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TECHNICAL REPORT

Airborne Manganese Particulate Matter

East Liverpool, Ohio

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EXECUTIVE SUMMARY

INTRODUCTION

In July 2016, U.S. Environmental Protection Agency (EPA) Region 3 requested, in conjunction with EPA Region 5, EPA's National Enforcement Investigations Center (NEIC) to examine manganese (Mn)-bearing particulate material found in air filters collected in East Liverpool, Ohio; Glasgow, Pennsylvania; and Chester and Lawrenceville Park (Lawrenceville), West Virginia, and from nine commercial facilities in the East Liverpool and Midland areas to determine the primary sources of Mn-bearing airborne particulate material.

Based on data collected at three Ohio monitoring stations through 2009, the Agency for Toxic Substances and Disease Registry (ATSDR) concluded that exposure to Mn concentrations in the East Liverpool community posed a public health hazard because the highest measured concentrations approached the low end of manganese air concentrations that have been associated with neurological impacts documented in occupational studies (ATSDR, 2010, 2016). Although substantial work has been done to control Mn emissions in East Liverpool, Mn concentrations in ambient air have increased since 2013, reaching as high as 32 micrograms per cubic meter ($\mu g/m^3$) at the water treatment plant (WTP) air monitoring site. ATSDR (2017) has set the minimum risk level (MRL) for respirable Mn at 0.3 $\mu g/m^3$ for chronic exposure, and the EPA (1993) has established a reference concentration for respirable Mn (RfC) at 0.05 $\mu g/m^3$ for chronic exposure. The MRL and the RfC are both estimates of the concentrations of Mn that anyone could be exposed to without experiencing adverse health effects (ATSDR, 2016).

Air filters collected between January 2014 and October 2015 were shipped to NEIC from the West Virginia Department of Environmental Protection (WVDEP), the Ohio Environmental Protection Agency (OEPA), and the Pennsylvania Department of Environmental Protection (PADEP). NEIC received 10 total suspended particulate (TSP) air filters collected in Chester (air monitor 54-029-0008), 9 collected in Lawrenceville (air monitor 54-029-0015), 63 collected at the WTP in East Liverpool (air monitor 39-029-0020), and 40 TSP and 40 PM_{10} filters collected in Glasgow (air monitors 35IQ and 35IP, respectively). PM_{10} refers to inhalable particles, with diameters that are generally 10 micrometers (µm) and smaller. The Chester, Lawrenceville, and WTP air monitoring sites were part of the state or local air monitoring sites network (SLAMS). The air monitoring site in Glasgow was part of a special air toxics study established in 2014 (EPA, 2016a). All TSP filters received were analyzed, and six PM_{10} filters from Glasgow were selected for analysis for comparison to the TSP filters from Glasgow. **Figures 1a–b** show the relative locations of these air monitoring sites.

EPA Region 3 (EPA, 2016b) and EPA Region 5 (Benisek, pers. comm., 2018) sampled Mn-bearing particulate material from commercial facilities in the Midland and East Liverpool areas, respectively. Composite samples of Mn-bearing particulate materials consisting of

multiple aliquots were collected from commercial facilities with the potential of producing Mn-bearing airborne particulate emissions. Commercial facilities handling Mn-bearing particulate materials in the Midland area were: First Energy/Bruce Mansfield Power Plant (First Energy), Harsco Metals (Harsco), Shell Chemical (Shell), Watco Industries (Watco), and Whemco Steel Castings, Inc. (Whemco) (EPA, 2016b). Commercial facilities handling particulate materials in East Liverpool were S.H. Bell Co. (S.H. Bell) and Hall China. **Figures 1a–b** show the relative locations of these commercial facilities.

From January 2014 to October 2015, TSP filters were collected in East Liverpool at the WTP air monitoring site, which was located adjacent to and west of the S.H. Bell facility and approximately 0.1−0.2 mile east of the Hall China facility. On the opposite side of S.H. Bell, TSP filters were collected at the Glasgow air monitoring site, located approximately 0.1−0.2 mile to the east-northeast. The Glasgow air monitoring site was also located approximately 2−5 miles west-northwest of the Midland area facilities which were approximately 0.4−0.5 mile farther away from the WTP air monitoring site in the same direction. The Chester and Lawrenceville air monitoring sites were located approximately 2.5 and 1.8 miles, respectively, to the southwest of the WTP, across the Ohio River in West Virginia.

S.H. Bell provides shipping, handling, storage, and processing services for producers, traders, and consumers of metals, minerals, and semi-finished industrial materials (S.H. Bell, 2018). S.H. Bell's processing services includes crushing, drying, screening, blending, and packaging at a river-side facility extending approximately one-half mile and straddling the Ohio-Pennsylvania border. S.H. Bell stores materials in open sheds and in outdoor piles and ships materials by river barge, truck, and railroad. Hall China produces various porcelain products using high-temperature kilns in a 12-acre building (Hall China, 2018). However, Hall China's quantity and use of Mn-bearing materials is extremely limited (Benisek, pers. comm., 2018).

This report (NEICVP1222E01) presents analytical results of Mn-bearing particulate matter on TSP filters collected at the WTP air monitoring site in East Liverpool and at air monitoring sites in Chester, Lawrenceville, and Glasgow. Results of Mn-bearing particulate matter in process materials from S.H. Bell, Hall China, and Midland area facilities are also presented. Characterization of individual particles, including morphology, size, and composition, was determined by scanning electron microscopy with energy dispersive spectrometry (SEM/EDS). Relative elemental abundances were determined by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). Mn concentrations reported from the TSP filters (EPA, 2018; WVDEP, 2016) were sufficiently elevated for the associated Mn particulate to be characterized by LA-ICP-MS. LA-ICP-MS results are presented for 71 samples of particulate material and 2 air filters from facilities in the East Liverpool and Midland areas and for 122 TSP and 6 PM_{10} air filters collected in the East Liverpool and surrounding areas. Data analysis and findings pertaining to these materials and filters and follows.

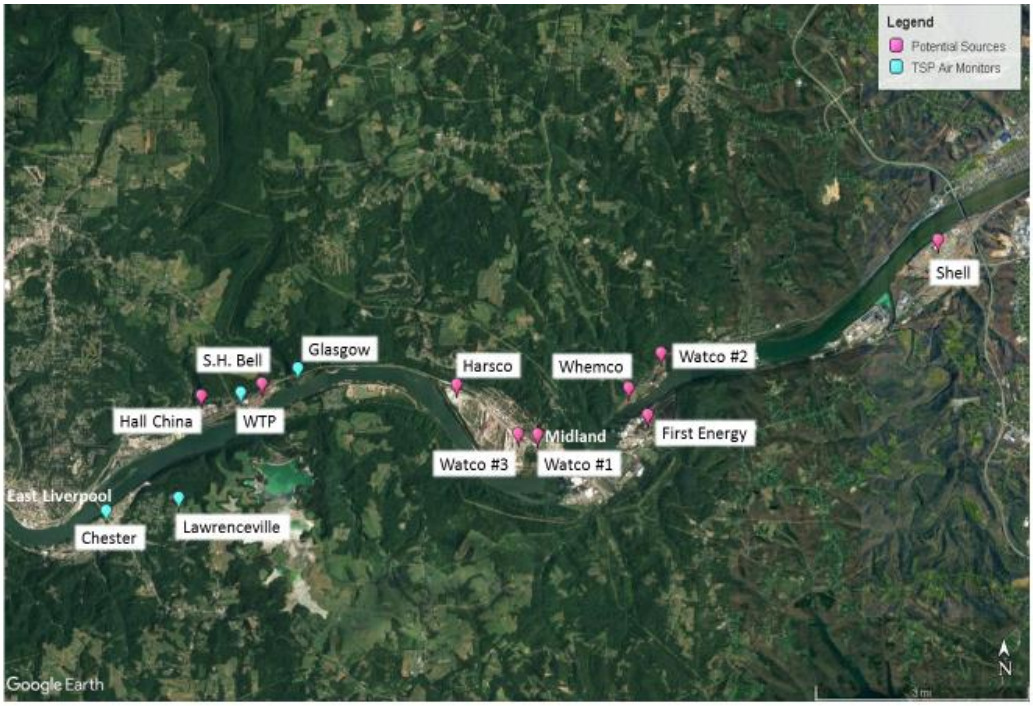


Figure 1a. Overview map of the East Liverpool, Ohio, and Midland, Pennsylvania, study area showing locations of the Hall China, S.H. Bell, First Energy, Harsco, Shell, Watco, and Whemco properties and the air monitoring sites in Chester, Lawrenceville, and Glasgow and at the WTP in East Liverpool.

Figure 1b. Detailed map of the East Liverpool, Ohio, study area showing locations of the Hall China and S.H. Bell properties and the air monitoring sites in Chester, Lawrenceville, and Glasgow and at the WTP in East Liverpool.

SUMMARY OF FINDINGS

LA-ICP-MS responses (elemental intensities in counts per seconds [cps]) were directly related to elemental abundances and indicated associations of Mn with cobalt (Co) and iron (Fe) on air filters collected in East Liverpool and surrounding areas. Scatterplots of Mn versus Co and Mn versus Fe showed the relationships of these elements on TSP filters and in particulate process materials from the Midland area facilities of First Energy, Harsco, Shell, Watco, and Whemco and from the Hall China and S.H. Bell facilities in East Liverpool. Spearman's rank correlation coefficients, r_s, were calculated from Mn, Co, and Fe responses for TSP filters collected at the WTP, Glasgow, Chester, and Lawrenceville air monitoring sites.

The relationships, i.e., relative responses, of Mn, Co, and Fe in particulate matter on TSP filters from the WTP and Glasgow air monitoring sites were inconsistent with most materials of particulate material from First Energy, Harsco, and Shell; i.e., process materials were not aligned with the TSP filter trends. Although the relative responses of Mn and Co and Mn and Fe in a few samples were consistent with the TSP filter trends, abundances of Mn, Co, and Fe were too low compared to the highest abundances on the TSP filters for those process materials to account for the bulk of the particulate matter on the filters. Typically, instrument responses (cps) of an order of magnitude or greater for facility particulate material are expected to account for airborne dispersion of the particulate and any dilution with ambient dust on TSP filters (NEIC, 2010, 2011, 2012, 2014).

Although many Watco and Whemco facility materials aligned with the TSP filter trends, differences in the overall responses of Mn, Co, and Fe in particulate matter on filters from the WTP and Glasgow air monitoring sites were not consistent with particulate materials from the Watco and Whemco facilities contributing significantly to the Mn-bearing particulate matter on WTP filters. The Glasgow air monitoring site was located west of the Watco and Whemco facilities, and the WTP air monitoring site was located approximately 0.4−0.5 mile farther west from the Glasgow site. The upper range of Mn responses for particulate matter on filters from the WTP air monitoring site was an order of magnitude greater than the upper range of Mn responses for filters from the Glasgow site, although the Glasgow site was approximately one-half mile closer to the Watco and Whemco facilities. These results indicated that a source of Mn other than the Watco and Whemco facilities was responsible for contributing most of the Mn-bearing particulate to the WTP filters.

Because the WTP air monitoring site was located between the S.H. Bell and Hall China facilities, WTP filters were categorized with respect to discriminating wind direction during filter collection periods, including downwind of S.H. Bell and downwind of Hall China. Significant differences in the relative intensities of Mn, Co, and Fe in particulate matter on filters from the WTP that were downwind of S.H. Bell versus downwind of Hall China were not consistent with Hall China particulate materials contributing significantly to the Mn-bearing particulate matter on WTP filters. In particular, the upper range of Mn responses for particulate matter on WTP

filters downwind of S.H. Bell was an order of magnitude greater than the upper range of Mn responses for filters downwind of Hall China, indicating S.H. Bell, rather than Hall China, was responsible for contributing most of the Mn-bearing particulate on the WTP filters.

Results of SEM/EDS and LA-ICP-MS analysis of TSP filters and process materials indicated Mn-bearing particles from S.H. Bell were the major contributor of airborne Mn-bearing particulate matter in the East Liverpool area from January 2014 to October 2015 based on the following:

- The typical Mn-bearing particle type observed in the WTP filters consisted of micrometer-scale, angular, Mn-oxide containing significant calcium (Ca), Fe, and/or silicon (Si), corresponding to particles of S.H. Bell's Mn-rich materials. In contrast to the abundant Mn-oxide particles observed in the WTP filters, oxide particles with distinctive proportions of chromium (Cr), Mn, and Fe and lacking significant Ca were not observed in WTP filters, nor were Mn-oxide particles containing barium (Ba) but lacking significant Cr, Fe, or Ca, suggesting particles such as those found in Hall China materials were not common on the filters.
- Mn abundance and its relationship with Co and Fe in particulate material from First Energy, Harsco, and Shell were not consistent with these materials contributing significantly to the Mn-bearing particulate matter on WTP filters.
- Significantly greater responses for Mn in particulate matter on filters from the WTP air monitoring site compared to filters from the Glasgow air monitoring site were not consistent with particulate material from the Watco and Whemco facilities contributing significantly to the Mn-bearing particulate matter on WTP filters.
- Significantly greater responses for Mn in particulate matter on WTP filters downwind from S.H. Bell compared to filters downwind from Hall China were not consistent with particulate materials from Hall China contributing significantly to the Mn-bearing particulate matter on WTP filters. However, the significantly greater Mn responses, along with the above findings, indicated particulate materials from S.H. Bell contributed significantly to the Mn-bearing particulate matter on WTP filters.
- The absence of filters collected downwind from Hall China with high Mn concentrations indicated that Hall China contributed negligible Mn to WTP filters.
- The relatively high frequency of filters collected downwind from S.H. Bell with high Mn concentrations and the lack of other potential sources, indicated that S.H. Bell contributed the majority of Mn-bearing particulate material to WTP filters.

LABORATORY ACTIVITIES

Laboratory activities included analysis by SEM/EDS and LA-ICP-MS of air filters from the WTP, Glasgow, Chester, and Lawrenceville air monitoring sites and particulate process materials from Hall China, S.H. Bell, First Energy, Harsco, Shell, Watco, and Whemco. SEM/EDS and LA-ICP-MS analyses were conducted in accordance with the NEIC quality system and are within the scope of NEIC's ISO/IEC 17025 accreditation issued by ANSI-ASQ National Accreditation Board (ANAB) (certificate No. AT-1646).

SAMPLE RECEIPT AND DESCRIPTION

OEPA environmental scientists collected process materials from S.H. Bell and Hall China on August 31 and September 1, 2016. Source materials from process material storage and waste collection areas were sampled using clean, dedicated, disposable scoops (Benisek, pers. comm., 2018). The samples were photographed, and the locations were recorded. NEIC chemist Steve Machemer received 36 process materials from Hall China and S.H. Bell on September 12, 2016. Facility process materials were powders and were received in 8-ounce glass jars.

PADEP environmental scientists collected process material similarly from facilities in the Midland area from October 11 through October 13, 2016. Details of the sampling and process materials can be found in EPA (2016b). Steve Machemer received 35 process materials from the First Energy, Harsco, Shell, Watco, and Whemco facilities on October 21, 2016. Facility process materials were powders and also were received in 8-ounce glass jars. Two air filters collected by Shell on October 12, 2016 were also included. For each process material analyzed, **Table 1a** lists the facility, facility location, particulate sample description, laboratory identification number, field station number, and sampling date.

Table 1a. FACILITY PROCESS MATERIALS
Airborne Manganese Particulate Matter
East Liverpool, Ohio

Facility	Location	Particulate Sample Description[a]	Laboratory (LIMS)[b] No.	Field Station No.	Sample Date
First Energy	Midland	Coal	N610002-EO	BM001	10/11/2016
First Energy	Midland	Waste	N610002-ET	BM002	10/11/2016
First Energy	Midland	Waste	N610002-EU	BM003	10/11/2016
First Energy	Midland	Waste/product	N610002-EV	BM004	10/11/2016
First Energy	Midland	Duplicate of BM004	N610002-EW	BM005	10/11/2016
Harsco	Midland	Raw material	N610002-EX	HAR006	10/11/2016
Harsco	Midland	Raw material	N610002-EY	HAR007	10/11/2016
Harsco	Midland	Duplicate of HAR007	N610002-EZ	HAR008	10/11/2016
Harsco	Midland	Pulverized slag	N610002-FA	HAR009	10/11/2016
Shell	Midland	Soil	N610002-EP	SH-032	10/13/2016
Shell	Midland	Duplicate of SH-032	N610002-EQ	SH-033	10/13/2016
Shell	Midland	Soil	N610002-ER	SH-034	10/13/2016
Shell	Midland	Soil	N610002-ES	SH-035	10/13/2016
Shell	Midland	Air filter particulate[c]	N610002-DW	PM10Q-PM01A	10/12/2016

Table 1a. FACILITY PROCESS MATERIALS
Airborne Manganese Particulate Matter
East Liverpool, Ohio

Facility	Location	Particulate Sample Description[a]	Laboratory (LIMS)[b] No.	Field Station No.	Sample Date
Shell	Midland	Air filter particulate[c]	N610002-DX	PM10Q-PM03B	10/12/2016
Watco #1	Midland	Waste	N610002-01	WA1-016	10/12/2016
Watco #1	Midland	Duplicate of WA1-016	N610002-DY	WA1-017	10/12/2016
Watco #1	Midland	Product	N610002-DZ	WA1-018	10/12/2016
Watco #1	Midland	Waste	N610002-EA	WA1-019	10/12/2016
Watco #1	Midland	Product	N610002-EB	WA1-020	10/12/2016
Watco #1	Midland	Raw material/product	N610002-EC	WA1-021	10/12/2016
Watco #1	Midland	Waste	N610002-EG	WA1-015	10/12/2016
Watco #2	Midland	Raw material/product	N610002-ED	WA2-022	10/12/2016
Watco #2	Midland	Waste	N610002-EE	WA2-023	10/12/2016
Watco #2	Midland	Waste	N610002-EF	WA2-024	10/12/2016
Watco #2	Midland	Waste	N610002-EH	WA2-025	10/12/2016
Watco #2	Midland	Raw material/product	N610002-EI	WA2-026	10/12/2016
Watco #2	Midland	Raw material	N610002-EJ	WA2-027	10/12/2016
Watco #2	Midland	Waste	N610002-EK	WA2-028	10/12/2016
Watco #3	Midland	Waste	N610002-EL	WA3-029	10/12/2016
Watco #3	Midland	Waste	N610002-EM	WA3-030	10/12/2016
Watco #3	Midland	Waste	N610002-EN	WA3-031	10/12/2016
Whemco	Midland	Waste	N610002-FB	WH010	10/11/2016
Whemco	Midland	Duplicate of WH010	N610002-FC	WH011	10/11/2016
Whemco	Midland	Waste	N610002-FD	WH012	10/11/2016
Whemco	Midland	Waste	N610002-FE	WH013	10/11/2016
Whemco	Midland	Waste	N610002-FF	WH014	10/11/2016
S.H. Bell	East Liverpool	Mn truck hopper	N610002-BT[d]	S01	8/31/2016
S.H. Bell	East Liverpool	Load out F dust collector	N610002-BU	S02	8/31/2016
S.H. Bell	East Liverpool	MEV dust collector	N610002-BV	S03	8/31/2016
S.H. Bell	East Liverpool	Under KUX Crusher	N610002-BW	S04	8/31/2016
S.H. Bell	East Liverpool	Road sweeping Bin 365 RT	N610002-BX	S05	8/31/2016
S.H. Bell	East Liverpool	Road sweeping Bin 365 LT	N610002-BY	S06	8/31/2016
S.H. Bell	East Liverpool	Load out O dust collector	N610002-BZ	S07	8/31/2016
S.H. Bell	East Liverpool	Bin 322 dust/fines	N610002-CA	S08	8/31/2016
S.H. Bell	East Liverpool	Bin 329 dust/fines	N610002-CB[d]	S09	8/31/2016
S.H. Bell	East Liverpool	Bin 331 dust/fines	N610002-CC	S10	8/31/2016
S.H. Bell	East Liverpool	Bin 341 dust/fines	N610002-CD	S11	8/31/2016
S.H. Bell	East Liverpool	Bin 343 dust/fines	N610002-CE	S12	8/31/2016
S.H. Bell	East Liverpool	Bin 351 dust/fines	N610002-CF	S13	8/31/2016
S.H. Bell	East Liverpool	Bin 364 dust/fines	N610002-CG	S14	8/31/2016
S.H. Bell	East Liverpool	Bin 902 dust/fines	N610002-CH	S15	8/31/2016
S.H. Bell	East Liverpool	Bin 939 dust/fines	N610002-CI	S16	8/31/2016
S.H. Bell	East Liverpool	Bin 920 dust/fines	N610002-CJ	S17	8/31/2016
S.H. Bell	East Liverpool	Bin 976 dust/fines	N610002-CK[d]	S18	8/31/2016
S.H. Bell	East Liverpool	Bin 966 dust/fines	N610002-CL[d]	S19	8/31/2016
S.H. Bell	East Liverpool	Bin 836 dust/fines	N610002-CM	S20	9/1/2016
S.H. Bell	East Liverpool	Bin 840 dust/fines	N610002-CN	S21	9/1/2016
S.H. Bell	East Liverpool	Area C crusher dust collector west side sack	N610002-CO	S22	9/1/2016
S.H. Bell	East Liverpool	Area C crusher dust collector fines from lip	N610002-CP	S23	9/1/2016
S.H. Bell	East Liverpool	Area C crusher long belt	N610002-CQ	S24	9/1/2016

Table 1a. FACILITY PROCESS MATERIALS
Airborne Manganese Particulate Matter
East Liverpool, Ohio

Facility	Location	Particulate Sample Description[a]	Laboratory (LIMS)[b] No.	Field Station No.	Sample Date
S.H. Bell	East Liverpool	Area C center building screener side	N610002-CR	S25	9/1/2016
S.H. Bell	East Liverpool	Area C dust screener dust collector	N610002-CS	S26	9/1/2016
S.H. Bell	East Liverpool	Packaging Torit	N610002-CT	S27	9/1/2016
S.H. Bell	East Liverpool	Number 2 dust collector	N610002-CU	S28	9/1/2016
S.H. Bell	East Liverpool	Number 2 dust collector	N610002-CV	S29	9/1/2016
S.H. Bell	East Liverpool	Number 4 dust collector	N610002-CW	S30	9/1/2016
Hall China	East Liverpool	GS-874 mixed phase oxide	N610002-CX	S01	9/1/2016
Hall China	East Liverpool	MnO_2 Manganese dioxide	N610002-CY[d]	S02	9/1/2016
Hall China	East Liverpool	GS-815 Pemco Black	N610002-CZ	S03	9/1/2016
Hall China	East Liverpool	Mixed metal pigment 26431	N610002-DA[d]	S04	9/1/2016
Hall China	East Liverpool	Dust collection bin	N610002-DB	S05	9/1/2016
Hall China	East Liverpool	Bin of floor sweeping	N610002-DC	S06	9/1/2016

[a] Particulate sample description for Midland samples from EPA (2016b) and for East Liverpool samples from chain-of-custody forms
[b] LIMS = Laboratory Information Management System
[c] Collected by Shell (EPA 2016b)
[d] Analyzed by SEM/EDS

From September to October 2016, Steve Machemer received the following TSP filter sets from OEPA, WVDEP, and PADEP: 10 from Chester, 9 from Lawrenceville, 63 from the WTP in East Liverpool, and 40 from Glasgow. Forty PM_{10} filters from Glasgow were also received. Air filters had been collected over 24-hour sampling periods for which associated ambient air Mn concentrations had been determined (EPA, 2018; WVDEP, 2016). TSP filter portions received were approximately 3 to 5 centimeters (cm) by 20 cm each.

For each filter analyzed, **Table 1b** lists the air monitoring site number and location, laboratory sample number, TSP (or PM_{10}) filter number, filter collection date, the discriminating wind direction at the WTP relative to the Hall China or S.H. Bell operations, and ambient air Mn concentration derived from the filter. The location of the WTP air monitoring site between S.H. Bell and Hall China (**Figure 1b**) allowed wind direction (OEPA, 2016) at the WTP during the 24-hour airborne particulate sampling period to be employed as a discriminator between S.H. Bell and Hall China materials in conjunction with elemental abundances or Mn concentrations from filter particulate. ATSDR (2016) has demonstrated the discriminating utility of wind data in East Liverpool. Thus, WTP TSP filters were categorized as downwind of S.H. Bell when significant wind (>20%) occurred at the WTP from the direction of S.H. Bell, i.e., from the north-northeast to south-southeast, with negligible wind from the direction of Hall China (<20 relative percent difference). Similarly, filters were categorized as downwind of Hall China when significant wind occurred at the WTP from the direction of Hall China, i.e., from the northwest to southwest, with negligible wind from the direction of S.H. Bell. Filters were categorized as having indeterminate wind direction when significant wind from the direction of both S.H. Bell and Hall China occurred at the WTP. Wind data collected before early 2015 was invalidated because the weather station at the WTP at the time was placed below the required height.

Table 1b. AIR FILTERS
Airborne Manganese Particulate Matter
East Liverpool, Ohio

Air Monitoring Site	Location	Laboratory (LIMS)[a] No.	TSP (PM_{10}) Filter No.	Filter Collection Date	Discriminating Wind Direction at the WTP Relative to Hall China or S.H. Bell	Ambient Air Mn Concentration from Filter ($\mu g/m^3$)[b]
54-029-0015	Lawrenceville	N610002-DD	Q1551476	11/13/2014	Not relevant	0.014
54-029-0015	Lawrenceville	N610002-DE	Q1551696	12/13/2014	Not relevant	0.0065
54-029-0015	Lawrenceville	N610002-DF	Q1551719	1/18/2015	Not relevant	0.0070
54-029-0015	Lawrenceville	N610002-DG	Q1551733	2/17/2015	Not relevant	0.0010
54-029-0015	Lawrenceville	N610002-DH	Q1551740	2/23/2015	Not relevant	0.018
54-029-0015	Lawrenceville	N610002-DI	Q1551746	3/13/2015	Not relevant	0.021
54-029-0015	Lawrenceville	N610002-DJ	Q1551761	4/12/2015	Not relevant	0.027
54-029-0015	Lawrenceville	N610002-DK	Q1551779	5/18/2015	Not relevant	0.022
54-029-0015	Lawrenceville	N610002-DL	Q1551794	6/17/2015	Not relevant	0.089
54-029-0008	Chester	N610002-DM	Q1551477	11/13/2014	Not relevant	0.038
54-029-0008	Chester	N610002-DN	Q1551697	12/13/2014	Not relevant	0.012
54-029-0008	Chester	N610002-DO	Q1551720	1/18/2015	Not relevant	0.013
54-029-0008	Chester	N610002-DP	Q1551734	2/17/2015	Not relevant	0.024
54-029-0008	Chester	N610002-DQ	Q1551747	3/13/2015	Not relevant	0.32
54-029-0008	Chester	N610002-DR	Q1551762	4/12/2015	Not relevant	Not reported
54-029-0008	Chester	N610002-DS	Q1551768	4/18/2015	Not relevant	0.050
54-029-0008	Chester	N610002-DT	Q1551780	5/18/2015	Not relevant	0.074
54-029-0008	Chester	N610002-DU	Q1551795	6/17/2015	Not relevant	0.68
54-029-0008	Chester	N610002-DV	Q5520216	7/5/2015	Not relevant	0.074
35IQ	Glasgow	N610002-11	13Q1536053	10/26/2014	Not relevant	0.16
35IQ	Glasgow	N610002-12	14Q4517672	11/1/2014	Not relevant	0.15
35IQ	Glasgow	N610002-13	14Q4517675	11/7/2014	Not relevant	0.18
35IQ	Glasgow	N610002-14	14Q4517676	11/13/2014	Not relevant	1.5
35IQ	Glasgow	N610002-16	14Q4517679	11/19/2014	Not relevant	1.6
35IQ	Glasgow	N610002-17	13Q1536045	12/1/2014	Not relevant	0.14
35IQ	Glasgow	N610002-18	13Q1536046	12/7/2014	Not relevant	0.041
35IQ	Glasgow	N610002-19	14Q4517693	12/25/2014	Not relevant	0.037
35IQ	Glasgow	N610002-20	14Q4517690	12/31/2014	Not relevant	1.3
35IQ	Glasgow	N610002-15	14Q4517684	1/6/2015	Not relevant	1.4
35IQ	Glasgow	N610002-21	14Q4517687	1/12/2015	Not relevant	0.47
35IQ	Glasgow	N610002-22	14Q4517689	1/18/2015	Not relevant	0.27
35IQ	Glasgow	N610002-23	14Q4517846	1/24/2015	Not relevant	0.17
35IQ	Glasgow	N610002-24	14Q4517844	1/30/2015	Not relevant	0.089
35IQ	Glasgow	N610002-25	14Q4517842	2/5/2015	Not relevant	0.29
35IQ	Glasgow	N610002-26	14Q4517840	2/11/2015	Not relevant	1.3
35IQ	Glasgow	N610002-27	14Q4517838	2/17/2015	Not relevant	0.38
35IQ	Glasgow	N610002-28	14Q4517838	2/23/2015	Not relevant	0.095
35IQ	Glasgow	N610002-29	14Q4517990	3/1/2015	Not relevant	0.084
35IQ	Glasgow	N610002-30	14Q4517994	3/7/2015	Not relevant	0.77
35IQ	Glasgow	N610002-31	14Q4517995	3/13/2015	Not relevant	0.18
35IQ	Glasgow	N610002-32	14Q4517997	3/19/2015	Not relevant	0.17
35IQ	Glasgow	N610002-65	14Q4518023	3/25/2015	Not relevant	0.34
35IQ	Glasgow	N610002-66	14Q4518025	3/31/2015	Not relevant	0.41
35IQ	Glasgow	N610002-67	14Q4518028	4/6/2015	Not relevant	1.2
35IQ	Glasgow	N610002-68	14Q4518030	4/12/2015	Not relevant	0.089
35IQ	Glasgow	N610002-69	14Q4518032	4/18/2015	Not relevant	0.088

Table 1b. AIR FILTERS
Airborne Manganese Particulate Matter
East Liverpool, Ohio

Air Monitoring Site	Location	Laboratory (LIMS)[a] No.	TSP (PM_{10}) Filter No.	Filter Collection Date	Discriminating Wind Direction at the WTP Relative to Hall China or S.H. Bell	Ambient Air Mn Concentration from Filter ($\mu g/m^3$)[b]
35IQ	Glasgow	N610002-70	14Q4518240	4/24/2015	Not relevant	0.51
35IQ	Glasgow	N610002-71	14Q4518232	4/30/2015	Not relevant	0.097
35IQ	Glasgow	N610002-72	14Q4518235	5/6/2015	Not relevant	0.12
35IQ	Glasgow	N610002-73	14Q4518237	5/12/2015	Not relevant	1.7
35IQ	Glasgow	N610002-74	14Q4518238	5/18/2015	Not relevant	0.15
35IQ	Glasgow	N610002-75	14Q4518385	5/24/2015	Not relevant	0.18
35IQ	Glasgow	N610002-76	14Q4518387	5/30/2015	Not relevant	0.072
35IQ	Glasgow	N610002-77	14Q4518389	6/5/2015	Not relevant	0.084
35IQ	Glasgow	N610002-45	14Q4518391	6/11/2015	Not relevant	0.26
35IQ	Glasgow	N610002-78	14Q4518393	6/17/2015	Not relevant	2.2
35IQ	Glasgow	N610002-79	14Q4518414	6/23/2015	Not relevant	2.0
35IQ	Glasgow	N610002-80	14Q4518416	6/29/2015	Not relevant	0.40
35IQ	Glasgow	N610002-81	14Q4518418	7/5/2015	Not relevant	0.037
35IP	Glasgow	N610002-42	14Q4517691 (PM_{10} filter)	12/31/2014	Not relevant	0.35
35IP	Glasgow	N610002-43	14Q4517685 (PM_{10} filter)	1/6/2015	Not relevant	0.42
35IP	Glasgow	N610002-51	14Q4517839 (PM_{10} filter)	2/11/2015	Not relevant	0.34
35IP	Glasgow	N610002-FG	14Q4518236 (PM_{10} filter)	5/12/2015	Not relevant	0.49
35IP	Glasgow	N610002-07	14Q4518392 (PM_{10} filter)	6/17/2015	Not relevant	0.57
35IP	Glasgow	N610002-08	14Q4518413 (PM_{10} filter)	6/23/2015	Not relevant	0.86
39-029-0020	WTP, East Liverpool	N610002-82	G-3502263	1/2/2014	Wind data invalid	5.0
39-029-0020	WTP, East Liverpool	N610002-83	G-3502262	1/5/2014	Wind data invalid	5.0
39-029-0020	WTP, East Liverpool	N610002-84	G-3502283	1/29/2014	Wind data invalid	5.6
39-029-0020	WTP, East Liverpool	N610002-85	G-3502303	2/19/2014	Wind data invalid	5.9
39-029-0020	WTP, East Liverpool	N610002-86	G-3502307	2/28/2014	Wind data invalid	5.6
39-029-0020	WTP, East Liverpool	N610002-87	G-3534902	9/8/2014	Wind data invalid	7.3
39-029-0020	WTP, East Liverpool	N610002-88	G-3534914	9/23/2014	Wind data invalid	7.6
39-029-0020	WTP, East Liverpool	N610002-89[c]	G-3534918	9/26/2014[c]	Wind data invalid	32[c]
39-029-0020	WTP, East Liverpool	N610002-90	G-3534933	10/14/2014	Wind data invalid	7.0
39-029-0020	WTP, East Liverpool	N610002-91	G-3534943	10/26/2014	Wind data invalid	0.23
39-029-0020	WTP, East Liverpool	N610002-92	G-3534947	11/1/2014	Wind data invalid	0.35
39-029-0020	WTP, East Liverpool	N610002-93	G-3534952	11/7/2014	Wind data invalid	0.07
39-029-0020	WTP, East Liverpool	N610002-94	G-3534958	11/13/2014	Wind data invalid	0.13
39-029-0020	WTP, East Liverpool	N610002-95	G-3534962	11/19/2014	Wind data invalid	0.093
39-029-0020	WTP, East Liverpool	N610002-96	G-3534967	11/25/2014	Wind data invalid	1.8
39-029-0020	WTP, East Liverpool	N610002-97	G-3534972	12/1/14	Wind data invalid	2.7
39-029-0020	WTP, East Liverpool	N610002-98	G-3534978	12/7/14	Wind data invalid	2.6
39-029-0020	WTP, East Liverpool	N610002-99	G-3534983	12/13/14	Wind data invalid	0.055
39-029-0020	WTP, East Liverpool	N610002-AA	G-3534988	12/19/14	Wind data invalid	0.33
39-029-0020	WTP, East Liverpool	N610002-AB	G-3534992	12/25/14	Wind data invalid	0.24
39-029-0020	WTP, East Liverpool	N610002-AC	G-3534997	12/31/14	Wind data invalid	0.076
39-029-0020	WTP, East Liverpool	N610002-AD	G-3535002	1/6/2015	Wind data invalid	0.41
39-029-0020	WTP, East Liverpool	N610002-AE	G-3535006	1/12/2015	Downwind from S.H. Bell	1.1
39-029-0020	WTP, East Liverpool	N610002-AF	G-3535011	1/18/2015	Downwind from Hall China	0.67
39-029-0020	WTP, East Liverpool	N610002-AG	G-3535017	1/24/2015	Downwind from Hall China	0.24
39-029-0020	WTP, East Liverpool	N610002-AH	G-3535022	1/30/2015	Indeterminate wind direction	0.25

Table 1b. AIR FILTERS
Airborne Manganese Particulate Matter
East Liverpool, Ohio

Air Monitoring Site	Location	Laboratory (LIMS)[a] No.	TSP (PM_{10}) Filter No.	Filter Collection Date	Discriminating Wind Direction at the WTP Relative to Hall China or S.H. Bell	Ambient Air Mn Concentration from Filter ($\mu g/m^3$)[b]
39-029-0020	WTP, East Liverpool	N610002-AI	G-3535027	2/5/2015	Indeterminate wind direction	0.35
39-029-0020	WTP, East Liverpool	N610002-AJ	G-3535032	2/11/2015	Downwind from Hall China	1.2
39-029-0020	WTP, East Liverpool	N610002-AK	G-3535102	2/17/2015	Indeterminate wind direction	0.60
39-029-0020	WTP, East Liverpool	N610002-AL	G-3535106	2/23/2015	Downwind from Hall China	0.21
39-029-0020	WTP, East Liverpool	N610002-AM	G-3535111	3/1/2015	Indeterminate wind direction	0.47
39-029-0020	WTP, East Liverpool	N610002-AN	G-3535117	3/7/2015	Downwind from Hall China	0.49
39-029-0020	WTP, East Liverpool	N610002-AO[c]	G-3535118	3/10/2015[c]	Downwind from S.H. Bell	18[c]
39-029-0020	WTP, East Liverpool	N610002-AP	G-3535122	3/13/2015	Downwind from S.H. Bell	5.3
39-029-0020	WTP, East Liverpool	N610002-AQ	G-3535127	3/19/2015	Downwind from S.H. Bell	6.7
39-029-0020	WTP, East Liverpool	N610002-AR	G-3535132	3/25/2015	Indeterminate wind direction	1.9
39-029-0020	WTP, East Liverpool	N610002-AS	G-3535137	3/31/2015	Indeterminate wind direction	1.7
39-029-0020	WTP, East Liverpool	N610002-AT	G-3535142	4/6/2015	Indeterminate wind direction	7.9
39-029-0020	WTP, East Liverpool	N610002-AU	G-3535146	4/12/2015	Downwind from S.H. Bell	1.2
39-029-0020	WTP, East Liverpool	N610002-AV	G-3535152	4/18/2015	Indeterminate wind direction	1.5
39-029-0020	WTP, East Liverpool	N610002-AW	G-3535157	4/24/2015	Indeterminate wind direction	1.2
39-029-0020	WTP, East Liverpool	N610002-AX	G-3535162	4/30/2015	Indeterminate wind direction	1.4
39-029-0020	WTP, East Liverpool	N610002-AY	G-3535297	5/6/2015	Downwind from S.H. Bell	3.5
39-029-0020	WTP, East Liverpool	N610002-AZ	G-3535302	5/12/2015	Downwind from Hall China	0.24
39-029-0020	WTP, East Liverpool	N610002-BA	G-3535307	5/18/2015	Downwind from S.H. Bell	1.1
39-029-0020	WTP, East Liverpool	N610002-BB	G-3535312	5/24/2015	Downwind from S.H. Bell	1.5
39-029-0020	WTP, East Liverpool	N610002-BC	G-3535317	5/30/2015	Indeterminate wind direction	0.43
39-029-0020	WTP, East Liverpool	N610002-BD	G-3535322	6/5/2015	Downwind from Hall China	1.1
39-029-0020	WTP, East Liverpool	N610002-BE	G-3535327	6/11/2015	Downwind from S.H. Bell	0.37
39-029-0020	WTP, East Liverpool	N610002-BF[c]	G-3535332	6/17/2015[c]	Indeterminate wind direction	13[c]
39-029-0020	WTP, East Liverpool	N610002-BG	G-3535333	6/20/2015	Downwind from S.H. Bell	6.8
39-029-0020	WTP, East Liverpool	N610002-BH	G-3535337	6/23/2015	Indeterminate wind direction	5.2
39-029-0020	WTP, East Liverpool	N610002-BI	G-3535343	6/29/2015	Indeterminate wind direction	0.72
39-029-0020	WTP, East Liverpool	N610002-BJ	G-3535347	7/5/2015	Downwind from S.H. Bell	0.43
39-029-0020	WTP, East Liverpool	N610002-BK	G-3535357	7/17/2015	Downwind from S.H. Bell	5.4
39-029-0020	WTP, East Liverpool	N610002-BL	G-3535373	8/7/2015	Downwind from S.H. Bell	7.3
39-029-0020	WTP, East Liverpool	N610002-BM[c]	G-3535377	8/10/2015[c]	Downwind from S.H. Bell	18[c]
39-029-0020	WTP, East Liverpool	N610002-BN	G-3535417	9/27/2015	Indeterminate wind direction	5.6
39-029-0020	WTP, East Liverpool	N610002-BO	G-3535422	10/3/2015	Downwind from S.H. Bell	5.7
39-029-0020	WTP, East Liverpool	N610002-BP[c]	G-3535423	10/6/2015[c]	Downwind from S.H. Bell	14[c]
39-029-0020	WTP, East Liverpool	N610002-BQ	G-5501952	10/9/2015	Indeterminate wind direction	8.9
39-029-0020	WTP, East Liverpool	N610002-BR	G-5501953	10/12/2015	Indeterminate wind direction	5.1
39-029-0020	WTP, East Liverpool	N610002-BS[c]	G-5501967	10/27/2015[c]	Downwind from S.H. Bell	18[c]

[a] LIMS = Laboratory Information Management System
[b] Mn concentrations from EPA (2018) and WVDEP (2016)
[c] Analyzed by SEM/EDS

LA-ICP-MS ANALYSIS

In December 2016, NEIC chemist Theresa Hosick collected elemental responses using LA-ICP-MS for 73 facility process materials, 122 TSP filters, and 6 PM_{10} filters. To compare

TSP and PM_{10} filter trends at higher Mn concentrations, a limited number of PM_{10} filters were randomly selected (6 out of 40) for this purpose. LA-ICP-MS results of process materials and filters were compared and evaluated for elemental relationships and trends. LA-ICP-MS provides direct ICP-MS analysis of solid samples, eliminating the need for labor-intensive digestion and dissolution of particulate material. Although there are no certified reference materials for matrices in this study, such as particulate on glass fiber filters, it has been demonstrated that the LA-ICP-MS responses for a given analyte are directly proportional to the concentration of that analyte (Arroyo et al., 2009; Latkoczy et al., 2005; NEIC, 2010; NEIC, 2011; NEIC, 2012; NEIC, 2014). And, even though concentrations, such as those expressed in $\mu g/m^3$, are not directly obtainable by this method without matrix-matched standards, relative responses for Mn and other elements are measured reliably.

LA-ICP-MS Sample Preparation

Although most of the process materials were dry powders, because several appeared damp, the damp materials were oven dried overnight at 85 degrees Celsius (°C). Process materials were sieved using an 80-mesh sieve (180-micrometer mesh opening) using a Retsch AS200 ultrasonic sieve shaker. The smaller sieved fraction of the samples allowed for better comparison to the smaller wind-transported particulate matter on the filters (EPA, 1999; Industrial Specialties Manufacturing and IS Med Specialties [ISM], 2017). The sieved fractions were pressed into 10-millimeter (mm) diameter pellets using approximately 0.5-gram (g) boric acid (EMD Millipore, 99.5 percent purity, Lot #47288752) and 0.5 g sample. A Carver laboratory press was used to press the sieved samples at a pressure of 5−7 metric tons into 10-millimeter-diameter pellets for LA-ICP-MS analysis.

Filter samples were prepared by cutting an approximately 1- by 1.5-cm section from the filter with a clean razor blade. The samples were handled with forceps and gloved hands and were cut on a clean Kimwipe®. Each filter section was placed into a small, plastic sample container with a snap-top lid. The Kimwipe® was replaced, and the forceps were rinsed and dried between samples. The remaining filter sample was returned to its original sample envelope.

LA-ICP-MS Method of Analysis

The analysis was performed using a Teledyne Analyte G2 excimer laser with Chromium software, version 2.2, coupled to a PerkinElmer® NexION 300D ICP-MS with NexION software, version 1.5. The ICP-MS system was tuned and optimized to minimize oxides and doubly-charged ions as recommended by the instrument manufacturer. Analysis was performed using a modified ASTM method for trace elements in glass (ASTM, 2013). The laser power was adjusted such that filter particulate was ablated while avoiding ablation of the glass fiber filter. Intensities (in counts per second) of blank filter ablation were negligible compared to intensities of sample filter ablation for all analytes of interest, as were boric acid blanks when compared to

facility source material samples. Four separate lines, each 1.0 mm long and 500 microns apart, were ablated for each sample with a 250-µm spot size, a scan speed of 10 µm/second (sec), and a repetition rate of 10 hertz (Hz).

The collection method consisted of 30 seconds of data acquisition without laser ablation, followed by 60 seconds of acquisition with laser ablation, and then 40 seconds without laser ablation. The ICP-MS acquisition was in peak hopping mode, standard resolution, a dwell time of 10 milliseconds (ms), 1 sweep/reading, 320 readings/replicate, 1 replicate/line, 4 lines/sample. The data were then exported to Iolite software, version 3.32 (University of Melbourne). Baselines and sample response regions were selected in the Iolite software using the automatic selections option, which ensured the same ranges of baseline and signal were selected for every sample for comparison. Mean counts per second (background subtracted) were imported into a Microsoft Excel spreadsheet where the mean, standard deviation, and the relative standard deviation were calculated for the four replicate lines for each sample.

Quality control measures included instrument performance standards, blank filter samples, boric acid blank samples, daily analysis of National Institute of Standards (NIST) standard reference material (SRM) 2710, and replicate filter analysis within and across analysis dates.

Correlation Analysis

Log-log scatterplots were created, and correlation analysis was performed to evaluate relationships between Mn and other elements within sample sets. Similar evaluations have been conducted by others (U.S. Geological Survey [USGS], 2003; Myers and Thorbjornsen, 2004; Thorbjornsen and Myers, 2007; Anderson and Kravitz, 2010). Results of correlation analysis were given as the Spearman rank correlation coefficient, r_s, because a normal distribution of data in sample populations is not assumed for its application, and because it is a better indicator in the case of a non-linear relationship. An r_s is calculated by correlating *rankings* of the data values in data sets rather than correlating the data values themselves. The Spearman rank correlation coefficient is more robust than the Pearson product-moment correlation coefficient for the reasons stated above, and because it tends to minimize the effects of extreme values (outliers). An r_s indicates the strength or weakness of a relationship between the concentrations of a pair of elements. An r_s of unity (1), either positive or negative, indicates a perfect correlation, and an r_s of zero indicates that there is no evidence of a correlation. Weak correlations may be indicated by $|r_s| < 0.3$, moderate correlations by $0.3 < |r_s| < 0.7$, and strong correlations by $0.7 < |r_s| < 1$ (Gerstman, 2017; Laerd, 2017). Thus, an r_s of 0.90 indicates a relatively strong positive relationship, while an r_s of 0.40 indicates a much weaker relationship. The sign (+ or -) of the r_s indicates a positive or negative correlation between the parameters of a pair of elements, increasing for both in a positive monotonic relationship, and decreasing for one element while increasing for the other in a negative relationship.

For each r_s, a p-value was calculated. P-values are probabilities based, in part, on the number of data pairs, n, used in the correlation analysis. Typically, p-values less than a significance level set at $\alpha = 0.05$ suggest a high level of confidence that a statistically significant, non-zero correlation exists between the concentrations of a pair of elements. Thus, a p-value of 0.0001 or less indicates a high level of confidence that the variables are correlated, and a p-value of 0.0500 or greater indicates a lower level of confidence. Both the r_s and the p-value are used to evaluate the strength of association between two variables (Miller and Miller, 1993; Rumsey 2017; Good and Hardin, 2003).

SCANNING ELECTRON MICROSCOPY

Steve Machemer conducted scanning electron microscopy with energy dispersive spectrometry in March, August, and September 2017 in glass fiber TSP air filters collected at the WTP in East Liverpool and in process materials from S.H. Bell and Hall China. The purpose of the SEM/EDS analysis was to document size, morphology, texture, and elemental composition of Mn-bearing particulate matter found on TSP filters associated with elevated airborne Mn concentrations (EPA, 2018) and in relevant process materials from nearby facilities. Six WTP TSP filters collected between January 2014 and October 2015 with high associated ambient air Mn concentrations were chosen for examination by SEM/EDS. In addition, four S.H. Bell process materials and two Hall China process materials were chosen for examination based on their alignment with WTP TSP filters in data plots, in particular, the Mn versus Co plot to be presented later. Results were compared to evaluate similarities between the dominant Mn-bearing particles in the TSP filters and process materials.

SEM/EDS Sample Preparation

The less-than-180-µm-size fraction of the six process materials analyzed by SEM/EDS was dab-mounted onto carbon adhesive tabs attached to 12-mm-diameter, aluminum (Al) SEM specimen stubs. Portions, approximately 1-cm square, of six exposed and one unexposed glass fiber air filters were mounted onto 12-mm-diameter, aluminum SEM specimen stubs using carbon adhesive tabs. Edges of the filter specimens were dabbed with carbon paint to provide adequate grounding with the stub. Filter and particulate specimens were carbon-coated using a Denton Vacuum BTT-IV bench-top carbon evaporator.

SEM/EDS Method of Analysis

Process materials and filter specimens were analyzed in accordance with the NEIC operating procedure *Scanning Electron Microscope Operation*, NEICPROC/00-072R5. A JEOL JSM-6460LV SEM with Control User Interface v6.95 software and a Thermo Scientific energy dispersive X-ray spectrometer (EDS) with a silicon drift detector (SDD) and Noran System Seven (NSS version 3.0) software were used for the analysis. The following instrument parameters were used: acceleration voltage was 20 kiloelectronvolts (keV), working distance

was 10 mm, spot size setting was 60, magnification was varied as needed, and the count acquisition time for spectra was 30 seconds. Backscattered electron imaging (BEI) was used to aid in locating Mn-bearing particles, and secondary electron imaging (SEI) was used to document particle size, morphology, and texture. Energy dispersive spectra were collected at selected spots and areas to document particle composition. Spectra were presented at 0 to 14 keV.

SEM stub mounts were systematically scanned in BEI mode at approximately 1000x magnification to search for Mn-bearing and other metal-bearing particles, which tend to be more responsive in BEI mode due to higher average atomic number (Z) than surrounding particles. However, SEI was used to document particle size, morphology, and texture of the Mn-bearing particle types observed. Examination of each stub was concluded after documentation of approximately 12 to 25 particles. EDS spectra were collected at selected spots and areas to qualitatively document particle composition and to evaluate spectral response of background materials. EDS spectra were used for qualitative data collection. Proper EDS calibration was verified daily with aluminum, copper, and cobalt standards in an SPI Supplies reference set. No metal-bearing particles were observed on the unexposed TSP filter blank analyzed for comparison to exposed filters.

ANALYTICAL RESULTS AND DISCUSSION

LA-ICP-MS and SEM/EDS analytical results of process materials and ambient air particulate matter collected in WTP TSP filters between January 2014 and October 2015 are presented below, with a discussion of the results that considers: (1) the relative locations of facility operations and the air monitoring sites and (2) wind data for the TSP filter 24-hour collection periods.

LA-ICP-MS RESULTS

Process materials from these facilities were compared with particulate matter on TSP filters collected over time frames ranging from 22 months at the WTP air monitoring site (January 2014−October 2015) to approximately 8 months at the Glasgow, Chester, and Lawrenceville air monitoring sites (November 2014−July 2015). Only the less-than-180-µm-size fraction of the process materials was analyzed for a better comparison to particles on the TSP filters

Results of LA-ICP-MS analyses for elemental abundance presented in the following sections were background-corrected raw counts (cps). The LA-ICP-MS intensity response for Mn (in cps) was proportional to ambient air Mn concentrations (EPA, 2018) measured for the WTP TSP filters by OEPA (r_s = 0.89, p-value < 0.0001) and for the Glasgow TSP filters measured by PADEP (r_s = 0.82, p-value < 0.0001). To compare particulate matter on TSP filters to particulate matter in process materials, LA-ICP-MS responses were examined for elemental relationships and relative intensities.

Spearman rank correlation coefficients, r_s, were calculated from Mn, Co, and Fe responses for TSP filters collected at the WTP, Glasgow, Chester, and Lawrenceville air monitoring sites (**Figure 1b; Table 2**). In addition, Spearman rank correlation coefficients were calculated for WTP TSP filters that were collected on days when the wind was predominantly from the west, downwind of Hall China, or predominantly from the east, downwind of S.H. Bell.

Table 2. SPEARMAN'S RANK CORRELATION COEFFICIENTS
Airborne Manganese Particulate Matter
East Liverpool, Ohio

Elements	TSP Filter Collection Location	r_s for TSP Filters	Number of TSP Filters (n)	p-value
Mn and Co	Glasgow	0.72	40	<0.0001
Mn and Co	WTP	0.81	63	<0.0001
Mn and Fe	Glasgow	0.50	40	<0.0001
Mn and Fe	WTP	0.79	63	<0.0001
Mn and Co	Chester	0.87	10	0.0012
Mn and Co	Lawrenceville	0.78	9	0.0125
Mn and Fe	Chester	0.87	10	0.0012
Mn and Fe	Lawrenceville	0.88	9	0.0016
Mn and Co	WTP downwind of Hall China	0.61	7	0.1482
Mn and Co	WTP downwind of S.H. Bell	0.80	17	0.0001
Mn and Fe	WTP downwind of Hall China	0.71	7	0.0713
Mn and Fe	WTP downwind of S.H. Bell	0.61	17	0.0096

For most of the TSP filter sets in **Table 2**, r_s values indicated moderate-to-strong positive correlation for Mn with Co and Fe. For the filter set, WTP downwind of Hall China, p-values were greater than the typically accepted value of 0.05 (95 percent confidence level) likely due to the smaller sample size (n=7) and not statistically significant.

Based on r_s results indicating moderate-to-strong positive associations of Mn with Co and Fe for most of the filters sets, log-log scatterplots of Mn versus Co and Mn versus Fe were prepared and evaluated. The following scatterplots show the relationships of Mn, Co, and Fe on TSP filters from the four air monitoring sites and in particulate material from First Energy, Harsco, Shell, Watco, Whemco, Hall China, and S.H. Bell.

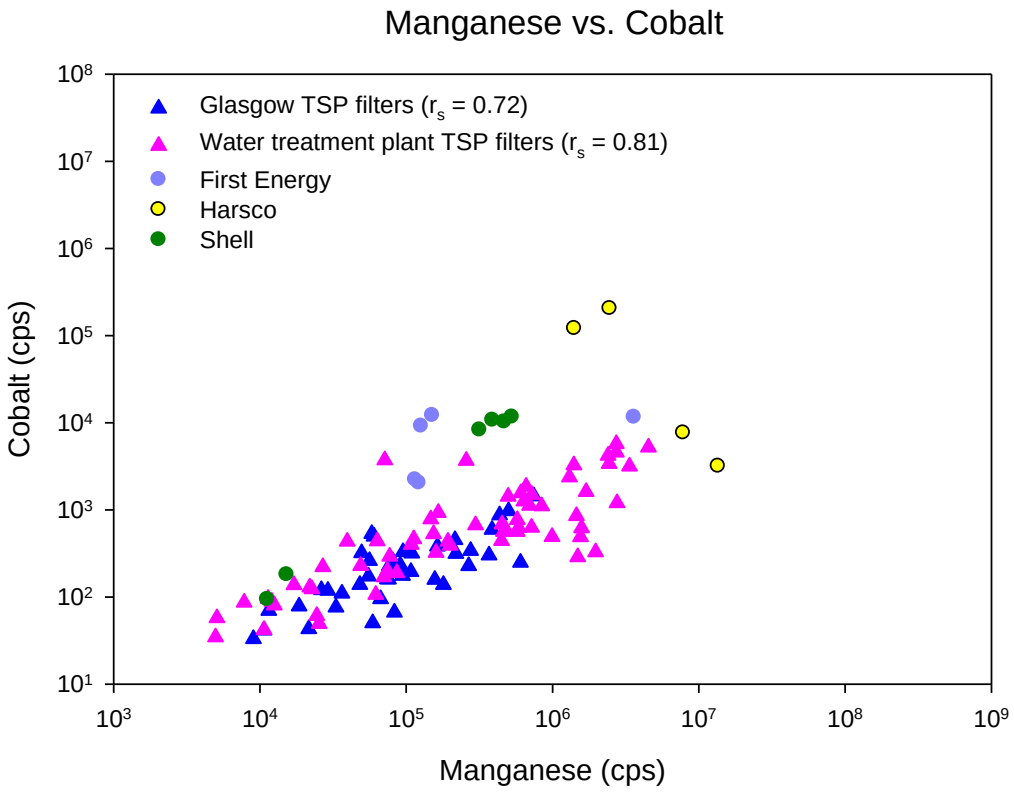
- **Figures 2a–b.** Mean background-corrected counts of Mn versus mean background-corrected counts of (**a**) Co and (**b**) Fe for Glasgow and WTP TSP filters and process materials from three facilities, First Energy, Harsco, and Shell. These plots were evaluated because Co and Fe correlated with Mn **(Table 2)** and are associated with raw Mn materials such as ore (Olsen et. al., 2007; NEIC, 2005).

- **Figures 3a–b**. Mean background-corrected counts of Mn versus mean background-corrected counts of (**a**) Co and (**b**) Fe for Glasgow and WTP TSP filters and process materials from four facilities, Watco 1, Watco 2, Watco 3, and Whemco.

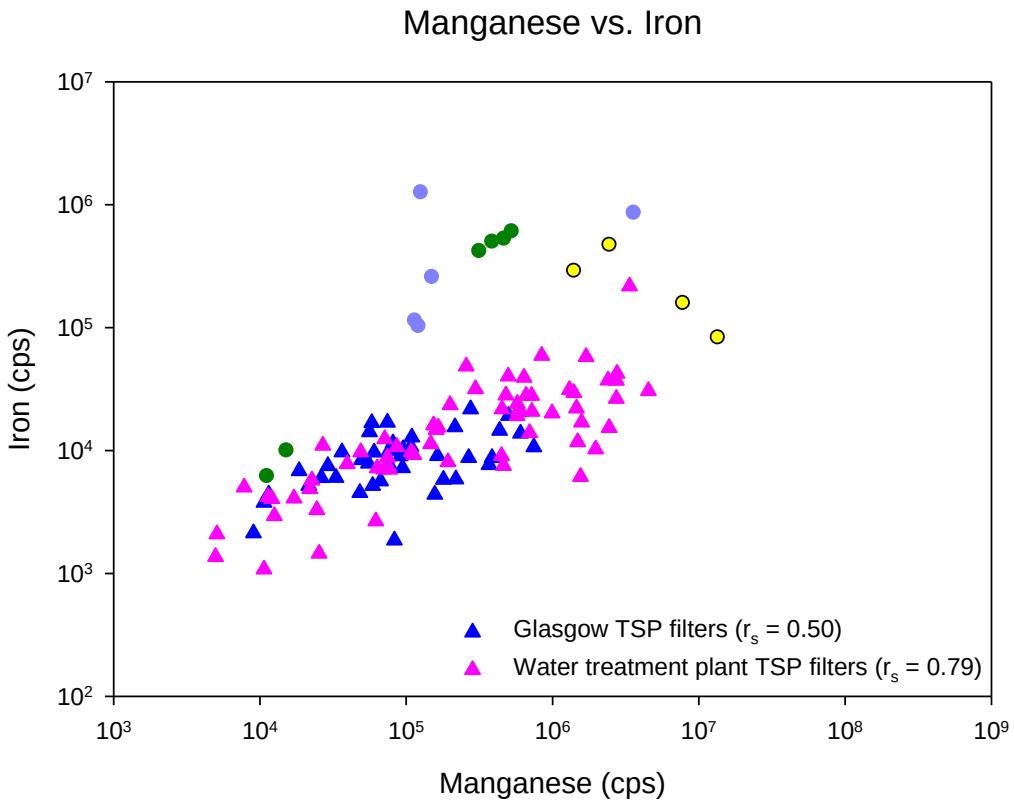
- **Figures 4a–b.** Mean background-corrected counts of Mn versus mean background-corrected counts of (**a**) Co and (**b**) Fe for the Glasgow TSP filters and for PM_{10} filters associated with higher Mn ambient air concentrations.

- **Figures 5a–b**. Mean background-corrected counts of Mn versus mean background-corrected counts of (**a**) Co and (**b**) Fe for TSP filters collected at the WTP, Chester, and Lawrenceville air monitoring sites.

- **Figures 6a–b**. Mean background-corrected counts of Mn versus mean background-corrected counts of (**a**) Co and (**b**) Fe for WTP TSP filters downwind from S.H. Bell and downwind from Hall China and from process materials from Hall China and S.H. Bell.

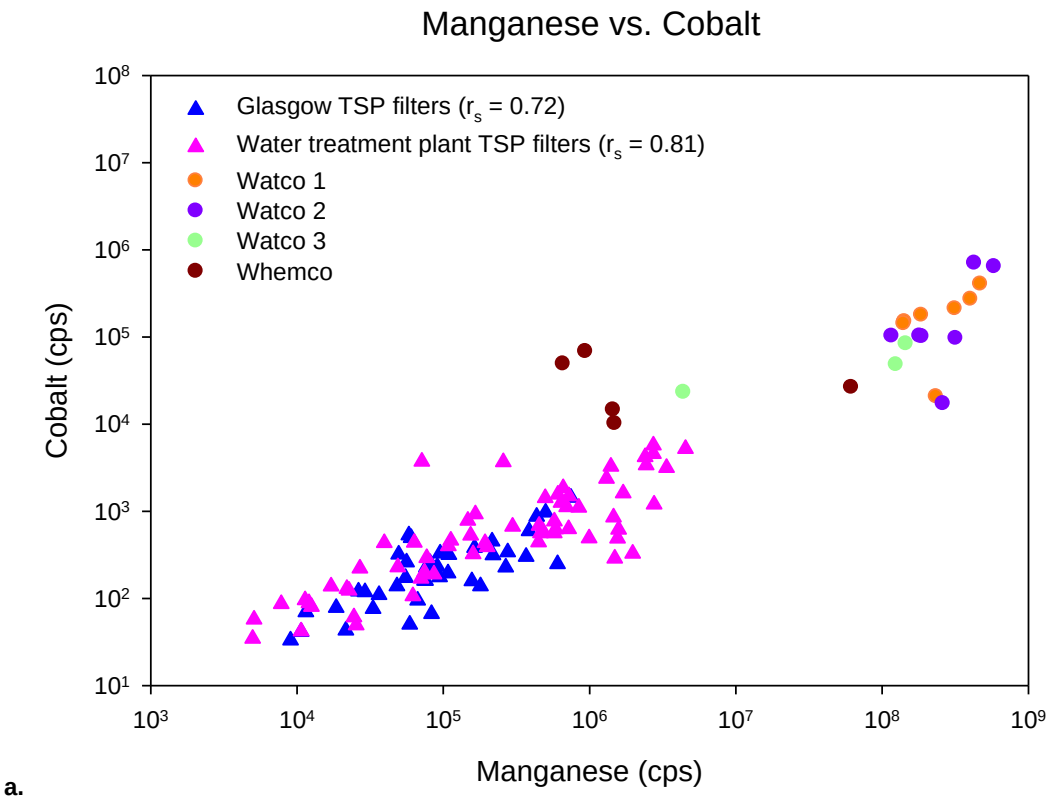


a.

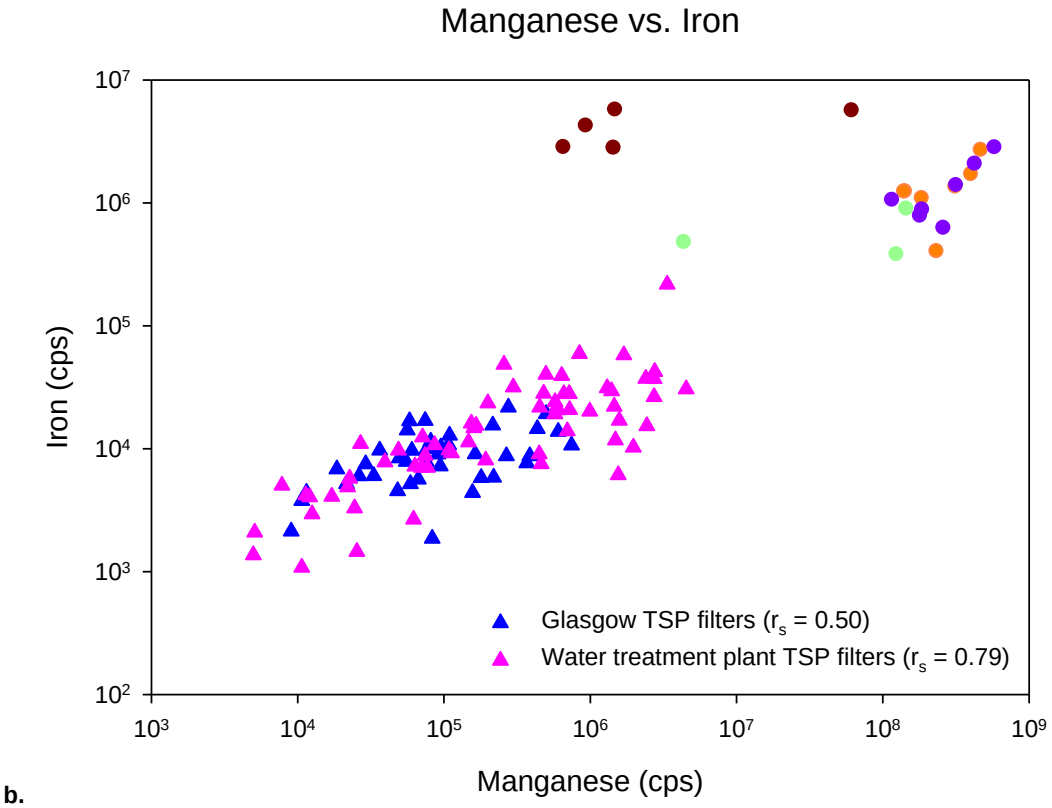


b.

Figure 2. The Mn versus Co (a) and Mn versus Fe (b) trends of airborne Mn-bearing particulate at the WTP and Glasgow air monitoring sites were not aligned with most First Energy, Harsco, and Shell materials from the Midland area. For a few facility materials aligning with the TSP filter trends, Mn abundances were too low compared to the highest abundances on the TSP filters to account for the bulk of the Mn-bearing particulate on the filters. Also, the further distant WTP filters contained the highest abundances of Mn, whereas the closer Glasgow filters contained much lower abundances of Mn.

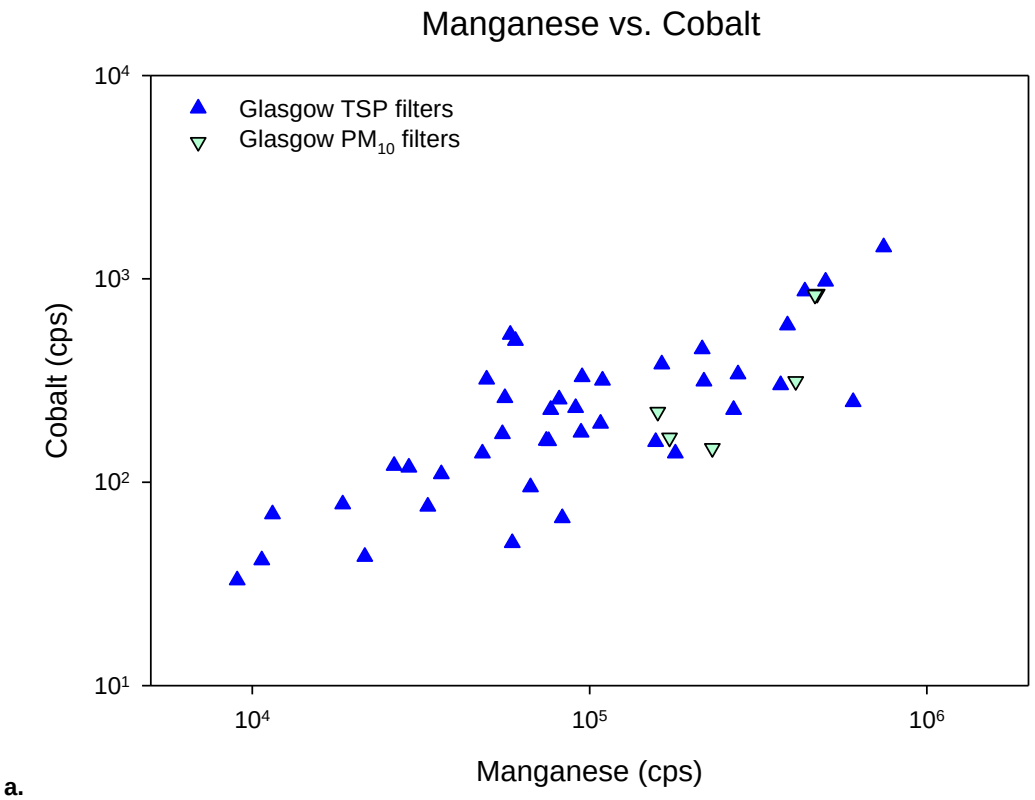


a.

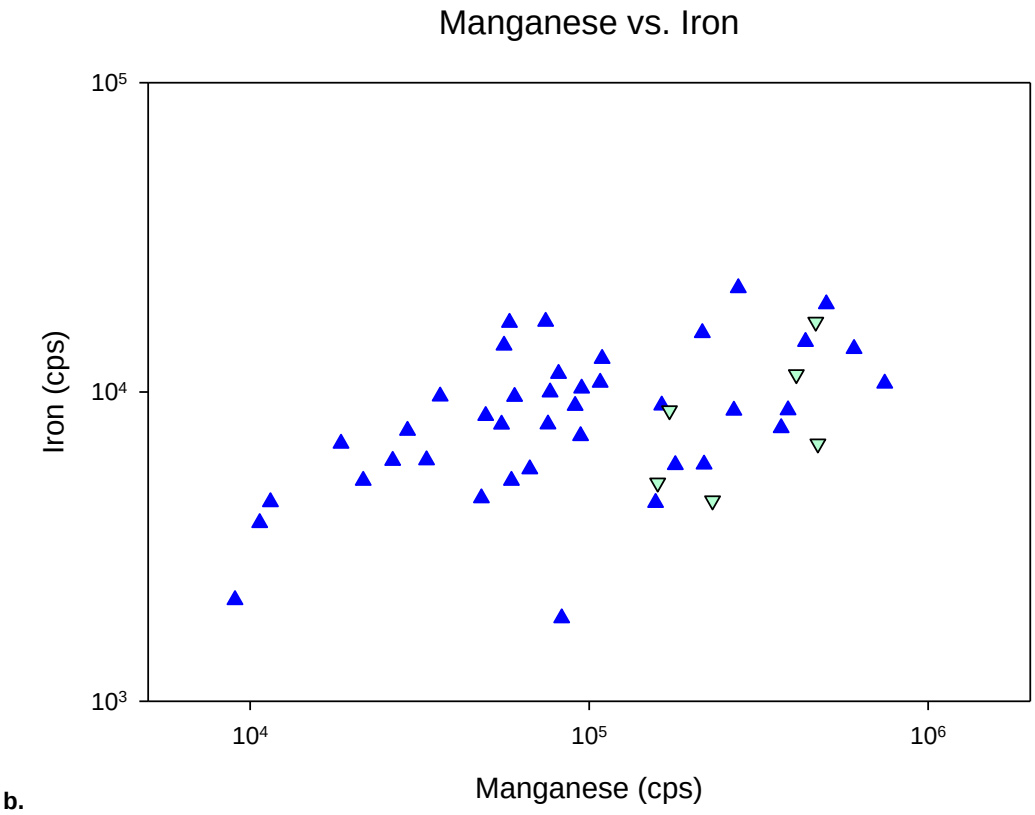


b.

Figure 3. The Mn versus Co (a) and Mn versus Fe (b) trends of airborne Mn-bearing particulate at the WTP and Glasgow air monitoring sites relative to the Watco and Whemco process materials. Although many Watco and Whemco facility materials aligned with the TSP filter trends, the order-of-magnitude-greater range of Mn responses for high level Mn on the further distant WTP filters relative to the closer Glasgow filters indicated a Mn source other than the Watco and Whemco facilities was responsible for contributing most of the Mn-bearing particulate matter to the WTP filters.

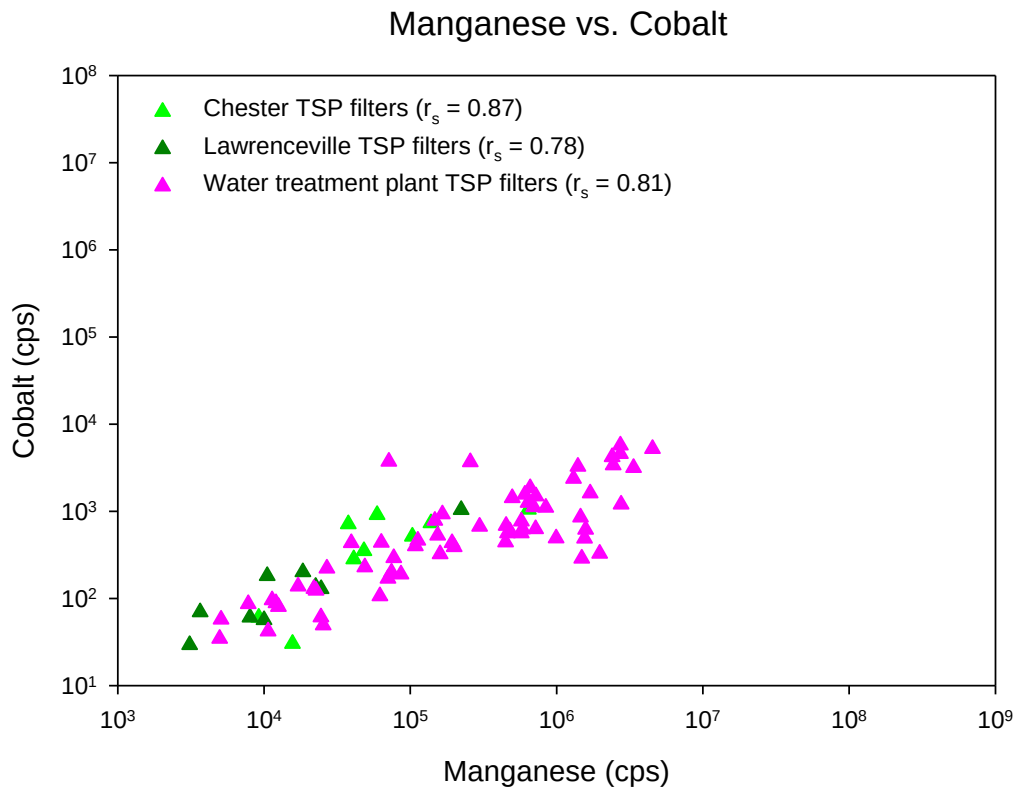


a.

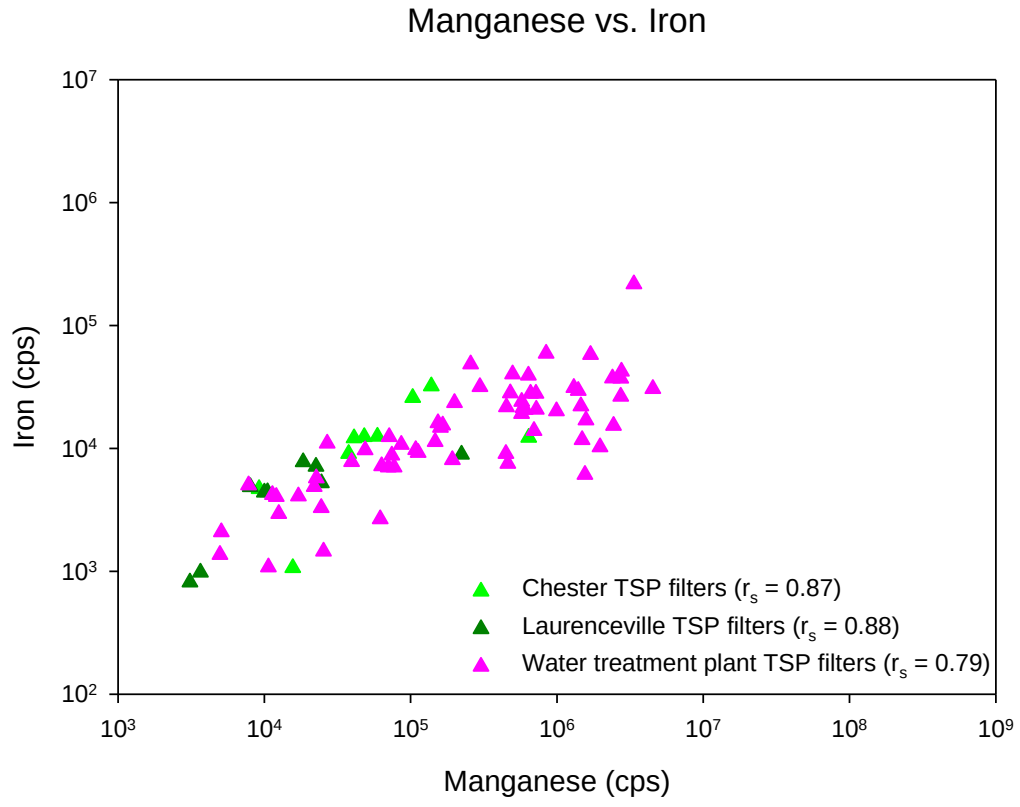


b.

Figure 4. The Mn versus Co (a) and Mn versus Fe (b) trends of airborne Mn-bearing particulate at the Glasgow air monitoring site comparing the TSP and PM_{10} filters.

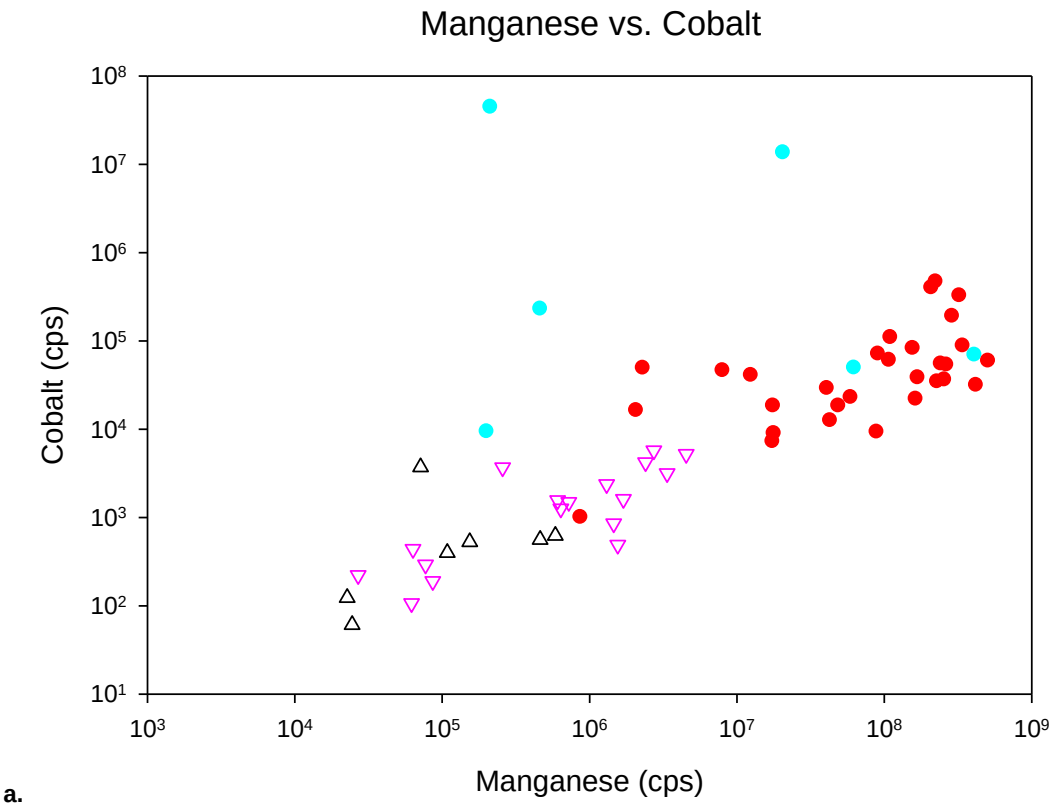


a.

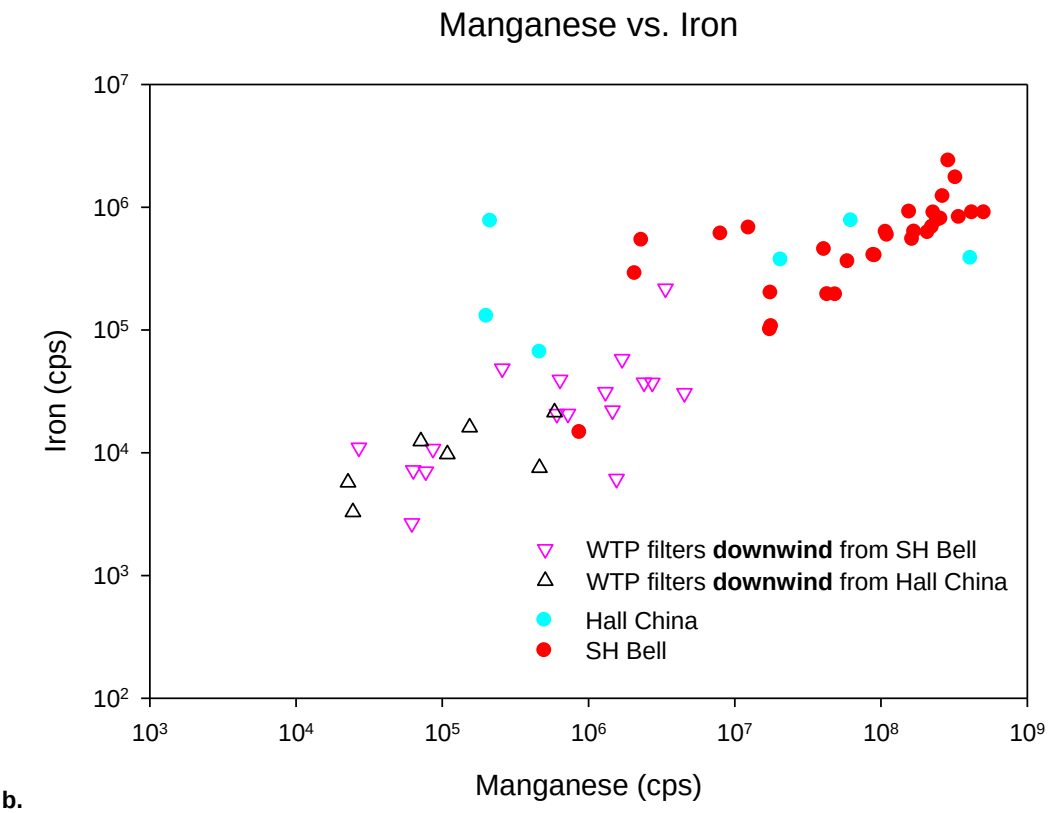


b.

Figure 5. The Mn versus Co (a) and Mn versus Fe (b) trends of airborne Mn-bearing particulate at the WTP, Chester, and Lawrenceville air monitoring sites. The order-of-magnitude-greater range of Mn responses for high level Mn on the WTP filters relative to the Chester and Lawrenceville filters indicated a Mn source closer to the WTP air monitor was responsible for contributing most of the Mn-bearing particulate matter to the WTP filters.



a.



b.

Figure 6. The Mn versus Co (a) and Mn versus Fe (b) trends of airborne Mn-bearing particulate at the WTP air monitoring site relative to Hall China and S.H. Bell process materials. Although a two or three Hall China process materials aligned with the TSP filter trends at high Mn responses, the order-of-magnitude-greater range of high Mn responses on filters downwind from S.H. Bell relative to filters downwind from Hall China indicated S.H. Bell's process materials and not Hall China's were the major contributors of Mn-bearing particulate on the WTP filters. (Omitted were WTP filters corresponding to invalid or indeterminate wind data).

COMPARISON OF LA-ICP-MS ELEMENTAL RESPONSES

The correlation coefficients (**Table 2**) and scatterplots (**Figures 2−6**) of elemental responses on TSP filters from the WTP, Glasgow, Chester, and Lawrenceville air monitoring sites indicated significant positive correlations of Mn with Co and Fe. Moderate-to-strong correlation of LA-ICP-MS results of Mn with Co and Fe suggested that these elements have been added to the TSP filters largely from the same material or process rather than as independently distributed constituents. This application of correlation analysis has been demonstrated previously by others (USGS, 2003; Myers and Thorbjornsen, 2004; Thorbjornsen and Myers, 2007; and Anderson and Kravitz, 2010). These correlations suggested Co and Fe were concomitant in Mn-bearing particulate matter from a source with a relatively consistent composition, even though Co was not detectable in individual particles by SEM/EDS. The correlations also suggested that multiple major sources of Mn were not likely, because additional major sources of Mn not associated with Co and/or Fe would tend to obscure the correlations. As indicated previously, Co and Fe are associated with raw Mn materials such as ore (Olsen et. al., 2007; NEIC, 2005).

The relationships, i.e., relative LA-ICP-MS responses or intensities in cps, of Mn, Co, and Fe in particulate matter on TSP filters from the WTP and Glasgow air monitoring sites and in materials from First Energy, Harsco, and Shell are shown in **Figures 2a–b**. Typically, instrument responses of an order of magnitude or greater for facility process materials compared to responses on TSP filters are expected to account for airborne dispersion of the particulate and dilution with ambient dust on TSP filters (NEIC, 2010, 2011, 2012, 2014). Thus, responses of Mn in process materials from First Energy, Harsco, and Shell were too low compared to the relatively high intensities of Mn in many WTP filters to account for the bulk of the Mn-bearing particulate matter on the filters. In addition, trends formed by Mn, Co, and Fe intensities for the filters represented dilution lines consistent with airborne dispersion and filter deposition. Relative responses of Mn, Co, and Fe in most of the process materials from First Energy, Harsco, and Shell did not align well with the trends of filters from the WTP and Glasgow air monitoring sites. In particular, 11 out of 15 facility materials did not align with the Mn versus Fe TSP filter trend, indicating their compositions were not consistent with material on the filters. Furthermore, the upper range of Mn responses for WTP filters was approximately an order of magnitude greater than for the Glasgow filters. Because of the relative locations of the air monitoring sites, with the Glasgow site situated much closer to the Midland facilities than the WTP site, these different responses on filters from the sites were consistent with the source of airborne Mn originating in East Liverpool rather than in the Midland area.

Similar to **Figures 2a–b**, relatively low Mn intensities for five of the Watco and Whemco materials compared to the relatively high Mn intensities for many WTP filters indicated those materials were not major sources of airborne Mn (**Figures 3a–b**). In addition, several process materials from the Watco and Whemco facilities did not align well with the WTP and Glasgow TSP filter trend for Mn versus Fe, plotting well above the filter trend and exhibiting much

greater abundance of Fe relative to Mn than particulate collected on the filters. The compositions of these particulate materials were not consistent with the composition of the Mn-bearing particulate matter on the TSP filters because the greater abundance of Fe eliminated the possibility those particulate materials could have been a major source of the airborne Mn found on the Glasgow and WTP filters. Furthermore, although many Watco and Whemco process materials did align with the TSP filter trends, an order of magnitude approximate difference in the maximum range of Mn, Co, and Fe intensities of particulate matter in WTP and Glasgow filters indicated that the source of the airborne Mn was in or near East Liverpool (west of Glasgow) and not from the Midland area. Because the Glasgow air monitoring site was located one-half mile or more west of the Watco and Whemco facilities and the WTP air monitoring site was located approximately 0.4−0.5 mile farther west from the Glasgow site, the Watco and Whemco facilities could not have contributed significantly to the WTP filters without elemental responses for the Glasgow filters being significantly greater than for the WTP filters. In other words, the opposite differential pattern in the maximum range of Mn, Co, and Fe intensities for WTP and Glasgow filter particulate matter would be necessary because the Glasgow filters were collected significantly closer to the Watco or Whemco facilities. The observed data pattern for the filters was consistent with correlation values (r_s) generally weakening with distance from a pollution source, as seen in **Table 2** (WTP = 0.81 and 0.79 versus Glasgow = 0.72 and 0.50, respectively). Thus, the remaining process materials from Watco and Whemco could be excluded as major sources of the airborne Mn because Watco and Whemco were located in the Midland area east of Glasgow.

Scatterplots in **Figures 4a–b** compare the relative intensities of Mn, Co, and Fe in particulate on TSP filters and co-located PM_{10} filters associated with higher Mn ambient air concentrations collected at the Glasgow air monitoring site. The relative intensities of Mn, Co, and Fe in total suspended airborne particulate and airborne particulate matter less than 10 micrometers in size corresponded well at higher Mn intensities, consistent with originating from the same source.

Scatterplots in **Figures 5a–b** compare relative intensities of Mn, Co, and Fe in particulate on TSP filters collected in Chester and Lawrenceville with WTP filters. Although the elemental trends on filters from the Chester and Lawrenceville sites appeared indistinguishable, the upper range of Mn, Co, and Fe intensities for WTP filters was approximately an order of magnitude greater than for the Chester and Lawrenceville filters. The greater upper range of intensities for the WTP filters was consistent with a source of airborne Mn originating in East Liverpool, where the WTP was located, and not from northern West Virginia.

In **Figures 6a–b**, relatively low Mn intensities for three to four Hall China process materials compared to the relatively high Mn intensities for many WTP filters excluded those materials from being a major source of airborne Mn. However, relative responses of Mn, Co, and Fe provided an effective signature for distinguishing some of Hall China materials. In other

words, the response of Co was too high relative to Mn in several materials from Hall China compared to relative responses for the WTP filters for those materials to be a major source of airborne Mn. Only the two Hall China process materials (mixed metal pigment and manganese dioxide) aligned with the WTP filter trend for Mn versus Co, exhibiting compositions consistent with WTP filters and indicating they were candidates for further analysis relative to predominant wind direction and examination by SEM/EDS. However, trends of Mn, Co, and Fe intensities of the WTP filters were consistent with airborne dispersion and filter deposition of most of S.H. Bell's Mn-bearing particulate materials; i.e., most of S.H. Bell's process materials aligned with the WTP filters (4 were selected for analysis by SEM/EDS).

As described previously, WTP filters were categorized with respect to discriminating wind direction during filter collection periods, including downwind of S.H. Bell and downwind of Hall China (**Table 1b**). Significant differences in the relative intensities of Mn, Co, and Fe in particulate matter on filters from the WTP that were downwind of S.H. Bell versus downwind of Hall China were not consistent with Hall China particulate materials contributing significantly to the Mn-bearing particulate matter on WTP filters (**Figures 6a–b**). In particular, elevated responses of Mn in particulate matter on WTP filters downwind of S.H. Bell (violet triangles) ranged an order of magnitude greater than elevated responses of Mn on filters downwind of Hall China (black triangles), indicating S.H. Bell, rather than Hall China, was responsible for contributing most of the Mn-bearing particulate on the WTP filters.

SEM/EDS RESULTS

A summary of SEM/EDS results of observed Mn-bearing particle types in six TSP filters, four S.H. Bell process materials, and two Hall China process materials is presented in **Table 3**. To illustrate typical occurrences of the Mn-bearing particles observed, SEI and EDS spectra are shown in **Figures 7–10**. Particle types were identified based on the dominant morphologies and elemental compositions observed.

The Mn-bearing process material from Hall China described as a mixed metal pigment (N610002-DA) was composed of angular particles of Cr-Mn-Fe-oxide with relatively consistent abundances of Mn, Cr, and Fe and ranged from micrometer to 10s of micrometers in scale (**Figure 7**). The Mn-bearing process material from Hall China described as manganese dioxide (MnO_2) (N610002-CY) was composed of angular particles of Mn-oxide, typically 10s of micrometers in scale, with traces of Al, Ba, Fe, potassium (K), sodium (Na), and/or Si (**Figures 8a–b**). The occurrence of Ba was a distinguishing feature of some particles in this Hall China material.

The four Mn-bearing particulate materials from S.H. Bell appeared similar to each other and consisted of angular, Si-rich, Mn-oxide, or Mn-rich Si-oxide particles, micrometer to 10s of micrometers in scale, and commonly occurred with significant Ca or Fe and traces of Cr (**Figures 9a–e**).

TSP filters collected at the WTP in East Liverpool contained abundant micrometer-scale, angular, Mn-oxide particles with significant Ca, Fe, and/or possible Si and common traces of Cr (**Figures 10a–b**). Occurring less frequently were micrometer-scale, angular, Mn-rich Fe-oxide and Mn-rich Si-oxide particles.

Table 3. HALL CHINA AND S.H. BELL PROCESS MATERIALS AND WTP TSP FILTERS ANALYZED BY SEM
Airborne Manganese Particulate Matter
East Liverpool, Ohio

Site	Material	LIMS No.	Field Tag No. (Filter No.)	TSP Filter Date	Ambient Air Mn Concentration from Filter ($\mu g/m^3$)[a]	Typical Mn-bearing Particle Type
Hall China	Mixed metal pigment (26431)	N610002-DA	5-110912	Not applicable	Not applicable	Angular Cr-Mn-Fe-oxide with consistent proportions
Hall China	MnO_2 manganese dioxide	N610002-CY	5-110914	Not applicable	Not applicable	Angular Mn-oxide (some with Ba)
S.H. Bell	Mn truck hopper	N610002-BT	5-110931	Not applicable	Not applicable	Angular Mn-oxide with variable Ca, Fe, Si
S.H. Bell	Bin 329 dust/fines	N610002-CB	5-110939	Not applicable	Not applicable	Angular Mn-oxide with variable Ca, Fe, Si
S.H. Bell	Bin 976 dust/fines	N610002-CK	5-110936	Not applicable	Not applicable	Angular Mn-oxide with variable Ca, Fe, Si
S.H. Bell	Bin 966 dust/fines	N610002-CL	5-110938	Not applicable	Not applicable	Angular Mn-oxide with variable Ca, Fe, Si
East Liverpool WTP	TSP filter	N610002-AO	(G-3535118)	03/10/2015	18	Angular Mn-oxide with variable Ca, Fe, (Si)[b]
East Liverpool WTP	TSP filter	N610002-BF	(G-3535332)	06/17/2015	13	Angular Mn-oxide with variable Ca, Fe, (Si)[b]
East Liverpool WTP	TSP filter	N610002-BM	(G-3535377)	08/10/2015	18	Angular Mn-oxide with variable Ca, Fe, (Si)[b]
East Liverpool WTP	TSP filter	N610002-BP	(G-3535423)	10/06/2015	14	Angular Mn-oxide with variable Ca, Fe, (Si)[b]
East Liverpool WTP	TSP filter	N610002-BS	(G-5501967)	10/27/2015	18	Angular Mn-oxide with variable Ca, Fe, (Si)[b]
East Liverpool WTP	TSP filter	N610002-89	(G-3534918)	09/26/2014	32	Angular Mn-oxide with variable Ca, Fe, (Si)[b]

[a] EPA (2018) provided airborne Mn concentrations from TSP filters.
[b] (Si) in parentheses indicates possible matrix interference due to the silica glass fiber of the filter.

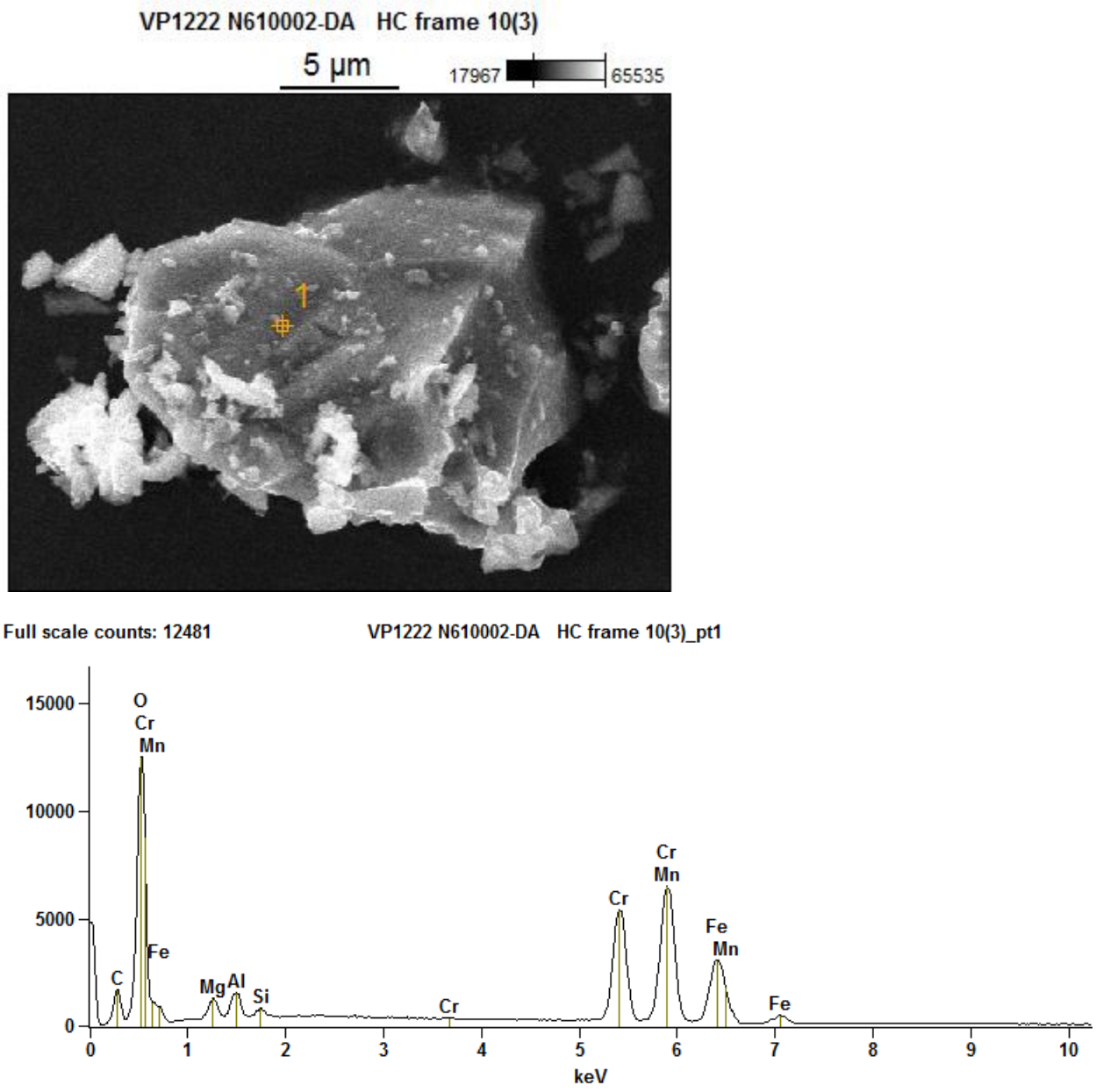


Figure 7. SEI image and EDS spectrum of typical Cr-Fe-Mn-bearing particle from Hall China's process materials in East Liverpool, Ohio (N610002-DA).

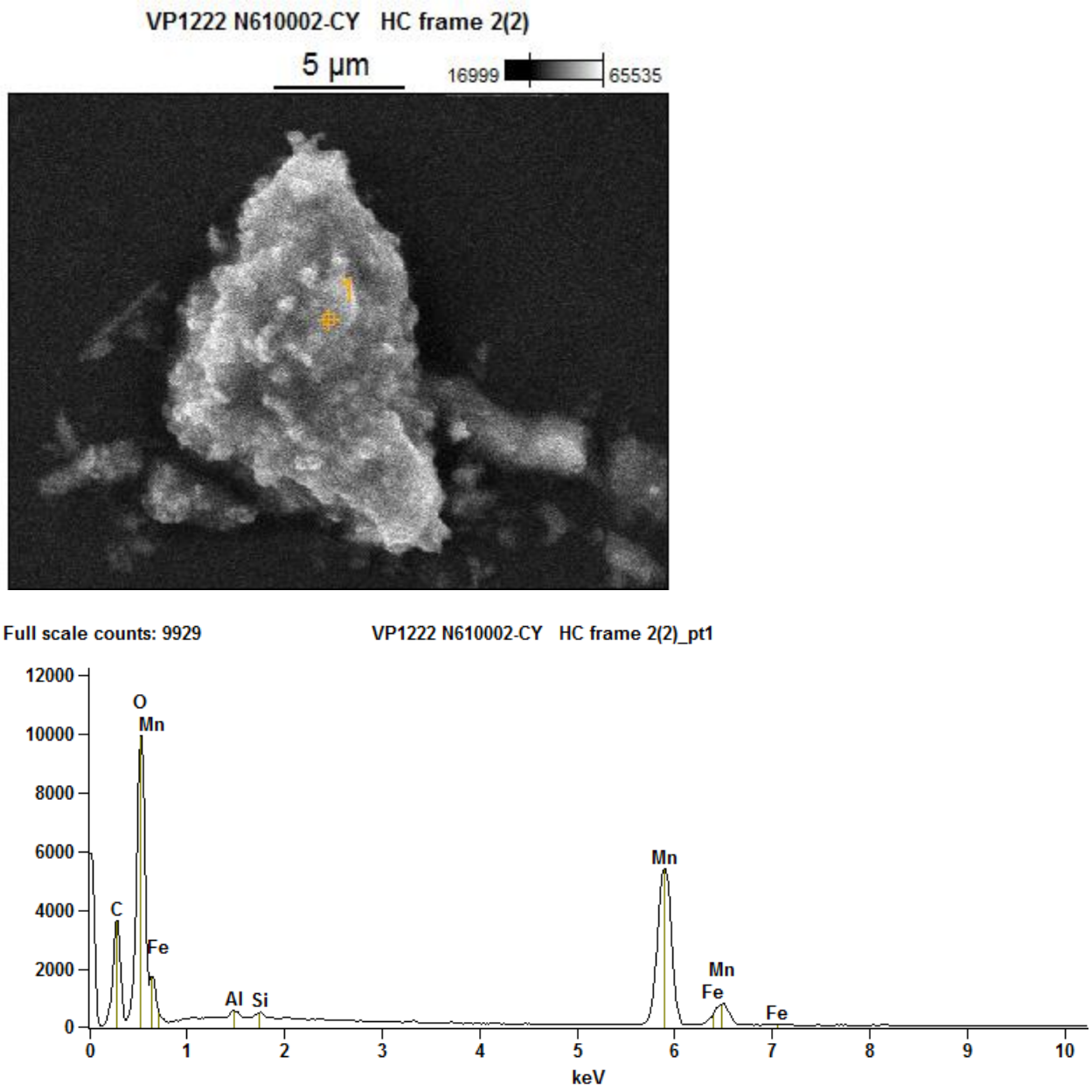


Figure 8a. SEI image and EDS spectrum of typical Mn-bearing particle from Hall China's process materials in East Liverpool, Ohio (N610002-CY).

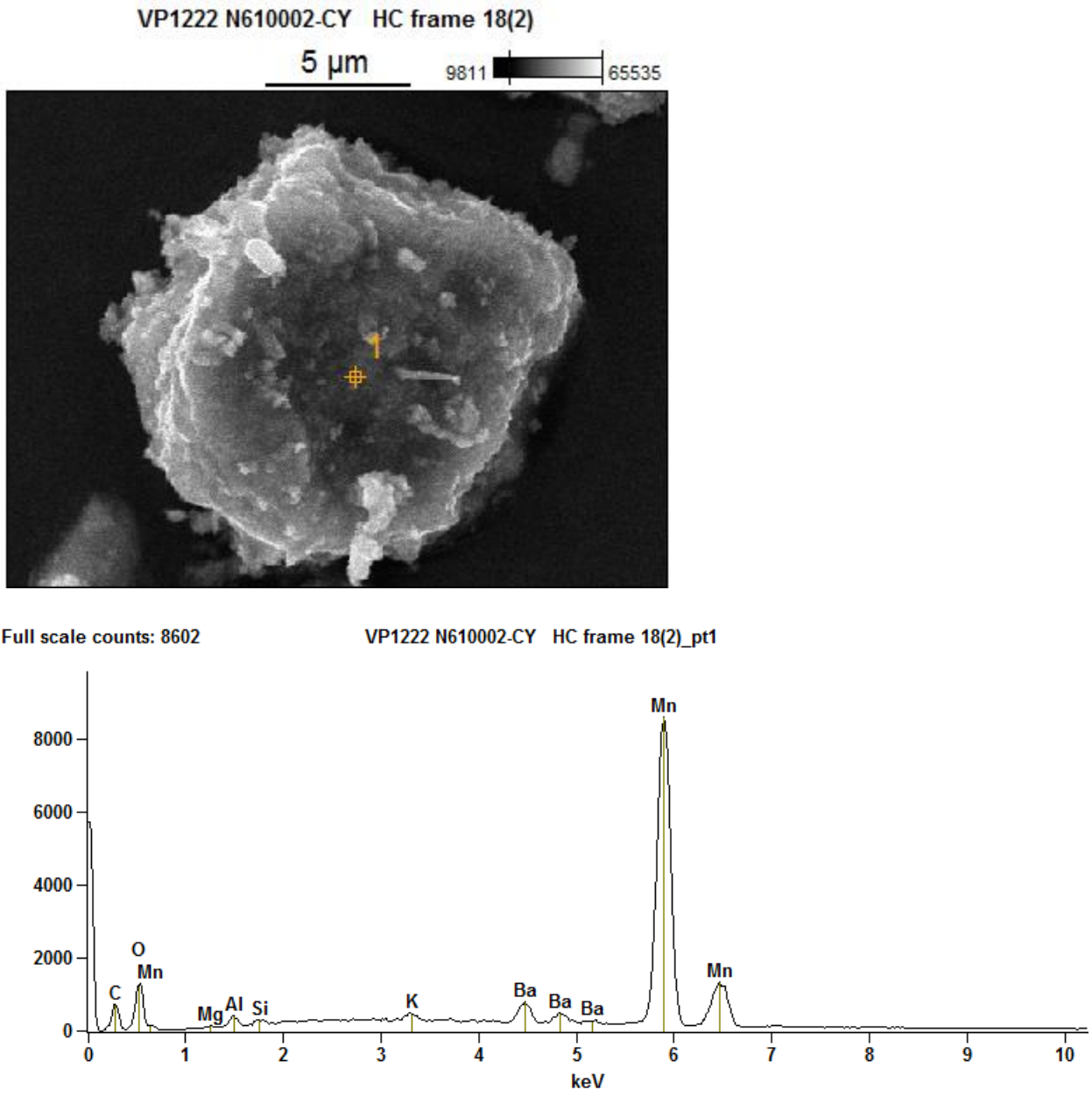


Figure 8b. SEI image and EDS spectrum of typical Mn-bearing particle with a trace of Ba from Hall China's process materials in East Liverpool, Ohio (N610002-CY).

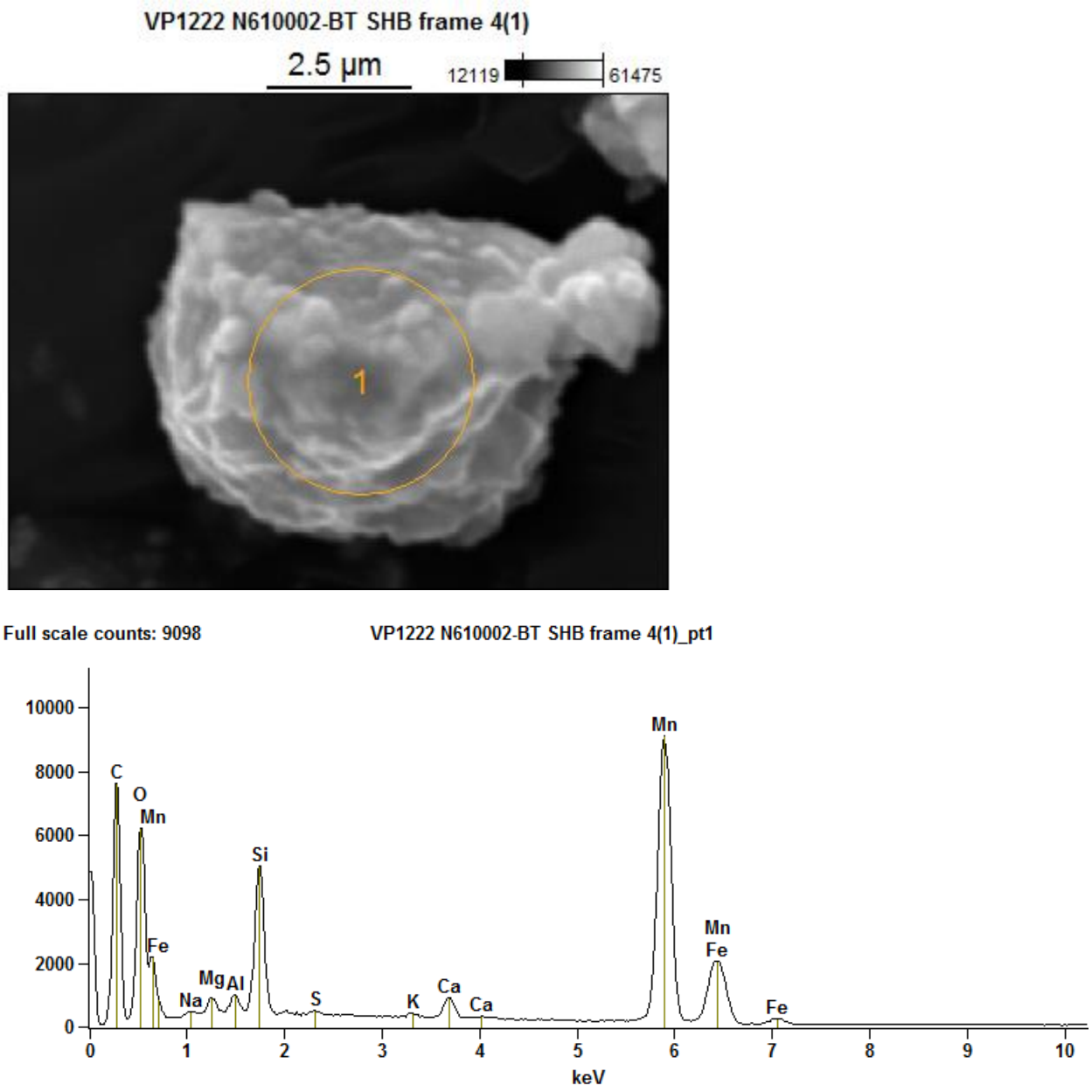


Figure 9a. SEI image and EDS spectrum of typical Mn-bearing particle from S.H. Bell's process materials in East Liverpool, Ohio (N610002-BT).

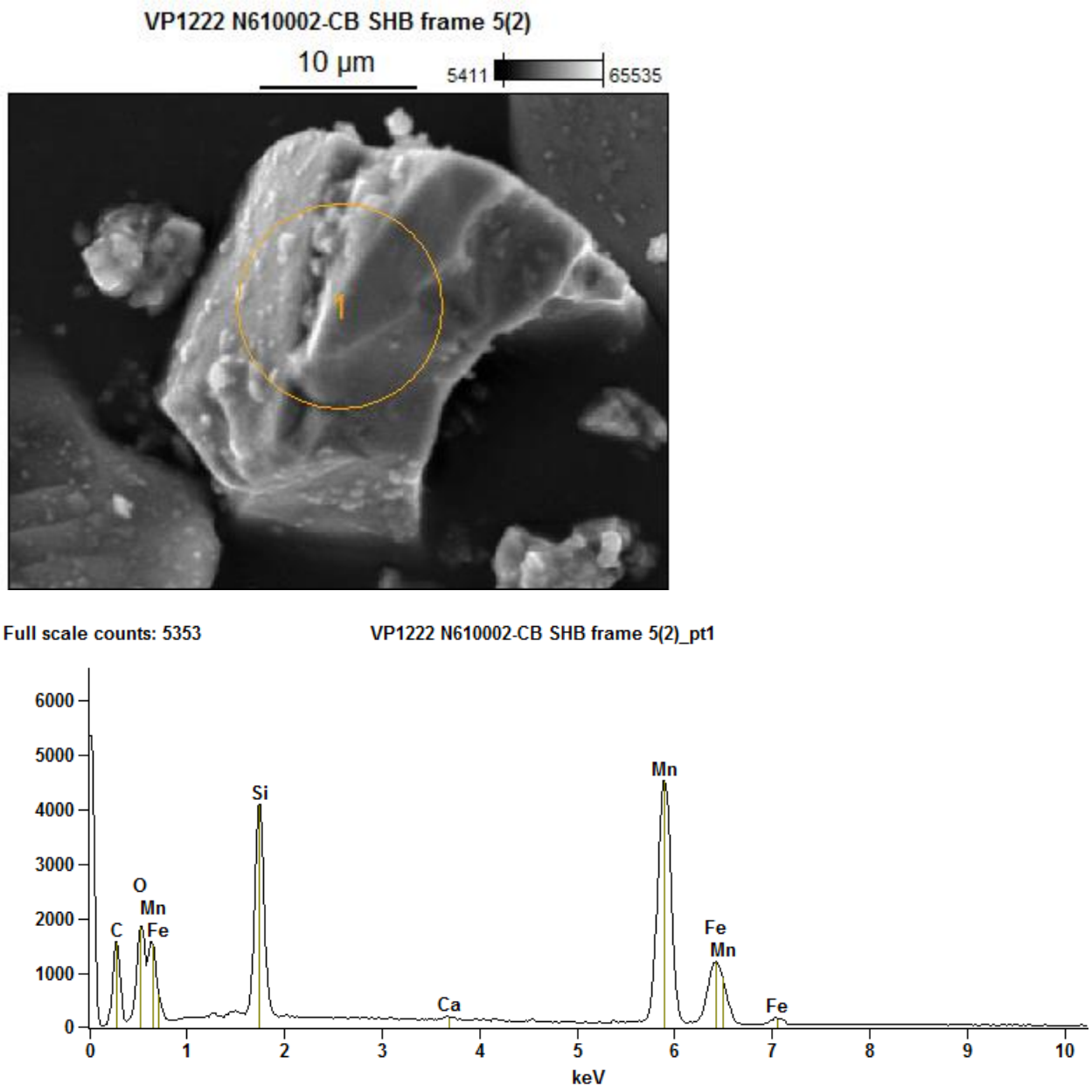


Figure 9b. SEI image and EDS spectrum of typical Mn-bearing particle from S.H. Bell's process materials in East Liverpool, Ohio (N610002-CB).

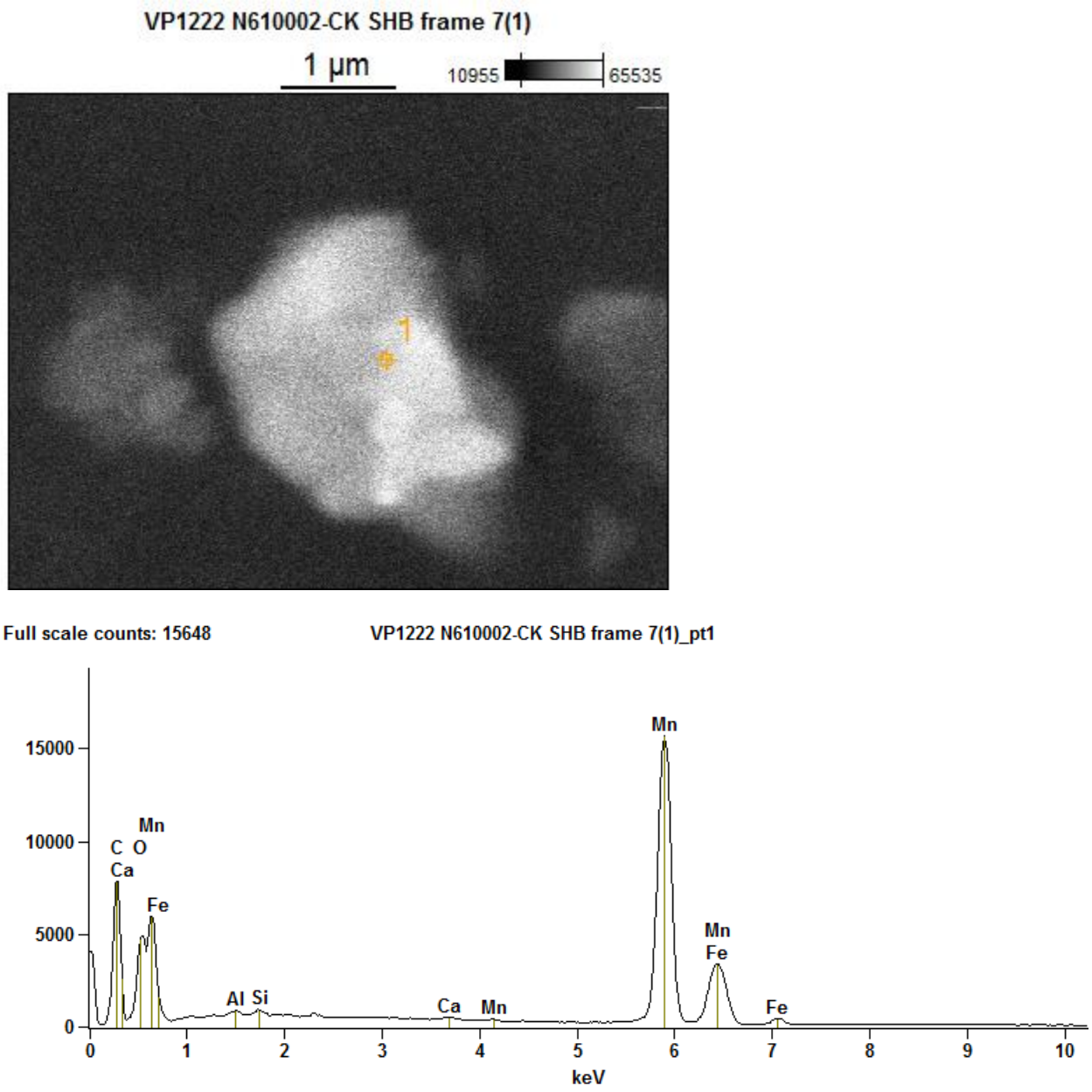


Figure 9c. SEI image and EDS spectrum of typical Mn-bearing particle from S.H. Bell's process materials in East Liverpool, Ohio (N610002-CK).

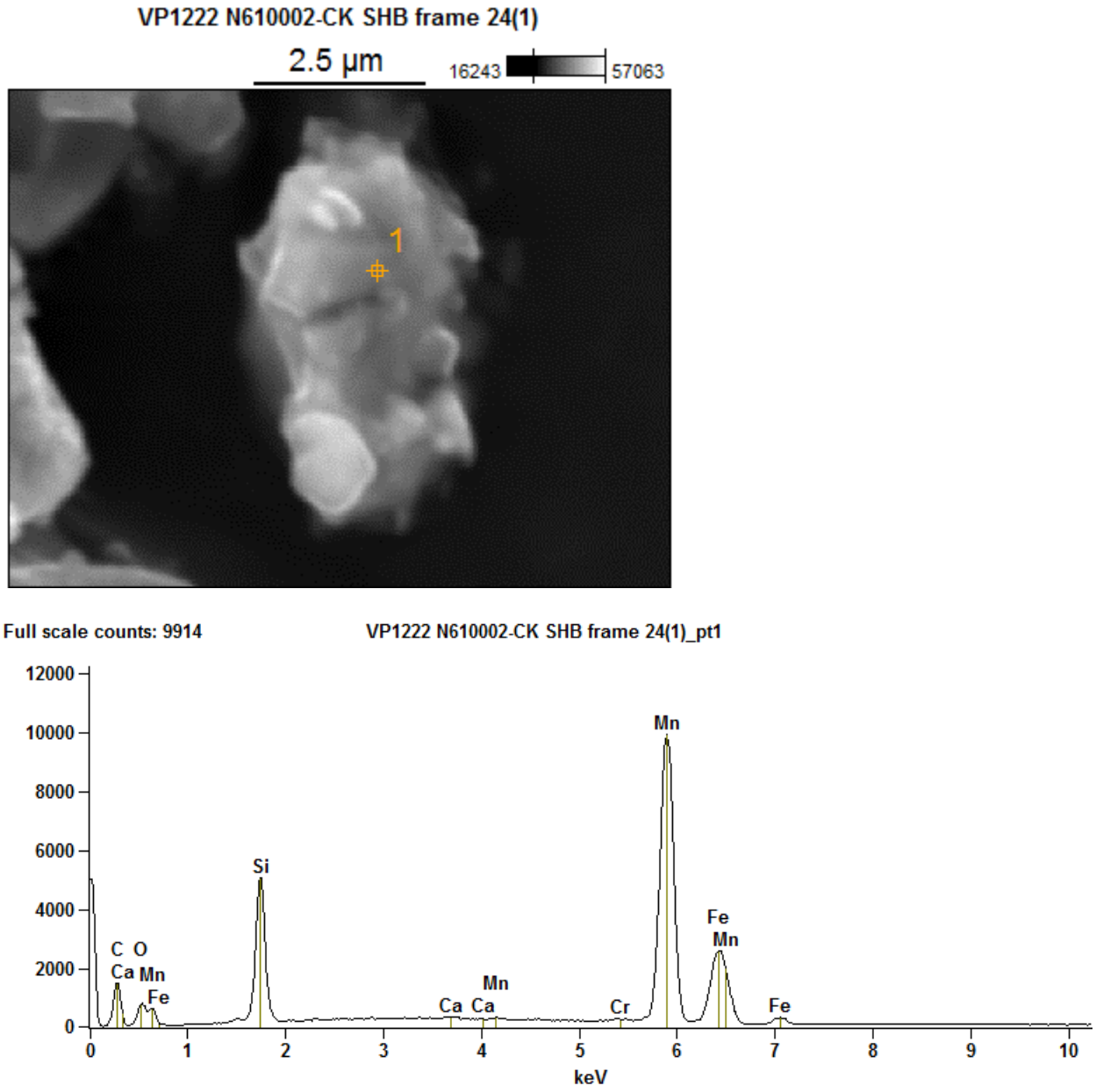


Figure 9d. SEI image and EDS spectrum of typical Mn-bearing particle from S.H. Bell's process materials in East Liverpool, Ohio (N610002-CK).

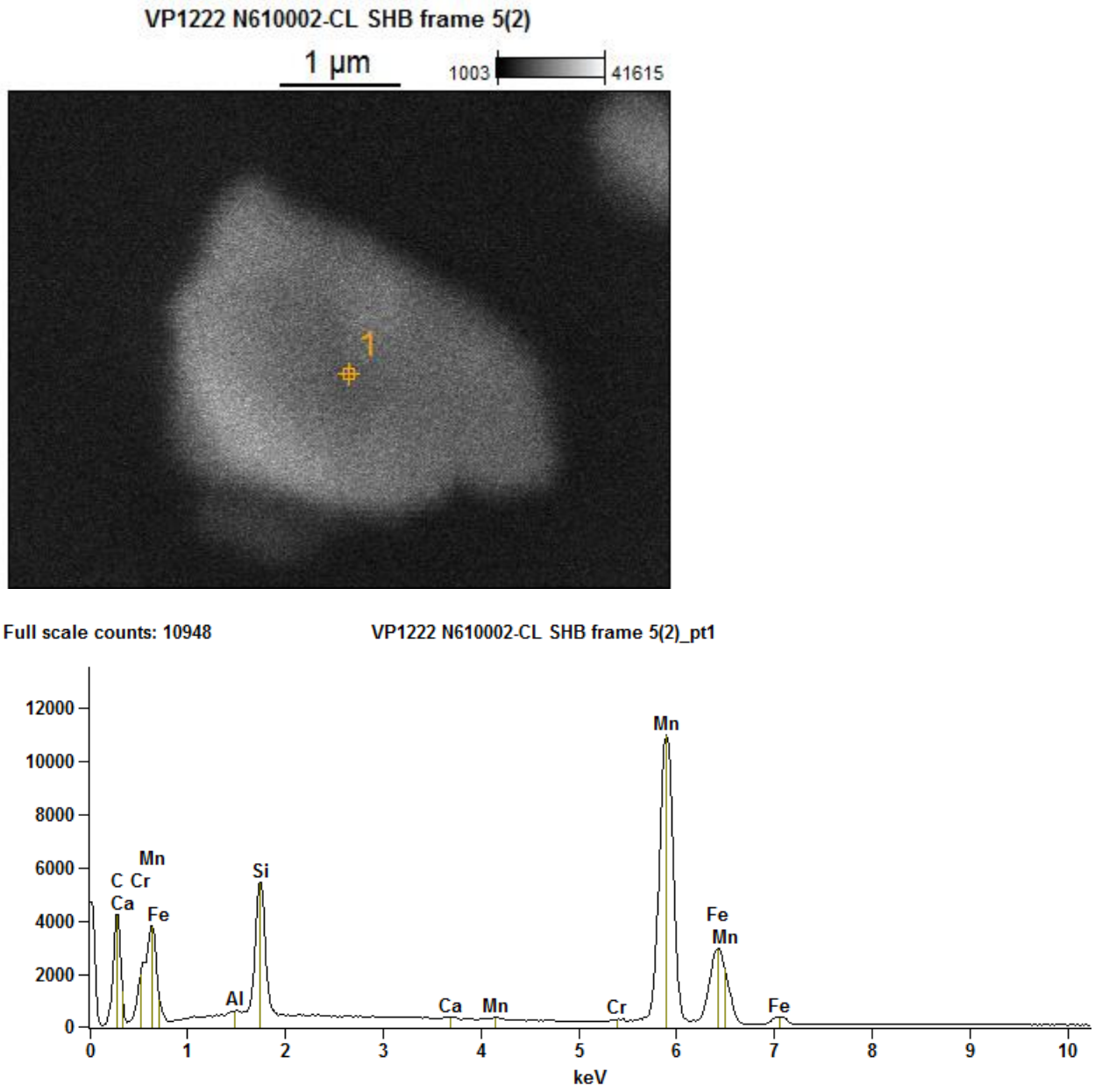


Figure 9e. SEI image and EDS spectrum of typical Mn-bearing particle from S.H. Bell's process materials in East Liverpool, Ohio (N610002-CL).

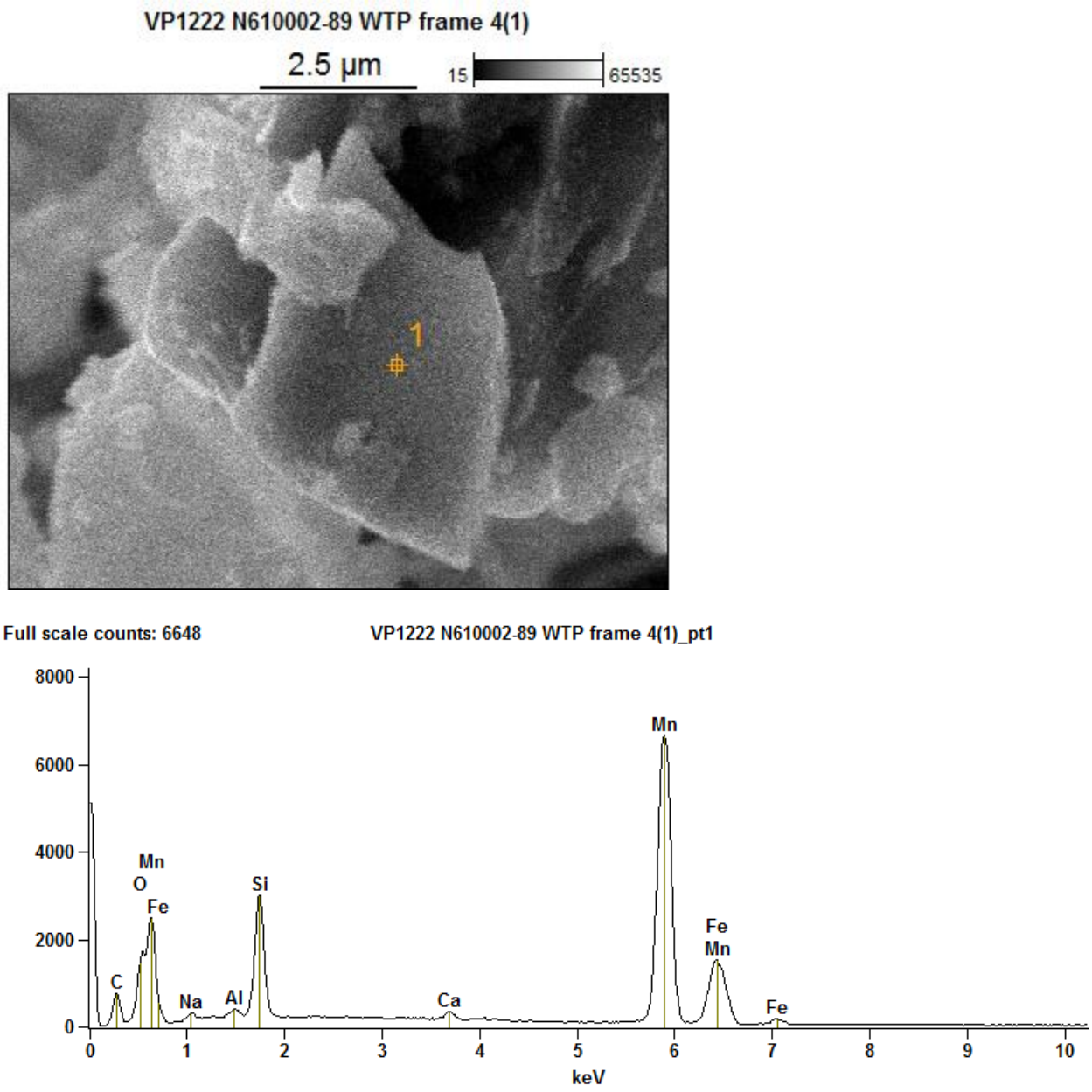


Figure 10a. SEI image and EDS spectrum of typical Mn-bearing particle on a TSP filter collected at the WTP in East Liverpool, Ohio (N610002-89).

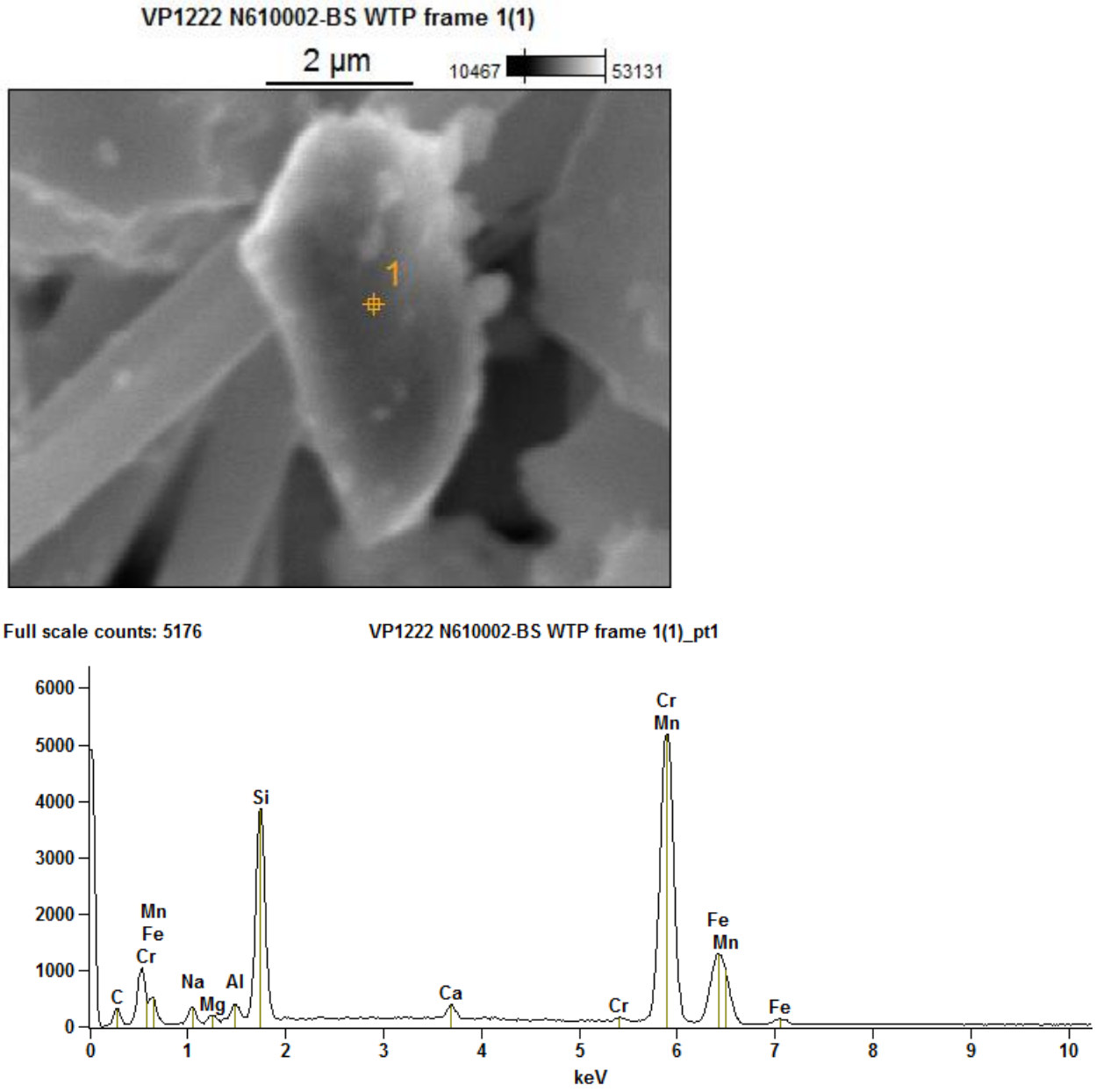


Figure 10b. SEI image and EDS spectrum of typical Mn-bearing particle with trace of Cr on a TSP filter collected at the WTP in East Liverpool, Ohio (N610002-BS).

COMPARISON OF SEM/EDS RESULTS

The Mn-bearing particles observed in the six process materials and six TSP filters were consistently angular in morphology. Furthermore, the type of Mn-bearing particles found in the four process materials examined from S.H. Bell were not distinctive from each other in either morphology or chemical composition. For example, the four Mn-rich materials examined from S.H. Bell consistently contained angular particles of Mn-oxide, micrometer to 10s of micrometers in scale, with variable Ca, Fe, and Si compositions. In contrast, the types of Mn-bearing particles found in the two process materials examined from Hall China were distinctive in chemical composition from each other and from particles in process materials from S.H. Bell. For example, in contrast to Mn-oxide particles in materials from S.H. Bell, Hall China's mixed metal pigment material consisted of oxide particles with distinctly consistent proportions of Cr, Mn, and Fe but without significant Ca or Si. Also, in contrast to Mn-oxide particles in materials from S.H. Bell, Hall China's manganese dioxide material consisted of Mn-oxide without significant Ca, Fe, or Si but occasionally contained Ba.

The typical Mn-bearing particle type observed in the WTP TSP filters consisted of micrometer-scale, angular, Mn-oxide containing significant Ca, Fe, and/or possible Si, corresponding to particles of S.H. Bell's Mn-rich materials. In contrast to the abundant Mn-oxide particles observed in the TSP filters, oxide particles with distinctive proportions of Cr, Mn, and Fe and lacking significant Ca were not observed on TSP filters, nor were Mn-oxide particles containing Ba but lacking significant Cr, Fe, or Ca, suggesting particles such as those comprising Hall China materials were not common on the filters, if they occurred at all. Less frequent occurrences of Mn-rich Fe-oxide and Mn-rich Si-oxide particles were consistent with S.H. Bell materials but not consistent with Hall China's.

MANGANESE IN RELATION TO WIND DIRECTION

Comparing wind direction to Mn abundances showed WTP filters with the highest LA-ICP-MS responses for Mn (cps) were consistently downwind of S.H. Bell (**Figures 6a-b**). To illustrate wind as a discriminator, wind speed and direction for each 24-hour collection period were plotted as wind roses. Wind roses shown as an overlay on each map in **Figures 11a-b** visually represent how wind speed and direction were distributed in the East Liverpool area over 24-hour periods. Wind direction is plotted relative to compass direction, with the length of the spoke (rose petal) proportional to the frequency of the wind in the indicated direction over the 24-hour period. The length of the color bands on each spoke indicates the frequency of the wind speed within a given range for that wind direction. The point of the longest spoke of the wind rose points in the direction the wind was blowing most frequently (National Resources Conservation Service [NRCS], 2017). The center of the wind rose for each sampling date is overlaid at the air monitoring site. The longest wind rose spoke indicates the predominant direction from which the wind blew. The LA-ICP-MS responses for Mn (cps) indicated the relative abundances of Mn found on the TSP filter for that 24-hour sampling period. The

ambient air Mn concentration determined for the associated 24-hour sampling period was also given in **Table 1b**.

The examples shown in **Figures 11a-b** indicated how the 24-hour wind roses, along with the relative Mn abundance and site locations, limited the possible location of the source of airborne particulate matter collected. Relatively low Mn responses were observed at the WTP air monitoring site when the predominant wind was from the west, the direction opposite from which S.H. Bell was located **(Figure 11a)**. In contrast, relatively high Mn responses were consistently observed at the WTP air monitoring site when the predominant wind direction was from the east, the direction in which S.H. Bell was located. In **Figure 11b**, when the predominant wind direction at the WTP was from the east with negligible wind from the direction of Hall China, Mn abundances (cps) were approximately 47x greater compared to when the wind was from the direction of Hall China with negligible wind from the direction of S.H. Bell. Similarly, ambient air Mn concentrations (EPA, 2018) were approximately 32x greater.

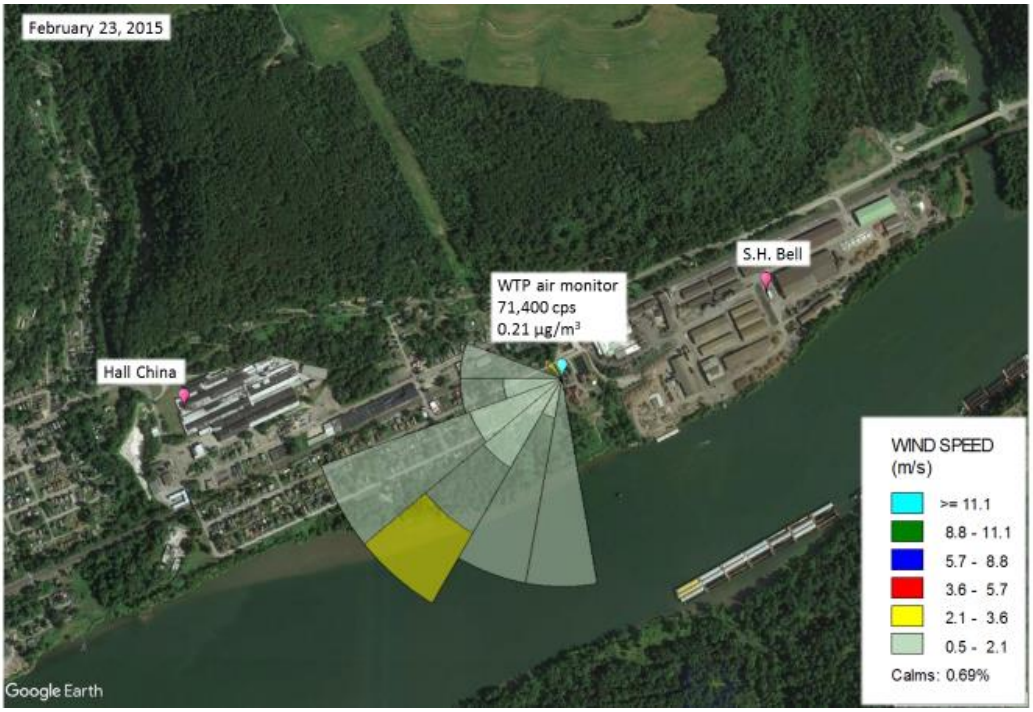


Figure 11a. On February 23, 2015, wind from the west and west-southwest put the WTP air monitor downwind of Hall China with negligible wind from the direction of S.H. Bell. The ambient air Mn concentration of 0.21 µg/m3 and the LA-ICP-MS response for Mn (<72K cps) in the TSP filter collected that day were relatively low.

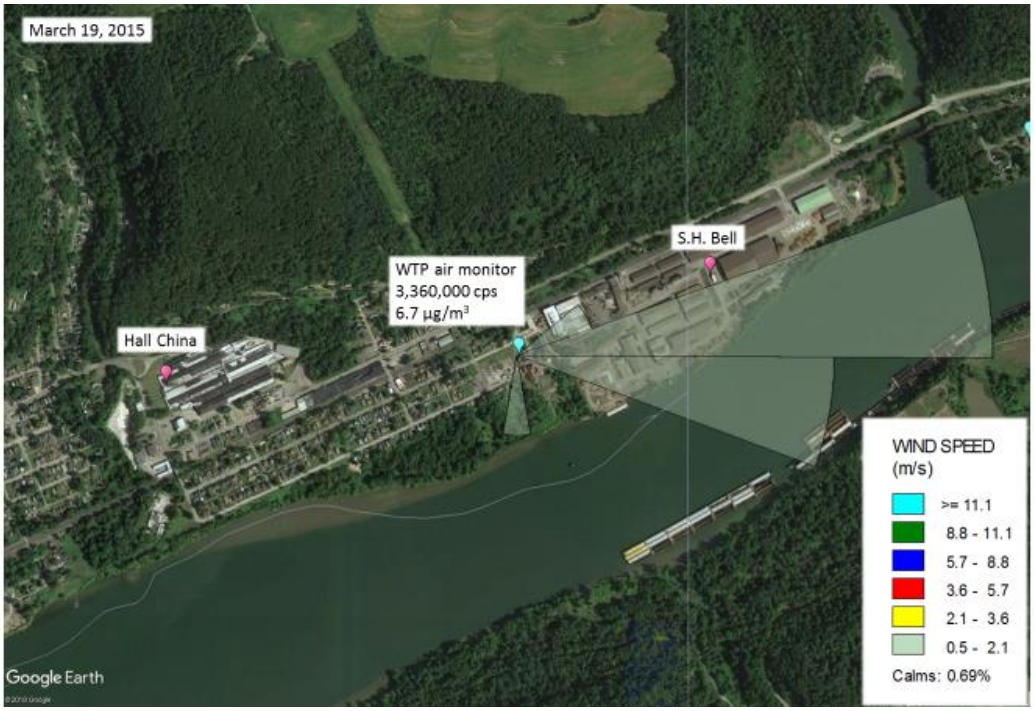


Figure 11b. On March 19, 2015, wind was predominantly from the east, putting the WTP air monitor downwind of S.H. Bell with negligible wind from the direction of Hall China. The ambient air Mn concentration of 6.7 µg/m^3 and the LA-ICP-MS response for Mn (>3M cps) in the TSP filter collected that day were significantly elevated, approximately 32x and 47x greater for Mn, respectively, compared to when the wind was from the direction of Hall China as shown in above Figure 11a.

As depicted in **Figures 6a–b**, the maximum Mn intensities on WTP filters was elevated by approximately an order of magnitude for the downwind S.H. Bell filters (violet triangles) compared to the downwind of Hall China filters (black triangles). Thus, wind direction recorded during the 24-hour filter collection periods was considered to evaluate relative amounts of Mn on WTP filters that may have originated from S.H. Bell or Hall China. On the basis of the results shown in **Figures 2** and **3**, the impact from the seven Midland facilities could be considered negligible. Because no other facilities with possible emissions of Mn particulate material were reported in the surrounding East Liverpool area (Benisek, pers. comm., 2018), only S.H. Bell and Hall China were considered, with all other sources of Mn assumed to be negligible, including background sources.

The stacked bar histogram in **Figure 12** shows the frequency of filters within distinct Mn concentration ranges and wind direction categories. Categories included indeterminate wind direction, invalid wind data, downwind from Hall China, and downwind from S.H. Bell. Although all four wind categories were represented in the lowest concentration range spanning 1 $\mu g/m^3$, only the downwind from Hall China wind category was not present in any of the greater Mn concentration ranges, suggesting any Mn contribution from Hall China was minimal. Conversely, filters downwind from S.H. Bell were represented in five greater Mn concentration ranges. The sum of Mn concentrations for filters collected downwind from Hall China compared to the sum of Mn concentrations for filters collected downwind from S.H. Bell revealed Hall China and S.H. Bell contributed 4.15 and 114 $\mu g/m^3$ Mn, respectively. Based on these Mn concentrations, S.H. Bell contributed approximately 27x times more Mn than Hall China, implicating S.H. Bell as the major source of Mn-bearing particulate matter impacting WTP filters. This finding was consistent with possible significant fugitive dust emissions as a result of S.H. Bell storing Mn-bearing materials in open sheds and outdoor piles and transferring large quantities of these materials in bulk to river barges, trucks, and railcars for shipping.

Furthermore, as a percentage of all the filters analyzed, including those categorized as indeterminate and invalid, any contribution of Mn attributable to Hall China was less than 2 percent of the Mn collected at the WTP air monitoring site. This finding was consistent with no Mn-rich particles similar in composition to those found in process materials from Hall China being definitively observed on WTP filters, which was also consistent with Hall China's limited quantity and use of Mn-bearing materials. These findings and observations suggested emissions from Hall China were negligible.

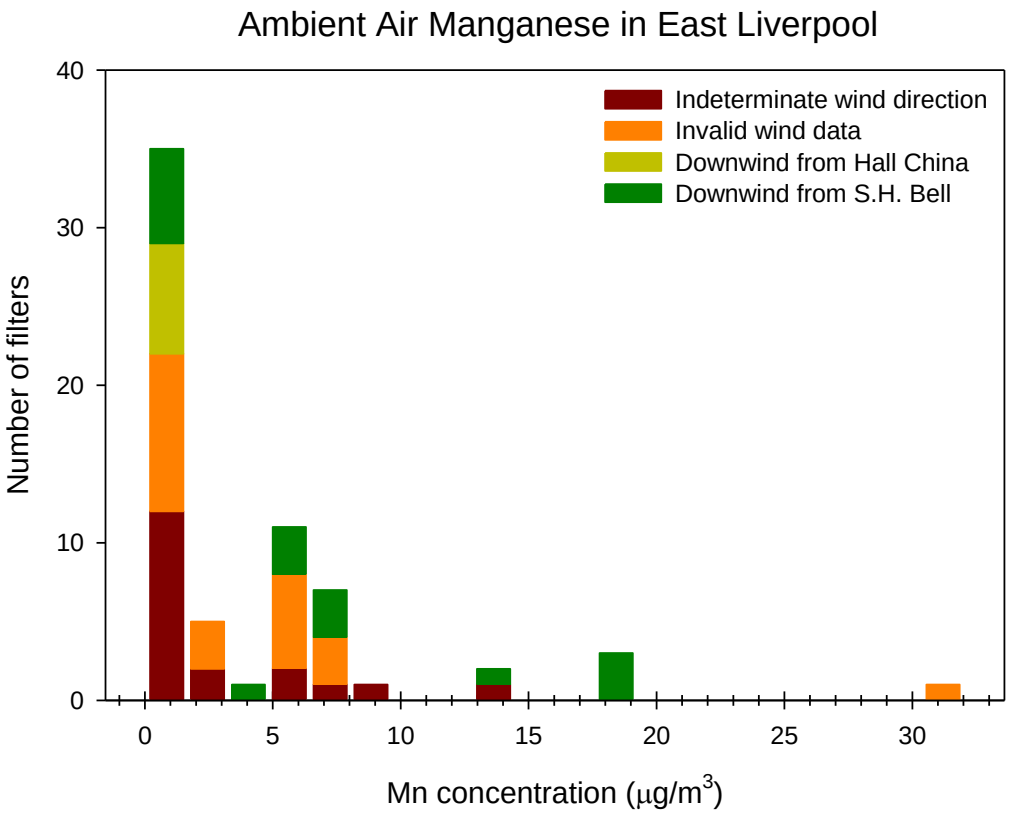


Figure 12. Histogram of ambient air Mn concentration (µg/m^3) at the WTP from January to October 2015 with wind data categories: indeterminate wind direction, invalid wind data, downwind from Hall China, downwind from S.H. Bell.

SUMMARY AND CONCLUSIONS

Abundances of Co and Fe in airborne particulate matter indicated a consistent Mn source composition on WTP filters with high Mn levels. Mn responses by LA-ICP-MS on WTP filters and 24-hour wind data were consistent with an airborne source of Mn particulate matter at the approximate location of the S.H. Bell facility. In addition, angular Mn-bearing particles consistent with Mn-bearing particles from S.H. Bell were the predominant Mn-bearing particle type in WTP filters with high Mn levels. Mn-bearing particles from S.H. Bell were identified as the major contributor of airborne Mn-bearing particulate matter in the East Liverpool area from January 2014 to October 2015. Important findings are summarized below.

- The typical Mn-bearing particle type observed in the WTP filters consisted of micrometer-scale, angular Mn-oxide containing significant Ca, Fe, and/or Si, corresponding to particles of S.H. Bell's Mn-rich materials. In contrast to the abundant Mn-oxide particles observed in the WTP filters, oxide particles with distinctive proportions of Cr, Mn, and Fe and lacking significant Ca were not observed in WTP filters, nor were Mn-oxide particles containing Ba but lacking significant Cr, Fe, or Ca, suggesting particles such as those in Hall China materials were not common on the filters.
- Mn abundance and its relationship with Co and Fe in particulate material from First Energy, Harsco, and Shell were not consistent with these materials contributing significantly to the Mn-bearing particulate matter on WTP filters.
- Significantly greater responses for Mn in particulate matter on filters from the WTP air monitoring site compared to filters from the Glasgow air monitoring site were not consistent with particulate material from the Watco and Whemco facilities contributing significantly to the Mn-bearing particulate matter on WTP filters.
- The relative intensities of Mn, Co, and Fe in TSP and PM_{10} filters corresponded well at higher Mn intensities, suggesting the same source of ambient air Mn for both the smaller and total particle size fractions.
- The upper range of Mn, Co, and Fe intensities for WTP filters were approximately an order of magnitude greater than for Chester and Lawrenceville filters, consistent with a source of airborne Mn originating in East Liverpool and not from northern West Virginia.
- Significantly greater responses for Mn in particulate matter on WTP filters downwind from S.H. Bell compared to filters downwind from Hall China were not consistent with particulate materials from Hall China contributing significantly to the Mn-bearing particulate matter on WTP filters. However, those same significantly greater responses, along with the above findings, indicated particulate materials from S.H. Bell contributed significantly to the Mn-bearing particulate matter on WTP filters.
- The absence of filters collected downwind from Hall China with high Mn concentrations indicated that Hall China contributed negligible Mn to WTP filters.
- The relatively high frequency of filters collected downwind from S.H. Bell with high Mn concentrations and the lack of other potential sources, indicated that S.H. Bell contributed the majority of Mn-bearing particulate material to WTP filters.

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