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Original Article

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Exploring Manganese Fractionation Using a Sequential Extraction Method to Evaluate Welders' Gas Metal Arc Welding Exposures during Heavy Equipment Manufacturing

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Abstract

The National Institute for Occupational Safety and Health (NIOSH) has conducted an occupational exposure assessment study of manganese (Mn) in welding fume at three factories where heavy equipment was manufactured. The objective of this study was to evaluate exposures to different Mn fractions using a sequential extraction procedure. One hundred nine worker-days were monitored for either total or respirable Mn during gas metal arc welding. The samples were analyzed using an experimental method to separate different Mn fractions based on selective chemical solubility. The full-shift total particle size Mn time-weighted average (TWA) breathing zone concentrations ranged 0.38–26 for soluble Mn in a mild ammonium acetate solution; 3.2–170 for $Mn^{0,2+}$ in acetic acid; 3.1–290 for $Mn^{3+,4+}$ in hydroxylamine-hydrochloride; and non-detectable (ND)–130 µg m^{-3} for insoluble Mn fractions in hydrochloric and nitric acid. The summation of all the total particulate Mn TWA fractions yielded results that ranged from 6.9 to 610 µg m^{-3}. The range of respirable size Mn TWA concentrations were 0.33–21 for soluble Mn; 15–140 for $Mn^{0,2+}$; 14–170 for $Mn^{3+,4+}$; 5.3–230 for insoluble Mn; and 36–530 µg m^{-3} for Mn (sum of fractions). Total particulate TWA GM concentrations of the Mn (sum) were 53 (GSD = 2.5), 150 (GSD = 1.7), and 120 (GSD = 1.8) µg m^{-3} for the three separate factories. Although all of the workers' exposures were measured below the OSHA regulatory permissible exposure limit and NIOSH recommended exposure limit for Mn, 70 welders' exposures exceeded the ACGIH Threshold Limit Values® for total Mn (100 µg m^{-3}) and 29 exceeded the recently adopted respirable Mn TLV (20 µg m^{-3}). This study shows that a welding fume exposure control and

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management program is warranted for Mn, which includes improved exhaust ventilation and may necessitate the use of respiratory protection, especially for welding parts that impede air circulation.

Keywords: GMAW; metal inert gas; MIG; Mn; oxidation state; solubility

Introduction

The principal objective of this research study was to evaluate workers' exposures to manganese (Mn) in welding fume (WF), often associated with mild carbon steel (CS) welding. The specific aim was to evaluate Mn in WF collected in field settings by applying extraction methods to measure different fractions based on solubility, utilizing industrial hygiene air sampling and analytical methods. The focus of this manuscript is to report on three site evaluations at heavy equipment manufacturers in 2010. The vast majority of the hot work for these manufacturing jobs used gas metal arc welding (GMAW) on CS. A few welders were exposed to lesser amounts of grinding dust.

Currently, occupational evaluation criteria for Mn are based on chemical measurement of elemental, inorganic Mn without further characterization. However, Mn in WF binds with many other elements (Jenkins and Eagar, 2005), and Mn can exist in six different oxidation states (CRC, 2013). Although Mn neurotoxicity has been reported for many years, the mechanism is not fully understood (Pal *et al.*, 1999). Archibald and Tyree (1987) proposed that Mn can produce varying toxicities contingent upon oxidation state. Oberdoster and Cherian (1988) reported that they believed Mn^{3+} and Mn^{4+} were the most toxic oxidation states. However, the World Health Organization (1999) reported that 'little is known about the relative toxicity of different Mn compounds'.

An *in vitro* study conducted by Chen *et al.* (2001) examined the effect of Mn oxidation state on some mitochondrial enzymes containing Fe-S. Their results suggest that Mn^{3+} species appear more cytotoxic than Mn^{2+} compounds, possibly due to higher oxidative reactivity. The rate of (saturable) Mn^{2+} transport through the blood–brain barrier is believed to be an important determinant of Mn neurotoxicity (Pal, 1999). Transferrin-mediated transfer across cell membranes is another proposed pathway into cellular tissues; Mn is in the trivalent form when conjugated with transferrin (Aschner and Aschner, 1991). The olfactory nerve route, which directly transports Mn from the nasal cavities to the olfactory bulb, is also a factor for Mn deposition in the brain (Tjalve and Henriksson, 1999; Sunderman, 2001).

Frequently, symptomatic workers have presented with Mn accumulation in the brain in area(s) normally associated with divalent Mn which may impact transport regulation (Pal *et al.*, 1999; Olanow, 2004) The chemical and biological solubility of Mn compounds is not easily characterized with conventional analytical methods (Taube, 2012). The paucity of occupational exposure studies regarding Mn oxidation states served as the impetus of the present study to evaluate welders' breathing zone (BZ) exposures because the oxidation state and solubility of Mn in welding aerosols may affect the transport of Mn across cellular membranes, influence brain deposition, and may have implications for Mn cytotoxicity and neurotoxicity (Chen *et al.*, 2001; Aschner and Guilarte, 2007; Roth, 2009).

New methods for measuring Mn fractions were explored by applying the sequential extraction procedures reported by Tessier *et al.* (1979) and modified by Thomassen *et al.* (2001). In the latter study, workers were monitored for dust exposures from raw materials, intermediate materials and finished products, and metal fume in the Mn alloy industry in Norway. This method measures four Mn fractions based on chemical solubility of Mn compounds optimized for soluble Mn; $Mn^{0,2+}$; $Mn^{3+,4+}$; and insoluble Mn. Thomassen *et al.* (2001) and Ellingsen *et al.* (2003) proposed that Mn compounds one could expect in each extraction include: (i) MnF_2, $MnCl_2$ in soluble Mn fraction; (ii) Mn metal, MnO, divalent Mn of Mn_3O_4 in $Mn^{0,2+}$ fraction; (iii) trivalent Mn of Mn_3O_4, Mn_2O_3, MnO_2 in $Mn^{3+,4+}$ fraction; and (iv) SiMn in insoluble Mn fraction. The method was critiqued with Mn in WF by Berlinger *et al.* (2009) using area sampling with Higgens-Dewell cyclones. X-ray diffraction results did not fully confirm the inductively coupled argon plasma–atomic emission spectroscopy (ICP-AES) results but, even with this limitation, data for different Mn species in complex WF emissions may prove useful for assessing bio-accessibility in future research.

Background

In excess of 300 000 US workers are defined as welders, brazers, and solders (US Bureau of Labor Statistics, 2011), most of whom are employed in the manufacturing, construction, energy, and transportation sectors. Approximately 100 different welding and thermal cutting processes exist (Linnert, 1994). Details of GMAW, also called metal inert gas (MIG) welding, are published elsewhere (Burgess, 1995; Harris, 2002). In short, GMAW uses electric current to produce a molten metal pool from a consumable wire at the joint; an inert gas protects the molten metal to minimize oxidation. As a result of high process temperatures, welders are exposed to aerosol emissions composed of metals, metal oxides, silicates, and fluorides (NIOSH, 1988; Burgess, 1995; Harris, 2002; Antonini, 2003). Occupational studies have reported a number of health effects in welders, such as lung disease and possibly neurotoxicity. Epidemiologic studies and case reports of welders have shown an excessive incidence of acute and chronic respiratory diseases (NIOSH, 1988).

The particle sizes of WF aerosol is variable but the primary particle is typically in nanometer sizes (i.e. <0.1 μm), which will form larger aggregates and agglomerates, most of which are produced in sub-micrometer particle sizes (AWS, 1983; Hewett, 1995; Zimmer and Biswas, 2001; Jenkins *et al.*, 2005; Cena, 2014). The size of the welding aerosol will determine the location of particle penetration and deposition within the nasopharnyx and respiratory system; even the larger welding particle clusters are typically of respirable sizes, much of which deposits in the pulmonary alveoli.

Manganese is a common ingredient of many steels, welding rods/wires to impart strength, hardness, and ductility to the metal (Linnert, 1994). The principal health effects of excessive occupational Mn exposure are neurological abnormalities and respiratory effects (e.g. irritation, bronchitis, pneumonitis) (Hathaway *et al.*, 1996; ACGIH, 2008). Most notably, excessive Mn exposure can cause manganism, a neurological syndrome with well-recognized movement disorders (e.g. poor hand-eye coordination, reduced response speed, slow movement, disturbed gait, and increased tremor) (Roels *et al.*, 1992; Mergler *et al.*, 1994; Korczynski, 2000; Antonini, 2003; Antonini *et al.*, 2006; Bowler *et al.*, 2006a,b). Manganism is a progressive occupational disease which develops gradually over time, but is often unrecognized until the worker is irreversibly affected (Rodier, 1955).

Manganism has been reported in workers who had high Mn exposures in ore mining and refining, ferroalloy, and dry cell battery industries (ACGIH, 2008). Yet the relationship between chronic low level Mn exposure, including those associated with welding, and manganism is unclear because the initial signs and symptoms may be subtle, subclinical neurobehavioral effects (i.e. mild abnormalities that may not be recognized as a medical problem). Baker *et al.* (2015) reported in an inception cohort of asymptomatic welding trainees, that T1-weighted index changes in magnetic resonance images of the brain were associated with increased cumulative exposure to low level Mn before any clinical symptoms were evident. Other studies of welders have shown neurobehavioral effects from low level Mn exposures (<200 μg m^{-3}) including short-term memory loss, mood swings, altered reaction times, and eye-hand coordination deficits (Bowler *et al.*, 2007; Wastensen *et al.*, 2012). However, the association of exposure to WF with the development of clinical neurological disease is inconclusive (Santamaria *et al.*, 2007), and the use of neurobehavioral tests for epidemiological and risk assessment studies is not universally accepted (Lees-Haley *et al.*, 2004; Olanow, 2004; Jancovik, 2005).

Occupational exposure criteria

The occupational exposure limits (OELs) available for Mn are inconsistent. The NIOSH REL for Mn is an 8–10 h (40 h week) time-weighted average (TWA) concentration of 1000 μg m^{-3}, with a short-term exposure limit (STEL) of 3000 μg m^{-3} over 15 min, based on central nervous system effects and pneumonitis (NIOSH, 1992). The OSHA PEL for Mn is a ceiling limit of 5000 μg m^{-3} for protection against eye and respiratory irritation (OSHA, 2015). The ACGIH TLV for total (inhalable) inorganic Mn is 100 μg m^{-3}, measured as an 8-h TWA which was established to reduce central nervous system impairment (e.g. psychomotor abnormalities) (ACGIH, 2008, 2015). In 2012, ACGIH adopted a respirable Mn 8-h TLV of 20 μg m^{-3}. For WF exposures, sampling total Mn using closed-face filter cassettes approximates the inhalable levels (conversion factor = 1.0) because of the very small particle size distribution of the fume emissions (Werner *et al.*, 1996). OELs for Mn are not specific to Mn in WF but are applicable to all sources of Mn aerosols.

Materials and methods

One hundred nine worker-days were monitored throughout three heavy equipment plants in 2010. At all three factories, welders were monitored when working on CS parts. Three consecutive days of monitoring were conducted with 46 different welders in the summer at Plant A using American Welding Society (AWS) ER70S-3 (0.045 mm; 1% Mn) class wire and 95:5% argon (Ar):carbon dioxide (CO_2) shielding gas mixture. Plant B was also monitored over three consecutive days in the summer with 33 participating welders who used AWS ER70S-6 (0.052 mm; <2% Mn) wire with 90:10% (Ar:CO_2) gas. Plant C was a smaller factory so only two consecutive days were needed to sample 30 welders during the winter. American Welding Society ER70S-3 (0.045 mm; 1% Mn) class wire and 95:5% (Ar:CO_2) gas mixture was utilized in Plant C, the same as in Plant A.

Eighty total and 29 respirable particulate Mn TWA concentrations were measured as specified in Table 1.

Full-shift BZ exposure concentrations were measured on each welder over 10–12 h work shifts, either for total or respirable Mn, but not both. No welder was monitored more than once. The number of respirable samples collected each day was contingent on the number of impactor devices and number of welders available each day. When a department had multiple welders, an effort was made to include a respirable measurement. Personal air sampling pumps were used at nominal flow rates of 2.5 lpm for total particulate or 2.0 lpm for respirable particulate. Total particulate samples were collected using 25-mm diameter, 0.8 µm pore size, mixed cellulose ester (MCE) sample filters in closed-face cassettes (SKC, Inc.). The filter cassettes were attached on workers' lapels close to their neck such that the filter position was inside of their welding helmets when closed in accordance with the ISO welding standard (ISO, 2011). Respirable particulate Mn samples were collected on 37 mm, 0.8 µm pore size, MCE filters (SKC, Inc.) which were placed in a SKC Parallel Particle Impactor®, a respirable particle size selecting device reported to more closely approximate the alveolar particle penetration curve (CEN, 1993; ISO, 1995; ACGIH, 2015) than cyclone samplers. The respirable samples were collected outside of the welding helmets because the dimensions of the impactor precluded placement inside the helmet.

Welders' BZ samples were analyzed for four fractions of Mn based on a procedure published by Thomassen *et al.* (2001) with modifications. Speciation of the Mn fractions was accomplished using a sequential extraction procedure to extract Mn based on chemical solubility. The cassette and impactor filters were extracted in polypropylene tubes with 25-ml filter cup inserts equipped with 0.2-µm polyvinylidene fluoride membranes (Grace Davidson) and prepared using a triplicate sequential extraction procedure: (i) 10-ml of 0.01 M ammonium acetate at room temperature for 90 min (optimized for and defined as soluble Mn); (ii) 10-ml of 25% acetic acid, heated at 75°C for 90 min (defined as Mn^0 and Mn^{2+} oxidation states); and (iii) 10-ml of 0.5% hydroxylamine-hydrochloride in 25% acetic acid, heated at 75°C for 90 min (defined as Mn^{3+} and Mn^{4+} oxidation states). The fourth extraction step in the method described by Thomassen *et al.* (2001) was modified to measure insoluble Mn remaining after the first three extractions using the same digestion procedure as published in NIOSH Manual of Analytical Methods (NMAM) 7303 (NIOSH, 2003): (i) 2.5-ml of 12.1 M hydrochloric acid, hot block heated at 95°C for 15 min, cooled; (ii) 2.5-ml of 15.6 M nitric acid added to the extract, hot block heated at 95°C for 15 min, cooled; and (iii) dilution to 25-ml with deionized water.

Between each extraction step, the samples were spun in a centrifuge; the extract was collected and the filter cup was transferred to a clean 50-ml polypropylene centrifuge tube. The sample extracts were analyzed by ICP-AES using the instrumental parameters described in NMAM 7303. The LODs were 0.08; 0.02; 0.29; and 0.15 µg per filter for soluble Mn; $Mn^{0,2+}$; $Mn^{3+,4+}$; and insoluble Mn fractions, respectively. Percent recovery of QC laboratory standards were 91.7% for soluble Mn (using Mn nitrate as the test compound); 98.2% for Mn^0 (using Mn powder); 102.6% for Mn^{2+} (using MnO); 88.1% for Mn^{3+} (using Mn_2O_3); 89.9% for Mn^{4+} (using Mn_3O_4), and 75.1% for insoluble Mn (using SiMn). Details of the laboratory evaluation of this extraction procedure were previously published (Andrews *et al.*, 2015). Spike QC tests were conducted in triplicate; the percent difference between the high and low recoveries were 2.4% for soluble Mn, 12.5% for $Mn^{0,2+}$, and 8.0% for $Mn^{3+,4+}$.

While certified WF laboratory standard materials are not available to fully validate the sequential extraction procedure, suitable representative materials were tested. Andrews *et al.* (2015) evaluated Mn speciation for GMAW-CS using chamber-generated bulk WF. Using Mn(sum) from the sequential extraction method (52.5 mg g^{-1}-WF), and hot block acid method NMAM 7303 as a reference value (57.5 mg g^{-1}-WF), the percent difference of 7.1% was judged not to have practical importance for industrial hygiene field samples.

Various exposure groups stratified by manufacturing plant and particle size were compared using simple descriptive statistics. Assumptions of normality were better met by taking logarithms of the TWA exposure data for both total and respirable particulate. All statistical analyses were performed using SAS Software (version 9.2, SAS Institute Inc., Cary, NC). Data were summarized by reporting the minimum, maximum, geometric mean (GM), and geometric standard deviation (GSD). In the case of values below the LOD, the maximum likelihood (Jin, 2011) GM and GSD were calculated by analyzing

Table 1. Distribution of total and respirable samples collected by survey day for three heavy equipment plants.

Plant	Particle size	Day 1	Day 2	Day 3	All days
A	Total	14	13	10	37
	Respirable	4	3	2	9
B	Total	11	9	3	23
	Respirable	4	4	2	10
C	Total	10	10	0	20
	Respirable	5	5	0	10

the log of the values in the PROC LIFEREG procedure of SAS (9.3). To create box plots (presented in Fig. 1), the minimum, maximum, median, 25th and 75th percentiles were calculated stratified by plant, particle size, and Mn fraction. In addition, the ratio of each Mn fraction to the Mn(sum) were calculated as a percentage for each TWA measurement. These percentages were also summarized by reporting minimum, maximum, GM, and GSD, using the maximum likelihood estimate of the minimum detectable concentrations in the case of values below the LOD. To compare the difference between total and respirable particulate for all three plants combined, a two sample *t*-test comparing the means of the log of the measurements was conducted for each Mn fraction. Each TWA measurements were independent because the samples were collected separately on only one welder at high production welding plants without discernible differences between sampling days. The results are presented as difference ratios with 95% confidence intervals and *P* values.

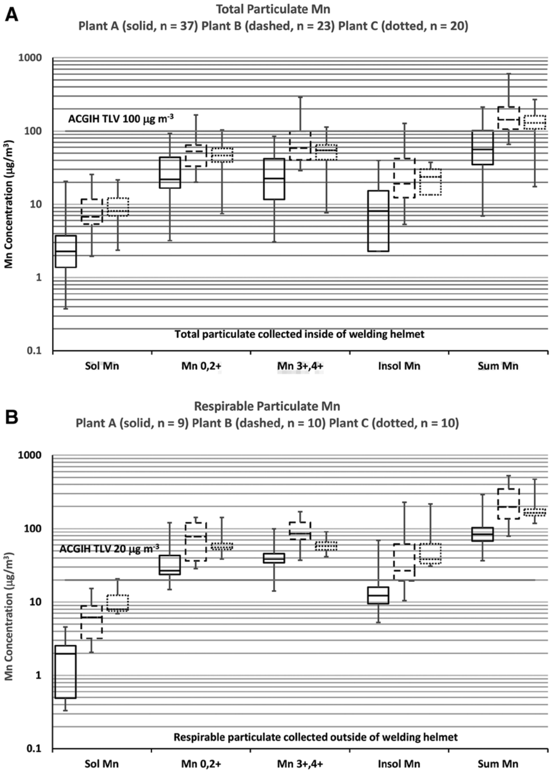

Figure 1. Total and respirable particulate TWA breathing zone concentrations (µg m^{-3}) of manganese fractions from gas metal arc welding at three heavy equipment manufacturing plants. Sol Mn, manganese concentration dissolved in first sequential extraction solution: 0.01 molar ammonium acetate, room temperature (over 90 min); Mn 0, 2+, manganese concentration dissolved in second solution: 25% acetic acid, 75°C (over 90 min); Mn 3+, 4+, manganese concentration dissolved in third solution: 0.5% hydroxylamine-hydrochloride in 25% acetic acid, 75°C (over 90 min); Insol Mn, manganese concentration dissolved in fourth solutions: hydrochloric acid, 95°C (over 15 min) and nitric acid, 95°C (over 15 min); Sum Mn, addition of all four previous extraction manganese concentrations.

Results

Total particulate manganese

Welders' full-shift TWA concentrations for total particulate Mn fractions are presented in Table 2, stratified by three manufacturing plants and all plants combined. Overall, the Mn speciation results (µg m^{-3}) ranged 0.38–26 for soluble Mn; 3.2–170 for $Mn^{0,2+}$; and 3.1–290 for $Mn^{3+,4+}$; and non-detectable (ND)–130 for insoluble Mn fractions. The summation of all the total particulate Mn fractions ranged from 6.9 to 610 µg m^{-3} and the GM (GSD) for all plants was 88 µg m^{-3} (2.4). All of the total Mn(sum) TWA exposure levels were well below the OSHA ceiling PEL for Mn (5000 µg m^{-3}) and NIOSH REL (1000 µg m^{-3}).

The highest total Mn TWA concentrations were measured in the summer at Plant B where larger equipment was made. At this plant, the GM (GSD) concentrations (µg m^{-3}) were 7.7 (1.8) for soluble Mn; 54 (1.7) for $Mn^{0,2+}$; 65 (1.7) for $Mn^{3+,4+}$; 23 (2.2) for insoluble Mn fractions; and 150 (1.7) for Mn(sum). Nineteen (out of 23) welders' total Mn(sum) exposures exceeded the ACGIH TLV for inorganic, elemental Mn (100 µg m^{-3}), which was lowered from 200 µg m^{-3} in 2012. The lowest BZ levels were observed in Plant A in the summer when doors and windows were opened, yet 11 (out of 37) exposures measured with filter cassettes exceeded the total Mn TLV; 9 more were elevated over 100 µg m^{-3} using respirable samplers. The GM (µg m^{-3}) (GSD) Mn(sum) concentrations were 150 (1.7), 120 (1.8), and 53 (2.5) for Plant B, C, and A, respectively. The GM concentrations exceeded the TLV for total particulate Mn for Plants B and C but not for Plant A. Further, some individual measurements of $Mn^{0,2+}$ and $Mn^{3+,4+}$ fractions also exceeded the total Mn TLV in plants B and C.

Respirable particulate manganese

Respirable particulate full-shift Mn TWA concentrations are summarized for each plant separately and combined in Table 3. Overall, the respirable Mn speciation results (µg m^{-3}) ranged 0.33–21 for soluble Mn; 15–140 for $Mn^{0,2+}$; 14–170 for $Mn^{3+,4+}$; and 5.3–230 for insoluble Mn fractions. The summation of all the respirable particulate Mn fractions ranged from 36 to 530 µg m^{-3} and the GM (GSD) for all plants was 150 µg m^{-3} (1.9). The same trend was apparent as with the total particulate data:

Table 2. Welders' TWA breathing zone concentrations (µg m^{-3}) of total particle size manganese (Mn) fractions measured at three heavy equipment plants.

Plant	Parameter	TWA concentration				
		Mn (Sol)	Mn (0, +2)	Mn (+3, +4)	Mn (Insol)	Mn (Sum)
A	*n*	37	37	37	33	37
	Minimum	0.38[a]	3.2	3.1	ND[b]	6.9
	GM (GSD)	2.2 (2.5)	23 (2.5)	21 (2.4)	4.7 (5.1)	53 (2.5)
	Maximum	21	93	84	40	210
B	*n*	23	23	23	23	23
	Minimum	2.0	20	29	5.3	66
	GM (GSD)	7.7 (1.8)	54 (1.7)	65 (1.7)	23 (2.2)	150 (1.7)
	Maximum	26	170	290	130	610
C	*n*	20	20	20	19	20
	Minimum	2.4	7.4	7.7	ND[b]	18
	GM (GSD)	8.9 (1.6)	44 (1.7)	46 (1.9)	17 (2.5)	120 (1.8)
	Maximum	22	100	110	37	270
All	*n*	80	80	80	75	80
	Minimum	0.38	3.2	3.1	ND[b]	6.9
	GM (GSD)	4.5 (2.7)	34 (2.3)	35 (2.5)	10 (4.2)	88 (2.4)
	Maximum	26	170	290	130	610

Sol Mn, manganese concentration dissolved in first sequential extraction solution: 0.01 molar ammonium acetate, room temperature (over 90 min); Mn 0, 2+, manganese concentration dissolved in second solution: 25% acetic acid, 75°C (over 90 min); Mn 3+, 4+, manganese concentration dissolved in third solution: 0.5% hydroxylamine-hydrochloride in 25% acetic acid, 75°C (over 90 min); Insol Mn, manganese concentration dissolved in fourth solutions: hydrochloric acid, 95°C (over 15 min) and nitric acid, 95°C (over 15 min); Sum Mn, addition of all four previous extraction manganese concentrations.

[a] Data in this table reported with two significant figures.

[b] ND = non-detectable. *n* lists the number of detectable samples. The GM (GSD) calculations used a maximum likelihood method to account for values below the minimum detectable concentration.

the highest exposures occurred in Plant B and the lowest exposures in Plant A. The GM respirable Mn(sum) were 200, 190, and 85 µg m^{-3}, respectively, for Plant B, C, and A with GSDs ranging between 1.5 and 1.8. OSHA PEL and NIOSH REL for respirable particulate Mn are not available and the ACGIH respirable Mn TLV was not adopted until 2 years after the data was collected for this field survey. However, in all 29 measurements obtained with an impactor sampler, the ACGIH TLV for elemental respirable Mn (20 µg m^{-3}) was exceeded; many of which were greater than an order of magnitude higher than the TLV. Moreover, the GM respirable concentrations for the Mn$^{0,2+}$ and Mn$^{3+,4+}$ fractions were greater than the TLV for all three plants.

Ratio of manganese fractions to manganese summation

The ratios of the four Mn fractions with the summation of all Mn fractions were calculated individually for each TWA measurement. Table 4 presents the GM and GSD for these fractional ratios for each plant site stratified by particle size. As shown, the vast majority of the Mn(sum) is partitioned in the Mn$^{0,2+}$ and Mn$^{3+,4+}$ fractions (e.g. the average of the ratio summations for these two Mn fractions were 79 and 75% for total and respirable particulate, respectively). Soluble Mn occurred in the lowest proportions, which ranged 2–8% of Mn(sum), while the insoluble Mn results ranged 9–28% of Mn(sum).

Discussion

Analyzing the Mn fractions with the sequential digestion procedure is an experimental method. As such, the OELs from NIOSH, OSHA, and ACGIH are not directly relevant because the OELs are published for all inorganic Mn, measured as elemental Mn, and OELs for evaluating the specific Mn fractions have not been established. Summing the component Mn fractions, however, may approximate the full elemental Mn concentration, which may be used for comparison to legacy data and applied to OELs.

Total particulate BZ air samples collected during this survey were initially placed inside of the welding helmets in accordance with the International Organization for Standardization (ISO, 2011). Monitoring within the

Table 3. Welders' TWA breathing zone concentrations (μg m^{-3}) of respirable particle size manganese (Mn) fractions measured at three heavy equipment plants.

Plant	Parameter	TWA concentration				
		Mn (Sol)	Mn (0, +2)	Mn (+3, +4)	Mn (Insol)	Mn (Sum)
A	*n*	9	9	9	9	9
	Minimum	0.33[a]	15	14	5.3	36
	GM (GSD)	1.3 (2.6)	32 (1.9)	37 (1.7)	13 (2.0)	85 (1.8)
	Maximum	4.6	120	100	69	290
B	*n*	10	10	10	10	10
	Minimum	2.1	28	37	10	79
	GM (GSD)	5.7 (1.9)	70 (1.8)	87 (1.6)	35 (2.4)	200 (1.8)
	Maximum	15	140	170	230	530
C	*n*	10	10	10	10	10
	Minimum	6.9	38	42	31	120
	GM (GSD)	9.7 (1.4)	63 (1.5)	60 (1.3)	52 (1.9)	190 (1.5)
	Maximum	21	140	90	220	470
All	*n*	29	29	29	29	29
	Minimum	0.33	15	14	5.3	36
	GM (GSD)	4.3 (2.9)	53 (1.9)	58 (1.7)	29 (2.6)	150 (1.9)
	Maximum	21	140	170	230	530

Sol Mn, manganese concentration dissolved in first sequential extraction solution: 0.01 molar ammonium acetate, room temperature (over 90 min); Mn 0, 2+, manganese concentration dissolved in second solution: 25% acetic acid, 75°C (over 90 min); Mn 3+, 4+, manganese concentration dissolved in third solution: 0.5% hydroxylamine-hydrochloride in 25% acetic acid, 75°C (over 90 min); Insol Mn, manganese concentration dissolved in fourth solutions: hydrochloric acid, 95°C (over 15 min) and nitric acid, 95°C (over 15 min); Sum Mn, addition of all four previous extraction manganese concentrations.

[a] Data in this table reported with two significant figures.

Table 4. Geometric mean ratios of Mn fractions to Mn (sum) stratified by particle size for three heavy equipment plants.

Plant	Parameter	Total particulate		Respirable particulate		Both total and respirable particulate	
		***n* (*n* < LOD)**	**GM (GSD)**	***n* (*n* < LOD)**	**GM (GSD)**	***n* (*n* < LOD)**	**GM (GSD)**
A	Sol Mn:Mn(sum)	37 (0)	0.04 (1.9)	9 (0)	0.02 (2.8)	46 (0)	0.03 (2.3)
	Mn(0,2+):Mn(sum)	37 (0)	0.43 (1.2)	9 (0)	0.37 (1.1)	46 (0)	0.42 (1.2)
	Mn(3+,4+):Mn(sum)	37 (0)	0.39 (1.2)	9 (0)	0.44 (1.1)	46 (0)	0.40 (1.2)
	Insol Mn:Mn(sum)	33 (4)[a]	0.09 (2.4)	9 (0)	0.15 (1.3)	42 (4)[a]	0.10 (2.3)
B	Sol Mn:Mn(sum)	23 (0)	0.05 (1.3)	10 (0)	0.03 (1.3)	33 (0)	0.04 (1.5)
	Mn(0,2+):Mn(sum)	23 (0)	0.35 (1.2)	10 (0)	0.34 (1.2)	33 (0)	0.35 (1.2)
	Mn(3+,4+):Mn(sum)	23 (0)	0.43 (1.2)	10 (0)	0.43 (1.2)	33 (0)	0.43 (1.2)
	Insol Mn:Mn(sum)	23 (0)	0.15 (1.4)	10 (0)	0.17 (1.5)	33 (0)	0.16 (1.4)
C	Sol Mn:Mn(sum)	20 (0)	0.08 (1.4)	10 (0)	0.05 (1.2)	30 (0)	0.07 (1.4)
	Mn(0,2+):Mn(sum)	20 (0)	0.37 (1.2)	10 (0)	0.34 (1.1)	30 (0)	0.36 (1.2)
	Mn(3+,4+):Mn(sum)	20 (0)	0.39 (1.2)	10 (0)	0.32 (1.2)	30 (0)	0.36 (1.2)
	Insol Mn:Mn(sum)	19 (1)[a]	0.14 (1.4)	10 (0)	0.28 (1.3)	29 (1)[a]	0.18 (1.6)

Sol Mn, manganese concentration dissolved in first sequential extraction solution: 0.01 molar ammonium acetate, room temperature (over 90 min); Mn 0, 2+, manganese concentration dissolved in second solution: 25% acetic acid, 75°C (over 90 min); Mn 3+, 4+, manganese concentration dissolved in third solution: 0.5% hydroxylamine-hydrochloride in 25% acetic acid, 75°C (over 90 min); Insol Mn, manganese concentration dissolved in fourth solutions: hydrochloric acid, 95°C (over 15 min) and nitric acid, 95°C (over 15 min); Sum Mn, addition of all four previous extraction manganese concentrations.

[a] Some samples were below the limit of detection (lod); minimum detectable concentration (MDC) were calculated and these were applied as censored data to calculate GM (GSD) using maximum likelihood method.

helmet air space generally collects lower levels of WF (Goller and Paik, 1985; Liu *et al.*, 1995; ISO, 2011), unless the welder was exposed to high concentrations within a confined space (Harris *et al.*, 2005). However, due to the difficult nature of maintaining filter cassettes inside of welding helmets, particularly when welders frequently remove and reposition their helmets and move sampling filters, it is uncertain if the cassettes remained within the air space of the helmet when used throughout the entire work shift. Constant surveillance by the industrial hygiene survey team was not possible when multiple welders were simultaneously monitored in disperse locations throughout large factories.

The majority of particles associated with WF are of respirable sizes, most of which are submicrometer particles (AWS, 1983; Hewett, 1995; Zimmer and Biswas, 2001; Jenkins *et al.*, 2005). Thus, air samples collected in welders' BZ with total particulate filter cassettes may provide a reasonable estimate of respirable Mn exposure. Figure 1 compares all of the exposure measurements for both total and respirable particulate aerosol, which shows that median exposure levels and patterns of the Mn fractions and Mn(sum) appear similar. However, after statistical analyses of the total versus respirable Mn sample difference ratios [ratio (95% CI); P value] from all three plants combined, the soluble Mn fraction [0.97 (0.61, 1.53) $P = 0.890$] was essentially the same, but the $Mn^{0,2+}$ [1.54 (1.14, 2.07); $P = 0.013$], $Mn^{3+,4+}$ [1.66 (1.25, 2.20); $P = 0.001$], insoluble Mn [2.87 (1.79, 4.60); $P = 0.001$] fractions and Mn(sum) [1.71 (1.25, 2.33); $P = 0.001$] were statistically different. Although the relative ordinal rank patterns of the Mn fractions are consistent, the GM for respirable Mn(sum) (150 $\mu g\ m^{-3}$), collected outside of welding helmets, was significantly greater than that of total Mn(sum) (88 $\mu g\ m^{-3}$) collected within welding helmets. The ratio differences and 95% CI for each Mn fraction are consistent with these calculations showing that higher relative respirable Mn concentrations were observed with samples collected outside of the welding helmet. A definitive determination cannot be reached with these data because only a single measurement was collected on each individual welder for either respirable or total Mn particulate. Nonetheless, a hypothesis could be proposed that welding helmets may provide *some* level of exposure reduction in open-air industrial environments, but helmets do not provide adequate respiratory protection, as shown here, where the GM inside the helmet is over four times higher than the respirable Mn TLV.

In addition to WF, grinding dust particles may be collected in these BZ samples, as this task is often associated with welding. Grinding dust produces a larger particle size distribution than WF. However, given that the welders in these factories spent considerably more time welding than grinding, one could expect that their exposures to respirable Mn would be appreciable. Indeed, this was observed with these data, as many of the respirable measurements were in excess of an order of magnitude above the respirable Mn TLV, adopted 2 years after these field surveys.

Spatter is another factor which could cause larger particle emissions. This could create particles >20 µm, possibly contributing to the analysis results. These particles would not be collected in the respirable particulate impactors and are also less likely to enter into the air space within the welding helmet as particles greater than 20 µm do not remain suspended (Jenkins *et al.*, 2005). The heavy equipment factories in this study used 95:5 and 90:10% (Ar:CO_2) gas mixtures; the low CO_2 content reduces the potential for spatter (Daihen, 2016). Moreover, microspatter (i.e., < 1–20 µm) of GMAW was shown to be less than 10% of the total aerosol weight (Jenkins *et al.*, 2005).

This NIOSH research study evaluated the sequential extraction procedures reported by Thomassen *et al.* (2001) and Ellingsen *et al.* (2003) for Mn fractionation as applied to complex WF emissions found in welders' BZ. Thomassen *et al.* (2001) and Ellingsen *et al.* (2003) monitored workers' dust exposures from raw materials, intermediate materials and finished products, and metal fumes in the Norway Mn alloy industry. The present study shows that despite the differences in aerosol emission sources at Mn smelters, the Mn sequential extraction procedure can provide useful WF data. The NIOSH extraction method modified the Thomassen *et al.* procedures by eliminating the fourth extraction step due to its use of hydrofluoric acid because of safety concerns. NIOSH added a different fourth extraction step for dissolution of the 'insoluble' Mn in the previous extractions. This was important so that Mn(sum) would be more comparable to published OELs and legacy data measured with NMAM 7303 or similar method.

This manuscript presents Mn fraction data for GMAW on CS at three heavy equipment plants. This included open air work stations, partially enclosed work pieces and variable amount of jig set-up time causing a range of exposure concentrations both within and between plants. Yet the pattern of median Mn exposures to total particle size Mn showed that the ordinal ranks were consistent between the three plants: $Mn^{0,2+}$ and $Mn^{3+,4+}$ fractions were significantly greater than insoluble and soluble Mn fractions (refer to Fig. 1; $P < 0.0001$ for all three plants combined). The median respirable Mn exposures also demonstrated this same ordinal ranking and the insoluble Mn and soluble Mn levels were much lower than those of $Mn^{0,2+}$ and $Mn^{3+,4+}$ ($P < 0.0001$ for all three plants combined). Although the two predominant $Mn^{0,2+}$ and $Mn^{3+,4+}$ fractions observed in this study are consistent with that found by Hanley *et al.* (2015) at refinery construction projects using shielded metal arc welding (SMAW; stick welding), the prevalence rank is slightly different. In Hanley *et al.* (2015), more than 50 % of the Mn(sum) was due to $Mn^{0,2+}$; but, the $Mn^{3+,4+}$ fraction ranged 31–44% of the Mn(sum) in that SMAW study. In the present study of GMAW (i.e. MIG welding), the $Mn^{0,2+}$ and $Mn^{3+,4+}$ fractional ratios with Mn(sum) were found in close proportions with each other, with slightly elevated $Mn^{3+,4+}$:Mn(sum) ratios (i.e. 1.5% higher) which was statistically significant ($P = 0.061$).

In addition, the percent of the each Mn fraction to the Mn(sum) was calculated for individual total and respirable particulate TWA measurement collected with separate welders. The GM (GSD) for these ratios is summarized in Table 4 for all three factories, stratified by particle size. Again, the same ordinal rank was observed for both total and respirable particles (i.e. $Mn^{3+,4+}$ and $Mn^{0,2+}$ >> insoluble Mn > soluble Mn), with $Mn^{0,2+}$ and $Mn^{3+,4+}$ to Mn(sum) ratios in excess of 75% in all cases but one; insoluble Mn ranged 9–28% and soluble Mn from 2–8% of the Mn(sum). These data also show that the GSDs were quite low; most (30 out of 36) were 1.5 or less, which demonstrates relatively narrow variability for these Mn fractional ratios. The data reported in the present study are consistent with other studies which describe that GMAW-CS WF was largely iron (spinel phase, magnetite) mixed with Mn in divalent and trivalent forms (Jenkins and Eagar, 2005; Berlinger *et al.*, 2009).

The sequential extraction method is constrained by the inability to identify specific Mn compounds and discrete oxidation states. Rather, it grouped oxidation phases defined by solubility, which were tested using individual homogeneous laboratory standards with defined stoichiometries. The smallest mesh size (i.e. 325–60; ~44–250 µm) of the standards that were commercially available were used; however, these sizes are still much larger than the heterogeneous WF aerosols, many of which occur in submicrometer sizes. In theory, the smaller particles of the WF will have a larger surface area-to-mass ratio which could increase sample recoveries. Yet, Berlinger *et al.* (2009) reported that the Mn bound in the magnetite crystalline lattice may resist full dissolution. Nonetheless, the data generated using the sequential procedure is more informative than a single measurement for elemental Mn provided by NMAM 7303.

The bio-accessibility and neurotoxicity of Mn is influenced by several physiochemical parameters including particle size, chemical composition, solubility, surface area, and reactivity (Jenkins *et al.*, 2005; Taube, 2012). Ellingsen *et al.* (2013) observed that the bio-accessibility Mn in WF aerosols was relatively low using a simulated lung lining fluid. The average total (composition) Mn soluble in Hatch solution was 13.8% (95% CI = 12.7–15.8%; $n = 237$). However, most of the Mn will penetrate the naso-pharynx and respiratory system and $Mn^{0,2+}$ and $Mn^{3+,4+}$ fractions were most abundant (~75–80%) in the present GMAW, and SMAW studies (Hanley *et al.*, 2015) This may imply that alternate transport pathways, in addition to absorption in lung fluid (e.g. olfactory nerve, phagolysosomal fluid) cause Mn to deposit in brain tissue, or otherwise, be retained in or excreted from the respiratory system. The physiological solubility, distribution, accumulation, and elimination of Mn, partly determined by its oxidation state (Aschner and Aschner, 1991; Pal, 1999), underscores the importance of measuring Mn fractions and particle size in welders' BZ.

Conclusions

The sequential extraction analysis of Mn fractions has demonstrated, with gas metal arc welding on mild CS, that welders' are exposed to appreciable levels of Mn in several oxidation states with the vast majority (>75%) existing in the solutions optimized for $Mn^{0,2+}$ and $Mn^{3+,4+}$ fractions. Moreover, the prevalence patterns of Mn fractions were quite consistent at three heavy equipment factories regardless of particle size. $Mn^{3+,4+}$ fraction was observed in the highest quantities but only slightly higher than $Mn^{0,2+}$; both fractions were substantially greater than those of insoluble and soluble Mn. However, the prevalence patterns shown in this study with GMAW was slightly different than those observed with SMAW where $Mn^{0,2+}$ was most abundant (>50%) and in the Norway Mn alloy industry (47%, $Mn^{0,2+}$). The Mn fractional data discovered in this study may have future implications regarding welders' health risk.

Although all of the welders' exposure levels were below the OSHA regulatory PEL and NIOSH REL, there were numerous instances when their exposures exceeded the ACGIH TLV for total and respirable Mn adopted 2 years after this field survey. Although controversial, the signs of manganese toxicity may initially be subclinical, which may or may not progress to clinical disease but could possibly become irreversible. Moreover, in a criteria document addressing WF, NIOSH concluded that welders were potentially at risk for developing acute and chronic respiratory effects, and possibly, lung cancer. Thus, workplace exposures to Mn and welding emissions should be controlled to reduce the risk of chronic disease. Due to the very low exposure criteria of the recently adopted TLVs by ACGIH, it will be difficult for welding industries to reduce welders' exposures below these recommended levels, particularly for respirable Mn, which may necessitate the use of engineering controls or appropriate respiratory protection.

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