

Manganese fractionation using a sequential extraction method to evaluate welders' flux core arc welding exposures in a shipyard, structural steel and custom parts manufacturers

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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 flux core arc welding fume at three facilities. The objective of this study was to evaluate exposures to different Mn fractions using a sequential extraction procedure. Sixty-seven worker-days were monitored for either total or respirable Mn. The samples were analyzed using an experimental method to separate four Mn fractions based on chemical solubility: soluble Mn in a mild ammonium acetate solution; Mn^{0,2+} in 25% acetic acid; Mn^{3+,4+} in hydroxylamine hydrochloride in 25% acetic acid; and insoluble Mn fractions in hydrochloric/nitric acid. The full-shift total particle size Mn time-weighted average (TWA) breathing zone concentrations ranged from 0.51 to 43; 2.9 to 850; 1.7 to 620; and 0.56 to 331 $\mu\text{g}\cdot\text{m}^{-3}$, for the different Mn fractions, respectively. The summation of all the total particulate Mn fractions yielded results that ranged from 16 to 1,530 $\mu\text{g}\cdot\text{m}^{-3}$. The ranges of respirable size Mn TWA concentrations were 0.27 to 75 for soluble Mn; 1.6 to 690 for Mn^{0,2+}; 1.3 to 740 for Mn^{3+,4+}; 0.52 to 570 for insoluble Mn; and 3.8 to 1,800 $\mu\text{g}\cdot\text{m}^{-3}$ for Mn (sum of fractions). Total particulate TWA GM concentrations of the Mn (sum) were 56 (GSD = 4.0), 380 (GSD = 2.7), and 176 (GSD = 3.3) $\mu\text{g}\cdot\text{m}^{-3}$ for the shipyard, structural steel and custom parts facilities. Although most of the workers' exposures measured were below the NIOSH Recommended Exposure Limit for Mn (1,000 $\mu\text{g}\cdot\text{m}^{-3}$), 44 welders' exposures exceeded the ACGIH Threshold Limit Values® for total Mn (100 $\mu\text{g}\cdot\text{m}^{-3}$) and 46 exceeded the new respirable Mn TLV (20 $\mu\text{g}\cdot\text{m}^{-3}$). This study shows that a welding fume exposure control and management program is warranted for Mn, which includes improved exhaust ventilation and may necessitate the use of respiratory protection, especially for welding in enclosed or confined spaces.

Studie zur Bewertung der Exposition am Arbeitsplatz gegenüber Mangan (Mn) im Schweißrauch beim Fülldraht-Lichtbogenschweißen (flux core arc welding, FCAW) mithilfe eines sequentiellen Extraktionsverfahrens in einer Werft, bei Baustahl und Anlagen für Sonderteile

ZUSAMMENFASSUNG Das National Institute for Occupational Safety and Health (NIOSH) hat an drei Standorten eine Untersuchung zur Einschätzung der berufsbedingten Exposition gegenüber Mangan (Mn) im Schweißrauch beim Fülldraht-Lichtbogenschweißen durchgeführt. Ziel war es, mithilfe eines sequentiellen Extraktionsverfahrens die Exposition gegenüber verschiedenen Mn-Fractionen zu beurteilen. An 67 Arbeitstagen wurden die Gesamtmenge oder das lungengängige Mn überwacht. Die Proben wurden mit einer experimentellen Methode zur Trennung von vier Mn-Fractionen auf Grundlage ihrer chemischen Löslichkeit analysiert: lösliches Mn in einer milden Ammoniumacetatlösung; Mn^{0,2+} in 25%iger Essigsäure; Mn^{3+,4+} in Hydroxylaminhydrochlorid in 25%iger Essigsäure und nicht lösliche Mn-Fractionen in Salz-/Salpetersäure. Während der gesamten Schicht lagen die zeitgewichteten durchschnittlichen Gesamtkonzentrationen von Mn-Partikeln in der Atemluft für die unterschiedlichen Mn-Fractionen jeweils bei 0,51 bis 43; 2,9 bis 850; 1,7 bis 620 und 0,56 bis 331 $\mu\text{g}\cdot\text{m}^{-3}$. Die Addition aller Mn-Gesamtpartikelfractionen ergab Werte zwischen 16 und 1 530 $\mu\text{g}\cdot\text{m}^{-3}$. Die zeitgewichteten Mittelwerte für die Konzentrationen lungengängiger Mn-Partikel lagen für lösliches Mn bei 0,27 bis 75; für Mn^{0,2+} bei 1,6 bis 690; für Mn^{3+,4+} bei 1,3 bis 740; für unlösliches Mn bei 0,52 bis 570 und für Mn (Summe der Fractionen) bei 3,8 bis 1 800 $\mu\text{g}\cdot\text{m}^{-3}$. Die zeitgewichteten Mittelwerte für die Gesamtkonzentrationen an Mn-Partikeln (Summe) betrugen 56 (GSD = 4,0), 380 (GSD = 2,7) und 176 (GSD = 3,3) $\mu\text{g}\cdot\text{m}^{-3}$ für die Werft, Baustahl und Anlagen für Sonderteile. Obgleich die für die meisten Arbeiter ermittelten Expositionen unter dem vom NIOSH empfohlenen Expositionsgrenzwert für Mn (1 000 $\mu\text{g}\cdot\text{m}^{-3}$) lagen, überstiegen die Expositionen von 44 Schweißern die maximalen Arbeitsplatzkonzentrationen (Threshold Limit Values®) des ACGIH für die Mn-Gesamtbelastung (100 $\mu\text{g}\cdot\text{m}^{-3}$) und von 46 Schweißern die neue maximale Arbeitsplatzkonzentration für lungengängiges Mn (20 $\mu\text{g}\cdot\text{m}^{-3}$). Diese Untersuchung belegt, dass ein Programm zur Kontrolle und Steuerung der Schweißrauchbelastung für Mn gerechtfertigt ist, das eine bessere Be- und Entlüf-

tung beinhaltet und unter Umständen den Einsatz von Atemschutzgeräten erfordert, vor allem für Schweißarbeiten in engen oder abgeschlossenen Räumen.

1 Introduction

The International Agency for Research on Cancer (IARC) reported that eleven million workers worldwide have the job title of "welder" [1]. In the United States, as of 2018, there are over 400,000 production jobs that are classified as welders, cutters, solderers, and brazers. Welders mostly work in the manufacturing industry and commonly use arc welding methods which utilizes electrical currents to create heat and bond metals together [2]. One type of arc welding is flux core arc welding (FCAW), which uses electric current to produce a molten metal pool from a consumable wire and a flux material is released from the center of the filler wire to prevent oxidation of the metal pool at the joint; an inert gas may or may not be used as supplemental protection of the molten metal to minimize oxidation [3; 4].

As a result of high process temperatures produced during welding, welders are exposed to welding fumes (WF) composed of metals such as arsenic, beryllium, chromium, iron, lead, manganese, and vanadium and gases such as carbon dioxide, carbon monoxide, hydrogen fluoride, nitrogen oxide, nitrogen dioxide, and ozone [3 to 7]. In 2017, IARC concluded that there was "sufficient evidence" to determine that welding fume is a human lung carcinogen (Group 1 – carcinogenic to humans) [8]. Additionally, previous studies have demonstrated that when exposed to metals, such as lead, iron or manganese welders may be an increased risk of neurological and neurobehavioral health effects [9].

Manganese (Mn) is a common metal ingredient of many steels and used in welding rods/wires to impart strength, hardness, and ductility to the metal [10]. Mn can readily cross the blood brain barrier and lead to an increase in Mn concentration in brain regions, which produces manganism, a neurological syndrome similar to Parkinson's disease [11]. Studies of welders have shown neurobehavioral effects from low level Mn exposures (<200 $\mu\text{g}\cdot\text{m}^{-3}$) including short term memory loss, mood swings, altered reaction times and eye-hand coordination deficits [12; 13]. A prospective study of bridge construction welders reported that after 3.5 years of stopping confined space welding, olfactory, extrapyramidal, and mood disturbances remained constant or were exacerbated in welders; however, cognitive function improved significantly [14].

Although Mn neurotoxicity has been reported for many years, the mechanism is not fully understood [15]. The oxidation state and solubility of Mn in welding fume may affect the transport of Mn across cellular membranes, influence brain deposition, and may have implications for Mn cytotoxicity and neurotoxicity [16 to 18]. Previous research has reported that Mn^{2+} and Mn^{3+} are the Mn fractions predominantly found in biological tissues [19]. Frequently, the chemical and biological solubility of Mn compounds is not easily characterized with conventional analytical methods [20].

Based upon sequential extraction procedures reported by Tessier et al. [21], new methods for measuring Mn fractions were explored by Thomassen et al. [22]. In that 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; $\text{Mn}^{0,2+}$; $\text{Mn}^{3+,4+}$; and insoluble Mn. Thomassen et al. [22] and Ellingsen et al. [23] proposed that Mn compounds that could be expected in each extracted fraction include:

- i) MnF_2 , MnCl_2 in soluble Mn fraction;
- ii) Mn metal, MnO , divalent Mn of Mn_3O_4 in $\text{Mn}^{0,2+}$ fraction;
- iii) trivalent Mn of Mn_3O_4 , Mn_2O_3 , MnO_2 in $\text{Mn}^{3+,4+}$ fraction; and
- iv) SiMn in insoluble Mn fraction.

The method was tested with Mn in WF by Berlinger et al. [24] using area sampling with Higgins-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 will be useful for assessing bio-accessibility in future research.

The occupational exposure limits (OELs) available for Mn are inconsistent [9]. The National Institute for Occupational Safety and Health (NIOSH) Recommended Exposure Limit (REL) for Mn is an 8-h to 10-h (40-h week) time-weighted average (TWA) concentration of 1,000 $\mu\text{g}\cdot\text{m}^{-3}$, with a Short Term Exposure Limit (STEL) of 3,000 $\mu\text{g}\cdot\text{m}^{-3}$ over 15-min, based on central nervous system effects and pneumonitis [25]. The Occupational Safety and Health Administration (OSHA) Permissible Exposure Limit (PEL) for Mn is a ceiling limit of 5,000 $\mu\text{g}\cdot\text{m}^{-3}$ for protection against eye and respiratory irritation [26]. The American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Values (TLV[®]) for total (inhalable) inorganic Mn is 100 $\mu\text{g}\cdot\text{m}^{-3}$, measured as an 8-h TWA which was established to reduce central nervous system impairment (e.g., psychomotor abnormalities) [27; 28]. In 2012, ACGIH adopted a respirable Mn 8-h TLV of 20 $\mu\text{g}\cdot\text{m}^{-3}$. The German and European Union OEL for inorganic Mn respirable dust is also 20 $\mu\text{g}\cdot\text{m}^{-3}$ [29]. 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 [30].

It is the scarcity of occupational exposure studies regarding Mn oxidation states, and their potential for differential biological activity, which motivated the present study to evaluate welders' breathing zone (BZ) exposures. The primary objective of this research study was to evaluate Mn fractions for flux core arc welding (FCAW) on mild carbon steel (CS) welding at three different welding operations in 2010 – structural steel and custom parts manufacturers, and a shipyard. In addition, gas metal arc welding (GMAW) and grinding dust was measured on a few welders. This study evaluated Mn fractions in WF through data collection in field settings by applying extraction methods to measure different Mn fractions based on solubility, utilizing industrial hygiene air sampling and analytical methods. Results of this study were compared to previous studies examining shielded metal arc welding (SMAW) during a refinery turn-around, and GMAW at heavy equipment manufacturers [31; 32].

2 Materials and methods

Sixty-seven worker-days were monitored for either total Mn or respirable Mn throughout three facilities in 2010 as shown in Table 1. At all three facilities, welders were monitored when working on CS parts. Three consecutive days of monitoring were conducted with 20 welder-days in the summer at the shipyard using American Welding Society (AWS) E71T (0.045 mm; 1% Mn) class wire and 75:25% argon (Ar):carbon dioxide (CO₂) shielding gas mixture. The structural steel manufacturer was also monitored over three consecutive days in late summer with 40 welder-days when using AWS E71T (0.052 mm; <2% Mn) wire with 75:25% (Ar:CO₂) mixture or CO₂ gas. The customs part shop was a smaller factory, so only seven welder-days were monitored over five days during the summer. Here, AWS ER71T (0.045 mm; 1% Mn) class wire and 75:25% (Ar:CO₂) gas mixture was utilized, the same as in the shipyard. In all, 48 total and 19 respirable particulate Mn TWA concentrations were measured.

Full-shift BZ exposure concentrations were measured on each welder over 8 to 12 h work shifts, either for total or respirable Mn, but not both. 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 [33]. 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 than cyclone samplers [34; 35]. 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. [22] with modifications described and evaluated by Andrews et al. [36]. Differences in chemical solubility of the manganese valence states is the basis for the speciation. The four-step sequential extraction procedure included:

- 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 Mn⁰ and Mn²⁺ oxidation states); and
- iii) 10-mL of 0.5% hydroxylamine hydrochloride in 25% acetic acid, heated at 75°C for 90-min (defined as Mn³⁺ and Mn⁴⁺ oxidation states); and
- iv) 12.1 M hydrochloric acid/15.6 M nitric acid hot block digestion following NIOSH Manual of Analytical Methods (NMAM) 7303 [37].

The sample extracts were analyzed by ICP-AES using the instrumental parameters described in NMAM 7303. The limits of detection (LODs) were 0.08; 0.02; 0.29; and 0.15 µg/filter for

Table 1. Number and distribution of total and respirable welding samples collected by survey day.

Site	Particle Size	Day 1	Day 2	Day 3	All Days
Shipyard	Total	4	5	5	14
	Respirable	1	2	3	6
Structural Steel	Total	10	9	10	29
	Respirable	4	4	3	11
Custom Parts	Total	2	2	1	5
	Respirable	1	1	0	2

soluble Mn; Mn^{0,2+}; Mn^{3+,4+}; and insoluble Mn fractions, respectively.

Quality control (QC) samples containing (1) commercially-available, aqueous solution of Mn nitrate, (2) pure stoichiometrically-defined Mn compounds, and (3) a characterized SiMn alloy were analyzed alongside the field samples [22]. Percent recovery of QC samples were 91.7% for soluble Mn (using Mn nitrate as the test compound); 98.2% for Mn⁰ (using Mn powder); 102.6% for Mn²⁺ (using MnO); 88.1% for Mn³⁺ (using Mn₂O₃); 89.9% for Mn⁴⁺ (using Mn₃O₄) and 75.1% for insoluble Mn (using SiMn). Details of the laboratory evaluation of this extraction procedure were previously published and report the quantitative recovery of Mn compounds in the expected fraction and the Mn fractionation for laboratory-generated WF [36]. 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, including UK HSL WF materials certified for total Mn content and laboratory-generated welding fumes. Andrews et al. [36] evaluated Mn speciation for GMAW-CS using chamber-generated bulk WF. Using Mn(sum) from the sequential extraction method (52.8 mg/g-WF), and the result from hot block acid digestion method NMAM 7303 as a reference value (56.5 mg/g-WF), the percent difference of 6.8% was judged not to have practical importance for industrial hygiene field samples and confirmed the suitability of the sequential method for welding fume material.

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 limit of detection (LOD), the maximum likelihood GM and GSD were calculated by analyzing the log of the values in the PROC LIFEREG procedure of SAS 9.3 [38]. To create box plots (presented in Figure), the minimum, maximum, median, 25th and 75th percentiles were calculated which were stratified by facility, 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

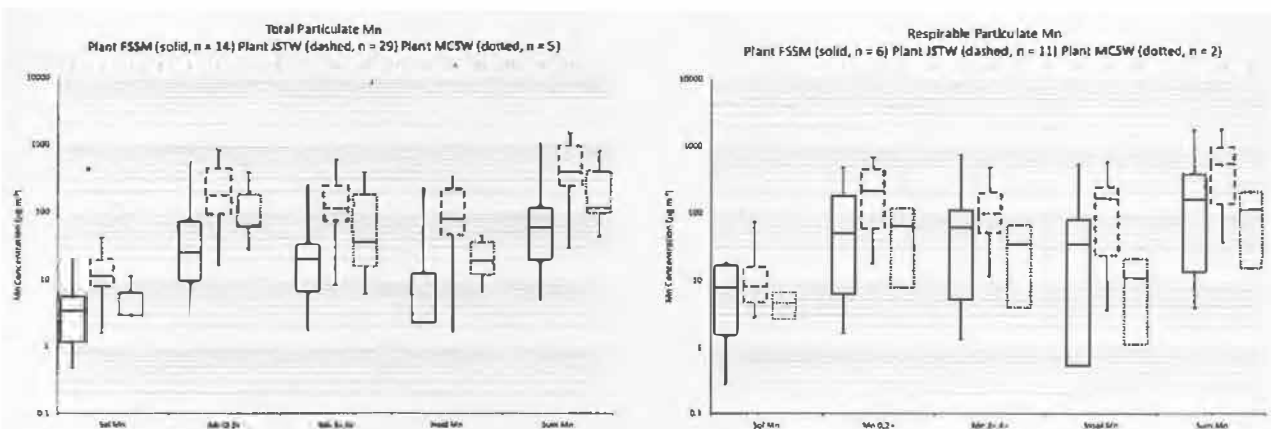


Figure. 8 and 9) Total and respirable particulate TWA breathing zone concentrations ($\mu\text{g}\cdot\text{m}^{-3}$) of Mn fractions from FCAW at a shipyard, structural steel and custom parts manufacturers.

the means of the log of the measurements was conducted for each Mn fraction. Each of the TWA measurements were independently collected separately on only one welder for various jobs. The results are presented as difference ratios with 95% confidence intervals and p-values.

3 Results and discussion

3.1 Total Particulate Manganese

Welders' full-shift TWA concentrations for total particulate Mn fractions are presented in Table 2, stratified by three facilities and all sites combined. Overall, the Mn speciation results ($\mu\text{g}\cdot\text{m}^{-3}$) ranged from 0.51 to 43 for soluble Mn; 2.9 to 850 for $\text{Mn}^{0,2+}$; and 1.7 to 620 for $\text{Mn}^{3,+4+}$; and 0.56 to 330 for insoluble Mn fractions. The summation of all the total particulate Mn

fractions ranged from 16 to $1,500 \mu\text{g}\cdot\text{m}^{-3}$ and the GM (GSD) for all plants was $200 \mu\text{g}\cdot\text{m}^{-3}$ (4.1). All of the total Mn(sum) TWA exposure levels were well below the OSHA ceiling PEL for Mn ($5,000 \mu\text{g}\cdot\text{m}^{-3}$). However, eight (of 29) Mn(sum) exposure measurements at the structural steel plant and one (of 14) at the shipyard exceeded the NIOSH recommended exposure limit, REL, ($1,000 \mu\text{g}\cdot\text{m}^{-3}$). Moreover, 33 (of 48) welders' total Mn(sum) exposures exceeded the ACGIH TLV for inorganic, elemental Mn ($100 \mu\text{g}\cdot\text{m}^{-3}$), which was lowered from $200 \mu\text{g}\cdot\text{m}^{-3}$ in 2012. The highest total Mn TWA concentrations were measured in the summer at the structural steel plant where larger equipment was made, necessitating larger amounts of weld wire and longer arc times. At this plant, the GM (GSD) concentrations ($\mu\text{g}\cdot\text{m}^{-3}$) were eleven (2.2) for soluble Mn; 190 (2.7) for

Table 2. Welders' TWA breathing zone concentrations ($\mu\text{g}\cdot\text{m}^{-3}$) of total Mn fractions during FCAW.

Site	Parameter	TWA concentration				
		Mn (soluble)	Mn (0, +2)	Mn (+3, +4)	Mn (insoluble)	Mn (sum)
Shipyard	n	14	14	14	9 ^c	9
	Minimum	0.51	2.9	1.7	0.56	16
	AM (SD)	4.6 (5.1)	76 (150)	43 (67)	35 (72)	200 (330)
	GM (GSD)	2.8 (2.9)	28 (3.9)	19 (3.8)	8.0 (6.1)	56 (4.0)
	Maximum	20	560	250	220	1000
Structural steel	n	29	29	29	29	29
	Minimum	1.6	16	8.2	1.6	29
	AM (SD)	14 (9.8)	270 (220)	160 (130)	120 (99)	560 (350)
	GM (GSD)	11 (2.2)	190 (2.7)	110 (2.7)	71 (3.5)	380 (2.7)
	Maximum	43	850	620	330	1500
Custom parts	n	5	5	5	5	5
	Minimum	2.9	28	6.0	6.6	44
	AM (SD)	5.9 (3.4)	140 (150)	130 (160)	24 (16)	300 (330)
	GM (GSD)	5.2 (1.8)	94 (2.8)	48 (5.6)	19 (2.2)	180 (3.3)
	Maximum	11	390	390	45	840
All	n	48	48	48	43	43
	Minimum	0.51	2.9	1.7	0.56	16
	AM (SD)	11 (9.3)	200 (210)	120 (130)	69 (96)	450 (420)
	GM (GSD)	6.9 (2.8)	100 (4.0)	59 (4.0)	38 (5.0)	200 (4.1)
	Maximum	43	850	620	330	1500

Table 3. Welders' TWA breathing zone concentrations ($\mu\text{g}\cdot\text{m}^{-3}$) of respirable Mn fractions during FCAW.

Site	Parameter	TWA concentration				
		Mn (soluble)	Mn (0, +2)	Mn (+3, +4)	Mn (insoluble)	Mn (sum)
Shipyard	n	6	6	6	5 ^c	5
	Minimum	0.27	1.6	1.3	0.52	3.8
	AM (SD)	8.6 (7.4)	130 (180)	160 (290)	140 (220)	480 (730)
	GM (GSD)	4.4 (5.1)	34 (8.5)	34 (9.8)	16 (23.0)	92 (9.6)
	Maximum	18	470	740	530	1800
Structural Steel	n	11	11	11	11	11
	Minimum	2.8	18	12	3.5	38
	AM (SD)	16 (21)	280 (220)	150 (130)	180 (160)	630 (520)
	GM (GSD)	9.7 (2.5)	180 (3.1)	99 (2.8)	98 (4.4)	410 (3.1)
	Maximum	75	690	470	570	1800
Custom Parts	n	2	2	2	2	2
	Minimum	2.6	7.7	3.8	1.1	15
	AM (SD)	4.6 (2.8)	63 (78)	35 (44)	11 (14)	110 (140)
	GM (GSD)	4.2 (2.8)	30 (6.9)	16 (7.6)	4.8 (7.9)	57 (6.4)
	Maximum	6.5	120	66	21	210
All	n	19	19	19	18	18
	Minimum	0.27	1.6	1.3	0.52	3.8
	AM (SD)	12 (16)	210 (210)	140 (180)	150 (180)	530 (560)
	GM (GSD)	6.9 (3.2)	89 (5.6)	58 (5.2)	42 (9.8)	210 (5.7)
	Maximum	75	690	740	570	1800

Mn^{0,2+}; 110 (2.7) for Mn^{3+,4+}; 71 (3.5) for insoluble Mn fractions; and 380 (3.5) for Mn(sum). The lowest BZ levels were observed in the shipyard due to many jobs being performed outdoors, yet four (out of 14) Mn(sum) exposures measured with filter cassettes exceeded the total Mn TLV when welding in tight enclosed areas or confined spaces; three more were elevated over 100 $\mu\text{g}\cdot\text{m}^{-3}$ using respirable size samplers. The GM ($\mu\text{g}\cdot\text{m}^{-3}$), GSD, and Mn(sum) concentrations were 380 (2.7); 180 (3.3); and 56 (4.0) for structural steel and custom parts manufacturers and shipyard, respectively. The GM concentrations exceeded the TLV for total particulate Mn for structural steel and custom parts plants but not the shipyard. Further, many individual measurements of Mn^{0,2+} and Mn^{3+,4+} fractions also exceeded the total Mn TLV for all three facilities.

3.2 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 ($\mu\text{g}\cdot\text{m}^{-3}$) ranged from 0.27 to 75 for soluble Mn; 1.6 to 690 for Mn^{0,2+}; 1.3 to 740 for Mn^{3+,4+}; and 0.52 to 570 for insoluble Mn fractions. The summation of all the respirable particulate Mn fractions ranged from 3.8 to 1,800 $\mu\text{g}\cdot\text{m}^{-3}$ and the GM (GSD) for all plants was 210 $\mu\text{g}\cdot\text{m}^{-3}$ (5.7). The highest BZ exposures occurred in structural steel plant and the lowest exposures in the custom parts shop. The GM respirable Mn(sum) were 410; 92; and 57 $\mu\text{g}\cdot\text{m}^{-3}$, respectively, for structural steel, shipyard, and custom parts facilities. GSDs ranged between 3.1 and 9.6 which demonstrates the diverse exposure patterns with these welding jobs, particularly with outdoor and confined space shipyard jobs. OSHA PEL and

Table 4. GM ratios of Mn fractions to Mn (sum) stratified by particle size for FCAW.

Plant	Parameter	Total particulate		Respirable particulate		Both total and respirable particulate	
		n	GM (GSD)	n	GM (GSD)	n	GM (GSD)
Shipyard	Sol Mn:Mn(sum)	9	0.04 (2.4)	5	0.04 (3.4)	14	0.04 (2.7)
	Mn(0,2+):Mn(sum)	9	0.47 (1.2)	5	0.38 (1.3)	14	0.44 (1.2)
	Mn(3+,4+):Mn(sum)	9	0.34 (1.2)	5	0.35 (1.1)	14	0.35 (1.2)
	Insol Mn:Mn(sum)	9	0.10 (2.0)	5	0.16 (2.3)	14	0.11 (2.2)
Structural Steel	Sol Mn:Mn(sum)	29	0.03 (2.1)	11	0.02 (2.8)	40	0.03 (2.3)
	Mn(0,2+):Mn(sum)	29	0.48 (1.2)	11	0.45 (1.2)	40	0.47 (1.2)
	Mn(3+,4+):Mn(sum)	29	0.28 (1.2)	11	0.24 (1.4)	40	0.27 (1.2)
	Insol Mn:Mn(sum)	29	0.18 (1.4)	11	0.24 (1.5)	40	0.20 (1.5)
Custom Parts	Sol Mn:Mn(sum)	5	0.03 (2.1)	2	0.07 (3.3)	7	0.04 (2.4)
	Mn(0,2+):Mn(sum)	5	0.54 (1.2)	2	0.53 (1.1)	7	0.53 (1.1)
	Mn(3+,4+):Mn(sum)	5	0.27 (1.8)	2	0.28 (1.2)	7	0.27 (1.6)
	Insol Mn:Mn(sum)	5	0.11 (1.6)	2	0.08 (1.2)	7	0.10 (1.5)
All	Sol Mn:Mn(sum)	43	0.03 (2.1)	18	0.03 (3.0)	61	0.03 (2.4)
	Mn(0,2+):Mn(sum)	43	0.49 (1.2)	18	0.44 (1.2)	61	0.47 (1.2)
	Mn(3+,4+):Mn(sum)	43	0.29 (1.3)	18	0.27 (1.3)	61	0.29 (1.3)
	Insol Mn:Mn(sum)	43	0.16 (1.7)	18	0.19 (1.9)	61	0.16 (1.8)

Table 5. Number and distribution of Mn(sum) measurements exceeding the OELs.

Site	> REL-total ^a	> TLV-total ^b	> TLV-respirable ^{c,d}
Shipyards	1	4	5
Structural Steel	8	25	10
Custom Parts	0	4	1
All	9	33	16
n ^e	48 ^f	48 ^f	19 ^g

^a NIOSH REL-total = 1000 µg · m⁻³; (NIOSH, 1992)

^b ACGIH TLV-total = 100 µg · m⁻³; (ACGIH, 2017)

^c ACGIH TLV-respirable = 20 µg · m⁻³; (ACGIH, 2017)

^d DFG (Germany) – Mn fume, respirable dust = 20 µg · m⁻³; (GESTIS, 2017)

^e n (total + respirable) = 48 + 19 = 67

^f n refers to number of sample measurements collected with filter cassettes.

^g n refers to number of samples collected with personal impactors, respirable particle size selectors.

NIOSH REL for respirable particulate Mn are not available and the ACGIH respirable Mn TLV was not adopted until two years after the data were collected for this field study. However, in 16 (of 19) individual BZ 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 both the Mn^{0,2+} and Mn^{3+,4+} fractions were greater than the respirable Mn TLV in five (out of six) sample sets for these three facilities.

3.3 Ratio of Mn fractions to summation of Mn fractions

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 site stratified by total versus respirable Mn as well as the ratios of respirable to total Mn for each fraction. As shown, the vast majority of the Mn(sum) is partitioned in the Mn^{0,2+} and Mn^{3+,4+} fractions (e.g., the mean of the ratio summations for these two Mn fractions were 78 and 71% for total and respirable Mn particulate, respectively for all sites combined). Soluble Mn occurred in the lowest proportions, that had GM ratios which ranged from 2 to 7% of Mn(sum), while the insoluble Mn results ranged from 8 to 24% of Mn(sum).

Table 5 presents the number of exposure excursions above the NIOSH REL and ACGIH TLVs for total and respirable particle size Mn(sum). Nine FCAW welders' exposures exceeded the NIOSH REL for total Mn, the vast majority of which occurred at the structural steel plant. The ACGIH TLV for total Mn was ex-

ceeded 33 times (n = 48) and 16 times (n = 19) for respirable Mn measured with a personal impactor in BZs. Again, most of the excessive exposures were observed at the structural steel facility due to the thick steel stock and longer arc times. Given the sub-micron WF particles, the samples collected with 'total' filter cassettes, were likely measuring respirable Mn. Hence, one could propose with these data, that 49 (of 67) exposures were above the respirable Mn TLV.

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 [33]. Monitoring within the helmet air space generally collects lower levels of WF, unless the welder was exposed to high concentrations within a confined space [33; 39 to 41]. Constant surveillance by the industrial hygiene survey team was not possible when multiple welders were simultaneously monitored in disperse locations throughout these factories and shipyard locations. 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.

The majority of particles associated with WF are of respirable sizes, most of which are sub-micrometer particles [42 to 45]. Thus, air samples collected in welders' BZ with total particulate filter cassettes may provide a reasonable estimate of respirable Mn exposure. The Figure compares all of the exposure measurements for both total and respirable particulate, which presents the median exposure levels and patterns of the Mn fractions and Mn(sum). Comparison of the GM for respirable Mn(sum) (210 µg·m⁻³), collected outside of welding helmets, was not significantly different than that of total Mn(sum) (200 µg·m⁻³) collected within welding helmets (p = 0.959). The ratio differences and 95% confidence intervals (CI) for each Mn fraction appear consistent with these calculations, showing that comparable respirable Mn concentrations were observed with total Mn samples collected inside of the welding helmet. The ratio of respirable GM to total GM for each FCAW Mn fraction relative to Mn(sum) (Table 6) are reasonably close to unity (e.g. 0.99, 0.90, 0.94 and 1.28 for soluble Mn, Mn^{0,2+}, Mn^{3+,4+}, and insoluble Mn, respectively.) The 95% CI also encompassed unity. Similar trends are observed in Table 6 for SMAW and GMAW [31; 32]. A definitive determination cannot be reached with these

Table 6. Geometric Mean Ratios of Mn fractions to Mn (sum) stratified by SMAW, GMAW, and FCAW.

Welding process	Parameter	Total particulate		Respirable particulate		Ratio of respirable GM/Total GM	
		n	GM (GSD)	n	GM (GSD)	Ratio	95%CI
SMAW ^a	Sol Mn:Mn(sum)	9	0.04 (2.4)	5	0.04 (3.4)	1.0	(0.22, 4.56)
	Mn(0,2+):Mn(sum)	9	0.47 (1.2)	5	0.38 (1.3)	0.81	(0.59, 1.12)
	Mn(3+,4+):Mn(sum)	9	0.34 (1.2)	5	0.35 (1.1)	1.03	(0.87, 1.21)
	Insol Mn:Mn(sum)	9	0.10 (2.0)	5	0.16 (2.3)	1.6	(0.87, 4.51)
GMAW ^b	Sol Mn:Mn(sum)	29	0.03 (2.1)	11	0.02 (2.8)	0.67	(0.32, 1.38)
	Mn(0,2+):Mn(sum)	29	0.48 (1.2)	11	0.45 (1.2)	0.94	(0.82, 1.07)
	Mn(3+,4+):Mn(sum)	29	0.28 (1.2)	11	0.24 (1.4)	0.86	(0.68, 1.08)
	Insol Mn:Mn(sum)	29	0.18 (1.4)	11	0.24 (1.5)	1.33	(1.00, 1.78)
FCAW ^c	Sol Mn:Mn(sum)	43	0.03 (2.1)	18	0.03 (3.0)	0.99	(0.58, 1.77)
	Mn(0,2+):Mn(sum)	43	0.49 (1.2)	18	0.44 (1.2)	0.9	(0.80, 1.00)
	Mn(3+,4+):Mn(sum)	43	0.29 (1.3)	18	0.27 (1.3)	0.94	(0.80, 1.11)
	Insol Mn:Mn(sum)	43	0.15 (1.7)	18	0.19 (1.9)	1.28	(0.91, 1.80)

^a[31] ^b[32] ^c Present study

data because only a single measurement was collected on each individual welder for either respirable or total Mn particulate.

Because grinding is associated with welding, both grinding dust particles and WF may be collected in these BZ samples. Grinding dust produces larger particle size distributions than WF. Given that the welders in these factories spent considerably more time welding than grinding, it was expected and observed that their exposures to respirable Mn would be appreciable. Many of the respirable measurements were in excess of an order of magnitude above the respirable Mn TLV. While it has been proposed that welding helmets may provide some level of exposure reduction in open-air industrial environments, the helmets do not provide adequate respiratory protection, as shown in this study, where the GM inside the helmet is over ten times higher than the respirable Mn TLV.

This article presents Mn fraction data for FCAW on CS at three different welding operations. 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 facilities. Yet the pattern of median Mn exposures showed Mn^{0,2+} and Mn^{3+,4+} fractions were significantly greater than insoluble and soluble Mn fractions (refer to the Figure; $p < 0.0001$ for total Mn and $p = 0.001$ for respirable Mn with all three FCAW sites combined). Although the two predominant Mn^{0,2+} and Mn^{3+,4+} fractions observed in this study are consistent with results reported by Hanley et al. [32] at refinery construction projects using SMAW (i.e., stick welding) and Hanley et al. [31] at heavy equipment manufacturers using GMAW (i.e., MIG welding), the proportions are slightly different. In the SMAW Hanley et al. [32] study, the GM Mn^{0,2+} ranged from 38 to 47% of the Mn(sum) and from 31 to 44% of the Mn(sum) for the Mn^{3+,4+} fractional ratio. In the study of GMAW, 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 the present study of FCAW (i.e., flux welding), the Mn^{0,2+} measurements were 1.7 times greater than that of Mn^{3+,4+} which was statistically significant ($p < 0.05$).

In addition, the percent of 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 are summarized in Table 4 for all three facilities, stratified by particle size. Again, the same ordinal rank was observed for both total and respirable particles (i.e., Mn^{0,2+} and Mn^{3+,4+} >> insoluble Mn > soluble Mn), with Mn^{0,2+} and Mn^{3+,4+} to Mn(sum) ratios in excess of 73% in all cases; insoluble Mn ranged from 8 to 24% and soluble Mn from 2 to 7% of the Mn(sum). These data also show relatively narrow variability for these Mn fractional ratios. The data reported in the present study are consistent with other welding studies which describe that WF was largely iron (spinel phase, magnetite) mixed with Mn in divalent and trivalent forms [24; 46].

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 stoichiometry. The smallest mesh size (i.e., 325–60 mesh; -44 – $250 \mu\text{m}$) of the standards that were commercially available were used. However, these sizes were still much larger than the heterogeneous WF aerosols, most of which

occur in nanometer and sub-micrometer 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. [24] 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 [37].

The bio-accessibility and neurotoxicity of Mn is influenced by several physiochemical parameters including particle size, chemical composition, solubility, surface area and reactivity [20; 44; 46]. Ellingsen et al. observed that the bio-accessibility Mn in welding fume aerosols was relatively low using a simulated lung lining fluid [47]. The average total (composition) Mn soluble in Hatch solution was 13.8% (95% CI = 12.7 to 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 (–71 to 78%) in the present FCAW study as well as the previous SMAW and GMAW studies shown in Table 6 [31; 32]. This may imply that alternate transport pathways, in addition to absorption in lung fluid (e.g., olfactory nerve, phagolysosomal fluid), might 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, highlights the importance of measuring Mn fractions and particle size in welders' BZ [15; 48].

4 Conclusions

During FCAW on mild carbon steel, we found that through the sequential extraction analysis of Mn fractions that welders are exposed to appreciable levels of Mn in several oxidation states, with the vast majority (>73%) existing in the extraction solutions optimized for Mn^{0,2+} and Mn^{3+,4+} fractions. Mn^{0,2+} fraction was observed in the highest quantities which was 1.7 times greater than Mn^{3+,4+} and both fractions were substantially greater than those of insoluble and soluble Mn. However, the prevalence patterns shown in this study with FCAW were slightly different than those observed with GMAW in heavy equipment plants where Mn^{0,2+} and Mn^{3+,4+} were measured at similar levels. The excessive Mn fractional data reported in this study may have future implications regarding welders' health risk.

The OELs from NIOSH, OSHA, and ACGIH are not directly relevant to individual fractions because the OELs are published for all inorganic Mn, measured as elemental Mn. OELs for evaluating the specific Mn fractions have not been established. The experimental nature of the sequential extraction procedure does not discount that summing the component Mn fractions can approximate the total elemental Mn concentration. This summation may be used for comparison to legacy data and applied to OELs. In this study, all of the welders' FCAW exposure levels were below the OSHA regulatory PEL, however, there were several instances when their exposures exceeded the NIOSH REL and there were numerous excursions above the ACGIH TLV for total and respirable Mn. Workplace exposures to Mn and welding emissions should be controlled to reduce the risk of acute and chronic disease [1; 9]. The very low exposure criteria adopted by ACGIH may necessitate the use of improved engineering controls and/or appropriate respiratory protection.

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DISCLAIMER

The findings and conclusions in this article are those of the authors and do not necessarily represent the views of the National Institute for Occupational Safety and Health (NIOSH) and the National Institute of Environmental Health Sciences (NIEHS). It does not represent and should not be construed to represent any agency determination or policy. Mention of company names and internet web sites does not constitute an endorsement by NIOSH and NIEHS.

DEFINITIONS FOR FIGURES AND TABLES (ANDREWS ET AL. [36]):

Sol Mn – Manganese dissolved in first sequential extraction solution: 0.01 molar ammonium acetate, room temperature (over 90 minutes)

Mn^{0, 2+} – Manganese dissolved in second solution: 25% acetic acid, 75°C (over 90 minutes)

Mn^{3+, 4+} – Manganese dissolved in third solution: 0.5% hydroxylamine hydrochloride in 25% acetic acid, 75°C (over 90 minutes)

Insol Mn – manganese concentration dissolved in fourth solutions: hydrochloric acid, 95 °C (over 15 minutes) and nitric acid, 95°C (over 15 minutes)

Sum Mn – Sum total of all four previous manganese extractions

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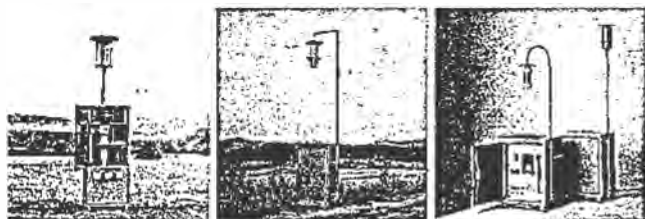
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