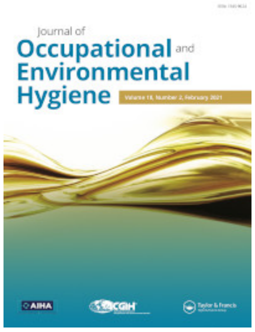

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Personal and area exposure assessment at a stainless steel fabrication facility: an evaluation of inhalable, time-resolved PM_{10}, and bioavailable airborne metals

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ABSTRACT
This study describes a comprehensive exposure assessment in a stainless steel welding facility, measuring personal inhalable PM and metals, time-resolved PM_{10} area metals, and the bioavailable fraction of area inhalable metals. Eighteen participants wore personal inhalable samplers for two, nonconsecutive shifts. Area inhalable samplers and a time-resolved PM_{10} X-ray fluorescence spectrometer were used in different work areas each sampling day. Inhalable and bioavailable metals were analyzed using inductively coupled plasma mass spectrometry (ICP-MS). Median exposures to chromium, nickel, and manganese across all measured shifts were 66 (range: 13–300) $\mu g/m^3$, 29 (5.7–132) $\mu g/m^3$, and 22 (1.5–119) $\mu g/m^3$, respectively. Most exposure variation was seen between workers ($0.79 < ICC < 0.55$), although cobalt and inhalable PM showed most variation within workers. Manganese was the most bioavailable metal from the inhalable size fraction ($16 \pm 3\%$), and chromium and nickel were $1.2 \pm 0.08\%$ and $2.6 \pm 1.2\%$ bioavailable, respectively. This comprehensive approach to welding-fume exposure assessment can allow for targeted approaches to controlling exposures based not only on individual measurements, but also on metal-specific measures and assessments of bioavailability.

KEYWORDS
Bioavailability; chromium; exposure; manganese; nickel; particulate matter; respiratory health; welding fumes

Introduction

Welding, the process of joining metals through coalescence (Jeffus 2004), is a rapidly growing occupation with approximately eleven million workers holding the job title worldwide and an additional 110 million workers incurring welding-related exposures (Guha et al., 2017). Although there are many different welding processes, two of the most common processes in occupational settings are gas metal arc welding (GMAW) and gas tungsten arc welding (GTAW). Welding fume is produced during arc welding when metal is vaporized in the electrical arc and condensed into fumes. These fumes typically have aerodynamic equivalent diameters less than one micrometer and are comprised of various particulate metals, including nickel, copper, manganese, chromium, lead, iron, and zinc (Antonini 2014). Additionally, supra-micron spatter particles may be produced and aerosolized from the surface of the molten weld pool where the welding arc joins the base metal and either the electrode or joining metal (Antonini 2014). These supra-micron particles can have a large impact on the total particle mass as mass increases cubically with diameter. The physicochemical characterization of welding fume is dependent on many factors, such as the metallurgical composition of the base metal and any joining metals (e.g., welding wires or electrodes), the presence of metal coatings or cores (such as fluxes), shield gases, and the welding process being used. In general, welding on stainless steel as opposed to mild steel produces higher fume concentrations of hazardous metals, particularly nickel and both trivalent and hexavalent chromium (Antonini 2014).

Exposure to welding fume can be difficult to assess comprehensively in occupational settings for several reasons. While personal exposure to total particulate

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matter in the air can be assessed gravimetrically with minor expense, exposure to airborne metals typically requires expensive laboratory analysis, on the order of $100 per sample. If performed, this analysis is usually only performed on a small subset of workers (Susi et al. 2000; Szram et al. 2013). Additionally, the welding plume is highly concentrated, often 10 to 100 times more concentrated near the weld than the area surrounding the welder (Antonini 2014). This can cause enormous variation in exposures between both welders who may spend different proportions of their day actively welding vs. performing other job tasks and between welders and other workers nearby who have incidental exposure to fumes but are not actively welding. As welding is typically performed intermittently and not constantly, exposure is also highly task-based and time-varying. Most metals exposure assessments use filter-based analysis, resulting in exposures that are time-weighted averages. However, the literature has indicated that there may be differences in biological response between high-intensity, low-duration exposures and low-intensity, long-duration exposures of similar magnitude (Smith 1992; de Vocht et al. 2015). These intra-day differences in exposure intensity cannot be captured using traditional time-weighted measurements.

Both nickel and hexavalent chromium are classified by the International Agency for Research on Cancer (IARC) as Group 1 human carcinogens, and manganese is known to be both cytotoxic and neurotoxic (Antonini et al. 2003; IARC 2012; Williams et al. 2012). There has been a renewed interest in occupational exposure to welding fume since an IARC working group reclassified welding fumes from a Group 2B to a Group 1 carcinogen in March of 2017 (IARC 2018).

Additionally, the bioavailability of welding fume components is highly variable based on welding process and the presence of certain shield gases and fluxes during fume generation (Berlinger et al. 2008). Several *in vitro* studies have shown that welding fumes with higher concentrations of bioavailable metals lead to increased adverse biological effects, including decreases in viability and function of lung macrophages and increases in cellular inflammatory response (Antonini et al. 1999; 2003; McNeilly et al. 2004). Additionally, a recent study by Han et al. suggests that the blood-solubility of inhaled manganese is an important determinant in the possible development of manganism or idiopathic Parkinsonism in welders (Han et al. 2008). However, relatively few studies in the literature directly assess the bioavailability of

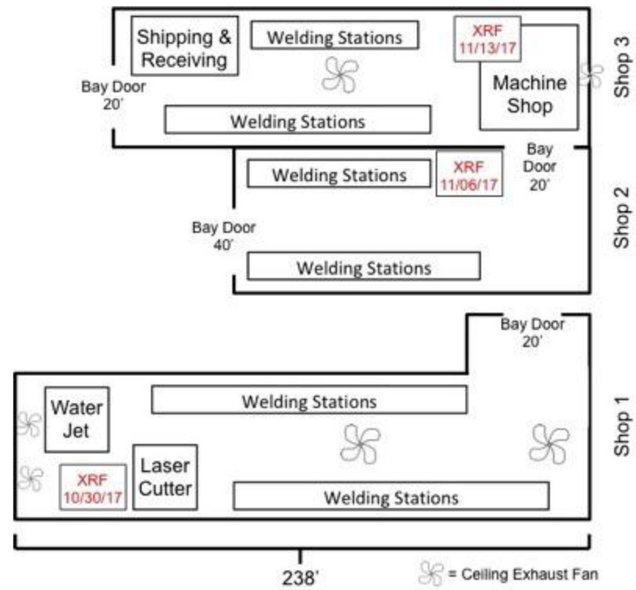

Figure 1. Shop layouts and XRF monitoring locations.

metals in sampled welding fume (Berlinger et al. 2008; Ellingsen et al. 2013; Berlinger et al. 2019). The assessment of metal bioavailability is currently limited by a lack of a standard analysis methodology for airborne samples and that most published methods require separate filters for the detection of bioavailable and total metals.

This study describes a comprehensive assessment of welding fume exposure at a stainless steel fabrication facility. To our knowledge, the first in the literature to combine personal inhalable metals exposure with both time-resolved area metals exposure and an assessment of the bioavailability of the metal components from area-sampled welding fume.

Methods

Site and participant information

This study was carried out in a stainless steel fabrication facility near Boise, Idaho in October and November of 2017. Twenty-four employees met the inclusion criteria of being employed at the facility as either a full-time welder/fabricator or a laser operator (for stainless steel sheet metal cutter). Eighteen workers were recruited to participate. All participants were administered informed consent and this study was approved by the Colorado Multiple Institutional Review Board (COMIRB).

The study site included three fabrications shops with marked areas reserved for different fabrication activities, including welding, machining, and laser cutting (Figure 1). Shop 2 was constructed in early 2017 and did not have a functioning general ventilation system installed during our study. Shops 1 and 3 had a functioning general ventilation system. Additionally, Shops 2 and 3 were interconnected via a 20-ft bay door in a shared wall. Employees at the site had assigned workstations in one of the three shops, although sometimes they moved between shops for specific tasks.

Each participant was monitored for the duration of their work-shift on two, nonconsecutive Mondays during the study period for personal exposure to inhalable PM and inhalable metals. The inhalable samplers were part of a side-by-side sampling set-up designed to validate a novel sampler for airborne lung-deposited metals (data not shown).

Pre-shift surveys were administered to collect demographic (age, ethnicity) and health information, including alcohol use, tobacco use, and history of physician-diagnosed asthma. Pre-shift surveys also asked whether or not the participant had performed any welding during the preceding 48 hr (e.g., Saturday or Sunday). Post-shift surveys were used to collect work task information and included time-task logs for all metal working (e.g., welding, cutting, grinding) performed that day, including shield gas, base metal, and any additional consumables used during welding. The time-task logs also collected information on what, if any, form of PPE (e.g., respiratory, gloves, local exhaust ventilation) was used during each metal working task. Information was also collected regarding during-shift use of tobacco or nicotine products, job title, years each participant welded professionally. Additionally, study personnel were allowed to accompany the site safety director to briefly monitor each participant twice per sample day to collect information on work activities and other exposure determinants, including PPE use and presence of any unusual exposure sources nearby (i.e., use of galvanizing spray). Half of the participants were sampled on each Monday for a total of 4 sample days.

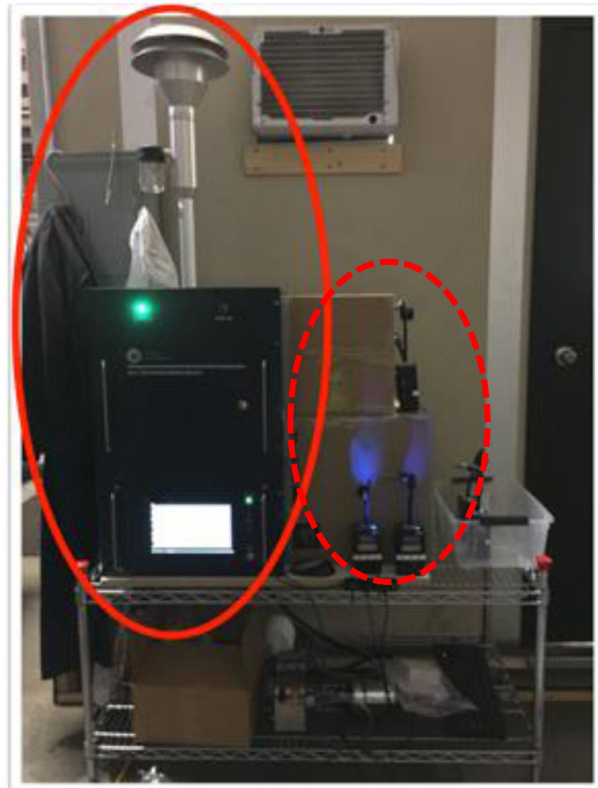

Figure 2. Area monitoring cart with EDXRF (circled) and triplicate IOMs (dashed circle).

Area air sampling

Beginning on the second study day (Monday, October 30, 2017), an area-monitoring cart holding a near real-time X-ray fluorescence (XRF) spectrometer for PM_{10} airborne metals was co-located with three IOM samplers for inhalable particles and placed in one of the three shops (Figure 2). Li et al. (2000) found that IOM samplers are suitable for area sampling in locations where windspeed is less than 0.5 m/sec; all sampling locations in this study were indoors.

The near real-time XRF was an XACT 625i Ambient Continuous Multi-Metals Monitor (Cooper Environmental, Beaverton, OR) using reel-to-reel filter tape sampling followed by energy dispersive X-ray fluorescence analysis (hereafter, EDXRF). The instrument was operated at 16.7 LPM (liters per minute) with a PM_{10} size-selective inlet, reporting concentrations for 13 elements (titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, molybdenum, tin, tungsten, and lead) every 15 min. Instrument limits of detection are reported in Table S1 of the online supplement.

Area monitoring locations in each shop are marked in Figure 1. The inhalable size fraction of particulate matter was also measured at each area sampling location using triplicate Institute of Medicine (IOM) samplers at a flow rate of 2 LPM (SKC Inc., Eighty Four, PA). The EDXRF ran continuously for 1 week in each of the three shops. Data reported in this manuscript are from Monday sampling times only (when personal sampling was also taking place), and the daily averages calculated from the time-resolved EDXRF data were truncated from 7 AM to 6 PM to better correspond with the shift-length personal samples. The EDXRF was not available for the first Monday of sampling, but is available for all subsequent sampling Mondays.

The triplicate inhalable samplers were co-located with the EDXRF on the area sampling cart and run on Mondays only, when personal samples were also collected. Of the three IOM samples (filters plus corresponding wipe of cassette walls), one was analyzed for inhalable metals and two were measured for the bioavailable fraction of the inhalable metals (Karthikeyan et al. 2006). One field blank was included per sampling day for each set of nine area IOM samplers.

Personal air sampling

Study participants wore an IOM sampler (SKC Inc., Eighty Four, PA) to measure inhalable particle exposure during their two monitored shifts. Samplers were located at the center of the collar, just below the bottom of the welding hood in order to minimize left shoulder/right shoulder exposure differences related to handedness. Filters and cassettes were measured gravimetrically and via inductively coupled plasma mass spectrometry (ICP-MS) for total metals analysis. One field blank was included per day for each set of nine personal IOM samplers.

Gravimetric analysis

Filters and their cassettes were pre- and post-weighed in a temperature and humidity-controlled weighing room at Johns Hopkins School of Public Health using a Mettler Toledo microbalance (Columbus, OH; ± 0.001 mg).

Chemicals and materials

All chemicals were analytical grade or higher and used as received without further purification. Single- and multi-element standards were purchased from Inorganic Ventures (Christiansburg, VA) and a certified reference material for stainless steel welding fume (SSWF-1 CRM) was purchased from Health and Safety Laboratory (Harpur Hill, Buxton, UK). SSWF-1 was specifically prepared as a CRM for stainless steel welding fume. The bulk material was collected from the ventilation ducts of an automobile assembly plant after spot welding of stainless steel components prior to certification (Butler et al. 2014). Concentrated nitric and hydrofluoric acid (TraceMetal grade) were purchased from Fisher Scientific (Waltham, MA) and hydrogen peroxide (Suprapur grade) was purchased from Millipore Sigma (Burlington, MA). IOM samplers, cassettes, and mixed cellulose ester (MCE) filters (25 mm, 0.8 µm) were purchased from SKC Inc. (Eighty Four, PA).

Metals analysis

All samples were prepared for ICP-MS analysis using a strong acid microwave-assisted digestion method. Particulate matter deposited on the sides of the IOM inlet was collected by wiping with 2 cm x 2 cm squares of KimWipe (Thomas Scientific, Swedesboro, NJ). IOM filters and IOM inlet wipes were placed in separate 50 mL Teflon microwave vessels with 4 mL 70% HNO_3, 2 mL 35% H_2O_2, and 0.35 mL 49% HF. The samples were then sealed and digested in a Mars Xpress scientific microwave (CEM Corporation, Matthews, NC) using a 17-min three-stage temperature-controlled program. The final temperature of 180 °C was held for 5 min with intermediate 2-min ramps and 3-min holds at 9 °C and 135 °C.

Digested samples were then diluted and analyzed using an Agilent 7500 Series Octopole ICP-MS (Agilent Technologies, Santa Clara, CA). Percent recovery for all elements was verified as 95 ± 5% using the stainless steel welding fume CRM. Laboratory blanks, laboratory spikes, and duplicates were carried out at a rate of 1 in every 10 samples during ICP-MS analysis. All laboratory blanks were below the method-calculated LOD for reported analytes.

Nine metals were assessed in the diluted digests from the IOM samples: vanadium, chromium, manganese, cobalt, copper, nickel, zinc, molybdenum, and lead Eight IOM filters were below the method LOD for lead (7 ng/filter), and $LOD/\sqrt{2}$ was imputed for those exposures. All other metals for all samples were above element specific LODs in ICP-MS analyses.

Bioavailable metals analysis

Karthikeyan et al. (2006) report a bioavailable metals analysis digestion and analysis method suitable for measuring the bioaccessible, or water-soluble, metals fraction on filters in detail. Briefly, duplicate IOM filters and sampler wipes were microwave digested in Millipore water for 10 min at 100 W power prior to ICP-MS analysis.

Statistical analysis

Summary statistics were calculated for personal and area exposures and boxplots were created to indicate metals exposure across categories of exposure determinants (i.e., base metal, welding process). Wilcoxon rank-sum tests were performed to test for statistically different levels of metals exposure between the three shops and by amount of time spent welding. A one-way random effect analysis of variance (ANOVA) model was used to determine between-worker and within-worker exposure variance, as well as F ratios and intra-class correlation coefficients.

A Shapiro–Wilk W test was used to check for normality on log-transformed exposure variables. Of the 10 exposure variables tested, five rejected the null hypothesis that the values were normally distributed (manganese, copper, zinc, molybdenum, total inhalable mass) and five did not reject the null hypothesis (vanadium, chromium, cobalt, nickel, and lead). It is well known, however, that exposure data are generally log-normally distributed (Hinds 1999) and the authors believe it is likely that the small sample size ($n = 35$) was a factor in the rejection of the null hypothesis. Thus, all exposure variables were log-transformed prior to any parametric analysis. Mean square between-worker variance ($\hat{\sigma}^2_{by}$), and mean square within-worker variance ($\hat{\sigma}^2_{wy}$) were tabulated from the ANOVA output. In order to show the partitioning of worker exposure variance into between-worker and within-worker fractions, intra-class correlation coefficients were calculated using the formulas described by Rappaport et al., where $\widehat{ICC} = \frac{\hat{\sigma}^2_{by}}{\hat{\sigma}^2_{Y}}$, where $\hat{\sigma}^2_{by}$ is the between-worker variance for the group and $\hat{\sigma}^2_{Y}$ is the total variance, or $\hat{\sigma}^2_{by} + \hat{\sigma}^2_{wy}$ (Rappaport and Kupper 2008). Stata 14 was used for all statistical analyses (StataCorp, College Station, TX).

Results

Characteristics of study population

Eighteen participants were included in the study, 16 of whom were employed as full-time welders/fabricators and two of whom were employed as full-time laser or brake press operators. The population was predominately composed of Caucasian males with a median age of 30 years. Thirteen of the 18 participants reported welding for 1 hr or more during both of their shifts and the median inhalable PM exposure was 1.9 (range: 0.79–5.2) mg/m^3 as an 8-hr TWA. Participants with a self-reported welding time greater than 1 hr had a statistically significant increase ($p = 0.008$) in inhalable PM exposure.

Welding parameters

The most common form of welding (>85% total hours) was GTAW on stainless steel, followed by GMAW on mild steel. There were 35 total monitored shifts; one participant was called off-site prior to his second shift and was not able to be sampled. Of the 35 shifts, 68% ($n = 24$) reported only GTAW welding, 11% ($n = 4$) reported both GTAW and GMAW welding, 6% ($n = 2$) reported only GMAW welding, and 74% ($n = 26$) reported grinding. All GTAW welders used argon shield gas and all GMAW reported using 90/10 Ar:CO_2.

During 92% ($n = 22$) of the shifts sampled, workers reported only GTAW welding with stainless steel as the base metal. During the remaining 8% of shifts, mild steel or both mild and galvanized steel were reported as the base metal. 75% of the GMAW shifts welded on mild steel, and one of the four shifts was on stainless steel. Additionally, three of 18 welders reported having welded professionally for less than 1 year.

Personal inhalable exposures for chromium, manganese, and nickel are shown for different welding processes, base metals, and reported years welding professionally in Supplementary Figures S1–S3. In general, chromium exposures were highest in those who performed GTAW welding and manganese exposures were higher in those who performed either GMAW only or a combination of GMAW and GTAW. Additionally, welders who reported having less than 1 year of professional welding experience had higher median exposures to both chromium and nickel per shift than those who reported welding professionally for more than 1 year. The median shift length was 9 hr (range: 6–10 hr) and all exposures are reported as 8-hr time-weighted averages. No participants self-reported wearing respiratory personal protective equipment (i.e., N95, half-face respirator or similar) during welding and only one participant reported sometimes wearing respiratory PPE during grinding in the post-shift survey. No local exhaust ventilation was provided in any of the shops.

Personal exposure monitoring

Gravimetric and metals analysis was performed on each of the two shift-length IOM inhalable samplers for the eighteen study participants. Figure 3 presents box plots for all participant personal exposures to chromium, manganese, and nickel. Results for all 10 elements and the gravimetric mass analysis are presented in Table 1, separated by participant's assigned shop location and by amount of self-reported welding time.

A nonparametric Wilcoxon rank-sum test was used to compare the median inhalable metals exposures between both welding time categories and between each shop pairing. There was a significant difference in

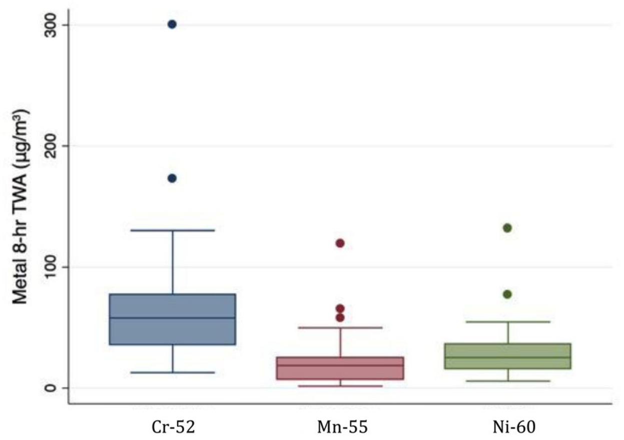

Figure 3. Personal inhalable chromium, nickel, and manganese exposure across all shifts.

exposure for all metals between those who welded more than 1 hr and those who welded 1 hr or less ($p < 0.01$). Those who welded for more than 1 hr had between two- and four-fold higher geometric mean metals exposures than those who welded less than 1 hr. Geometric mean exposure levels in Shops 2 and 3 were between 2- and 10-fold higher compared to Shop 1 ($p < 0.01$) with the exception of cobalt, which showed no statistically significant difference between the shops. No metals exposures were statistically significantly different between Shops 2 and 3 ($0.08 \leq p \leq 0.90$).

Area air monitoring

Area monitoring results are presented in Table 2. Inhalable total particulate metals and inhalable bioavailable metals were measured at the area monitoring stations with the collocated EDXRF in Shop 1 on October 30th, Shop 2 on November 6th, and Shop 3 on November 13th. PM_{10} metals from the EDXRF are presented as the mean of the 15-minute time-resolved data from 7AM–6PM.

The 15-min time-resolved data for selected elements is presented in Figure 4 for Shop 2 on Monday, November 6th as an example of typical patterns observed. Six metals are shown in panel A and five metals are shown in panel B. Clear activity peaks are present for many elements associated with stainless steel welding (Antonini et al. 2003), particularly aluminum, manganese, and chromium. The elements in Figure 4(a) show a ramp in concentration at the beginning of the workday, a sharp decrease during the lunch period, and a slower ramp down at the end of the workday. Peaks can also be seen when a laser-cutter was operated adjacent to the EDXRF at approximately 1:15 PM and 3:00 PM on November 6, 2017. With the exception of the peaks associated with the laser cutter (which is only present in Shop 2), these trends are similar across all shops and all days.

Several elements, however, show trends that are not associated with an increase in welding activity and were poorly correlated with the overall temporal trends for the other metals (Figure 4(b)). Tungsten had its highest peaks corresponding with workers sharpening their tungsten electrodes before performing GTAW welding at the beginning of the workday and after lunch. Vanadium exposure exhibited several discrete peaks, but was not always present at detectable levels in shop air using the 15-min time-resolved readings from the EDXRF.

Exposure variance

Values for the intraclass correlation coefficient can be found in Table 3. Values greater than 0.5 indicate that most variance in the indicated exposure was found between workers, while values less than 0.5 indicate that more variance in exposure occurred within participants. For most elements, a majority of the variance is attributed to differences between workers. However, for cobalt and inhalable PM most variation is seen within workers.

Discussion

This study aimed to assess comprehensively welder exposure at a stainless steel fabrication facility, including assessing the bioavailability of the primary welding fume metals. Although welding fume as a mixture does not currently have an occupational exposure limit in the United States, participant personal exposures to inhalable metals were all under the relevant Occupational Health and Safety Administration (OSHA) metal-specific permissible exposure limits (PELs). However, one participant's manganese exposure was over the $0.1\,mg/m^3$ threshold limit value (TLV®) set by the American Conference of Governmental and Industrial Hygienists (ACGIH®). Furthermore, median nickel and chromium exposures were higher for those participants who reported welding professionally for less than 1 year. Inexperience in welding has been suggested by other researchers to increase personal exposure as a result of less efficient techniques (Korczynski 2000; Graczyk et al. 2016).

Given that approximately 85% of the welding hours reported were for GTAW on stainless steel, participant personal exposures to nickel and chromium were generally higher than has been reported in similar

Table 1. Personal inhalable PM and inhalable metals by shop location and welding time category.

Elements, 8-hr TWA, $\mu g/m^3$ Geometric mean (range)	^{51}V	^{52}Cr	^{55}Mn	^{59}Co	^{60}Ni	^{63}Cu	^{66}Zn	^{95}Mo	^{208}Pb	Inhalable PM mg/m^3 (range)
All Shifts (n = 35)	0.27 (0.07–1.4)	51 (13–300)	13 (1.5–119)	0.68 (0.14–2.5)	22 (5.7–132)	3.3 (0.58–24)	7.3 (1.0–290)	0.97 (0.23–4.8)	0.17 (0.04–1.2)	1.7 (0.31–5.2)
Shop 1 (n = 10)	0.11 (0.07–0.25)	22 (13–61)	3.0 (1.5–8.0)	0.46 (0.14–2.4)	9.6 (5.7–26)	1.0 (0.58–2.4)	1.6 (1.0–2.1)	0.44 (0.23–1.1)	0.06 (0.04–0.12)	0.74 (0.31–1.6)
Shop 2 (n = 19)	0.37 (0.14–1.42)	65 (26–300)	25 (10–119)	0.76 (0.39–2.5)	29 (12–132)	5.1 (3.1–11)	16 (3.4–290)	1.3 (0.46–4.8)	0.24 (0.13–0.60)	2.4 (1.4–5.2)
Shop 3 (n = 6)	0.45 (0.28–0.90)	91 (49–173)	19 (9.2–50)	0.93 (0.51–1.6)	41 (20–77)	5.8 (3.0–24)	8.2 (2.5–42)	1.5 (0.87–3.3)	0.33 (0.20–1.2)	2.4 (1.3–4.4)
Welding Time										
One Hour or Less (n = 9)	0.12 (0.07–0.40)	23 (12.7–74)	4.3 (1.52–30)	0.35 (0.14–1.4)	10 (5.7–33)	1.3 (0.58–4.8)	3.3 (1.0–46)	0.49 (0.25–1.3)	0.09 (0.04–0.30)	0.97 (0.31–2.6)
1+ Hours (n = 26)	0.36 (0.07–1.4)	67 (15–300)	19 (3.3–119)	0.86 (0.45–2.5)	29 (6.3–132)	4.5 (0.79–24)	9.6 (1.5–290)	1.2 (0.23–4.8)	0.22 (0.04–1.2)	2.1 (0.39-5.2)

studies (Bonde 1990; Wallace et al. 2001; Weiss et al. 2013). The 2013 WELDOX study by Weiss et al., for example, reported median inhalable chromium and nickel exposures for GTAW welders of 10.5 and $<5.10\,\mu g/m^3$ when excluding those wearing powered air-purifying respirators and including only those whose weld material had chromium or nickel content higher than 5%. In contrast, our study had median total inhalable chromium and nickel exposures of 58 and $25\,\mu g/m^3$, respectively.

Additionally, all exposures in this study were measured on a Monday after a 2-day weekend (the study site only operated Monday through Friday for the duration of the study). Mondays may not be fully representative of the exposures occurring on other days of the week, warranting caution in extrapolating these results as unbiased average daily-exposures for each participant.

A limitation of this study is that chromium was not able to be speciated in the analysis and thus only total chromium and not hexavalent chromium can be reported. Relatively high levels of inhalable total chromium were measured in this study compared to similar field studies reporting on stainless steel welding exposures (Bonde 1990; Wallace et al. 2001; Weiss et al. 2013) and previous studies have reported that 4–20% of the total chromium present in GTAW fumes can be present in the hexavalent state (Bonde 1990; Edme et al. 1997; Emmerling et al. 1987).

Although the true concentration of hexavalent chromium is unknown, assuming 4% as the minimum percent of hexavalent chromium present and applying this to the inhalable total chromium measured in this study, four of 35 readings could be over the OSHA PEL of $5\,\mu g/m^3$ and 14 could be over the OSHA action level of $2.5\,\mu g/m^3$. However, hexavalent chromium is generally water-soluble and the bioavailability analyses of our area samplers showed a mean water-soluble chromium fraction of 1.2%. Limiting the possible hexavalent fraction to 1.2% would suggest that none of the samples were above the OSHA PEL and only two samples were at or above the action level. One should use caution, however, in using area sampler data to interpret personal exposures as the area samplers may not be fully representative of the welding-associated aerosols generated by the participants. Additionally, hexavalent chromium is known to reduce to trivalent chromium on filters within hours of collection (Shin and Paik 2000), and thus the soluble chromium fraction measured in this study may be biased low.

Table 2. Total inhalable, bioavailable, and PM10 area results from each shop.

	October 30, 2017 Shop 1			November 6, 2017 Shop 2			November 13, 2017 Shop 3		
Element	Inhalable ($\mu g/m^3$)	PM_{10}^A ($\mu g/m^3$)	Bioavailable Inhalable^B($\mu g/m^3$)	Inhalable ($\mu g/m^3$)	PM_{10}^A ($\mu g/m^3$)	Bioavailable Inhalable^B($\mu g/m^3$)	Inhalable ($\mu g/m^3$)	PM_{10}^A($\mu g/m^3$)	Bioavailable Inhalable^B ($\mu g/m^3$)
^{52}Cr	11	2.6	0.06	57	10	0.59	14	7.4	0.35
^{55}Mn	1.1	0.96	0.19	22	17	4.17	15	15	2.9
^{60}Ni	4.8	0.89	0.07	25	3.3	0.49	6.1	1.9	0.26
^{63}Cu	0.43	0.20	0.11	5.8	2.8	1.6	2.6	1.7	0.75
^{66}Zn	0.33	0.11	0.49	48	104	28	8.4	1.6	6.5
$^{208}Pb^C$	<LOD	0.001	<LOD	0.37	0.25	0.08	<LOD	0.03	<LOD

[A]From EDXRF; daily average of 15-min time-resolved concentrations (7am–6pm).
[B]Bioavailable metals fraction from IOM filter; average of two samplers.
[C]Method Limit of Detection (LOD) for lead was 0.007 μg/filter for total metals and 0.001 μg/filter for bioavailable metals.

Shop 2 had mean area concentrations of all metals at least a factor of three higher than in Shop 1, with the largest difference in concentrations exhibited by zinc. With the exception of zinc, Shop 2 metals concentrations were similar to those in the interconnected Shop 3. Zinc had significantly higher airborne concentrations in Shop 2 than Shop 3. Welder personal exposures showed similar trends across metals by participant's primary shop assignment (Table 1), although exposures were more similar across shops for vanadium and cobalt (all shops within 40% of group mean for cobalt and 67% for vanadium).

Zinc fume exposure is associated with oxygen radical formation and a cytokine-mediated pulmonary inflammatory response (Blanc et al. 1993; Lindahl et al. 1998; Brand et al. 2014). Nineteen of the 35 measured shifts were from welders reporting a primary shop assignment of Shop 2. The increased personal and area zinc levels are unlikely to solely be a result of a higher number of welders in the space or the lack of a general ventilation system because other welding-fume associated metals did not exhibit the same magnitude of increase in concentration. It was noted in the field observations, however, that some welders in Shop 2 used galvanizing spray. Galvanizing spray is an aerosolized spray comprised of >90% zinc, intended to coat the sprayed metal with a layer of zinc to protect from corrosion and rust. This spray could have contributed to the elevated zinc levels in Shop 2, although the use of such galvanizing sprays is rarely reported in the literature.

The near-real time metals analysis by the EDXRF allowed for visualization of intra-day variation in airborne metals concentrations. Many welding-associated metals exhibited three-fold or higher concentration changes throughout study days, with peaks in airborne levels consistently occurring in mid-morning and mid-afternoon. This likely is a result of preparation activities (such as tacking or cutting) occurring immediately after the start of the workday and after the lunch break, with most welding tasks taking place after the preparation is finished. This time-resolved information could be used to target fume exposure reduction activities, such as increasing ventilation or encouraging the use of PPE when area fume levels are likely to be highest.

The time-resolved information also allows for detection of task-based peaks in metals concentrations, especially those associated with large, stationary equipment. A time-series of the EDXRF-measured concentrations in Shop 1, for example, showed clear peaks that correlated with the use of the laser-cutting instrument (see location in Figure 1).

The element-specific fraction of bioavailable metals (representing the systemic absorption) is the predominate indicator of biological effect for respiratory exposures (Berlinger et al. 2008). The increased bioavailability of manganese ($16 \pm 3\%$), as compared to chromium ($1.2 \pm 0.08\%$) and nickel ($2.6 \pm 1.2\%$), in the inhalable metals fraction indicates a potential concern with respect to neurotoxicity. Recent studies in the literature have indicated that the blood-solubility of manganese directly impacts its ability to uptake into the CNS through the blood-brain barrier and that the solubility modulates its neurotoxicity (Aschner and Aschner 1991; Han et al. 2008). Bioavailability of metals in welding fume is directly impacted by the choice of welding process, the presence of certain fluxes and alkalis, and other determinants (Antonini et al. 2003), leading to the possibility of targeted approaches in decreasing risk of particularly hazardous exposures.

One-way random effects intra-class correlation coefficients (ICC) were calculated to determine the between- and within-worker variance components using the formulas described by Rappaport and Kupper (2008). Using this framework, ICCs close to zero indicate repeated measures that appear random, and ICCs close to 1 suggest clustered measures. The inhalable PM and inhalable cobalt both have ICCs of 0.30, indicating that most of the variance in these

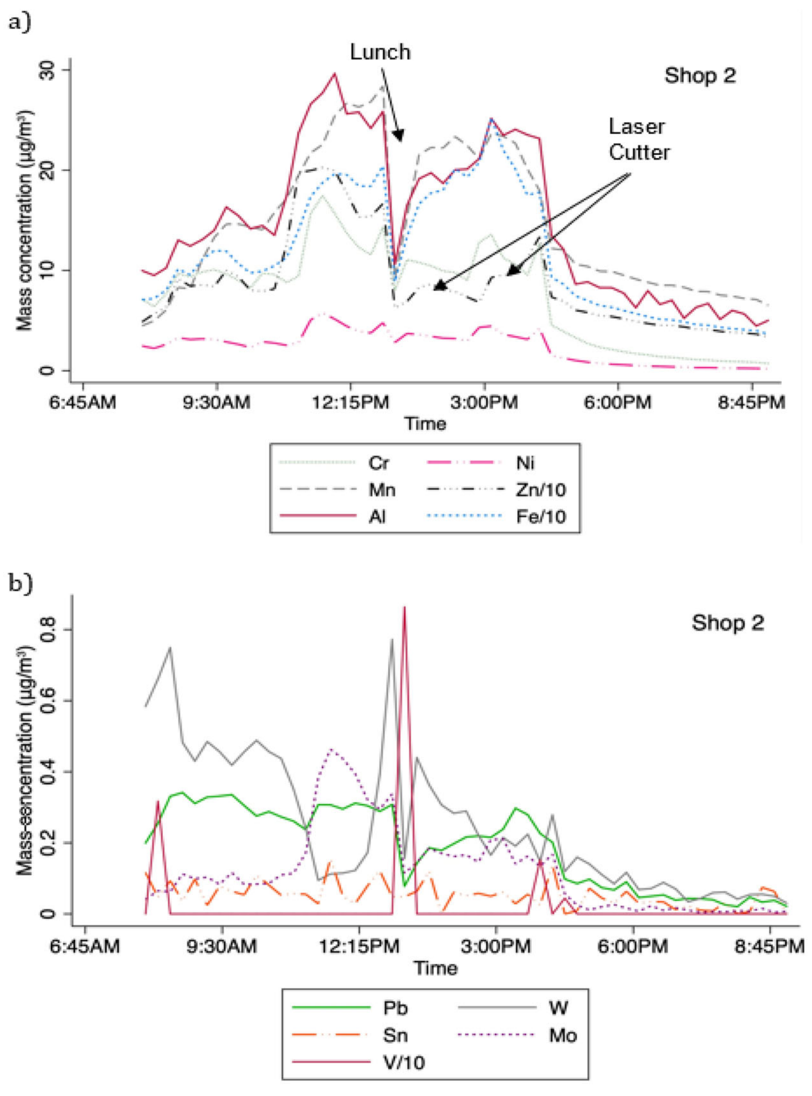

Figure 4. (a) Time-resolved Cr, Mn, Al, Ni, Zn, and Fe in Shop 2 on 11/6/17. (b) Time-resolved Pb, Sn, V, W, and Mo in Shop 2 on 11/6/17.

Table 3. Intraclass correlation coefficients (ICC) for inhalable metals and inhalable PM exposure (describing between and within worker variance in exposure).

Element	^{51}V	^{52}Cr	^{55}Mn	^{59}Co	^{60}Ni	^{63}Cu	^{66}Zn	^{95}Mo	^{208}Pb	Inhalable PM
$ICC = \frac{\hat{\sigma}^2_{by}}{\hat{\sigma}^2_{Y}}$	0.74	0.67	0.79	0.30	0.70	0.68	0.55	0.65	0.69	0.30

exposures occurs within-worker rather than between workers. All other metals have ICCs greater than 0.65, suggesting that most of the variation occurs between workers. The high within-worker variance component in the inhalable and total particle size fraction is in line with recent studies (Liu et al. 2011). The between-worker variance components for the other welding fume-associated metals indicate that the enrolled participants had heterogeneous task-based exposures, even between similar job titles. This between-worker variability implies a need for individual-level controls, such as local exhaust ventilation or other OSHA recommended means to reduce exposures for those workers most highly exposed (Rappaport and Kupper 2008; OSHA 2013).

Conclusions

This comprehensive approach to welding-fume exposure assessment can allow for targeted approaches to controlling exposures based not only on individual measurements, but also on metal-specific measures, such as the use of galvanizing spray in unventilated areas. Additionally, assessments for bioavailability can also lead to targeted approaches in decreasing element-specific exposures, such as manganese, that may carry increased risk of adverse health outcomes.

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Conflict of interest

The authors declare no conflict of interest relating to the material presented in this article.

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