Characterization of Total and Size-Fractionated Manganese Exposure by Work Area in a Shipbuilding Yard

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ABSTRACT

Background: Shipbuilding involves intensive welding activities, and welders are exposed to a variety of metal fumes, including manganese, that may be associated with neurological impairments. This study aimed to characterize total and size-fractionated manganese exposure resulting from welding operations in shipbuilding work areas.

Methods: In this study, we characterized manganese-containing particulates with an emphasis on total mass \( m = 86 \), closed-face 37-mm cassette samplers) and particle size-selective mass concentrations \( n = 86, 8 \)-stage cascade impactor samplers), particle size distributions, and a comparison of exposure levels determined using personal cassette and impactor samplers.

Results: Our results suggest that 67.4% of all samples were above the current American Conference of Governmental Industrial Hygienists manganese threshold limit value of 100 \( \mu g/m^3 \) as inhalable mass. Furthermore, most of the particles containing manganese in the welding process were of the size of respirable particulates, and 90.7% of all samples exceeded the American Conference of Governmental Industrial Hygienists threshold limit value of 20 \( \mu g/m^3 \) for respirable manganese.

Conclusion: The concentrations measured with the two sampler types (cassette: total mass; impactor: inhalable mass) were significantly correlated \(( r = 0.964, p < 0.001)\), but the total concentration obtained using cassette samplers was lower than the inhalable concentration of impactor samplers.

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1. Introduction

Shipbuilding refers to the construction of ships and other floating vessels. It normally takes place in a specialized facility known as a shipbuilding yard. Welding is a major task in shipbuilding yards that generates welding fumes. Owing to the condensation of the high-temperature metal vapor released into the air from the welding arc, welding fume is generated during the transfer of molten metal from the electrode to the base metal. The constituents of the welding fume and its contents depend on welding type, welding condition, materials being fused, and filler materials. A significant amount of welding in shipbuilding yards is performed on steel. Inevitably, manganese (Mn) is present in the base metals being joined and the filler wire being used, and, hence, in the fumes to which workers are exposed.

Manganese is an essential element and is required for adequate functioning of the human central nervous system. However, high, long-term occupational exposure to manganese can result in manganism, a severe neurological disorder characterized by movement disturbances and cognitive deficits [1,2].

In 1985, the first case of occupational disease due to exposure to manganese was reported at a welding rod manufacturing company in Republic of Korea [3]. Prior to 2002, a total of 10 cases of occupational disease due to manganese were reported: three workers involved in crushing materials containing manganese, one metal assembly line worker, and six welders [3]. Thus, minimizing the concentration of manganese that welders are exposed to is very important for protecting their health.

Currently, the Occupational Safety and Health Administration [4] in the USA has a permissible exposure limit for welding fume as individual metals or total particulate mass. The permissible exposure limit for manganese is 5,000 \( \mu g/m^3 \), set as a ceiling for total fume and dust, while for iron oxide fume it is 10,000 \( \mu g/m^3 \), set as an 8-hour time-weighted average (TWA) [4]. The Ministry of
Table 1

| Substance type                  | Year     | TLV (g/m³) |
|--------------------------------|----------|------------|
| Manganese                      | 1948–1959| TWA: 6,000 |
|                               | 1960–1962| TWA: 5,000 |
|                               | 1963–1969| Ceiling: 5,000 |
| Manganese and inorganic        | 1970–1981| Ceiling: 5,000 as Mn |
| Manganese fume                 | 1977 proposed| TWA: 1,000 as Mn |
|                               | 1979–1994| TWA: 1,000 as Mn |
|                               |          | STEL: 3,000 as Mn |
| Manganese dust and compounds   | 1982–1987| TWA: 5,000 as Mn |
|                               | 1988–1994| TWA: 5,000 as Mn |
| 1.1. Manganese, element, and inorganic compounds | 1.1. 1992 proposed| TWA: 200 as Mn |
|                               | 1.1. 1995–2012| TWA: 200 as Mn |
|                               | 1.1. 2009 proposed| TWA: 100 (I), 20 (R) as Mn |
|                               | 1.1. 2013–present| TWA: 100 (I), 20 (R) as Mn |

ACGIH, American Conference of Governmental Industrial Hygienists; I, inhalable fraction; Mn, manganese; R, respirable fraction; STEL, short-term exposure limit; TLV, threshold limit value; TWA, time-weighted average.

2. Materials and methods

All samples were collected from the main work areas at one shipbuilding yard in Republic of Korea. The job contents, welding types used, and number of workers sampled in the work areas were as follows. In steel cutting, steel plates are cut into the parts that will form the hull and deck sections of a ship typically using a thermal plasma cutting technique, and 10 workers were sampled in this work area. In the block assembly, the cut steel is assembled into smaller blocks. Almost 95% of the work in this work area was CO2 arc welding, and the remainder was grinding. A total of 32 workers in this work area were sampled. In block erection, smaller blocks are assembled into larger sections that are mounted together, which finally becomes a complete ship. All work in this area was CO2 arc welding. We sampled 21 workers in this work area. Ships should be outfitted with support equipment, such as plumbing, electrical installation, etc. There are two major processes for outfitting: outfitting preparation and outfitting installation. The CO2 arc welding workload of outfitting preparation and installation was smaller than that in the other work areas (preparation: 80%; installation: 90%). However, these work areas used tungsten inert gas (argon) welding (preparation: 20%; installation: 10%). We sampled seven (preparation) and 16 (installation) workers in these work areas.

2.1. Personal air sampling and analysis

A total of 86 samples of air particulates were collected from employees in five main processes using a closed-face 37-mm cassette sampler, and the total manganese was analyzed. All cassette samples were collected on mixed cellulose ester substrates at a flow rate of 2.0 L/min using personal air sampling pumps (Gilian BDX-II; SediStyle, St Petersburg, FL, USA). Each 37-mm cassette sampler was positioned in the personal breathing zones of employees during their normal work activities.

In the same employees, 86 impactor samples were collected using eight-stage cascade impactor samplers (Marple Series 290; MSP Corporation, Shoreview, MN, USA), which were also positioned in employees’ personal breathing zones and analyzed for manganese.

All impactor samples were collected on Mylar substrate (from Stage 1 to Stage 8) and polyvinyl chloride substrate (backup stage) at a flow rate of 2.0 L/min, using personal air sampler pumps (Gilian BDX-II; Sensidyne). The aerodynamic diameter cut points for the impactor samplers at a flow rate of 2.0 L/min were > 21.3 μm (Stage 1), 14.8 μm (Stage 2), 9.8 μm (Stage 3), 6.0 μm (Stage 4), 3.5 μm (Stage 5), 1.55 μm (Stage 6), 0.93 μm (Stage 7), 0.52 μm (Stage 8), and < 0.52 μm (final backup stage). All impactor samples were collected on the substrates, which were sprayed with silicone to minimize particle bounce during sampling.

Manganese content analyses were performed by inductively coupled plasma/mass spectrometry according to the National Institute for Occupational Safety and Health analytical method 7302, which has a limit of detection of 0.02 μg/sample [11].

2.2. Data analysis

The concentration of manganese in air was determined by dividing the sum of analyte masses on all filters in a sample by the volume of sampled air. The inhalable, thoracic, and respirable mass concentrations of manganese on the impactor samples were calculated using the ACGIH/International Organization for Standardization dust criteria [12]. Size-selective mass concentrations were calculated using Simpson’s rule in a tabular–graphical approach to estimate the contribution of each impactor stage to the
The GM concentration of out
terations measured using 37-mm cassette samplers by work area.

3. Results

3.1. Samples of 37-mm cassette

Table 3 presents the total airborne manganese mass concentrations by work area using 37-mm cassette samplers placed in breathing zones of workers, and excess rate of Korean MoEL’s OES for manganese.

Table 2

Inhalable, thoracic, and respirable factors for each stage obtained from ACGIH/ISO size-selective curves and Simpson’s rule

| Stage       | Size range (µm) | Respirable factors | Thoracic factors | Inhalable factors |
|-------------|-----------------|--------------------|------------------|------------------|
|             | Lower limit     | Upper limit        | Midpoint*        |                   |
| 1           | 21.3            | 42                 | 31.55            | 0.00             | 0.010             | 0.580             |
| 2           | 14.8            | 21.1               | 17.95            | 0.00             | 0.104             | 0.671             |
| 3           | 9.8             | 14.8               | 12.30            | 0.005            | 0.338             | 0.740             |
| 4           | 6               | 9.8                | 7.90             | 0.065            | 0.669             | 0.812             |
| 5           | 3.5             | 6                  | 4.75             | 0.360            | 0.861             | 0.876             |
| 6           | 1.55            | 3.5                | 2.53             | 0.819            | 0.930             | 0.930             |
| 7           | 0.93            | 1.55               | 1.24             | 0.962            | 0.964             | 0.964             |
| 8           | 0.52            | 0.93               | 0.73             | 0.979            | 0.979             | 0.979             |

* The midpoint of the lower and upper limits for each stage (MP = [(UL – LL)/ 2] + LL).

ACGIH, American Conference of Governmental Industrial Hygienists; ISO, International Organization for Standardization; LL, lower limit; MP, midpoint; UL, upper limit.

Table 3

Total airborne manganese mass concentrations by work area using 37-mm cassette samplers placed in breathing zones of workers, and excess rate of Korean MoEL’s OES for manganese

| Work area          | n  | GM (µg/m³) | GSD | Range (µg/m³) | Excess rate (%) |
|--------------------|----|------------|-----|---------------|-----------------|
| Steel cutting      | 10 | 60.5       | 4.0 | 52.0–407.4    | 0.0             |
| Block assembly     | 32 | 198.4      | 5.7 | 58.2–2,335.3 | 18.8            |
| Block erection     | 21 | 98.1       | 6.4 | 43–2,596.6    | 14.3            |
| Outfitting preparation | 7 | 25.0       | 3.4 | 2.4–109.9     | 0.0             |
| Outfitting installation | 16 | 99.4   | 4.9 | 8.0–1,345.2  | 6.3             |
| Total              | 86 | 108.1      | 5.7 | 2.4–2,596.6   | 11.6            |

GM, geometric mean; GSD, geometric standard deviation; MoEL, Ministry of Employment and Labor; n, number of samples; OES, occupational exposure standard for manganese of MoEL in Republic of Korea = 1,000.0 µg/m³.

Overall particle size fraction of interest [13]. Table 2 gives the particle size range, midpoint, and factors applied to each impactor stage to estimate the inhalable, thoracic, and respirable mass concentrations. Size distributions of manganese-containing particles in air were estimated for each impactor sample [13].

All statistical analyses were performed using PC-SPSS version 18.0 (IBM Corporation, Armonk, NY, USA). For the concentration of data below the limit of detection, a value of one-half the limit of detection was assigned to the data [14]. Distributions of the data on exposure to airborne manganese-containing particles were examined by the Kolmogorov–Smirnov test. As a result, all log-transformed data were found to be normally distributed; hence, the geometric mean (GM) and geometric standard deviation were calculated. The analysis of variance (ANOVA) procedure was used to conduct a comparison of the differences between the means of five different work areas in the shipbuilding yard. One-way ANOVA were used to investigate these differences between means using the general linear model procedure. In these procedures, the logarithm of exposure was used as the outcome variable, and Scheffe’s test option was specified to identify specific differences between the different means. Pearson’s correlation coefficients were obtained to assess the relationships between the sampler types and the concentrations of exposure agents using the Proc Corr procedure. Graphs of the sampler types and exposure agents were prepared in SigmaPlot 10.0 (Systat Software Inc., San Jose, CA, USA).

3.3. Eight-stage impactor samples

Table 5 summarizes the airborne manganese mass concentrations of all size fractions measured using eight-stage impactor samplers and mass median aerodynamic diameter by work area. The GM concentration of the outfitting preparation area (55.8 µg/m³) was significantly lower than that of the block assembly (323.0 µg/m³), block erection (193.2 µg/m³), and outfitting installation areas (186.0 µg/m³; Scheffe’s test: p = 0.04). Although the GM concentration of the block assembly area was the highest, there were no significant differences among the total airborne manganese mass concentrations in the block assembly, block erection, and outfitting installation areas (p = 0.33). Similar to cassette samplers, the mass concentrations for all sizes of manganese-containing particles collected with impactor samplers were higher in the block assembly area than in all other areas. All work areas except for steel cutting indicated that the range of mass median aerodynamic diameters was 0.21–0.31 µm.

Table 4 summarizes the inhalable, thoracic, and respirable mass concentrations using impactor samplers, and the excess rate of ACGIH’s TLV for manganese. In all work areas, exposure to respirable manganese components existed, indicating the potential for exposure to airborne manganese-containing particles of sizes suitable for depositing in the alveolar region of the lung. In addition, inhalable and thoracic mass concentration exposure components existed, suggesting the potential for exposure to manganese-containing particles in the upper airways.

Fig. 1 depicts the content proportions of respirable, thoracic, and inhalable mass concentrations of all size fractions. The respirable mass concentration contents of all work areas except for the steel cutting work area exceeded 80.0%: block assembly, 85.9%; block erection, 87.4%; outfitting preparation, 82.6%; and outfitting installation, 87.9%. However, the respirable mass concentration content of all size fractions in the steel cutting work area was 39.5%.

Regarding the respirable fraction, the percentages of samples that exceeded the ACGIH TLV of 20 µg/m³ in the steel cutting, block assembly, block erection, outfitting preparation, and outfitting...
installation work areas were 80.0%, 96.9%, 90.5%, 85.7%, and 87.5%, respectively.

3.3. Comparison of sample types

Fig. 2 shows a scatterplot constructed utilizing the airborne manganese concentrations measured using 37-mm cassette samplers (total) relative to the inhalable concentrations measured using impactor samplers. The concentrations measured by the two sampler types were significantly correlated ($r = 0.964$, $p < 0.001$), and the relationship is described by the regression equation:

$$\log \text{total (cassette)} = 1.099 \log \text{inhalable (impactor)} - 0.456. \quad (1)$$

4. Discussion

The data in Tables 2 and 3 present the airborne exposure to total manganese in the studied work areas. Workers with the highest exposure were from the block assembly, block erection, and outfitting installation work areas. One possible explanation for this result is that these work areas may be partially confined spaces, and thus, it may be very difficult to remove the welding fumes using a local or general ventilation system. Confined and enclosed spaces are common in shipbuilding, because work is frequently required on the interior of vessels due to the structure of ships and the nature of their construction. Workers who worked in open areas, such as the steel cutting and outfitting preparation areas, were exposed to much smaller manganese concentrations. The GM value of 86 samplers of 108.1 $\mu g/m^3$ in this study is much smaller than the values of 180 $\mu g/m^3$ found in the shipbuilding yard studies of Choi et al [15] and Kang et al [16], respectively. In a National Institute for Occupational Safety and Health Hazard Evaluation program, Kifer et al [17] reported on the personal exposure of welders in a shipbuilding yard involved in stick welding, arc gouging, and flux-cored welding primarily on mild steel, and the manganese results ranged from 240 $\mu g/m^3$ to 7,330 $\mu g/m^3$. Bellido-Milla et al [18] studied welding fume exposure in a shipbuilding yard in Spain. They collected 166 personal samples and 14 area samples over a 3-month period at various locations in the facility. The mean value for manganese ranged from nondetectable to 3,890 $\mu g/m^3$, and the majority of samples exceeded the TLV for manganese. The manganese concentration range of this study was similar to that found in our study (3.6–3,141.8 $\mu g/m^3$). Ellingsen et al [19] reported on exposure of welders to manganese from a shipbuilding yard and a plant that manufactured machinery. The GM of all the samples ($n = 188$) for manganese was 97 $\mu g/m^3$ (range, 3–4,620 $\mu g/m^3$).

Even though the concentration of manganese that welders are exposed to in shipbuilding yards depends on welding methods, with or without the use of fume extractors or efficient ventilation systems, this concentration has been decreasing lately. However, many samples exceeded the occupational exposure limits (i.e., ACGIH’s TLV and MoEL’s OES). Of all the samples in our study, 67.4% exceeded the TLV for inhalable manganese.

The slope of the plot of the inhalable concentrations measured using impactor samplers relative to the total concentrations measured using 37-mm cassette samplers was not significantly different from 1.0, and there was a small but significant intercept in the model. The overall mean ratio of total to inhalable concentration was 0.59, suggesting that the total mass was substantially lower than the inhalable fraction. Dufresne et al [20] reported that eight-stage impactor sampler has more collection efficiency than the 37-mm cassette sampler for beryllium aerosol in the magnesium and aluminum transformation industry.

It has long been recognized that the regional pattern of particle deposition in the respiratory tract affects the pathogenic potential of inhaled aerosols. Sampling the total air concentration of particulate matter provides a crude estimate of exposure that may not be correlated with health effects if the risk is associated only with those particles that may enter the thorax or penetrate beyond the ciliated airways. Although controversial, many studies suggest that neurological impairments are associated with manganese exposure [1,2,9,10]. In our study, the respirable mass concentration content of all size fractions of all work areas except for the steel cutting work area exceeded 85.0%. In addition, the range (0.21–0.31 $\mu m$) of mass

### Table 4

| Facility                  | Work area          | n  | Inhalable GM ($\mu g/m^3$) | GSD | Excess rate (%) | Thoracic GM ($\mu g/m^3$) | GSD | Excess rate (%) | Respirable GM ($\mu g/m^3$) | GSD | Excess rate (%) |
|---------------------------|--------------------|----|---------------------------|-----|-----------------|---------------------------|-----|-----------------|-------------------------------|-----|-----------------|
| Shipbuilding yard         | Steel cutting      | 10 | 88.6                      | 3.3 | 40.0            | 62.2                      | 3.3 | 43.3            | 3.4                           | 40.0 | 80.0            |
| Block assembly            | 32                 |    | 307.4                     | 4.4 | 71.9            | 292.7                     | 3.3 | 277.6           | 4.3                           | 90.0 |                 |
| Block erection            | 21                 |    | 185.0                     | 5.2 | 71.4            | 178.8                     | 5.1 | 168.9           | 5.1                           | 90.5 |                 |
| Outfitting preparation    | 7                  |    | 52.6                      | 3.8 | 42.9            | 49.4                      | 3.8 | 46.1            | 3.8                           | 85.7 |                 |
| Outfitting installation   | 16                 |    | 178.5                     | 3.9 | 81.3            | 172.0                     | 3.9 | 163.5           | 3.9                           | 87.5 |                 |
| Total                     | 86                 |    | 184.0                     | 4.6 | 67.4            | 169.6                     | 4.7 | 155.1           | 4.8                           | 90.7 |                 |

### Table 5

| Facility                  | Work area          | n  | GM ($\mu g/m^3$) | GSD | AM (SD) |
|---------------------------|--------------------|----|-----------------|-----|---------|
| Shipbuilding yard         | Steel cutting      | 10 | 109.5           | 3.4 | 51.1    |
| Block assembly            | 32                 | 323.0 | 4.4 | 171.9  | 5.2 |
| Block erection            | 21                 | 193.2 | 5.2 | 6.8     | 3,141.8 |
| Outfitting preparation    | 7                  | 55.8  | 3.7 | 3.6    | 165.2 |
| Outfitting installation   | 16                 | 186.0 | 3.9 | 16.4   | 182.1 |
| Total                     | 86                 | 196.5 | 4.6 | 3.6    | 1,341.8 |

ACGIH, American Conference of Governmental Industrial Hygienists; GM, geometric mean; GSD, geometric standard deviation; ISO, International Organization for Standardization; n, number of samples; TLV, threshold limit value of ACGIH – 100.0 $\mu g/m^3$ as inhalable mass and 20.0 $\mu g/m^3$ as respirable mass.
Respirable size. The ACGIH currently presents the limit for manganese as 20 μg/m³ as respirable dust based on neurobehavioral and neuropsychological changes [8]. The percentage of impacter samples that exceeded the ACGIH’s TLV for manganese as respirable mass was 90.7%. Therefore, we think that exposure to manganese from welding fumes in shipbuilding yards has more adverse health effects than exposure to manganese from any other sources, such as manganese alloy and nonferrous alloy manufacturing.

The level of manganese in welding fume could be affected by welding conditions, such as arc current or voltage, welding speed, and the characteristics of the welding stick, such as manganese content of the welding stick and the amount of the stick used per shift. However, we did not obtain adequate information on those kinds of welding conditions and characteristics. Despite this limitation of our study, we thought that our results could reflect the concentration of manganese that welders in shipbuilding yards are exposed to.

**Fig. 1.** Content proportions of respirable, thoracic, and inhalable mass concentrations of all size fractions estimated using impactor samplers.

Fig. 2. Airborne manganese concentration measured using 37-mm cassette samplers relative to the inhalable fraction estimated using impactor samplers.

With the measurements with inhalable aerosol (cascade impactor sampler), the slope between the two sampling methods was not significantly different from 1.0. The data analyzed here by characterizing size-selective mass concentrations indicate that the manganese-containing particles inhaled by welders in shipbuilding yards could mostly be of respirable particle size.

**Conflicts of interest**

All contributing authors declare no conflicts of interest.

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