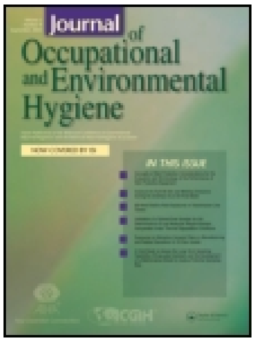

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Exposure to Fuel-Oil Ash and Welding Emissions During the Overhaul of an Oil-Fired Boiler

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The health effects of exposure to vanadium in fuel-oil ash are not well described at levels ranging from 10 to 500 μg/m^3. As part of a larger occupational epidemiologic study that assessed these effects during the overhaul of a large oil-fired boiler, this study was designed to quantify boilermakers' exposures to fuel-oil ash particles, metals, and welding gases, and to identify determinants of these exposures. Personal exposure measurements were conducted on 18 boilermakers and 11 utility workers (referents) before and during a 3-week overhaul. Ash particles <10 μm in diameter (PM_{10}, mg/m^3) were sampled over full work shifts using a one-stage personal size selective sampler containing a polytetrafluoroethylene filter. Filters were digested using the Parr bomb method and analyzed for the metals vanadium (V), nickel (Ni), iron (Fe), chromium (Cr), cadmium (Cd), lead (Pb), manganese (Mn), and arsenic (As) by inductively coupled plasma mass spectrometry. Nitrogen dioxide (NO_2) was measured with an Ogawa passive badge-type sampler and ozone (O_3) with a personal active pump sampler.

Time-weighted average (TWA) exposures were significantly higher ($p < 0.05$) for boilermakers than for utility workers for PM_{10} (geometric mean: 0.47 vs. 0.13 mg/m^3), V (8.9 vs. 1.4 μg/m^3), Ni (7.4 vs. 1.8 μg/m^3) and Fe (56.2 vs. 11.2 μg/m^3). Exposures were affected by overhaul time periods, tasks, and work locations. No significant increases were found for O_3 or NO_2 for boilermakers or utility workers regardless of overhaul period or task group. Fuel-oil ash was a major contributor to boilermakers' exposure to PM_{10} and metals. Vanadium concentrations sometimes exceeded the 2003 American Conference of Governmental Industrial Hygienists (ACGIH®) threshold limit value.

Keywords boilermakers, exposure assessment, occupational health, respiratory health, toxic metals, vanadium

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Boiler repair work in power plants is associated with significant exposure to a complex mixture of toxic agents consisting of fuel-oil ash, vanadium and other metal oxides, and nitrogen dioxide and ozone from welding emissions.(1–3) Exposure to vanadium oxides in particular has long been known to cause acute respiratory symptoms or illness, ranging from mild irritation to bronchitis and pulmonary edema.(4–12) Reduced pulmonary function has also been reported in boilermakers.(13–14)

Most early studies, however, were based on limited environmental sampling, and personal exposure assessment was rare. In addition, earlier studies were done primarily at high levels of exposure where severe clinical symptoms were often observed. With improvements in power plant technology, exposures in recent years have been reduced significantly.(2,3,14) While significant health effects at these lower levels are still observed,(14) the dose-response relationship for vanadium has not been well defined for exposure levels in the range of approximately 10–500 μg/m^3.(2) It is important to continue developing and applying better measurement techniques for assessing personal exposures and to develop specific and sensitive biological indicators to detect any early adverse health effects of vanadium exposure. In addition, it is important to investigate the combined health effects from the mixture of toxic metals in fuel-oil ash and welding emissions.

The current study was part of a prospective epidemiologic survey that aimed to assess whether low-level, fuel-oil ash exposure would lead to an early airway inflammatory response and then progress, or predispose, individuals to the development of chronic lung diseases.(14,15) One objective was to evaluate personal exposures to fuel-oil ash, metals, and welding gases for a larger percentage of person-days and to provide more accurate dose indices that could be used to detect early airway responses induced by these exposures. Another objective was to identify important determinants of exposure, such as certain job tasks, that might significantly modify a worker's exposures so that appropriate control measures could be identified and implemented. These exposure determinants could also be used to estimate exposures of those workers for whom actual measurements were not available. The primary hypothesis of this study was that average exposure to particles, metals, and welding gases differed by work group (boilermakers vs. utility workers), task performed, overhaul time period, and work location.

MATERIALS AND METHODS

Process Description

The study was conducted at a large, urban, oil-fired power plant that had the capacity to produce 565 megawatts of electricity. The boiler was housed in a 10-story building. The unit produced power by burning oil in a large combustion chamber (boiler). Oil was injected into the boiler through burners, while water in tubes lining the walls of the boiler was heated to produce steam, which was superheated at the top of the boiler (superheater). The resulting high-pressure steam turned a turbine to generate electricity. The steam was cooled in the condenser and the water was recirculated through the muddrum (a large settling chamber). Incoming air was preheated in the air heater using a heat exchanger to capture heat in the effluent combustion gases. Combustion gases were then cleaned in the precipitator before being discharged via the stack into the open air. The boiler, firebox, and related structures were regularly overhauled to replace damaged and deteriorating parts, such as water tubes in the boiler walls or in the superheater section.

A summary of job activities for boilermakers during the overhaul is presented in Table I. The major work of this overhaul was cutting by plasma or flame torch to remove damaged tubes, grinding of the cuts, and welding new parts in place. Major work locations were the superheater, burners, air heater, and precipitator. These locations provided the greatest opportunities for boilermakers to come into contact with ash. The ash pit, at the bottom of boiler, was another location with potentially high exposure.

Selection of Worker Population

The study was approved by the Human Subjects Review Board at the Harvard School of Public Health, and informed consent obtained from all subjects and management. Two worker groups, boilermakers and utility workers, were selected based on their work locations and tasks performed during the overhaul. The boilermakers came from the Boilermakers' Union, which provided workers to the power plant on a contract basis. Utility workers were full-time regular employees of the power plant and served as the referent group. The latter group included mechanics, welders, laborers, painters, precipitator operators, work crew supervisors, and laboratory workers. During the overhaul, utility workers helped repair the turbine and related facilities in areas adjacent to the boiler where there was little direct contact with fuel-oil ash.

Time Schedule for Overhaul and Field Sampling

The overhaul was divided into two time periods. In the *pre-overhaul* period (May 15–21), boilermakers did preparatory work outside the boiler. During the *overhaul* period (May 22–June 11), both boilermakers and utility workers conducted the repair work. Boilermakers worked both inside and outside the boiler; utility workers worked outside the boiler in adjacent areas. From June 1–8, most of the work done by the boilermakers was inside the boiler. During the overhaul, boilermakers worked from 6:30 a.m. to 5:30 p.m. and utility workers from 7:00 a.m. to 3:30 p.m. Work continued on Saturdays but not Sundays.

The field sampling was conducted in accordance with the overhaul schedule. There were two major sampling periods: pre-overhaul sampling to determine background exposure levels, and overhaul sampling to quantify exposures during overhaul activities.

TABLE I. Major Repair Tasks During the Boiler Overhaul by Location and Hazard

Work Location	Tasks Performed	Exposed Hazards
Furnace wall	Cutting and welding to replace damaged tubes	Ash, metals, welding gases
Superheater	Cutting and welding to replace damaged tubes	Ash, metals, welding gases
DMWs	Grinding and welding to repair failed DMWs.	Ash, metals, welding gases
Burners	Burning, welding, and mechanical work to replace various components	Ash, metals, welding gases
Air heater	Cutting and burning to remove heating element; welding and mechanical work to install new element	Ash, metals, welding gases
Muddrum	Welding, cutting, and mechanical work to remove and replace failed parts and install new parts	Metals, welding gases
Precipitator	Cutting and welding to repair or replace various parts	Ash, metals, welding gases

Note: Welding gases = ozone and nitrogen dioxide; DMWs = dissimilar metal welds, which connect the water tubes with the steam tubes in the superheater.

Measurement of Fuel-Oil Ash Particles

Since the fuel-oil ash particles and metals, such as vanadium and cadmium, may have irritational and inflammatory effects on both the pulmonary region and respiratory tract, we were interested in collecting all particles that would deposit in the pulmonary region and airways and have the potential to cause harm there. Hence, we measured personal exposures to ash particles $<10\ \mu$m in aerodynamic diameter (PM_{10}) that would include both the thoracic fraction of particulate mass(16) and respirable particulate mass. PM_{10} was collected using Gillian (Wayne, N.J.) personal air sampling pumps with the flow rate set at 4 L/min, and the personal environmental monitor (or PEM, model 200, MSP Corp., Shoreview, Minn.), which had an impaction plate with a cut point of 10 μm at 4 L/min to remove the large particles before collection on a filter. The filter used was polytetrafluoroethylene (PTFE) with a 0.3 micron pore size (Millipore, Billerica, Mass.).

Each morning, workers came to the study trailer before starting their work shift. After they completed a short questionnaire, they were asked to wear personal pumps and PEMs. Pumps were hooked on the waist belts and PEMs clipped on the uniform lapels. Workers were told to report immediately any abnormal pump sound or interruption in pump operation during sampling. If a pump stopped working, the pump automatically recorded the time sampled. Then a new pump was used and the time and flow rate recorded. The sampling period covered the entire work shift, 8–12 hours for boilermakers and 8–10 hours for utility workers. The start and finish times were recorded in the daily sampling logs.

Measurement of Nitrogen Dioxide and Ozone

Exposure to nitrogen dioxide (NO_2) and ozone (O_3) during the overhaul process was expected to come from flame- or plasma-cutting and welding. Personal exposure to NO_2 was measured using Ogawa passive badge-type samplers (Ogawa & Company, USA, Inc., Pompano Beach, Fla.). Both boilermakers and utility workers were asked to wear badge samplers. The badge was clipped on the uniform lapel. At the end of a worker's shift, the badge was removed, sealed, and the time recorded in the sampling log. The sampling duration covered the full work shift. Samples were then sent for laboratory analysis by spectrometry following the procedure defined by the manufacturer. The limit of detection (LOD) for 8 hours was 32 ppb of NO_2.

Personal exposure to O_3 was measured using an active sampler and a small low-flow rate sampling pump (PAS-500 personal air sampler, Spectrex Corp., Redwood City, Calif.).(17) This sampler was less likely to be affected by wind velocity, relative humidity, variation in O_3 concentration, and total O_3 exposure. It was also lightweight, convenient to use, and four times more sensitive than the O_3 passive sampler. The small pump was placed in the worker's breast pocket and the sampling inlet fixed on the uniform lapel. The O_3 sampling also covered the full work shift. O_3 sample analysis was conducted using the method described by Geyh et al.(17) The LOD was 1.4 ppb of O_3.

Work Diary

All subjects were asked to fill out an exposure diary at the end of the work shift. This included: (a) name, ID#, and date; (b) total hours worked; (c) time spent at primary job location for that day; (d) time spent (if any) working in areas other than the primary location; (e) job tasks (e.g., cutting, welding) and time spent at each task; (f) type of welding and welding rods used (if applicable); (g) use of personal protective equipment; and (h) number of cigarettes smoked during the day. Cutting, grinding, and welding (CGW) tasks were identified from the work diary and combined as the CGW task group. Other tasks, such as area setup, materials handling, or supervising were identified separately. A boilermaker was classified in the CGW task group for those days on which he cut, ground, or welded for any part of the shift.

Analytical Methods

The mass of PM_{10} collected on the filters was determined by the gravimetric method using a 6-place electronic microbalance (Cahn model 21; Cahn Instruments, Madison, Wis.). PTFE filters were weighed pre- and post-sampling, after equilibrating for 48 hours in a room controlled for temperature (65–75°F) and relative humidity (40 ± 5%).

Particles collected and the filters were acid-digested using the Parr bomb microwave method modified from Loring and Rantala.(18) The filter containing the particles was placed in a Teflon vessel with 1 mL concentrated nitric acid and 1 mL high-purity hydrofluoric acid. The vessel was then placed inside a casing and microwaved at 750 watts for 2 min. After cooling for 1 hour in water, the vessel was opened in a hood and 8 mL of 15% boric acid was added. The resulting digestate was then analyzed using inductively-coupled plasma mass spectrometry (ICP-MS) (ELAN model 5000; Perkin-Elmer, Norwalk, Conn.), for vanadium, nickel, iron, cadmium, chromium, manganese, arsenic, and lead. Tellurium, germanium, and indium were used as internal standards for arsenic, and indium and iridium used as standards for other metals.

The National Institute of Standards and Technology (NIST) standard reference materials 1643c, "Metals in Water," was used as the external standard to control for drift by the ICP-MS. Accuracy and precision of metal recovery were assessed by adding a known amount of metal standard (spikes) onto a blank filter that was digested in the same way as samples. Metal extraction efficiency from particles was evaluated using the NIST 1648, "Urban Particulate Matter." The LOD of this method was assessed using three standard deviations of the blank filter metal levels divided by the filter mass (blank metal concentration per mg of filter). Metals in each sample were corrected for metal background in that batch of filters by subtracting the filter blank metal concentration times the filter tare weight.

Quality Control and Assurance Procedures

Personal air sampling pumps for PM_{10} were calibrated in the field pre- and post-sampling for particles using a calibrated rotameter, and pumps for O_3, using a pocket bubble flow meter (Spectrex Corp., Redwood City, Calif.) following the manufacturer's guidelines for calibration. Variation between each flow rate reading was controlled to less than 5%. A mean flow rate was obtained by averaging the pre- and post-sampling flow rates, and used to calculate the concentrations.

For NO_2, 10% field duplicates and 17% field blanks were used. For O_3, 5% lab blanks and 30% field blanks were used. For PM$_{10}$ and metals, one filter was used each day as the field blank. For the filter sample acid digestion, 16 samples were digested each day, which included two metal spikes on filters, one lab filter blank and one standard reference material on a filter, the NIST 1648. For metal analysis, the actual accuracy for both NIST 1643c and metal spikes were obtained at 100% ± 10% as the acceptable quality range. For particle metal recovery, actual accuracy was 100% ± 20%. Overall precision (coefficient of variation or CV) was obtained at 10% or below.

Exposure Metric

The time-weighted average (TWA) full-shift exposure was used as the exposure measure for all subjects and both overhaul periods. The TWA exposure was calculated using the measured mass gain divided by the air volume sampled across the work shift without adjusting to a standard shift length.

Statistical Methods

All exposure data (PM$_{10}$, metals, NO_2, and O_3) were log-transformed to approximate normality. Since some workers performed same or similar tasks over the overhaul time periods, a geometric mean (GM) exposure was calculated for each worker based on all available measurements to avoid the self correlation from repeated measurements. The GMs from all workers in the same job or task group, or a time period, were then averaged to obtain the overall GM and geometric standard deviation (GSD). These GMs and GSDs were then used for statistical testing. Comparisons of exposure levels for boilermakers versus utility workers, and between boilermaker task groups, were conducted using two-sample t-tests, and between overhaul time periods and work locations using the analysis of variance (ANOVA). To determine which exposures of PM$_{10}$ and welding gases were most correlated with metal exposures, a Pearson correlation matrix was constructed. All statistical analyses were performed using Statistical Analysis Software (SAS Release 6.12 for Windows, SAS Institute, Cary, N.C.).

RESULTS

Due to the low levels and limited measurements, results on arsenic and lead are not reported here.

Exposure Differences Between Overhaul Time Periods

Table II shows TWA exposures to PM$_{10}$, gases, and metals for boilermakers and utility workers before and during the overhaul as compared with 2003 American Conference of Governmental Industrial Hygienists (ACGIH®) threshold limit values (TLVs).(19) Boilermakers' exposure to PM$_{10}$ was significantly higher than that of utility workers in both the pre-overhaul ($p < 0.05$) and overhaul ($p < 0.01$) time periods. The PM$_{10}$ exposure for boilermakers averaged 0.47 mg/m^3 during the overhaul compared with 0.13 mg/m^3 for utility workers. Before the overhaul, exposures to vanadium and nickel were not statistically different between boilermakers and utility workers, whereas exposure to iron was significantly ($p < 0.05$) higher in boilermakers. During the overhaul, however, exposure to all the above metals was significantly higher in boilermakers than in utility workers. Exposure to other metals (data not provided) was not significantly different between the two groups either before or during the overhaul. Exposures

TABLE II. Time-Weighted Average, Full-Shift Personal Exposures to PM$_{10}$, Metals, and Gases by Group and Overhaul Period

	Pre-Overhaul Work				During Overhaul Work				
Exposure	Boilermakers	N[A]	Utility Workers	N[A]	Boilermakers	N[A]	Utility Workers	N[A]	2003 TLV[B]
PM$_{10}$ (mg/m^3)	0.40 (1.6)[C]	5	0.10 (2.7)	8	0.47 (1.9)[D]	15	0.13 (4.0)	7	10.0
Vanadium (μg/m^3)	1.20 (1.4)	4	1.10 (1.2)	3	8.90 (2.3)[E,F]	15	1.40 (1.6)	7	50.0
Nickel (μg/m^3)	2.80 (4.0)	5	0.90 (1.0)	3	7.40 (3.4)[C]	15	1.80 (1.4)	4	1500.0
Iron (μg/m^3)	41.80 (3.7)[C]	5	4.20 (5.5)	8	56.20 (2.7)[C]	15	11.20 (4.4)	7	1000.0
O^3 (ppb)	4.5 (1.2)	5	1.6 (1.5)	3	3.7 (2.2)	13	4.8 (2.2)	5	100.0
NO_2 (ppb)	Not measured	—	Not measured	—	53.6 (1.6)	13	91.2 (2.6)	4	3000.0

Note: Geometric means and geometric standard deviation in parentheses.

[A] N = number of workers, each contributing 2–11 measurements.

[B] ACGIH 2003 threshold limit values. Value of PM$_{10}$ is for inhalable particles.

[C] $p < 0.05$ comparing boilermakers with utility workers.

[D] $p < 0.01$ comparing boilermakers with utility workers.

[E] $p < 0.001$ comparing boilermakers with utility workers.

[F] $p < 0.01$ comparing boilermakers during with pre-overhaul work.

to O_3 and NO_2 during the overhaul were not statistically significant comparing boilermakers to utility workers (3.7 vs. 4.8 ppb for O_3 and 53.6 vs. 91.2 ppb for NO_2). The levels of these exposures were well over an order of magnitude lower than the TLVs.(19)

Within groups, Table II shows that boilermakers had higher exposure to metals during versus pre-overhaul. The exposure ratios comparing the during- to pre-overhaul periods were 1.3 for Fe, 2.6 for Ni, and 7.2 for V. However, the increase was statistically significant ($p < 0.01$) only for vanadium. Exposure to PM_{10} was higher during the overhaul but not at a statistically significant level. No significant differences were observed for utility workers' exposures to particles, metals, or ozone across overhaul time periods.

In general, TWA exposures to particles and metals were lower than their respective 2003 TLVs. For utility workers, this was true regardless of overhaul period. For boilermakers, vanadium exposure during the overhaul was the closest to its TLV, and the highest vanadium exposure was 307.5 $\mu g/m^3$, six times the current TLV.

Exposure Differences Between Job Tasks

Boilermakers' TWA exposures to particles, metals, and welding gases between the CGW task group and non-CGW task group are presented in Table III. There was no statistically significant difference in exposure to PM_{10} between the two task groups. For metals, TWA exposure showed a two- to threefold increase comparing the CGW task group with other tasks, and the observed increase was statistically significant ($p < 0.05$) for vanadium. No statistically significant differences were found for TWA exposure to welding gases between task groups.

TABLE III. Boilermakers' Time-Weighted Average, Full-Shift Personal Exposures to PM_{10}, Metals, and Welding Gases by Task

Exposure	CGW^A Tasks	N^B	Non-CGW Tasks	N^B	CGW/ Non-CGW Ratio
PM_{10} (mg/m^3)	0.6 (1.8)	13	0.4 (2.1)	11	1.4
Vanadium ($\mu g/m^3$)	10.0 (3.1)^C	13	3.7 (2.0)	11	2.7
Nickel ($\mu g\ m^3$)	10.0 (4.6)	13	4.7 (4.5)	11	2.1
Chromium ($\mu g/m^3$)	4.7 (3.7)	11	2.6 (2.5)	7	1.8
Iron ($\mu g/m^3$)	100.2 (2.5)	13	45.5 (3.4)	11	2.2
Manganese ($\mu g/m^3$)	4.6 (2.9)	13	2.2 (2.0)	7	2.1
NO_2 (ppb)	46.2 (1.7)	9	59.1 (1.6)	10	0.8
O^3 (ppb)	2.6 (1.9)	10	6.2 (2.2)^C	9	0.4

Note: Geometric means and geometric standard deviation in parentheses.
^{A}CGW tasks = cutting, grinding, and welding tasks.
^{B}N = number of workers, each contributing 2–11 measurements.
^{C}$p < 0.05$ comparing CGW task group with non-CGW task group.

Similar comparisons for utility workers did not reveal any significant increases in TWA exposure to particles, metals, or welding gases between task groups (data not shown). In general, exposures in the referent group were low, similar in magnitude to those of boilermakers doing non-CGW tasks.

Exposure Differences at Work Locations

Boilermakers' TWA exposure to particles and metals in major work locations is presented in Table IV. Overall, boilermakers worked in 36 different locations inside and outside the boiler. Data for exposure analysis, however, were restricted to a limited number of locations where the large majority of work activities were conducted. The superheater, air heater, burner, and ash pit were the work locations where most repair activities were performed, and they were the focus of the exposure analysis. Other work locations related to boiler structure or inside the boiler housing, such as the precipitator, air duct, condenser, steam drum, economizer, and muddrum had fewer repair activities and were combined into one group as "other." Locations that could not be classified into these major categories (mostly locations outside the boiler or its housing) were grouped together as "others."

Although individual exposure to PM_{10} at various job locations ranged from 0.12 to 4.48 mg/m^3, no statistically significant difference was observed for mean TWA exposures across work locations.

For metals, boilermakers' geometric mean TWA exposure showed wide variations: 2.3 to 30.4 $\mu g/m^3$ for vanadium, 2.3 to 97.4 $\mu g/m^3$ for nickel, 25.6 to 78.6 $\mu g/m^3$ for iron (data not shown in Table IV), 1.2 to 57.0 $\mu g/m^3$ for chromium, and 1.3 to 18.0 $\mu g/m^3$ for manganese. The differences across locations were statistically significant for V ($p < 0.05$), Ni ($p < 0.01$), Cr ($p < 0.001$), and Mn ($p < 0.05$). Besides the ash pit and burners, dissimilar metal welding on the water tubes and work on the air heater also had high exposures. The geometric mean of TWA full-shift exposure to vanadium at the ash pit was 30.4 $\mu g/m^3$, more than 50% of the TLV.

Time Profiles for Work and Respirator Use

The work patterns and respirator use as collected by work diaries are presented in Table V. Both boilermakers and utility workers spent over 90% of each work shift at a primary location. Typically, less than 1 hour per shift was spent working in areas other than the primary work location. Time used to cut, grind, and weld accounted for 30% of the total work time for boilermakers and 28% for utility workers. Boilermakers and utility workers showed a significantly different pattern in respirator use. Boilermakers used a respirator almost 40% of the time vs. 2% for utility workers.

Correlation of Particles, Welding Gas, and Metal Exposures

Results of the Pearson correlation analysis are presented in Table VI. There were significant ($p < 0.001$) positive correlations between PM_{10} and metals with correlation coefficients at 0.50, 0.66, 0.77, 0.71, and 0.69 for V, Ni, Fe, Cr, and

TABLE IV. Boilermakers' Time-Weighted Average, Full-Shift Personal Exposures to PM$_{10}$, and Metals by Work Location

Location	PM$_{10}$ mg/m^3	N[A]	Vanadium μg/m^3	N[A]	Nickel μg/m^3	N[A]	Chromium μg/m^3	N[A]	Manganese μg/m^3	N[A]
Ash pit	0.74 (3.2)	4	30.4 (5.5)	4	21.0 (1.6)	4	4.4 (2.0)	4	4.5 (2.0)	4
Burner	1.03 (1.9)	3	21.6 (2.2)	3	97.4 (1.8)	3	57.0 (1.7)	3	18.0 (2.2)	3
DMW[B]	0.52 (2.5)	3	22.8 (4.4)	3	8.6 (3.4)	4	22.8 (3.9)	3	1.7 (2.7)	3
Superheater	0.39 (1.5)	4	11.6 (3.0)	4	2.3 (1.9)	4	NA[C]	0	1.3 (—)	1
Air heater	0.46 (1.0)	7	5.3 (3.8)	7	2.6 (4.0)	7	1.2 (1.4)	3	2.2 (2.9)	6
Other[D]	0.46 (3.2)	7	2.3 (2.3)	4	8.6 (4.2)	7	1.9 (2.9)	5	1.9 (2.2)	4
Others[E]	0.51 (3.2)	5	4.2 (2.2)	5	4.0 (4.0)	5	1.4 (1.7)	4	2.2 (1.6)	4
p-value[F]	0.77		0.02		0.003		0.0001		0.03	

Note: Geometric mean and geometric standard deviation in parentheses.

[A] N = number of workers each contributing 2–11 measurements. Measurements that were below the LOD are not included.

[B] DMW = dissimilar metal welds that joined the water and steam tubes in the superheater.

[C] Insufficient measurements above LOD to calculate geometric mean.

[D] Other boiler structures including the precipitator, dearator, steam drum, and muddrum.

[E] Other non/boiler structures including the water treatment plant, tool room, and outside work.

[F] ANOVA test of the null hypothesis of no difference in geometric means across work locations.

Mn, respectively. However, no correlation was found between welding gases (NO_2 and O_3) and any metals or PM$_{10}$.

DISCUSSION

This boiler overhaul was short, lasting only 3 weeks with less than 2 weeks' work inside the boiler. Typically, a full overhaul would last for several weeks or even months. In addition, there were relatively few places in the boiler areas that needed extensive repair, and a separate contractor had washed down the inside boiler walls before the overhaul work began. Therefore, in this study, the level of boilermakers' exposures to PM$_{10}$ during the overhaul was unusually low with a geometric mean of 0.47 mg/m^3. This is well below values reported in earlier studies,(1–2) and in studies reported more recently.(3,8,14) Most PM$_{10}$ values measured in this study were also well below the TLV. However, even at this low-level exposure, a statistically significant difference for PM$_{10}$ was found between boilermakers and utility workers in both the pre-overhaul and during overhaul time periods. This provided a good opportunity to study the health effects below the TLV. In fact, the epidemiologic study with which this exposure analysis was associated found that both within boilermakers and between boilermakers and utility workers there were significantly increased levels of adverse respiratory health effects comparing during to pre-overhaul periods.(15,20) This indicates that this low-level exposure to fuel-oil ash during the short period of boiler repair work had adversely affected boilermakers' respiratory health.

TABLE V. Distribution of Work Hours and Respirator Use by Group and Area

	Total[A] (hours)	Cutting (hours)	Grinding (hours)	Welding (hours)	CGW (%)[C]	Others[B] (hours)	Respirator Use (hours)
Boilermakers							
Primary areas[D]	8.59	0.43	0.73	1.55		5.63	3.42
Secondary areas[E]	0.44	0	0.01	0.02		0.41	0.09
Total	9.03	0.43	0.74	1.57	30.3	6.29	3.51
Utility Workers							
Primary areas[D]	8.53	0.21	1.34	0.76		6.13	0.13
Secondary areas[E]	0.47	0	0.05	0.16		0.24	0.03
Total	9.00	0.21	1.39	0.92	28.0	6.37	0.16

[A] Total hours may not equal additive task time exactly because of unincluded fractional times spent in unspecified areas.

[B] All noncutting, grinding, or welding (CGW) tasks.

[C] Percentage of total work hours involved in CGW tasks.

[D] Primary area = area specified on work diary as location where a subject spent the majority of his work time.

[E] Secondary area = any work area (other than the primary location) specified on the work diary.

TABLE VI. Pearson Correlation Coefficients (r) Between PM_{10}, Welding Gases, and Metals

	V	Ni	Fe	Cr	Mn
PM_{10}	$r = 0.50$ $p < 0.001$	$r = 0.66$ $p < 0.001$	$r = 0.77$ $p < 0.001$	$r = 0.71$ $p < 0.001$	$r = 0.69$ $p < 0.001$
O_3	$r = -0.22$ $p = 0.12$	$r = -0.13$ $p = 0.37$	$r = -0.06$ $p = 0.68$	$r = -0.12$ $p = 0.41$	$r = -0.10$ $p = 0.49$
NO_2	$r = -0.22$ $p = 0.15$	$r = 0.00$ $p = 0.98$	$r = -0.08$ $p = 0.62$	$r = 0.03$ $p = 0.84$	$r = 0.04$ $p = 0.79$

Note: Not shown are the correlation coefficients between metals, which were all positive and highly significant.

For the eight metals analyzed, exposures to three (V, Ni, and Fe) were significantly higher in boilermakers. Vanadium is the major constituent of concern in fuel-oil ash. It has been associated with acute respiratory symptoms and decreased lung function. However, as stated earlier, the World Health Organization has indicated that health effects due to vanadium exposure between 10 and 500 $\mu g/m^3$ have been poorly described.(2) Mean exposure to vanadium for boilermakers in this study was approximately 9 $\mu g/m^3$, and exposure in cutting, grinding, and welding tasks averaged 10 $\mu g/m^3$. Exposure around the ash pit averaged 30 $\mu g/m^3$, with the highest exposure being 307.5 $\mu g/m^3$. These exposure levels provided an appropriate range for studying health effects that have not been well described in the literature.

A major strength of this study was that by using a good referent group, several determinants were found to affect exposure to fuel-oil ash, metals, and welding emissions during the overhaul. Job title was a major factor. Boilermakers had significantly higher exposures to ash particles and metals compared with utility workers. This finding is most likely because boilermakers worked primarily around structural areas inside the boiler and thus had the opportunity for direct inhalation of fuel-oil ash. Vanadium was found to be significantly elevated for various tasks and work locations inside but not outside the boiler. This suggests that fuel-oil ash was the main source of exposure to vanadium in boilermakers. Utility workers typically worked away from those areas where direct contact with fuel-oil ash was likely, and their exposures to ash particles and metals were significantly lower than those for boilermakers. In addition, while boilermakers showed increased levels of exposure to ash particles and metals during the overhaul, exposure levels for utility workers were not affected by overhaul period.

Tasks were another important determinant of exposure. Boilermakers who performed cutting, grinding, and welding tasks showed higher levels of metal exposures, especially to vanadium, compared with those who performed other tasks. The probable explanation was that most cutting, grinding, and welding tasks were performed in less ventilated areas where considerable fuel-oil ash had deposited, such as the superheater area and the burners inside the firebox. Cutting, grinding, and welding processes might have not only aerosolized the ashes deposited on the water tubes but also could have generated some metal fumes from the metal tubes, further contributing to metal exposures of boilermakers It is noteworthy that no significant differences in PM_{10} exposures were observed between boilermakers who performed cutting, grinding, and welding tasks and those who performed other tasks. A possible explanation could be that boilermakers who handled materials outside the boiler might have been exposed to other sources of particles in other areas (e.g., water plant), which did not have a high metal content, such as road dust when materials were being moved around outdoors.

Work location also influenced exposure levels. Most metal exposures were found to be the highest at the ash pit (where the bottom ash was collected) and burners (where the oil was injected into the furnace). A substantial number of repair activities took place at these locations where measured ash particles and vanadium exposure levels were high. The ash pit area also served as the primary entrance into the boiler during overhaul, providing additional exposure opportunities. These results provide further evidence that fuel-oil ash was the major source of exposure to metals, particularly vanadium.

To further define source-exposure relationships and assist in identifying exposure determinants, a Pearson correlation analysis was performed for boilermakers. The results demonstrated that PM_{10}, but not welding gases, was highly correlated with metal exposures. This supports our conclusion that vanadium (and other metals) came more from fuel-oil ash than from welding emissions.

Exposure determinants identified from this study provided us with clues on where and how the exposure to vanadium-rich fuel-oil ash should be controlled, namely, boilermakers who enter the inner boiler structure during the overhaul to perform cutting, grinding, and welding tasks on the water tubes should be well equipped with appropriate types of respirators (half mask organic vapor cartridge respirators with HEPA filter combinations). Respiratory protection should be used at all times for inside boiler repair work. During the study its use was inadequate. Increased boiler ventilation and more thorough washing of the high exposure boiler areas before the work started would also help reduce the exposures.

The major limitations of this study were the small sample size and the relatively low number of measurements taken. Although subjects were encouraged to wear sampling devices, only 23% of available worker-days were sampled, and three boilermakers were not measured at any time during the overhaul. Since it was especially cumbersome to wear personal exposure monitors and sampling pumps for those workers who had to crawl into the narrow spaces (e.g., among the water tubes) to perform cutting, grinding, and welding tasks, workers from this group were the most likely to refuse to wear a sampling pump. Therefore, more workdays were missed from cutting, grinding, and welding tasks in high exposure areas. This could have led to underestimation of actual exposures. We have developed an algorithm to estimate exposures for unmeasured times and the results of that analysis were reported separately.(21)

Exposure measurements in this study were all external, which did not take into account the use of a respirator and personal breathing rate. An exposure metric without adjusting for respirator use would certainly overestimate the actual quantities inhaled, and subsequently affect the health risk analysis. While the time for using the respirators for boilermakers was inadequate to assess the protective effects of respirator use, we observed that there was a significant difference for boilermakers in using their respiratory protective equipment compared with utility workers. This needs to be considered when internal dosage of exposure is developed for workers in these two job groups. Evaluation of this effect is described in another publication.(22)

Two other issues of potential concern in this type of study are repeated measurements for a subject and multiple comparisons. Exposure measurements for the same individual from one day to the next are not independent. To deal with the repeated measurement issue, we first calculated the mean exposure for each worker, then calculated the mean for boilermakers and utility workers as a whole or for boilermaker task groups. This avoided the self-correlation of data points. However, we did not adjust for multiple comparisons; therefore, individual p-values should be interpreted with caution.

CONCLUSION

We found that exposure levels of fuel-oil ash particles and vanadium in this study were relatively lower than from other studies of boilermakers conducted in recent years. We also found that, for boilermakers, direct inhalation of fuel-oil ash was the major source of exposure to PM_{10} and metals, particularly vanadium. In addition to job title, overhaul time period, tasks performed, and work locations were identified as major exposure determinants. Vanadium exposure was found to be consistently higher for boilermakers and was considered a good indicator of exposure to fuel-oil ash. More respiratory protection and better boiler cleaning and ventilation are recommended for boilermakers in performing boiler repair work.

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