Estimation of Personal Exposures to Particulate Matter and Metals in Boiler Overhaul Work

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Objective: *We sought to develop an algorithm and estimate unmeasured exposures to particulate matter (PM) and metals in an epidemiologic study of boilermakers.* ***Methods:*** *The algorithm was based on limited measurements and workers' task and time activity patterns. Half of the measurements were used to develop exposure estimates for unmeasured person days. The other half was used for method validation.* ***Results:*** *The validation demonstrated good approximations of actual exposures with differences less than 5% for PM and vanadium (V). Average estimated exposures to PM (mg/m^3) and V (μg/m^3) were significantly higher for workers doing boiler repair than utility work (0.36 vs. 0.09 for PM and 5.99 vs. 0.38 for V).* ***Conclusions:*** *This algorithm provided reasonably accurate exposure indices for our epidemiologic study in this population. It also is likely applicable to similar exposure scenarios in other studies.* (J Occup Environ Med. *2005; 47:68–78*)

Workers repairing large fuel-oil-fired boilers are exposed to a complex mixture of toxic agents, including fuel-oil ash that is rich in vanadium[1–3] and other toxic metals, ozone, and nitrogen dioxide from welding. Exposure to vanadium oxides has long been recognized to cause acute respiratory symptoms and illnesses,[4,5] ranging from mild irritation and bronchitis,[6] to asthma,[7] or even acute poisoning with pulmonary edema.[8–10] Reduced pulmonary functions also have been reported in boilermakers.[11] However, exposure levels that caused the more serious health effects seen in early times are rarely encountered today. Health effects associated with current low exposures of vanadium, in the range of 0.10 to 0.50 mg/m^3, are not well defined.[1] In addition, possible adverse effects to boiler workers from coexposures to other metals (such as nickel) present in fuel-oil ash or welding fumes are rarely investigated.

We therefore initiated a series of prospective epidemiologic studies to assess whether low-level fuel-oil ash and metal exposures would lead to an early airway inflammatory response[2] and then progress, or predispose, individuals to the development of chronic lung diseases and reduced pulmonary function[12,13] In this current evaluation of molecular markers,[14] pulmonary function,[15] and respiratory symptoms,[16] we concurrently measured both exposures to fuel-oil ash, metals, and respiratory health effects among 18 boilermakers and 11 utility workers. In the exposure assessment,

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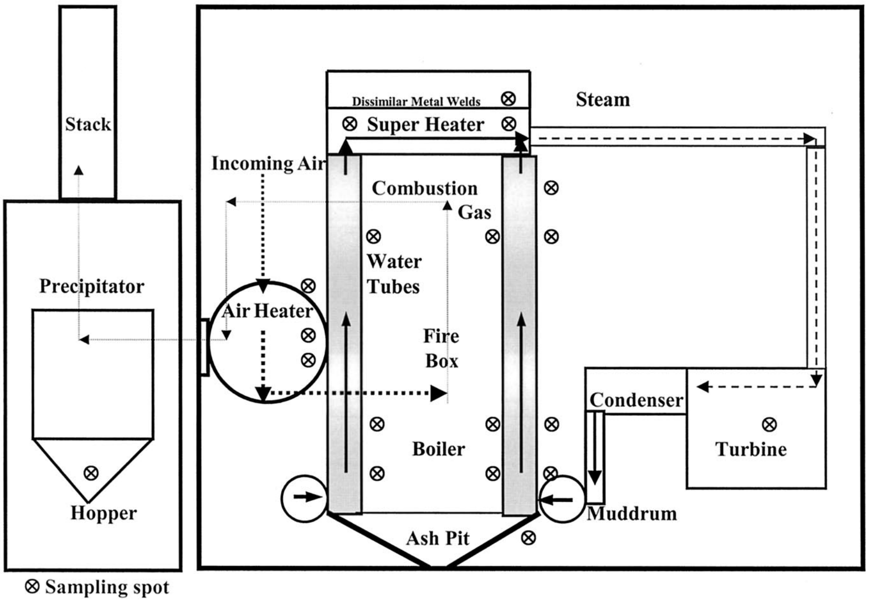

Fig. 1. Schematic diagram of boiler structure and sampling locations. See text for details.

we measured full work shift, time-weighted average concentrations of particulate matter 10 μm or smaller aerodynamic diameter (PM_{10}) of the fuel-oil ash, and its metal components: vanadium (V), nickel (Ni), iron (Fe), chromium (Cr), cadmium (Cd), lead (Pb), manganese (Mn), and arsenic (As), plus the concurrent gaseous welding emissions of nitrogen dioxide and ozone. PM_{10} in the subject's breathing zone was chosen as the exposure of interest because the target tissues for the exposures were both the airways and alveoli, not just the deep lung tissues, which are exposed to $PM_{2.5}$.

As with many other cross-sectional and prospective studies with volunteer subjects or retrospective surveys, cost and practical limitations prevented us from obtaining personal air monitoring data from all participants and all workdays during the study period. Full-shift, time-weighted average exposures in this survey were collected during 23% of worker-days. A large part of the subject's daily exposures had to be estimated by developing an exposure estimation algorithm.

Traditionally, industrial hygienists conduct exposure assessment and estimation to determine the compliance of current exposure with occupational exposure limits. However, it has become more common that exposure estimation methods are developed and used to derive personal exposure metrics for all types of observational occupational epidemiologic studies, when no direct measurements are available.[17–22] Industrial hygiene analysis and statistical modeling have been the two major methods used for exposure estimation. In industrial hygiene analysis, a panel of experienced industrial hygienists uses basic principles and background information to sort workers into different exposure categories and to assign exposure values.[23] In statistical modeling, determinants of exposure are identified as independent variables and measurements are used to fit models. The coefficients and derived models are then used to predict unmeasured exposures.[24] However, statistical models require extensive measurement data and are limited to the use in similar exposure situations where the measurements were made.[19] Errors can result from the underlying assumptions used to build the models.[25]

The objective of this study was to develop and evaluate an industrial hygiene type of exposure algorithm and use it to reconstruct personal exposure metrics of PM_{10} and metals for unmeasured boilermakers and utility workers on unmeasured workdays, based on available exposure measurements and daily work activity diaries. These exposure estimates were then used to calculate risks of respiratory health effects associated with boiler repair work.

Materials and Methods

Population

A total of 18 contract boilermakers who participated in the overhaul of a large boiler in a power plant were recruited from the Boilermakers' Union as the study population. Also enrolled were 11 utility workers who were regular employees of the power plant and used as the referent group. The referent group included mechanics, welders, laborers, painters, precipitator operators, work crew supervisors, and laboratory workers. More details on the study population are provided in previous publications.[14–16] The Institutional Review Board of the Harvard School of Public Health approved the human subjects protocol used for the study.

Boiler Overhaul Work Process

The study was conducted at a large urban fuel-oil-fired power plant when one of its boilers was being repaired (overhaul). The boiler was housed in a big building. Figure 1 shows the structural and functional components. The boiler itself was the main structure that had a large combustion chamber for burning oil. Inside was a big firebox with oil injection burners in the four corners, water tubes in the walls and in the super-heater to generate steamed air, and an ash pit on the bottom to collect fuel-oil ash. Steamed air was led out of the boiler in pipes to the turbine for electricity generation with steam condensed at the condenser, and water recycled at mud-drums. There was also a big air heater for warming up incoming air and a precipitation hopper for air pollution control. Also attached to the boiler outside were 10 floors of structure with open space and stairways leading to each floor for boiler repair and maintenance. The major task of the overhaul was to repair the damaged burners and deteriorated water tubes in the boiler walls and super-heater by cutting to remove damaged tubes, grinding the cuts, and welding new parts in place. Minor tasks involved maintenance repairs or preparatory work (such as making stages and scaffolds or preparing materials used in overhaul) around boiler locations. The overhaul was scheduled in three time periods: pre-overhaul from May 15 to 21, 1995 when most work was preparatory; overhaul from May 22 to June 11, 1995 in which actual repairs took place inside the boiler; and post-overhaul from June 12 to 21, 1995 when boilermakers had left the job and only utility workers remained working in the facility on aftermath maintenance.

Exposure Measurement

Although 29 workers took part in the overhaul and study, only three to five volunteered each day to participate in the air sampling. PM_{10} was chosen as a surrogate metric for the thoracic fraction of aerosol because we were interested in a particle range that could deposit in both the bronchial tree and alveolar regions. A personal environmental monitor (PEM, Model 200, MSP Co, Shoreview, MN) was used to measure PM_{10}. The PEM had an impactor with a particle size cut point of 10 μm at 4 L per minute. Particulate was collected on polytetrafluoroethylene filters with 0.3-μm pore size and 37 mm diameter. The PEM was attached to the uniform collar and connected to a GilAir pump (Gillian, West Caldwell, NJ). Personal air sampling was taken at main work locations and covered the whole work shift, 12 hours on average for boilermakers and 8 hours for utility workers. Exposure measurements were conducted during each of the three overhaul time periods. In the post overhaul time period, only utility workers were measured because boilermakers had finished their part of the repair job. Post-overhaul was so designated as part of the health measurement protocol.

Stationary sampling of PM_{10} in designated work areas was also conducted to provide supplemental exposure levels for major and minor work locations where overhaul tasks were performed. These locations were distributed on various floors of the boiler outside structure and facilities (see Fig. 1 for details). Harvard impactors[26] were used for area sampling. The impactors also had a particle cut point of 10 μm at 4 L per minute, and the same polytetrafluoroethylene filters were used. Area sampling also covered the whole work shift. In total, eight area samples were taken each day at various locations.

Job Activity Diary (Exposure Log)

All workers were asked to complete an exposure log each day at the end of the work shift. It included: 1) name, ID#, and date of work; 2) total hours worked; 3) job locations and task duration at each location; 4) job and task activity; 5) time spent specifically at cutting, grinding, and welding; and 6) type and duration of respirators used. There were a total of 36 different work locations inside and outside the boiler, but only a major work location and a minor location were asked. The major location was defined as the area where the worker spent the majority of his workday, while a minor location defined as any place where the worker spent the most time in addition to the major location. Information from the work diary was used to reconstruct exposures for each individual.

Analytical Methods

After sampling, the filters were taken to the laboratory to determine quantities of particulate collected on the filter by gravimetric method. Filters were then acid digested using the Parr bomb microwave digestion method[27] with some modifications. One filter was placed in a Parr bomb Teflon vessel each time. One milliliter of concentrated nitric acid and extra-pure hydrofluoric acid each was added. The vessel was placed in a plastic casing and heated in a microwave at 750 Watts for 2 minutes. The plastic casing and vessel were cooled in cold water for one hour. Then, 8 mL of 15% boric acid was added to the sample. The digestate was then analyzed on the induced-coupling plasma-mass spectrometry ELAN Model 5000 (Perkin-Elmer, Norwalk, CT) for metals: V, Ni, Cr, Cd, Fe, Pb, Mn, and As.

Quality Control and Assurance

Indium and iridium were used as internal standards. The accuracy and precision were assessed by adding known amounts of standard metals onto blank filters. Additionally, the standard particle material NIST 1648: Urban Particulate Matter, were digested and analyzed to determine the metal extraction efficiency from particulates. The limit of detection of this method was determined by using 3 standard deviations from mean blank filter metal levels divided by the filter mass. Each sample value was adjusted for the blank filter metal content. The limit of detection was 0.34 $\mu g/m^3$ for PM_{10} and 0.53, 0.46, 0.40, and 0.24 ng/m^3 for V, Ni, Cr, and Mn, respectively. The accuracy was greater than 99% for PM_{10} and 90% to 100% for metals. The precision was less than 5% for PM_{10} and less than 10% for metals. The metal recovery was 90% to 110%.

Exposure Metric

The full-shift time-weighted average (TWA) concentration was used as the exposure metric in exposure measurement and estimation. The TWA concentrations were determined as mass of particles or metals collected on the filter divided by the air volume, normalized to 8 or 12 hours.

Exposure-Estimating Algorithm

The TWA concentrations were entered into a spreadsheet database and merged with work diary data. The measured exposures only showed significant differences for V, Ni, Cr, and Mn among job titles and locations. Therefore, estimation of exposure was only performed for these four metals and PM_{10}. Cutting, grinding, and welding were found to be major tasks associated with high exposures to fuel-oil ash and metals and, therefore, these tasks were the focus in exposure estimation. Because most workers worked in a major and a minor work location and performed either high-exposure tasks such as cutting, grinding, and welding or low-exposure tasks such as material handling, their average exposures can be estimated using the following equation as the algorithm:

$$\mathrm{TWA} = \frac{t_1{*}C_1 + t_2{*}C_2 + t_3{*}C_3 \ldots + t_i{*}C_i}{T} \qquad (1)$$

where TWA = time-weighted average concentration measured or estimated for a worker on a specific day; t_1 = time spent in welding; C_1 = concentration in welding; t_2 = time spent in cutting and grinding; C_2 = concentration in cutting and grinding; t_3 = time spent in doing other tasks; C_3 = concentration in doing other tasks; t_i = time spent in minor locations doing minor tasks; C_i = concentrations in minor locations; and T = sum of $t_1 + t_2 \ldots + t_i$, the total time worked over the day.

The estimation process was performed in two steps: calculation of task-specific concentrations from the data of measured workers, and estimation of TWA concentrations for unmeasured workers or unmeasured days. In the first step, all suitable full shift data were identified where only single-task activities were performed: cutting, grinding, welding, and others. If a single task concentration was not directly available, it was estimated from the TWA concentration of measured workers by inverting Equation 1. In the second step, task-specific concentrations from step 1 and area concentrations were used as base exposures and the time on each task as the weight to calculate full-shift TWA concentrations for unmeasured workers on unmeasured days. The above estimation process can be summarized as follows, where PM_{10} is used to illustrate the procedure:

Worker A:

$$PM_{10}\,(\text{measured}) = \frac{[hr_{task\text{-}i}]{*}[C_{task\text{-}i}] + [hr_{area\text{-}j}]{*}[C_{area\text{-}j}]}{[hr_{task\text{-}i}] + [hr_{area\text{-}j}]} \qquad (2)$$

In Equation 2, $C_{task\text{-}i}$ is the unmeasured concentration in a major task performed by worker A (for example, cutting, grinding or welding). $C_{area\text{-}j}$ is the concentration in a minor task (for example, material handling), which is assumed to be similar to the area concentration. Solving for $C_{task\text{-}i}$ (mg/m^3) gives a PM_{10} concentration for a major task, which can then be used to estimate total PM_{10} exposure for an unmeasured fellow worker in the same area based on his reported work hours, as shown below.

Worker B:

$$PM_{10}\,(\text{estimated}) = \frac{[hr_{task\text{-}k}]{*}[C_{task\text{-}i}\ (\text{from Worker A})] + [hr_{area\text{-}1}]{*}[C_{area\text{-}1}]}{[hr_{task\text{-}k}] + [hr_{area\text{-}1}]} \qquad (3)$$

In Equation 3, the full-shift exposure to PM_{10} is estimated using Worker A's major task concentration plus the area concentration from a minor task weighted by Worker B's work time on each task. Some examples of using this approach to derive task concentrations and exposure estimates are given below.

Example #1:

On May 30, subject 104 performed cutting and grinding for 6 hours at the super heater inside the boiler on the 8th floor and did some area setup work for 1.5 hours at the same location. The measured area concentration at this major work location was 0.08 mg/m^3. He also did setup work for 2 hours at a minor location, for a total of 9.5 work hours. His total measured PM_{10} (TWA) for the day was 0.50 (mg/m^3). For the minor location, it was not clear from the work diary if it was inside or outside the boiler. To compensate for the missing data, measurements from both inside (0.18 mg/m^3) and outside (0.09 mg/m^3) levels on May 31 (data were not available for May 30) were averaged to obtain 0.14 mg/m^3. The concentration ($C_{task\text{-}i}$) during cutting and grinding was therefore estimated from the measured TWA as:

$$0.50\ \text{mg/m}^3 = (6{*}C_{task\text{-}i} + 1.5{*}0.08 + 2{*}0.14)/9.5$$

or

$$C_{task\text{-}i} = C_{cutting/grinding} = 0.72\ \text{mg/m}^3$$

This worker's $C_{cutting/grinding}$ could then be used to calculate the TWA exposure for an unmeasured fellow worker who was also cutting and grinding at the same location on the same day. It could also be used to estimate the TWA concentration for welding as in Example #2.

Example #2:

On May 31, subject 126 did welding for 6 hours, grinding for 1 hour, and setup work for 1 hour (8 hours total) all at a same location in the super heater. The area concentration of PM_{10} for this location was 0.23 mg/m^3 on that day. The subject's measured full shift TWA exposure was 1.46 mg/m^3. Using the cutting and grinding concentration ($C_{task\text{-}i}$ = 0.72 mg/m^3) from his fellow worker 104 above, we estimated the concentration ($C_{task\text{-}k}$) during welding as:

$$1.46\ \text{mg/m}^3 = (6{*}C_{task\text{-}k} + 1{*}0.72 + 1{*}0.23)/8$$

or

$$C_{task\text{-}k} = C_{welding} = 1.79\ \text{mg/m}^3$$

Example #3:

On May 26, subject #135 did welding for 4 hours and fitting for another 4 hours inside the super heater, where on May 27 (data for May 26 not available) the area concentration of PM_{10} was 0.075 mg/m^3. Using the welding concentration from Example #2, we estimated the TWA for this worker as:

$$\text{TWA (estimated)} = (4*1.79 + 4*0.075)/8 = 0.93 \text{ mg/m}^3.$$

Some assumptions and rules were made before starting the estimation. We assumed: 1) Fellow workers performing same tasks at same locations had similar mean exposures. 2) Area measurements could be used as personal exposure surrogates when no major sources of exposure were present in the area although some underestimation would be possible. 3) For unmeasured areas, the area concentration on the same day at a nearby location (eg, lower or upper floor) could be used as a surrogate. 4) Similar tasks generated similar mean exposures at the same location and could be used for substitutes. 5) If a same-day concentration was not available, a concentration from the nearest day for the same operation and location could be used. 6) The 4th floor area sampling spot was designated as a clean location because it was outside the boiler, facing a door, and there were no repair activities in the area. Concentrations from the 4th floor were used for assigning exposures to outdoor tasks or office work. 7) An average of all-floor area concentrations for a given day represented exposures for the location category "somewhere in the boiler area." Averages were made separately for boilermakers and utility workers. 8) Post-overhaul area measurements from utility workers were used to represent exposures of utility workers working in other boiler units where no overhaul was conducted. The priority hierarchy for selecting a value to estimate a subject's exposure was: 1) the worker's own measurements, 2) nearest fellow workers' data, and 3) relevant area sampling data.

The overhaul time periods were also considered in the exposure estimation. In general, measured data from the same period was used to derive estimates, and pre-June 3 and post June 3 exposures were clearly distinguished because June 3 was the day when the repair at the burners started.

Validation of Exposure Estimates

The original measured data were divided into two sets by assigning "estimation" and "validation" alternatively to each measurement. The "estimation" data set was used to reconstruct exposures on unmeasured days. The "validation" data were assumed not available and estimated in a same way using the "estimation" data. The real measurements from the "validation" data set were then compared with their respective estimates. For each agent, a geometric mean for both the estimates and real measurements was computed, and the absolute and percentage differences between the means were also calculated. The percentage difference was calculated as: [(estimated-measured)/measured] × 100. An overall 95% confidence interval for the mean of estimates was also calculated (data not presented). When two choices of similar data points were available for estimation (for example: area concentrations before the day versus after the day or above the floor versus below the floor), we calculated the absolute and percent differences for both.

Statistical Methods

Field data, laboratory reports, and exposure estimates were checked manually for accuracy before and after data entry. Statistical analyses were performed using SAS (version 8.12; SAS Statistical Institute, Inc., Cary, NC). Exposure data were approximately log-normally distributed; hence a geometric mean exposure and a geometric standard deviation for each variable were computed. A paired *t* test was used to compare the differences of estimates and actual measurements for each exposure agent in the validation process. A simple regression analysis was also performed between the estimates and measurements.

A two-sample *t* test was also used to compare the differences of estimated exposures between boilermakers and utility workers, between the two overhaul time periods as before versus after June 3, and between workers who performed cutting, grinding, welding, and minor tasks and workers who performed minor tasks only. In addition, one-way analysis of variance was used to compare estimated exposure among various work locations.

Results

Measured Exposures

Table 1 summarizes the results from measured full-shift, time-weighted average personal exposures to PM_{10} and metals as compared to 2003 threshold limit values (TLVs) recommended by the American Conference of Governmental Industrial Hygienists.[28] In pre-overhaul work, there was a significant difference in exposures to PM_{10} and iron (Fe) between boilermakers and utility workers, whereas during overhaul work, the difference also was significant for metals V and Ni. Overall, exposures to PM_{10} and metals were all higher in boilermakers than in utility workers. Boilermakers had significantly higher (eight times as high) exposure to V during overhaul work than in the pre-overhaul work. Such a significant difference was not found for PM_{10} and other metals. Exposure to V also was found significantly higher in cutting, grinding and welding tasks than in other tasks (9.9 versus 3.7 $\mu g/m^3$). Average exposures to V, Ni, Fe, Cr, and Mn were significantly different among work locations with the ash pit (30.4 $\mu g/m^3$ for V) and burners (21.6 $\mu g/m^3$ for V) as the places

TABLE 1

Measured Full-Shift, Time-Weighted Average Exposures [GM(GSD)]† to PM_{10} (mg/m^3) and Metals (μg/m^3) by Group and Overhaul Time

	Pre-Overhaul Work				During Overhaul Work				2003
Exposure	**Boilermakers**	**N‡**	**Utility Workers**	**N**	**Boilermakers**	**N**	**Utility Workers**	**N**	**TLV§**
PM_{10}	0.4 (1.6)*	5	0.1 (2.7)	8	0.5 (1.9)**	15	0.1 (4.0)	7	10.0‖
V	1.2 (1.4)	4	1.1 (1.2)	3	8.9 (2.3)***###	15	1.4 (1.6)	7	50.0
Ni	2.8 (4.0)	5	0.9 (1.0)	3	7.4 (3.4)*	15	1.8 (1.4)	4	1500.0
Fe	41.8 (3.7)*	5	4.2 (5.5)	8	56.2 (2.7)*	15	11.2 (4.4)	7	1000.0

† Geometric mean (geometric standard deviation).
‡ Number of workers, each contributing several measurement samples.
§ Threshold Limit Values from ACGIH 2003. ‖ Value for inhalable particulates.
* $P < 0.05$ comparing boilermakers to utility workers.
** $P < 0.01$ comparing boilermakers to utility workers.
*** $P < 0.001$ comparing boilermakers to utility workers.
$P < 0.001$ comparing pre-overhaul to during overhaul work.

TABLE 2

Exposure Bias for Estimated PM_{10} (mg/m^3) and Metals (μg/m^3) (N = 42)

	Measured Values (Geometric Mean)	Estimated Values (Geometric Mean)	Bias*	% Difference†
PM_{10}	0.340	0.325	−0.015	−4.4
V	3.005	2.834	−0.171	−5.7
Ni	2.767	2.177	−0.590	−21.3
Cr	0.488	0.499	0.011	2.2
Mn	0.931	1.435	0.504	54.1

* Bias = estimated value - measured value.
† % difference = (estimated value - measured value)/(measured value) * 100.

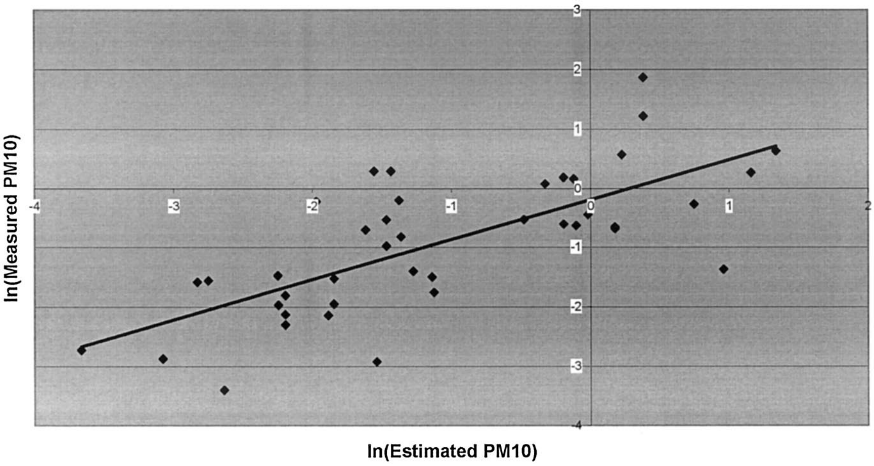

Fig. 2. Estimated and measured exposures to PM_{10}. Estimates of PM_{10} were correlated with measurements of PM_{10}. (ln measured PM_{10}) = 0.68 (ln estimated PM_{10}) − 0.19 (r = 0.719, $P <$ 0.0001, $n = 42$).

with highest exposures to both particulate matter and metals. Although these exposures were generally well below the current TLVs, individual exposures to V often had exceeded the TLV. For example, the highest measured personal exposure to V was found to be 307.2 μg/m^3, a value more than 6 times as high as the American Conference of Governmental Industrial Hygienists's 8-hour TWA exposure guideline.

Validation of Exposure Estimates

Using the algorithm, a total of 42 measured samples were estimated in a same way as other unmeasured exposures. Table 2 summarizes the validation results. PM_{10}, V, and Ni tended to be underestimated whereas Cr and Mn were overestimated. The bias (absolute difference) was small for PM_{10}, V and Cr (less than 0.2) with percent difference all less than 10%. The bias was larger for Ni and Mn (greater than 0.5) with percent differences all greater than 20%. However, measured PM_{10} and metals were all within the 95% confidence intervals of the estimated exposures (data not shown). The paired *t* test showed that the average differences were not statistically significant ($P < 0.05$). Figure 2 shows that estimates of PM_{10} were positively correlated with measurements of PM_{10} in a power function: (ln measured PM_{10}) = 0.68 (ln estimated PM_{10}) − 0.19 (r = 0.720, $P <$ 0.0001, $n = 42$). Figure 3 shows that estimates of V were also positively correlated with measurements of V: (ln measured V) = 0.91 (ln estimated V) + 0.33 (r = 0.798, $P < 0.0001$, $n = 42$). We also found positive correlations between the estimates and measurements for other metals with correlation coefficients at 0.798 for Ni, 0.699 for Cr, and 0.675 for Mn, respectively, all statistically

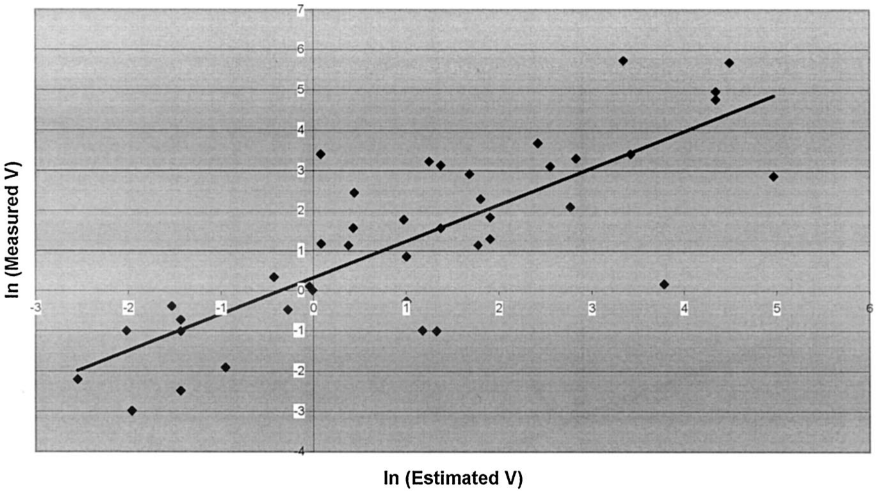

Fig. 3. Estimated and measured exposures to V. Estimates of V were correlated with measurements of V. (ln measured V) = 0.91 (ln estimated V) + 0.33 ($r = 0.797$, $P < 0.0001$, $n = 42$).

highly significant. The average percent difference between different choices of data (sensitivity) was 60% for PM_{10}, 76% for V, 58% for Ni and Cr, and 32% for Mn.

Estimated Exposures

A total of 133 exposure values were estimated for 18 boilermakers and 89 exposures for 11 utility workers. Table 3 summarizes the full-shift, time-weighted average exposures estimated for both groups. Except for one estimate in each group that fell within the pre-overhaul time period (May 15 to May 21), the estimates represented unmeasured exposures from May 24 to June 7, a major part of the overhaul period (May 22 to June 11). The table shows that boilermakers' estimated exposures to PM_{10} and metals were all significantly higher than those of utility workers. Average estimated exposure to V was 5.99 $\mu g/m^3$, a value comparable to that of measured exposures (see Table 1).

When we further looked at boilermakers' exposures during actual repair at burners inside the firebox after June 3, we saw significant increases in all exposed agents (see Table 4). Average exposure to V was 23.99 $\mu g/m^3$, six times as high as that before June 3 time period. In contrast, such an exposure difference was not seen in utility workers who never entered the boiler for any repair work. This may suggest that the fuel-oil ash from the boiler repair work was a major source of V exposure for boilermakers.

Table 5 shows that boilermakers doing cutting, grinding and welding tasks together with other tasks had significantly higher exposures to PM_{10} and metals, especially to V and Ni, compared with those doing other tasks only. This significant difference was also found in utility workers even though their tasks were performed outside the boiler, and exposures were of a lower magnitude, suggesting cutting, grinding and welding as another possible significant source of exposure to toxic metals.

Table 6 shows that boilermakers' estimated exposures to PM_{10} and metals were highly variable among work locations. Exposures at the major boiler structural components, where most repair work took place, were much higher than in the locations where most utility workers performed their jobs such as the turbine area. The highest exposures were found at the ash pit and burners, where there were major sources of vanadium-rich ash particulate. The average estimated exposure to V at the ash pit was very close to the measured exposure, all around 30 $\mu g/m^3$.

Discussion

As part of a prospective study of respiratory health of workers involved in the overhaul of a large, oil-fired boiler, we developed and evaluated an exposure algorithm and used it to estimate personal exposures to ash particulate matter and toxic metals in boiler repair activities. This exposure reconstruction was applied to subjects who, for practical reasons, did not have actual measurements on some workdays. In the algorithm, we used their daily work diaries that recorded and characterized jobs, task profiles, and time spent working in each assigned area. Because actual measurement data indicated that cutting, grinding, and welding were major tasks affecting boilermakers' exposures to ash and metals, we focused our efforts on developing task specific concentrations for cutting, grinding, and welding from available measurements. These task specific concentrations were combined with area concentrations to estimate unmeasured daily exposures location by location. The major underlying assumption was that similar tasks, performed at the same or nearby locations, on the same or adjacent days, would generate similar mean exposures. In addition, we assumed that minor tasks performed mostly in areas outside boiler were less important determinants of exposure. We verified these assumptions with measured data. This algorithm and its assumptions enabled us to develop estimates on a personal and daily basis.

The internal validation test revealed that this algorithm provided reasonably accurate and reliable exposure estimates for particulate matter and toxic metals for boiler overhaul work activities. Vanadium was well estimated with PM_{10}. The estimated means of vanadium and PM_{10} were very close to the means from actual measurements during the overhaul. Although biases were rel-

TABLE 3

Estimated Full-shift, Time-Weighted Average Exposures [GM(GSD)]* to PM_{10} (mg/m^3) and Metals (μg/m^3) by Group

Group	N†	n‡	PM_{10}	V	Ni	Cr	Mn
Boilermakers	18	133	0.36 (3.8)***	5.99 (8.1)***	3.64 (7.9)***	0.95 (15.2)***	1.40 (5.4)***
Utility Workers	11	89	0.09 (2.6)	0.38 (3.8)	0.35 (5.0)	0.10 (13.2)	0.30 (8.2)

* Geometric mean (geometric standard deviation).

† Number of subjects contributing estimates.

‡ Number of estimates.

*** $P < 0.001$ comparing boilermakers to utility workers.

TABLE 4

Estimated Full-Shift, Time-Weighted Average Exposures [GM(GSD)]* to PM_{10} (mg/m^3) and Metals (μg/m^3) by Group and Time Period

Group/Time Period	N†	n‡	PM_{10}	V	Ni	Cr	Mn
Boilermakers							
Before June 3	18	100	0.27 (3.0)	3.79 (5.1)	2.18 (5.6)	0.62 (15.4)	1.05 (4.8)
After June 3	15	33	0.87 (5.0)***	23.99 (14.9)***	17.19 (9.7)***	3.41 (9.8)**	3.38 (5.6)***
Utility workers							
Before June 3	9	57	0.08 (2.4)	0.36 (3.3)	0.26 (3.9)	0.08 (10.4)	0.28 (6.6)
After June 3	11	32	0.10 (2.8)	0.40 (4.8)	0.56 (6.7)	0.15 (19.1)	0.33 (11.8)

* Geometric mean (geometric standard deviation).

† Number of subjects contributing estimates.

‡ Number of estimates.

** $P < 0.01$ comparing boilermakers after June 3 to before June 3.

*** $P < 0.001$ comparing boilermakers after June 3 to before June 3.

TABLE 5

Estimated Full-Shift, Time-Weighted Average Exposures [GM(GSD)]* to PM_{10} (mg/m^3) and Metals (μg/m^3) by Group and Task

Group/Tasks	N†	n‡	PM_{10}	V	Ni	Cr	Mn
Boilermakers							
CGW tasks§	15	79	0.69 (3.2)**	18.57 (5.6)**	10.70 (6.4)**	2.60 (16.9)**	2.99 (4.9)**
Other tasks¶	15	54	0.14 (2.5)	1.14 (3.9)	0.76 (3.2)	0.22 (5.6)	0.46 (3.0)
Utility workers							
CGW tasks	3	20	0.30 (2.4)###	1.58 (2.8)###	1.49 (4.6)###	0.46 (6.7)***	2.06 (4.6)###
Other tasks	11	69	0.06 (1.9)	0.25 (3.0)	0.23 (4.0)	0.06 (13.4)	0.17 (6.7)

* Geometric mean (geometric standard deviation).

† Number of subjects contributing estimates.

‡ Number of estimates.

§ Cutting, grinding and welding tasks. ¶ Area setup, rigging, staging, and material handling.

** $P < 0.001$ comparing boilermakers' CGW tasks to other tasks.

*** $P < 0.01$ comparing utility workers' CGW tasks to other tasks.

$P < 0.001$ comparing utility workers' CGW tasks to other tasks.

atively larger for Ni and Mn, the overall differences were not statistically significant.

The results from this survey were comparable with those from another overhaul job in our previous surveys. The measured PM_{10} concentrations in that survey ranged from 1.44 to 6.69 mg/m^3, with a mean (SD) of 3.22 (1.42) mg/m^3 and the vanadium concentration ranged from 2.2 to 31.3 μg/m^3, with a mean (SD) of 12.2 (9.1) μg/m^3.[2,12] Although measured and estimated average PM_{10} concentrations were lower in this overhaul than in the previous one, the average vanadium concentrations were close. The overestimation of Cr and Mn exposures may be due to the fact that Cr and Mn were generally at low levels in measured samples and estimates were more easily affected by a few high concentrations from cutting, grinding and welding tasks used in estimation. The use of area sampling provided supplemental data and an alternative to personal exposures, which facilitated our exposure reconstruction. Since area concentrations might have been lower than personal exposures, some underestimation of PM_{10}, V and Ni could have been introduced this way.

TABLE 6

Boilermakers' Estimated Full-Shift, Time-Weighted Average Exposures [GM(GSD)]* to PM_{10} (mg/m^3) and Metals (µg/m^3) by Work Location

Location	N†	PM_{10}	V	Ni	Cr	Mn
Ash pit	3	1.98 (2.8)	30.05 (3.5)	10.93 (10.4)	2.17 (11.1)	23.24 (3.7)
Burners	3	1.10 (3.8)	26.89 (13.6)	76.38 (26.9)	23.73 (19.9)	11.87 (5.6)
DMW‡	9	0.68 (3.9)	22.12 (9.2)	11.09 (5.7)	2.57 (11.0)	1.79 (3.8)
Water plant	3	0.86 (1.1)	6.51 (1.1)	3.77 (1.2)	0.87 (1.9)	1.33 (1.4)
Heat exchanger	3	0.59 (9.2)	15.6 (30.5)	9.24 (19.4)	3.79 (26.6)	1.70 (8.3)
Mud drum	2	0.40 (1.3)	2.22 (3.3)	9.82 (2.7)	0.73 (1.2)	2.89 (6.3)
Precipitator	2	0.35 (4.9)	3.71 (13.4)	5.75 (13.8)	1.48 (301.2)	1.92 (8.6)
Super heater	9	0.34 (2.2)	10.61 (2.9)	3.46 (2.9)	0.81 (5.1)	0.94 (4.4)
Condenser	2	0.34 (1.0)	3.65 (1.0)	1.73 (1.0)	0.44 (1.0)	0.45 (1.0)
Mixed areas	7	0.20 (2.4)	1.79 (2.7)	2.29 (5.4)	0.97 (6.3)	1.59 (4.0)
Air heater	8	0.18 (2.4)	2.17 (3.8)	0.77 (3.4)	0.13 (12.4)	0.80 (3.9)
Steam drum	5	0.15 (4.5)	1.46 (10.8)	2.11 (9.9)	1.14 (26.3)	0.51 (6.8)
Turbine area	2	0.10 (1.7)	0.44 (1.7)	0.36 (3.3)	0.10 (5.7)	0.81 (2.6)
F statistic:		5.52	8.76	4.88	2.59	2.80
P value:		<0.0001	<0.0001	<0.0001	<0.01	<0.01

* Geometric mean (geometric standard deviation).

† Number of subjects contributing estimates.

‡ Dissimilar metal welds. These connect the water tubes with the steam tubes in the superheater.

We tried to use personal measurements as much as possible in the estimation process to compensate for this difference.

Vanadium is a natural component of fuel oil. The content is variable in crude oil depending on the source. The burning process concentrates the vanadium in the fuel oil ash, which may contain as high as 40% by weight vanadium oxides.[16] Our results suggest that direct contact with fuel-oil ash in boiler repair activities, especially inside the boiler at burners and ash pit, was the main source of vanadium exposure. Although a separate contractor washed walls inside the firebox prior to the repair work, collection of fuel-oil ash at the ash pit bottom was evident and presented as a great potential for exposures. Our results also suggested that it was possible for boilermakers to be exposed to high levels of particulate matters at other locations outside boiler area such as the wastewater treatment plant, but such particulate matter was not as rich in vanadium as the boiler ash particles. Therefore, they may not have contributed similarly to the health effects as from vanadium-rich fuel ash particles. These all point to the possibility of using vanadium as an indicator of exposure to fuel oil ash particulates.

Cutting, grinding, and welding were major tasks performed during the boiler overhaul for both boilermakers and utility workers. These work processes inside the boiler could both aerosolize the fuel-oil ash particles deposited on the water tubes and generate welding fumes in the same process, especially Ni, Cr, and Mn. Our results showed that boilermakers who performed cutting, grinding and welding tasks had a magnitude higher exposures to V and Ni than utility workers who also performed these tasks outside the boiler. It is also noticeable that boilermakers who did not perform these tasks had similar or lower exposures to both particulate matter and metals as utility workers, who were cutting, grinding and welding, outside the boiler. This points to cutting, grinding, and welding tasks as another potential source of exposure to toxic metals during the boiler overhaul activities. This may also explain why pre- and during-overhaul levels of Ni and Fe were not significantly different in boilermakers (Table 1).

In occupational epidemiologic studies, high-quality exposure data from actual measurements are not always available, especially for retrospective exposure assessment. Exposure-estimating algorithms often need to be developed so that valid exposures could be estimated. On the basis of different exposure scenarios and exposed agents, exposure models and algorithms can be different and developed separately for each study. Armstrong and colleagues used a multiplicative model to estimate past exposures of petroleum marketing and distribution workers in the United States to benzene and total hydrocarbons.[29] They used recent measurements as the base exposure and adjusted for change in exposure modifiers such as difference in workplace, materials handled and tasks performed. They also used part of measured data for exposure estimate validation. Glass et al[21] used another algorithm to estimate past benzene exposure in Australian petroleum industry workers, but they validated their estimates against the reported value in literature. Others used a similar approach to estimate exposure to respirable man-made mineral fibers in the European insulation wool industry.[30] Compared with difficulties in historic exposure assessments in these studies where exposure modifiers may be more variable and less reliable, the exposure data in our study were measured simultaneously and well matched with exposure determinants such as tasks, work locations and time spent doing each task This allowed us to derive more reliable and accurate estimates as shown in the validation testing. It also allowed us to develop exposure estimates on a personal basis, rather than group averages. This is essential to estimating personal risks for respiratory symptoms and lung function of the epidemiologic study.

One potential weakness of this study was the fact that we did not use the common cyclone samplers to collect particles of respirable fraction. Instead, we used PM_{10} as the representative metric, indicative of the thoracic fraction, and PM_{10} personal samplers to collect particulate matter. In the occupational health field, aerosol is traditionally sampled and defined in inhalable, thoracic, and respirable fractions, each of which covers different deposition probability curves based on particle size and density.[28] The thoracic fraction particles are those that have 10 μm as mass median aerodynamic diameter and can enter and deposit in the bronchial tree or the lung parenchyma,[31] where they may affect both the airways and alveolar region. It was the health effects in these regions that we were most interested in, not just the alveolar region. PM_{10} as defined by the United States Environmental Protection Agency also is a probability curve that includes both fine and coarse particles and is an indicator of thoracic fraction particles.[32]

The exposure described in this report is the external exposure of workers. It did not take into account of other factors that may have affected the quantity of particulate inhaled, such as the use of respirators, breathing rate, and actual particle deposition rates in different regions of the respiratory system. These also may significantly modify the internal dosage of particulate matters and metals workers received. It was these internal doses that might have induced the biologic effects as assessed in the epidemiologic study.[16] The estimation of internal dose from these exposures will be presented elsewhere using different modeling approaches.

In summary, we developed and validated an algorithm to reconstruct exposures to particulate matter and toxic metals for unmeasured workdays during a major boiler overhaul work. This algorithm was a step-by-step process, easy to use, and needed no sophisticated statistical modeling. It used the available measurement data, took into account of daily tasks performed, time activity patterns and work locations, and provided reasonably accurate and reliable, individually based exposure metrics, which not only allowed the analysis on individual health risks associated with the exposures to fuel oil ash and component metals, but also might have helped reduce the exposure misclassifications in the epidemiologic study of boilermakers if as in other studies group average exposures were used for individuals. This method also may be applicable to assessment strategies in other exposure scenarios, assuming workplace mean concentrations do not vary significantly across time.

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