Comparing Exposure Zones by Different Exposure Metrics Using Statistical Parameters: Contrast and Precision

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Recently, the appropriateness of using the ‘mass concentration’ metric for ultrafine particles has been questioned and surface area (SA) or number concentration metrics has been proposed as alternatives. To assess the abilities of various exposure metrics to distinguish between different exposure zones in workplaces with nanoparticle aerosols, exposure concentrations were measured in preassigned ‘high-’ and ‘low-’exposure zones in a restaurant, an aluminum die-casting factory, and a diesel engine laboratory using SA, number, and mass concentration metrics. Predetermined exposure classifications were compared by each metric using statistical parameters and concentration ratios that were calculated from the different exposure concentrations. In the restaurant, SA and fine particle number concentrations showed significant differences between the high- and low-exposure zones and they had higher contrast (the ratio of between-zone variance to the sum of the between-zone and within-zone variances) than mass concentrations. Mass concentrations did not show significant differences. In the die cast facility, concentrations of all metrics were significantly greater in the high zone than in the low zone. SA and fine particle number concentrations showed larger concentration ratios between the high and low zones and higher contrast than mass concentrations. None of the metrics were significantly different between the high- and low-exposure zones in the diesel engine laboratory. The SA and fine particle number concentrations appeared to be better at differentiating exposure zones and finding the particle generation sources in workplaces generating nanoparticles. Because the choice of an exposure metric has significant implications for epidemiologic studies and industrial hygiene practice, a multimetric sampling approach is recommended for nanoparticle exposure assessment.

Keywords: contrast; exposure metric; nanoparticle; precision

INTRODUCTION

Traditionally, mass concentration has been used as the metric for exposure assessment of airborne particles and the basis for regulation. Recently, however, the appropriateness of the mass concentration metric for nano-sized particles has been questioned. The concern is that exposure assessments that rely on mass concentration could lead to underestimates of ultrafine particle toxicity. This is because these particles do not contribute much to total mass concentration despite their high numbers. No scientific agreement exists for appropriate exposure metrics for nano-sized particles (Maynard and Aitken, 2007; Paik et al., 2008).
New exposure metrics for the nano-sized particles have been proposed. McCawley et al. (2001) showed that particle number concentration was a more appropriate metric than mass concentration for relating beryllium particle exposure to chronic beryllium disease and found no correlation between mass and number concentrations. Peters et al. (1997) found that a decrease of peak expiratory flow among 27 nonsmoking asthmatics had a stronger association with number concentration than with mass concentration.

Surface area (SA) concentration has been highlighted as a biologically more relevant metric for the effective dose than mass concentration because the adverse health effects of nanoparticles may be associated with surface reactivity (Li et al., 1996; Oberdo¨rster, 2000; Tran et al., 2000; Brown et al., 2001). Schwartz and Marcus (1990) related daily mortality with number concentration than with mass concentrations. Contrast and precision can be assessed using statistical parameters, such as contrast between zones and precision within a location. Using the same data set, but converting the mass concentrations into SA concentrations, Maynard and Maynard (2002) showed a linear relationship between the particle SA and mortality. This indicates that SA may be a more suitable metric than mass for ambient aerosol exposure. Although these studies suggest that either SA or number concentration may be a better metric than mass concentration for ultrafine particles, further investigations are required to confirm their appropriateness in occupational and environmental settings through epidemiological studies.

The choice of the most appropriate exposure metric will be critical. In epidemiological studies, zones of workers are split into different exposure categories based on exposure information, such as exposure concentration, job profile, and duration of exposure, to name a few. If exposure concentration by a less health-relevant exposure metric is used to determine exposure categories, workers could be misclassified into incorrect categories resulting in a weaker exposure–response association (Flegal et al., 1991).

The efficiency of zonings to detect an exposure–response relationship in an epidemiologic study can be assessed using statistical parameters, such as contrast between zones and precision within a zone (Kromhout and Heederik, 1995). Here, a zone refers to an exposure zone that contains a set of specific locations expected to have similar particle concentrations. Contrast and precision can be derived from the estimates of variance between-zones (S^2_{BZ}), within-zones (S^2_{WZ}), and within-location (S^2_{WL}) for a set of measurements. Contrast (\varepsilon) in exposure levels between zones is calculated as follows:

\[ \varepsilon = \frac{S^2_{BZ}}{S^2_{BZ} + S^2_{WZ}}. \]  

Contrast approaches a value of 1 as within-zone variability approaches 0, i.e. each zone based on this exposure metric is getting more homogeneous. On the contrary, contrast approaches a value of 0 as the between-zone variability becomes negligible.

The precision (\pi) of each zone’s mean exposure is calculated as a reciprocal of the pooled standard errors for within-zones and within-locations:

\[ \pi = \frac{1}{\sqrt{(S^2_{WZ}/n_1 + S^2_{WL}/n_2)}.} \]

where \( n_1 \) is the number of locations and \( n_2 \) is the number of measurements in a zone. Precision is a measure of repeatability within each zone and/or within each location in a zone. Higher precision indicates that exposure concentrations from different locations within a zone and/or repeated measurements within a location are relatively similar to each other compared to the case of lower precision. Better classification of zones improves precision and contrast by decreasing the within-zone variance component (S^2_{WZ}).

In this study, exposure assessments were carried out in three workplaces generating incidental nanoparticles. Simultaneous real-time measurements of particle SA, number, and mass concentrations were obtained. The abilities of various exposure metrics to distinguish between different exposure zones were assessed using contrast and precision, exposure ranking, and concentration ratios between different exposure categories.

**METHODS**

**Sampling strategy**

The study was conducted in three workplaces—a restaurant, a diesel engine laboratory, and a die cast facility—where incidental nanoparticles were being generated. In a previous study, we obtained aerosol measurements in the restaurant and die cast facility to construct particle maps that helped us to visualize spatial variability of aerosol concentration distributions in those workplaces for different exposure metrics and to identify exposure zones based on exposure levels (Park et al., 2010). In that study, concentrations for all metrics in the kitchen of the restaurant were significantly higher than in the serving
area. The kitchen area was identified as the high-exposure zone and the serving area was identified as the low-exposure zone. In the die-casting plant, exposure rankings and the statistical significance of differences among the three primary areas of the facility varied based on the exposure metrics chosen. The SA or fine particle number concentrations were used to create three exposure zones because these metrics were found to be more appropriate for distinguishing between the exposure zones. The die-casting, trim/repair, and machining areas were identified as the high-, medium-, and low-exposure zones, respectively.

For the diesel engine laboratory, two exposure zones were chosen based on the activities being conducted. The laboratory was the high-exposure zone and the office area was the low-exposure zone. For the exposure assessments reported in this paper, two exposure zones (high and low) were selected for each facility.

Because there are currently no SA or number concentrations instruments suitable for full-shift personal worker sampling, area sampling was used as a surrogate to measure personal exposures. This was done using real-time instruments for the various exposure metrics of interest at three or four locations for every exposure zone. Sampling time was ~4 to 6 h with 3-min averaging times for each instrument. Two sets of samples were taken at each of the six or seven workplace locations.

Descriptions of workplaces

Restaurant. The restaurant had two major job categories: cooking and serving. The cooking workers spent most of their time in the kitchen. The serving workers spent the majority of their time in the serving areas, such as the serving station and seating area.

The high-exposure zone contained an oven area, grill area, and a dishwasher area (Fig. 1). Most entrees were prepared in the oven area. Some foods were warmed up and made-to-order in the grill area. The oven area had gas burners, flat top grills, and gas convection ovens that generated combustion particles. The grill area was for serving food to customers during lunchtime. The deep fryers, flat top grills, and gas grill were located in the corner of the grill area. The dishwashing area was located adjacent to the oven area and was divided by a wall that had a door, which was open most of the time. The restaurant was ventilated by HVAC (heating, ventilation, and air conditioning) systems, and canopy hoods were installed above cooking appliances to draw air away.

The serving area did not have any combustion sources and included a serving station, a bar, a general seating area, private rooms, and a hallway. Three representative locations for this zone were selected: the serving station, the bar, and the seating area.

Diesel engine laboratory. The diesel engine laboratory was in the Department of Mechanical Engineering at the University of Minnesota (Fig. 2). It had two sections: a laboratory area and an office area. Seven diesel engines were located in the laboratory area where students and researchers performed their experiments. When they were not conducting experiments in the laboratory area, the students spent their time in the office area. When

![Fig. 1. Floor plan of the restaurant (sampling locations are indicated on the diagram).](https://academic.oup.com/annweh/article-abstract/54/7/799/202708/0)
an experiment was being performed, researchers turned on fans, drawing outdoor air from windows on one side through the laboratory to windows on the other side. Diesel engine experiments were performed infrequently according to research needs. Because only one engine was operating at any given time during the days of this study, the nanoparticle source was clearly identified. Therefore, no mapping measurements were performed to establish exposure zones. The office area included a study room, teaching assistants office, and preparation room. The preparation room was right next to the laboratory area, separated by a wall, but contained no diesel engines.

**Die-casting facility.** The die-casting facility produced aluminum alloy products. The plant was divided into three sections by walls containing passageways on either side. As indicated in Fig. 3, the sections were the die-casting, trim/repair, and machining areas. Aluminum was melted in the furnaces and delivered to each die-casting machine by forklift trucks. In the trim/repair area, castings were trimmed in trim presses and stacked. Dies were also repaired in the tool repair section. In the machining area, the trimmed castings were finished using milling, broaching, and turning machines. The die cast facility had four job categories: die casting, trimming, machining, and maintenance. Most workers in the first three categories spent >90% of their time in their corresponding work zone. However, some of the trimming employees worked in the die-casting zone because two of the seven trim presses were located there.

The exposure zones were ranked based on mapping of the fine particle number concentrations. The die cast area was the high-exposure zone, the trim/repair area was the medium zone, and the machining area was the low-exposure zone. Two die cast machines and one trim press were selected for the investigation because workers near these machines were in the high-exposure zone. In the machining area, trimmed castings were finished through milling, turning, or broaching processes that used metalworking fluids. Two milling machines and one turning machine were chosen for the low-exposure zone.

**Particle measurement**

Real-time measurements of particle mass, number, and SA concentrations and size distribution by number, as well as gravimetric filter measurements for calibration of the real-time mass monitor, were...
obtained simultaneously. Three aerosol photometers (DustTrak Model 8520; TSI Inc., Shoreview, MN, USA) with PM2.5, PM1.0, and respirable sampling inlets were used for mass concentration.

The DustTrak measurements were calibrated to the average aerosol concentration from the corresponding gravimetric measurements for the respirable and PM2.5 size fractions. The gravimetric PM2.5 and respirable mass concentrations were obtained using a PM2.5 sampler (PEM™ Model 200; MSP Inc., Minneapolis, MN, USA) and a nylon cyclone (Dorr–Oliver 10 mm cyclone; Sensidyne, Clearwater, FL, USA). Pumps drew air through sampling inlets at 4.0 and 1.7 l min \(^{-1}\), respectively.

Filters were weighed before sampling using a microbalance with a sensitivity of 5 μg in a weighing room where the temperature and humidity were controlled. After sampling, filters were equilibrated in the weighing room and then reweighed.

The DustTrak measurements were recalculated using a specific calibration factor for each measurement as follows:

Calibration factor

\[
\text{Calibration factor} = \frac{\text{Gravimetric concentration}}{\text{Time-integrated DustTrak concentration}}
\]  

(3)

Each DustTrak measurement was multiplied by this factor to estimate the true mass concentration. No gravimetric sampling was conducted for PM1.0. The calibration factor for PM1.0 was calculated using the concentration ratio between PM2.5 and PM1.0 and the gravimetric PM2.5 concentration:

PM1.0 Calibration factor

\[
\text{PM1.0 Calibration factor} = \frac{\text{Gravimetric PM2.5 concentration}}{\text{Time-integrated DustTrak PM1.0}} \times \frac{\text{Size-integrated PM1.0}}{\text{Size-integrated PM2.5}}.
\]  

(4)

Size-integrated PM2.5 and PM1.0 concentrations were calculated from size distribution measurements obtained from a scanning mobility particle sizer (SMPS Model 3034; TSI Inc.) and an optical particle counter (OPC, AeroTrak™ Model 8220; TSI Inc. or HHPC-6; Hach Ultra, Grants Pass, OR, USA). The gravimetric mass concentration and integrated DustTrak concentrations were highly correlated (\(R^2 = 0.84\) for respirable matter and 0.97 for PM2.5) and the mean calibration factors for respirable matter, PM2.5, and PM1.0 were 0.31, 0.35, and 0.37 with standard errors of 0.01, 0.03, and 0.01, respectively.

For each run, blank filters (20% of total sample filters) were weighed at the same time as the sample filters. The detection limit, calculated as three times the standard deviation of the field blank weight gains divided by the sampled air volume, was 0.024 mg m \(^{-3}\).

The SA monitor (AeroTrak™ Model 9000; TSI Inc.) had the ability to measure the SA concentrations of particles that could be deposited in the tracheobronchial or alveolar regions of the human lung (Shin et al., 2007). The amount of charge on particles charged with unipolar positive ions by diffusion is proportional to the SA of lung-deposited particles based on the International Commission on Radiological Protection lung deposition model for a reference worker with specific physiological and activity-related parameters (Fissan et al., 2007). For this study, the monitor was set on the alveolar deposition mode.

For number concentration, a condensation particle counter (CPC, P-Trak Model 8525; TSI Inc.) was utilized. The P-Trak is a real-time CPC that counts single particles 0.02 μm in diameter to >1 μm. The particle counts from the P-Trak will be referred to henceforth as fine particle number concentration in this study. An OPC was used to measure size distribution by number. The OPC simultaneously counts and sizes particles into six channels (0.3–0.5, 0.5–0.7, 0.7–1.0, 1.0–2.0, 2.0–5.0, and >5.0 μm) via light scattering. Particle counts from summing all size bins will be referred to henceforth as coarse particle number concentrations.

The SMPS was used to obtain information on particle size distribution by number based on the electrical mobility diameter. The SMPS can measure particles between 10 and 487 nm in diameter in up to 32 size channels.

For easy portability, a mobile sampling cart was used to carry the instruments. A mannequin was placed on the top section of the sampling cart to locate sampling tubes from the different instruments at breathing zone height. The inlets of sampling tubes were set closely together. All instruments were connected to a wall outlet using AC power. Data from each device were downloaded to a laptop computer.

**Data analysis**

All statistical analyses were conducted using SAS 9.1 (SAS Institute Inc., Cary, NC, USA). The real-time instrument data were organized into 3-min averages. To compare aerosol concentrations representing different exposure metrics from the simultaneous measurements, data were needed from all
seven real-time instruments. If a time point did not have any one of the seven instrument readings, it was excluded from the analysis. More than 90% of time intervals had all seven measurements and were included in the analysis.

The distributions of concentrations for all exposure metrics were approximately lognormal. The geometric means were calculated for each location and each zone. Significant mean differences between high and low zones by each metric in each workplace were detected using t-tests on the log scale. Data taken from the same location at different times were autocorrelated. To correct for the autocorrelation in the real-time measurements, the most suitable covariance structure should be selected. For this study, general linear models with compound symmetry (homogeneous variances and constant correlation regardless of how far apart in time they are) were used for the repeated measures of real-time monitoring instruments. These models were more appropriate to compare high- and low-exposure zone measurements than models assuming independence among different measurements. The level of statistical significance for all analyses was 0.05.

A two-way random effects analysis of variance (ANOVA) model based on Kromhout and Heederik (1995) was constructed using ‘PROC MIXED with random statements’ to estimate the between-zone, within-zone, and within-location components of the variance of the logged exposure concentrations as follows:

\[ Y_{ijk} = \ln X_{ijk} = \mu_y + \alpha_i + \beta_{ij} + \epsilon_{ijk}, \]  

for \( i = \) high and low zones, \( j = 1–4 \)th locations, and \( k = 1–240 \) time points, where \( X_{ijk} \) = exposure concentration of the \( i \)th zone’s \( j \)th location at the \( k \)th time point, \( \mu_y \) = mean of \( Y_{ijk} \), \( \alpha_i \) = random deviation of the \( i \)th zone’s true exposure (\( \mu_{y,i} \)) from \( \mu_y \), \( \beta_{ij} \) = random deviation of the \( j \)th location’s true exposure (\( \mu_{y,ij} \)) from \( \mu_{y,i} \), and \( \epsilon_{ijk} \) = random deviation of the \( i \)th zone’s \( j \)th location’s exposure on the \( k \)th time point from its true exposure, \( \mu_{y,ij} \).

This model assumed that \( \alpha_i, \beta_{ij}, \) and \( \epsilon_{ijk} \) are normally distributed and can be expressed as \( \alpha_i \sim N(0, \sigma^2_{BZ}), \beta_{ij} \sim N(0, \sigma^2_{WZ}), \) and \( \epsilon_{ijk} \sim N(0, \sigma^2_{WL}). \) The distribution of \( X_{ijk} \) is lognormal. The variance components of the samples—\( S^2_{BZ}, S^2_{WZ}, \) and \( S^2_{WL} \)—were used as estimates of the variance components in the population—\( \sigma^2_{BZ}, \sigma^2_{WZ}, \) and \( \sigma^2_{WL} \)—and they were used to calculate standard deviation for distributions between-zone (\( S_{BZ} \)), within-zone (\( S_{WZ} \)), and within-location (\( S_{WL} \)). The antilogs of the standard deviations were the corresponding geometric standard deviations \( \text{GSD}_{BZ}, \text{GSD}_{WZ}, \) and \( \text{GSD}_{WL}. \)

The number concentration obtained by summing the counts in all size channels of the SMPS was assumed as the reference number concentration (\( N_{\text{Ref}} \)) for particles in the 10–487 nm size range. To compare \( N_{\text{Ref}} \) with the P-Trak and an OPC, the ultrafine particle number concentration (\( N_{\text{UFP}} \)) for particles 20–500 nm was calculated as:

\[ N_{\text{UFP}} = N_{\text{P-Trak}} - \sum_{k=2}^{3} N_{\text{OPC},k}. \]

The concentrations ratios between high- and low-exposure zones were obtained by taking the antilog of the differences between least square means of the two zones in the logarithmic scale. These ratios were used to evaluate the ability of each metric to differentiate between two exposure zones.

**RESULTS**

Aerosol concentrations and exposure ranks by different metrics

The aerosol concentrations measured for various exposure metrics and exposure ranks in the three workplaces are summarized in Table 1. The column named ‘rank’ lists the exposure rankings for each location within a workplace according to each exposure metric.

Restaurant. SA and fine particle number concentrations were the highest in the oven area followed by the grill and dishwashing areas. These concentrations were significantly higher than those in the low-exposure zone. In the high-exposure zone, the coarse particle number concentrations were significantly higher than in the low-exposure zone. Respirable mass concentration was higher in the low-exposure zone than in the high zone. PM2.5 and PM1.0 concentrations showed no significant difference between the zones.

The top three rankings based on SA and fine and coarse particle number concentrations were all from the high-exposure zone. In marked contrast, the top three rankings were all from the low zone for respirable mass concentration.

Figure 4 presents the ratios of the mean concentrations of the high- and low-exposure zones for each concentration metric in the three workplaces. In the restaurant, the highest ratios were observed for SA and fine particle number concentrations. The
coarse particle number concentration ratio was lower. The ratios of respirable mass and PM2.5 concentrations were <1.

**Diesel engine laboratory.** Table 1 shows that SA and fine particle number concentrations were highest near Engine 1 followed by the Engines 3 and 2. PM2.5 was highest in the preparation room. Rankings based on SA and fine particle number concentration tracked each other, but coarse particle number and mass concentrations did not show any similarity. As shown in Fig. 4, the ratios of SA and fine particle number concentrations were higher than those of mass concentrations.

**Die cast facility.** In the die-casting facility, all concentrations were significantly higher in the high-exposure zone than in the low-exposure zone. The top three ranks of SA, respirable matter, PM1.0, and fine and coarse particle number concentrations came from the high-exposure zone. However, the three highest ranks for PM2.5 were not
all from the high-exposure zone. The ratio of concentrations in the high- and low-exposure zones was highest for SA (Fig. 4).

**Exposure variability for different exposure metrics**

The contrast and precision of different exposure metrics and exposure variability from the two-way ANOVA are presented in Table 2.

**Restaurant.** In the restaurant, the GSD_{BZ} for SA, fine, and coarse particle number concentrations were higher than those for mass concentrations. SA, respirable mass, fine, and coarse particle number concentration showed high contrast, but PM2.5 and PM1.0 had very low contrast. Respirable mass concentration showed high contrast, but the concentrations were lower in the high-exposure zone than in the low-exposure zone. Fine particle number concentration showed relatively high contrast but the lowest precision.

**Diesel engine laboratory.** No statistically significant difference in GSD_{WL}, GSD_{WZ}, and GSD_{BZ} was observed for SA and fine and coarse particle number concentrations. As shown in Table 2, GSD_{WZ} was slightly greater than GSD_{BZ} for all metrics. PM2.5 and PM1.0 had the lowest contrast. The other metrics showed higher contrasts ranging between 0.21 and 0.39.

**Die cast facility.** GSD_{BZ} was substantially greater than GSD_{WZ} for all metrics except PM2.5 and PM1.0. Fine particle number concentration had the highest contrast and precision. SA concentration showed a similar contrast but lower precision compared to the fine particle number concentration. PM2.5 and PM1.0 had the lowest contrast and precision in this facility.

**Particle size distribution by number for particles <500 nm in diameter**

The reference number concentration ($N_{\text{Ref}}$) measured by the SMPS and corresponding ultrafine particle number concentrations calculated from the P-Trak and OPC ($N_{\text{UFP}}$) are summarized in Table 3. The size distribution parameters—count median diameter and GSD—obtained from the SMPS measurement are also included.

$N_{\text{Ref}}$ was greater than $N_{\text{UFP}}$ in all locations of the three workplaces. Figure 5 shows $N_{\text{UFP}}$ versus $N_{\text{Ref}}$ from all time points. At lower concentrations, $N_{\text{UFP}}$ was close to $N_{\text{Ref}}$ with little variation. However, at high levels, $N_{\text{UFP}}$ underestimated the number concentration.

**DISCUSSION**

**SA and fine particle number concentrations: more sensitive metrics for differentiating exposure zones**

Based on this study, SA and fine particle number concentrations are more sensitive measures to detect
spatial variation of nanoparticles than mass concentrations, which cannot always be a substitute or surrogate metric for the others. The restaurant had relatively simple particle generation characteristics: incidental nanoparticle sources located only in the kitchen and no particle source in the serving area. The high-exposure zone had significantly higher concentration than the low-exposure zone in terms of SA, fine, and coarse number concentrations. However, mass concentrations did not differ between the two zones.

Within the high-exposure zone of the restaurant, the strength of particle sources varied by location. For SA and fine particle number concentrations, the oven area was highest followed by the grill and the dishwashing areas. However, coarse particle number concentration, which represented particles >300 nm in diameter that were not produced by combustion sources, was highest in the dishwashing area. Incidental nanoparticles transported from the grill and oven areas to the dishwashing area could agglomerate in this area; ultrafine particles could also be created in this area by drying of droplets. In addition, particles could grow by condensation of water vapor in the high humidity environment, causing a higher coarse particle number concentration in the dishwashing area than in the oven and grill areas.

A one-way ANOVA test was used to determine if there were differences among the three locations within the high-exposure zone. SA and fine particle number concentrations showed significant differences ($P = 0.02$ and $0.003$, respectively) between locations but coarse particle number concentration did not ($P = 0.43$). Table 1 shows that the dishwasher area has significantly different SA and fine number concentrations than the grill and oven areas, but the coarse number concentrations were similar in all three locations. Indeed, the SA and fine number concentrations in the dishwasher area are closer to those observed in the low-exposure zone. This suggests a need to reclassify the exposure zones in the restaurant with the dishwasher location being placed in the low zone rather than the high zone.

The diesel engine laboratory had even more distinct particle generation conditions than the restaurant. Seven engines were located in the laboratory but only one engine at a time was operating during our measurements. However, unlike the restaurant, no exposure metrics were significantly different between the two zones in the engine laboratory. Two reasons for this are that outdoor air was provided to the laboratory through the entire period of our experiments and each engine was equipped with a local ventilation system to remove exhaust from the work area. In the restaurant, on the other hand, the oven

### Table 2. GSD_{WL}, GSD_{WZ}, and GSD_{BZ} and contrast and precision for all exposure metrics

<table>
<thead>
<tr>
<th>Workplace/exposure metric</th>
<th>GSD_{WL}</th>
<th>GSD_{WZ}</th>
<th>GSD_{BZ}</th>
<th>Contrast, $\epsilon$</th>
<th>Precision, $\pi$</th>
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<tbody>
<tr>
<td><strong>Restaurant</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SA</td>
<td>2.14</td>
<td>2.02</td>
<td>3.77</td>
<td>0.78</td>
<td>2.7</td>
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<tr>
<td>Fine number</td>
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<td>4.89</td>
<td>0.64</td>
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<tr>
<td>Coarse number</td>
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<td>1.55</td>
<td>2.96</td>
<td>0.86</td>
<td>3.8</td>
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<tr>
<td>RPM</td>
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<td>1.16</td>
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<tr>
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<td>0.00</td>
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<tr>
<td>PM1.0</td>
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<td>1.46</td>
<td>1.00</td>
<td>0.00</td>
<td>4.6</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
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<td>SA</td>
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<td>1.76</td>
<td>1.42</td>
<td>0.28</td>
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<tr>
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<td>1.48</td>
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<tr>
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<td>1.38</td>
<td>1.00</td>
<td>0.00</td>
<td>6.2</td>
</tr>
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<td>1.40</td>
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<td>3.25</td>
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<td>1.72</td>
<td>0.54</td>
<td>4.0</td>
</tr>
</tbody>
</table>

RPM, Respirable particulate mass.
and grill areas had many cooking appliances and most of them were used simultaneously. Although all cooking appliances were installed with canopy hoods to exhaust emissions from cooking, they were not efficient enough to remove all the particles being generated during the lunchtime peak.

All concentrations in the die-casting facility were significantly greater in the high-exposure zone than in the low-exposure zone, but the ratio of SA between high- and low-exposure zones was higher than those of other exposure concentration metrics. Concentrations for all metrics in the die-casting facility were high because this facility was operated for 20 h a day with two shifts and, due to cold weather, general ventilation through the doors with outside air did not occur. The die-casting facility generated a broad size range of particles from the multiple particle generation sources. Nano-sized metal oxide particles are produced by furnaces and die cast machines like those found in the high-exposure zone (Chang et al., 2005). Submicrometer and larger particles are generated by machining processes like those present in the low-exposure zone (Thornburg and Leith, 2000).

SA and fine particle number concentrations appear to be more appropriate to detect spatial variation of nanoparticles and provide greater contrast between nominally ‘high’- and ‘low’-exposure zones in this study. Of course, this by itself does not mean that

<table>
<thead>
<tr>
<th>ID</th>
<th>Zone</th>
<th>Location</th>
<th>$N_{\text{Ref}}$ (10–487 nm, particles cm$^{-3}$)</th>
<th>$N_{\text{UFP}}$ (20–500 nm, particles cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Count median diameter (GSD)</td>
<td>Mean 5% 95%</td>
</tr>
<tr>
<td>Restaurant</td>
<td>High</td>
<td>Dishwasher</td>
<td>57.0 (2.19) 2860 1200 8770</td>
<td>2680 1130 8550</td>
</tr>
<tr>
<td>Grill</td>
<td>32.2 (1.83) 25,000 9300 75,200</td>
<td>23,800 8840 59,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oven</td>
<td>25.5 (2.13) 87,610 11,800 526,000</td>
<td>77,000 13,200 260,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>18,100</td>
<td>16,700</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Low</td>
<td>Bar</td>
<td>76.2 (2.13) 1480 1170 1960</td>
<td>1400 1100 1190</td>
<td></td>
</tr>
<tr>
<td>Serving station</td>
<td>68.3 (2.06) 1320 394 4060</td>
<td>1310 394 4000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sitting area</td>
<td>82.2 (2.09) 1780 851 4550</td>
<td>1740 790 4590</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>1430</td>
<td>1420</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$P$</td>
<td>0.009</td>
<td>&lt;0.001</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diesel</td>
<td>Engine1</td>
<td>High</td>
<td>27.4 (1.83) 50,600 13,500 631,000</td>
<td>42,600 14,400 292,000</td>
</tr>
<tr>
<td>Engine2</td>
<td>30.5 (2.20) 13,100 7500 23,500</td>
<td>7140 3230 16,200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Engine3</td>
<td>30.1 (1.97) 24,500 14,000 53,900</td>
<td>20,300 11,200 45,700</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Engine4</td>
<td>34.3 (2.29) 6100 3380 11,400</td>
<td>4990 2840 8630</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>15,600</td>
<td>11,700</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Low</td>
<td>Office</td>
<td>40.1 (2.10) 7590 5420 11,500</td>
<td>6270 4360 10,000</td>
<td></td>
</tr>
<tr>
<td>Study area</td>
<td>38.2 (2.08) 7330 3840 28,200</td>
<td>6160 3060 24,200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Teaching assistants office</td>
<td>45.5 (2.08) 6100 3780 10,900</td>
<td>5450 3290 10,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>7180</td>
<td>6320</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$P$</td>
<td>0.16</td>
<td>0.26</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Die cast facility</td>
<td>High</td>
<td>Die cast1</td>
<td>38.0 (1.78) 845,600 511,000 1,510,000</td>
<td>307,000 280,000 370,000</td>
</tr>
<tr>
<td>Die cast2</td>
<td>37.7 (1.92) 919,000 347,000 1,840,000</td>
<td>318,000 263,000 404,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trim press</td>
<td>44.4 (1.93) 901,000 689,000 1,160,000</td>
<td>296,000 281,000 312,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>891,000</td>
<td>309,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Low</td>
<td>Turning</td>
<td>42.2 (2.11) 104,000 56,000 216,000</td>
<td>91,000 53,700 151,000</td>
<td></td>
</tr>
<tr>
<td>Milling1</td>
<td>62.7 (2.51) 113,000 97,000 130,000</td>
<td>102,000 89,400 118,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Milling2</td>
<td>43.2 (2.22) 126,000 104,000 251,000</td>
<td>107,000 89,400 171,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>114,000</td>
<td>99,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$P$</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*aantilog of the least squares mean of the logarithms of concentrations.*
these metrics are better than mass concentration metrics for nanoparticle exposure assessment. The choice of an exposure metric should be based on the toxicological evidence and biological relevance (Nieuwenhuijsen, 2003).

The toxicological mechanisms of nanoparticles have been explored and their unique characteristics—small size, increased SA per unit mass, and surface reactivity—are believed to play an important role in adverse health effects (Gwinn and Vallyathan, 2006; Nel et al., 2006). Recent studies have reported that the inflammatory responses in the lungs by low solubility ultrafine and fine particles showed a better dose–response relationship with SA deposited than mass concentrations regardless of particle size (Oberdörster, 2000; Tran et al., 2000; Brown et al., 2001; Monteiller et al., 2007). While the mechanism is not clear, it is thought that reduced phagocytosis could increase interaction between nanoparticles and the epithelium and increase oxidative stress due to the large SA of nanoparticles (Donaldson et al., 2001).

While there is no consensus on the issue of appropriate exposure metrics for nanoparticles exposure (Maynard and Aitken, 2007), it appears that SA or number concentration metrics might be more appropriate than the mass metric. This study shows that these two metrics are also better suited for distinguishing between exposure zones for nanoparticles. In the absence of personal exposure monitoring, these zones loosely correspond to similarly exposed groups (SEGs).

Using contrast and precision for exposure zoning

It is important to recognize and evaluate exposure variability (Kromhout and Heederik, 1995). Exposure variability has significant implications for epidemiological studies designed to assess risk and for the development of sampling strategies and exposure control measures by industrial hygienists.

Using a two-way random effects ANOVA model, exposure variability in this study was partitioned into its components: between-zone, within-zone, and within-location. In epidemiological studies, these variance components can be used to optimize zoning of workers. Kromhout and Heederik (1995) developed statistical parameters based on the variance components—contrast and precision—to evaluate various exposure zoning schemes in the rubber industry. Contrast is the ratio of between-zone variance to the sum of between-zone and within-zone variances. Precision is a measure of how homogeneous exposure concentrations are within a zone and within a location. From an epidemiological point of view, higher contrast and precision indicate ‘well-formed’ exposure zones or SEGs that facilitate the detection of an exposure–response relationship using a given exposure metric.

In this study, contrast and precision were used to compare the capability of different exposure metrics to distinguish between two predefined exposure zones and to provide information on statistical differences between high and low zones. In the die-casting facility, the contrast and precision for fine

![Fig. 5. Comparison of ultrafine particle concentrations measured by the SMPS (N\textsubscript{Ref}) and calculated from measurements made by the P-Trak and the OPC (N\textsubscript{UFP}).]
particle number and SA concentrations were highest indicating that they were the most efficient metrics to differentiate between the two exposure zones. In the diesel engine laboratory, no metric was observed to be efficient in differentiating between the two zones. Small between-zone variability may cause low contrast indicating a higher probability of overlap between the distributions of exposure concentration of the two zones. In case of low contrast, comparing precision from different metrics may not be useful.

Precision can be used to evaluate homogeneity within an exposure zone and refine exposure groupings. In the restaurant, the concentrations of incidental nanoparticles showed large spatial variations in the cooking area. In addition, there was large time variation in the cooking area due to peak periods of service. The lower precision for the SA and fine particle concentration metrics reflected larger variation by location and time in the high-exposure zone despite their high contrast.

As described before, the SA and fine number concentrations in the dishwashing area of the restaurant were significantly lower than in other locations in the high-exposure zone, leading to lower precision and contrast for these metrics. Therefore, exposure zones were refined by reassigning the dishwashing area to the low-exposure zone. The statistical analyses were repeated with results shown in Table 4. The refined zone classification yielded higher contrast and precision for fine particle number and SA concentrations. This occurred because the within-zone variance component for SA and fine particle number concentrations decreased while the between-zone variance component increased dramatically.

Precision was also used to identify significant measurement errors in this study. In the die-casting facility, the precision of fine particle number concentration zoning was exceptionally high compared to precision of SA even though both metrics had similar values for contrast. This occurred, as shown in Fig. 5, because the P-Trak substantially underestimated the highest fine particle number concentrations with the consequence that variance in the readings was suppressed.

Reducing measurement error in the P-Trak

The P-Trak is a handheld version of a CPC and is designed for qualitative investigations. It counts particles enlarged in a saturated vapor environment using optical sensing. In a high concentration environment, this instrument can experience coincidence errors, i.e. more than one particle can pass through the sensing region at a time and then can be counted as a single particle (Hameri et al., 2002).

At extremely high concentrations such as near the die-casting machines or when the gas oven was open, significant underestimation by as much as a factor of 3 was observed in comparisons of \( N_{\text{UFP}} \) to \( N_{\text{Ref}} \). As shown in Fig. 5, these large differences started to occur at \( \sim 2 \times 10^5 \) particles cm\(^{-3} \), which was lower than the manufacturer’s maximum concentration of \( 5 \times 10^6 \) particles cm\(^{-3} \).

Both \( N_{\text{UFP}} \) and \( N_{\text{Ref}} \) concentrations in the die-casting facility showed statistically significant differences between the high- and low-exposure zones, but the ratio of concentrations in the high and low zones using \( N_{\text{Ref}} \) was 7.8, which was much greater than the ratio of 3.1 using \( N_{\text{UFP}} \). These data also show that the P-Trak underreported the fine particle number concentrations in the high zone of the die-casting plant due to coincidence errors. This error could cause weaker association between exposure and related health outcomes than actually exists. An accurate measurement as well as the choice of appropriate exposure metrics is essential in exposure assessment. The use of a dilution system with the P-Trak would have improved its performance in this study and decreased measurement error (Knibbs et al., 2007; Peters et al., 2006).

CONCLUSIONS

Multimetric aerosol monitoring was performed in three workplaces generating incidental nanoparticles to assess the efficiency of various metrics at

<table>
<thead>
<tr>
<th>Exposure metric</th>
<th>GSD(_{\text{WL}})</th>
<th>GSD(_{\text{WZ}})</th>
<th>GSD(_{\text{BZ}})</th>
<th>Contrast, ( \epsilon )</th>
<th>Precision, ( \pi )</th>
</tr>
</thead>
<tbody>
<tr>
<td>SA</td>
<td>2.13</td>
<td>1.78</td>
<td>4.64</td>
<td>0.88</td>
<td>3.1</td>
</tr>
<tr>
<td>Fine number</td>
<td>2.02</td>
<td>1.68</td>
<td>9.52</td>
<td>0.95</td>
<td>3.3</td>
</tr>
<tr>
<td>Coarse number</td>
<td>1.90</td>
<td>2.44</td>
<td>1.52</td>
<td>0.18</td>
<td>2.4</td>
</tr>
<tr>
<td>RPM</td>
<td>1.47</td>
<td>1.14</td>
<td>1.08</td>
<td>0.28</td>
<td>7.8</td>
</tr>
<tr>
<td>PM2.5</td>
<td>1.56</td>
<td>1.39</td>
<td>1.12</td>
<td>0.10</td>
<td>5.3</td>
</tr>
<tr>
<td>PM1.0</td>
<td>1.68</td>
<td>1.43</td>
<td>1.19</td>
<td>0.19</td>
<td>4.7</td>
</tr>
</tbody>
</table>
differentiating concentrations between exposure zones. In a workplace with a distinct source of nanoparticles, SA and fine particle number concentrations were more appropriate metrics to detect and locate nanoparticle sources than mass and coarse particle number concentrations. However, in the case of a distinct nanoparticle generation source situation with low workload or infrequent activity such as the diesel engine laboratory in this study, none of the metrics were found to be useful. In a plant having multiple particle generation sources with high concentration levels, all exposure metrics showed significant mean differences between the high- and low-exposure zones, but SA and fine particle number concentrations showed higher concentration ratios with higher precision and contrast than mass and coarse number concentrations. Therefore, in the workplaces generating nanoparticles, the SA and fine particle number concentration metrics appear to be better at differentiating exposure zones than mass concentrations.

The choice of appropriate exposure metrics is critical for industrial hygiene exposure management as well as for epidemiological studies. Even though there is no consensus on the most health-relevant exposure metric, toxicological evidence to date suggests that the SA or number concentration metrics might be more appropriate than the mass concentration metric in many situations. The results from this study indicate that these metrics also provide for better contrast and precision. Thus, they are better at distinguishing between exposure zones and reducing exposure misclassification. However, until the most health-relevant metric is definitively established from toxicological and epidemiological studies, a multiple metric sampling approach including SA or fine particle number concentration measurements with mass concentrations is recommended for exposure assessment of nanoparticles. Efforts to reduce measurement error will also improve the ability to find associations in these studies.

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REFERENCES


