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Comparison of two estimation methods for surface area concentration using number concentration and mass concentration of combustion-related ultrafine particles

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ABSTRACT

Recent research has suggested that the adverse health effects caused by nanoparticles are associated with their surface area (SA) concentrations. In this study, SA was estimated in two ways using number and mass concentrations and compared with SA (SA_{meas}) measured using a diffusion charger (DC). Aerosol measurements were made twice: once starting in October 2002 and again starting in December 2002 in Mysore, India in residences that used kerosene or liquefied petroleum gas (LPG) for cooking. Mass, number, and SA concentrations and size distributions by number were measured in each residence. The first estimation method (SA_{PSD}) used the size distribution by number to estimate SA. The second method (SA_{INV}) used a simple inversion scheme that incorporated number and mass concentrations while assuming a lognormal size distribution with a known geometrical standard deviation. SA_{PSD} was, on average, 2.4 times greater (range = 1.6–3.4) than SA_{meas} while SA_{INV} was, on average, 6.0 times greater (range = 4.6–7.7) than SA_{meas}. The logarithms of SA_{PSD} and SA_{INV} were found to be statistically significant predictors of the logarithm of SA_{meas}. The study showed that particle number and mass concentration measurements can be used to estimate SA with a correction factor that ranges between 2 and 6.

1. Introduction

Ultrafine particles are defined as particles smaller than 100 nm in diameter. As these particles have a larger surface area (SA) per unit mass and also more atoms on their surface than fine or coarse particles (Welland and Porter, 2005), they may have increased surface reactivity in technical applications and biological activity in the human body. Since the hypothesis of a possible causal relationship between adverse health effects and exposure to ultrafine particles was first proposed, many papers have been published to support this assertion (Schwartz et al., 1996; Fairley, 1999; Wichmann et al., 2000; Oberdörster and Utell, 2002).

Traditionally, mass concentration has been regarded as most appropriately associated with ill health for particle exposure assessment. As the adverse health effects of ultrafine particles have been investigated, researchers have questioned the appropriateness of mass concentration measurements for ultrafine particles' exposure (e.g., Kent et al., 2001; McCawley et al., 2001). Exposure assessment using mass concentration may not reflect the toxicity of ultrafine particles because these particles do not contribute much to total mass concentration even when they dominate the particle number concentration. Therefore, alternative exposure metrics for the ultrafine and fine particles have been proposed. McCawley et al. (2001) showed that particle number concentration was a more appropriate metric for chronic beryllium disease and found no correlation between mass and number concentration. Peters et al. (1997) found that a decrease in peak expiratory flow among twenty-seven non-smoking asthmatics was more associated with number concentration than mass.

SA concentration has been proposed as biologically more relevant to the effective dose than other exposure metrics because the adverse health effects of ultrafine particles may be associated with surface reactivity and the portion of the size distribution that contributes most to SA does not contribute much to the mass concentration (Li et al., 1996; Oberdörster, 2000; Tran et al., 2000). Several toxicological studies have shown that inflammatory responses in the lung caused by ultrafine and fine particles (Tran et al., 2000; Brown et al., 2001) and translocation to the lymph nodes (Tran et al., 2000) were proportional to SA deposited regardless of particle composition, size, or shape. Driscoll (1996) demonstrated that overload tumors were best correlated with SA, and not number or mass concentration.

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Only a few devices to measure SA concentrations directly are available commercially. The first device developed for SA measurement was the epiphaniometer, which can measure active SA. However, it is not suitable for workplaces because it has a radioactive source (Maynard, 2003). TSI Inc. (Shoreview, MN) developed a portable nanoparticle SA monitor suitable for workplaces that measures the SA of particles likely to be deposited in the tracheobronchial or alveolar regions of the respiratory system rather than total aerosol SA (Fissan et al., 2006). The LQ1-DC diffusion charger (Matter Engineering, Switzerland) consists of an aerosol diffusion charger and an electrometer to measure the attachment rate of unipolar ions to particles that in turn is directly related to active SA. The portable diffusion charger (DC) also can be utilized in occupational settings. While the SA of monodisperse particles which were smaller than 100 nm was comparable to the geometric SA, it underestimated SA for particles larger than 100 nm in diameter (Ku and Maynard, 2005).

Alternative methods can be used to estimate SA based on particle size distribution statistics. Woo et al. (2001) tried estimating aerosol SA concentrations with two methods based on indirect size distribution modeling using measurements of number, charge, and mass concentration and direct aerosol size distribution measurement by an SMPS (Scanning Mobility Particle Sizer) and an LPS (laser particle sizer). The authors obtained optimal values for three parameters defining a lognormal size distribution by minimizing the difference between measured signals and expected values. They then calculated the total SA concentration by integrating the lognormal size distribution function. The estimated total SA concentration was compared with SA concentrations obtained from the SMPS–LPS system. The calculated SA concentration from the parametric measurements was higher by a factor of 2 than the SA obtained from the particle size distribution measurement, although there was a high degree of correlation between them ($R^2 = 0.91$). However, the devices used for measurement in that study are not widely and easily used in occupational and ambient environments for exposure assessment.

Maynard (2003) developed an SA estimation method using mass and number concentration measurements by assuming a lognormal particle size distribution with a specific geometric standard deviation (GSD). When compared to actual SA concentrations determined by integrating known size distributions obtained from published papers (McCawley et al., 2001; Zimmer and Maynard, 2002), SA concentrations estimated using his algorithm were between 0.95 and 1.45 times the actual values for a unimodal size distribution when the GSD value was set equal to 1.8 and were between 1.66 and 3.06 times actual concentrations for a bimodal size distribution using GSD = 1.8 for both modes of the size distribution. However, Maynard's estimates correlated well with the measurements ($R^2 = 0.98$). This study provided a positive prospect for estimating SA concentration based solely on measurements routinely made in occupational health.

In this paper, two estimation methods are described and applied to estimate SA concentrations based only on number and mass measurements, and using only devices easily available in the field. These estimates are compared with SA concentrations measured directly. The objective of this study is to determine if estimated SA concentrations can be used to predict the actual SA concentrations measured with a direct-reading instrument.

2. Methods

2.1. Study design

This work is part of a larger study dealing with women's exposure to particulate matter in India reported in Andresen et al. (2005). Cooking is primarily a woman's role in India and cooking heaters are considered one of the major ultrafine particle sources in Indian homes. Therefore, exposure measurements were performed in Mysore, India in residential homes that used kerosene or liquefied petroleum gas (LPG) as cooking fuels. Sampling was conducted in kitchens twice: once starting in October 2002 and again beginning in December 2002. In the first period, the assessments were conducted in seven homes (three kerosene, four LPG). In the second period, assessments were conducted in ten homes (five kerosene, five LPG).

2.2. Instrumentation

Four real-time instruments for particle mass, number, and SA concentrations and size distribution by number and one gravimetric sampler for calibration of the real-time mass monitor were used simultaneously in each location. All devices were used as area samplers for 24 h and were placed near the combustion sources at table-top level.

The DustTrak (Model 8520, TSI, Shoreview, MN) with PM2.5 inlet was used for mass concentration. It measures scattered light which is a function of particle mass concentration, size distribution, and composition. The DustTrak measurements were calibrated to the average aerosol concentration from the gravimetric measurements. The gravimetric PM2.5 concentrations were obtained using a PM2.5 sampler (PEM™ Model 200, MSP Inc., Minneapolis, MN) that collected particles on Teflon filters by inertial impaction. Air pumps drew air through sampling inlets at 10 L min^{-1}. Filters were weighed before and after sampling using a microbalance with a sensitivity of 5 μg in a weighing room where the temperature and humidity were environmentally controlled. After sampling, filters were equilibrated in the weighing room and then reweighed. For each run, blank samples were weighed at the same time as the sampled filters. The detection limit was calculated as three times the standard deviation of the field blank weight gains divided by the sampled air volume. The DustTrak measurements were recalculated using a specific calibration factor for each measurement as follows:

$$\text{Calibration Factor} = \frac{24-\text{h average gravimetric concentration}}{24-\text{h time integrated DustTrak concentration}} \qquad (1)$$

Each DustTrak measurement was multiplied by this factor to estimate the true mass concentration. The gravimetric concentration and integrated DustTrak concentrations were highly correlated ($R^2 = 0.93$) and the mean calibration factor was 0.216 with a standard error of ±0.021.

The CPC 3007 (TSI, Shoreview, MN), a real-time single-particle counting instrument, was used for measuring number concentration of ultrafine particles by condensational growth and optical detection. The LQ1-DC (Matter Engineering, Switzerland) was used to measure the aerosol active SA. It measures the attachment rate of unipolar ions sticking to the surface of particles. The HHPC-6 (Hach Ultra, Grants Pass, OR) is an optical particle counter which has a laser beam and photodetector installed in it to simultaneously count and size particles into six channels via light scattering. It was used for size distribution by number. All real-time instrument data were organized into two-min averages.

The average relative humidity in sampling seasons I and II was 40% and 22% respectively, and not high enough to significantly affect the performance of the DustTrak (e.g., Ramachandran et al., 2003) or the CPC 3007 (TSI, Inc).