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Passive measurement of coarse particulate matter, $PM_{10–2.5}$

Darrin K. Ott, William Cyrs, Thomas M. Peters*

Department of Occupational and Environmental Health, The University of Iowa, 102 IREH, 100 Oakdale Campus, Iowa City, IA 52242, USA

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Abstract

This work developed a passive sampling method to measure ambient $PM_{10–2.5}$. The coefficient of variation (CV) of $PM_{10–2.5}$ measured with collocated passive samplers was 20.1% in laboratory tests and 11.6% in field tests. $PM_{10–2.5}$ measured passively deviated from that measured with a filter-based dichotomous sampler by 29% in field tests. The strong correlation between $PM_{10–2.5}$ derived passively with the dichotomous sampler ($r = 0.97$) suggests that the bias observed in field tests was systematic and may be empirically corrected. The limit of detection of the method was determined to be 2.3 $\mu g\,m^{-3}$ for a 5-day sample. A bootstrap analysis suggests that at least 300 particles should be imaged to stabilize the analytical variability of the method. Repeated analysis suggests that the CV for the analytical method is 5%. This method offers an inexpensive means to assess $PM_{10–2.5}$ that may be incorporated into compliance networks or epidemiological studies.

Keywords: Passive sampling; Coarse particulate matter; $PM_{10–2.5}$; Aerosol

1. Introduction

Exposure to ambient coarse particulate matter, $PM_{10–2.5}$, has been associated with adverse respiratory (Chen et al., 2004; Fung, Khan, Krewski, & Chen, 2006; Lin, Chen, Burnett, Villeneuve, & Krewski, 2002) and cardiovascular health effects (Burnett, Brook, Yung, Dales, & Krewski, 1997; Lipsett, Tsai, Roger, Woo, & Ostro, 2006). In general, however, these associations are weaker than those for fine particulate matter, $PM_{2.5}$ (Brunekreef & Forsberg, 2005; Schwarze et al., 2006). Although coarse particles are known to be more spatially heterogeneous than fine particles (Monn, 2001; Wilson & Suh, 1997), epidemiological studies usually rely on exposure data from compliance networks of filter-based samplers that have limited spatial resolution (Wilson, Kingham, Pearce, & Sturman, 2005). Consequently, weaker associations between adverse health effects and exposure to $PM_{10–2.5}$ may be attenuation of statistical power from inadequate exposure assessment rather than a true lack of effect (Jerrett et al., 2005).

Passive sampling is an inexpensive means to measure particulate matter in many locations and thus offers a way to bolster exposure assessment (Brown, Wake, Thorpe, Hemingway, & Roff, 1994; Noll, Fang, & Watkins, 1988; Vinzents, 1996; Wagner & Leith, 2001a; Yamamoto et al., 2006). Wagner and Leith (2001a) presented a method where particle number concentration by size is estimated from the surface loading of particles collected onto a substrate over time and knowledge of the flux, or rate of transfer, of these particles to the sampler. In their method, surface loading is

* Corresponding author. Tel.: +1 319 335 4436.
E-mail address: thomas-m-peters@uiowa.edu (T.M. Peters).

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determined by counting and sizing particles that have deposited on the substrate, typically with an electron microscope, and flux is estimated from a semi-empirical model that is a function of the aerodynamic diameter of a particle, d_a. The number concentration by size data may then be converted into mass concentration by size and summed to estimate atmospheric PM.

Following Wagner and Leith (2001a), d_a may be calculated from the projected area diameter of a particle, d_{pa}, derived from microscopic analysis as

$$d_a = d_{pa}/S_V[\rho_p/(S_D\rho_0)]^{1/2}, \tag{1}$$

where S_V is the volumetric shape factor, ρ_p is the particle density, S_D is the aerodynamic shape factor, and ρ_0 is unit density ($1\,g\,cm^{-3}$). The mass of a particle, m, may be estimated as

$$m = (\pi/6)\rho_p[d_{pa}/S_V]^3. \tag{2}$$

Although important to accurately estimate each of the parameters in Eqs. (1) and (2), Wagner and Leith showed that ρ_p and S_D have relatively minor influence on particle mass concentration compared to S_V. Whereas a 10% error in the estimate of ρ_p or S_D results in a 5% error in calculated mass, the same error in the estimation of S_V translates into a 21% error in calculated mass.

Researchers have assumed mean values for density, volumetric shape factor, and dynamic shape factor when estimating ambient mass concentration from microscopic data. Wagner and Macher (2003) assumed a mean value of $2.0\,g\,cm^{-3}$ for ρ_p because particles are made up of a combination of crustal materials and less dense man-made or natural organic material. Assigning a mean value for S_V and S_D for ambient particles is more difficult. Davies' (1979) work is often cited to justify a mean value of 1.4 for S_D for ambient particles, although this value appears to be the average of the specific dusts studied—quartz, sand, talc, anthracite coal, and bituminous coal. Alternatively, Wagner and Leith (2001a) and Davies (1979) suggested selecting from a list of d_a/d_{pa} ratios for eight dusts, including $d_a/d_{pa} = 1.0$ for sand if S_D is unknown. Noll et al. (1988) identified values of S_V for coarse particles ($> 1\,\mu m$) ranging from 1.35 to 3.15 in 34 atmospheric samples. More recent studies have used shape information from scanning electron microscopy (SEM) to derive shape factors (Franck & Herbarth, 2002; Pratesi, Zoppi, Vaiani, & Calastrini, 2007). Pratesi et al. (2007) found substantial heterogeneity in the shape of coarse particles.

This work presents a revised method to estimate ambient $PM_{10-2.5}$ from samples collected with the passive sampler of Wagner and Leith (2001a). This method uses low-cost method light microscopy combined with digital imagery to determine particle surface loading by size. Particle mass concentration is then estimated from surface loading with an assumed ρ_p and S_D but with S_V derived from microscopy. In this way, the most sensitive parameter in calculating mass concentration from microscopic data, S_V, is based on individual characteristics of each particle. Laboratory and field tests were conducted to evaluate the precision and accuracy of this method. The limit of detection (LOD) of the method was derived through analysis of blank samples. The precision of the analytical portion of the method was derived through a bootstrap analysis and a repeated measures analysis.

2. Methods and materials

2.1. Passive sampler operation

As shown in Fig. 1, the passive samplers used in this work were identical to those described by Wagner and Leith (2001a) with the following exceptions. A 12-mm-diameter cover glass (Catalog #12-545-80, Fisher Scientific, Pittsburgh, PA) was used as the collection substrate. The mesh cap was increased in diameter from 15 to 18 mm to accommodate two retaining screws that held the cap to an aluminum SEM sample mount. Prior to assembly, the mesh cap and SEM mount were inspected visually and cleaned with compressed air.

Each substrate was cleaned by gently rubbing the cover glass with several layers of antistatic laboratory wipes (Model #34155, Kimberly Clark, Dallas, TX) placed between the index finger and thumb. It was then inspected under a microscope to ensure that the sample surface was free from shards of glass. The substrate was held within 1 cm above a polonium-210 strip (Catalog #1U200, Amstat Industries, Glenview, IL) to neutralize any static charge. The substrate was placed into the mesh cap, which was inverted to receive it. A circle was drawn on the substrate with a permanent

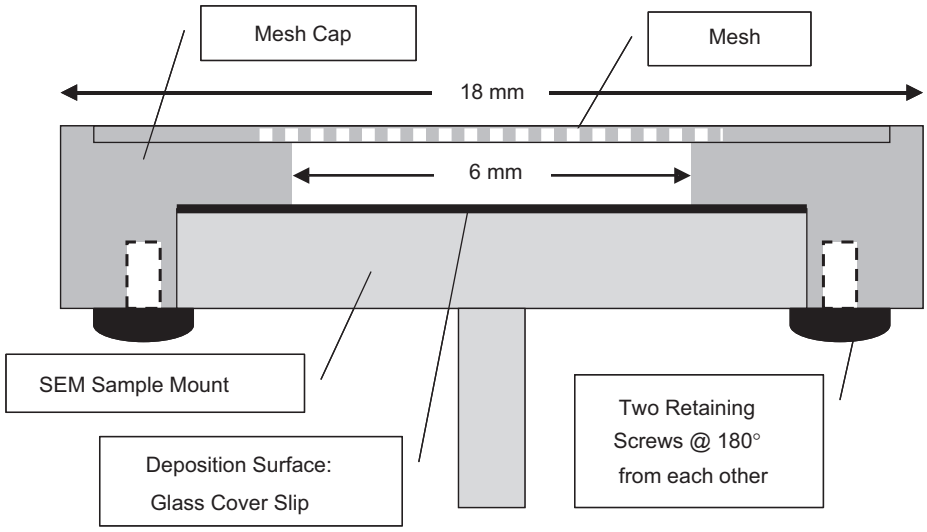

Fig. 1. Modified Wagner–Leith passive sampler.

marker to delineate the boundary of the area open to sampling. The SEM mount was placed on the substrate and secured to the mesh cap with the retaining screws.

The sampler remained covered with tape tabs (Arrow Flags, 3M, St. Paul, MN) until put into use. Sample collection was started by removing the tape tab and ended by re-covering the passive sampler with a clean tape tab. The sample was prepared for analysis in a clean, designated area of the laboratory by removal of the mesh cap and placement of the SEM mount in a holder. The cover glass was marked with a focusing dot just outside of the circle drawn to delineate the boundary of the sample area. This dot facilitated focus of the microscope on the plane of particle deposition. With forceps, the substrate was inverted and placed face down on the center of a clean microscope slide that had been cleaned in the same manner as the substrate described above. The substrate was then held in place on the slide with two pieces of tape. Care was taken to ensure that the tape did not cover the marked circle or the focusing dot.

2.2. Sample analysis

Digital images of the particles on the cover glass were captured at 100X magnification (10X objective lens) with a light microscope (Leica DMLSP, Leica Microsystems, Wetzlar, Germany) equipped with a digital camera (Leica DFC 280, Leica Microsystems, Wetzlar, Germany). A stage micrometer was used to determine that the pixel resolution of digital images was 0.524 μm per pixel. Thus, the smallest particles included in the analysis for $PM_{10–2.5}$ contained at least 18 pixels (area = 4.93 μm^2 and diameter = 2.51 μm). The size of each image was 1064 × 1280 pixels.

For each sample, an average of 40 images was taken systematically over about 70% of the total surface area available for deposition. These images were placed into a common computer folder, and particles were counted and sized automatically within ImageJ (NIH, Bethesda, MD) using a custom macro. This macro converted raw images to a binary image (black indicating a particle and white being the background) using autothresholding and a "fill holes" command to blacken any internal white pixels in the interior of a particle. The macro outputted a list of projected area, image coordinates, and circularity for each particle detected in the images.

This imaging process was validated by sizing borosilicate glass microspheres (Catalog #9005, Duke Scientific, Fremont, CA) with a 5-μm physical diameter certified to NIST traceable standards. Adjustments were made to the microscope and camera setup to ensure that the diameters of particles measured with this automated counting and sizing procedure were within 5% of the certified diameter before samples were analyzed. Image edge effects were neglected because the area of the image was very large compared to the size of the particles of interest.

2.3. Computation of mass concentration

Following Wagner and Leith (2001a), deposition velocity, V_{dep}, was estimated for each particle, i, as

$$V_{dep,i} = V_{ambient,i}\gamma_{mesh,i}, \tag{3}$$

where $V_{ambient}$ is the particle settling velocity and γ_{mesh} is an empirical modifier to account for the presence of the mesh cap. $V_{ambient}$ and γ_{mesh} were calculated as

$$V_{ambient} = \tau g \quad \text{and} \tag{4}$$

$$\gamma_{mesh} = 0.00595(d_a \tau g/\nu)^{-0.439}, \tag{5}$$

where τ is the relaxation time of the particle, g is the gravitational constant, and ν is the kinematic viscosity of air. The relaxation time, τ, was calculated as

$$\tau = (\rho_p d_a^2)/(18\eta), \tag{6}$$

where η is the dynamic viscosity of air. A Cunningham slip correction factor was not included in the calculation of τ due to its minor influence on the calculation for particles of the coarse size range. Particle aerodynamic diameter, d_a, was assumed equal to the projected area diameter, d_{pa}, obtained from microscopy to eliminate the need to estimate the aerodynamic shape factor, S_D. This assumption is supported by Davies' (1979) work that showed that d_a/d_{pa} was equal to one for sand and near one for most other coarse mineral dusts (Wagner & Macher, 2003). It is also supported by the fact that S_D has a relatively minor influence on mass calculation (Wagner & Leith, 2001a).

The mass of a single particle, m_i, was then calculated using Eq. (2). The known particle density of test dust ($\rho_p = 2.65\,g\,cm^{-3}$) was used for laboratory tests. For field tests, particle density was assumed to be $2.0\,g\,cm^{-3}$ following Wagner and Macher (2003). Volumetric shape factor, S_V, was determined for each particle from particle circularity, C_p, output by ImageJ as

$$S_{V,i} = 1/C_{p,i} = 1/[4\pi(A_i/P_i^2)], \tag{7}$$

where P is the perimeter and A is the projected area of the particle. A circularity of unity indicates that the particle is a perfect circle, while circularity progressively decreases from unity the more irregularly shaped a particle appears.

The contribution of a single particle to mass concentration, C, was calculated as

$$C_i = \frac{F_i}{V_{dep,i}} = \left(\frac{m_i}{A_T t}\right)\frac{1}{V_{dep,i}}, \tag{8}$$

where F is the mass flux of the particle to the deposition surface, A_T is the total area of the sample that was imaged (A_T is the number of images times the area of one image), and t is the sample time. $PM_{10-2.5}$ was calculated as

$$PM_{10-2.5} = \sum_{i=1}^{n} C_i E_i \quad (\text{if } d_{a,i} > 2.5\,\mu m), \tag{9}$$

where E is the PM_{10} curve as defined by Hinds (1999):

$$\begin{aligned} E_i &= 0.9585 - 0.00408 d_{a,i}^2 \quad \text{for } d_{a,i} < 15\mu m \\ E_i &= 0 \qquad\qquad\qquad\quad \text{for } d_{a,i} > 15\mu m, \end{aligned} \tag{10}$$

and $d_{a,i}$ is in μm.

Alternatively for field tests, ambient particle mass concentration was computed using the method presented Wagner and Macher (2003). This method used a constant dynamic shape factor, $S_D = 1.41$, and a constant volumetric shape factor, $S_V = 1.61$.

2.4. Laboratory tests

Laboratory tests were conducted in a straight, 20-m-long wind tunnel with a square cross-sectional test section (61 cm × 61 cm). Test dust (primarily road dust, $\rho_p = 2.65\,g\,cm^{-3}$, ISO 12103-1, A3 Medium, Powder Technology,

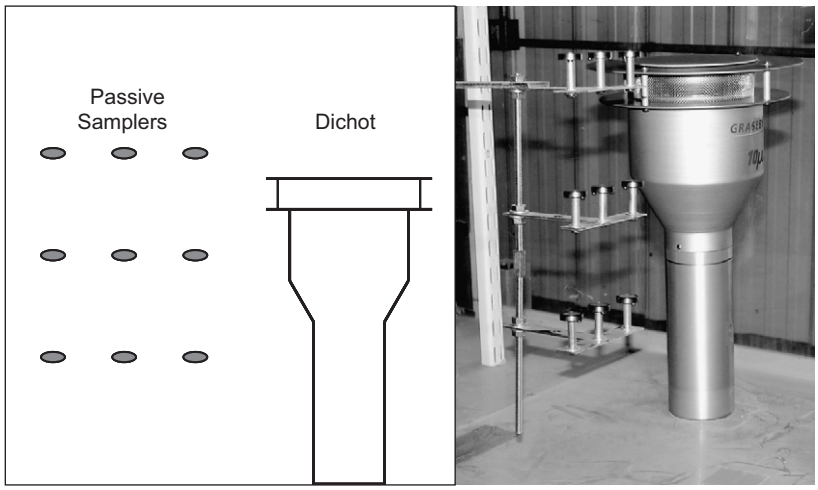

Fig. 2. Cross-section of wind tunnel showing position of passive samplers and dichotomous sampler.

Inc., Burnsville, MN) was injected into the tunnel 13 m upstream of the test section with a Venturi nozzle (Vaccon, Medfield, MA). A panel that blocked the center two-thirds of the tunnel was positioned 1 m downstream of the dust injection port to force mixing. A perforated sheet (McMaster-Carr, Atlanta, GA) 4 m further downstream of the mixing panel provided a uniform air flow in the test section. Samplers were placed in the test section 5 m downstream of the laminar-flow panel. The air flow velocity in the center of the test section was set to 2 km h^{-1} using a thermal anemometer (Velocicalc 8347, TSI, Incorporated, Shoreview, MN). This wind speed is the lowest wind speed of three required for performance tests of PM_{10} samplers (USEPA, 40 CFR Part 53.42). Wind velocity was measured to be uniform in the test section at nine points equally spaced across the face of the test section.

Nine passive samplers were placed in a 3 × 3 vertical grid centered in one-half of the test section and oriented perpendicular to the air flow (Fig. 2). The samplers were separated from each other by 4 cm horizontally and 10 cm vertically. The inlet of a dichotomous sampler (Model SA241CUM, Graseby-Andersen, Fulton, GA) was centered in the other half of the test section.

Three tests of 90 min each were conducted at a target mass concentration of 6 mg m^{-3}. This test is equivalent to five days of sampling 70 μg m^{-3}, the mass concentration proposed as the 24-h air quality standard for $PM_{10-2.5}$ (USEPA, 2006). Thirty-seven-millimeter PTFE filters (Part #R2PJ037, Gelman Sciences, Ann Arbor, MI) were used to collect coarse and fine particulate in the dichotomous sampler. Using a volumetric flow meter (TriCal, BGI, Inc., Waltham, MA), the coarse and fine air flows of the dichotomous sampler were set before and verified after each run to be within 5% of their design values (coarse flow = 1.67 Lpm and fine flow = 15.0 Lpm). These filters were analyzed gravimetrically with a micro-balance (Model # MT5, Mettler-Toledo, Columbus, OH). The coarse mass concentration was adjusted for fine particle contamination in the calculation (Poor et al., 2002). All filters were equilibrated in a relative humidity (40 ± 10%) and temperature (20 ± 3 °C) controlled weigh room for 24 h prior to pre- and post-run weighing.

Three blank passive samplers and a blank filter were transported and analyzed for each test. Passive sampler blanks were treated exactly as samples with the exception that the tape tab was removed and immediately replaced. Airborne mass concentration from blank passive samplers was subtracted from the corresponding samples. This subtraction accounted for 0.3% of the total mass on average.

2.5. Field tests

Eight 7-day field trials were conducted at three sites in Iowa City, IA. In each trial, three passive samplers were collocated with a dichotomous sampler and meteorological equipment that recorded temperature, relative humidity, and wind speed (Weather Transmitter WXT510, Vaisala, Helsinki, Finland). Each passive sampler was placed in its own shelter to isolate it from wind turbulence and precipitation. The development and testing of this shelter are provided in a companion paper (Ott & Peters, submitted for publication). All samplers were placed within 6 m from each other. The

dichotomous sampler was operated as described in the laboratory tests. Three blank passive samplers and one blank filter were taken into the field for each of the five trials.

2.6. Statistical analysis

Precision was expressed as the coefficient of variation (CV), also referred to as relative precision by the USEPA, of $PM_{10-2.5}$ measured by three collocated passive samplers. As prescribed by the USEPA, CV was calculated as the sample standard deviation divided by the sample mean times 100%. CV across sites or tests was determined by taking the square root of the squared CV sets, which the USEPA refers to as the root mean square (rms). Accuracy was calculated as the difference between the mean $PM_{10-2.5}$ measured with the passive sampler and that measured with the dichotomous sampler expressed as a percentage of the dichotomous sampler.

For laboratory tests, ANOVA was performed to test the hypothesis that the mean $PM_{10-2.5}$ measured at each of the nine passive sampler locations were equal. For field tests, a linear regression was performed with $PM_{10-2.5}$ measured with the passive samplers as the dependent variable and that measured with the dichotomous sampler as the independent variable. The slope, intercept, and Pearson correlation coefficient from this regression were compared to the criteria established by the USEPA for acceptable performance of equivalent methods for $PM_{10-2.5}$ samplers (USEPA, 40 CFR Part 53.35). Statistical analyses were carried out in SAS (SAS Institute Inc., Cary, NC) and Microsoft Excel (Microsoft Corp., Redmond, WA).

2.7. Uncertainty analysis

The blanks from both field and laboratory tests were used to calculate the LOD and limit of quantitation (LOQ). LOD may be defined as the threshold for asserting the presence of an analyte and calculated as three standard deviations of $PM_{10-2.5}$ measured for blanks (NIOSH, 1995). LOQ represents a theoretical threshold of acceptable precision and was calculated as 10 standard deviations of $PM_{10-2.5}$ measured for blanks. Since the blanks were not exposed, LOD and LOQ were expressed as if the blank had been exposed over a range of assumed sample times of one to seven days.

A bootstrap analysis was performed to determine the number of particles that should be counted to stabilize the analytical uncertainty. Analysis of the microscopy images from one of the passive samplers was performed following Hoozemans, van der Beek, Frings-Dresen, and van der Molen (2001). Airborne mass concentration was calculated for each image in the set ($n = 46$). A subset of a predetermined number of the images was then randomly chosen and averaged to obtain a new mass concentration estimate. This process was repeated for image subset sizes that ranged from 1 to 20 images. One thousand mass concentration estimates were generated randomly for each set size and a concentration was calculated for each set. The 95th and 5th percentile concentration values were determined for each image grouping and the difference was reported. These calculations were carried out in an Excel spreadsheet.

Repeated measurements of three passive samples randomly selected from the laboratory tests were conducted to estimate uncertainty microscopic analysis and image analysis portion of the method. Each sample was imaged and analyzed three times. The CV was calculated for each sample.

2.8. Estimation of volumetric shape factor

For laboratory and field tests, Eq. (7) was used to estimate mean S_V by particle size. Mean and standard deviation of S_V were also calculated for each run.

3. Results

3.1. Laboratory tests

In laboratory tests, the precision of $PM_{10-2.5}$ measured with the passive samplers was 20.1% ($n = 27$), while that of the dichotomous sampler was 7% ($n = 3$). The accuracy of the passive sampler was −16% relative to the dichotomous sampler.

Fig. 3 summarizes $PM_{10-2.5}$ measured by each passive sampler compared to that measured by the dichotomous sampler. Physical location in the wind tunnel affected both the mean and the variation of $PM_{10-2.5}$ measured with the

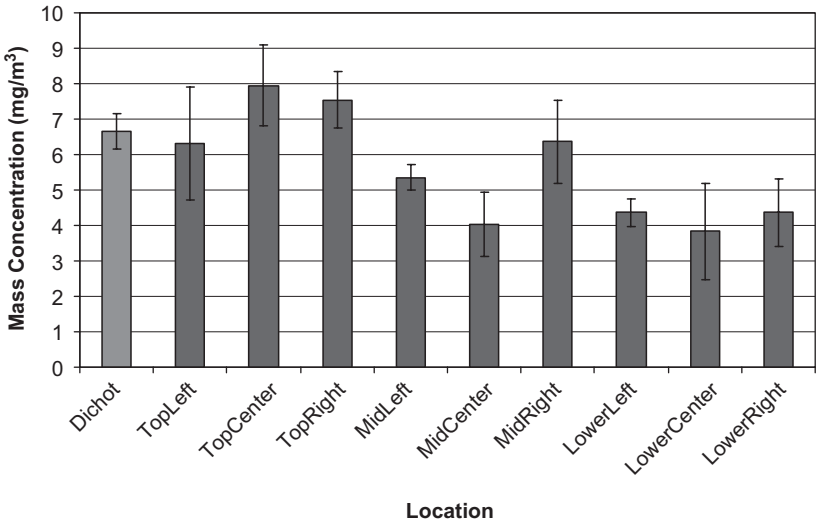

Fig. 3. $PM_{10–2.5}$ measured at each passive sampler location ($n = 3$); error bars indicate one standard deviation.

Table 1
Summary of field test results

Test #	$PM_{10–2.5}$ dichot ($\mu g\,m^{-3}$)	$PM_{10–2.5}$ passive sampler ($\mu g\,m^{-3}$)	Passive/dichot ratio	Passive CV (%)	Wagner method passive/dichot ratio
1	21.2	29.4	1.39	3.8	1.08
2	13.9	17.7	1.27	7.3	0.84
3	12.8	14.2	1.11	19.9	0.70
4	13.4	16.8	1.25	7.2	0.82
5	3.7	4.4	1.18	9.4	0.72
6	20.9	29.8	1.43	4.1	1.07
7	12.5	19.5	1.56	3.9	1.14
8	13.4	14.9	1.11	20.8	0.89
Mean	13.98	18.33	1.29	9.5	0.91
St. dev.	5.48	8.29	0.16	6.98	0.17

passive samplers. ANOVA confirmed that the nine positions had different mean values ($p = 0.0007$). The CV for a given location varied from 6.8% to 35.2%.

3.2. Field tests

Table 1 provides a summary of the eight field tests. The CV of $PM_{10–2.5}$ measured with the passive samplers during each test ($n = 3$) ranged from 3.8% to 20.8% with six of the eight values less than 10%. The rms CV was 11.6%. The mean $PM_{10–2.5}$ measured with the passive samplers, $18.3 \pm 8.3\,\mu g\,m^{-3}$, was greater than that measured with the dichotomous sampler, $14.0 \pm 5.5\,\mu g\,m^{-3}$. Also reported in the last column of Table 1 is the comparison of the passive samplers to the dichot if Wagner and Macher's original assumptions for ambient PM are used. The mean passive result was $13.2 \pm 6.7\,\mu g\,m^{-3}$ calculated by that method.

The linear regression of $PM_{10–2.5}$ measured with the passive samplers on the dichotomous sampler is reported in Table 2. The resulting slope was 1.47 and the intercept was −2.2 and the Pearson correlation coefficient, r, was 0.97. This slope was statistically different from zero ($p = 0.05$) and the intercept was not statistically different from zero ($p = 0.05$). The results with Wagner's original assumptions in the calculations were also included in a regression analysis with the dichot as reported in Table 2; r was 0.96.

Table 2
Regression analysis summary

Parameter	Estimate	Std. error	*p*-Value
Study model			
Intercept	−2.22	2.20	0.352
Slope	1.47	0.15	<0.0001
$r^2 = 0.943$			
Model with Wagner's original assumptions			
Intercept	−3.17	2.11	0.18
Slope	1.17	0.14	0.0002
$r^2 = 0.919$			

Table 3
Particle count summary

	Blanks	Laboratory tests	Field tests
Mean particle count per sample (st. dev.)	33.8 (22.7)	1323 (408)	393 (168)

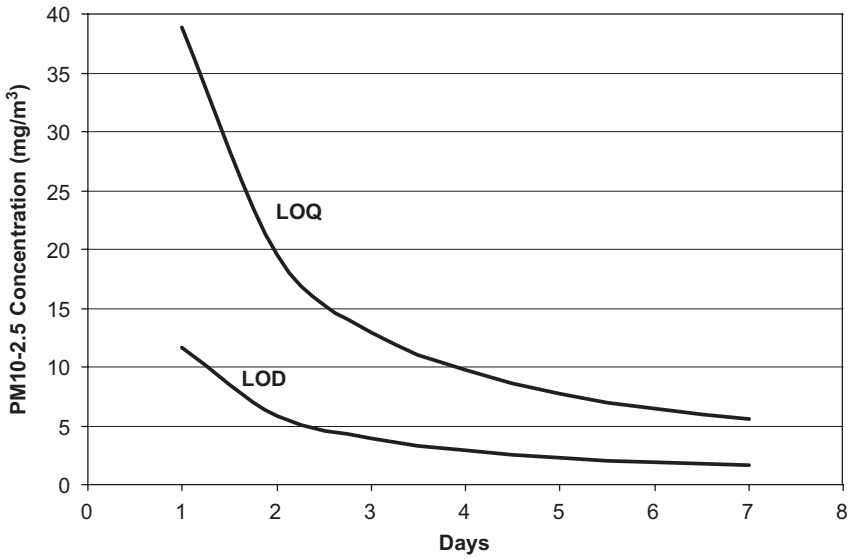

Fig. 4. LOQ and LOD calculated for different sampling durations.

3.3. Uncertainty analysis

A total of 18 blank passive samplers from laboratory and field tests were analyzed. As shown in Table 3, the particle counts on the blanks 34(0.84 particles image^{-1}) were substantially less than those in samples collected in laboratory or field tests.

If these particle counts were collected during a 1-day sample, they would translate to a mean $PM_{10–2.5}$ of 5.7 μg m^{-3} with a standard deviation of 3.9 μg m^{-3}. The 95% confidence limits on the mean were 3.9–7.5 μg m^{-3}. The LOD was 12 μg m^{-3} and the LOQ was 39 μg m^{-3}. To adjust these values to different sample periods in days, one simply divides by the number of days as shown in Fig. 4.

Fig. 5 presents the 95th–5th percentile $PM_{10–2.5}$ range as a function of the number of images in each set of the bootstrap analysis. A smaller value of 95th–5th percentile range indicates that there is less uncertainty in the results.

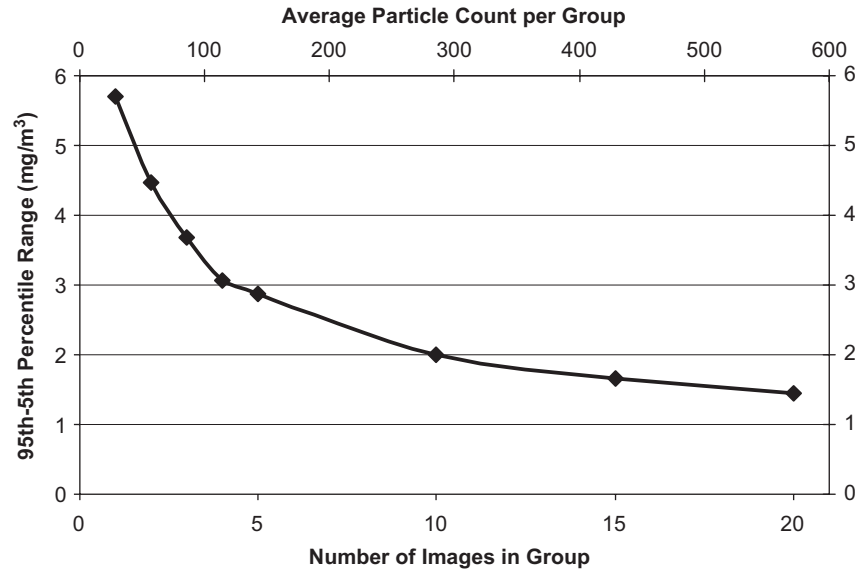

Fig. 5. Bootstrap analysis results.

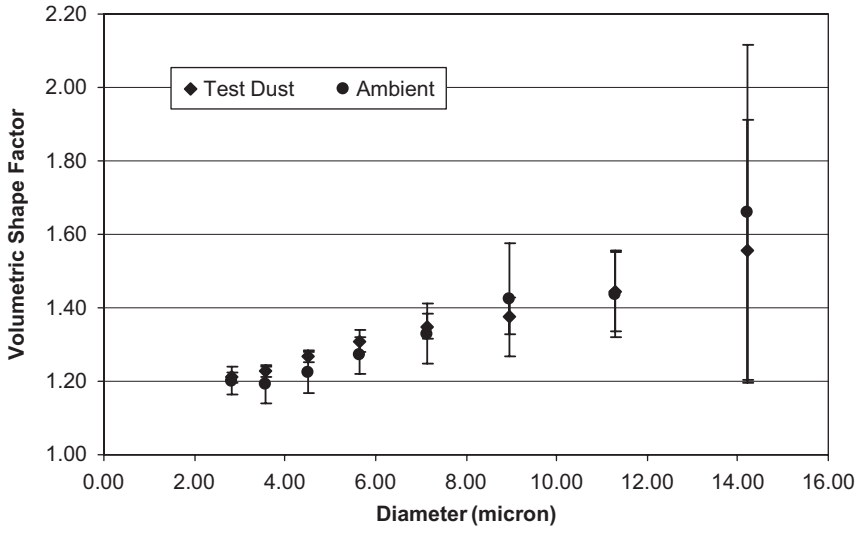

Fig. 6. Mean volumetric shape factor; error bars indicate one standard deviation.

The associated particle counts with the number of images in each image set are reported as a secondary x-axis. The laboratory sample used for this analysis had a mean of 25 particles per image and a calculated concentration with the original 46 pictures of 4.56 $\mu g\, m^{-3}$. The initial sharp slope leveled off at around 10 images which translates to about 300 particles counted.

In the repeated imaging analysis, the CV of each of the three samples that were repeatedly analyzed three times was 5.5%, 6.4%, and 2.1%. The rms of these CVs was 5.0%.

3.4. Estimation of volumetric shape factor

Fig. 6 shows S_V by diameter for the ambient particles and the test dust used in the wind tunnel. A general trend of increasing S_V as diameter increases is evident. Also notable is that there is greater variability in the volumetric shape factor of the field samples than in the laboratory samples.

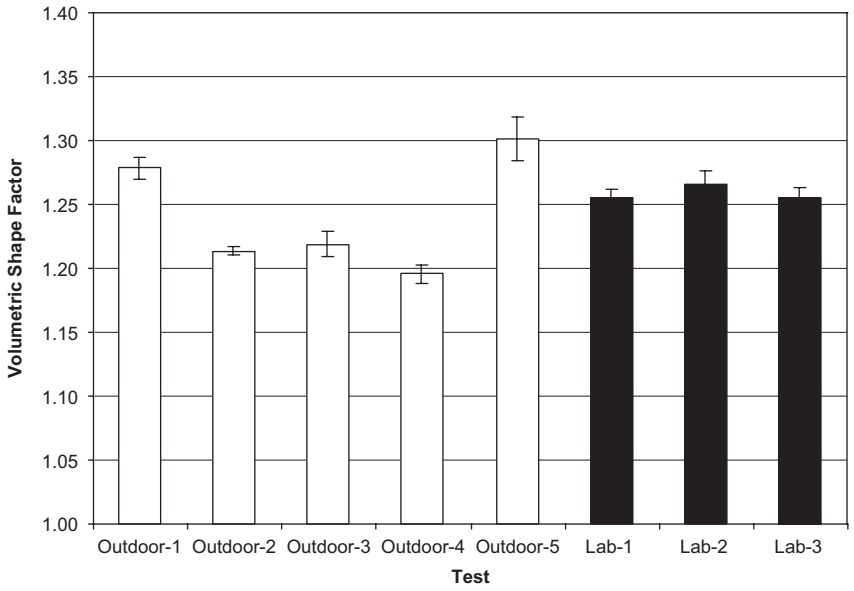

Fig. 7. Volumetric shape factor by run; error bars indicate one standard deviation.

Table 4
Comparison of field measurements to EPA acceptance criteria for federal equivalent methods

	Field tests	Calculated with Wagner method	EPA acceptance criteria
Slope of regression	1.47	1.17	1 ± 0.12
Intercept of regression	−2.2	−3.2	−7 to 7
r^2	0.94	0.92	–
Pearson correlation coefficient, r	0.971	0.958	0.946
Precision (rms CV) (%)	11.6	13.5	15

Fig. 7 shows the difference in S_V of the individual run results of the field study for five of the sites and the laboratory tests. The runs with the test dust in the lab are consistent as expected, while the ambient particles appear to have had changes in shape characteristics over the different runs.

4. Discussion

This work presents an inexpensive method to passively measure ambient $PM_{10–2.5}$. This method includes systematic imaging of most of the deposition surface to increase particle counts, and automated sizing and counting to reduce analysis time. It also relies on a simplified data reduction scheme compared to that proposed by Wagner and Leith (2001a). First, the aerodynamic diameter was assumed to be equal to the diameter of the projected area of the particle from imaging, $d_a = d_{pa}$, to eliminate the need to estimate dynamic shape factor, S_D. Second, the use of a new shelter eliminated the need to estimate the friction velocity, u^*, in the Wagner and Leith (2001a) deposition velocity model. This term accounts for turbulent inertial deposition and is unnecessary with the shelter described in a companion paper to this work (Ott & Peters, submitted for publication). Lastly, the volumetric shape factor, S_V, was estimated for each particle from circularity output by ImageJ. Thus, microscopic information was leveraged to estimate the most sensitive parameter, S_V, in the estimation of particle mass concentration, and mean values were assumed for the least sensitive parameters, S_D and ρ_p.

$PM_{10–2.5}$ measured with the revised passive sampling method had favorable precision within runs (Table 1) and when compared to the dichotomous sampler (Table 4). Precision of $PM_{10–2.5}$ measured with the passive sampler (11.6%) compared adequately with the USEPA acceptance criterion (15%) for field performance of federal equivalent methods

(FEMs) (40 CFR Part 53). It was slightly better than the CV for the dichotomous sampler (13.5%). The somewhat worse precision identified in laboratory tests (20%) was attributed to spatial heterogeneity of particles in the test section of the wind tunnel. Thus, precision measured in the field tests is probably a better estimate of method precision than that measured in the laboratory.

Previous researchers reported a CV of 32.2% for PM_{10} in wind tunnel studies (Wagner & Leith, 2001b). The improved precision reported here is attributed to sizing more particles per sample. Wagner and Leith analyzed fewer than 100 particles per sample, while over 1300 per sample were analyzed in the laboratory segment of this study. Such numerous counts are more practical to achieve with the automated particle counting and sizing used in this work.

$PM_{10-2.5}$ measured with the passive sampler was highly correlated with that measured with the dichotomous sampler ($r = 0.971$) and compares favorably with EPA's criterion for FEM samplers ($r > 0.946$). However, $PM_{10-2.5}$ measured with the passive sampler was biased positive (28.8%) with regard to the dichotomous sampler. This bias was reflected in the fact that the slope of the regression was 1.47, which is outside the tolerance set by USEPA's acceptance criterion for FEMs. The fact that $PM_{10-2.5}$ measured with the passive sampler correlated well with that measured with the reference sampler suggests that this bias is systematic. Such systematic bias may be attributed to the assumptions made in calculating mass concentration with the passive sampler, such as particle density or dynamic shape factor. Improved estimates for particle density may be obtained by analyzing passively collected samples by SEM with chemical speciation capability. Alternatively, seasonal and/or site correction factors could be developed and applied to adjust passive sampler data.

An important source of uncertainty in mass concentration estimates may be eliminated by deriving volumetric shape factor, S_V, from microscopy. Substantial variability in this parameter (Fig. 6) was observed within one site and one season. This variability is incorporated into mass concentration estimates when volumetric shape factors are derived from microscopy. Inclusion of this unique information is important because volumetric shape factor is the most sensitive parameter in converting count data from microscopy to particle mass concentration.

The uncertainty analysis provides a framework to optimize sampling time in context of sampling and analytical error. The blank analysis provides an estimate of LOD and LOQ that are important in determining the sample time required with regard to expected $PM_{10-2.5}$. Although a seven-day sample time was needed to collect a sufficient number of particles because of the low $PM_{10-2.5}$ in these field tests, shorter times would be acceptable for environments with greater $PM_{10-2.5}$. It does, however, seem unlikely that the methods here could be very effective for a broad exposure assessment using 24-h samples unless $PM_{10-2.5}$ greater than the method LOQ of about $40\,\mu g\,m^{-3}$ is expected. Further efforts to clean more thoroughly or identify less contaminated substrates are warranted. The bootstrap analysis suggests that 250–300 particles are needed to stabilize analytical uncertainty. Repeated analysis identified that imaging contributes about 5% error to the overall method. More complete scanning of the surface could improve this.

The trend of increasing volumetric shape factor with particle size (Fig. 7) may indicate a genuine difference in the particles or possibly be an artifact introduced in imaging. Smaller particles are represented by a smaller number of pixels and thus information regarding the shape can be lost. This issue may be investigated further by increasing magnification to better estimate the smaller particles. However, there are trade-offs to increasing magnification. For example, more images would have to be made to get a similar surface area analyzed and getting a sharp focus on the edge of larger particles could become difficult because of a shallow depth of field.

A limitation of this method is that some particles may not be counted because they are not visible in the optical microscope. While this issue may be important for occupational settings (e.g., oil mist in metalworking facilities or asbestos fibers in buildings), it is unlikely to have biased our measurements in this work because this type of aerosol is rare in atmospheric coarse mode aerosol. Moreover, our overestimate of mass concentration compared to filter-based measurements suggests that this issue was of minor importance.

In conclusion, this work presents a simplified method to passively measure ambient $PM_{10-2.5}$ with the Wagner–Leith passive sampler. This work provides data on method accuracy and precision needed to estimate statistical power in the design of epidemiological studies. The systematic imaging, automatic particle counting and sizing, and simplified data reduction scheme presented here provide measurements of ambient $PM_{10-2.5}$ comparable to those made with a dichotomous sampler. The passive sampler may now be used to characterize $PM_{10-2.5}$ in different settings, such as rural versus urban environments, with the caveat that seasonal and/or site-specific correction factors may improve the accuracy compared to filter-based samplers. Future work that aims to better identify values of and variability in these parameters in ambient settings would be valuable to determine the extent to which correction factors are needed.

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