

Abstract

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Precision of Measurements with the UNC Passive Aerosol Sampler

(Under the direction of David Leith)

The UNC passive aerosol sampler measures mass concentrations and size distributions of indoor, outdoor, and occupational particulate matter. This study assessed the precision of passive sampler measurements using data from duplicate pairs of samplers that were deployed in a large field study. Particle count and size data were used to calculate $PM_{2.5}$ and PM_{10} concentrations. To determine precision, the concentrations measured by duplicate samplers were compared to one another. Results showed that this sampler provides mass concentrations of $PM_{2.5}$ and PM_{10} in the field with relative standard deviations that approach about 15%, with greater precision associated with higher concentrations. Variability between measurements was associated with counting statistics and with differences in the open area of the passive sampler mesh screen.

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Chapter Overview

Chapter 1 presents the need to further investigate the precision of measurements made with the UNC passive aerosol sampler and introduces the objective of the work presented in subsequent chapters. Chapter 2 presents a technical note in its entirety that will be submitted to the *Journal of Aerosol Science*. Due to word count limitations of the journal, the technical note contains a shortened version of the methods and results. Therefore, further analysis of the results is presented in Chapter 3 and a detailed methods section is presented in Appendix A. Implications of this work can be found in Chapter 4. Comparison of the calculated mass concentrations with the RJ Lee Group concentrations is presented in Appendix C followed by an analysis on mesh cap variability in Appendix D.

Chapter I: Introduction

Background

By the end of the nineteenth century, the industrial revolution had brought vast economic growth and affluence to many cities in the U.S. While these industrial cities benefitted economically from the influx of laborers and factories and increased manufacturing, this growth caused hazy skies and pollution from increased coal burning and industrial processes, which added a new complexity to the burden of domestic coal use. Thus, the industrial revolution did not mark the birth of air pollution, but it brought the problem of particulate matter and its related health and environmental concerns to the attention of early environmentalists (Bachmann 2007).

Particulate matter (PM) is defined as solid particles or liquid droplets that can vary in size, shape, and composition. Particulates can be released into the air directly from stationary and mobile sources or can be formed in the atmosphere through gas phase reactions. The degree to which particulate matter is an environmental or health concern depends on its properties. For example, the size of a particle determines its uptake and deposition in the lungs, with larger particles impacting in the larger airways and smaller particles depositing deeper in the lungs (Hinds 1999). The location where particles collect in the lungs affects health consequences, and the composition of the deposited particles elicits different bodily responses.

Public interest in particulates has developed over time and was marked by notable events of extreme fog or haze both in the U.S. and Europe. In 1930, a temperature inversion resulted in a four-day air pollution episode in the Meuse Valley of Belgium that caused 60 deaths (Nemery et al. 2001). Donora, Pennsylvania was affected in 1948 by an inversion that

caused emissions from a sulfuric acid plant and local zinc and steel smelters to collect in the low level atmosphere. Twenty people died in the Donora incident, and approximately 6,000 people experienced respiratory problems caused by the accumulation of PM and SO_x in the fog (Bachmann 2007). The deadliest of all reported air pollution events was the Great London Smog of 1952, which killed approximately 4,000 people in a one-week period. The heavy fog that settled over the city led to an increase of 200-300% in mortality (Vardoulakis 2010).

Each subsequent event increased public concern and solidified the belief that air pollution affects health. Finally in 1971, the newly-formed United States Environmental Protection Agency (U.S. EPA) utilized results from British research and developed the first National Ambient Air Quality Standards (NAAQS) for PM and SO₂ to protect human health and the environment (Bachmann 2007). The original NAAQS for particulates regulated total suspended particles (TSP) by mass concentration. Eventually, the EPA classified particulate matter by size based on research indicating that particle size affects health. PM_{2.5} was defined as the mass concentration of particles having an aerodynamic diameter less than 2.5 μm and PM₁₀ as the mass concentration of particles having an aerodynamic diameter less than 10 μm.

Since these early studies of major pollution events, researchers have shown a clearer link between exposure to particulate matter and adverse health effects (Dockery et al. 1993, Schwartz et al. 1993, Samet et al. 2000). The severity of adverse effects ranges from asthmatic episodes that result from acute exposure to mortality associated with lung cancer and cardiopulmonary disease (Dockery et al. 1993, Schwartz 1993). The Harvard Six Cities

Study conducted by Dockery et al. (1993) found an adjusted mortality rate ratio of 1.26 when the most polluted of the cities was compared to the least polluted of the cities.

In addition to health effects, particulate matter can have detrimental environmental effects that include reduced visibility, aesthetic damage, and adverse ecological impact (Rodrigues et al. 1996, Grantz et al. 2003, Hyslop et al. 2009). Therefore, the EPA has designated primary and secondary standards for particulate matter. The intent of primary standards is to protect public health, including the health of sensitive populations such as children, asthmatics, and the elderly. The aim of secondary standards is to protect public welfare, including protection against decreased visibility and damage to crops, vegetation, wildlife, and buildings. The current 24-hour NAAQS for particulate matter is $35 \mu\text{g}/\text{m}^3$ for $\text{PM}_{2.5}$ and $150 \mu\text{g}/\text{m}^3$ for PM_{10} (40 CFR Part 50).

Particulate Matter Sampling Methods

To ensure that standards are met, accurate and precise air sampling is necessary. Particulate matter can be sampled using active or passive methods. Active sampling methods utilize a pump to collect air with the entrained particles, whereas passive samplers collect particles without the use of external energy sources. Both methods have advantages and disadvantages. Active samplers can give accurate results with low uncertainty but are expensive, require continuous power, and have high operational and maintenance costs (Assael et al. 2010). Passive samplers may provide comparable results without a power supply and at a lower cost but have higher uncertainty and cannot provide real-time measurements.

Active sampling is the common method for sampling ambient air and measuring occupational exposure. However, active sampler measurements may not represent true

exposure. The expense of active monitors and their power requirements may limit the number of deployed samplers and their placement, thus preventing active samplers from providing representative ambient exposure measurements over a large area. Noisy, heavy, or bulky sampling pumps worn by workers can influence or limit behavior during the sampling period; such restrictive behaviors can affect measurements of occupational exposure and introduce bias (Wiener and Rodes 2001).

UNC Passive Aerosol Sampler

Recognizing the limitations of existing sampling methods, Wagner and Leith (2001a) developed the UNC passive aerosol sampler (RJ Lee Group, Monroeville, PA) to measure particle concentrations and size distributions in ambient, indoor, and occupational settings. This sampler measures a wide range of concentrations and particle sizes including coarse, fine, and ultrafine particles, yet is lightweight, inexpensive, and easy to deploy (Wagner and Leith 2001b, Leith et al. 2007, Nash and Leith 2010). The sampler, pictured in Figure 1, consists of an annular stainless steel cap with a mesh top held into place with screws on top of an SEM stub outfitted with a substrate for particle collection. The sampler sits in a plastic SEM stub holder with a cover that is removed at the beginning of an exposure period and replaced at the end of the sampling period.

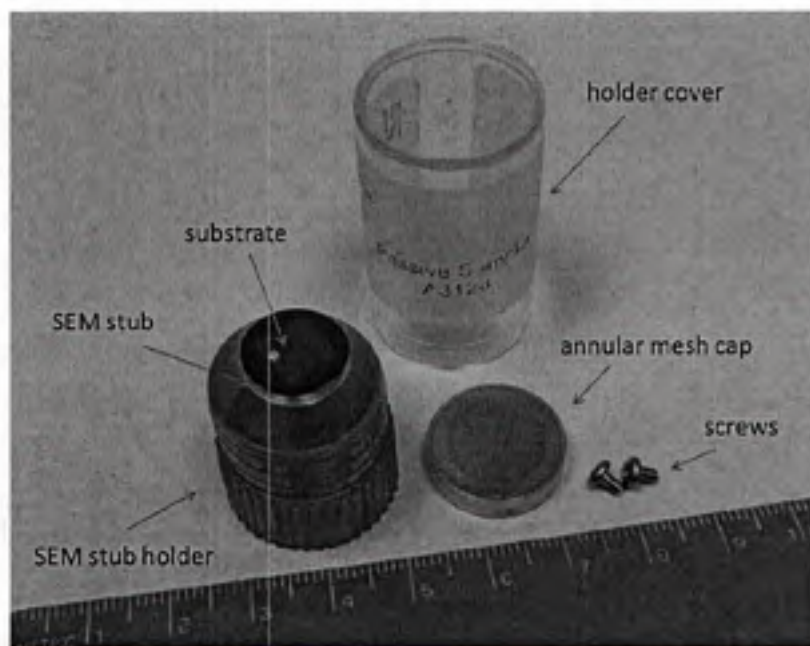


Figure 1. UNC passive sampler measuring 18 x 12 mm

Aerosol particles passively deposit onto the sampler substrate through gravitational settling, diffusion, and inertia. Particles collected on the substrate are imaged using a scanning electron microscope (SEM) or an optical microscope to be counted and sized (Wagner and Leith 2001a, Assael et al. 2010). Figure 2 shows a sample microscope image of a sampler substrate; the particles and the pores present in the substrate can be clearly seen at the set magnification. The particle count and size obtained from the generated images are used to calculate the flux of the particles to the substrate. Subsequently, through use of deposition velocity models, the flux can be used to calculate the average particle concentration in the air during the sampling period (Wagner and Leith 2001a, Nash and Leith 2010).

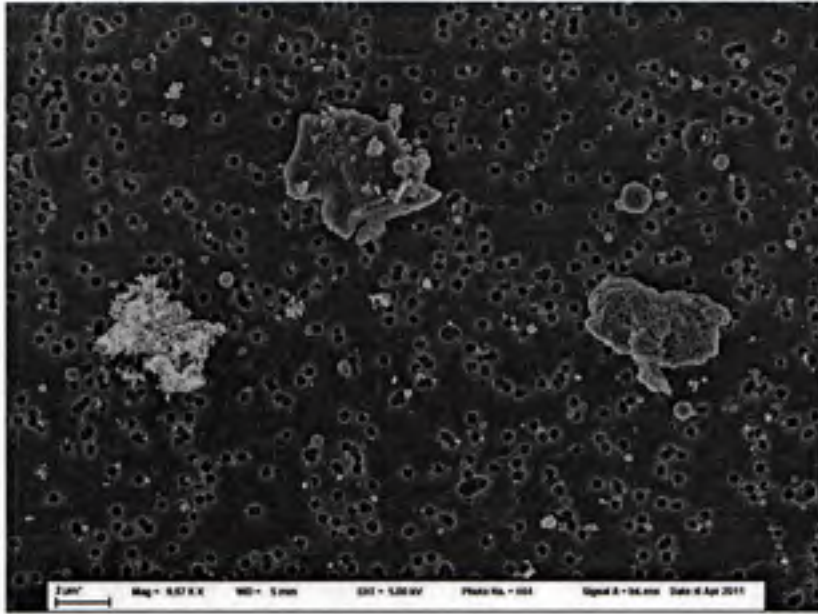


Figure 2. Scanning Electron Microscope (SEM) image of particles on collection surface

Because of their low cost and portability, passive samplers can be deployed in large numbers to investigate the spatial and temporal variability of particle concentration and composition (Wagner and Leith 2001a, Lagudu et al. 2011, Kumar et al. 2011). With the commercial availability of the passive sampler and its increased popularity as an ambient sampler, performance data for the passive sampler are essential.

Previous Passive Aerosol Sampler Research

Because the passive sampler is capable of sampling indoor, outdoor, and occupational particulates, it has been tested in a variety of settings for precision and accuracy. Each study using the sampler had different sampling conditions and objectives, and provides a different insight into sampler utility and performance.

Accuracy

Accuracy has been defined by the U.S. EPA as “the degree of agreement between an observed value and an accepted reference value.” This definition includes “a combination of random error (imprecision) and systematic error (bias) components which are due to sampling and analytical operations” (40 CFR Part 58 Appendix A). To test accuracy, investigators have compared the measurements of the passive sampler against various reference methods. When first developed, Wagner and Leith (2001b, 2001c) tested the passive sampler against an Andersen eight-stage cascade impactor. The passive sampler demonstrated reasonable agreement with the impactor in wind tunnel experiments and provided mass concentration measurements in an occupational setting that correlated well with those of the impactor with $R^2 = 0.80$ and 0.93 for $PM_{2.5}$ and PM_{10} (Wagner and Leith 2001b,c).

Other researchers have supported Wagner’s results by comparing the accuracy of the passive sampler measurements with other reference methods. In a chamber study, Whitehead and Leith (2008) tested the sampler against a dichotomous sampler and an aerodynamic particle sizer (APS) and showed that the measurements made by the passive sampler “were more variable than those of the active instruments, but generally tracked” size distribution and mass concentration measurements made by the reference samplers. A best fit line between the passive sampler concentration and active sampler average concentration had an R^2 value of 0.67 (Whitehead and Leith 2008).

For ambient conditions in several cities, Leith et al. (2007) tested the accuracy of the passive sampler for coarse aerosol measurements with collocated Federal Reference Method (FRM) samplers; they found that overall passive sampler measurements of $PM_{10-2.5}$ ranging

from $<10 \mu\text{g}/\text{m}^3$ to $\sim 40 \mu\text{g}/\text{m}^3$ were within ~ 1 standard deviation of concentrations measured with the FRM samplers. An R^2 value of 0.95 was found for a best fit line between FRM concentrations and passive sampler concentrations with an intercept not significantly different from zero and a slope not significantly different from unity (Leith et al. 2007).

Because environmental factors are harder to control in ambient conditions, Ott et al. (2008a) developed a shelter for the passive sampler to protect it from precipitation and eliminate the need to account for wind effects. In the initial development of the shelter, wind tunnel tests demonstrated that the ratio of $\text{PM}_{10-2.5}$ measured with the passive sampler to that measured by a reference sampler was 1.04 in the lab and 1.29 in the field; both values are close to the ideal ratio of 1.0 (Ott et al. 2008a). In further studies using the sampler shelter, Ott et al. (2008b,c) found that the sampler shows a “strong correlation” ($R=0.97$) to a dichotomous sampler in ambient conditions when measuring $\text{PM}_{10-2.5}$ and is capable of capturing the spatial variation of PM in the field.

Assael et al. (2010), using their own outdoor shelter design, found “very good [agreement] with an overall uncertainty of about $\pm 10 \mu\text{g}/\text{m}^3$ ” between the passive and active samplers. Deployed in the field, the passive samplers “agree[d] very well” with the active PM monitoring stations in Thessaloniki, Greece and were able to detect high concentrations near industrial areas (Assael 2010).

Precision

Precision has been defined by the U.S. EPA as “a measurement of mutual agreement among individual measurements of the same property usually under prescribed similar conditions, expressed generally in terms of the standard deviation” (40 CFR Part 58 Appendix A). Although studies on accuracy have shown good agreement between the

passive sampler and FRM measurements, the precision of the sampler is not understood as fully. Existing studies have analyzed precision by deploying replicate samplers and comparing measurements. The coefficient of variation (CV) between sampler measurements has been used as a measure of precision in many studies, while other studies have analyzed the level of agreement between replicate measurements (Wagner and Leith 2001b, 2001c, Ott et al. 2008a, Whitehead and Leith 2008, Lagudu et al. 2011).

In wind tunnel studies, Wagner and Leith (2001b) reported log-based CVs of 18.1% and 32.2% for $PM_{2.5}$ and PM_{10} . They found no statistically significant dependence of $CV_{PM_{2.5}}$ and $CV_{PM_{10}}$ on wind speed, relative humidity, and concentration, but attributed differences in measurements to slight differences between mesh caps and to counting statistics. These researchers suggested that sampler precision would improve under normal sampling conditions, and in an occupational field test they found the CV improved to an average of 16% and 20% for non-hygroscopic $PM_{2.5}$ and total PM_{10} , respectively (Wagner and Leith 2001c). Hygroscopicity of particles affected precision with a CV value for hygroscopic $PM_{2.5}$ of 59%.

In initial shelter design experiments, Ott et al. (2008a) found CV values of 16.1%-49.9% in a laboratory setting and 2.4%-20.8% in a field study. In a related study, Ott et al. (2008b) reported a root mean square (rms) CV of 11.6% in field trials conducted in Iowa City, IA using the shelter and an rms CV of 20.1% in lab testing without the shelter for $PM_{10-2.5}$. They explained the difference in rms CV between lab and field tests by the spatial heterogeneity of particles in laboratory wind tunnel studies (Ott et al. 2008a).

Researchers have found greater uncertainty in the precision of the passive sampler in laboratory experiments where sampling times may be shorter and particle counts reduced

(Wagner and Leith 2001b, 2001c, Ott et al. 2008b, Whitehead and Leith 2008). A series of three-hour chamber studies conducted by Whitehead and Leith (2008) found that size intervals of the standard deviation about the mean mass concentration were larger for the passive sampler than those for the APS due to the small number of particles counted. In contrast, studies using the sampler in ambient conditions have reported better precision (Ott et al. 2008b). In ambient conditions, the passive sampler provides measurements of coarse particulates that are in “generally good agreement” with its replicates with a moderate correlation ($R^2 = 0.43$) found between the concentration of replicate sampler and its corresponding base sampler (Lagudu et al. 2011). Although the precision of passive sampler measurements has been analyzed previously, further studies are needed to explore sampler performance in other settings.

Research Objectives

This work aims to supplement existing studies by analyzing passive sampler performance in a field study with a focus on measurement precision of $PM_{2.5}$ and PM_{10} concentrations. This study examines the precision of 44 duplicate passive aerosol samplers that exhibit a wide range of $PM_{2.5}$ and PM_{10} concentrations.

Chapter II: Precision of PM Measurements with the UNC Passive Aerosol Sampler

This technical note is in preparation for submission to *Journal of Aerosol Science*.

Introduction

The UNC passive aerosol sampler has application as a personal sampler and as an aerosol monitor in indoor and outdoor environments (Wagner and Leith 2001a). Because the device weighs only 6.5 g, measures 18 x 12 mm, and does not require pumps or auxiliary support, it is easy to deploy and remains unobtrusive throughout the sampling period. The capability of the passive sampler to measure particle number and mass concentration, size distribution, and elemental composition makes it an effective method to sample coarse, fine, and ultrafine particles (Leith et al. 2007, Whitehead and Leith 2008, Nash and Leith 2010). These characteristics have led to its use in outdoor environments to assess the spatial distribution of fine particles (Assael et al. 2010, Lagudu et al. 2011).

Both the accuracy and the precision of measurements made with this sampler are important to characterize. Tests of accuracy in laboratory and field environments have shown that passive sampler measurements agree reasonably well with measurements from active samplers such as a cascade impactor, Aerodynamic Particle Sizer, and U.S. EPA federal reference methods for $PM_{2.5}$ and PM_{10} (Wagner and Leith 2001b, 2001c, Leith et al. 2007, Whitehead and Leith 2008, Assael et al. 2010).

In contrast, the precision of data from this sampler has been evaluated in only a few studies. Wagner and Leith (2001c) assessed the precision of passive sampler measurements in an occupational setting and found good precision for $PM_{2.5}$ and PM_{10} when measuring high concentrations of non-volatile particles for short sampling periods. Ott et al. (2008b) and

Lagudu et al. (2011) deployed multiple samplers at a limited number of field locations and found favorable and moderate precision, respectively, for coarse PM. Generally, these studies have concluded that moderate to good precision can be expected with some imprecision associated with differences in particle type (Wagner and Leith 2001).

The present study examines $PM_{2.5}$ and PM_{10} concentrations measured using replicate UNC passive aerosol samplers that were deployed in a large field study. The objectives of the present study are to examine the precision of these measurements and examine differences between samplers as a source of variation in PM concentration measurements between replicate samplers. A better understanding of measurement precision will help investigators who use this device to understand the reliability of the data collected.

Methods

The data analyzed here were obtained for a study conducted in the United Arab Emirates (Yeatts et al. 2012). As part of this study, 88 passive samplers were prepared in the United States, shipped to the United Arab Emirates, and deployed as collocated pairs for one week – indoors in 41 residences and outdoors at three homes. After deployment, the samplers were shipped back to the United States in lots of 25 and analyzed by computer controlled scanning electron microscopy (RJ Lee Group, Monroeville, PA) to determine particle characteristics including size and count.

From these data, concentrations of $PM_{2.5}$ and PM_{10} were calculated in $\mu\text{g}/\text{m}^3$ as explained by Wagner and Leith (2001a). From these paired PM values, precision was investigated in two ways: first, by calculating the correlation between the paired PM measurements; and second, by comparing the coefficient of variation (CV) for each paired

measurement to the CV specified by the United States Environmental Protection Agency (U.S. EPA) for PM_{2.5} (40 CFR Part 58 Appendix A).

To examine physical differences between passive samplers, image analysis was used to determine the fractional open area of the mesh caps of 24 randomly selected samplers. The mesh caps were placed on a light box to provide contrast for the openings in the mesh. Each mesh cap was then imaged from above with a digital camera equipped with a bellows and macro lens. The fractional open area of each mesh cap was estimated using the histogram tool in ImageJ software (NIH).

Results

Figure 3 compares the mass concentration measured by each sampler to its corresponding average concentration calculated for it and its pair for PM_{2.5} and for PM₁₀. The coefficient of determination, R^2 , is 0.94 for PM_{2.5} and 0.96 for PM₁₀. High correlations imply that samplers measured a mass concentration comparable to an average value and thus exhibited high precision. High correlations for both PM_{2.5} and for PM₁₀ also imply that particle size does not substantially affect the strength of the correlation, and thus, the precision of these measurements.

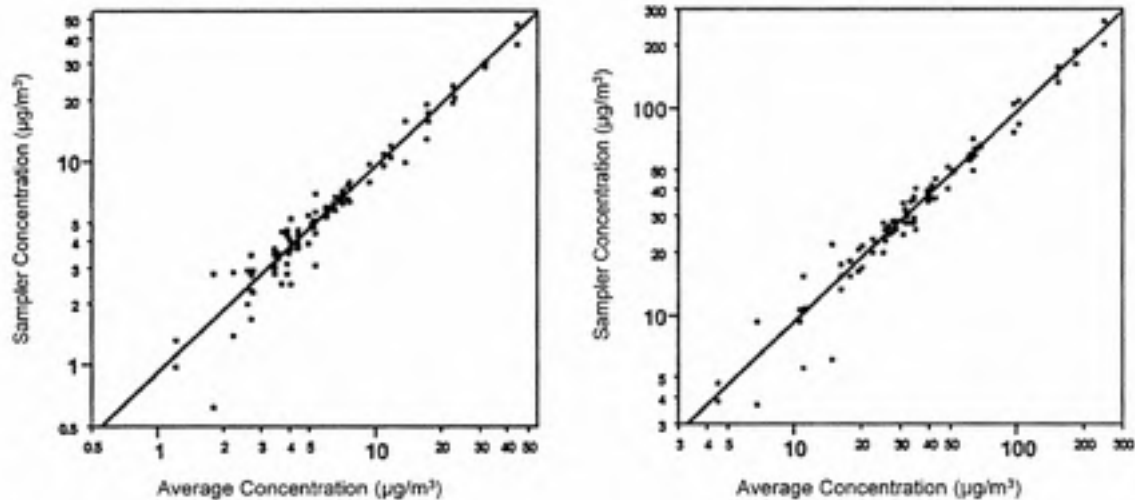


Figure 3. Sampler concentration ($\mu\text{g}/\text{m}^3$) vs. average concentration ($\mu\text{g}/\text{m}^3$) for $\text{PM}_{2.5}$ (left) and PM_{10} (right).

Figure 4 compares the average PM concentrations for the sampler pairs to their respective coefficients of variation (CV) for $\text{PM}_{2.5}$ and for PM_{10} . These plots suggest that CV decreases as PM concentration increases. The better precision observed for higher concentrations is likely due to better counting statistics (Leith and First 1976). Because the substrate area in which particles were counted was the same for all samplers, more particles were counted for samplers with higher concentrations, thereby improving the precision of the measurements and decreasing the corresponding CVs.

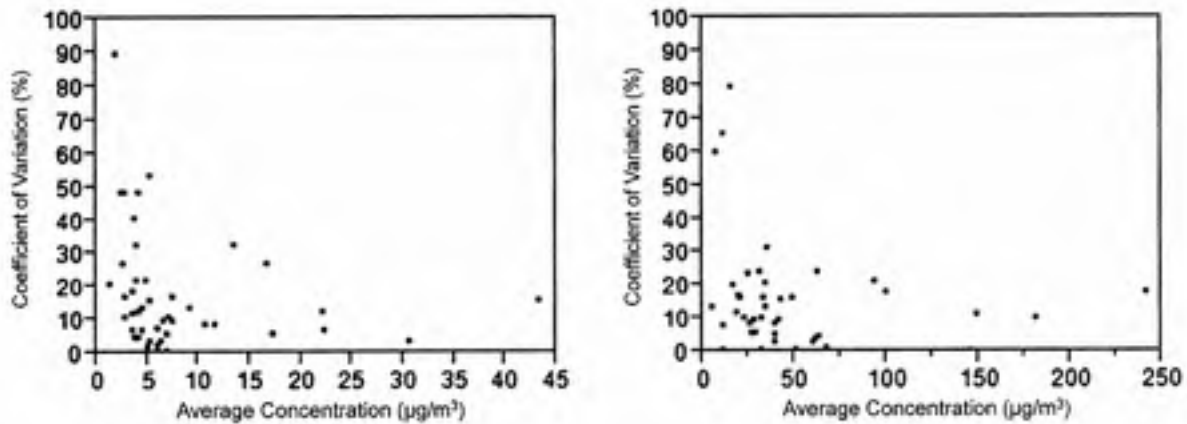


Figure 4. Coefficient of variation (%) vs. average concentration ($\mu\text{g}/\text{m}^3$) for $\text{PM}_{2.5}$ (left) and PM_{10} (right).

The data quality objective of the U.S. EPA for the operational precision of $\text{PM}_{2.5}$ monitoring is a CV of 10% or lower (40 CFR Part 58 Appendix A). Our study shows that 39% of the data pairs for $\text{PM}_{2.5}$ and 43% of the data pairs for PM_{10} meet this objective. Precision improves as concentration increases; the percentage of pairs that meet the EPA objective increases to 52% for $\text{PM}_{2.5}$ concentrations greater than $5 \mu\text{g}/\text{m}^3$, and to 49% for PM_{10} concentrations greater than $20 \mu\text{g}/\text{m}^3$. Further, 74% of $\text{PM}_{2.5}$ concentrations greater than $5 \mu\text{g}/\text{m}^3$ and 67% of PM_{10} concentrations greater than $20 \mu\text{g}/\text{m}^3$ meet the less restrictive CV objective of 15% or lower as specified by the U.S. EPA for the measurement uncertainty for $\text{PM}_{10-2.5}$ methods. The UNC passive aerosol sampler has never been suggested as a reference method for measuring $\text{PM}_{2.5}$ or PM_{10} , nor should it be; however, that the precision of measurements made with this simple device is not much worse than the data quality

objective set by the U.S. EPA for measurements using a federal reference method is worthy of note.

Results of the image analysis of the mesh caps from 24 samplers indicate that the average fractional open area is 0.27 with a standard deviation of 0.029. Fractional open area ranged from 0.192 to 0.326. These variations may be responsible for a substantial portion of the variability in measured PM concentrations between replicates, particularly at high PM concentrations. Nash and Leith (2010) proposed a model in which the estimated PM concentration is proportional to the reciprocal of the fractional open area. The mean and standard deviation of the reciprocal of the fractional open area is 3.76 and 0.45, respectively. The CV of this reciprocal is 12%, comparable to the CV of the estimated PM concentrations at high concentration as shown in Figure 4.

Conclusions

The passive sampler investigated in this study provided reasonably precise measurements of PM_{2.5} and PM₁₀ over a wide range of concentrations in a field setting. The conditions for sampler use in this study were challenging as the samplers were shipped overseas, deployed for a week either indoors or outdoors without supervision, and then shipped back overseas for analysis. Even under these conditions, the device was able to produce reasonably precise measurements. The variability in results obtained for paired samplers may be largely explained by differences in the porosity of the mesh cap for the samplers used. Precision improved as concentration increased, because more particles could be collected and analyzed. Longer sampler deployment will allow more particles to be collected and, in turn, improve precision.

Chapter III: Additional Analysis of Results

Additional analysis of CV values for the sampler pairs was conducted but not included in the technical note to further understand the precision of the passive sampler measurements and to explore particle count as a source of measurement variations. Measurement variability due to mesh caps is explained further in Appendix D. The average CV for the 44 pairs of passive samplers was calculated as 18.2% and 15.2% for PM_{2.5} and PM₁₀, respectively. Of the samplers measuring concentrations greater than 5 µg/m³ and 20 µg/m³ for PM_{2.5} and PM₁₀, the average CV values were 12.3% and 11.3%. These values are comparable to or better than CV values in previous studies.

In comparison to Wagner and Leith (2001c), Ott et al. (2008b) attributed their lower CV values to a higher number of particles sized per sample analyzed. Average counts per passive sampler analyzed by Wagner and Leith (2001c) were 15.4 and 177 particles for PM_{2.5} and PM₁₀ respectively, whereas Ott et al. (2008b) analyzed over 1300 particles per sample. In this study, the number of particles analyzed for each sampler ranged from approximately 50 to 10,000.

Counting statistics have been invoked to explain improved precision associated with higher particle counts in past studies (Wagner and Leith 2001c, Ott et al. 2008b). Wagner and Leith (2001c) found that precision was generally better for PM₁₀ than for PM_{2.5} and attributed greater precision to better counting statistics. Better PM₁₀ precision was seen in samplers with higher PM₁₀ counts. This study supports past findings showing that precision, being partly driven by counting statistics, increases with a greater measured PM concentration

Chapter IV: Implication of Results

This study has shown that reasonable precision can be expected from the UNC passive aerosol sampler for a wide range of particle mass concentrations measured indoors and outdoors. The implication of this finding is that the passive sampler can be deployed with a certain level of confidence in a variety of settings. Increased precision is expected with higher measured mass concentrations, making the passive sampler ideal for measuring high occupational exposures and outdoor air. As discussed in the introduction, active personal samplers can be bulky and affect exposure measurements. Passive samplers can be used as personal samplers to provide fairly precise measurements because they are unobtrusive and do not impede worker behavior. In an outdoor setting, the passive sampler can be utilized to determine spatial and temporal variability of particulates. In all settings, the passive sampler can provide researchers with a better understanding of actual exposure which can be affected by behavior and spatial variation.

This study has also shown that the variability between sampler measurements can be attributed to the number of particles collected on the sampler and by the variability in mesh cap openings. By identifying possible sources of variability, precision of measurements can be improved. Both sources of variability identified in this study are controllable.

The issue of low particle count affecting precision can be improved by a longer deployment time. The longer a sampler is deployed, the more particles will be collected. However, if particles are collected over a longer period of time, mass concentrations must be averaged over that longer period and variations due to time are not well-represented.

The variability between mesh caps must be controlled by the manufacturer of the passive sampler. However, recognizing that there is a possibility for differences between

mesh caps, users can image mesh caps for quality assurance before deploying samplers. If these sources of variations are controlled, better precision can be expected from passive sampler measurements.

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Appendix A: Detailed Methods

Field study

The data used in this study were obtained from outdoor duplicate samplers from three households and indoor duplicate samplers from 41 households for a total of 88 deployed samplers. Data from outdoor samplers were included in the analysis to give a greater range of concentrations. All samplers were deployed for approximately one week. The date and time of sampler deployment was recorded along with the time and date of sampler collection. Once samplers were collected they were capped and shipped to RJ Lee Group in lots of 25 for analysis.

Particle analysis

RJ Lee Group imaged particles from all samplers using Computer-Controlled Scanning Electron Microscopy (CCSEM). Particle diameter and area were reported for each particle imaged for each sampler. The number of particles varied by sample and ranged from approximately 50 particles to 10,000 particles.

RJ Lee Group reported values of $PM_{2.5}$, PM_e , and PM_{10} mass concentrations for each sampler. For each sampler, they also provided the average diameter and area for each particle counted on the sampler for low and high magnification. The substrate area over which particles were counted was always 1.85 mm^2 and 20.48 mm^2 for high and low magnifications, respectively.

Combining magnifications

Because high magnification images capture small particles and low magnification images capture large particles, low magnification and high magnification data needed to be

combined to obtain a good representation of the range of particle diameters. All particles on low magnification were included and particles imaged on high magnification with a diameter, as calculated from reported areas, less than the smallest particle imaged on low magnification were included. Low magnification particles were normalized to the high magnification particles.

Excel spreadsheet

All calculations were performed in Excel using equations given by Wagner and Leith (2001a). Once low and high magnification particle data were combined, they were input into an Excel sheet with the parameters listed in Appendix B. The mass concentrations of PM_{2.5} and PM₁₀ that were used in subsequent precision analyses were calculated by considering each particle's individual contribution to total mass without grouping similarly sized particles. Cutoff curves were then applied to determine the fractional contribution of each particle. For PM₁₀, the fraction of particles of diameter d_a that was included in the PM₁₀ mass concentration, PF_{10} , was given by the following equations:

$$PF_{10} = 1.0 \quad \text{for } d_a < 1.0\mu\text{m}$$

$$PF_{10} = 0.9585 - 0.00408d_a^2 \quad \text{for } 1.0 < d_a < 15\mu\text{m}$$

$$PF_{10} = 0 \quad \text{for } d_a > 15\mu\text{m}$$

based on the U.S. EPA PM₁₀ sampling criteria for ambient particulate sampling, which are for $d_a < 1.5\mu\text{m}$, $1.5 < d_a < 15\mu\text{m}$, and $d_a > 15\mu\text{m}$ (Hinds 1999). Similarly for PM_{2.5}, the fraction of particles of diameter d_a included in the PM_{2.5} mass fraction, $PF_{2.5}$, was given by

$$PF_{2.5} = [1 + \exp(3.233d_a - 9.495)]^{-3.368}$$

where d_a is in μm (Hinds 1999).

Determination of precision

Once the mass concentrations were calculated for all samplers, precision was determined by comparing the mass concentration of each sampler to its duplicate. Precision was determined in two ways: looking at the general level of agreement and determining the coefficient of variation between duplicate sampler measurements.

To analyze the level of agreement between replicate measurements, duplicate sampler mass concentrations were averaged and graphed against each sampler concentration for a total of 88 data points. Statistical analyses were conducted in JMP (SAS, Cary, NC). For the comparison of individual sampler concentrations to its corresponding average concentration, the logarithms of the data were taken before analysis to determine the correlation as shown in Figure 3. JMP (SAS, Cary, NC) also generated the coefficient of determination for each plot.

To determine the coefficient of variation the following equation was used:

$$CV = \frac{\textit{standard deviation}}{\textit{mean}} \times 100\%.$$

Coefficient of variation values between samplers was calculated for all 44 duplicate pairs and was graphed against the average mass concentration of the duplicate pairs as seen in Figure 4.

Appendix B: PM Mass Concentration Calculation Parameters

Parameter	Value
Gas Density	0.00118 g/cm ³
Dynamic Viscosity	0.0000181 g/(cm s)
Kinematic Viscosity	0.1534 g/(cm s)
Particle Density	2 g/cm ³
Volume Shape Factor	1.6
Dynamic Shape Factor	1.4
Mean Free Path	0.066 μ m
Gravitational Constant	981 cm/s ²
Boltzmann's Constant	1.38E-16
Temperature	283K
Turbulence Reference Height	0.2 m
Mean Wind Speed	0.2 m/s
Area	1.85 mm ²
Sampling Time	Varies by sampler in seconds

Appendix C: Comparison to RJ Lee Group

In their analysis of the passive samplers, RJ Lee Group reported particle count and size information, and calculated $PM_{2.5}$ and PM_{10} mass concentrations. There were differences between the mass concentrations calculated in this study using the methods previously explained and the mass concentrations for the same samplers reported by RJ Lee Group. The differences can be attributed to differing methods for PM calculation. RJ Lee grouped particles of similar diameters together to determine mass contributions on a group-by-group basis, whereas in this study calculations were conducted on a particle-by-particle basis. Also, this study utilizes cutoff curves to determine fractional contributions of different particle sizes, whereas the analysis of RJ Lee does not.

However, Figure 5, which presents a log-based plot of mass concentrations reported by RJ Lee Group versus mass concentrations measured in this study, shows general agreement between the two sets of measurements with slope 1.019 ± 0.007 and intercept -0.049 ± 0.013 for $PM_{2.5}$ and slope 0.997 ± 0.007 and intercept -0.102 ± 0.023 for PM_{10} where the \pm values correspond to the standard error. Analysis in JMP statistics (SAS, Cary, NC) shows the coefficient of determination, R^2 , is 0.996 for $PM_{2.5}$ and 0.996 for PM_{10} .

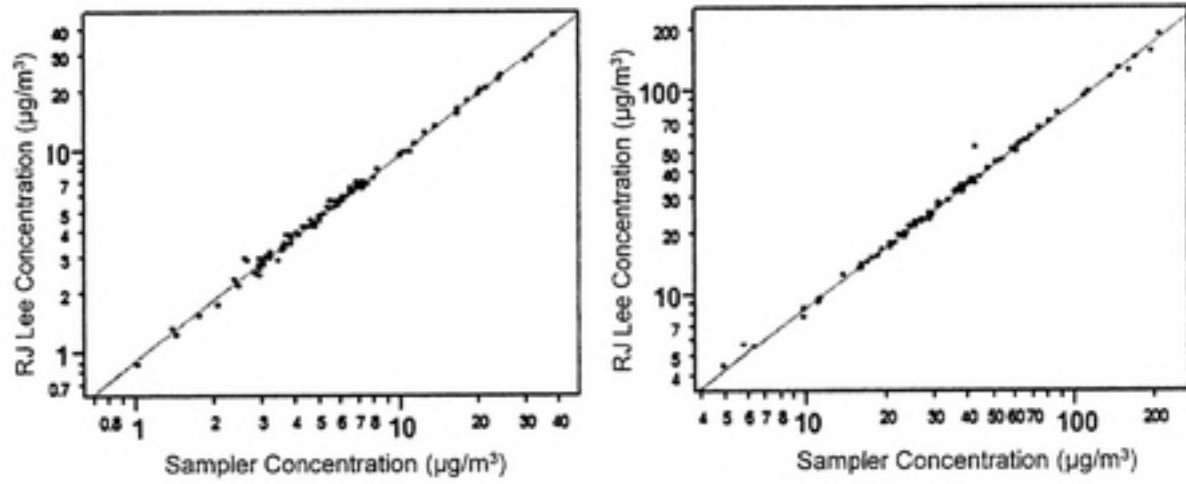


Figure 5. RJ Lee Group reported sampler concentration ($\mu\text{g}/\text{m}^3$) vs. calculated sampler concentration ($\mu\text{g}/\text{m}^3$) for $\text{PM}_{2.5}$ (left) and PM_{10} (right).

Appendix D: Analysis of Mesh Cap

The following work was conducted by Dr. Joe Pedit to analyze the variations in the fractional open area of the mesh caps of the passive aerosol sampler. Knowing the variations between mesh caps is important because they may contribute to variations between sampler measurements. Different porosities for different mesh caps will cause the number of particles collected on the substrate surface to differ, if all else remains the same.

Mesh cap imaging

A total of 24 mesh caps were imaged to determine differences in fractional open areas. Each mesh cap was imaged by placing it on a lightbox and using a Canon EOS Rebel T3i DSLR camera equipped with a Nikon PB-6 bellows and a Nikon 55mm f/2.8 AIS Micro-Nikkor lens to capture images from above. In preparation for image analysis, the raw image file was converted to a TIFF file using ImagesPlus software (version 4.5, Rootstown, Ohio) to obtain a non-stretched image (i.e., gamma=1) and cropped using Adobe Photoshop CS4 software (San Jose, California) to isolate the area over which particle deposition occurs. The image analysis was done using ImageJ software (NIH) and yielded estimations of the fractional open area for each of the mesh caps. The average fractional open areas were 0.27 with a standard deviation of 0.029. The mean and standard deviation of the reciprocal of the fractional open area were 3.76 and 0.45, respectively with a CV of 12%. The results are presented graphically in Figure 6 which shows a plot of the cumulative distribution versus the inverse fractional open area with a 3rd order polynomial fit.

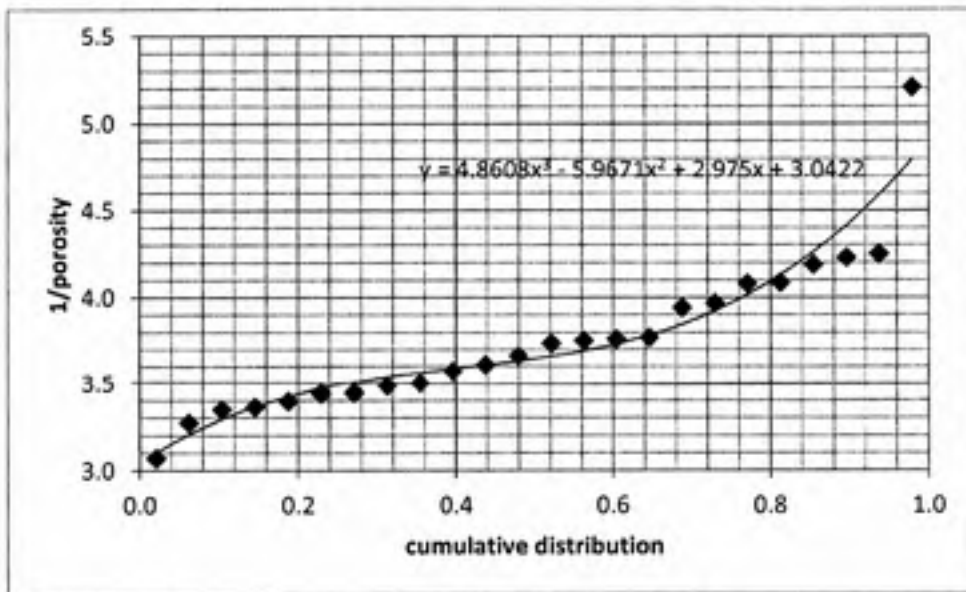


Figure 6. Cumulative distribution vs. inverse fractional open area fit with a 3rd order polynomial.

Excel Analysis

To further understand the implications of fractional open area variability on measurement variability between duplicate samplers, an average CV value between simulated duplicate pairs was determined. An Excel sheet was set up so random draws from a uniform distribution over 0 to 1 could be made to represent random draws on the cumulative distribution function. For each analysis, two random draws were made to simulate a duplicate pair and the inverse fractional open area for each random draw was calculated based on the 3rd order polynomial given in Figure 6. This process was repeated 10,000 times and the average CV between the randomly drawn pairs was calculated to be 8.5%

Appendix E: Contents of Data CD

HH PM Calculations	Calculation of $PM_{2.5}$ and PM_{10} for each of the 44 households
Particle by particle data	Particle diameter and area for each sampler on high and low magnification
CV calculations	Analysis of coefficient of variation between duplicate sampler mass concentrations
Comparison to RJ Lee	Compilation of all calculated mass concentrations for each sampler compared to reported values from RJ Lee