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Assessment of the temporal relationship between daily summertime ultra-fine particulate count concentration with PM2.5 and Black Carbon Soot in Washington DC

George Allen, Eileen Abt, Petros Koutrakis
Harvard School of Public Health
665 Huntington Ave
Boston, MA 02115

Robert Burton
NERL, US EPA
MD-56
RTP, NC 27711

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INTRODUCTION

Several recent epidemiological studies have shown a significant relationship between ambient daily particulate mass concentrations and human health effects as measured by cardio-pulmonary morbidity and mortality (Schwartz, 1994). Much of the current research aimed at determining causal agents of these PM health effects focuses on fine mass (PM2.5), which is primarily the combustion-related component of PM10. Some studies have suggested that ultra-fine aerosols (typically defined as those particles that are less than 0.1 or 0.15μm in diameter) may be an important category of particulate matter to consider, as opposed to or in addition to other measures of fine particle mass (Ferin et al., 1990; Ferin, et al., 1992; Oberdorster et al., 1995). One of the postulated toxicological mechanisms for ultra-fine particles is that it is the number of particles which is most important, and not necessarily their composition or mass (Seaton et al., 1995; Chen et al., 1995). Some studies suggest that the count concentration could be important by overwhelming macrophages (Miller et al., 1995). Another possible particle metric that could be important in health-effect outcomes is particle surface area, which may serve as a condensation surface for gas phase components that are then deposited deep in the lung.

To provide more detailed temporal and size distribution data on ambient PM, the Harvard School of Public Health, in conjunction with the US EPA, has recently conducted intensive aerosol size characterization measurements in two east-coast cities during the summer peak pollution season: Washington DC during the summer of 1994, and Nashville TN during the summer of 1995. At this time, only a portion of the Washington DC data are available for analysis and presented here; the Nashville data are not currently ready for analysis.

During July and August of 1994, continuous ambient particle size distributions were measured in Washington, DC. Size distributions from 0.02 to greater than 10 μm were continuously measured using the TSI (St. Paul, MN) Scanning Mobility Particle Sizer (SMPS) and the TSI Model 3310A Aerodynamic Particle Sizer (APS). The SMPS samples particles from 0.02 to 0.7 μm, and the APS samples particles with sizes from 0.7 to greater than 10 μm. Data from the SMPS and the APS were merged to determine hourly total particle counts, total fine mass concentrations, and size distributions for count and mass concentrations. Continuous PM2.5 and black carbon soot (BC, a surrogate for elemental carbon) were measured at the same site with a Rupprecht and Patashnick (Albany, NY) TEOM and Magee Scientific (Berkeley, CA) Aethalometer respectively. Integrated low-volume 24-hour (9am to 9am local time) PM2.5 samples were also collected for method validation purposes. This paper presents the temporal relationship for 24-hour means between these pollutants and discusses the implications of these results.

METHODS

Aerosol measurements were made 4 km north northeast of downtown Washington, DC, in an urban residential area. The monitoring site was on the grounds of the McMillan Reservoir, located approximately two and one quarter miles north northeast of downtown Washington D.C. in an open clearing at the south-western end of McMillan Reservoir. Howard University borders the entire western side of the reservoir site, while three hospitals are situated along the north border. A moderately traveled road with 4 lanes (1st Street) runs parallel with the reservoir on the eastern side, approximately 200 meters from the monitoring site.

Samples were collected outdoors at 5 meters above ground level. For particle size methods, both the sampled air and the instruments were maintained at ambient temperature and relative humidity to prevent distortion of size distributions resulting from changes in the aerosol's particle bound water. All particle data reported here for the calculation of temporal associations are 24-hour means of hourly datasets (midnight to midnight local

standard time), since the relevant health effects epidemiology is based on that time interval (EPA, 1996).

Particle Size and Count Measurement Methods

SMPS. To characterize particle size distribution in the 0.02 to 0.7 μm range, a TSI Inc. Scanning Mobility Particle Sizer (SMPS) Model 3934L, consisting of a Model 3071A electrical mobility size classifier and a Model 3010 Condensation Particle Counter (CPC), was used to count particles and classify them by size based on electrical mobility characteristics. The nominal sample scan time was six minutes; the mean results of two scans were recorded. Sample aerosol for the SMPS is drawn through an impactor to remove particles above the measurement range and then exposed to a Kr-85 neutralizer to reduce the particle charge distribution to one described by the Boltzmann equilibrium. For a given particle size and rod voltage charge, the mobility is just enough to allow the measured particles to be swept past a charged rod and through a slit into a particle counter. All particles with greater mobilities than the desired size precipitate on the charged rod, and those with smaller mobilities are removed with the sheath air. Corrections are made in data processing for multiple charges on particles.

APS. The size distribution of particles in the range from 0.7 to greater than 10 μm aerodynamic diameter was measured using the TSI, Inc. Aerodynamic Particle Sizer (APS) model 3310A, a laser-Doppler velocimeter. The principle of operation is the measurement of the time of flight in an accelerating air stream. Results are stored every 5 minutes in 58 channels of logarithmic size intervals between 0.5 and 30 μm. The aerodynamic particle size distribution is calculated from a previously stored calibration curve. Calibration is performed with standardized polystyrene latex spheres. Data below 0.7 μm were discarded for this study. Data above 15 μm are reported here, but are likely to be underestimated due to sampling losses in the APS inlet.

Merging of data from particle sizing instruments. The SMPS and APS data were merged by analyzing the response from both methods in the size range where the measurement capabilities of the two instruments overlap at 0.7 μm. The APS measures aerodynamic diameter, which is a function of particle shape and particle density, while the SMPS measures electrical equivalent diameter, which is a function of particle size and shape, but not density (the equivalent diameter of a particle is the diameter of a sphere that would have the same particular physical property as the non-spherical particle). The electrical equivalent diameter was considered to be equal to the volume equivalent diameter, since a spherical particle shape was assumed (Peters et al. 1993).

Data from the SMPS and APS were each processed independently and then merged using a determined density. Data from the SMPS, which consisted of twelve minute samples, were charge corrected using TSI's SMPS software (version 1.1) and then averaged for each hour. APS data, which consisted of five minute samples, were averaged for each hour and corrected for coincidence using TSI Inc.'s APS Extra software. The SMPS data was then converted from volume equivalent diameter to aerodynamic diameter using an assumed spherical particle geometry and various aerosol densities, ranging from 1.0 to 1.4 g/cm^3. Particulate number and mass distributions were analyzed for multiple hours on various days to determine the density at which the data achieved the best fit in the overlapping region. The converted SMPS data was then merged with the APS data (Peters et al., 1995) to provide particle count and mass size distributions over the entire range of 0.02 to greater than 10 μm.

Black Carbon (Aethalometer)
The Aethalometer (Magee Scientific Inc., Berkeley CA) measures "black carbon soot" (BC), a surrogate of elemental carbon (EC), in real time. The method is similar in principle and highly correlated to the coefficient of haze (COH) parameter that has been monitored for several years in many urban areas (Allen et al., 1996).

The Aethalometer BC data is much more sensitive and stable than COH, and it is scaled to elemental carbon atmospheric concentrations. Measurements are made every five minutes; the one hour LOD is 50 ng·m^{-3} BC. The method is based on the optical attenuation of light by particles collected on a 47 mm diameter pre-fired quartz fiber filter. The light source is an incandescent bulb, with an effective center wavelength of 820 nm. Using the internal, empirically determined conversion factor, the BC data from this instrument has agreed well with EC in previous comparisons. This instrument does *not* measure organic carbon or the *atmospheric* light absorption of the elemental carbon aerosol. The method is documented in detail elsewhere (Hansen et al, 1984).

Continuous Mass (TEOM®)

The Rupprecht and Patashnick (Albany, NY) model 1400a Tapered Element Oscillating Microbalance (TEOM®) is an EPA designated equivalent method for measuring PM_{10}. The TEOM provides continuous mass concentration by collecting particles on a small heated (50 °C) filter mounted on the end of a hollow tapered oscillating glass rod. The frequency of oscillation decreases as the mass on the filter increases. For fine mass measurements, a 2.5 µm size fractionating impactor replaces the 10 µm inlet. The fine mass inlet and impactor used in this study is the same design as is used in the Harvard Impactor (HI) integrated PM sampler (Marple et al., 1988). To accommodate the HI inlet, the total sample flow of the TEOM is increased from 16.7 to 20 l·min^{-1}, with the filter flow increased from 3.0 to 3.6 lpm. The performance of the TEOM for PM2.5 has been evaluated previously (Allen et al, 1995); for east-coast US sites in warm weather seasons when the aerosol composition is primarily non-volatile mass, the comparison with integrated 24-hour PM2.5 gravimetric samples collected with the Harvard Impactor sampler is within 5%.

RESULTS

At this time, only 14 days of data from the summer of 1994 in Washington DC are available. One of those days had insufficient hours for the day, and was removed from the data set. For the remaining days, the coefficient of determination (R^2) for Pearson regression analysis was calculated for both PM2.5 and black carbon (BC) against particle counts. The results are shown in Table I. There was nosignificant relationship between PM2.5 and total count concentrations or BC and total count concentration. A scatter plot and a time-series plot of the mass and count data are shown in Figures 1 and 2 respectively. A significant relationship [p=0.05] was observed between BC and PM2.5, with an adjusted R^2 of 0.25. This is shown in Figure 3.

Figure 4 shows a typical cumulative distribution for particle count and mass between .02 and 10 µm aerodynamic size. Ultra-fine particles dominate the total particle count, with about 85% having sizes less than 0.2 µm diameter at ambient relative humidities. Only about 4% of the mass is in particles smaller than 0.2 µm. These data are from midnight to 1 AM on July 31, 1994, when relative humidity was high (85%) and particles would be expected to have had significant amounts of particle bound water (PBW) associated with them, causing them to grow in size. Even with the PBW in this example, 97% of particles by count are less than 0.5µm in diameter, and 99% are less than 0.6µm. Figure 5 shows mass distribution by size for two hours on August 3, 1994 (5 AM with an RH of 92%, and 2 PM with an RH of 57%), in Washington, DC. For both hours, the mass peaks at about 0.6µm. As expected, the size distribution is shifted slightly to the right (larger diameter) for the more humid early morning hour of data. The Y axis of this plot shows the relative mass, normalized to be independent of the size measurement interval (the "bin" width).

DISCUSSION

The lack of an observable association between particle count and mass concentration in ambient urban

atmospheres as shown here is consistent with the characteristic lifetimes, sources, and sinks of the different types of ambient particles in urban areas. Ultra-fine particles are typically generated from local, ground level combustion sources. Their lifetime in the atmosphere is very short (typically less than one or two hours), thereby limiting the distance they can be transported to a few kilometers. This implies that their chemical composition reflects local source emissions of secondary aerosol precursors, and may not be similar to transported aerosols that tend to be aged and larger than fresh aerosols. The exception to this would be freshly formed sulfate aerosol when local SO_2 concentrations and humidities were high.

Ultra-fine particles are removed as they age, primarily by combining to form larger particles (agglomeration). The higher the concentration of ultra-fine particles, the more rapidly they grow out of that size category, since for a given particle size, the rate of coagulation is proportional to the square of the particle number concentration. In addition, the smaller the particle size, the higher the rate of coagulation (the rate of change in number concentration); given an identical particle number concentration, a 0.01 μm particle will have an 8-fold higher coagulation rate than a 0.1 μm particle. This short lifetime of ultra-fine particles also prevents the formation of high count concentrations during prolonged periods of poor dispersion conditions that cause elevated PM2.5 concentrations, as demonstrated by the lack of correlation between PM2.5 and particle counts.

Aerosol theory dictates that large particles (greater than a few microns aerodynamic diameter) *also* have much shorter lifetimes in the atmosphere (typically a few hours at most) as compared to particles between 0.3 and 1.0μm (with lifetimes of many days) where most of the combustion source-related mass is found. The large particles are rapidly removed by settling. A 10μm particle has a settling velocity of 0.3 cm/s, or 9 meters in 5 minutes. By comparison, a 0.1 μm particle's settling velocity is 0.00025 cm/s (with the slip correction factor applied), or 10 meters in 46 days, slow enough for the other factors (discussed above) to account for removal of particles in the ultra-fine size range.

With the exception of black carbon which is discussed below, the size of a fine mode (combustion source-related) particle generally indicates its age. Particles larger than ultra-fines but smaller than about 0.4 to 0.5 μm. are typically not fresh, but are also not usually older than about one day (eg., the sources in this size range could generally be expected to be from the regional urban area, but not from long-distance transport sources). The number concentration of particles in this size range is smaller than that of the ultra-fine size range. However these mid-size particles still have substantially higher count concentrations than the aged aerosols typical of long distance transport, and usually dominate the particle surface area measurement (surface area being proportional to the square of the spherical particle diameter). The aged aerosols (typically between 0.5 and 1 μm) are primarily from long-distance transport sources (or regional sources during periods of severe stagnation), and are the size group of combustion aerosol particles that dominate the temporal variation of PM2.5 and PM10 measurements, driving the high episodic regional concentrations of PM2.5. Note that high ambient levels of relative humidity can increase the upper limit of all of the size classifications discussed here. A good discussion of particle sources, lifetimes and sinks as a function of size can be found elsewhere. (Wilson et al., 1996).

Black Carbon (BC) was included in this analysis since it is distinctly different from the other combustion aerosols. Combustion aerosols are condensed from the gas phase and are products of post-emission chemical reactions. BC is a primary (directly emitted) pollutant with particle sizes usually peaking around 0.3 μm. Because of this, BC is useful as a surrogate for local fossil fuel (vehicular and space heating sources) or biomass combustion sources. As a result of this difference in sources, temporal patterns of BC are distinctly different from the sulfate dominated aerosols. BC peaks with morning rush hour (Allen, 1996), while sulfates have a diurnal pattern similar to ozone, peaking in the mid-day (Wilson et al.,1991). It should be noted that the size range of BC aerosols is such that they may account for a larger percentage of the aerosol surface area than their mean mass concentration (typically about 2 to 3 $\mu g/m^3$ in urban/sub-urban areas) suggests.

Although data for surface area were not available for this paper, the relationship between number, area, and mass (volume) is well established for spherical particles, and given number distributions, the surface area can be predicted. For a density of 1.0 and spherical shape, particulate surface area increases as the square of the particle diameter, and mass increases as the cube of the particle diameter. For example, a 1.0 μm diameter particle has 400 times more surface area than a 0.05 μm particle of similar composition and shape, and a 1.0 μm particle weighs 8000 times more than a 0.05 μm particle of similar composition and shape. If particle counts peak at approximately 0.1 μm (and assuming a log-normal number concentration distribution), surface area peaks at 0.3 ($0.1^{0.5}$), and mass peaks at 0.5 ($0.1^{0.33}$) μm. The assumption above of spherical shape is reasonable for east-cost US areas where ambient humidity is usually higher than 40%, since there would be water associated with the aerosol most of the time. The density of combustion-related aerosols, including the associated water, is usually between 1.1 and 1.4, so the mass size distribution peak used in this example would actually be somewhat higher, at 0.6 to 0.7 μm.

Given these relationships between count, area, and mass, and that none of the various epidemiological models based on mass have shown any clear indication of a highly non-linear (cubic) dose-response relationship, it is unlikely that count concentration alone is the best indicator for the health effect response. However, particle surface area may still be an important parameter in this respect, since there is enough uncertainty in the dose-response curves to allow a second-order particle-related effect to account for the observed response.

CONCLUSIONS

No temporal association was observed between particle count and mass concentrations for 24 hour mean measurements. These results are consistent with the characteristics of ultrafine particles, which are generated primarily by local sources, have short lifetimes, and show small day-to day temporal variability. In contrast, the larger sub-micron particles that dominate PM2.5 concentrations in east coast urban areas (0.3 to 1 μm) are primarily from regional or long-distance transport sources and have lifetimes of many days.

If the lack of an association between count and mass concentration reported here holds over other seasons and locations, this may make it more difficult to support theories of causal mechanisms for PM health effects which rely on a temporal association between particle counts or ultra-fine mass and measures of PM2.5 or PM10. However, particulate surface area may still be an important metric in assessing the health effect response to particles.

It should be noted here that these are preliminary, limited results from a single site and single season. With the small sample size used here, the ability to detect a significant association is weak. To make definitive statements on the associations presented here, additional data would be needed that includes broader seasonal and spatial measurements. However, there is nothing to suggest that these results would not be representative for population-based monitoring sites in east-coast urban areas during the warm weather seasons.

Further work on this topic will analyze data from additional days in Washington DC and two additional sites (Nashville TN and Boston, MA). Surface area is a particle measurement of interest with regard to health effects assessment, and will be examined along with the count and mass measurements.

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Table 1. Pearson regression analysis.

N=13 days

	adj R^2
#/cc vs FM:	0.09 [Regression slope not significant at p=.05]
BC vs FM:	0.25
#/cc vs BC:	0.06 [Regression slope not significant at p=.05]

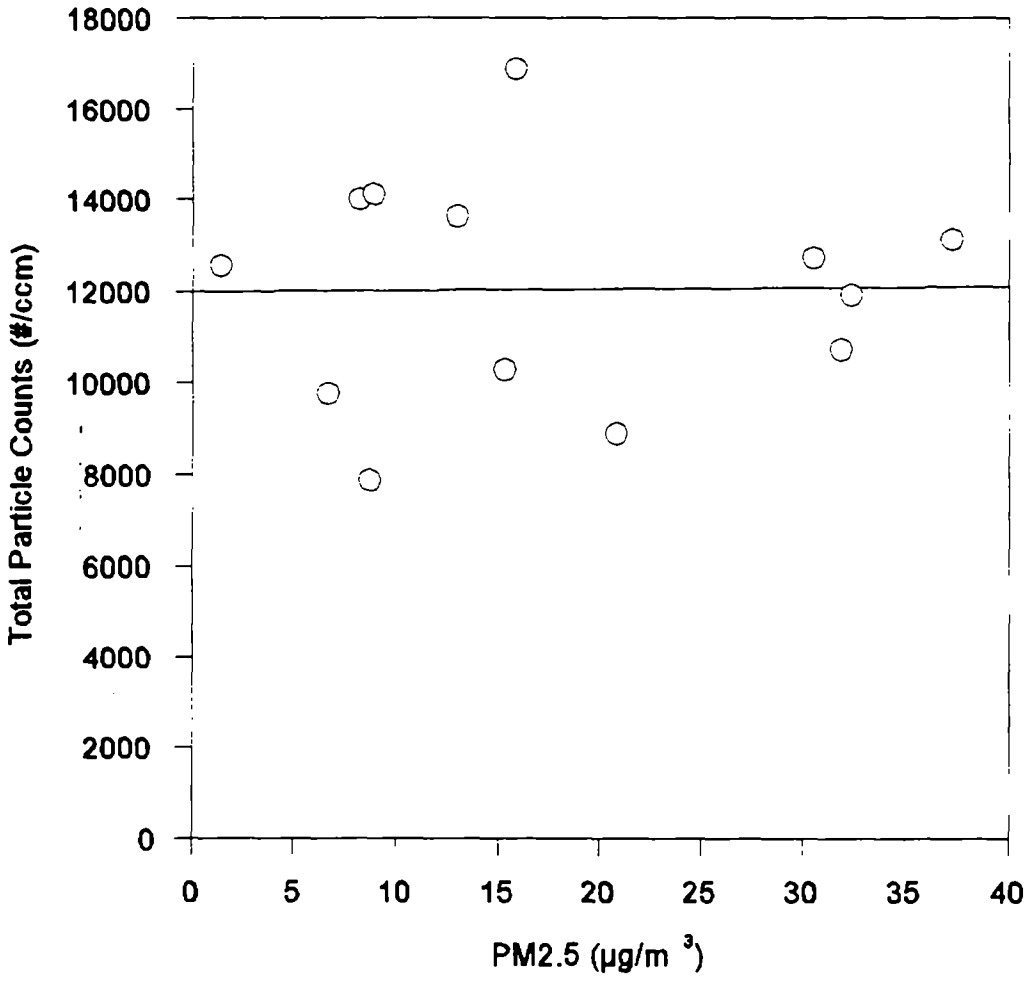

Figure 1. PM2.5 vs. Total Counts per ccm; 24-hour Means, Washington DC, Summer 1994 (13 days).

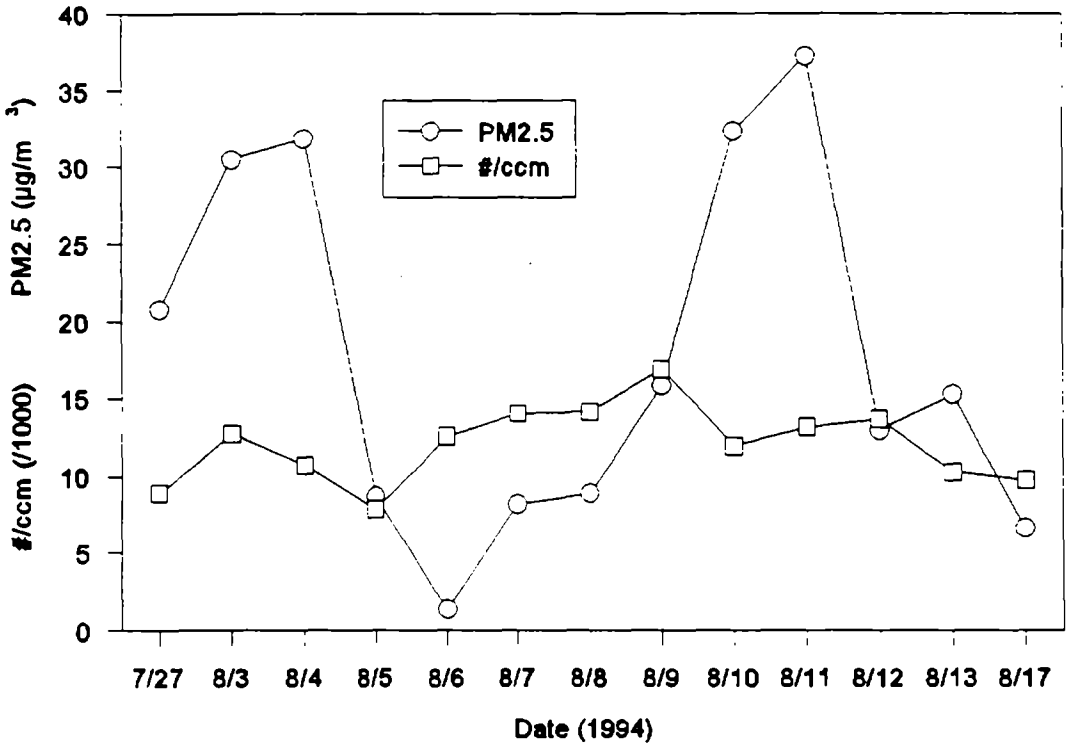

Figure 2. PM2.5 and Total Particle Counts per ccm; 24-hour means, Washington DC, Summer 1994

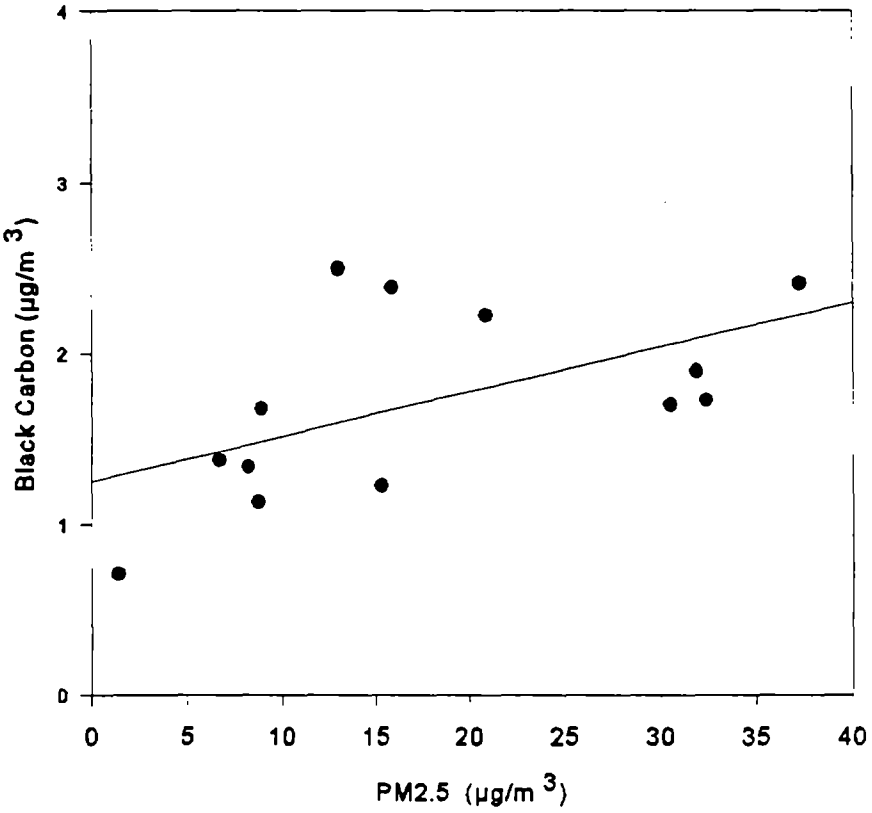

Figure 3. Black Carbon vs. PM2.5 (Regression line is shown).

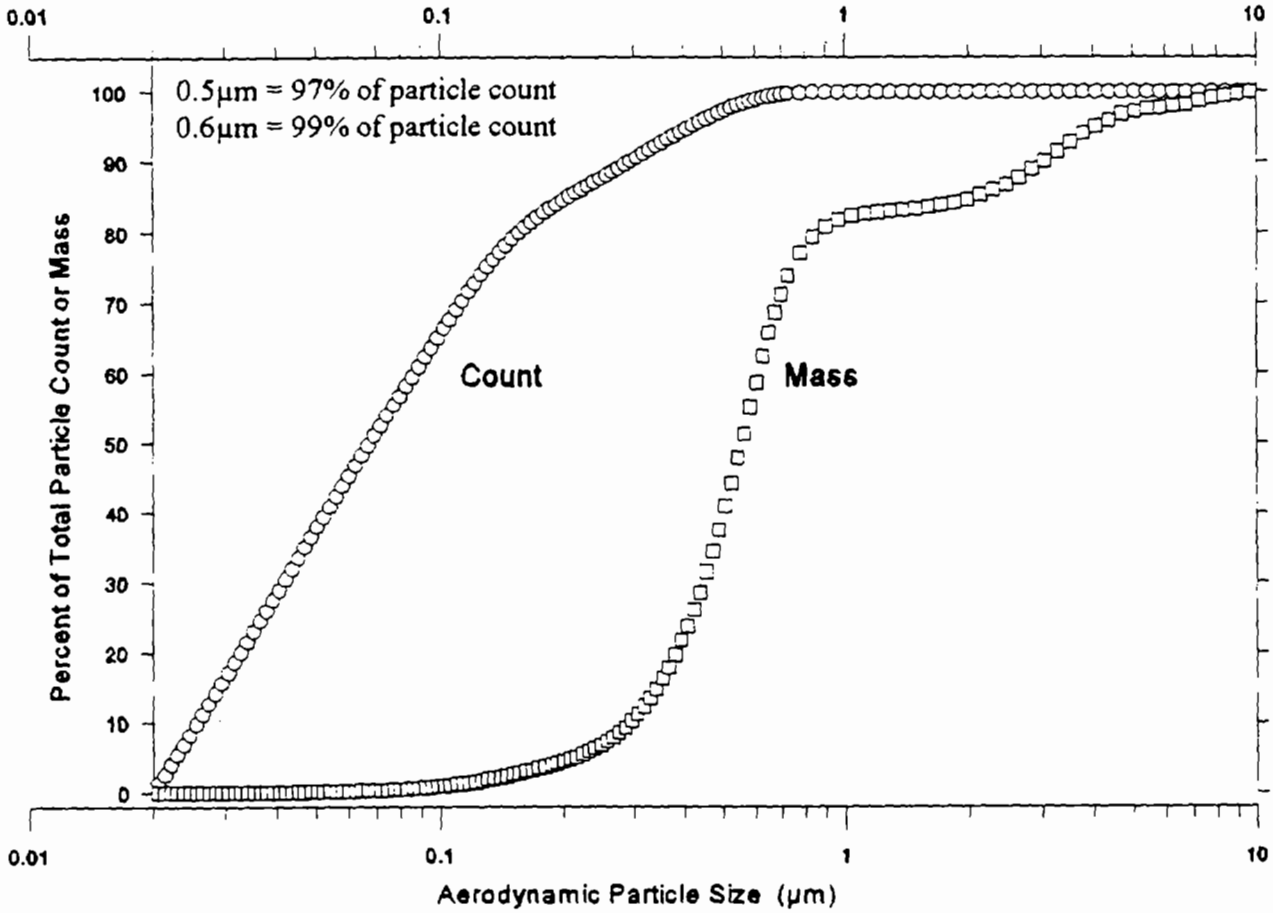

Figure 4. Typical Distribution of Cumulative Particle Counts and Mass, 0.02 to 10 µm (RH = 85%).

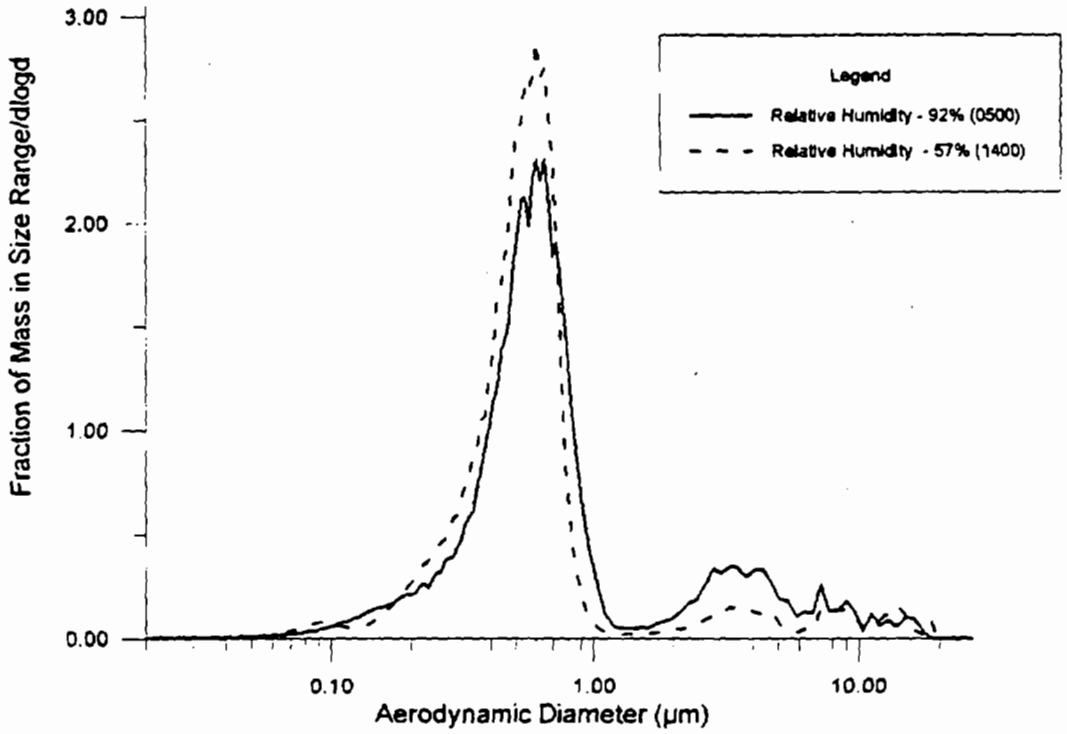

Figure 5. Typical Distribution of Particle Mass, 0.02 to 10 µm. Aerodynamic Diameter