Urban Air Monitoring Strategy – Preliminary Results Using Aethalometer™ Carbon Measurements for the Seattle Metropolitan Area

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ABSTRACT

Air toxics assessments performed for the Seattle Metropolitan Area suggest that Diesel Particulate Matter and Wood Smoke pose significant health risks to our community. Using data from the Washington State Department of Ecology's Beacon Hill National Air Toxics Trends and Assessments (NATTS) site and a small network of Aethalometers™, we measured black carbon (BC) at two sites in Seattle. We used a standard operating procedure comparable to the Draft Technical Assistance Document for the NATTS program. Initial efforts focused on determining the suitability of the Aethalometer™ method for use in ambient conditions by comparing 24-hour averages to the PM 2.5 Speciation Elemental Carbon (EC) method and by correlating the Aethalometer™ continuous data with other PM 2.5 continuous methods. Preliminary analysis indicates that hourly BC measurements have exhibited the temporal patterns that we expected based on local knowledge of traffic patterns. BC measurements have correlated with other PM 2.5 continuous monitors including the Nephelometer and the Tapered Element Oscillating Microbalance (TEOM). Average daily BC measurements have correlated with collocated speciation samplers monitoring for Elemental Carbon and the Federal Reference Method for PM 2.5. The network has been supplemented by two additional Aethalometers that are now sited in locations where wood smoke is present during winter months. Initial analysis indicates that hourly BC and Ultraviolet (UV) measurements exhibit the distinctive patterns that we would expect due to wood burning during the winter. Additionally, initial analysis seems to indicate that the relative quantities of BC versus UV absorption could potentially assist in differentiating between the WS and the other components of BC. BC and UV data could potentially be used as indicators to develop sound scientific risk reduction strategies.

INTRODUCTION

Diesel particulate matter (DPM) and wood smoke (WS) are combustion mixtures that include unknown amounts of black carbon (BC). BC includes particles from other combustion sources as well. On average, diesel soot accounts for somewhere between 70 to 85 percent of the total cancer risk from air toxics in our area.[1] According to source apportionment studies, WS is also a significant contributor to the fine particulate aerosol throughout the Puget Sound.[2]

BC has physiological effects including the ability to adsorb other species, such as air toxics. These particles are small enough to penetrate the human pulmonary system, by-passing protective mechanisms in the nose and throat and causing substantial accelerated mortality. BC also has a large optical absorption cross-section.[3] The large optical absorption cross-section causes the extinction of IR, visible radiation, and heat absorption into the atmosphere. This leads scientists to suspect BC of causing reduced visibility and contributing to global warming.[4]

The Puget Sound Clean Air Agency monitors BC by using a Magee Scientific, Inc. Aethalometer™. The Aethalometer™ is a tape sampler that takes in air at a controlled flow rate, and then passes the air through a special glass fiber filter tape. As the pollutant accumulates, the Aethalometer™ measures the attenuation of light at two channels. The BC channel is at 880 ηm and the UV channel is at 370 ηm. The light attenuation has been assigned a calibration factor that converts the attenuation information into Micrograms per Cubic Meter ($\mu g/m^3$). While the assignment of this calibration factor has been quantified in the case of the BC channel, the UV channel calibration is not easily quantified due to the absorption cross-section variability of the hydrocarbon compounds found at 370 ηm.[5] Consequently, UV data is qualitative and not quantitative. A 5-minute average is determined for both channels and then recorded onto a data disk, which is replaced periodically. We review, validate, and archive the data.

Standard Operating Procedures were used in conjunction with the EPA Draft Technical Assistance Document for the NATTS program, the Magee Scientific Operator Guide, and the Washington State Department of Ecology (WA DOE) Aethalometer™ Procedure. In December of 2003, we installed a PM2.5 (particulate matter with an aerodynamic diameter less than 2.5 microns) head onto the inlet hose in order to comply with the newly approved WA DOE Aethalometer™ Procedure. Research indicates that this change is insignificant because optical absorbance is most significant in particles less than .3 microns in size.[6] Additionally, we conducted informal experiments that indicated no change to the data after the PM 2.5 head was installed. Based on our experience, the only advantage to having a PM 2.5 head on this device is the prevention of mechanical tape advance problems associated with water, insects, or pollen impingement.

EXPERIMENTAL METHODS

Our goal was to monitor impacts of BC in areas where either DPM or WS would be the main source contributor to the fine particulate aerosol. The first step was to determine suitability of the Aethalometer™ method. During the Environmental Technology Verification of the Aethalometer™, the correlation between BC Aethalometer™ method and the TOR (thermal/optical reflectance) method for EC measurement was used. Using this test result as the benchmark, we measured our own BC vs EC correlation. The second step to achieving our goal was to site the Aethalometers™ in strategic locations where we had the opportunity to use factual data, historical monitoring data from other methods, and observational data gathered over many years to set expectations regarding the temporal patterns that we would see in the BC data.

In conjunction with the National Air Toxics Trend network, WA DOE sited an Aethalometer™ at their Beacon Hill Site that began operating in January 2003. This site is representative of the urban neighborhood scale in the Seattle area and is considered the Urban Background site in our study. This site is also a fine particle speciation trends site and provides EC and OC data. It is located at a reservoir in the Beacon Hill neighborhood with sources typical of a Seattle neighborhood scale present.

The Industrial/Arterial site is located in the heart of the Duwamish valley, with a variety of major particulate sources including Highway 99, which is a common arterial for diesel truck traffic in and out of the Port of Seattle. Approximately 70,000 vehicles per day drive by this site[7], many of which include diesel trucks. Our expectation was that the mobile sources present here would produce the highest levels of BC during the period between 7:00 AM and 6:00 PM when the Port of Seattle is most active. We expected to find that on Sundays, inactivity at the Port of Seattle would cause Sunday averages to be less than the rest of the days of the week. The Industrial site Aethalometer™ was operational October 2002. This neighborhood scale site is considered the maximum fine particle concentration site in Washington State. Speciation sampling and a suite of continuous fine particle sampling is performed at the Industrial/Arterial site.

The Freeway site is located on top of a two-story apartment building located about 20 meters from I-5 in downtown Seattle. This micro scale/middle scale site is dominated by the freeway. Over 200,000 vehicles drive by this site per day.[8] We expected to see the highest levels of BC during rush hour traffic peaks surrounding the hours of 8:00 AM and 5:00 PM. We expected to find that typical light traffic on Sundays would cause Sunday averages to be less than the rest of the days of the week. The Freeway Aethalometer™ was operational January 2003. Impacts from industrial sources or from wood smoke are believed to be minimal at this site. Speciation and continuous fine particles data are collected at this site.

The two wood smoke sites (Wood Smoke North, and Wood Smoke South) were not operational until December 2003. Wood smoke is a significant area source in the aerosol during the winter months and is most prevalent during evening and midnight hours. We expected to see the highest levels of BC between the hours of 6:00 PM and 6:00 AM. The north site is proximate to several suburban arterials where we also expected to see impacts from mobile sources. Due to the strong seasonal signature of wood smoke, a fuller understanding of the aerosol will be achieved when more data has been collected.

Comparing the data to our expectations was extremely challenging because of the meteorology and the inconsistent nature of the WS sources. In cases where we analyzed data, we attempted to choose periods of time where meteorology was similar and constant for multiple days in a row at multiple locations. We found that stagnant periods gave us the best opportunity to analyze the data. Additionally, we chose to utilize other particulate methods to gather insight into the BC data. For example, to objectively evaluate our BC data, we correlated the data with other PM 2.5 methods such as the FRM (Federal Reference Method for PM 2.5), the TEOM (Tapered Element Oscillating

Microbalance) and the Nephelometer. Our experimental design had three main objective tests including:

- BC correlation with EC
- BC temporal patterns matching our expectations
- BC data correlating with other PM 2.5 sensors

In addition to our experimental design, in this text we are documenting our initial observations regarding the potential usefulness of the Aethalometer™ UV channel with respect to WS.

RESULTS AND DISCUSSION

BC Correlation with EC

Figure 1. PM 2.5 Speciation Sampling Elemental Carbon Parameter vs Aethalometer BC (both methods in ug/m3) at the Industrial Site.

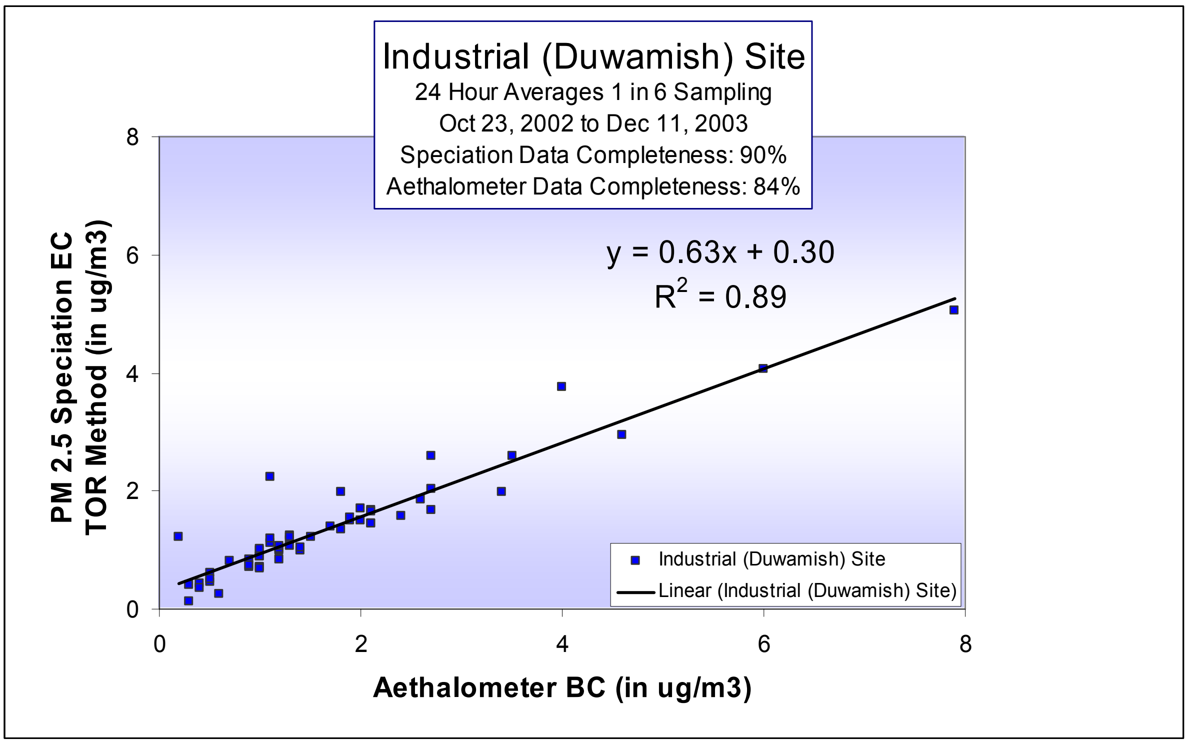


Figure 2. PM 2.5 Speciation Sampling Elemental Carbon Parameter vs Aethalometer BC (both methods in ug/m3) at the Freeway Site.

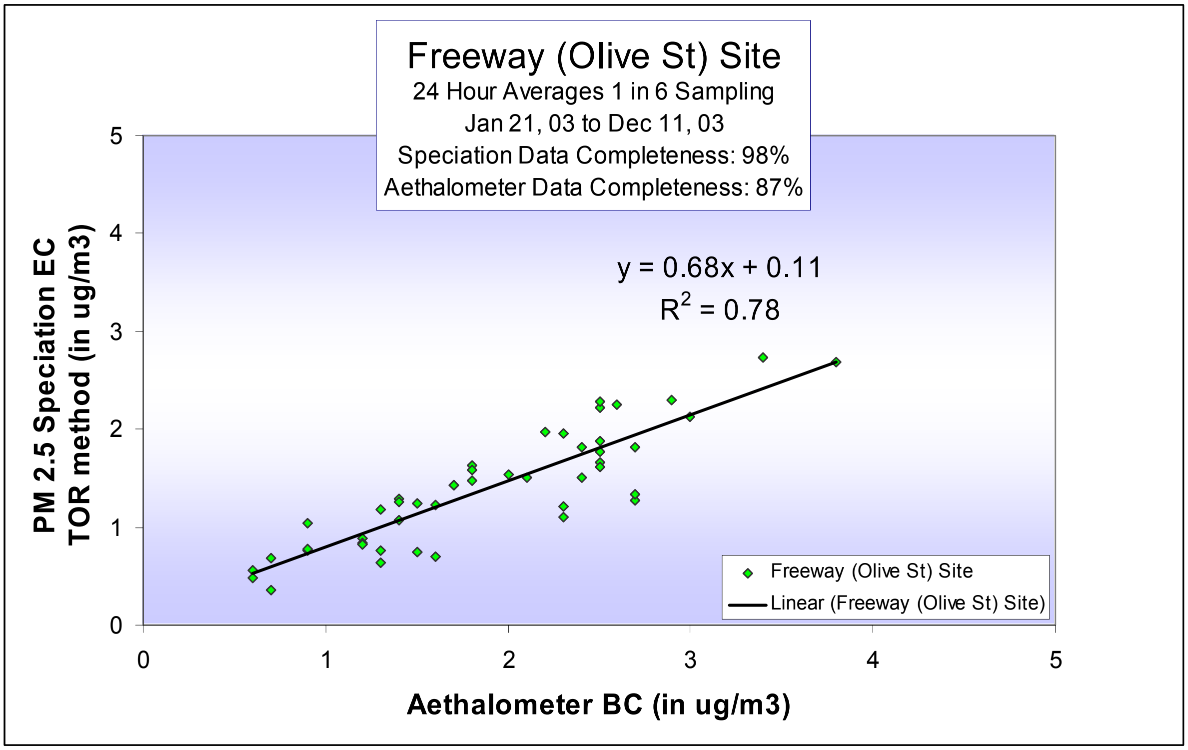


Table 1. Environmental Technology Verification Report Results, August 2001.

City	ETV Program Results	Slope	Y-Intercept	R^2
Pittsburgh, PA	Monitor 1	.815 (.280)	0	.590
	Monitor 2	.791 (.270)	0	.593
Fresno, CA	Monitor 1	.711 (.031)	.54 (.25)	.930
	Monitor 2	.735 (.031)	.47 (.25)	.934

Figures 1 and 2 show the correlation between PM 2.5 speciation EC TOR method on the y-axis versus the Aethalometer™ BC on the x-axis using the data gathered at our Industrial/Arterial site and at our Freeway site respectively. Table 1 summarizes the results of the ETV test.[9] Our Industrial site showed a slope of .63 and our Freeway site showed a slope of .68 compared to a slope ranging from .711 to .815 found during the ETV test. This shows that there was more of a bias between methods at our Industrial site and our Freeway site than what was found during the Pittsburgh and Fresno studies. It is possible that this bias is caused by either factors inherent in the method, differences in the operating procedures being used, differences in the nature of the aerosol, or a combination of these factors. At our Industrial site, $R^2 = .89$ and at our Freeway site, $R^2 = .78$ compared to $R^2 = .59$ in Pittsburgh and $R^2 = .93$ in Fresno. Our correlation coefficients compared well to those found in the Pittsburgh and Fresno studies. In general, our test compared well enough with the ETV test that we can have initial confidence in our BC method. Additional tests are needed for more conclusive validation.

Temporal Patterns

Theoretically, diesel combustion activity causes the levels of BC to increase. Some temporal patterns are illustrated in the following figures. We have seen hourly averages as high as 20 μg/m^3. In figure 3, at the Industrial/Arterial site and the Freeway site, the peaks in BC occur during the same time that the peaks in rush hour and mid day diesel truck traffic are present. Figure 3 shows evidence that our expectations were met by the Aethalometer™ in its capability to see DPM peaks as increases in the BC channel. Figure 3 also shows that at the Urban Background site, the peaks occur at these same times. We think that these peaks are smaller because the distance from the Urban Background Site to the I-5 Freeway (the closest major highway) is greater than the distance from the Industrial/Arterial site to Highway 99 and the distance from the Freeway site to the I-5 Freeway. The distances from the site to the closest highway are illustrated in Table 2.

Figure 3. One Week in July 2003. Temporal Patterns at Urban Background Site (pink), Industrial/Arterial Site (green), and Freeway Site (blue).

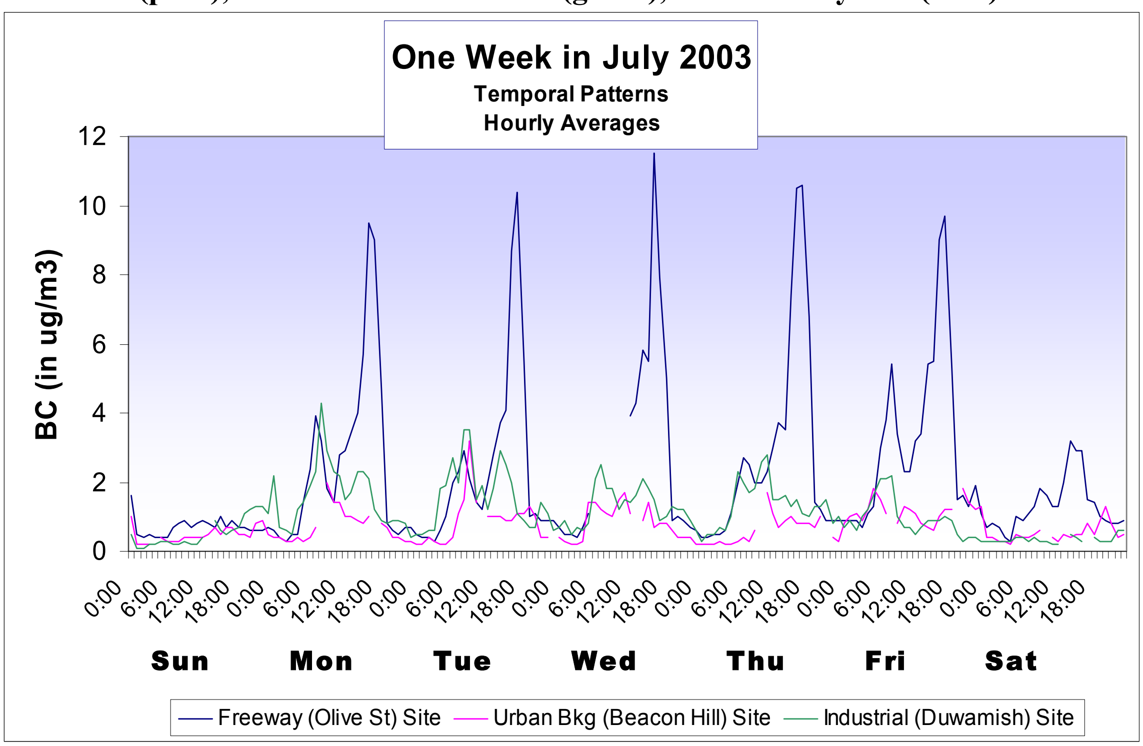


Table 2. Freeway, Urban Background and Industrial/Arterial Site Relative Distance from Closest Major Highway.

Study Site Description	Distance From	Closest Major Highway
Urban Background Site	600 Meters	Interstate 5
Industrial/Arterial Site	30 Meters	State Highway 99
Freeway Site	20 Meters	Interstate 5

We expected that due to the lack of activity in the diesel truck activity near the Industrial/Arterial Site and the Freeway Site, the BC levels on Sundays would be lower on average than the average during the rest of the week. Figure 4 shows BC data gathered during the month of April 2003 at the Freeway site. The Sundays are highlighted by a pink box. The figure clearly shows that the Sunday BC peaks are not as high as the BC peaks found during the rest of the week. Also, we performed a simple statistical analysis which showed that the mean BC daily average on Sundays during the First Quarter in 2004 was lower than the total mean BC daily averages at the Industrial/Arterial Site and the Freeway Site. This data is shown in Table 3. Significance was not calculated.

Figure 4. Freeway Site monthly BC data April 2003. Sundays are highlighted with pink boxes.

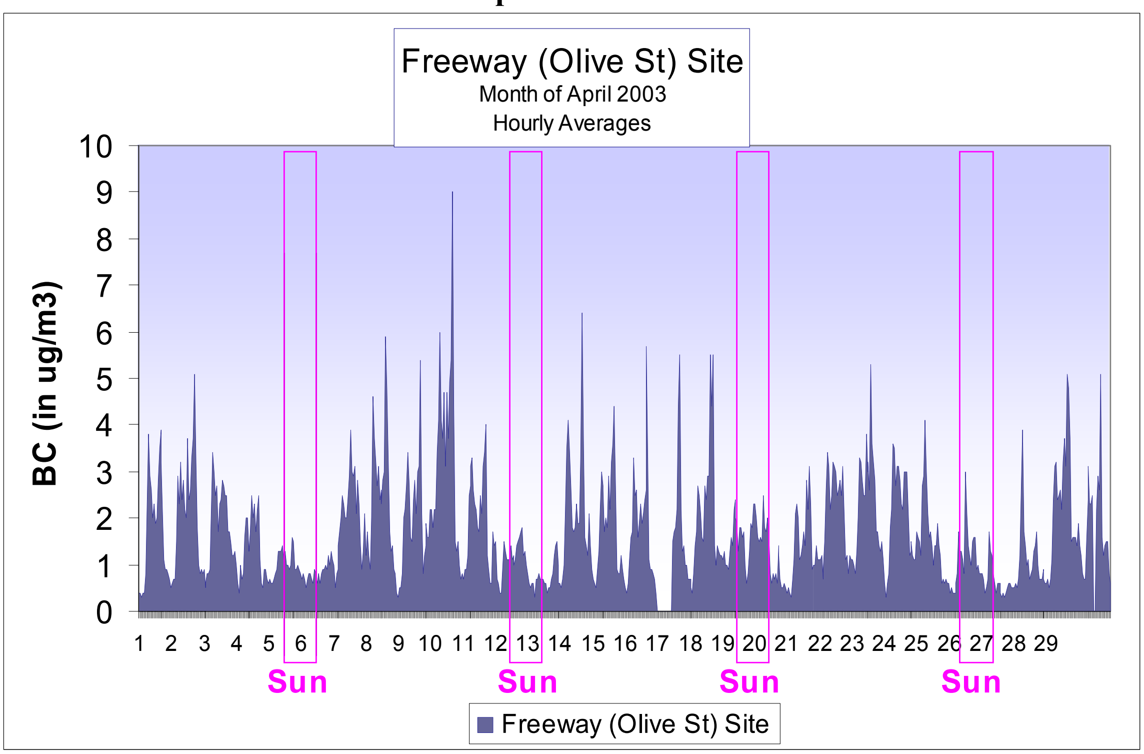


Table 3. Mean Daily BC compared with Sunday Mean BC during Q1 of 2004 for Industrial/Arterial Site and Freeway Site.

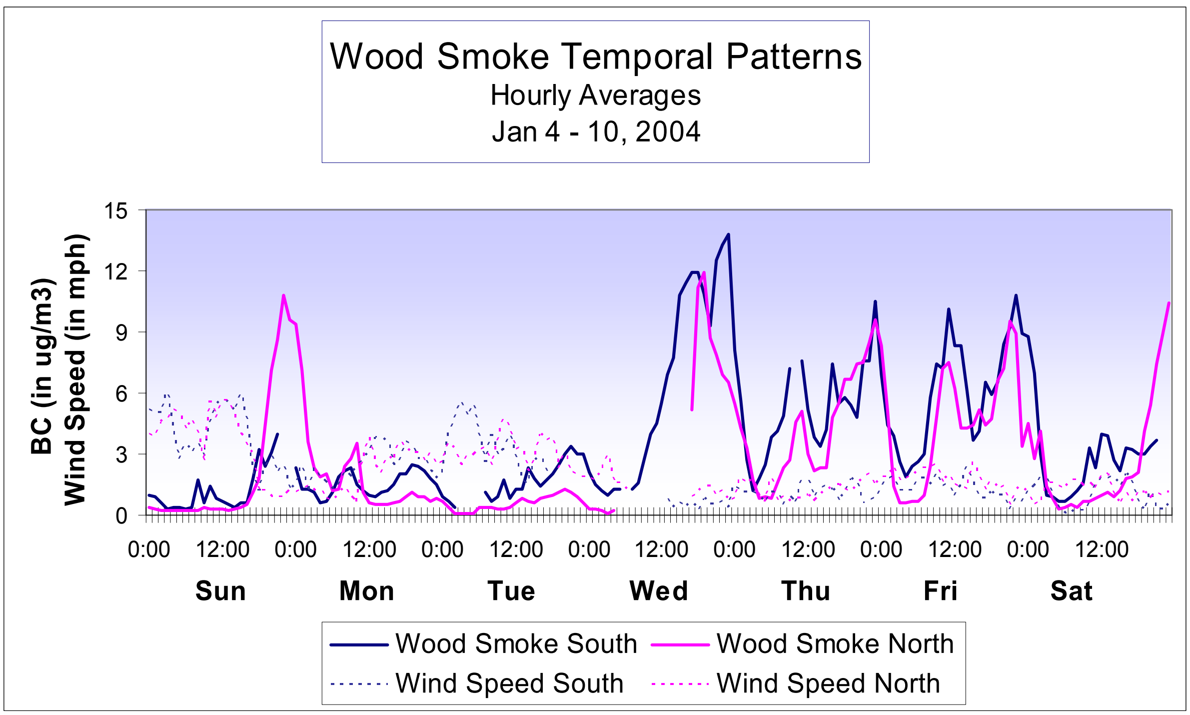
	Industrial/Arterial Site	Freeway Site
Mean Daily BC	2.50	1.94
Sunday Mean BC	1.65	1.32

Indications of Wood Smoke Temporal Patterns

We expected to see the peaks in BC at the wood smoke sites occur between the hours of 6:00 PM and 6:00 AM. Figure 5 illustrates preliminary data comparing the two wood smoke sites in the context of the wind speed at each site.

As shown in Figure 5, during periods where wind speed is consistently low, the sources present at these sites tend to build up the BC pollutant. When wind speed increases to about 3 mph or higher, the figure shows that BC levels drop rapidly. This inverse relationship between wind speed and BC level has been observed at all of our sites. The meteorology plays a significant role in the analysis because it is difficult to find periods when mixing and dispersion is inhibited for longer than a few hours.

Figure 5. Temporal BC patterns at Wood Smoke Sites during a stagnant period in January.



At both sites, we see peaks occurring both during the middle of the day (around 12:00 Noon) and during the evening hours (around 12:00 Midnight). Clearly, what we found at the wood smoke sites was not exactly the same as what we expected. The source of the mid-day peak, especially at the south site, is undetermined but may be either a function of wood smoke due to rekindling of fireplaces for daytime heating or a function of mobile sources or both. In order for us to confirm that the sources peaks are wood smoke, we will have to analyze what happens during stagnant periods at these sites in the spring and summer when wood smoke season is over.

Correlations of BC vs PM 2.5 Methods

Since BC is theoretically a part of the PM 2.5 fraction, we objectively evaluated our BC data by correlating the Aethalometer™ BC measurement with both continuous and non-continuous PM 2.5 methods. As shown in Figure 6, the correlation between the 24-hour averages of BC and the PM 2.5 Nephelometer method gave us an $R^2 = .75$. Also, the correlation between the 24-hour averages of BC and the PM 2.5 TEOM method gave us an $R^2 = .78$. Using the slopes from the regressions between BC and the Nephelometer, the TEOM, and the FRM, the data indicates that BC makes up approximately 25 to 30% of the PM 2.5 fraction. In a previously conducted study, PM 2.5 FRM filters from the Wood Smoke North site were analyzed for Carbon Mass using a Carbon 14 dating method. Based on a small data set, the indication was that the Carbon Mass made up 61.8% of the PM 2.5 fraction of the samples gathered at the WS North site.[10] Our monitoring data from the Aethalometer is significantly less and based upon a larger set of data. We have not yet attempted to account for these differences.

Figure 6. Correlation at the Wood Smoke North site between Aethalometer BC and two Continuous PM 2.5 methods.

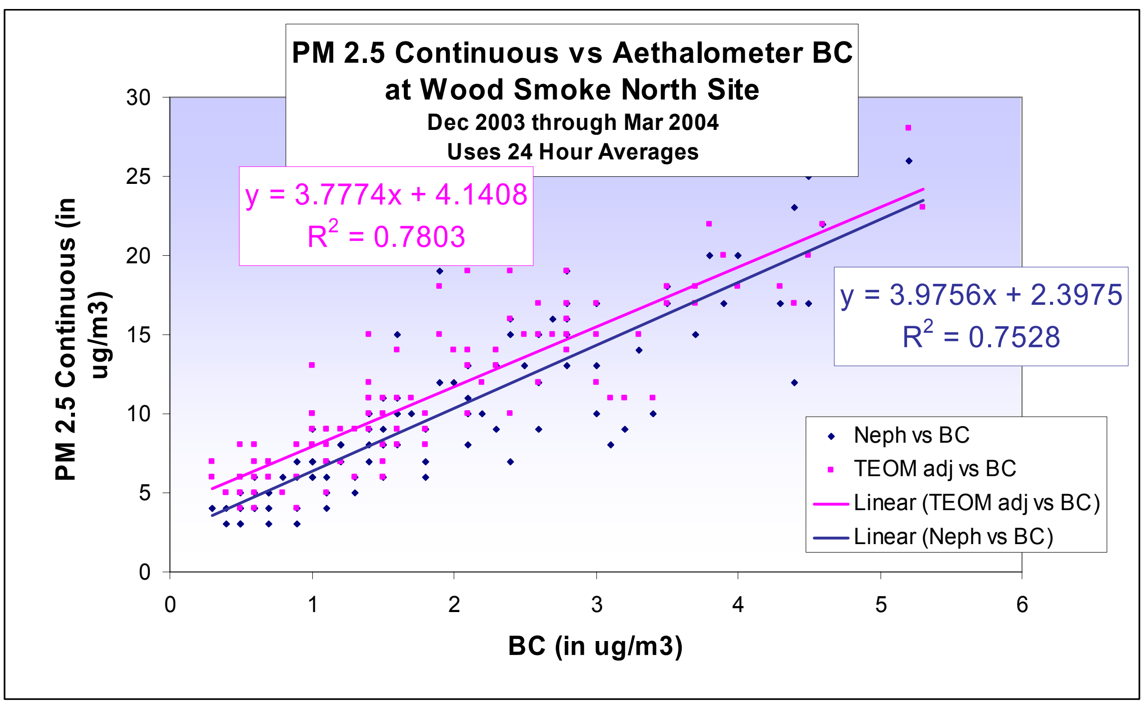


Figure 7. Correlation at the Industrial/Arterial Site between Aethalometer BC and the FRM PM 2.5 method.

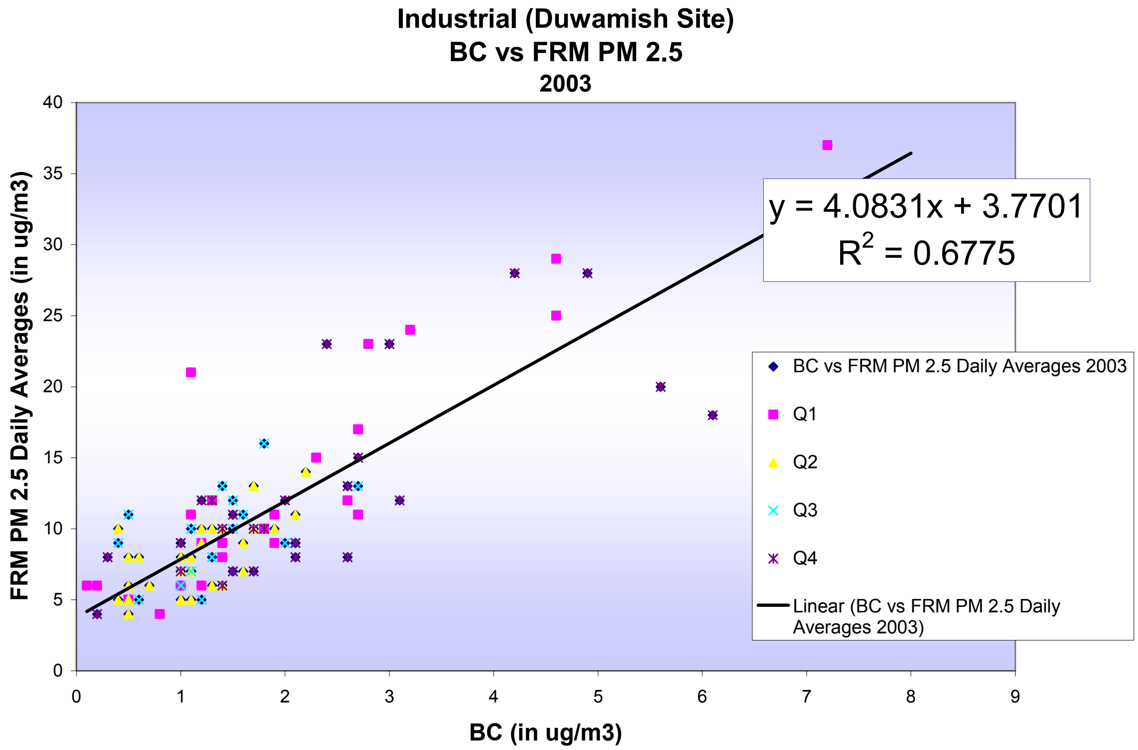
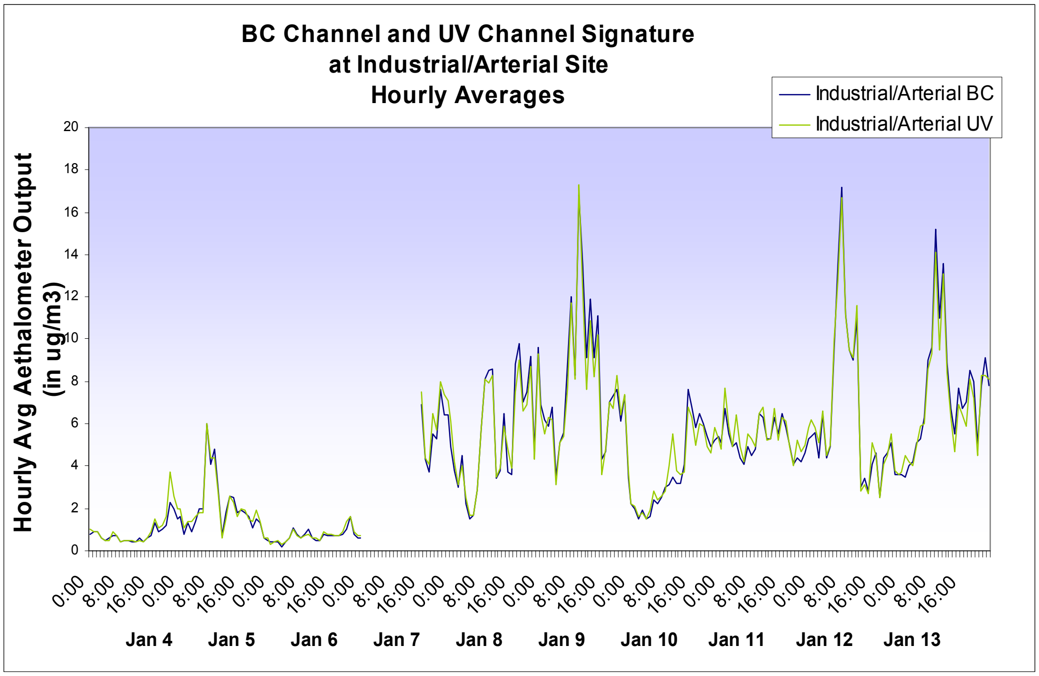


Figure 7 shows the correlation between the Aethalometer™ BC and the PM 2.5 Federal Reference Method, broken down by quarters. The slope and R^2 are similar to the graphs shown with the comparison to continuous methods. The breakdown by quarter shows that the highest values occur in the First and fourth quarter of the year. This is consistent with our typical pattern because most of the air inversions occur during winter. In general, correlations between Aethalometer™ BC and other PM 2.5 methods support the use of the BC indicator. However, BC should not be used as a substitute for PM 2.5 monitoring due to lack of strong correlation. BC is a variable subset of PM 2.5. Additional work would need to be performed in order to assess the extent of this variability.

Other Initial Observations Regarding the Aethalometer™

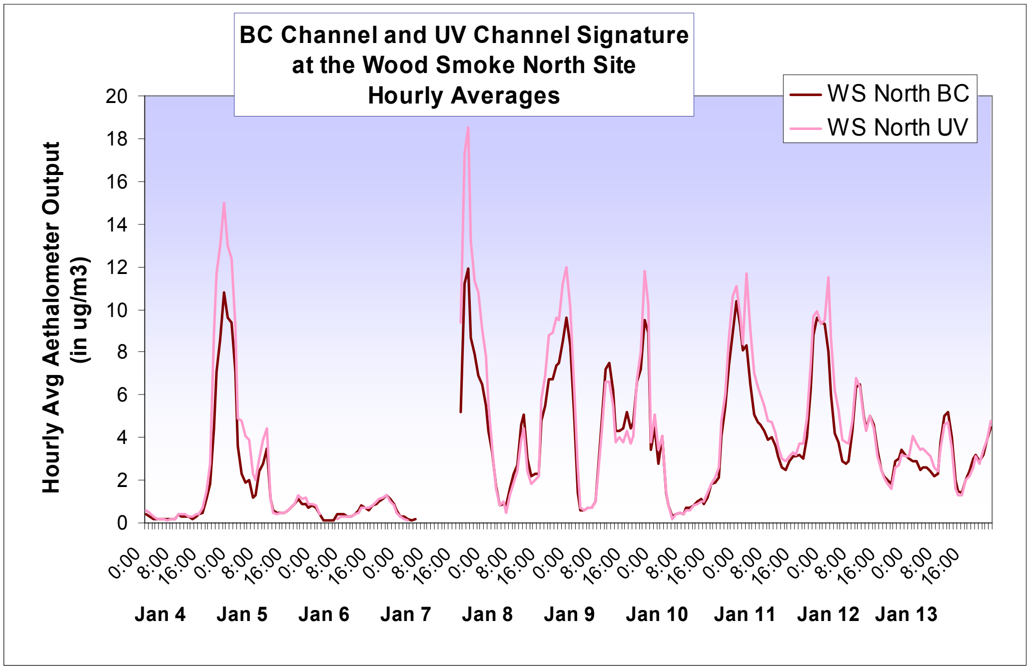
Use of the Aethalometer™ UV channel is currently under investigation. Our hypothesis is that the UV channel can potentially be used as a marker for the presence of WS in the local aerosol. We compared initial data from two sites to determine if we would find differences in the UV channel patterns. Although we need to gather additional data to confirm this hypothesis for the Seattle area, we have some initial observations that seem to indicate that this hypothesis might be true. The WS indicator has been described as data where the UV channel is significantly greater than the BC channel.[11] Figure 8 shows both the BC and UV channels for the Industrial/Arterial Site. At this site, we would not expect WS to be a major contributor, so we would expect to see the UV and BC channels tracking together, and we would see peaks in the middle of the day. In fact, this is what we do see from this data set.

Figure 8. BC & UV channel Data from the Industrial/Arterial Site in January 2003



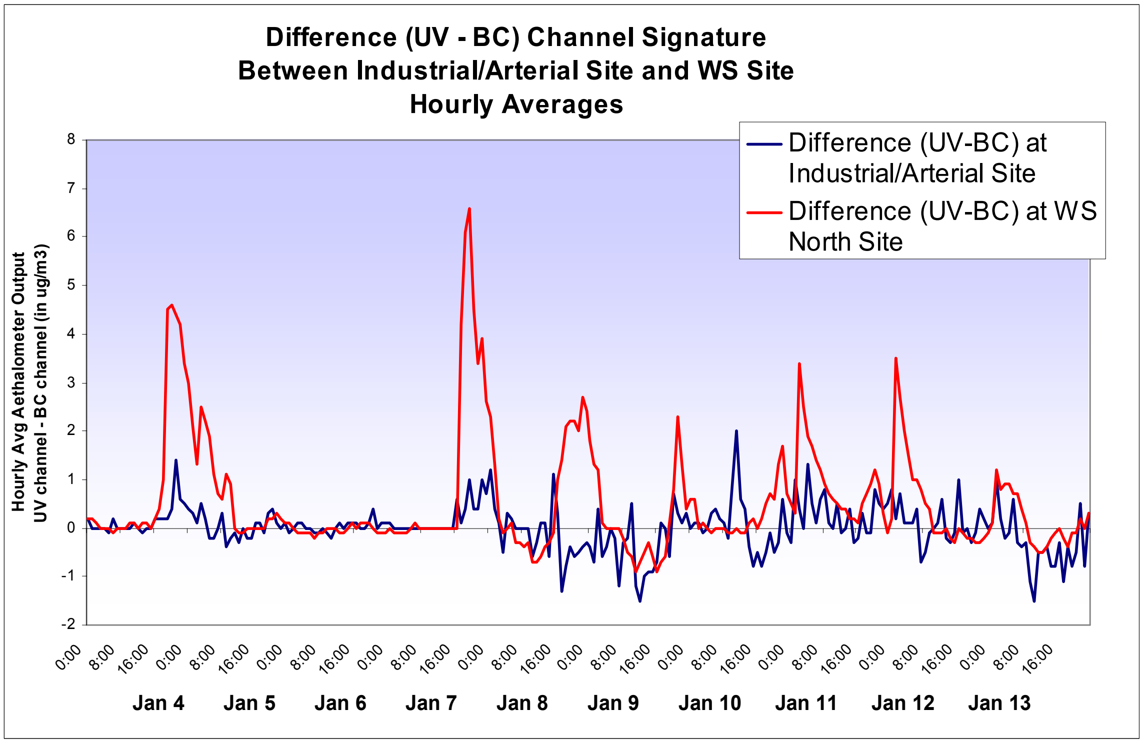
At our WS North Site, we would expect to see periods between the hours of 6:00 PM and 6:00 AM where the UV trace is significantly higher than the BC trace. Also, we would see the BC peaks during the hours between 6:00 PM and 6:00 AM. This is what we see.

Figure 9. BC & UV channel Data from the Wood Smoke North Site in January 2004



In order to quantify the UV trace as it compared to the BC trace, we graphed the Difference parameter over the same period of time to find out what the peaks looked like. Figure 10 shows the Difference parameter (UV channel – BC channel) over the same period of time for the Industrial/Arterial Site and the Wood Smoke North Site. The hypothesis would suggest that the peaks in the Difference parameter would be shown in the WS trace more than the Industrial/Arterial trace, and that they would be seen between the hours of 6:00 PM and 6:00 AM. In fact, this is what we do see.

Figure 10. Difference (UV – BC) Signature Between Industrial/Arterial and WS Site



In order to calculate the magnitude of this difference, we took the mean hourly readings and averaged them over four time periods of the day. Between the hours of 6:00 PM and 6:00 AM, we expected the WS signature to be present at the WS North site. Between the daylight hours, we expected a much smaller WS signature to be present at the WS North site. We expected a smaller WS presence to be noticed at the Industrial/Arterial site. Table 4 illustrates that we found that between the hours of 18:00 and 06:00, the UV was higher on average (1.2667 and .787 respectively) than 06:00 to 18:00 (.115 and .035 respectively). We also found that at the Industrial/Arterial site, the evening mean differences were greater than zero while the daytime mean differences were less than zero. This could indicate that there is some wood smoke being detected at the Industrial/Arterial site. This initial data does not conclusively prove the hypothesis that the UV channel can potentially be used as a marker for the presence of WS in the local carbon aerosol. However, it does give us initial indications that this may be true. Additionally, we can now more effectively design experiments which are better suited to prove or disprove this hypothesis.

Table 4. Mean Difference (UV – BC) signature by Site and by Time (in µg/m^3)

Time	Industrial/Arterial Site	WS North Site
00:00 to 06:00	0.139	0.787
06:00 to 12:00	-0.062	0.115
12:00 to 18:00	-0.145	0.035
18:00 to 24:00	0.102	1.2667

CONCLUSIONS AND NEXT STEPS

The Aethalometer™ appears to be a good indicator that can be used with other tools to more comprehensively understand the BC component of the PM 2.5 fraction. This data set was gathered in an urban ambient air network. This implies that other urban areas could potentially use this method in their networks successfully. For this method to become more accepted, work needs to be continued in developing successful operating procedures and instrument design features that maximize the instrument's precision and accuracy.

Preliminary results indicate that this method could be a tool to help us understand how to monitor more effectively for WS. Along with BC monitoring, speciation samplers and/or open path monitors may be used as a next step in understanding the patterns associated with WS. More resources, research, and data are needed to fully understand this problem.

The hypothesis that the UV channel could potentially be used for identifying sites where WS is present needs to be challenged by continuing work in this area. Incorporating organic carbon (OC) data from the speciation network is an important element in furthering our understanding of the WS issue. We intend to compare our results with results from data gathered this spring and summer when wood smoke season is over.

We need to continue work correlating our BC measurements with other PM 2.5 devices. It would be very useful if we could understand the BC variability as a component of the PM 2.5 fraction.

In order to more specifically relate BC temporal patterns to diesel and other mobile sources, additional traffic data and statistical analysis is needed. We expect to begin this work in May 2004.

The data and initial conclusions suggested in this paper do not indicate that the Aethalometer™ is the silver bullet. Rather, the Aethalometer™ represents a very useful method of gathering highly resolved temporal data that can be used to help indicate patterns and potential quantities of BC in our urban environment.

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KEY WORDS

black carbon
Aethalometer
elemental carbon
PM 2.5
particulate carbon
diesel particulate matter
wood smoke
Magee Scientific