

APPENDIX VI

MATES IV

FINAL REPORT

Black Carbon Measurements at Fixed Sites

Authors

Payam Pakbin

Andrea Polidori

Appendix VI Black Carbon Measurements at Fixed Sites

VI.1 Introduction

A common goal of the MATES studies is to identify and quantify health risks associated with major known toxic air contaminants within the South Coast Air Basin (SCAB). In the MATES III study, diesel particulate matter (DPM) was identified as one of the major contributors to carcinogenic risk due to exposure to air toxics, accounting for 84% of the total carcinogenic risk (SCAQMD MATES III Report, 2008). Diesel particulate emissions are primarily in the $PM_{2.5}$ size range and are mostly comprised of impure carbon particles (soot) resulting from the incomplete combustion of diesel-type fuels and is often emitted along with other combustion products such as organic carbon (OC) and trace amounts of inorganic compounds (Abu-Allaban, 2004; Lloyd, 2001). The OC fraction contains mostly heavy hydrocarbons from lubricating oils and low volatility PAHs. Soot is often referred to as black carbon (BC) or elemental carbon (EC) depending on the measurement method used. The presence of high fractions of EC and BC within diesel exhaust is a unique property of this combustion source; therefore in urban areas, EC and BC are often considered good surrogates for DPM (Schauer J. J., 2003). While the major source of EC and BC in an urban area is from diesel-powered vehicles, non-road mobile machinery, ship emissions, residential heating (such as wood burning stoves) and open biomass burning (e.g. forest fires or burning of agricultural waste) also contribute to the observed levels. For example, in some areas of the world, residential burning of wood or coal, or open biomass burning from wildfires, may be even more important sources of BC. In industrial regions, harbors and industrial facilities may have a pronounced effect on BC concentrations. Although EC and BC are currently unregulated, the implementation of national, state and local regulations and programs to mitigate fine PM (i.e. $PM_{2.5}$) and the toxic impacts of diesel emissions often result in the control of EC and BC.

Soot consists of agglomerates of small roughly spherical elementary carbonaceous particles that are emitted directly into the atmosphere predominantly during combustion processes along with some organic carbon (OC). Soot particles absorb organic vapors when the combustion byproducts cool down, thus accumulating significant quantities of potentially toxic organic compounds. While soot may not be a major direct toxic component of fine particles ($PM_{2.5}$), it may operate as a universal carrier of a wide variety of chemicals that cause adverse health effects.

Various analytical methods have been developed to quantify the concentration of atmospheric soot particles. Depending on the measurement method used, the non-OC fraction of soot is referred to as BC or EC. Unlike OC, which is both emitted from primary sources (primary OC) and formed in the atmosphere from chemical reactions involving low-volatility precursors (secondary OC), BC (and EC) is only emitted directly into the atmosphere from combustion processes. Measurements of EC and BC are defined by the method of analysis. Soot can be analyzed by several different methodologies. When its light-absorbing properties are measured, soot is often referred to as BC. When its concentration is measured by thermal or thermal-optical techniques however, it is generally referred to as EC. A significant advantage of monitoring BC by absorption photometry is that it delivers results in real time with a high time resolution (e.g. minutes). The absorption properties of BC are the reason it is considered a short-lived climate forcer, and thus this type of measurement is relevant for climate impact assessment.

Laboratory-based EC methods can be time consuming as soot is sampled on a filter and then subsequently analyzed in a laboratory. These methods do not necessarily yield directly comparable results, although they are generally correlated (Chow, 2001).

The measurement of optically-absorbing material on a filter is performed by Aethalometers. This optical method measures the attenuation of a light of a specific wavelength that is transmitted through a sample collected on a quartz fiber filter, while the filter is continuously collecting ambient aerosols. The measured attenuation is proportional to the mass of BC in the filter deposit. This measurement is affected by the wavelength of the light with which it is made. By using the appropriate value of the specific attenuation for that particular combination of filter and optical components, the concentration of the BC content of the aerosol deposit can be determined at each measurement time.

In the most common thermal analysis EC methods, the particles are collected on a quartz fiber filter. OC can be volatilized and separated from the sample deposit by heating the sample in a non-oxidizing/inert helium (He) atmosphere. EC is also oxidized by raising the temperature and introducing oxygen. The combusted compounds are then converted to CO₂ using manganese dioxide (MnO₂) as the oxidizer. Subsequently CO₂ is converted to methane (CH₄), and the concentration of CH₄ is quantified with a flame ionization detector (FID).

Both optical and thermal measurement techniques are important and complement each other. However, a significant advantage of monitoring BC by absorption photometry is that it delivers results in real time with a high time resolution (minutes), in contrast to measuring EC by a time-consuming analytical method where soot is sampled on a filter and then analyzed. Field deployable versions of the EC/OC methods that provide real-time semi-continuous are also available, but require more maintenance than Aethalometers. Therefore BC measurements are suitable for deployment in monitoring networks for health impact and trend analyses.

VI.1.1 Health Effects Associated with BC

In the U.S., the mass concentration of PM_{2.5} and PM₁₀ currently serves as the regulatory metric for population exposure to ambient particles. EPA, however, recognizes that it is highly plausible that the chemical composition of PM would be a better predictor of health effects than the particle size alone (U.S. EPA, 2009b, 6-202). The focus of the scientific community on trying to identify the health impacts of particular PM constituents (or group of constituents) associated with specific source categories of particles (Janssen et al., 2011; Ostro et al., 2010) has provided evidence of effects associated with exposure to BC, among other PM constituents (Pope et al., 2009). Consequently, research and data collection activities focused on particle composition could improve our understanding of the relative toxicity of different particle constituents associated with specific sources to inform future regulatory activities and benefit assessments.

BC is a component of both fine and coarse PM (PM_{2.5} and PM_{2.5-10}, respectively); however, these two PM size fractions can have substantially different sources and sinks. Therefore, their fractions can be composed of varying chemical species contributing to potentially different health outcomes. Coarse particles arise predominantly from mechanical processes including windblown soil and dust (mostly containing iron, silica, aluminum and base cations from soil), sea salt and bio-aerosols such as plant and insect fragments, pollen, fungal spores, bacteria and

viruses, as well as fly ash, brake lining abrasion and tire wear. Fly ash, brake lining abrasion and tire wear are associated with urban and industrial activities and often contain BC. Fine particles, on the other hand, primarily originate from combustion activities and from gas-to-particle conversion processes in the atmosphere. BC is known to be an important contributor to the total $PM_{2.5}$ mass. Generally, combustion-related particles are widely thought to be potentially more harmful to human health than PM that is not generated from combustion.

Regulation of $PM_{2.5}$ and PM_{10} concentrations in the U.S. during the past two decades has resulted in significant declines in PM concentrations. However, $PM_{2.5}$ remains a significant risk factor for public health considering that many areas of the country are still in non-attainment for the $PM_{2.5}$ National Ambient Air Quality Standards (NAAQS). While BC is currently unregulated, as a component of $PM_{2.5}$, control of BC emissions is also beneficial for attaining the PM mass-based concentration standards.

There are not enough clinical or toxicological studies to allow for an accurate evaluation of the differences between the health outcomes from exposure to BC or PM mass, or of identification of any distinctive mechanism of BC effects. Distinguishing between the effects of highly correlated air pollutants (i.e. pollutants from the same sources such as BC, PM, VOCs, CO and other combustion products) is always challenging because of inherent problems caused by multi-co-linearity in statistical models. A review of the results of all available toxicological studies suggested that BC itself may not be a major toxic component of $PM_{2.5}$, but it may serve as a carrier of a wide variety of, especially combustion-derived, chemical constituents of varying toxicity to sensitive targets in the human body such as the lungs, the body's major defense cells and possibly systemic blood circulation. In urban areas such as Southern California, BC (and EC) is considered as a tracer for diesel PM, which is the most important contributor to the carcinogenic risk due to air toxics exposure in the South Coast Air Basin.

VI.1.2 Climate

BC is one of the major anthropogenic components of atmospheric particles, and has significantly different optical and radiative properties compared to the other PM constituents. It is the most effective form of PM, by mass, at absorbing solar energy and can absorb a million times more energy than carbon dioxide (CO_2) per unit mass. There is a general consensus within the scientific community that BC is contributing to climate change globally and regionally. BC influences climate through multiple mechanisms, directly and indirectly. Direct radiative forcing by BC is caused by absorption and scattering of sunlight. BC contributes to warming of the atmosphere by absorbing both incoming and outgoing radiation of all wavelengths (in contrast to greenhouse gases (GHGs), such as CO_2 that mainly trap outgoing infrared radiation from the Earth surface) which in turn heats the atmosphere where the BC is present.

BC also deposits on snow and ice significantly reducing the total surface *albedo* available to reflect solar energy back into space, thereby increasing energy absorption and accelerating ice melting. Furthermore, BC can affect the climate indirectly, like other atmospheric particles, by altering cloud formation, distribution, reflectivity and lifetime. BC influences the properties of clouds through diverse and complex processes, including changing the number of liquid cloud droplets and altering the atmospheric temperature structure within the cloud, which consequently alters cloud distributions. These effects may have either negative or positive climate forcings. Thus, the climate effects of BC via interaction with clouds are more uncertain, and their net

climate influence is an open subject of research.

Other than different mechanisms by which BC and long-lived GHGs affect climate, one of the distinguishing differences between BC and other GHGs is due to the relatively short atmospheric lifetime of BC (days or weeks as opposed to years or decades). BC concentrations respond quickly to reductions in emissions because BC is rapidly removed from the atmosphere by dry and wet deposition. Consequently, targeted strategies to reduce BC emissions can be expected to provide immediate results that could reduce global climate forcing from anthropogenic activities in the short term and slow the associated rate of climate change (Bond, Doherty, 2013; Molina, et al. 2009; Ramanathan and Xu, 2010). While reduction in GHG emissions is necessary for limiting climate change over the long-term, it will take much longer to influence atmospheric concentrations and will have less impact on climate on a short timescale. Accordingly, mitigation of BC emissions from on-road and off-road (e.g. agricultural, construction and other diesel-engine mobile equipment) diesel sources may have the best potential to reduce near-term climate forcing, as well as reducing public exposure to toxic air contaminants.

VI.2 BC and EC Measurements during MATES IV

The Aethalometer continuous measurements were carried out at all 10 fixed MATES IV locations from July 2012 until the end of June 2013 or beyond. Only data collected from July 1, 2012 through June 30, 2013 have been used for the present report. Monthly-averaged ambient data from samples collected at all fixed MATES IV sites [West Long Beach (W LB), North Long Beach (N LB), Compton (COMP), Huntington Park (HNPK), Pico Rivera (PICO), Central Los Angeles (CELA), Burbank (BURK), Inland Valley San Bernardino (IVSB), Rubidoux (RUBI), and Anaheim (ANAH)] were used. Details of the sites, their characteristics and sampling protocols are given in Chapter 2 of MATES IV.

VI.2.1 Black Carbon Measurements

The Aethalometer (Magee Scientific, Berkeley, CA) is an instrument which collects airborne particulate matter on a filter while continuously measuring the light transmission through the filter. Aethalometers are small, reliable and easy to use, provide continuous real-time measurements and are the most common instruments used to measure BC. The operating principles of the Aethalometer are described in detail elsewhere (Hansen, et al., 1984). Briefly, this instrument utilizes light-absorbing properties of BC-containing particles in order to gain a light absorption coefficient. This coefficient can be translated into a unit that measures particulate BC mass.

During MATES IV, aerosol particles were sampled through a ¼" inlet with a PM_{2.5} cyclone with a sampling flow rate of 5 L.min⁻¹. The Aethalometers were operated in air-conditioned trailers. Typical maintenance operations include flow rate calibration, zero tests, filter taper replacement (once every two weeks in locations with high BC concentrations), and cleaning.

One drawback of this measurement method, inherent in all filter-based photometers, is the non-linearity of the measurements due to PM loading on the filter media, which reduces the sensitivity of the measurements. The Aethalometer relies on measurements of light transmission through the collection filter; this needs to be post-processed to obtain ambient aerosol absorption coefficients which are then converted to BC concentrations. Numerous studies have focused on

developing methodologies to correct the Aethalometer non-linearity and the Aethalometer model AE33 performs the correction automatically.

VI.2.2 Elemental Carbon Measurements

OC and EC are determined by thermal-optical analysis of integrated PM samples collected over a period of 24 hours. It should be noted that there are several different protocols to measure OC and EC, and results may differ by up to a factor of 2 (Health Effects Institute (HEI) 2010). This means extra caution is required when comparing EC measurements from different studies, or when comparing BC and EC measurements. Currently, 24-hr integrated EC concentrations are available for regional and urban monitoring sites throughout the U.S. Interagency Monitoring of Protected Visual Environments (IMPROVE) Network and the U.S. Environmental Protection Agency Chemical Speciation Network.

In the MATES IV Study, the EC concentrations were quantified using DRI Model 2001 Thermal/Optical Carbon Analyzer using IMPROVE_A thermal protocol. The operation of the DRI Model 2001 Thermal/Optical Carbon Analyzer is based on the preferential oxidation of organic carbon (OC) compounds and elemental carbon (EC) at different temperatures. Its function relies on the fact that organic compounds are volatilized from the sample deposit in a non-oxidizing helium (He) atmosphere, while elemental carbon is combusted by an oxidant, in this case oxygen. The analyzer operates by: 1) liberating carbon compounds under different temperature and oxidation environments from a small sample punch of known surface area taken from a quartz-fiber filter; 2) converting these compounds to carbon dioxide (CO₂) by passing the volatilized compounds through an oxidizer (heated manganese dioxide, MnO₂); 3) reducing CO₂ to methane (CH₄) by passing the flow through a methanizer (hydrogen-enriched nickel catalyst); and 4) quantifying CH₄ equivalents with a flame ionization detector (FID).

The principal function of the optical (laser reflectance and transmittance) component of the analyzer is to correct for pyrolysis charring of OC compounds into EC. Without this correction, the OC fraction of the sample might be underestimated and the EC fraction might include some pyrolyzed OC. The correction for pyrolysis is made by continuously monitoring the filter reflectance and/or transmittance (via a helium-neon laser and a photodetector) throughout an analysis cycle. The reflectance and transmittance, largely dominated by the presence of light absorbing EC, decrease as pyrolysis takes place and increase as light-absorbing carbon is liberated during the latter part of the analysis. By monitoring the reflectance and transmittance, the portion of the EC peak corresponding to pyrolyzed OC can be accurately assigned to the OC fraction. The correction for the charring conversion of OC to EC is essential for reducing bias in the measurement of carbon fractions (Johnson et al., 1981). The Thermal Optical Reflectance (TOR) and Thermal Optical Transmittance (TOT) charring corrections are not necessarily equivalent due to charring of organic vapors adsorbed within the quartz fiber filter (Chow et al., 2004; Chen et al., 2004). AQMD reports both OC and EC as determined by both methods to the EPA. Seven temperature fractions, as well as the TOR and TOT charring correction, are individually quantified and reported when the IMPROVE A (Chow et al., 1993, 2001) temperature protocol is applied. Values routinely reported include total OC, total EC, total carbon (TC, sum of total OC and total EC), and pyrolyzed carbon, monitored by both reflectance (OPR) and transmittance (OPT). Depending on the thermal/optical protocol applied for quantification, thermally-derived sub-fractions of OC and EC are reported.

VI.2.3 Aethalometer™ Data Review and Validation

The SCAQMD is committed to achieving the highest possible data quality level. In order to produce accurate and precise data from the Aethalometers, the raw data, laboratory notebook entries and logbooks were first reviewed before being used in statistical calculations.

Data from the Aethalometers were recorded every 1 to 5 minutes on an internal floppy disk or memory drive, and downloaded on a laptop once per week throughout the entire duration of the study. The data is recorded in tabular format showing the time and the high time resolution BC concentrations. The data is imported directly into a spreadsheet for analysis. In addition to the BC concentrations, the system also records diagnostic signals such as Sensing Beam signal, Reference Beam signal, the mean air flow rate, and the calculated optical attenuation which is screened for any abnormality.

The Aethalometer needs to measure extremely small changes in optical transmission in order to calculate BC concentrations with speed and accuracy which may introduce noise in the data. The major source of noise is due to small, random fluctuations of digitized signals. These fluctuations have the effect of causing the calculated value of attenuation (ATN) to deviate from a smooth, monotonic increase with time: instead, individual values of ATN may be artificially higher or lower than would be predicted from the rate of accumulation of BC from the air stream. Such error in signals will usually not be repeated in the following measurement cycle, and, therefore, the calculated ATN will revert to its 'correct' value: but with an intervening false number.

If the error condition produced an artificially high value of ATN for one measurement, the algorithm will interpret that large increase as a large value of the BC concentration for that period. This calculated value may be much larger than the preceding and following data, and the event will be obvious. However, this large value of ATN is used as the starting value for the calculation of the increment in the following cycle. The increase from this value to the 'correct' value at the end of the next period will be much smaller than it should be, resulting in a reduced value for the BC calculation. The result of the single error value of ATN in this case is an artificially large value of BC, followed by an artificially small value. The 'true' value is recovered by replacing the value for each of the periods with the arithmetic mean of the two distorted values. This is equivalent to simply ignoring the one bad signal measurement; determining the increase in ATN between the periods before and after the bad measurement; and calculating the increment in ATN and hence the mean BC concentration over a time interval of two periods rather than one.

In extreme cases, the error in voltage measurement may generate a value of ATN that deviates from the expected smooth progression by a large amount. The algorithm will process these deviations in the same manner; however, if the apparent value of ATN during the 'error' measurement exceeds the subsequent 'correct' value of ATN, the program is presented an optical attenuation value that is smaller than its predecessor. The mathematics will produce a negative apparent value of BC for this situation. This negative value will be adjacent to a slightly larger positive value: the arithmetic mean of the two numbers will still allow a recovery of the correct mean BC concentration for the double period. The derivative nature of the algorithm is such that a single error value in recorded signals produces a symmetrical plus-minus (or minus-plus in some cases) derivative event in the calculated BC result.

Note, however, that the appearance of ‘negative’ numbers for the deduced BC concentration is a natural consequence of the algorithm if either (i) there are occasional corrupting events on the voltages being recorded, or (ii) the instrument is being used to study extremely small concentrations of BC. These negative numbers do not imply malfunction of the instrument; they are the consequence of differentiating a quantity (ATN) whose increase with time is not perfectly smooth and monotonic. In subsequent data reduction, one must average the BC numbers appropriately until the negative numbers disappear, i.e., effectively increase the averaging time until the increment of BC collected on the filter easily exceeds the minimum amount detectable by the electronics.

The measurements are performed with a one-minute time base period that is considerably shorter than the final desired time resolution (hourly), and should subsequently undergo data post-processing. The reasons for this strategy are two-fold: firstly, to minimize the damage to the resulting data due to one bad voltage reading; and, secondly, to allow the instrument to respond rapidly to ‘real’ events in the local atmosphere, while retaining the possibility of averaging the data into longer time base periods during quiescent periods. In these events the large positive excursion is not followed by a compensating negative number.

Firstly, the instrument logbooks were studied to identify instrument malfunction events. The raw data spreadsheet includes diagnostic signals in addition to BC data and time stamps. The stability of the sensor signals and the flow rate was checked prior to conducting statistical analysis of the raw data.

Aethalometers tend to have a glitch where four consecutive zero readings are occasionally reported that have to be removed prior to the final data analysis and averaging for hourly data. In some cases, instead of four consecutive zeros, the instruments report three consecutive zeros followed by a large negative number (in the order of negative millions). These data points were removed from the database.

Outliers are then identified by flagging the BC concentration values that exceed 10 times the average value for each given site. These flagged data points are then studied to determine occasional short-duration events of actual BC concentration excursions (e.g. emissions from a diesel vehicle operating upwind of the measurement site). These events are typically identified in the database as those in which a large positive excursion is not followed by a compensating negative number. If flagged data-points were indeed caused by an instrument glitch, they were removed from the data-set. The same procedure was repeated for negative values exceeding five times the overall average BC concentration.

Following this preliminary data screening, the ‘cleaned’ database was used for the calculation of hourly averages and to study temporal and spatial BC variations at the 10 MATES IV sites. If the hourly averages were negative, the high time resolution data associated to that particular hour were re-examined, to remove negative values. All final (valid) hourly BC data points were larger than zero. The data screening yielded excellent data completeness, with an average data recovery of 96% over the 10 sites, well above the targeted 75% completeness established prior to the beginning of this study (Figure 1).

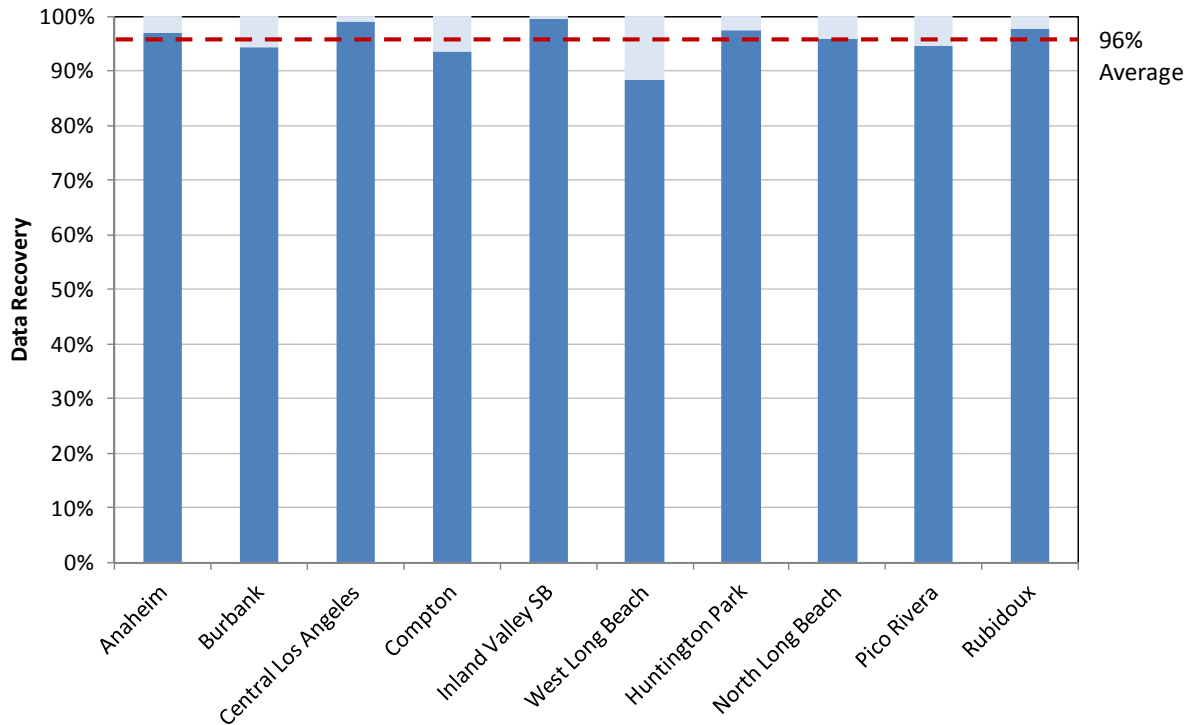


Figure 1 - Black Carbon Data Completeness at each of the MATES IV sites.

VI.2.4 Results

Diurnal, daily, seasonal and yearly variations in BC concentration were examined to study the temporal variations in BC concentrations. Spatial variations were also studied by comparing the collected BC data across each sampling site. Temporal and spatial variations in BC concentrations present invaluable information regarding daily and seasonal patterns and, more importantly, potential source contributions throughout SCAB.

VI.2.5 Spatial Variations

Figure 2 shows a box plot, summarizing the distribution of hourly BC concentrations for MATES IV. Data is displayed based on six number values (in order): 90th quartile, 75th quartile, mean, median (50th quartile), 25th quartile and 10th quartile. The inner rectangle spans the mean and median, while the outer rectangle spans the 75th and 25th quartiles. The “whiskers” above and below the box extend to the 90th and 10th, respectively.

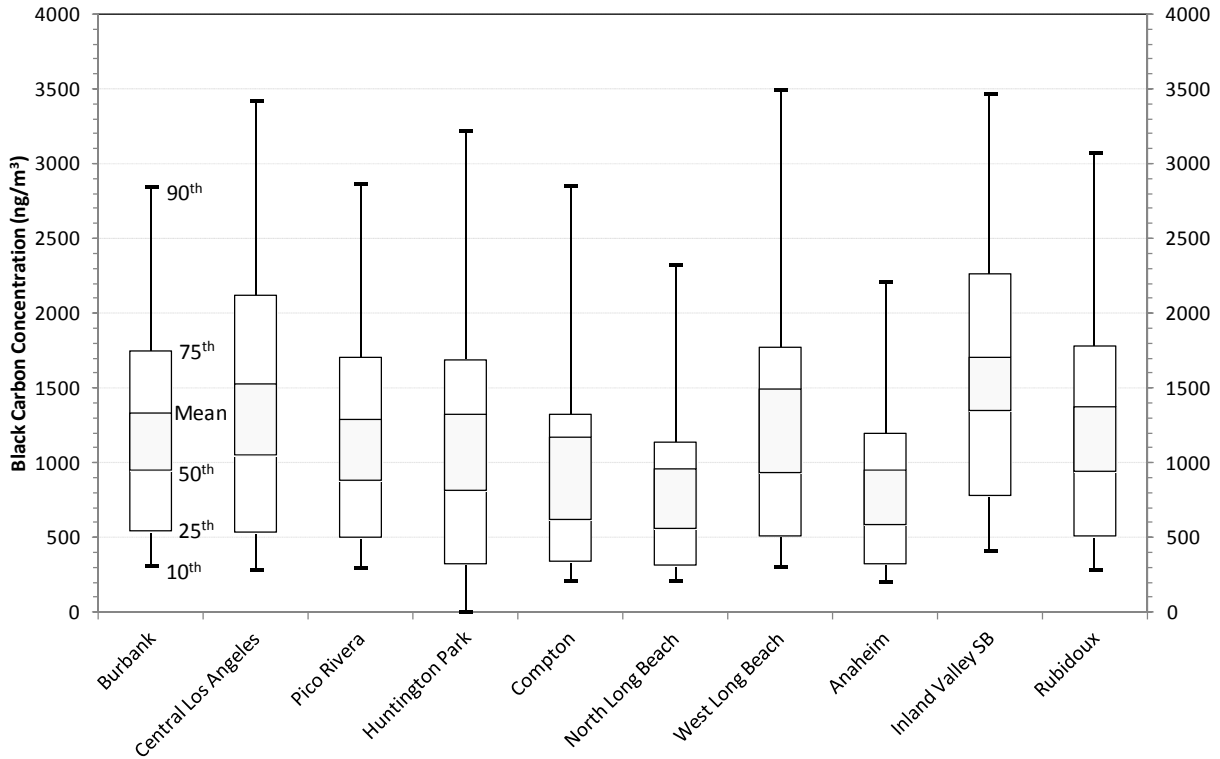


Figure 2 - Spatial Distribution of Black Carbon Concentrations Across All MATES IV Sites.

Figure 3 presents only the average BC concentration at each site for the duration of the study, along with the Basin average BC concentration [MATES IV (AVG)] and the Basin average EC concentration for the current and previous MATES studies [MATES III (EC) and MATES IV (EC), respectively]. Generally, BC concentrations at the urban sites closer to traffic corridors (i.e. Burbank, Central Los Angeles, Pico Rivera and Huntington Park) were higher than those at more suburban sites (e.g. Compton and Anaheim). Elevated concentrations were also observed at inland/receptor sites such as Rubidoux and Inland Valley San Bernardino (probably due to truck traffic in those areas). While BC was not measured during MATES III, the average EC levels decreased substantially (about 35% reduction) from MATES III to MATES IV (See Chapter 2).

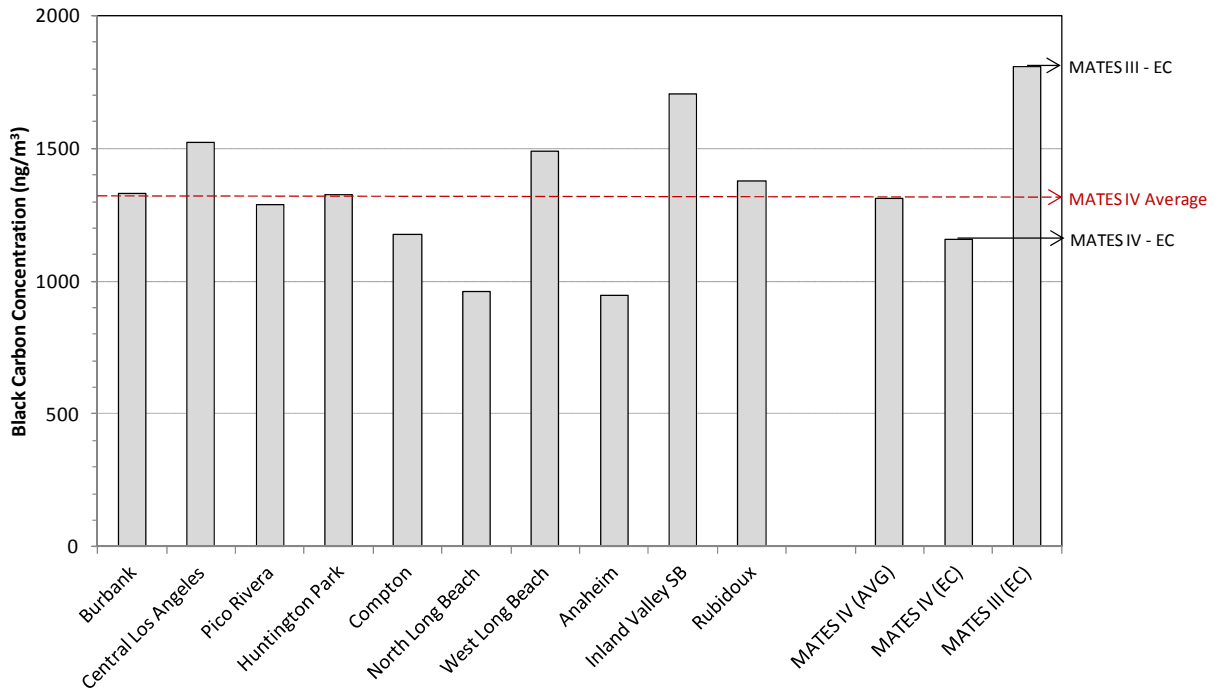


Figure 3 - Distribution of average Black Carbon concentrations during MATES IV and comparison with MATES IV and MATES III Elemental Carbon study averages.

VI.2.6 Temporal Variations

BC exhibits considerable daily, seasonal and annual variations. Studying BC variations over different time intervals can yield insights into the contributions of local and urban scale sources and into short- and long-term exposure levels.

Figure 4 shows monthly average BC concentrations that were calculated based on the high time resolution BC measurements for the entire sampling period. A general seasonal trend can be discerned from this plot, with elevated BC concentrations observed during the colder months.

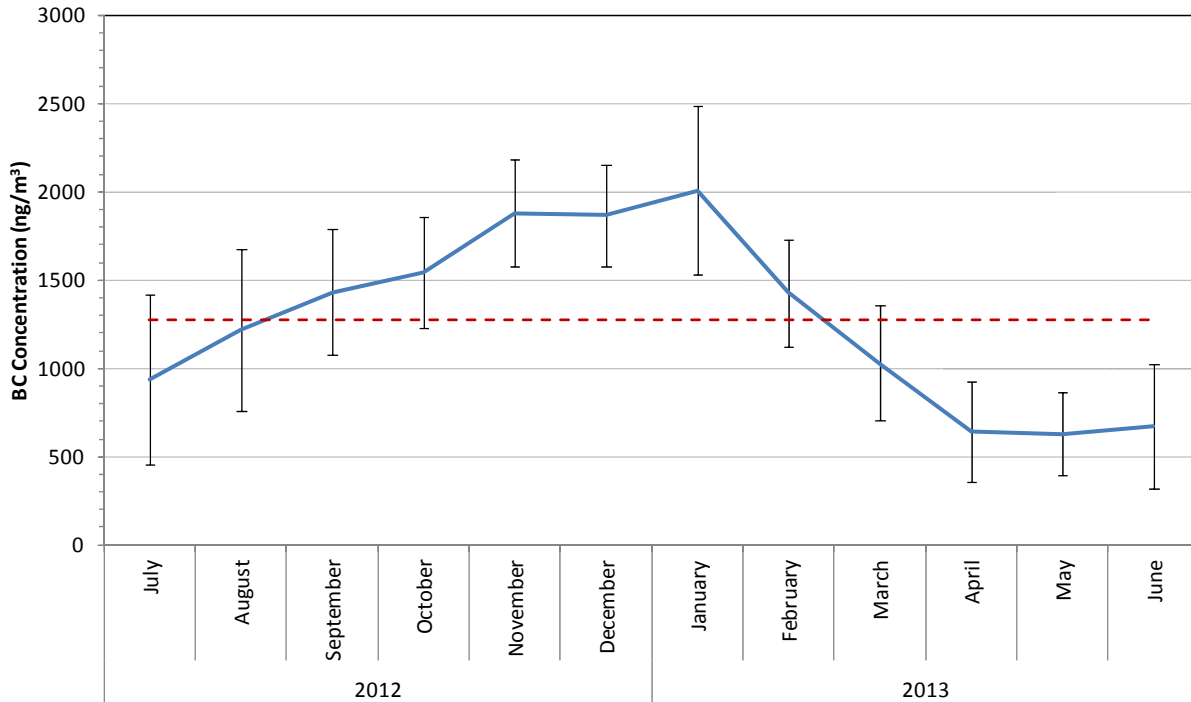


Figure 4 - Monthly Average Black Carbon Concentration Trends in the South Coast Basin During MATES IV. Red Line Indicating the MATES IV Average Concentration.

As mentioned earlier, in addition to diesel exhaust, other sources contribute to increasing the total BC content of atmospheric PM. These may include biomass burning, meat charbroiling and fuel oil combustion (ship emissions). Emissions from these sources often show some seasonality and may impact the spatial distribution of BC within the Basin (Magliano, 1999; Reinhart, 2006). For instance, during colder winter months an increase in residential wood burning would be expected (Fine et al., 2004). Hence, the higher BC concentrations observed during the winter season can be partly attributed to enhanced BC emissions from increased residential wood burning. However, the winter months are characterized by lower mixing height which is likely the most significant factor increasing the atmospheric concentrations of several atmospheric pollutants, including BC.

These seasonal trends are further highlighted in Figure 5, where the BC concentrations for each site were averaged over a period of three months (i.e. summer: June, July and August; fall: September, October and November; winter: December, January and February; and spring: March, April and May).

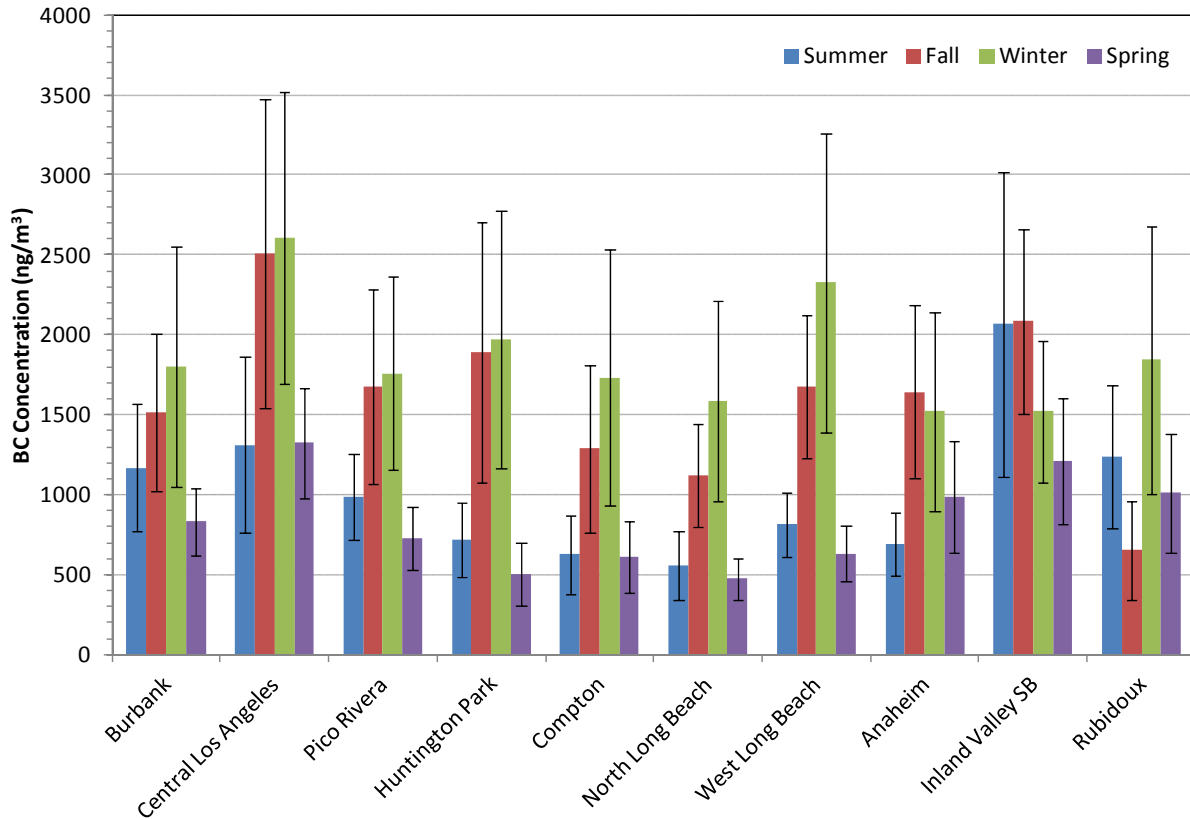


Figure 5 - Seasonal Variations of Black Carbon Concentrations at Each MATES IV Site.

BC concentrations during the warmer months were substantially higher in Inland Valley San Bernardino with respect to all other MATES IV sites, with the highest monthly mean concentration observed in July, August and September 2012, and March, April, May and June 2013. In contrast the BC concentration at the same Inland Valley San Bernardino location in January 2013 was the lowest amongst all sites (Figure 6). This different seasonal trend may be due to potential unknown local sources of BC at this site that follow a different seasonal pattern.

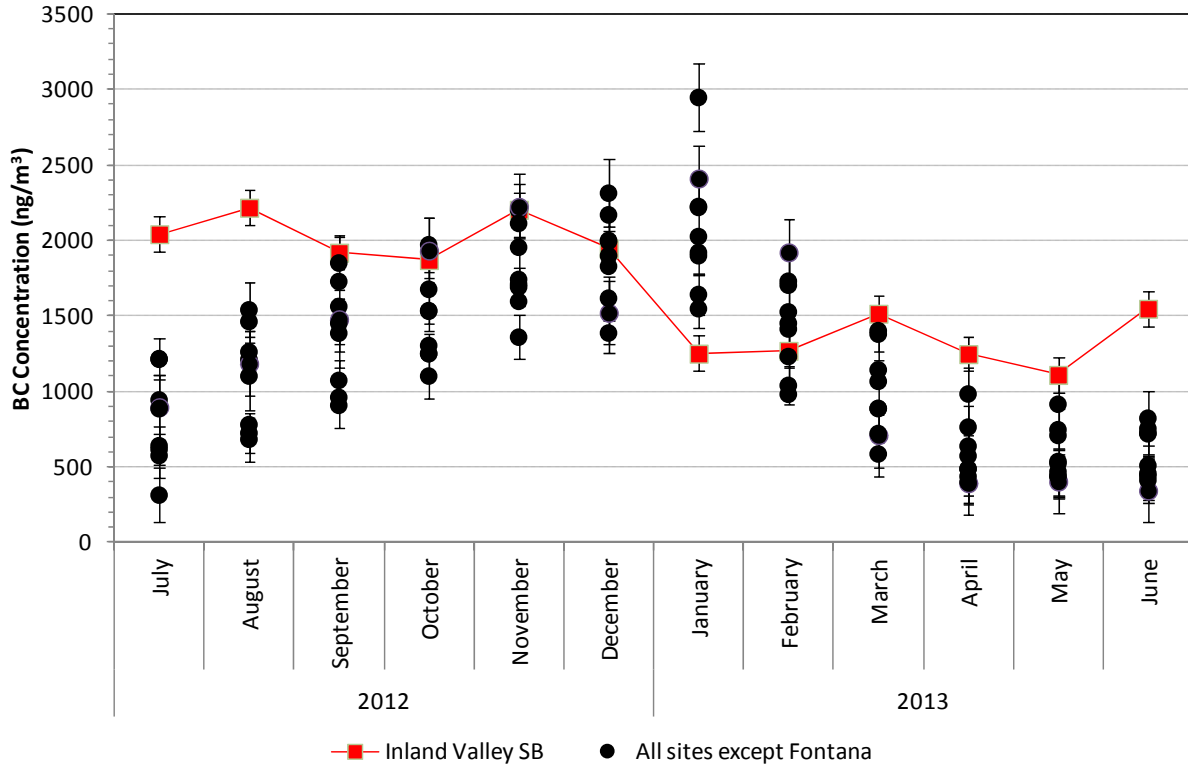


Figure 6 - Inland Valley San Bernardino (Fontana) Exhibits a Different Temporal Variation Compared to All Other MATES IV Sites.

In order to assess the temporal associations between each site pair, a linear regression analysis was performed. Figure 7 summarizes the correlation coefficients for all site pairs. All r^2 values are highlighted with colors ranging from blue (poor correlation) to red (strong correlation).

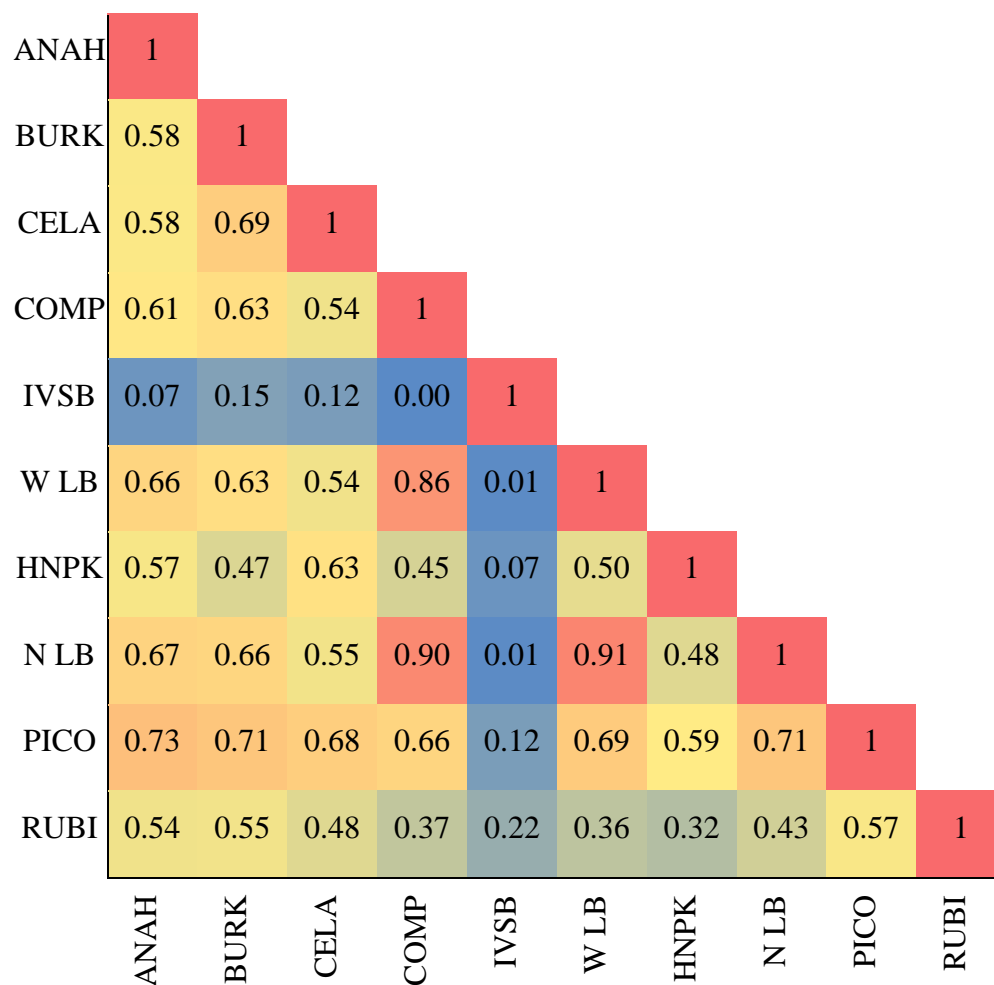


Figure 7 - Coefficients of Determination (r^2) of Black Carbon Trends between Each Site Pair.

Among all site pairs, the highest correlation coefficients were obtained between sites located nearer the port area (i.e. Compton, West Long Beach and North Long Beach sites) with r^2 values higher than 0.80. The relatively high r^2 values between these sites and more inland sites (i.e. Anaheim, Burbank and Pico Rivera) suggest that the major sources of BC at these sites are similar and concentrations vary with a relatively similar temporal pattern. Other than Inland Valley San Bernardino which was not correlated with any other site, Rubidoux also exhibits relatively low r^2 values, which suggests different temporal trends of BC concentration in Riverside.

VI.2.6.1 Diurnal Variations

Typically, BC exhibits a distinct diurnal profile at most locations. BC is associated with primary combustion activities and is widely considered as one of the best indicators of local mobile source diesel emissions in urban environments.

The 10-site average diurnal variation of BC concentrations (indicative of the typical diurnal BC trend in the South Coast Air Basin) is shown in Figure 8. The distinct increase in BC mass concentration between 0600 and 0900 PST is associated with rush-hour traffic during stagnant atmospheric conditions in the morning.

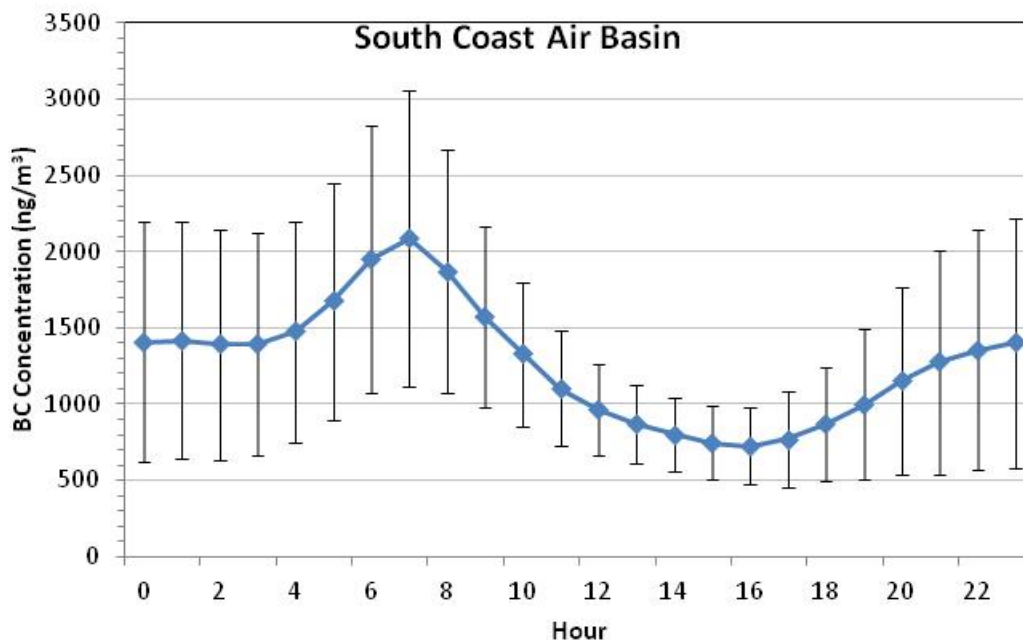


Figure 8 - Diurnal Variation of Black Carbon Concentration in South Coast Air Basin During MATES IV.

As the day progresses, the increased solar heating leads to greater dispersion of aerosols due to increased turbulent effects and deeper boundary layer. The dispersion of aerosols causes a dilution of BC near the surface resulting in a gradual decrease in BC concentrations in the afternoon along with diminished traffic density. The BC concentration continues to be relatively low until 17:00 when it slowly increases in the evening hours, which can be partly attributed to the evening rush hour traffic. In addition, lower wind speeds during night and shallow inversion layer leads to a rapid decline in ventilation. Overnight, there is a progressive and strong reduction in the traffic density and BC generation, but stable conditions persist until the morning.

VI.2.6.2 Seasonal Variations of BC Diurnal Trends

In order to examine the seasonal changes on the BC diurnal variations, the BC concentrations were averaged over a period of three months, to compare the diurnal variations of BC during each season at each site. In this analysis, the hourly BC concentrations are averaged for the months of June, July and August, representing summer; September, October and November, representing fall; December, January and February, representing winter; and March, April and May, representing spring. Each data point represents the average concentration for that hour for the entire three month period. Results are presented in Figure 9(a – j).

In general, there is a distinct seasonal dependence on the diurnal variations of BC. With the exception of Inland Valley San Bernardino, as compared to winter, the morning peak is less pronounced in summer and the evening peak is completely absent. It is evident that the BC concentrations during the winter season show the strongest diurnal variations. This can be mainly attributed to the seasonal changes in the boundary layer dynamics. Due to meteorological conditions, the boundary layer in winter is much shallower compared to its summer counterparts, resulting in the increased confinement of aerosols, causing an increase in the BC concentrations in winter. Moreover, the secondary evening peak is prominent only during the winter season, gradually diminishing during fall and spring seasons, and almost disappearing during the summer months when afternoons are characterized by strong on-shore sea breezes.

It is important to note that during the winter months, there can be additional BC emissions due to residential wood burning, particularly during night-time when the temperatures drop, which would contribute to the observed secondary, evening peak in winter.

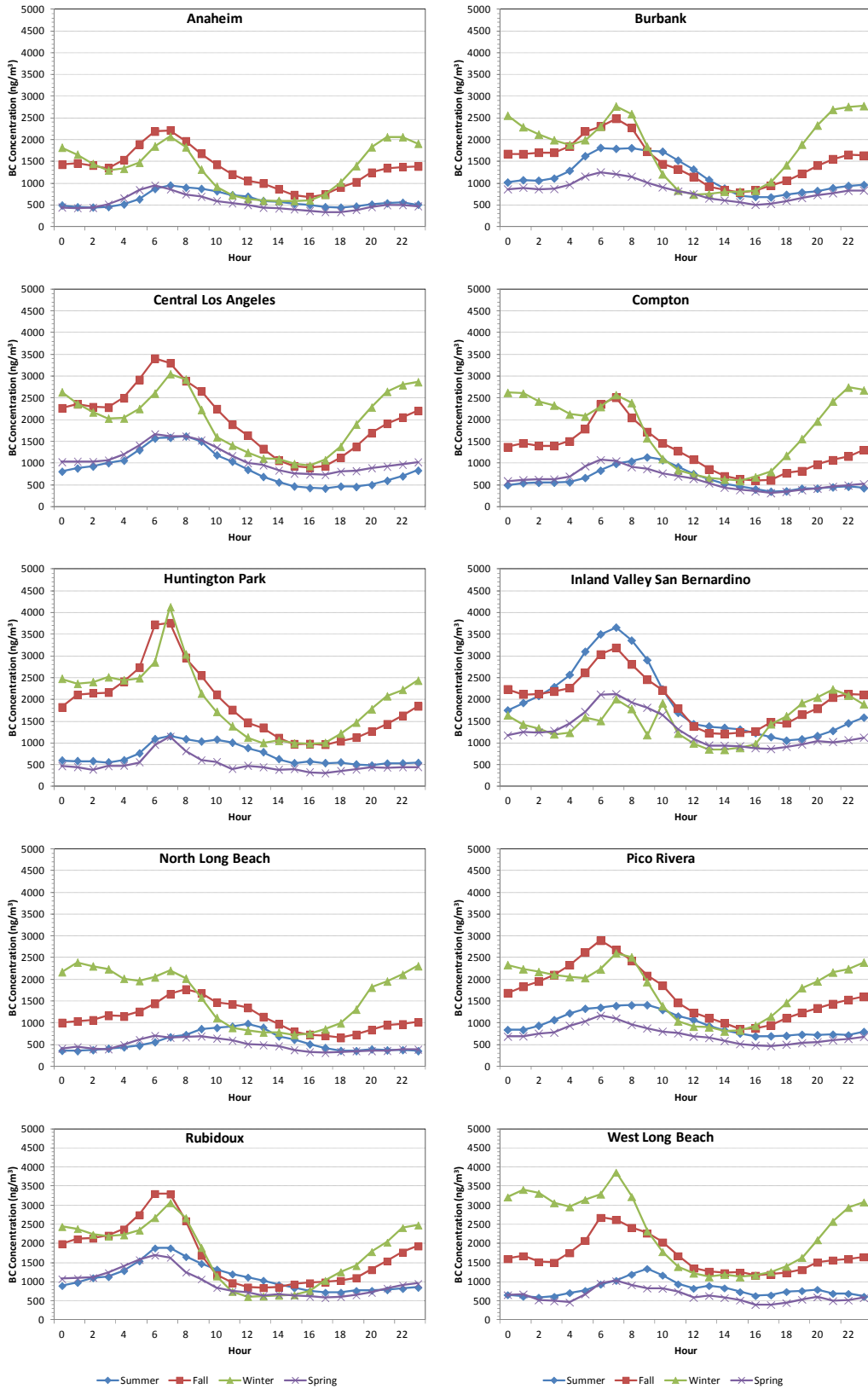


Figure 9 - Seasonal Diurnal Trends of Black Carbon Concentrations at Each Site.

VI.2.6.3 Weekday vs. Weekends

Motor-vehicle traffic (diesel traffic, in particular) has a direct impact on ambient BC concentrations. At most locations, traffic density during weekdays (i.e. Monday through Friday) is usually higher than on weekends (i.e. Saturday and Sunday). This is reflected in Figure 10, where for each season the BC concentration measured during weekdays is typically higher than that on Saturdays and Sundays.

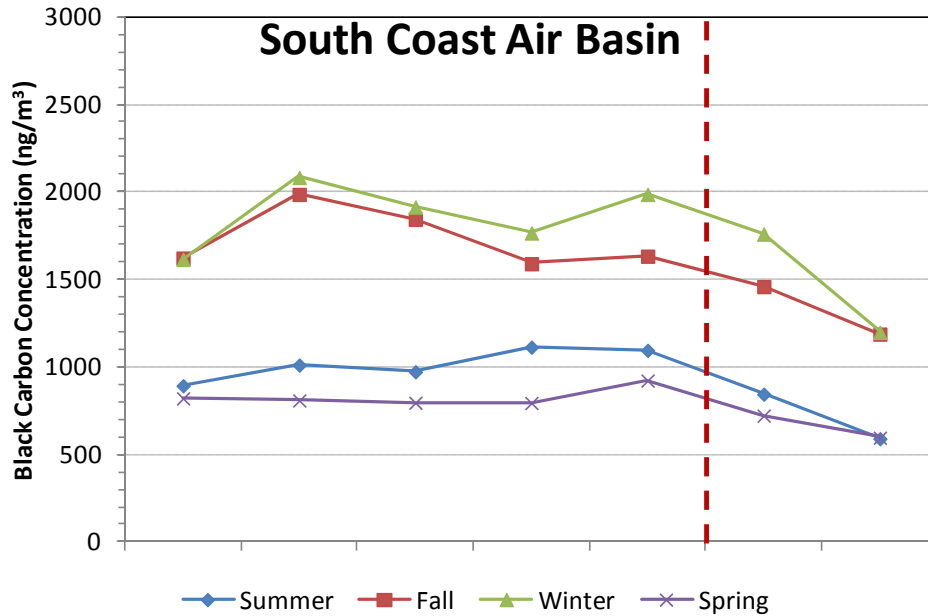


Figure 4 - Seasonal Weekday/Weekend Comparison in the South Coast Air Basin During MATES IV.

VI.2.7 Comparison Between BC and EC Measurement

Continuous BC monitors (i.e. AE22 and AE33 Aethalometers) and 24-hr integrated speciation samplers (i.e. SASS; used to collect the particle samples that were then analyzed for EC and other major components of PM_{2.5}) were operated at all 10 MATES IV sites. Both samplers were operated in air-conditioned trailers through PM_{2.5} inlets, approximately 10 m above the ground level and subsequently, the quartz-fiber filters were analyzed for OC and EC.

As shown in Figure 11, a comparison between the 24-hr. average BC concentrations and the corresponding EC levels for all MATES IV sites shows a good correlation ($r^2 = 0.81$).

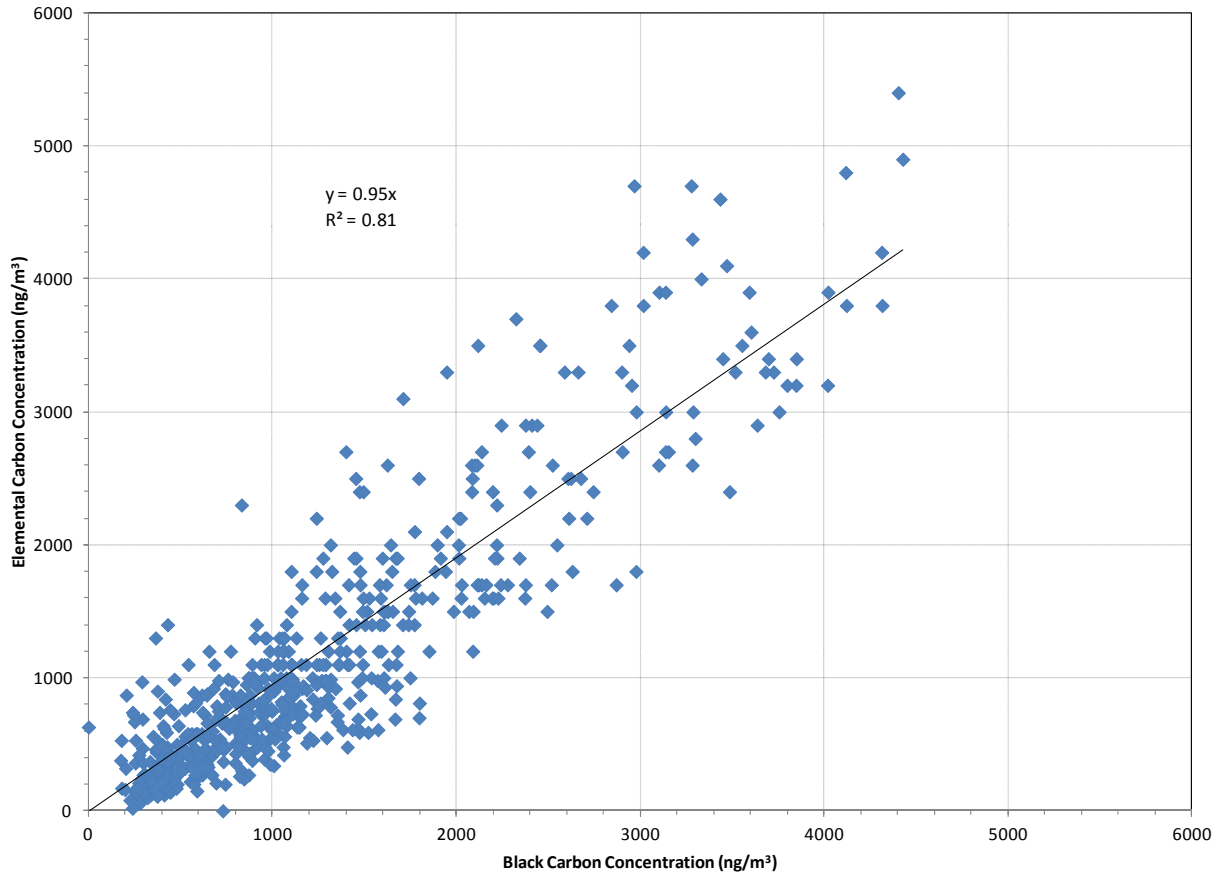


Figure 11 - Comparison of Daily Average BC and EC Concentrations in South Coast Air Basin During MATES IV.

The relationship between BC and EC measurements has been the subject of extensive research. Such comparisons usually indicate satisfactory correlation coefficients but various degrees of bias (slope). This is probably related to the choice of the coefficients used to convert absorption measurements to BC estimates or to assumptions inherent in the thermal-optical methods used to measure EC. Figure 12 show the regression analysis between BC and EC measurements at each site. While the high correlation coefficients ($0.67 < r^2 < 0.90$) show good agreement between the two measurements, the slopes can be either higher or lower than unity. Of all 10 sites, the slopes of the EC/BC regressions were higher than 1 at five sites (i.e. North Long Beach, Pico Rivera, Anaheim, Burbank and Compton) and smaller than 1 at the other five sites (i.e. West Long Beach, Huntington Park, Rubidoux, Inland Valley San Bernardino and Central Los Angeles). Therefore, a universal correction factor for converting optical BC measurements to thermal-optical EC equivalents may impose significant biases. Such conversions are desirable since current chemical transport models are mostly based on time-consuming and relatively expensive EC measurements, whereas BC measurements can be performed relatively cheaply, continuously, with higher time resolution and with much lower required maintenance. One solution might be applying site-specific correction factors calculated based on actual measurements.

It should be noted that prior to the beginning of the MATES IV Study, an intensive co-located study was designed and conducted by I-710 Freeway, to measure BC and EC concurrently in order to evaluate the instruments and the comparability of BC and EC measurements methods. A summary report for this study will be completed separately from the MATES IV Report.

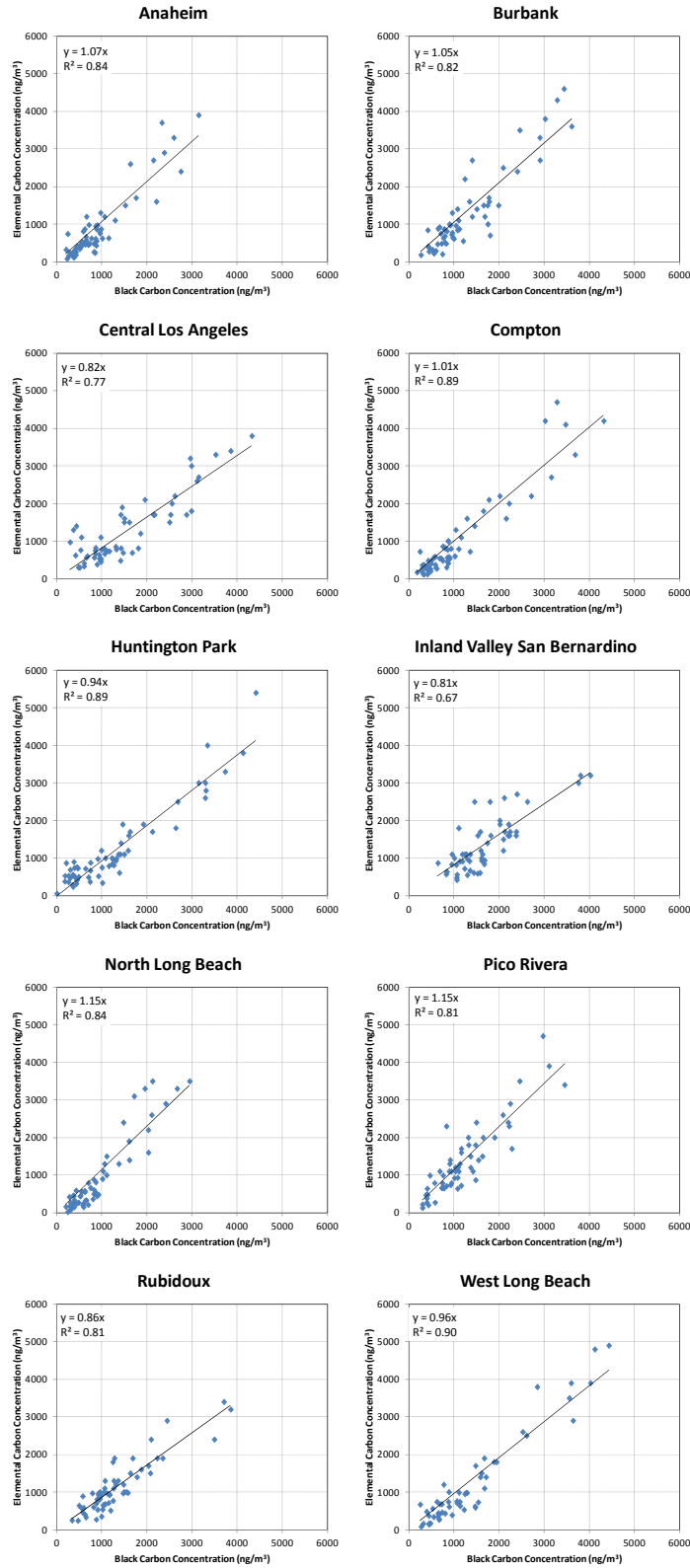


Figure 5 - Comparison of Daily Average BC and EC Concentration at Each MATES IV Site.

Generally, particulate BC measured by the Aethalometer is a reliable surrogate for particulate EC measured by subsequent chemical analysis on the filter, especially in the cases where the trends and changes of ambient BC concentrations are of interest, or in large air quality monitoring networks. The concurrent measurement of BC and EC with both optical and thermal-optical methods however, provides additional information for identifying emission sources.

VI.3 Summary

Long-term measurements of BC concentrations carried out from July 2012 to July 2013 in a network of 10 sampling sites located in the SCAB, were used to characterize the spatial and temporal variations in BC concentrations and their association to meteorology and local sources, most notably, vehicular traffic.

One of the major areas of interest in air monitoring is to evaluate relatively cheap continuous monitoring technologies in order to reduce the frequency and amount of filter based technologies that are extremely expensive and time consuming. Aethalometers offer a tremendous opportunity to move towards more desired continuous, higher time resolution sampling (as short as 1-min) and supplement or reduce the need for expensive, time consuming filter based sampling. As discussed in this Appendix, BC show significant temporal variations in all scales; annual, seasonal and diurnal (in addition to weekday/weekend). The diurnal variations at most sites have a distinct morning peak that is probably associated with increased traffic density during rush hours. The diurnal variations are more pronounced during winter season. This effect is particularly pronounced during the colder months, when higher traffic density is coupled with a shallower mixing height.

The seasonal variations are mostly related to changes in meteorology and the boundary layer dynamics. High concentrations are generally observed in colder months. Moreover, biomass burning smoke may contribute to the observed elevated BC concentrations in winter. In general, local traffic sources, meteorological conditions and boundary layer dynamics are the most important parameters influencing the BC concentrations.

Various existing regulations and emission reduction strategies are designed to control the atmospheric concentration of BC, either directly by reducing diesel emissions, or indirectly by reducing total PM emissions. Measures to mitigate BC will probably also reduce OC and PM emissions. Therefore, mitigating emissions from diesel-engine sources may offers the potential to reduce near-term climate forcing, air toxic exposure, as well as PM exposure.

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