APPENDIX VI

MATES V

FINAL REPORT

Black Carbon Measurements at Fixed Sites

Appendix VI

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VI.1 Preface

Black carbon, or soot, is part of fine particulate air pollution ($PM_{2.5}$). The main sources of black carbon (BC) are incomplete burning of biofuels, burning of fossil fuels, and open biomass burning (e.g. open agriculture burning). Black carbon sources vary by region and anthropogenic activity. Multiple studies reported strong correlation between black carbon concentration and diesel vehicle traffic and that exhaust from diesel engines is the major source of soot in urban areas. Therefore, soot is often considered a good proxy for diesel particulate matter in urban areas (Diesel PM) (Schauer, 2003).

The comparison between the average levels of black carbon during MATES V and MATES IV, and temporal variability of these levels are discussed in Chapter 5. This appendix elaborates on the sampling and analytical methods used for this report and provides a further detailed analysis of the temporal and spatial variability of black carbon. In addition, this appendix includes a detailed comparison between optical and thermo-optical methods that are in use for quantifying soot emissions.

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 Quality Management District (South Coast AQMD), with a particular focus on the South Coast Air Basin (SCAB). Previous MATES studies assessed the carcinogenic risk due to inhalation exposure to air toxics and found that emissions from diesel-powered engines and boilers accounted for 84% and 68% of this risk during MATES III and MATES IV, respectively (South Coast Air Quality Management District, 2008, 2015a).

VI.2 Analytical Methods for Quantifying Atmospheric Soot

Various analytical methods have been developed to quantify the concentration of atmospheric soot particles. Depending on the measurement method used, the non-organic carbon fraction of soot is referred to as black carbon (BC) or elemental carbon (EC). When optical methods that quantify the amount of soot by measuring its interaction with light are used, soot is often referred to as BC. However, when its concentration is measured by thermal or thermal-optical techniques, it is generally referred to as EC.

The measurement of optically absorbing material on a filter is performed by Aethalometers. This instrument measures the attenuation of 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 atmosphere. EC is also oxidized by raising the temperature and introducing oxygen. The combusted compounds are then converted to CO_2 using manganese dioxide (MnO_2) as the oxidizer. Subsequently, CO_2 is converted to methane (CH_4) using a nickel catalyst, and the concentration of CH_4 is quantified with a flame ionization detector (FID).

Both optical and thermal measurement techniques are important and considered complementary to 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 where soot is collected on a filter, usually for 24 hours, 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. It should be noted that EC and BC methods do not necessarily yield directly comparable results, although they are generally correlated (Chow et al., 2001; Lack et al., 2014). A comparison between EC and BC measurements during MATES V is provided in the Appendix XIII. Due to higher sampling frequency and lower maintenance and operating costs, BC measurements are often favored for deployment in monitoring networks.

VI.3   BC and EC Measurements during MATES V

BC and EC were measured at all 10 fixed MATES V locations: Anaheim, Burbank Area, Central Los Angeles (Central LA), Compton, Inland Valley San Bernardino (Inland Valley SB), West Long Beach (W. Long Beach), Huntington Park, Long Beach, Pico Rivera, and Rubidoux. Details of the sites, their characteristics and sampling protocols are given in Appendix III of MATES V.

Continuous measurements of BC were carried out from January 2018 until the end of April 2019. Only data collected from May 1, 2018 through April 30, 2019 have been used for the present report to match the sampling period for the MATES V time-integrated samples. For EC and OC analysis, time-integrated PM samples were collected over a period of 24 hours from May 1, 2018 through April 30, 2019 at all fixed MATES V sites.

We note that the locations of three stations: Burbank Area, Long Beach, and Huntington Park have changed from their previous locations during MATES IV. Figure VI-1 presents the locations of all ten sites and the changes of these three sites.
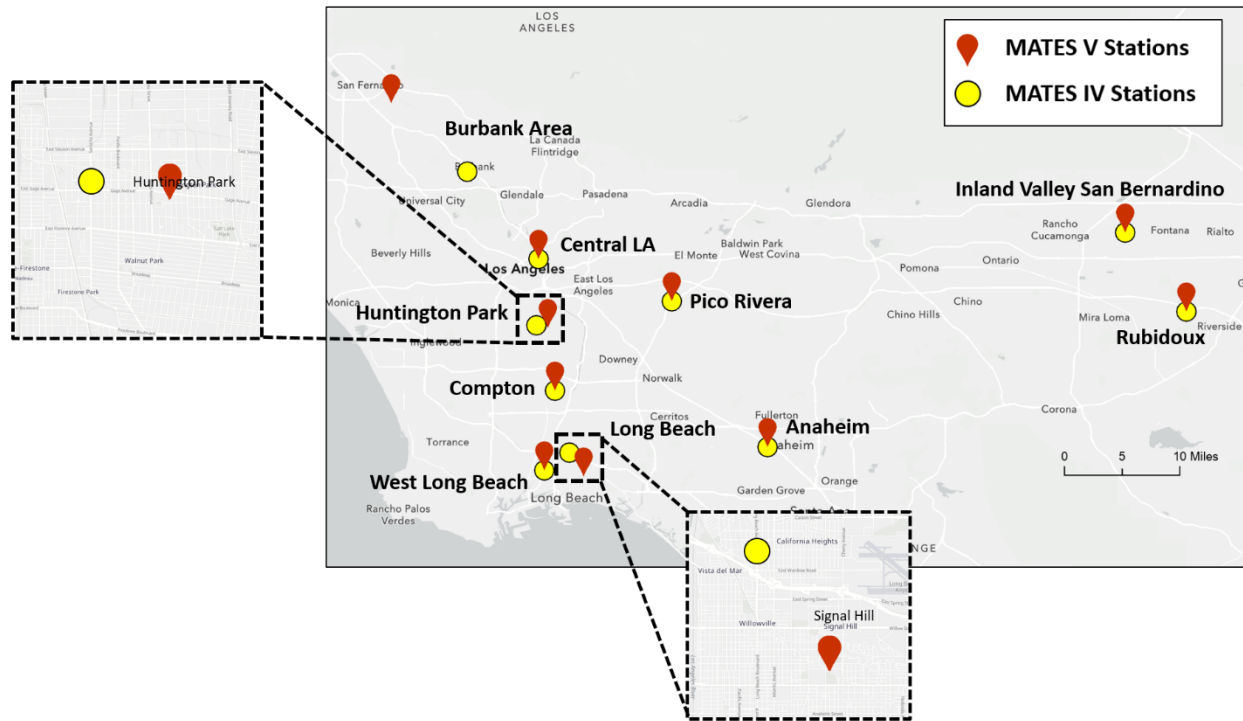
Figure VI-1. The locations of MATES V and their location during MATES IV

VI.3.1   Black Carbon Measurements

The Aethalometer (Magee Scientific, Berkeley, CA) is a photometer that provides a real-time readout of the concentration of black carbon aerosol particles in an air stream. The operating principles of the Aethalometer are described in detail elsewhere (Hansen et al., 1984). Briefly, the instrument collects airborne particulate matter on a filter while continuously measuring the light transmission through the filter. The attenuation in light intensity is caused by light absorption of BC-containing particles that accumulate on the filter over time. This measurement needs to be post-processed to obtain ambient aerosol absorption coefficients which are then converted to BC concentrations. One drawback of this measurement method, inherent in all filter-based photometers, is the nonlinearity of the measurements due to PM loading on the filter media, which reduces the sensitivity of the measurements. Numerous studies have focused on developing algorithms to correct the Aethalometer non-linearity. The Magee Aethalometer model AE33 performs this correction automatically.

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

VI.3.2   Elemental Carbon Measurements

OC and EC are determined by thermal-optical analysis of time-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 (HEI, 2010). Hence, extra caution is required when comparing EC measurements from different studies, or when comparing BC and EC measurements. Currently, 24-hour 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 MATES V, the EC concentrations were quantified using DRI Model 2001 Thermal/Optical Carbon Analyzer using the IMPROVE_A thermal protocol (South Coast Air Quality Management District, 2020). 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 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 (CO_2) by passing the volatilized compounds through an oxidizer (heated manganese dioxide, MnO_2); 3) reducing CO_2 to methane (CH_4) by passing the flow through a methanizer (hydrogen-enriched nickel catalyst); and 4) quantifying CH_4 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 (Chen et al., 2013; Chow et al., 2004). South Coast AQMD reports both OC and EC as determined by both methods to U.S. 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., 2001, 1993) 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.4   Results

The procedures of data collection, review, analysis, and validation are described in detail in MATES IV, Black Carbon Measurements at Fixed Sites (South Coast Air Quality Management District, 2015b). The screening processes of the data collected from by the aethalometers yielded excellent data completeness, with average data recovery of 98% overall MATES V sites, an improvement over the 96% completeness of the dataset of MATES IV.

VI.4.1 The Seasonal and diurnal variations in MATES V sites

Typically, BC exhibits a distinct diurnal profile at most locations. BC is associated with primary combustion emissions and is widely considered as one of the best indicators of local mobile sources i.e. diesel exhaust 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 VI-2. The distinct increase in BC mass starts as early as 4 AM. BC concentration reaches its maximum around 7 AM (all reported times are Pacific standard time) and decreases during the morning hours. This pattern is associated with a shallow atmospheric boundary layer in early morning enhanced with emissions from morning commute traffic.
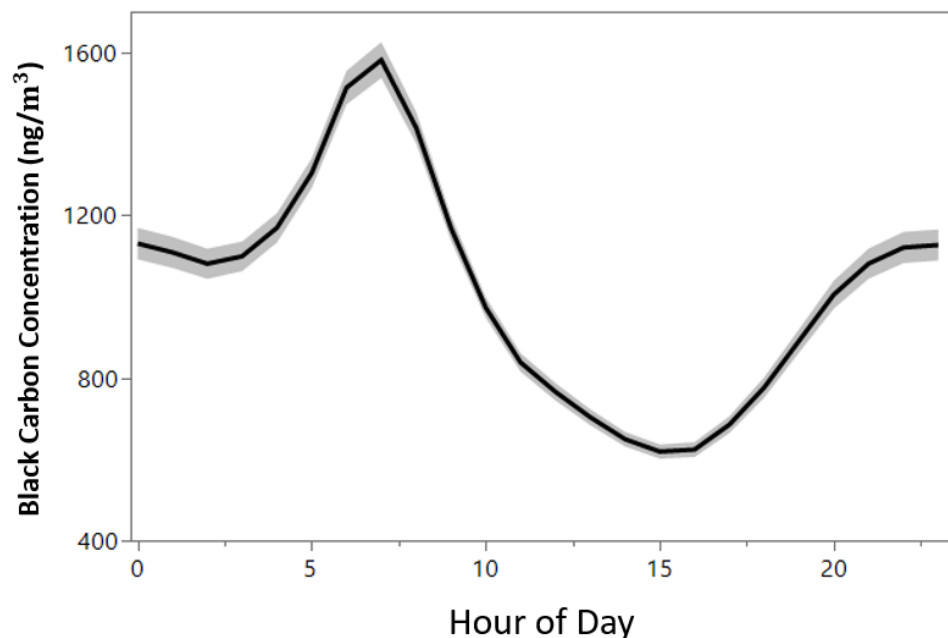

Figure VI-2. Diurnal variation of black carbon concentration in the South Coast Air Basin during MATES V. The shaded areas represent the 95 percent confidence level of the measurement

As the day progresses, the increased solar heating leads to greater dispersion of aerosols due to increased turbulent mixing 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, reaching daily minimum concentration around 3pm in the afternoon, when the atmospheric convective mixing is the highest. The BC concentration continues to be relatively low until 4 pm and then increases again during the evening hours as the atmospheric boundary layer collapses. Evening commute traffic contribute to the increase too. In addition, lower wind speeds during the night and shallow inversion layer lead to a rapid decline in ventilation. Overnight, there is a progressive and strong reduction in the traffic density and other industrial and commercial activities generating BC emissions, however, stable meteorological conditions, and a lower boundary layer result in the accumulation of BC near the surface until the next morning.

The daily and seasonal levels in each MATES V site are presented in Figure VI-3. The seasonal time periods 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).

In general, there is a distinct seasonal dependence on the diurnal variations of BC (Figure VI-3). BC concentrations during the winter season show the strongest diurnal variations, mainly attributable 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 lower dispersion and ventilation of aerosols in the Basin, 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 nighttime when the temperatures drop, which would contribute to the evening peak seen in winter.

BC concentrations vary by season significantly with winter showing the highest concentration followed by fall, summer and spring. Burbank Area and Inland Valley San Bernardino stations are exceptions with the highest BC measured during the summer months.
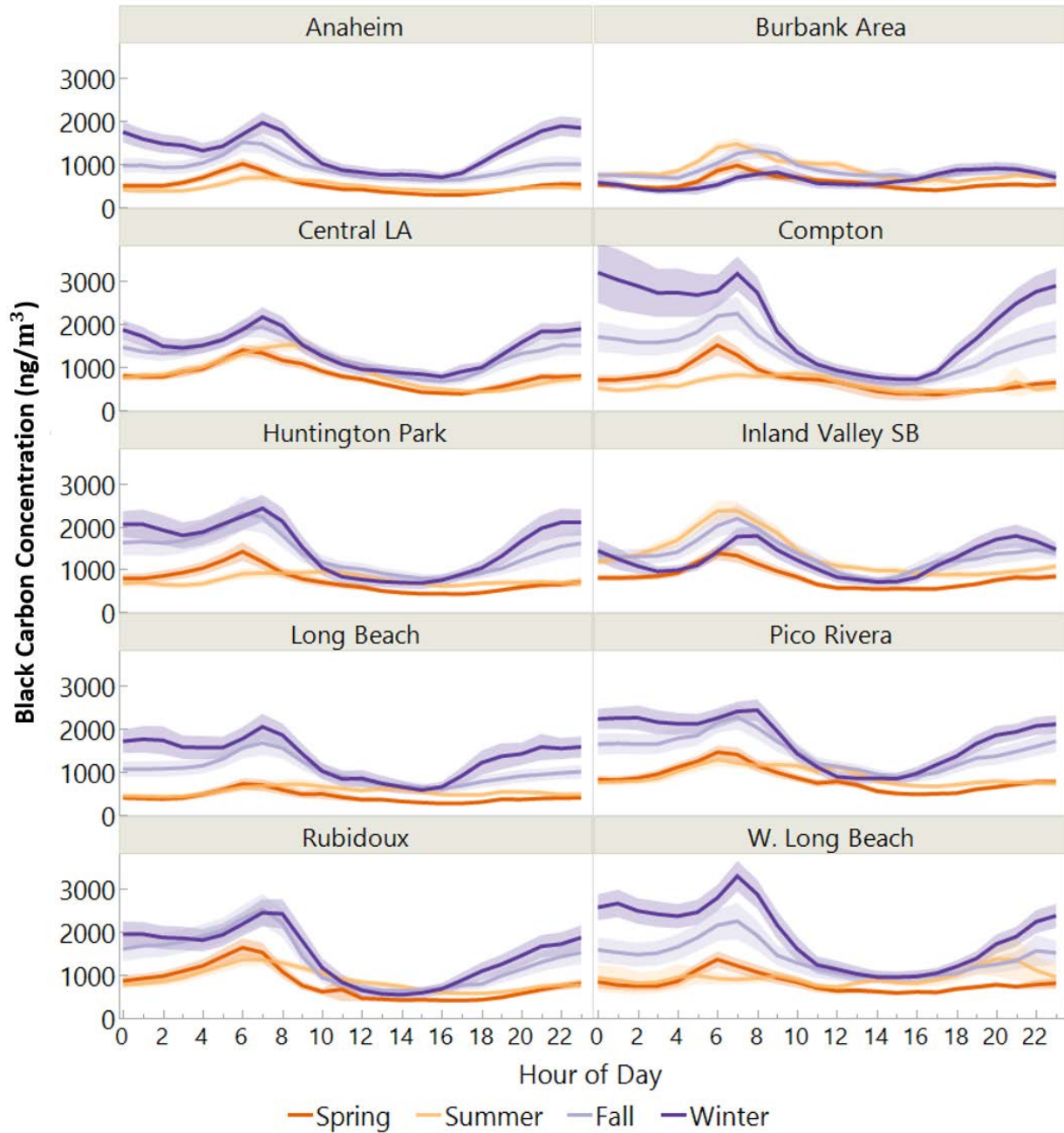
Figure VI-3. Seasonal diurnal trends of black carbon concentrations at each site. The shaded areas represent the 95 percent confidence level of the measurement

In order to assess the temporal associations between each site pair, a linear regression analysis was performed. Figure VI-4 summarizes the correlation coefficients for all site pairs.
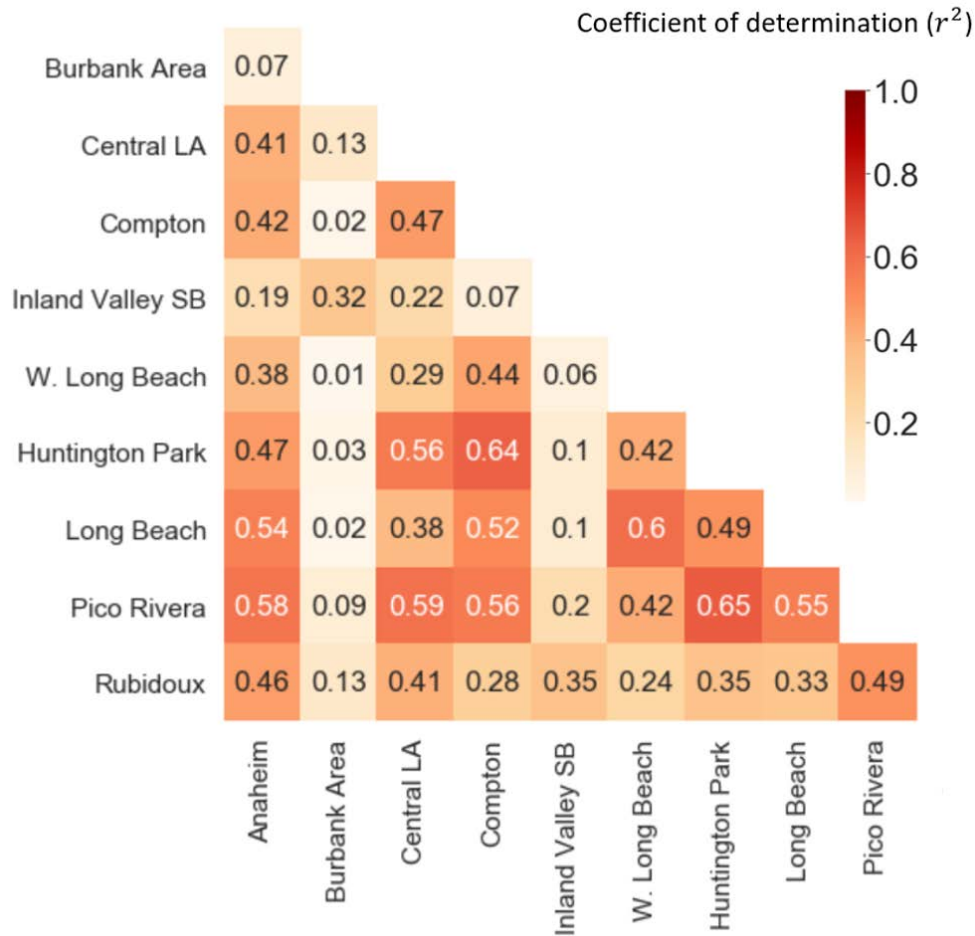
Coefficient of determination (r^2)

	Anaheim	Burbank Area	Central LA	Compton	Inland Valley SB	W. Long Beach	Huntington Park	Long Beach	Pico Rivera
Burbank Area	0.07								
Central LA	0.41	0.13							
Compton	0.42	0.02	0.47						
Inland Valley SB	0.19	0.32	0.22	0.07					
W. Long Beach	0.38	0.01	0.29	0.44	0.06				
Huntington Park	0.47	0.03	0.56	0.64	0.1	0.42			
Long Beach	0.54	0.02	0.38	0.52	0.1	0.6	0.49		
Pico Rivera	0.58	0.09	0.59	0.56	0.2	0.42	0.65	0.55	
Rubidoux	0.46	0.13	0.41	0.28	0.35	0.24	0.35	0.33	0.49

Figure VI-4. Coefficients of determination (r^2) of black carbon trends between each site pair

Among all site pairs, the highest correlation coefficients were obtained between Huntington Park and Pico Rivera, (r^2=0.65) and Huntington Park and Compton (r^2=0.64). A high correlation was also found between West Long Beach and Long Beach, which are both located close to the ports. On the other hand, Rubidoux, Inland Valley San Bernardino, and Burbank Area which are each located relatively far away from any other station, showed low correlation with the other stations.

The relatively high r2 values between the stations that are in the urban areas and between those that are located near the ports suggest that the meteorological patterns and major sources of BC at each of those are similar and that the concentrations vary with a relatively similar temporal pattern. On the other hand, the lack of correlation between the inland stations (Inland Valley San Bernardino and Rubidoux) and Burbank Area (as a more suburban site) with the urban sites indicates that the temporal trends for BC concentrations at these sites are impacted by different emission sources and meteorological patterns.

VI.4.2   The Directionality of BC Enhancements

The polar plots in Figure VI-5 show the average BC concentration organized by direction and time of day.   The polar angle of the data shows the direction from which that average concentration was observed and the distance from the center of each plot (0 – 23) indicates the time of day. For example, the plot for West Long Beach shows that the highest average BC concentrations during the MATES V period come from the northeast direction and usually occur around the morning which can be the result of the proximity of two major highways (Interstates 405 and 710) to the north and east. Stagnant wind condition caused by the transition of the nocturnal offshore wind to the daytime onshore wind is expected to contribute to the high concentration too.
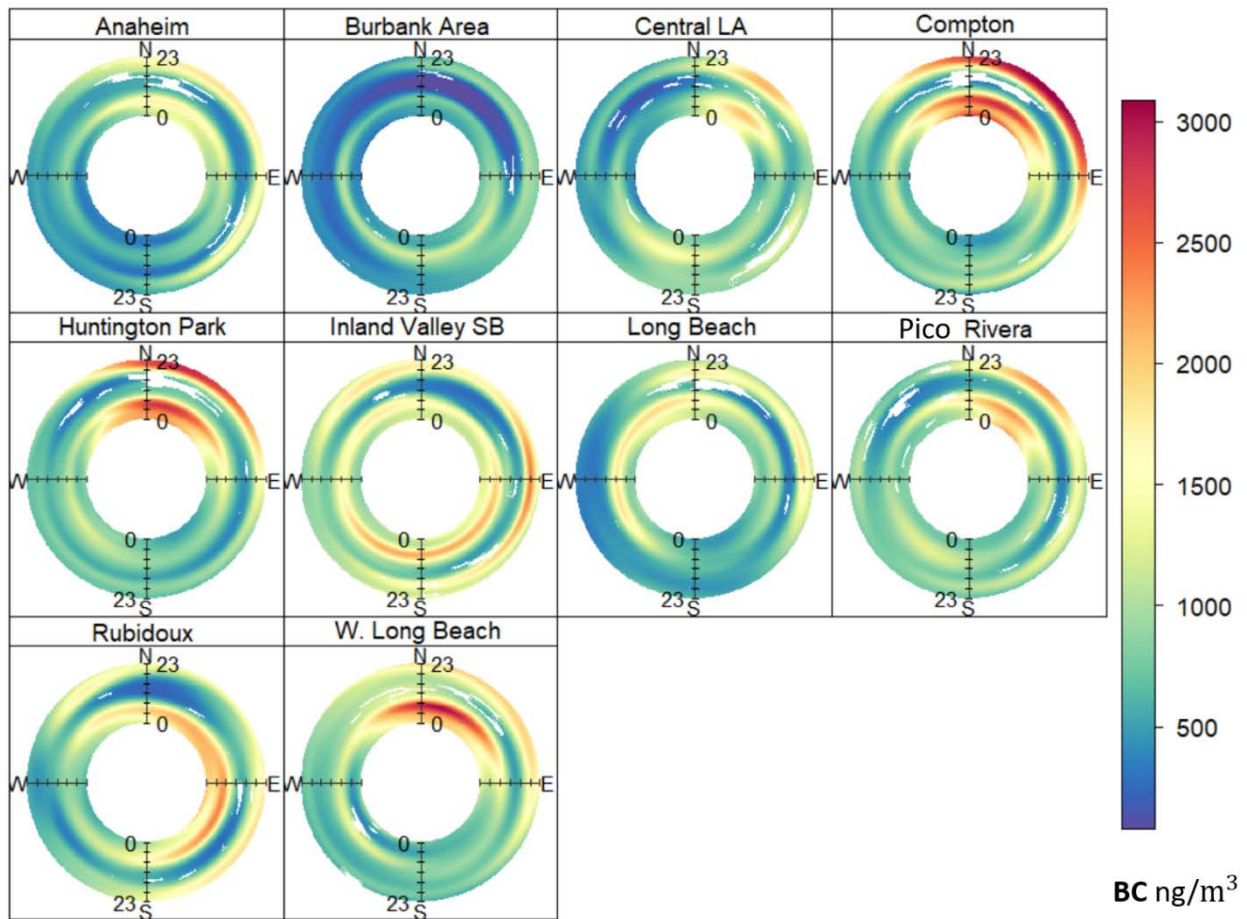

Figure VI-5. Polar time plots of BC concentration at each MATES V station

Compton, Central Los Angles, Anaheim, Pico Rivera, and Huntington Park have morning and evening peaks when winds from the northeast direction. Rubidoux, Burbank Area, and Inland Valley San Bernardino have higher concentrations coming from the southeast direction. The morning peaks are usually associated with nearby on-road and off-road mobile source activities and transport by prevailing wind directions, while the midnight peaks are produced by a

combination of lower boundary layer height and higher wood-burning activities during the cold months.

VI.5 Summary

Long-term measurements of BC concentrations carried out from May 2018 to April 2019 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.

Based on the MATES V data, BC concentrations show significant temporal variations on all time scales; annual, seasonal, and diurnal (see Chapter 5 for detailed analysis). The diurnal variations at most sites have a distinct morning peak, which was primarily caused by the diurnal variation of the atmospheric boundary layer and emissions from commute traffic. The diurnal variations are more pronounced during the winter. This effect is particularly pronounced during the colder months when the mixing height is the lowest.

The seasonal variations are mostly related to changes in meteorology and the boundary layer dynamics. High concentrations are generally observed in colder months, when there is less convective mixing. 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 also reduce OC and PM emissions. Therefore, mitigating emissions of BC from diesel-engine and biomass burning sources helps to reduce short-lived climate forcing, air toxic exposure, as well as PM exposure.

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