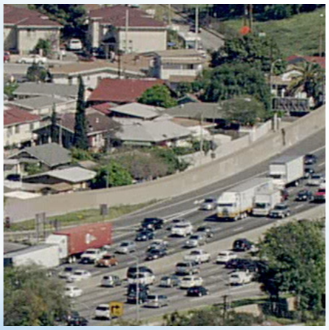
DRAFT FINAL APPENDICES

Multiple Air Toxics Exposure Study in the South Coast Air Basin

MATES-IV



APRIL 2015

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List of Appendices

APPENDIX I

MATES IV

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List of Substances and Their Associated Risk Factors

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Appendix I

List of Substances and their Associated Risk Factors Including Updated OEHHA Methodology (final Column)

Compound	Class	CAS	Acute REL (µg/m3)	8-Hour REL (µg/m3)	Chronic REL (µg/m3)	Previous Unit risk (µg/m3)$^{-1}$	Inhalation Slope Fator (mg/kg-day)-1	Calculated Updated Unit Risk (µg/m3)$^{-1}$
Acetaldehyde	Carbonyls	75-07-0	470	300	140	2.7E-06	1.0E-02	6.77E-06
Formaldehyde	Carbonyls	50-00-0	55	9	9	6.0E-06	2.1E-02	1.42E-05
Methyl Ethyl Ketone(2-Butanone)	Carbonyls	78-93-3	13000					
Arsenic	Metal	7440-38-2	0.2	0.015	0.015	3.3E-03	1.2E+01	8.12E-03
Cadmium	Metal	7440-43-9			0.02	4.2E-03	1.5E+01	1.01E-02
Copper	Metal	7440-50-8	100					
Cr+6	Metal	18540-29-9			0.2	1.5E-01	5.1E+02	3.45E-01
Lead	Metal	7439-92-1				1.2E-05	4.2E-02	2.84E-05
Manganese	Metal	7439-96-5		0.17	0.09			
Nickel	Metal	7440-02-0	0.2	0.06	0.014	2.6E-04	9.1E-01	6.16E-04
Selenium	Metal	7782-49-2			20			
Benz(a)anthracene	PAH	56-55-3				1.1E-04	3.9E-01	2.64E-04
Benzo(a)pyrene	PAH	50-32-8				1.1E-03	3.9E+00	2.64E-03
Benzo(b)fluoranthene	PAH	205-99-2				1.1E-04	3.9E-01	2.64E-04
Benzo(k)fluoranthene	PAH	207-08-9				1.1E-04	3.9E-01	2.64E-04
Chrysene	PAH	218-01-9				1.1E-05	3.9E-02	2.64E-05
Dibenz(ah)anthracene	PAH	53-70-3				1.2E-03	4.1E+00	2.77E-03
Indeno(123-cd)pyrene	PAH	193-39-5				1.1E-04	3.9E-01	2.64E-04
Naphthalene	PAH	91-20-3			9	3.4E-05	1.2E-01	8.12E-05
Benzene	VOC	71-43-2	27	3	3	2.9E-05	1.0E-01	6.77E-05
Butadiene, 1,3-	VOC	106-99-0	660	9	2	1.7E-04	6.0E-01	4.06E-04
Carbon Tetrachloride	VOC	56-23-5	1900		40	4.2E-05	1.5E-01	1.01E-04
Chloroethene (Vinyl Chloride)	VOC	75-01-4	180000			7.8E-05	2.7E-01	1.83E-04
Chloroform	VOC	67-66-3	150		300	5.3E-06	1.9E-02	1.29E-05
Dibromoethane,1,2- (Ethylene Dibromide)	VOC	106-93-4			0.8	7.1E-05	2.5E-01	1.69E-04
Dichlorobenzene, p-	VOC	106-46-7			800	1.1E-05	4.0E-02	2.71E-05
Dichloroethane, 1,2- (Ethylene Dichloride)	VOC	107-06-2			400	2.1E-05	7.2E-02	4.87E-05
Ethylbenzene	VOC	100-41-4			2000	2.5E-06	8.7E-03	5.89E-06
Methyl tertiary-butyl ether (MTBE)	VOC	1634-04-4			8000	2.6E-07	1.8E-03	6.09E-07
Methylene Chloride (Dichloromethane)	VOC	75-09-2	14000		400	1.0E-06	3.5E-03	2.37E-06
Perchloroethylene (Tetrachloroethylene)	VOC	127-18-4	20000		35	5.9E-06	2.1E-02	1.42E-05
Styrene	VOC	100-42-5	21000		900			
Toluene	VOC	108-88-3	37000		300			
Trichloroethene	VOC	79-01-6			600	2.0E-06	7.0E-03	4.74E-06
Xylene, m-	VOC	108-38-3	22000		700			
Xylene, o-	VOC	95-47-6	22000		700			
Xylene, p-	VOC	106-42-3	22000		700			
Diesel Particulate Matter		n/a	5			3.0E-04	1.1E+00	7.44E-04

Values from the Consolidated Table of OEHHA/ARB Approved Risk Assessment Health Values available at http://www.arb.ca.gov/toxics/healthval/healthval.htm. The Calculated Revised Unit Risk Values were calculated using the updated methodology adopted by OEHHA in February, 2015 assuming an exposure value of 1 µg/m^3, 90th percentile breathing rates for age groups up to 2 years and 80th percentile breathing rates for age groups above 2 years, fraction of time at home of 1 for ages up to 16 yrs and 0.73 for age above 16 yrs, and 30 year exposures.

APPENDIX II

MATES IV

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Technical Advisory Group Members

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MATES IV Technical Advisory Group

Member Name	**Affiliation**
Diane Bailey	National Resources Defense Council
Michael Benjamin	California Air Resources Board
Judith Chow	Desert Research Institute
Maria Costantini	Health Effects Institute
Kenneth Davidson	U.S. Environmental Protection Agency
Rob Farber	Southern California Edison
Elfego Felix	U.S. Environmental Protection Agency
Dennis Fitz	University of California, Riverside
John Froines	University of California, Los Angeles
Scott Fruin	University of Southern California
Michael Kleinman	University of California, Irvine
Fred Lurmann	Sonoma Technology
Andrew Salmon	Office of Environmental Health Hazard Assessment
Constantinos Sioutas	University of Southern California
Samuel Soret	Loma Linda University
Yifang Zhu	University of California, Los Angeles

APPENDIX III

MATES IV

DRAFT FINAL REPORT

MATES IV Monitoring and Laboratory Analysis Protocol

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Solomon Teffera
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MATES IV

APPENDIX III

MONITORING AND LABORATORY ANALYSIS PROTOCOL

SEPTEMBER 2014

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South Coast Air Quality Management District

DISCLAIMER

Any or all reference made in this Appendix to a specific product or brand name does not constitute an endorsement of that product or brand by the South Coast Air Quality Management District.

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Chapter 1.0
Introduction

This appendix document provides detailed information about the procedures and processes which were used to conduct the field measurement and laboratory analysis elements of the Multiple Air Toxics Exposure Study IV (MATES IV).

1.1 BACKGROUND

In 1998, the South Coast Air Quality Management District (SCAQMD) conducted an intensive ambient air toxics monitoring program, the Multiple Air Toxics Exposure Study II (MATES II). The objective of MATES II was to establish a baseline of existing air toxics ambient emissions, exposure and risk level data and an assessment of model accuracy. The SCAQMD conducted MATES II over a one-year period at ten sampling sites in the South Coast Air Basin (Basin). The MATES II Final Report was approved by the SCAQMD Board in March 2000[1].

As a follow up study to MATES II, MATES III was conducted from April 2004 through March 2006. The initial scope of the study was for one year, however, due to heavy rains in the first year of the study a second study year was added over concern of atypical meteorology. The MATES III Final Report was published in September 2008[2].

MATES IV was conducted to build upon prior ambient toxics data sets, evaluate spatial and temporal trends and better understand current risk associated with air toxics in the Basin.

For MATES IV, organic and metal compounds were sampled and analyzed. These compounds are identified in Appendix A. Compounds listed in Appendix A were measured on a routine one-in-six day basis.

Field sampling began July 2012 and continued for one year. This document describes the monitoring, laboratory analysis, quality control (QC), and quality assurance (QA) activities necessary to support the MATES IV program.

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[1] South Coast Air Quality Management District (2000). *MATES II Final Report*. Diamond Bar, CA

[2] South Coast Air Quality Management District (2008). *MATES III Final Report*, Diamond Bar, CA

Chapter 2.0
Monitoring Equipment

2.1 INTRODUCTION

For the purposes of this appendix, the descriptions and operational and maintenance procedures of the following equipment are stated.

TABLE 2-0 MATES IV Samplers

Sampler Type	Vendor and Model Number
Volatile Organic Compounds (VOC)	XonTech 910A/ 912
Metals; Carbonyls, Cr^{+6}	XonTech 924
$PM_{2.5}$ Speciation Air Sampling System	Met One Instruments SASS
Wind, Speed, and Direction (WSD)	R.M. Young Mechanical Wind Sensor
PM_{10}	Graseby-GMW 1200 PM_{10} Sampler
Aethalometer	Teledyne API 602
UFP (CPC)	Teledyne TSI 651

The siting, acceptance testing, and calibration functions for each type of equipment identified above are defined below. Non-generic functions are discussed under each equipment heading.

2.2 EQUIPMENT CHARACTERISTICS

2.2.1 Siting

A) Monitoring site selection criteria was the same for all fixed sites. Site uniformity was achieved to the greatest degree possible. Descriptions have been prepared for all sampling sites and can be found in the annual network plan at www.aqmd.gov/home/library. The description includes, at a minimum, the type of ground surface, the direction, distance, and approximate height to any airflow obstruction, and the direction and distance to any local pollutant sources.

B) The sampler platform was located in an area with unobstructed airflow, especially in the direction of any recognized sources of the sampled compounds. This is critical since turbulence and eddies from obstructions will cause non-representative results. The distance between an obstruction and the sampler is not to be closer than two times the height of the obstruction.

C) Locations significantly influenced by nearby pollutant sources, activities potentially impacting air quality or where reactive surfaces may cause chemical changes in the air sampled were avoided. Micro-meteorological influences caused by nearby hills, bodies of water, valley drainage flow patterns, etc. were considered when selecting a monitoring site.

D) The recommended intake probe height for criteria pollutants is 3 to 15 meters above ground level as near breathing height as possible with the additional criteria that a site will not be placed where a building is an obstruction or where equipment is easily vandalized.

E) The probe should extend at least two meters away from the supporting structure. If the probe is located on a building, it must be mounted on the prevailing windward side.

2.2.2 Acceptance Testing

Acceptance testing was performed on all instrumentation and sampling equipment approximately one month after receipt. After acceptance testing was completed and instruments were found to meet acceptance criteria, they were deployed in the field and ambient sampling commenced. Acceptance testing was conducted according to the following steps:

A) All instruments were carefully unpacked from their shipping containers and checked for completeness, broken parts, and correct subunits.

B) The units were assembled according to manufacturer guidelines and prepared for start-up.

C) The flowrate/flow meter portion of the pneumatic system, if any, was checked using the most appropriate calibration-transfer standard to verify the operating flow/flowrate.

D) Timer accuracy was evaluated by comparing it to an elapsed-timer standard. All timers must hold their accuracy to ±5 minutes over a 24-hour period.

E) Any deficiency was corrected and addressed following the manufacturer’s recommendations and procedures as stated in the operations manuals.

2.2.3 Calibration

At each sampling site, final dynamic calibrations were performed on each analyzer and sampler prior to the start of the program. At the end of the sampling period, an “As Is” calibration was performed on each analyzer to ascertain the amount of analyzer drift.

2.2.4 Sample Pickup

The SCAQMD Senior Chemist sample custodian distributed the sampling media to the field technician. Filters and carbonyl cartridges were transported in coolers with blue ice and the canisters were kept capped at all times during transportation. Once the filter and carbonyl cartridge were used to collect a sample, they were refrigerated until returned to the SCAQMD Laboratory. The sampling media was returned to the sample custodian as soon as possible following sampling.

2.2.5 Troubleshooting

For instrument usage overlapping the NATTS program usage, the routine maintenance and quality control checks were based on U.S. EPA *Quality Assurance Project Plan for the Air Toxics Monitoring Network* (EPA-454/R-01-007) and U.S. EPA National Air Toxics Trends Station (NATTS) technical assistance document (NATTS TAD, 2009) and are listed in Appendix P. For the instruments that were not present in the NATTS program, a maintenance guide based on the equipment manufacturers’ suggested operating procedures was made available for each instrument. If an instrument fell out of the correct operating range, or if there was a component failure, the operator immediately placed a call to the SCAQMD STA/AM Support and Repair Section to schedule a repair.

2.2.6 Repair

The potential failure of instrument and equipment components such as pumps and flow controllers was addressed by SCAQMD maintaining an inventory of staff replaceable spare parts.

2.3 SAMPLING EQUIPMENT

2.3.1 XonTech 910A and 912

2.3.1.1 XonTech 910A - Description

The XonTech 910A air sampler is designed to take air samples at a constant flow rate for a known sampling period. It is durable, serviceable and accurate making it useful for sampling a wide variety of gases. Its compact, constructed simply, and offers long term reliability.

Specifically, the 910A sampler takes air from the sample inlet and injects it into a canister at a constant flow rate for the preset period of time. Excess air is exhausted through a bypass exhaust. The constant flow rate and elapsed time allow the operator to calculate the integrated air sample volume. The sample was pumped through a metal bellows pump that develops sufficient pressure to control the flow with a mass flowmeter. The XonTech 910A is operated according to the guidelines set forth in XonTech's *Model 910 Toxic Air Sampler Operations Manual*[3].

2.3.1.2 XonTech 912 - Description

The XonTech 912 adapter may be added to the XonTech 910A to enhance sampling capability over a reduced period of time. It cannot operate independent of the 910A. It is designed to route gas samples to a maximum of 16 canisters. An internal time base can be used to step a rotary valve from canister to canister at a user-selected rate. The 912 also accepts timing signals from the model 910A. The XonTech 912 adapter was operated according to the guidelines set forth in XonTech's *Model 910 Toxic Air Sampler Operations Manual*[4].

2.3.1.3 Pre-Testing

All canister samplers were field tested prior to and during field sampling.

2.3.1.4 Cleanliness Check

To perform a system bias check, ultra-pure air or nitrogen was injected into the sample manifold to fill one, 3-hour canister. Additionally, the 24-hour sampler was tested by maximally increasing its sample flow to fill a canister in approximately 6 hours. A field blank canister was filled at the site by flowing pure air or nitrogen into an evacuated cylinder. A difference of less than 1 part per billion (ppb) per compound between the field blank and the bias test samples is the acceptance criteria for this test and indicates that the system is not contaminated (non-biasing). A value greater than 1 ppb per compound required investigation and corrective action. A system bias check was repeated until all biases are demonstrated to be eliminated. The SCAQMD's Ambient Monitoring Support Group performed system repairs. This group assembled, leak checked, disassembled, and cleaned the sample manifold, and the Auditing Group calibrated the mass flow controller (MFC) for flow.

2.3.1.5 Canister Sample Pickup

An SCAQMD Instrument Specialist picked up clean verified clean silica lined stainless steel canisters from the Laboratory. Evacuated canisters were transported by vehicle to the respective air monitoring stations. Each canister has a tag attached (Appendix F). This tag was completed and contained the following information: sample site, operator initials, and sample date. The air monitoring station operator completed this tag once the canister was set up for sampling. Once the canister is filled and disconnected from the 910A or 912 sampler, and prior to returning the sampled canister to the Laboratory, the canister number, start

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[3] XonTech, Inc. (1987). *Model 910 Toxic Air Sampler Operations Manual*. Van Nuys, CA.

[4] Ibid.

vacuum, end pressure (psig), and elapsed time was recorded on the MATES IV sample log (Appendix E). The time on the QC chart was also checked and adjusted. This value must be within ± 10 minutes of actual Local Standard Time. The canister was delivered to the sample custodian in the Laboratory as soon as possible.

2.3.2 XonTech 924

2.3.2.1 Description

The Model 924 Toxic Air Samplers are designed to collect ambient air particulate samples on a variety of filter materials and sorbent media in unattended field use. These samples were brought to the SCAQMD headquarters for Laboratory analysis. The sampler precisely controls the sampling time and flowrate through each sampling head using a microprocessor and mass flow controller (MFC). Sampler design is modular to facilitate installation of individual sampling channels. Each sampler may accommodate eight sampling channels for two types of sample collection media: one that accepts 37 or 47 millimeter filters and another that accepts sorbent tubes.

The sampler consists of three modules, each contained in a separate enclosure. The heart of the system is the control module. This module contains the microprocessor, controller, mass-flow controllers, and front panel, displays, printer, and keypad. The difference between the Model 920 and 924 is the electronics have been upgraded to reflect the increase in microprocessor functionality presently available that was not available in the circa 1995 Model 920. The sampling module is equipped with isolation valves that protect the sampling media from passive sampling before or after sampling or sample loss after sampling. The sampling inlet height is 1.2 meters above ground level. The third element of the sampler is the pump module. It contains the vacuum pump that provides adequate capacity for simultaneous operation of three, 30 liters per minute (lpm) and 200 cubic centimeters per minute (ccm) sampling channels.

2.3.2.2 Operation

To use the sampler, the operator inserted the sample filter cassette or sorbent tube into the sampling head and keyed in the filter or sorbent head number. Start and stop times, and flow rates are pre-programmed or can be manually input. Following the sampling period, a report is automatically printed which was removed from the printer and submitted to the Laboratory with the filter for analysis.

The XonTech 924 samples carbonyl compounds for an integrated 24-hour period only. Warm and cold-start options as well as all other operational specifications are discussed in XonTech, Inc. *Model 924 Toxic Air Sampler Operations Manual*[5]and SCAQMD SOP 00094, *RM Environmental Systems Inc. (RMESI) 924 Toxics Sampler*.

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[5] XonTech, Inc. (1987). *Model 924 Toxic Air Sampler Operations Manual*. Van Nuys, CA.

2.3.3 MET One SASS

2.3.3.1 Description

The MET One Speciation Air Sampling System (SASS) accommodates up to five sampling canisters which may hold multiple 47 millimeter filters to capture $PM_{2.5}$ particles. The $PM_{2.5}$ separation is produced by a sharp cut cyclone (SCC) that removes both solid and liquid coarse particles. Particle penetration through the SCC mimics the $PM_{2.5}$ cutoff curve of the WINS impactor as defined by the U.S. Environmental Protection Agency. All routine maintenance can be done in the field. Filter containers are transported to the Laboratory for inspection, cleaning and unloading/loading of sampling substrates. Every element of the sampler contacted by the sampled air stream ahead of the filter, including the inlet can be cleaned with each sample change. The SASS was designed with individual sharp cut cyclone inlets. Particles larger than 2.5 micron aerodynamic diameter are removed by the cyclonic inlet mounted with each filter container. The filter containers may be equipped with a diffusion denuder ahead of the filter to remove selected gaseous compounds[6].

2.3.3.2 Module and Media Description

The integrated SASS canister contains the following components: a sharp cut cyclone, a denuder to remove nitric acid or ammonia gases, a 47 mm front filter for particle capture, a 47 mm tandem or backup filter as needed, and a cover to protect the components.

Several types of filter media are needed for assaying the different chemical constituents of ambient particles. The chosen filter media are suitable for the type of analysis to be conducted. For example, Teflon filters were used for gravimetric mass and trace metal determinations. Quartz fiber filters were used for elemental and organic carbon analysis as well as anions and cations analysis.

2.3.4 R.M. Young Mechanical Wind Sensor

2.3.4.1 Description

The R.M. Young Mechanical Wind Sensor is used to measure wind speed and direction (WSD) data. The performance specifications of this wind system are delineated in Table 2-1. Data is stored in a data logger until it is telemetered to the SCAQMD's information system.

For a complete description of anemometer operations, refer to *R.M. Young AQ Wind Monitor User Manual and Product Specification*[7].

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[6] MET One Instruments, Inc. (2001), *Model SASS & SuperSASS $PM_{2.5}$ Ambient Chemical Speciation Samplers*, Grants Pass, Oregon.

[7] R.M. Young Company. *SAQ Wind Monitor User Manual (05305) and Product Specification* http://www.youngusa.com/products/7/6.html

TABLE 2-1 Performance Specifications - R.M. Young Mechanical Wind Sensor

Wind Speed	Wind Direction
1. Starting Threshold 0 mph	0 degrees
2. Range 0-112 mph	0-360 degrees
3. Accuracy ± 1%	±3 degrees

2.3.4.2 Siting

WSD measurement, barometric pressure, relative humidity, and temperature monitoring equipment were housed in monitoring stations. The stations meet Environmental Protection Agency (EPA) criteria for National Air Monitoring Stations (NAMS) and State and Local Air Monitoring Stations (SLAMS) as cited in part 40 Code of Federal Register (CFR) Part 58.

When the meteorological equipment was located at a permanent air monitoring station, it was installed on a 10-meter tower in an unobstructed position. When the equipment was installed in a mobile platform, it was mounted on a 6.1-meter mast.

2.3.4.3 Installation

WSD equipment was assembled and oriented according to the manufacturer's instructions. The manufacturer’s manuals are used as the primary installation guide.

Once the WSD monitoring equipment was assembled, mounted on the mast, and raised to its full height in the correct orientation, the direction sensor was aligned to true north using a true-north-calibrated compass. Although alignment was performed from a distance, accuracy within five degrees was achieved and is considered acceptable.

2.3.4.4 Telemetry Interfacing

At each fixed monitoring site an existing telemetry system was used to transfer WSD data from the station to the SCAQMD central computer.

2.3.4.5 Routine Servicing

The air quality instrument specialist responsible for each monitoring site performed routine servicing and periodic checks of the WSD system, barometric pressure, relative humidity, and temperature. The instrument specialist also noted and initialed the type of service performed and the results of each periodic check in the system’s logbook, and on the WSD Monthly Quality Control Maintenance Sheet (Appendix C).

Any suspected operational problem were communicated in detail by the instrument specialist to the appropriate supervisor. The supervisor, when informed of the problem, contacted the station operator to determine if the problem could be corrected in-house. If the problem could not be corrected in-house, the supervisor arranged for a replacement of the WSD system. Anemometer servicing was conducted as described below.

A) Weekly Checks

The mechanical anemometer, barometric pressure, and temperature were checked for daily trends as an indication of acceptable operation.

B) Monthly Checks

The mechanical anemometer was lowered from the tower and visually checked, relative humidity and temperature aspirators were cleaned as necessary. The mounting of all three sensors was checked to verify they were securely attached.

2.3.4.6 Calibration

The RM Young Model 05305VP/101283-G2 Wind Monitor-AQ type wind speed and wind direction sensors are calibrated at the factory before receipt. Prior to the deployment of the sensor to the field, an initial calibration check was performed. Field calibrations were performed annually and/or immediately after sensor repair (bearing replacement), rewiring or replacement of the sensor per Draft SOP00070, October, 2011.

2.3.4.7 Data Handling

All data generated from the WSD system was stored in a data logger before being transmitted to SCAQMD headquarters. Data was also recorded on an electronic strip chart recorder on site. During site visits any maintenance or repair work was noted on the strip chart. Strip chart data is uploaded to the SCAQMD quarterly.

2.3.5 Graseby-GMW 1200 PM_{10} Sampler

2.3.5.1 Description

The Graseby-GMW Model 1200 two-stage, size-selective inlet (SSI) head sampler is used to sample particulates with an aerodynamic diameter of 10 microns and less at Pico Rivera, Compton, Huntington Park and the Hudson school site in Long Beach . The inlet head is symmetrical and therefore insensitive to wind direction and relatively insensitive to wind speed. The air is drawn through the acceleration nozzles at 40 cfm. Particles larger than 10 microns (aerodynamic diameter) pass through the nozzel and are deposited onto the flat surface below the nozzles. The air sample is then drawn through vent tubes, the second-stage fractionator, and the filter where particulate matter is collected. The height of the vent-tube inlets above the acceleration nozzle plate prevents re-suspension and transport of particles.

The PM_{10} sampler draws air into a specially shaped inlet at a flowrate of 40 ±4 cubic feet per minute (cfm). PM_{10} particulate matter collects on an 8 x 10 inch matted quartz fiber filter. The concentration of PM_{10} particulate matter (in micrograms per cubic meter) is calculated by weighing the particulates collected on the filter and dividing by the measured air sample volume. The standard sampling frequency is every sixth day.

To initiate sampler start-up, the operator completes a PM_{10} sampler site report and sends it to the appropriate SCAQMD supervisor for review using the criteria of compliance with SLAMS total suspended particulates (TSP) siting as stated in 40 CFR Part 58, Appendix E. The PM_{10} sampler may be calibrated according to Appendix A, Section A.5.9 of the SCAQMD's *Quality Assurance Plan for Air Monitoring*[8].

The matted, quartz-fiber filter is very delicate and can be easily torn or gouged. Because a damaged filter invalidated results, it was important to carefully handle it by the edges. Complete operational details are contained in *Instruction and Operation Manual High Volume* PM_{10} *Sampler*[9].

2.3.6 Black Carbon as Measured Using an Aethalometer

The term soot often refers to impure carbon particles resulting from the incomplete combustion of fossil fuels and various types of biomass burning. Soot is a key component of atmospheric aerosols because of its strong ability to absorb solar radiation, causing a warming effect on global and regional climate. Soot is also of interest because of its potential 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-Organic Carbon fraction of soot is referred to as Black Carbon (BC) or Elemental Carbon (EC). While BC is an "optical term" that is used to denote strong light-absorbing carbon, EC is a "chemical term" that refers to thermally-refractory carbon with a graphite-like structure. Thus, BC and EC are two methodologically defined species that are typically measured using optical (summarized here and described in greater detail in Appendix VI) and thermal-optical methods (described in section 3.3 of this Appendix), respectively.

BC Measurements

The Aethalometer® (developed by Magee Scientific, Berkeley, CA) is an instrument that uses optical analysis to determine the mass concentration of BC particles collected from an air stream passing through a filter. Aethalometers are the most common instruments used to measure BC in real time. The principal and working of the Aethalometer are described in detail elsewhere [Hansen et al., 1984]. Briefly, the gas stream (frequently ambient air) passes through a filter material which traps the suspended particulates, creating a deposit of increasing density. A light beam projected through the deposit is attenuated by those particles which are absorbing ('black') rather than scattering ('white'). Measurements are made at successive regular time intervals. The increase in attenuation from one measurement to the next is proportional to the increase in the density of optically absorbing material on the filter. This, in turn, is proportional to the concentration of the material in the sampled air stream. The sample is collected as a spot on a roll of filter tape. When the density of the deposit spot reaches a pre-set limit, the tape advances

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[8] Applied Science & Technology. (1996). *Quality Assurance Plan For Air Monitoring.* Diamond Bar, CA: South Coast Air Quality Management District.

[9] Graseby Anderson. (1988). *Instruction and Operation Manual High Volume* PM_{10} *Sampler.* Atlanta, GA.

to a fresh spot and the measurements continue. Measurement of the sample gas flow rate and knowledge of the instrument's optical and mechanical characteristics permit a calculation of the average concentration of absorbing particles in the gas stream during the sampling period. Aethalometers may operate on time-base periods as rapid as 1 second, providing quasi-real-time data. One minute to one hour averages are commonly used in most field applications. Comparison of aethalometer data with other physical and chemical analyses allows the output to be expressed as a concentration of BC. A more detailed description of the Magee Scientific Aethalometer along with monitoring results can be found in Appendix VI.

2.3.7 Ultra Fine Particulate (UFP)

Ultrafine Particles (UFPs) are typically defined as particles with an aerodynamic diameter less than 100 nm. UFPs are emitted from both natural and anthropogenic sources, although in most urban environments vehicular fossil fuel combustion constitutes the major contributing source. The terms UFPs and nanoparticles (NP; diameter < 0.05 µm) are often used interchangeably, and the definitions of each generally vary with the study or application. While fine particulate matter ($PM_{2.5}$) dominates the mass distribution of atmospheric particles, UFPs account for about 90% of the total particle number. For this reason, their concentration is usually expressed in terms of total particle count (i.e. # per cubic centimeter of sampled air, or $\#/cm^3$), even though a small fraction of the particles being counted may be above 100 nm.

Condensation Particle Counters (CPCs) are instruments that provide the total number concentration of particles above a lower size limit (~3-20 nm, depending on make and model) in real-time. By mean of CPCs, UFPs are grown through condensation in a controlled super-saturation environment to larger sizes and then measured/counted using a photodetector. Although CPCs are the most widely used instruments in most applications, they do not provide any information on the original size of the particles counted.

UFP Measurements

The CPC used to measure the ambient number concentration of UFPs at the ten fixed MATES IV sites is commercialized by Teledyne Advanced Pollution Instrumentation PI (Teledyne API, Sand Diego, CA). This particular model (651) was specifically designed for network operation and its performance was thoroughly evaluated by SCAQMD Staff prior to the beginning of MATES IV. The Teledyne 651 CPC utilizes a patented laminar-flow, water-based condensation growth technique. Particles which are too small (nanometer scale) to scatter enough light to be detected by conventional optics are grown to a larger size by condensing water on them. An air sample is continuously drawn through the CPC inlet via an external pump and a portion of the flow is sent to the exhaust as bypass flow. The aerosol sample is pulled through a cool region saturated with water vapor and its temperature is equilibrated. The sample then passes to a growth section where wetted walls are heated to produce an elevated vapor pressure resulting in a thermodynamic "supersaturation" condition. The small cool particles in the flow stream act as nuclei for condensation, and grow into micron sized droplets. The droplets are passed through a laser beam and create a large light pulse. Every particle pulse event is detected and counted. In this technique particle concentration is measured by counting every individual particle in the air stream. The CPC model 651 is able to detect particles as small as 7 nm in diameter and has a detection range between 0 and 1,000,000 #/cm^3. A more detailed discussion of the Teledyne 651 CPC monitoring results can be found in Appendix VI.

2.3.8 Polycyclic Aromatic Hydrocarbons (PAH)

Polycyclic Aromatic Hydrocarbons (PAHs) on polyurethane foam (PUF) sampling media were analyzed by Eastern Research Group (ERG), Morrisville, North Carolina. Sampling was performed by SCAQMD staff of Instrument Technicians and Laboratory Technicians. Chain of Custody was maintained from receipt of sampling materials received from ERG through the return of the samples for analysis. SCAQMD staff was responsible for calibration, calculating and reporting of the total air volume of each sample. This included calibration of the sampling instrument flow rate. A short method description is given in Appendix L.

Chapter 3.0
Laboratory Procedures

3.1 INTRODUCTION

Since 1994, the SCAQMD has implemented the U.S. EPA Photochemical Assessment Monitoring Stations (PAMS) program to gather data on ozone precursors. In 2008 the National Air Toxics Trends Stations (NATTS) was implemented in the South Coast Air Basin. Some of the same sampling instruments currently used in the PAMS and NATTS programs were used in MATES IV. Hence, many of the procedures and protocols for the MATES IV program were based on the SCAQMD *Quality Management Plan for Environmental Measurement Programs*[10] (January 2009). QAPP, Chemical Speciation of PM2.5 Filter Samples (2005), and National Air Toxics Trends Stations Technical Assistance Document (NATTS TAD, 2009). However, MATES IV also utilizes several analytical methods not performed under the federal programs and the protocols included herein are based upon manufacturer's measurement and quality control procedures that are intended to ensure that the data quality is suitable for the intended purposes of MATES IV.

The SCAQMD utilized Air Quality Instrument Specialists to collect field samples and deliver them to the Laboratory sample custodian. The Laboratory sample custodian handled logging and distribution within the SCAQMD Laboratory. Procedures for proper sampling and initial chain-of-custody are outlined in the SCAQMD *PAMS Air Monitoring Network Quality Assurance Plan*[11], Section 7E Parts 1 and 2.

3.2 SAMPLE HANDLING

All sampling media were handled according to the Laboratory practice for implementation of toxics analysis and particulate matter network programs, as applicable. Field instrument specialists completed the sampling information and chain-of-custody forms[12], and delivered the samples to the Laboratory sample custodian.

3.2.1 Canister Cleaning

The SCAQMD Laboratory has a canister cleaning oven system. Per SOP00091 entitled "Canister Cleaning System (CCS) Ovens 3 & 4 Toxics," these systems utilize humidified nitrogen to flush and clean canisters in a heated oven to less than 5 ppb carbon of total organic compounds. The canisters are held at 80°C and are flushed a minimum of seven times over a 2 ½ -hour period. Every canister is removed from the canister cleaning oven and analyzed for residual hydrocarbons. Data collected in performance of SOP00091 demonstrates the cleaning procedures satisfy cleanliness requirements and long-term experience has proven that the

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[10] Applied Science & Technology. (2009). *Quality Management Plan for Environmental Measurement Programs.* Diamond Bar, CA: South Coast Air Quality Management District.

[11] Applied Science & Technology. (1992). *PAMS Air Monitoring Network Quality Assurance Plan.* Diamond Bar, CA: South Coast Air Quality Management District.

[12] These forms consist of the Size-Selective Inlet PM_{10} Sampler Envelope (Appendix B), MATES IV Sample Log (Appendix E), and VOC Canister Tag (Appendix F).

canister-cleaning oven system is sufficient to provide clean canisters. Any hydrocarbons (above the threshold concentrations) found in canister trigger investigation and corrective action. All canisters (8) in the batch are re-cleaned and tested again to assure they meet cleanliness requirements. The cleaning date and operator are noted on the canister tag and in an electronic database that serves as the primary chain-of-custody.

3.2.2 Field Canister Use

Canisters were transported by the instrument specialist to the site and installed in accordance with the sampling SOP00080 included in the *PAMS Air Monitoring Network Quality Assurance Plan*. Once the sample was taken and the sample time, canister number, and start and stop vacuum were noted on the MATES IV Sample Log (Appendix E) that accompanied the canister starting with sample collection. All samples were promptly returned to the Laboratory for log-in and distribution to the appropriate Senior AQ Chemist.

3.2.3 Sample Distribution in the Laboratory

The Laboratory sample custodian (Senior Chemist) logs in received samples and distributes them to the appropriate AQ Chemist following established Laboratory procedures. The sample custodian distributed samples to Laboratory personnel starting with the responsible Senior AQ Chemist.

3.3 ANALYSIS METHODS – APPENDIX A COMPOUNDS

Gaseous compounds listed in Appendix A were analyzed using gas chromatography with mass spectrometry and flame ionization detection (FID) after cryo-focusing. This technique provides for instrument sensitivity sufficient for meeting MATES IV measurement criteria. The method generally follows the EPA Method TO-15; *Determination of Volatile Organic Compounds (VOCs) in Specially Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS),* as found in SCAQMD SOP0008B. Carbonyl analysis was conducted using EPA Method TO-11*, Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Pressure Liquid Chromatography*. These methods are detailed in the EPA *Compendium of Methods for the Determination of Toxic Organic Compounds*[13] and SCAQMD SOP0006. A short method description for sampling and analysis of VOCs by GC/MS can be found in Appendix K.

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[13] Winberry, William, Murphy, Norma & Riggan, R.M. (1988). *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*. Research Triangle Park, NC: Quality Assurance Division, Environmental Monitoring Systems Laboratory, Office of Research and Development, US Environmental Protection Agency. (EPA-600/4-84-041)

Carbonyl measurements were performed using the NATTS sampling and analysis methodology delineated in the NATTS TAD (2009). The California Air Resources Board (CARB) toxic network design method was followed using the XonTech 924 with a carbonyl channel. A potassium-iodide-coated ozone denuder was also used in all carbonyl samplers. Waters ® silica gel cartridge impregnated with dinitrophenyl hydrazine was used to sample for carbonyl compounds. A short method description for the carbonyl sampling and analysis can be found in SOP #00094 and in Appendix G.

Metals collected on Teflon filters using XonTech 924 samplers were analyzed by Energy Dispersive X-ray Fluorescence (XRF) following the procedure found in SCAQMD SOP00004 *Standard Operating Procedure for the Analysis of $PM_{2.5}$ Filter Samples by Energy Dispersive X-Ray Fluorescence Spectrometry*. For $PM_{2.5}$ samples, a Teflon filter was also used, and XRF was used for metals analysis. A short method description for sampling and analysis of elements by XRF is attached to this document as Appendix H. Filters were also analyzed by ICP/MS following the procedure found in SCAQMD SOP#00005, *The Determination of Metals in Ambient Particulate Matter by Inductively Coupled Plasma Mass Spectrometry (ICP/MS),* March 9, 2010.

Hexavalent chromium in ambient air is measured by collecting total suspended particulate matter on 37-mm cellulose filters impregnated with 0.12M sodium bicarbonate solution using the Xontech 924 Toxic Air Sampler. The samples were analyzed by a Dionex® ion chromatograph (IC) equipped with a UV-Vis detector. Hexavalent chromium is detected at 530 nm after a post-column derivatization reaction with diphenylcarbazide. The method description for hexavalent chromium sampling and analysis is found in Appendix M.

Particulate filter samples for both PM_{10} and $PM_{2.5}$ were analyzed for metals, ions, total mass, organic carbon (OC), elemental carbon(EC), and total carbon (TC). The procedure for mass and ion determinations follows the methodology used in support of the SCAQMD (federally recognized) PM_{10} Network activity. Analysis for EC, OC and TC of the PM_{10} and $PM_{2.5}$ filter samples was analyzed using the Interagency Monitoring of Protected Visual Environments A (IMPROVE A) method. The method evolves carbon from filters by heating and optically monitors carbon as it is evolved from the filter. After catalysts oxidize then reduce the carbon, it is measured by a flame ionization detector. A more detailed description of the IMPROVE A method can be found in Appendix J.

The compounds listed in Appendix A were sampled on a one-day-in-six sampling schedule synchronized with the national PM_{10} and $PM_{2.5}$ network schedules. These samples were integrated 24-hour samples. SCAQMD personnel conducted both the sampling and analysis. Contract Instrument Technicians and Chemists assisted SCAQMD employees.

Some of the compounds listed in Appendix A do not have consensus methods of analysis; however, ASTM International or American Industrial Hygiene Laboratory test methods and test methodologies were followed or adapted as needed.

3.4 SAMPLING SCHEDULE

MATES IV sampling was conducted on the same schedule as used by the air-monitoring network. The air monitoring network sampling schedule can be found on the U.S. EPA website at; www.epa.gov/tnn/amtic , and follows a six-day monitoring schedule for TSP, Pb, PM_{10}, $PM_{2.5}$ and VOCs. This sampling schedule has several benefits:

1) Data from MATES IV can be correlated with ambient data taken on the same day.
2) Additional staff time to service and maintain MATES IV sampling equipment and instrumentation was minimized.
3) Sample set-up, retrieval, and delivery time to the Laboratory was minimized.

3.5 COMPARISON OF ICP/MS TO XRF

For MATES IV, in addition to the use of XRF for the analysis of ambient metals collected on filters; Inductively Coupled Plasma Mass Spectrometry (ICP/MS) was also employed. While both the XRF and ICP/MS instruments are designed for metals analysis, the principals of analysis are vastly different. In short, XRF is a whole sample non-destructive technique requiring no sample preparation. ICP/MS, however, requires a vigorous acid extraction process prior to analysis. A more detailed of these methods can be found in Appendix N along with charts for selected metals comparing analytical results.

3.6 NICKEL ANALYSIS BY ICP/MS

Nickel overestimation by ICP/MS was determined to be caused by the ubiquitous and proportionally very high concentration of Calcium and Sodium which form interfering molecular ions in the plasma. The subsequent correction for Ni by changing the isotope of acquisition to 58 Amu from 60 Amu is described in Appendix O.

Chapter 4
Quality Assurance and Quality Control

4.1 INTRODUCTION

To achieve the maximum data quality in the MATES IV program, SCAQMD implemented the following Quality Assurance/Quality Control (QA/QC) plan. This Chapter contains the objectives, procedures, documentation, and data review techniques that were used by the SCAQMD to assure that MATES IV produced data that met or exceeded the accepted criteria for its intended use as described below.

4.2 OBJECTIVES

There were two major objectives for the MATES IV Quality Assurance Project Plan. These objectives were: (1) to provide one year MATES IV monitoring which would meet SCAQMD data requirements for accuracy and precision to serve as inputs to accepted risk assessment model(s) and comparisons to other air toxics measurements and (2); to provide time and spatially resolved comparison of black carbon and ultrafine particle concentrations. Thus MATES IV provides data that meets the measurement objectives (MQOs) displayed in Table 4-1. Where practicable, MATES IV MQOs were designed to meet or exceed U.S. EPA Monitoring Programs MQOs such as NATTS and PM2.5 Speciation for comparability to other national air toxics monitoring data, including historical SCAQMD NATTS and PM2.5 speciation data. Measurements not present in the Federal programs such as black carbon and ultrafine particles, are not intended to directly calculate risk. They serve as real time indicators of pollution for comparison over time and space and thus have MQOs that are appropriate.

TABLE 4-1 Measurement Quality Objectives

			CRITERIA/PARAMETER			
ASSESSMENT	**MEASURES**	**PROCEDURE**	VOCs	Carbonyls	PM_{10}	$PM_{2.5}$
Accuracy	Percent Deviation from True Value	Audits	± 25%	± 25 %	± 10%	± 10%
	95% Probability Limits		< 30%	< 30%	< 15%	< 15%
Precision	Percent Deviation from True Value	Collocation	± 25%	± 25%	< 10%	< 10%
	95% Probability Limits		< 30%	< 30%	< 15 %	< 15 %
Completeness	Percent of Valid Data		85%	75%	90%	90%

4.3 PROCEDURES

4.3.1 Quality Assurance Procedures

The SCAQMD is one of the four Primary Quality Assurance Organizations (PQAO) responsible for air monitoring in California, and is committed to achieving the highest possible data quality level in the MATES IV programs. The Quality Management Plan (QMP), which is the foundation document for ensuring high quality and defensible data (approved in 2009) presents SCAQMD quality system and describes the organizational structure, functional responsibilities of management and staff, lines of authority, and general methodology for assessing all activities conducted in support of air monitoring and analysis, air quality assessment and other environmental measurement activities conducted by the agency.

The quality goals and QA requirements for the particle and gaseous pollutants measured during MATES IV are found in various Quality Assurance Project Plan (QAPP) documents as outlined in the following paragraphs. These QAPPs also describe the responsibilities within the organization for carrying out each program and meeting specific QA/QC objectives. They address the Data Quality Objectives (DQOs) of accuracy, bias, comparability, completeness, detectability and representativeness, list the Method Quality Objectives (MQOs) of precision, bias, completeness, sensitivity and, where applicable, flow rate accuracy for the analytes of interest. They document the Standard Operating Procedures (SOPs) and Operational Assistance Guides (OAGs) which are directions for specific performing measurement activities. Finally, they list the required QA/QC requirement for each activity and provide instructions for data review, QA oversight, and corrective actions.

The quality goals and QA requirements (with the exception of siting) for monitoring ambient levels of volatile organic compounds (VOCs), carbonyls, hexavalent chromium , and polycyclic aromatic hydrocarbons (PAHs) were adopted from the US EPA National Air Toxics Trends Stations (NATTS) program. These requirements can be found in the SCAQMD NATTS QAPP, which was last revised in 2013 and is currently under review by the US EPA Region 9.

The quality goals and QA requirements (with the exception of siting) for monitoring the main components of fine particulate matter (PM2.5) including Organic and Elemental Carbon (OC/EC), Anion and Cations, and trace metals were adopted from the US EPA Chemical Speciation Network (CSN) program. These requirements can be found in the SCAQMD PM2.5 Speciation QAPP, which was last revised in 2013 and was approved by the US EPA Region 9 in 2014.

The quality goals and QA requirements (with the exception of siting) for monitoring fine and coarse PM (PM2.5 and PM10 FRM) were adopted from the US EPA Criteria Pollutant Monitoring Program. These requirements can be found in the SCAQMD Criteria Pollutant Monitoring Program QAPP,, which was last revised in 2012 and approved by the US EPA Region 9 in 2013.

The quality goals and QA requirements (with the exception of siting) for monitoring ultrafine particles (UFPs) and black carbon (BC) can be found in the SCAQMD Special Monitoring Program QAPP, which also describes the protocols and procedures followed by SCAQMD for monitoring other "non-criteria" pollutants and performing short-term measurement studies similar to those conducted during MATES IV (see Chapter 5 for details). The current version of this QAPP was last revised in 2013 and is currently awaiting approval by the US EPA Region 9.

The SCAQMD objectives, procedures, documentation, and data review techniques assure the MATES IV program will produce data that are accurate, precise, reliable and legally defensible. The technical procedures for QA/QC include annual system audits on all equipment in the laboratory and at all MATES sampling sites. Quality control procedures also include proper record keeping, standard checks, routine calibrations of the sampling and analytical equipment, and collecting collocated samples at regular intervals and are described in the next section.

4.3.2 Quality Control Procedures

The SCAQMD performed annual flow audits on all PM_{10} and $PM_{2.5}$ samplers. These flow audits were conducted according to the procedures outlined in the SCAQMD's *Quality Assurance Plan for Ambient Monitoring*, *Appendix K*. In addition, the California Air Resources Board (CARB) performs quarterly audits of flows at District air monitoring stations. The CARB also annually audits laboratory systems related to mass measurement in the $PM_{2.5}$ and PM_{10} networks. The EPA and CARB annually audits the performance of the SCAQMD Laboratory for VOCs, carbonyls and lead (Pb) using the EPA's National Performance Audit Program and the CARB's toxic VOC performance audit.

A) Field Checks

SCAQMD staff performed a number of activities concurrent with conducting field checks. Specifically, staff:

1) observed and recorded all required data for each sampler's monthly maintenance sheet, chain-of-custody form, and sample identification tag
2) checked and reset all timers if off by more than ± 5 minutes Local Standard Time
3) checked and adjusted the flow settings if they are not within ± 5% of the calibrated setting

B) Laboratory Daily Checks

SCAQMD staff monitored the PM 2.5 room balance using a NIST traceable check standard; conducted a gas chromatograph standard check using a NIST traceable gas standard; observed, recorded, and corrected all sample media equilibration conditions if they were out of tolerance.

C) Semi-Annual Checks

SCAQMD staff conducted multipoint calibrations of mass-flow controllers in samplers; performed instrument leak checks; and cleaned PM_{10} inlet heads for all instruments and samplers used in support of MATES IV.

D) Annual Checks

SCAQMD staff cleaned sample probes using de-ionized water and a soft cloth; conducted sample probe leak checks and repaired them as necessary; and conducted 24-hour timer tests by operating the sampler to observe actual run length. Actual start and stop were observed. The timer was repaired if the sample period varied by more than ± 20 minutes from 24 hours.

4.4 DOCUMENTATION

A critical element of an effective QA/QC system is complete and accurate documentation. To ensure that all samples are properly handled, inspected, collected, analyzed, and reported, a comprehensive set of QA/QC documents was prepared and completed. The information reported in these documents was crucial in validating reported data quality. Lack of properly documented data could be grounds for data invalidation. A summary of QA/QC sampling activities is attached as Appendix P.

A) Chain-of-Custody Forms

Sample forms (Appendices B, D, and E) are necessary to identify and control the disposition of the samples through the multiple steps of preparation, sampling, retrieval, analysis, and data reporting. As appropriate, chain-of-custody forms accompanied samples collected under MATES IV. These forms originated with field operators, were delivered to the Laboratory, and submitted to the assigned Laboratory staff. The Laboratory is responsible for storing all chain-of-custody documents.

B) Maintenance Check Sheets

Maintenance sheets (Appendices C and D) were completed by field instrument operators for PM_{10} samplers and wind speed and direction systems. These monthly maintenance sheets were submitted to senior field operators for review, approval, and storage.

Other types of QA/QC, station and laboratory documentation and their descriptions are listed in Table 4-1 through 4-4 and 4-6.

TABLE 4-2 QA/QC Records

Document Name	Brief Description	Format	Storage Location
Training Files	Records substantiating the training and proficiency of staff relevant to this program	Hard copy	AM Branch: File Cabinet in "Bullpen" in AM Area; LSST Branch: Training Binder at Laboratory Front Desk, PDF copies: e:\astd\quality assurance\laboratory \training\scanned forms
QAPP	Master version of QAPP, including pending revisions	Hard copy or electronic	QA Branch Records or M&A online resources and e:\astd\quality assurance\ current_documentation \QAPP_SOPs
SOPs	Current version of all SOPs	Hard copy or electronic	QA Branch Records or M&A online resources and e:\astd\quality assurance\ current_documentation \QAPP_SOPs
Performance Evaluations and Audits	Results of internal and external assessments	Hard copy and/or electronic	QA Branch Records; AM Branch: Principal AQIS Operations; LSST Branch: Laboratory Report Binder and e:\astd\quality assurance\quality assurance branch\audits
Corrective Action Reports	Results or identified QA problems and their resolution	Electronic	Program Office, QA Office and e:\astd\quality assurance\quality assurance branch\QA CAR

TABLE 4-3 Laboratory Records

Document Name	Brief Description	Format	Location
Laboratory Notebooks	Includes the following types of notebooks and bound data sheets: - analysts' notebooks - instrument maintenance logs - reagent preparation logs - materials acceptance tests	Hard copy	Instrument benches
Calibration Certificates and Records	Includes certificates of NIST traceability and similar records	Hard copy	Instrument benches
Control Charts or Equipment	QC information displayed in sequence to help diagnose problems with analytical instruments. Usually includes acceptance limits that are periodically recomputed.	Hard copy or spreadsheet	Hardcopies: Instrument benches. Electronic: instrument control PCs.
SOPs	Current copies of SOPs relevant to the analyses performed in a particular laboratory	Hard copy	Instrument benches, M&A online resources and e:\astd\quality assurance\ current_documentation \QAPP_SOPs
QAPP	A current copy of this QAPP. The Principal Chemist must ensure that each analyst has access to a current copy of the QAPP	Hard copy	QA Branch Records or M&A online resources and e:\astd\quality assurance\ current_documentation \QAPP_SOPs
Analytical Results Database	Results for each chemical analysis with identifying information	Spreadsheet or LIMS	Analyst computer/ LIMS Server
Analytical QC Database	Includes all QC information for each weighing session including standard weights, duplicates, field blanks, and laboratory blanks.	Spreadsheet or LIMS	Analyst computer/ LIMS Server

TABLE 4-4 Station Records

Document Name	Brief Description	Format	Location
Station Notebooks	Logs station activity	Hard copy	Station
Instrument User's Manual and/or Manufacturer's Instructions	Information for setting up, using, and troubleshooting the continuous gaseous monitors	Hard copy	Station
Calibration Certificates and Records	Includes certificates for gases and other chemicals used for calibration	Hard copy/ Electronic	Station/ Shared Drive
QC Records	Results of instrument blanks, calibrations, standard recoveries, and replicate precision	Computer files and hard copy	Maintenance Sheets/ Calibration Sheets/ Database
Raw Data Records	Results of instrument analyses (including supporting data that is not uploaded to the database)	spreadsheets; hard copy; and DMS, chessell, custom database	Database/ Server

4.5 DATA REVIEW

MATES IV data validity was based upon the appropriate implementation of operational and QA/QC procedures described in this appendix. To assure that the program's DQOs were met, responsibility for data review was distributed between the field operators, calibrators, auditors, and supervisors, Laboratory Chemists and Supervisors, QA Supervisors, and the Laboratory and Atmospheric Measurement Managers.

TABLE 4-5 Position Responsibilities

Position	Responsibilities	Upward Lines of Communication
Health Effects Officer	Principal Investigator of MATES IV responsible for direction and implementation of the study; coordinate MATES IV TAC	ADEO: Planning, Rules and Area Sources
Laboratory Services and Source Test Engineering Manager	Responsible for preparation of sampling media and analysis of samples submitted to laboratory	ADEO: Science Technology Advancement
Atmospheric Measurements Manager	Responsible for establishment, operation and maintenance of monitoring stations	ADEO: Science Technology Advancement
Quality Assurance Manager	Responsible for reviewing, developing, documenting, and implementing QA/QC practices and procedures	ADEO: Science Technology Advancement
Principal Air Quality Chemist: Aerosol Analysis	Responsible for laboratory operations of the Aerosol Analysis group which conducts analysis of $PM_{2.5}$ and PM_{10} Mass and TSP Lead filters.	Manager: Laboratory Services and Source Test Engineering
Senior Air Quality Chemist: Aerosol Analysis	Responsible for supporting Aerosol Analysis group operations and 2nd level data validation of data analyzed from $PM_{2.5}$ and PM_{10} Mass and TSP Lead filters.	Principal AQ Chemist: Aerosol Analysis
Principal Air Quality Chemist: Ambient VOC/ Toxics	Responsible for laboratory operations of the Ambient VOC/ Toxics group which conducts carbonyl and VOC analysis	Manager: Laboratory Services and Source Test Engineering
Senior Air Quality Chemist: Ambient VOC/ Toxics	Responsible for supporting Ambient VOC/ Toxics group operations and 2nd level data validation on carbonyl and VOC analyses.	Principal AQ Chemist: Aerosol Analysis
Air Quality Chemist and Assistant Air Quality Chemist	Responsible for following SOPs and GLP in the analysis of samples; submittal of data into LIMS	Principal AQ Chemist: Aerosol Analysis
Laboratory Technician	Responsible for following SOPs and GLP for the preparation of samples or sampling media	Principal AQ Chemist: Aerosol Analysis
Principal Air Quality Instrument Specialist	Responsible for station operations and deployment and/or coordinating repair and calibrations	Atmospheric Measurements Manager
Senior Air Quality Instrument Specialist	Responsible for supporting operations and 2nd level data validation	Principal Air Quality Instrument Specialist
Air Quality Instrument Specialist I and II	Responsible for following SOPs and GLP in the collection of samples from the field sites, maintaining the station site, and/or repair and calibration of instruments	Principal Air Quality Instrument Specialist

A) Field Supervisors

Field supervisors were responsible for locating and setting up field sites, scheduling operators, training field operators, coordinating supply ordering, supply receipt and distribution, and review of monthly QC maintenance sheets. The field supervisors were also responsible for notifying the appropriate supervisor in the Laboratory of every event that could invalidate the sample.

B) Field Operators

Field operators were responsible for operating all samplers and analyzers according to the operating procedures specified in this document. Field operators annotated all information in the monthly QC maintenance sheets, chain-of-custody forms, sample tags, and logbooks. Field operators were also responsible for notifying their supervisors of every out-of-control flow setting, timer setting, expected start or ending pressure, or any other instrument malfunction.

C) Field Calibrators

Field calibrators were responsible for performing semiannual multipoint calibrations on flow control-devices according to SCAQMD calibration procedures. Any as-is calibration showing a deviation from design flowrate in excess of acceptable criteria was reported to the field supervisor. Any samples collected while flow percentage deviation from design flow exceeds acceptable criteria were invalidated back to the previous flow calibration, audit, or malfunction date.

D) Field Auditors

SCAQMD field auditors conducted flow audits on 25 percent of the entire network each calendar quarter. Auditors were responsible for notifying the QA Manager of any audit indicating a greater than ± 15% average percent deviation from design flow for follow up.

F) Laboratory Chemists

Laboratory Chemists were responsible for receiving field samples, maintaining and storing chain-of-custody documents, performing and documenting QC activities on the QC monthly maintenance sheets, performing Laboratory audit analyses, and conducting preliminary data review for outliers and out-of-control conditions.

G) Laboratory Supervisors

Laboratory supervisors were responsible for final raw data review; calculation of precision based upon collocated sampling; reviewing monthly QA/QC sheets; making final evaluation of data validity based on reports from the QA group and field supervisor; and assessment of Laboratory precision data.

H) Atmospheric Measurements Manager

The Atmospheric Measurements Manager was responsible for overseeing MATES IV field operations.

I) Laboratory Services and Source Testing Engineering Manager

The Laboratory Services and Source Test Engineering Manager was responsible for overall coordination of field and analytical activities for MATES IV.

J) Quality Assurance Manager

The Quality Assurance (QA) Manager was responsible for implementing the quality assurance program for the MATES IV program including independent performance and system evaluations, the corrective action process, establishing acceptance criteria for sample validity once with consideration of quality control data and review of quality control procedures.

4.6 ASSESSMENTS AND RESPONSE ACTIONS

SCAQMD participates in field and laboratory assessment or proficiency programs established by U.S. EPA and CARB, and maintained any analyst or laboratory certification required for the program. Examples of assessments applicable to the MATES IV program are listed in Table 4.6. The QA Manager, or his designee, performed or arranged performance of periodic technical systems audits of SCAQMD activities. These audits covered all aspects of SCAQMD's work, including sample receipt, custody, conditioning, weighing, chemical/speciation analysis, shipping, data reduction and reporting. Prior to each audit, a checklist was prepared, based on the MATES IV workplan, SOPs, and applicable guidance documents. After audits, the QA Manager communicated to the Atmospherics Measurement Manager and/or the Laboratory Manager to specify areas in which corrective action were necessary and prepared a corrective action report (CAR) tracked by the QA Branch. If any serious problems were identified that required immediate action, such as a large, systematic analytical bias, the QA Manager informed the respective manager verbally or through electronic mail the day that such problems are identified as well as issued a Corrective Action Report. The corrective action followed the Corrective Action Process as described in the SCAQMD QMP (2009).

TABLE 4-6 QA Assessments Applicable to the MATES IV Program

Audit Name	Description	Frequency	Agency
SCAQMD Speciation network Performance Evaluation	Flow check, temperature, and pressure evaluation of the samplers (PM10, PM2.5, TSP, and SASS)	Twice a year	SCAQMD, QA Branch and/or an Approved Contractor
EPA Chemical Speciation Monitoring Program and IMPROVE Laboratory Performance Audit Samples.	1. Anions/Cations collected on nylon/quartz filters and analyzed by ion chromatography. 2. Organic and elemental carbon collected on quartz filters and analyzed by TOR/TOT 3. Metals collected on 47mm Teflon filters and analyzed by EDXRF and ICP/MS. 4. $PM_{2.5}$ mass collected on 47mm Teflon filters and analyzed by gravimetry.	Annual	U.S. EPA OAQPS
$PM_{2.5}$ Weighing Room Evaluation	Conditioning Room Audit	Annually	SCAQMD, QA Branch
$PM_{2.5}$ Weighing Room Evaluation	Gravimetric Mass Analysis performance evaluation and Conditioning Room Audit	Annually	CARB
U.S. EPA Systems Audit	All lab and field instrumentation, practices and procedures used to collect data for Federal Programs	Every 3 – 5 Years	U.S. EPA Region 9
CARB Ambient Gaseous Toxic Inter-laboratory Comparison Check.	Intercomparison of TO-15 compounds in ambient air matrix	Annually	CARB
CARB Ambient Gaseous Toxic Performance Evaluation.	Single Blind Challenge PE of TO-15 compounds in a standard VOC mix	Annually	CARB
SCAQMD QA Branch Carbonyl PE	Carbonyls – As specified by the PAMS/NATTS Programs	Annual and as needed	SCAQMD QA Branch

TABLE 4-6 QA Assessments Applicable to the MATES IV Program (Continued)

Audit Name	Description	Frequency	Agency
NATTS Carbonyl PT	Carbonyls: Formaldehyde and Acetaldehyde	Annually	EPA-OAQPS-AQAD
SCAQMD QA Branch VOC PE	TO-15 compounds	As needed or follow up to CAR	SCAQMD QA Branch
NATTS PT	NATTS VOCS on Select TO-15 compounds in a canister & metals by ICP/MS.	Annually	EPA-OAQPS-AQAD
Quarterly Pb Performance Evaluation	Technical evaluation on manual filter samplers (TSP)	Quarterly	SCAQMD, QA Branch
Annual Performance Evaluation	Technical evaluation on manual filter samplers (PM2.5, PM10)	Annually	SCAQMD, QA Branch
Meteorological Evaluation	Technical evaluation on surface meteorology instruments	PAMs stations; Annually	SCAQMD, QA
National Performance Evaluation Program	PM2.5 PM10, and TSP collected on appropriate filters from FRM samplers and analyzed by independent, certified, EPA approved laboratory.	Annual; 20% of the network	U.S EPA OAQPS/ Region 9
National Performance Audit Program – Pb Analysis	Technical evaluation of Pb Analysis from strips; Quarterly audit strip analysis	Quarterly	U.S. EPA Region 9; SCAQMD, QA Branch

4.6.1 Total Systems Audits (TSAs)

During MATES IV, a series of internal systems audits were conducted on the monitoring network and data quality, under the oversight of the QA Manager. Due to the number of methods and the size of the monitoring network for MATES IV, the systems audit was an on-going process. The systems audit included inspections of monitoring sites, a periodic review of the Laboratory by section or types of analyses, and a review of the data validation systems from the initial source of the data through the archiving and reporting of that data. The various aspects of the annual systems audit were conducted by QA staff or under contract with an independent contractor working under the oversight of the QA Manager.

In addition, as part of Federal air monitoring programs, external systems audits are carried out by the U.S. EPA and CARB, at their discretion and using either agency staff or through independent consultants working under the oversight of U.S. EPA or CARB. SCAQMD also contracts with independent consultants to conduct an external audit of selected systems in addition to the regular annual internal audit. These audits include a majority of methods and analyses conducted under MATES IV and review and follow-up of the audit findings, if necessary, is conducted through the QA Branch.

4.6.2 Performance Evaluations (PEs)

Performance evaluations are conducted for determining the accuracy and precision of monitoring and analytical instrumentation and procedures that provide the data for the various monitoring programs, including MATES IV. All performance audits whether performed by SCAQMD QA staff, independent consultants or other entities are required to satisfy requirements under the appropriate QAPPs and SOPs. These audits may be internal and/or external.

Internal performance audits may be conducted by QA staff or through independent consultants under the oversight of the QA Manager. Due to the size and scope of the program, performance evaluations were conducted on an on-going basis. Performance audits were scheduled for each specific instrument and target U.S. EPA measurement criteria (when applicable).

External performance evaluations are carried out by the U.S. EPA and CARB, at their discretion and using either agency staff or through independent consultants working under the oversight of the U.S. EPA or CARB. SCAQMD QA Branch may also conduct an performance evaluation or contract with independent consultants to conduct an external audit of selected systems in addition to the regular annual internal audit.

Chapter 5.0
Data Processing and Reporting

5.1 INTRODUCTION

MATES IV monitoring of ambient air toxics developed a large data base which is available for future analysis. Appendix A compounds, given the frequency of sampling in MATES IV, resulted in more than 25,000 individual data points including data for concentration, time and location of sampling. The purpose of this chapter is to outline the data handling of this large database. This section will only pertain to laboratory work performed and not to the meteorological, criteria pollutant, or monitor calibration data.

The SCAQMD Laboratory has experience handling large data bases including those generated under MATES II and III. Reporting templates for carbon analysis and XRF elemental analysis (inorganics) were based upon those used in MATES II and III and US EPA's PM Speciation Network requirements. Reporting templates for the VOCs, halogenated hydrocarbons, and carbonyls adhered to the PAMS and NATTS formats.

The aim of reporting is to generate Excel data files for electronic transfer to interested parties. The data has been checked for transcription errors, to assure that it meets DQOs and for adherence to other QA criteria such that the data represent the most accurate determinations possible. The Laboratory made every effort to disseminate the data in a timely fashion to facilitate feedback.

5.2 DATA BASE COMPILATION

Laboratory chemists generated data presenting the concentration of a particular compound found over a particular time period at a particular site. Samples were analyzed and results presented as the volume concentration on a parts-per-billion or ng/m^3 basis. These concentrations have been compiled into a spreadsheet along with the name of the sampling site and the date the sample was taken. The chemist (analyst) was responsible for checking data accuracy. The technician in charge of copying the data into the spread sheet was responsible for their accurate transcription. The Senior AQ Chemist was responsible for double checking the chemists' and technicians' data entry and transcription work.

As resources permitted, one AQ Chemist operated a particular instrument while another AQ Chemist reduced the data and transcribed it to an Excel spreadsheet. This structure led to the most efficient data handling. Chemists also reduced the data from several instruments depending on their workload.

MATES IV data encompasses PM$_{10}$ and PM$_{2.5}$ mass and ions, VOCs, carbonyls, metals, PAHs, and carbon results. Run dates are encoded with the year, month, and day in six numerals. This information is followed by a two-letter acronym representing the station and concentration. The column header has the name of the compound and the concentration units. Uncertainties encompass the calculated limits for the sampling and analysis errors introduced into the measurement system.

The MATES IV data has been compiled into several spreadsheets. These spreadsheets will conjugate components along the lines of the analysis technique. Each instrument will have a separate spreadsheet for the compounds it analyzes.

The Laboratory will work with data end users to supply the electronic version in whatever file length or configuration is desired. The data can also be translated into ASCII flat files.

5.3 PERIODIC REPORTS

The Laboratory’s goal was to meet a two-month turnaround time from the date of sample receipt to the finished and checked report. VOCs, carbonyls, metals, and carbon will be sampled individually, but in similar fashion. Duplicate and other QC samples were analyzed with each batch analysis run. The reports are available in electronic file and as printed spreadsheets.

5.4 FINAL REPORT

Experience with MATES II and III report preparation has demonstrated that the final MATES IV report including QA information may take in excess of six months to complete after the last day of sampling. Laboratory staff have migrated Excel spreadsheets to an Access database. The final report has been stored in several files segregated by date and type of analysis.

Glossary

Accuracy
A determination of how closely reported data values are to true values. Annually conducted performance audits will challenge the various samplers and instruments used in this program to assess their accuracy. All program data accepted as valid will meet the criteria set forth in Table 4-1. Accuracy is expressed as “percent” deviation from true and is calculated as follows:

$$\text{Percent Deviation from True} = \frac{\text{Indicated Value - True Value}}{\text{True Value}} \times 100$$

Collocated Sampling
The process of running two identical samplers concurrently at the same location. Collocated data measures a method’s precision. One of the samplers is designated *A* and is treated as the true value; while the other sampler is designated *B* and is regarded as the indicated value.

Data Completeness (DC)
The percent of valid data points actually collected out of the total number of data points possible. The data completeness objectives for the MATES II and MSS programs are presented in Table 4-1. DC is calculated using the following formula:

$$\text{percent DC} = \frac{\text{Total valid data points}}{\text{Total number of possible data points}} \times 100$$

Performance Audit
A procedure conducted to establish individual analyzer and overall sampling and analysis accuracy. Probe audits are used to measure the integrity of both the sampling and analysis systems. Flow audits measure the accuracy of the flow metering devices that assure the sample’s temporal representativeness. Gas standard audits determine accuracy of laboratory analyzers in measuring known concentrations of toxic compounds.

Precision
The measure of monitoring system repeatability. Precision is determined by amassing a variety of measurements of the same true value over a period of time and assessing the variability of those measurements. Precision objectives for the various monitoring methods used in MATES II and MSS programs are presented in Table 4-1.

Quality Assurance (QA)
The practice of establishing procedures external to the day-to-day monitoring operations that indicate whether or not air quality data is accurate, representative, precise and complete enough to satisfy the needs of the data users. QA activities include, but are not limited to, system and performance audits and collocated and parallel sampling. These activities are described in detail in Chapter 4.

Quality Control (QC)

Any procedure incorporated into the internal, day-to-day operations of collection and analysis of air quality samples to satisfy the data user's need for valid data. These activities are described in detail in Chapter 4.

Representativeness
The goal that samples are representative of both temporal and/or spatial scales at all sites. This is accomplished by conforming to 40CFR58 siting and sampling requirements for PM_{10}.

System Audit
An on-site inspection and review of the entire monitoring program.

ACRONYM LIST

AC	alternating current
AIHL	American Industrial Hygiene Laboratory
AM	Air Monitoring
ARB	Air Resources Board
AST	Applied Science and Technology
ASTM	American Society of Test Methods
Basin	South Coast Air Basin
cc	cubic centimeters
ccm	cubic centimeters per minute
cfm	cubic feet per minute
CFR	Code of Federal Records
DC	direct current
DNPH	2, 4-dinitrophenyl-hydrazine
EDB	ethylene dibromide
EDC	ethylene dichloride
EJ-2	Environmental Justice Initiative Number 2
EPA	Environmental Protection Agency
EPROM	erasable prompt chip
ERN	equipment relocation notice
ETM	elapsed time meter
FPC	filter paper cartridge
HPLC	High Performance Liquid Chromatograph
ICP/MS	Inductively Coupled Plasma/Mass Spectrometry
LIMS	Laboratory Information Management System
LOD	Level of Detection
lpm	liters per minute
MATES II	Multiple Air Toxics Study II
MATES III	Multiple Air Toxics Study III
MATES IV	Multiple Air Toxics Study IV
MFC	mass flow controller
mph	miles per hour
MTBE	methyl tert butyl ether
NAMS	National Air Monitoring Stations
NATTS	National Air Toxics Trends Stations
NEMA	National Equipment Manufacturer’s Association
PAH	polycyclic aromatic hydrocarbon
PAMS	Photochemical Assessment Monitoring Station
PE	performance evaluation
PM	particulate matter
ppb	parts per billion
ppbC	parts per billion carbon
PSI	pounds per square inch
PST	Pacific Standard Time
PTEP	Particulate Technical Enhancement Program

PUF	polyurethane foam
QA	quality assurance
QC	quality control
RAM	random access memory
rms	root mean standard
SASS	speciation air sampling system
SCAQMD	South Coast Air Quality Management District
SCC	sharp cut cyclone
SCFM	standard cubic feet per minute
SLAMS	State and Local Air Monitoring Stations
SOP	standard operating procedure
SSI	size selective inlet
TAC	toxic air contaminant
TSA	Total System Audit
TSP	total suspended particulates
V	Volt
VOC	volatile organic compound
WSD	wind speed and direction
XRF	X-ray fluorescence

APPENDIX A Air Contaminants Measured in MATES IV Program

CAS No.	Chemical Name	Lab Test Method	Comment
VOCs			
67-63-0	**Acrolein (2-propenal)**		**No Ambient Method**
71-43-2	**Benzene**	**GC/MS/FID**	
106-99-0	**Butadiene [1,3]**	**GC/MS/FID**	
(o-) 95-50-1	Dichlorobenzene [ortho- & para]	GC/MS/FID	
100-41-4	Ethyl Benzene	GC/MS/FID	
100-42-5	Styrene	GC/MS/FID	
108-88-3	Toluene	GC/MS/FID	
(m-) 108-38-3	Xylene [m+p, o-]	GC/MS/FID	
75-01-4	**Vinyl chloride**	**GC/MS/FID**	
Halo-HCs			
56-23-5	**Carbon tetrachloride**	**GC/MS/FID**	
67-66-3	**Chloroform**	**GC/MS/FID**	
107062	Ethylene dichloride {EDC}	GC/MS	
	(1,2 Dichloroethane)		
75-09-2	**Methylene chloride (Dichloromethane)**	**GC/MS/FID**	
127-18-4	**Perchloroethylene (tetrachloroethene)**	**GC/MS/FID**	
78-87-5	**Propylene Dichloride (1,2-dichloropropane)**	**GC/MS/FID**	**Not in Mates II**
79-01-6	**Trichloroethylene**	**GC/MS/FID**	
Carbonyls			
75-07-0	**Acetaldehyde**	**HPLC**	
67-64-1	Acetone	HPLC/ GC/MS/FID	Not Reported
50-00-0	**Formaldehyde**	**HPLC**	
78-93-3	Methyl ethyl Ketone (MEK)	HPLC/GC/MS/FID	Not Reported
1634-04-4	Methyl tert-Butyl Ether (MTBE)	HPLC/GC/MS/FID	Not Reported
Inorganics			
7429-90-5	Aluminum	ICP/MS:XRF	
7440-38-2	**Arsenic**	**ICP/MS:XRF**	
7440-41-7	**Beryllium**	**ICP/MS:XRF**	
7440-43-9	**Cadmium**	**ICP/MS:XRF**	
7440-70-2	Calcium	ICP/MS:XRF	
7440-47-3	Chromium (total)	ICP/MS:XRF	
	Chromium (hexavalent)	**IC**	
7440-48-4	Cobalt	ICP/MS:XRF	
7440-50-8	Copper	ICP/MS:XRF	
7439-89-6	Iron	ICP/MS:XRF	
7439-92-1	**Lead**	**ICP/MS:XRF**	
7439-95-4	Magnesium	ICP/MS:XRF	
7439-96-5	**Manganese**	**ICP/MS:XRF**	
7440-02-0	**Nickel**	**ICP/MS:XRF**	
7723-14-0	Phosphorous	ICP/MS:XRF	
7440-09-7	Potassium	ICP/MS:XRF	
7782-49-2	Selenium	ICP/MS:XRF	
7440-21-3	Silicon	ICP/MS:XRF	
7440-62-2	Vanadium	ICP/MS:XRF	
7440-66-6	Zinc	ICP/MS:XRF	
Others			
	Elemental & organic carbon	C analyzer	
Criteria Pollutants			
	$PM_{2.5}$	SASS	Speciation
	PM_{10}	SSI-Hivol	PM network

APPENDIX B Size-Selective Inlet PM_{10} Sampler Envelop

South Coast Air Quality Management District
Applied Science & Technology

Size-Selective Inlet PM_{10} Sampler Envelop

FIELD OPERATOR USE	LABORATORY USE ONLY
STATION #________________________	SAMPLE #___________________________
LOCATION________________________	FLOWRATE, CFM____________________
SAMPLER #_______________________	VOLUME OF AIR, M^3_______________
QUARTZ FILTER #_________________________	FINAL WEIGHT (gm)_________________
DATE_____________________________	TARE WEIGHT (gm)_________________
TIME	SAMPLE WEIGHT (gm)______________
END_________________________	PM_{10}(μg/M^3)____________________
START______________________	SAMPLE RECV'D____________________
TOTAL______________________	
REMOVED FROM SAMPLER_______	SAMPLE WEIGHED__________________
SENT TO HQ______________________	SAMPLE EXTR._____________________
RECEIVED AMB__________________	SAMPLE ANALYSIS_________________
	REF. _______________________________

DATE SAMPLER CALIBRATION______________________________

STATION OPERATOR____

Remarks (unusual activities sampling conditions, etc.):

APPENDIX C WSD Monthly Quality Control Maintenance Check Sheet

SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT

MONTHLY QUALITY CONTROL MAINTENANCE CHECK SHEET

MAKE/MODEL________________________________Wind Speed and Direction System

Location ____________________________________ Month/Year _________________________
Station No.__________________________________ Specialist __________________________
Control No._______________ Reviewed by ________________________ Date _______________

Date	Zero Speed		Zero Direction		Visual Wind Transmitter Check	Chart Time	
	As Found	Final	As Found	Final		As Found	Final

OPERATOR INSTRUCTIONS:

Daily Checks: Chart trace and time.
Weekly Checks: Zero speed and direction inking system
Visual wind transmitter check. The station operator will visually check the wind transmitter to confirm the direction coincides with recorder. Notify supervisor immediately if problem occurs.

Bi-monthly
Maintenance:

DATE	COMMENTS OR MAINTENANCE PERFORMED

Calibration Date:__________________ Operator _____________________

APPENDIX D High Volume Monthly Quality Control Maintenance Check Sheet

High Volume
Monthly Quality Control Maintenance Check Sheet

MAKE/MODEL HIGH VOLUME SAMPLER

Location________________________________
Station No.______________________________
Control No.______________________________
Operating Set Point_______________________
Date SSI Head Cleaned____________________

Month/Year_____________________
Specialist_______________________
Reviewed by/Date_______________
Cubic Feet per Meter_____________
Due Date________________________

Sample Date	Initial Flow cfm	Final Flow cfm	Filter No.	Initial Elapsed Time	Final Elapsed Time	Total Time
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
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28						
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31						

APPENDIX E MATES IV Sample Log

South Coast Air Quality Management District

Mates IV Sample Log

Location:___________________________

Sample Date:_________________________

Station No.:__________________________

Retrieved By:_________________________

Retrieval Date:________________________

Lab No.:________________________

Date Sample Received:____________

Reference No.:___________________

Analyst:__________________________

Canister Log – XonTech 910

Sample Time	Canister No.	Start Vacuum	End Pressure	Comments
24 hour				
Blank				
Collocated				

DNPH Cartridge Log – XonTech 924

Sample Time	Cartridge No.	Elapsed Time	Flow Rate	Comments
24 hour				
Blank				
Collocated				

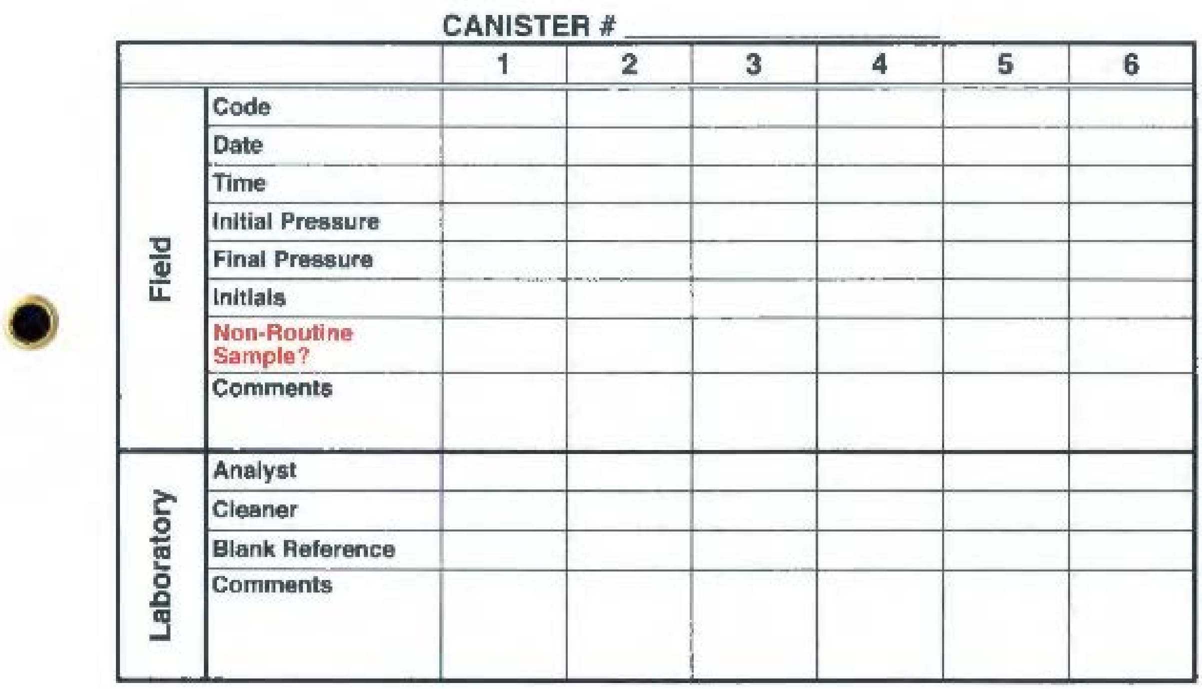
Filter Log – XonTech 924

Sample Time	Filter No.	Flow Rate	Comments
Teflon (Metals)			
Cellulose (Chrome VI)			
PM_{10} (Hi-Vol)			

(Staple Printout Here)

APPENDIX F VOC Canister Tag

VOC CANISTER TAG



CANISTER # ____________________

		1	2	3	4	5	6
Field	Code						
	Date						
	Time						
	Initial Pressure						
	Final Pressure						
	Initials						
	Non-Routine Sample?						
	Comments						
Laboratory	Analyst						
	Cleaner						
	Blank Reference						
	Comments						

APPENDIX G Method Description for Sampling and Analysis of Carbonyls by HPLC at the SCAQMD Laboratory

Sampling - Ambient air is drawn through a dinitrophenylhydrazine (DNPH) coated silica cartridges mounted in the Xontec 924 sampler. The sampler is located on a stand outdoors to EPA siting specifications. The Xontec 924 incorporates a potassium iodide (KI) impregnated filter upstream of the cartridge for ozone destruction. The sampling cartridges are coated with a minimum of 300 mg of DNPH on Waters Sep-Pak silica cartridges. The sample is pulled through the cartridge at approximately 0.7 lpm for 24-hour sampling. Before and after sampling the cartridges are kept capped and refrigerated in small vials to prevent loss or contamination.

Laboratory Analysis - The laboratory uses a Waters Millennium system high performance liquid chromatograph (HPLC) with autosampler. After elution of the Sep-Pak cartridge with three milliliters of acetonitrile, the samples are placed in the autosampler. Samples are run isocratically (55% acetonitrile and 45 % H_20) on a Waters C-18, 5 micron, 4.6 mm by 250-mm column. Flow is one milliliter per minute. Twenty microliters are injected onto the column by the autosampler.

Quantification - A calibration curve is derived from multipoint injections of standards obtained from two separate sources. One point control standards are run every 10 samples with the batch analysis. PAMS/NATTS compounds, acetaldehyde, formaldehyde, and acetone, are quantified by comparison to the calibration curve.

QA/QC - The instrument Minimum Detection Level (MDL) is determined for the HPLC response (EPA Appendix B to Part 136, 40CFR Ch.1) and the system MDL is calculated for a typical air volume sampled. A collocated cartridge is run every 6 days of sampling in the field. Blank cartridges are run at a similar frequency. All samples are run in duplicate.

APPENDIX H Method Description for Sampling and Analysis of Elements by Energy Dispersive X-ray Fluorescence (XRF) Spectrometry at the SCAQMD Laboratory

Sampling - Ambient air is drawn through a 47 mm Teflon filter loaded in a TSP or $PM_{2.5}$ sampler. Typically, 24 hour sampling at about 20 lpm provides sufficient sample mass on the filter for a successful analysis. The sampler must collect a homogeneous sample across the surface of the filter. The Panalytical Epsilon5 XRF instrument examines a very small cross section of the filter near the center.

Laboratory Analysis - A Panalytical Epsilon5 Energy Dispersive X-ray Fluorescence spectrometer is used to analyze 43 elements in the filter sample. There is no need for sample preparation other than bringing the filters to room conditions. Each filter is loaded onto an autosampler, brought to a sample chamber kept under vacuum and scanned under ten different instrumental conditions. Each condition is optimized for certain groups of elements. After spectral acquisition, an identification and deconvolution process extracts the net contributions of counts of each of the 43 elements.

Speciation and Quantification - Each element has a unique spectral pattern. After accounting for overlaps, each of the elements is identified qualitatively. By using previously calibrated standard values the net counts for each element are converted to actual concentrations in $\mu g/cm^2$. Using air volume data gathered during sampling, the µg/filter concentrations of the elements are converted to ng/M^3.

QA/QC - The X-ray instrument is calibrated using 35 single element standards. These calibration standards are checked using an NIST multi-element film standard. The NIST is run at the beginning and end of each sequence. Filter blanks are analyzed and used to subtract background from subsequent runs using the Epsilon 5 software. Field blanks are taken at specified times depending on the frequency of sampling. Field blank results are either subtracted or reported in accordance with data reporting and analysis requirements. Finally, all runs are checked in duplicate for precision.

APPENDIX I Method Description for Sampling and Analysis of Elements by Inductively Coupled Plasma Mass Spectrometry (ICP/MS) at the SCAQMD Laboratory

Sampling - Ambient air is drawn through a 47 mm Quartz filter loaded in a TSP sampler. Typically, 24 hour sampling at about 12 lpm provides sufficient sample mass on the filter for a successful analysis. The Perkin Elmer ICP/MS instrument examines total metal concentrations on the whole filter.

Laboratory Analysis - A Perkin Elmer ICP/MS is used to analyze 38 elements in the filter sample. Sample preparation procedures include digesting the whole filter in 11% nitric acid in a microwave oven, centrifuging the digested solution and diluting 10 times with 2% nitric acid. The diluted solution is then analyzed by ICP/MS.

Speciation and Quantification - The elements in the samples are ionized with inductively coupled plasma and are separated in the mass spectrometer based on their mass to charge ratio and then their concentrations are determined by the detector based on the intensities of ion counts. Using air volume data gathered during sampling, the μg/L concentrations of the elements are converted to ng/m^3.

QA/QC - The ICP/MS instrument is calibrated using a calibration standard mixture containing all the interested elements. The standard is diluted to eight concentrations and a 9 point calibration curve is generated and used to determine the concentration of samples. After the initial calibration is completed, a calibration check is required at the beginning and end of each analysis period for one analytical batch and at intervals of ten samples to verify the calibration. A blank filter and a blank filter spike sample is also digested and analyzed in each batch to examine the extraction efficiency and matrix effect.

Nickel Analysis by ICP/MS - Nickel overestimation by ICP/MS was determined to be caused by the ubiquitous and proportionally very high concentration of Calcium and Sodium which form interfering molecular ions in the plasma. The subsequent correction for Ni by changing the isotope of acquisition to 58 Amu from 60 Amu is described in section 3.6 and Appendix O.

APPENDIX J Method Description for Sampling and Analysis of Organic and Elemental Carbon by Thermal/Optical Carbon Analyzer at the SCAQMD Laboratory

Sampling - Ambient air is drawn through a 47-mm quartz filter loaded in a $PM_{2.5}$ sampler or an 8 x 10 inch quartz fiber filter loaded in a SSI-Hi-Vol sampler. Typically, 24-hour sampling provides sufficient sample mass on the filter for a successful analysis. The sampler must collect a homogeneous sample across the surface of the filter. A one-centimeter diameter punch from any quadrant of the filter is used in the instrument.

Laboratory Analysis - A Desert Research Institute (Reno, Nevada) thermal/optical carbon analyzer is used to determine the total carbon content of aerosol deposited on quartz filters. The analyzer is able to distinguish and characterize organic and inorganic carbon by a thermal/optical method with flame ionization detection. There is no need for sample preparation other than bringing the filters to room conditions. A small circular filter area is punched out from the quartz filter and loaded on to the carrier quartz tube. The filter is pushed into an oven whose temperature is raised in steps from ambient to approximately 850 degrees Celsius. An inert gas, such as nitrogen is continuously passed over the filter. At the same time the surface of the filter is monitored with a laser beam to determine the exact point at which all the elemental carbon (soot) is burned off. The combusted carbon forms carbon dioxide that is carried over to a methanizer. The methanizer (active nickel with the addition of hydrogen gas) converts the carbon dioxide to methane. The methane flows to a flame ionization detector. The detector output is integrated and converted to μg of carbon per filter using previously calibrated standards.

Speciation and Quantification - The light organic fraction is driven off the filter at the early stages of heating. The elemental carbon fraction is then oxidized at a higher temperature with an oxygen enriched carrier gas. A laser beam constantly scans the filter surface indicates the exact point at which the organic and elemental carbon fractions are removed from the filter. The two fractions are summed to give the total carbon concentration of the sample. The analysis results in the elemental, organic, and total carbon content of the sample. Using air volume data gathered during sampling, the μgC/filter concentrations are converted to $\mu gC/M^3$ of air.

QA/QC - The optical-thermal carbon analyzer is calibrated using two types of standards. One set consists of carbon containing gases, methane and carbon dioxide in an inert gas mixture. These are passed through the entire system to calibrate the instrument. In addition, filters impregnated with solution containing a known concentration of carbon are run as external standards. Filter blanks are analyzed for subsequent background correction during the run. Field blanks are taken at specified times depending on the frequency of sampling. Field blank results are reported in accordance with the data reporting and analysis requirements. Finally, collocated runs are utilized in checking precision.

APPENDIX K Method Description for Sampling and Analysis of VOCs by GC/MS/FID at the SCAQMD

Sampling - Ambient air is pumped into an evacuated Summa® polished and/or a silonite coated (Entech ^{TM}) 6 liter canister by a Xontech 910A air sampler at the sample location through a properly sited probe and manifold. The sample is integrated over 24 hours to fill the canister to approximately 12 PSI, following SOP00080 “XonTech 910 Canister Sampler/Multichannel Controller.” The canister is returned to the laboratory for subsequent analysis by Gas Chromatography with a Mass Spectrometer and Flame Ionization Detector (GC/MS/FID).

Laboratory Analysis - The Laboratory uses an Agilent 6890 Gas Chromatograph with an Agilent 5973 Mass Selective Detector. The sample is concentrated with an Entech 7100A cryo-concentrator for input to the GC/MS/FID. The sample canister is attached to the cryo-concentrator and a 600-milliliter aliquot is chilled in a trap to minus 150 degrees centigrade. For removal of the ambient humidity (water), the trap is heated to 10 degrees centigrade and transferred to a second trap cooled to -45 C for mitigation of the CO_2 collected. The concentrator loop is then heated and the contents cryo-focused at the head of the GC column for subsequent separation of the VOCs. The mass selective detector records the mass spectrum of each peak (compound) and the analyst uses previously determined standards to compare selected ions for each compound to determine the concentration. The FID quantifies non-toxic hydrocarbons per SOP 0008B “Standard Operating Procedure for TO15 (VOC).”

Quantitation - A calibration curve is derived by injection of a gas standard containing the compounds of interest at ppb levels. Every sample run is preceded and ended with a calibration check. Every analysis day is begun with a system blank run. Selected quantitation ions for each compound are compared to the gas standards injected to determine concentration in parts per billion. Non-toxic hydrocarbons are quantified by FID by a split from the column to the MS detector.

QA/QC - The Method Detection Limit (MDL) is determined for the GC/MS/FID by multiple injections of the lowest standard amount available (EPA Appendix B to Part 136, 40CFR Ch.1). Collocated samples are run in the field at one station. All canisters from the canister cleaning system are filled with the purified humidified nitrogen and tested for the presence of the compounds of interest. Above 0.2 ppb of any compound of interest or 10 ppb total of all compounds (compared to the benzene response factor) is cause for corrective action.

APPENDIX L Method Description for Sampling and Analysis of PAH Compounds

Sampling - Ambient air is drawn through an Andersen Instruments Poly-Urethane Foam (PUF) sampler. The method uses a high volume (Hi-Vol) air sampler equipped with a quartz fiber filter and PUF/Tenax glass adsorbent module for sampling between 325 and 400 cubic meters of air in a 24 hour sampling period. The laboratory is responsible for receipt of the quartz fiber filter and PUF/Tenax sorbent collection module, pre-cleaned and blanked, from Eastern Research Group (ERG), transported in a cold pack. The received modules are refrigerated until needed and then constructed for sampling by a Laboratory Technician for use by the field Instrument Technician. The Instrument Technician then installs the filter with PUF/Tenax collection module onto the Hi-Vol sampling unit and collects the sample on the appropriate day. The Instrument Technician returns the sample immediately after sampling and places it in the laboratory refrigerator. The Laboratory Technician then deconstructs the sampling module for shipment to ERG in a cooler with blue ice. Turnaround time for the sample to reach ERG from the sampling date is 7 days.

Laboratory Analysis- Analysis of the collected sample (in accordance with the chain of custody) is performed by ERG, Morrisville, North Carolina. The protocol used is EPA Compendium Method TO-13. The results are reported to the SCAQMD Project Manager and US EPA Air Quality System (AQS). Per ERG, “The test results are in compliance with NELAC accreditation requirements for certified parameters. All analyses are performed as described in the US EPA approved QAPP, under the contract for NATTS.”

QA/QC- Quality Assurance/Quality Control is limited to the sampling process. The Thermo Andersen PUF sampler is calibrated using an orifice transfer standard that has been standardized against a primary standard Roots meter. The orifice transfer standard is referenced to 25 degrees centigrade and 760 millimeters of mercury (Hg). In the field leak checks and sampling flow rate checks are performed each run. Field blanks are run at the prescribed frequency as found in the National Air Toxics Trends study work plan. Non-contaminating and cold transfer of all materials is maintained up through the shipment under cold conditions to ERG.

APPENDIX M Method Description for Sampling and Analysis of Hexavalent Chromium by Ion Chromatography at the SCAQMD Laboratory

Sampling - Ambient air is drawn through a 37-mm sodium bicarbonate treated cellulose filter loaded in a Xontech 924 sampler. Ambient air is pulled though the filter at a rate of approximately 12.0 liters per minute for 24 hours with an aggregate total air volume of approximately 17.2 m^3. Samples must be refrigerated to minimize the reduction of hexavalent chromium to trivalent chromium.

Laboratory Analysis - A Dionex ICS-3000 ion chromatograph (IC) is utilized to determine the hexavalent chromium concentration in ambient air samples. The entire filter sample is extracted in 10 mL of 20mM sodium bicarbonate solution via sonication for one hour. The extract is then filtered to remove solids/particles and analyzed by the Dionex IC. This system is comprised of an autosampler, guard column, analytical column, post-column derivatization module, a UV-Vis detector, and Chromeleon software. Hexavalent chromium is detected by a visible lamp at a wavelength of 530nm after forming a complex with diphenylcarbazide in a post-column reaction.

Quantification - A five point calibration curve is generated from prepared standards ranging from 50 to 1000 part per trillion (ppt). The hexavalent chromium sample concentrations are quantified by area comparisons to the area obtained for the calibration standards. The Chromeleon® software calculates the concentrations for each sample based on the calibration curve. (The ppt concentrations are then converted to ng/m^3 by multiplying the ppt by the extraction volume (in Liters) and dividing by the air volume (m^3).

Quality Control - All analyses are performed following the Standard Operating Procedure for The Analysis of Hexavalent Chromium in Ambient Air by Ion Chromatography (SOP 0046). Performance qualifications are conducted annually to determine the LOD for the Dionex IC. Linearity of the calibration curve is also an important aspect of instrument performance. The IC is calibrated weekly to achieve a minimum correlation coefficient of 0.9990. MDLs are obtained annually to determine the analytical method sensitivity. Blank and check standard analyses are performed every 10 samples to verify the precision of the analytical data. Additionally, an external standard is prepared for every batch of samples to verify the accuracy of the calibration standard. Blank and spike QCs are extracted with every sample batch. Spike QCs are spiked with known hexavalent chromium concentrations and are prepared with the samples. The amount of the spike concentration recovered during the analytical procedure will indicate the accuracy of the method. All samples require duplicate injections, which test precision of IC measurements. Field blanks are collected throughout the sampling duration to determine if there are errors and/or contamination in sample acquisition and the analytical process. The field blank results are reported in accordance with data reporting and analysis requirements. Collocated samples are collected at specified sites and times. The collocated data is used to verify sampling and analytical precision.

Method Enhancements - The analytical method has improved since MATES III in several aspects. A newer Dionex ion chromatograph replaced the previous instrument used in the analysis of MATES III samples for hexavalent chromium. The detection limit for the previous system and the new system were 0.06 ng/m^3 and approximately 0.02 ng/m^3, respectively. The detection limit was further improved by the implementation of additional filter pre-sampling treatment procedures, such as nitric acid washing followed by deionized (DI) water rinsing, and impregnation with sodium bicarbonate. The incorporation of nitric acid washing of cellulose filters eliminated the hexavalent chromium background concentrations prior to sampling. This resulted in the removal of a positive hexavalent chromium bias and improved the precision and accuracy during the MDL determination for the analytical method. The resulting MDL after the implementation of these protocols was 0.002 ng/m^3.

There were also additional enhancements to the sample preparation procedure. The efficiency of the sample extraction process was improved by decreasing the sonication time from 3 hours to 1 hour. This minimized the sample preparation time prior to analysis and prevented the possible change in hexavalent chromium concentration during the sonication process. Further improvement to the detection limit was done by decreasing the extraction volume from 15 mL to 10 mL. The older method of higher extraction volume would have diluted the samples and could have decreased the accuracy of the results for samples near the detection limit. Prior to sampling, the sodium bicarbonate treated cellulose filters had little variability in pH. However, during sampling, the pH of the filters could change depending on proximity to sources or different environmental conditions. In order to ensure that the pH of the extracts was consistent among all samples post-sampling, the extraction solution was changed from DI water to 20mM sodium bicarbonate. The addition of dilute sodium bicarbonate stabilizes the pH, reducing the variability in pH in the samples. For consistency, all standard solutions were also prepared in a 20mM sodium bicarbonate solution. Improvements in the hexavalent chromium method follow the procedures outlined in the National Ambient Toxics Trend Stations Technical Assistance Document (NATTS TAD).

APPENDIX N Comparison of ICP/MS to XRF

Background:

Energy Dispersive XRF has been used to determine metals in the previous two air toxics study; MATES II & MATES III. The two important differences between the two methods are sample pretreatment and sensitivity. ICP/MS requires acid digestion of filter samples, whereas filters can be run as is on the XRF method. However, for all the air toxic metals, the ICP/MS has significantly better detection limit. Further, the XRF method is not as well suited for TSP filters as it is for PM2.5. The presence of coarse particles on TSP filters creates serious absorption effects on many metals, requiring multiple and complicated corrections. Even these corrections may not work well because they require knowledge of the mass density of each individual filter. As TSP filters are never weighed, XRF determinations on TSP samples are not the ideal matrix for the XRF method. The only advantage of XRF over ICP/MS was the ability to measure crustal elements such as Aluminum & Silicon without sample prep which otherwise would have required very strong acid mixture (including HF) for ICP/MS. Since the toxic metals list for MATES did not include these crustal elements, it was decided to analyze all MATES IV TSP filters for selected toxic metals using ICP/MS.

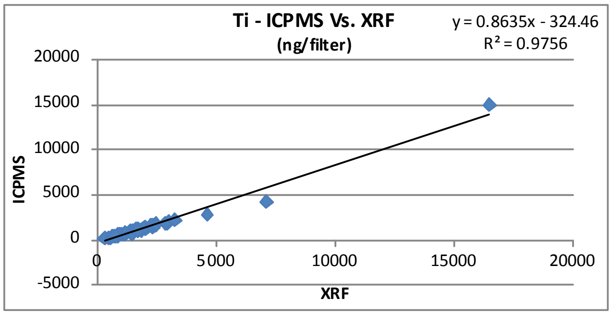
Method:

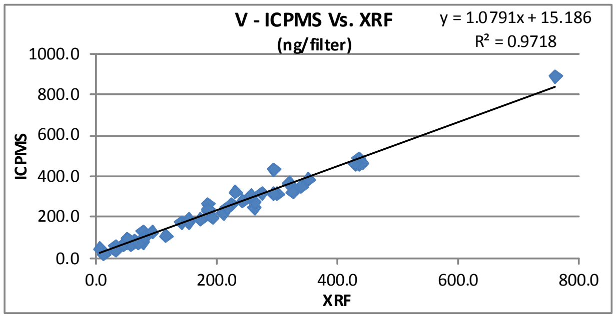
Comparison between the two methods was performed using 50 TSP filters from two sites from a previous project. These filters were run on the PANAlytical Epsilon 5 EDXRF analyzer in accordance with SCAQMD S.O.P. #0004. The same filters were then digested in nitric acid and analyzed by ICP/MS in accordance with the SCAQMD S.O.P. #0005. Data from both methods were reported in µg/filter unit and compared to each other. Charts comparing these methods for selected metals are found below.

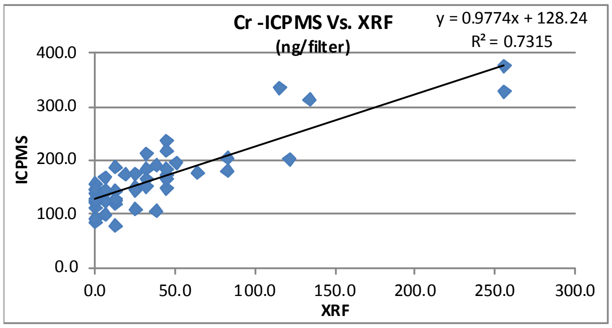
Results:

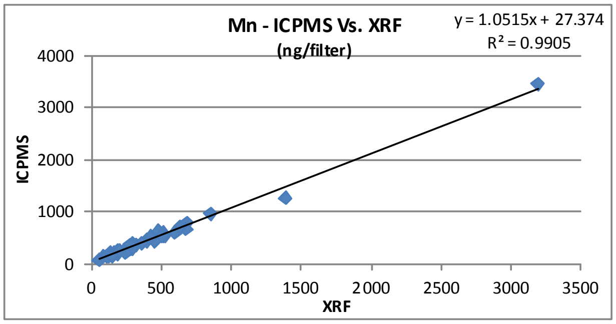
- Comparison for most metals was very good with slope in the range of 0.8 to 1.1.
- Metals such as Co, As, and Se did not fare well, primarily because the superior detection limit of ICP/MS over XRF. Almost all non-detect values by XRF were quantitatively reported by the ICP/MS. This was especially serious for Se where most XRF reported values are below the MDL.

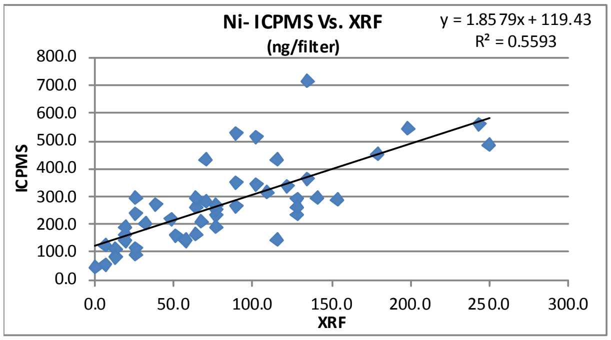
Nickel overestimation by ICP/MS was determined to be caused by the ubiquitous and proportionally very high concentration of Calcium and Sodium which form interfering molecular ions in the plasma. The subsequent correction for Ni by changing the isotope of acquisition to 58 Amu from 60 Amu is described in section 3.6 and Appendix O.

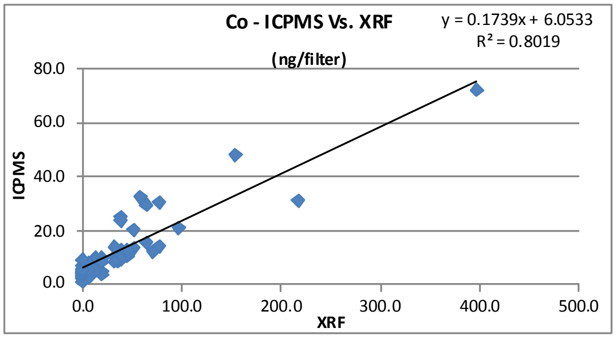

Ti - ICPMS Vs. XRF
(ng/filter)
y = 0.8635x - 324.46
R² = 0.9756
ICPMS
XRF
20000
15000
10000
5000
0
-5000
0
5000
10000
15000
20000

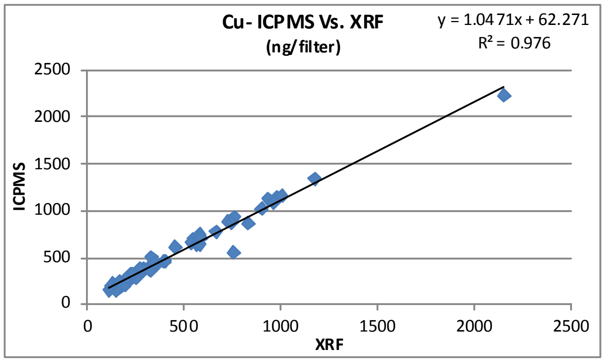

V - ICPMS Vs. XRF
(ng/filter)
y = 1.0791x + 15.186
R² = 0.9718
ICPMS
XRF
1000.0
800.0
600.0
400.0
200.0
0.0
0.0
200.0
400.0
600.0
800.0

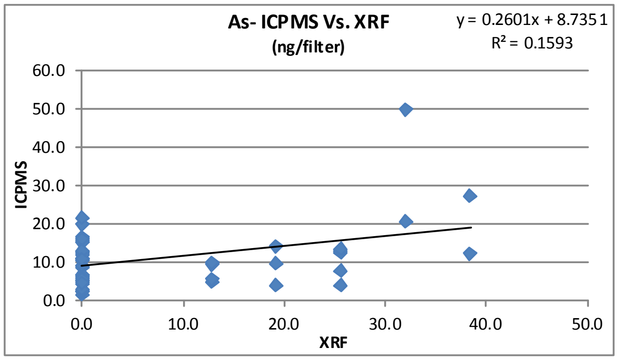

Cr -ICPMS Vs. XRF
(ng/filter)
y = 0.9774x + 128.24
R² = 0.7315
ICPMS
XRF
400.0
300.0
200.0
100.0
0.0
0.0
50.0
100.0
150.0
200.0
250.0
300.0

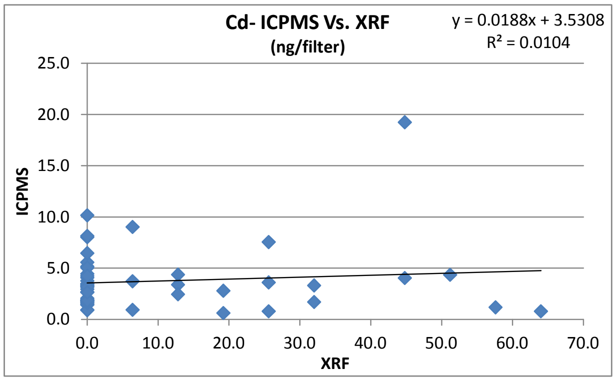

Mn - ICPMS Vs. XRF
(ng/filter)
y = 1.0515x + 27.374
R² = 0.9905
ICPMS
XRF
4000
3000
2000
1000
0
0
500
1000
1500
2000
2500
3000
3500

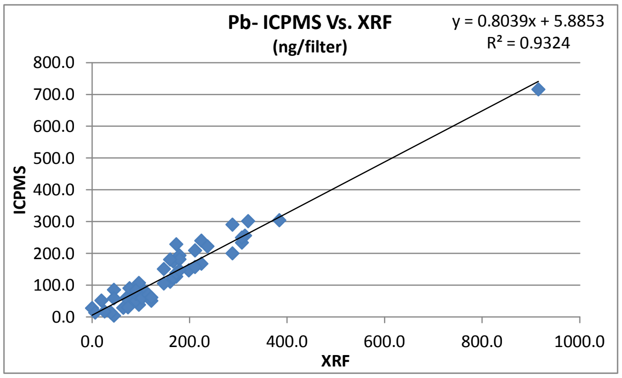

Ni- ICPMS Vs. XRF
(ng/filter)
y = 1.8579x + 119.43
R² = 0.5593
ICPMS
XRF
800.0
700.0
600.0
500.0
400.0
300.0
200.0
100.0
0.0
0.0
50.0
100.0
150.0
200.0
250.0
300.0

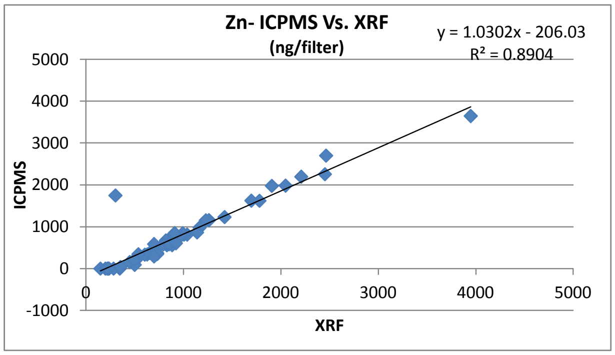

Co - ICPMS Vs. XRF
(ng/filter)
y = 0.1739x + 6.0533
R² = 0.8019
ICPMS
XRF
80.0
60.0
40.0
20.0
0.0
0.0
100.0
200.0
300.0
400.0
500.0


Cu- ICPMS Vs. XRF
(ng/filter)
y = 1.0471x + 62.271
R² = 0.976
ICPMS
XRF
2500
2000
1500
1000
500
0
0
500
1000
1500
2000
2500


As- ICPMS Vs. XRF
(ng/filter)
y = 0.2601x + 8.7351
R² = 0.1593
ICPMS
XRF
60.0
50.0
40.0
30.0
20.0
10.0
0.0
0.0
10.0
20.0
30.0
40.0
50.0


Cd- ICPMS Vs. XRF
(ng/filter)
y = 0.0188x + 3.5308
R² = 0.0104
ICPMS
25.0
20.0
15.0
10.0
5.0
0.0
0.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
XRF


Pb- ICPMS Vs. XRF
(ng/filter)
y = 0.8039x + 5.8853
R² = 0.9324
ICPMS
800.0
700.0
600.0
500.0
400.0
300.0
200.0
100.0
0.0
0.0
200.0
400.0
600.0
800.0
1000.0
XRF


Zn- ICPMS Vs. XRF
(ng/filter)
y = 1.0302x - 206.03
R² = 0.8904
ICPMS
5000
4000
3000
2000
1000
0
-1000
0
1000
2000
3000
4000
5000
XRF

APPENDIX O Nickel Analysis by ICP/MS

Background:

Average Nickel Basin-wide concentrations were found to be significantly higher during the first half of MATES IV when compared to same period during MATES III. This apparent increase in Nickel concentration occurred while all other metals either did not change or showed reduction in concentrations during the same period. This observation prompted a re-examination of the data.

Although quality control criteria were met for each of the batches analyzed by the ICP-MS, it became clear that an unknown interference with significant additive properties was responsible for the elevated values of Nickel. The target mass used in the ICP-MS determination of Nickel was 58 atomic mass units (AMU). The primary interferant was determined to be several molecular ions whose combined molecular weight equaled 58, including $^{23}Na^{35}Cl^{+}$, $^{40}Ar^{18}O^{+}$, $^{40}Ca^{18}O^{+}$, as well as other ions found at lower concentrations with smaller impacts. Once this was determined, the analysis method was changed such that ^{60}Ni isotope was selected as the target for analysis instead of ^{58}Ni.

Method:

The samples that were received after the method change to ^{60}Ni were analyzed and reported as is. All available filter samples and extracts previously analyzed with the ^{58}Ni target ion were re-analyzed using ^{60}Ni as the target isotope. These re-analyzed samples were then reported using the ^{60}Ni values. There were however a limited number of samples for which no filters or extracts were available. The re-analyzed samples generated data that was used to calculate an average ratio of $^{58}Ni/^{60}Ni$ concentration at each sampling site which was used to correct previously analyzed data from samples for which no filters or extracts were available to repeat the analysis under the new analytical condition. Instead of using one average ratio for all MATES IV sites, average ratios for each individual site were calculated and used to correct values at each respective site. Each of the initial concentration values was corrected by multiplying that value with appropriate site ratio. These interference corrected Nickel data have been flagged. The table below shows the ratio of ^{58}Ni to ^{60}Ni at each of the MATES IV sites.

Station	**Average ^{58}Ni /^{60}Ni**
Anaheim	3.315
Burbank	4.233
Compton	2.813
Fontana	4.843
Hudson	3.338
Huntington Park	2.614
Long Beach	2.909
Los Angeles A	3.921
Pico Rivera	3.009
Rubidoux A	5.213

APPENDIX P QA/QC Matrix Summary

Process	Interval	Activity	Criteria	Corrective Action
Field Canister	Before & After Each	QC - Note Activities in Log Book, Canister	Notes For Each Canister	N/A
Sampler		QC - Check Chart Time	± 10 Minutes of Actual PST	AQIS Resets
	Annually	QC - Clean Manifold	Pass Leak Check	AM Support Repairs
		QC - Calibrate Flow	± 5 % True Flow	AM Operations Calibrates
	1 Day in 6	QA - Collocated Sample	10 % Of Network	Run A + B Make-Ups if Possible
	Annually	QA - ARB Through-the-Probe Audit	Within ± 25 % of True For all Compounds	Isolate & Repair, Validate Data
		QA - Flow Audit	Indicated Flow Must Be Within ± 10 % of True Flow	Notify Operations If Outside Limits, Delete Data
	Before & After Each	QC - Note Activities in Log Book	N/A	N/A
	Sampling Event	QC - Check Start & Stop Times & Volume	Note On Canisters Log Sheet	AQIS Resets Time
Field Carbonyl		QC - Clean Manifold	Pass Leak Check	AQIS Cleans & Tests
Sampler	Annually	QC - Calibrate Flow Controller	± 5 % True Flow	AM Operations Calibrates
If Equipment	1 Day in 6	QA - Collocated Sample	10 % of Network	Run A + B Make-Ups if Possible
Available	Annually	QA - Through-the-Probe Audit By ARB	Within ± 25 % of True For All Compounds	Isolate & Repair, Validate Data
		QA - Flow Audit	Indicated Flow Must be Within ± 10 % of True Flow	Notify Operations if Outside Limits, Delete Data
		QC - Chain-of-custody	Log Sheet & Cartridge Numbers Agree	Chemist Corrects Any Errors
		QC - Propane Peak	± 10 % Of Previous	Chemist Adjusts Span
	Daily	QC – System Blank	< 10 ppb/C Total NMOC	Chemist Repairs/ Leak Checks
		QC – Replicate Sample	Visual Evaluation of Chromatogram	Chemist Repairs/Leak Checks
Laboratory	Semiannually	QC – Replicate Standard Analysis	± 10 % on All Compounds	Chemist Repairs
		QC - Bias Check	2 ppb/C Per Compound	Chemist Repairs/Leak Checks
	Annually	QC - LOD Check	All Loads Must Be Less Than 1 ppb/C	Chemist Repairs/Rechecks
	1 Day In 6	QA – Collocated Samples	± 25 % On All Compounds	Chemist Repairs
	Quarterly	QA – Parallel Sampling	All Compounds Must Be Within ± 30 %	
	Annually	QA – NPAP Performance Audit	Within ± 30 % of True For All Compounds	Chemist Repairs
		QC – Standard Response	± 10 % of Previous	Chemist Repairs/Adjusts Span
	Daily	QC – Purge Cycle	System Pressure Between 800 & 1700 PSIG	Chemist Leak Checks
Laboratory	Semiannually	QC – Multipoint Calibration	± 10 % Of Previous	Chemist Develops New Calibration Curve
		QC - Bias Check	<3 ppb Per Compound	Chemist Repairs
	Annually	QC - LOD Check	<1 ppb Per Compound	Chemist Repairs/Leak Checks
	Quarterly	QA – Parallel Sampling	All Compounds Must Be Within ± 30 %	
	Annually	QA – NPAP Performance Audit	Within ± 30 % of True For All Compounds	Chemist Repairs
	Before & After Each	QC - Note the Maintenance Sheet, Log	Notes as Required	N/A
	Semiannually	QC – Change Motor & Multipoint	Create New Calibration Curve	N/A
		QC - Clean Inlet		
Field PM_{10} SSI	Annually	QC - Timer Check	Timer Tested For Start With 20 Minutes of Setting & Elapsed	Repair or Replace
	1-Day-in- 6	QA - Collocate	Run At 10 % Of Sites	N/A
	Annually	QA - Flow Audit	Actual Flow Must be Within ± 10 % of True Flow	Request Repair; Investigate & Confirm Data Validity
		QC - Balance Checks		
aboratory	Daily	QC - Inspect Filters	No Light Leaks or Tears	
PM_{10} SSI		QC - Equilibrate Filters		
	1 Day in 6	QA - Collocate Filters	Agreement Within ± 20 %, all Compounds	

APPENDIX IV

MATES IV

DRAFT FINAL REPORT

Summaries for the MATES IV Fixed Monitoring Sites

Appendix IV
Summaries for the MATES IV Fixed Monitoring Sites

IV.1 Method Detection Limit (MDL) and Data Reporting

Guidance for determination of the method detection limit (MDL) and data reporting was taken from the U. S. EPA's National Air Toxics Pilot City Monitoring Program. The MDL, as defined in 40 CFR Appendix B, Part 136, "Definition and Procedure for Determination of the Method Detection Limit" was used. The MDL is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given sample matrix containing the analyte (EPA, 2001) [1]

The AQMD Laboratory used this MDL determination method for the analyses conducted. It consists of seven replicate analyses of a sample containing the analyte of interest at a level not to exceed five times the projected MDL. A standard deviation is determined using results of the analysis. The standard deviation times 3.14 (from the Tables of Student's t Values at the 99% confidence level) is the reported MDL.

It was recognized by the Science Advisory Board (EPA, 2001) that just because a value is below the MDL does not mean the laboratory has not been able to measure a value, but rather the measurement has less reliability than others above the MDL. From this study, the convention is to report every value, even those below the MDL. These values were flagged as being below the MDL but above the Limit of Detection (LoD). For analytes that had concentrations that were below the LoD, no concentration is ascertained in the analysis; and the data are reported as zero.

In calculating the average concentrations, the reported analytical values are used. Other reporting conventions include reporting a value equal to ½ the MDL for all values below the MDL. However, this can lead to potential biases in calculating average values.

The station abbreviations used in the following tables are listed below.

Station	Abbreviation
Anaheim	AN
Burbank	BU
Central Los Angeles	LA
Compton	CO
Inland Valley San Bernardino	SB
Huntington Park	HP
North Long Beach	NLB
Pico Rivera	PR
Rubidoux	RU
West Long Beach	WLB

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[1] Reference: Pilot City Air Toxics Measurements Summary, EPA454/R-01-003, February 2001

Method detection limits for the analytes are given in the Tables below

Analyte	**ppb**
2_Butanone	0.001
Acetaldehyde	0.008
Acetone	0.005
Formaldehyde	0.014
1,2-Dibromoethane	0.070
1,2-Dichlorobenzene	0.095
1,2-Dichloroethane	0.044
1,2-Dichloropropane	0.022
1,3-Butadiene	0.028
1,4-Dichlorobenzene	0.057
2-Butanone	0.022
2-Propenal	0.079
Acetone	0.053
Benzene	0.026
Carbon Tetrachloride	0.046
Chloroform	0.054
Ethylbenzene	0.050
m+p-Xylene	0.072
Methyl Tert Butyl Ether	0.051
Methylene Chloride	0.076
o-Xylene	0.065
Styrene	0.069
Tetrachloroethylene	0.065
Toluene	0.024
Trichloroethylene	0.072
Vinyl Chloride	0.051

Analyte	**ng/M3**
TSP Antimony	0.08
TSP Arsenic	0.09
TSP Barium	2.40
TSP Beryllium	0.09
TSP Cadmium	0.08
TSP Calcium	0.29
TSP Cesium	0.29
TSP Chromium	1.05
TSP Cobalt	0.12
TSP Copper	0.93
TSP Hexavalent Chromium	0.00
TSP Iron	0.29
TSP Lead	0.49
TSP Manganese	0.37
TSP Molybdenum	0.12
TSP Nickel	0.72
TSP Potassium	0.29
TSP Rubidium	0.29
TSP Selenium	0.87
TSP Strontium	0.21
TSP Tin	0.44
TSP Titanium	0.88
TSP Uranium	0.08
TSP Vanadium	0.20
TSP Zinc	0.29
PM10 EC	0.01
PM10 Mass	0.06
PM10 OC	0.10
PM10 TC	0.10

Analyte	ng/M3
$PM_{2.5}$ Aluminum	42.20
$PM_{2.5}$ Ammonium Ion	43.75
$PM_{2.5}$ Antimony	59.83
$PM_{2.5}$ Arsenic	13.08
$PM_{2.5}$ Barium	123.19
$PM_{2.5}$ Cadmium	42.75
$PM_{2.5}$ Calcium	13.90
$PM_{2.5}$ Cesium	154.49
$PM_{2.5}$ Chloride Ion	150.00
$PM_{2.5}$ Chlorine	12.44
$PM_{2.5}$ Chromium	8.86
$PM_{2.5}$ Cobalt	10.27
$PM_{2.5}$ Copper	11.67
$PM_{2.5}$ EC	37.50
$PM_{2.5}$ Iron	15.83
$PM_{2.5}$ Lead	22.23
$PM_{2.5}$ Manganese	14.66
$PM_{2.5}$ Mass	104.17
$PM_{2.5}$ Nickel	8.03
$PM_{2.5}$ Nitrate Ion	150.00
$PM_{2.5}$ OC	500.00
$PM_{2.5}$ Phosphorus	15.43
$PM_{2.5}$ Potassium	7.16
$PM_{2.5}$ Potassium Ion	81.25
$PM_{2.5}$ Rubidium	13.33
$PM_{2.5}$ Selenium	25.63
$PM_{2.5}$ Silicon	28.75
$PM_{2.5}$ Sodium Ion	15.63
$PM_{2.5}$ Strontium	16.41
$PM_{2.5}$ Sulfate Ion	150.00
$PM_{2.5}$ Sulfur	31.35
$PM_{2.5}$ TC	500.00
$PM_{2.5}$ Tin	49.81
$PM_{2.5}$ Titanium	17.48
$PM_{2.5}$ Uranium	23.41
$PM_{2.5}$ Vanadium	15.53
$PM_{2.5}$ Yttrium	15.67
$PM_{2.5}$ Zinc	8.37

Table IV-1 Ambient Concentrations (ppb) of Carbonyls at the Fixed Sites

		Measurement Site									
Pollutant	**Statistic**	**AN**	**BU**	**LA**	**CP**	**SB**	**HP**	**NLB**	**PR**	**RU**	**WLB**
Acetaldehyde	Avg	0.59	1.08	0.94	0.83	0.99	1.04	0.67	1.25	0.84	0.75
	SD	0.47	0.56	0.43	0.59	0.49	0.61	0.42	0.56	0.39	0.60
	N	60	59	59	60	59	57	59	59	59	55
	95% CI	0.12	0.15	0.11	0.15	0.13	0.16	0.11	0.15	0.10	0.16
	Max	3.07	2.70	2.00	2.94	2.44	2.94	2.07	2.61	1.95	2.79
	Min	0.11	0.22	0.32	0.02	0.21	0.41	0.18	0.42	0.12	0.15
Acetone	Avg	1.65	2.34	1.91	1.62	1.43	2.59	1.17	1.92	1.14	1.23
	SD	3.55	3.77	2.21	2.77	0.98	4.12	1.83	2.44	0.86	2.05
	N	59	59	59	60	59	57	59	60	59	55
	95% CI	0.93	0.98	0.58	0.72	0.26	1.09	0.48	0.63	0.23	0.56
	Max	21.79	19.47	9.97	12.45	4.77	19.75	8.95	11.38	5.05	9.93
	Min	0.02	0.10	0.08	0.06	0.08	0.11	0.10	0.15	0.14	0.02
Formaldehyde	Avg	1.19	2.58	2.93	2.05	2.63	2.73	1.86	2.81	2.00	1.55
	SD	0.82	1.13	0.99	0.81	1.19	0.95	0.71	1.04	1.10	0.95
	N	58	59	59	60	59	57	59	59	57	51
	95% CI	0.22	0.29	0.26	0.21	0.31	0.25	0.18	0.27	0.29	0.27
	Max	3.73	4.72	5.06	4.18	5.14	5.40	3.79	6.32	4.40	4.06
	Min	0.25	0.29	0.92	0.12	0.26	1.14	0.40	0.36	0.34	0.13
Methyl Ethyl Ketone	Avg	0.07	0.11	0.08	0.08	0.09	0.11	0.06	0.15	0.07	0.07
	SD	0.10	0.14	0.08	0.12	0.06	0.16	0.08	0.17	0.05	0.11
	N	57	59	59	59	58	57	59	60	59	53
	95% CI	0.03	0.04	0.02	0.03	0.01	0.04	0.02	0.04	0.01	0.03
	Max	0.57	0.62	0.35	0.55	0.23	0.77	0.39	0.76	0.29	0.47
	Min	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.00

Table IV-2 Ambient Concentrations (ppb) of Organic Gases at the Fixed Sites

			Measurement Site									
Pollutant	**Period**	**Statistic**	**AN**	**BU**	**LA**	**CP**	**SB**	**HP**	**NLB**	**PR**	**RU**	**WLB**
Benzene		Avg	0.33	0.46	0.40	0.50	0.29	0.52	0.33	0.35	0.28	0.36
		SD	0.25	0.29	0.21	0.46	0.14	0.38	0.19	0.21	0.15	0.29
		N	51	55	51	57	53	53	54	57	52	57
		95% CI	0.07	0.08	0.06	0.12	0.04	0.10	0.05	0.05	0.04	0.08
		Max	1.33	1.23	1.15	1.77	0.91	1.72	0.84	0.91	0.91	1.17
		Min	0.08	0.17	0.13	0.11	0.10	0.02	0.11	0.10	0.11	0.07
1,3-Butadiene		Avg	0.08	0.11	0.10	0.12	0.05	0.14	0.07	0.07	0.06	0.07
		SD	0.09	0.11	0.07	0.15	0.05	0.13	0.07	0.07	0.06	0.09
		N	51	55	51	57	53	53	54	57	52	57
		95% CI	0.02	0.03	0.02	0.04	0.01	0.04	0.02	0.02	0.02	0.02
		Max	0.41	0.39	0.36	0.58	0.22	0.53	0.28	0.30	0.21	0.32
		Min	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Carbon Tetrachloride		Avg	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08
		SD	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
		N	47	49	45	51	49	47	50	51	49	53
		95% CI	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
		Max	0.12	0.11	0.11	0.11	0.11	0.10	0.11	0.11	0.11	0.11
		Min	0.06	0.06	0.06	0.07	0.06	0.06	0.06	0.06	0.06	0.06
Chloroform		Avg	0.04	0.05	0.04	0.03	0.04	0.03	0.03	0.04	0.04	0.03
		SD	0.02	0.03	0.02	0.01	0.02	0.02	0.01	0.02	0.01	0.01
		N	51	55	51	57	53	53	54	57	52	57
		95% CI	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
		Max	0.08	0.14	0.09	0.07	0.08	0.10	0.06	0.10	0.08	0.06
		Min	0.02	0.02	0.01	0.00	0.00	0.00	0.00	0.01	0.02	0.02

Table IV-2 Ambient Concentrations (ppb) of Organic Gases at the Fixed Sites

		Measurement Site									
Pollutant	**Statistic**	**AN**	**BU**	**LA**	**CP**	**SB**	**HP**	**NLB**	**PR**	**RU**	**WLB**
Dibromoethane	Avg	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	SD	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	N	51	55	51	57	53	53	54	57	52	57
	95% CI	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Max	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.00
	Min	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1,2-Dichlorobenzene	Avg	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	SD	0.00	0.01	0.01	0.00	0.00	0.02	0.00	0.02	0.00	0.00
	N	51	55	51	57	53	53	54	57	52	57
	95% CI	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Max	0.00	0.04	0.04	0.00	0.01	0.12	0.02	0.12	0.02	0.00
	Min	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1,4-Dichlorobenzene	Avg	0.00	0.01	0.01	0.01	0.00	0.01	0.00	0.00	0.00	0.00
	SD	0.01	0.02	0.02	0.01	0.00	0.03	0.01	0.01	0.01	0.01
	N	51	55	51	57	53	53	54	57	52	57
	95% CI	0.00	0.00	0.01	0.00	0.00	0.01	0.00	0.00	0.00	0.00
	Max	0.03	0.08	0.11	0.04	0.02	0.24	0.05	0.03	0.05	0.02
	Min	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1,2-Dichloroethane	Avg	0.01	0.01	0.01	0.02	0.02	0.01	0.01	0.02	0.01	0.01
	SD	0.01	0.01	0.01	0.02	0.01	0.02	0.01	0.02	0.01	0.02
	N	51	55	51	57	53	53	54	57	52	57
	95% CI	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Max	0.05	0.06	0.05	0.05	0.05	0.06	0.04	0.06	0.05	0.05
	Min	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table IV-2 Ambient Concentrations (ppb) of Organic Gases at the Fixed Sites

		Measurement Site									
Pollutant	**Statistic**	**AN**	**BU**	**LA**	**CP**	**SB**	**HP**	**NLB**	**PR**	**RU**	**WLB**
1,2-Dichloropropane	Avg	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
	SD	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.02	0.00
	N	51	55	51	57	53	53	54	57	52	57
	95% CI	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Max	0.03	0.02	0.03	0.00	0.01	0.01	0.01	0.01	0.06	0.00
	Min	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ethylbenzene	Avg	0.12	0.18	0.72	0.20	0.11	0.24	0.11	0.12	0.15	0.13
	SD	0.12	0.14	0.74	0.21	0.07	0.24	0.07	0.09	0.10	0.14
	N	51	55	51	57	53	53	54	57	52	57
	95% CI	0.03	0.04	0.21	0.06	0.02	0.07	0.02	0.02	0.03	0.04
	Max	0.63	0.58	4.75	0.81	0.42	1.43	0.32	0.35	0.43	0.73
	Min	0.00	0.04	0.11	0.00	0.00	0.01	0.04	0.00	0.04	0.00
Methylene Chloride	Avg	0.64	0.24	0.32	0.17	0.28	0.24	0.91	0.17	2.00	0.48
	SD	1.97	0.14	0.21	0.08	0.43	0.18	4.98	0.08	3.15	1.83
	N	51	55	51	57	53	53	54	57	52	57
	95% CI	0.55	0.04	0.06	0.02	0.12	0.05	1.36	0.02	0.88	0.49
	Max	13.79	0.86	1.16	0.44	2.56	1.05	36.83	0.45	17.07	13.59
	Min	0.08	0.08	0.07	0.08	0.06	0.00	0.07	0.08	0.10	0.07
Methyl t-Butyl Ether	Avg	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	SD	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	N	51	55	51	57	53	53	54	57	52	57
	95% CI	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Max	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00
	Min	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table IV-2 Ambient Concentrations (ppb) of Organic Gases at the Fixed Sites

		Measurement Site									
Pollutant	**Statistic**	**AN**	**BU**	**LA**	**CP**	**SB**	**HP**	**NLB**	**PR**	**RU**	**WLB**
Perchloroethylene	Avg	0.03	0.04	0.03	0.04	0.04	0.04	0.02	0.02	0.01	0.02
	SD	0.04	0.03	0.02	0.04	0.04	0.03	0.02	0.02	0.01	0.02
	N	51	55	51	57	53	53	54	57	52	57
	95% CI	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.01	0.00	0.00
	Max	0.17	0.15	0.10	0.26	0.23	0.12	0.07	0.10	0.05	0.07
	Min	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Styrene	Avg	0.07	0.06	0.03	0.08	0.01	0.05	0.03	0.03	0.04	0.07
	SD	0.14	0.08	0.04	0.12	0.02	0.06	0.05	0.03	0.04	0.09
	N	51	55	51	57	53	53	54	57	52	57
	95% CI	0.04	0.02	0.01	0.03	0.00	0.02	0.01	0.01	0.01	0.02
	Max	0.85	0.33	0.16	0.49	0.10	0.25	0.26	0.11	0.14	0.32
	Min	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Toluene	Avg	0.87	1.32	1.15	1.42	0.84	1.61	0.74	0.97	0.81	0.89
	SD	0.83	0.96	0.70	1.51	0.49	1.21	0.52	0.68	0.50	0.83
	N	51	55	51	57	53	53	54	57	52	57
	95% CI	0.23	0.26	0.20	0.40	0.13	0.33	0.14	0.18	0.14	0.22
	Max	4.60	3.78	3.76	6.15	2.92	5.67	2.33	2.81	2.71	3.58
	Min	0.15	0.30	0.19	0.21	0.11	0.10	0.19	0.19	0.24	0.12
Trichloroethylene	Avg	0.00	0.01	0.02	0.00	0.00	0.01	0.00	0.00	0.00	0.00
	SD	0.01	0.01	0.03	0.01	0.01	0.01	0.00	0.01	0.01	0.01
	N	51	55	51	57	53	53	54	57	52	57
	95% CI	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Max	0.03	0.07	0.10	0.03	0.04	0.03	0.01	0.07	0.03	0.07
	Min	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table IV-2 Ambient Concentrations (ppb) of Organic Gases at the Fixed Sites

		Measurement Site									
Pollutant	**Statistic**	**AN**	**BU**	**LA**	**CP**	**SB**	**HP**	**NLB**	**PR**	**RU**	**WLB**
(m+p)-Xylenes	Avg	0.40	0.61	2.50	0.67	0.35	0.86	0.34	0.39	0.38	0.43
	SD	0.42	0.50	2.48	0.76	0.23	1.01	0.25	0.28	0.25	0.46
	N	51	55	51	57	53	53	54	57	52	57
	95% CI	0.12	0.14	0.70	0.20	0.06	0.28	0.07	0.07	0.07	0.12
	Max	2.31	2.19	16.22	3.06	1.42	6.62	1.09	1.08	1.03	2.53
	Min	0.07	0.13	0.37	0.07	0.06	0.06	0.08	0.07	0.10	0.05
o-Xylene	Avg	0.12	0.17	0.52	0.19	0.09	0.23	0.09	0.11	0.12	0.12
	SD	0.14	0.16	0.52	0.25	0.06	0.32	0.08	0.08	0.09	0.15
	N	51	55	51	57	53	53	54	57	52	57
	95% CI	0.04	0.04	0.15	0.07	0.02	0.09	0.02	0.02	0.02	0.04
	Max	0.79	0.72	3.17	1.01	0.30	2.03	0.34	0.34	0.35	0.86
	Min	0.01	0.02	0.07	0.02	0.00	0.02	0.00	0.00	0.02	0.00
Vinyl Chloride	Avg	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	SD	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	N	51	55	51	57	53	53	54	57	52	57
	95% CI	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Max	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00
	Min	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table IV-3 Ambient Concentrations (ng/m^3) of TSP Components at the Fixed Sites

		Measurement Site									
Pollutant	**Statistic**	**AN**	**BU**	**LA**	**CP**	**SB**	**HP**	**NLB**	**PR**	**RU**	**WLB**
Antimony	Avg	2.45	5.07	6.06	3.97	4.50	4.95	3.28	6.09	3.98	2.76
	SD	2.18	3.74	4.36	3.36	1.98	3.63	2.87	4.43	3.39	2.50
	N	60	58	59	59	56	55	59	60	58	58
	95% CI	0.56	0.98	1.14	0.87	0.53	0.98	0.75	1.15	0.89	0.66
	Max	11.40	21.40	19.00	13.90	9.01	16.60	11.80	30.40	23.70	11.40
	Min	0.04	1.18	0.80	0.92	0.46	0.81	0.00	1.38	0.96	0.51
Arsenic	Avg	0.23	0.44	0.64	0.50	0.91	0.56	0.39	0.56	0.76	0.50
	SD	0.14	0.22	0.41	0.36	0.43	0.35	0.24	0.25	0.81	0.32
	N	60	58	59	59	56	55	59	60	58	58
	95% CI	0.04	0.06	0.11	0.09	0.12	0.10	0.06	0.06	0.21	0.09
	Max	0.52	0.96	2.10	2.08	2.35	1.67	1.02	1.19	6.33	1.46
	Min	0.00	0.00	0.14	0.00	0.21	0.11	0.00	0.01	0.16	0.07
Barium	Avg	29.42	57.33	67.12	46.28	69.70	55.60	43.39	61.06	58.49	56.95
	SD	26.62	39.88	48.40	31.21	55.09	35.39	29.78	36.98	54.08	38.66
	N	60	58	59	59	56	55	59	60	58	58
	95% CI	6.87	10.48	12.61	8.13	14.75	9.56	7.76	9.55	14.21	10.16
	Max	159.00	216.00	216.00	139.00	306.00	158.00	115.00	162.00	371.00	159.00
	Min	1.05	14.00	9.77	12.40	11.20	15.70	3.53	16.10	6.80	8.61
Beryllium	Avg	0.02	0.01	0.02	0.01	0.03	0.01	0.01	0.02	0.03	0.02
	SD	0.03	0.01	0.02	0.02	0.03	0.01	0.01	0.02	0.03	0.02
	N	60	58	59	59	56	55	59	60	58	58
	95% CI	0.01	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.01	0.00
	Max	0.15	0.05	0.08	0.09	0.10	0.05	0.06	0.08	0.23	0.09
	Min	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table IV-3 Ambient Concentrations (ng/m^3) of TSP Components at the Fixed Sites

		Measurement Site									
Pollutant	**Statistic**	**AN**	**BU**	**LA**	**CP**	**SB**	**HP**	**NLB**	**PR**	**RU**	**WLB**
Cadmium	Avg	0.05	0.12	0.25	0.15	0.28	0.17	0.21	0.11	0.11	0.11
	SD	0.05	0.12	0.83	0.16	0.22	0.16	0.44	0.10	0.12	0.10
	N	60	58	59	59	56	55	59	60	58	58
	95% CI	0.01	0.03	0.22	0.04	0.06	0.04	0.11	0.02	0.03	0.03
	Max	0.20	0.65	6.50	0.70	1.45	0.76	3.19	0.59	0.84	0.42
	Min	0.00	0.00	0.00	0.00	0.03	0.00	0.00	0.00	0.00	0.00
Calcium	Avg	640	903	1133	986	2332	1022	879	1149	2324	1303
	SD	584	554	852	613	2181	581	645	770	2072	988
	N	60	58	59	59	56	55	59	60	58	58
	95% CI	151	145	222	159	583	157	168	198	544	259
	Max	3540	2880	4610	3090	11200	3420	3340	3800	9220	4640
	Min	103	169	248	257	325	330	96	211	230	157
Cesium	Avg	0.04	0.06	0.07	0.06	0.13	0.06	0.06	0.07	0.12	0.08
	SD	0.03	0.04	0.05	0.04	0.11	0.04	0.04	0.04	0.12	0.05
	N	41	39	40	40	39	40	41	42	39	41
	95% CI	0.01	0.01	0.02	0.01	0.04	0.01	0.01	0.01	0.04	0.02
	Max	0.13	0.16	0.26	0.20	0.63	0.21	0.19	0.22	0.67	0.23
	Min	0.01	0.01	0.01	0.01	0.02	0.01	0.00	0.00	0.01	0.01
Chromium	Avg	1.91	3.15	3.74	3.66	5.54	5.28	3.72	3.53	4.19	3.36
	SD	0.97	1.56	1.54	2.33	3.38	7.44	6.05	1.54	4.14	1.77
	N	60	58	59	59	56	55	59	60	58	58
	95% CI	0.25	0.41	0.40	0.61	0.90	2.01	1.58	0.40	1.09	0.47
	Max	4.60	7.94	6.92	13.10	19.90	49.50	47.70	8.17	31.50	8.83
	Min	0.37	0.88	0.48	1.05	0.99	1.19	0.28	1.08	0.40	0.49

Table IV-3 Ambient Concentrations (ng/m^3) of TSP Components at the Fixed Sites

		Measurement Site									
Pollutant	**Statistic**	**AN**	**BU**	**LA**	**CP**	**SB**	**HP**	**NLB**	**PR**	**RU**	**WLB**
Chromium Hexavalent	Avg	0.03	0.04	0.07	0.11	0.04	0.10	0.04	0.05	0.04	0.03
	SD	0.02	0.03	0.06	0.14	0.03	0.24	0.04	0.03	0.04	0.03
	N	60	57	59	60	58	55	60	61	59	58
	95% CI	0.00	0.01	0.02	0.04	0.01	0.07	0.01	0.01	0.01	0.01
	Max	0.09	0.19	0.39	0.85	0.12	1.80	0.20	0.17	0.25	0.14
	Min	0.00	0.01	0.01	0.01	0.00	0.01	0.00	0.01	0.00	0.00
Cobalt	Avg	0.20	0.48	0.42	0.41	0.79	0.46	0.36	0.46	0.64	0.56
	SD	0.15	0.34	0.21	0.24	0.43	0.32	0.23	0.24	0.52	0.54
	N	60	58	59	59	56	55	59	60	58	58
	95% CI	0.04	0.09	0.05	0.06	0.11	0.09	0.06	0.06	0.14	0.14
	Max	0.66	1.92	1.00	1.04	1.96	1.74	0.98	1.26	3.57	3.70
	Min	0.00	0.00	0.00	0.00	0.13	0.14	0.00	0.05	0.06	0.08
Copper	Avg	17.35	38.05	42.18	29.62	42.48	49.69	31.98	46.86	33.45	31.65
	SD	15.74	26.35	32.87	20.14	28.48	40.28	59.06	34.38	26.87	35.46
	N	60	58	59	59	56	55	59	60	58	58
	95% CI	4.06	6.93	8.56	5.25	7.62	10.89	15.38	8.88	7.06	9.32
	Max	74.10	127.00	160.00	87.40	147.00	261.00	459.00	140.00	162.00	251.00
	Min	1.12	7.55	5.69	9.70	4.73	9.03	2.60	8.04	4.53	4.50
Iron	Avg	613	1157	1424	1153	2727	1244	1037	1474	2148	1495
	SD	613	691	1042	701	2421	770	792	969	1888	1145
	N	60	58	59	59	56	55	59	60	58	58
	95% CI	158	182	272	183	648	208	206	250	496	301
	Max	4050	3310	5560	3000	11600	3660	3920	4470	9440	5730
	Min	43	215	192	216	344	367	57	222	149	152

Table IV-3 Ambient Concentrations (ng/m^3) of TSP Components at the Fixed Sites

		Measurement Site									
Pollutant	**Statistic**	**AN**	**BU**	**LA**	**CP**	**SB**	**HP**	**NLB**	**PR**	**RU**	**WLB**
Lead	Avg	2.11	5.27	7.34	6.24	9.80	9.46	4.39	5.89	6.21	5.83
	SD	1.28	2.84	3.35	4.10	4.79	10.76	2.31	2.43	4.52	5.90
	N	60	58	59	59	56	55	59	60	58	58
	95% CI	0.33	0.75	0.87	1.07	1.28	2.91	0.60	0.63	1.19	1.55
	Max	6.84	16.80	15.60	20.10	19.30	81.70	13.00	12.60	32.30	43.30
	Min	0.03	1.28	1.62	2.20	1.43	2.81	0.00	1.68	1.31	1.22
Manganese	Avg	8.32	15.21	19.20	18.62	51.97	22.73	14.37	21.16	32.99	21.28
	SD	5.42	8.36	8.91	12.69	30.04	20.89	8.30	9.94	25.08	13.18
	N	60	58	59	59	56	55	59	60	58	58
	95% CI	1.40	2.20	2.32	3.31	8.04	5.65	2.16	2.57	6.59	3.47
	Max	28.30	40.20	38.80	77.50	120.00	103.00	42.60	40.30	178.00	61.70
	Min	0.80	3.30	3.92	3.99	6.63	6.37	0.13	3.68	2.58	2.84
Molybdenum	Avg	0.83	1.81	3.36	1.90	2.13	2.39	1.74	1.66	1.39	1.58
	SD	0.63	1.13	2.61	1.42	1.78	2.62	1.66	1.09	1.25	1.35
	N	60	58	59	59	56	55	59	60	58	58
	95% CI	0.16	0.30	0.68	0.37	0.48	0.71	0.43	0.28	0.33	0.35
	Max	2.84	5.27	12.60	6.62	9.78	17.00	7.25	5.88	8.48	7.35
	Min	0.17	0.46	0.25	0.35	0.36	0.56	0.08	0.42	0.24	0.35
Nickel	Avg	1.74	3.90	3.37	4.06	4.05	5.40	3.59	4.47	3.35	3.73
	SD	1.03	7.66	3.65	2.60	2.28	6.98	2.65	2.66	2.48	2.10
	N	60	58	59	59	56	55	59	60	58	58
	95% CI	0.27	2.01	0.95	0.68	0.61	1.89	0.69	0.69	0.65	0.55
	Max	5.80	44.50	29.40	13.70	13.37	50.00	14.80	17.50	14.62	13.00
	Min	0.27	0.56	0.75	0.99	0.33	1.45	0.04	1.06	0.31	0.59

Table IV-3 Ambient Concentrations (ng/m^3) of TSP Components at the Fixed Sites

		Measurement Site									
Pollutant	**Statistic**	**AN**	**BU**	**LA**	**CP**	**SB**	**HP**	**NLB**	**PR**	**RU**	**WLB**
Potassium	Avg	250	320	382	398	812	371	357	454	985	475
	SD	217	191	284	237	814	224	269	318	964	356
	N	60	58	59	59	56	55	59	60	58	58
	95% CI	56	50	74	62	218	61	70	82	253	94
	Max	1150	998	1490	1240	4420	1350	1350	1470	4170	1920
	Min	6	79	63	82	85	90	0	87	83	61
Rubidium	Avg	0.62	1.13	1.11	1.16	2.24	1.14	0.93	1.24	2.18	1.44
	SD	0.37	0.72	0.66	0.68	1.47	0.66	0.58	0.75	1.52	1.00
	N	41	39	40	40	39	40	41	42	39	41
	95% CI	0.12	0.23	0.21	0.22	0.48	0.21	0.18	0.23	0.49	0.32
	Max	1.63	3.24	3.41	2.77	5.77	3.39	2.07	3.18	5.57	4.48
	Min	0.10	0.18	0.18	0.16	0.33	0.24	0.00	0.00	0.20	0.15
Selenium	Avg	0.44	0.54	0.95	0.80	0.75	1.67	0.76	0.98	0.73	0.63
	SD	0.31	0.39	0.65	0.72	0.45	1.96	1.19	0.67	0.66	0.68
	N	60	58	59	59	56	55	59	60	58	58
	95% CI	0.08	0.10	0.17	0.19	0.12	0.53	0.31	0.17	0.17	0.18
	Max	1.46	1.73	2.52	5.21	2.14	12.60	9.26	3.32	4.06	5.19
	Min	0.00	0.00	0.00	0.00	0.00	0.22	0.00	0.00	0.00	0.00
Strontium	Avg	7.27	10.90	16.11	10.86	17.82	11.91	9.60	12.73	20.14	15.56
	SD	6.31	6.36	11.47	6.13	15.57	6.91	6.32	7.92	17.34	11.69
	N	60	58	59	59	56	55	59	60	58	58
	95% CI	1.63	1.67	2.99	1.60	4.17	1.87	1.65	2.05	4.56	3.07
	Max	37.60	34.00	58.80	33.00	75.30	40.50	28.50	36.90	83.80	56.00
	Min	0.28	2.61	2.11	2.28	2.79	3.43	1.14	2.90	1.79	2.55

Table IV-3 Ambient Concentrations (ng/m^3) of TSP Components at the Fixed Sites

		Measurement Site									
Pollutant	**Statistic**	**AN**	**BU**	**LA**	**CP**	**SB**	**HP**	**NLB**	**PR**	**RU**	**WLB**
Tin	Avg	1.89	5.26	6.50	2.86	3.97	5.83	3.25	20.04	2.89	2.55
	SD	1.53	3.42	5.36	2.01	3.26	6.42	4.51	71.12	2.35	1.95
	N	60	58	59	59	56	55	59	60	58	58
	95% CI	0.40	0.90	1.40	0.52	0.87	1.73	1.18	18.37	0.62	0.51
	Max	7.70	18.40	31.10	8.93	17.70	33.50	32.80	549.00	13.20	8.63
	Min	0.13	1.07	0.93	0.80	0.27	0.83	0.60	0.84	0.82	0.57
Titanium	Avg	30.00	53.92	59.71	58.81	145.75	56.17	51.55	71.50	132.87	73.14
	SD	28.48	32.44	43.60	34.92	133.47	34.11	42.50	49.85	119.57	60.83
	N	60	58	59	59	56	55	59	60	58	58
	95% CI	7.35	8.53	11.36	9.10	35.73	9.22	11.07	12.87	31.43	15.99
	Max	183.00	147.00	221.00	145.00	636.00	169.00	215.00	238.00	554.00	324.00
	Min	3.19	9.58	7.62	10.30	15.10	14.80	4.49	7.87	7.27	5.83
Uranium	Avg	0.04	0.05	0.06	0.04	0.10	0.04	0.04	0.06	0.10	0.05
	SD	0.05	0.04	0.05	0.04	0.09	0.03	0.03	0.07	0.10	0.05
	N	60	58	59	59	56	55	59	60	58	58
	95% CI	0.01	0.01	0.01	0.01	0.02	0.01	0.01	0.02	0.03	0.01
	Max	0.24	0.18	0.25	0.24	0.54	0.11	0.19	0.46	0.61	0.29
	Min	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
Vanadium	Avg	1.81	2.10	2.64	3.14	5.63	2.67	3.53	3.11	4.72	4.58
	SD	2.82	1.20	1.95	1.73	5.44	1.50	3.06	2.32	4.48	3.38
	N	60	58	59	59	56	55	59	60	58	58
	95% CI	0.73	0.32	0.51	0.45	1.46	0.40	0.80	0.60	1.18	0.89
	Max	21.10	6.09	10.00	8.50	28.10	8.08	12.30	11.10	22.30	18.00
	Min	0.06	0.47	0.28	0.91	0.54	0.44	0.00	0.55	0.37	0.72

Table IV-3 Ambient Concentrations (ng/m^3) of TSP Components at the Fixed Sites

		Measurement Site									
Pollutant	**Statistic**	**AN**	**BU**	**LA**	**CP**	**SB**	**HP**	**NLB**	**PR**	**RU**	**WLB**
Zinc	Avg	43.40	53.74	72.38	54.11	109.69	74.11	61.05	73.01	64.27	71.74
	SD	44.44	32.47	52.21	32.62	91.64	57.20	50.33	57.39	44.44	49.45
	N	60	58	59	59	56	55	59	60	58	58
	95% CI	11.48	8.53	13.60	8.50	24.53	15.46	13.11	14.82	11.68	13.00
	Max	219.00	162.00	264.00	138.00	496.00	305.00	267.00	351.00	250.00	225.00
	Min	1.46	11.10	14.00	15.60	20.10	29.10	11.40	16.60	13.70	11.20

Table IV-4 Ambient Concentrations (ng/m^3) of PM$_{2.5}$ Components at the Fixed Sites

		Measurement Site									
Pollutant	**Statistic**	**AN**	**BU**	**LA**	**CP**	**SB**	**HP**	**NLB**	**PR**	**RU**	**WLB**
Aluminum	Avg	42.20	44.59	48.17	41.20	71.22	48.18	44.90	50.57	56.42	64.18
	SD	38.01	28.33	43.45	42.68	47.98	48.41	45.42	33.07	39.90	57.61
	N	59	58	59	61	60	57	61	58	60	61
	95% CI	9.90	7.45	11.32	10.93	12.39	12.84	11.63	8.69	10.30	14.75
	Max	176.00	119.00	214.00	286.00	286.00	317.00	285.00	130.00	161.00	290.00
	Min	0.00	0.00	0.00	0.00	8.00	0.00	0.00	0.00	0.00	0.00
Antimony	Avg	19.61	19.52	18.83	18.44	17.63	20.02	19.36	15.16	19.48	18.77
	SD	17.72	16.36	17.38	14.41	14.76	15.45	17.37	15.04	15.69	16.95
	N	59	58	59	61	60	57	61	58	60	61
	95% CI	4.62	4.30	4.53	3.69	3.81	4.10	4.45	3.95	4.05	4.34
	Max	72.00	69.00	59.00	54.00	59.00	53.00	61.00	55.00	65.00	63.00
	Min	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Arsenic	Avg	0.15	0.21	0.08	0.34	0.20	0.18	0.41	0.28	0.33	0.11
	SD	0.74	0.64	0.47	1.21	0.71	0.57	1.60	0.89	1.08	0.49
	N	59	58	59	61	60	57	61	58	60	61
	95% CI	0.19	0.17	0.12	0.31	0.18	0.15	0.41	0.24	0.28	0.12
	Max	4.00	3.00	3.00	8.00	4.00	2.00	11.00	4.00	6.00	3.00
	Min	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Barium	Avg	33.76	41.81	45.37	34.15	35.98	33.65	35.87	38.50	30.58	35.21
	SD	34.39	32.18	32.91	29.89	28.31	23.68	30.17	28.67	25.70	28.17
	N	59	58	59	61	60	57	61	58	60	61
	95% CI	8.96	8.46	8.57	7.65	7.31	6.28	7.72	7.54	6.64	7.21
	Max	206.00	173.00	135.00	115.00	97.00	96.00	118.00	89.00	89.00	107.00
	Min	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table IV-4 Ambient Concentrations (ng/m^3) of $PM_{2.5}$ Components at the Fixed Sites

			Measurement Site									
Pollutant	**Period**	**Statistic**	**AN**	**BU**	**LA**	**CP**	**SB**	**HP**	**NLB**	**PR**	**RU**	**WLB**
Cadmium		Avg	13.86	12.57	13.83	13.93	12.93	13.67	14.57	13.00	13.33	11.61
		SD	6.51	7.47	5.93	6.94	5.64	5.96	5.98	6.90	7.11	5.67
		N	59	58	59	61	60	57	61	58	60	61
		95% CI	1.70	1.96	1.55	1.78	1.46	1.58	1.53	1.81	1.84	1.45
		Max	33.00	31.00	30.00	41.00	26.00	29.00	31.00	27.00	34.00	32.00
		Min	0.70	0.00	2.00	0.00	2.00	4.00	4.00	0.00	3.00	0.00
Calcium		Avg	45.00	55.34	53.14	41.77	91.97	51.04	45.99	51.21	72.80	79.72
		SD	30.88	33.50	44.96	41.22	74.81	33.52	33.18	32.84	51.41	64.83
		N	59	58	59	61	60	57	61	58	60	61
		95% CI	8.05	8.81	11.71	10.55	19.32	8.89	8.50	8.63	13.28	16.60
		Max	166.00	132.00	298.00	259.00	424.00	142.00	194.00	138.00	260.00	288.00
		Min	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.00
Cesium		Avg	58.29	62.21	55.11	62.87	55.88	63.75	57.33	58.84	64.18	58.61
		SD	29.65	40.44	34.34	38.45	30.21	36.70	36.16	33.43	33.38	33.81
		N	59	58	59	61	60	57	61	58	60	61
		95% CI	7.73	10.63	8.95	9.84	7.80	9.73	9.26	8.79	8.62	8.66
		Max	156.00	153.00	143.00	145.00	146.00	160.00	160.00	142.00	144.00	141.00
		Min	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Chromium Total		Avg	1.15	1.64	1.68	1.86	1.09	5.42	3.28	1.60	1.49	1.64
		SD	1.43	1.95	2.86	1.86	1.10	11.01	9.86	2.51	1.80	2.33
		N	59	58	59	61	60	57	61	58	60	61
		95% CI	0.37	0.51	0.74	0.48	0.28	2.92	2.52	0.66	0.47	0.60
		Max	6.00	11.00	20.00	8.00	4.00	68.00	76.00	18.00	10.00	14.00
		Min	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table IV-4 Ambient Concentrations (ng/m^3) of PM$_{2.5}$ Components at the Fixed Sites

		Measurement Site									
Pollutant	**Statistic**	**AN**	**BU**	**LA**	**CP**	**SB**	**HP**	**NLB**	**PR**	**RU**	**WLB**
Cobalt	Avg	0.81	0.83	0.59	0.61	0.68	0.73	0.72	0.52	0.61	0.62
	SD	0.97	1.28	1.07	0.92	1.00	1.17	0.94	0.84	0.92	0.91
	N	59	58	59	61	60	57	61	58	60	61
	95% CI	0.25	0.34	0.28	0.23	0.26	0.31	0.24	0.22	0.24	0.23
	Max	3.00	5.00	7.00	4.00	5.00	4.00	4.00	3.00	4.00	4.00
	Min	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Copper	Avg	6.63	9.31	9.54	6.90	9.87	14.66	5.77	13.03	6.22	7.24
	SD	6.82	6.44	6.96	6.35	7.07	23.73	5.47	6.84	3.81	7.73
	N	59	58	59	61	60	57	61	58	60	61
	95% CI	1.78	1.69	1.81	1.63	1.83	6.29	1.40	1.80	0.98	1.98
	Max	35.00	28.00	30.00	33.00	51.00	175.00	24.00	29.00	21.00	44.00
	Min	0.00	0.00	0.00	0.00	0.00	0.90	0.00	4.00	0.00	0.00
Iron	Avg	99	147	156	91	184	139	96	138	119	148
	SD	107	97	121	116	114	138	90	90	80	159
	N	59	58	59	61	60	57	61	58	60	61
	95% CI	28	26	31	30	29	37	23	24	21	41
	Max	608	472	653	716	657	612	399	379	474	1060
	Min	2	41	20	14	31	24	23	39	25	19
Lead	Avg	6.04	6.05	6.56	6.92	8.15	7.84	7.00	5.97	6.61	6.69
	SD	3.78	3.65	3.57	4.50	4.60	3.97	3.96	4.00	4.18	5.75
	N	59	58	59	61	60	57	61	58	60	61
	95% CI	0.99	0.96	0.93	1.15	1.19	1.05	1.02	1.05	1.08	1.47
	Max	17.00	14.00	14.00	17.00	17.00	18.00	18.00	18.00	17.00	33.00
	Min	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table IV-4 Ambient Concentrations (ng/m^3) of PM$_{2.5}$ Components at the Fixed Sites

		Measurement Site									
Pollutant	**Statistic**	**AN**	**BU**	**LA**	**CP**	**SB**	**HP**	**NLB**	**PR**	**RU**	**WLB**
Manganese	Avg	3.31	2.38	4.51	2.64	5.49	6.94	3.52	4.73	2.83	3.32
	SD	5.29	3.83	5.72	3.99	7.80	14.18	4.94	5.88	4.49	5.17
	N	59	58	59	61	60	57	61	58	60	61
	95% CI	1.38	1.01	1.49	1.02	2.01	3.76	1.26	1.54	1.16	1.32
	Max	23.00	14.00	22.00	14.00	32.00	82.00	16.00	23.00	17.00	18.00
	Min	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Nickel	Avg	1.16	1.27	1.39	1.29	1.03	2.39	1.57	1.56	1.27	1.46
	SD	1.42	2.09	1.93	1.63	1.34	4.60	3.30	1.88	1.47	2.91
	N	59	58	59	61	60	57	61	58	60	61
	95% CI	0.37	0.55	0.50	0.42	0.35	1.22	0.85	0.49	0.38	0.74
	Max	5.00	13.00	8.00	8.00	5.00	32.00	24.00	8.00	5.00	20.00
	Min	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Phosphorous	Avg	14.96	18.16	19.42	17.66	18.09	20.21	16.13	17.72	17.16	16.85
	SD	13.14	15.75	15.86	14.09	15.66	16.46	13.81	13.81	13.93	12.62
	N	59	58	59	61	60	57	61	58	60	61
	95% CI	3.42	4.14	4.13	3.61	4.04	4.37	3.54	3.63	3.60	3.23
	Max	48.00	64.00	69.00	54.00	55.00	74.00	60.00	46.00	52.00	49.00
	Min	0.00	0.00	0.00	0.00	0.00	0.40	0.05	0.00	0.00	0.00
Potassium	Avg	68.53	75.00	70.07	71.15	74.43	70.35	61.18	73.72	74.85	71.77
	SD	44.47	37.06	34.13	49.14	39.97	39.31	33.68	34.57	33.73	42.84
	N	59	58	59	61	60	57	61	58	60	61
	95% CI	11.58	9.74	8.89	12.58	10.32	10.43	8.62	9.09	8.71	10.97
	Max	290.00	191.00	213.00	229.00	187.00	203.00	152.00	176.00	183.00	245.00
	Min	22.00	20.00	12.00	13.00	15.00	17.00	16.00	26.00	27.00	21.00

Table IV-4 Ambient Concentrations (ng/m^3) of PM$_{2.5}$ Components at the Fixed Sites

		Measurement Site									
Pollutant	**Statistic**	**AN**	**BU**	**LA**	**CP**	**SB**	**HP**	**NLB**	**PR**	**RU**	**WLB**
Rubidium	Avg	0.06	0.02	0.04	0.03	0.03	0.01	0.00	0.04	0.01	0.03
	SD	0.20	0.13	0.18	0.16	0.13	0.03	0.00	0.16	0.04	0.26
	N	59	58	59	61	60	57	61	58	60	61
	95% CI	0.05	0.03	0.05	0.04	0.03	0.01	0.00	0.04	0.01	0.07
	Max	1.00	1.00	1.00	1.00	0.70	0.20	0.00	1.00	0.30	2.00
	Min	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Selenium	Avg	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	SD	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	N	59	58	59	61	60	57	61	58	60	61
	95% CI	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Max	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Min	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Silicon	Avg	80.85	102.09	100.56	79.57	160.83	103.30	82.16	95.07	129.85	134.56
	SD	68.66	62.49	79.89	99.73	109.70	83.73	89.60	60.15	82.56	119.39
	N	59	58	59	61	60	57	61	58	60	61
	95% CI	17.89	16.42	20.81	25.53	28.33	22.21	22.94	15.81	21.32	30.57
	Max	300.00	268.00	399.00	664.00	615.00	398.00	552.00	223.00	352.00	567.00
	Min	0.00	8.00	0.00	0.00	7.00	3.00	0.00	14.00	2.00	11.00
Strontium	Avg	3.14	2.93	3.53	1.82	2.45	2.24	1.93	2.72	2.54	3.38
	SD	3.66	2.26	3.82	1.94	1.89	2.00	1.85	2.20	2.27	4.83
	N	59	58	59	61	60	57	61	58	60	61
	95% CI	0.95	0.59	0.99	0.50	0.49	0.53	0.47	0.58	0.58	1.24
	Max	24.00	8.00	25.00	5.00	8.00	7.00	7.00	7.00	8.00	35.00
	Min	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Capture										

Table IV-4 Ambient Concentrations (ng/m^3) of PM$_{2.5}$ Components at the Fixed Sites

		Measurement Site									
Pollutant	**Statistic**	**AN**	**BU**	**LA**	**CP**	**SB**	**HP**	**NLB**	**PR**	**RU**	**WLB**
Sulfur	Avg	520	518	554	547	501	591	558	546	474	595
	SD	318	327	363	347	341	368	347	335	301	346
	N	59	58	59	61	60	57	61	58	60	61
	95% CI	83	86	94	89	88	98	89	88	78	88
	Max	1320	1260	1720	1480	1350	1640	1470	1510	1100	1670
	Min	94	90	88	93	40	97	103	110	74	105
Tin	Avg	25.25	26.09	26.80	27.64	25.68	27.86	25.38	47.33	25.55	24.54
	SD	11.30	12.13	11.03	16.48	10.28	14.31	10.67	124.68	11.09	11.27
	N	59	58	59	61	60	57	61	58	60	61
	95% CI	2.94	3.19	2.87	4.22	2.66	3.80	2.73	32.77	2.86	2.88
	Max	61.00	63.00	59.00	81.00	58.00	77.00	52.00	966.00	53.00	55.00
	Min	5.00	0.00	7.00	0.00	6.00	5.00	8.00	5.00	6.00	0.00
Titanium	Avg	5.85	8.01	8.81	6.80	8.34	7.18	8.67	8.17	5.98	9.62
	SD	5.68	5.43	6.49	8.40	7.05	6.22	13.06	6.88	4.52	13.83
	N	59	58	59	61	60	57	61	58	60	61
	95% CI	1.48	1.43	1.69	2.15	1.82	1.65	3.34	1.81	1.17	3.54
	Max	32.00	24.00	30.00	45.00	34.00	29.00	55.00	30.00	26.00	77.00
	Min	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Uranium	Avg	10.60	10.60	10.42	11.33	10.45	10.02	10.92	10.74	11.52	11.49
	SD	7.16	7.49	7.11	8.41	7.34	7.43	7.66	7.99	8.32	8.10
	N	59	58	59	61	60	57	61	58	60	61
	95% CI	1.87	1.97	1.85	2.15	1.90	1.97	1.96	2.10	2.15	2.07
	Max	32.00	31.00	27.00	33.00	34.00	29.00	31.00	32.00	33.00	31.00
	Min	0.50	1.00	1.00	0.00	1.00	0.00	2.00	1.00	1.00	0.00

Table IV-4 Ambient Concentrations (ng/m^3) of PM$_{2.5}$ Components at the Fixed Sites

			Measurement Site									
Pollutant	**Period**	**Statistic**	**AN**	**BU**	**LA**	**CP**	**SB**	**HP**	**NLB**	**PR**	**RU**	**WLB**
Vanadium		Avg	0.37	0.22	0.47	0.46	0.29	0.36	0.56	0.43	0.33	0.60
		SD	0.76	0.49	0.84	0.73	0.72	0.62	1.08	1.01	0.78	1.10
		N	59	58	59	61	60	57	61	58	60	61
		95% CI	0.20	0.13	0.22	0.19	0.18	0.16	0.28	0.27	0.20	0.28
		Max	4.00	2.00	3.00	3.00	4.00	2.00	4.00	6.00	4.00	5.00
		Min	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Yttrium		Avg	1.12	0.93	1.04	1.04	1.08	1.32	0.93	0.94	1.50	1.28
		SD	1.51	1.16	1.26	1.25	1.25	1.35	1.05	1.11	1.62	1.59
		N	59	58	59	61	60	57	61	58	60	61
		95% CI	0.39	0.31	0.33	0.32	0.32	0.36	0.27	0.29	0.42	0.41
		Max	8.00	5.00	5.00	5.00	5.00	6.00	4.00	4.00	7.00	7.00
		Min	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Zinc		Avg	21.42	9.26	11.05	10.23	24.34	19.44	13.76	17.82	10.44	12.58
		SD	40.93	7.62	11.19	12.37	17.10	31.54	15.84	44.42	11.09	14.73
		N	59	58	59	61	60	57	61	58	60	61
		95% CI	10.66	2.00	2.92	3.17	4.42	8.36	4.06	11.67	2.86	3.77
		Max	210.00	36.00	58.00	61.00	72.00	189.00	72.00	332.00	56.00	64.00
		Min	0.00	0.00	0.00	0.00	0.06	0.00	0.00	0.00	0.00	0.00

Table IV-5 Ambient PM$_{10}$ Carbon Concentrations (ug/m^3) at the Fixed Sites

			Measurement Site									
Pollutant	**Period**	**Statistic**	**AN**	**BU**	**LA**	**CP**	**SB**	**HP**	**NLB**	**PR**	**RU**	**WLB**
PM$_{10}$ Mass		Avg	22.46	26.16	27.30	26.26	35.64	27.37	22.40	27.32	33.45	30.02
		SD	7.19	8.44	8.84	8.87	15.37	8.25	7.25	8.74	13.14	13.01
		N	61	57	60	57	61	52	60	50	60	51
		95% CI	1.84	2.24	2.28	2.35	3.94	2.29	1.87	2.48	3.39	3.66
		Max	43.00	40.00	45.00	52.00	63.00	41.00	36.00	48.00	66.00	78.00
		Min	8.00	6.00	7.00	9.00	7.00	8.00	6.00	11.00	11.00	8.00
PM$_{10}$ Elemental Carbon		Avg	1.17	1.74	1.67	1.50	1.74	1.65	1.29	1.87	1.48	1.78
		SD	0.87	1.02	0.93	1.21	0.81	1.05	0.88	0.99	0.75	1.32
		N	61	57	60	57	61	52	58	50	59	51
		95% CI	0.22	0.27	0.24	0.32	0.21	0.29	0.23	0.28	0.20	0.37
		Max	4.76	4.54	4.24	4.68	3.98	5.15	3.69	4.39	3.96	5.98
		Min	0.26	0.54	0.52	0.29	0.33	0.66	0.30	0.58	0.57	0.38
PM$_{10}$ Organic Carbon		Avg	3.71	4.86	4.44	4.44	5.32	4.54	3.64	4.82	5.29	4.45
		SD	1.52	1.79	1.48	2.36	1.73	1.75	1.57	1.57	1.58	2.45
		N	61	57	60	57	61	52	58	50	59	51
		95% CI	0.39	0.47	0.38	0.63	0.44	0.49	0.41	0.45	0.41	0.69
		Max	9.32	10.30	8.22	12.10	9.27	9.26	7.96	9.28	9.17	12.20
		Min	1.79	2.38	2.13	1.84	2.05	2.44	1.70	2.43	3.02	1.60
PM$_{10}$ Total Carbon		Avg	4.88	6.60	6.12	5.94	7.05	6.19	4.92	6.69	6.77	6.23
		SD	2.35	2.76	2.37	3.53	2.46	2.75	2.42	2.50	2.14	3.71
		N	61	57	60	57	61	52	58	50	59	51
		95% CI	0.60	0.73	0.61	0.94	0.63	0.76	0.64	0.71	0.56	1.04
		Max	14.10	14.20	12.40	16.80	12.90	13.60	11.60	13.70	13.10	18.20
		Min	2.05	3.06	2.64	2.27	2.42	3.27	2.06	3.01	3.68	1.98

Table IV-6 Ambient $PM_{2.5}$ Carbon Concentrations (ug/m^3) at the Fixed Sites

		Measurement Site									
Pollutant	**Statistic**	**AN**	**BU**	**LA**	**CP**	**SB**	**HP**	**NLB**	**PR**	**RU**	**WLB**
$PM_{2.5}$ Mass	Avg	12.37	14.40	14.14	12.91	14.33	14.40	12.95	14.21	13.83	13.21
	SD	4.45	5.00	4.94	4.96	6.20	5.62	4.47	4.75	5.58	4.58
	N	59	59	59	61	60	57	61	58	61	60
	95% CI	1.16	1.30	1.29	1.27	1.60	1.49	1.14	1.25	1.43	1.18
	Max	31.64	27.89	27.37	29.59	34.08	35.40	27.05	29.52	30.27	28.11
	Min	5.47	3.31	4.13	2.58	4.45	4.33	4.34	6.61	4.75	4.96
$PM_{2.5}$ Elemental Carbon	Avg	0.90	1.32	1.23	1.06	1.36	1.28	0.90	1.40	1.11	1.13
	SD	0.90	1.07	0.87	1.11	0.88	1.08	0.97	0.97	0.69	1.18
	N	59	58	60	61	60	59	61	59	61	61
	95% CI	0.24	0.28	0.22	0.28	0.23	0.28	0.25	0.25	0.18	0.30
	Max	3.90	4.60	3.80	4.70	5.00	5.40	3.50	4.70	3.40	4.90
	Min	0.08	0.18	0.30	0.12	0.02	0.06	0.02	0.13	0.24	0.08
$PM_{2.5}$ Organic Carbon	Avg	3.74	4.81	4.47	4.00	4.84	4.68	3.59	4.68	4.62	3.67
	SD	1.53	1.75	1.48	1.97	1.83	1.85	1.84	1.63	1.50	1.94
	N	59	58	60	61	60	59	61	59	61	61
	95% CI	0.40	0.46	0.38	0.50	0.47	0.48	0.47	0.42	0.38	0.50
	Max	8.00	9.50	8.10	10.00	11.00	10.00	11.00	10.00	9.80	9.90
	Min	1.50	2.10	1.90	1.50	1.50	1.90	1.20	2.00	1.90	1.00
$PM_{2.5}$ Total Carbon	Avg	4.64	6.12	5.70	5.06	6.20	5.97	4.47	6.06	5.75	4.82
	SD	2.33	2.70	2.22	3.05	2.62	2.84	2.70	2.42	1.94	3.11
	N	59	58	60	61	60	59	61	59	61	61
	95% CI	0.61	0.71	0.57	0.78	0.68	0.74	0.69	0.63	0.50	0.80
	Max	12.00	14.00	12.00	15.00	17.00	15.00	14.00	14.00	12.00	15.00
	Min	1.70	2.30	2.30	1.60	1.50	2.20	1.20	2.20	2.20	1.30

APPENDIX V

MATES IV

DRAFT FINAL REPORT

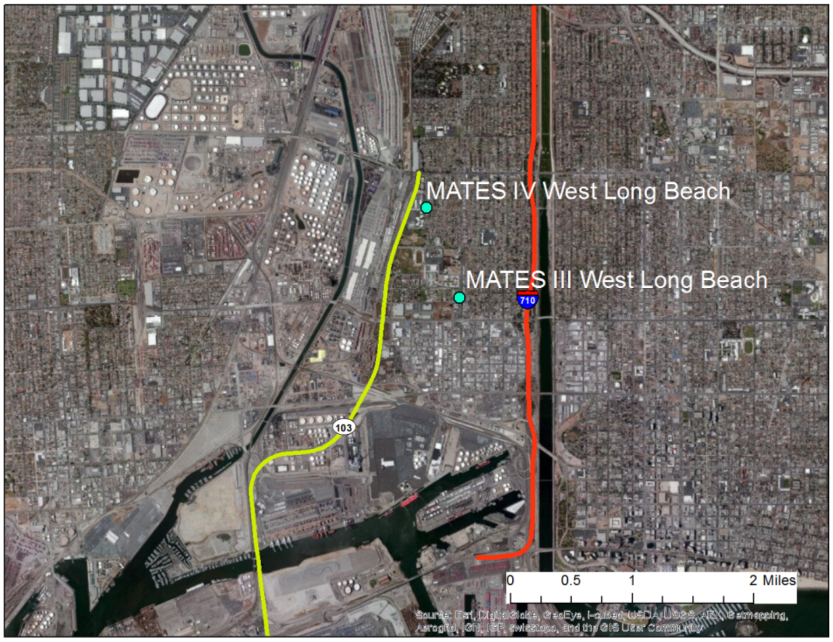
Comparison Between the West Long Beach Sites in MATES III and MATES IV

<u>Author</u>

Kalam Cheung

Appendix V. Comparison between the West Long Beach Sites in MATES III and MATES IV

The monitoring station that represents the West Long Beach (WLB) area in MATES IV is located about 0.8 mile northwest of the WLB site in MATES III. Figure V-1 shows the imagery of the two stations and the surrounding environment. MATES IV WLB is a neighborhood-scale sampling site that aims to represent an area of the community with relatively uniform land use within 0.3 to 2.5 miles. To evaluate the comparability of the two stations, linear regression analyses are performed on PM mass and major $PM_{2.5}$ species including organic carbon (OC), elemental carbon (EC), and nitrate and sulfate ions. Gaseous species, including benzene, 1,3-butadiene, acetaldehyde and formaldehyde, are also evaluated. The comparisons are conducted for two time periods when the sampling was concurrent at the two stations, namely February to November of 2007, and April to December of 2008. Sampling was carried out once every six days, each for a duration of 24 hours.



Source: Esri, DigitalGlobe, GeoEye, i-cubed, USDA, USGS, AEX, Getmapping, Aerogrid, IGN, IGP, swisstopo, and the GIS User Community

Figure V-1. Location of MATES III and MATES IV West Long Beach monitoring stations

The average concentration of selected PM, VOC and carbonyl species, and their respective 95% confidence interval are presented in Table V-1. Only days when concentrations are present at both stations are included in the calculation. With the exception of acetaldehyde, the differences in average levels between the two stations are not statistically significant ($p > 0.05$).

Table V-1. Average concentration of selected PM, VOC and carbonyl species, their respective 95% confidence interval, and the p-value for the difference between the mean at the MATES III and MATES IV West Long Beach sites.

	PM2.5 Mass (μg/m^3)	PM2.5 OC (μg/m^3)	PM2.5 EC (μg/m^3)	Nitrate (μg/m^3)	Sulfate (μg/m^3)	1,3-Butadiene (ppb)	Benzene (ppb)	Formaldehyde (ppb)	Acetaldehyde (ppb)
MATES III WLB Site	17.6 ± 2.0	6.50 ± 0.82	2.22 ± 0.44	3.07 ± 0.70	3.67 ± 0.55	0.048 ± 0.01	0.39 ± 0.06	2.47 ± 0.27	0.98 ± 0.14
MATES IV WLB Site	18.5 ± 2.1	6.30 ± 0.74	2.77 ± 0.51	3.34 ± 0.78	3.87 ± 0.57	0.058 ± 0.01	0.39 ± 0.07	2.50 ± 0.23	1.24 ± 0.15
p-value	0.26	0.36	0.06	0.31	0.32	0.15	0.45	0.44	0.01

Table V-2 shows the correlation coefficient (R), slope (m) and number of data point (n) from the linear regression analyses between the two stations for the PM, VOC and carbonyl species. The associations are high (R > 0.80) with the exception of OC and sulfate. For OC, the agreement improves considerably in 2008 (R = 0.85, m = 0.76, n = 31). The moderate association of sulfate is mainly driven by a few outliers. With the removal of four outliers out of 63 data points, the correlation is good (R = 0.80, m = 0.83).

Table V-2. Correlation coefficient (R), slope (m) and number of data point (n) from linear regression analyses between the MATES III and MATES IV West Long Beach sites.

	PM2.5 Mass	PM2.5 OC	PM2.5 EC	Nitrate	Sulfate	1,3-Butadiene	Benzene	Formaldehyde	Acetaldehyde
R	0.92	0.46	0.89	0.85	0.68	0.94	0.91	0.91	0.94
m	0.90	0.40	1.02	0.94	0.68	1.19	1.00	0.77	0.97
n	72	68	67	64	63	84	86	90	90

The scatterplots between the two monitoring stations, segregated by year, are presented in Figures V-2 to V-10. Overall, the concentrations of PM, VOC and carbonyl species at MATES IV WLB correlate well with those from MATES III WLB.

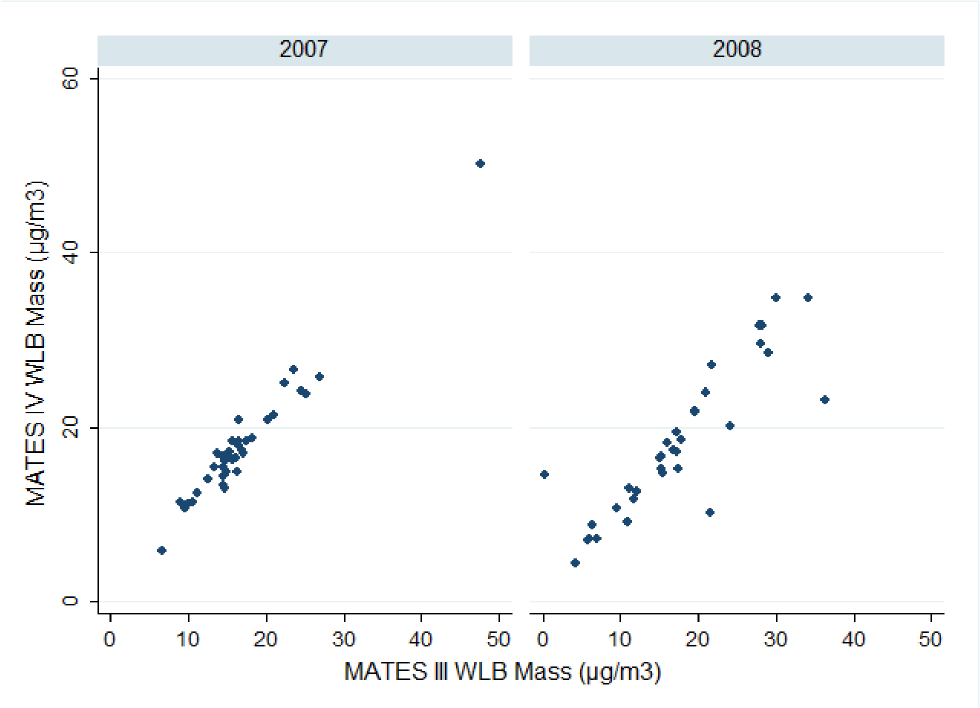


Figure V-2. Scatterplot of PM2.5 mass concentration between the MATES III and MATES IV West Long Beach sites.

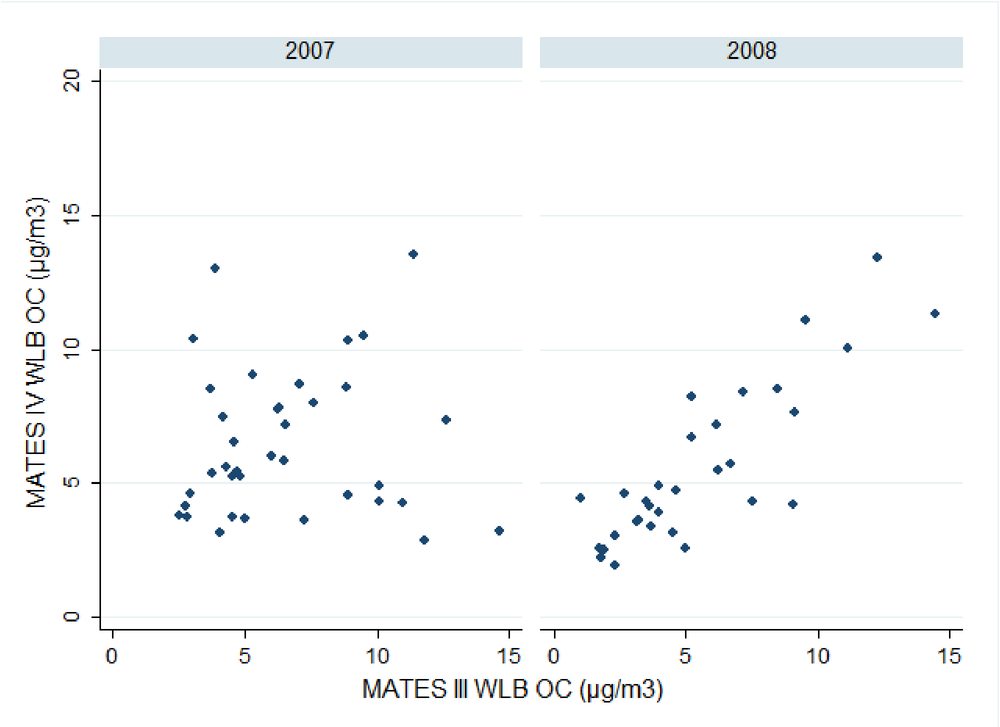


Figure V-3. Scatterplot of PM2.5 OC concentration between the MATES III and MATES IV West Long Beach sites.

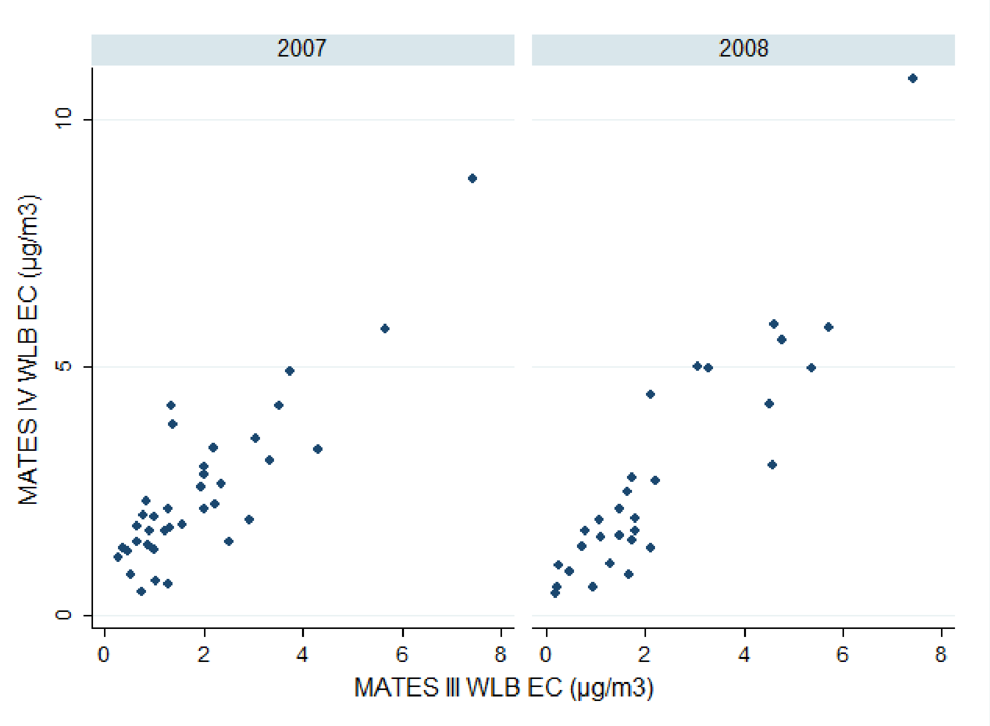


Figure V-4. Scatterplot of PM2.5 EC concentration between the MATES III and MATES IV West Long Beach sites.

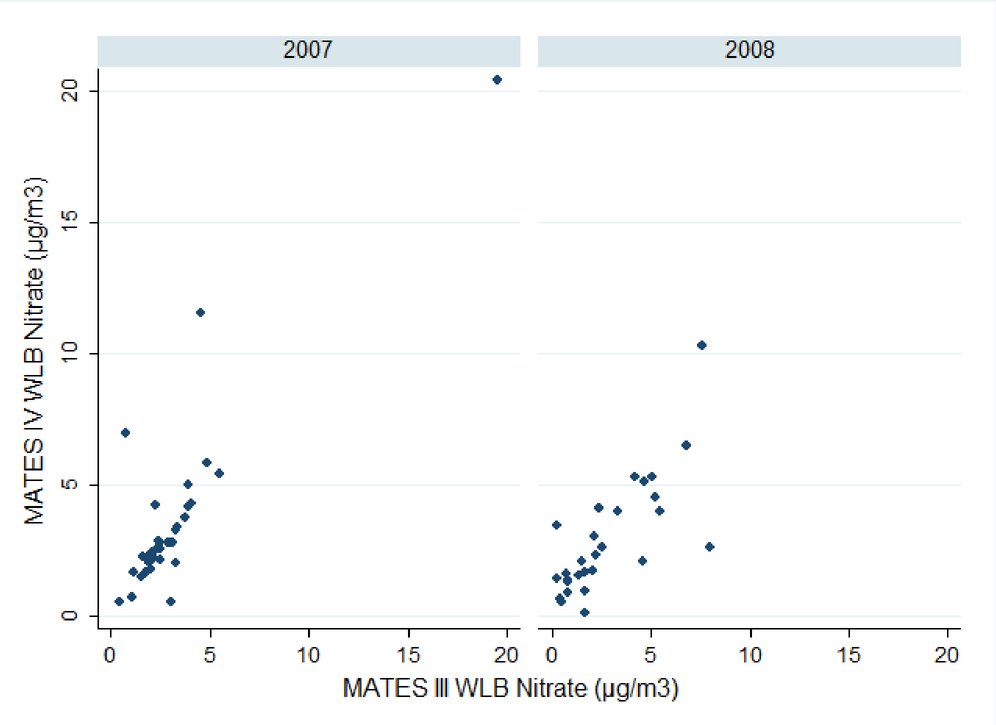


Figure V-5. Scatterplot of nitrate concentration between the MATES III and MATES IV West Long Beach sites.

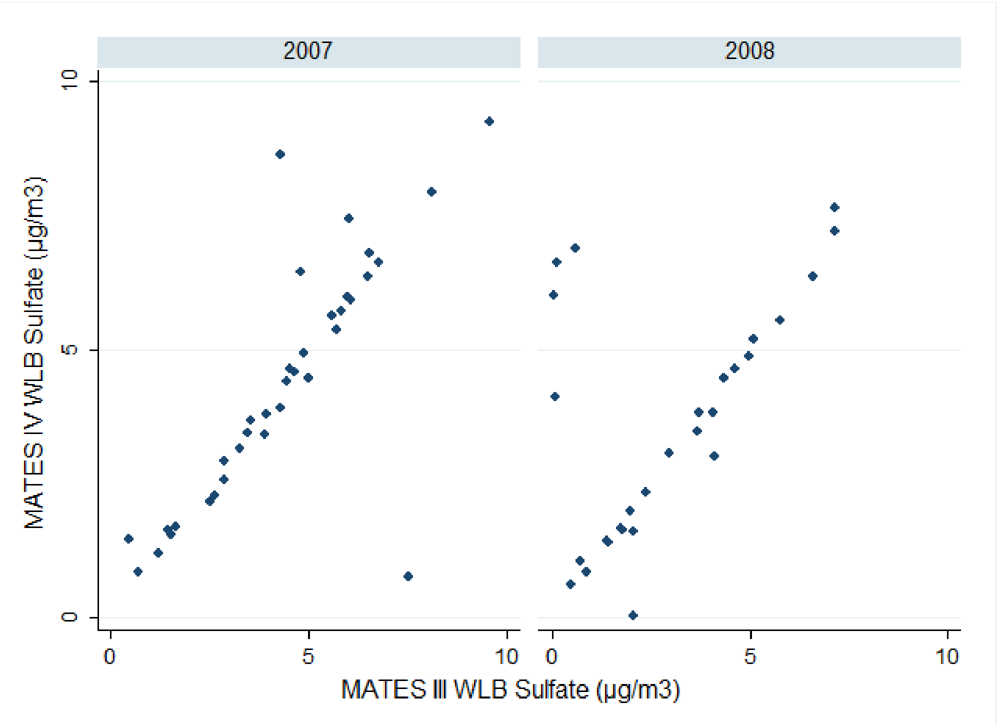


Figure V-6. Scatterplot of sulfate concentration between the MATES III and MATES IV West Long Beach sites.

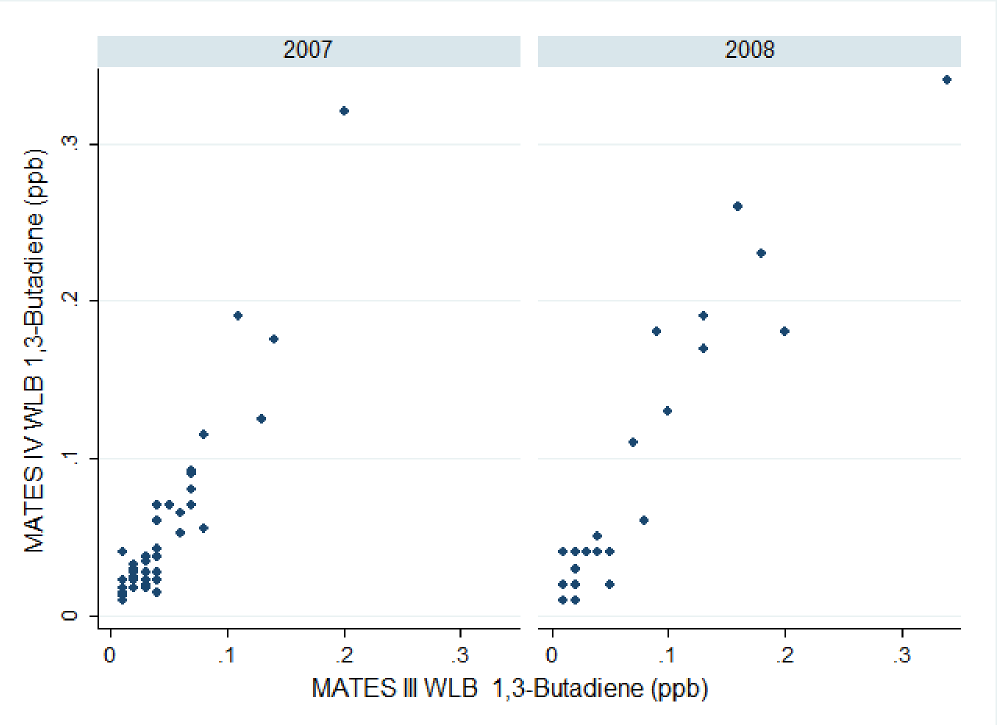


Figure V-7. Scatterplot of 1,3-butadiene concentration between the MATES III and MATES IV West Long Beach sites.

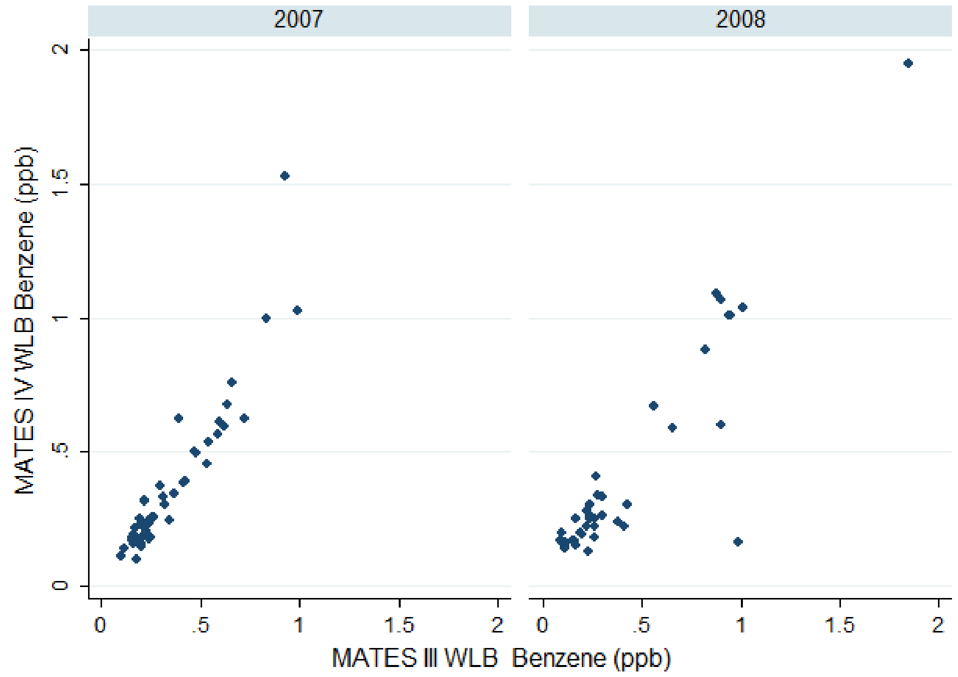


Figure V-8. Scatterplot of benzene concentration between the MATES III and MATES IV West Long Beach sites.

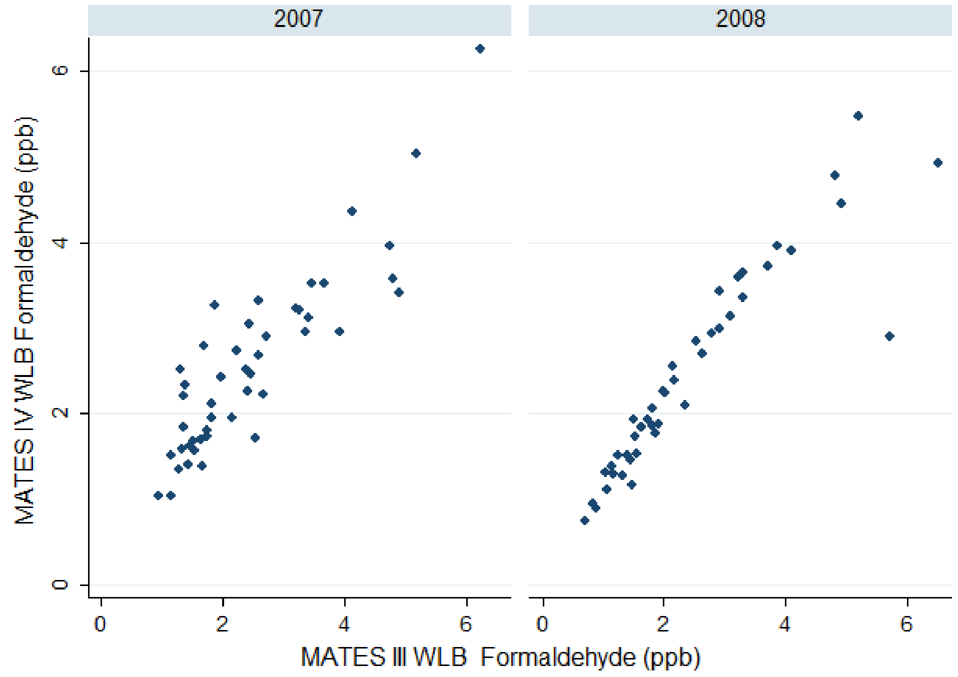


Figure V-9. Scatterplot of formaldehyde concentration between the MATES III and MATES IV West Long Beach sites.

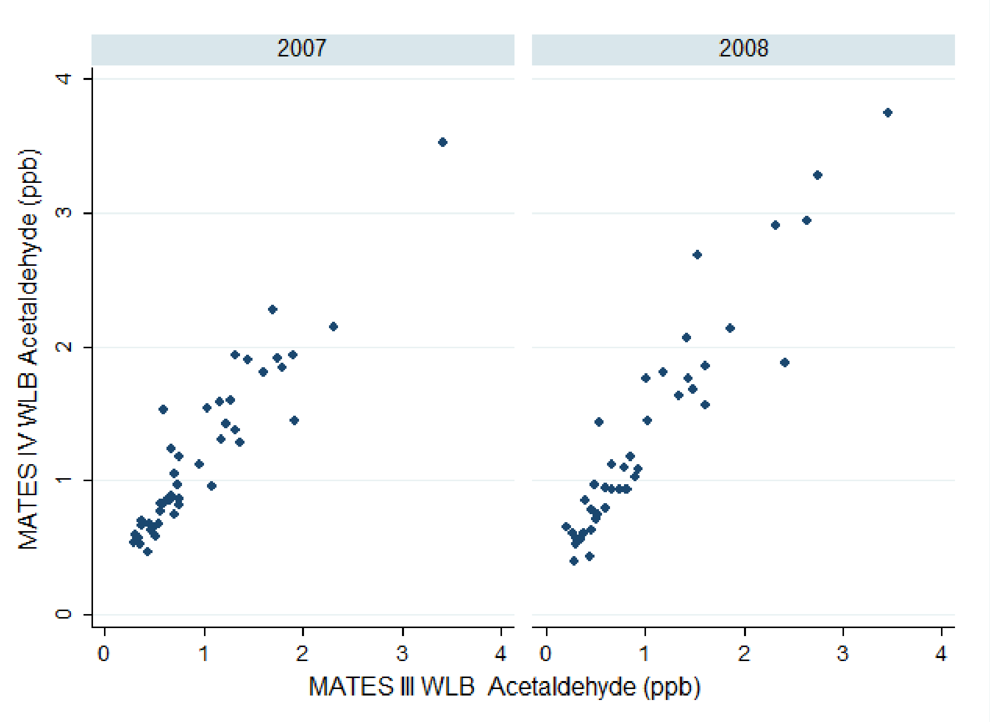


Figure V-10. Scatterplot of acetaldehyde concentration between the MATES III and MATES IV West Long Beach sites.

APPENDIX VI

MATES IV

DRAFT FINAL REPORT

Black Carbon Measurements at Fixed Sites

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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 CO_2 using manganese dioxide (MnO_2) as the oxidizer. Subsequently CO_2 is converted to methane (CH_4), and the concentration of CH_4 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 PM_{10} 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 $PM_{2.5\text{-}10}$, 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 inherit 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 though 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 though 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 (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 OpticalTransmittance (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 pyrolized 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 establish prior to the beginning of this study (Figure 1).

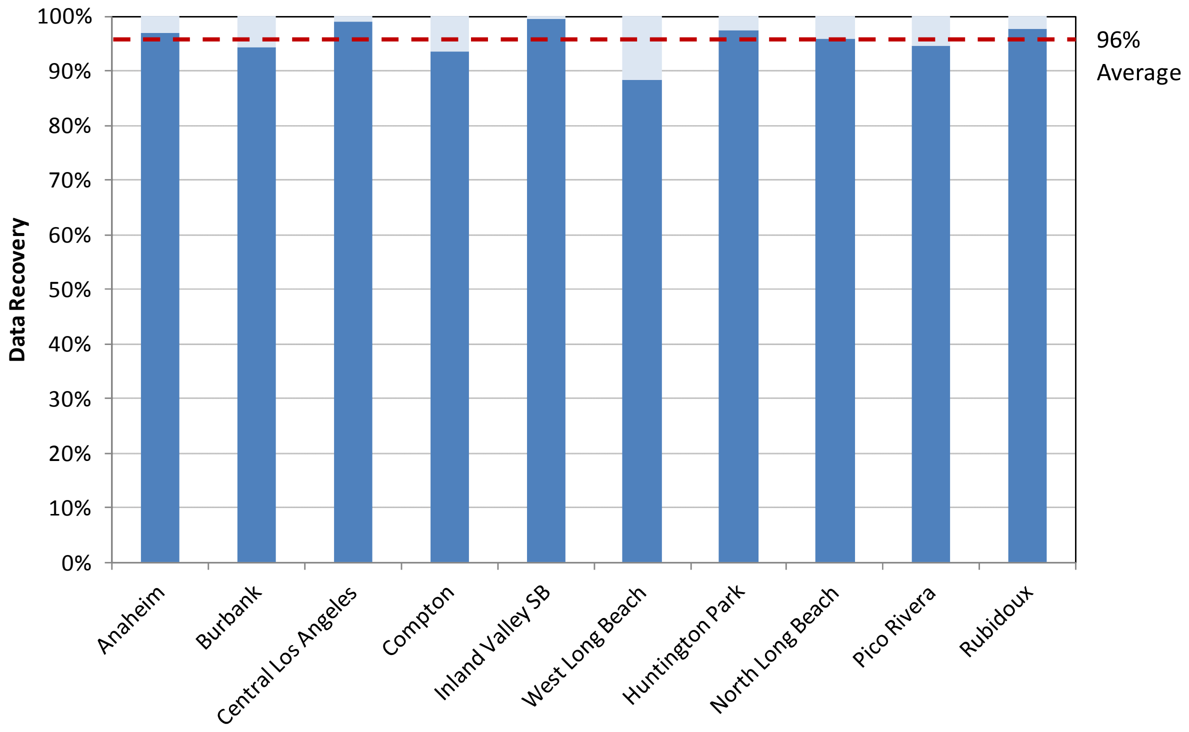


Figure 1 - Black Carbon Data Completeness at each of the MATES IV sites.

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.

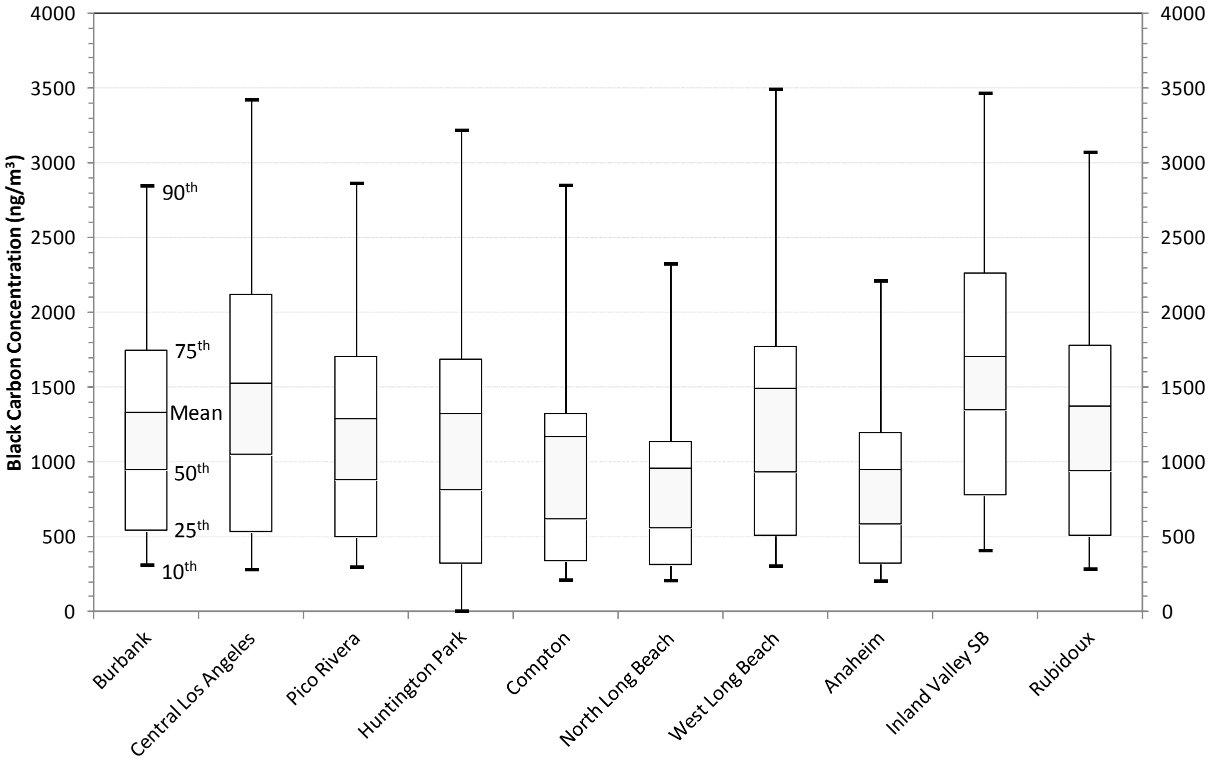


Figure 2 - Spatial Distribution of Black Carbon Concentrations Across All MATES IV Sites.

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).

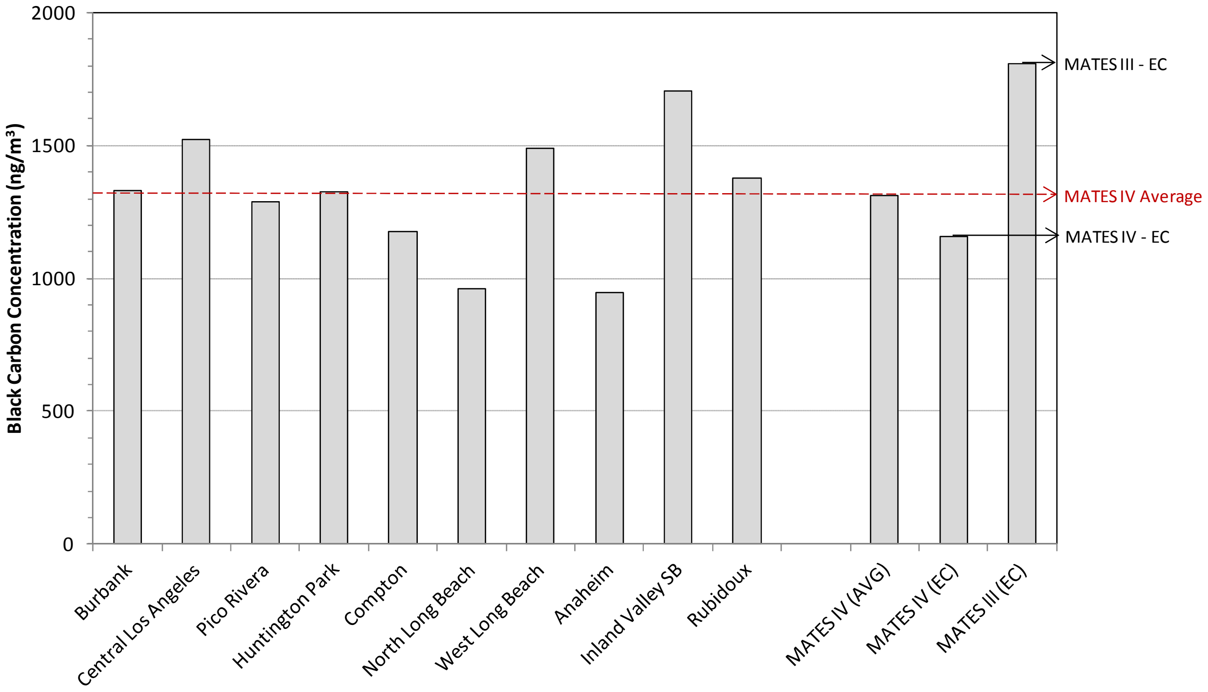


Figure 3 - Distribution of average Black Carbon concentrations during MATES IV and comparison with MATES IV and MATES III Elemental Carbon study averages.

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.

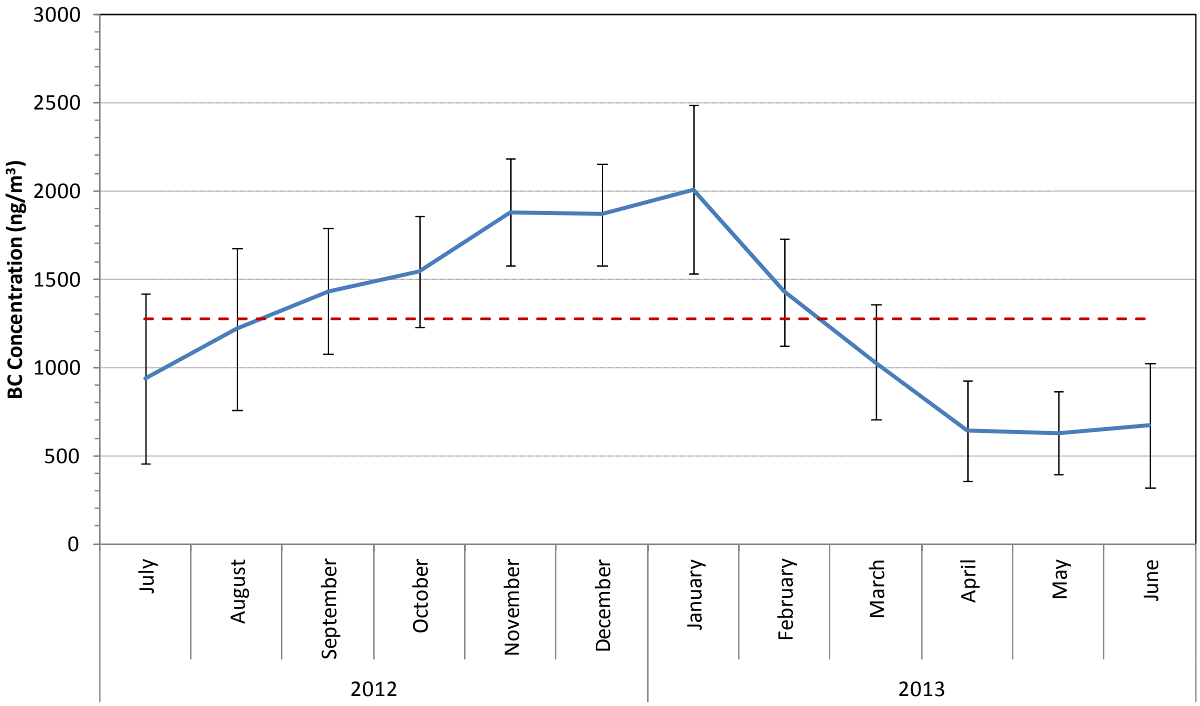


Figure 4 - Monthly Average Black Carbon Concentration Trends in the South Coast Basin During MATES IV. Red Line Indicating the MATES IV Average Concentration.

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).

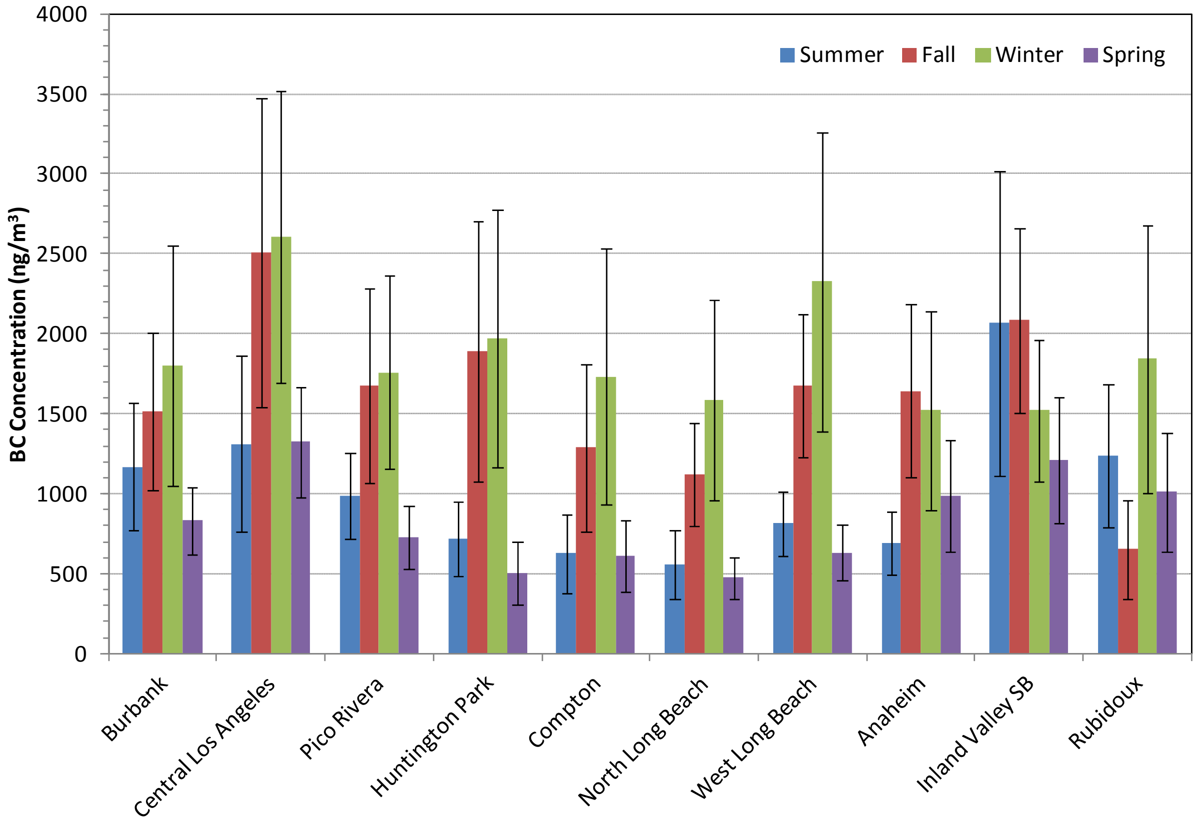


Figure 5 - Seasonal Variations of Black Carbon Concentrations at Each MATES IV Site.

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.

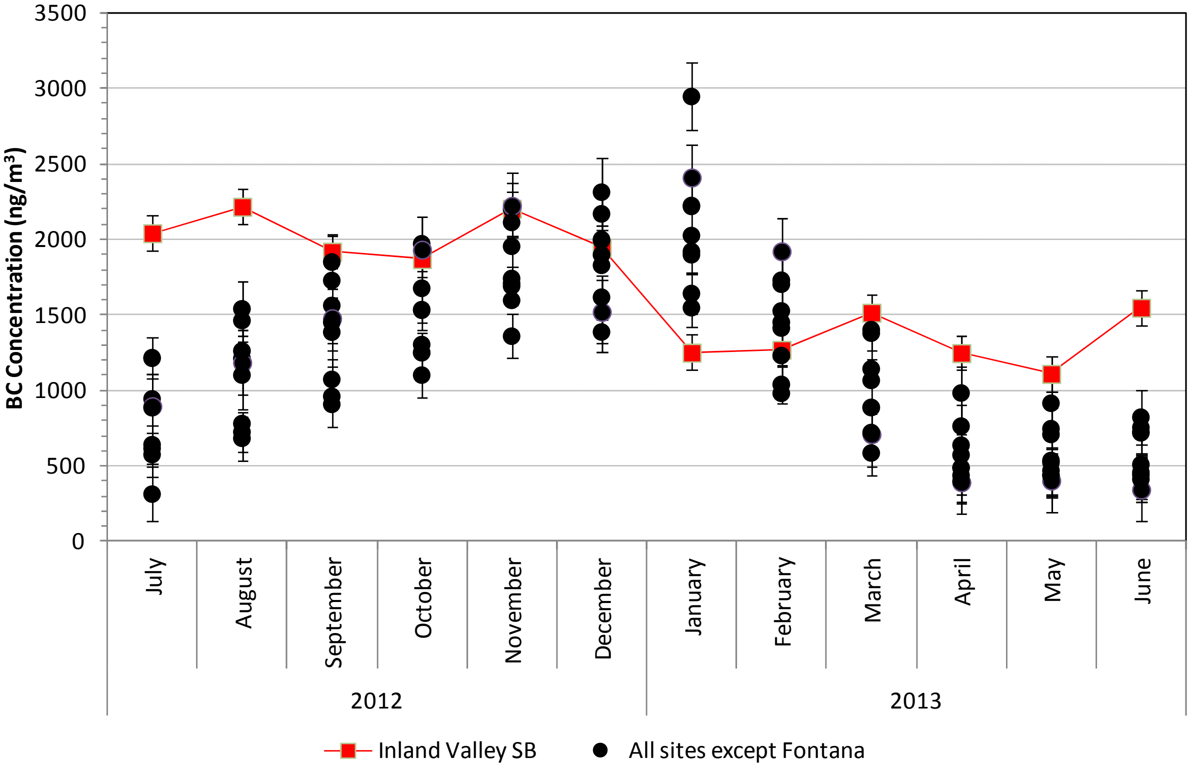
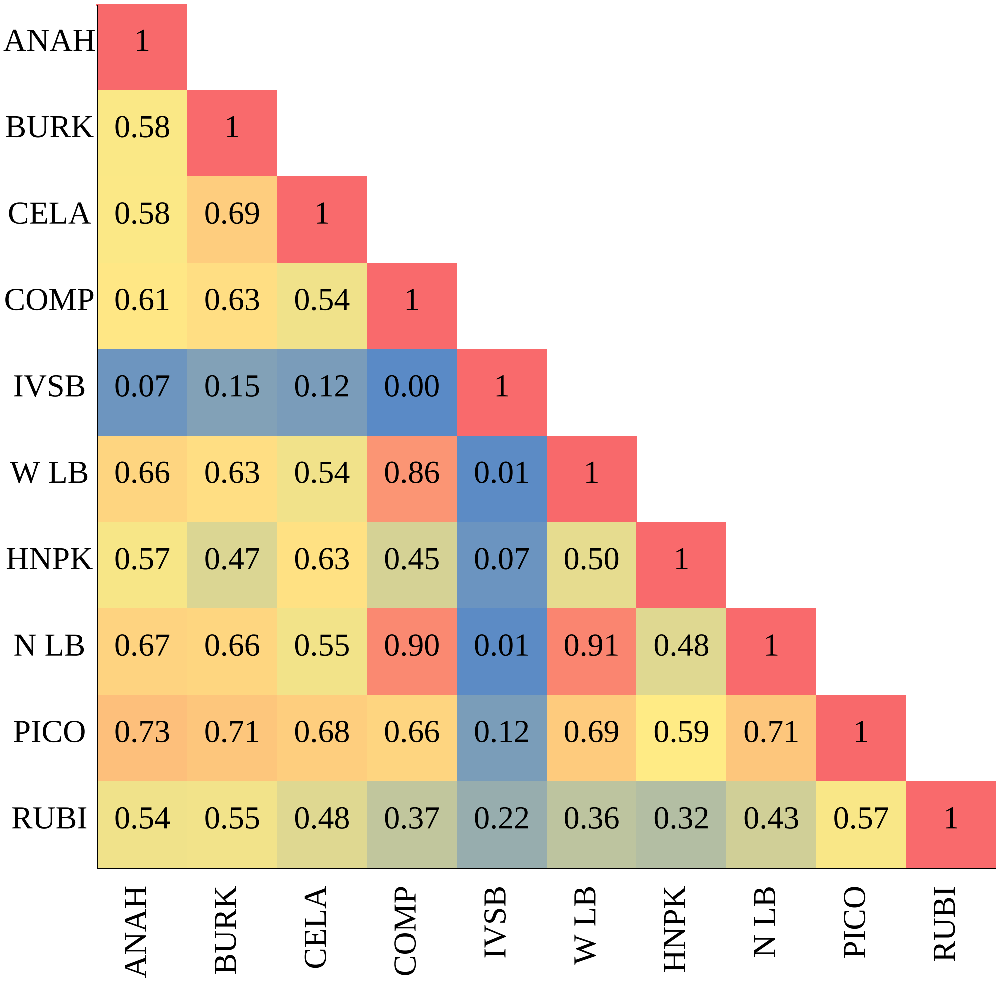


Figure 6 - Inland Valley San Bernardino (Fontana) Exhibits a Different Temporal Variation Compared to All Other MATES IV Sites.

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).



	ANAH	BURK	CELA	COMP	IVSB	W LB	HNPK	N LB	PICO	RUBI
ANAH	1									
BURK	0.58	1								
CELA	0.58	0.69	1							
COMP	0.61	0.63	0.54	1						
IVSB	0.07	0.15	0.12	0.00	1					
W LB	0.66	0.63	0.54	0.86	0.01	1				
HNPK	0.57	0.47	0.63	0.45	0.07	0.50	1			
N LB	0.67	0.66	0.55	0.90	0.01	0.91	0.48	1		
PICO	0.73	0.71	0.68	0.66	0.12	0.69	0.59	0.71	1	
RUBI	0.54	0.55	0.48	0.37	0.22	0.36	0.32	0.43	0.57	1

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.

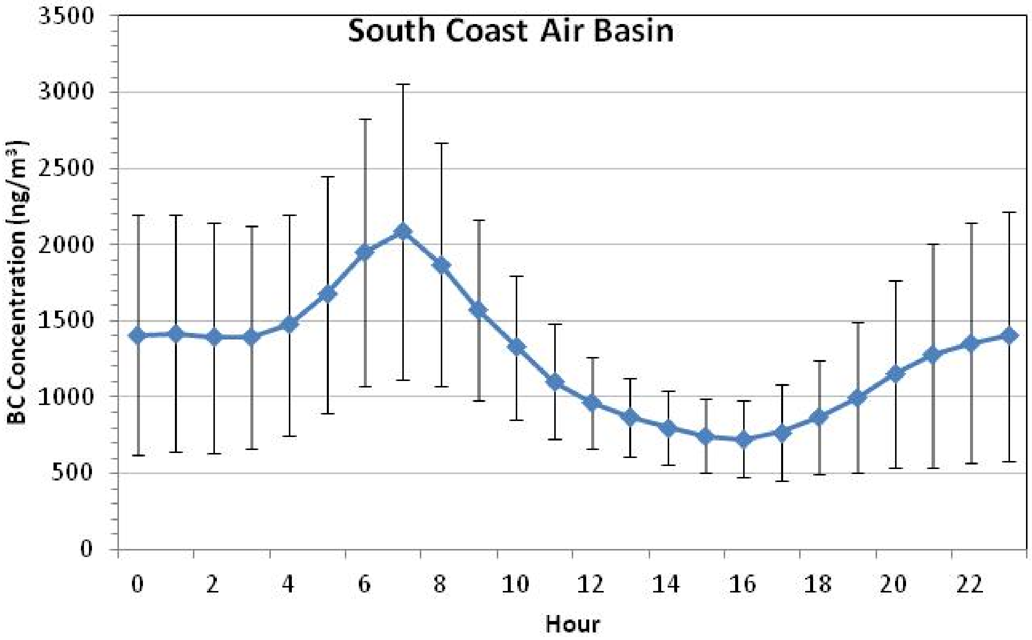


Figure 8 - Diurnal Variation of Black Carbon Concentration in South Coast Air Basin During MATES IV.

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.

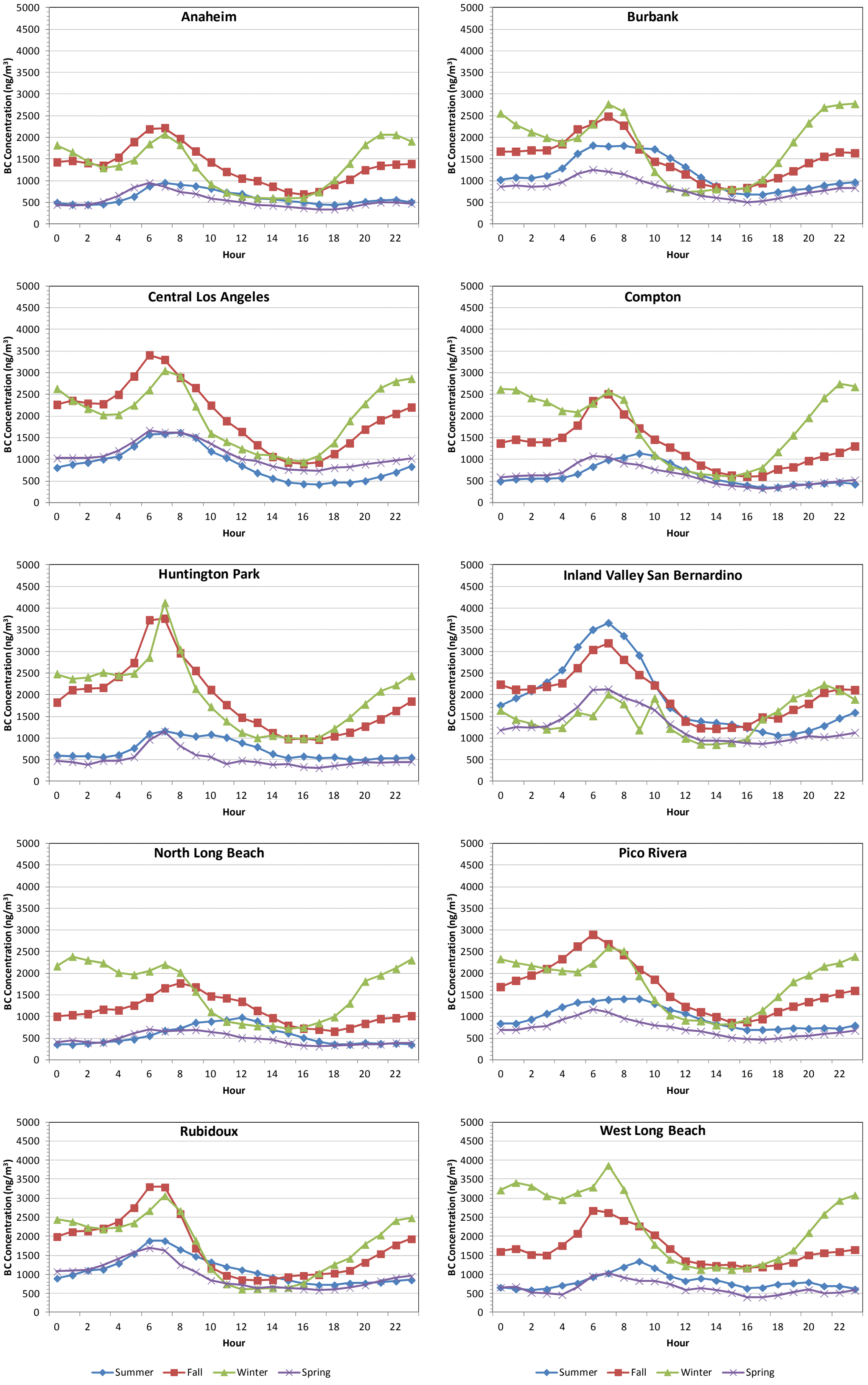


Figure 9 - Seasonal Diurnal Trends of Black Carbon Concentrations at Each Site.

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.

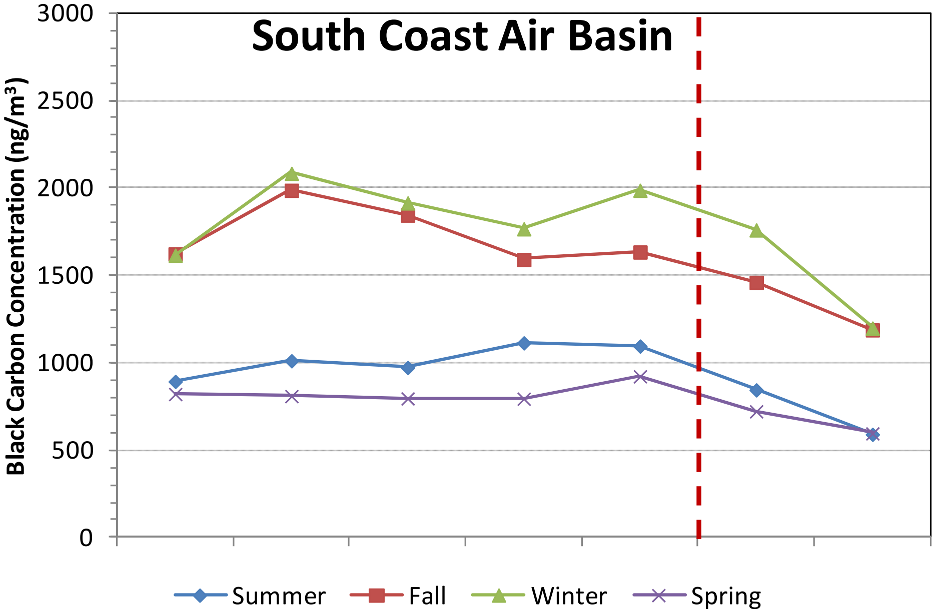


Figure 4 - Seasonal Weekday/Weekend Comparison in the South Coast Air Basin During MATES IV.

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 PM2.5) 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 ($r^2 = 0.81$).

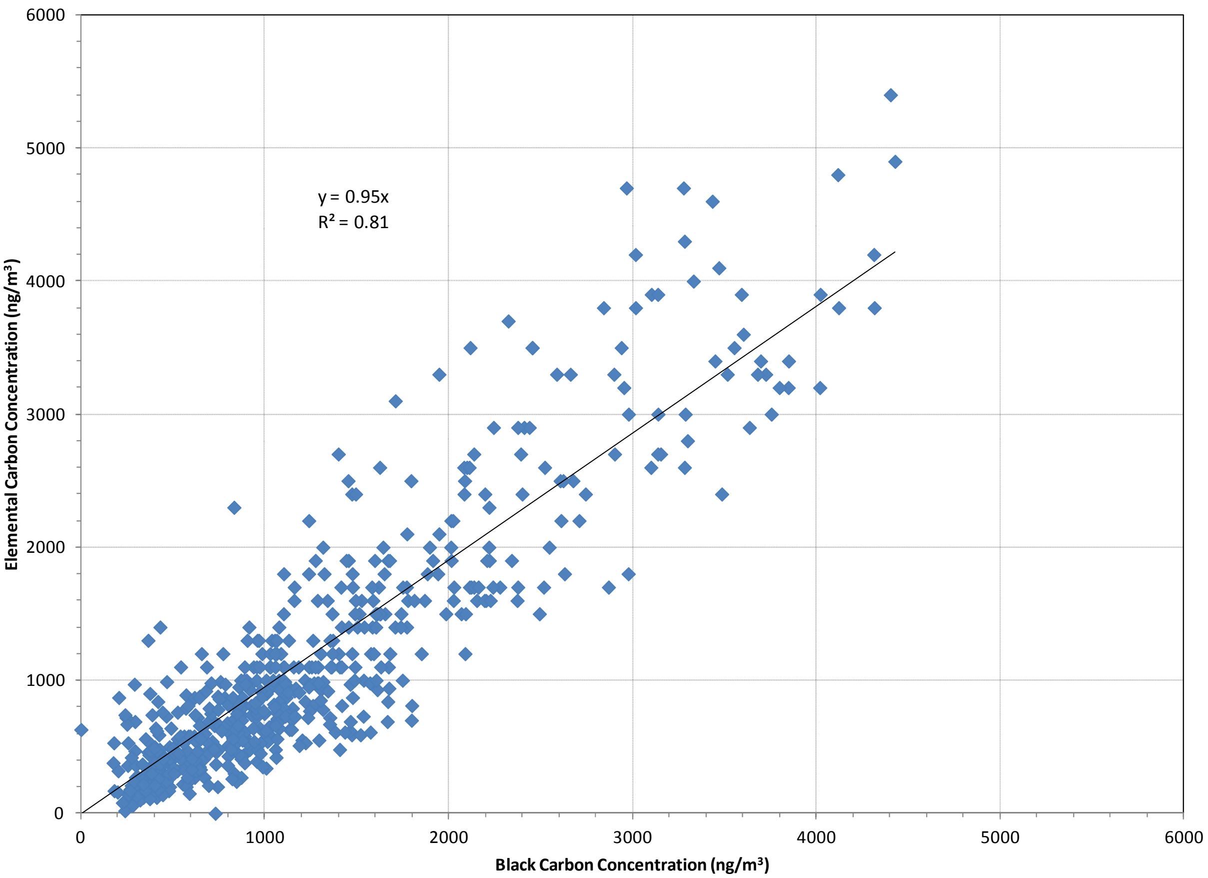


Figure 11 - Comparison of Daily Average BC and EC Concentrations in South Coast Air Basin During MATES IV.

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.

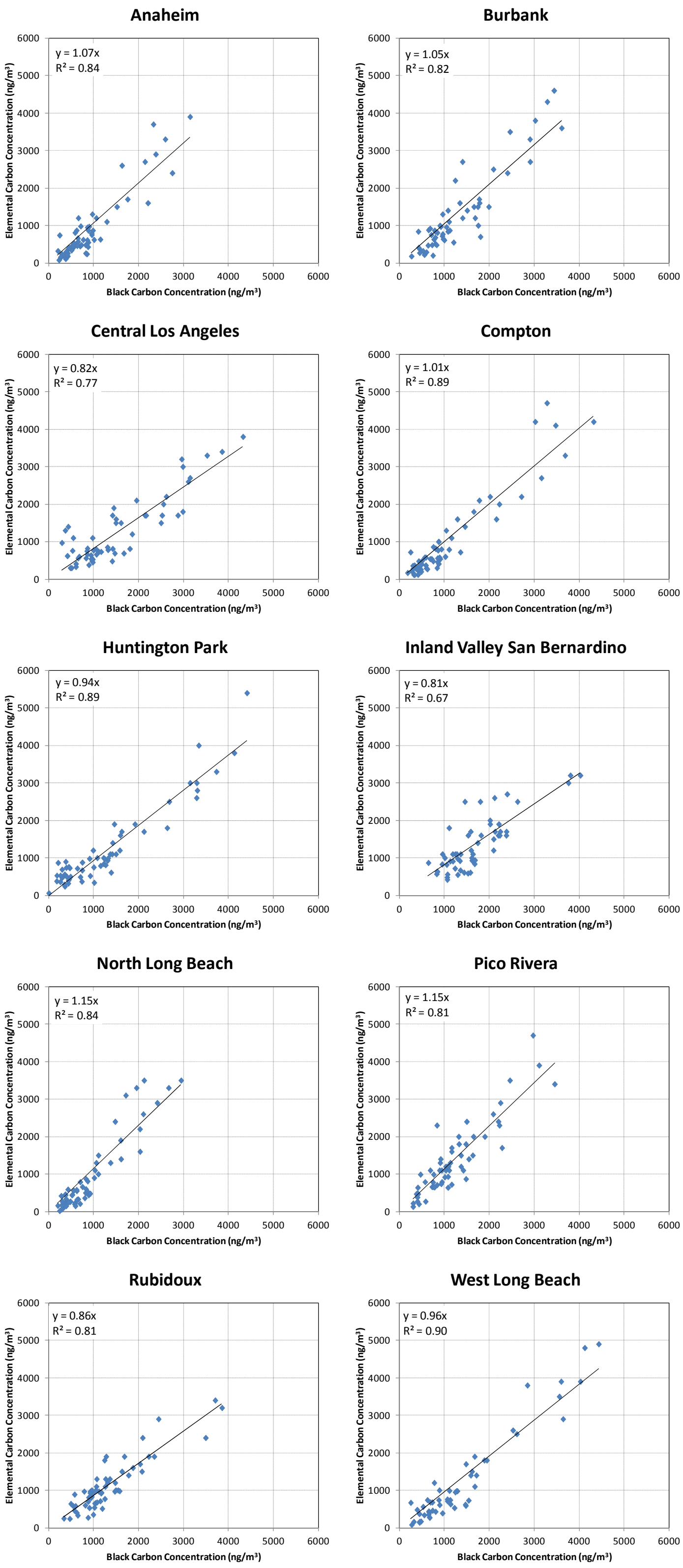


Figure 5 - Comparison of Daily Average BC and EC Concentration at Each MATES IV Site.

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.

VI.4 References:

Abu-Allaban, M., Rogers, C. F., & Gertler, A. W. (2004). A quantitative description of vehicle exhaust particle size distributions in a highway tunnel. *Journal of the Air & Waste Management Association*, *54*(3), 360-366.

Allen, G. A., Babich, P., & Poirot, R. L. (2004, October). Evaluation of a new approach for real time assessment of wood smoke PM. In *Proceedings of the Regional and Global Perspectives on Haze: Causes, Consequences, and Controversies, Air and Waste Management Association Visibility Specialty Conference* (pp. 25-29).

Bond, T. C., and Bergstrom, R. W. (2006) Light absorption by carbonaceous particles: An investigative review, Aerosol Science and Technology.

Chen, L.-W.A.; Chow, J.C.; Watson, J.G.; Moosmüller, H.; and Arnott, W.P. (2004). Modeling reflectance and transmittance of quartz-fiber filter samples containing elemental carbon particles: Implications for thermal/optical analysis. *J. Aerosol Sci.*, **35**(6):765-780.

Chow, J. C., Watson, J. G., Pritchett, L. C., Pierson, W. R., Frazier, C. A., & Purcell, R. G. (1993). The DRI thermal/optical reflectance carbon analysis system: description, evaluation and applications in US air quality studies. *Atmospheric Environment. Part A. General Topics, 27*(8), 1185-1201.

Chow, J. C., Watson, J. G., Crow, D., Lowenthal, D. H., & Merrifield, T. (2001). Comparison of IMPROVE and NIOSH carbon measurements. *Aerosol Science & Technology, 34*(1), 23-34.

Chow, J.C.; Watson, J.G.; Chen, L.-W.A.; Arnott, W.P.; Moosmüller, H.; and Fung, K.K. (2004). Equivalence of elemental carbon by Thermal/Optical Reflectance and Transmittance with different temperature protocols. *Environ. Sci. Technol.*, **38**(16):4414- 4422.

Fine, P. M., Cass, G. R., & Simoneit, B. R. (2004). Chemical characterization of fine particle emissions from the fireplace combustion of wood types grown in the Midwestern and Western United States. *Environmental Engineering Science, 21*(3), 387-409.

HEI, 2010. Traffic Related Air Pollution: A Critical Review of the Literature on Emissions, Exposure and Health Effects. HEI Special Report 17. Boston: Health Effects Institute.

Janssen, N. A., et al. (2011), Black carbon as an additional indicator of the adverse health effects of airborne particles compared with PM10 and PM2.5, Environ. Health Perspect., 119, 1691–1699, doi:10.1289/ehp.1003369.

Johnson, R. L., J. J. Shah, R. A. Cary, and J. J. Huntzicker, An automated thermal-optical method for the analysis of carbonaceous aerosol, *in ACS Symposium Series 167, pp. 223–233,* Am. Chem. Soc., Washington, D.C., 1981.

Lloyd, A. C., & Cackette, T. A. (2001). Diesel engines: environmental impact and control. *Journal of the Air & Waste Management Association, 51*(6), 809-847.

Magliano, K. L., Hughes, V. M., Chinkin, L. R., Coe, D. L., Haste, T. L., Kumar, N., & Lurmann, F. W. (1999). Spatial and temporal variations in PM_{10} and $PM_{2.5}$ source contributions and comparison to emissions during the 1995 integrated monitoring study. *Atmospheric Environment, 33*(29), 4757-4773.

Molina, M., D. Zaelke, K. M. Sarma, S. O. Andersen, V. Ramanathan, and D. Kaniaru (2009), Reducing abrupt climate change risk using the Montreal Protocol and other regulatory actions to complement cuts in CO2 emissions, P. Natl. Acad. Sci. USA, 106(49), 20616–20621, doi:10.1073/pnas.0902568106.

Ostro, B., M. Lipsett, P. Reynolds, D. Goldberg, A. Hertz, C. Garcia, K. D. Henderson, and L. Bernstein (2010), Long-term exposure to constituents of fine particulate air pollution and mortality: Results from the California teachers study, Environ. Health Perspect., 118(3), 363–369, doi:10.1289/ehp.0901181.

Pope, C. A., M. Ezzati, and D. W. Dockery (2009), Fine-particulate air pollution and life expectancy in the united states, N. Engl. J. Med., 360(4), 376–386.

Ramanathan, V., and Y. Y. Xu (2010), The Copenhagen Accord for limiting global warming: Criteria, constraints, and available avenues, P. Natl. Acad. Sci. USA, 107(18), 8055–8062, doi:10.1073/pnas.1002293107.

Rinehart, L. R., Fujita, E. M., Chow, J. C., Magliano, K., & Zielinska, B. (2006). Spatial distribution of $PM_{2.5}$ associated organic compounds in central California. *Atmospheric Environment*, *40*(2), 290-303.
Schauer, J. J. (2003). Evaluation of elemental carbon as a marker for diesel particulate matter. *Journal of Exposure Science and Environmental Epidemiology*, *13*(6), 443-453.

South Coast Air Quality Management District (AQMD) (2008) “Multiple Air Toxics Exposure Study III”

U.S. EPA (2009b) Integrated science assessment for particulate matter. Report by the U.S. Environmental Protection Agency, Washington, DC, EPA/600/R-08/139. Available on the Internet at *http://cfpub.epa.gov/ncea/cfm/recordisplay.cfm?deid=216546*.

Wang, Y., Hopke, P. K., Rattigan, O. V., & Zhu, Y. (2011). Characterization of ambient black carbon and wood burning particles in two urban areas. *Journal of Environmental Monitoring*, *13*(7), 1919-1926.

APPENDIX VII

MATES IV

DRAFT FINAL REPORT

Ultrafine Particle Measurements at Fixed Sites

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Payam Pakbin
Andrea Polidori

VII-1 Background

There is continuing concern about the potential health effects caused by exposure to criteria pollutants and air toxics emitted from both gasoline and diesel vehicles (HEI, 2010), especially for people living in urban areas. Motor-vehicle emissions consist of a complex mixture of solid, liquid and gaseous hydrocarbons, metals, black carbon (BC), volatile organic compounds (VOC), sulfates and nitrates that range in size from a few nanometers to several microns in aerodynamic diameter. Over the past decade, regulators in the United States and California have taken major steps to reduce the adverse human health impacts from vehicular emissions. In 1998, the California Air Resources Board (CARB) classified diesel exhaust PM as a toxic air contaminant, citing its potential to cause cancer and other health problems. The U.S. EPA concluded that long-term exposure to diesel engine exhaust is likely to pose a lung cancer hazard to humans and can also contribute to other acute and chronic health effects. The International Agency for Research on Cancer (IARC), part of the World Health Organization (WHO), recently classified diesel exhaust as a human carcinogen (Benbrahim-Tallaa et al., 2012). The MATES studies conducted by the South Coast Air Quality Management District (SCAQMD) are designed 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 the major contributor to carcinogenic risk due to exposure to air toxics, accounting for 84% of the total carcinogenic risk (SCAQMD MATES III Report, 2008). In the current MATES IV assessment, DPM accounts for 68% of the average carcinogenic risk in the SCAB (Executive Summary - Figure ES-2).

Federal, state and local regulatory efforts have been focused on reducing the mass of PM emitted in the ambient air. Current PM regulations are focused on two size fractions: PM_{10} (particles with a diameter less than 10 µm) and $PM_{2.5}$ (diameter < 2.5 µm). Recently, however, there is a growing concern in the public health community about the contribution of the ultrafine particles (UFPs; diameter < 0.1µm) to the overall health impacts of PM. While substantial effort has been made to characterize the health risks associated with exposure to diesel PM, information about the health impacts of UFPs is just recently emerging. These very minute particles (consisting primarily of organic material, soot, and trace elements) have a different chemical composition than the larger PM fractions ($PM_{2.5}$ and PM_{10}). Due to their small size, UFPs are not a major factor in measurements of overall PM mass, but comprise a significant majority (90%) of the number of airborne particles in the atmosphere (Stanier et al., 2004a and Zhang et al., 2004). For this reason, their concentration is usually expressed in terms of total particle count (i.e. # per cubic centimeter of sampled air, or $\#/cm^3$), even though a small fraction of the particles being counted may be above 100 nm. UFPs are emitted from almost every fuel combustion process, including diesel, gasoline, and jet engines. Although there are many sources of UFPs in the atmosphere, vehicle exhaust is the major contributor to UFP concentrations in urban areas, particularly in proximity to major roads. Consequently, there is growing concern that people living in close proximity to highly trafficked roadways and other sources of combustion-related pollutants (e.g. airports, refineries, and railyards) may be exposed to significant levels of UFPs as well as air toxics. In a seminal study conducted in the Los Angeles Basin, the number concentration of UFPs dropped dramatically with increasing distance from busy freeways (Zhu et al., 2002a,b). UFP concentrations were typically highest on or in close proximity to freeways and decreased exponentially to upwind background levels. One type of ultrafine combustion particles are formed in the engine or tailpipe, and are mostly sub-micrometer agglomerates of carbonaceous material ranging in size from 30 to 500 nm. These particles may also contain metallic ash (from lubricating oil additives and from engine wear), adsorbed or condensed hydrocarbons, and sulfur compounds (Morawska et al., 2008). Another type of ultrafine particle is formed as hot exhaust gases are expelled from the tailpipe. They quickly cool and either condense on existing particles or nucleate to form large numbers of very small particles in the air. They consist mainly of hydrocarbons and hydrated sulfuric acid, are generally 30 nm or less in diameter and are most commonly observed near busy freeways, especially those where a large fraction of heavy-duty diesel vehicles is present (Westerdahl et al., 2005; Ntziachristos et al., 2007; Keskinen and Ronkko, 2010). Once released into the atmosphere, UFPs undergo dilution with ambient air and are subject to chemical reactions and physical processes such as evaporation, condensation, and coagulation. Thus, particles measured away from roadways and other emission sources generally have different characteristics than those measured immediately after formation. Wind speed and direction, precipitation, relative humidity, and temperature are the main meteorological factors affecting UFP transport. In addition to primary UFP emissions, secondary formation of UFPs in the atmosphere through photochemical reactions also contributes to total number concentrations. Particle formation by secondary processes depends strongly on the intensity of solar radiation and is more distinct in summers. Once formed, secondary particles are also transformed by coagulation and condensation in the atmosphere.

VII-2 UFP Measurements During MATES IV

There are very few if any long-term studies of human population exposure to UFPs, as this species is not typically measured in monitoring networks throughout the U.S. Concentrations of UFPs vary geographically, and it is not clear how well central site monitors may capture actual local exposures. Generally there is little or no correlation between ambient particle numbers and mass (Sardar et al., 2004); therefore, measurements of ambient particle number concentrations are necessary to complement the existing PM mass measurements. UFPs have a relatively short lifespan and are strongly dependent on local sources and atmospheric conditions; thus, their number concentrations can vary significantly on short temporal and spatial scales. In order to accurately estimate human exposure and the subsequent health impacts of UFPs, particle number would need to be measured across more spatially resolved monitoring networks.

The purpose of the MATES program is to conduct a series of studies to assess cancer risk from exposure to toxic air contaminants in the SCAB. These studies are comprised of air toxics monitoring and analysis, development of toxic emissions inventories, and regional modeling and evaluations. MATES IV is intended as a follow-up study to MATES II and III; unique to MATES IV is the incorporation of continuous UFP and BC concentration measurements, even though they are not technically specified as air toxics. Details of the sites, their characteristics and sampling protocols are given in MATES IV, Chapter 2. The sampling duration for all fixed stations was one year, ranging from July 1, 2012, to June 30, 2013, excluding Huntington Park, where sampling begun in August 1, 2012, and ended in July 31, 2013. Additionally, local-scale near source monitoring of UFP and BC concentrations was performed in the vicinity of the Los Angeles International Airport (LAX), San Bernardino Railyards, and Mira Loma to assess near-source air toxic emissions. This appendix will focus on the fixed site UFP measurements in the

SCAB as part of MATES IV. Results from the local-scale UFP measurements will be reported separately.

Since there is no “standard” measurement technique or calibration standard by which different instruments can be evaluated and compared, UFP measurements are somewhat operationally defined. The MATES IV UFP continuous real-time minute data was collected at 10 fixed sites utilizing the Teledyne Advanced Pollution Instrumentation (TAPI) Ultrafine Particle Monitor Model 651. This is a continuous laminar flow condensation particle counter (CPC) that uses water to grow UFPs to a larger, detectable size. UFPs are grown through condensation in a controlled super-saturation environment to larger sizes and then measured (counted) using a photodetector. CPCs provide the total number concentration of particles above 7 nm, in real-time. Although CPCs are the most widely used instruments for measuring particle number concentrations, they do not provide any information on the original size of the particles counted. Additional technical details on this CPC model and the results of a test evaluation conducted by SCAQMD and UCLA prior to the beginning of MATES IV are reported elsewhere (Lee et al., 2013). For further information and maintenance instructions, please refer to the Teledyne Advanced Pollution Instrumentation (TAPI) Ultrafine Particle Monitor Model 651 Operation Manual.

VII-3 Data Validation

The particle number count data was downloaded from the instrument using USB drives on a weekly basis. Minute data for each site was validated and examined for anomalies. During the sampling period we experienced minor problems with the USB drives, which led to some data loss and a slightly decreased data recovery. Hourly average particle number concentrations were calculated for each station (i.e., Anaheim, Burbank, Central Los Angeles, Compton, Inland Valley San Bernardino, Huntington Park, North Long Beach, Pico Rivera, Rubidoux, and West Long Beach) from the corresponding one minute data only when the data recovery was 75% or higher (i.e., when more than 45 one minute data within the hour were valid). The hourly data recoveries for each sampling location are provided in Figure VII-1. The overall hourly data recovery for the ten MATES IV sites combined was 82%.

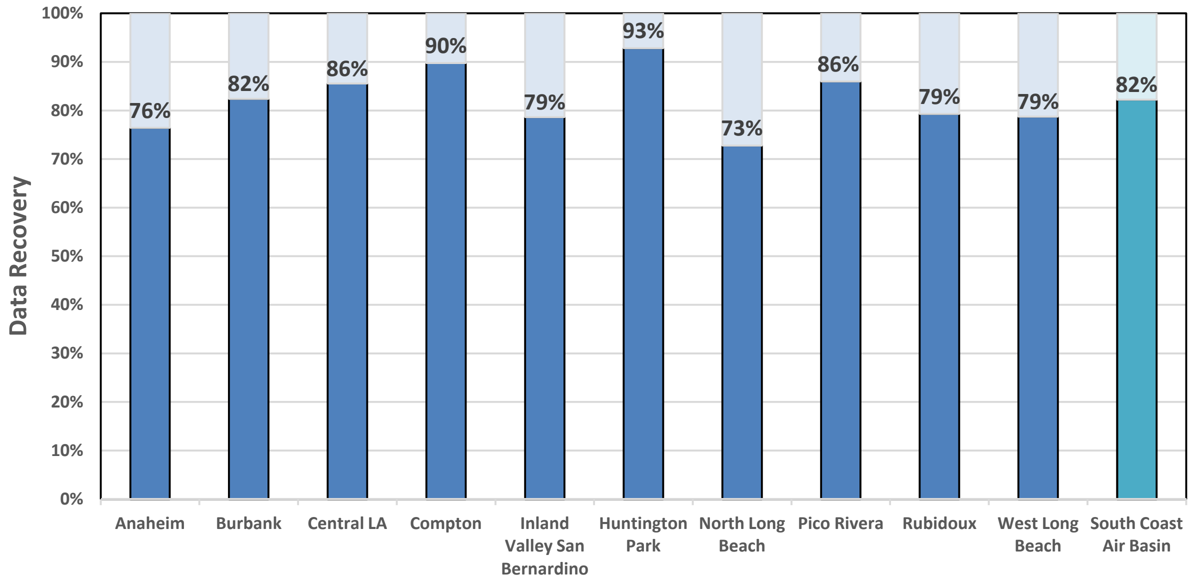

Figure VII-1: Ultrafine particle hourly data completeness for the MATES IV sites.

Three collocation studies were performed against a "Gold Standard" CPC (i.e., a reference instrument that was only used for collocation purposes) as a QA/QC check and to determine if correction factors should have been applied to the data to account for intra-model variations between CPC performances. These studies indicated that all ten site instruments were in good agreement with the "Gold Standard" CPC (i.e., high correlation coefficients; slopes close to one, and small intercepts). Thus, no corrections were applied to the field data.

VII-4 Results and Discussion

Annual Trends

The UFP annual means and standard deviation (error bars) for each site and the SCAB are shown in Figure VII-2. The UFP concentrations varied from site to site, with the highest annual averages measured at West Long Beach and Huntington Park. These sites are near potential emission sources associated with goods movement to and from the San Pedro Bay Ports and other vehicular sources. West Long Beach is located in a mixed residential and industrial area, approximately 2 km inland of the Port of Los Angeles and the Port of Long Beach, the busiest port complex in the USA. It is situated immediately downwind of a railyard and the Terminal Island Freeway 103, where heavy truck traffic consists of 22-25% of the average annual daily traffic (AADT; http://traffic-counts.dot.ca.gov/). Sampling locations with high AADT comprising of a greater percentage of heavy-duty diesel trucks (HDDT) have been shown to have elevated levels of particle number count compared to sites with less traffic and more gasoline vehicles (Zhu et al. 2004). The Huntington Park location is in a residential area, downwind of the Alameda Corridor, a freight rail connecting the downtown Los Angeles rail system to the San Pedro Bay Ports. Although Compton is also located in a residential area downwind from the railroad, it is further east than Huntington Park, potentially resulting in a decreased average annual UFP concentration. The Central L.A. site experienced some construction activity during the sampling duration, which might have caused increased UFP concentrations. Rubidoux, an inland receptor site, had the lowest annual UFP concentration average.

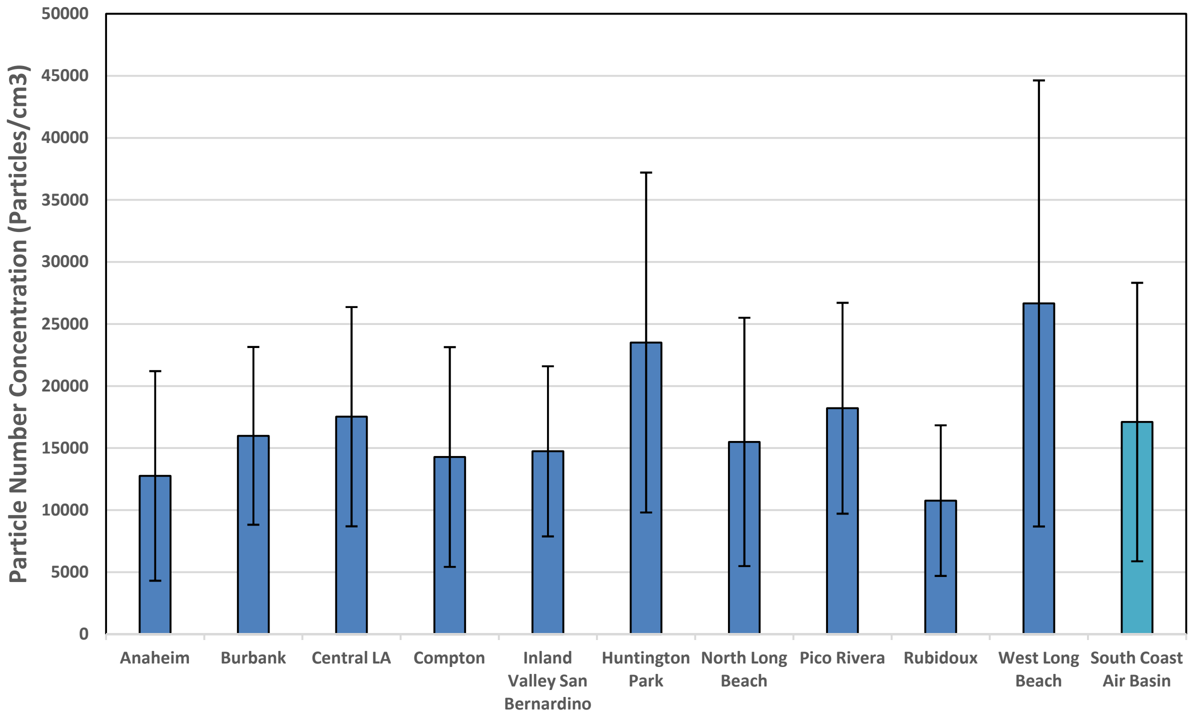

Figure VII-2: Mean and standard deviation for the MATES IV sites.

The box whisker plot in Figure VII-3 summarizes the 10th percentile, first quartile, median, mean, third quartile, and 90th percentile hourly UFP concentrations at each MATES IV site in the SCAB. The plot indicates that the Anaheim, Burbank, Central L.A., Compton, Inland Valley San Bernardino, Pico Rivera, and Rubidoux sites were characterized by a relatively low UFP variability, while the Huntington Park, North Long Beach, and West Long Beach stations had wider UFP ranges and distributions. The relatively high variability among these sites is indicative of their vicinity to one or more emission sources of UFPs (e.g., major roadways).

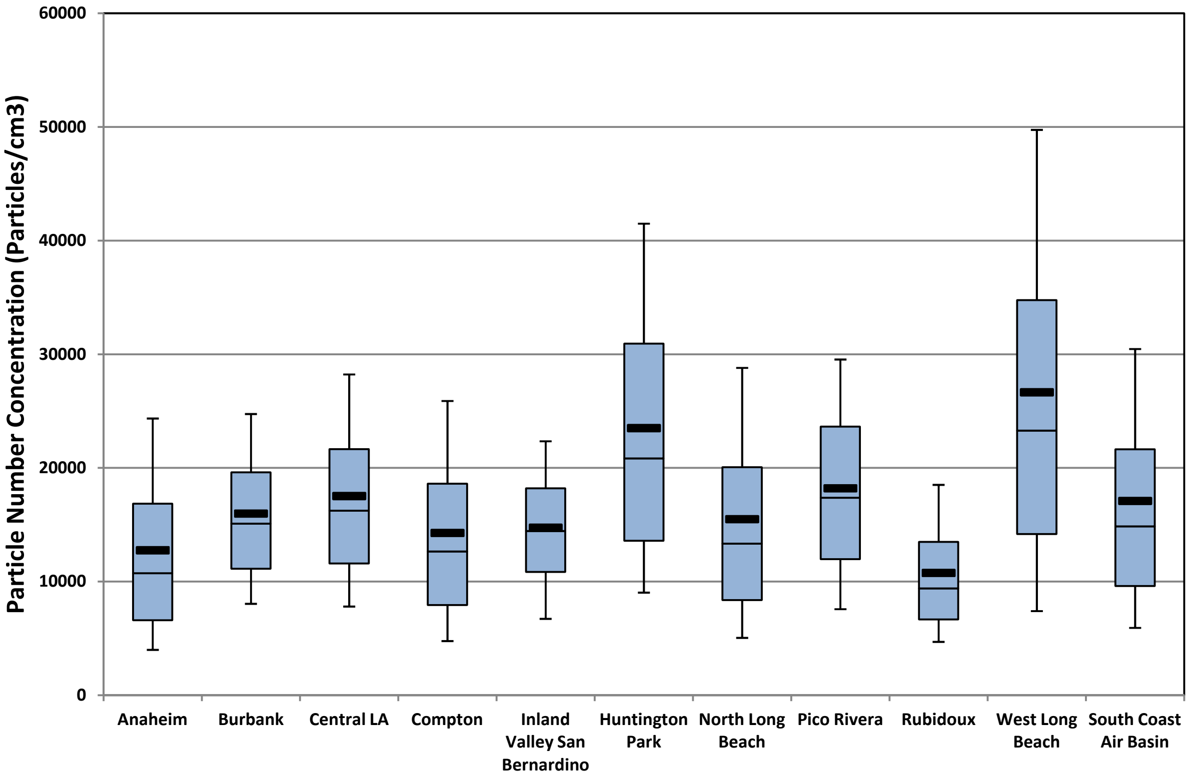

Figure VII-3: Box whisker plot showing the 90% quartile, first quartile, median, mean, third quartile and 10% quartile observed values for the MATES IV sites.

The annual mean SCAB UFP diurnal trend based on data from the 10 fixed MATES IV sites is presented in Figure VII-4. This trend is characterized by a trimodal distribution consisting of a morning peak (05:00 to 09:00), midday peak (10:00 to 16:00), and a less distinct evening peak (17:00 to 02:00). During the early morning, there is a pronounced UFP increase probably due to heavy rush hour traffic and a lower atmospheric mixing height. As the day progresses and the atmosphere is heated, the mixing height rises, leading to a dilution and subsequent decrease of traffic emissions. In the late morning and early afternoon, a second peak emerges due to the formation of secondary UFPs from photochemical processes. The UFP concentration decreases towards the late afternoon, but background levels remain elevated. A third, less pronounced peak due to the trapping of overnight emissions by the nocturnal inversion emerges towards the early evening and persists throughout the night.

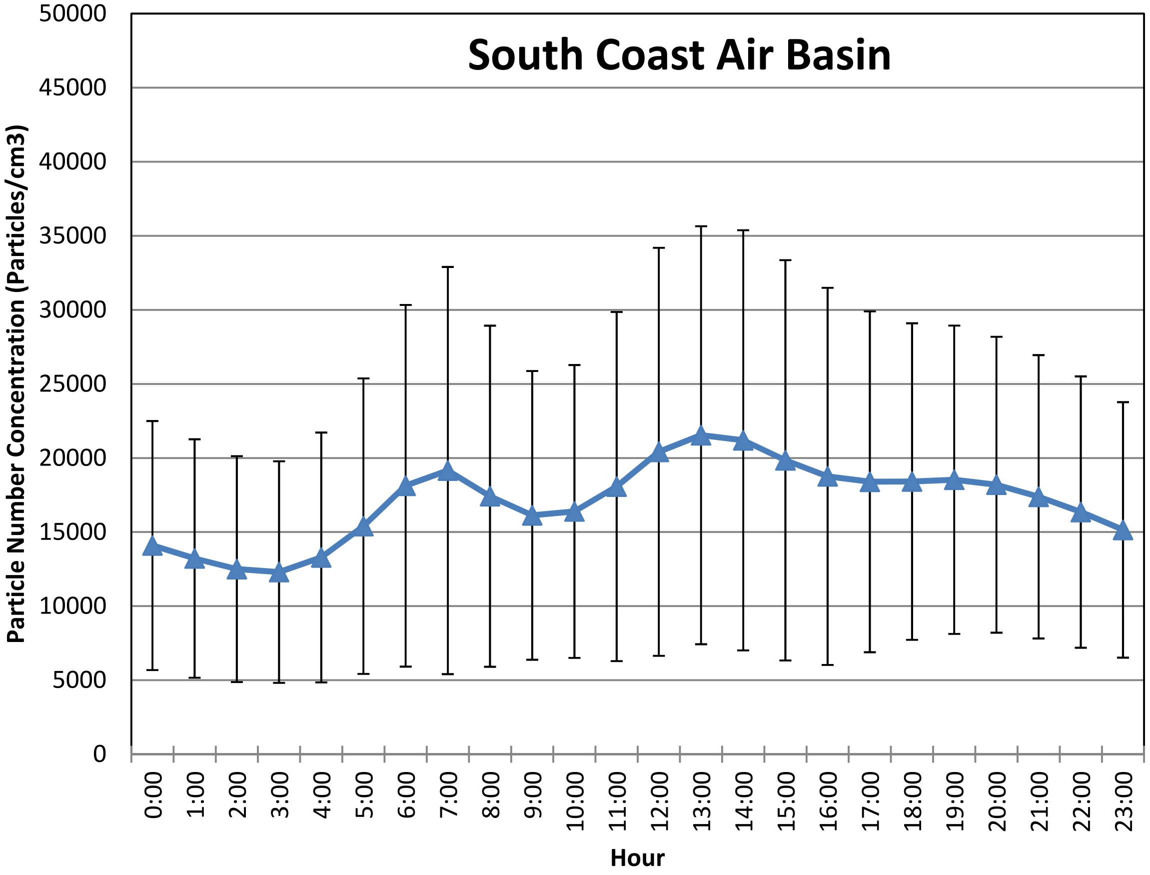

Figure VII-4: Diurnal variation of ultrafine particle concentration in the South Coast Air Basin during MATES IV.

Seasonal Trends

UFP concentrations were averaged by season to characterize seasonal variations. Seasons were divided into fall (September-November), winter (December-February), spring (March-May), and summer (June-August). Figure VII-5 displays the averaged seasonal UFP concentrations at all 10 fixed monitoring sites and for the SCAB. Huntington Park and West Long Beach showed the highest mean seasonal UFP concentrations throughout the entire duration of sampling. The maximum UFP levels observed for all seasons were in West Long Beach, except during winter, when the UFP concentration at Huntington Park was the highest. In most instances, the maximum average particle number concentrations at all sites were observed during winter months with the exception of Inland Valley San Bernardino, where the winter average was the lowest and the summer average the highest. In the wintertime, emissions from primary sources dominate the UFP concentrations due to stagnant atmospheric conditions. In addition, the coastal region experiences surface temperature inversions and weak onshore wind flow during this time of the year, leading to increased UFP levels near the coastal regions, especially near emission sources, such as freeways. During the summertime, increased UFP concentrations inland are influenced by local emission sources and long range advection of upwind sources due to a strong onshore flow and enhanced photochemical activities. Differences in particle number concentration between the winter and summer seasons are consistent with previous studies that found higher UFP levels in the winter versus the summer months (Kittleson 1998, Kim, et al. 2000, Wang, et al. 2013). In a study conducted to compare seasonal air pollution variations near the I-710 and the I-405 freeways, lower ambient temperatures produced fewer particles in the 50-200nm size range (on the lower size limit of the accumulation mode) and a larger amount of particle number concentrations in the 6-25nm (nuclei mode) size range at both sites (Zhu et al. 2004).

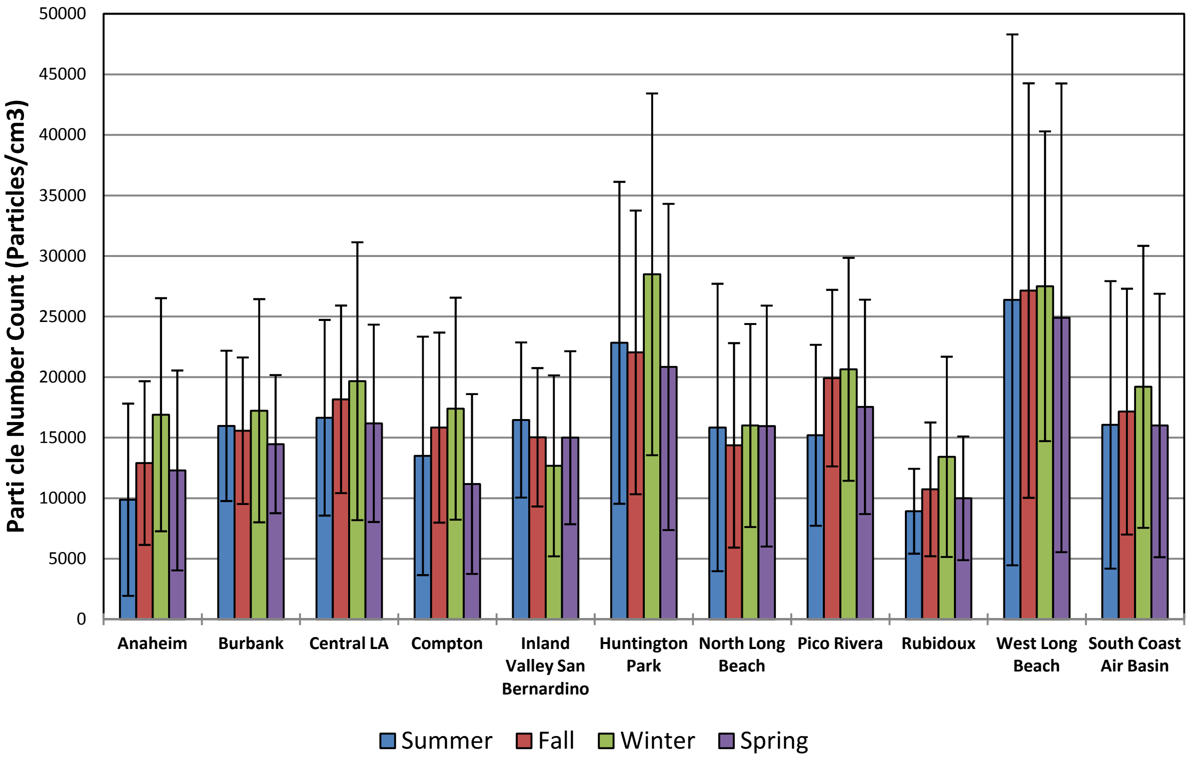

Figure VII-5: Averaged seasonal particle number concentration for the MATES IV sites.

The influence of meteorological conditions on UFP concentrations is further demonstrated in the diurnal trend differences between winter and summer profiles for the SCAB (Figure VII-6) and for each individual MATES site (Figure VII-7). The winter profile is characterized by a bimodal distribution and is distinctly different from that observed in the summer. Traffic emissions generated during the winter morning commute produces a peak during rush-hour that extends until late morning. All sites show a peak during the early morning commute hours (05:00 to 10:00) and evening commute hours (19:00 to 22:00) due to a combination of decreased atmospheric mixing height and enhanced coagulation and nucleation. As the temperature increases in the afternoon, the mixing height rises and the UFP concentrations drop, reaching a minimum in midday. When evening approaches, the nocturnal inversion layer causes an elevation in particle number count, producing a peak that persists throughout the late evening hours. Previous studies by Singh et al. 2006 and Wang, et al. 2012 have found similar winter diurnal trends. However, these patterns are less pronounced in the spring and fall. During these seasons, especially in the spring, the morning commute peak decreases to near background levels at all stations. This observation was most likely due to warmer overnight temperatures, a higher mixing height, and a subsequent dispersion of air pollutants. Comparable spring and fall diurnal profiles were also observed in previous studies conducted in the SCAB (Sioutas et al. 2011). Throughout the summer, secondary formation of UFP through photochemical reactions generates a midday peak (10:00 to 17:00). Particles smaller than 60nm in aerodynamic diameter have been shown to contribute to this increase in particle number concentration (Singh et al. 2006). This midday photochemical peak is more pronounced in the coastal region and less distinct in the inland sites (Inland Valley San Bernardino, Rubidoux). The Inland Valley San Bernardino location did not reflect the same seasonal trends as Rubidoux. In fact, a large broad peak begins in the early morning commute hours at 04:00, reaches a maximum at 14:00, and remains elevated during the evening. This was the only site where the summer evening particle number concentrations were higher than the winter evening concentrations. The photochemical peak was also in an earlier time frame compared to the other sampling locations.

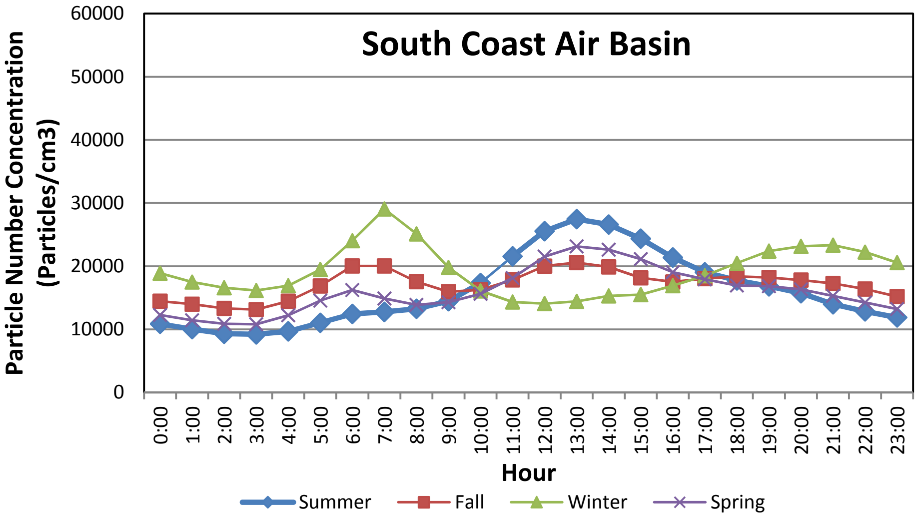

Figure VII-6: Averaged seasonal diurnal particle number concentration for SCAB.

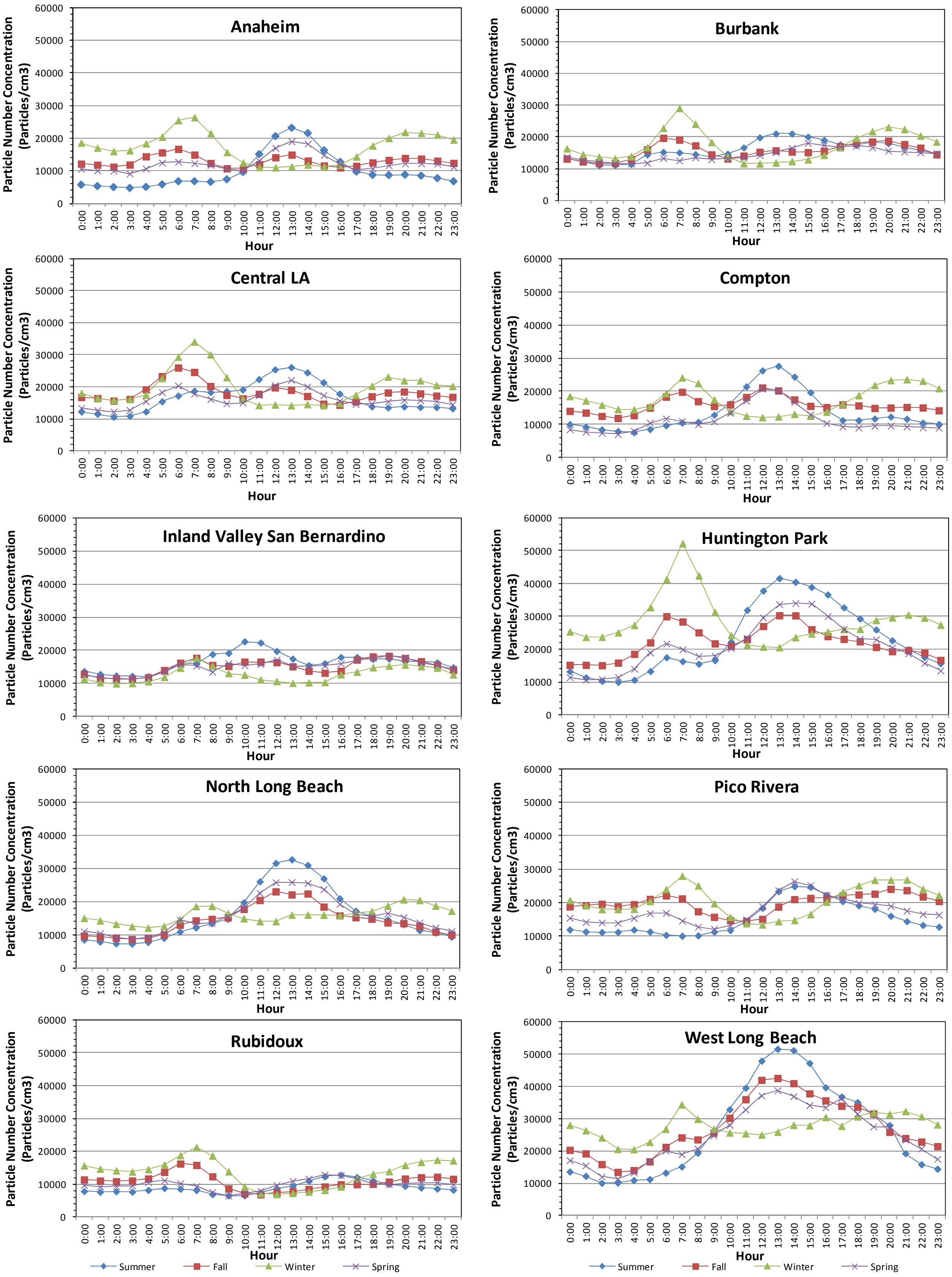

Figure VII-7: Averaged seasonal diurnal particle number concentration at each site.

Weekday/Weekend Diurnal Trends

The effect of traffic emission sources and of meteorological factors is also reflected in the day of the week diurnal UFP distribution plots. Figure VII-8 and Figure VII-9 display seasonal averages for each day of the week for the SCAB and for each individual MATES IV site, respectively. The lowest UFP averages were typically observed on Sundays during all seasons, which is consistent with previous studies (Sabaliauskas et al. 2013, Sioutas 2011, Tiwary et al. 2012). Conversely, the highest UFP levels were observed on Tuesdays and/or Fridays. UFP concentrations were generally higher on weekdays and followed a similar weekly pattern, with the exception of Monday which is associated with lower concentrations than the other weekdays. Similar differences between weekdays and weekends patterns have been observed in various studies (Morawska et al. 2002, Fine et al. 2004). West Long Beach had the highest weekday and weekend average, and the greatest difference between the weekdays and weekends (Figure VII-9). Rubidoux had the lowest weekday and weekend average, with the lowest difference between weekdays and weekends. This weekday/weekend distinction is attributed to vehicular traffic emissions generated during the weekday commute. Sioutas et al. (2011) also observed day of the week differences between sites near the ports versus near Downtown Los Angeles. There was a larger particle number reduction at sampling locations near the vicinity of the ports on weekends versus weekdays when compared to L.A. This greater reduction in UFP concentrations demonstrates that heavy-duty diesel vehicles are important contributors to ambient UFP.

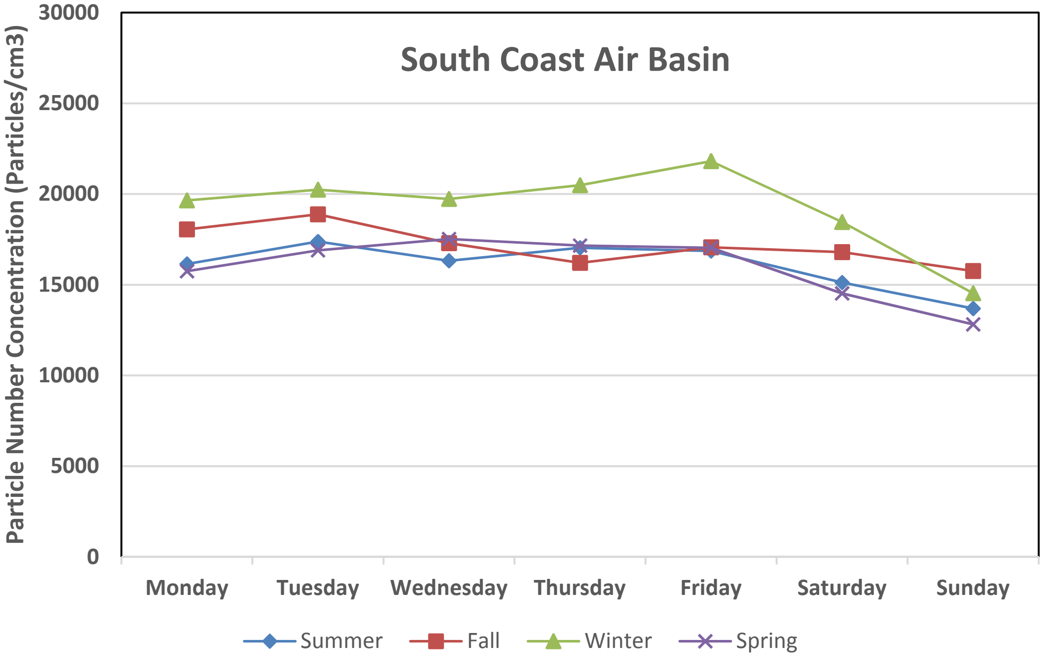

Figure VII-8: Averaged seasonal day of the week particle number concentration for the South Coast Air Basin.

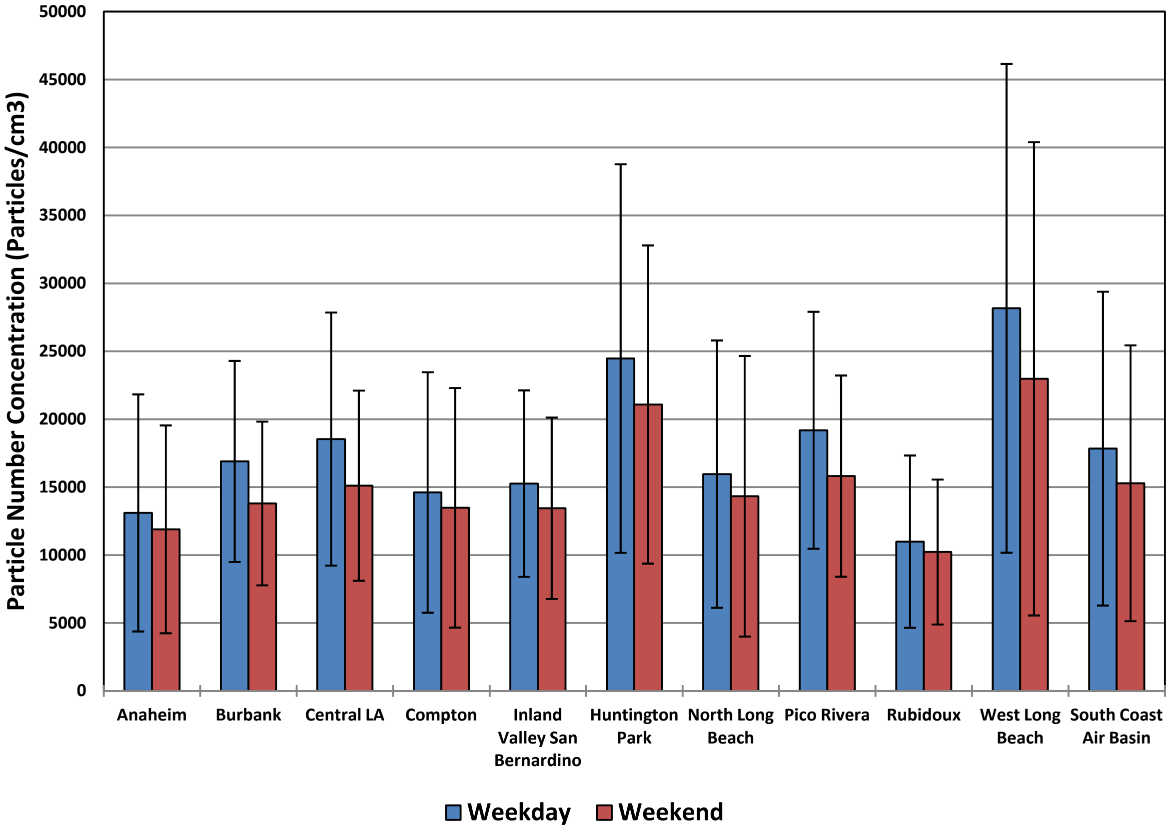

Figure VII-9: Averaged weekday and weekend particle number concentrations for each MATES IV site.

VII-5 Summary

Continuous real-time UFP measurements collected at ten SCAQMD sites during MATES IV showed high temporal and spatial variability. A variety of factors, such as the distance to the nearest emission source, the type of emission source, the traffic volume, wind speed, wind direction, relative humidity, and temperature (among other factors) could all influence the concentration, composition, and dispersion of UFPs. Atmospheric parameters could fluctuate rather rapidly throughout the day, therefore short time scales, particularly on an hourly or less basis, should be used to examine the diurnal trends of UFPs. Despite the high spatial and temporal differences measured across the SCAB, the average diurnal UFP concentrations at most MATES IV sites followed a similar trend, rising and falling throughout the day, with distinct peaks during the early morning commute, midday, and evening commute. As shown here and reported in previous studies, the ambient UFP concentration in urban environments is closely related to the temporal variation in traffic density, with highest levels observed on weekdays during rush hours (Hussein, et al., 2004; Morawska, et al., 2008; AQMD, 2012). Photochemical particle formation also contributes to increasing the afternoon number concentration of UFPs, especially in the summer.

Due to the sharp drop in UFP concentrations over short distances from the emission sources, more detailed local-scale studies are needed to develop a better understanding of the spatial UFP concentrations in the SCAB. For example, in a recent study conducted by the SCAQMD near the Santa Monica Airport (SMO; a general aviation airport), 1-min average UFP levels as high as 2,600,000 #/cm^3 were measured 35 m downwind of the runway during jet aircraft take-off (AQMD, 2011). One-minute maxima between 1,500,000 and 2,000,000 #/cm^3 (also associated with jet aircraft departures) were observed 100 m downwind of the runway in the backyard of a local residence.

Several meteorological factors contribute to the seasonal variability in the concentration of atmospheric PM and UFPs; these include:

- Lower mixing layer height and greater atmospheric stability in winter, which tend to increase particle levels by limiting vertical atmospheric mixing
- Lower winter temperature, which leads to increased nucleation of volatile combustion products, particularly during morning rush hours
- Higher photochemical activity in the summer, which favors photochemical particle formation

In the wintertime most of the factors leading to an increase in particle concentration tend to occur early in the morning (i.e. rush hour traffic, low mixing height, low wind speed and temperature). Summer minima are usually associated with increased ambient temperature (which does not favor the nucleation process), although increased photochemical activity can lead to new UFP formation, which typically occurs midday.

VII-6 References

Benbrahim-Tallaa, L., Baan, R.A., Grosse, Y., et al. (2012) “ Carcinogenicity of diesel-engine and gasoline-engine exhausts and some nitroarenes”, Lancet Oncology, 13.7: 663-664

Fine, P. M., Cass, G. R., & Simoneit, B. R. (2004). Chemical characterization of fine particle emissions from the fireplace combustion of wood types grown in the Midwestern and Western United States. Environmental Engineering Science, 21(3), 387-409.

Health Effects Institute (HEI) (2010) “Traffic-Related Air Pollution: A Critical Review of Literature on Emissions, Exposure, and Health Effects”, http://pubs.healtheffects.org/getfile.php?u=553

Hussein, T., Puustinen, A., Aalto, P., Makela, J., Hameri, K., Kulmala, M. (2004) “Urban aerosol number size distributions”, Atmospheric Chemistry and Physics Discussions 4, 391–411

Keskinen, J. and Ronkko, T. (2010) “Can Real-World Diesel Exhaust Particle size Distribution be Reproduced in the Laboratory? A Critical Review”, Journal of the Air & Waste Management Association, 60: 1245-1255

Kim, B.M., Teffera, S., Zeldin, M.D. (2000) “Characteristics of PM2.5 and PM10 in the South Coast Air Basin of Southern California: Part I – Spatial Variations” Journal of Air and Waste Management Association, 50: 2034-2044

Kittelson, DB. (1998) “Engines and nanoparticles: a review”, Journal of Aerosol Science, 29 (5/6): 575-588

Lee, E.S., Polidori, A., Koch, M., et al. (2013) “Water-based condensation particle counters comparison near a major freeway with significant heavy-duty diesel traffic”, Atmospheric Environment, 68: 151-161

Morawska, L., Jayaratne, E.R., Mengersen, K., et al. (2002) “Differences in airborne particle and gaseous concentrations in urban air between weekdays and weekends”, Atmospheric Environment, 36: 4375-4383

Morawska, L., Ristovski, Z., Jayaratne, E.R., et al (2008) “Ambient nano and ultrafine particles from motor vehicle emissions: characteristics, ambient processing and implications on human exposure”, Atmospheric Environment, 42: 8113-8138

Ntziachristos, L., Ning, Z., Geller, M.D., Sioutas, C. (2007) “Particle concentration and characteristics near a major freeway with heavy duty diesel traffic”, Environmental Science and Technology 41, 2223–2230

Sabaliauskas, K., Jeong C., Yao, X., et al. (2013) “Cluster analysis of roadside ultrafine particle size distributions”, Atmospheric Environment, 70: 64-74

Sardar, S.B., Fine, P.M., Yoon, H., et al. (2004) "Associations between particle number and gaseous co-pollutant concentrations in the Los Angeles Basin", Air and Waste Management, 54: 992-1005

Singh, M., Phuleria, H.C., Bowers, K., et al. (2006) " Seasonal and spatial trends in particle number concentrations and size distributions at the children's health study sites in Southern CA", Journal of Exposure Science and Environmental Epidemiology, 16: 3-18

Sioutas, C. (2011) "Fine-Scale Spatial and Temporal Variability of Particle Number Concentrations within Communities and in the Vicinity of Freeway Sound Walls", University of Southern California

South Coast Air Quality Management District (AQMD) (2008) "Multiple Air Toxics Exposure Study III"

South Coast Air Quality Management District (AQMD) (2011) "General Aviation Airport Air Monitoring Study: Follow-up Monitoring Campaign at the Santa Monica Airport"

Stanier, C., Khlystov, A., Pandis, S. (2004a) "Ambient aerosol size distributions and number concentrations measured during the Pittsburgh Air Quality Study (PAQS)", Atmospheric Environment 38, 3275–3284

Tiwary, A., Namdeo, A, Pareira, A. (2012) "Spatial Variation on Personal Exposure of Parking Attendants to Traffic Emissions in an Urban Conurbation", The Open Atmospheric Science Journal , 6: 78-83

Wang, J., McGraw, R.L., Kuang, C. (2013) "Growth of atmospheric nano-particles by heterogenous nucleation of organic vapor", Atmospheric Chemistry and Physics, 13: 6523-6531

Wang, Y., Hopke, P.K., Utell, M.J. (2012) "Urban-Scale Seasonal and Spatial Variability of Ultrafine Particle Number Concentrations", Water Air and Soil Pollution, 223: 2223-2235

Westerdahl, D., Fruin, S., Sax, T., Fine, P., Sioutas, C. (2005) "Mobile platform measurements of ultrafine particles and associated pollutant concentrations on freeways and residential streets in Los Angeles", Atmospheric Environment 39, 3597–3610

Zhang, Q., Stanier, C., Canagaratna, M., Jayne, J.,Worsnop, D., Pandis, S., Jimenez, J. (2004) "Insights into the chemistry of new particle formation and growth events in Pittsburgh based on aerosol mass spectrometry", Environmental Science and Technology 38, 4797–4809

Zhu, Y. ,Hinds, W.C., Shen S., et al. (2004) "Seasonal Trends of Concentration and Size Distribution of Ultrafine Particles Near Major Highways in Los Angeles", Aerosol Science and Technology, 38 (S1): 5-13

Zhu, Y., Hinds, H.C., Kim, S., et al. (2002a) "study of ultrafine particles near a major highway with heavy-duty diesel traffic", Atmospheric Environment, 36 (27): 4323-4335

Zhu, Y., Hinds, H.C., Kim, S., et al (2002b) “Concentration and size distribution of ultrafine particles near a major highway”, Journal of Air and Waste Management Association, 52: 1032-1042

APPENDIX VIII

MATES IV

DRAFT FINAL REPORT

2012 Emissions by Major Source Category

Authors

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Tom Chico

RETURN↑

Appendix VIII

2012 Emissions by Major Source Category

The 2012 toxic inventory by major source category is contained in a table in this appendix. Toxic gases are provided first, in alphabetical order, followed by the toxic particulates, also in alphabetical order. The particulates are estimated total mass from all size fractions.

Table VIII-1. 2012 Emissions (lbs/day) by Major Source Category for the South Coast Air Basin.

Code	Source Category	Acetaldehyde	Acetone	Benzene	1,3 Butadiene	Carbon tetrachloride	Chloroform	1,1 Dichloroethane	1,4 dioxane	Ethylene dibromide
	Fuel Combustion									
10	Electric Utilities	21.82	19.99	91.08	0.51	0.00	0.00	0.00	0.00	0.00
20	Cogeneration	0.18	0.00	0.67	0.00	0.00	0.00	0.00	0.00	0.00
30	Oil and Gas Production (combustion)	1.89	1.58	25.39	0.04	0.00	0.00	0.00	0.00	0.00
40	Petroleum Refining (Combustion)	1.85	0.07	12.80	0.12	0.00	0.00	0.00	0.00	0.00
50	Manufacturing and Industrial	23.28	11.95	174.17	0.40	0.00	0.00	0.00	0.00	0.00
52	Food and Agricultural Processing	0.62	0.57	8.22	0.03	0.00	0.00	0.00	0.00	0.00
60	Service and Commercial	26.13	23.24	720.80	1.11	0.00	0.00	0.00	0.00	0.00
99	Other (Fuel Combustion)	35.19	35.18	17.62	3.95	0.00	0.00	0.00	0.00	0.00
	Total	**110.96**	**92.58**	**1050.76**	**6.16**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**
	Waste Disposal									
110	Sewage Treatment	0.24	0.26	1.52	0.00	0.11	11.72	0.00	0.05	0.04
120	Landfills	0.00	114.60	244.08	0.00	0.12	0.83	65.52	0.00	0.00
130	Incineration	0.00	0.00	59.87	0.00	0.00	0.00	0.00	0.00	0.00
140	Soil Remediation	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
199	Other (Waste Disposal)	0.00	72.23	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Total	0.24	187.08	305.47	0.00	0.23	12.56	65.52	0.05	0.04
	Cleaning and Surface Coatings									
210	Laundering	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
220	Degreasing	0.00	2981.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00
230	Coatings and Related Processes	0.00	941.43	1.80	0.00	0.00	0.00	0.00	0.00	0.00
240	Printing	0.00	1.32	0.00	0.00	0.00	0.00	0.00	0.00	0.00
250	Adhesives and Sealants	0.00	999.62	1.46	0.00	0.00	0.00	0.00	0.00	0.00
299	Other (Cleaning and Surface Coatings)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Total	**0.00**	**4923.39**	**3.26**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**
	Petroleum Production and Marketing									
310	Oil and Gas Production	0.00	0.00	31.65	0.00	0.00	0.00	0.00	0.00	0.00
320	Petroleum Refining	0.00	0.00	46.54	0.00	0.00	0.00	0.00	0.00	0.00
330	Petroleum Marketing	0.03	0.00	211.16	0.00	0.03	0.03	0.00	0.00	0.03
399	Other (Petroleum Production and Marketing	0.00	0.00	0.35	0.00	0.00	0.00	0.00	0.00	0.00
	Total	**0.03**	**0.00**	**289.70**	**0.00**	**0.03**	**0.03**	**0.00**	**0.00**	**0.03**

Table VIII-1. 2012 Emissions (lbs/day) by Major Source Category for the South Coast Air Basin.

Code	**Source Category**	**Acetaldehyde**	**Acetone**	**Benzene**	**1,3 Butadiene**	**Carbon tetrachloride**	**Chloroform**	**1,1 Dichloroethane**	**1,4 dioxane**	**Ethylene dibromide**
	Industrial Processes									
410	Chemical	34.88	47.04	240.40	428.03	5.63	0.75	0.00	0.00	0.00
420	Food and Agriculture	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
430	Mineral Processes	0.04	0.06	13.70	0.02	0.01	0.00	0.00	0.00	0.00
440	Metal Processes	0.36	0.54	3.13	0.18	0.06	0.01	0.00	0.00	0.00
450	Wood and Paper	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
460	Glass and Related Products	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
470	Electronics	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
499	Other (Industrial Processes)	4.36	259.11	58.23	1.60	0.74	0.14	0.00	0.00	0.05
	Total	**39.64**	**306.75**	**315.47**	**429.83**	**6.43**	**0.90**	**0.00**	**0.00**	**0.05**
	Solvent Evaporation									
510	Consumer Products	0.00	11441.16	2.18	0.00	0.00	0.00	0.00	0.00	0.00
520	Architectural Coatings and Related Solvent	7.57	1674.86	18.29	0.00	0.00	0.00	0.00	0.00	0.00
530	Pesticides/Fertilizers	0.00	0.14	0.00	0.00	0.00	0.00	0.00	0.00	0.00
540	Asphalt Paving/Roofing	0.00	0.00	4.02	0.00	0.00	0.00	0.00	0.00	0.00
	Total	**7.57**	**13116.16**	**24.48**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**
	Miscellaneous Processes									
610	Residential Fuel Combustion	1328.39	980.24	229.10	0.00	0.00	0.00	0.00	0.00	0.00
620	Farming Operations	0.00	1342.81	0.00	0.00	0.00	0.00	0.00	0.00	0.00
630	Construction and Demolition	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
640	Paved Road Dust	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
645	Unpaved Road Dust	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
650	Fugitive Windblown Dust	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
660	Fires	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
670	Waste Burning and Disposal	0.00	0.00	0.00	106.36	0.00	0.00	0.00	0.00	0.00
690	Cooking	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
699	Other (Miscellaneous Processes	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Total	**1328.39**	**2323.05**	**229.10**	**106.36**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**

Table VIII-1. 2012 Emissions (lbs/day) by Major Source Category for the South Coast Air Basin.

Code	Source Category	Acetaldehyde	Acetone	Benzene	1,3 Butadiene	Carbon tetrachloride	Chloroform	1,1 Dichloroethane	1,4 dioxane	Ethylene dibromide
	Onroad Motor Vehicles									
710	Light Duty Passenger Auto (LDA)	282.65	169.56	1973.24	368.37	0.00	0.00	0.00	0.00	0.00
722	Light Duty Trucks 1 (T1)	70.59	41.14	529.74	93.70	0.00	0.00	0.00	0.00	0.00
723	Light Duty Trucks 2 (T2)	111.42	65.52	797.25	148.61	0.00	0.00	0.00	0.00	0.00
724	Medium Duty Trucks (T3)	124.55	73.75	810.35	166.38	0.00	0.00	0.00	0.00	0.00
732	Light Heavy Duty Gas Trucks 1 (T4)	50.82	31.11	314.79	68.66	0.00	0.00	0.00	0.00	0.00
733	Light Heavy Duty Gas Trucks 2 (T5)	5.39	3.32	33.80	7.30	0.00	0.00	0.00	0.00	0.00
734	Medium Heavy Duty Gas Trucks (T6)	12.97	8.14	74.63	17.59	0.00	0.00	0.00	0.00	0.00
736	Heavy Heavy Duty Gas Trucks ((HHD)	2.67	1.58	15.18	3.59	0.00	0.00	0.00	0.00	0.00
742	Light Heavy Duty Diesel Trucks 1 (T4)	101.57	103.70	27.64	2.62	0.00	0.00	0.00	0.00	0.00
743	Light Heavy Duty Diesel Trucks 2 (T5)	33.92	34.63	9.23	0.88	0.00	0.00	0.00	0.00	0.00
744	Medium Heavy Duty Diesel Truck (T6)	224.41	229.11	61.07	5.80	0.00	0.00	0.00	0.00	0.00
746	Heavy Heavy Duty Diesel Trucks (HHD)	821.62	838.83	223.59	21.23	0.00	0.00	0.00	0.00	0.00
750	Motorcycles (MCY)	60.92	33.40	365.88	80.25	0.00	0.00	0.00	0.00	0.00
760	Diesel Urban Buses (UB)	92.50	94.44	25.17	2.39	0.00	0.00	0.00	0.00	0.00
762	Gas Urban Buses (UB)	3.46	1.85	20.10	4.58	0.00	0.00	0.00	0.00	0.00
771	Gas School Buses (SB)	0.96	0.53	5.64	1.27	0.00	0.00	0.00	0.00	0.00
772	Diesel School Buses (SB)	20.44	20.87	5.56	0.53	0.00	0.00	0.00	0.00	0.00
777	Gas Other Buses (OB)	3.59	2.30	19.77	4.89	0.00	0.00	0.00	0.00	0.00
779	Diesel Other Buses (OB)	37.06	37.84	10.09	0.96	0.00	0.00	0.00	0.00	0.00
780	Motor Homes (MH)	5.40	4.44	13.60	2.93	0.00	0.00	0.00	0.00	0.00
	Total	**2066.93**	**1796.06**	**5336.32**	**1002.51**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**
	Other Mobile Sources									
810	Aircraft	272.81	24.42	122.44	109.86	0.00	0.00	0.00	0.00	0.00
820	Trains	305.03	311.42	83.01	7.88	0.00	0.00	0.00	0.00	0.00
833	Ocean Going Vessels	138.48	141.38	37.68	3.58	0.00	0.00	0.00	0.00	0.00
835	Commercial Habor Crafts	82.31	84.03	22.40	2.13	0.00	0.00	0.00	0.00	0.00
840	Recreational Boats	472.63	253.97	1567.46	363.59	0.00	0.00	0.00	0.00	0.00
850	Off-Road Recreational Vehicles	32.38	15.63	150.06	27.64	0.00	0.00	0.00	0.00	0.00
860	Off-Road Equipment	1640.64	1371.10	2392.51	508.26	0.00	0.00	0.00	0.00	0.00
870	Farm Equipment	138.85	140.35	47.36	5.76	0.00	0.00	0.00	0.00	0.00
890	Fuel Storage and Handling	0.00	0.00	54.20	0.00	0.00	0.00	0.00	0.00	0.00
	Total	**3083.14**	**2342.30**	**4477.12**	**1028.69**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**
Total	**Stationary**	**1486.84**	**20949.02**	**2218.24**	**542.34**	**6.69**	**13.49**	**65.52**	**0.05**	**0.11**
Total	**On-Road Vehicles**	**2066.93**	**1796.06**	**5336.32**	**1002.51**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**
Total	**Other Mobile**	**3083.14**	**2342.30**	**4477.12**	**1028.69**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**
Total	**Anthropogenic**	**6636.90**	**25087.38**	**12031.67**	**2573.54**	**6.69**	**13.49**	**65.52**	**0.05**	**0.11**

Table VIII-1. 2012 Emissions (lbs/day) by Major Source Category for the South Coast Air Basin.

Code	Source Category	Ethylene dichloride	Ethylene oxide	Formaldehyde	Methyl ethyl ketone	Methylene chloride	MTBE	Naphthalene	p-Dichlorobenzene	Perchloroethylene
	Fuel Combustion									
10	Electric Utilities	0.00	0.00	259.45	3.93	0.00	0.00	0.23	0.00	0.00
20	Cogeneration	0.00	0.00	4.91	0.00	0.00	0.00	0.00	0.00	0.00
30	Oil and Gas Production (combustion)	0.00	0.00	60.69	0.31	0.00	0.00	0.02	0.00	0.00
40	Petroleum Refining (Combustion)	0.00	0.00	284.39	0.01	0.00	0.00	0.02	0.00	0.00
50	Manufacturing and Industrial	0.00	0.00	1287.79	2.35	0.00	0.00	0.15	0.00	0.00
52	Food and Agricultural Processing	0.00	0.00	18.13	0.11	0.00	0.00	0.01	0.00	0.00
60	Service and Commercial	0.00	0.00	1548.25	4.55	0.00	0.00	0.34	0.00	0.00
99	Other (Fuel Combustion)	0.00	0.00	88.62	6.92	0.00	0.00	0.47	0.00	0.00
	Total	**0.00**	**0.00**	**3552.22**	**18.19**	**0.00**	**0.00**	**1.24**	**0.00**	**0.00**
	Waste Disposal									
110	Sewage Treatment	0.06	0.05	1.25	0.00	18.02	0.00	0.00	1.78	14.68
120	Landfills	11.44	0.00	98.41	143.90	341.88	0.00	0.00	0.00	174.16
130	Incineration	0.00	0.00	1.89	0.00	0.00	0.00	0.00	0.00	0.00
140	Soil Remediation	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
199	Other (Waste Disposal)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Total	11.50	0.05	101.55	143.90	359.90	0.00	0.00	1.78	188.84
	Cleaning and Surface Coatings									
210	Laundering	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2246.76
220	Degreasing	0.00	0.00	0.00	1112.36	5681.30	0.00	32.89	0.00	813.25
230	Coatings and Related Processes	0.00	0.00	0.00	2148.61	6.81	0.00	5.60	0.00	136.44
240	Printing	0.00	0.00	0.00	382.44	0.00	0.00	3.55	0.00	1.32
250	Adhesives and Sealants	0.00	0.00	0.00	840.54	26.75	0.00	0.00	0.00	0.00
299	Other (Cleaning and Surface Coatings)	0.00	3.38	0.00	0.00	0.00	0.00	0.00	0.00	0.18
	Total	**0.00**	**3.38**	**0.00**	**4483.95**	**5714.86**	**0.00**	**42.05**	**0.00**	**3197.96**
	Petroleum Production and Marketing									
310	Oil and Gas Production	0.00	0.00	9.93	0.00	0.00	0.00	0.00	0.00	0.00
320	Petroleum Refining	0.00	0.00	621.16	0.00	0.00	0.00	0.12	0.00	0.00
330	Petroleum Marketing	0.00	0.00	0.03	0.00	0.00	0.03	3.44	0.00	0.00
399	Other (Petroleum Production and Marketing	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Total	**0.00**	**0.00**	**631.12**	**0.00**	**0.00**	**0.03**	**3.55**	**0.00**	**0.00**

Table VIII-1. 2012 Emissions (lbs/day) by Major Source Category for the South Coast Air Basin.

Code	Source Category	Ethylene dichloride	Ethylene oxide	Formaldehyde	Methyl ethyl ketone	Methylene chloride	MTBE	Naphthalene	p-Dichlorobenzene	Perchloroethylene
	Industrial Processes									
410	Chemical	47.26	1.31	0.56	37.39	0.00	0.00	0.03	60.39	0.00
420	Food and Agriculture	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
430	Mineral Processes	0.05	0.00	14.42	0.04	0.00	0.00	13.39	0.07	0.00
440	Metal Processes	0.49	0.01	0.53	0.37	0.00	0.00	0.03	0.63	0.00
450	Wood and Paper	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
460	Glass and Related Products	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
470	Electronics	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
499	Other (Industrial Processes)	5.84	0.17	3.10	5.15	31.19	0.05	18.35	7.47	106.06
	Total	**53.65**	**1.50**	**18.62**	**42.96**	**31.19**	**0.05**	**31.79**	**68.55**	**106.06**
	Solvent Evaporation									
510	Consumer Products	0.00	0.00	1.91	1569.14	3721.28	0.00	87.35	2945.14	3152.78
520	Architectural Coatings and Related Solvent	0.00	0.00	0.00	38.24	73.28	0.00	1.81	0.00	24.75
530	Pesticides/Fertilizers	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00
540	Asphalt Paving/Roofing	0.00	0.00	0.00	0.00	0.00	0.00	69.32	0.00	0.00
	Total	**0.00**	**0.00**	**1.91**	**1607.39**	**3794.56**	**0.00**	**158.49**	**2945.14**	**3177.53**
	Miscellaneous Processes									
610	Residential Fuel Combustion	0.00	0.00	1890.54	0.00	0.00	0.00	0.00	0.00	0.00
620	Farming Operations	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
630	Construction and Demolition	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
640	Paved Road Dust	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
645	Unpaved Road Dust	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
650	Fugitive Windblown Dust	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
660	Fires	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
670	Waste Burning and Disposal	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
690	Cooking	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
699	Other (Miscellaneous Processes	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Total	**0.00**	**0.00**	**1890.54**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**

Table VIII-1. 2012 Emissions (lbs/day) by Major Source Category for the South Coast Air Basin.

Code	Source Category	Ethylene dichloride	Ethylene oxide	Formaldehyde	Methyl ethyl ketone	Methylene chloride	MTBE	Naphthalene	p-Dichlorobenzene	Perchloroethylene
	Onroad Motor Vehicles									
710	Light Duty Passenger Auto (LDA)	0.00	0.00	951.40	26.48	0.00	0.00	104.38	0.00	0.00
722	Light Duty Trucks 1 (T1)	0.00	0.00	246.10	6.22	0.00	0.00	29.85	0.00	0.00
723	Light Duty Trucks 2 (T2)	0.00	0.00	380.69	10.08	0.00	0.00	42.65	0.00	0.00
724	Medium Duty Trucks (T3)	0.00	0.00	418.27	11.50	0.00	0.00	37.72	0.00	0.00
732	Light Heavy Duty Gas Trucks 1 (T4)	0.00	0.00	158.75	5.11	0.00	0.00	14.50	0.00	0.00
733	Light Heavy Duty Gas Trucks 2 (T5)	0.00	0.00	16.70	0.55	0.00	0.00	1.60	0.00	0.00
734	Medium Heavy Duty Gas Trucks (T6)	0.00	0.00	38.17	1.39	0.00	0.00	3.09	0.00	0.00
736	Heavy Heavy Duty Gas Trucks ((HHD)	0.00	0.00	8.98	0.25	0.00	0.00	0.53	0.00	0.00
742	Light Heavy Duty Diesel Trucks 1 (T4)	0.00	0.00	203.25	20.40	0.00	0.00	1.17	0.00	0.00
743	Light Heavy Duty Diesel Trucks 2 (T5)	0.00	0.00	67.87	6.81	0.00	0.00	0.39	0.00	0.00
744	Medium Heavy Duty Diesel Truck (T6)	0.00	0.00	449.07	45.08	0.00	0.00	2.59	0.00	0.00
746	Heavy Heavy Duty Diesel Trucks (HHD)	0.00	0.00	1644.14	165.04	0.00	0.00	9.50	0.00	0.00
750	Motorcycles (MCY)	0.00	0.00	233.38	4.55	0.00	0.00	12.36	0.00	0.00
760	Diesel Urban Buses (UB)	0.00	0.00	185.10	18.58	0.00	0.00	1.07	0.00	0.00
762	Gas Urban Buses (UB)	0.00	0.00	13.88	0.24	0.00	0.00	0.59	0.00	0.00
771	Gas School Buses (SB)	0.00	0.00	3.65	0.07	0.00	0.00	0.19	0.00	0.00
772	Diesel School Buses (SB)	0.00	0.00	40.90	4.11	0.00	0.00	0.24	0.00	0.00
777	Gas Other Buses (OB)	0.00	0.00	9.98	0.40	0.00	0.00	0.78	0.00	0.00
779	Diesel Other Buses (OB)	0.00	0.00	74.16	7.44	0.00	0.00	0.43	0.00	0.00
780	Motor Homes (MH)	0.00	0.00	15.36	0.79	0.00	0.00	0.40	0.00	0.00
	Total	**0.00**	**0.00**	**5159.81**	**335.11**	**0.00**	**0.00**	**264.03**	**0.00**	**0.00**
	Other Mobile Sources									
810	Aircraft	0.00	0.00	783.16	0.30	0.00	1.11	34.76	0.00	0.00
820	Trains	0.00	0.00	610.39	61.27	0.00	0.00	3.53	0.00	0.00
833	Ocean Going Vessels	0.00	0.00	277.11	27.82	0.00	0.00	1.60	0.00	0.00
835	Commercial Habor Crafts	0.00	0.00	164.71	16.53	0.00	0.00	0.95	0.00	0.00
840	Recreational Boats	0.00	0.00	1403.36	36.19	0.00	0.00	58.41	0.00	0.00
850	Off-Road Recreational Vehicles	0.00	0.00	99.71	2.02	0.00	0.00	4.41	0.00	0.00
860	Off-Road Equipment	0.00	0.00	3910.93	251.50	0.00	0.00	89.16	0.00	0.00
870	Farm Equipment	0.00	0.00	280.68	27.53	0.00	0.00	1.93	0.00	0.00
890	Fuel Storage and Handling	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Total	**0.00**	**0.00**	**7530.04**	**423.16**	**0.00**	**1.11**	**194.75**	**0.00**	**0.00**
Total	**Stationary**	**65.15**	**4.92**	**6195.97**	**6296.38**	**9900.51**	**0.08**	**237.11**	**3015.48**	**6670.38**
Total	**On-Road Vehicles**	**0.00**	**0.00**	**5159.81**	**335.11**	**0.00**	**0.00**	**264.03**	**0.00**	**0.00**
Total	**Other Mobile**	**0.00**	**0.00**	**7530.04**	**423.16**	**0.00**	**1.11**	**194.75**	**0.00**	**0.00**
Total	**Anthropogenic**	**65.15**	**4.92**	**18885.82**	**7054.65**	**9900.51**	**1.18**	**695.89**	**3015.48**	**6670.38**

Table VIII-1. 2012 Emissions (lbs/day) by Major Source Category for the South Coast Air Basin.

Code	**Source Category**	**Propylene oxide**	**Styrene**	**Toluene**	**Trichloro-ethylene**	**Vinyl chloride**	**Arsenic**	**Cadmium**	**Chromium**	**Diesel PM (DPM)**
	Fuel Combustion									
10	Electric Utilities	0.00	0.15	49.82	0.00	0.00	0.04	0.00	0.51	8.32
20	Cogeneration	0.00	0.00	3.91	0.00	0.00	0.00	0.00	0.04	0.00
30	Oil and Gas Production (combustion)	0.00	0.01	12.64	0.00	0.00	0.13	0.01	0.21	25.02
40	Petroleum Refining (Combustion)	0.00	0.02	6.31	0.00	0.00	0.00	1.13	12.78	0.00
50	Manufacturing and Industrial	0.00	0.11	104.94	0.00	0.00	0.62	0.17	2.10	115.78
52	Food and Agricultural Processing	0.00	0.01	4.20	0.00	0.00	0.01	0.02	0.19	3.13
60	Service and Commercial	0.00	0.26	356.85	0.00	0.00	1.23	0.15	1.94	231.19
99	Other (Fuel Combustion)	0.00	0.27	14.07	0.00	0.00	0.18	0.04	0.48	108.98
	Total	**0.00**	**0.83**	**552.75**	**0.00**	**0.00**	**2.22**	**1.53**	**18.25**	**492.42**
	Waste Disposal									
110	Sewage Treatment	0.01	0.07	8.37	1.80	0.08	0.00	0.00	0.00	0.00
120	Landfills	0.00	0.00	4279.85	104.35	129.13	0.00	0.00	0.00	0.00
130	Incineration	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.00
140	Soil Remediation	0.00	0.00	1.05	0.00	0.00	0.00	0.00	0.00	0.00
199	Other (Waste Disposal)	0.00	0.00	395.52	0.00	0.00	0.02	0.02	0.25	0.00
	Total	0.01	0.07	4684.79	106.16	129.21	0.03	0.03	0.27	0.00
	Cleaning and Surface Coatings									
210	Laundering	0.00	0.00	0.00	0.13	0.00	0.00	0.00	0.00	0.00
220	Degreasing	0.00	2.61	737.85	675.38	0.00	0.00	0.00	0.00	0.00
230	Coatings and Related Processes	0.00	0.42	11065.26	81.41	0.00	0.00	0.00	0.00	0.00
240	Printing	0.00	0.00	5.60	0.00	0.00	0.00	0.00	0.00	0.00
250	Adhesives and Sealants	0.00	0.00	257.45	0.00	0.00	0.00	0.00	0.00	0.00
299	Other (Cleaning and Surface Coatings)	0.00	0.00	79.11	0.00	0.00	0.00	0.00	0.00	0.00
	Total	**0.00**	**3.03**	**12145.29**	**756.92**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**
	Petroleum Production and Marketing									
310	Oil and Gas Production	0.00	0.00	17.46	0.00	0.00	0.00	0.00	0.00	0.00
320	Petroleum Refining	0.00	0.00	97.99	0.00	0.00	2.32	0.00	0.00	0.00
330	Petroleum Marketing	0.03	0.00	2926.10	0.00	0.00	0.00	0.00	0.00	0.00
399	Other (Petroleum Production and Marketing	0.00	0.00	0.70	0.00	0.00	0.00	0.00	0.00	0.00
	Total	**0.03**	**0.00**	**3042.25**	**0.00**	**0.00**	**2.32**	**0.00**	**0.00**	**0.00**

Table VIII-1. 2012 Emissions (lbs/day) by Major Source Category for the South Coast Air Basin.

Code	Source Category	Propylene oxide	Styrene	Toluene	Trichloro-ethylene	Vinyl chloride	Arsenic	Cadmium	Chromium	Diesel PM (DPM)
	Industrial Processes									
410	Chemical	0.38	1210.62	733.53	0.00	33.26	0.00	0.42	0.08	0.00
420	Food and Agriculture	0.00	0.00	12.11	0.00	0.00	0.00	0.00	0.07	0.00
430	Mineral Processes	0.00	0.11	4.78	0.00	0.03	10.38	2.78	8.78	0.00
440	Metal Processes	0.00	1.15	14.79	0.00	0.31	0.21	0.42	7.30	0.00
450	Wood and Paper	0.00	0.00	0.14	0.00	0.00	0.00	0.01	0.02	0.00
460	Glass and Related Products	0.00	0.00	1.44	0.00	0.00	3.20	0.00	0.88	0.00
470	Electronics	0.00	0.00	0.07	0.00	0.00	0.00	0.01	0.01	0.00
499	Other (Industrial Processes)	0.09	11.19	422.78	12.34	3.73	0.78	0.22	0.09	0.00
	Total	**0.46**	**1223.07**	**1189.63**	**12.34**	**37.33**	**14.57**	**3.84**	**17.24**	**0.00**
	Solvent Evaporation									
510	Consumer Products	0.22	6.71	6690.65	746.06	0.00	0.00	0.00	0.00	0.00
520	Architectural Coatings and Related Solvent	0.00	1.08	144.69	0.00	0.00	0.00	0.00	0.00	0.00
530	Pesticides/Fertilizers	0.00	0.00	0.17	0.00	0.00	0.00	0.00	0.00	0.00
540	Asphalt Paving/Roofing	0.00	0.00	9.55	0.00	0.00	0.00	0.00	0.00	0.00
	Total	**0.22**	**7.79**	**6845.05**	**746.06**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**
	Miscellaneous Processes									
610	Residential Fuel Combustion	0.00	0.00	533.69	0.00	0.00	0.13	0.05	1.66	0.00
620	Farming Operations	0.00	0.00	0.00	0.00	0.00	0.04	0.05	0.54	0.00
630	Construction and Demolition	0.00	0.00	0.00	0.00	0.00	1.18	1.46	15.56	0.00
640	Paved Road Dust	0.00	0.00	0.00	0.00	0.00	2.67	0.62	3.49	0.00
645	Unpaved Road Dust	0.00	0.00	0.00	0.00	0.00	0.30	0.26	0.34	0.00
650	Fugitive Windblown Dust	0.00	0.00	0.00	0.00	0.00	0.12	0.16	1.63	0.00
660	Fires	0.00	0.00	55.11	0.00	0.00	0.00	0.02	0.01	0.00
670	Waste Burning and Disposal	0.00	0.00	1.08	0.00	0.00	0.24	0.02	0.01	0.00
690	Cooking	0.00	0.00	404.01	0.00	0.00	0.04	0.04	0.29	0.00
699	Other (Miscellaneous Processes	0.00	0.00	0.08	0.00	0.00	0.00	0.00	0.00	0.00
	Total	**0.00**	**0.00**	**993.96**	**0.00**	**0.00**	**4.70**	**2.67**	**23.51**	**0.00**

Table VIII-1. 2012 Emissions (lbs/day) by Major Source Category for the South Coast Air Basin.

Code	Source Category	Propylene oxide	Styrene	Toluene	Trichloro-ethylene	Vinyl chloride	Arsenic	Cadmium	Chromium	Diesel PM (DPM)
	Onroad Motor Vehicles									
710	Light Duty Passenger Auto (LDA)	0.00	99.67	6339.51	0.00	0.00	0.18	0.06	20.30	79.64
722	Light Duty Trucks 1 (T1)	0.00	24.56	1728.45	0.00	0.00	0.02	0.01	2.48	4.03
723	Light Duty Trucks 2 (T2)	0.00	39.97	2559.18	0.00	0.00	0.06	0.02	7.06	4.08
724	Medium Duty Trucks (T3)	0.00	45.59	2477.88	0.00	0.00	0.05	0.02	5.62	6.10
732	Light Heavy Duty Gas Trucks 1 (T4)	0.00	20.33	976.78	0.00	0.00	0.01	0.00	1.20	0.00
733	Light Heavy Duty Gas Trucks 2 (T5)	0.00	2.18	106.20	0.00	0.00	0.00	0.00	0.13	0.00
734	Medium Heavy Duty Gas Trucks (T6)	0.00	5.49	229.41	0.00	0.00	0.00	0.00	0.10	0.00
736	Heavy Heavy Duty Gas Trucks ((HHD)	0.00	0.99	41.87	0.00	0.00	0.00	0.00	0.02	0.00
742	Light Heavy Duty Diesel Trucks 1 (T4)	0.00	0.80	20.35	0.00	0.00	0.01	0.02	0.75	300.77
743	Light Heavy Duty Diesel Trucks 2 (T5)	0.00	0.27	6.79	0.00	0.00	0.00	0.01	0.30	108.12
744	Medium Heavy Duty Diesel Truck (T6)	0.00	1.77	44.96	0.00	0.00	0.02	0.03	1.59	2174.00
746	Heavy Heavy Duty Diesel Trucks (HHD)	0.00	6.48	164.59	0.00	0.00	0.05	0.09	1.89	7120.00
750	Motorcycles (MCY)	0.00	18.41	943.84	0.00	0.00	0.00	0.00	0.16	0.00
760	Diesel Urban Buses (UB)	0.00	0.73	18.53	0.00	0.00	0.02	0.03	1.73	470.00
762	Gas Urban Buses (UB)	0.00	0.99	47.64	0.00	0.00	0.00	0.00	0.02	0.00
771	Gas School Buses (SB)	0.00	0.30	14.37	0.00	0.00	0.00	0.00	0.00	0.00
772	Diesel School Buses (SB)	0.00	0.16	4.09	0.00	0.00	0.00	0.00	0.35	142.00
777	Gas Other Buses (OB)	0.00	1.59	61.25	0.00	0.00	0.00	0.00	0.03	0.00
779	Diesel Other Buses (OB)	0.00	0.29	7.42	0.00	0.00	0.00	0.01	0.15	338.00
780	Motor Homes (MH)	0.00	0.61	30.44	0.00	0.00	0.00	0.00	0.10	52.00
	Total	**0.00**	**271.17**	**15823.57**	**0.00**	**0.00**	**0.43**	**0.30**	**44.01**	**10798.74**
	Other Mobile Sources									
810	Aircraft	0.00	20.75	72.06	0.00	0.00	0.00	0.00	0.53	0.00
820	Trains	0.00	2.41	61.11	0.00	0.00	0.00	0.08	0.01	1226.42
833	Ocean Going Vessels	0.00	1.09	27.74	0.00	0.00	0.00	0.00	0.00	1043.46
835	Commercial Habor Crafts	0.00	0.65	16.49	0.00	0.00	0.00	0.02	0.01	519.39
840	Recreational Boats	0.00	58.23	3425.27	0.00	0.00	0.00	0.00	1.57	31.09
850	Off-Road Recreational Vehicles	0.00	4.41	409.43	0.00	0.00	0.00	0.00	0.02	0.00
860	Off-Road Equipment	0.00	85.20	4913.11	0.00	0.00	0.01	0.17	1.55	5739.73
870	Farm Equipment	0.00	1.43	51.63	0.00	0.00	0.00	0.02	0.02	620.77
890	Fuel Storage and Handling	0.00	0.00	256.23	0.00	0.00	0.00	0.00	0.00	0.00
	Total	**0.00**	**174.18**	**9233.07**	**0.00**	**0.00**	**0.01**	**0.28**	**3.71**	**9180.86**
Total	**Stationary**	**0.73**	**1234.79**	**29453.72**	**1621.47**	**166.54**	**23.85**	**8.07**	**59.26**	**492.42**
Total	**On-Road Vehicles**	**0.00**	**271.17**	**15823.57**	**0.00**	**0.00**	**0.43**	**0.30**	**44.01**	**10798.74**
Total	**Other Mobile**	**0.00**	**174.18**	**9233.07**	**0.00**	**0.00**	**0.01**	**0.28**	**3.71**	**9180.86**
Total	**Anthropogenic**	**0.73**	**1680.14**	**54510.36**	**1621.47**	**166.54**	**24.29**	**8.65**	**106.98**	**20472.02**

Table VIII-1. 2012 Emissions (lbs/day) by Major Source Category for the South Coast Air Basin.

Code	Source Category	DPM2.5	Elemental carbon (EC)	EC2.5	Hexavalent chromium	Lead	Nickel	Organic carbon	Selenium	Silicon
	Fuel Combustion									
10	Electric Utilities	8.04	670.83	668.97	0.03	0.05	0.47	4.05	0.00	0.05
20	Cogeneration	0.00	15.18	15.06	0.00	0.00	0.04	0.00	0.00	0.00
30	Oil and Gas Production (combustion)	24.19	51.17	50.84	0.01	0.14	0.09	0.00	0.03	0.00
40	Petroleum Refining (Combustion)	0.00	453.57	441.44	0.02	1.13	12.78	0.00	12.46	0.00
50	Manufacturing and Industrial	111.98	947.71	945.20	0.04	0.75	1.54	0.00	1.29	0.00
52	Food and Agricultural Processing	2.86	42.01	41.83	0.00	0.02	0.18	0.00	0.18	0.01
60	Service and Commercial	223.50	1049.04	1046.51	0.08	1.31	0.82	0.00	0.50	0.00
99	Other (Fuel Combustion)	73.02	84.23	60.78	0.02	0.19	2.46	18.06	0.04	0.18
	Total	**443.60**	**3313.74**	**3270.63**	**0.20**	**3.60**	**18.38**	**22.11**	**14.50**	**0.24**
	Waste Disposal									
110	Sewage Treatment	0.00	7.73	7.73	0.00	0.05	0.00	0.00	0.00	0.00
120	Landfills	0.00	130.10	130.10	0.00	0.00	0.00	0.00	0.00	0.00
130	Incineration	0.00	32.81	32.80	0.00	0.01	13.46	0.00	0.00	13.46
140	Soil Remediation	0.00	3.29	3.04	0.00	0.00	0.00	0.00	0.00	0.00
199	Other (Waste Disposal)	0.00	5.20	0.34	0.00	0.63	0.07	49.38	0.00	213.67
	Total	0.00	179.12	174.01	0.00	0.69	13.53	49.38	0.00	227.13
	Cleaning and Surface Coatings									
210	Laundering	0.00	0.43	0.29	0.00	0.00	0.00	1.21	0.00	0.00
220	Degreasing	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
230	Coatings and Related Processes	0.00	1744.98	1614.22	0.00	0.00	0.00	0.00	0.00	0.00
240	Printing	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
250	Adhesives and Sealants	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
299	Other (Cleaning and Surface Coatings)	0.00	11.65	10.78	0.00	0.00	0.00	0.00	0.00	0.00
	Total	**0.00**	**1757.06**	**1625.29**	**0.00**	**0.00**	**0.00**	**1.21**	**0.00**	**0.00**
	Petroleum Production and Marketing									
310	Oil and Gas Production	0.00	7.10	7.10	0.00	0.00	0.00	0.00	0.00	0.00
320	Petroleum Refining	0.00	235.08	240.79	0.00	2.32	2.32	0.00	0.00	456.10
330	Petroleum Marketing	0.00	0.23	0.21	0.00	0.00	0.00	0.00	0.00	0.00
399	Other (Petroleum Production and Marketing	0.00	0.52	0.48	0.00	0.00	0.00	0.00	0.00	0.00
	Total	**0.00**	**242.93**	**248.58**	**0.00**	**2.32**	**2.32**	**0.00**	**0.00**	**456.10**

Table VIII-1. 2012 Emissions (lbs/day) by Major Source Category for the South Coast Air Basin.

Code	Source Category	DPM2.5	Elemental carbon (EC)	EC2.5	Hexavalent chromium	Lead	Nickel	Organic carbon	Selenium	Silicon
	Industrial Processes									
410	Chemical	0.00	11.66	8.60	0.01	0.09	0.47	25.16	0.00	24.81
420	Food and Agriculture	0.00	108.84	1.08	0.00	0.00	0.04	0.00	0.00	72.65
430	Mineral Processes	0.00	317.04	169.52	0.10	12.01	12.28	20.52	3.39	5425.22
440	Metal Processes	0.00	77.69	47.05	0.07	10.14	2.06	15.79	0.01	0.56
450	Wood and Paper	0.00	16.37	5.37	0.00	0.02	0.03	41.48	0.00	0.30
460	Glass and Related Products	0.00	18.24	18.48	0.04	0.88	0.08	0.00	6.08	0.00
470	Electronics	0.00	0.30	0.10	0.00	0.09	0.01	1.22	0.00	0.79
499	Other (Industrial Processes)	0.00	77.82	57.87	0.00	1.19	0.09	38.44	0.01	28.24
	Total	**0.00**	**627.96**	**308.07**	**0.23**	**24.42**	**15.04**	**142.62**	**9.48**	**5552.57**
	Solvent Evaporation									
510	Consumer Products	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
520	Architectural Coatings and Related Solvent	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
530	Pesticides/Fertilizers	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
540	Asphalt Paving/Roofing	0.00	21.10	19.51	0.00	0.00	0.00	0.00	0.00	0.00
	Total	**0.00**	**21.10**	**19.51**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**
	Miscellaneous Processes									
610	Residential Fuel Combustion	0.00	2755.99	2022.78	0.00	0.22	2.83	8712.53	1.93	8.97
620	Farming Operations	0.00	23.88	6.13	0.00	0.15	0.13	511.02	0.01	442.49
630	Construction and Demolition	0.00	321.13	21.02	0.00	38.68	4.10	3052.59	0.14	13209.84
640	Paved Road Dust	0.00	1582.39	109.19	0.00	25.42	2.46	12248.67	0.41	62260.91
645	Unpaved Road Dust	0.00	22.96	1.35	0.00	2.56	0.73	664.29	0.06	6406.25
650	Fugitive Windblown Dust	0.00	24.27	1.40	0.00	2.49	0.40	207.54	0.01	1417.80
660	Fires	0.00	219.29	193.06	0.00	0.05	0.00	215.66	0.00	37.27
670	Waste Burning and Disposal	0.00	2222.73	1847.17	0.00	0.46	0.00	5821.75	0.03	14.32
690	Cooking	0.00	1079.86	1079.86	0.00	2.90	0.67	13750.72	0.00	53.43
699	Other (Miscellaneous Processes	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Total	**0.00**	**8252.50**	**5281.97**	**0.00**	**72.94**	**11.33**	**45184.79**	**2.60**	**83851.27**

Table VIII-1. 2012 Emissions (lbs/day) by Major Source Category for the South Coast Air Basin.

Code	Source Category	DPM2.5	Elemental carbon (EC)	EC2.5	Hexavalent chromium	Lead	Nickel	Organic carbon	Selenium	Silicon
	Onroad Motor Vehicles									
710	Light Duty Passenger Auto (LDA)	73.27	1573.00	710.97	1.01	2.31	11.48	4137.66	0.40	1154.01
722	Light Duty Trucks 1 (T1)	3.71	236.08	129.29	0.12	0.41	1.43	585.39	0.05	141.83
723	Light Duty Trucks 2 (T2)	3.76	540.74	241.64	0.35	0.81	3.99	1422.99	0.14	401.12
724	Medium Duty Trucks (T3)	5.61	432.40	193.95	0.28	0.64	3.18	1136.59	0.11	319.22
732	Light Heavy Duty Gas Trucks 1 (T4)	0.00	88.20	37.11	0.06	0.12	0.68	234.40	0.02	68.25
733	Light Heavy Duty Gas Trucks 2 (T5)	0.00	8.89	3.54	0.01	0.01	0.07	23.87	0.00	7.12
734	Medium Heavy Duty Gas Trucks (T6)	0.00	8.52	3.67	0.01	0.01	0.06	21.62	0.00	5.81
736	Heavy Heavy Duty Gas Trucks ((HHD)	0.00	0.87	0.29	0.00	0.00	0.01	2.69	0.00	1.11
742	Light Heavy Duty Diesel Trucks 1 (T4)	276.71	114.70	85.25	0.04	0.06	0.42	318.53	0.02	43.24
743	Light Heavy Duty Diesel Trucks 2 (T5)	99.47	41.78	30.90	0.02	0.02	0.17	116.96	0.01	17.26
744	Medium Heavy Duty Diesel Truck (T6)	2000.08	1256.45	1125.29	0.08	0.08	0.82	722.83	0.03	83.08
746	Heavy Heavy Duty Diesel Trucks (HHD)	6550.40	4077.28	3648.16	0.09	0.17	0.88	2206.05	0.04	84.16
750	Motorcycles (MCY)	0.00	11.09	3.97	0.01	0.01	0.09	30.32	0.00	9.30
760	Diesel Urban Buses (UB)	432.40	161.10	130.76	0.09	0.09	0.96	482.77	0.03	99.19
762	Gas Urban Buses (UB)	0.00	1.33	0.71	0.00	0.00	0.01	3.61	0.00	1.17
771	Gas School Buses (SB)	0.00	0.05	0.02	0.00	0.00	0.00	0.22	0.00	0.14
772	Diesel School Buses (SB)	135.04	92.60	83.71	0.02	0.02	0.19	68.25	0.01	20.03
777	Gas Other Buses (OB)	0.00	1.57	0.51	0.00	0.00	0.02	4.72	0.00	1.81
779	Diesel Other Buses (OB)	321.44	207.59	194.21	0.01	0.01	0.08	103.31	0.01	9.14
780	Motor Homes (MH)	47.84	19.15	14.78	0.01	0.01	0.06	52.42	0.00	6.04
	Total	**9949.72**	**8873.40**	**6638.74**	**2.18**	**4.80**	**24.61**	**11675.20**	**0.87**	**2473.02**
	Other Mobile Sources									
810	Aircraft	0.00	312.32	163.70	0.29	0.71	1.08	800.43	0.00	13.69
820	Trains	1128.20	315.35	298.25	0.00	0.04	0.02	842.68	0.01	3.52
833	Ocean Going Vessels	990.23	63.65	60.40	0.00	0.00	0.00	571.81	0.00	0.00
835	Commercial Habor Crafts	480.19	332.47	307.38	0.00	0.00	0.00	118.99	0.00	1.17
840	Recreational Boats	28.56	574.89	527.19	0.08	4.19	4.18	2155.07	0.00	56.87
850	Off-Road Recreational Vehicles	0.00	8.73	5.93	0.00	0.07	0.07	33.80	0.00	0.89
860	Off-Road Equipment	5275.28	4203.95	3865.38	0.09	3.71	3.81	3190.02	0.05	62.55
870	Farm Equipment	570.72	400.09	367.79	0.00	0.03	0.03	152.77	0.00	1.68
890	Fuel Storage and Handling	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Total	**8473.19**	**6211.46**	**5596.02**	**0.47**	**8.74**	**9.18**	**7865.58**	**0.06**	**140.38**
Total	**Stationary**	**443.60**	**14394.40**	**10928.05**	**0.43**	**103.98**	**60.61**	**45400.11**	**26.59**	**90087.31**
Total	**On-Road Vehicles**	**9949.72**	**8873.40**	**6638.74**	**2.18**	**4.80**	**24.61**	**11675.20**	**0.87**	**2473.02**
Total	**Other Mobile**	**8473.19**	**6211.46**	**5596.02**	**0.47**	**8.74**	**9.18**	**7865.58**	**0.06**	**140.38**
Total	**Anthropogenic**	**18866.52**	**29479.26**	**23162.82**	**3.09**	**117.52**	**94.39**	**64940.89**	**27.52**	**92700.72**

Table VIII-2. 2012 Criteria Emissions (tons/day) by Major Source Category for the South Coast Air Basin.

Code	Source Category	TOG	VOC	CO	NOx	SOx	TSP	PM10	PM2.5
	Fuel Combustion								
10	Electric Utilities	4.90	0.90	8.77	0.20	0.28	0.96	0.95	0.95
20	Cogeneration	0.33	0.04	0.31	0.01	0.01	0.05	0.04	0.04
30	Oil and Gas Production (combustion)	0.88	0.10	0.54	0.61	0.01	0.10	0.10	0.10
40	Petroleum Refining (Combustion)	4.42	1.28	5.06	0.00	0.00	1.62	1.56	1.54
50	Manufacturing and Industrial	25.60	5.59	17.11	13.53	0.45	1.24	1.23	1.22
52	Food and Agricultural Processing	0.18	0.05	0.99	0.12	0.00	0.06	0.06	0.06
60	Service and Commercial	14.23	4.41	16.40	10.14	0.87	1.36	1.35	1.35
99	Other (Fuel Combustion)	1.54	0.34	3.02	3.78	0.22	0.36	0.28	0.20
	Total	**52.08**	**12.71**	**52.20**	**28.39**	**1.85**	**5.73**	**5.58**	**5.46**
	Waste Disposal								
110	Sewage Treatment	0.09	0.05	0.01	0.01	0.00	0.01	0.01	0.01
120	Landfills	595.86	8.44	0.48	0.49	0.30	0.13	0.13	0.13
130	Incineration	0.39	0.07	0.36	0.90	0.07	0.17	0.07	0.06
140	Soil Remediation	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
199	Other (Waste Disposal)	4.23	3.50	0.01	0.00	0.03	0.56	0.27	0.03
	Total	**600.58**	**12.06**	**0.87**	**1.40**	**0.41**	**0.87**	**0.49**	**0.23**
	Cleaning and Surface Coatings								
210	Laundering	1.25	0.13	0.00	0.00	0.00	0.00	0.00	0.00
220	Degreasing	50.36	9.73	0.00	0.00	0.00	0.00	0.00	0.00
230	Coatings and Related Processes	20.68	19.78	0.01	0.01	0.00	1.59	1.52	1.47
240	Printing	1.73	1.73	0.00	0.00	0.00	0.00	0.00	0.00
250	Adhesives and Sealants	4.02	3.50	0.00	0.00	0.00	0.00	0.00	0.00
299	Other (Cleaning and Surface Coatings)	0.52	0.52	0.04	0.04	0.00	0.01	0.01	0.01
	Total	**78.57**	**35.39**	**0.04**	**0.04**	**0.00**	**1.60**	**1.54**	**1.48**
	Petroleum Production and Marketing								
310	Oil and Gas Production	2.38	1.35	0.06	0.08	0.00	0.01	0.01	0.01
320	Petroleum Refining	6.14	4.11	4.98	0.19	0.56	2.84	1.82	1.58
330	Petroleum Marketing	117.92	34.67	0.00	0.01	0.01	0.00	0.00	0.00
399	Other (Petroleum Production and Marke	0.02	0.02	0.00	0.00	0.00	0.00	0.00	0.00
	Total	**126.46**	**40.13**	**5.05**	**0.28**	**0.57**	**2.85**	**1.83**	**1.59**

Table VIII-2. 2012 Criteria Emissions (tons/day) by Major Source Category for the South Coast Air Basin.

Code	Source Category	TOG	VOC	CO	NOx	SOx	TSP	PM10	PM2.5
	Industrial Processes								
410	Chemical	7.67	6.24	0.16	0.00	0.00	0.65	0.50	0.42
420	Food and Agriculture	1.44	1.42	0.00	0.00	0.00	0.44	0.22	0.10
430	Mineral Processes	0.44	0.39	0.83	0.03	0.01	8.41	5.54	3.03
440	Metal Processes	0.15	0.12	0.19	0.03	0.01	0.54	0.37	0.24
450	Wood and Paper	0.13	0.13	0.00	0.00	0.00	5.56	3.88	2.34
460	Glass and Related Products	0.01	0.01	0.00	0.00	0.00	0.11	0.10	0.09
470	Electronics	0.00	0.00	0.00	0.00	0.00	0.02	0.01	0.01
499	Other (Industrial Processes)	6.27	5.63	0.23	0.03	0.00	1.22	0.84	0.52
	Total	**16.12**	**13.94**	**1.42**	**0.08**	**0.03**	**16.94**	**11.46**	**6.74**
	Solvent Evaporation								
510	Consumer Products	103.58	84.43	0.00	0.00	0.00	0.00	0.00	0.00
520	Architectural Coatings and Related Solv	20.34	18.83	0.00	0.00	0.00	0.00	0.00	0.00
530	Pesticides/Fertilizers	1.02	1.02	0.00	0.00	0.00	0.00	0.00	0.00
540	Asphalt Paving/Roofing	0.78	0.71	0.00	0.00	0.00	0.02	0.02	0.02
	Total	**125.72**	**104.99**	**0.00**	**0.00**	**0.00**	**0.02**	**0.02**	**0.02**
	Miscellaneous Processes								
610	Residential Fuel Combustion	19.78	8.63	48.54	20.20	0.49	7.77	7.39	7.19
620	Farming Operations	33.57	2.69	0.00	0.00	0.00	2.36	1.21	0.31
630	Construction and Demolition	0.00	0.00	0.00	0.00	0.00	34.72	16.98	1.70
640	Paved Road Dust	0.00	0.00	0.00	0.00	0.00	102.51	46.85	7.07
645	Unpaved Road Dust	0.00	0.00	0.00	0.00	0.00	9.86	5.86	0.58
650	Fugitive Windblown Dust	0.00	0.00	0.00	0.00	0.00	3.70	1.85	0.26
660	Fires	0.34	0.24	3.02	0.08	0.00	0.45	0.44	0.41
670	Waste Burning and Disposal	5.66	3.23	50.64	1.52	0.47	5.37	5.16	4.60
690	Cooking	2.48	1.73	0.00	0.00	0.00	10.39	10.39	10.39
699	Other (Miscellaneous Processes	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	NOX/SOX RECLAIM				26.51	11.78			
	Total	**61.83**	**16.52**	**102.20**	**48.31**	**12.74**	**177.13**	**96.14**	**32.53**

Table VIII-2. 2012 Criteria Emissions (tons/day) by Major Source Category for the South Coast Air Basin.

Code	Source Category	TOG	VOC	CO	NOx	SOx	TSP	PM10	PM2.5
	Onroad Motor Vehicles								
710	Light Duty Passenger Auto (LDA)	58.49	53.92	528.58	41.78	0.81	10.73	10.53	4.61
722	Light Duty Trucks 1 (T1)	16.11	14.88	141.71	11.13	0.11	1.38	1.35	0.64
723	Light Duty Trucks 2 (T2)	23.29	21.43	240.28	26.88	0.39	3.72	3.65	1.59
724	Medium Duty Trucks (T3)	21.75	19.78	241.75	28.70	0.39	2.96	2.91	1.27
732	Light Heavy Duty Gas Trucks 1 (T4)	7.92	7.23	71.08	16.41	0.09	0.63	0.62	0.26
733	Light Heavy Duty Gas Trucks 2 (T5)	0.86	0.79	7.75	1.69	0.01	0.07	0.06	0.03
734	Medium Heavy Duty Gas Trucks (T6)	1.78	1.63	21.15	3.17	0.01	0.05	0.05	0.02
736	Heavy Heavy Duty Gas Trucks ((HHD)	0.33	0.29	9.40	1.11	0.00	0.01	0.01	0.00
742	Light Heavy Duty Diesel Trucks 1 (T4)	0.69	0.58	3.34	19.77	0.02	0.51	0.50	0.28
743	Light Heavy Duty Diesel Trucks 2 (T5)	0.23	0.19	1.14	6.47	0.01	0.20	0.19	0.11
744	Medium Heavy Duty Diesel Truck (T6)	1.53	1.28	5.07	29.95	0.05	1.73	1.71	1.26
746	Heavy Heavy Duty Diesel Trucks (HHD)	5.59	4.68	23.36	92.14	0.15	4.39	4.38	3.57
750	Motorcycles (MCY)	8.51	7.30	66.36	2.23	0.00	0.08	0.08	0.03
760	Diesel Urban Buses (UB)	0.63	0.53	2.55	14.21	0.02	0.96	0.95	0.52
762	Gas Urban Buses (UB)	0.41	0.33	4.20	0.73	0.00	0.01	0.01	0.00
771	Gas School Buses (SB)	0.12	0.10	1.82	0.14	0.00	0.00	0.00	0.00
772	Diesel School Buses (SB)	0.14	0.12	0.41	2.33	0.00	0.22	0.21	0.13
777	Gas Other Buses (OB)	0.46	0.43	5.73	0.98	0.00	0.02	0.01	0.01
779	Diesel Other Buses (OB)	0.25	0.21	0.94	4.79	0.01	0.23	0.23	0.19
780	Motor Homes (MH)	0.29	0.24	7.72	1.78	0.01	0.08	0.08	0.04
	Total	**149.38**	**135.93**	**1384.33**	**306.42**	**2.06**	**27.97**	**27.55**	**14.58**
	Other Mobile Sources								
810	Aircraft	3.38	3.30	35.87	13.53	1.44	0.86	0.81	0.40
820	Trains	2.07	1.74	6.05	20.21	0.02	0.61	0.61	0.56
833	Ocean Going Vessels	0.94	0.83	1.49	14.71	2.98	0.52	0.52	0.50
835	Commercial Habor Crafts	0.56	0.47	2.27	6.04	0.00	0.26	0.26	0.24
840	Recreational Boats	33.52	31.68	102.78	5.97	0.00	1.99	1.91	1.82
850	Off-Road Recreational Vehicles	6.91	6.63	7.79	0.11	0.01	0.03	0.03	0.02
860	Off-Road Equipment	57.66	52.80	592.14	70.52	0.08	4.71	4.64	4.33
870	Farm Equipment	1.23	1.06	6.76	5.36	0.01	0.32	0.32	0.29
890	Fuel Storage and Handling	7.53	7.50	0.00	0.00	0.00	0.00	0.00	0.00
	Total	**113.79**	**106.01**	**755.17**	**136.45**	**4.53**	**9.30**	**9.10**	**8.17**
Total	**Stationary**	**1061.36**	**235.74**	**161.78**	**78.51**	**15.60**	**205.14**	**117.05**	**48.05**
Total	**On-Road Vehicles**	**149.38**	**135.93**	**1384.33**	**306.42**	**2.06**	**27.97**	**27.55**	**14.58**
Total	**Other Mobile**	**113.79**	**106.01**	**755.17**	**136.45**	**4.53**	**9.30**	**9.10**	**8.17**
Total	**Anthropogenic**	**1324.54**	**477.69**	**2301.27**	**521.38**	**22.19**	**242.42**	**153.70**	**70.80**

APPENDIX IX

MATES IV

DRAFT FINAL REPORT

Regional Modeling Analyses

Authors

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IX.1 Introduction

The MATES IV regional modeling analysis is presented in Chapter 4 of the main document. This appendix provides the analyses to complement and support the regional modeling demonstration. These include: characterization and validation of the meteorological input data, development of the MATES IV modeling emissions inventory, discussion of the development of the boundary conditions, model performance, and risk.

The Comprehensive Air Quality Model with Extensions enhanced with a reactive tracer modeling capability (CAMx RTRAC, Environ, 2006) provided the dispersion modeling platform and chemistry used to simulate annual impacts of both gaseous and aerosol toxic compounds in the Basin. The version of the RTRAC "probing tool" in CAMx used in the modeling simulations includes an air toxics chemistry module to treat the formation and destruction of reactive air toxic compounds.

Numerical modeling was conducted on a domain that encompassed the Basin and the coastal shipping lanes located in the Southern California Bight portions of the Basin using 2 km by 2 km computational grids. The domain was extended by 80 km to the east to include Coachella Valley and 10 km to the south to include the entire Orange County beyond the MATES III domain. An updated version of the 2012 AQMP emissions inventory for model year 2008, which included detailed source profiles of air toxic sources, provided mobile and stationary source input for the MATES III CAMx RTRAC simulations. Back-casting to the previous MATES modeling inventories was not performed due to the complications involved in the map projections and speciation profiles used in the inventory.

Grid-based, hourly meteorological fields were generated from the Weather Research Forecast (WRF) mesoscale model (Skamarock, 2008). The National Weather Service (NWS) North American Model (NAM) analysis field was employed as initial and lateral boundary values for the WRF modeling. Four dimensional data assimilation was performed using the NAM output enhanced with available upper and surface measurements. WRF was simulated for the period of July 1, 2012, to June 20, 2013, which provided the dispersion platform for the chemical transport modeling using CAMx.

IX.2 Background

MATES IV regional modeling analyses relied on the CAMx RTRAC model to simulate annual impacts of both gaseous and aerosol toxic compounds in the Basin. The 2000 MATES II analysis used the Urban Airshed Model with TOX (UAMTOX) chemistry to simulate the advection and accumulation of toxic compound emissions throughout the Basin. UAMTOX was simulated for 2 km by 2 km grid domain that overlaid the Basin. The analysis relied on the 1997-1998 emissions projection from the 1997 AQMP and meteorological data fields for 1997-1998 generated from objective analysis using a diagnostic wind model. These tools were consistent with those used in both the 1997 and 2003 AQMP attainment demonstrations.

For MATES III, the regional modeling dispersion platform and chemistry simulations progressed from the UAMTOX model to CAMx RTRAC. The second major change in the MATES III modeling analysis was the incorporation of the Mesoscale Meteorological Model 5 (MM5, Grell, 1994) to drive the meteorological data simulation. At that time, MM5 was the state-of-the-art meteorological model used in numerous regional modeling analyses, worldwide. The transition to CAMx and MM5 was made based on suggestions from peer review for the 2003 AQMP modeling efforts.

During MATES III, MM5 was simulated for two periods to provide the dispersion profile for the CAMx simulations: April 1998 through March 1999 and all days in 2005. As for emissions, an updated version of the 2007 AQMP inventory for model year 2005 was used. This included detailed source profiles of air toxics and mobile and stationary sources for CAMx RTRAC simulations. An additional back-cast of the 2007 AQMP emissions inventory was generated for 1998 to re-simulate MATES II in a framework identical to the MATES III, which enabled a direct comparison of risk assessments of the two previous MATES studies.

The CAMx-MM5 modeling platform from MATES III was updated to the CAMx-WRF coupled system in MATES IV. The WRF, state-of-the-science meteorological modeling tool offers a variety of user options to cover atmospheric boundary layer parameterizations, turbulent diffusion, cumulus parameterizations, land surface-atmosphere interactions, which can be customized to specific geographical and climatological situations. SCAQMD performed extensive sensitivity tests and developments to improve the WRF performance for the South Coast Basin, of which geographical and climatological characteristics impose great challenges in predicting complex meteorological structures associated with air quality episodes. For MATES IV, CAMx with RTRAC algorithms continued to serve as the chemical transport platform, given the importance of tracking chemically active toxic elements individually to assess the contribution of each source category. The RTRAC algorithm provides a flexible approach for tracking the emission, dispersion, chemistry, and deposition of multiple gas- and particle-phase species that are not otherwise included in the model’s chemistry mechanisms.

IX.3 CAMx Modeling Domain

Modeling was conducted on a domain that encompassed the South Coast Air Basin and the coastal shipping lanes located in the Southern California Bight portions of the Basin using a 2 km by 2 km grid. Figure IX-1 depicts the MATES IV modeling domain, which was extended by 80 km in the east and 10 km to the south beyond the MATES III domain, which was presented as the shaded area in the figure. The discrepancy of the two domains, other than the size, results from the map projection used in the grid configuration. MATES III employed a UTM coordinate map projection, an orthogonal grid system. MATES IV used a Lambert conformal map projection (reference point was located at 120° 30′ W and 37° N) which complements the meteorological simulations and more accurately represents the geographical setting. Offsets in the orientation of the domain and the shape of the computational grid make it impossible to compare the two modeling results directly on an individual grid level, but meaningful comparisons can be made when averaging results over an extended area, such as a countywide or Basin total. The total integrated risks for each county and the South Coast Basin total were presented in Chapter 4 and the modeling results section later in this Appendix. Concentrations simulated for a specific location in the domain consisted of a nine-cell distance weighted average.

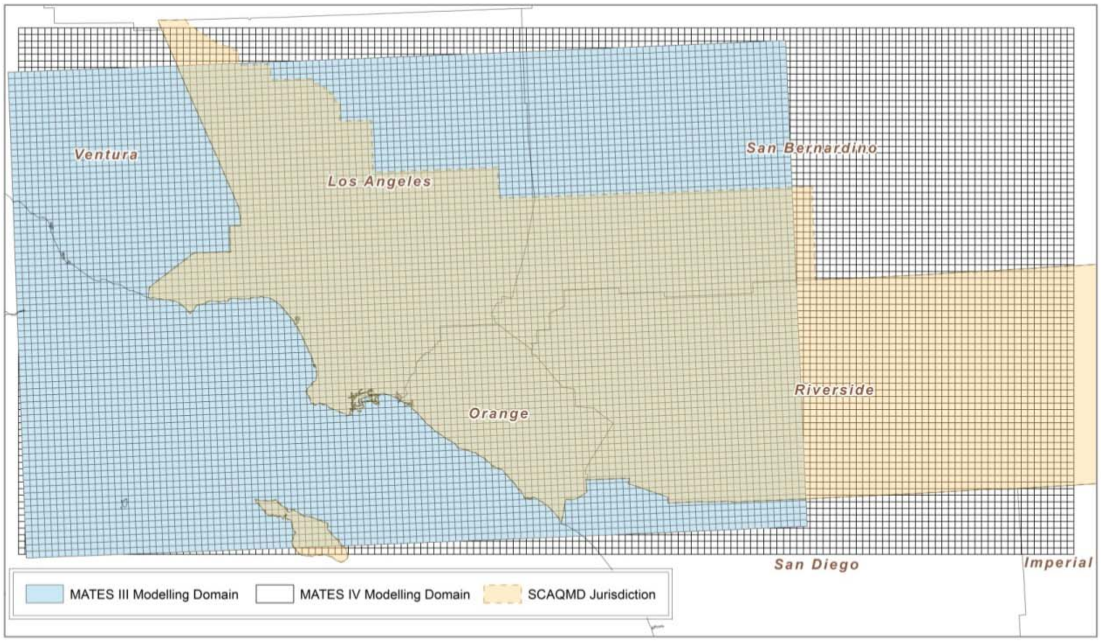


Figure IX-1
MATES IV Modeling Domain. Shaded area represents the MATES III modeling domain.

IX.4 Meteorological Summary for MATES IV Period

Most of the rainfall in Southern California occurs between late fall and early spring, with most rain typically in the months of January and February. Overall, the MATES IV time period from July 2012 through June 2013 had recorded precipitation well below normal (38% of normal), consistent with the developing drought conditions in Southern California. The total rainfall measured at the National Weather Service Downtown Los Angeles station, on the University of Southern California (USC) campus, measured a total of 5.67 inches of rain during the one-year MATES IV period, 38% of the 30-year normal value of 14.93 inches. The monthly precipitation and average temperatures are shown in Table 1. While the typically wet months of November and December 2012 had close to normal rainfall, the other typically wet months of October 2012 and January through April of 2013 all had very low rain amounts. For the calendar year of 2013, only 3.60 inches of precipitation were measured at Downtown Los Angeles, making it the driest calendar year measured in the downtown areas since records began in 1877. The drought-impacted low-rainfall conditions at Downtown Los Angeles were generally consistent with stations throughout southwestern California.

Table IX-1
Monthly Precipitation and Average Temperatures
at Downtown Los Angeles between July 2012 and June 2013

	Precipitation			Average Temperature		
Month	**Measured (in.)**	**30-Year Normal (in.)**	**Percent of Normal**	**Measured (°F)**	**30-Year Normal (°F)**	**Percent of Normal**
Jul-12	0.01	0.01	100	70.5	73.3	96.2
Aug-12	0.00	0.04	0	76.6	74.3	103.1
Sep-12	Trace	0.24	0	76.3	73.1	104.4
Oct-12	0.02	0.66	3	71.2	68.6	103.8
Nov-12	1.03	1.04	99	63.3	62.4	101.4
Dec-12	2.16	2.33	93	56.7	57.6	98.4
Jan-13	1.18	3.12	38	59.1	58.0	101.9
Feb-13	0.02	3.80	1	57.6	58.9	97.8
Mar-13	0.54	2.43	22	58.3	60.6	96.2
Apr-13	Trace	0.91	0	62.6	63.1	99.2
May-13	0.71	0.26	273	65.5	65.8	99.5
Jun-13	0.00	0.09	0	68.0	69.2	98.3
MATES-IV Period	**5.67**	**14.93**	**38**	**65.5**	**65.4**	**100.1**

The annual averaged temperature at Downtown Los Angeles for the entire MATES IV period was 0.1 degree F above the 30-year normal annual average temperature of 65.4. The months of August through November of 2012 were warmer than normal, along with January 2013. The months of July 2012, December 2012, and February through June of 2013 temperatures were slightly below normal.

Some notable weather events occurred in Southern California during the MATES IV period. A period of excessive heat occurred in the Inland Empire between August 5 through August 20, 2012, with temperatures between 96 and 110 degrees F. The southwestern monsoon was active between about July 21 and September 21, 2012, causing convection and thunderstorms in the desert and mountain areas, occasionally spilling into the South Coast Air Basin. Thunderstorms that occurred over the San Bernardino Mountains and the High Desert on August 9, 11, and 17 of 2012 led to some strong downburst winds and flooding. Thunderstorms that developed over Southern California on August 30, 2012, caused flash flooding in Moreno Valley and Redlands, as well as in the Coachella Valley. Between September 9 and 11, 2012, severe thunderstorms and flash flooding occurred in the desert and mountain areas, the Coachella Valley, and in vicinity of Temecula and Lake Elsinore.

Synoptic conditions were evaluated using 850 hPa temperature and dew point temperature measured via a rawinsonde launched at Miramar Marine Corps Air Station, the closest World Meteorological Organization's weather sounding station to the Basin. Average temperature and dew point temperature during the MATES IV period were 14.9 C and -4.6 C, respectively at 850 hPa height. These values are very close to those measured during the MATES III period: 14.1 C and -4.7 C. The difference in the ambient and dew point temperature confirms that the MATES IV period was drier than the MATES III period, confirming that drought conditions affected all of Southern California. Note that an ambient temperature close to dew point indicates that the atmosphere is near saturation. In other words, the closer the two temperatures are, the wetter the atmosphere is. When air is fully saturated, the relative humidity is 100 % and the ambient and dew point temperatures become identical.

IX.5 WRF Numerical Model Configuration

The WRF mesoscale model developed by National Center for Atmospheric Research (NCAR) was employed to produce meteorological fields for CAMx RTRAC simulations. The WRF simulations were comprised of four nested domains with horizontal grid distances of 36, 12, 4, and 2 km respectively. The first three domains were configured in a two-way nested approach, and the innermost domain was developed as one-way nesting from the 4 km domain. The relative sizes and locations of each domain are given in Figure IX-2. The innermost domain spans 334 km X 174 km in east-west and north-south directions, respectively, which overlaps the CAMx domain by three additional rows and columns in each lateral boundary. The initial guess field and lateral boundary values for the outermost domain were extracted from the operational National Center for Environmental Prediction North American Model (40 km grid resolution) grid analysis. The databases contain variables of air temperature, geopotential height, heat flux, humidity, precipitable water, sea level pressure, shortwave radiation, snow water equivalent, surface air temperature, surface winds, thermal infrared, upper level winds, vertical wind, and vorticity at each isobaric level of 1000, 975, 950, 925, 900, 875, 850, 800, 750, 700, 650, 600, 550, 500, 450, 400, 350, 300, 275, 250, 225, 200, 175, 150, 100, 50 hPa. (Refer to http://dss.ucar.edu/datasets/ds609.2 for further dataset information).

Four dimensional data assimilation (FDDA) was conducted by utilizing the National Weather Service (NWS) twice-daily sounding data and hourly surface measurements. Each simulation was conducted for a four-day period with the first 24 hours used as a spin up period. The detailed configuration and physical options used in the WRF simulation are listed in Table IX-2.

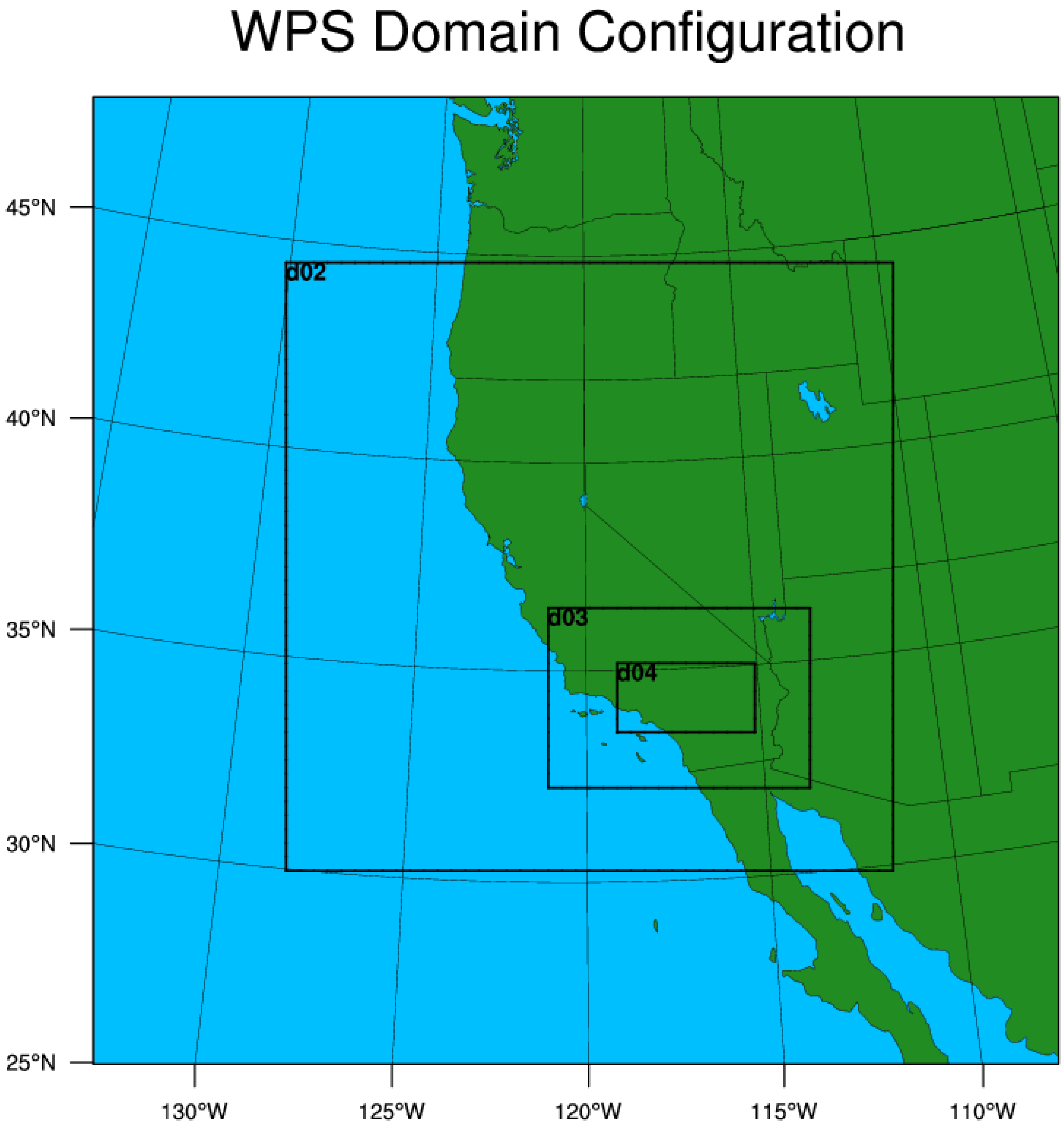


Figure IX-2.
The relative locations and sizes of the four WRF nested domains.

Table IX-2
WRF configuration and its comparison to MM5 used in the MATES III

Component	MATES IV (July 2012-June 2013)	MATES III (2005)
Numerical Platform	WRF version 3.4.1	MM5 version 3.7
Number of grids	(167 X 87) in east-west and north-south respectively	(127 X 82) in east-west and north-south respectively
Number of vertical layers	30 layers with the lowest layer being approximately at 20 m agl.	29 layers with the lowest layer being approximately at 20 m agl.
Initial and boundary values	NCEP NAM analysis field (40 km grid distance)	NCEP ETA 218 grid analysis field (12 km grid distance)
Boundary layer scheme	YSU	Blackadar
Soil model	Five-layer soil model	Five-layer soil model
Cumulus parameterization	Explicit	Explicit
Micro physics	Simple ice	Simple ice
Radiation	Cloud radiation	Cloud radiation
Four dimensional data analysis	Analysis nudging with NWS surface and upper air measurements	Analysis nudging with NWS surface and upper air measurements

IX.6 Meteorological Model Performance

The WRF performance was extensively evaluated using NWS surface measurements and Environ's METSTAT (ENVIRON, 2001) statistical software to compute mean, bias, gross error, root mean square error (RMSE), and index of agreement.

Figure IX-4 shows the time series of hourly observed and predicted temperature at 2 m above ground level (agl) for October 2012. The model successfully resolved overall cooling and warming trend induced by synoptic scale motions, while both daily minimum temperatures in the beginning of the month and daily maximum in the end of the month were slightly under-predicted. This can be partly attributed to inaccurate representation of surface characteristics such as soil moisture content and land use category.

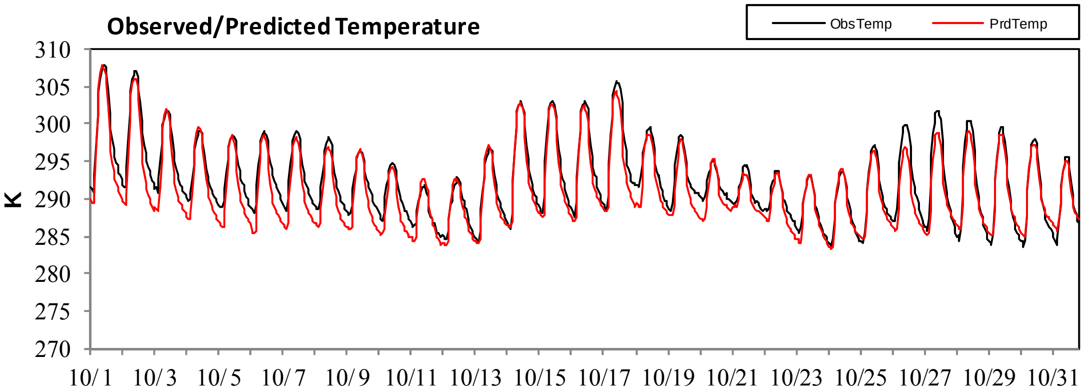


Figure IX-3

Time series of observed and predicted temperature at 2 m above ground level for October 2012. The data are hourly average observations of all available measurements within the domain and the corresponding predictions.

In all, the model has less than 4 degrees of bias and gross error and approximately 4 degrees of RMSE, which are approximately equivalent to WRF performance for 2012 Air Quality Management Plan (AQMP) modeling case. Wind speed turned out to be underpredicted by less than 1.7 m s^{-1}. In general, all conventional surface parameters including wind speed, direction, temperature and water vapor mixing ratio showed good agreement with the observations (Figures IX-4 through IX-6).

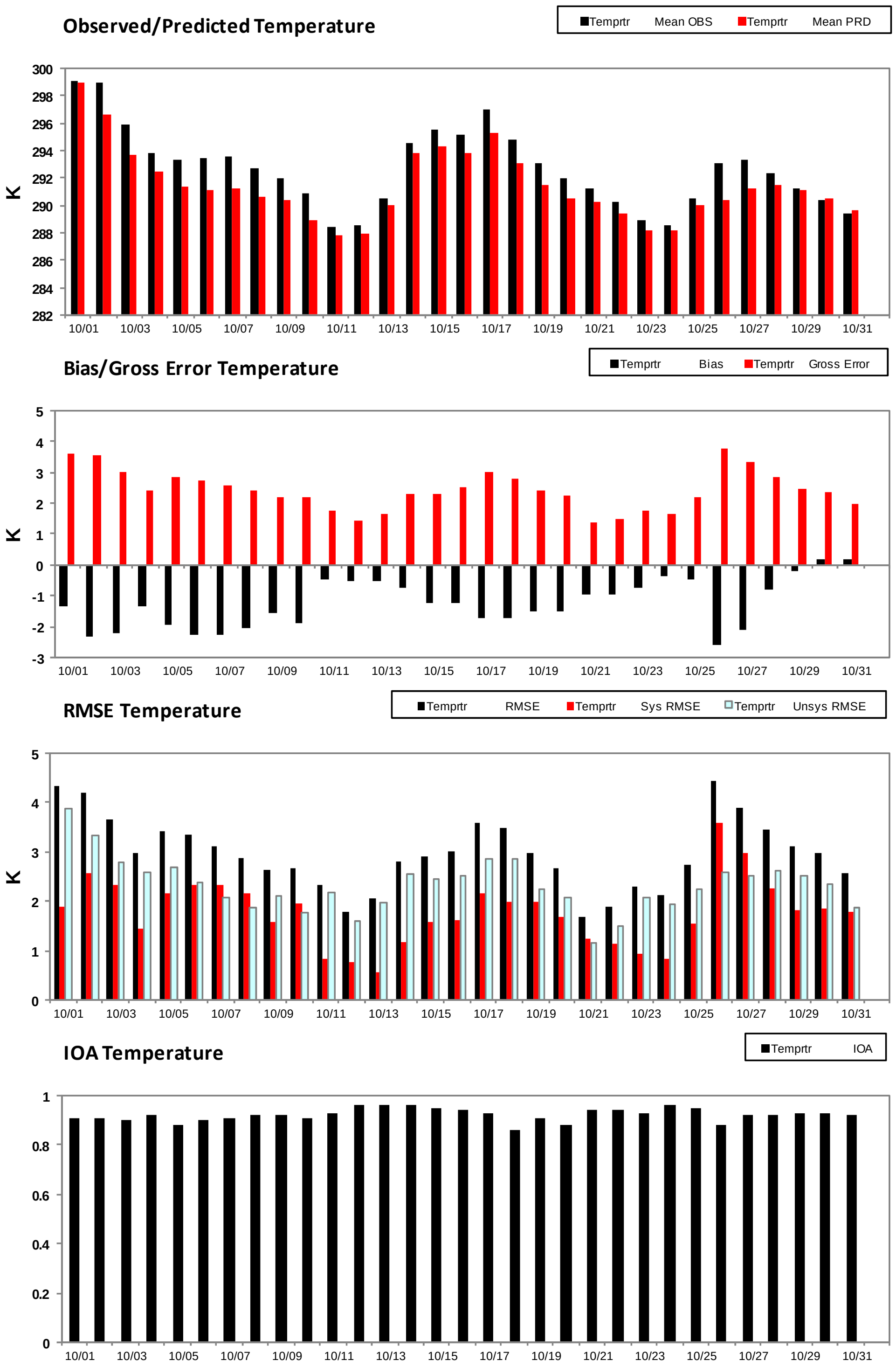


Figure IX-4

Daily averaged (a) mean, (b) bias and gross error, (c) root mean square error, and (d) index of agreement for observed and predicted temperature at 2 m agl.

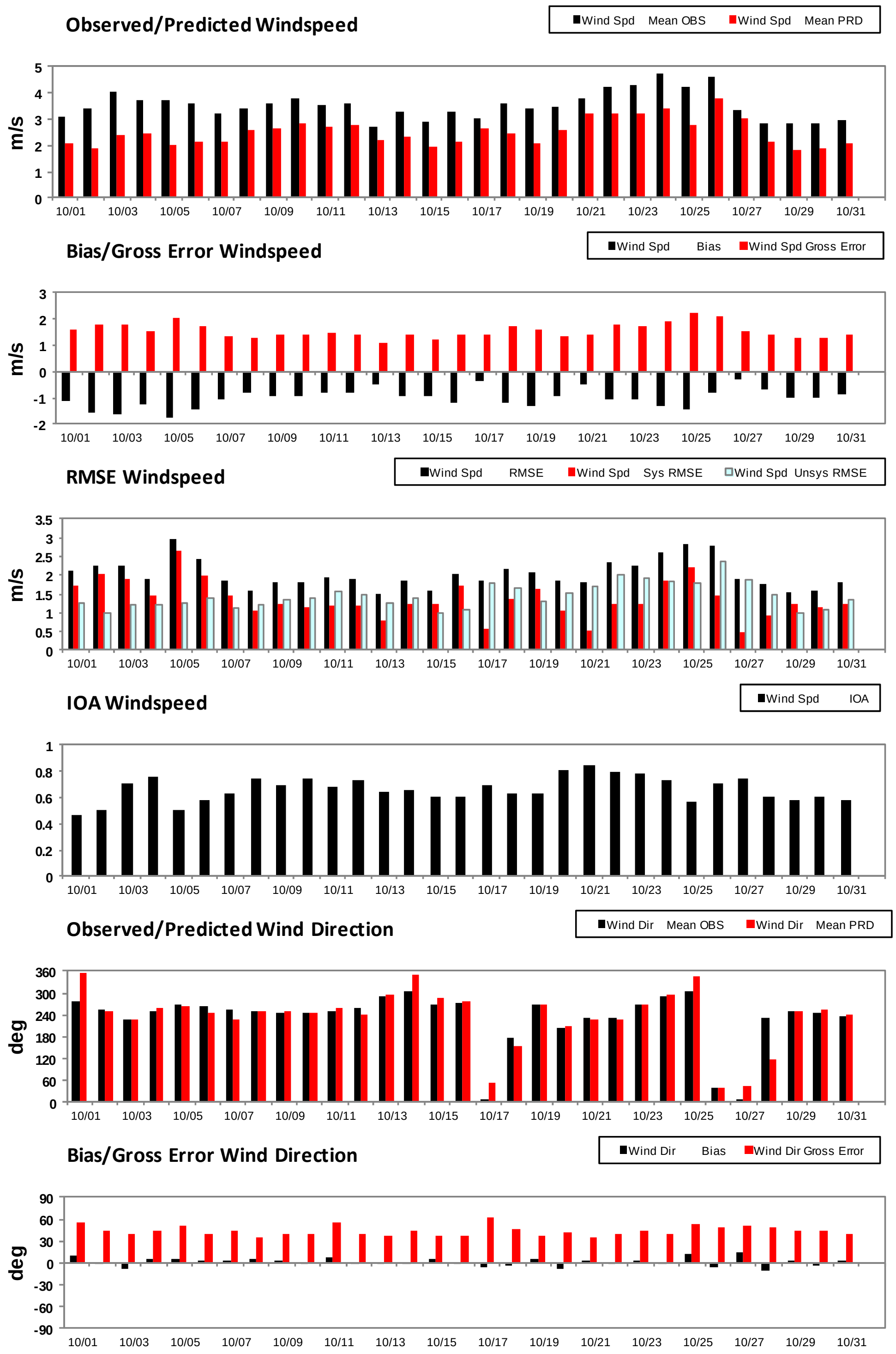


Figure IX-5

Daily averaged (a) mean, (b) bias and gross error, (c) root mean square error, and (d) index of agreement for observed and predicted wind speed. (e) Mean and (f) bias and gross error of wind direction are presented as well.

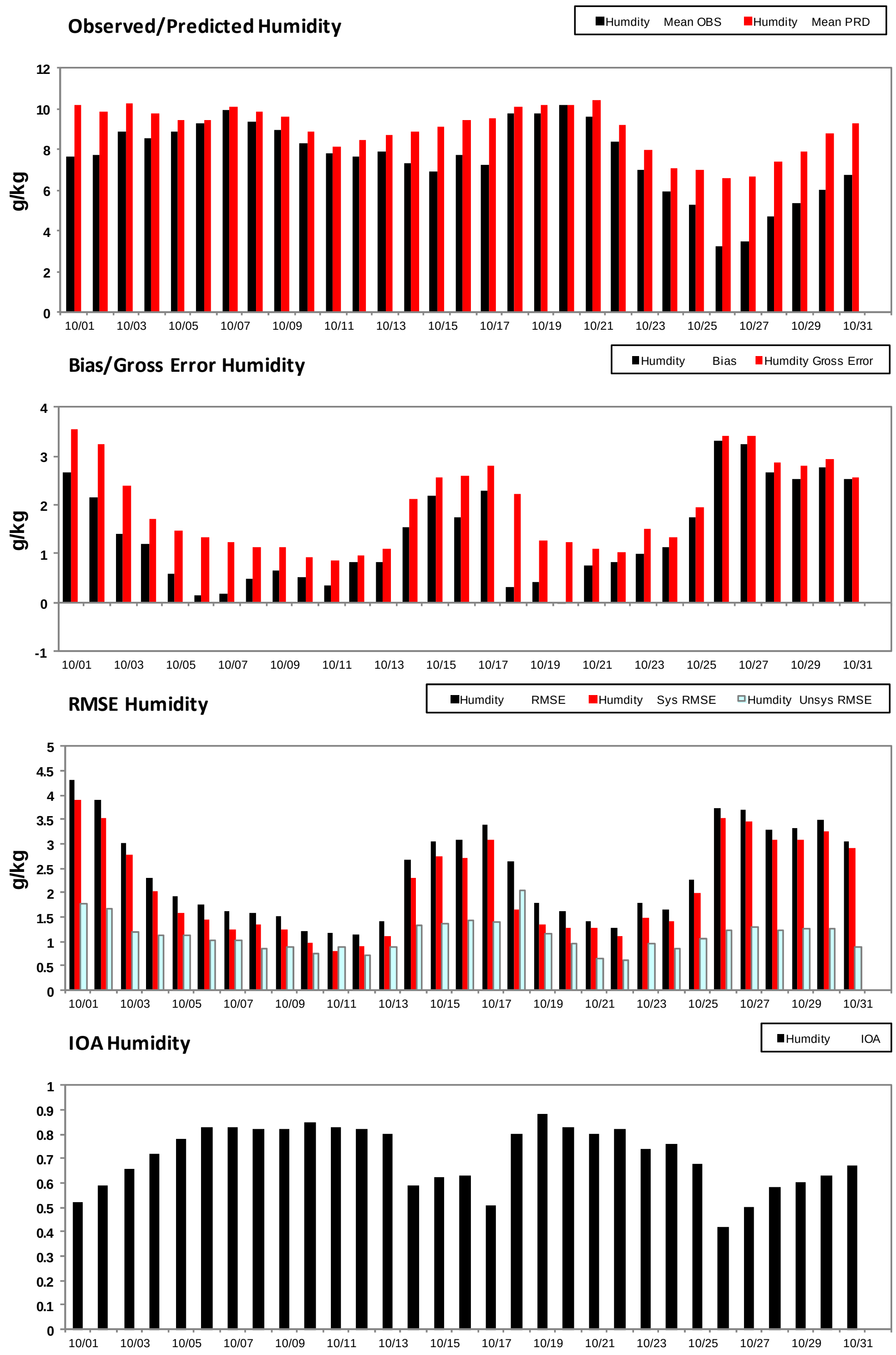


Figure IX-6

Daily averaged (a) mean, (b) bias and gross error, (c) root mean square error, and (d) index of agreement for observed and predicted humidity at 2 m agl.

IX.7 Wind Rose Comparison

While the METSTAT evaluation is a useful tool to assess the performance of the regional WRF simulations, it is important to examine the capability to recreate observed annual local scale wind patterns. To assess the local scale prevailing flow, wind roses were generated from the hourly WRF model output for the 2 km by 2 km grid cell and measurements from NWS stations. The WRF winds were retrieved from a grid in which a NWS station is located. An exact replication of the measured winds was not expected in the analysis. However, comparison of the modeled and measured annual average wind roses offers a visual comparison of the fit of the simulation to the local scale and assists in the evaluation of chemical transport model performances.

Figures IX-7a through IX-7f depict the wind roses for Fullerton, Burbank, San Bernardino, Long Beach, Santa Monica, and Riverside during the MATES IV sampling period from July 2012, to June 2013. Subtle nuances between the simulated and observed winds are observed at all stations. In general, wind speeds are slightly lower for the WRF simulation. The directional frequencies are reasonably well-captured at most sites, with an offset in the primary wind vector of less than one sector (22.5 degrees). It is important to note that the local emissions sources (particularly ground level) directly upwind of the monitoring site have a significant impact to the measured concentration profile. As such, a minor one-sector difference in the simulated wind direction may impact the CAMx RTRAC performance.

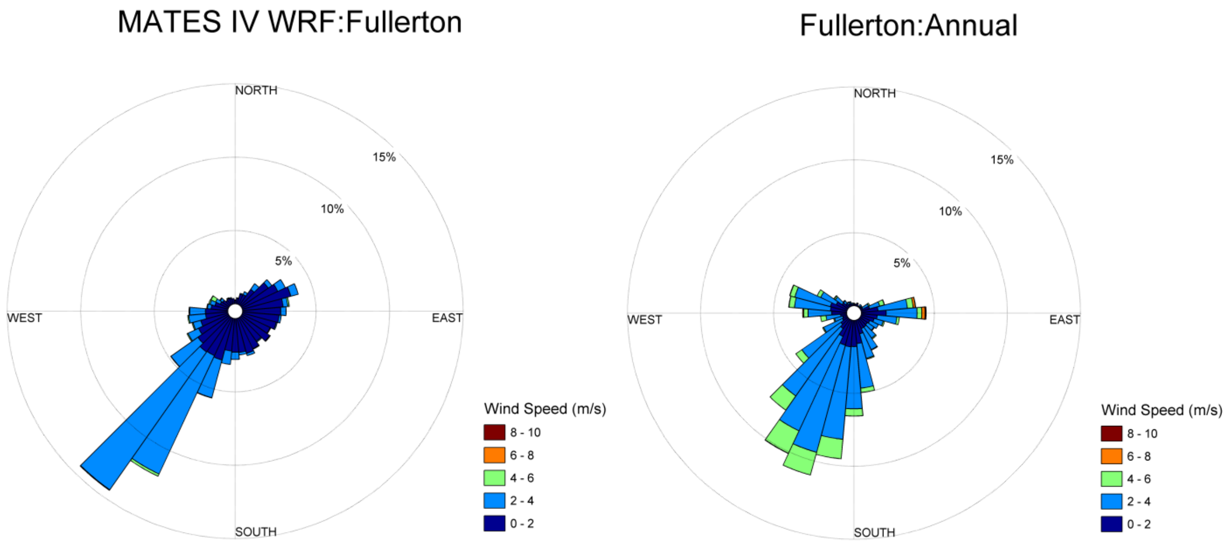


Figure IX-7a.
WRF Simulated and Observed Annual Wind Roses at Fullerton.

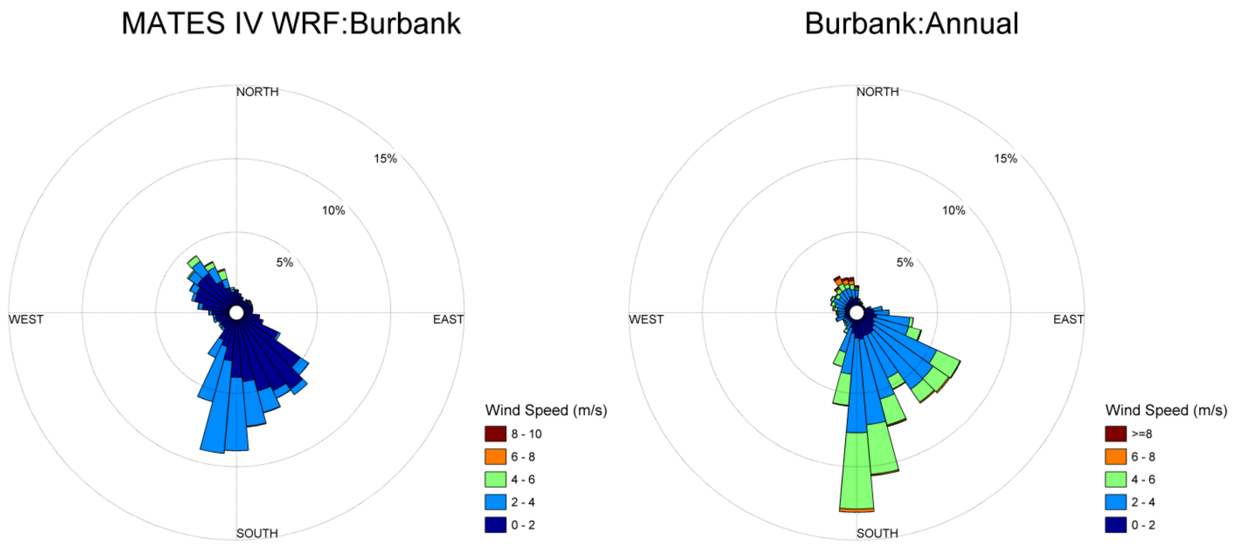


Figure IX-7b.
WRF Simulated and Observed Annual Wind Roses at Burbank.

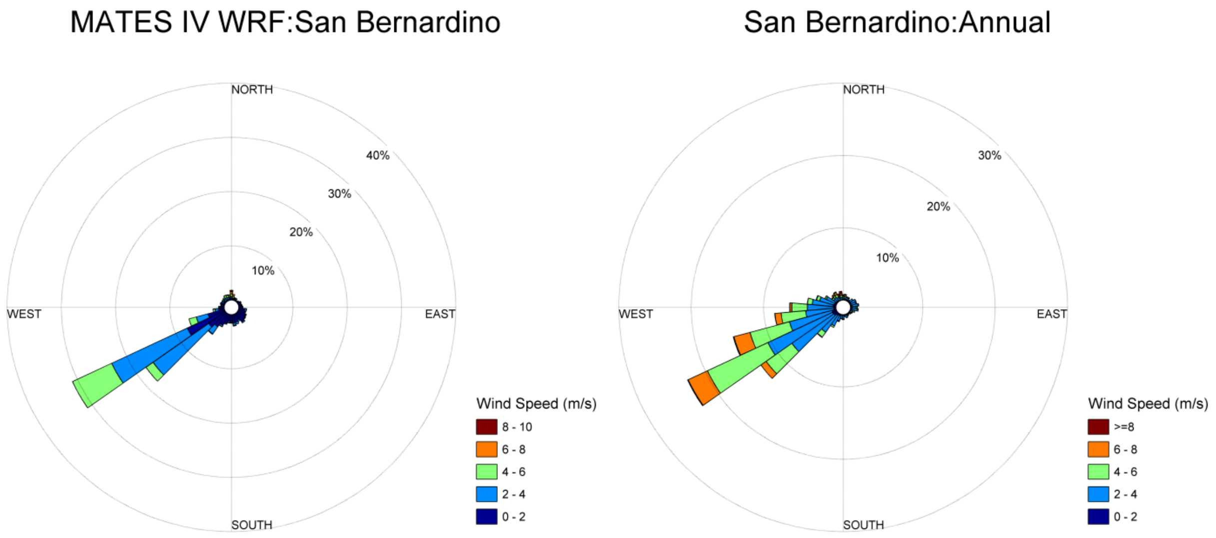


Figure IX-7c.
WRF Simulated and Observed Annual Wind Roses at San Bernardino.

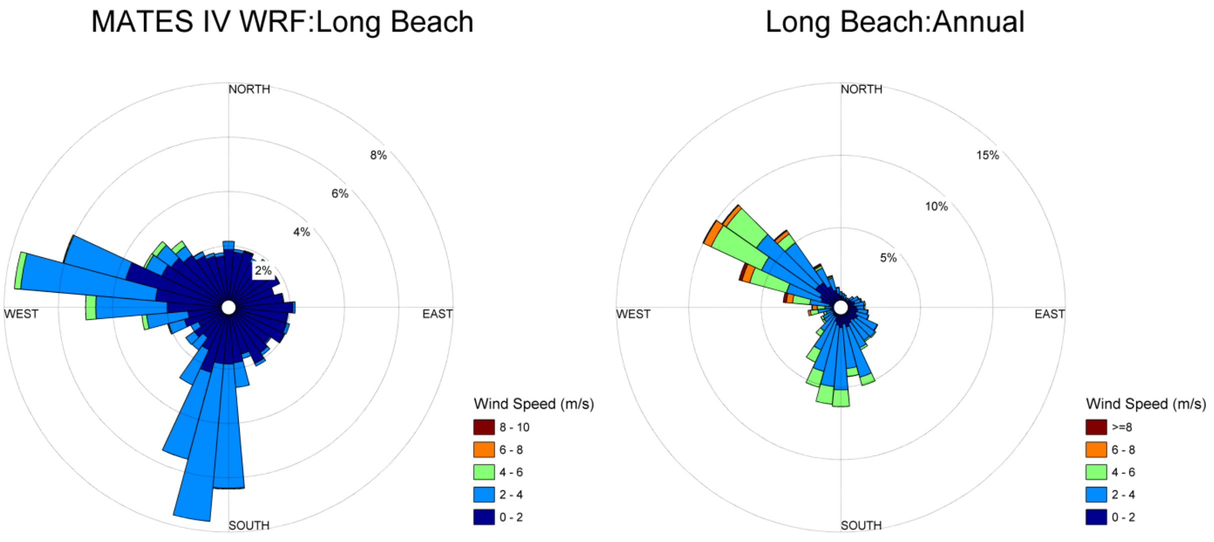


Figure IX-7d.
WRF Simulated and Observed Annual Wind Roses at Long Beach.

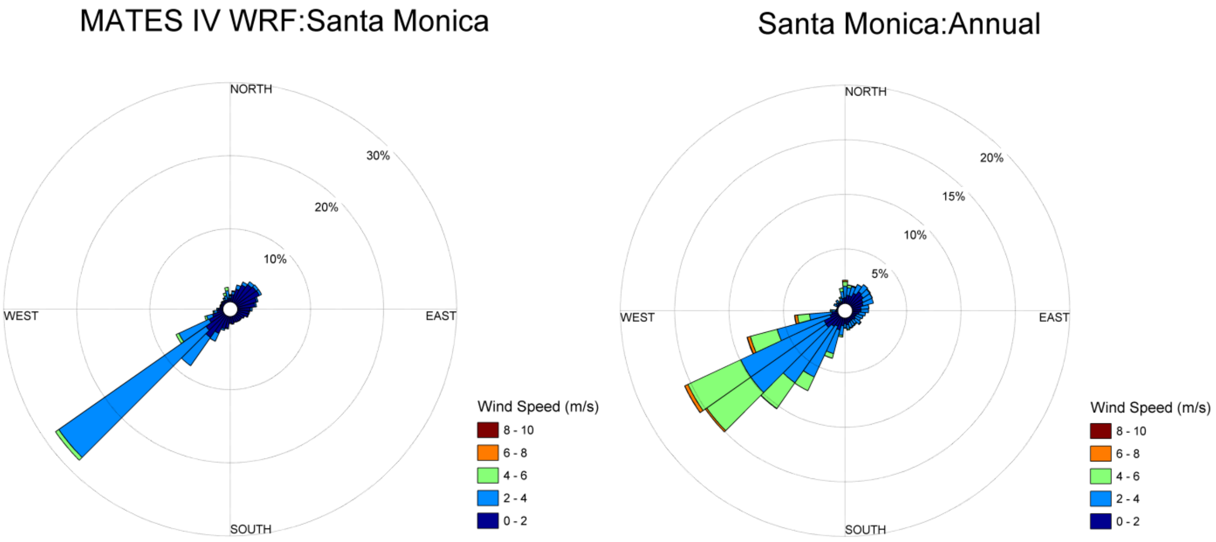


Figure IX-7e.
WRF Simulated and Observed Annual Wind Roses at Santa Monica.

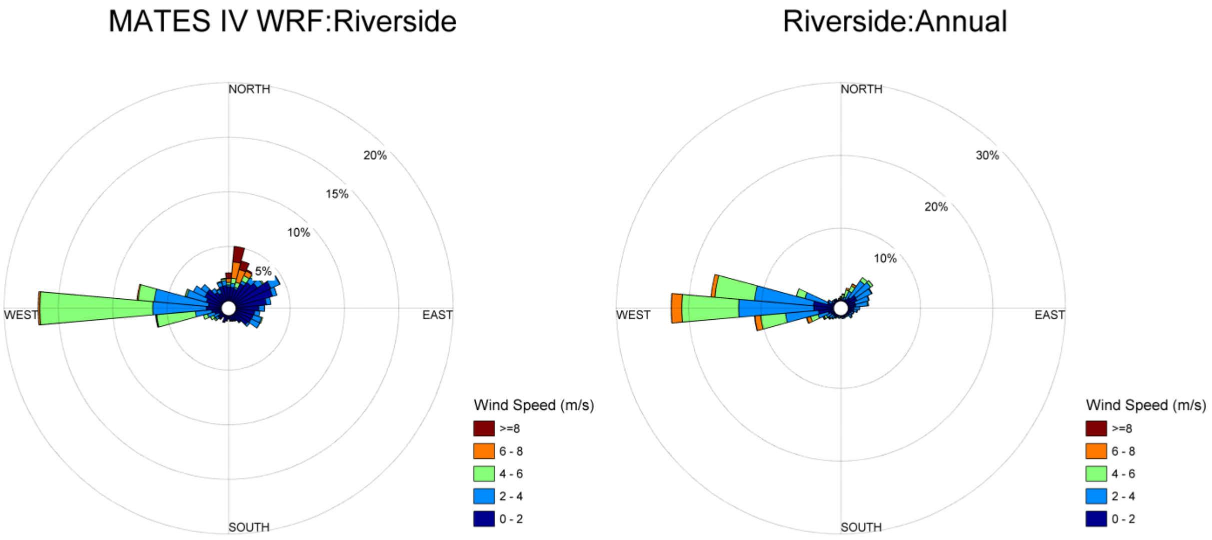


Figure IX-7f.
WRF Simulated and Observed Annual Hourly Averaged Wind Roses at Riverside.

IX.8 Vertical Dispersion

The WRF output was converted to the CAMx RTRAC format using ‘wrfcamx_v3.2’ software. Vertical diffusivity (*Kv*), which is critical in vertical dispersion, was computed using CMAQ vertical diffusivity scheme with a minimum value of 1.0 m^2/sec. The number of vertical layers was reduced to 18 layers from the 30 layer configuration used in the WRF. The layers of which height was below 2 km from the ground level were not modified. The layers above 2 km were collapsed to four layers in order to reduce computation cost. Note that the vertical structure was chosen carefully to optimize computational efficiency and numerical accuracy after an extensive sensitivity study to evaluate the impact of vertical layer structure using various numbers of computational layers.

During the development phase of the meteorological data sets, WRF was tested using a variety of mixing scheme including CMAQ (Byun and Ching, 1999) and the O’Brien 70 [OB70] (O’Brien, 1970), with various values of default minimum vertical diffusivity, ranging from 0.1 to 1.0 m^2/sec.

Based on peer review comments from MATES III and experiences from previous MATES and AQMP attainment demonstrations, the *Kv* patch algorithm (Environ, 2006) was applied in the dispersion calculation. The *Kv* patch algorithm imposes minimum *Kv* values that are pre-assigned for each land use category, regardless of the diffusivity estimated from the WRF simulated meteorological condition. In the current study, the first and second computational layers, which are centered approximately 80 m and 140 m above ground level, respectively, were subject to the direct modification of the *Kv* through the *Kv* patch.

$EC_{2.5}$ concentration from CAMx RTRAC revealed that that the *OB70* scheme predicted higher concentrations at key sites. This overprediction occurred in the CMAQ scheme with 0.1 m^2/sec minimum diffusivity, as well. All of the combinations, regardless of layer structure or minimum *Kv*, resulted in overprediction at Long Beach and West Long Beach and underprediction to varying degrees at Rubidoux and Inland Valley San Bernardino. The use of *Kv* patch modestly improved the bias. This nominal impact was attributed to the fact that 1.0 m^2/sec chosen as default minimum *Kv* was relatively large so that the *Kv* patch did not introduce significant changes in tracer dispersion.

In all, after careful evaluation of various sensitivity analyses, the vertical dispersion profile used in the final MATES IV CAMx RTRAC simulations relied on a 16-layer structure using the CMAQ diffusivity scheme overlaid with the *Kv*-patch option set at 1.0 m^2/sec value of *Kv*.

IX.9 MATES IV Modeling Emissions

An updated version of the 2012 AQMP emissions inventory for the year 2012 provided mobile and stationary source input for the MATES IV CAMx RTRAC simulations. Mobile source emissions were adjusted for time-of-day and day-of-week travel patterns based on CalTrans weigh-in-motion data profiles. Table IX-3 lists the annual average day emissions projected for 2012. (A comprehensive breakdown of the planning VOC, NOx, CO, SO2 and particulate emissions for 2012 used in the MATES IV simulation is provided in Chapter 3 and Appendix XIII). Table IX-3 also includes the MATES III TSP and $PM_{2.5}$ diesel emissions for 2005 for comparison.

A comparison of the MATES IV (2012 AQMP) 2012 projection of the $PM_{2.5}$ diesel emissions shows a 66% reduction in emissions from the 2005 emissions used in MATES III. The most significant area of diesel particulate matter emissions reduction occurs in the off-road categories. While most of those emissions reductions are real, reflecting control efforts and fleet turnover in the past several years, some of the changes are due to methodological changes in emissions inventories employed in the two AQMPs.

Figures IX-8a through IX-8x provide the grid-based weekday modeling emissions for selected toxic pollutant and precursor emissions categories.

IX.10 MATES IV vs. MATES III: Key Emissions Modeling Assumptions

Since the regional modeling effort in MATES II, the basic approach in preparing modeling emissions remained the same, i.e., based on the corresponding AQMP inventories and speciation profiles. Three relatively minor changes to emissions data preparation were implemented in the MATES IV modeling. First, emissions from ocean-going vessels in the shipping lanes and ports were assumed emitted into the stacks with stack parameters based on Mason, *et al.* (2008) while emissions from harbor craft and commercial boats were released at sea level. In MATES III, the combined shipping emissions were assumed to be 70% released through stacks while the rest at sea level.

Table IX-3
Annual Average Diesel/EC Emissions in the SCAB (TPD)

Compound	MATES IV 2012		MATES III 2005	
	PM$_{2.5}$	TSP	PM$_{2.5}$	TSP
EC	11.58	14.74	14.38	19.44
Total Diesel Particulate Matter (DPM)	9.43	10.24	27.99	30.34
DPM per Major Source Category				
On-road	4.97	5.40	10.20	11.08
Off-road	2.94	3.20	11.23	12.21
Ships	0.74	0.78	5.18	5.55
Trains	0.56	0.61	0.86	0.94
Stationary	0.22	0.25	0.52	0.55
Total DPM	9.43	10.24	27.99	30.34

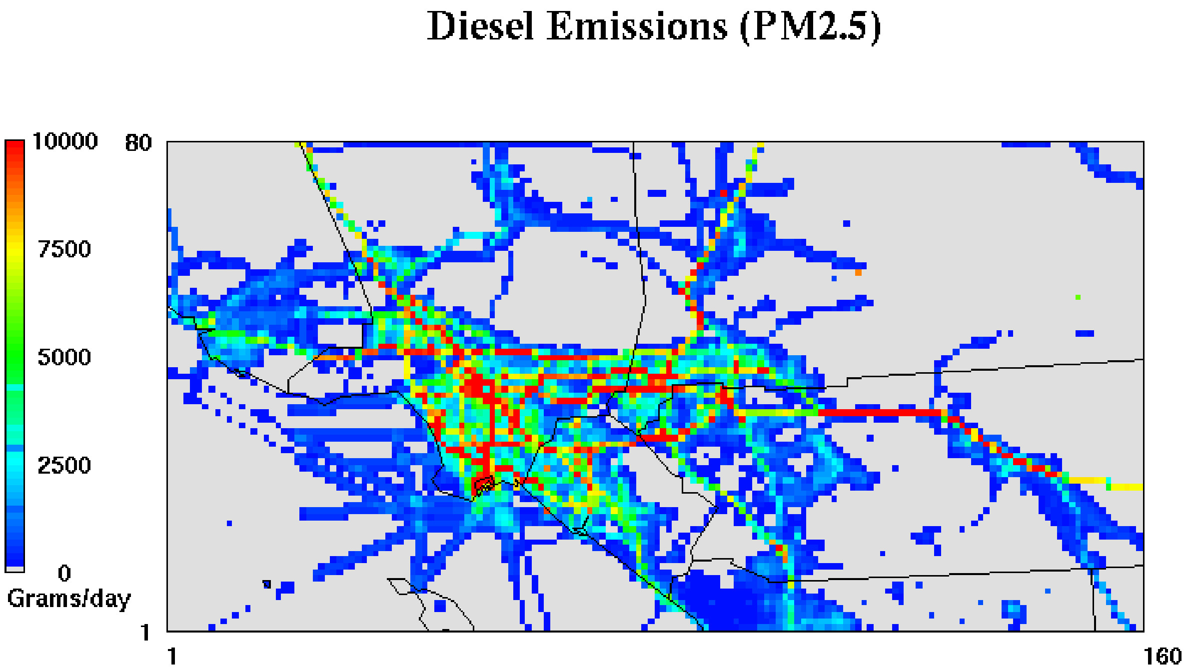

Diesel Emissions (PM2.5)

Figure IX-8a
Weekday average emissions pattern for Total Diesel PM$_{2.5}$.

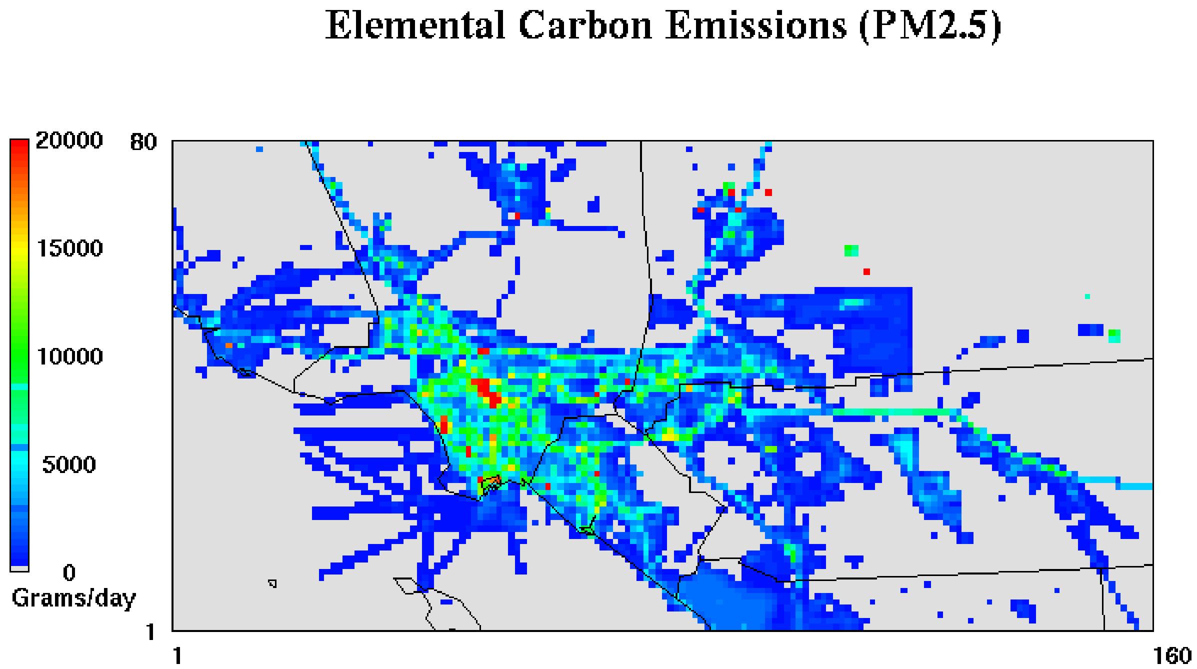


Figure IX-8b
Weekday average emissions pattern for Elemental Carbon.

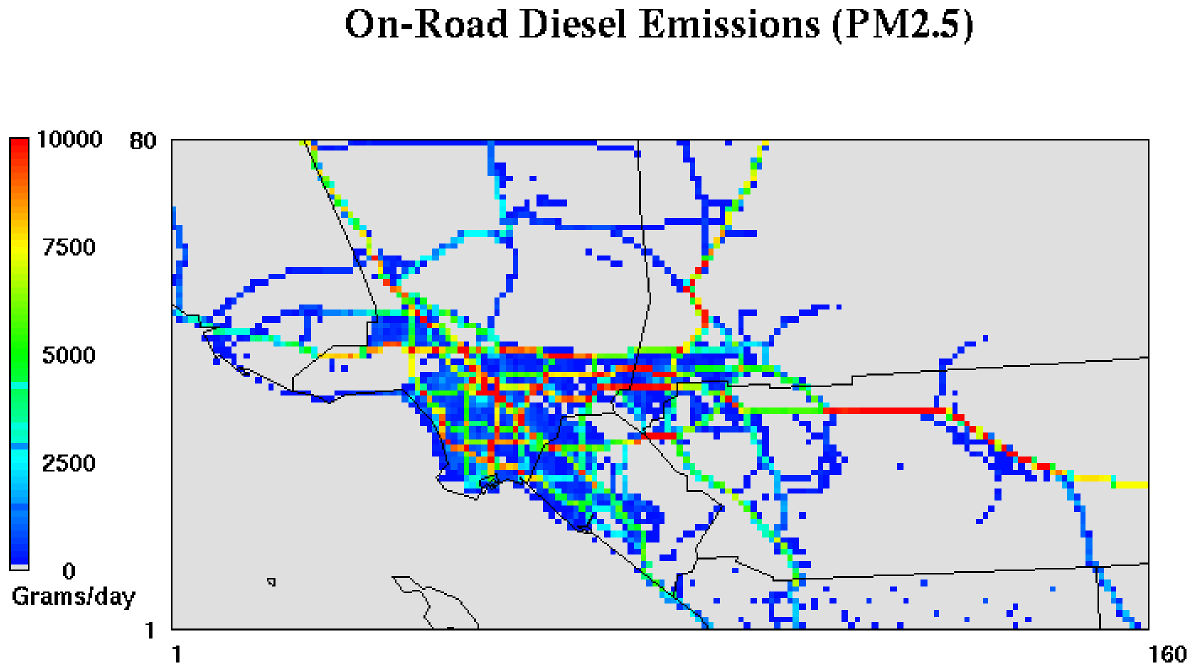
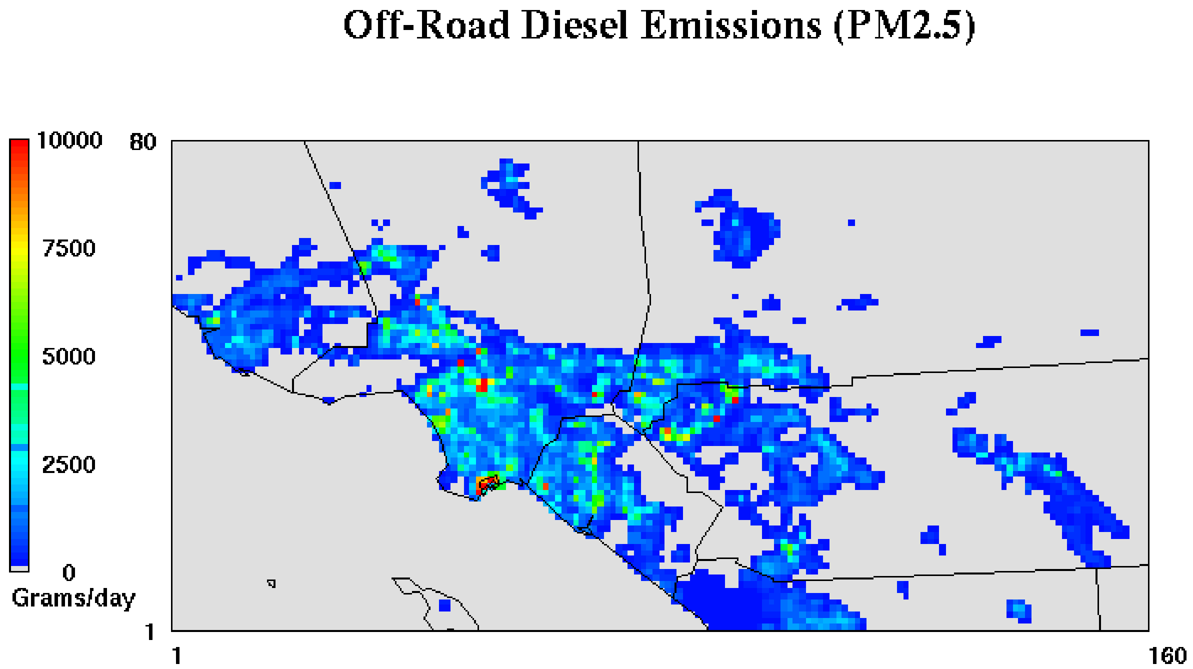
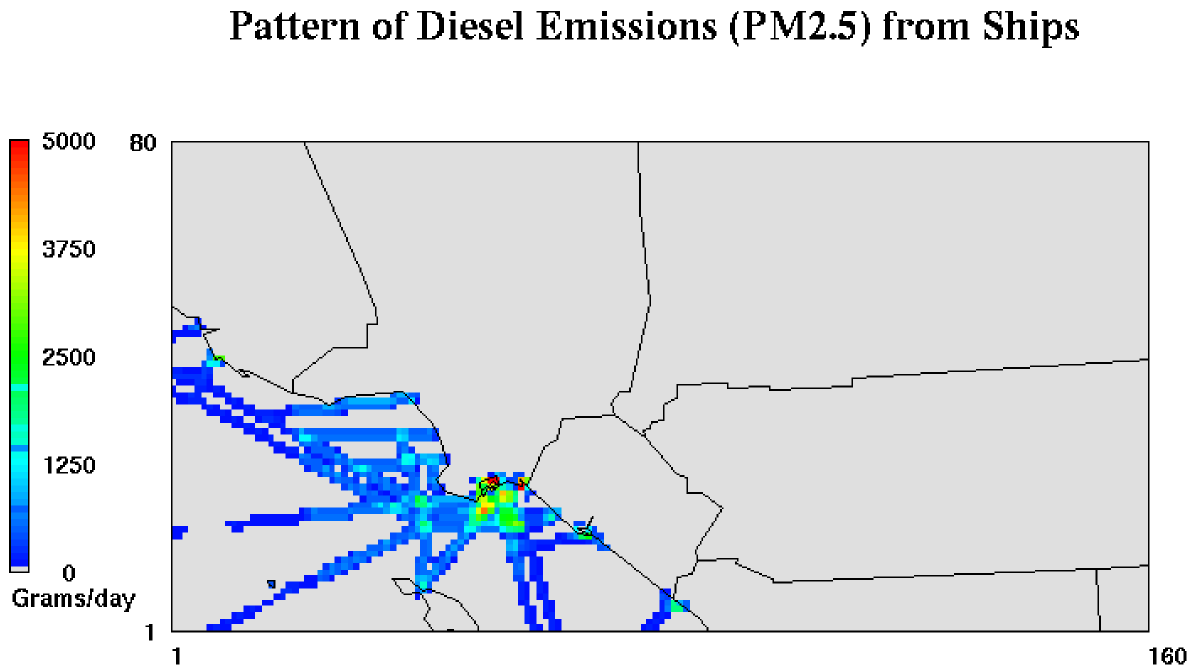


Figure IX-8c
Weekday average emissions pattern for On-Road Diesel $PM_{2.5}$.



Off-Road Diesel Emissions (PM2.5)

Figure IX-8d
Weekday average emissions pattern for Off-Road Diesel $PM_{2.5.}$



Pattern of Diesel Emissions (PM2.5) from Ships

Figure IX-8e
Weekday average emissions pattern Diesel $PM_{2.5}$ from Ships.

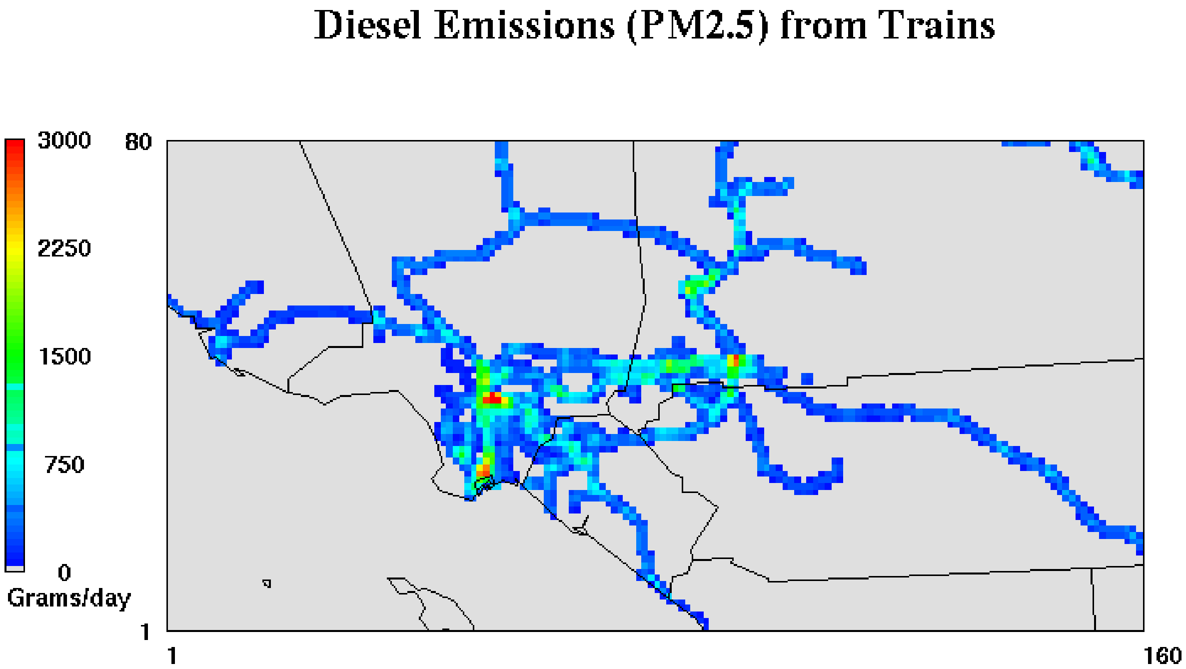


Figure IX-8f
Weekday average emissions pattern Diesel $PM_{2.5}$ from Trains.

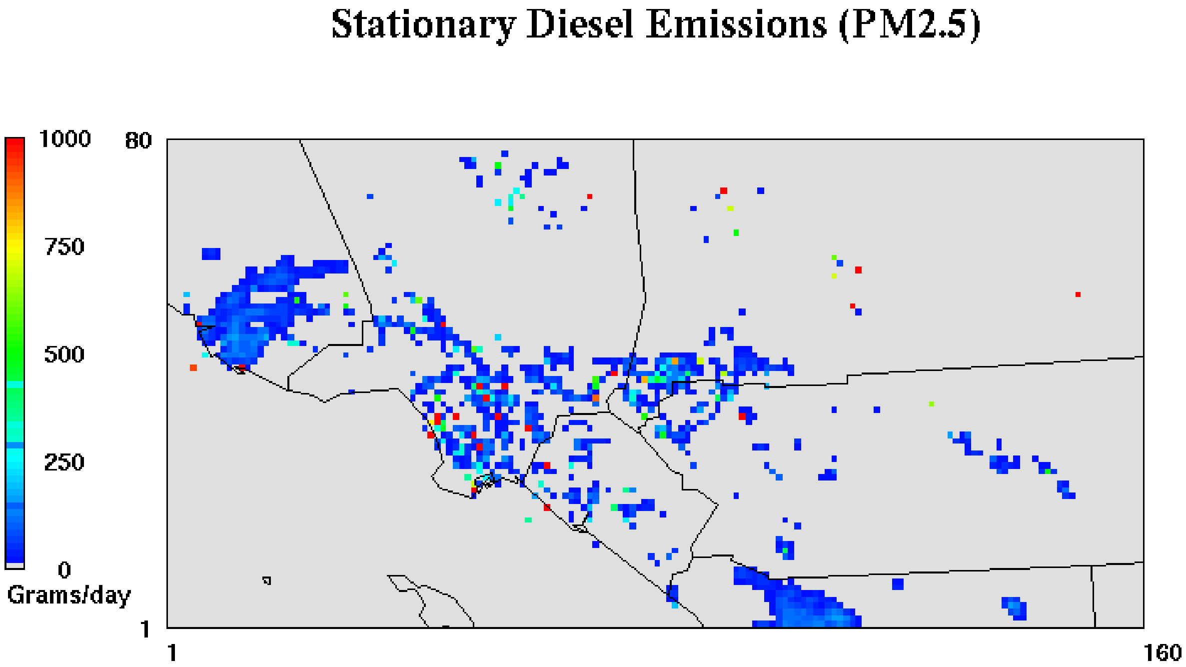
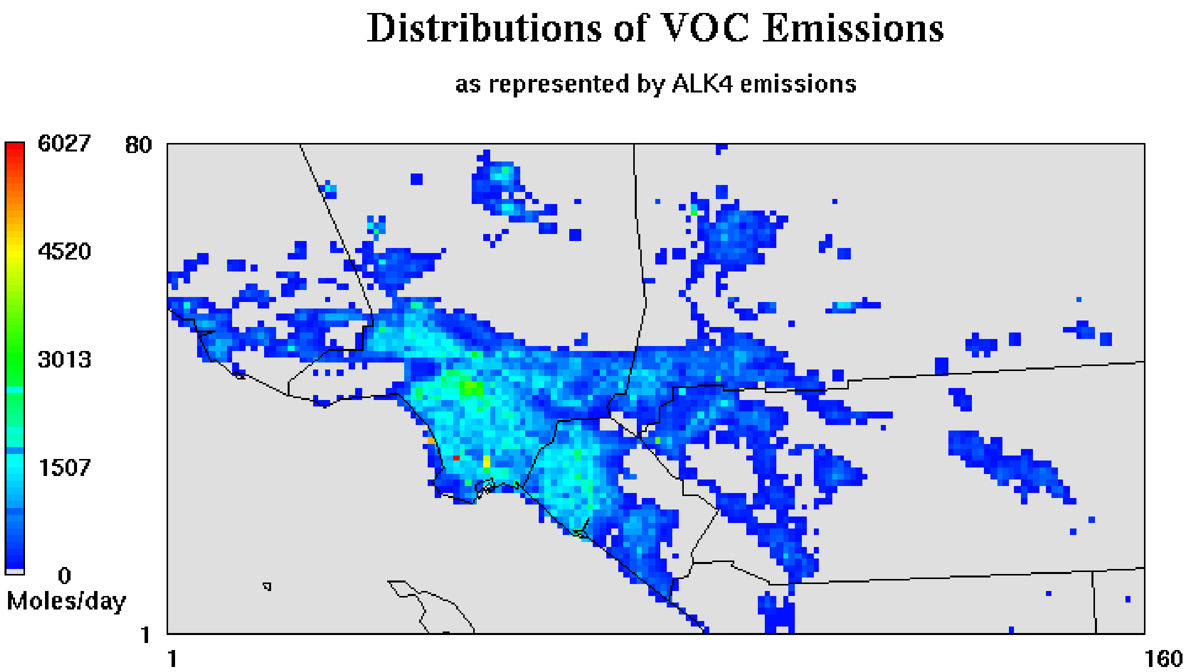


Figure IX-8g
Weekday average emissions pattern Diesel $PM_{2.5}$ from Stationary Sources.


Distributions of VOC Emissions

as represented by ALK4 emissions

Figure IX-8h
Weekday average VOC emissions pattern.

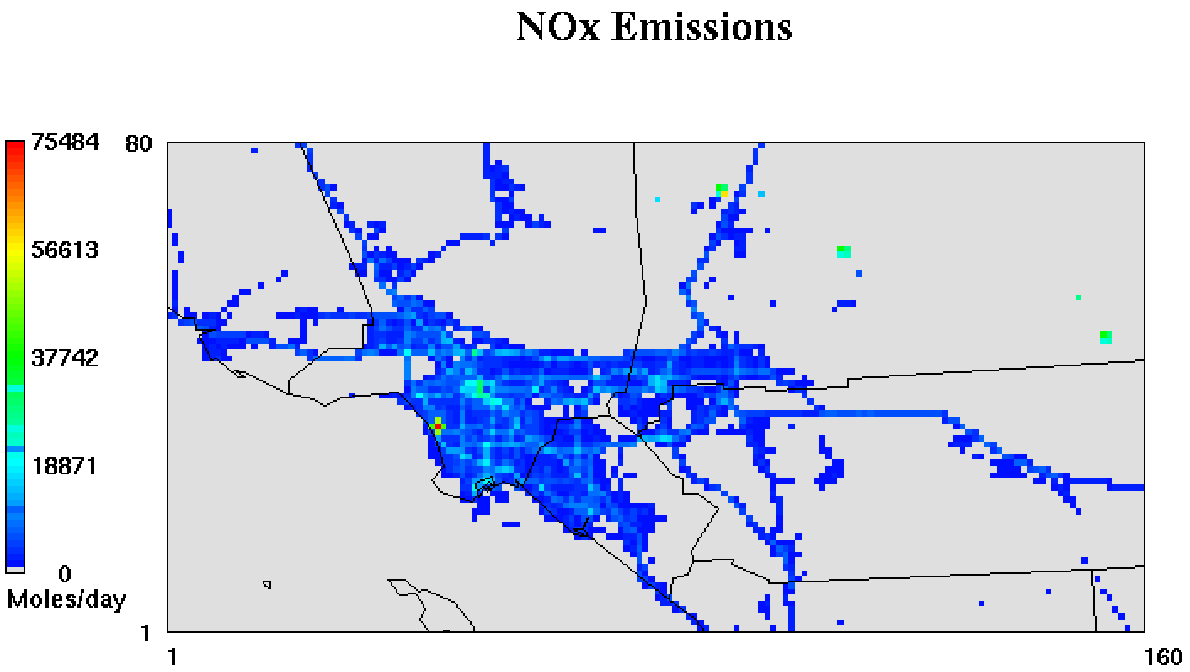

NOx Emissions

Figure IX-8i
Weekday average NOx emissions pattern.

CO Emissions

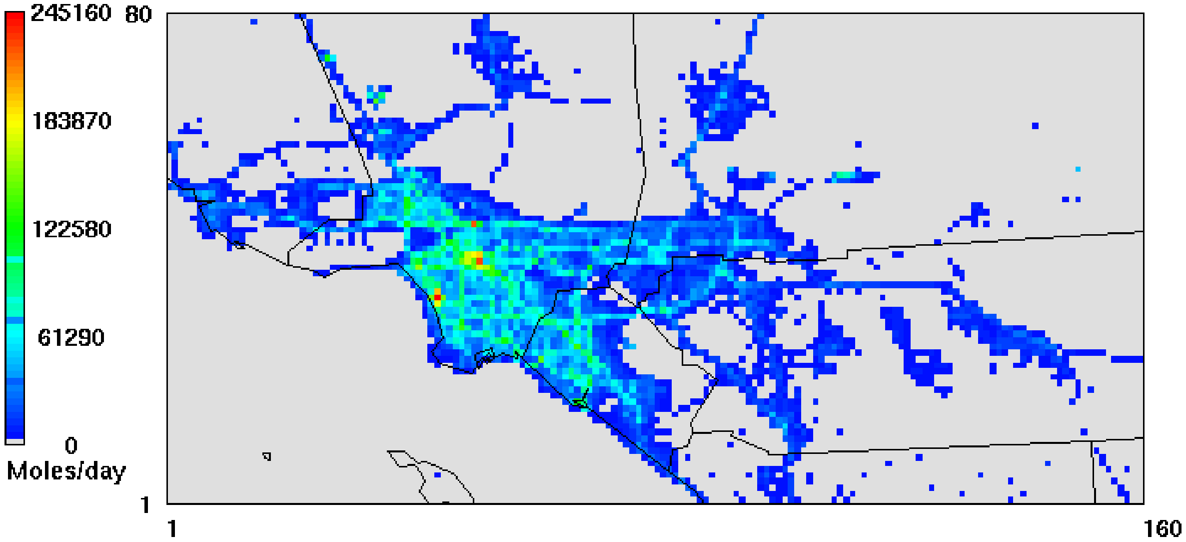


Figure IX-8j
Weekday average CO emissions pattern.

Acetaldehyde Emissions

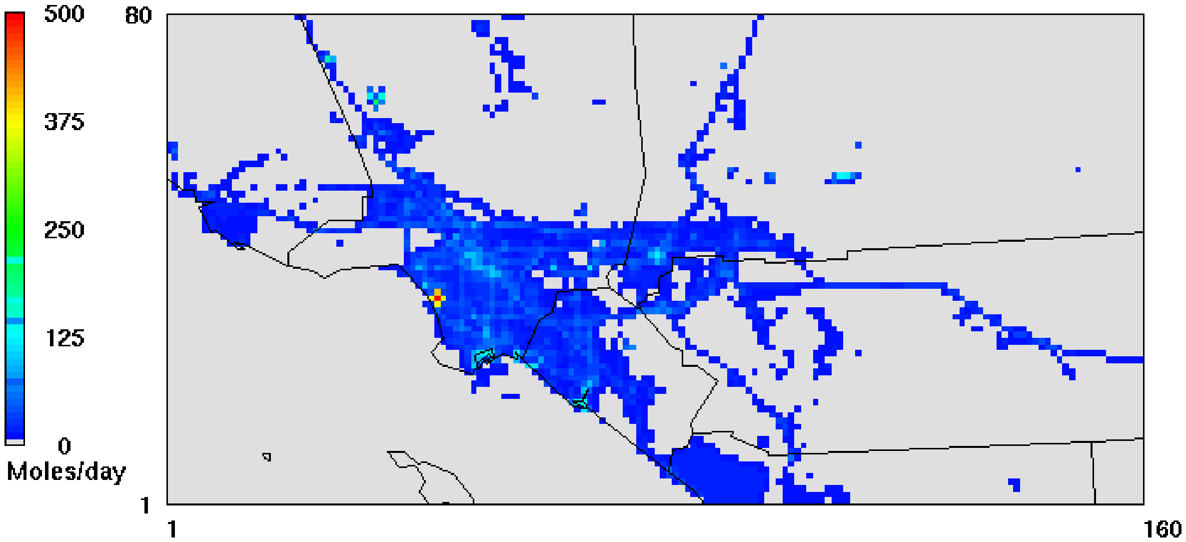


Figure IX-8k
Weekday average emissions pattern for Acetaldehyde.

Arsenic Emissions (PM2.5)

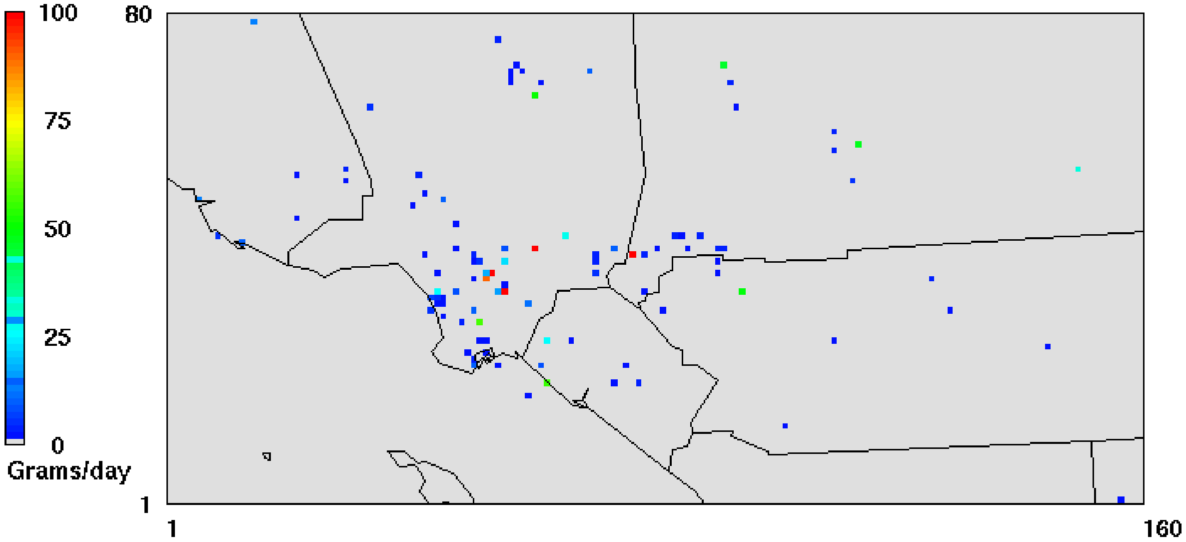


Figure IX-8l
Weekday average Arsenic emissions pattern.

Benzene Emissions

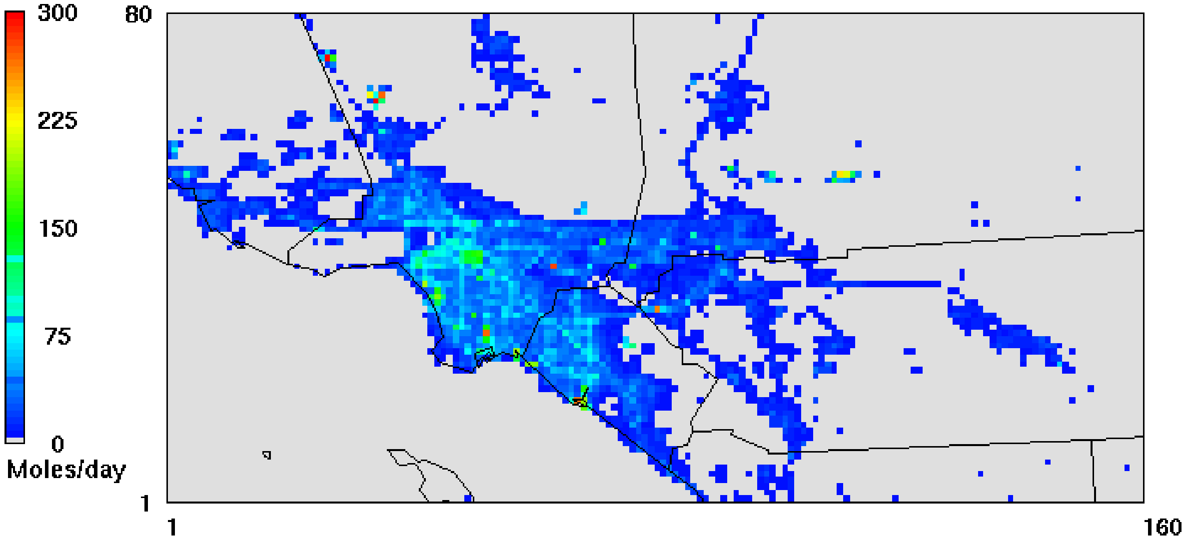


Figure IX-8m
Weekday average Benzene emissions pattern.

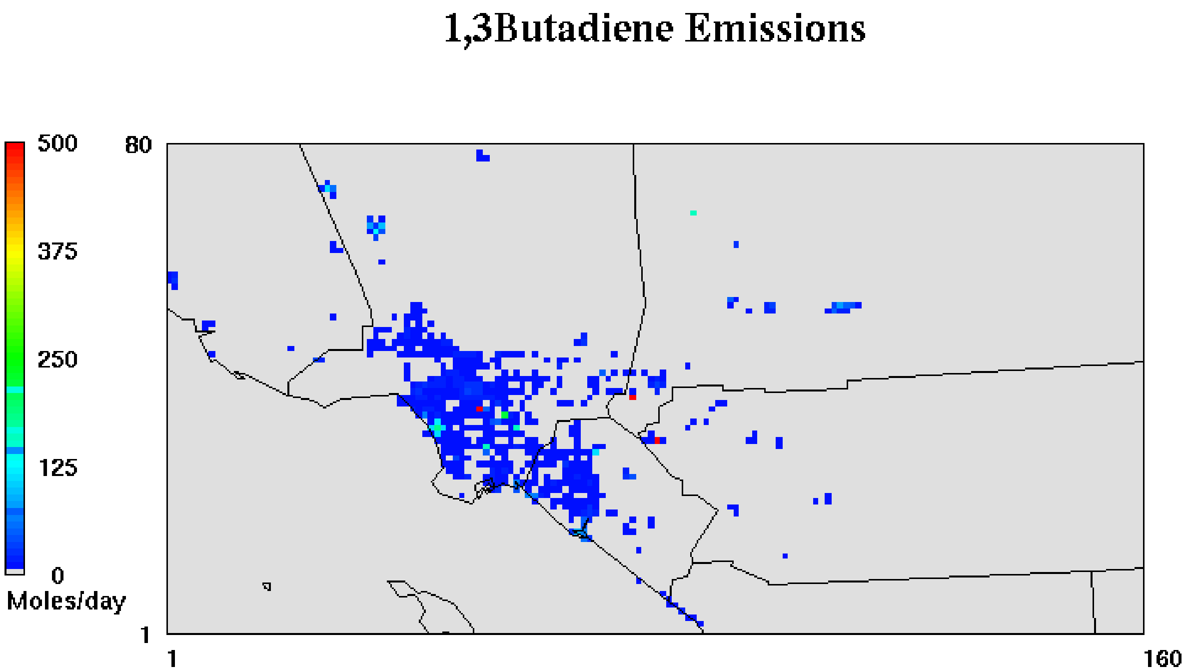


Figure IX-8n
Weekday average 1,3-Butadiene emissions pattern.

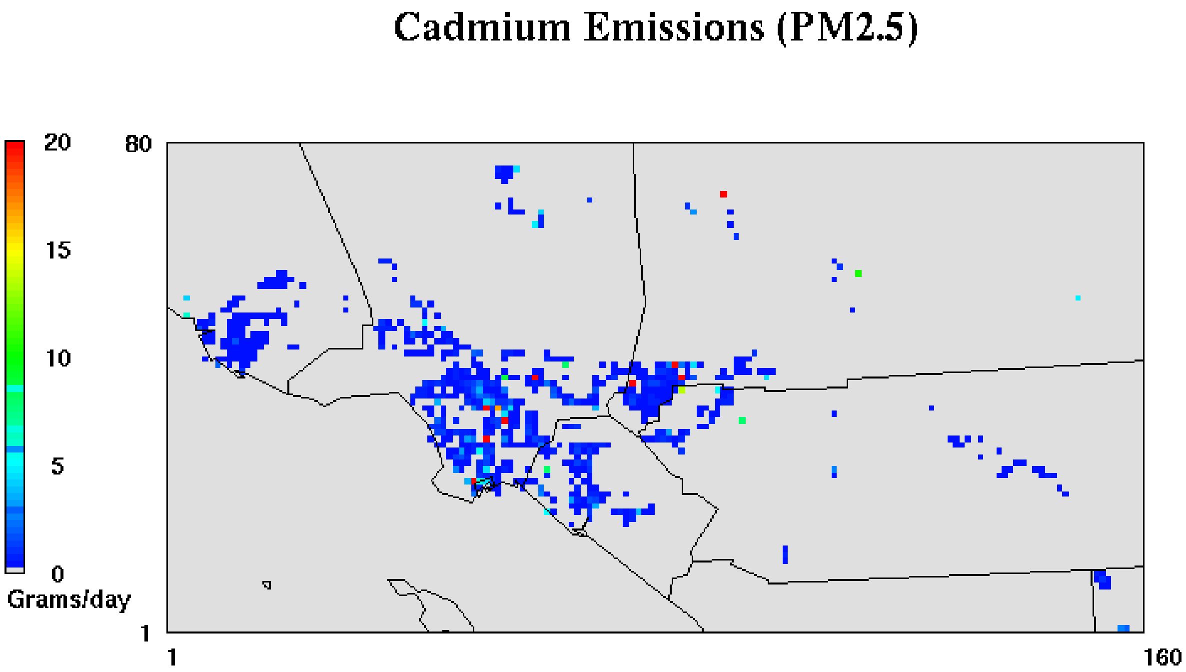


Figure IX-8o
Weekday average Cadmium $PM_{2.5}$ emissions pattern.

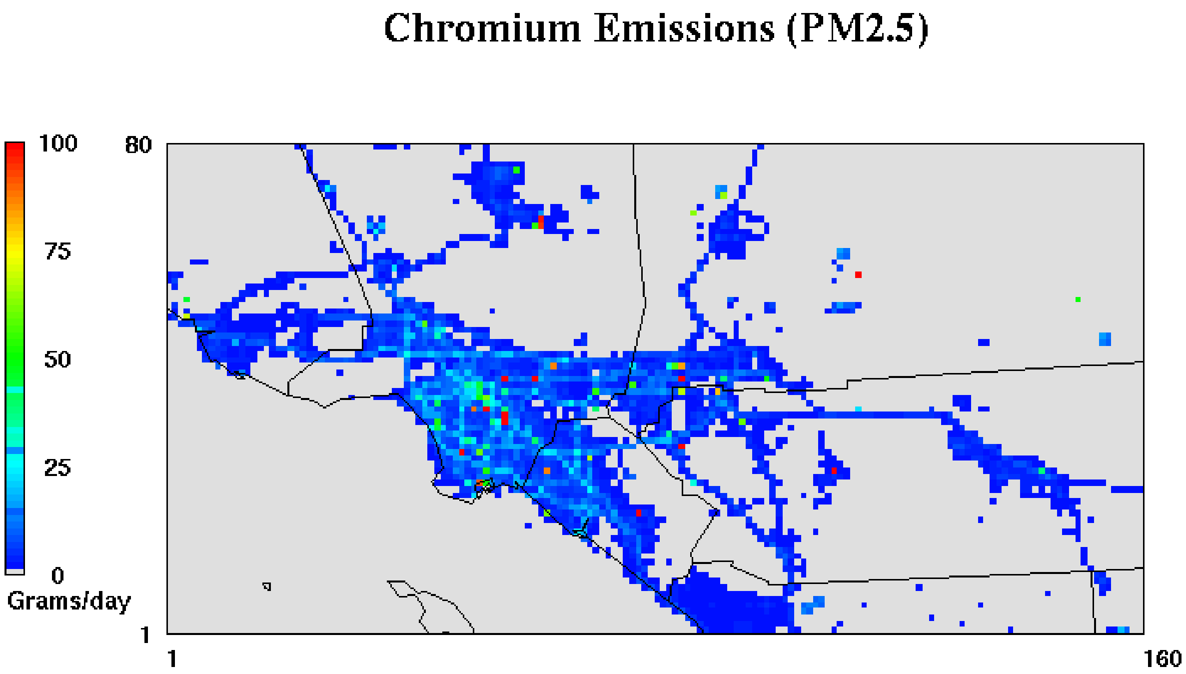


Figure IX-8p
Weekday average Chromium $PM_{2.5}$ emissions pattern.

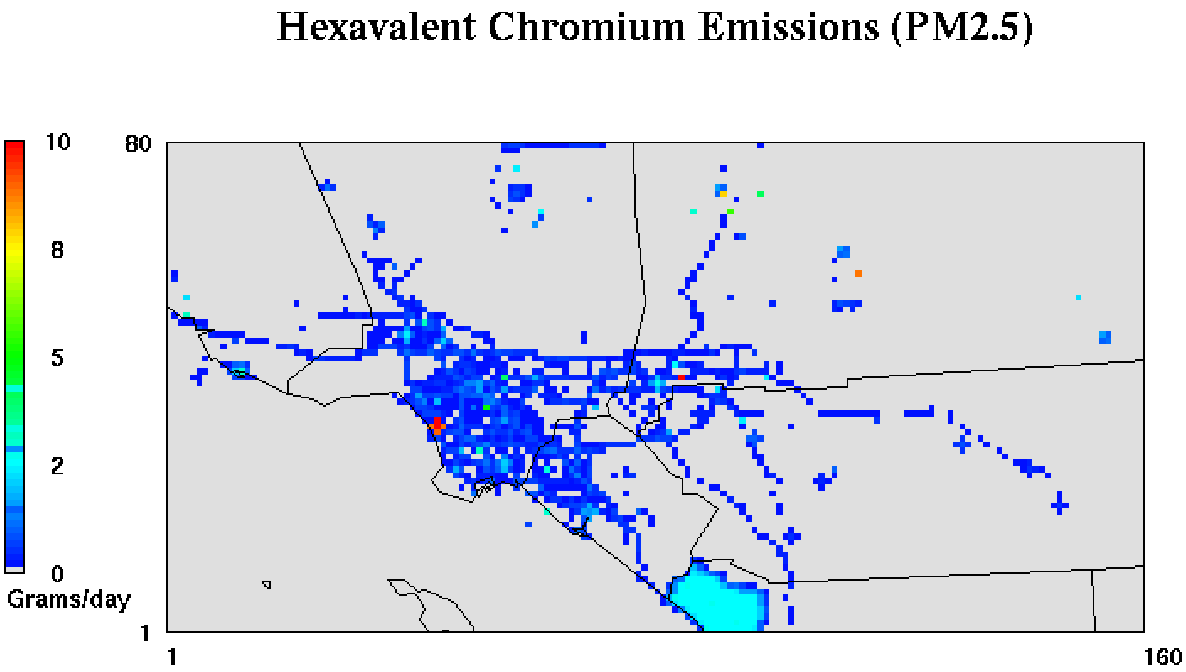


Figure IX-8q
Weekday average Hexavalent Chromium $PM_{2.5}$ emissions pattern.

Lead Emissions (PM2.5)

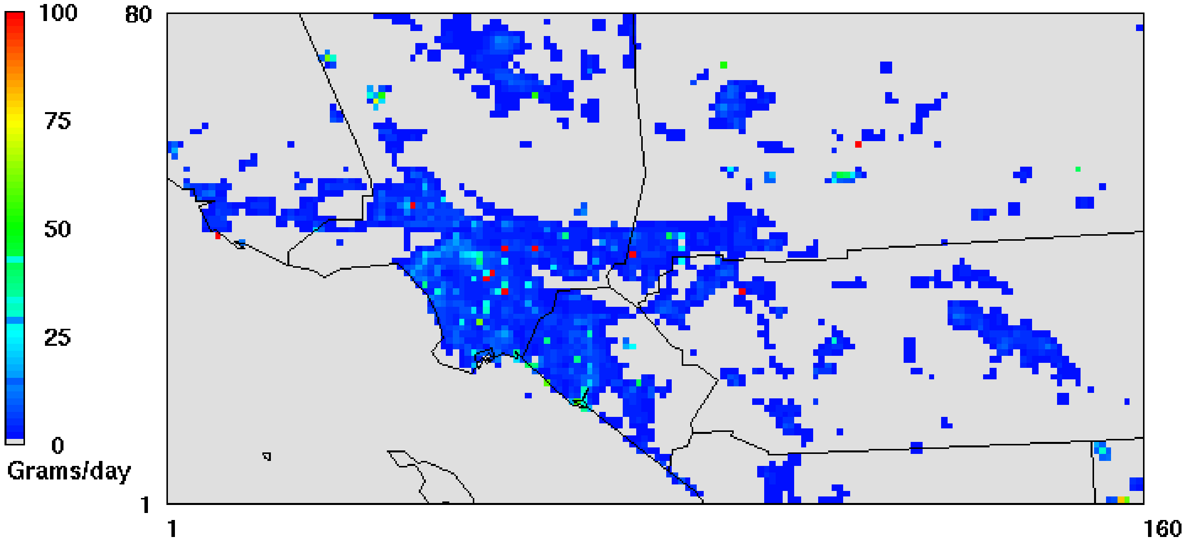


Figure IX-8r
Weekday average Lead $PM_{2.5}$ emissions pattern.

Methylene Chloride Emissions

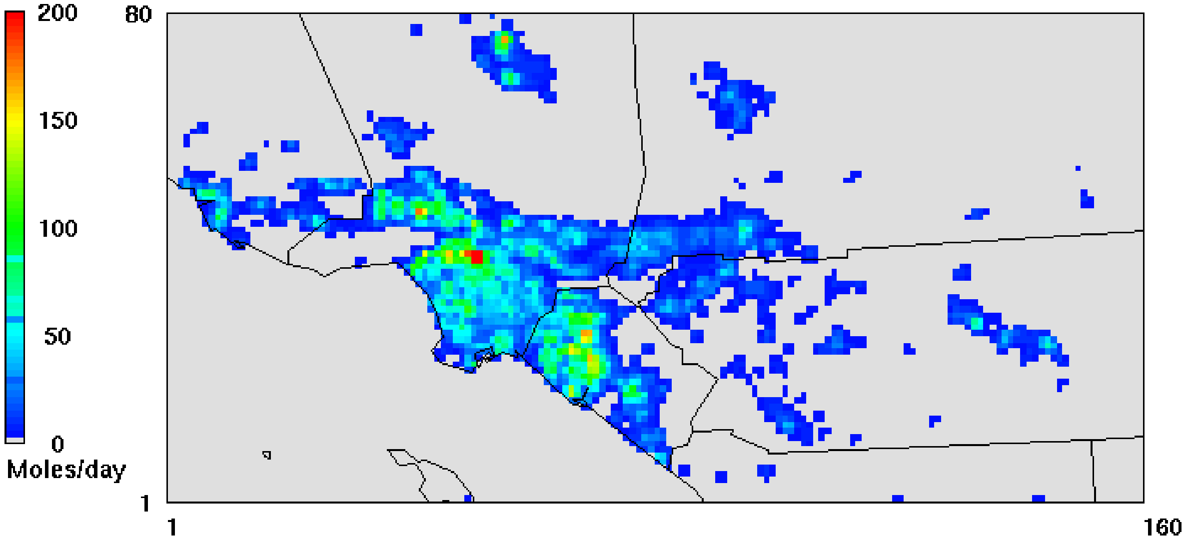


Figure IX-8s
Weekday average Methylene Chloride emissions pattern.

Naphthalene Emissions

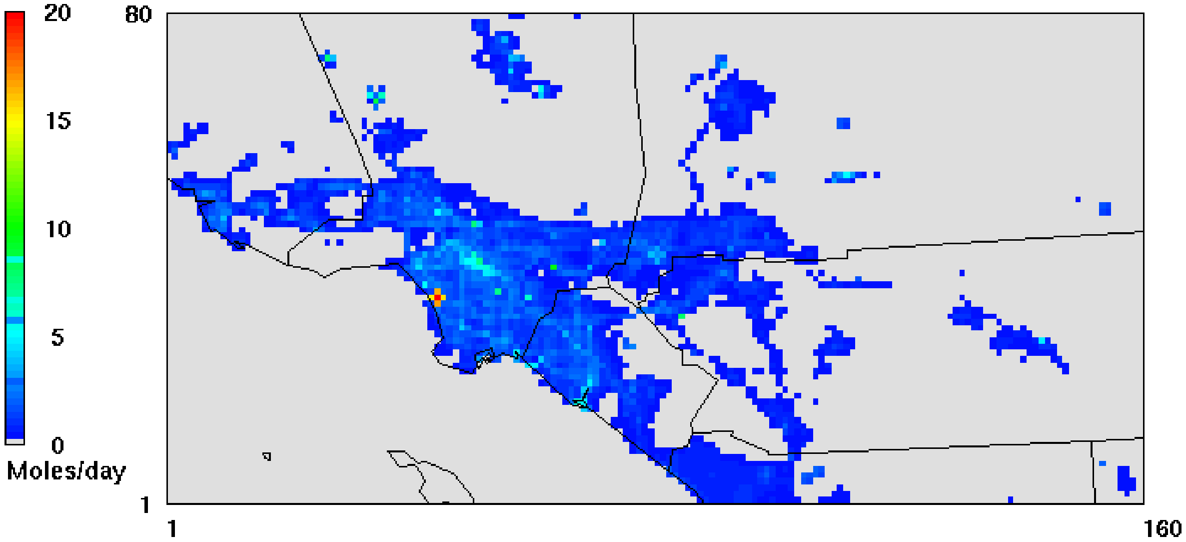


Figure IX-8t
Weekday average Naphthalene emissions pattern.

Nickel Emissions (PM2.5)

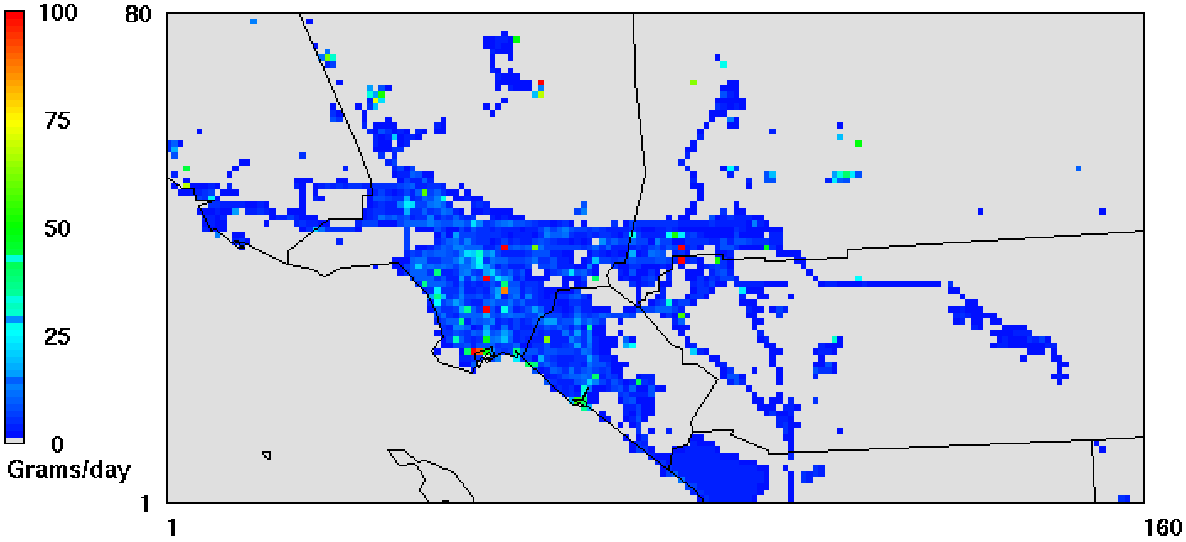


Figure IX-8u
Weekday average Nickel $PM_{2.5}$ emissions pattern.

p-Dichlorobenzene Emissions

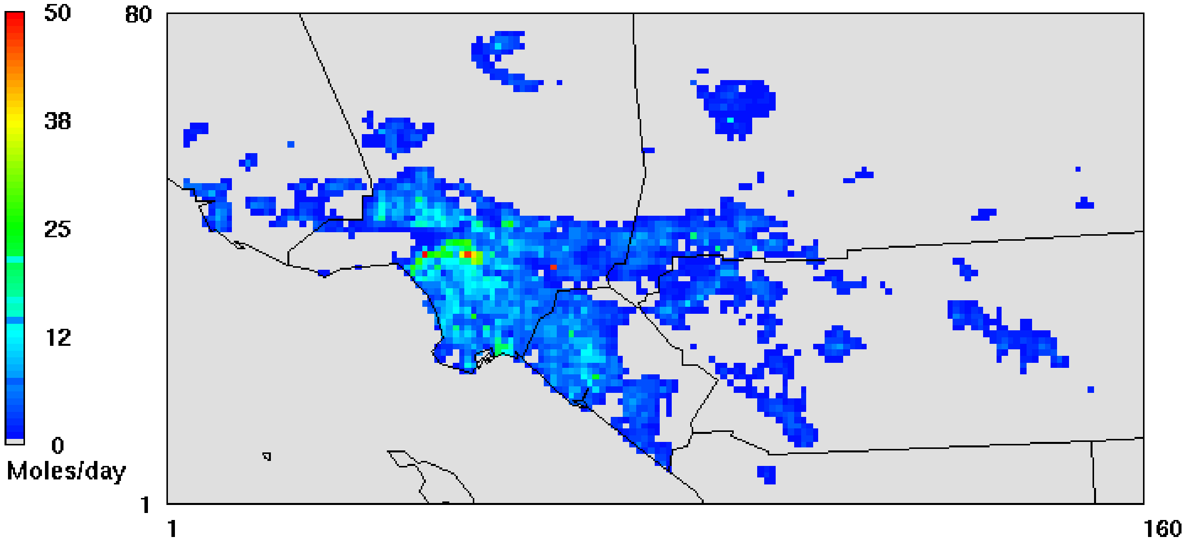


Figure IX-8v
Weekday average p-Dichlorobenzene emissions pattern.

Perchloroethylene Emissions

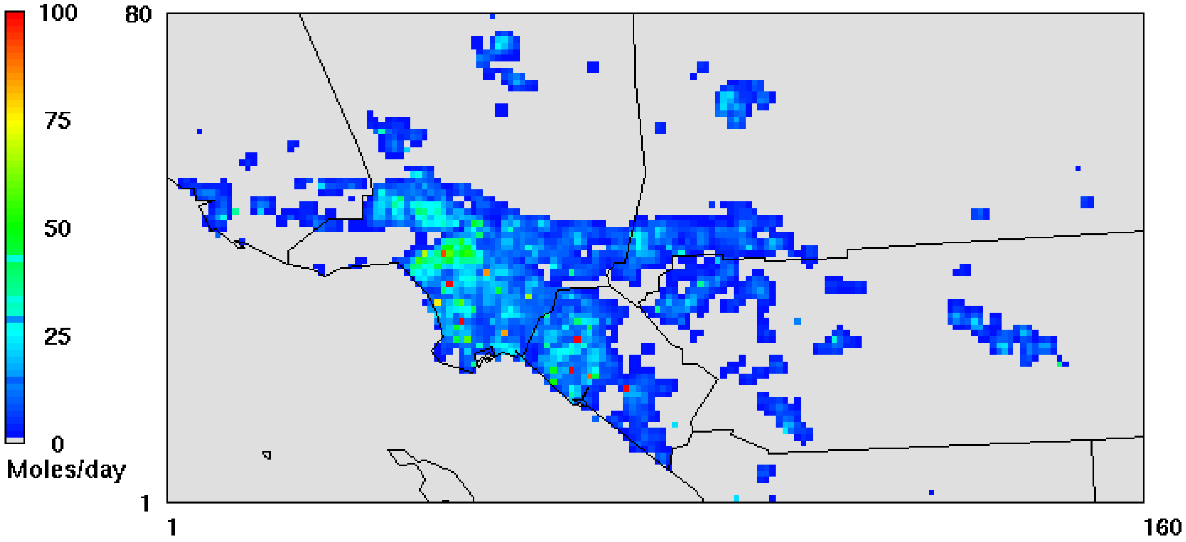


Figure IX-8w
Weekday average Perchloroethylene emissions pattern.

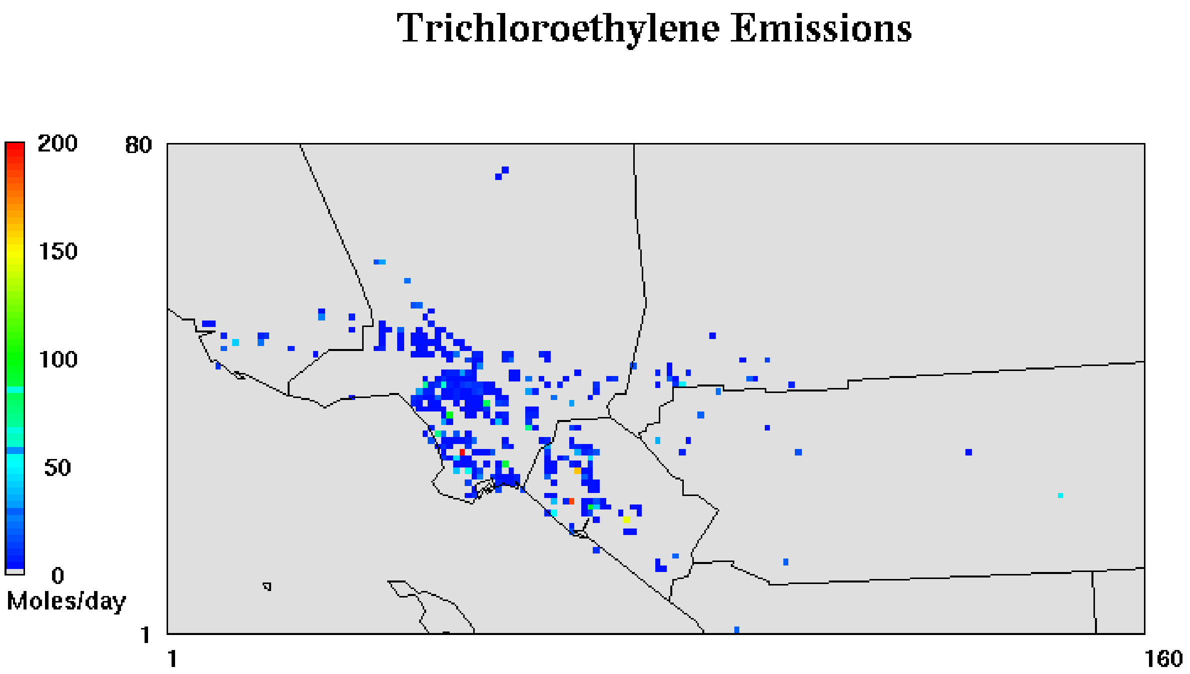


Figure IX-8x
Weekday average Trichloroethylene emissions pattern.

The California Air Resources Board (CARB) maintains the speciation profile library for the California emissions and provides periodic updates. Compared to the MATES III, there are some significant changes in the speciation profiles. In particular, elemental carbon content in diesel emissions increased substantially. In addition, the preparation of on-road emissions was modified. For MATES IV, on-road emissions were prepared based on day-specific temperature and relative humidity with vehicular activities for Monday, Friday, Saturday, Sunday and a single profile representing Tuesday through Thursday, while the MATES III on-road inventories were made with monthly averages of Weekday, Saturday, and Sunday emissions.

IX.11 Boundary and Initial Conditions

The initial and boundary condition files were prepared using the *icbcprep* utility included in the CAMx standard package. The utility prepares uniform boundary and initial conditions with prescribed values. Those values were presented in the Table IX-4. However, the initial values turn out to be not significant in the annual modeling, since the footprint of the initial values typically disappear in approximately seven to 10 days of time integration, depending on grid size and chemical mechanism.

Table IX-4

Boundary Condition Values

Gas (ppm)				Particle (ug/m^3)			
Compound	Value	Compound	Value	Compound	Values	Compound	Value
NO	0.000	ARO1	0.00021	DSL	0.05	DSLC	0.003
NO2	0.0001	ARO2	0.00007	EC	0.05	ECC	0.003
O3	0.03	OLE1	0.00018	OC	0.10	OCC	0.01
HCHO	0.00093	PHCHO	0.0001	CR	0.00001	CRC	0.00001
CCHO	0.00053	PACET	0.0001	CR6	0.00	CR6C	0.00
RCHO	0.00025	SFORM	0.00083	AR	0.00001	ARC	0.00001
ISOP	0.00002	SACET	0.00043	CD	0.00001	CDC	0.00001
MEOH	0.0001	BENZ	0.0001	NI	0.00001	NIC	0.00001
COOH	0.00005	BUTA	0.00001	PB	0.00001	PBC	0.00001
CO	0.2	PDIC	0.00001	DPMa	0.045	DPMaC	0.0001
ETHE	0.00018	MCHL	0.00001	DPMb	0.020	DPMbC	0.0001
ALK1	0.0025	PERC	0.00001	DPMc	0.010	DPMcC	0.0001
ALK2	0.0023	TCE	0.00001	DPMd	0.010	DPMdC	0.0001
ALK3	0.00093	NAPH	0.00001	DPMe	0.001	DPMeC	0.0001

IX.12 Modeling Results

The performance of the CAMx regional modeling simulation is summarized through statistical and graphical analysis, including time series of key pollutant concentrations. Summarized in Table IX-5 are the measurements and model predictions of toxic components during the sampling period. Prediction Accuracy (PA), defined as the percentage difference between the mean observed and simulated concentrations, is given as an indicator for the model performance.

For 2012-2013 period, the model simulated concentrations of particulate matter species, such as $EC_{2.5}$, $EC_{10,}$ and TSP metals, were biased high; this bias was the result, to a large extent, of uncertainties in emission inventory as well as the model's inability to accurately predict extremely low concentrations of PM species present during spring and summer. The model performed better for gaseous species. Concentrations of perchloroethylene, p-dichloroebenzene, trichloroethylene, 1,3-butadiene and naphthalene have become low enough that model performances for those pollutants are immaterial. Benzene, formaldehyde, and acetaldehyde were relatively well-simulated. Modeled and observed concentrations of methylene chloride compared well except at the Rudidoux site. Monitors at this site have experienced a dramatic increase in methylene chloride concentrations since 2009. The source(s) of this increase have not been determined.

Simulated annual average $EC_{2.5}$ and EC_{10} were used to assess overall model performance for the 2012-2013 MATES IV period. Tables IX-6a and IX-6b summarize the 2012-2013 MATES IV $EC_{2.5}$ and EC_{10} model performance, respectively.

EPA guidance (U.S. EPA, 2006) recommends evaluating gaseous and particulate modeling performance using measures of prediction bias and error. PA goals of ±20% for ozone and ±30% for individual components of $PM_{2.5}$ or PM_{10} have been used to assess simulation performance in previous modeling attainment demonstrations.

As shown in the Tables IX-6a and IX-6b, five of the 10 MATES IV sites meet the $PM_{2.5}$ PA goal. The model performed significantly better with predictions of PM_{10} concentrations, with only the Long Beach site exhibiting a large degree (34%) of overprediction of the annual average concentrations. In general, the model underpredicts annual average concentrations in places like Burbank, Inland Valley San Bernardino and Rubidoux, consistent with what was observed in our past modeling effort. On the contrary, concentrations in locations such as Long Beach, Compton, and Los Angeles are overpredicted.

For $EC_{2.5,}$ overprediction was more pronounced than underprediction. Five of the 10 sites did not meet the performance goal due to overprediction. The greatest tendency for overprediction is at the West Long Beach site, with a PA of 67%. The mean error of the simulated versus measured concentrations ranges from 0.40 $\mu g/m^3$ to 1.00 $\mu g/m^3$. For $EC_{10,}$ the model performance is markedly better. PA at nine of the10 MATES IV sites meets the particulate goal with only Long Beach exhibiting a large degree (34%) of overprediction of the annual average concentration. Of the remaining sites, Compton, Los Angeles and West Long Beach are overpredicted by 21, 30 and 21%, respectively. For the remaining sites, PA falls within ±20% of observations. The mean error of the simulated versus measured concentrations ranges from 0.44 $\mu g/m^3$ to 0.86 $\mu g/m^{3.}$

Table IX-7 provides the CAMx RTRAC performance for benzene at the 10 MATES IV monitoring sites. Benzene model performance is included in the evaluation because of the confidence in the benzene measurement data based on the long-term monitoring conducted in the Basin and throughout California. With the exception of West Long Beach (15% over), the annual average benzene concentrations are underpredicted with Compton showing the largest low bias (43 %). This underprediction, can be mostly attributed to lower boundary values than used in the MATES III. Benzene emissions have been reduced by 47% since MATES III. Consequently, a boundary value of 0.15 ppb was used in MATES IV compared to 0.2 ppb in MATES III. In hindsight, since benzene has a long atmospheric residence time, its background value is influenced more by the global emissions. Reduction in the boundary value due to local emissions reductions is probably not warranted. Even with the negative bias, the overall model performance for benzene is reasonable.

The time series fit of the simulated $EC_{2.5}$ and EC_{10} concentrations to measurements for each station is depicted in Figures IX-9a through IX-9j. As evident in the plots, for the four sites (Burbank, Inland Valley San Bernardino, Pico Rivera, and Rubidoux) with moderate under-predictions, the negative bias is mostly due to uncertainties associated with emissions inventory as well as meteorological conditions inductive for high concentrations occurred during winter. In contrast, at the sites where the model overpredicts, low concentrations measured during spring and summer were not simulated accurately, indicating a limitation that a current numerical model has for an exceptionally low concentration case.

IX.13 Comparison with MATES III Simulation

Tables IX-8 and IX-9 provide a comparison of the 2012-2013 MATES IV and 2005 MATES III model performance for $EC_{2.5}$ and benzene, respectively. Listed in each table are PA, bias, and mean error.

As presented in Table IX-9, compared to MATES III modeling, where only one site (Burbank) exhibited substantial underprediction, MATES IV modeling exhibited an overall tendency to overpredict $EC_{2.5}$. The overall characteristics of the two sets of modeling are similar: i.e. the sites with under or overpredictions are consistent. The two sets of modeling results for benzene behaved similarly. The model underpredicted concentrations in places like Burbank and Compton and overpredicted concentrations in West Long Beach.

IX.14 Simulation Evaluation Averaged Over the Monitoring Network

For this comparison, the monitored data for six stations are combined to provide an estimate of average Basin-wide conditions for the two sampling periods: 2012-2013 and 2005. Table IX-10 summarizes the network average measured and predicted pollutant concentrations over the eight sites. Two stations in 2005, Huntington Park and Pico Rivera, did not have complete measurement records for the full 12 months and were excluded from the analysis. CAMx RTRAC simulated pollutant concentrations for the eight stations that have complete data for the two measurement periods were calculated from the grid data using the distance weighted nine-cell average. Measured concentrations of naphthalene were available for Long Beach, Central

Los Angeles, and Rubidoux. Each of the four counties is represented by at least one station. The eight stations' average measured and simulated concentrations provide an estimate of the regional profile but with a bias towards impacts to the coastal communities in the heavily transited areas of the Basin. Moreover, the assessment provides a direct comparison for model performance evaluation.

For 2012-2013, the model simulated concentrations of particulate matter species, such as $EC_{2.5}$, EC_{10}, and TSP metals were biased high. The model performed better for gaseous species. Concentrations of perchloroethylene, p-dichloroebenzene, trichloroethylene, 1,3-butadiene and naphthalene have become low enough that model performances for those pollutants are immaterial. Benzene, formaldehyde and acetaldehyde were well-simulated. Modeled and observed concentrations of methylene chloride compared exceptionally well except at the Rubidoux site. Monitors at this site have experienced a dramatic increase in methylene chloride concentrations since 2009. The source(s) of this increase have not been determined.

In general, 2005 model simulated particulate $EC_{2.5}$, EC_{10}, hexavalent chromium and $PM_{2.5}$ nickel average annual toxic compound concentrations compared well with the measured annual average values. The majority of gaseous components were well-simulated with the sole exception of acetaldehyde, which was underpredicted. Arsenic and TSP lead exhibit the greatest tendency for overprediction. Cadmium and $PM_{2.5}$ lead concentrations tend to be underpredicted. In general, the concentrations of the gaseous compounds are closely recreated.

IX.15 Simulation Estimated Spatial Concentration Fields

Figures IX-10a through IX-10u depict the CAMx projected annual average concentration distributions of selected toxic compounds as well as the impacts of five emissions categories of diesel particulates in the Basin. In general, the distribution of diesel particulates follows the major arterials. The highest concentration (2.9 $\mu g/m^3$) was simulated to occur around the Ports of Los Angeles and Long Beach. The peak diesel concentration is much lower than the previous MATES studies, due, in a large part, to emission reductions from ocean-going vessels at near coastal waters and at ports. Figures IX-10h and IX-10i provide the distributions of benzene and 1,3-butadiene, respectively, whereby the toxic compounds are almost uniformly distributed throughout the Basin (reflecting patterns of gasoline fuel consumption). The ambient concentrations of formaldehyde in the SCAB are made up from direct emissions, primarily from combustion sources, secondary formation from the oxidation of anthropogenic and biogenic VOCs. The formaldehyde profile, shown in Figure IX-10j, depicts this characteristic of its origins, with measurable concentrations in the heavily traveled western and central Basin and additional elevated levels in the downwind areas of the Basin that are impacted by higher levels of ozone formation. Due to continued reduction of combustion source emissions, the formaldehyde concentrations are dominated by secondary formation. The peak formaldehyde concentrations are now in the areas with elevated biogenic emissions.

Table IX-5

2012-2013 Station Observed and CAMx Simulated MATES IV Annual Average Concentrations

Compound	Units	Anaheim			Burbank			Compton			Inland Valley San Bernardino		
		Obs	Model	PA	Obs	Model	PA	Obs	Model	PA	Obs	Model	PA
1,3-Butadiene	ppb	0.09	0.04	-57	0.12	0.04	-71	0.14	0.05	-62	0.07	0.02	-65
Acetaldehyde	ppb	0.59	0.90	53	1.08	0.98	-9	0.84	0.87	3	1.03	0.99	4
As (2.5)	ηg/m^3	N/A	0.40	N/A	N/A	0.37	N/A	N/A	0.62	N/A	N/A	0.36	N/A
As (TSP)	ηg/m^3	0.24	0.53	121	0.46	0.58	27	0.52	1.42	175	0.91	0.87	-5
Benzene	ppb	0.33	0.28	-14	0.46	0.28	-38	0.50	0.28	-43	0.29	0.22	-24
Cd (2.5)	ηg/m^3	N/A	0.15	N/A	N/A	0.12	N/A	N/A	0.54	N/A	N/A	0.35	N/A
Cd (TSP)	ηg/m^3	N/A	0.25	N/A	N/A	0.23	N/A	N/A	0.69	N/A	N/A	0.70	N/A
Cr6 (TSP)	ηg/m^3	0.03	0.15	470	0.04	0.16	575	0.12	0.19	60	0.05	0.18	296
EC$_{10}$	µg/m^3	1.17	1.39	18	1.74	1.43	-18	1.50	1.81	21	1.74	1.42	-18
EC$_{2.5}$	µg/m^3	0.90	1.10	22	1.32	1.19	-9	1.06	1.48	39	1.38	1.13	-18
Formaldehyde	ppb	1.19	1.67	40	2.58	1.89	-27	2.08	1.66	-20	2.63	1.89	-28
Methylene Chloride	ppb	0.37	0.30	-20	0.24	0.28	18	0.17	0.26	50	0.28	0.13	-53
Naphthalene	ppb												
Ni (2.5)	ηg/m^3	N/A	2.87	N/A	N/A	1.85	N/A	N/A	6.98	N/A	N/A	3.07	N/A
Ni (TSP)	ηg/m^3	1.74	4.72	171	3.90	3.02	-22	4.06	8.31	105	4.05	4.57	13
Pb (2.5)	ηg/m^3	N/A	1.25	N/A	N/A	1.27	N/A	N/A	1.96	N/A	N/A	3.69	N/A
Pb (TSP)	ηg/m^3	2.14	3.37	57	5.27	3.82	-28	6.24	4.83	-23	9.80	9.67	-1
p-Dichlorobenzene	ppb	0.02	0.06	273	0.02	0.06	146	0.02	0.06	233	0.01	0.04	282
Perchloroethylene	ppb	0.04	0.09	118	0.05	0.08	83	0.04	0.09	113	0.05	0.05	6
Trichloroethylene	ppb	0.01	0.04	266	0.02	0.04	112	0.01	0.05	342	0.01	0.03	108

Table IX-5 (Continued)

2012-2013 Station Observed and CAMx Simulated MATES IV Annual Average Concentrations

Compound	Units	Huntington Park			North Long Beach			Central Los Angeles			Pico Rivera		
		Obs	Model	PA	Obs	Model	PA	Obs	Model	PA	Obs	Model	PA
1,3-Butadiene	ppb	0.15	0.18	21	0.09	0.05	-48	0.11	0.05	-52	0.09	0.04	-57
Acetaldehyde	ppb	1.04	0.97	-7	0.67	0.85	27	0.94	1.05	11	1.25	1.00	-20
As (2.5)	ηg/m^{3}	N/A	5.21	N/A	N/A	0.98	N/A	N/A	0.64	N/A	N/A	1.14	N/A
As (TSP)	ηg/m^{3}	0.56	6.11	997	0.41	1.45	256	0.64	1.45	72	0.57	1.77	209
Benzene	ppb	0.53	0.33	-38	0.33	0.30	-10	0.40	0.37	-8	0.35	0.27	-21
Cd (2.5)	ηg/m^{3}	N/A	0.40	N/A	N/A	0.49	N/A	N/A	0.22	N/A	N/A	0.27	N/A
Cd (TSP)	ηg/m^{3}	N/A	0.62	N/A	N/A	0.64	N/A	N/A	0.40	N/A	N/A	0.46	N/A
Cr6 (TSP)	ηg/m^{3}	0.07	0.28	289	0.04	0.19	334	0.07	0.24	247	0.05	0.17	251
EC$_{10}$	µg/m^{3}	1.65	1.98	20	1.29	1.72	34	1.67	2.17	30	1.87	1.69	-10
EC$_{2.5}$	µg/m^{3}	1.30	1.70	31	0.91	1.45	59	1.23	1.81	47	1.39	1.30	-6
Formaldehyde	ppb	2.73	1.92	-30	1.86	1.76	-6	2.93	2.11	-28	2.81	1.81	-36
Methylene Chloride	ppb	0.24	0.33	37	0.24	0.23	-1	0.32	0.42	0.32	0.17	0.23	38
Naphthalene	ppb				0.015	0.011	-27	0.029	0.014	-51			
Ni (2.5)	ηg/m^{3}	N/A	4.03	N/A	N/A	6.92	N/A	N/A	2.76	N/A	N/A	2.77	N/A
Ni (TSP)	ηg/m^{3}	5.40	5.68	5	3.65	8.59	136	3.37	4.57	36	4.48	4.11	-8
Pb (2.5)	ηg/m^{3}	N/A	3.75	N/A	N/A	2.26	N/A	N/A	2.14	N/A	N/A	1.80	N/A
Pb (TSP)	ηg/m^{3}	9.46	7.66	-19	4.47	4.99	12	7.34	6.17	-16	5.89	4.69	-20
p-Dichlorobenzene	ppb	0.03	0.07	180	0.01	0.06	321	0.03	0.09	203	0.01	0.06	293
Perchloroethylene	ppb	0.04	0.11	165	0.02	0.10	390	0.03	0.09	203	0.03	0.08	192
Trichloroethylene	ppb	0.02	0.06	300	0.01	0.07	550	0.03	0.04	35	0.02	0.03	120

Table IX-5 (Continued)
2012-2013 Station Observed and CAMx Simulated MATES IV Annual Average Concentrations

Compound	Units	Rubidoux			West Long Beach		
		Obs	Model	PA	Obs	Model	PA
1,3-Butadiene	ppb	0.08	0.02	-77	0.11	0.05	-55
Acetaldehyde	ppb	0.84	0.97	16	0.75	0.87	16
As (2.5)	ηg/m^3	N/A	0.38	N/A	N/A	0.57	N/A
As (TSP)	ηg/m^3	0.76	0.62	-18	0.50	2.15	333
Benzene	ppb	0.28	0.21	-24	0.36	0.41	15
Cd (2.5)	ηg/m^3	N/A	0.15	N/A	N/A	1.04	N/A
Cd (TSP)	ηg/m^3	N/A	0.44	N/A	N/A	1.24	N/A
Cr6 (TSP)	ηg/m^3	0.04	0.12	180	0.03	0.19	471
EC$_{10}$	µg/m^3	1.48	1.26	-14	1.78	2.15	21
EC$_{2.5}$	µg/m^3	1.11	0.98	-12	1.13	1.88	67
Formaldehyde	ppb	2.00	1.76	-12	1.55	2.12	37
Methylene Chloride	ppb	2.11	0.13	-94	0.24	0.22	-10
Naphthalene	ppb	0.017	0.011	-35			
Ni (2.5))	ηg/m^3	N/A	2.18	N/A	N/A	13.29	N/A
Ni (TSP)	ηg/m^3	3.35	3.17	-5	3.73	15.42	313
Pb (2.5)	ηg/m^3	N/A	1.16	N/A	N/A	3.04	N/A
Pb (TSP)	ηg/m^3	6.21	3.70	-41	5.83	5.74	-1
p-Dichlorobenzene	ppb	0.02	0.04	123	0.01	0.06	417
Perchloroethylene	ppb	0.02	0.05	179	0.02	0.09	355
Trichloroethylene	ppb	0.01	0.03	133	0.03	0.07	127

Table IX-6a

MATES IV 2012-2013 $EC_{2.5}$ Model Performance

Location	$EC_{2.5}$ Observed (µg/m^3)	Samples	Modeled Sampling Days (µg/m^3)	Prediction Accuracy	Mean Bias (µg/m^3)	Mean Error (µg/m^3)	Normalized Mean Bias	Normalized Mean Error
Anaheim	0.90	59	1.10	22	0.20	0.56	1.08	1.24
Burbank	1.32	58	1.19	-9	-0.12	0.64	0.43	0.73
Compton	1.06	61	1.48	39	0.42	0.76	1.52	1.64
Inland Valley San Bernardino.	1.38	59	1.13	-18	-0.25	0.46	-0.03	0.31
Huntington Park	1.30	58	1.70	31	0.40	0.67	0.85	0.93
Long Beach	0.91	60	1.45	59	0.53	0.80	2.18	2.27
Central L.A.	1.23	60	1.81	47	0.58	0.70	0.91	0.96
Pico Rivera	1.39	60	1.30	-6	-0.09	0.48	0.26	0.52
Rubidoux	1.11	61	0.98	-12	-0.13	0.40	0.12	0.44
West Long Beach	1.13	61	1.88	67	0.75	1.00	2.10	2.17
All Stations	1.17	597	1.40	20	0.23	0.65	0.95	1.13

Table IX-6b

MATES IV 2012-2013 EC_{10} Model Performance

Location	$EC_{2.5}$ Observed (μg/m^3)	Samples	Modeled Sampling Days (μg/m^3)	Prediction Accuracy	Mean Bias (μg/m^3)	Mean Error (μg/m^3)	Normalized Mean Bias	Normalized Mean Error
Anaheim	1.17	61	1.39	18	0.22	0.49	0.44	0.54
Burbank	1.74	57	1.43	-18	-0.31	0.60	-0.03	0.34
Compton	1.50	57	1.81	21	0.32	0.66	0.58	0.68
Inland Valley San Bernardino.	1.74	61	1.42	-18	-0.32	0.47	-0.08	0.27
Huntington Park	1.65	52	1.98	20	0.33	0.54	0.36	0.43
Long Beach	1.29	58	1.72	34	0.44	0.59	0.61	0.68
Central L.A.	1.67	60	2.17	30	0.50	0.61	0.46	0.51
Pico Rivera	1.87	50	1.69	-10	-0.18	0.44	-0.02	0.24
Rubidoux	1.48	59	1.26	-14	-0.22	0.44	-0.06	0.29
West Long Beach	1.78	51	2.15	21	0.37	0.86	0.53	0.69
All Stations	1.58	566	1.69	7	0.11	0.57	0.28	0.47

Table IX-7
2012-2013 Simulation Performance Statistics for Benzene

Location	Observed (ppb)	Samples	Predicted (ppb)	PA	Mean Bias (ppb)	Mean Error (ppb)	Normalized Mean Bias	Normalized Mean Error
Anaheim	0.33	51	0.28	-14	-0.05	0.16	0.24	0.58
Burbank	0.46	55	0.28	-38	-0.17	0.22	-0.18	0.39
Compton	0.50	57	0.28	-43	-0.21	0.26	-0.09	0.40
Inland Valley San Bernardino	0.29	53	0.22	-24	-0.07	0.09	-0.13	0.28
Huntington Park	0.53	52	0.33	-38	-0.20	0.22	-0.21	0.30
North Long Beach	0.33	54	0.30	-10	-0.03	0.10	0.07	0.31
Central L.A.	0.40	51	0.37	-8	-0.03	0.12	0.05	0.30
Pico Rivera	0.35	57	0.27	-21	-0.07	0.12	-0.03	0.33
Rubidoux	0.28	51	0.21	-24	-0.07	0.10	-0.10	0.32
West Long Beach	0.36	57	0.41	15	0.05	0.20	0.77	0.95

Table IX-8
Comparative Simulation Performance Statistics for **$EC_{2.5}$**

	MATES IV (2012-2013)					MATES III (2005)				
Location	Observed Days ($\mu g/m^3$)	Modeled Sampling Days ($\mu g/m^3$)	PA	Bias ($\mu g/m^3$)	Mean Error ($\mu g/m^3$)	Observed Days ($\mu g/m^3$)	Modeled Sampling Days ($\mu g/m^3$)	PA	Bias ($\mu g/m^3$)	Mean Error ($\mu g/m^3$)
Anaheim	0.90	1.10	22	0.20	0.56	1.41	1.35	-4	-0.06	0.54
Burbank	1.32	1.19	-9	-0.12	0.64	2.04	1.03	-50	-1.02	1.11
Compton	1.06	1.48	39	0.42	0.76	1.76	1.88	7	0.12	0.61
Inland Valley San Bernardino	1.38	1.13	-18	-0.25	0.46	2.18	1.77	-19	-0.41	0.91
Huntington Park	1.30	1.70	31	0.40	0.67	-	-	-	-	-
North Long Beach	0.91	1.45	59	0.53	0.80	1.40	1.71	21	0.30	0.61
Central L.A.	1.23	1.81	47	0.58	0.70	1.93	2.04	6	0.11	0.76
Pico Rivera	1.39	1.30	-6	-0.09	0.48	-	-	-	-	-
Rubidoux	1.11	0.98	-12	-0.13	0.40	1.69	1.32	-22	-0.38	0.74
West Long Beach	1.13	1.88	67	0.75	1.00	2.07	2.14	3	0.07	0.79

Table IX-9
Comparative Simulation Performance Statistics for Benzene

	MATES IV (2012-2013)					MATES III (2005)				
Location	Observed Days (ppb)	Modeled Sampling Days (ppb)	PA	Bias (ppb)	Mean Error (ppb)	Observed Days (ppb)	Modeled Sampling Days (ppb)	PA	Bias (ppb)	Mean Error (ppb)
Anaheim	0.33	0.28	-14	-0.05	0.16	0.44	0.50	15	0.06	0.22
Burbank	0.46	0.28	-38	-0.17	0.22	0.71	0.47	-34	-0.24	0.34
Compton	0.50	0.28	-43	-0.21	0.26	0.80	0.57	-29	-0.23	0.39
Inland Valley San Bernardino.	0.29	0.22	-24	-0.07	0.09	0.49	0.44	-11	-0.05	0.17
Huntington Park	0.53	0.33	-38	-0.20	0.22					
North Long Beach	0.33	0.30	-10	-0.03	0.10	0.50	0.57	13	0.07	0.21
Central L.A.	0.40	0.37	-8	-0.03	0.12	0.59	0.69	16	0.10	0.25
Pico Rivera	0.35	0.27	-21	-0.07	0.12					
Rubidoux	0.28	0.21	-24	-0.07	0.10	0.44	0.44	2	0.01	0.16
West Long Beach	0.36	0.41	15	0.05	0.20	0.53	0.60	14	0.07	0.21

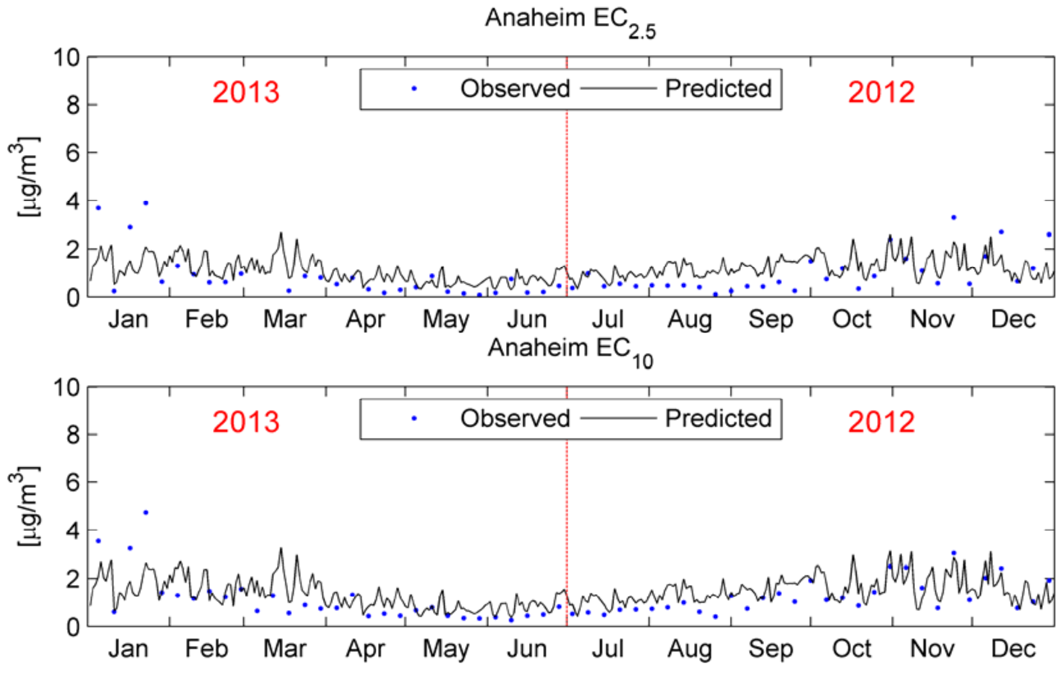


Figure IX-9a

$EC_{2.5}$ and EC_{10} Time Series: Simulated vs. Measured at Anaheim.

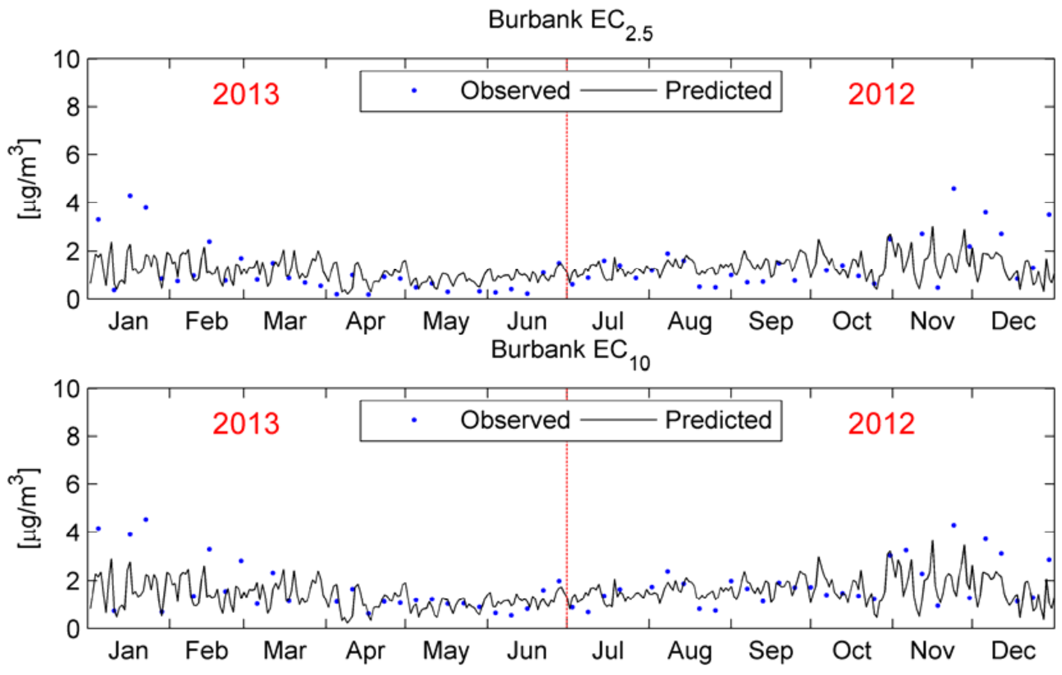


Figure IX-9b

Same as Figure IX-9a except Burbank.

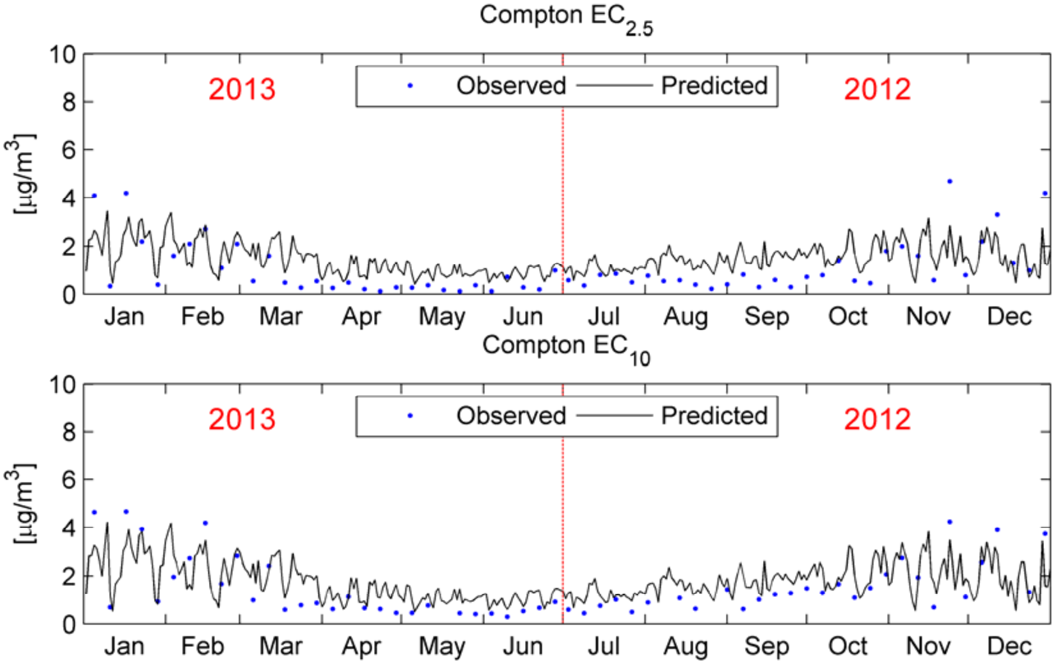


Figure IX-9c
Same as Figure IX-9a except Compton.

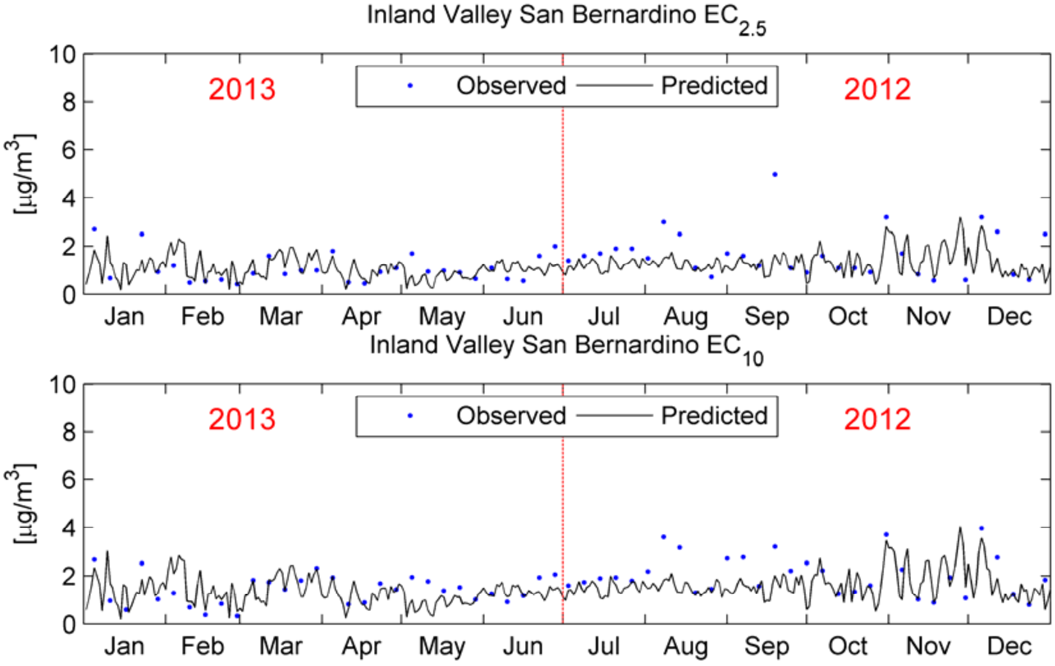


Figure IX-9d
Same as Figure IX-9a except Inland Valley San Bernardino.

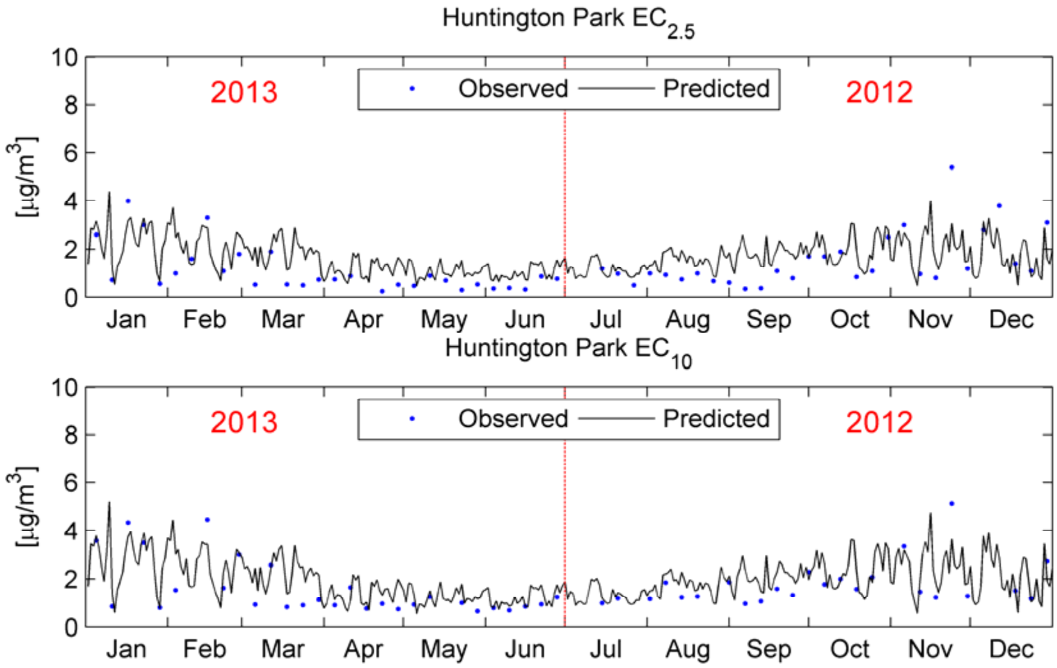


Figure IX-9e

Same as Figure IX-9a except Huntington Park

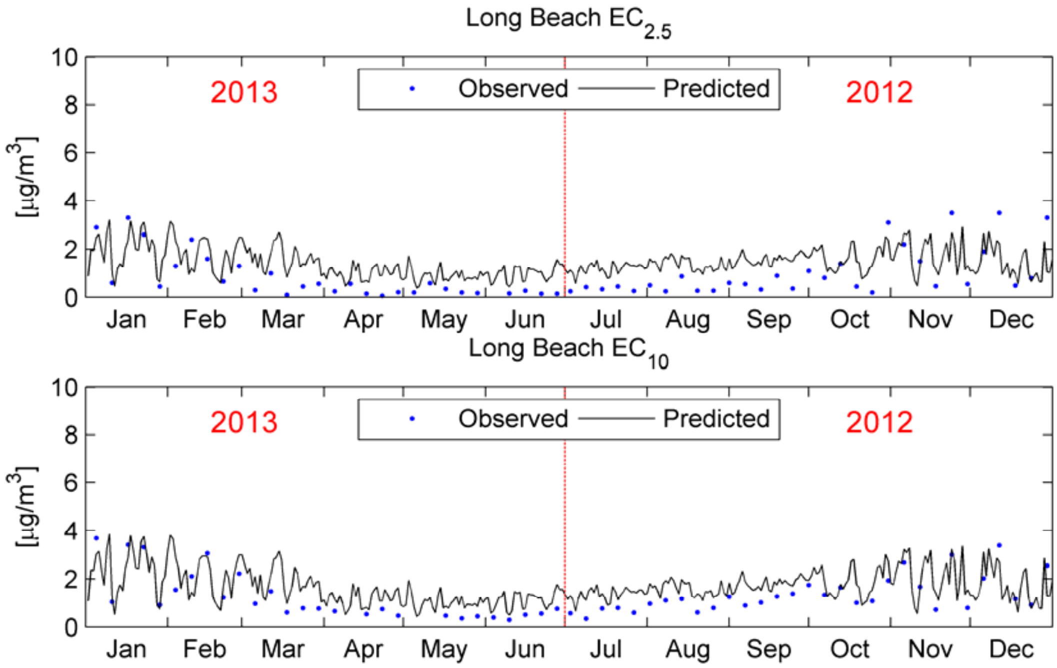


Figure IX-9f

Same as Figure IX-9a except North Long Beach.

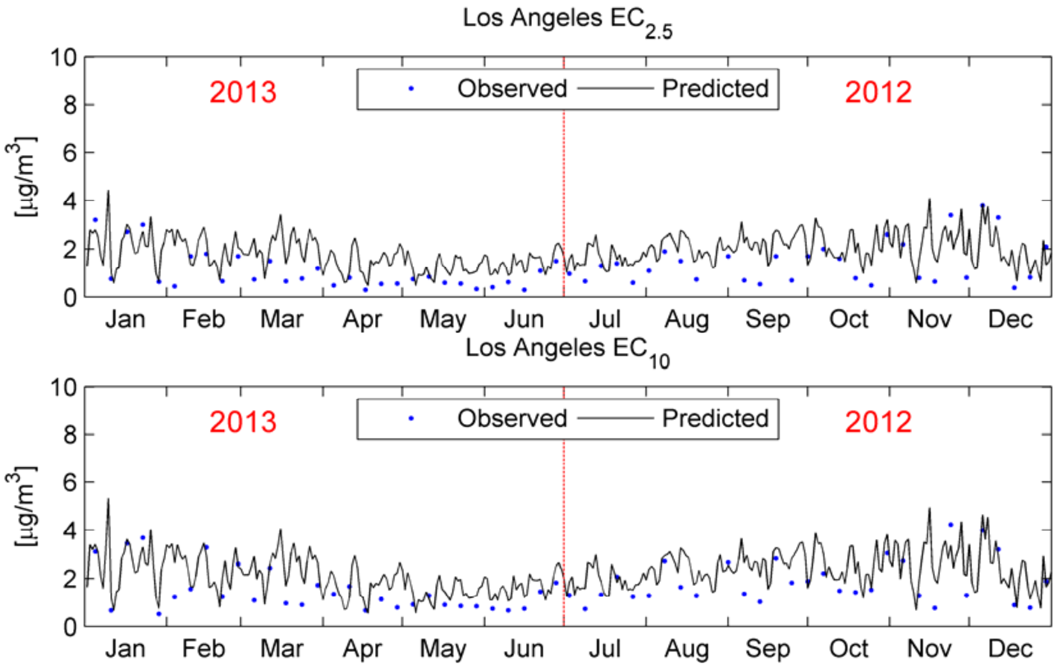


Figure IX-9g
Same as Figure IX-9a except Central Los Angeles.

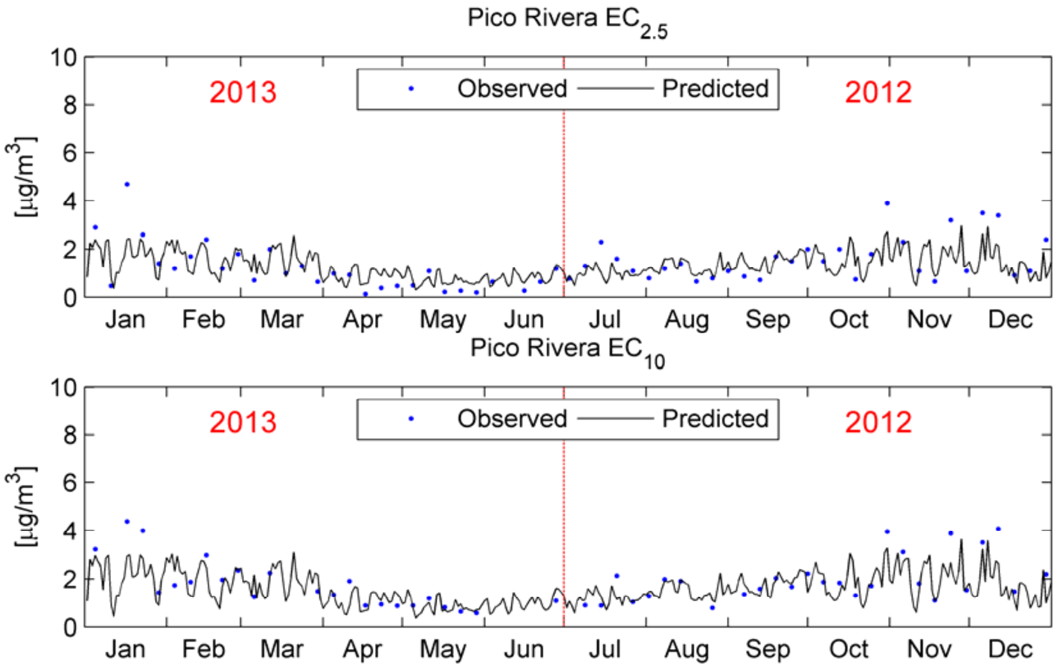


Figure IX-9h
Same as Figure IX-9a except Pico Rivera.

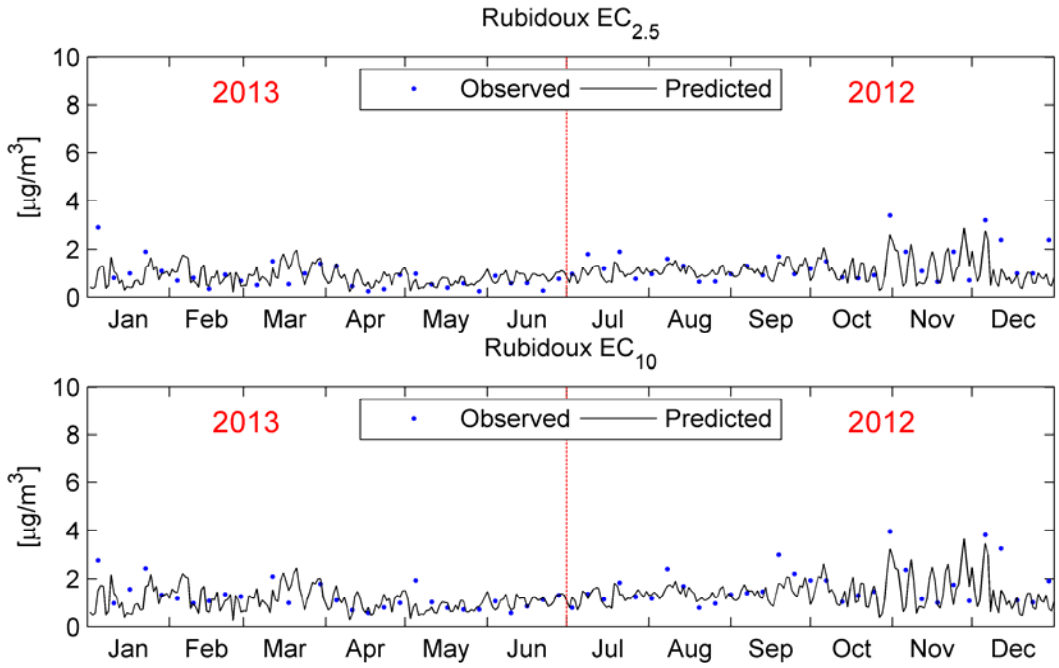


Figure IX-9i

Same as Figure IX-9a except Rubidoux.

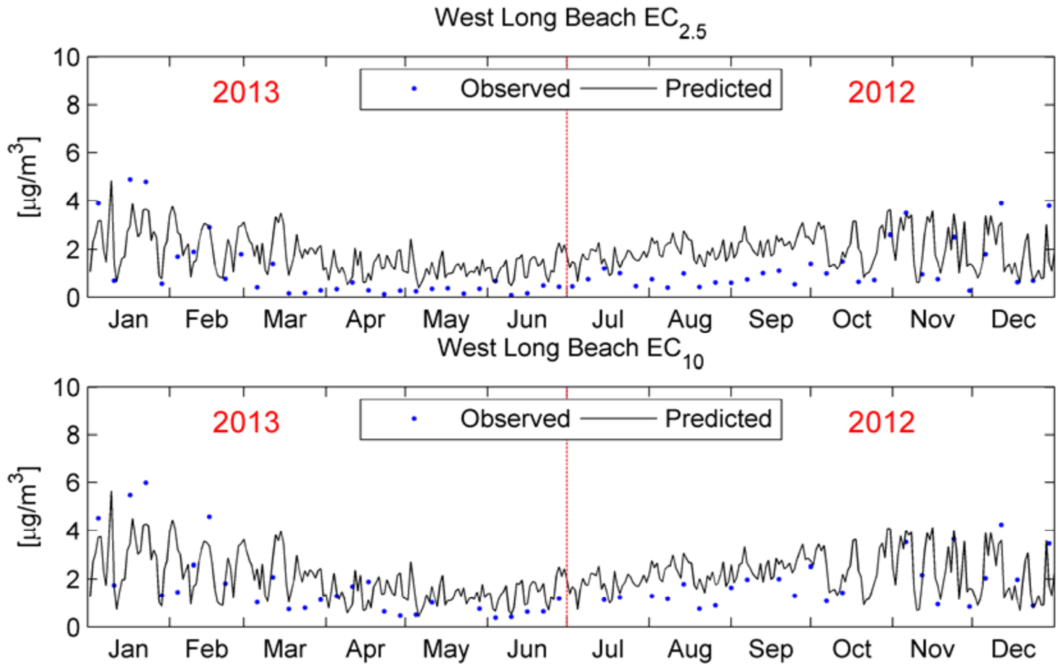


Figure IX-9j

Same as Figure IX-9a except West Long Beach.

Table IX-10
Toxic Compounds Simulated and Measured Eight-Station Annual Average Concentrations
For 2012-2013 MATES IV and 2005MATES III periods using CAMX RTRAC

Compound	Units	2012-2013MATES IV		2005 MATES III	
		Measured Annual Average	Simulated Annual Average	Measured Annual Average	Simulated Annual Average
$EC_{2.5}$	μg/m^3	0.96	1.39	1.81	1.69
EC_{10}	μg/m^3	1.33	1.68	2.05	2.15
Cr 6 (TSP)	ηg/m^3	0.05	0.18	0.23	0.21
As (2.5)	ηg/m^3	N/A	0.66	0.49	1.07
As (TSP)	ηg/m^3	0.44	1.07	0.68	2.57
Cd (2.5)	ηg/m^3	N/A	0.38	1.49	0.59
Cd (TSP)	ηg/m^3	0.13	0.56	1.53	0.88
Ni (2.5))	ηg/m^3	N/A	4.58	4.44	4.88
Ni (TSP)	ηg/m^3	2.98	6.64	5.40	7.55
Pb (2.5)	ηg/m^3	N/A	2.10	5.32	2.53
Pb (TSP)	ηg/m^3	4.69	5.26	10.64	8.68
Benzene	ppb	0.33	0.29	0.56	0.54
Perchloroethylene	ppb	0.03	0.08	0.06	0.10
p-Dichlorobenzene	ppb	0.02	0.04	0.04	0.08
Methylene Chloride	ppb	0.46	0.24	0.32	0.33
Trichloroethylene	ppb	0.02	0.04	0.03	0.03
1,3-Butadiene	ppb	0.09	0.04	0.11	0.09
Formaldehyde	ppb	1.78	1.91	3.52	3.26
Acetaldehyde	ppb	0.71	0.95	1.60	1.11
Naphthalene	ppb	0.02*	0.01	0.02*	0.01

* Three station average

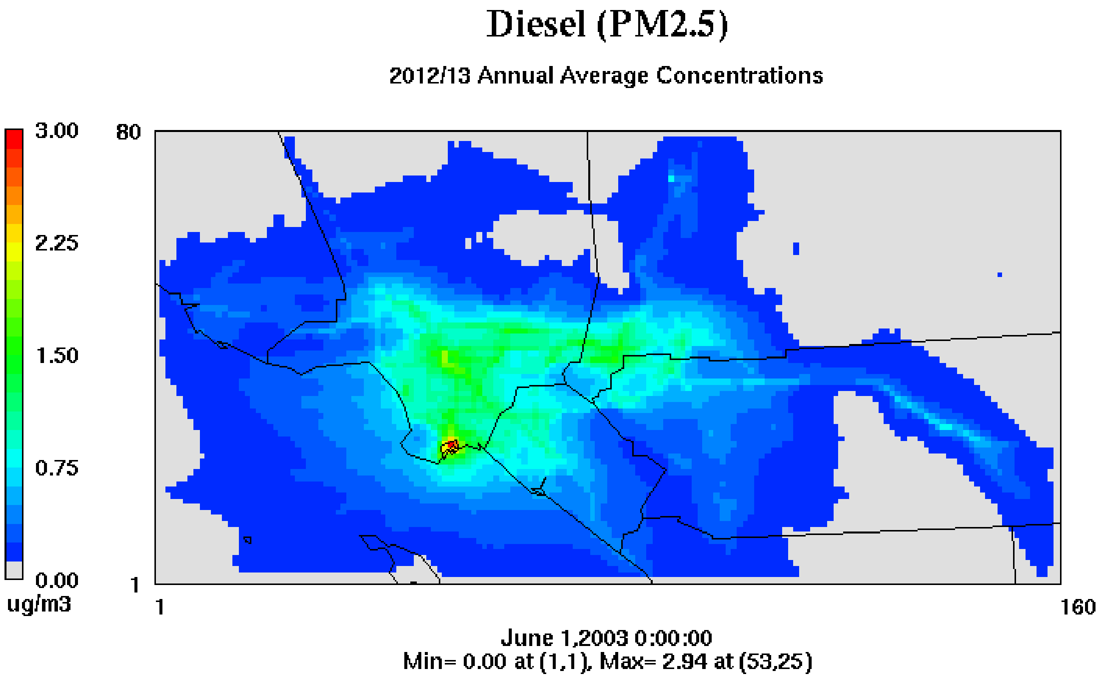


Figure IX-10a

CAMx simulated 2012 annual average Diesel $PM_{2.5}$.

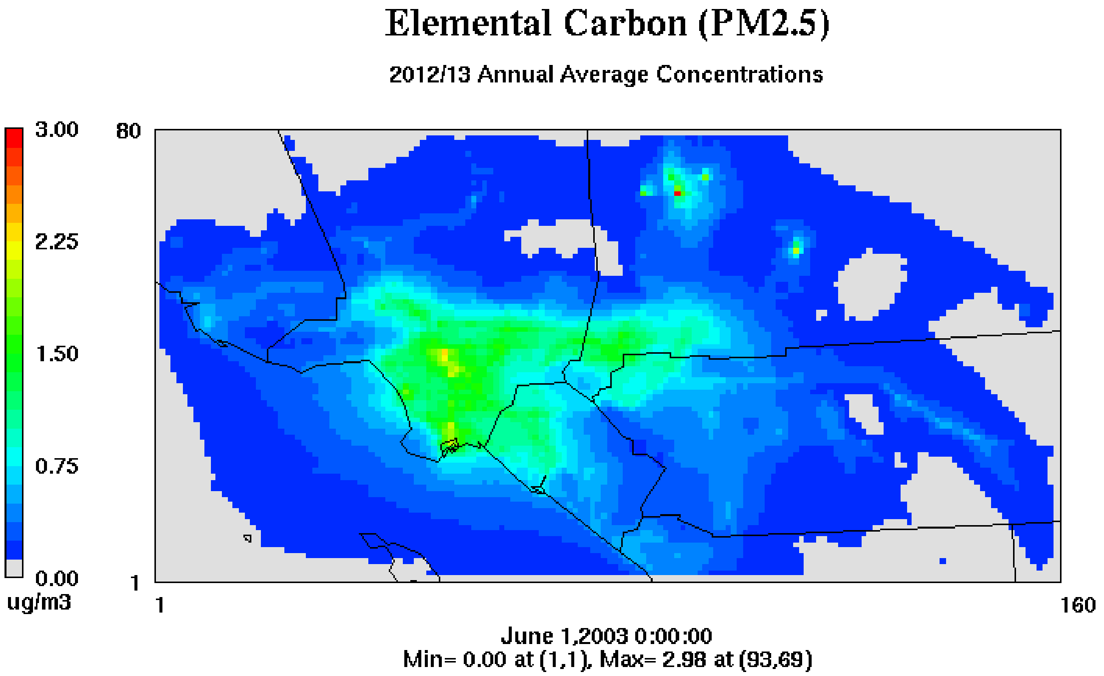


Figure IX-10b

CAMx simulated 2012 annual average Elemental Carbon $PM_{2.5}$.

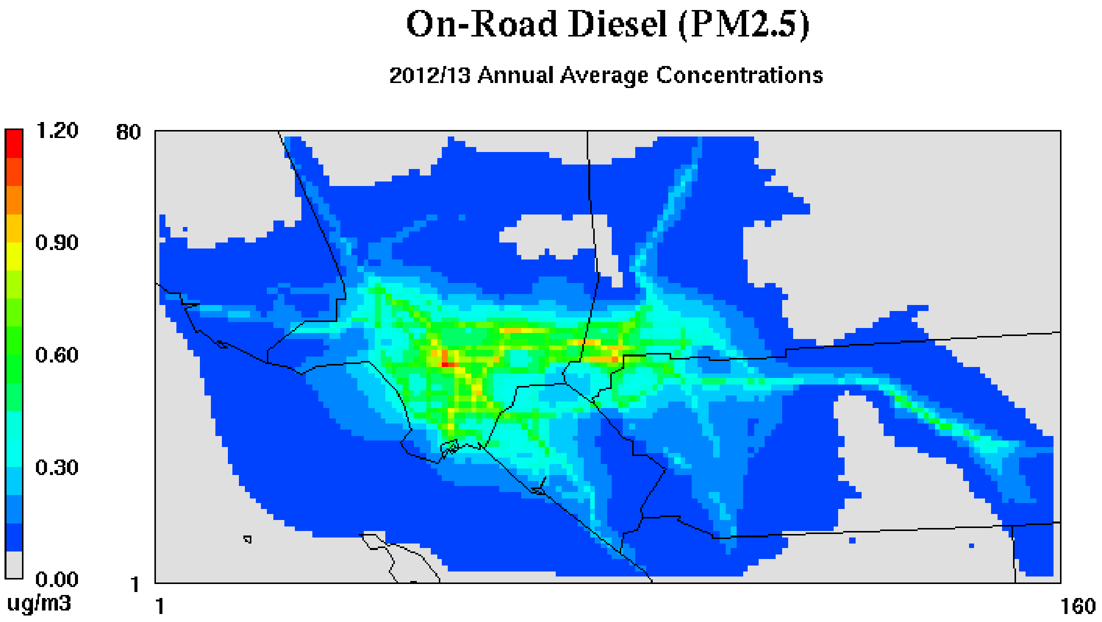


Figure IX-10c
CAMx simulated 2012 annual average On-Road Diesel $PM_{2.5}$.

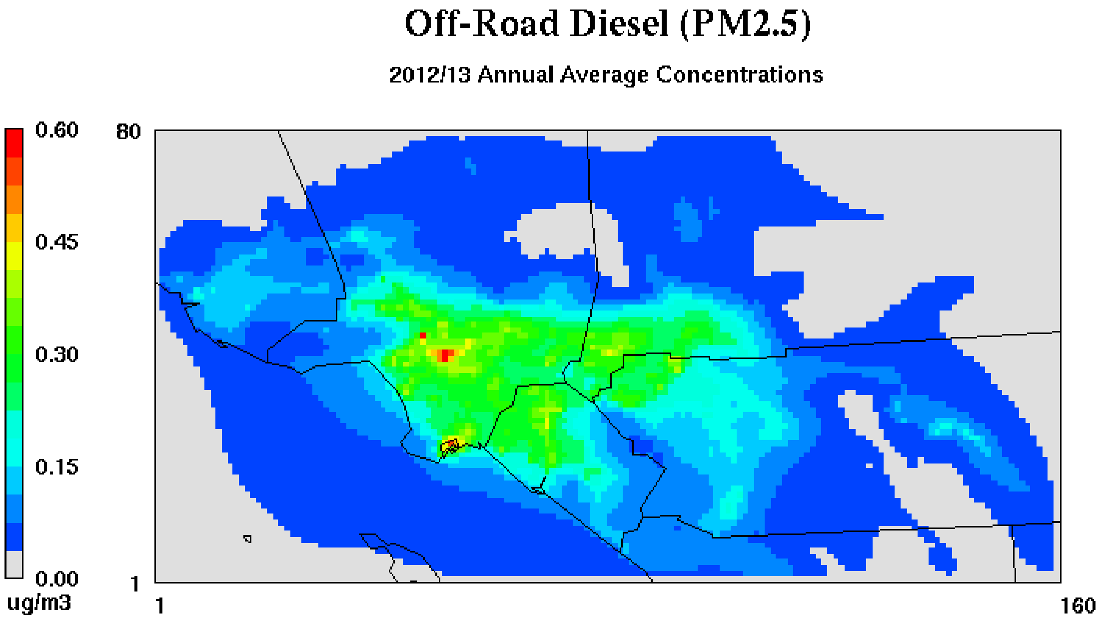


Figure IX-10d
CAMx simulated 2012 annual average Off-Road Diesel $PM_{2.5}$.

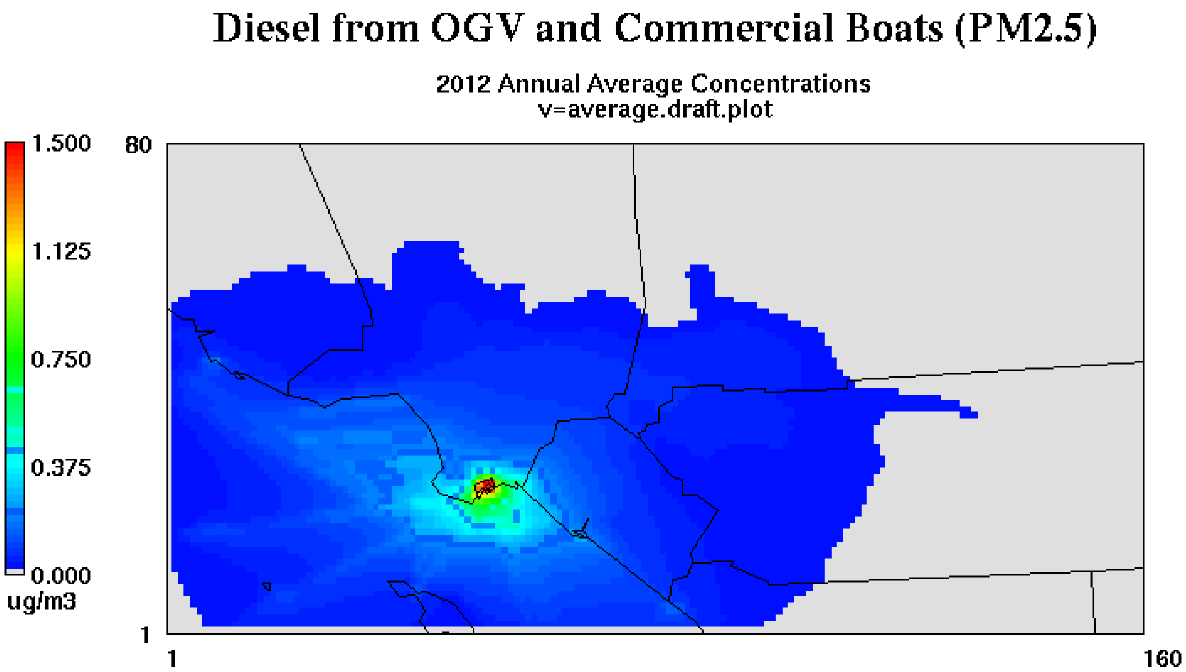


Figure IX-10e
CAMx simulated 2012 annual average Diesel from Ships $PM_{2.5}$.

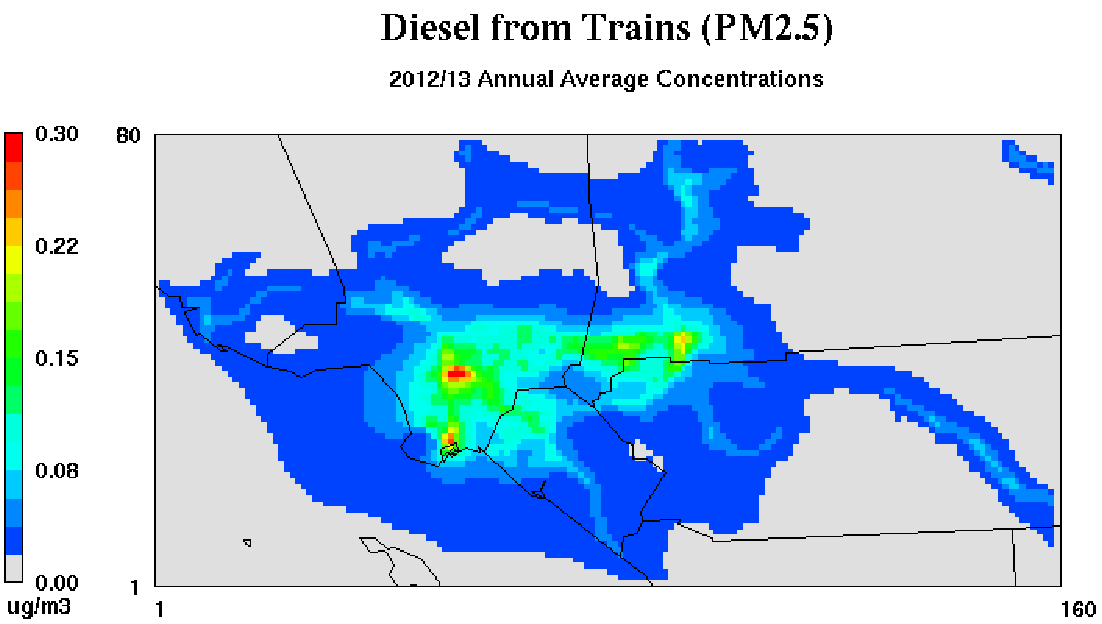


Figure IX-10f
CAMx simulated 2012 annual average Diesel from Trains $PM_{2.5}$.

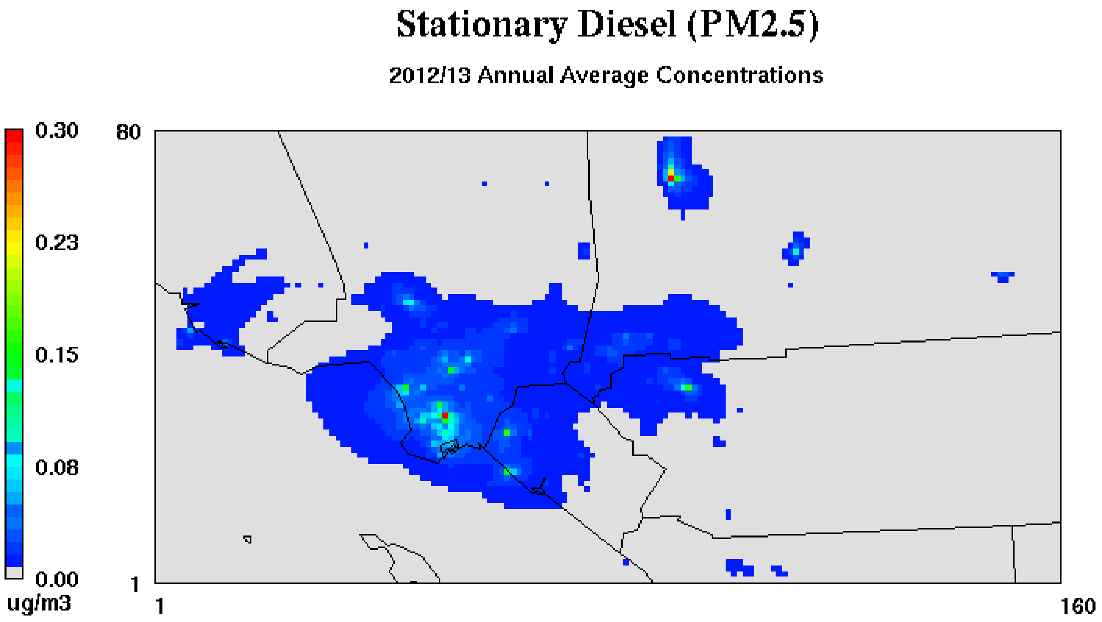


Figure IX-10g
CAMx simulated 2012 annual average Diesel from Stationary Sources $PM_{2.5}$.

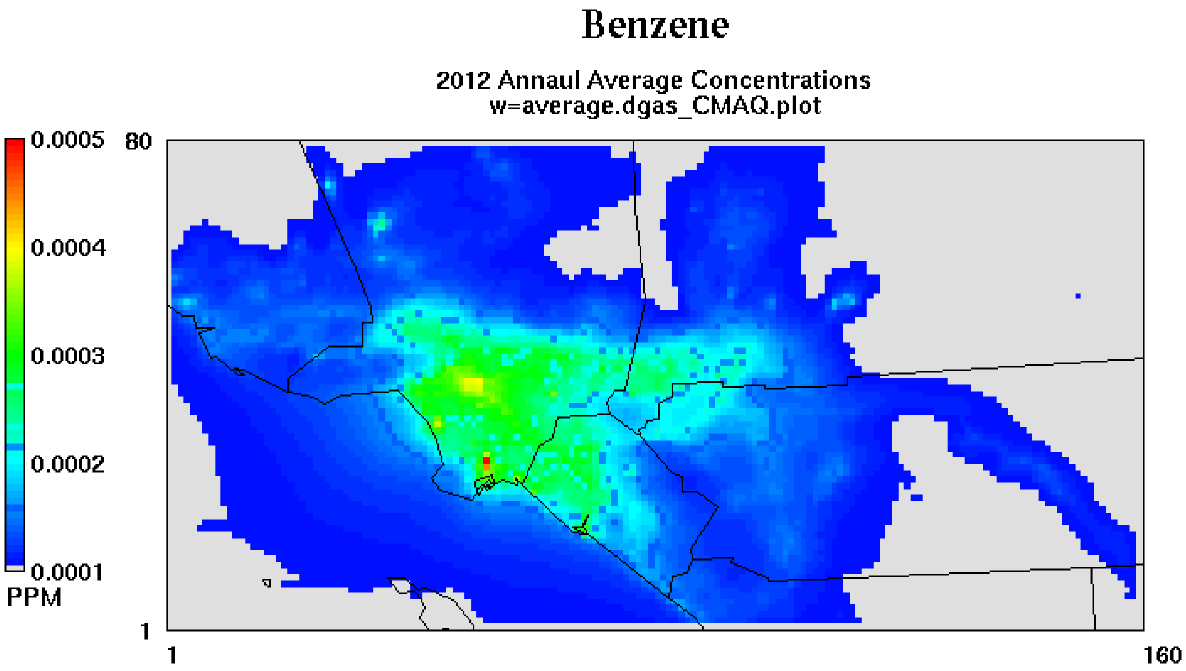


Figure IX-10h
CAMx simulated 2012 annual average Benzene.

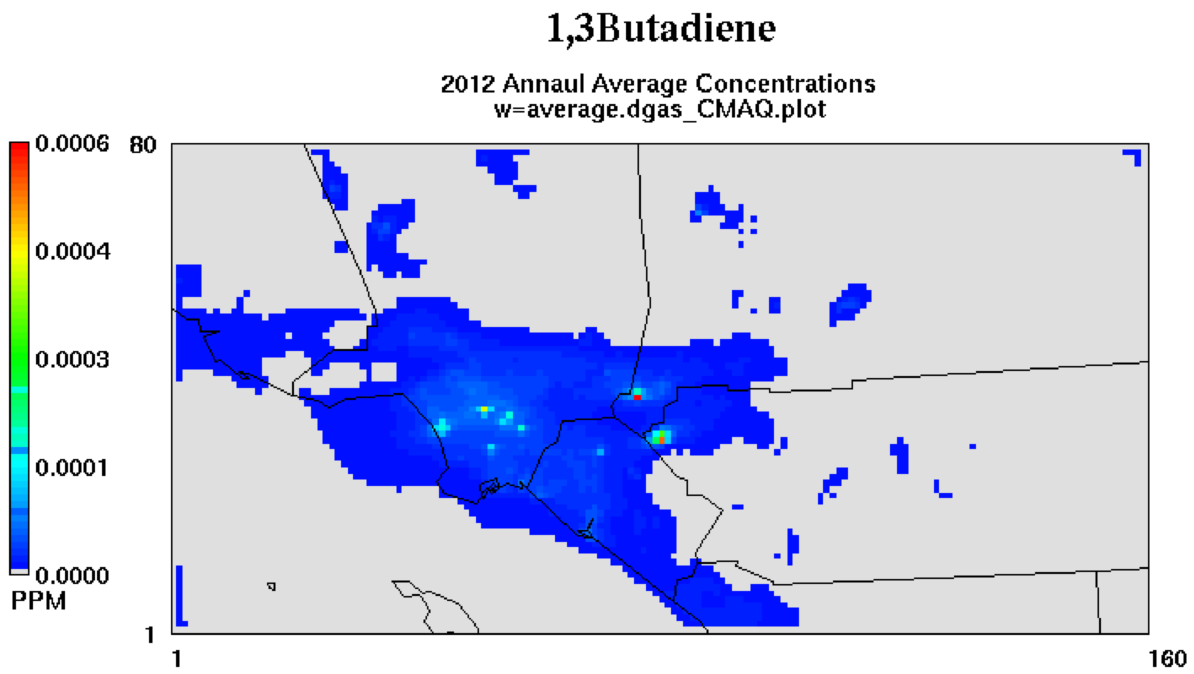


Figure IX-10i
CAMx simulated 2012 annual average 1,3-Butadiene.

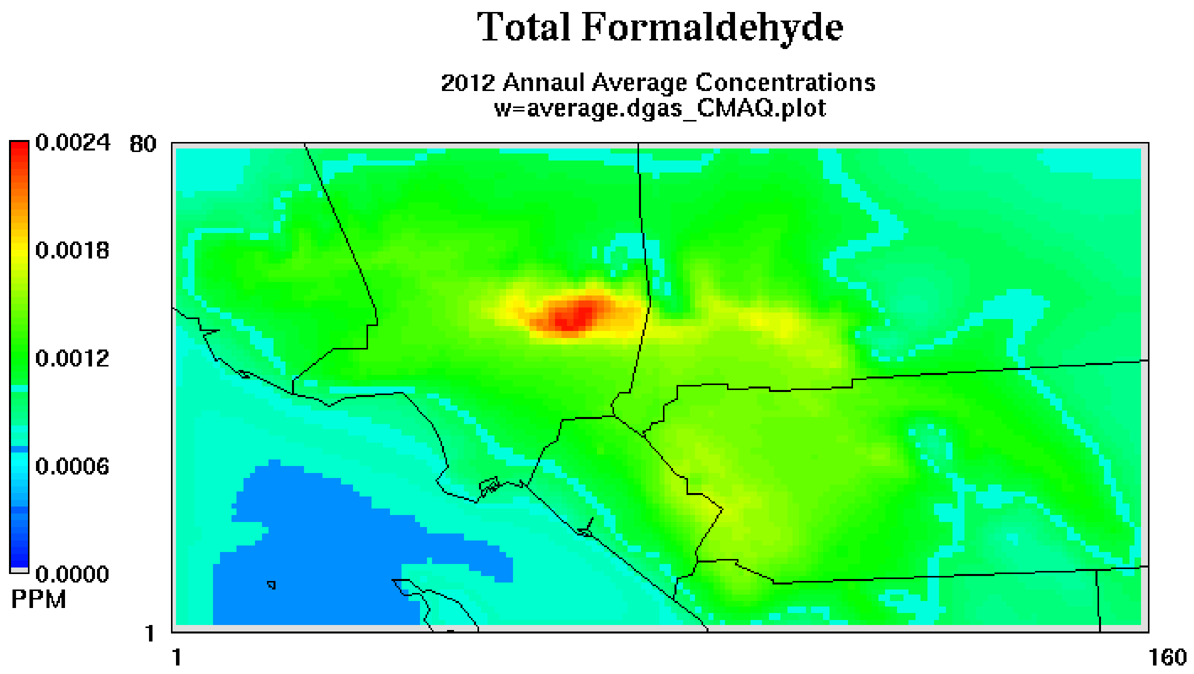


Figure IX-10j
CAMx simulated 2012 annual average for Total Formaldehyde.

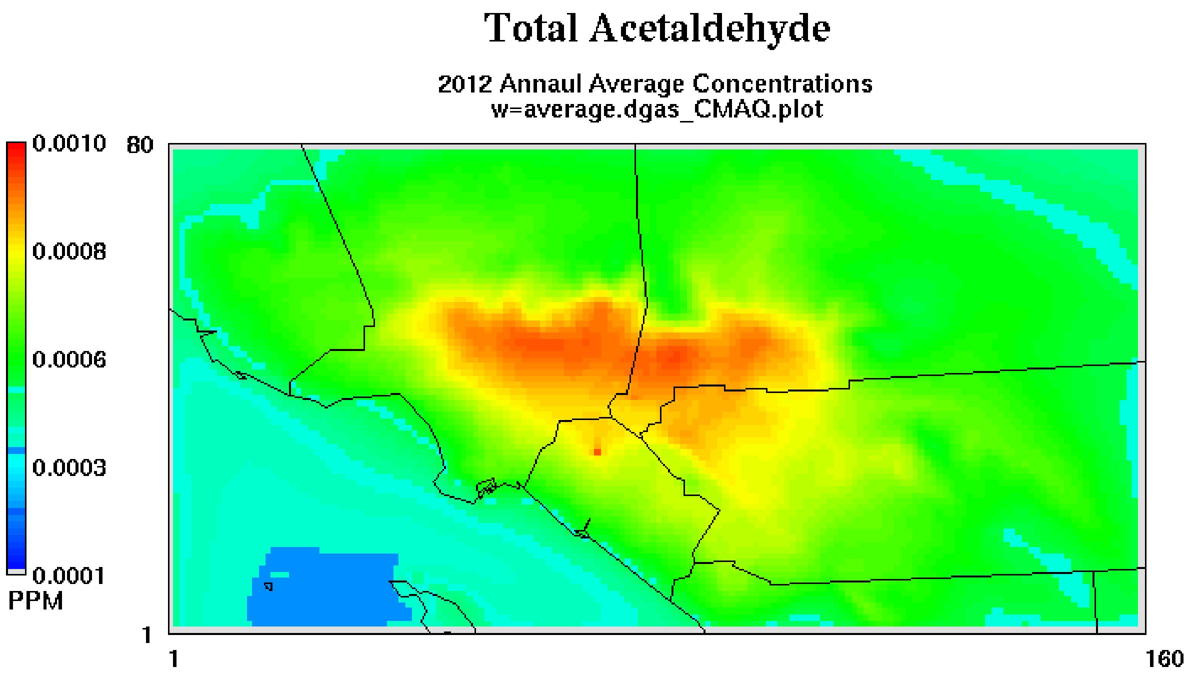


Figure IX-10k
CAMx simulated 2012 annual average Acetaldehyde.

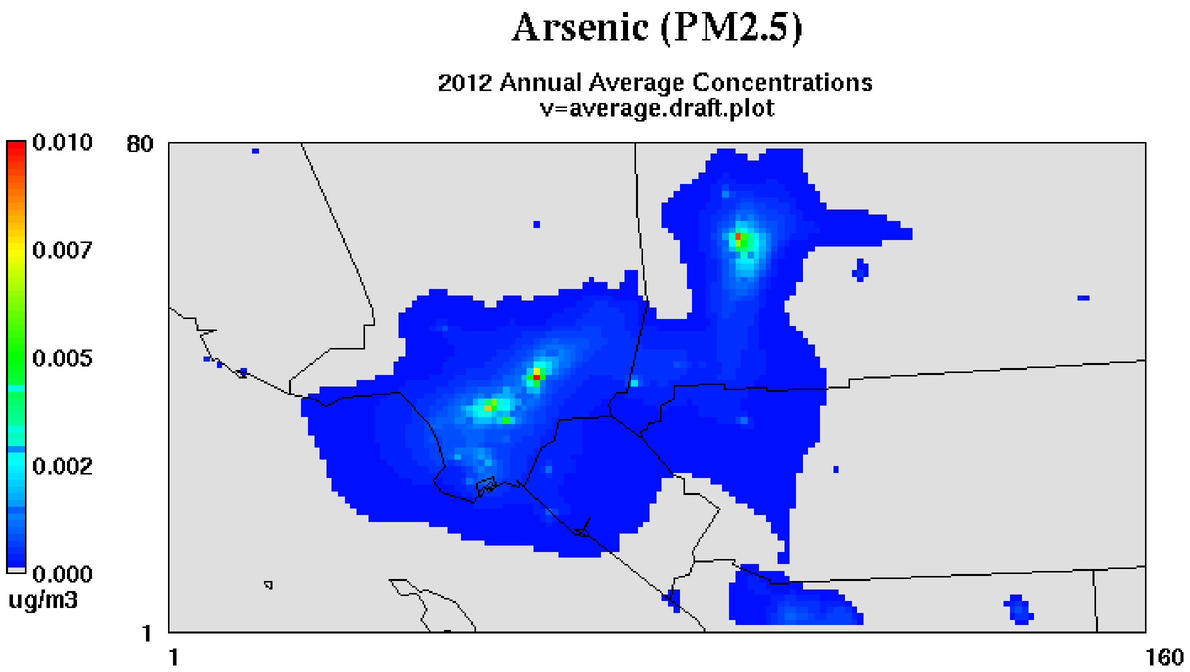


Figure IX-10l
CAMx simulated 2012 annual average Arsenic $PM_{2.5}$.

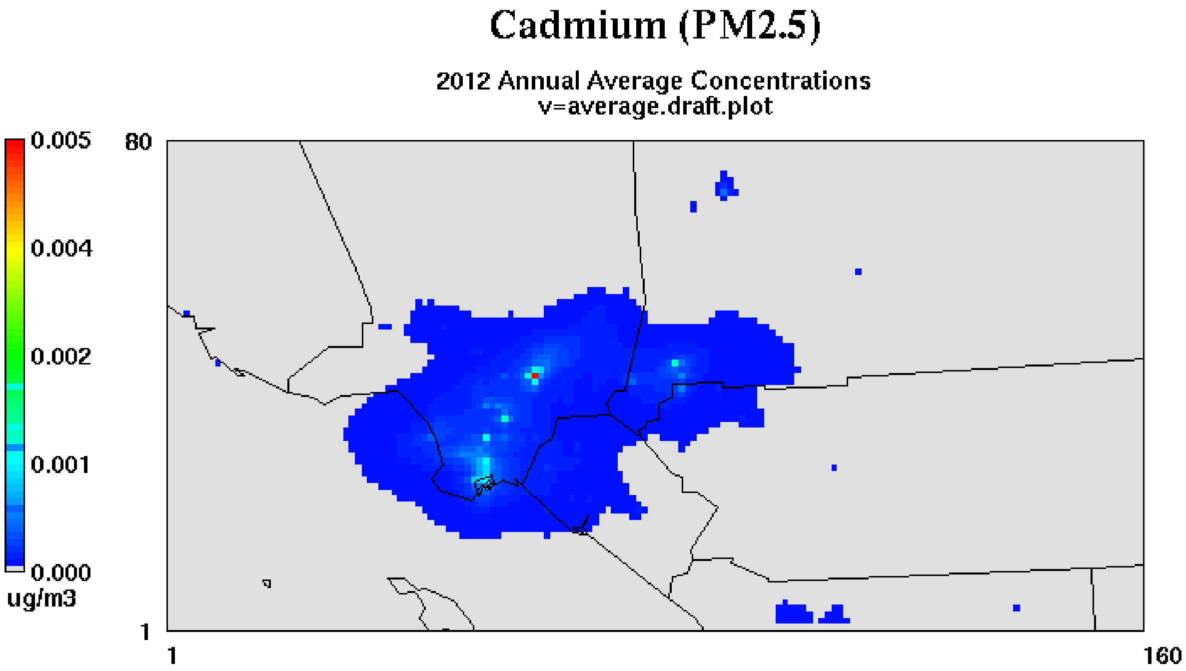


Figure IX-10m
CAMx simulated 2012 annual average Cadmium $PM_{2.5}$.

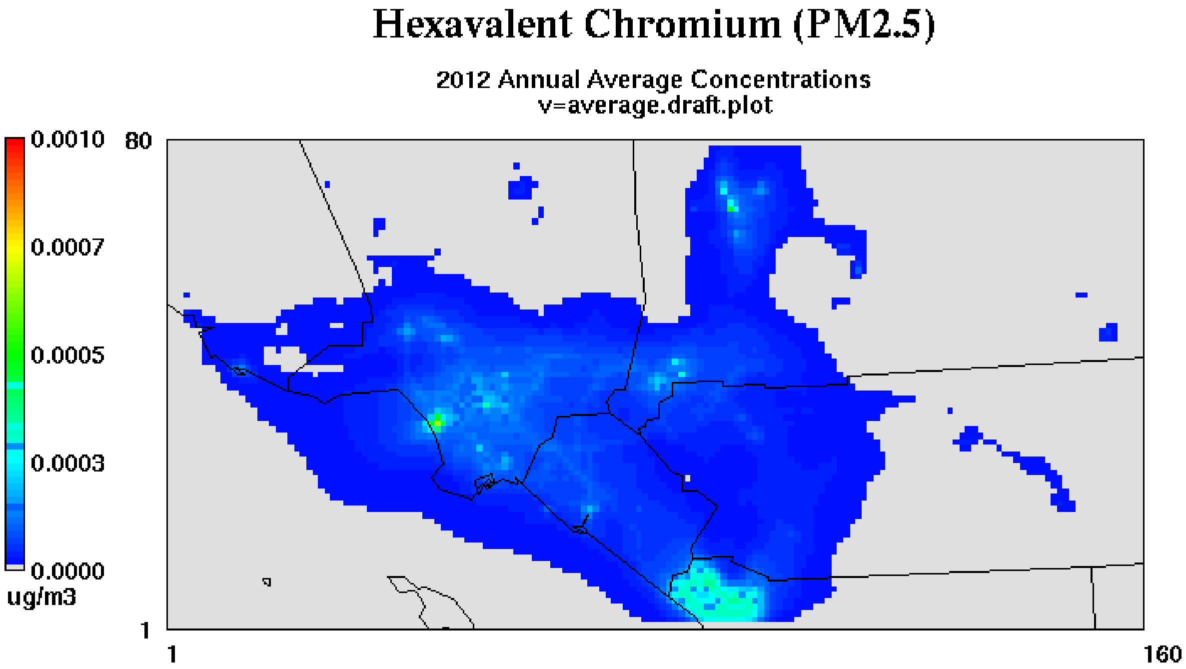


Figure IX-10n
CAMx simulated 2012 annual average Chromium $PM_{2.5}$.

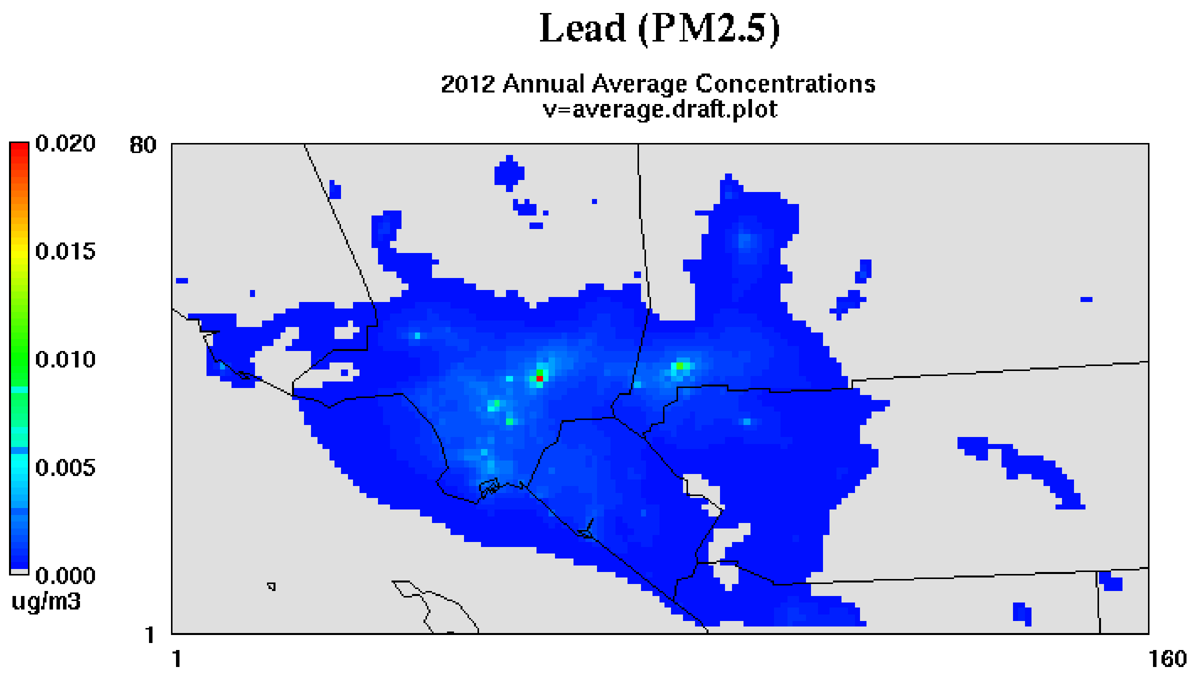


Figure IX-10o

CAMx simulated 2012 annual average Lead $PM_{2.5}$.

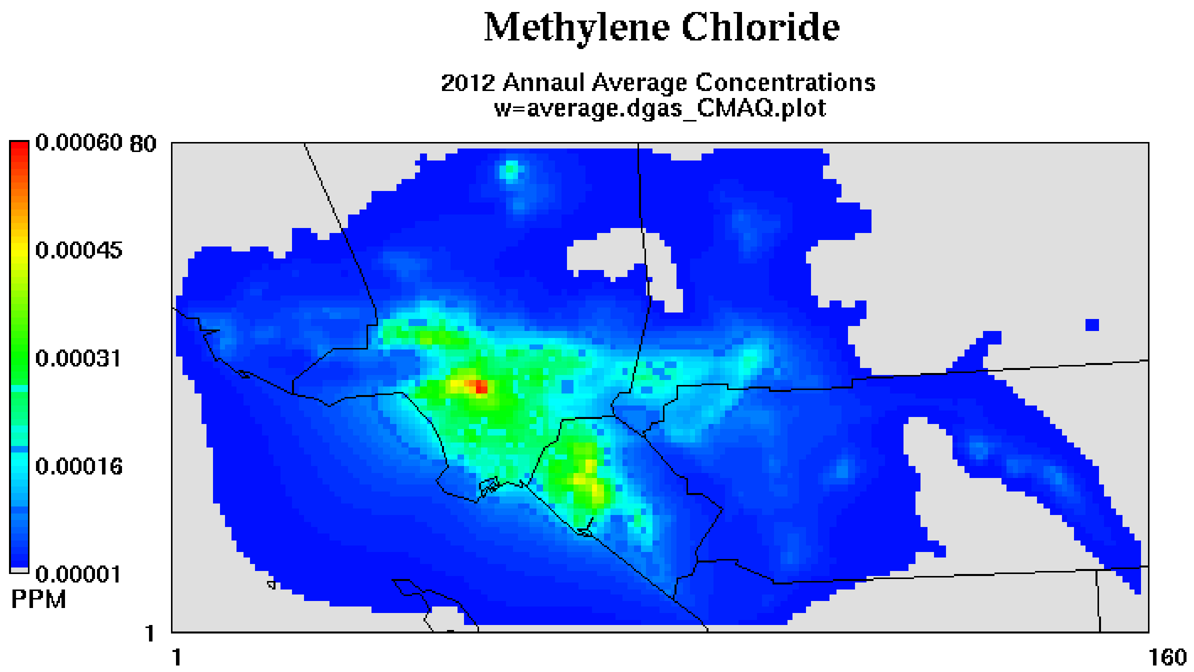


Figure IX-10p

CAMx simulated 2012 annual average Methylene Chloride.

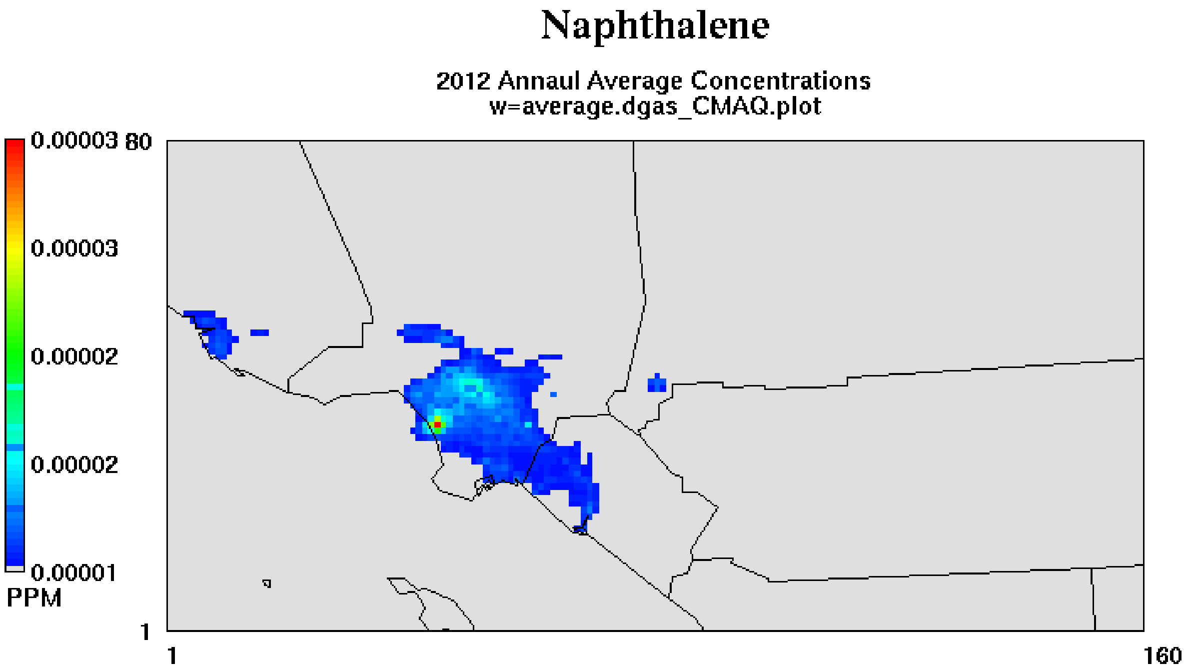


Figure IX-10q
CAMx simulated 2012 annual average Naphthalene.

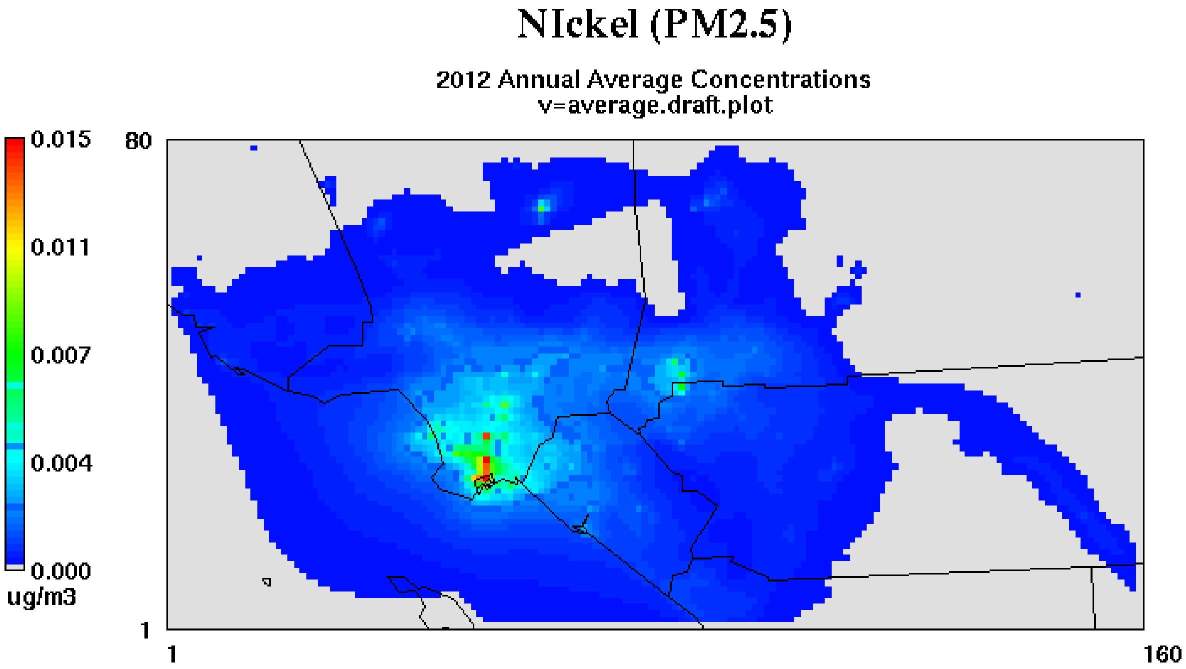


Figure IX-10r
CAMx simulated 2012 annual average Nickel $PM_{2.5}$.

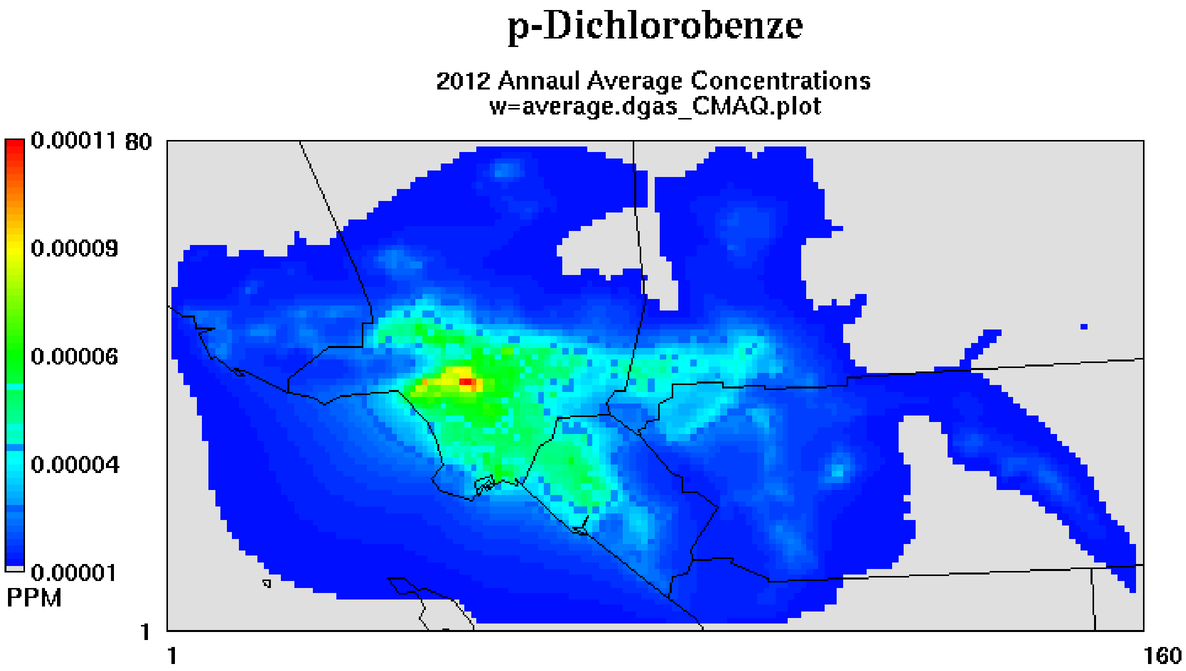


Figure IX-10s
CAMx simulated 2012 annual average p-Dichlorobenzene.

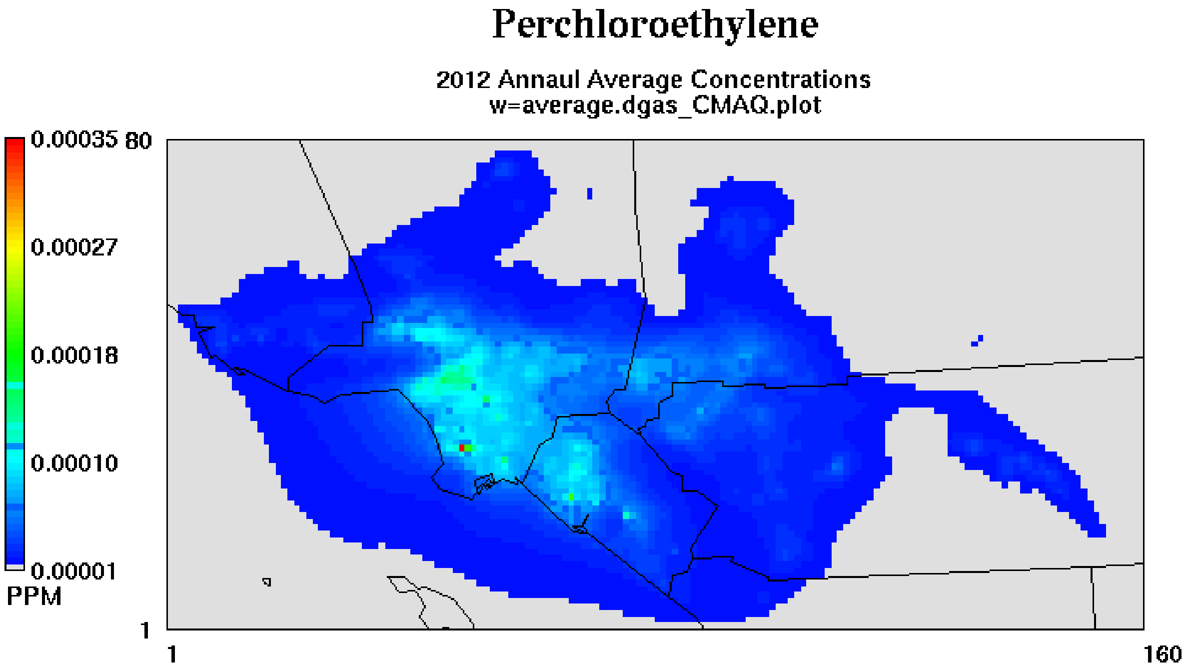


Figure IX-10t
CAMx simulated 2012 annual average Perchloroethylene.

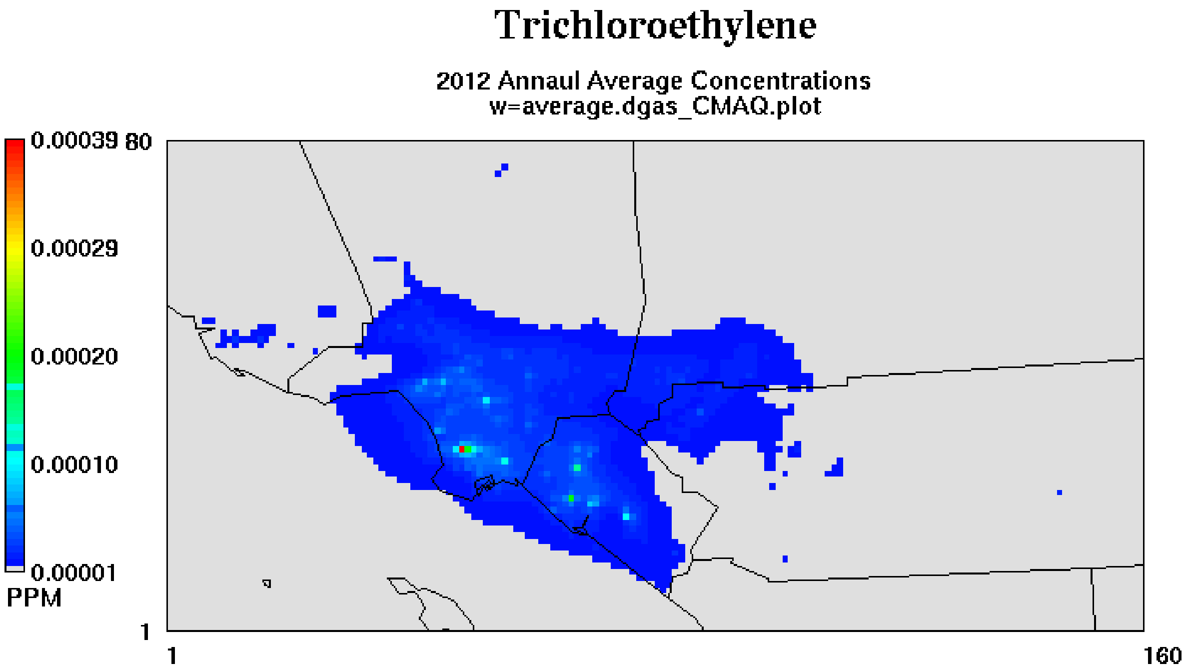


Figure IX-10u
CAMx simulated 2012 annual average Trichloroethylene.

IX.17 Estimation of Risk

Figure IX-11 depicts the distribution of risk estimated from the predicted annual average concentrations of the key toxic compounds. Risk is calculated for each grid cell as follows:

$$\text{Risk}_{i,j} = \Sigma \text{ Concentration}_{i,j,k} \text{ X Risk Factor}_{i,j,k},$$

where i,j is the grid cell (easting, northing) and k is the toxic compound.

The grid cell having the maximum simulated risk of 1,057 was located in the Ports of Los Angeles and Long Beach. In addition to the cluster of cells around the port area with high risk, a second cluster of high risk area is centered on the railyard in Los Angeles. In general, as in the past studies, the higher risk areas tend to be along transportation corridors.

Figure IX-12 provides the CAMx RTRAC simulated air toxics risk for the 2005 MATES III period. Figure IX-13 depicts the changes in risk from 2005 to 2012-2013 estimated from the CAMx RTRAC simulations. The greatest decrease in risk occurred in the port area, reflecting the emission reductions from shipping and port operations. Overall, air toxics risk improves significantly, consistent with air toxic emissions reductions that occurred over the period.

The 2012-2013 Basin average population-weighted risk summed for all the toxic components yielded a cancer risk of 367 in a million. The average risk included all populated over-land cells that reside within the Basin portion of the modeling domain. The MATES III Basin average risk was 853 per million. From the MATES III to the MATES IV period, the simulated risk decreased by 57%. This reduction in Basin risk can be attributed to several factors, most notably changes in diesel emissions between 2005 and 2012. While weather profiles between the two monitoring periods varied, no appreciable difference was observed in the meteorological dispersion potential.

Figures IX-14a through IX-14f depict risk associated with diesel and its specific emissions categories. Figure IX-15 provides the Basin risk excluding the contribution of diesel particulates. On and off-road diesel impacts are spread throughout the Basin following the transportation corridors and off-road facilities such as the intermodal transfer sites. The shipping impacts are concentrated in the vicinity of the Ports of Los Angeles and Long Beach and the adjacent downwind communities.

Regional risk from nondiesel sources (Figure IX-15) is also uniformly distributed throughout the Basin with values typically around 100 in one million, with only a few selected cells showing values in excess of 200.

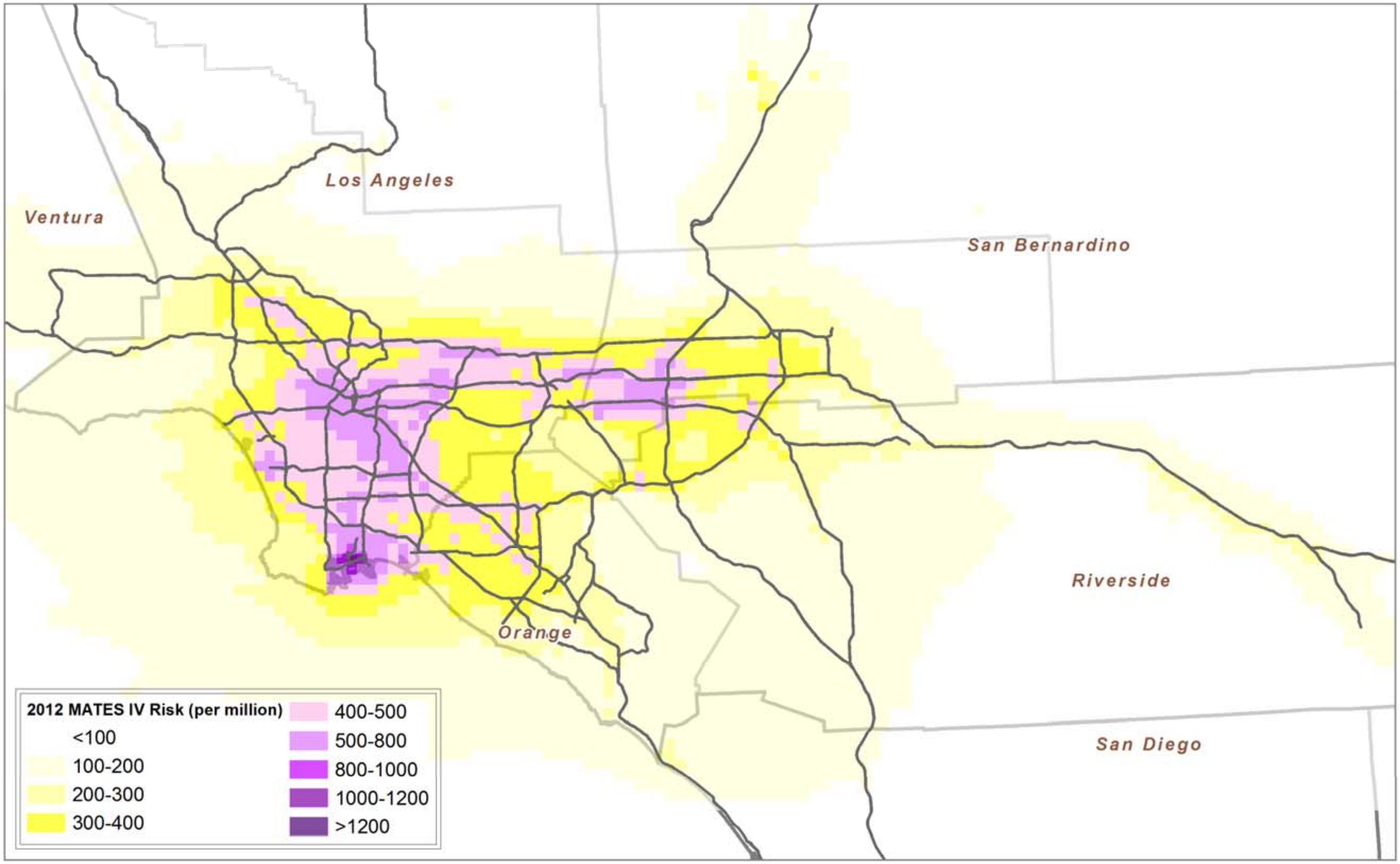


Figure IX-11
2012 MATES IV CAMx RTRAC Simulated Air Toxic Risk.

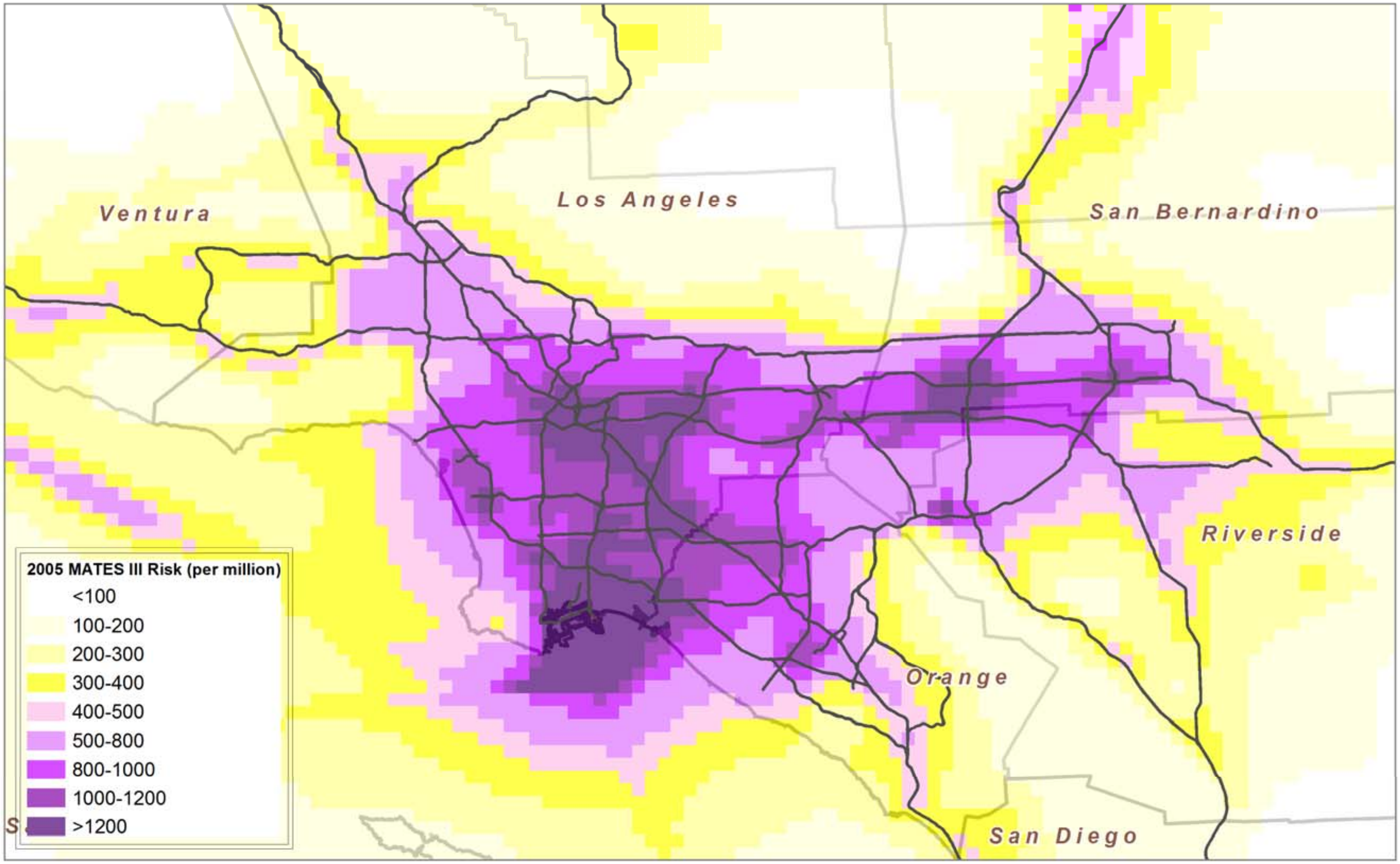


Figure IX-12
2005 CAMx RTRAC Simulated Air Toxic Risk.

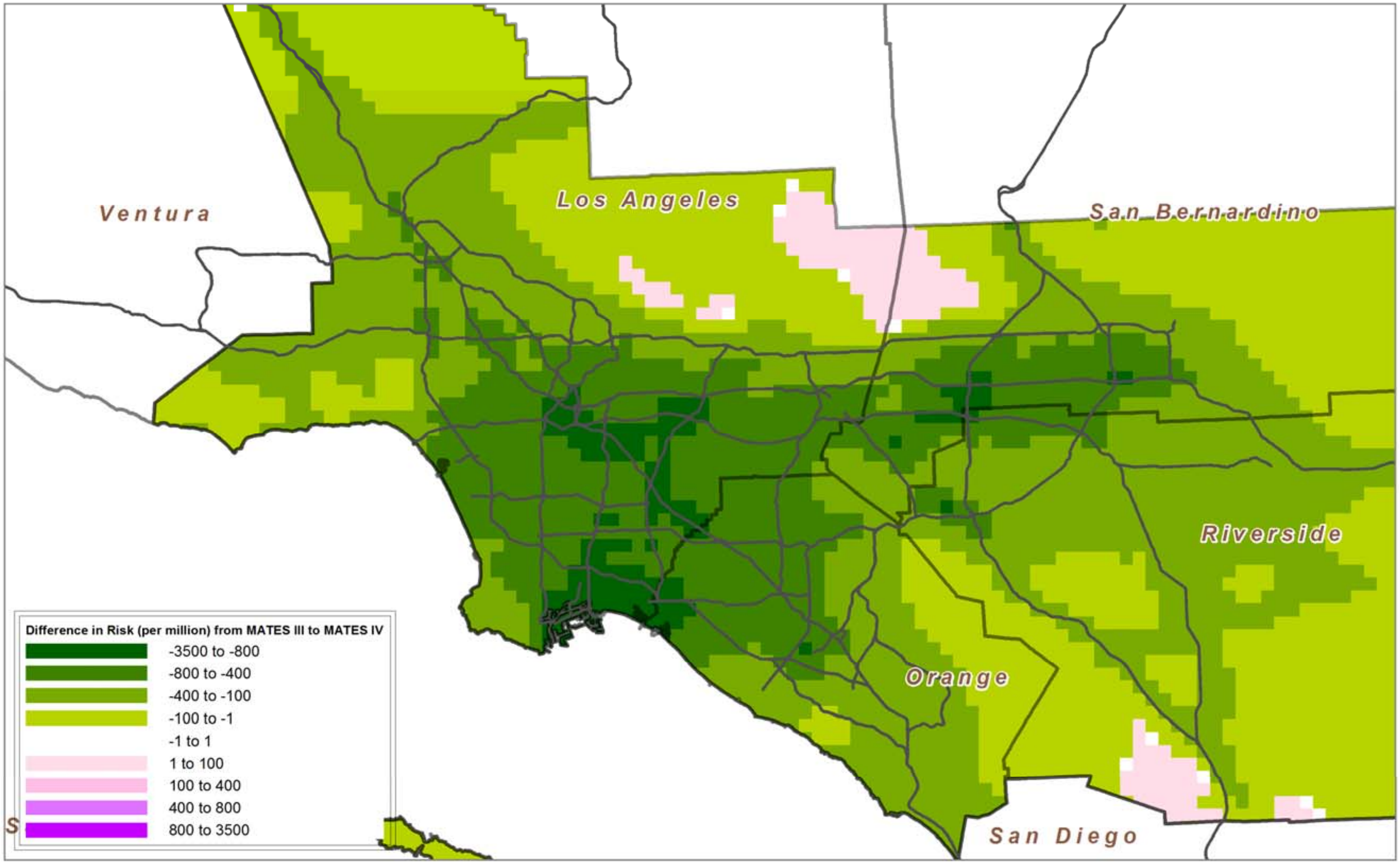


Figure IX-13
Change in CAMx RTRAC simulated risk from the 2005 to 2012

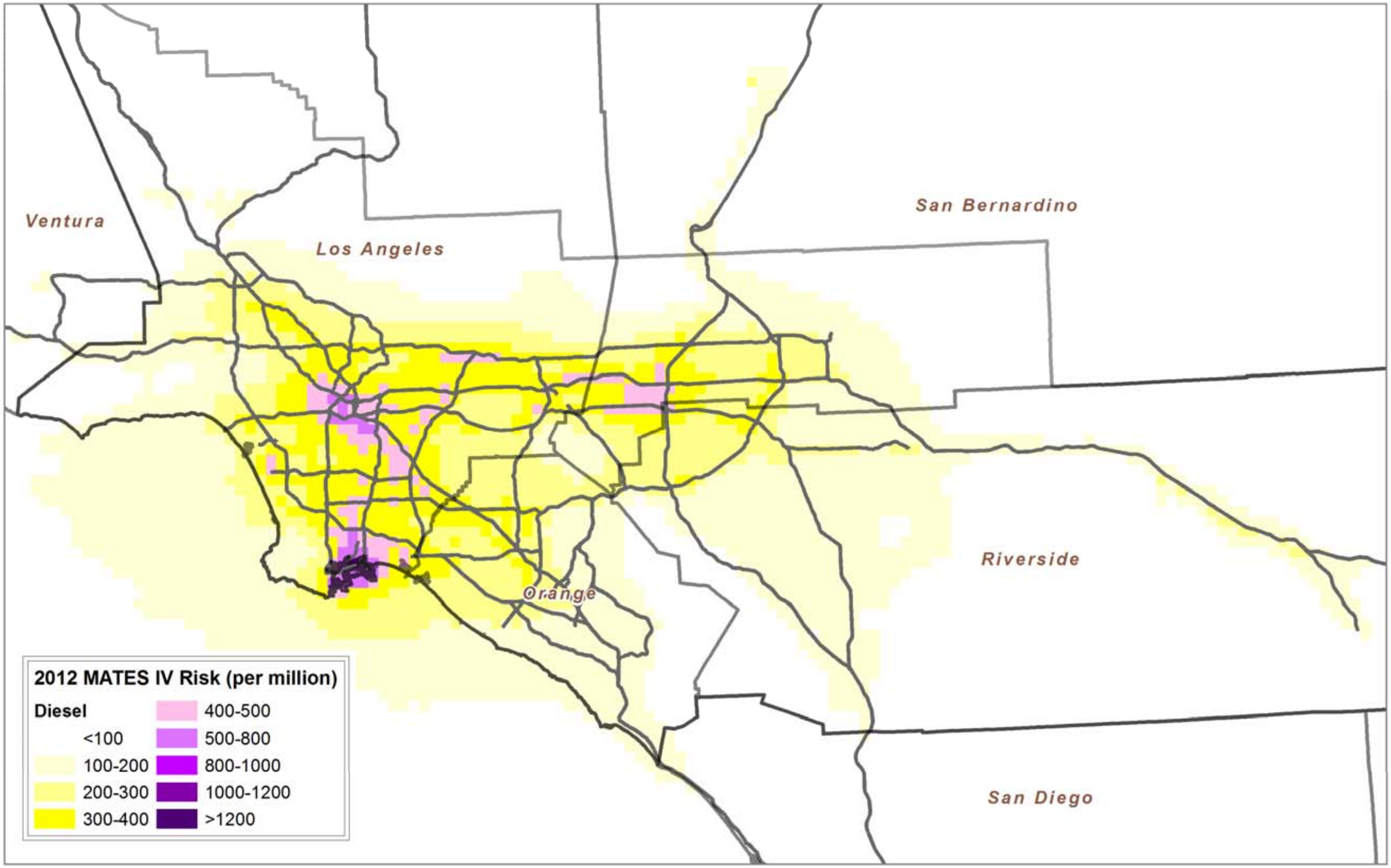


Figure IX-14a
MATES IV Risk from Diesel

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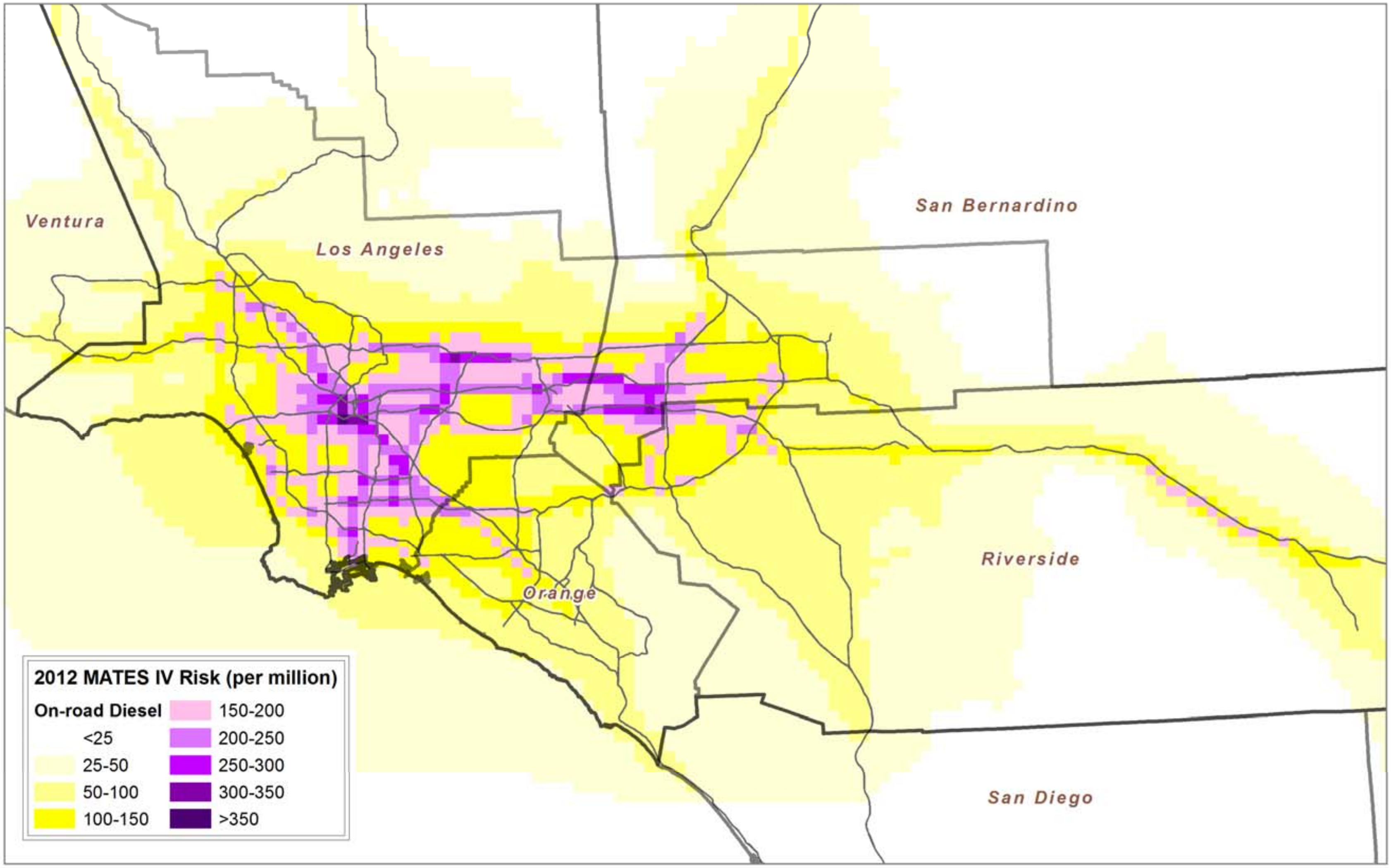

Figure IX-14b
MATES III Simulated Risk from On-Road Diesel.

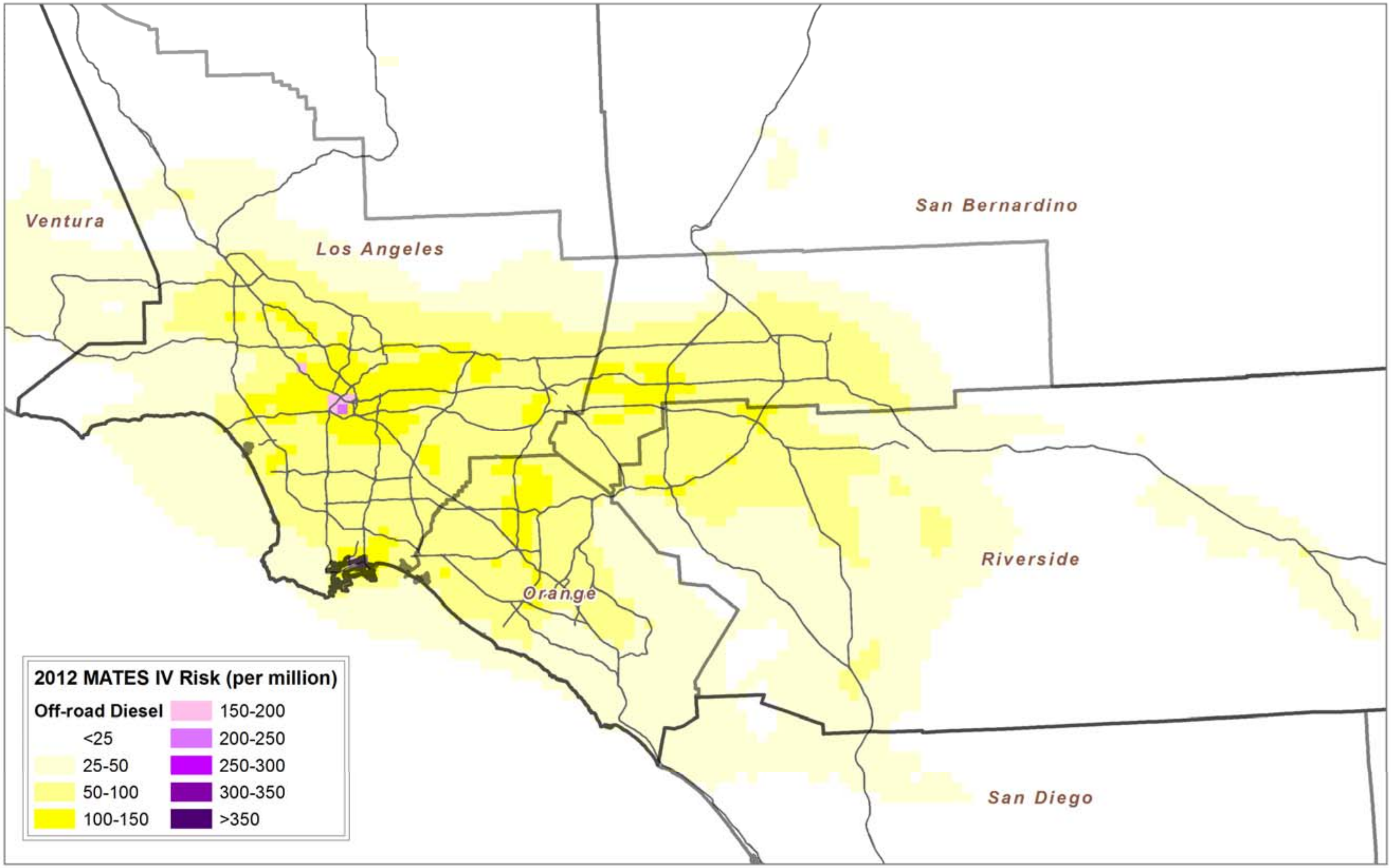

Figure IX-14c
MATES IV Simulated Risk from Off-road Diesel (including railyards but excluding trains and ships).

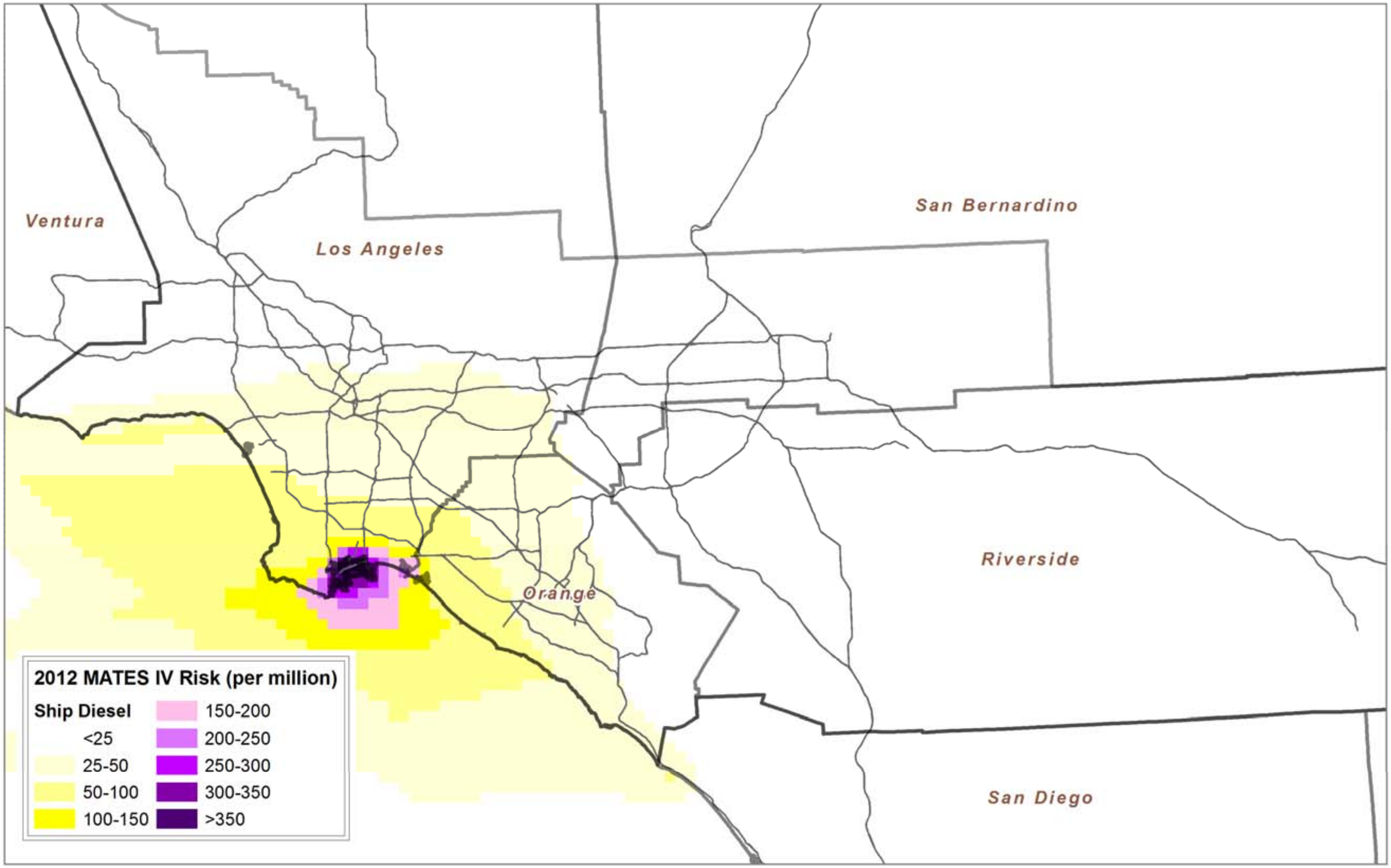

Figure IX-14d
MATES IV Simulated Risk from Ship Diesel.

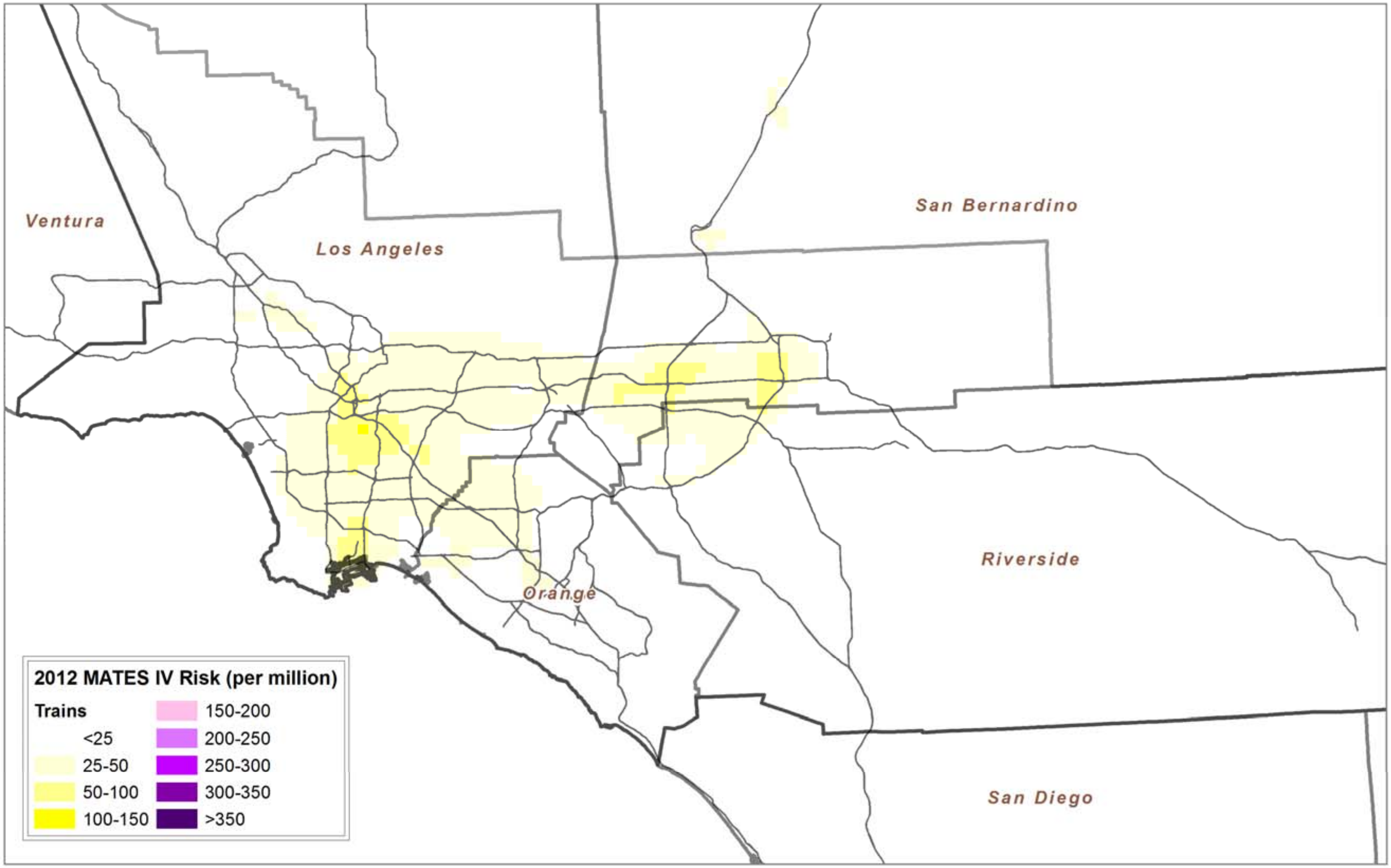

Figure IX-14e
MATES IV Simulated Risk from Trains (Excluding Railyards Equipments).

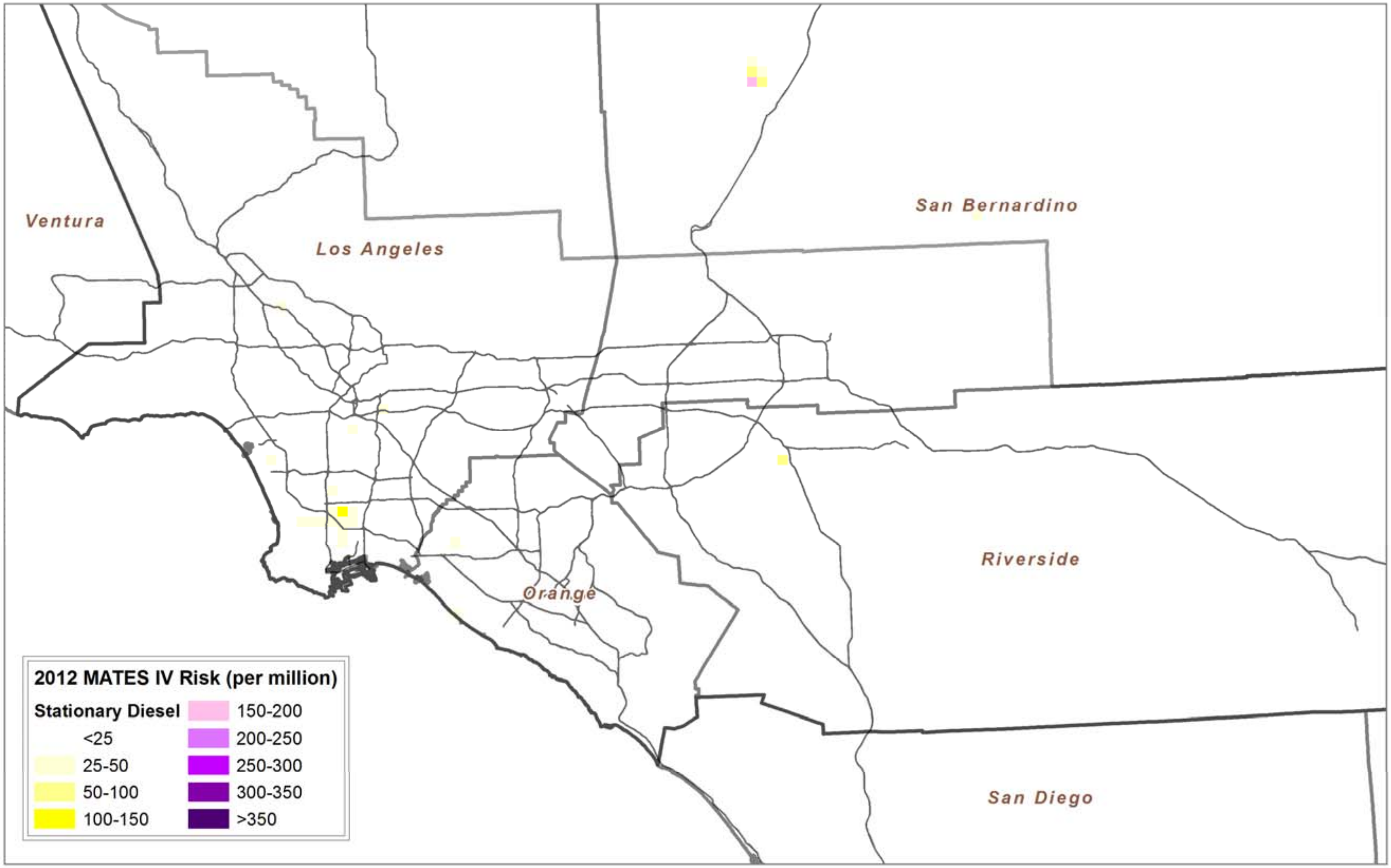

Figure IX-14f
MATES IV Simulated Risk from Stationary Diesel.

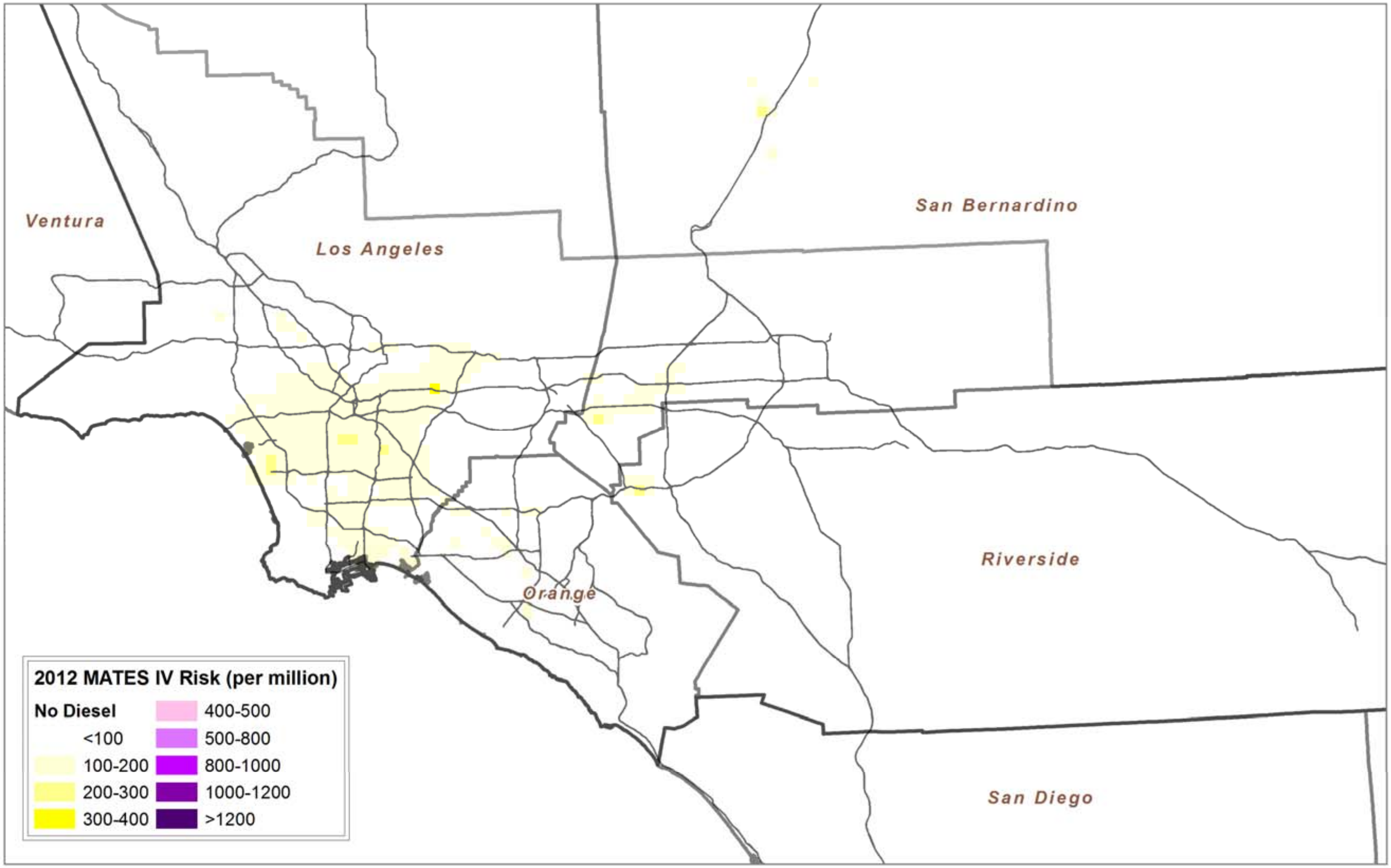

Figure IX-15
MATES IV Simulated Risk No-Diesel.

Figure IX-16 provides a close-up plot of risk in the ports area. Table IX-11 provides a summary risk estimated for the Basin, for the Ports area, and for the Basin excluding the ports area. For this assessment, the ports area includes the populated cells roughly bounded by the Interstate 405 to the north, San Pedro to the west, Balboa Harbor to the east and Pt. Fermin to the south. The 2012-2013 average population-weighted air toxics risk in the ports area (as defined above) was 480 in one million. The Basin average population-weighted air toxics risk, excluding the grid cells in the ports area, was 359 in one million. It is important to note that the downwind impacts resulting from port area activities are reflected in the toxics risk estimates for the grid cells categorized as "Basin minus Ports." Similarly, the MATES III simulations for 2005 indicated that the ports area air toxics risk was 1,415; and the Basin, minus the ports area, was 816 in one million. Overall, the ports area experienced an approximate 66% decrease in risk, while the average population-weighted risk in other areas of the Basin decreased by about 56%.

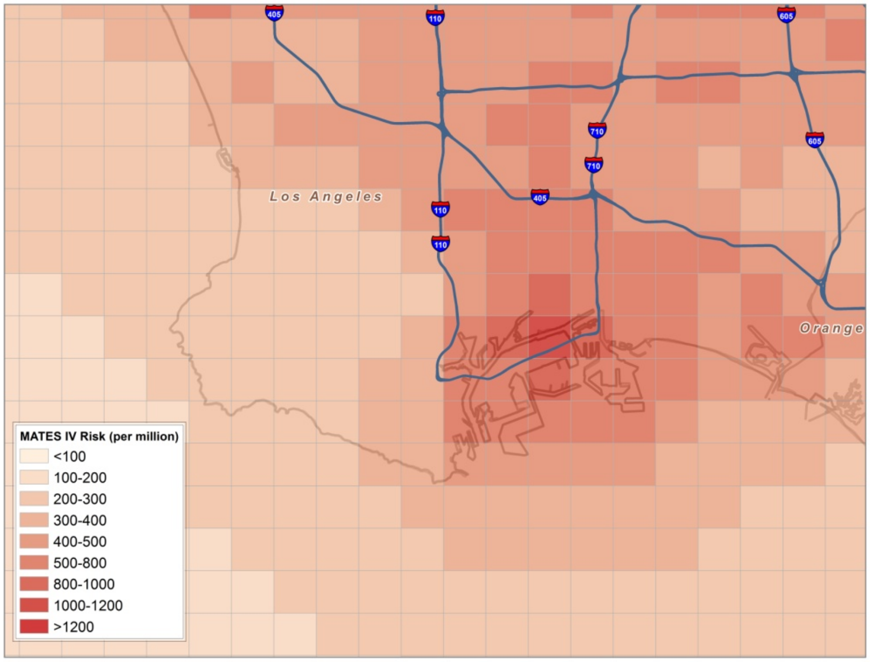

Figure IX-16
2012 Ports area MATES IV Simulated Air Toxic Risk.

Table IX-11

Basin and Port Area Population Weighted Risk

Region	MATES IV		MATES III		Average Percentage Change in Risk
	2012 Population	Average Risk (Per Million)	2005 Population	Average Risk (Per Million)	
Basin	15,991,150	367	15,662,620	853	-57
Ports Area	998,745	480	959,761	1,415	-66
Basin Excluding Ports Area	14,992,806	359	14,702,859	816	-56

IX.18 County Risk Assessment

Figures IX-17 through IX-20 provide close up depictions of air toxics risk to Central Los Angeles, Mira Loma/Colton, Central Orange County and West Los Angeles areas, respectively;, and Table IX-12 provides the county breakdown of air toxics risk to the affected population. As presented in the spatial distribution, Los Angeles County bears the greatest average risk at 415 per one million person population. The SCAB portion of San Bernardino County has the second highest projected risk at 339 per one million person population. The estimated risk for Orange County is 315 per million, and Riverside was estimated to have the lowest population-weighted risk at 223. The Coachella Valley of Riverside County, as expected, has the lowest toxic risk at 139. It should be noted that these are county-wide averages, and individual communities could have higher risks than the average if they are near emissions sources, such as railyards or intermodal facilities.

Comparison of the county-wide population-weighted risk shows that the greatest reduction occurred in Orange County with nominal variations among counties. Reductions in emissions from mobile sources including benzene, 1,3-butadiene, and diesel particulate have contributed to the improved county-wide risk. It is noteworthy that San Bernardino County now has higher population-weighted risk than Orange County. This is because the port area has a proportionally larger impact in Orange County than in San Bernardino County.

Table IX-12
County-Wide Population Weighted Air Toxic Risk

Region	MATES IV		MATES III		Average Percentage Change in Risk
	2012 Population	Average Risk (Per Million)	2005 Population	Average Risk (Per Million)	
Los Angeles	9,578,586	415	9,887,127	951	-56
Orange	3,067,909	315	2,764,620	781	-60
Riverside	1,784,872	223	1,548,031	485	-54
San Bernardino	1,560,183	339	1,462,842	712	-52
SCAB	15,991,550	367	15,662,620	853	-57
Coachella Valley	465,064	139	N/A	N/A	N/A

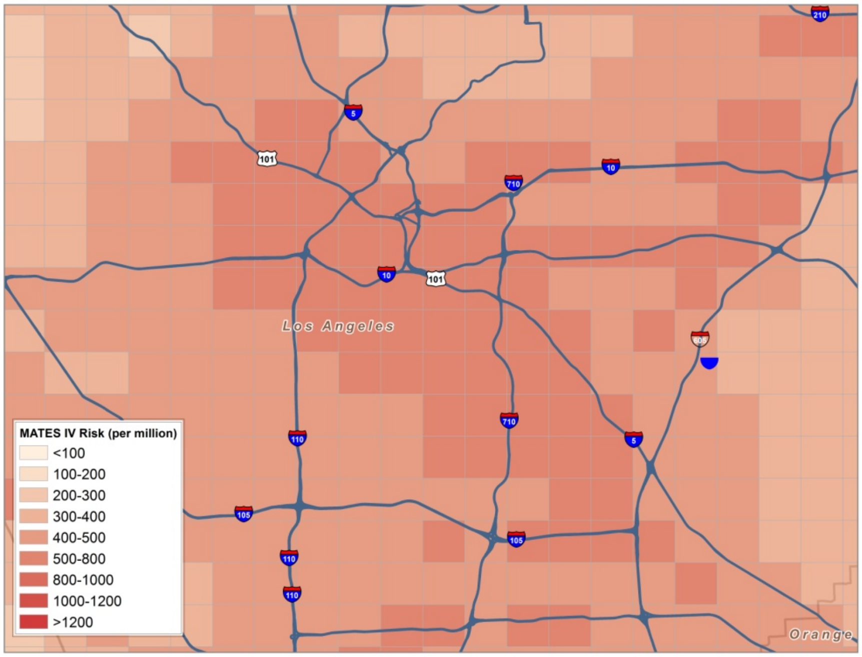

Figure IX-17
2012 Central Los Angeles MATES IV Simulated Air Toxic Risk.

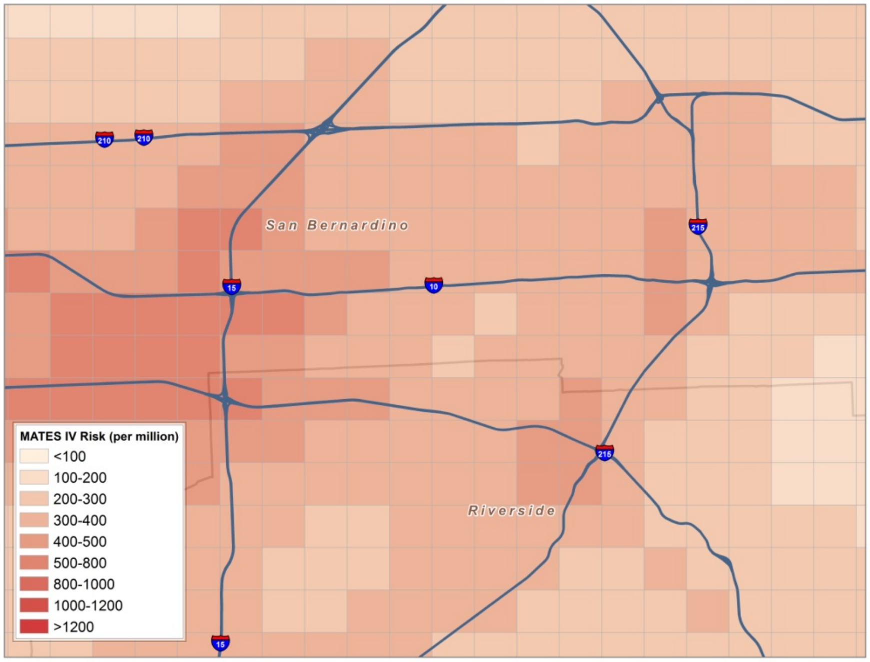

Figure IX-18
2012 Mira Loma/Colton MATES IV Simulated Air Toxic Risk.

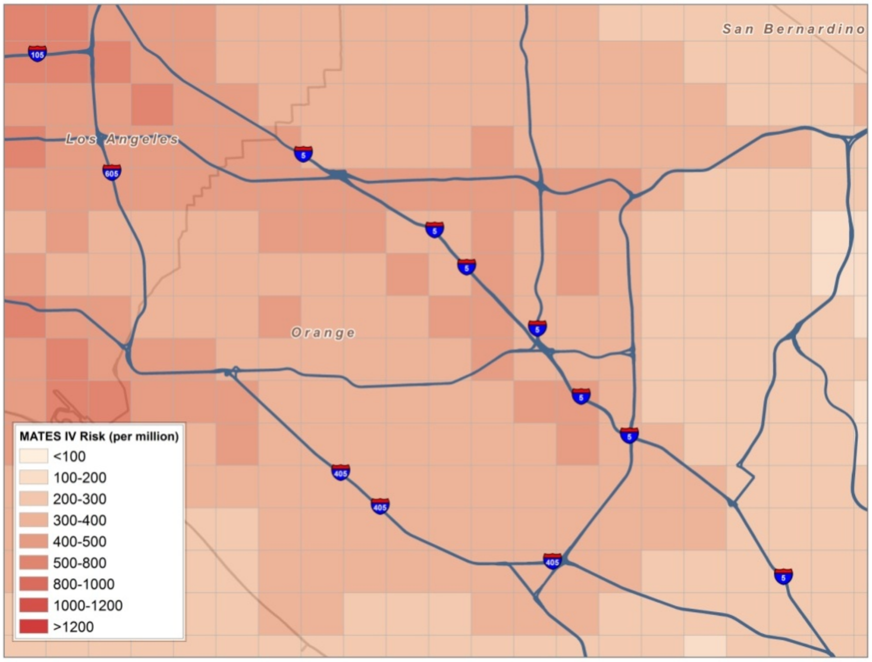

Figure IX-19
2012 Central Orange County MATES IV Simulated Air Toxic Risk.

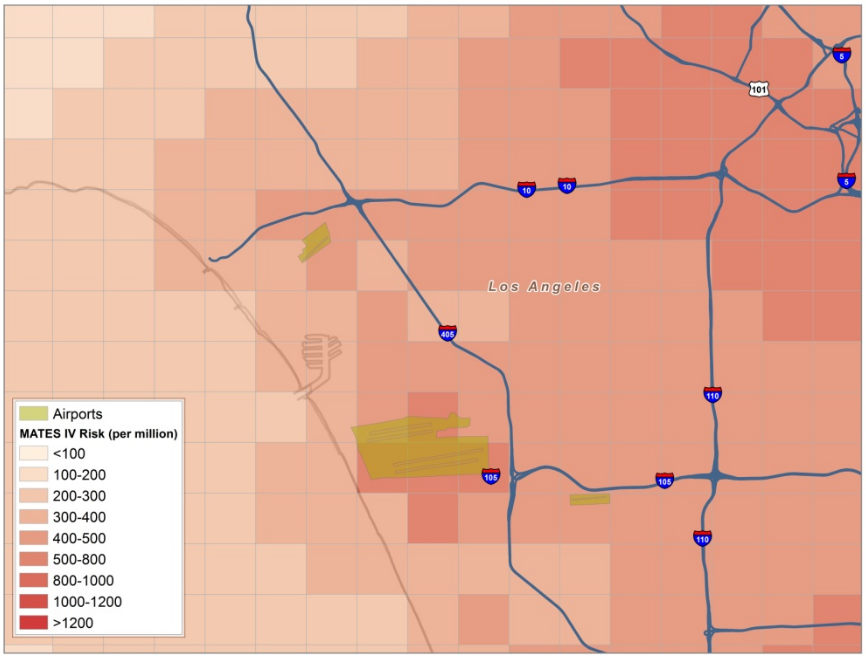

Figure IX-20
2012 West Los Angeles MATES IV Simulated Air Toxic Risk.

IX.19 Risk from Key Compounds

Table IX-13 provides the Basin average breakdown of risk associated with each of the key compounds simulated in the analysis. Diesel particulate ranked highest (76%) as the toxic compound contributing to the overall risk to the population. The next three highest contributors included benzene, hexavalent chromium and 1,3-butadiene. The four top toxic pollutants contribute over 91% toxic risk. Formaldehyde (primary and secondary) and acetaldehyde (primary and secondary) contribute 3.5% and 1.3%, respectively, while the remaining compounds combined accounted for less than 4% of the total.

IX.20 Network Risk Evaluation

Table IX-14 provides the simulated air toxics risk at each of the 10 stations for the three main toxic compounds and the remaining aggregate based on the regional modeling. Risk is calculated using the predicted concentrations of each toxic component for the specific monitoring station location (based on a nine-cell weighted average concentration). The summary also provides the comparison between simulated average risk for the 10 stations combined and the average risk calculated using the annual toxic compound measurements and the estimated diesel concentrations at those sites.

Table IX-13

2012-2013 MATES IV Risk from Simulated Individual Toxic Air Contaminants

Toxic Compound	Risk Factor (μg/m^3)	Peak Annual Average Concentration	Population Weighted Annual Average Concentration	Units	Cumulative Risk (per million)	% Contribution
Diesel	3.00E-04	17.4	0.93	μg/m^3	279.67	76.2
Benzene	2.90E-05	0.51	0.25	ppb	22.82	6.2
Hexavalent Chromium	1.50E-01	0.001	1.37E-04	μg/m^3	20.52	5.6
1,3-Butadiene	1.70E-04	0.58	0.03	ppb	12.54	3.4
Secondary Formaldehyde	6.00E-06	2.35	1.24	ppb	9.12	2.5
Primary Formaldehyde	6.00E-06	2.71	0.50	ppb	3.7	1.0
Secondary Acetaldehyde	2.70E-06	0.93	0.73	ppb	3.56	1.0
Arsenic	3.30E-03	0.043	9.97E-04	μg/m^3	3.29	0.9
p-Dichlorobenzene	1.10E-05	0.11	4.38E-02	ppb	2.90	0.8
Perchloro-ethylene	5.90E-06	0.356	0.07	ppb	2.71	0.7
Naphthalene	3.40E-05	0.03	9.87E-03	ppb	1.76	0.5
Cadmium	4.20E-03	0.014	3.29E-04	μg/m^3	1.38	0.4
Nickel	2.60E-04	0.11	3.69E-03	μg/m^3	0.96	0.3
Primary Acetaldehyde	2.70E-06	0.67	0.16	ppb	0.80	0.2
Methylene Chloride	1.00E-06	0.59	0.21	ppb	0.74	0.2
Trichloroethylene	2.00E-06	0.39	3.08E-02	ppb	0.33	0.1
Lead	1.20E-05	0.065	4.17E-03	μg/m^3	0.05	<0.1

The highest simulated risk was estimated for West Long Beach followed by Los Angeles, Huntington Park, North Long Beach, and Compton. The lowest modeled risk was simulated at Anaheim. As previously discussed, simulation performances at those high risk sites showed a tendency for overprediction; consequently, this feature resulted in the higher risk calculation.

Risk averaged over the 10 stations was simulated as 505 in a million, which is approximately 25% higher than the value estimated from measurements. This includes the contribution of diesel particulates. An emission-based adjustment factor, 0.82, was applied to estimate the diesel portion from the $EC_{2.5}$ measurements.

The nondiesel portion of the simulated risk can be directly compared to risk calculated from the toxic compound measurements. Figure IX-21 presents a comparison of the model simulated and measurement estimated nondiesel risk at each monitoring site, as well as the 10-station average. Simulated nondiesel risk is within 30% of measurements at all stations. The simulated 10-station average risk is essentially equal to the risk estimated from the measurements.

Simulated total risk, including the contribution of diesel particulates, taken as an eight-station average, is 505 in a million. The 10-station average simulated risk is approximately 25% lower than the risk calculated from the measured toxic compound concentrations and the estimates of diesel concentrations using the emissions based factor (0.82) applied to the $EC_{2.5}$ average concentration.

Table IX-14

Comparison of Network Averaged CAMx RTRAC 2012-2013 Modeled Risk to Measured Risk at the 10 MATES IV Sites

	2012-2013 MATES IV CAMX RTRAC Simulation				
Location	Benzene	1,3-Butadiene	Others	Diesel	Total
Anaheim	26	14	54	301	395
Burbank	27	13	59	333	431
Central LA	33	19	78	516	646
Compton	26	17	63	383	489
Inland Valley San Bernardino	21	9	61	309	400
Huntington Park	30	62	96	389	576
North Long Beach	27	16	65	395	503
Pico Rivera	25	13	62	358	459
Rubidoux	20	7	46	296	369
West Long Beach	32	15	69	662	778
10-Station Average Modeled	27	18	65	394	505
10-Station MATES IV Average Measured (EC$_{2.5}$ *0.82 for Diesel)	35	33	47*	287	402

* Including modeled species only, Risk from some species, such as carbon tetrachloride, chloroform and PAHs are excluded.

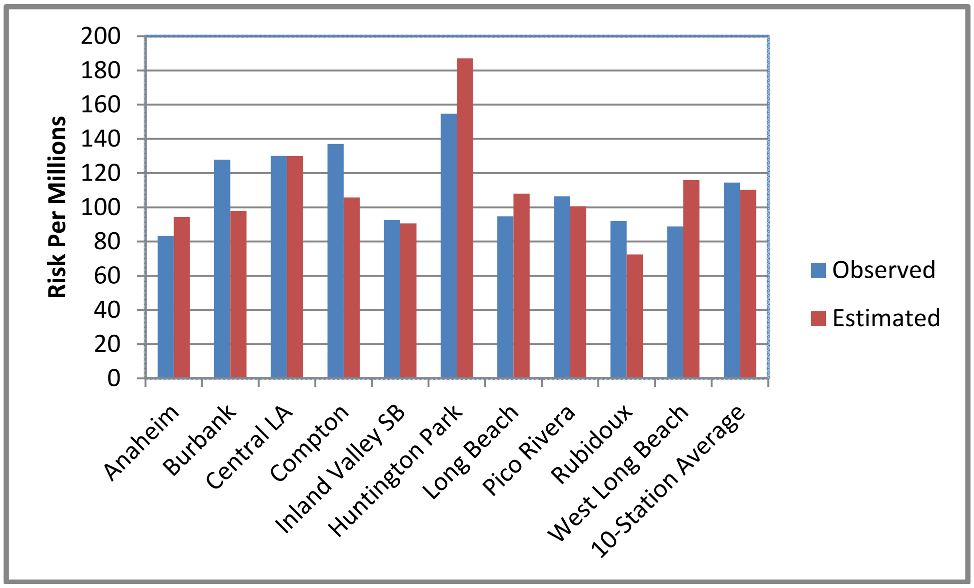

Figure IX-21
2012 MATES IV Simulated vs. Measured Non-Diesel Air Toxics Risk

IX.21 Evaluation

The population-weighted average Basin air toxics risk (367 per million) simulated using CAMx RTRAC for the 2012-2013 MATES IV period was estimated to be 57% lower than estimated (853 in a million) for the MATES III period. The areas of the Basin with the highest risk continued to be the Ports of Los Angeles and Long Beach with a secondary maximum occurring in an area around the railyard in the Los Angeles.

A majority of the risk reduction can be tied to changes in diesel emissions, which were reduced by 66% from 2005 to 2012. The emissions reductions of benzene (11%), 1,3-butadiene (50%), arsenic (43%) and other air toxics contribute to the overall reduction in 2012-2013 simulated risk, as well. A general assessment of the observed meteorological profile suggests that the two monitoring periods were comparable in dispersion potential.

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IX.22 References

Byun, D.W., and Ching, J.K.S., 1999, Science Algorithms of the EPA Models-3 Community Multiscale Air Quality (CMAQ) Modeling system, U.S. Evironmental Protection Agency, EPA/600/R-99/030

ENVIRON, Inc., 2008, CAMx User's Guide Version 4.5. ENVIRON. Novato, CA 94945

ENVIRON, Inc., 2005, "METSTAT software for MM5 version 3 (02/11/05)," ENVIRON. Novato, CA 94945, http://www.camx.com/down/support.php

ENVIRON, Inc., 2006, "KVPATCH software for CAMx," ENVIRON. Novato, CA 94945, http://www.camx.com/down/support.php

Grell, G.A., Dudhia, J., Stauffer, D.R., 1994, A Description of the Fifth-Generation Penn State/NCAR Mesoscale Model (MM5), NCAR/TN-398+STR, NCAR Technical Note

Mason, R., Dolwick, P., Carey, P., Kinnee, E., Wilson, M., 2008. Emissions processing and sensitivity air quality modeling of category 3 commercial marine vessel emissions. In: Proceedings from 17th Annual International Emission Inventory Conference, Portland, OR.

O'Brien, J.J., 1970, A note on the vertical structure of the eddy exchange coefficient in the planetary boundary layer. J. Atmos. Sci., 27, 1213-1215

Skamarock, W.C., Klemp, J.B., Dudhia, J., Gill, D.O., Barker, D.M., Duda, M.G., Huang, X.-Y., Wang, W., Powers, J.G., 2008. A Description of Advanced Research WRF version 3. NCAR/TN-475+STR, NCAR Technical Note

U.S. EPA, 2006," Guidance on Use of Modeled and Other Analyses for Demonstrating Attainment of Air Quality Goals for Ozone, $PM_{2.5}$ and Regional Haze NAAQS," U.S. EPA, Office of Air Quality Planning and Standards, Emissions, Monitoring, and Analysis Division, Air Quality Modeling Group, Research Triangle Park, North Carolina, September, 2006

WRAP, 2007, Western Regional Air Partnership, Technical Support System, Emissions Method, Offshore Emissions, http://vista.cira.colostate.edu/

APPENDIX X

MATES IV

DRAFT FINAL REPORT

The Spatial and Temporal Trends of $PM_{2.5}$, PM_{10}, and TSP Components in the South Coast Air Basin

Author

Kalam Cheung

Appendix X. The Spatial and Temporal Trends of $PM_{2.5}$, PM_{10}, and TSP Components in the South Coast Air Basin

X.1. Summary

To characterize the ambient level of toxic pollutants in the South Coast Air Basin, $PM_{2.5}$, PM_{10} and Total Suspended Particles (TSP) samples are collected once every six days at 10 monitoring stations from July, 2012 to June, 2013. The spatial and seasonal trends of chemical components in $PM_{2.5}$ are examined. Organic matter (OM) is the most dominant category, accounting for ~44% of the reconstructed mass, while approximately one-third (36%) is attributable to the group of inorganic ions. Elemental carbon (EC) contributes by 8.6%, followed by crustal materials (5.9%) and sea salt (5.3%). Due to limited atmospheric ventilation in cooler months, EC, OM and crustal materials concentrations are higher in the winter than in the summer in the source areas. In the inland receptor areas, regional transport is less pronounced in winter. Thus, their mass fractions in winter are generally similar to, or lower than those in summer. An air pollution episode occurred in early December, and fine particulate mass is elevated by 57 ± 30% across the Basin. In particular, the levels of EC, nitrate and ammonium are higher than the annual average by 2.5, 2.6 and 2.5 times, respectively. Overall, the levels of toxic air pollutants reduce considerably compared with MATES II and MATES III. Fine particulate EC is 36% lower than MATES III, due to reduction of tailpipe emissions. The decline is less pronounced (24%) for EC in PM_{10}. Additional analysis suggests that abrasion emissions induced by heavy-duty diesel vehicles may be a significant source of coarse PM-bound EC. For TSP, arsenic and cadmium concentrations are much lower than those observed in MATES II and MATES III, although the reductions are partly driven by the lower detection limits in the current study. Compared to MATES III, average levels of lead, nickel, vanadium, and hexavalent chromium decrease by 50, 36, 68 and 69% respectively.

X.2. Mass Reconstruction of $PM_{2.5}$

In the $PM_{2.5}$ samples, levels of EC, organic carbon (OC), inorganic ions and metals are quantified. For the purpose of chemical mass reconstruction, these chemical components are grouped into five categories: EC, OM, crustal materials (CM), inorganic ions and sea salt. Reconstructed PM mass is calculated based on the sum of the five categories:

Reconstructed mass = elemental carbon + organic matter + crustal materials + inorganic ions + sea salt

EC is assumed to contain only carbon and requires no multiplier. OM is estimated from OC with a multiplier of 1.4 that accounts for the unmeasured hydrogen (H), oxygen (O), nitrogen (N), and sulfur (S) (Malm et al., 1994). Crustal materials (CM) consist of the typical geological materials including Al, Ca, Fe, Ti and Si. They are multiplied by 2.2, 1.63, 2.42, 1.94 and 2.49 respectively to account for the oxygen associated with these elements (Malm et al., 1994). Inorganic ions represent the sum of sulfate (SO_4^{2-}), nitrate (NO_3^-), and ammonium (NH_4^+). Previous studies in this Basin show that these are present in $PM_{2.5}$ samples as ammonium sulfate $(NH_4)_2SO_4$ and ammonium nitrate (NH_4NO_3); contributions from fugitive dust and salt are small, and do not affect $PM_{2.5}$ mass reconstruction. Sea salt is estimated from the sum of sodium ion (Na^+) and chloride ion (Cl^-).

Daily reconstructed mass is calculated for each site and compared with gravimetric measurements. The reconstructed mass agrees well with the filter-based measurements (R^2 = 0.69, n = 589). The average ratio of reconstructed to gravimetric mass concentration is 1.03 ± 0.29. The lower fraction occurs at the sampling stations of Anaheim (0.95 ± 0.19) and North Long Beach (0.91 ± 0.24). The uncertainty of the above-mentioned mass reconstruction method could be attributed to the uncertainty in the OC multiplication factor, which greatly depends on source characterization of organic component that may have consideration seasonal and spatial variation. Additionally, the higher relative humidity at coastal locations could hydrate particles during sample collection, which may still retain water content after equilibration at 30-40% relative humidity, thereby causing the discrepancy between the gravimetric and the reconstructed mass (Andrews et al., 2000).

Figure X-1 illustrates the chemical closure of $PM_{2.5}$. Overall, OM is the most dominant category, contributing an average of 44.2 ± 1.0% to the reconstructed mass. The levels of OM are relatively higher in sites that are further from the coast, namely Pico Rivera (annual avg. = 6.53 $\mu g/m^3$), Burbank (annual avg. = 6.73 $\mu g/m^3$), Inland Valley San Bernardino (annual avg. = 6.77 $\mu g/m^3$) and Rubidoux (annual avg. = 6.47 $\mu g/m^3$), although their contributions to the reconstruction mass are similar with other sites. The group of inorganic ions (36.0 ± 1.5%) is another major source category, with 16.0, 11.2 and 8.7% attributable to nitrate, sulfate and ammonia, respectively. EC accounts for an average of 8.6% of the reconstructed mass, and higher fractions are found at Pico Rivera (9.5%) and West Long Beach (9.3%). In general, the standard deviations of the site-wide annual average contribution of EC, OM and inorganic ions are less than 10% of their corresponding averages, highlighting the relatively low spatial variation of the three major source categories in this Basin. Approximately 5.9% of the reconstructed mass is attributed to crustal materials, with higher fractions at West Long Beach (8.1%) and Inland Valley San Bernardino (7.8%). Sea salt accounts for 5.3% of the reconstructed mass. Higher fractions are observed at West Long Beach (6.8%) and North Long Beach (7.2%), while the inland stations of Inland Valley San Bernardino and Rubidoux record lower fractions at 3.6% and 3.7%, respectively.

Meteorological conditions such as wind direction and speed, mixing height and temperature play an important role in the formation and removal mechanisms of PM components, thereby impacting ambient pollutant concentrations in different time of the year. EC shows a seasonal variation, with higher concentrations in winter (avg. = 1.88 ± 1.2 $\mu g/m^3$) than summer (avg. = 0.82 ± 0.54 $\mu g/m^3$). Such trend is more distinct in the source areas and less pronounced at the two inland sites. Mean monthly levels of EC in $PM_{2.5}$ ranged from 0.58 to 0.89 $\mu g/m^3$ in summer to 1.34 to 2.15 $\mu g/m^3$ in winter. In this Basin, EC predominantly arises from vehicular emissions. In winter, the level of atmospheric dispersion is generally lower due to lower temperature and weaker prevailing winds, facilitating the accumulation of air pollutants in the western side of the Basin. OM, predominantly arises from anthropogenic emissions in the fine mode, displays a similar seasonal trend with EC, with higher concentrations in winter (avg. = 6.93 ± 2.7 $\mu g/m^3$) than other seasons (avg. = 5.72 ± 2.34 $\mu g/m^3$). The seasonal characteristics of CM vary by location. At the two inland sites, winter CM levels are lower than or similar to those of summer. At most other sites, CM levels are higher in winter than summer. Generally, sea salt levels are lower in winter (avg. = 0.52 ± 0.43 µg/m^3) than other seasons (avg. = 0.79 ± 0.51 µg/m^3). In this Basin, prevailing onshore wind is stronger in spring and summer, transporting marine emissions from the coast to the inland areas. The lower concentrations in winter result from the lower wind speed and the change of predominant wind direction (from westerly in summer to northerly and northeasterly in winter) in certain sites. The seasonal and spatial trend of inorganic ions is determined by sulfate, nitrate and ammonium. Winter sulfate levels are lower than summer levels by 77.7 ± 4.6%. Across the 10 monitoring sites, winter concentrations range from 0.31 to 0.67 µg/m^3, while summer levels vary from 1.95 to 2.39 µg/m^3. The higher temperature in summer favors the photochemical oxidation of SO_2 and enhances the formation of particulate sulfate. Winter nitrate levels, on the other hand, are higher than or similar to those of summer. The seasonal variation is more distinct near the coast (North Long Beach, West Long Beach, Compton and Anaheim). Gas-to-particle conversion of ammonium nitrate is generally stronger in wintertime, when temperature is lower and more favorable for the formation of particulate nitrate (Seinfeld and Pandis, 2006). The seasonal variation of ammonium is similar to that of nitrate, with slightly higher concentration in winter than summer.

Note that an air pollution episode, defined as three or more continuous days of daily 24-hour average $PM_{2.5}$ concentration exceeding 35 µg/m^3, occurred from December 7 to December 9, 2012. PM levels are elevated (>30% above annual average) from December 5 to December 11 at most sampling stations. As a result, the samples collected on December 5 and 11 of 2012 show considerably higher levels of PM components compared with other data collected in winter. Figure X-2 shows the chemical composition of $PM_{2.5}$ on December 11. Compared to the yearly averages (Figure X-1), the contributions of EC and inorganic ions to the reconstructed mass are higher on December 11, while the fractions of OM, crustal and sea salt decrease. Inorganic ion is the most abundant category, accounting for 43.0 ± 3.1% of the reconstructed mass. In particular, nitrate is a major constituent, and its contribution on December 11 (26.0%) is considerably higher than the yearly average contribution (16.0%). About one-third (35.8%) of the reconstructed mass is attributed to OM. EC's average contribution is 13.6 ± 1.8%. Note that the episode is more pronounced at the source area, where both the gravimetric and reconstructed mass increase by more than 50% relative to the yearly averages. Given the spatial variation of the episode's magnitude, the increase levels of EC and inorganic ions in the source area, and the examination of meteorology (temperature, dew point, wind speed, etc.), the episode is likely due to an event of fog in stagnant conditions, which is characterized by an increase in relative humidity and reduction in atmospheric dilution. These atmospheric conditions favor the formation of secondary ions, resulting in their high concentrations in the source areas (Seinfeld and Pandis, 2006).

Chemical mass reconstruction is not conducted on PM_{10} and TSP measurement due to the absence of metal and/or inorganic ion data. Nonetheless, the ratios of EC and OC to gravimetric mass concentrations are compared. On average, EC accounts for 8.6 ± 6.5% and 5.9 ± 3.1% of $PM_{2.5}$ and PM_{10}, respectively. This is consistent with the understanding that EC is more abundant in fine PM than coarse PM in areas with dominant primary emissions. OC contributes to 33.7 ± 14% of $PM_{2.5}$ and 17.5 ± 6.6% of PM_{10}. The source of OC is distinct in the fine and coarse fraction in this Basin. OC in the fine mode primarily originates from anthropogenic emissions, while a significant fraction of coarse PM-bound OC arises from biogenic sources such soil-derived dust and humic substances (Cheung et al., 2011). The mass fraction of OC in coarse mode aerosols is generally lower.

X.3. Elemental Carbon in $PM_{2.5}$ and PM_{10}

EC was measured in both $PM_{2.5}$ and PM_{10} samples in the MATES III and MATES IV Study, while the MATES II Study quantified EC only in PM_{10}. Their levels are shown in Figures X-3 and X-4.

In the PM_{10} samples, average EC level is 1.58 ± 0.08 µg/m^3. EC decreased by 24% compared to MATES III and 52% compared to MATES II. The reduction is more significant for fine particles. Average EC in $PM_{2.5}$ is 1.17 ± 0.99 µg/m^3, which is 36% lower than MATES III. Fine particulate EC primarily arises from fossil fuel combustion in this Basin, whereas the contribution of biomass burning could be significant in the coarse mode in the inland areas, particularly in winter. Additionally, nonexhaust emissions, namely tire and brake wear, as well as road surface wear, could be a major source of EC in coarse PM. The higher reduction in fine particulate EC suggests the sources of EC in fine PM (i.e. emission from fossil fuel combustion) is more efficiently controlled than the sources in the coarse mode. Due to proximity to the Ports of Long Beach and Los Angeles, the two Long Beach sites are heavily influenced by heavy-duty diesel vehicle (HDDV). Although HDDV is a major source of EC, the levels of EC in Long Beach are similar to other monitoring sites, suggesting the reduction of tailpipe emissions of HDDVs and/or stronger dilution of air pollutants along the coast in MATES IV. In 2006, the Clean Air Action Plan was adopted by the Ports of Long Beach and Los Angeles. Incentives were provided to the trucking industry to switch to newer and cleaner trucks. Starting in 2012, trucks that do not meet the 2007 Federal Clean Truck Emission Standards are not allowed to service the Ports' terminals. The significant reductions of fine particulate EC at West Long Beach (44%), and to a lesser extent North Long Beach (38%), relative to MATES III are in line with the monitoring data from the ports. Note that the levels of some PM constituents measured at the MATES IV West Long Beach site were slightly higher than those measured concurrently at the MATES III West Long Beach site (more details about the location and comparison of the two sites can be found in Appendix V). Therefore, the percentage reduction of PM species from the ambient monitoring program in West Long Beach might be a low estimate.

On average, $PM_{2.5}$-bound EC contribute to 68% of the EC measured in the PM_{10} samples. Interestingly, the ratio of $PM_{2.5}$-bound EC to PM_{10}-bound EC shows a spatial variation. The lower fractions at West Long Beach (57%) and North Long Beach (58%) indicate that a higher fraction of EC resides in the coarse mode at Long Beach compared to other areas. Wear from tires, brake, and road surface is a significant nonexhaust source of coarse particle emissions, particularly at Long Beach where HDDV is a major source of air pollutants. The lower ratios suggest that EC originating from HDDV, either as direct or indirect emissions, may contribute significantly to coarse particles. Additionally, the coarse fraction of EC, calculated as the difference between PM_{10} and $PM_{2.5}$, is significantly higher at West Long Beach (avg. = 0.63 µg/m^3; 95% CI = 0.08 µg/m^3) than the nine other sites (avg. = 0.44 µg/m^3; 95% CI = 0.03 µg/m^3). West Long Beach is 100 m. east of the Terminal Island Freeway and 1.2 km. west of the Long Beach Freeway (I-710). It is heavily impacted by the large volume of HDDVs from port activity. Furthermore, the relative humidity is usually a few percent higher in Long Beach than

Central Los Angeles and the inland areas, thereby impeding the degree of particle re-suspension. The lower ratio at Long Beach suggests a local source, either in the form of emission or re-suspension of coarse particulate EC. HDDVs are known to have higher emissions of tire and brake wear due to the stronger abrasion processes, and they also induce a greater magnitude of particle re-suspension from the road than light-duty traffic (Charron and Harrison, 2005). Given that this site experiences similar fine particulate EC levels with other sites, it is likely that coarse PM-bound EC originate from the mechanical processes of abrasion from the HDDVs.

As mentioned previously, both $PM_{2.5}$ and PM_{10} EC levels are higher in winter than other seasons due to meteorology (Figures X-5 and X-6). During cooler months, the mixing height is generally lower. Furthermore, particle re-entrainment by wind reduces due to lower wind speed in the source area. Consequently, the effect of vehicle-induced re-suspension becomes more pronounced, resulting in higher fractions of traffic-related coarse particles. The seasonal trend is consistent at all sites with the exception of Central Los Angeles. $PM_{2.5}$ EC winter level is 1.88 $\mu g/m^3$ (95% CI = 0.20 $\mu g/m^3$), doubling the average level of 0.93 $\mu g/m^3$ in other seasons (95% CI = 0.21 $\mu g/m^3$). Similar results are found for EC in PM_{10}. Winter average is 2.27 $\mu g/m^3$ (95% CI = 0.21 $\mu g/m^3$), compared with 1.34 $\mu g/m^3$ (95% CI = 0.07 $\mu g/m^3$) in other seasons.

X.4. Metals in TSP

Concentrations of selected metals in TSP in MATES IV, and their levels in MATES II and III, are shown in Figures X-7 to X-14.

Figures X-7 and X-8 show arsenic and cadmium concentrations. The average level of arsenic is 0.55 ng/m^3, with higher levels at the inland areas. In Inland Valley San Bernardino, the average level is 0.91 ng/m^3. In Rubidoux, the higher average of 0.76 ng/m^3 is driven by a spike of 6.34 ng/m^3 on July 14, 2012. Most measured elements recorded a considerably higher concentration (> 4 times higher than average) on that day. Note that the lower arsenic levels relative to MATES II is partly driven by the lower detection limits in the current study. The average concentration of cadmium is 0.16 ng/m^3. Although MATES IV cadmium levels are considerably lower, these trends are largely due to the lower reporting limits for MATES IV (LOD = 0.08 ng/m^3), compared with the previous studies (LOD = 10 ng/m^3 for MATES II and 2 ng/m^3 for MATES III). Inland Valley San Bernardino records higher cadmium levels at an average of 0.28 ng/m^3, followed by Central Los Angeles at 0.25 ng/m^3. With the exception of Central Los Angeles and the two inland sites, cadmium levels are usually higher in winter than other seasons.

Figure X-9 shows the decline of lead, and the trend is consistent at all sites. Average lead concentration is 6.21 ng/m^3, which is 50% lower than MATES III and 75% lower than MATES II. Inland Valley San Bernardino records higher lead levels at an average of 9.80 ng/m^3, followed by Huntington Park at 9.46 ng/m^3. The highest daily lead concentration of 81.7 ng/m^3 is observed at Huntington Park on February 15, 2013. All measured concentrations are below the Ambient Air Quality Standard of lead at 1,50 ng/m^3.

Nickel and vanadium concentrations are shown in Figures X-10 and X-11. Compared with MATES III, vanadium reduces by 68% across the 10 sites, with higher reductions at Anaheim (80%), North Long Beach (78%) and West Long Beach (83%). The reduction of nickel is 36%, and the decline is again more pronounced at West Long Beach (67%), Anaheim (59%) and North

Long Beach (50%). Ni and V are impurities of bunker and fuel oil used in ships (Krudysz et al., 2008). Their declines at Long Beach suggest potential emissions reduction from ports activity. On the other hand, average nickel and vanadium concentrations are similar between MATES III and MATES IV at the two inland locations (Rubidoux and Inland Valley San Bernardino). Given their reductions at Long Beach, the higher levels at the inland sites suggest soil and road dust as a significant source of Ni and V in TSP. Nickel concentration is highest (avg. = 5.40 ng/m^3) at Huntington Park, which is largely driven by a few data points in winter, as reflected in the higher confidence interval. With the exception of the two inland sites, winter nickel levels are higher than or similar to those of summer. Vanadium in fine PM could originate from oil combustion and industrial activities, while street and road dust is another source for coarser particles (Pakbin et al., 2011). Except for Anaheim, the level of vanadium is about two to four times higher in August (avg. = 9.05 ng/m^3) than other months. Vanadium started to increase in late July, reached its peak in August, and declined in early September. Similar temporal trend is observed for other elements, namely, titanium, strontium, potassium, iron, molybdenum, copper, calcium, barium and zinc. Higher levels of windblown dust are usually observed in warmer months due to the stronger wind and lower relative humidity. The higher monthly concentration of vanadium and other crustal elements in August across the Basin could result from dust re-suspension.

Figure X-12 shows hexavalent chromium concentrations. In MATES II, half of the PM samples were analyzed by ARB and half were analyzed by SCAQMD. The ARB laboratory had higher method detection limits for hexavalent chromium, likely resulting in the lower reported concentrations than the SCAQMD samples. For comparison purposes, only results from the SCAQMD laboratory analyses are shown. Site-wide average hexavalent chromium level is 69% lower compared to MATES III. Winter levels are generally higher than other seasons. In particular, Compton and Huntington Park recorded higher concentrations on February 27, 2013, at 0.85 and 1.80 ng/m^3 ,respectively. In MATES III, staff identified cement production as a source of elevated levels of hexavalent chromium near the Rubidoux site. In the current study, the annual average at Rubidoux is 0.041 ng/m^3, lower than the levels at MATES III (avg. = 0.39 ng/m^3) and the site-wide average of 0.056 ng/m^3 in the current study.

Figures X-13 and X-14 illustrate the average level of selenium and manganese, both of which are in the EPA original list of hazardous air pollutants. In MATES III, all measured selenium levels were under the method detection limits of 2 ng/m^3. For MATES IV, the average concentration is 0.82 ng/m^3, with higher levels at Huntington Park (avg. = 1.67 ng/m^3). The average concentration of manganese is 22.4 ng/m^3. The highest average level is observed at Inland Valley San Bernardino (52.0 ng/m^3), followed by Rubidoux (33.0 ng/m^3). Overall, the reduction of manganese (28% relative to MATES III) is not as significant as other metals examined in this section. Manganese is an element in the upper continental crust. The high correlations (R^2 range from 0.60 to 0.93) between manganese and titanium, a dust tracer, suggesting that manganese in TSP primarily originates from crustal materials in this Basin. To examine the relative contributions of anthropogenic vs. crustal origins of manganese, crustal enrichment factors (CEFs) are calculated using the reference element of titanium. In brief, the level of observed manganese is divided by the level of observed titanium in this study, which is then normalized to the average abundance of manganese in the upper continental crust (UCC) obtained in Usher et al. (2006). Note that this calculation is typically conducted in reference to aluminum, which is not quantified in TSP in this study. CEF > 10 is indicative of anthropogenic sources. Across the 10 sites, the average CEF range from 1.8 to 2.5. The highest CEF (10.9) is found at Compton on March 17, 2013. At the inland sites, all CEFs are below 5.

X.5. References

E. Andrews, P. Saxena, S. Musarra, L. M. Hildemann, P. Koutrakis, P. H. McMurry, I. Olmez, and W. H. White, Concentration and composition of atmospheric aerosols from the 1995 SEAVS experiment and a review of the closure between chemical and gravimetric measurements, *Journal of the Air & Waste Management Association*, 50, 5: 648-664, 2000.

A. Charron and R. M. Harrison, Fine (PM2.5) and coarse (PM2.5-10) particulate matter on a heavily trafficked London highway: Sources and processes, *Environmental Science & Technology*, 39, 20: 7768-7776, 2005.

K. Cheung, N. Daher, W. Kam, M. M. Shafer, Z. Ning, J. J. Schauer, and C. Sioutas, Spatial and temporal variation of chemical composition and mass closure of ambient coarse particulate matter (PM10-2.5) in the Los Angeles area, *Atmospheric Environment*, 45, 16: 2651-2662, 2011.

M. A. Krudysz, J. R. Froines, P. M. Fine, and C. Sioutas, Intra-community spatial variation of size-fractionated PM mass, OC, EC, and trace elements in the Long Beach, CA area, *Atmospheric Environment*, 42, 21: 5374-5389, 2008.

W. C. Malm, J. F. Sisler, D. Huffman, R. A. Eldred, and T. A. Cahill, Spatial and seasonal trends in particle concentration and optical extinction in the United States, *Journal of Geophysical Research: Atmospheres*, 99, D1: 1347-1370, 1994.

P. Pakbin, Z. Ning, M. M. Shafer, J. J. Schauer, and C. Sioutas, Seasonal and Spatial Coarse Particle Elemental Concentrations in the Los Angeles Area, *Aerosol Science and Technology*, 45, 8: 949-U156, 2011.

J. H. Seinfeld and S. N. Pandis, Atmospheric Chemistry and Physics - From Air Pollution to Climate Change, (Second edition ed.), John Wiley & Sons, Inc, New York, 2006.

C.R. Usher, A. E. Michel and V.H. Grassian, Reactions on Mineral Dust, *Chemistry Reviews*, 103:4883-4939, 2003.

**Error bars in the charts denote 95% confidence interval*

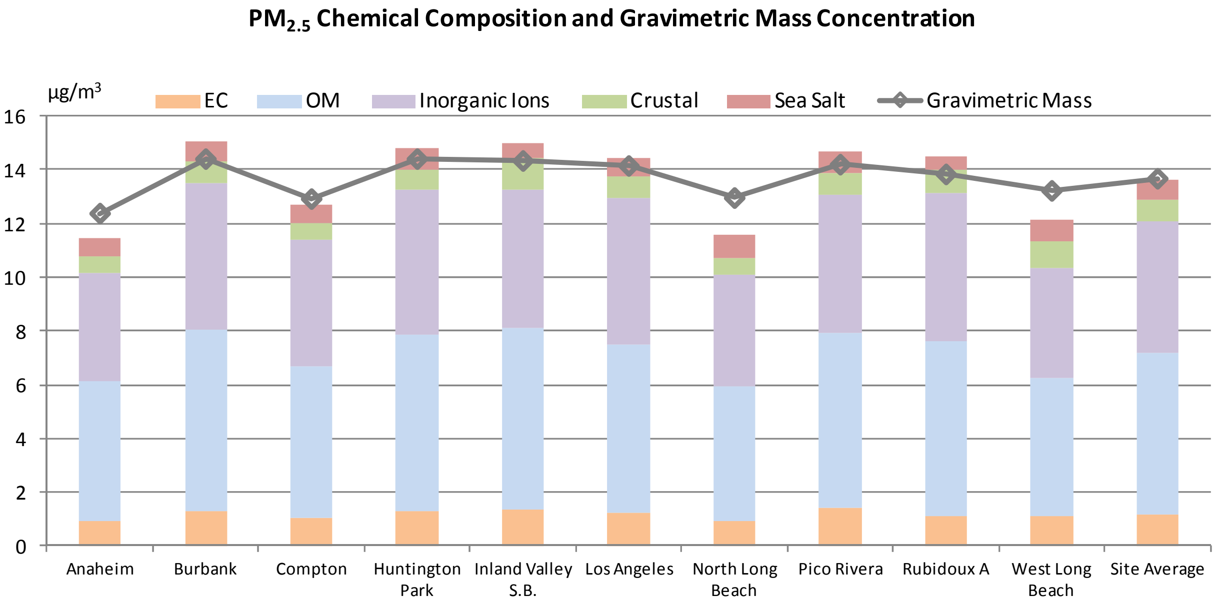

Figure X-1 Annual Average Chemical Composition and Gravimetric Mass Concentrations in $PM_{2.5}$

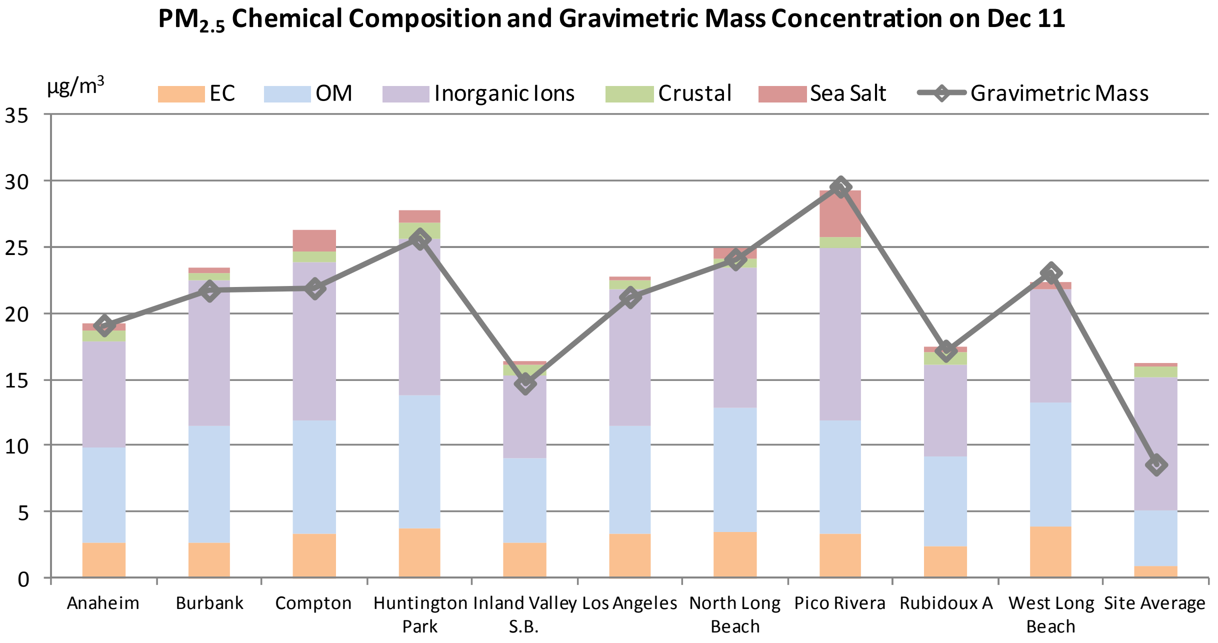

Figure X-2 Chemical Composition and Gravimetric Mass Concentrations in $PM_{2.5}$ on December 11, 2012

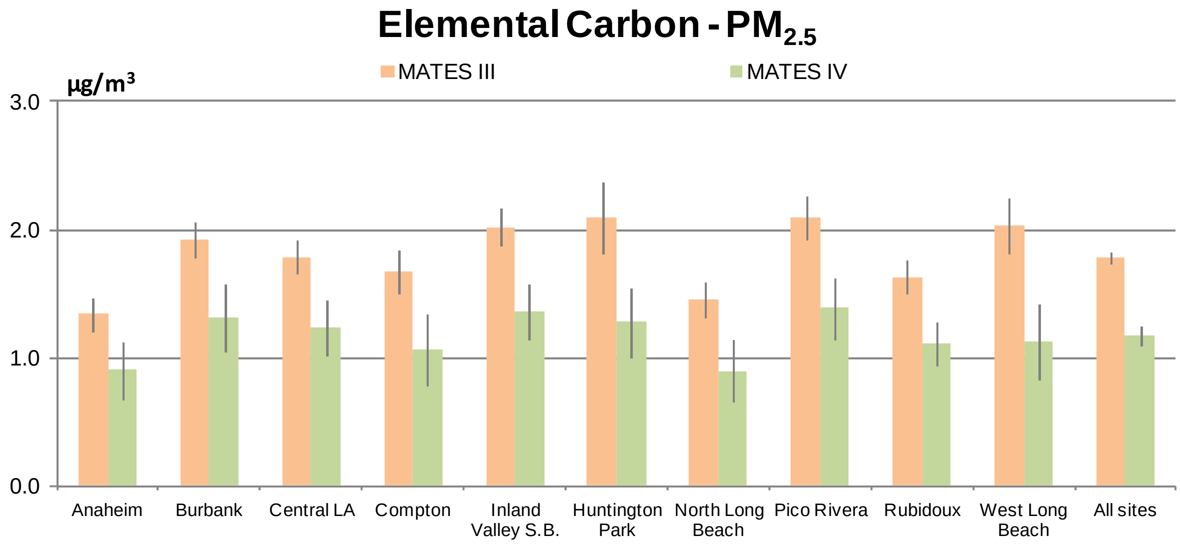

Figure X-3 Average Concentrations of Elemental Carbon in $PM_{2.5}$

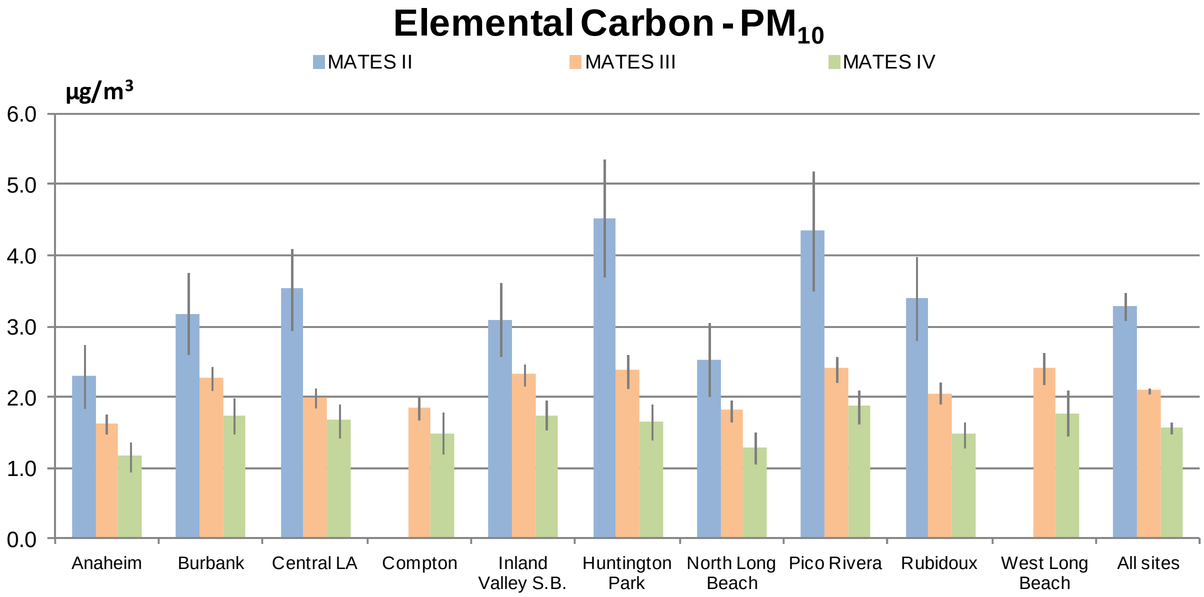

Figure X-4 Average Concentrations of Elemental Carbon in PM_{10}

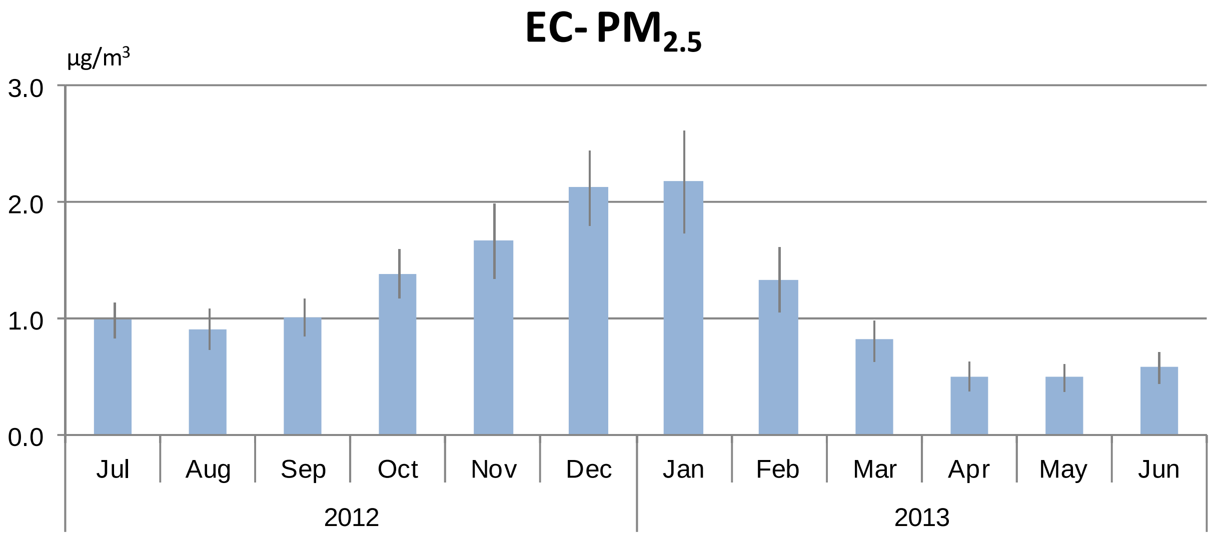

Figure X-5 Monthly Average Concentrations of Elemental Carbon in $PM_{2.5}$

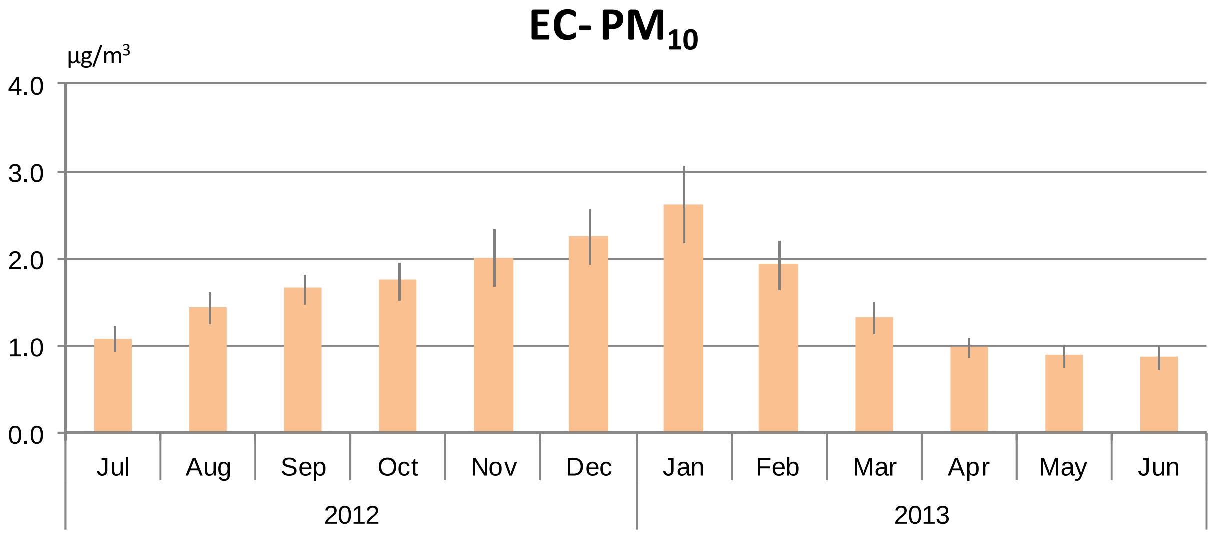

Figure X-6 Monthly Average Concentrations of Elemental Carbon in PM_{10}

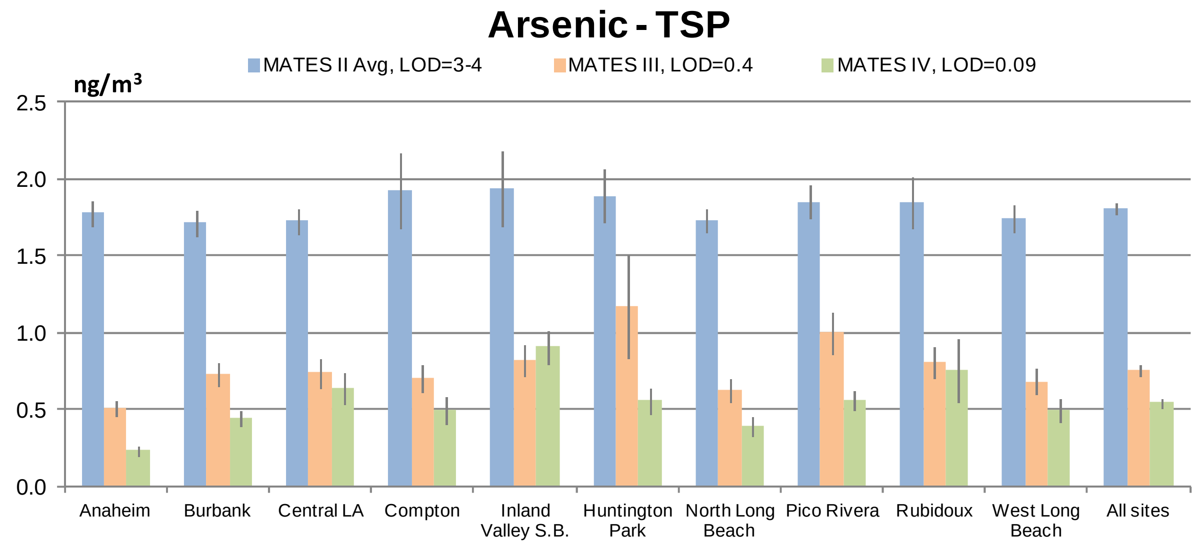

Figure X-7 Average Concentrations of Arsenic in Total Suspended Partiulate (TSP)

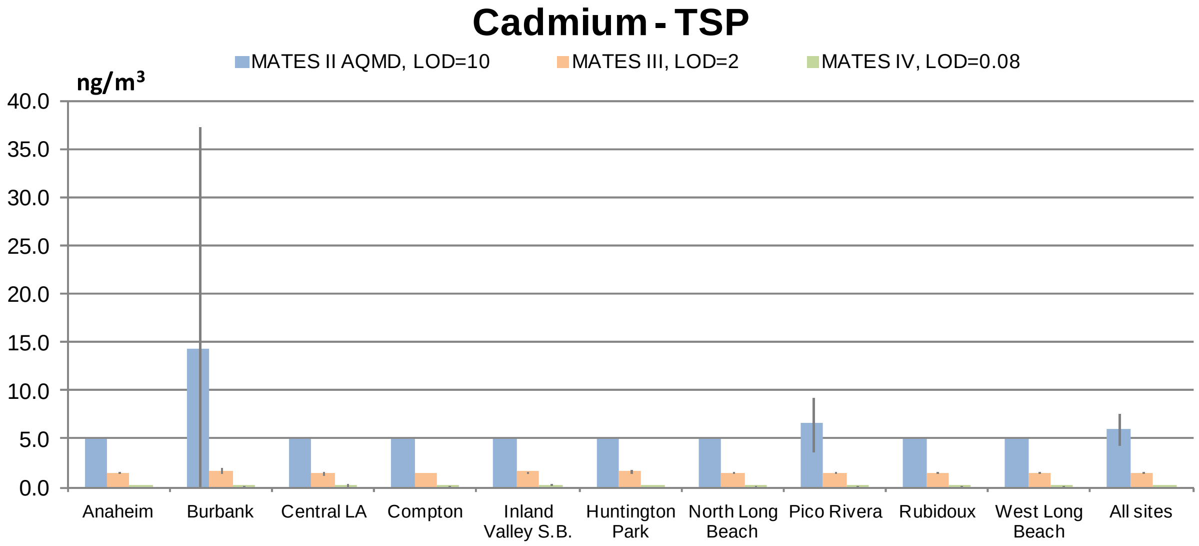

Figure X-8 Average Concentrations of Cadmium in Total Suspended Partiulate (TSP)

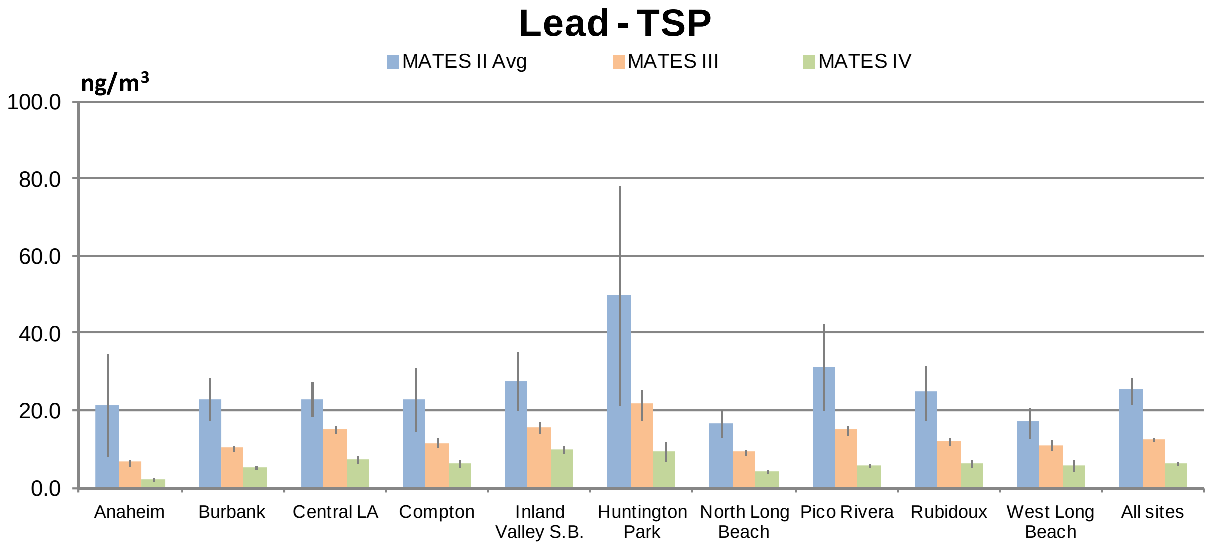

Figure X-9 Average Concentrations of Lead in Total Suspended Partiulate (TSP)

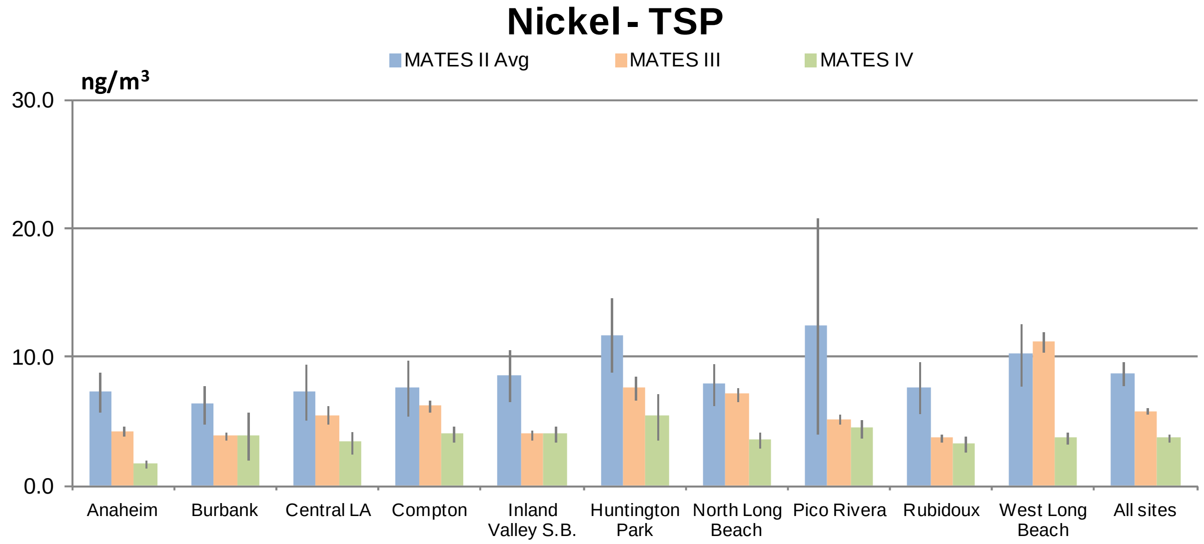

Figure X-10 Average Concentrations of Nickel in Total Suspended Partiulate (TSP)

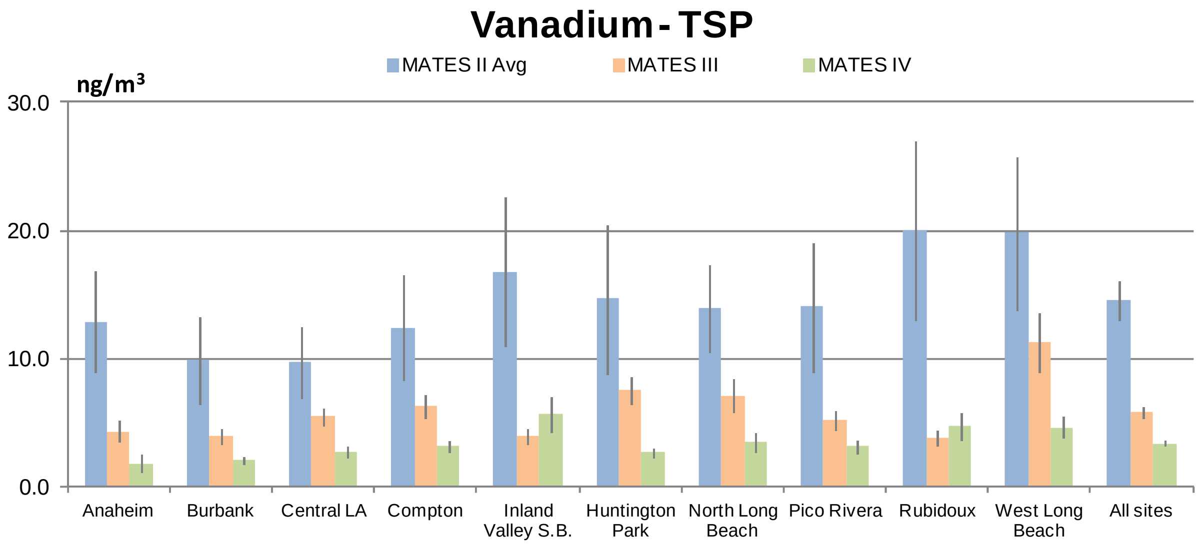

Figure X-11 Average Concentrations of Vanadium in Total Suspended Partiulate (TSP)

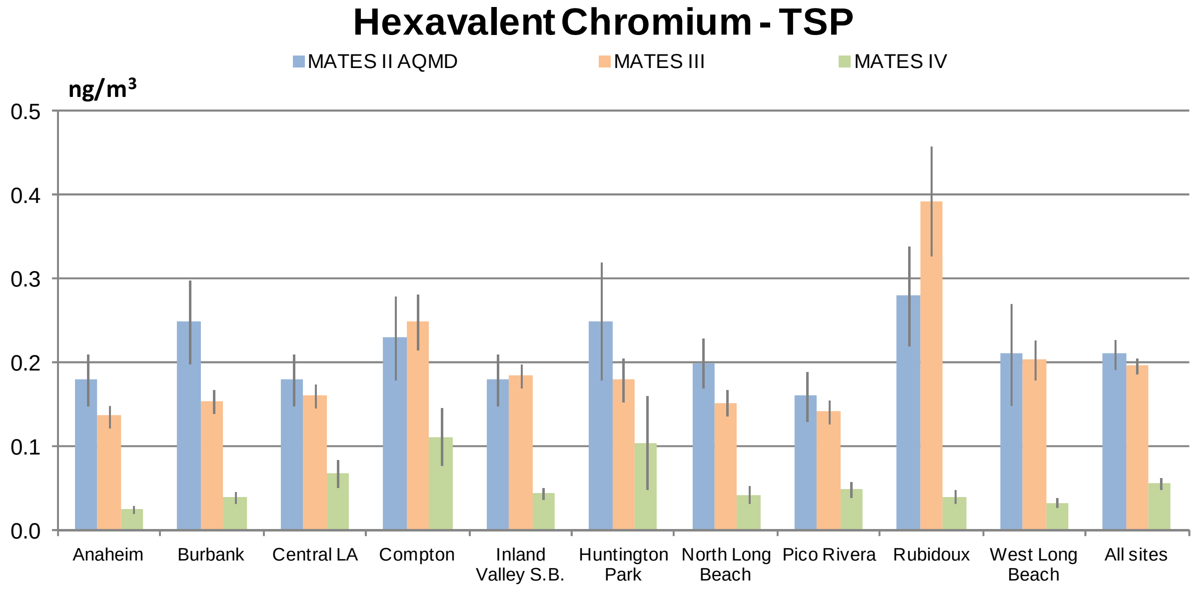

Figure X-12 Average Concentrations of Hexavalent Chromium in Total Suspended Partiulate (TSP)

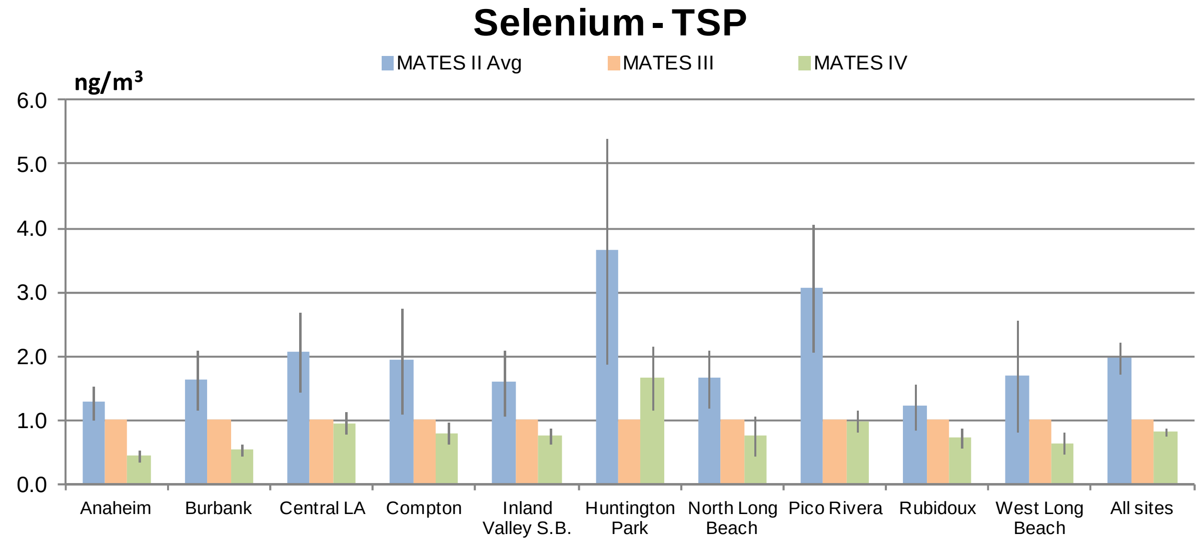

Figure X-13 Average Concentrations of Selenlium in Total Suspended Partiulate (TSP)

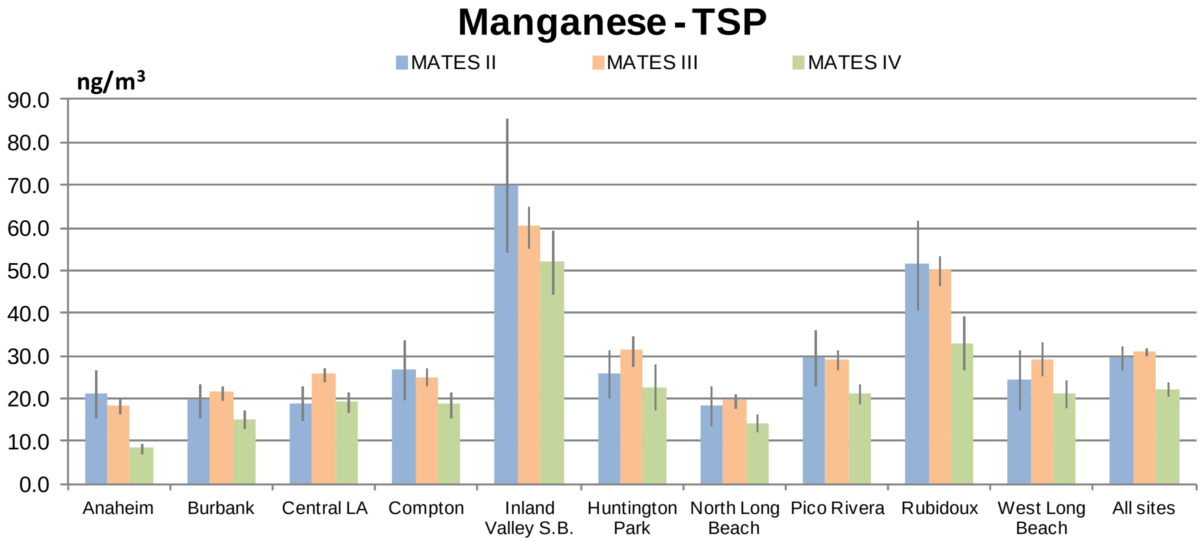

Figure X-14 Average Concentrations of Manganese in Total Suspended Partiulate (TSP)

APPENDIX XI

MATES IV

DRAFT FINAL REPORT

Estimating Diesel Particulate Matter

Authors

Philip Fine

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Appendix XI. Estimating Diesel Particulate Matter

XI.1. Introduction

Ambient diesel PM concentrations cannot be measured directly, but were estimated using ambient EC measurements multiplied by the ratio of diesel particulate matter (DPM) to elemental carbon (EC) based on the emissions inventory. The ratio estimated for MATES IV is 0.81, which is smaller than a ratio of 1.95 found in MATES III. This chapter describes factors contributing to this change and uncertainties associated with the estimates.

XI.2. Methodology

The ratio of diesel particulate matter (DPM) to elemental carbon (EC) can be rewritten, under well-mixed atmospheric conditions,

$$Ratio = \frac{DPM_{total}}{EC_{total}} = \left(\frac{PM_{diesel}}{EC_{diesel}}\right) \cdot \left(\frac{EC_{diesel}}{EC_{total}}\right). \qquad [1]$$

The first term, the ratio of PM from diesel to EC from diesel is determined by the combined speciation profiles of all diesel PM sources, which provides the fraction of each PM species including EC, organic matter, sulfate, nitrate and others. The speciation profiles used in MATES IV were significantly different from those used in MATES III. In the new PM speciation profile, which was developed based on recent dynamometer experiments and comprehensive source testing, heavy-duty diesel trucks have an EC fraction ranging from 23% to 68% depending on engine model year, emission control technology, driving cycle, etc. An example of the new speciation profile from heavy duty diesel truck is presented in Figure XI-1, which shows EC fraction as a function of calendar year. It increases from 50% for calendar year 2005 to 56% in 2010. Calendar year fleet is an aggregated fleet composed of various engine model years, technology groups, fuel types, operating conditions, etc.

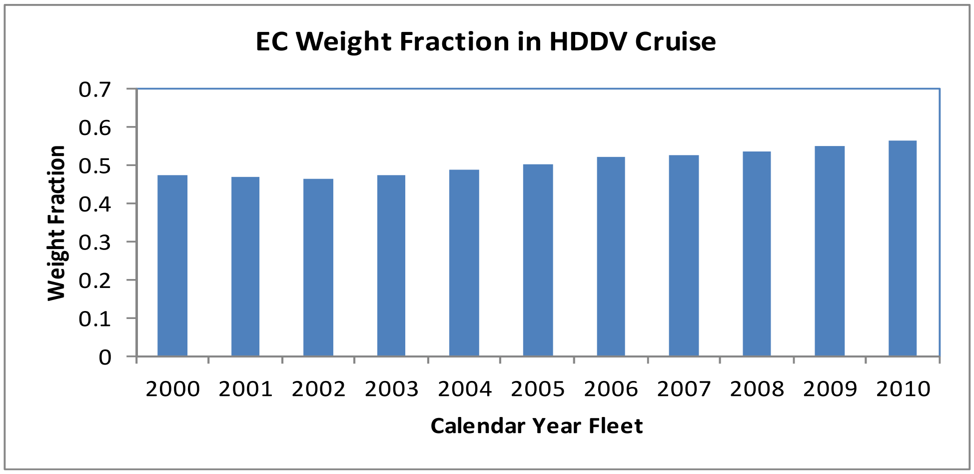

Figure XI-1. The EC fraction by weight from Heavy Duty Diesel Vehicles Exhaust in Cruise mode

On the contrary, the MATES III inventory was developed using a diesel profile based on source tests conducted on diesel tractors more than 20 years ago (Houck 1989, CARB 2008). In addition, only one speciation profile was applied to all diesel fueled mobile source categories, regardless of the fleet type, operating condition, engine technology, etc. However, at the time of MATES III, this profile was considered state-of-the-science. This PM profile assumes that 26.4% of total diesel exhaust is EC, while the MATES IV profile for heavy-duty vehicles has closer to 50% EC (Figure XI-1).

A majority of diesel emissions come from heavy-duty diesel trucks, diesel buses, ocean-going vessels, and off-road equipments categories, as shown in Table XI-1. These categories account for approximately 92% of total DPM emission in the Basin. Corresponding EC fractions and DPM/EC ratios are presented as well.

Note that the total DPM/EC ratio is an average of category specific DPM/EC ratios weighted by DPM mass from the category. So shifts among relative emissions from all diesel sources will also change the total combined speciation profile.

Some of the changes in the DPM/EC ratio could result from recent regulatory actions. Changes in PM speciation from OGV show the impact of such actions. During the period between the MATES III and MATES IV, OGV fuel regulation by California Air Resources Board became effective. The regulation requires OGVs to switch from heavy fuel oil (HFO, 1.0-2.5% sulfur content) to distillate marine diesel oil (MDO) of ~0.1% sulfur within 200 nautical miles of California coast. This requirement decreased sulfate in diesel exhaust more effectively than the other components including EC. In fact, replacement of 2.5% HFO marine fuel to 0.1% MDO marine fuel leads to a decrease in sulfate emissions of almost one-half while EC emissions remain nearly constant (CARB, 2012). The reduction in DPM emissions is well reflected in the MATES IV inventory (Table XI-1).

In all, the changes in the speciation profiles along with shifts in the relative amount of DPM emission from different diesel sources led to a lower value of the 1st term in Eq [1].

Table XI-1. Emissions for major DPM/EC source categories, total anthropogenic sources for the South Coast Air Basin and percentage change of DPM and EC from 2005 to 2012

Category	2005			2012			Changes	
	DPM (lb/day)	EC (lb/day)	DPM/ EC Ratio	DPM (lb/day)	EC (lb/day)	DPM/ EC Ratio	DPM (%)	EC (%)
Diesel Heavy Duty Trucks & Buses	19596	5231	3.75	9816	5298	1.85	49.91	-1.29
Other On-Road	795	3233	0.25	134	1340	0.10	83.12	58.54
Ocean Going Vessels	10365	415	25.00	990	60	16.39	90.45	85.43
Off-Road Equipment	21567	6207	3.47	5275	3865	1.36	75.54	37.72
Other Off-Road	2614	1720	1.52	2208	1670	1.32	15.55	2.88
Total Stationary and Area Sources	1045	11957	0.09	444	10928	0.04	57.55	8.60
Total Anthropogenic	55983	28761	1.95	18867	23163	0.81	66.30	19.47

The last term in Eq [1] represents the amount of diesel EC relative to the total EC emissions based on the Basin-wide inventory. The total EC, EC_{total} in Eq [1] can be split into diesel originated EC and non-diesel EC. In the Basin, the diesel EC accounts for the majority of total EC (64%). Non-diesel EC from sources such as biomass burning, cooking, residential fuel combustion, explain 36% of the total. While EC emissions from both diesel and non-diesel categories decreased between the MATES III and MATES IV, the reduction is more pronounced in the diesel category (24% reduction in diesel EC vs. 10% in non-diesel sources). A portion of changes in the non-diesel sources were driven by socio-economic growth in the Basin. Cleaning and Coating processes and Petroleum Production and Marketing categories are among those that have led to additional EC emissions between the MATES III and MATES IV period. This change in total EC decreased in the 2nd term of Eq [1]. Therefore, the overall ratio was decreased from the MATES III to MATES IV.

XI.3. Discussion and Summary

To estimate the impact of the updated speciation profile on measurements-based comparisons between the MATES III and MATES IV results, EC emissions from major diesel source categories in the MATES IV inventory were re-calculated using the older MATES III speciation profile, in which EC accounts for 26.4% of DPM. This retrospective calculation was applied to heavy-duty diesel trucks, diesel buses, off-road equipment, and farm equipment (Table XI-2).

The retrospective calculation yielded 23% less total anthropogenic EC emissions with most of the difference coming from the mobile source category. This in consistent with a ~30% reduction of EC from traffic emissions in LA and Riverside counties from the 2002-2006 to the 2008-2012 period as determined by source apportionment study (Hasheminassab, et al. 2014).

The overall DPM/EC ratio from this sensitivity calculation was 1.06 and thus the overall average ambient DPM concentration was estimated to be 1.24 ug/m^3 (1.17 ug/m^3 basin-wide averaged measured ambient EC concentration during MATES IV, multiplied by the ratio 1.06). Using the updated profiles in MATES IV with a DPM/EC ratio of 0.81 (TableXI-1), and the measured ambient EC of 1.17 ug/m^3, the overall average DPM concentration is estimated to be 0.95 ug/m^3.

This sensitivity test indicates that the effect of the speciation methodology change between MATES III and MATES IV is an overall lower estimated DPM concentration from 1.24 to 0.95 ug/m^3. This difference can be viewed in terms of the estimated DPM reductions based on EC measurements between MATES III (2005) and MATES IV (2012). Using the updated profiles for MATES IV and the previously published MATES III results using the older profiles, the basin-wide average reduction in DPM is 73% as cited in this report. Using the older speciation profiles for both MATES III and MATES IV yields a 2005 to 2012 DPM reduction of 64.3%. Thus, the methodology changes in the DPM speciation profile account for at most about 9% of the total stated 73% stated DPM reduction. It is also worth of note that, despite the uncertainties associated with emission inventory and measurements, the estimated DPM concentration stays within 25% of variation.

Note that the effect of this speciation methodology change only affects MATES III vs. MATES IV comparisons between estimated DPM based on EC measurements. Comparisons between 2005 and 2012 based on inventories and modeling results are not affected by the EC speciation profiles as DPM is estimated directly. Furthermore, given that the speciation profiles used in MATES IV are more recent and applied in a more detailed manner, the MATES IV results represent a refined analysis that is likely an improvement over the MATES III methods.

Table XI-2. Estimation of EC fractions from major diesel sources using the MATES III profile

Category	**MATES IV**			**Using MATES III profile**	
	DPM (lb/day)	EC (lb/day)	DPM/EC Ratio	EC (lb/day)	DPM/EC Ratio
Diesel Heavy-Duty Trucks & Buses	9816	5298	1.85	2594	3.78
Other On-Road	134	1340	0.10	1340	0.10
Ocean Going Vessels	990	60	16.39	60	16.39
Off-Road Equipment	5275	3865	1.36	1394	3.78
Other Off-Road	2208	1670	1.32	1453	1.52
Total Stationary and Area Sources	444	10928	0.04	10928	0.04
Total Anthropogenic	18867	23163	0.81	17771	1.06

The DPM/EC ratio discussed above is the basin average, yet the ratio can change from location to location depending on the dominant emission categories. The geographical variation of the ratio was evaluated using CAMx model output, which calculates atmospheric transport and mixing as well as chemistry and removal processes. The average of the predicted DPM/EC ratio is approximately 0.87 with a standard deviation of 0.06, indicating spatial variations were relatively small. Still, the ratio was higher near coastal sites and lower in inland regions, confirming the geographical dependency of diesel exhaust compositions. Non-diesel EC sources, such as biomass burning, partially contributed to the lower ratio in the inland areas, as well.

Overall, the DPM/EC ratio estimated in the current MATES IV is 0.81, significantly lower than 1.95 calculated in the MATES III. Several factors that contributed to this change include the revision of diesel exhaust profiles that provide more refined and detailed speciation data. Secondly, regulatory actions reduced some components of PM species more effectively than EC. In addition, changes in social demographics contributed to the changes of diesel originated EC to the total EC emissions, and consequently lowered the DPM/EC ratio.

XI.2 References:

California Air Resources Board, Main Speciation Profiles. In May 19, 2008 ed.; California Air Resources Board: 2008.

California Air Resources Board, Heavy Duty Diesel Vehicle Exhaust PM Speciation Profiles, Available at the following URL, http://www.arb.ca.gov/ei/speciate/profilereference/HDDV%20PM%20Profiles%20Final.pdf

California Air Resources Board, Ocean-Going Vessel (OGV) PM Speciation Profile Preparation, Available at the following URL, http://www.arb.ca.gov/ei/speciate/profilereference/OGV_PM1191-93&4251.pdf

California Air Resources Board, 2012, OGV PM Speciation Profile Development and Assignment, Available at the following URL, http://www.arb.ca.gov/ei/speciate/profilereference/OGV_PM4252.pdf

Hasheminassab, S.; Daher, N; Ostro, B.D.; Sioutas, C, 2014, Long-term source apportionment of ambient fine particulate matter (PM2.5) in the Los Angeles Basin: A focus on emissions reduction from vehicular sources, Environmental Pollution **193**, 54-64.

Houck, J. E.; Chow, J. C.; Waston, J. G.; Simons, C. A.; Pritchett, L. C.; Coulet, J. M.; Frazier, C. A. *Determination of Particle Size Distribution and Chemical Composition of Particulate Matter from Selected Sources in California*; California Air Resources Board: June 30, 1989.

RETURN↑

MATES IV Comments
(Comment Period: October 3, 2014 – January 2, 2015)

Joseph K. Lyou, Ph.D.
President and CEO, Coalition for Clean Air and
Governor's Appointee to SCAQMD Governing Board

David Pettit, Senior Attorney
Natural Resources Defense Council

Constantinos Sioutas, Sc.D.
Fred Champion Professor
Civil and Environmental Engineering,
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Joseph L. Suchecki, Vice President, Public Affairs
Engine Manufacturers Association

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Christopher Cannon, Director of Environmental Management
Port of Los Angeles &
Heather Tomley , Director of Environmental Planning
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John Pastore, P.E.
Executive Director, SCAP

Scott Fruin
USC Occupational & Environmental Health

C. L. Stathos, Environmental Coordinator, Region 9
Department of Defense

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From: Joe Lyou <joe@ccair.org>
Date: October 6, 2014 11:47:50 AM PDT
To: "Barry Wallerstein (bwallerstein@aqmd.gov)" <bwallerstein@aqmd.gov>
Subject: MATES IV

I was just reading the draft MATES IV report, pp. 5-14 to 5-15, re speculation that I-405 Freeway traffic emissions may have contributed to the elevated UFP concentrations at site 8.

The LAX Air Quality Source Apportionment Study includes evidence that the freeway did not influence UFP concentrations measured east of the freeway. Specifically to address this question, the researchers collected simultaneous measurements downwind of the runway and the same distance from the freeway about a mile and a half south of the runway. See Phase III of the LAX AQSA Study, pp. 5-99 to 5-113.

The results showed that the elevated UFP concentrations could be attributed to aircraft, not the freeway. The language on pp. 5-14 to 5-15 of MATES IV should be revised to acknowledge the LAX AQSA study finding and suggest instead that, while the freeway could be a source of UFP, existing evidence shows that the elevated concentrations result from aircraft.

Joe

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From:	Pettit, David
To:	Philip Fine
Cc:	Leben, Danielle; Jean Ospital
Subject:	RE: MATES IV draft
Date:	Wednesday, October 08, 2014 5:27:21 PM

Thanks.

David Pettit
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From: Philip Fine [mailto:pfine@aqmd.gov]
Sent: Wednesday, October 08, 2014 5:26 PM
To: Pettit, David
Cc: Leben, Danielle; Jean Ospital
Subject: RE: MATES IV draft

Good suggestions. You are reading table IX-5 correctly.

-Phil

Philip M. Fine, Ph.D.
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From: Pettit, David [mailto:dpettit@nrdc.org]
Sent: Wednesday, October 08, 2014 3:54 PM
To: Philip Fine
Cc: Leben, Danielle; Jean Ospital; Pettit, David
Subject: RE: MATES IV draft

Phil, I think that those are good comparisons for the public to see, and you might want to think about a comparison with local GDP also.

A question on the draft: do I read Table IX-5 correctly as setting out modeled vs observed data for 2012-2013 for the locations listed?

Thanks.

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From: Philip Fine [mailto:pfine@aqmd.gov]
Sent: Tuesday, October 07, 2014 1:54 PM
To: Pettit, David
Cc: Leben, Danielle; Jean Ospital
Subject: RE: MATES IV draft

Since the MATES studies are just single year snapshots, it is hard to do a regression analysis with just two or three data points. The total combined ports container throughput in 2005 (MATES III) was about 14.2 million TEU vs. 14.1 million TEU in 2012 (MATES IV). So with similar throughput, the risks have dropped significantly.

We have also looked at container throughput vs. ambient Elemental Carbon (a marker for diesel PM which drives most of the risk) levels over time. It shows that since the 2009 recession period, container throughput at the ports has increased while Elemental Carbon has significantly decreased.

Let me know if you have any suggestions for additional analyses that could be conducted related to this.

-Phil

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From: Pettit, David [mailto:dpettit@nrdc.org]
Sent: Tuesday, October 07, 2014 1:00 PM
To: Philip Fine
Cc: Leben, Danielle; Pettit, David

Subject: MATES IV draft

Phil: I'm reading through the MATES IV draft and I wondered if the District has run a regression analysis against POLA and POLB throughput to see what effect, if any, higher or lower throughput has had on cancer risk.

David

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From: Constantinos Sioutas [mailto:sioutas@usc.edu]
Sent: Saturday, November 01, 2014 3:29 PM
To: Jean Ospital; Marilyn Traynor
Cc: Philip Fine; Andrea Polidori
Subject: Re: MATES IV Technical Advisory Group meeting at 1:00 p.m. on November 6, 2014 @ SCAQMD in Conference Room GB

Given the significance of traffic sources in our basin, and the fact that you/AQMD use EC as a marker of carcinogenic diesel emissions, I attach our latest paper in which we used PMF on the speciation network data from 2002-2012 to do source apportionment, and showed that in LA and Riverside counties, the traffic emissions were reduced from the 2002-2006 to the 2008-2012 period by ~30% (a very impressive number) following the 2007 emission standards ; this was despite an actual increase in overall traffic volume in the post standard period. This is very relevant to the work presented in your draft document and corroborates the effectivenss of the emission standard

Please use the paper “Long-term source apportionment of ambient fine particulate matter (PM2.5) in the Los Angeles Basin: A focus on emissions reduction from vehicular sources,” authors Hasheminassab, Daher, Ostro, Sioutas (Environmental Pollution 193 (2014) 54-64) for your reference and let me know if you have any comments

cs

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November 3, 2014

VIA E-MAIL

Dr. Jean Ospital
Health Effects Officer
South Coast Air Quality Management District
21865 Copley Drive
Diamond Bar, CA 91765

Re: EMA's Comments on Draft MATES-IV Report

Dear Dr. Ospital:

The Truck and Engine Manufacturers Association (EMA) hereby submits the following comments and recommendations regarding the draft report of the Multiple Air Toxics Exposure Study (MATES-IV) that was released for public comment on October 3, 2014. EMA is the trade association that represents the world's leading manufacturers of heavy-duty trucks, as well as the leading manufacturers of internal combustion engines utilized in a wide variety of other mobile and stationary applications. One of EMA's core functions is to represent its 29 member companies in working with the United States Environmental Protection Agency, the California Air Resources Board, and other state and local agencies on a broad range of air quality issues and initiatives. In that role, EMA has been involved in reviewing and commenting on the SCAQMD's MATES initiative since the issuance of the first MATES report.

In its MATES-IV draft report, the South Coast Air Quality Management District (SCAQMD) states that it has used the same monitoring, modeling, and risk assessment methods that were used in the previous three MATES reports. The draft report acknowledges the shortcomings and caveats regarding those methods, and in particular the uncertainties in estimating ambient levels of diesel particulate matter (diesel PM) and actual human exposure to air toxics, as well as the uncertainties in interpreting the estimates of cancer health risks. These uncertainties are significant, since, as acknowledged in the draft report, the real value to the public of the MATES-IV report stems from its ability to document and communicate clearly and accurately the long-term trends of reduced air toxics in the South Coast Air Basin.

In general, EMA has no new comments on the methodologies or analyses used in the MATES-IV draft report. That said, we remain in fundamental disagreement with the Elemental Carbon/Organic Carbon (EC/OC) apportionment method used in MATES, and also continue to believe that the unit risk factor (URF) applied for diesel PM is not based on sound science, stemming as it does from flawed dose-response assumptions derived from the 1987 and 1988 Garshick, et al. studies of railroad workers. We also are very concerned that EMA was excluded from the MATES technical advisory committees, and that, in fact, no industry representatives were included on that committee. That basic lack of industry representation calls into question the objectivity of the MATES-IV report, and needs to be addressed.

With those long-standing objections in mind, EMA offers the following specific recommendations and suggestions regarding the presentation and reporting of the MATES-IV results, with emphasis on the draft report's discussion of the emission of diesel PM and other air toxics from mobile sources.

The MATES-IV Report does not adequately convey the very significant reductions in ambient levels of air toxics or the successful efforts to reduce air toxics risk in the South Coast Basin.

As noted above, the most significant public benefit from the periodic MATES reports is providing accurate and up-to-date information regarding the long-term trends in air quality in the South Coast Air Basin, and, in particular, the downward trends in ambient levels of air toxics. In that regard, the air toxics monitoring and modeling completed as part of MATES-IV demonstrate that there have been very significant reductions in ambient levels of air toxics between 2006 (MATES III) and 2013 (MATES-IV). For example, estimated Basinwide risk has decreased from 1,194 per million in 2006 to 418 per million in 2013, based on the fixed-site monitoring data. Similarly, modeled risk estimates have decreased from 853 per million in MATES III to 367 per million in MATES-IV. Equally significant, estimated average concentrations of diesel PM in the Basin have decreased from approximately 3.5 ug/m^3 in 2006 to less than 1.0 ug/m^3 in 2013, and the estimated risk attributable to diesel PM has declined by 70% (or more) over that time period. Equivalent reductions can be seen for all other air toxics as well. Reductions in levels of ambient air toxics are even greater if compared to the earlier MATES reports (MATES-I and MATES-II), although the results may not be directly comparable due to changes in certain measurement methods. All of those trends are very positive, and are testaments to the fact that the current programs to promote advanced emission-control technologies, especially ultra-clean new-technology diesel engines and vehicles, are working.

Although the overall results of the MATES-IV draft report are contained in the Executive Summary, the draft report does not place sufficient emphasis on the remarkable reductions in air toxics that have been achieved. The reductions in ambient levels of air toxics, and therefore the reductions in exposures and estimated public health risk, are very significant accomplishments that need to be highlighted in the report. In its current format, the draft report does not present the most relevant information in a "user-friendly" manner that clearly shows the very significant reductions that have been achieved over the last seven years. The Executive Summary, as well as other portions of the report, needs to be revised to present and emphasize more fully the improvements in air quality that have been confirmed through the MATES-IV findings.

EMA has the following specific recommendations to improve the Executive Summary of the draft MATES-IV report to better convey the results of the study to the general public.

Page ES-4 Conclusion

The conclusion section of the Executive Summary should explain in more detail the very significant reductions in ambient levels of air toxics, as well as estimated cancer risk, in the Basin. To that end, the conclusion should provide a direct comparison of the current results with past studies showing the greater than 70% reduction in risk over the time period of the four MATES reports, highlighting the especially large reductions in diesel PM emissions (which have resulted from the development of ultra-clean new-technology diesel engines), and clearly indicating that all major air toxics are continuing to decline in a very significant manner. In essence, the conclusion needs to highlight the tremendous success of the regulatory programs to reduce air toxics and diesel PM in the Basin.

Page ES-5 Policy Implications

The discussion of policy implications states that remaining risks are unacceptably high, that OEHHA's revised risk calculation methods will make those risks appear higher, and that, as a result, there is a need for continued focus on air toxic reductions, particularly diesel PM. Rather than focusing on OEHHA's new modeling approach to assessing childhood exposures, however, the policy implications section should focus on the programs and regulations that are in place and that have contributed to the very large reductions in ambient air toxics, as confirmed in MATES-IV. In the case of diesel PM emissions, the existing suite of mobile source regulations has worked exceedingly well to reduce diesel emissions and hence exposure to diesel PM for all residents in the South Coast Air Basin. More specifically, the current EPA and CARB regulations governing emissions from on-highway and nonroad diesel engines have reduced PM emissions to essentially-zero levels. As the entire diesel fleet transitions to the new-technology diesel vehicles, the benefits of zero-PM emissions will continue to multiply across the Basin.

Thus, this section should acknowledge that the current regulations and incentive programs governing diesel emissions will continue to reduce the amount of diesel emissions and ambient concentrations of diesel PM below the levels identified in MATES-IV, which are already less than 1 ug/m^3. Consequently, it should be stated that the existing programs in California are sufficient to reduce any health risks attributable to diesel PM to acceptable levels in the near future, and that the diesel PM issues have been essentially resolved, as evidenced in part, by the attainment demonstrations that have been made for the PM NAAQS in the South Coast Air Basin. Failing to mention the many positive aspects of the remarkable improvements and reductions in ambient air toxics, especially diesel PM, renders the draft MATES-IV report both incomplete and fundamentally misleading to the general public.

Page ES-7 Figures ES-2 and ES-3

Figure ES-2 should be revised to include a pie chart of the MATES-III results in addition to the current MATES-IV results to show, again, the very significant reductions in risk and to provide a better visual perspective of the changes between 2006 and 2013. The area of the pie charts should be proportional to the Basinwide risk estimates at the fixed monitoring sites. For example, the MATES-IV pie chart should be 70% smaller than the MATES-III pie chart.

In addition, a second bar chart should be added to the Executive Summary comparing the MATES-III and MATES-IV air toxics risks. The second chart should provide a comparison of the change in risk between the two studies and clearly show that risk have decreased from 1,200 in 2006 to 400 in 2013.

Page ES-8, Figure ES-4

Figure ES-4 presents the results of the estimated Basinwide risk for the MATES-IV modeling results. Although the changes in modeled risk between the two studies are presented in Figure ES-9, the impact of the significant reductions is not clear from the two figures. EMA recommends that an additional figure be added to the Executive Summary that shows the modeled risks from the MATES-III report. That figure should present the MATES-III results using the same color scheme and scale so that the reader can readily see and understand how the modeled concentrations and risks have been reduced so dramatically between the two study periods. Inclusion of the additional graphic will greatly enhance the lay reader's understanding of the positive changes that have occurred.

Additional Comments on Specific Sections of the Report

Page 1-3 Dose-Response Assessment

One topic that should be mentioned in this section, as well as in the other sections relating to diesel PM, is that the OEHHA Unit Risk Factor (URF) for diesel PM that is used in the reported risk calculations (which EMA continues to believe is flawed) is based on an assessment of exposures to emissions from uncontrolled diesel locomotive engines from the 1950s, 1960s and 1970s, prior to the development and deployment of modern emission-control technologies, including catalyzed diesel particulate filters (DPFs). New-technology diesel engines have completely different emissions profiles that are qualitatively and quantitatively different from the emissions assessed in developing the OEHHA unit risk factor. New-technology diesel engines are equipped with DPFs that reduce particulate matter emissions and hydrocarbons by over 99%. In addition, new-technology engine emissions no longer contain high levels of organic carbon or adsorbed hydrocarbons that were characteristic of the emissions from the 1950-1980 time frame.

Because there has been no re-evaluation of the URF to address the significantly different emissions profile of new-technology diesel engines, application of the "old" OEHHA risk value to today's diesel engines is not valid. This adds to the uncertainty of MATES-IV, and most certainly overestimates the risk ascribed to diesel PM emissions in MATES-IV. This issue needs to be addressed.

One of the necessary additions to the MATES-IV report to address this critical issue is to highlight the discussion regarding new-technology diesel engines that the International Agency for Research on Cancer (IARC) included in its Monograph 105. See IARC Monograph 105: "Diesel and Gasoline Engine Exhausts and Some Nitroarenes." More specifically, Monograph 105 includes the following conclusions regarding new-technology diesel engines, which conclusions should be stated in the body of the MATES-IV report to highlight the fact that the risks ascribed to diesel PM are being controlled and managed effectively:

> To meet the most stringent current emission-control regulations, diesel engines must be designed and constructed according to modern technology, which includes wall-flow particulate filters and diesel oxidation catalysts, in combination with the use of diesel fuel that has a very low sulfur content. The new diesel engine technology has been shown to reduce particulate mass emissions by more than two orders of magnitude. Although the implications for carcinogenicity are not yet know, *the "new technology" diesel engines, due to their much lower emissions of particulate matter, will probably bring about an improvement with regard to public health.* It should be noted that the human epidemiological studies reviewed in this Monograph [and that underly the OEHHA URF] were conducted before the introduction of the modern diesel engine technology. (Monograph 105, p. 34, emphasis added.)

* * *

> [E]vidence has also been found that exhaust aftertreatment can contribute to substantial reductions in the activity of extracts of diesel engine particulate matter or of exhaust semi-volatile organic compounds as expressed per unit of engine work or volume of emitted exhaust. No comparative data were available to the Working Group to evaluate the genetic and related effects of new-technology diesel exhaust. (Monograph 105, p. 457.)

Like IARC, the SCAQMD needs to acknowledge that the emissions from new-technology diesel engines are significantly different from earlier diesel technologies, that diesel PM levels are essentially zero, and that the old assumptions about the potential health effects of diesel emissions may no longer be applicable to assessments of current and, more especially, future risks.

Page 5-12 Summary of Fixed Sites

The discussion indicates that there are ongoing concerns that the application of advanced emissions control technologies to diesel engines has led to uncertainties regarding the potential formation of ultrafine particles (UFPs). The issue stems from concerns that the new technologies may actually increase emissions of UFPs.

Notwithstanding that speculation, extensive emissions testing has shown that the use of DPFs and selective catalytic reductions systems actually reduces the number of fine particles emitted from new-technology diesel engines. EMA refers AQMD staff to the recently completed Phase 2 Report from the Advanced Collaborative Emissions Study (ACES), published by the Health Effects Institute and the Coordinating Research Council, for a comprehensive presentation on the dramatic reductions in particle mass and number (as well as all other air pollutants) from today's new-technology diesel engines. Thus, the statement regarding increased ultrafine and particle number emissions in the MATES-IV report is wrong, and should be removed from the text.

Page 5-13 Gradient Studies

The report refers to UFPs and black carbon (BC) as air toxics. Neither UFPs nor BC are considered or regulated as air toxic contaminants in California. The text of the MATES-IV report should be changed to reflect their correct classification throughout the document.

Conclusion

EMA appreciates the opportunity to offer the foregoing comments and recommendations on the MATES-IV Draft Report. Please do not hesitate to contact me should you have any questions regarding EMA's comments and concerns.

Very truly yours,

Joseph L. Suchecki

Joseph L. Suchecki
Vice-President, Public Affairs

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From: Constantinos Sioutas [sioutas@usc.edu]
Sent: Wednesday, November 05, 2014 2:22 PM
To: Jean Ospital; Marilyn Traynor
Cc: Philip Fine; Andrea Polidori
Subject: Re: MATES IV Technical Advisory Group meeting at 1:00 p.m. on November 6, 2014 @ SCAQMD in Conference Room GB

Dear all

Few comments on the ultrafine section after reviewing your draft:

1. Overall a very fine job!

2. Please note that at least last time that I checked , the Appendix associated with the Ultrafine PM section is blank, it has no contents

3. Adding error bars in the plots and .or some metric of standard deviations or uncertainty in tables would make the presented data more defensible and the conclusions drawn more robust-this is a MUST in almost any scientific publications, as those you have been former members of my group know!

4. The use of a mobile or portable platform for freeway measurements , proposed as an upcoming activitiy, will add tremendous value to your work in characterizing exposures to UFP. I would even propose to devise a coherent sampling stately, currently missing in the draft, and I could even help you with it if need me to, whereby yo monitor by rotation different freeways every weekday, and/ or as many as you can afford depending on number of mobile platforms that you plan to employ . Regardless, I feel that knowing the freeway levels of UFP concurrently with measurements in stationary sites are essential in developing exposure models of these pollutants.

5. The elevated BC levels at the Inland Valley SB , not accompanied by equally high levels of UFP, are intriguing and require some further thoughts and investigation – are there any BC sources other than traffic in the area?

6. Fig 5-7 are these data averages across sites ? Here again SD/SE would be vey helpful

7. Same comment about figures 5-8 and 5-9 ;are these averages across sites? If so, error bars need to be added

8. The LAX pilot study is very well presented and in concert with our earlier work by Westerdahl, D., Fruin, S. A., Fine, P. L., & Sioutas, C. (2008). The Los Angeles International Airport as a source of ultrafine particles and other pollutants to nearby communities. *Atmospheric Environment*, *42*(13), 3143-3155.

I think that is all for now - let me know if you have any additional questions, comments or requests

cs
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December 30, 2014

Dr. Jean Ospital
Health Effects Officer
South Coast Air Quality Management District
21865 Copley Drive
Diamond Bar, California 91765

Dear Dr. Ospital:

SUBJECT: COMMENTS ON THE DRAFT SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT MULTIPLE AIR TOXICS EXPOSURE STUDY (MATES IV) REPORT

The Ports of Long Beach and Los Angeles (Ports) appreciate the opportunity to comment on the Draft South Coast Air Quality Management District Multiple Air Toxics Exposure Study (MATES IV) Report, and to submit the attached technical comments focused on Appendix V and Appendix VI.

In summary, Appendix V states that the differences in average levels of various gaseous species and pollutants between the West Long Beach (WLB) MATES III and MATES IV sites are not statistically significant (except for acetaldehyde), even though the sites are 0.8 miles away from each other. However, to the contrary and most notably, there was wide variability in elemental carbon (EC) concentrations between the WLB MATES III and MATES IV sites.

Additionally, Appendix VI gives the impression that the major contributors of black carbon (BC) emissions measured at the WLB site are from Ports' operations. Instead, our findings strongly suggest that weather conditions and BC emissions from other areas played a significant role in the measurements seen in Appendix VI.

The Ports appreciates your consideration of our comments into the Final MATES-IV Report. If you have any comments or questions, please contact Janna Watanabe at the Port of Long Beach at (562) 283-7100; or Amber Coluso at the Port of Los Angeles at (310) 732-3950.

Sincerely,

CHRISTOPHER CANNON
Director of Environmental Management
Port of Los Angeles

HEATHER TOMELY
Director of Environmental Planning
Port of Long Beach

CC:LW:TJD:AC:yo
APP No: 120626-996

Enclosure: Technical Comments on MATES IV Draft Report

APPENDIX

TECHNICAL COMMENTS ON MATES IV DRAFT REPORT

Prepared by Leidos, Inc., in Consultation with the Ports of Long Beach and Los Angeles

These technical comments are focused on two areas: Appendix V, entitled *Comparison between the West Long Beach Site in MATES III and MATES IV;* and Appendix VI, entitled *Black Carbon (BC) Measurements at Fixed Sites.*

APPENDIX V - COMMENTS

1. While there was only a 5% increase in $PM_{2.5}$ concentrations in comparing data from the West Long Beach (WLB) MATES III to IV sites, an almost 25% increase in elemental carbon (EC) concentrations was observed, as shown in Table V.1 (summarized below). In addition, review of Figure V-4 in Appendix V indicates several days when EC at the MATES IV site are more than 2x the EC at the MATES III site. Appendix V states the change in EC concentrations between the MATES III and IV sites is not statistically significant at the 95% level. However a comparison of the data in Table V-1 shows that the average EC concentration at the MATES IV site is outside the 95% confidence limits of the EC concentrations at the MATES III site, and the average EC concentration at the MATES III site is outside the 95% confidence limits of the EC concentrations at the MATES IV site. Therefore, this analysis shows that the differences in average concentrations between the two stations are statistically significant ($p> 0.05$), and the two stations do not have equivalent EC levels.

Re-creation of Table V-1 in Appendix V

	$PM_{2.5}$ Mass (µg/m3)	**$PM_{2.5}$ OC (µg/m3)**	**$PM_{2.5}$ EC (µg/m3)**	**Nitrate (µg/m3)**	**Sulfate (µg/m3)**	**1,3-Butadiene (ppb)**	**Benzene (ppb)**	**Formaldehyde (ppb)**
MATES III WLB Site	17.6 ±2.0	6.50 ±0.82	2.22 ±0.44	3.07 ±0.70	3.67 ±0.55	0.048 ±0.01	0.39 ±0.06	2.47 ±0.27
MATES IV WLB Site	18.5 ±2.1	6.30 ±0.74	2.77 ±0.51	3.34 ±0.78	3.87 ±0.57	0.058 ±0.01	0.39 ±0.07	2.50 ±0.23
% Difference	5.11%	-3.08%	**24.77%**	8.79%	5.45%	20.83%	0.00%	1.21%

2. Table V-2 (reproduced below for $PM_{2.5}$ mass, $PM_{2.5}$ OC and $PM_{2.5}$ EC, with an added estimate of R^2), shows the correlations between the MATES-III and MATES-IV data set for $PM_{2.5}$ mass, OC and EC. The R^2 value (coefficient of determination) provides an indication of how much of the variance of one variable is predictable from the other variable. Here, we agree that $PM_{2.5}$ mass and EC have statistically high correlations with both at $R^2 = 0.80$. It appears OC at the sites are minimally related at $R^2 = 0.20$.

   Two data sets that are highly correlated do not necessarily equate to equivalency. It may be that a high correlation simply indicates a consistency where data points increase or decrease together on the same date. The increase in EC at the MATES IV site compared to the MATES III site is concerning in terms of representativeness since the MATES IV site is located much closer to a localized source.

   Table V-2 with added R^2

	$PM_{2.5}$ Mass	**$PM_{2.5}$ OC**	**$PM_{2.5}$ EC**
R	0.92	0.46	0.89
m	0.90	0.40	1.02
n	72	68	67
R^2	0.8464	**0.2116**	0.7921

3. Based on the data collected in the POLA and POLB monitoring programs, it appears that the measured pollutant which has the highest spatial variability is ultrafine particle (UFP) counts. This also seems to be the case for the UFP analysis in Chapter 5 of the Draft MATES IV report, although the full analysis is apparently not completed (Appendix VII, Particle Counts at Fixed Sites is listed as *In Preparation*). UFP measurements were not taken in MATES III, but it would be useful to compare UFP measurements from the MATES IV and MATES III in WLB. The MATES-IV WLB site is located 0.8 miles to the northwest of the MATES-III site, closer to major emission sources such as a rail yard. Given that UFP counts may be the most sensitive indicator of nearby emission sources, as shown in the studies near LAX, San Bernardino Railroad, and near a freeway, as discussed in Chapter 5.roadways. Detailed analysis of the UFP data from MATES-IV (especially with wind speed and direction data) would be useful.

4. Presented below are the $PM_{2.5}$ Mass, EC and OC concentrations at POLB's Inner Harbor station (located approximately 1 mile south of the MATES III site) for the estimated dates used in this study. All PM concentrations presented below were measured using a DRI Sequential Filter Sampler (SFS). Assumptions were made on the exact start and end dates for the averaging period, but comparatively the results show that the Port monitoring stations are consistently lower. The POLB Inner Harbor station's measurements were the highest of the six stations in the POLA/POLB monitoring program. For this study, the SCAQMD

deployed filter-based SASS units for their PM monitoring, so some discrepancy in concentrations might be expected due to the difference in instruments.

Comparison of $PM_{2.5}$ Mass, EC, and OC Levels at 3 Sites during the MATES IV Study

	$PM_{2.5}$ Mass (µg/m3)	$PM_{2.5}$ Mass (% Reduction)	$PM_{2.5}$ EC (µg/m3)	$PM_{2.5}$ EC (% Reduction)	$PM_{2.5}$ OC (µg/m3)	$PM_{2.5}$ OC (% Reduction)
MATES IV WLB Site	18.5	-	2.77	-	6.30	-
MATES III WLB Site	17.6	5%	2.22	20%	6.50	-3%
POLB Inner Harbor	15.3	17%	1.71	38%	3.33	47%

It should be noted that measured $PM_{2.5}$ Mass, EC and OC concentrations presented above all decrease moving south as the POLB Inner Harbor station is located approximately 1 mile due south of the MATES III West Long Beach station. Thus, the monitoring stations located closest to the Ports have lower concentrations than the MATES IV WLB stations, indicating that sources outside the vicinity of the Ports are producing higher ambient levels of $PM_{2.5}$ Mass, EC and OC.

5. The data collected in this MATES IV monitoring program were affected by seasonal meteorological and dispersion conditions during the timeframe of the study. Appendix V states the data was collected from February to November 2007 and April to December 2008. Typically, the highest levels of $PM_{2.5}$ and EC (in particular) are measured during the winter months from November to February. While emissions remain generally constant throughout the year, ground level concentrations tend to increase during these timeframes due to the lower dispersion of ground-based emissions.

   It might be instructive to conduct a more detailed review of the data. For example:

   a. There are at least three days on which EC at the MATES IV site > 4 µg/m^3, while EC at the MATES III site < 2 µg/m^3 which is more than 100% higher. Are these anomalies, or were there special atmospheric conditions or other events that affected the data?

   b. During this study, not much data was collected during the winter months for these two time periods. Under southerly or southwesterly winds, common during spring and summer months when most of the measurements took place, the sites are likely exposed to the same general sources to the south and southwest. However under light northerly or northwesterly flow, localized sources may impact the MATES IV site due to its close proximity to Route 163 and rail yard sources. Since the MATES IV site is 0.8 mile closer to both Route 163 and the rail yard, it is feasible that measured EC levels (and potentially OC) could be higher under the light northerly winds commonly found during the nighttime hours (stable nocturnal boundary layer) in the fall and winter months.

APPENDIX VI - COMMENTS

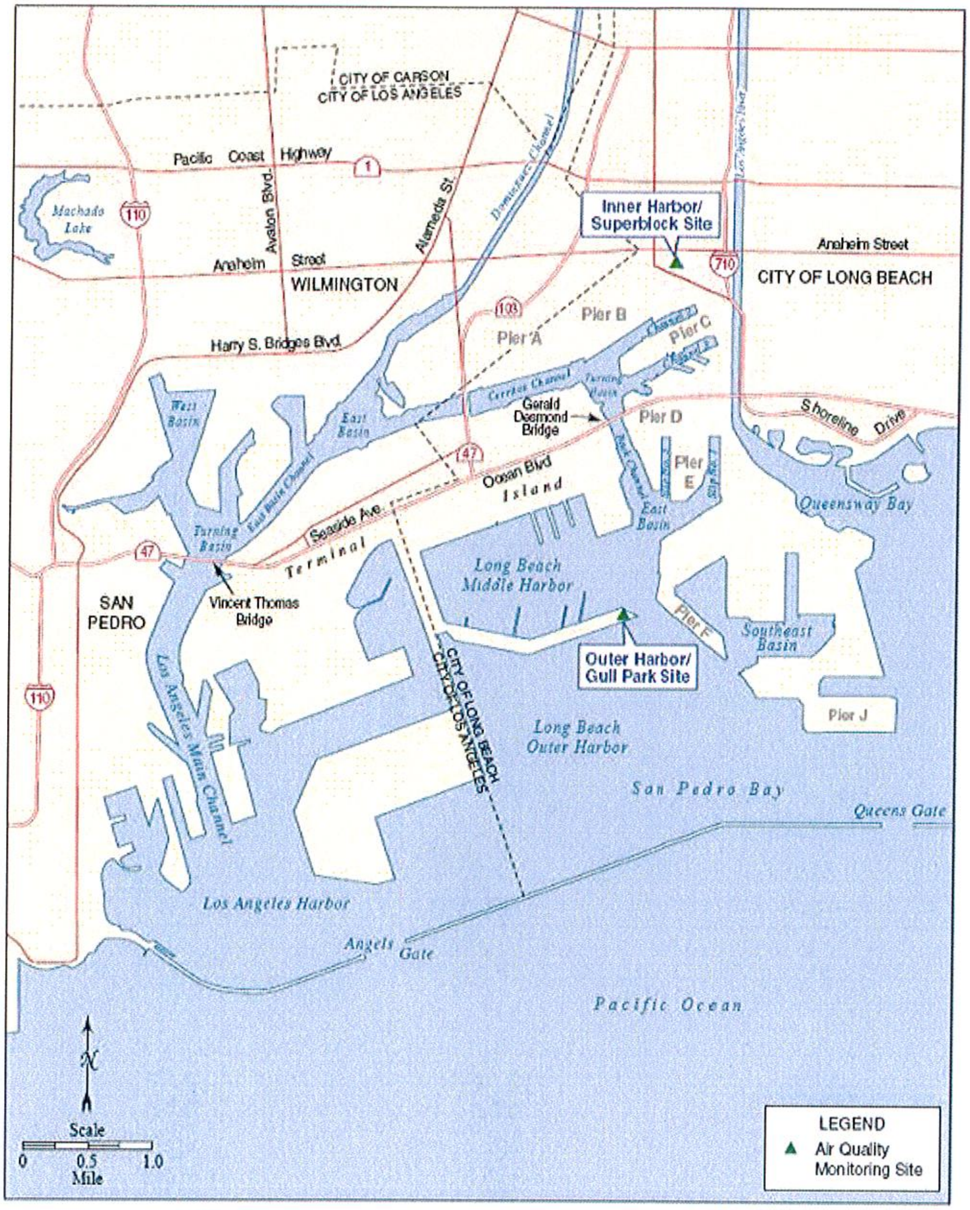
Most sites presented in Appendix VI, Figure 6 indicate that maximum BC concentrations occurred during the fall and winter seasons. The WLB site, the monitoring station closest to the Ports area in the MATES-IV program, has the second-highest winter average BC concentration of the 10-site MATES-IV monitoring program, estimated at approximately 2.3 $\mu g/m^3$ from Figure 6. In this report and in a presentation to the MATES-IV Technical Advisory Group (Polidori, 2014), the impression is given that the major contributors of BC emissions measured at the WLB site are diesel-powered vehicles, non-road mobile machinery, and ships.

The Ports would like to offer some general findings from their BC monitoring program to provide additional insight into BC levels in the Ports area, specifically BC data collected at the Inner and Outer Harbor stations in the POLB monitoring network. A brief description of these stations is presented below and Figure 1 shows the locations of the two monitoring sites:

a. The Inner Harbor station is located in a heavy industrial area at the north end of the POLB complex. There are several truck distribution depots in the vicinity, and two busy roads are located nearby, West Anaheim Ave and I-710, both of which are used by large numbers of diesel trucks.

b. The Outer Harbor station is located at the end of the "Navy Mole" (i.e. eastern end of Nimitz Road), a peninsula that terminates at the Long Beach Channel. It is located near the southern end of the POLB complex, and diesel-powered mobile sources will primarily be located at Port terminals, located some distance away (except for the occasional ship that passes nearby while moving through the Long Beach Channel). The two POLB stations are located approximately 2.7 miles apart, in a roughly north-south line.

Figure 1. Locations of Air Monitoring Stations for Port of Long Beach BC Study



Because the highest average BC concentrations measured in the MATES-IV program were found during the winter season, the focus of this analysis is the winter season (assumed to be December 2012 through February 2013). Average winter season BC concentrations at the two POLB monitoring stations are comparable to the average observed at the WLB station, as shown in the table below.

BC Concentrations at Three Monitoring Stations in the Ports Area

Period	Average BC Concentration at Selected Sites (µg/m3)		
	MATES IV West Long Beach	POLB Outer Harbor	POLB Inner Harbor
2012 - 2013 Winter Season	2.3	2.3	3.0

Detailed Review of the Black Carbon Hourly Data

Figure 7 in Appendix VI illustrates that across the 10 stations in the MATES IV study, the highest monthly BC concentrations during the winter were recorded in January 2013. The Aethalometers deployed at the Ports' monitoring stations also measured the highest monthly BC concentrations during January 2013. Detailed analysis of the 1-minute BC data channel on the Aethalometers, in conjunction with meteorological data collected at the Port's monitoring sites, yields insight into the potential origin and transport of the BC material measured during January 2013.

The 24-hour average BC concentrations measured at the Inner and Outer Harbor stations on January 3, 2013 were 6.92 $\mu g/m^3$ and 5.83 $\mu g/m^3$, respectively. However, the Aethalometers also provide 1-minute average BC concentrations, which allow in-depth analysis of BC concentrations and correlations with key meteorological parameters to assess changes in BC levels with changes in boundary layer and transport parameters.

Mr. George Allen of NESCAUM (Northeast States for Coordinated Air Use Management) has performed research suggesting that stable 1-minute BC data can be evaluated to differentiate BC sources on multiple scales (Allen, 2014). His research states that local sources (within a few hundred meters) will produce rapid spikes in the BC signal. Sources that are on a larger scale (urban and regional) will drive smoother increases and decreases in BC levels that can occur over a morning or evening. Through the analysis of the 1-minute BC data, it is possible to develop some conclusions on the spatial scales that are influencing the measured BC data.

Through review of the simultaneous 1-minute data at the Inner and Outer Harbor stations, we can draw insights into the spatial scales of the measured BC. The Inner Harbor station would likely be influenced by a combination of regional, urban, and local sources; the Outer Harbor station would be expected to be influenced primarily by regional and urban sources.

The following three figures illustrate 1-minute BC concentrations measured at the POLB Inner Harbor and Outer Harbor stations on January 3, 2013, which was selected as a typical weekday in January that had high BC concentrations.

Figure 1 provides the raw 1-minute BC concentrations at the Inner (green) and Outer (red) Harbor stations over the 24-hour period. There are two major features of the BC concentrations at these two stations that can be seen in Figure 1:

1. The general pattern of BC concentrations measured throughout the day on January 3rd at the two stations is very similar. Elevated BC concentrations at both stations occur during the morning (averaging around 10-15 μg/m^3) until about 9 AM, when BC concentrations begin decreasing to the low of the day which was reached in early afternoon. The BC concentrations remain relatively constant (averaging 2-3 μg/m^3) until early evening, when they begin to increase again.
2. Elevated 1-min spikes of BC concentrations (up to 40 μg/m^3) are much more prevalent at the Inner Harbor station, indicating that there are a number of BC sources close to that station. These measurements reflect the environment around the two stations, because nearby BC sources appear to be common at the Inner Harbor station and less common at the Outer Harbor station. The other feature evident in the 1-min BC measurements is that elevated BC spikes are common only during certain parts of the day, primarily in the early morning and late afternoon/evening hours.

Assessment of the co-located meteorological parameters measured on January 3rd indicates an overnight low temperature of 41° F, which is quite cold for the South Coast Air Basin. This can be used to infer a strong nocturnal boundary layer with a low capping inversion and little mechanical turbulence. None of the nighttime hours record a wind speed measurement over 3 mph. Wind direction measurements indicating light northerly winds persist throughout the nocturnal hours until 11AM, so we have light flow from the greater LA air basin south towards the Port's monitoring stations. Around 11AM, the winds switch to a more south-southwest direction indicating a more onshore flow regime. On the graphic, the vertical black line at 11AM (as well as the wind rose graphic) provides a visual indication of when the winds switch from northerly to more southwesterly flow. The onshore flow remains until about 8PM, when once again the winds become light and turn north-northeast for the remainder of the evening. The meteorological parameters in combination with the 1-minute BC data provide strong evidence that the Aethalometers are being influenced by a variety of sources from several directions.

Figures 2 and 3 estimates the contribution from local scale BC sources and from urban and regional scale BC contributions. This was done by using the approach pioneered by John Watson and Judy Chow (JAWMA, 2001) at the Desert Research Institute (DRI), in which a moving average subtraction method was applied to BC measurements taken at stations around Mexico City. In this method, an hourly average BC concentration is calculated for each 1-min BC measurement, using the 60 1-min BC averages centered on the 1-min BC measurement. The hourly average BC calculation is then subtracted from the 1-min BC measurement, which provides an estimate of the contributions from local BC sources (the 1-min BC measurement minus the hourly BC moving average), and the contributions from urban and regional BC sources (the hourly BC moving average). These calculations were conducted for each minute of the day and then averaged over the day, to provide an estimate of the contribution to the BC concentrations from the two spatial scales.

Figure 2 shows the estimated contribution at the Inner Harbor station from urban and regional BC sources ("baseline BC level") and from local BC sources. Local sources contributed approximately 19% of the 24-hour average BC concentration (6.92 µg/m^3) on January 3rd, while the baseline BC level was 81% of the 24-hour average BC contribution. Figure 3 shows the estimated contribution at the Outer Harbor station from the local and baseline BC sources. Local sources contributed approximately 15% of the 24-hour average BC concentration (5.83 µg/m^3) on January 3rd, while the baseline BC level was 85%.

This analysis shows that local BC sources (within a few hundred meters) contributed between 15% and 19% of the total measured BC concentrations on January 3rd, which is comparable to the 12% contribution from local sources in Mexico City estimated in the John Watson and Judy Chow paper. Their paper also estimated that the neighborhood contribution (1-5 km) was an additional 23%, indicating that BC sources from larger scales contributed the majority to their BC measurements.

This analysis was conducted on only one day in January 2013. However, the POLB monitoring stations collected BC and meteorological data throughout the winter (December 2012 through February 2013), and a preliminary review of the data indicates this was not an isolated event. There are many other days, particularly in January 2013, where similar BC levels and meteorological conditions persist, indicating that there are significant urban and regional contributors to the levels of BC measured at the Port monitoring stations. We encourage the South Coast AQMD to conduct a similar analysis for the winter months to see if the WLB data agrees with the Ports' data presented above.

References

Allen, G., 2014. Email correspondence between G. Allen (Northeast States for Coordinated Air Use Management, NESCAUM) and G. Bertolin (Leidos, Inc.), December 2014.

Watson, J.G. and J.C. Chow, 2001. *Estimating Middle-, Neighborhood-, and Urban-Scale Contributions to Elemental Carbon in Mexico City with a Rapid Response Aethalometer*, J. Air & Waste Management Association, **51**:1522-1528.

Figure 1: Inner and Outer Harbor BC Concentrations (1-min) on January 3, 2013

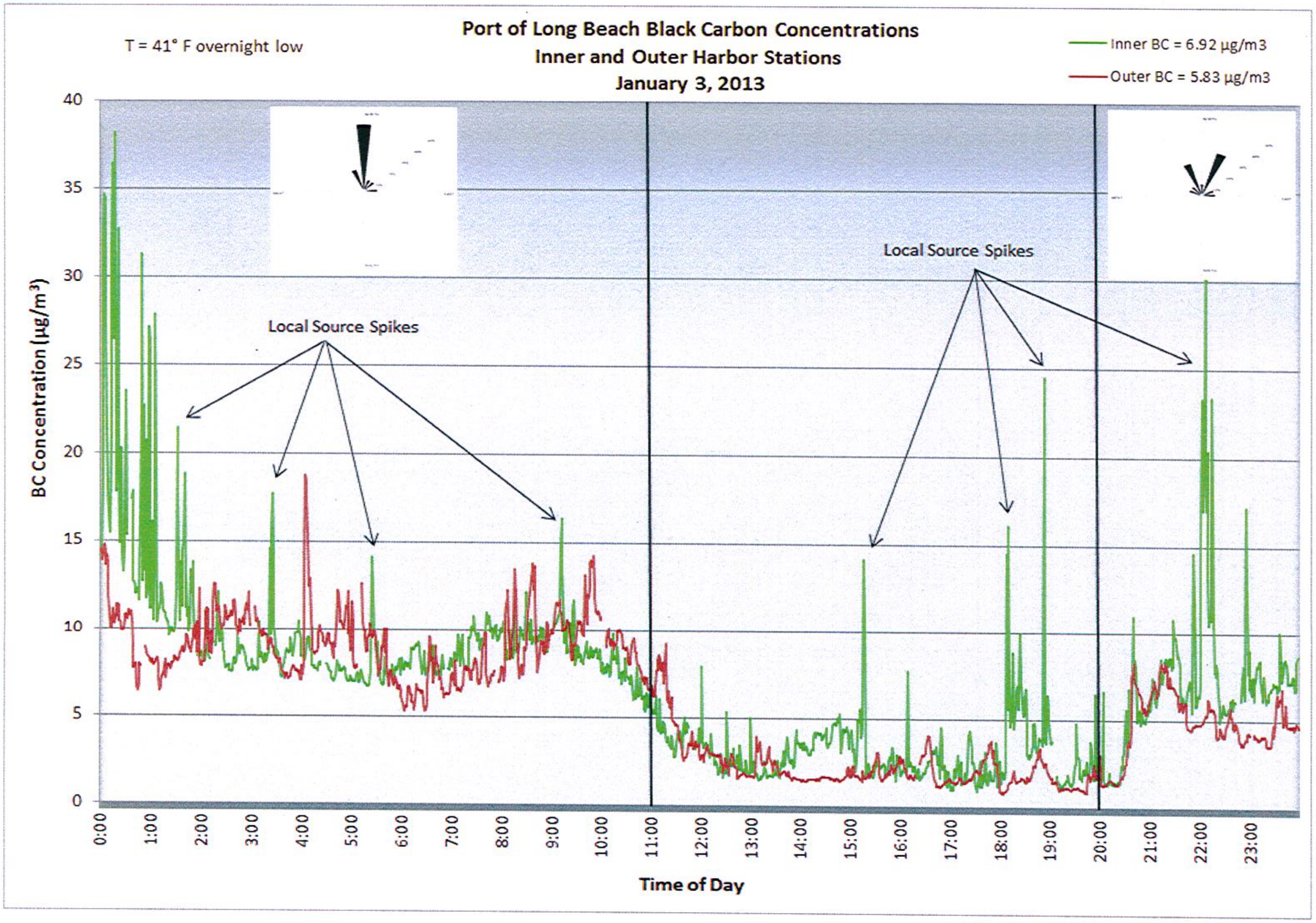


Figure 2: Detailed Inner Harbor BC Concentrations (1-min) on January 3, 2013

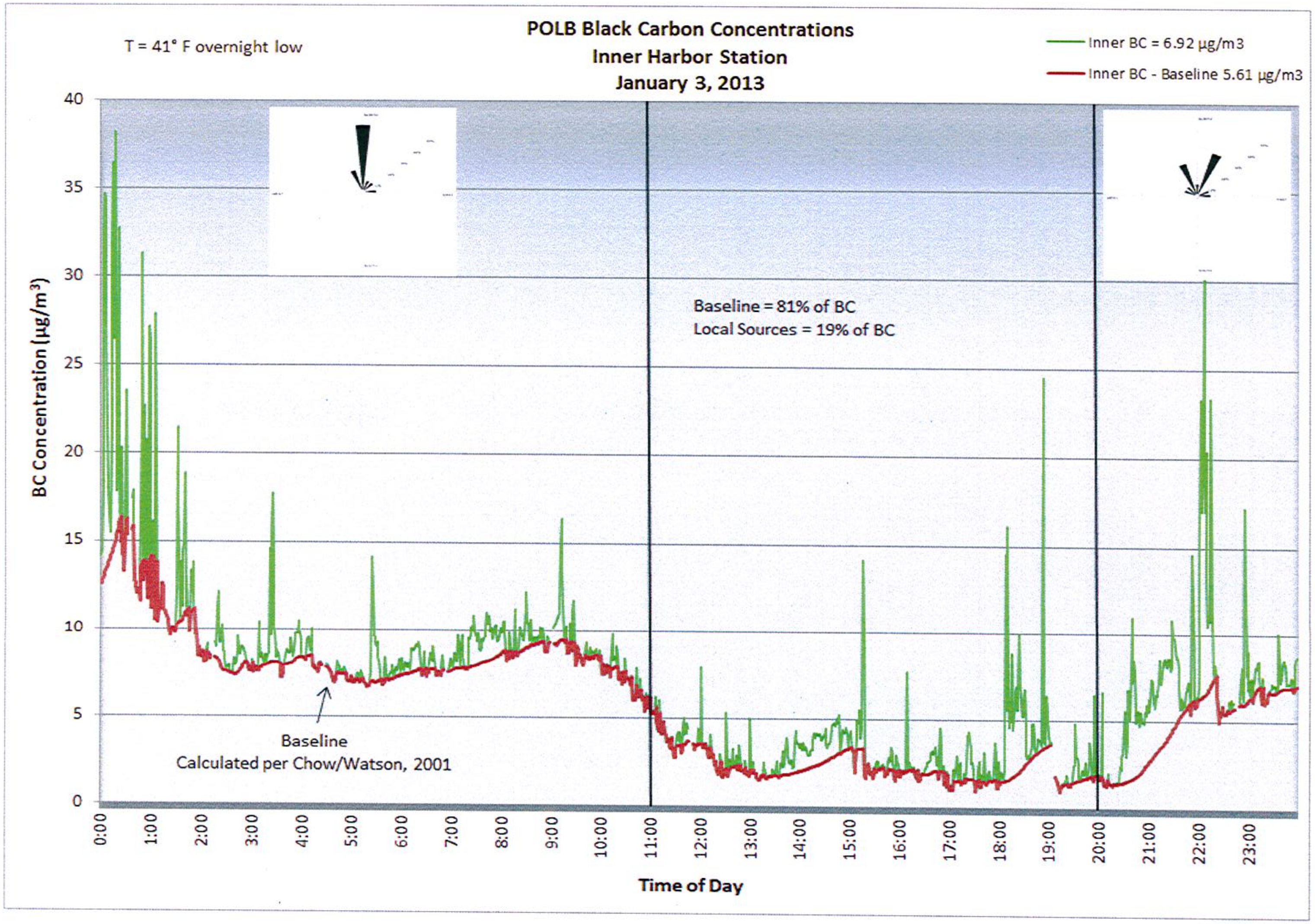
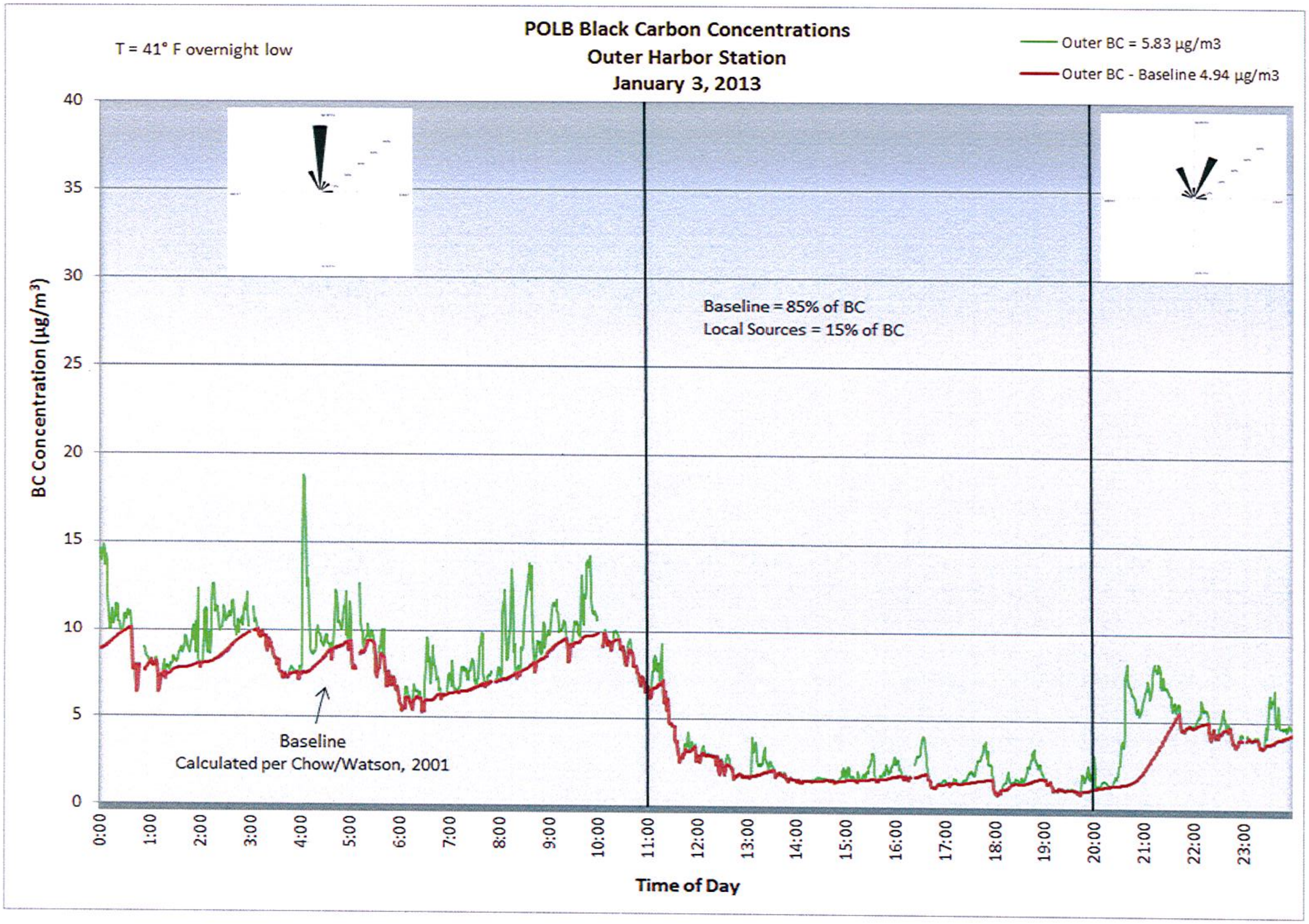


Figure 3: Detailed Outer Harbor BC Concentrations (1-min) on January 3, 2013



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SCAP
SOUTHERN CALIFORNIA ALLIANCE OF
PUBLICLY OWNED TREATMENT WORKS

December 30, 2014

Dr. Jean Ospital, Health Effects Officer
South Coast Air Quality Management District
21865 Copley Drive
Diamond Bar, CA 91765-4178

Re: Comments on the MATES IV Draft Report

Dear Dr. Ospital:

The Southern California Alliance of Publicly Owned Treatment Works (SCAP) represents 82 public agencies that provide essential water and wastewater treatment to nearly nineteen million people in Los Angeles, Orange, San Diego, Santa Barbara, Riverside, San Bernardino and Ventura counties. We provide environmentally sound, cost-effective management of more than two billion gallons of wastewater each day and, in the process, convert wastes into resources such as recycled water and renewable energy.

SCAP appreciates this opportunity to comment on the MATES IV Draft Report (Draft Report). SCAP has followed all the MATES efforts, and we continue to remain impressed at the level of scientific rigor and dedication we find in each report. The most recent Draft Report continues this laudable trend.

It seems logical and appropriate that MATES should discuss, where valid, comparisons of its results to those from other reputable and scientifically valid sources. Thus, we are concerned about the inclusion of CalEnviroScreen results in Section 4.8 of the Draft Report. While we understand the interest to include a discussion regarding CalEnviroScreen, SCAP respectfully requests that the Final Report explain the substantial differences between this screening tool and a comprehensive risk analysis. For example, CalEnviroScreen has been used to estimate a community's combined "pollution burden and population characteristics" score, while MATES provides a lifetime risk estimate from exposure to air toxics.

SCAP's comments on Section 4.8 of the Draft Report are incorporated into the attached document for your consideration. Our membership believes that it is important to communicate that CalEnviroScreen scores are not an expression of health risk, and this screening tool is not intended to be used as a health or ecological risk assessment for a specific area or site.

We appreciate your consideration of our comments, and look forward to working with SCAQMD on our mutual goal of cleaning the air. If you have any questions regarding these comments, please do not hesitate to contact me at (760) 479-4121.

Sincerely,

John Pastore

John Pastore, Executive Director

cc: Elaine Chang, SCAQMD
Philip Fine, SCAQMD

ATTACHMENT
SCAP's Recommended Revised Section 4.8 of the MATES IV Draft Report

4.8 California Communities Environmental Health Screening Tool (CalEnviroScreen)

Since the completion of the MATES III Study, the California Environmental Protection Agency (CalEPA) and Office of Environmental Health Hazard Assessment (OEHHA) developed a screening tool for evaluating multiple pollutants and stressors in communities, called the California Communities Environmental Health Screening Tool (CES). This tool has been used to estimate a community's "Pollution Burden and Population Characteristics" score, while MATES provides a lifetime risk estimate from exposure to air toxics. The purpose of this section is to outline the fundamental difference between MATES and CES.

In August 2014, CES version 2.0 was released. This version produces results at the census tract level for approximately 8,000 census tracts in California and approximately 3,600 tracts within the jurisdiction of SCAQMD. The model consists of two component groups – pollution burden and population characteristics. Unlike MATES, which provides a traditional health risk assessment approach using measured air toxic contaminants, CES considers pollution surrogates and community characteristics that have been shown to affect vulnerability to pollution, such as socioeconomic factors or underlying health status. A set of statewide indicators (Table 4-8), selected based on existing environmental, health, demographic and socioeconomic data, is used by CES to create a screening score for communities across the state.

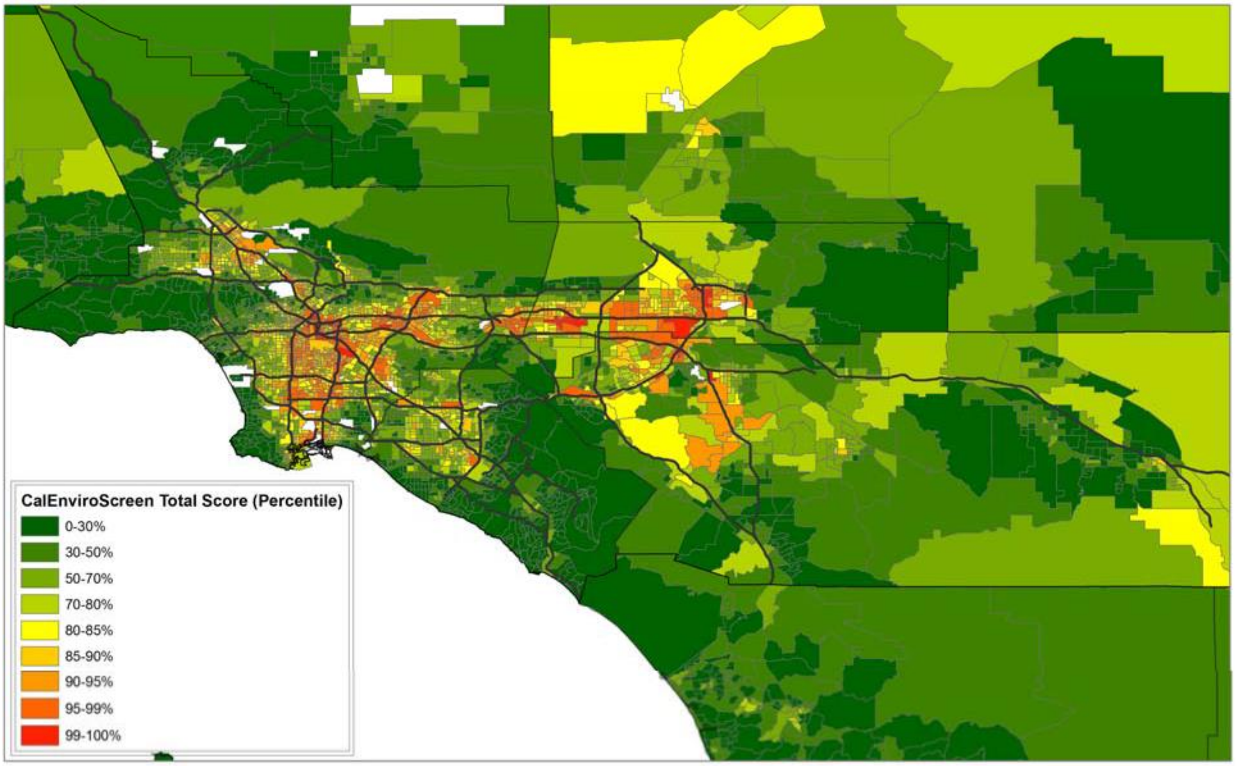
Table 4-8
Indicators used to Represent Pollution Burden and Population Characteristics
in CES Version 2.0

Component Group 1: Pollution Burden		**Component Group 2: Population Characteristics**	
Exposures	Environmental Effects	Sensitive Populations	Socioeconomic Factors
PM 2.5 concentrations Ozone concentrations Diesel PM emissions Pesticide use Toxic releases from facilities Traffic density Drinking water quality	Cleanup sites Groundwater threats Impaired water bodies Solid waste sites and facilities Hazardous waste	Children and elderly Asthma emergency department Low birth weight births	Educational attainment Linguistic isolation Poverty Unemployment

For each indicator, a value is assigned for each census tract. Among the areas with an indicator value, the values are ranked from highest to lowest and a statewide percentile score is created for each indicator in each census tract. The percentile score for all individual indicators is averaged in each component group and then divided by the maximum value observed in the State. In the pollution burden component group, environmental effects indicators are weighted half as much as the exposure indicators. The component group scores are both scaled to a maximum of 10 with a possible range of zero to 10. Finally, the overall CES score is calculated by multiplying the scaled component group score for pollution burden by the scaled component group score for population characteristics. The highest possible CES percentile score is 100 with an equal contribution from the two component groups. An area with a high score would be expected to have higher pollution burdens and vulnerabilities than other areas with low scores. Results produced by CES can help decision-makers determine how to focus available time, resources and programs to improve the environmental health of Californians.

Figure 4-17 depicts the CES score in SCAQMD highlighting the census tracts scoring in the highest percentiles across the state. Most urbanized areas are in the top 30% score, indicating these tracts have higher pollution burden and population characteristics compared to other communities in the State. In particular, a significant fraction of census tracts in the Los Angeles, Riverside and San Bernardino counties are in the top 10% of the relative statewide scoring.

Figure 4-17



CES Version 2.0 Overall Scores. ***Data retrieved from OEHHA in September 2014.***

While CES can assist CalEPA in prioritizing resources and helping promote greater compliance with environmental laws, it is important to note some of its limitations. The tool’s output provides a relative ranking of communities based on a selected group of available datasets, through the use of a summary score. Unlike MATES, the CES score is not an expression of health risk, and does not provide quantitative information on increases in cumulative impacts for specific sites or projects. Further, as a comparative screening tool, the results do not provide a basis for determining when differences between scores are significant in relation to public health or the environment. Accordingly, the tool is not intended to be used as a health or ecological risk assessment for a specific area or site.

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Keck School
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of USC

Scott Fruin
Assistant Professor

Dr. Jean Ospital
Health Effects Officer
South Coast Air Quality Management District
21865 Copley Dr,
Diamond Bar, CA 91765

Re: Comments on MATES Ill Report

Dear Dr. Ospital:

I appreciate the opportunity to comment on the October 2014 draft of the MATES IV study. This study importantly demonstrates the continuing success of SCAQMD and CARB regulations and policies to improve air quality and reduce exposures in the South Coast Air Basin. I have grouped my recommendations into three major areas:

1) presentation and interpretation of results;
2) conversion of elemental carbon (EC) to diesel particulate matter (DPM) concentrations; and
3) characterization of uncertainties.

PRESENTATION AND INTERPRETATION OF RESULTS

The reduction in air toxic exposures of 65% since MATES III should be presented clearly as an unqualified success story. In fact, the MATES III basin *average* would be considered a hot spot by MATES IV standards. However, I do not feel this message comes across as strongly as it should when multiple results covering changes in the OEHHA exposure estimation are presented.

A key point is that the exposure and risk reductions measured by MATES IV are not affected by the changes in the OEHHA exposure methodology. The OEHHA changes can and should apply to all MATES studies and any risk calculations and risk maps comparing different MATES studies should be based on a single, consistent method. Using different exposure methodologies (such as was done in the maps of ES-4 and ES-6) sends a confusing message that the risk reductions measured in MATES IV are somehow offset due to previous flaws in assessing exposure.

I also suggest that differing exposure methodologies not be used in any presentations of risk, as it likely will result in confusion for policy makers and the public. If you disagree, I suggest that any presentations of MATES III risk in the MATES IV report that use the new OEHHA exposure methods be put in appendices, along with detailed explanations of the changes in the exposure calculation methodology.

Other recommendations for presenting results are listed in the Appendix under “Specific Suggestions for Data Presentation.”

Keck School
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of USC

Scott Fruin
Assistant Professor

CALCULATION OF DIESEL PM CONCENTRATIONS

Because a large part of the reduction in cancer risk was due to changes in the DPM/EC ratio, more detail should be provided about the changes in this ratio along with estimates of uncertainty.

Appendix XI should be expanded and included in the main report due to its importance. Because the overall risk numbers are dominated by diesel PM exposure, the uncertainty in the conversion of measured EC to DPM may dominate the overall cancer risk uncertainty. This conversion factor should be given a detailed uncertainty analysis based on estimated uncertainties in the emission inventories and speciation profiles. (Another large uncertainty in the risk numbers that should be mentioned is the large uncertainty in the DPM cancer potency factor.)

Below are some questions that I feel should be addressed in an expanded Appendix XI:

1. Were the large changes in DPM/EC ratios from MATES III to IV due to actual reductions in this ratio or were they primarily due to better speciation profiles (e.g., better methods, larger sample numbers, etc.)? For example, was the single 2005 exhaust profile (based on much older engines) appropriate to use for 2005? How uncertain was this profile? Were sample numbers adequate and were the tested engines sufficiently representative of 2005 engines?
2. Were there improvements or important changes in the DPM emission inventory from MATES III to IV?
3. Was the decrease in DPM/EC ratio expected or reasonable due to changes in engine technology and fleet turnover? This was discussed briefly for ocean-going vessels but not for other source categories.
4. In light of the above information, is it reasonable that the DPM/EC ratio changed from 1.04 to 1.95 then back down to 0.85 over the course of the last three MATES studies?
5. Were different contributions by source category in different parts of the basin taken into account? If not, should they have been? One example might be a decrease in DPM/EC ratio as one goes inland and the average ratio is less influenced by the high ratio for ocean-going vessels.
6. The sensitivity test of using the MATES III profiles for MATES IV data was a good idea but the results were not presented clearly.

UNCERTAINTY

A detailed uncertainty analysis including all uncertainties should be part of this report. It is clear that there are large differences in relative uncertainties between the analysis methods, emission inventories, DPM/EC ratios and cancer potency factors. As described above, the uncertainty in the DPM/EC ratio may dominate the overall risk numbers and be worthy of increased attention, as described below.

Besides giving readers an appreciation for the sometimes large uncertainties present in cancer risk estimations, knowing what uncertainties contribute most to the overall risk uncertainty can be useful in determining where future resources and efforts should be focused. At the same time, any measurements contributing significantly less total risk than the overall risk uncertainty could be considered for elimination. This would allow diverting resources to other study needs such as increased DPM measurements and/or reducing the measurement and analysis uncertainty for Cr(VI) and 1,3-butadiene, two challenging compounds to measure with good accuracy.

Any uncertainty analysis should also include the spatial uncertainty. For example, DPM shows near road and near-freeway concentrations several times higher than ambient. While these may have been included in the 2 x 2 km grid average, there are large, socioeconomic-related differences in proximity to roadways across the basin. These should be an explicit concern in a study of this type.

Please feel free to contact me regarding any of these recommendations.

Best regards,

Scott Fruin

Dr. Scott Fruin, P.E.
Assistant Professor
Environmental Health Sciences
USC Keck School of Medicine

Keck School
of Medicine
of USC

Scott Fruin
Assistant Professor

APPENDIX

Additional Recommendations

One important caveat to include is that people who live, work, attend school, or drive in locations of elevated DPM may be subject to significantly higher risks than these calculations indicate.

One new aspect of the large downward temporal trend in concentrations is that the risk reductions in a year or two are now larger than the site-to-site differences within a given year. This might justify the continuous temporal coverage of one location, such as Central Los Angeles, which matches the overall basin average for most compounds, and fewer numbers of sites or reduced sampling frequencies at sites that do not differ very much.

In absolute terms, the big reductions are from on-road diesel. The actual decreases in the inventory as modeled should be highlighted up front, along with the regulations and programs that are believed to be behind them. The other risk reductions should be prioritized by quantity.

Specific Suggestions for Data Presentation

One alternative inter-study mapping strategy that might be useful would be to make maps of the percent of basin average risk. This would allow direct inter-study comparisons of spatial differences that would not have been produced in previous reports. These will show a reduction in spatial disparities from MATES III to IV.

For credibility, the results should not be presented with three or four digit precision. If the uncertainty is +/- 50%, for example, only two digit precision is justified.

Table 2-2 (Sampling locations): It would be useful to list distance from and orientation to the nearest busy road.

Section 3.8 and Table 3-6: More discussion of these results seems warranted. Table 3-6 seems to show fairly large discrepancies in MATES III versus IV inventory changes and changes in the air measurements. Cr(VI), 1,3-butadiene and benzene are important since they contribute significantly to total risk. For Cr(VI) and 1,3-butadience, relatively large discrepancies may be due to measurement challenges and may be deserving of more resources while other compounds contributing little risk might be considered for elimination if that results in a cost savings.

Calculating spatial correlations would highlight which compounds are global (e.g., high correlations for CCl_4), which are regional and which are more localized (with lower correlations). It is important to show where BC/EC fits in this picture—it may be localized most of the time but build up to be a regional pollutant during times of summer inversions.

In Appendix IV, correlation matrices for elements and VOCs would be useful to present. Also, readings below the Limit of Detection (LOD) should be set to 2/3 of the LOD rather than zero. This is less conservative and also more appropriate if the fraction of readings below the LOD is moderate, i.e., fewer than 20 or 30%.

Appendix G seems repetitive in some places. Some graphs are not readable (Figures 4, 13).

Suggest listing emissions by contribution to risk rather than just alphabetically for enhanced public understanding.

Linear regressions for scatter plots like Fig 14 in Appendix G (EC vs BC) should probably be log transformed.

↑ Return to first page

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5090
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January 5, 2015

Jean Ospital
South Coast Air Quality Management District
21865 Copley Drive
Diamond Bar, CA 91765

Subject: DRAFT MULTIPLE AIR TOXICS EXPOSURE STUDY MATES IV

Thank you for the opportunity to comment on the Draft Multiple Air Toxics Exposure Study IV (MATES IV) on behalf of the military services in California. The Study validates the efforts of the South Coast Air Quality Management District (SCAQMD) to reduce air toxics since MATES III was conducted in the 2004-2006 timeframe.

However, we understand the MATES IV Study is not consistent in the use of scientific advancements in the assessment of risk. While recent advancements in modeling and exposure assessment were incorporated into MATES IV, the latest scientific updates were not applied for the dose-response assessment portion of the Study. This is in specific reference to page 1-3 in the Dose Response Assessment, "For this study, the dose-response estimates developed by OEHHA are used to estimate the potential for adverse health effects." The Study and SCAQMD would be best served by using the best and most current dose-response data and unit risk cancer potency factors from U.S. EPA.

Unfortunately, some of the key OEHHA cancer dose response/ potency factors are over 20 years old and thus do not reflect current knowledge, which the Study as a whole is to be based on. While MATES IV acknowledges on page 1-3 that OEHHA cancer potency "estimates sometimes differ from those developed by the U.S. EPA", the MATES IV report does not affirm that it applied any dose-response advancements since the MATES series began. Specifically, key inhalation cancer potency values used (as per Appendix I of MATES IV and as shown on Table 4-6 of the Draft Report) were proposed in October 1990 (for trichloroethylene, TCE) and October 1991 (for perchloroethylene, PCE), suggesting 23-24 years have passed since the OEHHA toxicity studies for these chemicals were developed. The MATES IV Report should incorporate in their risk assessment process the best and most current dose-response science as it has incorporated recent exposure assessment science.

Specifically, OEHHA's outdated unit risk cancer potency factor for PCE is based on a toxicological study from 1986. The current state of knowledge for PCE toxicity was reviewed on a national scale from 2004-2012, with an updated unit risk cancer potency factor established using a 1993 study with a 2010 National Research Council panel report, that was documented by written and oral comments from scientists within the U.S. EPA, other federal agencies, and the Office of Management and Budget, as well as the public (Regulations.gov 2008). The output of the national PCE unit risk update effort was finalized by the EPA Integrated Risk Information System (IRIS) in February 2012 (http://www.epa.gov/iris/subst/0106.htm). A similar update for TCE was completed on a national scale in September 2011 (http://www.epa.gov/iris/subst/0199.htm.

The MATES IV practice of retaining the outdated TCE unit risk cancer potency factor that has been in use since October 1990 means the MATES IV risk calculations use 24-year old dose-response science, whereas other OEHHA and California DTSC guidance directs the use of the updated (U.S. EPA IRIS) TCE toxicity value by way of HERO Note 3 (posted 14 Jul 14 at http://www.dtsc.ca.gov/assessingrisk/humanrisk2.cfm), making the California MATES IV approach using the 1990 OEHHA value for TCE inconsistent with HERO Note 3. In particular, HERO Note 3 (http://www.dtsc.ca.gov/AssessingRisk/upload/HHRA-Note-3-2.pdf) now directs risk assessors at California "hazardous waste sites and permitted facilities" to use the U.S. EPA Regional Screening Level for TCE (i.e., to use the U.S. EPA TCE IRIS unit risk cancer potency factor). Thus, SCAQMD and the MATES IV study should be consistent with DTSC guidance and incorporate the latest scientific knowledge of dose-response and unit risk factor selection.

Additionally, the MATES IV use of OEHHA cancer potency values contradicts the U.S. EPA OSWER Guidance Directive 9285.7-6, *Use of IRIS Values in Superfund Risk Assessment* which directs a hierarchy of cancer potency values be used in certain federal (i.e., Superfund) risk assessments. The OSWER guidance is clear to state that a Tier 1 value from U.S. EPA IRIS is to be used in risk assessment if one exists for a given chemical, which is the case for PCE and TCE. Please note that the OEHHA inhalation cancer potency values are considered Tier 3 values in the OSWER

Guidance hierarchy. Since a Tier 1 value exists for PCE and TCE, it is the best value to use particularly at federal sites subject to compliance with U.S. EPA guidance.

The Study notes in the Executive Summary that uncertainty in the risk estimates may be reduced with further scientific studies. Uncertainty in the risk estimates would be reduced by the use of the most current cancer potency value published in the U.S. EPA IRIS database, produced by rigorous nationwide scientific and peer-reviewed efforts.

On behalf of the military services in California, please consider this input to improve the Final MATES IV Study by consistently applying the most credible and current state of dose-response knowledge.

My point of contact for this is David Bell who can be reached at (415)977-8845 or Michael Huber at (619)532-2303.

Sincerely,

C. L. Stathos

C. L. STATHOS
By direction

APPENDIX XIII

MATES IV

DRAFT FINAL REPORT

Responses to Comments Received on the MATES IV Draft Report

Below is a compilation of comments received on the MATES IV Draft Report, followed by staff responses.

Comment: The draft MATES IV report, pp. 5-14 to 5-15, speculates that I-405 Freeway traffic emissions may have contributed to the elevated UFP concentrations at site 8.

The LAX Air Quality Source Apportionment Study includes evidence that the freeway did not influence UFP concentrations measured east of the freeway. Specifically to address this question, the researchers collected simultaneous measurements downwind of the runway and the same distance from the freeway about a mile and a half south of the runway. See Phase III of the LAX AQSA Study, pp. 5-99 to 5-113.

The results showed that the elevated UFP concentrations could be attributed to aircraft, not the freeway. The language on pp. 5-14 to 5-15 of MATES IV should be revised to acknowledge the LAX AQSA study finding and suggest instead that, while the freeway could be a source of UFP, existing evidence shows that the elevated concentrations result from aircraft.

Response: In the Phase III of the LAX AQSA Study, pp. 5-99, it is indicated that: "*The particle size distribution (PSD) data from the Winter Season indicates the 7-30 nm particles are likely associated with jet exhaust while the 30-160 nm particles were likely associated with aged aerosol and directly emitted vehicle exhaust emissions*." which is not inconsistent with conclusions in MATES IV report. In the comprehensive LAX AQSA Study, the diurnal variations of PSD and other pollutants were measured and studied. The correlations of specific particle size ranges with other pollutants provide information regarding the relative contributions of different possible sources. The LAX AQSA Study (pp. 113) concludes: *"[d]ifferences in correlations of UFP with other pollutants and day-of-week variations in diurnal profiles in 7-30 nm and 30-160 nm particles suggest that particles in the two size ranges may have different origins. Good correlations of the 30-160 nm particles with CO, NO, and BC and strong weekday dependence of diurnal variations indicates an association of these particles with vehicle emissions. In contrast, the poorer correlations with* SO_2 *and* NO_2 *suggest contributions of jet exhaust and possibly secondary particles."* identifying vehicular traffic as a possible contributor to the measured ultrafine particles.

Our findings from the LAX local-scale study show the influence of aircrafts on the measured UFP concentrations, however elevated concentrations adjacent to freeways were also observed. In the MATES IV LAX local study, considering that site 8 is located immediately downwind of the I-405 freeway, this site is most susceptible to be affected by emissions originated from the freeway; therefore it is hypothesized in the report that the slightly higher measured UFP concentrations at site 8 (e.g. compared to site 4, also downwind but further away from the freeway) may be due to the contribution of vehicular emissions. The report has been revised to refer to the Phase III LAX AQSA Study for more information.

Comment: Has the District run a regression analysis against POLA and POLB throughput to see what effect, if any, higher or lower throughput has had on cancer risk.

Response: Since the MATES studies are just single year snapshots, it is hard to do a regression analysis with just two or three data points. The total combined ports container throughput in 2005 (MATES III) was about 14.2 million TEU vs. 14.1 million TEU in 2012 (MATES IV). So with similar throughput, the risks have dropped significantly. We have also looked at container throughput vs. ambient Elemental Carbon (a marker for diesel PM which drives most of the risk) levels over time. It shows that since the 2009 recession period, container throughput at the ports has increased while Elemental Carbon has significantly decreased.

Comment: Given the significance of traffic sources in the Basin, and the fact that AQMD uses EC as a marker of carcinogenic diesel emissions, I attached our latest paper in which we used PMF on the speciation network data from 2002-2012 to do source apportionment, and showed that in L.A. and Riverside counties, the traffic emissions were reduced from the 2002-2006 to the 2008-2012 period by ~30% following the 2007 emission standards ; this was despite an actual increase in overall traffic volume in the post standard period . This is very relevant to the work presented in your draft document and corroborates the effectiveness of the emission standard.
Reference: Long-term source apportionment of ambient fine particulate matter (PM2.5) in the Los Angeles Basin: A focus on emissions reduction from vehicular sources, Sina Hasheminassab, Nancy Daher, Bart D. Ostro, Constantinos Sioutas, Environmental Pollution 193 (2014) 54-64.

Response: Staff appreciates the reference, and it is included in Appendix XI.

Comment: Adding error bars in the plots and/or some metric of standard deviations or uncertainty in tables would make the presented data more defensible and the conclusions drawn more robust.

Response: Standard deviations have been added to the diurnal variation plots of BC and UFP in Appendix VI.

Comment: The elevated BC levels at the Inland Valley SB, not accompanied by equally high levels of UFP, are intriguing and require some further thoughts and investigation – are there any BC sources other than traffic in the area?

Response: The highest annual average black carbon concentration measured during the MATES IV Study was observed in Inland Valley San Bernardino site. Similarly, elemental carbon concentration measured at this site during the MATES III Study, conducted between April 2004 and March 2006, was among the highest measured in the fixed sites throughout the basin. These observations suggest presence of local diesel sources. The addition of particulate matter number concentration measurements in MATES IV Study provides additional insight which may be helpful in identifying possible sources of BC emissions in this region, considering that the identification of such potential sources in this region was non-conclusive in the MATES III Study. Typically high BC concentrations not accompanied by high UFP concentrations could be attributed to heavy-duty diesel vehicle and locomotive emissions. In one of the local-scale studies of the MATES IV, BC and UFP were measured in vicinity of the San Bernardino Railyard as one of the potential sources of the observed elevated BC concentrations (Chapter 5 – Page 5-15). Railyards are a complex mix of many source types including trains, stationary equipment, terminal operations and on-road vehicles, particularly heavy-duty diesel trucks. Generally, elevated BC concentrations are expected in vicinity of a railyard facility due to high traffic activity of heavy-duty diesel vehicles. This is evident from higher measured BC concentrations around the railyard compared to the concentrations measured at the fixed Inland Valley San Bernardino site during the same period. The railyard and the chosen sampling sites in this study were all located upwind of I-215, and the light-duty vehicle traffic around the railyard is not significant; therefore, the measured concentrations mostly reflect emissions of heavy-duty diesel vehicles. This may explain highly elevated BC concentrations not accompanied by equally high UFP concentrations around the San Bernardino Railyard. Similar observation at the fixed Inland Valley San Bernardino site may also suggest higher contribution of diesel emissions compared to gasoline traffic in this region. It should be noted that the relative contribution of light-duty and heavy-duty vehicles to the measured BC and UFP levels and identification of other possible sources of BC and UFP is difficult to assess with this limited dataset.

Comment: Fig 5-7, 5-8 and 5-9 are these averages across sites? If so, error bars need to be added.

Response: The error bars were not added to these plots in order to simplify the report for general public, since this report is intended mainly for an audience with a non-scientific background. Some of the plots in this chapter are presented with the error bars (including Figures 5-7 and 5-9; Figure 5-8 with the error bars is not readable) in Appendix VI – Black Carbon Measurements at Fixed Sites and Appendix VII – Ultrafine Particle Measurements at Fixed Sites, where more details and scientific discussions are included for more technical readers.

Comment: The LAX pilot study is very well presented and in concert with earlier work by Westerdahl, D., Fruin, S. A., Fine, P. L., & Sioutas, C. (2008). The Los Angeles International Airport as a source of ultrafine particles and other pollutants to nearby communities. Atmospheric Environment, 42(13), 3143-3155.

Response: Thank you for your comment and the reference. This study echoes the findings of the MATES IV Study and the reference has been added to the report.

Comment: Commenter notes a fundamental disagreement with the Elemental Carbon/Organic Carbon (EC/OC) apportionment method used in MATES.

Response: There was no apportionment of EC or OC in the MATES IV Study, other than the use of EC as a surrogate for diesel PM. Staff acknowledges that there is no specific method to measure diesel PM in ambient air. The method used employs EC as a surrogate measure and estimates diesel PM levels by applying the emissions ratio of diesel PM and EC from the emissions inventory to the measured EC concentrations. Additional details are provided in Appendix XI.

Comment: The unit risk factor (URF) applied for diesel PM is not based on sound science, stemming as it does from flawed dose-response assumptions derived from the 1987 and 1988 Garshick, et al. studies of railroad workers.

Response: The risk factors used for diesel PM and other air toxics, as noted in the report, are those adopted by the California EPA Office of Health Hazard Assessment.

Comment: There is concern that EMA was excluded from the MATES Technical Advisory Committee, and that, in fact, no industry representatives were included on that committee. That basic lack of industry representation calls into question the objectivity of the MATES IV Report, and needs to be addressed.

Response: A Technical Advisory Group was selected to give input to SCAQMD staff on a range of technical areas. We note that all meetings of the Advisory Group were open to the public, notice of meetings were sent to interested stakeholders, and anyone with interest or relevant information was invited to provide comments.

Comment: The MATES IV Report does not adequately convey the very significant reductions in ambient levels of air toxics or the successful efforts to reduce air toxics risk in the South Coast Basin.

Response: Staff believes that the substantial reductions in air toxics was emphasized and conveyed appropriately, including specific graphical comparisons of ambient levels measured with those from prior MATES studies. Staff has added additional language to point out the reductions.

Comment: The Policy Implications section should acknowledge that the existing programs in California are sufficient to reduce any health risks attributable to diesel PM to acceptable levels in the near future, and that the diesel PM issues have been essentially resolved, as evidenced in part, by the attainment demonstrations that have been made for the PM NAAQS in the South Coast Air Basin.

Response: While staff may share the commenter’s optimism that reductions in air toxics will continue into the future, staff believes that only future study of ambient levels of air toxics can provide the information needed to determine if future risks will indeed be reduced and to what extent. Whether future residual risk levels from diesel PM are acceptable is a question of policy and risk management that is beyond the scope of this report. Also note that the Basin is still in non-attainment for both the annual and 24-hour $PM_{2.5}$ standards

Comment: Suggest including additional figures and charts in the Executive Summary comparing estimated risks from MATES IV to MATES III:

- A pie chart of the MATES-III results in addition to the MATES-IV results showing the area of the pie charts proportional to the risk estimates at the fixed monitoring sites

- A bar chart should be added to the Executive Summary comparing the change in risk between the two studies and clearly show that risk have decreased from 1,200 in 2006 to 400 in 2013

Response: These reductions were noted in the summary text, and a chart showing the reductions in risks across the Basin is also included to show both the magnitude as well as the spatial extent of estimated risks in MATES IV compared to MATES III.

Comment: There has been no re-evaluation of the Diesel PM URF (Unit Risk Factor) to address the significantly different emissions profile of new-technology diesel engines. Application of the "old" OEHHA risk value to today's diesel engines is not valid. This adds to the uncertainty of MATES IV and most certainly overestimates the risk ascribed to diesel PM emissions in MATES IV.

Response: While the PM mass emissions of "new technology" diesel engines are substantially lower on a per mile or per hour operating basis, there is a lack of data that would indicate whether such emissions differ in terms of toxic potency per mass emitted. Again, staff used the potency factors established by OEHHA. Should OEHHA develop a different potency factor, staff will employ it in our estimates. Staff also notes a recent report from the Health Effects Institute describing the lack of tumors found in a laboratory animal study of "new technology" diesel exhaust, where the study's Review Panel states that "whether the toxicity per unit mass of the PM emitted from the 2007-compliant engines was changed compared with older engines, the Panel pointed out that ACES was not designed to investigate this question." And further that the most straightforward inference would be that the steep drop in particle mass and levels of organic components in exhaust significantly decreased the observed overall toxicity of exhaust compared with the toxicity of exhaust from older engines. That is, the decrease in toxic effects observed was likely due to the substantial reduction in the exposure level of diesel particulate, and not necessarily a change in the per unit mass risk factor.

Comment: The statement regarding increased ultrafine and particle number emissions in the MATES IV Report is wrong, and should be removed from the text. Page 5-12 Summary of Fixed Sites - The discussion indicates that there are ongoing concerns that the application of advanced emissions control technologies to diesel engines has led to uncertainties regarding the potential formation of ultrafine particles (UFPs). Extensive emissions testing has shown that the use of DPFs and selective catalytic reductions systems actually reduces the number of fine particles emitted from new-technology diesel engines.

Response: Staff concurs that proper controls on diesel engines can reduce both particle mass (PM) and particle number (ultrafines). A full discussion of the different emissions controls and their impacts is beyond the scope of this report, and thus this discussion has been removed.

Comment: Page 5-13 Gradient Studies - The report refers to UFPs and black carbon (BC) as air toxics. Neither UFPs nor BC are considered or regulated as air toxic contaminants in California. The text of the MATES-IV report should be changed to reflect their correct classification throughout the document.

Response: This erroneous statement has been removed.

Comment: There is concern expressed that the difference between the MATES III and MATES IV West Long Beach sites are considerable, especially with EC.

Response: The two-sample T-test was used to test the difference between the average pollutant concentration in the MATES III and MATES IV West Long Beach sites. Except for acetaldehyde, p values are above 0.05 for other species listed in Table V-1. Therefore, the differences between the MATES III and MATES IV West Long Beach sites are not statistically significant ($p>0.05$) for most constituents.

Note that ambient monitoring data is used to provide temporal and spatial trends of VOC/carbonyl/PM species. Cancer risk calculations and source identification are based on the emission inventory, which does not rely on monitoring data. More details about development of the 2012 emission inventory can be found in Chapter 3. Nonetheless, the following text has been added in Appendix X (page X-4) to highlight the potential observed differences:

"… relative to MATES III are in line with the monitoring data from the ports. Note that the levels of some PM constituents measured concurrently at the MATES IV West Long Beach site were slightly higher than those at the MATES III West Long Beach site (more details about the location and comparison of the two sites can be found in Appendix V). Therefore, the percentage reduction of PM species from the ambient monitoring program at West Long Beach might be a low estimate.

Comment: The impression is given that the major contributors of BC emissions measured at the WLB site are from the Port's operations - diesel-powered vehicles, non-road mobile machinery, and ships. However other area sources play a significant role in the measurements in Appendix VI. Commenter presented an analysis of BC measurements conducted by the port, and concluded that local BC sources (within a few hundred meters) contributed between 15% and 19% of the total measured BC concentrations on January 3rd" and that on the days that "similar BC levels and meteorological conditions persist", "there are significant urban and regional contributors to the levels of BC measured at the port monitoring stations".

Response: This is in line with what is presented in MATES IV Appendix 6, where the major sources of BC in the port area are associated with the port activities, including ship emissions, port related traffic, goods movement and other activities related to the ports; while acknowledging other potential BC sources, such as the seasonal residential wood burning and other local sources. It should also be noted that the BC measurements in the MATES studies were not conducted for source apportionment analysis. Identifying and quantifying the contribution of various sources are achieved from the emission inventories and were not the purpose of BC measurements or Appendix 6. However, high time resolution BC measurements provide important information including the temporal trends which are helpful in identifying major and dominating sources.

Comment: In the analysis presented by commenter, based on 1-min BC concentration measurements, "*[e]levated 1-min spikes of BC concentrations (up to 40 ug/m*^{3}*) are much more prevalent at the Inner Harbor station, indicating that there are a number of BC sources close to that station. These measurements reflect the environment around the two stations, because nearby BC sources appear to be common at the Inner Harbor station and less common at the Outer Harbor station. The other feature evident in the 1-min BC measurements is that elevated BC spikes are common only during certain parts of the day, primarily in the early morning and late afternoon/evening hours.*"

Response: The sharp BC spikes in the 1-min data probably originate from nearby sources, which are most likely direct emissions from diesel trucks on the nearby roads since the continuous point-source emissions and neighborhood contributions are expected to appear as more slowly varying concentrations rather than sharp, short-lived spikes (Watson and Chow, 2001). Moreover, as the commenter indicated as well, these spikes are more common during the rush hours with higher vehicular traffic (coupled with shallower mixing heights). Given that the major vehicular emitters of BC are diesel trucks, these spikes are most likely related to the goods movements to and from the ports which are considered as port activities in this report.

The commenter concludes that "*local BC sources (within a few hundred meters) contributed between 15% and 19% of the total measured BC concentrations on January 3rd*". Based on the locations of the measurement stations the commenter expects that "*the Inner Harbor stations, would likely be influenced by a combination of regional, urban and local sources; the Outer Harbor station would be expected to be influenced primarily by regional and urban sources*", meaning that the Inner Harbor station is affected by local sources more than the Outer Harbor station. However based on the analysis presented by the commenter, the difference between the estimated contribution from local sources are only 4%, suggesting that the local sources at the Inner Harbor station are not a significant contributor to the total measured BC concentrations.

In the report it is clearly acknowledged that other than major BC sources, depending on the region, other sources may also contribute to the measured concentrations. For example it is mentioned in the report (Appendix VI – Page VI-1) that: "*While the major source of EC and BC in an urban area is 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 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.*" and also (Appendix VI – Page VI-13) "*As mentioned earlier, other than diesel exhaust other sources contribute to increasing the total BC content of atmospheric PM. These may include biomass burning, coal burning, meat charbroiling and fuel oil (ship emissions).*"

Comment: The high correlation between two data sets collected comparing the MATES III and MATES IV West Long Beach sites might indicate a consistency where data points increase or decrease together on the same date. The increase in EC at the MATES IV WLB site might be due to its proximity to a localized source.

Response: The BC levels at the MATES IV West Long Beach site are probably affected by emissions from the Terminal Island Freeway 103, located only 300 feet upwind of the sampling station, where vehicular traffic from goods movement associated with the San Pedro Bay Ports is particularly pronounced.

Comment: Suggested a comparison between UFP of the MATES III and MATES IV WLB sites.

Response: Unfortunately, particle counts were not in part of the sampling campaign in 2007-8 at the MATES III site. A detailed analysis of UFP spatial and temporal variation of the current MATES is presented in Appendix VII.

Comment: The Port's monitoring data at POLB's Inner Harbor station (1 miles south of the MATES III site) shows lower concentration of PM2.5 mass, EC and OC compared to both the MATES III and MATES IV WLB sites.

Response: The MATES III and MATES IV West Long Beach sites are closer to the Terminal Island Freeway (300 feet and 0.7 mile downwind, respectively) than the Inner Harbor station (1 mile downwind). The Terminal Island Freeway is heavily impacted by heavy-duty diesel trucks traveling to and from the Ports. Vehicular traffic from goods movement associated with Ports' activities could be a significant source of PM emission at the WLB sites.

Comment: Suggested a more detailed analysis of the data due to seasonal meteorological and dispersion conditions in the study timeframe.

Response: Excluding low EC days (< 1 ug/m3), there are 3 days when the difference between MATES III and IV West Long Beach site exceeds 2x. For these 3 days, westerly wind prevailed most of the time, and wind speed was moderate to moderately low in the Long Beach area. For the diurnal profile of BC, please refer to Appendix VI.

Comment: The reduction in air toxic exposures of 65% since MATES III should be presented clearly as an unqualified success story. However, this message does not come across as strongly as it should when multiple results covering changes in the OEHHA exposure estimation are presented.

Response: Staff believes this description was included in the report. Regarding the changes in OEHHA risk estimation procedures, this is included to show what the changes are for the MATES IV modeling results that will be compared to future MATES studies using the new methodology. For consistency with previous MATES study results, the previous risk estimations were used to describe the changes in potential air toxics risks.

Comment: A key point is that the exposure and risk reductions measured by MATES IV are not affected by the changes in the OEHHA exposure methodology. The OEHHA changes can and should apply to all MATES studies and any risk calculations and risk maps comparing different MATES studies should be based on a single, consistent method. Using different exposure methodologies (such as was done in the maps of ES-4 and ES-6) sends a confusing message that the risk reductions measured in MATES IV are somehow offset due to previous flaws in assessing exposure.

Response: Staff's view is that the changes in risk estimation methodology are important, and should be described. Also that the changes in the methodology, as pointed out by the commenter, do not imply that exposures and risks have gone up compared to previous MATES studies. Staff does not agree that the implication is that reductions in exposures are "offset" due to changes in the calculations for estimating risk. Staff has added revised language in the report to more fully address this.

Comment: Differing exposure methodologies should not be used in any presentations of risk, as it likely will result in confusion for policy makers and the public. Any presentations of MATES III risk in the MATES IV Report that use the new OEHHA exposure methods should be put in appendices, along with detailed explanations of the changes in the exposure calculation methodology.

Response: Staff considered a number of approaches to present the risks resulting from the revised OEHHA calculation methodology, and chose to use the method used in previous MATES reports to provide a comparison of exposures and estimated risks in the previous studies, and then to point out the magnitude of difference in the MATES IV Study when using the revised methodology. It is staff's view that these changes are important to acknowledge and describe for the public and for policy makers.

Comment: Because a large part of the reduction in cancer risk was due to changes in the DPM/EC ratio, more detail should be provided about the changes in this ratio along with estimates of uncertainty. Appendix XI should be expanded and included in the main report due to its importance. Specific questions that should be addressed in an expanded Appendix XI, include the following, presented as

Response: Staff appreciates the detailed and valuable comments from the reviewer. The Appendix XI was revised to address the concerns raised by the reviewer.

Comment: Were the large changes in DPM/EC ratios from MATES III to IV due to actual reductions in this ratio or were they primarily due to better speciation profiles

Response: In addition to the speciation profile, some regulatory actions and demographic changes, even though small, contributed to the change. More discussions about the changes are now incorporated in the Appendix XI.

Comment: Were there improvements or important changes in the DPM emission inventory from MATES III to IV?

Response: DPM and EC emissions are calculated using VMT estimated by SCAG and emission factors from EMFAC 2011. Other than the speciation profiles and updates made to EMFAC2011, there was no significant changes in methodology to estimate emissions.

Comment: Was the decrease in DPM/EC ratio expected or reasonable due to changes in engine technology and fleet turnover? This was discussed briefly for ocean-going vessels but not for other source categories.

Response: A figure (XI-1) is added to demonstrate the changes in speciation profile over time. The calendar year fleet represent an aggregated fleet with different engine type, control technology, engine operation mode, etc. More references are added as well.

Comment: In light of the above information, is it reasonable that the DPM/EC ratio changed from 1.04 to 1.95 then back down to 0.85 over the course of the last three MATES studies?

Response: The ratios were estimated strictly based on the emissions inventory which were the state-of-art at the time of the study. As more advanced and refined data become available, the emission inventory has been updated based on them. Note that MATES II was conducted in 1998-1999 which is over 16 years ago and MATES III is almost a decade old. The changes in the ratio are largely driven by changes in the relative contribution of various EC sources and DPM sources, in addition to updates to speciation profiles.

Comment: Were different contributions by source category in different parts of the Basin taken into account? If not, should they have been? One example might be a decrease in DPM/EC ratio as one goes inland and the average ratio is less influenced by the high ratio for ocean-going vessels.

Response: A new paragraph is added in the Appendix XI to discuss the geographical variation of the ratio.

Comment: The sensitivity test using the MATES III profiles for MATES IV data was a good idea but the results were not presented clearly.

Response: A paragraph and a table are now added to Appendix XI to clarify the calculation.

Comment: A detailed uncertainty analysis including all uncertainties should be part of this report. It is clear that there are large differences in relative uncertainties between the analysis methods, emission inventories, DPM/EC ratios and cancer potency factors. As described above, the uncertainty in the DPM/EC ratio may dominate the overall risk numbers and be worthy of increased attention. Besides giving readers an appreciation for the sometimes large uncertainties present in cancer risk estimations, knowing what uncertainties contribute most to the overall risk uncertainty can be useful in determining where future resources and efforts should be focused.

Response: The effect of the DPM/EC ratio change due to the speciation methodology change only affects MATES III vs. MATES IV comparisons based on EC measurements. The overall risk assessment using numerical modeling results is not affected by the EC speciation profiles as DPM is estimated directly, and results from the modeling were consistent with the measurement approach. In addition, the DPM concentration estimated using MATES III diesel profile showed less than 25% of variation.

Comment: Uncertainty analysis should also include the spatial uncertainty. For example, DPM shows near road and near-freeway concentrations several times higher than ambient. While these may have been included in the 2 x 2 km grid average, there are large, socioeconomic-related differences in proximity to roadways across the basin. These should be an explicit concern in a study of this type.

Response: Programs such as MATES are designed to monitor and characterize toxic emissions over the entire Basin. However, ambient monitoring is necessarily conducted at a limited number of locations, and modeling is limited to a spatial resolution of 2km. For this reason, communities located close to industrial sources or large mobile source facilities (such as marine ports, railyards and commercial airports) can be affected by higher air contaminant levels that cannot be captured in the typical MATES analysis. Near-road monitoring studies and dispersion modeling results for point sources indicate that exposure can vary greatly over distances much shorter than 2 km. The local-scale monitoring program of MATES IV aimed to characterize the impacts of large sources on nearby communities by utilizing portable platforms designed to sample for a period of several weeks at selected locations with an emphasis on diesel particulate matter (DPM) and ultrafine particle (UFP) emissions. The studies are designed to assess gradients in ambient pollutant levels within communities as well as provide a comparison to the fixed MATES monitoring sites. The communities chosen for sampling were selected based on proximity to potential sources as well as environmental justice concerns. Please refer to Chapter 5.4 (Page 5-12).

Comment: One important caveat to include is that people who live, work, attend school, or drive in locations of elevated DPM may be subject to significantly higher risks than these calculations indicate.

Response: Staff appreciates the comment, but the study was designed on a regional scale and thus may not pick up exposures that would be influenced by a nearby source. The modeled risk based on the emissions inventory point out graphically that risks are higher near sources of emissions. For this reason the local-scale program was designed as part of the MATES IV Study to characterize the impacts of some of the large sources in selected locations and assess gradients in ambient pollutant levels within these communities. This local-scale program specifically focused on DPM emissions.

Comment: One new aspect of the large downward temporal trend in concentrations is that the risk reductions in a year or two are now larger than the site-to-site differences within a given year. This might justify the continuous temporal coverage of one location, such as Central Los Angeles, which matches the overall basin average for most compounds, and fewer numbers of sites or reduced sampling frequencies at sites that do not differ very much.

Response: The MATES studies are, of course, very resource intensive. Staff appreciates the comment and will take the suggestion into consideration for future studies. It should be noted as well that high-time resolution continuous measurement of black carbon concentrations will continue in four of the fixed MATES IV sites, including the suggested Central Los Angeles site (as well as Anaheim, Rubidoux and Inland Valley San Bernardino sites), in order to monitor the year-to-year variations. Moreover, some of the sampling stations in MATES IV Study, are also part of the National Air Toxics Trends Stations (NATTS), or National Core (NCore) Multi-Pollutant Monitoring Station, or the Speciation Trends Network (STN) which provide the measured ambient levels of air toxics every year.

Comment: In absolute terms, the big reductions are from on-road diesel. The actual decreases in the inventory as modeled should be highlighted up front, along with the regulations and programs that are believed to be behind them. The other risk reductions should be prioritized by quantity.

Response: Staff believes that the relative contributions to risks from the various air toxics measures have been presented in the report. Additional detail on risk weighted emissions is in Chapter 3, which also shows the large reduction from on road vehicles.

Comment: One alternative inter-study mapping strategy that might be useful would be to make maps of the percent of basin average risk. This would allow direct inter-study comparisons of spatial differences that would not have been produced in previous reports. These will show a reduction in spatial disparities from MATES III to IV.

Response: Staff's view is that the actual estimates are most appropriate to convey the results. A map with percent of Basin average risk would look very similar to the absolute risks presented.

Comment: For credibility, the results should not be presented with three or four digit precision. If the uncertainty is +/- 50%, for example, only two digit precision is justified.

Response: Staff appreciates the comment. While most of the data are presented with two decimal points, there are small exceptions with an added digit to accommodate low concentrations observed in certain species.

Comment: Table 2-2 (Sampling locations): It would be useful to list distance from and orientation to the nearest busy road.

Response: The sampling location addresses are given. It was not the purpose to list nearby potential sources of emissions, as this was a regional scale study with sites generally chosen to be representative of regional or urban scale levels. When local sources are thought to be influencing measurements, they are mentioned in the discussion.

Comment: Section 3.8 and Table 3-6: More discussion of these results seems warranted. Table 3-6 seems to show fairly large discrepancies in MATES III versus IV inventory changes and changes in the air measurements. Cr(VI), 1,3-butadiene and benzene are important since they contribute significantly to total risk. For Cr(VI) and 1,3-butadiene, relatively large discrepancies may be due to measurement challenges and may be deserving of more resources while other compounds contributing little risk might be considered for elimination if that results in a cost savings.

Response: Changes in benzene air quality should show a lower percentage change than emissions. This is so because benzene has a relative long atmospheric residence time, i.e, there is a large global background benzene concentration.

Changes in 1,3-butadiene emissions are consistent with formaldehyde and acetaldehyde. These pollutants come from similar sources. While changes in air quality for acetaldehyde and formaldehyde are consistent with emissions, changes in 1,3-butadiene are smaller than changes in emissions. Like the commenter alluded to, there is significant measurement challenge in measuring 1,3-butadiene. This is so due to both challenges in analytic technique and the ambient concentrations of 1,3-butadiene have come down significantly over last decade and to levels frequently below analytical detection limit.

The Cr6 inventory increases are primarily due to the increases of brake wear emissions between the two versions of EMFAC used in MATES III and IV. The brake wear increases are also resulting in higher nickel emissions. The other part of nickel increases is due to changes in off-road diesel profile. Therefore, these increases in emissions are due to inventory methodology changes and are not necessary real emissions changes. As shown in Chapter 2, ambient levels for both of these metals showed a decrease from MATES III to MATES IV.

Comment: Calculating spatial correlations would highlight which compounds are global (e.g., high correlations for CCl_4), which are regional and which are more localized (with lower correlations). It is important to show where BC/EC fits in this picture—it may be localized most of the time but build up to be a regional pollutant during times of summer inversions.

Response: Intersite correlations are a good suggestion for further analysis, but the MATES Study focused more on determining risk levels from the combined impact of all sources, local or regional

Comment: In Appendix IV, correlation matrices for elements and VOCs would be useful to present. Also, readings below the Limit of Detection (LOD) should be set to 2/3 of the LOD rather than zero. This is less conservative and also more appropriate if the fraction of readings below the LOD is moderate, i.e., fewer than 20 or 30%.

Response: Staff appreciates the comments. Presenting such correlations may be of interest to some, and the data is publically available for further analyses. Regarding presenting data below the limits of detection, staff chose to present the actual readings from the analyses. Setting an arbitrary fraction of the LOD for non-detects may artificially bias the averages high.

Comment: Appendix G seems repetitive in some places. Some graphs are not readable (Figures 4, 13).

Response: Staff assumes the reference is to Appendix VI. Both figures (Figure 4 and Figure 13) are removed from the Appendix VI. Figure 4 that presented the daily BC concentrations at each site was not readable because daily concentrations for all ten sites were presented in one graph, with an intention to highlight generally higher concentrations during colder months. Figure 5 shows the trend of monthly (average) BC concentrations averaged over all ten sites which conveys same conclusion as Figure 4; therefore, figure 4 is deleted from the report.

Similarly, Figure 13 presents the correlations between EC and BC measurements for each of the ten sites combined in one plot, which as the commenter pointed out, is not readable in the printouts. Figure 14 presents the same correlation plots, for each site separately; therefore, with the same logic, figure 13 is also removed from the report.

Comment: Suggest listing emissions by contribution to risk rather than just alphabetically for enhanced public understanding.

Response: Table 3-5 in Chapter 3 (Development of the Toxics Emissions Inventory) lists emissions on a potency weighted basis.

Comment: Linear regressions for scatter plots like Fig 14 in Appendix G (EC vs BC) should probably be log transformed.

Response: Staff presumes this is Appendix VI. Generally the daily BC concentrations measured in this study range from a few hundred to below 5,000 ng/m^3, therefore log-scale plots were not used.

Comment: The latest scientific updates were not applied for the dose-response assessment portion of the study. Specific examples are for trichloroethylene and perchloroethylene, where more recent potency factors are available from the U.S. EPA Integrated Risk Information System. Commenter also noted that the reports use of OEHHA potency factors in not in line with EPA guidance "Use of IRIS Values in Superfund Risk Assessment"

Response: Staff has acknowledged in the report that the risk factors from OEHHA are often different than those in the EPA IRIS System. Should OEHHA revise the California risk factors, staff will apply such revised factors.

Comment: Concerned about the inclusion of CalEnviroScreen results in Section 4.8 of the Draft Report. Request that the Final Report explain the substantial differences between this screening tool and a comprehensive risk analysis and communicate that CalEnviroScreen scores are not an expression of health risk.

Response: Staff agrees that the difference between MATES and CalEnviroScreen should be emphasized. Section 4.8 has been revised to include the commenter's recommendation.