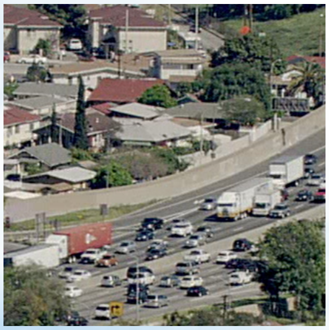
DRAFT APPENDICES

Multiple Air Toxics Exposure Study in the South Coast Air Basin

MATES-IV



OCTOBER 2014

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APPENDICES

Multiple Air Toxics Exposure Study in the South Coast Air Basin

MATES IV

Draft Report

October 2014

South Coast Air Quality Management District
21865 Copley Drive
Diamond Bar, CA 91765

List of Appendices

APPENDIX I

MATES IV

DRAFT REPORT

List of Substances and Their Associated Risk Factors

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Appendix I

List of Substances and their Associated Risk Factors

Compound	Class	CAS	Acute REL (µg/m3)	8-Hour REL (µg/m3)	Chronic REL (µg/m3)	Unit risk (µg/m3)$^{-1}$
Acetaldehyde	Carbonyls	75-07-0	470	300	140	2.7E-06
Formaldehyde	Carbonyls	50-00-0	55	9	9	6.0E-06
Methyl Ethyl Ketone(2-Butanone)	Carbonyls	78-93-3	13000			
Arsenic	Metal	7440-38-2	0.2	.015	0.015	3.3E-03
Cadmium	Metal	7440-43-9			0.02	4.2E-03
Copper	Metal	7440-50-8	100			
Cr+6	Metal	18540-29-9			0.2	1.5E-01
Lead	Metal	7439-92-1				1.2E-05
Manganese	Metal	7439-96-5		0.17	0.09	
Nickel	Metal	7440-02-0	0.2	0.06	0.014	2.6E-04
Selenium	Metal	7782-49-2			20	
Benz(a)anthracene	PAH	56-55-3				1.1E-04
Benzo(a)pyrene	PAH	50-32-8				1.1E-03
Benzo(b)fluoranthene	PAH	205-99-2				1.1E-04
Benzo(k)fluoranthene	PAH	207-08-9				1.1E-04
Chrysene	PAH	218-01-9				1.1E-05
Dibenz(ah)anthracene	PAH	53-70-3				1.2E-03
Indeno(123-cd)pyrene	PAH	193-39-5				1.1E-04
Naphthalene	PAH	91-20-3			9	3.4E-05
Benzene	VOC	71-43-2	27	3	3	2.9E-05
Butadiene, 1,3-	VOC	106-99-0	660	9	2	1.7E-04
Carbon Tetrachloride	VOC	56-23-5	1900		40	4.2E-05
Chloroethene (Vinyl Chloride)	VOC	75-01-4	180000			7.8E-05
Chloroform	VOC	67-66-3	150		300	5.3E-06
Dibromoethane,1,2- (Ethylene Dibromide)	VOC	106-93-4			0.8	7.1E-05
Dichlorobenzene, p-	VOC	106-46-7			800	1.1E-05
Dichloroethane, 1,2- (Ethylene Dichloride)	VOC	107-06-2			400	2.1E-05
Ethylbenzene	VOC	100-41-4			2000	2.5E-06
Methyl tertiary-butyl ether (MTBE)	VOC	1634-04-4			8000	2.6E-07
Methylene Chloride (Dichloromethane)	VOC	75-09-2	14000		400	1.0E-06
Perchloroethylene (Tetrachloroethylene)	VOC	127-18-4	20000		35	5.9E-06
Styrene	VOC	100-42-5	21000		900	
Toluene	VOC	108-88-3	37000		300	
Trichloroethene	VOC	79-01-6			600	2.0E-06
Xylene, o-	VOC	95-47-6	22000		700	
Xylenes, (m+p)-	VOC	108-38-3/ 106-42-3	22000		700	
Diesel Particulate Matter			5			3.0E-4

Values for the above table are from the Consolidated Table of OEHHA/ARB Approved Risk Assessment Health Values available at http://www.arb.ca.gov/toxics/healthval/healthval.htm.

APPENDIX II

MATES IV

DRAFT REPORT

Technical Advisory Group Members

RETURN↑

Appendix II

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 REPORT

MATES IV Monitoring and Laboratory Analysis Protocol

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Solomon Teffera
Na Mon Trinh
Payam Pakbin

MATES IV

APPENDIX III

MONITORING AND LABORATORY ANALYSIS PROTOCOL

SEPTEMBER 2014

Science and Technology Advancement
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:

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

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

STATION #_______________________

LOCATION_______________________

SAMPLER #______________________

QUARTZ
FILTER #________________________

DATE____________________________

TIME

END________________________

START______________________

TOTAL______________________

REMOVED FROM SAMPLER_______

SENT TO HQ______________________

RECEIVED AMB__________________

LABORATORY USE ONLY

SAMPLE #__________________________

FLOWRATE, CFM___________________

VOLUME OF AIR, M^3________________

FINAL WEIGHT (gm)________________

TARE WEIGHT (gm)_________________

SAMPLE WEIGHT (gm)______________

PM_{10}($\mu g/M^3$)___________________

SAMPLE RECV'D___________________

SAMPLE WEIGHED_________________

SAMPLE EXTR.______________________

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						
16						
17						
18						
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21						
22						
23						
24						
25						
26						
27						
28						
29						
30						
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				

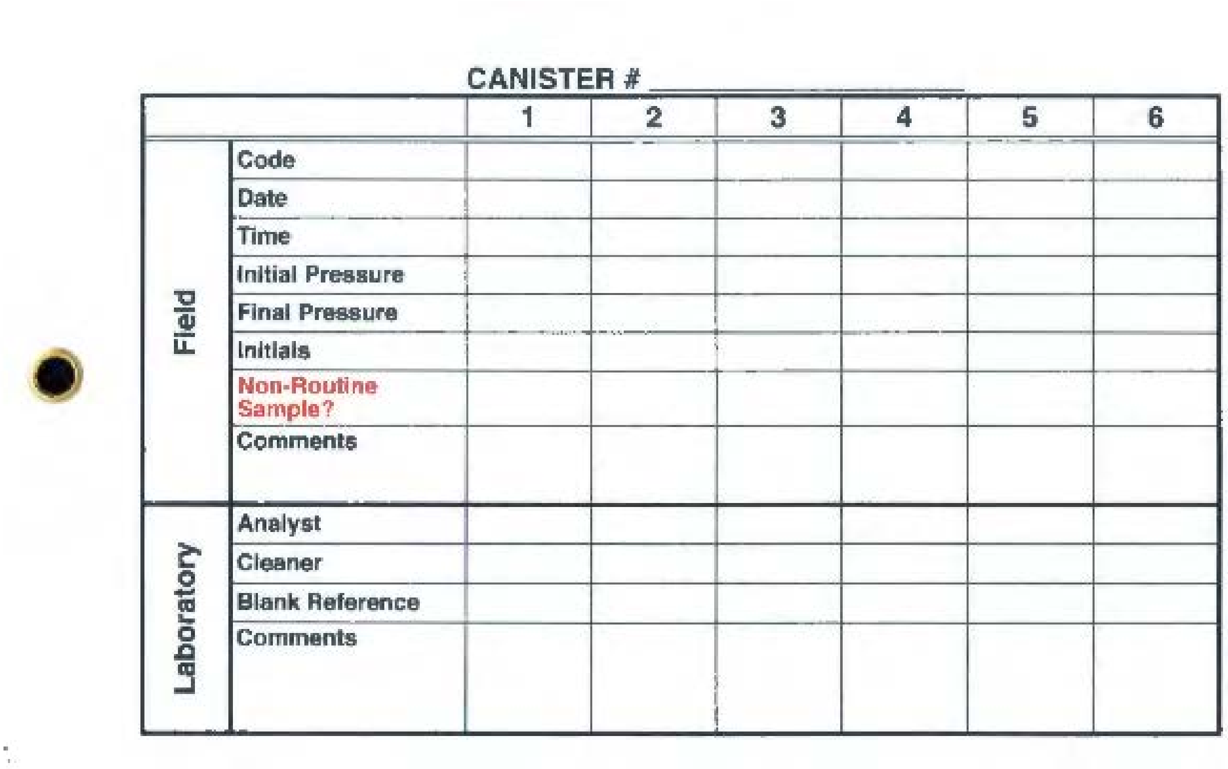
Filter Log – XonTech 924

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.

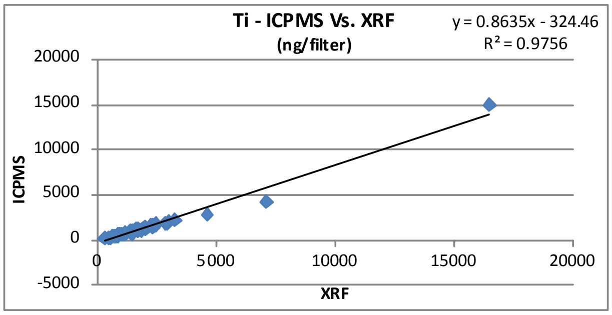
Method:

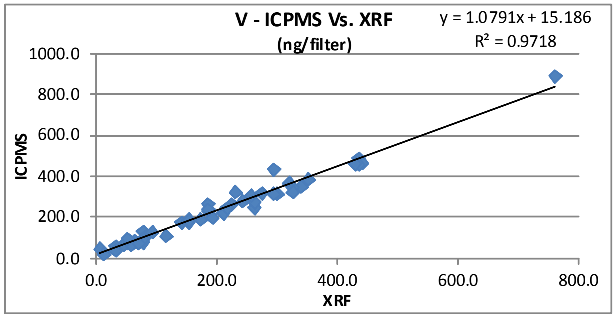
Comparison between the two methods was performed using 50 TSP filters from two sites from a previous project. These filters were run on the PANAlytical Epsilon 5 EDXRF analyzer in accordance with SCAQMD S.O.P. #0004. The same filters were then digested in nitric acid and analyzed by ICP/MS in accordance 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.

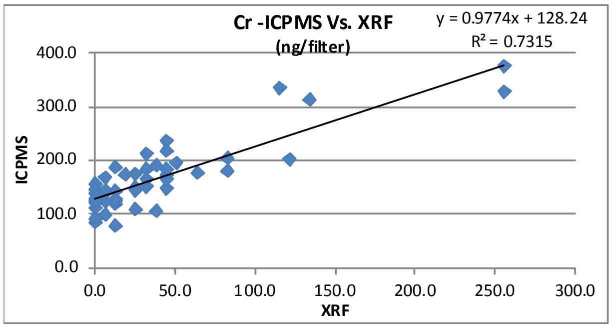
Results:

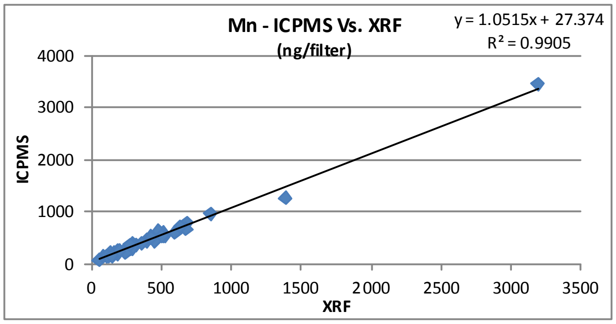
- Comparison for most metals was very good with slope in the range of 0.8 to 1.1.
- Metals such as Co, As, and Se did not fare well, primarily because the superior detection limit of ICP/MS over XRF. Almost all non-detect values by XRF were quantitatively reported by the ICP/MS. This was especially serious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

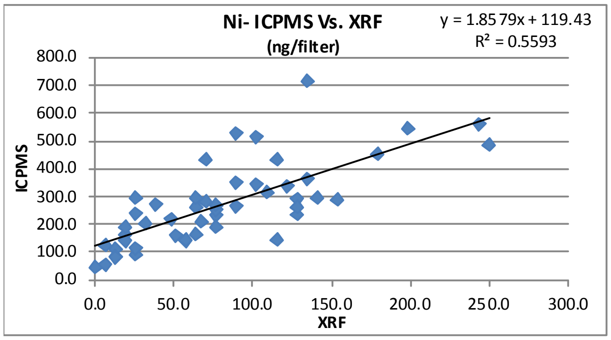
Nickel overestimation by ICP/MS was determined to be caused by the ubiquitous and proportionally very high concentration of Calcium and Sodium which form interfering molecular ions in the plasma. The subsequent correction for Ni by changing the isotope of acquisition to 58 Amu from 60 Amu is described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

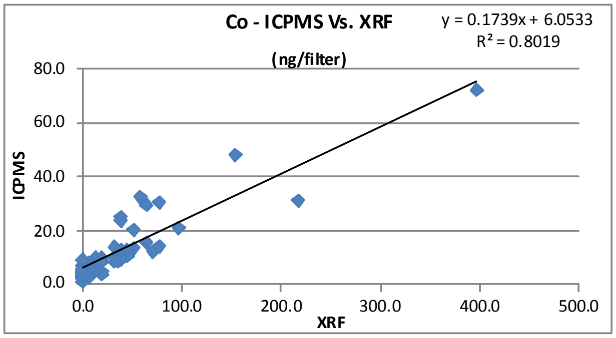

Ti - ICPMS Vs. XRF
(ng/filter)
y = 0.8635x - 324.46
R² = 0.9756
ICPMS
20000
15000
10000
5000
0
-5000
0
5000
10000
15000
20000
XRF

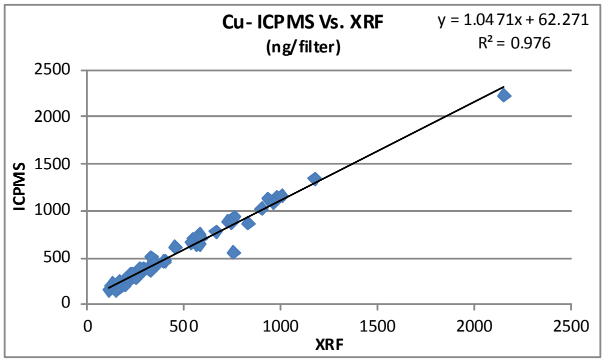

V - ICPMS Vs. XRF
(ng/filter)
y = 1.0791x + 15.186
R² = 0.9718
ICPMS
1000.0
800.0
600.0
400.0
200.0
0.0
0.0
200.0
400.0
600.0
800.0
XRF

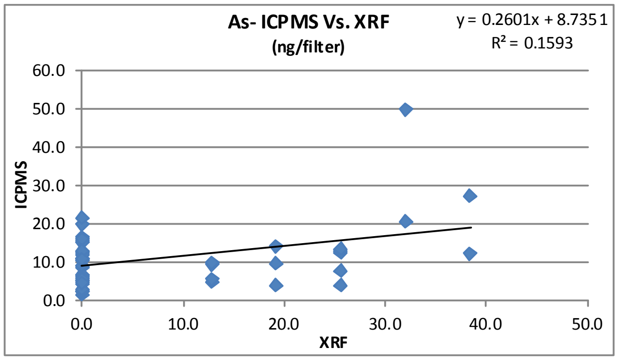

Cr -ICPMS Vs. XRF
(ng/filter)
y = 0.9774x + 128.24
R² = 0.7315
ICPMS
400.0
300.0
200.0
100.0
0.0
0.0
50.0
100.0
150.0
200.0
250.0
300.0
XRF

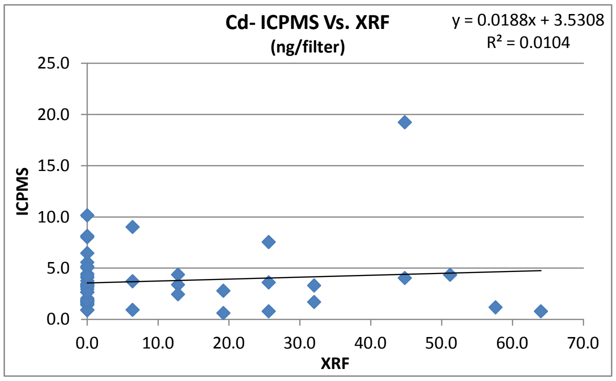

Mn - ICPMS Vs. XRF
(ng/filter)
y = 1.0515x + 27.374
R² = 0.9905
ICPMS
4000
3000
2000
1000
0
0
500
1000
1500
2000
2500
3000
3500
XRF

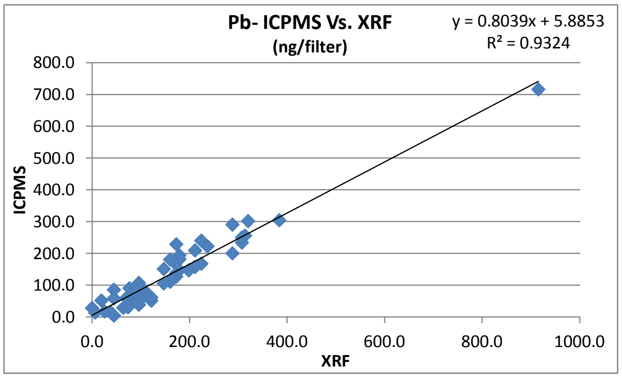

Ni- ICPMS Vs. XRF
(ng/filter)
y = 1.8579x + 119.43
R² = 0.5593
ICPMS
800.0
700.0
600.0
500.0
400.0
300.0
200.0
100.0
0.0
0.0
50.0
100.0
150.0
200.0
250.0
300.0
XRF

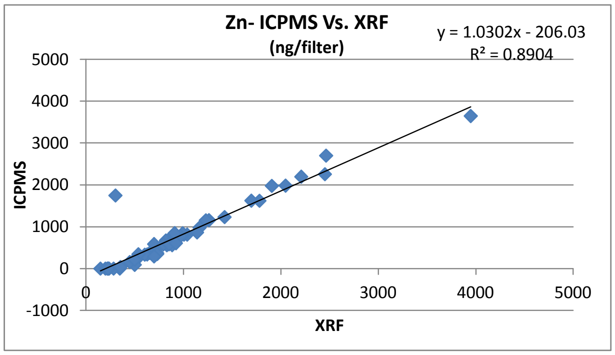

Co - ICPMS Vs. XRF
(ng/filter)
y = 0.1739x + 6.0533
R² = 0.8019
ICPMS
80.0
60.0
40.0
20.0
0.0
0.0
100.0
200.0
300.0
400.0
500.0
XRF


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


As- ICPMS Vs. XRF
(ng/filter)
y = 0.2601x + 8.7351
R² = 0.1593
ICPMS
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
XRF


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 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

Pollutant	Statistic	Measurement Site 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

Pollutant	Statistic	Measurement Site									
		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 REPORT

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

Author

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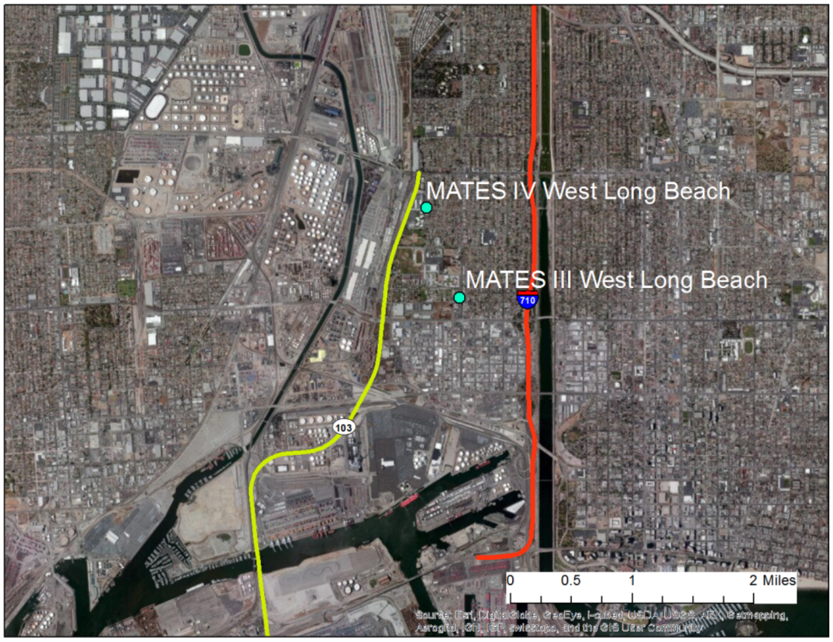
Appendix V. Comparison between the West Long Beach Sites in MATES III and MATES IV

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 samplings are coincident 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, and their respective 95% Confidence Interval 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

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.

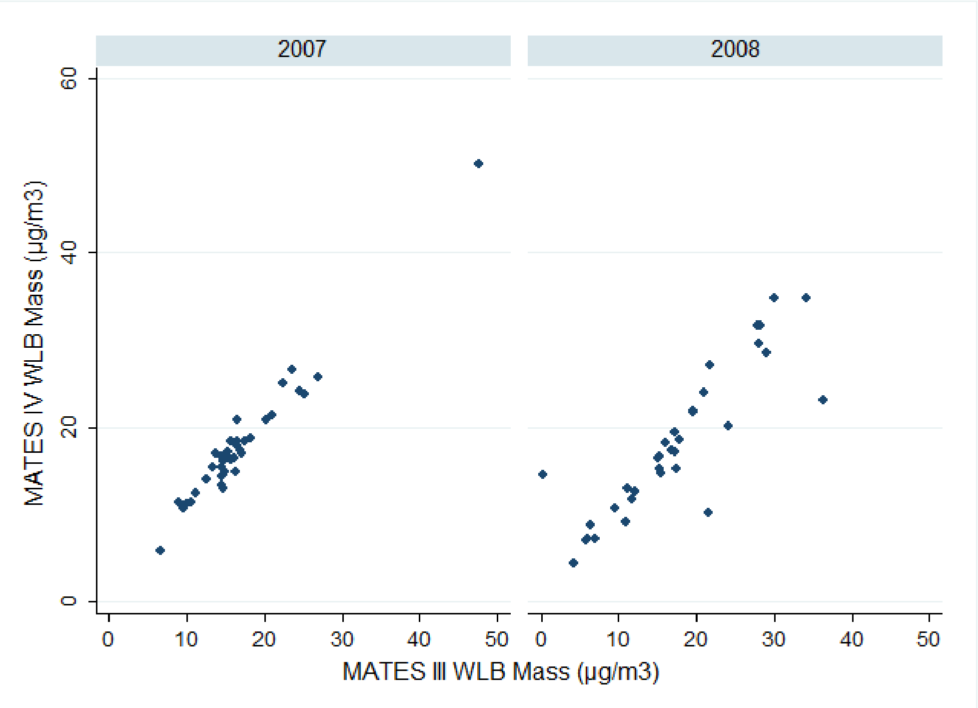


Figure V-2. Scatterplot of $PM_{2.5}$ Mass Concentration between the MATES III and MATES IV West Long Beach Sites.

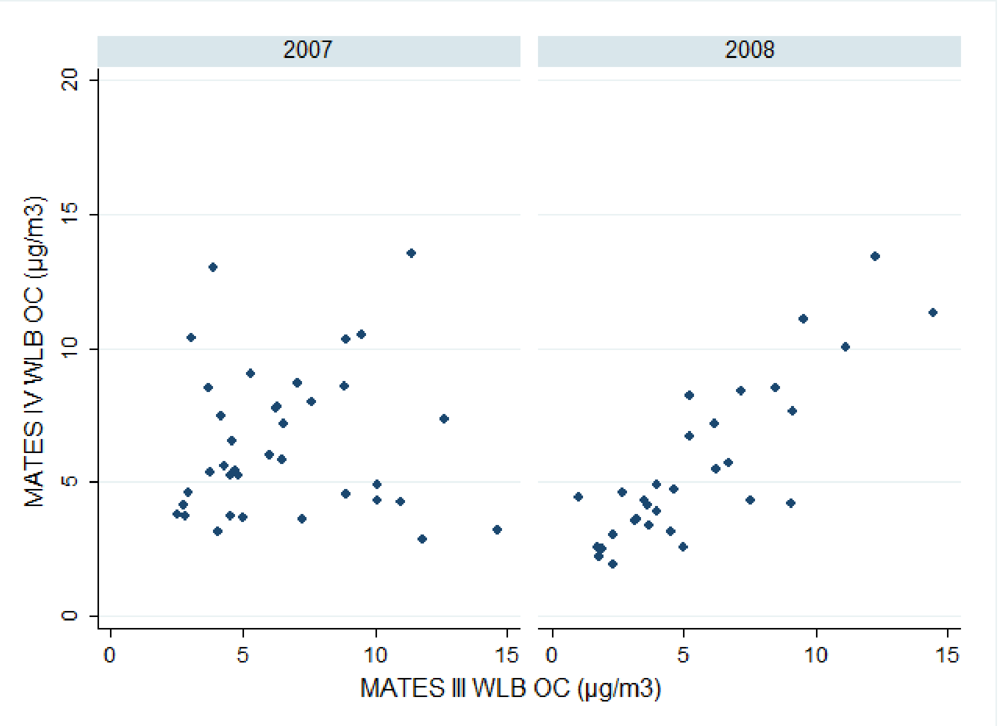


Figure V-3. Scatterplot of $PM_{2.5}$ OC Concentration between the MATES III and MATES IV West Long Beach Sites.

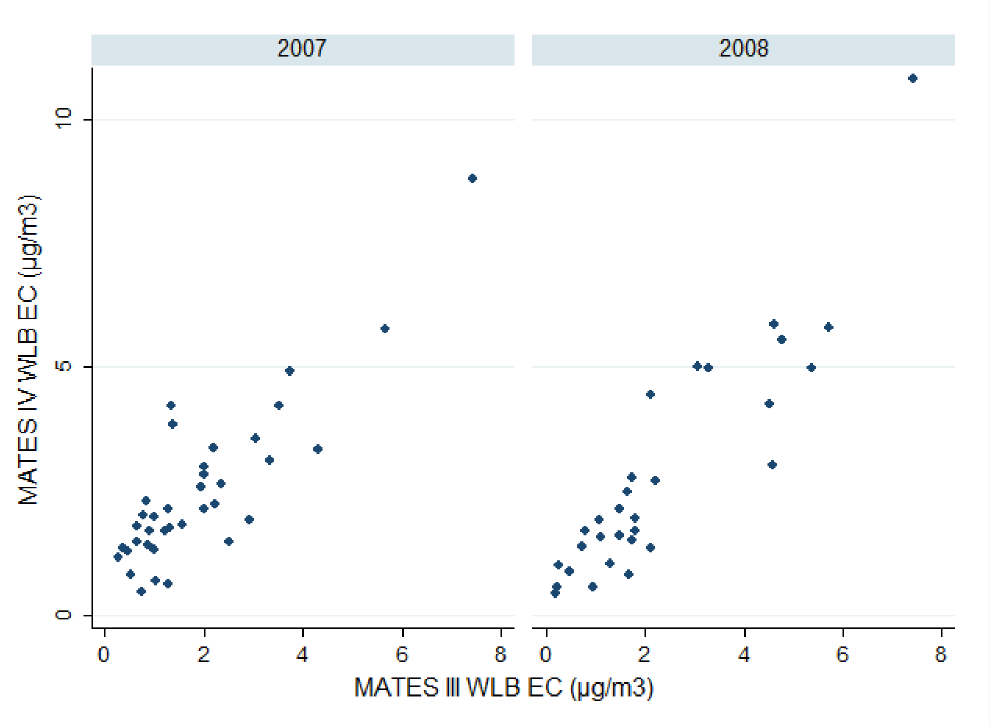


Figure V-4. Scatterplot of $PM_{2.5}$ EC Concentration between the MATES III and MATES IV West Long Beach Sites.

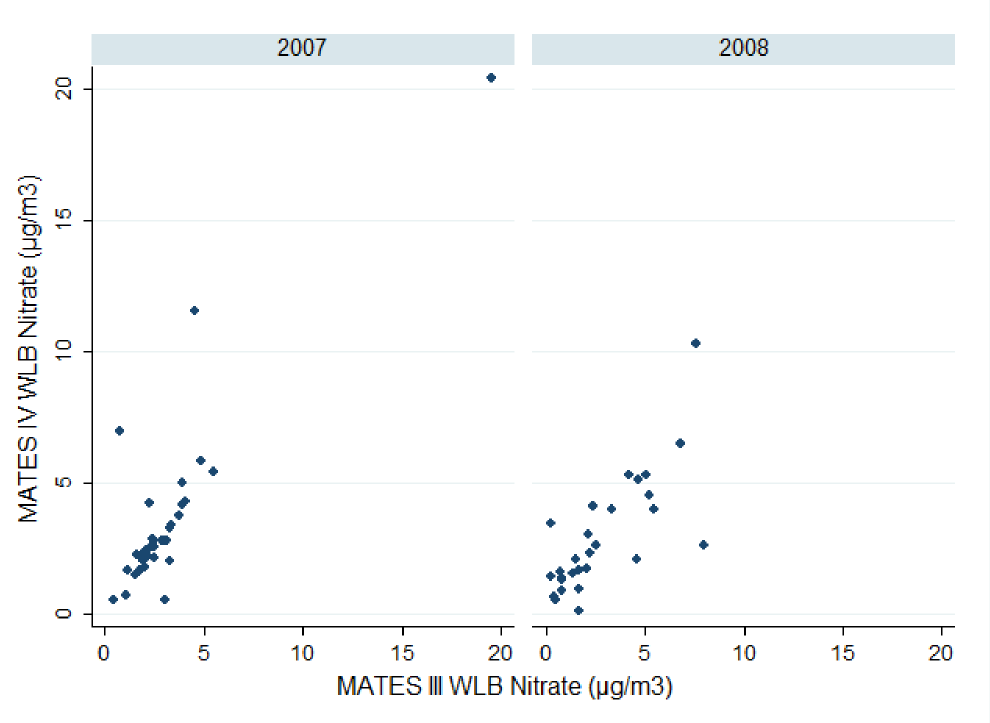


Figure V-5. Scatterplot of Nitrate Concentration between the MATES III and MATES IV West Long Beach Sites.

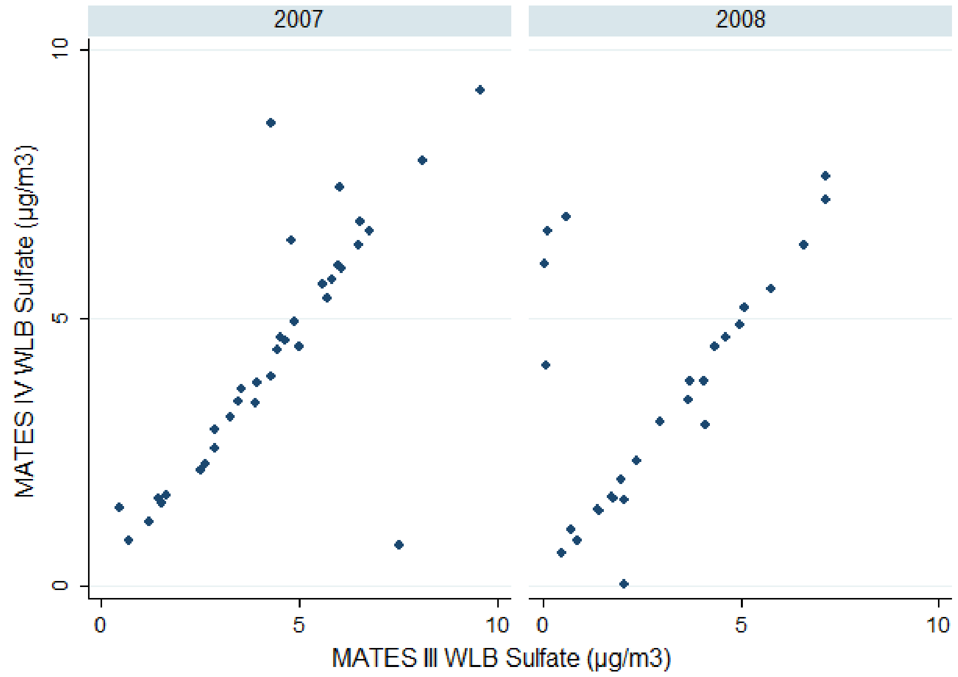


Figure V-6. Scatterplot of Sulfate Concentration between the MATES III and MATES IV West Long Beach Sites.

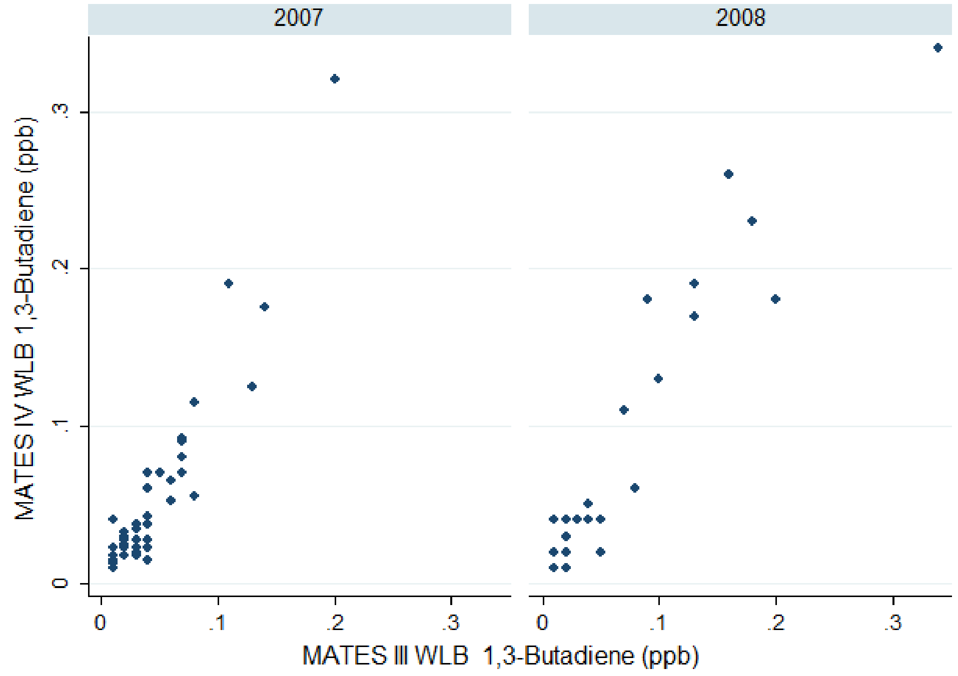


Figure V-7. Scatterplot of 1,3-Butadiene Concentration between the MATES III and MATES IV West Long Beach Sites.

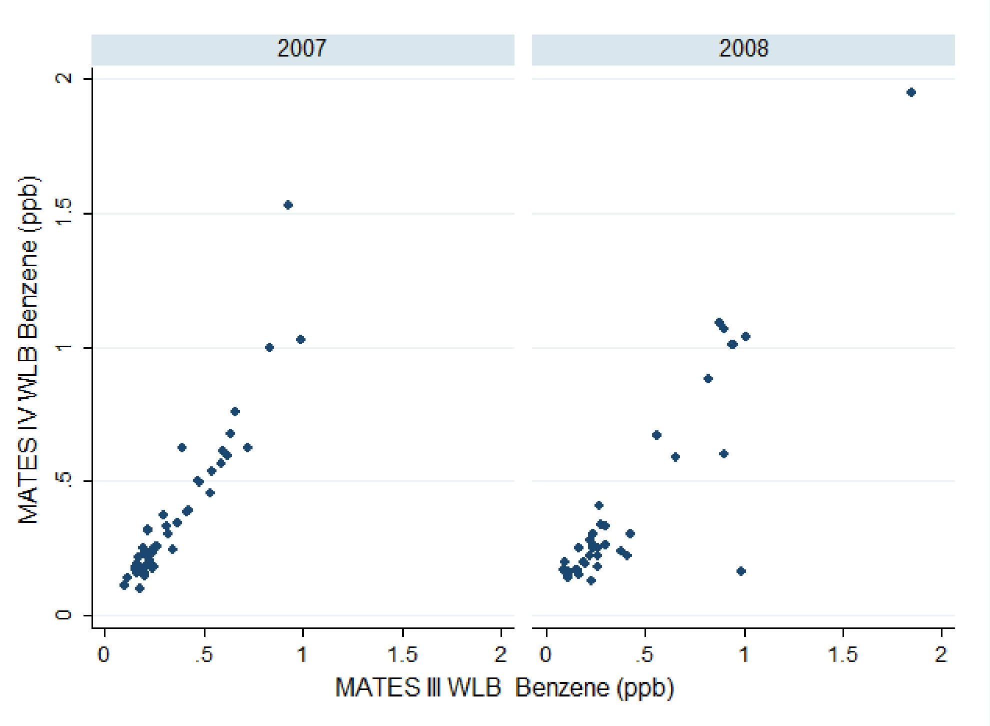


Figure V-8. Scatterplot of Benzene Concentration between the MATES III and MATES IV West Long Beach Sites.

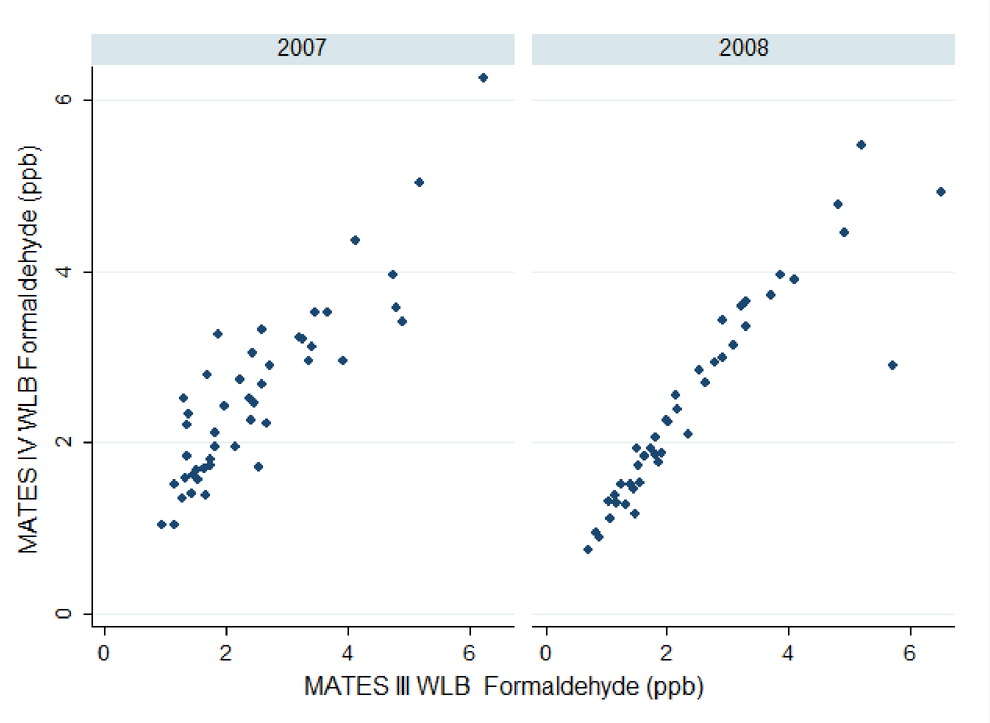


Figure V-9. Scatterplot of Formaldehyde Concentration between the MATES III and MATES IV West Long Beach Sites.

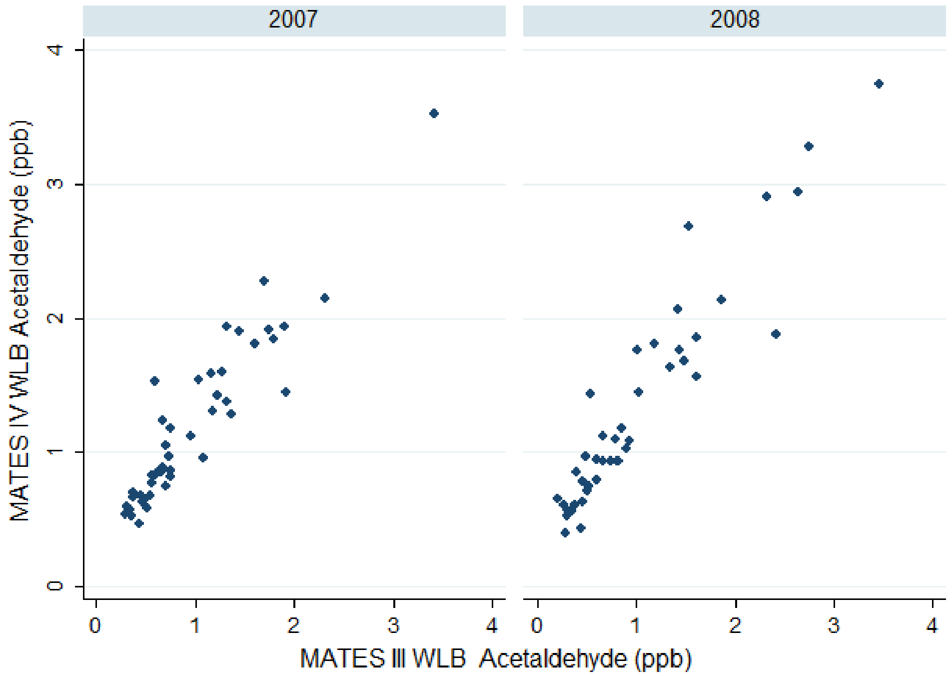


Figure V-10. Scatterplot of Acetaldehyde Concentration between the MATES III and MATES IV West Long Beach Sites.

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). DPM is comprised of gaseous and particle phases. The gaseous phase contains typical combustion products which include carbon dioxide, nitrogen oxides, carbonyl compounds, and volatile and semi-volatile hydrocarbons (Kirchstetter, 1999; Shah, 2005). Diesel particulate emissions are primarily in the $PM_{2.5}$ size range and is 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 levels 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 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. 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 diesel emissions often results 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 promote 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 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 means of different methodologies. When its light-absorbing properties are measured, soot is referred to as BC. When its concentration is measured by thermal-optical techniques however, it is 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), in contrast to measuring EC by a time−

consuming analytical method where soot is sampled on a filter and then analyzed. These methods do not necessarily yield directly comparable results (Chow, 2001).

The measurement of optically-absorbing material is performed by Aethalometers. This optical method, measures the attenuation of a beam of light transmitted through the sample collected on a quartz fiber filter, while the filter is continuously collecting an aerosol sample. The measured attenuation is linearly 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 BC content of the aerosol deposit can be determined at each measurement time.

In thermal analysis used to measure EC, 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. Therefore they 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 basis to assess 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), as well as evidence that many different constituents of the particle mixture (for example groups of constituents associated with specific source categories) are linked to adverse health effects. Consequently, research and data collection activities focused on particle composition could improve our understanding of the relative toxicity of different particle constituents or groups of constituents associated with specific sources of particles to inform future regulatory activities and benefits assessments. Developing additional air quality standards to address the effects of road vehicle PM emissions that are not well captured by $PM_{2.5}$ mass appears to be advantageous.

BC is a component of both fine and coarse PM ($PM_{2.5}$ and PM_{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 or are coated with BC. Fine particles, on the other hand, are known to primarily originate from combustion activities and from gas-to-particle conversion processes in the atmosphere. BC is known to be one of the most important contributors to the $PM_{2.5}$ total mass. Generally combustion-related particles are widely thought to be 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 $PM_{2.5}$ 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 mass concentration standards.

There are not enough clinical or toxicological studies to allow for an accurate evaluation of the qualitative 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 may not be a major toxic component of $PM_{2.5}$, but it may operate as a universal 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 the systemic blood circulation. 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 as 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). However, BC influences climate through multiple mechanisms, directly and indirectly. There is a general consensus within the scientific community that BC is contributing to climate change globally and regionally. Direct radiative forcing of 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 traps outgoing infrared radiation from the Earth surface) which in turn heats the atmosphere where the BC is present and reduces the sunlight that reaches the surface.

BC also deposits on snow and ice significantly reducing the total surface *albedo* available to reflect solar energy back into space, thereby increasing absorption and accelerating ice melting.

Furthermore, BC can affect the climate indirectly, like other atmospheric particles, by altering clouds formation, distribution, reflectivity and lifetime. BC influences the properties of clouds though diverse and complex processes, including changing the number of liquid cloud droplets, 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 distinguished differences between BC and other GHGs is due to the relatively short atmospheric lifetime of BC (days / weeks as opposed to years / 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 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. Sampling was conducted for a year period from July 2012 to July 2013. Details of the sites, their characteristics and sampling protocols are given in MATES IV Chapter 2.

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 deposition on 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 principle and working 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. In recent years, two wavelengths (880 nm and 370 nm) or seven wavelengths (370 nm, 470 nm, 520 nm, 590 nm, 660 nm, 880 nm, and 950 nm) Aethalometers have become widely used to measure ambient BC concentrations. These instruments offer the opportunity to measure light absorption across a wider selection of near UV to near IR wavelengths, and this ability has been exploited to estimate the concentrations of other atmospheric aerosol components including wood smoke. Numerous studies have suggested that certain organic aerosol components of wood burning particles have enhanced optical absorption at 370 nm relative to 880 nm. Therefore, the difference between the two, defined as Delta-C, has been suggested as a qualitative indicator of wood burning particles (Allen et al., 2004).

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. The 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, inherited by 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 sampling artifacts 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.

The EC concentrations are 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 Optical

Transmittance (TOT) charring corrections are not necessarily equivalent due to charring of organic vapors adsorbed within the quartz fiber filter (Chow et al., 2004; Chen et al., 2004). AQMD reports both OC and EC as determined by both methods to the EPA and AQMD staff. 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.

VI.2.4 General Principles

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 database 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).

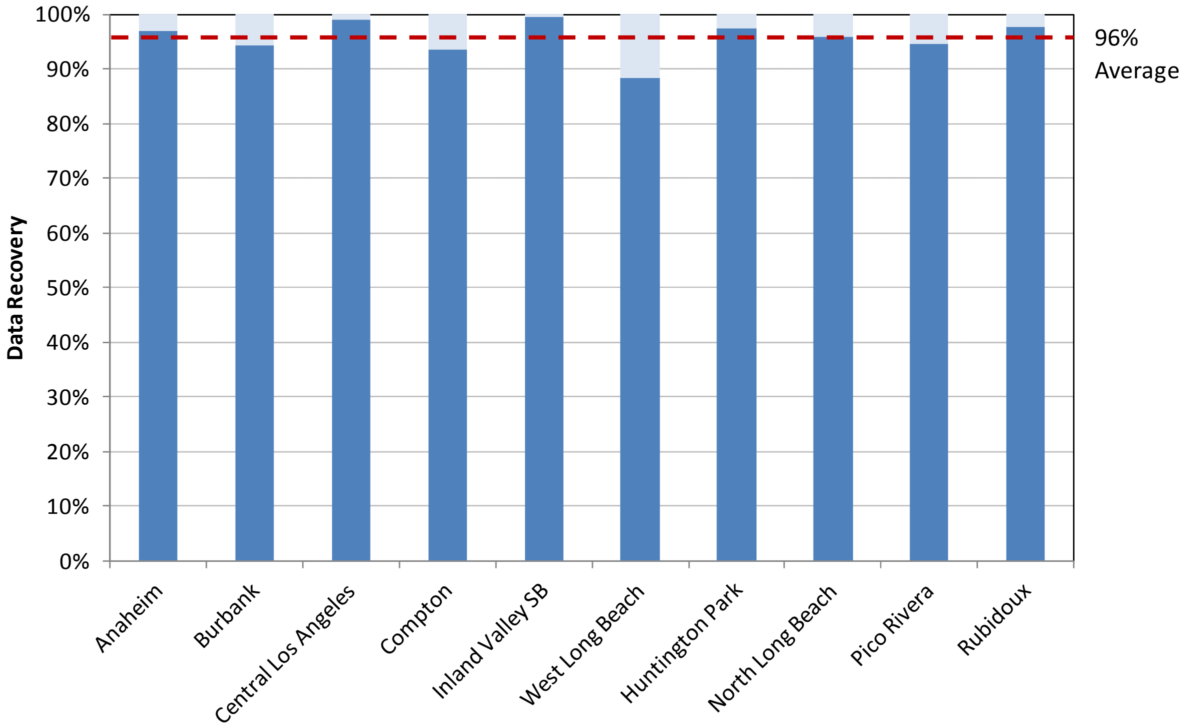


Figure 1 - Black Carbon Data Completeness at each of the MATES IV sites.

VI.3 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.3.1 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.

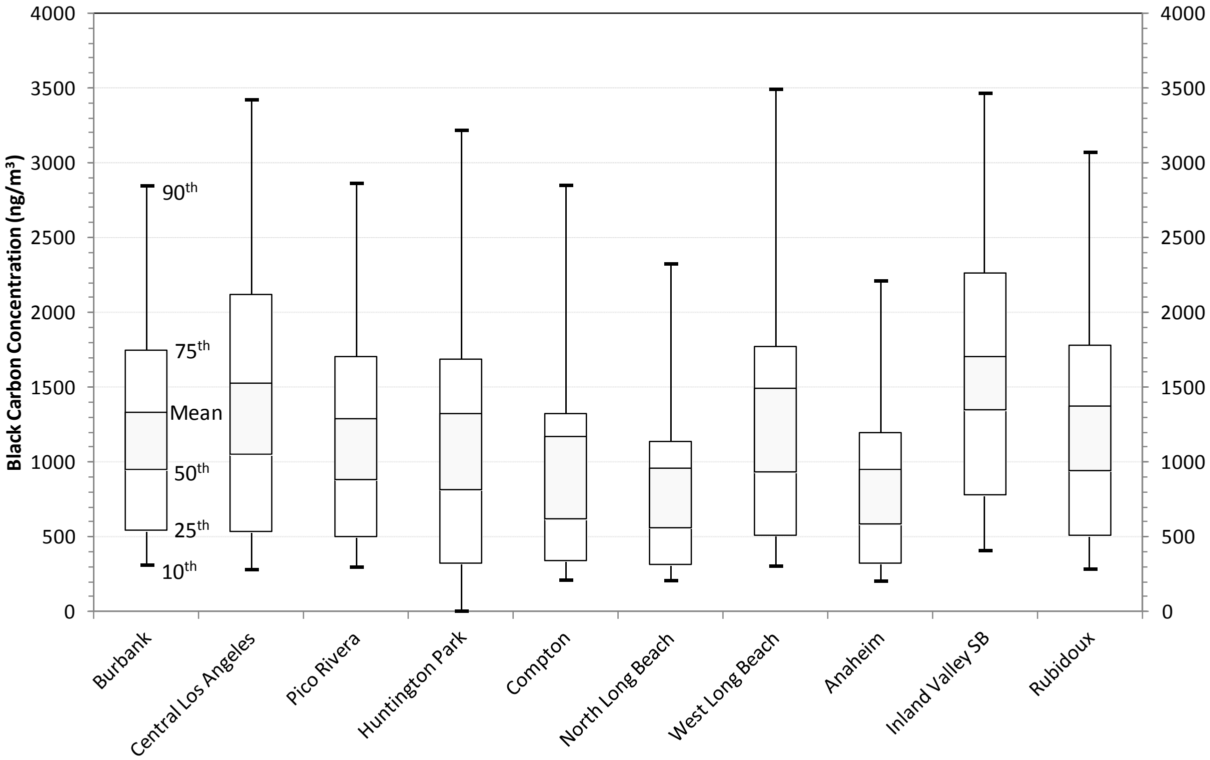


Figure 2 - Spatial Distribution of Black Carbon Concentrations Across All MATES IV Sites.

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 adjacent to major freeways (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 Inland Valley San Bernardino (probably due to activities at the San Bernardino Railyard and the movement of goods at from the port 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).

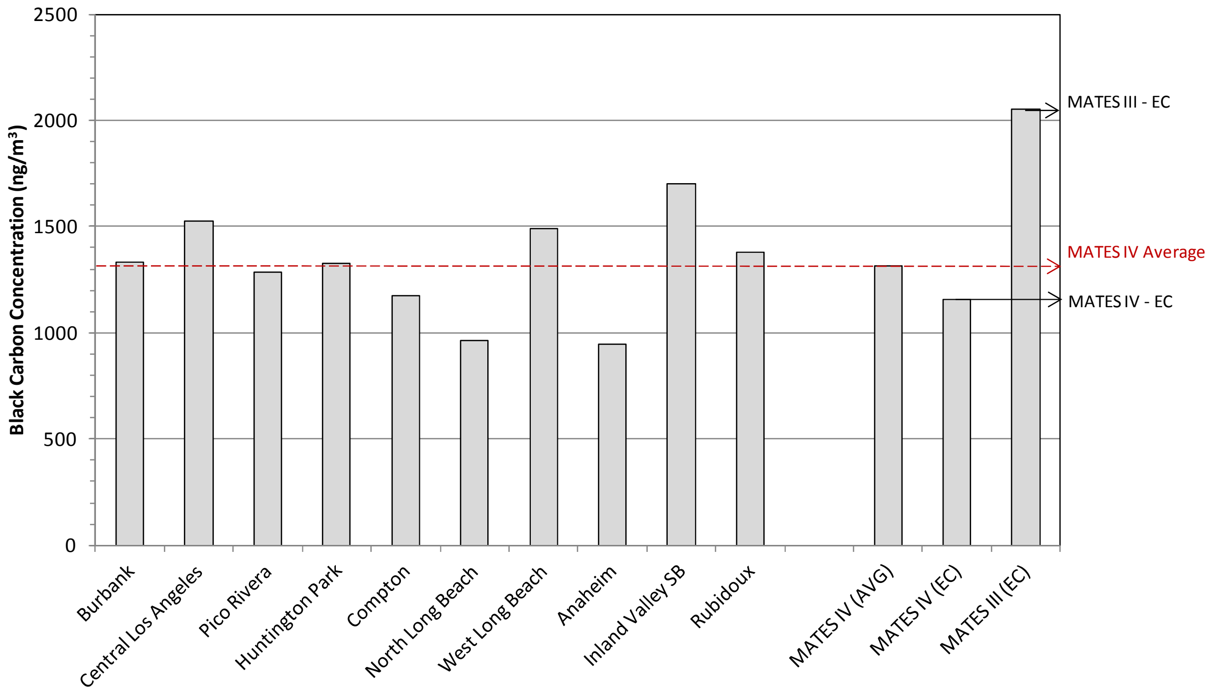


Figure 3 - Distribution of average Black Carbon concentrations during MATES IV and comparison with MATES IV and MATES III Elemental Carbon study averages.

VI.3.2 Temporal Variations

BC exhibits considerable daily, monthly, 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 daily BC concentrations at each site for the entire sampling period. A general seasonal trend can be discerned from this plot, with elevated BC concentrations observed during the colder months. To better characterize this trend, monthly average BC concentrations were calculated based on the high time resolution BC measurements (Figure 5).

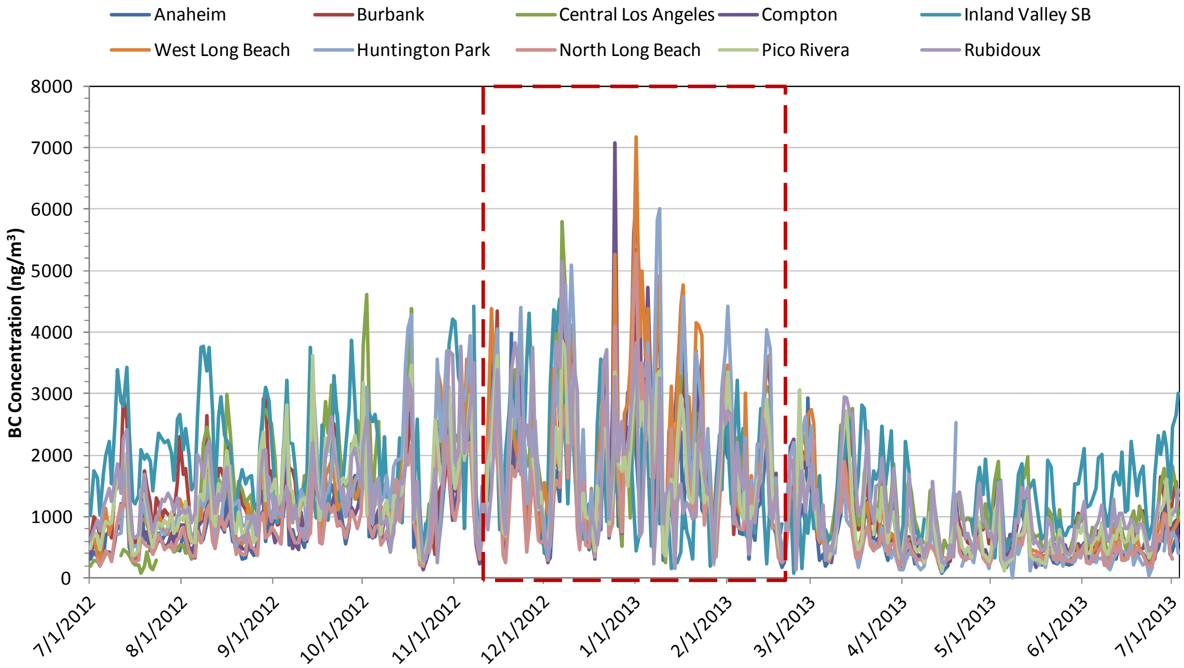


Figure 4 - Daily Black Carbon Concentration Trends at Each MATES IV Site. Red Rectangle Representing Elevated Levels in Colder Months.

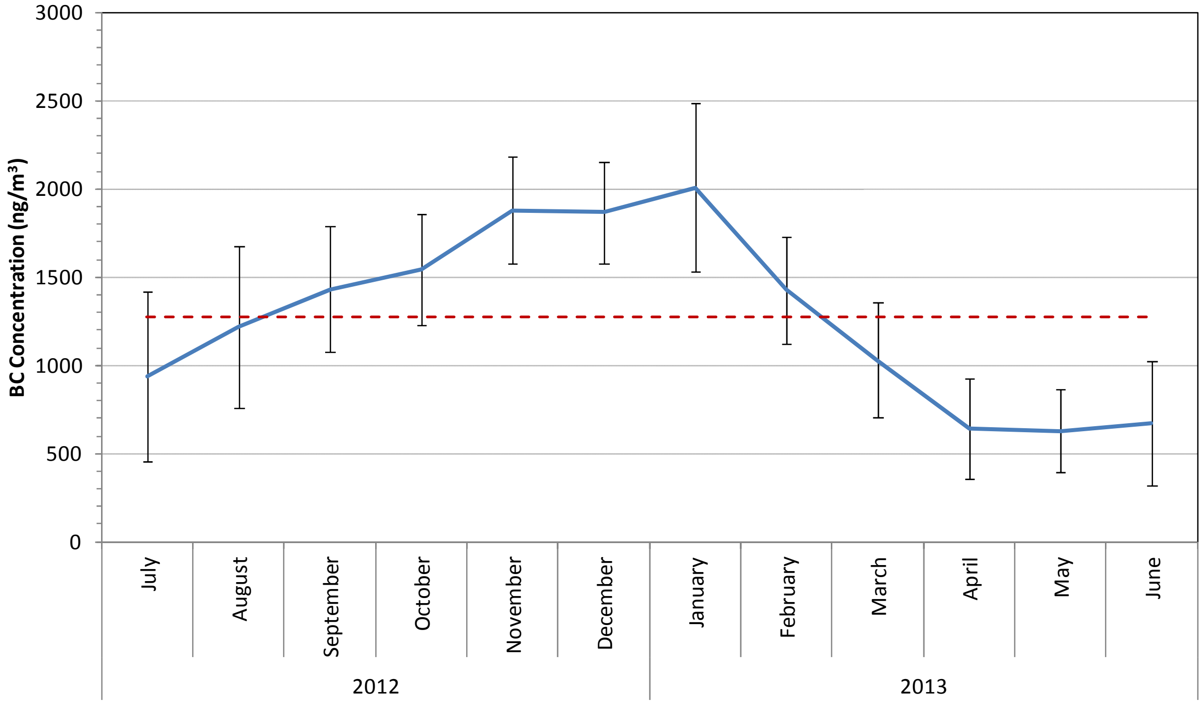


Figure 5 - Monthly Average Black Carbon Concentration Trends in the South Coast Basin During MATES IV. Red Line Indicating the MATES IV Average Concentration.

As mentioned earlier, 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). 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 usage of wood burning for space heating. In the meantime, the winter months are characterized by lower mixing height which, in turn, contributes to increase the atmospheric concentrations of several atmospheric pollutants, including BC.

These seasonal trends are further highlighted in Figure 6, 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).

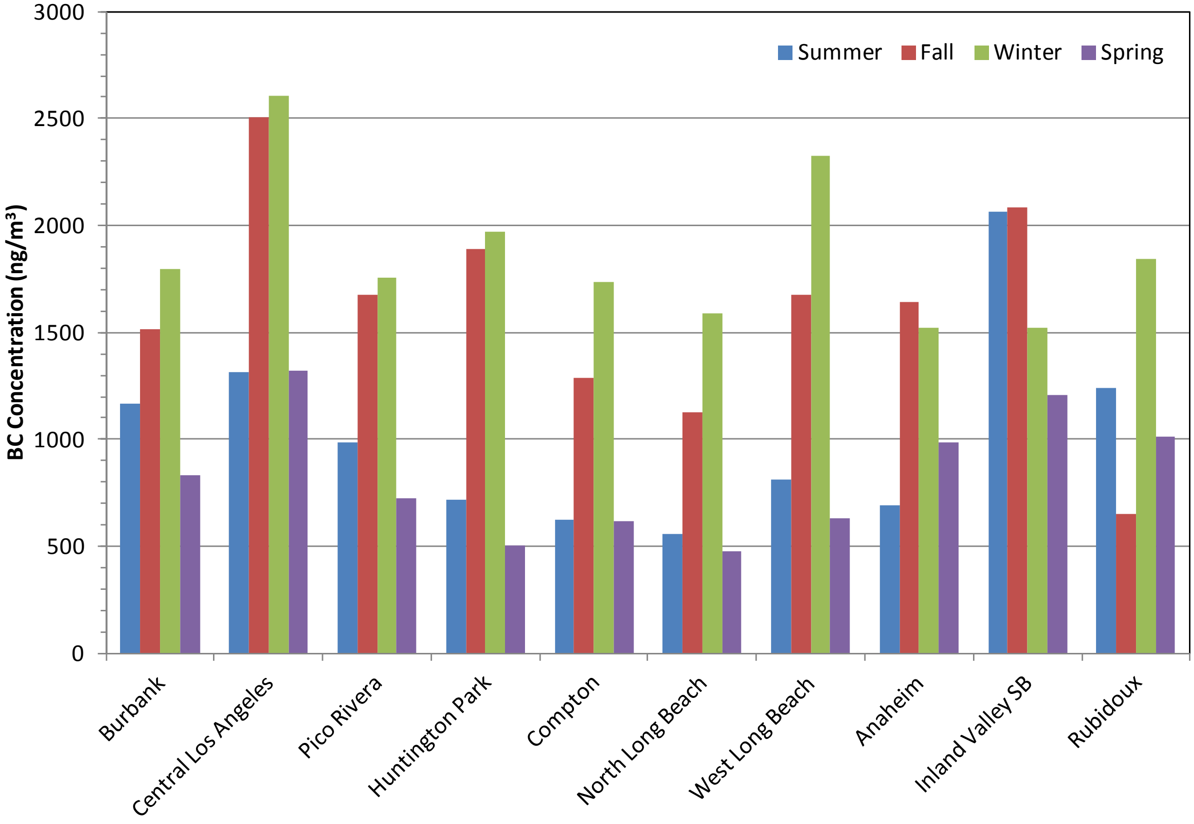


Figure 6 - Seasonal Variations of Black Carbon Concentrations at Each MATES IV Site.

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 7). This different seasonal trend may be due to potential sources of BC other than motor-vehicle emissions at this site (e.g. San Bernardino Railyard).

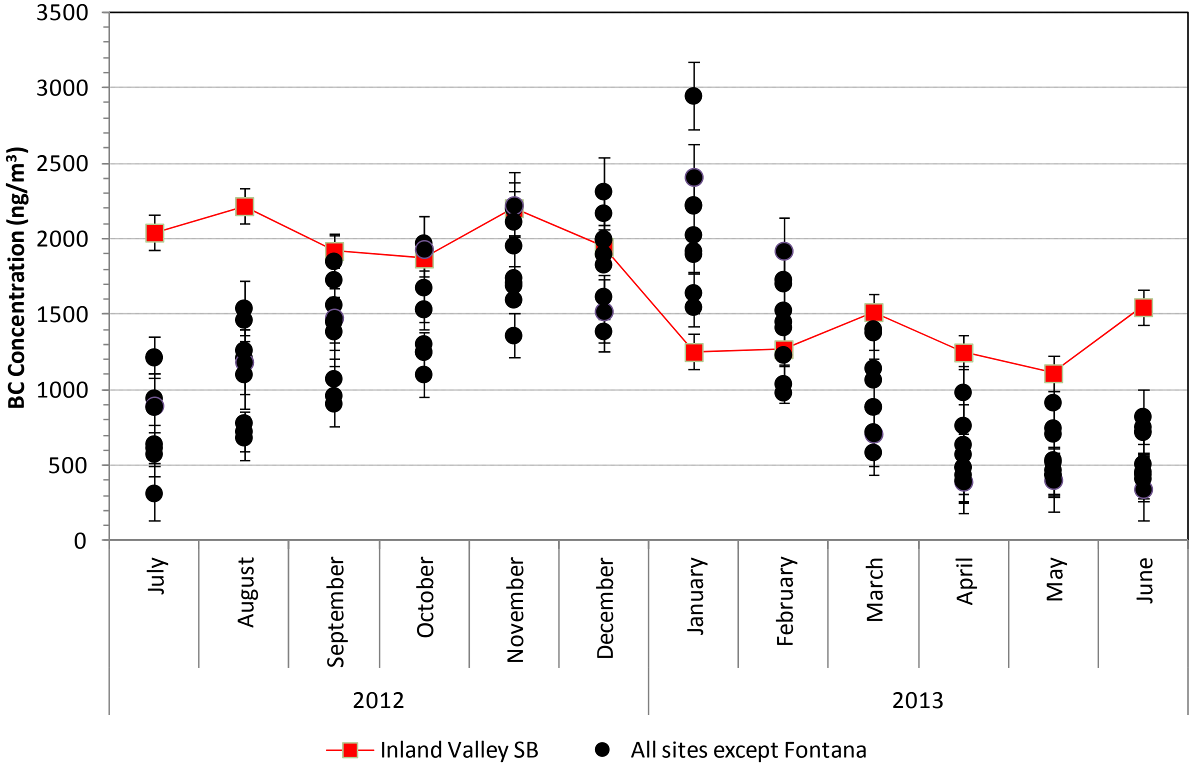
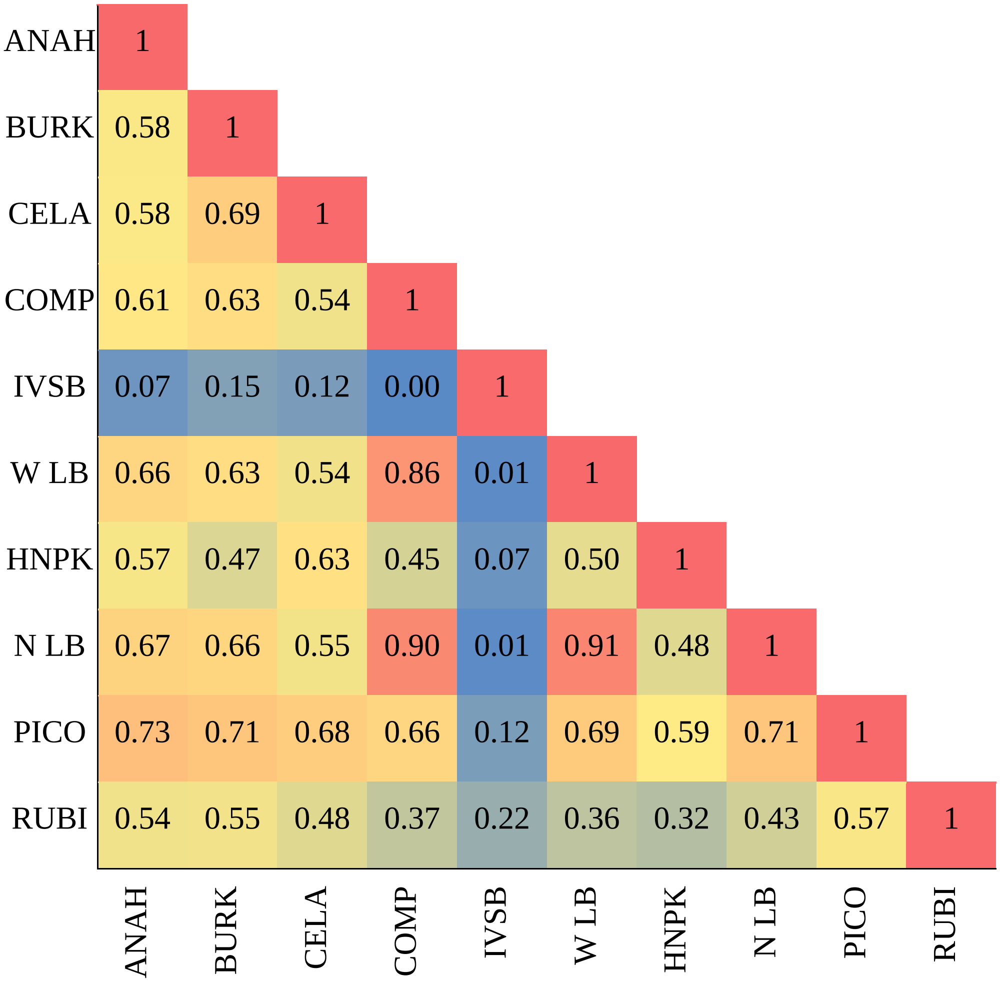


Figure 7 - Inland Valley San Bernardino Exhibits a Different Temporal Variation Compared to All Other MATES IV Sites.

In order to assess the temporal associations between each site pair, a linear regression analysis was performed. Figure 8 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 8 - 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 near the port area (i.e. Hudson, Compton and Long Beach sites) with r^2 values higher than 0.80. The relatively high r^2 values between the inland sites (i.e. Anaheim, Burbank and Pico Rivera) and between the near the port area (i.e. Hudson, Compton and Long Beach sites) suggest that the source of BC at these sites are similar (e.g. port traffic) 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.3.2.1 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 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 9. The distinct increase in BC mass concentration between 0600 and 0900 PST is probably associated with rush-hour traffic.

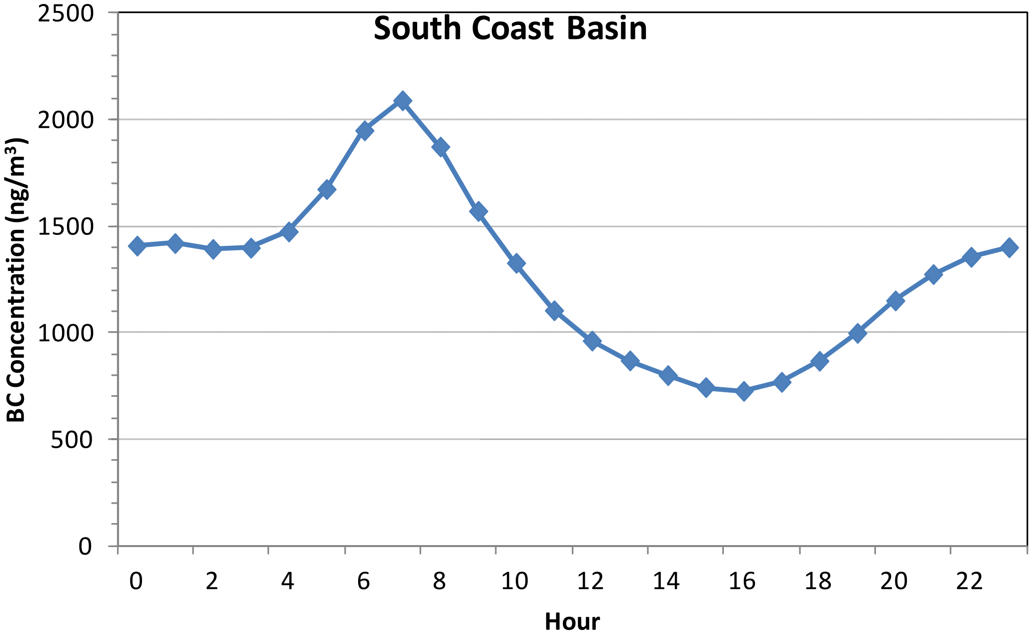


Figure 9 - Diurnal Variation of Black Carbon Concentration in South Coast Air Basin During MATES IV.

As the day progresses, the increased solar heating leads to faster dispersion of aerosols due to increased turbulent effects and deeper boundary layer. The faster dispersion of aerosols causes a dilution of BC near the surface resulting in a gradual decrease in BC concentrations in the afternoon. 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 more scattered evening rush hour traffic. In addition, lower wind speeds during night and shallow inversion layer leads to a rapid decline in the ventilation effects. Overnight, there is a progressive and strong reduction in the traffic density and BC generation, leading to stable conditions until the early morning.

VI.3.2.2 Seasonal Variations of BC Diurnal Trends

In order to examine the seasonal changes on the BC diurnal variations, the BC concentrations are 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 10(a – j).

In general, there is a distinct seasonal dependence on the diurnal variations of BC (Figure 10).

With 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.

It is important to note that it can also be expected that, during the winter months, there can be additional BC emissions due to usage of space heating, particularly during night-time when the temperatures drop, which would contribute to the observed secondary, evening peak in winter.

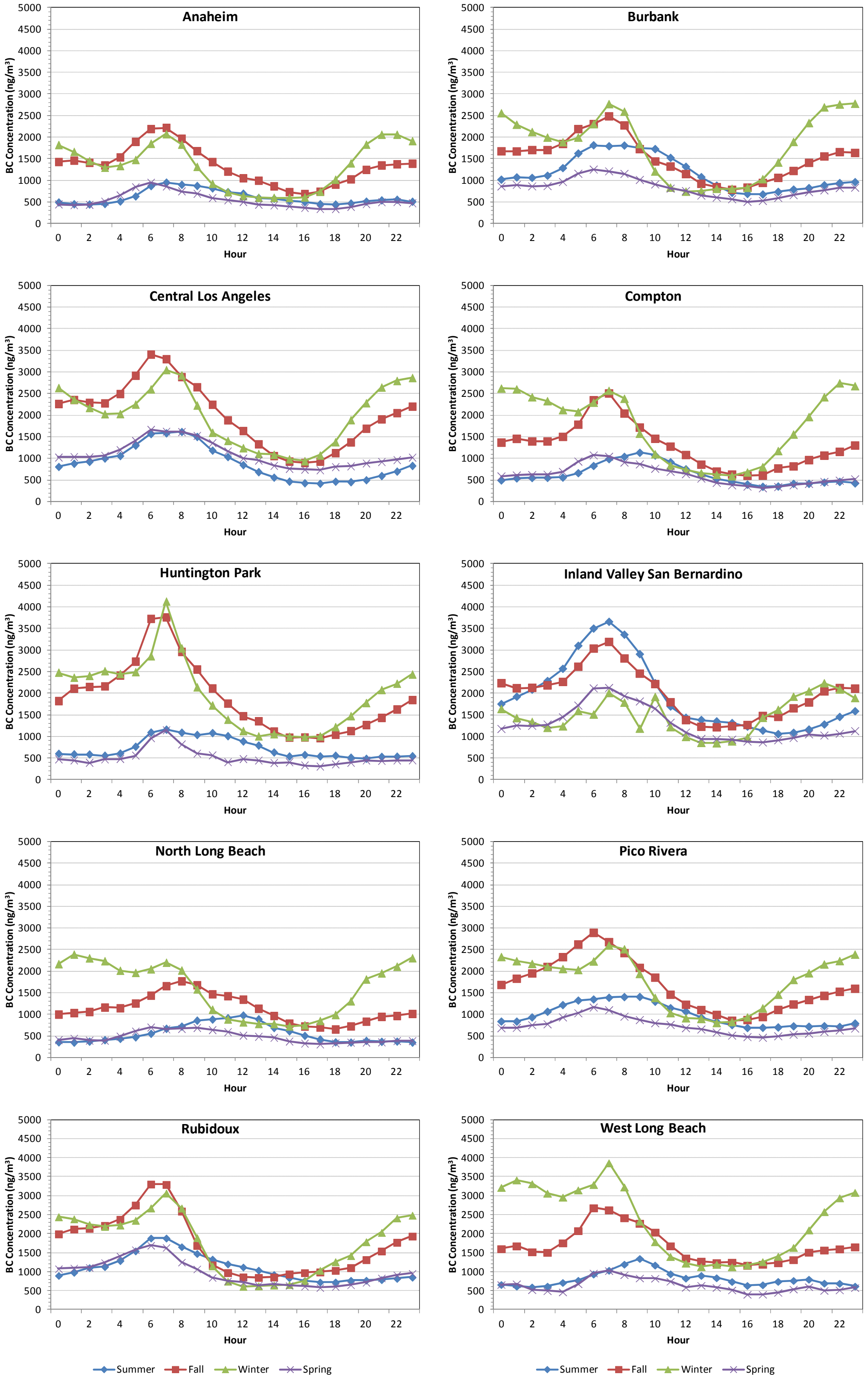


Figure 10 - Seasonal Diurnal Trends of Black Carbon Concentrations at Each Site.

VI.3.2.3 Weekday/Weekend Effect

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 11, where for each season the BC concentration measured during weekdays is typically higher than that on Saturdays and Sundays.

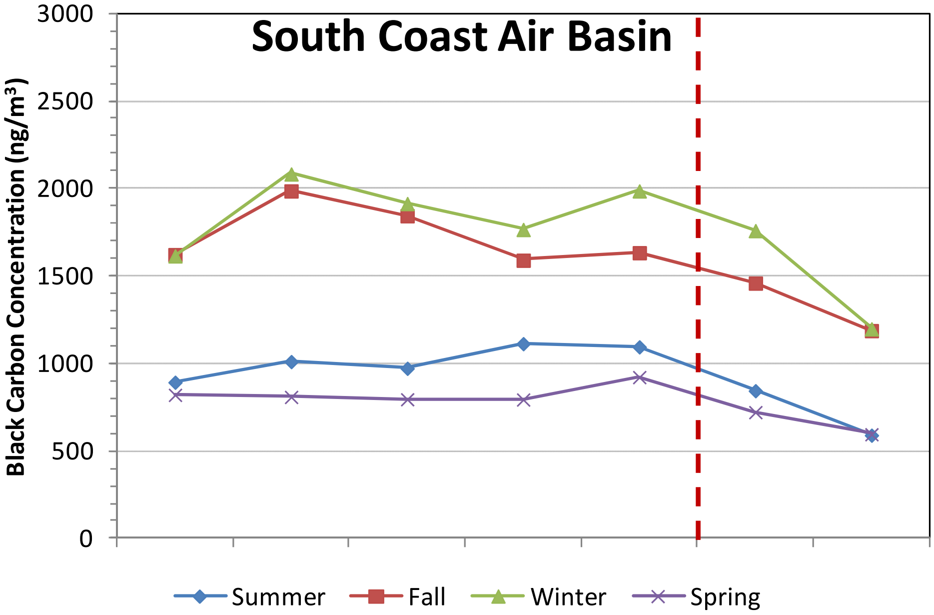


Figure 11 - Seasonal Weekday/Weekend Comparison in the South Coast Air Basin During MATES IV.

VI.3.3 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 from the FRM and HiVol samplers were analyzed for OC and EC.

As shown in Figure 12, a comparison between the 24-hr. average BC concentrations and the corresponding EC levels for all MATES IV sites shows a good correlation ($r^2 = 0.81$).

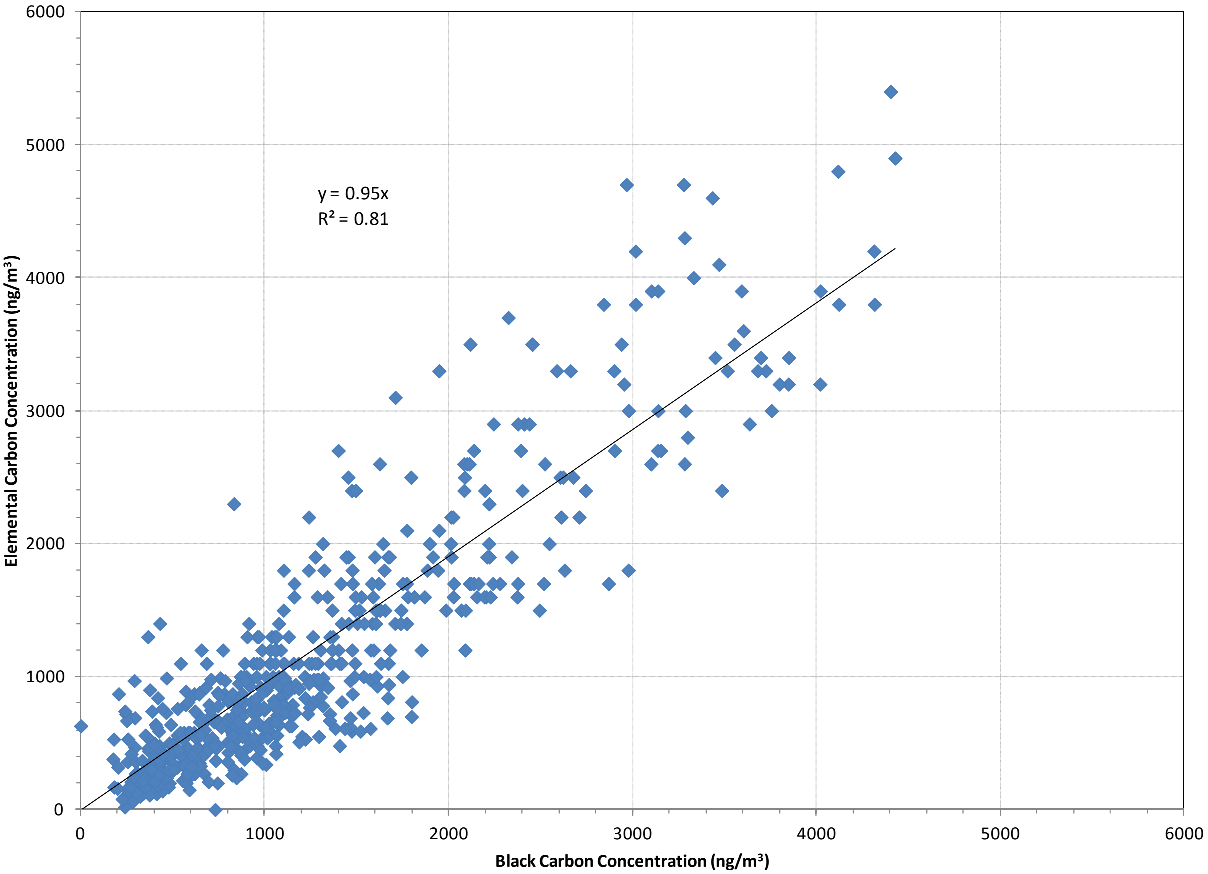


Figure 12 - Comparison of Daily Average BC and EC Concentrations in South Coast Air Basin During MATES IV.

The relationship between BC and EC measurements has been the subject of extensive research. Such comparison usually indicates a satisfactory correlation coefficient but various degrees of slope variations. This is probably related to the choice of the coefficients used to convert absorption measurements to BC estimates or to assumptions inherited to the thermal-optical methods used to measure EC. Figures 13 and 14 show the regression analysis between BC and EC measurements at each site (all sites combined and individually). 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 1. 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 conversion is 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 MATES IV study an intensive co-located study was designed and conducted by I710 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 report.

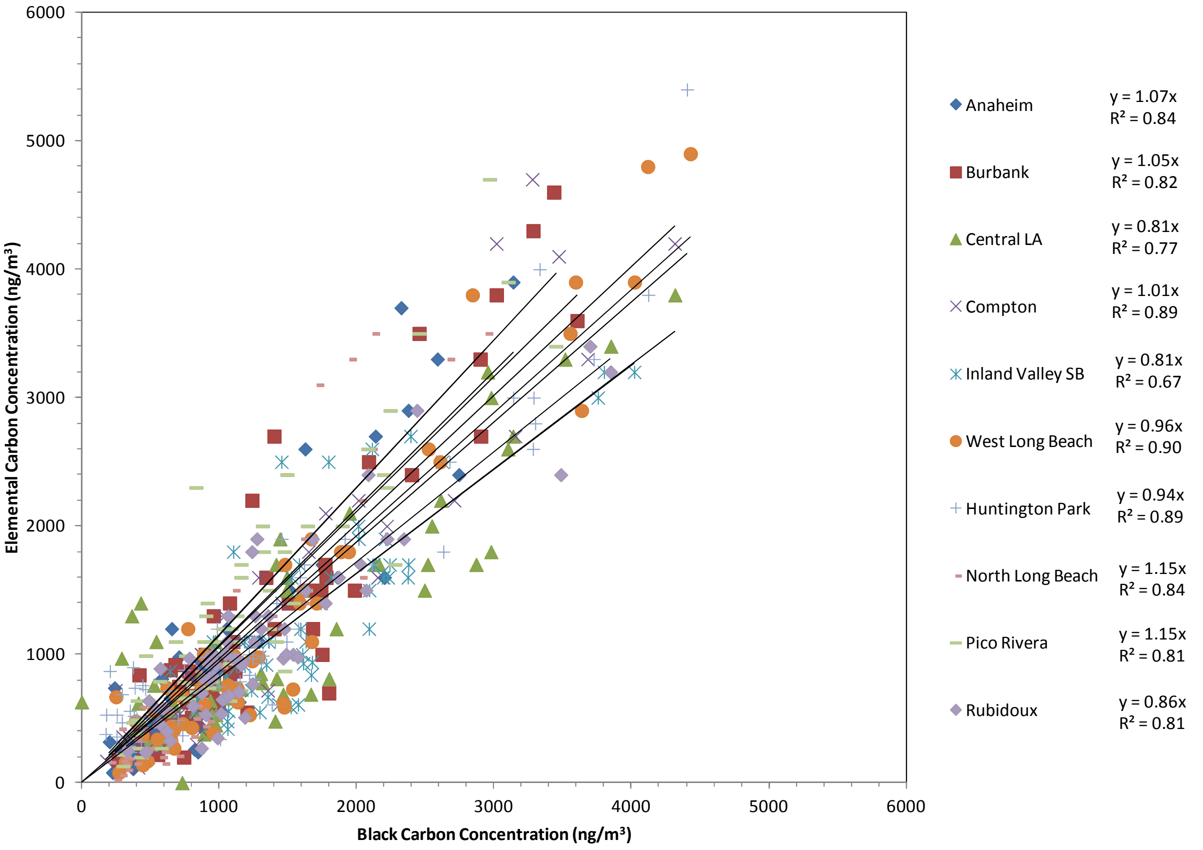


Figure 13 - Comparison of Daily Average BC and EC Concentration at Each MATES IV Site (All Sites Combined).

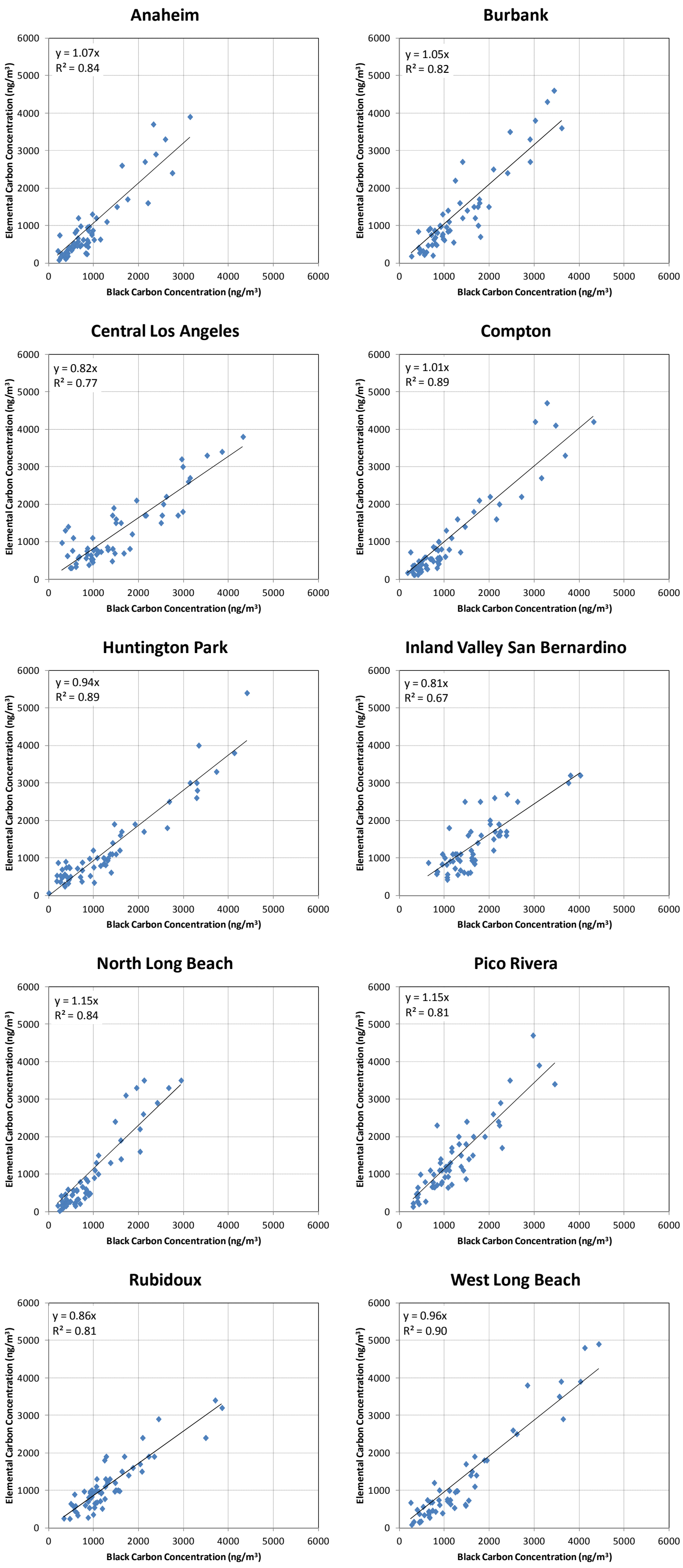


Figure 14 - Comparison of Daily Average BC and EC Concentration at Each MATES IV Site (Sites Shown Separately).

Generally, Particulate BC measured by the Aethalometer is a reliable surrogate for particulate EC measured by subsequent chemical analysis on the filter collected PM, 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 and sinks, as well as presence of OC and secondary organic aerosol.

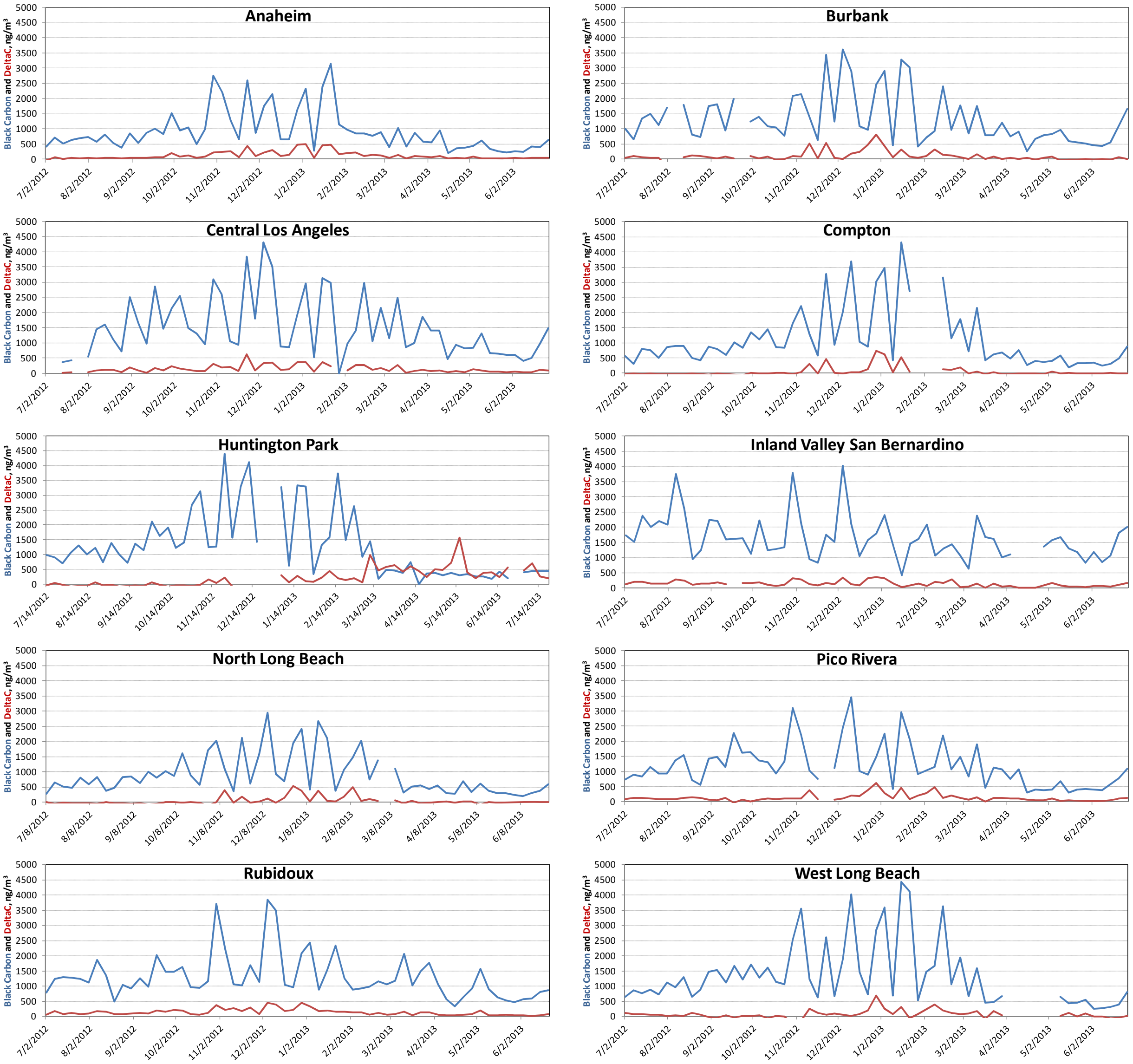
VI.3.3.1 Temporal and Spatial Variations of Biomass Burning Smoke

Certain organic aerosol components of wood smoke have enhanced ultraviolet absorption at 370 nm relative to 880 nm in Aethalometer BC measurements. This enhanced absorption has been used as an indicator of wood combustion particles and is defined as Delta-C, where:

$\text{Delta-C} = \text{UVBC}_{370\text{nm}} - \text{BC}_{880\text{nm}}$

It is important to note that the Delta-C values are not a direct quantitative measurement of mass concentration.

Delta-C values were calculated from MATES IV data in order to estimate the contribution of biomass burning smoke to total ambient BC and are presented in Figure 15(a – j). The Delta-C values in summer, spring and fall were mostly negative, indicating no impact from wood smoke (Wang et at., 2011). Studying the temporal variations in BC concentration and Delta-C values, reveal a distinct seasonal trend with elevated BC concentrations and Delta-C values during winter months, suggesting higher contribution of biomass burning smoke. The Huntington Park site represents an exception; in fact, despite higher BC concentration in the winter, the peak of Delta-C values was observed between March and July 2013. Delta-C in Inland Valley San Bernardino also exhibits the least temporal variation.



Anaheim

Burbank

Central Los Angeles

Compton

Huntington Park

Inland Valley San Bernardino

North Long Beach

Pico Rivera

Rubidoux

West Long Beach

Figure 15 - Comparison Between BC and Delta-C Temporal Variations.

VI.4 Summary

Long-term measurements of BC concentrations carried over a year from July 2012 to August 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.

Comprehensive speciation of carbonaceous aerosols provides invaluable data on the composition, properties and sources of carbonaceous aerosols; however, this type of analysis is extremely time consuming and expensive. Therefore, such analysis is usually only possible for a small number of sampling sites and for short duration periods. One alternative is to measure bulk carbonaceous aerosol properties with thermal/optical techniques used to analyze particulate matter samples for EC and OC, respectively. The U.S. Environmental Protection Agency currently operates two major sampling networks in the Unites States, the Interagency Monitoring of Protected Visual Environments network (IMPROVE) and the EPA’s Chemical Speciation Network (CSN) are responsible for collecting samples across the country and conducting regular speciated aerosol analyses that characterize carbonaceous species, in addition to ionic and elemental species. The long-term monitoring of carbonaceous aerosols provides the opportunity to study the changes in carbonaceous aerosols over time and assess the success of regulatory efforts in reducing emissions.

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. Some examples include: (a) promoting regular vehicle emissions testing and retrofitting older diesel powered vehicles and equipment; (b) controlling ship emissions by regulating idling at terminals and mandating fuel standards for ships seeking to dock at port; (c) requiring the use of cleaner fuels; (d) controlling and limiting biomass burning; (e) requiring permits for operation of industrial, power-generating and oil refining facilities; and (f) promoting filtering and after-treatment technologies. Measures to mitigate BC will probably also reduce OC and PM emissions and may reduce the net climate forcing. Therefore, mitigating emissions from diesel-engine sources may offer the best mitigation potential to reduce near-term climate forcing, and regardless of net climate forcing, all BC mitigation strategies bring health benefits through reduced PM exposure.

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APPENDIX VII

MATES IV

DRAFT REPORT

Particle Counts at Fixed Sites

(IN PREPARATION)

APPENDIX VIII

MATES IV

Draft REPORT

2012 Emissions by Major Source Category

Authors

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Tom Chico

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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	Formalde-hyde	Methyl ethyl ketone	Methylene chloride	MTBE	Naphthalene	p-Dichloro-benzene	Perchloro-ethylene
	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

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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.

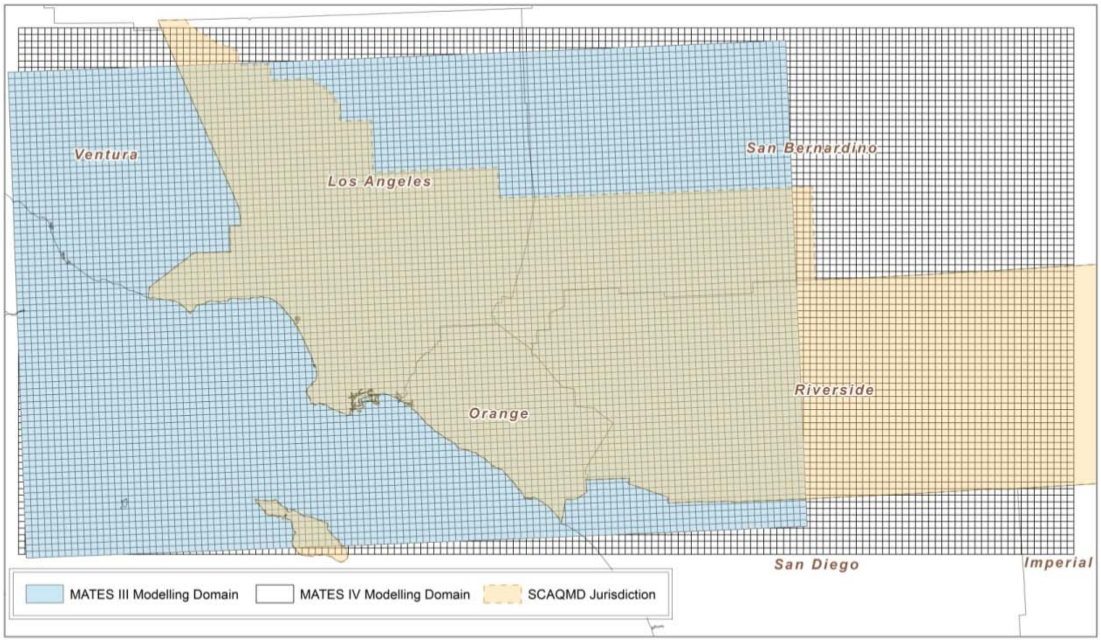


Figure IX-1
MATES IV Modeling Domain. Shaded area represents the MATES III modeling domain.

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 percent 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 percent 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.

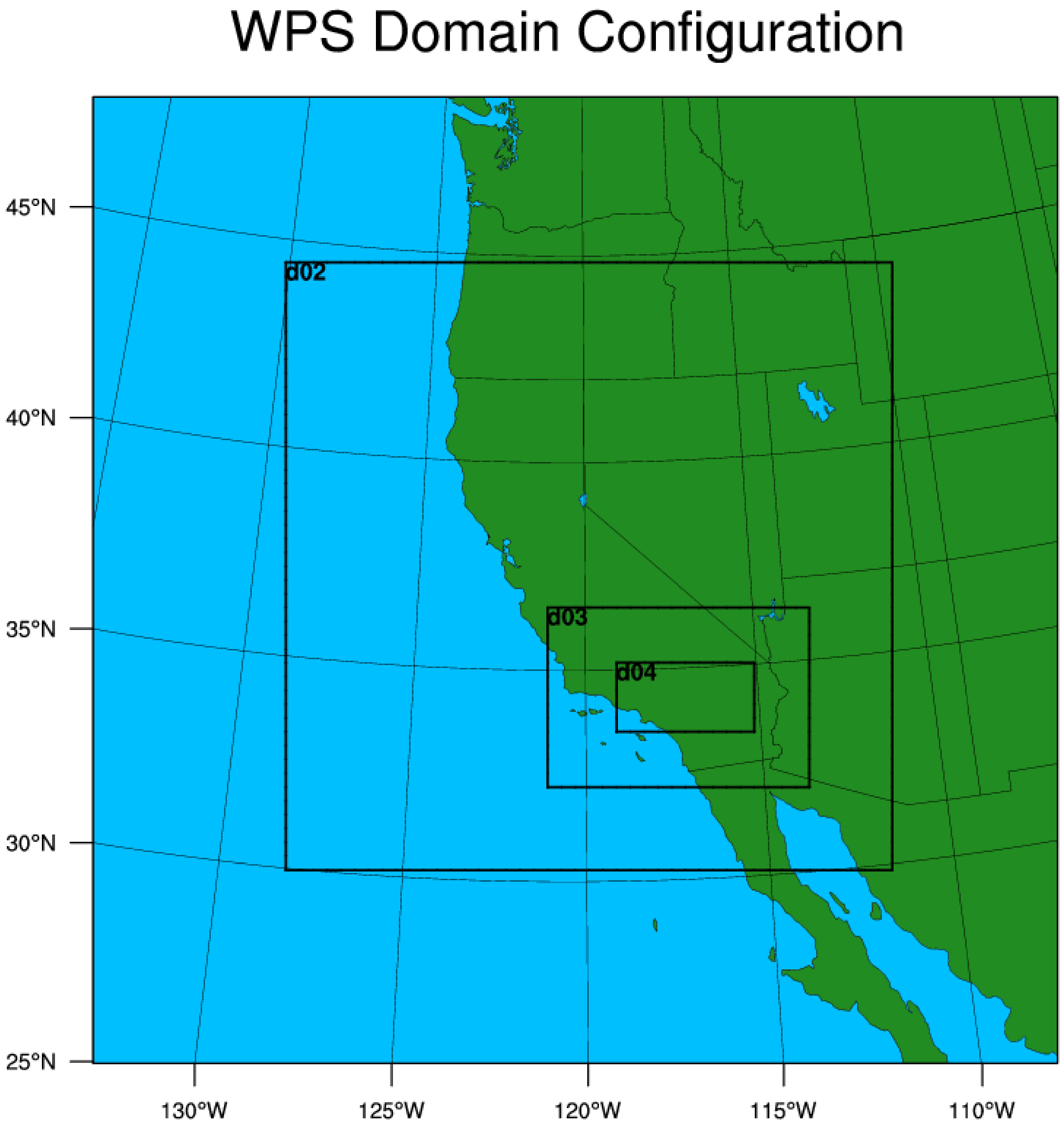


Figure IX-2.
The relative locations and sizes of the four WRF nested domains.

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.

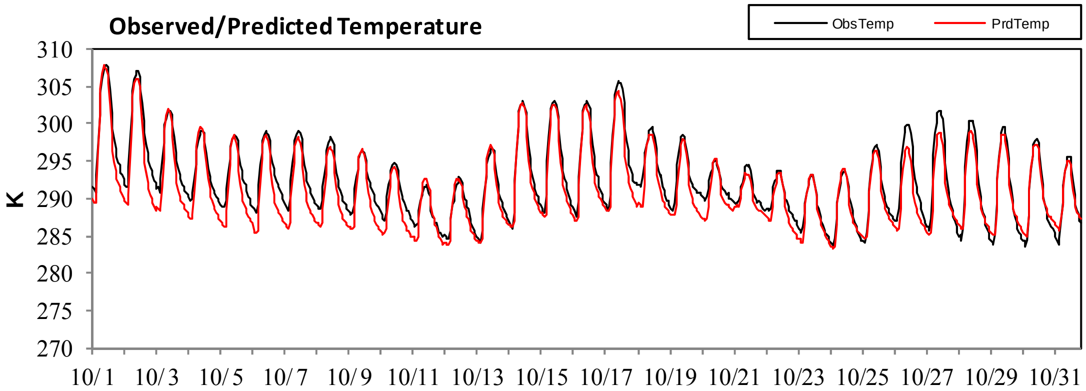


Figure IX-3

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).

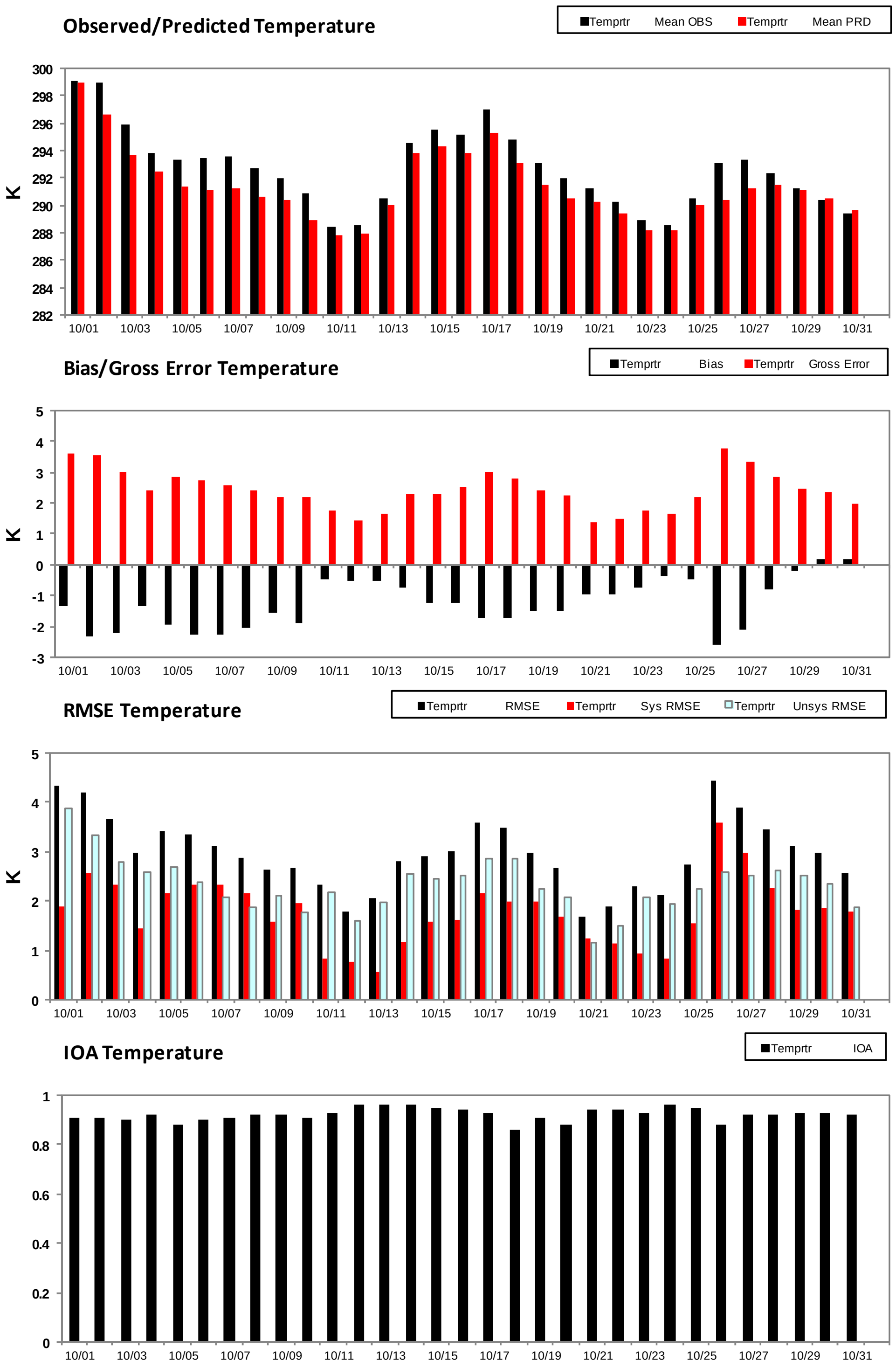


Figure IX-4

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.

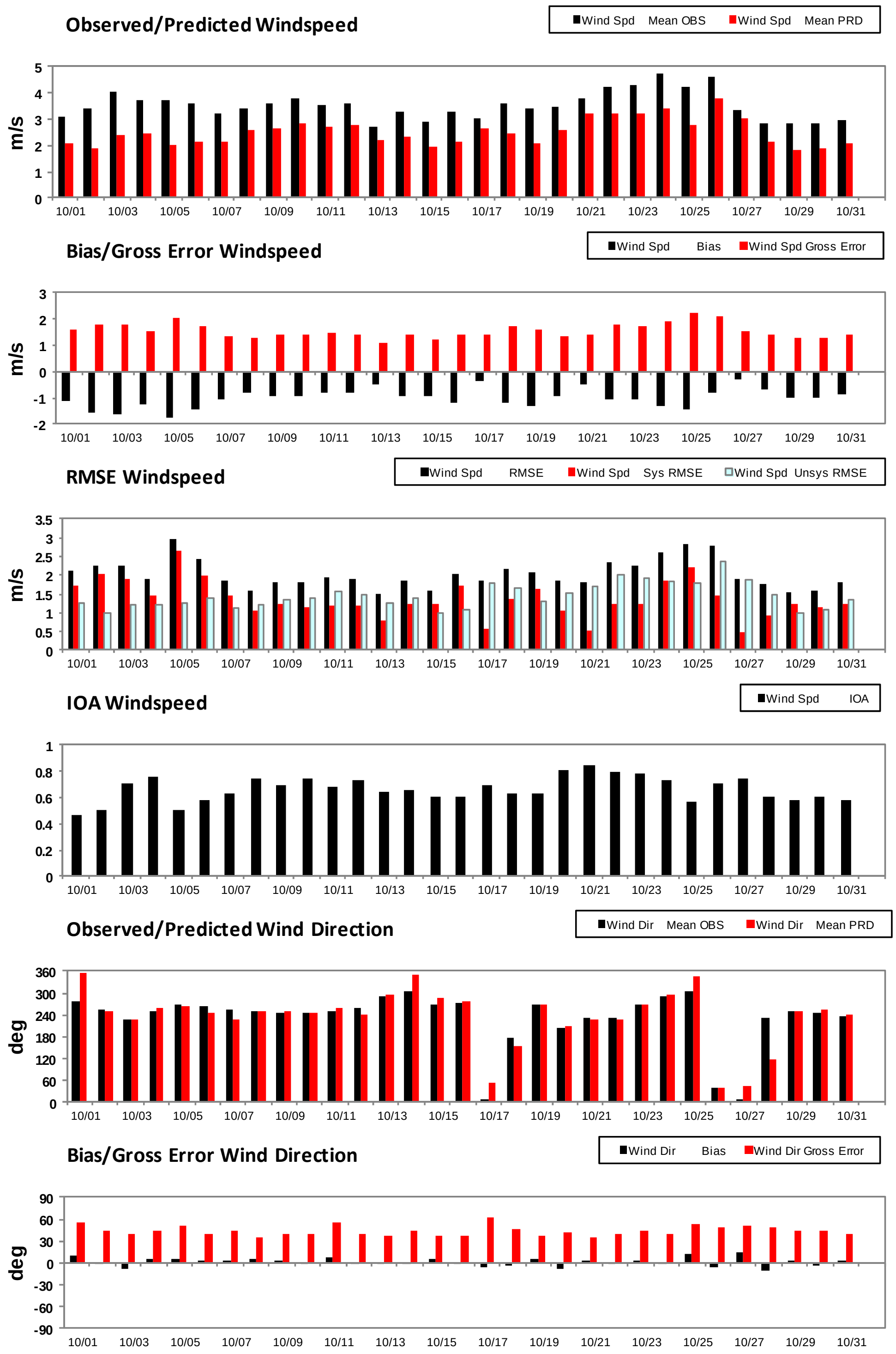


Figure IX-5

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.

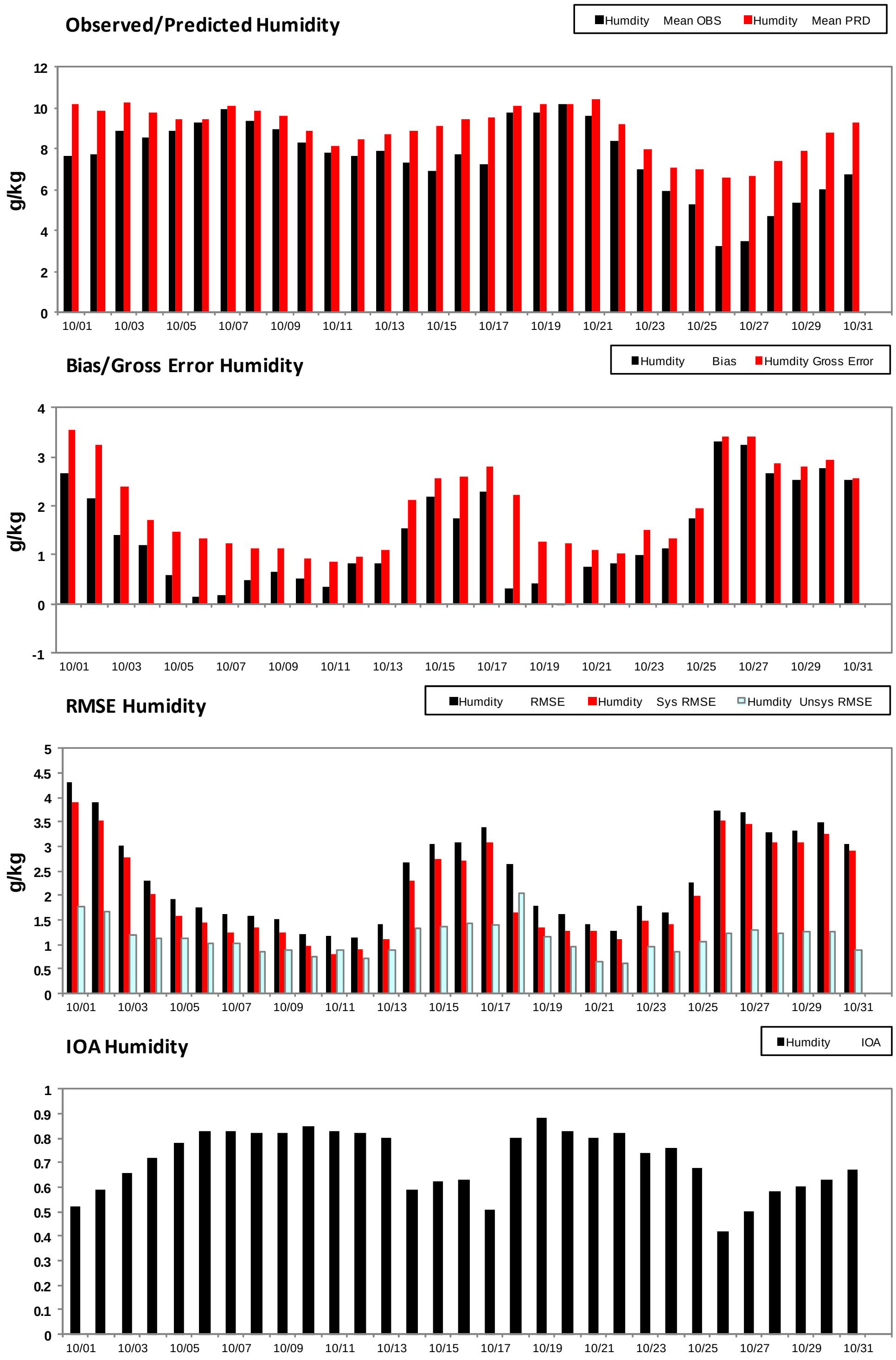


Figure IX-6

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.

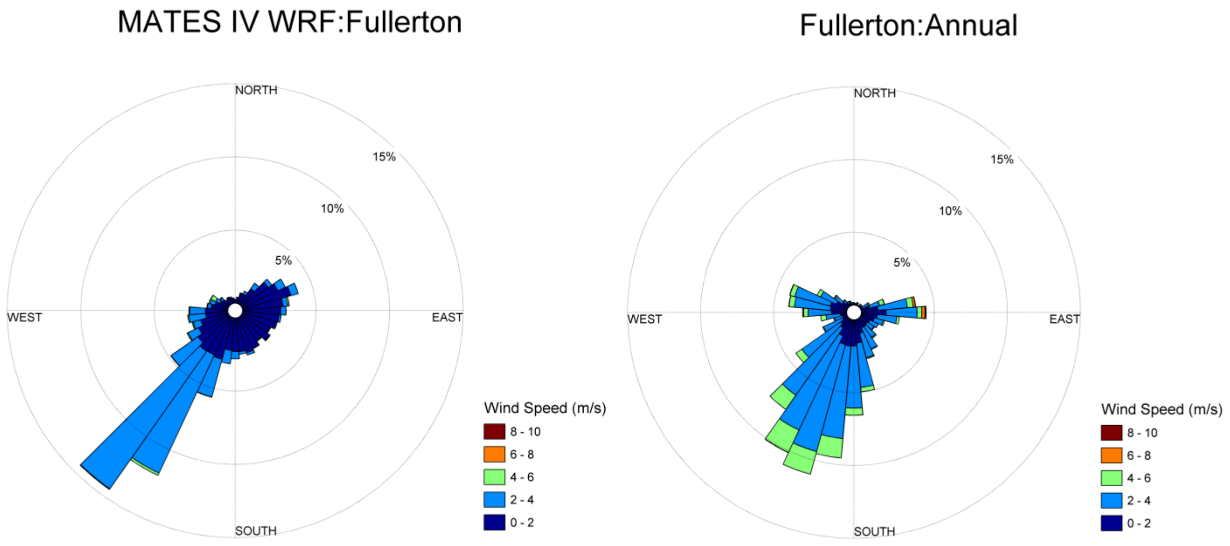


Figure IX-7a.
WRF Simulated and Observed Annual Wind Roses at Fullerton.

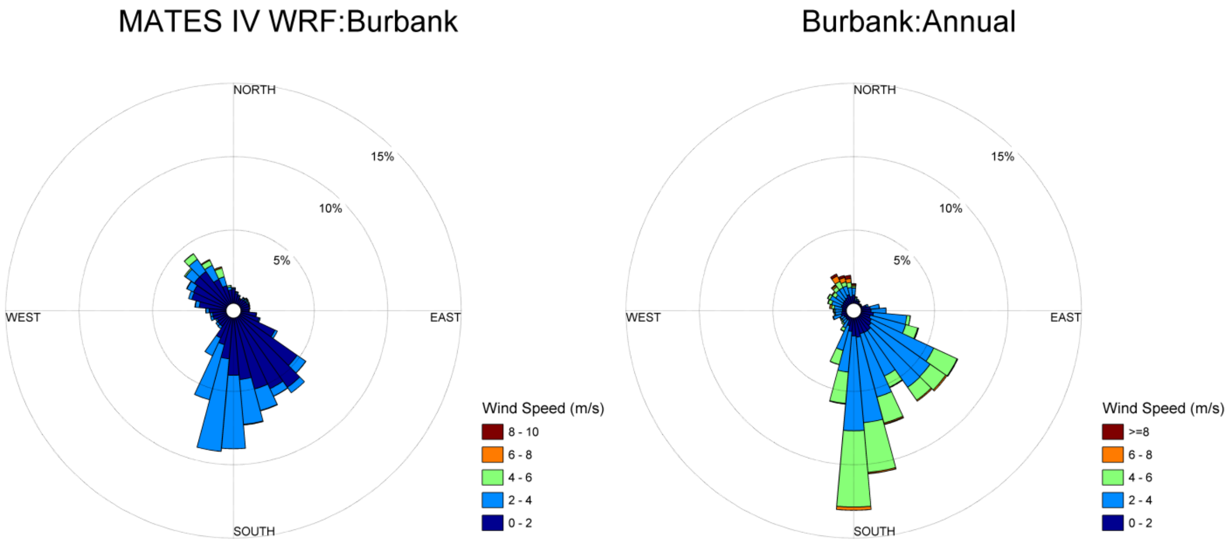


Figure IX-7b.
WRF Simulated and Observed Annual Wind Roses at Burbank.

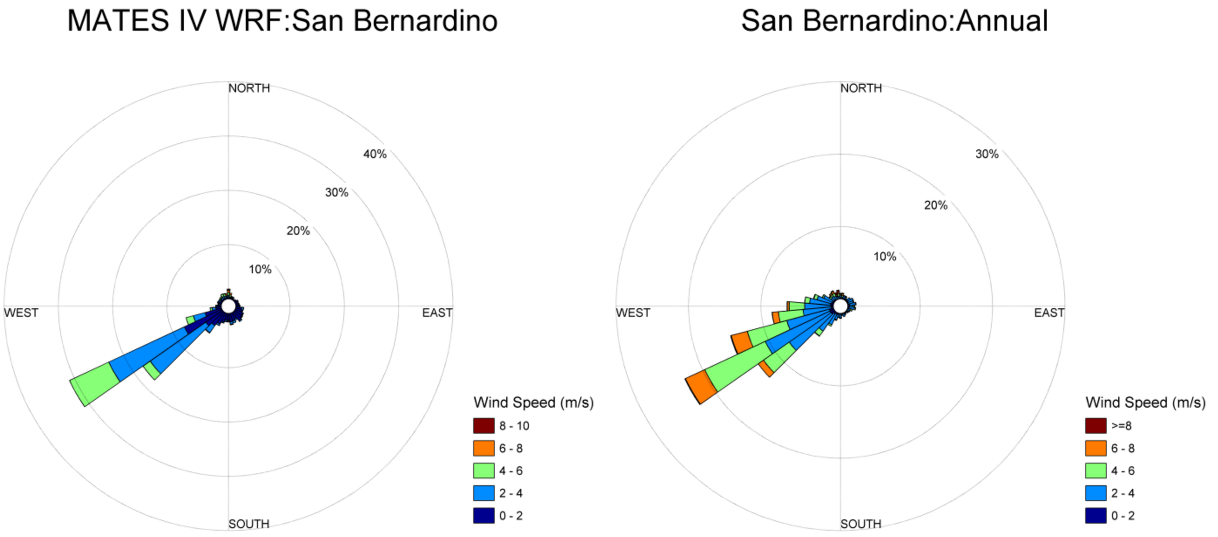


Figure IX-7c.
WRF Simulated and Observed Annual Wind Roses at San Bernardino.

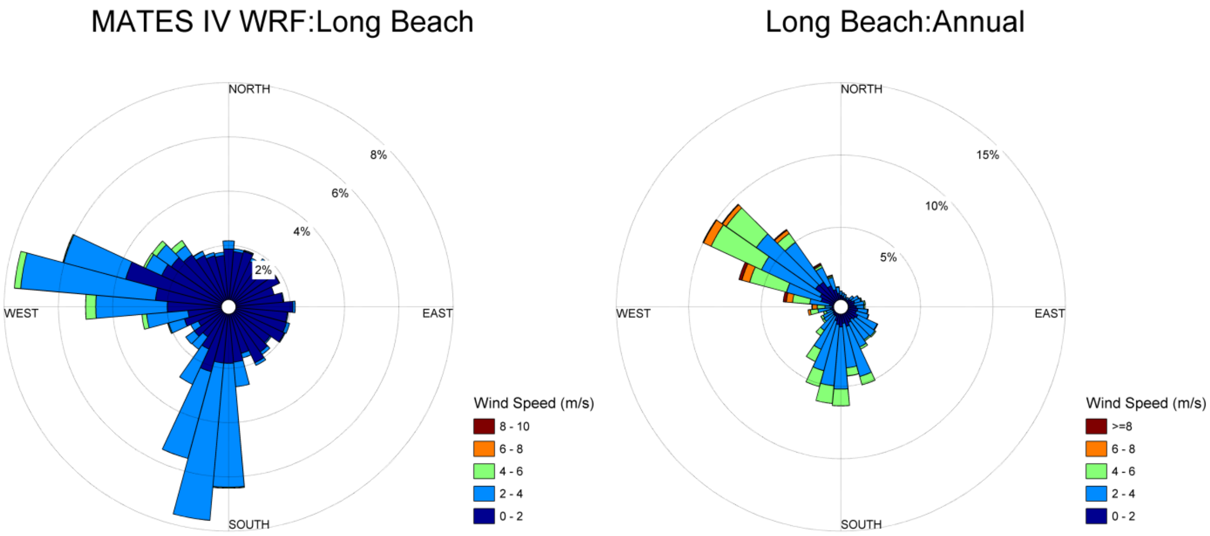


Figure IX-7d.
WRF Simulated and Observed Annual Wind Roses at Long Beach.

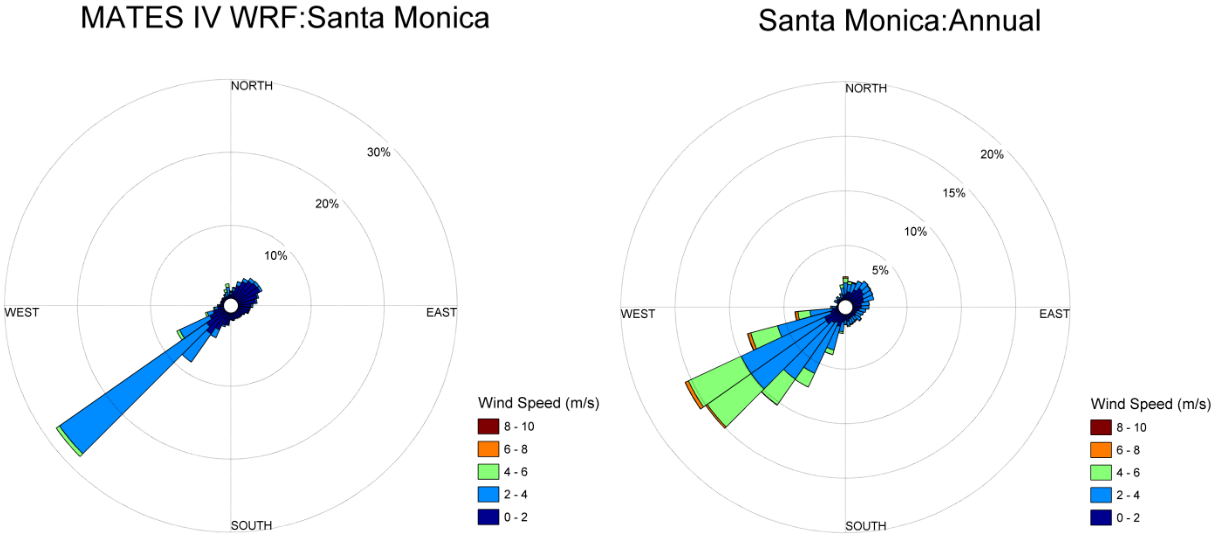


Figure IX-7e.
WRF Simulated and Observed Annual Wind Roses at Santa Monica.

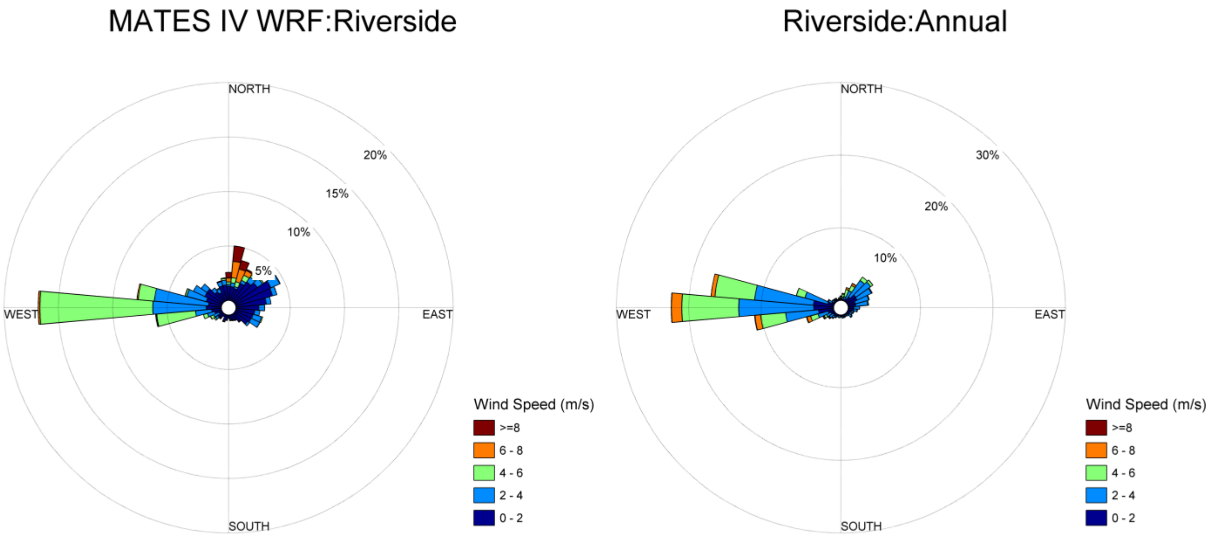


Figure IX-7f.
WRF Simulated and Observed Annual Hourly Averaged Wind Roses at Riverside.

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

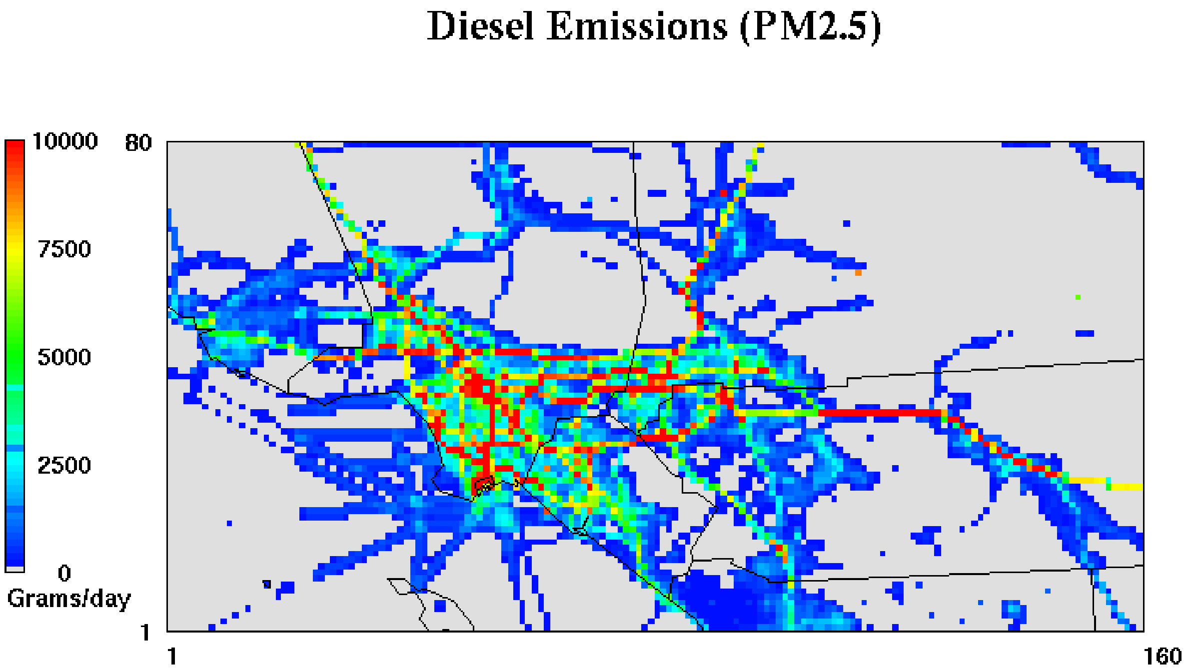


Figure IX-8a
Weekday average emissions pattern for Total Diesel $PM_{2.5}$.

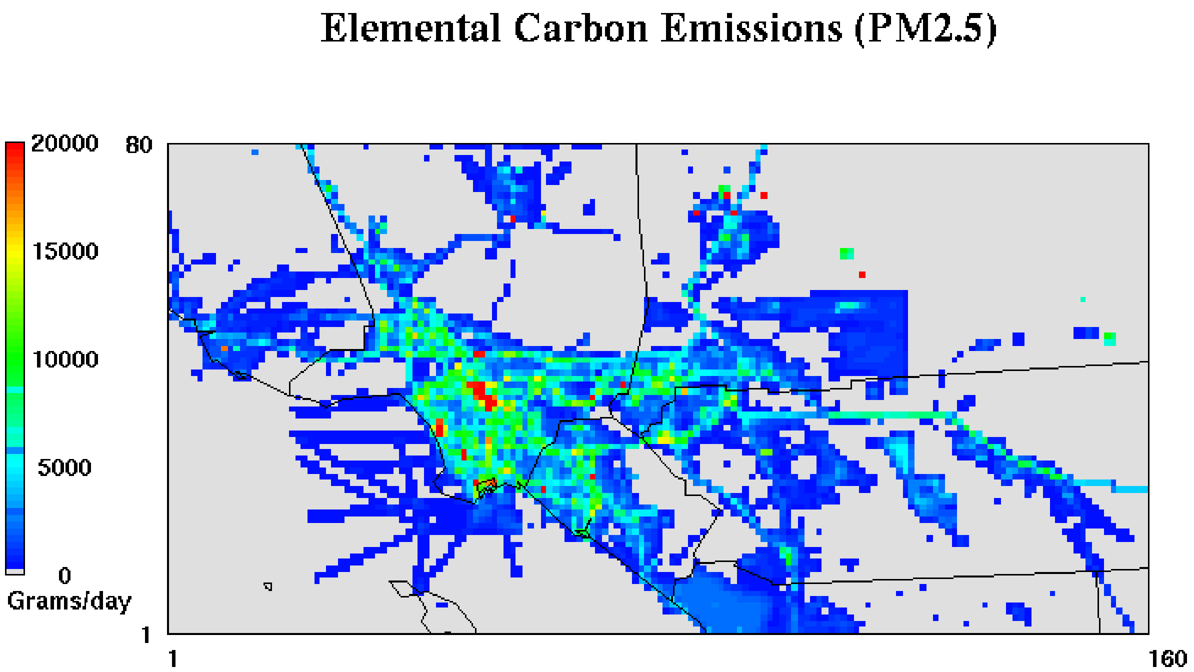


Figure IX-8b
Weekday average emissions pattern for Elemental Carbon.

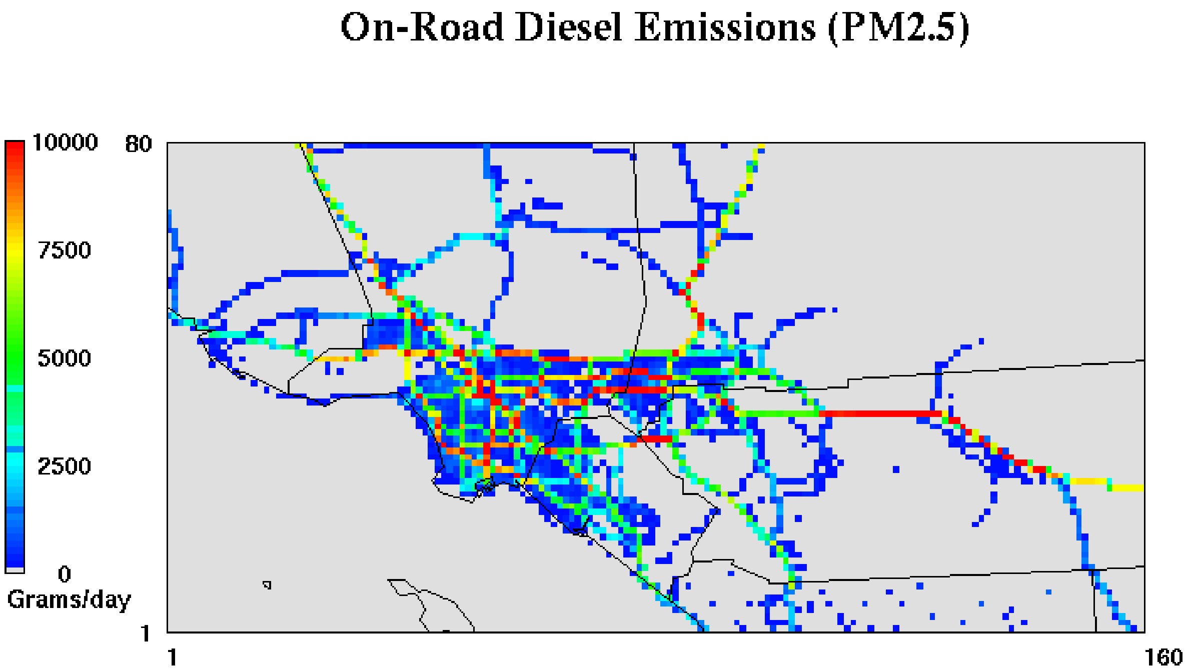


Figure IX-8c
Weekday average emissions pattern for On-Road Diesel $PM_{2.5}$.

Off-Road Diesel Emissions (PM2.5)

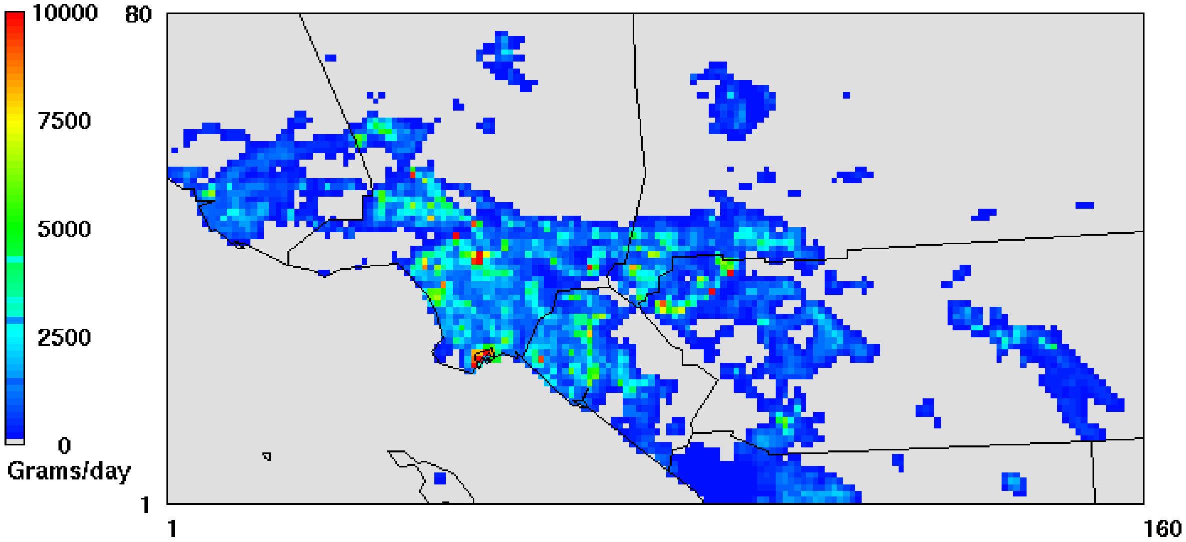


Figure IX-8d
Weekday average emissions pattern for Off-Road Diesel $PM_{2.5}$.

Pattern of Diesel Emissions (PM2.5) from Ships

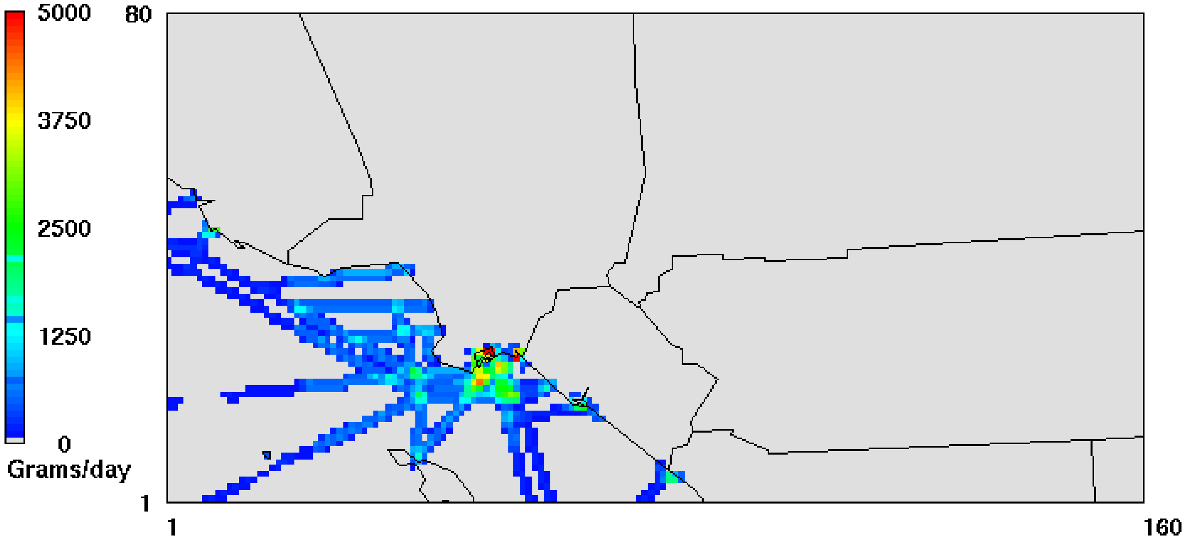


Figure IX-8e
Weekday average emissions pattern Diesel $PM_{2.5}$ from Ships.

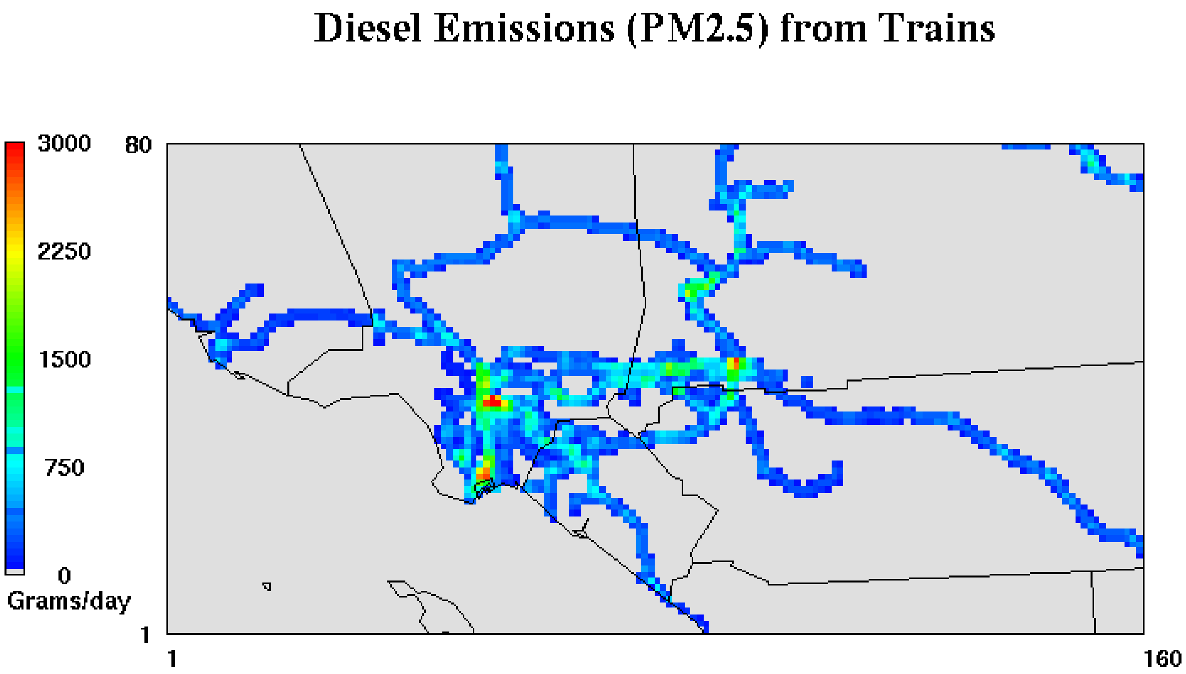


Figure IX-8f
Weekday average emissions pattern Diesel $PM_{2.5}$ from Trains.

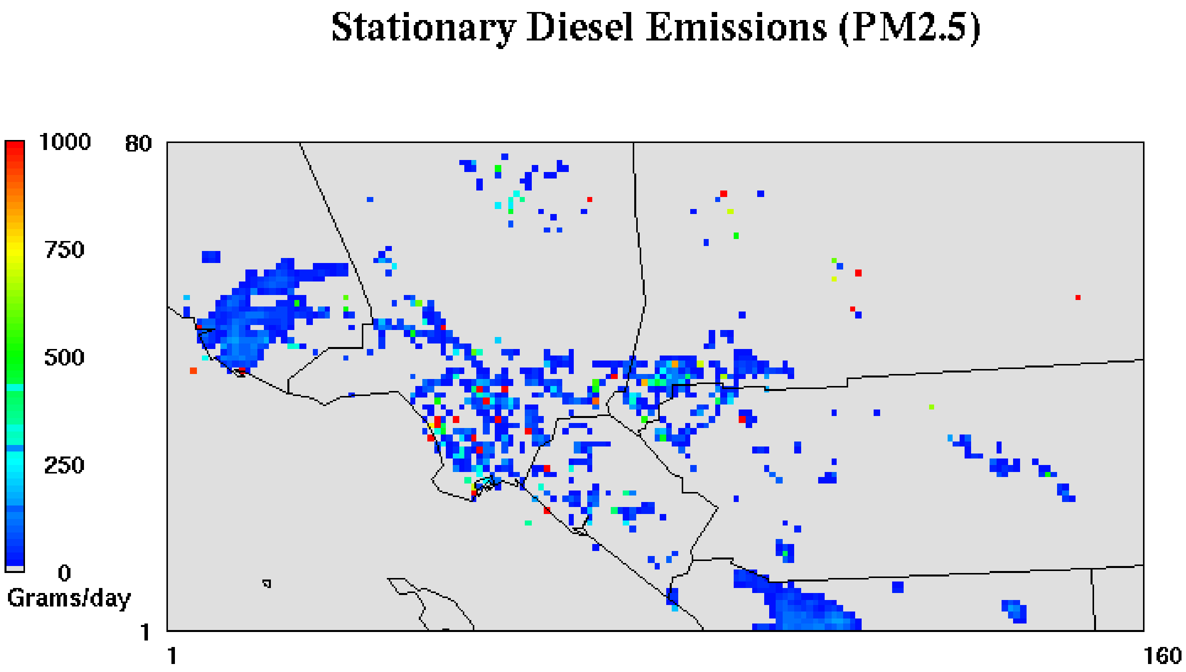
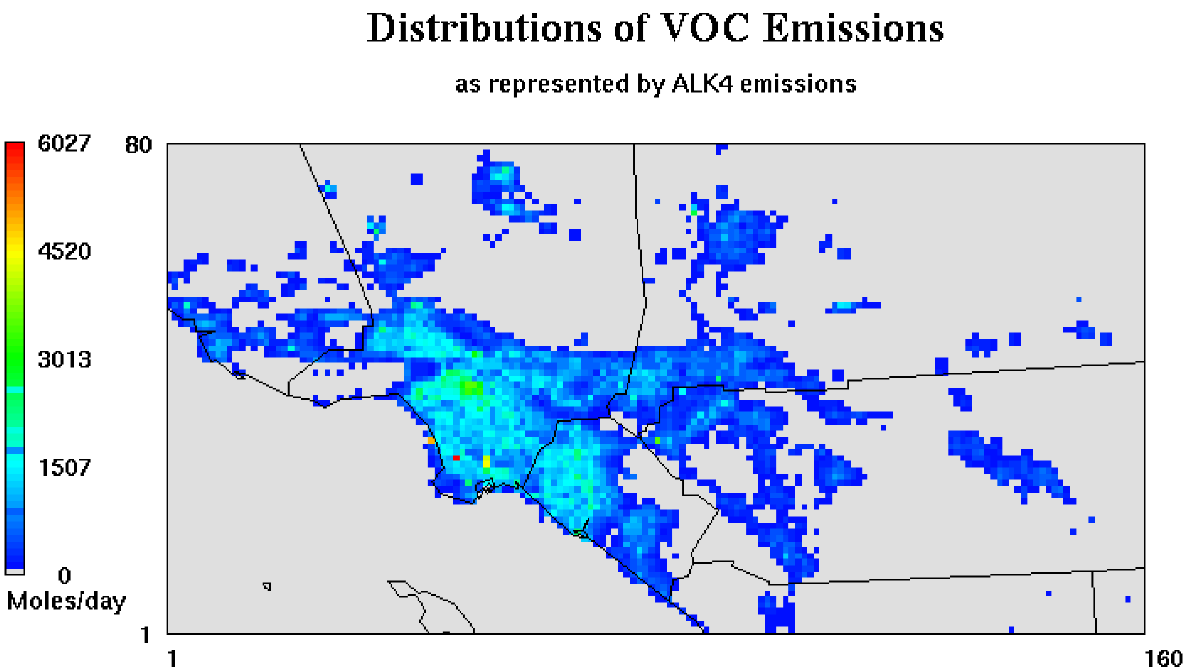


Figure IX-8g
Weekday average emissions pattern Diesel $PM_{2.5}$ from Stationary Sources.


Distributions of VOC Emissions

as represented by ALK4 emissions

Figure IX-8h
Weekday average VOC emissions pattern.

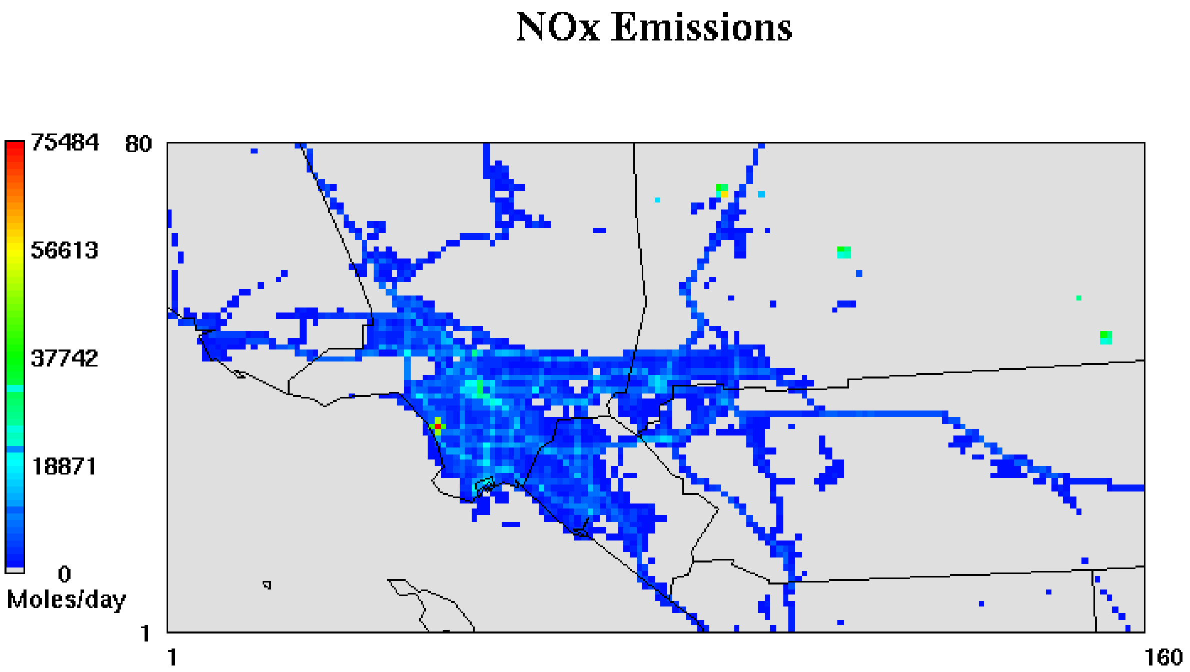

NOx Emissions

Figure IX-8i
Weekday average NOx emissions pattern.

CO Emissions

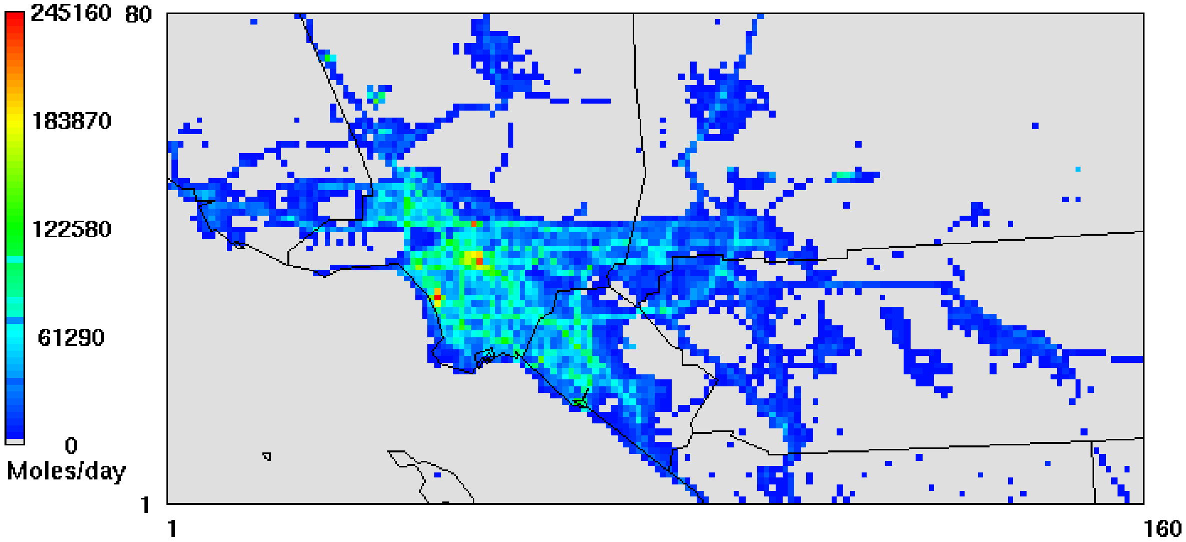


Figure IX-8j
Weekday average CO emissions pattern.

Acetaldehyde Emissions

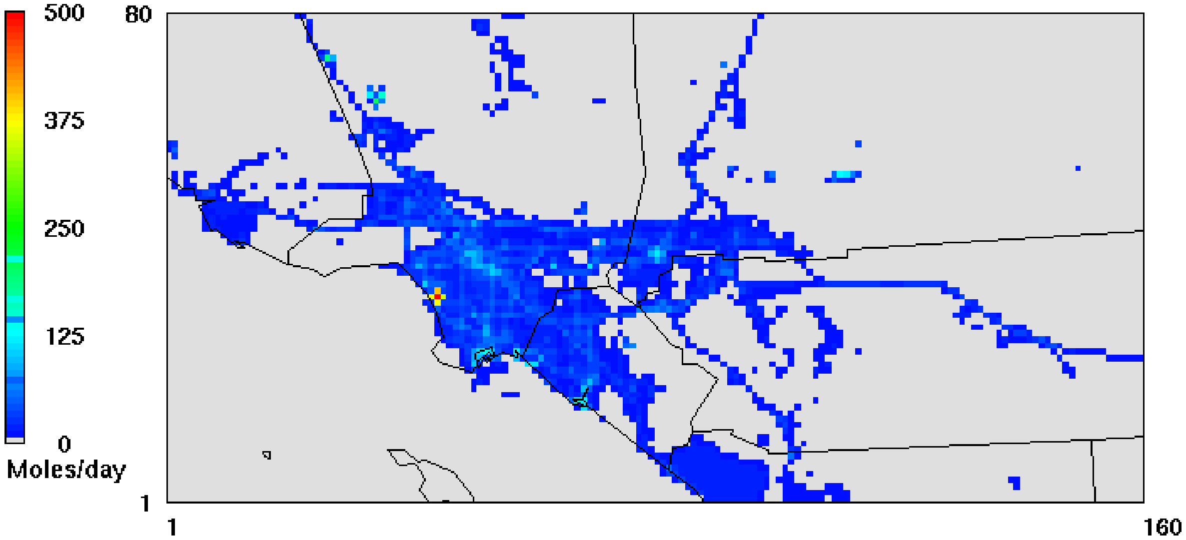


Figure IX-8k
Weekday average emissions pattern for Acetaldehyde.

Arsenic Emissions (PM2.5)

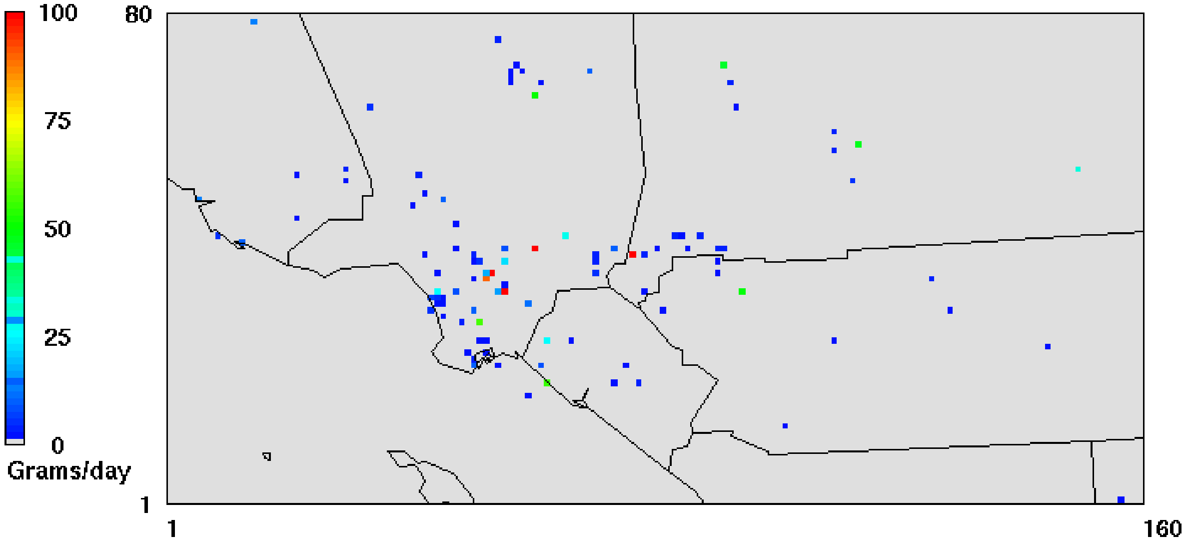


Figure IX-8l
Weekday average Arsenic emissions pattern.

Benzene Emissions

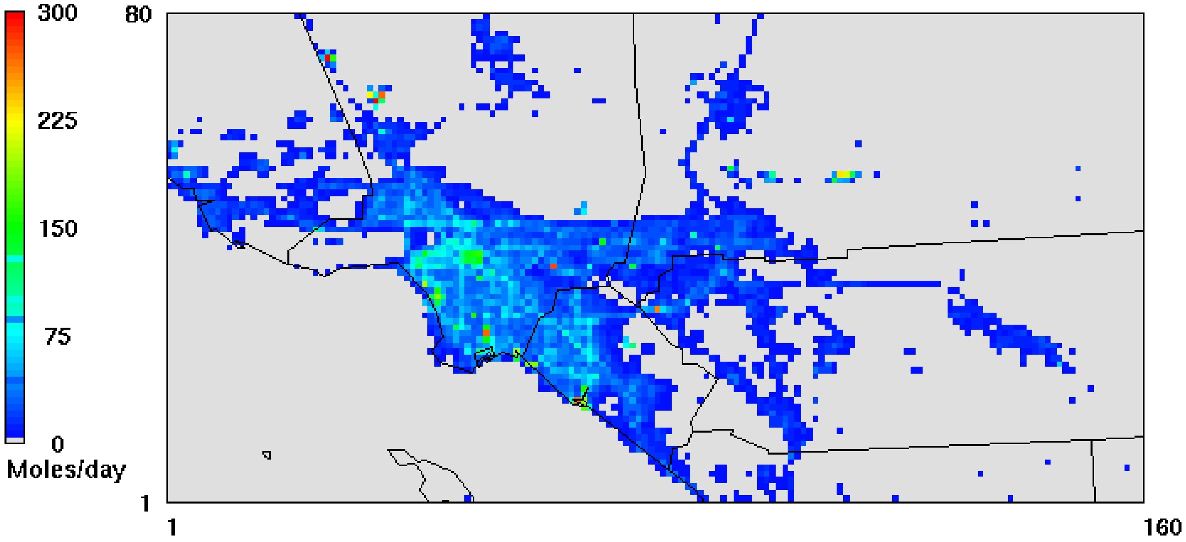


Figure IX-8m
Weekday average Benzene emissions pattern.

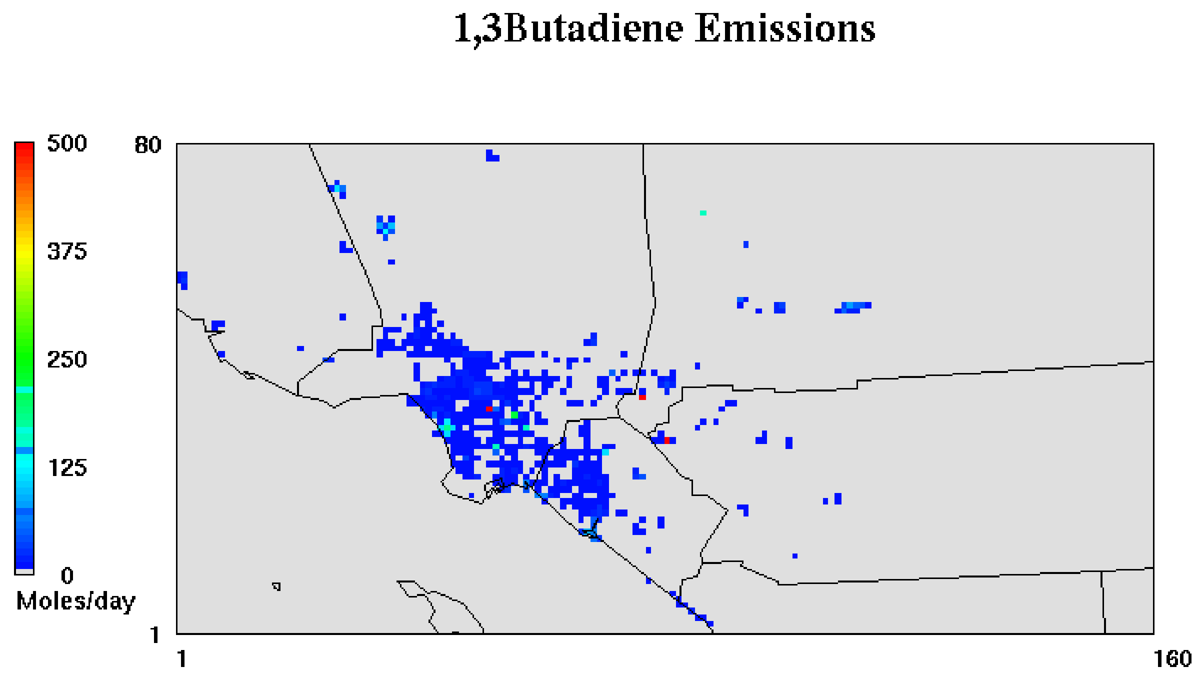


Figure IX-8n
Weekday average 1,3-Butadiene emissions pattern.

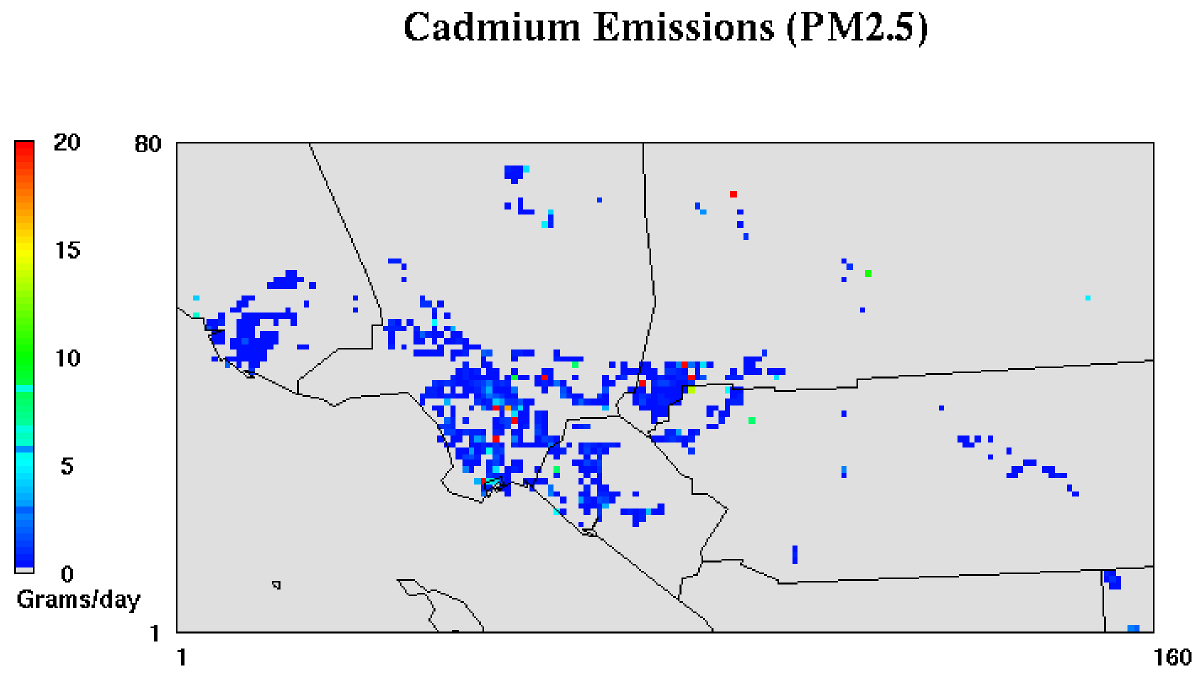


Figure IX-8o
Weekday average Cadmium $PM_{2.5}$ emissions pattern.

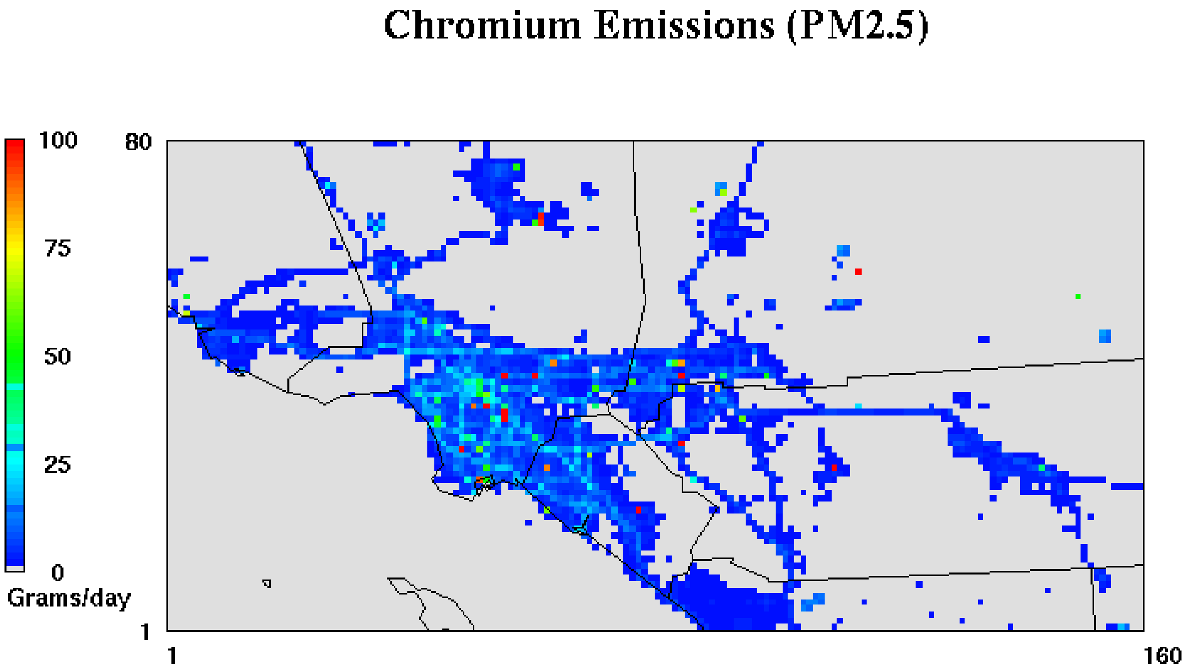


Figure IX-8p
Weekday average Chromium $PM_{2.5}$ emissions pattern.

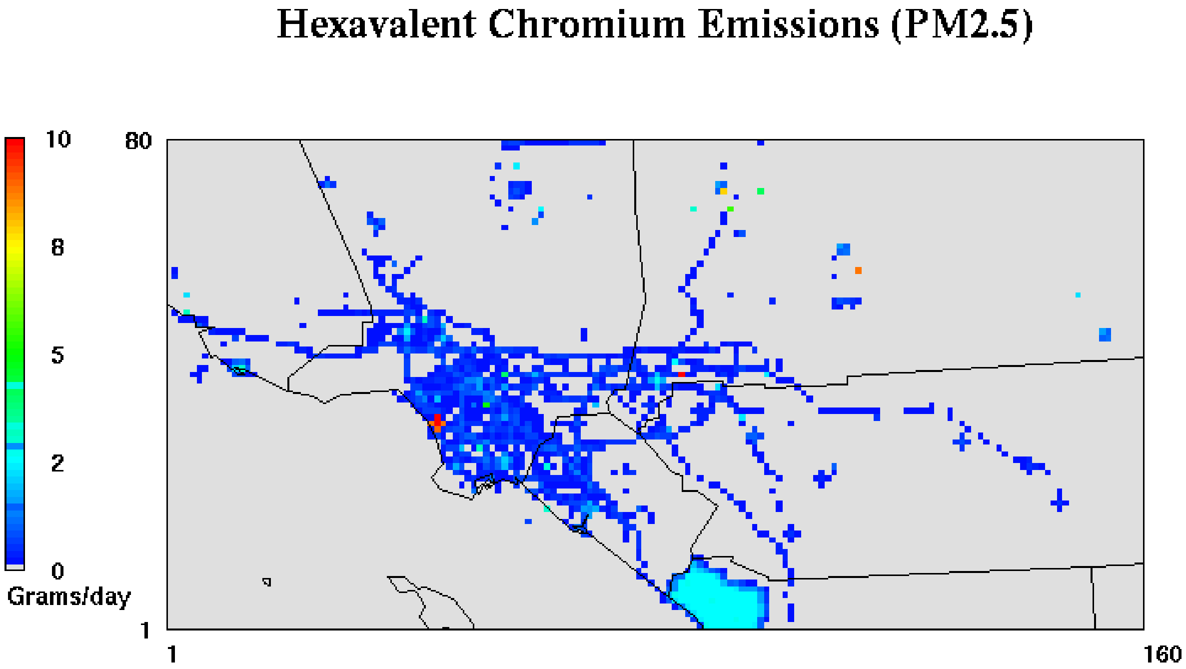


Figure IX-8q
Weekday average Hexavalent Chromium $PM_{2.5}$ emissions pattern.

Lead Emissions (PM2.5)

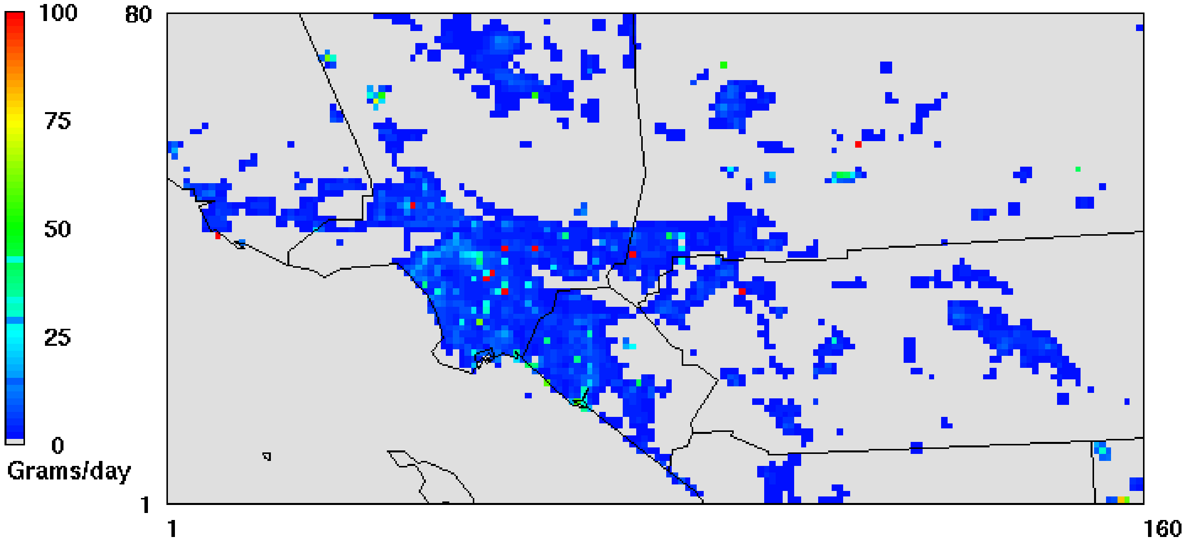


Figure IX-8r
Weekday average Lead $PM_{2.5}$ emissions pattern.

Methylene Chloride Emissions

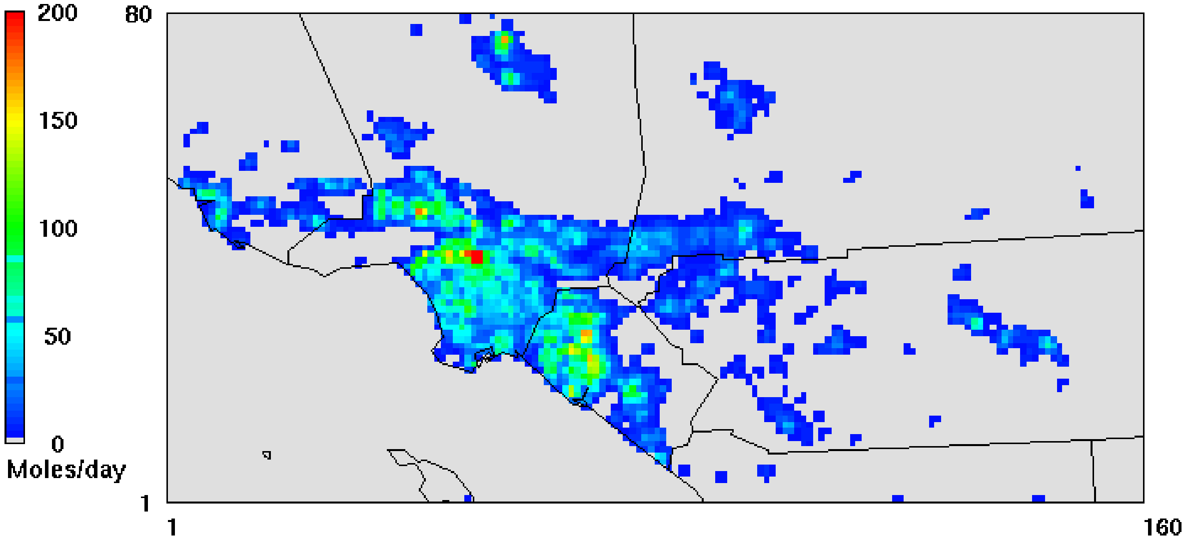


Figure IX-8s
Weekday average Methylene Chloride emissions pattern.

Naphthalene Emissions

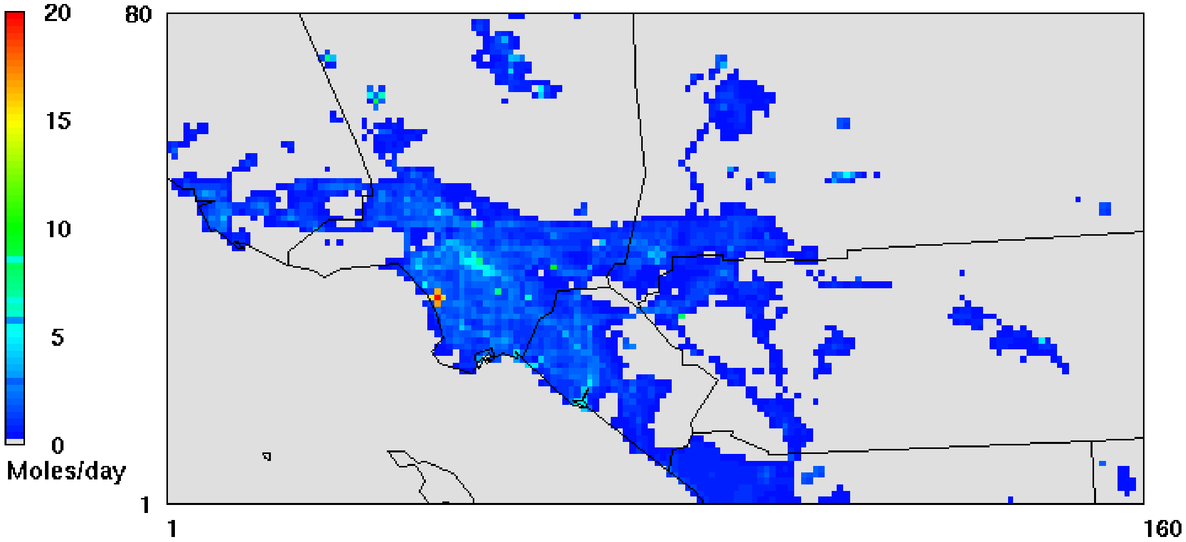


Figure IX-8t
Weekday average Naphthalene emissions pattern.

Nickel Emissions (PM2.5)

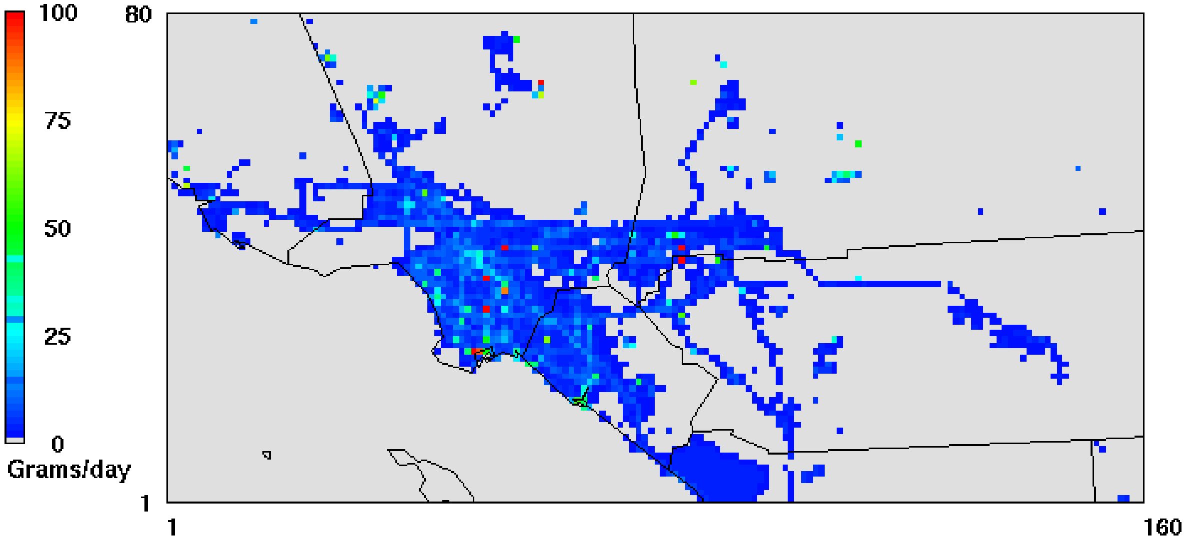


Figure IX-8u
Weekday average Nickel $PM_{2.5}$ emissions pattern.

p-Dichlorobenzene Emissions

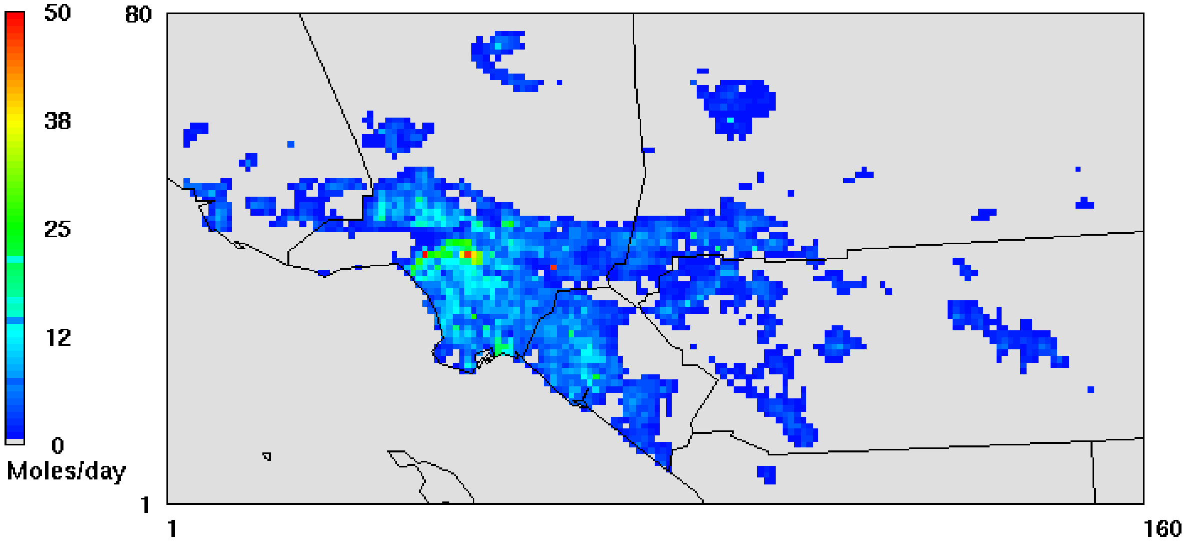


Figure IX-8v
Weekday average p-Dichlorobenzene emissions pattern.

Perchloroethylene Emissions

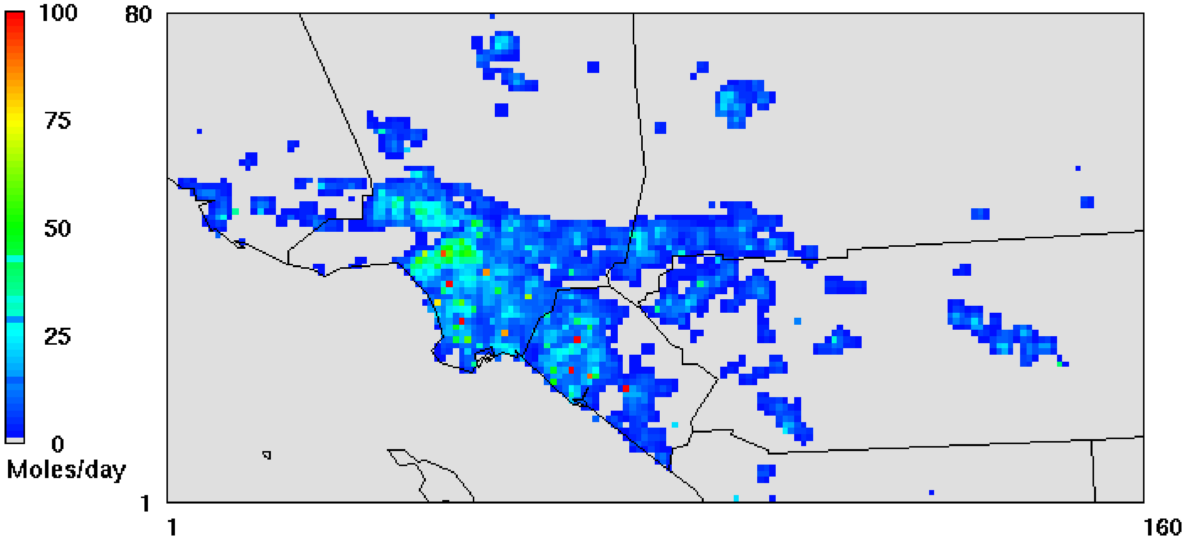


Figure IX-8w
Weekday average Perchloroethylene emissions pattern.

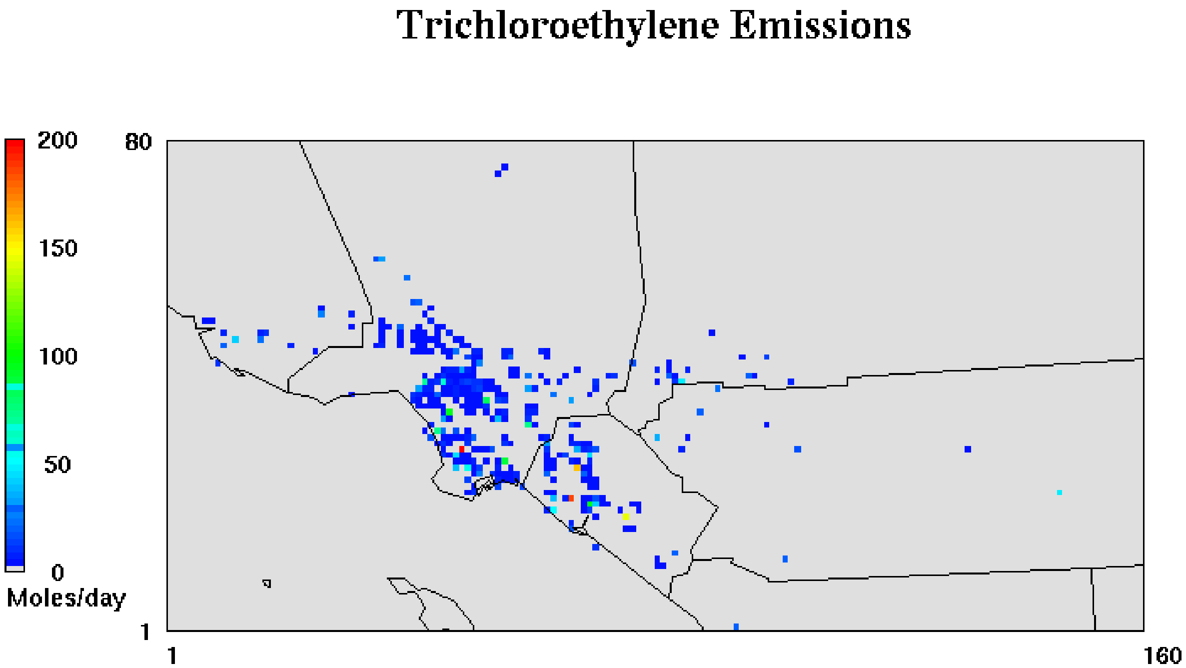


Figure IX-8x
Weekday average Trichloroethylene emissions pattern.

The California Air Resources Board (ARB) 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 ($\mu g/m^3$)	Samples	Modeled Sampling Days ($\mu g/m^3$)	Prediction Accuracy	Mean Bias ($\mu g/m^3$)	Mean Error ($\mu g/m^3$)	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 $\mathbf{EC_{2.5}}$

	MATES IV (2012-2013)					MATES III (2005)				
Location	Observed Days (µg/m^3)	Modeled Sampling Days (µg/m^3)	PA	Bias (µg/m^3)	Mean Error (µg/m^3)	Observed Days (µg/m^3)	Modeled Sampling Days (µg/m^3)	PA	Bias (µg/m^3)	Mean Error (µg/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

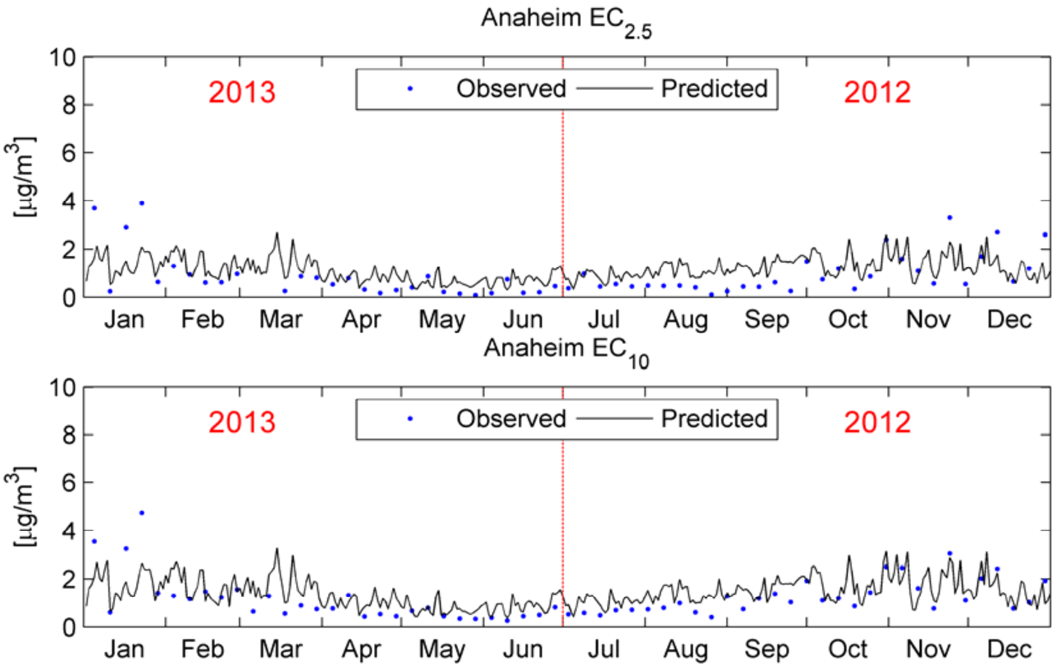


Figure IX-9a

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

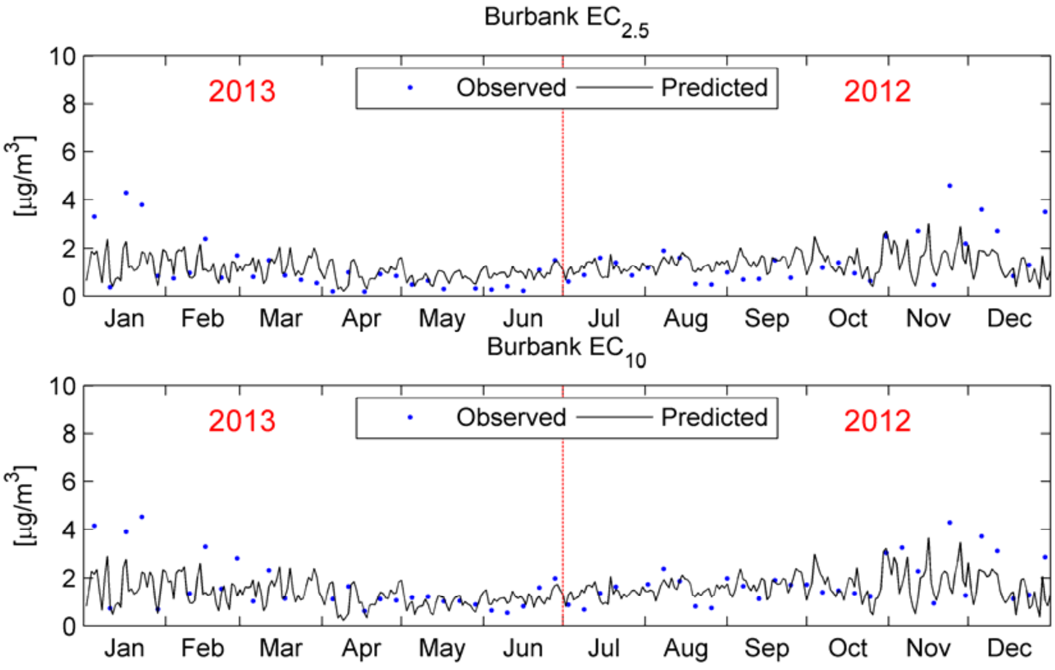


Figure IX-9b

Same as Figure IX-9a except Burbank.

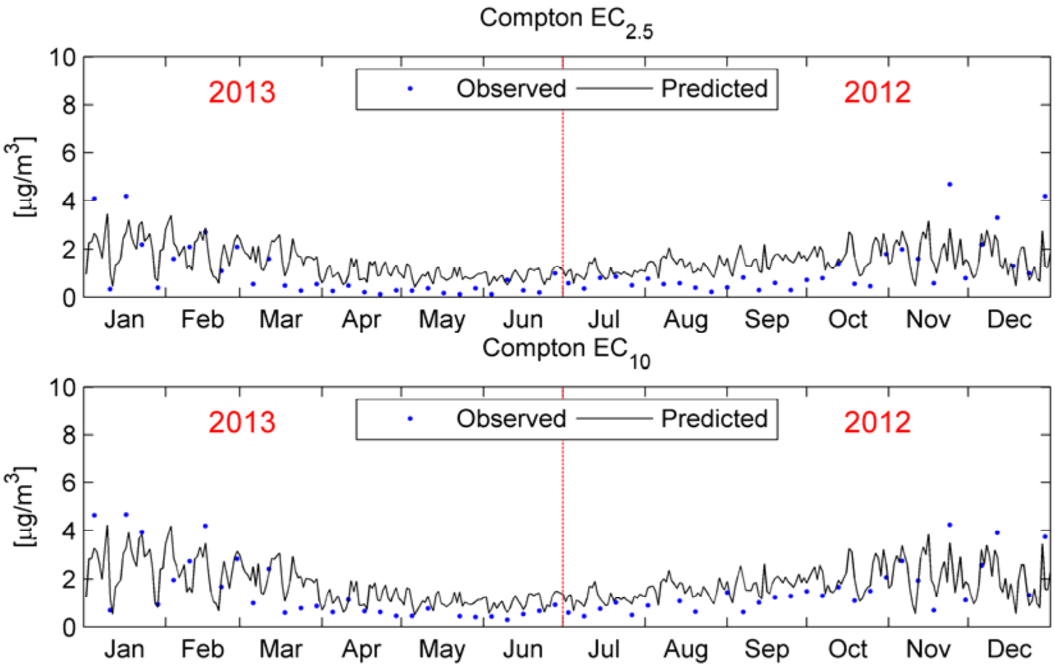


Figure IX-9c

Same as Figure IX-9a except Compton.

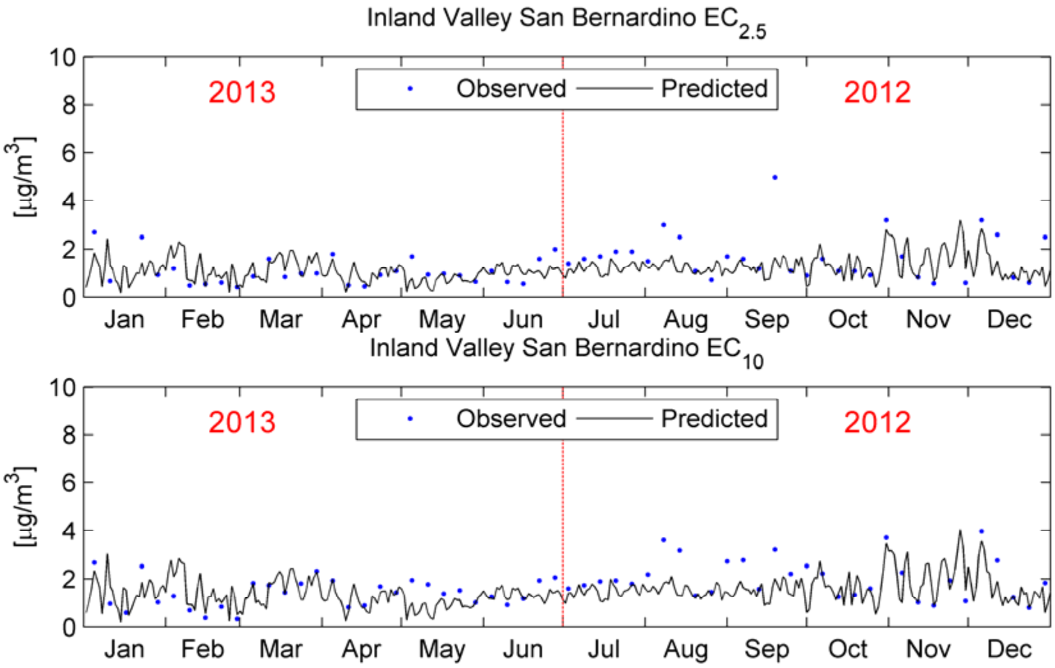


Figure IX-9d

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

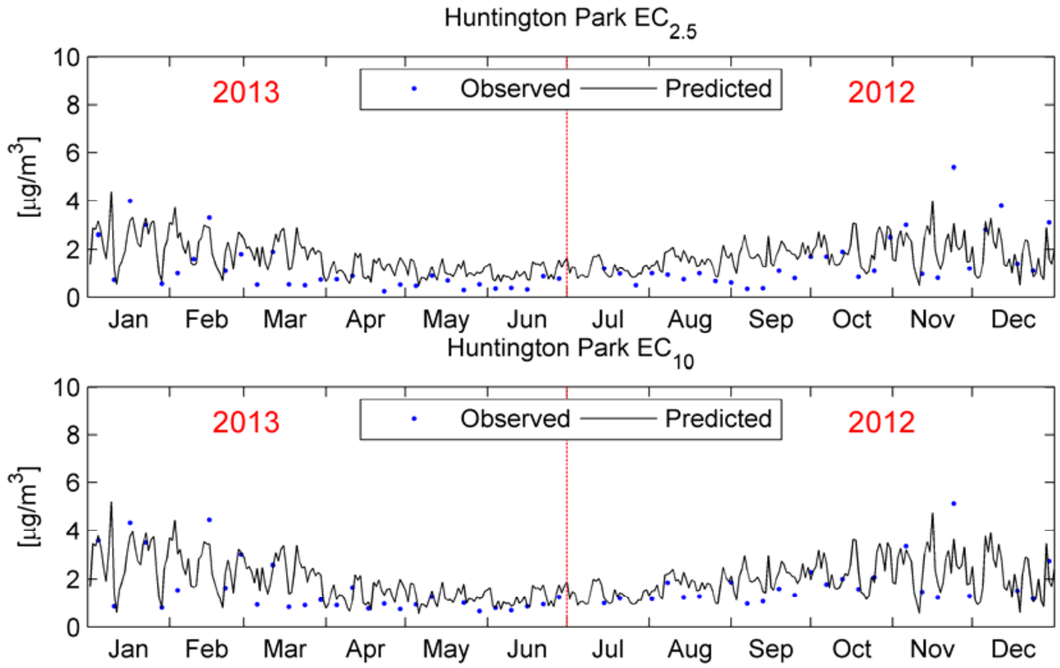


Figure IX-9e
Same as Figure IX-9a except Huntington Park

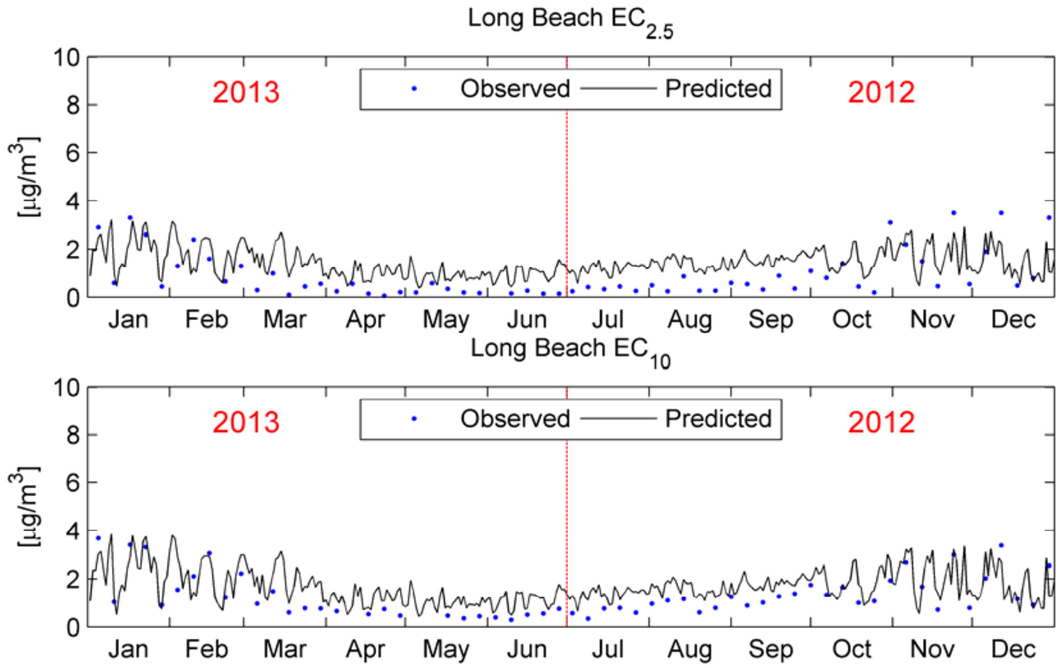


Figure IX-9f
Same as Figure IX-9a except North Long Beach.

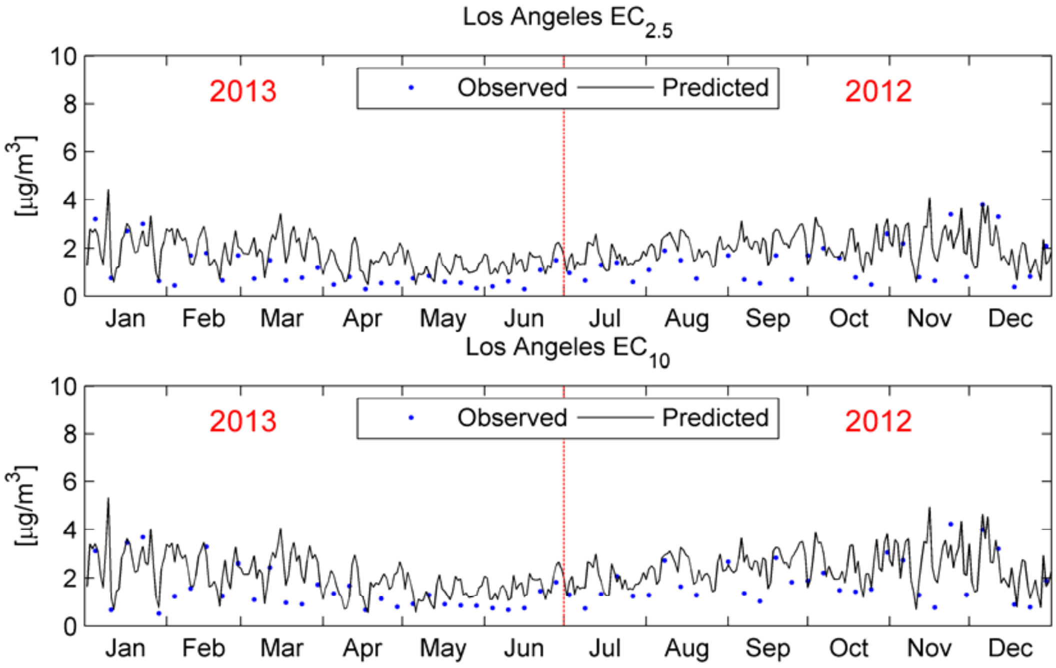


Figure IX-9g

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

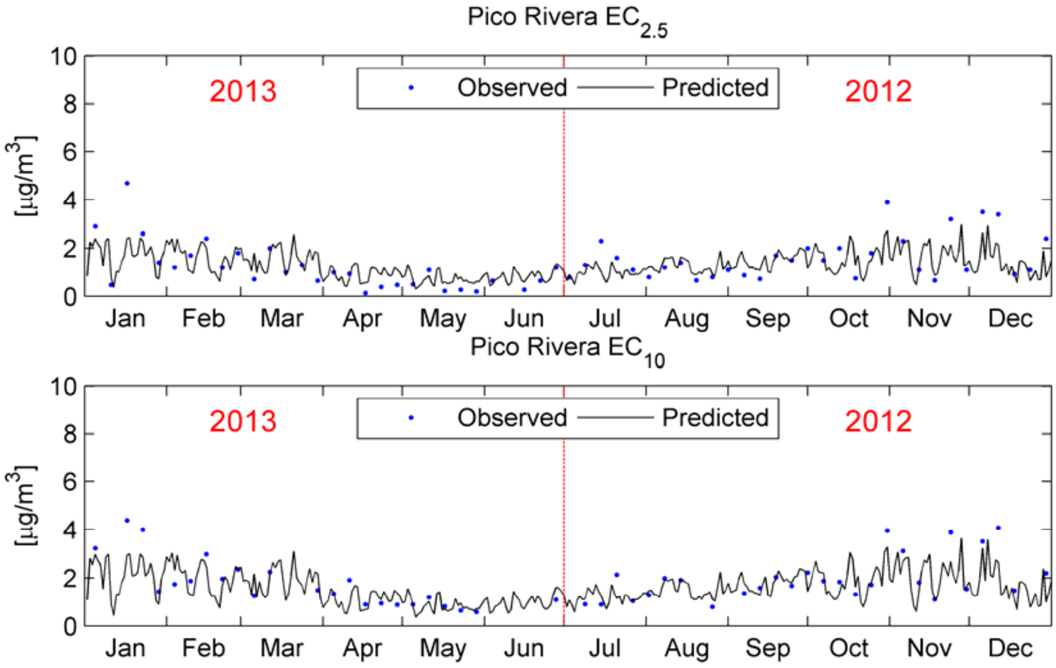


Figure IX-9h

Same as Figure IX-9a except Pico Rivera.

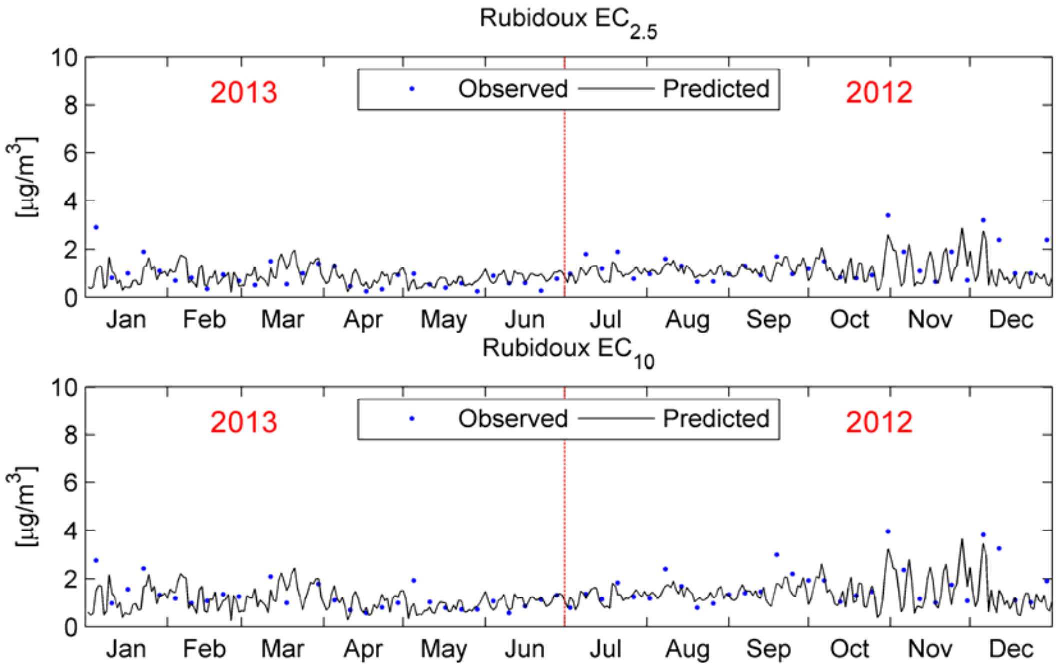


Figure IX-9i

Same as Figure IX-9a except Rubidoux.

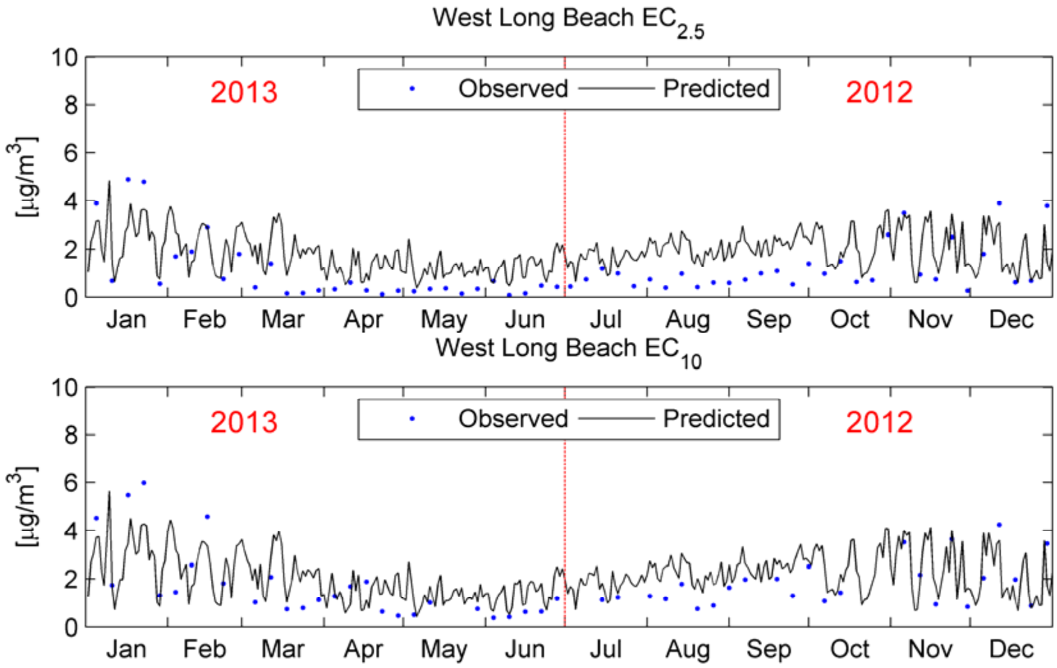


Figure IX-9j

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
$EC_{2.5}$	$\mu g/m^3$	0.96	1.39	1.81	1.69
EC_{10}	$\mu g/m^3$	1.33	1.68	2.05	2.15
Cr 6 (TSP)	$\eta g/m^3$	0.05	0.18	0.23	0.21
As (2.5)	$\eta g/m^3$	N/A	0.66	0.49	1.07
As (TSP)	$\eta g/m^3$	0.44	1.07	0.68	2.57
Cd (2.5)	$\eta g/m^3$	N/A	0.38	1.49	0.59
Cd (TSP)	$\eta g/m^3$	0.13	0.56	1.53	0.88
Ni (2.5))	$\eta g/m^3$	N/A	4.58	4.44	4.88
Ni (TSP)	$\eta g/m^3$	2.98	6.64	5.40	7.55
Pb (2.5)	$\eta g/m^3$	N/A	2.10	5.32	2.53
Pb (TSP)	$\eta g/m^3$	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

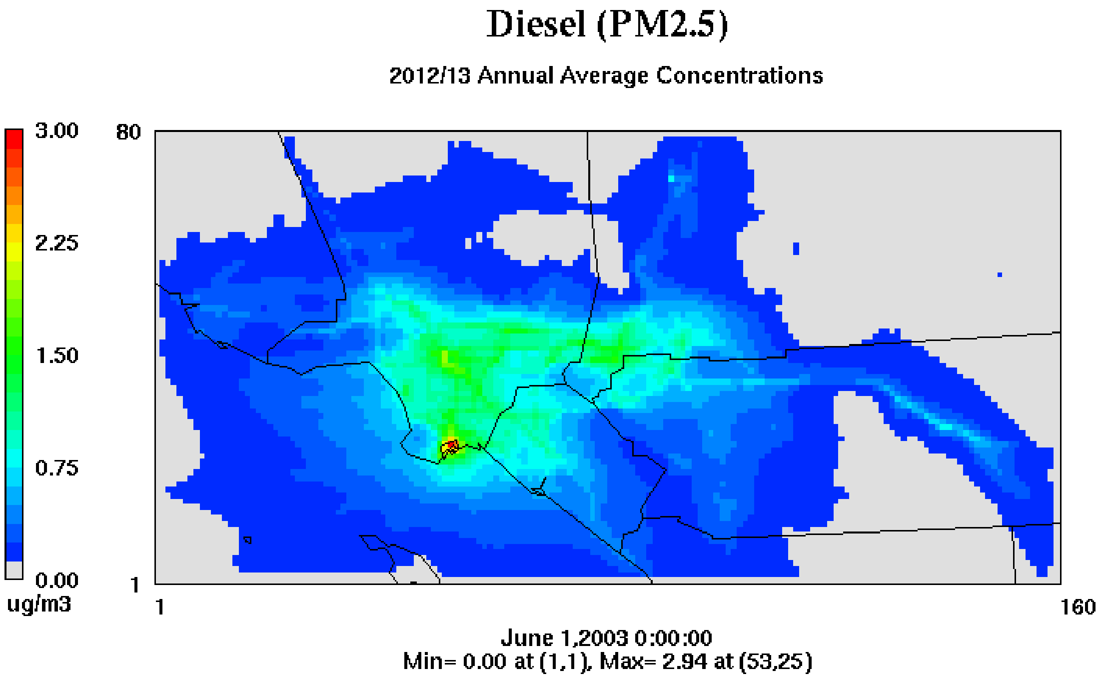


Figure IX-10a

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

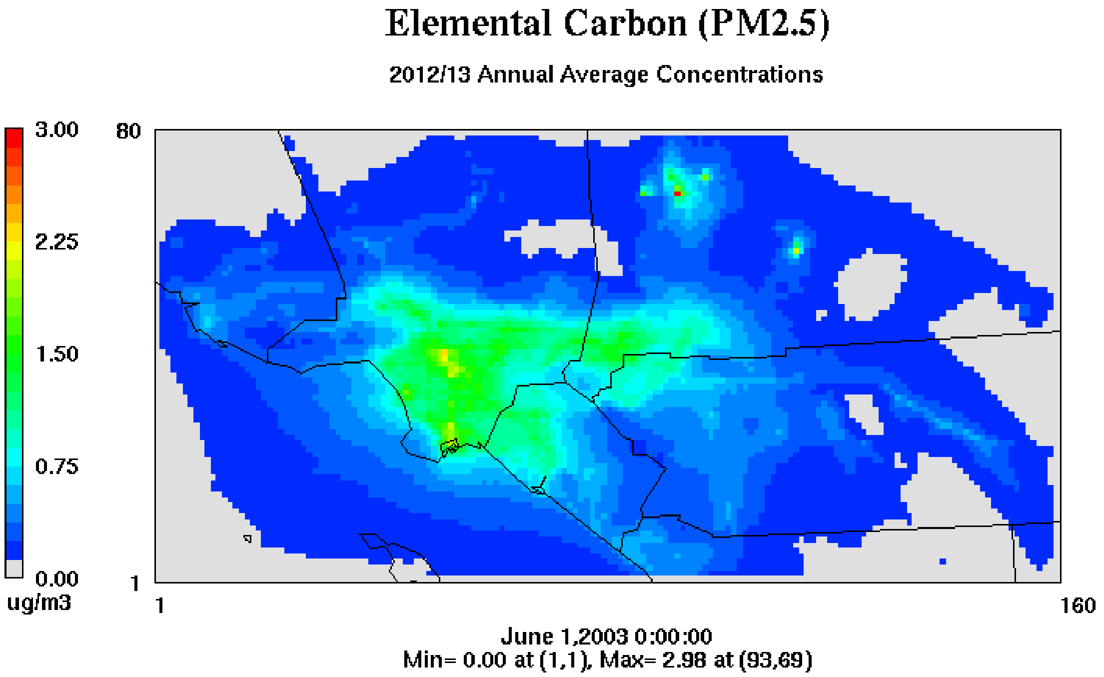


Figure IX-10b

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

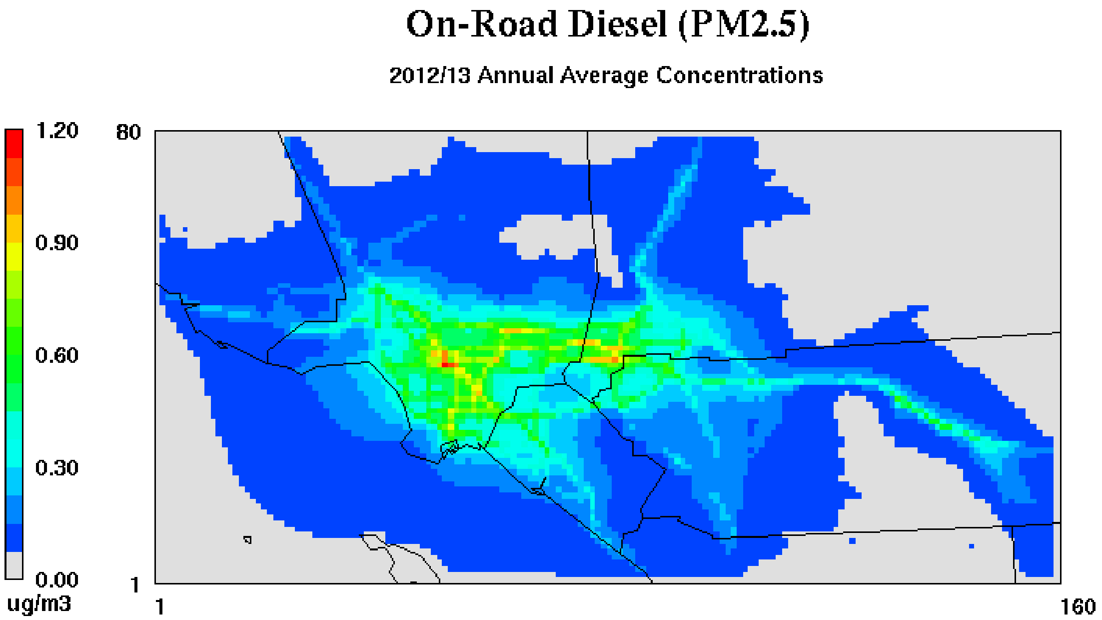


Figure IX-10c

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

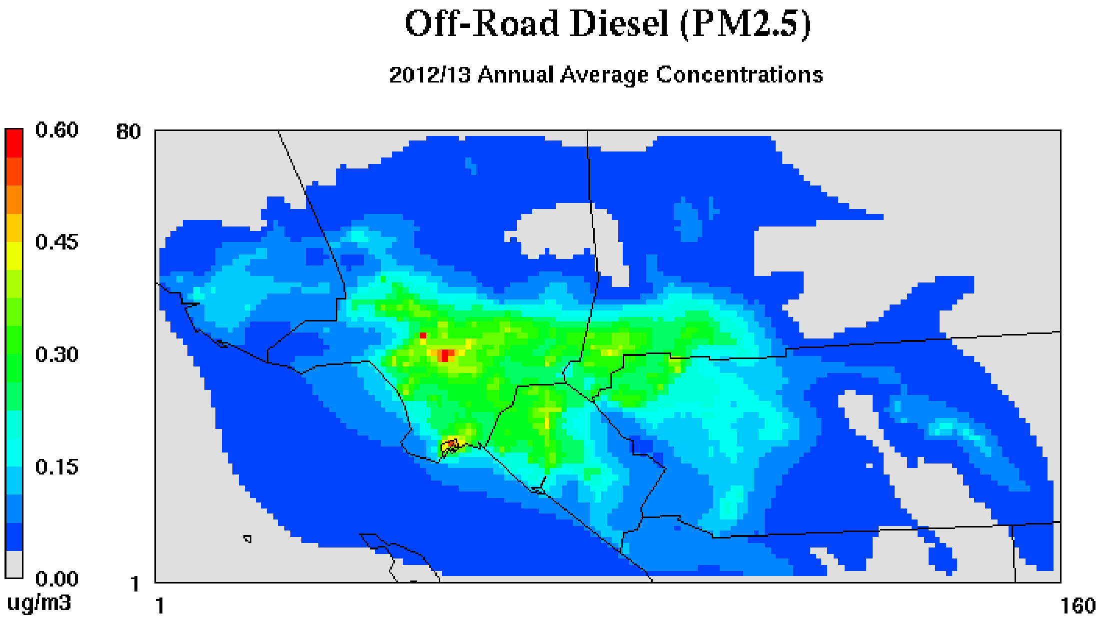


Figure IX-10d

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

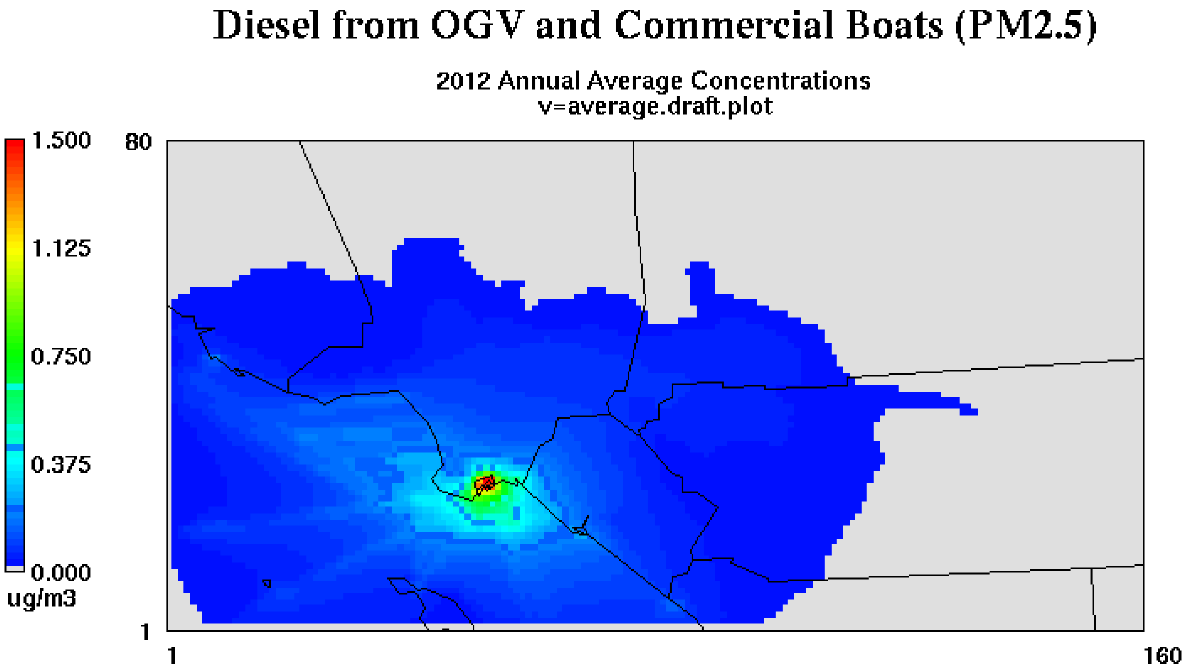


Figure IX-10e
CAMx simulated 2012 annual average Diesel from Ships $PM_{2.5.}$

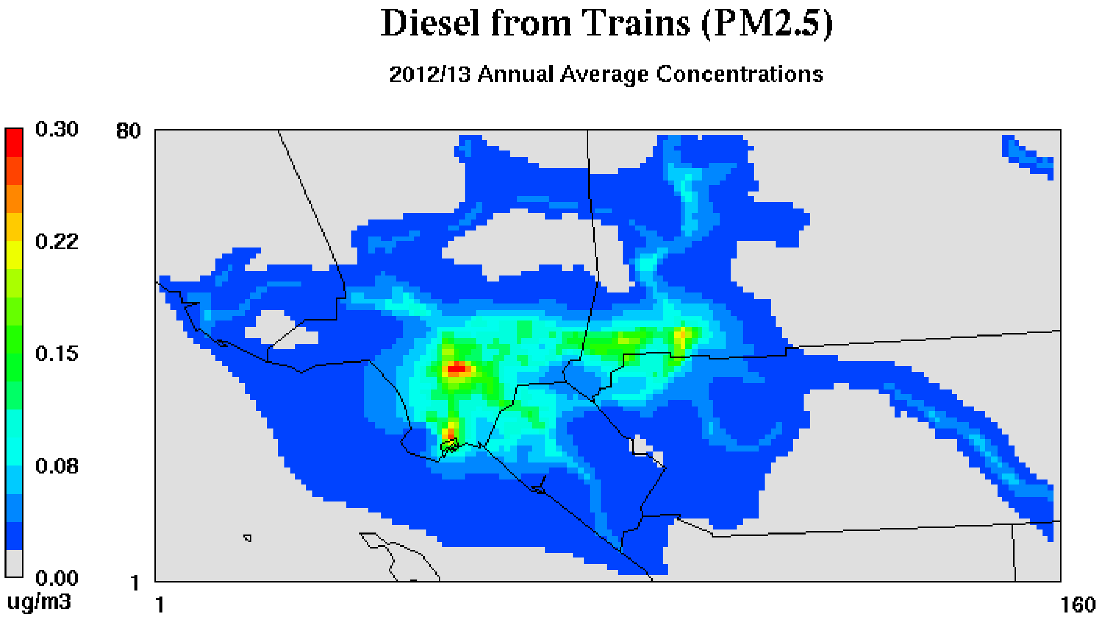


Figure IX-10f
CAMx simulated 2012 annual average Diesel from Trains $PM_{2.5}$.

Stationary Diesel (PM2.5)

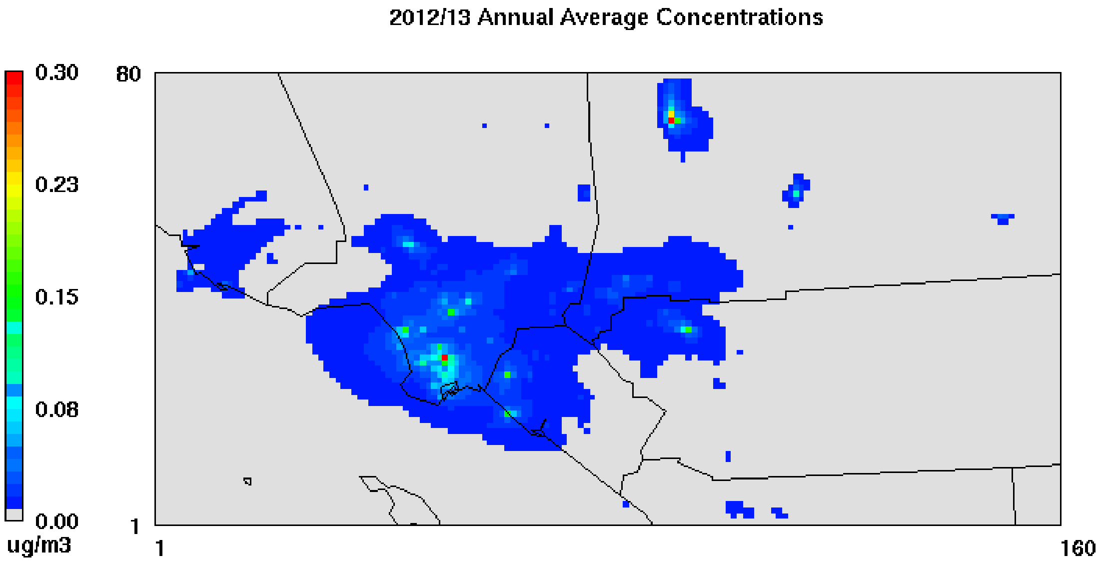


Figure IX-10g
CAMx simulated 2012 annual average Diesel from Stationary Sources $PM_{2.5}$.

Benzene

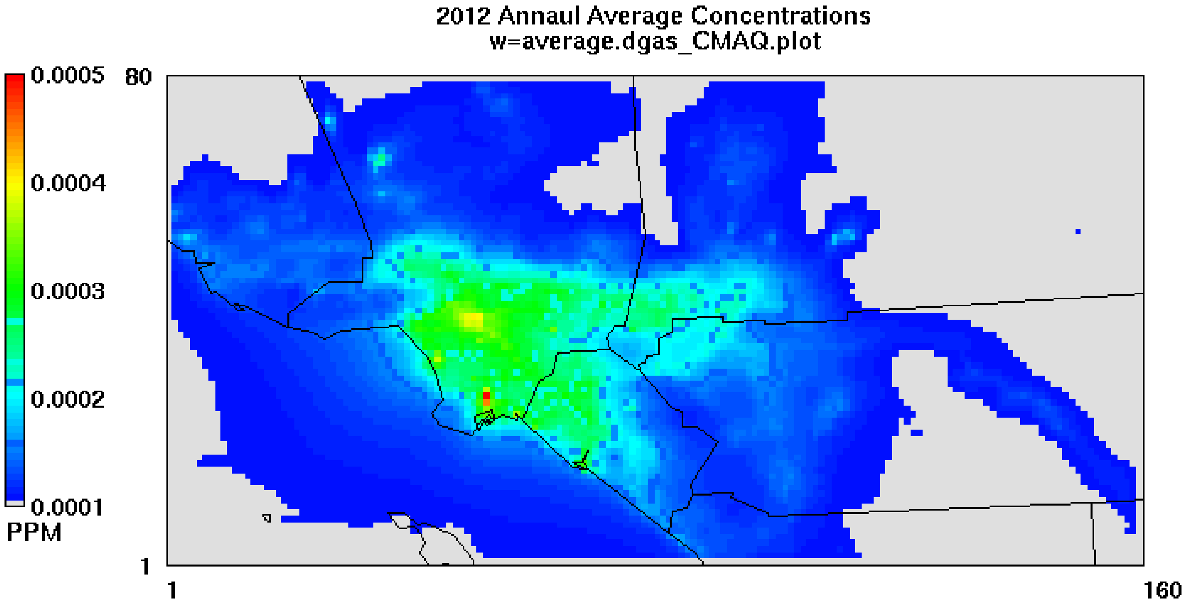


Figure IX-10h
CAMx simulated 2012 annual average Benzene.

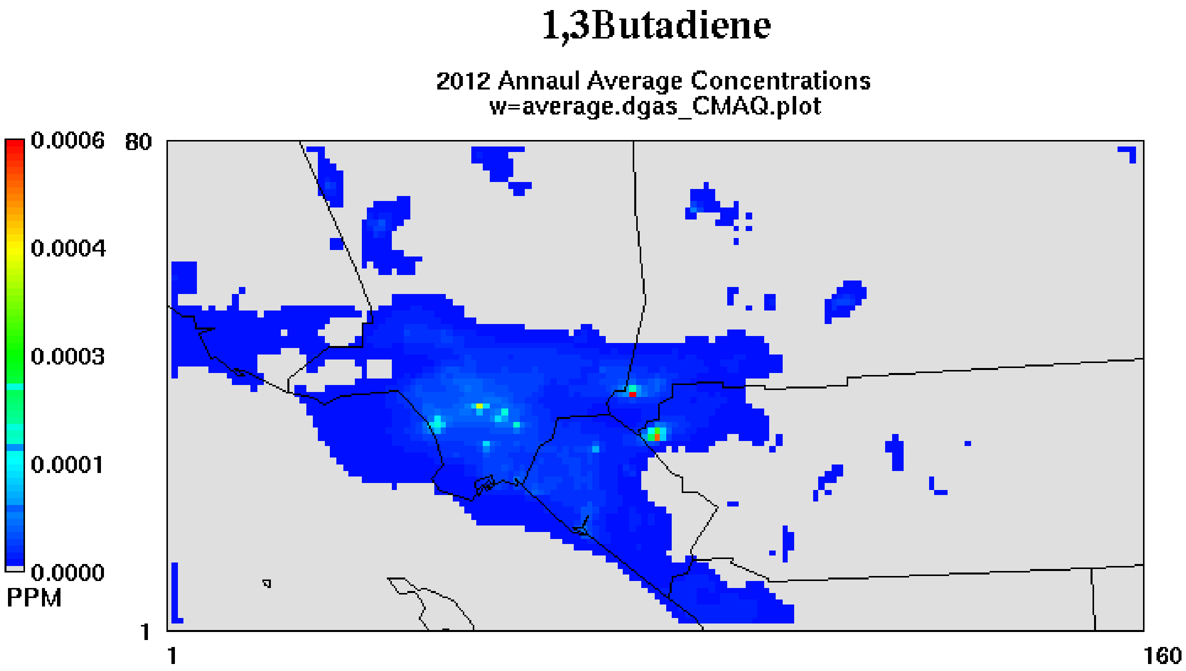


Figure IX-10i
CAMx simulated 2012 annual average 1,3-Butadiene.

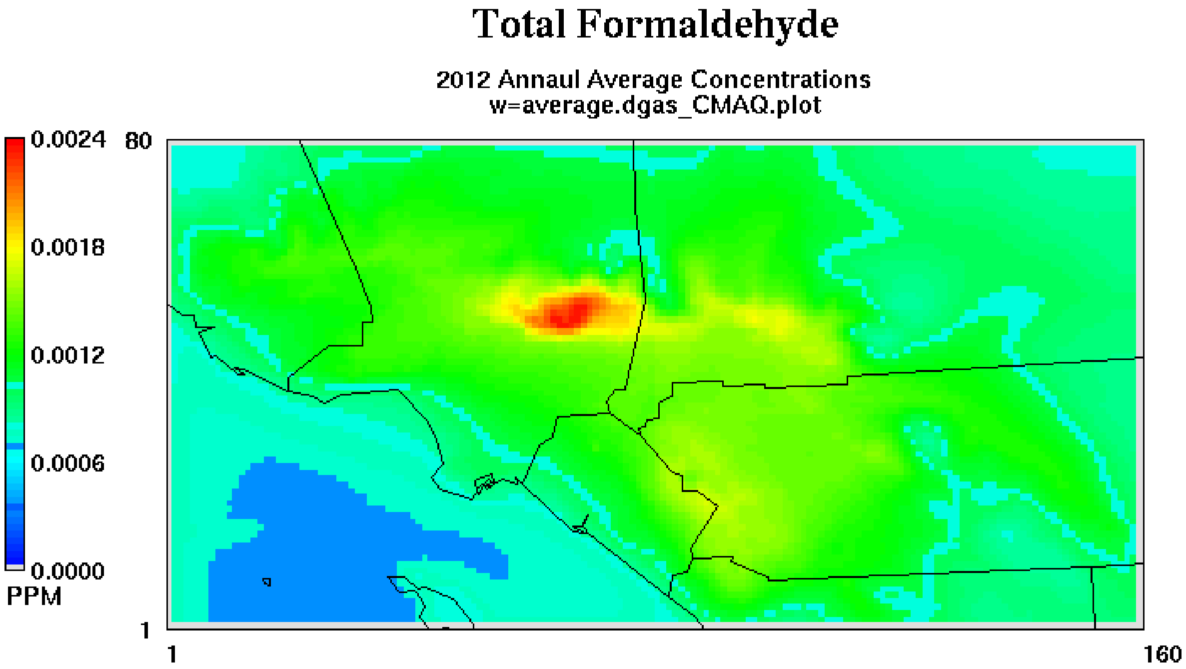


Figure IX-10j
CAMx simulated 2012 annual average for Total Formaldehyde.

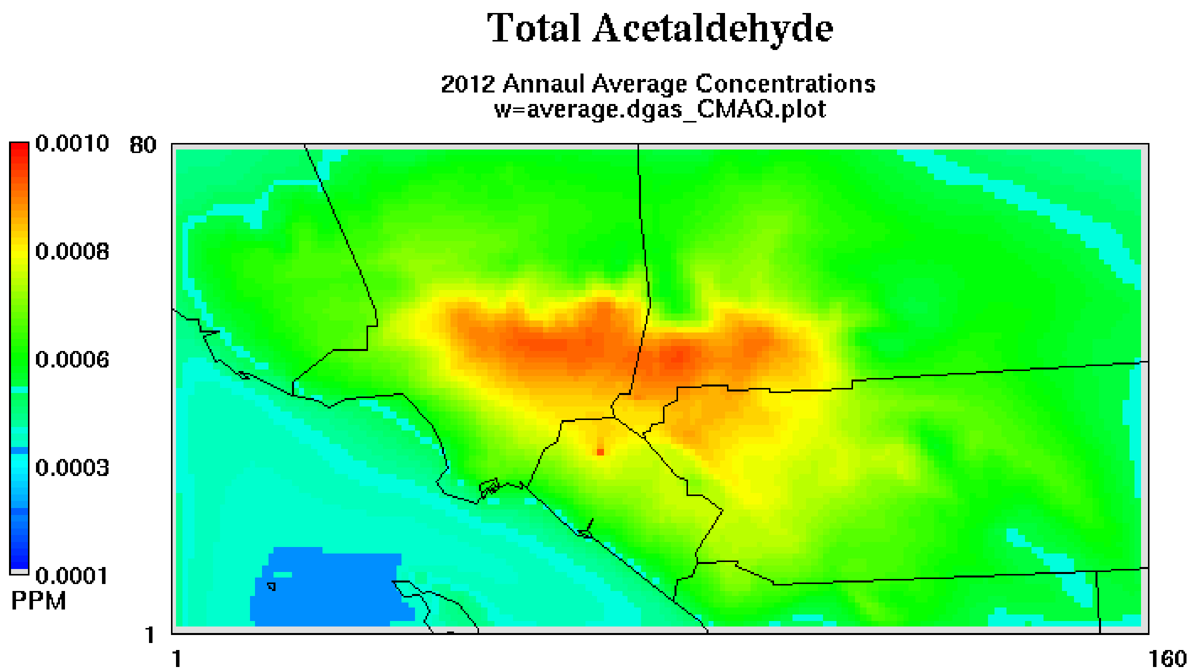


Figure IX-10k
CAMx simulated 2012 annual average Acetaldehyde.

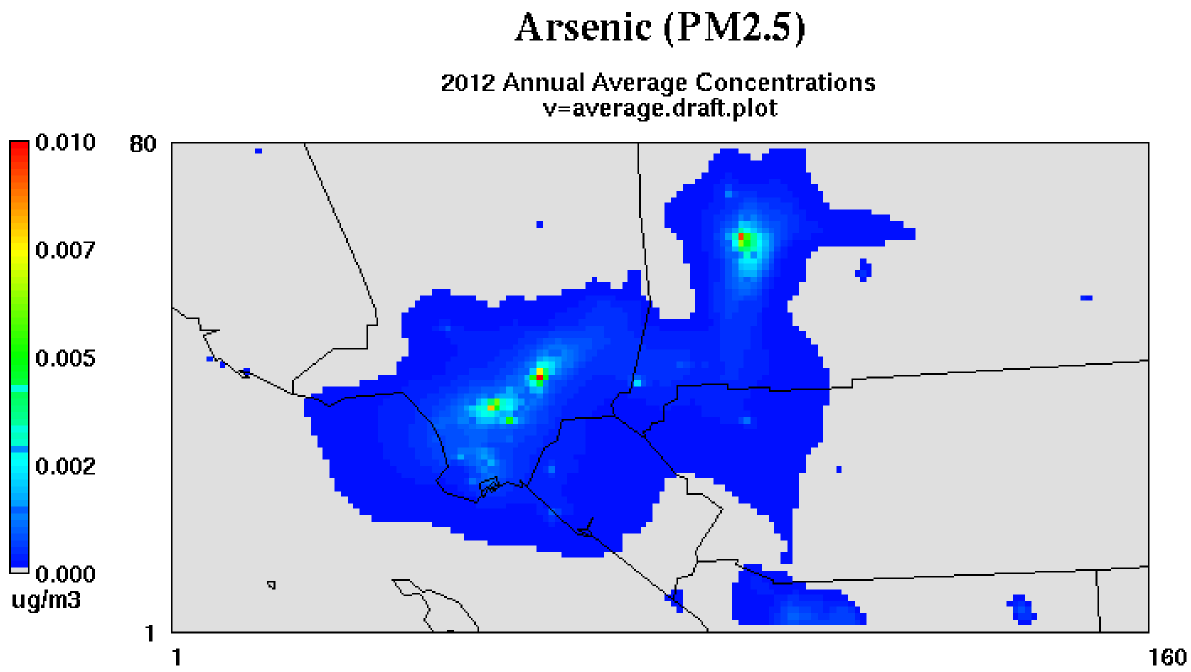


Figure IX-10l
CAMx simulated 2012 annual average Arsenic $PM_{2.5}$.

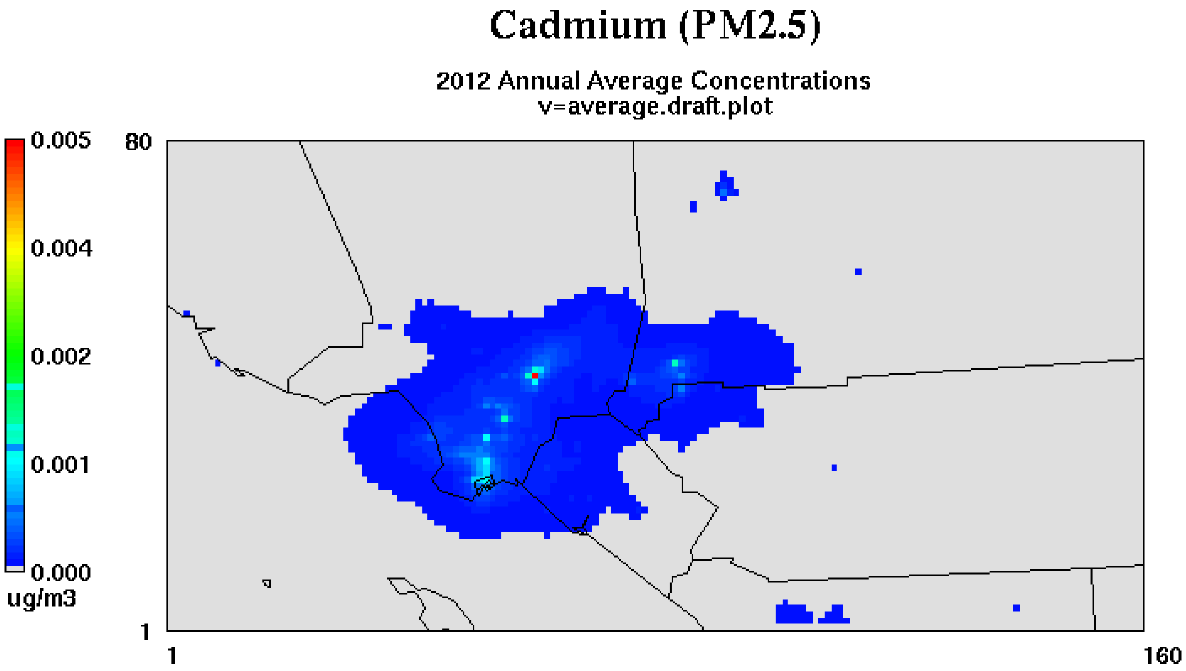


Figure IX-10m
CAMx simulated 2012 annual average Cadmium $PM_{2.5}$.

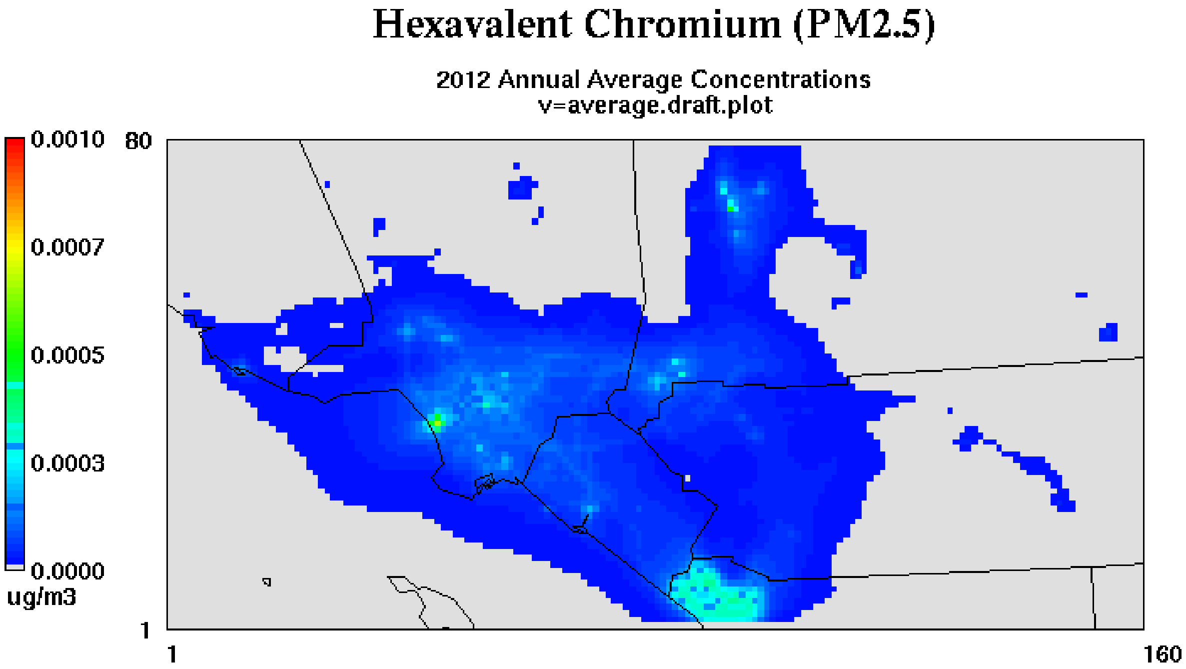


Figure IX-10n
CAMx simulated 2012 annual average Chromium $PM_{2.5}$.

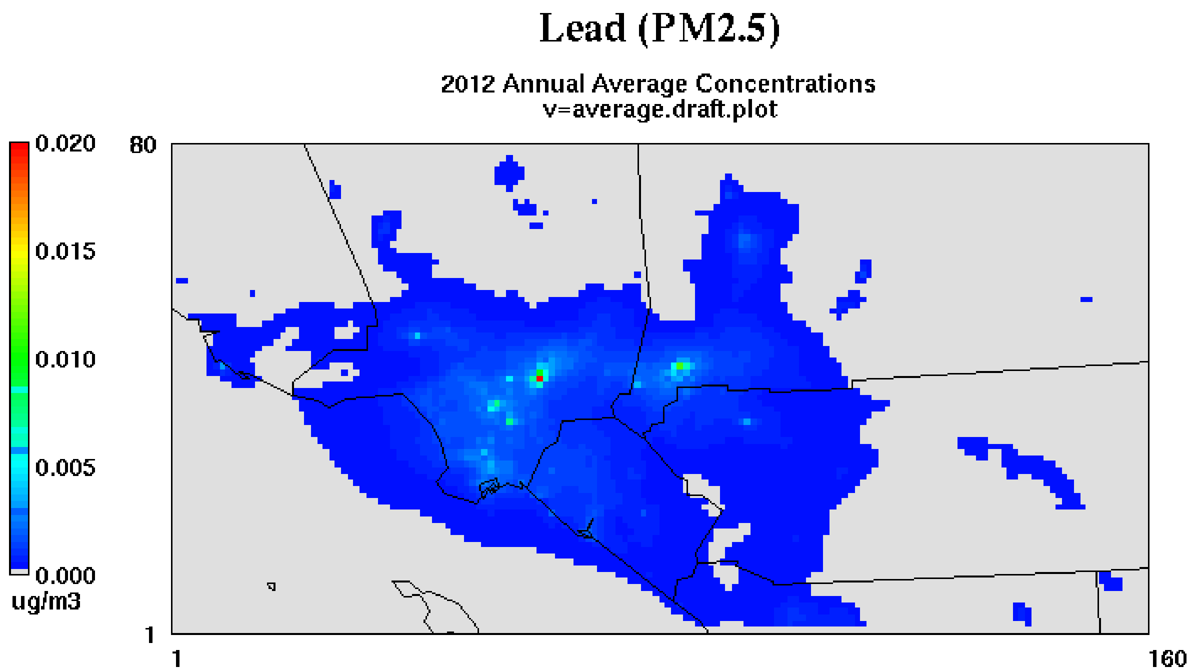


Figure IX-10o
CAMx simulated 2012 annual average Lead $PM_{2.5}$.

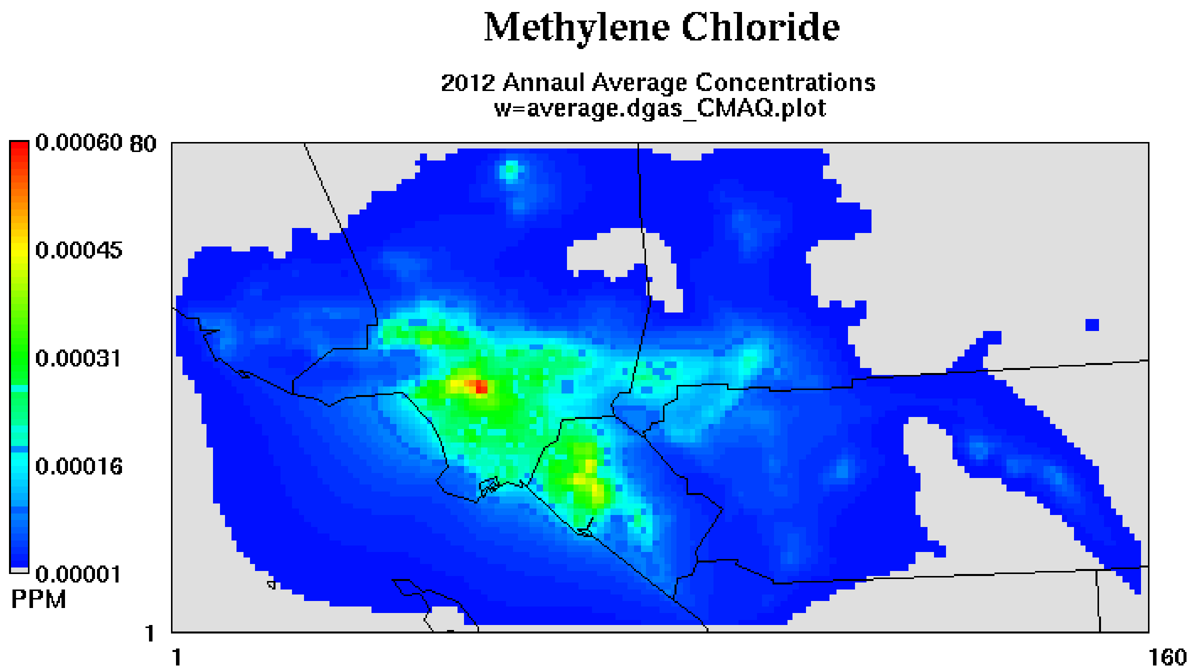


Figure IX-10p
CAMx simulated 2012 annual average Methylene Chloride.

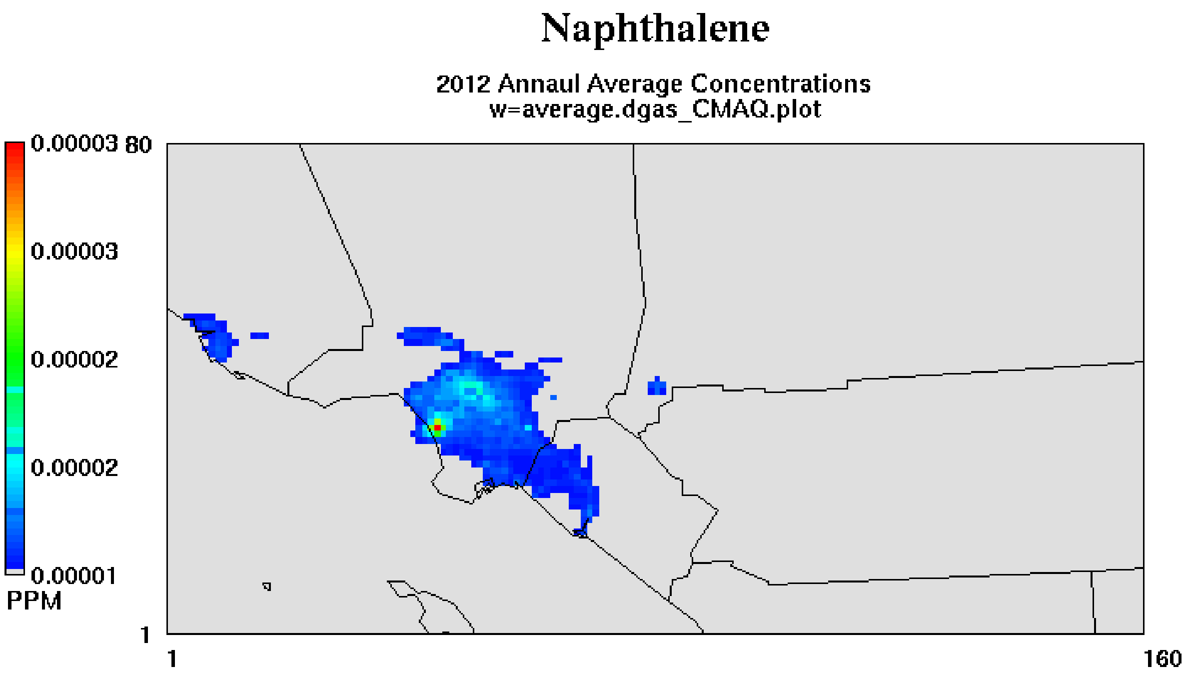


Figure IX-10q
CAMx simulated 2012 annual average Naphthalene.

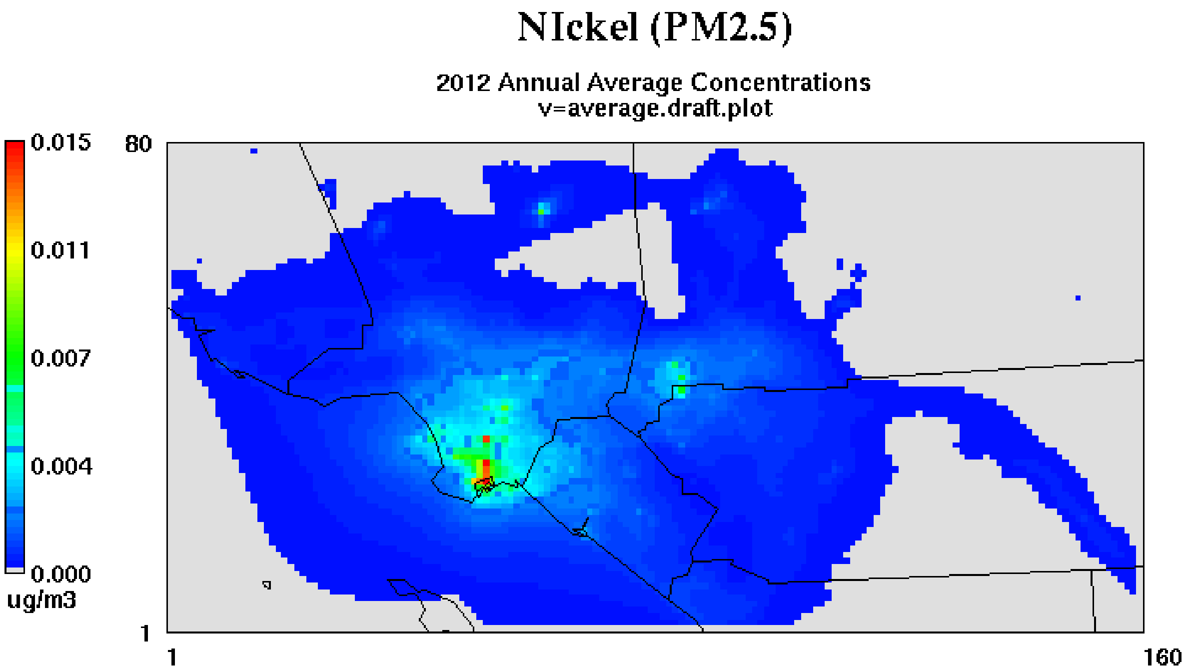


Figure IX-10r
CAMx simulated 2012 annual average Nickel $PM_{2.5}$.

p-Dichlorobenze

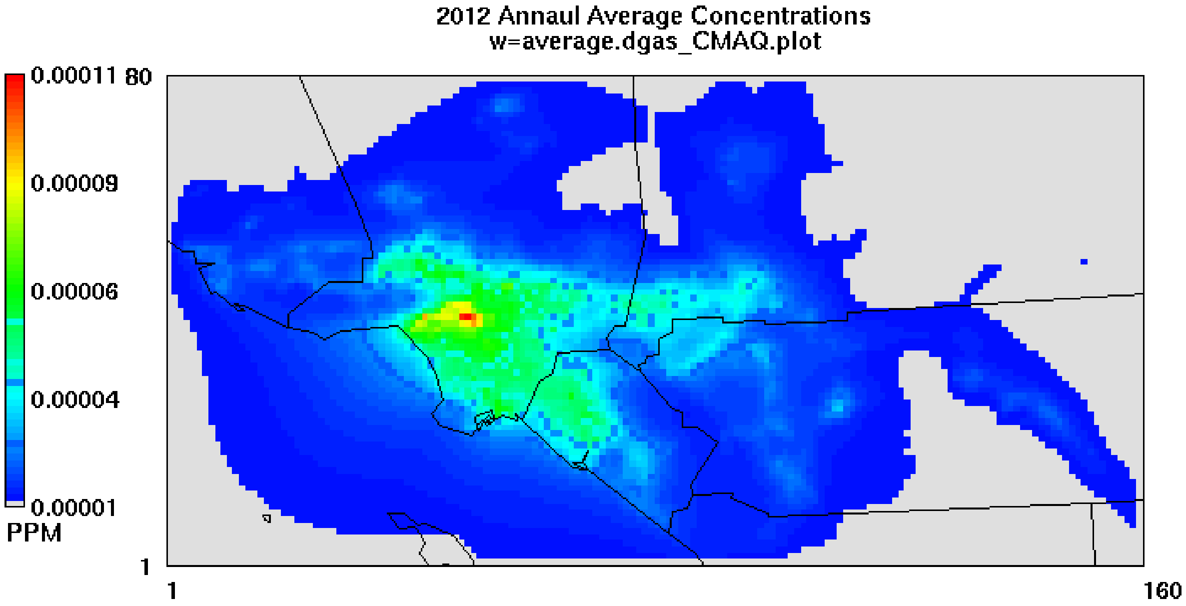


Figure IX-10s
CAMx simulated 2012 annual average p-Dichlorobenzene.

Perchloroethylene

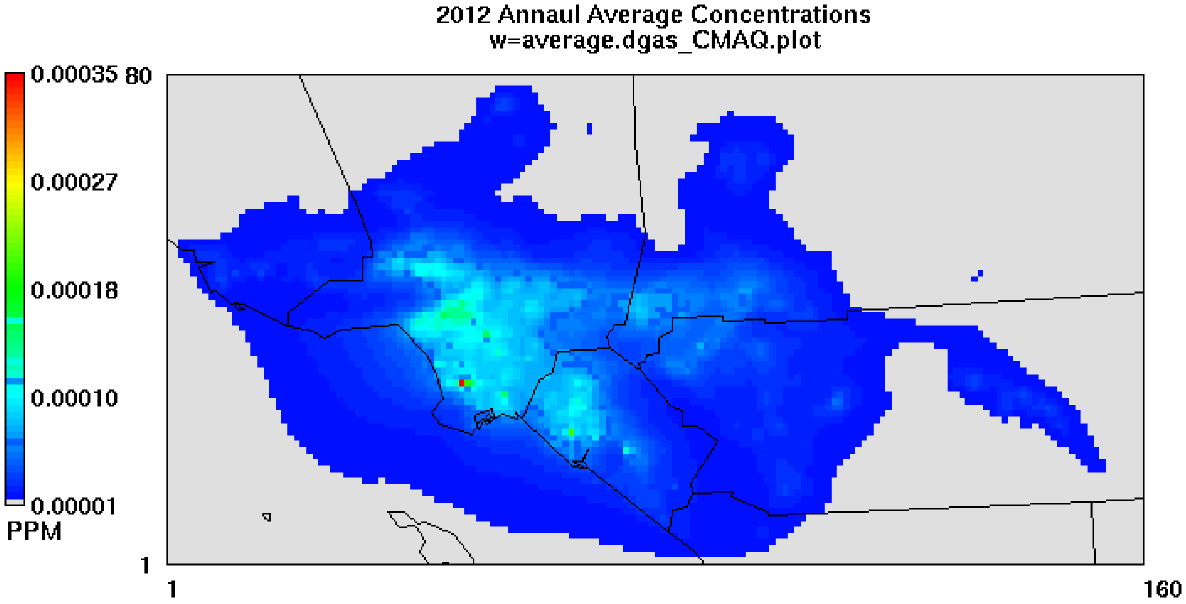


Figure IX-10t
CAMx simulated 2012 annual average Perchloroethylene.

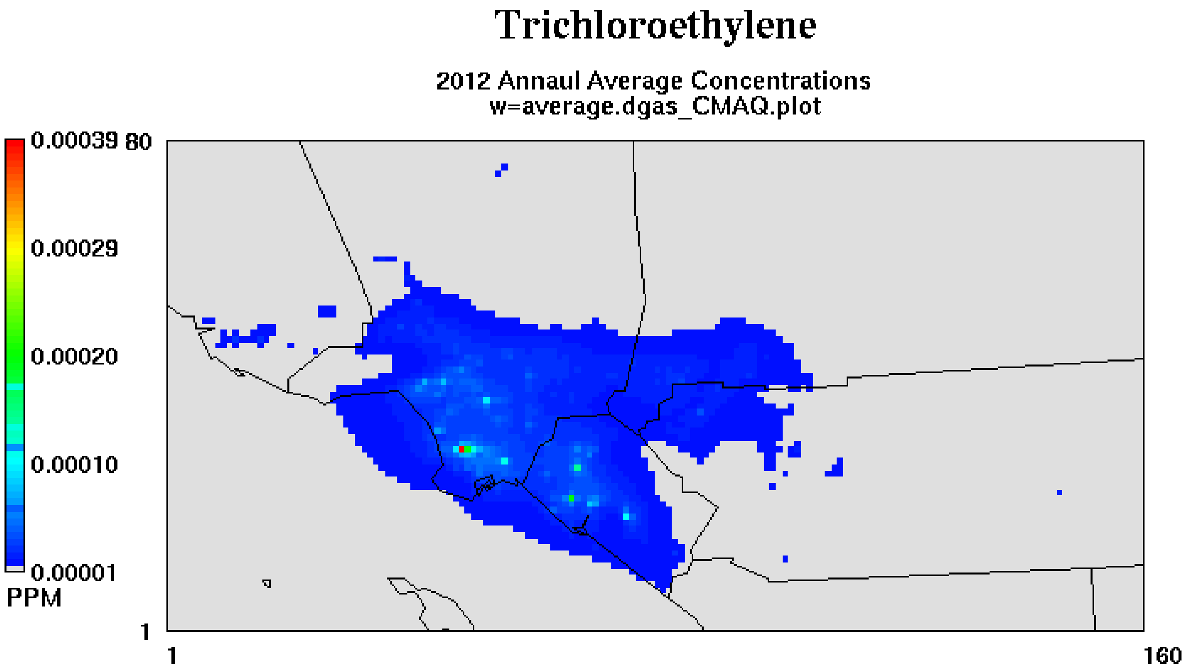


Figure IX-10u
CAMx simulated 2012 annual average Trichloroethylene.

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.

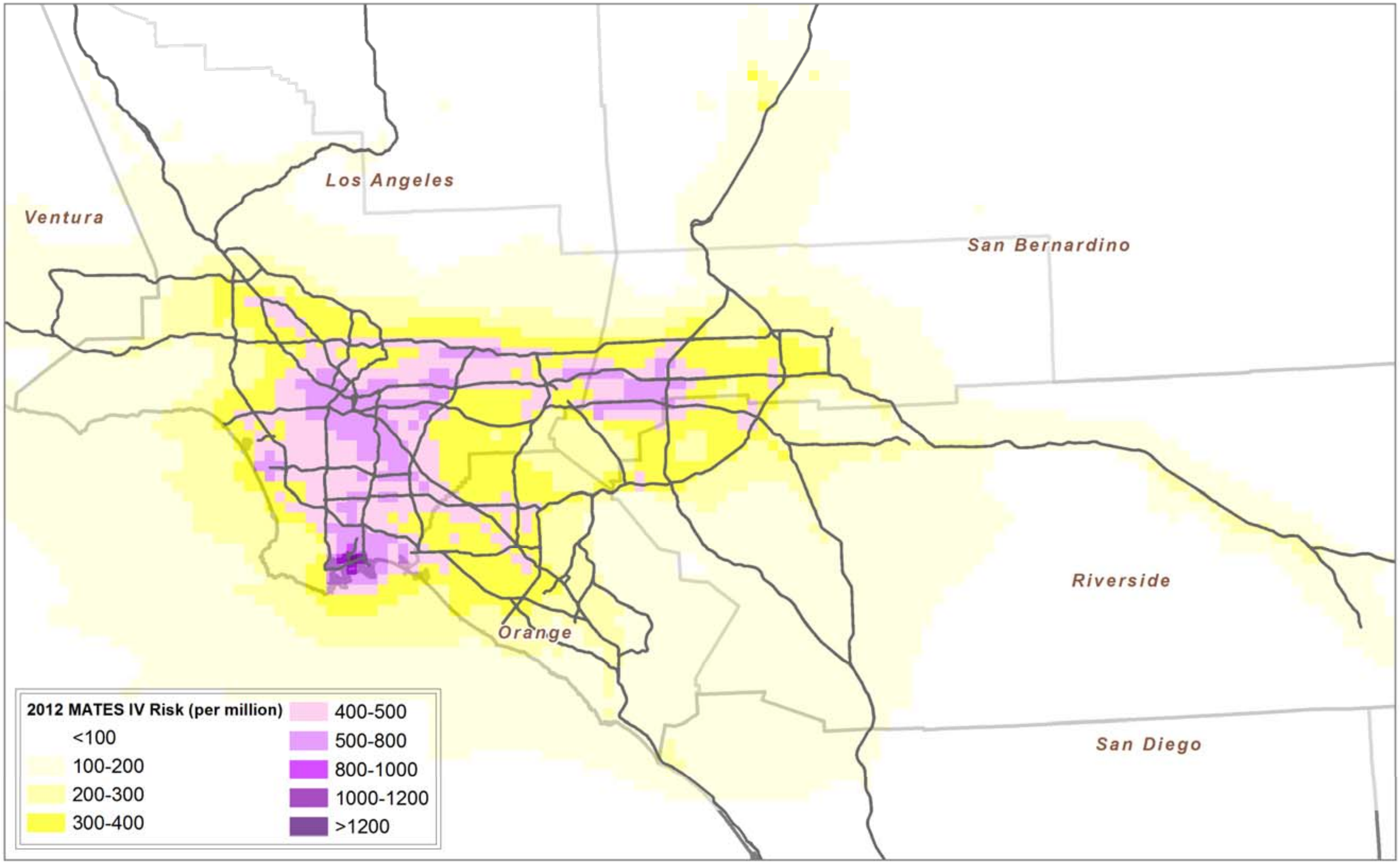


Figure IX-11
2012 MATES IV CAMx RTRAC Simulated Air Toxic Risk.

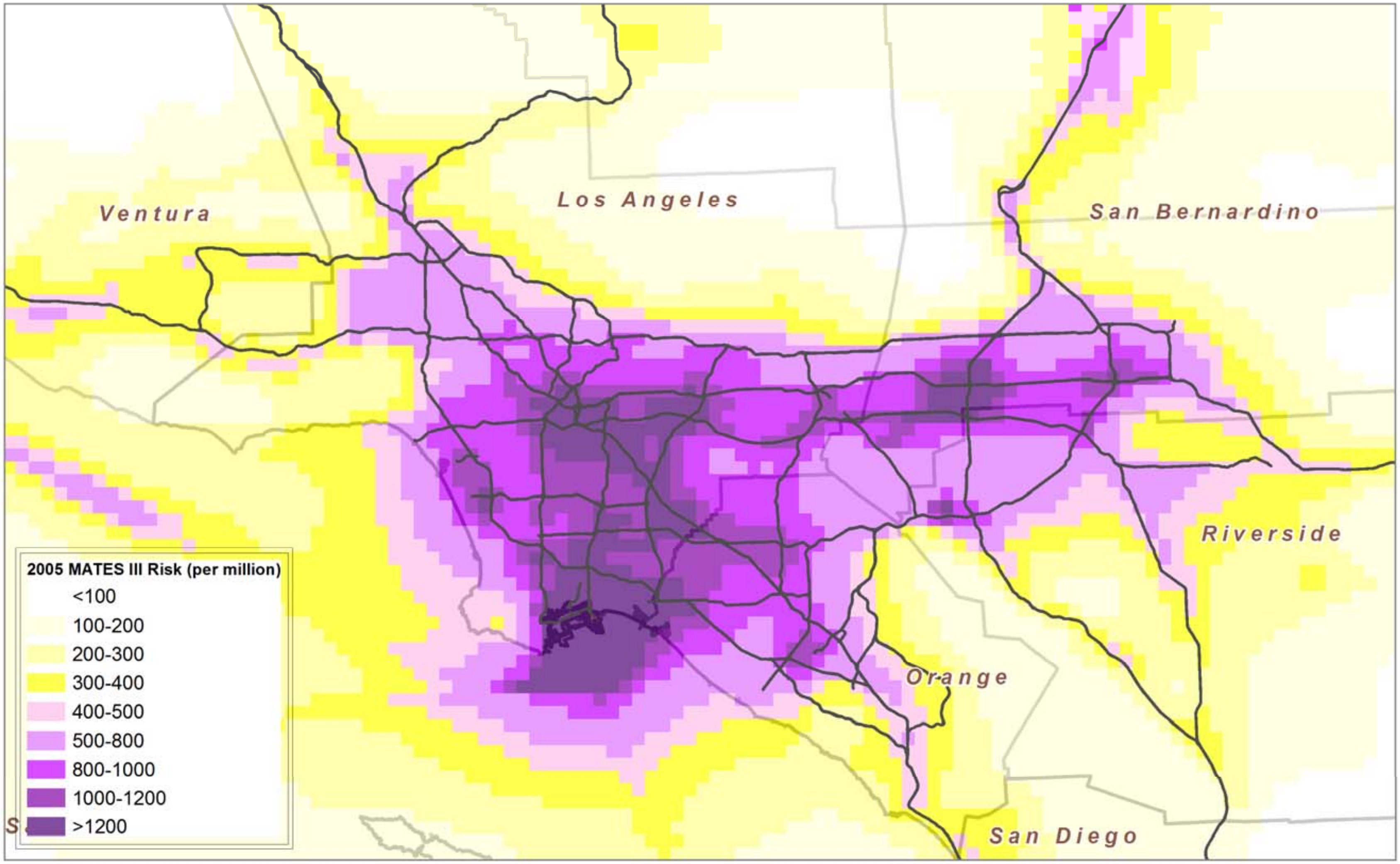


Figure IX-12
2005 CAMx RTRAC Simulated Air Toxic Risk.

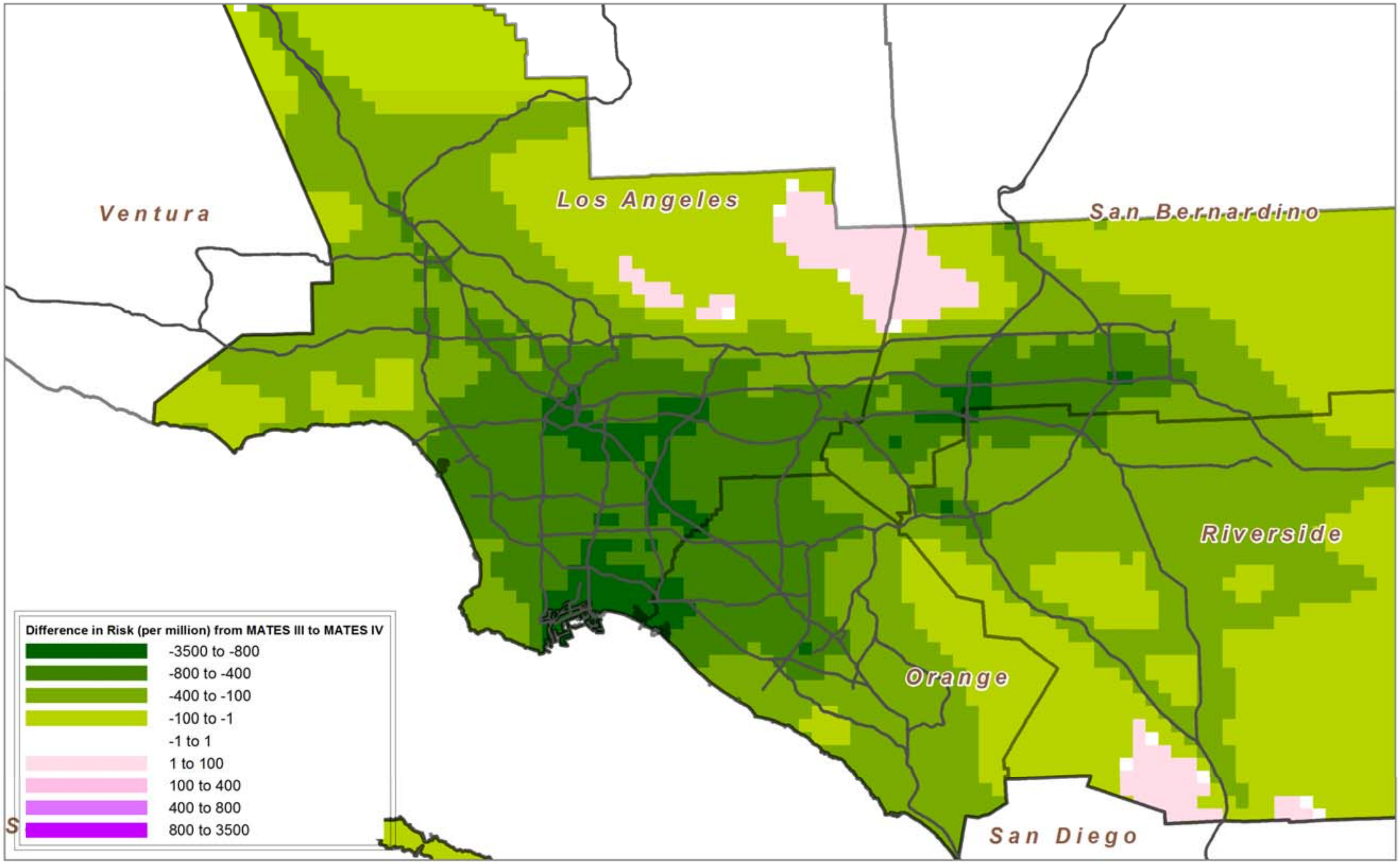


Figure IX-13
Change in CAMx RTRAC simulated risk from the 2005 to 2012

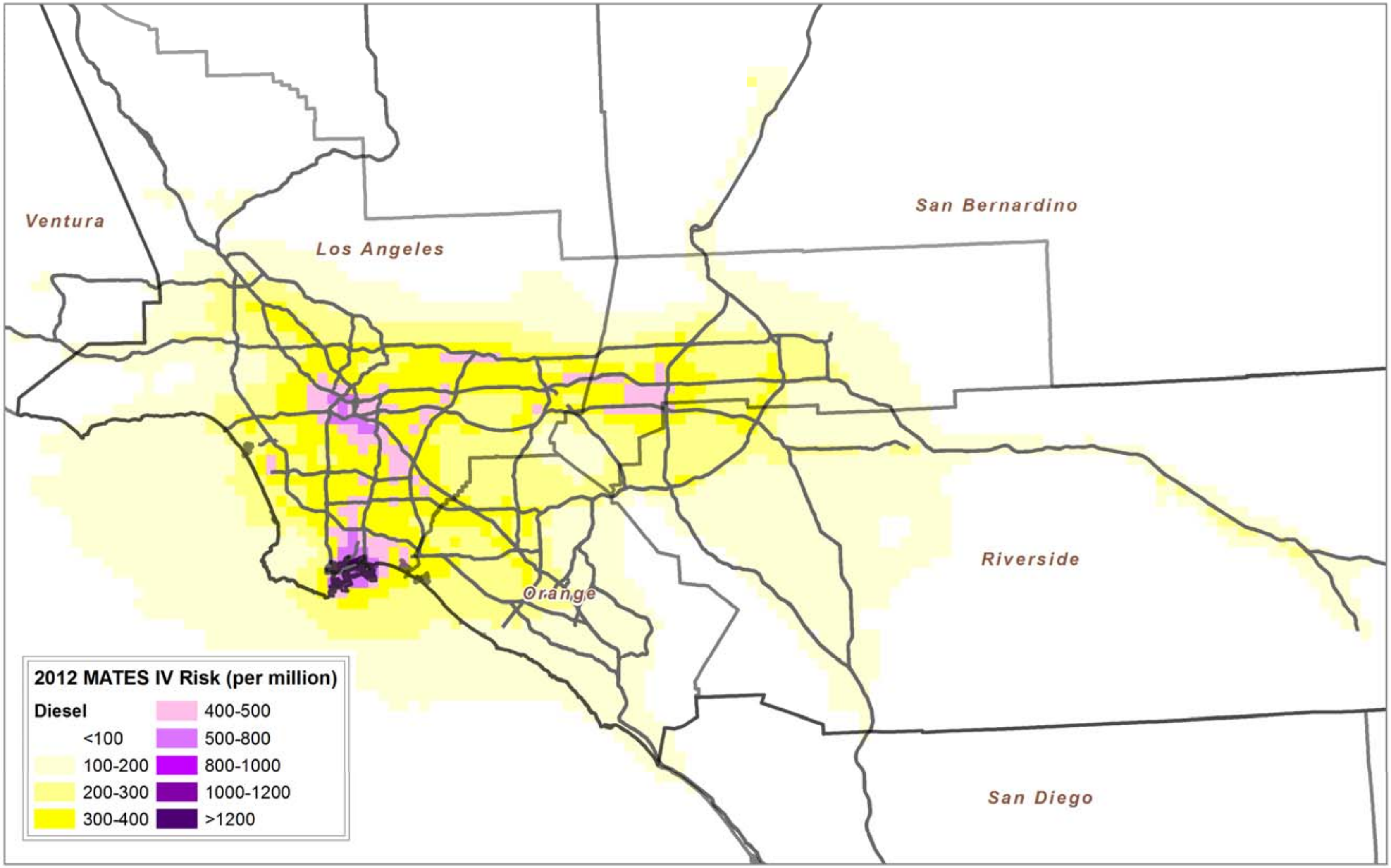


Figure IX-14a
MATES IV Risk from Diesel

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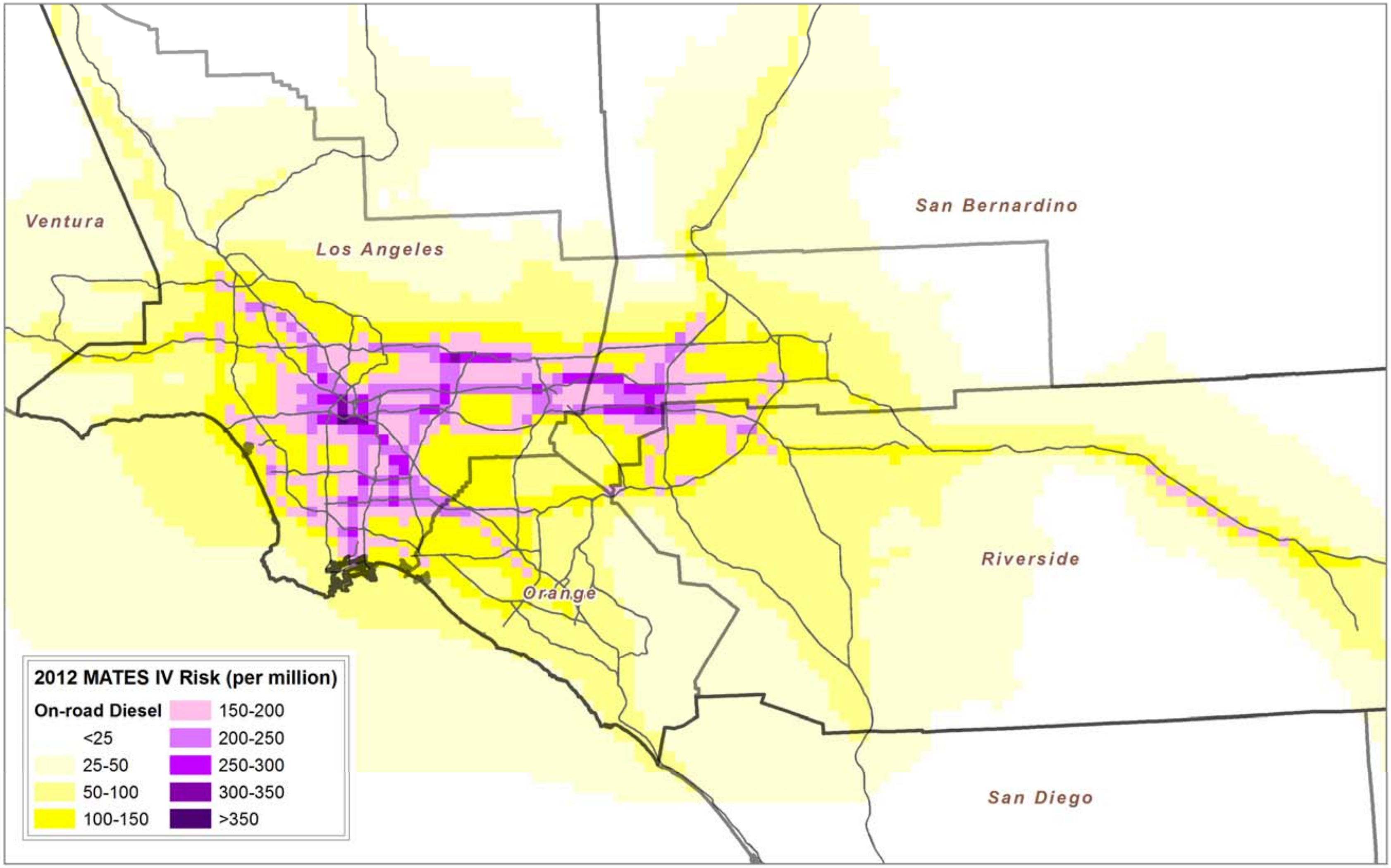

Figure IX-14b

MATES III Simulated Risk from On-Road Diesel.

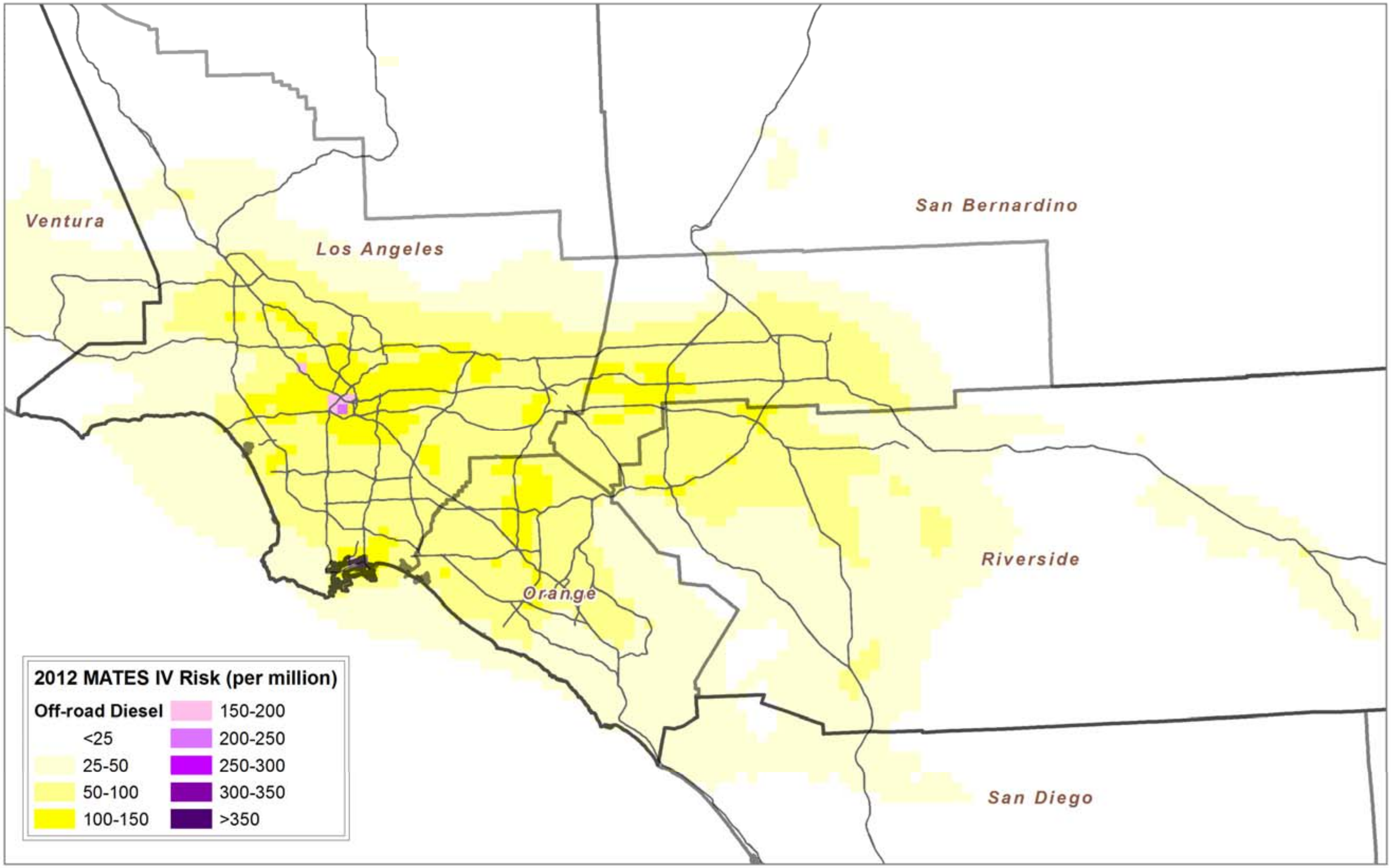

Figure IX-14c

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

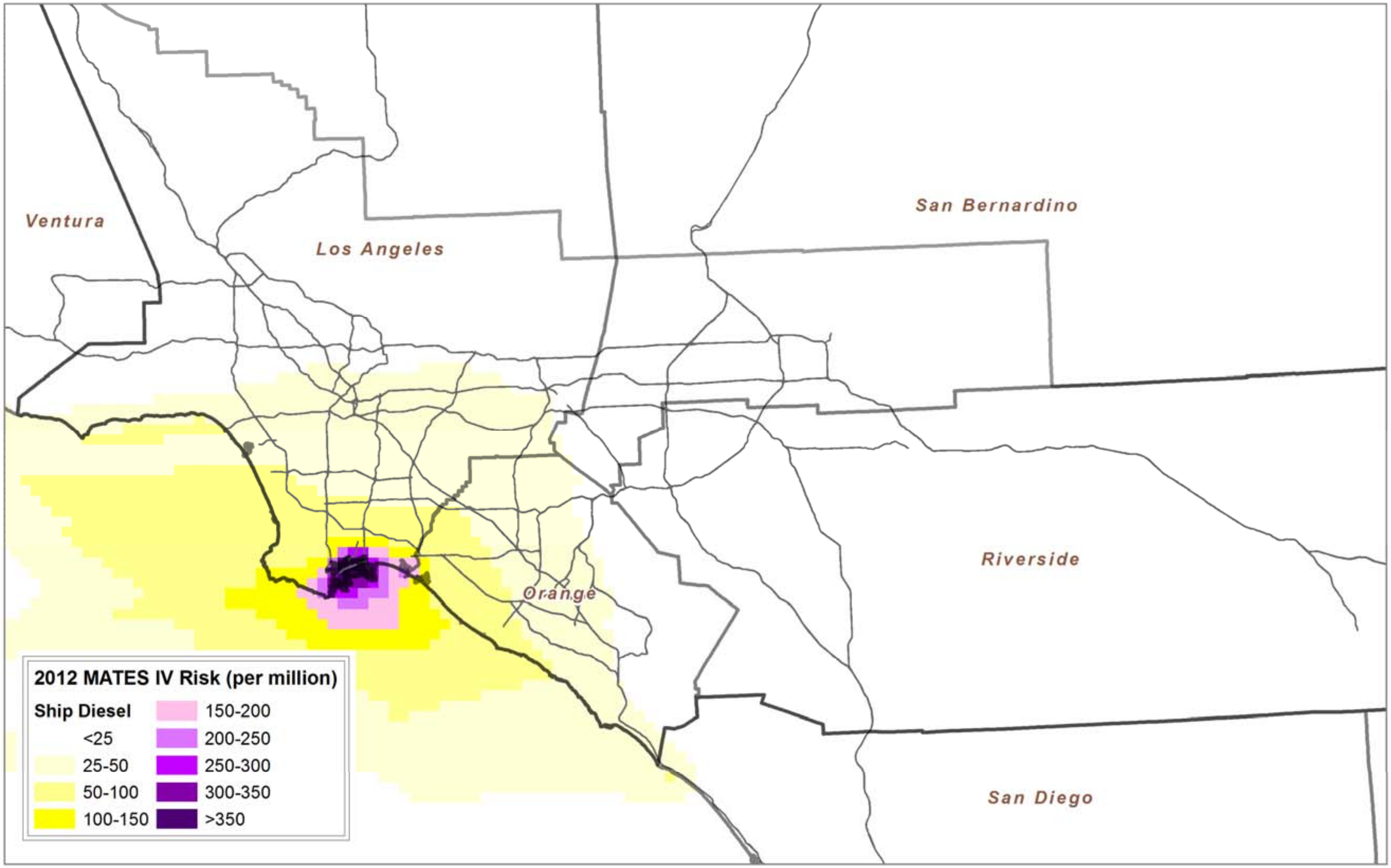

Figure IX-14d
MATES IV Simulated Risk from Ship Diesel.

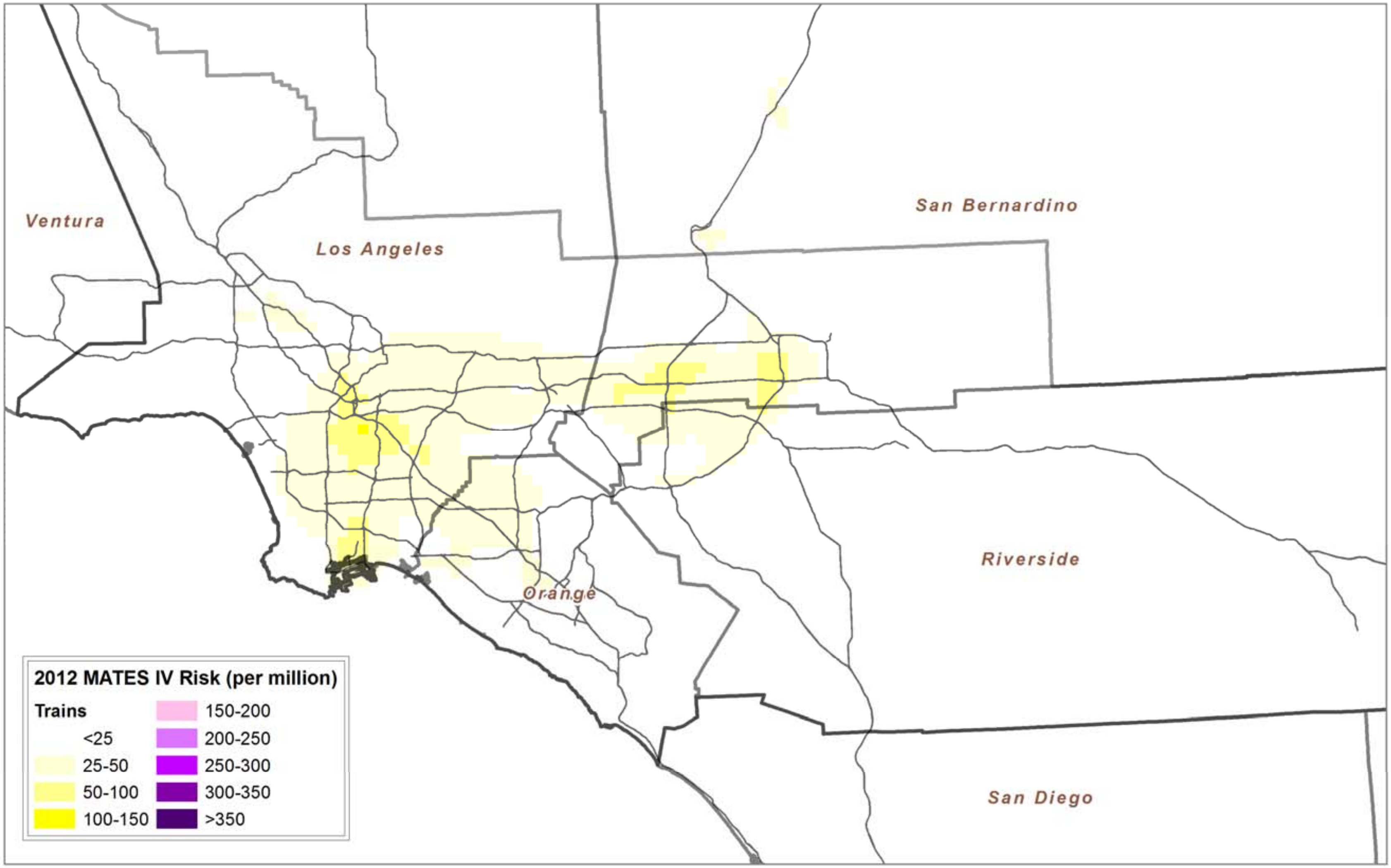

Figure IX-14e
MATES IV Simulated Risk from Trains (Excluding Railyards Equipments).

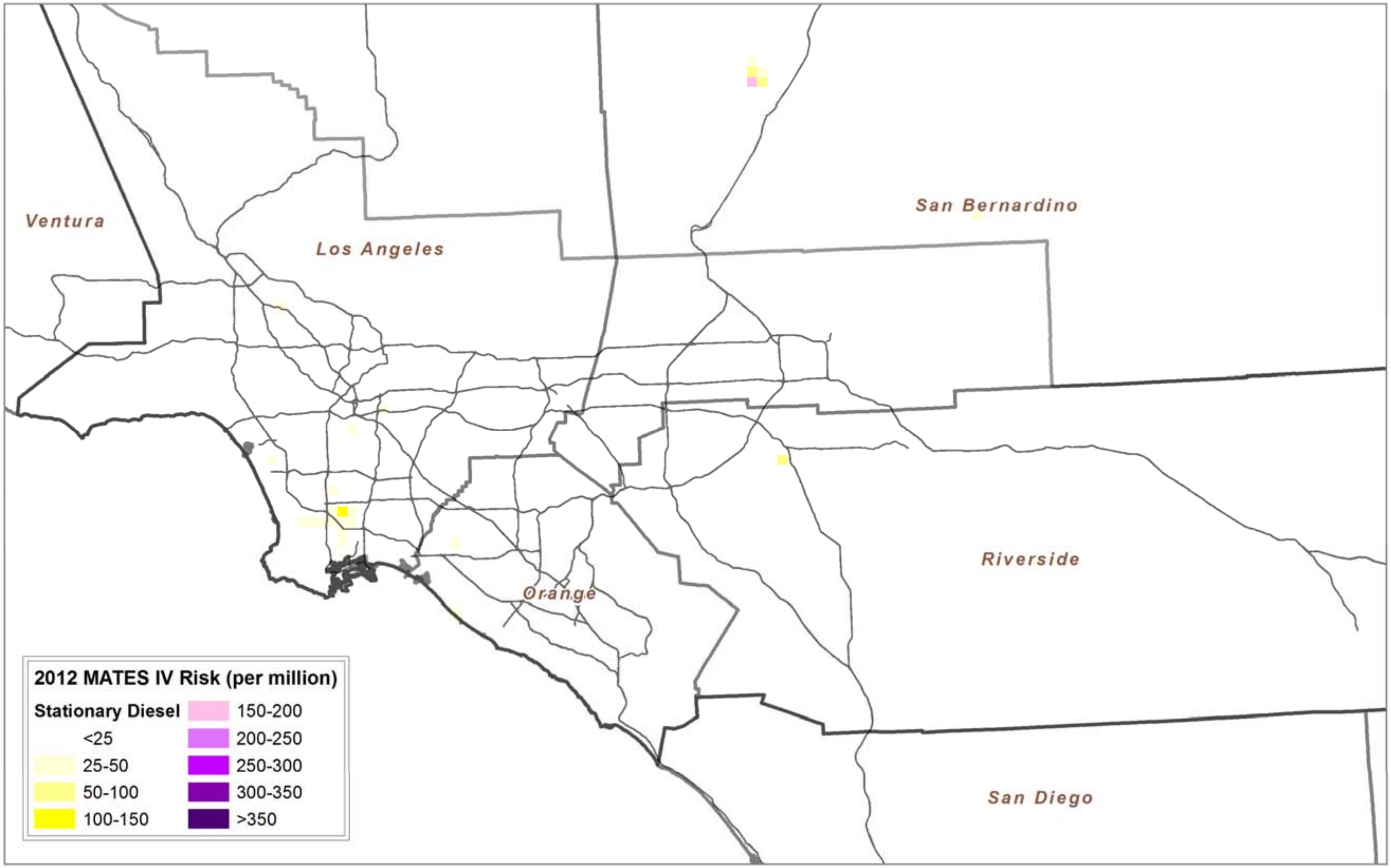

Figure IX-14f
MATES IV Simulated Risk from Stationary Diesel.

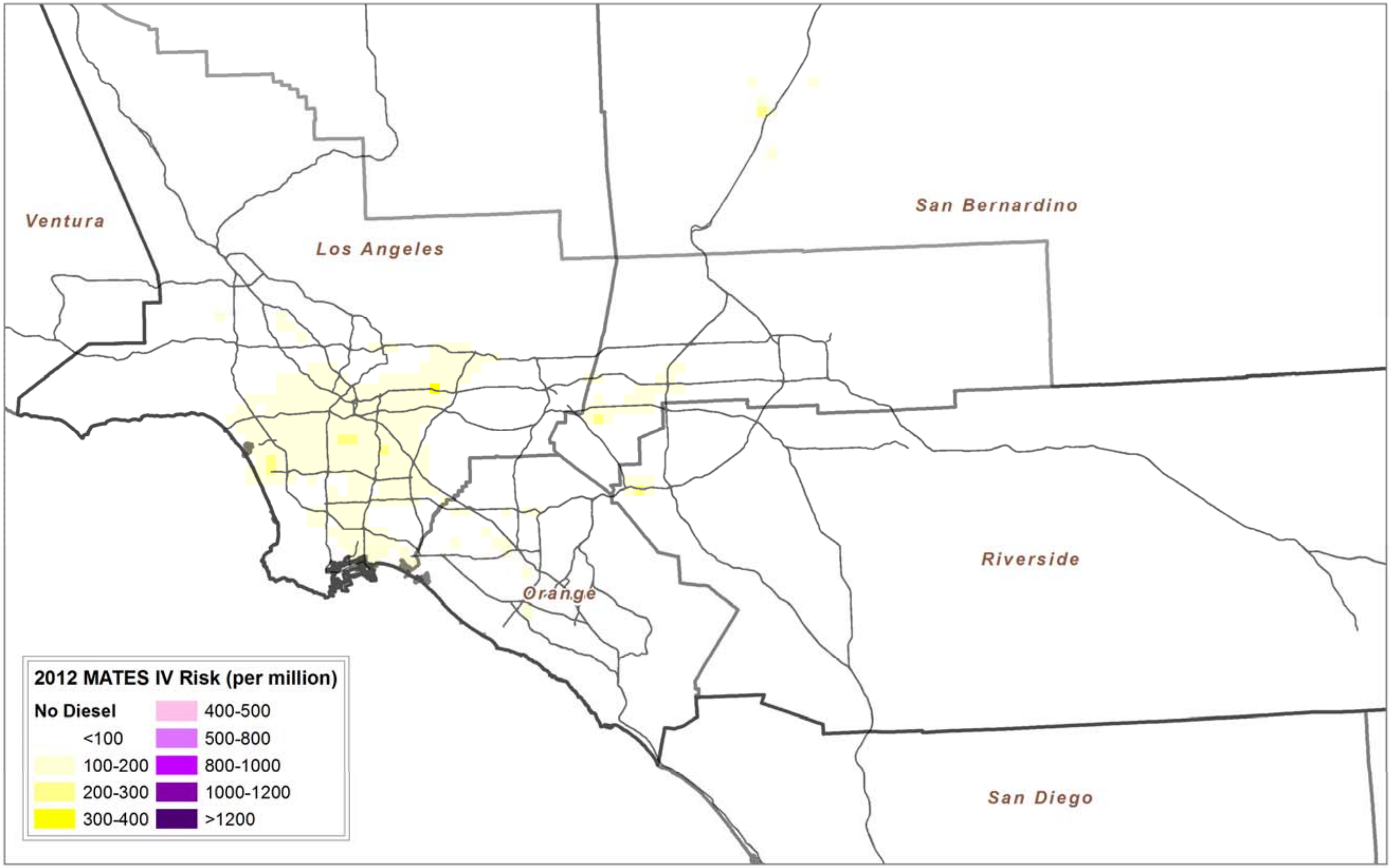

Figure IX-15
MATES IV Simulated Risk No-Diesel.

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%.

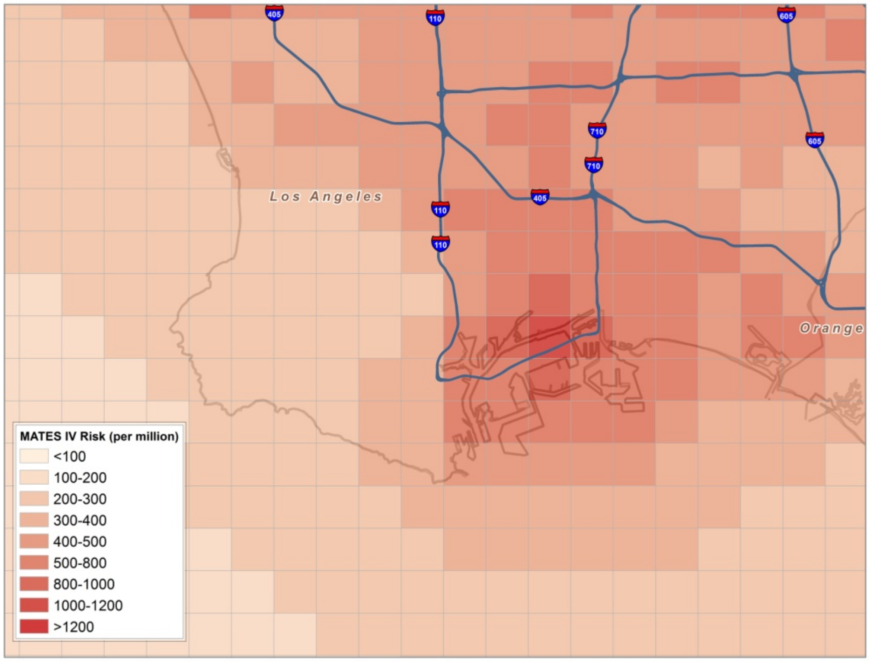

Figure IX-16
2012 Ports area MATES IV Simulated Air Toxic Risk.

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

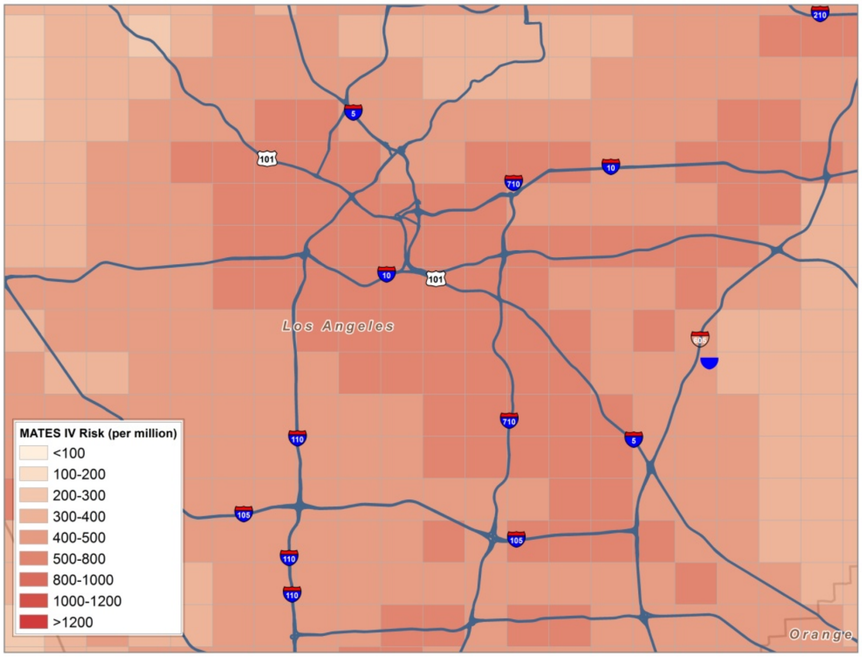

Figure IX-17
2012 Central Los Angeles MATES IV Simulated Air Toxic Risk.

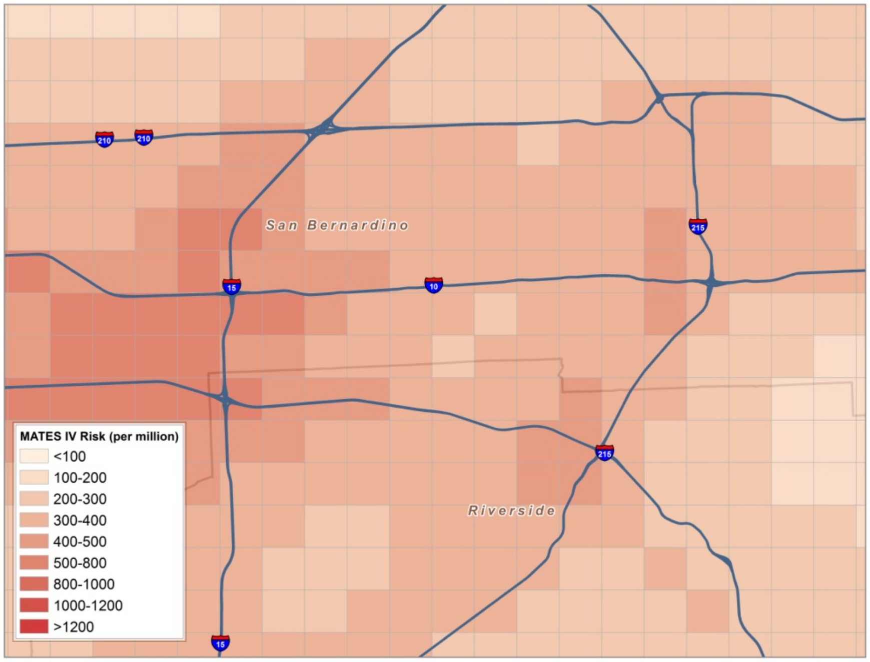

Figure IX-18
2012 Mira Loma/Colton MATES IV Simulated Air Toxic Risk.

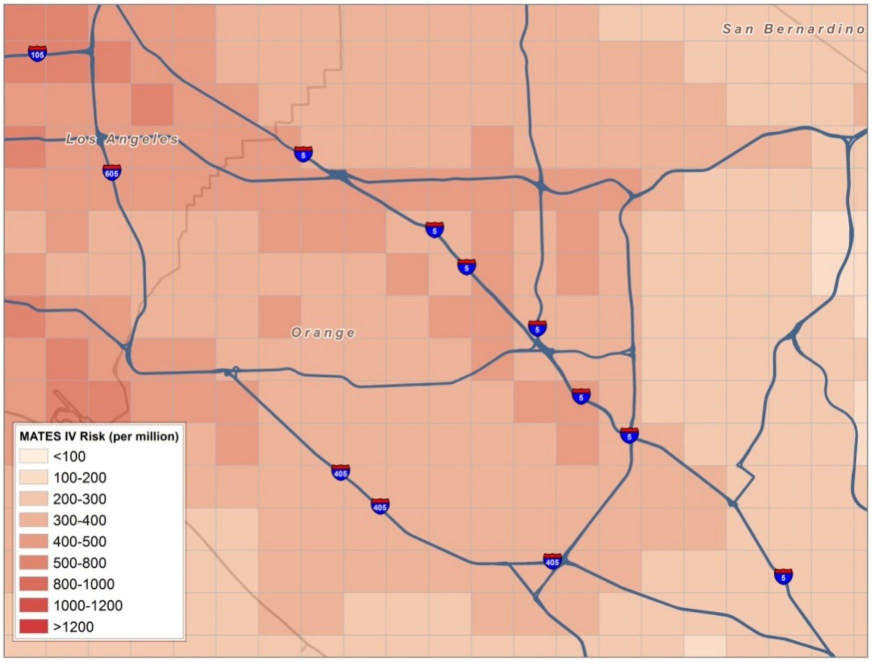

Figure IX-19
2012 Central Orange County MATES IV Simulated Air Toxic Risk.

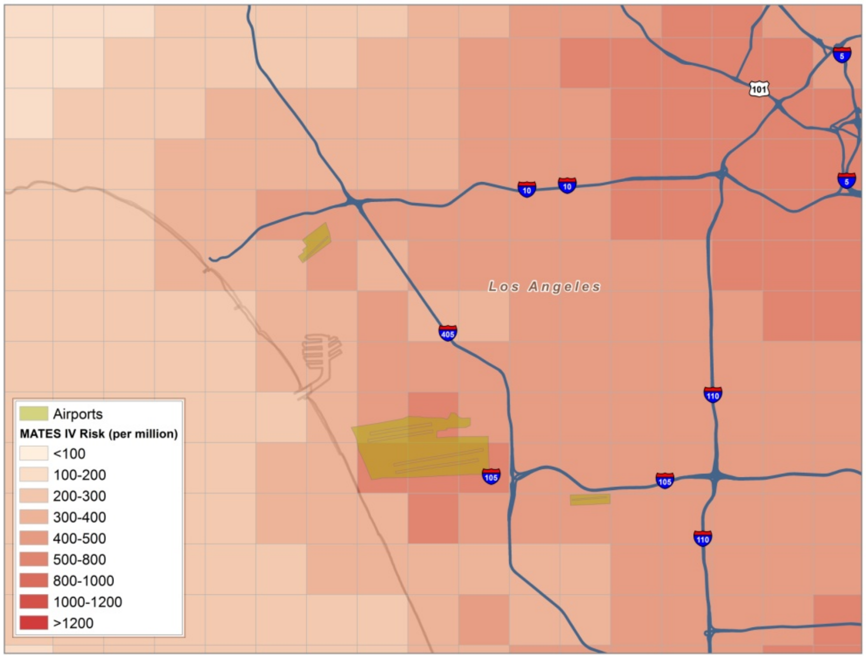

Figure IX-20
2012 West Los Angeles MATES IV Simulated Air Toxic Risk.

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

Location	2012-2013 MATES IV CAMX RTRAC Simulation				
	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.

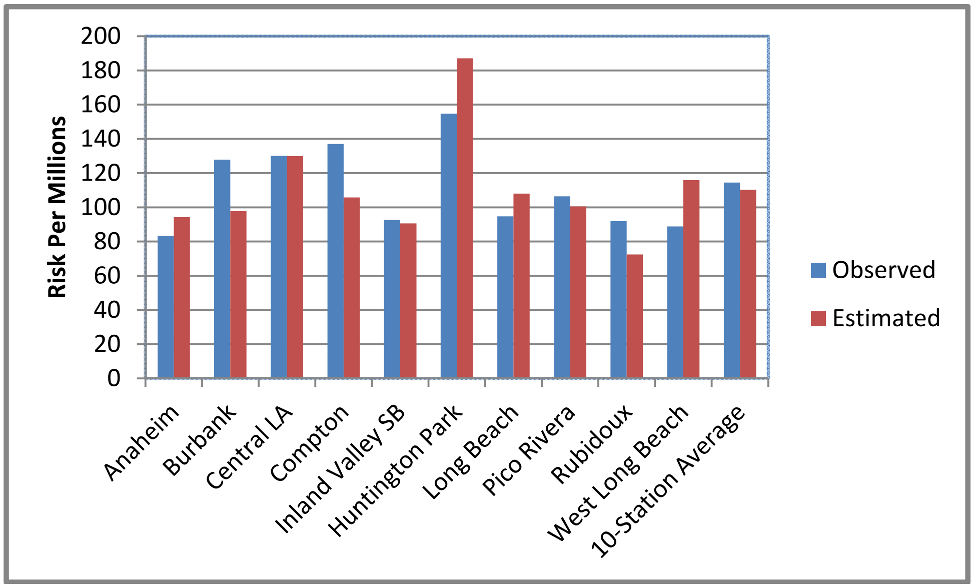

Figure IX-21
2012 MATES IV Simulated vs. Measured Non-Diesel Air Toxics Risk

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

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APPENDIX X

MATES IV

DRAFT REPORT

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

Author

Kalam Cheung

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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 $\mu g/m^3$. 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 $\mu g/m^3$, 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.

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 $\mu g/m^3$; 95% CI = 0.08 $\mu g/m^3$) than the nine other sites (avg. = 0.44 $\mu g/m^3$; 95% CI = 0.03 $\mu g/m^3$). 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

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

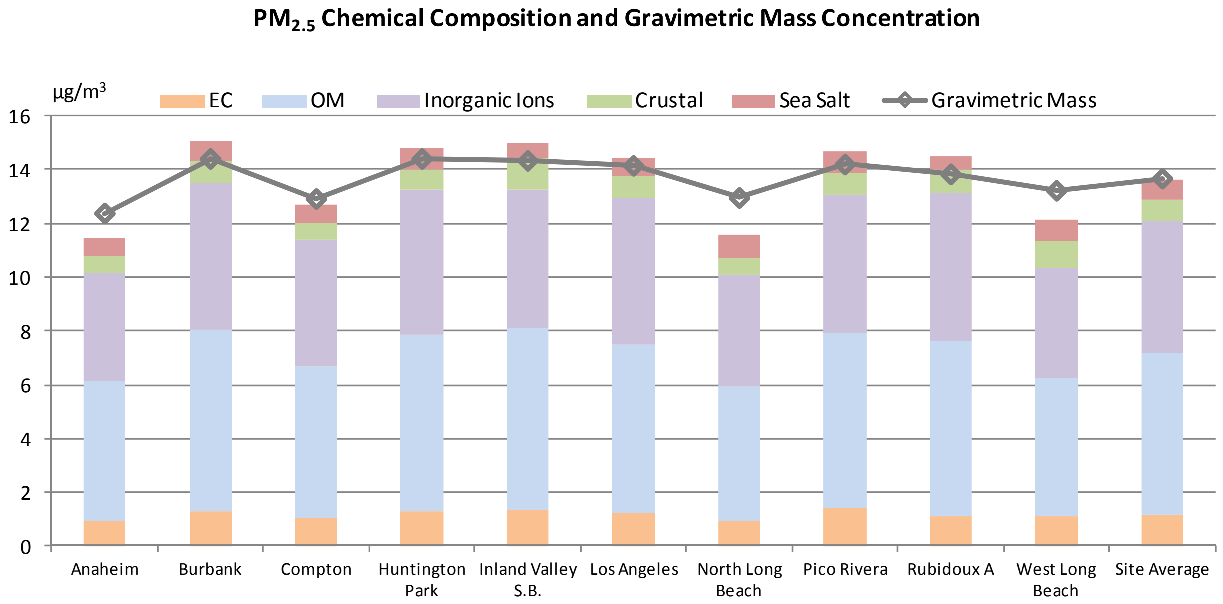

Figure X-1 Annual Average Chemical Composition and Gravimetric Mass Concentrations in $PM_{2.5}$

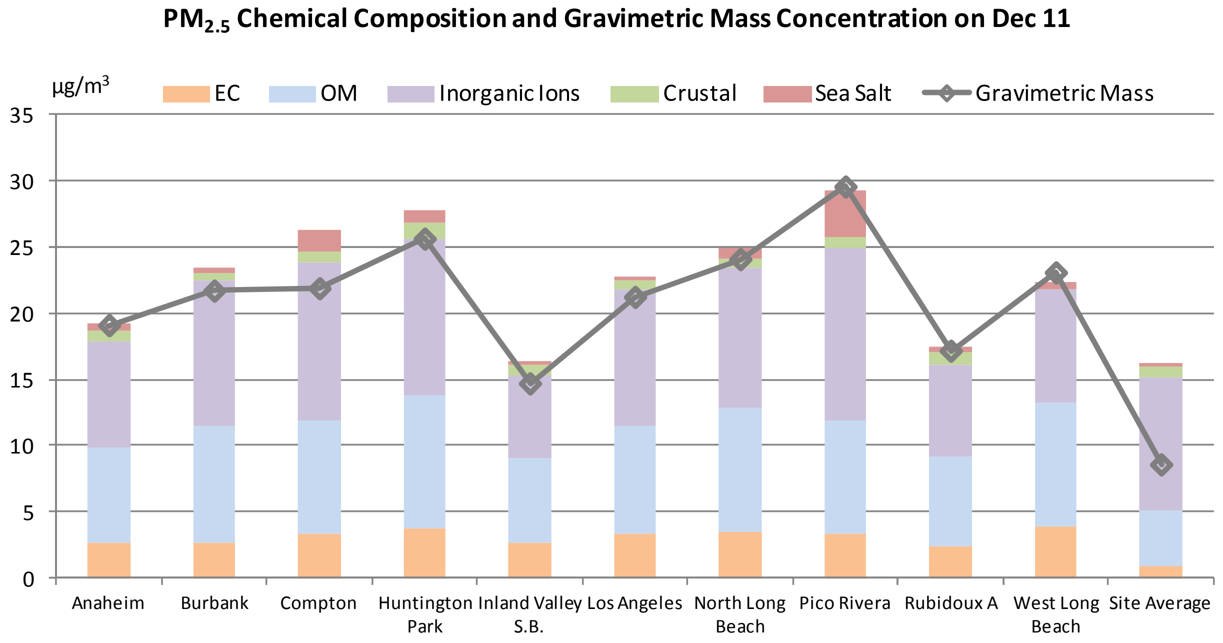

Figure X-2 Chemical Composition and Gravimetric Mass Concentrations in $PM_{2.5}$ on December 11, 2012

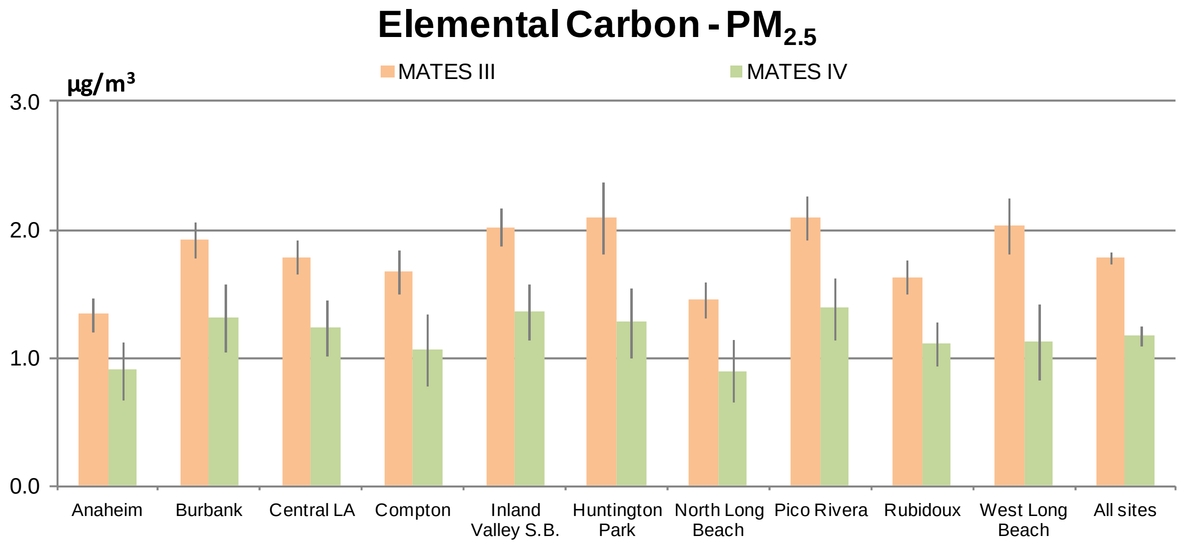

Figure X-3 Average Concentrations of Elemental Carbon in PM$_{2.5}$

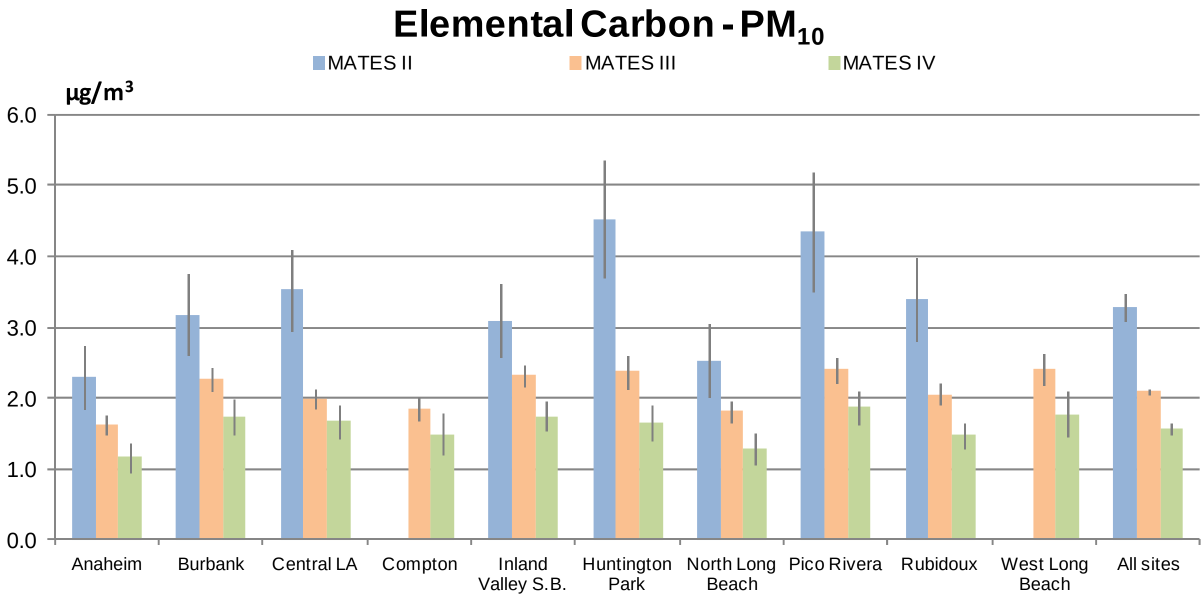

Figure X-4 Average Concentrations of Elemental Carbon in PM$_{10}$

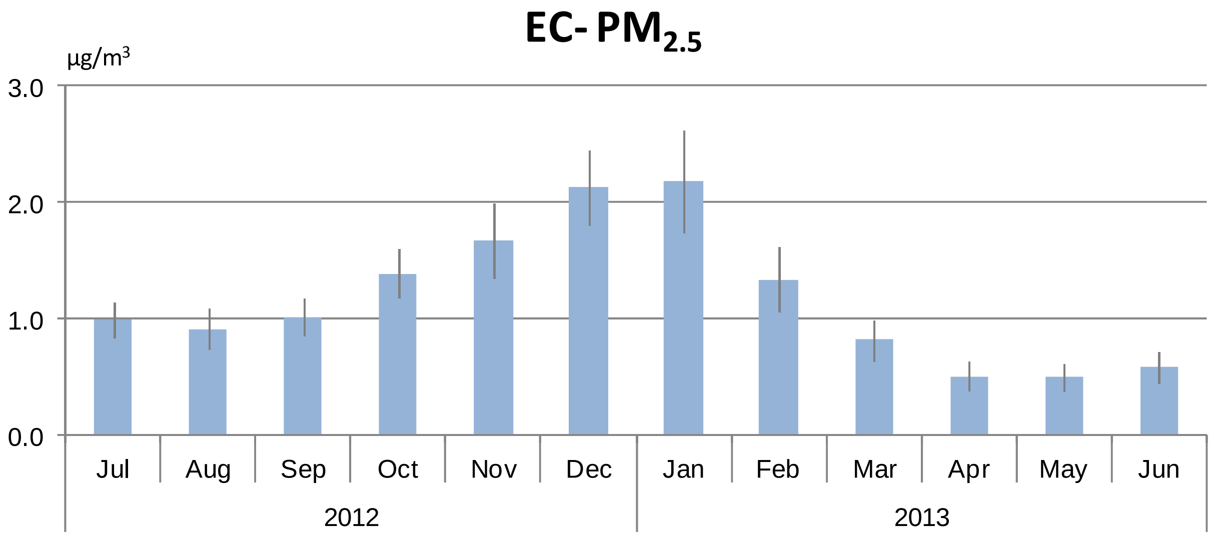

Figure X-5 Monthly Average Concentrations of Elemental Carbon in $PM_{2.5}$

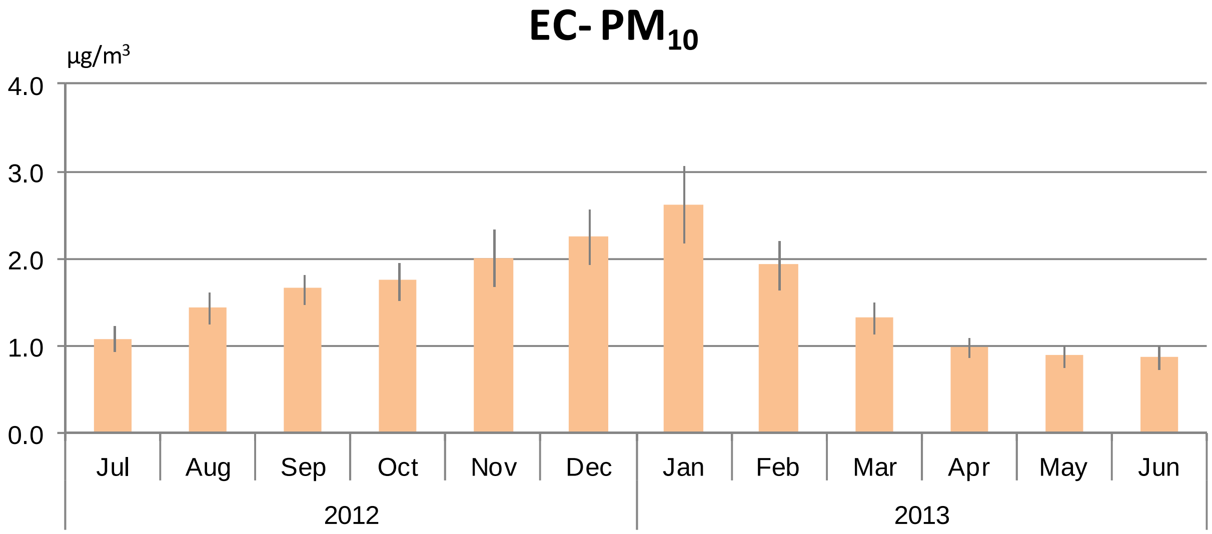

Figure X-6 Monthly Average Concentrations of Elemental Carbon in PM_{10}

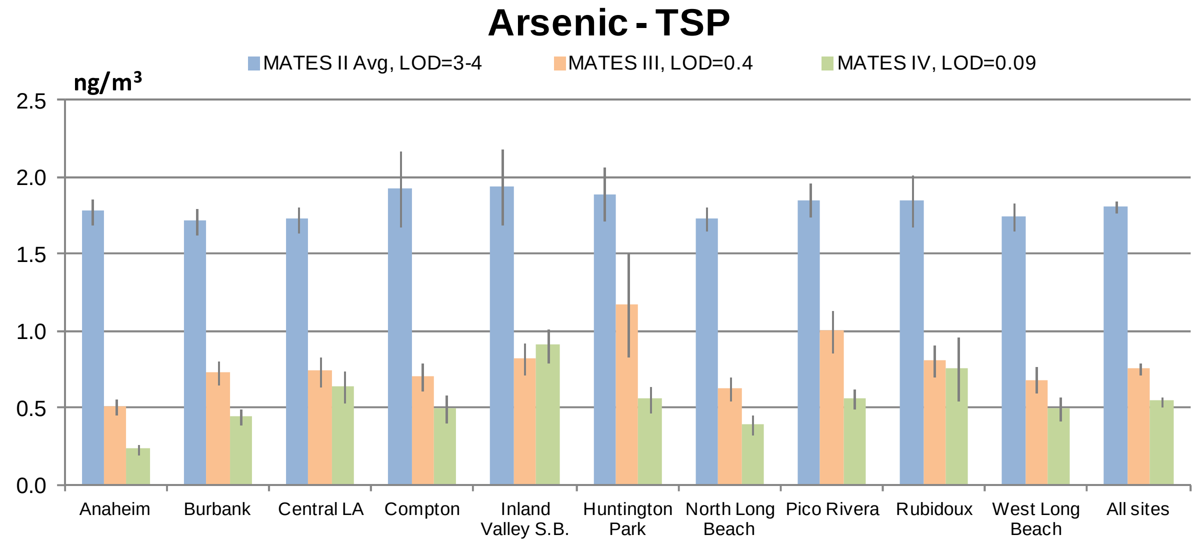

Figure X-7 Average Concentrations of Arsenic in Total Suspended Partiulate (TSP)

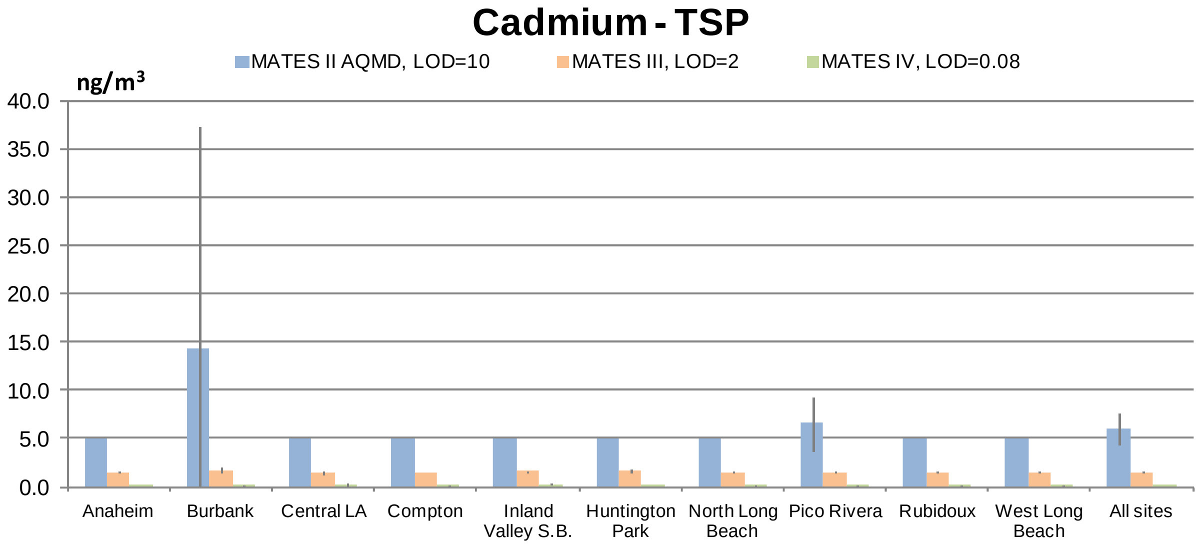

Figure X-8 Average Concentrations of Cadmium in Total Suspended Partiulate (TSP)

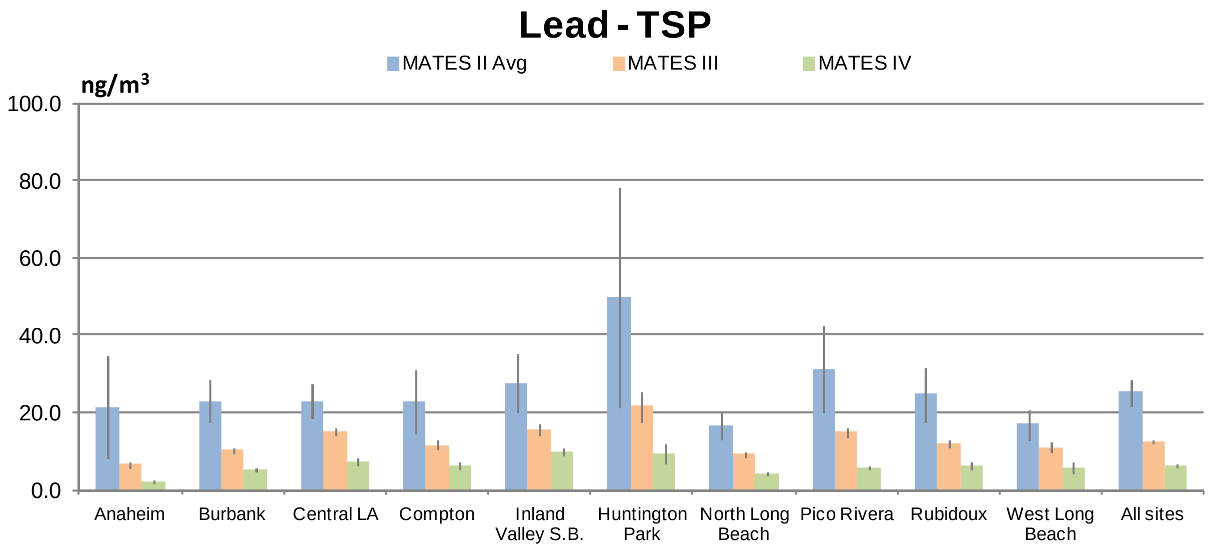

Figure X-9 Average Concentrations of Lead in Total Suspended Partiulate (TSP)

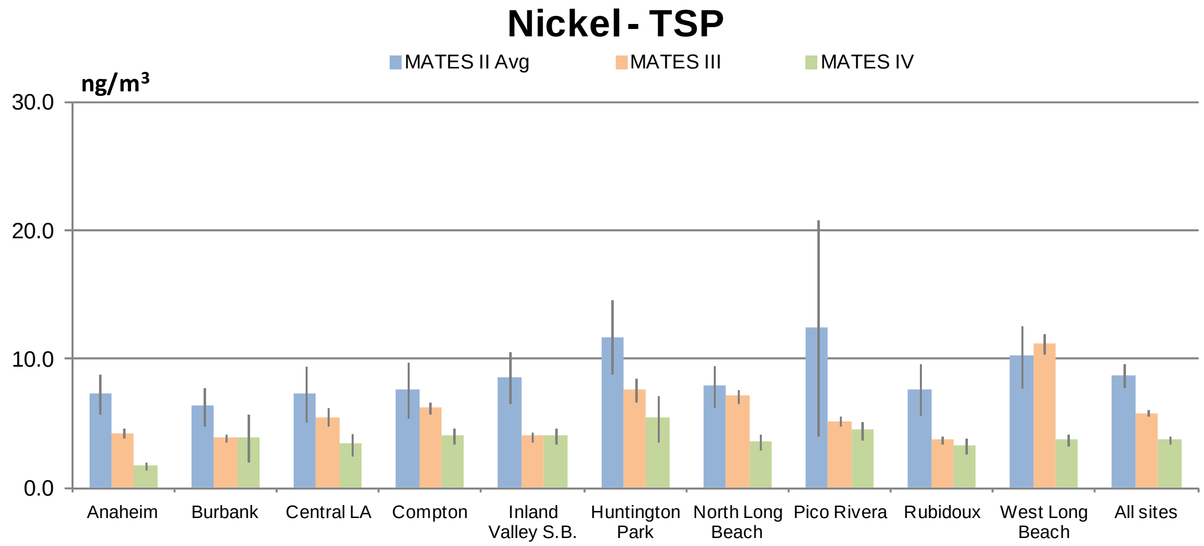

Figure X-10 Average Concentrations of Nickel in Total Suspended Partiulate (TSP)

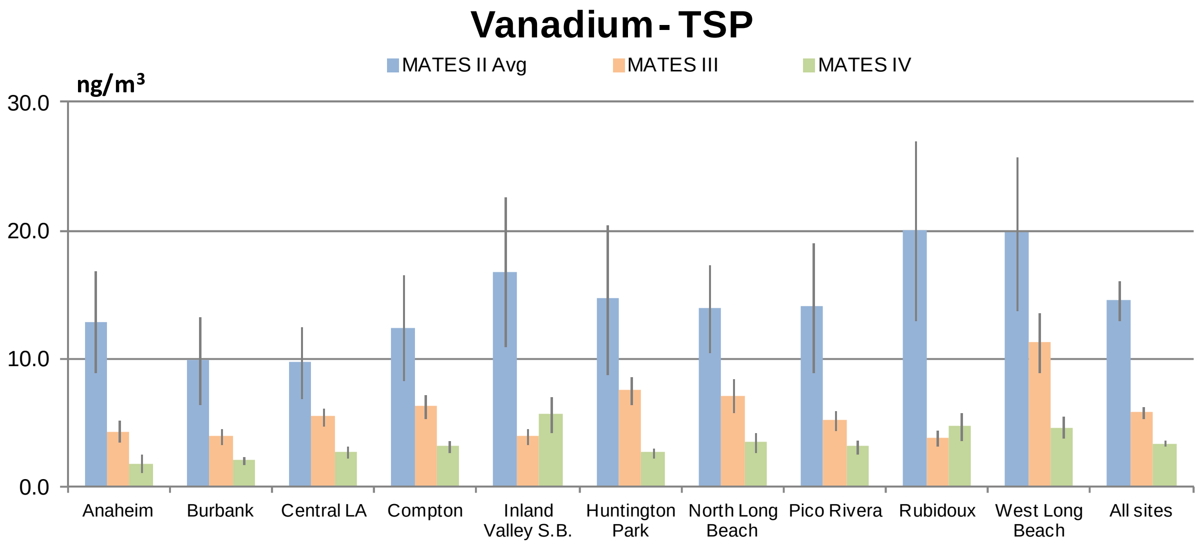

Figure X-11 Average Concentrations of Vanadium in Total Suspended Partiulate (TSP)

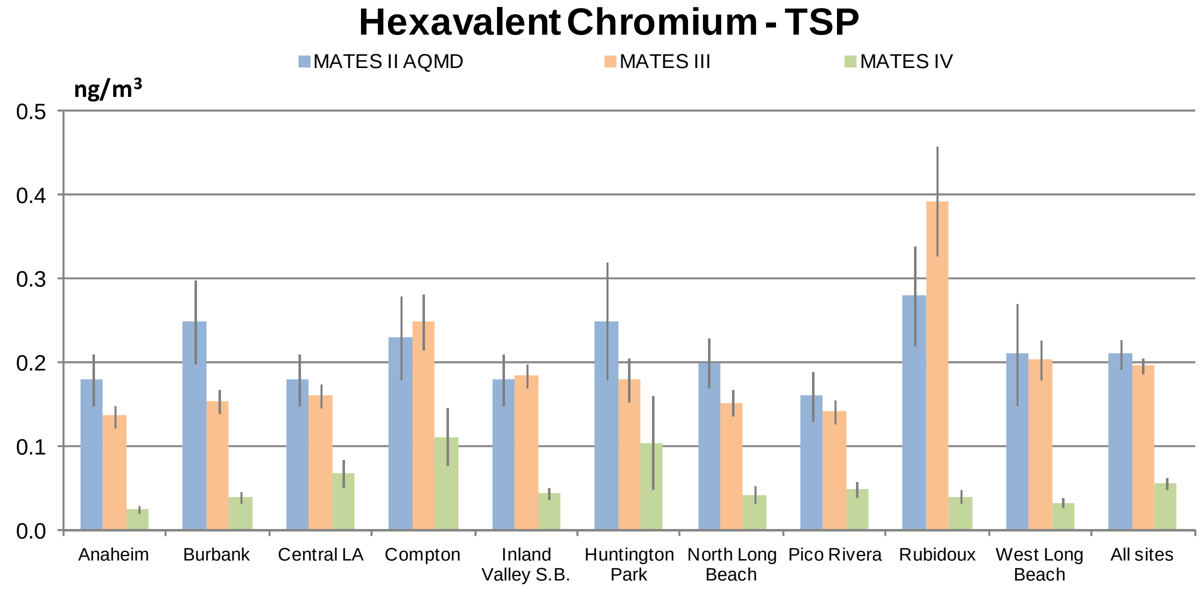

Figure X-12 Average Concentrations of Hexavalent Chromium in Total Suspended Partiulate (TSP)

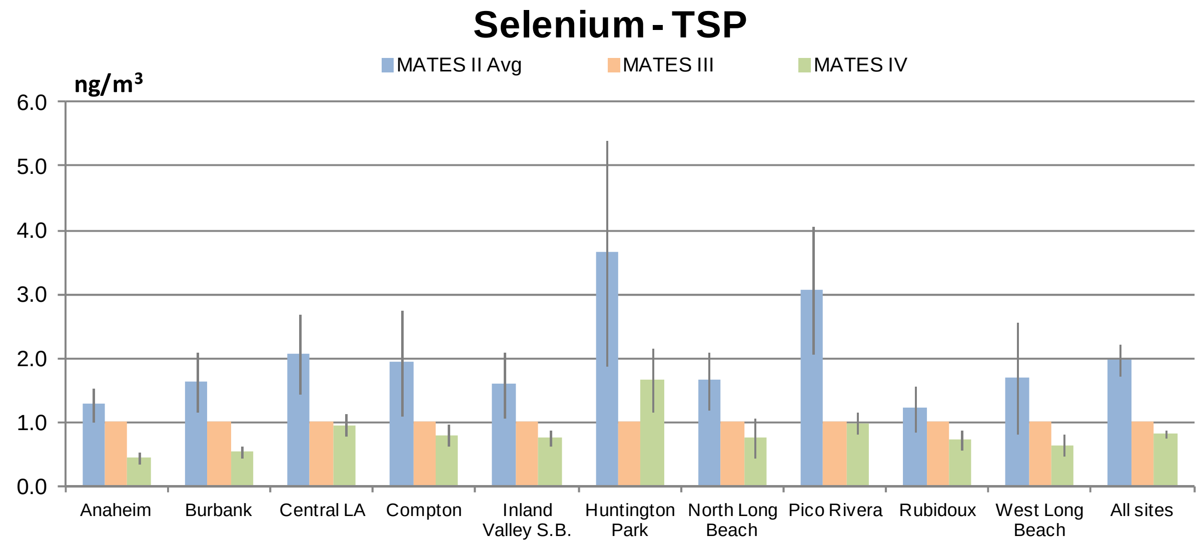

Figure X-13 Average Concentrations of Selenlium in Total Suspended Partiulate (TSP)

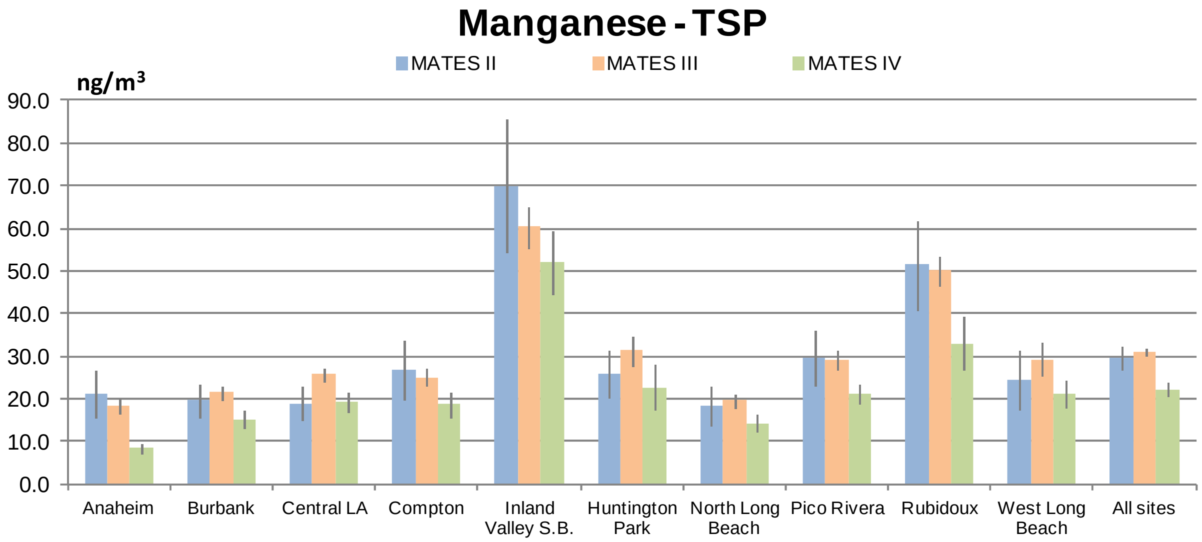

Figure X-14 Average Concentrations of Manganese in Total Suspended Partiulate (TSP)

APPENDIX XI

MATES IV

DRAFT REPORT

Estimating Diesel Particulate Matter

Authors

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Appendix XI. Estimating Diesel Particulate Matter

XI.1 Summary

Ambient diesel PM concentrations cannot be directly measured. It can be estimated using a diesel particulate matter (DPM) to elemental carbon (EC) ratio based on the emission inventory, which is then multiplied by ambient EC concentrations. The PM emission speciation profile that includes EC is specific to each source category, and the emissions ratio of DPM to EC could vary from 0 (non-diesel sources that emit EC such as residential fuel combustion and cooking) to above 10 (diesel-powered emissions with high fraction of inorganic ions and organic matter and a low fraction of EC such as ocean-going vessels). For diesel engine emissions, the fraction of EC in DPM is a function of engine parameters, fuel formulations, emission control types, etc., all of which vary as technology evolves to meet tighter emissions standards.

In the 2012 emissions inventory, off-road equipment, ocean- going vessels and diesel heavy-duty trucks and buses are the major sources of DPM, accounting for 85% of total anthropogenic emissions. Their DPM/EC ratios are 1.32, 16.39, and 1.85, respectively. In the 2005 inventory used in MATES III, these three categories account for 92% of the total diesel emissions, and their DPM/EC ratios were significantly higher than the 2012 inventory used in MATES IV (Table XI-1). The changes in the ratio for on-road and off-road equipment are primarily due to updates to the source speciation profiles applied to the particulate emissions from these sources. These changes are based on the most recent emissions testing and more detailed speciation profile assignments by source type, model year and control technology.

For instance, in the 2005 inventory, only one diesel exhaust PM speciation profile was used to calculate diesel-related emissions in all emission categories and inventory years. This PM profile was created based on source tests conducted on diesel tractors more than 20 years ago (Houck 1989, CARB 2008). The EC fraction in the 2005 profile was 26.4%, which is close to the DPM/EC ratios for on-road diesel heavy-duty trucks and buses, and off-road equipment shown in Table XI-1. Since then, more comprehensive dynamometer experiments were conducted to refine and improve the emission inventory and speciation profiles. The new diesel exhaust PM speciation profiles, used in MATES IV, were developed to reflect the changes in fleet composition, technology advancement, and new regulations. In the new speciation profile, for example, heavy-duty diesel trucks have an EC fraction ranging from 23% to 68% depending on engine model year, technology types and driving cycle. These categories were aggregated into a calendar year specific profile via a weighted average of different model year and technology group profiles. The new profile also shows an increasing trend of EC fraction of DPM with calendar year. The 50% EC fraction for calendar year 2005 increases to 56% for calendar year 2010.

Some of the changes in the DPM/EC ratio could result from recent regulatory actions. For example, ocean-going vessels, another major source category of DPM, had the highest DPM/EC ratio of 25.0 among all source categories in 2005. The ratio is also substantially lower in 2012. This is likely due to the switching from heavy fuel oil (HFO) to distillate fuel of ~1% sulfur within 200 nautical miles of California coast as required by California Air Resources Board. This requirement decreased sulfate in diesel exhaust more effectively than the other components including EC, which consequently lowered the DPM/EC ratio.

Overall, due to the considerable reduction in DPM emission in the major source categories, the current MATES IV DPM/EC emissions inventory ratio is lower in 2012 (0.81) compared to the previous 2005 ratio (1.95) used in MATES III.

To estimate the impact of the updated speciation profile on measurements-based comparisons between 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. The retrospective calculation yielded 23% less total anthropogenic EC emissions with most of the difference coming from the mobile source category. 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 estimated DPM reduction 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 73% stated DPM reduction.

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 improved over the MATES III methods.

TableXI-1. Emissions for Major DPM/EC Source Category and total anthropogenic sources for the South Coast Air Basin

Category	**2005**			**2012**		
	DPM	EC	DPM/EC Ratio	DPM	EC	DPM/EC Ratio
Diesel Heavy Duty Trucks & Buses	19596	5231	3.75	9816	5298	1.85
Other On-Road	795	3233	0.25	134	1340	0.10
Ocean-Going Vessels	10365	415	25.00	990	60	16.39
Off-Road Equipment	21567	6207	3.47	5275	3865	1.36
Other Off-Road	2614	1720	1.52	2208	1670	1.32
Total Stationary and Area Sources	1045	11957	0.09	444	10928	0.04
Total Anthropogenic	55983	28761	1.95	18867	23163	0.815

XI.2 References:

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

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.