MATES V Monitoring Methods and Results

Aaron Katzenstein
Laboratory Services Manager
Payam Pakbin
Program Supervisor

Melissa Maestas
Air Quality Specialist
Scott Epstein
Program Supervisor

MATES V Technical Advisory Group Meeting

April 14, 2021

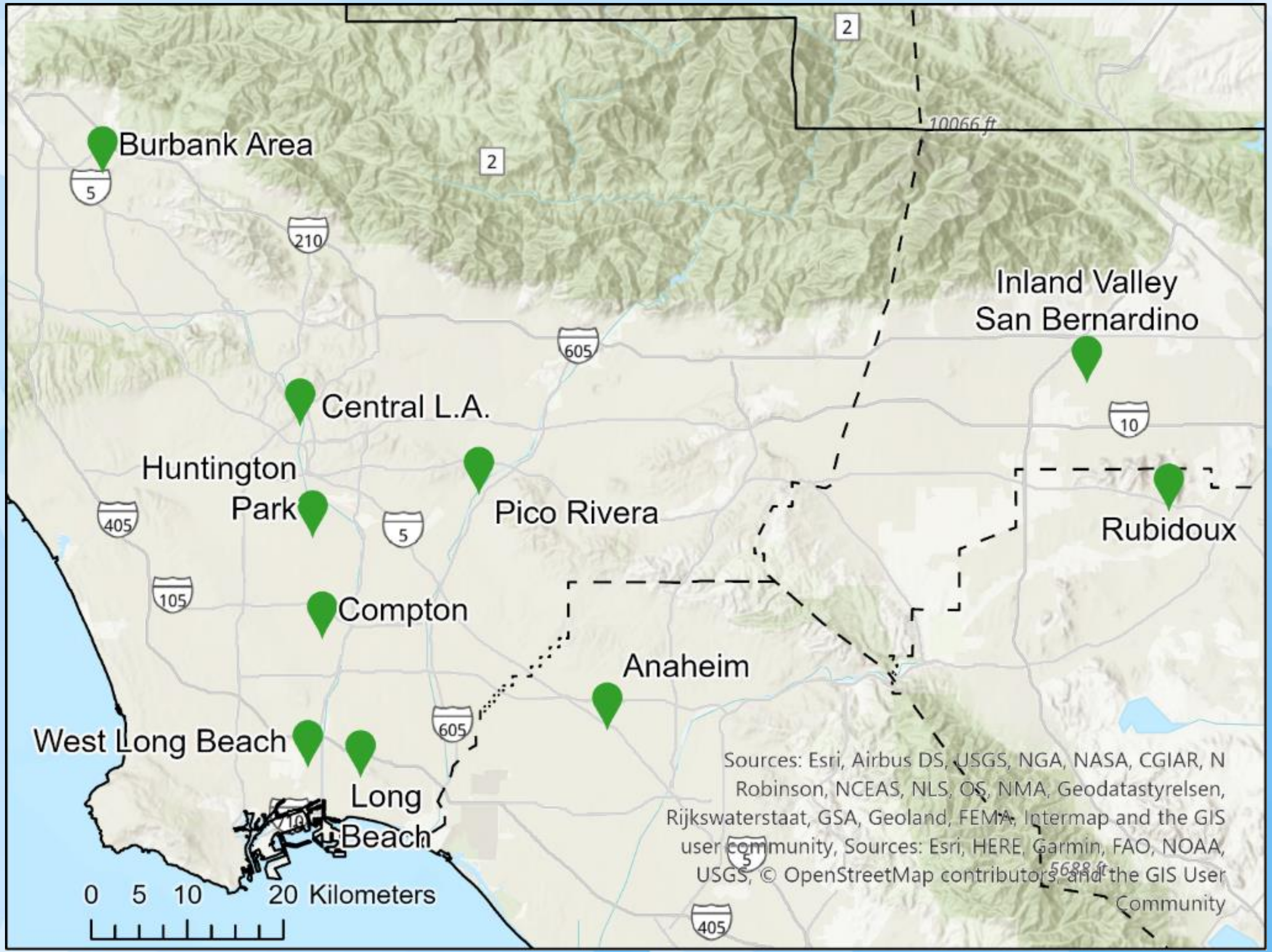
Summary of Sampling and Analysis

Aaron Katzenstein

Laboratory Services Manager

MATES V Monitoring

- Time period:
  - May 1, 2018-April 30, 2019
- Monitoring stations:
  - Mostly the same as previous MATES
  - Moved stations due to available locations:
    - Burbank Area
    - Huntington Park
    - Long Beach



Laboratory Sample & Analysis Summary

- 24 hour time integrated samples were collected on a 1-in-6 day frequency
- 121 analytes measured
- 3,185 samples collected
- 11,454 analyses conducted

Summary does not include field-based instruments

Pollutant Category		Measured Pollutants
Ultrafine Particles (UFPs)		UFPs
PM2.5	Ions	Ammonium Ion, Chloride, Nitrate, Potassium Ion, Sodium, Sulfate
	Sugars	Galactosan, Levoglucosan, Mannosan
	Metals	Aluminum, Antimony, Arsenic, Barium, Cadmium, Calcium, Cesium, Chlorine, Chromium, Cobalt, Copper, Iron, Lead, Magnesium, Manganese, Molybdenum, Nickel, Phosphorus, Potassium, Rubidium, Samarium, Selenium, Silicon, Strontium, Sulfur, Thallium, Tin, Titanium, Uranium, Vanadium, Yttrium, Zinc
	Other	PM2.5 mass, Black Carbon (BC), Elemental Carbon (EC), Organic Carbon (OC), Total Carbon (TC)
Total Suspended Particulate (TSP)	Metals	Antimony, Arsenic, Barium, Beryllium, Cadmium, Calcium, Cesium, Chromium, Cobalt, Copper, Cr6+ (hexavalent chromium), Iron, Lead, Manganese, Molybdenum, Nickel, Potassium, Rubidium, Selenium, Strontium, Tin, Titanium, Uranium, Vanadium, Zinc
Volatile Organic Compounds (VOCs)	Carbonyls	2-Butanone (Methyl Ethyl Ketone), Acetaldehyde, Acetone, Benzaldehyde, Formaldehyde, Propionaldehyde
	Other	1,2-Dibromoethane, 1,2-Dichlorobenzene, 1,2-Dichloroethane, 1,2-Dichloropropane, 1,3-Butadiene, 1,4-Dichlorobenzene, 2-Butanone (Methyl Ethyl Ketone), Acrolein (2-Propenal), Acetone, Benzene, Bromomethane, Carbon Tetrachloride, Chloroform, Ethylbenzene, m+p-Xylene, Methyl tert-Butyl Ether (MTBE), Methylene Chloride, o-Xylene, Styrene, Tetrachloroethylene (Perchloroethylene), Toluene, Trichloroethylene, Vinyl Chloride
Polycyclic Aromatic Hydrocarbons (PAHs)		9-Fluorenone, Acenaphthene, Acenaphthylene, Anthracene, Benzo(a)anthracene, Benzo(a)pyrene, Benzo(b)fluoranthene, Benzo(e)pyrene, Benzo(g,h,i)perylene, Benzo(k)fluoranthene, Chrysene, Coronene, Cyclopenta(c,d)pyrene, Dibenz(a,h)anthracene, Fluoranthene, Fluorene, Indeno(1,2,3-c,d)pyrene, Naphthalene, Perylene, Phenanthrene, Pyrene, Retene

What's new?

- Added sugars: levoglucosan, mannosan, and galactosan
  - Appendix XII – *Biomass Burning vs Fossil Carbon Contribution to PM2.5*
- Added bromomethane
- PM10 not included
- Used new statistical methods to account for data below detection limits
- Reanalyzed monitoring data from MATES II through IV.

Species	**Sampling**	**Laboratory Analysis**
Ions in Particulate Matter	PM Filters	Water extracts were analyzed by ion chromatography (IC) with conductivity detection
Sugars (Levoglucosan, Mannosan, Galactosan)	PM Filters	Acetonitrile extracts were derivatized and then analyzed by GC-MS
TSP Metals	Cellulose Fiber Filters	Nitric acid extracts were analyzed by inductively coupled plasma mass spectrometry (ICP-MS)
PM2.5 Metals	PM Filters	Filters were analyzed by energy dispersive x-ray fluorescence spectrometry (XRF)
Hexavalent Chromium	Cellulose Fiber Filters	Bicarbonate extracts were analyzed via ion chromatograph (IC) equipped with post-column derivatization, and UV-visible spectroscopic detection
Elemental and Organic Carbon	PM Filters	Section of PM filter removed and analyzed on a laser corrected carbon analyzer
Carbonyls	DNPH Cartridge	Acetonitrile recovery and subsequent analysis via high performance liquid chromatography (HPLC) or ultra high performance liquid chromatography (UHPLC) with UV-visible spectroscopic detection
Volatile Organic Compounds (VOCs)	Silica-Lined Canisters	Canisters analyzed by gas chromatograph – mass spectrometer (GC-MS) with automated pre-concentration and cryo-focusing
Black Carbon	Continuous	Aethalometer
UFP	Continuous	Condensation Particle Counters (CPC)

Sampling Issues

- Manifold leaks at: Rubidoux, CELA, Anaheim
- Large percentage of carbonyl data invalidated
- Anaheim biggest impact
- VOC and Carbonyl data not invalidated are flagged

Discussed in: Chapter 2- Monitoring and Analyses

	Rubidoux	Central Los Angeles	Anaheim
MATES V Sampling Period (1 Year): 5/1/2018 – 4/30/2019			
MATES V Manifold Leak Period	5/1/2018 – 2 /19/2019	8/18/2018 – 4/25/2019	5/1/2018 – 4/30/2019
Percent of Invalidated VOC Samples	0% (0 of 61 samples)	0% (0 of 61 samples)	100% (61 of 61 samples)
Percent of Invalidated Carbonyl Samples	80%* (49 of 61 samples)	69% (42 of 61 samples)	100% (61 of 61 samples)

* includes 2 Rubidoux carbonyl samples that invalidated due to other sampler run issues

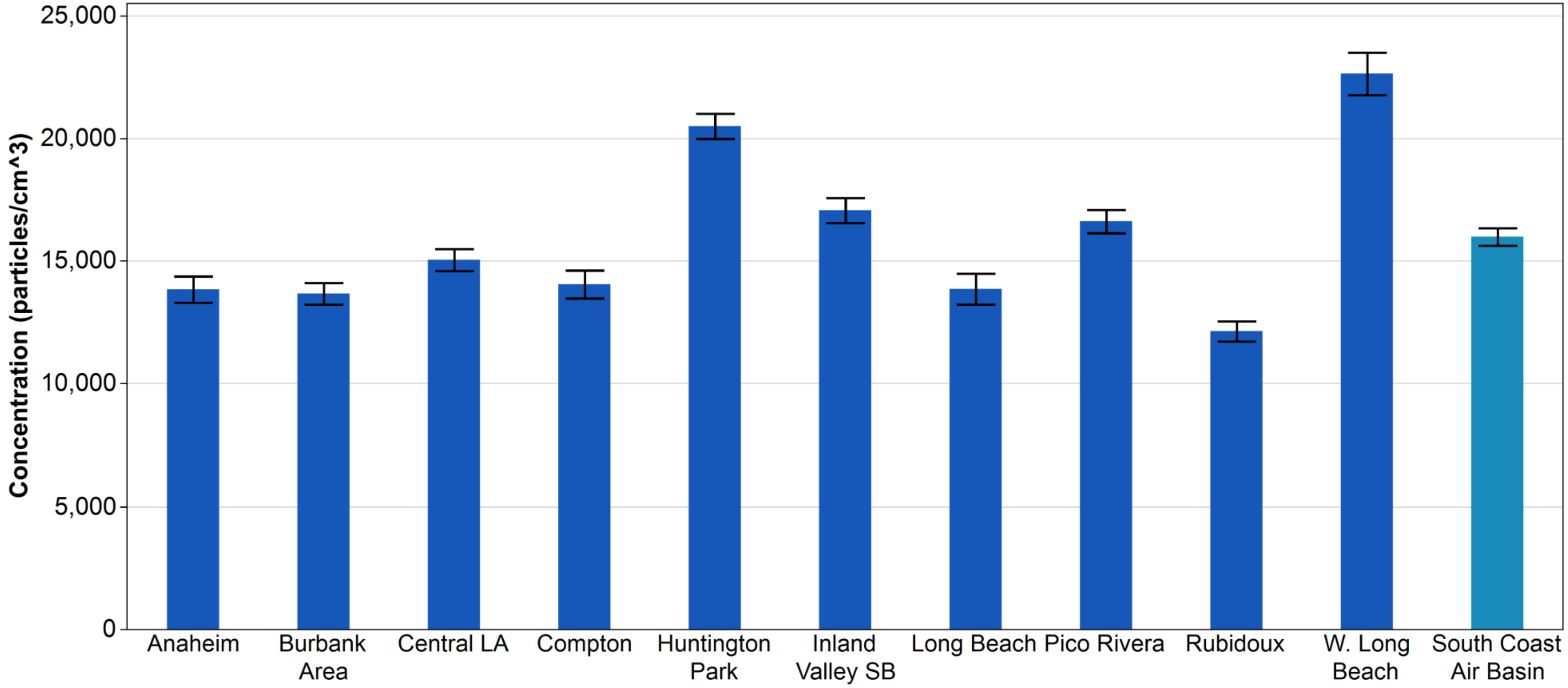
Summary of UFP and BC Measurements

Payam Pakbin

Program Supervisor

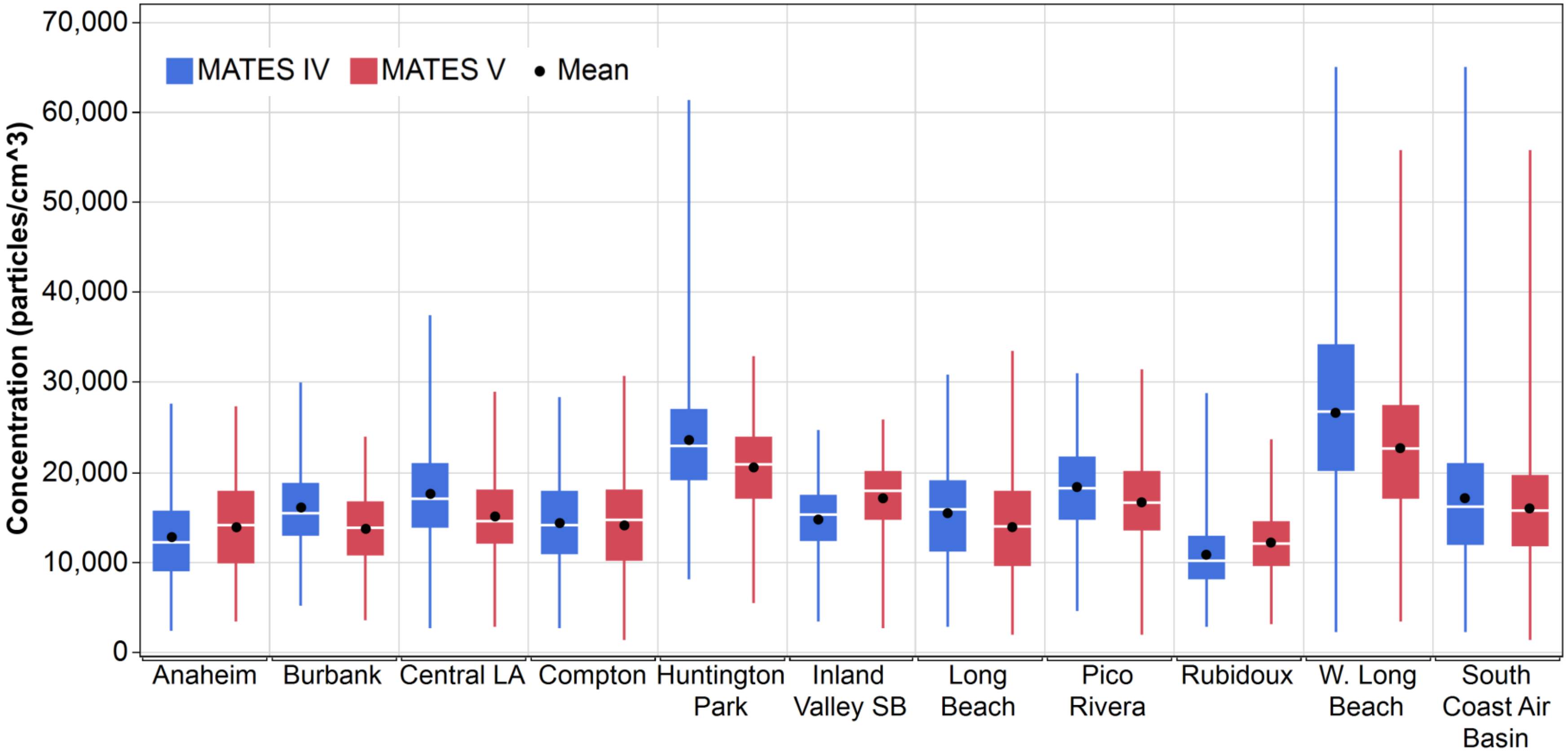
CHAPTER 5: ULTRAFINE PARTICLE (UFP) MEASUREMENTS

MATES V AVERAGE UFP CONCENTRATIONS



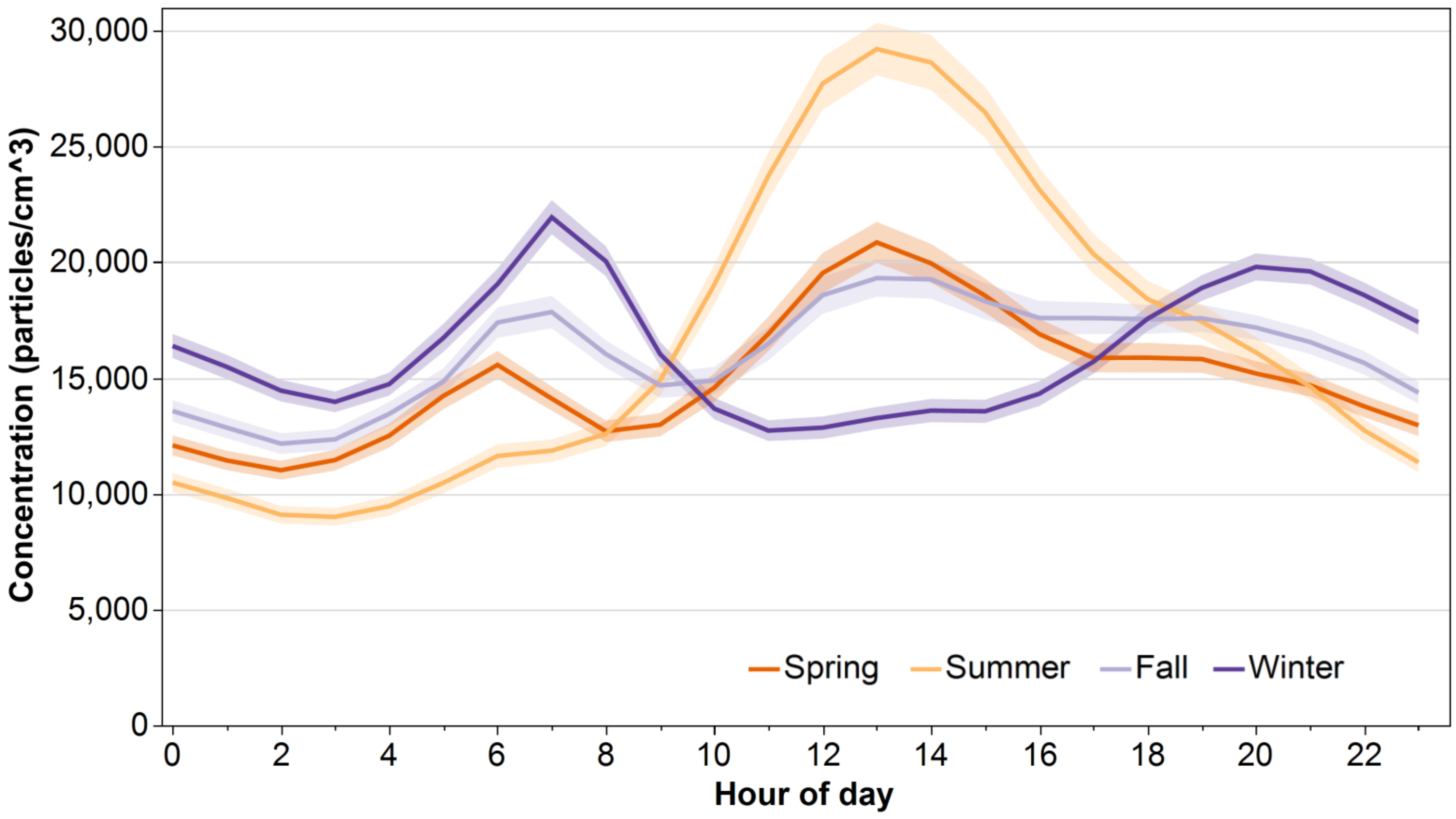
Overall UFP concentration for the South Coast Air Basin over MATES V is 15,971 particles/cm^3.
West Long Beach and Huntington Park show the highest average UFP concentrations

MATES IV AND MATES V COMPARISON



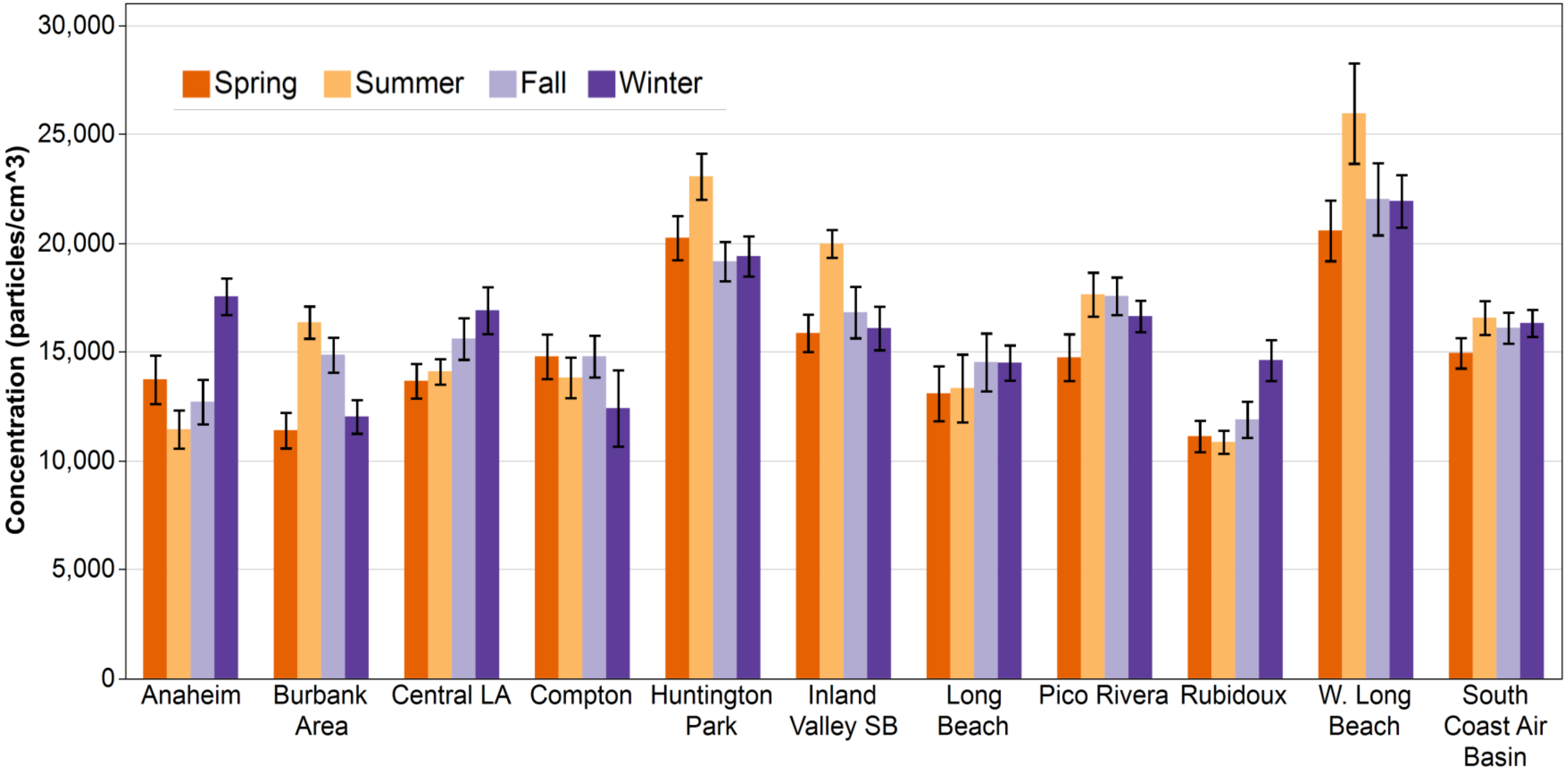
Overall UFP concentration decreased slightly, but there is no consistent trend in UFP concentrations going from MATES IV to MATES V across sites

DIURNAL UFP PROFILES BY SEASON



- UFP diurnal profiles vary significantly by season
- Summer profile shows a large peak around noon due to photochemistry (secondary particle formation)
- Winter profile shows peaks in the morning and evening due to rush hour traffic coupled with a shallow atmospheric mixing height

SEASONAL UFP AVERAGES



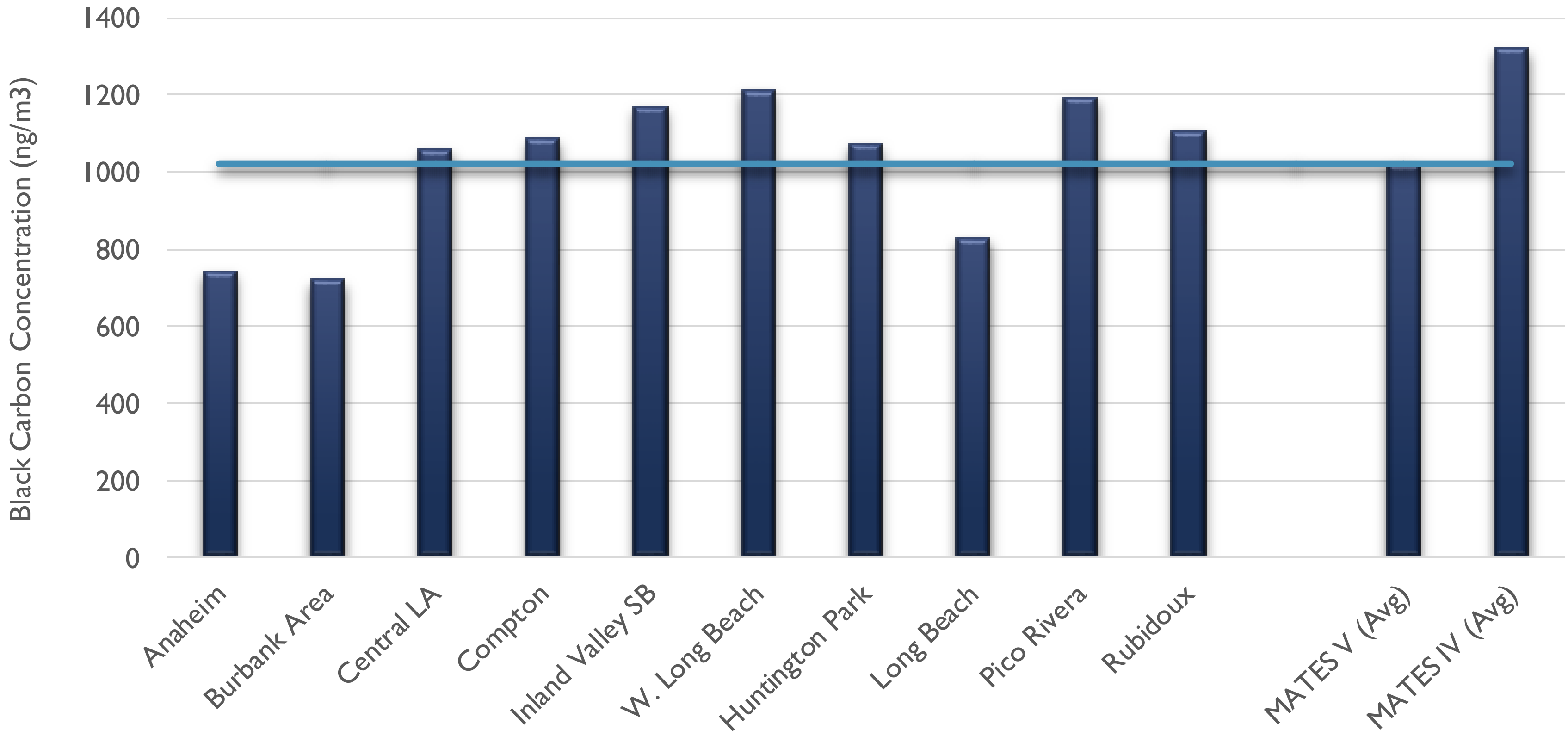
- Summer and winter typically show the highest UFP concentrations
- Variations in seasonal concentrations by site suggest that some sources be more important at some sites than others

SUMMARY OF UFP MEASUREMENTS

- UFP measurements over MATES V show high temporal and spatial variability
- Overall UFP concentrations decreased slightly between MATES IV (July 2012 – June 2013) and MATES V (May 2018 – April 2019), but there is no consistent trend across sites
- Clear differences are observed in the diurnal and seasonal UFP profiles that are influenced by:
  - Traffic volume, which peaks during the morning and evening rush hour periods
  - Photochemical activity, which is highest at noon and during the summer (and warmer days)
  - Atmospheric mixing layer height which varies by time of day and season
- Continued measurements of UFPs are needed to make robust conclusions on their long-term trends, spatial patterns, and important sources

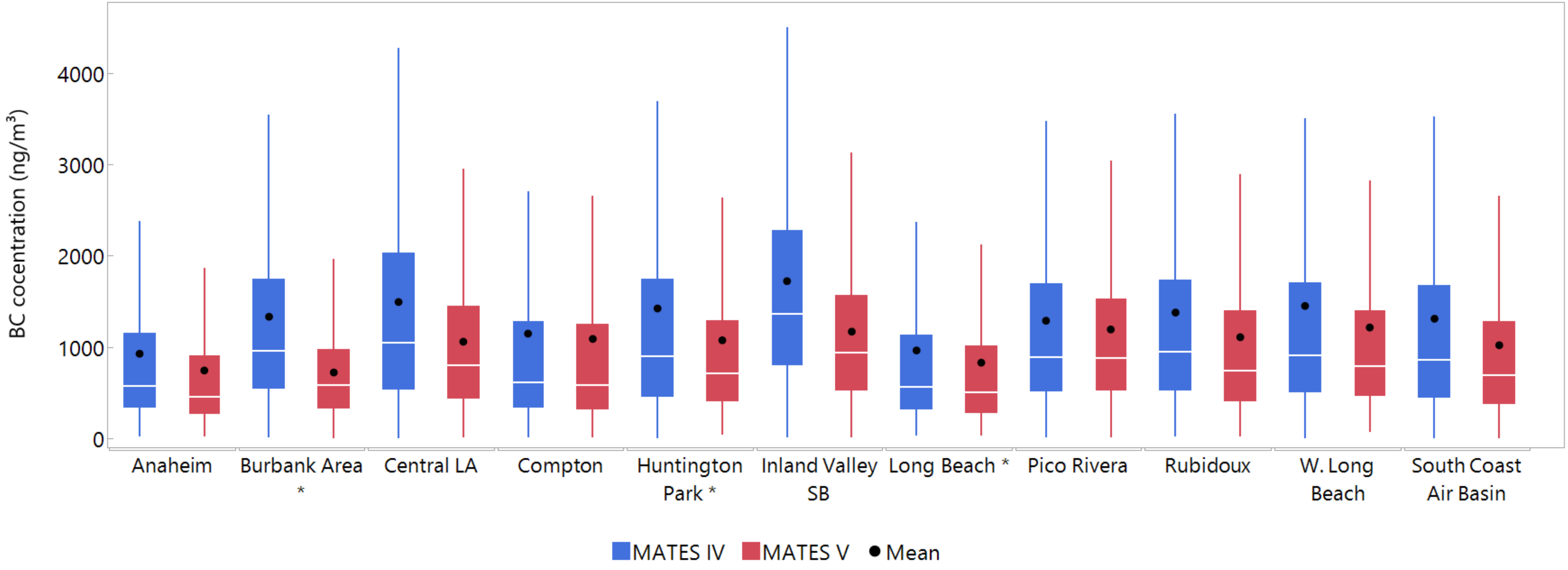
CHAPTER 5: BLACK CARBON (BC) MEASUREMENTS

MATES V AVERAGE BC CONCENTRATIONS



The annual average BC concentration in the South Coast Air Basin during MATES V is 1019 ng/m^3, lower by 22% than during MATES IV. West Long Beach, Huntington Park and Pico Rivera showed the highest BC concentrations

MATES IV AND MATES V COMPARISON

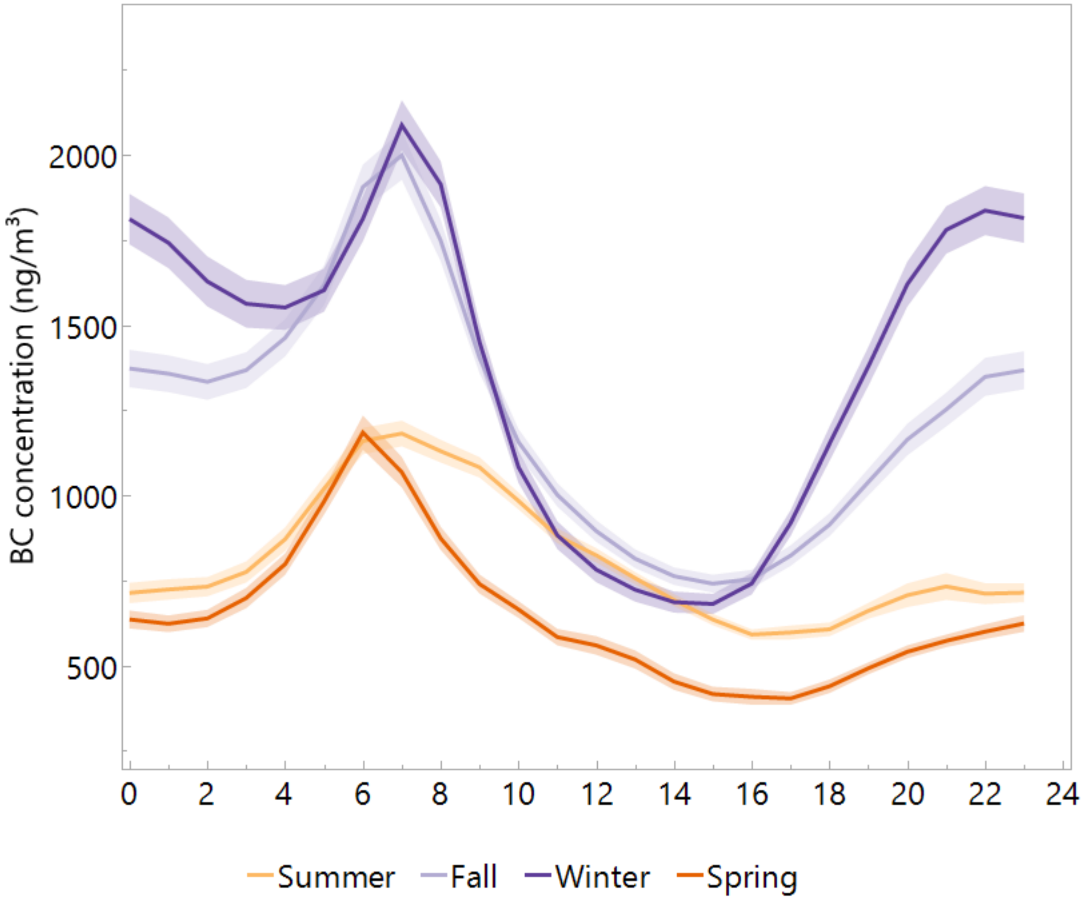


Overall BC concentration decreases in all stations except Compton. Significant reductions were observed in Burbank Area, Central LA, Huntington Park and Inland Valley SB

* denotes sites that changed location

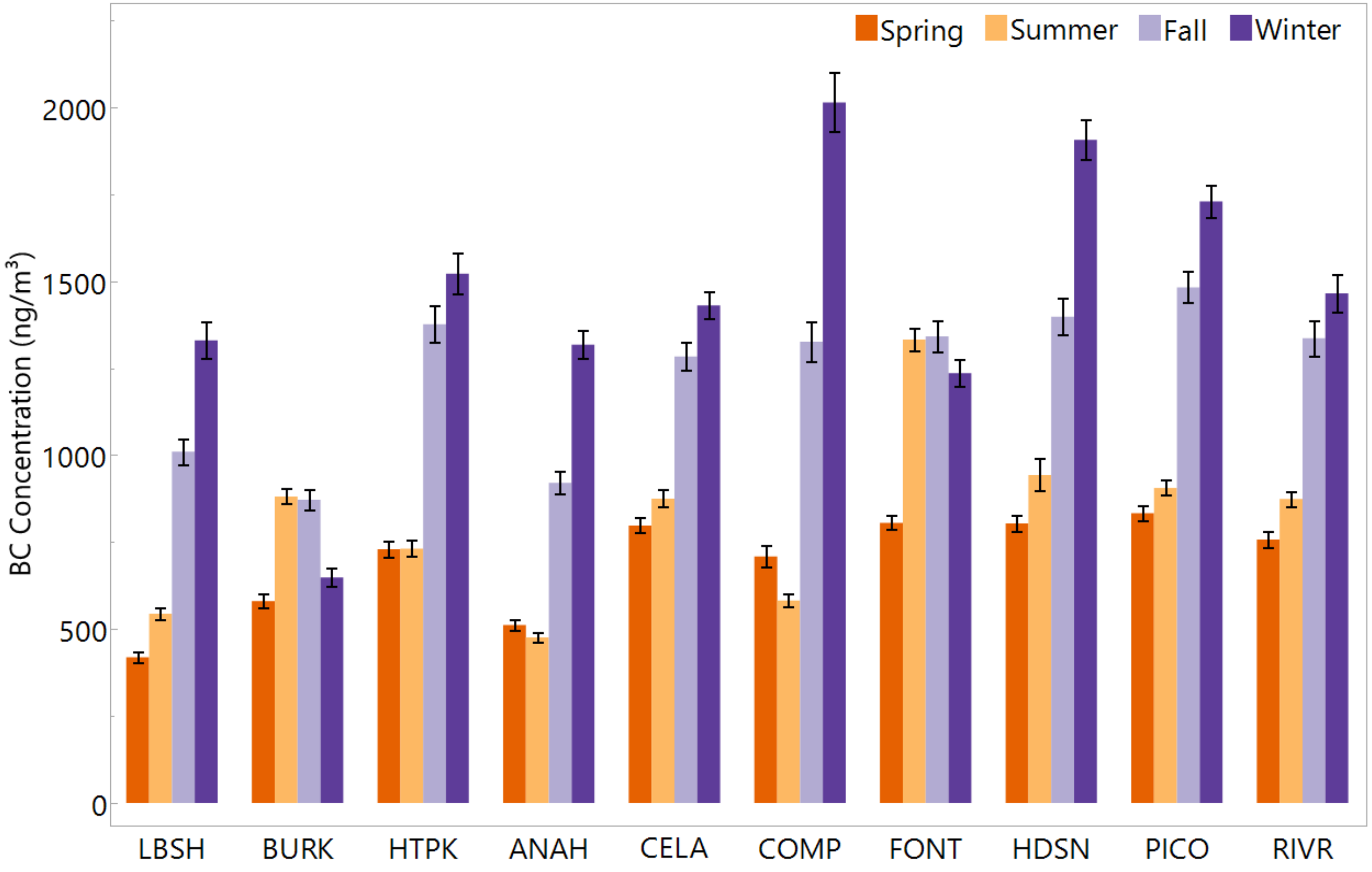
TEMPORAL TRENDS IN BC CONCENTRATION

Diurnal Pattern



- BC levels show distinct diurnal pattern. Its magnitude changes significantly by seasons
- BC levels during winter and fall show two high peaks at 6-7am hours and past 10pm
- These peaks are likely due to morning traffic and night meteorological conditions (e.g. shallower atmospheric mixing height)

SEASONAL BC AVERAGES



- Winter and Fall typically show the highest BC concentrations
- Variations in seasonal concentrations by site suggest that some sites might be more impacted by seasonal activity

SUMMARY OF BC MEASUREMENTS

- BC levels during MATES V were 22% lower than was measured during MATES IV
- Higher BC levels were measured in near-traffic sites than in MATES V sites
- BC levels were higher at near-traffic sites and are timely correlated with traffic rush hours
- Higher levels of BC are measured during the Winter and Fall, likely due to meteorological conditions (e.g., shallower atmospheric mixing heights)

Monitoring Results

Melissa Maestas
Air Quality Specialist

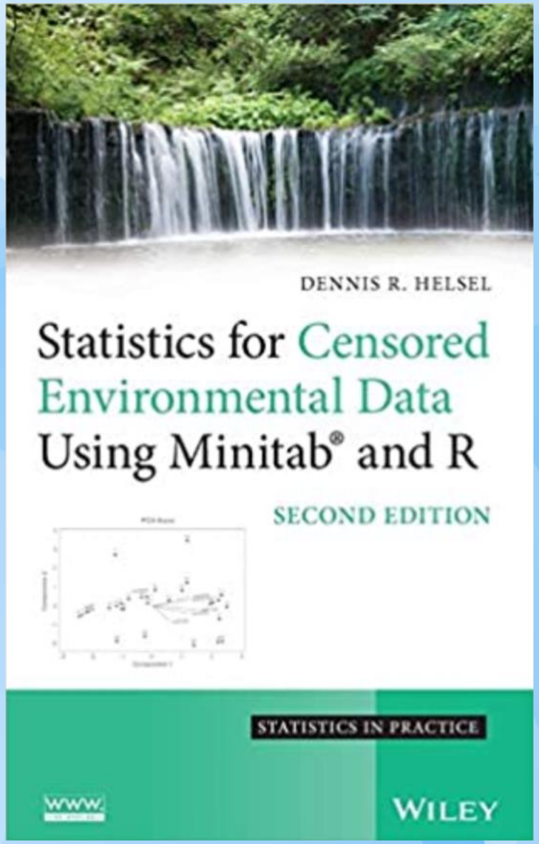
Scott Epstein
Program Supervisor

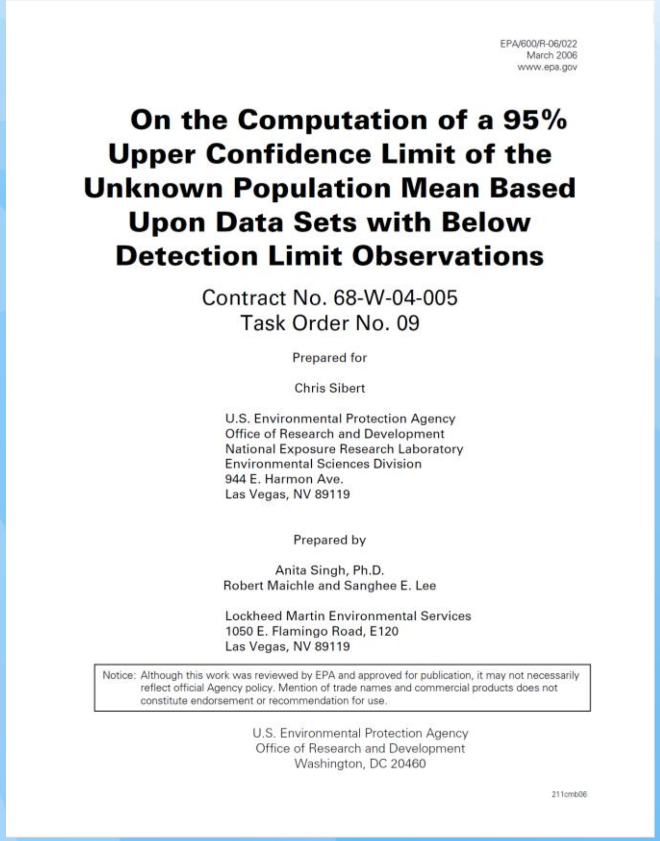
Handling Data Below Detection Limit

- Pollutant concentrations are occasionally below the method detection limit (MDL)
  - Upper bound estimate = MDL
  - Lower bound estimate = 0
    - Likely somewhere between
    - “nondetects”
- Laboratory technology tends to improve over time
  - MATES V MDLs generally much lower than for MATES II
- Statistical methods must account for nondetects to draw appropriate conclusions
- Statistical methods for nondetects have also improved over time
  - Improved methods becoming more widely used in environmental sciences

MATES II – V Analysis of Monitoring Data

- Re-analyzed MATES II – IV alongside MATES V data to allow for direct comparisons with consistent statistical methods
- Followed guidance of
  - Singh et al. (2006) – EPA-commissioned report about handling nondetects
  - Helsel (2012) – textbook about handling nondetects
- General guidance
  - Avoid substitution (e.g. ½ MDL)
  - Combine information about proportions of nondetects with numerical values of data above MDL
- See Appendix XI




EPA/600/R-06/022
March 2006
www.epa.gov

On the Computation of a 95% Upper Confidence Limit of the Unknown Population Mean Based Upon Data Sets with Below Detection Limit Observations

Contract No. 68-W-04-005
Task Order No. 09

Prepared for

Chris Sibert

U.S. Environmental Protection Agency
Office of Research and Development
National Exposure Research Laboratory
Environmental Sciences Division
944 E. Harmon Ave.
Las Vegas, NV 89119

Prepared by

Anita Singh, Ph.D.
Robert Maichle and Sanghee E. Lee

Lockheed Martin Environmental Services
1050 E. Flamingo Road, E120
Las Vegas, NV 89119

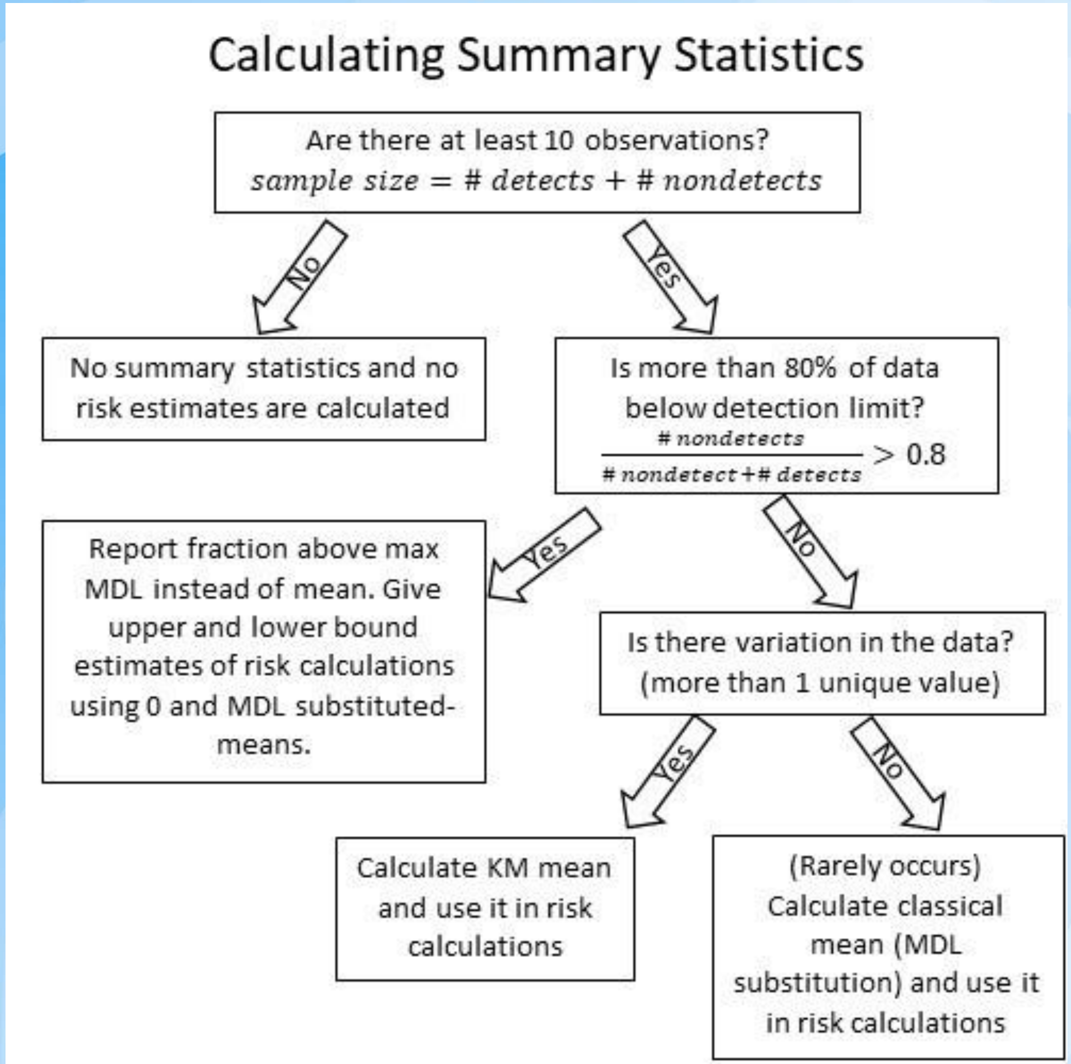
Notice: Although this work was reviewed by EPA and approved for publication, it may not necessarily reflect official Agency policy. Mention of trade names and commercial products does not constitute endorsement or recommendation for use.

U.S. Environmental Protection Agency
Office of Research and Development
Washington, DC 20460

211cmb06

Note: "censored" data means nondetect in this context

Annual Mean: Kaplan-Meier Method



- Kaplan-Meier (KM) method
  - with Efron's bias correction
  - Nonparametric survival analysis methods
- Minimum Sample Size = 10
  - # nondetects + # detects
    - Excluded invalidated data
- If > 80% sample are nondetects
  - Single estimate cannot be made
  - Upper and lower bound estimates using 0 and MDL substitution
    - clearly denoted in figures
- When # nondetect = 0
  - KM mean = classical mean

95% Confidence Intervals: Bootstrapping

When ≥ 20% of samples are above MDL:

1. KM mean is computed from a random sample of the data that is the same size as the data set
   - The random sampling is taken with replacement from the measurements, so that some measurements may be sampled multiple times while others may not have been sampled
2. Repeat 1000+ times with different random samples
3. The 2.5th and 97.5th percentiles of the distribution of 1000 KM mean estimates provides the 95% confidence interval

When > 80% sample are nondetects:

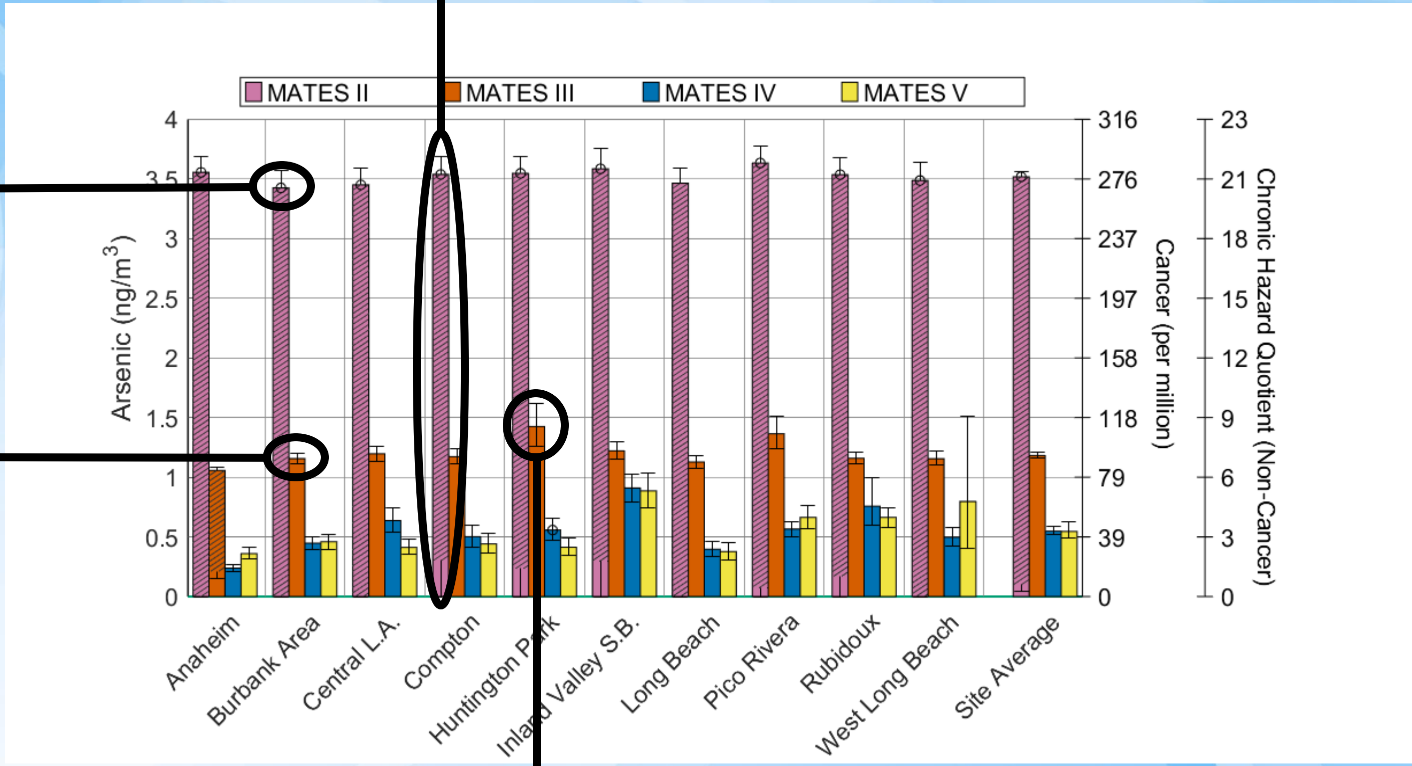
- Lower-bound of confidence interval: Bootstrapping for zero-substituted means
- Upper-bound of confidence interval: Bootstrapping for MDL-substituted means

TSP Arsenic

Diagonal lines (shading)
≥ 80% of data below MDL
Upper edge = MDL-substituted mean
Lower edge = zero-substituted mean

"o" = data incomplete on quarterly basis (75%)

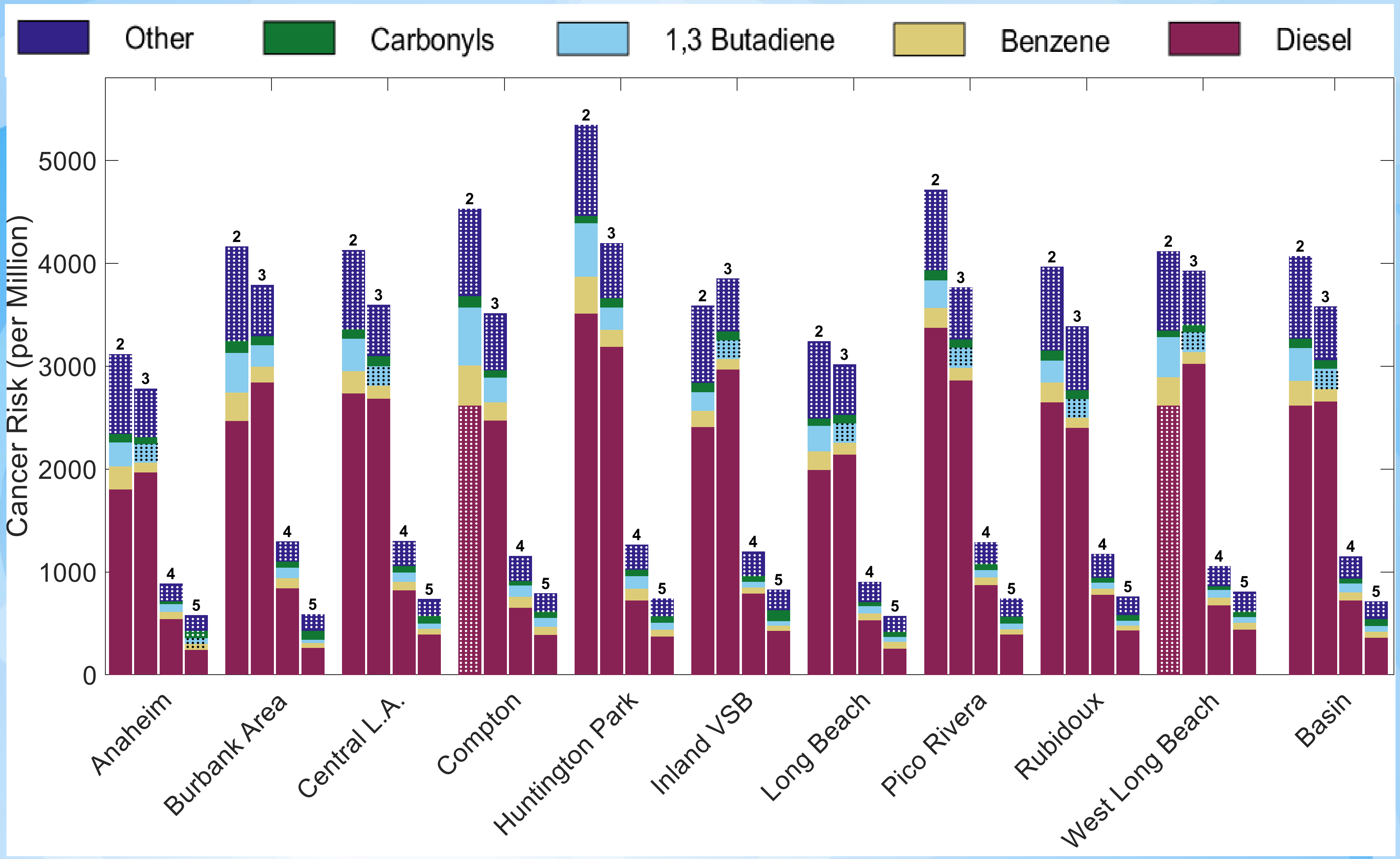
Bar height = KM mean (Except when ≥ 80% below MDL)



See Chapter 2 and Appendix IV for figures and tables for each analyte

Error bars denote the 95% confidence interval

Air Toxics Cancer Risk – Monitoring Data



Key Takeaways:

- Diesel PM remains the main risk driver
- Cancer risk decreased at every station
- Station with highest risk is Inland Valley San Bernardino

Chronic Non-Cancer Risk – Monitoring Data