# 2. Overview of Goals, Summary of Previous MATES Studies, and Projected Timeline

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**Planning, Rule Development, and Implementation**

MATES VI Technical Advisory Committee Mtg. #1

October 26, 2023

# The South Coast AQMD


**17 Million Residents**

*One-third of all U.S. containerized cargo*


# MATES Program Overview

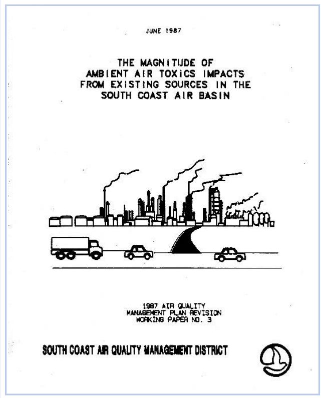
- Board Environmental Justice Initiative
- Focuses on regional air toxics impacts

<u>**Goals**</u>:

- Provide public information about air toxics and associated health risks throughout the region
- Evaluate progress in reducing air toxics exposure
- Provide direction to future toxics control programs

# Previous MATES Campaigns

1986-1987

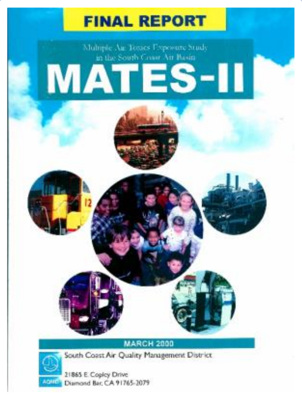



## MATES I

Limited Measurements

Impacts of benzene and hexavalent chromium (Cr6)

1998-1999

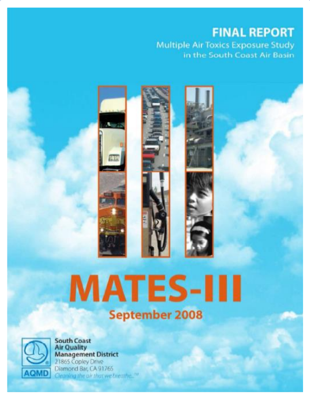



## MATES II

Downward trend for certain air toxics

Diesel exhaust accounted for 71% of cancer risk from air toxics

2004-2006



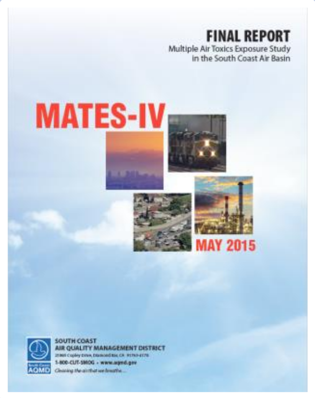

## MATES III

Continuing downward trends, other than Diesel Particulate Matter (PM)

Increased Diesel PM risk near ports

Cr6 traced to cement plant emissions

2012-2013




## MATES IV

>50% decrease in air toxic cancer risk since MATES III

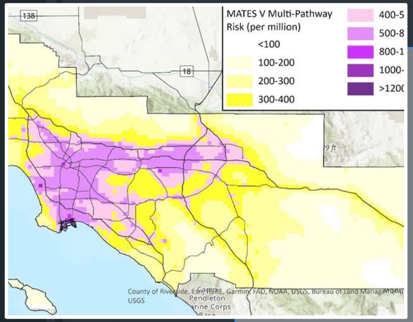
2/3 of air toxics cancer risk from Diesel PM

Continuous UFP and BC measurements

UFP = Ultrafine Particles
BC = Black Carbon

# MATES V: Summary of Results

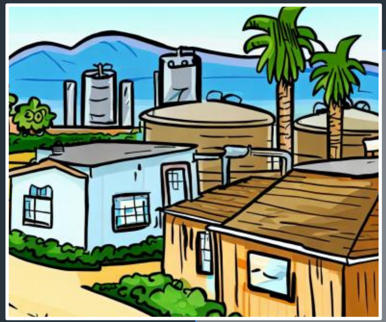
## (2018-2019 Monitoring, 2021 Report)




Air toxics cancer risk decreased by ~50% since 2012, but risks are still high

Highest air toxics cancer risk in and around the ports. Risk also elevated along goods movement corridors and major freeways

Diesel PM is the largest contributor to air toxics cancer risk



Environmental Justice (EJ) communities also had decreased air toxics levels, but still higher compared to Basin averages

Advanced air monitoring methods and techniques were evaluated at and near refineries

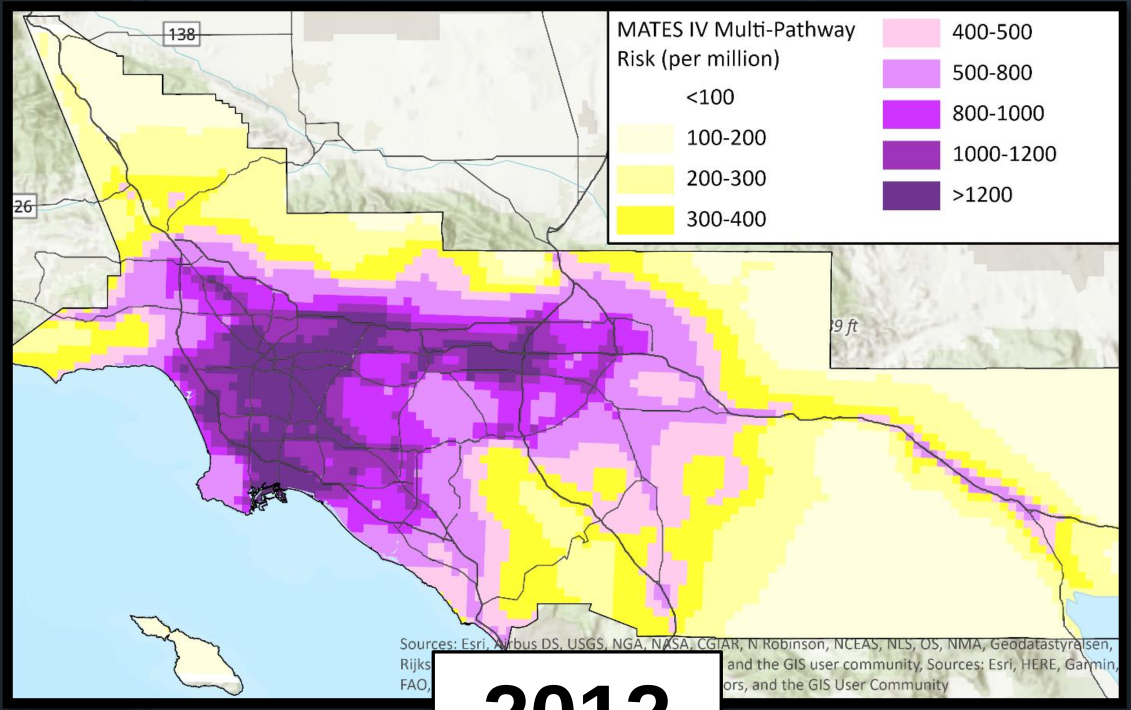
Chronic non-cancer health impacts were estimated for the first time, with a chronic hazard index of 5-9 across the 10 stations

MATES V webpage: http://www.aqmd.gov/MATES5

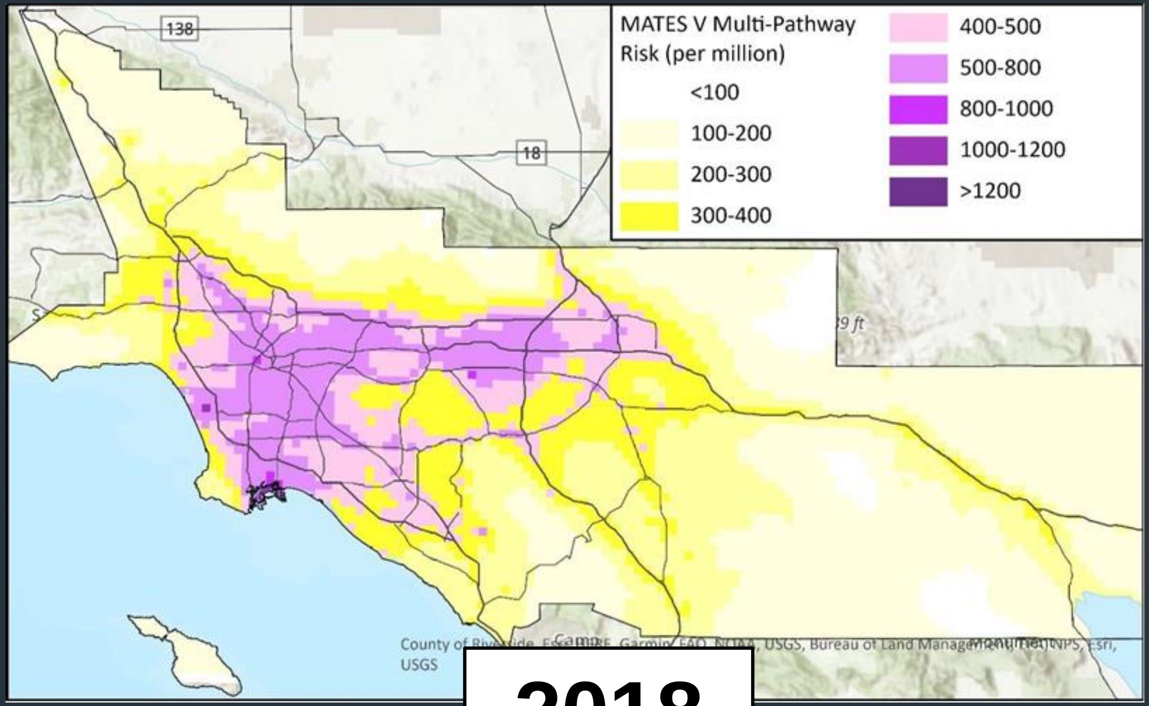
# Air Toxics Cancer Risk – Modeling Data

**MATES IV** (population-weighted):
South Coast Air Basin: **997-in-a-million**
Coachella Valley: **357-in-a-million**

**MATES V** (population-weighted):
South Coast Air Basin: **455-in-a-million**
Coachella Valley: **250-in-a-million**

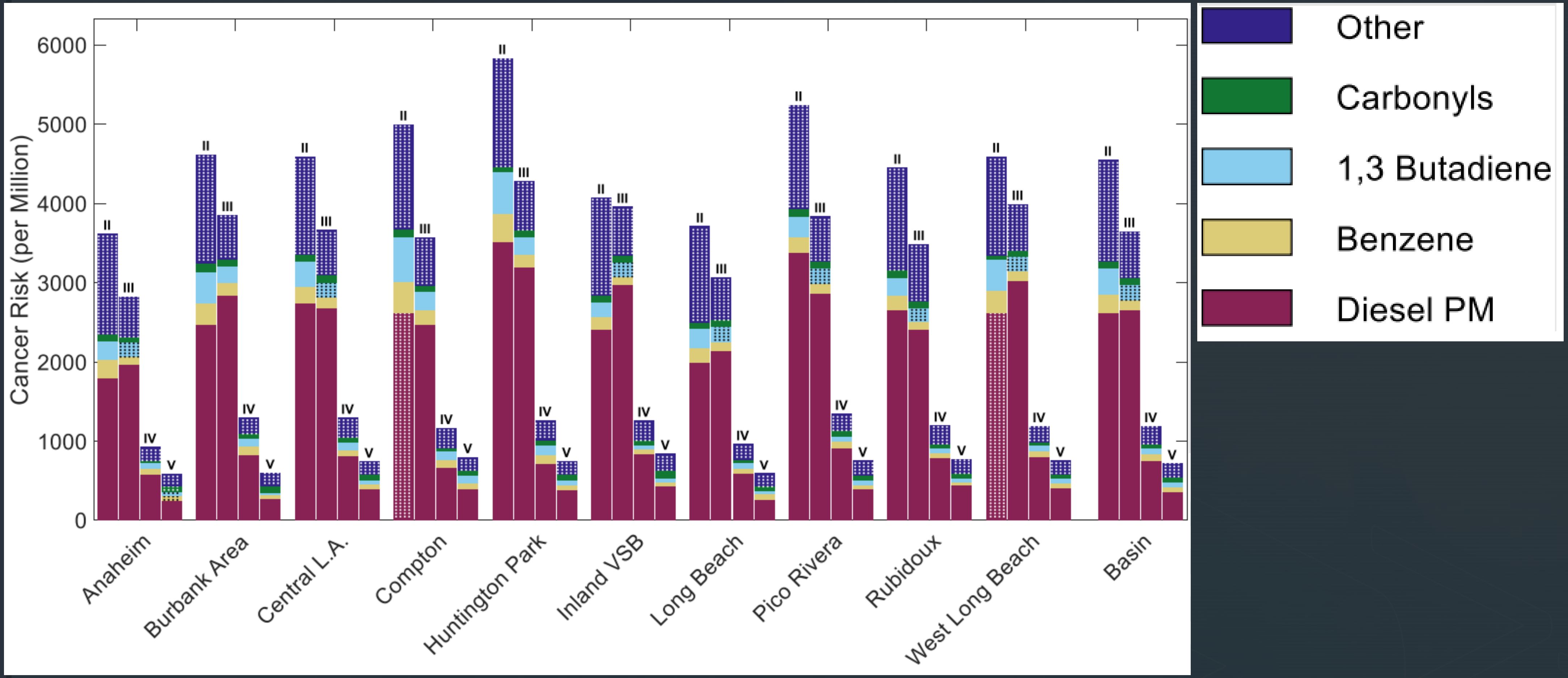



2012




2018

# MATES V Cancer Risk Trends
(based on monitoring data)




MATES V webpage and interactive web interface: http://www.aqmd.gov/MATES5

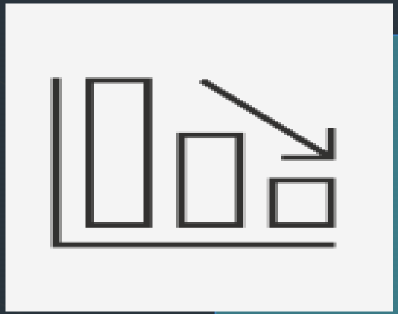
# MATES VI Approach

Solicit Feedback from 20 Member Technical Advisory Group


Air Monitoring Campaign at 10 Locations

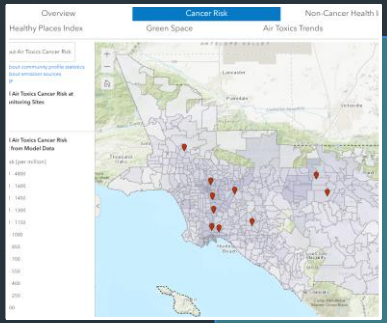
- South Coast Air Basin and Coachella Valley
- Two Near-Road Sites
- One Year

Comprehensive Modeling Analysis of Air Toxics Cancer Risk with Updated Emission Inventory



Analysis of Trends in Concentrations and Health Risk Over Past MATES Studies

Cancer Risk and Chronic Non-Cancer Health Impacts Determined with Measurement Data

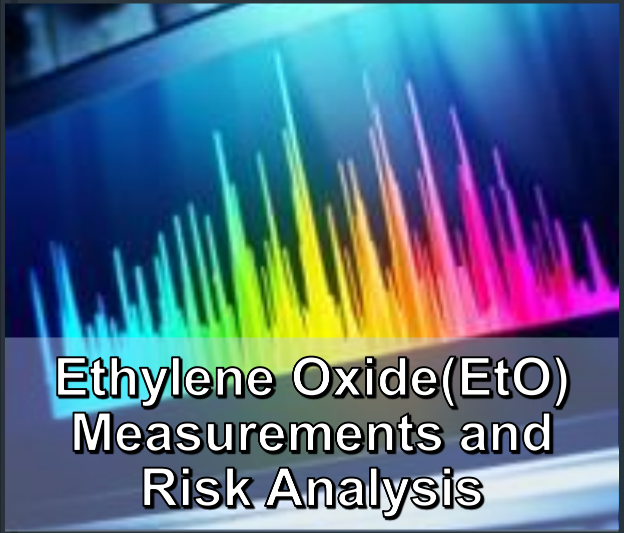


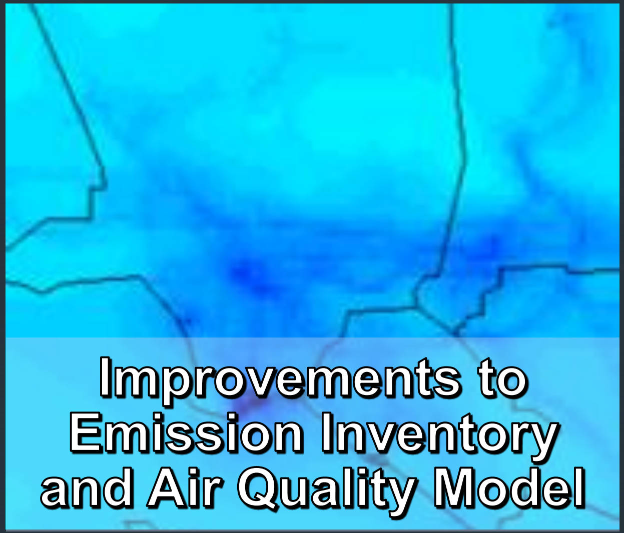

Online Interactive Data Display to Visualize Risk and Concentration Data

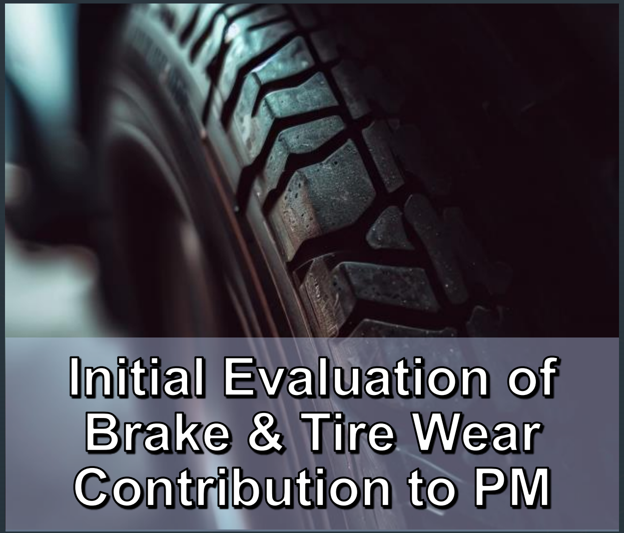
MATES VI webpage: http://www.aqmd.gov/MATES6

# What’s New for MATES VI?

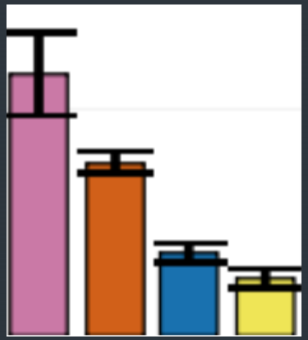


# How are MATES Results Used?



- Evaluate progress of air toxic control programs
- Help prioritize policy-making by determining major contributors to toxic risk
- Help interpret data from special air toxics monitoring studies and community air monitoring projects
- Identify unknown air toxics sources
- Help address public inquiries related to air toxics impacts

# MATES VI Process

## Planning & Preparation Stage (~1.5 years)

| Consultation with TAG | Obtaining Equipment & Supplies | Monitoring Site Preparation | Instrument Deployment & Testing |
|---|---|---|---|

## Field Measurements & Air Quality Modeling (~1.5 years)

| Instrument Operation & Maintenance | Collection & Lab Analysis of Samples | Emission Inventory Preparation | Meteorology & Air Toxics Modeling |
|---|---|---|---|

## Data Analysis (~1 year)

| Data QA/QC | Measured & Modeled Data Comparison | Cancer & Chronic Risk Calculation | Comparison to Past MATES Data | Source Apportionment Study |
|---|---|---|---|---|

## Dissemination (~9 months)

| Continued Consultation with TAG | Draft & Final Report | Design and Development of Interactive Tools | Public Outreach |
|---|---|---|---|

**Public Process**

# Tentative Timeline* & Next Steps

**2023**
1st TAG Meeting, Governing Board & Administrative Committee Meetings

**2024**
Instrument Acquisition and Testing

**2025-2026**
Air Monitoring Campaign

**2026-2027**
Analysis of Monitoring and Air Quality Modeling Data

**2027-2028**
Release of MATES VI Report and Online Interactive Data Visualization Tools

- November 9th Administrative Committee Meeting
- December 1st Governing Board Meeting
- MATES VI homepage: www.aqmd.gov/MATES6.

* Schedule subject to change

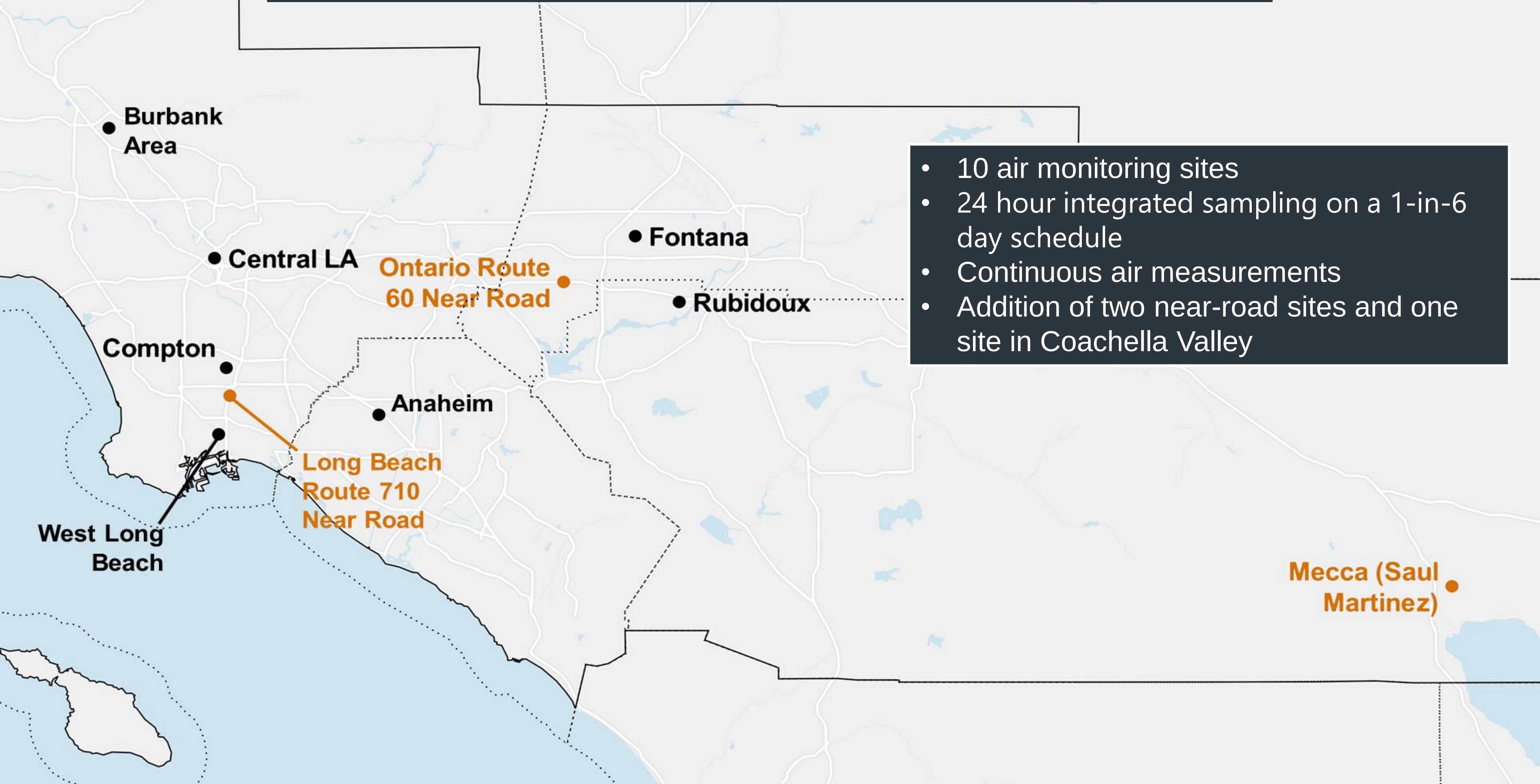
# 3. Overview of Fixed Site Measurements

**Payam Pakbin, Ph.D.**
**Atmospheric Measurements Manager**
**Advanced Monitoring Technologies**
**Monitoring & Analysis Division**

MATES VI Technical Advisory Committee Mtg. #1

October 26, 2023

# MATES VI Fixed Monitoring Stations

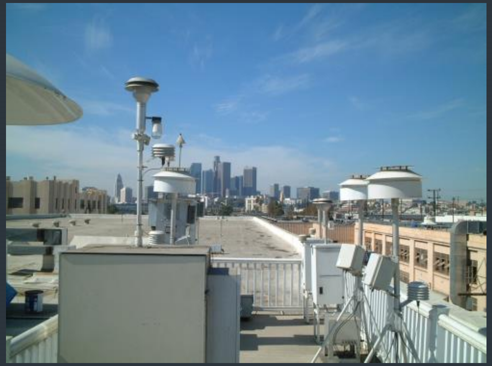


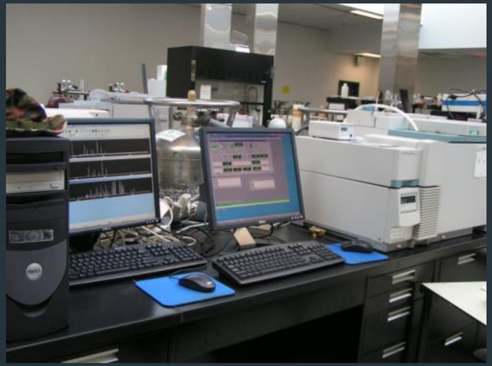

- 10 air monitoring sites
- 24 hour integrated sampling on a 1-in-6 day schedule
- Continuous air measurements
- Addition of two near-road sites and one site in Coachella Valley

# MATES VI Monitoring & Analysis Gaseous

All 10 sites

| Substance | Sampling Equipment | Analytical Method |
|---|---|---|
| VOCs | XonTech 910A/ 912 | TO-15A (GC-MS) |
| Carbonyls | ATEC 8000 | TO-11A (UHPLC) |
| SVOCs (PAH) | PUF | TO-13 (GC-MS) |





# MATES VI Monitoring & Analysis
# Gaseous

All 10 sites

| Substance | Sampling Equipment | Analytical Method |
|---|---|---|
| VOCs | XonTech 910A/ 912 | TO-15A (GC-MS) |
| Carbonyls | ATEC 8000 | TO-11A (UHPLC) |
| SVOCs (PAH) | PUF | TO-13 (GC-MS) |

- Benzene
- Bromomethane
- 1,3-Butadiene
- Carbon Tetrachloride
- Chloroform
- Dibromoethane
- 1,2-Dichlorobenzene
- 1,4-Dichlorobenzene
- 1,2-Dichloroethane
- Ethylbenzene
- Ethylene Oxide
- Methylene Chloride
- Methyl t-Butyl Ether
- Perchloroethylene
- Styrene
- Toluene
- Trichloroethylene
- (m+p)-Xylenes
- o-Xylene
- Vinyl Chloride

# MATES VI Monitoring & Analysis Gaseous

All 10 sites

| Substance | Sampling Equipment | Analytical Method |
| --- | --- | --- |
| VOCs | XonTech 910A/ 912 | TO-15A (GC-MS) |
| Carbonyls | ATEC 8000 | TO-11A (UHPLC) |
| SVOCs | PUF | TO-13 (GC-MS) |

Carbonyls:
- Acetaldehyde
- Formaldehyde
- Methyl Ethyl Ketone

# MATES VI Monitoring & Analysis Gaseous

All 10 sites

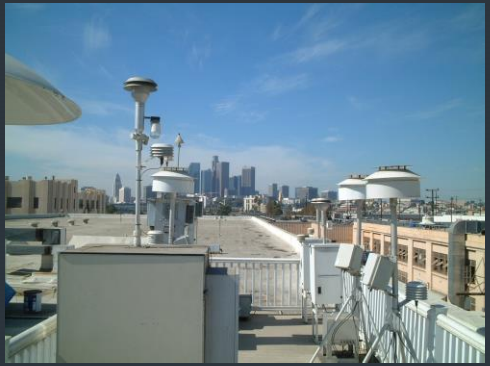
| Substance | Sampling Equipment | Analytical Method |
|---|---|---|
| VOCs | XonTech 910A/ 912 | TO-15A (GC-MS) |
| Carbonyls | ATEC 8000 | TO-11A (UHPLC) |
| SVOCs | PUF | TO-13 (GC-MS) |

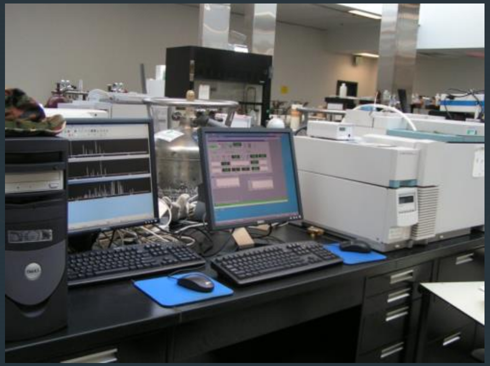
- Acenaphthene
- Acenaphthylene
- Anthracene
- Benz(a)anthracene
- Benzo(a)pyrene
- Benzo(b)fluoranthene
- Benzo(e)pyrene
- Benzo(g,h,i)perylene
- Benzo(k)fluoranthene
- Chrysene
- Coronene
- Dibenz(ah)anthracene
- Fluoranthene
- Fluorene
- Indeno(123-cd)pyrene
- Naphthalene
- Perylene
- Phenanthrene
- Pyrene

# MATES VI Monitoring & Analysis
# Particulate Matter Speciation – $PM_{2.5}$

6 Sites (Core Chemical Speciation Network (CSN) and 2 Near Road)

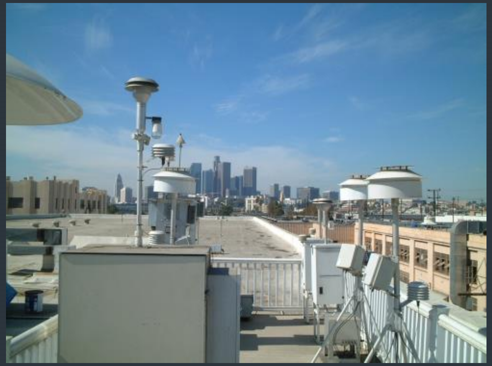
| Substance | Sampling Equipment | Analytical Method |
|---|---|---|
| Metals | Met One SASS | ED-XRF |
| EC/OC | Met One SASS | Thermal-optical |
| Ions | Met One SASS | IC |
| Mass | Met One SASS | Microbalance |

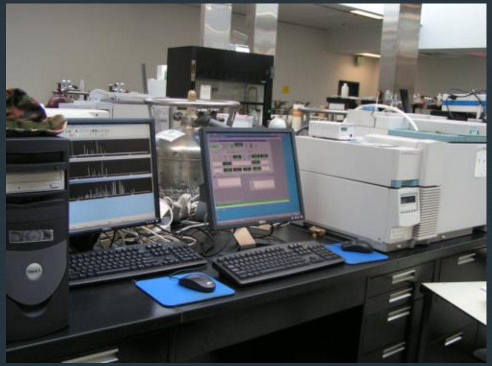




# MATES VI Monitoring & Analysis
# Particulate Matter Speciation – $PM_{10}$
All 10 sites

| Substance | Sampling Equipment | Analytical Method |
|---|---|---|
| Metals | SSI Hi-Vol | ICP-MS |
| EC/OC | SSI Hi-Vol | Thermal-optical |
| Ions | SSI Hi-Vol | IC |
| Levoglucosan | SSI Hi-Vol | GC-MS |
| Mass | SSI Hi-Vol | Balance |





# MATES VI Monitoring & Analysis Particulate Matter Speciation – PM10

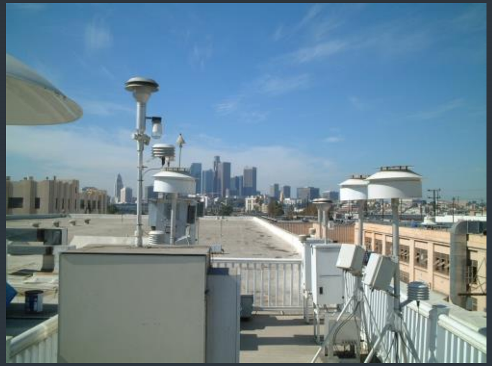
All 10 sites

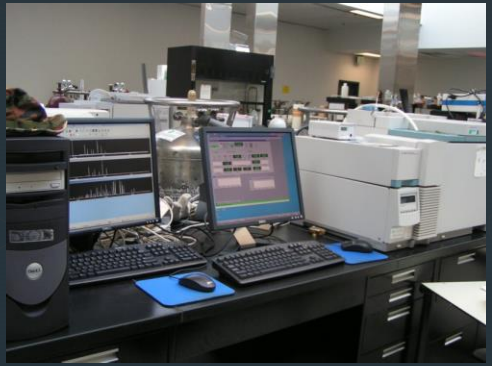
| Substance | Sampling Equipment | Analytical Method |
|---|---|---|
| Metals | SSI Hi-Vol | ICP-MS |
| EC/OC | SSI Hi-Vol | Thermal-optical |
| Ions | SSI Hi-Vol | IC |
| Levoglucosan | SSI Hi-Vol | GC-MS |
| Mass | SSI Hi-Vol | Balance |

- Antimony
- Arsenic
- Barium
- Beryllium
- Cadmium
- Calcium
- Cesium
- Chromium
- Cobalt
- Copper
- Iron
- Lead
- Manganese
- Molybdenum
- Nickel
- Potassium
- Rubidium
- Selenium
- Strontium
- Tin
- Titanium
- Uranium
- Vanadium
- Zinc

# MATES VI Monitoring & Analysis
# Particulate Matter Speciation – TSP
2 sites (Central Los Angeles & Riverside – Rubidoux)

| Substance | Sampling Equipment | Analytical Method |
|---|---|---|
| Metals | SSI Hi-Vol | ICP-MS |
| $Cr^{+6}$ | XonTech 924 | IC |





# MATES VI Monitoring & Analysis Continuous

| Substance | Sampling Equipment | Analytical Method |
|---|---|---|
| Black Carbon | Aethalometer | Optical absorption |
| Ultrafine PM | CPC | Optical counting |
| Elements & Metals (limited) | Xact | ED-XRF |
| Ammonia (limited) | Picarro | CRDS |
| Ethylene Oxide (limited) | Aerodyne | TILDAS |


# Quality Assurance Overview

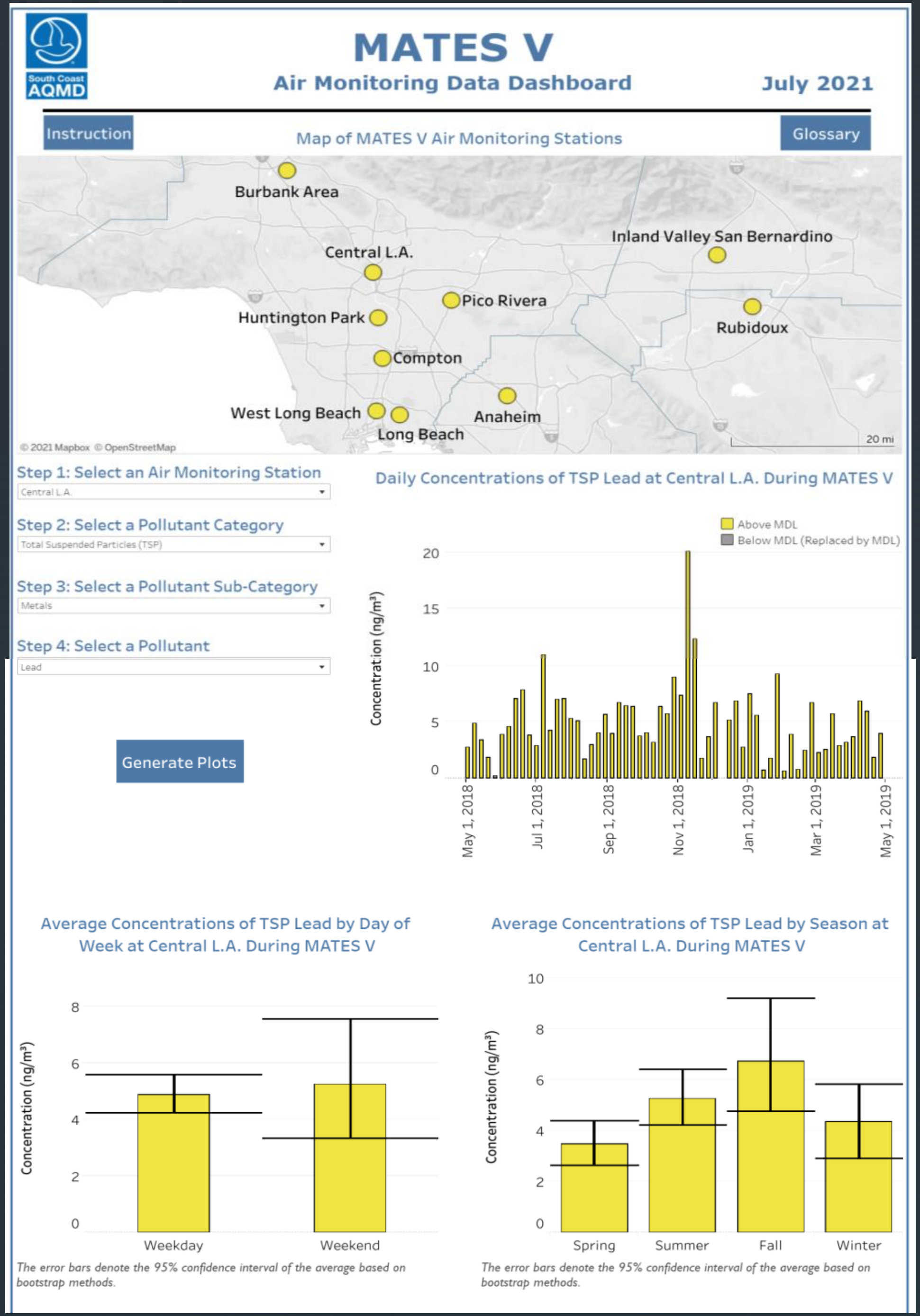
**<u>Objectives</u>:**

- Provide ambient air toxics data meeting the requirements for accuracy and precision to serve as inputs for risk assessment model(s)
- Develop an ambient air toxics database that is comparable to those for previous MATES and with other air toxics measurement program data (if applicable)
- QA criteria/parameter are based on NATTS and Appendix A for PM10/ PM2.5

**<u>Quality Control</u>:**

- Inspections and testing of consumables, instruments, and equipment
- Technical checks to evaluate meeting measurement criteria goals
  - Flow checks; calibrations; blanks; intercomparisons; replicates; duplicates
- Data validation

# MATES V
# Air Monitoring Data Dashboard



# 4. Diesel PM RISK Estimation in MATES VI

**Melissa Maestas, Ph.D.**
**Air Quality Specialist, Air Quality Assessment**
**Planning, Rule Development, and Implementation**

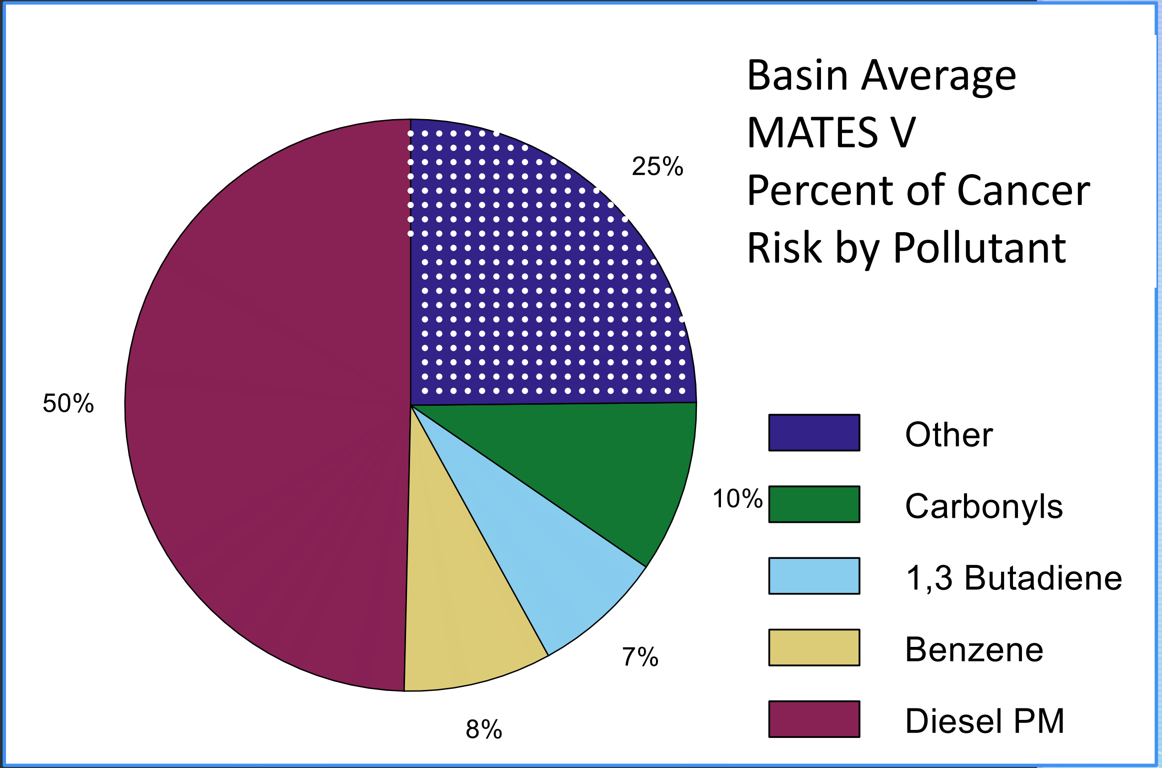
**Scott A. Epstein, Ph.D.**
**Program Supervisor, Air Quality Assessment**
**Planning, Rule Development, and Implementation**

MATES VI Technical Advisory Committee Mtg. #1

October 26, 2023

# Outline

- Describe strategy for estimating Diesel PM contribution to cancer risks
- Summarize impacts of removing EC measurements
- Questions for TAG




White dots indicate that some species in this category have higher uncertainty.

Glossary:
PM = particulate matter
EC = elemental carbon
TAG = Technical Advisory Group
MATES = Multiple Air Toxics Exposure Study

# Previous MATES – Calculation of Cancer Risk from Diesel

1. ‘Convert’ EC to diesel based on EC to diesel ratios from photochemical model at station locations
2. Calculate risk from simulated diesel concentrations

EC → Diesel → Risk

# EC → Diesel → Risk

DPM/EC ratio from model at station locations

$$Toxic\ Risk_{DPM} = EC \times \frac{DPM}{EC} \times Risk\ Factor$$

Average of measured EC (PM2.5) at station

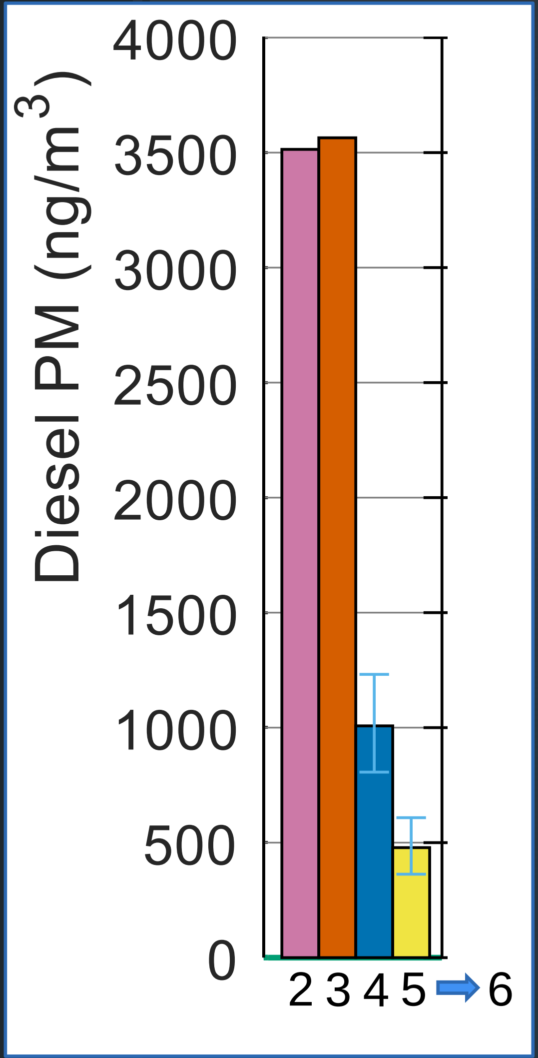
From OEHHA

No technique to directly measure diesel PM

Glossary:
OEHHA = California Office of Environmental Health Hazard Assessment

See pages ES-14 and ES-15 of MATES V report about uncertainties

# Requirements of Method to Estimate "Measured" Diesel Levels

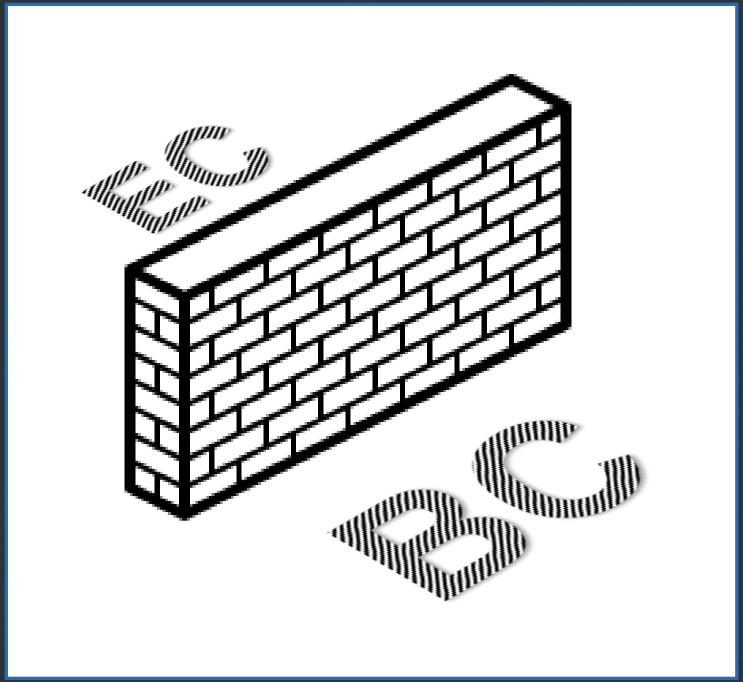



- Limited EC measurements proposed in MATES VI due to significant resource impacts
  - BC measurements at every station will still be available as in past MATES campaigns
- Clear metric that represents diesel and only diesel
  - Estimating diesel concentrations from source apportionment may not be practical due to difficulties in separating diesel from gasoline

Continue trend calculations

# Obstacles in Switching to BC for Risk Calculation

- BC is generally higher than EC so we cannot replace the EC values with BC without any correction
- The relationship of BC/EC changes over long periods
- There is no emission inventory for BC so DPM/BC cannot be calculated from emission inventory or from modeling BC values




Glossary:
BC = black carbon

# Proposed Approach for Estimation of "Measured" Diesel with BC Measurements

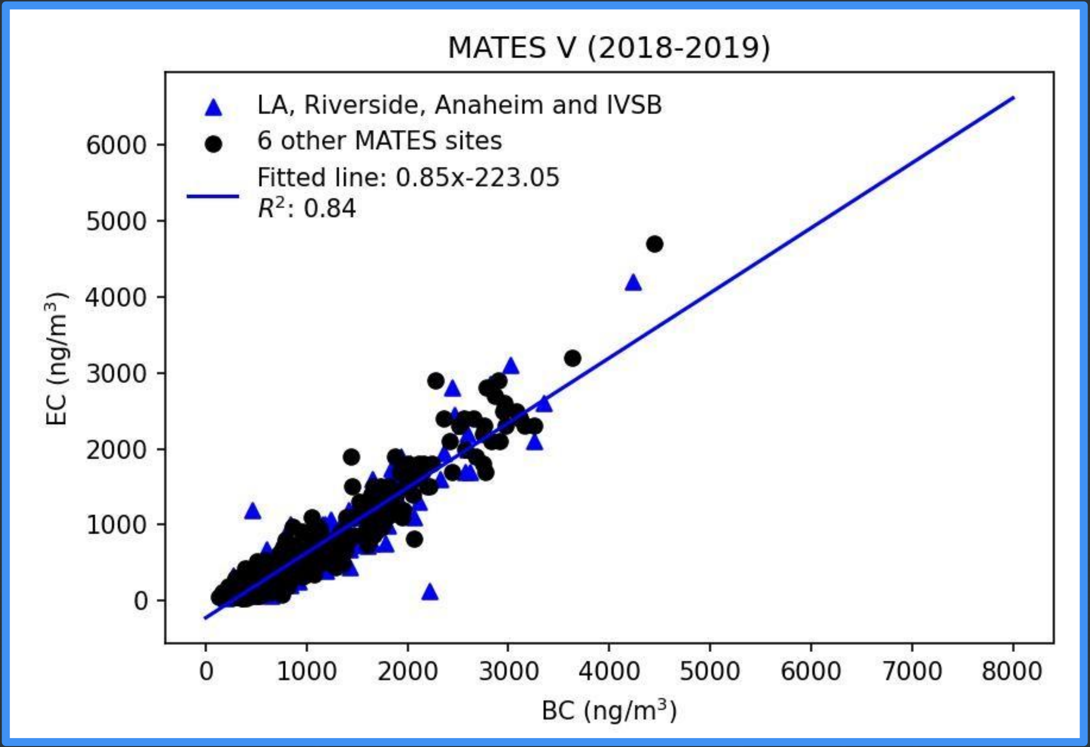
- Simultaneous measurement will be done at four sites to calibrate the relationship between EC and BC
- EC levels at each site can be estimated based on BC values and the EC to BC relationship calculated in the previous step
- The estimated EC will be used in risk calculation

BC → EC → Diesel → Risk

# Proposed method – Calculation of Cancer Risk from Diesel

New

1. Only measure EC at 4 Sites
   1. LA, Riverside, Anaheim, IVSB
   2. EC – logistical challenges & labor intensive
2. Fit equation of EC = slope*BC + intercept
3. 'Convert' annual BC to annual EC
4. 'Convert' calculated EC to diesel
5. Calculate risk




BC → EC → Diesel → Risk

Glossary: ISVB = Inland Valley San Bernardino

# BC → EC → Diesel → Risk

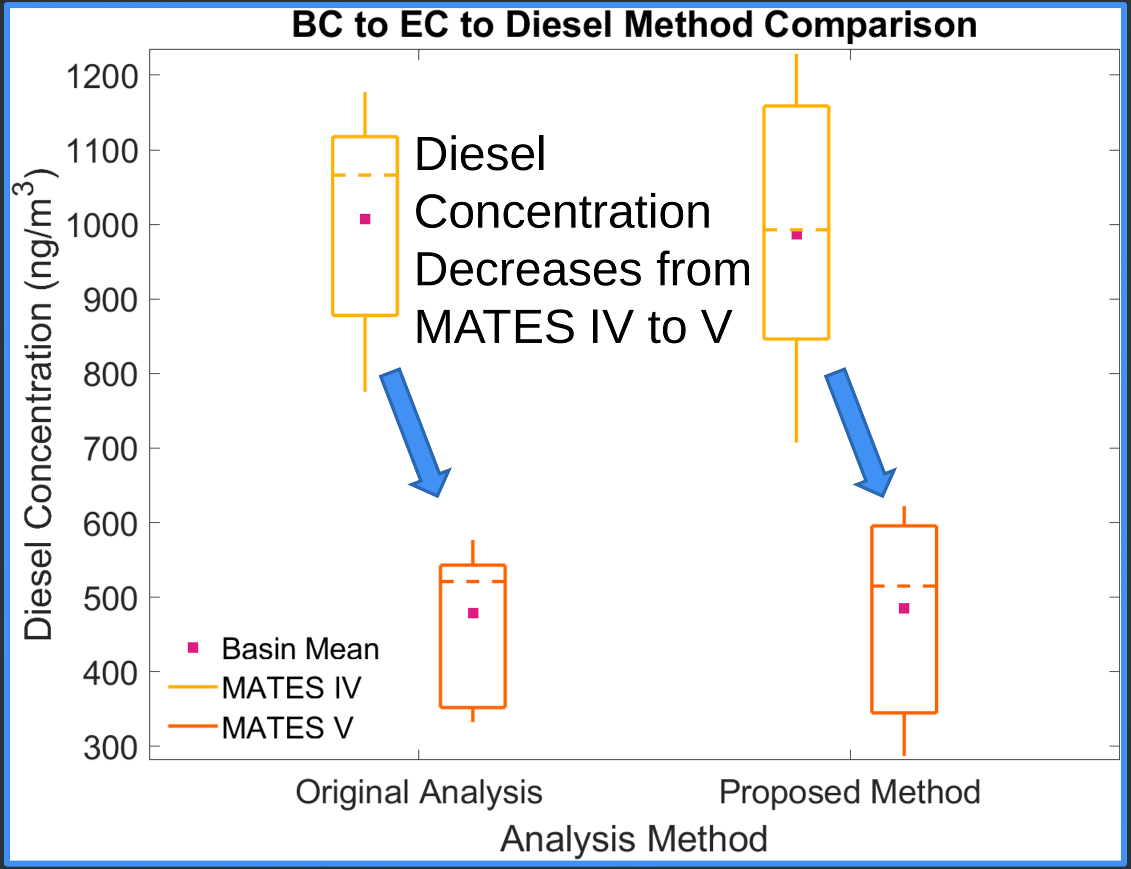
EC = a*BC + b
Fit from 4 sites with EC data

$$Toxic\ Risk_{DPM} = EC \times \frac{DPM}{EC} \times Risk\ Factor$$

4 sites with EC data:
- Los Angeles (LA)
- Rubidoux
- Anaheim
- Inland Valley San Bernardino (IVSB)

# Apply Proposed Method to Previous MATES Data

- Similar reduction in Diesel PM from MATES IV to V using original analysis and proposed method.
  - Conclusion is not dependent on choice of method




All data analyzed is at the annual time resolution

# Questions for TAG

- Are there better methods to estimate diesel contribution to risk?
- If we go with the described plan, are there any improvements we can make?
- Any other concerns from removing EC measurements at 6 of 10 MATES VI stations?

# 5. Exploration of Brake and Tire Wear Contribution to PM

**Scott A. Epstein, Ph.D.**
**Program Supervisor, Air Quality Assessment**
**Planning, Rule Development, and Implementation**

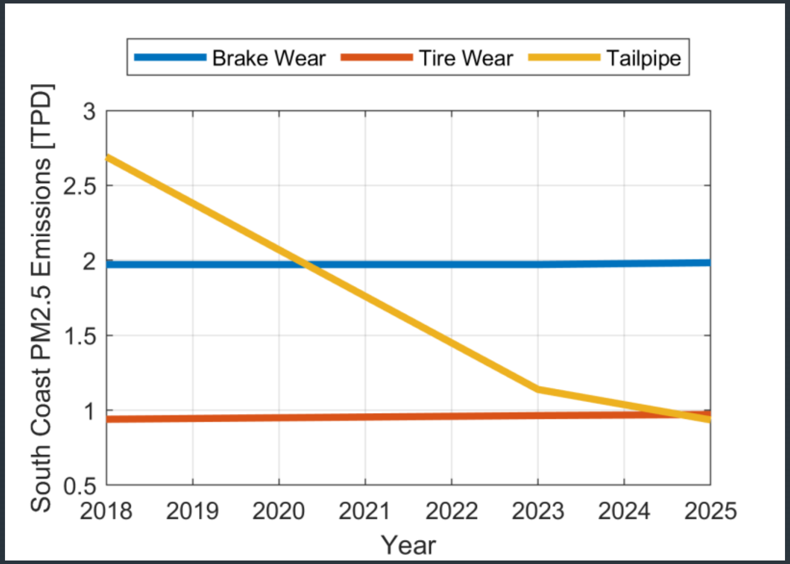
**Nick Molden**
**Founder & CEO**
**Emissions Analytics**

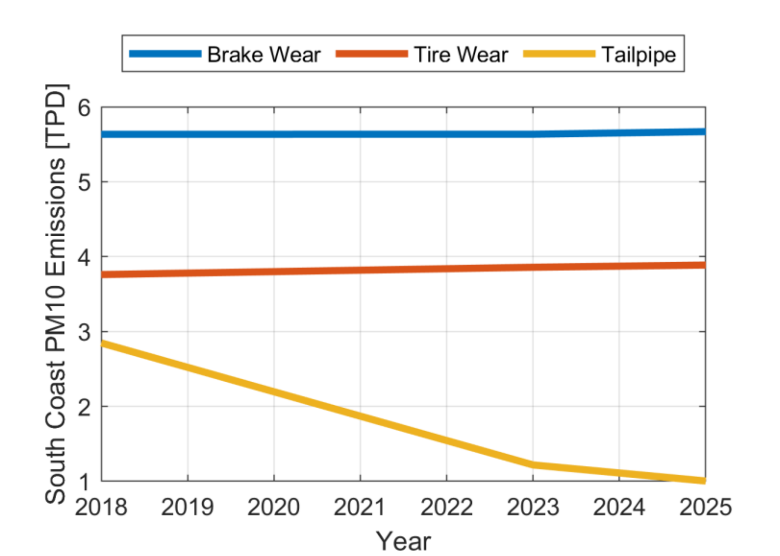
MATES VI Technical Advisory Committee Mtg. #1

October 26, 2023

# Background

- Contribution of non-exhaust emissions to total mobile source PM emissions is increasing
- Potential respiratory, cardiovascular, developmental & reproductive, and carcinogenic effects
- Important source of both fine and coarse particles



# Objectives

- Quantify the contribution of brake and tire wear emissions on PM levels throughout the region
  - Near road
  - Regional monitors
- Estimate the health effects of these emissions
  - Cancer risk
  - Chronic non-cancer risk

# Fingerprinting tyre emissions:

## *Characterising their chemical composition*

Presentation to the technical advisory group on MATES VI

Nick Molden

26 October 2023

ASSURED | INDEPENDENT | RESPONSIVE

# Overview

- State of the science
- Understanding non-exhaust emissions
- Approaches to measurement and fingerprint
- Speciation and potential health effects



**Source:** Emissions Analytics 2023

# Air pollutants

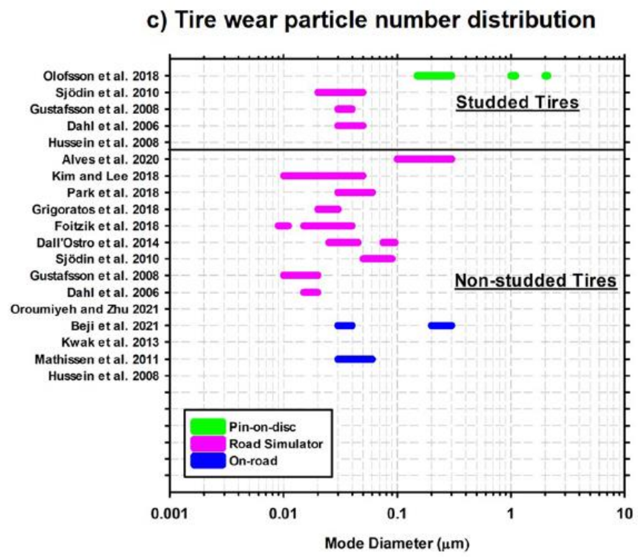
ASSURED | INDEPENDENT | RESPONSIVE

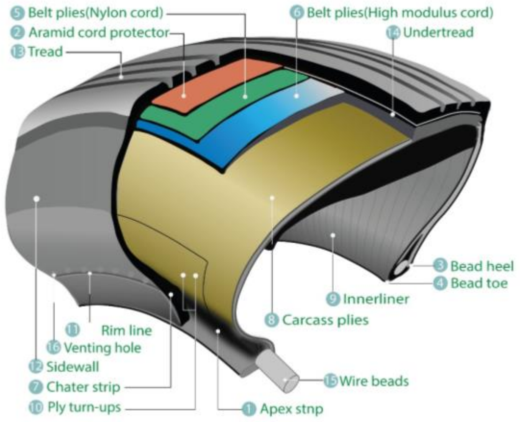
# Particles from tyres

- On-road test with ‘normal’ dynamics
- 11% of fine particle mass is below 2.5 μm diameter
- This mass accounts for almost 100% of particle number
- And ultrafines account for 92% by number
- Other potential source of ultrafines is from combustion, but influence from other vehicles eliminated
- Results borne out in academic literature

➢ Wide size distribution range

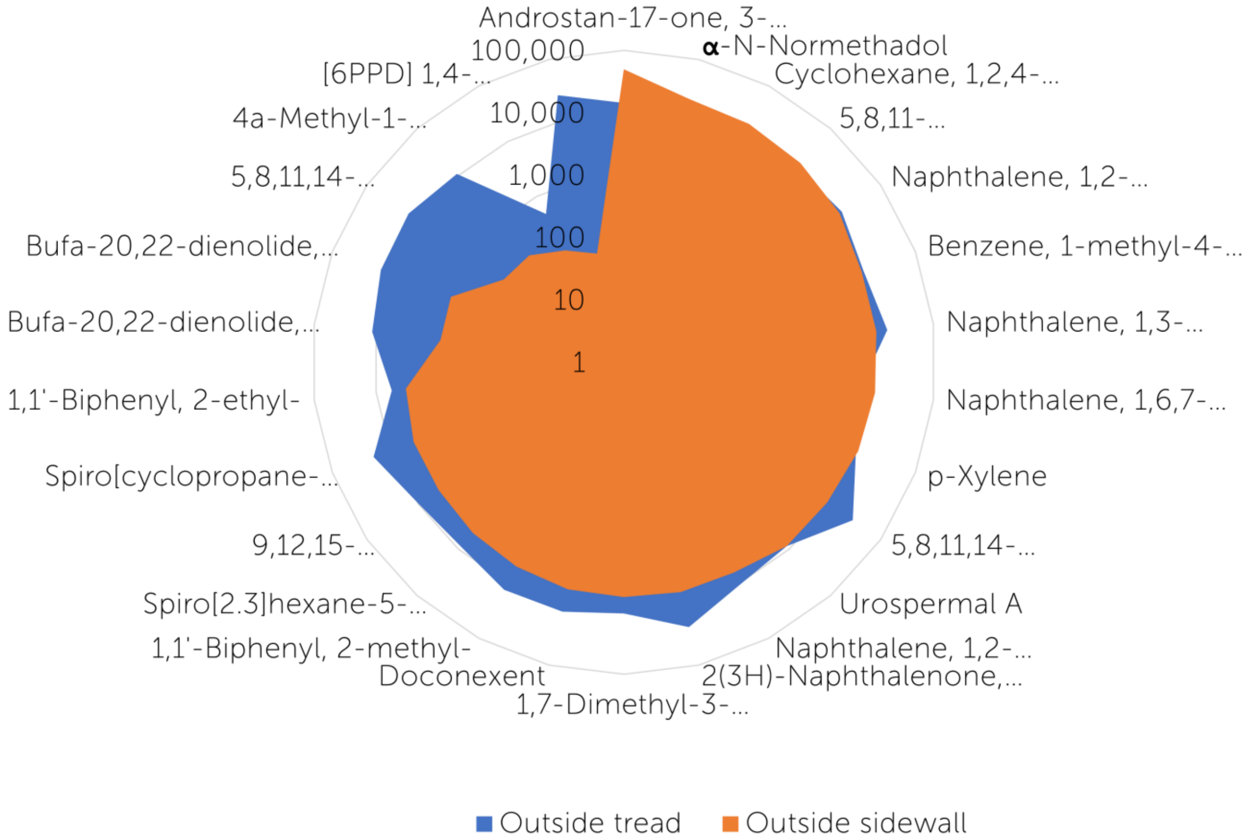
| Particulate mass | mg/km |
|---|---|
| | |
| PM 10 | 36.5 |
| PM 2.5 | 4.1 |
| | |
| PM 2.5 proportion of PM 10 | 11% |
| Ultrafine proportion of PM 10 | 0% |
| | |
| **Particulate number** | **# x10$^{11}$/km** |
| | |
| Down to 23 nm | 1.1 |
| Down to 6 nm | 14.5 |
| | |
| Fine as proportion of PM 10 | 8% |
| Ultrafine as proportion of PM 10 | 92% |






# Secondary pollutants

- Secondary organic aerosol formation from off-gassed VOCs reacting in air
- Mainly from tyre sidewall, which can be different chemical composition from tread
- SOA Yield of 4.01 μg/$m^3$ from toluene in recent research in Shanghai




BTAS brake and tyres analysis system

# Organic fingerprinting

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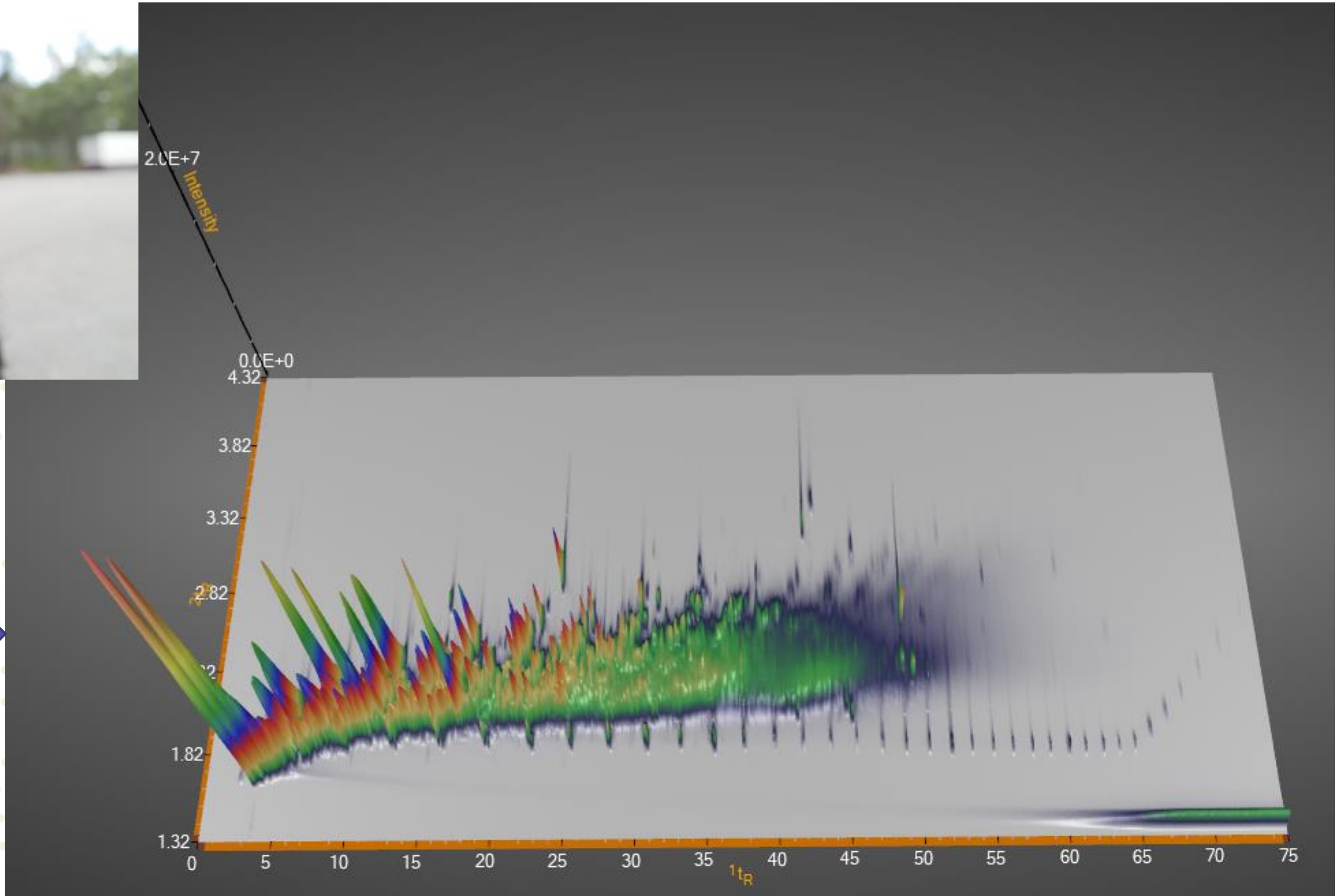
EQUA real-world test database

# Measurements – volatile organic compounds

- Two-dimensional gas chromatography with mass spectrometry from
- INSIGHT flow modulator from SepSolve Analytical for separation
- BENCH-TOF time-of flight mass spectrometer
- OPTIC-4 sample introduction


**Source:** Emissions Analytics 2023

# Two-dimensional pyrolysis chromatogram

# Fingerprint tyres to measure in environment

| Compound; peak area % | Androstan-17-one, 3-ethyl-3-hydroxy-, (5α)- | Limonene | β-Guaiene | Longifolene | Ursodeoxycholic acid | Cyclohexane, 1,2,4-triethenyl- | Desogestrel | 2-[4-methyl-6-(2,6,6-trimethylcyclohex-1-enyl)hexa-1,3,5-trienyl]cyclohex-1-en-1-carboxaldehyde | Doconexent |
|---|---|---|---|---|---|---|---|---|---|
| | $C_{21}H_{34}O_2$ | $C_{10}H_{16}$ | $C_{15}H_{24}$ | $C_{15}H_{24}$ | $C_{24}H_{40}O_4$ | $C_{12}H_{18}$ | $C_{22}H_{30}O$ | $C_{23}H_{32}O$ | $C_{22}H_{32}O_2$ |
| Tyre 1 | 16.8 | 3.8 | 5.8 | 2.7 | 5.4 | 3.1 | 1.4 | 1.9 | 3.0 |
| Tyre 2 | 17.2 | 5.2 | 4.9 | 2.4 | 5.3 | 2.6 | 0.5 | 2.8 | 4.1 |
| Tyre 3 | 8.0 | 5.6 | 5.4 | 4.0 | 10.5 | 2.0 | 1.1 | 3.0 | 2.4 |
| Tyre 4 | 7.7 | 4.9 | 4.3 | 4.4 | 6.7 | 1.4 | | 2.3 | 0.6 |
| Tyre 5 | 6.3 | 2.7 | 3.9 | 1.6 | | 3.3 | 3.4 | | |
| Tyre 6 | 10.1 | 3.9 | 4.3 | 6.2 | 0.6 | 1.8 | 2.5 | 1.5 | |
| Tyre 7 | 10.9 | 4.9 | 5.2 | 5.6 | | 2.7 | 3.7 | 1.5 | |
| Tyre 8 | 10.9 | 4.3 | 4.7 | 5.1 | 2.8 | 2.4 | 2.4 | 1.8 | |
| Tyre 9 | 7.9 | 3.8 | 4.9 | 6.3 | 0.7 | 1.6 | 2.5 | 1.4 | |
| Tyre 10 | | 6.3 | | | | 4.3 | | | 4.1 |
| Total | 95.7 | 45.4 | 43.3 | 38.3 | 32.0 | 25.1 | 17.6 | 16.1 | 14.3 |
| Description | Unknown | terpenic pine herbal peppery | sweet woody dry guaiacwood spicy powdery | sweet woody rose medical fir needle; irritant to skin and eyes | Drug to dissolve cholesterol; irritant to skin and eyes | Eye, skin, respiratory irritant | Hormone | Unknown | Fatty acid |

- Fragrances – citrus, sweet, woody, spicy
- Irritants – eyes, skin
- 2 unknowns

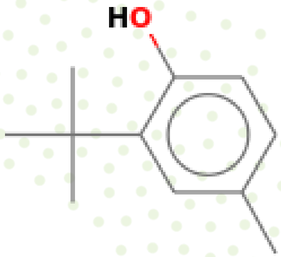
➢ Tyre 10 has very different composition

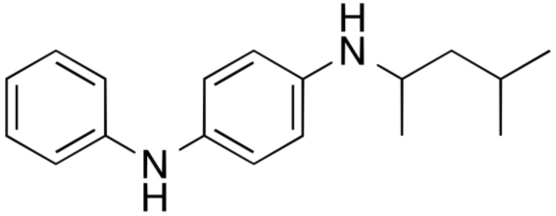
**Source:** Emissions Analytics 2023

# Notable compounds, but no individual tracer

Prevalent in Tyre 8

- phenol, 2-(1,1dimethylethyl)-4-methyl-
- Respiratory irritant, leathery smell




In all tyres, but significant concentration variation

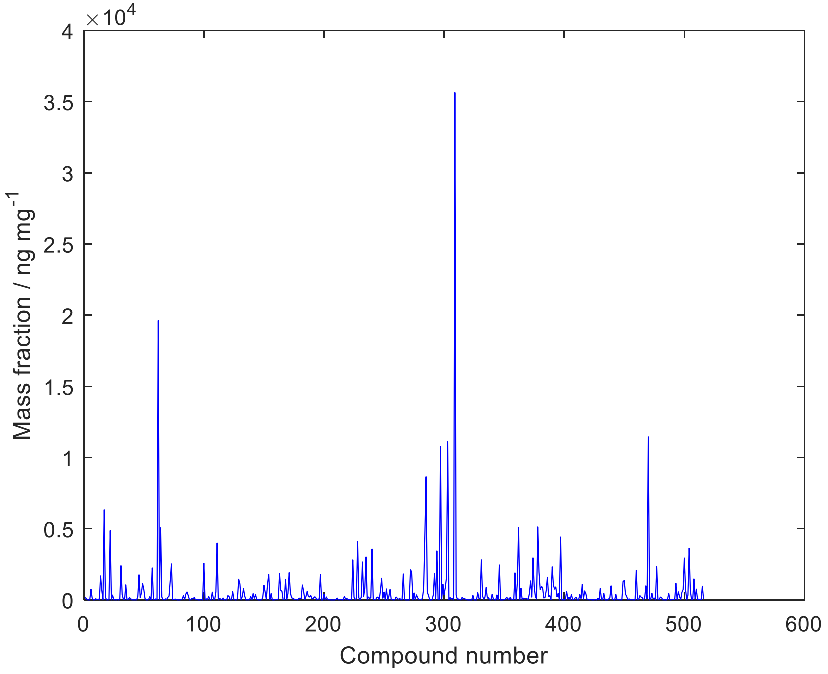
- N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine, aka 6PPD
- Preservative, reacts with ozone in the air
- 6PPD-quinone killed coho salmon in California



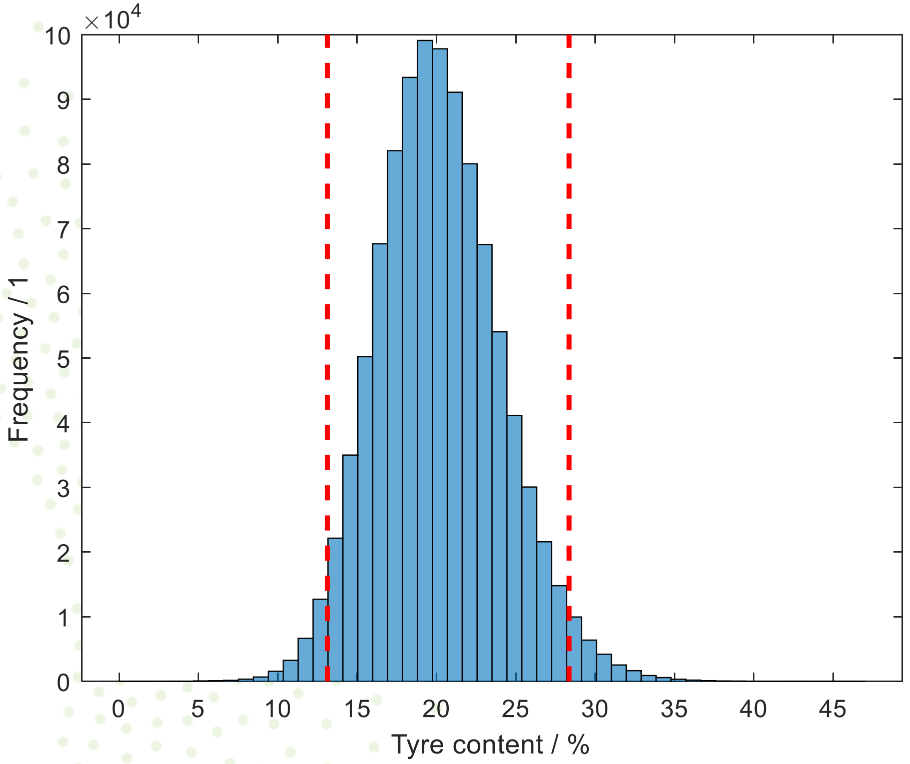
**Source:** Emissions Analytics 2023

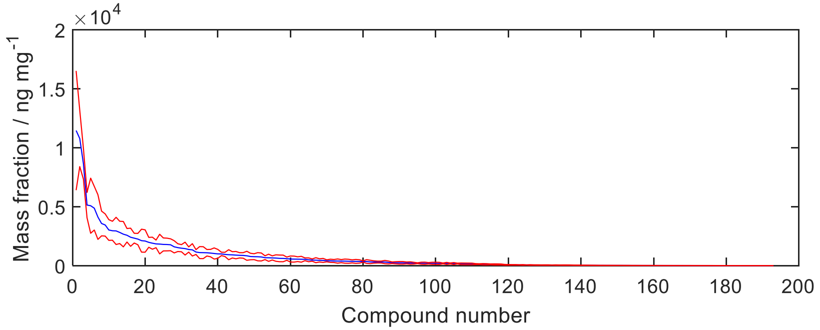
# Estimating air concentrations

- Pyrolyse environmental sample
- Compare to reference database of tyre material
- Use analytics to quantify concentrations




| Sample(s) | Number of unique compounds | Number of common compounds |
|---|---|---|
| Tyre | 516 | – |
| Wear | 1577 | – |
| Tyre and wear | 1900 | 193 |




**Source:** Emissions Analytics 2023

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# Inorganic fingerprinting

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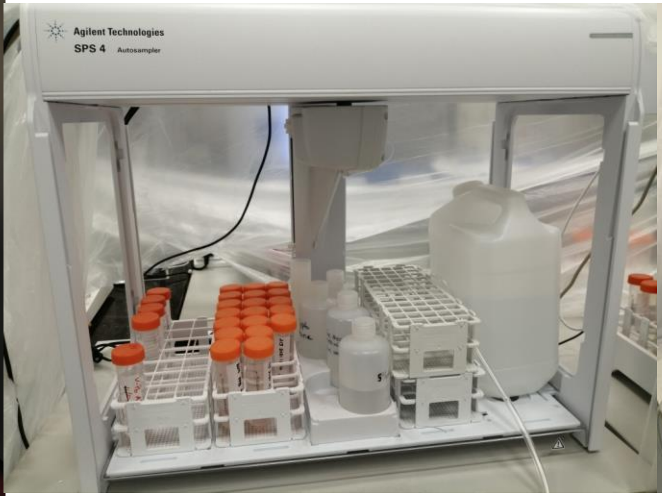
EQUA real-world test database

NPL National Physical Laboratory

# Metals analytical method

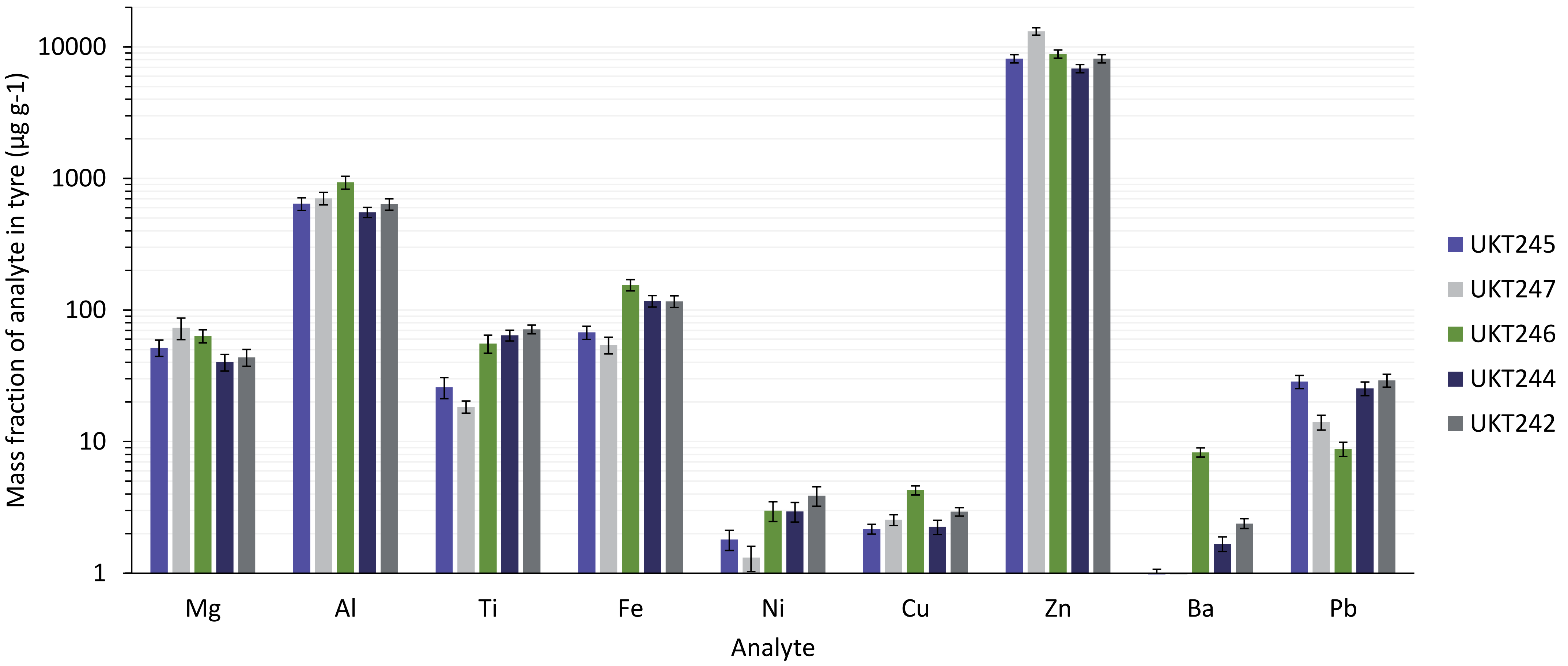




Weighed samples added to digestion vessels with nitric and sulfuric acid → Acid digestion in microwave at 140°C → Diluted aqueous samples put in autosampler → Analysis by tandem inductively coupled plasma mass spectrometry

BTAS brake and tyres analysis system

**Source:** Emissions Analytics 2023

# Mass fraction of metal analytes in tyres




**Source:** Emissions Analytics 2023

# Thank you.

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# Questions for the TAG

- What approaches are recommended?
  - Plan to allocate up to $850K for an RFP to study brake and tire wear.
- Any similar measurements conducted in Southern California?
- Are there other objectives that we should focus on in addition to or instead of what we proposed?

# 6. Open Discussion and Public Comments

MATES VI Technical Advisory Committee Mtg. #1

October 26, 2023

# Proposed TAG Discussion Topics for Next Meeting

- Interactive graphical tools for disseminating MATES results
- EtO literature review, monitoring strategy, and potential contribution to total risk
- Regional modeling analysis: emissions inventory and modeling
- In-depth discussion of RFP for brake and tire wear
- Any other topics to discuss in depth at the next TAG meeting?

# Discussion Topics

- Are proposed measurements adequate to conduct a comprehensive source apportionment study?
- Any other objectives we can accomplish with the current MATES framework?
- Are there any new risk drivers that may not be on our radar that we should measure?
- Other TAG feedback and public comment