TRACE METAL EMISSIONS FROM MOTOR VEHICLES

James Schauer, Glynis C Lough
and Martin M. Shafer

Environmental Chemistry and Technology Program
University of Wisconsin – Madison
Madison, Wisconsin

OUTLINE

- Objectives
- Sampling and analysis
- Measurement of motor vehicle emissions
- Ambient sampling and results

MOTIVATION

- Observed association between human health effects and increased atmospheric PM concentrations
  - Mechanisms of health effects from PM are not understood
  - Trace metals may be important components
- Origins, concentrations, and impacts of trace metals in atmospheric PM are not well defined
  - Traditional analytical methods are not sensitive enough for the low levels in many aerosol samples
- Improving understanding of the metals content of atmospheric PM will be important for
  - Source reconciliation modeling efforts
  - Health effects studies
- Motor vehicles may be an important source of metals to the atmosphere, especially in urban areas

OBJECTIVES

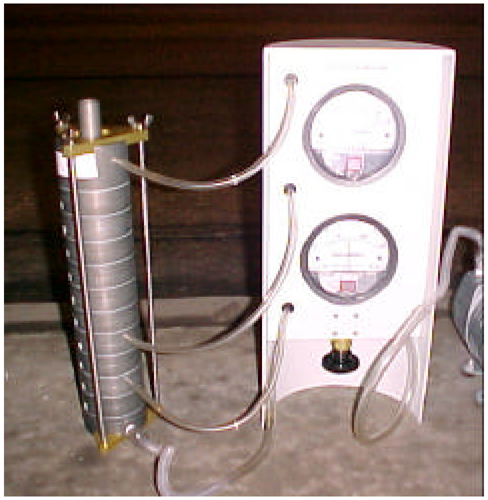
- Characterize total roadway particulate matter emissions from motor vehicles
- Construct source profiles for specific sources of roadway trace metal emissions, including:
  - Tailpipe emissions
  - Brake wear
  - Tire wear
  - Resuspended road dust
- Quantify and apportion contributions of these specific sources to measured total roadway emissions
- Understand the impact of motor vehicle emissions on metals levels in the ambient urban atmosphere

APPROACH

- Conduct tunnel tests to obtain a total roadway particulate matter emissions profile for on-road vehicles
- Develop source profiles for specific sources of trace metal and particulate matter emissions from vehicles
  - Conduct source characterization tests to develop profiles directly parallel to tunnel emission tests
    - Sample vehicles similar to tunnel fleet vehicles
    - Apply identical collection and analysis methods to all samples
- Characterize chemical composition of all PM emissions
  - Focus on trace metals analysis with ICP-MS
- Use chemical mass balance model to apportion total roadway emissions to specific sources
- Conduct parallel ambient sampling, and apply factor analysis to determine contribution of vehicle emissions

BACKGROUND

- PM sizes
  - PM10
    - smaller than 10 µm
    - primarily mechanically generated
  - PM2.5
    - smaller than 2.5 µm
    - primarily from combustion and chemical formation



MOUDI IMPACTOR

PM10 / PM2.5 SAMPLER

- Sampling
  - Sizes are separated with impactors or cyclones
  - Multiple filters of PM10 / PM2.5 collected simultaneously
  - Collected on filters selected and prepared for individual analyses

ANALYSIS

- Mass
- Elemental and Organic carbon
  - NIOSH 5040: thermal evolution and combustion
- Inorganic ions: Cl^-, NO_3^-, SO_4^{2-}, NH_4^+
  - Ion Chromatography
- Metals
  - Inductively-Coupled Plasma Mass Spectrometry (ICP-MS)
- Organic compounds
  - Gas Chromatography Mass Spectrometry (GC-MS)

Trace Metals Analysis by ICPMS

- Trace metals have historically been used to track crustal materials (XRF, PIXE)
- New opportunities using ICPMS techniques
  - Excellent sensitivity and accuracy for heavier elements
  - Can explore isotopes as tracers
  - Can begin speciation of metals
- Many sources can only be tracked by trace metal signatures
  - Brake wear
  - Some industrial source

Critical Issues for ICPMS

- Critical points in development of ICP-MS methods for analysis of particulate matter:
  - Effective sample solubilization
  - Minimization of contamination
  - Removal of instrumental polyatomic interferences
- Solubilization **-** Microwave-assisted acid digestion in Teflon bombs with high purity acids is the most robust method for solubilization of trace metals in environmental samples
- Contamination minimization
  - Pre-cleaning of Teflon filters
  - Use of rigorous cleaning methods and clean handling techniques
  - All work done in a dedicated Class 50 clean lab, analyses in a Class 100 lab

Digestion

- Complete digestion of all elements requires an acid mixture of HF, HCl and HNO_3
  - HF is required to digest clays
  - HCl is needed for digestion of platinum group metals
  - Closed bomb is needed to prevent vaporization of silicon fluoride compounds
  - Microwave assisted digestion using an acid mixture of HF, HCl, and HNO_3 has been validated with several Standard Reference Materials (SRM)

- Protocols have been developed to leach aerosols samples with surrogate fluids that can be used for ICP analysis and bioassays:
  - Artificial lake water – Sheesley et al. (2003)
  - Surrogate lung fluid – Schauer et al. (2003)

Trace Metal Clean Room

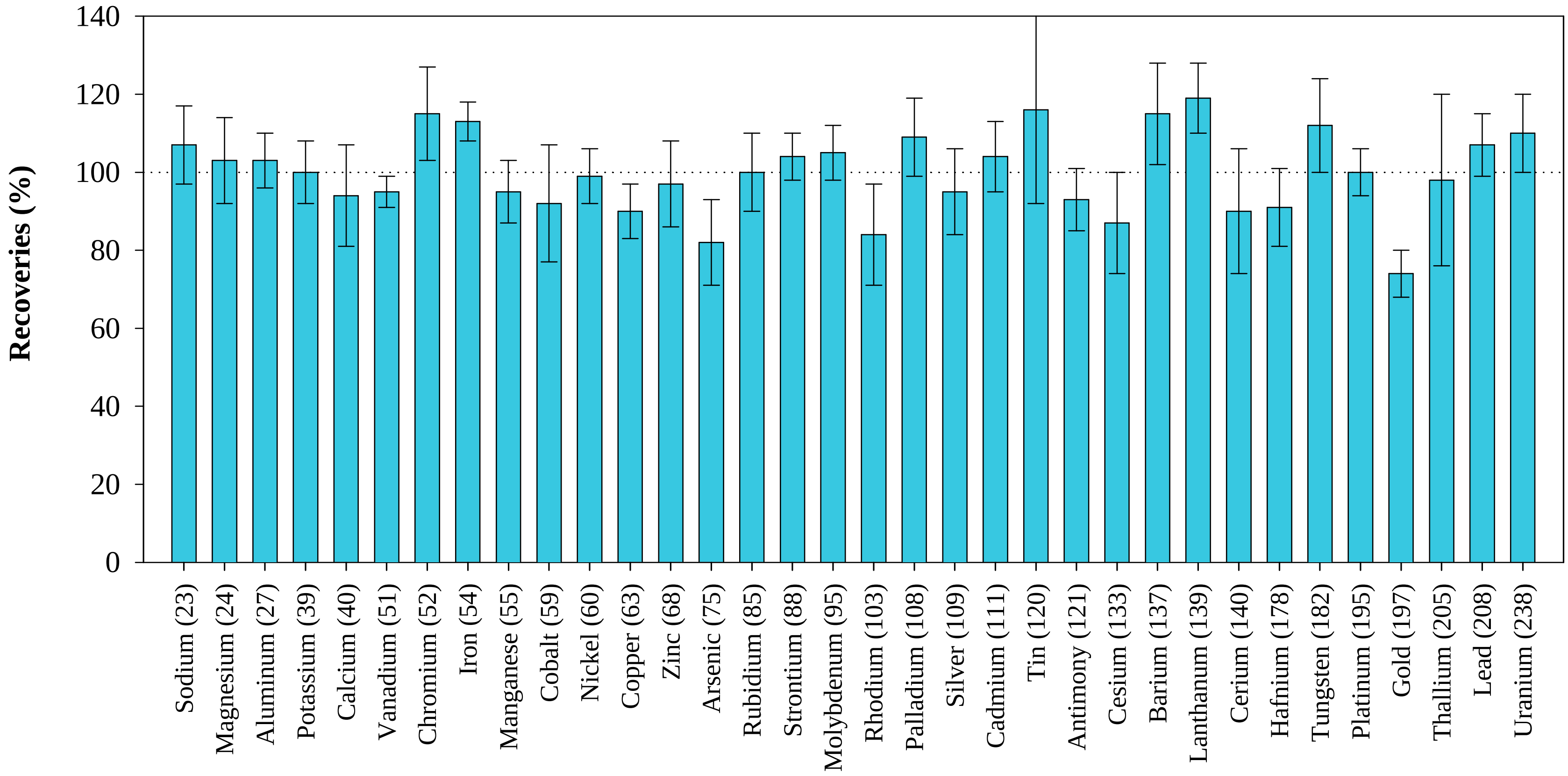
TRACE METAL ANALYSIS WITH ICP-MS

- ICPMS has excellent sensitivity
  - Detection limits for ICPMS analysis are determined by field and lab blanks and not instrument detection limits
  - Key issue for quantification is addressing polyatomic interferences
- Broad range of ICPMS Instruments
  - Traditional ICPMS
  - Traditional ICPMS with collision cell and plasma shield technology
    - Allows analysis of light elements by removing polyatomic interferences
  - High resolution ICPMS
    - Allows analysis of virtually all elements increased mass accuracy
  - Multi-sector Multi-collector ICPMS
    - Allows analysis of isotopic distribution

Recoveries of Extraction and Analysis of NIST SRMs

UW-Madison ICP-MS

(Average and Standard Deviation of Multiple Extractions and Analyses)



NIST SRMs: San Joaquin Soil (NIST 2706), Used Auto Catalyst (NIST 2556) , and Urban Dust (NIST 1649a)

METAL SPECITAION

- Metal speciation has predominately been pursued to better understand toxicological effects
- Metal speciation is likely to aid source attribution efforts
  - Most metals present in minerals tend to have low water solubilities
  - Many processed metals are more oxidized and have higher solubilities
- Metal speciation includes
  - Valence state
  - Leachability
  - Isotopic analysis
- Need to consider potential impact of atmospheric processing

MOTOR VEHICLE EMISSIONS

TOTAL ROADWAY EMISSIONS

TUNNEL TESTS

- 2 Tunnels in Milwaukee, WI
- 12 Summer tunnel tests (total ~ 35,000 vehicles)
  - 3 distinct sampling conditions
    - Courthouse Tunnel - Afternoon Rush Hour
    - Airport Tunnel - Weekday Rush Hours
    - Airport Tunnel - Weekend Traffic
- 6 Winter tunnel tests (total ~ 45,000 vehicles)
  - Consistent sampling conditions
    - All Airport Tunnel
    - Weekdays, including afternoon rush hour
- Vehicle fleets characterized 3 ways:
  - DOT loops for basic vehicle counts
  - Videotaping for basic vehicle classification
  - Videotaping for license plate ID and detailed vehicle data

TUNNELS

AIRPORT

- Howell Ave
- 3 lanes in southbound direction
- Similar to Van Nuys Tunnel (CA)
  - Completely separate opposing bores
- 770 feet long - No curvature
- Constant speeds - very limited braking
- ~8% truck traffic on weekdays
- Not cleaned - noticeable road dust

COURTHOUSE

- I-43 entrance ramp
- 2 Lanes merge into one lane
- Forced ventilation, exit at center
- 1270 feet long - ~ 45 degree curve
  - Inlet section: 715 feet - sample collection
- Moderate braking and acceleration
- ~2% truck traffic on weekdays
- Minimal road dust

TUNNEL SAMPLING

- Samplers placed at the roadside at vehicle entrance and exit of tunnel
  - Upwind samples - 15 feet inside entrance
  - Inside Tunnel
    - Courthouse: 50 feet upwind of exhaust outlet
    - Airport: 50 feet upwind of tunnel outlet
  - Incremental concentration increase is vehicle emissions in the tunnel

- Dilution measurements with SF_6:
  - SUMMA cans filled at inlet and inside tunnel in selected tests
  - SF_6 released at inlet, downwind of samplers
  - Windspeed measured in all tests
  - SF_6 and windspeed used to calculate volumetric flow through tunnel for all tests

EMISSION RATES

- Increase in species concentration in the tunnel converted to emission rates
  - Measured concentration increase:

    (mass species) / (m^3)

  - Multiplied by SF6-derived dilution rate:

    m^3 air through tunnel

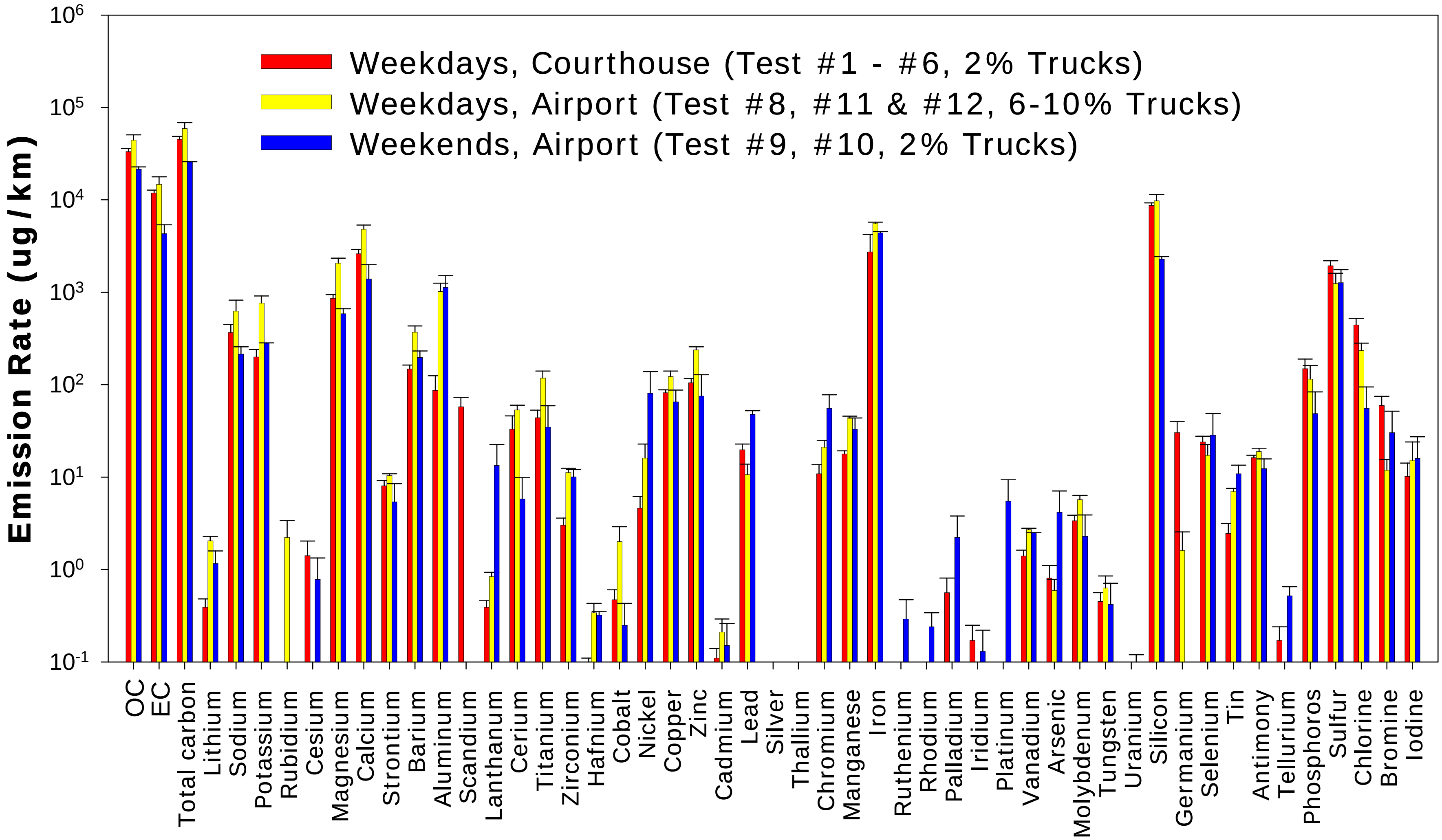
  - Divided by tunnel distance and number of vehicles passing through the tunnel during the test:

    total km driven

  - To yield emission rates:

    (mass species) / (km driven)

TUNNEL EMISSIONS PROFILE



Summer tunnel test data: average emission rates from on-road vehicles at Milwaukee, Wisconsin for PM10. Error bars indicate standard errors.

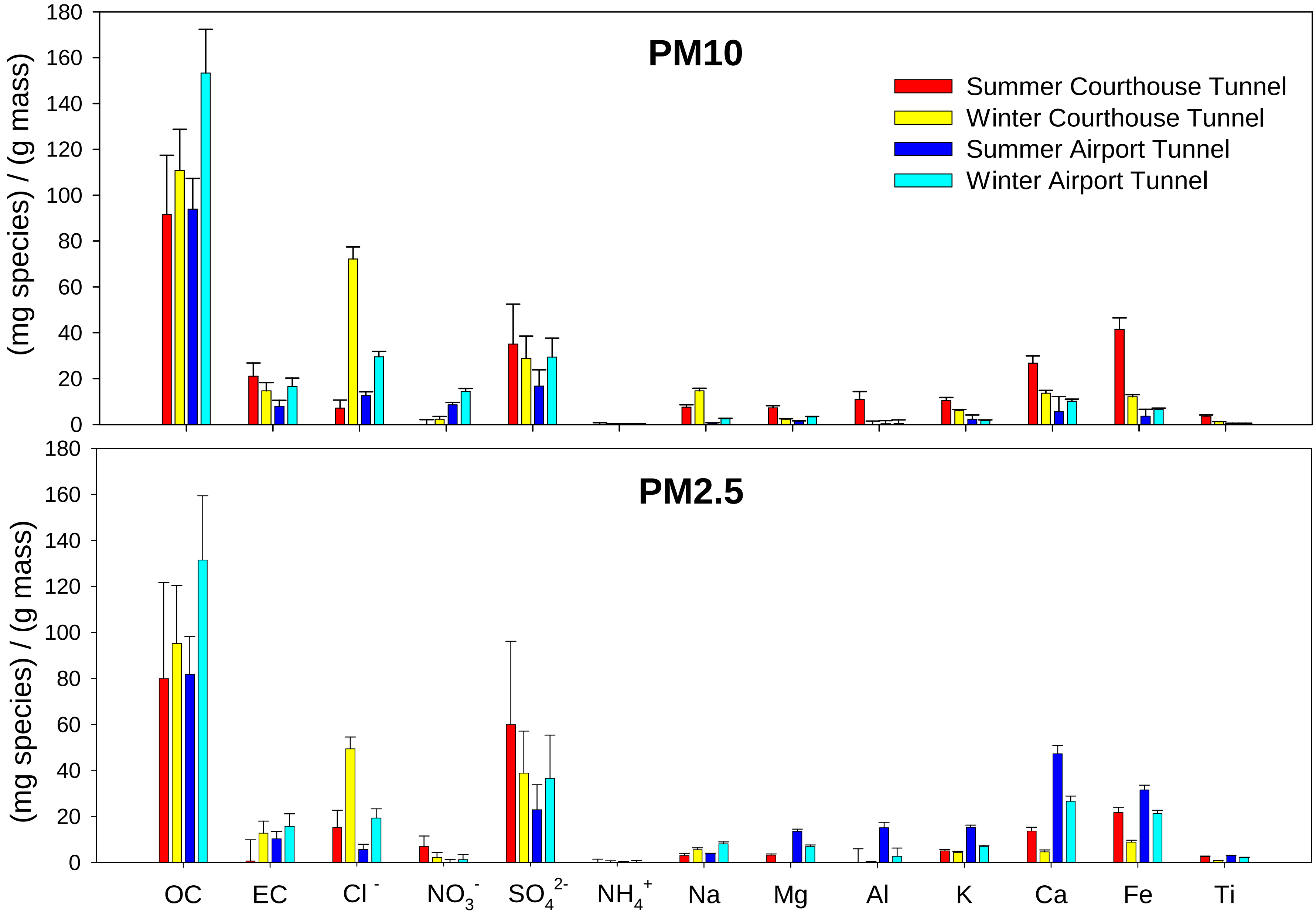
TUNNEL CONCLUSIONS

- Emissions in different seasons are similar, with exception of salt-impacted test
  - Several important elements emitted
    - Pb, expected from tailpipe emissions of older vehicles
    - Ba, high in brake wear emissions
    - Ce, expected in tailpipe emissions
    - Noble platinum group metals from catalytic converters not seen as high as expected
- Tunnel emissions are dominated by PM10
  - Low levels of PM2.5 in these tests

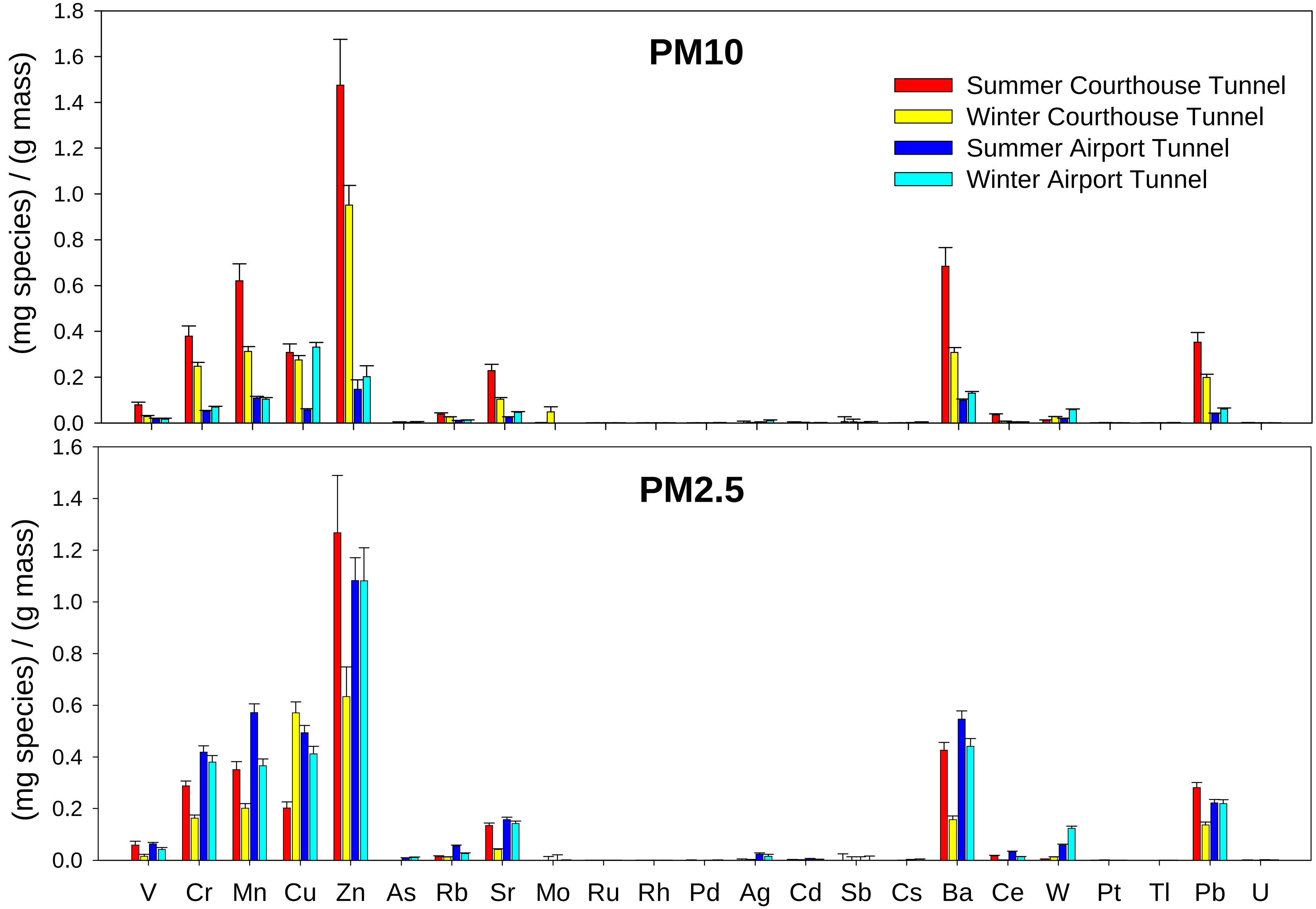
ROAD DUST

- Roadway dust is resuspended by passing vehicles
- Dirt was collected from the surface of the tunnel roadways
  - Ensured that samples were parallel to dust resuspended by tunnel fleet
  - Vacuumed from road surface in Summer and Winter tests
  - Dust was resuspended in a dilution chamber and sampled
    - PM 2.5 and PM 10: Bulk chemistry and trace metals

ROAD DUST


PM10
PM2.5
Summer Courthouse Tunnel
Winter Courthouse Tunnel
Summer Airport Tunnel
Winter Airport Tunnel
(mg species) / (g mass)
0
20
40
60
80
100
120
140
160
180
OC
EC
Cl -
NO3 -
SO4 2-
NH4 +
Na
Mg
Al
K
Ca
Fe
Ti

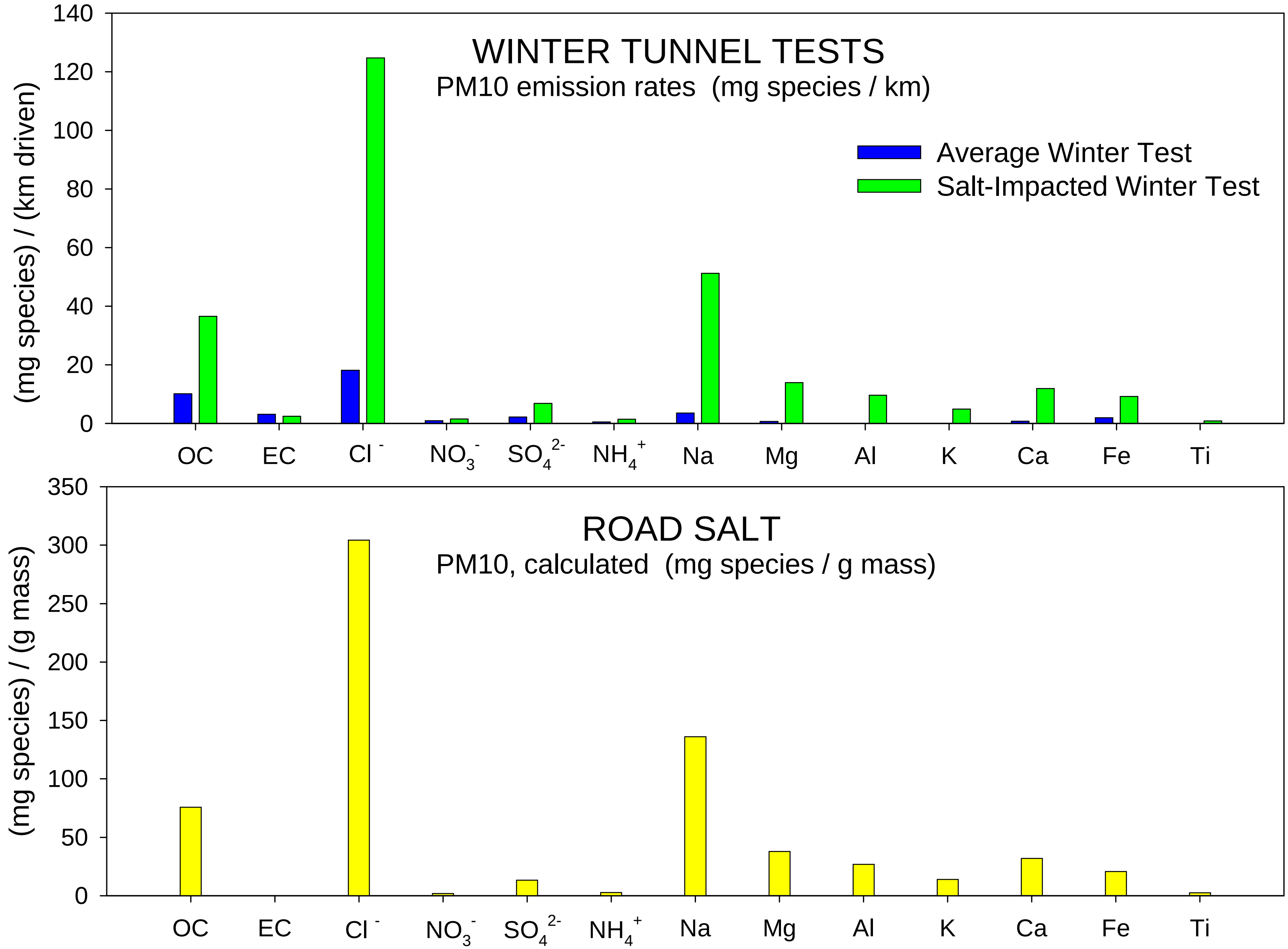
ROAD DUST


PM10
PM2.5
Summer Courthouse Tunnel
Winter Courthouse Tunnel
Summer Airport Tunnel
Winter Airport Tunnel
(mg species) / (g mass)
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
V
Cr
Mn
Cu
Zn
As
Rb
Sr
Mo
Ru
Rh
Pd
Ag
Cd
Sb
Cs
Ba
Ce
W
Pt
Tl
Pb
U

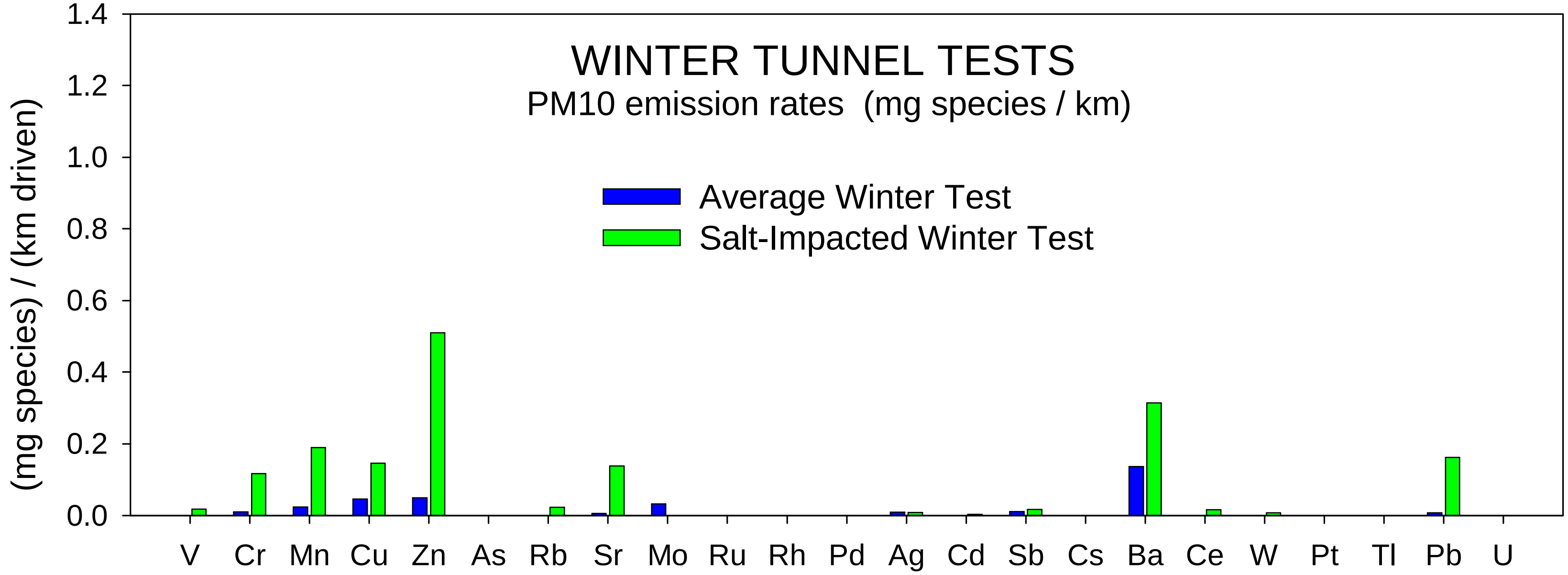
SALT-IMPACTED ROAD DUST

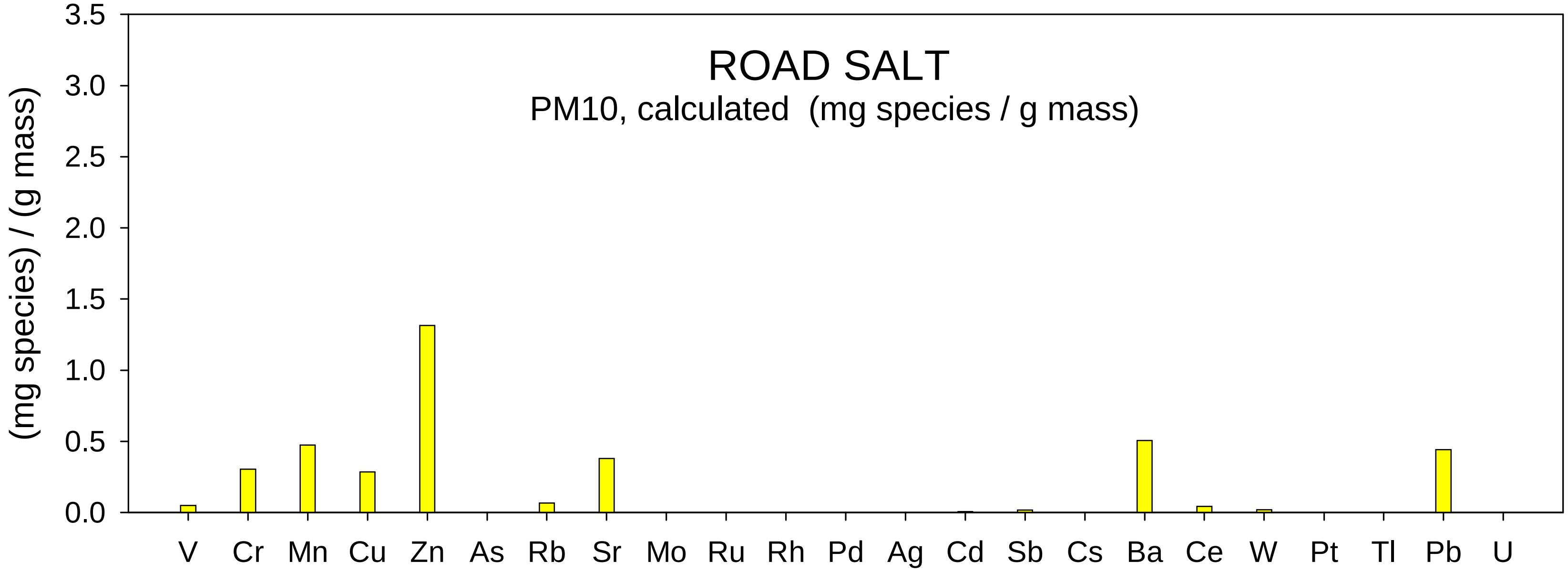
- High levels of road salt components were emitted from the roadway during one Winter Airport tunnel test
- Salt-impacted test was conducted on a cold, dry day, when the surface of the road had dried
  - Roadside snow had melted on several previous warmer days
  - Salt and slush dragged into tunnel by traffic
  - On the cold, dry day, no additional snow melt, and roadway dried
- Impact of road salt was determined by comparing elemental emission rates with similar winter tests
- Mole balance corroborates high emissions of road salt components NaCl, $MgCl_2$, KCl, and $CaCl_2$
- Profile is not pure salt, also shows components of sampled road dust from Airport Tunnel

SALT-IMPACTED ROAD DUST



SALT-IMPACTED ROAD DUST





ROAD DUST DISCUSSION

- Dust collected from the tunnels is enriched with elemental emissions from other sources
  - Ba from brake wear
  - Pb from older vehicles’ tailpipe emissions, leaded gasoline residues
  - Cr, Mn, Cu, Zn from brake wear, engine wear
- Salt applied to roads is an important factor in cold areas
- More road dust mass is PM10 than PM2.5

BRAKE WEAR

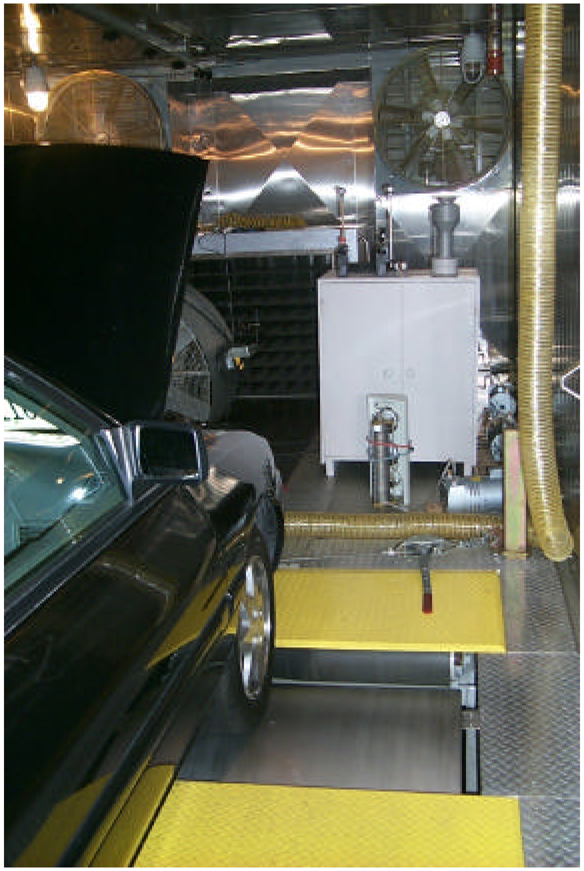
- Brake emissions are difficult to measure
  - Tunnel and dynamometer tests measure a mixture of emissions
  - Dynamometer tests are expensive, and access to dynos is limited
  - Specialized brake dynamometers are also expensive/limited
- Need method for estimating emissions composition
  - Relating emissions to brake pad composition would allow easy, inexpensive characterization of a wide range of brake types
- Set of tests conducted to characterize brake wear emissions and compare:
  - Actual brake wear emissions from driving cycles
  - Chemical composition of the bulk brake pads
  - Chemical composition of brake housing dust

BRAKE WEAR EMISSIONS

- Actual brake wear emissions
  - Specialized Dynamometer: California Air Resources Board Facility
  - RL-SHED: Running Loss - Sealed Housing for Evaporative Determinations
  - Sealed environment, stainless steel, constant volume and temperature, engine inlet air piped in, exhaust piped out
  - Emissions in the shed are:
    - Tire wear
    - Brake wear
    - Evaporative emissions
    - Resuspended dust
  - VEHICLE tests
    - 2 vehicles with original brakes
    - 3 types of driving cycle, plus background tests
    - Vehicle test results corrected with blank/background tests

DYNAMOMETER

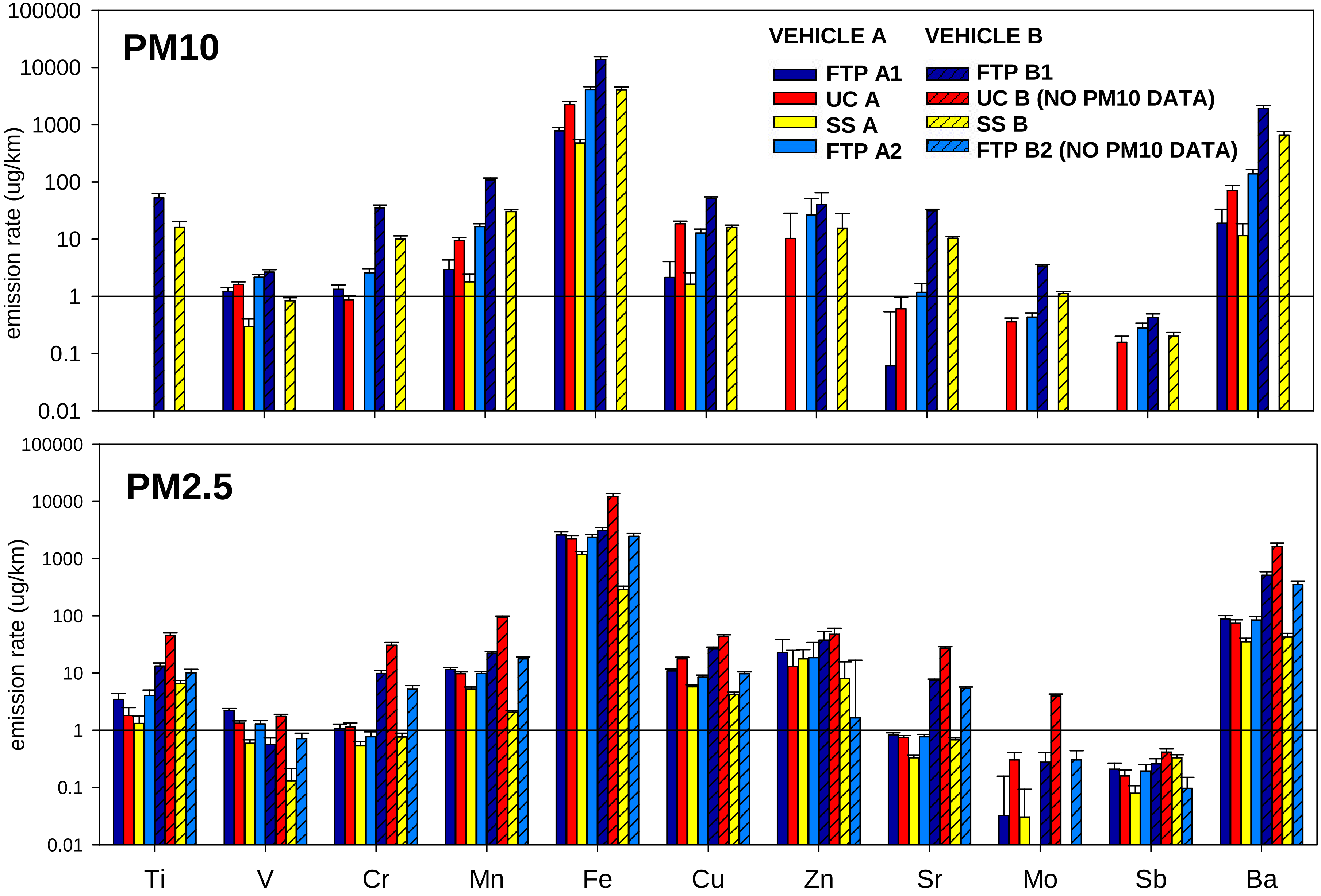
RUNNING LOSS SHED



SAMPLING SETUP

AIR INLET AND EXHAUST

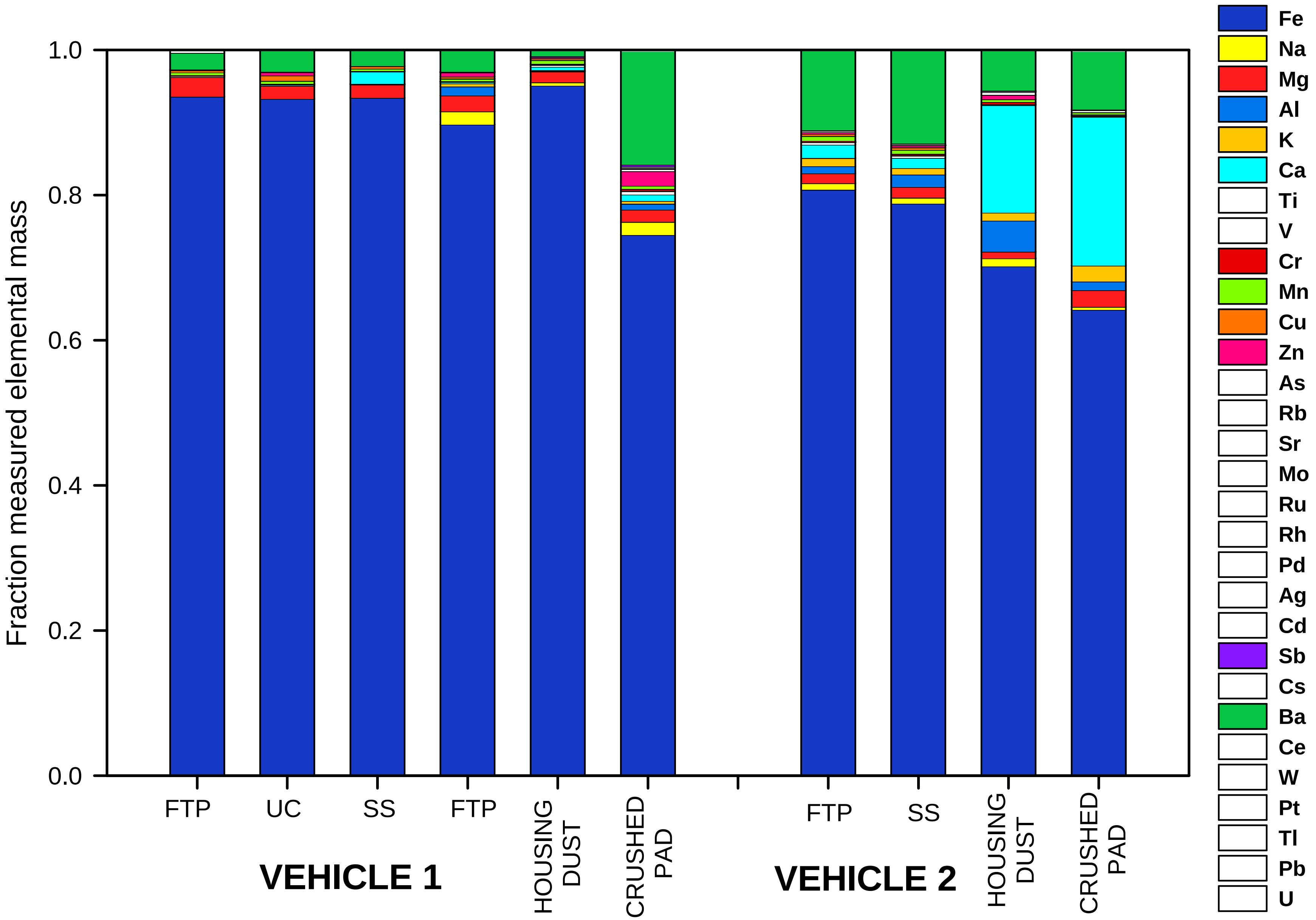
EMISSION RATES – selected abundant species, by test



BRAKE WEAR

- Relationships between composition of brake wear emissions, brake pad composition, and brake housing dust
  - Brake pads removed from dyno test vehicles and pulverized
  - Brake housing dust also collected from dyno test vehicles
  - Both dusts resuspended and sampled for PM10 and PM2.5

Elemental emissions compared to dust and pad compositions
PM10: SHED tests, resuspended brake dust and pads from test vehicles



BRAKE WEAR PROFILE

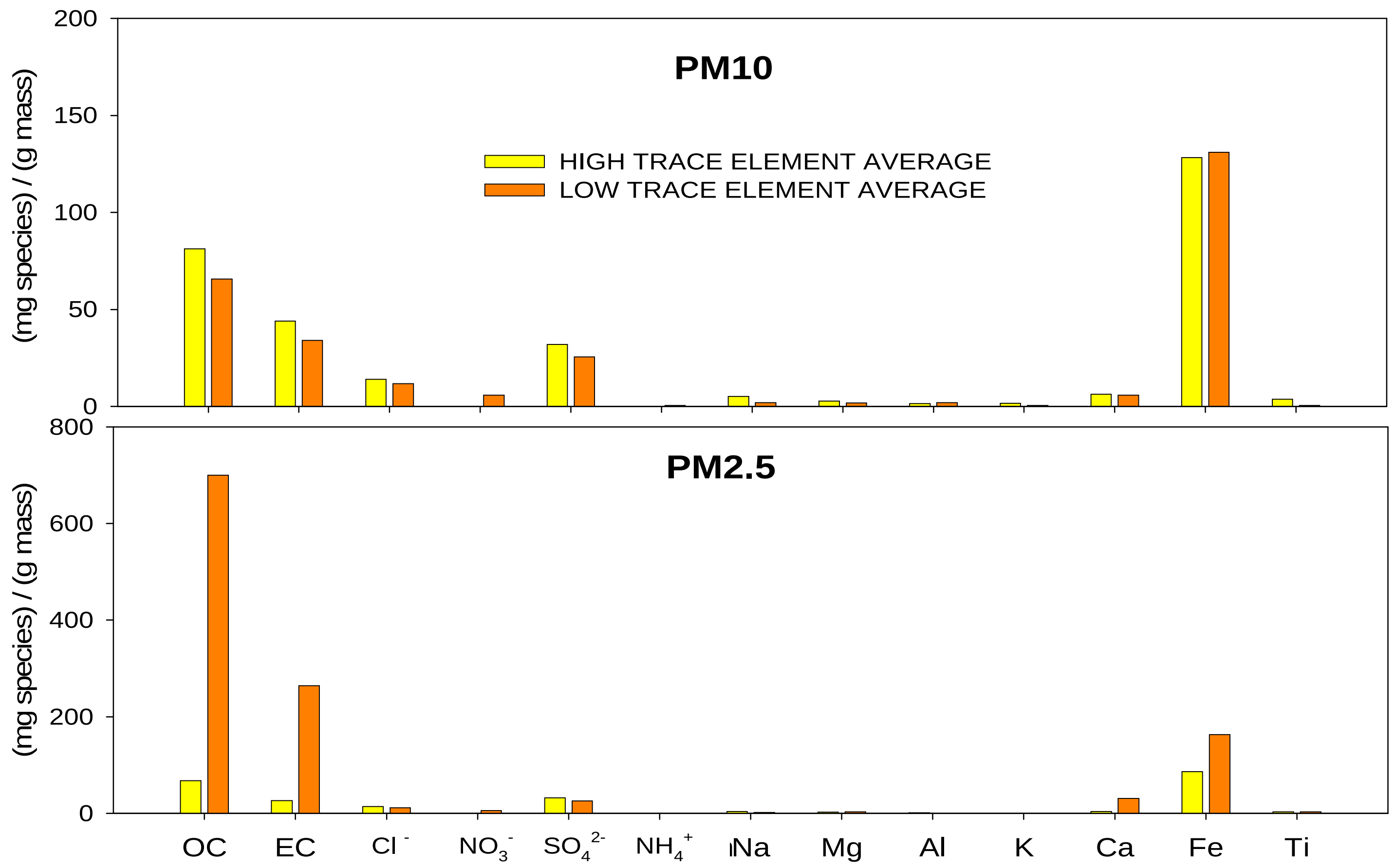
- Trace metal emissions are more similar to housing dust than to bulk pad composition
  - May reflect simultaneous grinding of the rotor, rivets, etc
    - could explain increased contribution of Fe, Cu in housing dust
  - Some species in the pad may be emitted in larger particle sizes (ie, larger than PM10)
    - may explain decreased contribution of Ba in housing dust
    - may explain disappearance of Ca in vehicle B dyno emissions
- Developing emissions profile for brake wear
  - Brake housing dust and brake pads sampled from random vehicles at local Wisconsin garages
    - Samples are parallel with WI tunnel emissions
  - Dusts resuspended for size segregation and chemical analysis

BRAKE WEAR PROFILE

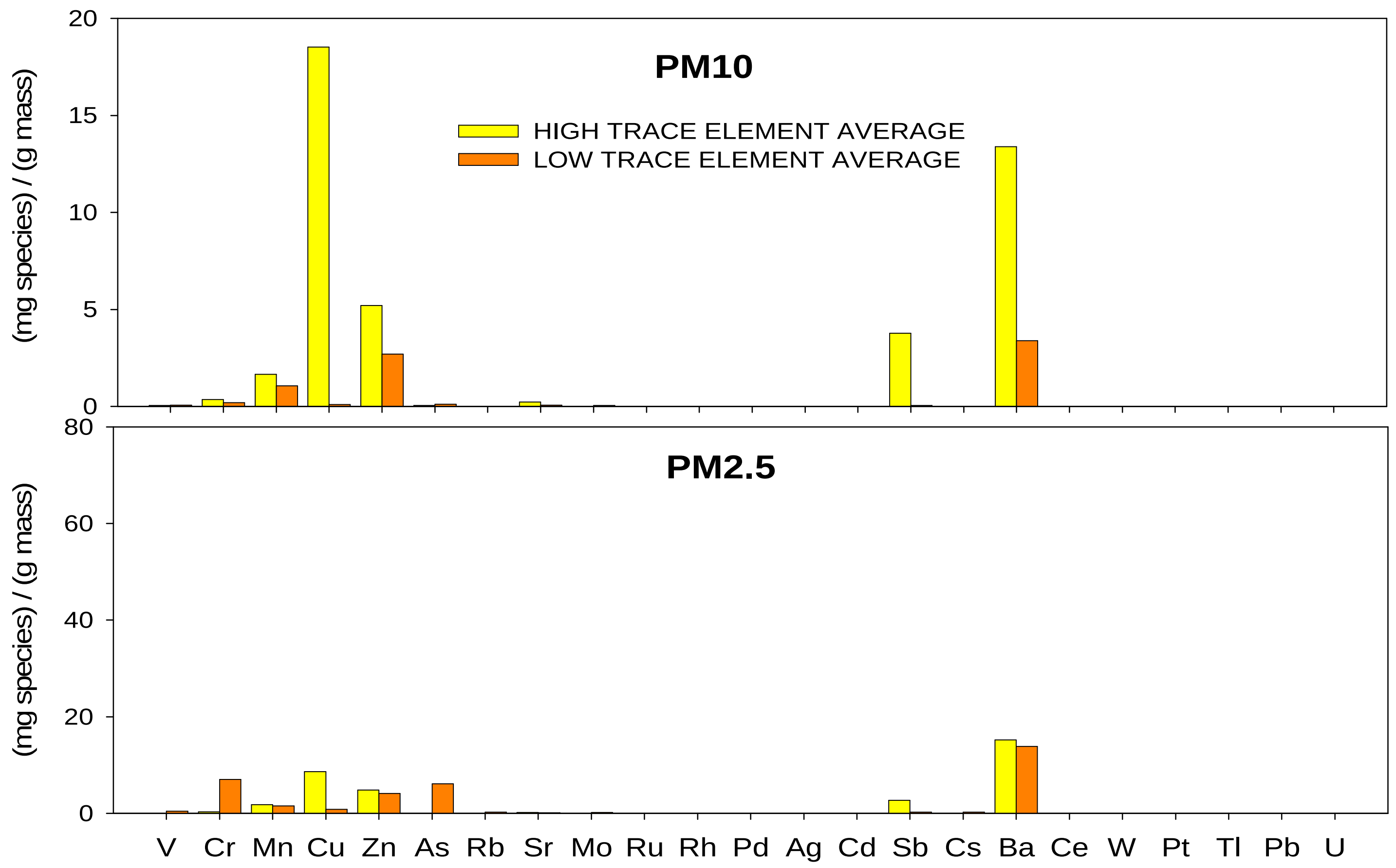
- Dust and pads from random vehicles show same composition trends as dyno test samples
  - increased Fe and Cu, Zn in housing dust
  - decreased Ba contribution on housing dust

- Housing dust samples averaged to create two profiles, as observed:
  - HIGH levels of Ba, Cu, and other ‘trace’ metals in dust
  - LOW levels of ‘trace’ metals in housing dust

BRAKE DUST PROFILE



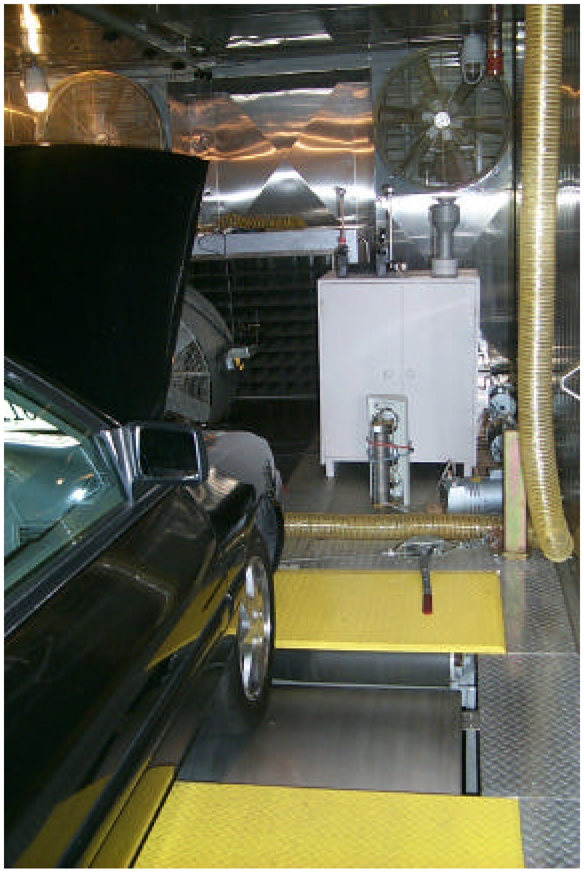
BRAKE DUST PROFILE



BRAKE WEAR DISCUSSION

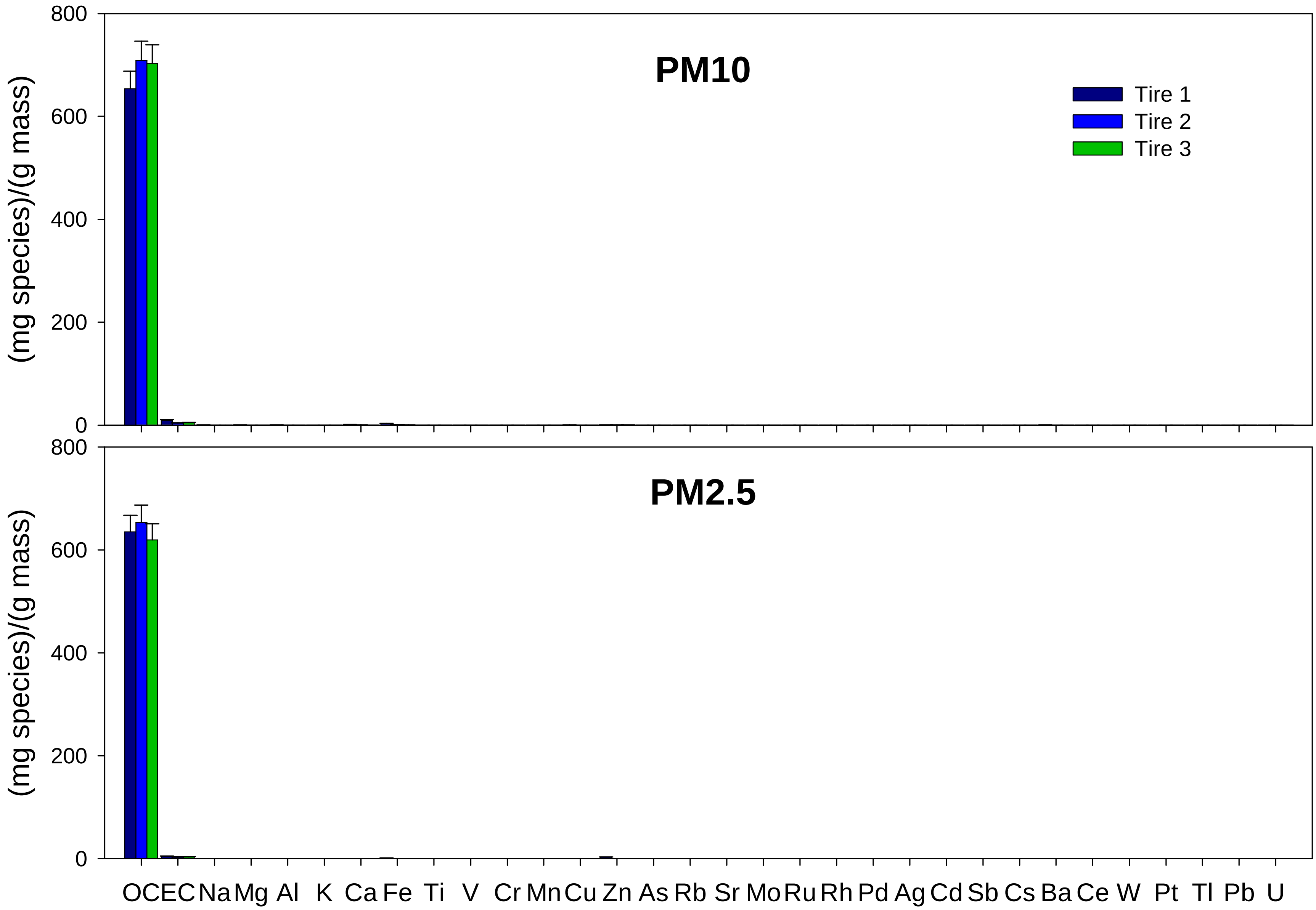
- Housing dust is more similar to actual brake wear emissions
  - Dust and pads from random vehicles show same composition trends as dyno test samples
  - Dust from a range of vehicles can be sampled to estimate emissions
- Emissions from brake wear are seen in the absence of braking
  - Tunnel tests and RL-SHED dynamometer test both showed brake wear from vehicles driven at 30mph with no braking
  - PM2.5 emissions are seen during braking, but little PM2.5 is seen during non-braking cycles
  - PM10 likely builds up in brake housing, and is emitted continuously during cycles with no braking

TIRE WEAR



- RL-SHED dynamometer test emissions also include tire wear
- Tires from dyno test vehicles sampled
  - Removed from vehicles
  - Abraded to obtain wear samples
  - Bulk chemistry and trace metals analysis
- Organic carbon dominates tire composition
  - Trace metal levels extremely low
  - Tires contribute negligible levels of metals to brake and tire wear dynamometer test emissions

TIRE WEAR


PM10
PM2.5
Tire 1
Tire 2
Tire 3
(mg species)/(g mass)
800
600
400
200
0
OC EC Na Mg Al K Ca Fe Ti V Cr Mn Cu Zn As Rb Sr Mo Ru Rh Pd Ag Cd Sb Cs Ba Ce W Pt Tl Pb U

TIRE WEAR DISCUSSION

- Tire wear contribution to metals levels is very low
  - Emissions from tires are 70% organic carbon
  - Zn is the only significant measured element (~0.1% by mass)
  - Brake wear dominates metals emissions in the SHED

TAILPIPE EMISSIONS

- Tailpipe emissions include
  - Unburned fuel
  - Partially combusted fuel
  - Lube oil
  - Engine wear
- Series of dynamometer tests done to investigate tailpipe emissions
  - More than 100 vehicles, both gasoline and diesel
  - Several different driving cycles tested on chassis dyno
  - Emissions collected with dilution source sampler
    - Allows exhaust to cool and condense before collecting particles
- Fuel and lube oil samples collected from test vehicles
  - Determine impact of lube oil and engine wear on tailpipe emissions of trace metals

TAILPIPE DISCUSSION

- Elemental content of emissions varies between vehicles
- Zn, Cu, and Fe generally have highest emissions
  - Expected to be from engine wear, seen in used motor oil
- Some vehicles emit high Ca
  - Also emit high Zn, and significant Fe and Cu, possibly indicating combustion of lube oil that contains engine wear products
  - Ca is consistently high in all used lubricating oil samples
  - Agrees with other studies
- Ce is detected in tailpipe emissions
  - significant primarily in gasoline-powered vehicles

VEHICLE EMISSIONS APPORTIONMENT

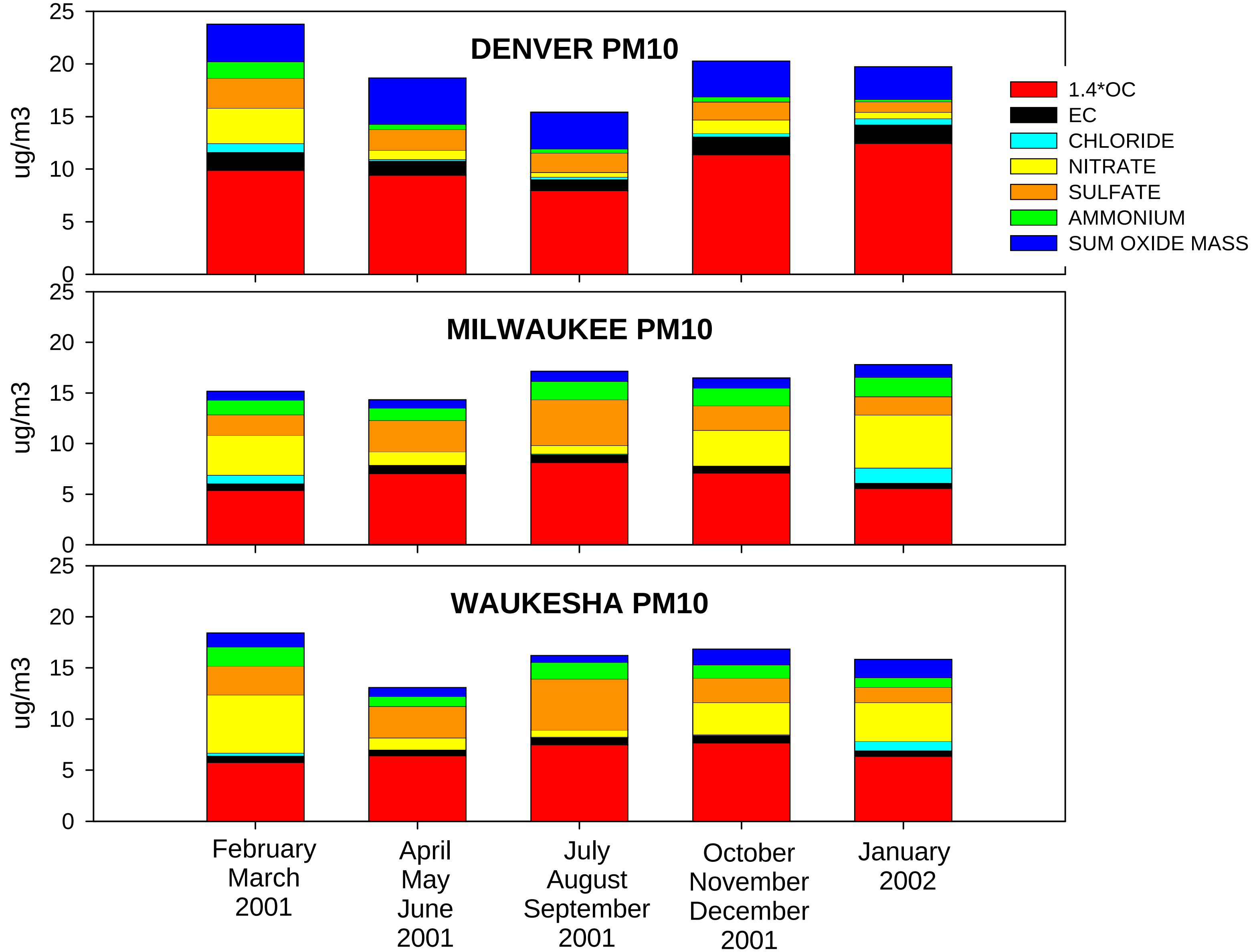
- PM2.5 is relatively low in the tunnels, PM10 is high
  - Bulk of road dust in the tunnels is PM10
  - Brake wear emitted during driving without braking is mainly PM10
- Basic, visual comparison of tunnel profiles with source profiles shows:
  - Roadway metal emissions from motor vehicles are dominated by brake wear and resuspended road dust
  - Resuspension of road salt is a very significant source of PM from roadways at some times

IMPACTS ON AMBIENT ATMOSPHERE

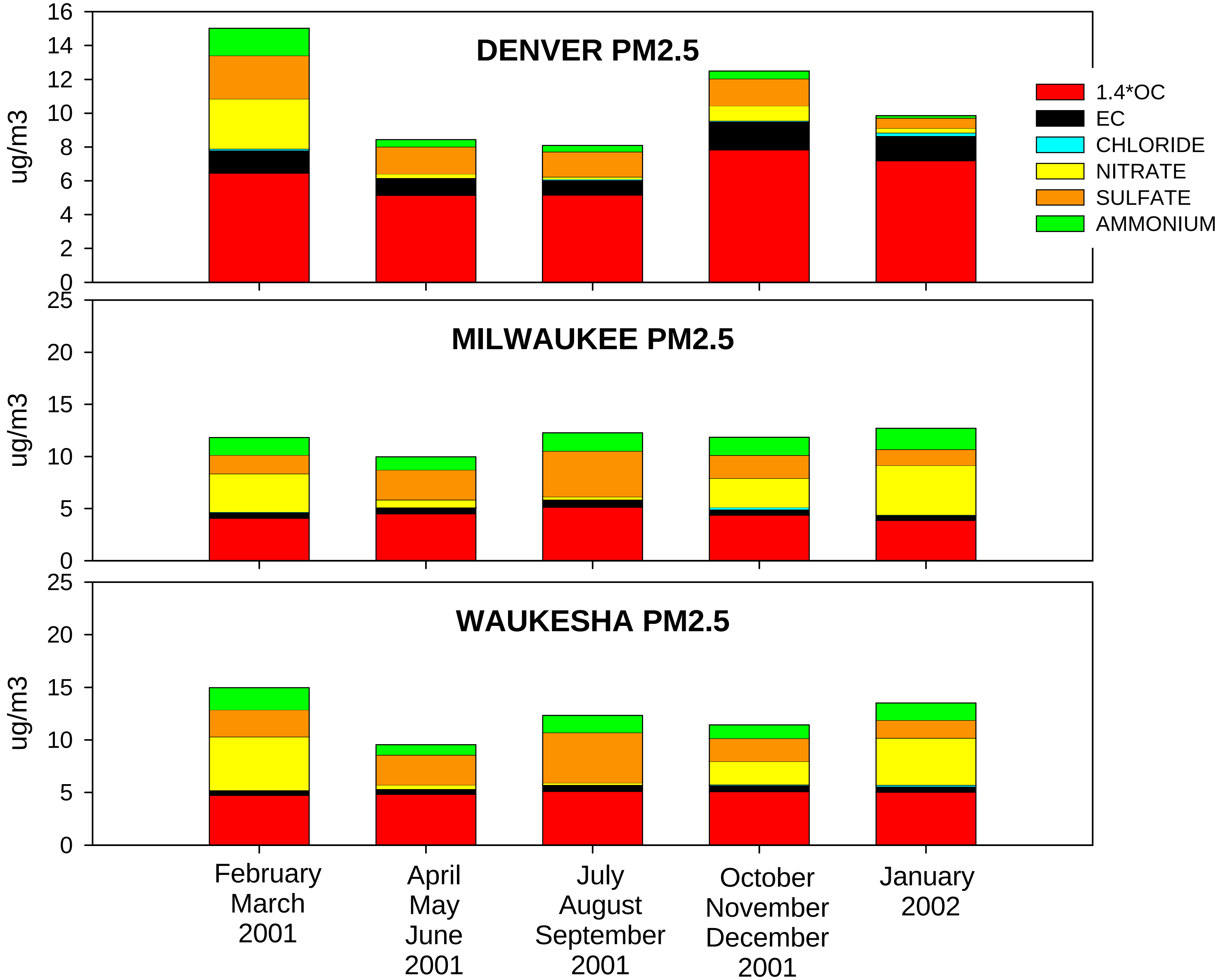
AMBIENT SAMPLING

- Ambient sampling network - Source apportionment
  - Determine the contribution of motor vehicles to total ambient PM in the urban atmosphere
  - Powerful molecular marker techniques have been developed with organic compounds as source tracers
  - The broad spectrum of metals that can be analyzed with ICP-MS provides many potential new tracers
  - Combination of metals data with organics data will allow very robust and accurate source reconciliation
- 3 sampling sites:
  - Milwaukee, WI - urban
  - Waukesha, WI - industrial
  - Denver, CO – industrial/residential
- EPA 6th day sampling schedule
  - February 2001 – January 2002
- PM 2.5 and PM 10
  - Same sampler design as source tests at each location
  - Chemical analyses parallel to source tests

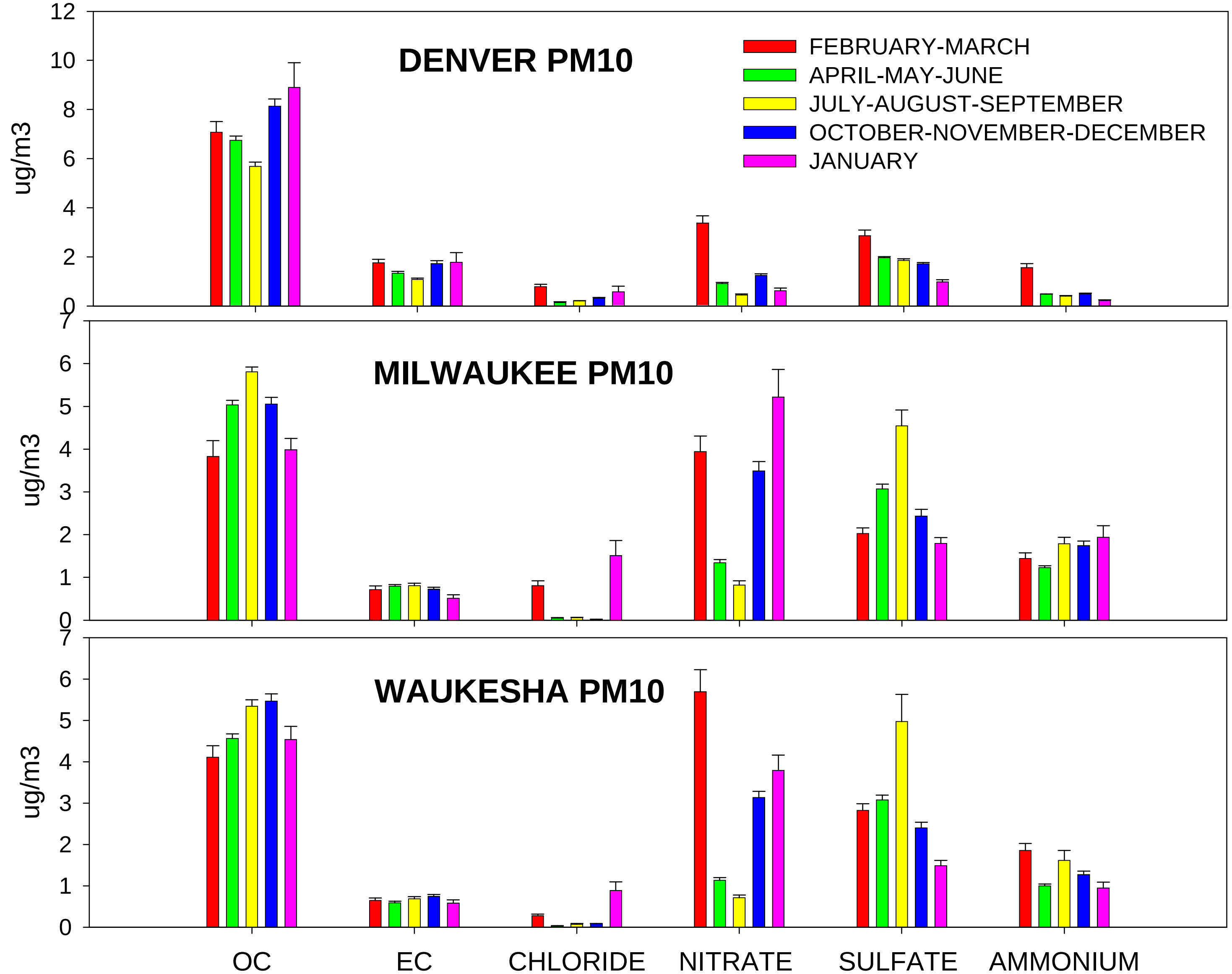
AMBIENT PM10 COMPOSITION



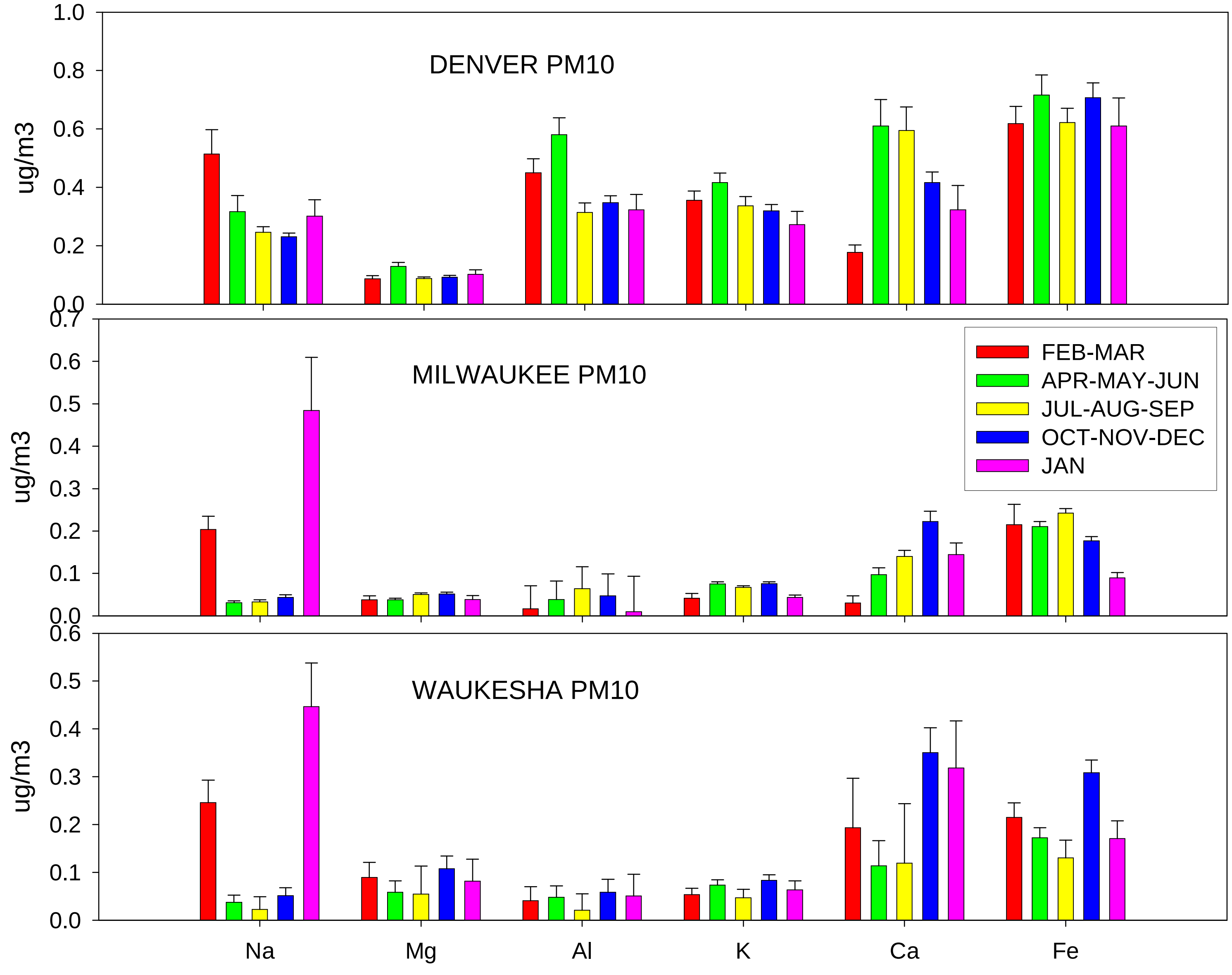
AMBIENT PM2.5 COMPOSITION



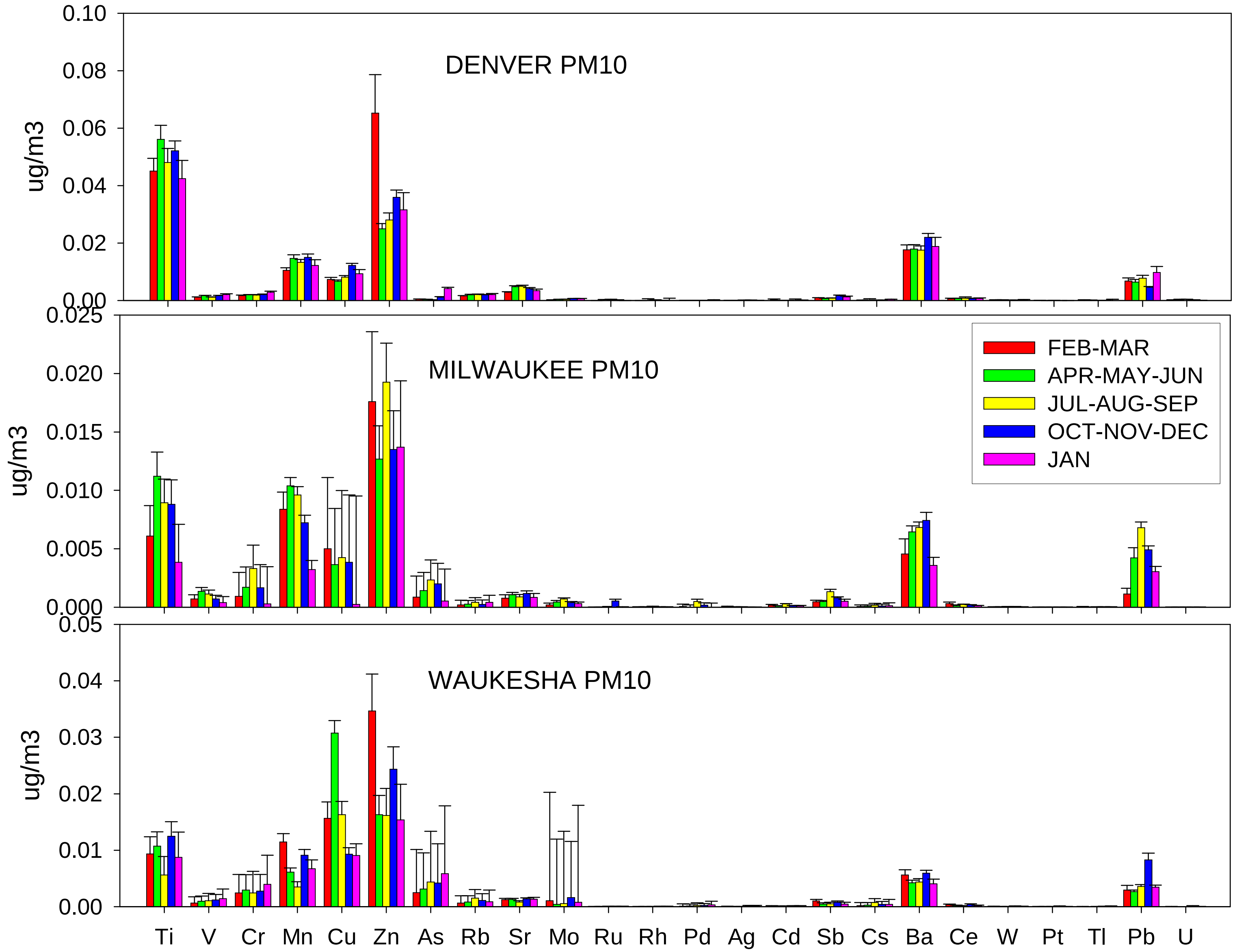
BULK CHEMISTRY
PM10: 3 Ambient sites 2001



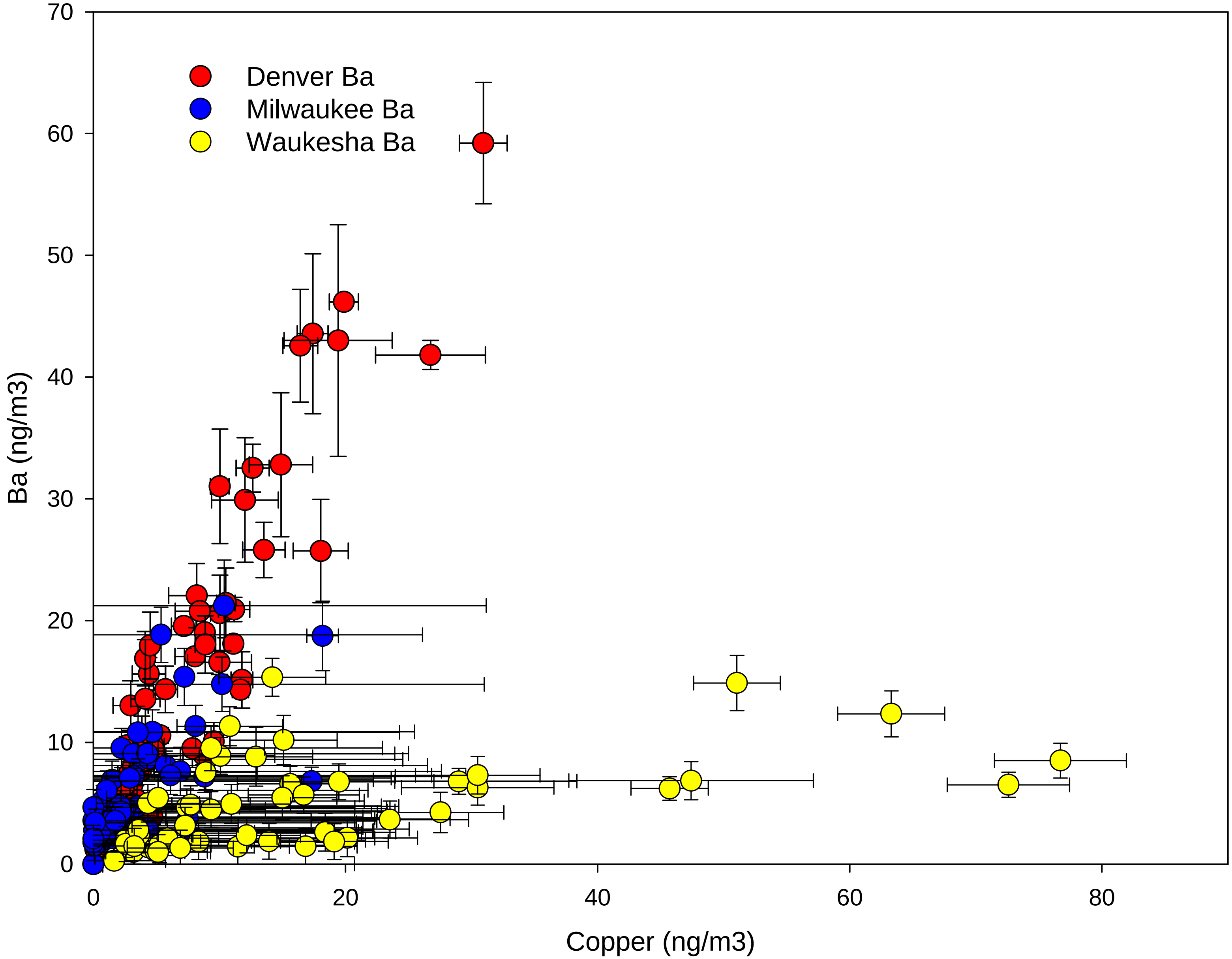
CRUSTAL ELEMENTS
PM10: 3 ambient sites 2001



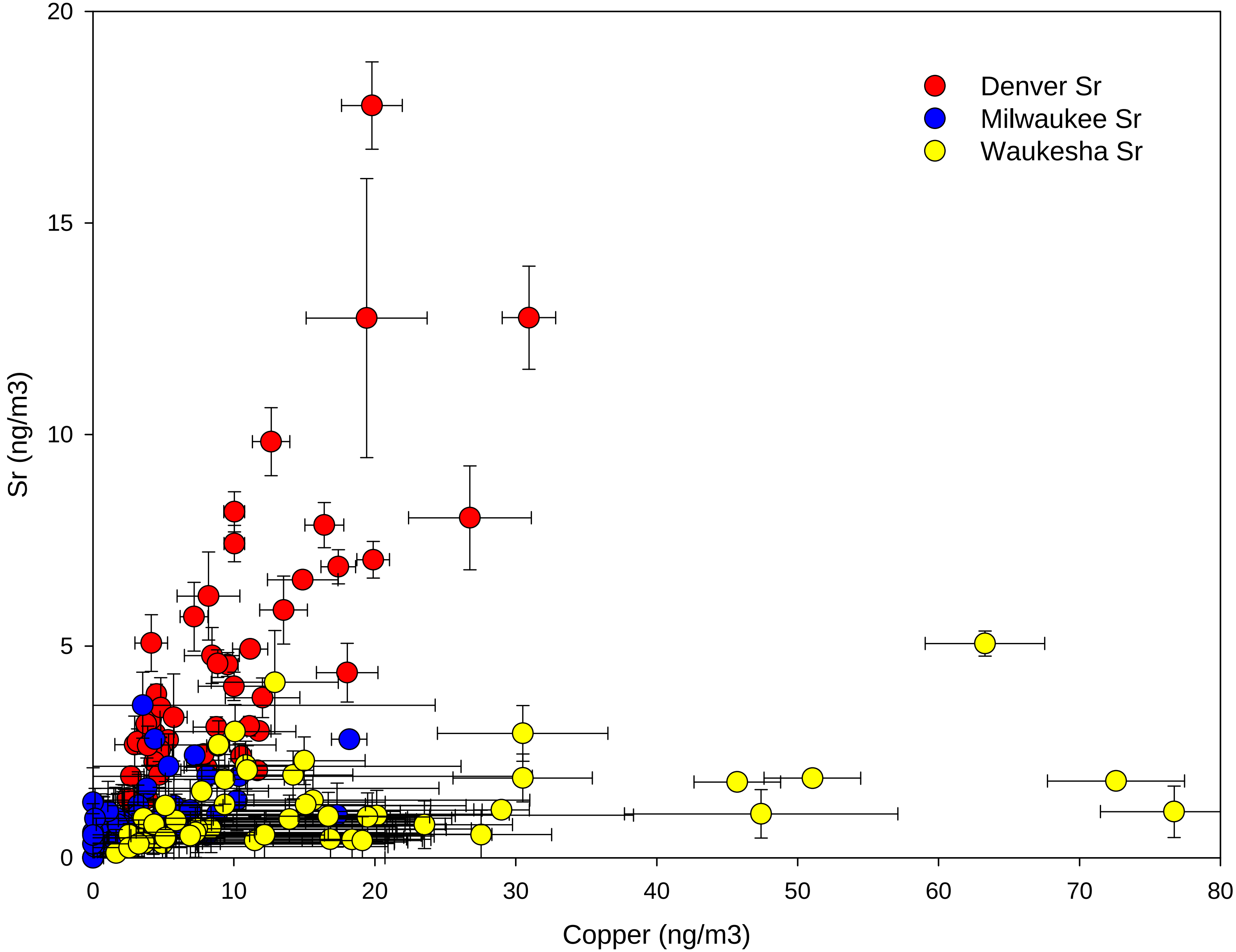
TRACE ELEMENTS
PM10: 3 Ambient sites 2001

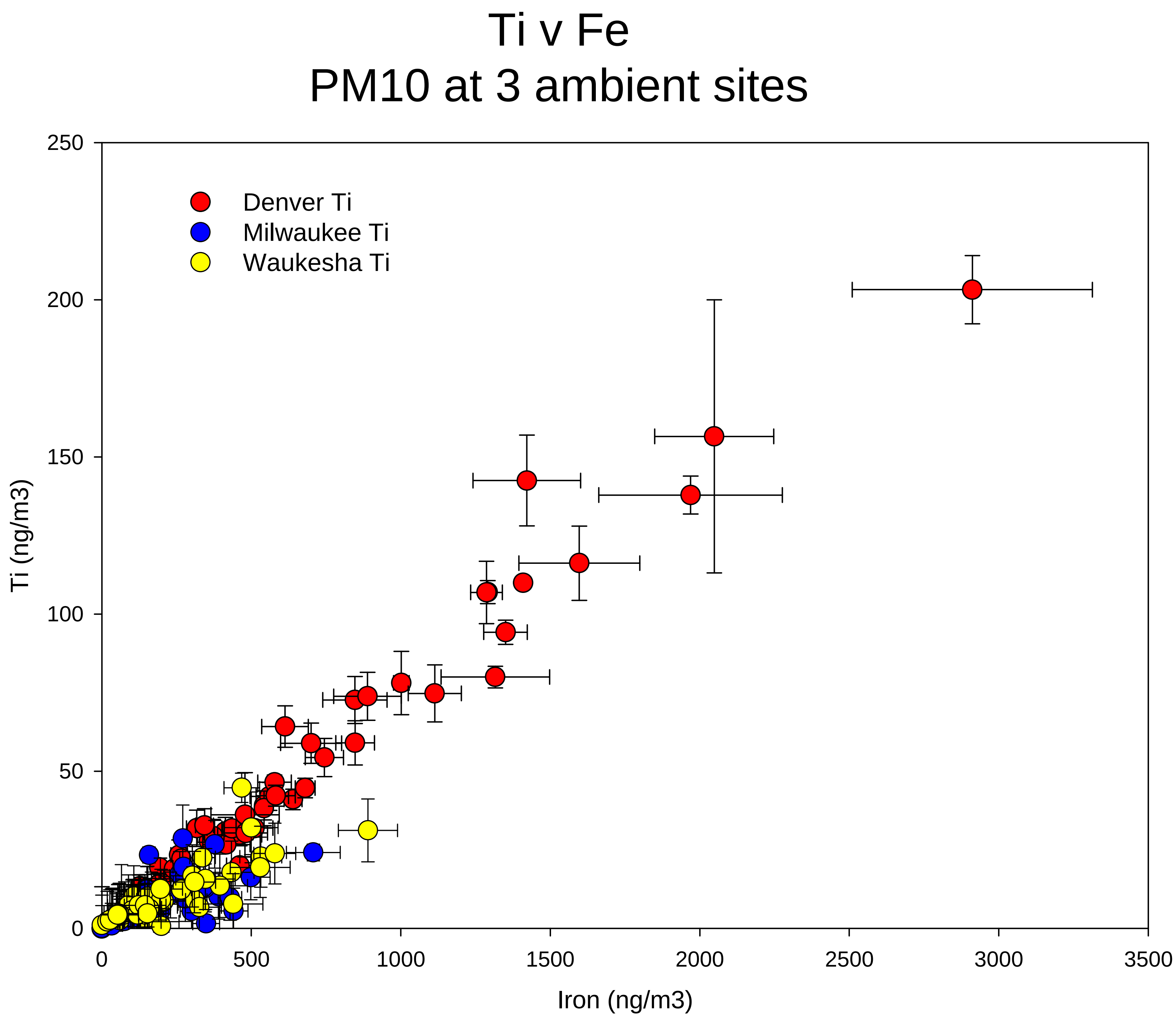


Ba v Cu
PM10 at 3 ambient sites

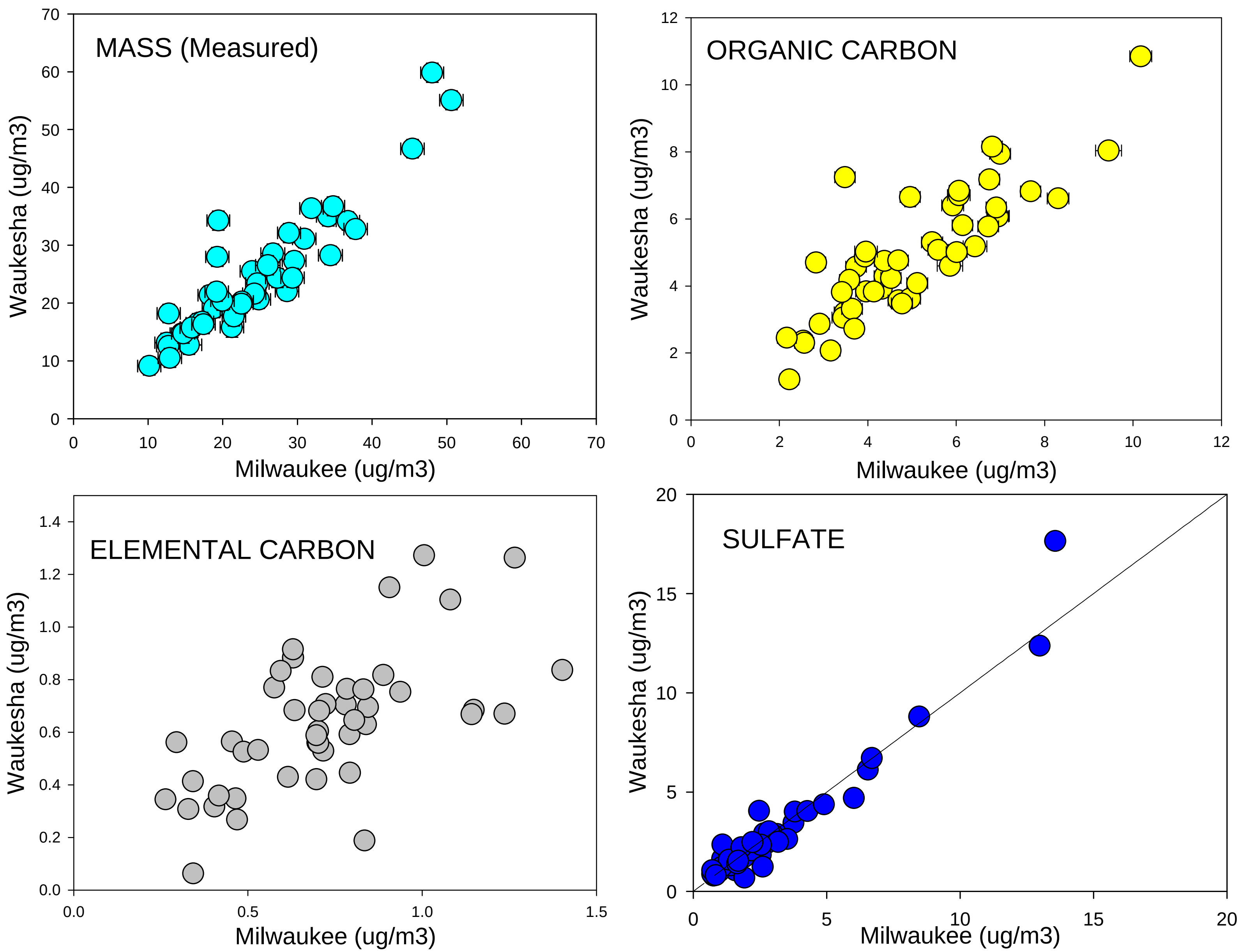


Sr v. Cu
PM10 at 3 ambient sites

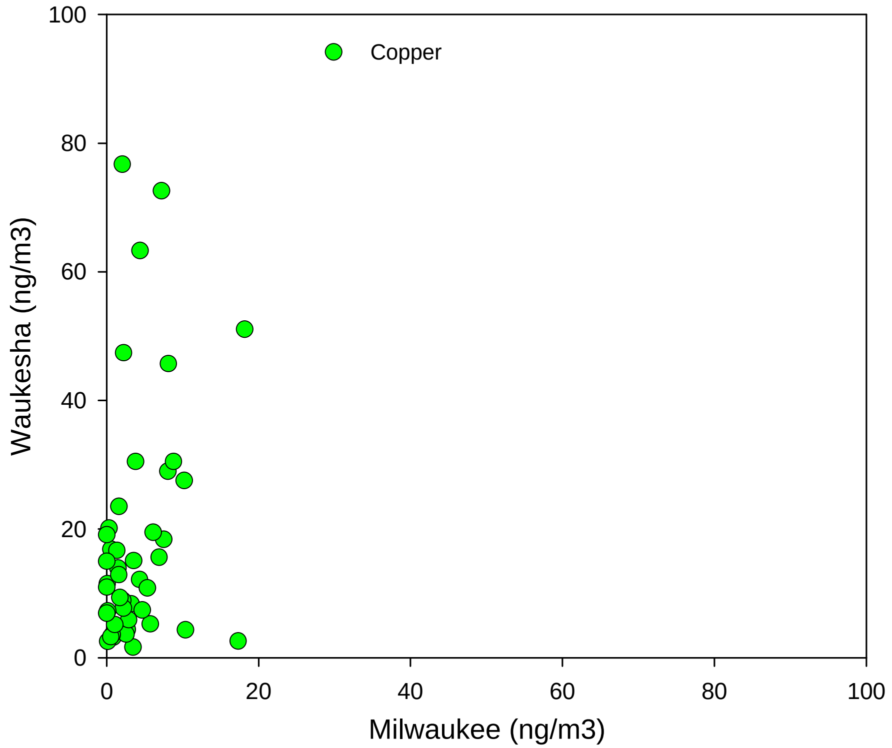


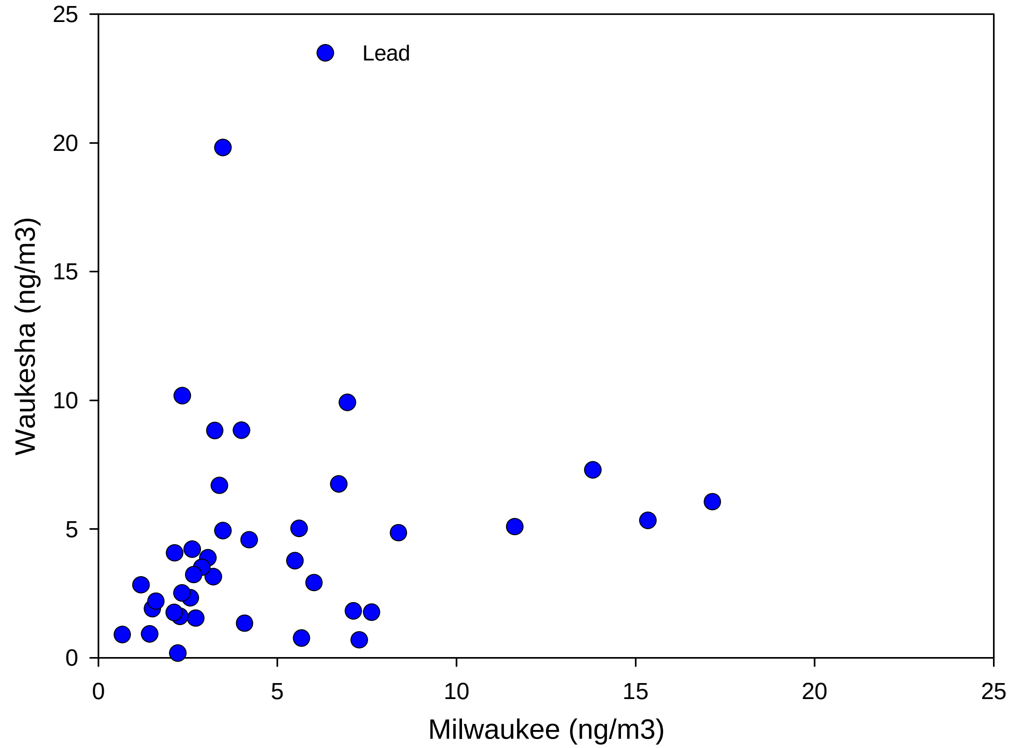

Ti v Fe
PM10 at 3 ambient sites
Denver Ti
Milwaukee Ti
Waukesha Ti
Ti (ng/m3)
Iron (ng/m3)
0
50
100
150
200
250
0
500
1000
1500
2000
2500
3000
3500

Waukesha v Milwaukee
2001 Ambient PM10



Waukesha v Milwaukee
PM10 Copper and Lead





AMBIENT DISCUSSION

- Metals emitted from motor vehicles are detected in ambient atmosphere
- Differences in regional sources at three ambient sites are apparent
  - Crustal materials, sources, altitude, vehicle operation
- Wisconsin sites
  - Data agree well for regionally-influenced species
  - Contribution of local sources is apparent
  - Chloride contribution to PM10 obvious in Winter months

Metal Speciation

- Dissolution of particles deposited in the lungs is a likely pathway to bioavailability
- Ultimate impact of PM on organisms may be more directly tied to the leachable fraction of metals than to the total metals concentration
- Leachability of trace metals in a biologically relevant fluid is sought
- Investigating leachability of trace metals in a biologically relevant fluid requires analytical methods that can handle the complex inorganic and organic matrix of a synthetic lung fluid

SYNTHETIC LUNG FLUID

- Natural extracellular lung fluid
  - coats the alveoli and walls of the lungs
  - is a buffered solution of salts with surfactants
- Two synthetic matrices used for extractions
  - Gamble Solution: buffered salt solution
  - Surfactant-Like Solution: Gamble solution plus an organic surfactant to more closely mimic the environment in the lungs
- Duplicate metals samples analyzed
  - analysis of complete digestion compared to the leachable fraction of the metals in synthetic lung fluid

CHEMICAL COMPOSITION

GAMBLE SOLUTION
INORGANIC SALTS

- Sodium 3350 mg/liter
- Potassium 160 mg/l
- Calcium 100 mg/l
- Magnesium 25 mg/l

- Chloride 4050 mg/l
- Bicarbonate 1900 mg/l
- Phosphate 100 mg/l
- Sulfate 50 mg/l

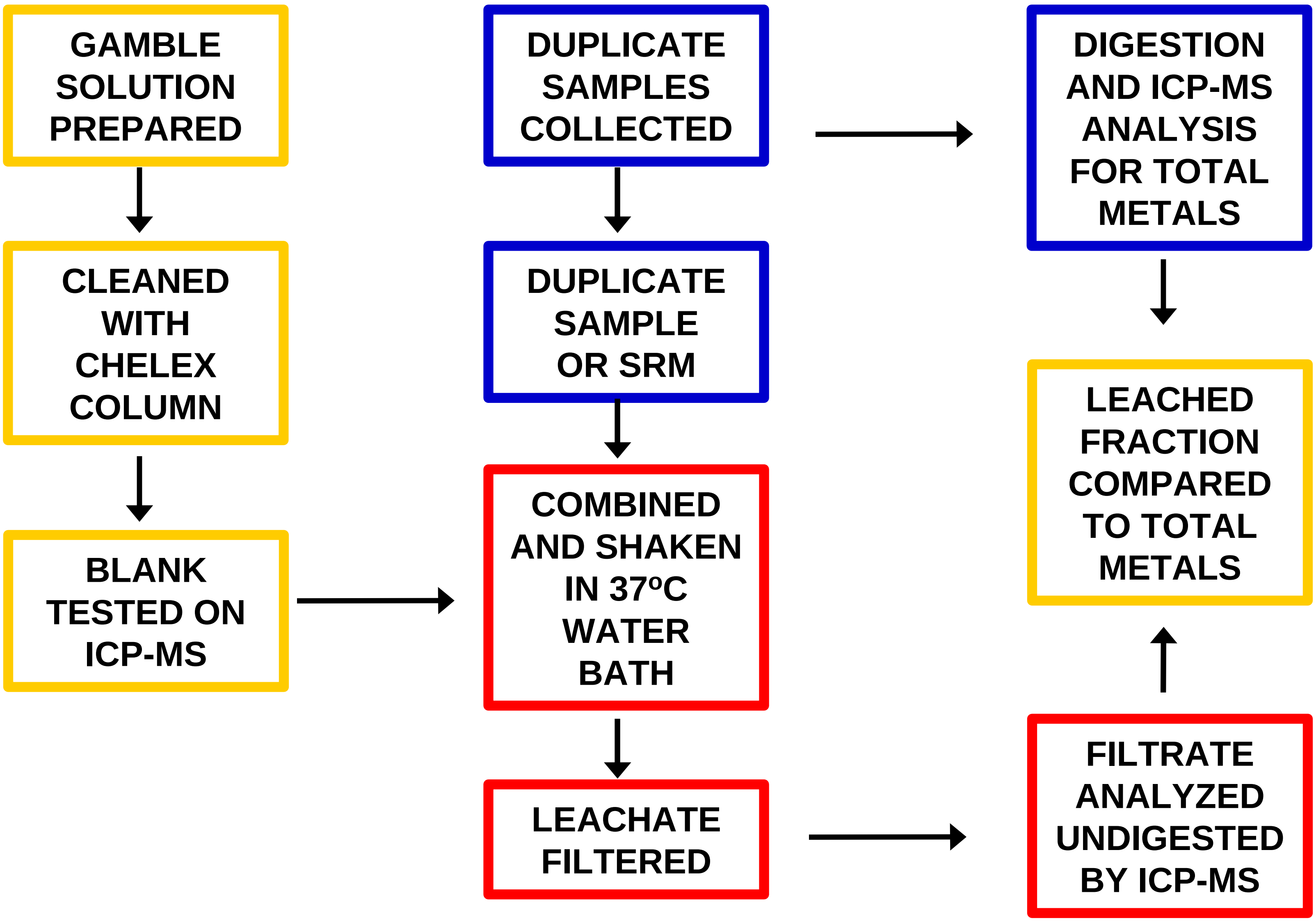
SURFACTANT
ORGANIC COMPONENTS

- Albumin 25 mg/l
- DPPC 730 mg/l
- Cetyl Alcohol 75 mg/l
- Tyloxapol 50 mg/l

- The DPPC, Cetyl Alcohol, and the Tyloxaphol are modeled after Exosurf Neonatal, a commercial lung surfactant for newborn babies

Gamble solution and surfactant are combined to closely mimic the composition of fluid in the lungs

METHOD: LEACHING

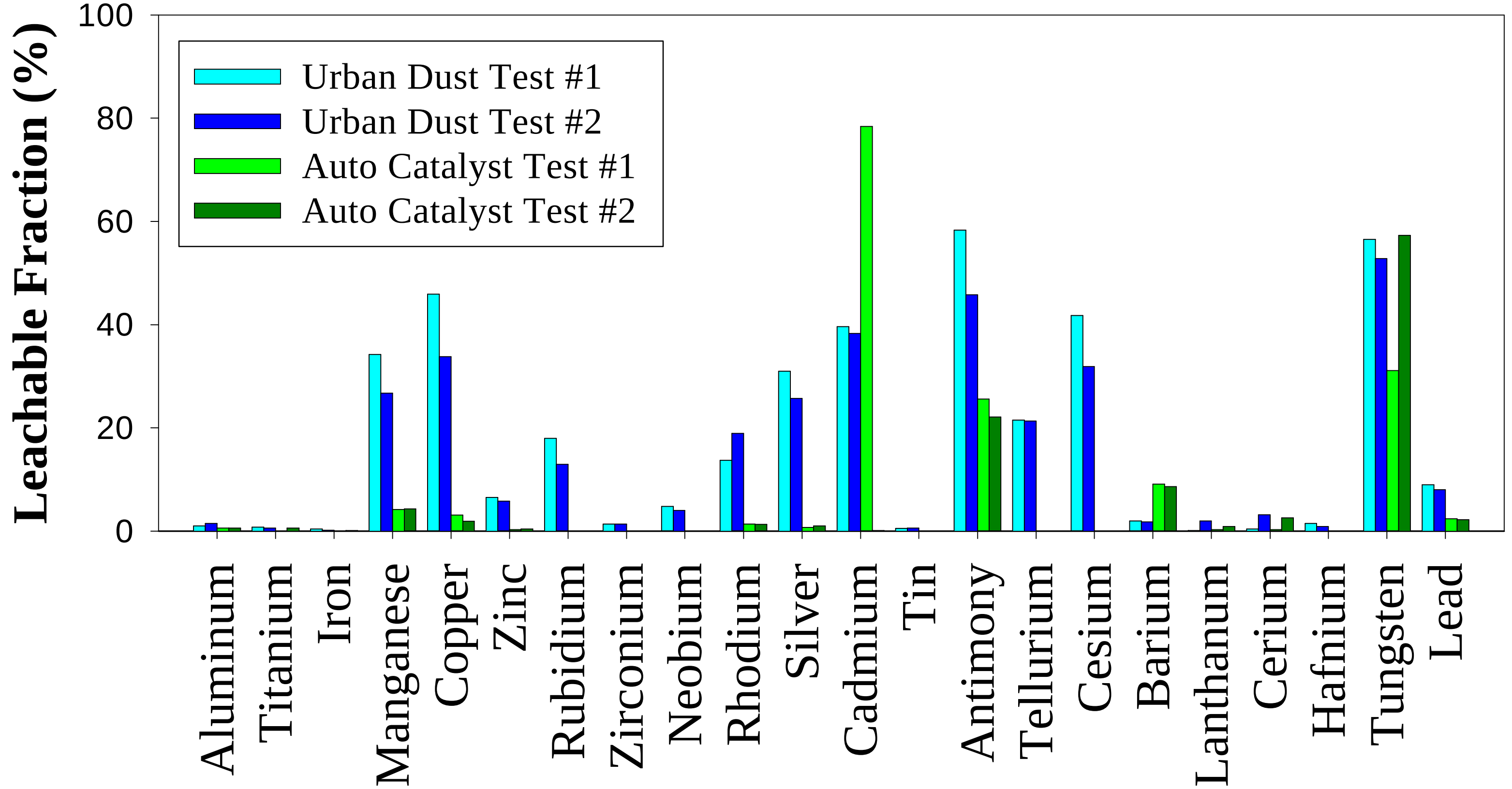


LEACHING SAMPLES

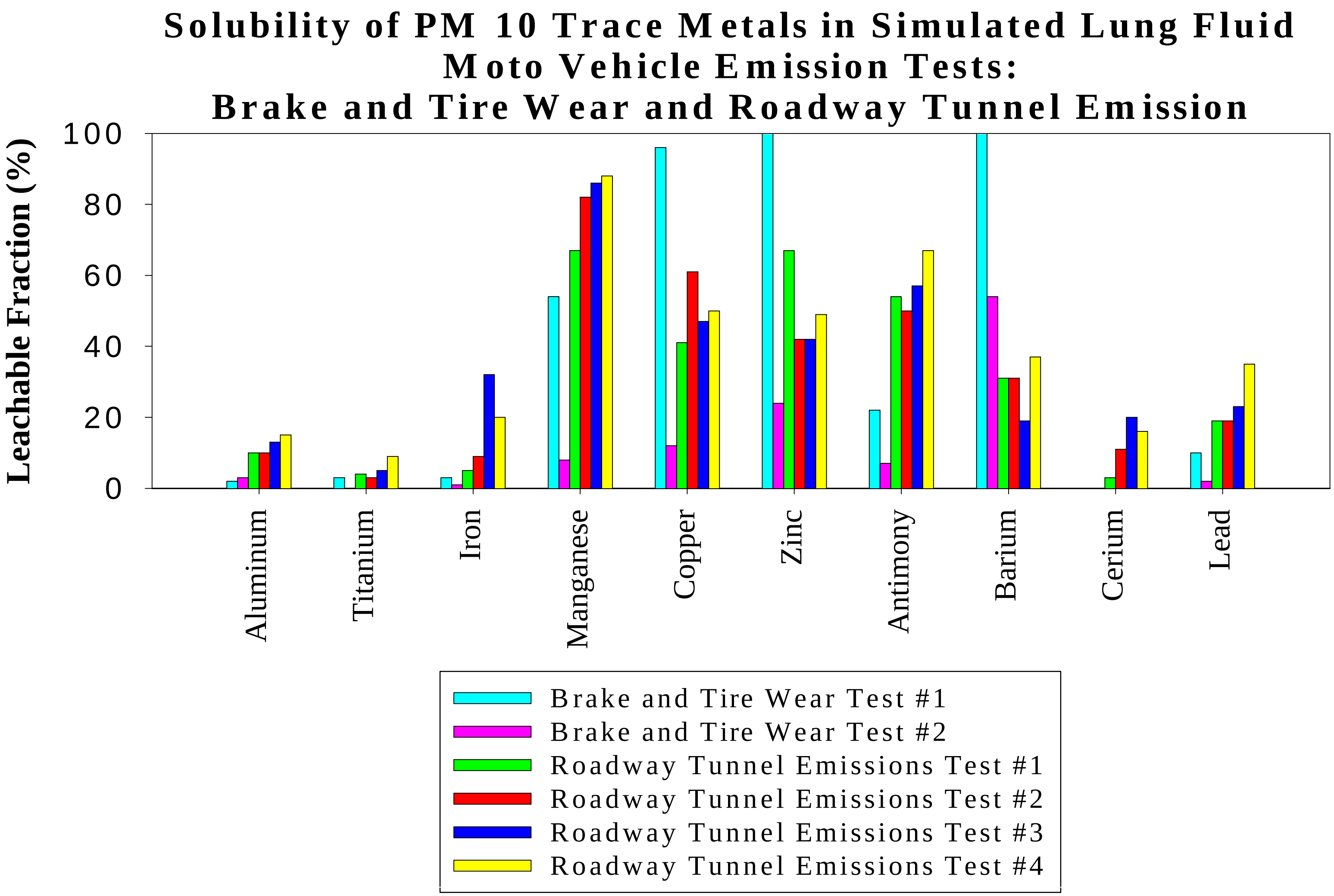
- NIST Standard Reference Materials (SRM's)
  - Used Auto Catalyst
  - Urban Dust
- Total Roadway Emissions from Motor Vehicles
  - PM10 samples from vehicle tunnel sampling
- Tire and Brake Wear emissions
  - PM10 samples from tire and brake wear dynamometer testing

RESULTS

Solubility of Trace Metals of Two Standard Reference Materials Urban Dust (NIST1649a) and Used Auto Catalyst (NIST2556) in Simulated Lung Fluid



RESULTS



Solubility of PM 10 Trace Metals in Simulated Lung Fluid
Moto Vehicle Emission Tests:
Brake and Tire Wear and Roadway Tunnel Emission
Leachable Fraction (%)
100
80
60
40
20
0
Aluminum
Titanium
Iron
Manganese
Copper
Zinc
Antimony
Barium
Cerium
Lead
Brake and Tire Wear Test #1
Brake and Tire Wear Test #2
Roadway Tunnel Emissions Test #1
Roadway Tunnel Emissions Test #2
Roadway Tunnel Emissions Test #3
Roadway Tunnel Emissions Test #4

CURRENT WORK

- CHEMICAL MASS BALANCE MODEL
  - Apportion specific sources of roadway emissions to total emissions from motor vehicles
    - Roadway profile and specific sources have been fully characterized
    - Use of parallel sampling and analysis techniques allows all profiles to be directly compared
    - CMB relates source profiles to overall profile to determine contributions of each

- FACTOR ANALYSIS OF AMBIENT DATA
  - Exploratory factor analysis
    - All sources of ambient PM are not fully defined
    - Parallel sampling and analyses available only for motor vehicle emissions
    - EFA can apportion ambient concentrations to various factors
    - Factors can be related to known sources

ACKNOWLEDGEMENTS

- Funded by Health Effects Institute (HEI#99-13)
- California Air Resources Board Haagen-Smit Laboratory staff
- Tailpipe emissions tests funded by NREL
- US EPA and Eastern Research Group

WI State Laboratory of Hygiene
Jeff DeMinter, John Strauss, Al Spallato,
Mike Arndt, Chris Worley, Dustan Helmer

Dr. June Soo Park, Min-Suk Bae, Rebecca Sheesley,
Charles Christensen, James Bucholz, M Danijarsa

Dr. Mike Hannigan, Sara Bruening, Clifton Hackbarth