Chemical Speciation of Ultrafine Particulate Matter

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ENVIRONMENTAL CHEMISTRY AND TECHNOLOGY PROGRAM
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Overview

- Big Picture Comments
- Sampling and Analysis Considerations
- Examples
  - California Ambient Data
  - DOE Cold-Cold Start Study
  - HEI Metals Study
  - Other Primary Sources
  - Metal Speciation
- Conclusions

Why Pursue Chemical Speciation of Ultrafine PM

- Mass Balance Closure
  - Focus on major components
  - Inherently provides some source information
- Source Apportionment
  - Key source tracers and their limitations are reasonable well understood
  - Tools are available for ultrafine PM
- Identify and Quantify Sources of Toxicity
  - Needs to be integrated with toxicology or epidemiological studies
  - "Chicken and the Egg" problem

Toxicity Focus

- Important to recognize that individual chemical analysis methods focus on groups of analytes
  - What we find is related to what we look for
  - Need to think beyond traditional analytes and methods
- Literally thousands of compounds in PM
  - Many are highly correlated and serve as surrogates for others compounds
- The toxicity of chemical species are:
  - Linked to the chemical form
  - Impacted by chemical and physical interaction with surroundings
- Need to direct chemical analysis by
  - Physical and chemical process associate with dose
  - Toxicity or health endpoints (i.e. bioassay directed chemical analysis)

Analytical Considerations

- Large set of tools available for quantification and speciation of ultrafine PM
  - Look to allied field of environmental chemistry as well as medicinal and pharmaceutical chemistry
  - Exploit new instruments and methods to improve detection limits, quantify a wider range of analytes and pursue speciation
    - ICPMS, LCMSMS, GC-NCI-MS, HR-MS
- Need to be directed by health relevant endpoints
- Clearly important directions to pursue
  - Polar organics
  - Metal speciation

Sampling Considerations

- Lab-based versus field-based measurements
  - Very closely related
  - Resource optimization
- Need to think beyond the traditional “filter analysis”
  - Chemical analysis is toxicity assay extracts
  - Aqueous collectors to mimic lung deposition and matrix interaction
  - Direct analysis of dose – Lung Condensate
  - Analysis of lung tissue
- Field blanks are now dominating almost all method detection limits – Critical issue

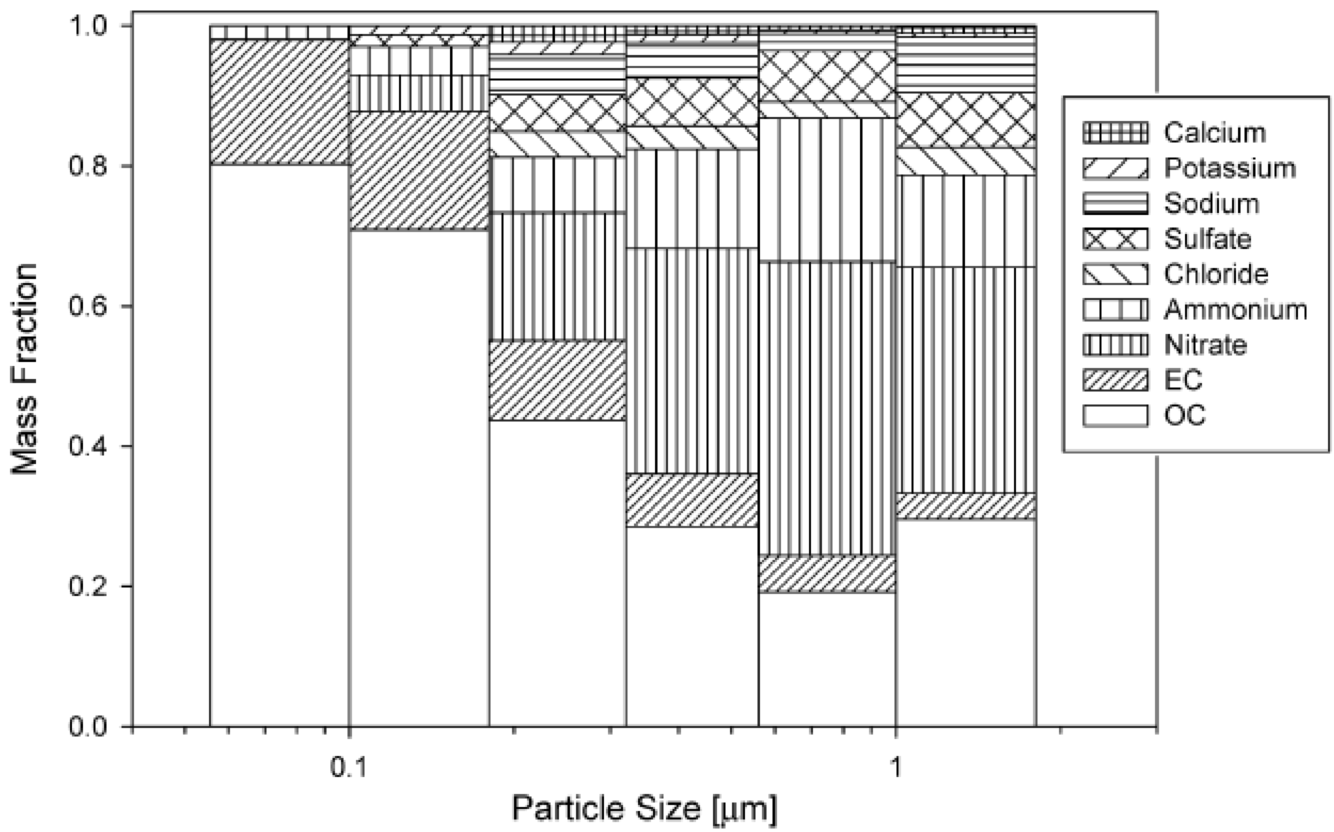

Figure 6. Relative size distribution of airborne particulate OC, EC, NH_4^+, NO_3^-, Cl^-, SO_4^{2-}, Na^+, K^+, and Ca^{2+} ions measured at Bakersfield on the evening of December 26, 2000. Results are typical of size distribution measured throughout the SJV during the study period.

Jorn D. Herner, Jeremy Aw, Oliver Gao, Daniel P. Chang, and Michael J. Kleeman
Department of Civil and Environmental Engineering, University of California at Davis, Davis, CA

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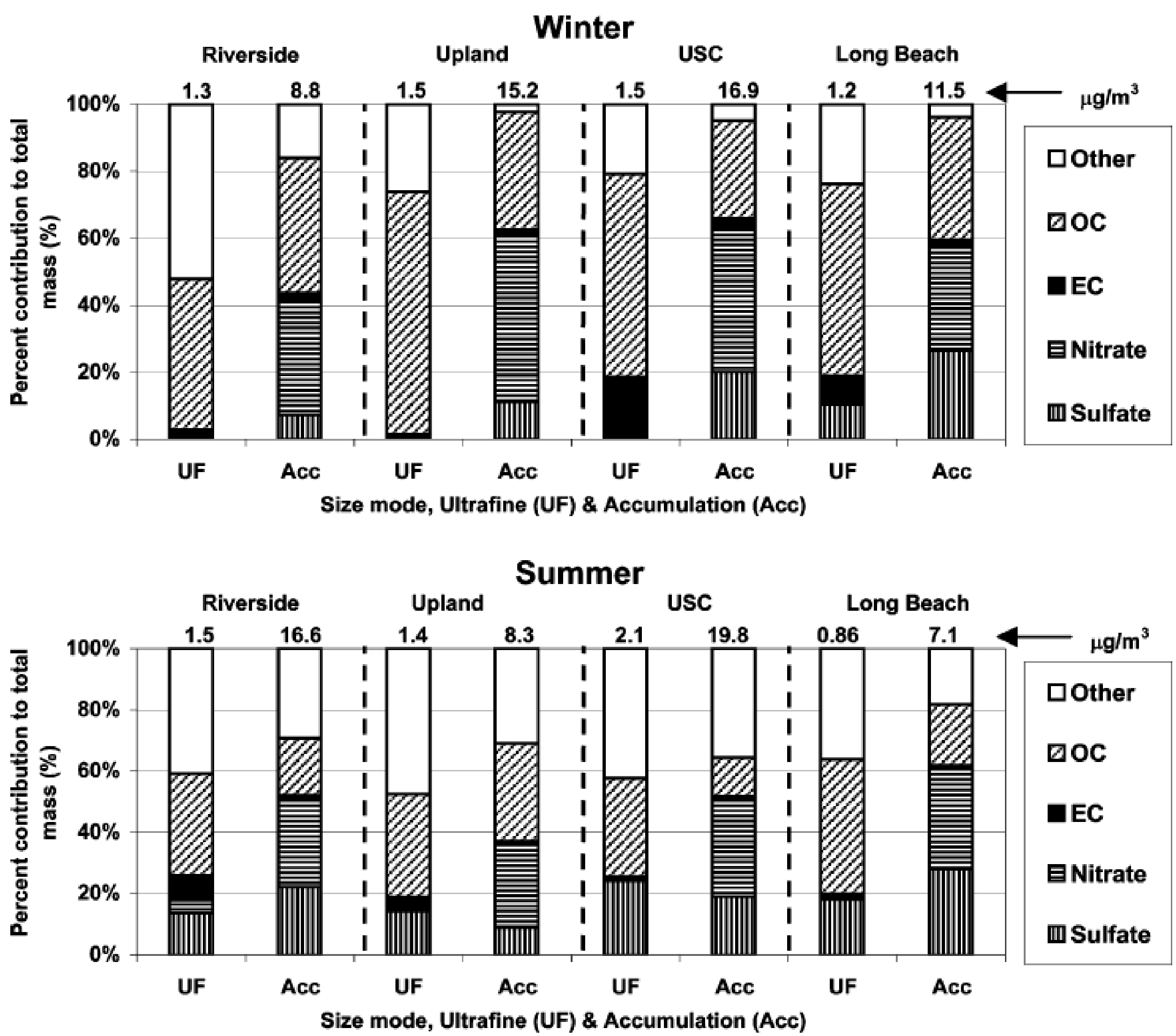

FIGURE 2. Contribution of chemical species to the total particulate mass in the ultrafine and accumulation modes.

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DOE Cold-Cold Start Study

Project Manager: Doug Lawson - NREL

- On-Road Gasoline (SI) Vehicle Tests
- Cold-Cold Dynamometer Test Cell
- Two-Stage Dilution
  - Primary Dilution Ratio of 10:1
  - Secondary Dilution Ratio of 30:1
- Samples collected from residence time chamber at ambient temperature
- Real Time Measurements – University of Minnesota
  - CO and CO2
  - Particle Number
  - Particle Size Distributions
  - Diffusion Charger

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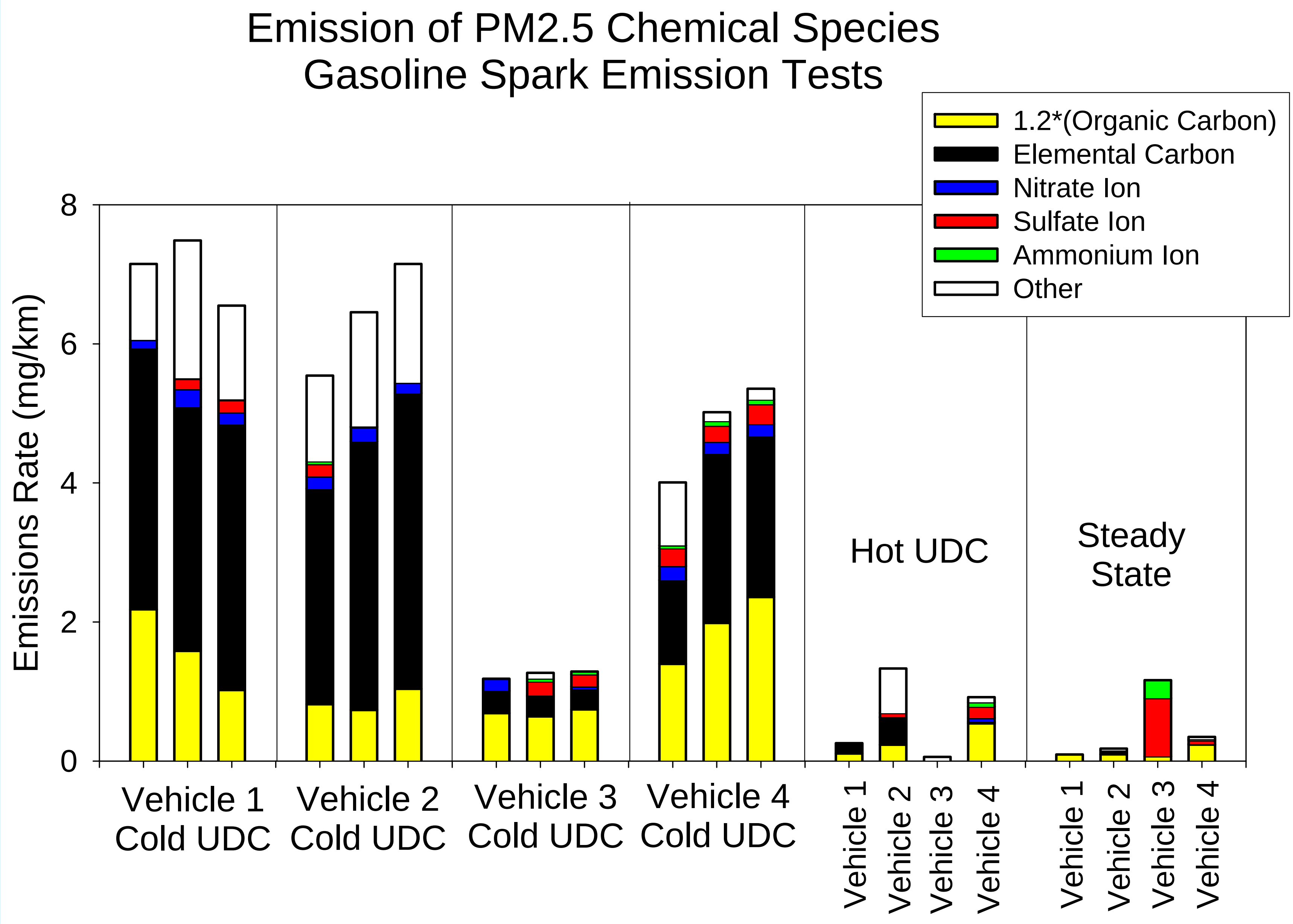

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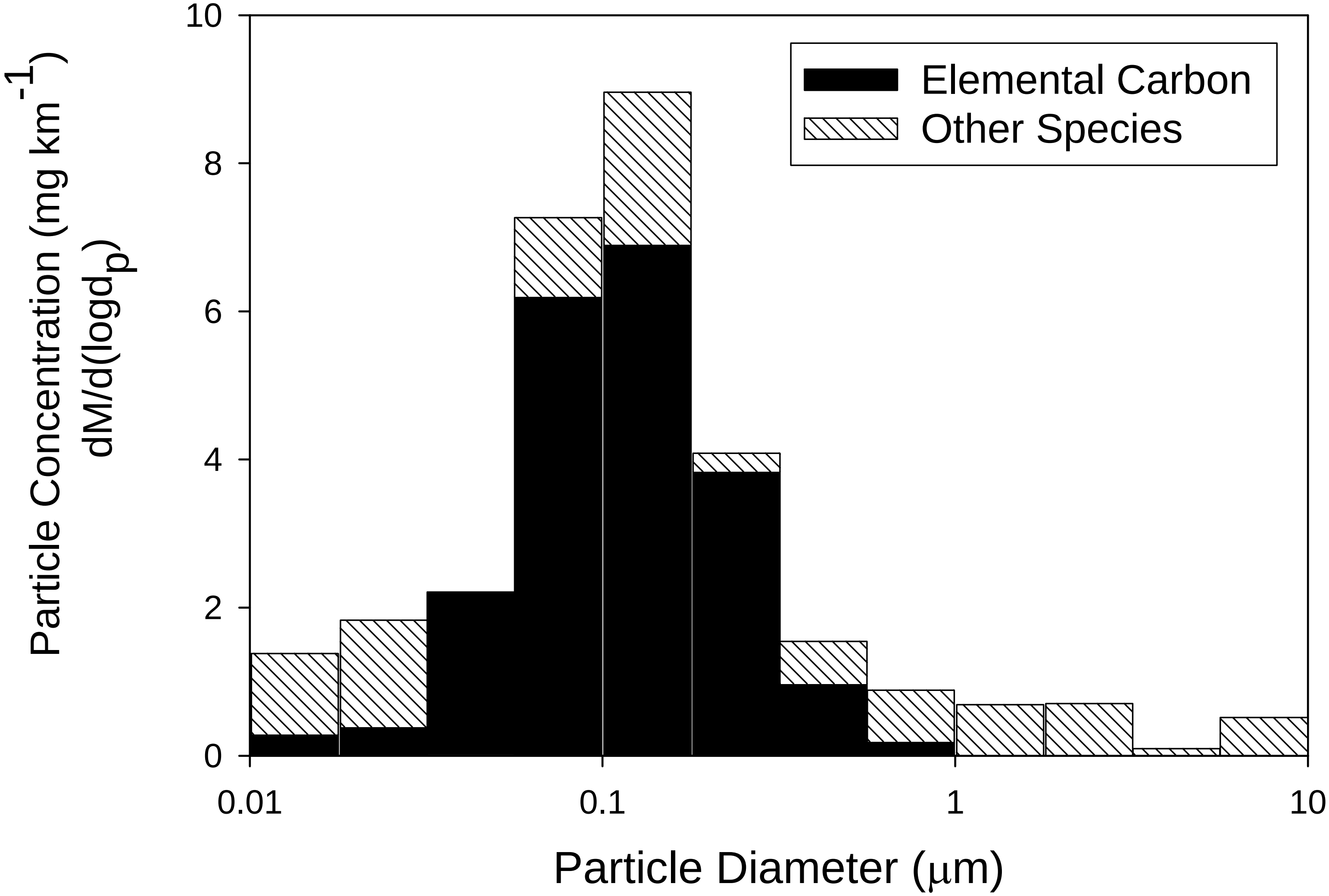
Particle Size Distribution for Cold-Cold Start UDC Driving Cycle
Test 13 - Vehicle 2 -Windstar



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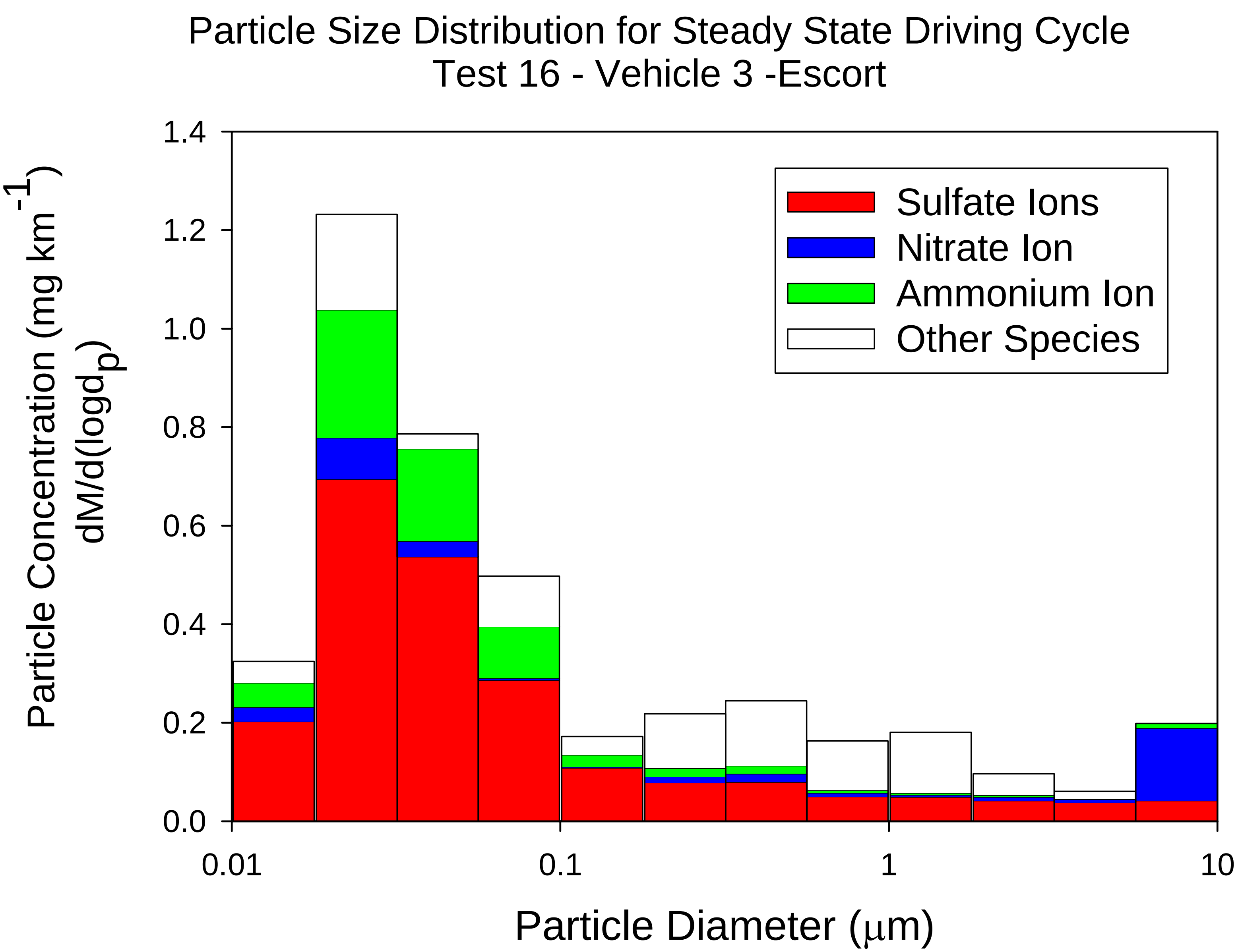

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Metal Emissions from Mobile Sources

HEALTH
EFFECTS
INSTITUTE

Number 133
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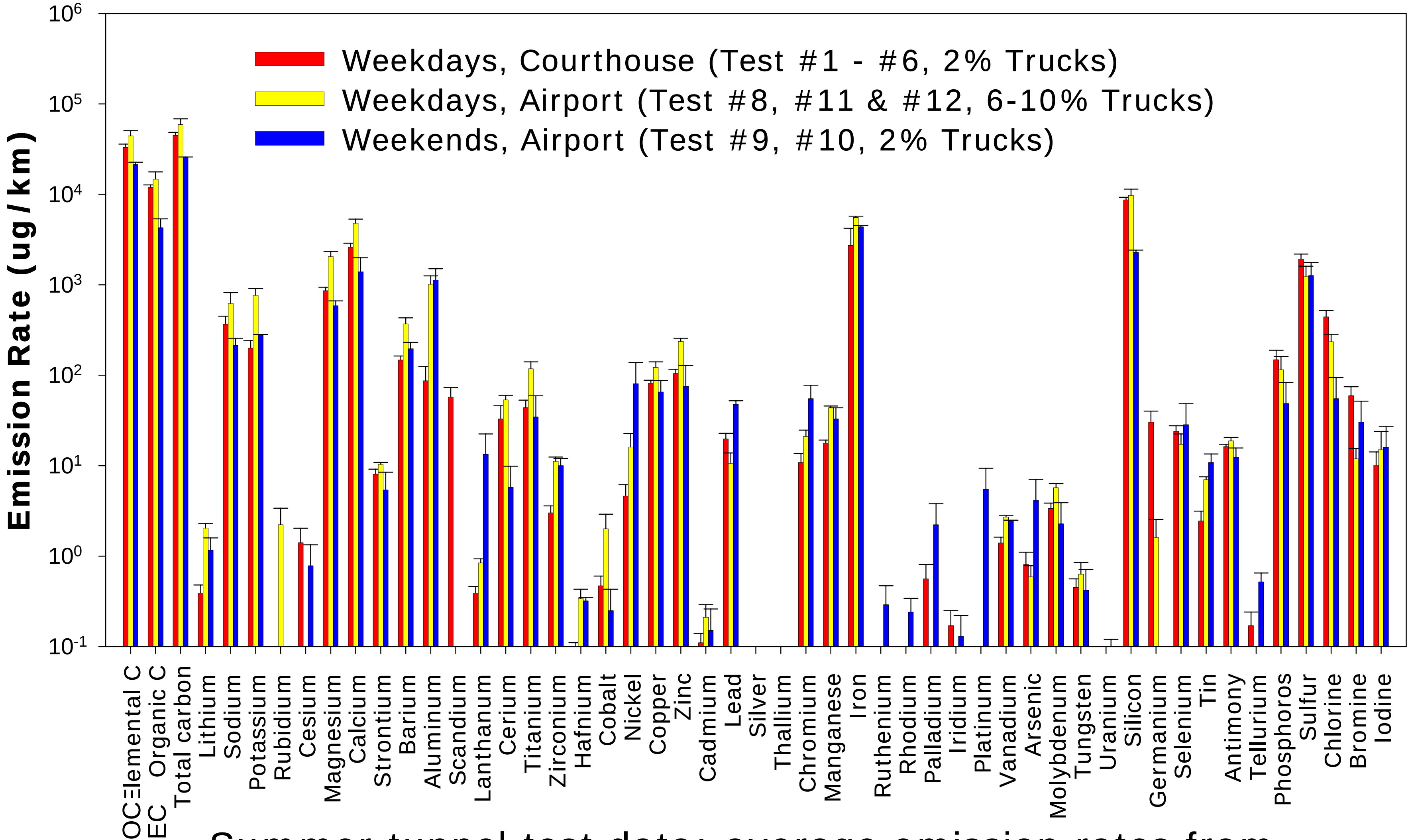
Characterization of Metals Emitted from Motor Vehicles

James J Schauer, Glynis C Lough, Martin M Shafer, William F Christensen, Michael F Arndt, Jeffrey T DeMinter, and June-Soo Park

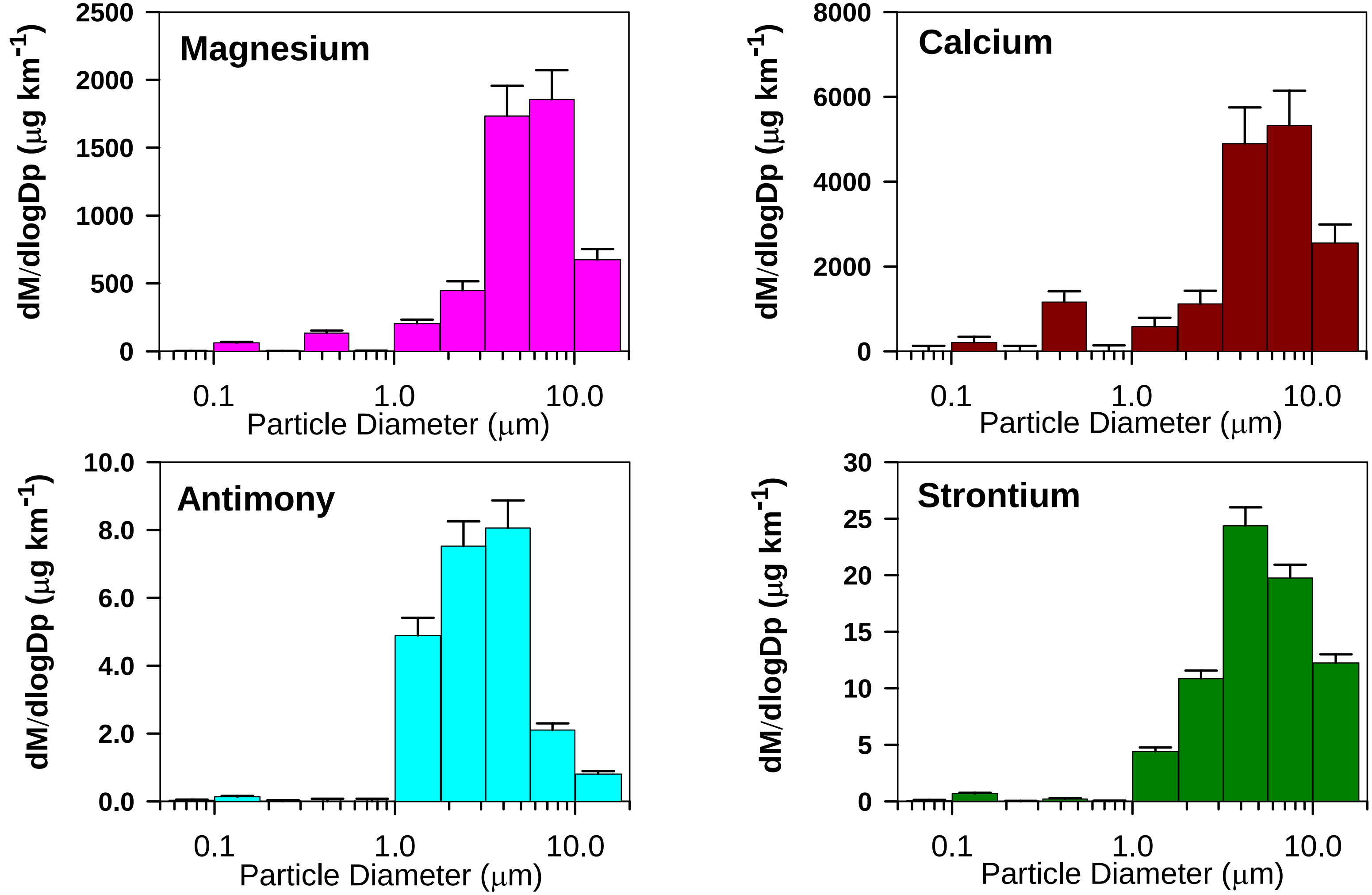
Milwaukee Airport

- 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



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

Size-resolved metals emissions from motor vehicle roadway tests



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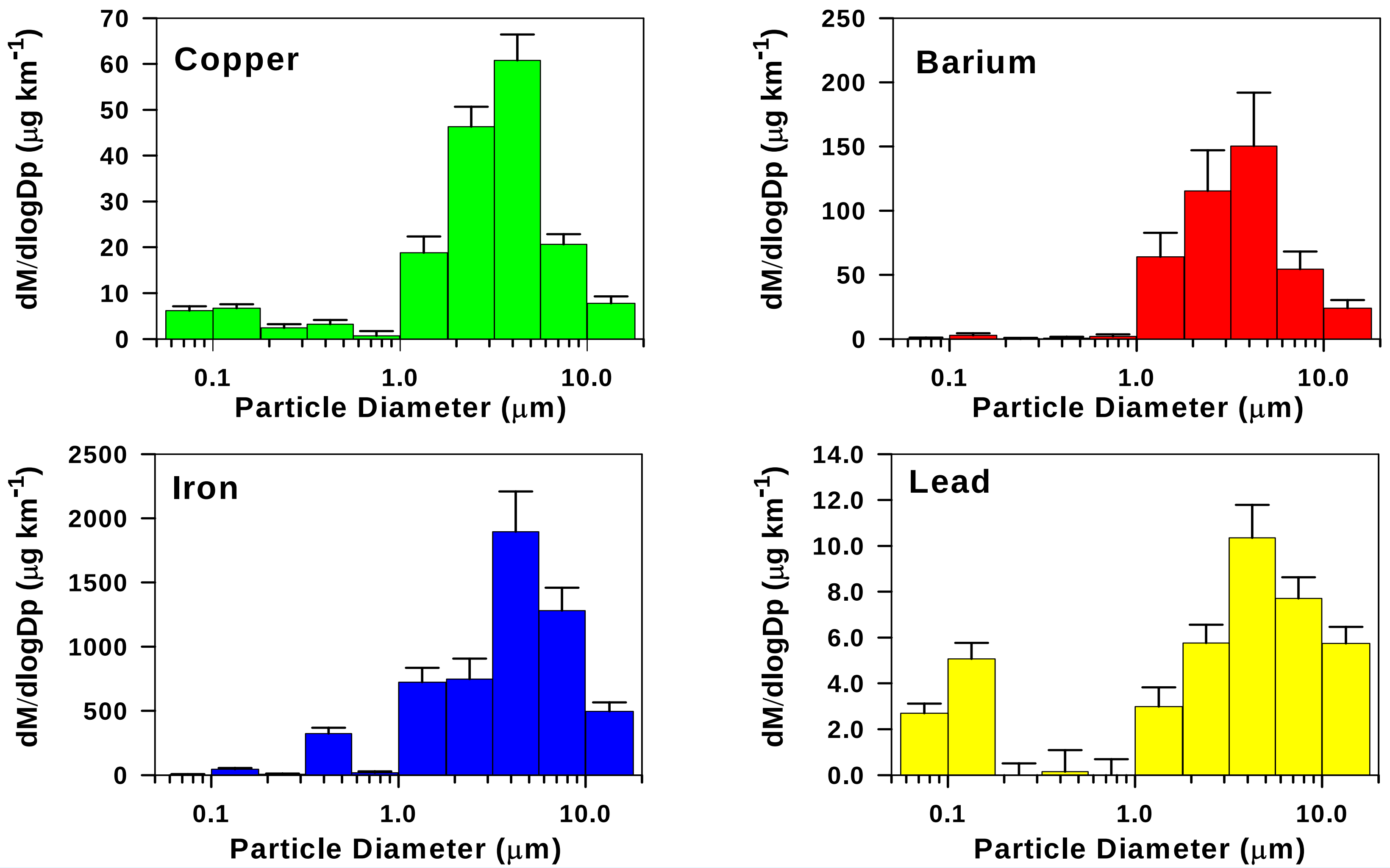
Size-resolved metals emissions from motor vehicle roadway tests



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Other Ultrafine Sources

- Secondary Ultrafine - Nucleation
  - Composition similar to secondary accumulations particles?
  - Are the secondary components are soluble in lung fluid?
- Non-Mobile Source Ultrafine
  - Sources can be important contributors to ultrafine particles without being important contributors to fine particulate matter
  - Bulk composition can be the same but the morphology and micro-contaminants can be very different

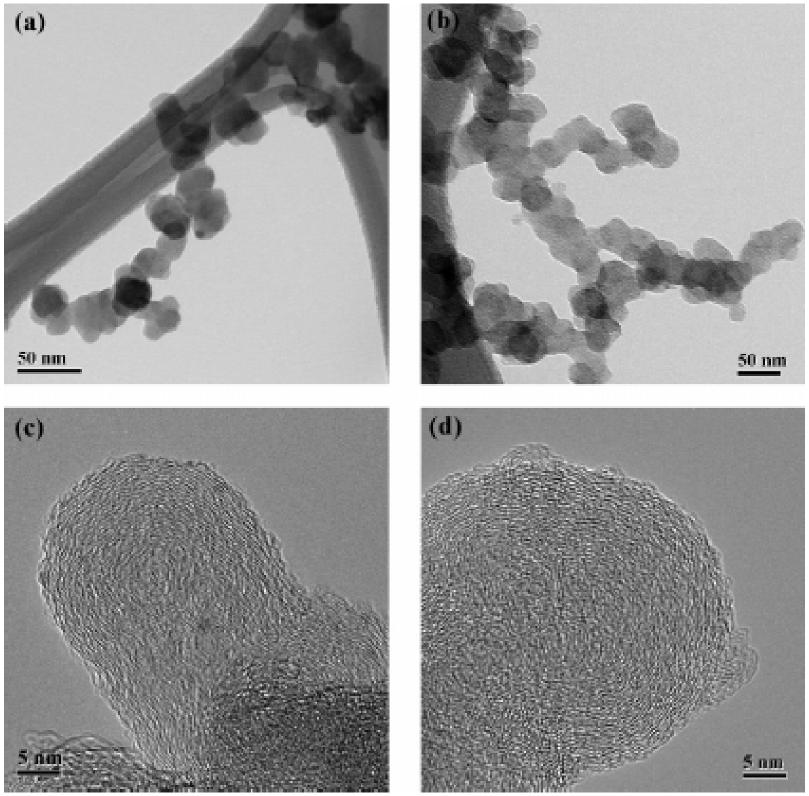

FIGURE 1. Comparison of the morphologies of coal fly ash soot (a) and diesel soot (b) aggregates. Both of them show chainlike branching structures. Microtextures consisting of concentrically stacked graphitic layers were observed in both the coal fly ash soot (c) and the diesel soot (d) primary particles.

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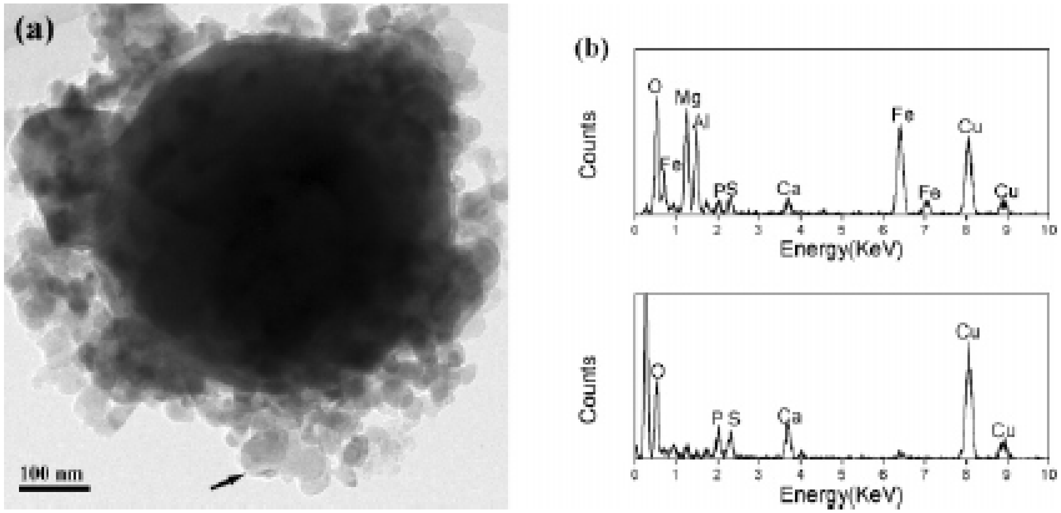

FIGURE 10. (a) Micrograph of a bunch of ultrafine Ca–P–S particles (indicated by the arrow) stuck on the surface of a submicrometer Mg–Al–Fe particle. (b) EDS spectra recorded from the Mg–Al–Fe particle (top) and the Ca–P–S particles (bottom), respectively (Wyoming PRB CFA).

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Metal Speciation

- Chemical form of metals in ultrafine, fine and coarse PM are critical to their fate and impacts
- Techniques exist to “speciate” metals in particulate matter samples
  - Leachability
  - Oxidation state
  - Chemical form
  - Bioavailability
- Need to utilize these methods for assessment of ultrafine PM

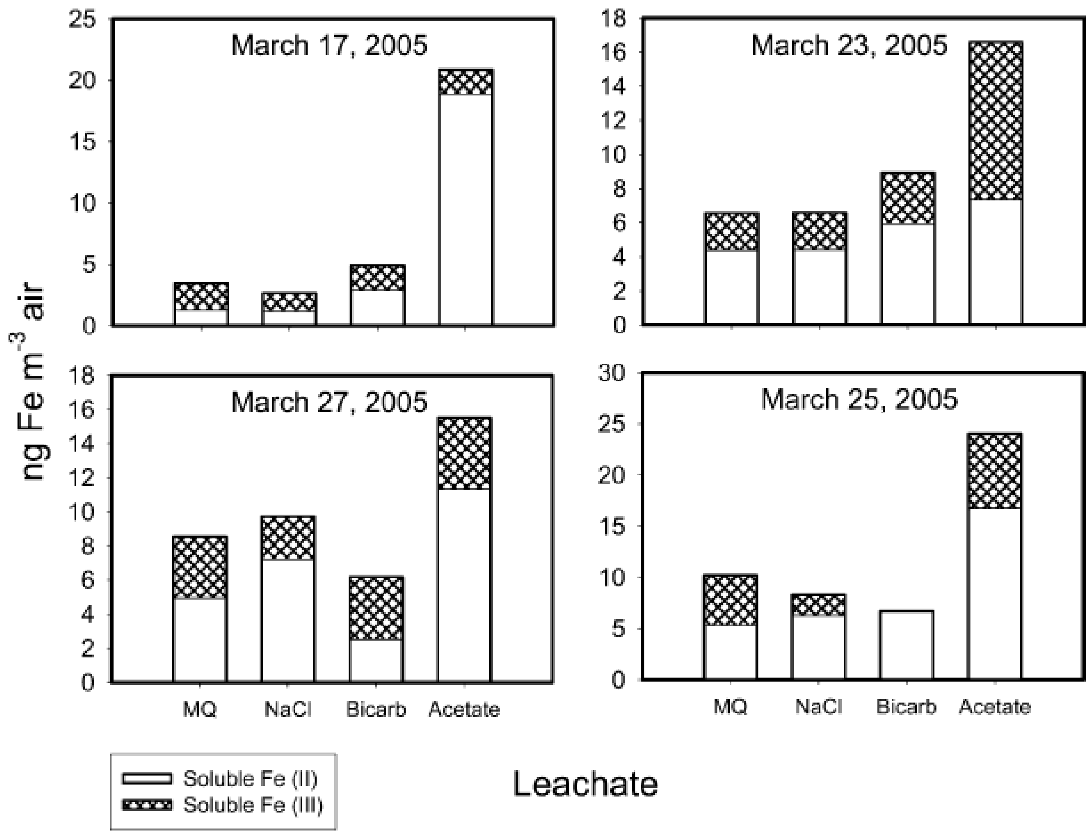

FIGURE 3. How leachate affects the soluble Fe(II) present in the collected PM. Each date consists of four co-located samples submitted to a different leach. In acetate solution, the fraction of the total iron extracted is 5.7%, 10%, 13%, and 7.4% for March 17, 23, 25, and 27, respectively.

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Conclusions

- Tools exist for the chemical speciation of ultrafine particulate matter
- Chemical analysis tools for ultrafine should be used that align with desired endpoint
- Organic and Elemental Carbon are important components of ultrafine PM
- Metals levels in ultrafine PM are important in the context of source apportionment and human health
- Caution is needed in applying conventional wisdom from PM2.5 directly to ultrafine PM