Source-Oriented Toxicology of Ambient Fine and Ultrafine PM

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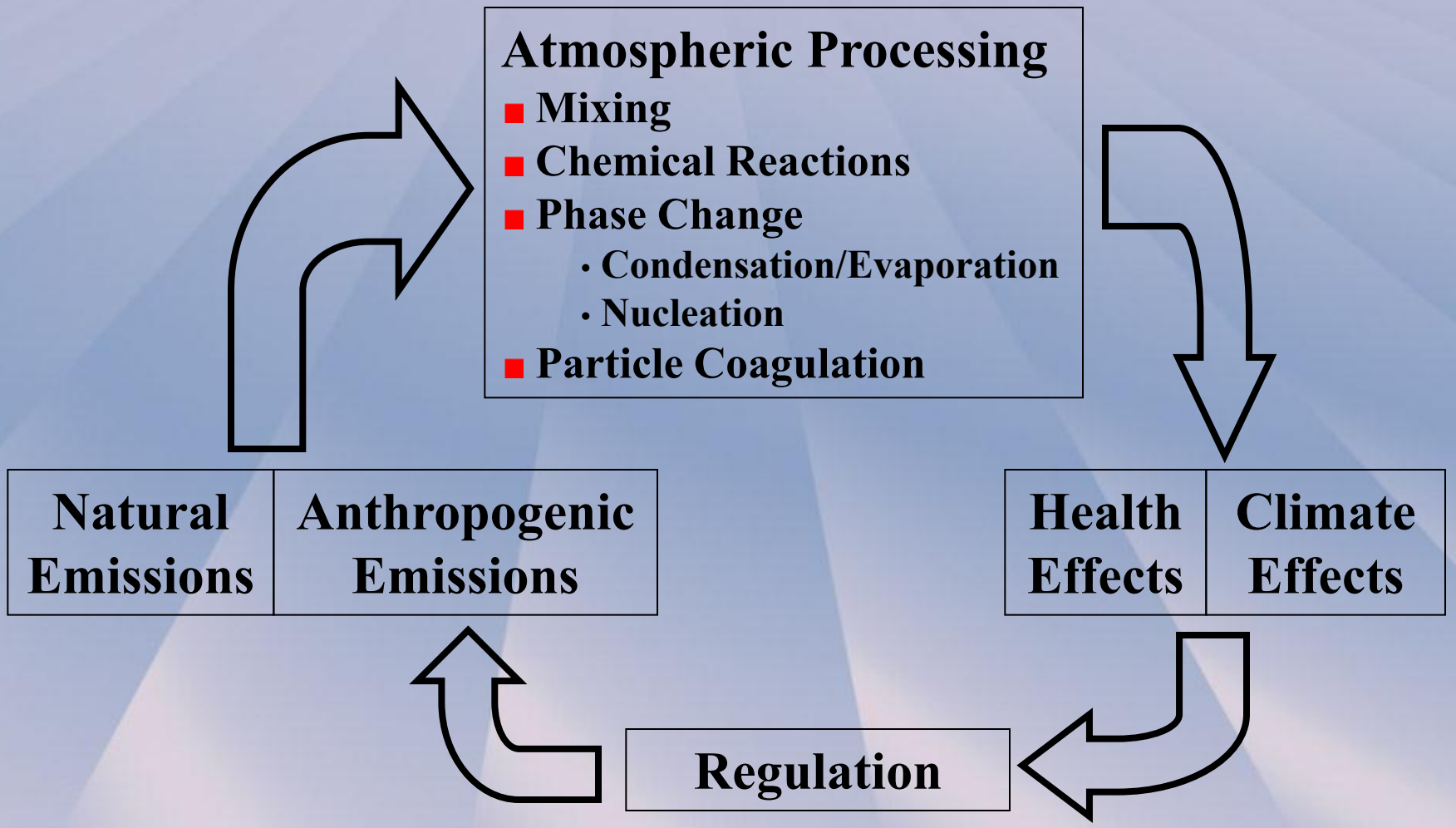
Work Sponsored by
California Air Resources Board and
Electric Power Research Institute

The Air Pollution Life Cycle



Which Sources are more Toxic?

Is all PM created equal?

Is some PM more equal than others?

(apologies to George Orwell)

-- Do sea spray and diesel exhaust have same toxicity?

-- Current mass-based NAAQS treats them the same

-- Can we differentiate sources by their toxicity?

Which Sources are more Toxic?

How do we deduce health effects of different sources?

Epidemiologically

-- High risk near freeways
-- High risk downwind of coal fired power plants
-- Many other studies
-- But correlative, not causative

Which Sources are more Toxic?

How do we deduce health effects of different sources?

Toxicologically directly from sources

-- Well how about those nasty secondary compounds?

-- And how about the atmosphere changing the toxicity?

-- Can we collect source-oriented PM from the atmosphere?

-- Isn’t the atmosphere well mixed?

Talk Outline

-- Source-Oriented Sampling (Wexler)

What did we do and how did we do it?

-- Source Attribution (Bein)

-- PM Extraction (Bein)

-- Source-Oriented Toxicity (Pinkerton)

Source-Oriented Sampling

The atmosphere is not well mixed on short time scales

-- Consider plumes hitting a sampling site

-- Single particle mass spectrometer observations in Atlanta, Houston, Baltimore and Pittsburgh

Source-Oriented Sampling

So what's the big idea?

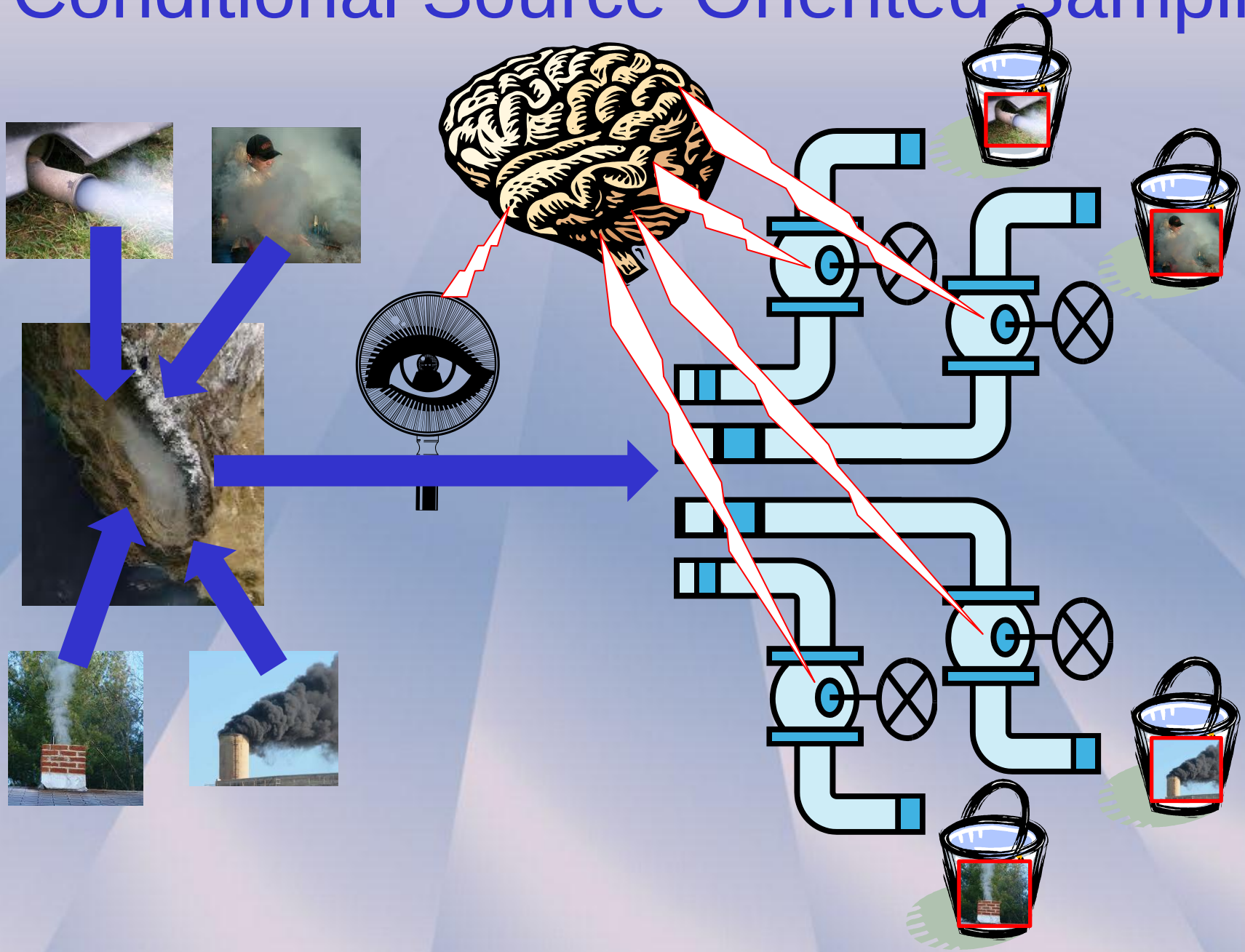
-- Run a single particle mass spectrometer to characterize the mixing state of the atmosphere

-- Assign prevailing sources or source combinations to each of 10 high-volume ChemVol samplers

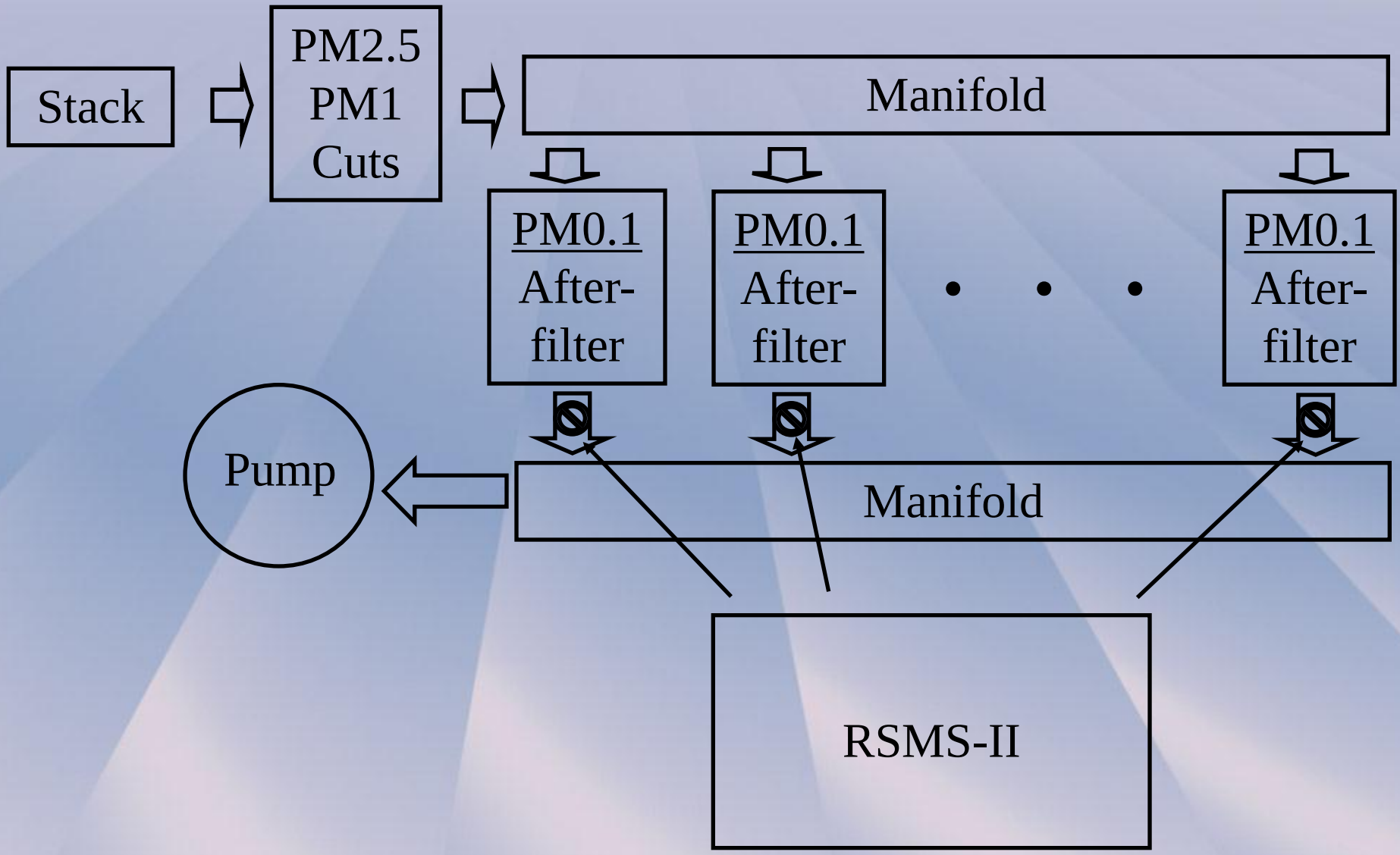
-- Use single particle mass spectrometer to select which ChemVol samples

-- Collect enough PM for tox studies

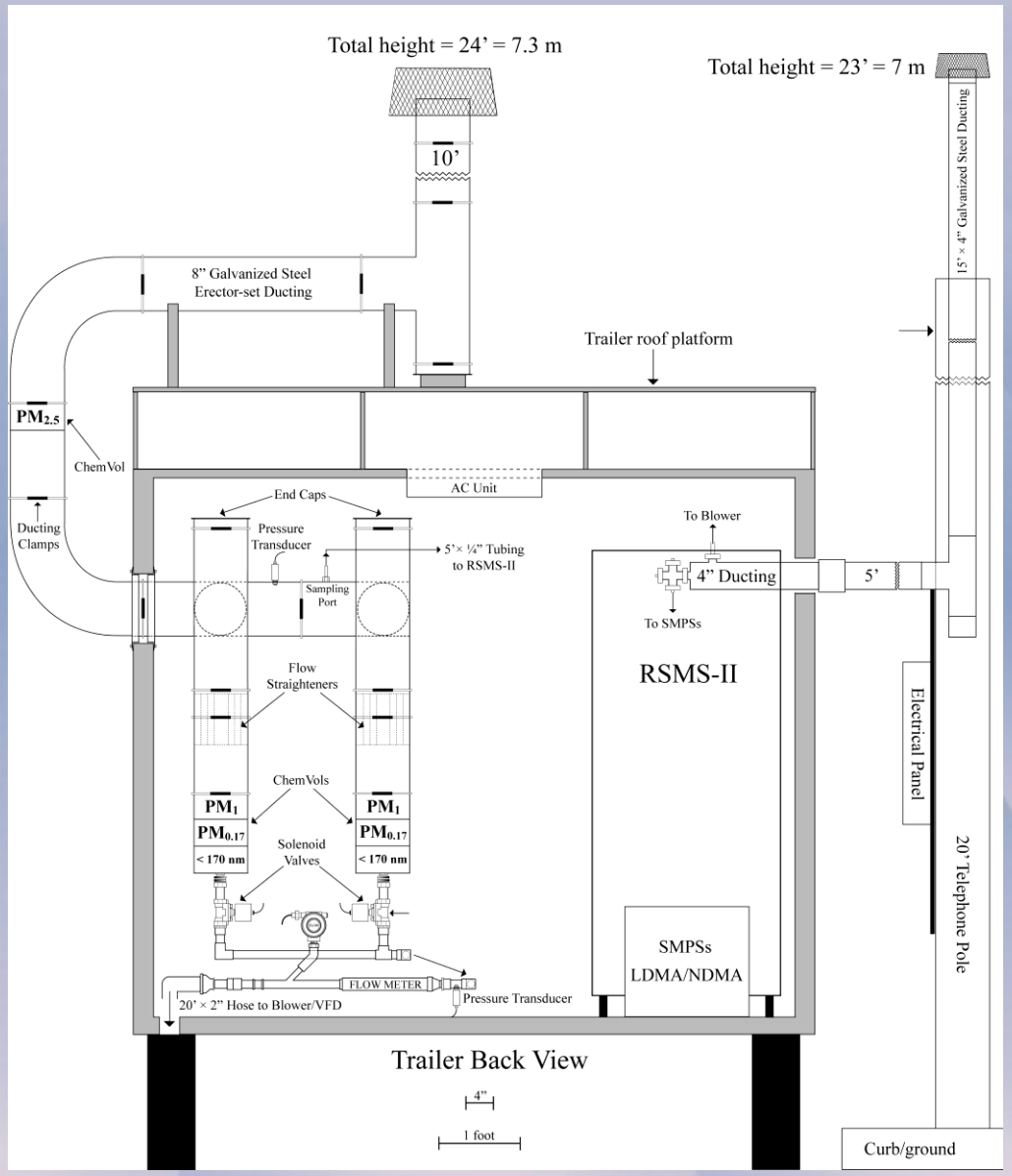
Conditional Source-Oriented Sampling



Conditional Source-Oriented Sampling



Sampling Train Schematic

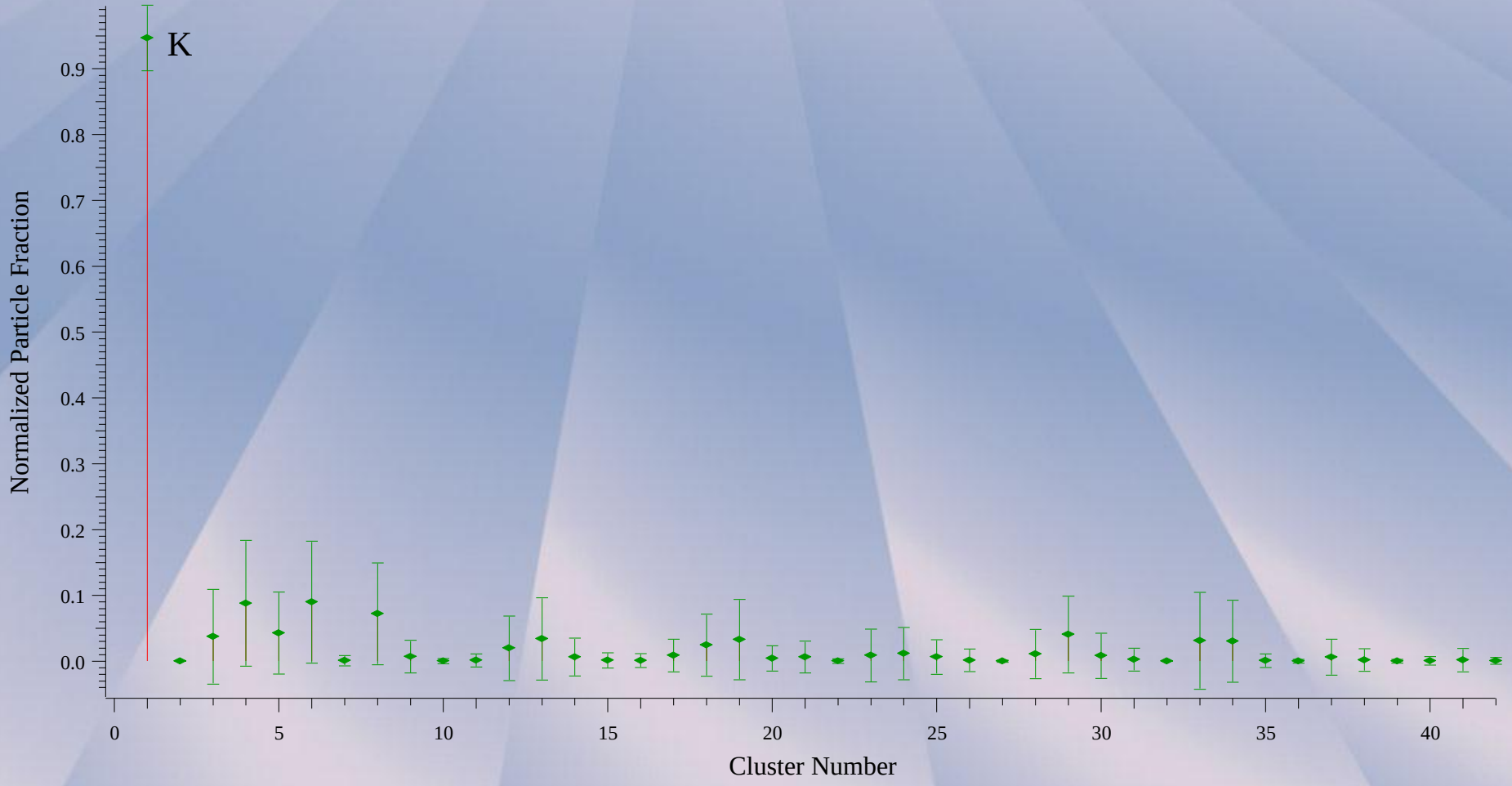


RSMS-II

Sampling Train

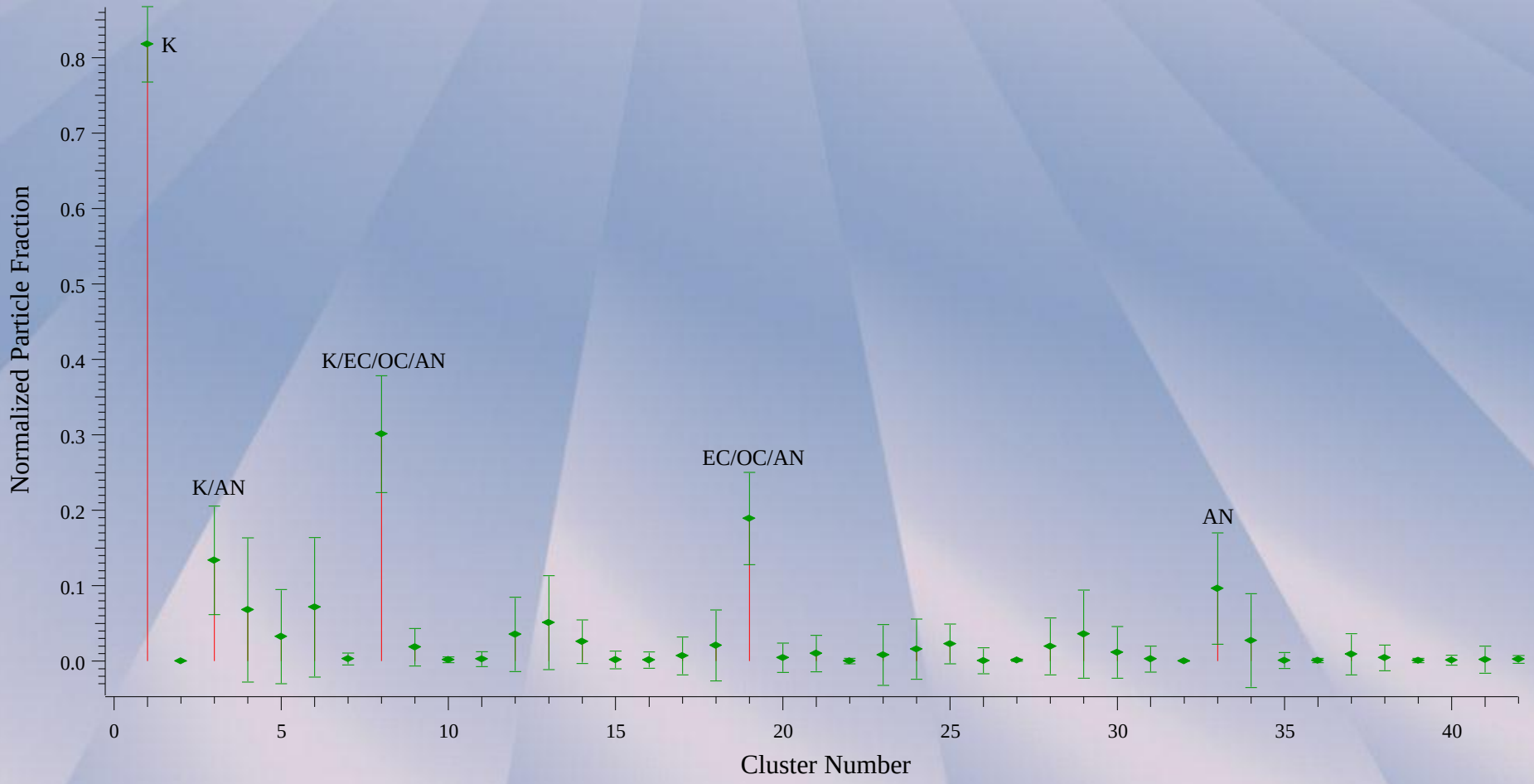
Source Combination 1 (D_p ~ 70-93 nm)

Relatively clean separation of primary wood smoke emissions



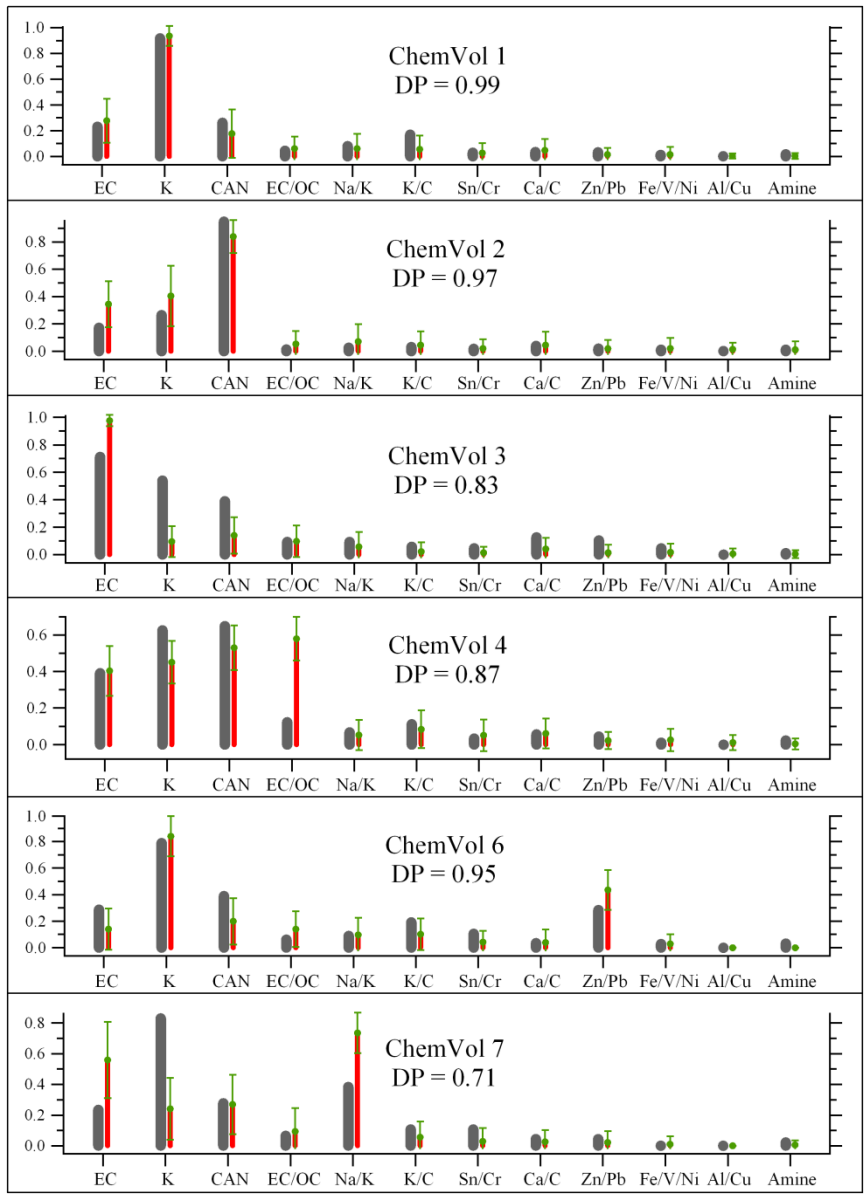
Source Combination 2 (D_p ~ 70-93 nm)

Mixture: wood smoke emissions (primary and w/ammonium nitrate), carbonaceous aerosol, and ammonium nitrate (AN) particles

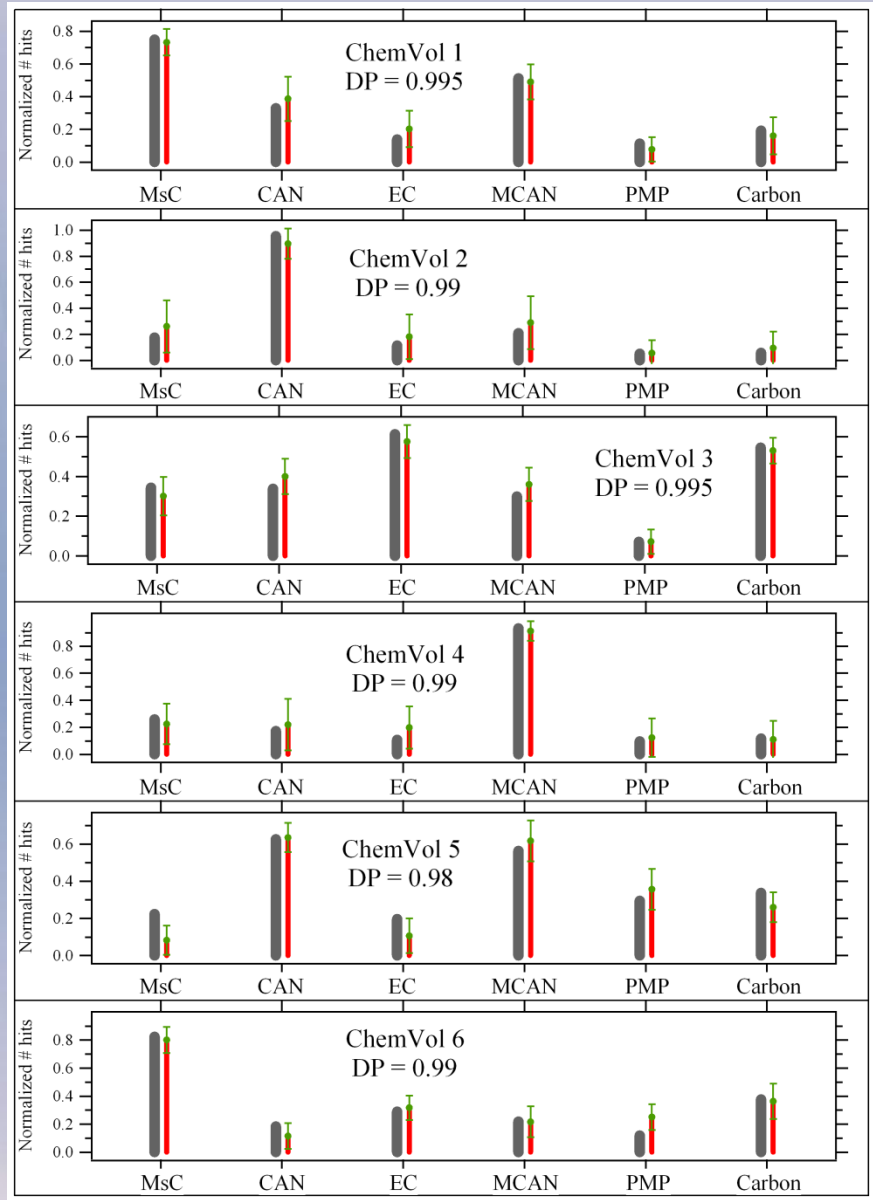


Fidelity

Summer 2008



Winter 2009



Source-Oriented Sampling

Summary

-- Collected source-oriented PM from Fresno
-- Two seasons: Summer ‘08 and Winter ’09
-- Two size ranges
    Ultrafine (UF): smaller than 170 nm
    Submicron Fine (SMF): 170 nm to 1 um
-- Sufficient sample in most sources/sizes for tox studies
-- Samples represent major sources in Fresno
-- Good separation of sources in the samples

Talk Outline

-- Source-Oriented Sampling (Wexler)

-- Source Attribution (Bein)

Where did the PM come from?

-- PM Extraction (Bein)

-- Source-Oriented Toxicity (Pinkerton)

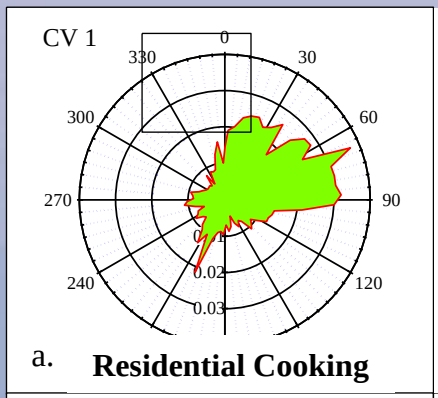
Source Attribution – Site-Source Relation

Emissions Sources

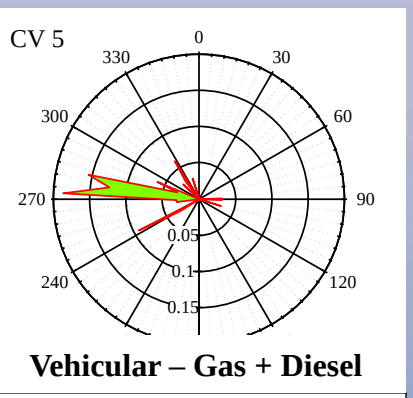
- Vehicular
  - Gasoline and diesel
  - Highways and residential
- Residential and Commercial
  - Cooking
  - Space heating
  - Construction/landscaping
- Agricultural
  - Ranching
  - Agricultural machinery
  - Waste/debris burning
  - Product transportation
- Regional Processing
  - Ammonium nitrate
  - Secondary Organic Aerosol
- Long-range Transport
  - Wildfires
  - Trans-Pacific transport

Source Attribution – Directional Relation

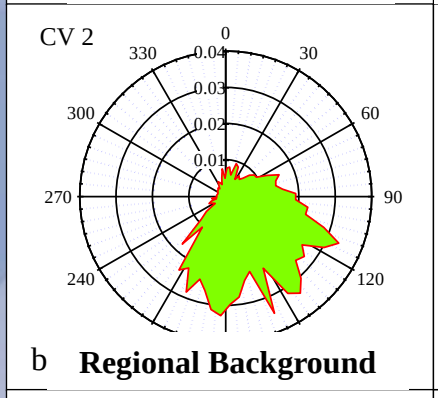
Summer 2008



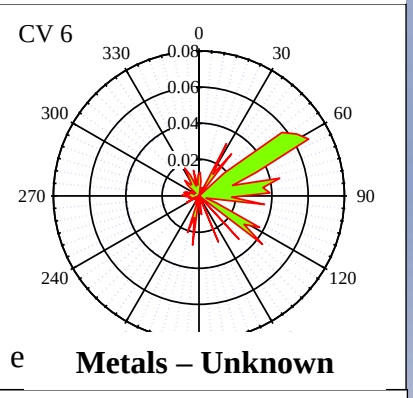
a. **Residential Cooking**



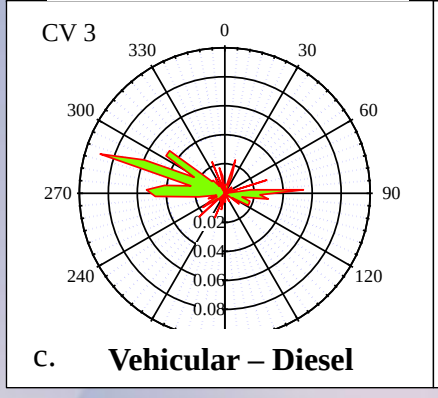
Vehicular – Gas + Diesel



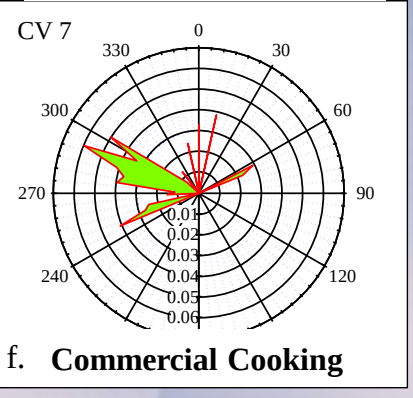
b **Regional Background**



e **Metals – Unknown**

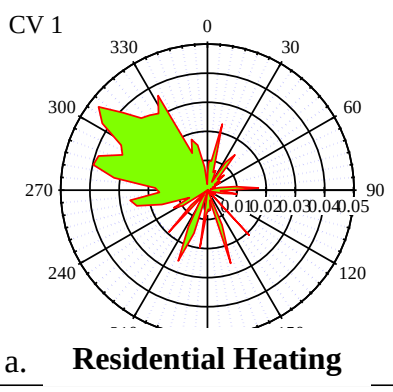


c. **Vehicular – Diesel**

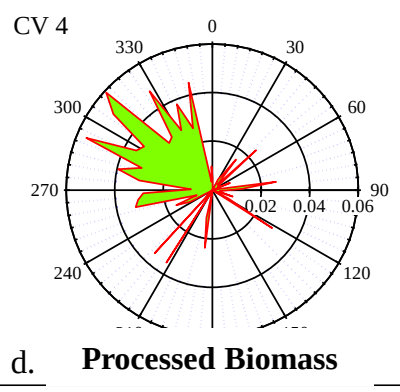


f. **Commercial Cooking**

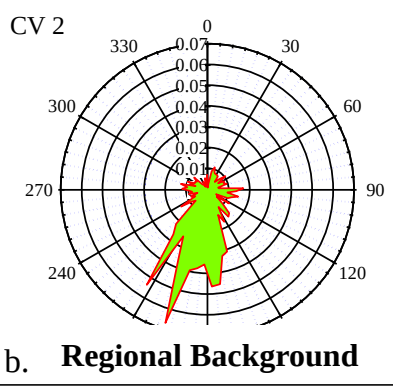
Winter 2009



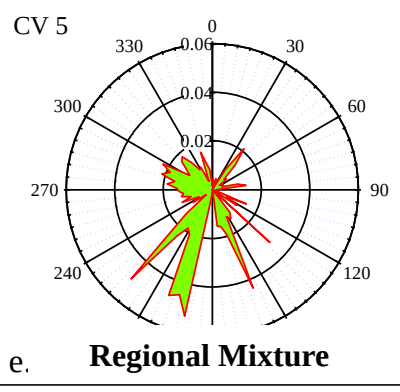
a. **Residential Heating**



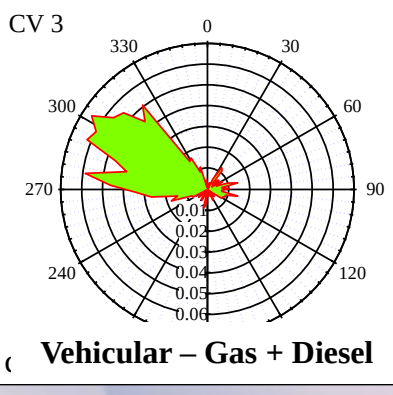
d. **Processed Biomass**



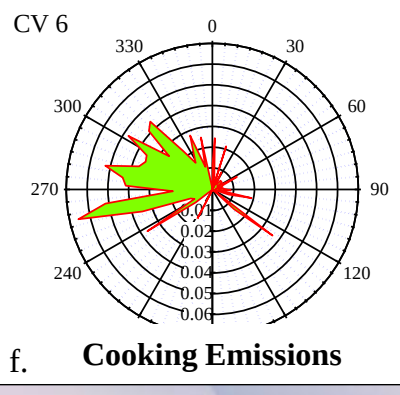
b. **Regional Background**



e. **Regional Mixture**



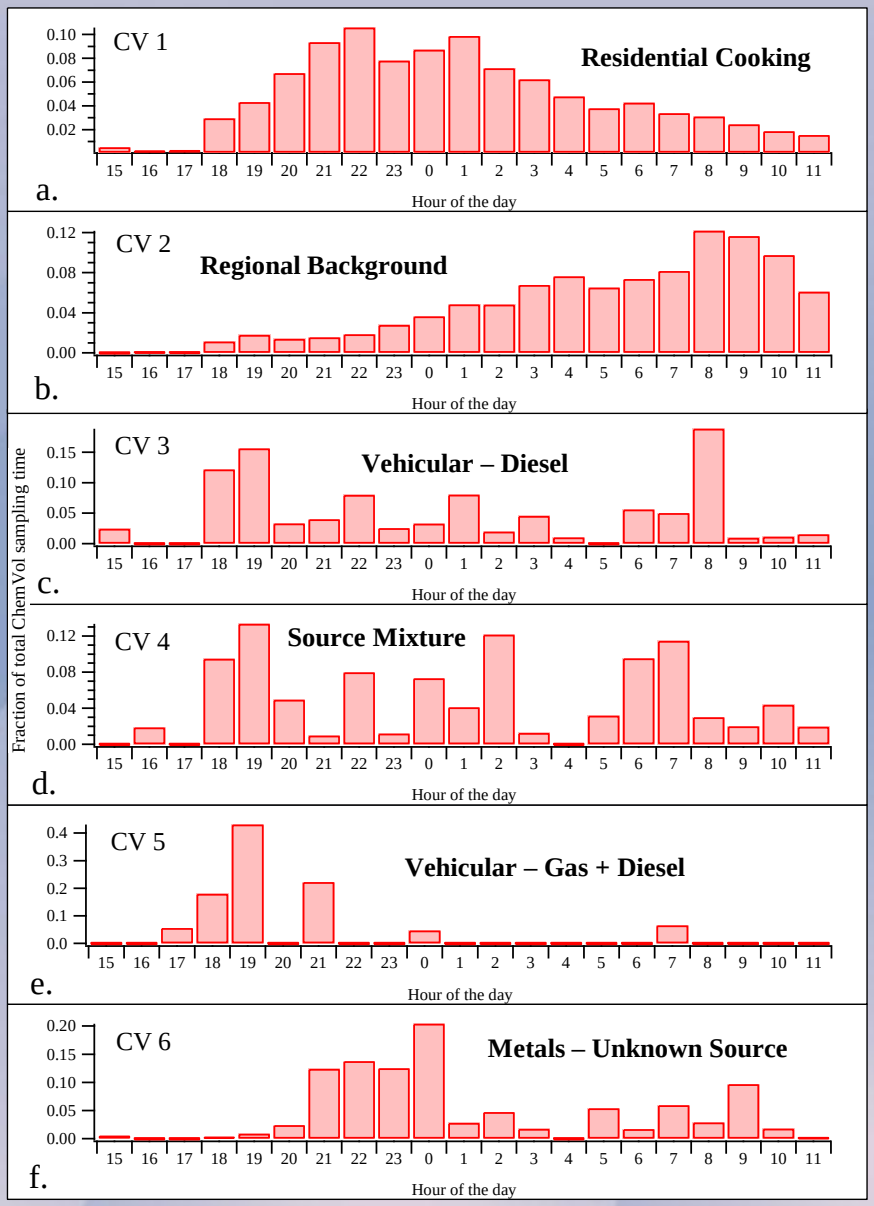
(**Vehicular – Gas + Diesel**



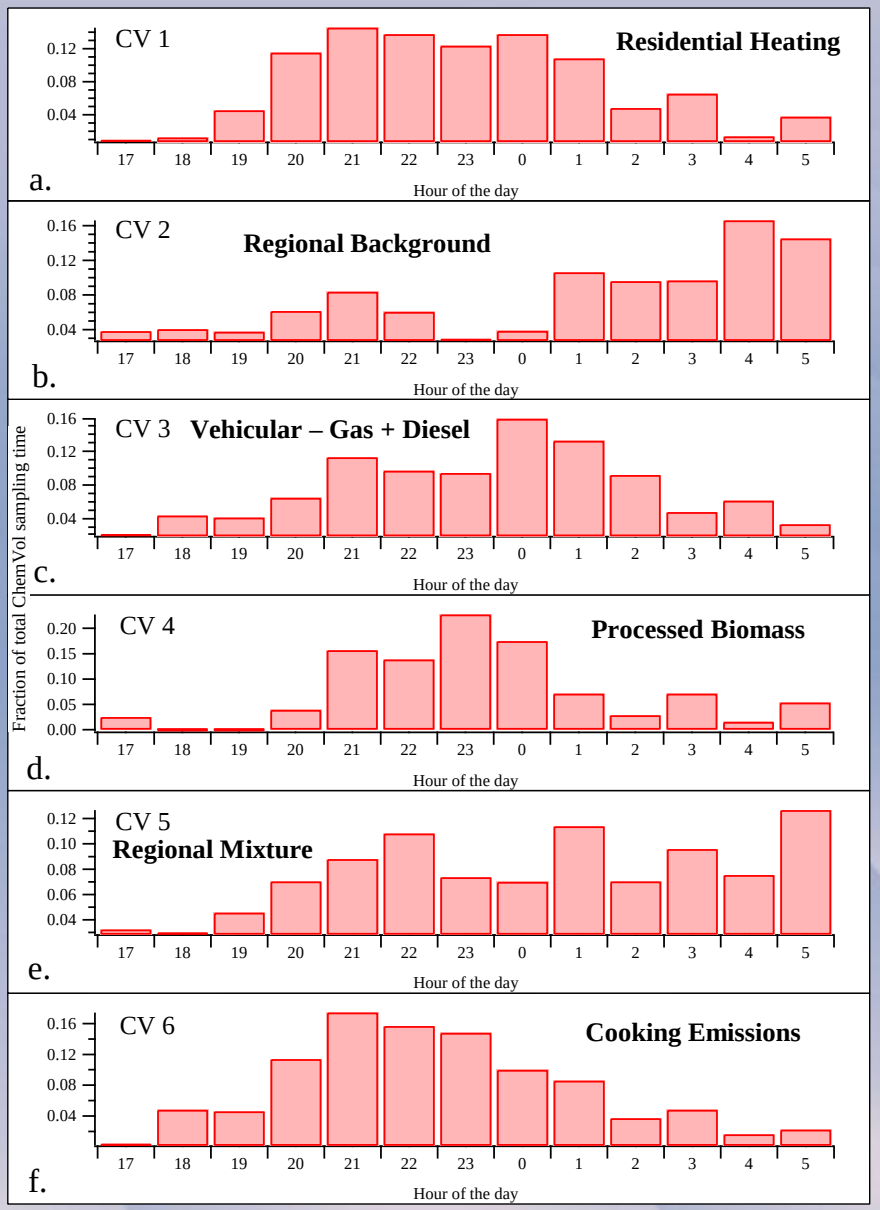
f. **Cooking Emissions**

Source Attribution – Temporal Relation

Summer 2008



Winter 2009



ChemVol Source Combination Reconciliation

Experiment:	Summer 2008		Winter 2009	
ChemVol	**Dominant Particle Type(s)**	**Dominant Source(s)**	**Dominant Particle Type(s)**	**Dominant Source(s)**
1	K	Local cooking emissions	K/EC/OC	Local residential heating
2	CAN	Highly processed regional background PM	CAN	Highly processed regional background PM
3	EC	Local vehicular emissions; diesel	EC; EC/OC	Local vehicular emissions; gas + diesel
4	CAN; K; EC/OC	Source Mixture	K/CAN	Highly processed biomass combustion PM
5	EC; EC/OC	Local vehicular emissions; gas + diesel	CAN; K/CAN	Regional source mix; vehicular, biomass + ag
6	Metals	Unknown	K/EC/OC	Local cooking emissions
7	K; Na/K	Local cooking emissions	Timed ChemVol ~ 17:00-20:00	Evening commute and dinnertime cooking
8	N/A	ChemVol not used	Timed ChemVol ~ 09:00-17:00	Morning commute
9	Timed ChemVol ~ 11:00-15:00	Daytime mixed layer	Timed ChemVol ~ 09:00-17:00	Daytime mixed layer
10	Undifferentiated	Nocturnal inversion	Undifferentiated	Nocturnal inversion

Talk Outline

-- Source-Oriented Sampling (Wexler)

-- Source Attribution (Bein)

-- PM Extraction (Bein)

How do we get the PM off the filters?

-- Source-Oriented Toxicity (Pinkerton)

Extracting PM from Filters
What are we doing?

- PM removed from atmosphere using filtration
- Need to remove PM from filters for toxicity tests
  - Different PM components have different properties
  - Some come off easy and others very “sticky”
- Conserve physical and chemical PM properties
  - Try to recreate PM as found in atmosphere
  - What are reasonable conservation objectives?
    - Physical integrity mostly lost
    - Mass and chemical composition

Extracting PM from Filters
What is the current state of science?

- Numerous SOPs available
- Different SOPs used by different groups
- No validation studies
- No comprehensive inter-comparison studies
- Different SOPs may elicit different toxicity
- New method developed for current study
  - Several motivating factors

Extracting PM from Filters
What are our objectives?

- Maximize Extraction Efficiency
  - Need as much PM as possible
- Minimize Compositional Biases
  - Conserve PM composition
- Minimize Extraction Artifacts
  - Evaporation/condensation
- Minimize Sources of Contamination
  - Filter material

Extracting PM from Filters
What are our new approaches?

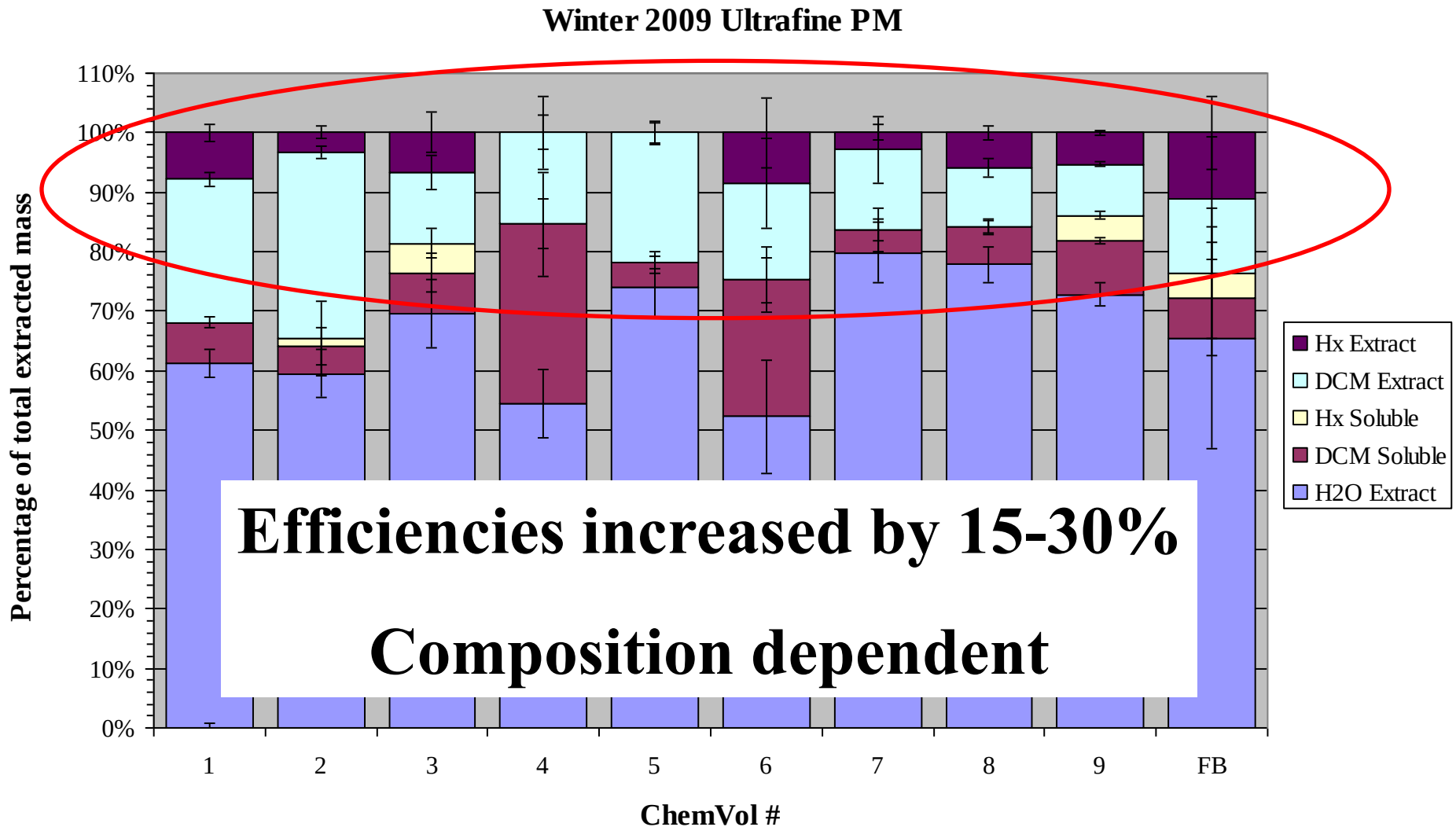
- Ultrasonic Sonication
  - Use sound waves to separate PM from filters
  - Different solvents remove different components
- Recovering PM from Solvents
  - Lyophilization, evaporation or distillation
- Solvent Washing
  - Immiscible solvents and differing volatility
- Selective Filtering
  - Removing contaminant filter material

Extracting PM from Filters
How much PM do we have?

- Gravimetric Analysis
  - PM mass is normalizing parameter for toxicity
  - Accuracy and precision are very important
    - Dose response studies
    - Inter-study comparisons
  - Two Methods
    - Filter Difference – traditional
      - Numerous artifacts
    - Direct Measurement – new approach

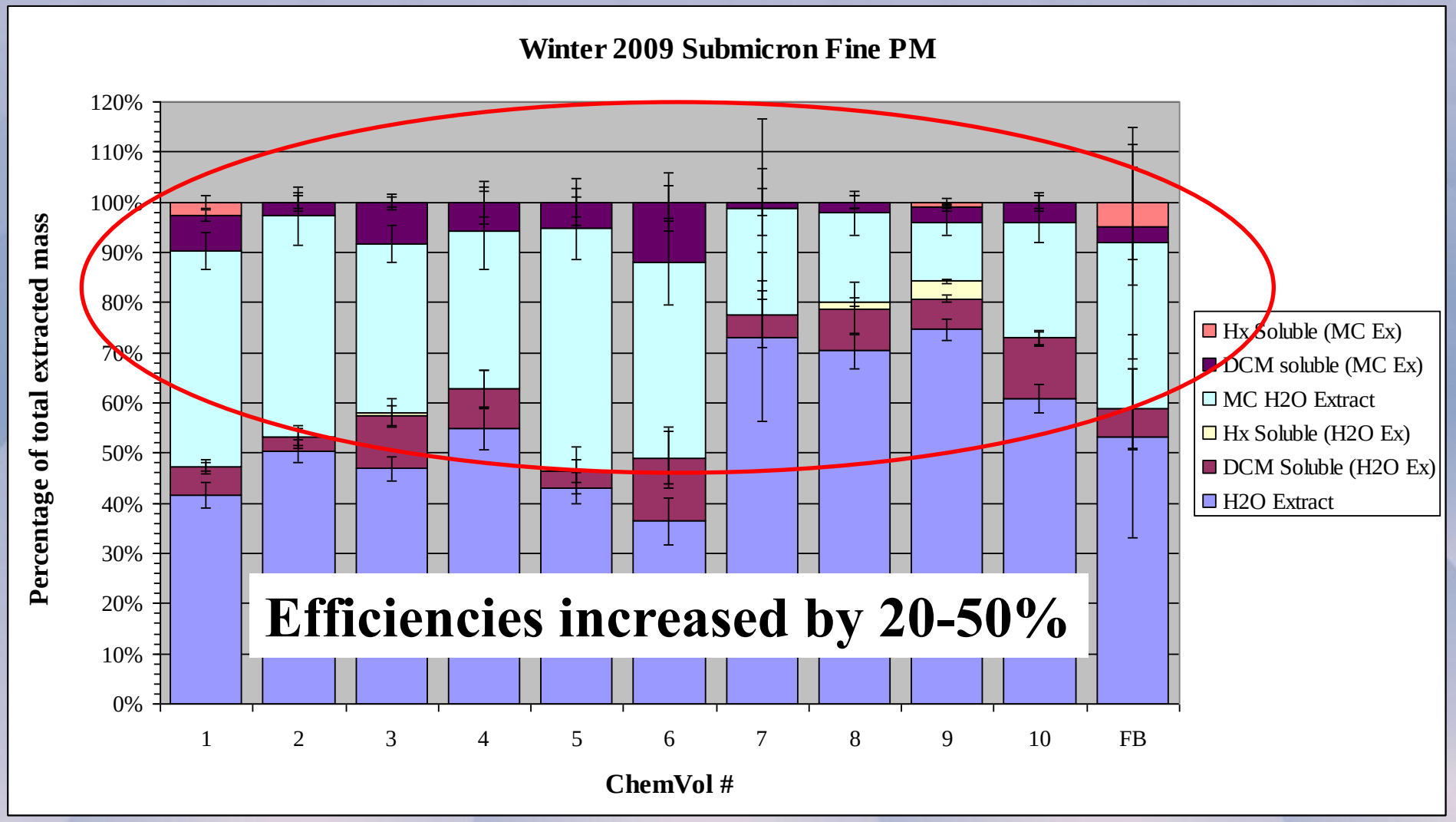
Extraction Efficiency

How well did we do for ultrafine PM?



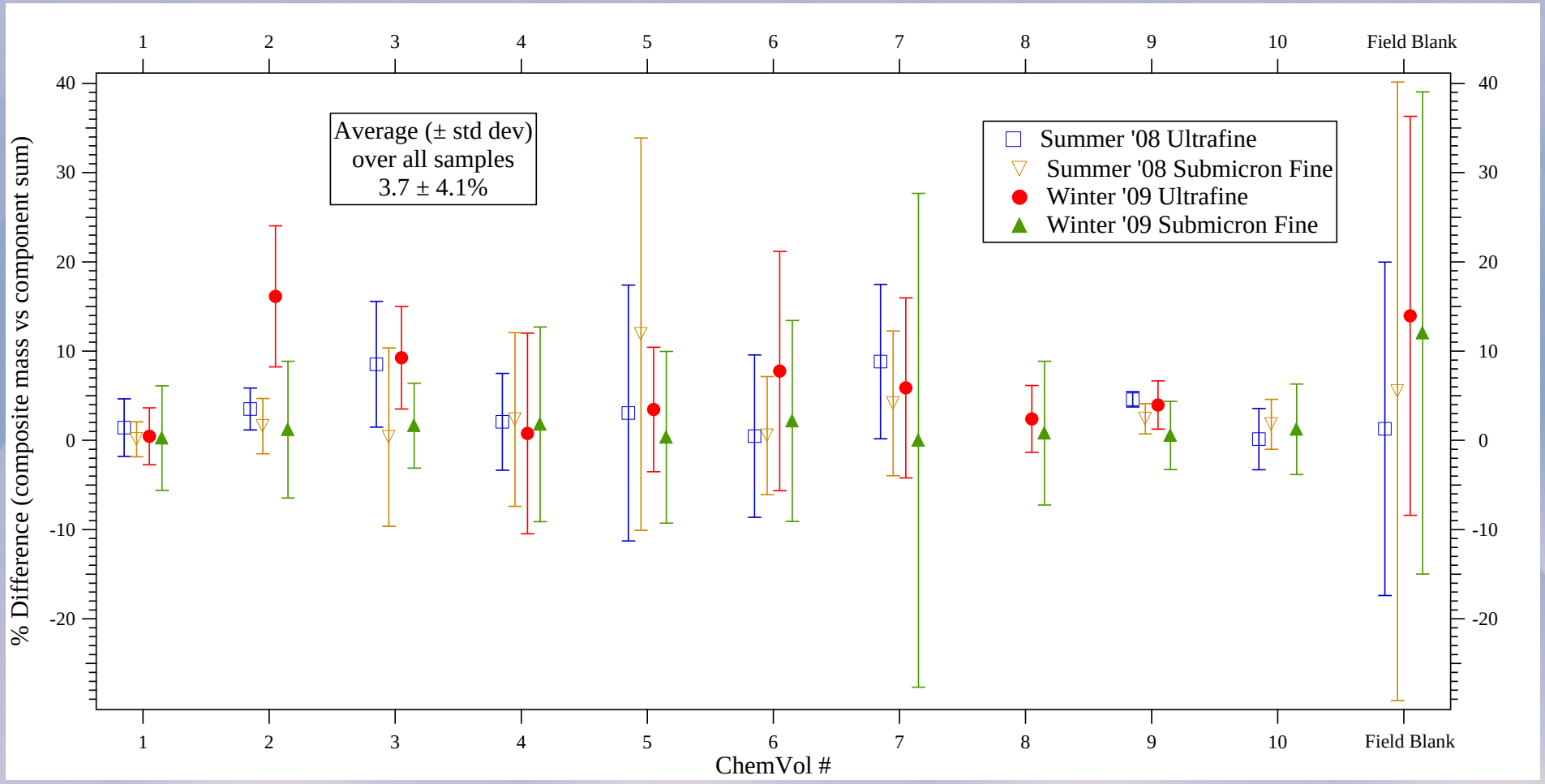
Extraction Efficiency

How well did we do for submicron fine PM?



Gravimetric Analysis

How good are our mass measurements?



Talk Outline

-- Source-Oriented Sampling (Wexler)

-- Source Attribution (Bein)

-- PM Extraction (Bein)

-- Source-Oriented Toxicity (Pinkerton)

Which sources are toxic and how are they toxic?

Source-Oriented Toxicity

- Single particle mass spectrometer controlled 10 ChemVols to collect source-oriented samples
- UF and SMF sampled during summer and winter in Fresno
- Source-oriented sampling captures
  - primary sources
  - secondary transformations
- Collected sufficient mass for toxicological testing

ChemVol Source Combination Reconciliation

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Source-Oriented Toxicity

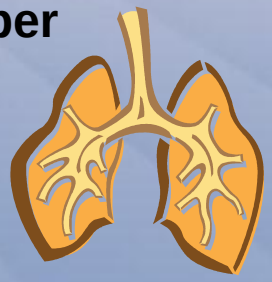
Study Design

50 μg Source-Oriented PM

24 hours post-exposure

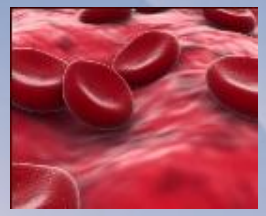
Bronchoalveolar Lavage (BAL)

- Total Cell Number
- Cell Differential
- Cell Viability
- Cytotoxicity
- Cell Damage



Blood (CBC)

- Total Cell Number
- Cell Differential
- Hematology



Reactive Oxygen Species

- Hydrogen peroxide
- Hydroxyl radical

Source-Oriented Toxicity

Definition of End Points

Bronchoalveolar Lavage (BAL)

- **Total Cell Number – elevation is indicator of injury**
- **Neutrophils – elevation indicates acute inflammation**
- **Eosinophils – elevation indicates allergic response**
- **Protein – elevation indicates cell injury**
- **LDH – elevation indicates cell death**

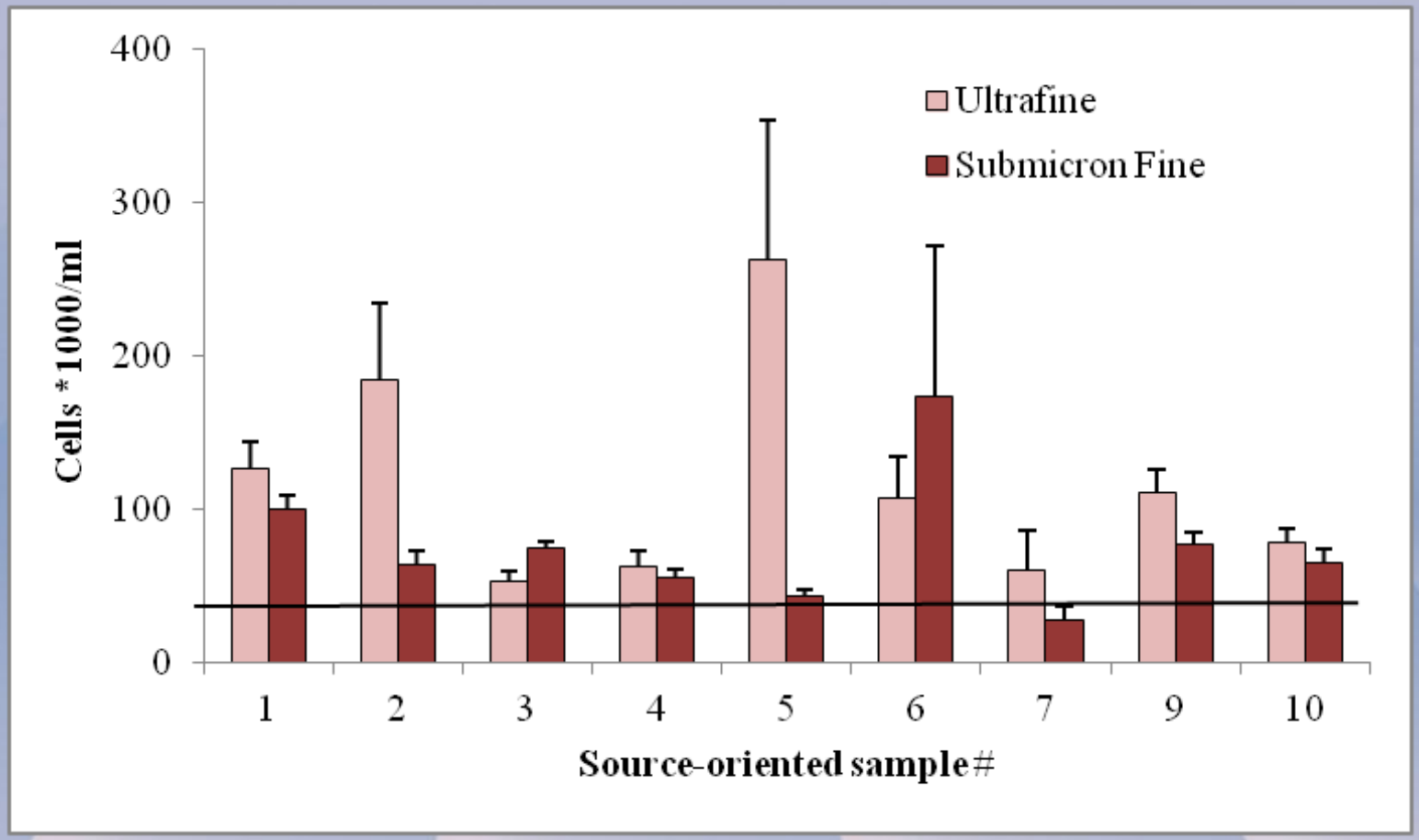
Blood (CBC)

- **Neutrophils – depletion suggests recruitment to lung**

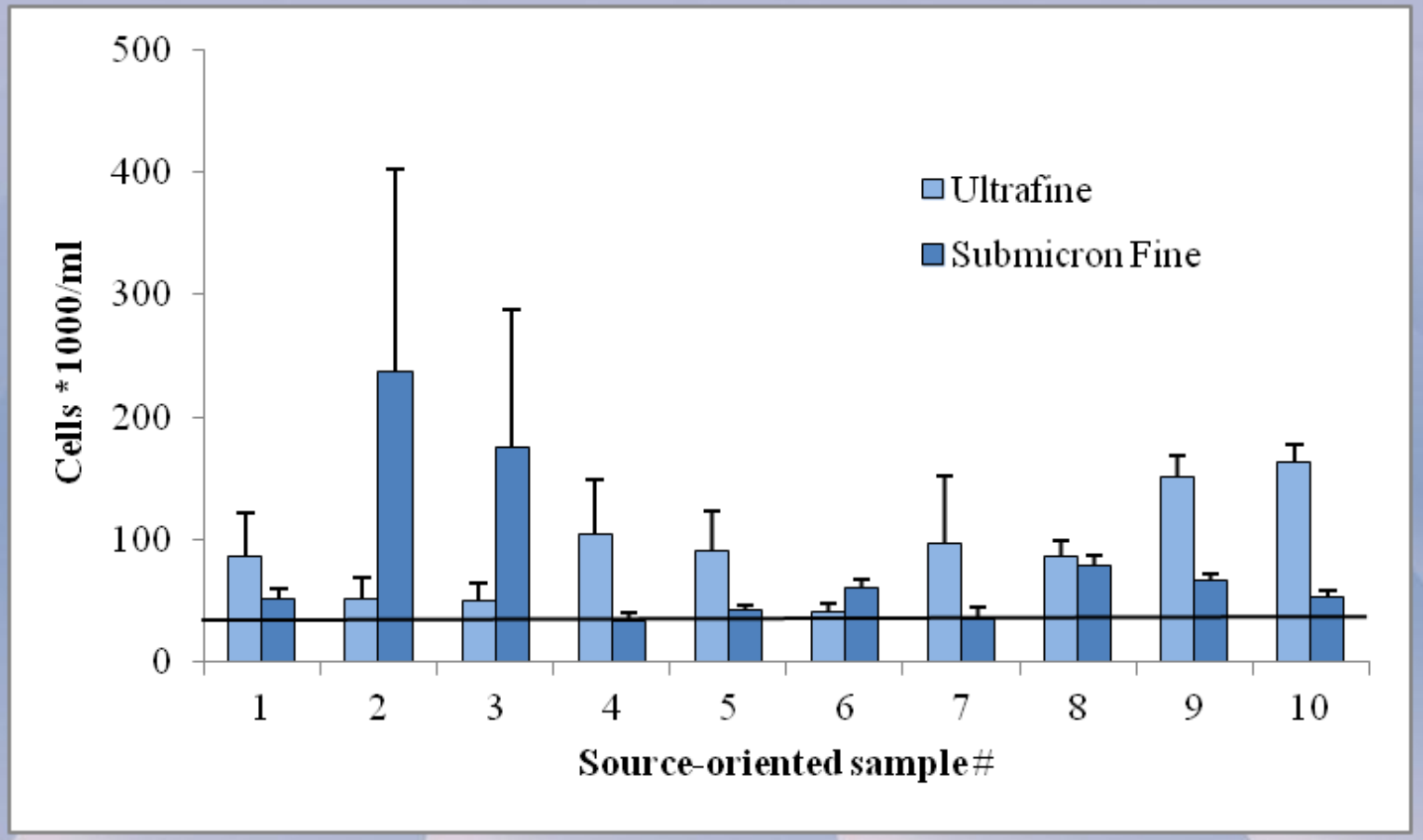
Reactive oxygen species – can induce DNA and cell membrane damage

- **Hydrogen peroxide**
- **Hydroxyl radical**

Summer Bronchoalveolar Lavage (BAL)

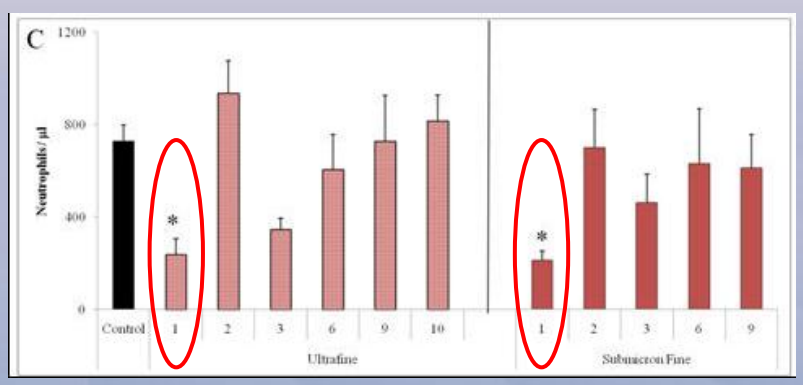


Winter Bronchoalveolar Lavage (BAL)



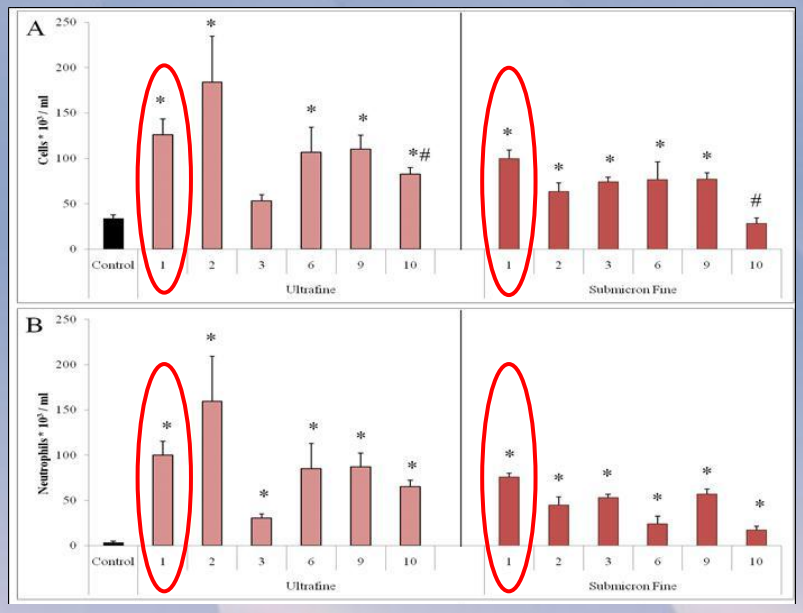
Summer Residential Cooking

Circulating Neutrophils



Lung BAL:

Total Cells



Neutrophils

Lung BAL protein:

Significant elevation in Summer Commercial Cooking

Winter Cooking

Relatively Little Pulmonary or Systemic Effects Found

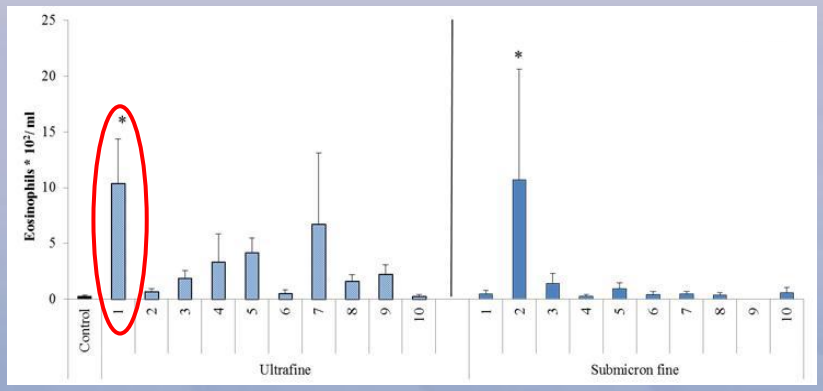
Winter Biomass Combustion

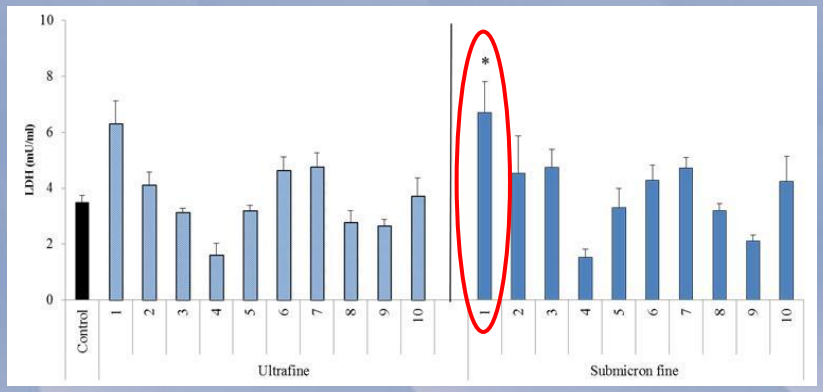
Lung BAL:

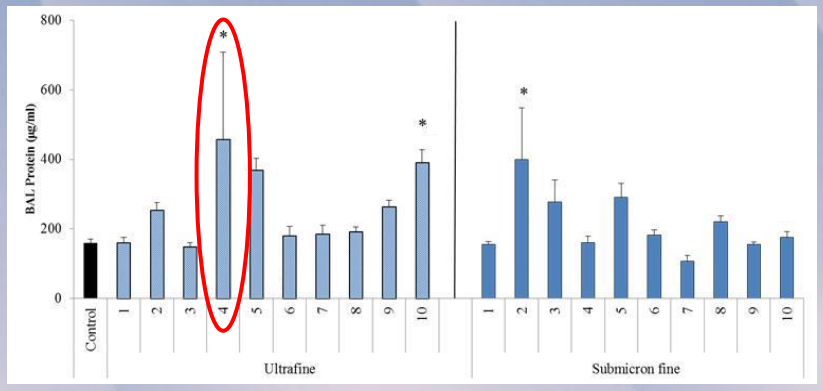
Eosinophils

LDH

Protein



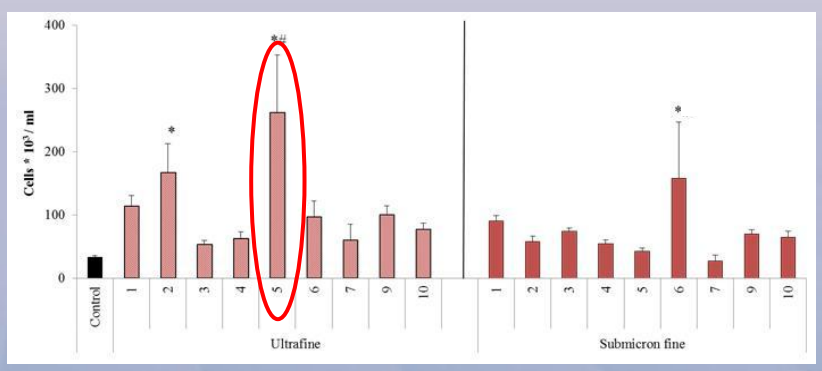




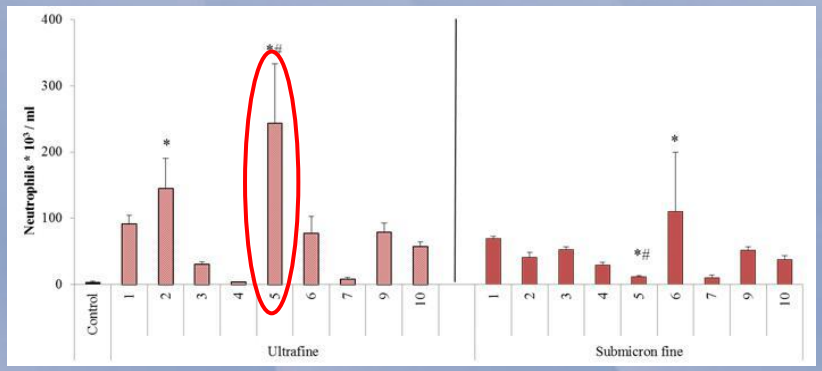
Vehicles in Summer

Lung BAL:

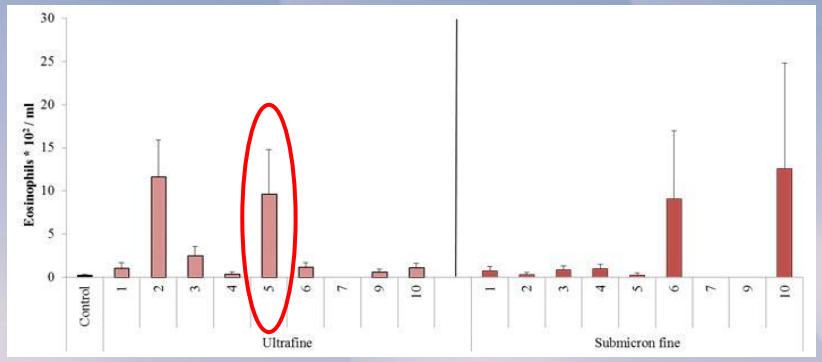
Total Cells



Neutrophils



Eosinophils

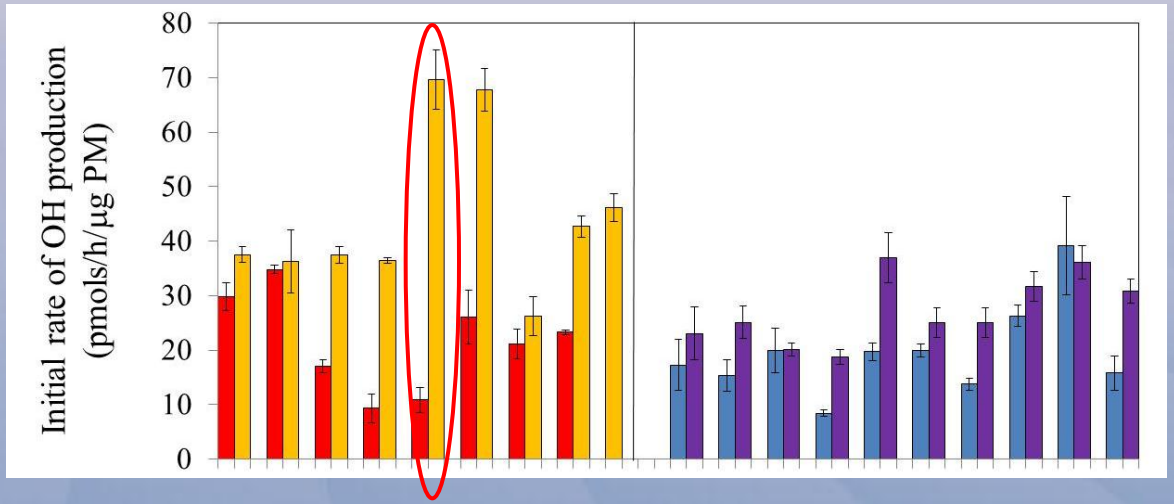


No Effects from the Vehicle mix with more Diesel

Vehicles in Summer

Reactive Oxygen Species: OH

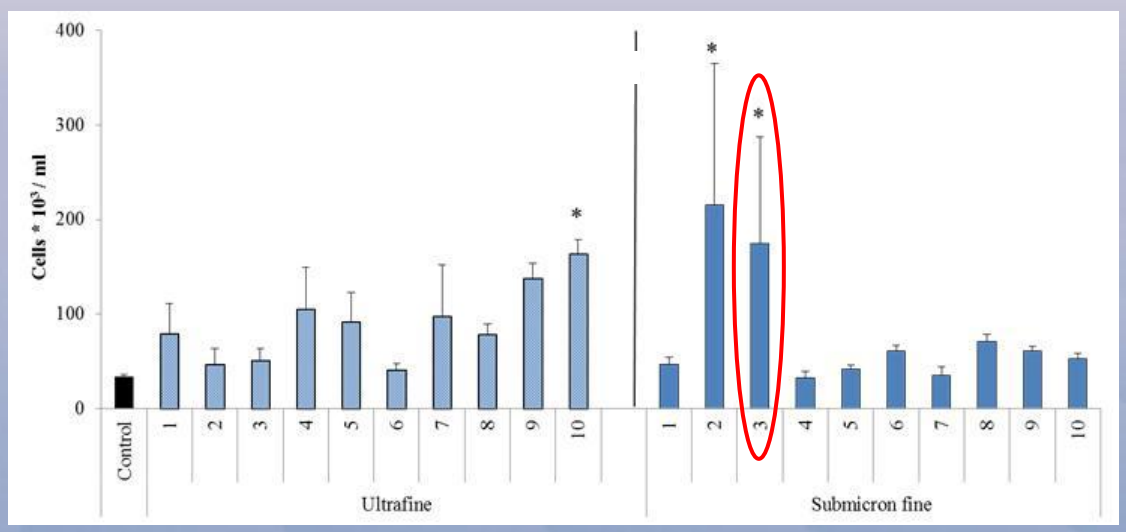
Submicron Fine



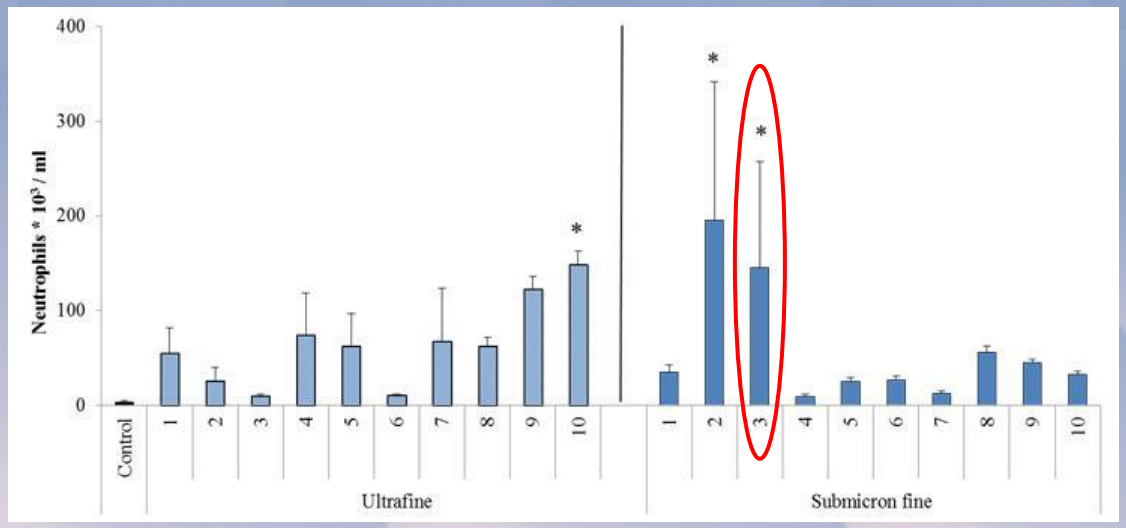
Vehicles in Winter

Lung BAL:

Total Cells



Neutrophils

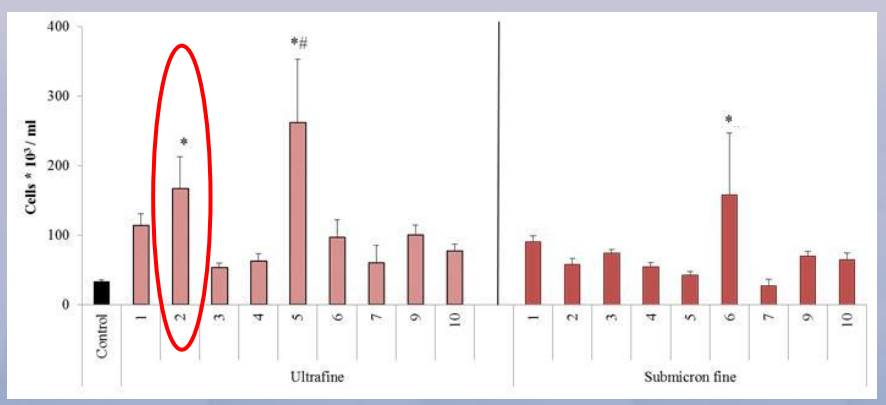


Systemic Effects in Morning Commute Hours

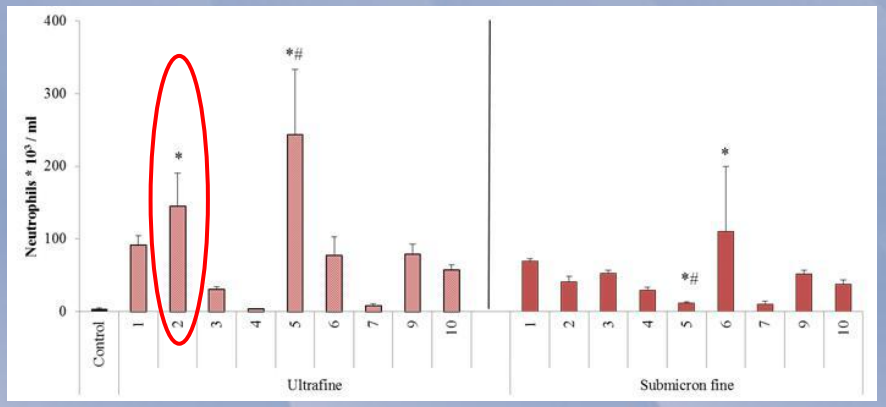
Summer Processed Regional Background

Lung BAL:

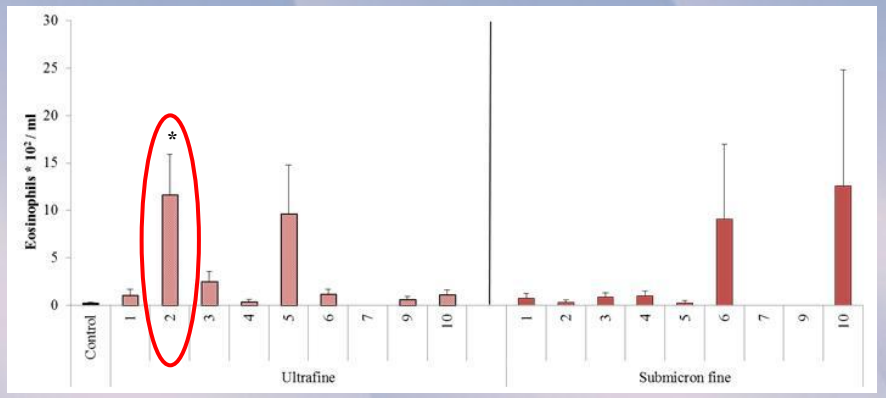
Total Cells



Neutrophils



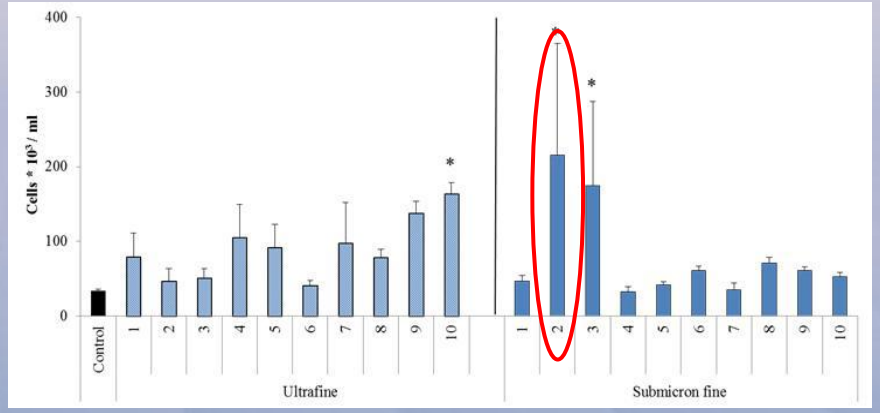
Eosinophils



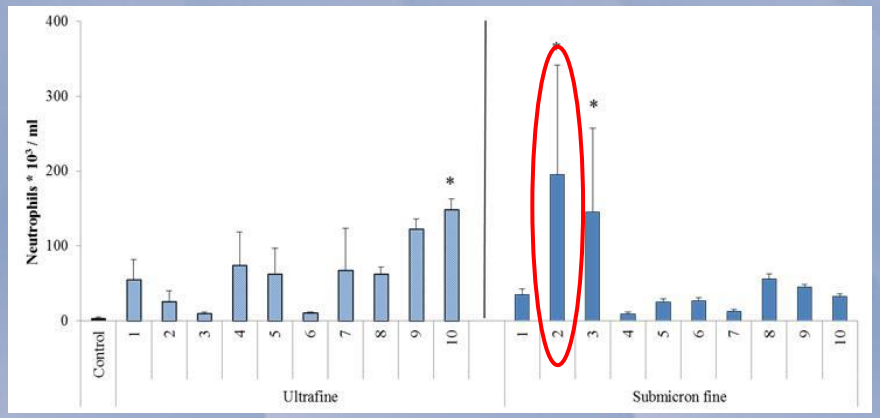
Winter Processed Regional Background

Lung BAL:

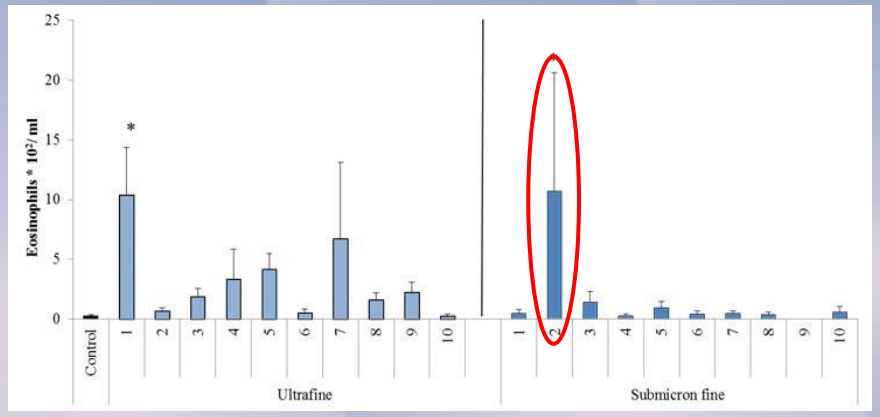
Total Cells



Neutrophils



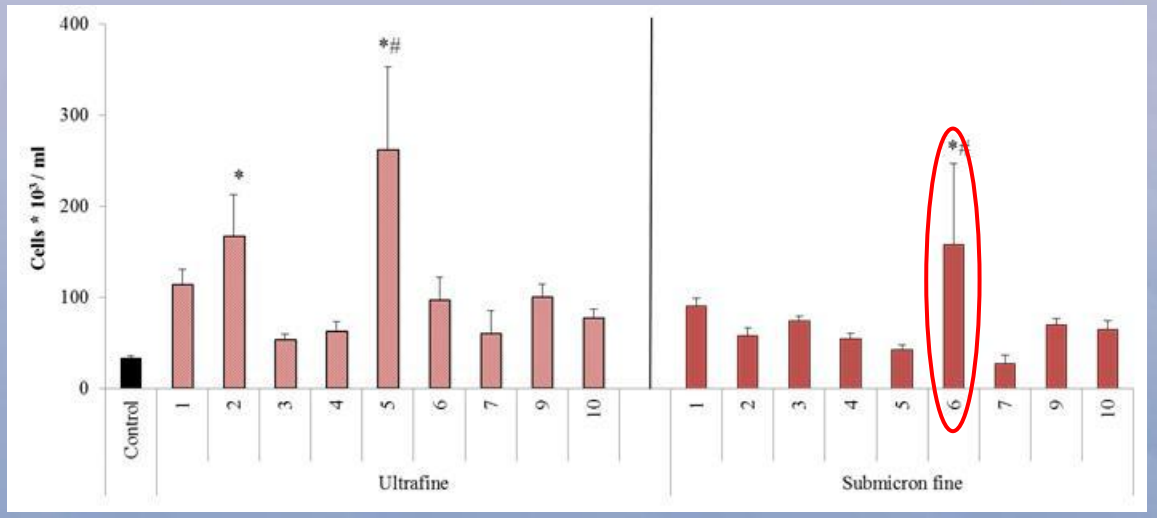
Eosinophils



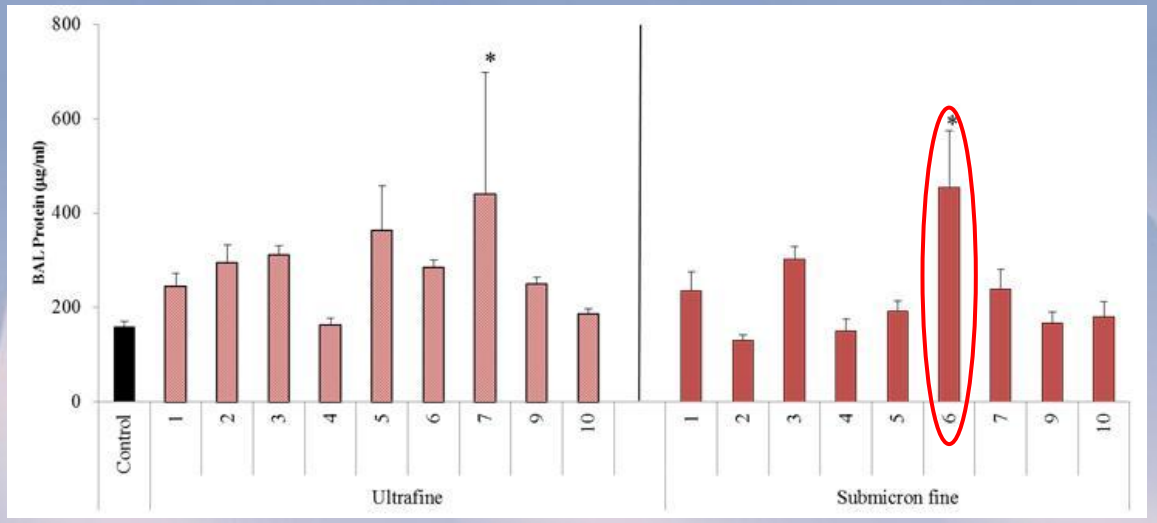
Summer Metals

Lung BAL:

Total Cells



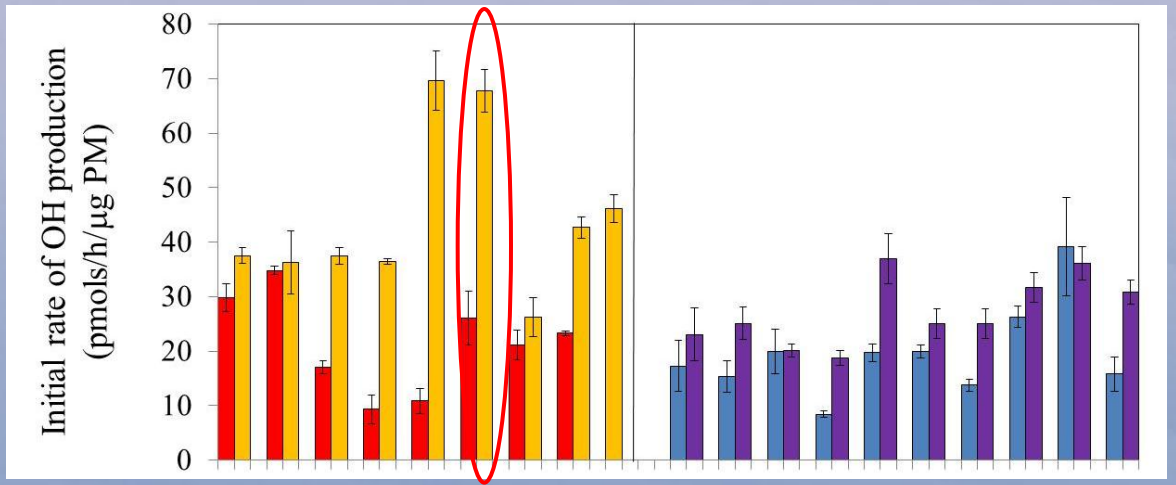
Protein



Summer Metals

Reactive Oxygen Species: OH

Submicron Fine



Conclusions
Source-Oriented Sampling

- Source-oriented sampling is FEASIBLE
  - Novel sampling method implemented successfully
  - Different PM samples attributable to different sources
  - Sufficient PM collected for toxicity studies
- PM extraction method MATTERS
  - Additional steps = additional PM mass
  - Additional solvents = additional chemical components
  - Direct mass measurement = more accurate dosing

Conclusions
Source-Oriented Toxicity

- Some particles MORE TOXIC than others
  - Summer PM: metal-containing and vehicular emissions have largest biological response
  - Winter PM: highly processed, vehicular emissions and nighttime mix have largest biological response
  - Ultrafine PM generally elicits greater biological response than submicron fine PM
- Different particles TOXIC in DIFFERENT ways