Weight of Evidence Validation of Source Contribution Estimates

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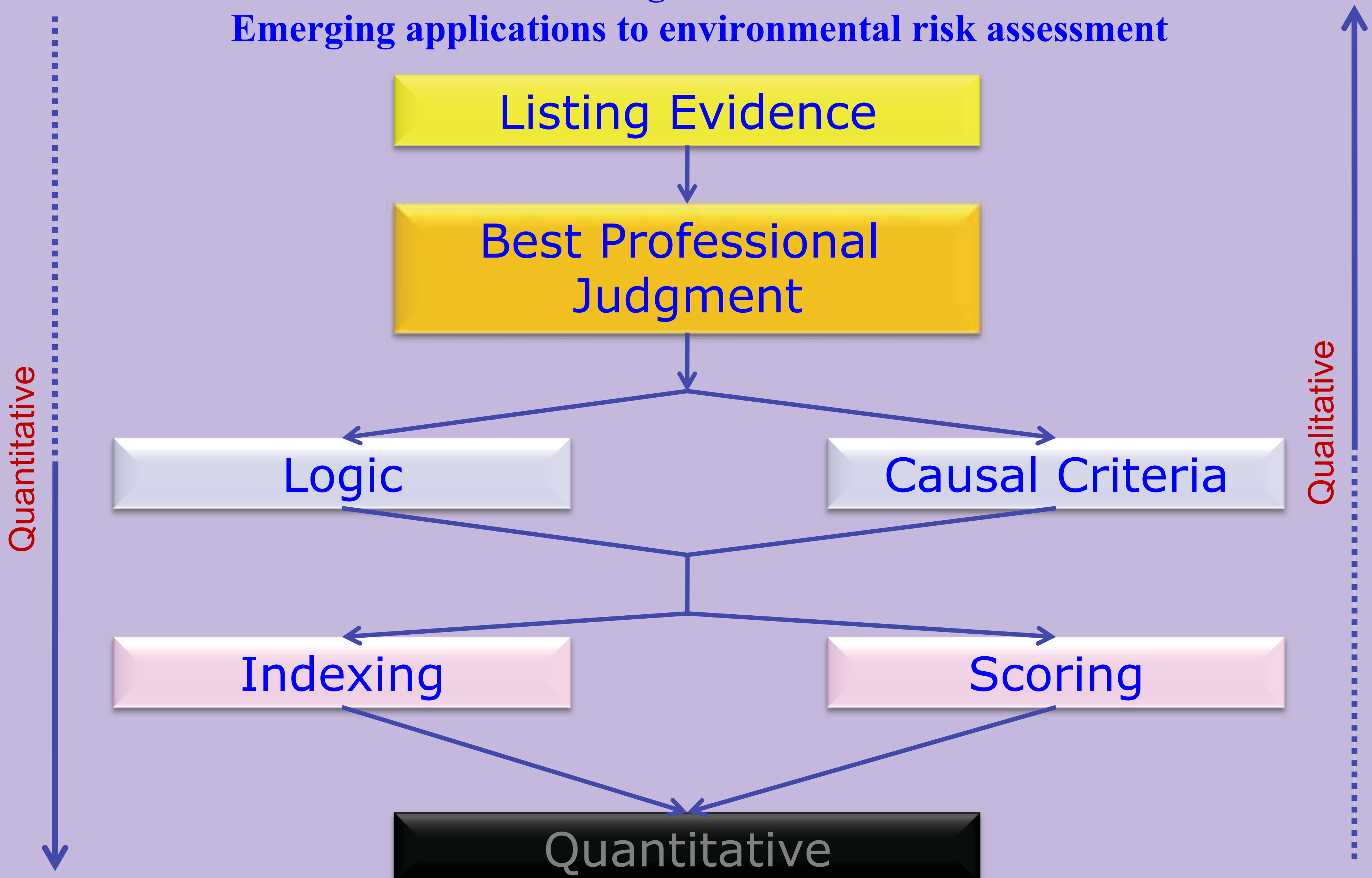
Objectives

- Define terms related to “Source Apportionment” and “Weight of Evidence”
- Summarize common pitfalls, limitations, and uncertainties in source apportionment studies and how to overcome them
- Identify some emerging technologies that might enhance the source apportionment weight of evidence

What do we mean by “Weight of Evidence”?

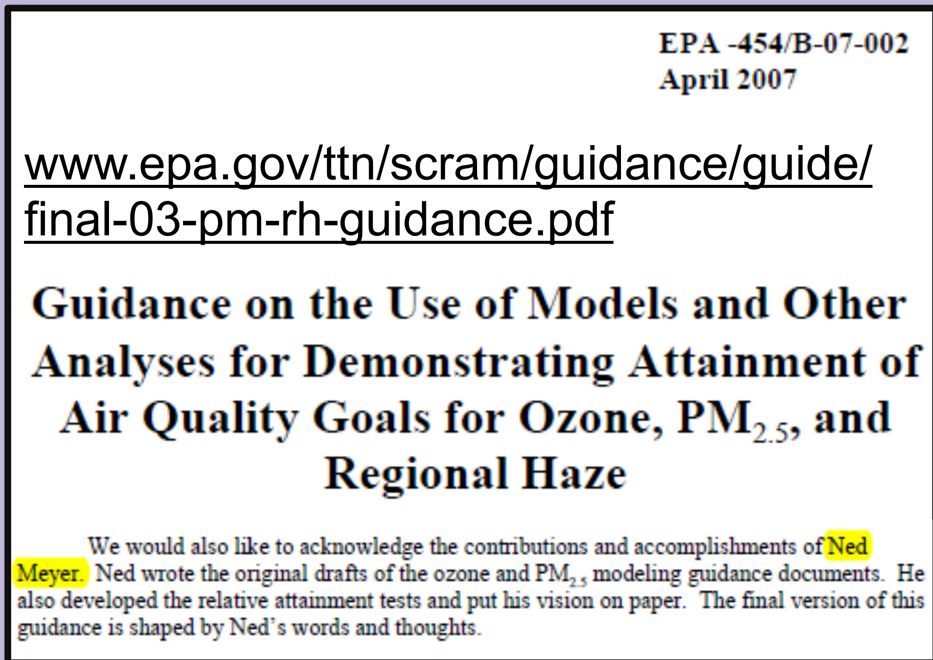
Derives from legal and medical fields

Emerging applications to environmental risk assessment



Linkov et al., 2009, *Sci. Total Environ.*

What do we mean by "Weight of Evidence"? (continued)

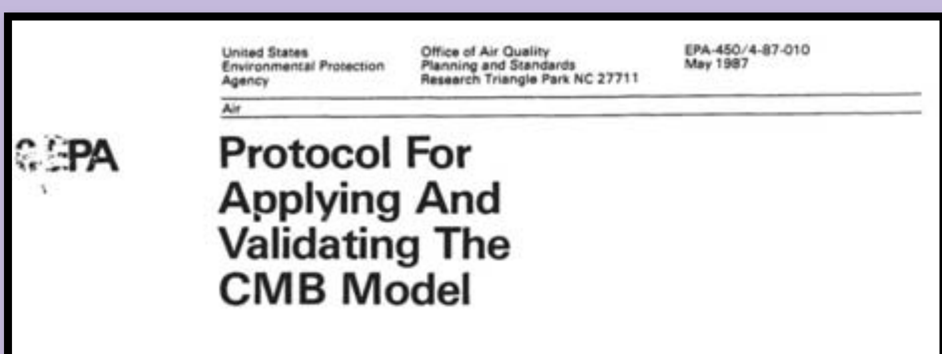


EPA -454/B-07-002
April 2007

www.epa.gov/ttn/scram/guidance/guide/final-03-pm-rh-guidance.pdf

Guidance on the Use of Models and Other Analyses for Demonstrating Attainment of Air Quality Goals for Ozone, $PM_{2.5}$, and Regional Haze

We would also like to acknowledge the contributions and accomplishments of Ned Meyer. Ned wrote the original drafts of the ozone and $PM_{2.5}$ modeling guidance documents. He also developed the relative attainment tests and put his vision on paper. The final version of this guidance is shaped by Ned's words and thoughts.



United States Environmental Protection Agency | Office of Air Quality Planning and Standards Research Triangle Park NC 27711 | EPA-450/4-87-010 May 1987

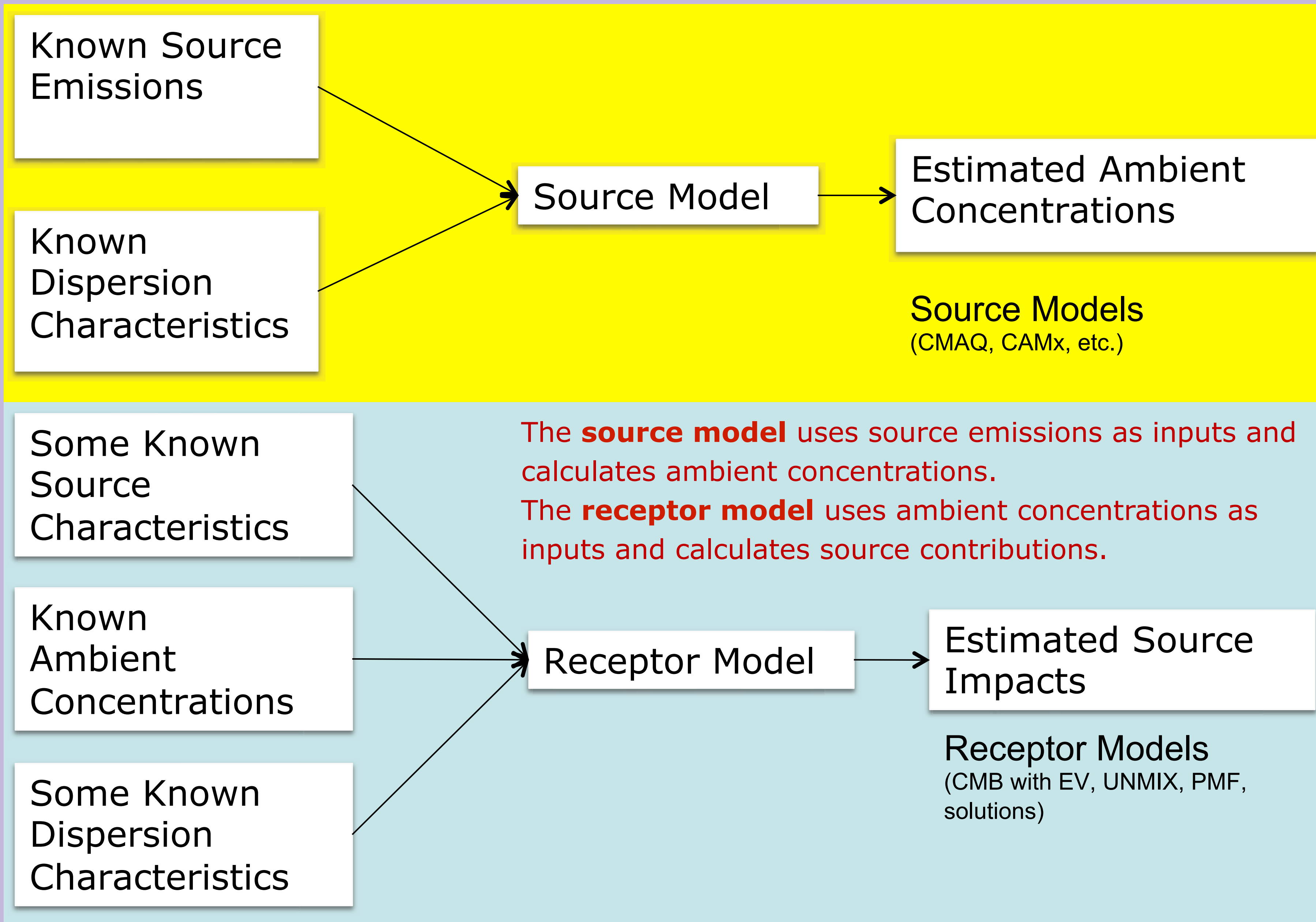
Air

Protocol For Applying And Validating The CMB Model

- Examine the problem using different methods
- Use discrepancies between model results to identify and correct weaknesses in models and input data
- Quantify confidence intervals
- Explain and qualify conclusions regarding source contribution estimates

U.S. EPA, 1987,2007

What do we mean by "Source Apportionment Model"?



Watson, 1979

Source and receptor models derive from the same physical construct

$$C_{ikl} = \Sigma_j \Sigma_m \Sigma_n F_{ij} T_{ijklmn} D_{kln} Q_{jkmn}$$

i	=	pollutant
j	=	source type
k	=	time period
l	=	receptor location
m	=	source sub-type, a specific source or groups of emitters with similar source compositions and/or locations
n	=	location of emitter m of source type j
C_{ikl}	**=**	**ambient concentration**
F_{ij}	=	fractional quantity of pollutant i in source j
T_{ijkmn}	=	transformation of pollutant i during transport
D_{kln}	=	dispersion and mixing between source and receptor
Q_{jkmn}	=	emissions rate

Adapted from Watson, 1984, *Atmos. Environ.*; Watson and Chow, 2005

Source and receptor model use different input data

Lagrangian Source Model

$$C_{ikl} = \Sigma_j \Sigma_m \Sigma_n T_{ijklmn} D_{kln} F_{ij} Q_{jkmn}$$

- **CALCULATED AT RECEPTOR**
- **CALCULATED BY CHEMICAL MODEL**
- **CALCULATED BY MET MODEL**
- **MEASURED AT SOURCE (INVENTORY)**

Chemical Mass Balance (CMB) Model

$$C_{ikl} = \Sigma_j T_{ijkl} F_{ij} \Sigma_m \Sigma_n D_{kln} Q_{jkmn}$$

- **MEASURED AT RECEPTOR**
- **MEASURED AT SOURCE (T=1 OR ESTIMATED BY OTHER METHOD)**
- **S_{ijkl}, SOURCE CONTRIBUTION ESTIMATE**

Source and receptor models complement each other rather than replacing each other

These equations reduce to the Chemical Mass Balance (CMB) receptor model

Equation: $$C_i = \sum_{j=1}^{J} F_{ij} S_j \quad \text{for } i = 1 \text{ to } N$$

Measurements:

- Size-classified mass, elements, ions, and carbon concentrations on both ambient and source samples

Model Input:

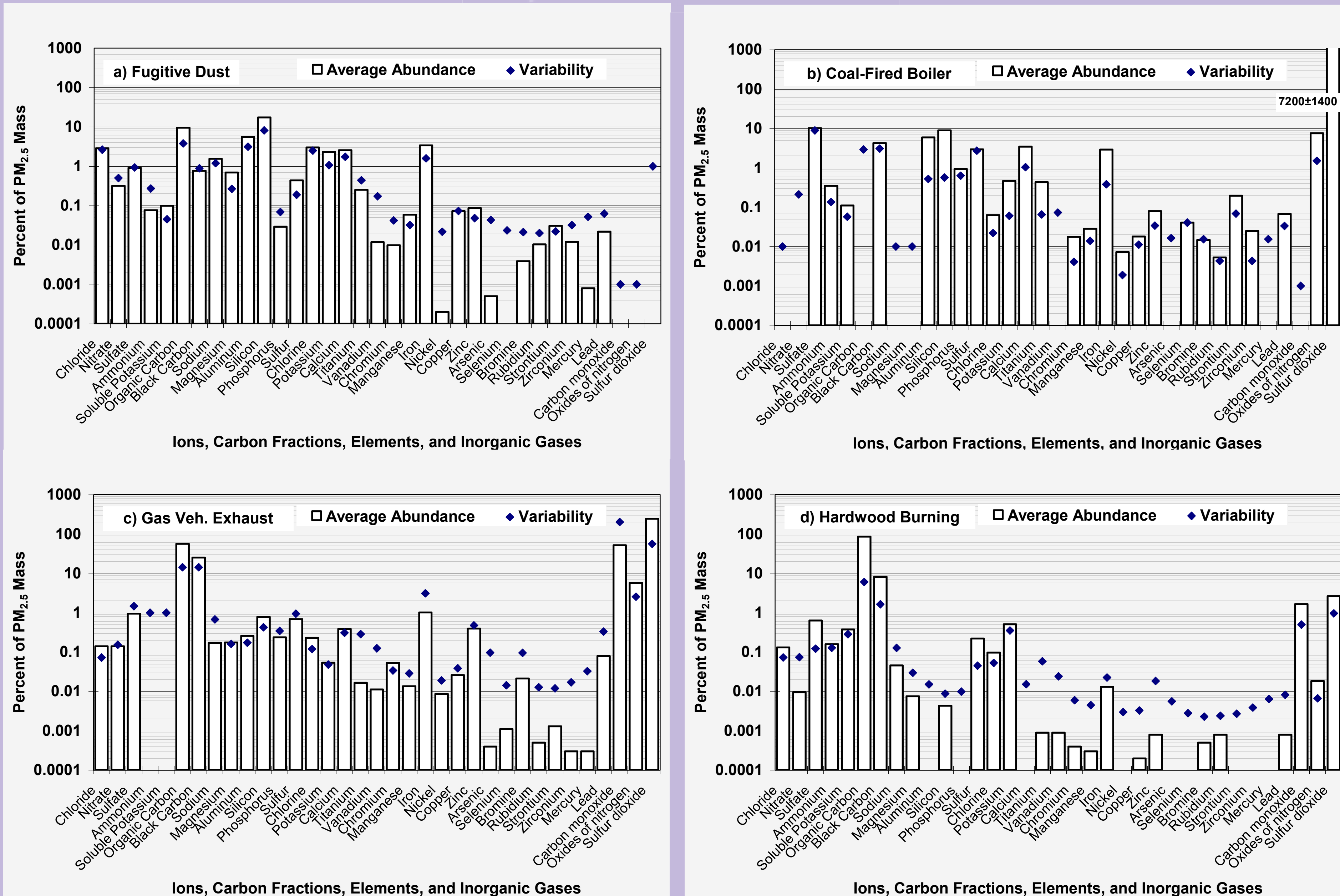
- Ambient concentrations (C_i) and uncertainties (σ_{Cj}), source profiles (F_{ij}), and uncertainties (σ_{Fij})

Model Output:

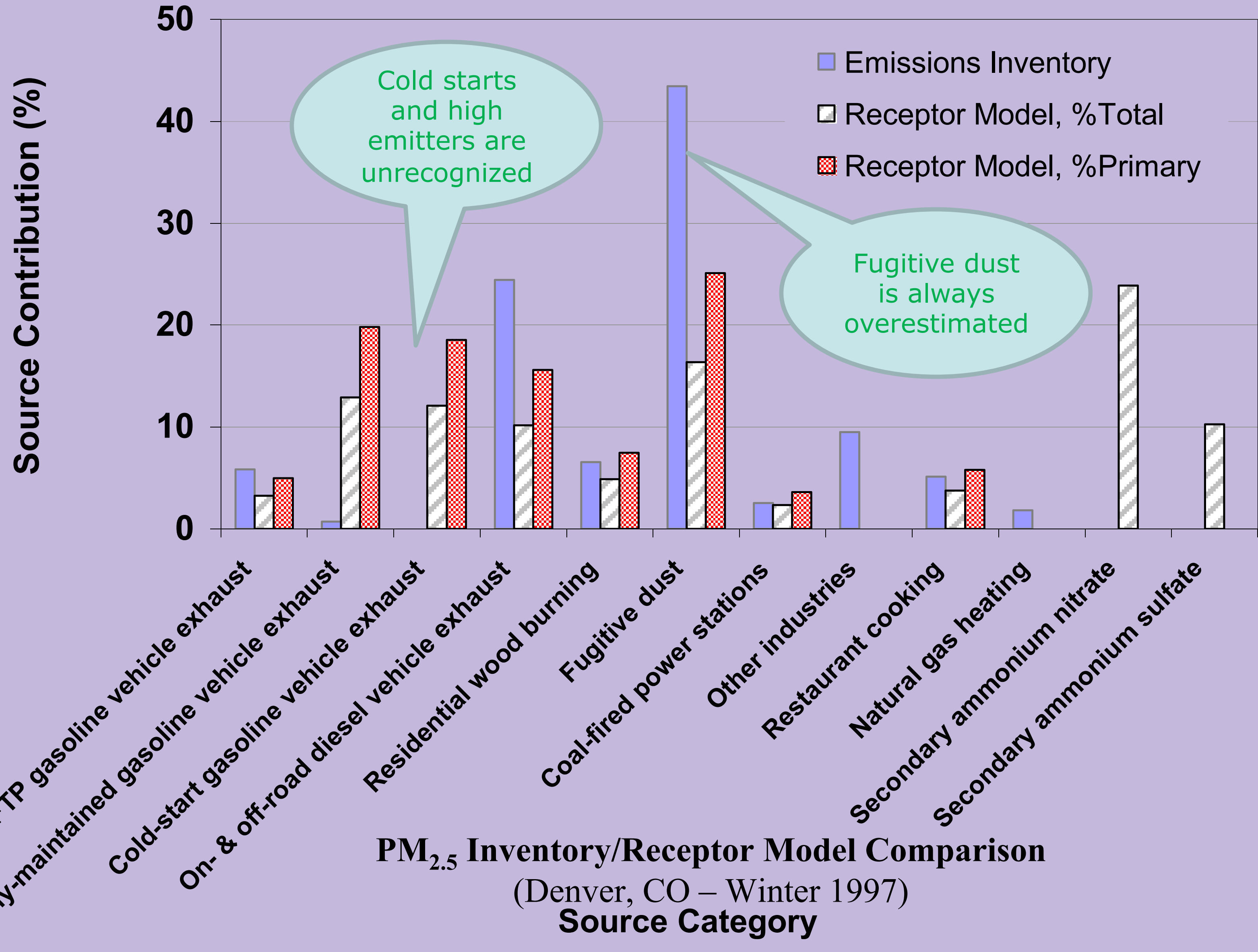
- Source contributions (S_j) and uncertainties (σ_{Sj})

Hidy and Friedlander, 1971

CMB solutions rely on chemical differences among source emissions, i.e., "Source Profiles"



Source and receptor models complement each other rather than replace each other

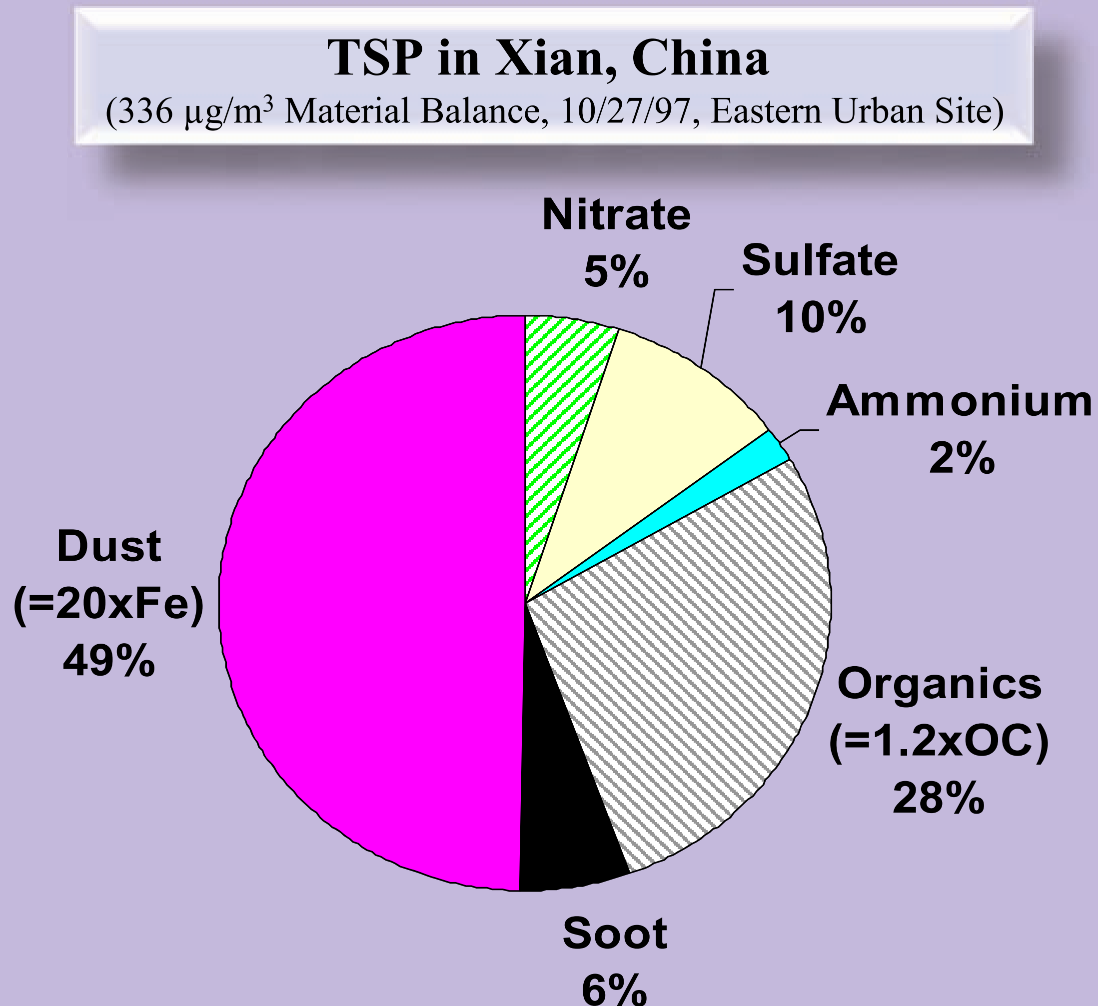


$PM_{2.5}$ Inventory/Receptor Model Comparison

(Denver, CO – Winter 1997)

Watson and Chow, 2007

"Xi'an emission inventories (EPA AP-42) show that TSP is nearly all from fugitive dust"-Shaanxi EPB official



Chow et al., 2002, *Chemosphere*

Effective Variance, PMF, and Unmix are solutions to the CMB equations, not separate models

$S_j = C_i / F_{ij}$

- Tracer solution, Hidy and Friedlander (1971), Winchester and Nifong (1971), single sample

$$\square^2 = \min \Sigma_i \left[(C_i - \Sigma_j F_{ij} S_j)^2 / \left(\sigma_{Ci}^2 + \Sigma_j \sigma_{Fij}^2 S_j^2 \right) \right]$$

- Effective Variance, single sample, Watson et al., 1984

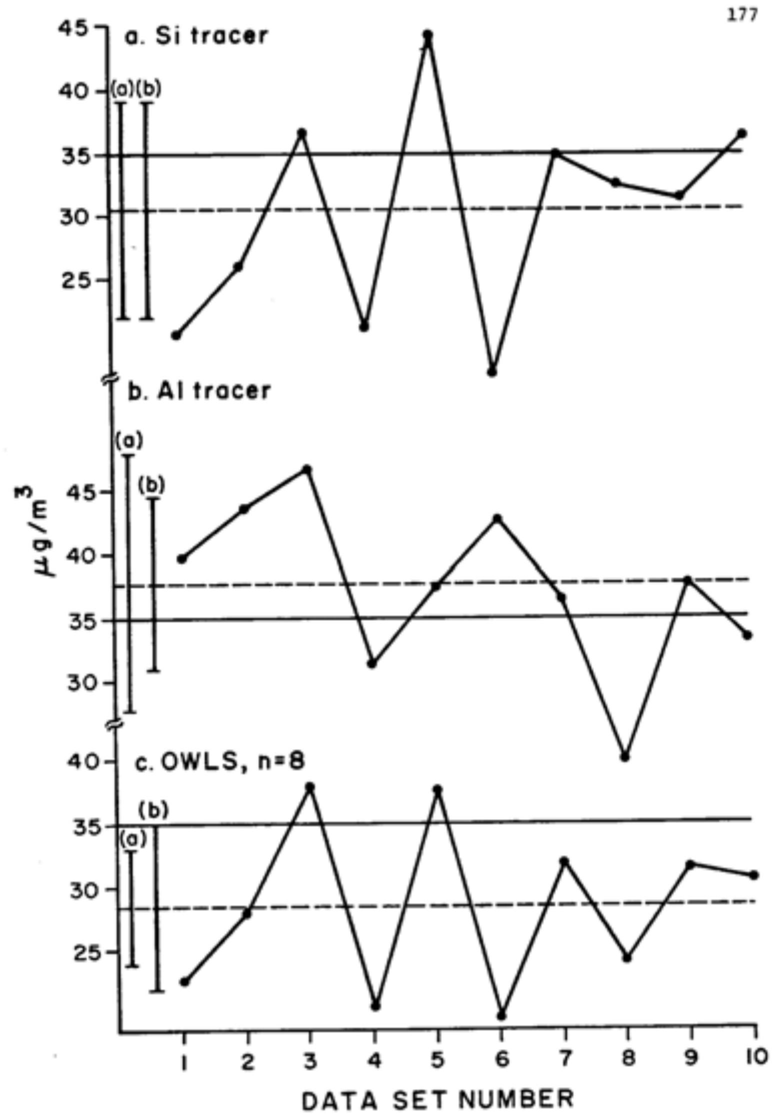
$$\square^2 = \min \Sigma_i \Sigma_k \left[(C_{ik} - \Sigma_j F_{ij} S_{jk})^2 / \sigma_{Cik}^2 \right]$$

- Positive Matrix Factorization, Paatero (1997), multiple samples

Marker (not "tracer") species have consistent ratios within a source type and different ratios between source types

- Elements, ions, and carbon are necessary, but insufficient for most source type
- Gas as well as particle components are useful
- Organic compounds are numerous, but have highly variable abundances
- Isotopic ratios of carbon, sulfur, lead, and other elements also vary among sources
- Particle size, morphology, and minerals are useful for dust sources
- Mass spectral patterns may not allow chemical identification, but can still distinguish among sources

What should you measure? Everything you can!



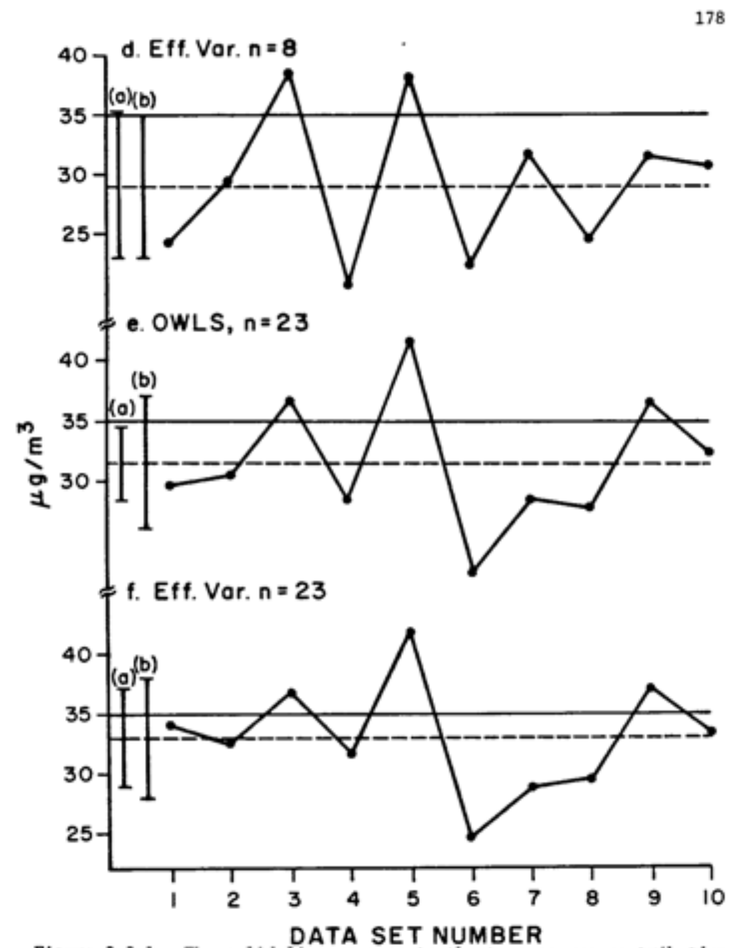
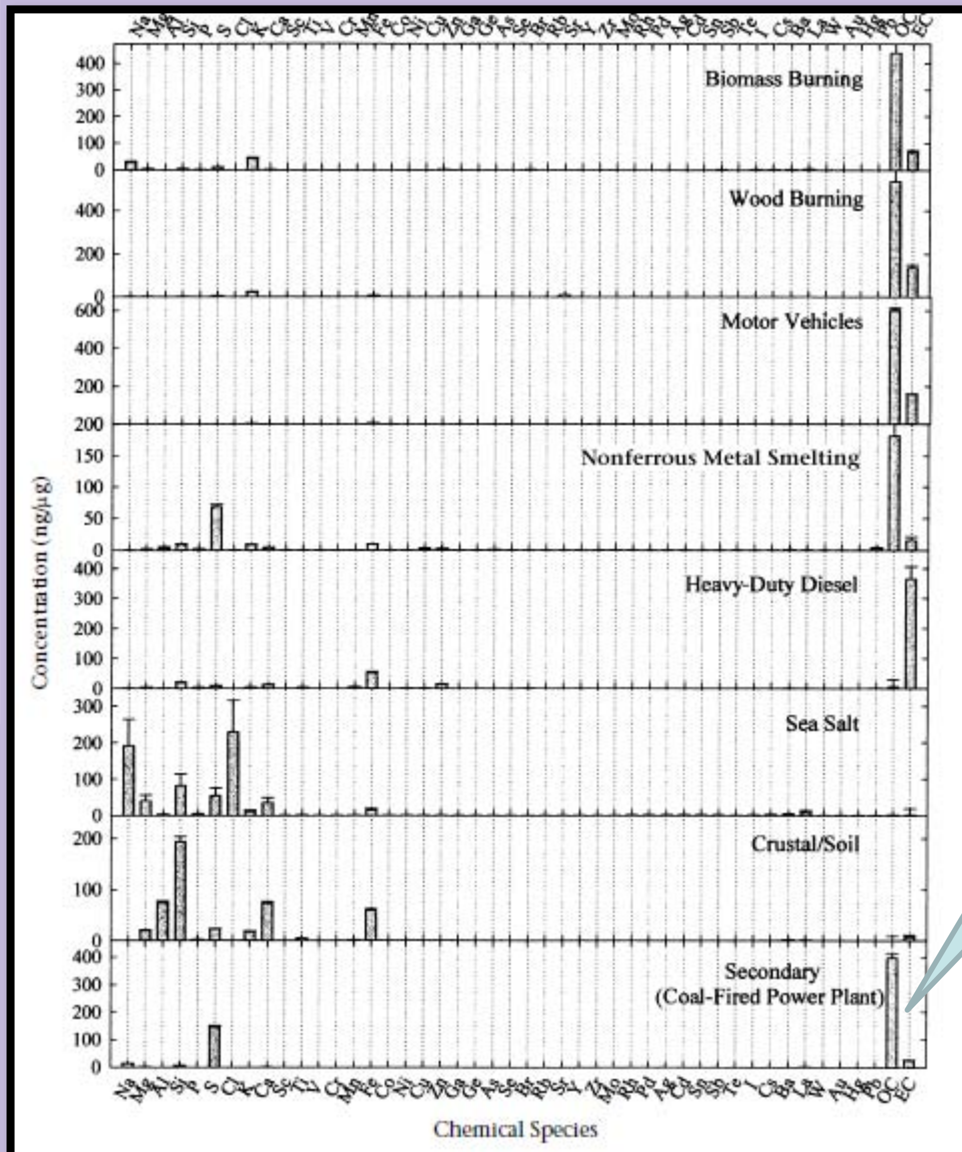


Figure 3.3.1. (continued) The solid line represents the true source contribution while the dotted line indicates the average of the ten data sets. Bar (b) is equal in length to two standard deviations of the ten data set values. Bar (a) is equal in length to two standard deviations as calculated by the receptor model applied to data set 8.

Watson, 1979

PMF and Unmix don’t need source profiles? WRONG!

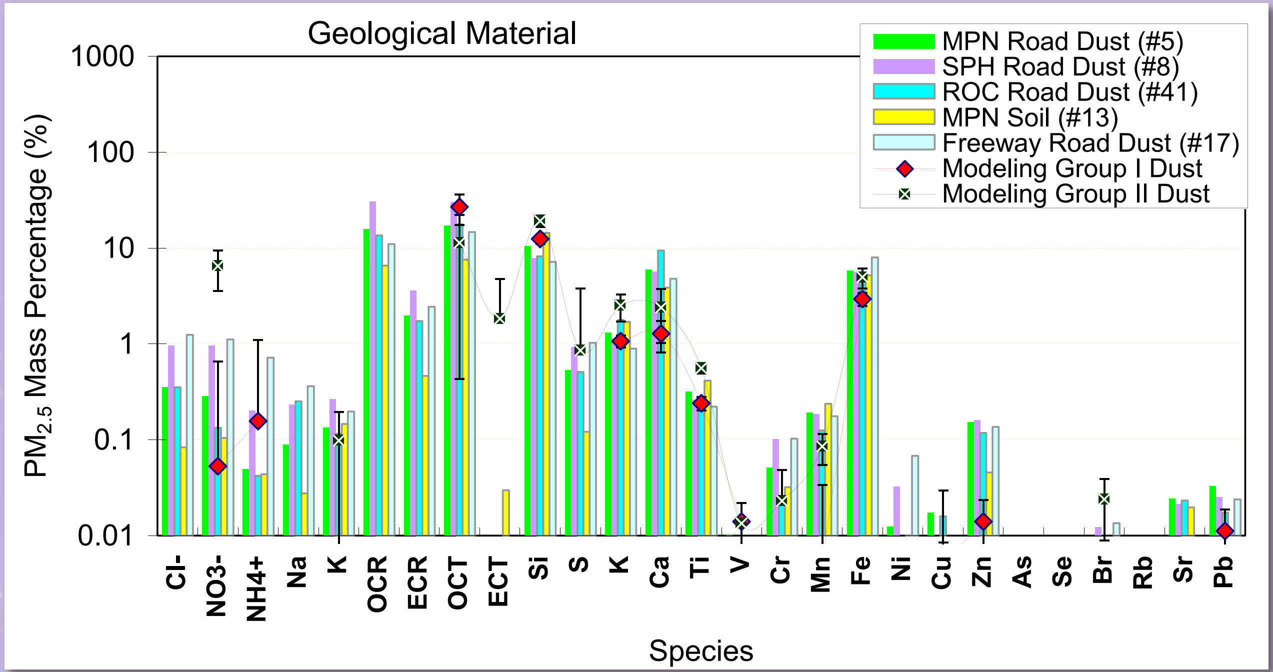


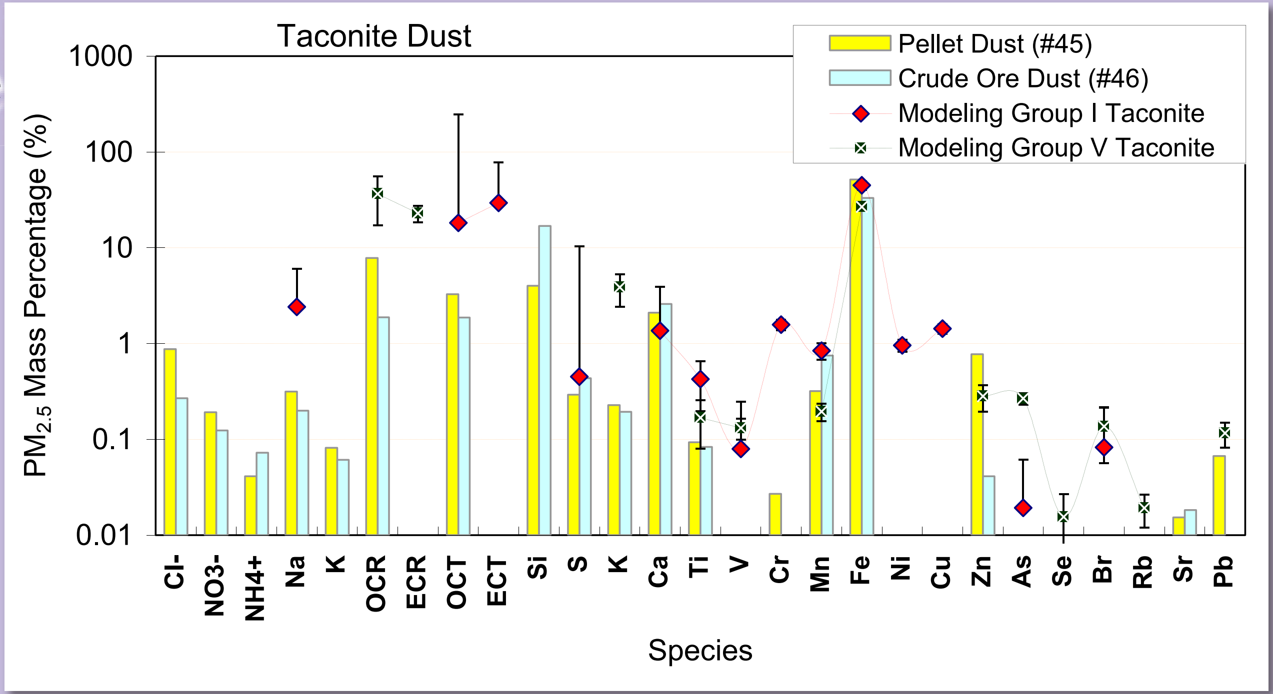
Why isn’t secondary coal dominated by sulfate?

Ramadan et al., 2000, *JAWMA*

PMF and Unmix source factors must correspond with at least one measured profile

Example from Minnesota

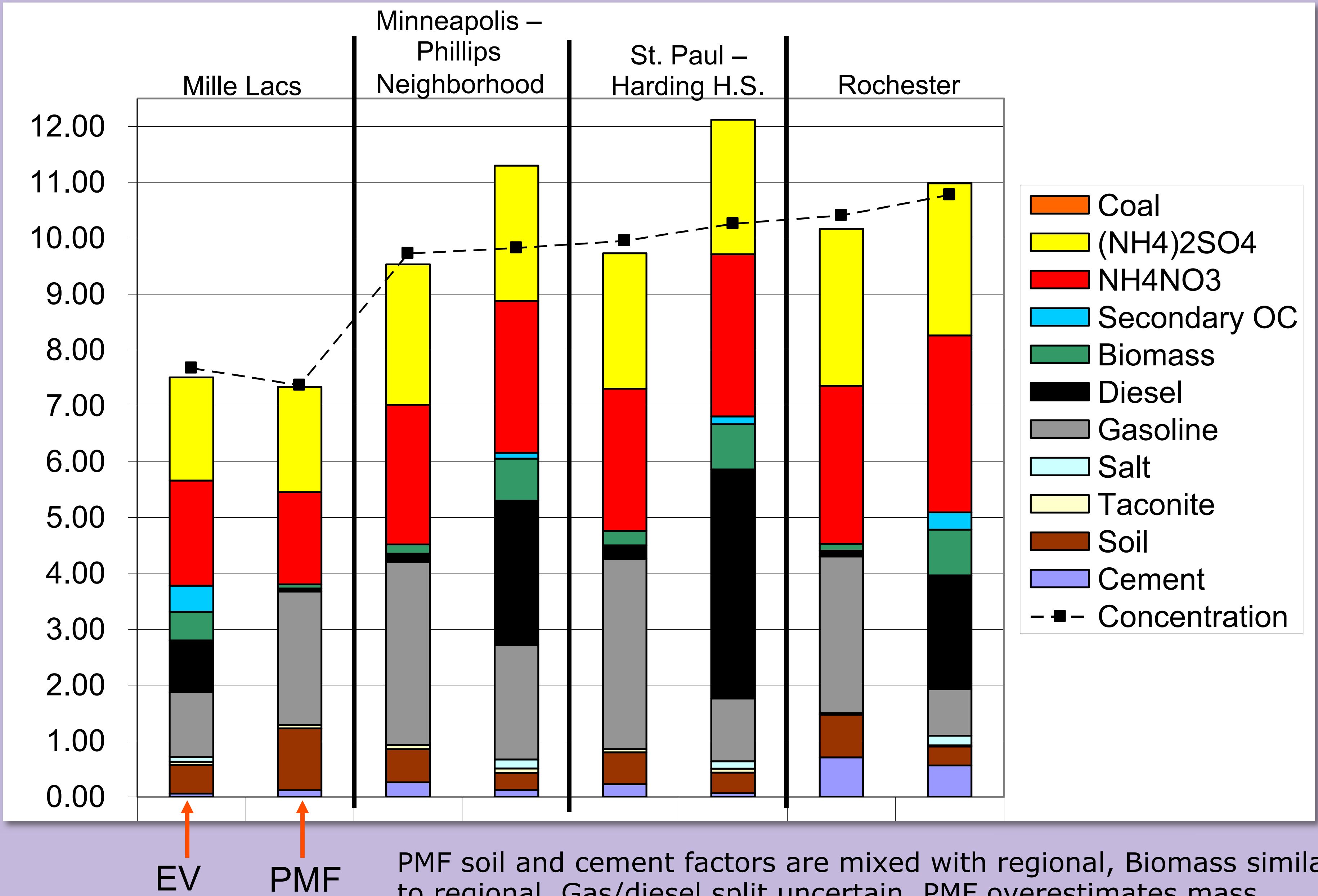




Chen et al. 2010, 2011, *JAWMA*

Applying different CMB solutions to the same data set aids in the Weight of Evidence

(Minnesota, 8/2003 – 7/2004, most samples passed validation tests)



PMF soil and cement factors are mixed with regional, Biomass similar to regional, Gas/diesel split uncertain, PMF overestimates mass

Chen et al., 2011, *JAWMA*

Considerations for a Source Apportionment Study

- Begin with a conceptual model. What has been done already? What are potential sources? What are useful markers? How does the wind blow?

- Plan measurement locations and times. Represent different spatial scales. Sample close to and away from sources. Obtain enough samples to cover different situations. Take advantage of interventions.

- Select the observables. Review prior source profiles. Sample on substrates appropriate for different analyses. Include source testing.

- Perform descriptive analysis prior to modeling. Averages and maxima by season, time of day. Case studies for maximum concentrations. Comparison with prior studies and those of similar situations.

Considerations for a Source Apportionment Study
(continued)

- Apply more than one CMB solution method and compare results. Compare PMF source factors with measured profiles. Conduct sensitivity and collinear tests. Stress the models.

- Refine emission inventory based on receptor model results and apply source model. Compare source and receptor model contributions.

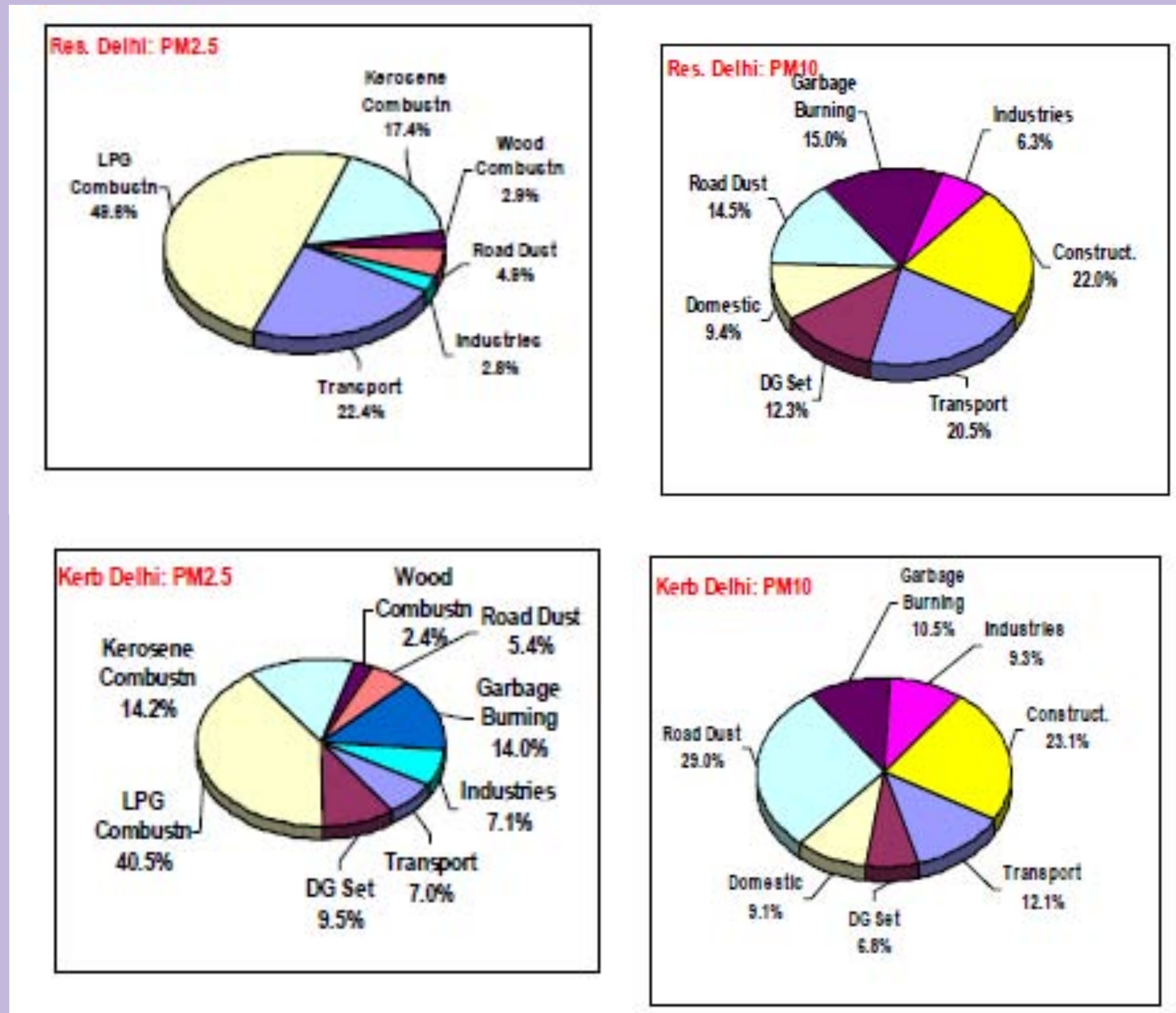
- Make input files available to others who would challenge conclusions.

- Refine the conceptual model and start over.

Danger of Ignoring the Weight of Evidence:

Example from India

- Good: Network design, source profiles, organic markers, emission inventory, dispersion model.
- Bad: No sensitivity/ collinearity tests, comparison among sites and cities, consistency of size fractions.



Danger of Ignoring the Weight of Evidence:

Example from India (continued)

LPG most polluting? Experts disagree

Chetan Chauhan
chetan@hindustantimes.com

EXPERTS SAY GOVT GIVING TRANSPORT SECTOR CLEAN CHIT FOR POLLUTION WITH STUDY SHOWING LPG AS BIGGEST POLLUTANT

NEW DELHI: A government claim that the source of the Capital's deadliest pollutant Particulate Matter 2.5 is liquid petroleum gas (LPG) in homes and not vehicles has miffed experts who term it as an attempt to give the transport sector a clean chit for air pollution.

PM 2.5, the smallest pollutant absorbed mostly by the human body, can trigger heart attacks and respiratory diseases.

Rise in number of vehicles was believed to be the major source of the pollutant.

This claim was countered by Indian Oil Corporation this week when it quoted a Central Pollution Control Board study saying LPG was the major contributor to rising PM 2.5 in the Capital.

An IOC presentation at a seminar organised by diesel vehicle manufacturers said that half of PM 2.5 in residential areas of Delhi was because of combustion of domestic LPG. In industrial areas, it was as high as 61 per cent and at traffic junctions 40.5 per cent.

"It is not a complete view," said CPCB chairperson S.P. Gautam. The board for the first time in India conducted an air pollution source appropriation study which was peer reviewed by air pollution experts from Europe and the US and is being examined by an inter-ministerial group. "I don't know what IOC had said but there are many factors which contribute to particulate matter."

The most intriguing findings were for residential areas in Delhi where vehicles contribute 22.4 per cent and kerosene combustion 17.4 per cent to total PM 2.5 pollution.

The presentation states vehicles contribute only seven per cent to particulate matter at traffic intersections and garbage burning for 14 per cent.

"It is shocking," said Anumita Roy Chowdhury, Associate Director with NGO Centre for Science and Environment. "Refinery and auto industries have hyped data in public forums to prove vehicles are the cleanest and must be left alone."

The CPCB study, which Environment Minister Jairam Ramesh has decided not to put in public domain, is likely to be the basis for India's future auto fuel policy. The government has constituted an inter-ministerial group to review the present policy, which expires in 2010, and create one for the new decade.

Environment ministry officials said the aim of the new policy would be to reduce the sources of air pollution.

Chowdhury said the government was framing a new policy without consulting people.

- Weight of evidence would include external data from vehicle and stove emission tests, comparisons with apportionments from different cities, examination of other data such as continuous gas and particle measurements.

More markers can be measured on existing and new samples

Chemical Analyses[a]

Teflon-membrane filter
- XRF for 51 elements[b]
- Acid Digestion
  - ICP-MS for rare-earth elements and isotopes[d]

Quartz-fiber filter
- ½ filter extracted in 20 ml distilled-deionized water (DDW)
  - 10 ml for anions and cations[e] by IC, AC, and AAS, acidified to pH 2 with
  - 1 ml for total WSOC by thermal/optical carbon
  - Filtration of 5 ml through 0.2 µm PTFE syringe filter
    - 1 ml speciated WSOC separated into three classes: NC, MDA, and PA by HPLC-IEC and UV/Vis detection at 254 nm
    - 1 ml for NC speciation (e.g., carbohydrates) by IC-PAD
    - 1 ml for MDA speciation (e.g., organic acids) by IC with conductivity detector
    - 1 ml for PA speciation (e.g., HULIS) by HPLC–SEC–ELSD–UV/VIS

Quartz-fiber filter
- $0.5\ cm^2$ punch
  - OC, EC, carbon fractions, carbonate by thermal/optical carbon
- $\sim 1\text{-}2\ cm^2$ punch
  - Organic Markers by TD-GC/MS[c]

Citric acid-impregnated cellulose-fiber filter
- ½ filter extracted in 10 ml DDW
  - Ammonia by AC

K_2O_3-impregnated cellulose-fiber filter
- ½ filter extracted in 10 ml 1:11 hydrogen peroxide: DDW dilution
  - Sulfur dioxide by IC

Silver nitrate-impregnated cellulose-fiber filter
- Whole filter without extraction
  - Hydrogen sulfide by XRF as sulfur

Nuclepore polycarbonate-membrane filter
- Elemental analysis or morphological analysis for lichen studies

[b] Al – U (see Table 7-1)
[c] 124 organic marker species (see Table 7-1)
[d] Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Pb204, 205, 206, 207, 208
[e] Cl^-, NO_2, NO_3^-, $PO_4^=$, $SO_4^=$ (by IC); NH_4^+ (by AC); Na^+, Mg^{++}, K^+, and Ca^{++} (by AAS)

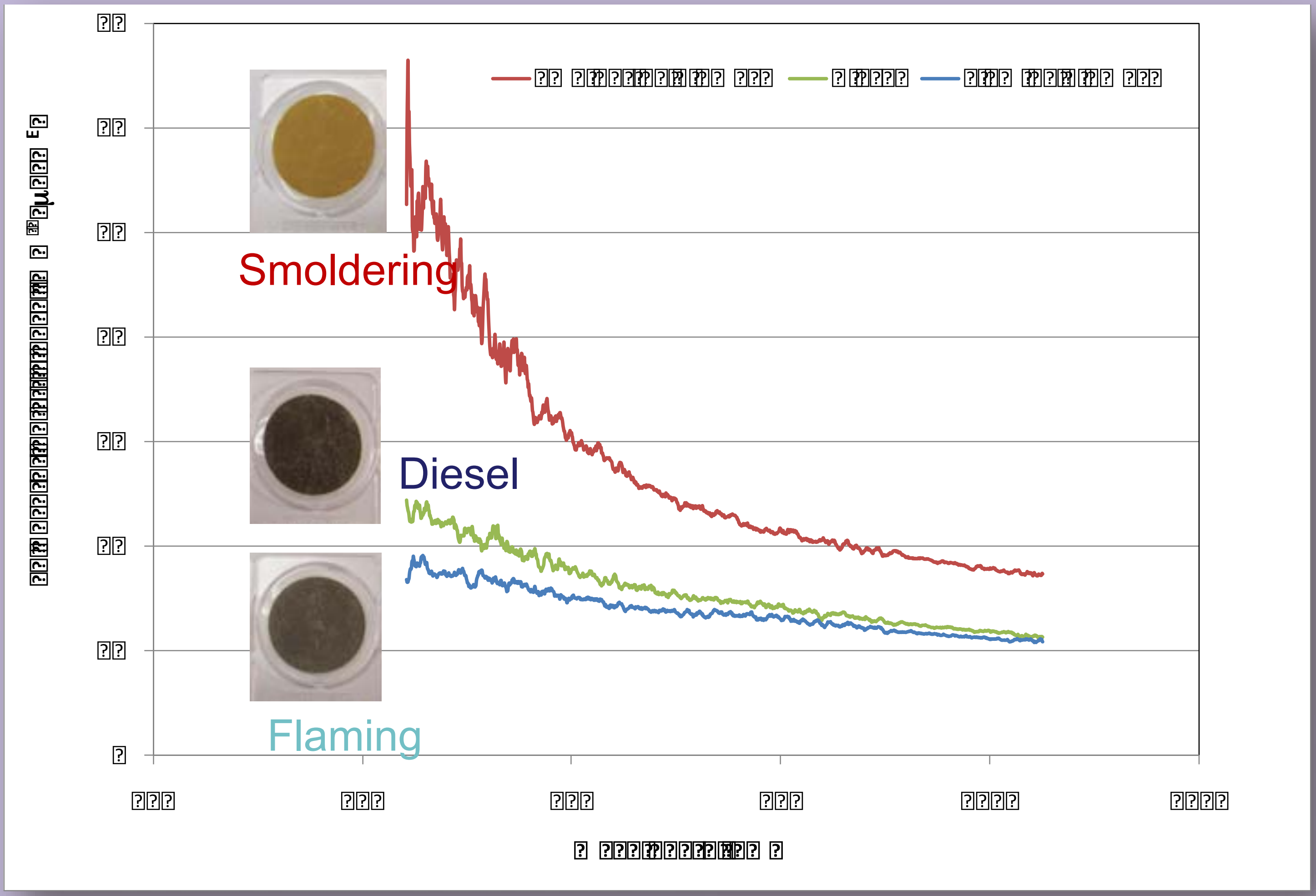
[a] *Analytical Instruments:*
AAS: Atomic absorption spectroscopy
AC: Automated colorimetry
ELSD: Evaporative light scattering detector
HPLC-IEC: High performance liquid chromatography with an ion exchange column
IC: Ion chromatography
IC-PAD: IC with pulsed amperometric detector
ICP-MS: Inductively coupled plasma – mass spectrometry
PTFE: Polytetrafluoroethylene
SEC: Size-exclusion chromatography
TD-GC/MS: Thermal desorption-gas chromatography/mass spectrometry
UV/VIS: Ultraviolet detector
XRF: X-ray fluorescence

Observables
OC: Organic carbon
EC: Elemental carbon
HULIS: Humic-like substances
MDA: Mono/dicarboxylic acids
NC: Neutral/basic compounds
PA: Polycarboxylic acids

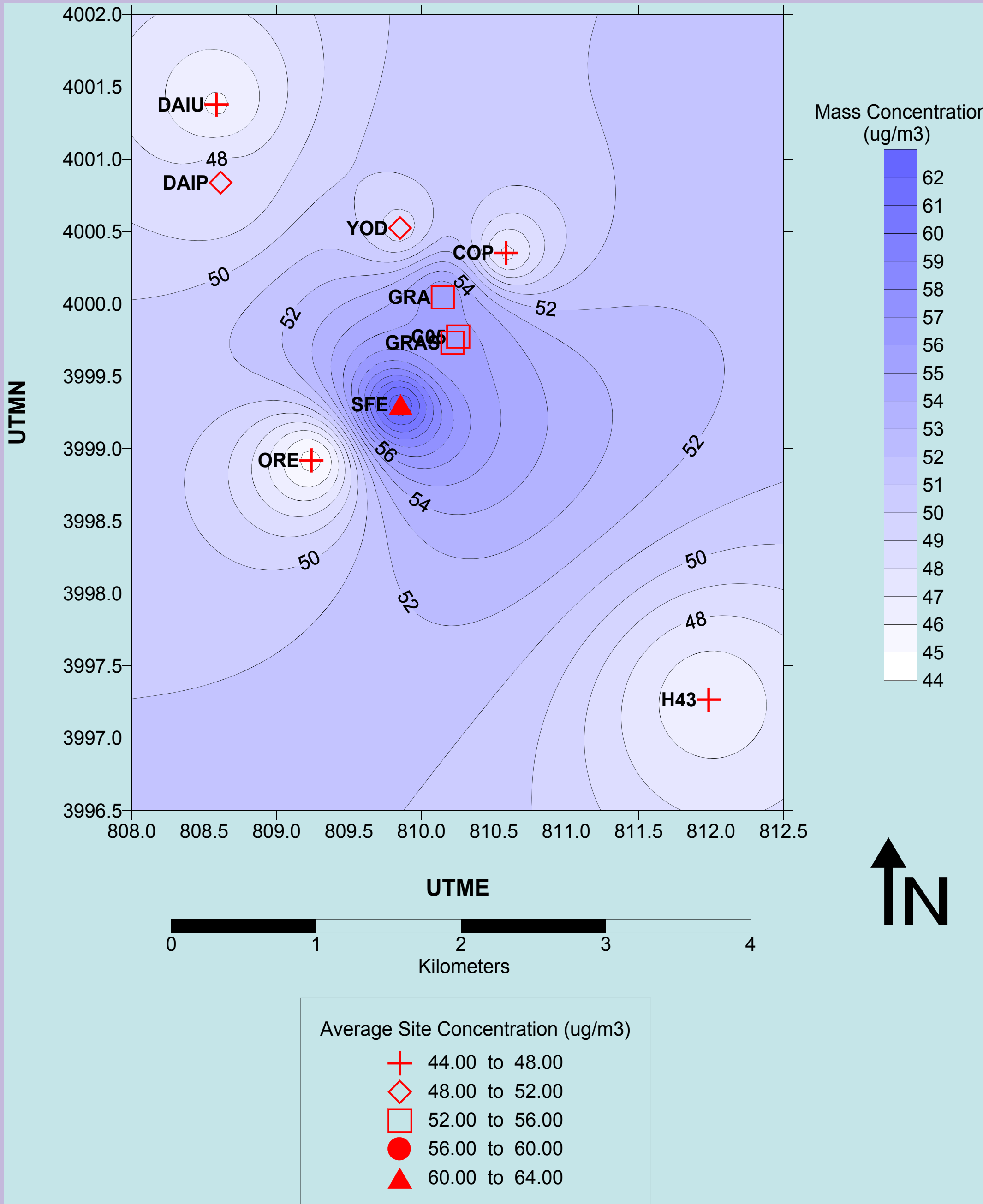
Chow and Watson, 2012;
Ho and Yu, 2004, *J. Chromatogr. A.*

Extending from single to multiple wavelengths can distinguish pollution sources

(EC absorption efficiency varies by source and wavelength)



Short-term dense monitoring can access PM_{10} spatial variation

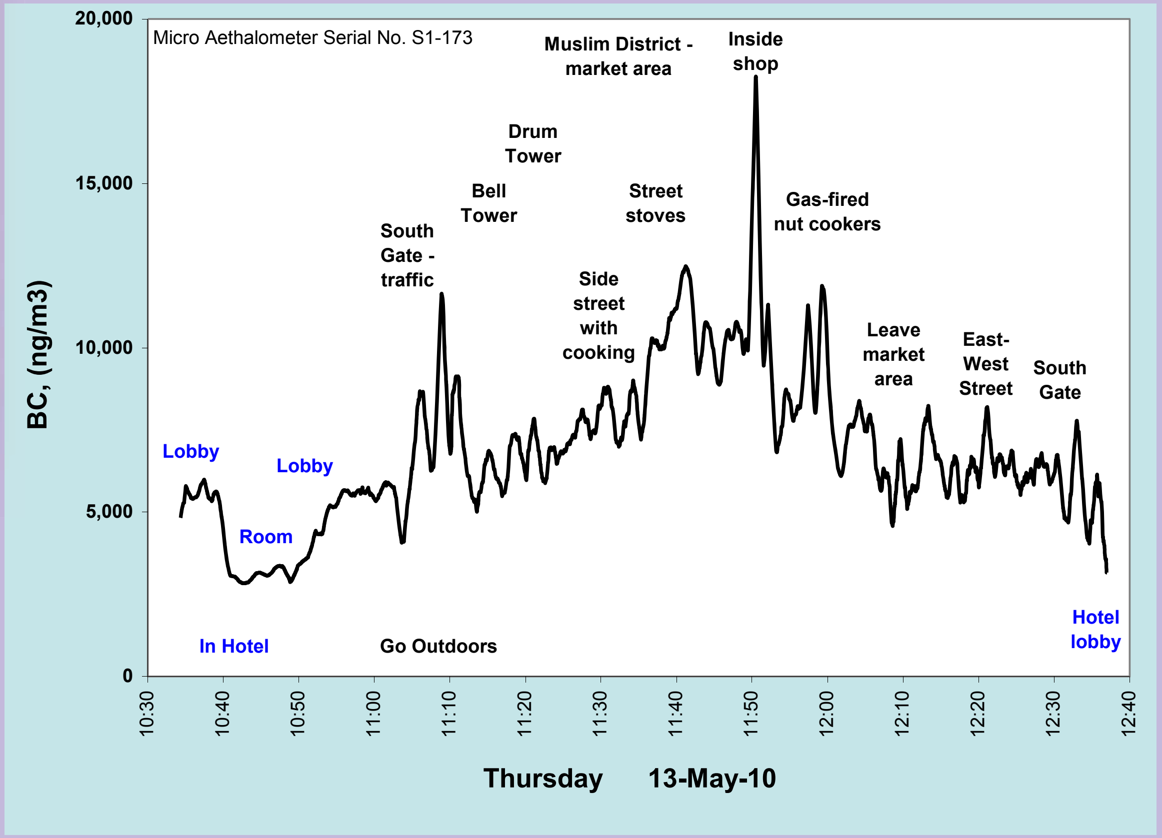


Corcoran, central California, USA (10/9/00 – 11/14/00)

Microaethalometer can be used to verify major black carbon emitters

Magee Scientific, Berkeley, CA

(Xian, China)

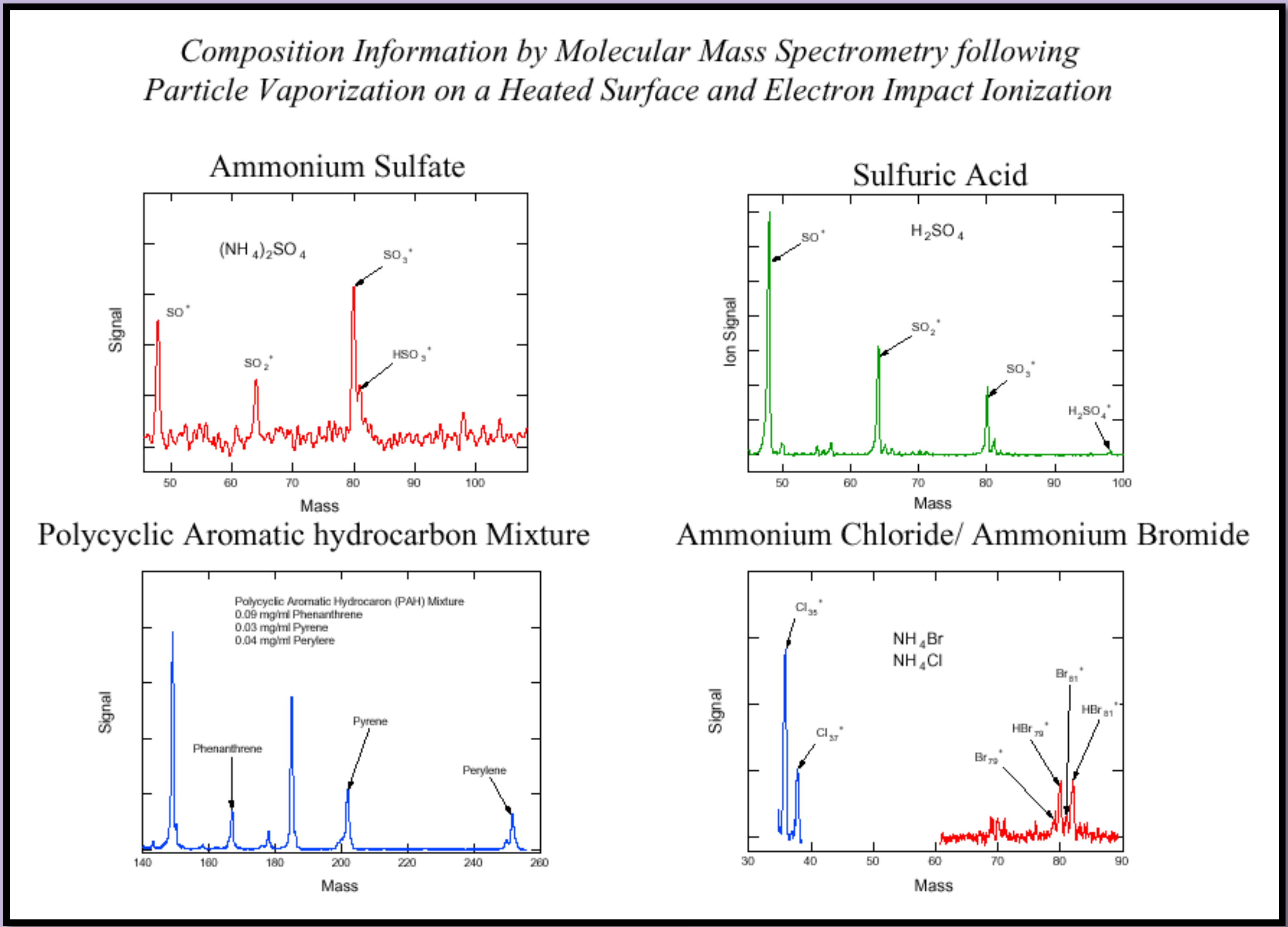


Hansen and Mocnik, 2010

UAVs are available to characterize aged plumes with microsensors
(Fooyin University, Taiwan)

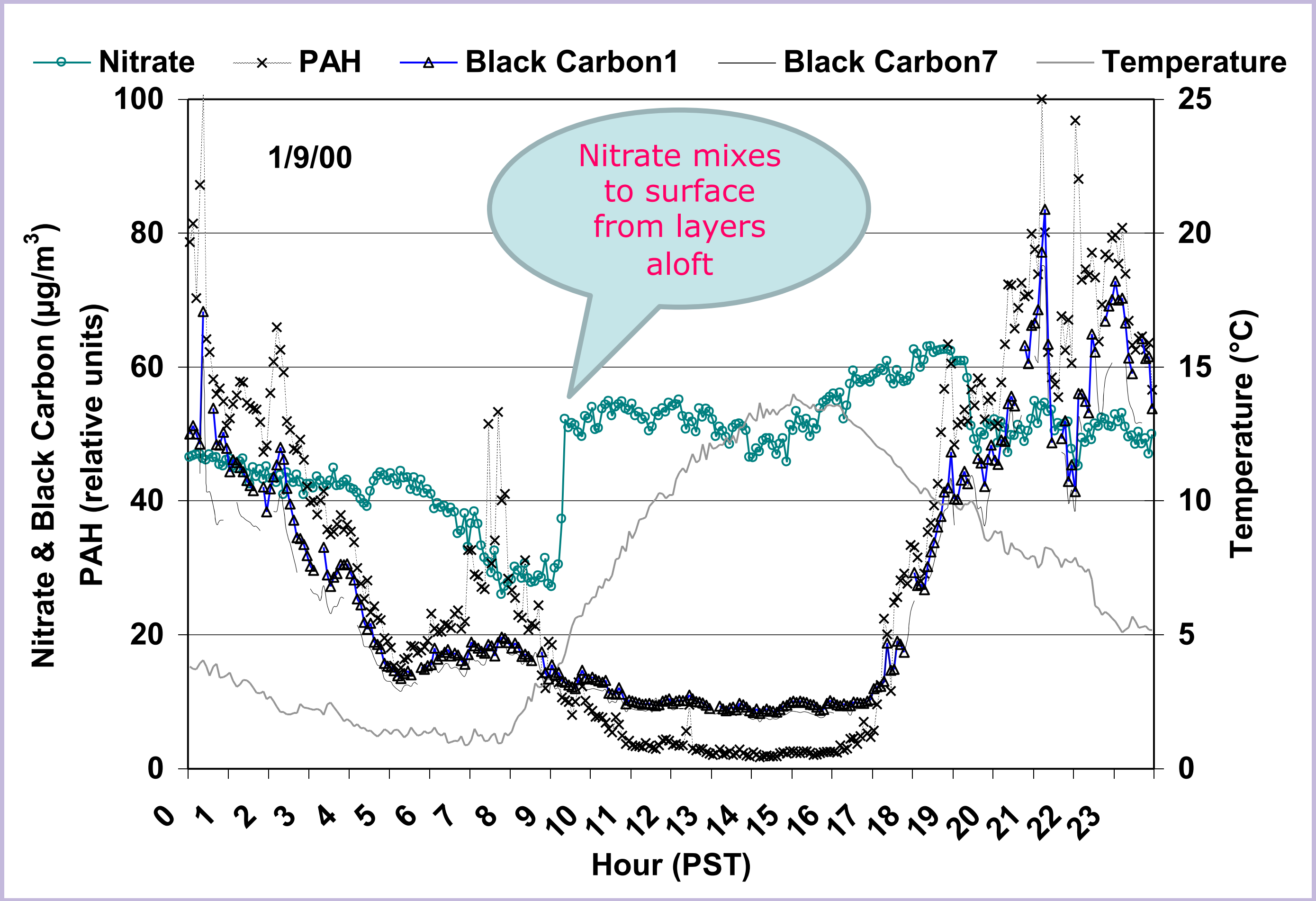
Char et al. 2010

Aerosol Mass Spectrometers are elucidating sources and chemical mechanisms



Middlebrook et al., 2003, *JGR*

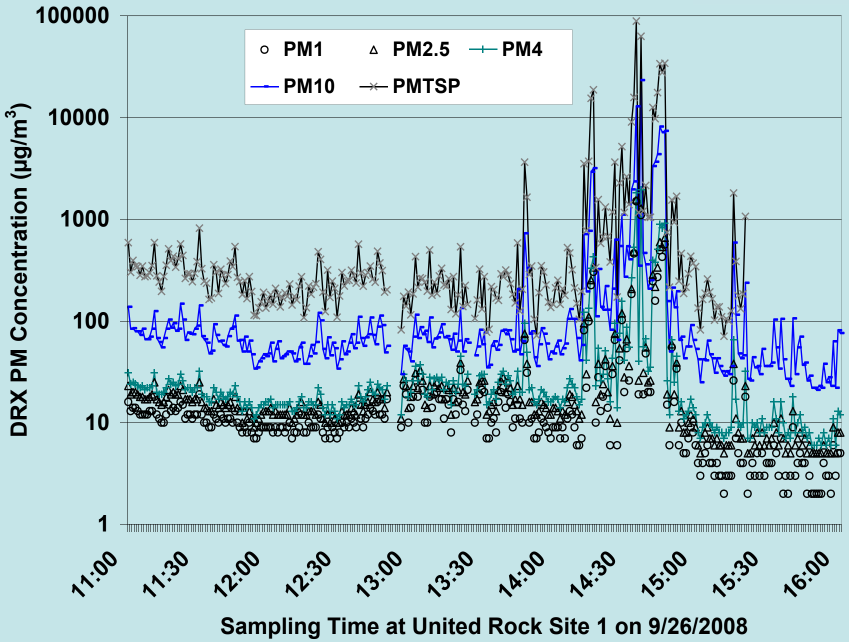
Continuous ion sensors show mechanisms

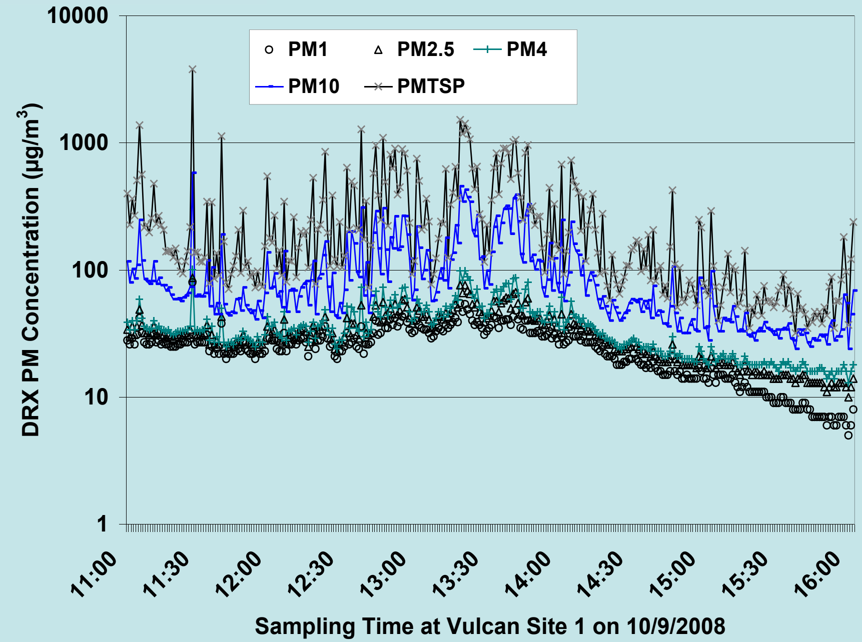


Liquid Diffusion Denuder

URG 9000D with IC (URG Corporation, Raleigh, NC, USA)

Rapid particle size measurements separate nearby from distant emitters





Sand/gravel Facility A

Sand/gravel Facility B







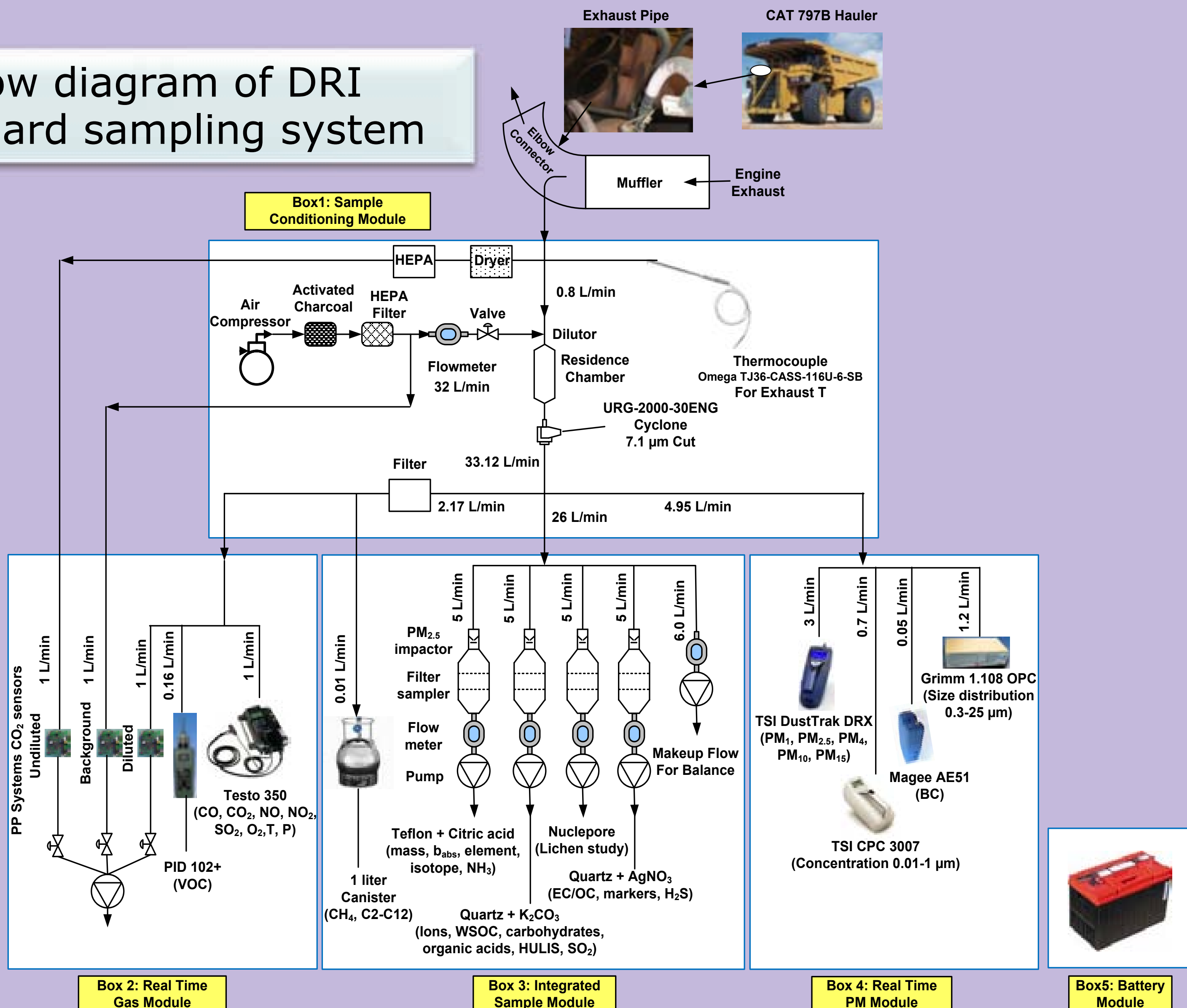


* Using TSI DustTrak DRX

Watson et al., 2011, *AAQR*

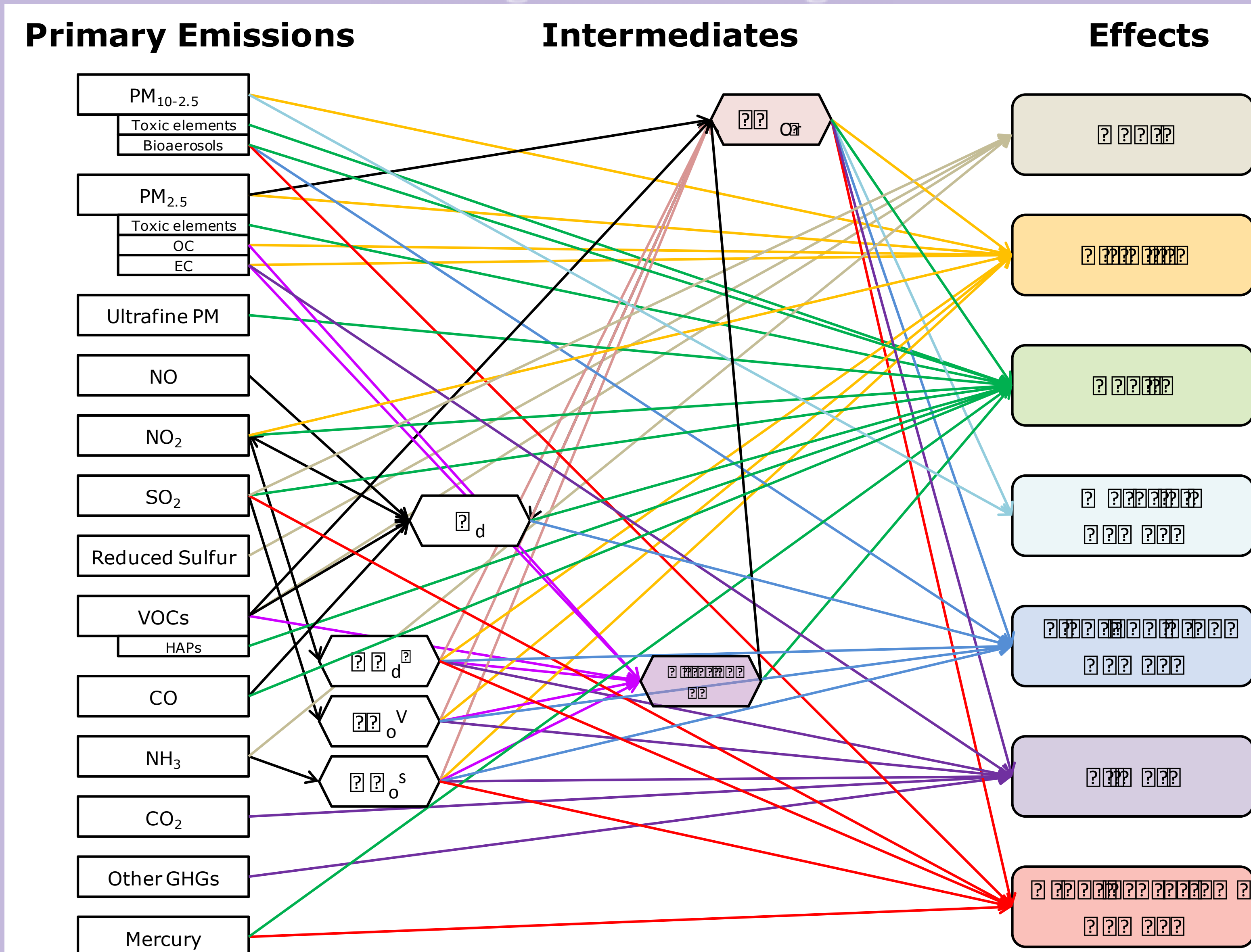
New technologies can be combined into complex systems to obtain source profiles as well as emission rates

Flow diagram of DRI on-board sampling system



Chow et al., 2010

Source apportionment studies are multi-pollutant by design, and their measurements will be useful for emerging air quality management strategies



Chow and Watson, 2011, *Air Quality and Climate Change Journal*

Take Home Messages

- Don’t just plug numbers into the software and expect to get a reasonable result.
- Find out what has been done already in the study area or similar areas. READ and don’t re-invent the wheel. Use all available resources to construct a conceptual model.
- Be critical of your own results and those of others.
- Expect to discover things you hadn’t thought of.

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