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

Listing Evidence

Best Professional Judgment

Logic  Causal Criteria

Indexing  Scoring

Quantitative  Qualitative

Quantitative

Linkov et al., 2009, Sci. Total Environ.
What do we mean by “Weight of Evidence”? (continued)

- 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

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.

Protocol For Applying And Validating The CMB Model


What do we mean by "Source Apportionment Model"?

The **source model** uses source emissions as inputs and calculates ambient concentrations.

The **receptor model** uses ambient concentrations as inputs and calculates source contributions.
Source and receptor models derive from the same physical construct

\[ C_{ikl} = \sum_j \sum_m \sum_n F_{ij} T_{ijklmn} D_{kln} Q_{jkmn} \]

- \( i \) = 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 \( j \)
- \( T_{ijklmn} \) = 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**

\[ C_{ijkl} = \sum_j \sum_m \sum_n T_{ijklmn} D_{kln} F_{ij} Q_{jkmn} \]

**Chemical Mass Balance (CMB) Model**

\[ C_{ijkl} = \sum_j T_{ijkl} F_{ij} \sum_m \sum_n D_{kln} Q_{jkmn} \]

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 \( \sigma_{C_j} \), source profiles \( F_{ij} \), and uncertainties \( \sigma_{F_{ij}} \)

**Model Output:**

- Source contributions \( S_j \) and uncertainties \( \sigma_{S_j} \)

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)

Source Category

- FTP gasoline vehicle exhaust
- Cold-start gasoline vehicle exhaust
- On- & off-road diesel vehicle exhaust
- Residential wood burning
- Fugitive dust
- Coal-fired power stations
- Other industries
- Restaurant cooking
- Natural gas heating
- Secondary ammonium nitrate
- Secondary ammonium sulfate

Watson and Chow, 2007
“Xi’an emission inventories (EPA AP-42) show that TSP is nearly all from fugitive dust”-Shaanxi EPB official

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TSP in Xian, China
(336 µg/m³ Material Balance, 10/27/97, Eastern Urban Site)

- Nitrate: 5%
- Sulfate: 10%
- Ammonium: 2%
- Organics (=1.2xOC): 28%
- Soot: 6%
- Dust (=20xFe): 49%

Chow et al., 2002, Chemosphere
Effective Variance, PMF, and Unmix are solutions to the CMB equations, not separate models

\[ S_j = \frac{C_i}{F_{ij}} \]

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

\[ \min \sum_i \left( \frac{(C_i - \sum_j F_{ij} S_j)^2}{\sigma_{C_i}^2 + \sum_j \sigma_{F_{ij}}^2 S_j^2} \right) \]

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

\[ \min \sum_i \sum_k \left( \frac{(C_{ik} - \sum_j F_{ij} S_{jk})^2}{\sigma_{C_{ik}}^2} \right) \]

- 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. 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.
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.
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)

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**

- **Teflon-membrane filter**
  - XRF for 51 elements

- **Quartz-fiber filter**
  - ½ filter extracted in 20 ml distilled-deionized water (DDW)

- **Quartz-fiber filter**
  - 0.5 cm² punch

- **Quartz-fiber filter**
  - ~1-2 cm² punch

- **Citric acid-impregnated cellulose-fiber filter**
  - ½ filter extracted in 10 ml DDW

- **K₂O₃-impregnated cellulose-fiber filter**
  - ½ filter extracted in 10 ml 1:11 hydrogen peroxide: DDW dilution

- **Silver nitrate-impregnated cellulose-fiber filter**
  - Whole filter without extraction

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

**Observables**

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

**Analytical Instruments:**

- AAS: Atomic absorption spectroscopy
- AC: Automated colorimetry
- ELSLD: 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

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

(Xian, China)

Hansen and Mocnik, 2010
UAVs are available to characterize aged plumes with microsensors
(Fooyin University, Taiwan)
Aerosol Mass Spectrometers are elucidating sources and chemical mechanisms

Composition Information by Molecular Mass Spectrometry following Particle Vaporization on a Heated Surface and Electron Impact Ionization

Ammonium Sulfate
(SO\textsubscript{4}\textsuperscript{2-}, SO\textsubscript{2}\textsuperscript{+}, HSO\textsubscript{4}\textsuperscript{+})

Sulfuric Acid
(SO\textsuperscript{-}, SO\textsubscript{2}\textsuperscript{+}, SO\textsubscript{3}\textsuperscript{2-}, H\textsubscript{2}SO\textsubscript{4}+)

Polycyclic Aromatic hydrocarbon Mixture
(Polycyclic Aromatic hydrocarbon (PAH) Mixture
0.03 mg/ml Phenanthrene
0.03 mg/ml Pyrene
0.04 mg/ml Naphthalene)

Ammonium Chloride/ Ammonium Bromide
(NH\textsubscript{4}Br, NH\textsubscript{4}Cl)

Middlebrook et al., 2003, JGR
Continuous ion sensors show mechanisms

Nitrate mixes to surface from layers aloft
Rapid particle size measurements separate nearby from distant emitters

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


• CPCB (2010). Air quality monitoring, emission inventory and source apportionment study for Indian cities. prepared by Central Pollution Control Board, New Delhi, India, http://www.cpcb.nic.in/FinalNationalSummary.pdf.


