Watson, J.G. and J.C. Chow 2005. *Receptor Models*. Chapter 16B of *AIR QUALITY MODELING - Theories, Methodologies, Computational Techniques, and Available Databases and Software. Vol. II – Advanced Topics* (P. Zannetti, Editor). Published by The EnviroComp Institute (http://www.envirocomp.org/) and the Air & Waste Management Association (http://www.awma.org/).

Chapter 16B

Receptor Models

John G. Watson (1) and Judith C. Chow (1)

(1) *Desert Research Institute, Reno, NV (USA)*
John.Watson@dri.edu
Judy.Chow@dri.edu

Abstract: Receptor models complement source models by independently identifying sources and quantifying their contributions using ambient measurements of different observables at different times and locations. Source apportionment is accomplished by solution of the mass balance equations that express concentrations of several measured pollutants as a linear sum of products of pollutant abundances in source emissions and source contributions. These equations can be solved by several methods, including maximum likelihood weighted least squares, singular value decomposition eigenvectors, and positive matrix factorization. A viable solution does not guarantee physical reality, so internal and external validation measures must be evaluated. Receptor models are best used in conjunction with source models to create a "weight of evidence" for justifying emission reduction measures on different source types.

Key Words: receptor model, source apportionment, chemical mass balance (CMB), ambient measurement, source profile, particulate matter (PM), volatile organic compound (VOC).

1 Introduction

1.1 Receptor Model Definition

Receptor models (Brook et al., 2003; Watson and Chow, 2002a; Watson et al., 2002a) include a wide range of multivariate analysis methods that use ambient air measurements to infer the source types, source locations, and source contributions that affect ambient pollutant concentrations. Receptor models contrast with the source models explained in other chapters. Source models begin with source emissions and calculate ambient concentrations using mathematical representations of meteorological dispersion, chemical transformation, and deposition. Applying source and receptor models to the same situation reveals deficiencies in each that, when remedied, lead to a better assessment of pollution sources.

1.2 Use and Applicability

Receptor models have been used to quantify source contributions from direct emissions of suspended particulate matter (PM) (Chow and Watson, 2002a) and volatile organic compounds (VOC) (Watson et al., 2001a), evaluate the zone of influence of source emissions (Watson and Chow, 2001a), determine limiting precursors for ammonium nitrate (Blanchard et al., 2000), estimate contributions to secondary sulfate from nearby emitters (Watson et al., 2002b), evaluate the effects of sulfate reductions on ammonium nitrate levels (Ansari and Pandis, 1998), identify uninventoried sources (Henry et al., 1997), improve emission inventories (Mendoza-Dominguez and Russell, 2000), and track the long-term effectiveness of pollution control strategies (Malm et al., 2002).

In addition to outdoor air applications, receptor models have been used to evaluate personal and animal exposure (Godleski et al., 2000), estimate source contributions to urban and regional haze (Chow et al., 2002a; Pitchford et al., 1999; Watson, 2002a, b), identify causes of nuisance and acid deposition (Anttila et al., 1994; Motelay-Massei et al., 2003), apportion toxic materials in water to their emitters (Pena-Mendez et al., 2001; Stout et al., 2001), and identify pollution sources in hazardous soil remediation (Murphy, 2000; Sims and Sims, 1995).

Receptor models complement, rather than replace, source models by providing an independent method of assessing the influence of nearby and distant sources. Their results are part of the "weight of evidence" (U.S. EPA, 2001a) that needs to be assembled to define and justify cost-effective emission reduction strategies. All air quality models are imperfect representations of reality, and input data are seldom complete. Using several types of models helps to identify and quantify model inaccuracies and to focus further investigation on the areas of greatest uncertainty. Watson et al. (2002a) present a framework for using receptor and source models to solve air quality problems that consists of: 1) formulating a conceptual model; 2) identifying potential sources; 3) characterizing source emissions; 4) obtaining and analyzing ambient gas and particle samples for major components and source markers; 5) confirming source types with multivariate receptor models; 6) quantifying source contributions with chemical mass balance (CMB); 7) estimating source profile changes and the limiting precursor gases for secondary aerosols; and 8) reconciling receptor modeling results with source models, emission inventories, and receptor data analyses. These steps systematize the weight of evidence approach.

1.3 Previous Receptor Model Reviews

This chapter summarizes and updates results from, rather than replicates, previous reviews and specialty conference proceedings that present theory, application examples, and measurement requirements for receptor models (Brook et al. [2003], Chow [1985], Chow and Watson [2002a], Cooper and Watson [1980], Gordon [1980, 1988], Gordon et al. [1984], Henry et al. [1984], Henry [1997, 2002], Hopke [1985, 1991, 1999, 2003], Hopke and Dattner [1982], Javitz and Watson [1988], Javitz et al. [1988], Pace [1986], Watson [1979, 1984], Watson et al. [1981, 1989, 2001a, 2002a], and Watson and Chow [2002a]). Watson et al. (2002a) classified more than 500 citations of receptor modeling theory and applications, and this list is still incomplete. Chow and Watson (2002a) summarized the results of 22 $PM_{2.5}$ and PM_{10} (particles with aerodynamic diameters <2.5 µm and <10 µm, respectively) source apportionment studies conducted between 1990 and 1998. Watson et al. (2001a) presented a similar summary for VOC receptor models.

Early receptor model research was motivated by the need to develop emission reduction strategies for the attainment of the Total Suspended Particulate (TSP, mass of particles with aerodynamic diameters < ~ 40 µm) standards and PM_{10} National Ambient Air Quality Standards (NAAQS) in many urban areas. Receptor modeling studies showed the importance of long-range sulfate transport (Lioy et al., 1982 and Mueller et al., 1983), fugitive dust (Gatz et al., 1981), vegetative burning (Watson, 1979), meat cooking (Rogge et al., 1996), and cold start/high emitting vehicles (Watson et al., 1998a) to ambient PM. These sources were previously omitted from local emission inventories, so no form of source-oriented modeling would estimate their contributions. When applied to VOCs (Fujita et al., 1992, 1994, 1995), receptor modeling resulted in major improvements to mobile source emission estimates (California Air Resources Board, 2000).

2 Receptor Model Types

Figure 1 categorizes receptor models based on their use of multivariate PM or VOC properties, measured at a receptor, and by their combination with source modeling concepts. Each receptor model type can be applied independently or in combination with other model types. Table 1 lists the types, strengths, and weaknesses of the different model types.

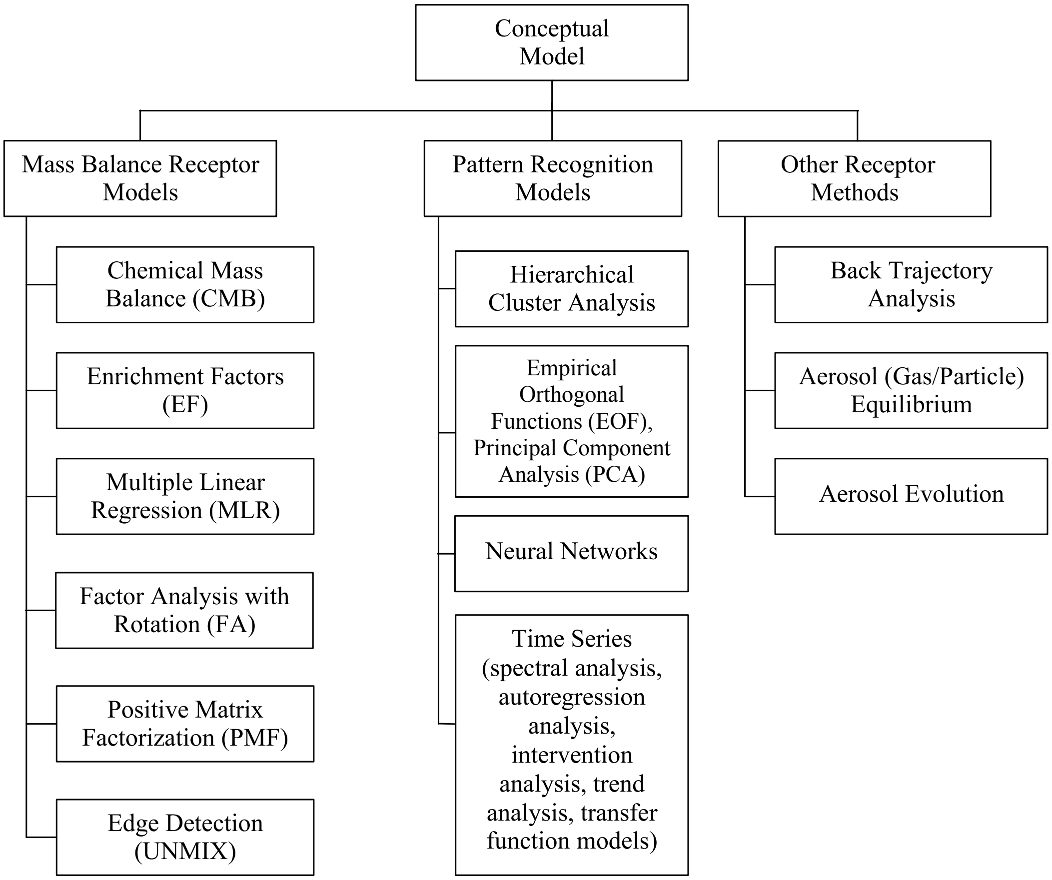

Figure 1. Summary of receptor models and source/receptor techniques.

Table 1. Strengths and weaknesses of different receptor model types (based on Brook et al., 2003 and Watson et al., 2002a). Citations given below are illustrative rather than comprehensive and are recommended for further details.

Receptor Model	Description	Strengths	Weaknesses
Chemical Mass Balance (CMB) (Hidy and Friedlander [1971], Watson [1979], and Watson et al. [1984, 1991])	Ambient chemical concentrations are expressed as the sum of products of species abundances and source contributions. These equations are solved for the source contribution estimates when ambient concentrations and source profiles are used as input. Several different solution methods have been applied, but the effective variance least squares estimation method is most commonly used because it incorporates precision estimates for both source and ambient input data into the solution and propagates these errors to the model outputs. The tracer solution is also commonly used, in which one chemical component is assumed to be unique and in a constant abundance in each source type.	• Simple to use, software available. • Quantifies major primary PM source contributions with element, ion, and carbon measurements, and VOC contributions with > 50 non-methane hydrocarbon measurements. • Quantifies contributions from source types with single particle and organic compound measurements. • Provides quantitative uncertainties on source contribution estimates based on input concentrations, measurement uncertainties, and collinearity of source profiles. • Has potential to quantify secondary sulfate contributions from single sources with gas and particle profiles when profiles can be "aged" by chemical transformation models.	• Requires representative source profiles, and common source and receptor measurements of observables, that are not always available. • Assumes all observed mass is due to the sources selected in advance, which involves some subjectivity. • Does not directly identify the presence of new or unknown sources. • Chemically similar sources may result in collinearity without more specific chemical markers. • Typically does not apportion secondary particle constituents to sources. Must be combined with profile aging model to estimate secondary PM.
Enrichment Factor (EF) (Dams et al. [1971] and Reimann and de Caritat [2000])	The ratios of atmospheric concentrations of elements to a reference element are compared to the same ratios in geological material, marine	• Simple, no software needed. • Indicates presence or absence of emitters. • Inexpensive. • Provides evidence of secondary PM	• Semi-quantitative method, often not source specific. • Requires source composition data. • More useful for source/process identification than for

Receptor Model	Description	Strengths	Weaknesses
	aerosol, or vehicle exhaust. Higher ratios are attributed to anthropogenic sources or secondary aerosol. Local soil and road dust compositions often differ from global crystal compositions. Heavy metal enrichments are attributed to industrial emitters. Potassium enrichment is attributed to burning and cooking. Sulfur enrichment is attributed to secondary sulfate. OC enrichment is attributed to secondary organics.	formation and changes in source impacts by changes in ambient composition.	quantification.
Multiple Linear Regression (MLR) (Kleinman et al. [1980], Morandi et al. [1991], and Malm and Gebhart [1997])	Mass, chemistry, or light extinction is expressed as linear sums of regression coefficients times source marker concentrations measured at a receptor. The regression coefficients represent the inverse of the chemical abundance of the marker species in the source emissions. The product of the regression coefficient and the marker concentration for a specific sample is the tracer solution to the CMB equation that yields the source contribution.	• Implemented by many statistical software packages. • Operates without source profiles. • Abundance of marker species in source is determined by inverse of regression coefficient. • Apportions secondary PM to primary emitters when primary markers are independent variables and secondary component (e.g., sulfate) is dependent variable.	• Requires a large number of ambient measurements. • Marker species must be from only the sources or source types examined. • Limited to sources or source areas with markers. • Abundance of marker species in emissions is assumed constant with no variability.
Hierarchical Cluster Analysis (Gether and Seip	Multivariate statistical procedure to group data based	• Simple, software available. • Detects natural	• Semi-quantitative method. • Requires large data

Receptor Model	Description	Strengths	Weaknesses
[1979], Hopke et al. [1976], Saucy et al. [1987], and Wilkinson [1990])	on similarities between observables. Usually presented by a Euclidian distance between each pair of observables.	data groupings without prior knowledge of group characteristics. • Can be used for either spatial or temporal analysis.	sets. • Requires prior knowledge of sources to select key species indicative of potential emission sources in the study area.
Eigenvectors (Principal Component Analysis [PCA], Factor Analysis [FA], Empirical Orthogonal Functions [EOF]) (Blifford and Meeker [1967], Henry and Hidy [1982], Henry [1987], Henry et al. [1991], Hopke [1988], Thurston and Spengler [1985], and White [1999])	Correlations or covariances are calculated from chemical measurements taken on simultaneous samples at a large number of locations. Eigenvectors of this correlation or covariance matrix represent a spatial distribution of source influence over the area, providing that the samplers have been located to represent the gradients in source contributions.	• Models such as PCA and FA identify major source types, and relate secondary components to source via correlations or covariances. • Sensitive to the influence of unknown and/or minor sources. • Influenced by extreme values. Can be used to identify data outliers.	• Large data sets required. • Most models are based on statistical associations (e.g., common variations or associations among groups of variables) rather than a derivation from physical and chemical principles. • Vectors or components are usually related to broad source types as opposed to specific categories or sources. • Many subjective rather than objective decisions and interpretations of eigenvectors as sources. • Do not always produce unique, physically valid solutions.
Non-Negative Least Squares (Positive Matrix Factorization [PMF]) (Hopke et al. [2003], Kim and Hopke [2004], Kim et al. [2004], Paatero and Tapper [1994] and Poirot et al. 2002)	Mass balance equations are solved by least squares minimization for many samples, not just for a single one. This provides an overdetermined set of equations that allows source profile abundances, as well as source contribution estimates, to be calculated.	• Software available. • Requires uncertainty estimates of ambient measurements. Can handle missing or below-detection-limit data. • Weights species concentrations by their analytical precisions. • Constrained to non-negative species concentrations or source contributions.	• Requires large ambient data sets. • Need to judge the number of retained sources. • Requires measured source profiles to assign categories to derived profiles. • Weights only by uncertainty of receptor measurements, not by uncertainties in source profiles. • Several adjustable parameters and initial

Receptor Model	Description	Strengths	Weaknesses
		• Provides solution evaluation tool (e.g., R^2, Chi-square). • Derives source profiles from ambient measurements as they would appear at the receptor.	conditions must be selected, often based on trial and error.
Edge Detection (RMAPS, UNMIX) (Henry [1997], and Henry et al. [1999])	Edges are constant ratios among chemical components that are detected in multi-dimensional space. Some samples in the input data must have no contribution from the sources to define an edge. The edges detected by models such as UNMIX are extensions of self-modeling curve resolution to *n* dimensions sources.	• Software available. • Does not require assumptions about number or composition of sources. • Provides source contribution estimate to each sample. • Provides evaluation tool (e.g., R^2, S/N ratio).	• Requires large ambient data sets. • Does not make explicit use of errors or uncertainties in ambient concentrations or source profiles. • Can produce an infinite number of solutions with the same root mean square error. • Need to assume or predetermine number of retained sources. • May result in no solution.
Time Series (e.g., spectral analysis, auto regression analysis, intervention analysis, trend analysis, transfer function models) (Perrier et al. [1995], Somerville and Evans [1995], Hies et al. [2000], Jorquera et al. [2000], and Watson and Chow [2001a])	Provides understanding of temporal variation of mass and chemical concentrations that coincide with meteorology and source information. Assists in formulating conceptual models and selecting sources for further modeling. Assumes that different source types or sub-types may have some periodicity to their emissions that allows separation of different source impacts.	• Can be used to determine statistical trends in data sequences. • Provides clues to influences from meteorology and sources.	• Requires continuous measurements. • Semi-quantitative descriptive data analysis does not provide specific source impact information.
Neural Networks (Bishop [1995], Chelani et al.	Attempts to simulate pattern recognition processes of the	• Makes no prior assumptions about data distributions.	• Semi-quantitative method. • Requires large

Receptor Model	Description	Strengths	Weaknesses
[2002], and Gao et al. [1994])	human brain by creating classification rules. Known inputs and outputs are presented to a neural network that simulates the human thought process. The network assigns weights to the inputs that reproduce the outputs. Once these patterns have been established for cases where outputs are known, weights can be applied to input data to estimate outputs.	• Deals with nonlinear relationships. • Neural networks can provide function relationships and represent a solution to the CMB equations.	ambient data sets. • Requires training set containing known source/receptor relationships. • Subjective association of outputs with sources.
Backward Trajectory Analysis (Ashbaugh [1983], Draxler [1999], and Green and Gebhart [1997])	Estimates the path and location of the air reaching a receptor based on prior wind movements. The simplest form classifies pollutant concentrations or source contributions by surface wind direction in a pollution rose. More complex backward trajectories add hourly wind vectors generated by a meteorological model.	• Traces or projects the route of air mass transport over hundreds to thousands of kilometers, and on the order of several days. • Can generate multiple trajectories with different time intervals. • Can represent plume spread from vertical wind shear at different hours of day, and provide better understanding of day/night transition.	• Relies on wind observations with limited temporal and spatial density. • Highly dependent on wind interpolation algorithm and start height/vertical dispersion parameters. • Accuracy and precision of the wind measurements dictate the model output. • Unable to resolve small-scale turbulence. • Provides history of air parcel travel path, but cannot tell how much pollution was picked up along the way or differentiate between pollutant contributions. • More useful in regional than in urban-scale applications.
Aerosol (Gas/Particle) Equilibrium (Ansari and Pandis [1998],	The portions of a semi-volatile species in the gas and particle phase are estimated based on receptor	• Estimates partitioning between gas and particle phases for ammonia, nitric acid,	• Highly sensitive to temperature and relative humidity. Short duration samples are not

Receptor Model	Description	Strengths	Weaknesses
Blanchard and Hidy [2003], Blanchard et al. [2000], Stelson and Seinfeld [1982], and Watson et al. [1994a])	measurements to determine which precursor is in excess and which needs to be diminished in order to reduce concentrations in the particle phase. The theory is most highly developed for ammonium nitrate/ammonium sulfate and has been used to determine the extent to which ammonia or oxides of nitrogen/sulfur dioxide reductions are needed to reduce ambient ammonium nitrate levels.	ammonium nitrate, and aerosol water content. • Allows evaluation of effects of precursor gas reductions on ammonium nitrate levels.	usually available. • Gas-phase equilibrium depends on particle size, which is not often known in great detail. • Sensitivity to aerosol mixing state, which is not completely understood or quantified.
Aerosol Evolution (Lewis and Stevens [1985], Stockwell et al. [2001], and Watson et al. [2002b])	Source profiles containing particle chemical components and gaseous precursors are mathematically "aged" using a chemical reaction scheme. Source profile evolution has been done using Lagrangian source models to simulate the conditions that a profile might encounter en route between source and receptor.	• Can be used parametrically to generate several profiles for typical transport and meteorological situations that can be used as input to mass balance equations.	• Very data-intensive. Input measurements are often unavailable. • Derives relative, rather than absolute, concentrations. • Level of complexity may not adequately represent profile transformations.

Receptor as well as source models start with a conceptual model that proposes plausible theories about the causes of an elevated pollutant concentration or effect. The conceptual model is formed from previous experience (e.g., tests on similar sources, gas and particle transport and transformation under similar meteorological conditions), the nature of the problem (e.g., exceeding an air quality standard, consistently poor visibility over a local area or large region), and available measurements (e.g., ambient, source, and meteorological). A conceptual model (Pun and Seigneur [1999], Watson et al. [1998b], Watson and Chow [2002b]) provides reasonable, though not necessarily accurate, explanations of: 1) potential sources; 2) precursor gas and particle emission characteristics; 3) meteorological conditions that affect emissions, transport, and transformation; 4) size, chemical, and temporal characteristics of precursor gas and particle emissions; and 5) frequency, magnitude, and composition of the PM or VOC levels. The conceptual model is used to design a measurement program that considers the location and number of monitoring sites, sampling frequencies and periods, sampling durations, properties that are quantified, samples that are selected for laboratory analysis, and the modeling and data analysis methods that will be applied.

Trajectory, aerosol evolution, and equilibrium models are described from a source-oriented point of view in other chapters and are not examined in detail here, except to note that they can also be used in a receptor-oriented mode, as cited in the references. An ammonium nitrate chemical equilibrium model, for example, can be used as a source model within the context of an air quality model. It can also be used as a receptor model to determine whether nitric acid (HNO_3) or ammonia (NH_3) limits ammonium nitrate formation when NH_3, HNO_3, hydrochloric acid (HCl), sulfur dioxide (SO_2), sulfuric acid (H_2SO_4), ammonium (NH_4^+), nitrate (NO_3^-,), sulfate ($SO_4^=$), temperature, and relative humidity measurements are available at a receptor. Wind models have source-oriented forward trajectory modes and receptor-oriented backward trajectory modes.

Chemical and physical analysis methods are often termed receptor models, but they serve as inputs to models. Carbon 14 (^{14}C) single particle microscopic analysis, gas chromatograms, x-ray spectra, and many other analytical outputs are analogous to source profiles (mass fractions of emitted chemical components) in that they represent a pattern that might allow a source contribution to be identified and quantified. Without the receptor model mathematics and applications framework, however, these methods do not provide valid, quantifiable source apportionments.

3 Multivariate Receptor Model Mathematics

Receptor models are incorrectly referred to as “statistical” methods (e.g., Seinfeld and Pandis, 1998). This is inaccurate because the statistical distributions, often-missing data, and variable uncertainties of the input measurements do not conform to the rigorous assumptions required for statistical tests. Furthermore, statistical significance tests are rarely used, and are not useful, for source apportionment studies. This misconception partially arises because much of the receptor modeling mathematics is also used to determine and test statistical associations in other areas of science. There are also situations where the physical basis for the receptor model formulation has not yet been clearly understood or demonstrated.

The derivation presented below (Watson, 1984) shows the physical and mathematical relationships between emission models, source models, and receptor models and the simplifying assumptions that are made when these models are applied.

Summation indices (lower case) are defined as follows:

- *i* = Pollutant, representing any quantifiable property such as an element (e.g., aluminum, arsenic, selenium, etc.), water soluble ions (e.g. $SO_4^=$, NO_3^-, NH_4^+, etc.), an operationally defined carbon fraction (organic carbon [OC], elemental carbon [EC]), a specific volatile or organic carbon compound (e.g., benzene, benzo(a)pyrene), an isotopic abundance (e.g., ^{14}C, lead 210 [^{210}Pb], sulfur 34 [^{34}S]), or particle property (e.g., vanadium- and nickel-rich particle, S-shaped spiny particle).
- *j* = Source type, a grouping of individual source emissions with similar compositions that differ from the compositions of other source types. Common source types include geological material, sea salt, vegetative burning, cooking, motor vehicle exhaust, evaporated gasoline, and architectural coatings.
- *k* = When the sample was taken (i.e., continuous hourly averages to days representing different seasons, days of the week, and times of day).
- *l* = Receptor location, often selected to be source dominated (e.g., near roadways or other emitters), exposure dominated (where people live, work, and play), transport dominated (between major source areas), and boundary dominated (to determine what is entering a monitoring domain). Source-dominated samples may be used to obtain source profiles.
- *m* = Source subtype, a specific source or groups of emitters within a source type that have similar source compositions or locations. Paved roads, unpaved roads, agricultural soil, and industrial dust are geological source subtypes. Diesel and gasoline engine exhaust are vehicle exhaust subtypes. Source subtypes may become source types with the measurement of additional chemical components or directional sampling that allow them to be distinguished by the receptor model.

Upper case indices designate the total number. Symbols used in the model equations and typical units are described as follows:

- A_{jkm} = Activity that causes emissions for source type *j* corresponding to time period *k* for subtype *m* (unit of activity/sec). Typical activities are vehicle miles traveled, amount of fuel consumed, or amount of product produced. Population densities are often used as surrogates for area source activities.
- C_{ikl} = Concentration of pollutant *i* for time period *k* at location *l* (unit of $\mu g/m^3$, ng/m^3, ppm, or ppb). This is the receptor concentration.
- D_{klm} = Dispersion and mixing of emissions from source type between subtype *m* and receptor *l* corresponding to time period *k* (sec/m^3).
- F_{ij} = Fractional quantity of pollutant *i* in source type *j* (unitless). These are elements of the source profile for different source types. For PM measurements, profile abundances are usually normalized to mass emissions from a source in the desired size range. They may also be normalized to the weighted sum of the major species emitted or to an individual element that is present in all of the source types being modeled. Owing to the large number of species, total VOC is not usually available

for normalization. Options for VOC source normalization are discussed below.

- Q_{jkm} = Emission rate from subtype *m* of source type *j* corresponding to time period *k* (µg/sec).
- R_{jkm} = Rate of emissions (emission factor) per unit of activity for subtype *m* of source type *j* corresponding to time period *k* (µg/unit of activity).
- T_{ijklm} = Transformation of pollutant *i* between source subtype *m* of type *j* and receptor *l* corresponding to time period *k* (unitless).
- S_{jkl} = Contribution from source type *j* for time period *k* at receptor *l* (µg/m^3, ng/m^3, ppm, or ppb).
- W_{ik} = Weighting of differences between measured and calculated concentrations for pollutant *i* on sample *k*.

3.1 Emission Model

Emission rates for a pollutant from a source are usually estimated in an inventory by:

$$Q_{jkm} = R_{jkm} A_{jkm} \tag{1}$$

The R_{jkm} emission factors are derived from a limited number of tests on representative emitters, and are applied over a wide range of emitters that may constitute *M* individual sources or *J* source types. An emission inventory may include a category of “electrical generation” that consists of emissions from diesel generators, coal-fired power stations, natural gas burners, and residual oil combustors. Each of these would be classified as a separate source type for receptor modeling. Diesel generators would be grouped with other diesel emissions from heavy-duty trucks, farm equipment, and construction equipment because their chemical source profiles would be similar. The activity level might be specific to location and time, but this is true only of specially constructed, gridded inventories. Most inventories for mobile and area sources are compiled as annual averages over countywide and statewide areas. Large point sources can usually be associated with a specific location.

Source models take the form of:

$$C_{ikl} = \sum_{j=1}^{J} \sum_{m=1}^{M} D_{klmn} T_{ijklm} F_{ij} Q_{jkm} \tag{2}$$

All of the values on the right side of Equation (2) are inputs that estimate the concentration of a specific pollutant *i* at a specific time *k* and location *l*. Other chapters in this book show that the linear form of this equation is a large, but necessary, simplification to show the relationship between the source and receptor models.

Receptor models used for source apportionment are based on the chemical mass balance equations:

$$C_{ikl} = \sum_{j=1}^{J} F_{ij} S_{jkl} \tag{3}$$

For this to be of use, species *i* must be such that $T_{ijlm} = 1$, meaning that there is little change in the F_{ij} between source and receptor, or that such changes can be adequately estimated with an aerosol evolution model and have been incorporated into the F_{ij}. A comparison of Equations (2) and (3) also implies that:

$$S_{jkl} = \sum_{m=1}^{M} D_{klm} Q_{jkm} \tag{4}$$

In contrast to the source model, the ambient concentrations (C_{ikl}) are known and the source contributions (S_{jkl}) are to be calculated. The mass balance equations (Equation 3) can be solved for single samples if the source profiles (F_{ij}) have been measured by minimizing the weighted sum of the squares of the differences between measured and calculated concentrations for individual samples:

$$\sum_{i=1}^{I} \left\{ \left(C_{ikl} - \sum_{j=1}^{J} F_{ij} S_{jkl} \right) / W_{ik} \right\}^2 = Minimum \tag{5}$$

The weights (W_{ik}) can be set to 1, but they are usually selected to represent uncertainties in the ambient measurements and variability of the source profile abundances (Watson et al., 1984). This minimization takes the same form as a multiple linear regression equation, but it is not used in the statistical sense that is usually associated with regression.

Positive matrix factorization (PMF) attempts to derive source profiles from the ambient data themselves. The PMF solution to the mass balance equations (Paatero and Tapper, 1994) minimizes the weighed sum of squares of the difference between measured and calculated concentrations over many samples:

$$\sum_{k=1}^{K} \sum_{i=1}^{I} \left\{ \left(C_{ikl} - \sum_{j=1}^{J} F_{ij} S_{jkl} \right) / W_{ik} \right\}^2 = Minimum \tag{6}$$

With multiple samples and with rigorous assumptions, there are sufficiently more equations than unknowns to estimate values of source profiles as well as source contributions. The derived profiles need to be associated with measured source compositions that can be determined only from source tests.

Watson (1984) showed how the eigenvector and multiple linear regression (MLR) models are derived from the mass balance equations and the simplifying assumptions that need to be made. When source profiles are not measured, unique solutions to Equation (6) do not exist, and subjective interpretation is needed to judge the validity of the derived source profiles.

4 Model Input Measurements

Receptor models require multivariate measurements that are specific to gaseous precursors, particle sizes, chemical/physical/optical characteristics, temporal variations, and source locations. Several sampling and analytical methods provide time-integrated samples of PM (ACGIH [2001], Baron and Willeke [2001], Chow [1995], Landsberger and Creatchman [1999]) and VOC (Zielinska and Fujita, 1994) that are collected in the field and analyzed in the laboratory. In-situ measurement systems (McMurry [2000], Middlebrook et al. [2003], Wang et al. [1999], Watson et al. [1998c], Yamamoto et al. [2002]) provide the opportunity to better associate ambient concentrations with specific wind directions and distances from the receptor. Source emissions need to be measured for the same pollutants with methods comparable to those used at receptors.

4.1 Source Profiles

Source profiles are intended to represent a category or type of source, rather than individual emitters. All receptor models require measured source profiles, even those that intend to derive these profiles from the ambient measurements. The derived profiles must always be compared and evaluated against measured profiles that represent a source type. The number and definition of these categories are limited by the degree of similarity between the profiles. Mathematically, this similarity is termed “collinearity” (Henry, 1992), which means that two or more of the CMB equations are redundant and the set of equations cannot be solved. Owing to measurement error, however, CMB equations are never completely collinear in a mathematical sense. When two or more source profiles are collinear, standard errors on source contributions are often very high. Some source contributions may be unrealistically high, while others may be negative. Determining the degree of collinearity is one of the main objectives of receptor model validation (Watson et al., 1998d).

4.1.1 Common Emission Sources

Emission inventories need to be examined before a receptor model is applied to determine which source profiles are needed, and which chemical components must be measured in local source emissions and ambient air. These inventories can be less quantitative than those needed for source modeling. Receptor models only need to identify potential emitters, not the individual emission rates. Source types that are often combined due to its similarity or collinearity for PM and VOCs are:

- Vegetative burning and cooking: Subtypes include fireplaces, wood stoves, prescribed burns, wildfires, char-broiling, and meat cooking. Some of these source subtypes may be separated when appropriate organic compounds are measured.
- Diesel exhaust: Subtypes include heavy- and light-duty cars and trucks, off-road equipment, stationary engines for pumps and generators, ship generators, and locomotives.
- Gasoline exhaust: Subtypes include heavy- and light-duty cars and trucks, and small engines. Emission inventories do not usually contain breakdowns by cold-starts and visible smoking vehicles, although these subtypes might be discriminated by certain organic compounds in a profile. Two-stroke engine profiles may differ from four-stroke engine profiles.
- Gasoline evaporative emissions: Subtypes include fueling stations and hot-soak vehicles.
- Fugitive dust: Subtypes include paved roads, unpaved roads, agricultural tilling, dairy/feedlot soil, construction, wind erosion, and industrial aggregate. These subtypes can sometimes be separated based on single particle profiles or the measurement of specific mineral composition (Ashbaugh et al. [2003], Chow et al. [2003]).
- Solvents and coatings: Subtypes include evaporation from paints, degreasers, and solvents. These subtypes can be separated when the specific solvent compounds are known.
- Metals: Subtypes include copper smelters, lead smelters, steel mills, and aluminum mills. These often have similar metal emissions but in different abundances depending on the process.
- Aggregate handling: Subtypes include cement, quarrying, and mining. Ores are often enriched in the materials being extracted, thereby allowing their separation. When low-level measurements of trace elements such as copper, zinc, and lead are made, metal processing operations that use these materials can be classified into separate source types.

Vehicle-related VOC emissions, including exhaust, evaporated fuel, and liquid fuel, are ubiquitous in all urban areas. Architectural (e.g., paints) and industrial solvents (e.g., cleaning and process solvents, as in printing) are also common, but highly variable, in most urban areas. Petrochemical production and oil refining are more specific to certain urban settings, such as the Texas coast, where these activities are numerous. Biogenic emissions are larger in the eastern U.S., where forests are lush, in contrast to the arid west. VOC emissions in inventories are often reported in equivalent units of methane or propane. Comparisons of relative source attributions to emission inventories require appropriate reconciliation between the inventory and source contribution units.

4.1.2 Source Profile Normalization Options

Both gaseous and particulate species can be included in a source profile. As noted in the definition of F_{ij} above, one of the difficulties in combining VOC and $PM_{2.5}$ in a source apportionment is that there are some particle sources (e.g., suspended dust) that have negligible VOC components and some VOC sources (e.g., solvents, evaporated gasoline, biogenics) that have negligible particle components. There are many sources, such as vehicle exhaust, cooking, and wood combustion, that have large VOC and PM components, and profiles that normalize both gas and particle components to $PM_{2.5}$ mass may increase the utility of the profiles for both VOC and PM source apportionment studies.

Individual profiles are formed from individual source samples, and the precisions of the numerator and denominator are propagated (Watson et al., 2001b) to obtain the individual profile uncertainties. These individual profiles are further combined to obtain the source profiles used as CMB model input or for comparison with those derived from ambient data. Chow et al. (2003) established a framework that uses statistical measures to composite similar profiles. The simplest composite consists of the averages and standard deviations of abundances for all individual profiles within a group. Outlier tests are applied to remove individual profiles that unduly bias the averages and standard deviations. There are always some outliers in any series of source tests owing to the difficulties in field sampling and emission variability. For this reason, it is important to obtain five or more samples that run the range of operating conditions and fuels for a given source type to obtain representative source profiles.

VOC abundances are defined by several different methods. Watson et al. (2001a) summarize VOC terms in common use that represent different fractions of atmospheric organic material. These include reactive organic gases (ROG), total organic gases, photochemical assessment monitoring station (PAMS) species, non-methane hydrocarbons (NMHC), heavy hydrocarbons (C_{10}-C_{20}), carbonyl compounds, non-methane organic compounds (NMOG), semi-volatile organic compounds (SVOC), and total VOC. Non-standard variable definitions and units are an impediment to VOC source apportionment. VOC concentrations are usually reported in ppbC or $\mu g/m^3$ at local temperature and pressure. Either unit is acceptable for receptor modeling, but the source profile ratios must be consistent with the ambient measurements. VOC fractional abundances have been normalized by: 1) NMHC, consisting of ROG and an unidentified fraction; 2) the sum of the quantified or most abundant measured compounds, which varies depending on the study; 3) the sum of all canister measurements, including non-reactive gases such as halocarbons; and 4) NMOG, the sum of all VOCs measured from all applied methods. These profile differences preclude the comparability and use of profiles from different studies. Watson et al. (2001a) advocate normalization to the sum of the 56 PAMS species in ppbC that are almost universally quantified in canister samples by the U.S. Environmental Protection

Agency (EPA) TO-14 method[1]. Measurements from other canister analyses, Tenax and 2,4-dinitrophenylhydrazine (DNPH), can also be normalized to this sum. With this common convention, re-normalization to NMOG or other categories is straightforward.

4.1.3 Requirements for a Source Profile Library

The current SPECIATE database (U.S. EPA, 1999) includes 376 PM and 610 VOC source profiles, most of which are dated before 1989. These source profiles need to be updated with more contemporary data to enhance their usefulness for both source and receptor models. The objectives of compiling source profile libraries are to: 1) identify chemical and physical characteristics of primary PM and VOC emissions; 2) tabulate and document chemical abundances and variabilities from source tests; and 3) provide data interfaces to receptor models and speciated emission inventories. These databases can be used to: 1) create speciated emission inventories for regional haze, $PM_{2.5}$, and ozone modeling; 2) estimate hazardous and toxic air pollutant emissions from primary PM and VOC emissions; 3) provide input to mass balance receptor models; and 4) verify profiles derived from ambient measurements by the multivariate receptor models listed in Table 1.

The minimum source profile requirements to compile a library are:

- No hot stack samples or hot stack/impinger analyses should be included. Only dilution sampler results come close to representing ambient air concentrations. Method 201/202 certification results (U.S. EPA [1996, 1997]) for PM_{10} do not represent actual, condensed, particle emissions (England et al., 2000).
- VOC profiles should include, at a minimum, the 56 PAMS species (U.S. EPA, 2001b), plus other available species (additional light hydrocarbons from canisters, heavy hydrocarbons from Tenax, and carbonyls from DNPH). PM profiles should include, at a minimum, major elements (at least those reported by the National Park Service [NPS], Interagency Monitoring of Protected Visual Environments [IMPROVE] [Malm et al., 2000], and EPA's $PM_{2.5}$ Speciation Trends Network [STN]); major water-soluble ions ($SO_4^{=}$ and NO_3^- at a minimum–preferably NH_4^+, water-soluble sodium, magnesium, potassium, calcium, chloride, fluoride, and phosphate); and carbon fractions (total carbon, OC, and EC, preferably with other fractions that are defined by the method such as the eight IMPROVE fractions [Chow et al., 1993, 2001, 2004a], and carbonate carbon [Chow and Watson, 2002b]). Organic functional groups, organic compounds, isotopic abundances, and single particle properties should be included where they are reported, well-defined, and can be normalized to PM mass or the sum of PAMS VOCs.
- Profiles must include their chemical abundances and variabilities (Chow et al. [2003, 2004b], Watson and Chow [2001b], Watson et al. [2001c]).

---

[1] http://www.epa.gov/ttnamti1/files/ambient/airtox/to-14ar.pdf

> Preference should be given to profiles that represent an average and standard deviation of individual samples. Analytical uncertainties for individual source profiles should be identified as such; they are typically smaller than the variability among several samples taken at different times from the same emitter or from samples taken from different, but similar, emitters (Chow et al., 2003). The method for estimating variabilities should be documented. Some references report emission rates instead of emission profiles. Emission rates that are not normalized are not useful for receptor modeling.

Necessary profile documentation includes:

- The primary reference document for the profile. Secondary references should be supplied when original profiles have been modified (i.e., by aerosol aging, different sample compositing, etc.). Gray literature reports should be scanned and made available with the database. Copyrighted journal articles and book chapters can be obtained from libraries.
- The profile database should include (in the notes column or other fields) the specific size fraction, type of source sampling (e.g., hot stack [presumably excluded], dilution stack, diluted plume [e.g., airborne], source dominated, grab/resuspension), background corrections, chemical analysis methods, sample compositing criteria and methods, and number and types of profiles in a composite.

4.2 Ambient Measurements

Receptor observables are a subset of the source profile species and must include at least those species in the source profiles that allow sources to be separated by the receptor model.

4.2.1 Physical and Chemical Characteristics of Receptor Concentrations

Table 2 associates VOC, semi-volatile organic compounds (SVOC), and PM measurements with measurement methods. For gas- and particle-phase organics, a standard set of species is needed for all studies. Table 3 contains C_2 to C_{12} VOCs that can be obtained by canister sampling, C_8 to C_{20} VOCs by Tenax sampling, and SVOC and PM organic compounds by Teflon-coated glass-fiber filter and PUF/XAD-4/PUF solid adsorbent sampling. These compounds are determined by thermal desorption/cryogenic preconcentration, followed by gas chromatography (GC) separation and flame ionization or electron capture detection and/or combined GC/mass spectrometry/Fourier transform infrared detection. One of the difficulties with organic compound measurements is that different researchers measure different compounds by different methods, so that ambient and source concentrations are not always compatible. Seinfeld and Pandis (1998) and Watson et al. (2002a) discuss which species are useful for identifying different source types and provide more extensive references to applications and analytical techniques.

Table 2. Inorganic and organic species and measurement methods commonly used for receptor modeling.

Observables	Chemical Analysis Method
Particulate mass on filters	Gravimetry
Particulate elements (Na to U) on filters	X-ray fluorescence (XRF) Proton-induced x-ray emission (PIXE) Instrumental neutron activation analysis (INAA) Inductively coupled plasma / emission spectroscopy (ICP/ES) Inductively coupled plasma / mass spectrometry (ICP/MS)
Particulate water-soluble anions on filters (F^-, Br^-, Cl^-, NO_3^-, $PO_4^{\equiv}$, $SO_4^=$)	Ion chromatography (IC) Automated colorimetry (AC)
Particulate cations on filters (NH_4^+, Na^+, Mg^{++}, K^+, Ca^{++})	Ion chromatography (IC) Atomic absorption spectrophotometry (AAS) (flame or graphite) Automated colorimetry (AC)
Particulate carbon (organic carbon [OC], elemental carbon [EC], carbonate, other fractions defined by thermal or optical properties)	Thermal/optical reflectance (TOR) Thermal/optical transmission (TOT) Thermal manganese oxidation (TMO)
Particulate single-particle morphology on filters	Computer-controlled scanning electron microscopy (CCSEM) Electron Microprobe Transmission Electron Microscopy
C_2-C_{10} organics, volatile organic compounds (VOC)	Canister and gas chromatography measurement with various detectors
C_{11}-C_{20} organics, VOCs and semi-volatile organic compounds (SVOC)	Tenax cartridge with thermal desorption and gas chromatography with various detectors
SVOC (polycyclic aromatic hydrocarbons [PAH])	Filter/PUF/XAD/PUF with extraction in solvents of different polarities and gas chromatography with various detectors
Carbonyl VOCs	2, 4-dinitrophenylhydrazone (DNPH)-coated C_{18} cartridge and gas or liquid chromatography
Oxygenated VOCs (e.g., alcohol, ethers, esters)	Carbotrap canister, solvent extraction, derivitization, and gas chromatography with various detectors

Table 3. List of volatile organic compounds (VOCs), photochemical assessment monitoring station (PAMS) target compounds, semi-volatile organic compounds (SVOCs), and particulate organic compounds.

1. C_2 to C_{12} VOC samples acquired by canister samplers using gas chromatography (GC) with mass spectrometry (MS) for analysis of 123 VOCs:

propene
propane
isobutane
1,3-butadiene
n-butane
methanol
t-2-butene
1&2-butyne
c-2-butene
3-methyl-1-butene
ethanol
isopentane
1-pentene
2-methyl-1-butene
n-pentane
isoprene
t-2-pentene
c-2-pentene
2-methyl-2-butene
2,2-dimethylbutane
cyclopentene
4-methyl-1-pentene
3-methyl-1-pentene
cyclopentane
2,3-dimethylbutane
methyl-t-butylether
2-methylpentane
2,2-dimethylpentane
3-methylpentane
2-methyl-1-pentene
1-hexene
n-hexane
t-3-hexene
t-2-hexene
2-methyl-2-pentene
cis-3-methyl-2-pentene
c-3-hexene
c-2-hexene
trans-3-methyl-2-pentene
methylcyclopentane
2,4-dimethylpentane
2,2,3-trimethylbutane
1-methylcyclopentene
benzene
3,3-dimethylpentane
cyclohexane
4-methylhexene
2-methylhexane
2,3-dimethylpentane
cyclohexene
3-methylhexane
1,3-dimethylcyclopentane
3-ethylpentane
1-heptene
2,2,4-trimethylpentane
t-3-heptene
n-heptane
2,4,4-trimethyl-1-pentene
methylcyclohexane
2,5-diemthylhexane
2,4-diemthylhexane
2,3,4-trimethylpentane
toluene
2,3-dimethylhexane
2-methylheptane
4-methylheptane
3-methylheptane
2,2,5-trimethylhexane
1-octene
1,1-dimethylcyclohexane
n-octane
2,3,5-trimethylhexane
2,4-dimethylheptane
4,4-dimethylheptane
2,6-dimethylheptane
2,5-dimethylheptane
3,3-dimethylheptane
ethylbenzene
m- & p-xylene
2-methyloctane
3-methyloctane
styrene
o-xylene
1-nonene
n-nonane
isopropylbenzene
isopropylcyclohexane
2,6-dimethyloctane
alpha-pinene
3,6-dimethyloctane
n-propylbenzene
m-ethyltoluene
p-ethyltoluene
1,3,5-trimethylbenzene
o-ethyltoluene
octanal
beta-pinene
1-decene
1,2,4-trimethylbenzene
n-decane
isobutylbenzene
sec-butylbenzene
1,2,3-trimethylbenzene
limonene
indan
indene
1,3-diethylbenzene
1,4-diethylbenzene
n-butylbenzene
1,2-diethylbenzene
1,3-dimethyl-4-ethylbenzene
isopropyltoluene
nonanal
1-undecene
n-undecane
1,2,4,5-tetramethylbenzene
1,2,3,5-tetramethylbenzene
1,2,3,4-tetramethylbenzene
2-methylindan
1-methylindan
1-dodecene
naphthalene
n-dodecane

2. Photochemical Assessment Monitoring Stations (PAMS) monitor 56 target VOCs:

ethylene	1-pentene	n-hexane	2,3,4-trimethylpentane	n-propylbenzene
acetylene	n-pentane	methylcyclopentane	toluene	m-ethyltoluene
ethane	isoprene	2,4-dimethylpentane	2-methylheptane	p-ethyltoluene
propylene	t-2-pentene	benzene	3-methylheptane	1,3,5-trimethylbenzene
propane	c-2-pentene	cyclohexane	n-octane	o-ethyltoluene
isobutane	2,2,-dimethylbutane	2-methylhexane	ethylbenzene	1,2,4-trimethylbenzene
1-butene	cyclopentane	2,3-dimethylpentane	m&p-Xylenes	n-decane
n-butane	2,3-dimethylbutane	3-methylhexane	styrene	1,2,3-trimethylbenzene
t-2-butene	2-methylpentane	2,2,4-trimethylpentane	o-xylene	m-diethylbenzene
c-2-butene	3-methylpentane	n-heptane	n-nonane	p-diethylbenzene
isopentane	2-methyl-1-Pentene	methylcyclohexane	isopropylbenzene	n-undecane

3. C_8 to C_{20} VOC samples acquired by glass cartridges filled with Tenax-TA (a polymer of 2,6-diphenyl-p-phenylene oxide) solid adsorbent. Samples were analyzed by the thermal desorption/cryogenic preconcentration method followed by high-resolution GC separation and flame ionization detection (FID) and/or combined MS/Fourier transform infrared (FTIR) detection for 63 VOCs:

1,2,4,5-tetramethylbenzene	1-methyl-3-ethylbenzene	1,3-di-n-propylbenzene	benzaldehyde
1(1,1-dimethylethyl)3-5-dimethylbenzene	1-methyl-4-ethylbenzene	2-methylnaphthalene	acetophenone
(1-methylethyl)benzene	4-methylindan	1-methylnaphthalene	2,5-dimethylbenzaldehyde
1-methyl-4-(1-methylethyl)benzene	2-methylindan	hexanal	ethanone-1(3-
1,4-diethylbenzene	5-methylindan	heptanal	methoxyphenol)
1,2-diethylbenzene	1,3-dimethyl-4-ethylbenzene	octanal	t-2,4-decadienal
1,3-diethylbenzene	1,2-dimethyl-3-ethylbenzene	nonanal	undecane
(1-methylpropyl)benzene	1,3-dimethyl-5-ethylbenzene	decanal	dodecane
1,2,3,4-tetramethylbenzene	1,2-dimethyl-4-ethylbenzene	undecanal	tridecane
2,3-dihydroindene (indan)	1-methyl-2-n-propylbenzene	dodecanal	tetradecane
1,2,3,5-tetramethylbenzene	1-methyl-3-n-propylbenzene	tridecanal	pentadecane
1-methyl-2-(1-methylethyl)benzene	1-methyl-4-n-propylbenzene	tetradecanal	hexadecane
1-methyl-3-(1-methylethyl)benzene	1-methyl-2-n-butylbenzene	pentadecanal	heptadecane
n-pentylbenzene	1,4-dimethyl-2-ethylbenzene	hexadecanal	octadecane
(2-methylpropyl)benzene	1,3-dimethyl-2-ethylbenzene	octadecanal	nonadecane
1-methyl-2-ethylbenzene	1-ethyl-2-n-propylbenzene	2-furaldehyde	eicosane

4. Carbonyl samples were acquired by carbonyl samplers containing dinitrophenylhydrazine (DNPH) cartridges, followed by high-performance liquid chromatography (HPLC) analysis of 14 carbonyls:

formaldehyde
acetaldehyde
acetone
acrolein
propanal
crotonal
methyl ethyl ketone
methacrolein
butanal
pentanal
glyoxal
hexanal
benzaldehyde and m-tolualdehyde

5. SVOCs and particulate organics acquired with a sampling train consisting of a Teflon-impregnated glass fiber filter backed up with a PUF/XAD-4/PUF sandwich solid adsorbent. Samples were analyzed by GC/MS for 151 SVOCs and particulate organic compounds:

Naphthalene
2-menaphthalene
1-menaphthalene
2,6+2,7-dimenaphthalene
1,7+1,3+1,6-dimenaphthalene
2,3+1,4+1,5-dimenaphthalene
1,2-dimenaphthalene
1,8-dimenapthalene
biphenyl
2-methylbiphenyl
3-methylbiphenyl
4-methylbiphenyl
trimethylnaphthalene Isomers
ethyl-Methylnaphthalenes
acenaphthylene
acenaphthene
phenanthrene
fluorene
methylfluorenes Isomers
1-methylfluorene
methylphenanthrenes Isomers
2-methylphenanthrene

4Hcyclopenta(def)phenanthren
benzo(c)phenanthrene
perylene
quinoline
dibenzo[a,e]pyrene
dibenzo[a,h]pyrene
dibenzo[a,i]pyrene
dibenzo[a,l]pyrene
dibenz[a,j]acridine
dibenz[a,h]acridine
7H-dibenzo[c,g]carbazole
5-methylchrysene
dibenz[a,h]anthracene
7,12-dimethylbenzanthracene
3-methylcholanthrene
oxy-PAH
9-fluorenone
xanthone
acenaphthenequinone
perinaphthenone
Anthraquinone
9-anthraldehyde

Hopanes&Steranes
18(H)-22,29,30-trisnorneohopane
17(H)-22,29,30-trisnorhopane
17(H)-21(H)-29-norhopane
17(H)-21(H)-hopane
20R,5(H),14 (H),17(H)-cholestane
20R,5(H),14(H),17(H)-cholestane
20R&S,5(H),14(H),17(H)-ergostane
20R&S,5(H),14(H),17(H)-sitostane

Carpanes
8, 13-dimethyl-14-n-butylpodocarpane
8, 13 dimethyl-14-[3'-methylbutyl] podocarpane
n-alkanoic Acids
octanoic acid
nonanoic acid
decanoic acid
undecanoic acid

Alkanes
n-pentadecane
n-hexadecane
n-heptadecane
n-octadecane
n-nonadecane
n-eicosane
n-heneicosane
n-docosane
n-tricosane
n-tetracosane
n-pentacosane
n-hexacosane
n-heptacosane
n-octacosane
farnesane
norpristane
norfarnesane
pristane
phytane

1-methylphenanthrene	benzanthrone	dodecanoic acid	Saturated Cycloalkanes
3,6-dimethylphenanthrene	benz(a)anthracene-7,12-dione	tridecanoic acid	
1,7-dimethylphenanthrene	1,4-chrysenequinone	tetradecanoic acid	tridecylcyclohexane
anthracene	9,10-dihydrobenzo(a)pyren-7(8H)-one	heptadecanoic acid	tetradecylcyclohexane
9-methylanthracene		octadecanoic acid	pentadecylcyclohexane
fluoranthene	nitro-PAH	nonadecanoic acid	hexadecylcyclohexane
pyrene	1-nitronaphthalene	eicosanoic acid	heptadecylcyclohexane
methylpyrene/fluoranthenes	2-nitronaphthalene	alkanedioic acids	octadecylcyclohexane
4-methylpyrene	methylnitronaphthalenes	octadecanedioic acid	nonadecylcyclohexane
retene	2-nitrobiphenyl	nonadecanedioic acid	
benzonaphthothiophene	4-nitrobiphenyl		Lower priority cycloalkanes
benz(a)anthracene	5-nitroacenaphthene	Aromatic acids	
7-methylbenz[a]anthracene	2-nitrofluorene	benzoic acid	heptylcyclohexane
chrysene/triphenylene	9-nitroanthracene	methylbenzoic acid	octylcyclohexane
benzo(b+j+k)FL	1-nitropyrene		nonylcyclohexane
BeP	4-nitropyrene		decylcyclohexane
BaP	3-nitrofluoranthene		undecylcyclohexane
7-methylbenzo[a]pyrene	7-nitrobenz(a)anthracene		dodecylcyclohexane
indeno[123-cd]pyrene	6-nitrochrysene		eicosylcyclohexane
dibenz(ah+ac)anthracene	6-nitrobenzo(a)pyrene		heneicosycyclohexane
benzo(b)chrysene	1,8-dinitropyrene		
benzo(ghi)perylene	1,6-dinitropyrene		
coronene	1,3-dinitropyrene		

4.2.2 Receptor Measurement Databases

Air quality monitoring networks in the U.S. are not designed for the application of receptor or source models (Demerjian, 2000). The major emphasis of networks is on NAAQS compliance rather than on the broader range of purposes that might include air quality forecasting, episode alerts, health studies, atmospheric process studies, evaluating source zones of influence, evaluating long-term effectiveness of control strategies, and source apportionment modeling (Chow et al. [2002b], U.S. EPA [2002]).

At least three levels of monitoring are needed:

- **Level III:** Portable, inexpensive filter and continuous sampling at a large number of locations with a minimum investment in site infrastructure and maintenance (Baldauf et al., 2001, 2002). Some accuracy and precision are traded for greater spatial coverage. Temporary, dense networks of this type surrounding Level I and Level II sites would establish the zones of representation for the permanent monitors.
- **Level II:** Fixed sites with proven technology, similar to compliance sites, but with observables and locations intended to serve the multiple purposes described above. Resources directed at urban sites that are no longer needed for compliance could be used to establish background, boundary, and transport sites.
- **Level I:** Fixed sites with proven, novel technology, similar to those of the U.S. EPA's current supersites program. These would have instrumentation similar to that of Level II and Level III sites to determine comparability, as well as detailed size distributions, PM chemistry, and precursor gases.

Special studies have been conducted to obtain data at representative receptors during periods when PM and/or VOC concentrations have been found to be excessive. Chow and Watson (1989), Lioy et al. (1980), and Watson and Chow (1992) summarize several chemically speciated data sets for suspended particles. The most complete chemical database to which receptor modeling can be applied is the IMPROVE network, which has acquired elemental, ionic, and carbon measurements at national parks and wilderness areas since 1987 (Eldred et al., 1989). The recently established STN may also be a source of data for receptor models in urban areas. The most comprehensive VOC data, derived from the PAMS, takes canister or continuous gas chromatographic measurements at urban and suburban sites during the summer.

4.2.3 Receptor Model Application Levels

There is no single sampling and analysis design that will permit successful receptor modeling in every urban area. Since measurements can be costly, it is useful to examine existing samples and data to assist in forming a conceptual model prior to designing a full-scale source apportionment study. Three sequential stages of complexity (U.S. EPA, 1984) can be applied, with each stage being progressively more costly, but providing more accurate and precise results than the previous stage.

Stage I uses existing data or data that can be readily obtained from analyses of existing samples (Gordon et al., 1984). Source profiles, related to local sources that were measured elsewhere, are also used. This effort confirms the selection of contributing sources from the preliminary analysis and eliminates minor contributors from further scrutiny. If the sources contributing to the high concentrations of PM or VOC are apparent and sufficiently certain, no further work will be needed. Alternatively, this step serves to reduce the areas to be studied in greater detail under an intermediate (Stage II) analysis.

Stage II involves additional chemical analyses on existing samples or the acquisition of additional samples from existing sampling sites. It is intended to fill the gaps in model input data that may have been discovered in Stage I, so as to reduce uncertainty in results of the Stage I source apportionment. This may require new source and ambient sampling activities. Local fugitive dust samples are acquired, resuspended, and analyzed, at a minimum. Ground-based vehicle exhaust and vegetative burning profiles may also be acquired. Industrial source profiles from other studies can often be adapted. C_2 to C_{12} hydrocarbons are measured for VOC apportionment studies, while elements, ions, and carbon are quantified for PM studies. Where additional sampling is possible, monitoring locations and times are selected to bracket suspected contributors.

Stage III analysis is applied only in the most complex airsheds, where the costs of emission reduction are high and their effectiveness is uncertain. A Stage III study involves original source testing and measurements beyond the basic PM or VOC species. C_{10} to C_{20} hydrocarbons and PM organic species are measured at source and receptor.

Many of the receptor modeling techniques described in Table 1 are appropriate for all three stages of PM or VOC assessment. Precision and validity estimates define the measurement requirements for the next level of analysis. These estimates can also be used to determine whether the model results at a given stage of PM or VOC assessment adequately eliminate the need for more extensive assessment.

4.3 Meteorological Variables

Concurrent with air quality measurements, meteorological measurements at the same or nearby locations are needed to better characterize the meteorological regimes affecting the sampled area. Meteorological measurements (typically at 10 meters above ground level) such as wind speed, wind direction, temperature, relative humidity, dew point, atmospheric pressure, cloud cover, solar radiation, mixing height, and precipitation are commonly used in principle component analysis (PCA) and factor analysis (FA). Temperature has been shown to be related to the intensity of photochemical reactions (Wolff and Lioy, 1978). Absolute humidity is related to the partial pressure of water vapor and can be associated with smog precursors. Inverse relative humidity is theoretically related to aerosol water content and is related to aerosol hydroscopic growth factors. Poor atmospheric dispersion (horizontal and vertical) is indicated by low wind speeds/mixing height and poor ventilation during cold winter periods. These variables are often correlated with atmospheric constituents that can also be used in time series and other receptor analyses. Nearby rawinsonde or radar profiler upper-air meteorology data can be used for backward air mass trajectory analysis (Draxler and Hess, 1997). These trajectories indicate the regions over which an air mass traveled, during the previous 12 to 120 hours, before arriving at the receptors.

4.4 Chemical Transformation Parameters

Appropriate gas and particle processes (Lewis and Stevens [1985], Watson et al. [2002b]) can be used for atmospheric "aging" of source profiles. "Aging" is assumed to occur in a confined "box" or "puff" from source to receptor along a trajectory path. Temperature, relative humidity, precursor gas concentrations, and particle composition affect changes in chemical abundances for different aging times. Watson et al. (2002a) provide an example of how to simulate changes in source profiles from nearby coal-fired power stations and how to use these aged profiles in receptor model applications for data acquired from the Mt. Zirkel Wilderness Area in northwestern Colorado. Watson et al. (1994b) also provide an example of the aerosol equilibrium model and the non-linearity of inorganic aerosol. These chemical transformation/equilibrium models require concurrent air quality and meteorological measurements of PM and their precursor gases such as NH_3, HNO_3, SO_2, HCl, VOC, temperature, and relative humidity. Shorter duration sampling of 1 to 6 hours is preferable to minimize the uncertainties of model simulation.

5 Receptor Model Assumptions, Performance Measures, and Validation Procedures

5.1 CMB Model Validation and Application Protocol

CMB software provides outputs and performance measures (Table 4) that can be adapted to other receptor models that follow the mass balance equations. The seven-step applications and validation protocol (Watson et al., 1998d) can also be applied to these receptor models (Watson, 2002c). The steps are: 1) determine the applicability of the receptor model; 2) format input files and perform initial model runs; 3) evaluate outputs and performance measures; 4) evaluate deviations from model assumptions; 5) modify model inputs to remediate problems; 6) evaluate the consistency and stability of the model results; and 7) corroborate receptor model results with other modeling and analyses. Elaborations are given below.

Table 4. Chemical mass balance (CMB) receptor model outputs and performance measures.

Output/Statistic/Code	Abbreviation	Description
Source Contribution Estimate	SCE	Contribution from the source type to the profile-normalizing component (usually PM mass or sum of PAMS VOCs).
Standard Error	STD ERR	The uncertainty of the source contribution estimate (SCE), expressed as one standard deviation of the most probable SCE. This is an indicator of the precision or certainty of each SCE. The STD ERR is estimated by propagating the precisions of the ambient measurements and source profiles through the effective variance least-squares calculations. Its magnitude is a function of the uncertainties in the input data and the amount of collinearity (i.e., degree of similarity) among source profiles. When the SCE is less than the STD ERR, the STD ERR is interpreted as an upper limit of the source contribution.
t-Statistic	TSTAT	Ratio of the SCE to its STD ERR. A high TSTAT suggests a non-zero SCE.
R-square	R-SQUARE	Variance in ambient species concentrations explained by the calculated species concentrations. A low R-SQUARE (<0.8) indicates that the selected source profiles have not accounted for the variance in the selected receptor concentrations. Ranges from 0 to 1.0.
Percent Mass Accounted For	PERCENT MASS (% MASS)	The sum of SCE divided by the PM mass or VOC concentration. A value approaching 100% is desired.

Output/Statistic/Code	Abbreviation	Description
Degrees of Freedom	DF	The number of species minus number of sources in fit. Solutions with larger degrees of freedom are typically more stable and robust than ones with small degrees of freedom.
Chi-square	CHI SQUARE	CHI SQUARE is the square root of the sum of the squares of the RATIO R/U that correspond to fitting species divided by the DF. Similar to R-SQUARE except that it also considers the uncertainties of the calculated species concentrations. A large CHI SQUARE (>4.0) means that one or more of the calculated species concentrations differ from the measured concentrations by several uncertainty intervals. The values for these statistics exceed their targets when: 1) contributing sources have been omitted from the calculation; 2) one or more source profiles have been selected which do not represent the contributing source types; 3) precisions of source profiles or ambient data are underestimated; and/or 4) source profiles or ambient data are inaccurate.
Ratio of Calculated to Measured Species	RATIO C/M	Ratio of calculated to measured concentrations and its uncertainty. Used to identify species that are over- or under-accounted for by the model. The ratios should be near 1.00 if the model has accurately explained the measured concentrations. Ratios that deviate from unity by more than two uncertainty intervals suggest that an incorrect set of profiles is being used to explain the measured concentrations.
Ratio of Residual to its Uncertainty	RATIO R/U	Ratio of the signed difference between the calculated and measured concentrations (i.e., the residual) divided by the uncertainty of that residual (i.e., square root of the sum of the squares of the uncertainty in the calculated and measured concentrations). Used to identify species that are over- or under-accounted for by the model. The RATIO R/U specifies the number of uncertainty intervals by which the calculated and measured concentrations differ. When the absolute value of the RATIO R/U exceeds two, the residual is significant. If it is positive, then one or more of the profiles is contributing too much to that species. If it is negative, then there is an insufficient contribution to that species and a source may be missing.

5.1.1 Determine the Receptor Model Applicability

The following conditions must be met for a receptor model to be applicable:

- A sufficient number of PM or VOC receptor samples have been taken with accepted sampling methods to fulfill study objectives. If objectives are to determine how to attain ambient air quality standards, samples should represent annual average and maximum concentrations for $PM_{2.5}$ and PM_{10}, and correspond to maximum 8-hour average ozone concentrations for VOCs. At least one ambient sample is needed for a CMB run, with the other methods in Table 1 requiring at least 50 to 100 ambient samples that encompass the variability of source contributions.
- Samples are amenable to or have been analyzed for a variety of chemical species. As noted above, elements, ions, and carbon are the minimal measurements for PM apportionment while the PAMS species listed in Table 3 are the minimal requirements for VOC apportionment.
- Potential source contributors can be identified and grouped into source types of distinct chemical compositions with respect to the available receptor species.
- Source profiles are available from the study area or from similar sources that represent the source compositions as they would appear at the receptors. Changes in source composition between source and receptor must be accommodated in order for the model to be physically meaningful.

5.1.2 Format Input Files and Perform Initial Model Runs

Modern receptor modeling software (Henry [2000], Hopke et al. [1983], Paatero [1998, 2000], Watson et al. [1997]) allows input data files to be prepared in spreadsheet or word processor formats and, with contemporary computer memories, there is no practical limit to the number of source profiles, chemical species, or individual samples that can be included in a single file. It is convenient, however, to group input data by site or season when data sets are large.

The initial model runs should include sensitivity tests (Watson et al., 1994b). For the CMB, this involves evaluating the effects of different combinations of source profiles and fitting species. For eigenvector, edge detection, and PMF models, this involves different selections of chemical species and subsets of the ambient samples, different selections of the number of factors, different rotation methods, and different settings for selectable variables.

In selecting source profiles for inclusion in a CMB or for associating a derived factor with a source type, wind direction data can be reviewed to disregard downwind sources that have little opportunity to contribute detectable concentrations. Source types that are likely to be dormant, such as wood smoke emissions during hot summer months, can also be eliminated, or they should be interpreted as wildfires or prescribed burning that might occur during that period.

Some sources have emissions that are chemically similar or consistent over time – that is, although the absolute magnitude of the emissions may vary, the abundances of the measured species may be stable. However, the chemistry of some species could be variable if an industrial source alternates its operating conditions, feedstock, or fuel. This variability must be reflected in the uncertainties that are assigned to each species abundance in the profile. These concerns about source profile variability are analogous to those faced by the dispersion modeler when estimating emission rates or dispersion parameters.

Because receptor models use the analytical results from all included species, mis-estimation of a single species, even so-called "tracer" species, may not appreciably affect the source contribution estimates. This is especially true if these species have been assigned and are inversely weighted by uncertainties, which reflect their variability in source emissions. When these uncertainties are adequately estimated, other less variable species abundances provide a larger influence on the source contribution estimates.

5.1.3 Evaluate Outputs and Performance Measures

Model outputs and performance measures are described in Table 4. These are examined for different combinations of profiles and species to determine the optimal fit to the data.

5.1.4 Evaluate Deviations from Model Assumptions

The performance measures and tests can often indicate when deviations from model assumptions may have occurred. These deviations do not necessarily invalidate the receptor model result, but they point out the potential for invalidity. This is why a separate step is necessary in the applications and validation protocol that evaluates the effects of these deviations from assumptions and determines whether these effects can be tolerated.

5.1.5 Modify Model Inputs to Remediate Problems

Receptor modeling results may be compromised by: 1) insufficient receptor measurements; 2) insufficient or non-representative source measurements; 3) incorrect profile combinations; and 4) source profile collinearity. Because of the complex interactions of all the data in a least squares estimate that occur in some CMB solutions (including the PMF solution), statistics or diagnostics may not always be adequate to conclusively isolate a problem with model input. Remedies for unacceptably high uncertainties due to collinearity include:

- Measure additional species that are abundant in one source, but not so abundant in other sources.

- Reduce the uncertainties in the source profiles of the collinear sources. This is applicable only if the uncertainties estimated for a composite profile are believed to be overestimated, owing to outliers in the compositing process.
- Combine the collinear source profiles into a single profile of a “composite source type” that chemically represents the source types identified by the estimable linear combinations of inestimable sources. For example, resuspended road dust and windblown soil dust are chemically similar, and some modelers include a single term to represent “crustal material” instead of the two individual source types. This aggregate source contribution estimate (SCE) might then be partitioned into its components by another method (e.g., source modeling, microscopy, or wind trajectory analysis).

5.1.6 Evaluate the Consistency and Stability of the Model Results

SCEs should not differ by more than two standard errors, with changes in input data (number of samples, number of species, and number of profiles). Portions of the input data may be perturbed randomly or systematically in proportion to their uncertainty. The sensitivity of SCEs to the species can be evaluated by eliminating and adding species to the calculation, and determining the change in source contributions.

5.1.7 Corroborate Receptor Model Results with Other Modeling and Analyses

The receptor analysis is considered valid if four criteria are met: 1) the receptor model is determined to be applicable; 2) the performance measures are generally within target ranges; 3) there are no significant deviations from model assumptions; and 4) the sensitivity tests reveal no unacceptable instabilities or inconsistencies. If uncertainties associated with source contributions are too high for decision-making purposes even after taking the steps recommended here, then the source compositions being used do not represent the sources in the airshed or they are too uncertain.

Source and receptor models may be used in a collaborative manner to perform an apportionment, provided that the source model is applicable and the receptor model is valid for the particular application. Spatial and time series distributions should be examined to determine that magnitudes of SCEs are consistent with the locations and timing expected from those sources.

5.2 Model Sensitivity Tests

An example of sensitivity testing for PM_{10} source apportionment along the Baja California, California (CA) border (Chow and Watson, 1997) is given in Table 5. Initial tests with different combinations of source profiles were done to determine which profiles best explained the data at the Calexico, CA, site. Several test CMB runs were performed for 24-hour samples collected on 12/02/92 with PM_{10} mass concentrations of 222.7 ± 11.2 $\mu g/m^3$. CMB performance measurements were examined to determine how well the ambient concentrations were explained by the SCEs. The results of these initial trials were used as guidance in CMB analysis of the entire sample set.

Based on the emission inventory and site survey, primary geological material, primary marine aerosol, salt flats or alkaline dust, primary vegetative burning, and primary motor vehicle sources were expected to be important contributors in the study area. Ambient measurements showed that high ambient concentrations of crustal species (e.g., aluminum, silicon, iron), marine and alkaline species (e.g., sodium, chloride), as well as OC, EC, and lead were observed. PM_{10} OC concentrations were enriched relative to EC in many samples. To account for this "excess" OC, either an agricultural burning profile, a charbroil cooking emission profile, or a composite of the two was used. Secondary ammonium nitrate and ammonium sulfate profiles explained NO_3^-, $SO_4^=$, and NH_4^+, which were unaccounted for by the primary emission profiles. Although soluble sodium was used in place of elemental sodium, magnesium was below the lower quantifiable limits (LQLs) in many of the source profiles. PM_{10} $SO_4^=$ was used in place of sulfur (S), and chloride (Cl^-) was used in place of chlorine (Cl), because the soluble fractions of these species are more typical of secondary sulfate and marine aerosol, or playa salt sources, than the total elemental fractions.

The test results of the source apportionments at each site are presented by a series of trials representing different combinations of source profiles in Table 5. The "best fit" or "default fit" is presented first as a reference. The SCEs and CMB performance measurements are shown for each trial.

Table 5 indicates that primary geological material was the largest contributor, followed by primary motor vehicle exhaust and vegetative burning emissions. The "best fit" was obtained using the Imperial County, CA, composite road dust profile (ICRDC) and the asparagus burning profile (ICABC2). While the Imperial County composite motor vehicle profile (ICRSC) produced a "good fit," the Mexicali, Mexico, motor vehicle profile (IMRSUC) gave better results because it accounted for more of the unusually high lead concentration (0.127 ± 0.0007 $\mu g/m^3$) in this sample. Meteorological data on 12/02/92 suggests that this sample was indeed impacted by cross-border transport.

Table 5. Example of sensitivity tests in chemical mass balance (CMB) receptor modeling (sample from Calexico, CA, on 12/02/94).

PROFILE[a]	BEST FIT	TRIAL 1	TRIAL 2	TRIAL 3	TRIAL 4	TRIAL 5	TRIAL 6
ICRDC (Road Dust)	143.6 ± 11.1	138.1 ± 11.1				136.0 ± 11.2	136.3 ± 13.4
ICBDC (Bulk Soil)			149.7 ± 15.6				
ICBD27 (Salt Flats)				74.5 ± 6.3			
IMRDC2 (Road Dust)					140.8 ± 6.6		
IMRSUC (Vehicle Exhaust)	18.1 ± 8.1						
ICRSBC (Vehicle Exhaust)		23.8 ± 7.4	33.6 ± 8.3	25.9 ± 10.1	27.0 ± 7.4		
ICRSC (Vehicle Exhaust)						36.6 ± 13.5	
ICRSHC (Vehicle Exhaust)							60.5 ± 12.0
ICRSIC3 (Vehicle Exhaust)							
ICRSIC2 (Vehicle Exhaust)							
MARIP (Marine Aerosol)	2.1 ± 1.3	2.2 ± 0.5	1.7 ± 2.5	-17.3 ± 3.0	2.0 ± 0.7	1.9 ± 0.6	1.4 ± 0.6
ICABC2 (Ag Burn)	30.2 ± 12.2	28.5 ± 11.6	17.7 ± 12.3	74.1 ± 20.4	24.0 ± 10.6	25.9 ± 12.2	14.4 ± 9.1
BAMAJC (Wood Stove)							
IMTSAC (Charbroiling)							
AB75TAL (Ag Burn/Cooking)							
ICPPMC (Power Station)							
IMGPEC (Glass Plant)							
AMSUL (Amm Sulfate)	4.2 ± 1.8	3.6 ± 1.6	2.0 ± 4.3	-15.9 ± 3.0	3.1 ± 1.1	2.6 ± 2.0	
AMNIT (Amm Nitrate)	17.6 ± 1.9	15.9 ± 2.1	14.9 ± 2.5	17.5 ± 2.4	15.7 ± 2.2	13.7 ± 5.0	1.2 ± 8.1
CHI SQUARE[b]	0.95	1.08	0.69	19.6	1.19	1.03	0.64
R SQUARE[b]	0.96	0.96	0.95	0.46	0.97	0.94	0.96
PERCENT MASS[b]	96.8	95.2	98.6	71.3	95.4	97.3	96.0
COLLINEARITY[c]			ICBDC ICABC2 ICRSBC	ICBD27 MAR100 AMSUL			ICRDC ICRSHC ICABC2

PROFILE[a]	TRIAL 7	TRIAL 8	TRIAL 9	TRIAL 10	TRIAL 11	TRIAL 12	TRIAL 13
ICRDC (Road Dust)	142.9 ± 12.1	142.0 ± 11.8	144.6 ± 11.3	147.2 ± 12.1	138.6 ± 11.2	137.7 ± 11.4	137.7 ± 11.2
ICBDC (Bulk Soil)							
ICBD27 (Salt Flats)							
IMRDC2 (Road Dust)							
IMRSUC (Vehicle Exhaust)							
ICRSBC (Vehicle Exhaust)			33.1 ± 11.5	44.4 ± 9.0	24.1 ± 7.6	23.9 ± 7.4	23.5 ± 7.4
ICRSC (Vehicle Exhaust)							
ICRSHC (Vehicle Exhaust)							
ICRSIC3 (Vehicle Exhaust)	32.5 ± 9.9						
ICRSIC2 (Vehicle Exhaust)		38.2 ± 19.1					
MARIP (Marine Aerosol)	2.4 ± 1.0	1.8 ± 0.8	3.3 ± 0.5	3.7 ± 0.6	2.2 ± 0.5	2.2 ± 0.5	2.1 ± 0.5
ICABC2 (Ag Burn)	20.6 ± 11.3	30.2 ± 14.4				28.2 ± 11.6	28.8 ± 11.7
BAMAJC (Wood Stove)			17.8 ± 12.0				
IMTSAC (Charbroiling)				-6.8 ± 14.9			
AB75TAL (Ag Burn/Cooking)					29.0 ± 12.4		
ICPPMC (Power Station)						0.26 ± 1.12	
IMGPEC (Glass Plant)							0.81 ± 0.62
AMSUL (Amm Sulfate)	3.0 ± 1.7	3.4 ± 1.9	3.3 ± 1.8	3.2 ± 1.8	3.6 ± 1.7	3.4 ± 1.8	3.2 ± 1.7
AMNIT (Amm Nitrate)	14.3 ± 3.1	16.8 ± 3.4	15.7 ± 2.5	15.1 ± 2.8	15.9 ± 2.1	15.9 ± 2.1	16.0 ± 2.1
CHI SQUARE[b]	ICRSIC3	ICRSIC2	ICRSBC	ICRSDC		AMSUL	AMSUL
R SQUARE[b]	ICABC2	ICABC2	BAMAJC	ICRSBC		AMNIT	AMNIT
PERCENT MASS[b]	AMSUL	ICRDC		IMTSAC		ICPPMC	IMAR100
COLLINEARITY[c]	AMNIT						IMGP15C

[a] See Chow and Watson (1997) for source profile descriptions.

[b] See Table 4 for details.

[c] Similar profiles representing subtypes that need to be combined into a single source type. Determined by the method of Henry (1992).

PM_{10} Na^+ and Cl^- concentrations were both present in elevated concentrations (1.13 ± 0.07 and 6.5 ± 0.4 μg/m^3, respectively). Because the Cl^-/Na^+ ratio is actually higher than ratios found in seawater, the "pure" unreacted marine profile (MARIP) was used to fit these species. The secondary ammonium nitrate profile (AMNIT) was the fourth largest component of PM_{10}, following the contributions from primary geological material (143.6 ± 11.1 μg/m^3), primary agricultural burning (30.2 ± 12.2 μg/m^3), and primary motor vehicle emissions (18.1 ± 8.1 μg/m^3).

The asparagus burning profile (ICABC2) was needed to fit OC, which had a concentration in this sample 5.6 times greater than that of EC. In the "best fit" case, the performance measurements, shown in Table 5, are excellent with a "CHI SQUARE" of 0.95, an "R-SQUARE" of 0.96, and a "PERCENT MASS" of 97%.

The first trial results in Table 5 were similar to the "best fit" solution except that an Imperial Valley motor vehicle profile (ICRSBC) was used. The major difference was a poorer fit for lead. In Trial 2, the Imperial County bulk soil profile (ICBDC) was substituted for the Imperial County road dust profile (ICRDC). This solution shows a potential collinearity among bulk soil composite (ICBDC), asparagus burning (ICABC2), and motor vehicle exhaust (ICRSBC) profiles, but the source contribution estimates are similar to those of the best fit solution.

For Trial 3, the bulk salt flats profile (ICBD27) was used by itself to represent fugitive dust contributions. The "CHI SQUARE" was high (19.6) and the "PERCENT MASS" was low (71.3%) in this case. The substitution of the Mexicali composite road dust profile (IMRDC2) for the "best fit" Imperial County road dust profile (ICRDC) caused little variation in the source contributions (Trial 4). This was also the case for Trial 5, where the Imperial County composite motor vehicle profile (ICRSC) was used, although less of the lead was accounted for in this case.

Substitution of the Imperial County motor vehicle profile with profile "ICRSHC" in Trial 6 resulted in a potential collinearity among road dust (ICRDC), motor vehicle exhaust (ICRSHC), asparagus burning (ICABC2), and ammonium nitrate (AMNIT) profiles. Similar results and higher "CHI SQUAREs" (2.21 and 2.64, respectively) were obtained by substituting the motor vehicle profiles with the profiles "ICRSIC3" and "ICRSIC2" in Trials 7 and 8, respectively.

Trial 1 combination was modified in Trial 9 by substituting the Bakersfield residential wood combustion (i.e., fireplace) profile (BAMAJC) for the asparagus burning profile (ICABC2). The solution is degraded, with a higher "CHI SQUARE" (3.54), lower "R-SQUARE" (0.88), and a potential collinearity among motor vehicle exhaust (ICRSBC) and residential wood combustion (BAMAJC). Substituting the taco restaurant charbroil cooking profile (IMTSAC) for the asparagus burning profile (ICABC2) produced a similar result, with potential collinearity among the road dust (ICRDC), motor vehicle exhaust (ICRSBS), and charbroil cooking (IMTSAC) profiles in Trial 10.

A composite profile (AB75TA25) constructed by combining 75% of asparagus burning (ICABC2) and 25% of charbroil cooking (IMTSCA) is tested in Trial 11. The results in this trial are similar to those obtained in Trial 1. The manure-fueled power plant profile (ICPPMC) was added to the Trial 1 combination in Trial 12. The SCEs from the manure-fueled power plant (ICPDMC) were not significant (0.26±1.12 $\mu g/m^3$) and a cluster was formed containing the ammonium sulfate (AMSUL), ammonium nitrate (AMNIT), and manure-fueled power plant (ICPPMC) profiles.

Finally, Trial 13 added the glass plant profile (IMGPEC) to the Trial 1 combination. Again, the SCEs from the glass plant (IMGPEC) were small (0.81 ± 0.62 $\mu g/m^3$), and this profile was potentially collinear with the ammonium sulfate (AMSUL), ammonium nitrate (AMNIT), and marine (MARIP) profiles. The "best fit" source combination provided a robust source apportionment because similar solutions were obtained using different combinations of profiles. The results shown in Table 5 for Trials 1, 4, 5, and 11 indicate similarly high performance indices and potential profile collinearities.

Therefore, the "best fit" solution shown in Table 5 is realistic, but the ICABC2 profile must be interpreted as a broader "vegetative burning" source that includes several source-types (e.g., agricultural field burning, backyard and trash burning, residential wood combustion, and restaurant charbroiler) rather than the asparagus field burning from which it was derived. SCEs calculated from either the charbroil cooking or asparagus burning source profile may represent more than any single source.

6 Summary and Conclusions

Receptor models are complementary to source models in that they infer source contributions from ambient concentrations, whereas source models estimate them from emissions. Agreement between the two independent models provides a weight of evidence in favor of the validity of both models. Disagreement points to areas where further measurements or more representative modeling is needed.

All multivariate receptor models are based on and are solutions to the CMB equations, which express ambient concentrations as a linear sum of source contributions and chemical abundances in those contributions. When there are substantial differences in the chemical abundances in the emissions, source contributions can be distinguished from each other with appropriate mathematical deconvolutions and simplifying assumptions. A wide variety of chemical and physical properties can be measured at source and receptor to distinguish one source type from another, but these measurements are not available from current compliance-oriented monitoring networks.

An application and validation protocol should be applied to all receptor model applications, including those that derive source profiles. This protocol includes performance measures and sensitivity tests that evaluate the extent to which simplifying assumptions are complied with, and how variability in the ambient and source measurements adds uncertainty to the source contribution estimates. Ultimately, the comparison between receptor and source models provides the most important estimate of the validity of both methods.

References

ACGIH (2001). *Air Sampling Instruments for Evaluation of Atmospheric Contaminants*, 9th ed., B.S. Cohen and C.S.J. McCammon, Eds. American Conference of Governmental Industrial Hygienists, Cincinnati, OH.

Ansari, A.S., and S.N. Pandis. 1998. Response of inorganic PM to precursor concentrations. *Environ. Sci. Technol.*, **32**(18):2706-2714.

Anttila, P., P. Paatero, U. Tapper and O. Järvinen. 1994. Application of positive matrix factorization to source apportionment: Results of a study of bulk deposition chemistry in Finland. *Atmos. Environ.*, **29**:1705-1718.

Ashbaugh, L.L. 1983. A statistical trajectory technique for determining air pollution source regions. *J. Air Pollution Control Assoc.*, **33**(11):1096-1098.

Ashbaugh, L.L., O.F. Carvacho, M.S. Brown, J.C. Chow, J.G. Watson and K.L. Magliano. 2003. Soil sample collection and analysis for the Fugitive Dust Characterization Study. *Atmos. Environ.*, **37**(9-10):1163-1173. doi: 10.1016/S1352-2310(02)01022-1.

Baldauf, R.W., D.D. Lane, G.A. Marotz and R.W. Wiener. 2001. Performance evaluation of the portable MiniVol particulate matter sampler. *Atmos. Environ.*, **35**:6087-6091.

Baldauf, R.W., R.W. Wiener and D.K. Heist. 2002. Methodology for siting ambient air monitors at the neighborhood scale. *J. Air & Waste Manage. Assoc.*, **52**(12):1433-1442.

Baron, P.A., and K. Willeke. 2001. *Aerosol Measurement: Principles, Techniques and Applications*, 2nd ed., P.A. Baron and K. Willeke, Eds. John Wiley & Sons, New York, NY.

Bishop, C.M. 1995. *Neural Networks for Pattern Recognition*. Clarendon Press, Oxford, UK.

Blanchard, C.L., P.M. Roth, S.J. Tanenbaum, S.D. Ziman and J.H. Seinfeld. 2000. The use of ambient measurements to identify which precursor species limit aerosol nitrate formation. *J. Air & Waste Manage. Assoc.*, **50**(12):2073-2084.

Blanchard, C.L., and G.M. Hidy. 2003. Effects of changes in sulfate, ammonia, and nitric acid on particulate nitrate concentrations in the southeastern United States. *J. Air & Waste Manage. Assoc.*, **53**(3):283-290.

Blifford, I.H., and G.O. Meeker. 1967. A factor analysis model of large scale pollution. *Atmos. Environ.*, **1**:147-157.

Brook, J.R., E. Vega and J.G. Watson. 2003. Chapter 7: Receptor methods. In *Particulate Matter Science for Policy Makers, A NARSTO Assessment, Part 2*. NARSTO, Pasco, WA, pp. 7-1-7-48.

California Air Resources Board. 2000. EMFAC2000 emission factor model, release 2.02. California Air Resources Board, Sacramento, CA. http://www.arb.ca.gov/msei/msei.htm.

Chelani, A.B., D.G. Gajghate and M.Z. Hasan. 2002. Prediction of ambient PM_{10} and toxic metals using artificial neural networks. *J. Air & Waste Manage. Assoc.*, **52**(7):805-810.

Chow, J.C. (1985). *A composite modeling approach to assess air pollution source/receptor relationships.* Sc.D. Dissertation, Harvard University, Cambridge, MA.

Chow, J.C., and J.G. Watson. 1989. Summary of particulate data bases for receptor modeling in the United States. In *Transactions, Receptor Models in Air Resources Management*, J.G. Watson, Ed. Air & Waste Management Association, Pittsburgh, PA, pp. 108-133.

Chow, J.C., J.G. Watson, L.C. Pritchett, W.R. Pierson, C.A. Frazier and R.G. Purcell. 1993. The DRI Thermal/Optical Reflectance carbon analysis system: Description, evaluation and applications in U.S. air quality studies. *Atmos. Environ.*, **27A**(8):1185-1201.

Chow, J.C. (1995). Critical review "Measurement methods to determine compliance with ambient air quality standards for suspended particles". *J. Air & Waste Manage. Assoc.*, **45**(5):320-382.

Chow, J.C., and J.G. Watson. 1997. Imperial Valley/Mexicali Cross Border PM_{10} Transport Study. Report No. 4692.1D1. Prepared for U.S. Environmental Protection Agency, Region IX, San Francisco, CA, by Desert Research Institute, Reno, NV.

Chow, J.C., J.G. Watson, D. Crow, D.H. Lowenthal and T. Merrifield. 2001. Comparison of IMPROVE and NIOSH carbon measurements. *Aerosol Sci. Technol.*, **34**(1):23-34.

Chow, J.C., and J.G. Watson. 2002a. Review of $PM_{2.5}$ and PM_{10} apportionment for fossil fuel combustion and other sources by the chemical mass balance receptor model. *Energy & Fuels*, **16**(2):222-260. doi: 10.1021/ef0101715.

Chow, J.C., and J.G. Watson. 2002b. $PM_{2.5}$ carbonate concentrations at regionally representative Interagency Monitoring of Protected Visual Environment sites. *J. Geophys. Res.*, **107**(D21):ICC 6-1-ICC 6-9. doi: 10.1029/2001JD000574.

Chow, J.C., J.D. Bachmann, S.S.G. Wierman, C.V. Mathai, W.C. Malm, W.H. White, P.K. Mueller, N. Kumar and J.G. Watson. 2002a. 2002 Critical review discussion - Visibility: Science and regulation. *J. Air & Waste Manage. Assoc.*, **52**(9):973-999.

Chow, J.C., J.P. Engelbrecht, J.G. Watson, W.E. Wilson, N.H. Frank and T. Zhu. 2002b. Designing monitoring networks to represent outdoor human exposure. *Chemosphere*, **49**(9):961-978.

Chow, J.C., J.G. Watson, L.L. Ashbaugh and K.L. Magliano. 2003. Similarities and differences in PM_{10} chemical source profiles for geological dust from the San Joaquin Valley, California. *Atmos. Environ.*, **37**(9-10):1317-1340. doi: 10.1016/S1352-2310(02)01021-X.

Chow, J.C., J.G. Watson, L.W. Chen, W.P. Arnott, H. Moosmüller and K.K. Fung, K.K., 2004a. Equivalence of elemental carbon by Thermal/Optical Reflectance and Transmittance with different temperature protocols. *Environ. Sci. Technol.*, **38**(16):4414-4422.

Chow, J.C., J.G. Watson, H.D. Kuhns, V. Etyemezian, D.H. Lowenthal, D. Crow, S.D. Kohl, J.P. Engelbrecht and M.C. Green. 2004b. Source profiles for industrial, mobile, and area sources in the Big Bend Regional Aerosol Visibility and Observational (BRAVO) Study. *Chemosphere*, **54** (2): 185-208.

Cooper, J.A., and J.G. Watson. 1980. Receptor oriented methods of air particulate source apportionment. *J. Air Pollution Control Assoc.*, **30**(10):1116-1125.

Dams, R., J.A. Robbins, K.A. Rahn and J.W. Winchester. 1971. Quantitative relationships among trace elements over industrialized N.W. Indiana. In *Nuclear Techniques in Environmental Pollution*. International Atomic Energy Agency, Vienna, Austria, pp. 139-145.

Demerjian, K.L. 2000. A review of national monitoring networks in North America. *Atmos. Environ.*, **34**(12-14):1861-1884.

Draxler, R.R., and G.D. Hess. 1997. Description of the HYSPLIT_4 Modeling System. *Report No. NOAA Technical Memorandum ERL ARL-224*. National Oceanic and Atmospheric Administration, Air Resources Laboratory, Silver Spring, MD. http://www.arl.noaa.gov/data/models/hysplit4/win95/arl-224.pdf.

Draxler, R.R. 1999. HYSPLIT User's Guide. *Report No. NOAA Technical Memorandum ERL ARL-230*. National Oceanic and Atmospheric Administration, Air Resources Laboratory, Silver Spring, MD. http://www.arl.noaa.gov/data/models/hysplit4/win95/user_man.pdf.

Eldred, R.A., T.A. Cahill, L.K. Wilkinson, P.J. Feeney and W.C. Malm.1989. Particulate characterization at remote sites across the U.S.: First year results of the NPS/IMPROVE Network. In 82nd Annual Meeting of the Air & Waste Management Association, Anaheim, CA.

England, G.C., B. Zielinska, K. Loos, I. Crane and K. Ritter. 2000. Characterizing $PM_{2.5}$ emission profiles for stationary sources: Comparison of traditional and dilution sampling techniques. *Fuel Processing Technology*, **65**:177-188.

Fujita, E.M., B.E. Croes, C.L. Bennett, D.R. Lawson, F.W. Lurmann and H.H. Main. 1992. Comparison of emission inventory and ambient concentration ratios of CO, NMOG, and NOx in California's South Coast Air Basin. *J. Air & Waste Manage. Assoc.*, **42**(3):264-276.

Fujita, E.M., J.G. Watson, J.C. Chow and Z. Lu. 1994. Validation of the chemical mass balance receptor model applied to hydrocarbon source apportionment in the Southern California Air Quality Study. *Environ. Sci. Technol.*, **28**(9):1633-1649.

Fujita, E.M., J.G. Watson, J.C. Chow and K.L. Magliano. 1995. Receptor model and emissions inventory source apportionments of nonmethane organic gases in California's San Joaquin Valley and San Francisco Bay Area. *Atmos. Environ.*, **29**(21):3019-3035.

Gao, N., M.D. Cheng and P.K. Hopke. 1994. Receptor modeling of airborne ionic species collected in SCAQS, 1987. *Atmos. Environ.*, **28**(8):1447-1470.

Gatz, D.F., G.J. Stensland, M.V. Miller and A.C.D. Leslie. 1981. Sources of airborne calcium in rural central Illinois. In *Atmospheric Aerosol: Source/Air Quality Relationships*, E.S. Macias and P.K. Hopke, Eds. American Chemical Society, Washington, DC, pp. 303-325.

Gether, J., and H.M. Seip. 1979. Analysis of air pollution data by the combined use of interactive graphic presentation and a clustering technique. *Atmos. Environ.*, **13**:87-96.

Godleski, J.J., R.L. Verrier, P. Koutrakis and P. Catalano. 2000. Mechanisms of morbidity and mortality from exposure to ambient air particles. *Report No. 91*. Health Effects Institute (HEI), Cambridge, MA.

Gordon, G.E. 1980. Receptor models. *Environ. Sci. Technol.*, **14**:792-800.

Gordon, G.E., W.R. Pierson, J.M. Daisey, P.J. Lioy, J.A. Cooper, J.G. Watson and G.R. Cass. 1984. Considerations for design of source apportionment studies. *Atmos. Environ.*, **18**(8):1567-1582.

Gordon, G.E. 1988. Receptor models. *Environ. Sci. Technol.*, **22**(10):1132-1142.

Green, M.C., K.A. Gebhart. 1997. Clean air corridors: A geographic and meteorologic characterization. *J. Air & Waste Manage. Assoc.*, **47**(3):403-410.

Henry, R.C., and G.M.Hidy. 1982. Multivariate analysis of particulate sulfate and other air quality variables by principal components - Part II, Salt Lake City, Utah and St. Louis, Missouri. *Atmos. Environ.*, **16**:929-943.

Henry, R.C., C.W. Lewis, P.K. Hopke and B.J. Williamson. 1984. Review of receptor model fundamentals. *Atmos. Environ.*, **18**(8):1507-1515.

Henry, R.C. 1987. Current factor analysis receptor models are ill-posed. *Atmos. Environ.*, **21**(8):1815-1820.

Henry, R.C., Y.J. Wang and K.A. Gebhart. 1991. The relationship between empirical orthogonal functions and sources of air pollution. *Atmos. Environ.*, **25A**(2):503-509.

Henry, R.C. 1992. Dealing with near collinearity in chemical mass balance receptor models. *Atmos. Environ.*, **26A**(5):933-938.

Henry, R.C. 1997. History and fundamentals of multivariate air quality receptor models. *Chemom. Intell. Lab. Sys.*, **37**(1):37-42.

Henry, R.C., C.H. Spiegelman, J.F. Collins and E.S. Park. 1997. Reported emissions of organic gases are not consistent with observations. *Proc. Natl. Acad. Sci. USA*, **94**:6596-6599.

Henry, R.C., Y. Mi and W. Moran. 1999. Multivariate receptor modeling of SCAQS VOC and airborne particle composition data. Report No. ARB-R-99/683; ARB-A832-131. Prepared for California State Air Resources Board, Sacramento, CA, by University of Southern California, Los Angeles, CA.

Henry, R.C. 2000. *UNMIX Version 2 Manual*. Ronald C. Henry, Ph.D., West Hills, CA.

Henry, R.C. 2002. Multivariate receptor models - Current practice and future trends. *Chemom. Intell. Lab. Sys.*, **60**(1-2):43-48. doi:10.1016/S0169-7439(01)00184-8.

Hidy, G.M., and S.K. Friedlander. 1971. The nature of the Los Angeles aerosol. In *Proceedings of the Second International Clean Air Congress*, H.M. Englund and W.T. Beery, Eds. Academic Press, New York, pp. 391-404.

Hies, T., R. Treffeisen, L. Sebald and E. Reimer. 2000. Spectral analysis of air pollutants Part 1. Elemental carbon time series. *Atmos. Environ.*, **34**(21):3495-3502.

Hopke, P.K., E.S. Gladney, G.E. Gorden, W.H. Zoller and A.G. Jones. 1976. The use of multivariate analysis to identify sources of selected elements in Boston urban aerosol. *Atmos. Environ.*, **10**:1015-1025.

Hopke, P.K., and S.L. Dattner. 1982. *Receptor Models Applied to Contemporary Pollution Problems*. Air & Waste Management Association, Pittsburgh, PA.

Hopke, P.K., D.J. Alpert and B.A. Roscoe. 1983. FANTASIA - A program for target transformation factor analysis to apportion sources in environmental samples. *Computers & Chem.*, **7**(3):149-155.

Hopke, P.K. 1985. *Receptor Modeling in Environmental Chemistry*. John Wiley & Sons, Inc., New York.

Hopke, P.K. 1988. Target transformation factor analysis as an aerosol mass apportionment method: A review and sensitivity study. *Atmos. Environ.*, **22**(9):1777-1792.

Hopke, P.K. 1991. *Receptor Modeling for Air Quality Management*, P.K. Hopke, Ed. Elsevier Press, Amsterdam, The Netherlands.

Hopke, P.K. 1999. An introduction to source receptor modeling. In *Elemental Analysis of Airborne Particles*, S. Landsberger and M. Creatchman, Eds. Gordon and Breach Science, Amsterdam, pp. 273-315.

Hopke, P.K. 2003. Recent developments in receptor modeling. *J. Chemometrics*, **17**(5):255-265.

Hopke, P.K., Z. Ramadan, P. Paatero, G.A. Norris, M.S. Landis, R.W. Williams and C.W. Lewis. 2003. Receptor modeling of ambient and personal exposure samples: 1998 Baltimore Particulate Matter Epidemiology-Exposure Study. *Atmos. Environ*., **37**(23):3289-3302. doi: 10.1016/S1352-2310(03)00331-5.

Javitz, H.S., and J.G. Watson. 1988. Feasibility study of receptor modeling for apportioning utility contributions to air constituents, deposition quality and light extinction. Prepared for Electric Power Research Institute, Palo Alto, CA, by SRI International, Menlo Park, CA.

Javitz, H.S., J.G. Watson, J.P. Guertin and P.K. Mueller. 1988. Results of a receptor modeling feasibility study. *J. Air Pollution Control Assoc.*, **38**(5):661-667.

Jorquera, H., W. Palma and J. Tapia. 2000. An intervention analysis of air quality data at Santiago, Chile. *Atmos. Environ.*, **34**(24):4073-4084.

Kleinman, M.T., B.S. Pasternack, M. Eisenbud and T.J. Kneip. 1980. Identifying and estimating the relative importance of sources of airborne particulates. *Environ. Sci. Technol*., **14**(1):62-65.

Kim, E. and P.K. Hopke., 2004. Source apportionment of fine particles at Washington, DC, utilizing temperature-resolved carbon fractions. *J. Air & Waste Manage. Assoc.*, **54**(7):773-785.

Kim, E., P.K. Hopke, and E.S. Edgerton. 2004. Improving source identification of Atlanta aerosol using temperature resolved carbon fractions in positive matrix factorization. *Atmos. Enviro.*, **38**(20):3349-3362.

Landsberger, S., and M. Creatchman. 1999. *Elemental Analysis of Airborne Particles*, S. Landsberger and M. Creatchman, Eds. Gordon and Breach, Newark, NJ.

Lewis, C.W., and R.K. Stevens. 1985. Hybrid receptor model for secondary sulfate from an SO2 point source. *Atmos. Environ.*, **19**(6):917-924.

Lioy, P.J., J.G. Watson and J.D. Spengler. 1980. APCA specialty conference workshop on baseline data for inhalable particulate matter. *J. Air Pollution Control Assoc.*, **30**(10):1126-1130.

Lioy, P.J., R.P. Mallon, M. Lippmann, T.J. Kneip and P.J. Samson. 1982. Factors affecting the variability of summertime sulfate in a rural area using principal component analysis. *J. Air Pollution Control Assoc.*, **32**(10):1043-1047.

Malm, W.C., and K.A. Gebhart. 1997. Source apportionment of sulfur and light extinction using receptor modeling techniques. *J. Air & Waste Manage. Assoc.*, **47**(3):250-268.

Malm, W.C., M.L. Pitchford, M. Scruggs, J.F. Sisler, R.G. Ames, S. Copeland, K.A. Gebhart and D.E. Day. 2000. Spatial and seasonal patterns and temporal variability of haze and its constituents in the United States: *Report III*. *Report No. ISSN: 0737-5352-47*. Cooperative Institute for Research in the Atmosphere, Colorado State University, Ft. Collins, CO. http://vista.cira.colostate.edu/IMPROVE/Publications/improve_reports.htm.

Malm, W.C., B.A. Schichtel, R.B. Ames and K.A. Gebhart. 2002. A ten-year spatial and temporal trend of sulfate across the United States. *J. Geophys. Res.*, **107**(D22):ACH 11-1-ACH 11-20. doi:10.1029/2002JD002107.

McMurry, P.H. 2000. A review of atmospheric aerosol measurements. *Atmos. Environ*. **34** (12-14):1959-1999.

Mendoza-Dominguez, A., and A.G. Russell. 2000. Iterative inverse modeling and direct sensitivity analysis of a photochemical air duality model. *Environ. Sci. Technol.*, **34**(23):4974-4981.

Middlebrook, A.M., D.M. Murphy, S.H. Lee, D.S. Thompson, K.A. Prather, R.J. Wenzel, D.Y. Liu, D.J. Phares, K.P. Rhoads, A.S. Wexler, M.V. Johnston, J.L. Jimenez, J.T. Jayne, D.R Worsnop, I. Yourshaw, J.H. Seinfeld and R.C. Flagan, R.C. 2003. A comparison of particle mass spectrometers during the 1999 Atlanta Supersite Project. *J. Geophys. Res.*, **108**(D7):SOS 12-1-SOS 12-13.

Morandi, M.T., P.J. Lioy and J.M. Daisey. 1991. Comparison of two multivariate modeling approaches for the source apportionment of inhalable particulate matter in Newark, NJ. *Atmos. Environ.*, **25A**(5/6):927-937.

Motelay-Massei, A., D. Ollivon, B. Garban and M. Chevreuil. 2003. Polycyclic aromatic hydrocarbons in bulk deposition at a suburban site: assessment by principle component analysis of the influence of meteorological parameters. *Atmos. Environ.*, **37**(22):3135-3146.

Mueller, P.K., G.M. Hidy, R.L. Baskett, K.K. Fung, R.C. Henry, T.F. Lavery, N.J. Nordi, A.C. Lloyd, J.W. Thrasher, K.K. Warren and J.G. Watson. 1983. Sulfate Regional Experiment (SURE): Report of findings. *Report No. EA-1901*. Electric Power Research Institute, Palo Alto, CA.

Murphy, B.L. 2000. Allocation by contribution to cost and risk at superfund sites. *Environ. Forensics*, **1**(3):117-120.

Paatero, P., and U. Tapper. 1994. Positive matrix factorization: A non-negative factor model with optimal utilization of error estimates of data values. *Environmetrics*, **5**:111-126.

Paatero, P. 1998. User's guide for positive matrix factorization programs PMF2 and PMF3 *Part 1: Tutorial*. University of Helsinki, Helsinki, Finland.

Paatero, P. 2000. User's guide for positive matrix factorization programs PMF2 and PMF3 *Part 2: Reference*. University of Helsinki, Helsinki, Finland.

Pace, T.G. 1986. *Transactions, Receptor Methods for Source Apportionment: Real World Issues and Applications*, T.G. Pace, Ed. Air Pollution Control Association, Pittsburgh, PA.

Pena-Mendez, E.M., M.S. Astorga-Espana and F.J. Garca-Montelongo. 2001. Chemical fingerprinting applied to the evaluation of marine oil pollution in the coasts of Canary Islands (Spain). *Environ. Poll.*, **111**(2):177-187.

Perrier, V., T. Philipovitch and C. Basdevant. 1995. Wavelet spectra compared to Fourier spectra. *J. Math. Phys.*, **36**(3):1506-1519.

Pitchford, M.L., M.C. Green, H.D. Kuhns, I.H. Tombach, W.C. Malm, M. Scruggs, R.J. Farber, V.A. Mirabella, W.H. White, C. McDade, J.G. Watson, D. Koracin, T.E. Hoffer, D.H. Lowenthal, J.C. Vimont et al. 1999. Project MOHAVE, Final Report. U.S. Environmental Protection Agency, Region IX, San Francisco, CA. http://www.epa.gov/region09/air/mohave/report.html.

Poirot, R.L., P.R. Wishinski, P.K. Hopke and A.V. Polissar. 2002. Errata: Comparative application of multiple receptor methods to identify aerosol sources in northern Vermont (vol. 35, pg 4622, 2001). *Environ. Sci. Technol.*, **36**(4):820.

Pun, B.K., and C. Seigneur. 1999. Understanding particulate matter formation in the California San Joaquin Valley: Conceptual model and data needs. *Atmos. Environ.*, **33**(29):4865-4875.

Reimann, C., and P. de Caritat. 2000. Intrinsic flaws of element enrichment factors (EFs) in environmental geochemistry. *Environ. Sci. Technol.*, **34**(24):5084-5091.

Rogge, W.F., L.M. Hildemann, M.A. Mazurek, G.R. Cass and B.R.T. Simoneit. 1996. Mathematical modeling of atmospheric fine particle-associated primary organic compound concentrations. *J. Geophys. Res.*, **101**:19379-19394.

Saucy, D.A., J.R. Anderson and P.R. Buseck. 1987. Cluster analysis applied to atmospheric aerosol samples from the Norwegian Arctic. *Atmos. Environ*., **21**:1649-1657.

Seinfeld, J.H., and S.N. Pandis. 1998. *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*. John Wiley & Sons, New York, NY.

Sims, R.C., and J.L. Sims. 1995. Chemical mass-balance approach to field-evaluation of bioremediation. *Environ. Prog.*, **14**(1):F2-F3.

Somerville, M.C., and E.G. Evans. 1995. Effect of sampling frequency on trend detection for atmospheric fine mass. *Atmos. Environ.*, **29**(18):2429-2438.

Stelson, A.W., and J.H. Seinfeld. 1982. Relative humidity and temperature dependence of the ammonium nitrate dissociation constant. *Atmos. Environ*., **16**(5):983-992.

Stockwell, W.R., H. Geiger and K.H. Becker. 2001. Estimation of incremental reactivities for multiple day scenarios: An application to ethane and dimethyoxymethane. *Atmos. Environ.*, **35**:929-939.

Stout, S.A., A.D. Uhler and K.J. McCarthy. 2001. A strategy and methodology for defensibly correlating spilled oil to source candidates. *Environ. Forensics*, **2**(1):87-98.

Thurston, G.D., and J.D. Spengler. 1985. A quantitative assessment of source contributions to inhalable particulate matter pollution in metropolitan Boston. *Atmos. Environ.*, **19**(1):9-25.

U.S. EPA. 1984. Receptor model technical series, vol. V: Source apportionment techniques and considerations in combining their use. *Report No. EPA-450/4-84-020*. U. S. Environmental Protection Agency, Research Triangle Park, NC.

U.S. EPA. 1996. *Method 202 - Determination of condensable particulate emissions from stationary sources*. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Technical Support Division, Research Triangle Park, NC. http://www.epa.gov/ttn/emc/promgate/m-202.pdf.

U.S. EPA. 1997. *Method 201A - Determination of PM_{10} emissions (constant sampling rate procedure)*. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Technical Support Division, Research Triangle Park, NC. http://www.epa.gov/ttn/emc/promgate/m-201a.pdf.

U.S. EPA. 1999. *SPECIATE: EPA's repository of total organic compound and particulate matter speciated profiles for a variety of sources for use in source apportionment studies.* U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC. http://www.epa.gov/ttn/chief/software/speciate/.

U.S. EPA. 2001a. *Draft guidance for demonstrating attainment of air quality goals for $PM_{2.5}$ and regional haze*. U.S. Environmental Protection Agency, Research Triangle Park, NC. http://vistas-sesarm.org/tech/draftpm.pdf.

U.S. EPA. 2001b. *PAMS information.* U.S. Environmental Protection Agency, Research Triangle Park, NC. http://www.epa.gov/ttn/amtic/pams.html.

U.S. EPA. 2002. *National ambient air monitoring strategy (Second draft).* U.S. Environmental Protection Agency, Research Triangle Park, NC. http://www.epa.gov/ttn/amtic/files/ambient/monitorstrat/compms.pdf.

Wang, J.L., C.J. Chang, W.D. Chang, C. Chew and S.W. Chen. 1999. Construction and evaluation of automated gas chromatography for the measurement of anthropogenic halocarbons in the atmosphere. *J. Chromatogr.*, **844**:259-269.

Watson, J.G. 1979. *Chemical element balance receptor model methodology for assessing the sources of fine and total suspended particulate matter in Portland, Oregon*. Ph.D. Dissertation, Oregon Graduate Center, Beaverton, OR.

Watson, J.G., R.C. Henry, J.A. Cooper and E.S. Macias. 1981. The state of the art of receptor models relating ambient suspended particulate matter to sources. In *Atmospheric Aerosol: Source/Air Quality Relationships*, E.S. Macias and P.K. Hopke, Eds. American Chemical Society, Washington, DC, pp. 89-106.

Watson, J.G. 1984. Overview of receptor model principles. *J. Air Pollution Control Assoc.*, **34**(6):619-623.

Watson, J.G., J.A. Cooper and J.J. Huntzicker. 1984. The effective variance weighting for least squares calculations applied to the mass balance receptor model. *Atmos. Environ.*, **18**(7):1347-1355.

Watson, J.G., J.C. Chow and C.V. Mathai. 1989. Receptor models in air resources management: A summary of the APCA International Specialty Conference. *J. Air Pollution Control Assoc.*, **39**(4):419-426.

Watson, J.G., J.C. Chow and T.G. Pace. 1991. Chemical mass balance. In *Receptor Modeling for Air Quality Management*, P.K. Hopke, Ed. Elsevier Press, New York, NY, pp. 83-116.

Watson, J.G., and J.C. Chow. 1992. Data bases for PM_{10} and $PM_{2.5}$ chemical compositions and source profiles. In *Transactions, PM_{10} Standards and Nontraditional Particulate Source Controls*, J.C. Chow and D.M. Ono, Eds. Air & Waste Management Association, Pittsburgh, PA, pp. 61-91.

Watson, J.G., J.C. Chow, F.W. Lurmann and S. Musarra. 1994a. Ammonium nitrate, nitric acid, and ammonia equilibrium in wintertime Phoenix, Arizona. *J. Air & Waste Manage. Assoc.*, **44**(4):405-412.

Watson, J.G., J.C. Chow, Z. Lu, E.M. Fujita, D.H. Lowenthal and D.R. Lawson. 1994b. Chemical mass balance source apportionment of PM_{10} during the Southern California Air Quality Study. *Aerosol Sci. Technol.*, **21**(1):1-36.

Watson, J.G., N.F. Robinson, C.W. Lewis, C.T. Coulter, J.C. Chow, E.M. Fujita, D.H. Lowenthal, T.L. Conner, R.C. Henry and R.D. Willis. 1997. *Chemical mass balance receptor model version 8 (CMB) user's manual.* Prepared for U.S. Environmental Protection Agency, Research Triangle Park, NC, by Desert Research Institute, Reno, NV. ftp://eafs.sage.dri.edu/cmb80/model/.

Watson, J.G., E.M. Fujita, J.C. Chow, B. Zielinska, L.W. Richards, W.D. Neff and D. Dietrich. 1998a. *Northern Front Range Air Quality Study. Final report.* Prepared for Colorado State University, Fort Collins, CO, by Desert Research Institute, Reno, NV. http://charon.cira.colostate.edu/DRIFinal/ZipFiles/.

Watson, J.G., D.W. DuBois, R. DeMandel, A.P. Kaduwela, K.L. Magliano, C. McDade, P.K. Mueller, A.J. Ranzieri, P.M. Roth and S. Tanrikulu. 1998b. *Field program plan for the California Regional $PM_{2.5}$/PM_{10} Air Quality Study (CRPAQS).* Prepared for California Air Resources Board, Sacramento, CA, by Desert Research Institute, Reno, NV. http://sparc2.baaqmd.gov/centralca/publications.htm.

Watson, J.G., J.C. Chow, H. Moosmüller, M.C. Green, N.H. Frank and M.L. Pitchford. 1998c. Guidance for using continuous monitors in $PM_{2.5}$ monitoring networks . *Report No. EPA-454/R-98-012*. Prepared for U.S. Environmental Protection Agency, Research Triangle Park, NC, by Desert Research Institute, Reno, NV. http://www.epa.gov/ttn/amtic/pmpolgud.html.

Watson, J.G., N.F. Robinson, C.W. Lewis, C.T. Coulter, J.C. Chow, E.M. Fujita, T.L. Conner and T.G. Pace. 1998d. CMB8 applications and validation protocol for $PM_{2.5}$ and VOCs. *Report No. 1808.2D1.* Prepared for U.S. Environmental Protection Agency, Research Triangle Park, NC, by Desert Research Institute, Reno, NV.

Watson, J.G., and J.C. Chow. 2001a. Estimating middle-, neighborhood-, and urban-scale contributions to elemental carbon in Mexico City with a rapid response aethalometer. *J. Air & Waste Manage. Assoc.*, **51**(11):1522-1528.

Watson, J.G., and J.C. Chow. 2001b. Source characterization of major emission sources in the Imperial and Mexicali valleys along the U.S./Mexico border. *Sci. Total Environ.*, **276**(1-3):33-47.

Watson, J.G., J.C. Chow and E.M. Fujita. 2001a. Review of volatile organic compound source apportionment by chemical mass balance. *Atmos. Environ.*, **35**(9):1567-1584. ftp://ftp.cgenv.com/pub/downloads/Watson.pdf.

Watson, J.G., B.J. Turpin and J.C. Chow. 2001b. The measurement process: Precision, accuracy, and validity. In *Air Sampling Instruments for Evaluation of Atmospheric Contaminants*, 9th ed., B.S. Cohen and C.S.J. McCammon, Eds. American Conference of Governmental Industrial Hygienists, Cincinnati, OH, pp. 201-216.

Watson, J.G., J.C. Chow and J.E. Houck. 2001c. $PM_{2.5}$ chemical source profiles for vehicle exhaust, vegetative burning, geological material, and coal burning in northwestern Colorado during 1995. *Chemosphere*, **43**(8):1141-1151.

Watson, J.G. 2002a. Visibility: Science and regulation. *J. Air & Waste Manage. Assoc.*, **52**(6):628-713.

Watson, J.G. 2002b. Visibility: Science and regulation - A summary of the 2002 Critical Review. *EM*, (June):36-43.

Watson, J.G. 2002c. Appendix S: Independent Review. In *Source Apportionment Analysis of Air Quality Data: Phase 1 - Final Report.* Mid-Atlantic Regional Air Management Assoc., Baltimore, MD, pp. S1-S63.

Watson, J.G., and J.C. Chow. 2002a. Particulate pattern recognition. In *Introduction to Environmental Forensics*, B.L. Murphy and R. Morrison, Eds. Academic Press, New York, NY, pp. 429-460.

Watson, J.G., and J.C. Chow. 2002b. A wintertime $PM_{2.5}$ episode at the Fresno, CA, supersite. *Atmos. Environ*., **36**(3):465-475.

Watson, J.G., T. Zhu, J.C. Chow, J.P. Engelbrecht, E.M. Fujita and W.E. Wilson. (2002a). Receptor modeling application framework for particle source apportionment. *Chemosphere*, **49**(9):1093-1136.

Watson, J.G., J.C. Chow, D.H. Lowenthal, N.F. Robinson, C.F. Cahill and D.L. Blumenthal. 2002b. Simulating changes in source profiles from coal-fired power stations: Use in chemical mass balance of $PM_{2.5}$ in the Mt. Zirkel Wilderness. *Energy & Fuels*, **16**(2):311-324.

White, W.H. 1999. Phantom spatial factors: An example. *J. Air & Waste Manage. Assoc.*, **49**(3):345-349.

Wilkinson, L. 1990. *SYSTAT: The System for Statistics*. SYSTAT Inc., Evanston, IL.

Wolff, G.T., and P.J. Lioy. 1978. An empirical model for forecasting maximum daily ozone levels in the northeastern U.S. *J. Air Pollution Control Assoc.*, **28**(10):1034-1038.

Yamamoto, N., M. Fujii, O. Endo, K. Kumagai and Y. Yanagisawa. 2002. Broad range observation of particle deposition on greased and non-greased impaction surfaces using a line-sensing optical microscope. *J. Aerosol Sci.*, **33**(12):1667-1679.

Zielinska, B., and E.M. Fujita. 1994. Organic gas sampling. In *Environmental Sampling for Trace Analysis*, B. Markert, Ed. VCH Publishers, New York, NY, pp. 163-184.