



Protocol for Applying and Validating the CMB Model for PM_{2.5} and VOC

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By:

John G. Watson *et al.*
Desert Research Institute
University and Community College System of Nevada
Reno, NV 89512

Prepared for:

C. Thomas Coulter and Charles W. Lewis, Project Officers
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

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Air Quality Modeling Group

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¹Air Quality Modeling Group, Office of Air Quality Planning & Standards; Research Triangle Park, NC 27711

²National Exposure Research Laboratory, Office of Research & Development; Research Triangle Park, NC 27711

Table of Contents

	<u>Page</u>
1. Introduction	1-1
1.1 Protocol Objectives	1-1
1.2 CMB Model Development and History	1-2
1.3 Protocol Overview	1-3
2. CMB Relationships with Other Air Quality Models	2-1
2.1 Conceptual Models	2-1
2.2 Emissions Models	2-1
2.3 Meteorological Models	2-2
2.4 Chemical Models	2-3
2.5 Source Dispersion Model	2-3
2.6 Receptor Models	2-4
3. CMB Source and Receptor Input Data	3-1
3.1 Source Profiles	3-1
3.1.1 Common Emissions Sources	3-1
3.1.2 Source Profile Normalization Options	3-2
3.1.3 PM _{2.5} Source Characteristics	3-6
3.1.4 VOC Source Characteristics	3-11
3.1.5 Source Characterization Methods	3-14
3.1.6 Source Profile Data Bases	3-16
3.2 Receptor Measurements	3-17
3.2.1 Physical and Chemical Characteristics of Receptor Concentrations	3-17
3.2.2 Receptor Characterization Methods	3-19
3.2.3 Sampler Siting	3-28
3.2.4 Temporal Variability	3-30
3.2.5 Receptor Measurement Data Bases	3-31
3.3 CMB Application Levels	3-31
4. Assumptions, Performance Measures, and Validation Procedures	4-1
4.1 Fundamental Assumptions and Potential Deviations	4-1
4.2 CMB Performance Measures	4-4
4.3 Protocol Steps	4-14
4.3.1 Determine the Applicability of CMB	4-14
4.3.2 Format Input Files and Perform Initial Model Runs	4-14
4.3.3 Evaluate Outputs and Performance Measures	4-17
4.3.4 Evaluate Deviations from Model Assumptions	4-17
4.3.5 Modify Model Inputs to Remediate Problems	4-17
4.3.6 Evaluate the Consistency and Stability of the Model Results	4-19
4.3.7 Corroborate CMB Results with Other Modeling and Analyses	4-20

Table of Contents (continued)

	<u>Page</u>
5. Example of Application and Validation for PM _{2.5}	5-1
5.1 Model Applicability	5-1
5.2 Initial Source Contribution Estimates	5-6
5.3 Model Outputs and Performance Measures	5-15
5.4 Deviations from Model Assumptions	5-15
5.5 Identification and Correction of Model Input Errors	5-17
5.6 Consistency and Stability of Source Contributions	5-17
5.7 Consistency with Other Simulations and Data Analyses	5-18
6. Example of Application and Validation for VOC	6-1
6.1 Model Applicability	6-1
6.2 Initial Source Contribution Estimates	6-1
6.3 Examine Model Outputs and Performance Measures	6-4
6.4 Test Deviations from Model Assumptions	6-5
6.5 Identify and Correct Model Input Errors	6-7
6.6 Evaluate Consistency and Stability of Source Contributions	6-7
6.7 Determine Consistency with Other Simulations and Data Analyses	6-7
7. Summary, Conclusions, and Future Prospects	7-1
8. References	8-1
APPENDIX A. 54 PAMS target compounds (hydrocarbons) listed in their elution sequence	A-1
APPENDIX B. Normalization for the VOC Source Profile	B-1
APPENDIX C. Internet Links to Modeling Software and Data Sets	C-1
APPENDIX D. CMB Mathematics	D-1
APPENDIX E. Summary of CMB PM ₁₀ Source Apportionment Studies	E-1
APPENDIX F. Summary of CMB VOC Source Apportionment Studies	F-1
APPENDIX G. Procedures for Treating Secondary Particles	G-1

List of Tables

	<u>Page</u>
Table 3.1-1	Chemicals from Particles in Different Emissions Sources 3-8
Table 3.1-2	Organic Compounds Found in Different Source Emissions and in Ambient Air 3-9
Table 3.2-1	Chemical Compounds, Mnemonics, and Measurement Methods for Particle and VOC Receptor Modeling 3-20
Table 4.2-1	CMB8 Outputs and Performance Measures 4-9
Table 5.1-1	Wintertime Emissions Inventory for Denver Metro Area 5-2
Table 5.1-2	Source Composition Profiles from NFRAQS 5-3
Table 5.1-3	Source Composition Profiles from the 1987 Scenic Denver Study and Other Studies 5-5
Table 5.2-1a	Sensitivity of Total Carbon Apportionment to Alternative Wood Combustion Profiles (Welby, 01/17/97 at 0600 to 1200 MST) 5-7
Table 5.2-1b	Sensitivity of Total Carbon Apportionment to Alternative Meat Cooking Profiles (Welby, 01/17/97 at 0600 to 1200 MST) 5-8
Table 5.2-2a	Sensitivity of Total Carbon Apportionment to Alternative Cold-Start Profiles (Welby, 01/17/97 at 0600 to 1200 MST) 5-9
Table 5.2-2b	Sensitivity of Total Carbon Apportionment to Alternative Hot-Stabilized and High Particle Emitter Profiles (Welby, 01/17/97 at 0600 to 1200 MST) 5-10
Table 5.2-2c	Sensitivity of Total Carbon Apportionment to Fitting Species (Welby, 01/17/97 at 0600 to 1200 MST) 5-11
Table 6.2-1	VOC Source Profiles for NARSTO-NE CMB 6-2
Table 6.2-2	PAMS Measured Species and CMB Fitting Species 6-3
Table 6.3-1	CMB Sensitivity Tests for Vehicle Exhaust Profiles 6-4
Table 6.3-2	CMB Sensitivity Tests for Different Profiles 6-5

List of Figures

	<u>Page</u>
Figure 3.2-1 Spatial distribution of average PM _{2.5} source contributions from gasoline exhaust, diesel exhaust, suspended dust, vegetative burning, secondary ammonium sulfate, secondary ammonium nitrate, and primary coal-fired power station fly ash in and near Denver, CO during winter, 1996-97.	3-29
Figure 3.2-2 PM _{2.5} source contributions at the Welby site north of Denver, CO during winter of 1996-97.	3-30
Figure 4.2-1 CMB8 source contribution display.	4-5
Figure 4.2-2 Eligible space collinearity display.	4-6
Figure 4.2-3 Species concentration display.	4-7
Figure 5.7-1 Average PM _{2.5} source contributions at the Welby site near Denver, CO during the winter of 1996-97.	5-18
Figure 6.7-1 Hourly average VOC source contributions by day of week at Lynn, MA.	6-8
Figure 6.7-2 Wind direction dependence of VOC source contributions at Lynn, MA.	6-9

1. INTRODUCTION

The Chemical Mass Balance (CMB) air quality model is one of several models that have been applied to air resources management. Receptor models use the chemical and physical characteristics of gases and particles measured at source and receptor to both identify the presence of and to quantify source contributions to receptor concentrations. Receptor models are generally contrasted with dispersion models that use pollutant emissions rate estimates, meteorological transport, and chemical transformation mechanisms to estimate the contribution of each source to receptor concentrations. The two types of models are complementary, with each type having strengths that compensate for the weaknesses of the other.

The CMB receptor model consists of a solution to linear equations that express each receptor chemical concentration as a linear sum of products of source profile abundances and source contributions. The source profile abundances (i.e., the mass fraction of a chemical or other property in the emissions from each source type) and the receptor concentrations, with appropriate uncertainty estimates, serve as input data to CMB. In order to distinguish among source type contributions, the measured chemical and physical characteristics must be such that they are present in different proportions in different source emissions and changes in these proportions between source and receptor are negligible or can be approximated. The CMB model calculates values for the contributions from each source and the uncertainties of those values.

The CMB model is applicable to multi-species data sets, the most common of which are chemically characterized particulate matter (PM) and volatile organic compounds (VOC). PM_{2.5} and PM₁₀ (mass of particles with aerodynamic diameters less than 2.5 and 10µm, respectively) are regulated by National Ambient Air Quality Standards (NAAQS, EPA, 1997a). VOC are not specifically regulated, but they are precursors for ozone, which is subject to NAAQS (EPA, 1997a).

CMB model results are used to determine how much different sources contribute to ambient concentrations. This knowledge is usually used with source attributions determined by other models to justify emissions reduction strategies.

1.1 Protocol Objectives

This protocol describes how to use the CMB model in practical applications to determine the contributions of different sources to PM_{2.5} and VOC. Its objectives are to:

- Document measurement approaches and data sources for source and receptor input data.
- Describe the seven step applications and validation protocol to be followed when using the CMB model for source apportionment.
- Present examples for PM_{2.5} and VOC apportionment using contemporary data sets and source types.

1.2 CMB Model Development and History

This protocol supplements and expands on the earlier protocol for applying and validating the CMB model (EPA, 1987a; Watson *et al.*, 1991) that was widely used to develop State Implementation Plans for the previous PM₁₀ NAAQS (EPA 1987b, 1987c). With the subsequent adoption of a PM_{2.5} NAAQS, as well as greater interest in apportioning VOC for its role in local formation of photochemical oxidants, EPA decided to produce this enhanced protocol, which supersedes the earlier edition.

The CMB software has evolved over more than two decades to facilitate model application and validation. The Chemical Mass Balance receptor model was first applied by Hidy and Friedlander (1971), Winchester and Nifong (1971), and Kneip *et al.* (1972). The original applications used unique chemical species associated with each source-type, the so-called "tracer" solution. Friedlander (1973) introduced the ordinary weighted least-squares solution to CMB equations, and this had the advantages of relaxing the constraint of a unique species in each source type and of providing estimates of uncertainties associated with the source contributions. Gordon (1980, 1988) and Kowalkzyk *et al.* (1978) subsequently applied this method to elemental concentrations measured in source and receptor samples. The ordinary weighted least squares solution was limited in that only the uncertainties of the receptor concentrations were considered; the uncertainties of the source profiles, which are typically much higher than the uncertainties of the receptor concentrations, were neglected.

The first interactive user-oriented software for the CMB model was programmed in 1978 in FORTRAN IV on a PRIME 300 minicomputer (Watson, 1979). The PRIME 300 was limited to 3 megabytes of storage and 64 kilobytes of random access memory. CMB versions 1 through 6 updated this original version and were subject to many of the limitations dictated by the original computing system. CMB7 was written in a combination of the C and FORTRAN languages for the DOS operating system. With Windows[®] 3.1, 95, and NT becoming the most widely used operating systems, CMB8 created a user interface for CMB7 calculations using the Borland Delphi object oriented language.

CMB1 was used in the Portland Aerosol Characterization Study (PACS) to develop a State Implementation Plan for the control of Total Suspended Particulate Matter (Watson, 1979). This modeling was the first to identify and quantify residential wood combustion as a major contributor to particulate levels in a U.S. urban area. CMB2 was installed on EPA's UNIVAC system in 1980 from which it could be operated by direct dial-up from a remote terminal. CMB3 streamlined the computer code in FORTRAN 77 for the EPA UNIVAC and added a ridge regression solution to the effective variance least-squares estimation method for solving the CMB equations (Williamson and DuBose, 1983). The ridge regression algorithm was thought to reduce the effects of collinearity (i.e., two or more source profiles which are too similar to be separated from each other by the model) on source contribution estimates. Henry (1982) showed, however, that the ridge regression solution was equivalent to changing the source profiles from their measured values until the collinearity disappeared. Henry (1982) determined that the source contribution estimates given by the ridge regression solution did not represent reality, and its use for air quality modeling was abandoned.

CMB4, created in 1984, ported the CMB3 software to an IBM/XT microcomputer and added the original effective variance solution of CMB1. CMB5 was an experimental version that contained several solution methods, performance diagnostics, and output displays. CMB5 was used as a test bed for evaluating model performance measures, and it was revised nine times in response to recommendations and findings of these scientists and regulators. These revisions resulted in CMB6 (EPA, 1987d) and the original protocol for applying and validating the CMB model (EPA, 1987a). A protocol for reconciling CMB source contribution estimates with those determined by dispersion modeling (EPA, 1987e) was also published.

While CMB7 (Watson *et al.*, 1990a; EPA, 1990) improved the ease of use, it did not appreciably modify the model validation performance measures. CMB8 (Watson *et al.*, 1997a) has major changes in the collinearity measures (Henry, 1992) that have resulted from more than ten years of experience in using the CMB6 and CMB7 methods for model evaluation. EPA-CMB8.2 (EPA, 2004; Coulter and Scalco, 2005) incorporates the upgrade features that CMB8 has over CMB7, but also corrects errors/problems identified with CMB8, updates the linear algebra library, adds enhancements for a more robust and user-friendly system, and employs code that has been reorganized, refactored, and is well-documented.

Although the protocol is applicable to earlier versions of the software (e.g., CMB7), the examples given are specific to Windows[®]-based versions developed since CMB7. Throughout this protocol, reference is made to CMB as well as to CMB8. For practical purposes, the protocol applies ideally to either CMB8 or EPA-CMB8.2. As implied in this protocol's title, our intention is to make this protocol "generic", applicable to any of the latest Windows[®] versions that have evolved since CMB7.

1.3 Protocol Overview

The CMB modeling procedure requires: 1) identification of the contributing sources types; 2) selection of chemical species or other properties to be included in the calculation; 3) estimation of the fraction of each of the chemical species which is contained in each source type (source profiles); 4) estimation of the uncertainty in both ambient concentrations and source profiles; and 5) solution of the chemical mass balance equations. The CMB model is implicit in all factor analysis and multiple linear regression models that intend to quantitatively estimate source contributions (Watson, 1984). These models attempt to derive source profiles from the covariation in space and/or time of many different samples of atmospheric constituents that originate in different sources. These profiles are then used in a CMB calculation to quantify source contributions to each ambient sample. Section 3 describes the types of data needed to apply and validate the CMB model.

The CMB model is intended to complement rather than replace other data analysis and modeling methods. The CMB model explains observations that have already been taken, but it does not predict the future. When source contributions are proportional to emissions, as they often are for PM and VOC, then a source-specific proportional rollback is used to estimate the effects of emissions reductions. Similarly, when a secondary compound (a substance formed in the atmosphere rather than directly emitted by sources) apportioned by CMB is known to be limited by a certain precursor, a proportional rollback is used on the controlling precursor.

The most widespread use of CMB over the past decade has been to justify emissions reduction measures in PM₁₀ non-attainment areas. More recently, CMB has been coupled with extinction efficiency receptor models to estimate source contributions to light extinction and with aerosol equilibrium models to estimate the effects of ammonia and oxides of nitrogen emissions reductions on secondary nitrates. Section 2 describes how CMB relates to other air quality models and Appendix C identifies Internet web sites where more information about these models may be obtained.

Several solution methods have been proposed for the CMB equations: 1) single unique species to represent each source (tracer solution) (Miller *et al.*, 1972); 2) linear programming solution (Houglund, 1983); 3) ordinary weighted least squares, weighting only by precision estimates of ambient measurements (Friedlander, 1973; Guardrail and Friedlander, 1975); 4) ridge regression weighted least squares (Williamson and Daboecia, 1983); 5) partial least squares (Larson and Long, 1989; Long *et al.*, 1988); 6) neural networks (Song and Hopke, 1996); 7) Britt and Luecke (1973) least squares; and 8) effective variance weighted least squares (Watson *et al.*, 1984). CMB8 software allows solutions 1, 3, 7, and 8 to be implemented, and this facilitates tests of the effect of solution method on model results. Appendix D shows how these solution methods relate to each other and documents the mathematical basis for CMB performance measures.

The effective variance weighted least squares solution is almost universally applied because it: 1) theoretically yields the most likely solutions to the CMB equations, providing model assumptions are met; 2) uses all available chemical measurements, not just so-called “tracer” species; 3) analytically estimates the uncertainty of the source contributions based on the uncertainty of both the ambient concentrations and source profiles; and 4) gives greater influence to chemical species with lower uncertainty estimates in both the source and receptor measurements than to species with higher uncertainty estimates. The effective variance is a simplification of a more mathematically exact, but less practical, generalized least squares solution proposed by Britt and Luecke (1973).

CMB model assumptions are: 1) compositions of source emissions are constant over the period of ambient and source sampling; 2) chemical species do not react with each other (i.e., they add linearly); 3) all sources with a potential for contributing to the receptor have been identified and have had their emissions characterized; 4) the number of sources or source categories is less than or equal to the number of species; 5) the source profiles are linearly independent of each other; and 6) measurement uncertainties are random, uncorrelated, and normally distributed.

The degree to which these assumptions are met in applications depends to a large extent on the particle and gas properties measured at source and receptor. CMB model performance is examined generically, by applying analytical and randomized testing methods, and specifically for each application by following an applications and validation protocol. The six assumptions are fairly restrictive and they will never be totally complied with in actual practice. Fortunately, the CMB model can tolerate reasonable deviations from these assumptions, though these deviations increase the stated uncertainties of the source contribution estimates. Section 4 explains these assumptions and summarizes the results of tests that evaluate deviations from them.

The seven-step applications and validation protocol: 1) determines model applicability; 2) selects a variety of profiles to represent identified contributors; 3) evaluates model outputs and performance measures; 4) identifies and evaluates deviations from model assumptions; 5) identifies and corrects of model input deficiencies; 6) verifies consistency and stability of source contribution estimates; and 7) evaluates CMB results with respect to other data analysis and source assessment methods. This protocol is illustrated for a PM_{2.5} example in Section 5 and for a Volatile Organic Compound (VOC) example in Section 6. These examples contain sufficient detail that the protocol can be followed for other source apportionment studies.

Appendix A lists the 54 PAMS (Photochemical Assessment Monitoring Sites) target compounds (hydrocarbons) listed in their elution sequence. Appendix B describes the normalization procedure for the VOC source profile. Appendix C lists Internet links (URLs) for modeling software and data sets. Appendix D describes the CMB mathematical formulations. Appendices E & F summarize applications of CMB to PM and VOC source apportionment. These are related to a comprehensive bibliography of methodological and application examples that can be consulted for greater detail. Appendix G explains procedures for treating secondary particles within the constraints of CMB.

2. CMB RELATIONSHIPS WITH OTHER AIR QUALITY MODELS

Most excessive pollutant to which large populations are exposed result from various source emissions that are transported and transformed by the atmosphere. In some cases, the emissions emit visible plumes that can be seen to traveling toward a receptor. It is more often the case, however, that plumes are invisible, or that many slightly visible plumes mix together and disperse over wide areas. Different models of emissions and the atmosphere are used to integrate science and measurements to determine the contributions from specific sources or source types. These models are imperfect representations of reality, making many assumptions and operating on limited data bases.

As much effort is needed to evaluate their veracity as to apply them. For this reason, several different and independent models are commonly applied, linked to one another and independent of each other, to quantify source. Discrepancies between model results helps to identify and improve their weakness and to apply uncertainty bounds that should be used when designing control strategies. Commonly used air quality models are: 1) conceptual models; 2) emissions models; 3) meteorological models; 4) chemical models; 5) source-oriented models; and 6) receptor models.

2.1 Conceptual Models

Conceptual models describe the relevant physical and chemical processes that affect emissions, transport, and transformation. They are the starting point for any source apportionment process. Conceptual models take advantage of the large body of scientific knowledge already acquired. They identify the sources that are likely to be present and eliminate those that are not. They examine meteorological conditions that affect concentrations and focus further modeling on the conditions conducive to the high concentrations. Although the conceptual models described earlier in this chapter are consistent with current information, they are not yet verified. Field study measurements are designed to test them as hypotheses, and they will likely change.

A conceptual model should be formulated prior to designing a CMB source apportionment study. This should include a conception of the sources, their zones of influence, transport from distant areas, timing of emissions throughout the day, and meteorology that affects transport, dispersion, and transformation. This conceptual model should be used to guide the location of monitoring sites, the time of samples, the selection of samples for laboratory analysis, and the species that are quantified in those samples.

2.2 Emissions Models

Emissions models estimate temporal and spatial emission rates based on activity level, emission rate per unit of activity, and meteorology (EPA, 1996). Emissions models are often empirically derived from tests on representative source types, such as paved and unpaved roads, motor vehicle exhaust, biota, and industries. Emissions models are used to construct emissions inventories that are used as the basis for control strategy.

Emissions models and their results are used to identify initial sources types for inclusion in a CMB analysis. When emissions rates are chemically speciated, the same profiles used for that speciation might also be applicable to the CMB apportionment. The CMB is often used to evaluate emissions models and to identify areas where they need improvement (e.g., Fujita *et al.*, 1994, 1995a, 1995b).

Emissions inventory models are often used to develop control strategies by linear rollback (Barth, 1970; deNevers and Morris, 1975; Cass, 1981; Cass and McRae, 1981, 1983). Rollback assumes that atmospheric concentrations in excess of background are proportional to aggregate emission rates. Reducing excessive concentrations of a pollutant to levels below a pre-set standard requires emissions reductions that are proportionally equal to the relative amount by which the standard is exceeded.

Linear rollback does not consider the effects of meteorological transport between source and receptor or the differences in gas-to-particle conversion for different precursor emitters. It is most valid for spatial and temporal averages of ambient concentrations that represent the entire airshed containing urban-scale sources. The effect of transport from distant sources located outside the airshed is compensated by subtracting background concentrations, measured nearby but outside the airshed, from ambient levels prior to determining needed emissions reductions. Linear rollback also assumes for secondary particles, such as ammonium nitrate and ammonium sulfate, that one of the precursors limits particle formation.

CMB is often used in conjunction with linear rollback to determine the contribution of source categories to excessive concentrations. The linear rollback is then performed on a category specific basis, starting with the largest contributors. This is often considered to be a more accurate method of justifying emissions reductions because the relative emissions from individual sources within a category are believed to be more accurate than the absolute emissions within the category or the relative emissions between categories.

2.3 Meteorological Models

Meteorological models describe transport, dispersion, vertical mixing, and moisture in time and space. Meteorological models consist of straight line, interpolation (termed diagnostic), and first principle (termed prognostic) formulations, with increasing levels of complexity and requirements for computational and data resources.

The straight line model is applied to hourly wind directions from a single monitor, assuming an air mass travels a distance equal to the wind velocity in the measured direction, regardless of the distance from the monitoring site. This model is applicable for a few hours of transport in flat terrain, typically for evaluating a single emission source. Interpolation models integrate wind speed and directions from multiple measurement locations, including upper air measurements provide by remote sensors or balloon launches. The more advanced of these models allow barriers, such as mountains, to be placed between monitors. Wind fields, therefore, show different directions and velocities at different horizontal and vertical positions. Interpolation wind models are applicable to domains with a large number of well-placed monitors and for estimating the movement of air masses from many sources over transport times of more than half a day. The number and placement of monitors, especially upper air monitors, is especially important in mountainous terrain and in coastal areas where winds are unusual.

First principle models (Stauffer and Seaman, 1994; Seaman *et al.*, 1995; Koracin *et al.*, 1993, Koracin and Enger, 1994) embody scientists' best knowledge of atmospheric physics and thermodynamics, employing basic equations for conservation and transfer of energy and momentum. Also known as "prognostic models," first principle models purport to need no data other than values from a sparse upper air network for interpolation. They are computationally intensive, often requiring supercomputers but are becoming more practical and cost-effective as workstation and desktop computers become more powerful. Modern versions use "four-dimensional data assimilation" that compare model-calculated wind, humidity, and temperature fields with measurements and "nudge" model outputs toward observations. A more complex meteorological model is not necessarily a better model for a specific application. The MM5 meteorological model has been adopted as the platform for central California air quality studies (Seaman *et al.*, 1995).

Meteorological models are useful in conjunction with a CMB analysis to determine where contributions might have come from. These models can often be used to determine the relative contributions from individual sources within a source category to better focus control strategies. These models are also useful adjunct analyses applicable to the seventh step of the applications and validation protocol.

2.4 Chemical Models

Chemical models describe transformation of directly emitted particles and gases to secondary particles and gases. Chemical models also estimate the equilibrium between gas and particle phases for volatile species. Chemical models have been or are being developed for: 1) photochemical formation of ozone, sulfate, nitrate, and organic particles in clear air (Seinfeld and Pandis, 1998); 2) sulfate and nitrate formation in fogs and clouds (Seinfeld and Pandis, 1998); 3) inorganic aerosol equilibrium (Kim *et al.*, 1993a, 1993b); and 4) organic aerosol equilibrium (Pankow, 1994a, 1994b). Chemical models are reasonably well developed for ozone and inorganic particles, but they are still under development for organic particles and gases.

Chemical models can be embedded in source-oriented dispersion models, or they can be applied to infer source contributions or limiting precursors as a receptor model using measurements from a monitoring site. Chemical equilibrium models, for example, are used to determine the extent to which ammonia or nitric acid reductions will reduce secondary ammonium nitrate concentrations estimated by CMB (Watson *et al.*, 1994a).

Chemical models have also been used to simulate changes between source and receptor (Friedlander, 1981; Lin and Milford, 1994; Venkatraman and Friedlander, 1994). These models are often overly simplified, and require additional assumptions regarding chemical mechanisms, relative transformation and deposition rates, mixing volumes, and transport times.

2.5 Source Dispersion Models

Source-oriented dispersion models use the outputs from emissions, meteorological, and chemical models to estimate concentrations measured at receptors. They include mathematical simulations of transport, dispersion, vertical mixing, deposition, and chemical models to represent transformation. The most common source dispersion models are Gaussian plume, puff, and grid formulations. Gaussian plume models (Schulze, 1990; Freeman *et al.*, 1986; Schwede

and Paumier, 1997) are most often associated with the straight line wind model and estimate a bell-shaped concentration field in the vertical and horizontal directions from the wind direction. These models are commonly used to evaluate potential effects of primary emissions from ducted sources, such as industrial stacks. Puff, or trajectory, models treat emissions from a variety of sources as independent entities that are moved in a curvilinear wind field generated by a diagnostic or prognostic wind model. Grid models place transfer pollutants between boxes with pre-defined vertical and horizontal dimensions (Bowman *et al.*, 1995; Byun and Dennis, 1995; Yamartino *et al.*, 1992). The 3-D grid-based photochemical SAQM-AERO model is the main platform that has been developed for central California studies.

2.6 Receptor Models

Receptor models (Cooper and Watson, 1980; Watson, 1984; Javitz *et al.*, 1988a, 1988b) infer contributions from different primary source emissions or precursors from multivariate measurements taken at one or more receptor sites. Receptor models are based on the same scientific principles as source dispersion models, but they are inferential rather than predictive of source contributions. They include CMB, factor analysis (and other forms of principal component analysis), empirical orthogonal functions, multiple linear regression, enrichment factors, neural networks, cluster analysis, Fourier Transform time series, and a number of other multivariate methods. In each case these other receptor models are used to identify patterns in chemical composition, time, or space.

Several of the model types described above can be used as either source-oriented or receptor-oriented models. 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 when ammonia, nitric acid, ammonium nitrate, temperature, and relative humidity measurements are available at a receptor. Wind models have source-oriented forward trajectory modes and receptor-oriented back-trajectory modes. Each of these formulations is useful and of value in any source apportionment effort.

Analysis methods are often termed receptor models, but they serve as inputs to models. Carbon-14 (^{14}C), microscopic analysis, gas chromatograms, x-ray spectra, and many other analytical outputs are analogous to source profiles 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 cannot provide valid quantifiable source apportionments.

3. CMB SOURCE AND RECEPTOR INPUT DATA

This section describes the types of measurements that are useful and available for both source and receptor input data to CMB. It provides references to publications and data bases that contain greater detail on these topics.

3.2 Source Profiles

Source profiles are the mass abundances (fraction of total mass) of a chemical species in source emissions. Source profiles are intended to represent a category of source rather than individual emitters. The number and meaning of these categories is limited by the degree of similarity between the profiles. Mathematically, this similarity is termed “collinearity,” 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” in a CMB solution, standard errors on source contributions are often very high. Some source contributions may be outlandishly high, while others may be negative. Determining the degree of collinearity is one of the main objectives of CMB validation.

3.1.1 Common Emissions Sources

Emissions inventories need to be examined before a CMB source apportionment to determine which source profiles will be needed and which chemical components must be measured in local source emissions and ambient air. Emissions inventories include thousands of individual emitters and dozens of source categories. To be useful for receptor modeling, the categories must be grouped into more generalized categories with similar source profiles. For example, an inventory will often contain separate entries for power generation, industrial, and institutional coal combustion. Since these combustion processes, and often the coal, are similar in a given airshed, it is unlikely that their contributions can be distinguished by CMB and they must be combined into a “coal-burning category.” The actual combinations depend on the profiles available or that are likely to be acquired for a CMB study. Other categories that are often combined for particulate and/or VOC are:

- Vegetative burning and cooking: Fireplaces, wood stoves, prescribed burns, wildfires, char-broiling, and meat cooking. Some of these subcategories may be separated when appropriate organic compounds are measured.
- Diesel exhaust: Heavy and light duty cars and trucks, off-road equipment, stationary engines for pumps and generators, and locomotives.
- Gasoline exhaust: Heavy and light duty cars and trucks, and small engines. Emissions inventories do not usually contain breakdowns by cold-starts and visibly smoking vehicles, although these might be discriminated by certain organic compounds in a profile. Since leaded fuels are no longer used in the U.S., there is no need to seek this separation.
- Gasoline evaporative emissions: Fueling stations, hot-soak vehicles.

- Fugitive dust: Paved roads, unpaved roads, agricultural tilling, construction, wind erosion, and industrial aggregate. These can sometimes be divided into subcategories based on single particle profiles or the measurement of specific mineral composition.
- Solvents and coatings: Paints, degreasers, and solvents. These can also be broken down into subcategories, not usually identified in emissions inventories, when the specific types of solvents have been determined.
- Metals: 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: Cement, quarrying, and mining. Ores, in particular, are often enriched in the materials being extracted and subcategories may be defined for these cases. 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 categories.

Most emissions inventories show 80% to 90% of suspended particles originating from suspended dust. This does not imply that other particle sources can or should be ignored. Appendix E shows that previous PM₁₀ source apportionment studies reported substantial contributions from other particle emitters.

VOC emissions inventories typically show stationary sources and on-road mobile sources contributing equally to total Reactive Organic Gases (ROG) emissions in an area. The summary of VOC source apportionment studies in Appendix F shows that source contributions from different vehicle components typically contribute the largest, and often the vast majority, of ambient VOC concentrations. Vehicle-related emissions, including exhaust, evaporated fuel, and liquid fuel are ubiquitous in all urban areas. Architectural (i.e., paints) and industrial solvents (i.e., cleaning and process solvents, as in printing) are also common to, 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 CMB source attributions to emissions inventories requires appropriate reconciliation between the inventory units and source contribution units.

3.1.2 Source Profile Normalization Options

Source profiles are created by sampling emissions from a variety of single emitters or small groups of emitters. These samples are then subjected to a variety of chemical and physical analyses to determine those properties that will allow contributions from the sources they represent to be distinguished at receptors. Each of these properties must be *normalized* (scaled) to some common property in the emissions from all sources. The two most widely used normalization properties are total particle mass or total volatile organic compound emissions that accompany the chemical components. The normalization procedure is one in which the measured concentrations are expressed as *ratios* (fractional abundances), and is necessary to construct source profile input files needed by CMB.

In a PM_{2.5} source apportionment study, the logical normalization factor is the PM_{2.5} mass emission, while in a VOC source apportionment study the total VOC is the logical normalization. One of the difficulties in combining PM_{2.5} and VOC 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. However, there are many sources, such as vehicle exhaust, cooking, and wood combustion, that have both large VOC and PM components, and profiles that are respectively normalized to both should be considered to increase the utility of the profiles for both VOC and PM source apportionment studies.

Individual profiles are formed from individual samples, and the uncertainty estimates of the numerator and denominator are propagated (Watson *et al.*, 1995) to obtain the individual profile uncertainties. These individual profiles are further composited to obtain the source profiles used for CMB source apportionment. The simplest composite consists of the average and standard deviation of abundances for all individual profiles within a group. For example, if ten tests of diesel vehicle exhaust are taken, each abundance is an average of the ten individual abundances and the uncertainty is the standard deviation of that average. Outlier tests are often applied to reject individual profiles that unduly bias the standard deviation of the composite (average) profile. In general, abundances that exceed two standard deviations calculated without the inclusion of that abundance should be omitted from a profile. There are always some outliers in any series of source tests, usually for reasons that can never be determined. For this reason it is important to obtain ten or more samples that run the range of operating conditions and fuels in an area to estimate source profiles.

Particle mass is well-defined and easy to measure, so most particle profiles for a stated size fraction are reasonably comparable, regardless of how they were measured. This is not the case for VOC profiles, where a wide variety of normalization factors and measurement units have been applied. Inventories employ different conventions for defining VOC. Many published VOC profiles are not comparable to each other, or with the ambient measurements, in terms of their normalization.

Several terms are used inconsistently but interchangeably to describe different fractions of atmospheric organic material. Common definitions and units must be used for ambient concentrations, source profiles, and emissions rates. The following terms are defined as they are used throughout this protocol, and these definitions are recommended for future CMB source apportionment projects:

- **C_x**: Molecules containing x carbon atoms (e.g., C₇ means the molecule contains seven carbon atoms). This notation is useful since many sampling and analysis techniques respond to different numbers of carbon atoms rather than to specific compounds.
- **Organic carbon**: Gases and particles containing carbon and hydrogen atoms in various ratios. Organic compounds found in ambient air may also be associated with other elements and compounds, particularly oxygen, nitrogen, sulfur, halogens, and metals. Various operational definitions based on measurement method are applied to different subsets of organic compounds.

- **Inorganic carbon:** Carbon dioxide and carbon monoxide are the most abundant inorganic gases found in the atmosphere, while amorphous graphite is the most common particulate component. Particulate elemental carbon is operationally defined by optical and combustion methods (Chow *et al.*, 1993), and it contains heavy organic material as well as inorganic carbon.
- **Hydrocarbons:** Organic compounds that consist only of carbon and hydrogen atoms.
- **Reactive organic gases (ROG):** Organic gases with potential to react (<30 day half-life) with the hydroxyl radical and other chemicals, resulting in ozone and secondary organic aerosol. The most reactive chemicals are not necessarily the largest contributors to undesirable end-products, however, as this depends on the magnitude of their emissions as well as on their reactivity (Carter, 1990; Carter and Lurmann, 1991).
- **Total organic gases (TOG):** Organic gases with and without high hydroxyl reactivity. TOG typically includes ROG plus methane and halocarbons.
- **Non-methane hydrocarbons (NMHC, also termed “light” hydrocarbons):** C₂ through C₁₂ (light) hydrocarbons collected in stainless steel canisters and measured by gas chromatography with flame ionization detection (GC-FID) by EPA method TO-14 (EPA, 1997b). NMHC excludes carbonyls, halocarbons, carbon dioxide, and carbon monoxide even though some of these may be quantified by the same method. NMHC is most often used to quantify ozone precursors.
- **Halocarbons:** NMHC with chlorine, fluorine, or bromine compounds attached, quantified from canisters by gas chromatography with electron capture detection (GC-ECD) (Farwell and Rasmussen, 1976). Methylchloride, methylchloroform, methylbromide, and various refrigerants (Freon-12, Freon-22, SUVA) are most commonly measured (Rasmussen *et al.*, 1980; Khalil *et al.*, 1985; Wang *et al.*, 1997). These compounds have long lifetimes and are not reactive enough to cause major changes in tropospheric ozone and secondary organic aerosol. Halocarbons have been implicated in the long-term depletion of stratospheric ozone (Lovelock *et al.*, 1973).
- **Heavy hydrocarbons:** C₁₀ through C₂₀ hydrocarbons collected on Tenax absorbing substrates and analyzed by thermal desorption and gas chromatography (Pellizzari *et al.*, 1984; Hawthorne and Miller, 1986; Walling *et al.*, 1986; Kamens *et al.*, 1988, 1989; Riba *et al.*, 1988; Zielinska and Fujita, 1994a; Zielinska and Fung, 1994; Zielinska *et al.*, 1996; Clausen and Wolkoff, 1997). These are sometimes termed “semi-volatile” compounds because the >C₁₅ compounds are often found as both gases and particles (Hampton *et al.*, 1982, 1983). Most of the total hydrocarbon mass is measured in the gas phase.
- **Carbonyls:** Aldehydes and ketones, the most common being formaldehyde, acetone, and acetylaldehyde (Carlier *et al.*, 1986; Altshuller, 1993). Carbonyls are operationally defined as C₁ through C₇ oxygenated compounds measured by collection on acidified 2,4-dinitrophenylhydrazine (DNPH)-impregnated C₁₈

cartridges and analyzed by high performance liquid chromatography with UV detection (HPLC/UV) (Cofer and Edahl, 1986; Zielinska and Fujita, 1994b; Grosjean and Grosjean, 1996; Kleindienst *et al.*, 1998).

- **Non-methane organic gases (NMOG):** NMHC plus carbonyls.
- **Semi-volatile organic compounds (SVOC):** Particles and gases collected on filters backed with solid absorbent such as polyurethane foam (PUF) and XAD, extracted in a variety of solvents, and analyzed by gas chromatography/mass spectrometry or HPLC/UV (Greaves *et al.*, 1985; Chuang *et al.*, 1987). This class includes compounds such as polycyclic aromatic hydrocarbons (PAHs), methoxyphenols and lactones, pesticides, and other polar and non-polar organic compounds. The heavy hydrocarbons are often classified as SVOC, but they are given a separate identity here for precision and clarity.
- **Volatile organic compounds (VOC):** NMHC plus heavy hydrocarbons plus carbonyls plus halocarbons, typically $<C_{20}$. VOC has been imprecisely used to describe most of the other categories defined above.

Non-standard variable definitions and units are an impediment to VOC source apportionment using CMB. VOC concentrations are usually reported in ppbC or $\mu\text{g}/\text{m}^3$ at local temperature and pressure.³ Either unit is acceptable for CMB analysis, but the source profile *ratios* must be consistent with the ambient measurements. Fortunately, the fractional abundances of most VOCs relative to NMHC vary by only a few percent when either ppbC or $\mu\text{g}/\text{m}^3$ are used for the numerator and the denominator. However, concentrations from all measurement methods must be in the same units. Since automated VOC analyzers inherently measure concentrations in ppbC, this unit is probably the best/most logical one for CMB applications.

VOC fractional abundances have been reported in ppbC or $\mu\text{g}/\text{m}^3$ and normalized by 1) total NMHC, as described above consisting of only the ROG including the unidentified fraction⁴; 2) the sum of the quantified or most abundant compounds in the chromatogram, which varies depending on the investigator; 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 comparability and use of profiles from different studies. Meaningful comparison of CMB results with emission inventories requires a common reference (Watson *et al.*, 2001). Since the TO-14 method is applied to PAMS (Lewis *et al.*, 1998a) at all severe ozone nonattainment areas, it is recommended that the sum of the 54 PAMS target hydrocarbons (Appendix A) should be the common normalization standard for source profiles. Measurements from other canister analyses, Tenax, and DNPH should also be normalized to the sum of the PAMS species. With this standard convention, renormalization to NMOG or other categories is straightforward. A discussion of the normalization procedure for a typical VOC source is provided in Appendix B.

³For any VOC, to convert from ppbC to ppbV, simply multiply the value by the # of carbon atoms in an individual molecule.

⁴Total NMOC is directly measured using EPA's Method TO-12 (EPA, 1985).

Note (however) that in many available source profiles, not all of the PAMS target compounds will be represented. They are usually best represented in vehicle exhaust profiles. Note also that most source profiles available in the literature (e.g., SPECIATE; see Appendix C) will not list uncertainties. Because CMB requires that uncertainties be input for its computation, nominal values of 5-10% may be assumed if there is no better information.

3.1.3 PM_{2.5} Source Characteristics

Table 3.1-1 identifies typical abundances of elements, ions, and carbon in different source emissions that have been found useful for CMB. Table 3.1-2 shows several of the organic aerosol compounds that are present in ambient aerosol and that are believed to originate in different source emissions. Note that many of these organic compounds are semi-volatile and may be predominantly in the gas or particle phase, depending on ambient temperature and other factors that affect equilibrium.

In geological material, aluminum (Al), silicon (Si), potassium (K), calcium (Ca), and iron (Fe) have large abundances with low variabilities. The total potassium (K) abundance is 15 to 30 times the abundance of soluble potassium (K⁺). Aluminum (Al), potassium (K), calcium (Ca), and iron (Fe) abundances are similar among the profiles, but the silicon (Si) abundances range from 14% in unpaved road dust to 20% in paved road dust. Lead (Pb) is sometimes abundant in paved road dust, but it is as low as 0.004% in the other geological profiles, probably due to deposition from previously emitted leaded-gasoline vehicle exhaust or remnants of lead from the exhaust trains of older vehicles. Elemental carbon (EC) abundances are highly variable in geological material, and are often negligible in natural soil samples. Organic carbon (OC) is typically 5% to 15% in geological emitters. It is most abundant in paved road and agricultural dusts, although the specific compounds are probably quite different for these two sources (Chow *et al.*, 1994). Motor vehicle emissions (e.g., brake and tire wear, oil drips) could result in greater abundances of Pb, EC, and OC in paved road dust. Soluble sulfate, nitrate, and ammonium abundances are low, in the range of 0 to 0.3%. Sodium and chloride are also low, with less than 0.5% in abundance. Larger abundances of these materials may be found temporarily soon after roadway de-icing, however.

Organic and elemental carbon are the most abundant species in motor vehicle exhaust, accounting for over 95% of the total mass. Watson *et al.* (1996a) found the lead (Pb) abundance is negligible and highly variable ($0.024 \pm 0.036\%$) in 1995 motor vehicle exhaust profiles from northwestern Colorado. The abundance of bromine (Br) was also low, in the range of 0.01% to 0.05%. Zinc was present in most exhaust profiles, usually at levels of 0.05% or less. The abundances of organic and total carbon can be quite variable in motor vehicle exhaust profiles. Organic carbon abundances ranged from 36% in highway vehicle emissions to 70% in local traffic emissions.

The ratio of organic to total carbon (OC/TC) was 0.58 in the composite vehicle profile for northwestern Colorado. This OC/TC ratio is similar to those reported by Watson *et al.* (1994b) in Phoenix, AZ, with 0.69 for gasoline-fueled vehicle exhaust, 0.55 for diesel-fueled vehicle exhaust, and 0.52 for a mixture of vehicle types in roadside tests. Earlier measurements in Denver, CO (Watson *et al.*, 1990b) reported an OC/TC ratio of 0.39 for the cold transient cycle and 0.81 for the cold stabilized cycle.

Watson *et al.* (1996a) also compared residential wood combustion (RWC), residential coal combustion (RCC), and forest fire PM_{2.5} profiles. Average OC abundances ranged from ~50% in RWC and the forest fire profiles to ~70% in the RCC profile. EC averaged 3% in forest fire, 12% in RWC, and 26% in RCC. The OC/TC ratio was highest in the forest fire profile (OC/TC = 0.94) and similar for the two residential combustion profiles, with 0.73 in RCC and 0.81 in RWC. Chow and Watson (1997c) measured profiles for asparagus field burning in California's Imperial Valley with OC/TC ratios of 0.93, similar to the 0.94 ratio found in the forest fire emissions. A similar observation was made for charbroil cooking emissions, with 60% to 70% OC abundances and high (>0.95) OC/TC ratios.

The K⁺/K ratios of 0.80 to 0.90 in burning profiles (Calloway *et al.*, 1989) are in large contrast to the low soluble to total potassium ratios found in geological material. Sulfate, nitrate, and silicon abundances in RCC are 2 to 4 times higher than those in the RWC and forest fire profiles. The ammonium abundance is highly variable, with an average of 1.4% in RCC and 0.1% in the RWC and forest fire profiles.

Table 3.1-1 Chemicals from Particles in Different Emissions Sources

Source Type	Dominant Particle Size	Chemical Abundances in Percent Mass			
		< 0.1%	0.1 to 1%	1 to 10%	> 10%
Paved Road Dust	Coarse	Cr, Sr, Pb, Zr	SO ₄ ⁼ , Na ⁺ , K ⁺ , P, S, Cl, Mn, Zn, Ba, Ti	Elemental Carbon (EC), Al, K, Ca, Fe	Organic Carbon (OC), Si
Unpaved Road Dust	Coarse	NO ₃ ⁻ , NH ₄ ⁺ , P, Zn, Sr, Ba	SO ₄ ⁼ , Na ⁺ , K ⁺ , P, S, Cl, Mn, Ba, Ti	OC, Al, K, Ca, Fe	Si
Construction	Coarse	Cr, Mn, Zn, Sr, Ba	SO ₄ ⁼ , K ⁺ , S, Ti,	OC, Al, K, Ca, Fe	Si
Agricultural Soil	Coarse	NO ₃ ⁻ , NH ₄ ⁺ , Cr, Zn, Sr	SO ₄ ⁼ , Na ⁺ , K ⁺ , S, Cl, Mn, Ba, Ti	OC, Al, K, Ca, Fe	Si
Natural Soil	Coarse	Cr, Mn, Sr, Zn, Ba	Cl ⁻ , NA ⁺ , EC, P, S, Cl, Ti	OC, Al, Mg, K, Ca, Fe	Si
Lake Bed	Coarse	Mn, Sr, Ba	K ⁺ , Ti	SO ₄ ⁼ , Na ⁺ , OC, Al, S, Cl, K, Ca, Fe	Si
Motor Vehicle	Fine	Cr, Ni, Y	NH ₄ ⁺ , Si, Cl, Al, Si, P, Ca, Mn, Fe, Zn, Br, Pb	Cl ⁻ , NO ₃ ⁻ , SO ₄ ⁼ , NH ₄ ⁺ , S	OC, EC
Vegetative Burning	Fine	Ca, Mn, Fe, Zn, Br, Rb, Pb	NO ₃ ⁻ , SO ₄ ⁼ , NH ₄ ⁺ , Na ⁺ , S	Cl ⁻ , K ⁺ , Cl, K	OC, EC
Residual Oil Combustion	Fine	K ⁺ , OC, Cl, Ti, Cr, Co, Ga, Se	NH ₄ ⁺ , Na ⁺ , Zn, Fe, Si	V, OC, EC, Ni	S, SO ₄ ⁼
Incinerator	Fine	V, Mn, Cu, Ag, Sn	K ⁺ , Al, Ti, Zn, Hg	NO ₃ ⁻ , Na ⁺ , EC, Si, S, Ca, Fe, Br, La, Pb	SO ₄ ⁼ , NH ₄ ⁺ , OC, Cl
Coal-Fired Boiler	Fine	Cl, Cr, Mn, Ga, As, Se, Br, Rb, Zr	NH ₄ ⁺ , P, K, Ti, V, Ni, Zn, Sr, Ba, Pb	SO ₄ ⁼ , OC, EC, Al, S, Ca, Fe	Si
Oil-Fired Power Plant	Fine	V, Ni, Se, As, Br, Ba	Al, Si, P, K, Zn	NH ₄ ⁺ , OC, EC, Na, Ca, Pb	S, SO ₄ ⁼
Steel Blast Furnace	Fine	V, Ni, Se,	Al, Si, P, K, Zn	Mn, OC, EC	Fe
Smelter Fire	Fine	V, Mn, Sb, Cr, Ti	Cd, Zn, Mg, Na, Ca, K, Se	Fe, Cu, As, Pb	S
Antimony Roaster	Fine	V, Cl, Ni, Mn	SO ₄ ⁼ , Sb, Pb	S	None reported
Marine	Fine and Coarse	Ti, V, Ni, Sr, Zr, Pd, Ag, Sn, Sb, Pb	Al, Si, K, Ca, Fe, Cu, Zn, Ba, La	NO ₃ ⁻ , SO ₄ ⁼ , OC, EC	Cl ⁻ , Na ⁺ , Na, Cl

Table 3.1-2 Organic Compounds Found in Different Source Emissions and in Ambient Air

<u>Species</u>	<u>Predominant Sources</u>	<u>Particle-Gas Phase Distribution</u>
PAH, for example		
naphthalene	Motor vehicles, wood smoke	Gas Phase
methylnaphthalenes	Motor vehicles, wood smoke	Gas Phase
dimethylnaphthalenes	Motor vehicles, wood smoke	Gas Phase
biphenyl	Motor vehicles, wood smoke	Gas Phase
acenaphthylene	Motor vehicles, wood smoke	Gas Phase
acenaphthene	Motor vehicles, wood smoke	Gas Phase
fluorene	Motor vehicles, wood smoke	Gas Phase
phenanthrene	Motor vehicles, wood smoke	Particle-Gas Phase
anthracene	Motor vehicles, wood smoke	Particle-Gas Phase
fluoranthene	Motor vehicles, wood smoke	Particle-Gas Phase
pyrene	Motor vehicles, wood smoke	Particle-Gas Phase
retene	Wood smoke -softwood	Particle-Gas Phase
benzo[b]naphtho[2,1]thiophene	Motor vehicles	Particle Phase
benz[a]anthracene	Motor vehicles, wood smoke	Particle Phase
chrysene	Motor vehicles, wood smoke	Particle Phase
benzo[b+j+k]fluoranthene	Motor vehicles, wood smoke	Particle Phase
benzo[e]pyrene	Motor vehicles, wood smoke	Particle Phase
benzo[a]pyrene	Motor vehicles, wood smoke	Particle Phase
indene[123-cd]pyrene	Motor vehicles, wood smoke	Particle Phase
dibenzo[ah+ac]anthracene	Motor vehicles, wood smoke	Particle Phase
benzo[ghi]perylene	Motor vehicles, wood smoke	Particle Phase
coronene	Motor vehicles, wood smoke	Particle Phase
Hopanes and Sterenes		
Cholestanes	Motor vehicles	Particle Phase
Trisnorhopanes	Motor vehicles	Particle Phase
Norhopanes	Motor vehicles	Particle Phase
Hopanes	Motor vehicles	Particle Phase
Guaiacols, for example		
4-methylguaiacol	Wood smoke	Gas Phase
4-allylguaiacol	Wood smoke	Particle-Gas Phase
isouegenol	Wood smoke	Particle-Gas Phase
Acetovanillone	Wood smoke	Particle Phase
Syringols, for example		
Syringol	Wood smoke, mostly hardwood	Particle-Gas Phase
4-methylsyringol	Wood smoke, mostly hardwood	Particle-Gas Phase
Syringaldehyde	Wood smoke, mostly hardwood	Particle Phase
Lactons, for example		
Caprolactone	Meat cooking	Gas Phase
Decanolactone	Meat cooking	Particle-Gas Phase
Undecanoic-G-Lactone	Meat cooking	Particle-Gas Phase
Sterols, for example		
Cholesterol	Meat cooking	Particle Phase
Sitosterol	Meat cooking, wood smoke	Particle Phase

Coal-fired power generation profiles differ substantially from residential coal burning, even though the fuels are similar, owing to the different emissions control technologies. Sulfate is one of the most abundant constituents in the particle phase and sulfur dioxide can be hundreds to thousands of times higher than the particle mass. Sulfur dioxide is a good indicator of contributions from nearby coal-fired power stations for which it has not reacted or deposited significantly during transport to a receptor. Crustal elements such as silicon (Si), calcium (Ca), and iron (Fe) in the coal-fired boiler profiles are present at 30% to 50% of the corresponding levels in geological material with the exception of aluminum (Al) which is present at similar or higher levels than those found in geological material. Other elements such as phosphorus (P), potassium (K), titanium (Ti), chromium (Cr), manganese (Mn), strontium (Sr), zirconium (Zr), and barium (Ba) are present at less than 1% levels.

Watson *et al.* (1996a) detected selenium (Se) at the level of 0.2% to 0.4% in coal-fired power station emissions with no scrubbers or wet scrubbers, but not in emissions from a unit with a dry limestone scrubber. Selenium is usually in the gaseous phase within hot stack emissions, and it condenses on particles when air is cooled in the dilution chamber. Abundances of calcium (15%), chloride (1%), and nitrate (1%) in the limestone-scrubbed unit were a few times higher than in the other units. These differences may have resulted from the dry lime scrubber, which added some calcium and absorbed the selenium in the vapor phase.

Sulfate, nitrate, and ammonium abundances in directly emitted particles are not sufficient to account for the concentrations of these species measured in the atmosphere. Ambient mass concentrations contain both primary and secondary particles. Primary particles are those which are directly emitted by sources; these particles often undergo few changes between source and receptor. Atmospheric concentrations of primary particles are, on average, proportional to the quantities that are emitted. Secondary particles are those that form in the atmosphere from gases that are directly emitted by sources.

Sulfur dioxide, ammonia, and oxides of nitrogen are the precursors for sulfuric acid, ammonium bisulfate, ammonium sulfate, and ammonium nitrate particles (Seinfeld, 1986; Watson *et al.*, 1994a). Several VOCs may also change into particles; the majority of these transformations result from intense photochemical reactions that also create high ozone levels (Grosjean and Seinfeld, 1989). Several of these particles, notably those containing ammonium nitrate, are volatile and transfer mass between the gas and particle phase to maintain a chemical equilibrium (Stelson and Seinfeld, 1982a-c). This volatility has implications for ambient concentration measurements as well as for gas and particle concentrations in the atmosphere.

Dust suspended from bare land, roadways, agricultural fields, and construction sites is predominantly a primary pollutant, but it does play a role in secondary particle formation (Chow and Watson, 1992; Chow *et al.*, 1994). Some components of dust, such as ammonium nitrate fertilizer, may volatilize into ammonia and nitric acid gases, thereby contributing to secondary aerosol. Alkaline particles, such as calcium carbonate, may react with nitric and hydrochloric acid gases while on the ground, in the atmosphere, or on filter samples to form coarse particle nitrates and chlorides. Ammonium sulfate fertilizers and minerals such as gypsum (calcium sulfate) may be mistaken for secondary sulfates when particle samples are chemically analyzed.

These examples show that although there are similarities in chemical compositions for different sources, using source profiles from one airshed or time period may not provide a valid CMB apportionment for ambient samples in another airshed or in another time period. Source emissions of precursor gaseous and primary particles are highly variable due to differences in fuel use, operating conditions, and sampling methods. Source and ambient measurements must be paired in time to establish reasonable estimates of source/receptor relationships. Trace metals acquired from elemental analysis of Teflon-membrane filters are only abundant in the geological and some industrial profiles. Elemental measurements by themselves are necessary, but insufficient, for a receptor modeling study. Chemical speciation must also include ammonium, sulfate, nitrate, organic carbon, and elemental carbon. Simultaneous gas measurements as well as other characteristics of suspended particles will be needed as more refined control strategies are developed using CMB.

3.1.4 VOC Source Characteristics

The largest body of knowledge about organic gas source compositions is related to mobile source emissions (Sampson and Springer, 1973; Black *et al.*, 1980; Carey and Cohen, 1980; Hampton *et al.*, 1982, 1983; Jensen and Hites, 1983; Nelson and Quigley, 1983, 1984; Kawamura *et al.*, 1985; Booker *et al.*, 1986; Sigsby *et al.*, 1987; Hlavinka and Bullin, 1988; Zweidinger *et al.*, 1988, 1990; McClenny *et al.*, 1989; Snow *et al.*, 1989; Stump *et al.*, 1989, 1990a, 1990b, 1992, 1996; Bailey *et al.*, 1990a, 1990b; Japar *et al.*, 1990, 1991; Trier *et al.*, 1990; Williams *et al.*, 1990; Chan *et al.*, 1991; Kaiser *et al.*, 1991; Wallington and Japar, 1991, 1993; Chock and Winkler, 1992; Corchnoy *et al.*, 1992; Hoekman, 1992; McCabe *et al.*, 1992; Siegl *et al.*, 1992; Stedman, 1992; Bailey and Eggleston, 1993; Diehl *et al.*, 1993; Chock *et al.*, 1994; Haszpra and Szilagyi, 1994; Zielinska and Fung, 1994; Conner *et al.*, 1995; Duffy and Nelson, 1996; Pierson *et al.*, 1996; Sagebiel *et al.*, 1996, 1997; Sjoren *et al.*, 1996; Zielinska *et al.*, 1996; Fujita *et al.*, 1997a, 1997b; Gelencsar *et al.*, 1997; Gertler *et al.*, 1997a, 1997b; Guicherit, 1997; Simo *et al.*, 1997). These tests include emissions from spark-ignition (gasoline-fueled) vehicle exhaust, compression ignition (diesel-fueled) vehicle exhaust, liquid gasoline, and evaporative gasoline emissions from fuel handling and vehicle operation.

With only the light hydrocarbons measured, the heavy-duty diesel and light-duty gasoline exhaust profiles are similar, and are often collinear in CMB calculations. Ethene, acetylene, 1-butene, iso-butene, propane, propene, isopentane, n-pentane, 2,2 dimethylbutane, 2-methylpentane, n-hexane, benzene, 3-methylhexane, toluene, ethyl benzene, *m*- & *p*-xylene, *m*-ethyltoluene, and 1,2,4-trimethylbenzene, are the most abundant compounds in either or both of these emissions. Several of these are short-lived and are only used in CMB calculations where fresh emissions are expected, as during early morning. Major differences between diesel and gasoline exhaust profiles are evident for acetylene, iso-butene, isopentane, n-hexane, and 2-methylhexane, which are most abundant in gasoline exhaust and for propene, propane, 2,2 dimethylbutane, n-decane, and n-undecane which are more abundant in diesel exhaust. Gertler *et al.* (1995) show that the CMB discrimination between diesel and gasoline exhaust is distinctive when the heavy hydrocarbons are included. Most of these compounds are highly enriched in diesel exhaust while having negligible abundances in normal-running gasoline vehicle exhaust.

Liquid gasoline contains many compounds in common with gasoline-vehicle exhaust. It is depleted in combustion products such as ethane, ethene, and acetylene. Evaporated gasoline is also depleted in these combustion compounds, as well as heavier hydrocarbons that volatilize more slowly from liquid fuels. Isobutane, n-butane, t-2 butene, and especially isopentane are enriched in evaporated gasoline. Methyl tertiary butyl ether (MTBE) stands out as a large constituent of all gasoline-related emissions that clearly separates these from diesel in areas where it is used as an additive. These differences are sufficient for CMB separation of gasoline exhaust from liquid and evaporated gasoline, and often from diesel exhaust, in ambient air. Gasoline compositions vary with location and time of year. Liquid gasoline and headspace evaporated gasoline samples should be analyzed at times and places consistent with ambient VOC measurements.

Petrochemical production, especially the refining of gasoline and other fuel oils (Sexton and Westberg, 1979, 1983; Fujita *et al.*, 1995a), can be a large contributor in areas such as Houston, TX. Ethane, propene, propane, n-pentane, t-2 hexene, benzene, n-heptane, toluene, and n-octane are abundant species. Most of these overlap with liquid and evaporated gasoline vapors. Refinery VOC measurements often contain a large fraction of unidentified NMHC that includes real, but unreported, chemical compounds that are not in the other profiles. If properly quantified, these could probably assist CMB resolution of refinery and other petrochemical sources.

Although solvents from paints and industrial uses are large components of all ROG inventories, their reported profiles are few (Kitto *et al.*, 1997; Guo *et al.*, 1998). Censullo *et al.* (1996) recently evaluated a large number of different solvent uses in southern California. These profiles are depleted in the species common to fuel use and production, with larger abundances of styrene, n-decane, and especially “other” compounds. The “other” VOCs are quantified and differ substantially among the different coatings tested. These are sufficient to separate various coating and solvent emissions from other contributors. California requires special solvent and coating formulations to comply with air quality emissions requirements, so these profiles are likely to be very specific to a particular area.

Printing ink solvents from offset (Wadden *et al.*, 1995a, 1995b) and rotogravure are commonly identified in emissions inventories. Most of these emissions are captured, condensed, and re-used by modern printing facilities, especially the toluene used for thin rotogravure inks. These may be enriched in styrene, n-nonane, and 1,2,4 trimethylbenzene, similar to the other solvents. Again, there is a large “other” fraction of identified compounds that allow the separation of solvent contributions to ambient VOC.

In addition to these common emissions sources, landfills are sometimes identified as large TOG emitters owing to their prodigious production of methane (Brosseau and Heitz, 1994; Eitzer, 1995). A variety of reactive organic gases may accompany the methane, depending of the nature of the landfill wastes and disposal practices. Brosseau and Heitz (1994) summarize measurements from many landfills, finding acetone, alpha terpinene, benzene, butyl alcohol, dichlorobenzene, dichloromethane, ethylbenzene, ethyl mercaptan, limonene, furans, terpenes, toluene, vinyl acetate, vinyl chloride, and xylene to be among the most abundant components of ROG.

Several of these compounds, such as vinyl chloride, are not common to widespread area sources and might be used to determine landfill source contributions by CMB. Kalman (1986) identifies several VOCs outgassed by plastics when they are heated. Acetone was consistently the most abundant ROG found in emissions from the surveyed landfills, probably resulting from the anaerobic decay of discarded organic material. Similar reactions in dumpsters and trash cans, as well as in the natural environment, may account for a portion of the unexplained acetone observed by Fujita *et al.* (1994) in Los Angeles and by Singh *et al.* (1994) at more remote locations. Acetone is also a product of photochemistry. Shonnard and Bell (1993) document substantial quantities of benzene emanating from contaminated soil, a situation that will presumably improve as modern amelioration methods are applied to these dumpsites (Fox, 1996).

Garcia *et al.* (1992) found small quantities of VOC emitted by several French coal-fired power stations, with benzene, toluene, ethylbenzene, xylenes, tetrachloroethane, benzaldehyde, and phenol being the most abundant compounds. Abundances of these compounds were substantially enriched over their abundances in the fuel, indicating that these compounds do not combust as well as other fuel components or that they form as part of the combustion process. Some data have also been reported for petroleum fires (Booher and Janke, 1997), food and beverage production (Passant *et al.*, 1993), household products and indoor building materials (Sack *et al.*, 1992, Sanchez *et al.*, 1987), ferry boats (Cooper *et al.*, 1996), hot asphalt application (Kitto *et al.*, 1997), fish rendering (Ohira *et al.*, 1976), and phytoplankton in the ocean (McKay *et al.*, 1996).

Biogenic VOC emissions from trees and shrubs (Tingey *et al.*, 1978, 1981; Arnts and Meeks, 1981; Tingey, 1981; Arnts *et al.*, 1982; Altshuller, 1983; Hov *et al.*, 1983; Shaw *et al.*, 1983; Lamb *et al.*, 1984, 1985, 1986, 1987, 1993; Oliver *et al.*, 1984; Roberts *et al.*, 1985; Gay, 1987; Riba *et al.*, 1987; Chameides *et al.*, 1988; Juttner, 1988; Yokouchi and Ambe, 1988; Das, 1992; Hewitt and Street, 1992; Khalil and Rasmussen, 1992; Nondek *et al.*, 1992; Winer *et al.*, 1992; Zhang *et al.*, 1992; Grosjean *et al.*, 1993a, 1993b, 1993c; Guenther *et al.*, 1993, 1994, 1996; Jobson *et al.*, 1994; Tanner and Zielinska, 1994, Ciccioli *et al.*, 1995, 1997a, 1997b; Fuentes *et al.*, 1996; Kempf *et al.*, 1996; Benjamin *et al.*, 1997; Bertin *et al.*, 1997; Cao *et al.*, 1997; Owen *et al.*, 1997; Pier *et al.*, 1997; Schuh *et al.*, 1997; Street *et al.*, 1997; Young *et al.*, 1997) are typically reported for isoprene and monoterpenes such as α -pinene and β -pinene. These compounds are very reactive and are usually detected only in forested areas. Isidorov *et al.* (1985) found a wide variety of heavy hydrocarbons in air dominated by different types of plants and trees that might be more stable indicators of biogenic contributions to ambient VOC.

Variations in biogenic emissions source profiles are difficult to quantify due to the variability in vegetation types, ambient temperature, seasonal growth cycles, and degree of drought. Despite its high reactivity, isoprene is commonly used as marker for biogenic emissions. Terpenes are not often quantified in ambient samples owing to measurement difficulties. Although the effects of photochemical reactions on the source contributions can be minimized for other major hydrocarbon sources by using fitting species with lifetimes comparable to air mass residence times, this is not possible for a single-species biogenic profile based upon isoprene with input data from conventional VOC measurement methods.

Fujita and Lu (1997) estimated an adjustment to biogenic contributions based on changes in the ratios of reactive hydrocarbons (e.g., isomers of xylene) to a relatively unreactive

hydrocarbon (e.g., benzene) between morning and afternoon samples to account for the loss of isoprene due to photochemical reactions. The average ratios of afternoon to morning xylenes/benzene ratios reflect the net fractional loss of xylenes due to atmospheric reactions. This fractional loss is adjusted to isoprene by applying the ratio of the OH* radical reaction rate constants for xylenes and isoprene. Adjustment factors of 6.6 to 10.0 were derived by this method for the biogenic contribution of ambient hydrocarbon in Phoenix, AZ (Fujita and Lu, 1997).

Biogenic contributions can be distinguished from fossil fuel contributions to ambient VOC by the ¹⁴C isotope which is much more abundant in recently-living organisms than in ancient coal, oil, and natural gas fuels (Conny and Currie, 1996; Klouda *et al.*, 1996; Rasmussen *et al.*, 1996; Lewis *et al.*, 1999). ¹⁴C is conserved with chemical transformations, thereby enabling the participation of biogenic emissions in photochemistry to be quantified by analysis of VOC end-products. Vegetative burning (Darley *et al.*, 1966; Rahmdal *et al.*, 1982; Khalil *et al.*, 1983; Rahmdahl, 1983; Ramdahl and Moller, 1983; Edgerton *et al.*, 1984, 1985, 1986; Edgerton, 1985; Isidorov *et al.*, 1985; Hawthorne *et al.*, 1988, 1989; Rau and Khalil, 1989; Ward and Hardy, 1989; Hurst *et al.*, 1994; Koppmann *et al.*, 1997) has also been identified by its contributions of methyl chloride and retene in ambient air, but the compounds in its NMHC and NMOG emissions are poorly characterized.

3.1.5 Source Characterization Methods

Several methods have been devised to extract samples from sources which will have chemical and physical properties similar to those found at a receptor (Gordon *et al.*, 1986; Chow *et al.*, 1988). In each of these methods, emitted particulate matter or gases are collected on substrates or in containers that are subsequently analyzed for chemical content in a laboratory.

The ideal source sampling method would allow for chemical and physical transformations of source emissions to occur prior to sample collection. Lacking this ideal, the sampling would at least quantify the precursors of the receptor profile so that a theoretically or empirically derived transformation could be applied. Methods used to sample source emissions in receptor model studies include: 1) hot exhaust sampling; 2) diluted exhaust sampling; 3) plume sampling from airborne platforms; 4) ground-based sampling of single-source dominated air; and 5) grab sampling and resuspension.

Hot exhaust sampling is well established for determining the emission rates of criteria pollutants, including primary particulate matter and some VOCs. Hot exhaust does not permit the condensation of vapors into particles prior to sampling, and it sometimes interferes with the sampling substrate or container. In vegetative burning, for example, many of the vapors do not condense until they are near ambient temperatures. In coal-fired station emissions, the selenium does not condense on other particles until temperatures approach ambient. Hot exhaust samples are not often taken on substrates or in containers amenable to extensive chemical analysis. Components of these compliance-oriented methods have been incorporated into other exhaust sampling procedures. Although most commonly applied, hot exhaust sampling rarely yields profiles that represent profiles as detected at receptors because it does not account for transformations which take place when the emissions cool. Hot exhaust sampling is not appropriate for receptor modeling studies.

Several dilution samplers have been developed to bring hot exhaust effluents to ambient temperature by mixing with clean, cool air (Cooper *et al.*, 1988, 1989; Heinsohn and Davis, 1980; Hildemann *et al.*, 1989; Houck *et al.*, 1982; Hueglin *et al.*, 1997; McCain and Williamson, 1984; McDonald *et al.*, 1998; Merrill and Harris, 1987; Sousa *et al.*, 1985; Westerholm *et al.*, 1988; Williamson and Smith, 1979). Dilution samplers draw hot exhaust gases into a chamber where they are mixed with filtered ambient air. After an aging period, the particles are drawn through a size-selective inlet and onto substrates or into sample containers. Multiple samples for different chemical analyses are obtained simultaneously or via sequential sampling of the same gas stream. Stainless steel or Teflon-coated chambers are used where species might be reactive. Recent sampling systems acquire gaseous as well as particulate samples that can be used to apportion both particles and VOC (McDonald *et al.*, 1998; Zielinska *et al.*, 1998) and measure emission rates as well as source profiles.

Diluted exhaust samplers lend themselves to laboratory simulations of emissions from individual sources. Dynamometer simulations of motor vehicle driving with exhaust sampled from a dilution tunnel can provide examples of aggregate emissions for a large number of separate vehicles. Similarly, wood stoves and fireplaces can be operated under different burning cycles with emissions sampled from a dilution tunnel.

Source sampling from airborne platforms to characterize the chemical and physical properties of emissions has been performed from airplanes (Small *et al.*, 1981; Richards *et al.*, 1981, 1985), tethered balloons (Armstrong *et al.*, 1980; Shah *et al.*, 1989) and helicopters. Sampling components of appropriate weight and packaging are elevated above the emissions, usually on the order of 100 to 500 meters, to draw samples of the effluent.

The major advantage of airborne sampling for source characterization is that source profile fractionation might be determined if the sample can be taken at a time after emission (i.e., distance) sufficient to have allowed transformations to take place. The drawbacks of airborne plume sampling are: 1) it is difficult to know when the sampler is in the plume and when it is in ambient air; 2) it is difficult to stay in the plume long enough to obtain a sample; and 3) ambient air mixes with the plume, so the source profile is really a combination of emissions and ambient air.

Ground-based source sampling is identical to receptor sampling, but it is applied in situations for which the air being sampled is known to be dominated by emissions from a given source. The requirements of this method are: 1) meteorological conditions and sampling times conducive to domination by a particular source; 2) samples short enough to take advantage of those conditions; and 3) a minimum of other interfering source contributions.

Tunnels, parking garages, vehicle staging areas, and isolated but heavily traveled roadways are often used to obtain samples for motor vehicle exhaust. Tunnels are especially useful for this because a large number of vehicles can be evaluated with little interference from sources other than suspended road dust (Benner *et al.*, 1989; Bishop *et al.*, 1996; Chang *et al.*, 1981; Dannecker *et al.*, 1990; Duffy and Nelson, 1996; Fraser *et al.*, 1998; Gertler and Pierson, 1996; Gertler *et al.*, 1997a; Gillies *et al.*, 1998; Hering *et al.*, 1984; Ingalls, 1989; Khalili *et al.*, 1995; Barrefors, 1996; Lonneman *et al.*, 1986; Miguel, 1984; Moeckli *et al.*, 1996; Pierson and Brachaczek, 1976, 1983; Pierson *et al.*, 1990, 1996; Rogak *et al.*, 1998; Staehelin *et al.*, 1998; Weingartner *et al.*, 1997; Zielinska and Fung, 1994).

Using source-dominated samples, Rheingrover and Gordon (1980) and Annergarn *et al.* (1992) characterized several point sources using ambient virtual impactor measurements when the sampling was downwind of the source. Chow (1985) examined the effects of an elevated coal-fired power plant emission on ground-based samples in a rural environment. The presence of the plume from corresponding SO₂ and wind direction measurements could be discerned, but it was not possible to discern other chemical concentrations contributed by the power plant owing to an overwhelming abundance of geological material in her 24-hour sample. This method may be much better for fugitive and area sources, however, because their influence is more constant over time.

The advantages of ground-based sampling are: 1) it is representative of fractionated (presuming transformations are complete) and composite (for area sources such as home heating, motor vehicles, and resuspended dust) source profiles; 2) it is relatively economical; and 3) it is compatible with other receptor samples. The disadvantages are: 1) sampling times may be too short to obtain an adequate deposit; and 2) contributions from other source types interfere with the source profile.

Grab sampling and resuspension in the laboratory (Chow *et al.*, 1994) is most often applied to fugitive dust sources that are usually not ducted and require numerous samples to represent a large population. Grab sampling and resuspension involves: 1) removal of a precipitated residue of the emissions; 2) resuspension and sampling onto substrates through size-selective inlets; and 3) analysis for the selected species. A simple sample swept, shoveled, or vacuumed from a storage pile, transfer system, or roadbed can be taken to represent these source types. Five to ten different samples from the same source are averaged to obtain a representative source profile. This method is semi-established, or at least as established as the chemical and physical analyses applied to it, because procedures are widely accepted and results are reproducible within a method, though not necessarily among methods. The main advantages of grab sampling and resuspension are simplicity, reliability, and low cost.

3.1.6 Source Profile Data Bases

Several compilations of particle profiles have been produced that might be applicable to a Level 1 source assessment described in Section 3.3 (Watson, 1979; EPA, 1988; Sheffield and Gordon, 1985; Core and Houck, 1987; Cooper *et al.*, 1987; Houck *et al.*, 1989; Chow and Watson, 1994a; Watson *et al.*, 1994a, 1996a, 1996b; Chow and Watson, 1997a, 1997b; Chow *et al.*, 1997). These include chemical abundances of elements, ions, and carbon for geological material (e.g., paved and unpaved road dust, soil dust, storage pile), motor vehicle exhaust (e.g., diesel-, leaded-gasoline-, and unleaded-gasoline-fueled vehicles), vegetative burning (e.g., wood stoves, fireplaces, forest fires, prescribed burning), industrial boiler emissions, and other aerosol sources. More modern, research-oriented profiles include specific organic compounds or functional groups, elemental isotopes, and microscopic characteristics of single particles.

As fuels, technologies, and use patterns have changed from 1970 to the present, so have the chemical profiles for many emissions sources. Lead has been phased out of U.S. and Canadian fuels, but it is still used in some Mexican gasolines that might affect PM_{2.5} in border areas. Catalytic converters on spark-ignition vehicles, improved compression-ignition engines (Pierson *et al.*, 1996), and newly-designed wood combustion appliances have substantially reduced carbon abundances in emissions from these small but numerous sources.

Similarly, process improvements and new source performance standards have resulted in changes in chemical component emissions from large industrial emitters. Source profiles must be paired in time with ambient PM_{2.5} chemical species measurements to establish a reasonable estimate of what is expected in ambient air.

Several compilations of VOC source profiles have also been assembled (Shah and Singh, 1988; EPA, 1988; Scheff *et al.*, 1989a, 1989b; Shah *et al.*, 1989; Doskey *et al.*, 1992; Harley *et al.*, 1992; Fujita *et al.*, 1997a) from original measurements and a combination of published and unpublished test results. Most of these profiles are limited for CMB use because: 1) they represent older technology and fuels that are different today; 2) documentation is lacking or insufficient; 3) compound abundances are normalized to different definitions of NMOG or NMHC and are derived from a variety of measurement units; and 4) reported VOCs are not the same among profiles.

The most complete and available compilation of organic speciation profiles are those associated with the example in Section 6. These are available with the CMB8 software.

3.2 Receptor Measurements

Receptor measurements need to be a subset of the source profile measurements. They must include at least those species in the source profiles that allow sources to be separated.

3.2.1 Physical and Chemical Characteristics of Receptor Concentrations

Several characteristics of VOC and particle emissions were discussed above. Major chemical components of PM_{2.5} or PM₁₀ mass in urban and non-urban areas consist of geological material, carbon, nitrate, sulfate, ammonium, sodium chloride, and liquid water:

- **Geological Material:** Suspended dust consists mainly of oxides of aluminum, silicon, calcium, titanium, iron, and other metal oxides (Chow and Watson, 1992). The precise combination of these minerals depends on the geology of the area and industrial processes such as steel-making, smelting, mining, and cement production. Geological material is mostly in the coarse particle fraction, and typically constitutes ~50% of PM₁₀ while only contributing 5 to 15% of PM_{2.5} (Chow *et al.*, 1992a; Watson *et al.*, 1994b).
- **Organic Carbon:** Particulate organic carbon consists of hundreds, possibly thousands, of separate compounds. The mass concentration of organic carbon can be accurately measured, as can carbonate carbon, but only about 10% of specific organic compounds that it contains have been measured. Vehicle exhaust (Rogge *et al.*, 1993a; Zielinska *et al.*, 1998), residential and agricultural burning (Rogge *et al.*, 1998; Zielinska *et al.*, 1998), meat cooking (Rogge *et al.*, 1991; Zielinska *et al.*, 1998), fuel combustion (Rogge *et al.*, 1993b, 1997), road dust (Rogge *et al.*, 1993c), and particle formation from heavy hydrocarbon (C₈ to C₂₀) gases (Pandis *et al.*, 1992) are the major sources of organic carbon in PM_{2.5}. Because of this lack of molecular specificity, and owing to the semi-volatile nature of many carbon compounds, particulate “organic carbon” is operationally defined by the sampling and analysis method (Chow *et al.*, 1993; Hering *et al.*, 1985).

- Elemental Carbon:** Elemental carbon is black, often called “soot.” Elemental carbon contains pure, graphitic carbon, but it also contains high molecular weight, dark-colored, non-volatile organic materials such as tar, biogenics, and coke. Elemental carbon usually accompanies organic carbon in combustion emissions with diesel exhaust (Watson *et al.*, 1994c) being the largest contributor.
- Nitrate:** Ammonium nitrate (NH_4NO_3) is the most abundant nitrate compound, resulting from a reversible gas/particle equilibrium between ammonia gas (NH_3), nitric acid gas (HNO_3), and particulate ammonium nitrate. Because this equilibrium is reversible, ammonium nitrate particles can easily evaporate in the atmosphere, or after they have been collected on a filter, owing to changes in temperature and relative humidity (Stelson and Seinfeld, 1982a, 1982b; Allen *et al.*, 1989). Sodium nitrate (NaNO_3) is found in the $\text{PM}_{2.5}$ and coarse fractions near sea coasts and salt playas (e.g., Watson *et al.*, 1994b) where nitric acid vapor irreversibly reacts with sea salt (NaCl).
- Sulfate:** Ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$), ammonium bisulfate ($(\text{NH}_4\text{HSO}_4)$), and sulfuric acid (H_2SO_4) are the most common forms of sulfate found in atmospheric particles, resulting from conversion of gases to particles. These compounds are water-soluble and reside almost exclusively in the $\text{PM}_{2.5}$ size fraction. Sodium sulfate (Na_2SO_4) may be found in coastal areas where sulfuric acid has been neutralized by sodium chloride (NaCl) in sea salt. Though gypsum (Ca_2SO_4) and some other geological compounds contain sulfate, these are not easily dissolved in water for chemical analysis. They are more abundant in the coarse fraction than in $\text{PM}_{2.5}$, and are usually classified in the geological fraction.
- Ammonium:** Ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$), ammonium bisulfate (NH_4HSO_4), and ammonium nitrate (NH_4NO_3) are the most common compounds. The sulfate compounds result from irreversible reactions between sulfuric acid and ammonia gas, while the ammonium nitrate can migrate between gases and particle phases (Watson *et al.*, 1994a). Ammonium ions may coexist with sulfate, nitrate, and hydrogen ions in small water droplets. While most of the sulfur dioxide and oxides of nitrogen precursors of these compounds originate from fuel combustion in stationary and mobile sources, most of the ammonia derives from living beings, especially animal husbandry practiced in dairies and feedlots.
- Sodium Chloride:** Salt is found in suspended particles near sea coasts, open playas, and after de-icing materials are applied. Bulk sea water contains $57\pm 7\%$ chloride, $32\pm 4\%$ sodium, $8\pm 1\%$ sulfate, $1.1\pm 0.1\%$ soluble potassium, and $1.2\pm 0.2\%$ calcium (Pytkowicz and Kester, 1971). In its raw form (e.g., deicing sand), salt is usually in the coarse particle fraction and classified as a geological material (Chow *et al.*, 1996a, 1996b). After evaporating from a suspended water droplet (as in sea salt or when resuspended from melting snow), it is abundant in the $\text{PM}_{2.5}$ fraction. Sodium chloride is often neutralized by nitric or sulfuric acid in urban air where it is often encountered as sodium nitrate or sodium sulfate (Pilinis *et al.*, 1987).
- Liquid Water:** Soluble nitrates, sulfates, ammonium, sodium, other inorganic

ions, and some organic material (Saxena and Hildemann, 1997) absorb water vapor from the atmosphere, especially when relative humidity exceeds 70% (Tang and Munkelwitz, 1993). Sulfuric acid absorbs some water at all humidities. Particles containing these compounds grow into the droplet mode as they take on liquid water. Some of this water is retained when particles are sampled and weighed for mass concentration. The precise amount of water quantified in a PM_{2.5} depends on its ionic composition and the equilibration relative humidity applied prior to laboratory weighing.

3.2.2 Receptor Characterization Methods

A variety of sampling and analysis methods have been applied to acquire measurements at source and receptor for both particles (Chow, 1995; Chow and Watson, 1994b, 1998) and VOC (Zielinska *et al.*, 1994, 1996). Table 3.2-1 specifies gas and particle chemical compounds that are quantified by these methods and are being reported in source profiles.

A mnemonic is given for each chemical species that is used by CMB8 to identify the compound. As can be seen in Table 3.2-1, most of these mnemonics bear a resemblance to the chemical compound names. These mnemonics are reasonably straightforward for elemental species, but they can be complex for organic species.

Several compounds can be measured by different methods, and it is a good idea to designate these mnemonics differently. For example, the elements in Table 3.2-1 might also be quantified by proton induced x-ray emission spectroscopy (PIXE), instrumental neutron activation analysis (INAA), inductively couple plasma emission spectroscopy (ICP/ES) in addition to or in place of x-ray fluorescence (XRF). The “X” in the third place of the mnemonic could be replaced with another identifier to designate these methods. As noted above, water soluble potassium (KPA) and total potassium (KPX) are measured by different methods, but also represent different characteristics that distinguish among source contributions. These need to be designated by different mnemonics.

Table 3.2-1 Chemical Compounds, Mnemonics, and Measurement Methods for Particle and VOC Receptor Modeling

Mnemonic	Species	Method^a	Group^b
MSG	Mass	GRAV	N
CO	Carbon monoxide	NDIR	G
HNO3	Nitric Acid	NACL/IC	G
NO2	Nitrogen Dioxide	TEA/AC	G
SO2	Sulfur dioxide	KOH/IC	G
NH3	Ammonia	CA/AC	G
CLI	Chloride	Q/IC	IP
N3I	Nitrate	Q/IC	IP
S4I	Sulfate	Q/IC	IP
N4C	Ammonium	Q/AC	IP
KPA	Soluble Potassium	Q/AA	IP
TCT	Total Carbon	Q/TOR	OP
OCT	Organic Carbon	Q/TOR	OP
ECT	Elemental Carbon	Q/TOR	OP
NAX	Sodium	T/XRF	IP
MGX	Magnesium	T/XRF	IP
ALX	Aluminum	T/XRF	IP
SIX	Silicon	T/XRF	IP
PHX	Phosphorus	T/XRF	IP
SUX	Sulfur	T/XRF	IP
CLX	Chlorine	T/XRF	IP
KPX	Potassium	T/XRF	IP
CAX	Calcium	T/XRF	IP
TIX	Titanium	T/XRF	IP
VAX	Vanadium	T/XRF	IP
CRX	Chromium	T/XRF	IP
MNX	Manganese	T/XRF	IP
FEX	Iron	T/XRF	IP
COX	Cobalt	T/XRF	IP
NIX	Nickel	T/XRF	IP
CUX	Copper	T/XRF	IP
ZNX	Zinc	T/XRF	IP
GAX	Gallium	T/XRF	IP
ASX	Arsenic	T/XRF	IP
SEX	Selenium	T/XRF	IP
BRX	Bromine	T/XRF	IP
RBX	Rubidium	T/XRF	IP
SRX	Strontium	T/XRF	IP
YTX	Yttrium	T/XRF	IP
ZRX	Zirconium	T/XRF	IP
MOX	Molybdenum	T/XRF	IP
PDX	Palladium	T/XRF	IP
AGX	Silver	T/XRF	IP
CDX	Cadmium	T/XRF	IP
INX	Indium	T/XRF	IP
SNX	Tin	T/XRF	IP
SBX	Antimony	T/XRF	IP
BAX	Barium	T/XRF	IP

Table 3.2-1 Chemical Compounds, Mnemonics, and Measurement Methods for Particle and VOC Receptor Modeling

Mnemonic	Species	Method^a	Group^b
LAX	Lanthanum	T/XRF	IP
AUX	Gold	T/XRF	IP
HGX	Mercury	T/XRF	IP
TLX	Thallium	T/XRF	IP
PBX	Lead	T/XRF	IP
URX	Uranium	T/XRF	IP
NAPHTH	Naphthalene	GC/MS	OG
MNAPH2	2-menaphthalene	GC/MS	OG
MNAPH1	1-menaphthalene	GC/MS	OG
DMN267	2,6+2,7-dimenaphthalene	GC/MS	OG
DM1367	1,7+1,3+1,6-dimenaphthalene	GC/MS	OG
D14523	2,3+1,4+1,5-dimenaphthalene	GC/MS	OG
DMN12	1,2-dimenaphthalene	GC/MS	OG
DMN18	1,8-dimenaphthalene	GC/MS	OG
BIPHEN	Biphenyl	GC/MS	OG
M_2BPH	2-Methylbiphenyl	GC/MS	OG
M_3BPH	3-Methylbiphenyl	GC/MS	OG
M_4BPH	4-Methylbiphenyl	GC/MS	OG
ATMNAP	A-Trimethylnaphthalene	GC/MS	OG
EM_12N	1-Ethyl-2-methylnaphthalene	GC/MS	OG
BTMNAP	B-Trimethylnaphthalene	GC/MS	OG
CTMNAP	C-Trimethylnaphthalene	GC/MS	OG
EM_21N	2-Ethyl-1-methylnaphthalene	GC/MS	OP
ETMNAP	E-Trimethylnaphthalene	GC/MS	OP
FTMNAP	F-Trimethylnaphthalene	GC/MS	OP
GTMNAP	G-Trimethylnaphthalene	GC/MS	OP
HTMNAP	H-Trimethylnaphthalene	GC/MS	OP
TM128N	1,2,8-Trimethylnaphthalene	GC/MS	OP
ACNAPY	Acenaphthylene	GC/MS	OP
ACNAPE	Acenaphthene	GC/MS	OP
PHENAN	Phenanthrene	GC/MS	OP
FLUORE	Fluorene	GC/MS	OP
A_MFLU	A-Methylfluorene	GC/MS	OP
M_1FLU	1-Methylfluorene	GC/MS	OP
B_MFLU	B-Methylfluorene	GC/MS	OP
C_MFLU	C-Methylfluorene	GC/MS	OP
A_MPHT	A-Methylphenanthrene	GC/MS	OP
M_2PHT	2-Methylphenanthrene	GC/MS	OP
B_MPHT	B-Methylphenanthrene	GC/MS	OP
C_MPHT	C-Methylphenanthrene	GC/MS	OP
M_1PHT	1-Methylphenanthrene	GC/MS	OP
DM36PH	3,6-Dimethylphenanthrene	GC/MS	OP
A_DMPH	A-Dimethylphenanthrene	GC/MS	OP
B_DMPH	B-Dimethylphenanthrene	GC/MS	OP
C_DMPH	C-Dimethylphenanthrene	GC/MS	OP
DM17PH	1,7-Dimethylphenanthrene	GC/MS	OP
D_DMPH	D-Dimethylphenanthrene	GC/MS	OP
E_DMPH	E-Dimethylphenanthrene	GC/MS	OP

Table 3.2-1 Chemical Compounds, Mnemonics, and Measurement Methods for Particle and VOC Receptor Modeling

Mnemonic	Species	Method^a	Group^b
ANTHRA	Anthracene	GC/MS	OP
M_9ANT	9-Methylanthracene	GC/MS	OP
FLUORA	Fluoranthene	GC/MS	OP
PYRENE	Pyrene	GC/MS	OP
A_MPYR	A-Methylpyrene	GC/MS	OP
B_MPYR	B-Methylpyrene	GC/MS	OP
C_MPYR	C-Methylpyrene	GC/MS	OP
D_MPYR	D-Methylpyrene	GC/MS	OP
E_MPYR	E-Methylpyrene	GC/MS	OP
F_MPYR	F-Methylpyrene	GC/MS	OP
RETENE	Retene	GC/MS	OP
BNTIOP	Benzonaphthothiophene	GC/MS	OP
BAANTH	Benz(a)anthracene	GC/MS	OP
M_7BAA	7-Methylbenz[a]anthracene	GC/MS	OP
CHRYSN	Chrysene	GC/MS	OP
BBJKFL	Benzo(b+j+k)FL	GC/MS	OP
BEPYRN	BeP	GC/MS	OP
BAPYRN	BaP	GC/MS	OP
M_7BPY	7-Methylbenzo[a]pyrene	GC/MS	OP
INCDPY	Indeno[123-cd]Pyrene	GC/MS	OP
DBANTH	Dibenz(ah+ac)anthracene	GC/MS	OP
BBCHRN	Benzo(b)chrysene	GC/MS	OP
BGHIPE	Benzo(ghi)Perylene	GC/MS	OP
CORONE	Coronene	GC/MS	OP
GCAPLA	A-Caprolactone	GC/MS	OP
GUACOL	Guaiacol	GC/MS	OP
M4GUCL	4-Methylguaiacol	GC/MS	OP
E4GUCL	4-Ethylguaiacol	GC/MS	OP
SYRGOL	Syringol	GC/MS	OP
PPGUCL	Propylguaiacol	GC/MS	OP
A4GUCL	4-Allylguaiacol	GC/MS	OP
GNONLA	G-Nonanoic Lactone	GC/MS	OP
F4GUCL	4-Formylguaiacol	GC/MS	OP
M4SYRG	4-Methylsyringol	GC/MS	OP
E4SYRG	4-Ethylsyringol	GC/MS	OP
ISOEUG	Isoeugenol	GC/MS	OP
GDECLA	G-Decanolactone	GC/MS	OP
ACETVA	Acetovanillone	GC/MS	OP
UNGLAC	Undecanoic-G-Lactone	GC/MS	OP
SYRALD	Syringaldehyde	GC/MS	OP
ERGOS	Ergostane	GC/MS	OP
SITOS	Sitostane	GC/MS	OP
C27SDS	Diasterane-1	GC/MS	OP
C27RDS	Diasterane-2	GC/MS	OP
C27RCH	Cholestane-1	GC/MS	OP
C27SBC	Cholestane-2	GC/MS	OP
C27RAC	Cholestane-3	GC/MS	OP
AABTNH	Trisnorhopane-1	GC/MS	OP

Table 3.2-1 Chemical Compounds, Mnemonics, and Measurement Methods for Particle and VOC Receptor Modeling

Mnemonic	Species	Method ^a	Group ^b
AB_TNH	Trisnorhopane-2	GC/MS	OP
AB30NH	Norhopane-1	GC/MS	OP
CHLSRL	Cholesterol	GC/MS	OP
BA30NH	Norhopane-2	GC/MS	OP
AB_HOP	Hopane-1	GC/MS	OP
STEROW	Steroid-w	GC/MS	OP
BA_HOP	Hopane-2	GC/MS	OP
SABHHP	Homohopane-1	GC/MS	OP
RABHHP	Homohopane-2	GC/MS	OP
SITOST	Sitosterol	GC/MS	OP
BB_HOP	Hopane-3	GC/MS	OP
STEROM	Steroid-m	GC/MS	OP
SABBHH	Bishomohopane-1	GC/MS	OP
RABBHH	Bishomohopane-2	GC/MS	OP
IDNMHC	Total Identified NMHC	F	N
UNID	Unidentified ¹	F	
METHAN	methane	F	P
ACETYL	acetylene	F	Y
CO_PPM	carbon monoxide	F	
ETHENE	ethene	F	O
MEACRO	methacrolein	F,D	AL
ETHANE	ethane	F	P
METOH	methanol	F	OH
FORMAL	formaldehyde	D	AL
PROPE	propene	F	O
CO2PPM	carbon dioxide	F	
ACETAL	acetaldehyde	F	AL
N_PROP	propane	F	P
ETHOH	ethanol	F	OH
BUDI13	1,3-butadiene	F	O
BUTYN	1&2-butyne	F	Y
ACETO	acetone	F,D	K
ACROLN	acrolein	D	AL
BEABYL	1-butene&i-butene	F	O
C2BUTE	c-2-butene	F	O
LBUT1E	1-butene	F	O
LIBUTE	iso-butene	F	O
T2BUTE	t-2-butene	F	O
PROAL	propionaldehyde	D	AL
I_BUTA	isobutane	F	P
N_BUTA	-butane	F	P
CPENTE	cyclopentene	F	O
I_PREN	isoprene	F	O
CROTON	crotonaldehyde	D	AL
B1E2M	2-methyl-1-butene	F	O
B1E3ME	3-methyl-1-butene	F	O
B2E2M	2-methyl-2-butene	F	O
CPENTA	cyclopentane	F	P

Table 3.2-1 Chemical Compounds, Mnemonics, and Measurement Methods for Particle and VOC Receptor Modeling

Mnemonic	Species	Method ^a	Group ^b
PENTE1	1-pentene	F	O
C2PENE	c-2-pentene	F	O
T2PENE	t-2-pentene	F	O
PRAL2M	2-methylpropanal	F	AL
BUAL	butanal	F,D	AL
BUONE	butanone	F	K
IPENTA	isopentane	F	P
N_PENT	n-pentane	F	P
BENZE	benzene	F	A
CPENE1	1-methylcyclopentene	F	O
CYHEXE	cyclohexene	F	O
C2HEXE	c-2-hexene	F	O
C3HEXE	c-3-hexene	F	O
C6OLE1	C6 olefin	F	O
CYHEXA	cyclohexane	F	P
HEX1E	1-hexene	F	O
MCYPNA	methylcyclopentane	F	P
P1E2ME	2-methyl-1-pentene	F	O
P1E3ME	3-methyl-1-pentene	F	O
P1E4ME	4-methyl-1-pentene	F	O
P2E2ME	2-methyl-2-pentene	F	O
P2E3MC	<i>cis</i> -3-methyl-2-pentene	F	O
P2E3ME	3-methyl-2-pentene	F	O
P2E3MT	<i>trans</i> -3-methyl-2-pentene	F	O
T2HEXE	t-2-hexene	F	O
T3HEXE	t-3-hexene	F	O
MECL2	methylene chloride	E	X
VALAL	valeraldehyde	D	AL
BU22DM	2,2-dimethylbutane	F	P
BU23DM	2,3-dimethylbutane	F	P
N_HEX	n-hexane	F	P
PENA2M	2-methylpentane	F	P
PENA3M	3-methylpentane	F	P
MTBE	methyl tertiary butyl ether (ppbv)	F	E
TOLUE	toluene	F,T	A
PHENOL	phenol	T	AL
MEBR	methylbromide	E	X
C12DCE	<i>cis</i> -1,2,-dichloroethylene	E	X
T12DCE	<i>trans</i> -1,2-dichloroethylene	E	X
VINECL	vinylidenechloride	E	X
C7OLE1	C7 olefin	F	O
CPA13M	1,3-dimethylcyclopentane	F	A
MECYHX	methylcyclohexane	F	P
T3HEPE	t-3-heptene	F	O
ETDC12	1,2-dichloroethane	E	X
HEXAL	hexanal	F,D	AL
BU223M	2,2,3-trimethylbutane	F	A

Table 3.2-1 Chemical Compounds, Mnemonics, and Measurement Methods for Particle and VOC Receptor Modeling

Mnemonic	Species	Method^a	Group^b
HEXA2M	2-methylhexane	F	P
HEXA3M	3-methylhexane	F	P
HEXE4M	4-methylhexene	F	P
N_HEPT	n-heptane	F	P
PEN22M	2,2-dimethylpentane	F	P
PEN23M	2,3-dimethylpentane	F	P
PEN24M	2,4-dimethylpentane	F	P
PEN33M	3,3-dimethylpentane	F	P
PA3ET	3-ethylpentane	F	P
STYR	styrene	F,T	A
HEPAL	heptanal	F	A
BENZAL	benzaldehyde	F,D,T	AL
ETBZ	ethylbenzene	F,T	A
MP_XYL	<i>m</i> - & <i>p</i> -xylene	F,T	A
O_XYL	<i>o</i> -xylene	F,T	A
CHX11M	1,1-dimethylcyclohexane	F	P
OCT1E	octene-1	F	O
P1E244	2,4,4-trimethyl-1-pentene	F	O
N_OCT	n-octane	F,T	P
HEP2ME	2-methylheptane	F	P
HEP3ME	3-methylheptane	F	P
HEX24M	2,4-dimethylhexane	F	P
HEX25M	2,5-dimethylhexane	F	P
HX23DM	2,3-dimethylhexane	F	P
PA224M	2,2,4-trimethylpentane	F	P
PA234M	2,3,4-trimethylpentane	F	P
INDENE	indene	F,T	A
INDAN	indan	F,T	A
CCL3	chloroform	E	X
ACPHONE	acetophenone	T	K
TOLUAL	tolualdehyde	D	AL
BZ123M	1,2,3-trimethylbenzene	F,T	A
BZ124M	1,2,4-trimethylbenzene	F,T	A
BZ135M	1,3,5-trimethylbenzene	F,T	A
IPRBZ	isopropylbenzene	F,T	A
M_ETOL	m-ethyltoluene	F,T	A
MEOCT	methyloctane	T	P
N_PRBZ	n-propylbenzene	F,T	A
O_ETOL	<i>o</i> -ethyltoluene	F,T	A
P_ETOL	<i>p</i> -ethyltoluene	F,T	A
F12	Freon 12	E	X
IPCYHX	isopropylcyclohexane	F	P
NONE1	1-nonene	T	O
OCTAL	octanal	F	AL
NAPHTH	naphthalene	F	A
HEP24D	2,4-dimethylheptane	F	P
HEP25D	2,5-dimethylheptane	F	P

Table 3.2-1 Chemical Compounds, Mnemonics, and Measurement Methods for Particle and VOC Receptor Modeling

Mnemonic	Species	Method ^a	Group ^b
HEP26D	2,6-dimethylheptane	F	P
HEP33D	3,3-dimethylheptane	F	P
HEP44D	4,4-dimethylheptane	F	P
HEP4ME	4-methylheptane	F	P
HEX225	2,2,5-trimethylhexane	F	P
HEX235	2,3,5-trimethylhexane	F	P
N_NON	n-nonane	F,T	P
OCT2ME	2-methyloctane	F	P
OCT3ME	3-methyloctane	F	P
TCENE	trichloroethylene	E	X
IND_1M	1-methylindan	F	A
IND_2M	2-methylindan	F	A
TCE112	1,1,2-trichloroethane	E	X
MECCL3	methyl chloroform	E	X
BZ1234	1,2,3,4-tetramethylbenzene	T	A
BZ1235	1,2,3,5-tetramethylbenzene	T	A
BZ1245	1,2,4,5-tetramethylbenzene	F	A
BZDME	1,3-dimethyl-4-ethylbenzene	F	A
DETBZ1	m-diethylbenzene	F	A
DETBZ2	<i>p</i> -diethylbenzene	F	A
DETBZ3	<i>o</i> -diethylbenzene	F	A
DMETBZ	dimethylethylbenzene	T	A
I_BUBZ	isobutylbenzene	F	A
IPRTOL	isopropyltoluene	F	A
N_BUBZ	n-butylbenzene	F	A
S_BUBZ	sec-butylbenzene	F	A
A_PINE	alpha-pinene	F	O
B_PINE	beta-pinene	F	O
LIMONE	limonene	T	O
F11	Freon 11	E	X
NONAL	nonanal	F	AL
NAP_1M	1-methylnaphthalene	T	A
NAP_2M	2-methylnaphthalene	T	A
DMOCT	dimethyloctane	T	P
N_DEC	n-decane	F	P
OCT26D	2,6-dimethyloctane	F	P
OCT36M	3,6-dimethyloctane	F	P
INDDM1	dimethylindan	T	A
MDCBZ	m-dichlorobenzene	E	X
ODCBZ	<i>o</i> -dichlorobenzene	E	X
PDCBZ	<i>para</i> -dichlorobenzene	T	X
DETMbz	diethylmethylbenzene	T	A
ACNAPY	acenaphthylene	T	A
CCL4	carbon tetrachloride	E	X
ACENPE	acenaphthene	T	A
DMN12	1,2-dimethylnaphthalene	T	A
DMN13	1,3-dimethylnaphthalene	T	A

Mnemonic	Species	Method ^a	Group ^b
DMN14	1,4-dimethylnaphthalene	T	A
DMN15	1,5-dimethylnaphthalene	T	A
DMN18	1,8-dimethylnaphthalene	T	A
DMN23	2,3-dimethylnaphthalene	T	A
DMN26	2,6-dimethylnaphthalene	T	A
DMN27	2,7-dimethylnaphthalene	T	A
NAP1ET	1-ethylnaphthalene	T	A
NAP2ET	2-ethylnaphthalene	T	A
N_UNDE	n-undecane	T,F	P
PERC	perchloroethylene	E	X
N_DODE	n-dodecane	F	P
DBRME	1,3-dibromomethane	E	X
PHENA	phenanthrene	T	A
N_TRID	n-tridecane	T	P
F113	Freon 113	E	X
F114	Freon 114	E	X
ETDB12	1,2-dibromoethane	E	X
N_TETD	n-tetradecane	T	P
CLDBRM	chlorodibromomethane	E	X
N_PEND	n-pentadecane	T	P
N_HEXD	n-hexadecane	T	P
N_HEPD	n-heptadecane	T	P
N_OCTD	n-octadecane	T	P
N_NOND	n-nonadecane	T	P
N_EICO	n-eicosane	T	P
N_HENE	n-heneicosane	T	P

^a AC=Automated colorimetry
CA/AC=Citric acid filter and automated colorimetry
D=DNPH with HPLC/UV
E=Canister with GC/ECD
F=Canister with GC/FID
GC/MS=Gas chromatography mass spectrometry
GRAV=Gravimetric,
IC=Ion chromatography
KOH/IC=Potassium hydroxide filter & ion chromatography
NACL/IC=Sodium chloride filter & ion chromatography
NDIR=Non-Dispersive Infrared
T=Tenax with GC/FID,
TEA/IC=Triethanolamine filter & automated colorimetry
XRF= X-ray fluorescence

^b Group codes:
A = aromatic VOC
AL = aldehyde VOC
E = ether VOC
IG=inorganic gas
IP=inorganic particle
K = ketone VOC
O = alkene (olefin) VOC
OG=organic gas
OH = alcoholVOC
OP=organic particle
P = parafin VOC
X = haogenatedVOC
Y = alkyne VOC

¹ Sum of unidentified hydrocarbons. Excludes halogenated and oxygenated compounds.

3.2.3 Sampler Siting

The chemical dimension can be supplemented by spatial separation of receptors to further define the source categories or the specific emitters represented by different source types. These sites are classified as background, transport, gradient, and source sites that are intended to measure the following (Watson *et al.*, 1997b):

- **Community Representative (CORE):** CORE sites are intended to represent concentrations of large populations that live, work, and play within 5 to 10 km surrounding the site. These sites are most affected by regional and urban scale contributions with relatively small neighborhood scale and smaller contributions.
- **Background:** Background sites intend to measure concentrations that are not influenced by emissions from the regulated study area. These are located in pristine areas, away from local or urban sources. Few background locations are completely devoid of anthropogenic emissions.
- **Interbasin transport:** These sites are intended to evaluate concentrations along established or potential transport pathways. In mountainous terrain, these are typically located at the mountain passes through which inflows and outflows have been documented. In flat terrain they are located between urban areas or industrial source areas and urban areas.
- **Intrabasin gradient:** These sites are located in large regional areas, such as the Great Lakes region, the northeast corridor, the Los Angeles area, and within California's San Joaquin Valley where urban complexes are in non-urban areas between core sites. They are intended to evaluate the extent to which one urbanized area in an airshed affects concentrations in another urban area, as well as the extent to which urban contributions arrive at non-urban locations within an airshed.
- **Source:** Source sites are located right next to, and downwind of, representative and identifiable emitters. Where practical, these are located within 1 km of gradient or core sites to further evaluate the zone of influence of these source emissions.

Figure 3.2-1 shows how sampler siting within and between urban areas can assist in determining which components are regional and which are nearby contributors. In this example it is apparent that most of the primary contributions from carbon and geological material are from urban and neighborhood sources, while secondary nitrate and sulfate are contributed from outside the urban area. This would not be discernible from a single sampling location in the city center. The source contributions in Figure 3.2-1 were determined by CMB applied to elemental, ionic, and carbon measurements without use of specific organic compounds.

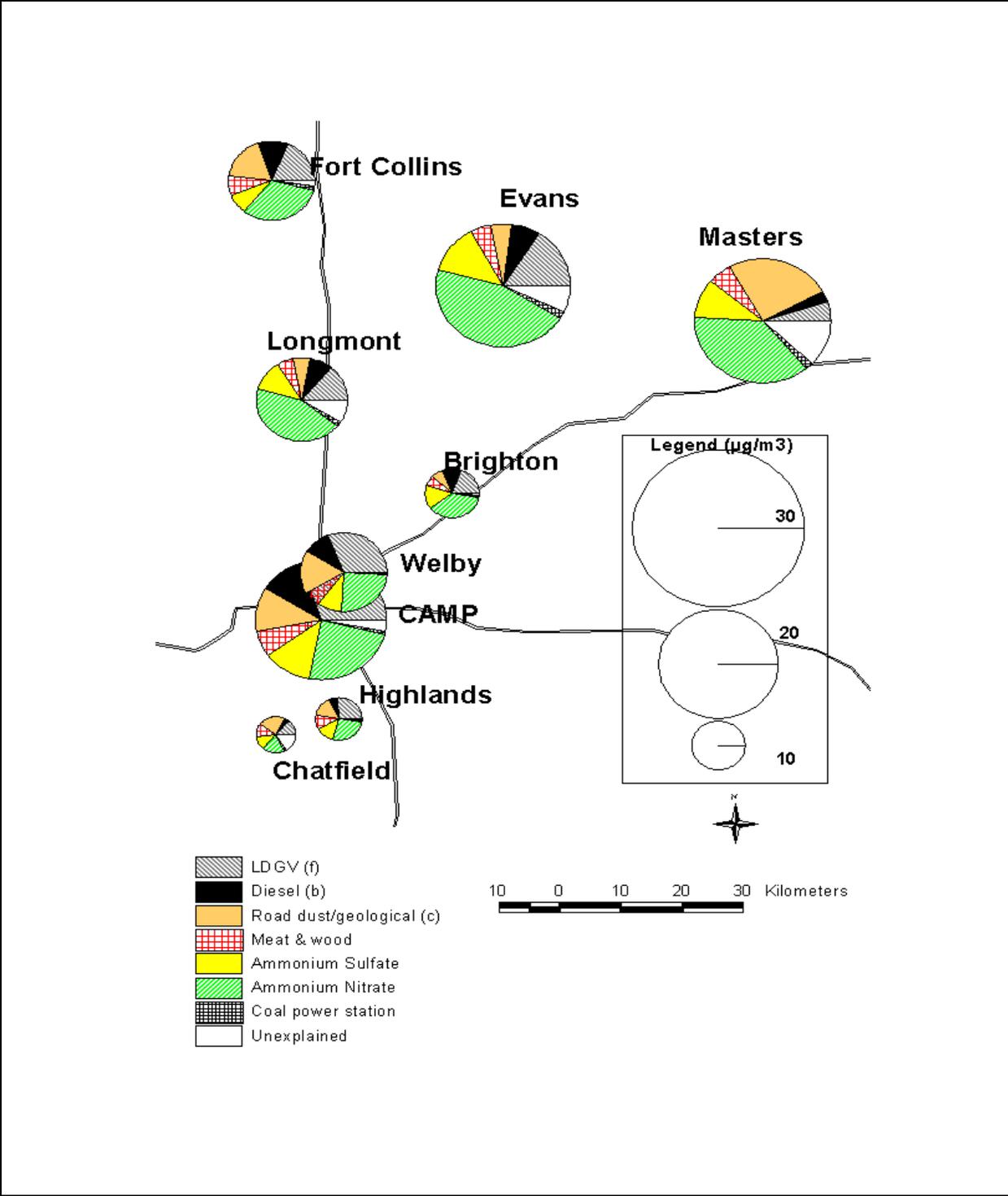


Figure 3.2-1. Spatial distribution of average PM_{2.5} source contributions from gasoline exhaust (LDGV), diesel exhaust (diesel), suspended dust (road dust/geological), vegetative burning (meat & wood), secondary ammonium sulfate, secondary ammonium nitrate, and primary coal-fired power station fly ash in and near Denver, CO during winter, 1996-97 (Watson *et al.*, 1998).

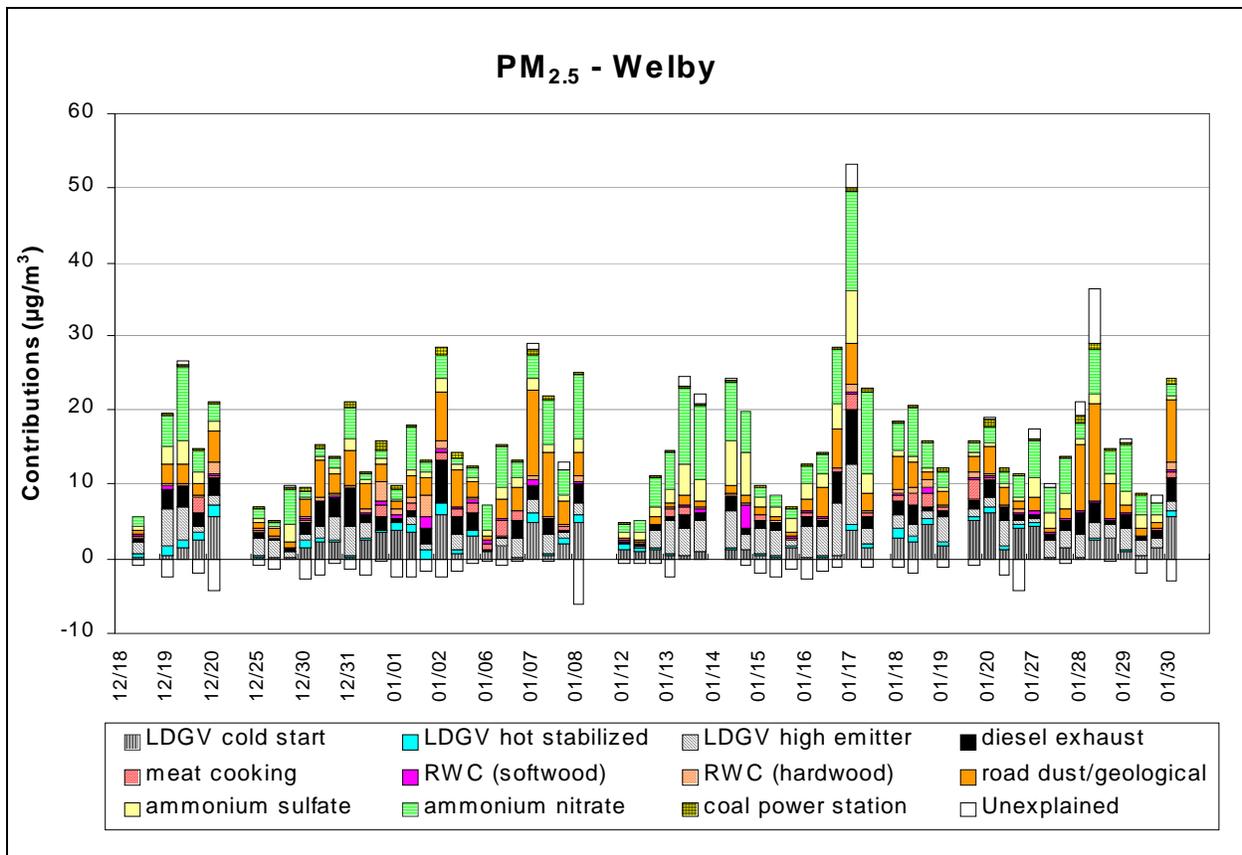


Figure 3.2-2. PM_{2.5} source contributions at the Welby site north of Denver, CO, during winter of 1996-97. Organic compounds were used in these apportionments, with resulting addition of source categories for gasoline exhaust for cold starts (LDGV cold start), normal running (LDGV hot stabilized), and poorly maintained (LDGV high emitter) vehicles. Vegetative burning is separated into meat cooking and residential wood combustion (RWC) for softwood and hardwood. Samples were taken from 0600-1200, 1200-1800, and 1800-0600 MST, with the morning sample directly over the date.

3.2.4 Temporal Variability

Temporal variability in concentrations is important because it helps to confirm source contributions by bracketing their emissions in time. Seasonal variations often allow vegetative burning contributions to be attributed to prescribed burning and wildfires during summer, when residential burning is at a minimum, and to woodstoves and fireplaces that are used during cool weather.

Figure 3.2-2 shows the temporal variation of source contributions at a site near Denver, CO. Motor vehicle exhaust contributions are typically largest during morning samples, and residential wood combustion is abundant in nighttime samples, especially near New Years Day.

3.2.5 Receptor Measurement Data Bases

Ambient chemical concentrations are not commonly available for CMB source apportionment. Special studies have been conducted to acquire the needed data at representative receptors during periods where PM or VOC concentrations have been found excessive. Appendices E and F identify many of these studies that have adequate data bases. Liroy *et al.* (1980); Chow and Watson (1989); and Watson and Chow (1992) summarize other chemically speciated data sets for suspended particles.

The most complete chemical data base to which CMB can be applied is the Interagency Monitoring of Protected Visual Environments (IMPROVE) network that has acquire elemental, ionic, and carbon measurements at National Parks and Wilderness areas since 1987. The most comprehensive VOC data base derives from the Photochemical Assessment Monitoring Sites (PAMS) that takes canister or continuous gas chromatographic measurements at urban and suburban sites during the summer.

New networks in support of the PM_{2.5} NAAQS will acquire speciated measurements at several hundred sites throughout the United States. One of the specific purposes of these measurements is to obtain source contributions via CMB modeling. Many of them will be collocated with PAMS sites, thereby offering the opportunity to use VOC and PM_{2.5} chemical components together in the source apportionment. Appendix C provides Internet links to data bases containing measurements useful for source apportionment studies.

3.3 CMB Application Levels

There is no single sampling and analysis design that will permit successful CMB source apportionment in every urban area. Since measurements can be costly, it is useful to examine existing samples and existing data to assist in forming a conceptual model prior to designing a full-scale source apportionment study. Three sequential levels of complexity (EPA, 1984) can be applied, with each level being more costly, but supplying more accurate and precise information than the previous level. The levels are useful as a shorthand notation of the general level of comprehensiveness of a CMB study but have no regulatory significance. A given level may not provide valid results because of data limitations. In such cases, the next higher level may need to be undertaken to complete the CMB analysis.

The basic level of CMB application (Level I) uses existing data or data that can be readily obtained from analyses of existing samples (Gordon *et al.*, 1984). Source profiles that were measured elsewhere, but that can be related to local sources, 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 PM₁₀ are apparent and sufficiently certain, no further work will be needed. Otherwise, this effort serves to reduce the areas to be studied in greater detail under an intermediate (Level II) analysis.

The intermediate (or Level II) analysis 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 which may have been discovered in Level I so as to reduce uncertainty in results of the Level I source apportionment. A comprehensive CMB analysis (Level II) involves the acquisition of new data from new source and ambient sampling activities.

Local dust samples are obtained and analyzed, at a minimum. Ground-based vehicle exhaust and vegetative burning profiles are also often acquired. Industrial source profiles are usually adapted from other studies. Light hydrocarbons are measured for a VOC apportionment study and elements, ions, and carbon are quantified for PM_{2.5} or PM₁₀. Where new sampling is possible, sampling locations and times are selected to bracket suspected contributors.

A Level III analysis is only applied in the most complex airsheds where the costs of emissions reduction are high and their effectiveness is uncertain. A Level III study involves original source testing and measurements beyond the basic particulate or VOC species. Heavy hydrocarbons and organic particles are measured at source and receptor. A Level III study usually involves a complex and detailed application of all model types specified in Section 2.

The CMB applications and validation protocol described here is appropriate to all three levels of PM and VOC assessment. It provides estimates of precision and validity that serve to define the measurement requirements for the next level of analysis. These estimates can also be used to determine whether or not the model results at a given level of PM and VOC assessment are certain enough to eliminate the need for more extensive assessment.

4. ASSUMPTIONS, PERFORMANCE MEASURES, AND VALIDATION PROCEDURES

4.1 Fundamental Assumptions and Potential Deviations

The CMB model assumptions are:

1. Compositions of source emissions are constant over the period of ambient and source sampling.
2. Chemical species do not react with each other, i.e., they add linearly.
3. All sources with a potential for significantly contributing to the receptor have been identified and have had their emissions characterized.
4. The source compositions are linearly independent of each other.
5. The number of sources or source categories is less than or equal to the number of chemical species.
6. Measurement uncertainties are random, uncorrelated, and normally distributed.

Assumptions 1 through 6 are fairly restrictive and will never be totally complied with in actual practice. Fortunately, CMB can tolerate deviations from these assumptions, though these deviations increase the stated uncertainties of the source contribution estimates.

The CMB model has been subjected to a number of tests to determine its abilities to tolerate deviations from model assumptions (Watson, 1979; Gordon *et al.*, 1981; deCesar and Cooper, 1982; Henry, 1982, 1992; Currie *et al.*, 1984; Dzubay *et al.*, 1984; deCesar *et al.*, 1985a, 1985b, 1986; Javitz and Watson, 1986; Lowenthal and Rahn, 1988a, 1988b, Lowenthal *et al.*, 1987, 1988, 1992, 1994; Javitz *et al.*, 1988a, 1988b; Cheng and Hopke, 1989; Kim and Henry, 1989; Henry and Kim, 1990; White and Macias, 1991). These studies all point to the same basic conclusions regarding deviations from the above-stated assumptions.

With regard to Assumption 1, source compositions, as seen at the receptor, are known to vary substantially among sources, and even within a single source over an extended period of time. These variations are both systematic and random and are caused by three phenomena: 1) transformation and deposition between the emissions point and the receptor; 2) differences in fuel type and operating processes between similar sources or the same source in time; and 3) uncertainties or differences between the source profile measurement methods. Evaluation studies have generally compared CMB results from several tests using randomly perturbed input data and from substitutions of different source profiles for the same source type. These tests consistently demonstrate that the error in the estimated source contributions due to biases in all of the elements of a source profile is in direct proportion to the magnitude of the biases. For random errors, the magnitude of the source contribution errors decreases as the difference between the number of species and sources increases.

Javitz *et al.* (1988b), for example, examined a simple 4-source urban airshed and a complex 10-source urban airshed using randomly perturbed source profiles and receptor concentrations with known source contributions. These tests with 17 commonly measured chemical species showed that primary mobile, geological, coal-fired power plant, and vegetative burning source types can be apportioned with uncertainties of approximately 30% when coefficients of variation in the source profiles are as high as 50%. This performance was demonstrated even without the presence of unique “tracer” species such as selenium for coal-fired power plants or soluble potassium for vegetative burning.

In a complex urban airshed, which added residual oil combustion, marine aerosol, steel production, lead smelting, municipal incineration, and a continental background aerosol, it was found that the geological, coal-fired power plant, and background source profiles were collinear with the measured species. At coefficients of variation in the source profiles as low as 25%, average absolute errors were on the order of 60%, 50%, and 130% for the geological, coal-burning, and background sources, respectively. All other sources were apportioned with average absolute errors of approximately 30% even when coefficients of variation in the source profiles reached 50%. These tests were performed with commonly measured chemical species, and results would improve with a greater number of species that are uniquely emitted by the different source types.

With regard to the nonlinear summation of species, Assumption 2, it is necessary to measure source profiles, or modify them by some objective method, to account for changes in the character between source and receptor. The conversion of gases to particles and reactions between particles are not inherently linear processes. This assumption is especially applicable to the end products of photochemical reactions and their apportionment to the sources of the precursors. Further model evaluation is necessary to determine the tolerance of CMB to deviations from this assumption.

The current practice is to apportion the primary material that has not changed between source and receptor. The remaining quantities of reactive species such as ammonium, nitrate, sulfate, and organic carbon are then apportioned to chemical compounds (*single constituent source type*) rather than directly to sources. While this approach is not as satisfying as a direct apportionment, it at least separates primary from secondary emitters, and the types of compounds apportioned give some insight into the chemical pathways that formed them. As noted in Section 3, when profiles are coupled with chemical reaction mechanisms and rates, deposition velocities, atmospheric equilibrium, and methods to estimate transport and aging time, it is possible to produce "aged" source profiles which will allow this direct attribution of reactive species to sources. This apportionment requires measurements of gaseous as well as particulate species at receptor sites, and is one of the main arguments for combining PM_{2.5} and VOC source apportionment studies together.

A major challenge to the application of CMB is the identification of the primary contributing sources for inclusion in the model, Assumption 3. Watson (1979) systematically increased the number of sources contributing to his simulated data from four to eight contributors while solving the CMB equations assuming only four sources. More sources were included in the least squares solution than those that were actually contributors.

These studies found that underrepresenting the number of sources had little effect on the calculated source contributions if the prominent species contributed by the missing sources were excluded from the solution. When the number of sources was underrepresented, and when prominent species of the omitted sources were included in the calculation of source contributions, the contributions of sources with properties in common with the omitted sources were overestimated. When source types actually present were excluded from the solution, ratios of calculated to measured concentrations were often outside of the 0.5 to 2.0 range, and the sum of the source contributions was much less than the total measured mass. The low calculated/measured ratios indicated which source compositions should be included. When the number of sources was overrepresented, the sources not actually present yielded contributions

less than their standard errors if their source profiles were significantly distinct from those of other sources. The over-specification of sources decreased the standard errors of the source contribution estimates.

Determining deviations from Assumption 4, the linear independence of source compositions, is one of the main goals of CMB validation. The degree of collinearity depends on the number of source categories contributing to influential fitting species, the relative contributions from source types with similar (but not identical) profiles, the variability of species abundances in the profiles, and the relative contribution from each category. These conditions vary from sample to sample, so it is not possible to state that two or more profiles are overly collinear prior to applying them to a specific sample. Similarly, the presence or absence of a “unique” or “tracer” species does not guarantee that collinearity is eliminated, especially if the “tracer” is at a very low abundance (e.g., <0.1%) and is highly variable. The variability of the profile abundances is more influential than the distinctness of the chemical species, in many cases.

Lowenthal *et al.* (1992), for example, showed that diesel and gasoline vehicle exhaust were non-collinear in a simple airshed where they were the major source of carbon. When a vegetative burning contribution was present, however, the diesel and gasoline exhaust profiles were too collinear to allow discrimination of their contributions, and only a composite “motor vehicle exhaust” contribution could be estimated.

Gordon *et al.* (1981) found instabilities in the ordinary weighted least square solutions to the CMB equations when species presumed to be “unique” to a certain source type were removed from the solution. Using simulated data with known perturbations ranging from 0 to 20%, Watson (1979) found that in the presence of likely uncertainties, sources such as urban dust and continental background dust cannot be adequately resolved by least squares fitting, even though their compositions are not identical. Several nearly unique ratios must exist for good separation.

Several “regression diagnostics” have been proposed for least squares estimation methods similar to the CMB effective variance solution (e.g., Belsley *et al.*, 1980; DeCesar *et al.*, 1985a, 1985b). Kim and Henry (1989) show that most of these diagnostics are not meaningful because they are based on the assumption of zero uncertainty in the source profiles. Kim and Henry (1989) demonstrate, through the examination of randomly perturbed model input data, that the values for these diagnostics vary substantially with typical random changes in the source profiles. Tests performed on simulated data with obviously collinear source compositions typically result in positive and negative values for the collinear source types as well as large standard errors in the collinear source contribution estimates. Unless the source compositions are nearly identical, the sum of these large positive and negative values very closely approximates the sum of the true contributions.

CMB8 makes the collinearity measures proposed by Henry (1992) more transparent to identify the degree of collinearity. These measure the degree of overlap among source profiles as if they were vectors in a multi-dimensional space. The user can set the overlap he or she is willing to tolerate for a selected maximum uncertainty in the quantity being apportioned (i.e., total VOC or PM mass to which the profiles are normalized). Little guidance is given in this protocol or elsewhere on how to select these overlaps and uncertainties, or on what the implication of that selection might be. By having these options available in CMB8, however, it

is hoped that such a body of knowledge can be acquired as more source apportionment studies are completed and the collinearity issue is studied in greater detail.

With most commonly measured species for particles (e.g., ions, elements, carbon) and common source types (e.g., motor vehicle, geological, residual oil, sea salt, steel production, wood burning, various industrial processes, secondary sulfuric acid, secondary ammonium bisulfate, secondary ammonium sulfate, secondary ammonium nitrate, secondary sodium nitrate), approximately five to seven source types are linearly independent of each other. About the same number of VOC source types (e.g., motor vehicle exhaust, liquid gasoline, evaporated gasoline, degreasers and coatings, graphic arts, biogenics) can be distinguished with most commonly measured species for VOC (e.g., C₂ - C₁₀ hydrocarbons in canisters). The degree of resolution and number of source types can be enhanced substantially, as will be shown in Section 5, when more detailed particle and gaseous organic compounds are measured at source and receptor, and when gas and particles are measured in conjunction with each other.

With regard to Assumption 5, the true number of individual sources contributing to receptor concentrations is generally much larger than the number of species that can be measured. It is therefore necessary to group sources into source types of similar compositions so that this assumption is met. For the most commonly measured species, meeting Assumption 4 practically defines these groupings.

With respect to Assumption 6 (the randomness, normality, and the uncorrelated nature of measurement uncertainties), there are few results available from verification or evaluation studies. Every least squares solution to the CMB equations requires this assumption, as demonstrated by the derivation of Watson *et al.* (1984). In reality, very little is known about the distribution of errors for the source compositions and the ambient concentrations. If anything, the distribution probably follows a log-normal rather than a normal distribution. Ambient concentrations can never be negative, and a normal distribution allows a substantial proportion of negative values, while a log-normal distribution allows no negative values. For small errors (e.g., less than 20%), the actual distribution may not be important, but for large errors it probably is important. A symmetric distribution becomes less probable as the coefficient of variation of the measurement increases. This assumption still requires further evaluation to determine the effects of its deviations.

4.2 CMB Performance Measures

Figures 4.2-1, 4.2-2, and 4.2-3 show the three segments of CMB model output that are displayed each time the model is applied to a set of source profiles and chemical species. These outputs accompany each application. Table 4.2-1 describes the model outputs and performance measures in these displays. The use of these measures to evaluate CMB solutions is explained in subsequent sections.

Chemical Mass Balance Version EPA-CMB8.2
 Report Date: 11/8/2004

SAMPLE:		OPTIONS:	INPUT FILES:	
SITE:	WELBY	BRITT & LUECKE:	No	INnfracqs.in8
SAMPLE DATE:	01/17/97	SOURCE ELIMINATION:	No	PRnfracqs.sel
DURATION:	6	BEST FIT:	No	SPnfracqs.sel
START HOUR:	06			.xxx
SIZE:	Fine			ADnfracqs.txt
				PRnfracqs.txt

Species Array: 5
 Sources Array: 1

FITTING STATISTICS:

R SQUARE	0.92	% MASS	93.8
CHI SQUARE	0.61	DEGREES FREEDOM	72

SOURCE CONTRIBUTION ESTIMATES:

SOURCE EST CODE	NAME	SCE($\mu\text{g}/\text{m}^3$)	Std Err	Tstat
YES N001	NVNSP	3.32689	2.06033	1.61474
YES N007	NVNSP2	0.92216	0.41334	2.23096
YES N010	NVSM	6.50609	3.73659	1.74118
YES N013	NWHD	7.23091	1.83963	3.93062
YES N050	NMc	1.86174	2.03008	0.91708
YES N055	NWFSc	0.81836	0.47345	1.72850
YES N067	NWSHc2	2.45221	1.30867	1.87383
YES N074	NRDC	6.37413	1.65625	3.84852
YES N082	AMSUL	6.84817	0.83248	8.22628
YES N084	AMNIT	13.68479	1.33685	10.23660
YES N124	PCHCLC1	-0.25354	1.24129	-0.20425

 49.77192

MEASURED CONCENTRATION FOR SIZE: Fine
 53.1+- 2.7

Figure 4.2-1. CMB8 source contribution display.

Eligible Space Display						
=====						
ELIGIBLE SPACE DIM. = 11 FOR MAX. UNC. = 10.61606 (20.% OF TOTAL MEAS. MASS)						
1 / Singular Value						

0.25514	0.37985	0.75550	0.86353	0.93826	1.34737	1.36735
1.86357	2.18762	4.20631				1.59420

NUMBER ESTIMABLE SOURCES = 11 FOR MIN. PROJ. = 0.95						
PROJ. SOURCE	PROJ. SOURCE	PROJ. SOURCE	PROJ. SOURCE	PROJ. SOURCE	PROJ. SOURCE	PROJ. SOURCE

1.0000 N001	1.0000 N007	1.0000 N010	1.0000 N013	1.0000 N050		
1.0000 N055	1.0000 N067	1.0000 N074	1.0000 N082	1.0000 N084		
1.0000 N124						

ESTIMABLE LINEAR COMBINATIONS OF INESTIMABLE SOURCES						
COEFF. SOURCE	COEFF. SOURCE	COEFF. SOURCE	COEFF. SOURCE	SCE		Std Err

Figure 4.2-2. Eligible space collinearity display.

Figure 4.2-3. Species concentration display.

SPECIES CONCENTRATIONS:					CALCULATED		RESIDUAL	
SPECIES	FIT	MEASURED	CALCULATED		MEASURED	UNCERTAINTY		
MSGC	MSGU	53.08030+-	2.70112	49.77192+-	2.80479	0.94+-	0.07	-0.8
CLIC	CLIU	* 0.45540+-	0.05500	0.19340+-	0.16807	0.42+-	0.37	-1.5
N3IC	N3IU	* 10.48780+-	0.69455	10.66432+-	1.06124	1.02+-	0.12	0.1
S4IC	S4IU	* 5.03660+-	0.39970	5.09540+-	0.50542	1.01+-	0.13	0.1
N4CC	N4CU	* 5.04460+-	0.26760	4.96436+-	0.37570	0.98+-	0.09	-0.2
KPAC	KPAU	* 0.06260+-	0.00540	0.02193+-	0.10357	0.35+-	1.65	-0.4
TCTC	TCTU	21.55080+-	1.38265	21.47394+-	0.57545	1.00+-	0.07	-0.1
OCTC	OCTU	* 13.42380+-	1.14530	13.44418+-	0.86062	1.00+-	0.11	0.0
ECTC	ECTU	* 8.12700+-	0.77460	8.02976+-	0.93415	0.99+-	0.15	-0.1
NAXC	NAXU	* 0.07980+-	0.04150	0.11505+-	0.10432	1.44+-	1.51	0.3
MGXC	MGXU	* 0.01450<	0.04340	0.05238<	0.06781	3.61<	11.78	0.5
ALXC	ALXU	* 0.13630+-	0.01320	0.34546+-	0.21019	2.53+-	1.56	1.0
SIXC	SIXU	* 0.52050+-	0.02830	1.13702+-	0.52088	2.18+-	1.01	1.2
PHXC	PHXU	* 0.00000<	0.01640	0.00529<	0.06631	0.00<	0.00	0.1
SUXC	SUXU	2.05200+-	0.10310	1.74683+-	0.17037	0.85+-	0.09	-1.5
CLXC	CLXU	* 0.34080+-	0.02290	0.20754+-	0.15976	0.61+-	0.47	-0.8
KPXC	KPXU	* 0.12110+-	0.00820	0.16756+-	0.06941	1.38+-	0.58	0.7
CAXC	CAXU	* 0.21120+-	0.01240	0.17604+-	0.11150	0.83+-	0.53	-0.3
TIXC	TIXU	* 0.00000<	0.02990	0.01525<	0.03837	0.00<	0.00	0.3
VAXC	VAXU	* 0.00000<	0.01660	0.00097<	0.01616	0.00<	0.00	0.0
CRXC	CRXU	* 0.00000<	0.00510	0.00151<	0.00388	0.00<	0.00	0.2
MNXC	MNXU	* 0.01120+-	0.00180	0.00385+-	0.00311	0.34+-	0.28	-2.0
FEXC	FEXU	* 0.34700+-	0.01770	0.24112+-	0.14516	0.69+-	0.42	-0.7
NIXC	NIXU	* 0.00010<	0.00140	0.00035<	0.00226	3.51<	54.03	0.1
CUXC	CUXU	0.01190+-	0.00120	0.00551+-	0.00513	0.46+-	0.43	-1.2
ZNXC	ZNXU	0.09250+-	0.00480	0.01933+-	0.01895	0.21+-	0.21	-3.7
ASXC	ASXU	* 0.00250<	0.00340	0.00020<	0.00464	0.08<	1.86	-0.4
SEXC	SEXU	* 0.00110+-	0.00100	-0.00004+-	0.00226	-0.04+-	2.06	-0.5
BRXC	BRXU	* 0.00490+-	0.00090	0.00141+-	0.00383	0.29+-	0.78	-0.9
RBXC	RBXU	* 0.00020<	0.00120	0.00077<	0.00213	3.87<	25.55	0.2
SRXC	SRXU	* 0.00170+-	0.00090	0.00150+-	0.00234	0.88+-	1.45	-0.1
ZRXC	ZRXU	* 0.00010<	0.00190	0.00079<	0.00277	7.88<	*****	0.2
HGXC	HGXU	* 0.00000<	0.00300	0.00010<	0.00404	0.00<	0.00	0.0
PBXC	PBXU	* 0.01120+-	0.00280	0.00576+-	0.01204	0.51+-	1.08	-0.4
NAPHTH	NAPHTH	1.15685+-	0.06375	1.10813+-	0.70144	0.96+-	0.61	-0.1
MNAPH2	MNAPH2	0.54554+-	0.03148	0.47372+-	0.23977	0.87+-	0.44	-0.3
MNAPH1	MNAPH1	0.32017+-	0.01963	0.25244+-	0.11945	0.79+-	0.38	-0.6
DMN267	DMN267	0.13343+-	0.00974	0.05868+-	0.02370	0.44+-	0.18	-2.9
DM1367	DM1367	0.21683+-	0.01504	0.08922+-	0.03454	0.41+-	0.16	-3.4
D14523	D14523	0.06834+-	0.00613	0.02964+-	0.01144	0.43+-	0.17	-3.0
DMN12	DMN12U	0.02676+-	0.00310	0.01277+-	0.00481	0.48+-	0.19	-2.4
BIPHEN	BIPHEN	0.08488+-	0.00494	0.02298+-	0.00887	0.27+-	0.11	-6.1
M_2BPH	M_2BPH	0.01973+-	0.00147	0.00207+-	0.00210	0.10+-	0.11	-6.9
M_3BPH	M_3BPH	0.07953+-	0.00443	0.01531+-	0.00639	0.19+-	0.08	-8.3
M_4BPH	M_4BPH	0.04232+-	0.00275	0.00831+-	0.00350	0.20+-	0.08	-7.7
ATMNAP	ATMNAP	0.06545+-	0.00444	0.02170+-	0.00843	0.33+-	0.13	-4.6
EM_12N	EM_12N	0.02026+-	0.00192	0.00753+-	0.00304	0.37+-	0.15	-3.5
BTMNAP	BTMNAP	0.06678+-	0.00496	0.02225+-	0.00791	0.33+-	0.12	-4.8
CTMNAP	CTMNAP	0.07318+-	0.00484	0.02223+-	0.00744	0.30+-	0.10	-5.7
EM_21N	EM_21N	0.00257+-	0.00056	0.00155+-	0.00174	0.60+-	0.69	-0.6
ETMNAP	ETMNAP	0.05283+-	0.00473	0.01536+-	0.00514	0.29+-	0.10	-5.4
FTMNAP	FTMNAP	0.04885+-	0.00378	0.01568+-	0.00527	0.32+-	0.11	-5.1
GTMNAP	GTMNAP	0.02637+-	0.00279	0.00904+-	0.00316	0.34+-	0.13	-4.1
HTMNAP	HTMNAP	0.00561+-	0.00100	0.00399+-	0.00197	0.71+-	0.37	-0.7
TM128N	TM128N	0.00283+-	0.00097	0.00128+-	0.00170	0.45+-	0.62	-0.8
ACNAPY	ACNAPY	0.02183+-	0.00300	0.09141+-	0.04484	4.19+-	2.13	1.5
ACNAPE	ACNAPE	0.02829+-	0.00216	0.01991+-	0.02033	0.70+-	0.72	-0.4
PHENAN	PHENAN	* 0.04598+-	0.00297	0.10035+-	0.03346	2.18+-	0.74	1.6

Figure 4.2-3 (continued). Species concentration display.

FLUORE	FLUORE	*	0.03263+-	0.00278	0.03197+-	0.01276	0.98+-	0.40	-0.1
A_MFLU	A_MFLU	*	0.01556+-	0.00144	0.01204+-	0.00448	0.77+-	0.30	-0.7
M_1FLU	M_1FLU	*	0.00697+-	0.00094	0.00559+-	0.00243	0.80+-	0.37	-0.5
B_MFLU	B_MFLU	*	0.00351+-	0.00057	0.00287+-	0.00189	0.82+-	0.55	-0.3
C_MFLU	C_MFLU	*	0.01187+-	0.00109	0.02067+-	0.00713	1.74+-	0.62	1.2
A_MPHT	A_MPHT	*	0.01087+-	0.00100	0.00989+-	0.00409	0.91+-	0.39	-0.2
M_2PHT	M_2PHT	*	0.01164+-	0.00105	0.01089+-	0.00442	0.94+-	0.39	-0.2
B_MPHT	B_MPHT	*	0.00065+-	0.00046	0.00330+-	0.00254	5.08+-	5.31	1.0
C_MPHT	C_MPHT	*	0.00797+-	0.00078	0.00680+-	0.00308	0.85+-	0.39	-0.4
M_1PHT	M_1PHT	*	0.00694+-	0.00079	0.00729+-	0.00321	1.05+-	0.48	0.1
DM36PH	DM36PH	*	0.00269+-	0.00064	0.00207+-	0.00187	0.77+-	0.72	-0.3
A_DMPH	A_DMPH	*	0.00325+-	0.00069	0.00268+-	0.00206	0.83+-	0.66	-0.3
B_DMPH	B_DMPH	*	0.00204+-	0.00047	0.00134+-	0.00176	0.66+-	0.88	-0.4
C_DMPH	C_DMPH	*	0.00650+-	0.00067	0.00426+-	0.00252	0.66+-	0.39	-0.9
DM17PH	DM17PH	*	0.00286+-	0.00064	0.00211+-	0.00189	0.74+-	0.68	-0.4
D_DMPH	D_DMPH	*	0.00236+-	0.00052	0.00171+-	0.00178	0.72+-	0.77	-0.4
E_DMPH	E_DMPH	*	0.00222+-	0.00064	0.00185+-	0.00184	0.83+-	0.86	-0.2
ANTHRA	ANTHRA		0.00408+-	0.00098	0.02458+-	0.00835	6.03+-	2.51	2.4
FLUORA	FLUORA		0.00579+-	0.00084	0.03360+-	0.01209	5.80+-	2.25	2.3
PYRENE	PYRENE		0.00694+-	0.00064	0.04160+-	0.01530	5.99+-	2.27	2.3
B_MPYR	B_MPYR	*	0.00118+-	0.00042	0.00079+-	0.00169	0.67+-	1.45	-0.2
D_MPYR	D_MPYR	*	0.00077+-	0.00042	0.00107+-	0.00169	1.39+-	2.33	0.2
F_MPYR	F_MPYR	*	0.00094+-	0.00042	0.00085+-	0.00170	0.90+-	1.84	-0.1
RETENE	RETENE	*	0.00074+-	0.00059	0.00035+-	0.00167	0.47+-	2.30	-0.2
BAANTH	BAANTH	*	0.00162+-	0.00126	0.00152+-	0.00176	0.94+-	1.30	0.0
CHRYSN	CHRYSN	*	0.00177+-	0.00067	0.00111+-	0.00169	0.62+-	0.98	-0.4
BBJKFL	BBJKFL	*	0.00183+-	0.00076	0.00214+-	0.00182	1.17+-	1.11	0.2
BEPYRN	BEPYRN	*	0.00157+-	0.00059	0.00075+-	0.00171	0.48+-	1.11	-0.5
BAPYRN	BAPYRN	*	0.00127<	0.00138	0.00093<	0.00177	0.73<	1.60	-0.2
INCDPY	INCDPY	*	0.00115+-	0.00113	0.00055+-	0.00172	0.48+-	1.56	-0.3
DBANTH	DBANTH	*	0.00027<	0.00163	0.00006<	0.00176	0.22<	6.74	-0.1
BGHIPE	BGHIPE	*	0.00260+-	0.00147	0.00169+-	0.00220	0.65+-	0.92	-0.3
CORONE	CORONE	*	0.00162<	0.00292	0.00122<	0.00216	0.75<	1.90	-0.1
GUACOL	GUACOL		0.04846+-	0.01833	0.02527+-	0.01222	0.52+-	0.32	-1.1
M4GUCL	M4GUCL		0.00080<	0.00109	0.02785<	0.01598	34.94<	51.70	1.7
E4GUCL	E4GUCL	*	0.00286+-	0.00105	0.00656+-	0.00394	2.29+-	1.61	0.9
SYRGOL	SYRGOL		0.00000<	0.00171	0.04130<	0.02025	0.00<	0.00	2.0
PPGUCL	PPGUCL	*	0.00000<	0.00046	0.00090<	0.00172	0.00<	0.00	0.5
A4GUCL	A4GUCL	*	0.00000<	0.00054	0.00417<	0.00266	0.00<	0.00	1.5
GNONLA	GNONLA	*	0.00487+-	0.00123	0.00444+-	0.00253	0.91+-	0.57	-0.2
F4GUCL	F4GUCL	*	0.01388+-	0.00709	0.01459+-	0.00660	1.05+-	0.72	0.1
M4SYRG	M4SYRG	*	0.00552<	0.00602	0.01250<	0.00437	2.26<	2.59	0.9
E4SYRG	E4SYRG	*	0.02555+-	0.00566	0.00551+-	0.00194	0.22+-	0.09	-3.4
ISOEUG	ISOEUG	*	0.02425+-	0.00359	0.01139+-	0.00457	0.47+-	0.20	-2.2
GDECLA	GDECLA	*	0.00227+-	0.00113	0.00176+-	0.00190	0.78+-	0.92	-0.2
ACETVA	ACETVA	*	0.00035<	0.00196	0.00408<	0.00246	11.52<	64.23	1.2
UNGLAC	UNGLAC	*	0.00313+-	0.00122	0.00706+-	0.00665	2.26+-	2.30	0.6
SYRALD	SYRALD		0.06167+-	0.01311	0.00321+-	0.00207	0.05+-	0.04	-4.4
C27SDS	C27SDS	*	0.00092+-	0.00067	0.00052+-	0.00168	0.57+-	1.88	-0.2
C27RDS	C27RDS	*	0.00080+-	0.00050	0.00041+-	0.00167	0.51+-	2.12	-0.2
C27RAC	C27RAC	*	0.00000<	0.00063	0.00081<	0.00172	0.00<	0.00	0.4
AB30NH	AB30NH	*	0.00139+-	0.00075	0.00120+-	0.00174	0.86+-	1.34	-0.1
CHLSRL	CHLSRL	*	0.00000<	0.00447	0.00115<	0.00190	0.00<	0.00	0.2
BA30NH	BA30NH	*	0.00092+-	0.00063	0.00074+-	0.00173	0.81+-	1.97	-0.1
AB_HOP	AB_HOP	*	0.00000<	0.00063	0.00095<	0.00170	0.00<	0.00	0.5
BA_HOP	BA_HOP	*	0.00012<	0.00042	0.00031<	0.00172	2.61<	17.28	0.1
SABHHP	SABHHP	*	0.00062+-	0.00050	0.00021+-	0.00168	0.34+-	2.72	-0.2
RABHHP	RABHHP	*	0.00035<	0.00042	0.00015<	0.00168	0.43<	4.76	-0.1
STEROM	STEROM		0.00000<	0.00731	0.00035<	0.00178	0.00<	0.00	0.0
SABBHH	SABBHH	*	0.00038<	0.00046	0.00015<	0.00168	0.40<	4.39	-0.1
RABBHH	RABBHH	*	0.00027<	0.00042	0.00009<	0.00422	0.36<	15.86	0.0
CO	COU		3.29642+-	0.34448	7.22289+-	6.74482	2.19+-	2.06	0.6
NOX	NOXU		0.60373+-	0.06120	0.32596+-	0.21088	0.54+-	0.35	-1.3
SO2	SO2U		9.15143+-	5.08306	-9.95237+-	5.06539	-1.09+-	0.82	-2.7

Table 4.2-1 CMB8 Outputs and Performance Measures

Output/Statistic/Code	Abbreviation	Description
<i>Source Contribution Display</i>		
Source Contribution Estimate	SCE	Contribution from the source type designated by the profile under NAME to the profile normalizing component (usually PM2.5 mass or total VOC). Units can be specified in the options menu of CMB8.
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 uncertainty estimates of the receptor data 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. Two or three times the standard error may be taken as an upper limit of the source contribution. [Target Std Err << SCE]
t-Statistic	Tstat	Ratio of the SCE to its Std Err. A high Tstat suggests a nonzero SCE. [Target > 2.0]
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. [Target 0.8 to 1.0.]
Percent Mass Accounted For	PERCENT MASS or %MASS	The sum of SCE divided by the total mass or VOC concentration. A value approaching 100% is desired. A %MASS near 100% can be misleading because a poor fit can force a high %MASS. [Target 100% ± 20%.]
Degrees of Freedom	DF	The number of species in fit 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. [Target > 5]
Chi-square	CHI SQUARE	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 differs 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 CMB calculation; 2) one or more source profiles have been selected which do not represent the contributing source types; 3) uncertainty estimates of receptor or source profile data are underestimated; and/or 4) source or receptor data are inaccurate. 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. [Target 0.0 to 4.0]

Table 4.2-1 CMB8 Outputs and Performance Measures

Output/Statistic/Code	Abbreviation	Description
<i>Source Contribution Display (cont.)</i>		
Site, sample duration, date, start hour, size		Describes the sample being modeled by location, time, and length of sample. Size refers to different particle size fractions, typically PM10 or PM2.5 (sometimes called “fine” particles).
Britt and Luecke Solution	B and L	A “Yes” flag indicates that the complex Britt and Luecke (1973) solution has been applied. A “No” flag means the default effective variance solution has been applied.
Source Elimination	SRC ELIM	The source elimination option automatically removes negative SCE or SCE less than the corresponding Std Err before printing the solution. A “Yes” flag means that the option is on and the default “No” means it is off. It is recommended that negative and negligible source types be removed manually as they may be indicators of collinearity that should be considered when interpreting the source categories represented by source profiles.
Weights for CHI SQR, R SQR, PCMASS, and FRCEST		Allows the “best” solution to be obtained automatically among up to ten combinations of source profiles based on a relative weighting of the chi-square, R-Square, Percent Mass, and Estimable Sources performance measures. The weights can be set in the options menu.
Estimable Source Profile	EST	A “Yes” flag in this column indicates that the source is estimable within the uncertainty parameters defined in the options menu. A “No” flag indicates that the source is not estimable within the uncertainty parameters.
Code and Name		The source code matches the profile with the source combinations in the source selection file. The name corresponds to a short mnemonic that designates the source profile.

Table 4.2-1 CMB8 Outputs and Performance Measures

Output/Statistic/Code	Abbreviation	Description
<i>Estimable Space Display</i>		
Eligible Space Dimension and Maximum Uncertainty		Replaces U/S CLUSTERS and SUM OF CLUSTER SOURCES in CMB7. This treatment (Henry, 1992) uses two parameters, maximum source uncertainty and minimum source projection on the eligible space. These are set to default values of 1.0 and 0.95, respectively, in CMB8. The maximum source uncertainty determines the eligible space to be spanned by the eigenvectors whose inverse singular values are less than or equal to the maximum source uncertainty. Estimable sources are defined to be those whose projection on the eligible space is at least the minimum source projection. Inestimable sources are sources that are not estimable. To modify these values click in the edit boxes and edit with keyboard entry.
Singular Value		The singular value decomposition of the source transfer matrix.
Number of Estimable Sources		The sources that are estimable given their source contributions and propagated uncertainties. This changes with the acceptable uncertainty specified in the options menu.
Estimable Linear Combinations	COEFF. SOURCE	Show clusters of sources which the model cannot easily distinguish between and that are likely to be interfering with the model's ability to provide a good set of SCE's. [Target - No clusters.]
	SCE Std Err	Estimates the sum of SCE's of the sources in a cluster and the standard error of the sum. Not needed if source profiles of cluster sources can be improved. The standard error of the SCE follows the \pm in the display.

Table 4.2-1 CMB8 Outputs and Performance Measures

Output/Statistic/Code	Abbreviation	Description
<i>Species Concentration Display</i>		
Selected Species In the Fit	I	A “*” in this column indicates the species is included in the calculation of the source contribution estimate.
Missing Measurement for Species	M	Status: M in column indicates missing measurement. These are indicated by -99 in the input data set.
Measured Species Concentration	MEAS	Ambient species concentrations (measurements and uncertainties)
Calculated Species Concentration	CALC	Calculated chemical concentrations and propagated uncertainties based on the selected profiles and the source contribution estimates. These are reported both for fitting and non-fitting species.
Ratio of Calculated to Measured Species	$\frac{\text{CALCULATED}}{\text{MEASURED}}$	Ratio of CALC/MEAS and its uncertainty Used to identify species that are over/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 indicate that an incorrect set of profiles is being used to explain the measured concentrations. [Target 0.5 to 2.0.]
Ratio of Residual to Its Uncertainty	$\frac{\text{RESIDUAL}}{\text{UNCERTAINTY}}$	Ratio of the signed difference between the calculated and measured concentration (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 2, 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. The sum of the squared RATIO R/U for fitting species divided by the degrees of freedom yields the CHI SQUARE. The highest RATIO R/U values for fitting species are the cause of high CHI SQUARE values. [Target <2.0 .]

Output/Statistic/Code	Abbreviation	Description
<i>Command Display</i>		
Modified Psuedo Inverse Matrix	MPIN	Shows which species most influence the source contribution estimate corresponding to each profile. It is examined to determine that the logical marker species are having the most influence on the apportionment.
Species – Source Contribution	SSCONT	Shows the fraction of each measured species concentration that is accounted for by the calculated species for each source or source category. This can be > 1.0 for a particular source if that species is over-accounted for by the fit. It is used to identify the sources which are accounting for particular species.

4.3 Protocol Steps

Each of the seven steps in the application and validation protocol is described below with respect to their general application. They are illustrated in greater detail for specific examples in Sections 5 and 6.

4.3.1 Determine the Applicability of CMB

The following conditions must be met for CMB to be applicable:

1. 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 NAAQS, samples should represent annual average and maximum concentrations for PM_{2.5} and PM₁₀ and correspond to maximum 8-hour average ozone concentrations for VOC.
2. Samples are amenable to or have been analyzed for a variety of chemical species. As noted above, elements, ions, and carbon are the minimal needs for PM apportionment and light hydrocarbons in canisters or automatic gas chromatographs are the minimal requirements for VOC apportionment.
3. Potential source contributors can be identified and grouped into source categories of distinct chemical compositions with respect to the receptor species available from requirement 2.
4. 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. The number of source types in a single application of CMB must be fewer than the number of chemical species measured above lower quantifiable limits at the receptor.

Unless all five of the above requirements are met, the Chemical Mass Balance receptor model is not applicable to the situation under study. These are necessary, but not sufficient, requirements, and it may still be found that even though these requirements are met, the precision and validity of CMB results are not adequate for control strategy decisions. The remaining steps in the applications and validation protocol must be completed to arrive at this conclusion.

4.3.2 Format Input Files and Perform Initial Model Runs

CMB8 allows input data files to be prepared in spreadsheet formats and, with contemporary computer memories, has no practical limit on the number of source profiles, chemical species, or individual samples that can be included in a single file. It is convenient, however, to divide input data into groups by site or season when data sets are large.

The initial model runs usually contain many more profiles than are used in production runs to determine how different composites might affect the precision and stability of the source contribution estimates. One or more initial arrays (combinations) of source profiles are usually examined during this step. Various arrays of fitting species are also examined.

During this step, it may be necessary to modify ambient data or source profiles by making additional assumptions. This is very often the case when some profiles are obtained from another study and may not report all of the species available in the other profiles or in the receptor samples. A default value of zero with a standard deviation equal to an analytical detection limit may be assigned to a species in a source profile if that species is known to be absent from that source type from previous tests of similar sources.

When selecting fitting species, only one of the different measurements of the same species (such as elemental carbon and total carbon or sulfur and sulfate) should be included in the fit. If more than one measurement of the same species is included in the CMB solution, then that species influences the source contribution estimates more than it should. This does not apply to soluble and insoluble species (such as potassium), which are really different species that distinguish among source types.

Concentrations with values below detection limits may be included only if their uncertainty is also included. Minimum detection limits may be used to estimate this uncertainty if it is not otherwise reported. If the uncertainty is underestimated or is not specified (and given a default value of zero), then these very imprecise measurements will have an excessive influence on the source contribution estimates.

Secondary components can be represented by their chemical form. In the simplest case, a single constituent source type (Section 4.1), such as secondary organic carbon that contains only an entry in the organic carbon column, may be used. These should be used sparingly, however, because a single constituent type effectively removes the influence of that source profile species on the source contribution estimates. A discussion and example application for PM₁₀ is presented in Appendix G.

Uncertainties assigned to the measurements for use in the CMB application should be reviewed to ensure that they are realistic estimates (see Appendix B). Measurement uncertainties should be provided as part of the measurement process. Typical measurement uncertainties are on the order of $\pm 5\%$ to $\pm 20\%$, with some species being more uncertain than others because of analytical interferences and proximity to detection limits. Uncertainties in source profiles could be much greater. The model considers these uncertainties when it develops the “fit”. Species with high uncertainties are unlikely to be very influential in the fit.

Chemical measurements are usually reported with their measurement uncertainties determined from error propagation of chemical analysis and flow rate uncertainties (e.g., Watson *et al.*, 1995). These uncertainties are determined from periodic performance tests and replicate analyses. The reporting of these uncertainties should be specified when the measurements are made. If chemical concentrations are available without uncertainties, typical uncertainties may be assigned based on those reported in previous analyses. The value of the diagnostics provided by the CMB software is substantially decreased without an adequate and accurate definition of measurement uncertainties in receptor data.

In most cases, the individual samples should be run separately in CMB. Compositing or combining the data from several samples will usually decrease the number of sources that CMB can resolve. Likewise, separate analysis of different PM size fractions is preferable to a “total” sample that combines the two size fractions. The sources contributing to these two size fractions are generally quite different.

Several source profiles for each source type may be included in the source profile input files, but only one profile from each type should be included in a fit. The set of profiles that best explains the measurements may differ from sample to sample, both because the profiles are different and because the source contributions change in magnitude. Several sources will nearly always contribute, and profiles should be included to represent vehicle exhaust, suspended dust, secondary sulfate, and possibly secondary nitrate or vegetative burning. Natural sources, such as sea salt or wind blown dust, should be included if these are in the proximity of the receptors. Point sources, such as coal-fired power stations, steel mills, cement production facilities, and other industrial sources in an emissions inventory are next in priority. These may be very directional, depending on which way winds are oriented between source and receptor. Finally, single constituent source types can be added as a last resort when there is no other explanation for a chemical species. This is sometimes done for zinc and copper, which are often in excess owing to nearby plating or metal handling operations.

In selecting source profiles for inclusion in a fit, it is helpful to review wind direction data and eliminate sources that have virtually no chance of contributing a detectable concentration because they are downwind of the receptor. Source types that are unlikely to be emitting during the period of time being studied (e.g., wood smoke emissions during hot summer months) can be omitted, or their profiles should be replaced with ones that represent wildfires or prescribed burning that might occur during that period.

The final selection of the most appropriate source types and the profiles to represent those source types results from interactive applications of CMB with an evaluation of the diagnostic measures. It is possible that more than one subset of source types and source profiles will fit the receptor data equally well. The interactive application of the model to different source subsets will identify these cases.

Some sources have emissions that are chemically similar or consistent over time, i.e., although the absolute magnitude of the emissions may vary, the relative composition of many of the measured species present in a source may be sufficiently stable. However, the chemistry of some species could be variable if the source changes its operating conditions, feedstock, or fuel. This variability must be reflected in the uncertainties that are assigned to each species 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 the CMB model uses the information provided by all species included in the fit, 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 uncertainties which reflect their variability. When these uncertainties are adequately estimated, other, less variable species provide a larger influence on the source contribution estimates.

4.3.3 Evaluate Outputs and Performance Measures

Model outputs and performance measures are described in Table 4.3-1. These are examined for different combinations of fitting profiles and fitting species to determine the optimal fit to the data. This process will become more evident when applied to the specific examples in Sections 5 and 6.

4.3.4 Evaluate Deviations from Model Assumptions

The CMB performance measures and tests using different profiles and fitting species can often indicate when deviations from model assumptions may have occurred. These deviations do not necessarily invalidate the CMB results – they merely indicate the potential for invalidity. This is why a separate step is necessary in the applications and validation protocol which evaluates the effects of these deviations from assumptions and determines whether or not these effects can be tolerated.

4.3.5 Modify Model Inputs to Remediate Problems

There are four main categories of problems which, once they have been identified, can be addressed to improve the performance of the model. The problem categories are: 1) insufficient receptor measurements; 2) insufficient source measurements; 3) incorrect profile combinations; and 4) source profile collinearity. Not all “indications” must persist for a problem to be present. The more “indications” that persist, the more evidence of a problem. Because of the complex interactions of all of the data in a least squares estimate, the statistics or diagnostics may not always be adequate to conclusively isolate a problem with model input. Additional physical evidence is also very helpful.

There may be inaccuracies in the receptor measurements that have not been uncovered in the routine data validation. If the data are “suspect” and there are no apparent data entry or analytical errors, the next step would be to eliminate the suspect species from the fit and rerun the model. Examine the changes in the estimates for each source. If the estimate changes by more than one standard error, and if the receptor concentration or a source profile value for the removed species is suspect, then either remeasure the species or use the SCE calculated without that species in the fit. A $RATIO\ R/U \ll -2.0$ for a species suggests either the ambient data are high or the profile data are low for that species while a $RATIO\ R/U \gg 2.0$ for a species would imply that the ambient data are low or the profile data for that species are high. In this case, it is prudent to:

1. Review the uncertainty assigned to the species with the high residuals. Make any justifiable and appropriate changes and rerun CMB. If this improves the $RATIO\ R/U$, Step 2 is not necessary.
2. Delete the suspect species from the list of fitting species and rerun. If the SCE changes by at least one standard error, do not use this species in the fit until it has been remeasured.

An unacceptable $RATIO\ R/U$ can also indicate that the set of profiles is not optimized or that the uncertainty for that species is underestimated in the receptor measurements or source profiles.

A gross error in the value of one or more species in a profile might result in a high standard error in the SCE and a high residual for those species. Therefore, one or more high residual values suggests that the uncertain source profile (and the associated species in particular) be checked and remeasured if necessary. This condition may be indicated by a SCE that is inconsistent with preliminary analyses or physical evidence. If one or more species has a “high” (positive or negative) residual which cannot be attributed to incorrect ambient data, one should examine the SSSCONT to see if one source contribution dominates that species. In this case, review profile data for the suspect species carefully. Correct or remeasure profile if necessary.

Missing source types are identified by a low percent mass explained (e.g., less than 80%) and/or a $RATIO\ R/U \ll -2.0$ for chemical species which are in the missing source. A “high negative” residual for one or more species and a high Chi-Square are also indicative of missing sources. The key to identifying these sources resides in the calculated to measured chemical concentrations listed in the species concentration display. “High negative” residuals imply that a source is needed which will supply a larger quantity of that species. The source profiles may be listed from CMB8 to assure that they have been properly formatted and read into the software. These profiles can be examined to determine which ones would supply sufficient quantities of the missing concentrations if they were added to the set of fitting sources. The CMB model can be reapplied as many times as is necessary to determine which source types and source profiles best account for the underestimated receptor concentrations. A source should not be included in the final fit just because it “explains” the data, however; there must be a physical justification for the source's contribution at a receptor if it is to be included in the fit.

Noncontributing source types, i.e., source types with contributions lower than detection limits, are identified by Tstat values below 2. Such source types may be eliminated from the fit if the source contribution is indeed small. If the source is present but with a very small contribution to total mass, it should only be removed from the fit if the SSSCONT shows that none of the species in the source account for more than 5% to 10% of the ambient concentration for those species.

Estimable linear combinations (of inestimable sources) may occur owing to high profile uncertainty or excessive collinearity with low profile uncertainty. To determine if the uncertainty in the SCE is due to high profile uncertainty, reduce the uncertainties in the profile to levels that might be reasonable to achieve if the source profiles were measured more precisely; then, rerun CMB – if the clusters containing those sources are no longer listed, it is likely that collinearity *per se* is not significant. Remeasurement of the profile will probably improve the uncertainties of the source contribution estimates. It is possible that reducing the uncertainty will not eliminate the clusters but the SCE uncertainty will likely be improved somewhat. This would suggest that collinearity is also present.

Remedies for unacceptably high uncertainties due to collinearity can take five forms, ranked from most to least desirable.

1. The profile of one or more of the cluster sources could be improved by measuring additional species.
2. Reduce the uncertainties in the source profiles of the cluster sources. If the Tstat becomes > 2.0 , and if these profile uncertainties are realistically achievable by remeasurement, then the “apparent” collinearity can be improved in large part by

improving the uncertainty in the profiles. Ideally, the cluster for that group of sources would disappear. Remeasure and rerun CMB with the improved measurements. More precise source profile measurements must be obtained before reapplying the model.

3. The estimate of the SCE of the source categories that are estimable linear combinations of inestimable sources. Obtain independent estimates of the contributions of the individual source categories and use them to apportion the SCEs into the source categories.
4. Combine the profiles of the collinear source profiles into a single profile of a “composite source category” that chemically represents the source categories 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 would result in improved source estimates of the crustal component, which can then serve as an estimate of the combined impact of the two sources. This aggregate source contribution estimate might then be partitioned into its components by another method (e.g., dispersion modeling, microscopy, or wind trajectory analysis).
5. Species that are causing the similarity in source profiles might be deleted from the fit. These species can often be determined from the display produced by the Contributions by Species tab in the Main Report. Often one of the inestimable sources will be $\gg 100\%$ for that species and the other will be negative. Unfortunately, eliminating too many species from the fit may cause the model to fail the applicability requirements. Also, the results should acknowledge that the deleted source may be present.

4.3.6 Evaluate the Consistency and Stability of the Model Results

The CMB estimates should be tested to see how sensitive they are to the various input data. Unstable estimates (source contribution estimates that change by more than one standard error) are an indication that the model may not be providing stable results. For CMB validation, the term “model stability tests” is usually taken to mean the evaluation of model estimates to changes in input parameters, such as the selected sources and their profiles, as well as selection of fitting species used to reach a solution with the CMB model.

The CMB model’s effective variance fitting procedure uses estimates of the source profile and receptor concentration uncertainties to “weight” their effect in arriving at source contribution estimates. It is helpful to explore how sensitive the source contribution estimates are to changes in the source profiles and these uncertainties. This can be done by introducing changes into the source profiles and rerunning the model for each change.

The model user can select several species from a source(s) of particular regulatory interest and assign worst case values to those species in the profile. The model can then be rerun with the worst case profile(s). A practical way to accomplish this sensitivity analysis is to include a “worst case” source profile along with the “best estimate” profile in the data file. The resulting source estimate(s) can be considered “brackets” to the source contribution estimates and can be compared to the uncertainty intervals calculated for each run. If the bracketing

interval is greater than the calculated uncertainty interval, then the model may be sensitive to changes in the source profiles.

The stability of source contribution estimates with respect to receptor concentrations is best tested with collocated chemical measurements from one of the sampling sites. These collocated measurements are usually included as part of the quality assurance plan for a subset of all samples. If nearly equivalent source contribution estimates are derived from these two independent measurements of the same ambient air, then the receptor data are not likely causing instabilities in the CMB results.

Lacking these collocated data, portions of the input data may be perturbed randomly or systematically in proportion to their uncertainty. The source contribution estimates for the sources of regulatory interest should not change by more than one standard error in response to small perturbations if the results are stable. (A “small” perturbation is defined as one standard error of the ambient species concentrations.) If the results are not stable, the validity of the CMB result for that particular data set are questionable.

The stability of CMB model results to the fitting species can be evaluated by identifying a species which SSCONT attributes in large part to a single source. Eliminate this species from the fit and examine how much the corresponding source contribution changes. If this change is greater than the Std Err, then that species must be greatly influencing the “fit”. Review the quality of both the source and ambient measurements for that species carefully because of its influence on the model estimates.

4.3.7 Corroborate CMB Results with Other Modeling and Analyses

If the CMB model is determined to be applicable, the summary statistics and diagnostics are generally within target ranges, there are no significant deviations from model assumptions, and the sensitivity tests reveal no unacceptable instability or consistency problems, the CMB analysis is considered valid. If uncertainties associated with source estimates are too high for decision-making purposes even after taking the steps recommended in this protocol, then the source compositions being used are not representative of the sources in the airshed, or they contain too much uncertainty associated with the influential species.

It is recommended that both a dispersion model and receptor model be used in a collaborative manner to perform an apportionment, provided that the dispersion model is applicable and the receptor model is valid for the particular application. Spatial and time series distributions, similar to the examples in Section 3, should be examined to establish that source contribution magnitudes are consistent with the locations and timing expected from those sources.

5. EXAMPLE OF APPLICATION AND VALIDATION FOR PM_{2.5}

This example demonstrates how the CMB applications and validation protocol is applied to PM_{2.5} measurements from the Northern Front Range Air Quality Study (NFRAQS, Watson *et al.*, 1998). NFRAQS is a preview of future PM_{2.5} source apportionment studies that have high stakes in terms of control strategy development. NFRAQS used a variety of the models described in Section 2, including CMB, to determine the source categories and individual emitters contributing to excessive contributions of primary suspended dust, carbon, and secondary ammonium, sulfate, and nitrate.

The PM_{2.5} CMB data set is used for this example because it is one of the few data sets that contains specific organic compounds in both source and receptor measurements. It is anticipated that, as organic aerosol measurement methods are standardized and the cost of their application decreases, these measurements will become more standard in future source apportionment studies.

Each of the seven steps in the protocol is illustrated using examples from this data set. The CMB input files are available with the other test data sets on EPA's website (www.epa.gov/scram001 ; Appendix C). The NFRAQS source profiles may be useful for Level I or Level II assessments in other airsheds in preparation for a more comprehensive source apportionment study.

5.1 Model Applicability

The requirements for CMB model applicability are: 1) a sufficient number of receptor samples is taken with an accepted method to evaluate temporal and spatial variations; 2) samples are analyzed for chemical species which are also present in source emissions; 3) potential source contributors have been identified and chemically characterized; and 4) the number of non-collinear source types is less than or equal to the number of measured species.

In NFRAQS, aerosol samples were taken by well-characterized methods and measurements were fully evaluated (Chow *et al.*, 1998). Samples were analyzed for 20 days throughout the winter of 1996-97. Two (i.e., Welby and Brighton) of the nine sampling sites acquired samples for organic aerosol analysis.

Table 5.1-1 shows an inventory that was especially compiled for NFRAQS, using published emission factors (not specific to the Denver area) and different activity estimates. According to this inventory, the major sources were: 1) normal hot-stabilized gasoline-powered vehicle exhaust; 2) gasoline-powered vehicle emitting visible smoke; 3) diesel exhaust; 4) meat cooking; 5) wood combustion; 6) road dust and sanding; 7) secondary ammonium sulfate; 8) secondary ammonium nitrate; and 9) industrial point sources, including coal-fired power stations, refineries, etc. Owing to previous source testing (Watson *et al.*, 1990b), it was believed that cold starts of gasoline vehicles might be a significant contributor and that soft wood (used mostly in fireplaces because it offers a nice flame) and hard wood (used in wood stoves because it heats more efficiently) might be distinguishable if the appropriate organic compounds were measured. Samples were acquired by dilution sampling of vehicles on dynamometers, wood burning on laboratory stoves, meat cooking in a laboratory kitchen, and grab sampling of suspendable dust. These samples were analyzed in the laboratory for elements, ions, carbon, organic aerosol compounds, and ¹⁴C using the same methods applied at the receptors. Profiles from coal-fired electrical generation were available from a previous study in the area (Watson *et al.*, 1988).

Table 5.1-1 Wintertime Emissions Inventory for Denver Metro Area

	Source emission rate estimates (tons/day) ^a						
	PM ₁₀	PM _{2.5}	SO ₂	NO _x	NH ₃	VOC	CO
Gas Exhaust	1.7	1.6	3.3	137.7		157.6	1340.8
Visibly Smoking Gas Exhaust	0.2	0.2					
Diesel Exhaust	5.0	4.9	1.5	36.1		8.4	30.9
Off-Road Exhaust	1.8	1.8	1.7	27.4		14.3	111.7
Wood Burning	1.8	1.8	0.0	0.0			
Road Dust & Sand	49.6	7.4	0.0	0.0			
Coal Power Stations	1.3	0.7	62.1	64.3			
Other Industries	7.8	2.6	16.7	47.8			
Natural Gas	0.5	0.5	0.0	28.4			
Unpaved Road Dust	28.2	4.2	0.0	0.0			
Restaurant Cooking	1.4	1.4	0.0	0.0			
Construction Dust	2.2	0.3	0.0	0.0			
Biogenic				3.0		31.3	0.0
Industrial						34.8	22.3
Area Sources				1.0		89.8	72.3
Total	101.6	27.5	85.2	345.7		336.2	1578.0

^aRegional Air Quality Council "Review of Blueprint for Clean Air Emissions Inventories"; April 8, 1998.

Tables 5.1-2 and 5.1-3 identify and describe the profiles available in the NFRAQS data base. A subset of these profiles was used for testing. The number of fitting species used in CMB (about 80-85 species with organic species, about 20-25 species with conventional element, ion, and carbon species) exceeds the number of source types (up to 11 source types). The CMB model is applicable to source apportionment of this PM_{2.5} data base.

Table 5.1-2 Source Composition Profiles from NFRAQS

PNO	Mnemonic	Size	Type	Description
N001	NWNSP	F	Composite	Winter, non-smoker, Phase 1 minus Phase 2, L2, ML1, M1, M2, M3, H1
N002	NWLP	F	Composite	Winter, non-smoker, Phase 1 - Phase 2, L2, ML1, ML2
N003	NWHP	F	Composite	Winter, non-smoker, Phase 1 - Phase 2, M1, M3, H1
N004	NWNSPI	F	Composite	Winter, non-smoker, Phase 1 - UPI, MLIP1, MIP1, M2P1, M3P1, HIP1
N005	NWNSP1mC	F	Composite	Winter, non-smoker, Phase 1 - UPI, MLIP1, MIP1, M2P1, M3P1, HIP1 minus backup carbon
N006	NWNSP1pC	F	Composite	Winter, non-smoker, Phase 1 - L2P1, MLIP1, MIP1, M2P1, M3P1, HIP1 plus backup carbon
N007	NWNSP2	F	Composite	Winter, non-smoker, Phase 2-LIP2, L2P2, MLIP2, MIP2, M2P2, M3P2, HIP2, H2P2
N008	NWNSP2mC	F	Composite	Winter, non-smoker, Phase 2 - LIP2, L2P2, MLIP2, MIP2, M2P2, M3P2, HIP2, H2P2 minus backup carbon
N009	NWNSP2pC	F	Composite	Winter, non-smoker, Phase 2 - LIPI, L2P2, MLIP2, MIP2, M2P2, M3P2, HIP2, H2P2 plus backup carbon
N010	NWSM	F	Composite	Winter, smokers, S2P1, S2P2, S2P3, S3P1, S3P2, S3P3
N011	NWSMmC	F	Composite	Winter, smokers, S2P1, S2P2, S2P3, S3P1, S3P2, S3P3 minus backup carbon
N012	NWSMpC	F	Composite	Winter, smokers, S2P1, S2P2, S2P3, S3P1, S3P2, S3P3 plus backup carbon
N013	NWHD	F	Composite	Winter, heavy-duty diesel, runs 2-15
N014	NWHDmC	F	Composite	Winter, heavy-duty diesel, runs 2-15 minus backup carbon
N015	NWHDpC	F	Composite	Winter, heavy-duty diesel, runs 2-15 plus backup carbon
N016	NWLCPI	F	Composite	Winter, low emitter, phase 1 - UPI, MLIP1, M2P1
N017	NWLCPI	F	Composite	Winter, low emitter, phase 2 - L2P2, MLIP2, M2P2
N018	NWLCPI	F	Composite	Winter, low emitter, phase 3 - L2P3, MLIP3, M2P3
N019	NWLCPC	F	Composite	Winter, low emitter, FTP composite - L2PC, MLIPC, M2PC
N020	NWL2PI	F	Individual	Winter, low emitter, phase 1 - L2PI
N021	NWL2P2	F	Individual	Winter, low emitter, phase 2 - L2P2
N022	NWL2P3	F	Individual	Winter, low emitter, phase 3 - L2P3
N023	NWL2C	F	Individual	Winter, low emitter, FTP composite - L2PC
N024	NWHCPI	F	Composite	Winter, high emitter, phase 1 - MIP1, M3P1, HIP1
N025	NWHCP2	F	Composite	Winter, high emitter, phase 2 - MIP2, M3P2, HIP2
N026	NWHCP3	F	Composite	Winter, high emitter, phase 3 - M1 P3, M3P3, H1 P3
N027	NWHCPC	F	Composite	Winter, high emitter, FTP composite - MIPC, M3PC, H1 PC
N028	NWHIPI	F	Individual	Winter, high emitter, phase 1, HIP1
N029	NWHIP2	F	Individual	Winter, high emitter, phase 2, HIP2
N030	NWHIP3	F	Individual	Winter, high emitter, phase 3, HIP3
N031	NWHIC	F	Individual	Winter, high emitter, FTP composite, HIPC
N032	NWnSPI	F	Composite	Winter, non-smoker, phase 1, UPI, MLIP1, ML2P1, M2P1, MIP1, M3P1, HIP1
N033	NWnSP2	F	Composite	Winter, non-smoker, phase 2, L2P2, MLIP2, ML2P2, M2P2, MIP2, M3P2, HIP2
N034	NWnSP3	F	Composite	Winter, non-smoker, phase 3, L2P3, MLIP3, ML2P3, M2P3, MIP3, M3P3, HIP3
N035	NWnSPC	F	Composite	Winter, non-smoker, FTP composite, L2PC, MLIPC, ML2PC, M2PC, MIPC, M3PC, HIPC
N036	NWSCPI	F	Composite	Winter, smoker, phase 1, SIP1, S2P1, S3P1
N037	NWSCP2	F	Composite	Winter, smoker, phase 2, SIP2, S2P2, S3P2
N038	NWSCP3	F	Composite	Winter, smoker, phase 3, SIP3, S2P3, S3P3
N039	NWSCPC	F	Composite	Winter, smoker, FTP composite, SIPC, S2PC, S3PC
N040	NWSaPI	F	Composite	Winter, smoker, phase 1, S2P1, S3P1
N041	NWSaP2	F	Composite	Winter, smoker, phase 2, S2P2, S3P2
N042	NWSaP3	F	Composite	Winter, smoker, phase 3, S2P3, S3P3
N043	NWSaPC	F	Composite	Winter, smoker, FTP composite, S2PC, S3PC
N044	NWLDCPI	F	Composite	Winter, light-duty diesel, phase 1, LDIP1, LD2P1, LD3P1, LD4P1, LD5P1
N045	NWLDCP2	F	Composite	Winter, light-duty diesel, phase 2, LDIP2, LD2P2, LD3P2, LD4P2, LD5P2
N046	NWLDCP3	F	Composite	Winter, light-duty diesel, phase 3, LDIP3, LD2P3, LD3P3, LD4P3, LD5P3
N047	NWLDCPC	F	Composite	Winter, light-duty diesel, FTP composite, LDIPC, LD2PC, LD3PC, LD4PC, LD5PC
N048	NWHDc	F	Composite	Winter, heavy-duty diesel, runs 2-15 (all)
N049	NWHDoc	F	Composite	Winter, heavy-duty diesel, runs 2,5,8,10,16,17,24,32 (others)
N050	NMc	F	Composite	Composite of NMAHa, NMCH, NMCCa, and NMCK
N051	NMAHa	F	Average	3 replicate samples, automated charbroiler, hamburger, samples MAHI, 2, and 3

Table 5.1-2 (cont.) Source Composition Profiles from NFRAQS

PNO	Mnemonic	Size	Type	Description
N052	NMCH	F	Individual	Charbroiled hamburger, sample MCHI
N053	NMCCa	F	Average	Charbroiled chicken w/skin, samples MCC1 and MCC2
N054	NMCK	F	Individual	Charbroiled steak, sample MCKI
N055	NWFSc	F	Composite	Fireplace burning soft woods
N056	NWFGPDa	F	Average	Fireplace, Pine, samples WFGPD1, 2 and 3 with Grate, Dry
N057	NWFEND	F	Individual	Fireplace, pinon, sample WFENDI, Empty, Dry
N058	NWFGAMD	F	Individual	Fireplace, Apple/Mesquite, sample WFGAMD1, with Grate, Dry
N059	NWFGBD	F	Individual	Fireplace, Bundled wood, sample WFGBD1, with Grate, Dry
N060	NWFHc	F	Composite	Fireplace burning hard woods
N061	NWFEHD	F	Individual	Fireplace, mixed Hardwood, sample WFEHDI, Empty, Dry
N062	NWFGHD	F	Individual	Fireplace, mixed Hardwood, sample WFGHD2, with Grate, Dry
N063	NWFGOD	F	Individual	Fireplace, Oak, sample WFGOD1, with Grate, Dry
N064	NWFGOW	F	Individual	Fireplace, Oak, sample WFGOWI, with Grate, Wet
N065	NWFGDD	F	Individual	Fireplace, Duraflame, sample WFGDDI, with Grate, Dry
N066	NWSHc	F	Composite	Woodstove burning hardwood
N067	NWSHDHH	F	Individual	Woodstove, mixed hardwood, sample WSHDHHI, Dry, High fuel, High burn
N068	NWSHDHL	F	Individual	Woodstove, mixed hardwood, sample WSHDHLI, Dry, High fuel, Low burn
N069	NWSHDLH	F	Individual	Woodstove, mixed hardwood, sample WSHDLHI, Dry, Low fuel, High burn
N070	NWSHDLL	F	Individual	Woodstove, mixed hardwood, sample WSHDLLI, Dry, Low fuel, Low burn
N071	NWSODHLa	F	Individual	Woodstove, Oak, sample WSODHLI, Dry, High fuel, Low burn
N072	NWSOWHL	F	Individual	Woodstove, Oak, WSOWHL2, Wet, High fuel, Low burn
N073	NRDC	F	Composite	Composite roaddust, NRD01 to 05
N074	NRDOI	F	Individual	Jewell, w of Kendall on 10/25/96, sample 717
N075	NRD02	F	Individual	Kipling at Federal on 3/3/97, sample 818
N076	NRD03	F	Individual	Kipling at Federal on 3/2/97, sample 819
N077	NRD04	F	Individual	Speer, Bannock to 11th on 12/21/96, sample 831
N078	NRD05	F	Individual	Jewell, w of Kendall on 12/24/96, sample 800
N079	AMSUL	F	Calculated	Secondary ammonium sulfate
N080	AMBSUL	F	Calculated	Secondary ammonium bisulfate
N081	AMNIT	F	Calculated	Secondary ammonium nitrate
N135	NSLCP1	F	Composite	Summer, Light-Duty, GasoSummer, LineL2P1
N136	NSLCP2	F	Composite	Summer, Light-Duty, GasoSummer, LineL2P2
N137	NSLCP3	F	Composite	Summer, Light-Duty, GasoSummer, LineL2P3
N138	NSLCP3	F	Composite	Summer, Light-Duty, GasoSummer, LineL2PC
N139	NSMCP1	F	Composite	Summer, Light-Duty, GasoSummer, LineMIP1
N140	NSMCP2	F	Composite	Summer, Light-Duty, GasoSummer, LineMIP2
N141	NSMCP3	F	Composite	Summer, Light-Duty, GasoSummer, LineMIP3
N142	NSMCPC	F	Composite	Summer, Light-Duty, GasoSummer, LineMIPC
N143	NSHCPI	F	Composite	Summer, Light-Duty, GasoSummer, LineHIP1
N144	NSHCPC	F	Composite	Summer, Light-Duty, GasoSummer, LineHIP2
N145	NSHCP3	F	Composite	Summer, Light-Duty, GasoSummer, LineHIP3
N146	NSHCPC	F	Composite	Summer, Light-Duty, GasoSummer, LineHIP3C
N147	NSSCPI	F	Composite	Summer, Light-Duty, GasoSummer, LineSIP1
N148	NSSCP2	F	Composite	Summer, Light-Duty, GasoSummer, LineSIP2
N149	NSSCP3	F	Composite	Summer, Light-Duty, GasoSummer, LineSIP3
N150	NSSCPC	F	Composite	Summer, Light-Duty, GasoSummer, LineSIPC
N151	NSLDCP1	F	Composite	Summer, Light-Duty, DieselDIP1
N152	NSLDCP2	F	Composite	Summer, Light-Duty, DieselDIP2
N153	NSLDCP3	F	Composite	Summer, Light-Duty, DieselDIP3
N154	NSLDCPC	F	Composite	Summer, Light-Duty, DieselDIPC

Table 5.1-3

Source Composition Profiles from the 1987 Scenic Denver Study and Other Studies

PNO	Mnemonic	Size	Type	Description
N082	BRAKE	B	Individual	radial tire (195/608-15 Toyo, 7200 miles)
N083	TRDST	B	Individual	
N084	GPHWYCI	F	Composite	3 samples. Interstate highway.
N085	GCYSTC3	F	Composite	2 samples. City street near civic center.
N086	GSCRDC4	F	Composite	2 samples. Secondary paved roads.
N087	GRSDMC5	F	Composite	2 samples. Road sanding material.
N088	GHWYTC6	F	Composite	2 samples. Stapleton Tunnel.
N089	GHWSTC7	F	Composite	3 samples. Stapleton Tunnel and adjacent dirt.
N090	GPRDVC8	F	Composite	6 samples. Paved roads (general).
N091	GUADVC9	F	Composite	5 samples. Unpaved roads (general).
N092	GAGSLC2	F	Composite	2 samples. Agricultural soil.
N093	MNDCC	F	Composite	9 samples. Dynamometer diesel, cold start.
N094	MNDCS	F	Composite	9 samples. Dynamometer diesel, cold stabilized.
N095	MNDCH	F	Composite	9 samples. Dynamometer diesel, hot transient.
N096	MLCC	F	Composite	10 samples. Dynamometer leaded, cold start.
N097	MLCS	F	Composite	10 samples. Dynamometer leaded, cold stabilized.
N098	MLCH	F	Composite	9 samples. Dynamometer leaded, hot transient.
N099	MUCCC	F	Composite	8 samples. Dynamometer unleaded, closed - loop catalyst, cold start.
N100	MUCCS	F	Composite	4 samples. Dynamometer unleaded, closed - loop catalyst, cold stabilized.
N101	MUCCH	F	Composite	3 samples. Dynamometer unleaded, closed - loop catalyst, hot transient.
N102	MUOCC	F	Composite	14 samples. Dynamometer unleaded, oxidation catalyst, cold start.
N103	MUOCS	F	Composite	8 samples. Dynamometer unleaded, oxidation catalyst, cold stabilized.
N104	MUOCH	F	Composite	5 samples. Dynamometer unleaded, oxidation catalyst, hot transient.
N105	MUCC	F	Composite	22 samples. Dynamometer unleaded, both catalyst types, cold start.
N106	MUCS	F	Composite	12 samples. Dynamometer unleaded, both catalyst types, cold stabilized.
N107	MUCH	F	Composite	8 samples. Dynamometer unleaded, both catalyst types, hot transient.
N108	MD50U50S	F	Composite	21 samples. Dynamometer, 50% diesel, 50% unleaded, cold stabilized
N109	MD75U25S	F	Composite	21 samples. Dynamometer, 75% diesel, 25% unleaded, cold stabilized
N110	MD95U5S	F	Composite	21 samples. Dynamometer, 95% diesel, 5% unleaded, cold stabilized
N111	ML50U50S	F	Composite	22 samples. Dynamometer, 50% leaded, 50% unleaded, cold stabilized
N112	ML25U75S	F	Composite	22 samples. Dynamometer, 25% leaded, 75% unleaded, cold stabilized
N113	ML5U95S	F	Composite	22 samples. Dynamometer, 5% leaded, 95% unleaded, cold stabilized
N114	MD5L2U3S	F	Composite	31 samples. Dynamometer, 50% diesel, 20% leaded, 30% unleaded, cold stabilized.
N115	MD75L5US	F	Composite	31 samples. Dynamometer, 75% diesel, 15% leaded, 10% unleaded, cold stabilized.
N116	MD85L0US	F	Composite	31 samples. Dynamometer, 85% diesel, 10% leaded, 5% unleaded, cold stabilized.
N117	MD3035US	F	Composite	31 samples. Dynamometer, 30% diesel, 35% leaded, 35% unleaded, cold stabilized.
N118	MD3050US	F	Composite	31 samples. Dynamometer, 30% diesel, 50% leaded, 20% unleaded, cold stabilized.
N119	PCHKC04	F		Cherokee Pow. Pt., #4 boiler burning coal, mech. collector., elec. precipitator, wet scrubber
N120	PCOOROI	F		Adolph Coors Co., #5 boiler burning coal and brewery sludge, wet scrubber.
N121	PCHKG03	F		Cherokee Pow. Pt., #3 boiler burning natural gas, no control equipment.
N122	PCHKC03	F		Cherokee Pow. Pt., #3 boiler burning coal, bag house.
N123	PCHCLCI	F		Composite, PCHKC03 & PCHKC04, boilers burning coal.
N124	PCOALC2	F		Composite, PCHKC03, PCHKC04 & PCOOROI, boilers burning coal.
N125	CCRCSCI	F		Composite, 3 samples. Fluidized Catalytic Cracker (FCC) regenerator.
N126	WFPLLOI	F		Fireplace, low burn rate.
N127	WFPLH02	F		Fireplace, high burn rate.
N128	WWSIN03	F		Fireplace insert (treated as woodstove).
N129	WWSTC04	F		Woodstove, thermostatically controlled.
N130	WWSLF05	F		Woodstove, large firebox.
N131	WWSF06	F		Woodstove, small firebox.
N132	WFIRECI	F		Composite of two fireplace tests.
N133	WSTOVC2	F		Composite of four woodstove tests.
N134	WRWCBC3	F		Composite of all six tests.

5.2 Initial Source Contribution Estimates

Initial CMB tests were performed to select a default combination of source profiles and fitting species for the ambient data. These tests were performed to apportion carbon, as this was a major focus of the NFRAQS. A preliminary set of source profiles consisting of at least one source profile from each source category was applied to NFRAQS Winter 97 organic speciated measurements. These initial apportionments were calculated in CMB's batch mode. No attempt was made to manually improve the apportionment. These tests were used to select a default set of fitting species and examine the sensitivity of total carbon and PM_{2.5} apportionment to alternative source profiles within source categories. Tables 5.2-1 and 5.2-2 show the results of the sensitivity tests for meat cooking and wood combustion profiles, and motor vehicle profiles, respectively, for the sample collected from the Welby sampling site on 01/17/97 at 0600 to 1200 MST. This sample had the highest PM_{2.5} and total carbon concentration during the study and showed detectable contributions from all major sources in the initial CMB tests.

The range of the carbonaceous fraction explained by alternative individual wood stove profiles (using hardwoods) was 5.7% to 21.7% of particulate carbon. Moisture content is the primary reason for the variability in apportionment. The composite profile that was used in the NFRAQS CMB as the default profile for this source category (NWSHc2) gives an average contribution of 14.0%.

Fireplace combustion profiles (using softwoods) yield contributions of 1.2% carbon for NWFGPDa and 4.4% for NWFEND. The composite of these two profiles (WFSc) gives a carbon contribution that is equal to the variability in the apportionments for individual softwood profiles.

With the exception of NWFGHD, the individual fireplace/hardwood profiles yield similar apportionments in the range of 0.7% to 0.8% carbon. The NWFGHD apportionment is a statistical outlier, and is excluded from the composite profile (NWFHc) for this source category. This composite profile gives an average apportionment of 0.8% carbon, which is similar to all other profiles within the composite. Apple and mesquite are both hardwoods, and their profile yields a carbon apportionment consistent with the majority of the hardwood profiles.

Synthetic log yields the highest apportionment among the fireplace profiles, with an average of 47% carbon. This profile is composed of an abundance of elemental carbon, with a lack of other key "marker" compounds. The high elemental carbon content of the synthetic log causes it to be collinear with the diesel profiles, which is why the apportionment for this profile is so high.

Several wood combustion profiles were used together in order to examine the potential for collinearity among subcategories of wood combustion. The softwood composite (NWFSc) gives similar apportionments with all alternative hardwood profiles regardless of the type of appliance, wood stove or fireplace. This softwood composite profile is not collinear with any other wood combustion profiles. Using the fireplace/hardwood composite profile with the wood stove/hardwood composite profile results in negative source contributions for the fireplace/hardwood profile. This fireplace/hardwood profile also causes an overall increase in the average predicted apportionment for wood stove. This indicates collinearity between the profiles for hardwood combustion in fireplaces and wood stoves. Because the contribution to

Table 5.2-1a Sensitivity of Total Carbon Apportionment to Alternative Wood Combustion Profiles (Welby, 01/17/97 at 0600 to 1200 MST)

Test	Base	W01	W02	W03	W04	W05	W06	W07	W08	W09	
Concentration of TC (ug/m3)	21.55 ± 1.38	21.55 ± 1.38	21.55 ± 1.38	21.55 ± 1.38	21.55 ± 1.38	21.55 ± 1.38	21.55 ± 1.38	21.55 ± 1.38	21.55 ± 1.38	21.55 ± 1.38	
R-squared	0.93469	0.93289	0.92899	0.93299	0.93631	0.92211	0.92392	0.93393	0.93264	0.93451	
Chi-squared	0.48714	0.49703	0.52859	0.49595	0.46708	0.57092	0.56866	0.48505	0.49967	0.47904	
Percent mass	99.56697663	99.40744659	99.32327338	99.14931232	99.51277911	99.08973217	99.23200067	98.82333834	98.85841825	98.82203909	
<u>Absolute Contribution (ugTC/m3)</u>	<u>Profile</u>										
LDGV, cold start	nvns	3.21 ± 0.28	3.24 ± 0.28	3.14 ± 0.27	3.46 ± 0.30	3.82 ± 0.33	3.44 ± 0.30	3.31 ± 0.29	3.43 ± 0.30	3.24 ± 0.28	3.40 ± 0.30
LDGV, hot stabilized	nvns2	0.80 ± 0.05	0.76 ± 0.05	0.71 ± 0.05	0.71 ± 0.05	0.81 ± 0.05	0.67 ± 0.04	0.64 ± 0.04	0.67 ± 0.04	0.69 ± 0.04	0.68 ± 0.04
LDGV, high particle emitter	nvsm	5.23 ± 0.21	5.65 ± 0.23	6.72 ± 0.27	5.53 ± 0.22	3.07 ± 0.12	7.35 ± 0.30	7.33 ± 0.30	7.41 ± 0.30	7.18 ± 0.29	7.38 ± 0.30
Diesel Exhaust	nwhdc	7.03 ± 0.28	6.92 ± 0.27	7.02 ± 0.28	6.87 ± 0.27	6.45 ± 0.26	6.86 ± 0.27	6.41 ± 0.25	6.89 ± 0.27	6.86 ± 0.27	6.91 ± 0.27
Meat composite	nmc	1.94 ± 0.15	1.98 ± 0.16	2.02 ± 0.16	2.03 ± 0.16	2.07 ± 0.16	2.19 ± 0.17	2.17 ± 0.17	2.18 ± 0.17	2.10 ± 0.17	2.17 ± 0.17
Road or geologic dust	nrdc	0.56 ± 0.18	0.57 ± 0.18	0.57 ± 0.18	0.57 ± 0.18	0.55 ± 0.18	0.59 ± 0.19	0.59 ± 0.19	0.57 ± 0.18	0.58 ± 0.18	0.58 ± 0.19
Coal power stations	pchcl1	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
Fireplace, softwood composite	nwfsc	-0.33 ± 0.11									
Wood stove hardwood composite	nwshe2	3.01 ± 0.14	2.32 ± 0.11								
Wood stove hardwood	nwsdhl			1.22 ± 0.08							
Wood stove oak	nwsodhla				2.20 ± 0.15						
Wood stove wet oak	nwsowhl					4.68 ± 0.30					
Fireplace, pine average	nwfcpda						0.26 ± 0.02				
Fireplace, pinion-no grate	nwfend							0.94 ± 0.05			
Fireplace, apple/mesquite	nwfgamd								0.14 ± 0.01		
Fireplace, bundled wood	nwfcbd									0.66 ± 0.04	
Fireplace, hardwood composite	nwfhc										0.18 ± 0.01
Test	Base	W10	W11	W12	W13	W14	W15	W16	W17	W18	
Concentration of TC (ug/m3)	21.55 ± 1.38	21.55 ± 1.38	21.55 ± 1.38	21.55 ± 1.38	21.55 ± 1.38	21.55 ± 1.38	21.55 ± 1.38	21.55 ± 1.38	21.55 ± 1.38	21.55 ± 1.38	
R-squared	0.93469	0.9299	0.93048	0.93243	0.93403	0.93187	0.93396	0.93392	0.93938	0.93508	
Chi-squared	0.48714	0.51275	0.51143	0.49398	0.48274	0.54105	0.49936	0.50149	0.49558	0.48035	
Percent mass	99.56697663	98.91832322	98.90180411	98.81614604	98.79851328	101.3780927	99.12935947	98.99405126	100.7689274	98.81582122	
<u>Absolute Contribution (ugTC/m3)</u>	<u>Profile</u>										
LDGV, cold start	nvns	3.21 ± 0.28	3.47 ± 0.30	3.34 ± 0.29	3.47 ± 0.30	3.44 ± 0.30	2.96 ± 0.26	3.39 ± 0.29	3.42 ± 0.30	3.04 ± 0.26	3.42 ± 0.30
LDGV, hot stabilized	nvns2	0.80 ± 0.05	0.67 ± 0.04	0.68 ± 0.04	0.67 ± 0.04	0.67 ± 0.04	0.82 ± 0.05	0.72 ± 0.05	0.69 ± 0.05	0.87 ± 0.06	0.68 ± 0.04
LDGV, high particle emitter	nvsm	5.23 ± 0.21	7.36 ± 0.30	7.50 ± 0.30	7.30 ± 0.30	7.37 ± 0.30	4.49 ± 0.18	6.34 ± 0.26	6.69 ± 0.27	3.50 ± 0.14	7.41 ± 0.30
Diesel Exhaust	nwhdc	7.03 ± 0.28	6.88 ± 0.27	6.93 ± 0.27	6.88 ± 0.27	6.89 ± 0.27	-0.50 ± 0.02	6.97 ± 0.28	6.91 ± 0.27	1.12 ± 0.04	6.94 ± 0.27
Meat composite	nmc	1.94 ± 0.15	2.18 ± 0.17	2.15 ± 0.17	2.22 ± 0.18	2.19 ± 0.17	3.31 ± 0.26	2.09 ± 0.17	2.12 ± 0.17	2.92 ± 0.23	2.18 ± 0.17
Road or geologic dust	nrdc	0.56 ± 0.18	0.58 ± 0.19	0.58 ± 0.18	0.58 ± 0.19	0.59 ± 0.19	0.60 ± 0.19	0.57 ± 0.18	0.56 ± 0.18	0.58 ± 0.18	0.58 ± 0.19
Coal power stations	pchcl1	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
Fireplace, softwood composite	nwfsc	-0.33 ± 0.11						-0.24 ± 0.08	-0.09 ± 0.03	-0.52 ± 0.17	-0.10 ± 0.03
Wood stove hardwood composite	nwshe2	3.01 ± 0.14						1.43 ± 0.07	0.92 ± 0.04	2.20 ± 0.10	
Fireplace, apple/mesquite	nwfgamd								0.10 ± 0.01		
Fireplace, bundled wood	nwfcbd										
Fireplace, hardwood composite	nwfhc										0.19 ± 0.01
Fireplace, hardwood-no grate	nwfhd		0.17 ± 0.01								
Fireplace, hardwood	nwfghd			0.13 ± 0.01							
Fireplace, oak	nwfgod				0.17 ± 0.01						
Fireplace, wet oak	nwfgow					0.15 ± 0.01					
Fireplace, synthetic log	nwfidd						10.18 ± 0.60			8.00 ± 0.47	

**Table 5.2-1b Sensitivity of Total Carbon Apportionment to Alternative Meat Cooking Profiles
(Welby, 01/17/97 at 0600 to 1200 MST)**

Test	Test	Base	M01	M02	M03	M04
Concentration of TC (ug/m3)	conc	21.55 ± 1.38	21.55 ± 1.38	21.55 ± 1.38	21.55 ± 1.38	21.55 ± 1.38
R-squared	rsquar	0.93	0.93	0.93	0.94	0.93
Chi-squared	chisquar	0.49	0.50	0.49	0.48	0.49
Percent mass	pcmass	99.6	99.9	99.6	99.5	99.5
<u>Absolute Contribution (ugTC/m3)</u>						
LDGV, cold start	nvnspl	3.21 ± 0.28	3.23 ± 0.28	3.40 ± 0.29	3.09 ± 0.27	3.19 ± 0.28
LDGV, hot stabilized	nvnspl2	0.80 ± 0.05	0.82 ± 0.05	0.82 ± 0.05	0.78 ± 0.05	0.80 ± 0.05
LDGV, high particle emitter	nvsm	5.23 ± 0.21	4.51 ± 0.18	4.45 ± 0.18	5.99 ± 0.24	5.33 ± 0.22
Diesel Exhaust	nwhdc	7.03 ± 0.28	7.08 ± 0.28	6.96 ± 0.28	7.09 ± 0.28	7.01 ± 0.28
Fireplace, softwood composite	nwfsc	-0.33 ± 0.11	-0.32 ± 0.11	-0.33 ± 0.11	-0.33 ± 0.11	-0.34 ± 0.11
Wood stove hardwood composite	nwshc2	3.01 ± 0.14	2.93 ± 0.14	3.04 ± 0.14	3.02 ± 0.14	3.05 ± 0.14
Road and geologic dust	nrdc	0.56 ± 0.18	0.55 ± 0.17	0.55 ± 0.18	0.57 ± 0.18	0.57 ± 0.18
Coal power station	pehclcl1	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
Meat composite	nmc	1.94 ± 0.15				
Hamburger, automated charbroiler	nmaha		2.72 ± 0.18			
Hamburger, under-fired charbroiler	nmch			2.58 ± 0.17		
Chicken, under-fired charbroiler	nmcca				1.24 ± 0.09	
Steak, under-fired charbroiler	nmck					1.84 ± 0.12

Table 5.2-2a Sensitivity of Total Carbon Apportionment to Alternative Cold-Start Profiles (Welby, 01/17/97 at 0600 to 1200 MST)

	Profile	Base	CS1	CS2	CS3	CS4	CS5
Concentration of TC (ug/m3)		21.6 ± 1.4	21.6 ± 1.4	21.6 ± 1.4	21.6 ± 1.4	21.6 ± 1.4	21.6 ± 1.4
R-square		0.96	0.95	0.95	0.96	0.96	0.96
Chi-square		0.27	0.47	0.38	0.31	0.31	0.29
Percent mass		99.1	102.1	100.3	99.5	99.6	99.0
<u>Absolute Contribution (ug/m3)</u>							
LDGV (cold start, l)	nvesl2		1.37 ± 0.11				
LDGV (cold start, l,ml)	nvlp			1.61 ± 0.18			
LDGV (cold start, l,ml,m)	nveslm				2.67 ± 0.25		
LDGV (cold start, l,ml,m)	nveslml					2.13 ± 0.24	
LDGV (cold start, l,ml,m,h)	nvnspl	3.50 ± 0.30					
LDGV (cold start, m,h)	nvhp						5.37 ± 0.24
LDGV (hot stabilized, l,ml,m,h)	nvnspl2	0.68 ± 0.04	0.58 ± 0.04	0.67 ± 0.04	0.69 ± 0.04	0.66 ± 0.04	0.80 ± 0.05
LDGV (phase 1,2&3, s)	nvsm	6.54 ± 0.27	9.78 ± 0.40	8.88 ± 0.36	7.09 ± 0.29	7.61 ± 0.31	5.61 ± 0.23
HD diesel	nwhdc	6.80 ± 0.27	7.80 ± 0.31	7.75 ± 0.31	7.40 ± 0.29	7.45 ± 0.30	5.99 ± 0.24
Meat cooking	nmc	2.17 ± 0.17	0.91 ± 0.07	1.19 ± 0.09	1.93 ± 0.15	1.97 ± 0.16	1.99 ± 0.16
Wood (fireplace, softwood)	nwfsc	0.07 ± 0.02	0.12 ± 0.04	0.16 ± 0.05	0.09 ± 0.03	0.10 ± 0.03	0.09 ± 0.03
Wood (woodstove, hardwood)	nwshe2	1.08 ± 0.05	0.86 ± 0.04	0.81 ± 0.04	1.06 ± 0.05	1.05 ± 0.05	0.95 ± 0.04
Road dust/geological	nrdc	0.50 ± 0.16	0.56 ± 0.18	0.55 ± 0.17	0.51 ± 0.16	0.51 ± 0.16	0.54 ± 0.17
Coal-fired power station	pchcl1	0.00 ± 0.00	0.02 ± 0.02	0.01 ± 0.01	0.01 ± 0.01	0.01 ± 0.01	0.01 ± 0.01
	Profile	CS6	CS7	CS8	CS9	CS10	CS11
Concentration of TC (ug/m3)		21.6 ± 1.4	21.6 ± 1.4	21.6 ± 1.4	21.6 ± 1.4	21.6 ± 1.4	21.6 ± 1.4
R-square		0.96	0.96	0.96	0.97	0.96	0.96
Chi-square		0.34	0.28	0.28	0.21	0.28	0.25
Percent mass		102.9	102.8	100.0	98.6	103.8	101.4
<u>Absolute Contribution (ug/m3)</u>							
LDGV (cold start, h)	nvsh1	3.08 ± 0.12					
LDGV (cold start, s,h)	nvssh		8.99 ± 0.44				
LDGV (cold start, s)	nvssh			12.61 ± 0.48			
LDGV (phase 1, l,ml,m,h)	nvnspl				7.49 ± 0.31		
LDGV (phase 1, s,h)	nvplsh					9.71 ± 0.43	
LDGV (phase 1, s)	nvplsh						16.83 ± 0.62
LDGV (hot stabilized, l,ml,m,h)	nvnspl2	0.91 ± 0.06	0.63 ± 0.04	0.54 ± 0.04		0.66 ± 0.04	0.67 ± 0.04
LDGV (phase 1,2&3, s)	nvsm	10.02 ± 0.41	6.58 ± 0.27	2.05 ± 0.08	4.99 ± 0.20	8.36 ± 0.34	4.14 ± 0.17
HD diesel	nwhdc	5.92 ± 0.23	5.26 ± 0.21	6.50 ± 0.26	4.62 ± 0.18	4.86 ± 0.19	4.93 ± 0.20
Meat cooking	nmc	0.83 ± 0.07	-0.51 ± 0.04	-1.32 ± 0.10	2.52 ± 0.20	-2.04 ± 0.16	-4.43 ± 0.35
Wood (fireplace, softwood)	nwfsc	0.23 ± 0.07	0.25 ± 0.08	0.29 ± 0.10	0.03 ± 0.01	0.40 ± 0.13	0.76 ± 0.25
Wood (woodstove, hardwood)	nwshe2	0.61 ± 0.03	0.41 ± 0.02	0.30 ± 0.01	1.14 ± 0.05	-0.15 ± 0.01	-1.64 ± 0.08
Road dust/geological	nrdc	0.56 ± 0.18	0.54 ± 0.17	0.55 ± 0.18	0.47 ± 0.15	0.57 ± 0.18	0.59 ± 0.19
Coal-fired power station	pchcl1	0.01 ± 0.01	0.00 ± 0.00	0.01 ± 0.01	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00

Table 5.2-2b Sensitivity of Total Carbon Apportionment to Alternative Hot-Stabilized and High Particle Emitter Profiles (Welby, 01/17/97 at 0600 to 1200 MST)

	Profile	Base	HS1	HS2	HE1	HE2	HE3
Concentration of TC (ug/m3)		21.6 ± 1.4	21.6 ± 1.4	21.6 ± 1.4	21.6 ± 1.4	21.6 ± 1.4	21.6 ± 1.4
R-square		0.96	0.96	0.97	0.97	0.96	0.96
Chi-square		0.27	0.29	0.20	0.18	0.26	0.19
Percent mass		99.1	100.9	99.2	92.6	93.2	93.0
<u>Absolute Contribution (ug/m3)</u>							
LDGV (cold start, l,ml,m,h)	nvnspl	3.50 ± 0.30	5.60 ± 0.49	2.74 ± 0.24	2.90 ± 0.25	5.60 ± 0.49	0.34 ± 0.03
LDGV (phase2, l)	nvhscl		0.87 ± 0.07				
LDGV (phase2, l,ml,m,h)	nvnspl2	0.68 ± 0.04			-0.94 ± 0.06	0.78 ± 0.05	0.60 ± 0.04
LDGV (phase2, h)	nvhsclh			2.42 ± 0.15			
LDGV (phase2, h,s)	nvp2sh				8.83 ± 0.39		
LDGV (phase2, s)	nvp2s					0.13 ± 0.01	
LDGV (cold & phase2, s)	nvcspl						10.65 ± 0.43
LDGV (phase123, s)	nvsm	6.54 ± 0.27	6.36 ± 0.26	6.39 ± 0.26			
HD diesel	nwhdc	6.80 ± 0.27	5.32 ± 0.21	5.99 ± 0.24	4.67 ± 0.19	5.97 ± 0.24	5.43 ± 0.22
Meat cooking	nmc	2.17 ± 0.17	2.03 ± 0.16	2.17 ± 0.17	2.76 ± 0.22	5.61 ± 0.44	1.49 ± 0.12
Wood (fireplace, softwood)	nwfsc	0.07 ± 0.02	0.07 ± 0.02	0.09 ± 0.03	0.03 ± 0.01	-0.07 ± 0.02	0.12 ± 0.04
Wood (woodstove, hardwood)	nwscl2	1.08 ± 0.05	1.01 ± 0.05	1.06 ± 0.05	1.19 ± 0.06	1.59 ± 0.07	0.89 ± 0.04
Road dust/geological	nrdc	0.50 ± 0.16	0.48 ± 0.15	0.51 ± 0.16	0.50 ± 0.16	0.47 ± 0.15	0.53 ± 0.17
Coal-fired power station	pchcl1	0.00 ± 0.00	0.00 ± 0.00	0.01 ± 0.01	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
	Profile	HE4	HE5	HE6	HE7	HE8	HE9
Concentration of TC (ug/m3)		21.6 ± 1.4	21.6 ± 1.4	21.6 ± 1.4	21.6 ± 1.4	21.6 ± 1.4	21.6 ± 1.4
R-square		0.96	0.97	0.97	0.97	0.97	0.97
Chi-square		0.27	0.18	0.16	0.14	0.15	0.18
Percent mass		93.3	95.8	94.6	94.6	97.0	97.9
<u>Absolute Contribution (ug/m3)</u>							
LDGV (cold start, l,ml,m,h)	nvnspl	4.95 ± 0.43	0.12 ± 0.01	0.13 ± 0.01	0.20 ± 0.02	-0.04 ± 0.00	1.44 ± 0.12
LDGV (phase2, l,ml,m,h)	nvnspl2	0.75 ± 0.05	0.66 ± 0.04	0.71 ± 0.05	-0.60 ± 0.04	0.75 ± 0.05	0.70 ± 0.05
LDGV (cold & phase3, s)	nvscsp2	1.03 ± 0.04					
LDGV (cold & phase23, s)	nvcsplsa		11.76 ± 0.45				
LDGV (phase12, s)	nvp1hs			11.27 ± 0.43			
LDGV (phase123, h,s)	nvsh				13.51 ± 0.62		
LDGV (phase123, h,s)	nvp1hsa					12.29 ± 0.47	
LDGV (phase123, s)	nvs						9.81 ± 0.38
HD diesel	nwhdc	6.20 ± 0.25	5.39 ± 0.21	5.50 ± 0.22	4.01 ± 0.16	5.49 ± 0.22	6.31 ± 0.25
Meat cooking	nmc	5.22 ± 0.41	1.21 ± 0.10	1.26 ± 0.10	1.71 ± 0.14	0.91 ± 0.07	1.31 ± 0.10
Wood (fireplace, softwood)	nwfsc	-0.10 ± 0.03	0.12 ± 0.04	0.14 ± 0.05	0.07 ± 0.02	0.14 ± 0.05	0.12 ± 0.04
Wood (woodstove, hardwood)	nwscl2	1.59 ± 0.07	0.87 ± 0.04	0.81 ± 0.04	1.01 ± 0.05	0.81 ± 0.04	0.90 ± 0.04
Road dust/geological	nrdc	0.47 ± 0.15	0.51 ± 0.16	0.56 ± 0.18	0.48 ± 0.15	0.54 ± 0.17	0.52 ± 0.17
Coal-fired power station	pchcl1	0.00 ± 0.00	0.00 ± 0.00	0.01 ± 0.01	0.00 ± 0.00	0.00 ± 0.00	0.01 ± 0.01

Table 5.2-2c Sensitivity of Total Carbon Apportionment to Fitting Species (Welby, 01/17/97 at 0600 to 1200 MST)

	Profile	Base	no OC	no EC	no OC & EC	no Hopa & Stera	no Lact & Stero
Concentration of TC ($\mu\text{g}/\text{m}^3$)		21.6 \pm 1.4	21.6 \pm 1.4	21.6 \pm 1.4	21.6 \pm 1.4	21.6 \pm 1.4	21.6 \pm 1.4
R-square		0.96	0.96	0.96	0.95	0.97	0.96
Chi-square		0.27	0.25	0.27	0.26	0.31	0.27
Percent mass		99.1	80.5	83.2	72.9	99.4	99.9
<u>Absolute Contribution ($\mu\text{g}/\text{m}^3$)</u>							
LDGV, cold start	nvnspp	3.50 \pm 0.30	4.62 \pm 0.40	3.38 \pm 0.29	4.14 \pm 0.36	3.41 \pm 0.30	3.73 \pm 0.32
LDGV, hot stabilized	nvnspp2	0.68 \pm 0.04	0.82 \pm 0.05	0.70 \pm 0.05	0.79 \pm 0.05	0.70 \pm 0.05	0.74 \pm 0.05
LDGV, high particle emitter	nvsm	6.54 \pm 0.27	1.49 \pm 0.06	6.67 \pm 0.27	3.28 \pm 0.13	6.56 \pm 0.27	4.72 \pm 0.19
Diesel Exhaust	nwhdc	6.80 \pm 0.27	6.55 \pm 0.26	2.50 \pm 0.10	2.83 \pm 0.11	6.88 \pm 0.27	6.92 \pm 0.27
Meat Cooking	nmc	2.17 \pm 0.17	2.22 \pm 0.18	3.03 \pm 0.24	3.01 \pm 0.24	2.23 \pm 0.18	3.80 \pm 0.30
Wood combustion, softwood	nwfsc	0.07 \pm 0.02	0.06 \pm 0.02	0.08 \pm 0.03	0.07 \pm 0.02	0.07 \pm 0.02	0.06 \pm 0.02
Wood combustion, hardwood	nwshe2	1.08 \pm 0.05	1.12 \pm 0.05	1.06 \pm 0.05	1.11 \pm 0.05	1.06 \pm 0.05	1.06 \pm 0.05
Road dust/geological	nrdc	0.50 \pm 0.16	0.48 \pm 0.15	0.51 \pm 0.16	0.49 \pm 0.16	0.50 \pm 0.16	0.48 \pm 0.15
Coal-fired power station	pchcl1	0.00 \pm 0.00	0.00 \pm 0.00	0.00 \pm 0.00	0.00 \pm 0.00	0.00 \pm 0.00	0.00 \pm 0.00
Test	Profile	no MeO-Phenols	no spec organics	with PAH (g)	with brake	with trdst	
Concentration of TC ($\mu\text{g}/\text{m}^3$)		21.6 \pm 1.4	21.6 \pm 1.4	21.6 \pm 1.4	21.55 \pm 1.38	21.55 \pm 1.38	
R-squared		0.97	1.00	0.88	0.93502	0.93493	
Chi-squared		0.27	0.04	0.58	0.5028	0.49487	
Percent mass		99.2		108.8	99.54957589	99.36452475	
<u>Absolute Contribution ($\mu\text{gTC}/\text{m}^3$)</u>							
LDGV, cold start	nvnspp	3.29 \pm 0.29	-10.65 \pm 0.93	12.19 \pm 1.06	3.09 \pm 0.27	3.61 \pm 0.31	
LDGV, hot stabilized	nvnspp2	0.65 \pm 0.04	11.67 \pm 0.76	-0.34 \pm 0.02	0.79 \pm 0.05	0.82 \pm 0.05	
LDGV, high particle emitter	nvsm	7.20 \pm 0.29	47.54 \pm 1.93	5.61 \pm 0.23	5.77 \pm 0.23	3.83 \pm 0.16	
Diesel Exhaust	nwhdc	6.31 \pm 0.25	-73.95 \pm 2.93	3.33 \pm 0.13	7.04 \pm 0.28	6.08 \pm 0.24	
Meat composite	nmc	2.15 \pm 0.17	-31.50 \pm 2.49	2.06 \pm 0.16	1.45 \pm 0.12	1.64 \pm 0.13	
Fireplace, softwood composite	nwfsc	1.73 \pm 0.57	223.95 \pm 73.84	0.09 \pm 0.03	-0.33 \pm 0.11	-0.34 \pm 0.11	
Wood stove hardwood composite	nwshe2	-0.45 \pm 0.02	1.7977E+308	0.01 \pm 0.00	3.04 \pm 0.14	3.08 \pm 0.14	
Road and geologic dust	nrdc	0.51 \pm 0.16	0.57 \pm 0.18	0.51 \pm 0.16	0.52 \pm 0.17	0.54 \pm 0.17	
Coal power station	pchcl1	0.00 \pm 0.00	-0.03 \pm 0.03	-0.01 \pm 0.01	-0.01 \pm 0.01	0.00 \pm 0.00	
Brake wear	brake				0.10 \pm 0.02		
Tire wear	trdst					2.14 \pm 0.43	

ambient carbon predicted from the fireplace/hardwood profile is negligible (0.5%), the wood stove/hardwood profile was selected as the default hardwood profile.

The fractions of ambient fine particles attributed to five alternative meat cooking profiles range from 5.7% to 12.6% of total ambient PM_{2.5} carbon with an average of 9.7%. This average is consistent with the apportionment results from the composite of all of these meat profiles (nmc), which was 9.0%. Because each of the alternative meat cooking profiles is collinear with each other, the composite profile, NMc, was selected as the default meat cooking profile.

Sensitivity tests were performed to examine the effect of alternative LDGV cold start profiles (Table 5.2-2a) and alternative LDGV hot stabilized and high particle emitter profiles (Table 5.2-2b) on the apportionment using a common set of default profiles for non-vehicular sources. The base case represents the set of default profiles used in the NFRAQS "extended species" CMB runs.

Each of the alternative LDGV cold start profiles was used individually with the default set of profiles. Tests CS1 to CS8 in Table 5.2-2 show the results for alternative incremental cold start profiles (i.e., FTP Phase 1 minus Phase 3), and are arranged according to increasing composite emission rates. The apportionment of total PM_{2.5} carbon ranges from 6.2% for incremental cold starts for low emitters to a high of 59% for visible smokers. The increase in contribution of cold starts with the inclusion of visible smokers is mostly at the expense of the high particle emitter category, which is comprised of visible smoking vehicles in both cold start and hot stabilized modes. Among the alternative incremental cold start profiles for non-smoking vehicles, the range in apportionment is 6.2% to 25.2%. The default profile for this category (nvns), which is an average of all non-smoking vehicles, gives an apportionment of 16.4% for cold start emissions.

In general, the apportionment (SCE) for other carbon sources varies less with alternative cold start profiles. The corresponding ranges in LDGV hot stabilized emissions, LDGV high particle emitters, diesel exhaust, meat cooking and wood combustion are 2.7% to 4.1%, 26.3% to 45.2%, 27% to 36%, 3.7% to 10.2%, 3.8% to 5.3%, respectively. In comparison to the default incremental cold start profile, the corresponding Phase 1 profile yields 35.2% contribution with zero hot stabilized emissions and lower contributions for LDGV high particle emitters and diesel exhaust. Compared to the profile for Phase 1, the incremental cold start is more distinguishable (chemically) from high emitters and non-smoking hot stabilized emissions.

All non-smoker Phase 2 profiles give lower carbon contributions than any of the Phase 1 profiles, regardless of the emitter category. With the exception of one sample, all of the alternative smoker profiles give about the same apportionment regardless of phase. The differences in apportionment between Phases 1 and 2 are within 15% and even lower with Phase 3. While the relative apportionment among the three spark-ignition profiles (i.e., Phase 1, Phase 2, and smoker) vary with alternative profiles for smokers, the amount apportioned to the default meat cooking profile is relatively insensitive to the use of alternative smoker profiles.

The initial CMB tests done for heavy-duty diesel exhaust showed that apportionment (SCE) of diesel exhaust is relatively insensitive to the differences in elemental carbon (EC) abundances in the profile. Diesel exhaust with relative abundances of EC of 86% and 63% show differences in apportionment (SCE) of total carbon of 10%. In addition to EC, the CMB

sensitivity matrix shows that particulate PAHs, especially methyl- and dimethyl-phenanthrene, have strong influence on the apportionment.

Table 5.2-2c shows the effects of using alternative sets of fitting species on the apportionment. The default fitting species included inorganic species and particle-phase organic species (particulate PAH, methoxy phenols, lactones, sterols, hopanes, and steranes) with R/U ratios between -2 and +2. The tests included the following changes to the default set of fitting species: 1) no organic carbon (OC); 2) no EC; 3) no OC and EC; 4) no hopanes and steranes; 5) no lactones and sterols; 6) no phenols; 7) no organic species; and 8) addition of gas-phase PAHs.

Removing OC from the set of fitting species reduces the apportionment of LDGV high particle emitter from 30.6% to 8.6%. However the PERCENT MASS is reduced from 99.1% to 80.5%, and a slight increase results in the other three vehicle exhaust profiles. Although organic carbon is the major component in the LDGV high emitter profile, it is incorrect to assume that the apportionment of this source is keyed simply on organic carbon. This statement would be true if the smoker profile is the only organic carbon source used in the fit. There are seven other sources of organic carbon that are used in the apportionment for NFRAQS.

The CMB sensitivity matrices show that organic carbon has the greatest influence on apportionment of LDGV high particle emitter and has little effect on the other sources of organic carbon. However, contributions of LDGV cold starts are strongly influenced by phenanthrene, fluorene, methylfluorene isomers, and heavy PAHs. Hot-stabilized particulate emissions from non-smokers are influenced by methylfluorene isomers, and methylphenanthrene and dimethylphenanthrene isomers. Lactones influence the apportionment for meat cooking and guaiacols and syringols affect apportionments of softwood and hardwood combustion, respectively. Diesel exhaust and road dust are predominantly influenced by elemental carbon and crustal elements, respectively. The attributions of carbon to the other seven sources are all influenced by species other than organic carbon.

Removing EC from the set of fitting species reduces the apportionment of diesel exhaust from 31.9% to 13.9%. As with the previous case with OC, the PERCENT MASS is reduced (to 83.2%) and contributions of LDGV high particle emitter and meat cooking increase by small margins. Removing both OC and EC cause decreases in contributions of both LDGV high particle emitter and diesel exhaust and correspondingly larger decrease in the percent of mass attributed (72.9%).

Removing hopanes and steranes has negligible effect on the apportionment. The effective variance weighted solutions in CMB8 gives greater influence to chemical species with lower uncertainty in both source and ambient measurements. As ambient levels approach detection levels for marker compounds, as was the case for these species, their influence on the CMB fit decreases.

According to the CMB sensitivity matrix, the expected marker species (i.e., lactones and sterols) have the greatest influence on the apportionment of meat cooking. Removing them resulted in an unexpected increase in apportionment for meat cooking and offsetting decrease in the prediction for LDGV high particle emitters. The long-chain g-lactones and cholesterol are considered "marker" species for meat cooking. However, motor vehicles were also found to emit "lactones", which raised questions regarding their proper identification. Since some of the light-duty gasoline and heavy-duty diesel vehicle exhaust samples, when analyzed by electron

impact/mass spectrometry (EI/MS), showed an m/z 85 ion (characteristic of lactones) at the same gas chromatographic retention time that correspond to some of the lactones, they were re-analyzed by chemical ionization/mass spectrometry (CI/MS) in order to confirm their identity.

None of the light-duty gasoline vehicle exhaust samples contains detectable amounts of lactones. All four lactones were found in heavy-duty diesel exhaust samples, but in much lower amounts than quantified by EI/MS. Six ambient samples (three from the Welby site and three from the Brighton site) were also re-analyzed for lactones using the CI/MS technique. All lactones, previously quantified by EI/MS in the ambient samples, were also identified and quantified by the CI/MS technique. Since all ambient samples were quantified by the EI/MS technique using the m/z 85 ion, some of the compounds emitted by motor vehicles could “artificially” contribute to the intensity of this ion. Thus, lactones were retained in all motor vehicle profiles, whether or not they were truly lactones. This situation is analogous to the application of “organic” carbon in CMB which contain a variety of unidentified organic compounds. The lactones are also imprecisely quantified, as reflected in measurement uncertainty estimates that approach or exceed 30% of their concentrations. Owing to these large uncertainties, the CMB8 effective variance solution reduces their influence on the apportionment relative to more precisely measured components. When lactones are removed as fitting species, however, the standard error of source contribution estimates for meat cooking increases.

Removing methoxyphenols from the fit results in a shift of the attribution from hardwood to softwood. This is expected since there are other markers for softwood (e.g., retene and 1,7 dimethylphenanthrene) while syringols are the primary markers for hardwoods. Including gas-phase PAH in the set of fitting species causes significant increase in the cold start contribution and an overestimation of mass because gas-phase organic species are generally not correlated with particulate mass.

Removing all organic species from the fit results in complete breakdown of CMB fit due to significant collinearity that results among the subcategories of motor vehicle as well as wood and meat combustion profiles. Tests were conducted using “conventional” species, which include only total organic carbon, elemental carbon, inorganic ions (nitrate, sulfate, ammonium), and elements. LDGV profiles were combined into one composite profile and meat cooking and wood combustion were combined for the conventional CMB. The effective variance weighted solutions in CMB8 uses all available chemical measurements, not just “tracer” species, and gives greater influence to chemical species with lower uncertainty in both source and ambient measurements.

As ambient levels approach detection levels for marker compounds, as was the case for many of the samples from Brighton, their influence on the CMB fit decreases. This situation could lead to overestimation of LDGV high particle emitter and underestimation of other sources of organic carbon, and could explain the differences that exist between the “extended” and “conventional” CMB results for Brighton. The low-concentration samples from Brighton contain less than 1 or 2 $\mu\text{g}/\text{m}^3$ of total carbon and are associated with transport from the north rather than from the Denver area, and are not representative of the urban source mix. In contrast, the samples from Welby are more representative of the urban source mix, and typically contain levels of total particulate carbon that allow for quantitative determination of organic markers. The “extended” and “conventional” CMB results are consistent with each other, and comparisons with isotopic carbon measurements are more consistent for this site than for

Brighton. The “conventional” CMB results for CAMP and Highlands indicate that results for Welby are likely representative of the Denver urban area.

Because tire wear and brake wear were not tested as part the NFRAQS study, chemical composition profiles were developed for these source from data published by Hildemann *et al.* (1991) and Rogge *et al.* (1993c). Hildemann *et al.* (1991) reports elemental data for tire wear and brake wear. Organic data were obtained from Rogge et al (1993b). The profiles were derived by converting the emission data into weight fractions normalized to total measured fine particle mass. A nominal uncertainty of 20% was applied to the weight fractions. Table 5.2-2c shows the average source contribution estimates for tire dust and brake wear for the sample that was examined as part of the sensitivity tests of alternative source profiles. The contributions of brake wear is negligible (<1%). Tire wear is about 10% of the total carbon. However, the apportionment of PM_{2.5} has high standard errors, which indicates that there is a high degree of uncertainty and/or collinearity in these profiles. These profiles were not used in the final NFRAQS apportionment.

5.3 Model Outputs and Performance Measures

Nearly 1,000 individual CMB calculations were performed for NFRAQS in various sensitivity tests. Apportionment of the NFRAQS ambient data included 132 apportionments using the “extended” data sets that include specific organic compounds measured at the Welby and Brighton sites of 6-hour or 12-hour durations for the Winter 97 samples. The CMB model was also applied to 150 24-hour average “conventional” data sets from all seven NFRAQS Winter 97 sites that included the elemental, ionic, and elemental/organic carbon concentrations that are most commonly measured on source and receptor samples. This allowed for comparison of source contribution estimates derived from the “extended” and “conventional” CMB calculations for the Welby and Brighton data.

For these source apportionments, R-SQUARE typically exceeded 0.9 and CHI-SQUARE values typically ranged from 0.3 and 0.6. PERCENT MASS values for organic carbon, elemental carbon, total carbon, and PM_{2.5} were within one standard deviation of 100% most of the time.

5.4 Deviations from Model Assumptions

Assumptions 1 and 2 of the CMB model specify that the compositions of source emissions are constant over the period of ambient and source sampling, and that chemical species do not react with one another. Once released into the atmosphere, primary emissions are subjected to dispersion and transport and, at the same time, to various physical and chemical processes that determine their ultimate environmental fate. Primary emissions from motor vehicles, residential wood combustion, meat cooking, etc., are complex mixtures containing thousands of organic and inorganic constituents in the gas and particulate phases.

These compounds have different chemical reactivities and are removed by dry and wet deposition processes at varying rates. Some of the gaseous species, by a series of chemical transformations, are converted into particles, forming secondary aerosol. Sulfates and nitrates are the most common secondary particles, though a fraction of organic carbon can also result from VOC via atmospheric reactions.

While the mechanisms and pathways for inorganic secondary particles are fairly well known, those for secondary organic aerosols are not well understood. Hundreds of precursors are involved in these reactions, and the rates at which these particles form are highly dependent on the concentrations of other pollutants and meteorological variables. Organic compounds present in the gas phase undergo atmospheric transformation through reactions with reactive gaseous species such as OH* radicals, NO₃* radicals, or O₃.

Atmospheric lifetimes can be estimated for several organic compounds in direct gas-phase emissions due to known tropospheric chemical removal reactions (Atkinson, 1988). These lifetimes (i.e., the time for the compound to decay to 1/e or 37% of its original concentration) are calculated from the corresponding measured reaction rate constants and the average ambient concentration of the tropospheric species involved. Although the individual rate constants are known to a reasonable degree of accuracy (in general, to within a factor of two), the tropospheric concentrations of these key reactive species are much more uncertain.

For example, the ambient concentrations of OH* radicals at any given time and/or location are uncertain to a factor of at least five, and more likely ten (Atkinson, 1988). The tropospheric diurnally and annually averaged OH* radical concentrations are more certain, to possibly a factor of two. For this reason, calculated lifetimes are approximate only for those reactive species concentrations that are listed in the footnotes. However, these data permit one to estimate the contribution of each of these atmospheric reactions to the overall removal rates of most pollutants from the atmosphere. The major atmospheric loss process for most of the direct emission constituents is by daytime reaction with OH* radicals.

For some pollutants, photolysis, reactions with ozone, and reactions with NO₃ radicals during nighttime hours are also important removal routes. For alkanes, the atmospheric lifetimes calculated from the corresponding measured reaction rate constant and the average ambient concentration of OH* radicals, ranges from ~19 days for propane (C₃H₈) to ~1 day for n-pentadecane (C₁₅H₃₂). For aromatic hydrocarbons, lifetimes range from 18 days for benzene to a few hours for methylnaphthalenes (assuming average 12-hour daylight OH* radical concentration of 1 x 10⁶ molecule/cm³).

Secondary organic compounds in particulate matter include aliphatic acids, aromatic acids, nitro aromatics, carbonyls, esters, phenols, and aliphatic nitrates (Grosjean, 1992; Grosjean and Seinfeld, 1989). However, these compounds can also be present in primary emissions (e.g., Rogge, 1993), thus they are not unique tracers for atmospheric transformation processes.

It has been reported that, in the presence of NO_x, the OH* radical reactions with fluoranthene and pyrene present in the gas phase lead to the formation of specific nitroarene isomers different from those present in the direct emissions (Arey *et al.*, 1986, 1989; Atkinson *et al.*, 1990; Zielinska *et al.*, 1990). The nighttime reactions with NO₃ radicals lead to the same product as OH* radical reactions which form nitro-fluoranthene and nitro-pyrene isomers (Zielinska *et al.*, 1986). In contrast, the electrophilic nitration reaction of fluoranthene, or pyrene, involving an NO₂⁺ ion, produces mainly 3-nitrofluoranthene from fluoranthene and 1-nitropyrene from pyrene and these isomers are present in direct emissions from combustion sources.

In order to assess the importance of atmospheric formation of secondary aerosol, the concentration of 2-nitrofluoranthene and 2-nitropyrene was measured during the NFRAQS at the Welby site (Watson *et al.*, 1998). Although 2-nitrofluoranthene and 2-nitropyrene are present in low amounts in daytime samples collected at the Welby site, their concentrations are not significantly different during sunny and cloudy days. Secondary organic aerosol formation was therefore considered negligible during the NFRAQS Winter 97 intensive operating period.

With respect to Assumption 3 involving the inclusion of all source types, it appears from the PERCENT MASS performance measures that all of the significant contributors have been included in most of the CMBs.

With respect to Assumption 4 concerning number of species and number of sources, 85 species and up to 11 source profiles were used in each calculation. The number of chemical species always exceeded the number of source types.

With respect to Assumption 5 concerning collinearity, this was largely eliminated by the inclusion of specific organic species in the extended data sets. These were sufficient to separate contributions from fireplaces, wood stoves, meat cooking, diesel exhaust, gasoline smoker exhaust, gasoline cold-start exhaust, and gasoline hot-stabilized exhaust. For the conventional data sets, wood burning and meat cooking were collinear and the gasoline exhaust contributors were collinear. Source-types for suspended dust, secondary ammonium sulfate and ammonium nitrate, and specific coal-fired power station contributions could not be resolved. Profiles for other industrial point sources were lacking, and their primary particle contributions could not be explicitly estimated by CMB.

The effects of deviations from Assumption 6 on the randomness and normality of measurement errors remain to be studied. For this study, all of the CMB assumptions are met to the extent that the source contribution estimates can be considered valid.

5.5 Identification and Correction of Model Input Errors

Many Level III validation deficiencies in the processing, formatting, compositing, and reporting of ambient concentration and source profile measurements were identified and corrected or flagged as a result of CMB8 source apportionment. Corrections and flags have been incorporated into the NFRAQS data base, and the results presented by Watson *et al.* (1998) reflect these changes. Some chemical species concentrations were physically unreasonable, as indicated by large CHI-SQUARE values with a large R/U value for the related species. The trimethylnaphthalenes and biphenyls consistently showed large R/U values. The reason is not readily apparent. In these cases the suspect species was removed from the fit. In general, the CMB modeling was robust enough that, when performance measures were within acceptable ranges around target values, there was little effect of suspect concentrations on the source contribution estimates.

5.6 Consistency and Stability of Source Contributions

The source contribution estimates and the statistics and diagnostic information were reviewed to determine the validity of the initial model results. The analysis was repeated by eliminating source profiles that gave negative source contribution estimates or standard errors that exceed the source contribution estimates. The good agreement between the calculated source

contributions and the measured ambient concentrations indicate that all major source types were included in the calculations, that ambient and source profile measurements are reasonably accurate, and that the source profiles are reasonably representative of actual emissions.

5.7 Consistency with Other Simulations and Data Analyses

Watson *et al.* (1998) demonstrate that the CMB8 source contribution estimates for carbon and PM_{2.5} are consistent with other NFRAQS data analysis and simulations. Figure 5.7-1 shows the CMB source apportionment at the Welby site. This chart shows substantial discrepancies with respect to the inventory⁵ in Table 5.1-1, in which diesel exhaust emissions are four times gasoline exhaust emissions. The cold start and high emitter portions of the gasoline exhaust reverse these proportions. These discrepancies should be further investigated.

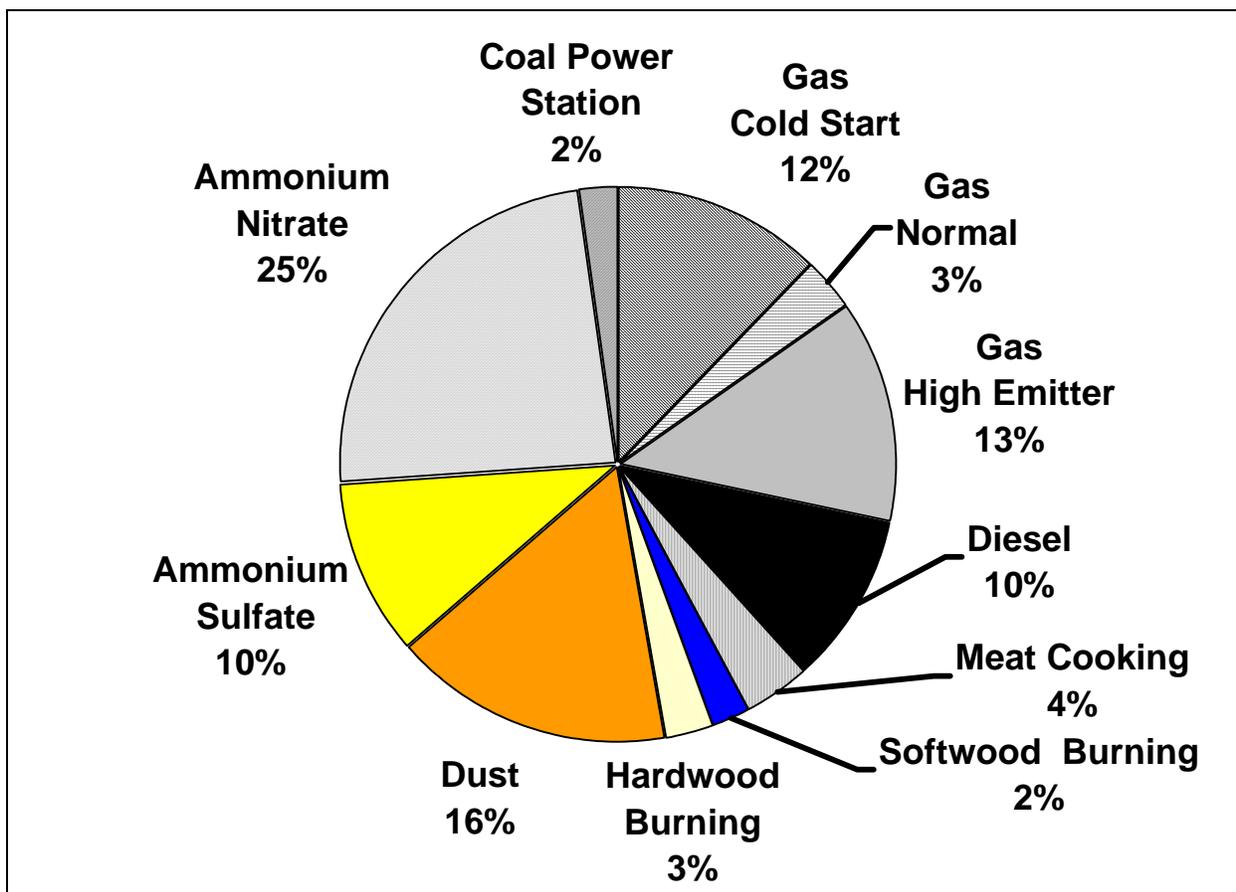


Figure 5.7-1. Average PM_{2.5} source contributions at the Welby site near Denver, CO during the winter of 1996-97.

⁵This SIP-planning inventory was compiled externally to the NFRAQS.

6. EXAMPLE OF APPLICATION AND VALIDATION FOR VOC

This example of VOC source apportionment is taken from the NARSTO-NE ozone study that took place between June 1 and August 31, 1995 in the region between Washington DC and Boston, MA (Fujita *et al.*, 1998). While several different types of VOC samples were taken, this example focuses on hourly measurements acquired with automated gas chromatographs at PAMS.

6.1 Model Applicability

The data set includes hydrocarbon measurements for 55 species⁶ measured hourly at eight PAMS sites in six source areas (E. Hartford, CT; McMillan Reservoir, DC; Chicopee, MA; Lynn, MA; Lake Clifton, MD; Bronx, NY) and two downwind (Type 1, 3, or 4) PAMS sites (Lums Pond, DE and Rider College, NJ). The speciated hydrocarbon data are hourly measurements by automated gas chromatographs providing more than 15,000 hydrocarbon samples covering the period from June 1, 1995 to August 31, 1995. The sites, number of samples, and number of species measured are sufficient to perform a CMB source apportionment.

6.2 Initial Source Contribution Estimates

Table 6.2-1 lists the mnemonic of the profiles that were considered in this study with short descriptions. The actual profiles are reported by Fujita *et al.* (1998) and are included as one of the CMB8 test data sets. As discussed in Section 3.1.2, the profiles are expressed as mass fractions of total NMHC. Compounds other than the PAMS target VOCs (Appendix A) that are in the profiles have been grouped into a category named “others”. The 28 species that were used as fitting species in the CMB analysis are identified in Table 6.2-2 with asterisks. Compounds reported as “unknown” were grouped into a category named “UNID”.

The PAMS target compounds typically account for about 80% of the ambient hydrocarbons in urban areas. Although MTBE is a major component in reformulated gasoline and in the exhaust of vehicles using reformulated gasoline, it was not included in the profiles because MTBE is not measured in the PAMS program. The source profile data reported in units of ppbC were converted to g/m³ prior to calculating the mass fractions (expressed as percentages) using species-specific conversion factors (Section 3.1.2). One-sigma uncertainties were derived from variations among multiple measurements for a particular source type or a nominal analytical uncertainty of ±15%. The assigned uncertainties are the larger of the two values.

In urban locations, motor vehicle exhaust and evaporative emissions of gasoline are often the major sources of hydrocarbon emissions. Composites of dynamometer measurements of vehicles of varying age and mileage are commonly used to represent fleet-averaged exhaust profiles. For these profiles to represent the actual fleet-average exhaust near ambient monitoring sites, the fuels in the dynamometer tests should resemble the fuels used in the study region and the mix of test vehicles should reflect the relative influence of non-catalyst vehicles or high emitters and catalyst-equipped normal emitters.

⁶Note that as of March 1998, the 2-Methyl-1-Pentene was removed; the list is now 54 species (see Appendix AA).

Table 6.2-1 VOC Source Profiles for NARSTO-NE CMB

No.	Mnemonic	Description
1	Tu_TusHD	Tuscarora Tunnel, Heavy duty emissions
2	Tu_MchHD	Ft. McHenry Tunnel, Heavy duty emissions
3	Exh_Cal0	Callahan Tunnel emissions with diesel contributions removed.
4	Exh_Lin0	Lincoln Tunnel emissions with diesel contributions removed.
5	Exh_Cal1	Callahan Tunnel emissions with diesel and 5~10% of running loss contributions removed.
6	Exh_Lin1	Lincoln Tunnel emissions with diesel and 5~10% of running loss contributions removed.
7	Exh_Cal2	Callahan Tunnel emissions with diesel and 15~25% of running loss contributions removed.
8	Exh_Lin2	Lincoln Tunnel emissions with diesel and 15~25% of running loss contributions removed.
9	WA_Tu1	Mt. Baker Tunnel emissions with diesel and 5~10% of running loss contributions removed.
10	Tu_Calla	Callahan Tunnel emissions
11	Tu_Lin	Lincoln Tunnel emissions
12	Tu_TusLD	Tuscarora Tunnel, Light duty emissions
13	Tu_MchLD	Ft. McHenry Tunnel, Light duty emissions
14	BoCS_Tip	Tip O'Neill Garage emissions, Boston, cold start
15	Exh801a	Derived from the FTP tests of Sigsby <i>et al.</i>
16	Bogl01	Boston liquid gasoline composite.
17	LA_liqGs	LA liquid gasoline composite.
18	WA_Liq	Washington liquid gasoline composite of 15 samples, weighted by brands and grades.
19	Bogv01	Boston headspace vapor composite
20	LA_Hsvap	LA headspace vapor composite
21	WA_Vap	Washington headspace composite of 15 samples, weighted by brands and grades.
22	COATcomp	Composite of various coating emissions, weighted by total emissions.
23	CNG	Commercial natural gas
24	GNG	Geogenic natural gas
25	LPG	Liquified petroleum gas
26	Biogenic	Constructed biogenic profile
27	Unid	Sum of unidentified species.

Previous studies showed that source attributions between tailpipe and evaporative emissions from receptor modeling can vary greatly depending on the particular profile chosen for tailpipe emissions (Harley *et al.*, 1992; Fujita *et al.*, 1994; Pierson *et al.*, 1996). This is because tailpipe emissions are a mixture of hydrocarbons produced during combustion along with unburned gasoline resulting from incomplete combustion. In the CMB calculation, liquid gasoline represents the additional unburned gasoline (due to misfiring and other engine malfunctions) that is not included in the exhaust profile, plus evaporative emissions from gasoline spillage, hot soaks, and some portion of resting losses (leaks, permeation). The profile for gasoline headspace vapor is taken to represent fuel tank vapor losses (e.g., migration of fuel vapor from the canister). Measuring exhaust in on-road tunnels is one way to obtain a composite profile for a larger mix of vehicles.

While tunnel measurements are reasonable approximations for exhaust profiles of the light-duty fleet, they also include varying amounts of diesel exhaust and running evaporative losses. The composite light-duty exhaust profiles that were derived by Fujita *et al.* (1997a) from measurements by Gertler *et al.* (1997a) in the Lincoln and Callahan Tunnels were used in this study.

Table 6.2-2 Measured PAMS Species and CMB Fitting Species

PAMS Species	CMB Fit	PAMS Species	CMB Fit
ETHANE	*	N_HEPT	*
ETHENE		MECYHX	*
ACETYL	*	PA234M	*
LBUT1E		TOLUE	*
PROPE		HEP2ME	*
N_PROP	*	HEP3ME	*
L_BUTA	*	N_OCT	*
N_BUTA	*	ETBZ	
T2BUTE		MP_XYL	
C2BUTE		STYR	
IPENTA	*	O_XYL	
PENTE1		N_NON	*
N_PENT	*	IPRBZ	
I_PREN	*	N_PRBZ	
T2PENE		M_ETOL	
C2PENE		P_ETOL	
B2E2M		BZ135M	
BU22DM	*	O_ETOL	
CPENTE		BZ124M	
P1E4ME		N_DEC	*
CPENTA	*	BZ123M	
BU23DM	*	DETBZ1	
PENA2M	*	DETBZ2	
PENA3M	*	N_UNDE	*
P1E2ME		UNID	
N_HEX	*		
T2HEXE			
C2HEXE			
MCYPNA	*		
PEN24M	*		
BENZE	*		
CYHEXA	*		
HEXA2M	*		
PEN23M	*		
HEXA3M	*		
PA224M	*		

6.3 Examine Model Outputs and Performance Measures

The tunnel-derived exhaust profiles, uncorrected tunnel profiles, and dynamometer-derived exhaust profiles were applied to the same ambient samples to determine the sensitivity of the CMB model to alternative exhaust profiles. Table 6.3-1 shows the effect of alternative vehicle exhaust profiles on the average source contributions for a set of 65 ambient samples from the PAMS site at Bronx, NY. Samples for this test were collected during the 0700 to 0800 EDT in the summer of 1995. Each of the ambient samples were apportioned with the diesel profile, TU_MCHHD, plus twelve alternative gasoline vehicle exhaust profiles (Exh801a, Exh_Cal0, Exh_Cal1, Exh_Cal2, Exh_Lin0, Exh_Lin1, Exh_Lin2, Tu_Calla, Tu_Lin, Tu_Mchld, Tu_Tusld, and Wa_Tu1) using only fitting species that are enriched in diesel and spark-ignition vehicle exhaust (ethene, acetylene, propene, benzene, nonane, decane, and undecane).

Table 6.3-1 CMB Sensitivity Tests for Vehicle Exhaust Profiles

# of samples ^a	TNMOC (µg/m ³)	r ²	χ^2	% of				
				NMHC	HD Profiles	LD Profiles	HD (%)	LD (%)
65	144.2	0.88	3.27	65.2	Tu_Mchhd	EXH801A	22.2	43.0
65	144.2	0.92	2.86	70.5	Tu_Mchhd	EXH_CAL0	22.0	48.6
65	144.2	0.92	2.81	66.6	Tu_Mchhd	EXH_CAL1	21.8	44.8
65	144.2	0.92	2.75	61.2	Tu_Mchhd	EXH_CAL2	21.9	39.3
65	144.2	0.93	2.40	78.8	Tu_Mchhd	EXH_LIN0	21.8	57.0
65	144.2	0.93	2.40	75.1	Tu_Mchhd	EXH_LIN1	21.6	53.5
65	144.2	0.93	2.28	68.7	Tu_Mchhd	EXH_LIN2	21.6	47.1
65	144.2	0.92	2.87	70.5	Tu_Mchhd	TU_CALLA	19.3	51.2
65	144.2	0.93	2.77	73.0	Tu_Mchhd	TU_LIN	14.5	58.5
65	144.2	0.88	4.83	66.6	Tu_Mchhd	TU_MCHLD	22.7	43.9
65	144.2	0.86	5.04	57.5	Tu_Mchhd	TU_TUSLD	24.3	33.2
65	144.2	0.91	3.46	52.2	Tu_Mchhd	WA_TU1	22.8	29.3

^a Samples collected between 0700 and 0800 EDT at Bronx, NY were used in the test.

Source contribution estimates using alternative gasoline vehicle exhaust profiles range from 50% to 70% of total NMHC. Exhaust profiles for relatively cleaner fleets (e.g., Tuscarora and Mount Baker Tunnels) yield lower contributions. Exhaust contributions varied by no more than 10% for the three levels of assumed headspace vapor contributions for both Lincoln and Callahan Tunnels profiles. The profiles corresponding to the maximum level of evaporative correction gave exhaust contributions about 5% to 6% greater than profiles corresponding to averages between no correction and maximum correction. Profiles derived from the tunnel measurements at the Lincoln Tunnel consistently yielded the best model performance.

Table 6.3-2 shows the effect of alternative gasoline profiles on the average source contributions for the same set of 65 ambient samples from the PAMS sites in Bronx, NY during the 0700 to 0800 EDT sampling period. Use of the vapor profiles for gasoline samples from either Boston or Los Angeles results in large overestimation of total NMHC. In contrast, the vapor profile for the Washington samples yield total predicted NMHC contributions that are, on average, about 90% of the observed ambient NMHC. Less than 100% is expected as only vehicle-related source profiles were included in these sensitivity tests. Adding the other default source profiles does not

Table 6.3-2 CMB Sensitivity Tests for Different Profiles

No. samples ^a	TNMOX ($\mu\text{g}/\text{m}^3$)	r^2	χ^2	% of			HD ^b (%)	LD ^b (%)	Liquid Gaso.		CNG	GNG	LPG	Biogenic	
				NMHC	Liq. Gaso.	Gasos. Vapor			Gasos.	Vapor Coating					
65	144.2	0.80	6.63	124.0	BOgl01	BOgv01	21.6	44.9	0.0	57.4					
65	144.2	0.86	4.61	115.7	BOgl01	LA_HsVap	21.6	43.3	0.0	50.8					
65	144.2	0.82	6.03	90.1	BOgl01	WA_Vap	22.0	44.6	0.0	23.5					
65	144.2	0.82	6.52	139.4	LA_liqGS	BOgv01	19.7	44.7	53.7	18.5					
65	144.2	0.86	4.54	114.6	LA_liqGS	LA_HsVap	22.1	42.7	0.0	51.1					
65	144.2	0.82	6.30	94.8	LA_liqGS	WA_Vap	21.7	44.8	6.5	21.8					
65	144.2	0.80	6.63	124.0	WA_liq	BOgv01	21.6	44.9	0.0	57.4					
65	144.2	0.86	4.61	115.7	WA_liq	LA_HsVap	21.6	43.3	0.0	50.8					
65	144.2	0.82	6.03	90.1	WA_liq	WA_Vap	22.0	44.6	0.0	23.5					
65	144.2	0.89	2.81	109.2	WA_liq	WA_Vap	7.7	50.9	5.0	18.0	13.5	8.8	2.9	1.4	0.9

^a Samples collected between 0700 and 0800 EDT at Bronx, NY were used in the test.

^b Tu_Mchhd and Exh_Lin2 were used to represent HD and LD, respectively.

significantly alter the contributions among the tailpipe and evaporative emissions for gasoline vehicles, but reduces the contribution of diesel exhaust from 22.0% to 7.7%. The difference is assigned to surface coating because decane and undecane are major components of both diesel exhaust and surface coatings. Because the sensitivity tests shown in Table 6.3-1 indicate that diesel exhaust is the correct source of the higher molecular weight species at the Bronx site, the surface coating profiles were not used in the default set of profiles in order to avoid potential for collinearity between these two profiles.

6.4 Test Deviations from Model Assumptions

Assumptions 1 and 2 of the CMB model specify that the compositions of source emissions are constant over the period of ambient and source sampling, and that chemical species do not react with one another. The CMB model was applied to the ten alternative diesel and evaporative emissions-corrected samples for each tunnel run with diesel exhaust and evaporative emissions as source profile. The model performance parameters and comparisons of calculated and measured amounts of total NMHC, isobutane, –butane, and isopentane were examined to determine the level of evaporative corrections that yield the best fit. These tests showed that the fit deteriorates rapidly beyond a certain level of assumed headspace vapor contribution. This level is typically 15% to 25%. The predicted vapor contributions do not increase above these levels of assumed vapor contribution. This is consistent with the expectation since there is a limit to the fractional contribution of running losses to hydrocarbons mixing ratios in roadway tunnels. Because the performance parameters for various levels of assumed headspace vapor contributions are similar up to the level at which the fit deteriorates, three sets of corrected profiles were derived for each tunnel run. One profile corresponded to no evaporative correction (i.e., only diesel correction), and a second set of profiles corresponded to the maximum level of evaporative correction before the fit begins to deteriorate (15% to 20%). In the 3rd profile, a composite of the best fitting diesel corrected profiles was made for the uncorrected tunnel measurements.

For PAMS sites, the significant contributors to the average 24-hour ambient NMHC are gasoline vehicle exhaust (40%), gasoline vapor (17%), and diesel exhaust (17%). Natural gas leak (9%), liquid gasoline (7%), liquefied petroleum gas (4%), and biogenic emissions (4%) are minor

contributors to NMHC. On average, only 4% of the identified NMHC are unexplained. Three of the Type 2 sites (Chicopee and Lynn, MA and Bronx, NY) account for the relatively high average contribution of diesel exhaust. Higher diesel contributions are possible at the Bronx site due to diesel buses.

However, there are no obvious sources of the high levels of heavy hydrocarbon at Chicopee and Lynn that result in high diesel contributions at those sites. Contributions of liquid gasoline and gasoline vapors are also much higher at Chicopee than for a typical Type 2 site. Removing Chicopee and Lynn from the average, decreases the average contribution of diesel exhaust for the remaining sites to 12% and increases gasoline vehicle exhaust to 46%.

The significant contributors to the average 24-hour ambient NMHC at downwind PAMS sites (Lums Pond, DE and Rider College, NJ) are gasoline vehicle exhaust (30%), gasoline vapor (18%), liquefied petroleum gas (18%), and natural gas (11%). Diesel exhaust (9%), liquid gasoline (6%), biogenic emissions (5%) are minor contributors to NMHC.

Biogenic emissions are a significantly larger fraction of total NMHC in suburban and rural areas than in urban area. The contributions of isoprene over a 24-hour average range from 4% to 12% in suburban and rural areas and are less than 2% in urban areas. Because isoprene is emitted only during daylight hours with peak emission rates occurring at midday, it is one of the larger sources of NMHC during the day in suburban and rural areas. For the CMB calculations performed in this study, only species with summertime lifetimes greater than that of toluene (~9 hours) were used as fitting species. An exception to this is isoprene. It was included as a fitting species despite its high reactivity because it serves as a marker for biogenic emissions. The source contribution estimates underestimated the actual source contributions of biogenic emissions, i.e., they provide a lower limit to biogenic contributions.

The actual contributions of isoprene may be estimated by examining changes between morning and afternoon samples in the ratios of reactive hydrocarbons (e.g., isomers of xylene) to a relatively unreactive hydrocarbon (e.g., benzene) from a common source (i.e., vehicle exhaust) as an indicator of the net fractional loss of reactive hydrocarbon between the two sampling periods. These ratios are invariant to atmospheric dispersion and include continuous injections of fresh emissions into the air parcel during its transport to the sampling site. The ratio of afternoon to morning xylenes/benzene ratios reflects the net fractional loss of xylenes due to atmospheric reactions. This fractional loss is adjusted to isoprene by applying the ratio of the OH* radical reaction rate constants for xylenes (18.8) and isoprene (101.0). Based on this approach, Fujita *et al.* (1997b) estimated that the actual daytime contributions of isoprene to total NMHC emissions may be 5 to 10 times greater than CMB estimates.

Unidentified compounds are not considered in the apportionment because a large fraction of these compounds are not quantified in the PAMS program. These compounds include terpenes and higher molecular weight aldehydes, which are relatively more abundant in non-urban areas.

6.5 Identify and Correct Model Input Errors

Substantial validation was done on the profiles and ambient data sets, and no major discrepancies were found as part of the source apportionment.

6.6 Evaluate Consistency and Stability of Source Contributions

The source contribution estimates and the statistics and diagnostic information were reviewed to determine the validity of the initial model results. The analysis was repeated by eliminating source profiles that gave negative source contribution estimates or standard errors that exceed the source contribution estimates. The good agreement between the calculated source contributions and the measured ambient concentrations indicate that all major source types were included in the calculations, that ambient and source profile measurements are reasonably accurate, and that the source profiles are reasonably representative of actual emissions.

6.7 Determine Consistency with Other Simulations and Data Analyses

Hourly data offers substantial opportunities to evaluate consistency with other analyses, especially expected diurnal, weekly, and spatial variations in source emissions. Figure 6.7-1 shows the diurnal variations of the absolute source contributions for each source category by day of the week at the Lynn, MA site. While motor vehicle exhaust contributions generally peak during morning and afternoon commute periods on weekday, the average contributions are significantly lower during weekend mornings. These patterns provide confidence in the proper apportionment of vehicle emissions. The diurnal and day-of-the-week patterns in the liquid gasoline contributions are essentially identical to motor vehicle exhaust, which suggests that a large fraction of the liquid gasoline contribution may be associated with tailpipe emissions rather than evaporative emissions from either vehicle or industrial sources.

The diurnal variations in the contribution of natural gas correlate with diurnal variations in vertical mixing. This diurnal pattern and lack of day-of-the-week variations are consistent with constant leakage of natural gas. Liquefied petroleum gas (LPG) generally shows the same diurnal variations. However, lower contributions for LPG during weekend mornings suggests some correlation with the vehicle exhaust profile since the latter profile is derived from roadside ambient measurements.

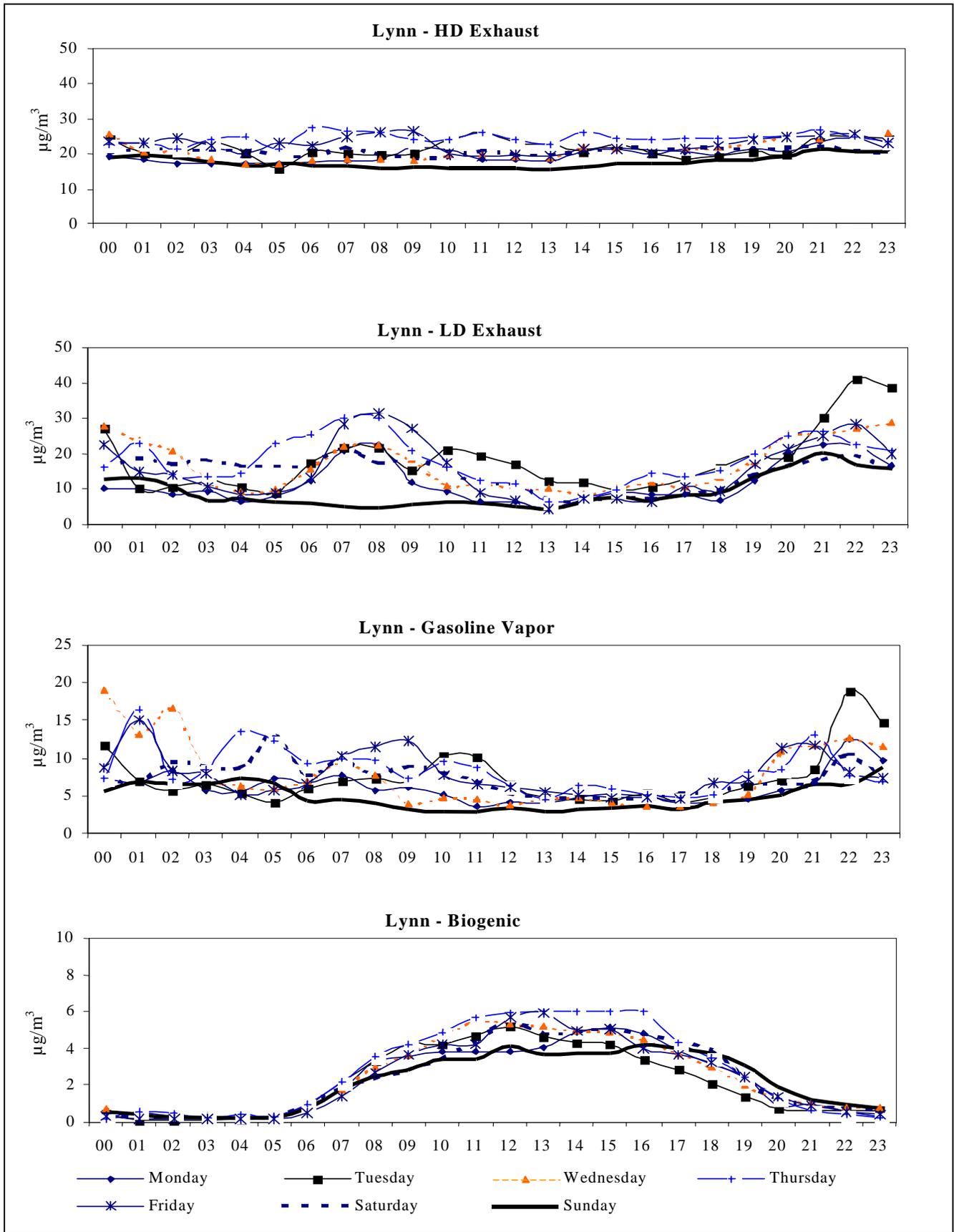


Figure 6.7-1. Hourly average VOC source contributions by day of week at Lynn, MA.

Figure 6.7-2 shows the average source contributions to NMHC by wind sector (centered on N, NE, E, SE, S, SW, W, NW) at the Lynn, MA site for the evening period. Contributions of gasoline vehicle exhaust are predominantly from the southeast, south, and southwest. In contrast, the contribution of diesel exhaust is more or less uniform from all directions. This pattern suggests a very strong local source that dominates the ambient VOC composition near the sampling site. It also indicates that the source of the heavy hydrocarbons that are ascribed to diesel exhaust is some source other than diesel vehicles.

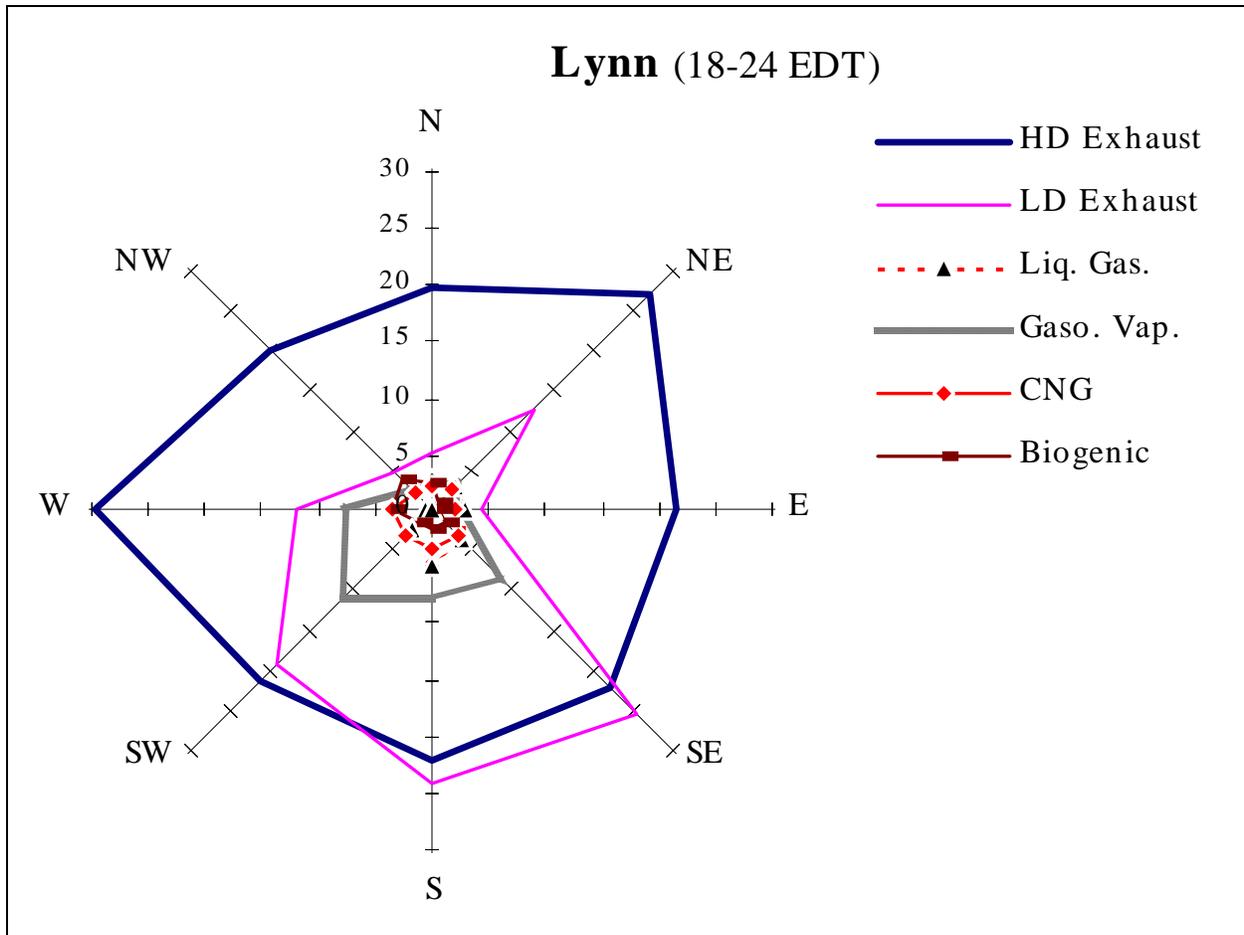


Figure 6.7-2. Wind direction dependence of VOC source contributions at Lynn, MA.

7. SUMMARY, CONCLUSIONS, AND FUTURE PROSPECTS

This applications and validation protocol has summarized knowledge on using the Chemical Mass Balance receptor model to determine source contributions to suspended particles and VOC measured at receptors. It describes new performance measures incorporated into CMB8 modeling software that facilitate the evaluation of similarity among different profiles.

Examples are given for PM_{2.5} source apportionment in Denver, CO, and for VOC source apportionment in the northeast corridor of the U.S. These examples demonstrate how the applications and validation steps can be used to build confidence in the source apportionment results.

New measurement methods, especially for organic aerosol and heavy hydrocarbons, will expand the ability of CMB to better distinguish sources from each other. Organic aerosol measurements allow cold-starts and high emitting gasoline exhaust to be distinguished from normal running vehicle exhaust. Initial indications are that emissions inventories do not adequately account for these emissions. Hourly gas chromatographic data allow the diurnal cycles and dominant wind directions of VOC sources to be estimated. These add confidence to the CMB apportionments, as well as elucidating temporal and spatial relationship between emissions and ambient concentrations.

Collocation of PM_{2.5} speciation sites with PAMS VOC sites will allow gas and particle properties to be used together in a single CMB apportionment. This holds the potential to provide more accurate source apportionments for a wider variety of chemical components.

CMB8 provides a myriad of options that can be applied to better understand the CMB source apportionment method. The new collinearity measures need to be better characterized to provide more specific guidance for their use in practical situations. Furthermore, the Britt-Luecke algorithm, as implemented in CMB8, has not undergone comprehensive testing. It is therefore not recommended for inexperienced users. Its inclusion as an option is mainly intended to provide the opportunity for interested advanced users to perform research investigations needed to establish its future viability.

This protocol will surely be revised as more and better data become available, and we gain more experience and skill in applying CMB to source apportionment studies.

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APPENDIX A. 54 PAMS TARGET COMPOUNDS (HYDROCARBONS) LISTED IN THEIR ELUTION SEQUENCE.

	Hydrocarbon	AIRS	CAS
1.	Ethylene	43203	74851
2.	Acetylene	43206	74862
3.	Ethane	43202	74840
4.	Propylene	43205	115071
5.	Propane	43204	74986
6.	Isobutane	43214	75285
7.	1-Butene ¹	43280	106989
8.	n-Butane	43212	106978
9.	<i>t</i> -2-Butene	43216	624646
10.	<i>c</i> -2-Butene	43217	590181
11.	Isopentane	43221	78784
12.	1-Pentene	43224	109671
13.	n-Pentane	43220	109660
14.	Isoprene	43243	78795
15.	<i>t</i> -2-Pentene	43226	646048
16.	<i>c</i> -2-Pentene	43227	627203
17.	2,2-Dimethylbutane	43244	75832
18.	Cyclopentane	43242	287923
19.	2,3-Dimethylbutane	43284	79298
20.	2-Methylpentane	43285	107835
21.	3-Methylpentane	43230	96140
22.	n-Hexane	43231	110543
23.	Methylcyclopentane	43262	96377
24.	2,4-Dimethylpentane	43247	108087
25.	Benzene	45201	71432
26.	Cyclohexane	43248	110827
27.	2-Methylhexane	43263	591764
28.	2,3-Dimethylpentane	43291	565593
29.	3-Methylhexane	43249	589344
30.	2,2,4-Trimethylpentane	43250	540841
31.	n-Heptane	43232	142825
32.	Methylcyclohexane	43261	108872
33.	2,3,4-Trimethylpentane	43252	565753
34.	Toluene	45202	108883
35.	2-Methylheptane	43960	592278
36.	3-Methylheptane	43253	589811
37.	n-Octane	43233	111659
38.	Ethylbenzene	45203	100414
39.	<i>m</i> & <i>p</i> -Xylene ²	45109	108383/106423
40.	Styrene	45220	100425
41.	<i>o</i> -Xylene	45204	95476
42.	n-Nonane	43235	111842
43.	Isopropylbenzene	45210	98828
44.	n-Propylbenzene	45209	103651
45.	<i>m</i> -Ethyltoluene	45212	620144
46.	<i>p</i> -Ethyltoluene	45213	622968
47.	1,3,5-Trimethylbenzene	45207	108678
48.	<i>o</i> -Ethyltoluene	45211	611143
49.	1,2,4-Trimethylbenzene	45208	95636
50.	n-Decane	43238	124185
51.	1,2,3-Trimethylbenzene	45225	526738
52.	<i>m</i> -Diethylbenzene ³	45218	141935
53.	<i>p</i> -Diethylbenzene	45219	105055
54.	n-Undecane	43954	1120214

¹Note that because 1-Butene and Isobutene elute at about the same time, they are difficult to resolve. The coeluting isomers are assigned AIRS Parameter Code 43127. Isobutene is assigned AIRS Parameter Code 43270 and CAS 115117.

²These isomers of xylene are also difficult to resolve. Individually, their AIRS Parameter Codes are 45205 & 45206, respectively. Respective CAS numbers are provided in the table.

³Also named 1,3-Diethylbenzene.

APPENDIX B. NORMALIZATION FOR THE VOC SOURCE PROFILE

As we stressed in Section 3.1.2, the different ways in which source profiles are constructed make it difficult in practice to compare and use VOC profiles from different studies. Furthermore, inventories employ different conventions for defining VOC. Meaningful comparison of CMB results with emission inventories requires a common reference. In this discussion we explain how normalized profiles are constructed for input to CMB, and also point out some differences to be seen in different normalization approaches.

In Table B-1 are shown data collected from the 1990 Atlanta Ozone Precursor Monitoring Study, in which motor vehicle emissions were sampled in canisters beside a roadway in a tunnel-like underpass during periods of heavy traffic. Roadway tunnels are usually good integrators of the mobile source fleet. In the first column is the average measured concentration for the top 83 NMOC appearing in the chromatogram, based on 9 samples. Two additional species, n-Tridecane and n-Tetradecane, were included to be consistent with the airport and aircraft profiles also collected in this study. The average sum of the 85 peaks is 1949.4, while the sum of *all* quantified NMOC chromatogram peaks is 2335.7 ppbC. Note that the example presented here - in which multiple samples were taken of a single source type for profile characterization, and subjected to averaging - is ideal. In some cases, only a single sample may be taken. It is important to understand exactly how the values appearing in Table B-1 were derived:

$$\text{Average Concentration for species } i = \bar{c}_i = \frac{\sum_{k=1}^n c_{ik}}{n}, \text{ where} \quad \text{B-1}$$

c_{ik} = measured concentration (ppbC) for species i in the chromatogram for sample k , and

n = number of samples available for constructing this source profile.

$$\text{Fractional abundance of species } i = \bar{f}_i = \frac{\sum_{k=1}^n f_{ik}}{n}, \text{ where} \quad \text{B-2}$$

$$f_{ik} = \frac{c_{ik}}{\text{summation}_k} \text{ (where } \text{summation}_k \text{ = sum of the concentration peaks for sample } k \text{ used in the normalization).} \quad \text{B-3}$$

$$\text{Uncertainty for fractional abundance of species } i = \sigma_{\bar{f}_i} = \sqrt{\frac{\sum_{k=1}^n (\bar{f}_i - f_{ik})^2}{n - 1}} \quad \text{B-4}$$

(the standard deviation of the mean fractional abundance determined from n samples).

In applying Eqns B-2, B-3, and B-4, professional judgement should of course be used in the matter of potential outliers. For example, if for a particular sample k , f_{ik} is greatly different from \bar{f}_i , especially for multiple species i , the sample k should probably be deleted from the calculations. For the VOC source profile presented in Table B-1, the uncertainties reported for

the mean fractional abundances were statistically analyzed. The mean is 12.7% and the median is 8.9%, with a minimum uncertainty of 2.6% (ethylbenzene) and a maximum uncertainty of 73.5% (2,3,3 trimethyl-1-butene). As indicated by these statistics, the routine practice of some laboratories to provide only a single, overall assessment of uncertainty/precision for an analysis is an oversimplification.

Ideally, the fractional abundances for each species i are determined individually for each source sample, and then averaged for the suite of samples taken. Note that the mean fractional abundance wasn't simply determined by taking the mean concentration for species i , and then dividing by the mean *summation* for the suite of samples, i.e.,

$$\bar{f}_i \neq \frac{\bar{c}_i}{\text{summation}} = \frac{\frac{1}{n} \sum_{k=1}^n c_{ik}}{\frac{1}{n} \sum_{k=1}^n \text{summation}_k} \quad \text{B-5}$$

Equations B-2 and B-5 are not equivalent and the value of \bar{f}_i determined via Eqn. B-5 in fact may be considerably biased. Note also that the uncertainty wasn't simply determined as the standard deviation of the mean concentration of species i for the suite of samples taken, i.e.,

$$\text{Unc.} \neq \sigma_{\bar{c}_i} = \sqrt{\frac{\sum_{k=1}^n (\bar{c}_i - c_{ik})^2}{n - 1}} \quad \text{B-6}$$

Equations B-4 and B-6 are not equivalent. Eqn. B-6, patterned after Eqn. B-1, is inappropriate because it isn't normalized (i.e., does not account for variations in *summation_k*). And because Eqn. B-5 is not a robust estimate of *relative* species abundance, the associated uncertainty ($\sigma_{\bar{c}_i}$) is not an accurate reflection of the uncertainty for species i .

As stated in Section 3.1.2, speciated VOC data are sometimes normalized to all the compounds in the chromatogram, as shown in the first set of paired columns in Table B-1. In fact, the values appearing in this set of columns are exactly as reported in Table 1 of the cited JAPCA article, except that the latter were expressed as percentages. Normalized fractional abundances are often presented as percentages because they are easier to read (fewer leading decimal places). However, CMB requires that abundances be in fractional form; the ratios represented in Table B-1 are appropriate for the source profile input file required by CMB. In this case, the value for *summation_k* in Eqn. B-3, with which the fractional abundances (f_{ik}) were determined, included the sum of all peaks in the chromatogram.

The 2nd set of paired columns represents a normalization to only the PAMS (Photochemical Assessment Monitoring Stations) species. Here, the ratio was constructed as before, but the value for *summation_k* in Eqn. B-3 included only the sum of the measured PAMS peaks.

Note that since the ratios appearing in column 2 include only 85 NMOC species, the sum of their fractional abundances normalized to total NMOC is less than unity. Conversely, since the ratios appearing in the 4th column are based on the sum of only the PAMS species, the sum of fractional abundances is greater than unity. Of course, had only PAMS species been sampled and measured, the sum would theoretically be unity in the 4th column. There is a 35% difference in fractional abundances normalized via the two approaches shown here. The ratio of 1.123 / 0.833 is 1.35, which is precisely the same ratio as 2335.7 / 1735.7 (sum of all measured peaks / sum of PAMS peaks). This relationship is shown most clearly in the last entry (total NMOC), in which the respective normalized values clearly reflect the 35% difference. It is worth noting that many published source profiles, including the source from which these data were reproduced, include an entry for total NMOC. When published profiles include a normalized value for total NMOC, the normalization approach becomes obvious. Beyond its practical purposes, it is useful to include an entry for total NMOC in the source profile input file for CMB provided it is normalized to the sum of the measured PAMS species. Ideally, the uncertainty for the normalized total NMOC abundance should be calculated as:

$$Unc_{.TNMOC} = \sqrt{(\sigma_{f_i})^2 + (\sigma_{f_{i+1}})^2 + (\sigma_{f_{i+2}})^2 + \dots + (\sigma_{f_m})^2}, \text{ where}$$

σ_{f_i} = normalized uncertainty computed via Eqn. B-4, and m = total number of NMOC species measured. For convenience, the value for this uncertainty reported in Table B-1 was based on $m = 85$ (only the 85 values in column 5 were used). If possible, all measured NMOC species should be used in this calculation.

We mentioned that the VOC source type characterized for this example is in many ways ideal. Roadway sources such as this one are likely to reflect most, if not all, of the PAMS species. However, many VOC source types may be sampled in which all or even most of the PAMS species will *not* be represented. So long as the sampling system is capable of collecting all of the PAMS species, and so long as the analytical system is capable of detecting all of the PAMS species, the normalization procedure described in Eqns. B-1 through B-4 should be followed. The value for n will reflect the number of samples taken, and the value for *summation_k* will include the sum of as many PAMS peaks measured in the chromatogram for any sample k .

**Table B-1. Measured VOC concentrations and their normalized fractional abundances.¹
(Species flagged with ‘•’ are PAMS target compounds listed in Appendix A)**

VOC Species	Average Concentration (ppbC)	Ratio to TNMOC		Ratio to PAMS	
		Abundance	Unc. ²	Abundance	Unc. ²
• Ethylene	99.77	0.043400	0.004700	0.058590	0.006345
• Acetylene	86.24	0.038000	0.006400	0.051300	0.008640
• Ethane	36.34	0.015500	0.001900	0.020925	0.002565
• Propene	45.11	0.019600	0.001800	0.026460	0.002430
• Propane	24.94	0.010500	0.001800	0.014175	0.002430
• Isobutane	27.16	0.011200	0.002500	0.015120	0.003375
• 1-Butene/Isobutene	27.67	0.011810	0.000900	0.015944	0.001215
• 1,3-Butadiene	9.34	0.003800	0.001100	0.005130	0.001485
• n-Butane	98.49	0.041100	0.007100	0.055485	0.009585
• <i>t</i> -2-Butene	9.70	0.004080	0.000280	0.005508	0.000378
• <i>c</i> -2-Butene	8.02	0.003340	0.000300	0.004509	0.000405
• 3-Methyl-1-Butene	3.74	0.001583	0.000091	0.002137	0.000123
• Isopentane	204.13	0.086400	0.008400	0.116640	0.011340
• 1-Pentene	7.78	0.003200	0.001600	0.004320	0.002160
• 2-Methyl-1-Butene	15.26	0.006360	0.000530	0.008586	0.000716
• n-Pentane	63.64	0.026600	0.002700	0.035910	0.003645
• Isoprene	7.89	0.003200	0.001700	0.004320	0.002295
• <i>t</i> -2-Pentene	17.78	0.007500	0.000450	0.010125	0.000608
• <i>c</i> -2-Pentene	9.79	0.004110	0.000290	0.005549	0.000392
• 2-Methyl-2-Butene	23.16	0.009300	0.002900	0.012555	0.003915
• 2,2-Dimethylbutane	12.07	0.004950	0.000850	0.006683	0.001148
• Cyclopentene	4.06	0.001720	0.000084	0.002322	0.000113
• 4-Methyl-1-Pentene	4.10	0.001790	0.000016	0.002417	0.000216
• Cyclopentane	5.86	0.002508	0.000077	0.003386	0.000104
• 2,3-Dimethylbutane	20.19	0.008630	0.000250	0.011650	0.000338
• 2-Methylpentane	57.25	0.024340	0.000990	0.032859	0.001336
• 3-Methylpentane	33.32	0.014180	0.000620	0.019143	0.000837
• 2-Methyl-1-Pentene	4.32	0.001830	0.000180	0.002471	0.000243
• 1-Hexene	3.13	0.001338	0.000055	0.001806	0.000074
• n-Hexane	25.68	0.010880	0.000580	0.014688	0.000783
• <i>t</i> -3-Hexene	6.11	0.002580	0.000570	0.003483	0.000769
• <i>t</i> -2-Hexene	5.85	0.002490	0.000210	0.003362	0.000284
• <i>c</i> -2-Hexene	2.99	0.001270	0.000110	0.001715	0.000149
• Methylcyclopentane	18.37	0.007830	0.000380	0.010571	0.000513
• 2,4-Dimethylpentane	16.62	0.007040	0.000580	0.009504	0.000783
• 2,3,3-Trimethyl-1-Butene	8.49	0.003400	0.002500	0.004590	0.003375
• Benzene	63.13	0.027300	0.001900	0.036855	0.002565
• Cyclohexane	3.83	0.001660	0.000110	0.002241	0.000149
• 2-Methylhexane	20.44	0.008740	0.000530	0.011799	0.000716
• 2,3-Dimethylpentane	21.29	0.009010	0.000600	0.012164	0.000810
• 3-Methylhexane	20.69	0.008880	0.000420	0.011988	0.000567
• <i>c</i> -1,3-Dimethylcyclopentane	4.49	0.001920	0.000130	0.002592	0.000175
• 3-Ethylpentane	6.98	0.002980	0.000150	0.004023	0.000203
• 2,2,4-Trimethylpentane	57.90	0.025100	0.002300	0.033885	0.003105
• n-Heptane	12.68	0.005400	0.000380	0.007290	0.000513
• Methylcyclohexane	7.08	0.003010	0.000170	0.004064	0.000230
• 2,5-Dimethylhexane	7.58	0.003290	0.000330	0.004442	0.000446
• 2,4-Dimethylhexane	12.82	0.005490	0.000440	0.007411	0.000594
• 2,3,4-Trimethylpentane	22.06	0.009500	0.001100	0.012825	0.001485
• Toluene	153.15	0.065900	0.003600	0.088965	0.004860

2,3-Dimethylhexane	6.57	0.002830	0.000350	0.003820	0.000472
• 2-Methylheptane	7.51	0.003240	0.000240	0.004374	0.000324
• 3-Methylheptane	8.30	0.003610	0.000440	0.004874	0.000594
2,2,5-Trimethylhexane	8.51	0.003720	0.000420	0.005022	0.000567
• n-Octane	6.68	0.002860	0.000120	0.003861	0.000162
2,5-Dimethylheptane	4.37	0.001888	0.000084	0.002549	0.000113
• Ethylbenzene	29.93	0.012800	0.000330	0.017280	0.000446
• <i>m/p</i> -Xylene	101.75	0.043500	0.001400	0.058725	0.001890
4-Methyloctane	5.70	0.002460	0.000220	0.003321	0.000297
3-Methyloctane	4.29	0.001860	0.000130	0.002511	0.000175
• Styrene	9.89	0.004370	0.000530	0.005900	0.000716
• <i>o</i> -Xylene	38.73	0.016620	0.000800	0.022437	0.001080
• n-Nonane	5.07	0.002140	0.000250	0.002889	0.000338
• Isopropylbenzene	3.60	0.001530	0.000150	0.002066	0.000203
• n-Propylbenzene	8.10	0.003530	0.000320	0.004766	0.000432
• <i>m</i> -Ethyltoluene	31.85	0.013810	0.000900	0.018644	0.001215
• <i>p</i> -Ethyltoluene	14.68	0.006330	0.000340	0.008546	0.000459
• 1,3,5-Trimethylbenzene	17.21	0.007490	0.000600	0.010112	0.000810
• <i>o</i> -Ethyltoluene	11.40	0.004990	0.000450	0.006736	0.000608
• 1,2,4-Trimethylbenzene	49.49	0.021600	0.002200	0.029160	0.002970
• n-Decane	6.05	0.002550	0.000400	0.003443	0.000540
• 1,2,3-Trimethylbenzene	12.23	0.005320	0.000420	0.007182	0.000567
n-Butylcyclohexane	5.55	0.002270	0.000330	0.003065	0.000446
• <i>m</i> -Diethylbenzene (1,3-Diethylbenzene)	4.37	0.001890	0.000110	0.002551	0.000149
• <i>p</i> -Diethylbenzene (1,4-Diethylbenzene)	17.25	0.007550	0.000650	0.010193	0.000878
1,3-Dimethyl-4-Ethylbenzene	5.52	0.002360	0.000220	0.003186	0.000297
• n-Undecane	5.57	0.002420	0.000240	0.003267	0.000324
1,2,4,5-Tetramethylbenzene	6.53	0.002720	0.000500	0.003672	0.000675
1,2,3,5-Tetramethylbenzene	7.99	0.003800	0.001000	0.005130	0.001350
<i>m</i> -Diisopropylbenzene	4.20	0.001570	0.000930	0.002119	0.001256
1,2,3,4-Tetramethylbenzene	4.69	0.001720	0.000890	0.002322	0.001202
naphthalene	18.53	0.008130	0.000810	0.010976	0.001094
n-Dodecane	5.64	0.002470	0.000280	0.003334	0.000378
n-Tridecane	2.11	0.000922	0.000098	0.001245	0.000132
n-Tetradecane	1.01	0.000420	0.000110	0.000567	0.000149
		Σ:	(0.833)	(1.12)	
Total NMOC	2335.66	1.000000		1.346	

Mean summation top 85 VOC peaks: **1949.35**

Mean summation PAMS peaks: 1735.72

Difference, TNMOC normalization vs. PAMS normalization: 34.6%

¹ Data used with permission from Conner, T.L., W.A. Lonneman, and R.L. Seila, 1995. Transportation-related volatile hydrocarbon source profiles measured in Atlanta. *JAWMA* 45: 383-394.

² Statistical analysis of these uncertainties is presented and discussed in the text.

APPENDIX C. INTERNET LINKS TO MODELING SOFTWARE AND DATA SETS

C.1 Receptor Models

- EPA-CMB8.2: www.epa.gov/scram001/

C.2 Source Profiles

- SPECIATE: www.epa.gov/ttn/chief/software/speciate
- Northern Front Range Air Quality Study Source Profiles (Particle Organics):
www.nfraqs.colostate.edu/nfraqs/index2.html

C.3 Ambient Measurements

- Center for Air Pollution Impact and Trend Analysis: capita.wustl.edu/
- IMPROVE Particle Measurements: www.epa.gov/ttn/amtic/visdata.html

C.4 Emissions Models and Inventories

- AP-42 Emissions Factors: www.epa.gov/ttn/chief/ap42/
- National Emissions Trends Report: www.epa.gov/ttn/chief/trends/trends98/
- National Emissions Inventory Data: www.epa.gov/ttn/chief/net/

C.5 Meteorological Models

- CALMET: www.epa.gov/scram001/
- MM5 (5th-Generation Penn State/NCAR Mesoscale Model):
www.mmm.ucar.edu/mm5/mm5v3/v3model.html
- WRF (Weather Research and Forecasting model): www.wrf-model.org
- National Centers for Environmental Prediction (NCEP) Products:
<http://nomads.ncdc.noaa.gov/data-access.html>

GFS (Global Forecast System)

HR GFS (High Resolution Global Forecast System)

Eta (regional mesoscale model)

NAM (North American Mesoscale)

NARR (North American Regional Reanalysis)

RUC (Rapid Update Cycle)

C.6 Dispersion Models

- AERMOD: www.epa.gov/scram001
- CALPUFF: www.epa.gov/scram001/
- CMAQ (Community Multi-Scale Air Quality Model):
www.epa.gov/asmdnerl/models3/

APPENDIX D. CMB MATHEMATICS

The source contribution (S_j) present at a receptor during a sampling period of length T due to a source j with constant emission rate E_j is

$$S_j = D_j \cdot E_j \quad (D-1)$$

where:

$$D_j = \int_0^T d[u(t), \sigma(t), x_j] dt \quad (D-2)$$

is a dispersion factor depending on wind velocity (u), atmospheric stability (σ), and the location of source j with respect to the receptor (x_j). All parameters in Equation A-2 vary with time, so the instantaneous dispersion factor, D_j , must be integrated over time period T (Watson, 1979).

Various forms for D_j have been proposed (Pasquill, 1974; Benarie, 1976; Seinfeld and Pandis, 1998), some including provisions for chemical reactions, removal, and specialized topography. None are completely adequate to describe the complicated, random nature of dispersion in the atmosphere. The advantage of receptor models is that an exact knowledge of D_j is unnecessary.

If a number of sources, J , exists and there is no interaction between their emissions to cause mass removal, the total mass measured at the receptor, C , will be a linear sum of the contributions from the individual sources.

$$C = \sum_{j=1}^J D_j \cdot E_j = \sum_{j=1}^J S_j \quad (D-3)$$

Similarly, the concentration of elemental component i , C_i , will be

$$C_i = \sum_{j=1}^J F_{ij} \cdot S_j \quad i = 1, \dots, I \quad (D-4)$$

where: F_{ij} = the fraction of source contribution S_j composed of element i . The number of chemical species (I) must be greater than or equal to the number of sources (J) for a unique solution to these equations.

Solutions to the CMB equations consist of: (1) a tracer solution; (2) a linear

programming solution; (3) an ordinary weighted least squares solution with or without an intercept; (4) a ridge regression weighted least squares solution with or without an intercept; and (5) an effective variance least squares solution with or without an intercept. An estimate of the uncertainty associated with the source contributions is an integral part of several of these solution methods.

Weighted linear least squares solutions are preferable to the tracer and linear programming solutions because: (1) theoretically they yield the most likely solution to the CMB equations, providing model assumptions are met; (2) they can make use of all available chemical measurements, not just the so-called tracer species; (3) they are capable of analytically estimating the uncertainty of the source contributions; and (4) there is, in practice, no such thing as a “tracer.” The effective variance solution developed and tested by Watson *et al.* (1984): (1) provides realistic estimates of the uncertainties of the source contributions (owing to its incorporation of both source profile and receptor data uncertainties); and (2) gives greater influence to chemical species with lower values for uncertainty in both the source and receptor measurements than to species with higher values for uncertainty. The effective variance solution is derived by minimizing the weighted sums of the squares of the differences between the measured and calculated values of C_i and F_{ij} (Britt and Luecke, 1973; Watson *et al.*, 1984). The solution algorithm is an iterative procedure which calculates a new set of S_j based on the S_j estimated from the previous iteration. It is carried out by the following steps expressed in matrix notation. A superscript k is used to designate the value of a variable at the k^{th} iteration.

1. Set initial estimate of the source contributions equal to zero.

$$S_j^{k=0} = 0 \quad j = 1, \dots, J \quad (\text{D-5})$$

2. Calculate the diagonal components of the effective variance matrix, V_e . All off-diagonal components of this matrix are equal to zero.

$$V_{e_{ii}}^k = \sigma_{C_i}^2 + \sum (S_j^k)^2 \cdot \sigma_{F_{ij}}^2 \quad (\text{D-6})$$

3. Calculate the $k+1$ value of S_j .

$$S^{k+1} = (F^T (V_e^k)^{-1} F)^{-1} F^T (V_e^k)^{-1} C \quad (\text{D-7})$$

4. Test the $(k+1)^{\text{th}}$ iteration of the S_j against the k^{th} iteration. If any one differs by more than 1%, then perform the next iteration. If all differ by less than 1%, then terminate the algorithm.

$$\text{if } |(S_j^{k+1} - S_j^k) / S_j^{k+1}| > 0.01, \text{ go to step 2} \quad (\text{D-8})$$

$$\text{if } |(S_j^{k+1} - S_j^k) / S_j^{k+1}| \leq 0.01, \text{ go to step 5}$$

5. Assign the (k+1)th iteration to S_j and σ_{S_j} . All other calculations are performed with these final values.

$$\sigma_{S_j}^2 = [\mathbf{F}^T (\mathbf{V}_e^{k+1})^{-1} \mathbf{F}_{jj}]^{-1} \quad j = 1, \dots, J \quad (\text{D-9})$$

where:

- \mathbf{C} = $(C_1 \dots C_i)^T$, a column vector with C_i as the i^{th} component
- \mathbf{S} = $(S_1 \dots S_j)^T$, a column vector with S_j as the j^{th} component
- \mathbf{F} = an $I \times J$ matrix of F_{ij} , the source composition matrix
- σ_{C_i} = one standard deviation uncertainty of the C_i measurement
- $\sigma_{F_{ij}}$ = one standard deviation uncertainty of the F_{ij} measurement
- \mathbf{V}_e = diagonal matrix of effective variances

The effective variance solution algorithm is very general, and it reduces to most of the solutions cited above with the following modifications:

- When the $\sigma_{F_{ij}}$ are set equal to zero, the solution reduces to the ordinary weighted least squares solution.
- When the $\sigma_{F_{ij}}$ are set equal to the same constant value, the solution reduces to the unweighted least squares solution.
- When a column is added to the \mathbf{F}_{ij} matrix with all values equal to 1, an intercept term is computed for the variable corresponding to this column.
- When the number of source profiles equals the number of species ($I = J$), and if the selected species are present only in a single, exclusive source profile, the solution reduces to the tracer solution.
- When the expression $(\mathbf{F}^T (\mathbf{V}_e^k)^{-1} \mathbf{F})$ is rewritten as $(\mathbf{F}^T (\mathbf{V}_e^k)^{-1} \mathbf{F} - \phi \mathbf{I})$, with ϕ equal to some non-zero number, known as the *smoothing parameter*, and \mathbf{I} equal to the identity matrix, the solution becomes the ridge regression solution (Williamson and Daboecia, 1983 and Henry *et al.*, 1984).

Formulas for the performance measures are:

$$\text{Reduced chi square} = \chi^2 = \frac{1}{I - J} \sum_{i=1}^I [(C_i - \sum_{j=1}^J F_{ij} S_j)^2 / V_{e_{ii}}] \quad (\text{D-10})$$

$$\text{Percent Mass} = 100 \left(\sum_{j=1}^J S_j \right) / C_t, \text{ where } C_t \text{ is the total measured mass} \quad (\text{D-11})$$

$$\text{R square} = 1 - [(I - J) \chi^2] / \left[\sum_{i=1}^I C_i^2 / V_{e_i} \right] \quad (\text{D-12})$$

$$\text{Modified Pseudo-Inverse Matrix} = (F^T (V_e)^{-1} F)^{-1} F^T (V_e)^{-1/2} \quad (\text{D-13})$$

The Singular Value Decomposition of the weighted **F** matrix is given by (Henry, 1992):

$$V_e^{1/2} F = U D V^T \quad (\text{D-14})$$

where **U** and **V** are I X I and J X J orthogonal matrices, respectively, and where **D** is a diagonal matrix with J nonzero and positive elements called the singular values of the decomposition. The columns of **V** are called the eigenvectors of the composition and their components are associated with the source types.

Appendix E. Summary of CMB PM₁₀ Source Apportionment Studies

Sampling Site	Time Period	Primary Geological	Primary Construction	Primary	Primary Vegetative Burning	Secondary Ammonium Sulfate	Secondary Ammonium Nitrate	Misc.	Misc.	Misc.	Misc.	Measured PM-10 Concentration
				Motor Vehicle Exhaust				Source 1	Source 2	Source 3	Source 4	
Central Phoenix, AZ (Chow <i>et al.</i> , 1991)	Winter 1989-90	33.0	0.0	25.0	2.3	0.2	2.8	0.0	0.0	0.0	0.0	64.0
Corona de Tucson, AZ (Chow <i>et al.</i> , 1992c)	Winter 1989-90	17.0	0.0	1.6	0.0	1.9	0.0	0.0	0.0	0.0	0.0	19.1
Craycroft, AZ (Chow <i>et al.</i> , 1992c)	Winter 1989-90	13.0	0.0	8.3	0.0	0.7	0.6	1.2 ^a	0.0	0.0	0.0	23.4
Downtown Tucson, AZ (Chow <i>et al.</i> , 1992c)	Winter 1989-90	26.0	5.1	14.0	0.0	1.0	0.2	1.3 ^a	0.0	0.0	0.0	48.0
Hayden 1, AZ (Garfield) (Ryan <i>et al.</i> , 1988)	1986	5.0	2.0 ^b	0.0	0.0	4.0	0.0	74.0 ^e	5.0 ^d	1.0 ^e	0.0	105.0
Hayden 2, AZ (Jail) (Ryan <i>et al.</i> , 1988)	1986	21.0	4.0 ^b	0.0	0.0	4.0	0.0	28.0 ^e	0.0	1.0 ^e	0.0	59.0
Orange Grove, AZ (Chow <i>et al.</i> , 1992a)	Winter 1989-90	20.0	0.0	15.0	0.0	0.4	0.4	0.0	0.0	0.0	0.0	34.2
Phoenix, AZ (Estrella Park) (Chow <i>et al.</i> , 1991)	Winter 1989-90	37.0	0.0	10.0	0.9	1.6	0.0	0.0	0.0	0.0	0.0	55.0
Phoenix, AZ (Gunnery Rg.) (Chow <i>et al.</i> , 1991)	Winter 1989-90	20.0	0.0	5.5	0.0	1.0	0.0	0.0	0.0	0.0	0.0	27.0
Phoenix, AZ (Pinnacle Pk.) (Chow <i>et al.</i> , 1991)	Winter 1989-90	7.0	0.0	2.9	1.0	0.9	0.0	0.0	0.0	0.0	0.0	12.0
Rillito, AZ (Thanukos <i>et al.</i> , 1992)	1988	42.7	13.8 ^b	1.2 ^f	0.0	0.0	0.0	11.6 ^e	0.0	0.0	0.0	79.5
Scottsdale, AZ (Chow <i>et al.</i> , 1991)	Winter 1989-90	25.0	0.0	19.0	7.4	0.6	3.6	0.0	0.0	0.0	0.0	55.0
West Phoenix, AZ (Chow <i>et al.</i> , 1991)	Winter 1989-90	30.0	0.0	25.0	10.0	0.4	3.1	0.0	0.0	0.0	0.0	69.0
Anacapa Island, CA (Chow <i>et al.</i> , 1996b)		2.2	0.0	4.9	0.0	3.4	1.0	9.6 ^h	0.0	0.0	0.0	26.0
Anaheim, CA (Gray <i>et al.</i> , 1988)	1986	21.2	0.0	4.1 ⁱ	0.0	7.0	9.8	0.4 ^j	1.4 ^h	8.2 ^k	0.0	52.1
Anaheim, CA (Summer) (Watson <i>et al.</i> , 1994a)	Summer 1987	11.4	0.0	8.5	0.0	9.0	2.9	0.0 ^j	6.5 ^h	0.0	0.0	51.3
Anaheim, CA (Fall) (Watson <i>et al.</i> , 1994c)	Fall 1987	13.2	0.0	37.2	0.0	3.7	38.5	0.0 ^j	3.1 ^h	0.0	0.0	104.0
Azusa, CA (Summer) (Watson <i>et al.</i> , 1994c)	Summer 1987	34.9	0.0	15.9	0.0	11.4	6.1	0.0 ^j	5.7 ^h	0.0	0.0	92.1
Bakersfield, CA (Magliano, 1988)	1986	27.4	3.0	5.5	9.6 ⁱ	5.6	0.0	0.5 ^j	0.0	0.0	0.0	67.6
Bakerfield, CA (Chow <i>et al.</i> , 1992a)	1988-89	42.9	1.6	7.7	6.5	5.5	12.7	1.0 ^m	1.5 ⁿ	0.6 ^k	0.0	79.6
Burbank, CA (Gray <i>et al.</i> , 1988)	1986	21.3	0.0	6.1 ⁱ	0.0	7.2	10.2	0.1 ^j	0.9 ^h	9.8 ^k	0.0	56.6
Burbank, CA (Summer) (Watson <i>et al.</i> , 1994c)	Summer 1987	14.0	0.0	17.0	0.0	12.4	6.5	0.0 ^j	5.7 ^h	0.0	0.0	72.3
Burbank, CA (Fall) (Watson <i>et al.</i> , 1994c)	Fall 1987	11.0	0.0	39.1	0.0	3.1	25.1	0.0 ^j	1.9 ^h	0.0	0.0	94.8
Chula Vista 1, CA (Bayside) (Cooper <i>et al.</i> , 1988)	1986	6.7	0.0	0.8	0.0	7.5	0.0	0.4 ^j	2.7 ^h	2.0 ^k	0.0	28.8
Chula Vista 2, CA (Del Ray) (Cooper <i>et al.</i> , 1988)	1986	8.2	0.3	1.5	0.0	8.9	0.0	0.6 ^j	1.8 ^h	0.0	0.0	31.1
Chula Vista 3, CA (Cooper <i>et al.</i> , 1988)	1986	9.7	0.3	1.4	0.0	8.2	0.0	0.6 ^j	1.7 ^h	0.0	0.0	29.6
Claremont, CA (Summer) (Watson <i>et al.</i> , 1994c)	Summer 1987	19.4	0.0	14.4	0.0	9.5	6.3	0.0 ^j	4.7 ^h	0.0	0.0	70.0
Crows Landing, CA (Chow <i>et al.</i> , 1992a)	1988-89	32.2	0.0	2.2	3.4	2.8	6.5	0.5 ^m	1.5 ⁿ	1.2 ^k	0.0	52.5
Downtown Los Angeles, CA (Gray <i>et al.</i> , 1988)	1986	23.8	0.0	6.4 ⁱ	0.0	7.6	11.2	0.0	1.3 ^h	7.9 ^k	0.0	60.2
Downtown Los Angeles, CA (Summer) (Watson <i>et al.</i> , 1994c)	Summer 1987	12.7	0.0	16.2	0.0	13.0	4.4	0.0 ^j	6.5 ^h	0.0	0.0	67.6
Downtown Los Angeles, CA (Fall) (Watson <i>et al.</i> , 1994c)	Fall 1987	9.4	0.0	41.1	0.0	3.9	27.5	0.0 ^j	1.8 ^h	0.0	0.0	98.6
Fellows, CA (Chow <i>et al.</i> , 1992a)	1988-89	29.0	1.4	2.1	3.4	5.1	7.5	7.0 ^m	1.4 ⁿ	1.4 ^k	0.0	54.6
Fresno, CA (Magliano, 1988)	1986	17.1	0.7	4.0	9.2 ⁱ	1.8	0.0	0.1 ^j	0.0	0.0	0.0	48.1
Fresno, CA (Chow <i>et al.</i> , 1992a)	1988-89	31.8	0.0	6.8	5.1	3.6	10.4	0.3 ^m	1.0 ⁿ	0.1 ^k	0.0	71.5
Hawthorne, CA (Summer) (Watson <i>et al.</i> , 1994c)	Summer 1987	7.5	0.0	5.6	0.0	15.0	0.6	0.0 ^j	7.0 ^h	0.0	0.0	45.9
Hawthorne, CA (Fall) (Watson <i>et al.</i> , 1994c)	Fall 1987	8.9	0.0	35.1	0.0	5.1	20.4	0.0 ^j	3.7 ^h	0.0	0.0	85.1
Indio, CA (Kim <i>et al.</i> , 1992)		33.0	3.0	4.4	7.1	3.6	4.1	0.2 ^j	1.0 ^h	0.0	0.0	58.0
Kern Wildlife Refuge, CA (Chow <i>et al.</i> , 1992a)	1988-89	15.1	2.0	2.2	4.0	3.3	1.5	0.5 ^m	1.5 ⁿ	0.7 ^k	0.0	47.8
Lennox, CA (Gray <i>et al.</i> , 1988)	1986	16.0	0.1	4.6 ⁱ	0.0	7.6	7.9	0.2 ^j	3.1 ^h	7.6 ^k	0.0	46.9
Long Beach, CA (Gray <i>et al.</i> , 1988)	1986	20.7	0.0	5.1 ⁱ	0.0	8.0	9.2	0.1 ^j	2.0 ^h	6.4 ^k	0.0	51.9

Appendix E. Summary of CMB PM₁₀ Source Apportionment Studies

Sampling Site	Time Period	Primary										Measured PM-10 Concentration
		Primary Geological	Primary Construction	Primary Motor Vehicle Exhaust	Primary Vegetative Burning	Secondary Ammonium Sulfate	Secondary Ammonium Nitrate	Misc. Source 1	Misc. Source 2	Misc. Source 3	Misc. Source 4	
Long Beach, CA (Summer) (Watson <i>et al.</i> , 1994c)	Summer 1987	11.1	0.0	6.3	0.0	10.9	0.8	0.1 ^l	2.2 ^h	0.0	0.0	46.1
Long Beach, CA (Fall) (Watson <i>et al.</i> , 1994c)	Fall 1987	11.3	0.0	42.8	0.0	3.8	23.2	0.0 ^j	2.7 ^h	0.0	0.0	96.1
Magnolia, CA (Chow <i>et al.</i> , 1992b)	1988	31.7	0.0	11.2	0.0	4.9	19.7	0.3 ⁱ	1.2 ^h	1.2 ^o	0.0	66.0
Palm Springs, CA (Kim <i>et al.</i> , 1992)		16.4	1.4	2.3	5.1	3.7	4.2	0.1 ^l	0.5 ^h	0.0	0.0	35.1
Riverside, CA (Chow <i>et al.</i> , 1992b)	1988	32.6	0.0	7.0	0.0	4.8	21.4	0.3 ⁱ	1.3 ^h	1.1 ^o	0.0	64.0
Rubidoux, CA (Gray <i>et al.</i> , 1988)	1986	43.1	4.0 ^j	5.6 ⁱ	0.0	6.4	21.3	0.3 ⁱ	1.0 ^h	5.9 ^k	0.0	87.4
Rubidoux, CA (Summer) (Watson <i>et al.</i> , 1994b)	Summer 1987	34.9	4.5	17.3	0.0	9.5	27.4	0.0 ^j	5.1 ^h	0.0	0.0	114.8
Rubidoux, CA (Fall) (Watson <i>et al.</i> , 1994b)	Fall 1987	19.2	16.1	30.3	0.0	2.1	31.6	0.0 ^j	1.1 ^h	0.0	0.0	112.0
Rubidoux, CA (Chow <i>et al.</i> , 1992b)	1988	48.0	0.0	10.2	0.0	5.3	21.7	0.4 ^j	1.5 ^h	5.7 ^o	0.0	87.0
San Jose, CA (4th St.) (Chow <i>et al.</i> , 1995b)		13.1	0.0	9.2	31.3	2.3	13.3	0.9 ^h	0.0	0.0	0.0	68.4
San Jose, CA (San Carlos St.) (Chow <i>et al.</i> , 1995b)		11.8	0.0	8.9	31.3	2.1	12.8	0.7 ^h	0.0	0.0	0.0	64.9
San Nicolas Island, CA (Summer) (Watson <i>et al.</i> , 1994c)	Summer 1987	1.6	0.0	0.9	0.0	3.7	0.5	0.0 ^j	4.3 ^h	0.0	0.0	17.4
Santa Barbara, CA (Chow <i>et al.</i> , 1996b)		9.5	0.0	14.7	0.0	3.2	1.0	6.4 ^h	0.0	0.0	0.0	34.0
Santa Barbara, CA (GTC) (Chow <i>et al.</i> , 1996b)		3.2	0.0	5.1	0.0	2.8	0.5	6.3 ^h	0.0	0.0	0.0	20.5
Santa Maria, CA (Chow <i>et al.</i> , 1996b)		7.4	0.0	7.6	0.0	3.1	1.4	5.7 ^h	0.0	0.0	0.0	27.0
Santa Ynez, CA (Chow <i>et al.</i> , 1996b)		4.6	0.0	6.8	0.0	2.2	0.6	4.0 ^h	0.0	0.0	0.0	19.0
Stockton, CA (Chow <i>et al.</i> , 1992a)	1989	34.4	0.5	5.2	4.8	3.1	7.0	0.7 ^m	1.8 ⁿ	0.0 ^k	0.0	62.4
Upland, CA (Gray <i>et al.</i> , 1988)	1986	25.4	0.4 ^j	4.1 ⁱ	0.0	6.4	14.5	0.6 ^j	0.6 ^h	7.8 ^k	0.0	58.0
Vandenberg AFB, CA (Watt Road) (Chow <i>et al.</i> , 1996b)		4.5	0.0	3.2	0.0	1.9	1.0	9.3 ^h	0.0	0.0	0.0	20.6
Telluride 1, CO (Central) (Dresser and Baird, 1988)	Winter 1986	32.0	0.0	0.0	98.7	0.0	0.0	61.3 ^p	0.0	0.0	0.0	208.0
Telluride 2, CO (Society Turn) (Dresser and Baird, 1988)	Winter 1986	12.1	0.0	0.0	7.3	0.0	0.0	7.3 ^p	0.0	0.0	0.0	27.0
Pocatello, ID (Houck <i>et al.</i> , 1992)	1990	8.3	7.5 ^q	0.1	0.0	0.0	0.0	0.0	0.0	84.1 ^r	0.0	100.0
S. Chicago, IL (Hope <i>et al.</i> , 1988)	1986	27.2	2.4	2.8	0.0	15.4 ^s	0.0	15.1 ^r	2.2 ^u	0.0	0.0	80.1
S.E. Chicago, IL (Vermette <i>et al.</i> , 1992)	1988	14.7 ^v	0.0	0.9 ^f	0.0	7.7	0.0	0.8 ^r	0.3 ^h	1.1 ^w	7.7 ^z	41.0
Reno, NV (Non-sweeping) (Chow <i>et al.</i> , 1990)	Winter 1987	9.7	0.0	8.7	0.1	0.6	0.2	0.0	0.0	0.0	0.0	20.4
Reno, NV (Sweeping) (Chow <i>et al.</i> , 1990)	Winter 1987	11.8	0.0	11.0	1.2	0.8	0.2	0.0	0.0	0.0	0.0	24.9
Reno, NV (Chow <i>et al.</i> , 1988)	1986-87	14.9	0.0	10.0	1.9	1.3	0.6	0.0	0.0	0.0	0.0	30.0
Sparks, NV (Chow <i>et al.</i> , 1988)	1986-87	15.1	0.0	11.6	13.4	2.7	0.9	0.0	0.0	0.2 ^k	0.0	41.0
Verdi, NV (Chow <i>et al.</i> , 1988)	1986-87	7.8	0.0	4.0	1.1	0.9	0.1	0.0	0.0	0.0	0.0	15.0
Follansbee, OH (Skidmore <i>et al.</i> , 1992)	1991	10.0	0.0	35.0	0.0	16.0	0.0	9.3 ⁱ	0.0	0.0	0.0	66.0
Mingo, OH (Skidmore <i>et al.</i> , 1992)	1991	12.0	0.0	14.0	4.1	15.0	0.0	3.4 ⁱ	11.0 ^x	0.0	0.0	60.0
Sewage Plant, OH (Skidmore <i>et al.</i> , 1992)	1991	22.0	0.0	12.0	0.0	13.0	0.0	6.6 ⁱ	8.7 ^x	0.0	0.0	62.0
Steubenville, OH (Skidmore <i>et al.</i> , 1992)	1991	8.3	0.0	14.0	0.8	14.0	0.0	3.8 ⁱ	5.0 ^x	0.0	0.0	46.0
WTOV Tower, OH (Skidmore <i>et al.</i> , 1992)	1991	7.4	0.0	16.0	0.2	15.0	0.0	3.4 ⁱ	7.9 ^x	0.0	0.0	49.0
Wuhan, China (Zelenka <i>et al.</i> , 1992)		55.0	21.4	1.2	49.2 ^l	28.1	17.0	49.5 ^y	13.6 ^z	1.2 ^{aa}	0.0	224.9

Appendix E. Summary of CMB PM₁₀ Source Apportionment Studies

- ^a Smelter background aerosol.
- ^b Cement plant sources, including kiln stacks, gypsum pile, and kiln area.
- ^c Copper ore.
- ^d Copper tailings.
- ^e Copper smelter building.
- ^f Heavy-duty diesel exhaust emission.
- ^g Background aerosol.
- ^h Marine aerosol, road salt, and sea salt plus sodium nitrate.
- ⁱ Motor vehicle exhaust from diesel and leaded gasoline.
- ^j Residual oil combustion.
- ^k Secondary organic carbon.
- ^l Biomass burning.
- ^m Primary crude oil.
- ⁿ NaCl + NaNO₃.
- ^o Lime.
- ^p Road sanding material.
- ^q Asphalt industry.
- ^r Phosphorus/phosphate industry.
- ^s Regional sulfate.
- ^t Steel mills.
- ^u Refuse incinerator.
- ^v Local road dust, coal yard road dust, steel haul road dust.
- ^w Incineration.
- ^x Unexplained mass.
- ^y Residential coal burning.
- ^z Aluminum processing.
- ^{aa} Primary lead smelter.

Appendix F. Summary of CMB VOC Source Apportionment Studies

Study, Location, and Period Measurements	Source Apportionment Method	Findings																											
<p>Lower Fraser Valley, British Columbia, Canada (7/89 to 8/91) (Jiang <i>et al.</i>, 1997).</p> <p>24-hour canister samples every sixth day at 8 sites in Lower Fraser Valley for non-methane organic compounds (NMOC)^a with 558 species.</p>	<p>Emissions profiles are grouped based on 74 SARVAP^b or AIRS^c and converted to molar emissions of emitted NMOC species for hydrocarbons (e.g., aromatics, alkanes [parafins], alkenes [olefins], alkynes, oxygenated compounds [esters, carboxylic acids, ketones, aldehydes, alcohols, ethers], others [Si-, S-, N-, or halogen-containing], and unidentified mixtures [C₁ to C₁₂ mixtures and >C₁₂ mixtures]). Descriptive data analyses were made to compile emissions and ambient measurements.</p>	<p>Overall high degree of similarity was found between emissions inventory and ambient NMOC measurements.</p> <p>Discrepancies between emissions inventory and ambient NMOC were found for biogenic compounds (isoprene, -pinene, -pinene) and some species related to light-duty vehicle exhaust.</p> <p>Emission profile is used to calculate rate constants and product yields of reactions in photochemical modeling.</p> <p>Light-duty gasoline vehicles account for ~80% of NMOC in the inventory.</p> <p>Speciated emission profiles for light-duty gasoline exhaust need to be updated periodically in the emissions inventory.</p>																											
<p>Western Washington Study, Seattle, WA (6/95 to 9/95, and 7/96 to 8/96) (Fujita <i>et al.</i>, 1997b).</p> <p>3-hour C₂ - C₁₀ canister and carbonyl DNPH^d samples beginning at 0600 and 1200 PDT twice per week (Tuesdays and Thursdays) at 7 sites during mornings and at 6 sites during afternoons during summer 1995. Hourly C₂ - C₁₀ canister and carbonyl DNPH samples beginning at 0900, 1200, and/or 1500 PDT at 8 sites during ozone episodes in summer 1996.</p> <p>Total NMHC^j = sum of 25 abundant hydrocarbons.</p>	<p>Effective variance weighted least squares CMB^e with composite motor vehicle exhaust (including tunnel, garage, roadside, and dynamometer for light-duty gasoline and diesel exhaust), gasoline evaporation, liquid gasoline, gasoline vapor, CNG^f, GNG^g, LPG^h, architectural coatings, industrial solvents and coatings, and biogenic profiles.</p> <p>14 to 27 stable species used in CMB calculation with 56 to 69 other species in profiles and ambient data for validation.</p>	<p>Average source contributions to total measured NMHC in % NMHC for:</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th></th> <th style="text-align: center;"><u>Summer 1995</u></th> <th style="text-align: center;"><u>Summer 1996</u></th> </tr> </thead> <tbody> <tr> <td>Vehicle exhaust</td> <td style="text-align: center;">39% to 57% (including 0% to 38% diesel exhaust and 19% to 54% light-duty vehicle exhaust)</td> <td style="text-align: center;">40% to 104% (including 0.8% to 66% diesel exhaust and 16% to 65% light-duty vehicle exhaust)</td> </tr> <tr> <td>Liquid gasoline</td> <td style="text-align: center;">2% to 23%</td> <td style="text-align: center;">0% to 37%</td> </tr> <tr> <td>Gasoline vapor</td> <td style="text-align: center;">7% to 15%</td> <td style="text-align: center;">7% to 36%</td> </tr> <tr> <td>Gas (CNG)</td> <td style="text-align: center;">0% to 7.7%</td> <td style="text-align: center;">0% to 5.7%</td> </tr> <tr> <td>Gas (GNG)</td> <td style="text-align: center;">0.6% to 12%</td> <td style="text-align: center;">0% to 7.1%</td> </tr> <tr> <td>Gas (LPG)</td> <td style="text-align: center;">0% to 3.1%</td> <td style="text-align: center;">0% to 2.4%</td> </tr> <tr> <td>Biogenics</td> <td style="text-align: center;">0.2% to 2.5%</td> <td style="text-align: center;">1.2% to 7.8%</td> </tr> <tr> <td>Unexplained</td> <td style="text-align: center;">0% to 28%</td> <td style="text-align: center;">-10% to -50%</td> </tr> </tbody> </table> <p>Larger errors in source contribution estimates were reported in 1996 because of uncertainties in quantifying unidentified sources and fewer samples collected.</p>		<u>Summer 1995</u>	<u>Summer 1996</u>	Vehicle exhaust	39% to 57% (including 0% to 38% diesel exhaust and 19% to 54% light-duty vehicle exhaust)	40% to 104% (including 0.8% to 66% diesel exhaust and 16% to 65% light-duty vehicle exhaust)	Liquid gasoline	2% to 23%	0% to 37%	Gasoline vapor	7% to 15%	7% to 36%	Gas (CNG)	0% to 7.7%	0% to 5.7%	Gas (GNG)	0.6% to 12%	0% to 7.1%	Gas (LPG)	0% to 3.1%	0% to 2.4%	Biogenics	0.2% to 2.5%	1.2% to 7.8%	Unexplained	0% to 28%	-10% to -50%
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Appendix F. Summary of CMB VOC Source Apportionment Studies

Study, Location, and Period Measurements	Source Apportionment Method	Findings																					
<p>San Joaquin Valley and San Francisco Bay Area, CA (7/90 to 8/90) (Fujita <i>et al.</i>, 1995b). 2-hour C₂ - C₁₂ canister and carbonyl DNPH samples at 0800, 1000, 1200, and 1400 PDT at 34 sites in central California representing urban, nonurban, oilfield background, and forested areas. NMOG = mass equivalent sum of all GC peaks from canister sample plus carbonyls from DNPH.</p>	<p>Effective variance weighted least squares CMB with motor vehicle exhaust, gasoline evaporation, liquid gasoline, CNG, GNG, LPG, oil production, architectural coatings, industrial solvents and coatings, biogenics, and acetone profiles from other studies. 26 stable species used in CMB calculation with 57 other species in profiles and ambient data for validation.</p>	<p>Typical average contributions to NMOG:</p> <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 60%;">Vehicle exhaust</td> <td style="width: 40%;">35% to 70%</td> </tr> <tr> <td>Gasoline evaporation</td> <td>10% to 40%</td> </tr> <tr> <td>Coatings and solvents</td> <td>1% to 2%</td> </tr> <tr> <td>Oil production</td> <td>30% to 50% (southern sites near oilfields), 5% to 15% (other sites)</td> </tr> <tr> <td>Biogenic:</td> <td>10% to 15% (Yosemite and Sequoia only, based on measured isoprene only)</td> </tr> <tr> <td>Others</td> <td>2% to 20% (morning), 20% to 60% (afternoon)</td> </tr> </table> <p>Most NMOG compounds were explained well by the profiles for the morning samples. Reactive precursors and end-products diverged from CMB estimates in afternoon samples, resulting in large contributions from "Others". Ambient motor vehicle contributions were ~twice proportions from inventory neighboring grid squares.</p>	Vehicle exhaust	35% to 70%	Gasoline evaporation	10% to 40%	Coatings and solvents	1% to 2%	Oil production	30% to 50% (southern sites near oilfields), 5% to 15% (other sites)	Biogenic:	10% to 15% (Yosemite and Sequoia only, based on measured isoprene only)	Others	2% to 20% (morning), 20% to 60% (afternoon)									
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<p>Los Angeles, CA (southern California and southeast desert areas) (6/74 to 9/74) (Mayrsohn and Crabtree, 1976; Mayrsohn <i>et al.</i>, 1977). 3-hour C₁ - C₁₀ samples were acquired starting 0200, 0600, 1100, 1200, and 1400 PDT at 6 south coast air basin sites (around Los Angeles, Long Beach, and El Monte) and at 2 southeast desert air basin sites (Banning and Palm Springs). NMHC = is the sum of 39 species plus C₁₁ - C₁₈ compounds.</p>	<p>Multi-regression analysis and ordinary least square equations were used with vehicle exhaust, liquid gasoline, gasoline vapor, CNG, GNG, and LPG profiles derived in 1973.</p>	<p>Average contributions to NMHC (C₁ to C₁₀):</p> <table style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 60%;"></th> <th style="width: 20%; text-align: center;"><u>CMB-calculated</u></th> <th style="width: 20%; text-align: center;"><u>Regression</u></th> </tr> </thead> <tbody> <tr> <td>Vehicle exhaust</td> <td style="text-align: center;">53%</td> <td style="text-align: center;">47%</td> </tr> <tr> <td>Liquid gasoline</td> <td style="text-align: center;">12%</td> <td style="text-align: center;">31%</td> </tr> <tr> <td>Gasoline vapor</td> <td style="text-align: center;">10%</td> <td style="text-align: center;">—</td> </tr> <tr> <td>CNG</td> <td style="text-align: center;">5%</td> <td style="text-align: center;">8%</td> </tr> <tr> <td>GNG</td> <td style="text-align: center;">19%</td> <td style="text-align: center;">14%</td> </tr> <tr> <td>LPG</td> <td style="text-align: center;">1%</td> <td style="text-align: center;">—</td> </tr> </tbody> </table>		<u>CMB-calculated</u>	<u>Regression</u>	Vehicle exhaust	53%	47%	Liquid gasoline	12%	31%	Gasoline vapor	10%	—	CNG	5%	8%	GNG	19%	14%	LPG	1%	—
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<p>Los Angeles, CA (8/86) (Harley <i>et al.</i>, 1992).</p> <p>Hourly, 4-, and 8-hour canister samples collected at 0400, 0600, 0800, and 1100 PDT at 9 sites between 8/10/86 and 8/21/86.</p>	<p>Effective variance least squares CMB with revised and respeciated organic gas emissions profiles for gasoline engine exhaust (non-catalyst, catalyst), unburned gasoline (whole liquid gasoline, headspace gasoline vapor), commercial jet exhaust, architectural coatings (solvent-borne, water-borne, thinning solvents), industrial coatings, and industrial adhesives.</p>	<p>Average contributions to NMOC:</p> <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 60%;">Gasoline engine exhaust</td> <td style="width: 20%;">31% to 37%</td> <td style="width: 20%;"></td> </tr> <tr> <td>Whole liquid gasoline</td> <td>32% to 38%</td> <td></td> </tr> <tr> <td>Headspace gasoline vapor</td> <td>5% to 13%</td> <td></td> </tr> <tr> <td>Waste and natural gas</td> <td>10% to 15%</td> <td></td> </tr> <tr> <td>Dry cleaning</td> <td>0% to 4%</td> <td></td> </tr> <tr> <td>Degreasing solvents</td> <td>5% to 12%</td> <td></td> </tr> </table> <p>Respeciation of organic gas emissions result in large changes in basin-wide emission estimates for 1,3-butadiene, ethylene glycol, methanol, and cyclohexane. Reactivity for surface coatings and thinning solvents are revised. Key discrepancies between CMB and the emissions inventory were found for unburned gasoline. Excess unburned gasoline is suspected to be a combination of emissions from tailpipe, hot-soak evaporative, and fuel spillage.</p>	Gasoline engine exhaust	31% to 37%		Whole liquid gasoline	32% to 38%		Headspace gasoline vapor	5% to 13%		Waste and natural gas	10% to 15%		Dry cleaning	0% to 4%		Degreasing solvents	5% to 12%	
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<p>Southern California Air Quality Study (SCAQS), Los Angeles, CA (7/87 to 9/97) (Fujita <i>et al.</i>, 1994)</p> <p>Hourly C₂ - C₁₂ canister samples at 0700, 1200, and 1600 PDT (PST during fall) at 8 sites during summer and at 6 sites during fall. Additional samples at 0300, 0900, and 1400 at two sites during the summer and fall in Southern California. Total NMHC = all GC/FID peaks except for oxygenated compounds.</p>	<p>Effective variance weighted least squares CMB with motor vehicle exhaust, gasoline evaporation, liquid gasoline, gasoline vapor, CNG, GNG, LPG, architectural coatings, industrial solvents and coatings, and biogenic profiles from CARB's modeling emissions data system and auto/oil program.</p> <p>27 stable species used in CMB calculation with 34 other species in profiles and ambient data for validation.</p>	<p>Average CMB-calculated source contributions to total NMHC in % NMHC in:</p> <table style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 40%;"></th> <th style="width: 20%; text-align: center;"><u>Summer</u></th> <th style="width: 20%; text-align: center;"><u>Fall</u></th> </tr> </thead> <tbody> <tr> <td>Vehicle exhaust</td> <td style="text-align: center;">49% to 54%</td> <td style="text-align: center;">54% to 68%</td> </tr> <tr> <td>Liquid gasoline</td> <td style="text-align: center;">11% to 17%</td> <td style="text-align: center;">14% to 15%</td> </tr> <tr> <td>Gasoline vapor</td> <td style="text-align: center;">10% to 11%</td> <td style="text-align: center;">7% to 11%</td> </tr> <tr> <td>Other</td> <td style="text-align: center;">21% to 30%</td> <td style="text-align: center;">11% to 21%</td> </tr> </tbody> </table> <p>CMB estimates for 0700 to 0800 PDT sampling periods are 2 to 3 times higher than the emissions inventory, with even larger discrepancies during midday. Non-motor-vehicle hydrocarbon emissions are overestimated in the inventory, while on-road motor vehicle emissions are underestimated. Photochemical modeling with adjusted (increased) on-road emissions improved model performance.</p>		<u>Summer</u>	<u>Fall</u>	Vehicle exhaust	49% to 54%	54% to 68%	Liquid gasoline	11% to 17%	14% to 15%	Gasoline vapor	10% to 11%	7% to 11%	Other	21% to 30%	11% to 21%			
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<p>Los Angeles, CA (7/95 to 10/95) (Fujita <i>et al.</i>, 1997b)</p> <p>3-hour C₂ - C₁₂ canister samples starting at 0700 and 1400 PDT for six 7-day periods at 3 ARB sites and for 3-day periods at 8 CRC^k sites.</p> <p>NMHC = sum of 25 species plus MTBE^l.</p>	<p>Effective variance weighted least squares CMB with composite motor vehicle exhaust (including tunnel, garage, roadside, and dynamometer for light-duty gasoline and diesel exhaust), gasoline evaporation, liquid gasoline, gasoline vapor, CNG, GNG, LPG, architectural coatings, industrial solvents and coatings, and biogenic profiles.</p> <p>27 stable species used in CMB calculation with 56 other species in profiles and ambient data for validation.</p>	<p>Average contributions to sum of NMHC and MTBE with 10 alternative gasoline vehicle profiles are:</p> <table style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 30%;"></th> <th style="width: 35%; text-align: center;"><u>3 ARB sites</u></th> <th style="width: 35%; text-align: center;"><u>8 CRC sites</u></th> </tr> </thead> <tbody> <tr> <td>Vehicle exhaust</td> <td style="text-align: center;">54% to 64% (including 11% to 15% diesel exhaust and 38% to 50% light-duty vehicle exhaust)</td> <td style="text-align: center;">56% to 68% (including 10% to 15% diesel exhaust and 42% to 54% light-duty vehicle exhaust)</td> </tr> <tr> <td>Liquid gasoline</td> <td style="text-align: center;">0.6% to 11%</td> <td style="text-align: center;">1% to 14%</td> </tr> <tr> <td>Gasoline vapor</td> <td style="text-align: center;">15% to 29%</td> <td style="text-align: center;">10% to 20%</td> </tr> <tr> <td>Gas (CNG)</td> <td style="text-align: center;">3.1% to 3.7%</td> <td style="text-align: center;">2.2% to 2.7%</td> </tr> <tr> <td>Gas (GNG)</td> <td style="text-align: center;">5.2% to 8.7%</td> <td style="text-align: center;">6.6% to 8.6%</td> </tr> <tr> <td>Gas (LPG)</td> <td style="text-align: center;">2.6% to 3.7%</td> <td style="text-align: center;">1.9% to 3.0%</td> </tr> <tr> <td>Biogenics</td> <td style="text-align: center;">0.2% to 0.3%</td> <td style="text-align: center;">0.1% to 0.2%</td> </tr> <tr> <td>Coatings (architectural)</td> <td style="text-align: center;">3.2% to 5%</td> <td style="text-align: center;">0.3% to 1.1%</td> </tr> <tr> <td>Coatings (industrial)</td> <td style="text-align: center;">1.7% to 9.3%</td> <td style="text-align: center;">4.1% to 6.9%</td> </tr> <tr> <td>Coatings (other)</td> <td style="text-align: center;">1.7% to 10%</td> <td style="text-align: center;">1.1% to 8.9%</td> </tr> <tr> <td>Unexplained</td> <td style="text-align: center;">-11% to -3.5%</td> <td style="text-align: center;">-0.9% to 7.8%</td> </tr> </tbody> </table> <p>Ratios of tailpipe to evaporative emissions are 2.4 in the morning and 1.7 in the afternoon. Morning samples attribute 48% to vehicle exhaust and 20% to evaporative emissions.</p> <p>Emission rates of heavy-duty diesel hydrocarbons are twice those of light-duty gasoline on a -per-mile basis. About 50% of diesel emissions are >C₁₀.</p> <p>Motor-vehicle-related emissions and sources of ethane and propane gas account for >90% of ambient NMHC. Evidence of emissions from solvent use were found, but not as significant as the 30% to 40% identified in the inventory.</p>		<u>3 ARB sites</u>	<u>8 CRC sites</u>	Vehicle exhaust	54% to 64% (including 11% to 15% diesel exhaust and 38% to 50% light-duty vehicle exhaust)	56% to 68% (including 10% to 15% diesel exhaust and 42% to 54% light-duty vehicle exhaust)	Liquid gasoline	0.6% to 11%	1% to 14%	Gasoline vapor	15% to 29%	10% to 20%	Gas (CNG)	3.1% to 3.7%	2.2% to 2.7%	Gas (GNG)	5.2% to 8.7%	6.6% to 8.6%	Gas (LPG)	2.6% to 3.7%	1.9% to 3.0%	Biogenics	0.2% to 0.3%	0.1% to 0.2%	Coatings (architectural)	3.2% to 5%	0.3% to 1.1%	Coatings (industrial)	1.7% to 9.3%	4.1% to 6.9%	Coatings (other)	1.7% to 10%	1.1% to 8.9%	Unexplained	-11% to -3.5%	-0.9% to 7.8%
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<p>Boulder, CO (2/91 to 1/91) (Goldan <i>et al.</i>, 1995).</p> <p>Hourly C₃ - C₁₀ NMHC with Auto-GC^m, NO, NO_x, NO_y, CO, and SO₂ at one traffic-dominated site between Boulder and Denver, CO.</p>	<p>Calculated correlations and ratios among measured components, especially with respect to NO_y. These were compared with speciated estimates from the 1985 National Acid Precipitation Assessment Program Emissions Inventory.</p>	<p>Did not explicitly calculate source contributions to NMHC.</p>																																				

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<p>1996 Phoenix Ozone Study, Phoenix, AZ (summer, 1996) (Fujita and Lu, 1997)</p> <p>Four-hour canister samples beginning at 0700 and 1130 at two sites and at 0700 at one site.</p>	<p>Effective variance weighted least squares CMB with composite motor vehicle exhaust (including tunnel, garage, roadside, and dynamometer for light-duty gasoline and diesel exhaust), gasoline evaporation, liquid gasoline, gasoline vapor, CNG, GNG, LPG, architectural coatings, industrial solvents and coatings, and biogenic profiles.</p> <p>27 stable species used in CMB calculation with 56 other species in profiles and ambient data for validation.</p>	<p>Average contributions to sum of NMHC at 3 sites are:</p> <table border="0" style="width: 100%;"> <tr> <td>Vehicle exhaust</td> <td>5.4% to 11.7%</td> <td>Gas (LPG)</td> <td>0.5% to 1.0%</td> </tr> <tr> <td>Gasoline exhaust</td> <td>51.5% to 59.0%</td> <td>Biogenics</td> <td>0.2% to 2.6%</td> </tr> <tr> <td>Liquid gasoline</td> <td>6.6% to 8.9%</td> <td>Coatings (architectural)</td> <td>0.4% to 2.2%</td> </tr> <tr> <td>Gasoline vapor</td> <td>2.8% to 7.3%</td> <td>Coatings (industrial)</td> <td>2.2% to 3.1%</td> </tr> <tr> <td>Gas (CNG)</td> <td>1.2% to 3.2%</td> <td>Unexplained</td> <td>7% to 8%</td> </tr> <tr> <td>Gas (GNG)</td> <td>5.6% to 8.0%</td> <td></td> <td></td> </tr> </table> <p>Because of the reactivity of isoprene, biogenic contributions are lower limits. Actual contributions may be 5 to 10 times higher than CMB estimates.</p>	Vehicle exhaust	5.4% to 11.7%	Gas (LPG)	0.5% to 1.0%	Gasoline exhaust	51.5% to 59.0%	Biogenics	0.2% to 2.6%	Liquid gasoline	6.6% to 8.9%	Coatings (architectural)	0.4% to 2.2%	Gasoline vapor	2.8% to 7.3%	Coatings (industrial)	2.2% to 3.1%	Gas (CNG)	1.2% to 3.2%	Unexplained	7% to 8%	Gas (GNG)	5.6% to 8.0%										
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<p>Coastal Oxidant Assessment for Southeast Texas (COAST) Study, Houston, TX (7/93 to 8/93) (Fujita <i>et al.</i>, 1995a; Lu, 1996).</p> <p>Hourly canister (C₂ - C₁₀ HC) and DNPH cartridge (C₁-C₇ carbonyl compounds) from 6 surface sites, 6 times per day, during summer 1993. Measurements aloft (aircraft) starting ~0600 and ~1200 CDT each day at 6 locations. Hourly auto-GC measurements at 2 sites.</p> <p>Total NMHC = sum of 25 abundant hydrocarbons.</p>	<p>Effective variance weighted least squares CMB with motor vehicle exhaust, gasoline evaporation, liquid gasoline, gasoline vapor, CNG, GNG, LPG, architectural coatings, industrial solvents and coatings, and biogenic profiles from CARB's modeling emissions data system and auto/oil program.</p> <p>27 stable species used in CMB calculation with 34 other species in profiles and ambient data for validation.</p>	<p>Average CMB-calculated source contribution to total NMHC in % NMHC for:</p> <table border="0" style="width: 100%;"> <thead> <tr> <th></th> <th style="text-align: center;">2 auto- GC sites</th> <th style="text-align: center;">6 surface sites</th> <th style="text-align: center;">6 aloft sites</th> </tr> </thead> <tbody> <tr> <td>Vehicle exhaust</td> <td>19% to 27%</td> <td>19% to 36%</td> <td>17% to 39%</td> </tr> <tr> <td>Liquid gasoline</td> <td>12% to 15%</td> <td>7% to 15%</td> <td>1% to 12%</td> </tr> <tr> <td>Gasoline vapor</td> <td>13% to 14%</td> <td>7% to 20%</td> <td>0% to 11%</td> </tr> <tr> <td>CNG</td> <td>11% to 12%</td> <td>3.5% to 6.4%</td> <td>8% to 16%</td> </tr> <tr> <td>Industrial</td> <td>9% to 18%</td> <td>22% to 50%</td> <td>19% to 52%</td> </tr> <tr> <td>Biogenic</td> <td>0.4% to 1.6%</td> <td>0.5% to 1.8%</td> <td>0.1% to 7%</td> </tr> <tr> <td>Unexplained</td> <td>22% to 27%</td> <td>-2% to 16%</td> <td>-1% to 39%</td> </tr> </tbody> </table> <p>Profiles need to be developed in Houston area to separate gasoline vs. diesel contribution. Vehicle exhaust and industrial sources (e.g., refinery) are the largest NMHC contributors. Source contributions aloft were 20% of those found at the surface. Emissions inventory overestimates biogenic emissions, but is comparable for the sum of liquid gasoline, gasoline vapor, industrial, and gas (CNG).</p>		2 auto- GC sites	6 surface sites	6 aloft sites	Vehicle exhaust	19% to 27%	19% to 36%	17% to 39%	Liquid gasoline	12% to 15%	7% to 15%	1% to 12%	Gasoline vapor	13% to 14%	7% to 20%	0% to 11%	CNG	11% to 12%	3.5% to 6.4%	8% to 16%	Industrial	9% to 18%	22% to 50%	19% to 52%	Biogenic	0.4% to 1.6%	0.5% to 1.8%	0.1% to 7%	Unexplained	22% to 27%	-2% to 16%	-1% to 39%
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<p>1996 Paso del Norte Ozone Study, El Paso, TX (8/96 to 9/96) (Fujita <i>et al.</i>, 1998)</p> <p>Hourly auto-GC measurements at one site and two-hour canister samples five times a day at four sites. Additional survey canister samples at five sites.</p>	<p>Effective variance weighted least squares CMB with diesel exhaust, gasoline vehicle exhaust, propane buses, gasoline evaporation, liquid gasoline, gasoline vapor, CNG, LPG, industrial, solvent-based primers and enamels and isoprene. 27 stable species used in CMB calculation with 34 other species in profiles and ambient data for validation.</p>	<p>Average CMB-calculated source contribution to total NMHC in % NMHC for:</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th></th> <th style="text-align: center;">El Paso GC sites</th> <th style="text-align: center;">El Paso sites</th> <th style="text-align: center;">Juarez sites</th> </tr> </thead> <tbody> <tr> <td>Diesel exhaust</td> <td style="text-align: center;">1% to 6%</td> <td style="text-align: center;">< 2%</td> <td style="text-align: center;">2% to 5%</td> </tr> <tr> <td>Gasoline exhaust</td> <td style="text-align: center;">26% to 44%</td> <td style="text-align: center;">50% to 65%</td> <td style="text-align: center;">50% to 65%</td> </tr> <tr> <td>Propane bus</td> <td style="text-align: center;">0.3% to 2.8%</td> <td style="text-align: center;">< 2%</td> <td style="text-align: center;">2% to 5%</td> </tr> <tr> <td>Liquid gasoline</td> <td style="text-align: center;">26% to 33%</td> <td style="text-align: center;">negligible</td> <td style="text-align: center;">2% to 8%</td> </tr> <tr> <td>Gasoline vapor</td> <td style="text-align: center;">0.3% to 3.7%</td> <td></td> <td style="text-align: center;">included with liquid</td> </tr> <tr> <td>LPG</td> <td style="text-align: center;">0.5% to 3.4%</td> <td style="text-align: center;">0 to 3%</td> <td style="text-align: center;">2% to 9%</td> </tr> <tr> <td>CNG</td> <td style="text-align: center;">1.7% to 5.8%</td> <td></td> <td></td> </tr> <tr> <td>Industrial</td> <td style="text-align: center;">7% to 21%</td> <td style="text-align: center;">10% to 20%</td> <td style="text-align: center;">10% to 30%</td> </tr> <tr> <td>Surface coating</td> <td style="text-align: center;">1.8% to 5.8%</td> <td style="text-align: center;">1% to 1.5%</td> <td style="text-align: center;">2% to 3%</td> </tr> <tr> <td>Biogenic</td> <td style="text-align: center;">0% to 0.1%</td> <td style="text-align: center;">negligible</td> <td style="text-align: center;">negligible</td> </tr> <tr> <td>Unexplained</td> <td style="text-align: center;">0% to 1.3%</td> <td></td> <td></td> </tr> </tbody> </table> <p>Source contribution estimates for auto-GC samples are averaged by day-of-the-week and by wind direction.</p>		El Paso GC sites	El Paso sites	Juarez sites	Diesel exhaust	1% to 6%	< 2%	2% to 5%	Gasoline exhaust	26% to 44%	50% to 65%	50% to 65%	Propane bus	0.3% to 2.8%	< 2%	2% to 5%	Liquid gasoline	26% to 33%	negligible	2% to 8%	Gasoline vapor	0.3% to 3.7%		included with liquid	LPG	0.5% to 3.4%	0 to 3%	2% to 9%	CNG	1.7% to 5.8%			Industrial	7% to 21%	10% to 20%	10% to 30%	Surface coating	1.8% to 5.8%	1% to 1.5%	2% to 3%	Biogenic	0% to 0.1%	negligible	negligible	Unexplained	0% to 1.3%		
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<p>Chicago, IL (9/85 to 10/85) (O'Shea and Scheff, 1988).</p> <p>45-minute Teflon bag samples at 1200 and 1300 LDT. NMHC = sum of <C4, isobutane, n-butane, isopentane, 2,3-dimethylbutane, 2-methylpentane, 3-methylpentane, hexane, and benzene analyzed by GC/FID.</p>	<p>Ordinary weighted least squares CMB with vehicle exhaust, petroleum refining, and gasoline vapor profiles.</p>	<p>Average contributions to NMHC:</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <tbody> <tr> <td>Vehicle exhaust</td> <td style="text-align: center;">47% to 62%</td> </tr> <tr> <td>Gasoline vapor</td> <td style="text-align: center;">7% to 13%</td> </tr> <tr> <td>Industry (refining)</td> <td style="text-align: center;">9% to 13%</td> </tr> <tr> <td>Others</td> <td style="text-align: center;">5% to 15%</td> </tr> </tbody> </table> <p>CMB calculations were compared with dispersion model results to verify emissions inventory and to develop pollution control strategies.</p>	Vehicle exhaust	47% to 62%	Gasoline vapor	7% to 13%	Industry (refining)	9% to 13%	Others	5% to 15%																																								
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Solvent (architectural coating)	3.1%	5.5%																											
Solvent (graphic arts)	1.0%	9.8%																											
Vapor degreasing	3.4%	3.1%																											
Dry cleaning	0.3%	0.1%																											
Industry (refining)	7.4%	1.3%																											

Appendix F. Summary of CMB VOC Source Apportionment Studies

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<p>Detroit, MI (7/88 to 8/88) (Chung <i>et al.</i>, 1996).</p> <p>1-hour canister samples at 0600, 0800, 1200, 1400, and 2200 LDT at 18 sites.</p> <p>NMHC = sum of 24 abundant hydrocarbons.</p>	<p>Ordinary weighted least squares CMB with vehicle exhaust, gasoline vapor, petrochemical, architectural coatings, graphic arts, polyethylene, refinery, and coke oven profiles from other studies.</p> <p>Sensitivity tests with 18 stable and 24 reactive species yielded similar source contribution estimates.</p>	<p>Average contributions to NMHC:</p> <table border="1" style="margin-left: 20px;"> <thead> <tr> <th></th> <th style="text-align: center;">CMB-calculated</th> <th style="text-align: center;">Emission Inventory</th> </tr> </thead> <tbody> <tr> <td>Vehicle exhaust</td> <td style="text-align: center;">28%</td> <td style="text-align: center;">33%</td> </tr> <tr> <td>Gasoline vapor</td> <td style="text-align: center;">9%</td> <td style="text-align: center;">7%</td> </tr> <tr> <td>Solvent (architectural coating)</td> <td style="text-align: center;">2.5%</td> <td style="text-align: center;">3.8%</td> </tr> <tr> <td>Solvent (graphic arts)</td> <td style="text-align: center;">4.7%</td> <td style="text-align: center;">0.7%</td> </tr> <tr> <td>Industry (refinery)</td> <td style="text-align: center;">17%</td> <td style="text-align: center;">0.7%</td> </tr> <tr> <td>Industry (coke oven)</td> <td style="text-align: center;">3.7%</td> <td style="text-align: center;">2.0%</td> </tr> <tr> <td>Other</td> <td style="text-align: center;">35%</td> <td style="text-align: center;">39%</td> </tr> </tbody> </table> <p>CMB model calculations can be used to verify the emissions inventory estimates prior to ozone modeling to derive more reliable source/receptor relationships.</p>		CMB-calculated	Emission Inventory	Vehicle exhaust	28%	33%	Gasoline vapor	9%	7%	Solvent (architectural coating)	2.5%	3.8%	Solvent (graphic arts)	4.7%	0.7%	Industry (refinery)	17%	0.7%	Industry (coke oven)	3.7%	2.0%	Other	35%	39%
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<p>Southeast Michigan Ozone Study (SEMOS), Detroit, MI (7/93 to 8/93) (Scheff <i>et al.</i>, 1996).</p> <p>2-hour canister data at 0600, 1000, and 1400 LDT at 4 sites for 8 days during summer 1993.</p> <p>NMOC = sum of chromatographic peaks.</p>	<p>Ordinary weighted least squares CMB with vehicle exhaust, gasoline vapor, petrochemical, architectural coatings, graphic arts, polyethylene, refinery, and coke oven profiles from other studies.</p> <p>Sensitivity tests with 18 stable and 24 reactive species yielded similar source contribution estimates.</p>	<p>Average CMB-calculated contributions to NMOC:</p> <table border="1" style="margin-left: 20px;"> <tbody> <tr> <td>Vehicle exhaust:</td> <td style="text-align: center;">37% to 40%</td> </tr> <tr> <td>Liquid gasoline</td> <td style="text-align: center;">2% to 9%</td> </tr> <tr> <td>Gasoline vapor</td> <td style="text-align: center;">1% to 3%</td> </tr> <tr> <td>Solvent (architectural coating)</td> <td style="text-align: center;">2% to 5%</td> </tr> <tr> <td>Solvent (graphic arts)</td> <td style="text-align: center;">1% to 4%</td> </tr> <tr> <td>Industry (refinery)</td> <td style="text-align: center;">3% to 10%</td> </tr> <tr> <td>Industry (coke ovens)</td> <td style="text-align: center;">1% to 4%</td> </tr> </tbody> </table> <p>Percent of total NMOC explained by CMB ranged from 54% during afternoon to 69% during early evening (i.e., 1800 LDT). Good agreement between CMB and emissions inventory for sum of vehicle and gasoline, architectural coatings, and coke ovens. CMB reports higher contributions from refinery and graphic arts industry than does inventory. Study demonstrated the effectiveness of CMB for development of emission control strategy.</p>	Vehicle exhaust:	37% to 40%	Liquid gasoline	2% to 9%	Gasoline vapor	1% to 3%	Solvent (architectural coating)	2% to 5%	Solvent (graphic arts)	1% to 4%	Industry (refinery)	3% to 10%	Industry (coke ovens)	1% to 4%										
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<p>Beaumont, TX, Detroit, MI, Chicago, IL, Washington, DC, and Atlanta, GA (summers of 1984 to 1988) (Kenski <i>et al.</i>, 1995).</p> <p>1-hour and 3-hour canister samples at 0600 and 0900 LDT, except at Detroit with 1-hour samples at 0600, 0900, 1200, 1400, and 2200 LDT. NMHC = sum of 24 abundant hydrocarbons.</p>	<p>Ordinary weighted least squares CMB with vehicle exhaust, gasoline vapor, petrochemical, architectural coatings, graphic arts, polyethylene, refinery, and coke oven profiles from other studies.</p> <p>Sensitivity tests with 18 stable and 24 reactive species yielded similar source contribution estimates.</p>	<p>Average CMB-calculated contributions to NMHC:</p> <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 60%;">Vehicle exhaust:</td> <td style="text-align: right;">28% to 55%</td> </tr> <tr> <td>Gasoline vapor</td> <td style="text-align: right;">9% to 20%</td> </tr> <tr> <td>Solvent (architectural coating)</td> <td style="text-align: right;">2% to 6%</td> </tr> <tr> <td>Solvent (graphic arts)</td> <td style="text-align: right;">5% to 12%</td> </tr> <tr> <td>Industry (refinery)</td> <td style="text-align: right;">9% to 17% (in cities with refineries)</td> </tr> <tr> <td>Industry (coke ovens)</td> <td style="text-align: right;">4% (in Detroit and Washington only)</td> </tr> <tr> <td>Polyethylene</td> <td style="text-align: right;">7% (in Beaumont only)</td> </tr> </table> <p>Motor vehicle fractions agreed with inventories, but refinery and graphic arts proportions were substantially different.</p>	Vehicle exhaust:	28% to 55%	Gasoline vapor	9% to 20%	Solvent (architectural coating)	2% to 6%	Solvent (graphic arts)	5% to 12%	Industry (refinery)	9% to 17% (in cities with refineries)	Industry (coke ovens)	4% (in Detroit and Washington only)	Polyethylene	7% (in Beaumont only)								
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<p>Boston, MA (8/95 to 9/95) (Fujita <i>et al.</i>, 1997b).</p> <p>Hourly C₂ - C₁₂ canister samples at 0700 and 1300 EST for 14 days at 3 main sites and 3 supplemental sites. Total NMHC = 25 most abundant NMHC species plus MTBE.</p>	<p>Effective variance weighted least squares CMB with composite motor vehicle exhaust (including tunnel, garage, roadside, and dynamometer for light-duty gasoline and diesel exhaust), gasoline evaporation, liquid gasoline, gasoline vapor, CNG, GNG, LPG, architectural coatings, industrial solvents and coatings, and biogenic profiles.</p> <p>27 stable species used in CMB calculation with 56 other species in profiles and ambient data for validation.</p>	<p>Average source contributions to sum of NMHC and MTBE:</p> <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 60%;">Vehicle exhaust:</td> <td style="text-align: right;">50% to 69% (including 17% to 26% diesel exhaust and 27% to 48% light-duty vehicle exhaust)</td> </tr> <tr> <td>Liquid gasoline</td> <td style="text-align: right;">2% to 19%</td> </tr> <tr> <td>Gasoline vapor</td> <td style="text-align: right;">3% to 10%</td> </tr> <tr> <td>Gas (CNG)</td> <td style="text-align: right;">3.1% to 3.5%</td> </tr> <tr> <td>Gas (GNG)</td> <td style="text-align: right;">2.0% to 4.4%</td> </tr> <tr> <td>Gas (LPG)</td> <td style="text-align: right;">0% to 0.3%</td> </tr> <tr> <td>Gas (biogenic)</td> <td style="text-align: right;">1.4% to 1.5%</td> </tr> <tr> <td>Solvent (architectural coating)</td> <td style="text-align: right;">0.4% to 0.6%</td> </tr> <tr> <td>Solvent (industrial coating)</td> <td style="text-align: right;">1.5% to 3.0%</td> </tr> <tr> <td>Unidentified</td> <td style="text-align: right;">6% to 11%</td> </tr> <tr> <td>Unexplained</td> <td style="text-align: right;">2% to 5%</td> </tr> </table> <p>Ratios of tailpipe to evaporative emissions with and without East Boston sites are 4.0 and 7.9 in the morning, and 3.9 and 7.4 in the afternoon, respectively. These ratios are 2 to 4 times those found in Southern California. Morning samples attribute 50.4% and 50.1% to vehicle exhaust and 12.5% and 7.9% to evaporative emissions with and without the East Boston sites, respectively.</p> <p>Motor-vehicle-related emissions and sources of ethane and propane gas account for >90% of ambient NMHC. Evidence of emissions from solvent use were found, but not as significant as the 30% to 40% identified in the inventory.</p>	Vehicle exhaust:	50% to 69% (including 17% to 26% diesel exhaust and 27% to 48% light-duty vehicle exhaust)	Liquid gasoline	2% to 19%	Gasoline vapor	3% to 10%	Gas (CNG)	3.1% to 3.5%	Gas (GNG)	2.0% to 4.4%	Gas (LPG)	0% to 0.3%	Gas (biogenic)	1.4% to 1.5%	Solvent (architectural coating)	0.4% to 0.6%	Solvent (industrial coating)	1.5% to 3.0%	Unidentified	6% to 11%	Unexplained	2% to 5%
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<p>1995 NARSTO-Northeast Ozone Study (6/95 to 8/95) (Fujita and Lu, 1998)</p> <p>Four, 3-hr canister samples at five sites and three, 3-hr samples at three sites. Also 13, hourly auto-GC and 7 canister-based PAMS sites operated by state and local air pollution agencies in the northeastern states.</p>	<p>Effective variance weighted least squares CMB with composite motor vehicle exhaust (including tunnel, garage, roadside, and dynamometer for light-duty gasoline and diesel exhaust), gasoline evaporation, liquid gasoline, gasoline vapor, CNG, LPG, and biogenic profiles.</p> <p>27 stable species used in CMB calculation with 56 other species in profiles and ambient data for validation.</p>	<p>Average CMB-calculated source contribution to total NMHC in % NMHC for:</p> <table style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th></th> <th style="text-align: center;">10 surface <u>PAMS sites</u></th> <th style="text-align: center;">6 surface <u>sites</u></th> <th style="text-align: center;">7 aloft <u>sites</u></th> </tr> </thead> <tbody> <tr> <td>Diesel exhaust</td> <td style="text-align: center;">3% to 44%</td> <td style="text-align: center;">6% to 8%</td> <td style="text-align: center;">6% to 9%</td> </tr> <tr> <td>Gasoline exhaust</td> <td style="text-align: center;">17% to 62%</td> <td style="text-align: center;">7% to 23%</td> <td style="text-align: center;">9% to 25%</td> </tr> <tr> <td>Liquid gasoline</td> <td style="text-align: center;">2% to 19%</td> <td style="text-align: center;">1% to 7%</td> <td style="text-align: center;">1.5% to 5.7%</td> </tr> <tr> <td>Gasoline vapor</td> <td style="text-align: center;">12% to 31%</td> <td style="text-align: center;">2% to 6%</td> <td style="text-align: center;">0.8% to 5.9%</td> </tr> <tr> <td>CNG</td> <td style="text-align: center;">7% to 12%</td> <td style="text-align: center;">3% to 34%</td> <td style="text-align: center;">7% to 11%</td> </tr> <tr> <td>LPG</td> <td style="text-align: center;">1% to 30%</td> <td style="text-align: center;">0.6% to 3.2%</td> <td style="text-align: center;">0.7% to 2.4%</td> </tr> <tr> <td>Biogenic</td> <td style="text-align: center;">1% to 12%</td> <td style="text-align: center;">2% to 10%</td> <td style="text-align: center;">0% to 5.8%</td> </tr> <tr> <td>Unidentified</td> <td></td> <td style="text-align: center;">46% to 72%</td> <td style="text-align: center;">59% to 75%</td> </tr> <tr> <td>Unexplained</td> <td style="text-align: center;">-8% to 17%</td> <td style="text-align: center;">-4% to -8%</td> <td style="text-align: center;">-6% to -11%</td> </tr> </tbody> </table> <p>Unidentified compounds are the largest fraction of total NMHC in NARSTO-Northeast supplemental hydrocarbon measurement. These samples were collected in area that reflect more regional air quality, rather than PAMS sites that reflect more urban/suburban area. Because of the reactivity of isoprene, biogenic contributions are lower limits. Actual contributions may be 5 to 10 times higher than CMB estimates (Fujita, 1997).</p>		10 surface <u>PAMS sites</u>	6 surface <u>sites</u>	7 aloft <u>sites</u>	Diesel exhaust	3% to 44%	6% to 8%	6% to 9%	Gasoline exhaust	17% to 62%	7% to 23%	9% to 25%	Liquid gasoline	2% to 19%	1% to 7%	1.5% to 5.7%	Gasoline vapor	12% to 31%	2% to 6%	0.8% to 5.9%	CNG	7% to 12%	3% to 34%	7% to 11%	LPG	1% to 30%	0.6% to 3.2%	0.7% to 2.4%	Biogenic	1% to 12%	2% to 10%	0% to 5.8%	Unidentified		46% to 72%	59% to 75%	Unexplained	-8% to 17%	-4% to -8%	-6% to -11%
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<p>Newark, NJ (7/80 to 8/90) (Scheff and Klevs, 1987).</p> <p>1-hour canister samples at 0600 and 0800 EDT at 2 sites: high traffic and industrial.</p> <p>NMHC = sum of 24 abundant hydrocarbons.</p>	<p>Ordinary weighted least squares CMB with vehicle exhaust, gasoline vapor, petrochemical, paint, and refinery profiles from other studies.</p> <p>Sensitivity tests with 18 stable and 24 stable and reactive species yielded similar source contribution estimates.</p>	<p>For average NMHC:</p> <table style="width: 100%; border-collapse: collapse;"> <tbody> <tr> <td>Vehicle Exhaust</td> <td style="text-align: center;">15% to 21%</td> </tr> <tr> <td>Gasoline vapor</td> <td style="text-align: center;">18% to 33%</td> </tr> <tr> <td>Petrochemical</td> <td style="text-align: center;">3% to 6%</td> </tr> <tr> <td>Paint</td> <td style="text-align: center;">1% to 7%</td> </tr> <tr> <td>Refinery</td> <td style="text-align: center;">24% to 27%</td> </tr> <tr> <td>Unexplained</td> <td style="text-align: center;">15% to 28%</td> </tr> </tbody> </table> <p>Industrial site showed three times the petrochemical and refinery contributions than the nearby urban site.</p>	Vehicle Exhaust	15% to 21%	Gasoline vapor	18% to 33%	Petrochemical	3% to 6%	Paint	1% to 7%	Refinery	24% to 27%	Unexplained	15% to 28%																												
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<p>Kanawha Valley, WV (Charleston, WV) (4/87 to 3/88) (Cohen <i>et al.</i>, 1991a, 1991b).</p> <p>12-hour VOC (Tenax-GC downstream of glass-fiber filter) and particles.</p> <p>Samples starting 0600 and 1800 EST for 15 days per month for 4 months at 3 sites. 19 VOCs were measured.</p> <p>A mobile van also collected NO₂, NO₃, O₃, light scattering, and meteorological measurements alone with VOC and particles at one in-valley site.</p>	<p>Univariate and multivariate correlation, analysis of variance (ANOVA), and factor analysis methods were used to resolve source contributions.</p>	<p>Factor analysis with % variance explained:</p> <table border="0"> <tr> <td style="padding-right: 20px;">Vehicle-related exhaust (including tailpipe emissions, fuel evaporation, and road dust)</td> <td>12% to 48% (e.g., high correlations for decane, <i>m</i>-xylene, and benzene)</td> </tr> <tr> <td>General VOCs</td> <td>15% to 17% (e.g., high correlations for styrene, methylchloroform, toluene)</td> </tr> <tr> <td>Chlorinated VOCs</td> <td>5% to 6% (e.g., high correlations for chloroform, carbon tetrachloride, methyl chloroform)</td> </tr> <tr> <td>Forest fire and combustion related emissions</td> <td>11% to 38% (e.g., high correlations for benzene, decane, particle organic and elemental carbon)</td> </tr> <tr> <td>Acid particles</td> <td>5% to 13% (e.g., high correlations for H₂SO₄, S)</td> </tr> </table> <p>VOC is a good indicator for motor vehicle exhaust if the atmosphere is enriched with alkylated-aromated compounds.</p> <p>Local and regional sources contributed to pollution levels at Kanawha Valley, WV, using a combination of gas and particle data.</p>	Vehicle-related exhaust (including tailpipe emissions, fuel evaporation, and road dust)	12% to 48% (e.g., high correlations for decane, <i>m</i> -xylene, and benzene)	General VOCs	15% to 17% (e.g., high correlations for styrene, methylchloroform, toluene)	Chlorinated VOCs	5% to 6% (e.g., high correlations for chloroform, carbon tetrachloride, methyl chloroform)	Forest fire and combustion related emissions	11% to 38% (e.g., high correlations for benzene, decane, particle organic and elemental carbon)	Acid particles	5% to 13% (e.g., high correlations for H ₂ SO ₄ , S)
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<p>1990 Atlanta Ozone Precursor Study, Atlanta, GA (7/90 to 8/90) (Henry <i>et al.</i>, 1994).</p> <p>Hourly C₂ - C₁₀ canister samples with auto-GC at 6 sites.</p> <p>Total NMOC = 54 hydrocarbon species with ethane excluded.</p>	<p>GRACEⁿ and SAFER^o statistical methods used to derive vehicle-related source compositions for vehicles in motion (tailpipe plus running losses), evaporative gasoline, and headspace gasoline vapor. Statistically derived compositions were compared with measured source compositions. 37 species were used to derive source profiles.</p>	<p>Unburned gasoline comprised ~50% of tailpipe emissions. There are other unaccounted sources for whole gasoline.</p> <p>Most studies include the whole gasoline contribution with the headspace gasoline vapor component.</p> <p>1990 Atlanta data shows that the whole gasoline component is considerably larger than the headspace gasoline vapor component. Relative source contributions were 62% roadway vehicle emissions, 15% whole gasoline, and 4% headspace vapor.</p> <p>GRACE/SAFER provide cost-effective alternatives to estimate source profiles, but require several hundred observations.</p>										

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<p>1990 Atlanta Ozone Precursor Study, Atlanta, GA (7/90 to 8/90) (Lin and Milford, 1994).</p> <p>Hourly C₂ - C₁₀ canister samples with auto-GC at 2 sites.</p> <p>Total NMOC = 54 hydrocarbon species with ethane excluded.</p>	<p>Source profiles were decay-adjusted to account for different reaction rates of VOCs for roadway vehicle and gasoline vapor emissions. PCA^P, CMB, and decay-adjusted CMB were applied to test synthetic and ambient data. 13 stable species used in CMB calculation with 36 other species in profiles and ambient data for validation.</p>	<p>Decay factors assumed for propylene were 0.78 to 0.92 (morning samples), 0.41 to 0.60 (afternoon samples), and 0.59 to 0.76 (average).</p> <p>Adjusted CMB source contributions to NMHC in % NMHC were:</p> <table style="margin-left: auto; margin-right: auto;"> <tr> <td></td> <td style="text-align: center;">CMB- <u>calculated</u></td> <td style="text-align: center;">Lewis et <u>al. (1993)</u></td> </tr> <tr> <td>Roadway vehicle emissions</td> <td style="text-align: center;">61% to 65%</td> <td style="text-align: center;">44%</td> </tr> <tr> <td>Whole gasoline</td> <td style="text-align: center;">not calculated</td> <td style="text-align: center;">15%</td> </tr> <tr> <td>Headspace gasoline vapor</td> <td style="text-align: center;">4% to 8.2%</td> <td style="text-align: center;">4%</td> </tr> <tr> <td>Total vehicle-related sources in summer 1990</td> <td style="text-align: center;">66% to 73%</td> <td style="text-align: center;">62%</td> </tr> </table> <p>CMB adjusted for decay factor gives small improvements to source contribution estimates.</p>		CMB- <u>calculated</u>	Lewis et <u>al. (1993)</u>	Roadway vehicle emissions	61% to 65%	44%	Whole gasoline	not calculated	15%	Headspace gasoline vapor	4% to 8.2%	4%	Total vehicle-related sources in summer 1990	66% to 73%	62%
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Headspace gasoline vapor	4% to 8.2%	4%															
Total vehicle-related sources in summer 1990	66% to 73%	62%															
<p>1990 Atlanta Ozone Precursor Study, Atlanta, GA (7/90 to 8/90) (Conner <i>et al.</i>, 1994).</p> <p>Hourly C₂ - C₁₀ canister samples with auto-GC at 6 sites.</p> <p>Total NMOC = 54 hydrocarbon species with ethane excluded.</p>	<p>Source profiles for roadway vehicle emissions, whole gasoline, and headspace gasoline vapor were developed. Profiles for pure propane, natural gas, and industrial coatings (auto painting) were used. 18 stable species used in CMB calculation with 35 other species in profiles and ambient data for validation.</p>	<p>Average contribution to total NMOC in % of total NMOC are:</p> <table style="margin-left: auto; margin-right: auto;"> <tr> <td>Roadway vehicle emissions</td> <td style="text-align: center;">69% to 79%</td> </tr> <tr> <td>Whole gasoline</td> <td style="text-align: center;">6% to 16%</td> </tr> <tr> <td>Headspace gasoline vapor</td> <td style="text-align: center;">4% to 15%</td> </tr> <tr> <td>Propane and natural gas</td> <td style="text-align: center;">2% to 5%</td> </tr> <tr> <td>Industrial coatings (auto painting)</td> <td style="text-align: center;">0% to 5%</td> </tr> </table> <p>Emissions inventory (based on MOBILE model for mobile sources) generally underestimate actual motor vehicle source contributions based on CMB results by 10% to 30%, assuming 2% to 47% biogenic emissions.</p> <p>Emissions inventory generally overestimate point and area sources by 10% to 20%.</p>	Roadway vehicle emissions	69% to 79%	Whole gasoline	6% to 16%	Headspace gasoline vapor	4% to 15%	Propane and natural gas	2% to 5%	Industrial coatings (auto painting)	0% to 5%					
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Industrial coatings (auto painting)	0% to 5%																

Appendix F. Summary of CMB VOC Source Apportionment Studies

Study, Location, and Period Measurements	Source Apportionment Method	Findings																
<p>1990 Atlanta Ozone Precursor Study, Atlanta, GA (7/90 to 8/90) (Lewis <i>et al.</i>, 1996).</p> <p>Hourly C₂ - C₁₀ canister samples with auto-GC at 1 site. Total NMOC = 54 hydrocarbon species with ethane excluded, using 5 weekday samples.</p>	<p>Source profiles for roadway vehicle emissions, whole gasoline, and headspace gasoline vapor were developed. Profiles for pure propane, natural gas, and industrial coatings (auto painting) were used. 16 fitting species used in CMB calculation with 31 remaining species in profiles and ambient data for validation.</p>	<p>Average contribution to total NMOC in % of total NMOC are:</p> <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 80%;">Roadway vehicle emissions</td> <td style="text-align: right;">49%</td> </tr> <tr> <td>Whole gasoline</td> <td style="text-align: right;">10%</td> </tr> <tr> <td>Headspace gasoline vapor</td> <td style="text-align: right;">3.7%</td> </tr> <tr> <td>Propane</td> <td style="text-align: right;">4.9%</td> </tr> <tr> <td>Natural gas</td> <td style="text-align: right;">2.9%</td> </tr> <tr> <td>Isoprene</td> <td style="text-align: right;">2.2%</td> </tr> <tr> <td>Industrial solvent</td> <td style="text-align: right;">2.6%</td> </tr> <tr> <td>Unexplained</td> <td style="text-align: right;">24.4%</td> </tr> </table> <p>Uncertainties in source contribution estimates are 9% to 14% for roadway vehicle, natural gas, propane-rich, and isoprene-rich emissions; 30% to 40% for evaporative gasoline emissions; and 50% for industrial solvent emissions. Using the VOC ¹⁴C abundance⁹ attributed 9% to 17% VOC as biogenic emissions for the mid-morning and late evening samples, respectively. Additional research is in progress using linear programming-factor analysis (e.g., GRACE/SAFER) to refine source profiles.</p>	Roadway vehicle emissions	49%	Whole gasoline	10%	Headspace gasoline vapor	3.7%	Propane	4.9%	Natural gas	2.9%	Isoprene	2.2%	Industrial solvent	2.6%	Unexplained	24.4%
Roadway vehicle emissions	49%																	
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Isoprene	2.2%																	
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Unexplained	24.4%																	
<p>Tokyo, Japan (7/81) (Wadden <i>et al.</i>, 1986).</p> <p>1- to 1.5-hour aloft Pyrex glass vessel (aircraft, 300 to 1,500m) samples from 2 days (7/16/81 and 7/18/81). NMHC = 18 compounds from C₂ to C₆.</p>	<p>Ordinary least squares CMB with 8 profiles (vehicle exhaust, gasoline vapor, petrochemical plants, paint solvents, degreasing, dry cleaning, petroleum refinery, and rubber production).</p>	<p>Average contributions to NMHC:</p> <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 80%;">Vehicle exhaust</td> <td style="text-align: right;">7%</td> </tr> <tr> <td>Gasoline vapor</td> <td style="text-align: right;">11%</td> </tr> <tr> <td>Paint solvents</td> <td style="text-align: right;">27%</td> </tr> <tr> <td>Petroleum refinery</td> <td style="text-align: right;">27%</td> </tr> <tr> <td>Unexplained</td> <td style="text-align: right;">29%</td> </tr> </table> <p>Short-term (~1 hour) samples are useful in providing diurnal and directional information to delineate source/receptor relationships.</p>	Vehicle exhaust	7%	Gasoline vapor	11%	Paint solvents	27%	Petroleum refinery	27%	Unexplained	29%						
Vehicle exhaust	7%																	
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Appendix F. Summary of CMB VOC Source Apportionment Studies

Study, Location, and Period Measurements	Source Apportionment Method	Findings										
<p>Sydney, Australia (9/79 to 6/80) Nelson and Quigley, 1982, Nelson <i>et al.</i>, 1983)</p> <p>Hourly C₂ - C₁₀ samples acquired on 400 ml glass gas pipettes between 0600 and 1200 on non-windy days at 3 sites.</p> <p>NMHC = sum of 69 compounds from C₂ to C₁₀.</p>	<p>Comparison between ambient measurements, source measurements (i.e. vehicle exhaust, evaporative gasoline, industrial solvents), and emissions inventory were made.</p>	<p>Average contributions to NMHC:</p> <table style="margin-left: 20px;"> <tr> <td>Vehicle exhaust</td> <td style="text-align: right;">36 ± 4%</td> </tr> <tr> <td>Evaporative gasoline</td> <td style="text-align: right;">32 ± 4%</td> </tr> <tr> <td>Evaporative solvents</td> <td style="text-align: right;">23 ± 4%</td> </tr> <tr> <td>Gas leakage</td> <td style="text-align: right;">3.5 ± 5%</td> </tr> <tr> <td>Industrial Processes</td> <td style="text-align: right;">5 ± 1%</td> </tr> </table> <p>Source contribution estimates vary significantly from the central business district (high concentration of vehicle exhaust) to the sites near the industrial area (high concentrations of evaporative and industrial process emissions). Sensitivity of source contribution estimates in source compositions is ~0.5 to 4.0%. Study results are in reasonable agreement with hydrocarbon emissions inventory. The study results indicate a somewhat greater contribution from evaporative gasoline relative to vehicle exhaust and solvent evaporation in the inventory.</p>	Vehicle exhaust	36 ± 4%	Evaporative gasoline	32 ± 4%	Evaporative solvents	23 ± 4%	Gas leakage	3.5 ± 5%	Industrial Processes	5 ± 1%
Vehicle exhaust	36 ± 4%											
Evaporative gasoline	32 ± 4%											
Evaporative solvents	23 ± 4%											
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Industrial Processes	5 ± 1%											
<p>The Netherlands (1974 to 1994) (cities of Delft, 1974 and 1977; Hague, 1974 and 1977; Kollumerwaard, winter and summer 1994; and Brabant, summer 1994) (Guicherit, 1997).</p> <p>Hourly C₂ - C₅ samples acquired with cold trap (stainless steel loop packed with glass beads) submerged into liquid nitrogen. Hourly C₃ - C₉ and preconcentrated C₆ - C₁₆ samples acquired with carbon trap (carbosieve, carbotrap, carbotrap C) at 3 sites.</p>	<p>Comparisons between ambient measurements, source measurements (tunnel and dynamometer), and emissions inventory were made for data collected over the last 20 years.</p>	<p>No quantitative calculations were provided. Using ambient measurements to validate emissions estimates, the study concluded that major hydrocarbon emissions are parafins (46%), aromatics (30%), and olefins (15%), with the remainder consisting of acetylene and aldehydes. Toluene concentrations were consistently >20%, which closely resembled vehicle emissions derived from tunnel and dynamometer measurements. Diesel exhaust accounted for 14% to 21% of NMHC with high alkanes. Elevated ambient temperature during summer resulted in higher evaporative emissions and increased photochemical degradation.</p>										

Appendix F. Summary of CMB VOC Source Apportionment Studies

- ^a NMOC = non-methane organic compounds.
- ^b SAROAD = U.S. EPA's Storage and Retrieval of Aerometric Data system.
- ^c AIRS = U.S. EPA's Aerometric Information Retrieval System.
- ^d DNPB = C₁₈ cartridge impregnated with 2,4-dinitrophenylhydrazine.
- ^e CMB = Chemical Mass Balance
- ^f CNG = compressed natural gas.
- ^g GNG = geogenic natural gas.
- ^h LPG = liquefied petroleum gas.
- ⁱ California Air Resources Board, Sacramento, CA.
- ^j NMHC = non-methane hydrocarbon.
- ^k CRC = Coordinating Research Council, Atlanta, GA.
- ^l MTBE = methyl-t-butyl ether, a major component in reformulated gasoline.
- ^m Auto-GC = automated gas chromatography with flame ionization detector (FID).
- ⁿ GRACE = Graphical Ratio Analysis for Composition Estimates, used to generate constraints (e.g., ratios) for SAFER model input.
- ^o SAFER = Source Apportionment by Factors with Explicit Restriction.
- ^p PCA = Principle Component Analysis.
- ^q Klouda *et al.* (1996)

APPENDIX G. PROCEDURES FOR TREATING SECONDARY PARTICLES

One of the key assumptions made by EPA-CMB8.2 is that chemical species do not react with each other; Section 1.2 of the EPA-CMB8.2 Users Manual (EPA, 2004) and Section 4.1 of this Protocol. This means that compositions for the source categories are obtainable which represent the source profile as it is perceived at the receptor for the chemical species of interest (Section 4.3.1 of this Protocol). Thus, EPA-CMB8.2 assumes no changes to the aerosol during transport and ideally apportions the primary material that has not changed between source and receptor. However, certain species, e.g., sulfur (S), that dominate polluted airsheds have both primary and secondary sources.

In such airsheds, secondary aerosols may contribute significantly to the ambient loading seen at receptors. These secondary materials are often in the form of reactive species such as NH_4^+ , SO_4^- , NO_3^- , and organic carbon. If sources of such materials are not explicitly treated, EPA-CMB8.2 will tend to underaccount for total particle mass (% MASS value in the Main Report (Table 4.2-1 of this Protocol). If a compound which is secondarily formed or is normally associated with regional scale pollution (such as sulfate) is included as a fitting species, a *single constituent source type* must also be included in the fit. Use of the *single constituent source profile* for secondary particles was initially suggested by Watson (1979) and is described briefly in the Section 4.3.2 of this Protocol. With this technique, the secondary species are apportioned to chemical compounds rather than directly to sources (Section 4.1 of this Protocol).

Table G-1 illustrates an example of the way the technique was used in an actual application for California's South Coast Air Basin (Watson *et al.*, 1994). Secondary source profiles consisting of "pure" ammonium sulfate (AMSUL), ammonium bisulfate (AMBSUL), ammonium nitrate (AMNIT), and organic carbon (OC) were used to apportion the remaining NH_4^+ , SO_4^- , NO_3^- , and OC that would not be apportioned to the primary particle profiles. For some secondary species thought to be significant (e.g., note the OC column), a source profile was created which includes only that component, in which the percentage composition in the profile is set to 100%. For other secondary species, only some chemical components may have been measured. For instance, elemental S and/or sulfate ion (SO_4^-) may be measured rather than ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$. In such a case, the respective species abundances in the $(\text{NH}_4)_2\text{SO}_4$ would equal the mass % of each species in $(\text{NH}_4)_2\text{SO}_4$. Thus, in the AMSUL profile the abundance of S in pure $(\text{NH}_4)_2\text{SO}_4$ is listed as 24.3% and the abundance of SO_4^- is listed as 72.7%. Examples are also given for other secondary species and their chemical components. In all cases, the uncertainty was arbitrarily set to 10%. In the EPA-CMB8.2 calculations, the portion of a measured secondary species not accounted for by other source types becomes assigned to its corresponding single constituent source type, as represented by profiles such as those described here.

The examples given above are described as profiles for secondary species. However, the secondary profile may not represent secondary aerosol exclusively. For example, Watson *et al.* (1994) indicated that the OC profile in Table G-1 may account for contributions from fugitive sources not included in the EPA-CMB8.2 calculation (e.g., cooking, plant parts, or tire wear) in addition to secondary sources. In such a case, the technique may be considered as a means to get an upper estimate of the amount of aerosol attributable to secondary formation.

One of the advantages of using the single constituent source profile technique is that it can account for that part of the ambient mass that is not accounted for by the primary sources included in the EPA-CMB8.2 calculations. However, this technique **cannot** yield any information on the specific source types contributing to the species in the single constituent profiles. Furthermore, the ambient mass may still be underestimated in some cases. For example, Conner *et al.* (1993) reported that fine particle mass may have been underaccounted for in their CMB calculations because of the likelihood for some amount of water associated with hygroscopic (or deliquescent) sulfates. The amount of mass due to this water depends of the form of the sulfate and relative humidity factors.

Table G-1. Secondary Aerosol Source Profiles (abundances are % of total mass)¹

Species ²	AMSUL			AMBSUL			AMNIT			OC		
	PM _{2.5} & Coarse ³			PM _{2.5} & Coarse ³			PM _{2.5} & Coarse ³			PM _{2.5} & Coarse ³		
	Conc. ± Unc. ⁴			Conc. ± Unc. ⁴			Conc. ± Unc. ⁴			Conc. ± Unc. ⁴		
Cl ⁻	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0
NO ₃ ⁻	0.0	±	0.0	0.0	±	0.0	77.5	±	7.8	0.0	±	0.0
SO ₄ ⁼	72.7	±	7.3	83.5	±	8.3	0.0	±	0.0	0.0	±	0.0
NH ₄ ⁺	27.3	±	2.7	15.7	±	1.6	22.6	±	2.3	0.0	±	0.0
Na ⁺	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0
TC	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0	100	±	10
OC	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0	100	±	10
EC	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0
Na	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0
Al	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0
Si	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0
P	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0
S	24.3	±	2.4	27.9	±	2.8	0.0	±	0.0	0.0	±	0.0
Cl	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0
K	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0
Ca	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0
Ti	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0
V	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0
Cr	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0
Mn	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0
Fe	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0
Ni	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0
Cu	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0
Zn	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0
As	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0
Se	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0
Br	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0
Sr	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0

¹Reproduced with permission from Watson *et al.* (1994)

²TC (Total Carbon) = OC + EC; sum does not include Na⁺, Cl⁻, S, or TC.

³PM₁₀ - PM_{2.5}

⁴Conc. is the average abundance (% of total mass) for several samples of emissions from the same source type. Unc. is the standard deviation of the abundances for these samples.

Mo	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0
Cd	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0
Sn	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0
Sb	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0
Ba	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0
Hg	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0
Pb	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0	0.0	±	0.0
Sum	100	±	8	99.1	±	8.5	100	±	8	100	±	10

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