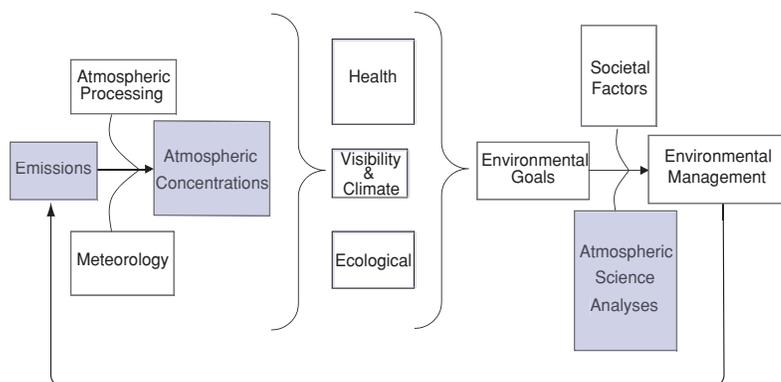


CHAPTER 7

Receptor Methods

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7.1 INTRODUCTION AND OVERVIEW

Receptor methods for source attribution or apportionment include the interpretation of physical and chemical measurements of ambient particles and their precursors to infer possible or probable sources and to quantify contributions from these sources. Source attribution implies that individual PM emitters are identified (e.g., a specific power plant), while apportionment identifies general source types or categories (e.g., vehicle exhaust, fugitive dust) responsible for the observed PM.

Receptor methods play a role at several points within the overall PM-management framework used in this Assessment (Figure 1.1). Application of the receptor methods described in this chapter helps to develop and refine conceptual models for explaining ambient PM concentrations and their precursors. When combined with information on emissions, receptor methods can provide insight on aspects of the inventory that may need improvement or on key atmospheric processes governing the observed PM. Receptor methods lead to a better understanding of the atmospheric environment. In areas with excessive $PM_{2.5}$ or PM_{10} concentrations, receptor methods can identify possible solutions, especially when applied systematically in combination with examination of the local emission inventory. Receptor methods also are useful for analysis and development of policy and/or specific PM management strategies.

Receptor methods encompass a variety of observationally based techniques that use differences in chemical composition, particle size, and concentration patterns in space and time, as well as

ratios among specific compounds (particles and/or gases), to identify source types and limiting precursors, and to quantify source contributions affecting particle mass concentrations, light extinction, or deposition. “Receptor models” are receptor methods that provide the theoretical and mathematical framework for quantifying source contributions.

Receptor models contrast with “source-oriented” CTMs, discussed in Chapter 8. Receptor models start with observations at given locations (receptors) and work backward, using as much information as is practical and available to determine the sources contributing to the observations and to quantify their contributions. CTMs combine estimated emission rates with meteorological transport, chemical changes and deposition rates to estimate concentrations and their temporal variations at different receptors, often an array of geographically-distributed grid points. CTMs can be used to predict how atmospheric concentrations or deposition fluxes could change if emission rates are changed. Receptor models explain events that have already occurred and are not used for predictive purposes, except for establishing current conditions for a source-category specific linear rollback (deNevers and Morris, 1975).

Complete understanding of the atmospheric environment and a thorough assessment of possible PM-management strategies are possible only when information from receptor methods, emission inventories, and CTMs is combined. This corroborative, or “weight-of-evidence,” approach (U.S. EPA, 2001) provides the strongest scientific basis for specific emission controls. Through this approach decisions can be made with greater

confidence when considering air-quality management options and costs in relation to other societal needs.

Several reviews and evaluations of receptor models have been published (Chow and Watson, 2002; Cooper and Watson, 1980; Gordon, 1980, 1988; Gordon et al., 1984; Henry et al., 1984; Henry, 1997a, 2002; Hopke, 1985, 1991, 1999, 2001; Javitz et al., 1988; Watson, 1984; Watson et al., 1981, 1989, 2001, 2002a; Watson and Chow, 2002). This chapter summarizes and complements these efforts, expanding them to a broader concept of receptor methods.

Receptor methods are most useful for: 1) identifying potential sources, especially those that are not included in emission inventories; 2) quantifying contributions from source types to ambient concentrations, initially to target emission reductions, and over the long-term to evaluate control-strategy effectiveness; 3) developing and refining conceptual models for source-receptor relationships; 4) evaluating and improving emission inventories; 5) guiding the application of CTMs; and 6) evaluating and improving CTM results. At present, receptor models have limited capability to distinguish sources of secondary PM compounds except when combined with elements of CTMs. CTMs play an important role in linking secondary PM to its sources while receptor methods can be used to refine the questions asked of the CTM. Successful application of all receptor methods depends on the quality and relevance of the measurements, the availability and specificity of source markers, and the interpretations made by the scientist and air-quality manager.

This chapter describes several receptor methods that have been applied to better explain $PM_{2.5}$ and PM_{10} source contributions and to reconcile emission inventories and source-model estimates. It provides examples of how PM, gas, and meteorological measurements are analyzed to identify and quantify contributions from PM and precursor gas emitters to $PM_{2.5}$ and PM_{10} concentrations measured at receptors.

Source apportionment by receptor methods begins with plausible hypotheses about the causes of high concentrations or effects. These initial hypotheses, which generally focus on various components of the overall conceptual model (Figure 1.1), are essential.

They should provide reasonable, although not necessarily accurate, explanations of: 1) potential sources; 2) size, chemical, and temporal characteristics of particle and precursor-gas emissions from these sources; 3) particle and precursor-gas emission rates; 4) meteorological conditions that affect emissions, transport, and transformation; and 5) frequency and intensity of the effect.

The initial hypotheses, as well as the conceptual model, are derived from previous experience (e.g., tests on similar sources, particle movement under similar meteorological conditions), the nature of the problem (neighborhood complaints, consistently poor visibility over a local area or large region, exceedance of air-quality standards), and available measurements (from existing air-quality and meteorological sensors). Sometimes evaluation of the hypotheses immediately quantifies contributions and implies appropriate remedial actions. More often the evaluation directs the application of appropriate receptor methods. The conceptual model, regardless of its level of sophistication, guides the location of monitoring sites, sampling periods, sampling frequencies, sample durations, selection of samples for laboratory analysis, and the particle properties that are quantified in those samples to test and discard hypotheses until, ideally, only one remains.

Several semi-quantitative, observationally based (receptor-oriented) data analyses should be performed prior to quantitative receptor modeling. These simple observational techniques, which are also a type of receptor method, can provide information about sources or source regions influencing the PM concentrations in an area. This helps to develop or refine the conceptual model. These methods often can be completed with data that are already available from existing networks. An overview of these methods and examples of the information they provide are listed below.

Time series plots of single-day, average, or median hourly $PM_{2.5}$ or PM_{10} concentrations. Continuous monitors, described in Chapter 5, acquire hourly (or shorter duration) PM measurements. Diurnal averages of weekend and weekday measurements may demonstrate morning traffic peaks that are accentuated during weekday rush hours. Summertime averages may show only a weekday

morning peak, and the evening rush-hour peak may not occur due to deeper atmospheric mixing layers. An evening peak is more likely in the wintertime because an earlier sunset results in a pollutant-trapping surface inversion before rush-hour traffic diminishes. Systematic evening peaks may also reveal other behavior, such as an increase in combustion (wood or fossil fuels) for home heating, which may occur with cooling after sunset and/or when people return to their homes at the end of the day. Hourly measurements from a single day may reveal that a relatively brief event dominates the 24-hr average concentration (e.g., windblown dust, nearby fire, truck idling near sampling inlet). Using short-duration measurements (e.g., 5 to 30 minutes, possible with TEOMs, nephelometers and aethelometers), concentration spikes caused by nearby emitters can be integrated and subtracted from hourly or 24-hr averages to estimate the effects of intermittent local sources (see Figure 7.1). High temporal-resolution measurements may help test the hypothesis that very high concentrations are caused by local sources and that these values do not represent human exposure over larger areas such as a neighborhood or a city.

Averaging by wind speed. When hourly or more frequent measurements of PM_{10} or coarse particles and wind speed are available, concentration averages can be calculated for different wind-speed categories to determine the extent to which wind speed affects dust suspension and the threshold for suspension. The hypothesis that “windblown dust” is a natural and uncontrollable PM_{10} contributor can be tested with measurements near natural surfaces, such as a crusted desert, and near surfaces with manmade disturbances, such as traffic or construction (see Figure 7.2).

Comparisons among source-oriented, neighborhood-scale and urban-scale PM mass and chemical concentrations. Spatial differences in chemical composition and/or mass concentration can indicate influence zones of different sources, which might arise from widespread emitters that affect an entire area, or from middle-scale emitters that affect a smaller population (see Figure 7.3). Large-scale urban/rural differences illustrated in Figure 6.21 can provide an estimate of the importance of upwind sources relative to the emissions within urban areas. PM_{10} and $PM_{2.5}$ mass, ion, element, and carbon

measurements are becoming more commonly available in long-term networks and from special studies. These provide a first estimate of the potential for different source types to affect ambient concentrations. High $SO_4^{=}$ levels imply that precursor SO_2 emissions must be reduced. Large geological contributions determined from Al, Si, Ca, and Fe concentrations imply that fugitive-dust sources require control. High proportions of BC imply primary emissions from incomplete combustion sources such as diesel and gasoline engine exhaust and vegetative burning (e.g., wood fireplaces). High OC levels can result from cooking, small vegetation fragments, and SOA formation (some of which is from biogenic hydrocarbon emissions), as well as vegetative burning and vehicle exhaust. Many trace metals (Fe, As, Se, Cr, Pb, Cu, Zn, Ni, V, Mn) result from industrial emissions. PM enriched in these elements identifies the presence of industrial contributions and the potential for secondary $SO_4^{=}$ and NO_3^- from SO_2 and NO_x gases that are co-emitted with the primary particles.

Concentration directionality. Particles move with wind-flow patterns. Averaging concentrations associated with wind-direction sectors or multi-day transport pathways narrows down the locations of influential sources. For nearby sources, a simple pollution rose that averages hourly concentrations by wind-direction sector may reveal higher concentrations from sectors that contain point sources or major roadways. This receptor method requires hourly resolution (or better) for PM and wind-direction measurements. For regional contributions, concentration averages may be classified by trajectories that pass over areas with high or low emissions to test the hypothesis that higher concentrations correspond with longer and more frequent transport over these source areas (see Figure 7.4). Transport or wind-direction sectors can be defined according to points on the compass, locations of suspected sources, or applications of cluster analysis or principal-component analysis to identify multivariate meteorological associations (e.g., Green et al., 1992). *There is a need for more observation-based analyses including the use of multiple data sources (e.g., meteorological, emissions, gaseous pollutant measurements). These analyses can provide valuable insight and will*

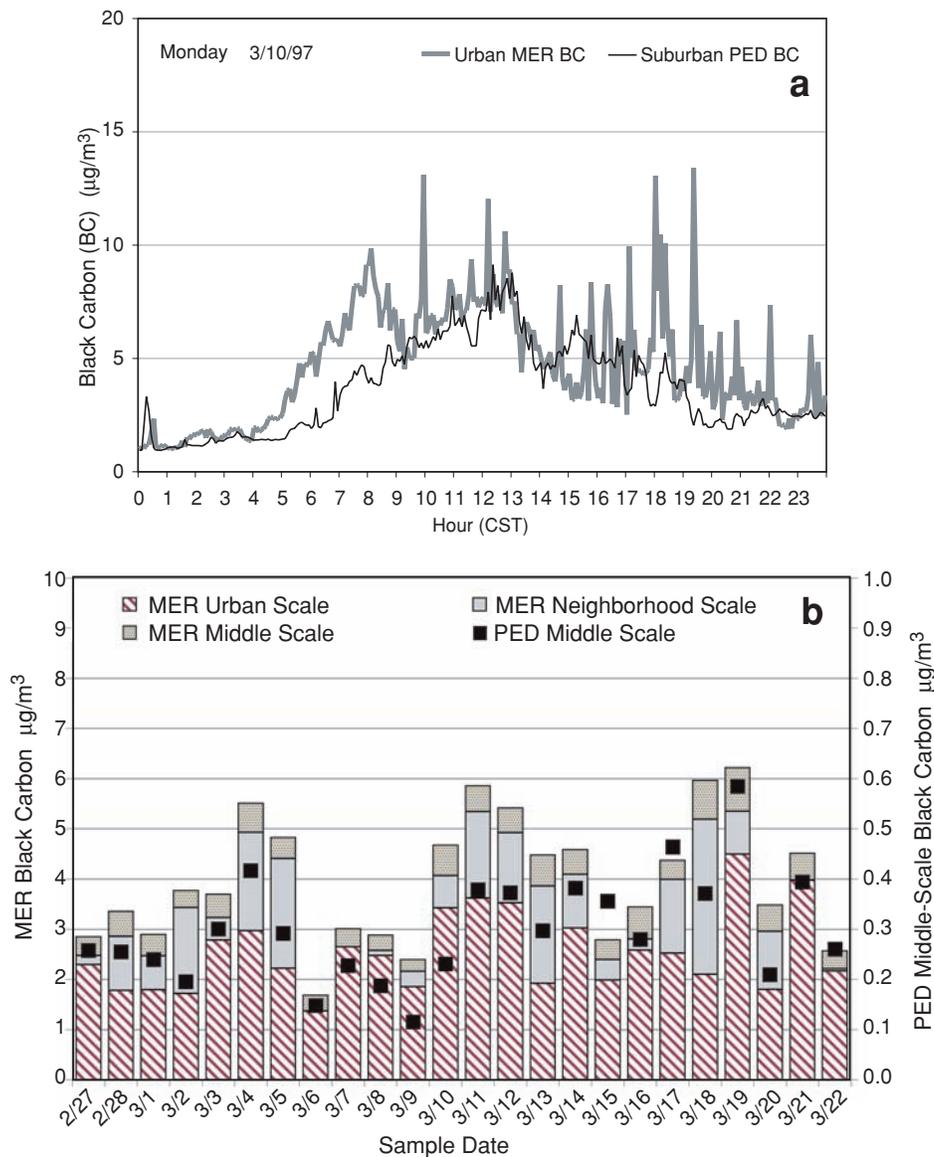


Figure 7.1. (a) Five-minute averages of BC measured with an aethalometer at a downtown (MER, La Merced) and a suburban site (PED, Pedregal) in Mexico City. The sharp spikes at MER are from middle-scale sources (within 0.5 km from the site). The morning traffic buildup (5:00 a.m. to 9:00 a.m.) around the downtown site is evident and is not seen at the suburban site. (b) To estimate the overall urban baseline, the short-term peaks in 7.1a are subtracted from BC at the suburban site (PED) before computing the daily, 24-hr average (peak-adjusted average). The difference between the peak-adjusted and non-adjusted 24-hr average at PED (black squares) is the suburban middle-scale BC. The difference between the peak-adjusted average at MER and PED yields an estimate of the neighborhood-scale (1 to 5 km) contribution at the downtown site (MER). The middle-scale contribution at the downtown site is obtained by subtracting the peak-adjusted 24-hr average at the downtown site from the unadjusted 24-hr average at this site. The magnitudes of the contributions from these 3 different spatial scales are shown for a series of days in 7.1b. This analysis indicates that only ~10 percent of the BC downtown at MER is of very local origin (middle-scale), and thus the site reasonably represents neighborhood exposures. Similar analyses can be performed on 5-minute PM_{10} and $\text{PM}_{2.5}$ mass measurements from TEOMs and light-scattering devices (See Chapter 5). (After Watson and Chow, 2001).

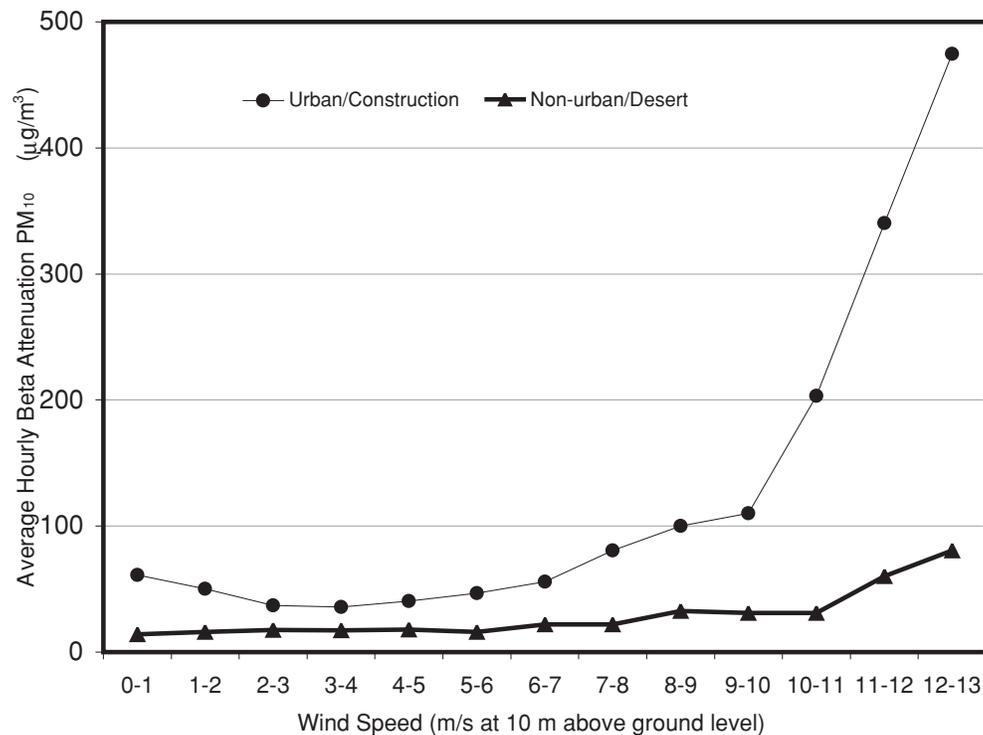


Figure 7.2. Average PM_{10} associated with different wind-speed categories at urban and non-urban locations in the Las Vegas, NV area, (Chow et al., 1999). Dust suspension at the construction site occurs at a lower wind speed, ~6 m/s, than at the desert site where PM_{10} increases are not observed until ~11 m/s. The concentrations are much higher near the disturbed land compared to the crusted desert surface at high wind speeds. This analysis convinced decision-makers that fugitive dust contributions were not just from, and were not dominated by, natural windblown dust. Methods to minimize land disturbances and to stabilize disturbed land during construction were needed to reduce excessive PM_{10} concentrations in Las Vegas. (After Watson et al., 2000).

increase in value as the size of the datasets with PM information grows. These semi-quantitative receptor-oriented data analyses (observational methods) should be performed prior to quantitative receptor modeling.

7.2 RECEPTOR MODEL TYPES

Table 7.1 summarizes receptor models that have been used for source apportionment/attribution along with their data requirements, strengths, and weakness. Watson et al. (2002a) provide more detailed references to their theory and application. Receptor models, such as the Chemical Mass Balance (CMB) model and its derivatives, are derived from the same physical principles as source models. Others, such as eigenvector analysis, are

statistically based, showing associations between variables from which causative factors may be inferred.

Receptor models are measurement-intensive, requiring many measurements of physical and chemical properties taken at monitoring sites that represent different spatial scales. Filter samples used for PM_{10} - or $PM_{2.5}$ -compliance measurements are not entirely suitable for the type and amount of chemical and physical analysis needed, so special sampling programs must be planned. Some techniques (e.g., CMB) require PM chemical-composition measurements of primary emissions for the sources influencing the ambient PM. Once these data are available, however, receptor methods do not require large manpower or computational resources. Costs for receptor-oriented studies range from ~\$US 50K

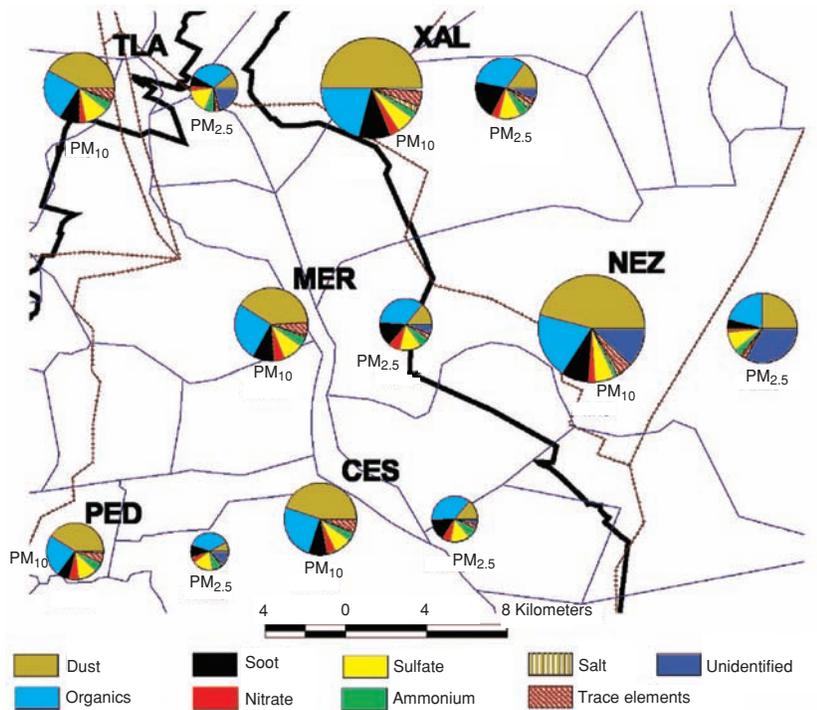


Figure 7.3. Material balance for PM₁₀ (larger circles) and PM_{2.5} (smaller circles) at six base sites in Mexico City averaged for the period of March 2 through 19, 1997. Most of the material is of primary origin composed of fugitive dust and carbon. NO₃⁻ and SO₄⁼ levels are relatively low. The effect of salt from dry Lake Texcoco, located in the upper right-hand corner, is evident at the XAL and NEZ sites, but not at the other sites. The XAL and NEZ sites appear to have larger local influences than the other sites, especially for the dust portion of PM₁₀. The MER, TLA, and CES locations have similar PM concentration and compositions. Differences in soot (BC), measured by the IMPROVE protocol (Chow et al., 1993a), between the MER and PED sites are similar to those derived independently in Figure 7.1. This plot is being used by the air-quality district to evaluate and improve the compliance and alert monitoring network operated in Mexico City. (After Chow et al., 2002a).

for a small community with an established air-quality network (e.g., Chow et al., 1992) to ~\$US 10M for a large region with a complex mixture of sources requiring establishment of a network and survey of potential sources (e.g., Pitchford et al., 1999). Many of the receptor-model measurements are the same as those that should be acquired to support a well-rounded source-model application.

Measurements of elements, ions, OC, and BC were usually sufficient in the past for successful source apportionment using receptor models. However, emission controls (e.g., precipitators and baghouses on stacks) and changes in processes and fuels (e.g., removal of lead from gasoline) have depleted many of the marker species, or have made their abundances more variable, in source emissions. Properties of

single particles, organic compounds, and operationally-defined carbon fractions are being measured to compensate. *There is a need to identify a greater variety of unique markers or tracers of specific sources and processes, particularly organic compounds, to improve the ability of receptor-modeling techniques to identify and quantify source contributions. This requires development of source and ambient sampling techniques and chemical extraction and analysis methods, and then testing of these new tools under a variety of situations.*

Multivariate receptor models require a large number of PM samples with chemical characterization. These models derive information from the temporal and spatial variability in the chemical concentrations and inter-relationships between the different chemical

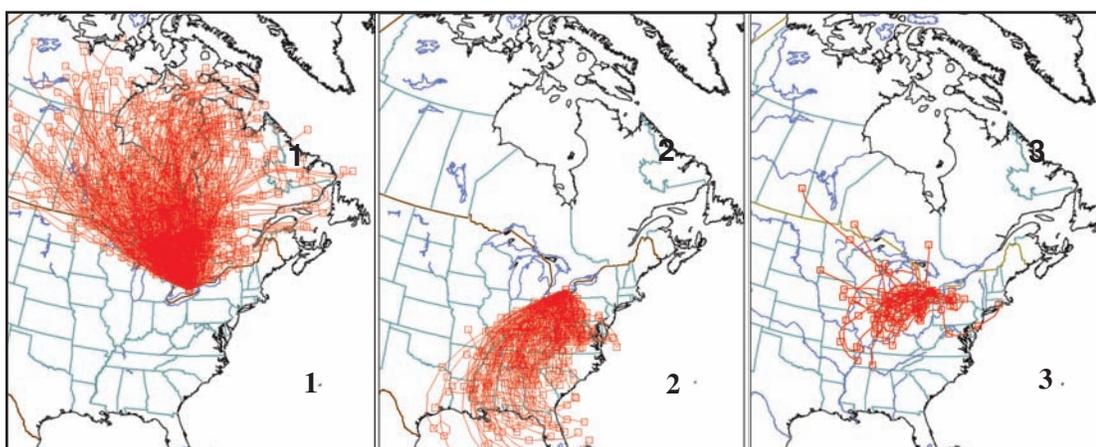


Figure 7.4. Three-day back-trajectories arriving at Simcoe, ON, during May-September of 1998 and 1999 were sorted by transport sector. Back-trajectories represent the most probable path that the air mass followed en route to Simcoe. Sectors 1 and 2 represent: 1) northerly flow over predominantly Canadian source regions, and 2) southerly flow over U.S. source regions. Six-hr average $PM_{2.5}$ loadings measured by a TEOM were $6.7 \pm 6.1 \mu\text{g}/\text{m}^3$ ($\pm 1\text{SD}$) for sector 1 and $22.4 \pm 11.7 \mu\text{g}/\text{m}^3$ for sector 2. Sector 3 includes trajectories corresponding to $PM_{2.5} > 30 \mu\text{g}/\text{m}^3$, which could not be classified into either of the other sectors because they cross over regions. The cut-off value of 30 was used because it approximates the Canadian standard for 24-hr average $PM_{2.5}$ (see Chapter 1 for details). The unclassifiable high-concentration cases (sector 3) were associated with very short transport distances, indicating stagnant conditions in the Midwest and Great Lakes region. There were 5 six-hr concentrations $> 30 \mu\text{g}/\text{m}^3$ in sector 1 and 51 in sector 2. This information is being used to estimate the portion of the $PM_{2.5}$ in the Simcoe and Toronto areas that is caused by local emissions vs. transport from other parts of Canada and the United States. (Brook et al., 2002).

concentrations. At least 50 samples are needed, and more than 100 samples from many locations and/or one location over a long time period are preferred. Samples should include high and low contributions from the suspected sources, usually requiring <24-hr averages. Sampling sites should be most densely located along strong concentration gradients for a pollutant or source. Network adequacy (Chow et al., 2002b) is not usually evident until after the measurements have been acquired.

7.2.1 Chemical Mass Balance

The CMB model (Friedlander, 1973) expresses ambient chemical concentrations as the sum of products of species abundances and source contributions. These equations are solved for the source contributions when ambient concentrations and source profiles are supplied as model input. Source profiles consist of the mass fractions of selected particle properties in source emissions; examples are given below. The CMB is the only

receptor air-quality model that calculates quantitative uncertainty values for source-contribution estimates. It provides the basic structure for other receptor models that can be derived from physical principles. The CMB model has been applied to evaluate PM control effectiveness (e.g., Chow et al., 1990; Engelbrecht et al., 2000), determine causes of high concentrations (Lowenthal et al., 1997; Schauer and Cass, 2000; Vega et al., 1997), quantify contributions to light extinction (e.g., Watson et al., 1988, 1996), and to estimate sources of particle deposition (Feeley and Liljestrand, 1983).

Several different CMB solution methods have been applied, but the multivariate, effective-variance, least-squares estimation method (Watson et al., 1984) is most commonly used because it incorporates precision estimates for all of the input data into the solution and propagates these errors to the model outputs. The tracer solution, in which a single chemical component or particle property is used to represent a single source or source type, is also in common use, but source-contribution estimates are

Table 7.1. Summary of receptor model source-apportionment models.

Receptor Model (Example Applications)	Data Requirements	Strengths	Weaknesses
7.2.1 Chemical Mass Balance	<ul style="list-style-type: none"> -Source and receptor measurements of stable aerosol properties that can distinguish source types. -Source profiles (mass abundances of physical and chemical properties) that represent emissions pertinent to the study location and time. -Uncertainties that reflect measurement error in ambient concentrations and profile variability in source emissions. -Sampling periods and locations that represent the effect (e.g., high PM, poor visibility) and different spatial scales (e.g., source dominated, local, regional). 	<ul style="list-style-type: none"> -Simple to use, software available. -Quantifies major primary source contributions with element, ion, and carbon measurements. -Quantifies contributions from source sub-types with single particle and organic compound measurements. -Provides quantitative uncertainties on source contribution estimates based on input data, uncertainties and colinearity of source profiles. -Has potential to quantify secondary SO₄ contributions from single sources with gas and particle profiles when profiles can be “aged” by chemical transformation models. 	<ul style="list-style-type: none"> -Completely compatible source and receptor measurements are not commonly available. -Assumes all observed mass is due to the sources selected in advance, which involves some subjectivity. -Does not directly identify the presence of new or unknown sources. -Typically does not apportion secondary particle constituents to sources. Must be combined with profile aging model to estimate secondary aerosol. -Much colinearity among source contributions without more specific markers than elements, ions, and carbon.
7.2.1 Injected Marker CMB Tracer Solution	<ul style="list-style-type: none"> -Non-reactive marker(s) added to a single source or set of sources in a well-characterized quantity in relative to other emissions. Sulfur hexafluoride, perfluorocarbons, and rare earth elements have been used. 	<ul style="list-style-type: none"> -Simple, no software needed. -Definitively identifies presence or absence of material from release source(s). -Quantifies primary emissions contributions from release source(s). 	<ul style="list-style-type: none"> -Highly sensitive to ratio of marker to PM in source profile; this ratio can have high uncertainty. -Marker does not change with secondary aerosol formation—needs profile aging model to fully account for mass due to “spiked” source. -Apportions only sources with injected marker. -Costly and logistically challenging.

Table 7.1. Summary of receptor model source-apportionment models. (continued)

Receptor Model (Example Applications)	Data Requirements	Strengths	Weaknesses
7.2.2 Enrichment Factor (EF)	<ul style="list-style-type: none"> -Inorganic or organic components or elemental ratios in a reference source (e.g., fugitive dust, sea salt, primary carbon). -Ambient measurements of same species. 	<ul style="list-style-type: none"> -Simple, no software needed. -Indicates presence or absence of emitters. -Inexpensive. -Provides evidence of secondary PM formation and changes in source profiles between source and receptor. 	<ul style="list-style-type: none"> -Semi-quantitative. More useful for source/process identification than for quantification.
7.2.3 Multiple Linear Regression (MLR)	<ul style="list-style-type: none"> -100 or more samples with marker species measurements at a receptor. -Minimal covariation among marker species due to common dispersion and transport. 	<ul style="list-style-type: none"> -Operates without source profiles. -Abundance of marker species in source is determined by inverse of regression coefficient. -Apportions secondary PM to primary emitters when primary markers are independent variables and secondary component (e.g. SO_4^{2-}) is dependent variable -Implemented by many statistical software packages. 	<ul style="list-style-type: none"> -Marker species must be from only the sources or source types examined. -Abundance of marker species in emissions is assumed constant with no variability -Limited to sources or source areas with markers. -Requires a large number of measurements.
7.2.4 Eigenvector Analysis ^a	<ul style="list-style-type: none"> -50 to 100 samples in space or time with source marker species measurements. -Knowledge of which species relate to which sources or source types. -Minimal covariation among marker species due to common dispersion and transport. -Some samples with and without contributing sources. 	<ul style="list-style-type: none"> -Intends to derive source profiles from ambient measurements and as they would appear at the receptor. -Intends to relate secondary components to source via correlations with primary emissions in profiles. -Sensitive to the influence of unknown and/or minor sources. 	<ul style="list-style-type: none"> -Most are based on statistical associations rather than a derivation from physical and chemical principles. -Many subjective rather than objective decisions and interpretations -Vectors or components are usually related to broad source types as opposed to specific categories or sources.

^aIncludes Principal Component Analysis [PCA], Factor Analysis {FA}, Empirical Orthogonal Functions [EOF], Positive Matrix Factorization [PMF], and UNMIX).

Table 7.1. Summary of receptor model source-apportionment models. (continued)

Receptor Model (Example Applications)	Data Requirements	Strengths	Weaknesses
7.2.5 Time Series	<ul style="list-style-type: none"> -Sequential measurements of one or more chemical markers. -100s to 1000s of individual measurements. 	<ul style="list-style-type: none"> -Shows spikes related to nearby source contributions. -Can be associated with highly variable wind directions. -Depending on sample duration, shows diurnal, day-to day, seasonal, and inter-annual changes in the presence of a source. 	<ul style="list-style-type: none"> -Does not quantify source contributions. -Requires continuous monitors. Filter methods are impractical.
7.2.6 Aerosol Evolution	<ul style="list-style-type: none"> -Emissions locations and rates. -Meteorological transport times and directions. -Meteorological conditions (e.g., wet, dry) along transport pathways. 	<ul style="list-style-type: none"> -Can be used parametrically to generate several profiles for typical transport/ meteorological situations that can be used in a CMB. 	<ul style="list-style-type: none"> -Very data intensive. Input measurements are often unavailable. -Derives relative, rather than absolute, concentrations. -Level of complexity may not adequately represent profile transformations.
7.2.7 Aerosol Equilibrium	<ul style="list-style-type: none"> -Total (gas plus particle) SO_4^-, NO_3^-, NH_4^+ and possibly other alkaline or acidic species over periods with low temperature and relative humidity variability. -Temperature and relative humidity. 	<ul style="list-style-type: none"> -Estimates partitioning between gas and particle phases for NH_3, HNO_3, and NH_4NO_3. -Allows evaluation of effects of precursor gas reductions on ammonium nitrate levels. 	<ul style="list-style-type: none"> -Highly sensitive to T and RH. Short duration samples are not usually available. -Gas-phase equilibrium depends on particle size, which is not usually known in great detail. -Sensitivity to aerosol mixing state not understood/quantified.

more uncertain than with the multivariate solution because they are highly dependent on the variability of the tracer-to-mass ratio. Artificial tracers (injected markers), such as rare-earth elements, sulfur hexafluoride, and halocarbon gases have been released with normal emissions and used in a CMB tracer solution to estimate contributions from many sources using the same fuel and from individual emitters (Horvath et al., 1988; Ondov et al., 1992; Pitchford et al., 1999).

The accuracy and precision of CMB source-contribution estimates depend on the variability of chemical abundances in the source profiles. Source profiles should represent source compositions as they would be perceived at a receptor. Profiles are most often measured at the source, and changes that take place during transport are not realized. These “fresh” profiles do not account for secondary PM formation and particle volatilization that may take place from source to receptor. Source profiles also must contain

several chemical components, which differ greatly in their abundances among different source types. Profiles often have not been measured on representative sources, or on enough different sources, to obtain reasonable estimates of profile variability. The propagated standard errors associated with CMB source-contribution estimates underestimate the true uncertainties of the apportionment in these cases.

The CMB attempts to explain the ambient chemical concentrations selected for its calculation with the source profiles provided. Excessive differences between calculated and measured concentrations usually indicate that profiles are insufficient, or that a contributing profile is missing. It is the responsibility of the modeler, not the CMB model, to evaluate the CMB uncertainties and performance measures, along with other data such as emission inventories, before accepting the results. This is true of all receptor- and source-oriented models.

Size-specific source profiles, including a variety of chemical species, need to be obtained. Consistent and well-characterized measurement techniques should be applied and a wide variety of sources, particularly those that are suspected to impact many geographic areas, should be surveyed. Enough source measurements from a series of representative sources to determine reasonable estimates of profile variability should be obtained. Gaseous pollutant measurements and extensive VOC and SVOC profiles should be obtained in conjunction with the PM source profiles. Not only will source-profile information benefit receptor modeling, leading to more confident results, but significant improvements in emission inventories and emission models will also result. This will improve the results from source-oriented models.

7.2.2 Enrichment Factors

The EF model (Sturges, 1989; Lawson and Winchester, 1979; Mason, 1990) compares ratios of chemical concentrations in the atmosphere to the same ratios in a reference material associated with a stable and well-characterized source, such as average crustal composition for a region, sea salt, or OC to BC in combustion sources. These ratios are often normalized to the Si concentrations in air and in soil,

as Si is the most abundant element in suspended soil. Reference ratios vary substantially between bulk soil and suspendable particles, and among different regions (Rahn, 1976). Differences are explained in terms of other sources, but not with quantitative apportionment as in the CMB.

Heavy-metal enrichments are usually attributed to industrial emitters. Sulfur enrichment is attributed to secondary SO_4^- -containing particles formed from gaseous SO_2 emissions. Organic carbon enrichment is attributed to SOA and non-reference primary emitters. Potassium, and sometimes Cl^- , enrichments are attributed to burning and cooking. Vanadium and Ni enrichments indicate contributions from residual oil combustion or refinery catalyst crackers, while enriched Se is usually attributed to coal-fired power stations. Iron, Mn, Cu, Zn, and Pb enrichments indicate steel-mill, smelting, or plating contributions. Calcium is often enriched near cement manufacture or the use of cement products in construction. Sodium and Cl^- are enriched near the coast and dry lake beds, and after de-icing materials are applied to streets.

For many applications, EFs can be determined by elemental analysis of Teflon filter samples, typical of those obtained with $\text{PM}_{2.5}$ compliance monitors. Enrichment factors are useful for forming a conceptual model of potential sources that might affect higher loadings, especially industrial emitters. The EF method also has been used to examine different geological strata to determine how specific elements, such as Pb, may have deposited over long time periods (Weiss et al., 1999).

7.2.3 Multiple Linear Regression on Marker Species

The MLR model expresses particle mass, a component of mass such as SO_4^- , light extinction, or another observable, as a linear sum of unknown regression coefficients multiplied by source-marker concentrations measured at a receptor. The markers, which may be chemical elements or compounds, must originate only in the source type being apportioned. The regression coefficients represent the inverse of the source-profile chemical abundance of the marker species in the source emissions. The product of the

regression coefficient and the marker concentration for a specific sample is the tracer solution to the CMB equations and yields the source-contribution estimate. MLR has been used to estimate source contributions to high PM concentrations (Morandi et al., 1991), to relate light extinction and SO_4^- to power-station and smelter emissions in the western United States (Malm et al., 1990), and to apportion SO_4^- to different source regions in the eastern United States (Lowenthal and Rahn, 1989).

7.2.4 Temporal and Spatial Correlation Eigenvectors

Principal Component Analysis (PCA), Factor Analysis (FA), Empirical Orthogonal Functions (EOF), Positive Matrix Factorization (PMF), and UNMIX are all variations on temporal and spatial eigenvectors (e.g., Henry, 1991; Hopke 1988; Paatero, 1997). There is a large variability in how these methods are applied and interpreted. The patterns from most of these methods are empirically derived, as a basic-principles derivation has not yet been formulated. PCA, FA, and EOF are applied to correlations between variables over time or space. Temporal correlations are calculated from a long time series (at least fifty, but preferably several hundred samples) of chemical concentrations at one or more locations. Eigenvectors of this correlation matrix (a smaller matrix of coordinates that can reproduce the ambient concentrations when added with appropriate coefficients) are determined and a subset is rotated in multi-dimensional space to maximize and minimize correlations of each vector with each measured species. These rotated vectors (also called “factors,” “principal components,” or “orthogonal functions”) are interpreted as source profiles by comparison of factor loadings with source measurements. Several different normalization and rotation schemes have been used, but this is where the physical derivation of the model is lost; the rotations depend on statistical or judgmental rather than physical criteria. The PMF method (Paatero, 1997) provides a physical basis for estimating eigenvectors that can be related directly to sources when a fairly stringent set of assumptions is met. This method is also reported to provide source profiles from the ambient data, but these have not been

verified against actual profile measurements in most cases. The UNMIX method (Henry, 2000) also has a physical justification by searching for “edges” in multi-dimensional space to determine ratios among ambient marker species.

For a large spatial network (25 to 50 locations), spatial correlations are calculated from chemical measurements taken on simultaneous samples across the monitoring locations (Henry, 1997b; White, 1999). Eigenvectors of this correlation matrix represent a spatial distribution of source influences over the area, provided that the samplers have been located to represent the gradients in source contributions. As with temporal correlation models, several normalization and rotation schemes have been applied and the physical derivation is still lacking.

Eigenvector receptor methods have been used to evaluate contributions to high particle concentrations that might affect health (Thurston and Spengler, 1985), distinguish regional contributors to $\text{PM}_{2.5}$ and SO_4^- concentrations (Poirot et al., 2001), and to determine SO_4^- contributions to light extinction over large regions (Henry, 1997c). They are used in exploratory analyses to identify the potential for emissions that are not yet inventoried. For example, Magliano (1988) identified an eigenvector containing a common variation between Cu and SO_4^- in California’s San Joaquin Valley. Further investigation determined that CuSO_4 was sprayed on orchards during winter to lower the freezing point of the fruit.

7.2.5 Time Series

Spectral analysis (Hies et al., 2000), intervention analysis (Jorquera et al., 2000), lagged regression analysis (Hsu, 1997), and trend analysis (Somerville and Evans, 1995) models separate temporal patterns for a single variable and establish temporal relationships between different variables. These models have been used to identify sources, to forecast future pollutant concentrations based on past experience, to infer relationships between causes and effects, and to relate long-term trends in PM chemical concentrations to emission changes. It is especially important to include meteorological indicators in time-series models (e.g., Shively and Sager, 1999; Weatherhead et al., 1998) and to use data sets with

comparable measurement methods and sampling frequencies (Henry et al., 2000).

7.2.6 Neural Networks

The neural-network approach (Reich et al., 1999; Wienke et al., 1994) involves constructing a synthetic logic network, patterned after biological reasoning systems, by presenting the neural network with known inputs and outputs representing the source-receptor system. These known inputs and outputs are referred to as training sets, and once the linkages are established by the neural net, it recognizes similar patterns and relationships among ambient variables with unknown causes. During training, the network assigns weights to the inputs that reproduce the outputs. Neural networks can provide functional relationships that generally turn out to be solutions to the MLR and CMB equations (Song and Hopke, 1996). Their results are only as good as the known relationships within the training sets and the extent to which the unknown data sets share the same patterns within the training sets.

7.2.7 Aerosol Evolution and Equilibrium

Atmospheric “aging” of source profiles containing PM chemical components (with or without size-distribution information) and gaseous precursors is modeled using appropriate chemical-reaction and aerosol-process schemes (Lewis and Stevens, 1985; Watson et al., 2002b). Aging is assumed to occur in a “box” or “puff” moving along a trajectory path from source to receptor (Kleeman et al., 1999a; Gordon and Olmez, 1986). Several of the substances reaching a receptor, such as $\text{NH}_3/\text{NH}_4^+$ and NO_3^- , may be in both the vapor and particle phases, depending on temperature, humidity, and precursor-gas concentrations. Aged profiles have been used to estimate SO_4^{2-} contributions to light extinction (Latimer et al., 1990).

Aerosol-evolution models provide the most explicit and useful link between source-oriented chemical-transport and receptor models. A source-oriented air-quality model with a range of inputs could develop individual source or regional source profiles, which might be used with the CMB or other receptor

samples. The results also could be used to evaluate source model inputs and representations of transformation processes. The profiles derived from specialized source-modeling experiments could be applied to future samples with similar meteorology but without a full source-modeling effort. *Methods for developing “aged” source profiles and for subsequent application of these profiles in receptor models, such as CMB, need to be evaluated. This could extend the capabilities of receptor models to include apportionment of secondary PM or to account for differential attrition of or addition to the primary emissions due to physical and chemical processes.*

Aerosol-equilibrium models (referred to in Chapter 8 as observation-based models) have been used to determine whether HNO_3 or NH_3 reductions are needed to reduce NH_4NO_3 (Ansari and Pandis, 1998; Blanchard et al., 2000; Watson et al., 1994a). Equilibrium models also have been used to determine the extent to which SO_4^{2-} reductions will free up NH_3 , potentially leading to an increase in NH_4NO_3 in $\text{PM}_{2.5}$ (West et al., 1999). These models are simpler than the aerosol-evolution models because fewer processes are considered and transport is not taken into account.

Chapter 3 includes some examples of the application of an equilibrium model for eastern North America. Equilibrium models have been combined with aerosol evolution models to determine the extent to which HNO_3 formation is limited by NO_x or VOC emissions and to determine PM credits for precursor NO_x emission reductions (Stockwell et al., 2000).

7.3 RECEPTOR-MODEL INPUT MEASUREMENTS

As previously noted, receptor models depend on emission characteristics that remain stable, or change in predictable ways, during transport from source to receptor. These include particle size, chemical composition, and variability in any of these parameters in space and time. Chapter 5 describes the methods used to quantify these characteristics. Chemical abundances and spatial/temporal variations are indicative of the main processes and sources, manageable or unmanageable, contributing to PM

concentrations. For example, the relative amount of SO_4^- decreases East to West in Canada and the United States, while the amounts of other compounds, such as NO_3^- and OC increase, indicating that SO_2 sources are a more important focus for $\text{PM}_{2.5}$ reductions in the East than in the West.

7.3.1 Particle Size

As explained in Chapter 3, different particle-size fractions are dominated by different source types. $\text{PM}_{2.5}$ and PM_{10} size fractions are most commonly measured, often at the same locations, and most receptor-modeling studies have used temporal or spatial variations in the bulk chemical composition of these fractions. Variations in particle size and chemical composition can be further exploited for quantitative source apportionment.

The ultrafine fraction is usually measured in terms of particle number by condensation particle counters or as mass concentration on the final stages of low-pressure impactors. Ultrafine particles are abundant in fresh combustion emissions, but they rapidly coagulate with each other and with larger particles shortly after emission (Preining, 1998). As a result, high ultrafine number counts typically indicate the influence of fresh combustion emissions, and lower particle-number concentrations indicate that nearby sources are not large contributors. Buzorius et al. (1999) measured 10,000 to 50,000 particles/ cm^3 near a heavily traveled street, while levels at a more pristine site were typically 2,000 to 3,000 particles/ cm^3 . Time series of the particle-number distribution, along with CO and NO_x concentrations, have been used together to apportion particle numbers to gasoline and diesel sources (Wahlin et al., 2001).

The accumulation mode usually contains most of the $\text{PM}_{2.5}$ mass and most of its chemical variability. Particle properties in the accumulation mode most often have been used for receptor modeling. These particles can be directly emitted “primary particles” or arise from rapid condensation of primary SVOC. Secondary particles that form in the atmosphere from gaseous emissions of SO_2 , NO_x , NH_3 , and some VOCs also occupy this mode. Within the accumulation mode there may be sub-modes

indicating secondary particle-formation processes (John et al., 1990). The condensation mode (peaking at $\sim 0.2 \mu\text{m}$) consists of smaller particles, which form from condensation and coagulation in dry air. The droplet mode (peaking at $\sim 0.7 \mu\text{m}$) forms from activated particles and gases adsorbed by, and reacted in, these cloud and fog droplets; when the water in the droplet evaporates, a larger amount of SO_4^- or NO_3^- remains than is in the condensation mode. The sub-mode occupied by SO_4^- in the size spectrum allows inferences about the history of the gases and processes that formed it.

Coarse particles, often reported as TSP minus $\text{PM}_{2.5}$ or PM_{10} minus $\text{PM}_{2.5}$ mass, result from the disaggregation of liquid or solid material, mostly fugitive dust or sea salt. Concentrations are bounded at larger particle sizes by gravitational settling. This settling results in dustfall nuisances near coarse-particle emitters such as heavily-traveled unpaved roads, construction sites, and mineral-handling facilities. As a result of settling, the peak of the coarse distribution shifts to smaller particles with transport distance from the point of emissions. Coarse particles can travel over long distances when they are injected high into the atmosphere by severe wind storms (Perry et al., 1997), but the peak of this transported coarse mode is closer to $3 \mu\text{m}$ than $10 \mu\text{m}$.

7.3.2 Chemical Composition

Chemical composition of particles provides the most information on their origins. The most abundant and commonly measured constituents of $\text{PM}_{2.5}$ or PM_{10} mass are OC, BC, geological material, SO_4^- , NO_3^- , and NH_4^+ . Soluble salts such as NaCl are often found near the ocean, open playas, and after road de-icing. Analysis for these common components indicates the extent to which mass concentrations result from fugitive dust, secondary particles, or carbon-generating combustion activities such as vehicle exhaust, vegetative burning, and cooking. More specific chemical characterization then can be focused on the components with the largest mass fractions.

For quantitative source apportionment, source profiles must contain chemical abundances (fractions of emitted $\text{PM}_{2.5}$ or PM_{10} mass) for a range of

components that differ among source types, that do not change appreciably during transport between source and receptor (or that allow changes to be simulated by measurement or modeling), and that are reasonably constant among different emitters of the same type (e.g., motor vehicles) and source operating conditions. Minor chemical components, constituting of less than 1 percent of particle mass, are needed for quantitative apportionment as they are more numerous and more likely to occur with patterns that allow differentiation among sources.

7.3.2.1 Soil, Dust, and Industrial Markers

Aluminum, Si, K, Ca, and Fe are most abundant in geological material, although the abundances vary by type and use of soil. Figure 7.5a is a profile from a paved road. Low levels of Pb deposited from exhaust and exhaust systems due to prior use of leaded gasoline is evident. Organic carbon from deposited exhaust, oil drippings, asphalt, tire wear and ground up plant detritus is often more abundant in road dust than in pristine desert soils. Trace metals such as Cu and Zn probably originate from brake and clutch linings as well as from metals used in vehicle construction. Water-soluble K is about one-tenth of the total K abundance in most fugitive dusts, indicating that other sources are responsible for water-soluble K in atmospheric samples when this ratio is exceeded.

Trace elements have been useful as markers for different industrial or combustion-source contributions (Biegalski et al., 1998). However, elements identified and quantified 1) in residual oil combustion and refinery catalyst crackers (V and Ni); 2) in leaded-gasoline combustion (Pb, Cl and Br); and 3) in metal smelting and refining processes (Cu, Fe, Mn, Cr, Zn, Zr, and As) have been removed from many fuels, processes, and industrial exhaust streams. While good for the environment, these modifications have decreased the utility of elemental abundances to distinguish among source contributions in receptor models. As highlighted above, additional chemical and physical properties beyond the commonly measured elements, ions, and carbon need to be examined to determine the ones that are useful in practical source-apportionment applications.

7.3.2.2 Combustion Markers

Figure 7.5b from a coal-fired power station contains many of the same elements found in fugitive dust, but in different proportions. Selenium, Sr, and Pb are enriched over the dust profile, and OC is depleted. The ratio of SO_2 to $\text{PM}_{2.5}$ emissions in this sample is large, and SO_2 is a good indicator of fresh emissions from this source type. This ratio changes with time, however, as SO_2 deposits more rapidly than $\text{PM}_{2.5}$ and augments $\text{PM}_{2.5}$ mass, generally within a day after emission, as it transforms into SO_4^{2-} .

The gasoline-vehicle exhaust profile in Figure 7.5c shows OC and BC as its major components, with OC two to three times BC. A wide variety of different elements is found in these emissions, but their abundances are highly variable. This is consistent with many of the metals originating from exhaust-system deterioration and motor oil that differ substantially from vehicle to vehicle. The CO to $\text{PM}_{2.5}$ ratio is highest for gasoline-vehicle exhaust, but it is also highly variable.

Figure 7.5d shows that wood-burning emissions are also dominated by carbon, but the OC abundance is usually much higher than the BC fraction. Most of the K is water-soluble, in contrast to the insoluble K in fugitive dust. Other soluble salts containing SO_4^{2-} , NO_3^- , NH_4^+ , and Cl^- are evident. Trace metals from dust deposited on the burned wood and from stove or fireplace deterioration are often evident in these emissions.

7.3.2.3 Secondary Sulfate and Nitrate

Sulfate, NO_3^- , and NH_4^+ abundances are low in the primary emission profiles shown in Figure 7.5 because most of these are formed in the atmosphere from primary emissions of gaseous SO_2 , NO_x , and NH_3 . Receptor models can easily separate primary from secondary origins when stoichiometric abundances in compounds such as H_2SO_4 , NH_4HSO_4 , $(\text{NH}_4)_2\text{SO}_4$, NH_4NO_3 , and NaNO_3 are included as source profiles. Although receptor models do not generally attribute these compounds to a specific source, the quantities of the different secondary compounds indicate the age of the material (e.g., H_2SO_4 is usually from a nearby emitter that has not been exposed to sufficient NH_3 for neutralization).

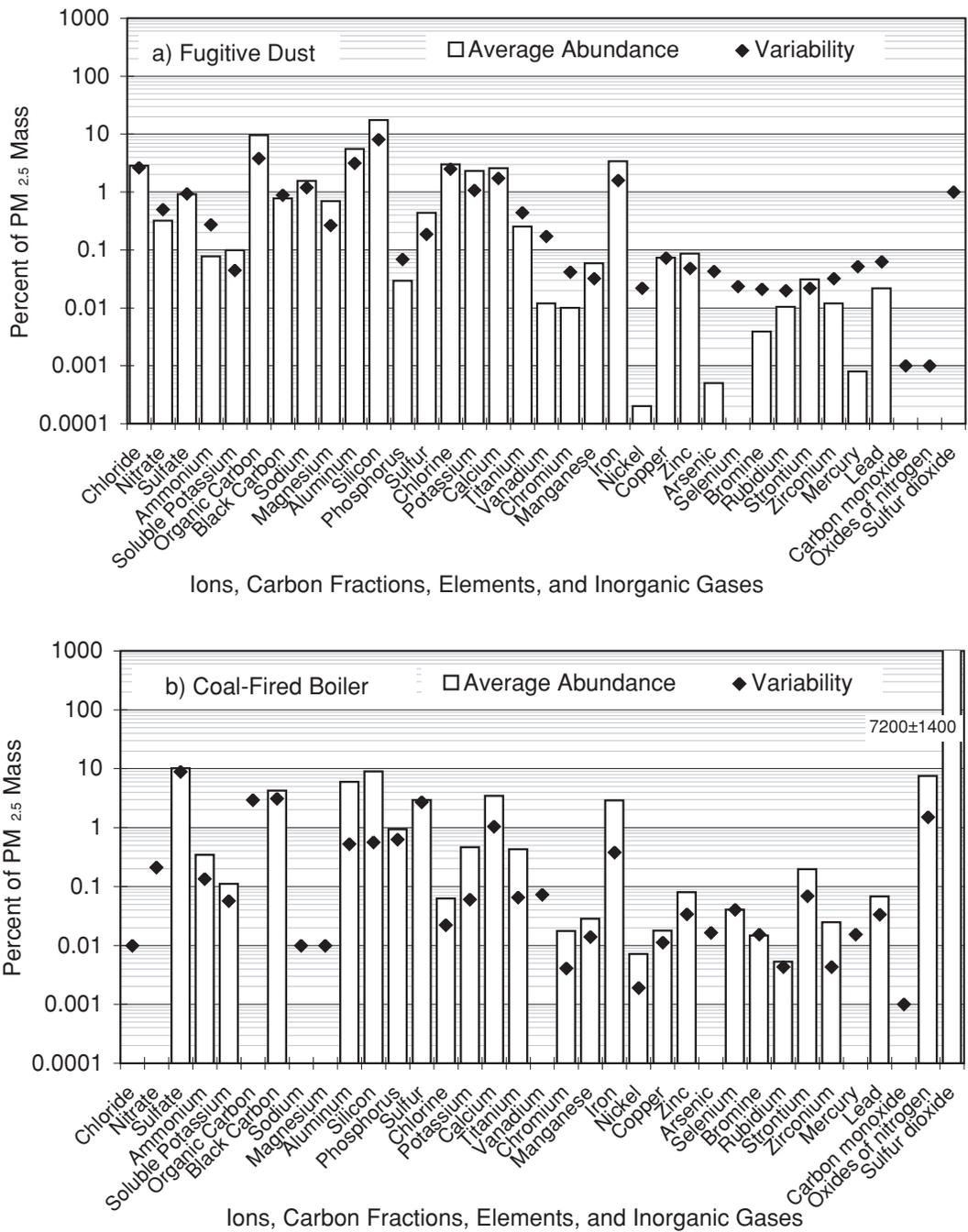


Figure 7.5. Examples of $PM_{2.5}$ source profiles determined from carbon, ion, and elemental analyses of diluted source samples from representative sources for a) fugitive dust, b) a coal fired power station, c) hot stabilized gasoline vehicle exhaust, and d) hardwood burning from emitters typical of Denver, CO, during winter, 1996 (Zielinska et al., 1998). The heights of the bars represent the average abundance of each species as determined by the average from several source tests and the diamonds represent the standard deviation of the average derived from the same tests. Ratios of CO , NO_x , and SO_2 to $PM_{2.5}$ mass emissions can also be included in source profiles and used in aerosol evolution models to determine how the profile might change during source/receptor transport. BC and OC were determined using the IMPROVE thermal/optical reflectance protocol (Chow et al., 1993a). (After Watson and Chow, 2002).

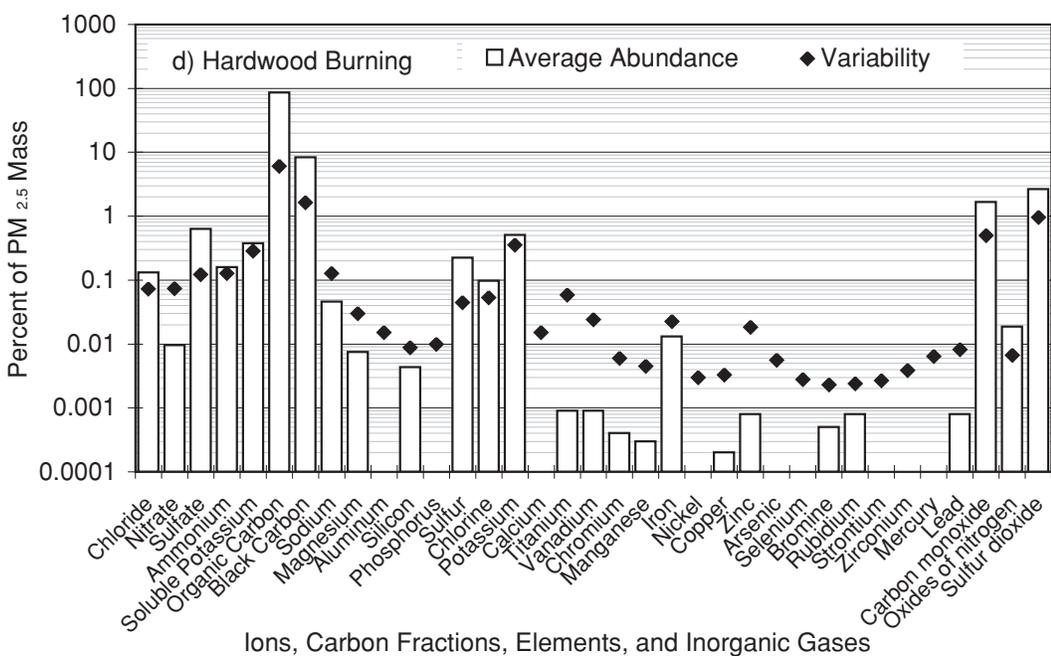
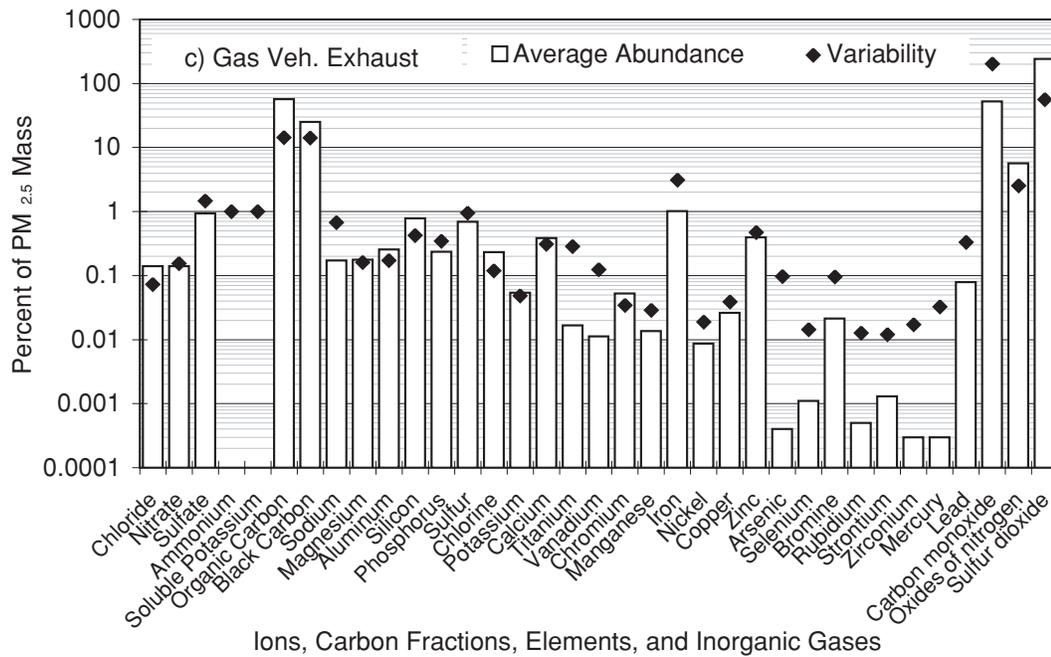


Figure 7.5. Examples of PM_{2.5} source profiles. (continued)

Over North America, anthropogenic emissions, specifically those from coal and oil combustion for power generation and metal smelting and refining, are the largest SO₂ emitters. Diesel fuel and gasoline contain some residual sulfur, but this is being reduced in the United States and Canada because it interferes with the effectiveness of catalytic converters (Lloyd

and Cackette, 2001). In remote areas, natural sources, such as DMS, H₂S, and OCS from marine and terrestrial biota, volcanoes, and biomass burning are important, but the resulting SO₄⁼ levels are typically <1 µg/m³.

Attributing SO₄⁼ to its original SO₂ source (e.g., smelters, power plants, steel manufacturing, natural

emissions) is uncertain because SO_2 in the atmosphere behaves the same regardless of its origin. However, within a large (~1000 km) geographic region, the largest SO_2 emitters, on average, probably contribute the largest fraction of $\text{SO}_4^{=}$. Direct or primary $\text{SO}_4^{=}$ emissions also can arise from combustion sources, although in much smaller amounts than SO_2 . Primary $\text{SO}_4^{=}$ is often part of a more complex molecule such as FeSO_4 , NiSO_4 , or organic sulfur. However, most (>90 percent) fine-particle $\text{SO}_4^{=}$ forms in the atmosphere and usually is associated with NH_4^+ .

Small amounts of PM NO_3^- are produced during combustion or formed in hot exhaust. As described in Chapter 3, most NO_3^- (>95 percent) derives from atmospheric oxidation of NO_x into species such as gaseous HNO_3 , N_2O_5 and NO_3 radical. Much of the N_2O_5 and NO_3 end up as HNO_3 , which can combine with NH_3 to produce NH_4NO_3 . NO_x is produced in the presence of high temperature (e.g., combustion), so fuel combustion is ultimately responsible for much of the NO_3^- . Similar to $\text{SO}_4^{=}$, attributing NO_3^- to a particular combustion source is uncertain. This is compounded by the interplay between NH_3 and HNO_3 and the fact that PM NO_3^- can convert back to these gaseous precursors.

NH_4^+ is usually associated with ammonium sulfate and ammonium nitrate, and derives from gaseous NH_3 emissions. Most NH_3 is of biogenic origin, associated with livestock waste products and vegetative decay. NH_3 is also emitted by some industries and in cities (due to people and pets, catalyst-equipped vehicles and wastewater). NH_3 rapidly neutralizes H_2SO_4 . Once the $\text{SO}_4^{=}$ -related acidity has been neutralized, the remaining NH_3 may react with HNO_3 to create NH_4NO_3 particles. In an NH_3 -depleted atmosphere containing HNO_3 , reducing $\text{SO}_4^{=}$ levels may free NH_3 that can then create NH_4NO_3 particles, as described in Chapter 3 and as exemplified later in this chapter.

7.3.2.4 Carbonaceous Particles

As defined in Chapter 1, carbonaceous particles refer to both BC and OC. Although total carbon is comparably measured by different methods, the observed OC and BC fractions depend on the analysis method. Several different methods are in common

use (e.g., Schmid et al., 2001; Currie et al., 2002), and their operational definitions for OC and BC do not always coincide. For receptor modeling, the definition of carbon fractions, especially OC and BC, must be the same for ambient and source-profile measurements. As noted in earlier chapters the terms BC, EC, soot, and LAC are used loosely and often interchangeably by air-quality, atmospheric, health, and industrial researchers. EC is not found in the atmosphere in its purest forms of diamond (four carbon bonds) or graphite (three carbon bonds). Therefore, referring to EC on atmospheric particles is misleading and a more ambiguous term like BC, as used here, is more appropriate. Atmospheric BC particles are believed to be the product of incomplete combustion of carbon-containing fuels in an oxygen-starved environment. Chang et al. (1982) define BC as "...a complex three-dimensional polymer with the capability of transferring electrons..." Seinfeld and Pandis (1998) refer to BC as soot that forms when carbon-to-oxygen ratios during combustion are less than one. This soot contains randomly oriented crystals 2 to 3 nm in diameter with a graphite-like structure, interspersed with other elements. Ebert (1990) found that fresh BC generated from incomplete combustion of diesel fuel was ~92 percent carbon, ~6 percent oxygen, ~1 percent hydrogen, ~0.5 percent sulfur, and ~0.3 percent nitrogen by weight. It is crucial when reporting OC and BC concentrations, as done in Chapter 6 and in Figures 7.3 and 7.5, to indicate the specific measurement method(s) that were utilized.

The most common sources of BC are combustion of fossil fuels, such as coal, oil, and natural gas (old carbon) and combustion of biomass, such as wood in fireplaces or forests/shrubs/grasses (new carbon). The amount of BC that forms during combustion depends on the combustion conditions (temperature, fuel-oxygen ratio). BC is emitted directly in the ultrafine or accumulation size ranges and in carbon aggregate chains that can be geometrically larger than 2.5 μm . Since BC arises from most oxygen-starved combustion processes, and since thermal measurements of total BC do not reveal much detail about its structure, BC is not easily relatable to specific sources without more information.

As shown in Chapter 6, OC makes up a large fraction of $\text{PM}_{2.5}$ in all locations. It also contains hundreds to

thousands of individual organic compounds. The main natural sources are: spores, bacteria, humic material and leaf litter in soils and abrasion of plant waxes; and heavy organic gases from biological processes that are oxidized and condense, partition, or react on particles (e.g., monoterpenes). Naturally-occurring forest and wildfires are also large contributors. Consequently, a fraction of the particle-phase OC is of natural origin, even in densely populated areas with manmade contributions. The main anthropogenic sources of OC are fossil-fuel combustion, burning of wood and other vegetation for heating or land clearance, cooking (both the fuel and the meat), wear/friction of carbon-containing material (e.g., tires and asphalt), and oxidation of some VOCs that condense or partition onto existing particles.

As described in previous chapters, OC may be emitted directly in the particulate phase or as an organic vapor (semivolatile OC or SVOC) that condenses on other particles shortly after being emitted. OC condensation that occurs quickly as the exhaust plume cools should be included as part of direct particle emissions, but this is not well-represented by hot-exhaust sampling (England et al., 2000). To realistically capture these condensables, source-profile tests should be made with cooling to ambient temperatures, dilution, and a short aging period prior to collection on filters (Hildemann et al., 1989). Considerable uncertainty exists regarding the true amount of direct particle-phase OC emissions because many source-profile tests have not followed this approach. Some SVOC compounds alternate between the gas and particle phase in the atmosphere, depending upon their concentrations and the ambient temperature. Typical diurnal, seasonal and geographic variations in temperature are large enough for some compounds to change phase several times during their atmospheric lifetime. Since gases often deposit more rapidly than particles, these phase changes alter the relative abundances among different components in a profile.

Past information on OC emissions needs to be examined to determine if appropriate sampling methods, capable of properly capturing SVOCs that condense rapidly, were utilized. The extent to which positive artifacts, due to VOC/SVOC adsorption onto the filter media, may have biased the OC emission

information and also needs to be assessed. Appropriate and consistent techniques need to be applied for a wide variety of sources to update the current source profile or speciation information.

The IMPROVE OC/BC fractions (Chow et al., 1993a, 2001) in Figure 7.5 are one of several ways to separate carbon into functional and repeatable categories (see Appendix B) for which the exact composition is not generally known. Watson et al. (1994b) found differences in the quantities of carbon that evolved at different temperatures, with diesel exhaust yielding more carbon at higher temperatures than gasoline-vehicle exhaust. Greaves et al. (1987) and Jeon et al. (2001) have experimented with thermal desorption followed by gas-chromatographic and mass-spectrometric detection, techniques that yield many carbon fractions, some of which can be associated with organic compounds, in receptor samples. These profiles have not yet been quantitatively related to source emissions via source testing. Thermal-desorption and pyrolysis methods may be less costly and more convenient to implement than detailed organic-compound analyses, which require large samples and laborious solvent-extraction operations. Comparisons must be made between the simple and complex analysis methods on source and receptor samples to demonstrate their utility.

Solvent extraction followed by gas or liquid chromatography with different detectors (e.g., Mazurek et al., 1987), and comparison with standards, has identified hundreds of organic compounds; but these account for only 10 percent to 20 percent of the OC in most ambient samples. Some organic compounds are dominant in certain source types and remain stable in the atmosphere; these are good source markers for receptor models. Figure 7.6 compares several different organic-compound abundances in hardwood burning with those in meat cooking. Meat-cooking profiles for elements, ions, and OC are similar to those for wood burning (Figure 7.5d), and this precludes separation of wood burning and meat cooking by the CMB. However, with the additional organic compounds shown in Figures 7.6a and 7.6b, these two sources can be distinguished. Hardwood burning is rich in guaiacols and syringols, but low in sterols such as steroid-m and cholesterol. Just the opposite is true for meat cooking, where

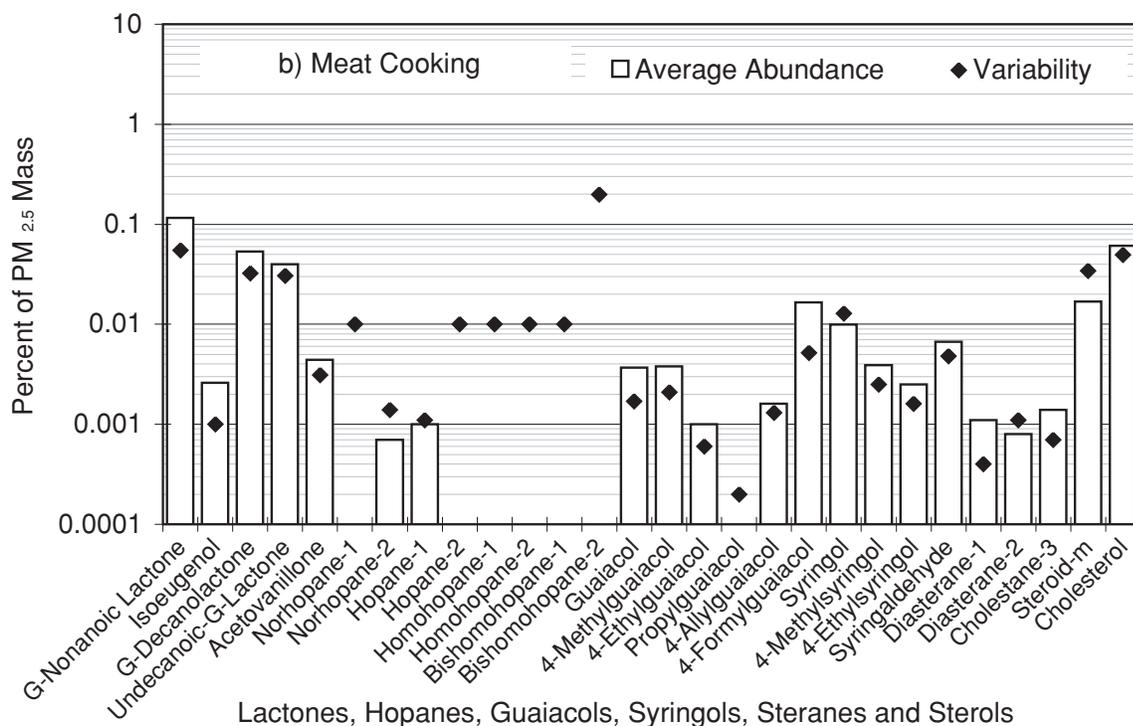
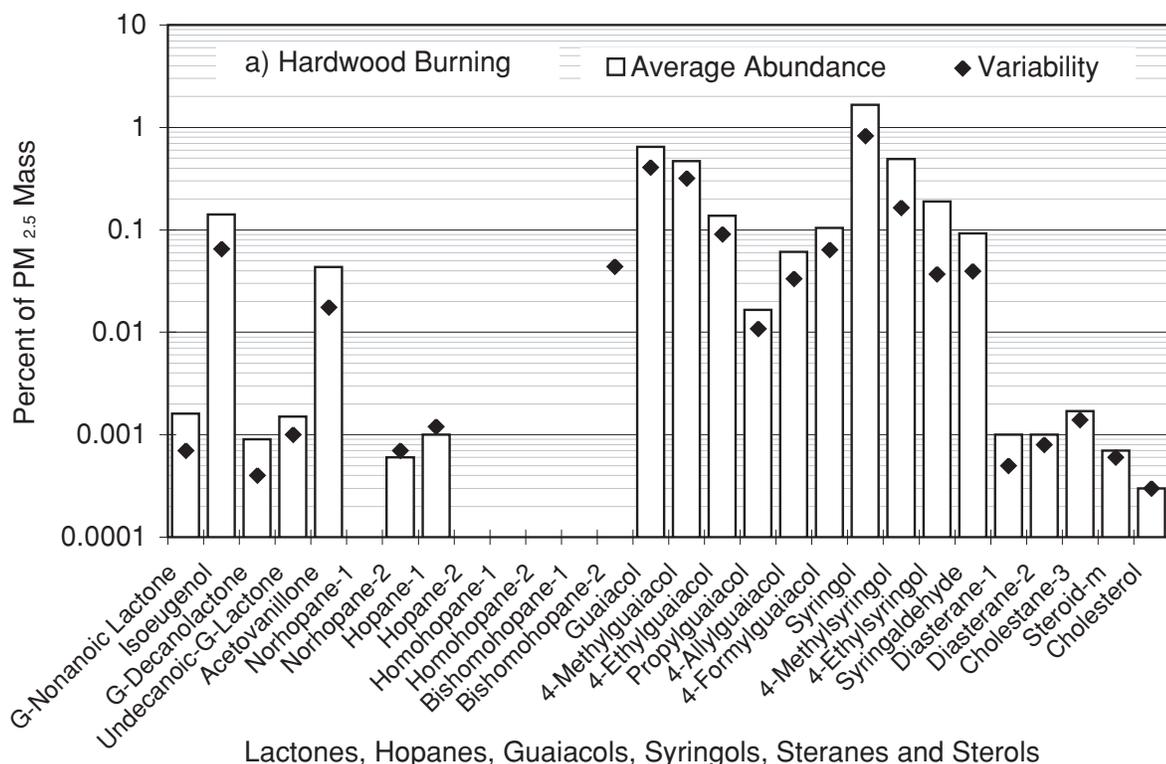


Figure 7.6. Examples of $PM_{2.5}$ source profiles for lactones, hopanes, guaiacols, syringols, steranes, and sterols for a) hardwood combustion and b) meat cooking (Zielinska et al., 1998). These are among many different categories of molecular organic markers measured by filter extraction and gas chromatography with mass-spectrometric detection. (After Watson and Chow, 2002).

cholesterol is among the most abundant species. Syringols are more abundant in hardwoods, such as oak or walnut, and they are depleted in softwoods such as pine, thereby allowing even greater differentiation to be achieved in source apportionment.

Some organic-compound source profiles have been measured for gasoline- and diesel-vehicle exhaust (Fraser et al., 1998; Kleeman et al., 2000; Schauer et al., 1999a, 2002a; Rogge et al., 1993a;), cooking (Nolte et al., 1999; Schauer et al., 1999b, 2002b), natural gas combustion (Rogge et al., 1993b), coal combustion (Oros and Simoneit, 2000), oil combustion (Rogge et al., 1997), wood burning and forest fires (Elias et al., 1999; Fine et al., 2002; Hays et al., 2002; McDonald et al., 2000; Rogge et al., 1998; Schauer et al., 1998; Simoneit et al., 1999; Standley and Simoneit, 1994), and fugitive dust (Rogge et al., 1993c). Most of these results are from emitters in southern California. Different investigators measure and use different markers for these sources, and these do not always correspond to the organic compounds measured at receptors. Organic-compound measurement methods are rapidly evolving and may soon be in widespread use for source profiles and receptor concentrations.

Simoneit (1999) cites several examples of odd- and even-numbered carbon molecules in the n-alkane series as indicating the presence or absence of OC from man-made sources along with ubiquitous contributions from natural sources. Biogenic materials, such as plant waxes, tend to have more molecules with odd numbers of carbon atoms, whereas n-alkanes from combustion processes have nearly equal quantities of even and odd carbon-numbered molecules. A Carbon Preference Index (CPI), the ratio of odd to even n-alkane masses, is used to assess the relative abundance of natural vs. anthropogenic contributions.

7.3.2.5 Secondary Organic Aerosol

SOAs are formed when some of the VOCs participate in photochemical reactions over short time periods under intense sunlight (Pandis et al., 1992), over longer time periods of stagnant conditions (Strader et al., 1999), or during long-range transport. The VOC classes that most commonly form SOAs are

described in Chapter 3. The relative importance of SOA vs. directly emitted OC is highly variable in time and space. Enrichment of the OC/BC ratio over that expected from source profiles of primary emissions has been used to estimate potential SOA contributions to OC (Turpin and Huntzicker, 1995). This approach assumes that the OC/BC ratio from primary emissions falls within a reasonable range (typically 1 to 4, depending on dominant primary contributions and OC/BC measurement method), that primary OC and BC disperse and deposit in the same way, and that all BC is of primary origin. Ambient OC/BC ratios are higher (e.g., >6) when secondary formation contributes OC in excess of that from primary emissions. Other primary OC emitters (e.g., vegetation fragments, cooking, unburned fuel, smoldering fires) can interfere with this interpretation. Organic vapors adsorbed onto quartz fiber filters may inflate OC measurements in pristine areas where actual particulate carbon concentrations are low. The same carbon analysis method must also be applied to the ambient samples and source emissions from which the primary OC/BC reference is derived (Dreher and Harley, 1998).

SOA may be a large fraction of OC during high PM_{2.5} episodes and/or at particular times of the day, such as the afternoon (Turpin and Huntzicker, 1995). Experiments in California's South Coast Air Basin (e.g., Hildemann et al., 1993; Schauer et al., 1996) and San Joaquin Valley (Strader et al., 1999; Schauer and Cass, 2000), which are discussed in Chapter 3, showed that, on average, SOA was a minor fraction of ambient OC. In the midwestern United States, Cabada et al., (2002) estimated 10 to 35 percent of annual average OC to be from SOA based on OC/BC enrichments. More specific PM end-products for SOA reactions would provide more definitive estimates of its contributions to ambient OC.

7.3.2.6 Other Chemical Markers

Isotopic abundances differ among source materials depending on formation processes and geologic origins. Radioactive carbon-14 (¹⁴C) is formed by cosmic rays in the atmosphere and is incorporated into living things through respiration and ingestion. Fossil fuels formed millions of years ago are depleted in ¹⁴C because its half life is ~5,000 years. ¹⁴C abundances allow the separation of biogenic or

“modern carbon” from carbon derived from fossil-fuel combustion (Currie et al., 1999). Estimates of fuel age must be made, as wood that grew before outdoor nuclear testing in the 1950s has much lower ^{14}C abundances than plant life that grew during and after that period. Other receptor-model applications using isotopic abundances include ^4He as a marker of continental dust (Patterson et al., 1999), ^{210}Pb to determine sources of lead in house dust (Adgate et al., 1998), and ^{34}S to determine sources of acid deposition (Turk et al., 1993) and to distinguish secondary SO_4^- contributions from residual-oil combustion (Newmann et al., 1975). Isotopes such as non-radioactive ^{34}S or radioactive ^{35}S follow the transformations of SO_2 to SO_4^- from a source type and offer a way to directly apportion the secondary PM in cases where there are large differences in profiles among contributing sources (Hidy, 1987).

Single particles can be identified in source emissions based on their shapes, sizes, mineralogy, optical properties, and elemental composition (Casuccio et al., 1983, 1989; Draftz, 1982; McCrone and Delly, 1973). Results from microscopic examination are semi-quantitative, as thousands of particles must be examined to obtain an adequate statistical representation of the millions deposited on a typical air-sampling filter. Computer-automated scanning systems with pattern-recognition methods are being developed to perform these analyses automatically (Hopke and Casuccio, 1991).

7.3.3 Temporal and Spatial Variability

Some emitters have source profiles so similar that their contributions cannot be distinguished from each other based on chemical and size characteristics. However, sources often can be discriminated by where and when the samples are taken. Although vegetative burning from wood stoves and forest fires cannot be differentiated chemically, high vegetative-burning contributions found in neighborhoods during winter logically result from residential wood combustion, while region-wide contributions during hot, dry summer months are more reasonably attributed to forest fires or prescribed burning.

Bracketing the morning traffic peak shown in Figure 7.1 with samples before, during, and after gives higher confidence that the carbon is from traffic rather than from other sources. Comparing measurements from within cities to those taken in nearby rural areas, as shown in Chapter 6, helps discriminate locally generated particles from those potentially transported into the area from upwind sources (Brook et al., 1999, 2002).

7.3.4 Combining Size, Composition, Space, and Time

Chapter 5 discusses many of the new technologies that are being developed for continuous measurements of carbon, SO_4^- , NO_3^- , and metals. As illustrated in Figure 7.1, higher time and chemical resolution will assist the association of chemical components with different sources and spatial scales. A semi-continuous elemental-analysis system (Kidwell and Ondov, 2001) shows clear, short-duration impacts from plume touchdown of nearby point sources. Several single-particle or particle-ensemble, sizing, and chemical-characterization methods are now being applied (Noble and Prather, 1996; Ge et al., 1998; Tan et al., 2002). Suess and Prather (1999) describe laser ablation of individual particles followed by on-line time-of-flight mass-spectroscopy to characterize particles from individual sources, such as biomass burning, automobile emissions, and suspended soils. Aerosol mass-spectrometers are also beginning to be applied to analyze emissions such as diesel exhaust (Jayne et al., 2001). Biomass particles are characterized by K clusters associated with Cl^- and SO_4^- (Silva et al., 1999). Vehicle-exhaust particles have been found to contain Pb, Ce, Pt, Mo, Ca, and Na (Noble and Prather, 1996; Silva and Prather, 1997). Soils are typified by individual particles containing Al, Fe, Na, Mg, K, Ca, Si, and Ti (Silva et al., 2000). Particle spectra containing Ca abundances are attributed to building materials, and K and Na have been associated with marine origins (Wiess et al., 1996). Particles containing C_2 and C_3 organic compounds with SO_4^- , NO_3^- , and Cl^- have been associated with combustion processes (Noble and Prather, 1996).

7.4 RECEPTOR MODELS AND DECISION-MAKING

Receptor methods have been widely used to justify pollution-control decisions. State Implementation Plans (SIPs) for several dozen PM_{10} non-attainment areas in the western United States were based almost entirely on receptor methods during the late 1980s and early 1990s. Many of these non-attainment areas were dominated by wood-smoke and fugitive-dust contributions under stagnant wintertime inversions (e.g., Chow et al., 1993b; Mathai et al., 1988), which were not amenable to accurate emission estimates or dispersion modeling. Watson (2002) details how receptor and source methods complemented each other to estimate contributions to haze in the Grand Canyon. Several recent examples are summarized below to demonstrate how receptor methods have been used in conjunction with other approaches in decision-making studies.

7.4.1 Sulfur Reductions in Canadian Gasoline

Removing sulfur from gasoline and diesel fuels helps decrease tailpipe emissions by improving catalyst performance and by direct reduction in the amount of primary SO_4^- and SO_2 produced. Based on this information, Canadian policy-makers considered new sulfur-content regulations. Receptor methods provided quantitative estimates of the potential improvement in air quality. These estimated improvements enabled determination of the health and economic benefits of lower sulfur in fuel – important information in the decision-making process. Health researchers initially requested that the estimated changes focus on ambient PM and SO_4^- because of the amount of quantitative information available on their health effects. Methods to estimate these changes included:

1. Source apportionment based on measurements from Canadian cities to establish that motor-vehicle exhaust was an important contributor to ambient PM levels.
2. A simple observation-based model, consisting of discrete and quantifiable sub-components

describing the processes linking vehicle emissions to $PM_{2.5}$ in urban areas.

3. Description of aerosol-related processes derived using an aerosol evolution/equilibrium observation-driven box model.
4. Application of the model and estimation of the uncertainties.

Previous Canadian and U.S. CMB studies were reviewed for information on the likely contribution of motor vehicles to PM. Combining the results of multiple, independent source-contribution estimates provided an understanding of uncertainties and similarities for different urban areas. The weight of evidence indicated that motor-vehicle exhaust was an important contributor to $PM_{2.5}$ in urban areas, regardless of location. Average primary motor-vehicle contributions were 44 ± 23 percent of $PM_{2.5}$.

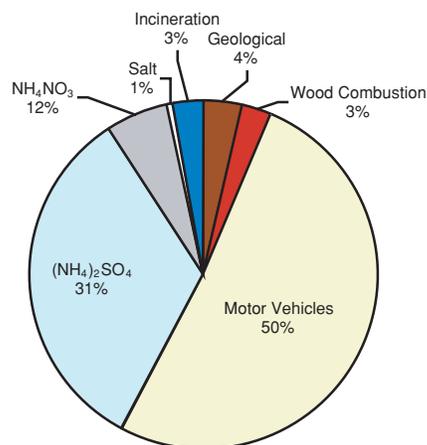
CMB source-contribution estimates from vehicle exhaust and other sources are shown for Toronto and the Lower Fraser Valley (e.g., Vancouver, BC, area) in Figure 7.7. These estimates, although uncertain because of the lack of locally-derived source profiles, were consistent with differences in carbon concentrations for different site locations and with estimates for U.S. cities with similar sources and meteorology.

An emission and air-quality modeling system, including appropriate measurements of emissions, meteorology, boundary conditions, and initial concentrations, was not available to credibly simulate the processes that would relate emission changes to ambient $PM_{2.5}$ in Canadian urban areas. A simpler, receptor-oriented conceptual model linking ambient $PM_{2.5}$ to vehicle emissions was constructed, as illustrated in Figure 7.8. The main assumptions, which were required in order to have quantifiable model sub-components, were: 1) particles in urban air can be separated into vehicle-related fractions that will and will not be affected by sulfur fuel reductions and that are independent of particles from other sources; 2) primary vehicular emissions of SO_4^- , and of SO_2 , NO_x , and VOC (PM precursors), disperse throughout an urban area, reaching typical ambient concentrations before chemical reactions take place; 3) after “inert” dispersion of the precursors, they form some SO_4^- , NO_3^- , and SOA before moving out of the

urban area; 4) the urban-air concentration of the vehicle-related $PM_{2.5}$ that is sensitive to fuel sulfur content is equal to the sum of the mass of secondary particles formed from the dispersed precursors and of the mass of the dispersed primary SO_4^- .

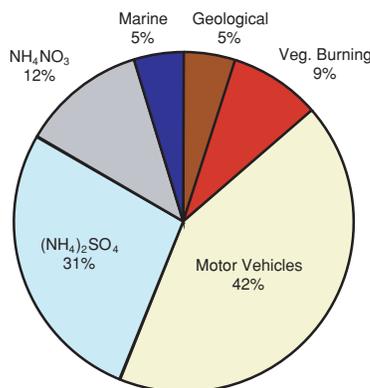
Although the conceptual model linking urban particles to tailpipe emissions in Figure 7.8 is simple, it identified the main processes and the chemical components that needed to be quantified (red and green boxes in Figure 7.8). The effects of sulfur fuel reductions on direct particle emissions of OC, BC, and other elements were unknown, and thus changes in their ambient concentration were assumed to be zero (gray boxes in Figure 7.8). Sulfate, SO_2 , NO_x and VOCs from the primary vehicle emissions were assumed to disperse like CO to estimate their ambient concentrations (red box). Observations and vehicle-emission rates for CO were used to derive a dispersion coefficient, which was then used in a CMB tracer solution to estimate vehicle-related primary pollutant concentrations. CO was used because most of it is emitted from vehicles and it does not react or deposit appreciably during the time required for dispersion throughout an urban area. A simple dispersion model and use of NO_x data in the CMB tracer solution were also considered. The primary-emission dispersion rates using these two approaches were similar to the CO-based estimate, thus lending confidence to the results and providing additional information for uncertainty estimates.

After instantaneous dispersion, SO_2 , NO_x and VOCs formed particles for a time-period equivalent to the length of time urban emissions typically remain over a city (green box in Figure 7.8). This residence time, accounting for the hours of possible photochemical transformations, was determined from available meteorological data using back-trajectories. Conversion factors allowing determination of the amount of secondary SO_4^- , NO_3^- and SOA formed during this time (green box) were derived using an aerosol-evolution model. This model was applied for several possible conditions (e.g., different seasons, different ambient NH_3 concentrations) to quantify changes in emission characteristics, and it was “tuned” to fit the observed conditions. This was done for Toronto, Montréal, and Vancouver (these conversion factors were also used for other cities where appropriate).



(a) Evans Ave., Toronto

Average $PM_{2.5} = 10.8 \mu g/m^3$



(b) Pitt Meadows, BC

Average $PM_{2.5} = 8.1 \mu g/m^3$

Figure 7.7. CMB $PM_{2.5}$ source-contribution estimates for two regions of Canada. The analyses demonstrate that, given the range of sources assumed to be important, motor vehicles contribute a large fraction. This information was used to support policy development focusing on S in gasoline. (a) Average motor-vehicle exhaust CMB contributions were 50 percent at Evans Ave., Toronto (average of twelve 24-hr observations from September 1995), which is within the range estimated for U.S. urban areas, but above the average. The Evans Ave. monitor is near high traffic volumes. (b) Average vehicle-exhaust $PM_{2.5}$ contributions in the Lower Fraser Valley of BC, at a site more distant from dense traffic, constituted ~42 percent of $PM_{2.5}$ (average for twenty-six 24-hr observations from July-August 1993). (From Bloxam et al., 1997).

The quantities of secondary SO_4^- , NO_3^- , NH_4^+ , and SOA formed from the dispersed precursors (Box 1) were added to the “dispersed primary SO_4^- concentration” (Box 2) to determine the $\text{PM}_{2.5}$ mass associated with vehicle emissions that is sensitive to fuel-sulfur content. This ‘fuel-sulfur-sensitive’ $\text{PM}_{2.5}$ was calculated using current emissions, based on actual fuel sulfur content and projected emissions,

based on several different options for sulfur content. Subtracting $\text{PM}_{2.5}^{\text{projected}}$ from $\text{PM}_{2.5}^{\text{current}}$ provided estimates of the changes in total ambient $\text{PM}_{2.5}$ mass due to the different fuel-sulfur scenarios. The structure of the conceptual model allowed uncertainties to be incorporated into the calculations. A range of probable values for emission changes, dispersion rates, and secondary-formation functions were defined and used to estimate uncertainty.

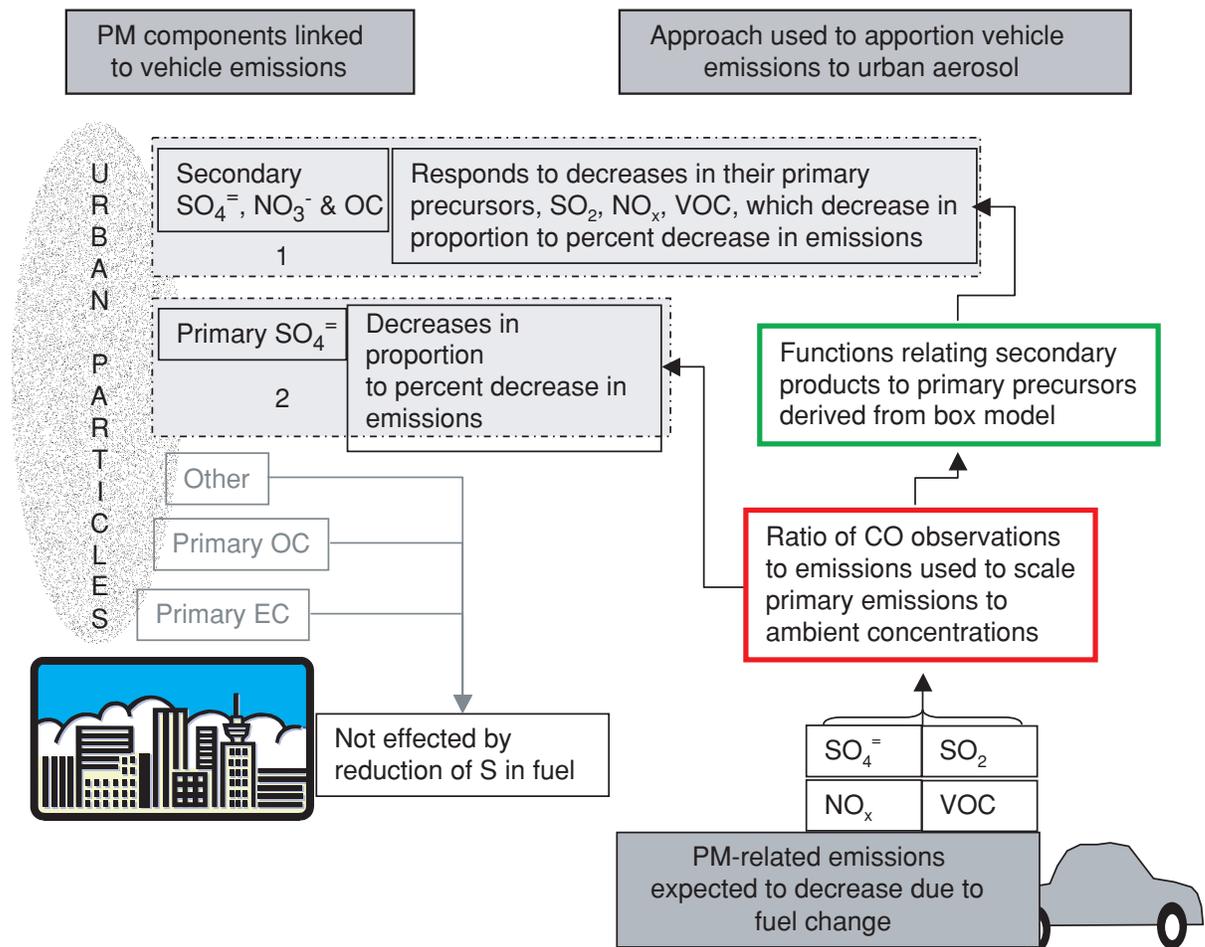


Figure 7.8. Conceptual model describing links between urban particles and tailpipe emissions of primary SO_4^- and particle precursors (NO_x , SO_2 , VOCs). Receptor methods were used to estimate the ambient concentrations of the precursors and primary SO_4^- , which were assumed to disperse like CO within an urban area (red box). After dispersion, a portion of the precursors were assumed to contribute to secondary SO_4^- , NO_3^- and SOA based on conversion rates determined from observational data and an aerosol evolution model (green box). The portion of the $\text{PM}_{2.5}$ from the tailpipe emissions that is expected to respond to reductions in fuel S was determined by summing the secondary products (box 1) and the ‘dispersed’ primary SO_4^- (box 2). Primary PM, OC, and BC emissions and other (e.g., trace elements, other inorganics) primary particle emissions were assumed to be unaffected by changes in fuel S. From this simple combination of models, estimates of the changes in urban $\text{PM}_{2.5}$ concentration due to decreasing fuel S were determined and subsequently related to health and economic benefits. (From Bloxam et al., 1997).

A gasoline sulfur reduction from 579 ppmw to 25 ppmw was estimated to result in a $0.27 \mu\text{g}/\text{m}^3$ decrease in the annual average $\text{PM}_{2.5}$ in Toronto, which represented a ~1.8 percent decrease from the current levels. Toronto was estimated to have the largest improvement, and hence the greatest potential health benefit, because its base-case sulfur levels in fuel were highest among the cities. Although a 1.8 percent reduction seems negligible, when combined with human mortality and morbidity concentration-response functions and summed over millions of people for 20 years, the estimated health and economic benefits were substantial (Thurston et al., 1998) and outweighed the estimated costs of the fuel reformulation. This information and additional health benefits arising from decreases in ambient CO , NO_2 and SO_2 (estimated from the red box in Figure 7.8) were key components in establishing the new Canadian regulations (Canada Gazette, 1998).

Although this Assessment was carried out through an open, multi-stakeholder process, and was supported through an external review, many gaps in knowledge became evident. For example, distinguishing diesel- and gasoline-powered vehicle contributions with the CMB was not possible with the available measurements. Emission rates and source profiles for Canadian vehicles using the current and reformulated fuels were not available, and it was not possible to assess how the proposed fuel changes might affect non-sulfur primary particle emissions, including those of OC and BC. The decision-making process helped identify knowledge gaps with strong relevance to policy. This provided guidance for research that could be expected to improve future assessment cycles.

7.4.2 $\text{PM}_{2.5}$ and Urban Haze in Denver, CO

The Denver Brown Cloud has been the subject of five major studies, and numerous smaller ones, since 1973. A 1987-88 study (Watson et al., 1988) identified secondary NH_4NO_3 and carbon as the largest chemical components, with wood smoke and vehicle exhaust being the largest contributors to the carbon as determined by the CMB model. With the available measurements, diesel contributions could not be distinguished from gasoline-vehicle exhaust,

and wood burning could not be distinguished from cooking contributions. A 1996-97 study (Watson et al., 1998) refined these CMB results by measuring organic markers (see Figures 7.5 and 7.6), which were sufficient to separate these source contributions, as well as gasoline-exhaust contributions from cold-starts and poorly-maintained vehicles. This more recent study also used an aerosol-equilibrium model to examine the limiting precursors for NH_4NO_3 .

Relative contributions from the emission inventory and CMB source apportionment are compared in Figure 7.9. Even when secondary SO_4^{2-} and NO_3^- contributions are removed from the total $\text{PM}_{2.5}$, there are substantial discrepancies. For fugitive dust, the inventory shows nearly twice the fraction compared to ambient observations and CMB model apportionment. This discrepancy has been attributed to inequivalence between suspendable and transportable dust in urban- and regional-scale fugitive dust inventories (Watson and Chow, 2000; Countess et al., 2001). A large part of the suspendable fraction deposits to the ground near its point of suspension and does not contribute ambient PM at larger distances.

The other discrepancy in Figure 7.9 is that between gasoline-vehicle exhaust and diesel exhaust contributions: the inventory indicates that diesel emissions are four times those of gasoline-vehicles. This is true for the hot-stabilized fraction of gasoline-vehicle exhaust. However, when the emissions from gasoline cold-starts and poorly-maintained vehicles are added, the ratio reverses. These results are confirmed from the emission rates measured during the source characterization tests (Cadle et al., 1998; Zielinska et al., 1998). Denver (Watson et al., 1998) and Los Angeles (Hildemann et al., 1994; Kleeman et al., 1999b) have included PM emissions from cooking in their inventories, but this and other potential sources have been neglected in most urban inventories. Through application of receptor models, the importance of these sources and others has been identified. This has led to improvements in emission inventories and has expanded the number sources that potentially could be controlled to reduce particle levels. *The discrepancy between the importance of dust to $\text{PM}_{2.5}$ emissions versus its importance to the observed ambient $\text{PM}_{2.5}$ observed in Denver is*

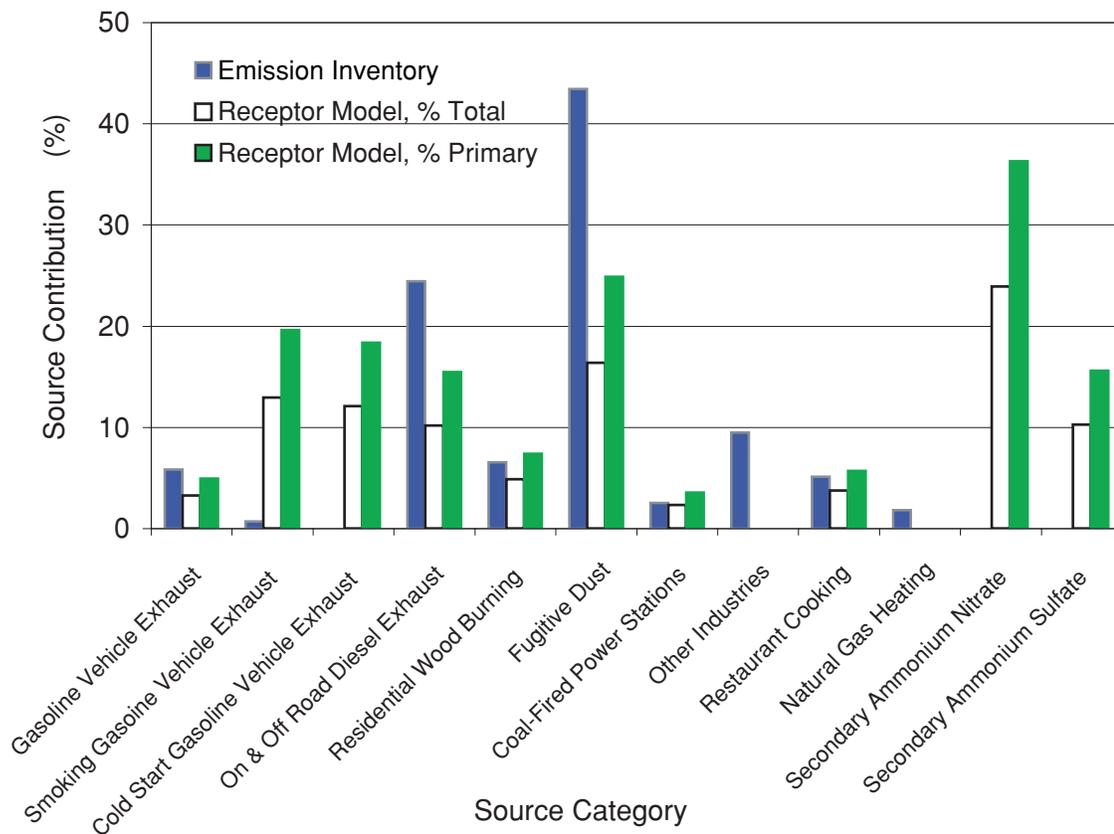


Figure 7.9. Comparison of fractional source contributions to $PM_{2.5}$ during 1996 in Denver, CO, (Watson et al., 1998) from an emission inventory, receptor-model source contributions as fraction of total $PM_{2.5}$, and receptor-model source contributions as fraction of primary $PM_{2.5}$ ($PM_{2.5}$ minus secondary NH_4NO_3 and $(NH_4)_2SO_4$ contributions). Fugitive dust emissions are overestimated by the inventory relative to quantities in ambient air. The cold-start gasoline category is not in the inventory because the standard Federal Test Procedure (FTP) for gasoline-vehicle exhaust emissions allows vehicles to equilibrate at summertime temperatures prior to testing. High emitters (poorly-maintained vehicles) are also underrepresented in most FTP testing. These discrepancies point toward improvements needed in the emission inventory. They also highlight the observation that inventories by themselves cannot be used to plan $PM_{2.5}$ reduction strategies. (After Watson and Chow, 2001b).

common throughout North America. This suggests that methods for estimating fine-particle dust emissions require significant improvement.

The 1996-97 Denver study showed that measures to reduce wood-burning emissions implemented as a result of the 1988 study had been effective. Approximately half of the $PM_{2.5}$ that would have been attributed to wood smoke without the organic markers was found to derive from meat cooking, as evidenced by the ambient sterol levels. Although diesel-emission reductions are still being considered, additional control measures are being investigated for the other sources.

Figures 7.10a through 7.10c show how changes in NH_3 , HNO_3 , and SO_4^{2-} affect ambient concentrations. This analysis was important for local decision-makers because NH_3 emission reductions were being considered (and were eventually implemented) by the South Coast Air Quality Management District (1996) to reduce PM_{10} concentrations in southern California. Logically, this was also being considered for Denver. Figure 7.10a shows that no increases in NH_4NO_3 result from increases in NH_3 concentrations where the present concentration (i.e., no change in NH_3) is given as 100 percent along the x-axis. A 25 percent reduction in NH_3 (from 100 percent to

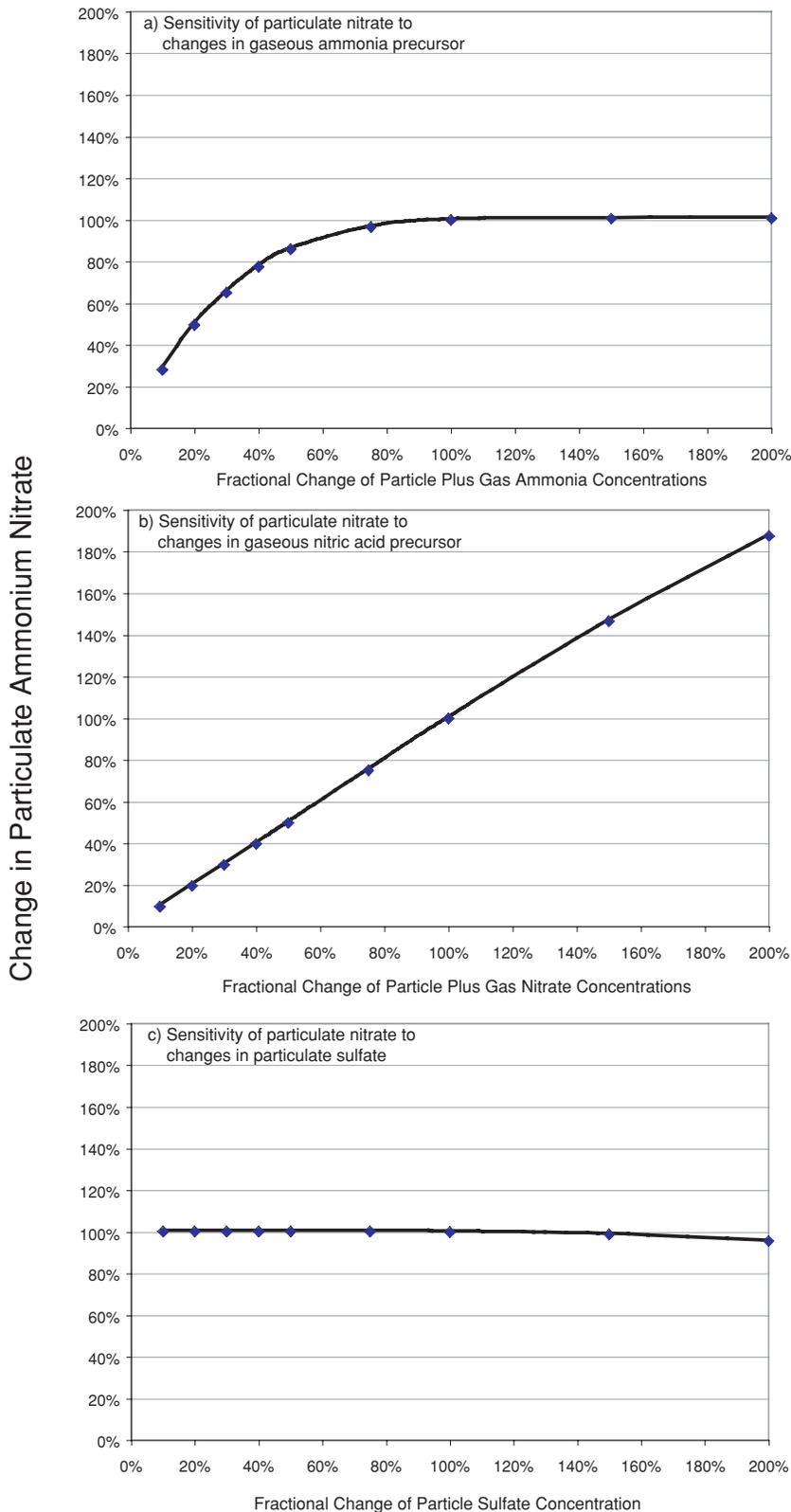


Figure 7.10. Effects of changes in (a) NH_3 , (b) HNO_3 , and (c) $\text{SO}_4^{=}$ levels that might result from emissions-control strategies on average NH_4NO_3 concentrations estimated using the Simulating Composition of Atmospheric Particles at Equilibrium (SCAPE) equilibrium model (Kim et al., 1993a, 1993b; Kim and Seinfeld, 1995). The aerosol-equilibrium receptor model apportions Na , NO_3^- , $\text{SO}_4^{=}$, NH_4^+ , and Cl^- among gas, liquid, and solid phases using thermodynamic equilibrium theory, as described in Chapter 3. These averages were derived from thousands of individual SCAPE simulations applied to 3-hour periods over which PM NO_3^- , $\text{SO}_4^{=}$, and NH_4^+ and gaseous HNO_3 and NH_3 were measured at urban and non-urban receptor sites in the Denver area. Ambient temperature and relative humidity corresponding to the samples are the other SCAPE inputs. This analysis is being used by decision-makers to focus emission-reduction efforts on HNO_3 precursors rather than NH_3 emissions. The horizontal axis represents the fraction of the measured 1996 concentration. (From Watson et al., 1998).

75 percent) results in a minor reduction in particle NO_3^- and a reduction of 50 percent NH_3 reduces particle NO_3^- by only 15 percent. After a 50 percent NH_3 reduction, however, PM NO_3^- decreases are nearly proportional to NH_3 reductions. Ammonia levels must be reduced by more than half before large reductions of PM NO_3^- are realized. This contrasts with Figure 7.10b, which examines effects of HNO_3 reductions on PM NO_3^- . Changes in HNO_3 , presumably resulting from changes in NO_x emissions that contribute to HNO_3 , result in a direct and proportional reduction in $\text{PM}_{2.5}$ NH_4NO_3 concentrations. Figure 7.10c shows that there is no sensitivity to changes in $\text{SO}_4^{=}$ levels. This is because there is sufficient free NH_3 in the Denver area that the small amount of NH_3 freed by removing $\text{SO}_4^{=}$ from the atmosphere has no effect on NH_4NO_3 levels.

7.4.3 Haze in the Grand Canyon

Frequent and intense hazes in Grand Canyon National Park have obscured natural vistas to the extent that a Grand Canyon Visibility Transport Commission (GVTC) was established to determine how particle concentrations should be reduced. Earlier studies (Malm et al., 1989; Richards et al., 1991) used receptor-oriented methods to attribute portions of the $\text{SO}_4^{=}$ measured in the Grand Canyon to the Navajo Generating Station located at the northeastern edge of the Canyon. The source-attribution methodology and results were contested (Markowski, 1992, 1993; Malm et al., 1993; Richards, 1993), but they were qualitatively similar to results from a follow-up study that used independent measurements and models (Richards et al., 1991). Sulfur dioxide scrubbers were installed and recently commenced operation at that facility.

Another uncontrolled coal-fired power station located southwest of the Canyon, the Mohave Power Project (MPP), was not found to be a wintertime contributor in these studies, but it was believed to be a contributor during summer. Another study (Pitchford et al., 1999) was undertaken during summer of 1992 to determine the MPP contribution to $\text{SO}_4^{=}$ and its subsequent contribution to the haze. This ~\$US 10M study included perfluorocarbon tracer gas releases from the MPP stack and two other source areas. Upper-air meteorological measurements, ground-based

chemistry measurements at more than 30 locations, special studies of PM size distributions, fogs, and peroxides, and compilation of measurements into a common data base were included. Project MOHAVE data were also used for the GVTC assessment related to regional haze (Mathai, 1995, 1996). This large data base allowed many different receptor and source models to be applied, as summarized in Table 7.2.

Source-contribution estimates from the applied models generally showed that MPP $\text{SO}_4^{=}$ contributions were a small fraction of the measured $\text{SO}_4^{=}$. However, the inert tracer gas could not mimic gas-to-particle conversion. It was useful to determine when MPP emissions were present or absent, but it did not add much information on $\text{SO}_4^{=}$ contributions. Tracer levels were typically highest when a receptor was directly impacted by a coherent plume, but generally there was insufficient time for conversion of SO_2 to $\text{SO}_4^{=}$ under these circumstances. Source-contribution estimates from the many models applied were inconsistent with each other, as illustrated in Figure 7.11. The weight-of-evidence was that the MPP contribution was detectable on several occasions, but that it was not the major cause of the haze and that quantitative MPP source contribution estimates were very uncertain.

Regulatory negotiations subsequent to the study used its results with other considerations to agree that the MPP would install state-of-the-art SO_2 scrubbers or cease operation by 2006.

Grand Canyon haze studies of individual source and regional source contributions have provided an evolving understanding of the cause of haze in the desert Southwest. The involvement of stakeholders (including power-station owners and operators) in the acquisition of this knowledge has resulted in commitments for progress toward continual improvement (Mathai et al., 1996; Chow et al., 2002b). The direct influence of individual studies on regulatory policy regarding emission controls on power stations and other sources was limited. However, their results have had a major influence on subsequent policy development employing air-quality models. The timing of this impact is ambiguous because of the lengthy cycle of assimilation of scientific results into the regulatory hierarchy. The results added an important perspective

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on the magnitude of expected benefits to visibility improvement associated with single sources. This perspective reinforced the need for a corroborative approach to establish the basis for regulatory involvement in prescribing emission controls for regional haze improvement. At this time, there is no

formal protocol for measuring the benefits of SO₂ emission reductions from power stations to visibility improvement in the Grand Canyon area. However, this appears to be an ideal location for tracking such progress, in the light of the influence of other regional sources (Watson, 2002).

Table 7.2. Receptor and source methods used to attribute SO₄⁼ in the Grand Canyon to Mohave generating station and other source emissions (Pitchford et al., 1999).

Method	Description	Inputs	Outputs
Receptor Data Analyses			
Tracer Max (Tracer Scaling)	Multiplies perfluorocarbon tracer (PFT) concentration at receptor by ratio of total sulfur to PFT in stack emissions. Provides upper bound for MPP SO ₄ ⁼ contributions.	PFT, SO ₂ , and PM sulfur concentrations at receptors; emission ratio of SO ₂ /PFT.	Contribution of PFT source to ambient S (SO ₂ + SO ₄ ⁼); upper bound estimate of contribution to PM sulfur.
Exploratory Data Analysis	Statistical analysis of SO ₂ , PM sulfur, and PFT measurements.	PFT, SO ₂ , and PM sulfur concentrations, and particle light scattering at receptors.	Spatial correlations of PM sulfur, temporal correlations of PFT, SO ₂ , and PM sulfur at specific sites.
Tracer Regression	Regression of total light extinction (b _{ext}) against PFT, industrial methylchloroform, and water vapor mixing ratio.	PFT, methylchloroform, and mixing ratio measurements at receptors.	Contributions to light extinction from emissions in source regions of the chosen tracers.
Tracer Aerosol Gradient Interpretative Technique (TAGIT)	PFT measurements identify nearby sites with and without MPP impact. MPP SO ₄ ⁼ contribution is the increment over unimpacted sites.	PFT, SO ₂ , and PM sulfur concentrations at multiple receptors.	SO ₂ and PM sulfur concentrations attributable to sources/source regions where PFT was emitted .
Modified CMB	CMB regional profiles modified to account for conversion and deposition of SO ₂ and SO ₄ ⁼ with aerosol evolution model.	Source/source-regions and receptor concentrations of SO ₂ , SO ₄ ⁼ , and markers elements, spherical aluminosilicate, light absorption (b _{abs}), relative transport times; ROME transport model estimates of relative conversion rates for emissions from different sources/source-regions.	SO _x and SO ₄ ⁼ attributable to sources/source- regions, including region containing MPP emissions.
Tracer Mass Balance Regression (TMBR)	Multiple linear regression of SO ₂ against PFTs and of PM sulfur against PFTs.	Concentrations at receptors of PFT, SO ₂ , and PM sulfur.	SO ₂ and PM sulfur concentrations attributable to MPP
Differential Mass Balance Regression (DMBR)	Combination of tracer-based dilution calculation with parameterized deposition and conversion.	Concentrations at receptors of PFT and SO ₂ ; times of travel from source to receptors; estimates of conversion rates; index of cloud cover.	SO ₂ and PM sulfur concentrations attributable to MPP.

Table 7.2. Receptor and source methods used to attribute $\text{SO}_4^{=}$ in the Grand Canyon to Mohave generating station and other source emissions (Pitchford et al., 1999) (continued).

Method	Description	Inputs	Outputs
Source Emissions Simulations			
HAZEPUFF (Modified)	Lagrangian puff model; interpolated wind field; first order SO_2 to SO_4 conversion; modified dispersion classes.	Vertical wind measurements, PFT and SO_2 emissions from MPP, relative humidity.	Plume locations and concentrations of PFT, SO_2 , SO_4 , and light scattering attributable to MPP.
CALPUFF/CALMET	Multi-layer Gaussian puff model with parameterized first order chemical conversion; diagnostic meteorological model.	Surface and upper air meteorological data, topography, PFT and SO_2 emissions from MPP, solar radiation, ambient O_3 .	Distribution of concentrations of PFT, SO_2 and SO_4 attributable to MPP.
ROME/RAPTAD/HOTMAC	Lagrangian plume model with explicit reaction chemistry; three-dimensional Lagrangian random puff dispersion; primitive equation meteorological model.	Meteorological soundings, topography and land use, solar radiation; MPP emissions of PFT, SO_2 , NO_x , and trace metals; background chemical concentrations; PFT concentrations at receptors.	Concentrations of PFT, SO_2 and SO_4 in MPP plume, at surface and aloft.

7.4.4 Understanding the Sources of PM_{10} and $\text{PM}_{2.5}$ in Mexico City

Much of the recent effort to understand the causes and control of PM in Mexico City has been directed at developing and using a technical infrastructure. A CMB source-apportionment study (Vega et al., 1997) was conducted at one site in 1989-1990. $\text{PM}_{2.5}$ was strongly influenced by primary carbon particles from motor-vehicle emissions, with substantial contributions from secondary particles ($\text{SO}_4^{=}$, NO_3^- , and NH_4^+), as well as dust. This study found refinery emissions to be a major contributor, and the large, but obsolete, refinery was eventually shut down. Infrastructure development for PM assessment then focused on an intensive wintertime field study in 1997 and a source-testing study in 1998. This involved several research groups from Mexico and the United States. This effort included application of several of the receptor-oriented methods described here. They are being used to develop a conceptual model of the causes of elevated concentrations (Molina and Molina, 2002).

Chemical analysis of the samples taken in the 1997 study provided a picture of spatial variation across

Mexico City (Figure 7.3). The study showed that fugitive dust was one of the largest PM_{10} contributors and affected some parts of the city more than others. $\text{PM}_{2.5}$ was dominated by carbon, with significant additions from secondary particles ($\text{SO}_4^{=}$ and NO_3^-), and dust. These results were consistent with the earlier work of Vega et al. (1997) and demonstrated the spatial extent of the problem and likely contributors. Evidence of the high $\text{SO}_4^{=}$ and trace metals caused by the closed-down refinery were not detected in 1997, indicating the success of the previous decision. The results confirm a continuing need for reduction in carbon sources, including motor-vehicle emissions, and fugitive dust, as a part of the Mexico City clean-air strategy. Equilibrium modeling (Moya et al., 2001) showed that NH_4NO_3 was not limited by available NH_3 , which was plentiful. Reductions in secondary $\text{SO}_4^{=}$ will require regional pollution controls, as 70 percent of $\text{SO}_4^{=}$ in the city was accounted for at the boundary monitors. Secondary PM reductions will require continuing efforts to reduce industrial emissions, combined with fuel sulfur reductions, and reductions in NO_x from stationary and mobile sources (e.g., Molina and Molina, 2002).

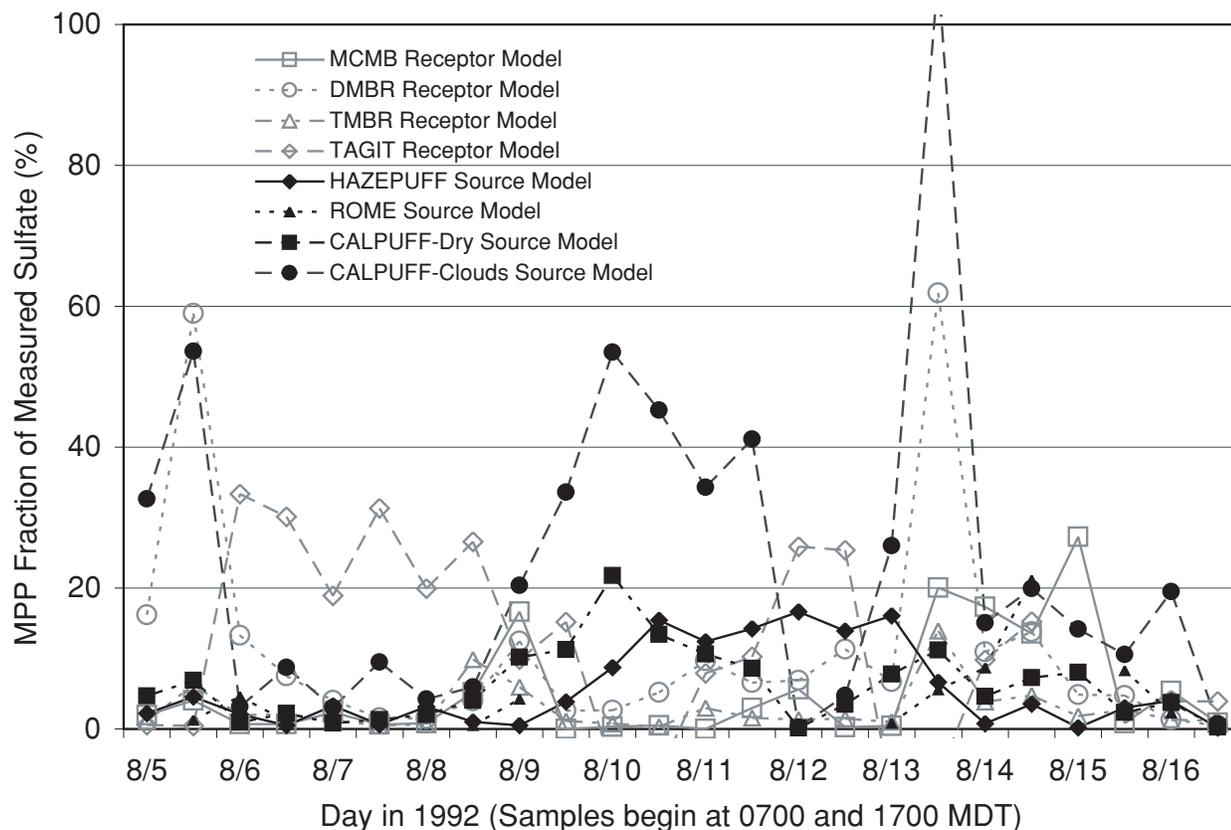


Figure 7.11. Comparison of fractions of $\text{SO}_4^{=}$ at Meadview, AZ, contributed by the MPP as estimated by different source and receptor models (Pitchford et al., 1999). This is a 12-day excerpt from the 7/12/92 through 8/31/92 results (Watson, 2002). Twelve-hour fractional contributions were estimated by a Modified Chemical Mass Balance (MCMB, Eatough et al., 2000), Differential Mass Balance Regression (DMBR, Malm et al., 1997), Tracer Mass Balance Regression (TMBR, Malm et al., 1997, the Tracer Aerosol Gradient Interpretive Technique (TAGIT, Kuhns et al., 1999,) U.S. EPA's HAZEPUFF plume model, Reactive and Optics Model of Emissions (ROME, Karamchandani et al., 2000), and the U.S. EPA's CALPUFF model with clear air (CALPUFF-Dry) and aqueous (CALPUFF-Clouds) $\text{SO}_4^{=}$ transformation. CALPUFF results were intended to represent low (dry) and high (clouds) transformation conditions to bound potential MGS contributions rather than estimate them. (After Watson, 2002).

7.5 DEVELOPING PM MANAGEMENT STRATEGIES

Receptor analyses can assist in determining how much of the observed PM is manageable and unmanageable, as well as the source types that contribute to undesirable concentrations. In some situations, receptor analyses may help identify specific sources of importance (attribution).

7.5.1 Manageable and Unmanageable Source Contributions

The broad distinctions between manageable and unmanageable sources were discussed in Chapters 1 and 3. Cases where unmanageable emissions cause exceedances are uncommon and usually identifiable as special events (e.g., visible smoke from wildfires or windblown dust plumes). These events need to be recorded so that they can be specially considered when determining compliance with air-quality

standards. Unmanageable natural emissions usually account for a minor (<20 percent) fraction of $PM_{2.5}$ during normal situations. Confidence in the contributions from natural OC and natural SOA is low.

From a practical standpoint, manageable sources can be classified as being either managed or unmanaged. Managed emitters are those that arise from human activities subject to permits and/or to emission-reduction strategies within a given political jurisdiction, such as a city, county, state, province or air-quality management district. Conversely, unmanaged emitters arise also from human activity, but they are not subject to such measures. This may be due to the nature of the emissions (e.g., difficult to control) and possibly because they are assumed to be relatively small. In this context, measures can be undertaken to reduce unmanaged emissions, albeit at a cost that may not be considered acceptable. Agricultural operations, for example, are often exempt from on-road emission standards for vehicles and dust controls applied to construction sites. *The fraction of OC from natural sources is unknown, but is potentially large. Detailed organic measurements and subsequent receptor-model studies need to be carried out to determine the importance of natural primary and secondary OC sources to $PM_{2.5}$ and PM_{coarse} .*

At a local level, emissions from human activities outside of an air-quality management district's jurisdiction can be viewed as being unmanageable. They may or may not be managed under the auspices of another jurisdiction, but the downwind districts have no direct management authority. Regional transport of $PM_{2.5}$ or its precursors across city, county, state/provincial, and international boundaries is common, especially for $PM_{2.5}$ and SO_4^{2-} . As the data in Chapter 6 show, this transport can cause high $PM_{2.5}$ concentrations in rural areas which are comparable to, and are part of, concentrations in nearby urban centers and which may affect downwind populations. Transported anthropogenic $PM_{2.5}$ is manageable, but management requires broader cooperation among jurisdictions and control strategies that are consistent among national and international governing bodies.

Receptor models that rely solely on chemical components cannot distinguish between manageable

and unmanageable sources, or between managed and unmanaged sources because their chemical compositions are often similar (e.g., natural vs. prescribed fire, natural windblown vs. construction dust). The greater the distance between the source and the receptor, the more difficult the distinction becomes, owing to the greater potential for atmospheric processes to alter the characteristics of the $PM_{2.5}$. Source apportionment on samples taken at different times and locations that maximize the potential differences between these managed, unmanaged, and unmanageable contributions can be contrasted to estimate contributions from each category.

7.5.2 Main Contributors to Manageable PM

Receptor methods are necessary, but not sufficient, for identifying source types and quantifying their contributions to PM. These methods depend on the measurements available, and quantitative apportionment is less likely to be accurate when applied to measurements that have not been taken for this specific purpose. As with all approaches for studying the relationship between emissions and ambient concentrations, receptor methods have strengths and weaknesses. Therefore, multiple observation-based, receptor- and source-oriented approaches, including detailed examination of emission inventories, should be undertaken to compensate. This corroborative approach helps characterize uncertainties and assess the consistency and strength of the results, which leads to more well-rounded information for decision-making, even when there are disagreements. Since receptor methods are based on actual observations, they provide an independent check on the emission inventories and some aspects of the source model (CTM) results.

From the discussion above, it is apparent that a sustained, iterative effort is needed to continually refine the conceptual model for high concentrations in an area. Building upon current knowledge leads to the design of measurement programs that make receptor- and source-modeling methods more effective. The cycle of assessments and measurement/modeling studies provides clearer focus on uncertainties identified in previous studies so that understanding of a problem improves over time.

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After undertaking case-studies employing simpler observational methods, which may be used directly to guide some decisions, the following steps, which fit into the overall framework for PM science and management (Figure 1.1), should be followed:

1. Formulate conceptual model. Use the conceptual model derived from analysis of existing data (observational methods) and studies in similar areas to guide the location of monitoring sites, sampling periods, sampling frequencies, sample durations, sampling methods, the selection of samples for laboratory analysis, and the species that are quantified in those samples. The conceptual model may also help identify which factors that affect PM concentrations in a given area (e.g., emissions, secondary formation, transport) are most important and/or most uncertain so that subsequent actions/activities are focused accordingly.
2. Compile emission inventory. Receptor models need to know which sources are potential contributors. The models then quantify those contributions and help focus resources on those emitters that are the most important contributors to PM concentrations. A receptor-model inventory requires only source categories, not the locations and rates of specific sources.
3. Characterize source emissions. Chemical or physical properties that are believed to distinguish among different source types are measured on a representative set of emitters. Source profiles are the mass abundances (fraction of total mass) of a chemical species in source emissions and the expected variability in the mass fraction. Source profiles are intended to represent a category of sources rather than individual emitters. Several compilations of particle profiles are available that might be applicable to an initial source apportionment, but these profiles will not necessarily represent the sources affecting the current area of interest if they were not measured from sources in this area.
4. Analyze ambient samples for mass, elements, ions, and carbon and other components from sources. Elements, ions ($\text{SO}_4^{=}$, NO_3^- , Cl^- , NH_4^+ , Na^+ , K^+), OC, and BC are sufficient to account for most of the particle mass, with reasonable assumptions about unmeasured oxides and hydrogen contents. Additional categories such as organic compounds, operationally-defined carbon fractions, isotopic abundances, and single-particle characteristics further distinguish source contributions from each other, even though they may not constitute large mass fractions.
5. Confirm source types with multivariate model. If a sufficient number of chemically characterized ambient samples is available (more than 50), multivariate analyses are helpful to determine the source types and profile characteristics that might be contributors.
6. Quantify source contributions. A CMB model estimates source contributions based on the degree to which source profiles can be combined to reproduce ambient concentrations. The CMB attributes primary particles to their source types and determines the chemical form of secondary PM when the appropriate chemical components have been measured. The PMF and UNMIX models are CMB applications that attempt to derive source profiles from the ambient measurements.
7. Estimate profile changes and limiting precursors. Source characteristics may change during transport to the receptor, the most common change being conversion of SO_2 and NO_x gaseous emissions to $\text{SO}_4^{=}$ and NO_3^- particles. These changes can be simulated with aerosol-evolution models under certain, but not all, conditions. Secondary $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 involve NH_3 from non-combustion sources that may be a limiting precursor. Chemical-equilibrium receptor models determine the extent to which one or the other precursor needs to be diminished to achieve reductions in NH_4NO_3 levels.
8. Apply source-oriented models. If available, source-oriented models can be used to examine the contribution of precursor-gas emissions from a variety of source categories to secondary particles and to contrast this contribution with the total particle mass. More advanced aerosol-evolution modeling, taking into account

horizontal/vertical transport, can be undertaken to test for limiting precursors. Depending on the spatial scale of the problem, it may be necessary to use the source-oriented model (CTM) to assess the role of upwind sources of primary and secondary particles relative to local sources.

9. Develop scenarios for source-oriented model (CTM) runs. Sources or source categories found to be significant contributors based upon the observational analyses or the receptor models should be targeted in emission-control scenarios set up for the CTM. This will help confirm the sensitivity of the PM levels to these sources and potentially identify optimum approaches for reducing PM.
10. Reconcile source contributions from the receptor models with other data analyses, with the inventories and with source models. Since no model, source, or receptor is a perfect representation of reality, the results must be independently challenged. Receptor-model source contributions should be consistent among locations in the current area of interest and across different sampling times and methods. If possible, discrepancies between source contributions suggested by the emission inventories and estimated by source and receptor models should be resolved. This will improve the models and/or the emission data. Remaining discrepancies should be made explicit to decision-makers.

7.6 SUMMARY

Receptor methods are useful for quantifying contributions from different sources to ambient concentrations, developing and refining conceptual models for source-receptor relationships, verifying emission inventories, and as an independent check on CTM or source model results. Given the complexity of the physical and chemical processes influencing PM-related emissions and atmospheric behavior, it is not surprising that receptor methods are not usually sufficient, by themselves, to characterize and quantify the source-receptor system. The approach to deal with the uncertainties and to obtain the best understanding of source-receptor

relationships involves careful analysis of all data and the application of multiple techniques, from analysis of emission data to CTMs. Receptor methods play an important role in this corroborative approach and new techniques that combine receptor models, which tend to be empirical, with physically based models will lead to further insights. As is the case for all approaches, successful receptor modeling depends on the quality of the measurements, ambient and source, and the availability of source markers, as well as the experience of the air quality analyst.

Source apportionment by receptor or source models must begin with plausible hypotheses about the causes of high concentrations or effects. These are derived from previous experience and background information/data, which might immediately suggest appropriate remedial actions or, if not, will direct the application of appropriate receptor methods and/or help guide the development of targeted field studies. With the available background information/data, semi-quantitative receptor-oriented data analyses should be performed prior to quantitative receptor modeling. These simple observational methods of analysis can provide insights regarding the sources or source regions influencing the PM concentrations in an area and possible limiting precursors, which will help develop or refine a conceptual model describing the source-receptor relationships in the region of interest.

Receptor methods apply to the measurement periods and locations where the required measurements are available, and the conceptual model should be used to select these sites and times. Receptor methods are measurement-intensive, requiring many chemical components taken over a representative period at a number of monitoring sites. Once these data are available, however, receptor methods are inexpensive to apply. However, it is important to realize that the required measurements are seldom available in retrospect and thus, must be planned for in advance.

Receptor methods that rely solely on chemical components do not distinguish between manageable and unmanageable emissions or between managed and unmanaged emissions because the particles from these different source categories can have very similar chemical compositions. The greater the distance from the source to the receptor, the more difficult the

distinction becomes due to the greater potential for atmospheric processes to alter the characteristics of the particles. Source apportionment on samples taken at different times and locations that maximize the differences between these managed, unmanaged, and unmanageable contributions can be contrasted to estimate contributions from each category. Multiple observation-based, receptor- and source-oriented approaches need to be applied to gain as complete of an understanding as is possible. Conclusions drawn from this corroborative approach will be more defensible for decision-making, even when there are disagreements, and agreement between approaches clearly increases confidence.

Specific answers to NARSTO science questions require specification of where and when they apply. Receptor methods have a role to play in obtaining answers that are accurate and precise enough to make well-informed decisions that are likely to result in successful emission-reduction strategies. The answers given below highlight the extent to which receptor methods have the potential to gain these answers with the appropriate data.

7.7 POLICY IMPLICATIONS

The contributions of different species to ambient PM concentrations can be assessed reasonably well. The major chemical components of fugitive dust, organics, BC, $(\text{NH}_4)_2\text{SO}_4$, and NH_4NO_3 can be separated by commonly used chemical analyses, although sampling and analysis methods give operational, rather than absolute, concentrations of OC and BC that are not always comparable (Chapter 4). The presence or absence of industrial contributions can be determined from trace-element measurements.

Anthropogenic and biogenic sources of PM species can be distinguished reasonably well. In areas with a PM problem, the large majority of the SO_4^- and NO_3^- is of anthropogenic origin. The main uncertainty currently lies with the carbon component of the PM. Carbon resulting from fossil-fuel combustion can be separated from carbon of more recent (modern or contemporary) origin because ^{14}C is depleted in fossil-fuel carbon. However, within the group of contemporary carbon compounds there

remain both natural and anthropogenic components (e.g., wildfires vs. fireplaces, vegetative emissions or decay vs. cooking). For primary particles, there is reasonable success in apportioning the modern or total OC to sources using specific organic markers or operationally-defined carbon fractions. In theory, this approach can distinguish between different types of vehicle exhaust, cooking, vegetative burning, vegetation fragments, etc. However, given the large fraction of OC on particles that cannot be identified through chemical analysis, there also may be more primary biogenic PM carbon compounds for which there are no clear marker species and which thus will not be apportioned properly. Carbon fractions that are not necessarily associated with specific compounds may yield different profiles for different source types. Unfortunately, at the present time there are insufficient data from source-characterization studies to fully test the use of organic markers to determine the extent to which they are successful at quantifying source contributions.

Relative contributions of primary and secondary PM can be distinguished. Secondary SO_4^- , NO_3^- , and NH_4^+ can be measured accurately and subtracted from total mass to estimate the fraction of PM composed of inorganic secondary material. A portion of $\text{PM}_{2.5}$ OC also results from the conversion of heavy hydrocarbons to condensable organic compounds. Polar oxygenated compounds are indicative of SOA formation, but they also result from primary PM emissions. Many of the SOA compounds are not quantified by existing measurement technologies. OC/BC ratios in excess of five or six may indicate an important contribution from SOA, but there are also primary OC sources that are depleted of BC. The OC/BC ratio is highly dependent on the thermal evolution protocol, and the method needs to be the same for primary emissions and receptor samples. However, this method may not be as appropriate in eastern North America due a greater impact from long-range transport and to the more “aged” air mass that affects the region. It also is not a very reliable method when BC concentrations are low, owing to measurement uncertainties. The ability to separate OC both in terms of natural vs. anthropogenic and primary vs. secondary (i.e., four groups) is limited at this time. This is a major knowledge gap that requires considerable research. Some secondary organic

products on particles formed from biogenic emissions (i.e., natural and secondary) can be chemically identified and apportioned to natural sources, but reliable separation of secondary organic carbon into natural and anthropogenic origin is not entirely possible at this time. An obvious complicating factor is that the distribution of OC into these four groups changes from place to place and over multiple time scales (i.e., daily and seasonally) at a given location. Consequently, a definitive answer may never be known, but through a corroborative approach enough can usually be learned to support specific policy decisions.

Relative contributions of local and long-range transport to $PM_{2.5}$ and coarse-particle concentrations can be distinguished. Source profiles are often similar for distant and nearby sources and thus, multiple techniques including detailed observation-based analyses need to be used to address this question. To gain insight into the relative importance of local and long-range transport, source-receptor models must be applied at locations and times that are expected to be more or less influenced by various scales of influence, nearby (<1 km of the monitor), neighborhood (1 to 5 km), urban (>10 km), and regional (100 to 1000 km). Conducting such an analysis clearly requires a well thought-out conceptual model and obviously, the situation varies geographically. Comparison of source-contribution estimates for short-term or long-term averages from the locations impacted over different time and space scales can be used to separate source contributions related to the different spatial scales. However, there has been very little work done on this issue at the present time and thus, new measurements and research are needed.

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