

A review of advancements in particulate matter sampling and analysis and its application to identifying source impacts at receptor locations

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Abstract

Time-integrated (typically 24-hr) filter-based methods (historical methods) form the underpinning of our understanding of the fate, impact of source emissions at receptor locations (source impacts), and potential health and welfare effects of particulate matter (PM) in air. Over the last 40 years, many of these methods have been thoroughly evaluated and there is reasonable confidence with what they measure and associated uncertainties. These methods require transport of samples collected in the field to a laboratory for analysis of PM properties of interest. Over the last decade, significant progress has occurred in the development and evaluation of continuous and semi-continuous methods that combine the collection and chemical or physical property analysis into one instrument. These methods are placed in the field, providing often near-real time data, most with hourly time-resolution or better from bulk to single particle information from a few nanometers to 10 μm . Many of the continuous chemical property methods developed and tested still require additional evaluation and comparison among themselves and to historical methods, the latter the primary basis for comparison since in-the-field, through the inlet reference standards are not available for most PM components. Despite lesser confidence in these methods relative to historical methods, data generated from these methods have greatly enhanced the application of approaches to link and quantify the impact of source emissions at receptor sites and to associate PM with health effects, as well as significantly advancing our understanding of atmospheric chemistry and the fate of PM in air. This paper briefly reviews the two primary modeling methods for estimating source contributions at receptor locations and current measurement methods with a focus on continuous measurements.

Keywords: continuous methods, chemical composition, real-time data, PM₁₀, PM_{2.5}

Introduction

Atmospheric particulate matter (PM) is a complex mixture of solid and liquid particles suspended in ambient air (i.e., the atmospheric aerosol) (Seinfeld and Pandis 1998; NARTSO 2004; Solomon and Hopke 2008). Ambient PM of interest to the regulatory and health communities are those that impact human health and welfare and range in size from a few nanometer (nm) to ~10 microns (μm), thus covering at least 4 orders of magnitude (EPA 2004; Davidson *et al.* 2005; Solomon and Costa 2009). Ambient PM arises from a wide-range of anthropogenic and natural sources, is emitted directly into the air (primary emissions) or formed in air through either homogeneous or heterogeneous chemical reactions. PM also consists of particles having a wide range of different shapes, compositions, and physicochemical properties that vary with particle size and many with environmental conditions (e.g., temperature, relative humidity). Typically, 6 major components are identified in routine PM air monitoring networks, some operationally defined*, and include sulfate, nitrate, ammonium, organic carbon*, elemental carbon*, and crustal material* (sum of the oxides of a series of trace metals abundant in soil, e.g., Fe, Ca, Si). The relative amounts of these components varies with particle size, location, and season (Blanchard 2004; Allen and Turner 2008; Turner and Allen 2008; Solomon *et al.* 2008). These factors make characterization of PM chemical and physical properties impossible currently with a single instrument (Fehsenfeld *et al.* 2004).

Over the last 40+ years, significant advances have occurred in the measurement of PM chemical and physical properties that has allowed us to better understand the accumulation and fate of PM on urban, regional, and global scales resulting in better quantification of source impacts at receptors from local sources (e.g., mining operations, motor vehicles) to long range transport over 1000s km (Chow *et al.* 2008; Solomon *et al.* 2008; Watson *et al.* 2008; Russell 2008; Turner and Allen 2008; Allen and Turner 2008). Two primary modeling tools are applied to help link and quantify concentrations of PM at a receptor back to its sources: observation-based (such as receptor modeling) and source-oriented methods (Viana *et al.* 2008; Watson *et al.* 2008; Russell 2008; also see Solomon *et al.* 2008). While large uncertainties still exist in the results achieved by these modeling approaches, they provide useful guidance for emissions reduction strategies.

This paper briefly reviews ambient data needs for observation-based and source-oriented modeling approaches focusing on ambient particulate matter in the size range less than 10 μm (PM₁₀) and less than 2.5 μm (PM_{2.5}) aerodynamic diameter, although applicable to any particle

size range of interest. Additional detail is given in the cited literature. The general components of a sampling system are briefly mentioned followed by brief descriptions of selected measurement methods useful for obtaining data for observation- and source-based modeling needs. Measurement methods range from basic filter-based methods typically employed for 24-hr sampling periods to advanced methods providing chemical and physical property data on an hourly average basis or less to methods that provide data on single particles as small as a few nanometers.

Methods for Estimating Source Contributions at Receptor Locations

Two general modeling approaches are used to quantitatively estimate pollution source contributions at a receptor location(s): observation-based and source-oriented methods (Viana *et al.* 2008; Watson *et al.* 2008; Russell 2008; also see Solomon *et al.* 2008). Observationally driven approaches apply statistical or similar approaches to ambient concentration data measured at a receptor site(s) (e.g., central site in a city, rural site or background site, or human receptor) to identify and quantify source contributions (to apportion) at the receptor site(s). The latter referring to source impacts at the receptor site. The most advanced source-oriented approaches start from the emissions source using advanced mathematical models or modeling systems (referred to herein as air quality models – AQM) to describe the transport, transformation, and fate of those emissions from the source to estimate source contributions at a receptor(s). Table 1 compares attributes of multi-variate receptor models, a widely used observation-based approach and chemical transport models, a source-oriented approach. Both approaches complement each other, each having different limitations and strengths (Seigneur *et al.* 1999; Solomon *et al.* 2008 and references within), and therefore, the most accurate results are obtained when both methods are applied to understanding source-receptor relationships. They also have different data needs, although many parameters overlap (Seigneur and Moran 2004; Brook *et al.* 2004; Solomon *et al.* 2008; Watson *et al.* 2008; Russell *et al.* 2008).

Observation-based approaches use chemical or physical properties of PM measured at a receptor site(s) to apportion the observed PM mass to sources or source categories. These may include simple analyses, such as time-series or correlation between or among pollutants, or more complex multivariate approaches, usually referred to as receptor modeling, the latter being the focus here. An example of a time series analysis is given in Figure 1. These data were collected in Las Vegas, Nevada, USA, using a semi-continuous sampler to measure organic carbon and

elemental carbon in 2-hr time intervals. Seen here is the buildup each weekday of OC and EC during the morning rush hour, the buildup of secondary organic aerosol in the afternoon, again during the weekdays and most pronounced on the first day, and the washout due to rain during the weekend.

A variety of multi-variate receptor models have been developed, most with different data needs or data applications (Watson *et al.* 2002; Watson *et al.* 2008; Solomon *et al.* 2008). In addition to ambient concentration data at the receptor site, receptor models require knowledge of sources or source types and for some (e.g., Chemical Mass Balance Model), source profiles (i.e., components emitted from sources and their relative or absolute abundances) including markers or tracer species (i.e., components that are emitted primarily from a specific source or source category and are essentially non-reactive between the source and receptor) to quantify source impacts at receptor sites. Useful tracers or markers include both inorganic and organic chemical components (see Solomon *et al.*, 2008; Watson *et al.* 2008 for a summary listing of relevant potential relevant species). More recent approaches include meteorological information or physical property data to help identify and quantify sources (Brook *et al.* 2004; Watson *et al.* 2008; also see summary in Solomon *et al.* 2008 and references within these).

The most advanced AQMs, actually modeling systems, are based on sources emissions information and a fundamental mathematical description of the atmosphere. AQMs consist of three major components: an emission model, meteorological model, and an atmospheric process model. Each model also may be composed of several modules (Seigneur and Moran 2004; Seigneur 2001). With the exception of data assimilation to nudge the model during processing or for use with inverse modeling, AQMs require emissions data (activity and emissions rate), initial and boundary conditions, meteorological fields (may require precipitation, fog, and cloud data), and physiographic data (e.g., location, land use) (Seigneur *et al.* 1999, 2001; Seigneur and Moran 2004; Russell 2008). Seigneur *et al.* (2000) indicate a 1-hr time resolution is highly desirable. These models use emissions and meteorology to generate oxidants and other secondary pollutants, and the most advanced models include 100s of chemical equations and detailed meteorological fields to solve the conservation equation (see brief description in Russell 2008). Primary emissions also are tracked to the extent possible, since, for example, grid cells in the models may be too large to track primary emissions with accuracy. Boundary and initial conditions also can be obtained from larger geographic fields (e.g., a regional model feeds boundary and initial conditions to an urban model). The most extensive data sets are required for model evaluation and include gas phase and condensed chemical components, the latter ideally by particle size distribution; droplet chemistry; wet and dry deposition fluxes; meteorological vari-

ables; and emissions estimates (see tables of parameters in Seigneur *et al.* 2000). However, different levels of data are needed depending on the level of model performance evaluation desired (see Seigneur *et al.* (2000). For the most complete evaluation of an AQM, comprehensive hourly data are needed for emissions, air quality, and meteorology.

This review is limited to measurements of the major and some minor components observed in PM_{2.5}/PM₁₀ in ambient air. A more detailed characterization of the ambient aerosol can improve model performance. Application of both model types likely allows for the best estimate of source impacts at receptors, thus allowing for the development of cost effective and efficient emissions management strategies to reduce levels of PM or other pollutants to levels deemed protective of human health and welfare at this time (e.g., EPA 2006).

Sampling Systems

Sampling systems for PM, independent of the size range of interest or purpose, consist of several basic components: inlet, transfer tubes, collection substrate and holder or detector, flow controller / flow meter, timer, and pump. Optional components include an additional PM size fractionator(s), additional sampling substrates behind the first filter, and one or more denuders. Characteristics of these components are described in Chow 1995; Fehsenfeld *et al.* 2004; and Watson and Chow 2009. Sampling systems for PM can be categorized several different ways, for example, bulk versus single particle; mass only versus chemical components; or time-integrated filter-based (TIFB) versus continuous or semi-continuous. Here we focus on the latter pair while integrating the former within these two subgroups. Characteristics TIFB methods include collecting particles of a defined size range on filters in the field, typically for 24-hr average sampling periods although shorter times are possible, with shipping of the filters to the laboratory for subsequent chemical analysis. (A discussion of chemical analysis methods is beyond the scope of this paper; see Chow 1995; Solomon *et al.* 2001, 2009; Chow *et al.* 2008; McMurry 2000 for additional information). Due to handling, shipping, and relatively long sampling times, TIFB methods are prone to both positive and negative sampling artifacts, which can be minimized if special methods are employed; although these are typically not employed in routing monitoring networks due to cost and additional labor needs. Real-time data are not available with TIFB methods and they are often labor intensive both in the field and laboratory. PM physical properties are not easily measured by TIFB methods.

Filters that are typically shipped to the laboratory for chemical analysis can be replaced by a detector that performs the collection and chemical analysis steps in-the-field in near-real time (i.e., the detector may include a filter) (Solomon and Sioutas 2008; Chow *et al.* 2008). These are referred to as continuous or semi-continuous methods (within continuous will represent both). The basic components of continuous samplers are the same as TIFB sampling methods; although some characteristics are different. For example, continuous methods are typically automated allowing for near real-time reporting of hourly average or better data, in most cases. As well, sampling artifacts and blanks levels are minimized due to shorter duration sampling periods and elimination of sample transport, handling, and storage. However, continuous methods may require highly skilled operators and many of the methods still require testing before use in routine monitoring networks (Solomon and Sioutas 2008). On the other hand, continuous PM physical property methods are robust and widely used (e.g., scattering, absorption, size distribution, and number concentration).

As briefly summarized below and in more detail elsewhere, the development and evaluation of these methods have advanced considerably in the last decade for the measurement of PM mass, chemical composition (Solomon and Sioutas 2008; Solomon *et al.* 2008; Wexler and Johnston 2008, Chow *et al.* 2008; Solomon *et al.* 2009; Canagaratna *et al.* 2007; Sullivan and Prather 2005) and physical properties (McMurry 2000; Solomon and Sioutas 2008). Continuous methods have advanced the abilities of receptor models allowing use of hourly or shorter time resolution data in line with changes in meteorology and source variations to better identify and quantify not only sources, but source locations (see discussion in Solomon *et al.* 2008). A recently developed hybrid model (Pseudodeterministic Receptor Model [PDRM]; Park *et al.* (2005); a combined dispersion and receptor model) includes the use of meteorological parameters needed for Gaussian plume dispersion estimates, stack engineering parameters (height, exit velocity, etc.), and high-time resolution chemical data to not only quantify source contributions at a receptor site, but to estimate emissions rates of specific pollutants from individual sources. Continuous data enhances performance evaluation of emissions-based models by allowing, for example, specific tracking and comparison of the diel cycle of pollutants as simulated in AQM against actual measurements, not obtainable with 24-hr ambient data (Seigneur *et al.* 2000; Russell 2008). In this sense, hourly data also improves hybrid modeling involving emissions-based models with inclusion of observational data through four dimensional data assimilation (FDDA) and FDDA in combination with inverse modeling, the latter pair used to better estimate parameters with significant uncertainty, such as emissions inventory validation (Mendoza-Dominguez and Russell 2001; Russell 2008). Continuous data also greatly enhance our ability to understand

chemical processing and fate of primary pollutants and precursor species on urban and regional scales (Wexler and Johnston 2008; Solomon *et al.* 2008). Over time, application of continuous methods in routine and research networks will greatly improve our ability to develop better emissions management strategies and link source emissions to health effects (Solomon and Costa 2009).

Measurement Methods

Time-integrated filter-based methods

Time-integrated filter-based measurements typically collected over 24-hr sampling periods underpin much of our knowledge about the spatial and temporal behavior of PM in ambient air. For example, Figure 2 illustrates the major chemical components of PM in Atlanta, Georgia, U.S. (upper plot) and across the Southeastern United States (SE U.S.) (lower plot). It shows a comparison of the chemical components between urban and rural areas across the SE U.S. as well as the representativeness of the Atlanta Supersites Experiment central site (JST in upper plot) (Solomon *et al.* 2003).

Many TIFB methods have been thoroughly evaluated over many years and uncertainties based on methods comparison studies are reasonably well defined for PM mass (5 – 10%) and for most major inorganic components (ions, trace elements) ranging from 10 – 35% (Solomon *et al.* 2003; Fehsenfeld *et al.* 2004; Chow *et al.* 2008; Solomon and Sioutas 2008). Uncertainties for major carbonaceous components (organic carbon - OC and elemental carbon - EC) and individual species have been estimated, ranging from 20-200%, but are still not well defined as yet, due to sampling artifacts and use of different, yet similar chemical analysis methods (Solomon *et al.* 2003; Subramanian *et al.* 2004; Chow *et al.* 2008). Physical property methods and uncertainties are summarized in McMurry (2000). Time-integrated filter-based measurement methods that may or may not include use of denuders and / or reactive filters, have been used to measure PM mass (routinely PM_{2.5}, PM₁₀, TSP, and PM_c – particles in the size range between PM_{2.5} μ m and 10 μ m); a number of major, minor, and trace chemical components; precursor species (e.g., HNO₃, NH₃); size distributions (up to about 10 fractions less than PM₁₀), including mass and composition; and physical properties such as light scattering and absorption. Individual particles have been examined for particle morphology and chemical composition on filters by techniques such as scanning electron microscopy. Additional details regarding TIFB methods can be found

in the literature cited within and elsewhere. The rest of this section will focus on continuous methods.

Continuous methods

The focus here will be continuous methods for chemical components. McMurry (2000) thoroughly reviews continuous methods for measurement of physical properties of the atmospheric aerosol. During the last decade, significant advances in development and evaluation of continuous methods were the result of the U.S. EPA PM Supersites Program (Solomon *et al.* 2008). Focus in the program was PM_{2.5}, but continuous methods were also developed for PM_c and ultrafine PM (particles less than 0.1 μm). Solomon and Sioutas (2008) and Chow *et al.* (2008) review measurement methods results with the former focusing on defining analytical capabilities of the methods (e.g., precision, bias, interferences, comparability), whereas the latter review focused on the readiness of continuous methods for routine field deployment, limited to research measurements, or requiring further development and evaluation. Both also describe the methods and provide references for more detailed information. Findings from these reviews are briefly summarized here.

Mass

Direct and indirect approaches have been developed to measure the mass of particulate matter in air. The mass range is usually limited to PM_{2.5}, PM₁₀, or PM_c. Uncertainty with indirect methods is high due to uncertainty in conversion factors from the measured parameter (e.g., light scattering, size distribution) to PM mass. However, several indirect methods are low in cost (e.g., nephelometer) and while not accurate tend to correlate well with direct methods making the results useful for receptor modeling where relative variability can be more important than absolute values. While several direct methods have been developed and tested, three seem to provide the most accurate representation of PM mass in air: the Tapered Element Oscillating Microbalance - Filter Dynamics Measurement System (FDMS-TEOM), the Beta Attenuation Monitor (BAM), and the Real-Time Ambient Mass Sampler (RAMS). The former two are available commercially; the third is a thoroughly evaluated research method (Eatough *et al.* 2001). Of the commercial units, under conditions tested and at several locations and seasons the FDMS-TEOM appears to provide the best estimate of PM as found in air, minimizing both positive and negative sampling artifacts (see Solomon and Sioutas 2008). For example, excellent agreement was observed when comparing an estimate of semi-volatile mass as obtained by subtracting the FDMS-TEOM mass from the mass obtained by a TEOM operated at 50 °C (the latter believed to

be a good measure of non-volatile mass) to the sum of semi-volatile organic carbon (SVOC) and nitrate showed (Figure 3). This comparison indicated that the semi-volatile mass measured by the FDMS-TEOM accounted for most of the negative artifact due to potential loss of SVOC and ammonium nitrate (Grover *et al.*, 2008; Solomon and Sioutas 2008 and references within). A fine and coarse PM FDMS-TEOM also is available commercially.

Ions

Continuous methods for cations and anions have been developed and tested over the last decade (Solomon and Sioutas 2008; Chow *et al.* 2008 and references within these) and include both direct and indirect approaches. Indirect approaches heat the aerosol either while in the gas phase or after collection on a substrate. The oxidized species (e.g., NO_x for determination of nitrate or ammonium, or SO₂ for sulfate) is measured by a standard high sensitivity gas monitor (e.g., chemiluminescence for NO_x). Conversion factors, interferences, and inefficient conversion of the species of interest appear to bias the results from what is found in air. Direct methods typically grow particles by condensation followed by impaction and on-line analysis by ion chromatograph. Results compare well with historical methods (Weber *et al.* 2003; Chow *et al.* 2008). Figure 4 illustrates one of the advantages of high time resolution data showing how the large sulfate peak on September 5 and 6, 2001 would have been essentially averaged out over both days showing little difference and no peak if only 24-hr average data were collected. Several commercial continuous ion methods units are available, but most still require additional evaluation before use in routine monitoring networks.

Carbonaceous components

Measurement of carbon components in PM can be divided into two main categories: major components, which are operationally defined, and determination of individual organic species. Major carbonaceous components are measured operationally by thermal and optical methods. Thermal methods are used to determine OC, EC, carbonate carbon (CC), and total carbon (TC, sum of OC, EC, and CC) from quartz-fiber filters. The two most widely used thermal protocols use an optical measurement (thermal-optical analysis – TOA) during analysis to correct for charring of OC during the OC analysis step. The different thermal protocols produce slightly different values of ambient OC (10-20%), but EC can be significantly different (up to 200%) (see Solomon *et al.* 2003; Chow *et al.* 2008 and references within these). Only one continuous TOA method is available commercially (Sunset Laboratory) for determining the major components of carbon in air. Good agreement was observed between this method and current TIFB methods (Solomon

and Sioutas 2008; Chow *et al.* 2008). The continuous and TIFB samplers use quartz-fiber filters to collect the PM sample. Quartz-fiber filters are prone to sampling artifacts that can add significant uncertainty to the results (Subramanian *et al.* 2004). Use of continuous methods greatly reduces the time the filter is in contact with ambient air to only the single sampling period and can significantly reducing this sampling artifact. Another major uncertainty in estimating the organic component in PM is converting the measured OC to organic material (OM), which provides an estimate of the organic component including elements other elements associated with organic compounds (e.g., O, N, S) (Turpin and Lim 2001). Figure 1 illustrates the application of the method as described earlier; noting also the loss in information if only 24-hr data had been collected.

Optical methods measure the light absorption properties of PM, which is dominated by black carbon (BC) or light absorbing carbon (LAC) (Bond and Bergstrom 2006). BC is similar to EC (they correlate and both represent a definition of the strong absorbing carbon found in the air) but since BC is an optical (units 1/m) indirect measurement a conversion factor (mass absorption coefficient or cross section) is required to convert it to ambient mass concentration. The Aethalometer measures BC and high correlations are observed with historical methods (Solomon and Sioutas 2008; Chow *et al.* 2008 and references within). Other approaches, such as, photoacoustic spectroscopy (PAS), Multi-Angle Absorption Photometer (MAAP), and Particle Soot Absorption Photometer (PSAP) provide estimates of BC in PM (see Chow *et al.* 2008). The Aethalometer (Magee Scientific) and MAAP, (Thermo Scientific) are commercially available.

Determining individual organic species in PM is challenging since there are 100s if not 1000s of possible organic compounds with a wide range of physiochemical properties. Organic species provide a suite of tracers now in use in receptor model applications (see Watson *et al.* 2008; Solomon *et al.* 2008). These have advanced the ability of receptor models to better estimate source contributions to ambient concentrations. Organic species also enhance the ability to evaluate the performance of emissions-based models, allowing, e.g., validation of secondary organic aerosol formation. Until recently, a suite of OC species were measured from filter samples collected over 24-hrs and often several days were composited to obtain sufficient material for analysis. Recently, individual species have been estimated from single filters collected over only 3 hrs using a high volume air sampler (Rogge *et al.* 2006). Individual species also have been estimated from particle mass spectrometers (MS) (single particle MS or aerosol MS) on short time scales, although more qualitative in nature (see Canagaratna *et al.* 2007). Thermal-desorption-gas chromatography-MS (TD-GC-MS) has recently emerged as a continuous method for organic

species (Kreisberg *et al.* 2009). The sample is collected for 30 min followed by analysis. An in-the-field calibration approach was described.

Trace elements

A continuous in-the-field collection and analysis method widely applicable to determining trace elements in ambient PM has not been developed. A method using X-ray fluorescence (XRF) is commercially available but has been applied only to emissions or near emissions sources (Yanca *et al.* 2006) due to the higher levels of PM in these areas. Two other collection methods provide high-time resolution data, although requiring subsequent analysis in the laboratory so real-time data are not available (see summary in Solomon *et al.* 2009). In one, PM is collected in several different size ranges using a Davis Rotating-drum Universal-size-cut Monitoring (DRUM) impactor, which provides samples suitable for a variety of laboratory analysis methods, such as proton induced X-ray emission (PIXE), proton elastic scattering analysis (PESA), and others. Depending on the speed of the tape in the sampler and size of the analysis spot, time resolutions of less than one hour can be obtained. More recently, particles as small as 80 nm are grown to greater than 3 μm in diameter by controlled condensational growth based on direct steam injection by the Semicontinuous Elements in Aerosol Sampler (SEAS) (Kidwell and Ondov 2004). A virtual impactor followed by a real impactor is used to concentrate and collect the droplets in vials with a 30 min sampling resolution. Samples vials are brought back to the laboratory for subsequent analysis by standard methods (ICP-MS, AAS, GF-AAS). Data from the SEAS have been used in PDRM mentioned earlier with excellent agreement between observed and predicted results (Park *et al.* 2005).

Particle mass spectrometers

Aerosol (AMS) and single particle (SPMS) mass spectrometers provide continuous data on a wide range of species and components in PM, typically in particles less than about 2 μm . SPMS provide qualitative data on the chemical components of single particles, although with proper calibration against other methods, SPMS have been shown to be quantitative for the bulk aerosol, but additional simultaneous measurements are required in the field. On the other hand, the AMS provides quantitative estimates of chemical data by size distribution after laboratory calibration. Figure 5 illustrates an example of the type of data obtained by an AMS. Here concentrations of four major components (organics, ammonium, nitrate, and sulfate) are plotted as a function of time of day (x-axis) and size distribution (y-axis of lower four plots). These data show not only when component concentrations peaked during the day (areas in red) but the size range

of particles responsible for those peak concentrations. This provides information on formation mechanisms and age of the aerosol, for example. For more information on these methods see Canagaratna *et al.* (2007) and Sullivan and Prather (2005).

Other components

Continuous methods for other chemical components and physical properties important to understanding the fate and source-receptor relationships of PM in air have been developed or evaluated over the last decade but are beyond the scope of this review. These components include particle bound water, water-soluble organic carbon, particle density (a function of composition), particle number, size distribution, and precursor species to PM (SO₂, NO_x, NH₃, and semi-volatile organic compounds). Cited literature within provides information and additional references on measurements of these components.

Uncertainty

Analytical capabilities of continuous methods are still being defined. Chow *et al.* (2008) and Solomon and Sioutas (2008) summarize results from the methods comparison performed during EPA PM Supersites Program. Accuracy, in the true sense is undefined for most methods since in-the-field standards are not available for most chemical measurement methods and some physical property methods, including mass, but excluding EPA's FRM for mass since the FRM is a regulatory standard and not an analytical standard (Fehsenfeld *et al.* 2004; Solomon and Sioutas 2008). The best estimate of accuracy is bias determined by comparison to historical methods, such as TIFB methods (Fehsenfeld *et al.* 2004; Solomon and Sioutas 2008). Bias ranges from $\pm 10 - 30\%$ for most species, although semi-volatile material (SVM) and differences in measurement protocols can result in much higher bias among continuous & integrated methods. Precision for most methods ranges between $\pm 5-30\%$, based on collocated sampling. Interferences and sampling artifacts, including both negative and positive sampling artifacts are likely minimized with continuous sampling but well defined measurements to quantify these interferences have not been widely performed and certainly depend on a number of variables as with TIFB methods. Interferences are discussed in Chow *et al.* (2008). Most continuous methods have a sensitivity of better than $0.1 \mu\text{g}/\text{m}^3$ for 1-hr average data for major components and ng/m^3 for trace elements & organic species. Data capture for continuous methods ranges from $70 - 90\%$; although some methods require highly skilled operators and are therefore, not ready for routine measurement networks (Solomon and Sioutas 2008; Chow *et al.* 2008). Additional information

regarding sampling artifacts and uncertainties associated with both TIFB and continuous methods can be found in the cited literature within this paper.

Conclusion

This brief review provides insights into data needs and methods available to support modeling and data analysis methods useful for linking source impacts observed at receptor locations back to the original source. Methods include both time-integrated filter-based methods with subsequent chemical analysis in the laboratory as well as in-the-field continuous methods that, in general, combine the collection and analysis methods into one instrument. The latter are capable of providing near real-time data that can support air quality forecasting and public warnings of potentially adverse pollutant conditions. Applications of methods described here have wide applicability from near source, such as coal, oil, and gas mining and use, to urban and long-range transport of PM in air. In particular, as continuous methods are more widely employed our understanding of the fate and source-receptor relationships of PM and precursor species in air will improve resulting in development of more cost effective and efficient emissions management strategies for reducing ambient levels of PM to below current ambient air quality standards or objectives.

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References

Allen D.T. and Turner J.R., 2008, Transport of atmospheric fine particulate matter: Part 1. Findings from recent field programs on the extent of regional transport within North America. *Journal of the Air & Waste Management Association*, **58**, 254-264.

- Blanchard C., 2004, Spatial and temporal characteristics of particulate matter, Chapter 6. In *Particulate Matter Science for Policy Makers, a NARSTO Assessment*, eds. P.H. McMurry, M. Shepherd, and J. Vickery, Cambridge University Press, Cambridge, U.K., pp. 191-234.
- Bond T.C. and Bergstrom R.W., 2006, Light absorption by carbonaceous particles: An investigative review. *Aerosol Science and Technology*, **40**, 27-67.
- Brook J.R., Vega E., and Watson J.G., 2004, Receptor methods, Chapter 7. In *Particulate Matter Science for Policy Makers, a NARSTO Assessment*, eds. P.H. McMurry, M. Shepherd, and J. Vickery, Cambridge University Press, Cambridge, U.K., 236-281.
- Canagaratna M.R., Jayne J.T., Jimenez J.L., Allan J.D., Alfarra M.R., Zhang Q., Onasch T.B., Drewnick F., Coe H., Middlebrook A., Delia A., Williams L.R., Trimborn A.M., Northway M.J., DeCarlo P.F., Kolb C.E., Davidovits P., and Worsnop D.R., 2007, Chemical and chemical and microphysical characterization of ambient aerosols with the aerodyne aerosol mass spectrometer. *Mass Spectrometry Reviews*, **26**, 185-222.
- Chow J.C., 1995, Measurement methods to determine compliance with ambient air quality standards for suspended particles. *Journal of the Air & Waste Management Association*, **45**, 320-382.
- Chow J.C., Doraiswamy P., Watson J.G., Chen L.-W.A., Ho S.S.H., and Sodeman D.A., 2008, Advances in integrated and continuous measurements for particle mass and chemical composition. *Journal of the Air & Waste Management Association*, **58**, 141-163.
- Davidson C.I., Phalen R.F., and Solomon P.A., 2005, Airborne particulate matter and human health: A review. *Aerosol Science and Technology*, **39**, 737-749.
- Eatough D.J., Eatough N.L., Obeidi F., Pang Y., Modey W., and Long R., 2001, Continuous determination of PM_{2.5} mass, including semi-volatile species. *Aerosol Science and Technology*, **34**, 1-8.
- EPA, 2004, *Air Quality Criteria for Particulate Matter*; EPA 600/P-99/002aF-bF. U.S. Environmental Protection Agency, Washington, DC.
- EPA, 2006, *National Ambient Air Quality Standards for Particulate Matter: Final Rule. 40 CFR Parts 50, 43, and 58*. Federal Register, **62(138)**. U.S. Environmental Protection Agency, Research Triangle Park, NC.

- Fehsenfeld F., Hastie D., Chow J., and Solomon P., 2004, Aerosol and gas measurements. In *Particulate Matter Science for Policy Makers, a NARSTO Assessment*, eds. P.H. McMurry, M. Shepherd, and J. Vickery, Cambridge University Press, Cambridge, U.K., pp. 159-189.
- Grover B.D., Kleinman M., Eatough N.L., Eatough D.J., Hopke P.K., Long R.W., Wilson W.E., Meyer M.B., Ambs J.L., 2005, Measurement of total PM_{2.5} mass (nonvolatile plus semi-volatile) with the Filter Dynamic Measurement System Tapered Element Oscillating Microbalance monitor. *Journal of Geophysical Research*, **110**, D07S03, doi: 10.1029/2004JD004995.
- Grover B.D., Eatough N.L., Woolwine W.R., Cannon J.P., Eatough D.J., Long R.W., 2008, Semi-continuous mass closure of the major components of fine particulate matter in Riverside, CA. *Atmospheric Environment*, **42**(2), 250-260.
- Kidwell C.B. and Ondov J.M., 2004, Elemental analysis of sub-hourly ambient aerosol collections. *Aerosol Science and Technology*, **38**, 205-218.
- Kreisberg N.M., Hering S.V., Williams B.J., Worton D.R., and Goldstein A.H., 2009, Quantification of hourly speciated organic compounds in atmospheric aerosols, measured by an in-situ thermal desorption gas chromatograph (TAG). *Aerosol Science and Technology*, **43**, 38-52.
- McMurry P.H. 2000, A review of atmospheric aerosol measurements. *Atmospheric Environment*, **34**, 1959-1999.
- Mendoza-Dominguez A. and Russell A.G., 2001, Emission strength validation using four-dimensional data assimilation: application to primary aerosol and precursors to ozone and secondary aerosol. *Journal of the Air & Waste Management Association*, **51**, 1538-1550.
- NARSTO, 2004, *Particulate Matter Science for Policy Makers, a NARSTO Assessment*, eds. P.H. McMurry, M. Shepherd, and J. Vickery, Cambridge University Press, Cambridge, U.K., 510 pp.
- Park S.S., Pancras P.J., Ondov J.M., and Poor N.A., 2005, New pseudo-deterministic multivariate receptor model for accurate individual source apportionment using highly time-resolved ambient concentrations. *Journal Geophysical Research*, **110**, D07S15; doi: 10.1029/2004JD004664.
- Rogge W.F., 2006, Character of Baltimore PM as derived from detailed characterization of molecular organic source markers in 3-hr samples. Presented at the 2006 National Air Monitor-

- ing Conference, Las Vegas, NV, November; available at <http://www.epa.gov/ttn/amtic/files/ambient/2006conference/rogge.pdf> (accessed 2008).
- Russell A.G., 2008, EPA Supersites Program-related emissions-based particulate matter modeling: Initial applications and advances. *Journal of the Air & Waste Management Association*, **58**, 289-302.
- Seigneur C., 2001, Current status of air quality models for particulate matter. *Journal of the Air & Waste Management Association*, **51**, 1508-1521.
- Seigneur C. and Moran M., 2004, Chemical-transport models. Chapter 8. In *Particulate Matter Science for Policy Makers, a NARSTO Assessment*, eds. P.H. McMurry, M. Shepherd, and J. Vickery, Cambridge University Press, Cambridge, U.K., pp. 283-323.
- Seigneur C., Pai P., Hopke P., and Grosjean D., 1999, Modeling atmospheric particulate matter. *Environmental Science and Technology*, **33**, 80A-86A.
- Seigneur C., Pun B., Pai P., Louis J.-F., Solomon P., Emery C.E., Morris R., Zahniser M., Worsnop D., Koutrakis P., White W., and Tombach I., 2000, Guidance for the performance evaluation of three-dimensional air quality modeling systems for particulate matter and visibility. *Journal of the Air & Waste Management Association*, **50**, 588-599.
- Seinfeld J.H. and Pandis S.N., 1998, *Atmospheric Chemistry and Physics from Air Pollution to Climate Change*, John Wiley and Sons, Inc., New York, NY, 1326 pp.
- Solomon P.A. and Hopke P.K., 2008, Special issue supporting key scientific and policy- and health-relevant findings from EPA's Particulate Matter Supersites Program and Related Studies: An integration and synthesis of results. *Journal of the Air & Waste Management Association*, **58(2)**, 137-139.
- Solomon P.A. and Sioutas C., 2008, Continuous and semicontinuous monitoring techniques for particulate matter mass and chemical components: A synthesis of findings from EPA's Particulate Matter Supersites Program and Related Studies. *Journal of the Air & Waste Management Association*, **58**, 164-195.
- Solomon P.A. and Costa D.L., 2009, Ambient tropospheric particles. In *Particle-Lung Interactions, Second Edition*, eds. P. Gehr, C. Mühlfeld, B.M. Rothen-Rutishauser, and F. Blank, Series: Lung Biology in Health and Disease, Vol. 241, Informa Healthcare, New York, NY, 328 pp.

- Solomon P.A., Tolocka M.P., Norris G., Landis M., 2001, Chemical analysis methods for atmospheric aerosol components. In *Aerosol Measurement: Principles, Techniques, and Application*, 2nd ed., eds., P. Baron and K. Willeke, John Wiley & Sons, Inc. New York, NY, pp. 261-293.
- Solomon P.A., Baumann K., Edgerton E., Tanner R., Eatough D., Modey W., Marin H., Savoie D., Natarajan S., Meyer M.B., and Norris G., 2003, Comparison of integrated samplers for mass and composition during the 1999 Atlanta Supersites Project. *Journal of Geophysical Research*, **108**, 8423, doi: 10.1029/2001JD001218.
- Solomon P.A., Hopke P.K., Froines J., and Scheffe R., 2008, Key scientific findings and policy- and health-relevant insights from the U.S. Environmental Protection Agency's Particulate Matter Supersites Program and Related Studies: An integration and synthesis of results. *Journal of the Air & Waste Management Association*, **58**(13), S1-S92.
- Solomon P.A., Fraser M.P., and Herckes P., 2009, Chemical analysis methods for atmospheric aerosol components. In *Aerosol Measurement: Principles, Techniques and Applications*, Third Edition, eds., P. Baron, P. Kulkarni, and K. Willeke, John Wiley & Sons, Inc., New York, NY, submitted, April.
- Subramanian R., Khlystov A.Y., Cabada J.C., and Robinson A.L., 2004, Positive and negative artifacts in particulate organic carbon measurements with denuded and undenuded sampler configurations. *Aerosol Science Technology*, **38**(S1), S27-S48.
- Sullivan R.C. and Prather K.A., 2005, Recent advances in our understanding of atmospheric chemistry and climate made possible by on-line aerosol analysis instrumentation. *Analytical Chemistry*, **77**, 3861-3886.
- Turner J.R. and Allen D.T., 2008, Transport of atmospheric fine particulate matter: Part 2. Findings from recent field programs on the intraurban variability in fine particulate matter. *Journal of the Air & Waste Management Association*, **58**, 196-215.
- Turpin B.J. and Lim H.J., 2001, Species contributions to PM_{2.5} concentrations: revisiting common assumptions for estimating organic mass. *Aerosol. Science and Technology*, **35**, 602-610.
- Viana M., Kuhlbusch T.A.J., Querol X., Alastuey A., Harrison R.M., Hopke P.K., Winiwarere W., Vallius M., Szidat S., Prévôt A.S.H., Hueglin C., Bloemen H., Wählin P., Vecchi R., Miranda A.I., Kasper-Giebl A., Maenhaut W., and Hitzenberger R., 2008, Source apportionment of atmospheric aerosols in the Paris area. *Journal of Geophysical Research*, **113**, D15307, doi: 10.1029/2007JD009278.

- tionment of particulate matter in Europe: A review of methods and results. *Journal of Aerosol Science*, **39**, 827-849.
- Watson J.C. and Chow J., 2009, Ambient aerosol sampling, Chapter 28. In *Aerosol Measurement: Principles, Techniques and Applications, Third Edition*, eds., P. Baron, P. Kulkarni, and K. Willeke, John Wiley & Sons, Inc., New York, NY, submitted, April.
- Watson J.G., Zhu T., Chow J.C., Engelbrecht J.P., Fujita E.M., and Wilson W.E., 2002, Receptor modeling application framework for particle source apportionment. *Chemosphere* **49**(9), 1093-1136.
- Watson J.G., Chen L.-W.A., Chow J.C., Doraiswamy P., and Lowenthal D.H., 2008, Source apportionment: findings from the U.S. Supersites Program. *Journal of the Air & Waste Management Association*, **58**, 265-288.
- Weber R., Orsini D., Duan Y., Baumann K., Kiang C.S., Chameides W., Lee Y.N., Brechtel F., Klotz P., Jongejan P., Ten Brink H., Slanina J., Dasgupta P., Hering S., Stolzenburg M., Edgerton E., Harstell B., Solomon P., Tanner R., 2003, Intercomparison of near real-time monitors of PM_{2.5} nitrate and sulfate at the U.S. Environmental Protection Agency Atlanta Supersite. *Journal Geophysical Research*, **108**, 8421, doi: 10.1029/2001JD001220.
- Wexler A. and Johnston M., 2008, What have we learned from highly time resolved measurements during EPA's Supersites Program and Related Studies? *Journal of the Air & Waste Management Association*, **58**, 303-319.
- Yanca C.A., Barth D.C., Petterson K.A., Nakanishi M.P., Cooper J.A., Johnsen B.E., Lambert R.H., and Bivins D.G., 2006, Validation of three new methods for determination of metal emissions using a modified Environmental Protection Agency Method 301. *Journal of the Air & Waste Management Association*, **56**, 1733-1742.
- Zhang Q., Canagaratna M.C., Jayne J.T., Worsnop D.R., and Jimenez J.L., 2005, Time and size-resolved chemical composition of submicron particles in Pittsburgh—Implications for aerosol sources and processes. *Journal of Geophysical Research*, **110**, doi:10.1029/2004JD004649.

Table 1. Comparison of Attributes of Multi-variate Receptor Models (MVRM) (Observationally Based Approach) and Chemical Transport Models (CTM) (Source-Oriented Approach)

<u>MVRM</u>	<u>CTM</u>
<ul style="list-style-type: none"> • Observationally Based, Requires Field Measurements, Typically Chemical Component Data, Physical Property & Meteorology Becoming More Useful • Emissions Source Profiles (Source Composition) Needed or Useful • Temporal Analysis Typical, Spatial Based on Multiple Site Locations • Hourly Data Improves Results Allows Integration of Meteorology to Provide More Specific Source Location Information • Predicts Primary Species More Effectively than Secondary • Not Able to Predict Changes in PM Due to Changes in Emissions 	<ul style="list-style-type: none"> • Chemical & Physical Property Data Not Required to Run Model Data Needed for Performance Evaluation, Nudging, & Inverse Modeling, Also Useful for Boundary & Initial Conditions • Meteorology & Emissions (Composition Rate & Activity) are Fundamental Inputs • Spatial Analysis Typical, Temporal Coverage Requires Modeling Multiple Hours & Days • Hourly Data Improves Results, Allowing for Diagnostic Model Evaluation, Improved Nudging, etc. • Predicts Secondary Species More Effectively than Primary Due in Part to Relatively Large Grid Size Restrictions • Can Predict Changes in Future PM Conc. Due to Changes in Emissions

Figure Captions

- Figure 1. Simple approach – Time Series Analysis. Time series of PM_{2.5} organic carbon (OC) and elemental carbon (EC) collected with a continuous (2-hr average sampling period) OC/EC analyzer (Sunset Lab). Plot shows diel variation with OC and EC peaks during the weekdays in the morning during rush hour, afternoon peaks indicating secondary organic aerosol formation, and washout due to rain on the weekend.
- Figure 2. Temporal and spatial representativeness of the Atlanta Supersites Project. (b) Spatial representativeness of PM_{2.5} mass and components observed at the Jefferson Street site compared with other sites within the Atlanta metropolitan area. Figures courtesy of ASACA. (c) Spatial representativeness of the Jefferson Street site compared with other sites within the southeast United States. Figures courtesy of the SEARCH project. Reproduced/modified with permission from Solomon et al. Copyright 2003 American Geophysical Union, Journal of Geophysical Research.
- Figure 3. Data from the Rubidoux July 2003 study. The circles indicate 1-hour average FDMS PM_{2.5} mass, the squares the difference between the 1-hour average FDMS and 50 °C TEOM monitor PM_{2.5} mass, and the bars the sum of 1-hour average R&P PM_{2.5} ammonium nitrate mass measurements and the modified Sunset monitor semi-volatile organic material (SVOM) mass measurements. This sum is indicated as SVM, semi-volatile material (as described in Grover et al. 2005). Reproduced/modified with permission from Grover et al. Copyright 2005 American Geophysical Union, Journal of Geophysical Research.
- Figure 4. Hourly average continuous sulfate measurements collected at the St. Louis, MO core Supersite from September 1 –9, 2001. Shown are hourly average data for sulfate measured by the Particle-into-Liquid sampler with ion chromatography detection (Applikon; squares) and the 5040 thermal reduction, gas detection sulfate analyzer (Thermo Scientific). 24-hr data are shown with black bars collected by the Harvard EPA annular denuder system (HEADS). Highlighted section shows a peak 48-hr period that was averaged out by the daily average data. Reproduced with permission from J. Turner, Washington University, St. Louis, MO.
- Figure 5. An example of the type of multi-dimensional information that can be obtained with the AMS. Panel a shows time trends in the mass concentrations of ambient aerosol

species observed during the Pittsburgh Air Quality Study in 2002 (modified from Zhang et al., 2005). Panels b–d show the corresponding time evolution of sulfate, nitrate, and organic mass-weighted size distributions. Measurements were averaged over 10-min timescales. Averages of the observed speciated size distributions over the entire time trend are shown in panels b'–d'. Reproduced/modified with permission from Canagaratna et. al. Copyright 2007, Wiley Periodicals, Inc., A Wiley Company, Mass Spectrometry Reviews.

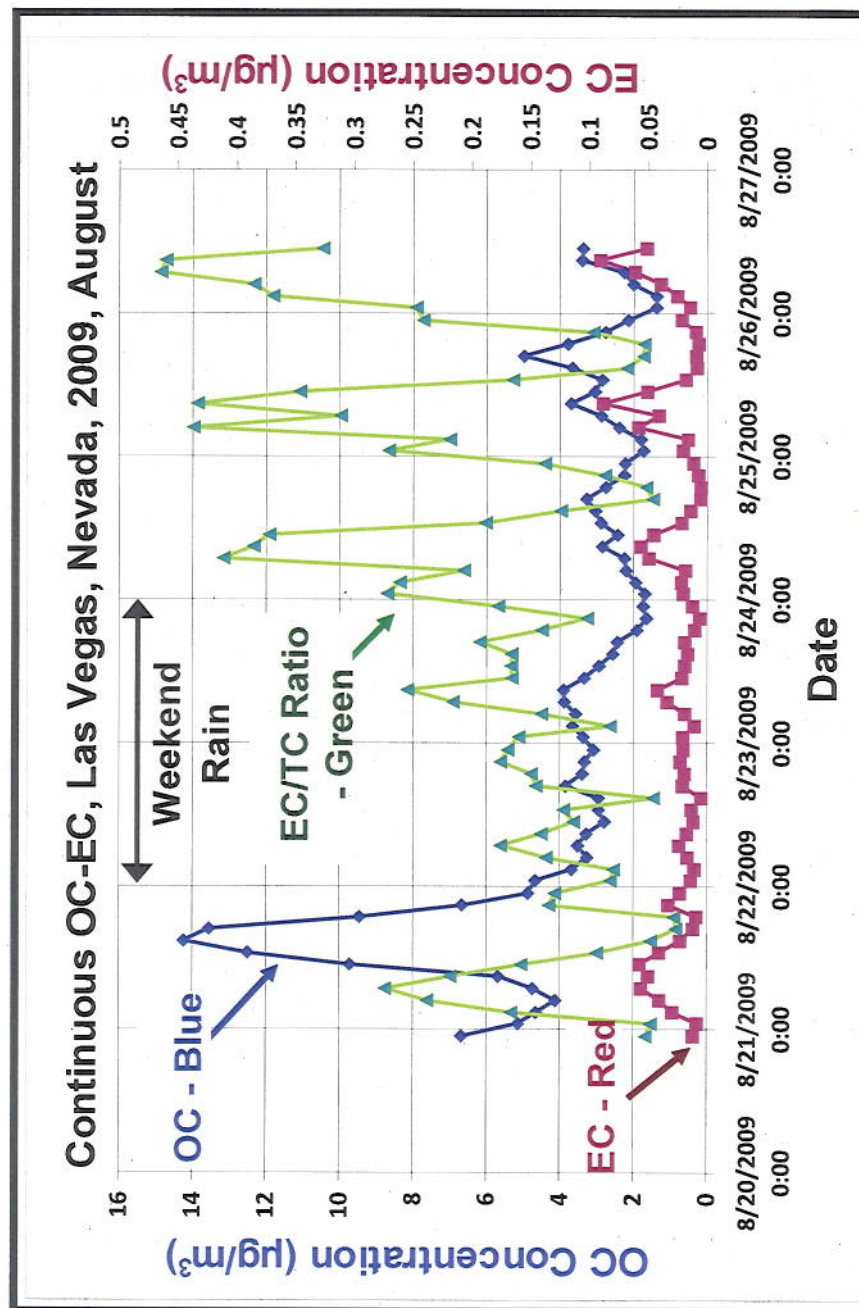


Figure 1

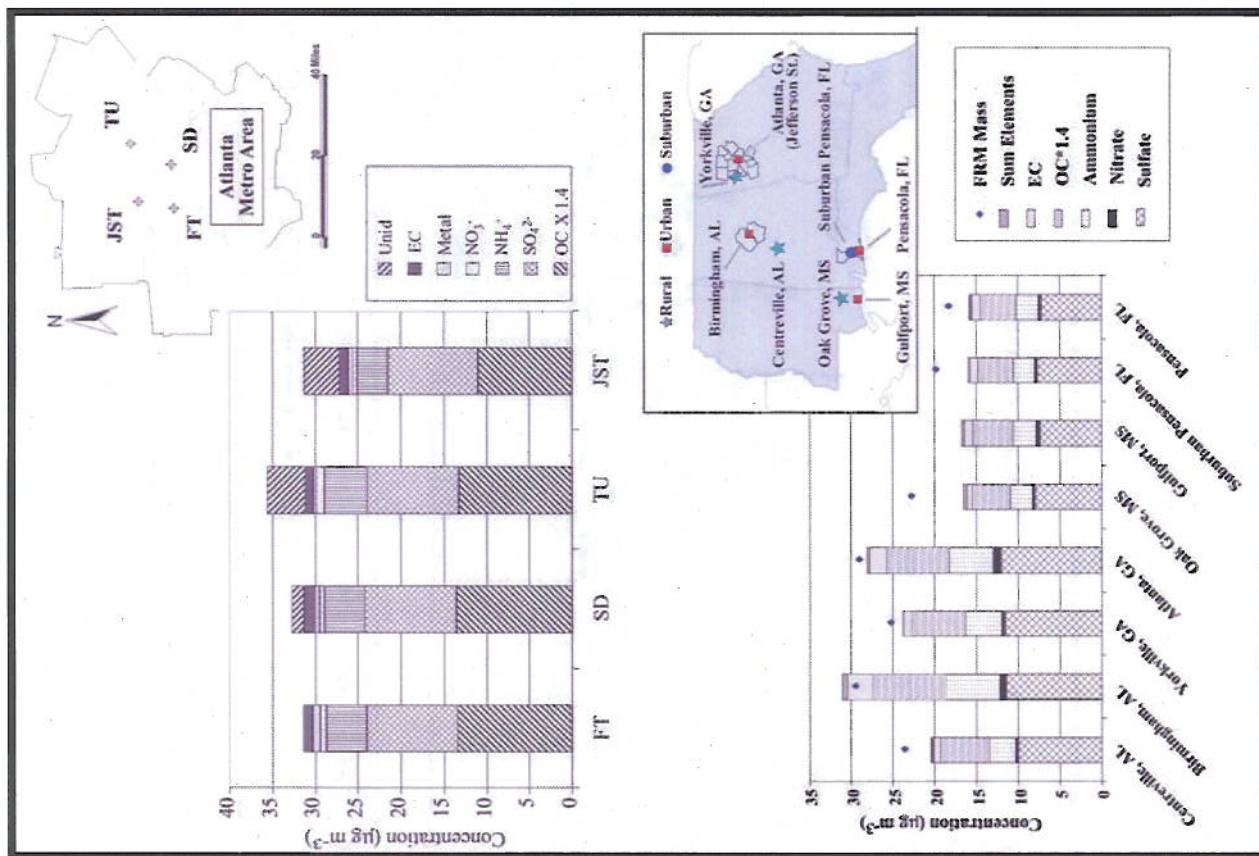


Figure 2

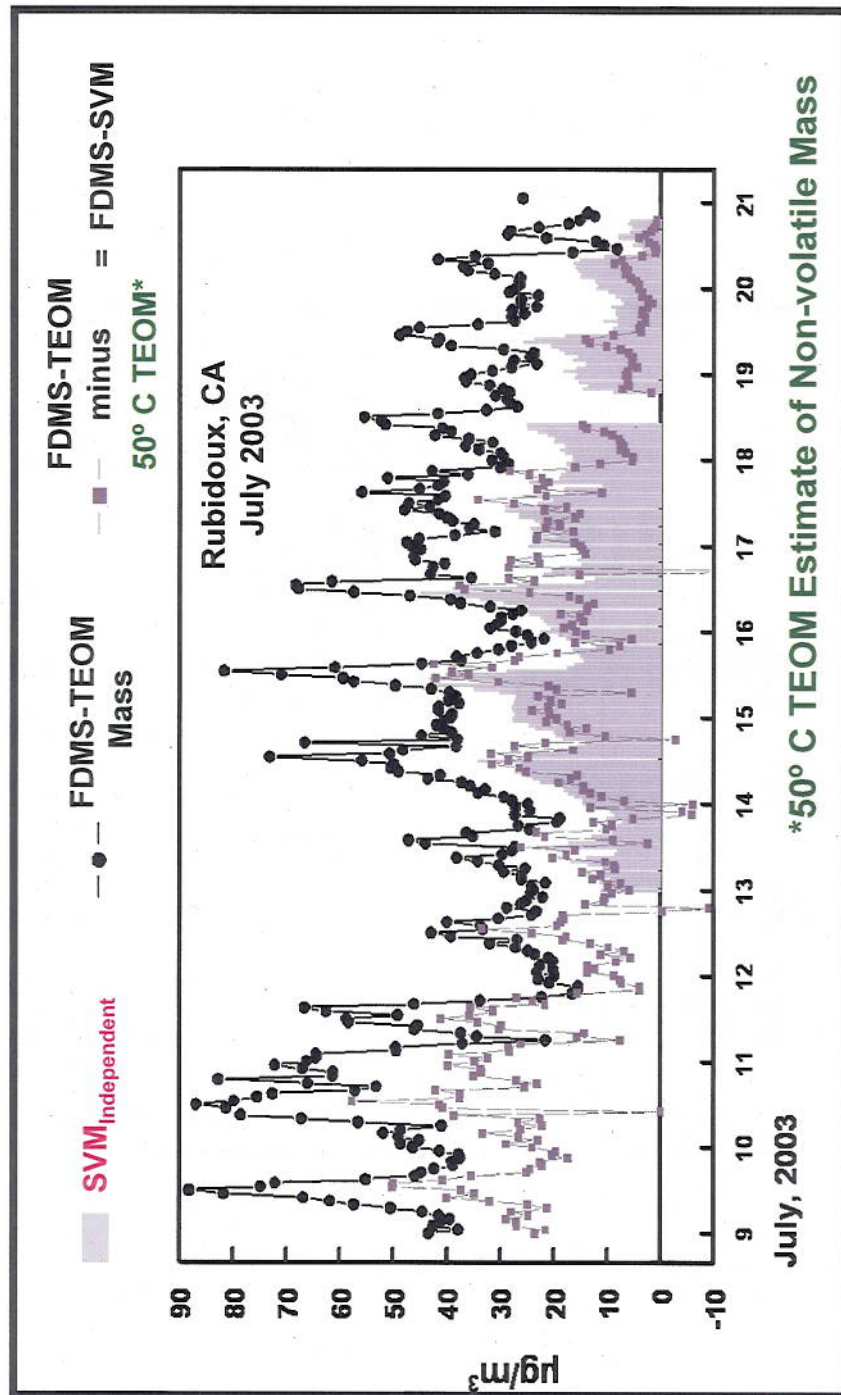


Figure 3

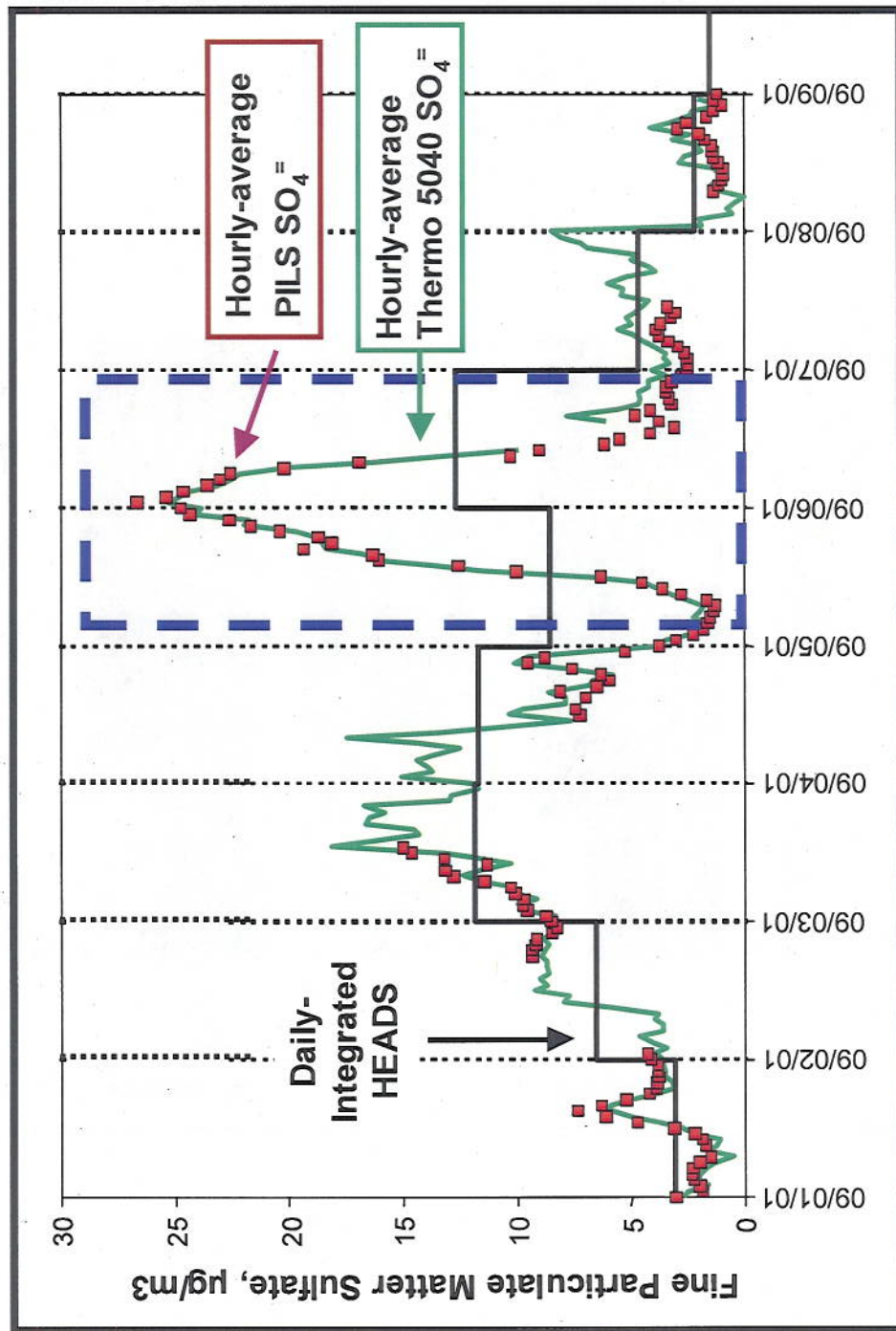


Figure 4

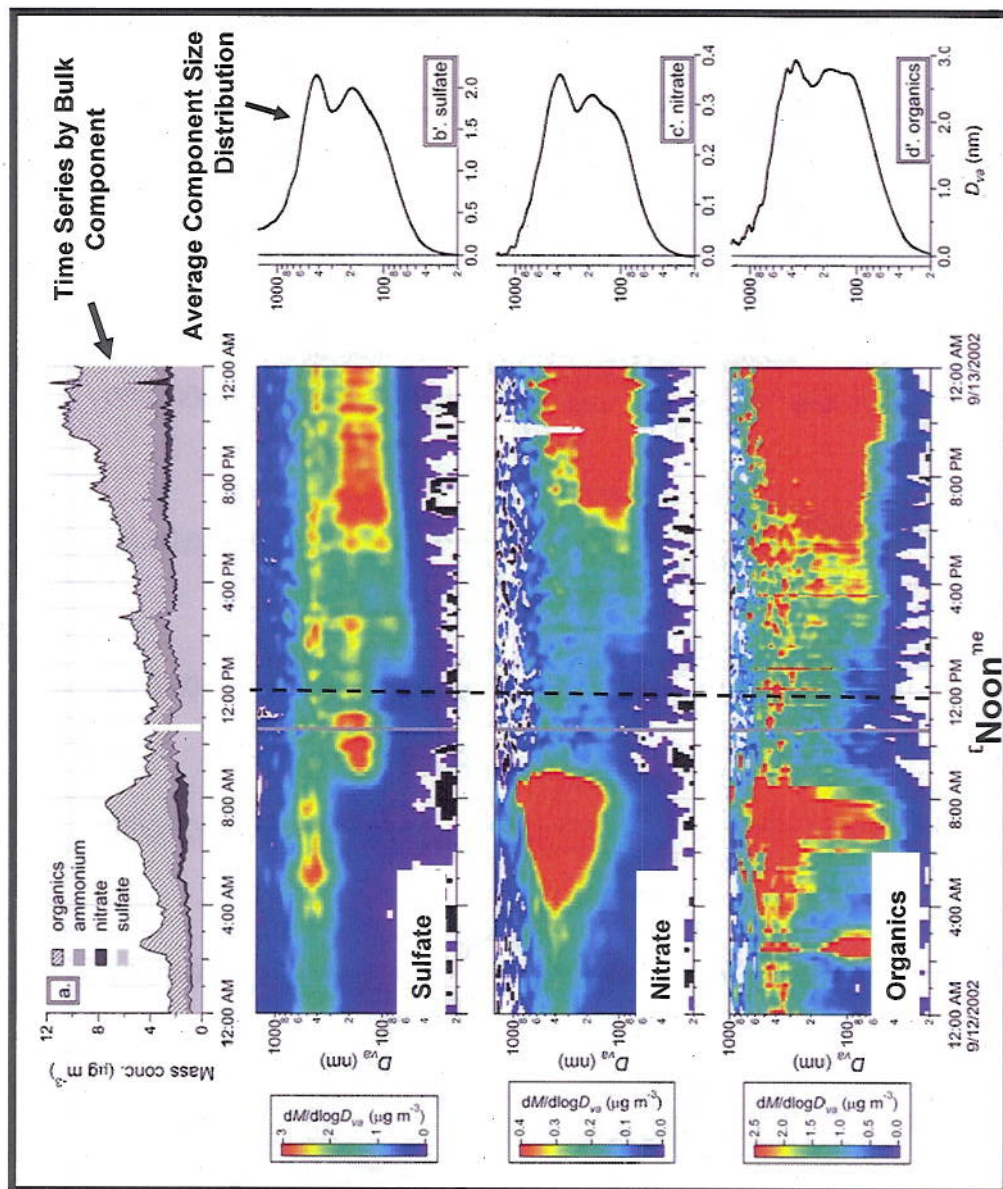


Figure 5

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