Project Title: Hybrid Source Apportionment Model: an operational tool to distinguish wildfire emissions from prescribed fire emissions in measurements of $PM_{2.5}$ for use in visibility and PM regulatory programs

Final Report: JFSP Project Number 05-3-1-04

Project Website: http://vista.cira.colostate.edu/improve/Studies/SmokeApp/ SmokeApp.htm

Principal Investigator:

Dr. Bret Schichtel, Physical Scientist, National Park Service
CIRA, Colorado State University, Foothills Campus, Fort Collins, CO 80523-1375
Telephone/Facsimile Number(s): (970) 491-8581; Fax: (970) 491-8598
E-mail:Schichtel@cira.colostate.edu

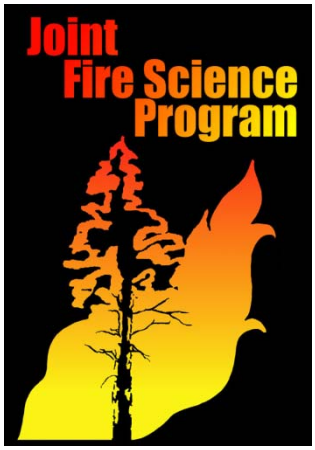
Co-Principal Investigators:

Dr. Douglas Fox, Colorado State University, Fort Collins, CO

Graduate Research Assistants and Technicians:

Ms. Leigh Patterson, Colorado State University, Fort Collins, CO
Ms. Amanda Holden, Colorado State University, Fort Collins, CO

This research was sponsored in part by the Joint Fire Science Program. For further information go to www.firescience.gov.



I. Abstract

Air quality regulations have the goal of reducing haze in national parks and wilderness areas to natural conditions and require that fine particulate matter ($PM_{2.5}$) be reduced below a threshold that adversely impacts health. The federally funded and managed Interagency Monitoring of Protected Visual Environments (IMPROVE) and Chemical Speciation Network (CSN) monitoring networks track the progress toward these goals. Carbonaceous material is often the largest contributor to haze and $PM_{2.5}$, and smoke from fire-related activities is a significant contributor to this carbonaceous material, particularly in the western and southeastern United States. However, federal land managers and policymakers currently lack the tools necessary to separate carbonaceous aerosols originating from natural and anthropogenic fires from industrial- and mobile-source activities and vegetation on a routine basis, which is necessary for developing meaningful control strategies.

Traditionally, source apportionment tools use either air quality models, which attempt to simulate the contributions of sources based upon first principles, or source-receptor models, which apportion measured $PM_{2.5}$ based upon measured marker species and their source profiles. Neither technique is adequate. In this project, a receptor-hybrid modeling methodology was developed. The methodology involves a four-phase approach, all beginning with measured particulate data and ending with the apportionment of smoke to fire types and source regions. Each successive phase requires more detailed data and information, resulting in refined results. The level of refinement is dependent on the availability of the detailed data and information. The first phase is a simple bounding calculation based upon measured elemental and total particulate carbon ratios to estimate the contribution of all biogenic sources, including biomass burning to particulate carbon. The second phase employs a hybrid receptor model to apportion the particulate carbon to biomass burning and other sources. Two hybrid models were developed, first, a hybrid chemical mass balance (hybrid CMB) method merging chemical transport modeling results with measured smoke marker species, and second, a hybrid positive matrix factorization (hybrid PMF) method in which chemical transport modeling (CTM) results are introduced as an additional constraint on the multivariate PMF receptor model. The third and fourth phases involve apportioning the biomass burning contribution to fire types, e.g., wild and prescribed fires and source regions. In addition, a semi-empirical CTM incorporating fire emissions, precipitation, and back dispersion calculations was develop to generate inputs for the hybrid models.

II. Background and Purpose

Carbonaceous compounds can account for over 50% of the fine particulate matter ($PM_{2.5}$) in rural and urban areas (Figure 1). Biomass burning from wild, prescribed, agricultural, and other fire types is a significant contributor to $PM_{2.5}$ carbon [Park et al., 2007], contributing to adverse health effects and haze and affecting the earth's radiation balance (global climate change). Biomass burning also contributes to ozone and nitrogen deposition [Nikolov, 2008]. These contributions can be large and easily identified near the fires, but they can also be significant hundreds of miles downwind where the smoke plume is diluted and has lost its clear identity. Ambient $PM_{2.5}$ and ozone concentrations are regulated under the Environmental Protection Agency's (EPA) National Ambient Air Quality Standards (NAAQS), which set limits on the concentrations allowed for hourly, daily, and annual average values to protect public health and the environment. Haze in our national parks and wilderness areas, collectively known as Class I areas (CIA), is regulated via the EPA's Regional Haze Rule (RHR), which requires each state to set "reasonable progress" goals to return visibility to natural conditions on the 20% haziest days by 2064 while preventing further degradation of visibility on the 20% clearest haze days.

Both the RHR and NAAQS have routine monitoring programs to support these regulations. The Interagency Monitoring of Protected Visual Environments (IMPROVE), a federal land management agency/EPA monitoring program that collects speciated $PM_{2.5}$ and PM_{10} concentrations in and near CIAs (Figure 1), was established to track progress toward this RHR goal. The Chemical Speciation Network (CSN) is a U.S. EPA monitoring network, similar to IMPROVE, established to help understand the causes of $PM_{2.5}$ exceedances and trends in $PM_{2.5}$ over time.

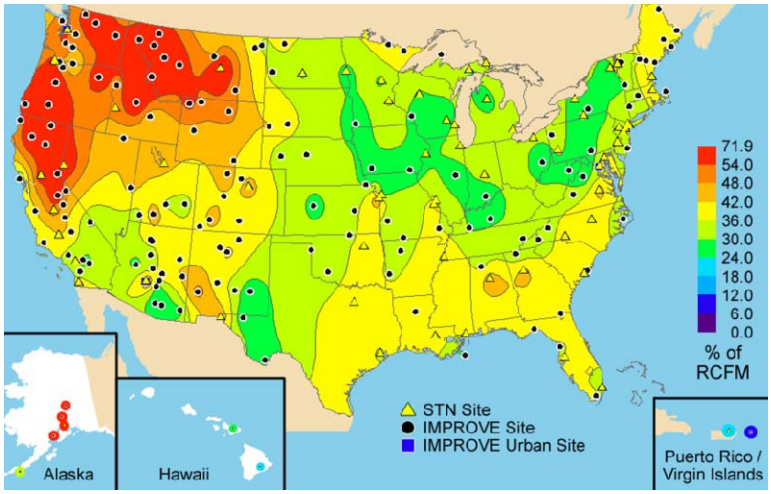


Figure 1. Fractional contribution of organic carbon to $PM_{2.5}$ as measured by IMPROVE and the CSN.

The PM and ozone NAAQS are violated at a number of communities [EPA, 2008a; EPA 2008b], and virtually all CIAs have haze above the natural background [Copeland et al., 2008]. State and federal organizations are required to develop and implement plans and programs to reduce emissions sufficient to attain and protect the NAAQS and make reasonable, steady progress to reduce anthropogenic emissions to achieve the long-term natural visibility goal in the RHR. Central to any meaningful implementation plan is an understanding of which sources

contribute to these pollutants, and regulators are beginning to look to sources of smoke to achieve needed decreases [Oregon, 2008].

Biomass burning occurs from natural fires (wildfire and wildland natural fires) and human-caused fires including prescribed, agricultural, and residential wood burning (RWB). The smoke source type is important since natural sources of haze are not controllable under the RHR, and recently the EPA implemented the Exceptional Event Rule, which provides for the exclusion of days strongly influenced by impacts from uncontrollable events, including smoke from wildfires, in assessing NAAQS violations. Although annual wildfire activity accounts for the majority of smoke emissions in the western United States, anthropogenic fires can significantly contribute to haze and $PM_{2.5}$ events.

Biomass burning emits $PM_{2.5}$ and volatile organic carbon (VOC). The VOCs participate in photochemical reactions, forming ozone and higher molecular weight VOCs that can condense out, forming secondary organic aerosols (SOA). VOCs are emitted as a by-product of the combustion processes, and Grieshop et al. [2008] have shown that in the presence of sunlight these VOCs can double the particulate organic carbon (OC) over the course of a day. During a fire, the heating of the vegetation prior to combustion can also emit biogenic VOCs such as isoprene and monoterpenes [Lee et al., 2008], which are known to generate SOAs. These SOAs are identical in composition to SOA formed from gases emitted by plant respiration, which is prevalent in the southeastern and northwestern United States where fire activity is high. The combination of combustion VOCs and increased biogenic VOCs can result in SOAs accounting for more than half the particulate matter from biomass burning, [Engling et al, 2006; Lee et al., 2008].

Current biomass burning emission inventories likely overestimate the particulate emissions and underestimate the VOC emissions due to biomass combustion and do not account for the increased emissions of biogenic VOCs. The effect of the poor understanding of these emissions was evident in a recent state-of-the-art modeling study conducted by the NPS where an unrealistically low 2% of the simulated smoke aerosol was SOA in the United States. One impact of underestimating the SOA contribution is that these models will overestimate the near-source impacts and underestimate the distant impacts.

To obtain the goals of the RHR and meet the requirements of the NAAQS, air quality regulators need a routine and cost-effective methodology and tools capable of apportioning primary and secondary aerosols in measured $PM_{2.5}$ to contributing sources, including different fire types, and their source regions, with associated uncertainties, on a daily basis. Long-term results are also needed to assess the successes of smoke-management policies. These regulatory needs are post-fire events, separate and complementary to the operational smoke forecasting done collaboratively by smoke managers and air quality agencies, and the methods and tools should be retrospective, taking advantage of all data and information generated during and after the events.

The purpose of this project was to develop source apportionment methods that are capable of satisfying the smoke management needs for air quality regulations. In order to do this, hybrid receptor modeling techniques were developed and began to be tested. This project was designed to develop a framework for apportioning smoke contributions to particulate matter and develop the theoretical basis and initial tools for performing the apportionment and testing them. However, it was not meant to develop operational tools suitable for use by the general air

quality regulators at this time.

III. Study Description

Traditionally, source apportionment is conducted using source-oriented chemical transport models (CTM) and receptor models. CTMs attempt to directly simulate pollutant emissions and their transport and fate. These models can simulate primary and secondary aerosols and contributions from specific source types and source regions. However, CTMs can suffer from large unconstrained errors [Pun et al., 2003; Nikolov, 2008], reducing the utility of modeling results.

Receptor models use measured chemical and physical characteristics of the particulate matter to apportion particulate mass to various source types, e.g., biomass-burning mobile and point sources. They rely on the fact that many sources emit a unique proportion of aerosols constituents known as their source profile. For example, the composition of biomass burning includes OC and elemental carbon (EC), as well as numerous trace compounds unique to biomass burning, such as levoglucosan, while emissions from power plants are dominated by sulfur species. The measured concentrations are then equal to these source profiles multiplied by the source contributions:

Receptor models are based on the chemical mass balance (CMB) equation [Gordon, 1980; Watson, 1984]. The CMB model relies on the assumption that the measured concentration of airborne aerosol species can be described by the sum of a number of source profiles such that

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} \qquad (1)$$

where
x_{ij} = concentration at a receptor for the j^{th} species on the i^{th} measurement
g_{ik} = contribution of the k^{th} source to the receptor on the i^{th} measurement
f_{kj} = fraction of the k^{th} source that is species j, also known as the source profiles
e_{ij} = residual for the j^{th} species in the i^{th} measurement

If $\boldsymbol{x}$ and $\boldsymbol{f}$ are known then equation 1 can be solved for the source contributions $\boldsymbol{g}$. This is known as the CMB model and has been extensively used in past studies to apportion primary aerosol species to individual and multiple samples [Watson et al., 2008, and references therein]. In general, the true source profiles at the receptor are not known and a number of limiting assumptions are made that are often violated, degrading the results [Watson and Robinson, 1984]. To date, there are few source profiles for secondary aerosol components and the CMB model cannot apportion the contribution of SOA to the source types [Schauer and Cass, 2000; Zheng et al. 2002; Watson et al., 2008].

Individual organic compounds known as molecular markers can also be used in CMB modeling analyses to apportion sources of primary organic carbon and fine particle mass [Robinson et al., 2006]. Molecular markers have a high degree of source specificity and in some cases are primarily associated with a single source type. For example, levoglucosan is primarily associated with biomass smoke. In these cases the CMB equation can be simplified to

$$x_i = g_i f_k + e_i \qquad (2)$$

The source contribution $\boldsymbol{g}$ is then simply the ratio of the measured molecular marker x divided by

the source profile ***f***, i.e., the molecular marker to OC ratio in the source's primary emissions. CMB with molecular marker species suffers from issues similar to traditional CMB modeling.

If the data set contains an adequate number of samples, multivariate algorithms can be used to derive the source profiles ***f*** and source contributions ***g*** using only measured aerosol composition. These techniques are based on regression and factor analyses [Hopke, 1985; Watson et al., 2008]. Since the source profiles are derived from the data, it is possible to apportion the average contributions of secondary and primary aerosols to the source types. Two receptor-oriented multivariate models often used are the Positive Matrix Factorization, PMF [Paatero, 1998], and UNMIX [Henry, 2000]. These tools have successfully been used with IMPROVE and CSN data to apportion measured $PM_{2.5}$ to biomass burning smoke and other sources [Poirot et al., 2001; Kim and Hopke, 2004].

The multivariate methods are powerful techniques and under the right circumstances can apportion the aerosols to specific source types including biomass burning. However, the derived source profiles often have large errors and are not necessarily unique to a specific source type but instead a mixture of covarying source types, and it is more correct to refer to these as source factors.

Hybrid source apportionment modeling. Air quality simulation and source-receptor models each have different strengths and weaknesses. Air quality simulation models can apportion secondary and primary species and identify contributions from individual fires, thus allowing the separation of wild, prescribed, and agricultural fires. However, the information requirements and chemical mechanisms of these models are incomplete and the results are subject to large unconstrained errors and biases. On the other hand, the source-receptor models are constrained by measured data, bounding their errors, but apportioning secondary particulate matter and between smoke types is problematic. Therefore neither technique adequately addresses the needs of the air quality regulations for smoke apportionment.

Hybrid source apportionment modeling directly combines measured data with air quality modeling results, ideally preserving the temporal and source type resolving power of the air quality model, but has results that are bounded by the measured data and satisfy the source profiles. Hybrid source apportionment models can be developed in either the source-oriented or receptor-oriented framework. In the source-oriented framework, measured data are used to constrain CTMs by either directly incorporating the measured data into the model through data assimilation methods, e.g., adjoint modeling [Henze et al., 2004] or as a post-processing of the model results, typically through inversion methods such as synthesis inversion [Enting, 2002; Schichtel et al., 2005; Schichtel et al., 2006] and Kalman filtering methods [Gilliland et al., 2003]. These are useful techniques but require extensive model development and/or do not incorporate many of the measured tracer species used in receptor models since air quality models do not simulate them. In the hybrid receptor models, the CTM results are incorporated directly into the CMB equation where they act as an additional constraint in the receptor model.

A hybrid receptor modeling methodology was developed as part of this project. The methodology involves a four-phase approach, all phases beginning with measured particulate data (Figure 2) and ending with the apportionment of smoke to fire types and source regions. Each successive phase requires more detailed data and information, resulting in refined results. The level of refinement is dependent on the availability of the detailed data and information.

The first phase is a simple bounding calculation based upon measured organic and

elemental carbon concentrations to apportion $PM_{2.5}$ carbon to contemporary, or biogenic, and fossil fractions [Bench et al, 2006; Schichtel et al., 2008a]. The fossil particulate carbon is due primarily to the combustion of coal, oil, and gas fuels, while contemporary carbon arises from biogenic sources. The biogenic carbon is then an upper bound for contributions from biomass burning.

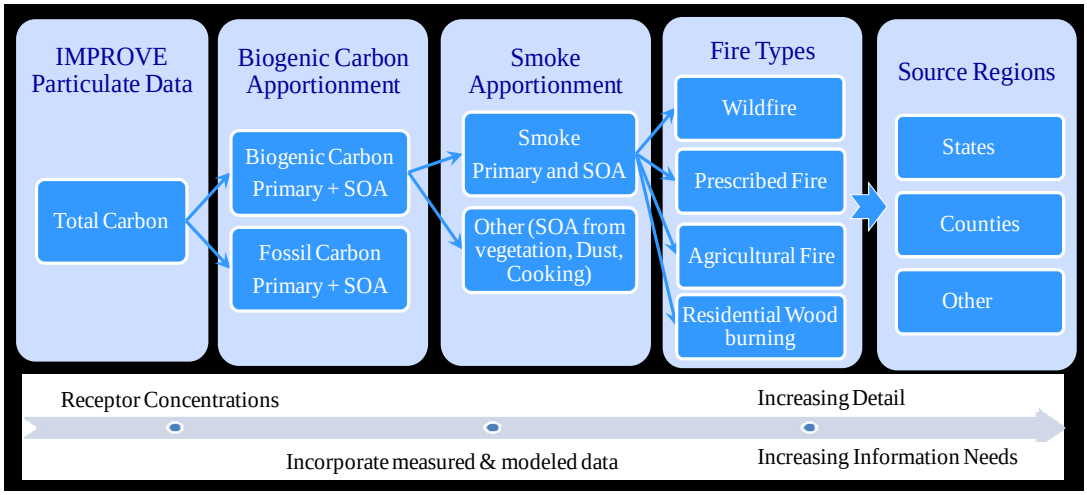


Figure 2. The different phases in apportioning measured particulate carbon to biomass burning and other sources.

The second phase employs the hybrid receptor model to apportion the organic carbon to biomass burning and other sources. Two hybrid models were developed. The first is a hybrid CMB, molecular marker approach. This method uses a simple CTM or back trajectories combined with biomass burning emission inventory and measured biomass burning molecular marker species and their source profiles to estimate the smoke contribution. This method can be used with one or more samples to apportion biomass contribution to primary organic carbon. The second hybrid model is a hybrid PMF method that directly incorporates CTM source attribution results into the PMF model solution as an additional constraint on the receptor model. The CTM results essentially aid in the identification and separation of the different source types contributing to the particulate carbon. This method requires multiple samples but can apportion average primary and secondary contributions from biomass burning to all of the samples.

The third phase of the methodology apportions the contributions of individual fire types. This is done using CTM results and relies on fire classifications in the emissions inventory. This information is generally missing from the inventories and represents an issue requiring future activity. The final phase apportions the biomass contributions to source regions such as individual states. This was not done as part of this project.

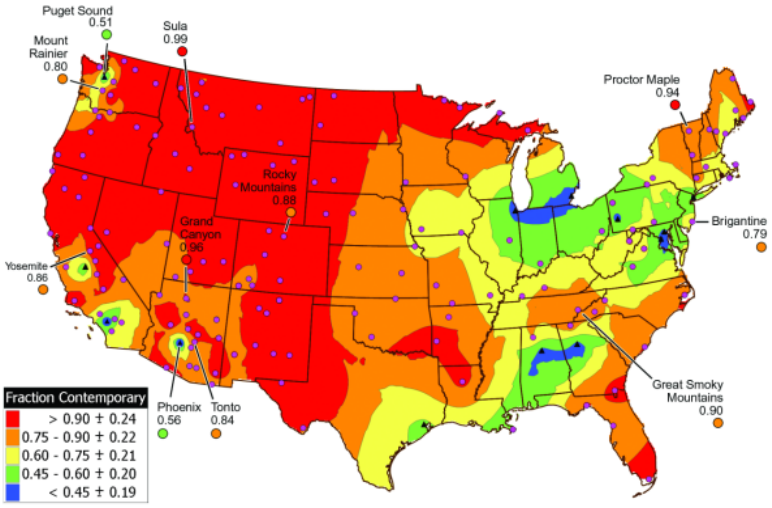
IV. Key Findings

The key findings section provides a brief summary of the methods developed for each phase of the biomass burning source apportionment as well as the inputs developed for the hybrid receptor models. More detailed descriptions, presentations, and documents, as well as data, are available from the project website.

IV.I. Bounding Biomass Burning Contributions by Estimating Biogenic Carbon Concentrations

The sources contributing to particulate carbon can be divided into two broad categories, one arising from the combustion of fossil fuels (fossil carbon) and the second arising from biogenic sources (biogenic carbon), such as biomass burning, meat cooking, and SOA from vegetation VOCs. In remote areas the majority of biogenic carbon is from biomass burning and vegetation SOA [Park et al., 2007]. Radiocarbon (^{14}C) is present at a small but approximately constant level in biogenic materials but is absent in fossil carbon; therefore ^{14}C can be used to partition particulate carbon into fossil and biogenic components. Biomass burning only contributes to the biogenic carbon; therefore the radiocarbon derived biogenic component is an upper bound for the biomass contributions to particulate carbon.

Radiocarbon measurements are expensive and conducted only for special studies. Such a study was conducted at 11 IMPROVE monitoring for different periods from 2004–2006 [Bench et al., 2006]. It was found that the biogenic and fossil fractions of particulate total carbon (TC) were strongly related to the ratio of particulate EC and TC as estimated by the thermal optical reflectance method used in the IMPROVE program [Schichtel et al., 2008a]. This relationship did vary by season. EC and TC are routinely measured at all IMPROVE monitoring sites. Therefore, the biogenic carbon to EC/TC relationship can be used to estimate the biogenic carbon at the IMPROVE sites and each sample. Figure 3 presents the average fraction of contemporary or biogenic carbon for the 2005 winter and summer seasons. We anticipate adding the estimated biogenic and fossil carbon concentrations to the IMPROVE database at http://vista.cira.colostate.edu/views/.



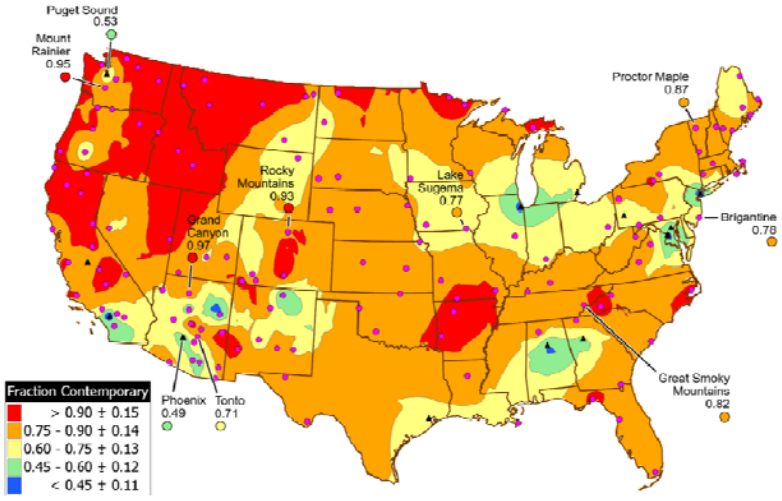


Figure 3. Average summer (top) and winter (bottom) 2005 contemporary fraction of $PM_{2.5}$ carbon at IMPROVE sites and spatially interpolated.

IV.II. Back-Dispersion Chemical Transport Model for Source Apportionment

The hybrid receptor models require a priori biomass burning source apportionment results as inputs, including contributions from different fire types and source regions. This information is not routinely available. Therefore a simple receptor-oriented, semi-quantitative CTM was developed. The CTM uses 6-day-back airmass histories generated from the CAPITA (Center for Air Pollution Impact and Trend Analysis) Monte Carlo (CMC) model [Schichtel and Husar, 1997], using meteorological data from the Eta Data Assimilation System (EDAS). The airmass history incorporates multiple air parcel trajectories to simulate the dispersion of the airmass. Every hour along each trajectory in the ensemble, the 3-D location, precipitation rate, mixing height, and other meteorological parameters are saved. Nonfire emissions are estimated using the Western Regional Air Partnership (WRAP) 2002 emission inventory. The biomass burning emissions were created from a moderate resolution imaging spectroradiometer (MODIS) satellite-derived inventory [Wiedinmyer et al., 2006]. This inventory identified some of the fires as agricultural.

$PM_{2.5}$ carbon concentrations are simulated by integrating the airmass histories forward in time. Trajectories below the mixed layer accumulated $PM_{2.5}$ carbon and VOCs from emissions evenly distributed throughout the mixed layer. First-order rate processes are applied for dry removal of $PM_{2.5}$ carbon and conversion of VOC to $PM_{2.5}$ carbon. Dry removal is applied only when the trajectories are below the mixing height. Wet removal is applied to all trajectories that encountered precipitation, with the rate coefficients dependent on the precipitation rate. The rate coefficients were determined in an optimization study where they were adjusted within physically reasonable ranges to best reproduce the average measured total $PM_{2.5}$ carbon, with SOA accounting for ~40% during the summer [Schichtel et al., 2008a].

Although this is a simple CTM model, it does capture much of the complexity of the atmospheric processes leading to particulate carbon concentrations, specifically dispersion, wet removal, and the temporal/spatial variability of biomass burning and other emissions. In addition, this model reproduced the measured $PM_{2.5}$ carbon concentrations with similar though somewhat lower performance at four western and eastern U.S. sites than the state-of-the-art

Community Multiscale Air Quality (CMAQ) CTM simulation conducted by WRAP for the RHR [Schichtel et al., 2008b]. Figure 4 presents the modeled source contributions from biomass burning, vegetation SOA, area, and other sources to the IMPROVE sites at Upper Buffalo, Akansas, and in the northern Rocky Mountains. These results are compared to the TC measured from the IMPROVE monitoring sites. As shown the sources contributing to the TC vary by season and from day to day. Overall, the model simulation reproduces the measured TC temporal variability.

The CTM has been run for every IMPROVE monitoring site from 2006 through 2008. The results are available from the project website. A simple tool, using Microsoft Excel pivot tables to compare the modeled measured TC and visualize the modeled results for each monitoring site, was also created and is available from the project website.

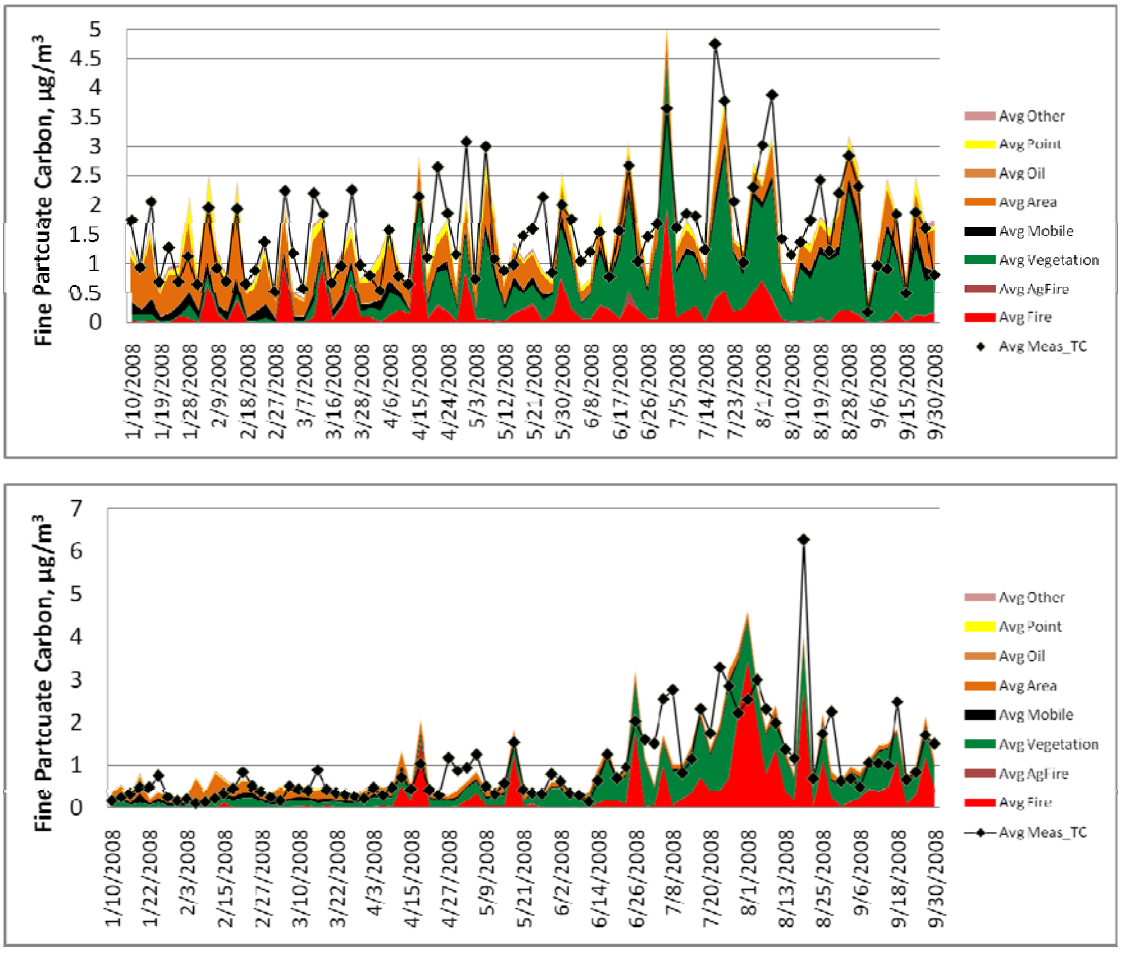


Figure 4. Simulated contributions of various sources to the TC at Upper Buffalo, Akansas (top), and in the northern Rocky Mountains (bottom). The measured TC from the IMPROVE network is also plotted for comparison.

IV.III. Biomass Burning Source Profiles

Source profiles for biomass burning and other sources are needed for input into the hybrid CMB model as well as for testing and evaluating the models. For this project, a database of biomass burning source profiles was compiled as well as a set of source profile biomass burning marker species that spatially vary based upon different vegetation and fuel loadings throughout the United States.

IV.III.I. Source profile database

A database of biomass burning smoke source profiles from 238 burns from 102 different fuels was compiled from the literature and the Fire Lab at Missoula Experiment (FLAME) study. FLAME was a companion JFSP-funded project to study the physical, chemical, and optical properties of primary smoke emissions [McMeeking et al., 2009]. As part of this study, source profiles from about 130 different burns from 39 fuels were measured. The source profiles contain elemental, ionic, and organic molecular marker species, as well as fine particulate mass, EC, OC, and TC. The database is available from the project website.

IV.III.II Spatially variable biomass burning molecular marker source profiles

As part of the FLAME study, levoglucosan, mannosan, galactosan, and other organic marker species were measured for each fuel burn [Sullivan et al., 2008]. In addition, an inexpensive method for measuring these species from a particulate sample was developed that is suitable for use in a routine monitoring network. These marker species have been shown to exhibit important characteristics for CMB modeling. Specifically, they are relatively unique to biomass burning and stable in the atmosphere. However, the source profiles can vary dramatically based upon the fuels burned [Sullivan et al., 2008] and combustion temperature [Simoneit et al., 1999].

To account for the variation due to fuel type and loading, smoke marker species source profiles for six vegetation types were constructed: softwood branches, shrub branches, hardwood leaves, shrub leaves, needles, and grasses. The spatial distribution, mixture, and loadings of these vegetation types were estimated from the Fuel Characteristic Classification System (FCCS) [Ottmar et al., 2007] on a 1-km by 1-km resolution for the conterminous United States. The combustion efficiency for each vegetation type in the mix was estimated from literature values and used to estimate the fractional contribution of each vegetation type to the fuel burned, which was then used to aggregate the source profiles in a given mixture.

Figure 5 presents the source profiles for levoglucosan/OC and mannosan/OC over the United States. A similar map was created for galactosan but is not shown. The levoglucosan/OC ratio can vary by about a factor of 2 over the United States and the mannosan/OC ratio can vary by a factor of 10. This variability translates to the potential variability in CMB modeling estimates of biomass burning contributions to particulate organic carbon from CMB modeling without using the proper source profiles. Note that the source profiles used to generate these maps are from laboratory burns. Therefore, they are most suited to low-intensity burns and may not be representative of wildfire or residential wood burning. These source profiles are available from the project website. See Patterson [2009] for detailed information on these source-profile maps.

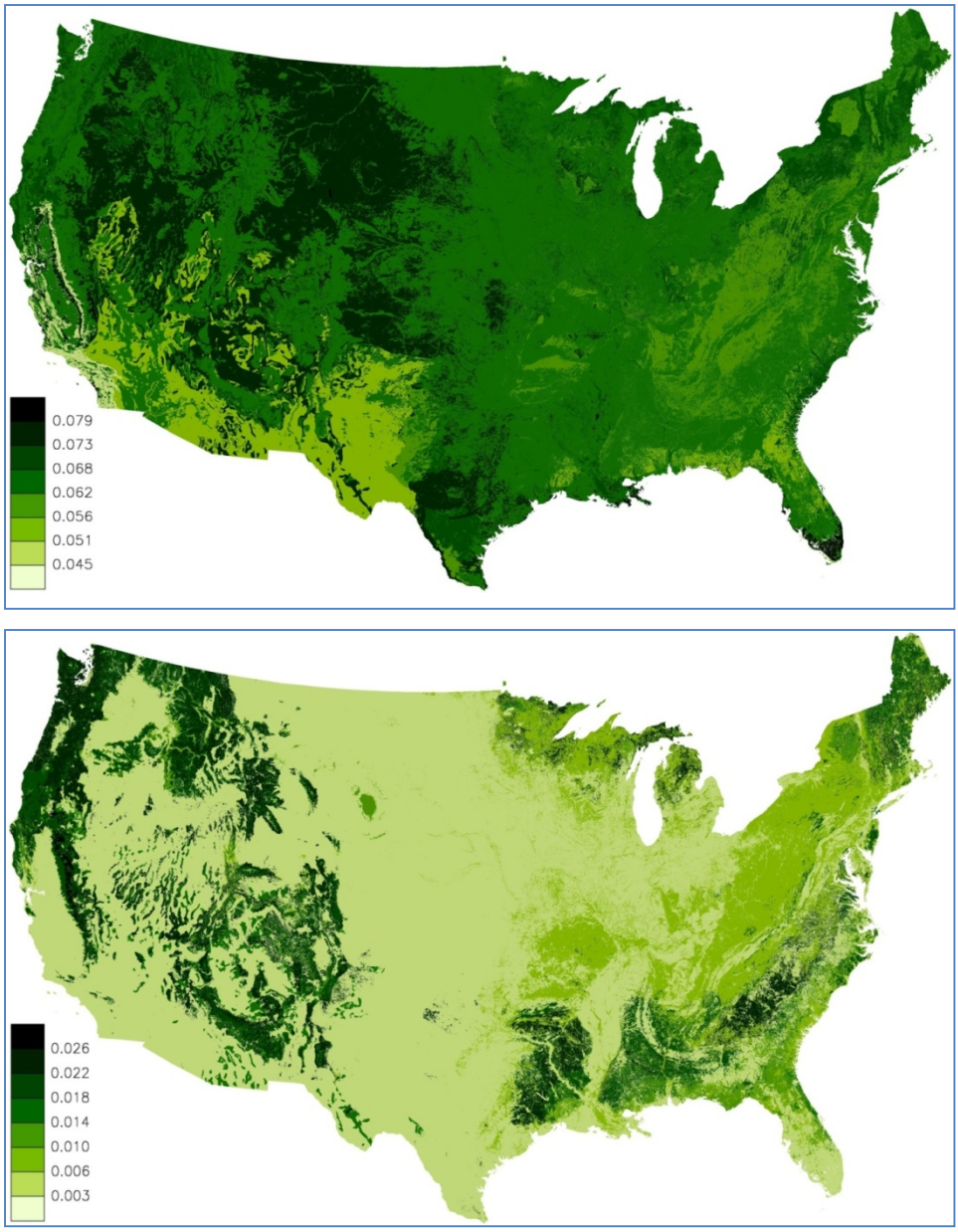


Figure 5. The biomass burning levoglucosan/OC (top) and mannosan/OC (bottom) source profiles.

IV.IV. Hybrid Chemical Mass Balance (CMB) Model

The smoke marker species levoglucosan, mannosan, and galactosan are relatively unique to biomass burning. Therefore the CMB model can be simplified to equation 2, and the contribution of biomass burning to primary particulate carbon or organic carbon is estimated by dividing the measured marker species by its source profile. However, as shown in Figure 5, the smoke marker species source profile can vary significantly depending on the location of the fire, potentially introducing large errors into the source apportionment. To reduce this error, a method was developed whereby fire location or emissions maps are combined with the source profile maps to estimate the source profiles for each fire. Then, using back trajectories from a receptor site, the fires that are likely to impact the monitoring site are identified, and the source profiles from these fires are aggregated together. Using these refined source profiles and

measured marker species, the contribution of the primary biomass burning emissions to the TC or OC at the receptor site is estimated using either equation 1 or 2, depending on available information.

This is illustrated in Figure 6, where levoglucosan was measured at Rocky Mountain National Park in 2005. Using a best estimate for the source profiles from the literature resulted in biomass burning contributions that were larger than the measured TC on the August 3 sample, a clear indication that the contribution of TC from the biomass burning was overestimated. Refined source profiles were created by combining fire locations with the source profiles and using 48-hour back trajectories. As shown, the refined source profiles decreased the biomass burning contribution for all samples, and on August 3 the biomass contribution is now estimated to be about half of the measured TC.

The basic concept and initial testing for this method is laid out in Holden [2008] and Patterson [2009]. A more formal method in which the source profiles are combined with fire emissions and the CMC-CTM is being developed by the NPS. The results will be presented at the American Association of Aerosol Research Biomass Burning Special Symposium sponsored by the JFSP in October 2009.

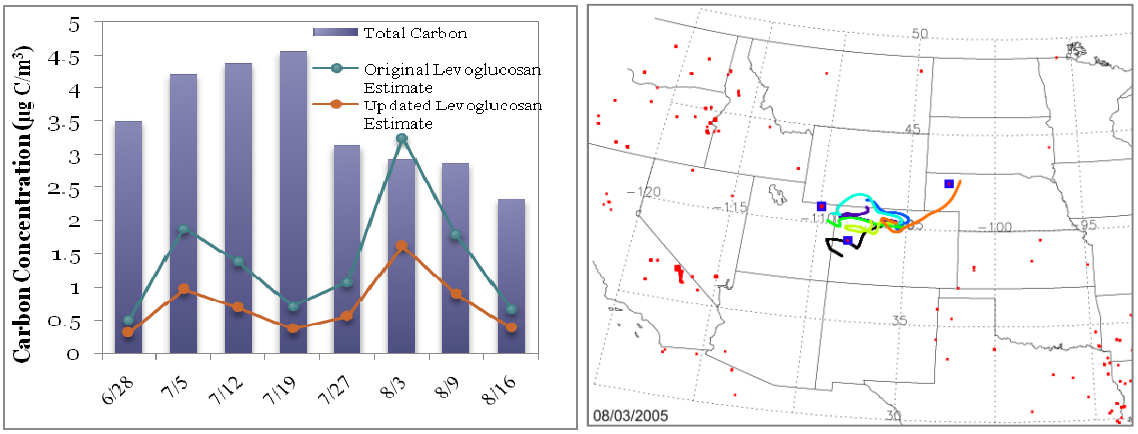


Figure 6. Left: estimated contributions of biomass burning to particulate carbon at Rocky Mountain National Park, using measured levoglucosan and an average levoglucosan/TC source profile and source profiles derived from back trajectories, fire emissions, and spatially variable source profiles. Right: location of fires and 48-hour HYSPLIT back trajectories used to develop the updated source profiles for the August 3 sample. From Patterson [2009].

IV.V. Hybrid Positive Matrix Factorization (PMF)

As developed, the hybrid CMB model does not apportion secondary organic carbon and does not take advantage of all of the measured data at IMPROVE and other similar monitoring sites. In addition it requires smoke marker species that are not routinely measured. To overcome these issues, a hybrid version of the PMF multivariate receptor model was created. The hybrid PMF directly incorporates a priori CTM modeling results, either as source attribution estimates or emission tracer species, into the CMB equation:

$$[x_{ij}, y_{ik}] = \sum_{k=1}^{p} g_{ik}[f_{kj}, I + b_{lk}] + [e_{ij}, e_{ik}] \qquad (3)$$

where

$y_{ik} = g_{ik} \pm e^{y}_{ik}$ are the prior estimated source contributions from the k^{th} source to the i^{th}

measurement at the receptor with residuals $e_{ik}^{y} = \sum_{l=1}^{p} g_{il} b_{lk} + e_{ik}$.

The CTM results are introduced as an additional constraint on the receptor model to aid the identification and separation of the different source types. In the current version, the measured concentrations and a priori source attribution results are assumed known and equation 3 is solved for ***g***, ***f***, and ***b***. This is done using the PMF receptor model, which solves equation 2 using a robust, constrained, weighted, least-square optimization technique in which the individual measured concentrations and prior source attribution estimates are weighted by their uncertainty.

The system was tested using synthetic data where the "truth", prior CTM source attribution, and measured data were known by using results from two CTM models and incorporating additional errors. The modeled smoke contributions were adjusted so that about 30% was SOA. As shown in Figure 7, the incorporation of the CTM results in the receptor model significantly reduced the systematic and random errors in the source attribution results compared to the CTM model results or receptor models alone. On average the hybrid receptor model results had little bias, indicating that the model was able to reproduce the large SOA contributions. The hybrid receptor model simulations included the primary smoke marker species, levoglucosan, mannosan, and galactosan. Excluding them from the analysis degraded the results; however, the hybrid model results were still superior to using PMF or the CTM results alone.

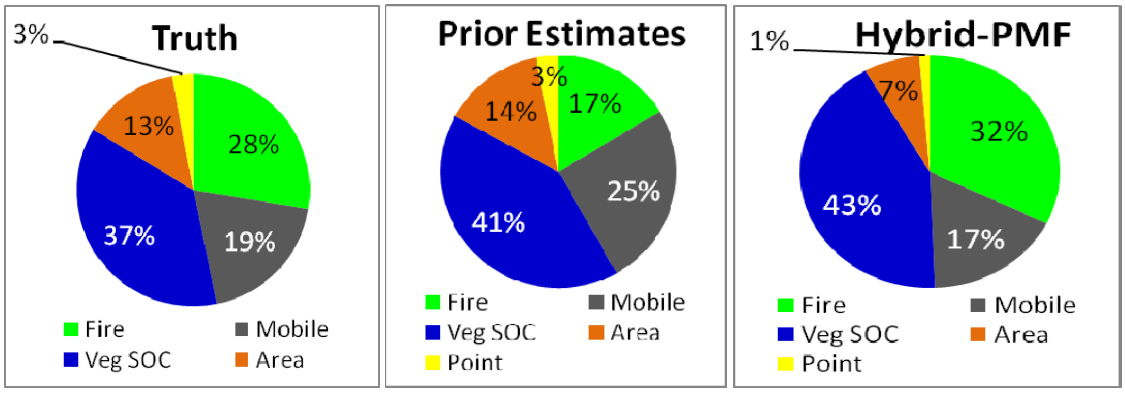


Figure 7. The relative contribution of sources to synthetic particulate carbon concentrations. Left: the truth or actual contributions; middle: the synthetic source contribution with large random and systematic errors added to them; right, the simulated source contribution using the hybrid PMF model incorporating the prior estimates.

IV.VI. Outreach

As part of this project there was extensive outreach conducted to the federal, state, and private scientific and regulatory communities. This outreach was conducted by means of the participation and sharing of results at a number of conferences, workshops, and meetings; see list below. In the original proposal a workshop was planned to share the results from this project and illustrate the use of the models. We believe that the extensive participation in other workshops and meetings accomplished this task and a formal workshop on the hybrid receptor modeling framework was not convened.

Publications and conference and workshop presentations wholly or partially supported by this project follow:

IV.VI.I. Publications:

Bench, G., S. Fallon, B.A. Schichtel, W.C. Malm, and C. McDade. 2007. Relative contributions of fossil and contemporary carbon sources to PM 2.5 aerosols at nine Interagency Monitoring for Protection of Visual Environments (IMPROVE) network sites. J. Geophysical Research-Atmosphere. 112 (D10): Art. No. D10205 MAY 19 2007

Schichtel, B. A. et al. 2008 Fossil and Contemporary Fine Carbon Fractions at 12 Rural and Urban Sites in the United States. *J. Geophys. Res.*, **113**, D02311.

Holden, A.S., A. P. Sullivan, S. Kreidenweis, J. L. Collett, Jr., B. A. Schichtel, W. C. Malm, and G. Bench. 2009. Estimating Contributions of Primary Biomass Combustion to Fine Particulate Matter at Sites in the Western United States. In progress.

Patterson, L.A., Schichtel, B.A., Sullivan, A. P., Collett, J.L. Jr., Holden, A. S., Kreidenweis, S. M., and Malm, W. C. 2009. Development of a Wildland Fire Smoke Marker Emissions Map for the Contiguous United States. In progress

Schichtel, B.A. W.C. Malm, J.L. Collett, Jr., A.P. Sullivan, A.S. Holden, L.A. Patterson, M.A. Rodriguez, M.G. Barna. 2008b. Estimating the contribution of smoke to fine particulate matter using a hybrid receptor model. In progress.

IV.VI.II. Master's Theses Partially Supported by This Project

Holden, A.S. 2008. Estimating Contributions of Primary Biomass Combustion to Fine Particulate Matter at Sites in the Western United States. Colorado State University Master's Thesis. (Http://)

Patterson, L.A. 2009. Development of Wildland Fire Smoke Marker Emissions Maps for the Conterminous United States. Colorado State University Master's Thesis. Http://

IV.VI.III. Conference Proceeding and Presentations

Schichtel, B. A., G. Bench, S. Fallon, C. E. McDade, J. C. Chow, and W. C. Malm. Apportionment of Particulate Carbon into Fossil and Contemporary Fractions at 12 Rural and Urban Sites in the United States. Presented at the AGU Fall Conference, December 2006, San Francisco, CA

Holden, A.S., A. P. Sullivan, S. Kreidenweis, J. L. Collett, Jr., B. A. Schichtel, W. C. Malm, and G. Bench. Application of Anion Exchange Chromatography with Pulsed Amperometric Detection for Measurement of Levoglucosan in Ambient Aerosol Samples, Presented at the AAAR Annual Conference, September, 2007 in Reno, NV.

Schichtel, B.A., W.C. Malm, J.L. Collett, A.P. Sullivan, A.S. Holden, L.A. Patterson, M.A. Rodriguez, M.G. Barna. 2008. Estimating the contribution of smoke to fine particulate matter using a hybrid-receptor model. Proceedings from Aerosol & Atmospheric Optics: Visual Air Quality and Radiation, April 2008, Moab UT.

Schichtel, B.A., W.C. Malm, J.L. Collett, A.P. Sullivan, A.S. Holden, L.A. Patterson, M.A. Rodriguez, M.G. Barna. Where There's Smoke There's Haze: Estimating the Contribution of Fires to PM2.5 and Haze. Presented at the BlueSky Smoke Modeling Framework Stakeholders' Meeting, May, 2008, Boise, ID.

Patterson, L.A., Schichtel, B.A., Sullivan, A. P., Collett, J.L. Jr., Holden, A. S., Kreidenweis, S. M., and Malm, W. C. 2008. Development of a Wildland Fire Smoke Marker Emissions Map for the Contiguous United States. Presented annual the AGU Fall Conference, December 2008, San Francisco, CA.

IV.VI.IV. Workshops and Meetings

Schichtel B.A, Bench, G. and Malm W.C. The Use of Carbon Isotope Analysis to Distinguish the Contribution of Biogenic and Anthropogenic Carbon. FLAME (Fire Lab at Missoula Experiment) Data Meeting held at Colorado State University, Fort Collins, February 22-23, 2007, Colorado State University. http://chem.atmos.colostate.edu/FLAME/feb_data_meeting.html

Schichtel, B. A., W. C. Malm, J. L. Collett, A.P. Sullivan, and A. S. Holden. Contribution of Smoke to PM2.5 and Haze: Development of Smoke Source Profiles and Routine Source Apportionment Tools. Presented at the International Biomass Smoke Health Effects (IBSHE) Conference, August 2007, at the University of Montana.

Each year the progress and results from the project were presented at the annual IMPROVE Steering Committee meetings. These presentations can be found on the IMPROVE websites: http://vista.cira.colostate.edu/improve/Activities/activities.htm

Developing fire emission products suitable for operational and retrospective analyses. A workshop held at Colorado State University, Fort Collins, CO in February 2008 with the National Park Service, Western Governors Association, Forest Service AirFire Team, and Forest Service Remote Sensing Application Center (RSAC) to discuss.

A new ad-hoc committee on cooperative operational biomass burning emissions has been formed to coordinate development of biomass burning emissions among federal agencies and key data providers. Two workshops have been held: First at the University of Maryland College Park Alumni Center, December 2&3 2008, and the second at Naval Research Laboratory, Monterey, California, June 25 & 26, 2009.

V. Management Implications

This project has developed methodologies and tools for use by experts to quantify what portion of measured fine particulate ($PM_{2.5}$) comes from fire, and of that amount, to determine how much comes from domestic natural wildfire, from agricultural burning, and from prescribed fire. This information can be directly used by air quality regulators in developing regional haze and $PM_{2.5}$ State Implementation Plans (SIPs) to reduce the haze and $PM_{2.5}$ below regulated thresholds. In addition, the results can be used to assess the usefulness of emissions reduction techniques for application in smoke management programs. This will ensure that fire managers are able to maintain the capability to use prescribed fire and quantify the effectiveness of emissions reduction techniques mandated to be applied by smoke management programs. Additional development is needed before the hybrid receptor models can be used in a more routine fashion by non-experts.

VI. Relationship to Other Recent Findings and Ongoing Work on This Topic

There are a number of issues and information gaps that still exist for estimating the contributions of biomass burning to $PM_{2.5}$, haze and other air quality issues. One important issue is that there is increasing evidence that SOA can significantly increase the contributions of biomass burning to $PM_{2.5}$. However, we currently lack an accurate inventory of smoke SOA precursor emissions and the mechanistic understanding to predict the amount of SOA from fires downwind. To begin to address this issue there is a recently funded JFS project# 09-1-03-1 involving Colorado State University, Carnegie Mellon University, Washington University, and the NPS. The objectives of the project are to 1) quantify SOA production as a function of smoke age in emissions produced by combustion of a variety of important wildland and agricultural fuel types; 2) quantify emissions of SOA precursors (traditional and nontraditional) in biomass combustion smokes for incorporation into air quality models; 3) parameterize the evolution of smoke organic aerosol concentrations for implementation in chemical transport models; and 4) develop simple analytical techniques for SOA marker species and their source profiles suitable for use in routine air monitoring networks.

A second issue is that the hybrid receptor models require addition development for use in a more routine fashion by non-experts as well as refinement to incorporate additional

information. As part of the JFS project# 09-1-03-1, the hybrid PMF model will be further developed to incorporate a priori source profiles to estimate the smoke contributions with associated uncertainties. In addition, the SOA marker species and source profiles will also be incorporated into the hybrid PMF model. Last, methods will be developed to reduce the user judgment required and determine a best set of default options.

The hybrid receptor models are dependent on a prior source attribution estimates from a CTM. There are several efforts to routinely generate this information including work on the Bluesky gateway (http://getbluesky.org/bluesky/sti/) at the National Oceanic and Atmospheric Administration (NOAA) (http://www.arl.noaa.gov/smoke.php) and the EPA. In addition, the NPS will continue to develop the CMC-CTM developed for this project. As part of this effort, the NPS is now in the process of collaborating with the EPA to compare modeled smoke impacts to those from the sophisticated Eulerian CMAQ model.

In concept, the hybrid receptor models can apportion the smoke to different fire types, provided this information exists in the emission inventories. The information classifying fire as wild, prescribed, etc., for many of the fires does exist in ground-based fire reports, but it is not integrated into any routine emission inventories. One outcome of the workshop on "developing fire emission products suitable for operational and retrospective analyses" was to initiate the "Collaborative fire emissions analysis and inventory (CFEAI) project integrating ground-based and remote sensing data" pilot study involving the USFS AirFire, USFS RSAC, WRAP, NPS, and EPA. In this study, protocols and methods will be developed and data sources identified to develop routine biomass burning inventories that incorporate additional metadata including the type of fire.

VII. Future Work Needed

As evidence by the on-going activities listed above, there is considerable work funded by the JFSP and others being conducted that will further our capabilities to perform retrospective biomass burning apportionment. Future work that still needs to be addressed includes

- Source profiles for smoke marker species were primarily developed from low-intensity burns in a laboratory. There is a need to gather more field data from actual prescribed and wildfires to evaluate and validate these profiles.

- Current smoke marker species source profile maps can be refined by including the temporal variations due to changes in vegetation with season as well as fire types and combustion temperatures.

- Develop routine a priori smoke apportionment estimates that include the types of biomass burning impacting the receptor sites and the source regions of the fires.

- Incorporate the hybrid receptor models and results into existing decision support systems (DSS). This could include incorporating into the Bluesky framework and adding to the VIEWS DSS (http://vista.cira.colostate.edu/views/).

VIII. Deliverables Cross-Walk

Deliverable	Description	Status
Annual reports	Annual report	Completed
Final report	Project final report, summarizing results and deliverables	Completed
Project Website	http://vista.cira.colostate.edu/improve/Studies/SmokeApport/ SmokeApport.htm	Updated as needed
Development of hybrid receptor	Development of hybrid receptor biomass burning apportionment framework	Completed
Workshop/training on hybrid model	Workshop and apportionment tool training session for air quality modeling centers, air regulators and fire planners and managers.	Incomplete. As discussed in IV.VI. Outreach instead of organizing a project workshop we participated in a number of related workshops and meetings sharing the methods and results developed in this project
Peer-reviewed journal articles	See publication list in IV.VI. Outreach	Some completed articles and some articlesin progress
Other documents, workshops and documents	Master's theses, conference presentations and proceeding and workshops and meeting are listed in IV.VI. Outreach	Completed

IX. Literature Cited

Bench, G., S. J. Fallon, B.A. Schichtel, W.C. Malm, C. McDade. 2007. Relative Contributions of Fossil and Contemporary Carbon sources to PM 2.5 Aerosols at Nine IMPROVE Network Sites, *J. Geophys. Res.*, **112**, D10205.

Copeland. S. A., M. Pitchford, R. Ames. 2008. Regional Haze Rule Natural Level Estimates Using the Revised IMPROVE Aerosol Reconstructed Light Extinction Algorithm. Submitted for review to *JAWMA.* Also see: http://vista.cira.colostate.edu/improve/Publications/GrayLit/032_NaturalCondIIpaper/Copeland_etal_NaturalConditionsII_Description.pdf.

Engling, G., Herckes, P., Kreidenweis, S., Malm, W. C., and Collett, Jr., J. L. (2006) Composition of fine organic aerosol in Yosemite National Park during the 2002 Yosemite Aerosol Char. Study. *Atmos. Env.* 40, 2959-2972.

Enting, I.G., *Inverse Problems in Atmospheric Constituent Transport*. Cambridge University Press, Cambridge, 2002**.**

EPA. 2008a. Area Designations for 2006 24-Hour Fine Particle ($PM_{2.5}$) Standards. http://www.epa.gov/pmdesignations/2006standards/index.htm

EPA. 2008b. 8-Hour Ground-level Ozone Designations. http://www.epa.gov/ozonedesignations/statedesig.htm.

Gilliland, A.B., Dennis, R.L.; Roselle, S.J.; Pierce, T.E. *J. Geophys. Res.-Atmospheres.* **2003**, *108(D15)*, Art. No. 4477.

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

Grieshop, A. P.; Logue, J. M.; Donahue, N. M.; Robinson, A. L. 2008. Laboratory investigation of photochemical oxidation of organic aerosol from wood fires 1: measurement and simulation of organic aerosol evolution. *Atmos. Chem. Phys. Disc.* 8, 15699-15737.

Henry, R. C., 2000. "UNMIX Version 2 Manual" Prepared for the U.S. Environmental Protection Agency.

Henze, D.K.; Seinfeld, J.H.; Liao, W.; Sandu, A.; Carmichael, G.R. *J. Geophys. Res.-Atmospheres*. **2004**, *109(D14)*, Art. No. D14201.

Holden, A.S. 2008. Estimating Contributions of Primary Biomass Combustion to Fine Particulate Matter at Sites in the Western United States. Colorado State University Master's Thesis. (Http://)

Hopke, P.K. 1985. Receptor modeling in environmental chemistry. Chemical Analysis. John Wiley & Sons (Eds.), New York, NY.

Kim, E. and Hopke, P.K. (2004) Comparison between Conditional Probability Function and Nonparametric Regression for Fine Particle Source Directions Atm Env 38 (2004) 4667–4673.

Lee, A., H. Kim, B. Yan, C. E. Cobb, C. Hennigan, S. Nichols, M. Chamber, E. S. Edgerton, J. J. Jansen, Y. Hu, M. Zheng, R. J. Weber, and A. G. Russell. 2008. Diagnosis of Aged Prescribed Burning Plumes Impacting an Urban Area. ES&T 42, NO. 5.

McMeeking, G. R., S. M. Kreidenweis, C.M.Carrico, A.Sullivan, M.Holden, J. L. Collett, Jr., S. Baker, C.E. Wold, W. M. Hao, W.C.Malm. 2009. Trace gases emitted by the combustion of several North American wildland plant species during the Fire Laboratory at Missoula Experiment (FLAME). Submitted to Submitted to *J. Geophys. Res.*

Nikolov, N. 2008. Impact of Wildland Fires and Prescribed Burns on Ground Level Ozone Concentration: Review of Current Science Concepts and Analytical Approaches. Report from the Rocky Mountain Center USDA FS Rocky Mountain Research Station. http://wrapair.org/forums/toc/meetings/080729m/Effect_of_Fires_on_Ozone.pdf.

Oregon, State of. 2008. State Implementation Plan Revision Adoption of Regional Haze Strategies in Oregon: A Plan for Implementing Section 308 (40CFR 51.308) of the Regional Haze Rule. State of Oregon, Department of Environmental Quality, 811 SW Sixth Avenue, Portland, OR 97204-1390. Available at: http://www.deq.state.or.us/aq/haze/docs/RegHazePlandr1.pdf.

Ottmar, R.D., Sandberg, D.V., Riccardi, C.L. and Prichard, S.J., 2007. An overview of the Fuel Characteristic Classification System - Quantifying, classifying, and creating fuelbeds for resource planning. Canadian Journal of Forest Research-Revue Canadienne De Recherche Forestiere 37 (12):2383-2393.

Paatero, P. 1998. "User's Guide for Positive Matrix Factorization Programs PMF2 and PMF3".

Patterson, L.A. 2009. Development of Wildland Fire Smoke Marker Emissions Maps for the Conterminous United States. Colorado State University Master's Thesis. Http://

Park, R.J., D.J. Jacob, and J.A. Logan. 2007. Fire and biofuel contributions to annual mean aerosol mass concentrations in the United States. *Atm. Env.* **41**, 7389–7400.

Poirot, R.L.; Wishinski, P.R.; Hopke, P.K.; and Polissar, A.V. 2001. Comparative Application of Multiple Receptor Methods To Identify Aerosol Sources in Northern Vermont. Environ. Sci. Technol., **35**,4622-4636.

Pun, B.K., S.Y. Wu, C. Seigneur, C., J.H. Seinfeld, R.J. Griffin, and S.N. Pandis. 2003. Uncertainties in modeling secondary organic aerosols: Three-dimensional modeling studies in Nashville/western Tennessee, *ES&T* **37**, 3647.

Robinson, A.L. Subramanian, R., Donahue, N.M., Bernardo-Bricker, A. and Rogge, W.F. 2006. Source Apportionment of Molecular Markers and Organic Aerosol. 2. Biomass Smoke. *Environ. Sci. Technol.*, **40**, 7803-7810.

Schichtel, B.A., and R.B. Husar. 1997. Regional Simulation of Atmospheric Pollutants with the CAPITA Monte Carlo Model. *J. Air & Waste Man. Ass.* **47**, 331–343.

Schichtel, B.A., K.A. Gebhart, W.C. Malm, M.G. Barna. (2005) Reconciliation and interpretation of Big Bend National Park particulate sulfur source apportionment: Results from the Big Bend Regional Aerosol and Visibility Observational study - Part I. *JAWMA*, **55 (11)**: 1709-1725.

Schichtel, B. A., W. C. Malm, K. A. Gebhart, M. G. Barna, and E. M. Knipping (2006), A hybrid source apportionment model integrating measured data and air quality model results, *J. Geophys. Res.*, **111**, D07301, doi:10.1029/2005JD006238.

Schichtel, B. A., W. C. Malm, G. Bench, S. Fallon, C. E. McDade, J. C. Chow and J. G. Watson. 2008a Fossil and Contemporary Fine Carbon Fractions at 12 Rural and Urban Sites in the United States. *J. Geophys. Res.*, **113**, D02311.

Schichtel, B.A. W.C. Malm, J.L. Collett, Jr., A.P. Sullivan, A.S. Holden, L.A. Patterson, M.A. Rodriguez, M.G. Barna. 2008b. Estimating the contribution of smoke to fine particulate matter using a hybrid receptor model. Proceedings from Aerosol & Atmospheric Optics: Visual Air Quality and Radiation, Moab, April 28.

Schauer, J.J., and Cass, G.R. 2000. Source apportionment of wintertime gas-phase and particle- phase air pollutants using organic compounds as tracers. Environmental Science & Technology, 34(9), 1821-1832.

Simoneit, B. R. T.; Schauer, J. J.; Nolte, C. G.; Oros, D. R.; Elias, V. O.; Fraser, M. P.; Rogge, W. F.; Cass, G. R. Levoglucosan, a tracer for cellulose in biomass burning and atmospheric particles. *Atmos. Environ.* **1999**, *33* (2), 173-182.

Sullivan, A.P., A.S. Holden, L.A. Patterson, S.M. Kreidenweis, W.C. Malm, W.M. Hao, C.E. Wold, and J.L. Collett, Jr.. 2008. A Method for Smoke Marker Measurements and its Potential Application for Determining the Contribution of Biomass Burning from Wildfires and Prescribed Fires to Ambient $PM_{2.5}$. *J. Geophys. Res.*, **113,** Article Number: D22302.

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

Watson, J.G., L.W.A. Chen, J.C. Chow, P. Doraiswamy, and D.H. Lowenthal. 2008. Source apportionment: Findings from the U.S. Supersites Program. *J. Air & Waste Man. Ass.* **58**, 265–288.

Watson, J.G., and Robinson, N.F. 1984. A method to determine accuracy and precision required of receptor model measurements. Presented at the APCA Quality Assurance in Air Pollution Measurements Meeting. Pittsburgh, PA.

Wiedinmyer, C., Quayle,B., Geronc, C., Belotea, A., McKenzied, D., Zhange, X., O'Neill, S., Wynnea, K. 2006. Estimating emissions from fires in North America for air quality modeling. *Atmos. Environ.* 40, 3419-3432.

Zheng M, Cass GR, Schauer JJ, Edgerton ES. Source apportionment of PM2.5 in the southeastern United States using solvent-extractable organic compounds as tracers ENVIRONMENTAL SCIENCE & TECHNOLOGY 36 (11): 2361-2371 JUN 1 2002