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Improving Source Apportionment of Fine Particles in the Eastern United States Utilizing Temperature-Resolved Carbon Fractions

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ABSTRACT

The objectives of this study were to examine the use of carbon fractions to identify particulate matter (PM) sources, especially traffic-related carbonaceous particle sources, and to estimate their contributions to the particle mass concentrations. In recent studies, positive matrix factorization (PMF) was applied to ambient fine PM ($PM_{2.5}$) compositional data sets of 24-hr integrated samples including eight individual carbon fractions collected at three monitoring sites in the eastern United States: Atlanta, GA, Washington, DC, and Brigantine, NJ. Particulate carbon was analyzed using the Interagency Monitoring of Protected Visual Environments/Thermal Optical Reflectance method that divides carbon into four organic carbons (OC): pyrolized OC and three elemental carbon (EC) fractions. In contrast to earlier PMF studies that included only the total OC and EC concentrations, gasoline emissions could be distinguished from diesel emissions based on the differences in the abundances of the carbon fractions between the two sources. The compositional profiles for these two major source types show similarities among the three sites. Temperature-resolved carbon fractions also enhanced separations of carbon-rich secondary sulfate aerosols. Potential source contribution function analyses show the potential source areas and pathways of sulfate-rich secondary aerosols, especially the regional influences of the biogenic, as well as anthropogenic secondary aerosol. This study indicates that temperature-resolved carbon fractions can be used to enhance the source apportionment of ambient $PM_{2.5}$.

IMPLICATIONS

The paper examines the regional similarities of key sources of the carbonaceous aerosol in the eastern U.S. PMF has been applied to composition data including eight carbon fractions collected at three Interagency Monitoring of Protected Visual Environments monitoring sites. The results suggest that temperature-resolved carbon fractions permit the separation between spark ignition exhausts and diesel emissions in $PM_{2.5}$ source apportionment studies. The compositional profiles for these two key sources show similarities among the three sites.

INTRODUCTION

Air quality studies have been undertaken since U.S. Environmental Protection Agency (EPA) promulgated new national ambient air quality standards for airborne particulate matter (PM).[1,2] As part of such studies, source apportionment methods for the airborne PM are required to understand the relationship between human exposure and source emissions. Positive matrix factorization (PMF)[3] has been developed to be a powerful receptor model for airborne PM[4–6] and has been used to assess ambient PM source contributions.[7–10] In these studies, carbon was typically measured by thermal optical methods.[11,12] Using the organic carbon (OC) and elemental carbon (EC), PMF generally could not separate multiple carbonaceous particle sources, especially traffic-related combustion sources. These sources were extracted as a mixture of traffic sources or as a carbon-rich source combined with other measured species, because they had similar chemical profiles, similar temporal emission patterns, or the variations in concentrations are averaged out over the 24-hr sampling interval.

The Interagency Monitoring of Protected Visual Environments/Thermal Optical Reflectance (IMPROVE/TOR) method measures several individual carbon types including OC and EC fractions and the pyrolyzed OC. A source composition study by Watson et al.[13] found differences between particles from diesel and spark ignition sources. Their results suggest that these sources might be separated and identified by using temperature-resolved fractional carbons in factor analysis studies. Initial source apportionment results in a Seattle, WA, study[14] showed

that the carbon fraction could be used to separate traffic-related carbonaceous particle sources into gasoline and diesel emissions. Thus, the use of temperature-resolved carbon fractions in PMF analysis has been examined in recent fine PM ($PM_{2.5}$) studies of Atlanta, GA,[15] Washington, DC,[16] and Brigantine, NJ.[17] PMF appears to have successfully separated diesel emissions from gasoline emissions and provided optimal solutions to maximize the benefit of using available data.

The objective of this study was to examine the use of carbon fractions in source apportionment studies to identify ambient $PM_{2.5}$ sources for three monitoring areas in the eastern United States. PMF-resolved source profiles and contributions presented in recent publications[15–17] were used in this study. The model-derived source profiles of the particulate carbon fractions are compared with measured profiles from chassis dynamometer tests. Also, the similarities among model-derived carbon fraction profiles, as well as weekday/weekend variations in three monitoring sites, are discussed. The potential source contribution functions (PSCFs) were calculated to help identify the likely locations and pathways of the PMF-identified secondary sulfate aerosol sources.

MATERIALS AND METHODS

Sample Collection and Chemical Analysis

Atlanta $PM_{2.5}$ samples were collected at the Southeastern Aerosol Research and Characterization[10,18] monitoring site located in Atlanta, GA. Daily integrated $PM_{2.5}$ samples were collected using the particulate composition monitor (Atmospheric Research and Analysis, Inc.) that permits simultaneous sampling on a three-stage filter pack (Teflon, Nylon, and cellulose filter), a Nylon filter, and a quartz filter.

$PM_{2.5}$ samples were collected on Wednesdays and Saturdays at the IMPROVE[19] monitoring sites located in Washington, DC, and Brigantine National Wildlife Refuge, NJ. Integrated 24-hr $PM_{2.5}$ samples were collected on Teflon, Nylon, and quartz filters.

The quartz filters were analyzed via the TOR method[11] for eight temperature-resolved carbon fractions (Desert Research Institute). This protocol volatilizes OC by four temperature steps in a helium atmosphere: OC1 at 120 °C, OC2 at 250 °C, OC3 at 450 °C, and OC4 at 550 °C. After OC4 response returns to baseline or a constant value, the pyrolyzed OC (OP) is oxidized at 550 °C in a mixture of 2% oxygen and 98% helium atmosphere before the return of reflectance to its original value. Then three EC fractions are measured in oxidizing atmosphere: EC1 at 550 °C, EC2 at 700 °C, and EC3 at 850 °C. The EC1 concentration reported in IMPROVE/TOR protocol includes OP concentration. Therefore, the OP was subtracted from EC1 and used as an independent variable in the PMF analysis.

For the Atlanta study, 529 daily samples and 28 chemical species collected between August 1998 and August 2000 were used. A total of 718 samples and 35 species collected between August 1988 and December 1997 were used for the Washington, DC, study. A total of 910 samples and 36 species collected between March 1992 and May 2001 were used for the Brigantine study. Detailed filter analyses and summaries of $PM_{2.5}$ speciation data used in these PMF analyses are shown in Kim and Hopke.[15–17]

Multivariate Receptor Modeling

The general receptor modeling problem can be stated in terms of the contribution from p independent sources to all of the chemical species in a given sample as follows:[20,21]

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

where x_{ij} is the jth species concentration measured in the ith sample, g_{ik} is the particulate mass concentration from the kth source contributing to the ith sample, f_{kj} is the jth species mass fraction from the kth source, e_{ij} is residual associated with the jth species concentration measured in the ith sample, and p is the total number of independent sources. PMF provides a solution that minimizes an object function, $Q(E)$, based on uncertainties for each observation.[3,22] This function is defined as:

$$Q(E) = \sum_{i=1}^{n} \sum_{j=1}^{m} \left[\frac{x_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj}}{u_{ij}} \right]^2 \tag{2}$$

where u_{ij} is an uncertainty estimate in the jth constituent measured in the ith sample.

The application of PMF requires the estimated uncertainties for each of the data values. The uncertainty estimation provides a useful tool to decrease the weight of missing and below-detection limit data in the solution. The procedure of Polissar et al.[22] was used to assign measured data and the associated uncertainties. In addition, the associated uncertainties were increased to reduce the weight of some specific species in the model fit,[23] as well as to take the temporal variability in the source profiles into account. The detailed estimation and increase of uncertainties are specified in Kim and Hopke.[15–17]

PSCF

To identify the likely locations of the regional sources for the secondary sulfate aerosols, the PSCF[24,25] was calculated using the source contributions estimated from PMF and backward trajectories calculated using the Hybrid single particle lagrangian integrated trajectory (HYSPLIT) model.[26,27] Five-day backward trajectories starting at a height of 500 m above the ground level were computed using the vertical mixing model every day producing 120 trajectories per sample. The geophysical region covered by the trajectories was divided into grid cells of 1° × 1° latitude and longitude. If a trajectory end point of the air parcel lies in the *ij*th cell, the trajectory is assumed to collect $PM_{2.5}$ emitted in the cell. Once the $PM_{2.5}$ is incorporated into the air parcel, it is assumed to be transported along the trajectory to the monitoring site. $PSCF_{ij}$ is the conditional probability that an air parcel that passed through the *ij*th cell had a high concentration on arrival at the monitoring site defined as:

$$PSCF_{ij} = \frac{m_{ij}}{n_{ij}} \quad (3)$$

where n_{ij} is the total number of end points that fall in the *ij*th cell, and m_{ij} is the number of end points in the same cell that is associated with samples that exceeded the threshold criterion. In this study, the average contribution of each source was used for the threshold criterion. The sources are likely to be located in the area that has high PSCF values.

To minimize the effect of small values of n_{ij} that result in high PSCF values with high uncertainties, an arbitrary weight function was applied to downweight the PSCF values for the cell in which the total number of end points was less than three times the average number of the end points per cell.[8,25]

RESULTS AND DISCUSSION

A variety of factor number solutions were explored, and finally the 11-, 10-, and 11-source models provided the most physically reasonable source profiles for the Atlanta, Washington, DC, and Brigantine studies, respectively. The average contributions of each source to the $PM_{2.5}$ mass concentrations among the Atlanta, Washington, DC, and Brigantine studies are compared in Table 1. In the present study, no other sources are examined than traffic sources and secondary sulfate aerosols of which the apportionments were changed using temperature-resolved eight carbon fractions. A complete set of the resolved source profiles and contributions are provided in the supplemental material to this paper.

In the previous analysis of ambient $PM_{2.5}$ compositional data from Atlanta, including total OC and EC,[10] diesel emissions could not be separated from gasoline emissions. Eight sources were identified by the PMF including a motor vehicle source that appears to be a mixture of gasoline and diesel emissions. In the reanalysis of the same Atlanta dataset including the eight carbon fractions, PMF derived four traffic-related combustion source profiles (gasoline vehicle, on-road diesel, railroad, and bus maintenance facility/highway traffic) containing high-carbon fractions of which the abundance was different among the sources. The on-road diesel emissions account for 11% of the $PM_{2.5}$ mass concentration. The gasoline vehicle, railroad traffic, and bus maintenance facility/highway traffic account for 6%, 3%, and 2%, respectively of the $PM_{2.5}$ mass concentration. The ratio of the average contributions of diesel emissions relative to gasoline emissions of 2.3 (= 2.46 $\mu g/m^3$ sum of diesel emissions/1.07 $\mu g/m^3$ gasoline vehicle emissions) is reasonably close to model-derived ratios of 3.2 in Pasadena, CA, and 3 in West Los Angeles.[28] The fraction of mass contributions from four traffic-related combustion sources is 21% of the $PM_{2.5}$ mass concentration. This is consistent with 22% of motor vehicle source from the Atlanta study using total OC and EC measurements.[10]

Table 1. The comparison of average source contributions (%) to $PM_{2.5}$ mass concentrations among PMF studies with eight carbon fractions.[15–17]

	Average Source Contribution (SE)		
Variable	**Atlanta, GA[15]**	**Washington, DC[16]**	**Brigantine, NJ[17]**
Secondary sulfate aerosol (summer and winter)	49.7 (1.7)		
Secondary sulfate aerosol (summer-high)		42.8 (1.4)	47.9 (1.6)
Secondary sulfate aerosol (winter-high)		6.0 (0.2)	5.4 (0.2)
Secondary sulfate aerosol (carbon-rich)	5.9 (0.2)	10.6 (0.4)	6.6 (0.2)
Diesel emissions	10.5 (0.4)	1.8 (0.1)	3.3 (0.1)
Gasoline vehicle	6.4 (0.3)	21.0 (0.6)	12.5 (0.4)
Secondary nitrate aerosol	8.5 (0.4)	8.4 (0.3)	5.7 (0.2)
Airborne soil	2.8 (0.1)	1.9 (0.1)	3.6 (0.2)
Incinerator		3.7 (0.1)	1.9 (0.1)
Aged sea salt		2.2 (0.1)	7.5 (0.3)
Oil combustion		1.5 (0.1)	1.2 (0.04)
Sea salt			4.4 (0.2)
Wood smoke	6.5 (0.2)		
Metal processing	3.4 (0.2)		
Railroad traffic	2.5 (0.06)		
Cement kiln/carbon-rich	2.0 (0.09)		
Bus maintenance facility/highway traffic	1.8 (0.1)		

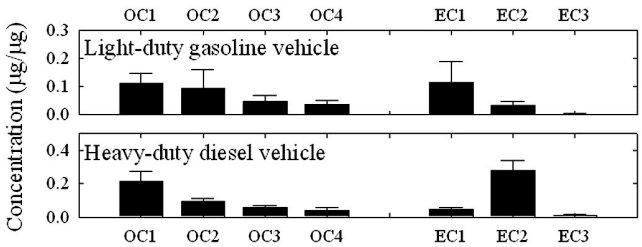

Figure 1. Measured carbon fractions from Watson et al.[13]

In contrast to the previous Washington, DC, and Brigantine studies using total OC and EC data,[9] PMF using the eight-carbon fractions separated traffic-related combustion sources into gasoline emissions and diesel emissions.[15–17] The ratios of the average contributions of diesel emissions relative to gasoline emissions are 0.09 in Washington, DC, and 0.26 in Brigantine, indicating limited diesel emissions in these areas. The fraction of mass contributions from gasoline and diesel emissions in Washington, DC, is 23%, which is consistent with the Atlanta study.[10,15] In Brigantine, the fraction of mass contributions from gasoline and diesel emissions is 16%, reflecting its more rural nature.

As shown in Figure 1, Watson et al.[13] reported the eight-carbon fractions measured by the IMPROVE/TOR method based on chassis dynamometer tests of light-duty gasoline vehicles and heavy-duty diesel vehicles. The model-derived carbon profiles of gasoline and diesel emissions are compared with these measured profiles in Figures 2 and 3. Similar to the measurements, the model-resolved gasoline emissions include the lower-temperature carbon fractions (OC1–OC4). The diesel emissions contain large amounts of the EC fractions (EC1–EC3). The Atlanta, Washington, DC, and Brigantine $PM_{2.5}$ studies show very similar carbon fraction profiles for gasoline emissions (Figure 2). In diesel emission profiles (Figure 3), OC fractions have different concentrations among the three sites. However, the large amount of EC1 in diesel emissions is consistent among three sites.

The average source contributions from gasoline and diesel emissions are compared between weekday and

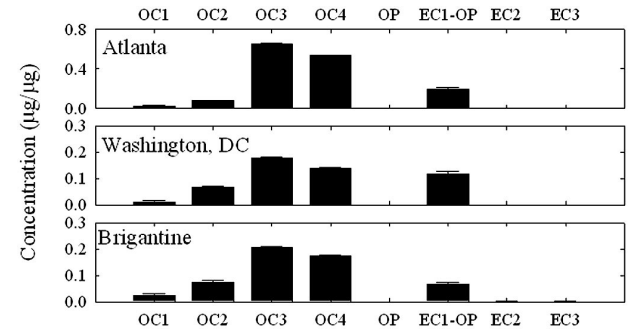

Figure 2. PMF-resolved carbon fractions of gasoline emissions at three monitoring sites.

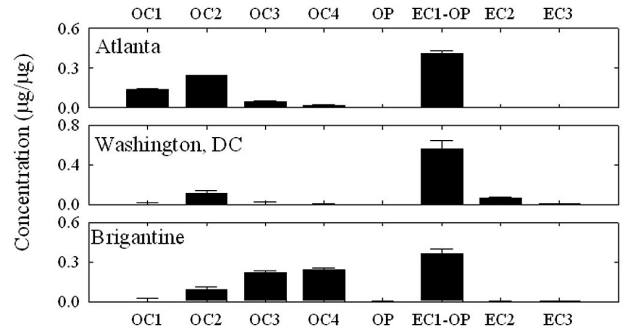

Figure 3. PMF-resolved carbon fractions of diesel emissions at three monitoring sites.

weekend in Figures 4 and 5. Gasoline emissions do not show strong weekday/weekend variations. The weekend-high variations of gasoline emissions in Brigantine, which is located northwest of Atlantic City, NJ, indicates the increased number of tourists traveling to Atlantic City on weekends. In contrast, the high weekday-to-weekend ratios for diesel emissions consistently shown in three sites (Figure 5) demonstrate that the diesel emissions are mostly from vehicles operating primarily on weekdays.

Comparison of the PMF-derived carbon fractions (Figures 2 and 3) with measured profiles (Figure 1) reveals interesting differences. The measured gasoline and diesel particles contain larger amount of OC1 fractions than those of model estimations. This difference may be because of the source-sampling artifact that is caused by the adsorption of fresh semivolatile organic compounds by quartz filters[29] in the dynamometer tests.

In addition, atmospheric chemical processing of lower molecular weight organic compounds between source and sampling sites may reduce the OC artifact. The source measurements showed that the gasoline emissions

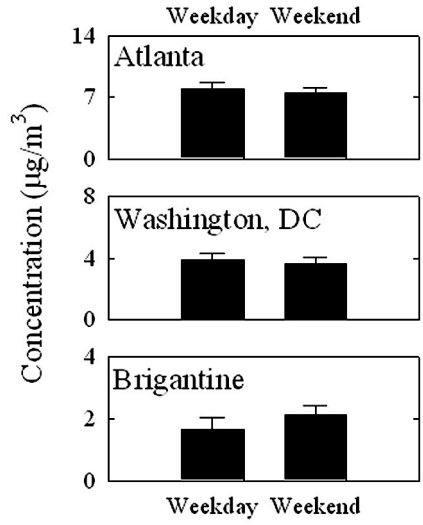

Figure 4. Weekday/weekend variations for PMF-resolved gasoline emissions.

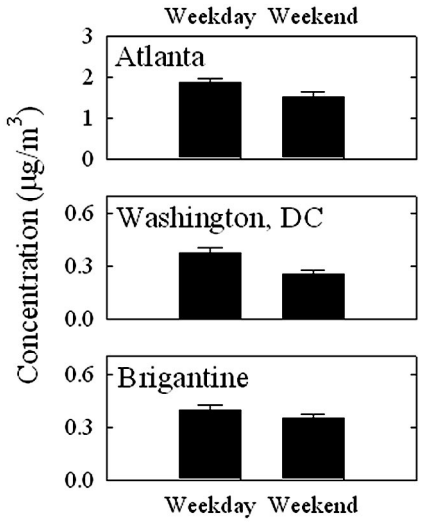

Figure 5. Weekday/weekend variations for PMF-resolved diesel emissions.

have a large concentration of OC4, and the diesel emissions contain a high concentration of EC2. In contrast, the model-derived carbon fraction profiles have high concentrations of OC3 and OC4 for the gasoline emissions and EC1 for the diesel emissions. The change in the carbon fractions in the thermal analysis may be influenced by the presence of other aerosol constituents. Transition metal oxides in the atmospheric aerosol may catalyze the oxidation of the OC and EC fractions at lower temperatures that results in higher concentrations of OC3 for the gasoline emissions and EC1 for the diesel emissions.[30]

In a previous northeastern U.S. aerosol study,[9] PMF separated the secondary sulfate aerosols into high-photochemistry aerosols and low-photochemistry aerosols with seasonal differences in the selerium/sulfur (Se/S) concentrations.[15] In the Atlanta $PM_{2.5}$ study, with Se data from less-sensitive analysis, PMF extracted two different secondary sulfate aerosols: carbon-low and carbon-rich secondary sulfate aerosols. The carbon-rich secondary sulfate aerosol shows a strong association between sulfate (SO_4^{2-}) and OC. Secondary aerosols typically become associated with carbon and tracer elements. Aerosol time-of-flight mass spectrometry studies of the Atlanta aerosol showed that secondary aerosols were combined with metals, carbons, nitrate, chloride, silicate, and phosphate.[31] This association is consistent with other studies that observed a similar profile in the data from Washington, DC,[16] and Brigantine, NJ.[17] Carbon-low secondary sulfate aerosol had the highest source contribution to $PM_{2.5}$ mass concentration in Atlanta (50%).

In the Washington, DC, and Brigantine $PM_{2.5}$ studies, PMF extracted three different secondary sulfate aerosols that have a high concentration of SO_4^{2-} and sulfur, respectively. The summer-high secondary sulfate aerosol has the highest source contribution to $PM_{2.5}$ mass concentrations both in Washington, DC, and Brigantine, of 43% and 48%, respectively. The observed seasonal variations may be because of the variation in source strength, in transport conditions, or both. The summer-high secondary sulfate aerosol shows strong seasonal variation with higher concentrations in summer when the photochemical activity is highest, indicating emissions from coal-fired power plants in summer.[8,9] With seasonal differences of the Se/SO_4^{2-} (or Se/S) concentrations, PMF separated winter-high secondary sulfate aerosol that has higher Se/SO_4^{2-} (or Se/S) concentration and showed higher contributions in winter indicating emissions from coal-fired power plants in winter.[8,9] Summer-high and winter-high secondary sulfate aerosols tend to have much less carbon associated with the profiles than has been observed in the prior studies[12,13] in which total OC and EC have been used instead of the eight-carbon fractions. The carbon now appears primarily in carbon-rich secondary sulfate aerosol.

Carbon-rich secondary sulfate aerosol shows a strong association between SO_4^{2-} (or sulfur) and OC. This carbon-rich secondary sulfatae aerosol was separated from other secondary sulfate aerosols with its high-carbon concentrations, especially the OP concentration. EC has been observed to be associated with SO_4^{2-} in individual particles.[31] An important question is the nature of the OC associated with these particles. Yu et al.[32] have observed an association between the water-soluble OC and OP formation in the thermal analysis of Hong Kong and China aerosols. Thus, the high OP in the carbon-rich secondary sulfate aerosol may be secondary OC produced from the oxidation of volatile precursors and that has become water-soluble in the atmosphere. The PSCF plot of the carbon-rich secondary sulfate aerosol described below shows the long distance transport of sulfur and OC.

It is suggested that this carbon-rich secondary sulfate aerosol may be, in part, the result of heterogeneous acid-catalyzed reactions between the acidic sulfate and gaseous organic compounds, which lead to additional secondary organic aerosol formation.[33] SO_4^{2-} particles can also provide a surface onto which semivolatile organic compounds can condense. There are several possible mechanisms for the formation of the carbon-rich secondary sulfate aerosol, and the exact nature of this factor cannot be deduced from the factor analysis alone.

The fraction of two secondary sulfate aerosols identified in Atlanta study was 56%. The fraction of three secondary sulfate aerosols identified in the Washington, DC, study was 59%, which is consistent with the 57% identified in previous studies with two carbon fractions.[9] In the Brigantine study, the fraction of three secondary sulfate

aerosols was 60%. This is consistent with the 59% contribution from the three secondary sulfate aerosols identified in closely situated Washington, DC. When the average source contributions from secondary sulfate aerosols to the $PM_{2.5}$ mass contributions are compared for the Atlanta, Washington, DC, and Brigantine studies, the summer-high and winter-high secondary sulfate aerosols do not show strong weekday/weekend variations. In contrast, carbon-rich secondary sulfate aerosol has weekend-high variations in three studies. The reasons for this apparently anomalous weekday/weekend variation of the carbon-rich secondary sulfate aerosol observed in the three studies need additional investigation.

PSCF plots for the secondary sulfate aerosols are compared in Figures 6, 7, and 8 in which PSCF values are displayed in terms of a color scale. As shown in Figure 6a, the PSCF plot of Atlanta carbon-low secondary sulfate aerosol shows the influence of midwestern coal-fired power plants in the Ohio River Valley.[34] Potential source areas and pathways that give rise to the high contribution to Atlanta are located in Pennsylvania and West Virginia, where known sulfur dioxide sources are located.[8] These identified areas also include areas where the secondary sulfate aerosols were formed in addition to areas where the sources were located. There are also areas of potential influence in Louisiana and Eastern Texas along the coast

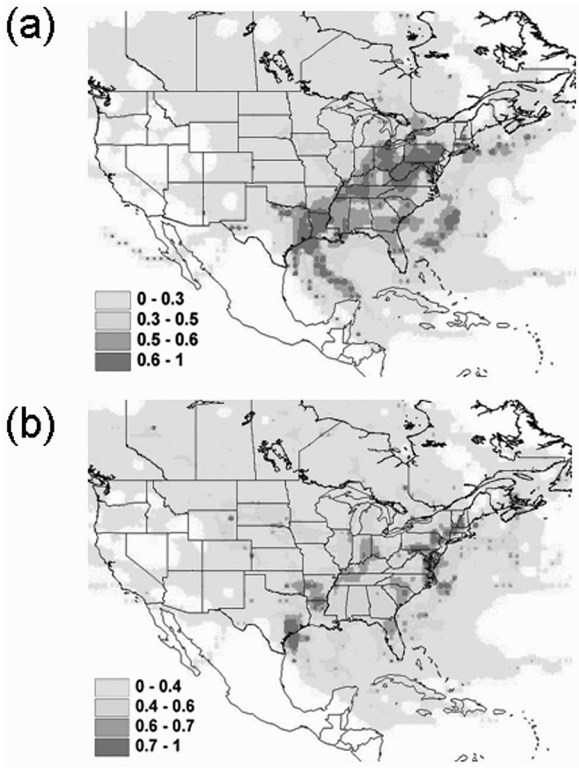

Figure 6. PSCF plots for Atlanta $PM_{2.5}$ study[15]; (a) carbon-low secondary sulfate aerosol; and (b) carbon-rich secondary sulfate aerosol.

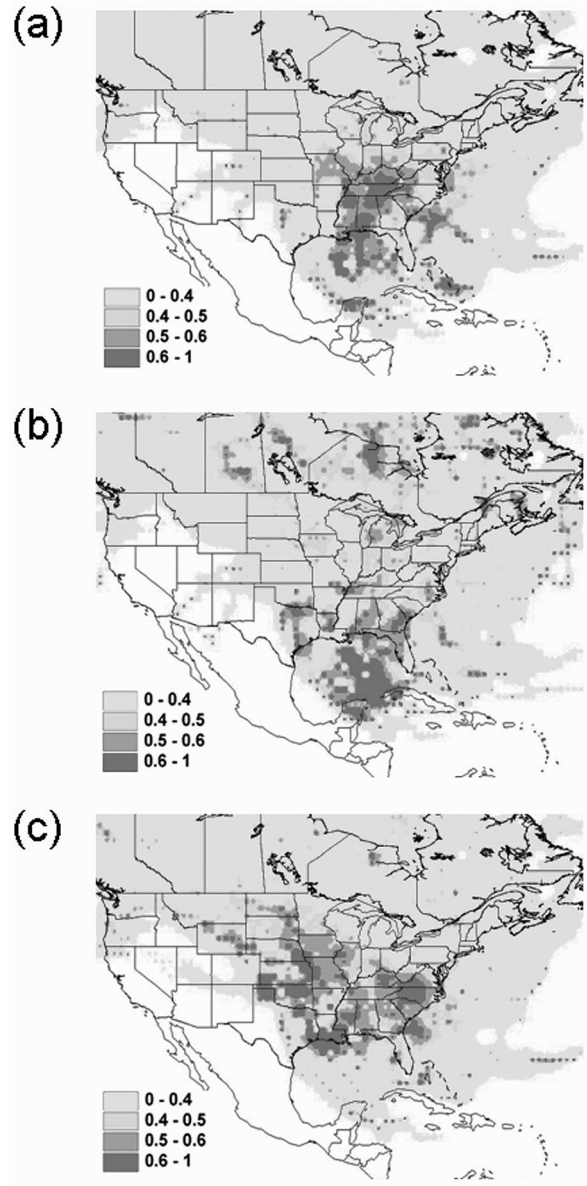

Figure 7. PSCF plots for Washington, DC, $PM_{2.5}$ study[16]; (a) summer-high secondary sulfate aerosol; (b) carbon-rich secondary sulfate aerosol; and (c) winter-high secondary sulfate aerosol.

where significant petrochemical industries and lignite-burning power plants are situated. The PSCF plots of summer-high secondary sulfate aerosols contributing to Washington, DC, and Brigantine in Figures 7a and 8a also show the Ohio River Valley, as well as areas in southern Louisiana, Mississippi, and Alabama. The Mississippi and Alabama areas might be associated with sulfur emissions. However, the detailed nature of these areas is uncertain. In Figures 7c and 8c, the high-potential areas and pathways of the winter-high secondary sulfate aerosol include the Ohio River Valley, South Louisiana, and Northwestern and Southwestern Missouri. In contrast to the high-PSCF value areas of summer-high secondary sulfate aerosols, those of winter-high secondary sulfate aerosols are

shifted toward the northwest because of the seasonal change of major wind direction that is consistent with PSCF results in the Vermont $PM_{2.5}$ study.[8]

The PSCF plot of carbon-rich secondary sulfate aerosol in Atlanta (Figure 6b) shows high values in urban areas along the East Coast and Southeastern Texas. These areas are likely to be related to the volatile OC emissions that then give rise to secondary organic aerosol. The potential source areas and pathways of the carbon-rich secondary sulfate aerosol in Washington, DC, and Brigantine (Figures 7b and 8b) include Southeastern Texas, Southern Louisiana, Mississippi, and Alabama. In addition, there are other high-potential areas around Hudson Bay in Canada, suggesting the potential for secondary OC contributions from Canadian boreal forest fires.

Figure 7b also shows high PSCF value areas in the Gulf of Mexico. This region may represent the influence of forest fire smoke from Central America that contributed to the high concentration of organic aerosol. The organic aerosols from forest fires and sulfate can come along, because the organic compounds support high-photochemistry enhancing SO_4^{2-} formation. The high correlation between wood smoke samples and OP formations in the thermal optical carbon analysis has been reported by Schauer et al.[35] and Chow et al.[36] In addition, the formation of the pyrolyzed carbon with increasing temperature was shown in Czimczik et al.[37] In Figure 8b, the potential source areas of Brigantine include Eastern Tennessee, Northeastern Georgia, and Western South Carolina. These areas may relate to the volatile OC emissions from biogenic sources that contribute to secondary organic aerosol or areas that also have frequent wildfire. Brigantine (Figure 8b) also shows the potential for Canadian boreal forest fires to contribute to this source. There remain some potential source areas in the Ohio River Valley. The PSCF plot of carbon-rich secondary sulfate aerosol indicates regional influences of the biogenic, as well as anthropogenic secondary aerosol. Therefore, more work is needed to fully identify the nature of this source that is found at all three of the sites.

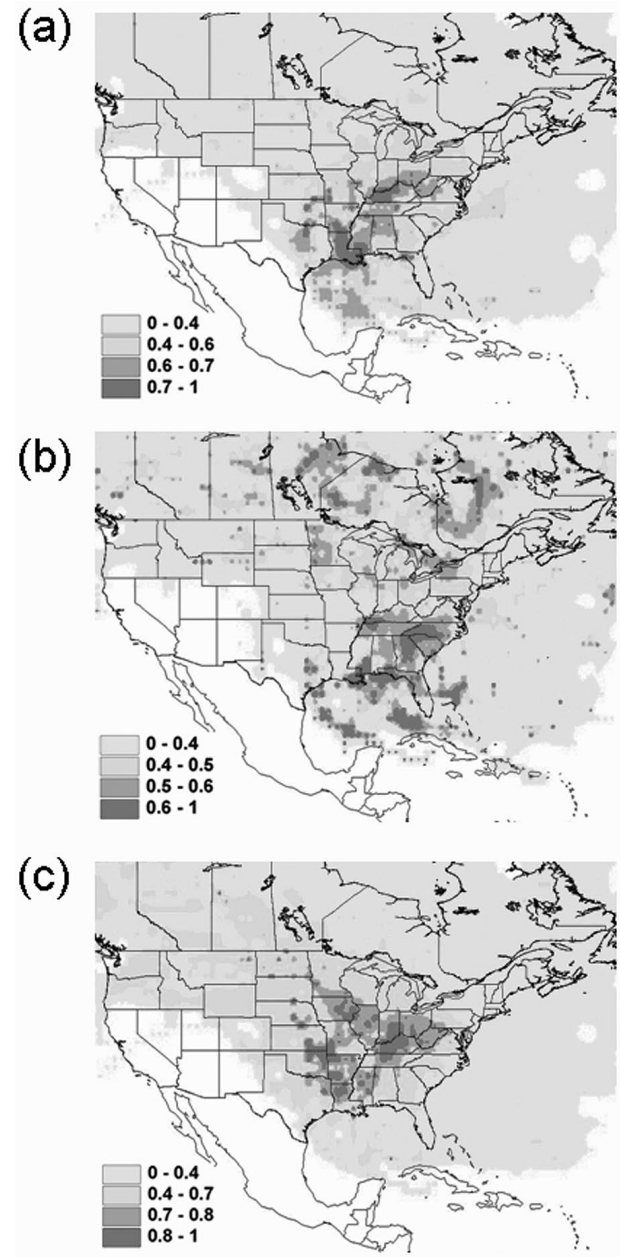

Figure 8. PSCF plots for Brigantine $PM_{2.5}$ study[17]; (a) summer-high secondary sulfate aerosol; (b) carbon-rich secondary sulfate aerosol; and (c) winter-high secondary sulfate aerosol.

CONCLUSIONS

The use of temperature-resolved carbon fractions to resolve carbonaceous particle sources was examined using previous PMF analyses of integrated $PM_{2.5}$ compositional data from samples collected at three monitoring site in the Eastern U.S. In contrast to the previous source apportionment studies that included two carbon fractions,[9,10] diesel emissions were separated from gasoline emissions in recent studies by using eight-carbon fractions of which the abundance differs between the two sources. The recent Atlanta, Washington, DC, and Brigantine $PM_{2.5}$ studies show very similar carbon fraction profiles for gasoline emissions and diesel emissions, although they are differently located. The diesel emissions contain large amounts of the EC fractions. The gasoline emissions show carbon fractions without significant EC. Secondary sulfate aerosols are the largest $PM_{2.5}$ source in three monitoring sites. Eight-carbon fractions also enhanced separations of carbon-rich secondary sulfate aerosols. The PSCF analyses for the secondary sulfate aerosols show the regional influences of the biogenic, as well as anthropogenic secondary aerosol.

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