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Research Article

Spatial and Temporal Trends in $PM_{2.5}$ Organic and Elemental Carbon across the United States

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The rural/remote IMPROVE network (Interagency Monitoring of Protected Visual Environments) and the Environmental Protection Agency's urban Chemical Speciation Network have measured $PM_{2.5}$ organic (OC) and elemental carbon (EC) since 1989 and 2000, respectively. We aggregated OC and EC data from 2007 to 2010 at over 300 sites from both networks in order to characterize the spatial and seasonal patterns in rural and urban carbonaceous aerosols. The spatial extent of OC and EC was more regional in the eastern United States relative to more localized concentrations in the West. The highest urban impacts of OC and EC relative to background concentrations occurred in the West during fall and winter. Urban and rural carbonaceous aerosols experienced a large (although opposite) range in seasonality in the West compared to a much lower seasonal variability in the East. Long-term (1990–2010) trend analyses indicated a widespread decrease in rural TC (TC = OC + EC) across the country, with positive, though insignificant, trends in the summer and fall in the West. Short-term trends indicated that urban and rural TC concentrations have both decreased since 2000, with the strongest and more spatially homogeneous urban and rural trends in the West relative to the East.

1. Introduction

Carbonaceous aerosols, including organic (OC) and elemental (EC) carbon, are ubiquitous in the atmosphere and therefore contribute significantly to particulate matter, both the $PM_{2.5}$ fraction [1] and coarse (PM_{10}–$PM_{2.5}$) fraction [2, 3], and they contribute to visibility degradation [4, 5] and climate forcing due to their ability to scatter and absorb solar radiation [6, 7]. Carbonaceous aerosols also adversely affect health [8, 9]. Organic carbon can be emitted directly from combustion activities or produced from secondary processes such as gas-to-particle formation. Elemental carbon, also known as light absorbing carbon or black carbon depending on the measurement method, is emitted directly from combustion sources. EC plays a significant role in climate forcing, and a recent review [10] suggests that the climate warming effects of EC are greater than previously thought, although large uncertainties still exist. Characterizing and predicting the complex nature of OC and EC are challenging from both a measurement and modeling framework. However, this characterization is necessary given the importance of OC and EC to many atmospheric processes and climate impacts.

Comprehensive speciation of carbonaceous aerosols is expensive and time-consuming and therefore usually possible only at a small number of sites for shorter-duration periods, such as the recent CARES study in California [11]. While these types of studies provide extremely useful data on the composition, properties, and sources of carbonaceous aerosols, they are limited in space and time. Large spatial-scale and long-term monitoring networks can provide this information but at the expense of detailed speciated data. An alternative is to measure bulk carbonaceous aerosol properties with methods that are suitable for routine monitoring programs. Such methods include thermal/optical techniques used to analyze particulate matter samples for OC and EC. Two major networks in the United States, the Interagency Monitoring of Protected Visual Environments network (IMPROVE) [12] and the Environmental Protection Agency's (EPA) Chemical Speciation Network (CSN) [13], are responsible for regularly

collecting samples at hundreds of rural and urban sites across the country, respectively, and conducting speciated aerosol analyses that characterize carbonaceous, ionic, and elemental species. In addition, the Southeastern Aerosol Research and Characterization (SEARCH) network collects data from several urban and rural sites in the southeastern United States, from which spatial and temporal trends in inorganic and carbonaceous aerosols in that region have been derived [14–16]. Integrating carbonaceous aerosol data from independent monitoring networks requires reconciliation of data obtained with different samplers, analytical techniques, and artifact corrections that can result in biases in OC and EC concentrations [17–20]. Several studies have reported on the differences and described methods for reconciling IMPROVE and CSN carbon data [1, 21, 22]. Hand et al. [1] aggregated IMPROVE and CSN data to examine the differences in urban and rural aerosols for data from 2005 to 2008. This work focused on the regional and seasonal trends in major aerosol species, including OC and EC.

Many studies have incorporated data from these large-scale networks to understand the sources of carbon aerosols. Jaffe et al. [23] examined interannual variations in IMPROVE $PM_{2.5}$ mass and OC concentrations in the western United States and attributed it to wildfire impacts. Malm et al. [24] used ratios of OC to EC to deduce source contributions from wildfire and mobile sources using IMPROVE data. Schichtel et al. [25] incorporated IMPROVE OC and EC data with radiocarbon data to estimate fossil and contemporary contributions to total carbon, and Schichtel et al. [26] further apportioned IMPROVE total carbon to major source types, including biomass burning, mobile, and vegetation. A source apportionment study [27] examined IMPROVE and CSN data across sites in Minnesota to determine mobile source contributions and local and regional pollution events. Buzcu-Guven et al. [28] used source apportionment of CSN data at Midwestern sites to determine mobile sources as a major contributor to OC mass. Yu et al. [29] used IMPROVE and SEARCH data to determine contributions from primary and secondary sources to measured OC. In addition to the IMPROVE and CSN, archived filters from the EPA Federal Reference Method (FRM) network from sites across three southeastern U.S. states have been used to determine the spatial and seasonal variability in water-soluble OC [30, 31]. In addition to these analyses, data from large-scale networks are very useful for model evaluation and studies of aerosol transport and processing [32–38] and constrain the role of carbonaceous aerosols in global climate models [39, 40].

The long-term availability of datasets such as those from IMPROVE, CSN, or SEARCH provides the opportunity to study the changes in carbonaceous aerosols over time and assess the success of regulatory efforts in reducing emissions. Trend studies are sensitive to changes in analytical techniques, so an evaluation of long-term trends in EC [41] focused on IMPROVE data from 1990 through 2004, before a hardware upgrade occurred for the carbon analysis. EC has decreased considerably (25%) across the rural United States, with higher rates of decrease in winter compared to summer due to increased EC in the West/Southwest, most likely due to impacts from biomass burning. Chen et al. [42] also reported on decreased EC concentrations from the IMPROVE network. From the SEARCH network in the southeastern United States, Blanchard et al. [16] reported that the annual mean organic matter and EC concentrations decreased by 3.3 to 6.5% yr^{-1} and 4.0 to 7.8% yr^{-1}, respectively, from 1999 through 2010. The greatest decrease in EC concentrations occurred at urban sites.

The contributions provided by this study include a recent analysis (2007–2010) and integration of IMPROVE and CSN OC and EC data, with specific focus on the integrated spatial and seasonal trends in absolute and relative concentrations. In addition, long-term (1990–2010) and short-term (2000–2010) trends in seasonal mean total carbon (TC = OC + EC) from integrated urban and rural sites are also examined.

2. Data and Methods

The IMPROVE network has been collecting samples for speciated aerosol analysis since 1989 [12] and currently operates 165 sites. IMPROVE sites are primarily in remote and rural areas, and the network's main purposes include tracking and characterizing aerosol composition and visibility in class I areas (federal visibility-protected areas), and determining trends in aerosol concentrations. Much of the monitoring performed by the network is in support of the EPA's Regional Haze Rule, and therefore considerable effort has been invested in maintaining consistency and data quality for the more than two decades the network has been operating. The network collects 24-hr samples every third day from midnight to midnight local time and reports concentrations at ambient conditions. $PM_{2.5}$ and PM_{10} samples are collected, and speciated analysis is performed only on the $PM_{2.5}$ filters. Characterization of anions is determined by IC analysis on nylon filters. Gravimetric $PM_{2.5}$ and PM_{10} mass are determined from the weighing of Teflon filters. Concentrations of $PM_{2.5}$ elemental species are characterized by X-ray florescence. Carbon species (OC and EC) are determined from quartz fiber filters analyzed by thermal optical reflectance [43]. OC concentrations reported by IMPROVE are corrected for a positive additive artifact [18, 44, 45] but not a multiplicative negative artifact [22]. We refer to the refractory carbon fraction as EC to reflect its operational definition while recognizing that the fraction contains nongraphitic carbon that absorbs light and complicates the split between EC and OC [46]. Additional details regarding IMPROVE instrumentation, sampling, analysis, artifact correction, and site information are available elsewhere [5, 12]. All IMPROVE data, metadata, and detailed descriptions of the network operations and data analysis and visualization results are available for download [47].

EPA's CSN urban network was deployed in 2000 [13] and currently operates over 200 sites. The objectives of the CSN are to track progress of emission reduction strategies through trend analyses, evaluate air quality models, support regulatory efforts for visibility, and for source apportionment and health effects studies. The CSN collects 24-h samples every third day on the same sampling schedule as the IMPROVE network. Its monitoring and analysis methods are similar to the IMPROVE network with the exception

that the CSN cold ships their filters and the IMPROVE network does not. The carbon analysis for the CSN was historically performed using thermal optical transmittance and the National Institute of Occupational Health (NIOSH) protocol. With the recognition that different IMPROVE and CSN samplers, as well as different analytical protocols, resulted in different OC and EC concentrations [21, 22, 44], CSN transitioned to an URG-3000N sampler to be more consistent with the IMPROVE sampler, as well as TOR and IMPROVE protocol analysis. The transition began in May 2007 and continued through 2010. Data during the period before transition were adjusted based on the method of Malm et al. [22] to agree with IMPROVE collocated data. Comparisons of adjusted collocated data from 2005 to 2008 showed close agreement [1], and comparisons for 2007–2010 data were similar. The CSN data are available for download [48].

We analyzed data from 2007 to 2010 and required 50% completeness of the data, resulting in 162 IMPROVE and 181 CSN "complete" sites. Seasonal means refer to winter (DJF), spring (MMA), summer (JJA), and fall (SON). The percent contributions of OC and EC to $PM_{2.5}$ reconstructed fine mass (RCFM) were determined by assuming the aerosols were comprised of ammonium sulfate, ammonium nitrate, particulate organic matter (POM = 1.8∗OC), EC, soil, and sea salt. A similar organic multiplier was used for urban and rural POM, although lower values may be more appropriate for urban OC [22, 49]. We combined and interpolated data from both networks using a Kriging algorithm. The resulting fields are not intended for strict interpretation but rather serve to guide the eye for spatial patterns. Interpolations are affected by site density, and the CSN has greater site density in the East, whereas the site density for the IMPROVE network is the highest in the West.

Linear Theil regression [50–52] was performed on total carbon (TC = OC + EC) data from "complete" sites, and 70% of "complete" years were required for a trend calculation over a given time period. Trend (% yr^{-1}) is defined as the slope from the Theil regression divided by the median concentration over the time period of the trend, multiplied by 100%. Total carbon was used to avoid possible biases in the OC and EC split due to the hardware upgrade in 2005 mentioned previously [41]. Trends were considered significant at the 90th percent significance level ($p < 0.10$) using Kendall tau statistics. Trends were computed for seasonal means for long-term IMPROVE sites over the time period from 1990 to 2010. In 2000, the IMPROVE network expanded, and the CSN began operation, therefore short-term trends were computed from 2000 to 2010.

3. Results and Discussion

3.1. Spatial and Seasonal Trends

3.1.1. POM. Isopleths of IMPROVE and CSN 2007–2010 seasonal mean POM concentrations for winter, spring, summer, and fall are provided in Figures 1(a)–1(d), respectively. The mean percent contribution of POM to RCFM is shown for the same seasons in Figures 2(a)–2(d). In the western United States, the regional POM (remote/rural) background was typically less than 1 $\mu g\,m^{-3}$, depending on season, with lower winter and spring concentrations (Figures 1(a) and 1(b), resp.). During summer, the western background concentration increased to 2-3 $\mu g\,m^{-3}$ (Figure 1(c)), and fall concentrations were closer to 2 $\mu g\,m^{-3}$ (Figure 1(d)). The increased summer background concentrations were likely due to the influence of biomass burning emissions and perhaps biogenic emissions [23, 53, 54], as the impacts were more regional in extent. In contrast, more localized high urban concentrations (>5 $\mu g\,m^{-3}$) in the West in winter occurred at a range of sites along the coast, and individual sites in Colorado, Utah, Montana, and Arizona. Winter urban sources included residential wood burning, although meteorological effects, such as low ventilation, likely contributed [55]. The fall season in the West appeared to be a transition season with influences from both the summer and winter sources. Contributions to RCFM were significant in the western United States (Figure 2), with values ranging from 40% to over 80% depending on season. The regional impacts in summer and fall were considerable due to the influence of biomass burning (Figures 2(c) and 2(d), resp.). Winter contributions in the West were fairly localized around urban sites and reached 75% or higher (Figure 2(a)), in contrast to spring time contributions of 20%–30% (Figure 2(b)).

In the eastern United States, the background POM concentrations were higher than in the West year-round (3-4 $\mu g\,m^{-3}$), due in part to regionally distributed sources of OC, including secondary organic aerosols from vegetation and wild and prescribed fires [7, 31]. Springtime concentrations were high in the Southeast (Figure 1(b)), most likely associated with biomass burning and a high fire year in 2007 [30, 56, 57]. Summer concentrations were the lowest, although more regional in extent (Figure 1(c)). Secondary organic aerosols from biogenic emissions are known to be important contributors to POM concentrations in the Southeast especially in summer [15, 25, 58, 59], and the higher background concentrations and large regional extent reflects this source. Residential wood burning was likely an important source in fall and winter [30, 57]. The contribution of POM to RCFM in the East was significantly lower than in the West (<50%) year-round. This difference mainly was due to the prevalence of other species, such as sulfate, which has abundant sources in the East and dominates RCFM, especially in summer [1].

3.1.2. EC. Seasonal mean EC isopleths are shown in Figures 3(a)–3(d), and seasonal mean percent contributions of EC to RCFM are shown in Figures 4(a)–4(d). Rural background EC concentrations ranged from 0.1 to 0.3 $\mu g\,m^{-3}$, with lower values in the West. In the West, especially winter and fall, localized impacts from individual urban sites produced higher concentrations (up to a factor of 10 higher) with steep spatial gradients, suggesting a limited spatial extent. Urban EC sources likely included residential heating and other urban combustion sources, including mobile sources [25, 58] that were most likely trapped due to low ventilation. EC hotspots did not occur necessarily at the same location

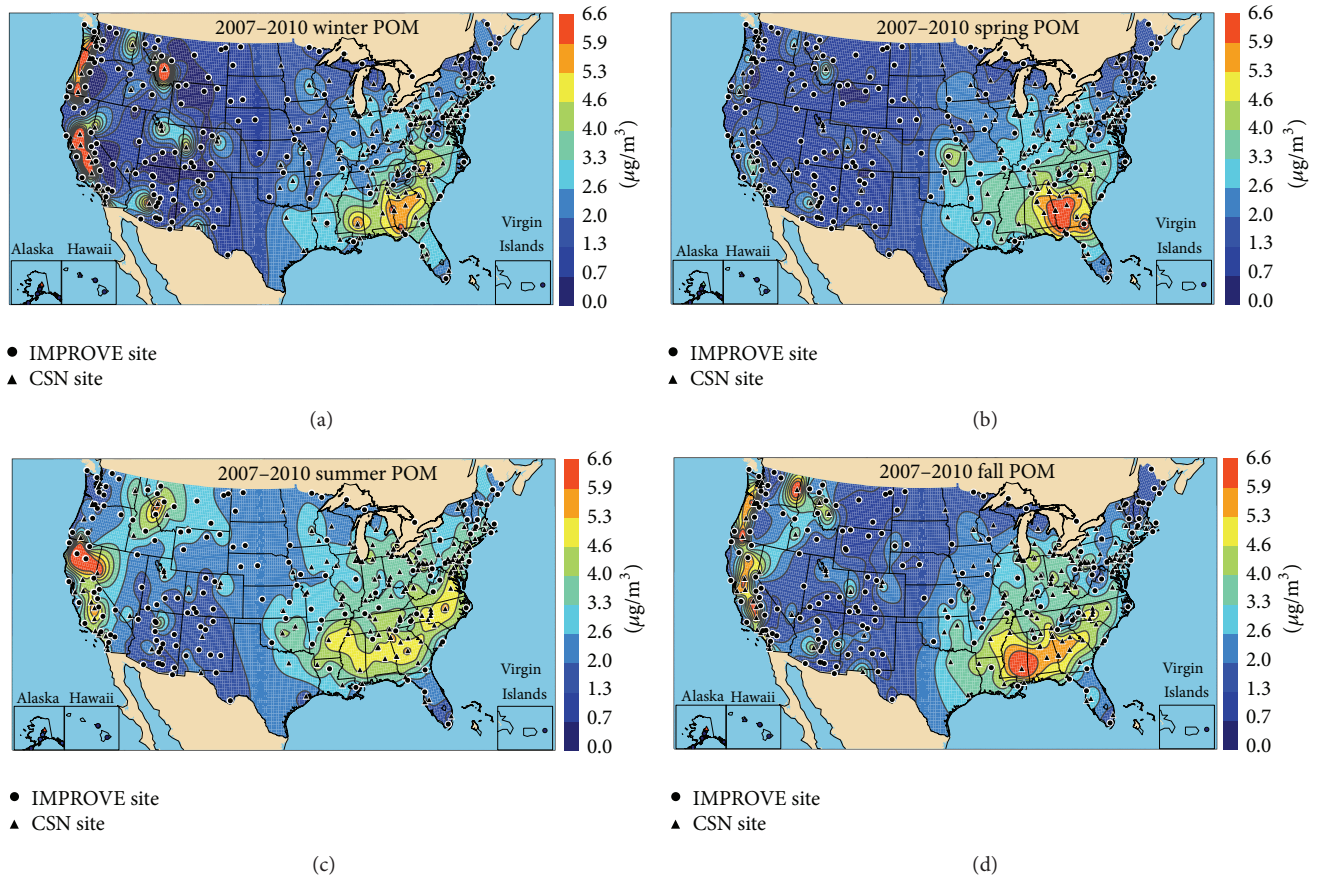

Figure 1: IMPROVE and CSN 2007–2010 seasonal mean $PM_{2.5}$ particulate organic matter (POM) ($\mu g\,m^{-3}$) for (a) winter (DJF), (b) spring (MAM), (c) summer (JJA), and (d) fall (SON). IMPROVE sites are shown as circles, and CSN sites are shown as triangles.

as high POM concentrations. The impacts from EC emitted from biomass burning in summer were not as great as the impacts from urban sources during fall and winter, probably because of meteorological effects. The contribution of EC to RCFM was quite low (Figure 4); generally the background EC contribution was less than 5%. However, at urban sites in the West, EC contributions were doubled relative to background contributions, with estimates greater than 10%, especially in winter and fall. Background summer contributions in the West reached 7%–9% in some locations, probably due to regional impacts of biomass burning (Figure 4(c)).

The EC influence in the eastern United States appeared to be more regional in extent relative to the West, with a somewhat higher rural background EC concentration of 0.5 $\mu g\,m^{-3}$ or less. Hecobian et al. [30] reported that biomass burning was the most significant source of brown carbon in the Southeast during colder months, and brown carbon would most likely be characterized as EC by the TOR method [60]. Urban impacts were not as significant in the East, especially compared to winter in the West, except for a few sites in the Southeast and Northeast in the fall. In fact, EC was the highest in general across the eastern United States in the fall. Meteorological effects, such as lower effective transport winds in the West in winter, may play a role in the differences seen between urban and rural EC (and POM) in the East and West [61]. EC contributions in the eastern United States were typically less than 10%, with its highest contributions in fall across most of the East (Figure 4(d)) and winter in the Southeast (Figure 4(a)). Although relative to other species EC contributions to fine mass were quite low; however, its optical effects were still important given its relatively high optical efficiency [6]. Hand et al. [5] showed that EC contributed as much as 10%–15% annually to reconstructed light extinction coefficients from 2005 to 2008 in the rural West, and 15%–20% or higher at western urban sites.

3.2. Seasonality. The seasonality of POM and EC was summarized by aggregating normalized monthly mean data (by annual mean) into broad regions. Regions were defined by separating the country into four large quadrants (Northeast, Southeast, Northwest, and Southwest) at roughly –100° longitude and 38° latitude based on the spatial patterns presented in the previous section. Normalized monthly mean POM is shown in Figures 5(a) and 5(b). Rural POM seasonality is characterized by maximum and minimum concentrations in warm and cold months, respectively, with timing and range of seasonality varying per region (Figure 5(a)). The largest range of seasonality occurred in the northwestern United States where the highest normalized concentrations in July and August were likely associated with biomass burning

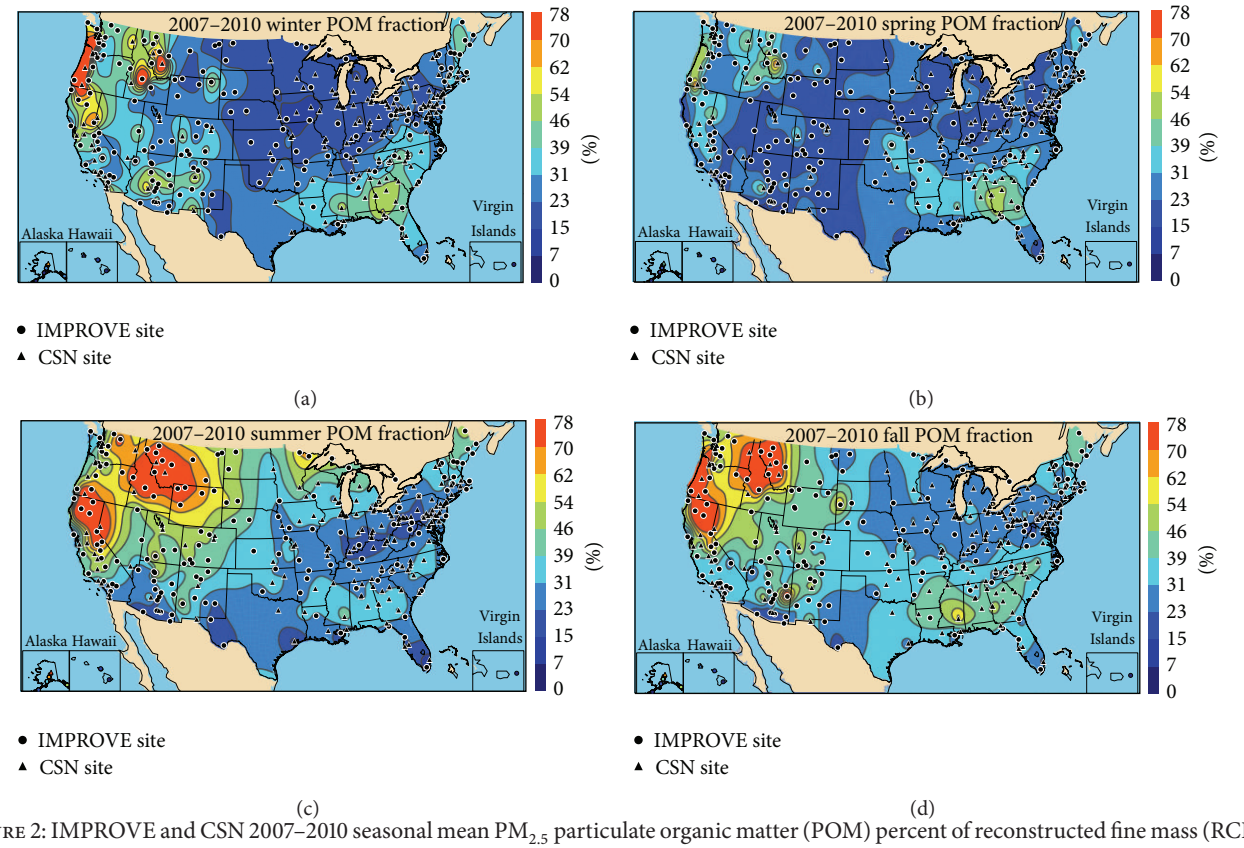

FIGURE 2: IMPROVE and CSN 2007–2010 seasonal mean $PM_{2.5}$ particulate organic matter (POM) percent of reconstructed fine mass (RCFM) for (a) winter (DJF), (b) spring (MAM), (c) summer (JJA), and (d) fall (SON). IMPROVE sites are shown as circles, and CSN sites are shown as triangles.

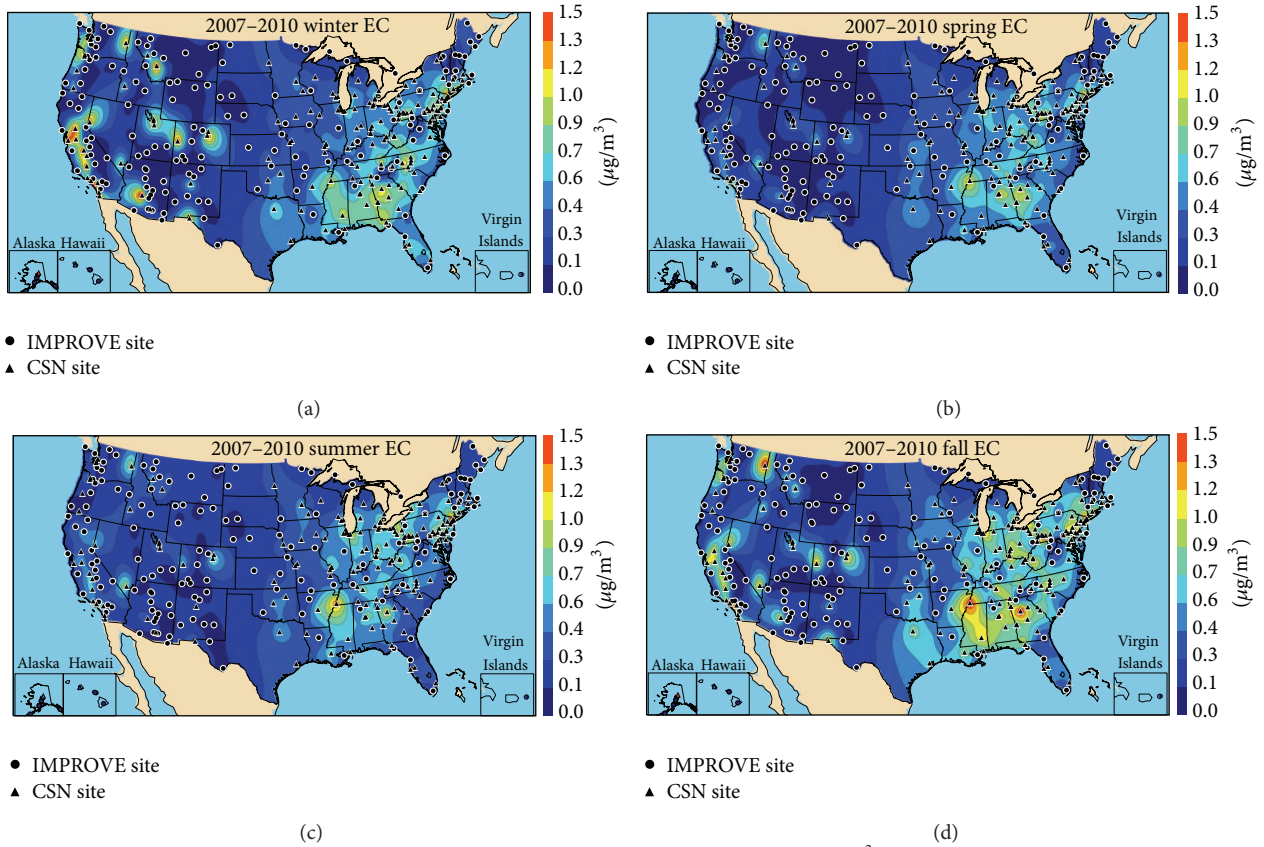

FIGURE 3: IMPROVE and CSN 2007–2010 seasonal mean $PM_{2.5}$ elemental carbon (EC) ($\mu g\,m^{-3}$) for (a) winter (DJF), (b) spring (MAM), (c) summer (JJA), and (d) fall (SON). IMPROVE sites are shown as circles, and CSN sites are shown as triangles.

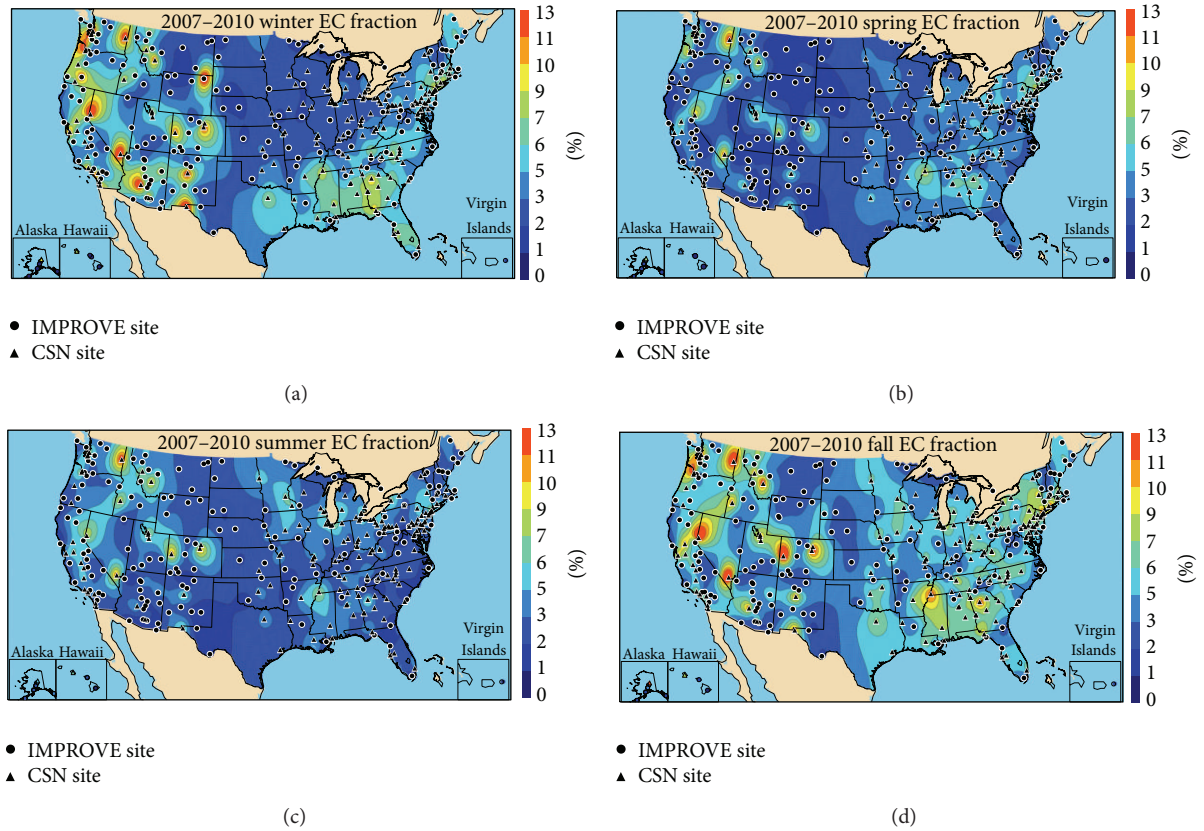

Figure 4: IMPROVE and CSN 2007–2010 seasonal mean $PM_{2.5}$ elemental carbon (EC) percent of reconstructed fine mass (RCFM) for (a) winter (DJF), (b) spring (MAM), (c) summer (JJA), and (d) fall (SON). IMPROVE sites are shown as circles, and CSN sites are shown as triangles.

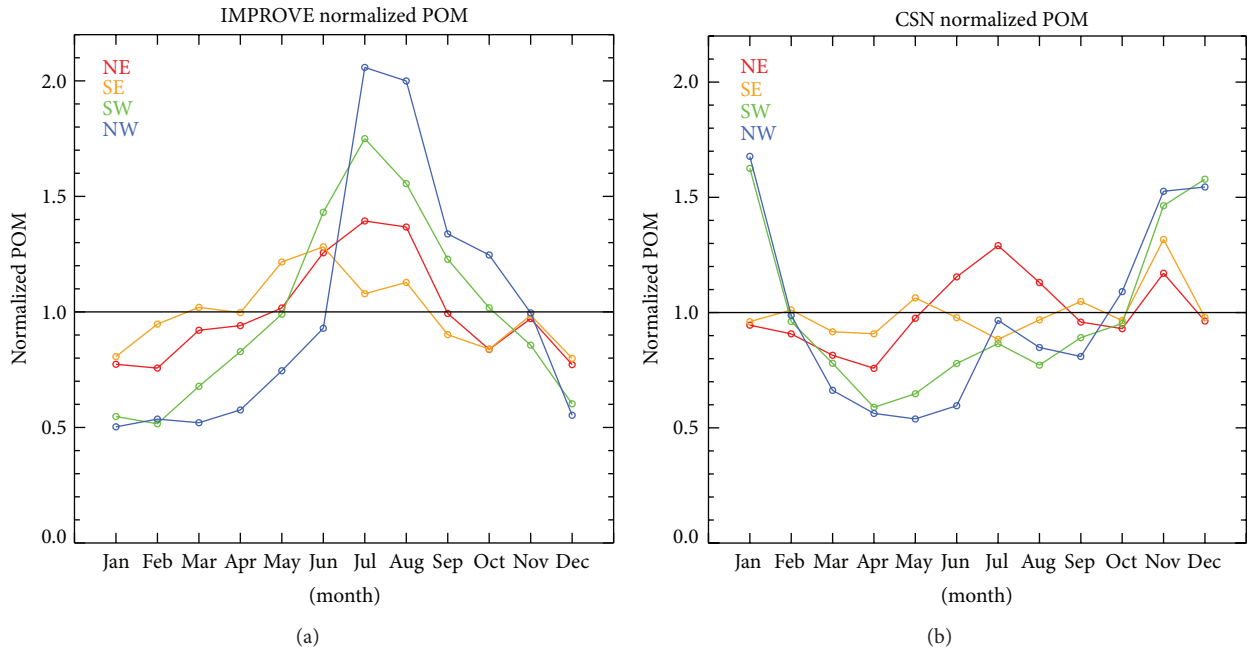

Figure 5: 2007–2010 regional monthly mean normalized (by annual mean) $PM_{2.5}$ particulate organic matter (POM) for (a) IMPROVE and (b) CSN. Regions correspond to the Northeast (NE), Southeast (SE), Southwest (SW), and Northwest (NW).

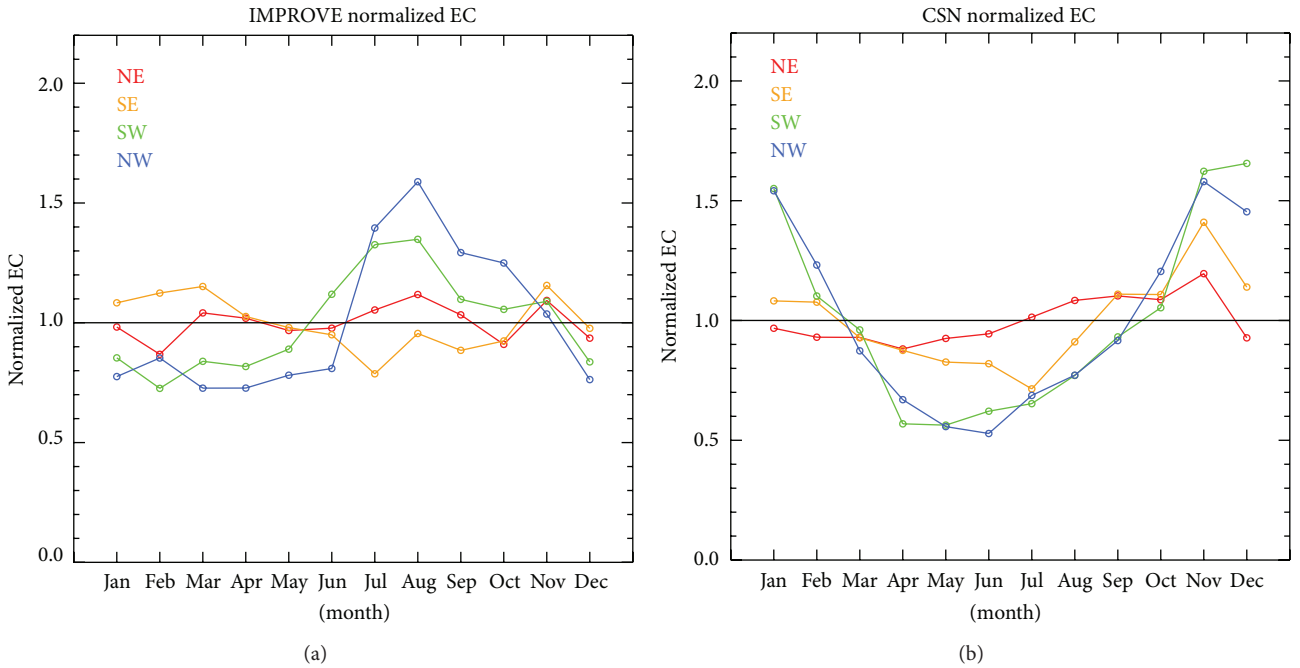

FIGURE 6: 2007–2010 regional monthly mean normalized (by annual mean) $PM_{2.5}$ elemental carbon (EC) for (a) IMPROVE and (b) CSN. Regions correspond to the Northeast (NE), Southeast (SE), Southwest (SW), and Northwest (NW).

impacts that extended into fall [25, 54]. The second largest range in seasonality occurred in the Southwest where spring relative contributions were more important and summer impacts began somewhat earlier than in the Northwest. In contrast to the West, the eastern United States experienced a much lower range in seasonality in rural POM, although still characterized by a winter minima and spring/summer maxima. In the southeastern United States, higher relative contributions occurred in the spring, particularly May, when prescribed burning occurs. Summer contributions peaked in June and extended through the summer when formation of secondary organic aerosol from vegetation is the highest. Summer relative maxima in the northeastern US region were higher than in the Southeast and encompassed the summer months, most likely due to biogenic emissions. A small increase in rural relative POM in November occurred at both eastern regions.

The opposite seasonality in urban and rural POM in the West is demonstrated clearly in Figure 5(b). The Northwest and Southwest regions had very similar behavior, with urban fall/winter maxima three times higher than spring/summer minima. Relative concentrations increased in summer but not to the extent of the fall/winter maxima. However, in the East, the range of seasonality was much lower, similar to rural regions. Seasonality in the Southeast was nearly flat with a slight increase in May when prescribed burning occurs. Urban POM contributions in the Northeast were highest in summer, similar to the rural region, indicating the regional impacts of biogenic sources of POM in the East. Both eastern regions experienced a peak in November, similar to but larger in magnitude to the rural regions. In addition to different sources, some of the differences in western and eastern POM seasonality were likely due to meteorological effects, with lower winter ventilation in the West, and higher dilution in the East [61].

Western rural EC seasonality patterns followed that of POM with a higher range in seasonality in the West (greater in the Northwest) likely associated with biomass burning (see Figure 6(a)). In the East the rural EC seasonality was fairly flat, although opposite for both eastern regions. In the Southeast, rural EC peaked in winter and was lowest in summer, while in the Northeast it was fairly flat but somewhat higher in summer. The peak in relative concentration of POM in May was not observed for EC. An increase in rural normalized EC in November in the East also occurred for urban sites (Figure 6(b)); in fact the maximum relative concentrations for both eastern urban regions occurred in November. Otherwise, the seasonality of urban EC was fairly flat in the Northeast, and somewhat greater in the Southeast with a pronounced summer minima. The seasonality of western urban EC relative concentrations followed urban POM closely, with strong winter maxima and summer minima.

3.3. EC to OC Ratios. Ratios of EC and OC concentrations provide some indication of source contributions, with higher ratios corresponding to combustion sources that directly emit both primary OC and EC, and relatively lower ratios reflecting the addition of OC from secondary formation processes. Mobile sources have EC/OC ratios around 1 [62], while rural [20, 24, 25] and biomass burning aerosols [63, 64] have much lower ratios (~0.1). Organic aerosols with significant secondary contributions are around 0.1-0.2 [65]. In contrast, EC/OC ratios of urban aerosols are relatively high depending on primary and secondary sources (~0.47–1.5) [15, 20]. EC/OC ratios are obviously sensitive to and can vary considerably depending on the analytical technique used,

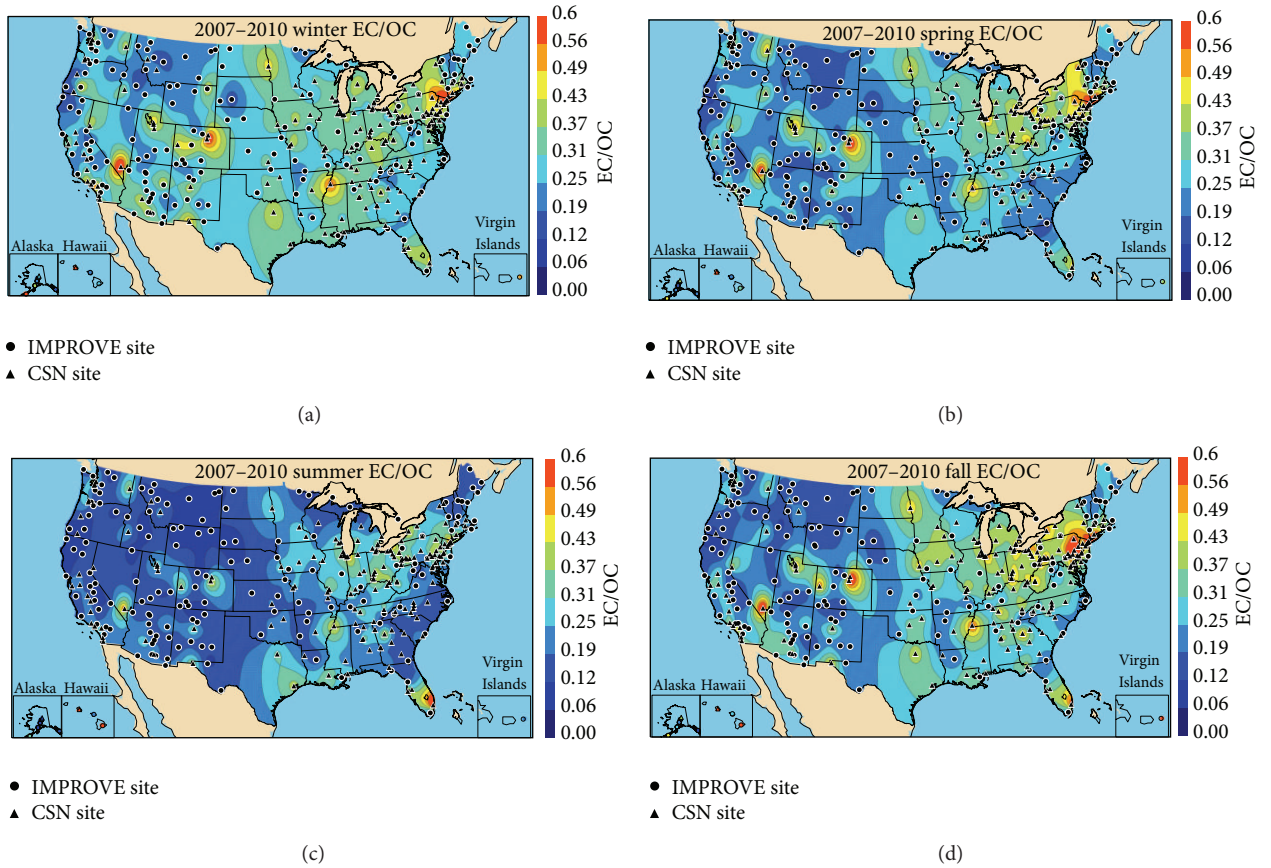

Figure 7: IMPROVE and CSN 2007–2010 seasonal mean $PM_{2.5}$ elemental carbon (EC) to organic carbon (OC) ratios for (a) winter (DJF), (b) spring (MAM), (c) summer (JJA), and (d) fall (SON). IMPROVE sites are shown as circles, and CSN sites are shown as triangles.

such as different temperature protocols applied in thermal optical techniques [17, 19, 20], and could be seasonally dependent due to different aerosol types [60]. This variability should be kept in mind when interpreting EC/OC ratios and comparing estimates from different studies.

The 2007–2010 seasonal mean EC/OC ratios are shown in Figures 7(a)–7(d). Urban "hot spots" in EC/OC (>0.6) in winter, spring, and fall emphasized the impact of urban and mobile sources on significantly lower ratios in surrounding regions. Locations with high EC/OC (~0.6) were coincident with locations corresponding to high EC concentrations, especially in Colorado and Utah (winter, spring, and fall; see Figures 3(a)–3(d)), but not in locations with high POM, such as along the West coast and the San Joaquin valley (winter and fall; see Figures 1(a) and 1(d)), suggesting secondary sources to urban POM. The high EC/OC hotspots in the West were fairly local in extent and surrounded by background EC/OC ratios of 0.1-0.2 that were the lowest in summer, likely due to high biogenic contributions and possibly biomass burning influences. Similar results were reported by Schichtel et al. [25] for rural sites in summer and for ratios at urban sites that had somewhat higher ratios (0.24–0.28); both urban and rural ratios increased in winter.

In the eastern United States, EC/OC ratios were the lowest (0.1-0.2) in regions and seasons that corresponded to high POM, such as the Southeast in summer, suggesting secondary sources. EC/OC ratios of 0.3-0.4 across the north-central and eastern United States year-round (with the exception of summer) suggested urban influences and were consistent with the higher EC/OC ratios corresponding to fossil carbon (0.54–0.85) [25]. The least seasonal variability in EC/OC ratios occurred in the Midwest, similar to the results reported by Zeng and Wang [64].

3.4. Trends in Total Carbon (TC). IMPROVE long-term trends (1990–2010) in seasonal mean TC are shown in Figures 8(a)–8(d). Sites with statistically significant trends ($p < 0.10$) are represented with a filled triangle pointing upward or downward depending on whether TC concentrations increased or decreased, respectively. Sites with insignificant trends are represented by unfilled triangles. Trends in TC, and not EC and OC separately, are shown to avoid possible biases due to hardware upgrades, as discussed previously; however, trends in TC are driven predominantly by OC. Since 1990, seasonal mean rural TC concentrations decreased across the country in winter and spring (Figures 8(a) and 8(b), resp.), with the strongest decrease along the West coast. However, in summer and to a lesser degree in fall, trends in the West were positive at many sites, although insignificant. This is the season when wildfires are most active, and wildfire activity has increased in the West [53] and most likely contributed to the positive trends. A similar conclusion was suggested by

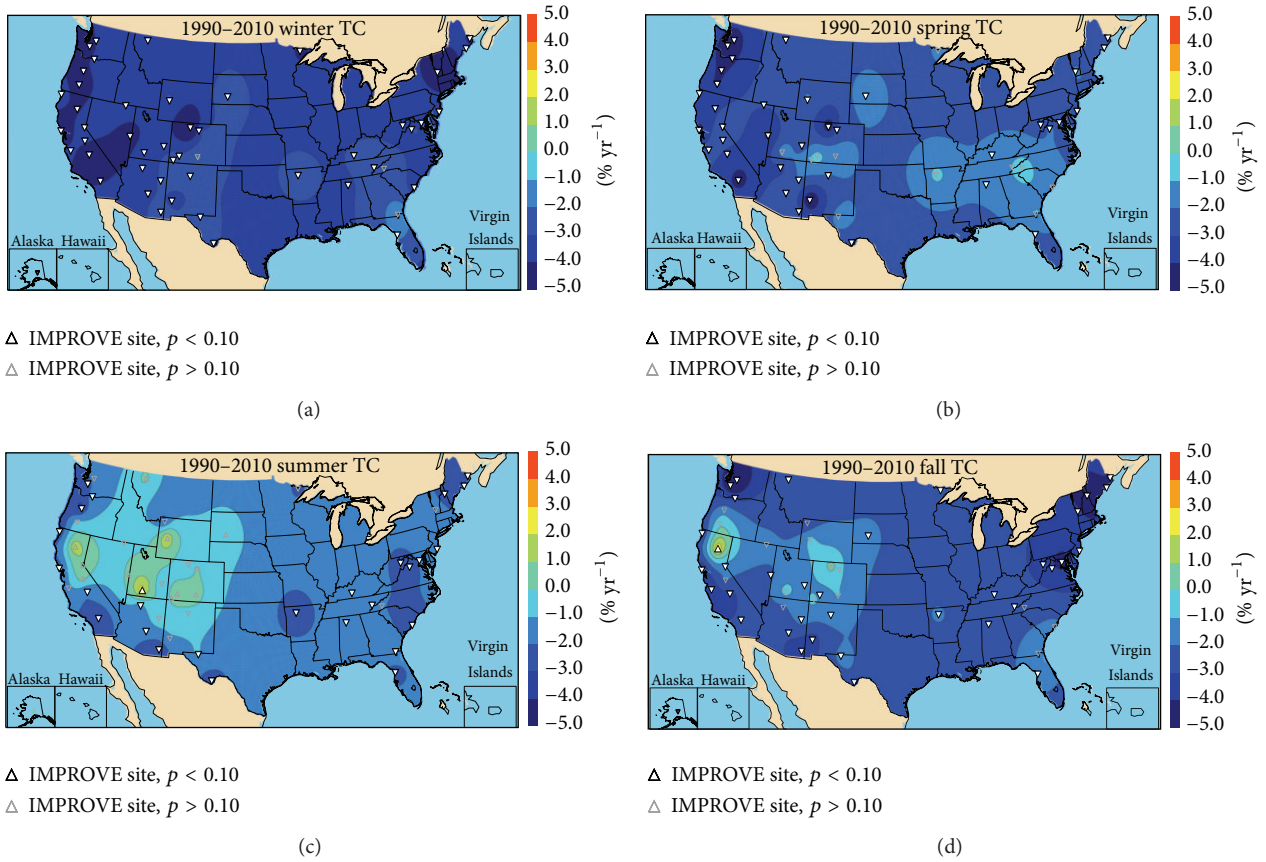

FIGURE 8: Long-term (1990–2010) trends (% yr^{-1}) in IMPROVE seasonal mean $PM_{2.5}$ total carbon (TC = OC + EC) for (a) winter (DJF), (b) spring (MAM), (c) summer (JJA), and (d) fall (SON). White triangles correspond to IMPROVE sites. Upward pointing triangles correspond to increased concentrations and vice versa. Trends with significance levels (p) less than 0.10 were considered significant. (filled triangles). Unfilled triangles correspond to insignificant trends.

Murphy et al. [41] who reported positive trends in summer time EC concentrations at IMPROVE sites in the West.

Combining trends from urban and rural sites over a shorter time period (2000–2010) resulted in greater spatial variability relative to the long-term trends. Short-term trends in urban and rural seasonal mean TC are shown in Figures 9(a)–9(d). In general, TC decreased more strongly in the West (−4% to −5% yr^{-1}), with winter and spring seasons corresponding to the highest rates of decrease (Figures 9(a) and 9(b), resp.). The long-term positive trends in TC in the West in summer did not occur for the shorter time period, although most of the summer trends in the West were insignificant (Figure 9(c)). The least negative trends in the West occurred during the fall (Figure 9(d)), although many were insignificant. Although the rural site density in the West is greater than that for urban sites, it still appears that urban and rural TC short-term trends in the West are fairly spatially consistent.

In contrast, in the eastern United States, trends were generally more spatially inhomogeneous, with rural sites having statistically significant negative trends nearby urban sites with insignificant positive or negative trends depending on the season. Overall, TC did not decrease as strongly in the East relative to the West (−1% to −2% yr^{-1}), and a number of urban sites experienced increased TC concentrations, such as in Iowa in winter, spring, and fall, and sites in New York year-round for reasons unknown. TC concentrations in winter and fall decreased at the strongest rates of all the seasons. Blanchard et al. [16] reported similar trends for annual mean OC and EC in the Southeast from sites in the SEARCH network. A thorough analysis of TC emission trends would help to reveal the cause of the spatial variability in urban and rural trends in the East; however, it is beyond the scope of this paper.

4. Summary and Conclusions

We presented an overview of the spatial and temporal variability in organic and elemental carbon concentrations and their contribution to $PM_{2.5}$ reconstructed fine mass from the rural IMPROVE network and the urban CSN for data aggregated from 2007 to 2010. Interpolating these data together provides large spatial patterns from which local and regional impacts of carbonaceous aerosols across the United States can be inferred.

Background rural/remote POM (= 1.8 ∗ OC) concentrations ranged from less than 1 μg m^{-3} in the West to around 2 μg m^{-3} in the East. High POM concentrations and

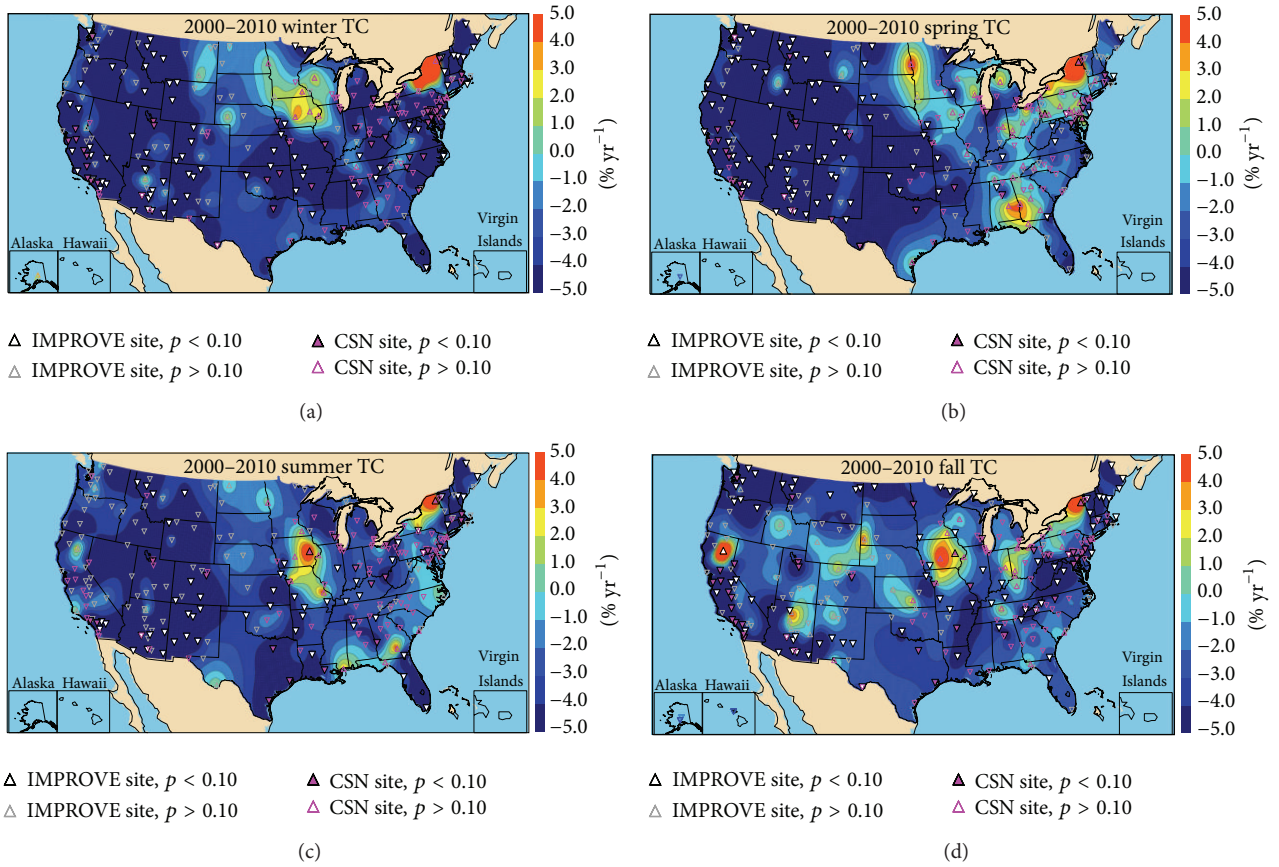

FIGURE 9: Short-term (2000–2010) trends (% yr^{-1}) in IMPROVE and CSN seasonal mean $PM_{2.5}$ total carbon (TC = OC + EC) for (a) winter (DJF), (b) spring (MAM), (c) summer (JJA), and (d) fall (SON). White and magenta triangles correspond to IMPROVE and CSN sites, respectively. Upward pointing triangles correspond to increased concentrations and vice versa. Trends with significance levels (p) less than 0.10 were considered significant. (filled triangles). Unfilled triangles correspond to insignificant trends.

contributions to RCFM up to 80% at both western urban and rural sites occurred during summer and fall when wildfires are most active. Urban impacts were the highest and more localized in the West in winter. Eastern POM concentration were the highest in the Southeast in spring when prescribed fires occur, but less regional in extent compared to summer concentrations that were most likely influenced by secondary sources. Contributions in the East were typically less than 50% year-round.

Background EC concentrations were 0.1–0.3 μg m^{-3} with lower values in the West. The influence of urban sources was significant (>10x higher) but fairly localized with high concentrations and tight spatial gradients around individual cities (especially in the West in winter). A more regional influence was observed in the East, although this could be due in part to site density. The highest eastern concentrations occurred in the Southeast in fall. Contributions from EC were typically 10% or less at rural sites and somewhat higher at urban sites.

Normalized monthly mean POM and EC concentrations were examined as a function of broad urban and rural regions. Rural POM in the West was characterized by a large range in seasonality, with a summer maximum that was most likely influenced by biomass burning and biogenic contributions. In contrast, urban POM in the West was characterized by winter maxima, although the influence of biomass burning in the summer can still be observed. Much of the western urban seasonality was probably due to meteorological effects such as low ventilation. In contrast, the seasonality in eastern rural and urban POM was fairly flat, with spring/summer maxima in the rural Southeast, likely associated with biomass burning and biogenic aerosols. The influence of secondary organic aerosols was inferred from the summer maxima in the urban and rural Northeast. Both urban and rural eastern regions experienced a peak in November. EC rural and urban seasonality in the East was also fairly flat and demonstrated somewhat different seasonality to POM, with a rural minimum in summer and maximum in winter in the Southeast. EC rural and urban seasonality in the West followed that of POM, reflecting different primary sources and influence of meteorological conditions, such as winter temperature inversions that trap urban sources.

Rural TC (OC + EC) concentrations have decreased across the country from 1990 through 2010 for most seasons except for positive summer trends in the West that may be associated with biomass burning impacts. Short-term (2000–2010) trends in rural and urban concentrations were

associated with greater spatial inhomogeneity, with higher rates of decrease in TC in the West for all seasons and variable trends at nearby urban and rural sites in the East.

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References

[1] J. L. Hand, B. A. Schichtel, M. Pitchford, W. C. Malm, and N. H. Frank, "Seasonal composition of remote and urban fine particulate matter in the United States," *Journal of Geophysical Research*, vol. 117, no. 5, Article ID D05209, 2012.

[2] W. C. Malm, M. L. Pitchford, C. McDade, and L. L. Ashbaugh, "Coarse particle speciation at selected locations in the rural continental United States," *Atmospheric Environment*, vol. 41, no. 10, pp. 2225–2239, 2007.

[3] E. S. Edgerton, G. S. Casuccio, R. D. Saylor et al., "Measurements of OC and EC in coarse particulate matter in the southeastern United States," *Journal of the Air & Waste Management Association*, vol. 59, no. 1, pp. 78–90, 2009.

[4] G. R. McMeeking, S. M. Kreidenweis, M. Lunden et al., "Smoke-impacted regional haze in California during the summer of 2002," *Agricultural and Forest Meteorology*, vol. 137, no. 1-2, pp. 25–42, 2006.

[5] J. L. Hand, S. A. Copeland, D. E. Day et al., "IMPROVE (Interagency Monitoring of Protected Visual Environments): spatial and seasonal patterns and temporal variability of haze and its constituents in the United States," CIRA Report 5, 2011, http://vista.cira.colostate.edu/improve/Publications/Reports/2011/2011.htm.

[6] T. C. Bond and R. W. Bergstrom, "Light absorption by carbonaceous particles: an investigative review," *Aerosol Science and Technology*, vol. 40, no. 1, pp. 27–67, 2006.

[7] A. H. Goldstein, C. D. Koven, C. L. Heald, and I. Y. Fung, "Biogenic carbon and anthropogenic pollutants combine to form a cooling haze over the southeastern United States," *Proceedings of the National Academy of Sciences of the United States of America*, vol. 106, no. 22, pp. 8835–8840, 2009.

[8] J. L. Mauderly and J. C. Chow, "Health effects of organic aerosols," *Inhalation Toxicology*, vol. 20, no. 3, pp. 257–288, 2008.

[9] A. C. Rohr and R. E. Wyzga, "Attributing health effects to individual particulate matter constituents," *Atmospheric Environment*, vol. 62, pp. 130–152, 2012.

[10] T. C. Bond, S. J. Doherty, D. W. Fahey et al., "Bounding the role of black carbon in the climate system: a scientific assessment," *Journal of Geophysical Research*, vol. 118, no. 11, pp. 5380–5552, 2013.

[11] R. A. Zaveri, W. J. Shaw, D. J. Cziczo et al., "Overview of the 2010 Carbonaceous Aerosols and Radiative Effects Study (CARES)," *Atmospheric Chemistry and Physics*, vol. 12, pp. 7647–7687, 2012.

[12] W. C. Malm, J. F. Sisler, D. Huffman, R. A. Eldred, and T. A. Cahill, "Spatial and seasonal trends in particle concentration and optical extinction in the United States," *Journal of Geophysical Research*, vol. 99, no. 1, pp. 1347–1370, 1994.

[13] U.S. Environmental Protection Agency, "$PM_{2.5}$ speciation network newsletter," Vol. 1, no. 1, 2004, http://www.epa.gov/ttn/amtic/files/ambient/pm25/spec/spnews1.pdf.

[14] D. A. Hansen, E. S. Edgerton, B. E. Hartsell et al., "The Southeastern Aerosol Research and Characterization Study: part 1—overview," *Journal of the Air & Waste Management Association*, vol. 53, no. 12, pp. 1460–1471, 2003.

[15] C. L. Blanchard, G. M. Hidy, S. Tanenbaum, and E. S. Edgerton, "NMOC, ozone, and organic aerosol in the southeastern United States, 1999–2007: 3. Origins of organic aerosol in Atlanta, Georgia, and surrounding areas," *Atmospheric Environment*, vol. 45, no. 6, pp. 1291–1302, 2011.

[16] C. L. Blanchard, G. M. Hidy, S. Tanenbaum, E. S. Edgerton, and B. E. Hartsell, "The Southeastern Aerosol Research and Characterization (SEARCH) Study: temporal trends in gas and PM concentrations and composition, 1999–2010," *Journal of the Air & Waste Management Association* , vol. 63, no. 3, pp. 247–259, 2013.

[17] J. C. Chow, J. G. Watson, L. W. A. Chen, W. P. Arnott, H. Moosmüller, and K. Fung, "Equivalence of elemental carbon by thermal/optical reflectance and transmittance with different temperature protocols," *Environmental Science and Technology*, vol. 38, no. 16, pp. 4414–4422, 2004.

[18] J. C. Chow, J. G. Watson, L.-W. A. Chen, J. Rice, and N. H. Frank, "Quantification of $PM_{2.5}$ organic carbon sampling artifacts in US networks," *Atmospheric Chemistry and Physics*, vol. 10, no. 12, pp. 5223–5239, 2010.

[19] Y. Cheng, K.-B. He, F.-K. Duan et al., "Ambient organic carbon to elemental carbon ratios: influences of the measurement methods and implications," *Atmospheric Environment*, vol. 45, no. 12, pp. 2060–2066, 2011.

[20] B. Khan, M. D. Hays, C. Geron, and J. Jetter, "Differences in the OC/EC ratios that characterize ambient and source aerosols due to thermal-optical analysis," *Aerosol Science and Technology*, vol. 46, no. 2, pp. 127–137, 2012.

[21] O. V. Rattigan, H. D. Felton, M.-S. Bae, J. J. Schwab, and K. L. Demerjian, "Comparison of long-term $PM_{2.5}$ carbon measurements at an urban and rural location in New York," *Atmospheric Environment*, vol. 45, no. 19, pp. 3228–3236, 2011.

[22] W. C. Malm, B. A. Schichtel, and M. L. Pitchford, "Uncertainties in $PM_{2.5}$ gravimetric and speciation measurements and what we can learn from them," *Journal of the Air & Waste Management Association*, vol. 61, no. 11, pp. 1131–1149, 2011.

[23] D. Jaffe, W. Hafner, D. Chand, A. Westerling, and D. Spracklen, "Interannual variations in $PM_{2.5}$ due to wildfires in the western United States," *Environmental Science and Technology*, vol. 42, no. 8, pp. 2812–2818, 2008.

[24] W. C. Malm, B. A. Schichtel, M. L. Pitchford, L. L. Ashbaugh, and R. A. Eldred, "Spatial and monthly trends in speciated fine particle concentration in the United States," *Journal of Geophysical Research*, vol. 109, no. 3, Article ID D03306, 2004.

[25] B. A. Schichtel, W. C. Malm, G. Bench et al., "Fossil and contemporary fine particulate carbon fractions at 12 rural and urban sites in the United States," *Journal of Geophysical Research*, vol. 113, no. 2, Article ID D02311, 2008.

[26] B. A. Schichtel, M. A. Rodriguez, M. G. Barna, K. A. Gebhart, M. L. Pitchford, and W. C. Malm, "A semi-empirical, receptor-oriented Lagrangian model for simulating fine particulate carbon at rural sites," *Atmospheric Environment*, vol. 61, pp. 361–370, 2012.

[27] L.-W. A. Chen, J. G. Watson, J. C. Chow, D. W. DuBois, and L. Herschberger, "Chemical mass balance source apportionment

for combined $PM_{2.5}$ measurements from U.S. non-urban and urban long-term networks," *Atmospheric Environment*, vol. 44, no. 38, pp. 4908–4918, 2010.

[28] B. Buzcu-Guven, S. G. Brown, A. Frankel, H. R. Hafner, and P. T. Roberts, "Analysis and apportionment of organic carbon and fine particulate matter sources at multiple sites in the mid-western United States," *Journal of the Air & Waste Management Association*, vol. 57, no. 5, pp. 606–619, 2007.

[29] S. Yu, R. L. Dennis, P. V. Bhave, and B. K. Eder, "Primary and secondary organic aerosols over the United States: estimates on the basis of observed organic carbon (OC) and elemental carbon (EC), and air quality modeled primary OC/EC ratios," *Atmospheric Environment*, vol. 38, no. 31, pp. 5257–5268, 2004.

[30] A. Hecobian, X. Zhang, M. Zheng, N. Frank, E. S. Edgerton, and R. J. Weber, "Water-soluble organic aerosol material and the light-absorption characteristics of aqueous extracts measured over the southeastern United States," *Atmospheric Chemistry and Physics*, vol. 10, no. 13, pp. 5965–5977, 2010.

[31] X. Zhang, Z. Liu, A. Hecobian et al., "Spatial and seasonal variations of fine particulate water-soluble organic carbon (WSOC) over the southeastern United States: implications for secondary organic aerosol formation," *Atmospheric Chemistry and Physics*, vol. 12, pp. 6593–6607, 2012.

[32] M. Chin, T. Diehl, P. Ginoux, and W. Malm, "Intercontinental transport of pollution and dust aerosols: implications for regional air quality," *Atmospheric Chemistry and Physics*, vol. 7, no. 21, pp. 5501–5517, 2007.

[33] R. J. Park, D. J. Jacob, M. Chin, and R. V. Martin, "Sources of carbonaceous aerosols over the United States and implications for natural visibility," *Journal of Geophysical Research*, vol. 108, no. 12, article 4355, 2003.

[34] R. J. Park, D. J. Jacob, N. Kumar, and R. M. Yantosca, "Regional visibility statistics in the United States: natural and transboundary pollution influences, and implications for the Regional Haze Rule," *Atmospheric Environment*, vol. 40, no. 28, pp. 5405–5423, 2006.

[35] H. Liao, D. K. Henze, J. H. Seinfeld, S. Wu, and L. J. Mickley, "Biogenic secondary organic aerosol over the United States: comparison of climatological simulations with observations," *Journal of Geophysical Research*, vol. 112, no. 6, Article ID D06201, 2007.

[36] E. Drury, D. J. Jacob, R. J. D. Spurr et al., "Synthesis of satellite (MODIS), aircraft (ICARTT), and surface (IMPROVE, EPA-AQS, AERONET) aerosol observations over eastern North America to improve MODIS aerosol retrievals and constrain surface aerosol concentrations and sources," *Journal of Geophysical Research*, vol. 115, no. 14, Article ID D14204, 2010.

[37] Y. H. Mao, Q. B. Li, L. Zhang et al., "Biomass burning contribution to black carbon in the western United States mountain ranges," *Atmospheric Chemistry and Physics*, vol. 11, no. 21, pp. 11253–11266, 2011.

[38] M. Huang, G. R. Carmichael, S. Kulkarni et al., "Sectoral and geographical contributions to summertime continental United States (CONUS) black carbon spatial distributions," *Atmospheric Environment*, vol. 51, pp. 165–174, 2012.

[39] M. Kanakidou, J. H. Seinfeld, S. N. Pandis et al., "Organic aerosol and global climate modelling: a review," *Atmospheric Chemistry and Physics*, vol. 5, no. 4, pp. 1053–1123, 2005.

[40] X. Liu, R. C. Easter, S. J. Ghan et al., "Toward a minimal representation of aerosols in climate models: description and evaluation in the Community Atmosphere Model CAM5," *Geoscientific Model Development*, vol. 5, pp. 709–739, 2012.

[41] D. M. Murphy, J. C. Chow, E. M. Leibensperger et al., "Decreases in elemental carbon and fine particle mass in the United States," *Atmospheric Chemistry and Physics*, vol. 11, no. 10, pp. 4679–4686, 2011.

[42] L. W. A. Chen, J. C. Chow, J. G. Watson, and B. A. Schichtel, "Consistency of long-term elemental carbon trends from thermal and optical measurements in the IMPROVE network," *Atmospheric Measurement Techniques*, vol. 5, pp. 2329–2338, 2012.

[43] J. C. Chow, J. G. Watson, L. C. Pritchett, W. R. Pierson, C. A. Frazier, and R. G. Purcell, "The DRI thermal/optical reflectance carbon analysis system: description, evaluation and applications in U.S. Air quality studies," *Atmospheric Environment*, vol. 27A, no. 8, pp. 1185–1201, 1993.

[44] J. G. Watson, J. C. Chow, L.-W. A. Chen, and N. H. Frank, "Methods to assess carbonaceous aerosol sampling artifacts for IMPROVE and other long-term networks," *Journal of the Air & Waste Management Association*, vol. 59, no. 8, pp. 898–911, 2009.

[45] A. M. Dillner, C. H. Phuah, and J. R. Turner, "Effects of post-sampling conditions on ambient carbon aerosol filter measurements," *Atmospheric Environment*, vol. 43, no. 37, pp. 5937–5943, 2009.

[46] J. L. Hand, W. C. Malm, A. Laskin et al., "Optical, physical, and chemical properties of tar balls observed during the Yosemite Aerosol Characterization Study," *Journal of Geophysical Research*, vol. 110, no. 21, Article ID D21210, pp. 1–14, 2005.

[47] "IMPROVE data," http://vista.cira.colostate.edu/improve/.

[48] "CSN data," http://views.cira.colostate.edu/fed/ or http://www.epa.gov/ttn/airs/airsaqs/.

[49] B. J. Turpin and H.-J. Lim, "Species contributions to $PM_{2.5}$ mass concentrations: revisiting common assumptions for estimating organic mass," *Aerosol Science and Technology*, vol. 35, no. 1, pp. 602–610, 2001.

[50] H. Theil, "A rank-invariant method of linear andpolynomial regression analysis I," in *Proceedings of the Koninklijke Nederlandse Akademie van Wetenschappen*, vol. A53, pp. 386–392, 1950.

[51] H. Theil, "A rank-invariant method of linear and polynomial regression analysis II," in *Proceedings of the Koninklijke Nederlandse Akademie van Wetenschappen*, vol. A53, pp. 521–525, 1950.

[52] H. Theil, "A rank-invariant method of linear and polynomial regression analysis III," in *Proceedings of the Koninklijke Nederlandse Akademie van Wetenschappen*, vol. A53, pp. 1397–1412, 1950.

[53] D. V. Spracklen, J. A. Logan, L. J. Mickley et al., "Wildfires drive interannual variability of organic carbon aerosol in the western U.S. in summer," *Geophysical Research Letters*, vol. 34, no. 16, Article ID L16816, 2007.

[54] A. S. Holden, A. P. Sullivan, L. A. Munchak et al., "Determining contributions of biomass burning and other sources to fine particle contemporary carbon in the western United States," *Atmospheric Environment*, vol. 45, no. 11, pp. 1986–1993, 2011.

[55] J. C. Chow, L.-W. A. Chen, J. G. Watson et al., "$PM_{2.5}$ chemical composition and spatiotemporal variability during the Californian Regional $PM_{10}/PM_{2.5}$ Air Quality Study (CRPAQS)," *Journal of Geophysical Research*, vol. 111, no. 10, Article ID D10S04, 2006.

[56] S. A. Christopher, P. Gupta, U. Nair et al., "Satellite remote sensing and mesoscale modeling of the 2007 Georgia/Florida fires," *IEEE Journal of Selected Topics in Applied Earth Observations and Remote Sensing*, vol. 2, no. 3, pp. 163–175, 2009.

[57] X. Zhang, A. Hecobian, M. Zheng, N. H. Frank, and R. J. Weber, "Biomass burning impact on $PM_{2.5}$ over the southeastern US during 2007: integrating chemically speciated FRM filter measurements, MODIS fire counts and PMF analysis," *Atmospheric Chemistry and Physics*, vol. 10, no. 14, pp. 6839–6853, 2010.

[58] G. Bench, S. Fallon, B. Schichtel, W. Malm, and C. McDade, "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," *Journal of Geophysical Research*, vol. 112, no. 10, Article ID D10205, 2007.

[59] L. Ke, X. Ding, R. L. Tanner, J. J. Schauer, and M. Zheng, "Source contributions to carbonaceous aerosols in the Tennessee valley region," *Atmospheric Environment*, vol. 41, no. 39, pp. 8898–8923, 2007.

[60] Y. Cheng, M. Zheng, K.-B. He et al., "Comparison of two thermal-optical methods for the determination of organic carbon and elemental carbon: results from the southeastern United States," *Atmospheric Environment*, vol. 45, no. 11, pp. 1913–1918, 2011.

[61] G. C. Holzworth, "Mixing heights, wind speeds, and potential for urban air pollution throughout the contiguous United States," Tech. Rep. AP-101, Environmental Protection Agency, Office of Air Programs Publication, 1972.

[62] J. A. Gillies and A. W. Gertler, "Comparison and evaluation of chemically speciated mobile source $PM_{2.5}$ particulate matter profiles," *Journal of the Air & Waste Management Association*, vol. 50, no. 8, pp. 1459–1480, 2000.

[63] J. D. Mcdonald, B. Zielinska, E. M. Fujita, J. C. Sagebiel, J. C. Chow, and J. G. Watson, "Fine particle and gaseous emission rates from residential wood combustion," *Environmental Science and Technology*, vol. 34, no. 11, pp. 2080–2091, 2000.

[64] T. Zeng and Y. Wang, "Nationwide summer peaks of OC/EC ratios in the contiguous United States," *Atmospheric Environment*, vol. 45, no. 3, pp. 578–586, 2011.

[65] B. J. Turpin and J. J. Huntzicker, "Secondary formation of organic aerosol in the Los Angeles basin: a descriptive analysis of organic and elemental carbon concentrations," *Atmospheric Environment*, vol. 25A, no. 2, pp. 207–215, 1991.