Concurrent Temporal and Spatial Trends in Sulfate and Organic Mass Concentrations Measured in the IMPROVE Monitoring Program

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Abstract Recent modeling and field studies have highlighted a relationship between sulfate concentrations and secondarily formed organic aerosols related to isoprene and other volatile biogenic gaseous emissions. The relationship between these biogenic emissions and sulfate is thought to be primarily associated with the effect of sulfate on aerosol acidity, increased aerosol water at high relative humidities, and aerosol volume. The Interagency Monitoring of Protected Visual Environments (IMPROVE) program provides aerosol concentration levels of sulfate (SO_4) and organic carbon (OC) at 136 monitoring sites in rural and remote areas of the United States over time periods of between 15 and 28 years. This data set allows for an examination of relationships between these variables over time and space. The relative decreases in SO_4 and OC were similar over most of the eastern United States, even though concentrations varied dramatically from one region to another. The analysis implied that for every unit decrease in SO_4 there was about a 0.29 decrease in organic aerosol mass (OA = 1.8 × OC). This translated to a 2 µg/m^3 decrease in biogenically derived secondary organic aerosol over 15 years in the southeastern United States. The analysis further implied that 35% and 27% in 2001 and 2015, respectively, of average total OA may be biogenically derived secondary organic aerosols and that there was a small but significant decrease in OA not linked to changes in SO_4 concentrations. The analysis yields a constraint on ambient SO_4–OC relationships that should help to refine and improve regional-scale chemical transport models.

1. Introduction

Atmospheric fine particulate matter—particles with aerodynamic diameters less than 2.5 µm ($PM_{2.5}$)—is the primary contributor to haze around the world and in the United States, is responsible for considerable numbers of human deaths and adverse health effects, and plays a significant role in climate forcing (Dockery et al., 1993; IPCC, 2013; Mauderly & Chow, 2008). Most atmospheric particulate matter contributing to these effects is secondary in nature in that it is formed from primary emissions of various gaseous species. In the case of ammoniated sulfate and nitrates, the gaseous precursors are sulfur dioxide (SO_2) and nitrogen oxides, respectively. For secondary organic aerosols (SOA), the gaseous precursor molecules are varied in nature and originate from many sources including vegetation, fire, and mobile sources (Carlton et al., 2010; Hallquist et al., 2009; Hoyle et al., 2011; Kleindienst et al., 2007; Weber et al., 2007).

With recent and significant reductions of SO_2 emissions, ammoniated sulfate is no longer the largest single contributor to $PM_{2.5}$ across the United States. In much of the East, the contributions of organic aerosol mass (OA) and ammoniated sulfate to $PM_{2.5}$ are similar. Attwood et al. (2014), Kim et al. (2015), and Marais et al. (2017) show that OA now makes a larger contribution than sulfate to $PM_{2.5}$ in the southeastern United States in summer. In much of the western United States, OA is the largest contributor to $PM_{2.5}$, the exceptions being the regions of southern Arizona and western Texas, where sulfates and soil are still the largest contributors to $PM_{2.5}$ (Hand, Schichtel, Malm, et al., 2012). During winter months, ammonium nitrate (ANO_3) contributes significantly to $PM_{2.5}$ in the Midwest, Ohio River valley, mid-South, and Southern California regions.

Tanner et al. (2015) and Budisulistiorini et al. (2016, 2013, 2015) have recently reported on aerosol measurements made at Look Rock, Great Smoky Mountains National Park (GRSM), Tennessee, and in downtown Atlanta, Georgia. Tanner et al. (2015) report on trends in, and relative composition of, $PM_{2.5}$ species over time from measurements made under the sponsorship of the Tennessee Valley Authority and by the Interagency

Monitoring of Protected Visual Environments (IMPROVE) program. They report that annual average concentrations of ammonium sulfate (ASO_4) have decreased from 6.8 $\mu g/m^3$ to 2.4 $\mu g/m^3$ from 1999 to 2013, while OA decreased from 4.4 $\mu g/m^3$ to 1.8 $\mu g/m^3$, factors of 2.8 and 2.4, respectively. In 1999 ASO_4 on the average made up 48% of $PM_{2.5}$, while in 2013 that fraction dropped to 41% because of the relative decrease of other species such as OA contributing to $PM_{2.5}$ mass. These annual averages should be contrasted with summer trends. Focusing on the summer months of June, July, and August, ASO_4 made up about 65% of $PM_{2.5}$ in 1999, 50% in 2013, and only 25% in 2015. Over this same time period, the fractional contribution of OA to $PM_{2.5}$ was about constant at 30% on the average for the summer months. The summer concentrations of ASO_4 went from about 12 $\mu g/m^3$ in 1999 to 3.1 $\mu g/m^3$ in 2013 and 2.4 $\mu g/m^3$ in 2015, and during that same time period, OA went from about 5.6 $\mu g/m^3$ to near 2.0 $\mu g/m^3$.

OA is associated with primary emissions as well as being formed secondarily from both anthropogenic and biogenic volatile organic carbon (VOC) gases. Carbon 14 measurements at GRSM (Bench et al., 2007; Ke et al., 2007; Schichtel et al., 2008; Tanner et al., 2004) indicate that the fraction of OA that is modern is consistently high year-round and >90% during the summer months. Tanner and Gaffney (1986) reported that modern carbon emissions did not change prior to 1986. More recently, Bauwens et al. (2016) report that on a global basis, there is little interannual variability in isoprene emissions from 2005 to 2014. Purves et al. (2004) report that isoprene emissions may have increased by 10–30% in the eastern United States prior to 2004 due to land use changes. If biogenic emissions have not changed or have increased and most OA is modern, why have OA concentrations decreased significantly over the past 10–15 years?

Isoprene is the most abundant nonmethane hydrocarbon emitted and may be a large contributor to organic concentrations in the eastern United States. Isoprene SOA is associated primarily with isoprene epoxydiols (IEPOX) and glyoxal (Marais et al., 2016). A strong relationship between IEPOX-SOA and SO_4 is thought to be primarily associated with the effect of SO_4 on aerosol acidity, increased aerosol water at high relative humidities, and aerosol volume (Marais et al., 2016; Xu et al., 2016).

To that end, Budisulistiorini et al. (2013, 2015) report on aerosol chemical speciation monitor (ACSM) measurements made during the Southern Oxidant and Aerosol Study (SOAS) and on a 2-year ACSM measurement program sponsored by the Electric Power Research Institute at GRSM and Atlanta, Georgia. For the yearlong measurement program at the GRSM site, Budisulistiorini et al. (2016) report on four organic aerosol types: low-volatility, oxygenated OA (30–66%), biomass burning OA (15–33%), IEPOX-OA (27–41%), and a 91Fac OA (21–23%). All species were weakly to moderately correlated with SO_4 and inorganics in general. The highest concentrations of OA and inorganics were during the summer season. During the SOAS measurement program (1 June to 17 July 2013), similar results to those described above were reported. IEPOX-SOA was fairly correlated with sulfate at $R^2 \approx 0.6$, suggesting that sulfate plays an important role in isoprene SOA formation. Pye et al. (2013) suggest that lowering sulfur oxide emissions by 25% could lower IEPOX-SOA by as much as 35–40%.

Hu et al. (2015) report on 24 IEPOX-SOA measurements made around the globe. Aircraft measurements made during the Studies of Emissions and Atmospheric Composition, Clouds and Climate Coupling by Regional Surveys ($SEAC^4RS$) campaign showed some of the highest IEPOX-SOA fractions of >30% of organic carbon (OC) in the southeastern United States, low concentrations across the Midwest and mountainous West, but higher concentrations in parts of the coastal West. Using daily averaged values, the slope between SO_4 and IEPOX was 0.64 ± 0.05 for SOAS and 0.78 ± 0.21 for boundary layer average values during $SEAC^4RS$.

Budisulistiorini et al. (2015) report that no association between IEPOX-SOA and NO or NO_2 was observed. Pye et al. (2013) report that a reduction in nitrogen oxides leads to small increases in IEPOX-SOA. However, Xu et al. (2015) report that the formation of less-oxidized oxygenated OA is a result of nighttime reactions of biogenic VOC (BVOC) and the NO_3 radical. They report, based on data collected in the Southeastern Aerosol Research and Characterization (SEARCH) network, that condensable organic nitrates contribute 19–34% of OA as a result of this mechanism at Centreville, Alabama, while 18–36% of OA is due to IEPOX-SOA.

Budisulistiorini et al. (2015) also report that no strong relationships were found between IEPOX-SOA formation and particle acidity. With SO_4 concentrations decreasing by more than 80% in much of the eastern United States from the early 1990s to current time periods (Hand, Schichtel, Malm, et al., 2012) and ammonia concentrations remaining about the same over the same time period (Saylor et al., 2015; Weber et al., 2016;

Xing et al., 2013), one might expect aerosol acidity to decrease and possibly inhibit the formation of IEPOX-SOA. However, Weber et al. (2016), Liggio et al. (2011), and Silvern et al. (2017) argue that for different reasons, as SO_2 and therefore SO_4 decrease and OA/SO_4 increases, aerosol acidity remains approximately unchanged, and therefore IEPOX-SOA would not be suppressed.

Budisulistiorini et al. (2017), in a modeling analysis, address the apparent lack of correlation between IEPOX-SOA and aerosol liquid water and pH during the SOAS study and reaffirm the importance of SO_4 and aqueous-phase chemistry in the formation of IEPOX-SOA. Carlton and Turpin (2013) suggest in a modeling experiment that the dominant SOA formation pathway in the Southeast is through liquid aerosol water. Nguyen et al. (2015) examined speciated ion and meteorological data collected from 2001 to 2012 in the SEARCH network with an eye toward understanding the relationship in decreasing trends in aerosol water, nitrate (NO_3), SO_4, ammonium (NH_4), and OA. Aerosol liquid water is predominantly linked to the hygroscopic characteristics of inorganic salts, primarily SO_4, under high relative humidity conditions. Because of relative decreases in inorganic salts, the fractional contribution of aerosol liquid water to $PM_{2.5}$ has decreased across the SEARCH network by 23% between 2001 and 2012.

Here we explore the relationships between SO_4 and OA collected by IMPROVE at 136 sites across the United States. Individual trends in OA and ASO_4 will be examined, as will the concurrent trends in OA and SO_4. Given the suggested strong relationship between SO_2 emission reduction and SOA, it is of interest to see if decadal reductions in SO_4 (Hand, Schichtel, Pitchford, et al., 2012) can be linked to similar reductions in OA (Hand et al., 2013). A decrease in OA concentration resulting from a decrease in fossil carbon emissions will be examined to further constrain the potential rate of decrease in OA linked to emissions of BVOCs such as isoprene and terpenes. SOA associated with all BVOC species will be referred to as BVOC-SOA.

2. The IMPROVE Monitoring Program

The Regional Haze Rule (United States Environmental Protection Agency, 1999) requires monitoring representative of 156 visibility-protected federal areas beginning in January 2001. This entails particle sampling and analysis of the major aerosol components using methods patterned after those used since 1987 by the IMPROVE network (Joseph et al., 1987; Malm et al., 1994). Although there are currently 157 monitoring sites, only 136 sites with the most complete records, starting in 2001, will be used for the analysis presented in the following two sections. These sites are shown in Figure 1 and listed by name and site number in Table S1 in the supporting information. Also shown in Figure 1 is a line representing longitude = −100°. The data from these sites are available on the IMPROVE web site at http://vista.cira.colostate.edu/improve/.

The 136 monitoring sites used in this analysis and operating in the IMPROVE network during 2001–2015 were grouped into 24 regions (Hand, Schichtel, Pitchford, et al., 2012; Malm et al., 2002). The regions were selected based upon topography and the expected spatial extent of fine aerosols. The groupings were further refined by examining the individual monthly aerosol composition patterns for each site within a region. Comparative analysis and regional trends in aerosol species will be presented based on these monitoring site groupings. This paper will focus on SO_4 and OA, primarily during the summer months when biogenic OC is expected to be high (Goldstein et al., 1998) and where there have been significant decreases in SO_4 mass concentration (Hand, Schichtel, Malm, et al., 2012).

3. Individual Site Trends

In the analysis presented in the next two sections, SO_4 is interpreted as ASO_4, primarily because the goal in presenting the information in the following section is to show how the relative contribution of ammoniated sulfate to $PM_{2.5}$ has dramatically decreased over the last 15 years. Furthermore, reconstructed fine mass ($RCPM_{2.5}$), the sum of $PM_{2.5}$ mass concentrations of individual aerosol species (ASO_4 + ANO_3 + OA + light absorbing carbon (LAC) + dust + sea salt) is used in lieu of measured gravimetric $PM_{2.5}$ mass because of significant artifacts linked to gravimetric mass concentrations (Malm et al., 2011).

Seasonal averages of aerosol species concentrations were calculated for each year for each of the 136 monitoring sites. Winter is defined as the average over December, January, and February, spring as March, April, and May, and so forth. A Theil regression (Theil, 1950) was performed with the seasonal average concentration data as the dependent variable and the year as the independent variable. Kendall tau statistics were used
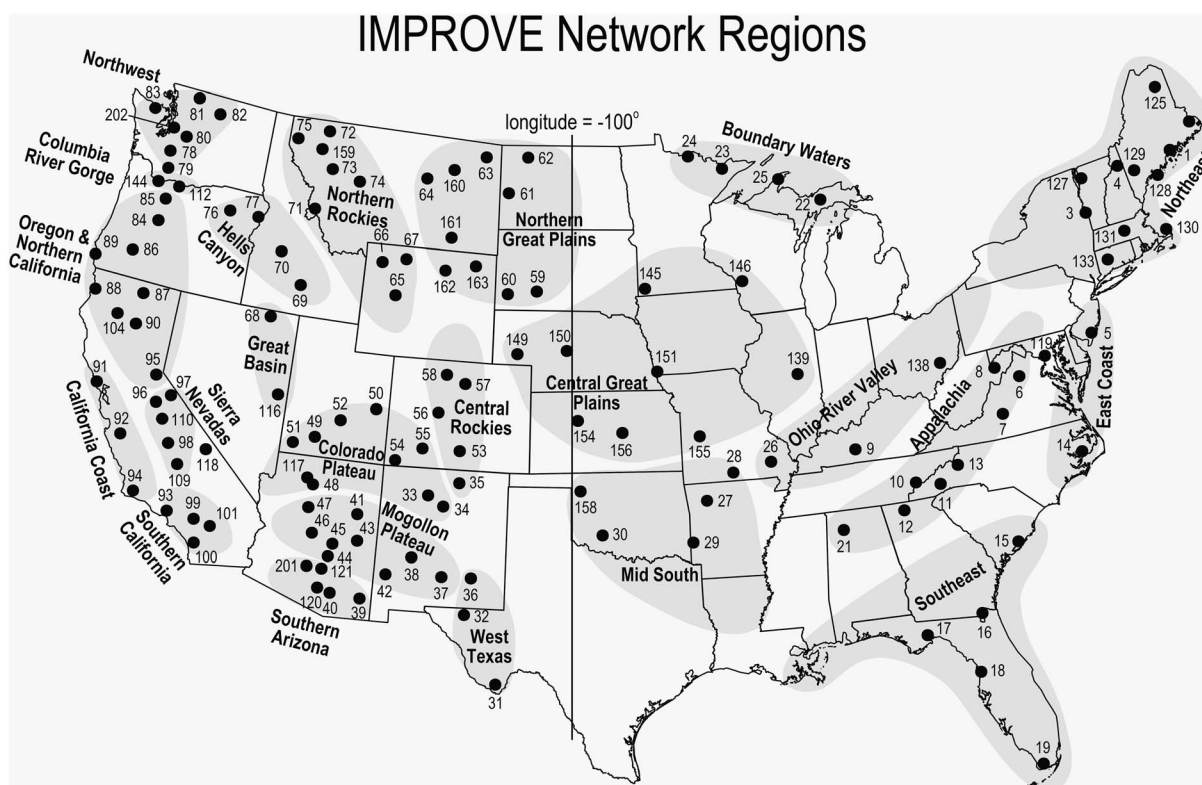
Figure 1. Map showing the location of IMPROVE monitoring sites as well as the grouping of the sites into regions. A line representing longitude = −100° is also shown. Each site is numbered to correspond to the respective names listed in Table S1.

to determine significance; a statistically significant trend was assumed at the 95th percentile significance level ($p < 0.05$), meaning that there was a 95% chance that the slope was not due to random chance. "Trend" is defined as concentration change per year ($\mu g/m^3/yr$).

Figure 2 shows a representative example of seasonally averaged trend data for Shenandoah National Park (site number 6 in Table S1 and Figure 1) for OA and ASO_4. Seasonal concentrations for both species are plotted as a function of time (year) along with the Theil regression line. The uncertainty bars represent one standard deviation of the mean. Trends for all seasons and for both species are significant at the 5% level. The winter, spring, summer, and fall trends are −0.06, −0.18, −0.49, and −0.22 $\mu g/m^3/yr$ for ASO_4 and −0.05, −0.04, −0.10, and −0.06 $\mu g/m^3/yr$ for OA, respectively. At Shenandoah National Park, the summer ASO_4 trend is about 5 times greater than OA and about the same as the OA trend during the winter months.

Figure 3 summarizes the average 2001–2015 summertime spatial trends for ASO_4 concentrations (Figure 3a), the fraction that it contributes to $RCPM_{2.5}$ (Figure 3b), the temporal trend in concentration ($\mu g/m^3/yr$) (Figure 3c), and the fractional change over the entire 15-year period relative to the concentration of the species in 2001 (Figure 3d). For the trend maps, the size of the arrow is proportional to the magnitude of the trend, and if the trend is significant at the 5% level, the arrow is plotted as green, while an insignificant trend is plotted as red. An up or down arrow indicates an increasing or decreasing trend, respectively. Similar results for OA are shown in Figure 4.

It is evident in Figure 3a that the highest summertime ASO_4 concentrations are found in the Appalachia region of the United States, with the Northeast and extreme Southeast being somewhat lower. The lowest concentrations occurred in the Intermountain West and northern California and Oregon, with intermediate concentrations found in Southern California and Arizona.

At 10% of the sites (see Figure 3b), primarily in the East, ASO_4 contributed more than 50% of summertime $PM_{2.5}$, while at 10% of the sites ASO_4 was less than 15% of $RCPM_{2.5}$. Across all sites, the median fractional contribution of ASO_4 to summertime $RCPM_{2.5}$ was 30%. Conversely, at 10% of the sites, primarily in the
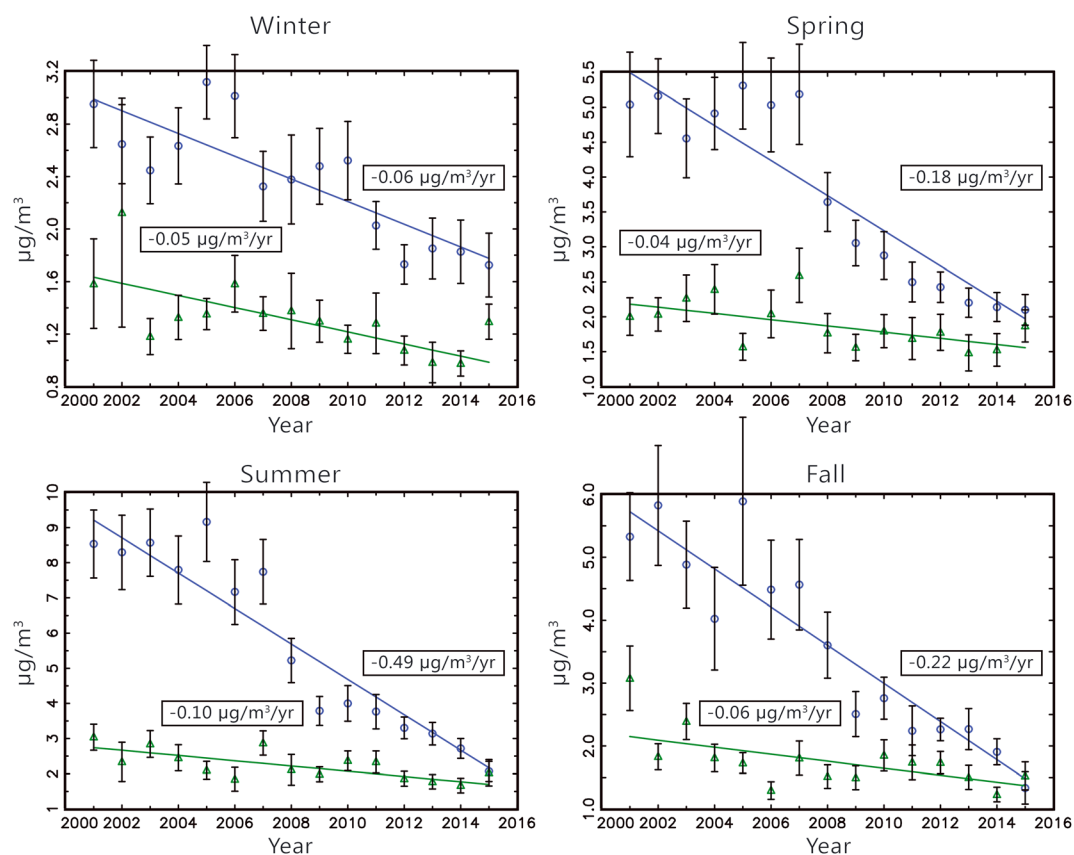
Figure 2. Seasonal average trends in ASO_4 (open circles) and OA (open triangles) concentrations ($\mu g/m^3$) at Shenandoah National Park for the years 2001–2015. Also shown in each panel are the respective trends in $\mu g/m^3/yr$.

West, OA contributed more than 60% of $PM_{2.5}$, while in the interior of the eastern United States, the percentage of OA in $PM_{2.5}$ was on the order of 25–30%.

As shown in Figure 3c, summertime ASO_4 decreased at a statistically significant rate at most sites in the continental United States. At more than 60% of the sites, the absolute downward trend in ASO_4 concentrations was less than 0.05 $\mu g/m^3/yr$, while at 15% of the sites the trend was greater than 0.3 $\mu g/m^3/yr$. At 10% of the sites, primarily in the central eastern United States, the downward trend in ASO_4 exceeded 0.5 $\mu g/m^3/yr$. The same trend information is plotted as a percent change in concentration relative to the year 2001 in Figure 3d. On a percentage basis, the trend in ASO_4 was less spatially variable across the United States. Over the entire 15-year time frame at 10% of the sites, ASO_4 has declined by more than 46%, and at most Intermountain West sites, the decreases in ASO_4 concentrations were on the order of 10–20%. The median percent decrease in ASO_4 concentrations across all sites was about 27%.

In Figures 4c and 4d, it is evident that summertime OA also decreased at most monitoring sites across the continental United States. However, many of the OA trends in the West were not statistically significant at the 5% level primarily because of episodic elevated concentrations that were a result of wildfires (Jaffe et al., 2008; Spracklen et al., 2007). The concentrations at these sites generally trend downward except for occasional extreme outliers. Ten percent of the sites had decreased trends of >0.12 $\mu g/m^3/yr$; sites having the greatest decreased trends occurred in Southern California and southern Arizona. OA decreased on the order of 0.09–0.11 $\mu g/m^3/yr$ at sites in the Southeast. The median OA trend is 0.05 $\mu g/m^3/yr$. On a percentage basis, trends across the United States were similar, with the majority of sites having decreased trends over the entire 15-year time frame of 15–30%. A few sites in southern Arizona and New Mexico had decreased percentage trends greater than 30%. The sites in the Southeast experienced a 25% decrease in OA.
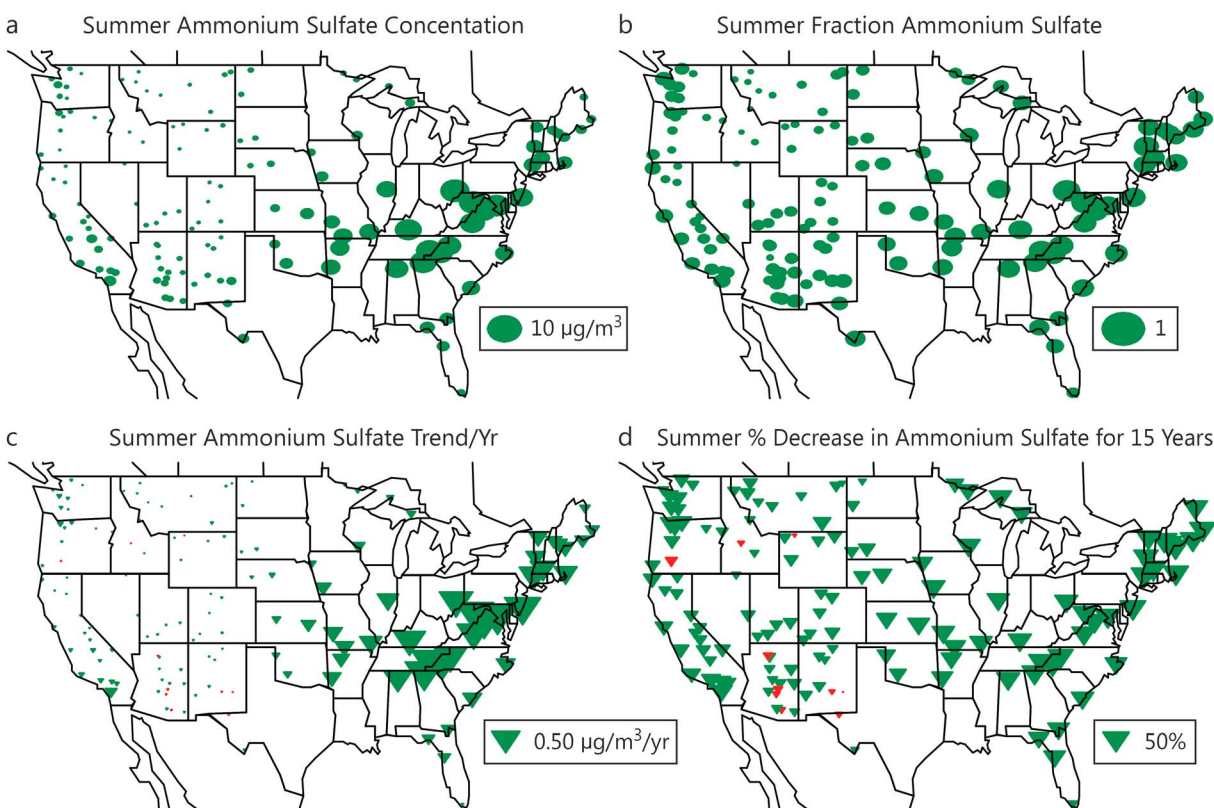
Figure 3. The 2001–2015 summer average of (a) ASO_4 concentration ($\mu g/m^3$), (b) ASO_4 fractional contribution to $RCPM_{2.5}$, (c) 2001–2015 trend in summer average of ASO_4 ($\mu g/m^3/yr$), and (d) 2001–2015 percent change in ASO_4. Green indicates a trend that is significant at the 0.05 level, while red represents a trend that is not significant. Upward-pointing triangles indicate positive trends, and vice versa.

4. Comparison of Average 2001–2002 to 2014–2015 Aerosol Mass Concentrations

Figures 5 and 6 show the average seasonal mass concentrations, in units of $\mu g/m^3$, of ASO_4, ANO_3, OA, and "remaining" for the average of years 2001–2002 and 2014–2015, respectively, grouped in accordance with the geographic regions shown in Figure 1.

In most cases, "remaining" is small, the exceptions being coastal sites, where sea salt can be significant, and the southwestern United States, where dust can be a substantial fraction of $PM_{2.5}$. For a more detailed discussion of the relative contributions of each species to $PM_{2.5}$, the reader is referred to Malm et al. (2004) and Hand, Schichtel, Malm, et al. (2012).

The concentration scale is the same for all regions and for both time periods, so the reader can easily compare the differences between eastern and western regions of the United States and between the two time periods. During the 2001–2002 time frame, in almost all cases $PM_{2.5}$ was highest during the summer months and lowest during wintertime. This trend was primarily due to ASO_4 in the East and OA in the West. ANO_3, on the other hand, tends to be highest during the winter months and lowest during summertime. This trend is most predominant for the Midwest and Southern California monitoring sites. This is likely due to higher temperatures during summer months inhibiting ANO_3 formation. Because of significant reductions in ASO_4 concentrations from 2001–2002 to 2014–2015, the seasonal trend in $PM_{2.5}$ has changed at a number of eastern sites but remains the same in the West. In the 2014–2015 time frame, the Boundary Waters, Midwest, Ohio River Valley, Northeast, and East Coast regions have the highest $PM_{2.5}$ concentrations during winter months; primarily because ASO_4 is a smaller fraction of $PM_{2.5}$, the seasonal variability of ASO_4 has decreased and in some cases is highest during wintertime, and the seasonal trend in ANO_3 has remained the same with higher concentrations during winter months.

National temporal trends in ASO_4 and their relationship to sulfur dioxide emission reductions have been explored in detail by Hand, Schichtel, Pitchford, et al. (2012). Referring to that paper and Figures 5 and 6, one
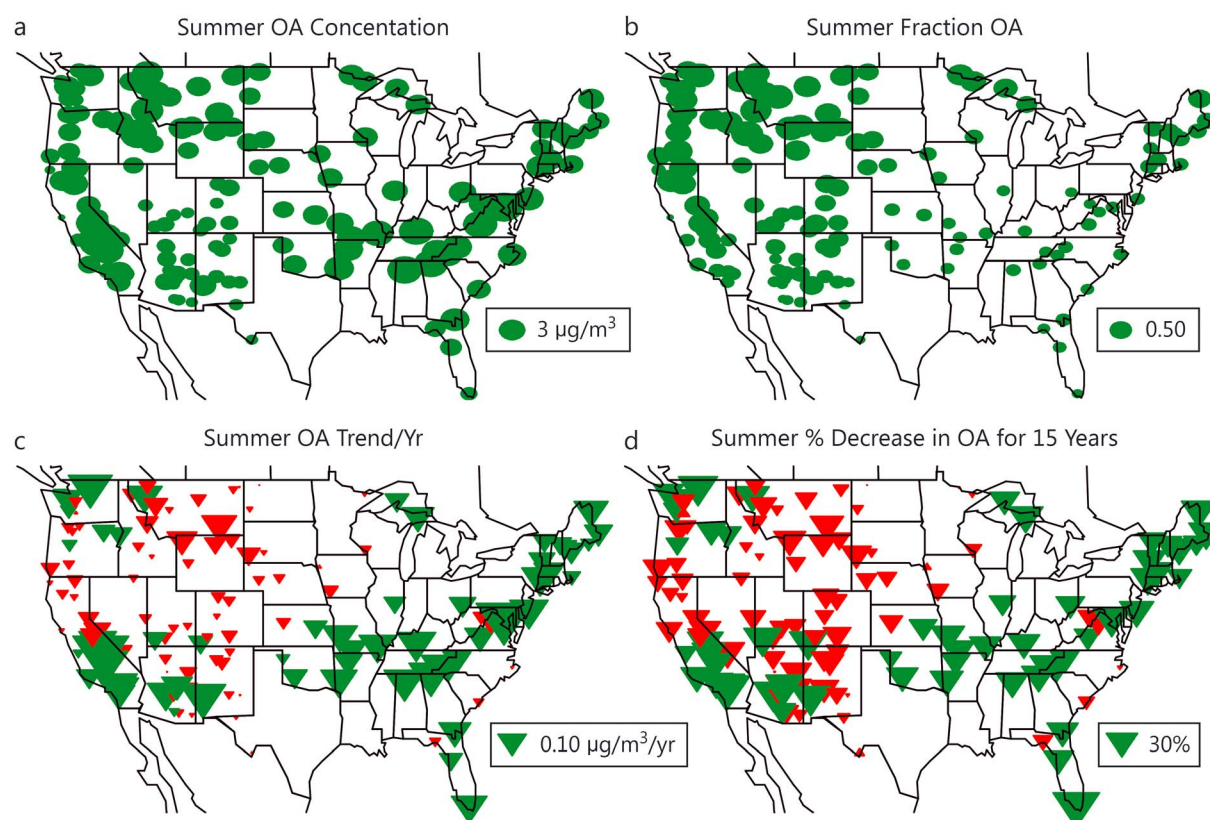
Figure 4. The 2001–2015 summer average of (a) OA concentration ($\mu g/m^3$), (b) OA fractional contribution to $RCPM_{2.5}$, (c) 2001–2015 trend in summer average of OA ($\mu g/m^3/yr$), and (d) 2001–2015 percent change in OA. Green indicates a trend that is significant at the 0.05 level, while red represents a trend that is not significant. Upward-pointing triangles indicate positive trends, and vice versa.

can see that during the 2001–2002 summer months the ASO_4 mass concentration in the eastern United States was on the average about 6 $\mu g/m^3$, while in the West it was near 1 $\mu g/m^3$ and about 2.5 $\mu g/m^3$ in Southern California. Figure 3 shows that by the 2014–2015 time frame, ASO_4 dropped by about 60–70% in the East to a level of 2–3 $\mu g/m^3$, while in the Intermountain West, the levels dropped by about 20–30% and in California, Oregon, and Washington by 30–40%. Summertime ANO_3, however, has dropped by about 30% across the United States, with the exception of the Northwest, where concentrations have stayed about the same.

For the most part, OA has also decreased across the United States but not as significantly or uniformly as ASO_4 concentrations. Much of the variation in the West is due to temporal variability in wildfire emissions. In the East, on the average summertime OA concentrations have decreased from 3.0–3.5 $\mu g/m^3$ to 2.0–2.5 $\mu g/m^3$, which represents a 20–40% decrease. The median decrease in OA east of longitude $-100.0°$ is 30%. In the West, concentrations and changes in concentrations are more varied. The regions of Colorado Plateau, Great Basin, and Boundary Waters exhibit almost no change; California regions showed a 30–40% decrease, while the remaining regions showed about a 20–30% decrease.

Concurrent with decreases in OA are decreases in LAC. In the eastern United States, the rate of summertime decrease in LAC exceeds that of OA, with a median value of 43% for those sites east of longitude $-100.0°$. For those same sites, the ratio of LAC to OA is decreasing, with a median value of 18% reflecting a more-rapid decrease in LAC than OA. These different rates of decrease for these two aerosol categories suggest different emission source types (Bond et al., 2007).

5. Direct Comparison of Site by Site SO$_4$ and OA Concentrations

The IMPROVE data set offers an opportunity to explore the commensurate decrease of SO$_4$ and OA in the eastern United States where, during late spring, summer, and early fall, BVOC emissions are elevated (Purves et al., 2004). Furthermore, in the following analysis, SO$_4$ ion concentrations will be used instead of
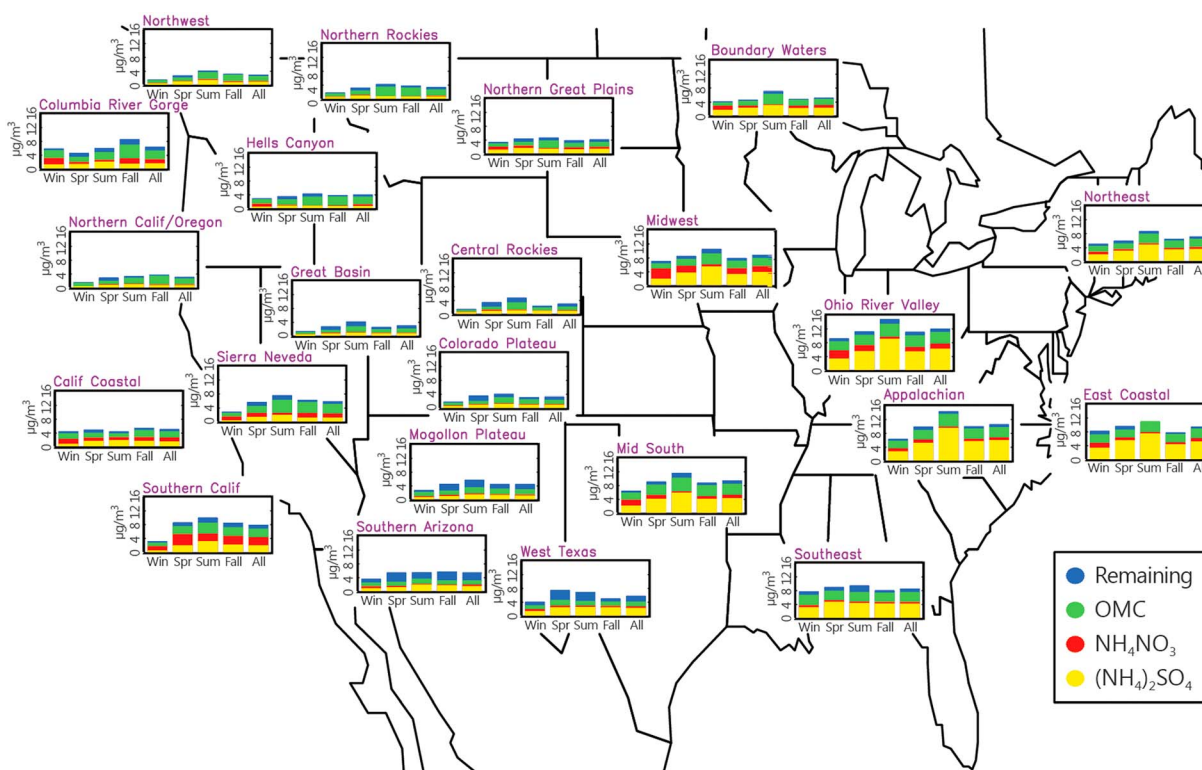
Figure 5. Average concentration, in units of $\mu g/m^3$, of ASO_4, ANO_3, OA, and "remaining" for years 2001–2002. The range for each graph is from 0.0 to 16.0 $\mu g/m^3$ for seasonal averages of winter, spring, summer, fall, and entire year.

ASO_4, as was done by most researchers investigating secondarily formed OA and which was reviewed in section 1. As an example of the relationship between SO_4 and OA in the eastern United States, Figure 7 shows a scatterplot of August–October average OA versus SO_4 for each year of the 15-year time period (2001–2015) at Shining Rock Wilderness Area in the southeastern United States (site number 11 in Table S1 and Figure 1). Combinations of other months, including the summer months of June, July, and August, were also explored, yielding similar results with slightly less statistical significance between the variables. In the following analysis, it is the average concentrations of the August–October data set that are used.

A Thiel regression line (Theil, 1950) with average concentrations of OA and SO_4 as the dependent and independent variables, respectively, is also shown. As before, Kendall tau statistics were used to determine significance, and a significance level of $p < 0.05$ was chosen. As shown, there is a strong linear relationship between the average OA and SO_4, with $R^2 = 0.73$ and a slope and intercept of 0.30 ± 0.04 and of 1.26 ± 0.19 $\mu g/m^3$, respectively. Here and in the following paragraphs, positive/negative uncertainty corresponds to one standard error. For a one-unit reduction in SO_4, there is a corresponding 0.30-unit decrease in OA.

Notice that if the intercept term was 0, a percent change in SO_4 would have the same percent change in OA, independent of the slope value. However, with an intercept greater than 0 this is not the case. For the relationship between SO_4 and OA shown in Figure 7, an 80% change in SO_4 corresponds to about a 15% change in OA.

This strong linear relationship, which occurred at most sites throughout the East, is shown in Figure 8, where the intercept and slope of the Thiel regression of OA against SO_4 for each of the 46 sites east of longitude $-100.0°$ is displayed. Green indicates a trend that is significant at the 0.05 level, while red represents a trend that is not significant. Thirty-five of the 46 sites have statistically significant trend lines.

The results are quite spatially uniform with a mean slope of 0.29 ± 0.14 and intercept of 1.68 ± 0.40 $\mu g/m^3$. The slope of 0.29 ± 0.14 is similar to those reported by reported by Marais et al. (2017), Xu et al. (2015), and Blanchard et al. (2016) of 0.24, 0.42, and ≈ 0.2, respectively.
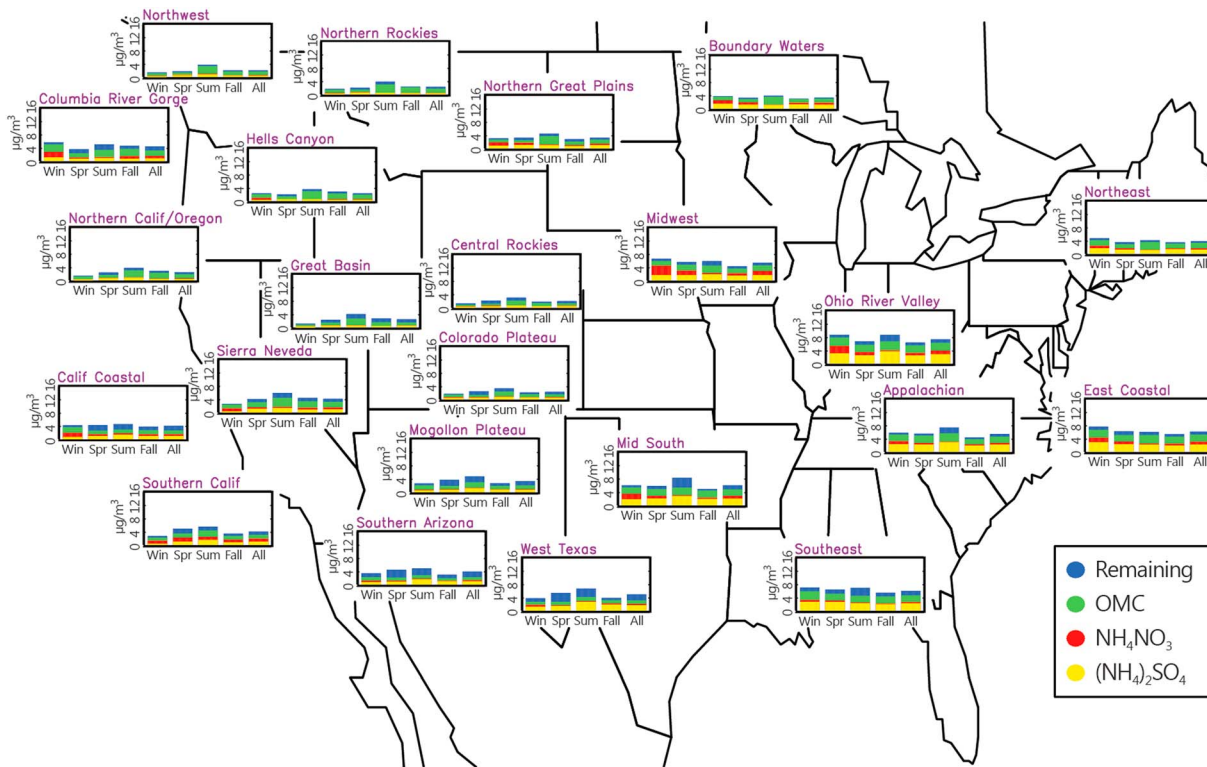
Figure 6. Average concentrations, in units of μg/m^3, of ASO$_4$, ANO$_3$, OA, and "remaining" for years 2014–2015. The range for each graph is from 0.0 to 16.0 μg/m^3 for seasonal averages of winter, spring, summer, fall, and entire year.

Also, the relationship between OA and the sum of NO$_3$ and SO$_4$ concentrations was explored. Because summer concentrations of NO$_3$ are low relative to SO$_4$, the relationship between this sum and OA are nearly the same as those shown in Figure 7.

The highly significant linear relationship between SO$_4$ and OA is consistent with the notion of sulfate-catalyzed BVOC-SOA. If this was the only cause of the relationship, then the slope could be interpreted as the average yield of BVOC-SOA associated with an incremental change of SO$_4$ and the intercept as the OA associated with fossil carbon emissions from mobile sources or other industrial sources, as well as biogenic carbon aerosol not related to BVOC-SOA-related SO$_4$. With this interpretation, there are some obvious questions. Are there other factors contributing to the correlation between OA and SO$_4$, such as meteorological conditions or concurrent decreases in precursor emissions to OA and SO$_4$? Because IMPROVE samples are collected over a 24-h period, could some BVOC-SOA be linked to nighttime NO$_3$ radical oxidation of monoterpenes (Xu et al., 2015)? Does the intercept term only represent non-BVOC-SOA?

If it is assumed that the relationship between SO$_4$ and OA is causal, then on the average across the eastern United States, for every unit decrease in SO$_4$, there is about a 0.29-unit reduction in OA. Also, the average intercepts are 65 ± 24% and 83 ± 27% of total OA for the years 2001 and 2015, respectively, implying that BVOC-SOA contributed 35% and 27% for the same years, respectively, to average total OA concentrations. This is consistent with ≈25% BVOC-SOA found in the southeastern United States as reported by Blanchard et al. (2016).
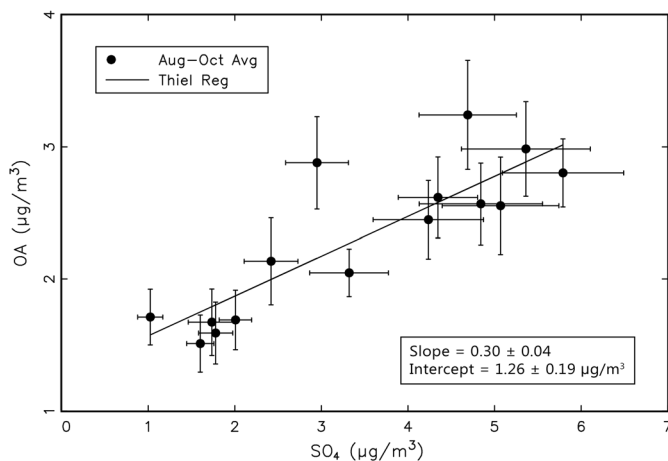
Figure 7. Scatterplot of August–October average OA as a function of average SO$_4$ for Shining Rock Wilderness Area. The slope is 0.30 ± 0.04 with an intercept of 1.26 ± 0.19 μg/m^3 and an R^2 of 0.73. The error bars represent ±1 standard error.
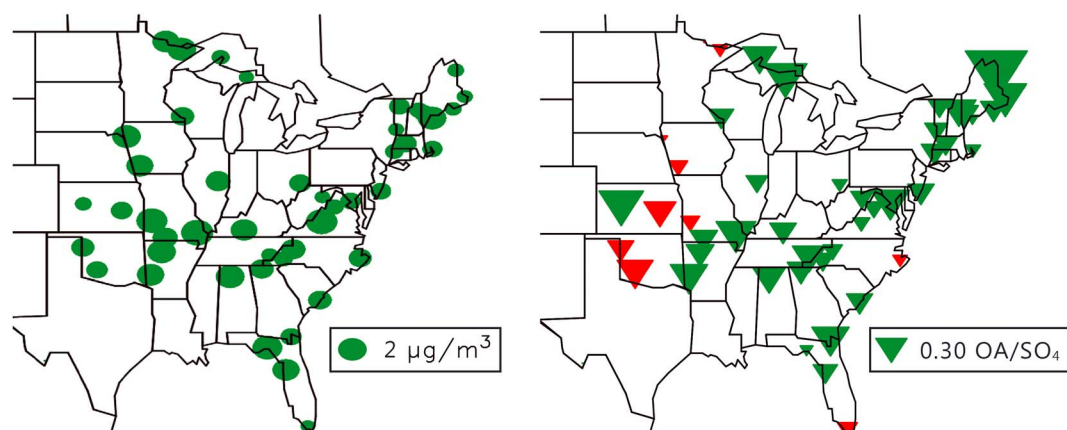
Figure 8. (left) Intercepts and (right) slopes of all monitoring sites for 2001–2015, east of longitude −100.0°. The mean intercept is 1.68 ± 0.40 μg/m^3, while the average slope is 0.29 ± 0.14.

As pointed out above, the interpretation that the slopes represented in Figure 8 are the amount of BVOC-SOA linked to SO$_4$ concentrations may be obscured by a change over time in fossil or BVOC-SOA that is collinear with changes in sulfate-related BVOC-SOA concentrations that could either suppress or enhance the slope between SO$_4$ and OA. These possibilities are further explored below.

5.1. Possible Trends in Fossil Carbon

Figure 9 shows the percent decrease in fossil VOC emissions by state for 1990–2015. The VOC emission data were obtained from the Environmental Protection Agency (EPA) National Emission Inventory (NEI) database (https://www.epa.gov/air-emissions-inventories/air-pollutant-emissions-trends-data). A Theil regression was performed with VOC emissions other than from wild or prescribed fire in ton/yr as the dependent variable and year as the independent variable. Kendall tau statistics were used to determine the significance level. The rate of decrease in VOC emissions in states east of the Mississippi River was nearly uniform at about 3.0%/yr or 45% over a 15-year period. The states with increased VOC trends were those states with significant oil and gas development, such as Wyoming. Because of decreased primary VOC emissions, it is likely that a fraction of fossil SOA has also decreased. Marais
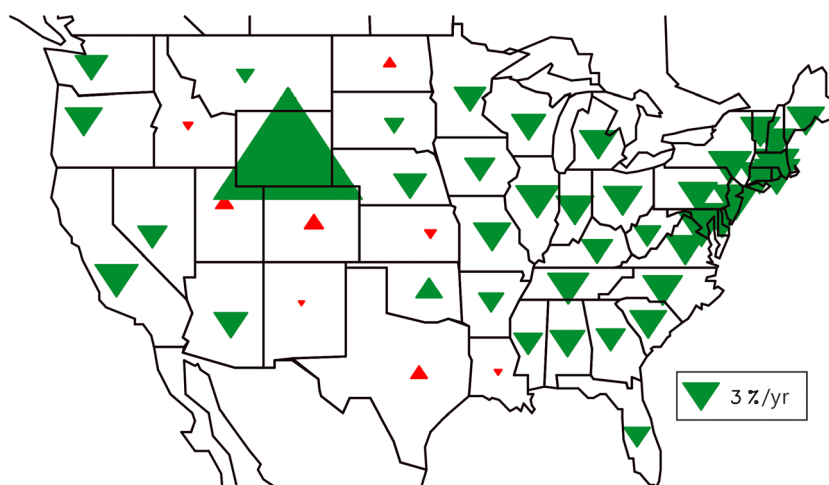
Figure 9. Percent change per year in EPA's National Emission Inventory VOC emissions on a state by state basis. Green indicates a significant trend at the 0.05 level, while red shows statistically insignificant trends.
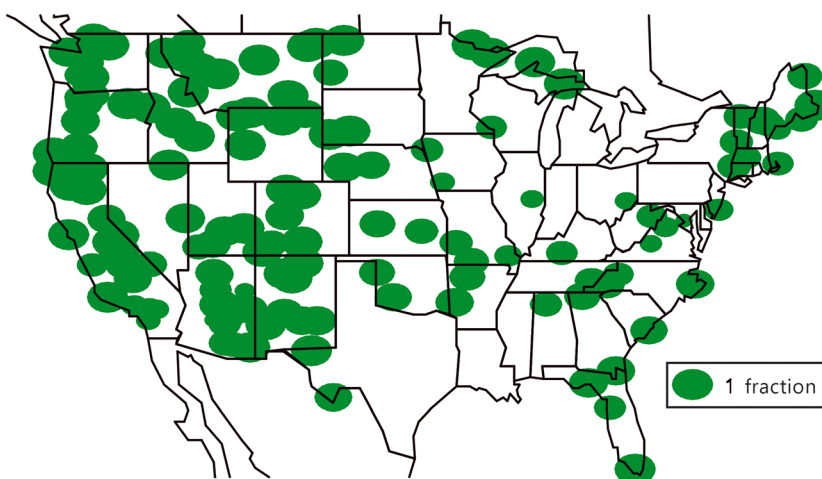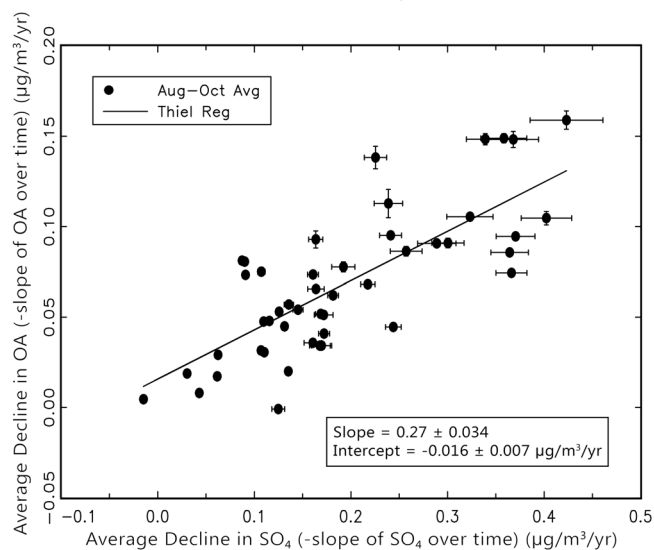
Figure 10. Fraction of OA that is biogenic at all IMPROVE sites, estimated using a hybrid receptor chemical transport model.

et al. (2017) estimate a small decline of 0.7%/yr in anthropogenic SOA due to a decline in anthropogenic VOC emissions.

5.2. How Much of OA Is Fossil?

Carbon 14 measurements in the eastern United States (Bench et al., 2007; Schichtel et al., 2017, 2008; Tanner et al., 2004) indicate that the fraction of OA that is modern is consistently high year-round and as high as 90% during the summer months. Schichtel et al. (2012) used a hybrid receptor chemical transport model to apportion 2006–2008 IMPROVE total particulate carbon to various anthropogenic and natural source types. The simulated contributions from vegetation SOA and fires were summed to obtain an estimate of the fraction of observed OA that is from biogenic sources during the summer months. Figure 10 presents the results for each IMPROVE site. Biogenic carbon, which includes vegetation SOA and biomass burning, in the summer months is almost always more than 70%. Note that if fossil SOA decreased at a rate of 3% per year and only 20% of OA were fossil carbon, then the reduction of OA due to fossil carbon would be on the order of 6% per year.
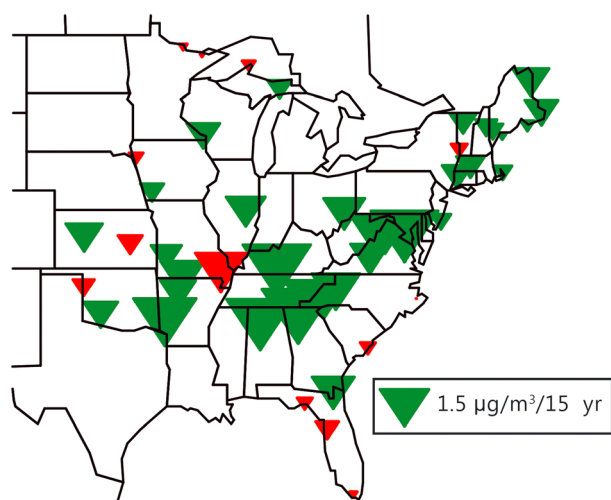
6. OA/SO$_4$ Temporal Trends

While Figure 8 is the result of data point by data point comparison of SO$_4$ and OA independent of time, a similar average OA/SO$_4$ relationship can be derived by comparing the ratio of slopes of SO$_4$ and OA over time, which yields a temporal average ΔOA/ΔSO$_4$.

Figure 11 shows minus the temporal trend of average (August–October) OA and SO$_4$ concentrations plotted against each other for monitoring sites east of longitude $-100.0°$ and for the years 2001–2015. Each data point corresponds to one monitoring site. As before, a Theil regression was performed with –slope of OA over time as the dependent variable and –slope of SO$_4$ as the independent variable. Kendall tau statistics were used to determine the significance level. The uncertainty bars on each data point represent the standard error of the Theil regression slope.

Figure 11 shows that over the 2001–2015 time period, the ΔOA/ΔSO$_4$ ratio is approximately constant at 0.27 ± 0.034 (the slope of the Theil regression line) over the entire region and independent of the magnitude of SO$_4$ and OA or ΔSO$_4$ and ΔOA concentration levels; that is, the change in SO$_4$

Figure 11. Plot of the declining trend in OA (μg/m^3/yr) versus the declining trend in SO$_4$ (μg/m^3/yr) for August–October averages from 2001 to 2015. The solid line is the Thiel regression line.

Figure 12. Derived trends in BVOC-SOA in in terms of $\mu g/m^3/15$ yr. Green indicates a significant trend at the 0.05 level, while red shows statistically insignificant trends.

(ΔSO_4) or OA (ΔOA) over time is not necessarily dependent on the magnitude of SO_4 or OA concentrations. The intercept is -0.016 ± 0.007 $\mu g/m^3/yr$, and R^2 is 0.60.

The implication of the slope of the regression line in Figure 11 is that on the average, for every unit change in SO_4, there is a corresponding 0.27-unit change in OA. The intercept term represents the year to year change in OA that is not correlated with changing SO_4 aerosol concentrations. It is approximately 6% of the average slope, implying that there is on the average a small amount of non-BVOC-SOA linked to the slope of $\Delta OA/\Delta SO_4$. The implication is that there may be a small amount of OA species, such as primary or fossil carbon or BVOC-SOA not dependent on SO_4 concentrations, that are correlated with OA concentrations in about the same way and at the same level across all monitoring sites and for all 15 years. As discussed above, because IMPROVE samples are collected over a 24-h period, it is possible that some collected BVOC-SOA is associated with nighttime NO_3 radical oxidation of monoterpenes.

The same analysis was carried out using the trend in $SO_4 + NO_3$ over time instead of just SO_4. The analysis yielded nearly an identical slope (0.26) and intercept (-0.14) but with a slightly degraded $R^2 = 0.59$.

If the data points in Figure 11 represent the yearly decrease in BVOC-SOA resulting from an incremental decrease in SO_4, it is possible to predict the total decrease in BVOC-SOA over the 2001–2015 time frame. Figure 12 shows a map of the estimated decrease in BVOC-SOA in terms of $\mu g/m^3/15$ yr. Triangles in green are significant at the 5% level. The median and mean BVOC-SOA reductions are 0.92 $\mu g/m^3$ and 0.95 $\mu g/m^3$, respectively, with a standard deviation of 0.56 $\mu g/m^3$. Sites in the mideastern United States show reductions of around 2.0 $\mu g/m^3$.

As shown in Figure 8, it is evident that the reduction in BVOC-SOA for a per unit change in SO_4 is quite uniform across the eastern United States, while Figure 12 shows that the reduction in BVOC-SOA per increment in time is greatest in the Southeast, where both SO_4 concentrations and BVOC emissions are highest.

7. Summary

Between 2001 and 2015, the downward trends in summer ASO_4 and OA on a percent change basis were quite uniform across much of the eastern United States. In the mid-Appalachian mountains (which includes the Great Smoky Mountains), the Northeast, and the eastern coastal regions, the decrease in sulfate mass concentration was 80% or greater, and at some sites the decrease approached 90%, while the commensurate change in OA was on the order of 60%. This corresponds to over a 6.0 $\mu g/m^3$ decrease in ASO_4 in the mid-Appalachian mountains and a 3.0 $\mu g/m^3$ decrease in the Northeast. In those same regions, OA decreased on the order of 2.0 $\mu g/m^3$ and 1.0 $\mu g/m^3$, respectively. In other areas of the eastern United States, the percent decrease in sulfates was on the order of 70% or greater, while OA decreased by about 30–40%.

The relative decreases in ASO_4 and OA are about the same over most of the eastern United States, even though the concentrations varied dramatically from one region to another, suggesting an underlying causal relationship between ASO_4 and OA concentrations.

Carbon 14 measurements in conjunction with hybrid receptor modeling show that the fraction of OA that is modern is high year-round and as high as 80% in summer months. Moreover, modern carbon emissions are reported to have not changed or even increased over recent time periods.

Average SO_4 and OA values were calculated for the August–October time period on a yearly basis (2001–2015) for data collected at each of the monitoring sites east of longitude $-100°$. A Thiel regression was performed on these averages with OA and SO_4 as the dependent and independent variables, respectively. The regression coefficient represents the average OA/SO_4 ratio for each site, while the intercept is an indication of background OA that is not dependent on the variability of SO_4. The intercept term is quite stable across all monitoring sites east of longitude $-100.0°$ at 1.68 ± 0.40 $\mu g/m^3$, while the average slope is 0.29 ± 0.14.

Interpreting the intercept term as background OA implies that BVOC-SOA made up 35% and 27% of average total OA in 2001 and 2015, respectively. The slope implies that on the average for every unit change in SO_4 there was a 0.29-unit change in BVOC-SOA, in spite of nearly constant BVOC emissions.

The above discussion is based on average year by year ratios of OA to SO_4, independent of whether adjacent years have higher or lower OA and SO_4 concentrations. A temporally averaged $\Delta OA/\Delta SO_4$ can be calculated by taking the ratio of the temporal trends in these two species. A Theil regression of the scatterplot of the OA and SO_4 trends yields a statistically significant, at a 5% level, intercept and slope of -0.016 ± 0.007 μg/m^3/yr and 0.27 ± 0.034, respectively. The interpretation of the intercept term in this case is that there is a small temporal trend in OA that is not linked to SO_4 of 0.016 ± 0.007 μg/m^3/yr. This corresponds to a decrease in OA over the 2001–2015 time frame of 0.24 μg/m^3 that is not linked to a decrease in SO_4. The $\Delta OA/\Delta SO_4$ relationship implies that the change in BVOC-SOA derived from a change in SO_4 levels on the average is 0.27. For every unit change in SO_4, there is a corresponding 0.27-unit change in BVOC-SOA, independent of SO_4 and OA concentrations. In the mideastern United States, this corresponds to a reduction in BVOC-SOA of about 2.0 μg/m^3. This $\Delta BVOC\text{-}SOA/\Delta SO_4$ should be contrasted with the average ratios of $\Delta IEPOX\text{-}SOA/\Delta SO_4$ of 0.64 and 0.78 reported during the SOAS and SEAC^{4}RS field campaigns, respectively (Marais et al., 2016), and to the $\Delta BVOC\text{-}SOA/\Delta SO_4$ of 0.24, 0.42, and ≈0.2 reported for the southeastern United States by Marais et al. (2017), Xu et al. (2015), and Blanchard et al. (2016), respectively.

The statistical and consistent relationships between declining ambient SO_4 and OA concentrations in nonurban locations in the eastern United States over 15 years (2001–2015) are consistent with the notion that BVOC-SOA formation is mediated by the presence of SO_4 aerosol. If the relationship between SO_4 and BVOC-SOA is causal, on the average a 1 μg/m^3 reduction in SO_4 has brought about a 0.27–0.29 μg/m^3 reduction in OA. It is anticipated that further reduction in SO_2 emissions will result in additional concurrent decreases in ambient SO_4 and BVOC-SOA concentrations. Therefore, health and environmental benefits of reduced particulate concentrations will be enhanced beyond those anticipated from just ambient SO_4 reduction.

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