Atmos. Chem. Phys., 12, 10353–10365, 2012
www.atmos-chem-phys.net/12/10353/2012/
doi:10.5194/acp-12-10353-2012

Atmospheric Chemistry and Physics

Particulate sulfate ion concentration and SO_2 emission trends in the United States from the early 1990s through 2010

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Received: 11 July 2012 – Published in Atmos. Chem. Phys. Discuss.: 3 August 2012
Revised: 12 October 2012 – Accepted: 23 October 2012 – Published: 7 November 2012

Abstract. We examined particulate sulfate ion concentrations across the United States from the early 1990s through 2010 using remote/rural data from the Interagency Monitoring of Protected Visual Environments (IMPROVE) network and from early 2000 through 2010 using data from the Environmental Protection Agency's (EPA) urban Chemical Speciation Network (CSN). We also examined measured sulfur dioxide (SO_2) emissions from power plants from 1995 through 2010 from the EPA's Acid Rain Program. The 1992–2010 annual mean sulfate concentrations at long-term rural sites in the United States have decreased significantly and fairly consistently across the United States at a rate of $-2.7\,\%\,yr^{-1}$ ($p < 0.01$). The short-term (2001–2010) annual mean trend at rural sites was $-4.6\,\%\,yr^{-1}$ ($p < 0.01$) and at urban sites (2002–2010) was $-6.2\,\%\,yr^{-1}$ ($p < 0.01$). Annual total SO_2 emissions from power plants across the United States have decreased at a similar rate as sulfate concentrations from 2001 to 2010 ($-6.2\,\%\,yr^{-1}$, $p < 0.01$), suggesting a linear relationship between SO_2 emissions and average sulfate concentrations. This linearity was strongest in the eastern United States and weakest in the West where power plant SO_2 emissions were lowest and sulfate concentrations were more influenced by non-power-plant and perhaps international SO_2 emissions. In addition, annual mean, short-term sulfate concentrations decreased more rapidly in the East relative to the West due to differences in seasonal trends at certain regions in the West. Specifically, increased wintertime concentrations in the central and northern Great Plains and increased springtime concentrations in the western United States were observed. These seasonal and regional positive trends could not be explained by changes in known local and regional SO_2 emissions, suggesting other contributing influences. This work implies that on an annual mean basis across the United States, air quality mitigation strategies have been successful in reducing the particulate loading of sulfate in the atmosphere; however, for certain seasons and regions, especially in the West, current mitigation strategies appear insufficient.

1 Introduction

Sulfate is an important secondary aerosol formed from photochemical reactions of sulfur dioxide (SO_2) emissions in the atmosphere. In the United States it is a major contributor to the $PM_{2.5}$ mass, accounting for 30–60 % of the fine monthly mean mass in the East (Hand et al., 2012a). Summertime peaks in sulfate concentrations are common for most areas of the United States due to available solar insolation, chemical reactions facilitated in high relative humidity environments, and stagnation events (e.g., Hidy et al., 1978; Tai et al., 2010); however, the maximum in the northwestern United States shifted to spring since 2000 (Hand et al., 2012a). Similar sulfate concentrations in urban and rural regions suggested that influences of sulfate are regional in extent due to formation processes, lifetimes, meteorological conditions, and transport (Hand et al., 2012a). The impacts of sulfate on the atmosphere and environment are well known. It contributes to visibility degradation (e.g., Malm, 1992; Hand et al., 2011) and acidification through wet deposition to aquatic

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and terrestrial ecosystems (e.g., Lehmann and Gay, 2011), is active as cloud-condensation nuclei and in cloud microphysical processes (e.g., Petters et al., 2009), interacts directly with incoming shortwave radiation and thereby contributes to global cooling (e.g., Kiehl and Briegleb, 1993), and is potentially harmful to human health (e.g., Rohr and Wyzga, 2012).

Regulatory and legislative mandates, such as Title IV of the 1990 Clean Air Act Amendment, were established to reduce SO_2 emissions in the United States. These mandates have been successful and, from 1990 to 2010, total annual SO_2 emissions in the United States have decreased 60 % (U.S. EPA, 2011a). Reductions in SO_2 emissions should lower particulate sulfate concentrations in the atmosphere and precipitation (Lehmann and Gay, 2011). Reductions could also significantly lower $PM_{2.5}$ mass concentrations in areas where sulfate is a dominant contributor, assisting goals in meeting the $PM_{2.5}$ and PM_{10} particulate matter National Ambient Air Quality Standards (NAAQS). The effects of emission reductions on visibility degradation are addressed by the Regional Haze Rule (RHR), promulgated by the EPA in 1999 (U.S. EPA, 1999). Its goals include reducing the worst haze days in class I areas to natural levels by 2064. Sulfate contributes $\sim$10–85 % of haze (Hand et al., 2011); therefore, reductions in sulfate concentrations are important for achieving RHR goals. A recent examination of progress toward RHR goals was reported in Hand et al. (2011).

Trend analyses are needed to track progress toward regulatory goals and to evaluate success of emission reduction programs by understanding how ambient concentrations respond to changes in emissions. Trend analyses require stable, long-term data sets obtained under consistent monitoring and analytical methods. The Interagency Monitoring of Protected Visual Environments (IMPROVE) program has monitored aerosol concentrations at remote and rural sites in the United States since 1988; one of its main purposes is to support trends analyses. Trends in aerosol species such as sulfate and nitrate ions, carbonaceous aerosols, and gravimetric fine mass using IMPROVE data suggest that across the rural United States the annual mean concentrations of major aerosol species generally decreased through 2008 (e.g., Hand et al., 2011; Murphy et al., 2011). Earlier work by Malm et al. (2002) also demonstrated that IMPROVE and CASTNet (Clean Air Status and Trends Network) sulfate concentrations decreased at most sites in the United States over a period of 10 yr (1988–1999), with the highest rates of decrease north of the Ohio River valley. Sulfate concentrations at Whiteface Mountain, New York, reportedly decreased by 59 % from 1979 through 2002 (Husain et al., 2004). Blanchard et al. (2012) reports decreased annual mean sulfate concentrations ranging from 3.7 ± 1.1 to $6.2 \pm 1.1\ \%\ yr^{-1}$ from 1999 to 2010 at sites in the southeastern United States as part of the SEARCH (Southeastern Aerosol Research and Characterization) program. Malm et al. (2002) also examined SO_2 emission data and found that although it varied by region, sulfate concentrations and SO_2 emissions tracked fairly closely. Husain et al. (1998) also reported a linear relationship between decreasing sulfate concentrations and SO_2 emissions (Husain et al., 1998). Reductions in sulfate concentrations in the atmosphere have decreased its concentration in precipitation as evidenced by Lehmann and Gay (2011). They performed trend analyses on precipitation data obtained from the National Atmospheric Deposition Program and demonstrated statistically significant decreases in sulfate concentrations in precipitation almost everywhere in the United States from 1985 through 2009. Although annual mean concentrations of major aerosol species generally have decreased, this may not be the case for specific seasons or regions. For example, wintertime particulate sulfate and nitrate ion concentrations have increased across the US northern and central Great Plains from 2000 through 2010 (Hand et al., 2012b).

Changes in sulfate concentrations over time are influenced not only by changes in local and regional emissions but also by changes in meteorology. Modeling studies to investigate the effects of future emission trends and meteorology on pollutant concentrations have been performed by several researchers. A study by Tai et al. (2010) showed that daily variations in meteorology can explain up to 50 % of $PM_{2.5}$ variability due to temperature, relative humidity, precipitation, and circulation. Sulfate was positively correlated with temperature and relative humidity and negatively correlated with precipitation, suggesting that changes in these meteorological variables can impact sulfate levels in the atmosphere. Further analysis by Tai et al. (2012) suggested these relationships were driven by synoptic transport in most locations.

Sulfate concentrations and trends in the United States are also influenced by the contributions of long-range transport of sulfate or its precursors. Several observational and modeling studies have pointed to the impacts of transpacific transport events from Asia in the spring that influence dust and sulfate concentrations at sites across the United States (e.g., Van Curen and Cahill, 2002; Park et al., 2004; Jaffe et al., 2005; Heald et al., 2006; Chin et al., 2007). Increased December monthly, regional mean sulfate concentrations at IMPROVE sites in the US Great Plains from 2000 through 2010 suggested possible long-range contributions from Canada at some sites (Hand et al., 2012b). Shipping emissions off the coast, such as in California, can impact sulfate concentrations across the western United States (Xu et al., 2006), and transport patterns off the West Coast could be responsible for transporting Asian pollution as well as local emissions (e.g., Peltier et al., 2008; Lin et al., 2012). Regions in the southern United States, such as in southwest Texas, experience contributions from sources in Mexico that increase sulfate levels in otherwise remote locations (Gebhart et al., 2006). Decreases in local emissions in the United States could lead to greater relative contributions from long-range sources, depending on emission trends of other countries, and thereby reduce progress towards national air quality goals. Untangling the influences of meteorology, long-range transport, and local emissions on sulfate trends requires a variety of data sets and tools, such as long-term observations, back trajectory analyses, and model simulations with changing emissions.

This paper builds on the previous work of Malm et al. (2002) by extending sulfate monthly, seasonal, and annual mean trend analyses through 2010 and by including both rural and urban sites across the United States. Trends in sulfate concentrations and SO_2 emissions from power plants were evaluated to investigate their relationships and potential effectiveness of emission control strategies. We also demonstrate that trends in seasonal mean concentrations can exhibit very different behaviors compared to trends in annual mean concentrations, highlighting the importance of understanding the impacts of meteorology and long-range transport to the interpretation of trends.

2 Data and methods

The IMPROVE program is a cooperative effort designed to monitor aerosol and visibility conditions in mandatory class I areas (Malm et al., 1994). The program began operating in remote areas in 1987 with approximately 30 sites and currently operates 170 remote and some urban sites across the United States. The network collects 24-h samples every third day from midnight to midnight local time and concentrations are reported at local conditions. Additional details regarding IMPROVE sampling are provided by Malm et al. (1994) and Hand et al. (2011). All IMPROVE data, metadata, detailed descriptions of the network operations, data analysis, and visualization results are available for download from http://vista.cira.colostate.edu/IMPROVE/.

We used $PM_{2.5}$ sulfate ion data collected on nylon filters, analyzed by ion chromatography, and artifact-corrected. Precisions for sulfate ion concentrations were 4 % as reported by Hyslop and White (2008) for collocated data. White et al. (2005) estimated sulfate trend uncertainty due to measurement error as 1 % yr^{-1} over a 5-yr period. We chose to use sulfate ion data, rather than sulfur data as used by Malm et al. (2002), due to biases in sulfur concentrations derived from X-ray fluorescence as described by White (2009) and Hyslop et al. (2012). However, in the late 1990s inadvertent manufacturer changes to the nylon filter resulted in clogged filters during periods with high mass concentrations (Eldred, 2001). Loss of filters due to clogging primarily affected sites in the East, where 30 % or more of the samples were invalidated during a given season, although some sites in the West were also affected. The issue was resolved by 2000. We determined that the missing samples resulted in biased monthly and annual mean sulfate concentrations because the clogging preferentially occurred during high mass events. To account for this bias, we replaced missing sulfate data before 2000 with sulfur concentrations that were scaled to sulfate mass.

The Speciated Trends Network (STN) and other urban monitoring sites are collectively known as the EPA's Chemical Speciation Network (CSN) and were deployed in the fall of 2000 (U.S. EPA, 2004), primarily in urban/suburban settings. The objectives of the CSN include tracking progress of emission reduction strategies through the characterization of trends. The CSN operates approximately 50 trend sites, with another ~150 sites operated by state, local, and tribal agencies. The CSN collects 24-h samples every third or sixth day, on the same sampling schedule as IMPROVE. Data are reported at local conditions. We used $PM_{2.5}$ sulfate ion concentrations collected on nylon filters and analyzed by ion chromatography. The methods for collecting and analyzing sulfate ion concentrations are similar for the CSN and IMPROVE network, with the exception that CSN does not correct for artifacts and cold-ships filters. Comparisons of data from collocated sites from 2005 to 2008 suggested close agreement between CSN and IMPROVE sulfate ion concentrations with a relative bias of 4.2 % (CSN higher) and a correlation of 0.99, and differences between urban and rural sites were typically low (Hand et al., 2012a). CSN data can be downloaded from http://views.cira.colostate.edu/fed/ or http://www.epa.gov/ttn/airs/airsaqs/.

Annual SO_2 emission data by source category for the entire United States were obtained from the EPA's National Emissions Inventory (NEI) database (U.S. EPA, 2011a). However, examining SO_2 emissions with finer spatial and temporal resolution required obtaining SO_2 emission data from the EPA's Clean Air Markets Division, Acid Rain Program (U.S. EPA, 2011b). As part of the Acid Rain Program, the EPA established requirements for continuous emissions monitoring (CEM) of SO_2 using SO_2 pollutant concentration monitors on regulated facilities. Power plant emissions are the dominant source of total SO_2 emissions; in 2010 electric utilities contributed ~65 % of NEI total SO_2 emissions. SO_2 emissions reported for each facility within a given state were aggregated to state-level monthly and annual total emission rates from 1995 to 2010. SO_2 emissions discussed in this paper refer to CEM SO_2 emissions.

Linear Theil regression (Theil, 1950) was performed on both the concentration and emission data. Fifty percent of the concentration data for given month and year had to be valid for a site to be considered "complete", and 70 % of "complete" years were necessary for a trend calculation over a given time period. We defined "trend" (% yr^{-1}) as the slope derived from the Theil regression divided by the median concentration value over the time period of the trend, multiplied by 100 %. Kendall tau statistics were used to determine the significance; a statistically significant trend was assumed at the 90th percentile significance level ($p < 0.10$), meaning that there was a 90 % chance that the slope was not due to random chance. Trends were computed for monthly, seasonal, and annual means for sulfate concentrations and monthly and annual total CEM SO_2 emissions. IMPROVE long-term trends were computed for 1989–2010 for individual site trends and 1992–2010 for regional trends. IMPROVE and CSN short-term trends for individual sites were computed for 2000–2010, while regional trends were computed for 2001–2010 and 2002–2010 for IMPROVE and CSN trends, respectively (see Sect. 3.4).

3 Results

3.1 Long-term trends in sulfate ion concentrations (1989–2010)

Long-term (1989–2010) annual mean sulfate trends at IMPROVE sites are presented in Fig. 1. Isopleths were produced by interpolating trend values at individual sites using a Kriging algorithm. Isopleths are meant to aid the visualization of spatial patterns and not for estimating trend values between monitoring sites. Sites with statistically significant trends ($p < 0.10$) were represented by filled triangles that point upward or downward for increased or decreased concentrations, respectively. Sites with statistically insignificant trends were represented by unfilled triangles. From 1989 to 2010 annual mean sulfate concentrations decreased at all but one of the 52 IMPROVE sites with 15 or more years of data; 49 sites corresponded to statistically significant trends (see Fig. 1). The largest decreases occurred in the East where sulfate generally decreased at a rate higher than $-2\,\%\,yr^{-1}$. In contrast, sulfate concentrations in the West decreased at a somewhat lower rate, especially closer to the coast. Long-term significant trends ranged from $-4.8\,\%\,yr^{-1}$ ($p < 0.01$) in Snoqualmie Pass, Washington (SNPA), to $-1.0\,\%\,yr^{-1}$ ($p = 0.01$) in Jarbidge, Nevada (JARB). Long-term trends in annual mean concentrations for all sites are included in the Supplementary material. Notice from Fig. 1 that most of the earliest IMPROVE sites are located in the southwestern, western, and eastern United States, with a lack of sites in the central United States, Great Plains, and Great Lakes regions.

3.2 Short-term trends in sulfate ion concentrations (2000–2010)

In 2000 the IMPROVE program expanded to 159 sites, filling gaps in the spatial distribution in the above-mentioned regions. The addition of these IMPROVE sites, as well as CSN sites that began operation in 2000, allowed for trends to be computed with finer spatial resolution but over a shorter time period (2000–2010). As Hand et al. (2011, 2012a) demonstrated, urban sulfate concentrations were only slightly higher than neighboring rural sites; however, generally good agreement suggested that urban and rural sites were influenced by similar regional sources. Since we focused only on the changes in sulfate concentrations, somewhat higher urban sulfate concentrations were of little consequence.

Annual mean sulfate concentrations from 2000–2002 and 2008–2010 are shown in Fig. 2a and b, respectively, for both

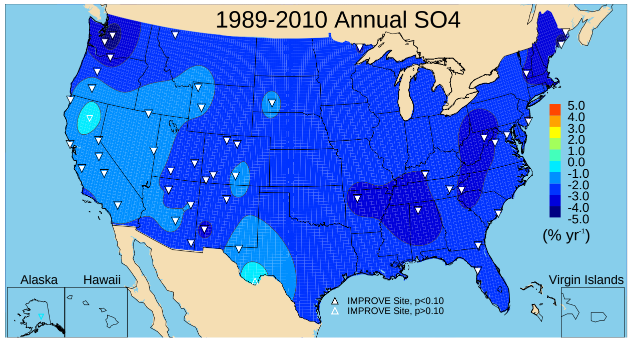

Fig. 1. IMPROVE 1989–2010 trends (% yr^{-1}) in annual mean particulate sulfate ion concentrations. Triangles correspond to IMPROVE sites; upward pointing triangles correspond to increased concentrations and vice versa. Trends with significance levels (p) less than 0.10 are considered significant.

IMPROVE and CSN data. These isopleth maps were generated by interpolating data from both networks. Sulfate concentrations were higher in the East where emissions were also highest (see Sect. 3.3). Comparisons of the two time periods demonstrated considerable reductions in concentrations at both rural and urban sites from the early to late 2000s.

Trend results demonstrating these reductions in short-term (2000–2010) annual mean sulfate concentrations are presented in Fig. 3. A total of 281 sites are shown (154 and 127 IMPROVE and CSN sites, respectively, with at least eight years of complete data). Most of the sites had statistically significant trends (80 % and 94 % of IMPROVE and CSN sites, respectively). Annual mean sulfate concentrations significantly increased at only three IMPROVE sites; the largest occurred at Hawaii Volcanoes, Hawaii (HAVO, $9.4\,\%\,yr^{-1}$, $p < 0.01$), Denali, Alaska (DENA, $6.0\,\%\,yr^{-1}$, $p = 0.04$), and Fort Peck, Montana (FOPE, $2.3\,\%\,yr^{-1}$, $p = 0.06$). The largest decrease in rural sulfate concentrations occurred in Martha's Vineyard, Massachusetts (MAVI, $-11.4\,\%\,yr^{-1}$, $p < 0.01$). The range in trends at the CSN sites were $-10.5\,\%\,yr^{-1}$ in Scranton, Pennsylvania (#420692006, $p < 0.01$), to $-1.3\,\%\,yr^{-1}$ in Portola, California (#060631009, $p = 0.012$). Short-term annual mean trends for IMPROVE and CSN sites are reported in the Supplement.

Not only have annual mean sulfate concentrations decreased nearly everywhere in the United States since 2000, but urban and rural concentrations decreased at similar rates, as indicated by the consistency in isopleths in Fig. 3 (this point will be discussed in more detail in Sect. 3.4). Concentrations in the eastern United States decreased more rapidly than in the West, where sulfate ion concentrations were 5–10 times lower (Fig. 2). To investigate these differences in more detail, we analyzed short-term seasonal mean trends to examine seasonal influence on the patterns seen in Fig. 3.

The spatial patterns in trends differed depending on the season. In winter (DJF) (see Fig. 4a), the sulfate trends were

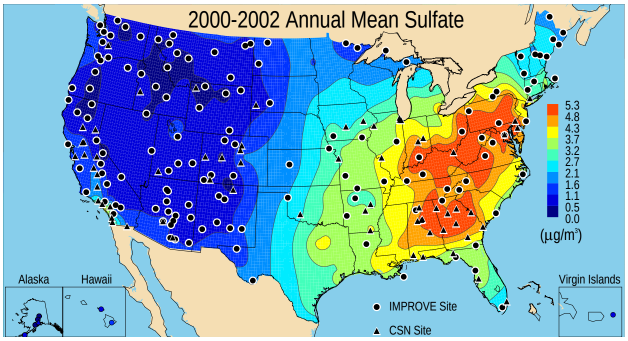

Fig. 2a. IMPROVE and CSN 2000–2002 annual mean particulate sulfate ion concentrations. Circles correspond to IMPROVE sites and triangles correspond to CSN sites.

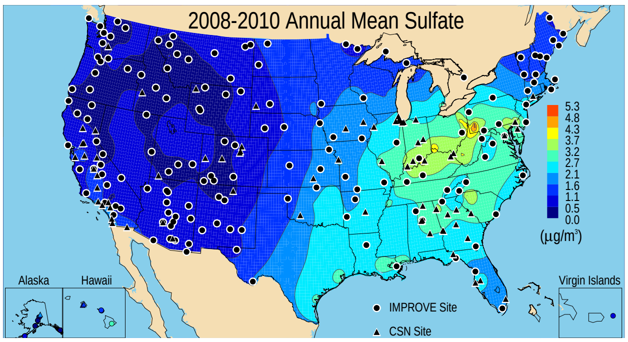

Fig. 2b. IMPROVE and CSN 2008–2010 annual mean particulate sulfate ion concentrations. Circles correspond to IMPROVE sites and triangles correspond to CSN sites.

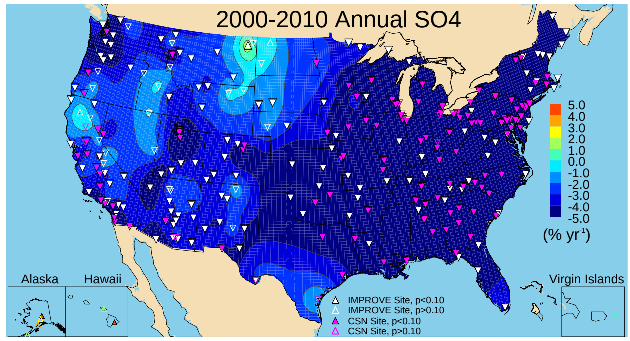

Fig. 3. IMPROVE and CSN 2000–2010 trends (% yr^{-1}) in annual mean particulate sulfate ion concentrations. White and magenta triangles correspond to IMPROVE and CSN sites, respectively; upward pointing triangles correspond to increased concentrations and vice versa. Trends with significance levels (p) less than 0.10 are considered significant.

flat to positive (see Fig. 4a) in the northern Great Plains and Great Lakes regions, relative to other regions of the country, although most trends were insignificant. Positive winter trends in the Great Lake region were influenced by many CSN sites with increased January monthly mean concentrations, such as at Rochester, Minnesota (#271095008, 7.1 % yr^{-1}, $p = 0.06$), and Youngstown, Ohio (#390990014, 4.6 % yr^{-1}, $p = 0.03$). These increased concentrations occurred during what was historically associated with the season of lowest sulfate concentrations during the year (Hand et al., 2012a).

In the northern Great Plains, winter trends were influenced by increased December monthly mean concentrations at a swath of sites extending southward from Montana into Oklahoma and parts of Texas. Hand et al. (2012b) reported on these trends only for IMPROVE sites, but sulfate concentrations at the few CSN sites within this area also increased. At the IMPROVE site at Fort Peck (FOPE), Montana, December monthly mean sulfate concentrations increased at the steep rate of 17.5 % yr^{-1} ($p = 0.06$), beginning sharply in 2006. Sulfate concentrations increased steadily at 5.4 % yr^{-1} ($p = 0.03$) at the CSN Omaha, Nebraska, site (#310550019). A less extensive spatial pattern occurred in February and was absent in January. Intriguingly, sites within this swath were also associated with increased nitrate concentrations (Hand et al., 2012b). This area is associated with relatively low sulfate concentrations that historically peaked in spring and summer (Hand et al, 2012a); in 2010 the maximum sulfate concentrations occurred in winter at most of these sites. In other regions of the country the winter seasonal mean concentrations significantly decreased at sites in the southeastern, northeastern, and southwestern United States.

Springtime (MAM) trends in the West were noteworthy and contributed to the differences seen between the East and the West in the annual mean trends (Fig. 4b). Most of the sites in the West were associated with concentrations that decreased at a much lower rate, or even increased, relative to sites in the East. Positive trends were insignificant, most likely due a drop in concentrations in 2009 and 2010 that was common at many sites (see Sect. 3.4). This drop in concentrations had a strong influence on the trends, and in fact trends from 2000 to only 2008 were positive and statistically significant at many sites. Increases in spring concentrations may have contributed to the shift in the maximum monthly seasonal concentrations from summer to spring at many north- and central-western sites since 2000 (Hand et al., 2012a).

In contrast to the increased sulfate concentrations in different regions in spring and winter, widespread decreases in summer (JJA) and fall (SON) concentrations occurred across the United States, although to a somewhat lower degree in the West compared to the East (Fig. 4c and d, respectively). However, in the fall the regions with less-decreasing concentrations stretched farther east compared to summer. Sites in Hawaii, Alaska, and the Virgin Islands demonstrated interesting trends for all seasonal means. Recall that the largest increase in short-term annual mean sulfate occurred in Denali, Alaska, and Hawaii Volcanoes, Hawaii (Fig. 3). In fact, the annual mean sulfate concentration and nearly every seasonal mean sulfate concentration increased at Denali since

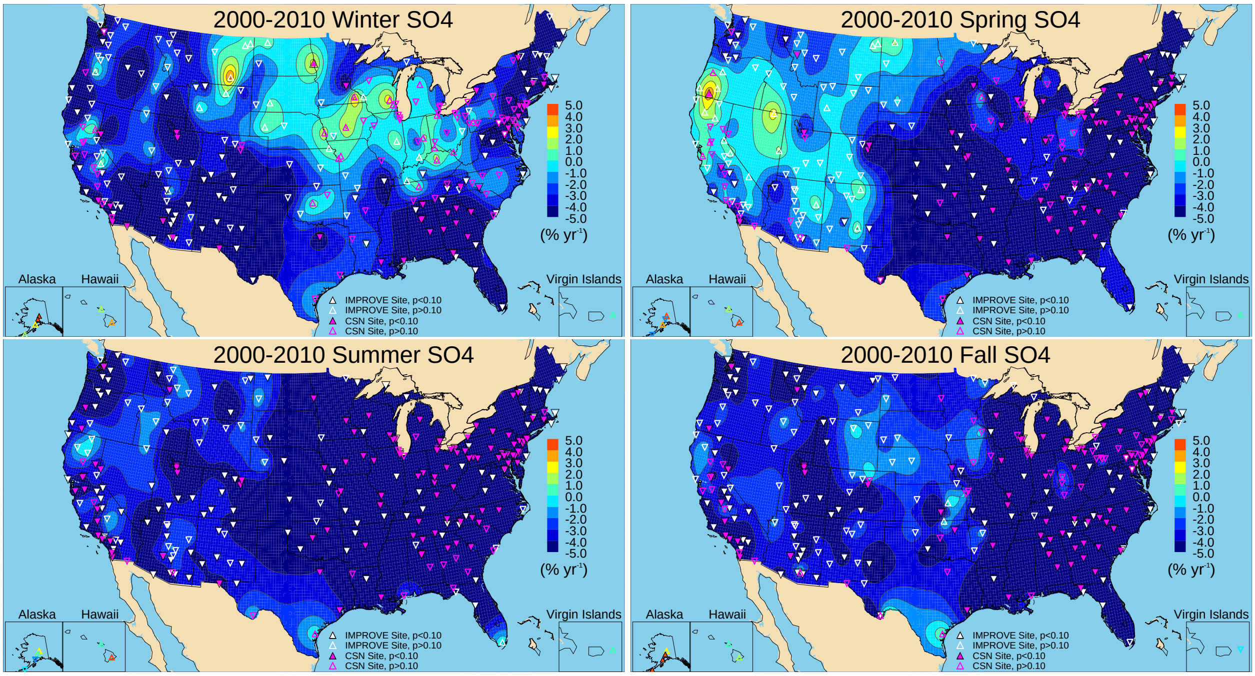

Fig. 4. IMPROVE and CSN 2000–2010 trends (% yr^{-1}) in seasonal mean particulate sulfate ion concentrations for **(a)** winter (DJF), **(b)** spring (MAM), **(c)** summer (JJA) and **(d)** fall (SON). White and magenta triangles correspond to IMPROVE and CSN sites, respectively; upward pointing triangles correspond to increased concentrations and vice versa. Trends with significance levels (p) less than 0.10 are considered significant.

2000. Hawaii Volcanoes also experienced increased concentrations for all seasonal means. Interestingly, concentrations dropped in 2010 for both sites, similar to other sites in the contiguous West discussed earlier.

3.3 Trends in SO_2 emissions

The 2000–2010 median total annual CEM SO_2 emissions for each of the contiguous United States are shown in Fig. 5a. Emissions are plotted on a logarithmic scale in units of million t yr^{-1}. Emissions in the eastern half of the country were orders of magnitude higher than emissions in the West, with Texas and states in the Southeast and around the Ohio River valley having the highest emissions ($> 5 \times 10^6$ t yr^{-1}). The 2000–2010 median total annual SO_2 emissions for the entire United States was 10.2×10^6 t yr^{-1}. Trends in these emissions from 2000 to 2010 are shown in Fig. 5b. The states are colored according to the magnitude of the trend and outlined in magenta if the trend was statistically significant ($p < 0.10$). The scale matches that of sulfate concentration trends shown in the previous section. Annual total CEM SO_2 emissions decreased significantly (rates greater than -5 % yr^{-1}) at most states in the northeastern, southeastern, and southwestern United States. Over half of the states were associated with decreased emissions; of the 32 states with significant trends, only one was associated with increased emissions (Rhode Island, 9.0 % yr^{-1}, $p < 0.01$); however, the median emissions in Rhode Island were extremely low (1.23 t yr^{-1}). Less negative trends were generally statistically insignificant, such as for states in the northern and central Great Plains and western states such as California, Oregon, and Idaho. Increased emissions in Idaho are noticeable in Fig. 4b and only just missed the criterion for significance (4.1 % yr^{-1}, $p = 0.102$); however, the magnitude of power plant SO_2 emissions in Idaho was also extremely low (3.04 t yr^{-1}). The largest decrease in SO_2 emissions occurred in Washington state (-68.6 % yr^{-1}, $p = 0.01$) due to a precipitous drop in emissions around 2002 when the Centralia Big Hanaford power plant transitioned some of its capacity to natural gas-fired units and SO_2 scrubbers were also installed (2000–2002). The 2000–2010 trend in the overall annual US power plant SO_2 emissions was -4.9 % yr^{-1} ($p < 0.01$) (computed by aggregating all of the state CEM data and then computing a trend). Incidentally, the trend in NEI total annual SO_2 emissions was -5.0 % yr^{-1} ($p < 0.01$) over the same time period.

3.4 Regional CEM SO_2 emissions and sulfate concentration trends

Changes in sulfate concentrations and SO_2 emissions through the late 1990s and early 2000s reported by Husain et al. (1998, 2004) and Malm et al. (2002) for certain regions of the United States implied a nearly linear relationship between local and regional contributions of SO_2 emissions and sulfate

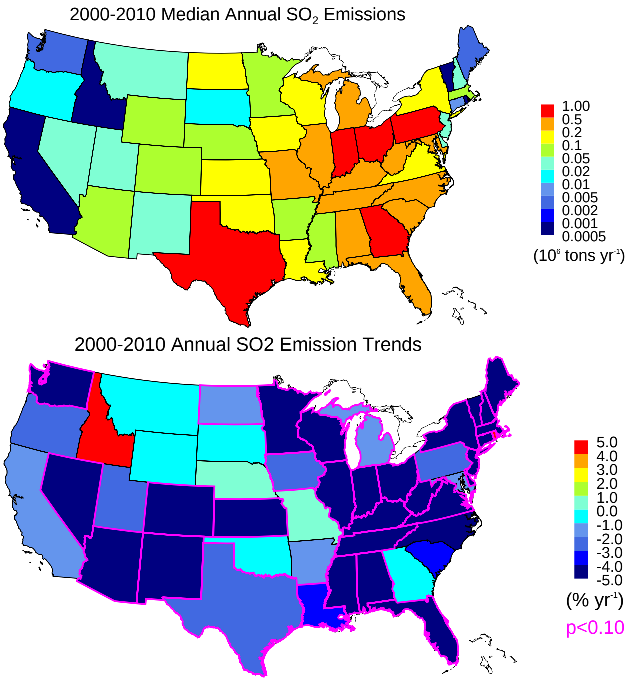

Fig. 5. (a) 2000–2010 median annual power plant SO_2 emissions (million t yr^{-1}) **(b)** 2000–2010 trends (% yr^{-1}) in annual total power plant SO_2 emissions. States with significant trends ($p < 0.10$) are outlined in magenta.

concentrations. We examined whether this relationship continued through 2010. We computed regional CEM SO_2 emissions and sulfate concentrations by aggregating from the state to regional level. Regional groupings were qualitative and based on the patterns observed in annual mean sulfate concentration and annual SO_2 emission trends seen in Fig. 3 and Fig. 5b, respectively. Regional-level trends allowed for a higher number of observations and summarized the observed state and site patterns. We did not account for meteorological influences, such as variability in air mass transport, chemical transformations, or deposition, as these effects were minimized by aggregating over large regions. Seven regions were defined: Southeast, Northeast, West, Southwest, Midsouth, Great Plains, and the contiguous United States. Similar regional groupings were defined by Malm et al. (2002) but for fewer regions due to lower spatial resolution of sites available. Regional annual and monthly mean sulfate concentrations were computed using "complete" sites from each region and trends were calculated on the regional mean. The same regions were used for IMPROVE and CSN sites, but trends were computed separately for each network. Regional monthly and annual SO_2 emissions were computed by summing the emissions from the states within a region for a given time period.

Regional trends can be sensitive to the geographical location and number of sites available for a given year (Schichtel et al., 2011). For example, the regional mean corresponding to initial years of network operation can be biased if the number of sites is too few to obtain a representative regional average. We observed this behavior with the regional annual mean IMPROVE data in the early 1990s and in 2000 during network expansion, and we also observed this behavior with CSN data in 2000 and 2001 during the initial years of that network. To avoid these biases, we filtered the regional data to include only data from years with numbers of sites that were within one standard deviation of the average number of sites per year for the entire time period. As a result, the length of the regional trends narrowed relative to the individual site trends shown in Figs. 1 and 3. Long-term (LT) regional IMPROVE trends were computed for 1992–2010 (19 yr); short-term (ST) regional IMPROVE trends were computed for 2001–2010 (10 yr), and CSN trends were computed for 2002–2010 (9 yr). Table 1 lists the number of IMPROVE and CSN sites used in the annual, regional analyses. The number of CSN sites used in the East was greater than IMPROVE sites, and vice versa in the West.

Timelines of annual mean sulfate concentrations and annual total CEM SO_2 emissions for the contiguous United States since the early 1990s are shown in Fig. 6. IMPROVE and CSN sulfate concentrations are shown on left axes and SO_2 emissions refer to the right axis. CSN and IMPROVE data are plotted with different scales so that the tracking of the timelines could be more clearly shown. The difference in IMPROVE and CSN data (signified by the shift in scales) should not be interpreted as urban excess, because the large-scale regional analysis includes sites beyond only nearby pairings of urban/rural sites. Also, recall from Fig. 2 that sulfate concentrations are highest in the East where the majority of CSN sites are located. LT IMPROVE data are shown in black, ST IMPROVE data are shown in green, and CSN data are shown in red. The LT and ST IMPROVE data are shown separately because the trends were computed with different numbers of available sites. The number of complete sites with valid data available for a given year is used as the plot symbol for each time series.

The US annual mean sulfate concentrations and SO_2 emissions have decreased steadily since the mid-1990s. LT IMPROVE sulfate concentrations decreased in 1992–1993, increased in 1997–1998, and increased again in 2005 and 2007 (along with ST IMPROVE and CSN data). Concentrations fell to their lowest values by 2010. In addition, the tracking of the LT IMPROVE, ST IMPROVE, and CSN data from 2000 was quite impressive. The temporal trends in SO_2 emissions were similar to sulfate concentrations. The annual mean sulfate LT IMPROVE trend was $-2.7\,\%\,yr^{-1}$ ($p < 0.01$). Since the early 2000s, ST IMPROVE sulfate decreased at a rate of $-4.6\,\%\,yr^{-1}$ ($p < 0.01$), slightly less than the CSN trend of $-6.2\,\%\,yr^{-1}$ ($p < 0.01$). CEM SO_2 emissions decreased by $-6.2\,\%\,yr^{-1}$ ($p < 0.01$) from 2001–2010 (see Table 1).

Annual mean regional data are shown in Fig. 7a–f and trends are listed in Table 1. The states included in each region are shaded gray on the map inset on each figure. Scales vary

Table 1. Trends in regional, annual mean IMPROVE and CSN particulate sulfate ion concentrations and annual total power plant (CEM) SO_2 emissions. The trend (% yr^{-1}) and significance (p) are on top and the number of sites and number of observations (in parentheses) are on the bottom for each region.

Region	LT IMPROVE (1992–2010)	ST IMPROVE (2001–2010)	CSN (2002–2010)	SO_2 Emission (2001–2010)
Northeast	−3.7 ($p<0.01$) 9 (166)	−6.4 ($p<0.01$) 33 (318)	−6.1 ($p<0.01$) 79 (656)	−6.6 ($p<0.01$)
Southeast	−3.1 ($p<0.01$) 6 (106)	−4.4 ($p=0.04$) 13 (126)	−6.6 ($p<0.01$) 34 (280)	−6.4 ($p<0.01$)
West	−2.0 ($p<0.01$) 16 (291)	−3.4 ($p<0.01$) 37 (362)	−5.0 ($p<0.01$) 20 (173)	−20.1 ($p<0.01$)
Southwest	−2.6 ($p<0.01$) 14 (260)	−3.1 ($p=0.03$) 33 (318)	−4.9 ($p<0.01$) 9 (75)	−8.5 ($p<0.01$)
Midsouth	−1.9 ($p<0.01$) 3 (56)	−5.3 ($p<0.01$) 13 (121)	−4.7 ($p<0.01$) 14 (118)	−2.6 ($p=0.02$)
Great Plains	−2.4 ($p<0.01$) 3 (56)	−1.3 ($p=0.13$) 21 (200)	−2.2 ($p=0.21$) 5 (40)	−1.3 ($p=0.03$)
United States	−2.7 ($p<0.01$) 53 (978)	−4.6 ($p<0.01$) 157 (1514)	−6.2 ($p<0.01$) 163 (1355)	−6.2 ($p<0.01$)

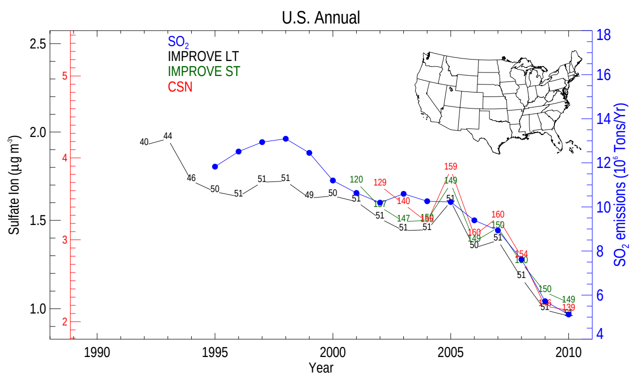

Fig. 6. United States annual mean particulate sulfate ion concentrations ($\mu g\,m^{-3}$) from long-term (LT) and short-term (ST) IMPROVE sites (left black axis) and CSN sites (left red axis), and power plant SO_2 emissions (million t yr^{-1}) (right blue axis). The number of complete sites with valid data available for a given year is used as the plot symbol for each time series.

for each figure. The highest annual total SO_2 emissions from power plants in the country were in the upper-right quadrant of the United States, referred to here as the Northeastern region, including the Ohio River valley and Boundary Waters regions and more "traditional" northeastern states. SO_2 emissions for this region were nearly double those in the southeastern United States due to relatively high emissions in the Ohio River valley region (see Fig. 5a); however, the 2000–2010 annual emissions decreased at similar rates in the Northeast (−6.6 % yr^{-1}) and Southeast (−6.4 % yr^{-1}) regions (all regional trends were statistically significant; significance levels are included in Table 1). SO_2 emissions in these regions tracked closely with sulfate concentrations. SO_2 emissions in the Midsouth region decreased at a lower rate (−2.6 % yr^{-1}) and did not track changes in sulfate concentrations as closely as the other eastern regions. This may be in part due to the geographic differences in the sites in the Midsouth region. Sulfate concentrations peaked in 2005 at all of the eastern regions and perhaps corresponded to a slight increase in SO_2 emissions during that year. SO_2 emissions and sulfate concentrations dropped in 2010, with the exception of sulfate concentrations in the Southeast region. Note that the temporal behavior of sulfate concentrations and SO_2 emissions for the contiguous United States (Fig. 6) were similar to those at the eastern regions (Fig. 7b, d, f), suggesting that that annual trends for the total United States were being driven by the emissions and concentrations in the eastern United States.

SO_2 emissions in the West region decreased at the highest rate of any region in the United States (−20.1 % yr^{-1}). Already decreasing SO_2 emissions dropped in 2002 due to the changes at the Centralia Big Hanaford power plant in Washington mentioned earlier and fell again in 2006 due to the closure of the Mohave power plant in Laughlin, Nevada. Emissions in the West after 2006 were the lowest in the country. Decreases in SO_2 emissions were flattest in the Great Plains region (−1.3 % yr^{-1}) compared to the Southwest region (−8.5 % yr^{-1}). In general, changes in sulfate concentrations at western regions did not track those of SO_2 emissions as closely or as strongly as was observed for eastern regions.

Recall from Fig. 4b and Sect. 3.2 that since 2000 sulfate concentrations increased in the western United States during spring months, especially in May. A timeline of May monthly mean sulfate concentrations and SO_2 emissions for the West region is presented in Fig. 8. Notice that compared to the annual mean concentrations for the West region

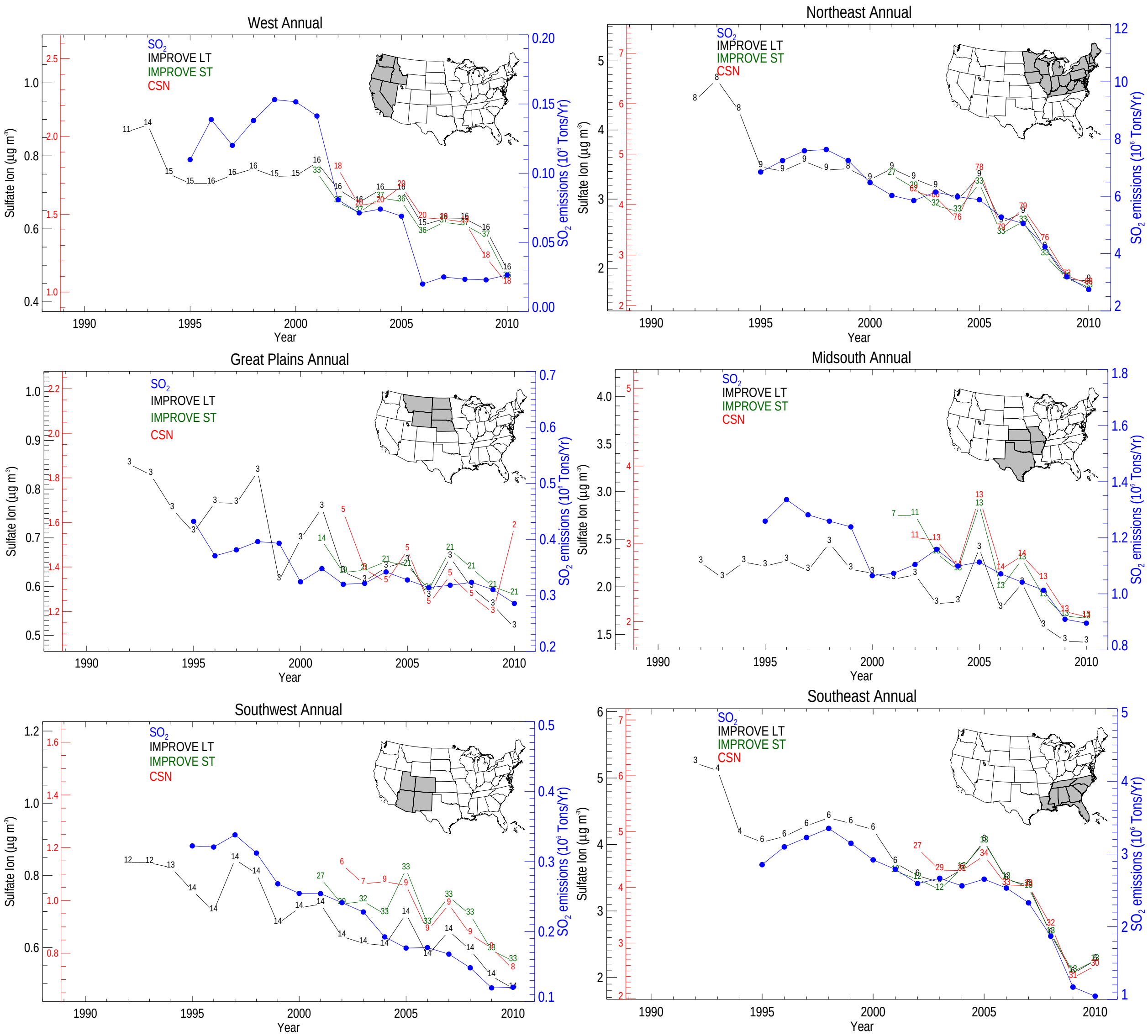

Fig. 7. Regional annual mean particulate sulfate ion concentrations (µg m^{-3}) from long-term (LT) and short-term (ST) IMPROVE sites (left black axis) and CSN sites (left red axis), and power plant SO_2 emissions (million tons yr^{-1}) (right blue axis) for **(a)** West **(b)** Northeast **(c)** Great Plains **(d)** Midsouth **(e)** Southwest **(f)** Southeast. The inset maps show the states in the region in gray. The number of complete sites with valid data available for a given year is used as the plot symbol for each time series.

(Fig. 7a), May monthly mean sulfate concentrations steadily increased from early 2000 through 2007, after which they dropped considerably and reached a low value in 2010. The regional pattern demonstrated that this behavior was typical for many urban and rural sites in the West region in spring. Clearly, the May SO_2 emissions demonstrated very different behavior. The correlation coefficient for May SO_2 emissions and ST rural monthly mean sulfate concentrations in the West was $r = 0.09$.

As another example of differing behavior between SO_2 emissions and sulfate concentrations, recall that winter mean sulfate concentrations increased at a swath of sites stretching from the northern into the central Great Plains (Fig. 4a), especially in December. A timeline of December monthly, regional mean SO_2 emissions and sulfate concentrations for the Great Plains region is shown in Fig. 9. Beginning in 2006 regional sulfate concentrations rapidly increased through 2010, at rates that reached 17.5 % yr^{-1} (recall the Fort Peck, Montana, site). In contrast, December regional SO_2 emissions from power plants were flat from 2000 through 2009 and decreased in 2010. The correlation coefficient for December SO_2 emissions and ST rural monthly mean sulfate concentrations in the central Great Plains was $r = -0.51$.

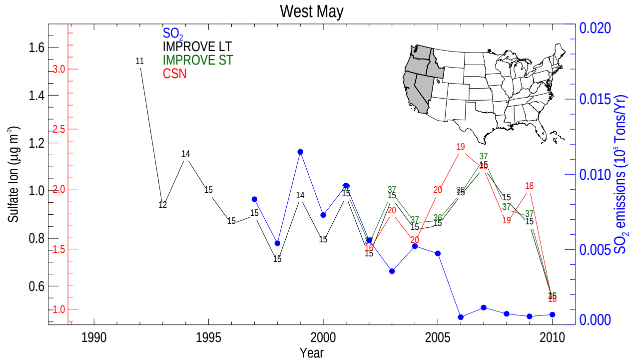

Fig. 8. May monthly and regional mean particulate sulfate ion concentrations (µg m^{-3}) for the West region (see gray states on inset map) from long-term (LT) and short-term (ST) IMPROVE sites (left black axis) and CSN sites (left red axis), and power plant SO_2 emissions (million t yr^{-1}) (right blue axis). The number of complete sites with valid data available for a given year is used as the plot symbol for each time series.

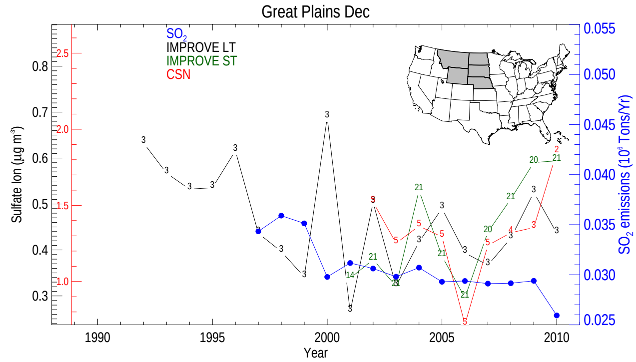

Fig. 9. December monthly mean particulate sulfate ion concentrations (µg m^{-3}) for the Great Plains region (see gray states on inset map) from long-term (LT) and short-term (ST) IMPROVE sites (left black axis) and CSN sites (left red axis), and power plant SO_2 emissions (million t yr^{-1}) (right blue axis). The number of complete sites with valid data available for a given year is used as the plot symbol for each time series.

Timelines of regional annual mean sulfate concentrations and annual total CEM SO_2 emissions tracked closely for most regions, suggesting a near-linear relationship between average changes in power plant SO_2 emissions and sulfate concentrations. This relationship was evident in the scatter plots of sulfate concentrations and CEM SO_2 emissions for regional short-term data shown in Fig. 10a and for NEI total SO_2 emissions in Fig. 10b. The LT IMPROVE data and the SO_2 emissions had a similar relationship. Linear correlation coefficients were highest for the Northeast and Southeast regions where SO_2 emissions and sulfate concentrations were largest. It is interesting to note that the apparent response of sulfate to SO_2 emissions was lower in the Northeast region relative to the rest of the country. The cause of this is unknown.

4 Discussion and summary

Significant progress has been made in reducing SO_2 emissions in the United States. The total US SO_2 emissions (NEI) have decreased from nearly 31 million tons in 1970 to 8 million tons in 2010, a nearly four-fold decrease (see Fig. 11). Source categories of the NEI include large electric utilities (power plants), industrial, commercial, and institutional sources, including residential heaters and boilers, chemical processes such as chemical production and petroleum refining, on-road vehicles, and non-road vehicles and engines. Since 1975 electric utilities consistently have accounted for roughly two-thirds or greater of total SO_2 emissions and reductions in power plant emissions primarily accounted for the decrease in total SO_2 emissions shown in Fig. 11. However, these SO_2 emissions are only from US sources. As mentioned in Sect. 1, transpacific transport from Asia can influence US sulfate concentrations. Modeling studies such as those performed by Park et al. (2004), Heald et al. (2006), and Chin et al. (2007) implied that SO_2 emissions from outside of the United States can be important contributors to background sulfate concentrations, especially in the West where power plant emissions are low. As SO_2 emissions in other countries change, it is possible that transboundary sulfate contributions could affect US sulfate trends, particularly as SO_2 emissions in the United States continue to decrease.

Sulfate concentrations decreased significantly at long-term IMPROVE sites in the United States from 1992 to 2010 ($-2.7\,\%\,yr^{-1}$). In 2000 the IMPROVE network expanded and the CSN came online, nearly tripling the number of sites available for trend analyses. Short-term annual mean urban (2002–2010) and rural (2001–2010) sulfate concentrations decreased by $-6.2\,\%\,yr^{-1}$ and $-4.6\,\%\,yr^{-1}$, respectively, with stronger rates for regions in the eastern compared to the western United States. Short-term trends in seasonal mean concentrations indicated specific seasons and regions where sulfate concentrations increased. For example, urban and rural mean sulfate concentrations in the western United States in May increased steadily from early 2000 until 2006–2007 after which they dropped (Fig. 8). Additionally, monthly mean maximum sulfate concentrations have shifted from summer to spring for many western sites since 2000 (Hand et al., 2012a). Contributions of sulfate from Asian sources are largest during the spring (Park et al., 2004), and Lu et al. (2011) reported timelines of Chinese SO_2 emissions that followed a similar temporal pattern as western May monthly mean sulfate concentrations. It is possible that western sulfate concentrations were responding to the Chinese emission trend, but other influences, such as changes in meteorology, transport, or oxidants, may have contributed. Monthly mean sulfate concentrations also increased in December at many sites in the northern and central Great Plains. Beginning

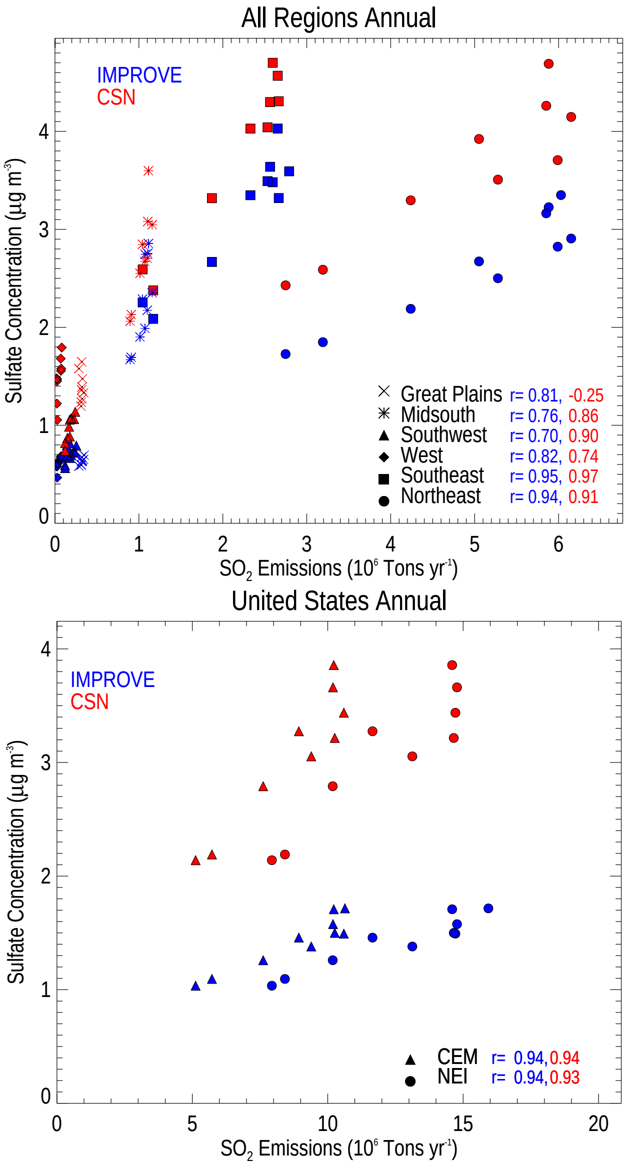

Fig. 10. (a) Regional annual mean short-term particulate sulfate ion concentration (µg m^{-3}) from IMPROVE and CSN versus annual total power plant SO_2 emissions (million t yr^{-1}) from continuous emission monitoring (CEM) power plants. **(b)** US annual mean short-term sulfate ion concentration (µg m^{-3}) for IMPROVE and CSN versus annual total SO_2 emissions (million tons yr^{-1}) from continuous emission monitoring (CEM) power plants and the National Emission Inventory (NEI). Correlation coefficients (r) are listed in blue for IMPROVE and red for CSN and are 99 % confident for values above 0.77 (IMPROVE) and 0.80 (CSN).

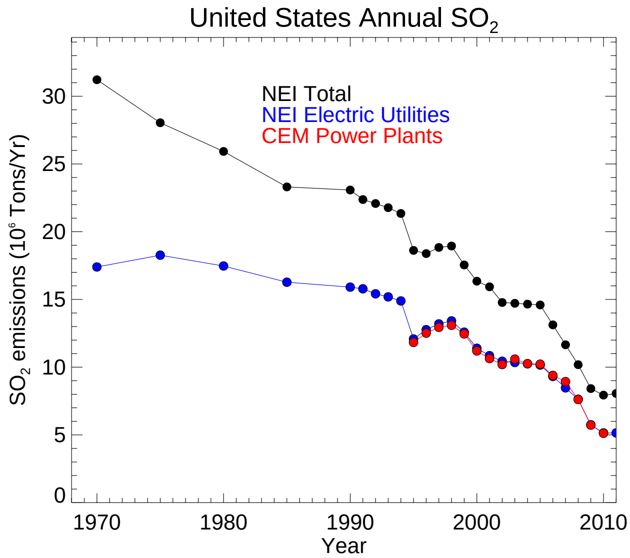

Fig. 11. US annual SO_2 emissions (million t yr^{-1}) from the National Emission Inventory (NEI) total sources, NEI electric utility sources, and continuous emission monitoring (CEM) power plant sources.

in 2006 concentrations increased rapidly and reached their highest values in 2010 (see Fig. 9). Hand et al. (2012b) speculated several possible causes, such as impacts from oil and gas development, transport from oil sand regions in Canada, meteorological influences, or a likely combination of all. In both the spring and winter cases, the known local and regional SO_2 emissions could not account for the sulfate concentration behavior.

The Regional Haze Rule (RHR) sets as the natural background goal aerosol concentrations corresponding to no US anthropogenic sources. RHR background levels of sulfate ion concentrations are 0.17 µg m^{-3} in the East and 0.09 µg m^{-3} in the West (U.S. EPA, 2003). As shown in Fig. 10a for all regions, as the US power plant SO_2 emissions approached zero, the sulfate concentrations did not. This offset is indicative of contributions from non-power-plant SO_2 emissions and non-US sources. The NEI SO_2 emissions, available only for the entire United States, included non-power plant emissions but did not account for natural sources (with the exception of a very small fire contribution). Therefore the intercept of the regression between sulfate concentrations and NEI SO_2 emissions provides an estimate of background sulfate due to natural sources, non-regulated sources, and international anthropogenic contributions (see Fig. 10b). Using Theil regression, the background sulfate concentrations for the United States were 0.39 ± 0.12 µg m^{-3} and 0.66 ± 0.24 µg m^{-3} for ST IMPROVE and CSN data, respectively. These values are larger than the RHR natural background estimates but are in line with those of Park et al. (2004), who estimated background sulfate ion concentrations of 0.31 µg m^{-3} and 0.28 µg m^{-3} for the western and eastern United States, respectively.

The results presented here imply that on an annual basis, the strategies for reducing SO_2 emissions from power plants have been successful in lowering particulate sulfate ion concentrations in the atmosphere, especially in the eastern United States where sources are largest, which has important ramifications for sulfate's role in visibility degradation, climate forcing, and health effects. However, this analysis also revealed that for certain regions and seasons, factors other than known local and regional power plant emissions have had significant impacts on sulfate concentrations. In general, the linear relationship between SO_2 emissions and sulfate concentrations in the western United States was not as robust as seen in the East. Understanding the sources of these increased concentrations has important implications for our current approach for air pollution mitigation strategies, as they appear to be insufficient for some seasons and regions.

Supplementary material related to this article is available online at: http://www.atmos-chem-phys.net/12/10353/2012/acp-12-10353-2012-supplement.pdf.

Acknowledgements. This work was funded by the National Park Service under contract H2370094000. The assumptions, findings, conclusions, judgments, and views presented herein are those of the authors and should not be interpreted as necessarily representing the National Park Service policies.

Edited by: R. Cohen

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