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The reduction of summer sulfate and switch from summertime to wintertime PM_{2.5} concentration maxima in the United States

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Abstract

Exposure to particulate matter air pollution with a nominal mean aerodynamic diameter less than or equal to 2.5 μm (PM_{2.5}) has been associated with health effects including cardiovascular disease and death. Here, we add to the understanding of urban and rural PM_{2.5} concentrations over large spatial and temporal scales in recent years. We used high-quality, publicly-available air quality monitoring data to evaluate PM_{2.5} concentration patterns and changes during the years 2000–2015. Compiling and averaging measurements collected across the U.S. revealed that PM_{2.5} concentrations from urban sites experienced seasonal maxima in both winter and summer. Within each year from 2000 to 2008, the maxima of urban summer peaks were greater than winter peaks. However, from 2012 to 2015, the maxima of urban summertime PM_{2.5} peaks were smaller than the urban wintertime PM_{2.5} maxima, due to a decrease in the magnitude of summertime maxima with no corresponding decrease in the magnitude of winter maxima. PM_{2.5} measurements at rural sites displayed summer peaks with magnitudes relatively similar to those of urban sites, and negligible to no winter peaks through the time period analyzed. Seasonal variations of urban and rural PM_{2.5} sulfate, PM_{2.5} nitrate, and PM_{2.5} organic carbon (OC) were also assessed. Summer peaks in PM_{2.5} sulfate decreased dramatically between 2000 and 2015, whereas seasonal PM_{2.5} OC and winter PM_{2.5} nitrate concentration maxima remained fairly consistent. These findings demonstrate that PM_{2.5} concentrations, especially those occurring in the summertime, have declined in the U.S. from 2000 to 2015. In addition, reduction strategies targeting sulfate have been successful and the decrease in PM_{2.5} sulfate contributed to the decline in total PM_{2.5}.

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Declaration of interest

Conflicts of interest

None.

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Abstract

Keywords

Air quality; Fine particulate matter; PM_{2.5}; Sulfate; Nitrate; Organic carbon

1. Introduction

Particulate matter (PM) is a heterogeneous mixture of solid and liquid substances suspended in the air. Exposure to PM has been associated with various health effects (Pope and Dockery, 2006). In particular, PM with an aerodynamic diameter of $2.5\ \mu\text{m}$ (PM_{2.5}) has been associated with increased risk of total mortality, death from cardiopulmonary disease, and death from lung cancer (U.S. EPA, 2009a). Airborne PM also adversely affects visibility, and major components of PM_{2.5} that are hygroscopic, such as sulfate and nitrate, can have a substantial impact on light extinction when the ambient relative humidity is high (Chan et al., 1999).

In addition to the nationwide network of monitors measuring PM_{2.5} mass concentrations, two networks monitor long-term trends in PM_{2.5} composition in the U.S., the Chemical Speciation Network (CSN, which evolved from the Speciation Trends Network) and the Interagency Monitoring of Protected Visual Environments (IMPROVE) network (Solomon et al., 2014). Both networks have been collecting data since at least 2000. CSN monitors are predominantly located in urban areas, whereas IMPROVE monitors are predominantly located in rural areas. Together, these networks provide nationwide data on the spatial and

temporal composition of PM_{2.5}. The purpose of this work is to understand the evolution of seasonal patterns (the time of year maximum and minimum concentrations are observed) and spatial variability in PM_{2.5} and its constituents at urban and rural sites across the U.S. over the years 2000–2015. Although it is well-understood that the concentration and composition of PM_{2.5} varies dramatically between the eastern and western U.S., differences in air quality between multi-state regions are less well-defined.

PM_{2.5} chemical composition data can be used to assess the efficacy of air pollution control efforts, as well as to better understand which major sources of PM_{2.5} remain. Major constituents of PM_{2.5} include sulfate, nitrate, and organic carbon (OC). Sulfate typically forms from the oxidation of SO₂ emitted by power plants and other industrial facilities. Much of the U.S. population resides in urban areas where sulfate has comprised a large portion of PM_{2.5} mass in the summertime, when the highest sulfate concentrations have historically been observed (Hand et al., 2012b, 2012c; Malm et al., 2002; U.S. EPA, 2009a).

Atmospheric ammonia plays a key role in the formation of both sulfate and nitrate (Seinfeld and Pandis, 2016). Nitrate typically forms in the atmosphere from nitrogen oxides emitted by motor vehicles, power plants, and other industrial facilities (U.S. EPA, 2016). Nitrate concentrations are greatest in winter and in urban areas across the U.S., especially in California and the western U.S. (Hand et al., 2012b, 2014, 2012c). OC is directly emitted and can also form in the atmosphere from a complex mixture of natural and anthropogenic sources. OC concentrations are highest in the west, in fall and winter (U.S. EPA, 2009b). In addition, estimates of the portion of organic aerosols that are secondary (formed in the atmosphere from gas phase biogenic and anthropogenic precursors) vary greatly, ranging from 20 to 70% (Baek et al., 2011; Millet et al., 2005; Weber et al., 2007). Determining the seasonal variability and amount of primary (emitted from combustion sources) and secondary organic aerosols could provide information regarding the contribution of various OC sources (Rohr and McDonald, 2016; Schichtel et al., 2017).

To better understand regional-, population-, and temporal-specific differences in U.S. air quality, we used quality-assured PM_{2.5} mass concentration measurements from 2000 to 2015 to analyze and compare average monthly urban and rural PM_{2.5} concentrations across the U.S. over time. We then resolved our analyses to more closely examine regional, temporal, and urban/rural PM_{2.5} changes. Similar analyses were also performed for PM_{2.5} sulfate and nitrate from 2000 to 2015 and PM_{2.5} OC from 2009 to 2015, to better understand patterns and changes in the composition of these major PM_{2.5} components across and within the U.S.

2. Methods

The 24-hour average PM_{2.5} mass and chemical composition data used in these analyses were obtained from the U.S. EPA's Air Quality System (AQS) and have a sampling frequency ranging from daily to every 6th day (U.S. EPA, 2015). The PM_{2.5} mass data collection follows specific quality assurance procedures required for regulatory use. All data from Federal Reference Method (FRM) or Federal Equivalent Method (FEM) monitors were included, regardless of the length of time each site reported data, the presence of an exceptional event flag, or whether they were used for regulatory purposes. PM_{2.5} data used were site-level (i.e., daily concentrations from the primary monitor per site, if available, or

the average of daily concentrations from co-located monitors), 24-hour (midnight to midnight) FRM/FEM average PM_{2.5} measurements (parameter code 88101) collected in the 50 U.S. states.

The AQS database (<https://www.epa.gov/outdoor-air-quality-data>) includes various metadata information for each site, including the city, county, state, EPA Region, and location setting. 'Location setting' includes the categories 'rural,' 'suburban,' 'urban and center city,' and 'unknown,' and are assigned by the local air quality agency that administers the network. Using recent U.S. census data, both 'urban and center city' and 'suburban' sites were determined to be located in areas of relatively high population, thus the two categories were combined and henceforth termed 'urban' (Supplemental Fig. 1). The 0.2% of measurements labeled as 'unknown' were excluded from the urban/rural analyses.

Monitor-level, 24-hour average (midnight to midnight) sulfate (parameter code 88403), nitrate (parameter code 88306), and OC (parameter codes 88320 [IMPROVE] and 88370 [CSN]) concentrations from the CSN and IMPROVE networks were also obtained from AQS and converted to the site-level using values from the lowest Parameter Occurrence Code monitor, to avoid the inclusion of multiple measurements from the same site. Although the CSN and IMPROVE networks measure similar parameters, each have slightly different measurement biases (Solomon et al., 2014). For example, the PM_{2.5} OC measurement biases are known to have changed between 2007 and 2009 for the CSN. In addition, the networks used different blank correction procedures throughout the time period of interest. IMPROVE data were blank corrected following the usual IMPROVE procedure of subtracting a monthly average field blank, and CSN data were not blank corrected. Although not all PM_{2.5} sites have chemical composition measurements and not all species were measured at each PM_{2.5} site, grouping measurements by EPA Region (Supplemental Fig. 2) and location setting enables unique analyses of the monthly average trends over time. EPA Regions were selected to divide the U.S. into smaller, more meteorologically-similar areas, and to provide a better understanding of Region-specific trends.

3. Results

3.1. Total PM_{2.5}

To better understand the seasonal patterns and long-term changes in PM_{2.5} concentrations at monitoring sites across the U.S., we obtained and compiled all daily, site-specific, rural and urban PM_{2.5} concentration measurements reported by FRM and FEM monitors from 2000 to 2015 in the U.S. Although the majority of PM_{2.5} monitors are located in urban areas, a significant subset (~18%) were positioned in rural areas (Supplemental Table 1). Urban monitors were more concentrated in the eastern U.S. and along the west coast, whereas rural monitors were fairly evenly distributed across the U.S. (Supplemental Fig. 3). It should also be noted that the number and distribution of monitors across the U.S. varied slightly each year.

To ensure that monitors collecting data over short periods of time (e.g., 1 year) did not greatly influence the data, we performed a sensitivity analysis using a subset of long-term monitors. We defined long-term monitoring sites as those reporting at least 11 measurements

per quarter from all four quarters and from 75% of the years 2000–2015 (Supplemental Fig. 4). Although this reduced the number of monitoring sites by approximately half, the overall $\text{PM}_{2.5}$ concentration trends of urban and rural sites remained consistent in the subset of long-term monitors. The only notable differences were slightly higher ($< 1 \mu\text{g}/\text{m}^3$) overall concentrations and higher summer rural maxima in the subset of monitors, though rural maxima never reached or surpassed summer urban maxima in this subset of monitors.

Monthly urban and rural $\text{PM}_{2.5}$ average concentrations over the 16 years of interest show distinct seasonal patterns (Fig. 1A). Intriguingly, the relative peak heights of monthly average urban $\text{PM}_{2.5}$ concentrations are higher in the summers (June, July, and August) than in the winters (December, January, and February) from 2002 to 2008, then switch so that winter peaks are higher than summer peaks during 2009–2015. Rural $\text{PM}_{2.5}$ concentrations peaked only in the summers between 2000 and 2008, but tended to display small peaks in both the winters and summers from 2009 to 2015. The average concentrations of $\text{PM}_{2.5}$ in rural areas has been consistently lower than in urban areas, and concentrations in both location types have decreased over time.

To determine monthly urban and rural $\text{PM}_{2.5}$ trends over a typical year, the monthly averages for each month from 2000 to 2015 were pooled, and an average concentration for each month in the year was calculated (Fig. 1B). On average, there were urban $\text{PM}_{2.5}$ concentration maxima of $\sim 12.5 \mu\text{g}/\text{m}^3$ in summer and winter and concentration minima of $9\text{--}10 \mu\text{g}/\text{m}^3$ in spring (March, April, and May) and fall (September, October, and November) across the U.S. Rural $\text{PM}_{2.5}$ concentrations reached $11 \mu\text{g}/\text{m}^3$ in summer, but only $\sim 9 \mu\text{g}/\text{m}^3$ in winter, and dipped below $8 \mu\text{g}/\text{m}^3$ in spring and fall.

The rural and urban U.S. averages were then grouped by location (Fig. 1C and Supplemental Fig. 2). Urban and rural locations in eastern (Regions 1–4) and central (Regions 5–7) states displayed both summer and winter $\text{PM}_{2.5}$ peaks, with maximum concentration occurring in the summertime. The seasonal pattern in eastern and central states differed greatly from the western states (Regions 8–10). Western urban sites displayed a strong winter peak, whereas rural western sites remained relatively low throughout the year. Rural $\text{PM}_{2.5}$ concentrations display slightly reduced summer peaks as compared to urban, and substantially reduced winter peaks.

When the monthly averages of each of the 16 years were superimposed, the consistent decrease in $\text{PM}_{2.5}$ over time at both rural and urban locations became clear (Fig. 1D). Although in general, the average $\text{PM}_{2.5}$ concentrations decrease over time, a clear distinction in the yearly concentration graphs between 2008 and 2009 is apparent at both rural and urban monitoring sites. The years 2000–2008 and 2009–2015 each group together, leaving a distinct separation that is most apparent in the summertime. Of note, the year 2002 averaged the highest summer concentrations, 2014 averaged the lowest summer concentrations, and 2015 has the lowest spring and fall concentrations of all years analyzed.

To understand how $\text{PM}_{2.5}$ concentrations changed over time within each EPA Region, we compared the average urban and rural monthly concentrations of each year in each EPA Region (Fig. 1E). EPA Regions were selected as a method to subset the country into a

manageable number of regions, while also retaining measurements collected in Alaska and Hawaii. While all EPA Regions display a general downward trend over time, substantial reductions in the summer peaks are evident in Regions 1–5 over time at both urban and rural sites. This reduction in summer peaks over time is less pronounced in EPA Regions located in the western U.S. In addition, Regions 1–5 show detectable wintertime peaks and troughs of similar magnitude in the spring and fall. While there are smaller reductions in total $PM_{2.5}$ over time in Regions 6–10, the overall yearly trends are rather different. $PM_{2.5}$ concentrations in Region 6 are reasonably consistent throughout all four seasons, whereas Region 7 displays discernible summer and winter peaks of similar magnitude. Regions 8–10 display distinct winter peaks at urban sites, as well as year-specific peaks in late summertime. In contrast, summer peaks of rural $PM_{2.5}$ are generally small or nonexistent in Regions 8–10. Also, rural concentrations are almost always lower than urban, in agreement with previous analyses (Hand et al., 2012c). Interestingly, the highest monthly average concentration (nearly $40 \mu\text{g}/\text{m}^3$) occurred at rural sites in Region 10 in September of 2012, which resulted from a wildfire (see the Discussion section for additional information).

3.2. $PM_{2.5}$ composition

Sulfate, nitrate, and organic carbon constitute a substantial portion of $PM_{2.5}$ mass throughout the U.S., although the relative contributions vary by region and season (U.S. EPA, 2009a). Both sulfate and nitrate are known to display seasonal patterns, with sulfate concentrations increasing in the summers and nitrate concentrations increasing in the winters (Hand et al., 2012c). In order to better understand if and how these components contribute to the seasonal variations in $PM_{2.5}$, the monthly average concentrations of $PM_{2.5}$ sulfate, nitrate, and OC were evaluated. Please note that the number of monitors reporting $PM_{2.5}$ sulfate, nitrate, and OC concentration measurements each year is smaller than the number of monitors reporting total $PM_{2.5}$ concentrations (Supplemental Tables 2–4 and Supplemental Figs. 5–7), though most sites do report a 24-h measurement every 3 or 6 days. In addition, just under 50% of $PM_{2.5}$ sulfate, nitrate, and OC monitors were located at urban sites, as compared to ~80% of $PM_{2.5}$ monitors.

3.3. $PM_{2.5}$ sulfate

We evaluated urban and rural $PM_{2.5}$ sulfate concentrations in a similar manner as total $PM_{2.5}$. In agreement with previous reports (Hand et al., 2012b, 2014, 2012c; Malm et al., 2002), we observed a distinct decrease in the magnitude of summer $PM_{2.5}$ sulfate peaks over the time period analyzed, especially after 2008 (Fig. 2A and D). In addition, trends from the subset of long-term monitors (sites reporting at least 11 measurements per quarter from all four quarters and from 75% of the years 2000–2015; Supplemental Fig. 8) appeared very similar to trends from all $PM_{2.5}$ sulfate monitors, even considering that only ~20% of urban $PM_{2.5}$ sulfate monitors satisfied the criteria to be considered long-term.

Both urban and rural monthly $PM_{2.5}$ sulfate concentration averages peaked in the summers, and urban concentrations were higher than rural (Fig. 2B). In addition, summer $PM_{2.5}$ sulfate concentrations were greater in the eastern and central U.S. (Regions 1–7) than in the western U.S. (Regions 8–10) (Fig. 2C). This result may be related to the distribution of urban monitor locations, which are more concentrated in the eastern U.S. (Supplemental Fig.

5), where sulfate concentrations are higher. In contrast, rural monitors are more evenly distributed across the U.S. It is also important to note that seasonal patterns of $\text{PM}_{2.5}$ sulfate differ between the eastern and western U.S., with summer peaks clearly visible at urban and rural sites in EPA Regions 1–7, but absent at rural monitors in Regions 8–10. Although it appears that rural $\text{PM}_{2.5}$ sulfate concentrations have decreased only slightly over time (Fig. 2D), when combined with Fig. 2C it is more likely that grouping rural areas masks the differences between $\text{PM}_{2.5}$ sulfate patterns observed in the eastern U.S. versus the western U.S. (Supplemental Fig. 5). Interestingly, summer $\text{PM}_{2.5}$ sulfate concentration maxima dramatically decreased in magnitude after 2008 (Fig. 2A, D, and 2E), similar to $\text{PM}_{2.5}$ (Fig. 1A).

3.4. $\text{PM}_{2.5}$ nitrate

Urban and rural $\text{PM}_{2.5}$ nitrate concentrations peaked in the winter months, with urban concentrations always greater than rural concentrations and the magnitude of both urban and rural $\text{PM}_{2.5}$ nitrate concentration maxima remained reasonably consistent over the 16 years analyzed (Fig. 3A and B). This is consistent with previous analyses of rural areas (Hand et al., 2012b, 2012c). Measurements from the subset of long-term monitors (those reporting > 75% of the time for at least 12 years) show that $\text{PM}_{2.5}$ nitrate trends behaved similarly, although urban monitors reached slightly higher maxima (Supplemental Fig. 9). $\text{PM}_{2.5}$ nitrate concentrations varied greatly by urban/rural status, with high wintertime concentrations reported from most urban Region groupings and some individual rural Regions (Fig. 3C, D, and 3E). While a study looking at the Great Plains found an increase in wintertime nitrate ion concentrations (Hand et al., 2012a), our analysis did not show considerable variation in wintertime maxima over time (Fig. 3D). It should be noted that previous analyses have identified that the highest $\text{PM}_{2.5}$ nitrate concentrations occur over a spatial scale smaller than that of EPA Regions, such as the Los Angeles Basin and the San Joaquin Valley (Hand et al., 2012c), and that classifying locations by EPA Regions does not capture this geographical characteristic (Supplemental Table 3 and Supplemental Fig. 6). However, the seasonal patterns of $\text{PM}_{2.5}$ nitrate shown here remain relevant and informative.

3.5. $\text{PM}_{2.5}$ OC

OC is a significant component of $\text{PM}_{2.5}$ in the U.S. and long-term normalized spatial and seasonal patterns of $\text{PM}_{2.5}$ OC have been reported (Attwood et al., 2014; Hand et al., 2013; Kim et al., 2015; Zhang et al., 2007). OC has many sources, such as wildland fires, various combustion sources, and secondary organic aerosol formation, of which the proportional contributions vary throughout the year (Kleindienst et al., 2007). The methods by which $\text{PM}_{2.5}$ OC were measured differed between the IMPROVE and CSN networks before 2007, but methods were modified in both networks from 2007 to 2009 to make measurements comparable after 2009 (Solomon et al., 2014). Although the full 16 years of data are available from many rural OC monitors from the IMPROVE network (Supplemental Fig. 10), we restricted our primary analysis to urban and rural $\text{PM}_{2.5}$ OC measurements collected from 2009 to 2015 in order to be able to directly compare measurements from both networks (Supplemental Table 4 and Supplemental Fig. 7).

Monthly urban PM_{2.5} OC concentration averages were higher than rural across the nation, and the two site categories displayed differing seasonal patterns (Fig. 4A and B). Urban PM_{2.5} OC concentrations peaked in the winters, whereas rural PM_{2.5} OC peaked in the summers. Seasonal patterns were less clear when only measurements from the subset of long-term PM_{2.5} OC monitors were included (Supplemental Fig. 11). When considering the average seasonal pattern of each EPA Region over the 7-year period spanning 2009–2015, urban sites in Regions 9 and 10 displayed distinct winter PM_{2.5} OC peaks, whereas only subtle summer peaks were visible in other Regions (Fig. 4C, D, and 4E). The lack of seasonal PM_{2.5} OC peaks in Region 4 was interesting because this area is thought to have very high summertime biogenic secondary organic aerosol concentrations (Carlton et al., 2010). Similar to PM_{2.5} nitrate (Fig. 3), PM_{2.5} OC concentrations have shown little change in the magnitude of the seasonal maxima and minima over time (Fig. 4D and E).

4. Discussion

This analysis presented publicly-available FRM and FEM PM_{2.5} mass measurements in a novel way that revealed clear, large-scale temporal and spatial patterns. Importantly, these findings demonstrate that summertime PM_{2.5} sulfate concentrations have dramatically decreased over time. This change likely contributed to both the continued decrease in total PM_{2.5} and the switch in average PM_{2.5} concentration maxima from summers to winters in the U.S.

The large summertime maxima in PM_{2.5} concentrations observed prior to 2009 in the eastern U.S. have been well-characterized and attributed to seasonal differences in meteorological conditions and sulfate oxidation from SO₂ (Bell et al., 2007; Hand et al., 2012c; Hidy et al., 1978; Hitchcock, 1976; Malm et al., 2002; Schwab et al., 2004; Wittig et al., 2004). Averaged across the U.S. and in most of the EPA Regions, a transition from an annual PM_{2.5} maxima in the summer to in the winter occurred between 2000 and 2015 in urban areas (Fig. 1). This can be partially explained by the substantial decrease in summer sulfate during the same period and in similar areas. Since sulfate is formed in the atmosphere by oxidation of SO₂, and a strong association between SO₂ emissions and sulfate concentrations has been well established in the eastern U.S. (Hand et al., 2012c; Husain et al., 1998; Malm et al., 2002), the decrease in summer sulfate maxima is a predictable consequence of reducing SO₂ emissions. Specifically, SO₂ emissions from coal-fired power plants, the largest source of U.S. SO₂ emissions in 1990, have decreased by > 70% between 1990 and 2010 (Xing et al., 2015) and national SO₂ emissions have declined by > 6% per year between 2000 and 2010 (Hand et al., 2012c). Because sulfate accounts for a greater fraction of PM_{2.5} in the summer, it follows that a decrease in PM_{2.5} concentrations due to a reduction of sulfate would be most noticeable in summer, resulting in a substantial reduction in the magnitude of summer PM_{2.5} peaks, as we have observed (Fig. 1A). While not a 1-to-1 relationship, EPA Regions in which summertime PM_{2.5} concentrations decreased over time also displayed a corresponding decrease in summertime PM_{2.5} sulfate.

The flattening of the seasonal sulfate concentration pattern may herald the end of summer as the season of highest annual PM_{2.5} concentrations. The reduction in the summer PM_{2.5} concentration peaks together with the emergence of winter as the season with the highest

nationwide $PM_{2.5}$ concentrations may have far-reaching implications for human exposure patterns and associations with co-pollutants, such as ozone. The near disappearance of the summer $PM_{2.5}$ sulfate peaks also provides a vivid visualization of a successful emission control strategy, namely the reduction of power plant SO_2 emissions.

Within the 2000–2015 time frame examined here, the highest monthly $PM_{2.5}$ concentration averages in EPA Regions 1–5 all occurred in July 2002. On July 6, 2002, lightning ignited several wildfires in Quebec, which produced a smoke plume that blanketed New England on July 7. Secondary analyses determined that this singular event was the primary cause of those high $PM_{2.5}$ concentrations. The highest monthly rural average occurred September 2012 in Region 10, which contributed to the only instance where the rural monthly average surpassed the urban monthly average. The cause of this was a single monitor in Lemhi County, Idaho that reported very high concentrations of $PM_{2.5}$ through August and September of that year due to wildfire smoke. In fact, late summer maxima that do not decrease over time generally coincide with large wildfires.

Although we show that $PM_{2.5}$ sulfate concentrations have decreased over time in EPA Regions 1–7 (the eastern and central U.S.), details of regional impacts resulting from these differences were not a focus of this analysis. Instead, the air quality trends highlighted here are those of long-term national scale data, such as national scale decreases in $PM_{2.5}$ sulfate due to reductions in SO_2 emissions and observations of extreme PM events due to wildfires. The dominance of electric power generating units as a national SO_2 source, their concentration in the eastern U.S., and the season-specific chemistry of sulfate formation combine to make an analysis based on seasonal and regional classification of a large data set a worthwhile approach for investigating the impact of decreases in SO_2 emissions from electric power generation. Similarly, extreme $PM_{2.5}$ concentrations from fire emissions on a given day have the potential to strongly influence average daily, and even monthly, concentrations across an entire state or region, and can be easily compared to wildfire data to pinpoint the cause.

There have been other major changes in $PM_{2.5}$ and precursor emissions that apparently did not result in obvious trends in national scale data. The most salient example is the decline in NO_x concentration. Total U.S. NO_x emissions decreased by 48% between 2002 and 2014 (U.S. EPA, 2017), resulting in a greater contribution from oil and gas production and natural gas emissions relative to coal (U.S. EPA, 2017). However, these emissions reductions and changes in source contributions do not appear to have resulted in major changes in ambient $PM_{2.5}$ nitrate concentration (Fig. 3), even though NO_x is a known precursor of particulate nitrate. Changes in emissions control and fuel composition of both diesel and gasoline vehicles have greatly reduced PM, NO_x , and SO_2 emissions from automobiles (CRC, 2013). In principle, reductions in sulfate and precursor SO_2 emissions from motor vehicles could impact regional ambient concentrations of $PM_{2.5}$ and $PM_{2.5}$ sulfate, as they are relatively long-lived can therefore undergo long distance transport. However, in practice SO_2 emissions from transportation accounts for less than 5% of national SO_2 emissions even before recent reductions in fuel sulfur content (U.S. EPA, 2008).

Combining our analyses with knowledge about seasonal emissions and sources may provide insight into the breakdown of OC into primary and secondary emissions. Combustion sources emitting primary organic aerosol emissions are abundant in winter due to home heating and in summer and fall due to wildfires, whereas industrial, transportation, and cooking sources emit year round. In contrast, increased biogenic precursor emissions and more rapid photochemical reaction rates lead to increased secondary organic aerosol in the summer (Baek et al., 2011; Millet et al., 2005; Weber et al., 2007). As we observed the highest rural PM_{2.5} OC concentrations in the summertime, it suggests that rural OC predominantly results from wildland fire smoke and secondary organic aerosols. In addition, as urban OC concentrations are highest in the wintertime, a substantial portion of urban OC may come from primary sources like home heating (Baek et al., 2011; Millet et al., 2005). Secondary OC production is enhanced when sulfate is present (Budisulistiorini et al., 2016; Pye et al., 2013), and aerosol water and aqueous processing may influence secondary organic aerosol formation (Adamson et al., 2004; Carlton and Turpin, 2013; Pye et al., 2017).

Although sulfate, nitrate, and OC are the three largest components of PM_{2.5} mass, other contributors include elemental carbon, crustal material, sea-salt, and ammonium. The contribution of these other components was beyond the scope of this analysis, and are not as likely to contribute to the changes we observed in total PM_{2.5} because they are not as abundant.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Abbreviations:

AQS	Air quality system
CSN	Chemical Speciation Network
EPA	Environmental Protection Agency

FEM	Federal Equivalent Method
FRM	Federal Reference Method
IMPROVE	Interagency Monitoring of Protect Visual Environments
NAAQS	National Ambient Air Quality Standard
OC	organic carbon
PM	particulate matter
SO₂	sulfur dioxide
U.S.	United States

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Fig. 1. Urban and rural PM_{2.5} concentration patterns and changes in the U.S. from 2000 to 2015.

A) Annual (thinner lines) and monthly (thicker lines) average concentrations of 24-hour PM_{2.5} urban (black) and rural (gray) measurements across the U.S. from 2000 to 2015. Faint grid lines indicate increments of 4 μg/m³ on the y-axis and January of each year on the x-axis. **B)** Average monthly urban (black) and rural (gray) U.S. PM_{2.5} concentrations. The monthly average, which was separated by year in panel A, was combined with the same months from other years. Seasons are demarcated by vertical dashed lines here, but are applicable to all figures. **C)** Average monthly urban and rural PM_{2.5} concentrations of the grouped EPA Regions. EPA Regions were combined by location, with the lightest line representing the eastern Regions (1–4), the medium-gray line representing the central Regions (5–7), and the darkest gray line representing the western Regions (8–10). **D)** Average national monthly urban and rural PM_{2.5} concentrations for each of the 16 years. Each year is colored by a different gradient of gray, from 2000 shown in the lightest gray line to 2015 shown in the darkest gray line. **E)** Average regional monthly urban and rural PM_{2.5} concentrations for each year for each of the 10 EPA Regions. Within each graph, years are colored by a different shade of gray, from 2000 shown in the lightest gray line to 2015 shown in the darkest gray line.

Fig. 2. Urban and rural PM_{2.5} sulfate concentration patterns and changes in the U.S. from 2000 to 2015.

A) Annual (thinner lines) and monthly (thicker lines) average concentrations of 24-hour PM_{2.5} urban (black) and rural (gray) sulfate measurements across the U.S. from 2000 to 2015. Faint grid lines indicate increments of 1 μg/m³ on the y-axis and January of each year on the x-axis. **B)** Average monthly urban (black) and rural (gray) U.S. PM_{2.5} sulfate concentrations. The monthly average, which was separated by year in panel A, was combined with the same months from other years. **C)** Average monthly urban and rural PM_{2.5} sulfate concentrations of the grouped EPA Regions. EPA Regions were combined by location, with the lightest line representing the eastern Regions (1–4), the medium-gray line representing the central Regions (5–7), and the darkest gray line representing the western Regions (8–10). **D)** Average national monthly urban and rural PM_{2.5} sulfate concentrations for each of the 16 years. Each year is colored by a different gradient of gray, from 2000 shown in the lightest gray line to 2015 shown in the darkest gray line. **E)** Average regional monthly urban and rural PM_{2.5} sulfate concentrations for each year for each of the 10 EPA Regions. Within each graph, years are colored by a different shade of gray, from 2000 shown in the lightest gray line to 2015 shown in the darkest gray line. Please note that some CSN monitors did not begin reporting data until the middle or end of 2000, leading to several missing data points in that year from various urban graphs of PM_{2.5} components in individual regions.

Fig. 3. Urban and rural PM_{2.5} nitrate concentration patterns and changes in the U.S. from 2000 to 2015.

A) Annual (thinner lines) and monthly (thicker lines) average concentrations of 24-hour PM_{2.5} urban (black) and rural (gray) nitrate measurements across the U.S. from 2000 to 2015. Faint grid lines indicate increments of 1 $\mu\text{g}/\text{m}^3$ on the y-axis and January of each year on the x-axis. **B)** Average monthly urban (black) and rural (gray) U.S. PM_{2.5} nitrate concentrations. The monthly average, which was separated by year in panel A, was combined with the same months from other years. **C)** Average monthly urban and rural PM_{2.5} nitrate concentrations of the grouped EPA Regions. EPA Regions were combined by location, with the lightest line representing the eastern Regions (1–4), the medium-gray line representing the central Regions (5–7), and the darkest gray line representing the western Regions (8–10). **D)** Average national monthly urban and rural PM_{2.5} nitrate concentrations for each of the 16 years. Each year is colored by a different gradient of gray, from 2000 shown in the lightest gray line to 2015 shown in the darkest gray line. **E)** Average regional monthly urban and rural PM_{2.5} nitrate concentrations for each year for each of the 10 EPA Regions. Within each graph, years are colored by a different shade of gray, from 2000 shown in the lightest gray line to 2015 shown in the darkest gray line. Please note that some CSN monitors did not begin reporting data until the middle or end of 2000, leading to several missing data points in that year from various urban graphs of PM_{2.5} components in individual regions.

Fig. 4. Urban and rural PM_{2.5} OC concentration patterns and changes in the U.S. from 2009 to 2015.

A) Annual (thinner lines) and monthly (thicker lines) average concentrations of 24-hour PM_{2.5} urban (black) and rural (gray) OC measurements across the U.S. from 2009 to 2015. Faint grid lines indicate increments of 1 μg/m³ on the y-axis and January of each year on the x-axis. **B)** Average monthly urban (black) and rural (gray) U.S. PM_{2.5} OC concentrations. The monthly average, which was separated by year in panel A, was combined with the same months from other years. **C)** Average monthly urban and rural PM_{2.5} OC concentrations of the grouped EPA Regions. EPA Regions were combined by location, with the lightest line representing the eastern Regions (1–4), the medium-gray line representing the central Regions (5–7), and the darkest gray line representing the western Regions (8–10). **D)** Average national monthly urban and rural PM_{2.5} OC concentrations for each of the 16 years. Each year is colored by a different gradient of gray, from 2009 shown in the lightest gray line to 2015 shown in the darkest gray line. **E)** Average regional monthly urban and rural PM_{2.5} OC concentrations for each year for each of the 10 EPA Regions. Within each graph, years are colored by a different shade of gray, from 2009 shown in the lightest gray line to 2015 shown in the darkest gray line. Please note that some CSN monitors did not begin reporting data until the middle or end of 2000, leading to several missing data points in that year from various urban graphs of PM_{2.5} components in individual regions.