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Ozone Trends Across the United States over a Period of Decreasing NOx and VOC Emissions

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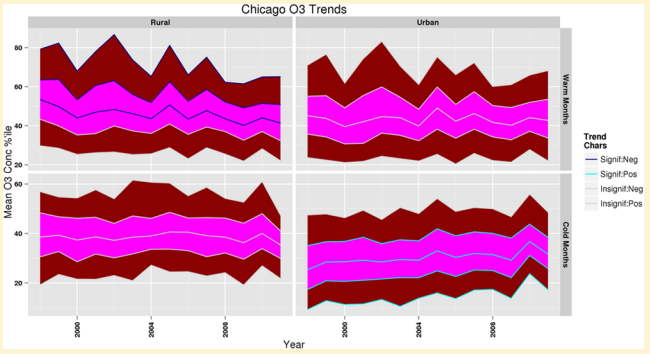
Supporting Information

ABSTRACT: In this work, we evaluate ambient ozone trends at urban, suburban, and rural monitoring sites across the United States over a period of decreasing NOx and VOC emissions (1998−2013). We find that decreasing ozone trends generally occur in the summer, in less urbanized areas, and at the upper end of the ozone distribution. Conversely, increasing ozone trends generally occur in the winter, in more urbanized areas, and at the lower end of the ozone distribution. The 95th percentile ozone concentrations decreased at urban, suburban, and rural monitors by 1−2 ppb/yr in the summer and 0.5−1 ppb/yr in the winter. In the summer, there are both increasing and decreasing trends in fifth percentile ozone concentrations of less than 0.5 ppb/yr at urban and suburban monitors, while fifth percentile ozone concentrations at rural monitors decreased by up to 1 ppb/yr. In the winter, fifth percentile ozone concentrations generally increased by 0.1−1 ppb/yr. These results demonstrate the large scale success of U.S. control strategies targeted at decreasing peak ozone concentrations. In addition, they indicate that as anthropogenic NOx emissions have decreased, the ozone distribution has been compressed, leading to less spatial and temporal variability.



INTRODUCTION

Ozone is one of six criteria air pollutants identified by the U.S. Environmental Protection Agency (EPA) pursuant to its authority under the Clean Air Act, and has been found to cause decreased lung capacity and respiratory system inflammation.[1] Additionally, ozone is associated with increased rates of emergency room visits, hospital admissions, and respiratory-related deaths.[1] The EPA sets National Ambient Air Quality Standards (NAAQS) for each criteria air pollutant to protect human health and welfare. For locations that have measured pollutant concentrations above the NAAQS, states are responsible for developing plans to bring these areas into compliance. The ozone NAAQS was set to 0.12 ppm (1-h averaging time, not be exceeded more than 1 day per year over a three year period) in 1979, and subsequently revised to 0.08 ppm in 1997 and 0.075 ppm in 2008 (8-h averaging time, fourth highest daily maximum averaged over 3 years) (http://www.epa.gov/ttn/naaqs/standards/ozone/s_o3_history.html).

Ground-level ozone, unlike many pollutants, is predominantly formed from chemical reactions in the atmosphere rather than being emitted directly. Two major ozone precursors are emitted from anthropogenic and natural sources: Oxides of Nitrogen (NOx = NO + NO_2) and Volatile Organic Compounds (VOCs).[2] NOx molecules participate in competing ozone creation and destruction reactions, but substantial ozone formation in the troposphere requires both NOx and VOC precursors. Consequently, the response of ambient ozone concentrations to changes in NOx or VOC emissions depends on the relative concentrations of the two in the atmosphere as well as the intensity of insolation. In cases where either the VOC/NOx ratio is low or insolation is very low, the effects of NOx on ozone are dominated by ozone destruction. These conditions are called VOC or oxidant limited. However, when the VOC/NOx ratio is high (NOx limited conditions), the ozone formation effects dominate. It is well documented that in regions with elevated ambient NOx concentrations due to high emissions densities (e.g., urban centers with significant traffic), VOC limited conditions often occur, leading to locally suppressed ozone concentrations relative to surrounding areas.[3−5] In those locations, reductions of NOx will lead to increases in local ozone concentrations although resulting ozone concentrations may still be lower than surrounding areas. Once the NOx is transported away from the source location, it mixes with VOCs in the atmosphere and forms ozone downwind. Consequently, locations that violate the ozone NAAQS are often at downwind suburban sites outside of core urban areas where NOx emissions are highest.[6] The same reduced NOx emissions which increase the low ozone concentrations near sources will also decrease the high ozone

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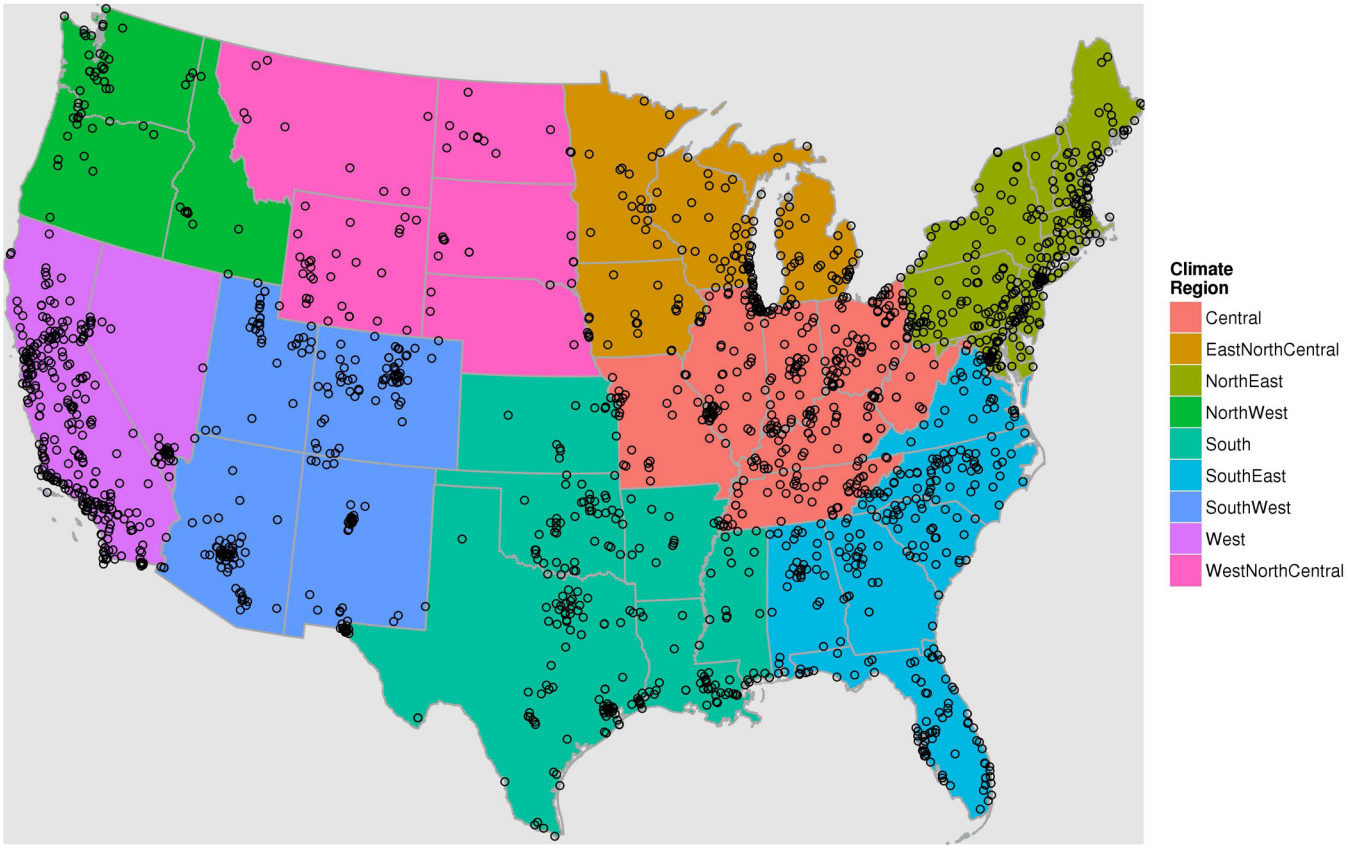

Figure 1. NOAA climate regions used to group ozone trends data and locations of AQS monitoring sites within each region.

concentrations downwind. Compliance with the ozone NAAQS focuses on reducing the magnitude and frequency of the highest ozone levels. Consequently, much of the federal and state regulatory efforts to reduce tropospheric ozone concentrations have focused on reducing NOx emissions.

Extensive measures have been taken to reduce ozone across the United States. Specifically, since adoption of the 1997 ozone NAAQS, EPA issued the NOx SIP Call and many rules that tighten emissions standards for mobile sources. The NOx SIP Call,[7] which was finalized in 1998 and fully implemented by 2004, dramatically reduced summertime NOx emissions from power plants and other large stationary sources in 22 states in the Eastern U.S., leading to a 57% reduction in NOx emissions from 2000 to 2005 for sources covered by this regulation.[8] Several rules issued by the EPA have reduced emissions of NOx and VOC from new onroad vehicles, including the Light Duty Tier 2 Rule, which took effect starting in 2004,[9] and the Clean Heavy Duty Bus and Truck Rule, which took effect for new heavy duty diesel vehicles starting in 2007.[10] In addition, EPA tightened emissions standards for nonroad engines between 2000 and 2008,[11−15] marine vessels between 1998 and 2011,[12,16−19] and locomotives between 2001 and 2005.[20] This article aims to characterize the multiyear trends in ozone concentrations that have occurred over the period from 1998 to 2013 in which these recent precursor control programs have been implemented. According to EPA's National Emissions Inventory (NEI), total U.S. anthropogenic NOx emissions from stationary and mobile sources have decreased by 18.4 million tons (39.6%) between 2002 and 2011, and VOC emissions decreased by 4.7 million tons (14%) (See section 3).

Previous studies have evaluated certain aspects of recent North American trends in ozone concentrations. A number of researchers have studied trends in "baseline" ozone concentrations at rural locations which are primarily influenced by transported emissions.[21−27] Cooper et al.[25] reported multiyear trends in the entire distribution of daytime hourly ozone concentrations measured in rural locations. They attributed sources such as international transport to increases in fifth percentile ozone concentrations at these locations, but also noted that decreasing NO emissions may contribute. They also showed that at these rural locations, 95th percentile ozone concentrations have decreased in the Eastern U.S., likely demonstrating the effectiveness of regional controls of ozone precursors. These same decreases in 95th percentile rural ozone concentrations were not seen in the Western U.S., which was not covered by the NOx SIP Call. Although that study evaluated the entire distribution of daytime ozone concentrations, the focus on rural sites was intended to isolate ozone that was not locally formed. Two other studies performed similar analyses for nonurban monitors in North America[22,23] yielding results that were generally consistent with those from Cooper et al.[25] These studies also found that increasing trends occurred more frequently in fifth percentile ozone concentrations than in monthly or seasonal averages of daily maximum concentrations. This increase in low ozone concentrations has also been observed at a select number of urban sites.[28,29] Other studies examining urban and nonurban trends in maximum daily 8-h average (MDA8) ozone concentrations reported decreases at the upper end of the distribution (4th highest or 99th percentile MDA8) at most sites across the U.S.[28−32] Although these studies provide useful insight into certain

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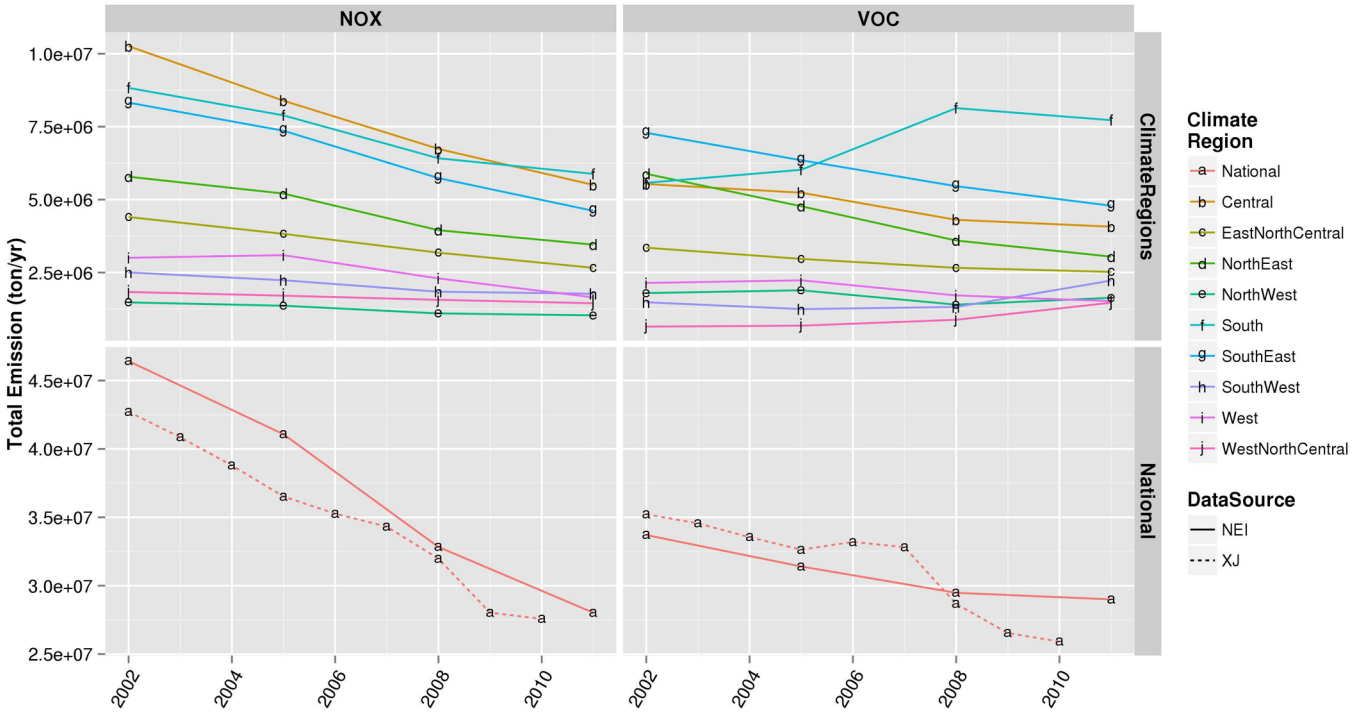

Figure 2. U.S. and regional annual NOx and VOC emissions from 2002 to 2011/2010 from the NEI and Xing et al.[42]

aspects of ozone trends, none have comprehensively compared observed ozone trends across seasons, regions of the U.S., urban and nonurban locations, and different portions of the ozone distribution. Here we take advantage of EPA's extensive monitoring database to provide a comprehensive assessment of trends in ozone concentrations across all of these factors over a period of dramatically decreasing U.S. NOx and VOC emissions (1998–2013).

DATA AGGREGATION METHODS

The EPA's Air Quality System (AQS) database includes air quality monitoring data for a range of air pollutant and meteorological parameters collected by state, local, and tribal air quality monitoring agencies across the United States (http://www.epa.gov/ttn/airs/airsaqs/). Nearly 1400 ambient monitoring sites across the U.S. currently report hourly ozone concentration data to the AQS database. All monitors in this network use a Federal Equivalent Method (FEM) approved by the EPA (most are UV absorption photometric analyzers) and must undergo biweekly quality control checks with a calibration gas. Collocated measurements show precision and bias to be less than 1%.[1] Ozone monitors in some locations are required to operate year-round, while in other locations may operate monitors for shorter time periods during the summer ozone season (40 CFR part 58, Appendix D). For the purpose of this analysis, we focus on MDA8 ozone concentrations and group these data by geographical region, season, and degree of urbanization. For regional definitions (Figure 1), we use climate regions defined by the National Oceanic and Atmospheric Administration (NOAA)[33] (http://www.ncdc.noaa.gov/monitoring-references/maps/us-climate-regions.php). NOAA routinely uses these "climatically consistent" regions to describe regional climate trends. These regions are appropriate for our analysis of ozone for three reasons. First, ozone patterns are partially driven by the same climatic features such as temperature and precipitation that define the climate regions. Second, the NOAA climate regions align well with areas containing similar emissions source types (e.g., the Central region contains a large concentration of coal-fired power plants, while the Northeast region encompasses much of the highly urbanized northeast corridor). Third, the NOAA climate regions match fairly closely with Principal Component Analysis factors determined by Chan et al.[22,23] based on spatial and temporal variability in daytime, warm-season ozone concentrations. We also group ozone data into summer season (May–September) and winter season (October–April) categories. Finally, we use the 2006 National Land Cover Database (NLCD 2006)[34] to characterize monitors as urban, suburban, and rural based on the land use designated for the 2 × 2 km^2 NLCD grid cell in which the monitor was located: urban is defined as "Developed High Intensity" and "Developed Medium Intensity", suburban is defined as "Developed Low Intensity" and "Developed Open Space", rural is defined as all other NLCD classifications. Figure S-1 in the Supporting Information (SI) displays the NLCD classifications for the United States and for four selected urban areas.

EMISSIONS TRENDS FOR OZONE PRECURSORS

Figure 2 presents U.S. NOx and VOC emissions totals from the NEI aggregated by climate region for 2002, 2005, 2008, and 2011 (data accessed at http://www.epa.gov/ttnchie1/trends/). NEI data are calculated within a few years of the emission year. Some methodologies and models for calculating emissions totals have changed over this time period and we make no attempt here to normalize for those changes. For instance, several large methodological changes occurred in 2008. First, the EPA updated the onroad emissions model from MOBILE6 to MOVES which uses new emissions factors and new temperature dependencies and generally results in higher NOx emissions estimates. Second, the EPA collaborated with state and regional planning organizations to create consistent approaches with updated algorithms and emissions factors for

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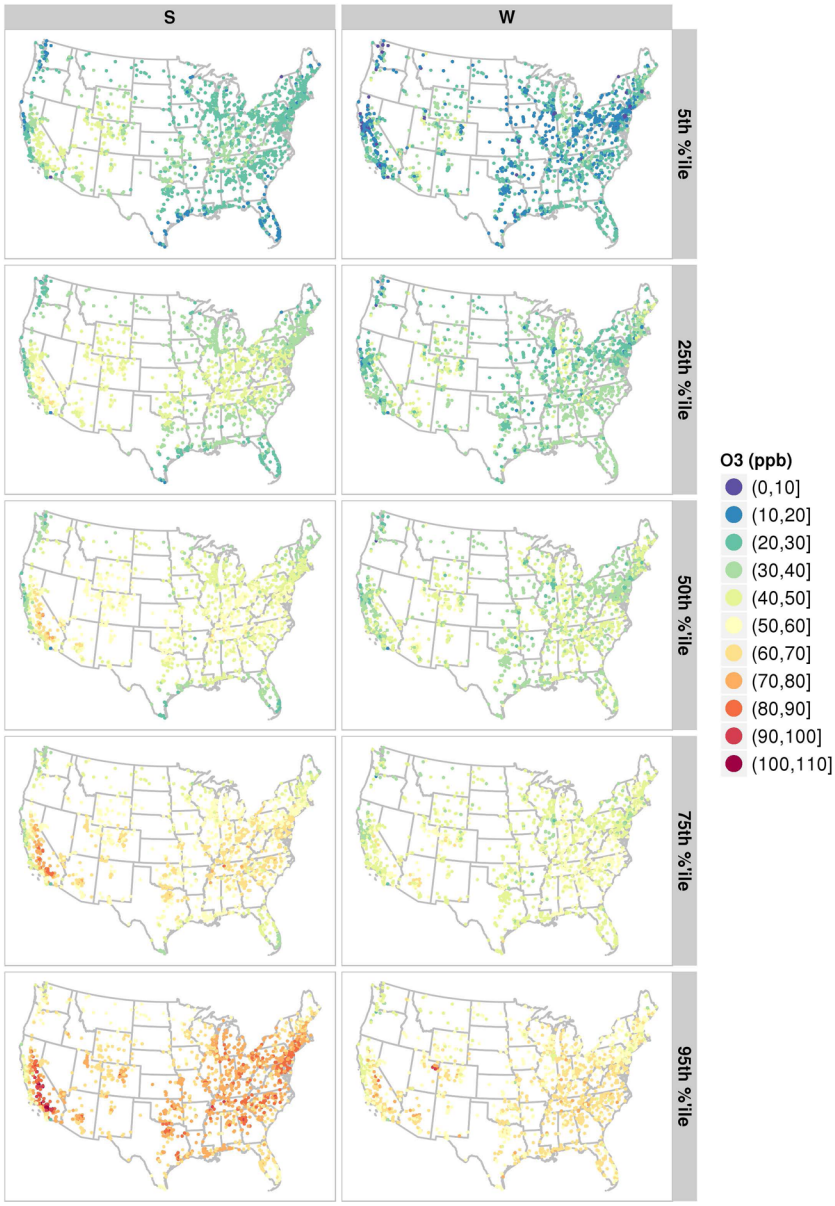

Figure 3. Measured 1998−2013 MDA8 ozone concentrations at U.S. monitoring sites. Summer (S: May−Sep) spatial patterns displayed in left-hand plots, winter (W: Oct−Apr) spatial patterns displayed in right-hand plots. Panels from top to bottom display 5th percentile, 25th percentile, 50th percentile, 75th percentile, and 95th percentile MDA8 ozone concentrations.

area sources.[35] Regional emissions are aggregated from county-level data in the NEI. Wildfires and biogenic emissions are absent from these analyses due to their nonanthropogenic origin and inconsistent emissions characterizations over the time period analyzed. From 2002 to 2011, nationwide anthropogenic NOx emissions declined from 46.2 to 28 million tons per year and nationwide VOC emissions declined from 33.7 to 29 million tons per year. These emissions reductions have not occurred uniformly across the country or throughout the year. As noted previously, the NOx SIP Call dramatically reduced summertime NOx emissions from power plants and other large industrial sources in the Eastern U.S. In addition, some urban areas which have had historically high ozone concentrations, like Houston and Los Angeles, have made specific efforts to reduce local sources of NOx as an approach to reduce ozone levels. Houston reduced NOx emissions from industrial point sources by 67% between 2000 and 2006.[36,37] Reductions in emissions from mobile source sectors have occurred more uniformly across the country due to tighter vehicle emissions standards for new cars and trucks. Other researchers have reported that these NOx reductions have led to decreasing satellite-measured tropospheric column NO_2 over this period for all regions of the U.S., although larger reductions were observed in the East.[25] Decreasing NO_2 measurements were observed even in areas of the Western U.S., likely due to tighter vehicle emission standards, despite substantial population growth. Some studies have shown that VOC emission trends in local areas differ from those in the NEI. For instance, VOC emissions have been found to be decreasing more quickly than regional NEI trends in Los Angeles,[38] Atlanta,[39] and the Southeast.[40] One study has suggested that VOC emissions in the Chicago area increased from 2005 to 2009,[41] while the East−North−Central NEI VOC trends are essentially flat. To address the nonuniformity in NEI methodologies between

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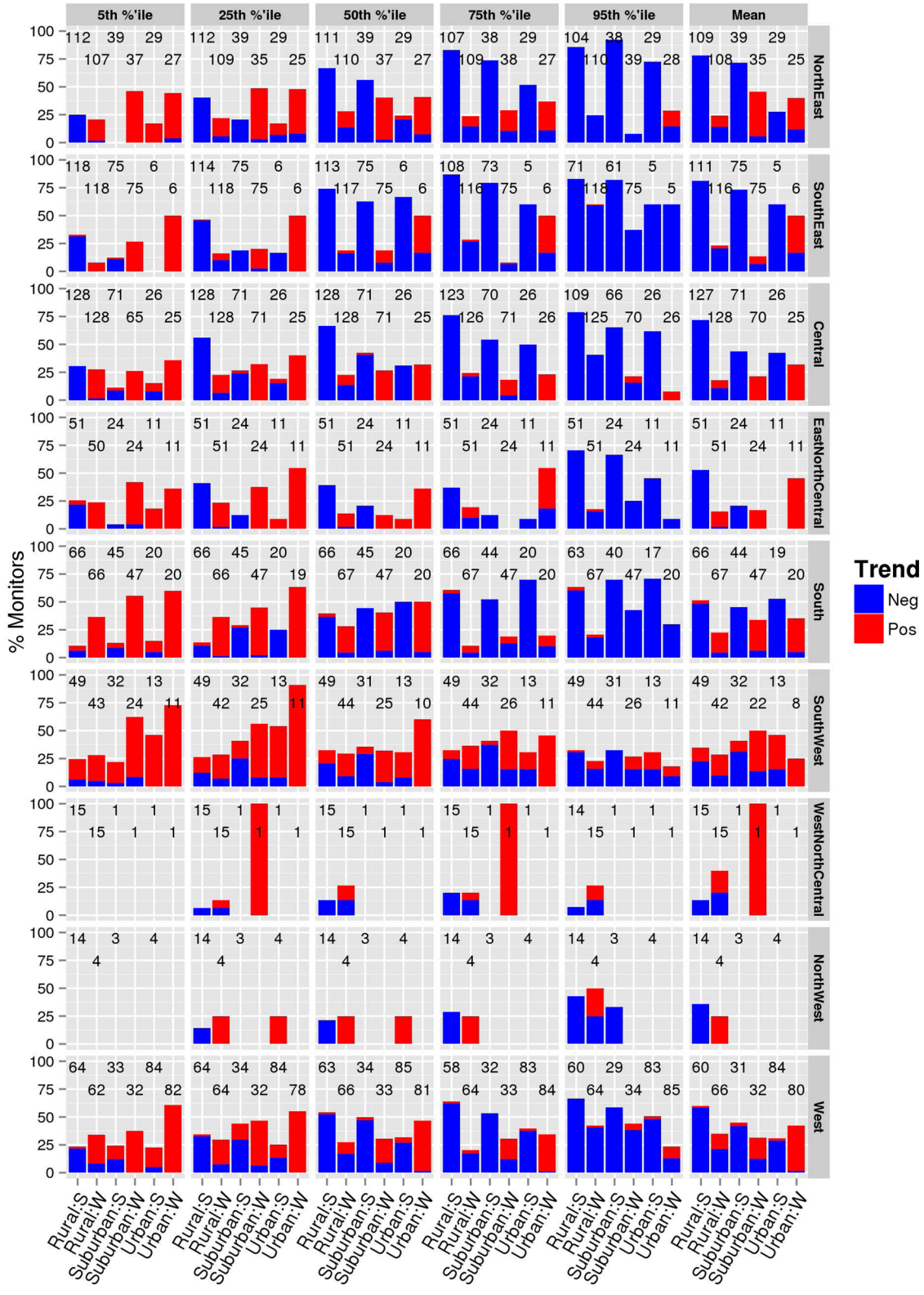

Figure 4. Percentage of sites by region in each seasonal and degree of urbanization classification which experienced statistically significant negative (decreasing) MDA8 ozone trends or statistically significant positive (increasing) MDA8 ozone trends. S and W labels refer to trends in summer and winter months, respectively. The difference between the top of each bar and 100% is the percentage of monitors that did not have statistically significant trends. The total number of monitors which were included in each classification is shown above each bar.

years, we compare the NEI national trends to those from Xing et al.,[42] who used a consistent framework across years to develop U.S. emissions estimates from 1990 to 2010 (Figure 2). Regional emissions trends from Xing et al.[42] are included in SI Figure S-2. These figures show comparable emissions trends from these two data sources, with the exception of VOC trends in the South, which are predicted to decrease between 2002 and 2010 by Xing et al.[42] and predicted to increase by the NEI.

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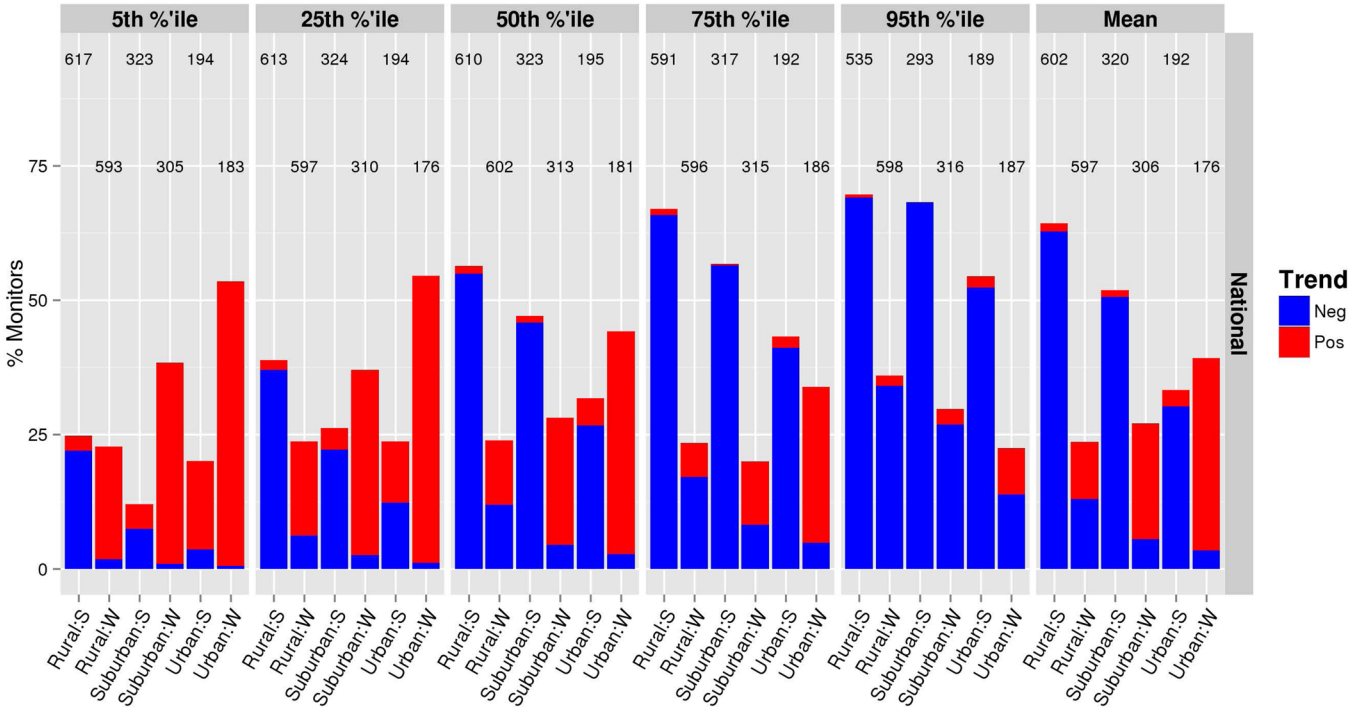

Figure 5. Percentage of sites nationally in each seasonal and degree of urbanization classification which experienced statistically significant negative (decreasing) MDA8 ozone trends or statistically significant positive (increasing) MDA8 ozone trends. S and W labels refer to trends in summer and winter months, respectively. The difference between the top of each bar and 100% is the percentage of monitors that did not have statistically significant trends. The total number of monitors which were included in each classification is shown above each bar.

OZONE CONCENTRATIONS AND TRENDS

Figure 3 displays 5th, 25th, 50th, 75th, and 95th percentile MDA8 ozone concentrations for summer and winter aggregated across years (1998−2013). The fifth percentile values in the summer range from 10 to 30 ppb except in the intermountain West where they range from 30 to 50 ppb. The summertime interquartile range covers a large span (30−60 ppb) at most sites, with Gulf and Pacific coast sites being about 10 ppb lower than most other locations, and some sites in the Southeast, Ohio Valley, central California, and the Southwest being about 10 ppb higher. Summertime 95th percentile values were about 70−90 ppb in most areas, with values up to 100 ppb in parts of California, and values in the 50−70 ppb range in the Northwest and West−North−Central regions. Cool season percentiles were about 10 ppb lower than warm season values for low and midrange portions of the ozone distribution, and 20−30 ppb lower than warm season values at high ozone concentrations.

We use AQS data from 1998 to 2013 to determine ozone trends for each individual monitor for the 5th, 25th, 50th, 75th, and 95th percentiles and mean of MDA8 ozone values, and aggregate results by region, degree of urbanization, and season. We determine direction and significance of multiyear ozone trends using the Spearman rank-order correlation coefficient, which is considered significant for p-values less than 0.05. Figure 4 displays the percent of sites in each region, season, and degree of urbanization classification that exhibit statistically significant increasing and decreasing trends. Figure 5 shows the same information aggregated nationally instead of by region. Results look similar when the figures are recreated with the subset of monitors that operate year round (SI Figures S-3 and S-4). Numbers corresponding to each stacked barplot in Figures 4 and 5 denote the total number of monitors that met each classification criteria. Throughout the country, there are many more monitoring sites classified as rural than urban or suburban. This is true in every climate region except the West, which has slightly more urban than rural monitors. All regions contained at least 75 monitoring sites in this analysis except the Northwest (21 monitors) and the West North Central (17 monitors).

Figures 4 and 5 show that 25−75% of monitoring sites, depending on the region and season, show no statistically significant trend. It is possible that trends have been occurring at these sites, but that they are not statistically significant at the 95% confidence level. This could occur if interannual meteorological variability were substantial enough to obscure longer-term trends due to emissions changes. It is also possible that the heterogeneity of emissions reductions means that some monitor locations are affected more strongly than others.

Among the sites that do show statistically significant trends, there are several consistent features. First, across all ozone metrics and all classifications, increasing trends are much more frequent in the winter, while decreasing trends are much more frequent in the summer. Previous analysis using indicator ratios from ambient measurements[43] and satellite data[44] has shown that locations in the U.S. can transition from NOx-limited in the summer to VOC-limited in the winter. Similarly, some modeling work[45] has also reported that across-the-board NOx cuts would result in more widespread increases in wintertime ozone than summertime ozone which suggests that increases are in part due to the elimination of NOx titration. Second, increasing trends were more common at more urbanized locations, while decreasing trends were more common at less urbanized sites. This clear linkage between degree of urbanization and direction of the ozone trends also indicates that these trends may be directly related to changes in NOx emissions. It is important to note that in many cities, the

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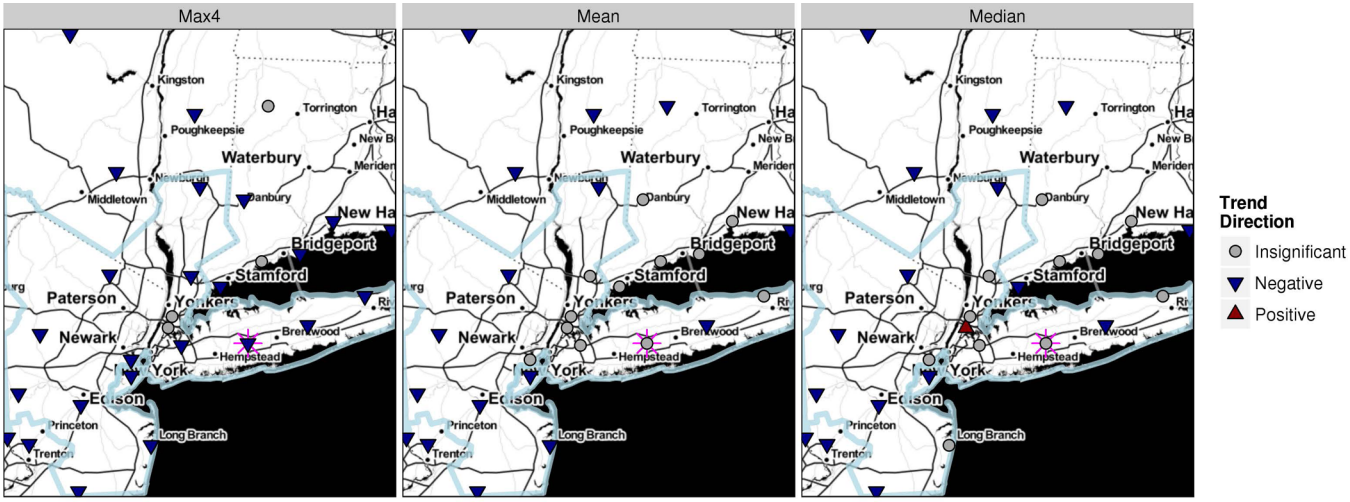

Figure 6. Map of summer season MDA8 ozone trends at specific monitors in the New York area. All upward and downward facing triangles represent statistically significant trends from 1998 to 2013 ($p < 0.05$), circles represent locations with no significant trends. Only monitors with at least nine years of data are displayed. The pink star indicates the site with the highest ozone concentration in 2013. The MSA border as defined by the U.S. census bureau is delineated by the light blue line. Left panel shows trends in summer season fourth highest MDA8 ozone values, center panel shows trends in summer season mean MDA8 ozone values, and right panel shows trends in summer season median MDA8 ozone values.

monitor with the highest 3-year average MDA8 ozone value is not located in the urban core.[6] Downward trends at suburban and rural monitors therefore represent the response of ozone at the locations with the highest ozone values. Finally, increases in ozone concentrations are seen most frequently on low ozone days, and decreases in ozone concentrations are seen most frequently on high ozone days. These trends are fairly consistent across all regions, although there are slightly larger percentages of monitors with increasing trends in the Southwest. In addition, slightly larger percentages of monitors with decreasing trends occur in the Southeast compared to the rest of the country. This is consistent with the fact that large biogenic VOC emissions in the Southeast make this portion of the U.S. more NOx limited than other regions. The next three paragraphs describe trends for high, low, and midrange ozone days in more detail.

Figures 4 and 5 show decreases in 95th percentile MDA8 ozone (summer and winter) and 75th percentile MDA8 ozone (summer) at almost all sites with significant trends. For the 95th percentile, exceptions are mostly found at urban sites in the West and Southwest, although these subcategories still show more decreasing trends than increasing trends. Winter 75th percentile MDA8 ozone trends varied by degree of urbanization, with suburban and rural sites showing mostly decreases and urban sites showing mostly increases. Nationally, the percentage of sites showing statistically significant decreases in high ozone diminishes with degree of urbanization.

Conversely, fifth percentile values (summer and winter) and 25th percentile values (winter) of MDA8 ozone generally either increased or had no trends. Only rural monitors during the summer showed more sites with decreasing than increasing fifth percentile MDA8 ozone trends. This is consistent with previous studies of baseline ozone.[22,25] Again, we note that increasing fifth percentile trends are more common in the more highly urbanized areas. This correlation with degree of urbanization suggests that, in addition to changes in baseline ozone, some of the increasing fifth percentile ozone concentrations may be tied to reductions in NOx emissions.

Trends in midrange ozone (mean and median MDA8 concentrations) are more varied and largely dependent on season and degree of urbanization. The vast majority of sites with significant trends show decreases in the summertime and increases in the wintertime, with the exception of rural sites for which trends are fairly evenly split between increasing and decreasing in the winter, but are predominantly decreasing in the summer.

Figure 6 visually depicts the urban versus nonurban summertime trends for the New York area, which has some of the most dramatic delineations between urban core and downwind ozone trends. This figure shows that summer median ozone is increasing at the most urbanized monitor in the area, but is decreasing downwind from 1998 to 2013. In addition, high ozone values are not changing significantly in the most urbanized areas, but are decreasing in the outlying areas including at the highest ozone monitor in the area indicated by the pink star. Similar figures can be found for Washington DC. Atlanta, Chicago Denver, Houston, and Los Angeles in the SI.

Figures S-5, S-6, and S-7 in the SI show the magnitude of urban, suburban, and rural statistically significant trends. Trends magnitudes are determined by the slope of regression lines for each monitoring site and are only shown for sites that had at least 9 years of data available. Decreasing 95th percentile ozone trends are generally in the range of 1−2 ppb/yr (15−30 ppb over the 15 year period) at urban, suburban, and rural monitoring sites in the summer and 0.5−1 ppb/yr in the winter, which demonstrates the substantial reduction of high ozone events that has been achieved in the U.S. Statistically significant trends in 50th percentile ozone concentrations show that the summer generally decreased by 0.5−2 ppb/yr. Conversely, wintertime trends in 50th percentile ozone generally show ozone increases of 0.1−1 ppb/yr, although some rural monitors show decreasing wintertime ozone concentrations of up to 2 ppb/yr. Similar to results reported by Cooper et al.,[25] ozone trends at rural sites show that median summertime ozone levels have decreased more dramatically in the Eastern U.S. than in the Western U.S., with most rural Eastern sites having decreasing trends of more than 0.5 ppb/yr

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Table 1. Broad Regional Annual Trends of Concurrent High and Low Percentile Summertime Ozone Concentrations (2008−2013) and Emissions of NOx and VOCs over the 2002−2011 Time Period[a]

Trend	Central	East North Central	Northeast	Northwest	South	Southeast	Southwest	West	West North Central
Urban ozone	5th % ↕ 95th % ↓	5th % ↑ 95th % ↓	5th % ↑ 95th % ↓	5th % - 95th % -	5th % ↕ 95th % ↓	5th % - 95th % ↓	5th % ↑ 95th % ↕	5th % ↑ 95th % ↓	5th % - 95th % -
Suburban ozone	5th % ↓ 95th % ↓	5th % ↓ 95th % ↓	5th % - 95th % ↓	5th % - 95th % ↓	5th % ↕ 95th % ↓	5th % ↓ 95th % ↓	5th % ↑ 95th % ↓	5th % ↕ 95th % ↓	5th % - 95th % -
Rural ozone	5th % ↓ 95th % ↓	5th % ↓ 95th % ↓	5th % ↓ 95th % ↓	5th % - 95th % ↓	5th % ↓ 95th % ↓	5th % ↓ 95th % ↓	5th % ↓ 95th % ↓	5th % ↓ 95th % ↓	5ht % ↓ 95th % -
NO_x emissions	↓	↓	↓	-	↓	↓	↓	↓	↓
VOC emissions	-	-	↓	-	↑	↓	↑	↓	↑

[a]The red upward ponting arrow indicates predominantly increasing trends, the blue downward pointing arrow indicates predominantly decreasing trends, − indicates no trends, and the green dual-pointing arrow indicates a mix of increasing and decreasing trends.

compared to rural Western sites where ozone concentrations increase or decrease at a rate of 0.1 to 0.5 ppb/yr. The magnitude of the decreasing trends in summertime 50th percentile ozone concentrations was greatest in the Southeastern U.S., with a substantial number of sites showing decreases of 1−2 ppb/yr. Finally, fifth percentile ozone concentrations generally increased by 0.1−1 ppb/year at urban, suburban, and rural monitors in the winter. In the summer, urban and suburban monitors show both increasing and decreasing trends of generally less than 0.5 ppb/yr, while rural monitors in the Eastern U.S. have decreasing trends of 0.1−1 ppb/yr, and rural monitors in California have decreasing trends of 0.1−0.5 ppb/yr. Generally, the magnitude of trends in fifth percentile ozone concentrations reported here for ground-level measurements is similar to those reported by Cooper et al.[25] for fifth percentile free tropospheric ozone concentrations between 1995 and 2011 (0.27 ± 0.39 ppb/yr). While the trends reported by Cooper et al. represent changes in transported ozone, the trends reported in this paper result from a combination of local and upwind emissions changes.

To demonstrate how changes in anthropogenic emissions of NOx and VOC might be driving these trends, Table 1 shows 1998−2013 trends of summer 5th and 95th percentile MDA8 ozone concentrations at urban and rural monitoring sites and of NEI NOx and VOC emissions from 2002 to 2011 aggregated by region. NO_x decreased from 2002 to 2011 in all regions. VOC emissions decreased in some regions, but increased or remained relatively constant in others. The regions with increasing or constant VOC emissions do not appear to show qualitatively different ozone trends than those regions in which VOC emissions have decreased. This suggests that the regional trends in ozone, which are fairly consistent across the U.S., are more likely being driven by decreasing NOx emissions which occur in every region. Lack of correspondence between VOC emissions decreases and ozone trends may be due to a variety of factors including (1) the mix of chemicals with a large range of reactivities (e.g., some urban areas are more VOC-limited than others); (2) complex nonlinear chemistry; and (3) the potential impact of the much larger magnitude of biogenic vs anthropogenic emissions on a regional scale. In addition, anthropogenic VOC reductions may cause local reductions in ozone in VOC-limited areas which are washed out when aggregated up to the climate region. Therefore, this high-level analysis should not be interpreted to mean that VOC controls have not been effective in specific locations in reducing ozone and producing other air quality benefits (e.g., reducing air toxics levels).

DISCUSSION

The ozone trends demonstrated by this analysis show that the highest U.S. ozone concentrations have been reduced over the past 15 years in response to a substantial decrease in ozone precursor emissions. These reductions have occurred during summer and winter, across urban, suburban, and rural locations and across all regions of the country. However, the substantial decrease in precursor emissions over this time period has produced seasonally varying changes in midrange ozone values (30−60 ppb) and increases on low days. This suggests that a different control strategy path (i.e., one that does not primarily target U.S. anthropogenic NOx emissions) may be required to reduce exposures to mid- and low-range ozone concentrations at certain times of year.

One interesting finding is that as a result of decreases on high days and increases on low days there has been a narrowing of the range of ozone concentrations over this period of decreasing NOx emissions. One other study has also shown this compression of the ozone range, but only for a few select urban sites.[29] Results from Cooper et al.[25] also suggest this is true for rural Eastern U.S. sites in the spring. To our knowledge, this is the first analyses to show this phenomenon may be occurring widely across the United States. The compression of the observed ozone distribution has also led to reductions in spatial gradients and temporal variability. Such changes in spatial and temporal ozone patterns have the potential to affect ozone exposure for individuals and populations. One implication is that health studies may benefit from more closely evaluating and accounting for effects of these changing patterns and the decreasing variability in order to reduce exposure measurement errors.

ASSOCIATED CONTENT

Supporting Information

Thirteen additional figures mentioned in the text, including regional emissions trends based on Xing et al.,[42] versions of Figure 4 and 5 created using the subset of monitors that operate year-round, maps of urban, suburban, and rural trends, and trends maps from six additional metropolitan areas. This material is available free of charge via the Internet at http://pubs.acs.org/

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Notes

The authors declare no competing financial interest.

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