

1 Author responses to all comments

2
3 Comments received 1 July 2015

- 4
- 5 • Comment 1 requested that the manuscript explicitly discuss to what extent manuscript
6 objectives were achieved.
 - 7 ○ Response: Conclusions section was revised (a paragraph added at beginning of
8 section) to summarize objectives and the degree to which they were met.
 - 9 • Comment 2 requested that Figure 1 be revised to include site elevation information.
10 ○ Response: Elevation data were added to a revised figure.
 - 11 • Comment 3 questioned to necessity of section 3.5 on diurnal air quality trends at the
12 monitoring site.
 - 13 ○ Section 3.5 was moved to the Supplementary Material along with all citations and
14 Table 4.
- 15

16 Comments received 1 July 2015

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- 18 • The primary comment (plus numbered comments 1, 2 and 3) requested a change in the
19 citation for parallel work done at the subject monitoring site.
 - 20 ○ Response: Changed the citation in the Reference list.
 - 21 • Comment 4 requested that Figure 2 be modified to enlarge text font.
22 ○ Response: Figure 2 was revised accordingly.
- 23
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1 **Trends in concentrations of atmospheric gaseous and**
2 **particulate species in rural eastern Tennessee as related to**
3 **primary emissions reductions**

4
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10

11 **Abstract**

12 Air quality measurements at Look Rock, Tennessee—on the western edge of the Great Smoky
13 Mountains National Park—were begun in 1980 and expanded during the 1980s to a National
14 Park Service (NPS) IMPROVE network station. Measurements were expanded again by the
15 Tennessee Valley Authority (TVA, 1999-2007) to examine the effects of electric generating unit
16 (EGU) emission reductions of SO₂ and NO_x on air quality at the station. Analysis of temporal
17 trends (1999-2013) has been conducted at the site in collaboration with activities related to the
18 2013 Southeast Atmosphere Study (SAS) at Look Rock and other southeastern U.S. locations.

19 Key findings from these trend studies include the observation that primary pollutant levels have
20 consistently tracked emissions reductions from EGUs and other primary sources in the region but
21 reductions in secondary pollutants such as particulate sulfate and, specifically, ozone have been
22 smaller compared to reductions in primary emissions. Organic carbonaceous material (OM)
23 remains a major contributor (30-40 percent in the period 2009-2013) to fine particulate mass at
24 the site, as confirmed by ACSM measurements at the site in 2013. A large portion (65-85
25 percent) of carbon in OM derives from modern carbon sources based on ¹⁴C measurements.
26 Important parameters affecting ozone levels, fine mass and visibility also include the specific
27 diurnal meteorology at this ridge-top site, its location in a predominantly mixed-deciduous forest,

1 and the presence of primary sources of precursors at distances of 50-500 km from the site in all
2 directions.

3 **1 Introduction**

4 Observations in and near the Great Smoky Mountains National Park (GSMNP) have been
5 included in many air quality trends analyses for national parks [e.g., Cai et al., 2011; Cooper et
6 al., 2012; U.S National Park Service, 2013]. Despite its rural location, the GSMNP is near
7 enough to major urban centers (e.g., Knoxville, TN; Chattanooga, TN; Birmingham, AL;
8 Atlanta, GA) and other areas of high air emissions (e.g., Ohio River and Tennessee River
9 valleys) that it represents a guidepost for tracking the progress and benefits of various air
10 pollution regulatory actions throughout recent history (e.g., acid rain emission reductions,
11 regional NO_x reductions for ozone control). Also, an era of low natural gas prices has made
12 switching from coal to natural gas very attractive to power producers facing the latest regulatory
13 pressures (U.S. Energy Information Administration, 2014) and these actions have triggered
14 further downward movement in emissions of both sulfur dioxide and nitrogen oxide emissions
15 that play a large role in determining air quality over the GSMNP. Deployment of a state-of-the-
16 art monitoring system for aerosol chemical speciation at the GSMNP Look Rock monitoring site
17 in 2013 (Budisulistiorini et al., 2015) offers a new opportunity to revisit air quality in the
18 GSMNP with a specific focus on aerosol composition. The 2013 deployment of an Aerodyne
19 Aerosol Chemical Speciation Monitor (ACSM)—with the ability to investigate the composition
20 of organic aerosol mass (abbreviated here as organic mass, or “OM”)—makes it especially useful
21 to understand the extent to which the air pollutant matrix over the region has changed since about
22 2000. This paper examines recent air quality trends at Look Rock to enable researchers to place
23 the 2013 data in proper perspective.

24 The Look Rock air quality research station in the GSMNP is located in a forest opening on the
25 ridge line of Chilhowee Mountain. This elongated mountain oriented southwest-northeast
26 borders the eastern edge of the Tennessee River valley. The ridge top lies 400-500 meters above
27 the valley floor while much higher mountains of the Great Smoky Mountains are found to the
28 east and south. Chilhowee Mountain is mostly covered by mixed deciduous forest and has been
29 forested for decades. Although low-density single-family housing lies in valleys on either side

1 of the site, its impact on gaseous and particulate concentrations at the site is infrequent and
2 usually small because of its elevation well below the monitoring site.

3 Look Rock has been the site of an IMPROVE network (Hand, 2011) station—designated
4 GRSM1—and operated by the U.S. National Park Service (NPS) since the 1980s. Activities at
5 the site have included intensive research studies (e.g., SEAVS, Day et al., 1996) in addition to
6 long-term IMPROVE network monitoring. The Tennessee Valley Authority (TVA)—in
7 collaboration with the NPS—added continuous measurements of gases in 1999 to complement
8 periodic intensive studies when aerosol composition was measured with time resolution of <24
9 hr (Cheng and Tanner, 2002; Tanner et al., 2005). Continuous measurements of fine mass,
10 sulfate, nitrate and aerosol carbon were also conducted in 2003-4 with the sponsorship of a
11 regional air management planning organization with the acronym “VISTAS” (“Visibility
12 Improvement State and Tribal Organization of the Southeast”) and described in Brewer and
13 Moore (2009). Other analyses of Look Rock data addressed the seasonal and diurnal variability
14 of aerosol composition and levels of precursor gases (Tanner et al., 2004b, 2005); the role of
15 aerosol acidity and meteorology on observed inorganic and organic aerosol levels (Olszyna et al.,
16 2005); and identification of the contribution of biogenic volatile organic compound (BVOC)
17 sources to aerosols based on ¹⁴C measurements from filtrated ambient air (Tanner et al., 2004a).

18 Subsequent advances in continuous measurement techniques for gases and aerosol constituents
19 led to enhanced measurement capabilities at the site beginning in late 2006. Supported by the
20 Tennessee Department of Environmental Conservation (TDEC) and the U.S. Environmental
21 Protection Agency (EPA), Look Rock was further instrumented (see Table 1) and designated a
22 rural NCore network station effective 1 January 2011. In addition to the continuous
23 measurements listed in Table 1, measurements of hourly aerosol organic and elemental carbon
24 levels have been made beginning in April 2011. Routine, continuous monitoring of aerosol
25 mass, sulfate, black carbon and primary and secondary gases—supplemented by enhanced
26 measurements during a series of intensive research studies—have produced a unique and
27 comprehensive air quality data base on background levels of species relevant to National
28 Ambient Air Quality Standards (NAAQS) for ozone and particulate matter for a high-elevation
29 site in the southeastern US.

1 Currently, special studies at the site include the deployment of an aerosol chemical speciation
2 monitor (ACSM) as described by Budisulistiorini et al. (2015) who also describe other
3 measurements made to accompany the aerosol data from the ACSM from February 2013 to
4 January 2014. An expanded research campaign was conducted 1 June – 15 July 2013 in
5 conjunction with the regional Southern Oxidant and Aerosol Study (SOAS) and the related
6 SENEX and NOMADSS airborne campaigns, all a part of the Southeast Atmosphere Study
7 (SAS) (UCAR, 2014/ https://www.eol.ucar.edu/field_projects/sas; U.S. National Atmospheric
8 and Oceanic Administration (NOAA), 2013, Southeast Nexus (SENEX): Studying the
9 Interactions between Natural and Anthropogenic Emissions at the Nexus of Air Quality and
10 Climate Change, Boulder, CO: NOAA/<http://www.esrl.noaa.gov/csd/projects/senex/>; EPA, 2014/
11 <http://blog.epa.gov/science/tag/southern-atmosphere-study-sas>). A review of the existing surface
12 data base is critically needed in light of an explosion of recent mechanistic studies of sources of
13 organic particles, their relation to precursor anthropogenic and BVOC emissions, and the role of
14 these emissions in the formation and accumulation of ambient secondary organic aerosol
15 (Hallquist et al., 2009; Hoyle et al., 2011; Schilling et al., 2013).

16 A comprehensive review is presented here of air quality trends at the Look Rock site covering its
17 period as an IMPROVE station, during periodic TVA activities from 1999 to 2007 and after
18 expanded continuous measurements were begun in 2007. This period is characterized as one
19 during which precursor emissions of species contributing to PM_{2.5} mass were being reduced
20 throughout the region. The following expands on analyses of visibility and ozone trends that
21 have been conducted using the site's long-term IMPROVE aerosol, light scattering, and gaseous
22 database (Hand et al., 2012; <http://vista.cira.colostate.edu/improve/Overview/Overview.htm>).
23 The objectives of this review are three-fold. First, this review determines the existence of
24 significant trends since 1999 in air emissions and air pollutant (including aerosol) precursors, and
25 associated changes in secondary air quality variables. Second, this study examines the degree to
26 which changes in emissions (of SO₂, NO_x and other species in the region) are associated with
27 reductions in ambient levels of secondary gaseous and particulate species. Finally, this effort
28 uncovers the extent to which changes in meteorological parameters may influence pollutant
29 trends.

1 **2 Analysis methods**

2 **2.1 Emissions in domain of influence**

3 A domain of highest potential impact from primary emissions on Look Rock air quality was
4 defined to evaluate the effects of changes in emissions on air quality at the site. This domain
5 (Figure 1) included most of Tennessee and Kentucky and portions of northern Alabama, northern
6 Georgia (including the Atlanta metropolitan area) and western portions of South Carolina, North
7 Carolina (including the Charlotte area), and Virginia. This “Look Rock emissions region” was
8 essentially an ellipse containing Look Rock and was 500 km along the longest (roughly west-
9 east) axis. The region was slightly skewed westward to account for prevailing winds. The intent
10 was to define an area in which changes in emissions of primary species could be expected to
11 cause the highest changes in concentrations of these and associated secondary species at Look
12 Rock with transport times of order 1-2 days at most (i.e., shorter in winter when winds are
13 greater and longer in summer when winds are lighter and atmospheric chemistry is more active).
14 It is likely that Look Rock concentrations of secondary species such as sulfate aerosol do not
15 respond proportionately to changes in precursor levels within the defined emission region.

16 Emissions data were obtained at the state level from the EPA as part of the National Emissions
17 Inventory (NEI) for each year from 1999 through 2013. These data are summarized online at
18 <http://www.epa.gov/ttnchie1/trends/>. County-wide emissions were taken from NEI inventories
19 released by EPA for 1999, 2002, 2005, 2008 and 2011. Electrical generating unit (EGU)
20 emissions were also obtained for SO₂ and NO_x for the domain on an annual basis over this period
21 (<http://ampd.epa.gov/ampd/QueryToolie.html>). Graphs of the NEI results (Figure 2a and b)
22 shows moderate downward trends in emissions—trends that accelerated for NO_x and SO₂ in the
23 period between 2008 and 2011. Downloaded data files obtained for the 1999 NEI inventory
24 were incomplete for CO, NH₃, NO_x, VOCs (volatile organic compounds) for unknown reasons
25 and both primary PM categories (PM₁₀-PRI and PM_{2.5}-PRI) are not shown. Also, county-level
26 and EGU data for 2013 were not available at the time this analysis was started so total domain
27 emissions were extrapolated from 2012 data and the 2013 state-level EGU:Total emission ratio
28 in the NEI data base. The NEI data for total SO₂ emissions (Figure 2b) are consistent with
29 trends in the EGU data. Total regional NO_x emissions (Figure 2b) are likely to be a better
30 predictor of Look Rock ozone than EGU NO_x emissions. For subsequent statistical analysis, the

1 annual variation in total NO_x emissions was estimated using the annual EGU NO_x emissions and
2 the ratio between EGU and non-EGU NO_x emissions determined when data from both were
3 available at the county level. Interpolation of this ratio (from a proportional comparison with the
4 annual state-wide ratios) to other years was done to estimate total NO_x within the Look Rock
5 domain for years without a detailed county-level inventory. The EGU:Total SO₂ emissions ratio
6 decreased from 75 to 51 percent over the 15-yr interval. The NO_x emissions ratio decreased
7 from 34 to 12 percent over the same time frame.

8 **2.2 Techniques and data sources for gases and aerosols**

9 The filter-based and continuous measurements made at Look Rock are listed in Table 1 and
10 represent methodologies used since 2007. The starting dates for the NPS vary from the 1980s
11 for IMPROVE filter measurements through about 2002 when the TEOM (Tapered Element
12 Oscillating Microbalance) instrument was installed. IMPROVE filter-based ammonium data are
13 available since 1998. Concentration data for gases—SO₂, NO-NO₂-NO_y, CO and O₃—and for
14 aerosol mass and chemical constituents [sulfate, organic carbon (OC), elemental carbon (EC) or
15 black carbon (BC)]—were acquired for the period from 1999 to 2013 for all time periods in which
16 there were continuous records from which valid annual, seasonal and monthly data could be
17 calculated.

18 Data for SO₂ at Look Rock are from several sources including the CASTNET station at Look
19 Rock, short-term campaign hourly data and continuous SO₂ data (reported as 1-hr averages)
20 acquired since March 2007 as part of the long-term monitoring initiative. Continuous hourly-
21 averaged data examined in the trends analyses below included sulfate, SO₂ and NO-NO_y data
22 from previous studies (e.g., VISTAS 2003 and 2004, and summer research intensives) at the site,
23 and used the same instruments or earlier prototypes as listed in Table 1. Organic and total
24 aerosol carbon were measured from April, 2003 through the end of 2004 by the R&P Model
25 5400 analyzer (an instrument description is available in Wittig and Hyslop, 2001); OC & EC
26 data obtained since April 2011 were obtained using Sunset Labs OCEC analyzer (Birch and
27 Cary, 1996; Bae et al., 2004). The annual average data for OC and EC at the site were obtained
28 from every-third-day, or twice-weekly 24-hr filter samples analyzed by the IMPROVE TOR
29 method (Chow et al., 1993). Operation of the instrumentation and the techniques used, their
30 limits of detection, precision, accuracy, and calibration procedures are consistent with EPA data

1 quality assurance requirements as outlined in EPA NCore network strategy (National Ambient
2 Air Monitoring Strategy: <http://www.epa.gov/ttn/amtic/files/ambient/monitorstrat>). The
3 IMPROVE TEOM PM_{2.5} mass had to be corrected to adjust for the fact that the NPS operated
4 the TEOM from the beginning at 30°C but used the calculation algorithm originally designed for
5 operation at 50°C. To avoid bias in reported mass (the lower temperature better preserves
6 ammonium nitrate and some semi-volatile OC) compared with standard filter-based PM_{2.5} data,
7 TEOM values were corrected based on an algorithm developed to produce results which were
8 highly correlated with reported FRM PM_{2.5} mass with essentially zero intercept

9 Annual quarters 1 (January-March), 2 (April-June), 3 (July-September) and 4 (October-
10 December) were defined as winter, spring, summer and autumn, respectively, for determining
11 seasonal data trends for investigating meteorological influences. The approach permits spring
12 and summer to be consistently the periods with highest temperature (*T*), solar radiation, and leaf
13 coverage, while fall and winter have lower *T* and solar radiation and very little deciduous leaf
14 cover. Major differences in trends are unlikely when compared to seasonal data binned
15 according to solstice and equinox dates or using alternate definitions such as winter = December-
16 February.

17 **2.3 Influence of meteorological patterns**

18 Temporal patterns in meteorology may influence Look Rock air quality due to the dependence of
19 atmospheric chemistry and pollutant transport on variations in temperature, solar radiation, cloud
20 cover, precipitation and wind patterns. Patterns were based on data collected at Look Rock and
21 the nearest National Weather Service (NWS) observations at the Knoxville airport. Data from
22 these two sites are described in Supplemental Material. Few significant (i.e., >95 percent
23 confidence) trends were identified over the time period from 1999 through 2013.

24 Atmospheric transport was inferred from computed three-dimensional air trajectories. Twenty-
25 four hour air trajectories ending at Look Rock were computed using the NOAA HYSPLIT Model
26 (www.arl.noaa.gov/HYSPLIT_info.php; Draxler and Hess, 1998; Draxler, 1999; Draxler and
27 Rolph, 2014). Trajectories were based on the NOAA-NCAR Global Reanalysis meteorological
28 data set and used diagnosed vertical velocity to determine vertical air parcel motion. Trajectories
29 were derived for days when TEOM data indicated fine particulate levels in either the lowest or

1 highest 5 percent of the distribution of all hourly PM_{2.5} concentrations in each month. This
2 ensured that we examined trajectory classes that contributed to the full range of particulate levels
3 at Look Rock. Two or more trajectory analysis days were selected monthly during 2007-2013
4 (ending in June of 2013) yielding a data set of 174 trajectories. Trajectories were computed to
5 arrive at 100, 500 and 1500 m above Look Rock at local midnight on the trajectory analysis
6 days. Trajectories arriving at 1500 m agl were so similar to those for 500 m that they provided
7 little additional information and were not included in a subsequent cluster analysis.

8 Cluster analysis is a useful aggregation tool for classifying data into groups with similar
9 locations in *K*-dimensional space (Wilks, 2006). Hourly upwind trajectory coordinates were
10 available for each combination of trajectory arrival date and trajectory height. Trajectory latitude
11 and longitude coordinates at 12 and 24 hours upwind and at 100 and 500 m arrival heights were
12 the focus of a cluster analysis designed to identify similar atmospheric transport pathways
13 approaching Look Rock. In this case *K*=2 and spatial coordinates were defined using latitude
14 and longitude transformed into orthogonal variables with unit variance and mean of zero. The
15 transformation was made using principal component analysis (Preisendorfer, 1988) for each
16 upwind time.

17 Cluster analysis yielded groupings (clusters) of trajectories that represented the full range of 5-hr
18 average PM_{2.5} concentrations centered on daily minimum or maximum hourly values. Cluster
19 PM_{2.5} averages showed a wide range in values suggesting that each cluster represented a unique
20 set of characteristics due to different combinations of trajectory geography and speed. Temporal
21 trends (2007-2013) within clusters were computed when possible and these trends were
22 arbitrarily sorted into three groups based on mean PM_{2.5} values [low (<10 μg m⁻³), medium (10-
23 20 μg m⁻³) and high (>20 μg m⁻³)]. Significant trends were only computable for the largest
24 clusters because they had sufficiently large numbers of trajectory days and represented years.
25 Even so, trend values for individual clusters are not as important as cluster trends sorted by PM_{2.5}
26 concentration groupings. A comparison across PM_{2.5} groups indicated that temporal trends were
27 significant and downward only for clusters that fell into the high PM_{2.5} group. In the subsequent
28 discussion, the trajectory cluster number refers to the hierarchy of clusters starting with the
29 cluster (assigned a value of one) having the most trajectories for which some predetermined
30 criteria are met that define a property of the trajectories. In the present study, Ward's method of
31 in-cluster variance minimization was used (Wilks, 2006). Subsequent (lower number) clusters

1 have fewer trajectories. Clusters are built starting with each trajectory in its own cluster and
2 aggregating trajectories on subsequent passes through the data. This process can continue only
3 until all trajectories are clustered into one group (such an endpoint has no value, however). The
4 analyst must select some number of clusters >1 for which the highest ranked clusters contain a
5 useful amount of trajectories that are classified. Once a trajectory is placed into a cluster it is not
6 removed.

7 **2.4 Trend determination**

8 In the subsequent discussion, a determination of “significance” when evaluating the presence of
9 a trend, when comparing changes in emissions and air pollutant concentrations or when
10 comparing air quality and meteorology was based on a statistical association computed (using
11 least-squares regression) to have a p value <0.05. Temporal changes in both domain-wide annual
12 NO_x and SO₂ emissions (all sources) were significant with p <0.001 (i.e., confidence exceeding
13 99.9 percent). Seasonal emissions were not estimated (seasonal emissions for non-EGU sources
14 must be modeled and this adds another level of complexity and uncertainty to the trends
15 analysis). Trends in total seasonal emissions are expected to be similar to annual trends with
16 some seasons experiencing more changes than others depending on the timing of specific
17 regulatory drivers. This assumption of similarity is used in all subsequent comparisons between
18 seasonal air quality values and emissions and contributes to uncertainty when comparing them.
19 The convention for comparing emissions, air quality and meteorological values averaged over
20 time (annual or seasonal) involved converting actual values into deviations from the 15-year
21 average and then normalizing the deviation by the standard deviation of the 15-year value:

$$22 \quad \hat{x} = \frac{x - \bar{x}}{\sigma_x}. \quad (1)$$

23 In Eq. (1) the overbar denotes the multi-year average of variable x while σ_x denotes its
24 corresponding standard deviation. This scaling of x reduces the impact of outliers (<5 percent of
25 all air quality values of \hat{x} fell outside $\pm 2\sigma_x$) and allows for a straightforward comparison between
26 different data sets. Thus, when comparing two variables \hat{x}_1 and \hat{x}_2 , a significant association
27 with mean regression slope $\Delta \hat{x}_2 / \Delta \hat{x}_1 = 1$ implies that a one-standard deviation change in variable
28 2 is associated with a one-standard deviation change in variable 1. Comparing different variable

1 associations in this manner allows a direct comparison between variable sensitivities (e.g.,
2 $\Delta \hat{x}_2 / \Delta \hat{x}_1$ versus $\Delta \hat{x}_3 / \Delta \hat{x}_1$). In the current context, x represents the annual or single-season
3 average (or sum as in the case of precipitation) of a variable such as ozone concentration or
4 temperature.

5 **3 Results**

6 **3.1 Annual trends in gaseous concentrations compared to emissions of primary** 7 **species**

8 **3.1.1 Ozone**

9 Annual and seasonal averages of one-hr O₃ data obtained from NPS for the period 1999-2013 are
10 plotted in Figure 3. The trend for the O₃ season (April-October) is not shown because it is nearly
11 indistinguishable from that for the third quarter (July-August) labeled “summer”. The trends are
12 similar to that observed for O₃ using the National Ambient Air Quality Standard (NAAQS)
13 metric—based on the annual fourth highest of the maximum daily 8-hr average (not plotted here)
14 and indicate only a slightly negative trend for 1999-2011. This change is much more modest
15 (about 0.3 ppbv yr⁻¹ or <1 percent yr⁻¹) than the trend in domain emissions of NO_x (an O₃
16 precursor) for the 2002-2011 period. The O₃ trends for the second (-0.5 ppbv yr⁻¹; -0.9 percent
17 yr⁻¹; -0.13σ yr⁻¹) and third quarters (-1.0 ppbv yr⁻¹; -1.9 percent yr⁻¹; -0.15σ yr⁻¹) were significant
18 at $p < 0.05$ but this was not true of the annual (-0.3 ppbv yr⁻¹ / -0.11σ yr⁻¹), first-quarter (0.2 ppbv
19 yr⁻¹ / 0.09σ yr⁻¹) and fourth-quarter (0.1 ppbv yr⁻¹ / 0.03σ yr⁻¹) changes. Likewise, the association
20 between quarterly O₃ and annual NO_x emissions was positive and highly significant for the
21 spring and summer quarters ($0.7 < \Delta \hat{x}_{O_3} / \Delta \hat{x}_{NO_x} < 0.8$), when high photochemical reactivity should
22 enable regional emissions to have the greatest impact on ozone observed at Look Rock, but not
23 for the other quarters when ozone had small, positive changes.

24 Zero or slightly upward O₃ patterns during the first and fourth quarters—when photochemistry is
25 low and contributions from local and regional sources are at a minimum—have occurred despite
26 reductions in regional NO_x emissions. These observations may be due in part to reduced emitted
27 NO_x titrating less O₃ during the winter and autumn periods. If true, this pattern implies the
28 relative importance of long-range (i.e., background) ozone transport during the cooler seasons.
29 Cooper et al. (2014) reviewed global ozone data trends and noted significant increases in ozone

1 across the Pacific Ocean (from Japan to Hawaii and the Pacific coast of western North America)
2 since at least 1990, with annual levels climbing from 30-40 ppbv in the early 1990s to 35-45
3 ppbv by 2010 along the U.S. west coast (changes equal to $0.27 \text{ ppbv yr}^{-1}$). Annual average Look
4 Rock data do not indicate similar increases but some influence from long-range transport cannot
5 be ruled out in light of the 0.2 ppbv yr^{-1} increases during the winter quarter. Large regional
6 decreases are noted across the eastern U.S. in summer and increases are reported in winter
7 (Cooper et al., 2014) during the first part of the 21st century, in agreement with Look Rock data.
8 However, the Look Rock springtime O_3 decrease contrasts with little change elsewhere in the
9 eastern U.S. but this discrepancy may be caused partly by a different definition of “spring”
10 (Cooper et al. used March-May).

11 Trends in the O_3 regulatory metric (annual 4th highest daily maximum 8-hr average, “4th8h”) in
12 the U.S. have been reported by the U.S. EPA (www.epa.gov/airtrends/ozone.html#oznat). These
13 more extreme values exhibit greater decreases since 1990 than found in annual average values, in
14 part because air management schemes are focused on reducing the highest concentrations. Using
15 over 100 sites in rural areas across the U.S, EPA shows changes in the 10th and 90th percentile
16 values of the 4th8h of -0.3 and $-1.1 \text{ ppbv yr}^{-1}$, respectively. At Look Rock the 4th8h has declined
17 at a comparatively rapid rate of 1.9 ppbv yr^{-1} since 1999. Thus, Look Rock data indicate
18 improvements in the worst O_3 levels at a faster rate than seen at most rural sites nationally.

19 **3.1.2 SO_2**

20 Annual SO_2 concentrations, based on high-sensitivity hourly pulsed fluorescence data measured
21 at Look Rock, are available from 2007 to present and show about a 25 percent yr^{-1} decrease over
22 the period, compared to a mean reduction rate of 11 percent yr^{-1} since 1999 based on CASTNET
23 weekly SO_2 data (Table 2). This reflects the large reductions in SO_2 emissions in the domain.
24 Compare the relative reduction rate of SO_2 with the reduction rate expressed as a fraction of a
25 standard deviation in the concentration (Table 2): 11 percent yr^{-1} is equivalent to an annual
26 decline of $0.42\sigma \text{ yr}^{-1}$ (i.e., almost a half of a standard deviation per year).

27 Annual averages of SO_2 concentrations from 1999 to the present from CASTNET weekly data
28 and continuous hourly pulsed fluorescence data are shown in Figure 4 along with a comparison
29 with NEI and EGU emissions of SO_2 in the domain (see discussion below). Hourly, continuous
30 data for SO_2 averaged on a shorter, monthly basis show much more month-to-month variability

1 (Figure 5) due to a combination of seasonal changes in emissions, gas-to-particle conversion and
2 meteorology-driven scavenging rates. Monthly comparison with hourly SO₂ data is less than
3 ideal because CASTNET SO₂ data are averaged weekly but, given the similarity in changes, it is
4 reasonable to expect that the conclusions would be the same. The CASTNet data do provide a
5 longer time series for comparison with emissions. A comparison of emissions and CASTNet
6 concentrations (i.e., $\Delta \hat{x}_{SO_2(emiss)}$ versus $\Delta \hat{x}_{SO_2(conc)}$) for 1999-2013 produces a highly significant
7 correlation ($p < 0.0001$) with $\Delta \hat{x}_{SO_2(emiss)} / \Delta \hat{x}_{SO_2(conc)} = 0.97$. A similar result was found comparing
8 annually-averaged hourly SO₂ with SO₂ emissions for 2007-2013: $p = 0.001$ and
9 $\Delta \hat{x}_{SO_2(emiss)} / \Delta \hat{x}_{SO_2(conc)} = 1.38$. The sensitivity value > 1 since 2007 is probably caused by large
10 additional SO₂ emission reductions outside the regional domain. Seasonal breakdowns in these
11 comparisons are further enumerated in Table S-2 of the Supplemental Material.

12 **3.1.3. NO_y**

13 Data for NO-NO_x-NO_y concentrations at the site are relatively sparse prior to March 2007
14 (Figure 5). Data since 2007 (Table 2) indicate a strong downward trend in NO_y at an average
15 rate of almost 15 percent per year. This compares with the negative trend in SO₂ (-25 percent yr⁻¹)
16 for the same period. The ambient NO_y trend was significantly negative for all 4 quarters of the
17 year (trend ≈ -0.4 ppbv yr⁻¹ independent of season). This result is similar to that for regional NO_x
18 annual emissions. However, despite similar tendencies, ambient NO_y was not significantly
19 associated with annual NO_x emissions except during the third and fourth quarters. This is likely
20 due to the extreme nonlinearity in NO-NO₂-NO_z (NO_z = NO_y - NO_x) chemistry and the spatial
21 inhomogeneity of NO_y. It is possible that the significant associations during two quarters were
22 coincidental or represented a serendipitous agreement between regional emissions trends and
23 trends for sources directly impacting Look Rock air quality during those periods.

24 In addition, O₃ was not significantly associated with NO_y except during the third (summer)
25 quarter when a positive association was determined ($\Delta \hat{x}_{O_3} / \Delta \hat{x}_{NO_y} = 0.76$). Again, this may be
26 because Look Rock NO_y data do not reflect regional NO_x emissions. Look Rock ozone appears
27 to only respond significantly (in a positive sense) to local NO_y levels during the summer quarter
28 when weak transport conditions and high photochemical rates coincide. In that quarter, NO_y was
29 significantly linked to only two variables: wind speed (positive sense) and cloud cover (negative
30 sense). This also supports the finding of positive trends observed in ozone for the first and fourth

1 quarters despite the fact that regional NO_x emissions were in strong decline. The conclusion
2 from these results is that local conditions at Look Rock that are influenced strongly by
3 atmospheric photochemical processes (especially ozone and secondary organic aerosol
4 formation) are only characterized by Look Rock measurements during the summer quarter. Data
5 from other times of the year indicate a blend of impacts from local and more distant emissions,
6 consistent with the stronger atmospheric transport and/or slower photochemical processing
7 typical for those seasons.

8 **3.2 Annual trends in aerosol mass and composition**

9 All aerosol species for which data are available exhibited an average 2007-2013 negative trend
10 of between 8 and 15 percent per year. Only ozone—which has had a modest upward trend in
11 winter and fall quarters—experienced a very small negative annual trend coinciding with the
12 strong negative trends for the other species.

13 Data used to evaluate trends in aerosol mass and composition at Look Rock include the
14 following: mass and composition data from the IMPROVE network from analysis of every-
15 third-day filter samples (twice-weekly prior to 1999) which were examined for the time period
16 1999 to the present for all trend analyses, and retrospectively back to 1988 for mass, sulfate,
17 ammonium (from 1998 only), OC and EC levels. The annual averages are shown in Figure 6
18 and show smoothly decreasing trends with an accelerated decrease in the 2007 to 2009 period for
19 sulfate that clearly influenced trends in PM_{2.5} mass. Annual percent reductions in concentrations
20 based on IMPROVE data are shown in Table 2 and range from 2.0 percent to 3.6 percent per yr⁻¹
21 since 1988. Note that the levels of OC as measured by the IMPROVE method actually increased
22 at Look Rock from 1988 to 1998 then decreased from 1998 to the present at a net rate of 2.7
23 percent yr⁻¹.

24 Comparing Look Rock PM_{2.5} trends with those from other locations is more complicated than for
25 O₃ because aerosols impacting a given site often come from a different mix of pollution source
26 types and pollutant precursor species. Across the eastern U.S. the predominant source of PM_{2.5}
27 has been sulfate from SO₂ emitted by fossil fuel combustion. However, some locations are more
28 influenced than others by biomass burning, biogenic organic aerosols, windblown dust and so
29 forth (see, for example, Chalbot et al., 2013 whose PM_{2.5} source analysis included many of the

1 same regions that impact Look Rock). Trends in these different source types influence overall
2 trends in PM_{2.5} pollution. The U.S. EPA tracks trends in annual average PM_{2.5} concentrations at
3 both the national and regional level (www.epa.gov/airtrends/pm.html#pmreg). Data from 2000-
4 2013 indicate national trends in 10th and 90th percentile levels of PM_{2.5} pollution of -0.19 and -
5 0.51 µg m⁻³ yr⁻¹, respectively. At Look Rock the trend for this same period was -0.46 µg m⁻³ yr⁻¹
6 ¹, or near the upper end of the nationally observed trends. Regionally, the Look Rock trend
7 compares with those from nearby regions (all units in µg m⁻³ yr⁻¹): -0.46 (Ohio River Valley
8 which includes Tennessee/Look Rock in EPA's regional definition), -0.42 (northeastern U.S.), -
9 0.41 (southeastern U.S. which includes states immediately south and east of Look Rock), and -
10 0.24 (south-central U.S., including Texas). Thus, the Look Rock PM_{2.5} trend is most similar to
11 that for the Ohio River Valley region which is a major source region for SO₂.

12 Since 1999 the changes in aerosol mass and its major constituents are all in a narrow range from
13 3.1 to 4.2 percent yr⁻¹ despite significant inter-annual variability. Comparing the results reported
14 in Table 2 for sulfate with trends reported by Hand et al.(2012), there is excellent agreement in
15 trends (-4.2 percent yr⁻¹ for Look Rock compared to -3.1 percent yr⁻¹ for six southeastern long-
16 term (1992-2010) IMPROVE sites) and -4.4 percent yr⁻¹ for 13 short-term southeastern sites
17 (2001-2010). This suggests that the trends observed at Look Rock are typical of the non-urban
18 southeast and that the observed decreases in PM_{2.5} mass levels are due to decreases in both
19 sulfate and organic carbon. Ammonium levels are expected to decrease with sulfate assuming
20 the extent of neutralization of aerosol sulfate does not change. However ammonium was not
21 measured at the site in a long-term context. Levels of other aerosol constituents not shown in
22 Figure 6 (e.g., metal oxides) may also have decreased during the period but, with the possible
23 exception of nitrate during winter months, these constituents contribute at most a few percent of
24 the PM_{2.5} mass. For example, in 2001, nitrate as NH₄NO₃ in FRM filter measurements made at
25 Look Rock averaged 12.9 percent of PM_{2.5} mass in winter but <1 percent averaged over the
26 remaining seasons (Tanner et al., 2004b). More recently, Budisulistiorini et al. (2015) reported
27 that in 2013 NH₄NO₃ varied between 4 (summer) and 9 (winter) percent of total PM₁ mass
28 ("PM₁" denotes aerosols with aerodynamic diameters <1 µm) mass.

29 Comparisons of aerosol components against emissions revealed that sulfate, OC and EC (and by
30 extrapolation, PM_{2.5}) were significantly associated with one or both emission species for at least
31 the spring and summer quarters. Details are provided in Table S-2 of Supplemental Material.

1 The strong covariance between SO₂ and NO_x emissions produces cross-correlations with any
2 aerosol component that is significantly associated with at least one of the emissions species.
3 However, sulfate was more closely associated (higher r^2 and lower p values; $p < 0.001$) with SO₂
4 emissions for each quarter of the year ($0.60 < \Delta \hat{x}_{sulf} / \Delta \hat{x}_{NO_x} < 0.76$ and $0.76 < \Delta \hat{x}_{sulf} / \Delta \hat{x}_{SO_2} < 1.0$).
5 Conversely, OC was strongly associated with NO_x emissions during the spring ($p < 0.01$) and
6 summer ($p < 0.001$) quarters and OC was associated to a lesser degree with spring, summer and
7 autumn SO₂ emissions ($0.66 < \Delta \hat{x}_{OC} / \Delta \hat{x}_{NO_x} < 0.76$ and $0.44 < \Delta \hat{x}_{OC} / \Delta \hat{x}_{SO_2} < 0.65$). One
8 relationship that stands out is between OC and ambient NO_{y(g)}. Similar to what was reported in
9 the previous section regarding ozone, OC was significantly associated with NO_{y(g)} only during
10 the third quarter ($\Delta \hat{x}_{OC} / \Delta \hat{x}_{NO_y} = 0.86$), perhaps reflecting a unique combination of factors
11 occurring only during summer. Finally, EC was more closely linked with SO₂ emissions than
12 NO_x emissions for each quarter ($p \leq 0.001$ for SO₂ in all seasons) although the SO_{2(emiss)}}:NO_{x(emiss)}}
13 covariance muddles interpretation of the data.

14 Another notable change in aerosol composition is reflected in the relative abundances among the
15 primary species measured at Look Rock. The change in relative abundances of the major fine
16 particle types is best seen by examining the IMPROVE data from 1999 and 2013 (Figure 7). The
17 ammonium sulfate component is much smaller in 2013 as already described. Ammonium nitrate
18 remained a very small component but did increase somewhat in response to the greater
19 availability of ammonium. The relative abundances of organic aerosol and EC mass remained
20 about the same despite decreases in concentrations. Even the “unknown” component—believed
21 to be associated with an unattributed organic contribution or water—decreased by just over 50
22 percent (nearly the same amount as the organic component). It is important to note that the
23 IMPROVE estimated organic mass is determined by applying a fixed adjustment factor of 1.8 to
24 measured OC concentrations to account for the other elements associated with the unidentified
25 organic compounds (Malm et al., 2011).

26 3.3 Relationship to long-term trends in meteorology

27 It is reasonable to consider whether these trends in aerosol and trace gas levels are associated
28 with meteorological trends at Look Rock. Data from the NWS at the nearby Knoxville airport in
29 Maryville and from Look Rock indicate similar patterns since 1999. There is no evidence of

1 either annual or seasonal precipitation or temperature trends, nor are these meteorological
2 variables correlated with measured air quality changes (details on the long-term trends in
3 temperature and precipitation and the year-to-year variability in those trends at Look Rock are
4 given in the Supplemental Material). Likewise, no significant 15-yr trends in wind direction
5 frequency, cloud cover or solar radiation have been detected. A slight upward trend in solar
6 radiation since 2007 was found which would suggest an increase in photochemistry, but the net
7 effect on secondary aerosol production is unclear.

8 A small decline (not statistically significant) since 1999 in the number of high moisture hours
9 (i.e., those with relative humidity >90 percent) was observed during all seasons but autumn.
10 Considering that the inter-annual variations in this parameter were large, the effect on observed
11 aerosol trends (such as through reduced heterogeneous chemistry) is likely to be small. The only
12 statistically significant, incontrovertible meteorological trend is that of wind speed which has
13 declined steadily since 1999 at Look Rock. This is consistent with wind speed measurements
14 elsewhere in the United States (Pryor et al., 2009; Milton, 2010; Pryor and Ledolter, 2010). The
15 source of this decline is unknown but could be linked to climate change (Pryor et al., 2009) or to
16 physical changes surrounding measurement sites. There is no evidence, however, that physical
17 characteristics have changed significantly in the Look Rock vicinity. A decline in wind speed
18 would reduce distances traveled by pollutants before arriving at Look Rock. This could increase
19 both primary pollutant concentrations—due to a decrease in atmospheric dilution—and
20 secondary pollutants by providing more time for atmospheric conversion. It would also mean an
21 increase in the relative contribution of local emissions to Look Rock compared to more distant
22 sources. In any case, declining wind speeds are not likely the reason behind the observed
23 decreases in pollutant concentrations at Look Rock unless a very non-linear process is involved.

24 Some meteorological factors, when viewed on a quarterly basis, were found to be significantly
25 associated with measured air quality values although they were not contributory to long-term
26 trends. Table 3 summarizes the notable linkages between air quality and meteorology at Look
27 Rock (in all cases $p < 0.05$). Details of these associations are described in Supplemental Material
28 to allow comparisons of relative sensitivities across different species and meteorological factors.
29 The quarter of the year when a significant association was identified is noted in the table for each
30 combination of air quality and meteorological factor. The summer (third) and autumn (fourth)
31 quarters had the most significant linkages. Wind speed was most frequently associated with air

1 quality (positively in all cases). Thus, speed is not an indicator of dilution but rather something
2 else, perhaps an increasing linkage between Look Rock air quality and local emissions with an
3 increasing role for “Look Rock domain” emissions as speed declines. Ozone, OC and EC are
4 occasionally negatively associated with precipitation which acts as a scavenger of pollutants.
5 Ozone and OC are both positively linked with temperature during summer with higher
6 temperatures associated with more biogenic precursor emissions (Lamb et al., 1993) and faster
7 photochemical reactions (e.g., Alley and Ripperton, 1962; Seinfeld and Pandis, 1998). Cloud
8 cover and solar radiation generally are anti-correlated. Insolation (reduced by cloud cover) is a
9 driver for photochemistry although neither it nor clouds appear as significant drivers during all
10 quarters. Insolation was negatively associated with sulfate during the spring quarter for reasons
11 that are not apparent. Also unexpected is the negative association between ozone/OC/EC and
12 high relative humidity conditions (i.e., frequency of humidity levels >90 percent) at Look Rock.
13 Typically, clouds impact the monitoring site directly (i.e., place the site in fog) under such humid
14 conditions. The occasional negative association between some air quality levels (i.e., ozone and
15 OC) on one hand and cloud cover and high humidity on the other might represent the same effect
16 on photochemistry but the physical basis for an impact on EC is not obvious.

17 **3.4 Seasonal trends in concentrations of primary and secondary aerosol** 18 **species**

19 Although located in the southeast US, the Look Rock site experiences four distinct seasons and
20 seasonal differences in meteorology and atmospheric chemistry can significantly affect trends in
21 concentrations and the degree to which changes in primary emissions are reflected in measured
22 air quality. Fine mass by either filter or continuous TEOM methods trends down for all seasons
23 (Figure 8), but the trend is dramatically sharper for the spring and summer data, especially for
24 the 2007-2009 period. This sharp decline is probably due to a combination of meteorology and
25 emissions reductions: 2009 was a wetter, cooler year than 2007, with 2008 being intermediate
26 between the two, which would reduce the amount of photochemical processing and secondary
27 aerosol formation. The period, 2007-2009, also saw the largest reductions in EGU emissions of
28 both SO₂ and NO_x within the domain. As a result, annual averages of TEOM-based PM_{2.5} mass,
29 hourly sulfate, and IMPROVE OC decreased by 42, 52 and 40 percent, respectively, from 2007

1 to 2009 compared to 54 percent and 63 percent reductions in total SO₂ and NO_x emissions
2 (respectively) in the domain.

3 Consistent with these observations, observed sulfate levels at Look Rock declined more sharply
4 in spring and summer compared to fall and winter (Figure 9) and again declines were most
5 pronounced in the 2007-2009 period. However, the trend in summer season sulfate was more
6 sharply downward than in the spring season and, since about 2009 there have been no significant
7 differences between average spring and summer values. Along with seasonal changes in
8 emissions, differences in meteorological parameters between spring and summer seasons—
9 specifically average wind speeds and precipitation totals (both lower in summer)—may have
10 contributed to accumulation of higher sulfate levels in summer vis-à-vis spring in the period
11 before these sharp decreases in SO₂ emissions occurred. However, it is unclear what this
12 observation implies about the relative importance of gas-phase and aqueous-phase SO₂-to-sulfate
13 conversion mechanisms and the relative pathways for SO₂ removal (reaction vs. deposition) in
14 the region in the future.

15 Figure 10 shows the IMPROVE data for OC, parsed by season for the 1999-2012 period. With
16 the exception of some anomalously high values of unknown origin in the fall seasons of 2000
17 and especially 2001, the trend in OC values is generally down (about 30 percent decrease in
18 2012 compared to 1999) but not as much as for fine mass and sulfate (55 percent and 58 percent,
19 respectively). There are two important caveats: comparing Figure 10 with the longer term OC
20 record in Figure 6 reveals that there was an upward trend in measured OC from the late 1980s to
21 the late 1990s prior to the decrease observed the last 10-15 years. Second, the seasonal decrease
22 in OC since 1999 is similar for all four seasons. This suggests that PM_{2.5} reductions at the site
23 derive from reductions in both carbonaceous and sulfate aerosol levels which have differing
24 seasonal patterns, likely because of different seasonal patterns in their respective emission
25 sources. The different seasonal behaviors of OC and sulfate in response to meteorological
26 factors—as illustrated by the data in Table 3—may also come into play. This is supported by
27 seasonal trends data for EC and BC illustrated in Figure 11.

~~3.5 Diurnal trends in primary and secondary species and their relation to meteorology~~

~~The relationship between diurnal variability of chemical variables and meteorology at this complex terrain site was examined in some detail in Tanner et al. (2005) for summer, 2001, conditions in which hourly PM_{2.5} mass and sulfate were available as well as data for temperature, wind speed and direction, and solar radiation. A similar diurnal variability plot was also reported for a month long summer study at Look Rock in 2002 (Olszyna et al., 2004). For both summer periods, nocturnal boundary breakup appeared to begin in the 0500-0600 (EST) time frame, and boundary layer growth reached the altitude of the site (about 815 m msl) in the 0800-1000 h (EST) time frame. In the absence of frontal boundaries, extensive cloudiness and/or precipitation, this was nearly always accompanied by a shift in wind direction from south/southeast (cross ridge followed by downslope) to the northwest direction (upslope), along with a modest increase in wind velocity. On average, the wind direction veered toward the southwest during the afternoon hours and backed to southerly or southeasterly (downslope) again around sunset. Meteorological trends are discussed in more detail in the Supplemental Material and suggest that, when data from all seasons are examined, the analysis becomes more complicated. In particular, surface trajectories at the Look Rock site appear to reflect wind field conditions over a more limited spatial range than previously assumed—at most a few hundred meters, and the timing for upslope-downslope wind direction changes may differ for seasons other than summer.~~

~~For this analysis, we have calculated an average diurnal variation of aerosol species for the mid-summer months (Jul-Aug) and mid-winter months (Jan-Feb) for three of the years since the initiation of continuous sulfate (and other species) monitoring, 2008, 2011 and 2013. For the summer periods we can compare the diurnal patterns with those obtained in previous scientific studies (2001, 2002) and in the VISTAS supported monitoring (2003-2004). For sulfate (Table 4) the patterns are weak with maxima only a few percent above the daily average. The patterns for all species (computed but not shown) were derived from a combination of chemical formation and removal processes that have been well documented (NAPAP, 1990), but also by the interaction of those processes with the characteristic meteorology resulting from Look Rock's ridge top location. For example, O₃ is a secondary species formed predominantly by photochemical processes in daylight hours but Look Rock daily maxima occur in the late evening hours (between 2200 hr and 0100 hr the following day; Tanner et al., 2005). It appears~~

~~that this timing of the maximum concentrations occurs because the collapse of the daytime boundary layer after sunset exposes the site to mid-tropospheric air which is not in contact with surface sources of NO and hence remains high even after daytime O₃ formation processes have subsided.~~

4 Sources of aerosol organic matter (OM)

A continuing source of uncertainty regarding the origin of secondary organic matter in atmospheric aerosols relates to the fraction of particle organic matter (OM) derived from anthropogenic activities versus that which originates from natural processes (Weber et al., 2007; Hoyle et al., 2011; Shilling et al., 2013). The most effective tool used to date to refine estimates of that fraction is measurement of the ¹⁴C content of aerosol samples from which the fractions of “modern” (f_m) and fossil carbon can be determined because ¹⁴C in fossil sources of carbon has decayed to zero (Stuiver and Polach, 1977). With respect to control strategies for atmospheric aerosol carbon in PM, this estimation is complicated by the fact that anthropogenic activities such as agricultural burning and prescribed forest burns contribute modern aerosol carbon as do vegetative emissions. An additional complication is the unexpected correlation of f_M with certain anthropogenic compounds (e.g. CO). Biomass burning samples present a challenge in interpretation of ¹⁴C content due to the varying age of carbonaceous material in biomass fuel and due to the fact that atmospheric ¹⁴C content is decaying to its cosmic ray background from higher levels caused by nuclear bomb tests in the 20th century. One approach to resolving this problem (not used herein) would involve using different correction factors for modern aerosol carbon from biomass burning (carbon of varying age) and for aerosol carbon from current biogenic emissions as has been recently reported by Zotter et al. (2014).

Measurements of the fraction of modern carbon, f_M , have been made at Look Rock and other sites in the southeast U.S. using 24-hr filter-based PM_{2.5} high-volume samples (Tanner et al., 2004a; Bench et al., 2007). These indicate that f_M is consistently high (60-90 percent) for rural locations in all seasons (see Table 54). As shown in Figure 6, OC concentrations have decreased (at least since 1998) at the Look Rock site at a rate comparable to that of inorganic constituents of PM_{2.5}, and there is no evidence to date that f_M in OM at southeastern U.S. sites such as Look Rock changed as the overall PM_{2.5} levels have dropped by 49 percent from 1988 to 2005 (see f_M data in Tanner and Gaffney, 1986). Since OM is now often the most abundant contributor to

1 PM_{2.5}, it is important to parse out which sources have the most contribution to PM_{2.5} and OM
2 mass. Until recently there were no reliable techniques which separately identify the f_M of
3 elemental and organic carbon in the same sample. This has hampered the use of aerosol mass
4 spectrometry results to identify and quantify contributions to OM from biomass burning, along
5 with SOA derived from biogenic emissions of isoprene and terpenes. Recent advances reported
6 by Zhang et al. (2012) and Zotter et al. (2014) may improve our ability to do so using
7 composited samples taken during the 2013 SOAS experiments.

8 **5 Atmospheric transport and aerosol trends**

9 Trends in PM_{2.5} were examined within trajectory coordinate clusters (Section 2.3) to determine
10 which transport scenarios contributed most to the observed overall negative PM_{2.5} trends
11 | previously described (Table 65). Cluster populations and the fraction of total variance (in
12 | transformed cluster coordinates) decrease as cluster number increases. Also, the lower cluster
13 | numbers usually included data from the largest range in years and, thus, most often provided
14 | statistically significant (with a minimum 95 percent confidence) trends in PM_{2.5}. Locations of
15 | the top 10 clusters (based on cluster-averaged 12-hr upwind trajectory locations) are illustrated in
16 | Figure 12. Numbered ellipses contain the 100-m and 500-m trajectory centroids for each cluster.
17 | Shaded clusters are those associated with significant downward trends in PM_{2.5} concentrations.
18 | Symbols denoting the locations of Look Rock and Knoxville are plotted for spatial reference.
19 | Table 56 lists the PM_{2.5} changes over time for the top eight 12- and 24-hr trajectory clusters
20 | (parts a and b, respectively). These clusters accounted for >60 percent of the total variance in
21 | cluster location for each upwind period and more than half the total number of trajectories
22 | analyzed. Although some clusters experienced increased PM_{2.5} over time, the weighted trend
23 | remains negative when higher-order/ lower numbered clusters are added together (see last
24 | column in each part of the table). The PM_{2.5} trend across all trajectories (there is no difference in
25 | trajectory age because all are associated with the same PM_{2.5} data) was $-1.35 \mu\text{g m}^{-3} \text{ yr}^{-1}$ which is
26 | significant at the 99 percent confidence level.

27 A plot of PM_{2.5} changes over time versus cluster-averaged PM_{2.5} (Figure 13) indicates that the
28 rate of change becomes increasingly negative as PM_{2.5} exceeds $12 \mu\text{g m}^{-3}$. The rate of change is
29 slightly positive when $\text{PM}_{2.5} < 12 \mu\text{g m}^{-3}$. The trajectory age (i.e., 12 or 24 hours upwind) makes
30 no difference. The downward trend in PM_{2.5} mass is caused principally by reductions in aerosol

1 mass when conditions are such that aerosol levels are high (i.e., there is no evidence of a
2 downward trend when aerosol levels are low), and that may be caused by a combination of
3 meteorological factors and emissions changes. As shown in Table 65, cluster 1 for both 12- and
4 24-hr upwind had the highest average PM_{2.5} and the largest decreases in PM_{2.5} over 2007-2013.
5 Note that the 12- and 24-hr (upwind) trajectory clusters were not the same because of differences
6 in upwind trajectory age and other factors. Also, most PM_{2.5} temporal changes within clusters
7 were not significant at the 95 percent confidence level, but when combined into a larger data set
8 that included all trajectories the preponderance of declining PM_{2.5} levels indicates a significant
9 negative trend.

10 In general, most trajectory clusters indicated declines in PM_{2.5} for 2007-2013. The exceptions
11 were for clusters over eastern Kentucky (at 24 hr upwind), central Georgia (-12 and -24 hr),
12 northern Alabama (-12 hr), and northern Mississippi (-24 hr). This analysis cannot assign
13 importance to changes in specific aerosol components due to a lack of data, but given the relative
14 contributions to PM_{2.5} we know that a trend must be associated with some combination of
15 changes in sulfate and organic particle mass.

16 6 Conclusions

17 As stated in the beginning, the three objectives of this effort were to (1) identify trends in
18 precursor emissions and air quality, (2) identify the degree of association between emissions and
19 air quality trends and (3) identify whether trends in meteorology influenced air quality trends.
20 All three objectives were met—as summarized here—and the only potential association between
21 air quality and meteorological trends (objective 3) appears to be small.

22 ~~The re evidence indicates are several conclusions that can be drawn from examining long-term~~
23 ~~trends in both gaseous and aerosol species at Look Rock. The first is that the~~ annual average
24 concentrations of SO₂ have gone down by more than 60 percent since 1999—more rapidly since
25 2007—although the decrease appears to level off recently. Concentrations of PM_{2.5} aerosol mass
26 and all of its major chemical constituents have decreased by about 50 percent during the same
27 period based on annual averages but the annual trends of about -3 to -4 percent per year have
28 been driven mostly by reductions in the spring and summer season. The PM_{2.5} mass trend
29 compares closely with the upper range in trends measured at other sites and in regions
30 (especially the Ohio River Valley) adjacent to Look Rock.

1 There have not been any significant changes in the modest diurnal patterns of major gaseous or
2 particulate sulfate over the past decade. It should be noted that there are large year-to-year
3 changes in most measured species concentrations which appear to be driven principally by
4 changes in meteorology—rainfall, clouds, solar radiation and temperature—and this is reflected
5 by some of the seasonal associations identified between air quality and meteorology.

6 The more pronounced reduction in SO₂ levels from 2007 to 2013—compared with changes in
7 sulfate levels over the same period (85 percent for SO₂ and 58 percent for sulfate based on
8 annual averages)—indicates that the spatial footprint of primary emissions of SO₂ in the region is
9 likely smaller than that for the largely secondary sulfate species. It appears that reductions in
10 SO₂ emissions have produced primary SO₂ concentration reductions closer to the sources than
11 those for sulfate whose levels depend on atmospheric SO₂-to-sulfate conversion processes that
12 respond to changes in precursor emissions over a larger region.

13 Statistical modeling revealed that a one standard deviation (1σ) decline in annual SO₂ emissions
14 in the emissions domain was associated with a 0.62σ decline in annual-average ambient SO₂. By
15 comparison, a similar emission decline was associated with 0.97σ decrease in spring and summer
16 and a 0.76σ decrease in winter. The OC association with NO_x emission was smaller with a 1σ
17 drop in emissions linked to a 0.44σ OC decrease in winter and 0.76σ OC decrease in summer.
18 Note that these statistical relations are all based on variances and do not reflect absolute
19 concentration responses to emissions. Changes in Look Rock air quality (1999-2013) appear to
20 be influenced little by meteorological trends (unless a slow but steady decrease in winds
21 somehow plays a role) but are instead primarily controlled by changes in precursor emissions.
22 Much of those changes have occurred nearby (as represented by the Look Rock emission domain
23 defined here) but some of those changes are also due to emissions changes farther upwind.

24 **Author contributions**

25 R. Tanner was the primary architect of this study and performed most of the air quality data
26 analysis. S. Bairai operated the Look Rock site and was primarily responsible for instrument
27 maintenance, data quality assurance and data archival. S. Mueller provided the meteorological,
28 trajectory modeling and statistical trends analyses. All three authors contributed to manuscript
29 preparation.

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20 [%2Fjournal.elementa.000029#sthash.QRLuOWtY.dpuf](http://elementascience.org/article/fetchArticleInfo.action?articleURI=info%3Adoi%2F10.12952%2Fjournal.elementa.000029#sthash.QRLuOWtY.dpuf))

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9

1 **Table 1.** Routine instrumentation deployed at Look Rock.

Responsible Agency	Species	Averaging Time	Method	Instrument	MDA
TVA	SO ₂	1 hr	Pulsed fluorescence	Thermo Model 43i	0.1 ppbv
TVA	NO-NO _y	1 hr	Chemilum. w Mo converter	Thermo Model 42c	NO: 0.1ppbv NO _y : 0.2ppbv
TVA	NO ₂ -NO _x	1 hr	Chemilum. w photolytic converter	Teledyne Model 200EU (trace level)	NO ₂ : 0.2 ppbv
TVA	CO	1 hr	NDIR-GFC	Thermo Model 48i TLE	50 ppbv
TVA	PM _{2.5} sulfate aerosol	1 hr	Thermal reduction /pulsed fluorescence	Thermo Model 5020	0.5 µg/m ³
TVA	PM _{2.5} BC	1 hr	Optical absorption on filter tape	Magee Sci Model AE 21 Aethelometer (Dual-beam BC/UV)	0.075 µg/m ³
TVA	PM _{2.5} OC and EC	1 hr	Thermal-optical CO ₂ NDIR	Sunset Labs Semi-Continuous Elem. Field Carbon Aerosol Analyzer	OC: 0.25 µg/m ³ EC: 0.05 µg/m ³
TVA	PM ₁₀ /PM _{2.5} aerosol mass	1 hr	Beta attenuation	BAMS-1020	PM _{2.5} : >1 µg/m ³
TVA					
NPS	PM _{2.5} aerosol mass	1 hr	TEOM	Thermo/R&P	PM _{2.5} : <1 µg/m ³
NPS-IMPROVE	PM _{2.5} aerosol mass	24 hr every 3 rd day, de-noted "24/3"	Filter pack	Gravimetry	See IMPROVE Data Protocols
NPS-IMPROVE	Sulfate/nitrate /ammonium /chloride mass	24/3	Filter pack	Ion chromatography /wet chemistry	
NPS-IMPROVE	PM _{2.5} Elemental composition	24/3	PIXE & XRF	-	
NPS-IMPROVE	PM ₁₀ Aerosol mass	24/3	Filter pack	Gravimetry	
NPS	b _{abs}	24/3	Filter pack	Optical absorption	
NPS	b _{sp}	1 hr	Light scattering	Nephelometer	
NPS-CASTNET	Temp., RH, wind speed & dir. (Θ), c _w & UV	1 hr	Various	-	

1
 2 **Table 2.** Trends in annual concentrations of selected aerosol fine mass and gas species at Look
 3 Rock.

Species	PM _{2.5} Mass	Sulfate	NH ₄ ⁺ ^a	OC	EC	SO ₂ , ppbv ^b	NO _y , ppbv	O ₃ , ppbv
Annual Change, 1999-2013	-0.45 μg/m ³	-0.23 μg/m ³	-0.053 μg/m ³	-0.088 μg/m ³	-0.019 μg/m ³	-0.14 ppbv	NA	-0.30
% Change yr ⁻¹ , 1999-2013	-5.0	-6.6	-4.9	-5.3	-5.5	-10.7	NA	-0.7
Ave. σ_f ^d Change yr ⁻¹ , 1999-2013	-0.21	-0.20	-0.20	-0.19	-0.19	-0.42	NA	-0.15
% Change yr ⁻¹ , 1988-2013	-2.6	-3.0	NA	-2.0	-2.6	NA	NA	NA
% Change yr ⁻¹ , 2007-2013	-8.3	-14.2	NA	-8.4	-9.4	-25.2	-14.6	-1.5

4 ^aData not available for 2013.

5 ^b CASTNET weekly data are shown except for the last row (2007-2013) that is based on continuous pulsed-fluorescence
 6 measurements.

7 ^c Average annual percent change was computed as the least-squares regression slope for mean annual concentration versus year
 8 (i.e., average concentration change per year) divided by the average concentration for the entire period.

9 ^d Mean interannual change expressed as a fractional standard deviation of the yearly concentration.

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Table 3. Quarters of the year when measured Look Rock air quality was significantly ($p < 0.05$) associated with observed meteorology.

Meteorological Parameter	Ozone	Sulfate	OC	EC
Temperature ¹	3		3	
Precipitation ²	3		3, 4	1, 4
Wind Speed ¹	2, 3	1, 2, 3	2, 3, 4	1, 3
Cloud Cover ²	3		3, 4	
Solar Radiation ³	4	2	4	
High RH ²	4		4	2

¹ Positive association.

² Negative association.

³ Positive for ozone and OC, negative for sulfate.

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Table 4. Summer average diurnal variation in sulfate concentrations at Look Rock.

Year	Ave. [SO₄⁼], μg/m³	Diurnal Var., % of Mean	Hr of Max. Conc.
2001	6.4	±15	1700
2002 ^a	10.3	±9	1700
2003 ^b	7.1	±9	1200-1700 (flat)
2004 ^c	7.6	±9	1500
2008	7.9	±7	1400-1500
2011	6.7	±9	1300, 1500
2013	2.4 ^e	±6	1400-1500

^a Data for mid July to mid August only.

^b Data for summer quarter (VISTAS).

^c Average 24 hr sulfate data may be low due to a conversion efficiency problem.

1
2 | **Table 45.** Summary of ^{14}C data for aerosol carbon in $\text{PM}_{2.5}$ samples from Look Rock and other
3 non-urban southeastern US sites, 2002-2005.

Sampling Location	Sample Season and Duration	Average [OC], $\mu\text{g}/\text{m}^3$	Average f_M^a , (Std. Dev.)	No. of Samples
Look Rock, GSMNP	24 hr, Summer, 2002	3.3	0.834 (0.082)	14
Muscle Shoals, AL	24 hr, Winter, 2003	2.7	0.787 (0.085)	12
Look Rock, GSMNP	24 hr, Spring, 2004	3.6	0.774 (0.091)	9
Look Rock, GSMNP	6-day, Summer, 2004 ^b	2.72	0.972 (0.082)	13
Look Rock, GSMNP	24 hr, Summer, 2004	3.2	0.712 (0.080)	11
Look Rock, GSMNP	24 hr, Fall, 2004	3.1	0.692 (0.108)	11
Look Rock, GSMNP	6-day, Winter, 2005 ^b	1.28	0.885 (0.057)	13
Look Rock, GSMNP	24 hr, Winter-Spring, 2005	2.8	0.746 (0.140)	12
Mammoth Cave NP	24 hr, Spring, 2004	NA	0.784 (0.078)	10
Mammoth Cave NP	24 hr, Summer, 2004	NA	0.749 (0.146)	12
Mammoth Cave NP	24 hr, Fall, 2004	NA	0.670 (0.080)	12
Mammoth Cave NP	24 hr, Winter-Spring, 2005	NA	0.656 (0.096)	13
Shenandoah NP	24 hr, Spring, 2004	NA	0.759 (0.124)	11
Shenandoah NP	24 hr, Summer, 2004	NA	0.741 (0.162)	12
Shenandoah NP	24 hr, Fall, 2004	NA	0.610 (0.130)	12
Shenandoah NP	24 hr, Winter-Spring, 2005	NA	0.592 (0.111)	10

4 ^aCorrected fraction of modern carbon.

5 ^bSamples collected by IMPROVE staff and analyzed by LLNL (Fallen and Bench, 2005).

Table 56.

(a) Cluster analysis results and associated PM_{2.5} changes over time for 12-hr trajectory clusters based on joint 100- and 500-m HYSPLIT trajectories.

Cluster (n)	Year Range ^a	Cumulative Fraction of Trajectory Data Set	Ave. Transport Dist. (km) to Look Rock	Ave. Traj. Height (m) at 12-hr Upwind ^b	Average PM _{2.5} ^c (µg m ⁻³)	PM _{2.5} Change ^d (µg m ⁻³ yr ⁻¹)	p>95%? ^e (Yes/No)	Cumulative Fraction of σ ² in Transformed Coordinates ^f	Cumulative Weighted Time Change in PM _{2.5} ^g (µg m ⁻³ yr ⁻¹)
1	2007-2012	0.09	111	324	22.9	-16.6	Y	18.6%	-16.6
2	2007-2013	0.20	256	433	8.0	-0.8	N	29.9%	-8.2
3	2007-2013	0.28	140	229	12.7	-1.9	Y	37.8%	-6.3
4	2007-2012	0.37	148	315	19.8	-4.0	Y	44.4%	-5.8
5	2007-2013	0.44	131	357	20.5	-0.9	N	49.4%	-5.0
6	2007-2013	0.50	258	316	12.9	0.8	N	53.5%	-4.3
7	2008-2012	0.55	295	289	13.0	0.0	N	57.3%	-3.9
8	2007-2013	0.59	320	284	11.3	1.1	N	60.4%	-3.5

(b) Same as (a) but for 24-hr trajectory clusters.

Cluster (n)	Year Range ^a	Cumulative Fraction of Trajectory Data Set	Ave. Transport Dist. (km) to Look Rock	Ave. Traj. Height (m) at 24-hr Upwind ^b	Average PM _{2.5} ^c (µg m ⁻³)	PM _{2.5} Change ^d (µg m ⁻³ yr ⁻¹)	p>95%? ^e (Yes/No)	Cumulative Fraction of σ ² in Transformed Coordinates ^f	Cumulative Weighted Time Change in PM _{2.5} ^g (µg m ⁻³ yr ⁻¹)
1	2007-2013	0.09	240	263	26.8	-9.3	Y	16.2%	-9.3
2	2009-2012	0.13	440	418	4.9	2.9	Y	30.1%	-5.4
3	2008-2013	0.18	337	284	18.0	-1.9	N	40.4%	-4.4
4	2007-2012	0.26	433	245	14.6	-0.7	N	45.6%	-3.2
5	2007-2013	0.34	298	263	19.7	-3.6	Y	50.5%	-3.3
6	2007-2013	0.47	299	239	15.1	-1.5	N	54.7%	-2.8
7	2007-2013	0.57	450	213	10.7	0.1	N	58.1%	-2.3
8	2008-2013	0.63	508	172	12.3	-3.0	Y	61.5%	-2.3

^a Range in years represented by data in the cluster.

^b Average cluster height of both trajectory levels at upwind time (ending average height was always 300 m).

^c Values are 5-hr averages centered on local midnight of the trajectory end date.

^d Time change in PM_{2.5} computed from a linear regression of midnight-centered 5-hr average PM_{2.5} versus year.

^e Confidence level *p* of computed time change in PM_{2.5}.

^f Running total of cluster (transformed coordinate) variance σ² from first through current cluster *n*.

^g PM_{2.5} time change (see column 7) weighted by cluster size and summed for clusters 1 through *n*.

1 **Figure Captions**

2 Figure 1. Spatial domain used to compare trends in air quality with trends in emissions of
3 precursor species.

4 Figure 2. (a) NEI emissions by species within the Look Rock domain for select years
5 between 1999 and 2011 (data other than SO₂ and NO_x were not considered reliable for 1999
6 and are not shown). (b) Yearly NEI SO₂ and NO_x emissions—EGU and all sources—within
7 the Look Rock domain for 1999-2013.

8 Figure 3. Ozone trends by season and annually at Look Rock, 1999-2013.

9 Figure 4. Comparison of annual SO₂ concentrations at Look Rock with corresponding total
10 SO₂ emissions in the Look Rock domain.

11 Figure 5. Average monthly SO₂ and NO_y concentrations at Look Rock, 2007-2013.

12 Figure 6. Trends in annual average IMPROVE PM_{2.5} mass, sulfate, NH₄⁺, OC, EC and BC at
13 Look Rock.

14 Figure 7. Comparison of IMPROVE PM_{2.5} mass chemical distributions for 1999 and 2013 at
15 Look Rock. “Light-Abs. C” denotes the EC component, “Soil” denotes particles of various
16 oxides (e.g., iron oxide) associated with soils and “Unknown” represents mass whose
17 composition is indeterminate (most likely some water along with mass associated with OC
18 that is not included in the 1.8 adjustment factor applied by IMPROVE to OC to estimate OM).
19 Numbers associated with each pie section denotes the annual mean mass (μg m⁻³) of that
20 chemical constituent.

21 Figure 8. Trends in seasonal PM_{2.5} mass at Look Rock.

22 Figure 9. Trends in seasonal PM_{2.5} sulfate mass at Look Rock.

23 Figure 10. Trends in seasonal IMPROVE PM_{2.5} OC mass at Look Rock.

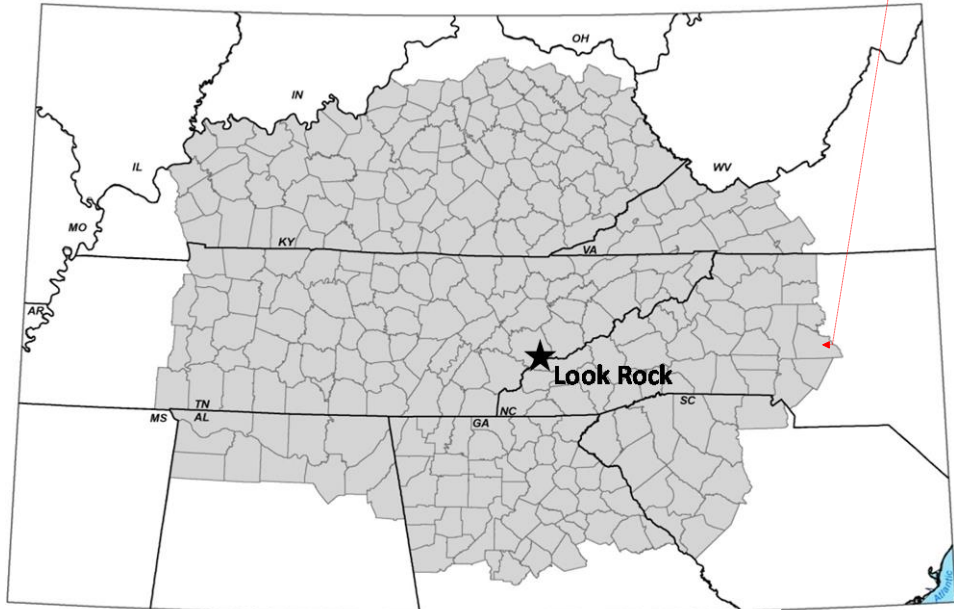
24 Figure 11. Trends in seasonal PM_{2.5} EC and BC mass at Look Rock.

25 Figure 12. Locations of cluster centroids (numbered ellipses) for computed 100- and 500-m
26 air trajectories at 12 hr upwind (pairs of squares within ellipses) from Look Rock (red square)
27 for selected extreme PM_{2.5} episodes during 2007-2013. Shaded ellipses denote clusters for
28 which significant negative PM_{2.5} mass trends at Look Rock were identified.

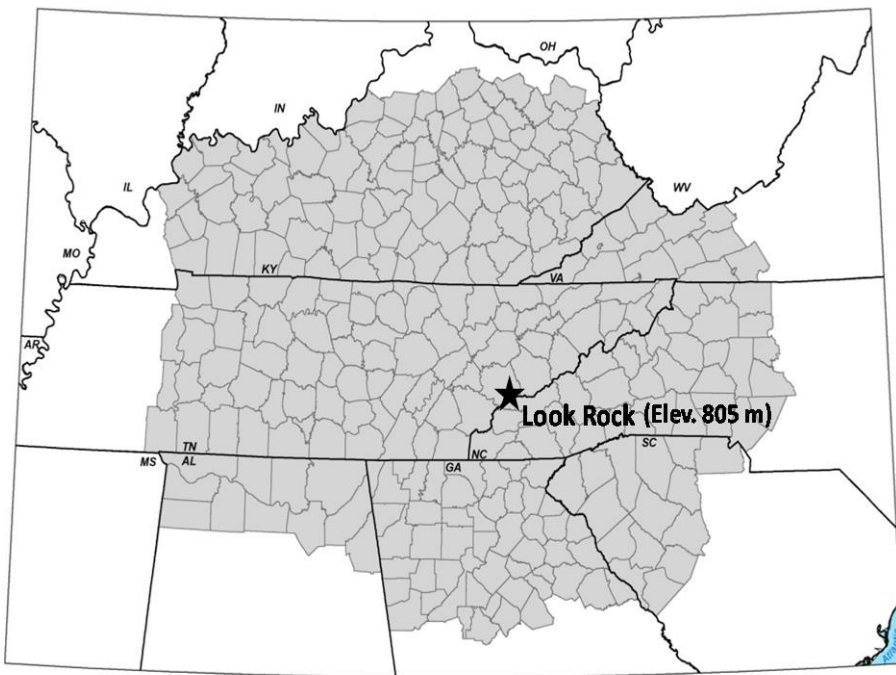
1 Figure 13. Weighted trend of PM_{2.5} mass by 12- and 24-hr trajectory clusters.

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Figure 1.

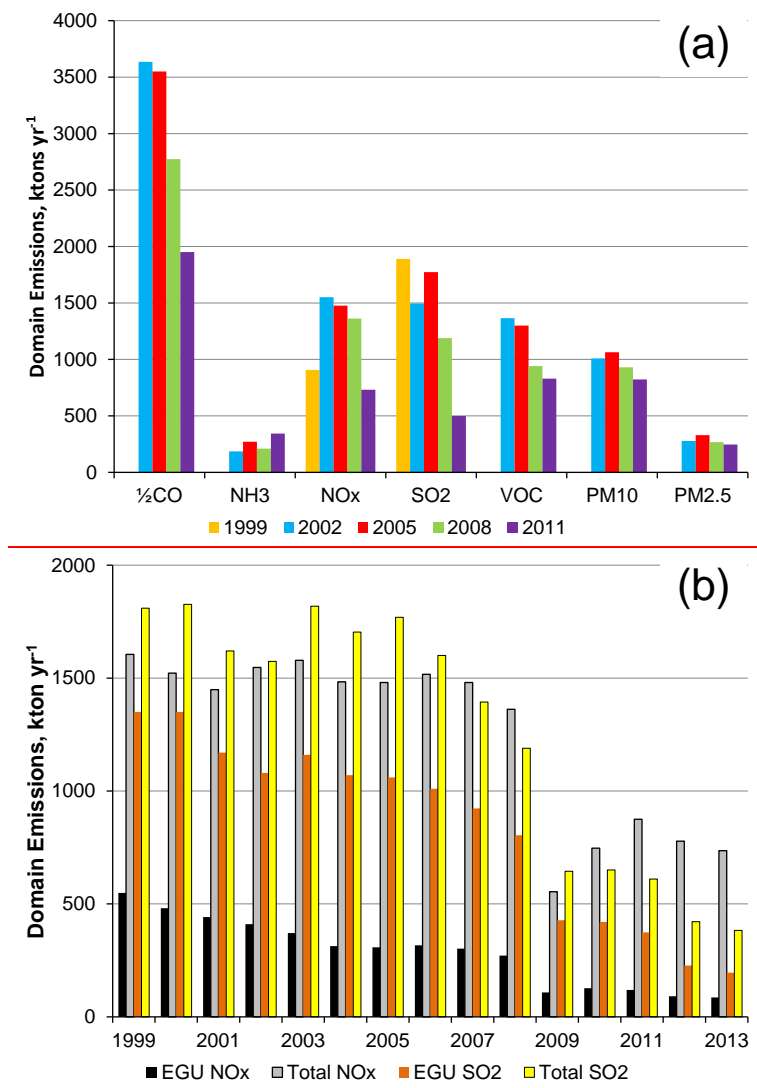


Figure 2.

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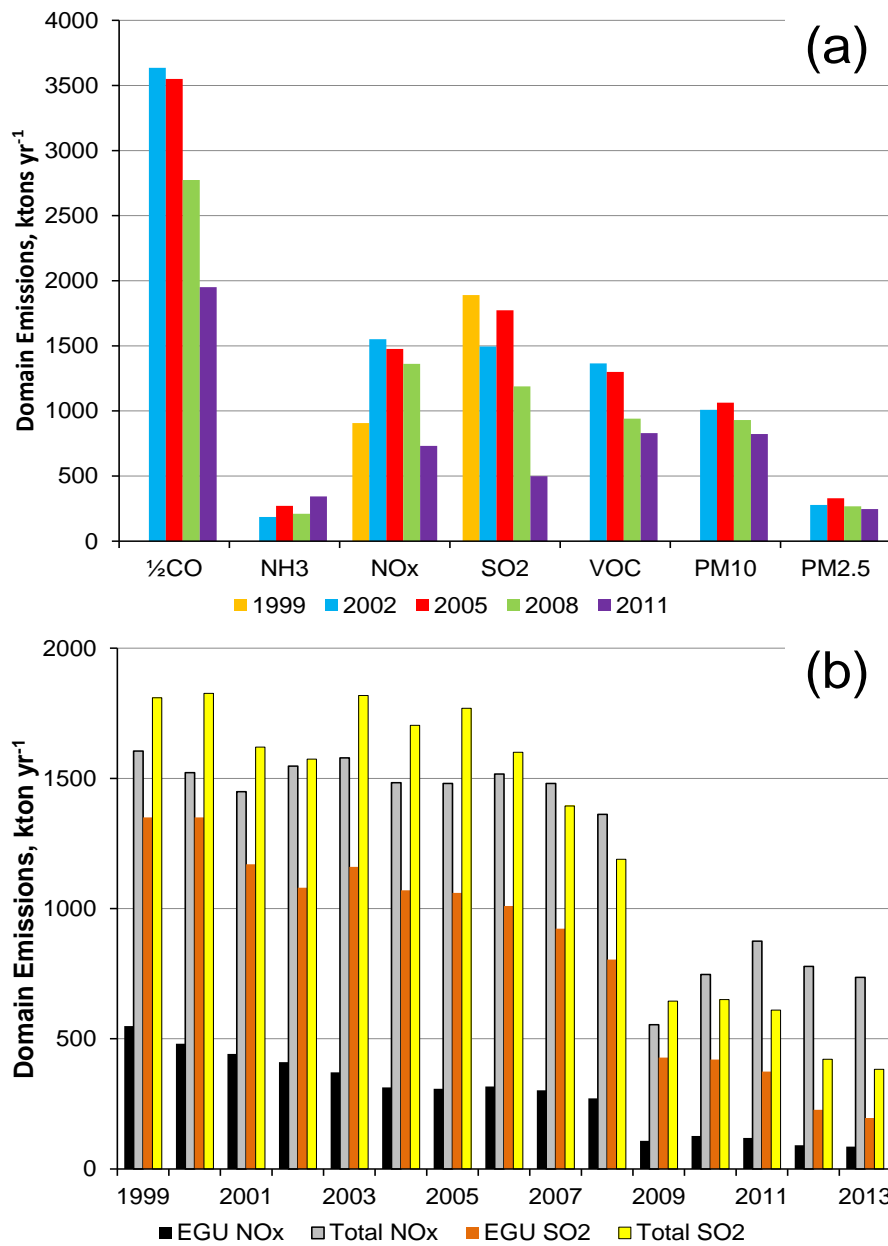


Figure 2

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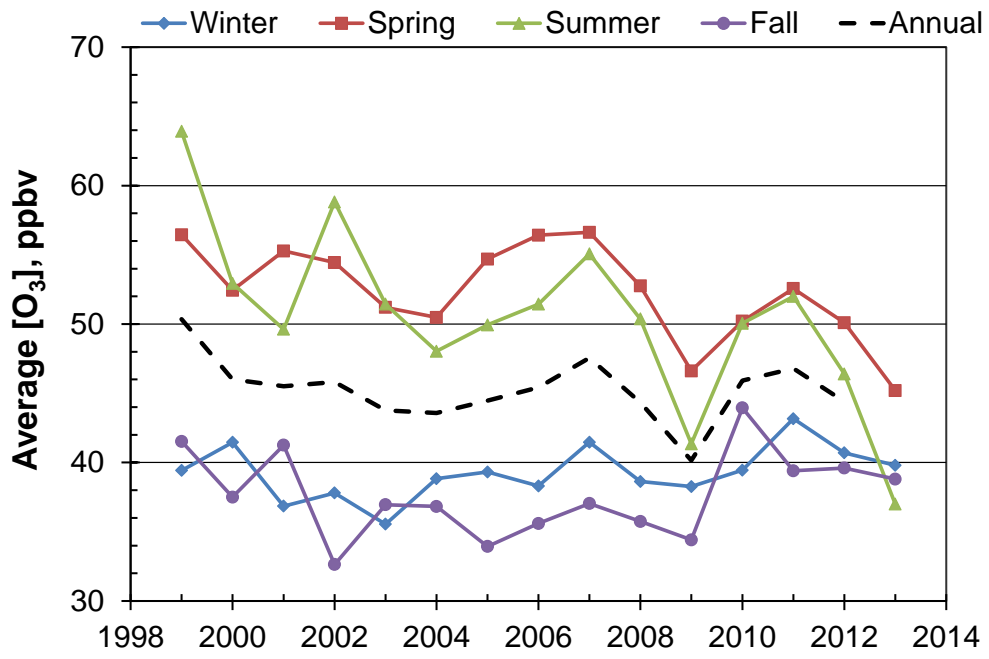


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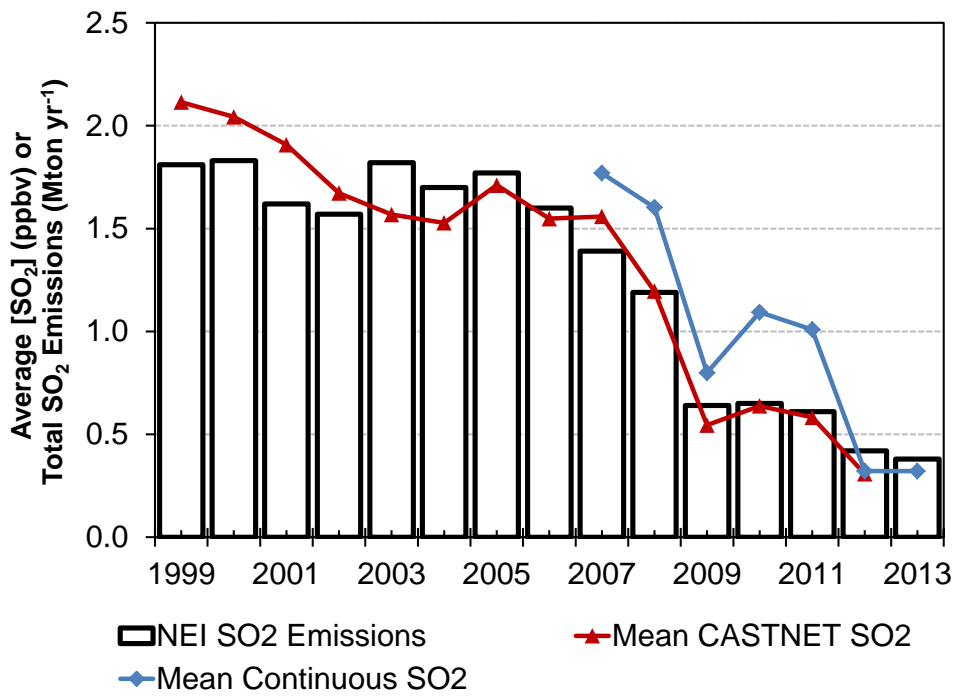


Figure 44.

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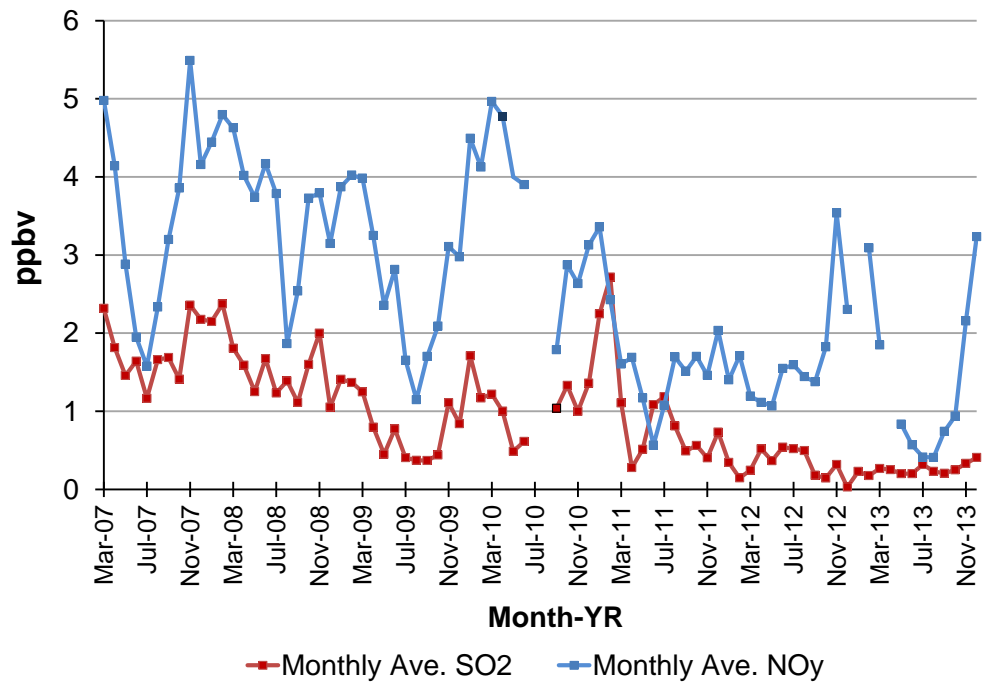


Figure 55.

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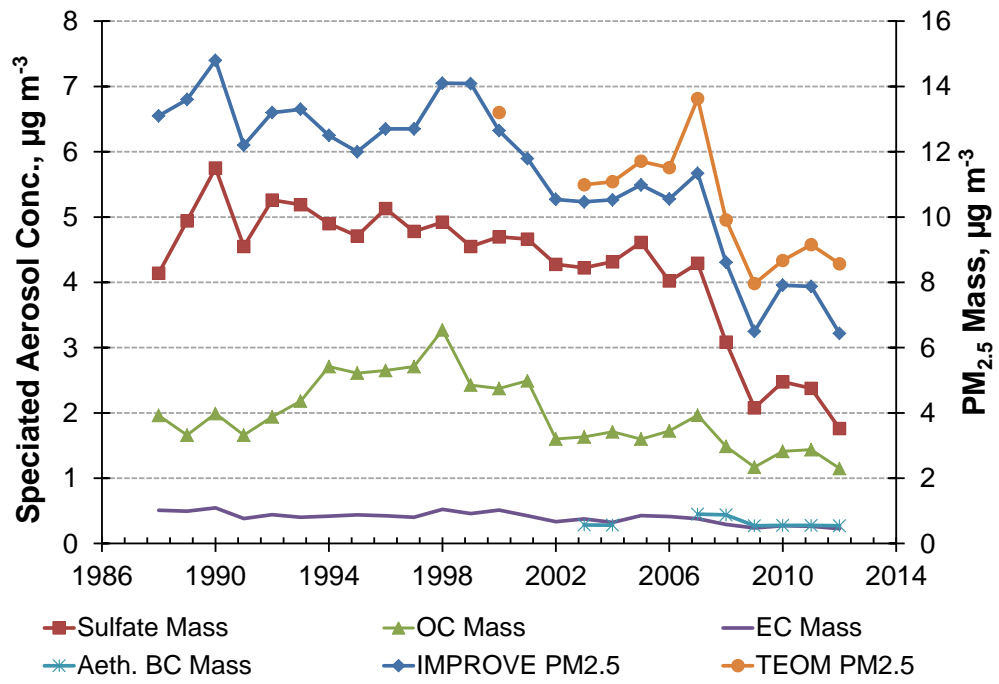


Figure 66.

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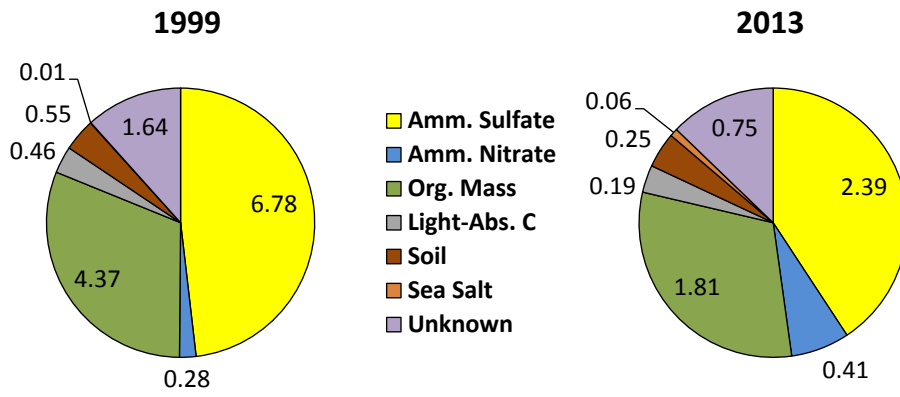


Figure 77.

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2

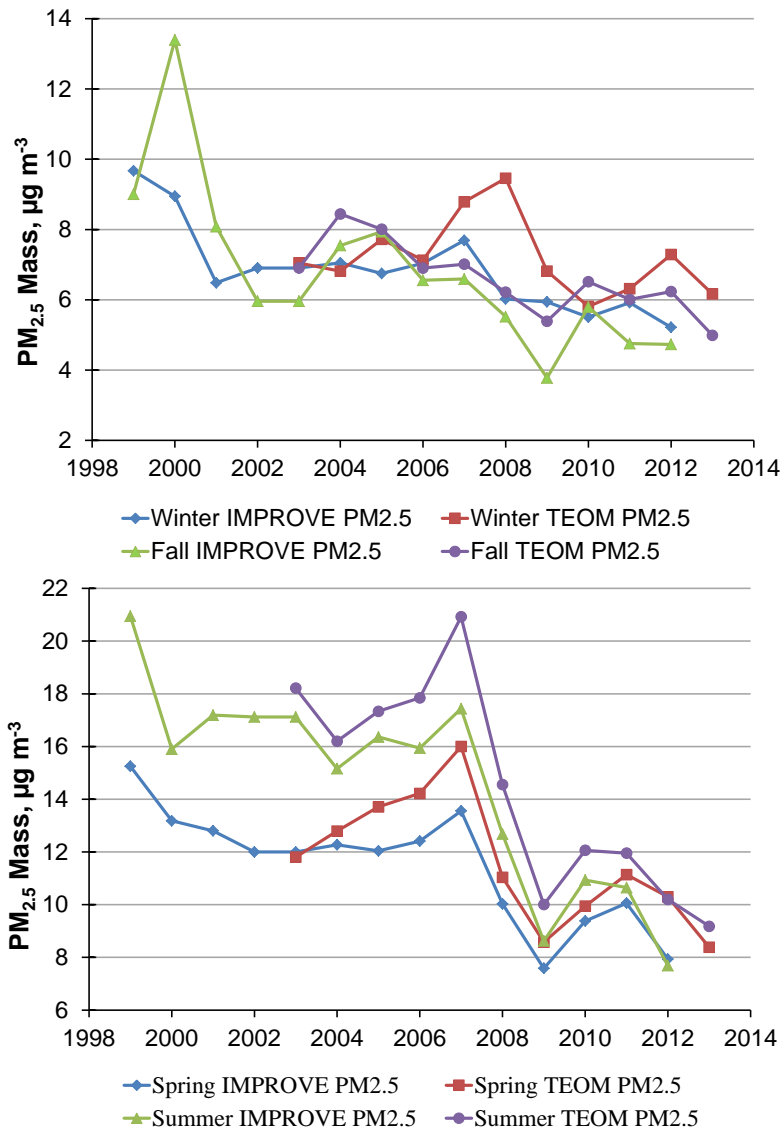


Figure 88.

1
2
3

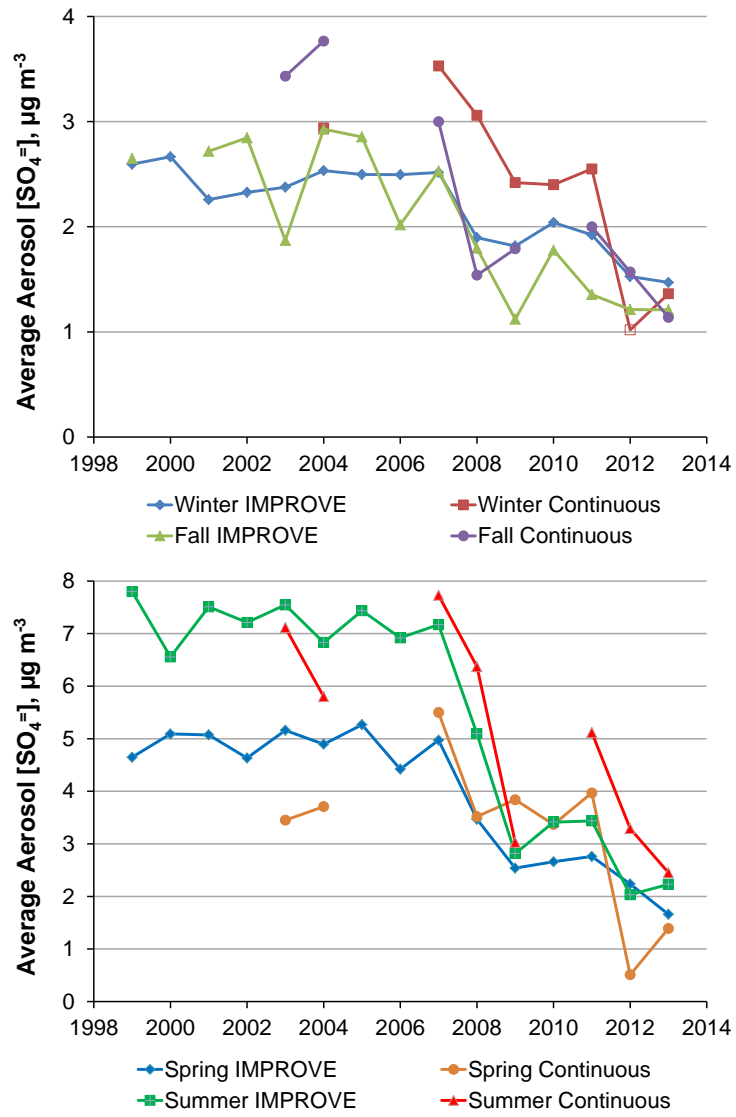


Figure 99.

1
2

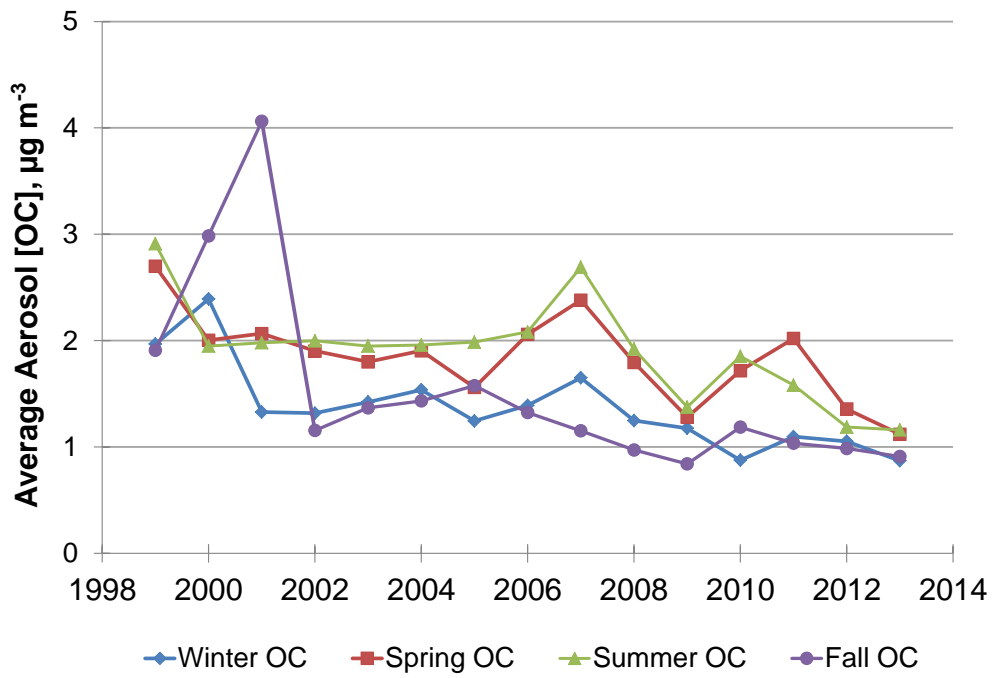


Figure 10-10.

1
2

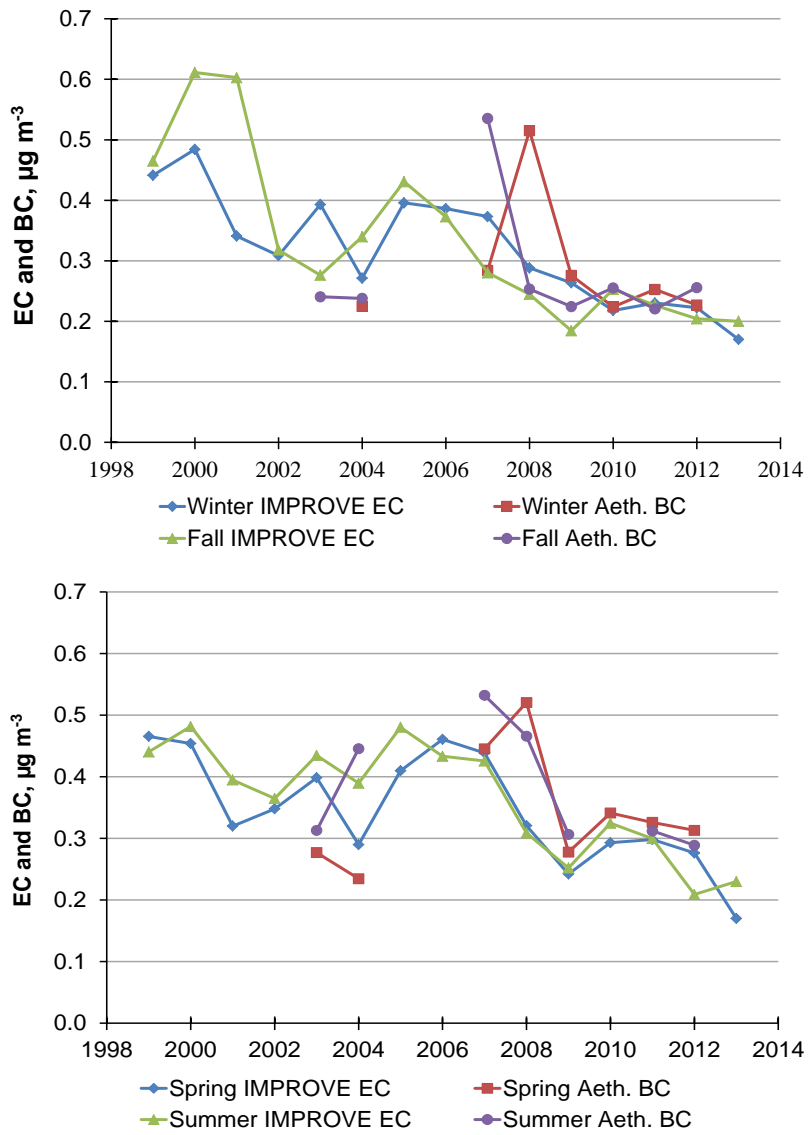


Figure 111.

1
2

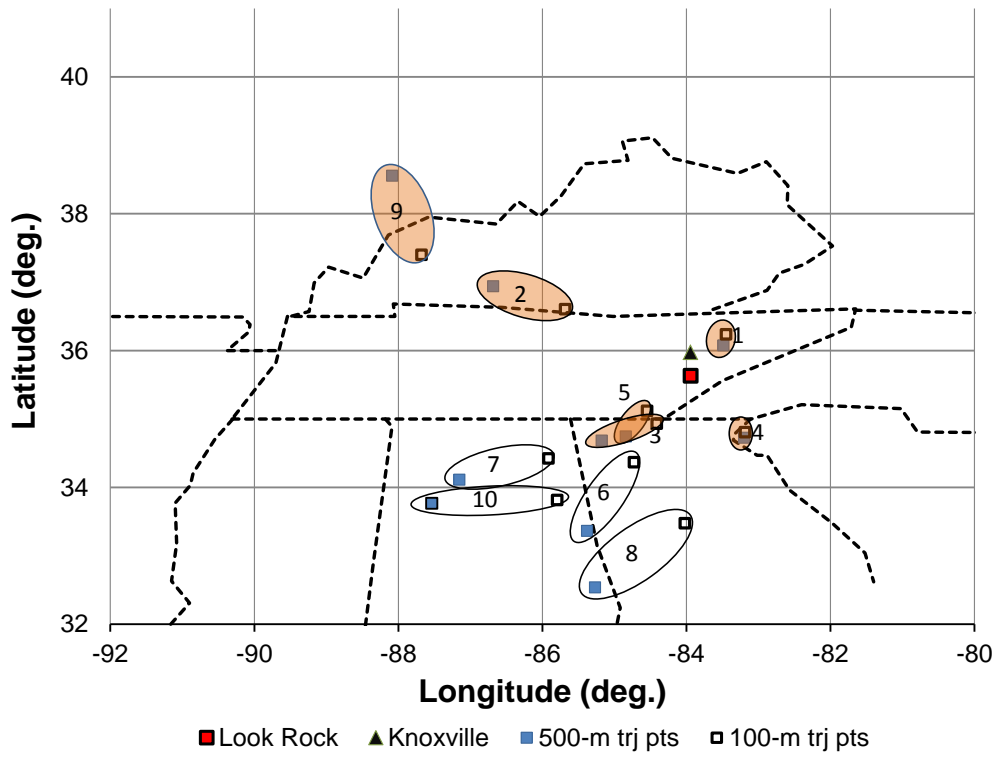


Figure 1212.

1
2
3

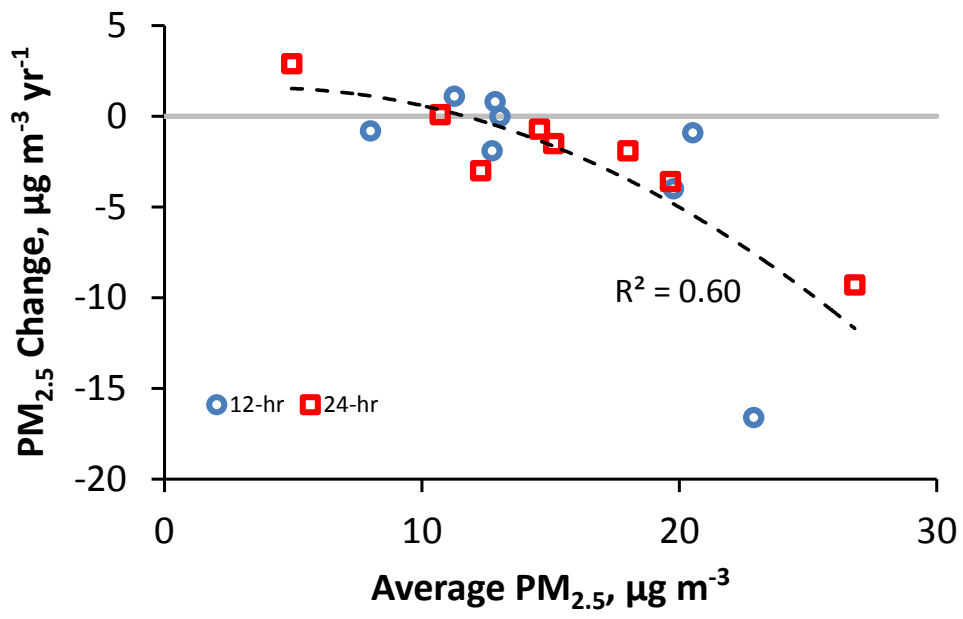


Figure 134.

1