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TECHNICAL PAPER

The Southeastern Aerosol Research and Characterization (SEARCH) study: Temporal trends in gas and PM concentrations and composition, 1999–2010

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The SEARCH study began in mid 1998 with a focus on particulate matter and gases in the southeastern United States. Eight monitoring sites, comprising four urban/nonurban pairs, are located inland and along the coast of the Gulf of Mexico. Downward trends in ambient carbon monoxide (CO), sulfur dioxide (SO_2), and oxidized nitrogen species (NO_y) concentrations averaged 1.2 ± 0.4 to 9.7 ± 1.8% per year from 1999 to 2010, qualitatively proportional to decreases of 4.7 to 7.9% per year in anthropogenic emissions of CO, SO_2, and oxides of nitrogen (NO_x) in the SEARCH region. Downward trends in mean annual sulfate (SO_4) concentrations ranged from 3.7 ± 1.1 to 6.2 ± 1.1% per year, approximately linear with, but not 1:1 proportional to, the 7.9 ± 1.1% per year reduction in SO_2 emissions from 1999 to 2010. The 95th percentile of the March–October peak daily 8-hr ozone (O_3) concentrations decreased by 1.1 ± 0.4 to 2.4 ± 0.6 ppbv per year (1.5 ± 0.6 to 3.1 ± 0.8% per year); O_3 precursor emissions of NO_x and volatile organic compounds (VOC) decreased at rates of 4.7 and 3.3% per year, respectively. Ambient particulate nitrate (NO_3) concentrations decreased by 0.6 ± 1.2 to 5.8 ± 0.9% per year, modulated in comparison with mean annual ambient NO_y concentration decreases ranging from 6.0 ± 0.9 to 9.0 ± 1.3% per year. Mean annual organic matter (OM) and elemental carbon (EC) concentrations declined by 3.3 ± 0.8 to 6.5 ± 0.3 and 3.2 ± 1.4 to 7.8 ± 0.7% per year. The analysis demonstrates major improvements in air quality in the Southeast from 1999 to 2010. Meteorological variations and incompletely quantified uncertainties for emission changes create difficulty in establishing unambiguous quantitative relationships between emission reductions and ambient air quality.

Implications: Emissions and secondary pollutants show complex relationships that depend on year-to-year variations in dispersion and atmospheric chemistry. The observed response of O_3 to NO_x and VOC emissions in the Southeast implies that continuing reductions of precursor emissions, probably achieved through vehicle fleet turnover and emission control measures, will be needed to attain the National Ambient Air Quality Standard for O_3. Reductions in fine particle concentrations have resulted from reductions of primary PM, especially EC and a portion of OM, and from reduction of gas precursors known to form particles, especially SO_4 from SO_2. Continued reduction of $PM_{2.5}$ mass concentrations will require attention to organic constituents, which may be complicated by potentially unmanageable biogenic species present in the Southeast.

Introduction

Detecting and quantifying trends in ambient concentrations of air pollutants depends on the relative influence of weather-driven and emission-driven variations on ambient pollutant concentrations, and on the quality and length of record of the monitoring data. In general, trends in mean ambient concentrations of emitted pollutants (primary pollutants) are expected to follow emission trends directly, while the products of reactions of emissions (secondary pollutants) exhibit trends that depend on both emissions and atmospheric processing.

The Clean Air Act of 1970 initiated large changes in local and regional pollutant emissions. With the Clean Air Act Amendments of 1990 (CAAA), commitments for emission reductions increasingly shifted from local to regional scales. From 1999 to 2010, U.S. Environmental Protection Agency (EPA) national and regional emission control programs affected emissions of sulfur dioxide (SO_2), oxides of nitrogen (NO_x), volatile organic compounds (VOC), carbon monoxide (CO), and particulate matter of less than 2.5 μm aerodynamic diameter ($PM_{2.5}$ mass). The U.S. EPA acid rain program (CAAA, Title IV) implemented a nationwide 10 million tons per year reduction of

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SO_2 emissions from electrical generating units (EGUs) in two phases, beginning in 1995 and 2000 (U.S. EPA, 2011a). The U.S. EPA NO_x SIP Call required further reductions in EGU NO_x emissions in 21 states in the eastern United States by May 31, 2004 (U.S. EPA, 2012a). The U.S. EPA Clean Air Interstate Rule, proposed in 2005, required 70% reductions of EGU emissions of SO_2 and NO_x in 28 states within the eastern United States; implementation of the program is ongoing but will be affected by the U.S. EPA response to a court remand (U.S. EPA, 2011b). The U.S. EPA established low-sulfur requirements for diesel fuel starting in 2006 (U.S. EPA, 2011c). The Tier 2 Vehicle and Gasoline Sulfur Control Program is aimed at reducing emissions from cars, trucks, and nonroad equipment by 77–95% relative to model year 2003; the rule covered 25% of the 2004 model year and all 2009 model year vehicles (U.S. EPA, 2011d).

Although there has been considerable attention to documenting national-scale emission reductions and ambient air quality improvements, less attention has been given to regional changes except in the Northeast (e.g., Gego et al., 2007, 2008; Gilliland et al., 2008; Godowitch et al., 2008). Hand et al. (2012) showed that $PM_{2.5}$ SO_4 trended downward from 1990 to 2010 at sites in the Interagency Monitoring of Protected Visual Environments (IMPROVE) network throughout the United States, but the regional responses of SO_4 to SO_2 emission changes were different among the six regions studied. Emissions, meteorological conditions, and atmospheric chemical regimes vary from region to region, so that regional studies are needed to evaluate ongoing improvements of air quality.

This paper describes temporal changes in air pollutant concentrations in the southeastern United States from 1999 to 2010 using data from a regional research network, the Southeastern Aerosol Research and Characterization (SEARCH) study. The data are used to assess the impacts of emission controls on the observed ambient trends for criteria (regulated) and related pollutants emitted in this region, and for secondary air pollutants.

Measurements

SEARCH network description

The SEARCH program was initiated in mid 1998 and has continued operating through 2012. SEARCH data are accessible from the SEARCH public archives (Atmospheric Research and Analysis, 2010). The SEARCH network was designed to provide long-term, detailed pollutant gas and aerosol chemistry for paired urban and nonurban sites in the southeastern United States (Figure 1). Pensacola (PNS) and Gulfport (GFP) are urban coastal sites; Pensacola–outlying (aircraft) landing field (OLF) and Oak Grove (OAK) are nonurban coastal sites along the Gulf of Mexico. Atlanta–Jefferson Street (JST) and North Birmingham (BHM) are urban inland sites; Yorkville (YRK) and Centreville (CTR) are nonurban inland sites. A companion paper (Blanchard et al., 2012a) discusses spatial variations, regionally as represented by the network, and within the Atlanta, GA, and Birmingham, AL, metropolitan areas, supplementing SEARCH data with measurements from other monitoring programs.

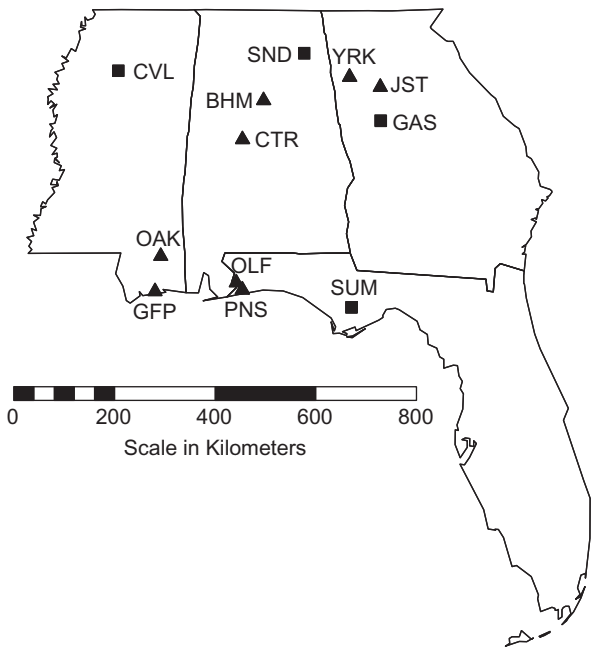

Figure 1. Locations of monitoring sites. Triangles, SEARCH; squares, CASTNet.

SEARCH operations, sampling, and measurement methods for gases and particles are documented in Hansen et al. (2003) and Edgerton et al. (2005, 2006, 2007, 2009). All sites have measurements of meteorological parameters and gas-phase species (i.e., criteria pollutants, 24-hr ammonia [NH_3], commencing mid-2003 [Edgerton et al., 2007; Saylor, 2010], and nitric acid [HNO_3]). Nonmethane organic compound (NMOC) measurements were made by SEARCH at JST through 2008 and by U.S. EPA at YRK (Blanchard et al., 2010a). "NMOC" is used here to refer to ambient concentration measurements of low-molecular-weight (C_2–C_{12}), gas-phase, nonmethane organic compounds, whereas the term "volatile organic compound" (VOC) is reserved for emissions of gas-phase organic compounds as defined in U.S. EPA (1996). Particulate measurements include mass concentration and bulk composition of inorganic and carbon species. SEARCH reports organic mass (OM) by scaling organic carbon (OC) by a constant factor of 1.4 ($OM = 1.4 \times OC$); that convention is followed here, recognizing that the actual scaling factor is not constant in time or space and may be higher on average. El-Zanan et al. (2009) conclude, for example, that the OM/OC ratio averages ~2:1 at SEARCH sites. A second SEARCH convention is to report concentrations of major metal oxides (MMO) as the sum of the highest oxidation states of six elements (i.e., $MMO = Al_2O_3 + SiO_2 + K_2O + CaO + TiO_2 + Fe_2O_3$). Although these elements may exist in different valence states, their oxidation states are specified here by the MMO convention. The individual concentrations of MMO and other elements are reported in the SEARCH database.

For this analysis, we focus on the gases CO, SO_2, NO_x, and NO_y, and on major $PM_{2.5}$ components (SO_4, NO_3, EC, and OM, which hereafter refer to the $PM_{2.5}$ fraction of these species unless otherwise noted). $PM_{2.5}$ mass concentration trends, which are dependent on complex, multisource primary emissions and

secondary production in the atmosphere, are also reported here for all SEARCH sites.

Comparison data

For comparison with SEARCH measurements, ambient measurement data were obtained from four sites in the U.S. EPA Clean Air Status and Trends Network (CASTNet; U.S. EPA, 2010a): Coffeeville, MS (CVL), Sand Mountain, AL (SND), Georgia Station, GA (GAS), and Sumatra, FL (SUM) (Figure 1). Distances from CASTNet to nonurban SEARCH sites are: CVL–OAK = 345 km, SND–CTR = 195 km, GAS–YRK 103 km, and SUM–OLF = 234 km. Additional data, especially for NMOCs, are available from U.S. EPA Photochemical Assessment Monitoring Stations (PAMS); three PAMS sites are in the Atlanta, GA, metropolitan area, and one is co-located with the YRK SEARCH site. NMOC measurements from JST and PAMS sites are discussed in Blanchard et al. (2010a).

Emissions data

Emissions data were obtained from the U.S. EPA National Emission Inventory (NEI). The NEI is released at 3-year intervals, and emissions estimation procedures are revised with each new NEI and between versions of an NEI (U.S. EPA, 2007). The NEI provides annual total emissions of criteria pollutants at county, state, and national levels, and at three levels of source disaggregation known as Tier 1, Tier 2, and Tier 3. The more recent inventories are the 2002 NEI version 3, release date October 15, 2007 (U.S. EPA, 2008b), the 2005 NEI version 2, release date March 11, 2009 (U.S. EPA, 2010b), the 2008 NEI version 1.5, release date May 16, 2011, and the 2008 NEI version 2, release date April 10, 2012 (U.S. EPA, 2011e). U.S. EPA prepares trend estimates by backcasting and forecasting from a base-year NEI (U.S. EPA, 2007). For years prior to 2002, U.S. EPA developed emission trends estimates based on the 1999 NEI, released September 20, 2005 (U.S. EPA, 2008a). Methodologically consistent national-level trends for Tier 1 categories are also available for 1970 through 2010 based on the 2005 NEI version 2 and 2008 NEI version 1.5 (U.S. EPA, 2011f). Version 2 of the 2008 NEI differs from version 1.5 totals due to changes in emission estimation methods compared with previous NEIs (U.S. EPA, 2012b). For the present study, state-level mobile-source trends were derived from 2005 NEI state-level emissions by applying scaling factors from the national mobile-source emission trends (U.S. EPA, 2011f). Although the reliability of the NEI is not well established for sources other than EGUs, the 2005 NEI emissions from Alabama, Georgia, Mississippi, and Florida are consistent with chemical mass balance (CMB) estimates of source contributions determined from measurements made at SEARCH sites from 2004 to 2007 (except for soil and road dust emissions) (Blanchard et al., 2012b).

EGU emission measurements have been obtained from continuous emissions monitoring (CEM) at facilities subject to U.S. EPA programs (U.S. EPA, 2010c). CEM data were summed by year for all reporting facilities located in AL, FL, GA, and MS. Within these states, CEMS measurements were made at 244 units in 1995, 518 units in 2005, and 693 units in 2010. These EGUs accounted for 2.9×10^{15} Btu in 1995, 3.4×10^{15} Btu in 1999 and 2000, 3.9×10^{15} Btu in 2005, and 4.0×10^{15} Btu in 2010 (1 Btu = 1055.06 J). Comparison of the CEM data to the 1999, 2002, 2005, and 2008 NEI estimates of all EGU emissions within the four study states showed that the CEM SO_2 emissions represented 99% of the NEI total EGU SO_2 emissions and the CEM NO_x emissions were 94 to 98% of the NEI total EGU NO_x emissions throughout the 1999–2010 study period. The comparison indicates that the NEI EGU emission estimates were consistent with the measured CEM values, and the 1999–2010 CEM data represent a nearly complete accounting of EGU emissions.

Methods of analysis

The analyses quantify gas and particle concentration trends across the SEARCH domain for (1) annual emissions, (2) annual-average and 95_{th} percentile ambient concentrations, with and without adjustment for meteorological variations, and (3) frequency distributions of ambient concentrations. Emphasis is placed on the relation between ambient and emission trends, assuming that SEARCH sites represent air quality in the four-state region (Blanchard et al., 2012a, 2012b).

Results

Emission trends

Within the four states hosting SEARCH sites, emissions of CO decreased from 18.2 to 9.2 million tons per year from 1990 to 2008, and SO_2 emissions declined from 2.8 to 1.5 million tons per year (Table 1). SO_2 emissions measured at EGUs within the four-state area decreased from 1.7 million tons per year in 1995 (~75% of total SO_2 emissions) to 0.62 million tons per year in 2010 (~70% of total SO_2 emissions) (Table 1). Emissions of anthropogenic VOCs were 2.6 and 1.5 million tons per year in 1990 and 2008, respectively. The VOC estimates from separate NEIs are incompatible, because changes in methods for estimating evaporative emissions affect the VOC inventory between 1999 and 2001 and 2002, and again between 2002 and 2005. Specifically, VOC emission factors in the 2005 NEI were higher relative to the 2002 and 1999 NEIs, and were also higher in the 2002 NEI relative to the 1999 NEI. The U.S. EPA emission trend analysis, backcast from the 2005 NEI, indicates declining national-level VOC emissions except from the Tier 1 "miscellaneous" category, for which VOC emissions increased eightfold from 2001 to 2002 due to a methods change (U.S. EPA, 2011f). Mobile-source VOC emissions decreased by 28% from 1999 to 2008 (U.S. EPA, 2011f; also see Table 1).

NO_x emissions were 2.6 and 1.8 million tons per year in 1990 and 2008. EGU NO_x emissions were 0.72–0.73 million tons per year from 1995 to 2000 (with a peak of 0.77 million tons per year in 1998), declining to 0.24 million tons per year as of 2010. EGU NO_x emissions were 27% of total NO_x emissions in 1999 and less than 20% in 2010 (Table 1). Uncertainty exists for non-EGU NO_x emission trends: Parrish (2006) reports that NEI estimates during the years 1990 through 2002 show decreases in CO,

Table 1. Annual emissions in the states of AL, FL, GA, and MS (U.S. EPA, 2007, 2008a, 2008b, 2010b, 20011b, 2011e, 2011f). Units of measurement are million tons per year. PM values account for primary emissions only and do not include precursors of secondary PM

Year	CO	NH_3	NO_x	PM_{10}	$PM_{2.5}$	SO_2	VOC	Mobile VOC[a]	On-road NO_x[a]	Nonroad NO_x[a]	EGU NO_x[b]	EGU SO_2[b]	EGU CO_2[b]
1990	18.22	0.34	2.62			2.80	2.59	1.69	1.25	0.40		2.17	
1991								1.62	1.23	0.41			
1992								1.56	1.21	0.42			
1993								1.49	1.19	0.43			
1994								1.42	1.17	0.43			
1995								1.35	1.15	0.44	0.72	1.70	274.6
1996	14.03	0.37	2.63	2.03	0.59	2.39	2.22	1.29	1.13	0.45	0.73	1.82	284.8
1997	13.72	0.37	2.66	2.12	0.61	2.46	2.20	1.23	1.14	0.45	0.73	1.88	298.8
1998	13.65	0.39	2.69	2.14	0.63	2.64	2.17	1.20	1.12	0.44	0.77	2.07	313.7
1999	15.99	0.36	2.70	2.66	1.03	2.46	2.42	1.17	1.09	0.44	0.73	1.91	316.1
2000	14.47	0.36	2.68	2.40	0.86	2.28	2.17	1.12	1.09	0.45	0.72	1.73	326.1
2001	15.16	0.32	2.62	2.39	0.88	2.23	2.19	1.06	1.01	0.44	0.68	1.66	318.8
2002	13.99	0.32	2.44	2.04	0.60	2.04	2.74	1.12	1.02	0.48	0.61	1.49	328.5
2003								1.07	0.96	0.50	0.56	1.56	335.8
2004								1.03	0.90	0.51	0.51	1.46	333.7
2005	12.48	0.33	2.25	2.12	0.68	2.11	2.66	0.98	0.84	0.52	0.50	1.57	349.8
2006								0.94	0.79	0.49	0.48	1.49	350.3
2007								0.90	0.74	0.45	0.46	1.47	361.0
2008[c]	9.22	0.30	1.75	1.75	0.43	1.46	1.54	0.86	0.69	0.42	0.42	1.20	339.0
2009								0.75	0.62	0.36	0.23	0.79	296.2
2010			1.33[d]			0.88[e]		0.63	0.56	0.31	0.24	0.62	338.6

Notes: [a]Annual values for 1990 through 2010 were generated by scaling the 2005 NEI on-road and nonroad emissions in AL, FL, GA, and MS using U.S. EPA 1990–2011 national trends data based on 2005 NEI version 2 and 2008 NEI version 1.5. [b]Continuous emissions monitoring (CEM) data. EGU emissions (U.S. EPA, 2011b) were summed over all reporting EGUs in AL, FL, GA, and MS. [c]According to Version 2 of the 2008 NEI, emissions of CO, NO_x, PM_{10}, $PM_{2.5}$, and VOC are 11.0, 2.15, 1.95, 0.63, and 1.98 million tons, respectively, differing from the version 1.5 totals reported here due to changes in emission estimation methods compared with previous NEIs (U.S. EPA, 2012b). Version 2 of the 2008 NEI lists emissions of NH_3 and SO_2 as 0.31 and 1.46 million tons, respectively, consistent with version 1.5. Version 1.5 totals are tabulated here for consistency with prior years. [d]NEI for 2010 is not available. Estimated by subtracting tabulated 2008–2010 EGU and mobile-source NO_x changes from 2008 NEI version 1.5 NO_x emissions. [e]NEI for 2010 is not available. Estimated by subtracting tabulated 2008–2010 EGU SO_2 changes from 2008 NEI version 1.5 SO_2 emissions.

VOC, and NO_x emissions, but ambient measurements indicate that NO_x emissions must have increased during that period.

EGU heat input and CO_2 emissions both act as indicators for energy production and fuel combustion, and insight about sector contributions to pollutant emissions can be gained from national and statewide CO_2 data by sector and year. From 2006 to 2010, a combination of reductions from new emission controls, fuel changes, and economic recession are present in CO_2 emission trends. EGU CO_2 emissions, which are calculated based on plant heat input data (heat rate), increased by 31% from 1995 to 2007, dropped by 18% from 2007 to 2009, then increased in 2010 to match the 2008 level (Table 1). Since CO_2 emissions reflect plant heat input, the data imply a reduction of electricity generation during the 2008–2009 economic recession or increased production efficiency due, for example, to switching from older coal-fired units to newer natural gas combined cycle plants.

National CO_2 emissions from energy consumption (> 99% fossil fuels plus < 1% nonbiomass waste; excludes biomass consumption) declined by 7% from 2008 to 2009, the largest absolute and percentage decrease since 1949 (U.S. Energy Information Administration [EIA], 2012a). The 7% decline was driven by a 2.4% reduction of gross domestic product (GDP) and additional reductions exceeding 2% each in energy intensity and the carbon intensity of the energy supply (U.S. EIA, 2012a). The reductions in energy and carbon intensity were in turn driven by the pattern of economic decline in 2009, in which energy consumption in the industrial sector decreased by 9.9%; total industrial output declined by 9.8%, but output from energy-intensive industries declined more, e.g., by 33.9% for primary metals and 17.4% for nonmetallic minerals (U.S. EIA, 2012a).

U.S. Energy Information Administration (EIA) data indicate that CO_2 emissions in Alabama, Georgia, and Mississippi declined by 14.1% from 2007 to 2009 (U.S. EIA, 2012b): 20.9% for the electrical sector, 17.7% for the industrial sector, and 5.0% for transportation (U.S. EIA, 2012c; Florida is not included here because statewide emissions do not represent the panhandle). In the east south central census region (Alabama, Mississippi, Tennessee, and Kentucky), electricity generation costs for natural gas combined cycle plants decreased by nearly 4 cents/kW-hr from 2008 to 2009, leading to increased frequency of generation of electricity from gas of ~10% and decreased frequency from coal (Lu et al., 2012).

EGU SO_2 and NO_x emissions depend on production rates, fuel type, and deployment of emission controls. EGU emissions

of NO_x and SO_2 decreased throughout the period from 1998 to 2010, with SO_2 decreasing by 60% from 2005 to 2010 and NO_x decreasing by 50% from 2005 to 2010. For EGUs, CO_2 emissions were equal in 2008 and 2010 (Table 1), whereas SO_2 and NO_x emissions were 48 and 43% lower, respectively, in 2010 than in 2008 (Table 1). Lower EGU SO_2 and NO_x emissions in 2010 compared to 2008 therefore derive from emission controls or fuel changes (U.S. EIA, 2012a; Lu et al., 2012), rather than lower production output. For other sectors, NEI emissions of CO, SO_2, and NO_x in 2009 and 2010 are not yet reported (Table 1), but likely declined from 2008 to 2009 in correspondence with reported declines in CO_2 emissions. Emissions of CO_2, SO_2, and NO_x in 2010 and later depend on the nature of economic recovery, with emission increases occurring if energy-intensive industries increase output (U.S. EIA, 2012a). The national 7.1% reduction in petroleum consumption by the transportation sector from 2007 to 2009 was driven by high petroleum prices in 2008 and economic recession in 2009, but the U.S. fleet average fuel economy also improved by 1.5 miles per gallon (U.S. EIA, 2012a). Future transportation sector emissions will depend on emission control requirements, fleet turnover, fuel economy, and miles driven.

Ambient SO_2 and SO_4 trends

Mean annual SO_2 concentrations at the SEARCH sites decreased at statistically-significant rates ranging from 5.1 ± 2.0 to 9.7 ± 1.8% per year (Table 2; the PNS decrease of 4.1 ± 8.4 was not statistically significant due to a shorter monitoring record and the occurrence of anomalously high concentrations in 2006 and 2007 that were not observed at nearby OLF). EGU SO_2 emissions declined at an average rate of 7.6 ± 1.6% per year from 1999 to 2010, but two-thirds of the decline occurred from 2007 to 2010 (Table 1). NEI total SO_2 emissions decreased by 7.9 ± 1.6% per year from 1999 to 2010, which is qualitatively comparable to the mean annual ambient SO_2 concentration reductions of 5.1 ± 2.0 to 9.7 ± 1.8% per year from 1999 to 2010. Mean annual $PM_{2.5}$ SO_4 concentrations decreased at statistically significant ($p < 0.05$) rates ranging from 3.7 ± 1.1 to 6.2 ± 1.1% per year (Table 2), and therefore did not follow a 1:1 proportionality with SO_2 emission reductions. As discussed in the following, the $PM_{2.5}$ SO_4 decrease was linear with respect to EGU SO_2 emissions, but less than 1:1 proportional due to a nondomain or non-EGU source of SO_4. SO_x (sum of SO_2 and SO_4 in common units) decreased at rates of 5.2 ± 1.9 to 8.4 ± 1.5% per year (except at PNS, as previously noted).

Higher 1999–2010 mean SO_2 concentrations of 4.2–4.3 ppbv in Atlanta and Birmingham compared with 1.3–2.3 ppbv at nonurban SEARCH sites (Blanchard et al., 2012a; also see Table 1) indicate that urban SO_2 sources contribute to the observed SO_2 concentrations in those cities, but a regional "baseline" SO_2 exists. The rural SEARCH sites exhibited higher mean SO_2 concentrations than did CASTNet sites (Figure 2). The SEARCH and CASTNet SO_2 measurement methods are different, and no co-located data are available for comparison; the rural SEARCH sites are closer to major point sources than are the CASTNet sites, suggesting significant local emission contributions to the measured ambient SO_2. The mean annual $PM_{2.5}$ SO_4 concentrations were 3.3–4.3 $\mu g\ m^{-3}$ at urban SEARCH sites and 3.2–4.1 $\mu g\ m^{-3}$ at nonurban SEARCH locations (Blanchard et al., 2012a), indicating a dominant regional presence of SO_4. SEARCH mean $PM_{2.5}$ SO_4 and CASTNet mean TSP SO_4 concentrations were similar within error limits (Figure 3), further supporting the evidence for the regional nature of $PM_{2.5}$ SO_4. For both SO_2 and SO_4, the temporal trends were similar for CASTNet and SEARCH.

Mean annual $PM_{2.5}$ SO_4 concentrations were adjusted for variations in meteorological conditions utilizing a statistical model developed by Camalier et al. (2007), as described in Blanchard et al. (2010b). Although the model was originally developed to assess meteorologically adjusted O_3 trends, it predicted the daily average SO_4 concentrations with R^2 values

Table 2. Rates of decrease of species concentrations,[a] 1999–2010.[b] Units are percent per year.[c] Uncertainties are one standard error of the regression slope

		Gas-phase species				Condensed-phase species ($PM_{2.5}$)				
State	Site[d]	SO_2	NO_y	O_3[e]	CO	SO_4	NO_3	NH_4[f]	EC	OM
AL	BHM	5.1 ± 2.0	6.6 ± 0.8	1.9 ± 0.9	6.0 ± 0.6	5.2 ± 1.0	5.8 ± 0.9	5.9 ± 1.0	6.6 ± 1.8	6.1 ± 1.3
AL	CTR	6.8 ± 1.4	6.1 ± 0.8	3.1 ± 0.8	1.6 ± 1.0	6.2 ± 1.1	3.3 ± 1.3	5.7 ± 1.1	1.3 ± 1.9	3.3 ± 0.8
GA	JST	9.1 ± 1.7	7.3 ± 0.8	1.8 ± 0.7	7.2 ± 0.4	5.5 ± 1.1	4.7 ± 0.6	6.6 ± 1.0	6.8 ± 1.3	5.0 ± 1.0
GA	YRK	7.6 ± 2.3	7.7 ± 0.7	2.8 ± 0.5	1.6 ± 0.7	5.3 ± 1.3	4.0 ± 0.9	5.6 ± 1.2	6.0 ± 1.8	4.0 ± 1.3
MS	GFP	7.1 ± 1.4	7.4 ± 1.1	1.5 ± 0.6	5.0 ± 0.8	4.6 ± 0.8	0.6 ± 1.2	5.1 ± 1.0	5.5 ± 1.6	4.1 ± 0.9
MS	OAK	8.0 ± 1.5	6.0 ± 0.9	1.9 ± 0.4	2.2 ± 0.7	4.2 ± 0.8	0.9 ± 1.2	4.0 ± 0.8	4.0 ± 1.6	4.9 ± 1.2
FL	PNS	4.1 ± 8.4	9.0 ± 1.3	2.2 ± 0.6	6.5 ± 0.5	3.7 ± 1.1	1.7 ± 0.8	4.1 ± 1.2	7.8 ± 0.7	6.5 ± 0.3
FL	OLF	9.7 ± 1.8	7.8 ± 0.7	2.0 ± 0.5	1.2 ± 0.4	4.4 ± 0.9	2.3 ± 1.1	4.4 ± 1.1	4.9 ± 1.3	4.5 ± 1.2

Notes: [a]Annual mean for all species except annual 95th percentile of peak daily 8-hr O_3. [b]BHM and GFP gas measurements began in 2001. PNS gas measurements began in 2002. No PNS measurements were made in 2010. [c]Logarithms of annual concentrations were regressed against year, yielding slope values having units of fractional change per year (Parrish, 2006). The slopes were converted to percent per year by multiplying by 100%. [d]Sites are listed by state with each urban site preceding its paired nonurban site. [e]The mean annual O_3 trends ranged from decreases of 0.1 ± 0.6 to 1.3 ± 0.5 at nonurban sites and increases of 0.1 ± 0.7 to 0.7 ± 1.0 at urban sites. [f]Trends are listed for $PM_{2.5}$ NH_4. NH_3 (gas) measurements commenced in 2004 and exhibited no statistically significant trends, ranging from decreases of 2.0 ± 1.5% per year to increases of 3.8 ± 4.2% per year from 2004 to 2010.

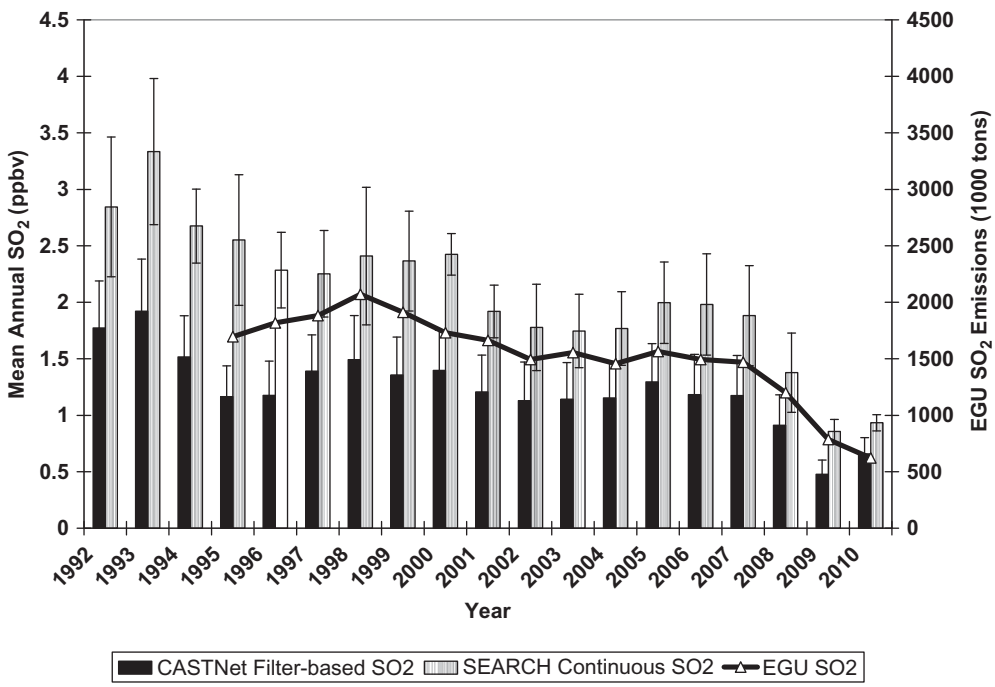

Figure 2. Comparison of mean annual SO_2 at three rural SEARCH sites, mean annual SO_2 at four CASTNet sites, and annual EGU SO_2 emissions (from Table 1). Error bars are one standard error of the mean annual site concentrations. Linear regression of ambient SO_2 against EGU SO_2 emissions is statistically significant (SEARCH: $p < 0.0001$, $r^2 = 0.88$, intercept = 0.03 ± 0.19 ppbv, slope = 1.23 ± 0.12 ppbv per 10^6 ton SO_2 emitted; CASTNet: $p < 0.0001$, $r^2 = 0.88$, intercept = 0.16 ± 0.10 ppbv, slope = 0.65 ± 0.06 ppbv per 10^6 ton SO_2 emitted).

ranging from 0.4 to 0.5 (i.e., meteorological factors accounted for 40 to 50% of the day-to-day SO_4 variations). The difference between meteorologically adjusted and unadjusted mean annual SO_4 concentrations was less than 0.1 to 0.4 μg m^{-3} for all sites and years, compared with the 2.3-μg m^{-3} decline in mean annual SO_4 concentrations (Figure 3). Meteorologically adjusted mean annual SO_4 concentrations for 2004 and 2005 were greater than, or equal to, unadjusted concentrations, indicating that the observed rise in mean annual SO_4 concentrations in 2004 and 2005 was not explained by meteorological variations.

Changes in EGU emissions of SO_2 account for the long-term declines in ambient concentrations of both SO_2 and SO_4 (Figures 2 and 3), since EGUs emitted 70–82% of total SO_2 over the period (Table 1). Mean ambient SO_2 concentrations at rural SEARCH sites decreased at a rate of 1.2 ± 0.1 ppbv per 10^6 tons SO_2 emitted by EGUs within the four-state domain (Figure 2). Mean ambient SO_4 concentrations decreased at a rate of 1.9 ± 0.2 μg m^{-3} SO_4 per 10^6 ton SO_2 emitted (Figure 3, average of SEARCH and CASTNet regressions). A statistically significant intercept of 1.1 ± 0.2 μg m^{-3} indicates a nondomain or non-EGU source of SO_4 equal to ~45% of the 2009–2010 mean ambient SO_4 concentrations. The ambient SO_4 reduction from 1999 to 2010 exhibited a linear response to EGU SO_2 emissions within the observed concentration range and uncertainties, but the regression intercept implies a nonproportional response of ambient SO_4 to EGU SO_2 emissions consistent with the results listed in Tables 1 and 2 and consistent with regional accumulation or a transport contribution to $PM_{2.5}$ SO_4.

A significant intercept term remained when the regressions were repeated using different methods and different emission domains. Nonparametric regression using the Theil–Sen procedure yielded a slope of 1.88 μg m^{-3} SO_4 per 10^6 ton SO_2 emitted and an intercept of 1.13 μg m^{-3} for SEARCH SO_4. For SEARCH met-adjusted SO_4, the nonparametric regression slope was 1.97 μg m^{-3} per 10^6 ton SO_2 emitted and the intercept was 0.98 μg m^{-3}. Since the domain of influence of SO_2 emissions is not limited by state boundaries, the regressions were repeated using EGU emissions from larger domains: (1) the original four states plus five surrounding states (LA, AR, TN, NC, SC), and (2) the preceding nine states plus TX and KY. Annual EGU SO_2 and NO_x emissions within the original four states correlated (r^2 ranging from 0.85 to 0.95) with EGU emissions in both the surrounding five states and in the two more distant states (TX and KY). Regression intercepts were essentially unchanged from the original four-state case, for example, 1.14 ± 0.21 μg m^{-3} ($r^2 = 0.94$, nine-state domain, SO_4 not adjusted for meteorology) and 0.83 ± 0.22 μg m^{-3} ($r^2 = 0.95$, 11-state domain, SO_4 not adjusted for meteorology).

Ambient NO_y trends

Mean annual NO_y concentrations declined at rates ranging from 6.0 ± 0.9 to 9.0 ± 1.3% per year (Table 2). The ambient NO_y declines are qualitatively consistent with the ~50% NO_x emission decrease from 1999 to 2010 (Table 1). Mean annual $PM_{2.5}$ NO_3 concentrations decreased at rates ranging from 0.6 ± 1.2 to 2.3 ± 1.1% per year (not significant at $p < 0.05$) at the four Gulf Coast sites and from 3.3 ± 1.3 to 5.8 ± 0.9% per year at the inland sites ($p < 0.05$) (Table 2), indicating that a statistically significant inland $PM_{2.5}$ NO_3 decline occurred. Mean $PM_{2.5}$

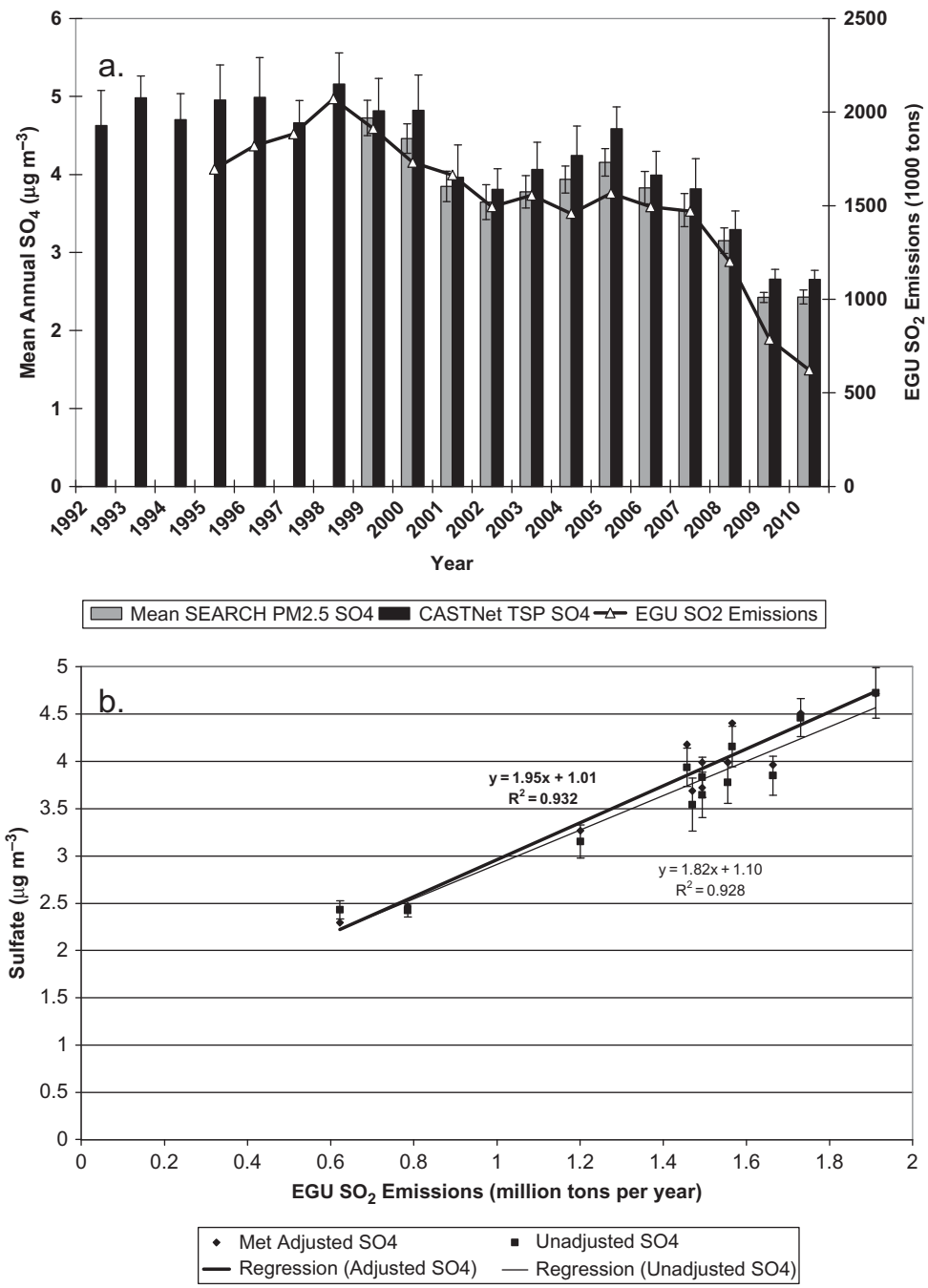

Figure 3. (a) Comparison of mean annual SO_4 at eight SEARCH sites, mean annual SO_4 at four CASTNet sites, and annual EGU SO_2 emissions (from Table 1). Error bars are one standard error of the mean annual site concentrations. (b) Linear regression of ambient SO_4 against EGU SO_2 emissions. SEARCH: $p < 0.0001$, $r^2 = 0.93$, intercept $= 1.09 \pm 0.23$ μg m^{-3}, slope $= 1.82 \pm 0.16$ μg m^{-3} per 10^6 ton SO_2 emitted; SEARCH met adjusted: $p < 0.0001$, $r^2 = 0.93$, intercept $= 1.01 \pm 0.22$ μg m^{-3}, slope $= 1.95 \pm 0.15$ μg m^{-3} per 10^6 ton SO_2 emitted; CASTNet: $p < 0.0001$, $r^2 = 0.88$, intercept $= 1.24 \pm 0.29$ μg m^{-3}, slope $= 1.91 \pm 0.19$ μg m^{-3} per 10^6 ton SO_2 emitted.

NO_3 concentrations are low (0.3–0.9 μg m^{-3}) (Blanchard et al., 2012a) and have not increased with decreasing $PM_{2.5}$ SO_4 concentrations (Table 2).

NO_x emissions are compared with ambient NO_y concentrations because NO_x is reactive and the NO_y measurements include both NO_x and NO_x reaction products. The composite NO_y trend at the rural SEARCH sites (OAK, CTR, YRK) was consistent with the trend in EGU NO_x emissions within measurement uncertainty (Figure 4). Linear regression of rural SEARCH NO_y with EGU NO_x emissions (using the data shown in Figure 4) was statistically significant ($p < 0.0001$, $r^2 = 0.84$, intercept $= 1.07 \pm 0.43$ ppbv, slope $= 6.25 \pm 0.73$ ppbv per 10^6

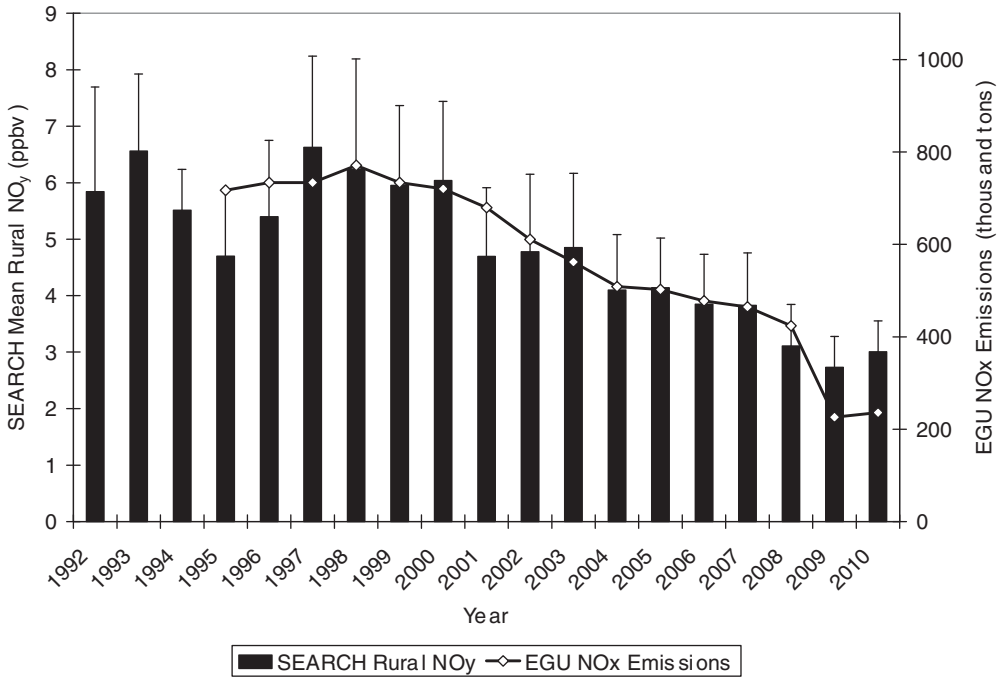

Figure 4. Comparison of annual EGU NO_x emissions from Table 1 with mean annual NO_y concentrations at three rural SEARCH sites. Linear regression of SEARCH NO_y against EGU NO_x emissions is statistically significant ($p < 0.0001$, $r^2 = 0.84$, intercept = 1.07 ± 0.43 ppbv, slope = 6.25 ± 0.73 ppbv per 10^6 ton NO_x emitted).

ton NO_x emitted). EGU emissions accounted for less than 28% of total NO_x emissions (Table 1), and CMB source apportionment indicates that point-source contributions accounted for 28–30% of mean 2004–2007 NO_y at the three rural SEARCH sites (Blanchard et al., 2012b). Concurrent declines in NO_x emissions from EGUs and other sources (Table 1) potentially confound determination of the link between rural NO_y and EGU NO_x emission trends using simple regressions or correlations. From 1995 to 2008, EGU and on-road vehicle NO_x emissions declined by 42 and 41%, respectively, in the four-state domain (Table 1).

Ambient O_3 trends

The annual O_3-season mean and the 95th percentile of the peak daily 8-hr O_3 concentrations declined at all SEARCH sites from 1999 to 2010. The 1999–2010 declines in the 95th percentile ranged from 1.5 ± 0.6 to 3.1 ± 0.8% per year (median 2.0% per year decrease) (Table 2), corresponding to decreases of 1.1 ± 0.4 to 2.4 ± 0.6 ppbv per year. Annual O_3-season mean peak 8-hr O_3 at the three rural SEARCH sites (CTR, OAK, YRK) did not decline in proportion to the decline in EGU NO_x emissions (Figure 5). The annual O_3-season means (Figure 5) and the 95th percentile of peak daily 8-hr O_3 increased from 1992 to 1999 and decreased from 1999 to 2010.

The U.S. EPA statistical model for meteorological adjustment of O_3 (Camalier et al., 2007; Blanchard et al., 2010b) was used to determine adjusted seasonal means (all days, March–October) and adjusted means for high-O_3 days (days exceeding the 90th percentile) for 1999–2010 (Figure 5). For all sites and years, and for both seasonal averages and high-O_3 days, adjusted and unadjusted means differed by ~5 to 10 ppbv. Meteorological adjustment reveals a network-average decline in annual O_3-season mean peak 8-hr O_3 concentrations of 1.1 ± 0.1 ppbv per year from 1999 to 2010 (Figure 6). From 2001 to 2007, the unadjusted network means increased by 3.5 ppbv, whereas the adjusted means decreased by 4.3 ppbv, revealing a downward trend otherwise obscured by year-to-year meteorological variability.

For comparison with the SEARCH peak 8-hr O_3 trends, peak 8-hr O_3 data were obtained from 107 U.S. EPA compliance-monitoring sites in AL, FL, GA, and MS. The trends in the annual 4th highest peak 8-hr O_3 were similar to the trends observed in the SEARCH 95th percentile peak 8-hr O_3 and mean peak 8-hr O_3: declining concentrations from about 2000 to 2004, a rise from 2004 to 2007, and another decline from 2007 to 2009. Urban, suburban, and rural sites exhibited the same peak 8-hr O_3 trends with approximately the same average peak concentrations, suggesting a regional as well as local component.

The 95th percentile peak 8-hr O_3 trends at JST were indistinguishable from the mean of the 95th percentile peak 8-hr O_3 trends at PAMS and other sites experiencing high O_3 in Atlanta. Atlanta peak 8-hr O_3 declined along with declining ambient NMOC and NO_y concentrations. Throughout the SEARCH domain, however, the O_3 declines are not attributed to a specific precursor using the data and methods reported here, because the mean concentrations of all O_3 precursors trended downward (Table 2).

Ambient CO, NMOC, EC, and OM trends

Mean annual CO concentrations declined at rates ranging from 1.2 ± 0.4 to 2.2 ± 0.7% per year at nonurban sites and at rates ranging from 5.0 ± 0.8 to 7.2 ± 0.4% per year at urban sites

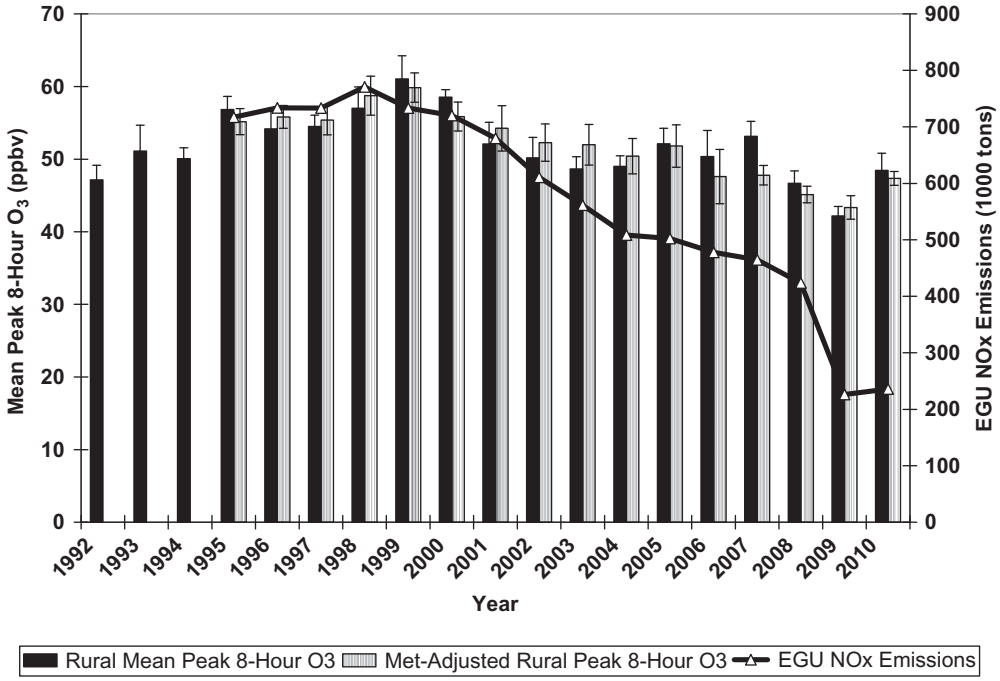

Figure 5. Comparison of annual EGU NO_x emissions from Table 1 with mean annual O_3 season (March–October) peak 8-hr O_3 concentrations at three rural SEARCH sites (CTR, OAK, YRK).

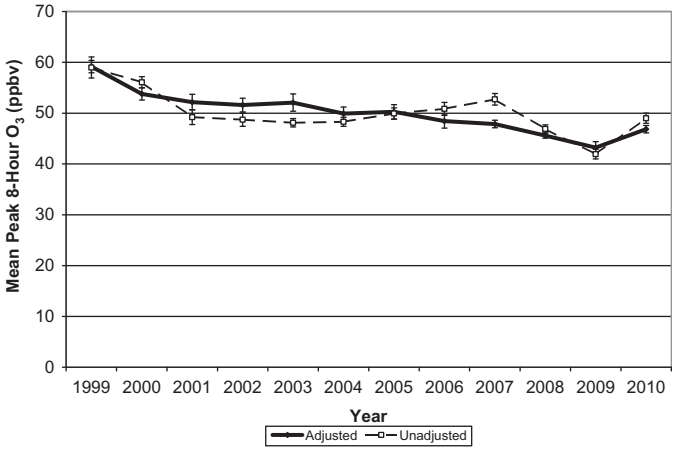

Figure 6. SEARCH network mean annual O_3 season peak daily 8-hr O_3 concentrations, with and without adjustment for meteorological variations. Error bars are one standard error of the intersite mean annual concentrations.

(Table 2). The difference between urban and nonurban rates of declines remained when CO concentrations were redetermined by subtracting 100 ppbv to approximately adjust for continental background CO concentrations (Parrish et al., 2002). The ambient CO declines were ~15 to 58%, qualitatively consistent with the 42% CO emission decrease from 1999 to 2008 (Table 1).

SEARCH NMOC measurements, described in Blanchard et al. (2010a), were made only at JST. The JST mean annual NMOC concentrations declined from 285 ppbC in 1999 to 120 ppbC in 2008, a 60% decline (Blanchard et al., 2010a, updated to include 2008 measurements). Trends in NMOC measurements at PAMS sites are not evident, due to data quality issues identified from year to year (Blanchard et al., 2010a).

Mean annual $PM_{2.5}$ EC concentrations decreased at statistically significant rates ranging from 4.0 ± 1.6 to 7.8 ± 0.7% per year (Table 2; the CTR downward trend of 1.3 ± 1.9% per year was not statistically significant due to the occurrence of anomalously high EC concentrations in 2009 that were not observed at other sites; excluding 2009, the CTR downward trend was statistically significant at 3.2 ± 1.4% per year). Mean annual $PM_{2.5}$ OM concentrations decreased at rates ranging from 3.3 ± 0.8 to 6.5 ± 0.3% per year (Table 2). The greatest reductions were for EC at urban sites, which declined by 5.5 ± 1.6 to 7.8 ± 0.7% per year (Table 2). The mean OM/EC was ~8:1 at rural sites and ~4:1 at the sites in the large urban areas (BHM and JST). No significant trend was evident in the mean OM/EC at any site, although year-to-year variation exists.

Comparisons with EC and OM emission trends cannot be made since EC and OM emissions are not reported in the NEI. A poorly quantified portion of OM consists of secondary organic aerosol (SOA). SOA is thought to derive from atmospheric oxidation of biogenic VOC precursors, such as isoprene and the terpenes, and from anthropogenic compounds. The complexities of SOA formation from different classes of organic material (volatile, semivolatile, or intermediate volatility) and loss are recognized but remain incompletely characterized (Hallquist, 2009; Hoyle, 2011; de Gouw et al., 2011).

Quarterly average EC, OM, and CO concentrations indicate roughly comparable magnitudes of downward trend and seasonal variation. Seasonal EC and CO maxima tend to occur in the fourth quarter, when high daily concentrations are associated with poor ventilation (Blanchard et al., 2012a).

Ambient $PM_{2.5}$ mass trends

Network-average mean annual $PM_{2.5}$ mass concentrations declined by 4.8 μg m^{-3} from 1999 to 2010 (Figure 7). The declines ranged from 1.7 μg m^{-3} to 5.2 μg m^{-3} at rural sites and from 3.0 μg m^{-3} to 7.4 μg m^{-3} at urban sites. The mean network $PM_{2.5}$ mass concentration declines were comprised of reductions of 2.3 μg m^{-3} SO_4, 2.2 μg m^{-3} OM, 0.9 μg m^{-3} NH_4, 0.6 μg m^{-3} EC, and 0.1 μg m^{-3} NO_3. Mean MMO and "other" concentrations increased by 0.2 μg m^{-3} and 1.1 μg m^{-3}, respectively. The latter increase is consistent with an average OM/OC ratio that was higher throughout the study period than the assumed value of 1.4, with improvements in measurement techniques yielding better mass closure over time. All mean species concentrations increased from 2009 to 2010, except that SO_4 maintained a near constant value (Figure 7).

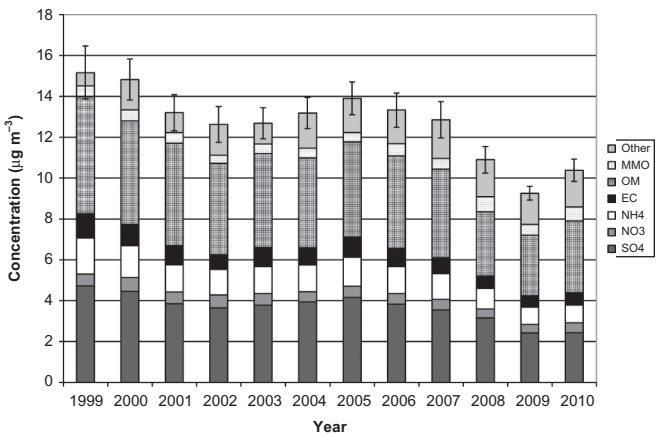

Figure 7. Trends in SEARCH network mean annual $PM_{2.5}$ mass concentration and composition. The mean annual federal reference method (FRM) mass concentrations, averaged across the eight SEARCH sites, are equal to the sum of measured components plus "other." Uncertainties are one standard error of the mean intersite FRM mass concentrations.

Trends in extrema

Changes occurred in the distributions of daily concentrations of gases, $PM_{2.5}$ mass, and $PM_{2.5}$ species over time, with fewer extreme high concentrations occurring in later years (Figure 8). $PM_{2.5}$ SO_4 concentrations decreased more at the 80th percentile and higher between 2004 and 2010 than between 1999 and 2004 (Figure 8). By 2010, over half the daily-average SO_2 concentrations were less than 1 ppbv at YRK (Figure 8) and the other rural sites. For some pollutants (e.g., CO), close proximity of the frequency curves for different years at the 10th percentile is potentially attributable to "baseline" or "background" conditions.

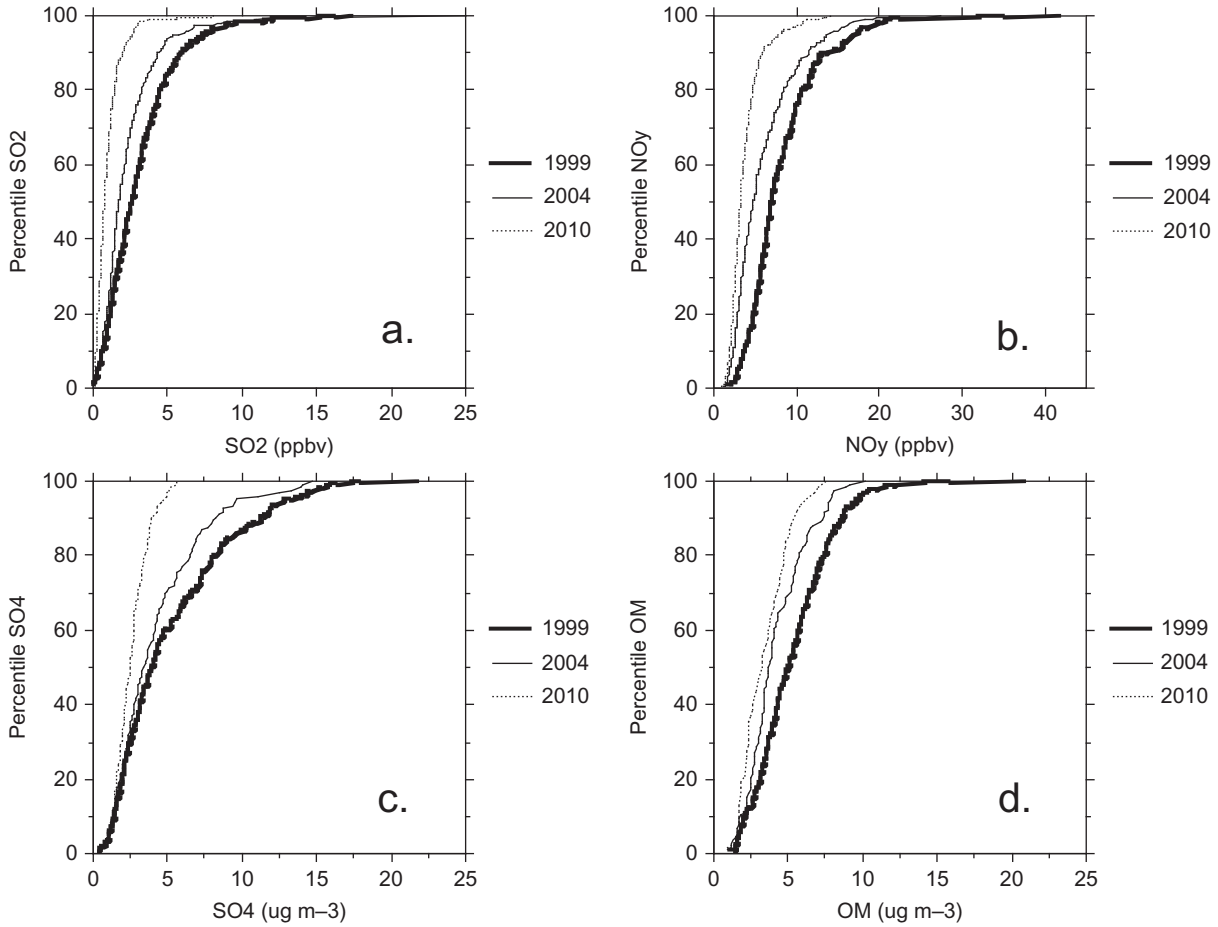

Figure 8. Statistical distributions of YRK 1999, 2004, and 2010 daily concentrations of (a) SO_2, (b) NO_y, (c) SO_4, and (d) OM.

Discussion

Comparisons of the trends in ambient primary pollutant concentrations with CO, SO_2, and NO_x emission changes in the SEARCH domain confirm expectations of approximately proportional relationships between emissions and ambient concentrations, with uncertainties related to emissions and dispersion variations. The direct CEM SO_2 and NO_x emissions data reported for EGUs are believed to be the most accurate emissions values. Emission estimates from other sources have higher uncertainties (NARSTO, 2005). Spatial averaging of monitoring data from rural sites reveals significant relationships between emissions and ambient concentrations of CO, SO_2, and NO_x or NO_y, but local emission changes affect these nominally regionally representative sites at times.

For secondary species, including O_3 and $PM_{2.5}$ components such as SO_4, NO_3, and SOA, the relation between ambient concentrations and precursor emissions depends on the relevant atmospheric chemistry and dispersion. In the case of $PM_{2.5}$ SO_4, the temporal pattern in ambient concentrations is qualitatively similar to changes in regional SO_2 emissions. From 1999 to 2010, mean annual $PM_{2.5}$ SO_4 concentrations decreased by more than 2 $\mu g\ m^{-3}$ throughout the region, providing a substantial contribution toward attaining the National Ambient Air Quality Standard for $PM_{2.5}$. Temporal trends in mean annual concentrations of SO_2 and SO_4 were similar for the CASTNet and SEARCH networks, indicating that year-to-year changes occurred over a more extended geographical scale than represented by the SEARCH sites.

When atmospheric chemistry is more complex, as for O_3, particulate NO_3, and SOA, the relationships between ambient concentrations and precursor emissions are less evident. SEARCH sites exhibit declining concentrations of NO and NO_y that are linked to reduced emissions of NO_x from EGUs and motor vehicles, but downward trends in $PM_{2.5}$ NO_3 (Table 2) are less than the decreases in ambient NO_y concentrations. Particulate NO_3 concentrations depend on an equilibrium relationship involving HNO_3, NH_3, SO_4, temperature, and moisture. Thermal equilibrium model applications indicate that $PM_{2.5}$ NO_3 formation in the Southeast is limited by the availability of NH_3 (Blanchard and Hidy, 2003, 2005; Blanchard et al., 2007). Statistically significant trends in gas-phase NH_3 were not observed, but $PM_{2.5}$ NH_4 trended downward with decreasing concentrations of $PM_{2.5}$ SO_4 and NO_3 (Table 2).

The relationship between O_3 and precursor concentrations is known to be nonlinear and dependent on multiple factors, including meteorological conditions, ambient concentrations of NO_x and NMOC, and the reactivity of the NMOC mix. In the late 1990s, the U.S. EPA adopted a regional approach to O_3 reduction, which included NO_x emission reductions from EGUs located mainly in the eastern and midwestern United States (U.S. EPA, 2012a). This approach to O_3 reduction was predicated on the hypothesis that regional O_3 concentrations were in a regime in which they would be roughly proportional to NO_x concentrations, and much less dependent on ambient anthropogenic NMOC concentrations. The NO_x-sensitivity hypothesis could apply to the southeastern United States as well and is testable in principle by comparing rural O_3 concentrations in the Southeast with EGU and mobile-source reductions of NO_x emissions. Peak 8-hr O_3 declined at SEARCH and other sites from 1999 to 2010. Meteorological adjustment confirms a consistent downward trend in mean peak 8-hr O_3 from ~60 ppbv in 1999 to ~45 ppbv in 2010. The O_3 trend is not comparable to the trend in EGU NO_x emissions alone, which represent less than 30% of total NO_x emissions. Mobile-source NO_x emissions dominate urban NO_y and contribute >50% at nonurban sites (Blanchard et al., 2012b). The largest O_3 decreases occurred from 1999 to 2001 and from 2007 to 2009. The test of O_3 sensitivity to total regional NO_x reductions is ambiguous, because the ~25% reduction of peak O_3 is coincident with reductions of both NO_x and VOC emissions. Because multiple O_3 precursor emissions decreased, declining O_3 trends cannot be attributed to a specific precursor with the available data.

At JST, the only SEARCH site with ambient NMOC data (Blanchard et al., 2010a), mean annual NMOC and NO_y concentrations declined by approximately the same magnitude since 1999. This result implies that the emissions ratio VOC/NO_x was nearly constant over the decade. The ratio of VOC/NO_x is an important determinant of peak O_3 concentrations. Speculatively, the lack of change in the emissions VOC/NO_x could have hindered O_3 reductions because of well-known nonlinear relations between O_3 concentrations and precursor concentrations (e.g., NRC 1991; NARSTO, 1999). Another complicating factor is a lack of change in the mean NMOC-OH reactivity over the study period, as the relative proportions of NMOC species changed little in spite of a 44% reduction in mean ambient NMOC concentrations at JST (Blanchard et al., 2010a).

For OM, there is a complex and ambiguous relationship between directly emitted particles and secondary material produced from oxidation of certain gas-phase species. SOA in the Southeast is believed to be strongly influenced regionally by biogenic VOC, especially isoprene. Urban SOA is likely to be influenced by oxidation of anthropogenic VOCs, including aromatic compounds, and by anthropogenic compounds of intermediate volatility (Hallquist et al., 2009; Hoyle et al., 2011; de Gouw et al., 2011). To first order, one would expect that the biogenic SOA component would not generate trends in the OM data. Trends in the anthropogenic SOA component are expected to depend on changes in the anthropogenic precursor emissions and the extent of oxidation taking place. The primary OM component derives from combustion sources, including diesel and gasoline engine emissions, and biomass combustion (Blanchard et al., 2012b). CO concentrations in urban environments are heavily influenced by gasoline-engine motor vehicle exhaust. The EC trend may be related to reductions of diesel-engine emissions. Despite the reductions of both OM and EC, a substantial amount of each remains present at the end of the monitoring record, and the remaining OM derives from an unquantified mix of primary and secondary pollutants. Further research and interpretation of carbon observations are needed to resolve these questions.

Conclusions

The data from the SEARCH network show that major improvements in air quality occurred in the Southeast from

1999 to 2010. Consistent monitoring at well-instrumented sites provides information necessary for relating these changes in air quality to emission changes and to atmospheric processing of emissions. Accurate emission trends are a key component of the analysis. Uncertainties in emissions estimates, especially from non-EGU sources, create ambiguities in comparison between emissions and ambient pollutant concentrations. These ambiguities are compounded by the aggregation of emissions over the four-state region in this study and by meteorological variability. Emissions and secondary pollutant concentrations show complex relationships that are dependent on year-to-year variations in dispersion and atmospheric chemistry.

In the Southeast, decision makers continue to be challenged by the presence of O_3, the further reduction of which will require continuing reductions of precursor emissions to achieve the National Ambient Air Quality Standard. Reductions of ambient concentrations of O_3 are smaller than reductions in NO_x and VOC precursor emissions.

Reduction in fine particles is recorded in the ambient air quality data, resulting in part from reductions of primary PM, especially EC and a portion of OM, and in part from reduction of gas precursors known to form particles, especially SO_4 from SO_2. Continued reduction of $PM_{2.5}$ will require attention not only to SO_2 emissions, but also to organic constituents. Controlling OM is likely to be complicated by unmanageable biogenic species present in the Southeast. Decreasing particulate nitrate concentrations by means of NO_x emission reductions does not appear to be an efficient approach for reducing $PM_{2.5}$ mass in the Southeast, because mean $PM_{2.5}$ NO_3 concentrations are low (0.3–0.9 $\mu g\ m^{-3}$) and have not increased with decreasing $PM_{2.5}$ SO_4 concentrations.

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References

Atmospheric Research and Analysis. 2010. http://www.atmospheric-research.com/studies/SEARCH/index.html (accessed April, 2010).

Blanchard, C.L., and G.M. Hidy. 2003. Effects of changes in sulfate, ammonia, and nitric acid on particulate nitrate concentrations in the southeastern United States. *J. Air Waste Manage. Assoc*. 53:283–290. doi:10.1080/10473289.2003.10466152

Blanchard, C.L., and G.M. Hidy. 2005. Effects of SO_2 and NO_x emission reductions on $PM_{2.5}$ mass concentrations in the southeastern United States. *J. Air Waste Manage. Assoc*. 55:265–272. doi:10.1080/10473289.2005.10464624

Blanchard, C.L., S. Tanenbaum, and G.M. Hidy. 2007. Effects of SO_2 and NO_x emission reductions on $PM_{2.5}$ mass concentrations: Regional comparisons. *J. Air Waste Manage. Assoc*. 57:1337–1350. doi: 10.3155/1047-3289.57.11.1337

Blanchard, C.L., G.M. Hidy, S. Tanenbaum, E.S. Edgerton, B.E. Hartsell, and J.J. Jansen. 2008. Carbon in southeastern U.S. aerosol particles: Empirical estimates of secondary organic aerosol formation. *Atmos. Environ*. 42:6710–6720. doi:10.1016/j.atmosenv.2008.04.011

Blanchard, C.L., G.M. Hidy, S. Tanenbaum, R. Rasmussen, R. Watkins, and E. Edgerton. 2010a. NMOC, ozone, and organic aerosol in the southeastern states, 1999–2007: 1. Spatial and temporal variations of NMOC concentrations and composition in Atlanta, Georgia. *Atmos. Environ*. 44:4827–4839. doi:10.1016/j.atmosenv.2010.08.036

Blanchard, C.L., G.M. Hidy, and S. Tanenbaum. 2010b. NMOC, ozone, and organic aerosol in the southeastern states, 1999–2007: 2. Ozone trends and sensitivity to NMOC emissions in Atlanta, Georgia. *Atmos. Environ*. 44:4840–4849. doi:10.1016/j.atmosenv.2010.07.030

Blanchard, C.L., G.M. Hidy, S. Tanenbaum, and E.S. Edgerton. 2011. NMOC, ozone, and organic aerosol in the southeastern states, 1999–2007: 3. Origins of organic aerosol in Atlanta, Georgia, and surrounding areas. *Atmos. Environ*. 45:1291–1302. doi:10.1016/j.atmosenv.2010.12.004

Blanchard, C.L., S. Tanenbaum, and G.M. Hidy. 2012a. The Southeastern Aerosol Research and Characterization (SEARCH) study: spatial variations and chemical climatology, 1999–2010. *J. Air Waste Manage. Assoc.* 63(3): 260–275. doi:10.1080/10962247.2012.748523

Blanchard, C.L., S. Tanenbaum, and G.M. Hidy. 2012b. Source contributions to atmospheric particulate matter and gaseous species in the southeastern United States. *Environ. Sci. Technol.* 46(10):5479–5488. doi 10.1021/es203568t.

Camalier, L., W. Cox, and P. Dolwick. 2007. The effects of meteorology and their use in assessing ozone trends. *Atmos. Environ*.41:7127–7137.doi:10.1016/j.atmosenv.2007.04.061

De Gouw, J., et al. 2011. Organic aerosol formation downwind from the Deepwater Horizon oil spill. *Science* 331:1295–1299. doi:10.1126/science.1200320

Edgerton, E., B.E. Hartsell, J.J. Jansen, and D.A. Hansen. 2001. Gas and particulate emissions from biomass burning in the Southeastern U.S. Presented at the Air &Waste Management Association Conference on Regional Haze and Global Radiation Balance, October 5.

Edgerton, E.S., J.J. Jansen, M. Zheng, and B.E. Hartsell. 2004. Sources of organic carbon in $PM_{2.5}$ based on ^{14}C and tracer analyses. Presented at the 8th International Conference on Carbonaceous Particles in the Atmosphere, Vienna, Austria, September 16.

Edgerton, E.S., B.E. Hartsell, R.D. Saylor, J.J. Jansen, D.A. Hansen, and G.M. Hidy. 2005. The Southeastern Aerosol Research and Characterization Study: Part 2—Filter-based measurements of $PM_{2.5}$ and PM_{coarse} mass and composition. *J. Air Waste Manage. Assoc*. 55:1527–1542. doi:10.1080/10473289.2005.10464744

Edgerton, E.S., B.E. Hartsell, R.D. Saylor, J.J. Jansen, D.A. Hansen, and G.M. Hidy. 2006. The Southeastern Aerosol Research and Characterization Study, part 3: Continuous measurements of fine particulate matter mass and composition. *J. Air Waste Manage. Assoc*. 56:1325–1341. doi:10.1080/10473289.2006.10464585

Edgerton, E.S., R.D. Saylor, B.E. Hartsell, J.J. Jansen, and D.A. Hansen. 2007. Ammonia and ammonium measurements from the southeastern United States. *Atmos. Environ.* 41:3339–3351. doi:10.1016/j.atmosenv.2006.12.034

Edgerton, E.S., G.S. Casuccio, R.D. Saylor, T.L. Lersch, B.E. Hartsell, J.J. Jansen, and D.A. Hansen. 2009. Measurements of OC and EC in coarse particulate matter in the southeastern United States. 2009. *J. Air Waste Manage. Assoc*. 59:78–90. doi:10.3155/1047-3289.59.1.78

El-Zanan, H.S., B. Zielinska, L.R. Mazzoleni, and D.A. Hansen. 2009. Analytical determination of the aerosol organic mass-to-organic carbon ratio. *J. Air Waste Manage. Assoc*. 59:58–69. doi:10.3155/1047-3289.59.1.58

Gego, E., A. Gilliland, J. Godowitch, S. T. Rao, P.S. Porter, and C. Hogrefe. 2008. Modeling analyses of the effects of changes in nitrogen oxides emissions from the electric power sector on ozone levels in the eastern United States. *J. Air Waste Manage. Assoc*. 58:580–588. doi: 10.3155/1047-3289.58.4.580

Gego, E., P.S. Porter, A. Gilliland, and S.T. Rao. 2007. Observation-based assessment of the impact of nitrogen oxides emissions reductions on ozone air quality over the eastern United States. *J. Appl. Meteorol. Climatol*. 46:994–1008. doi:10.1175/JAM2523.1

Gilliland, A., C. Hogrefe, R.W. Pinder, J. Godowitch, K.L. Foley, and S.T. Rao. 2008. Dynamic evaluation of regional air quality models: Assessing changes in O_3 stemming from changes in emissions and meteorology. *Atmos. Environ*. 42:5110–5123. doi:10.1016/j.atmosenv.2008.02.018

Godowitch, J., A. Gilliland, R.R. Draxler, and S.T. Rao. 2008. Modeling assessment of point source NO_x emission reductions on ozone levels in the eastern United States. *Atmos. Environ*. 42:87–100. doi:10.1016/j.atmosenv.2007.09.032

Hallquist, M., J.C. Wenger, U. Baltensperger, Y. Rudich, D. Simpson, M. Claeys, J. Dommen, N.M. Donahue, C. George, A.H. Goldstein, J.F. Hamilton, H. Herrmann, T. Hoffmann, Y. Iinuma, M. Jang, M.E. Jenkin, J.L. Jimenez, A. Kiendler-Scharr, W. Maenhaut, G. McFiggans, T.F. Mentel, A. Monod, A.S.H. Prévôt, J.H. Seinfeld, J.D. Surratt, R. Szmigielski, and J. Wildt. 2009. The formation, properties and impact of secondary organic aerosol: Current and emerging issues. *Atmos. Chem. Phys*. 9:5155–5236.doi:10.5194/acp-9-5155-2009

Hand, J.L., B.A. Schichtel, W.C. Malm, and M.L. Pitchford. 2012. Particulate sulfate ion concentration and SO2 emission trends in the United States from the early 1990s through 2010. *Atmos. Chem. Phys. Discuss*. 12:19311–19347. doi:10.5194/acpd-12-19311-2012

Hansen, D.A., E.S. Edgerton, B.E. Hartsell, J.J. Jansen, G.M. Hidy, K. Kandasamy, and C.L. Blanchard. 2003. The Southeastern Aerosol Research and Characterization Study (SEARCH): 1. Overview. *J. Air Waste Manage. Assoc*. 53:1460–1471. doi:10.1080/10473289.2003.10466318

Hansen, D.A., E. Edgerton, B. Hartsell, J. Jansen, H. Burge, P. Koutrakis, C. Rogers, H. Suh, J. Chow, B. Zielinska, P. McMurry, J. Mulholland, A. Russell, and R. Rasmussen. 2006. Air quality measurements for the aerosol research and inhalation epidemiology study. *J. Air Waste Manage. Assoc*. 56: 1445–1458. doi:10.1080/10473289.2006.10464549

Hoyle, C.R., M. Boy, N.M. Donahue, J.L. Fry, M. Glasius, A. Guenther, A.G. Hallar, K. Huff Hartz, M.D. Petters, T. Petaja, T. Rosenoern, and A.P. Sullivan. 2011. A review of the anthropogenic influence on biogenic secondary organic aerosol.*Atmos. Chem. Phys*. 11:321–343. doi:10.5194/acp-11-321-2011

Lu, X., J. Salovaara, and M.B. McElroy. 2012. Implications of the recent reductions in natural gas prices for emissions of CO_2 from the U.S. power sector. *Environ. Sci. Technol*. doi:10.1021/es203750k

NARSTO. 1999. An assessment of tropospheric ozone pollution: A North American perspective. http://www.narsto.org/section.src?SID=7 (accessed May 16, 2011).

NARSTO. 2005. Improving emission inventories for effective air quality management across North America. http://www.narsto.org/section.src?SID=8 (accessed April 23, 2011).

National Research Council. 1991. *Rethinking the Ozone Problem in Urban and Regional Air Pollution*. Washington, DC: National Academies Press.

Parrish, D.D., M. Trainer, D. Hereid, E.J. Williams, K.J. Olszyna, R.A. Harley, J.F. Meagher, and F.C. Fehsenfeld. 2002. Decadal change in carbon monoxide to nitrogen oxide ratio in U.S. vehicular emissions. *J. Geophys. Res*. 107 (D12):4140–4148. doi:10.1029/2001JD000720

Parrish, D. 2006. Critical evaluation of U.S. on-road vehicle emission inventories. *Atmos. Environ.* 40:2288–2300. doi:10.1016/j.atmosenv.2005.11.033

Saylor, R., E.S. Edgerton, B.E. Hartsell, K. Baumann, and D.A. Hansen, 2010. Continuous gaseous and total ammonia measurements from the southeastern aerosol research and characterization (SEARCH) study. *Atmos. Environ.* 44:4994–5004. doi:10.1016/j.atmosenv.2010.07.055

U.S. Energy Information Administration. 2012a. U.S. Carbon Dioxide Emissions in 2009: A Retrospective Review. http://www.eia.gov/oiaf/environment/emissions/carbon (accessed March 3, 2012). Monthly Energy Review, June 2012. http://www.eia.gov/totalenergy/data/monthly/pdf/sec12.pdf (accessed July 23, 2012).

U.S. Energy Information Administration. 2012b. http://www.eia.gov/environment/emissions/state/analysis/pdf/stateanalysis.pdf, http://www.eia.gov/totalenergy/data/monthly/pdf/mer.pdf (accessed March 3, 2012).

U.S. Energy Information Administration. 2012c. http://www.eia.gov/state/state-energy-profiles.cfm?sid=AL (accessed March 14, 2012).

U.S. Environmental Protection Agency. 1996. *Air Quality Criteria for Ozone and Other Photochemical Oxidants*. EPA/600/P-93/004aF. Research Triangle Park, NC: Office of Health and Environmental Assessment, Environmental Criteria Office; and Springfield, VA: NTIS. http://www.epa.gov/nscep (accessed September 16, 2009).

U.S. Environmental Protection Agency. 2007. National Emissions Inventory (NEI) air pollutant emissions trends data. http://www.epa.gov/ttn/chief/trends/index.html (accessed April 28, 2009).

U.S. Environmental Protection Agency. 2008a. Criteria pollutant emissions summary files. http://www.epa.gov/ttn/chief/net/critsummary.html (accessed May 21, 2010).

U.S. Environmental Protection Agency. 2008b. Criteria pollutant emissions summary files. http://www.epa.gov/ttn/chief/net/2002inventory.html (accessed May 1, 2008).

U.S. Environmental Protection Agency. 2010a. CASTNet home. http://www.epa.gov/castnet/ (accessed April 2010).

U.S. Environmental Protection Agency. 2010b. Criteria pollutant emissions summary files. http://www.epa.gov/ttn/chief/net/2005inventory.html (accessed April 28, 2009), ftp://ftp.epa.gov/EmisInventory/2005_nei/tier_summaries/tier_05v2/ (accessed May 21, 2010).

U.S. Environmental Protection Agency. 2010c. Continuous emissions monitoring fact sheet. http://www.epa.gov/airmarkets/emissions/continuous-factsheet.html (accessed May 21, 2010), http://camddataandmaps.epa.gov/gdm/index.cfm?fuseaction=emissions.wizard (accessed May 21, 2010).

U.S. Environmental Protection Agency. 2011a. Clean air interstate rule (CAIR) http://www.epa.gov/airmarkets/progsregs/cair/index.html (accessed April 16, 2011).

U.S. Environmental Protection Agency. 2011b. SO_2 reductions and allowance trading under the acid rain program http://www.epa.gov/airmarkets/progsregs/arp/s02.html (accessed April 16, 2011).

U.S. Environmental Protection Agency. 2011c. Diesel fuel. http://www.epa.gov/otaq/regs/fuels/diesel/diesel.htm (accessed April 16, 2011).

U.S. Environmental Protection Agency. 2011d. Tier 2 vehicle and gasoline sulfur program. http://www.epa.gov/tier2/ (accessed April 16, 2011).

U.S. Environmental Protection Agency. 2011e. Criteria pollutant emissions summary files. http://www.epa.gov/ttn/chief/net/2008inventory.html (accessed April 9, 2011, June 1, 2011, February 23, 2012).

U.S. Environmental Protection Agency. 2011f. National Emissions Inventory (NEI) air pollutant emissions trends data. www.epa.gov/ttn/chief/trends (accessed April 20, 2011).

U.S. Environmental Protection Agency. 2012a. The NOx SIP call. http://www.epa.gov/airmarkets/progsregs/nox/noxsipcall.html (accessed March 14, 2012).

U.S. Environmental Protection Agency. 2012b. 2008 National Emissions Inventory, version 2 technical support document. http://www.epa.gov/ttn/chief/net/2008neiv2/2008_neiv2_tsd_draft.pdf (accessed October 29, 2012).

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