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Chemical climatology of the southeastern United States, 1999–2013

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Abstract

A series of experiments (the Southern Oxidant and Aerosol Study-SOAS) took place in central Alabama in June–July 2013 as part of the broader Southern Atmosphere Study (SAS). These projects were aimed at studying oxidant photochemistry and for-
5 mation and impacts of aerosols at a detailed process level in a location where high biogenic organic vapor emissions interact with anthropogenic emissions, and the atmospheric chemistry occurs in a subtropical climate in North America. The majority of the ground-based experiments were located at the Southeastern Aerosol Research and Characterization (SEARCH) Centreville (CTR) site near Brent, Alabama, where
10 extensive, unique aerometric measurements of meteorology, trace gases and particles have been made from the early 1990s through 2013. The SEARCH network data permits a characterization of temporal and spatial context of the SOAS findings. The long-term measurements show that the SOAS experiments took place during the second wettest and coolest year in the 2000–2013 period, with lower than average solar radi-
15 ation. The pollution levels at CTR and other SEARCH sites were the lowest since full measurements began in 1999. This dataset provides a perspective for the SOAS program in terms of long-term average chemistry (chemical climatology) and short-term comparisons of summer average spatial variability across the Southeast at high temporal (hourly) resolution. Changes in anthropogenic gas and particle emissions between
20 1999 and 2013, account for the decline in pollutant concentrations at the monitoring sites in the region. The long-term and short-term data provide an opportunity to contrast SOAS results with temporally and spatially variable conditions in support for the development of tests for the robustness of SOAS findings.

1 Introduction

25 An important element of atmospheric science is the reconciliation of the results of short-term field campaigns with long-term measurements. Such comparisons are used

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to estimate the extent to which the results from special studies apply to other times, different locations, or under different aerometric conditions. Short-term campaigns for studying atmospheric processes are amenable to detailed observations of complex physicochemical processes. While it is impractical to obtain such detail over many years, long-term measurements can provide basic indicators of key atmospheric and chemical processes. The Southern Oxidant and Aerosol Study (SOAS) campaign was part of the Southern Atmosphere Study (SAS) held in the period of 1 June–15 July 2013 (EPA, 2014a; UCAR, 2014). SAS encompassed several major intensive field campaigns, of which SOAS was one. The campaigns involved a number of research groups in order to inform a series of coordinated research questions, which included the following: (1) the amounts, variations, and controlling processes for biogenic fluxes of organic carbon and nitrogen, (2) aerosol composition, secondary aerosol formation processes, associated driving factors, and impacts, (3) aqueous phase and cloud chemistry, (4) climate relevant properties of biogenic aerosol, (5) oxidation processes and oxidant concentrations, (6) cycling of reactive nitrogen compounds, and (7) mercury emissions, transformation, and fate. A key recurring theme of all the SAS research was to investigate how interactions of biogenic and anthropogenic emissions affect nitrogen, mercury, oxidant, and secondary organic aerosols (SOA) at the surface and aloft (e.g., Carlton et al., 2013; Hunt, 2013; NOAA, 2013).

This paper provides a context for, and an assessment of, the representativeness of the SOAS experimental period using long-term surface data, excluding mercury (mercury data are available for some sites in ARA, 2013), collected at the observational site at Centreville (Brent), Alabama (Supplement Fig. S1) and at nearby sites of the Southeastern Aerosol Research and Characterization (SEARCH) network (ARA, 2013; EPRI, 2013). Our approach first considers the climate of the southeastern United States in which the rural Centreville site (CTR) is located. This description is followed by a summary of pollutant emission trends in the region, and a survey of the role of meteorology in mediating the southeastern air chemical climatology. The post-1999 trends in concentrations of key natural and pollutant species at CTR and the region

are presented, with consideration of contrasts between rural and urban conditions, and between inland and coastal conditions. Finally, we discuss the long-term context and representativeness of the SOAS-SAS experiments from 1 June to 15 July 2013. The narrative is supported with additional tables and figures in the Supplement.

1.1 The infrastructure and climate of the Southeast

The southeastern US is characterized by a warm, moist, subtropical climate, with relatively isolated urban communities surrounded by agricultural areas and forests in hilly terrain. Anthropogenic activities in the region are known to emit volatile organic compounds (VOCs), CO, SO_x, NO_x, NH_3, and particles, including organic carbon (OC) and black (elemental) carbon (EC) (see Table A1 Glossary; e.g., SAMI, 2002; Ingram et al., 2013). The urban areas and the larger southeastern region have experienced a growth in population, transportation, and industry, resulting in increased air pollution since the 1960s, followed by post-1990s reductions in pollution (e.g., Irving, 1991; Ingram et al., 2013). Climatologically, summers are warm and humid, with occasional thunderstorms associated with continental frontal systems passing through the United States. Winter conditions are cooler, with occasional freezing and isolated snow or ice storms inland, but generally milder conditions along the northern coast of the Gulf of Mexico. The region also is known for its extreme weather conditions where drought occurs, tornadoes develop in large convective systems in summer and early fall, and tropical storms from the Atlantic Ocean and the Gulf of Mexico penetrate inland on occasion (e.g., Peterson et al., 2014). Extended summer periods of light winds and air mass stagnation are prevalent, leading to accumulation of pollution (e.g., McNider et al., 1998). The region is exposed to smoke from wild and prescribed fires, as well as intrusions of transported dust and other pollution from North America and Africa (e.g., Hidy, 2009).

1.2 Long-term observations

While multiple ground level monitoring sites were part of SOAS, including several in central Alabama, Look Rock Monitoring Station in Tennessee, and Research Triangle Park in North Carolina, by number the most measurements were made at the Centreville, Alabama SEARCH network site (CTR). The SEARCH network (Fig. 1) began in 1992 with three sites (CTR, Oak Grove (OAK), and Yorkville (YRK)) as part of the Southern Oxidant Study (SOS) measuring O_3, NO_y (oxidized nitrogen species, including NO_x [$NO + NO_2$], HNO_3, peroxyacetyl nitrate, other nitrogen oxide gases, and particulate nitrate [pNO_3]), other trace gases and meteorological variables (e.g., Chameides and Cowling, 1995; SOS, 2014). The sites were expanded to eight beginning in 1998 with the addition of discrete and continuous aerosol mass and composition instrumentation (Supplement Table S1). Selected sites, including CTR, have involved measurement methods development and deployed additional instrumentation over time (e.g., e.g., Solomon et al., 2003; Hansen et al., 2003, 2006; Edgerton et al., 2005, 2006, 2007; Hatch et al., 2011; Budisulistiorini et al., 2013). The SEARCH sites include continuous or semi-continuous measurements of indicators of pollutant emissions, reactants in the atmosphere, and products of chemistry. The basic, long-term measurements for gases, including CO, NO_y, SO_2, O_3, HNO_3 and NH_3, are listed in Supplement Table S1. At the Atlanta, Georgia site, Jefferson St. (JST), 24 h canister samples for determination of nonmethane organic compounds (NMOC) and oxygenated volatile organic compounds (OVOC) (subsets of VOC) were obtained from 1999–2008. These speciated NMOC observations complement measurements from four PAMS sites (Photochemical Assessment Monitoring Stations (http://www.epa.gov/ttn/amtic/pamsdata.html)) in the Atlanta metropolitan area (Tucker, South DeKalb, Conyers, and Yorkville, co-located with the YRK SEARCH site). The SEARCH gas and meteorological measurements are supplemented with ambient particle sampling for measurement of mass concentration and composition of $\lesssim PM_{2.5}$ range and PM_{10}–$PM_{2.5}$, and optical extinction (ambient and

dry; e.g., Hansen et al., 2003, 2006; Edgerton et al., 2005, 2006). In addition to the long-term measurements, SEARCH has hosted a number of studies supporting methods development and urban epidemiology. The data have been used for understanding ambient composition and chemistry, and a variety of analyses including characterization of trends (publications using SEARCH data for such purposes are found in http://www.atmosphericresearch.com/studies/SEARCH.index.html). SEARCH data also have been used in evaluation of air quality models, including Zhang et al. (2004), Morris et al. (2005), Marmur et al. (2006, 2009), Pun and Seigneur (2008), Pun et al. (2008), and Tesche et al. (2008). The SEARCH sites were established in urban-rural (or urban-suburban) pairs to represent urban-rural contrasts, and to capture the potential influences of inland-continental vs. marine aerometric conditions. A number of other monitoring sites for O_3, NO_y, and particulate matter are located in the region, including those of IMPROVE, CSN, ASACA and CASTNET (see glossary), and those data have been compared with SEARCH network data (e.g. Blanchard et al., 2013a).

CTR is believed to be a regionally representative location in an agricultural area surrounded by mixed deciduous-evergreen forest (e.g., Blanchard et al., 2013a). The region, represented by Alabama, Georgia, Mississippi, and northwestern Florida, is of particular interest in that relatively large quantities of natural biogenic emissions occur as VOCs and as detritus from vegetation. CTR is approximately 80 km SSW of the Birmingham, Alabama metropolitan area. The site is known to be exposed occasionally to pollution from Birmingham, Tuscaloosa ($\sim$ 45 km WNW), and Montgomery ($\sim$ 120 km SE), along with certain large point sources in the region, including power plants, pulp and paper mills, and metal processing (for regional gas and particle emissions, see Supplement Fig. S2; Blanchard et al., 2013b). The Southeast also experiences a substantial amount of biomass burning (Wade et al., 2000; Haines et al., 2001). Overall, the CTR aerometric conditions represent relatively low gas and aerosol concentrations typical of the rural Southeast from Louisiana eastward to Georgia, and from Tennessee and the Carolinas southward to the Gulf of Mexico (Blanchard et al., 2013a). In the Southeast, essentially all rural areas experience exposure to sustained

diluted air pollution (e.g., Goldan et al., 1995, 2000; SAMI, 2002). This regime of low, annual-average regional concentrations of monitored pollutants tends to approach nominal background concentrations characteristic of the eastern North American continent, e.g., estimated for different gases and particles, for example, by Seinfeld and Pandis (1998) for NO_x, Hidy and Blanchard (2005) for $PM_{2.5}$, and Lefohn et al. (2014) for O_3. The presence of anthropogenic pollution in the Southeast combined with large amounts of natural biogenic emissions yields the potential for a regional air chemistry that has elevated ozone levels, partially driven by isoprene from vegetation and anthropogenic non-methane organic compounds (NMOC) (e.g., Chameides et al., 1988; Chameides and Cowling, 1995; Meagher et al., 1998; SOS, 2014). Associated with the regional photochemistry are various species, including sulfur oxides, reactive nitrogen, VOC and the "secondary" pollutants, inorganic SO_4, (particle) pNO_3, O_3, and secondary organic compounds.

The Southern Oxidant Study (SOS), beginning in 1988, is of particular interest for elucidating ozone chemistry in the Southeast. This study involved several years of O_3 and precursor monitoring and major campaigns in Atlanta, and later in Nashville, Tennessee (SOS, 2014). The SOS provided evidence of the regional and urban character of summer O_3 concentrations, affected by precursor emissions distributions, active photochemistry, and meteorological influences. The accumulation of O_3 in the region depends on an interplay of urban plumes, high regional concentrations, and point-source plumes. SOS confirmed the hypothesis of Chameides et al. (1988), showing the importance of isoprene and the (regional) NO_x sensitivity of O_3 production. Observation-based O_3 modeling matured from the SOS experience, and the nature of O_3 production efficiency using the O_3/NO_z (or O_3/NO_2) ratio was proposed (e.g., Solomon et al., 2000). The role of southeastern meteorology, including multiple scale transport winds horizontally dispersing pollution and vertical mixing, was observed. Also of interest were the observations showing that nighttime winds in the boundary layer were potentially important in transporting O_3 over multiple days. The SOS experience served as basis for characterizing the long-term trends in chemical climatology of oxidants in

the Southeast, and catalyzed in part interest in the aerosol component of southeastern pollution. As discussed below, the aerometric conditions for O_3 accumulation currently remain the same in the Southeast, but both urban and regional concentrations of O_3 and its precursors have declined since the mid-1990s. Recent information about O_3 and precursor chemistry is derived from the SEARCH studies (e.g., Blanchard et al., 2010a, b; 2011).

Scientists recognized by the 1960s that SOC was present in atmospheric aerosols both naturally and from anthropogenic VOC oxidation (e.g., Went, 1960; O'Brien et al., 1975; Grosjean and Friedlander, 1980). Regional and urban SOC in the Southeast was expected, given the presence of isoprene and terpenes as precursors, as well as anthropogenic $>C_7$ VOCs. Lim and Turpin (2002), Zheng et al. (2002a, b), Saylor et al. (2006), Ding et al. (2008), and Blanchard et al. (2008, 2013c) reported estimates of SOC at SEARCH sites using different methods, all of which suggest that secondary organic carbon, SOC (vs. primary organic carbon, POC) is the smaller fraction of annual-average OC in the SEARCH region.

Theories linking oxidant-O_3 chemistry with reactions forming SOC are summarized in Seinfeld and Pandis (1998) based on hypothesized mechanisms mainly for $>C_7$ hydrocarbons (especially C=C containing compounds), and smog chamber experiments. In the 1990s, advanced laboratory experiments showed that lower carbon-number VOCs, including isoprene, could produce aerosols. Hallquist et al. (2009) reviewed the emerging homogeneous and heterogeneous chemical mechanisms and caveats relating to volatility or emitted and aging aerosols. A subset of mechanisms and observations have linked aqueous chemical reactions (e.g., Carlton and Turpin, 2013) and organo-sulfates and other tracers with SOC production (e.g., Takahama et al., 2006; Gao et al., 2006; Surratt et al., 2007; Froyd et al., 2010; Kleindienst et al., 2010; Budisulistiorini et al., 2013). Elucidation of these mechanisms is an important element of the goals of the SOAS experiments.

2 Indicators and trends in chemical climatology

2.1 Gas and particle emissions

The principal resource for post-2000 emissions and their trends in the SEARCH region is EPA's National Emissions Inventory (NEI). The NEI is formally revised and updated every three years, but its estimates have been extrapolated on an annual basis (e.g. Xing et al., 2013; Blanchard et al., 2013c). Revision and extrapolation since the 1990s have involved intermittent changes in emission modeling, revised interpretation of emission testing, and addition of major fugitive sources such as open burning, NH_3, and biogenic NMOC. These methodological changes are incompletely documented, which makes interpretation of differences difficult to follow (e.g., Xing et al., 2013; Blanchard et al., 2013c). In any case, the NEI provides a starting point for interpretation of changes in ambient air chemistry in response to annual emission changes.

Annual trends in the region are given in Supplement Fig. S2. Annual emissions from the states of Alabama, Georgia, Mississippi, and the 12 western counties of Florida are adopted for comparison with ambient data (Supplement Fig. S2). Analysis of the NEI data indicates that emissions of essentially all anthropogenic species of interest have decreased or remained nearly constant since 2000. Between 1999 and 2011, SO_2 emissions decreased by 65 % (Supplement Fig. S2a), NO_x emissions decreased by ~ 52 % (Fig. S2b in the Supplement), and anthropogenic NMOC emissions declined by ~ 36 % (Supplement Fig. S2c). Whereas NH_3 emissions have remained roughly constant during this period (15 % decrease – Supplement Fig. S2d), CO emissions decreased by 42 % (Supplement Fig. S2e). Fine particle emissions decreased by 19 % (Supplement Fig. S2f), and primary OC and EC emissions decreased by 17 and 40 %, respectively (Figs. S2g and S2h in the Supplement).

2.2   Role of meteorology

Once present in the atmosphere, constituents are dispersed by meteorological processes, and react chemically with one another, with varying temperature, humidity, and oxidant levels. It is widely known that meteorological factors have a strong influence on ambient concentrations of chemicals, including those produced in the atmosphere. This knowledge is imbedded in source-based air quality models that estimate spatial and temporal concentration distributions from sources (e.g., Seinfeld and Pandis, 1998; McMurry et al., 2004). While emissions of precursors are important, meteorology controls a major fraction of O_3 and SO_4 variability in multi-spatial studies from the 1970s through the 1990s (e.g., Rao et al., 1997; Hidy, 1994). Analysis of measurements shows relationships with meteorology independent of modeling. Relevant examples for the study of meteorological influences on secondary species include sulfate (SO_4) and O_3 (e.g., Hidy, 1994; Chameides and Cowling, 1995; Meagher et al., 1998; Hidy, 2000; Blanchard et al., 2010b, 2014a). Hidy (1994) summarized the key 1978–1980 findings of multiple spatial and temporal scale meteorology in the eastern US that affect SO_4 and O_3 concentrations. Rao et al. (1997) discuss the importance of synoptic scale processes in affecting ground level concentrations at temporal and spatial scales of 1–2 days and $\sim 600\,km$ in the Southeast. The SOS investigators describe meteorology and the multiscale O_3 climatology in the Southeast; Hidy (2000) summarized the role of meteorology in modulating O_3 chemistry, and Blanchard et al. (2010b, 2013a, 2014a) described pollutant species in the light of meteorological parameters in the SEARCH region.

The case of SO_4 on a regional scale in the eastern US, including parts of Tennessee, Virginia and North Carolina, was explored extensively in the 1980s, as reviewed by Hidy (1994). Using principal component analysis, Henry (e.g. Hidy, 1994, Chap. 5) showed that meteorological factors, primarily light winds, temperature, and humidity, accounted for much of the sulfate variability in the East during 1977–1978. As a part of SOS, Vukovich (1994, 1998) found that meteorological factors, including temperature,

humidity and winds, accounted for much of the variability in O_3 concentrations in the Southeast based on data from 1980–1991. SOS experiments in the Atlanta, Georgia (1991–1992) and Nashville, Tennessee areas (1994–1995; 1999) confirmed the strong influence of meteorological factors, especially temperature, on daily O_3 maxima (e.g., Banta et al., 2002; Frost et al., 1998; White et al., 2002).

A recent analysis of summer rural and urban mean O_3 concentrations using Camalier et al.'s (2007) generalized additive model (GAM) aimed to quantify statistically the impact of meteorology on O_3 formation in recent years (Blanchard et al., 2010b). The results indicated that meteorological factors accounted for $\sim 70\%$ of the variability in daily peak $8\,h$ O_3 concentrations over the 1999–2007 timeframe. Application of this method to 2002–2011 data from multiple sites confirmed this influence (Blanchard et al., 2013b). Temperature and relative humidity (RH) were the strongest factors influencing high O_3 concentrations (solar radiation correlated with RH and was a factor when RH was excluded). Other meteorological factors potentially important to O_3 concentrations include light winds and transport distances $< 200\,km$, signifying air mass stagnation with slow moving synoptic weather systems over the Southeast.

2.3 Ambient concentration trends

A conventional chemical climatology uses certain "macro" indicators for representing ambient chemistry at the ground (SO_2, NO_y, NMOC, CO, O_3 and particle mass and component concentration). The following discussion of these chemical indicators extends the recent downward trends in ambient concentration trends analyses of Blanchard et al. (2013b), which covered 1999–2010, through 2012.

2.3.1 Sulfur oxides

Historically, evolution of atmospheric conditions in the Southeast involved major urban expansion superimposed on a base of agriculture and silviculture. This evolution resulted in a sulfur dioxide (SO_2)-rich atmosphere inland from the Gulf of Mexico through

the early 1990s (e.g., Irving, 1991; Hidy, 1994). After this time, SO_2 emissions and ambient concentrations declined dramatically, both regionally and in cities such as Birmingham and Atlanta. A regional decline after 2000 is shown for SO_2 emissions and for annual-average ambient SO_2 and SO_4 concentrations in Fig. 2 (see also Figs. S2a and S3 in the Supplement). Regional ambient SO_2 concentrations follow the emissions throughout this period, and are consistent with emissions and ambient concentration changes over a longer period of time documented in other studies (e.g., pre-1990s, Irving, 1991; post-1990, Xing et al., 2013). SO_2 emissions from electrical generating units (EGUs) represented 77 % of total SO_2 emissions, on average, between 1999 and 2012. SO_4 tracks the SO_2 emission reductions (Supplement Fig. S2a). Statistically significant linear relations between annual SO_2 emissions and ambient SO_2 and SO_4 concentrations are indicated in Table 1. The SO_2 intercept is not statistically significant, while the statistically significant SO_4 intercept is $\sim 1.4\,\mu g\,m^{-3}$. We identify the SO_4 intercept with a continental background similar to that found to the west at this latitude (e.g. Hidy and Blanchard, 2005).

Seasonal averages of SO_4 are included in Supplement Fig. S3. An example of seasonally averaged changes for SO_4 is shown in Fig. 3 relative to changes in organic and elemental carbon (OC and EC). The concentrations of SO_4 in CTR are maximum in summer and minimum in winter over a twelve-year period, with a decline in seasonal amplitude after 2007. This is consistent with the known sulfur oxidation chemistry involving temperature, oxidant production and elevated moisture content in summer. The seasonal amplitude in SO_4 is greater than that of the carbon components, which correlate during the last three years. Unlike SO_4, which almost always peaks in summer (Q3), mean EC and OC concentrations do not show a consistent peak season, varying from spring (Q2) to fall (Q4) quarters. A consistent minimum occurs in winter (Q1), except for 2009. The OC concentration tends to rise in spring (Q2) with isoprene and terpene emissions and temperature dependent reaction potentially involving SO_4. But the continued OC and EC increase to summer (Q3) is inconsistent and delayed into fall, perhaps relating to weather, especially moisture levels.

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The presence of organic sulfur compounds hypothetically is a factor in SOC formation as postulated, for example, by Surratt et al. (2007). An upper estimate can be made of the mass of sulfur bound in such compounds through differencing methods. It is known from historic studies (e.g., Novakov, 1972; Hoffman et al., 1980) that particle S can include species other than SO_4 as acid, ammonium or other salts. The fraction of non-(inorganic) sulfate (NIS) component can be estimated by comparing sulfur measured by x-ray fluorescence (XRF) and the water-soluble component (WSSO4) measured by ion chromatography. This difference could reflect NIS compounds such as sulfite salts, methane sulfonate, or other organo-sulfur compounds, including isoprene-related sulfate esters. Comparison of the Atlanta (JST) daily average values by season for the period 1999–2000 is shown in Fig. 4. The comparison between XRF and WSSO4 in this urban area suggests small differences between the measures, in the range of −6 to +4 % of total sulfur as NIS, depending on season. The months with highest apparent contribution were May through September. If the differencing is an indicator of NIS, its S fraction in particles is small relative to inorganic sulfate, even in summer. Given the uncertainty in sampling and measurement expected from a differencing method (see also Supplement Table S2), the presence of NIS is not definitive for detecting small mass fractions of NIS in particles; however, the mass of organic sulfur particles would be a larger fraction of OC than of sulfate.

Recent studies of SOC formation from biogenic NMOC suggest that condensed material is facilitated with acid nuclei (e.g., Hallquist et al., 2009). Since sulfate is a major contributor to particle acidity, the degree of sulfate neutralization can be used as a qualitative surrogate for apparent acidity. The acidity in particles at rural Southeast locations, including CTR, and its relation to OC was investigated several years ago. Tanner et al. (2009) found no unambiguous evidence of acid catalyzed SOC formation from intercomparison of filter-based SO_4 and OC under varying conditions. However, the Lin et al. (2013) plume study of chemistry in high vs. low SO_2 and NH_3 conditions indicated a small enhancement in isoprene epoxydiol (IEPOX) related tracers in high SO_2 conditions.

Analysis of the SEARCH particle data, including NH_4, SO_4, and pNO_3, indicates that, stoichiometrically, sulfate can be interpreted, on average, as a mixture that lies between $(NH_4)_2SO_4$ and NH_4HSO_4 (e.g., letovicite), both in urban and rural locations. Even though the average sulfate neutralization is equivalent to letovicite, there are excursions in daily values of neutralization ranging from ammonium sulfate, and bisulfate to (rarely) unneutralized sulfuric acid. Analysis of the data by year from 2000–2011 (Fig. 5) suggests that acidic SO_4 neutralization has not changed appreciably over this period. Since neutralization has not changed, but sulfate concentrations have declined, the hydrogen ion concentrations associated with SO_4 would have decreased. This trend suggests that acid-promoted reactions of biogenic NMOC could be present, but potentially have changed with SO_4 concentrations unless other nucleophiles act as nuclei (as indicated in experiments of Nguyen et al., 2014).

2.3.2 Nitrogen oxides, NMOC and ozone

The nitrogen oxides and VOC are important elements of the oxidant photochemistry cycle in the troposphere, and are components involved in aerosol particle chemistry. Because of its importance, O_3 and its precursors have been studied extensively in the Southeast in major programs, including the SOS campaign in the Atlanta, Georgia and Nashville, Tennessee areas in the 1990s (e.g. Meagher et al., 1998). The urban-rural contrasts for O_3 production and atmospheric transport were investigated under the O_3 precursor conditions at that time. The SEARCH urban-rural site pairs are analogous to the 1994–1995 Nashville study, covering similar regional conditions inland, but distinctly different along the Gulf Coast. Thus, the Nashville study, combined with longer-term SOS measurements, yield insight into oxidant chemistry for 1990s conditions, with higher O_3 and precursor concentrations than seen since 2000 in the SEARCH region. NO and NO_y have been measured at all SEARCH sites since 1992; NO_2 has been measured at some SEARCH sites since 1992 and at all sites since 2002. NMOC was measured at JST through 2008, and is supplemented by the PAMS observations, including from the non-urban site at YRK. The sources of nitrogen oxides are mainly

combustion, from transportation, EGUs, and to a lesser extent, industrial, commercial and residential sources. Anthropogenic VOC emissions, including NMOC, deriving from transportation, industrial, and commercial sources, are superimposed as a small fraction on a much larger emissions component of natural sources (see Fig. S2c in the Supplement). In Table 1, linear regression models indicate statistically significant responses of ambient NO_y and NMOC concentrations to decreasing NO_x and (anthropogenic) VOC emissions, respectively, without statistically significant intercepts.

The SEARCH regional annual NO_x emissions are shown along with rural annual-average NO_y concentrations in Fig. 6. Reductions in ambient NO_y levels tracked the NO_x emission reductions between 2000 and 2011. The trends in CO emissions for transportation (Supplement Fig. S2e) have a similar pattern to NO_x emissions (Fig. S2b in the Supplement). Ambient CO concentrations have decreased at both urban and rural sites in the SEARCH region, with statistically significant linear relationships to CO emissions (Table 1). Blanchard et al. (2013b) showed that CO concentrations have an extra-regional "offset" of about 120 ppbv apparently associated with a regional or larger continental background. Such a "background" was not found for SO_2 or NO_y. This is supported by the linear model for ambient CO and emissions in Table 1, where the CTR relationship has an intercept of ~ 90 ppbv; the Birmingham data (BHM) show a strong local CO emissions relationship without a statistically significant intercept.

Emissions of VOC are indicated in Supplement Fig. S2c; the anthropogenic component is superimposed on a large natural component such that the decline in anthropogenic VOC emissions is a small increment of the total. Decreases in rural ambient NMOC are not well documented, but the urban-nonurban contrast is established with the PAMS and Atlanta-JST data. The annual averages of 24 h average NMOC at JST are shown with Georgia motor vehicle emissions in Fig. 7. The decline in urban NMOC is similar to the on-road VOC emissions reduction – as expected from a principal urban source, motor vehicles; NMOC trends and OH reactivity are discussed, for example, in Blanchard et al. (2010a). Evaluation of trends in NMOC at JST indicates that mean concentrations of anthropogenic species decreased between 1999 and 2007; however,

the average OH reactivity of the NMOCs decreased less, if at all. One of the important contributors to the JST OH reactivity was isoprene, and in summer at the nonurban Yorkville and Conyers sites where it contributed half of the estimated reactivity (Blanchard et al., 2010a). The dominant NMOC in the oxidant cycle at CTR is isoprene.

In the absence of long-term NMOC data at CTR, we rely on the PAMS data in the Atlanta area for potential qualitative indications of ambient NMOC characteristics or trends. The contrasting speciated NMOC data in summer from the PAMS sites in Atlanta and the site at YRK indicate the magnitudes of the decreases in species concentrations with distance from the urban area. The YRK concentrations are expected to be similar to those at CTR, with CTR possibly exhibiting still lower anthropogenic species concentrations relative to a nominally similar level of natural NMOC. Trends in the summer PAMS data (Fig. 8) are considered for selected species having measurements that appear robust (few values below detection limits; no obvious extreme outliers). These species include the anthropogenic groups of C_2-C_4 compounds, aromatics as benzene, toluene, ethyl benzene, and xylenes (BTEX), pentanes, and isoprene (representing biogenic species). The concentrations of BTEX have decreased over the years at the Atlanta urban sites but not at the non-urban sites (YRK and Conyers). Mean urban pentane concentrations began to decrease in 2004, followed by a three-year increase in 2007. The concentrations of the anthropogenic groups are substantially lower at YRK, about 60 km "upwind" from Atlanta, while isoprene tends to be larger in concentration away from the city, and slightly increasing by year. The reason for this seasonal increase in isoprene concentration has not been explained, but could be related to changes in biogenic emissions and chemistry in response to decreasing O_3 concentrations (e.g., Sharkey et al., 2008) since they don't appear to be consistent with changes in T and RH (e.g., Supplement Fig. S13 for a six-week early summer period).

Ozone (with NO_2 and NO_z) can be used as an indicator of the oxidation state of the air. Average 8 h maximum O_3 concentrations in the SEARCH region have declined along with decreasing emissions of its precursors, NO_x and NMOC (e.g., Fig. 9 and Fig. S2 in the Supplement). Linear regression results for decreasing O_3 concentrations

as a function of decreasing NO_x and (anthropogenic) VOC emissions are shown in Table 1. The O_3 decrease is less than a 1 : 1 proportionality with the precursor emission reductions, as indicated by the presence of intercept terms that are a large fraction of ambient O_3 concentrations. The intercepts of $\sim$ 33–37 ppbv are similar to background

5 levels projected for the South by Lefohn et al. (2014). The O_3 proportionality with its precursors would not necessarily be expected due to the nonlinear photochemistry involved, but given the substantial reduction in precursor emissions a relatively small change in ozone of about 1 % yr^{-1} has been observed.

Rural NO_z (NO_y– NO_x, a photochemical reaction product indicator) concentrations

10 have tended to level out since 2005, as indicated in Fig. 6, paralleling O_3 concentrations. The linear NO_z relationship with NO_x emissions is statistically significant (Table 1) with a variance higher than for other gases, and without a statistically significant intercept. Ozone concentrations vary with meteorological conditions, which need to be accounted for in long-term averages. Camalier et al. (2007) have developed a statis-

15 tical approach (GAM) employing meteorological variables to adjust mean summer O_3 concentrations locally and regionally, which has been adopted by EPA for inspecting O_3 trends (e.g. EPA, 2013). We have extended the GAM method to use air quality variables as well to improve the model for O_3 concentrations in the SEARCH region (Blanchard et al., 2014a). Evidence from JST compared with YRK indicates that Atlanta has

20 frequent periods of NMOC-sensitive O_3 formation, but the regional O_3 formation continues to be NO_x-sensitive as found earlier in the SOS studies, including the Atlanta and Nashville areas (e.g, Blanchard et al., 2010b; Chameides et al., 1988; Chameides and Cowling, 1995; (Meagher et al., 1998 considered urban Nashville in transition between NO_x and NMOC sensitive)).

25 Evidence for O_3 as an oxidant indicator derives from comparing diurnal O_3 concentra-tions with OH and HO_2 data. For example, at a suburban site 8 km NE of downtown Nashville, OH and HO_2 observations tracked the diurnal buildup and decline of O_3 (Martinez et al., 2003). This linkage also has been reported from observations in New York City (e.g. Ren et al., 2003). From the data taken in the New York City area,

OH concentrations empirically are roughly proportional to O_3 concentrations during the day (e.g., Supplement Fig. S4). If this urban-suburban pattern applies to rural conditions in the Southeast, one could expect to see a decline in daytime OH concentrations between 2000 and 2011. This assumption is tempered by recent evidence for the re-
5　generation of OH from isoprene reactions yielding an excess of OH from chemical model calculations (e.g. Fuchs et al., 2013). This also corroborates the potential importance of air mass transport with down-mixing of O_3 from a residual (upper boundary) layer during the break-up of the nocturnal inversion layer 2–3 h after sunrise (Baumann et al., 2000). As a part of the analysis of the SOAS data, a close look at relationships
10　between OH, HO_2, O_3 and VOCs would be of interest not only for SOC formation, but also for distinguishing rural from urban O_3 photochemistry.

2.3.3　Aerosol particles

Suspended particles and their origins are a key element of the SOAS experiments. The SO_4 component was discussed above with SO_2. Trends in regional and CTR par-
15　ticle mass concentration and composition are shown in Supplement Fig. S5. Mass concentrations of fine particles ($PM_{2.5}$) have decreased with primary emissions and secondary components (SO_4 and carbon). Sulfate has decreased in fine particles relative to EC and OC; NH_4 has not decreased as much, and pNO_3 decreased, even though increases in pNO_3 concentrations potentially could have occurred as declining
20　SO_4 made an increasing fraction of NH_3 available for reaction with HNO_3 (Blanchard et al., 2007). The major metal oxides (MMO) represent a small fraction of fine particle mass. Retained water (associated with species such as SO_4, and represented as one of the unmeasured components within "other") is relatively large. As shown above in Fig. 3, SO_4, EC, and OC display somewhat different seasonal variations. Regional OC
25　is identified with primary sources such as vehicle transportation and biomass burning (e.g., Lee et al., 2008; Zhang et al., 2010). Biomass burning is believed to be a significant portion of $PM_{2.5}$ concentrations especially in the rural Southeast. Various methods have been used to separate secondary (SOC) from primary (POC) (e.g., OC/EC

ratio method, Lim and Turpin, 2002; Saylor et al., 2006; organic tracer-chemical mass balance, Zheng et al., 2002a, b; Ding et al., 2008; regression, carbon mass balance, Blanchard et al., 2008, 2011; chemical composition particle and gases, Pachon et al., 2010; semi-empirical-air quality models, Yu et al., 2007). While these methods provide insight into the two components of OC, they do not yield a consistent quantitative picture of the fractions of each. The mean fraction of SOC estimated by different methods varies from $\sim 20\,\%$ to $> 50\,\%$ depending on the time of year data were obtained, and the method used.

The trends in rural annual average EC concentrations compared with EC emissions are shown in Fig. 10. At the rural SEARCH sites, ambient EC decreases over the decade from 2000, and tracks the EC emission decline occurring between 2005 and 2011. EC concentrations declined approximately coinciding with declining mobile source emissions (Fig. S6 in the Supplement). Mean OC concentrations followed similar trends as mean EC at both urban and rural SEARCH sites on an annual basis (Supplement Fig. S7). These and other results indicate that POC is a major part of average OC concentrations (e.g., Zheng et al., 2002a, b; Blanchard et al., 2013c, 2014b).

Linear regression models for relating decreases in rural EC and OC concentrations to decreasing emissions are shown in Table 1. Included are relationships between ambient concentrations with total EC and OC emissions and with mobile-source EC and OC emissions. The slopes for total and mobile EC are significant, but the intercepts are not. The slope and intercept for ambient OC vs. mobile source OC emissions are each significant, but neither the slope nor the intercept for regressions of rural ambient OC vs. total OC emissions is significant. Mobile OC comprises less than 10 % of the total POC emissions in the region (Blanchard et al., 2013c), but SOC derived from mobile VOC emissions could augment the mobile POC contributions; OC derived from a combination of motor-vehicle emissions of POC and of low-volatility VOC potentially represents a large enough fraction for the changes in mobile-source emissions to be detectable at CTR.

Birmingham EC and OC regression models are included in Table 1 for comparison with the rural case. This urban case is dominated by motor vehicle and industrial carbon emissions. The models for EC and OC vs. annual regional total carbon emissions and motor vehicle emissions show a much stronger annual rate of decline than the rural
5 cases do, without statistically significant intercepts. Regression models (not shown) for EC and OC in Atlanta (JST) are similar to those found for BHM. The linkages between motor-vehicle OC emissions and ambient OC are more evident at BHM and JST than at CTR because the higher motor vehicle emission density within the urban areas results in a stronger signal that is more readily observed within the variability associated with
10 meteorology and with year-to-year variations in biomass burning on small spatial scales (e.g., ∼ 10–100 km).

From source apportionment, wildfires and prescribed burns are a major factor in OC and EC concentrations in the SEARCH region, including at CTR (e.g. Blanchard et al. (2013c). The post-2005 NEIs indicate that the major contributors to EC
15 and POC derive from vehicle transportation emissions and biomass burning (Supplement Fig. S2g and h; Blanchard et al., 2013c). Over the period from 2000–2011, annual wildfires and prescribed burning are shown in Supplement Fig. S8. There is substantial variability in fires reported yearly and between states (e.g., Larkin et al., 2013). The prescribed burns in each of the states in the SEARCH regime are much more frequent
20 than the wildfires over this period. EPA (2014b) has tabulated major seasonal differences by state in occurrence of fires for use in the preparation of the NEI. According to EPA, the Georgia fire season is in late winter (January–March) while the Alabama season is apparently later, mainly in June; the information on which these temporal profiles were based is not documented. The implications of the temporal differences are
25 unclear for prescribed-burn EC and POC contributions relative to annual or seasonal ambient averages.

The SEARCH data have also given insight into the urban-rural contrasts in ambient EC and OC. For example, carbon isotope analysis has indicated that most of the total carbon – TC (OC + EC) at CTR is modern carbon compared with nearby Birmingham,

which has a major fraction of fossil carbon (e.g., Blanchard et al., 2008). The modern carbon fraction can be derived from primary emissions of smoke from fires, cooking, or from detritus and/or secondary atmospheric reactions of VOC. The secondary component of modern carbon comes from a host of potential biogenic reactions. The urban-rural contrasts between BHM and CTR indicate a large fraction of SO_4 and OC has a regional character, with SO_4 having a small increment and OC a larger increment associated with the urban emissions (Blanchard et al., 2013a).

Urban and rural contrasts are readily seen in Table 2, illustrating differences for the urban and rural pairs, and between inland and coastal sites. Strong urban-rural differences are found in the inland pair, CTR-BHM, for particles and gases. Interestingly, mean O_3 concentrations are higher at CTR than BHM. The urban-rural contrast is weaker for the coastal pair, OAK and Gulfport, Mississippi (GLF). The secondary species tend to have weaker urban-rural gradients than the primary species. The inland-coastal contrast is seen by comparing data from the two pairs of sites in Table 1. The data suggest the regional character for SO_4 (also NH_4) and O_3, while other species have lower mean concentrations along the coast than inland. The conditions along the Gulf Coast show lower concentrations, consistent with smaller cities, fewer major point sources along the coast than further inland, and mesoscale meteorological effects associated with marine conditions. Seasonal differences are shown in Table S3 in the Supplement.

2.3.4 Aerosol light extinction

Ground level estimates of light extinction have been made at the SEARCH sites between 1999 and present. Extinction apportionment gives additional insight into the role of chemical components including retained water. Extinction has tended to decrease over the 2000–2012 period, as expected from the decline in fine particle concentrations. A time series of observations for b_{ext} at CTR is shown in Supplement Fig. S9, including the dry light scattering component and the absorption component. The bulk of the extinction is from light scattering. Figure 11 shows a trend in combined fine

and coarse particle (PM_{10}) contributions to light extinction coefficient using a weighting relationship with particle composition, including Rayleigh scattering and also water through a hygroscopicity relationship with RH (Pitchford et al., 2007). On a dry basis, major contributors to "dry" extinction coefficient include SO_4 and organic matter (OM as 1.8 OC) at the SEARCH sites, including CTR. Water content, shown separately in Fig. 11, based on hygroscopicity of SO_4 and NO_3, is a major component of extinction at the average RH seen annually in CTR. Hygroscopicity of OM is not included; the inorganic component accounts for most of the water retention. This result is consistent with findings from other studies, including those in the Shenandoah, Virginia region of the Southeast (e.g., Malm et al., 2000) and in the Great Smoky Mountains (Lowenthal et al., 2009), and also with laboratory studies (e.g., Brooks et al., 2004). The black carbon component (light absorbing carbon or LAC) represents a relatively minor portion of the extinction coefficient annually, while the contribution of OM is larger than ammonium sulfate. For comparison, the contributions to the extinction coefficient based on chemical constituents without separation of water from SO_4 and NO_3 is given in Supplement Fig. S10.

3   Representativeness of 2013

The previous section provides a long-term context of air quality changes in the SEARCH domain. For the representativeness of the 2013 summer experiments, we turn to the long-term ambient data associated with the period of 1 June to 15 July. The discussion includes consideration of the representativeness of meteorological conditions as well as the ambient chemistry at CTR.

3.1   Diurnal emission characteristics

The annual emission trends derived from the NEIs provide no information about short-term emission patterns. Two major contributors to regional, diurnal emissions relevant

to the SOAS experiments are SO_2 and NO_x from electrical generation units, and NO_x and NMOC from transportation. Natural emissions for isoprene and terpenes are also of interest. The June–July diurnal EGU SO_2 and NO_x emissions for Georgia, Alabama, and Mississippi are shown in Supplement Fig. S11. A national average transportation emission pattern applied to NO_x and NMOCs is shown in Supplement Fig. S12 for comparison with the EGU pattern. The EGU emissions of SO_2 and NO_x show a "common" increase in daytime emissions, rising about 06:00 through the daytime followed by a decrease in evening after 18:00 (with stated exceptions, all data are given in local standard time [LST]). The annual trends in reduction in emissions across the states are consistent with the annual changes for SO_2 and NO_x in Supplement Fig. S2. The average diurnal changes in the on-road motor vehicle emissions (NO_x and NMOC) show an increase around 06:00 with morning urban commutes, with steady levels thereafter with a rise in traffic, followed by a decrease around 17:00. As indicated in the figure, there is a weekday-weekend difference in emission timing.

Natural VOC emissions of isoprene are influenced by rising and declining temperature and solar radiation, with rise at $\sim$ 06:00. in summer, modulated by O_3 concentrations (e.g. Sharkey et al., 2008). Terpene emissions are mainly temperature dependent and tend to rise at 06:00, before decreasing somewhat during midday and increasing again in the evening (Supplement Fig. S19; e.g., Guenther et al.,1993). NO_x emissions from soil emanations vary with temperature and soil moisture, with less-known average diurnal character; lightning-derived NO_x production is obviously intermittent depending on stormy conditions.

3.2 Meteorological conditions

Surface meteorological conditions are described in terms of box plots of the CTR data, directional pollution roses and diurnal plots of parameter variation. Box plots of wind speed, temperature, relative humidity and solar radiation are shown in Fig. 12 and Supplement Fig. S13 for 1 June to 15 July 2013. The period generally is characterized by light winds (air mass stagnation), warm daytime temperatures, high relative humidity,

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and reduced solar radiation relative to other years. Comparison of the box plots by year indicates that the period in 2013 was moist and cool relative to previous years, with slightly less solar radiation compared with earlier years. Meteorological conditions favorable to regional pollution episodes around CTR in current years are analogous to those found in the SOS Nashville experiment (McNider et al., 2002; Banta et al., 2002) and identified for the SEARCH region (Blanchard et al., 2013a). Conditions for elevated pollution involve large-scale, multiday periods of light winds, high SR and high RH, with limited nocturnal vertical mixing in an inversion in the lower boundary layer. In the morning the inversion tends to break up, permitting increased vertical mixing with pollution aloft reaching the ground. This is followed in the evening by re-formation of the inversion layer suppressing mixing. Occasional winds aloft, in the boundary layer, develop around the high pressure regime creating conditions for dispersion of pollution across the region, accompanied by decreases in ground level concentrations and concentrations aloft. The diurnal changes in summer EGU and transportation emissions, as well as natural VOC emissions tend to parallel changes associated with vertical mixing and changes in inversion conditions, providing increased daytime reactants. The morning increases tend to "fuel" the photochemistry of oxidants and SOC formation even with daytime dilution, while reducing nocturnal chemical reaction rates.

3.3 Chemical characterization

Box plots of trace gas and particle composition in Supplement Figs. S14 and S15 indicate the downward trend in pollutants at CTR in June–July, consistent with the trends in annual averages and emissions in the region discussed above. In some years the range of concentrations is large relative to the mean, but in recent years the range, based on the 25th and 75th percentiles, appears to have decreased along with the mean values.

Pollution-wind direction roses for the 1 June–15 July 2013 period are indicated in Fig. 13. Wind speed and frequency are also shown, indicating that northerly winds were rare in 2013; instead westerly winds occurred more frequently with higher wind

speeds than usual. The pollution roses suggest that SO_2 has some directionality that varies from year to year during the early summer, with a distinct source influencing the site from the southwest during this period. NO_y, CO, and EC show less directionality but broad enhancements in northern sectors, pointing to urban (traffic) influence from Birmingham and Tuscaloosa. O_3, $PM_{2.5}$, SO_4, NH_4, and OC show more regional character, indicated by near-symmetrical concentration distributions with direction. The OC/EC ratio has a distinct directional relationship. Although elevated EC derives mainly from the BHM and Tuscaloosa (northern) directions, OC/EC ratios show larger values from the west and south in association with low EC, while OC/EC ratios are lower from the north and east. These differences suggest that urban sources influence CTR from the northern and eastern sectors, but non-urban sources (including biomass burning and secondary material) are strongest from the southwest.

The time series and pollution roses indicate that the SOAS experiment observations include a range of conditions in which pollutants were seen at CTR in varying amounts and from different wind directions. Examples during SOAS include an urban plume (4 June, just before a biomass burn); power plant plume (26 June from the SW); open burning (4 June) and a dust intrusion from air transported over the Atlantic Ocean (9 June or 23). Examination of the air chemistry during these events compared with "non-event" days could provide key indicators of SOC formation in different polluted air conditions.

Diurnal plots of species are given in Figs. 14 and 15. SO_2 profiles show spikes during late morning when the convective boundary layer develops rapidly and mixing down from air in the residual layer occurs. Sporadically, this residual layer contains emissions from a power plant high in SO_2 emissions being mixed to the ground. The nature of this occurrence causes the standard deviation of these profile spikes to be relatively large. The height of the spikes and the frequency of occurrence decreased over the years. NO_y concentrations, in contrast, and similar to CO, show a broad morning peak around 06:00 CST associated with accumulation of local (traffic) emissions in a shrinking nocturnal inversion layer, which breaks up after sunrise and dilutes into the convective

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boundary layer. The level of midday NO_y, as well as its morning amplitude, decreased over the years, reaching a minimum in 2013. Ozone shows the well-known concentration variation with a sharp increase in the morning followed by a midday peak in response to combined precursor concentration increases and down-mixing from the residual layer during morning break-up of the inversion layer (e.g., Zhang and Rao, 1999). If OH and HO_2 concentrations follow a diurnal change (Martinez et al., 2003) similar to suburban Nashville, a maximum in SOC-OC concentration could be expected near midday. The midday O_3 maxima decrease at CTR over the years. Unlike a purely local development, the midday peak shows an extended decrease in ozone concentration into the late evening hours. The principal component of NO_y is NO_2 (e.g., Fig. S16 in the Supplement). NO_z follows a post-NO_2 diurnal pattern with a daytime elevation and a maximum just before 09:00 (local time, LT). The average NO_y levels at CTR are low, $\lesssim 1$ ppbv, with higher concentrations peaking at ~ 2 ppbv in the morning; the origins of these concentration levels may be local emissions of anthropogenic (most likely mobile) sources and naturally from soil exhalations that accumulate in a shrinking nocturnal inversion layer. A nitrogen oxide mass balance is shown Supplement Fig. S16. The composite diurnal composition indicates that NO_y is dominated at night mainly by NO_2, with NO_z (sum of pNO_3, HNO_3, alkyl nitrates (AN) and peroxalkylnitrates (PN)) prevailing during the day, wherein pNO_3 contributes very little. The measurements indicated in the NO_y mass balance nearly reach mass closure with only a minor fraction unidentified.

In contrast to SO_2 concentrations, which peak in the morning and evening at CTR, sulfate shows a weak midday to afternoon–evening enhancement (Fig. 15), with declining overall concentrations since 2000. The reactive species concentrations display a character consistent with recent lower hourly reaction rates associated with lower SO_2 and OH concentrations compared with earlier years. The diurnal EC and OC concentrations over the years have settled into low levels slightly enhanced around 09:00 – corresponding to a time similar to NO_y, thus possibly associated with the same sources such as a local traffic increase. The weak diurnal OC concentration pattern does not

indicate a strong daylight driven component with rapid rise in oxidant concentrations, but does not rule out the potential for SOC formation at night, as well as during the day. Periods prior to 2013 show an apparent spiky character of EC concentrations, possibly identified with local yard waste or trash burning, and less associate with the previously-discussed regional biomass burning (e.g. prescribed fires for forest management). Prescribed burning is a ubiquitous, widespread source for OC and EC with OC/EC emission ratios of 14 or larger (Lee et al., 2005) in the forests of the Southeast, including Alabama. In 2013, the Alabama Forestry Commission issued 14 137 burn permits for over one million acres, the largest total burn area since 2010 (B. Elliott, personal communication, 2014). Prescribed burning is regulated differently by state, making the NEI estimates of emissions for this source highly uncertain. Satellite observations are used to locate burns, but they do not reliably identify small burn areas below dense forest canopies.

The importance of aerosol water content in SOC reaction chemistry is hypothesized in Shen et al. (2013) and Carlton and Turpin (2013). A sample diurnal pattern of liquid water suggested in the difference between dry particle light scattering and ambient particle scattering is seen in Supplement Fig. S17. A maximum water uptake is at night with the highest RH, while the aerosol tends to lose water systematically with equilibration to lower midday RH. While ample water is present in the aerosol particles during the day, they are much wetter on average at night. This provides for an opportunity for both gas and aqueous phase oxidation reactions of NMOC to take place in the CTR environment. OC does not increase with drying out of the aerosol at morning to midday, which would indicate release of SOC from nocturnal reaction products.

Diurnal variations in NMOC concentrations are important for characterizing a portion of the potential for SOC production at CTR. While NMOC data were not obtained at CTR as part of the basic SEARCH observations, a long-term record of summer concentrations found at YRK can be compared qualitatively with results taken at a rural sites in the Southeast (Table S4 in the Supplement) at locations relevant to SOS, including CTR (e.g., SOS studies of Goldan et al., 1995; Hagerman et al., 1997; Riemer

et al., 1998). The data cited in Supplement Table S4 indicate the importance of iso-prene as a reactive species in the southeastern rural environment. The data suggest a varied but persistent regional presence of anthropogenic NMOC. In each of the locations, anthropogenic NMOC is mixed with the natural NMOC. These data suggest that the production of SOC in the rural sites may be dominated by natural NMOC, but the formation chemistry is complicated by low concentrations of anthropogenic species.

Figure S18 in the Supplement shows the diurnal changes at YRK in several NMOC groups: C_2-C_4, BTEX, pentanes, and isoprene. The first three groups show a concentration peak in the morning followed by a decrease through midday, with "recovery" of concentrations during the night. As noted earlier, this pattern is interpreted to be associated with the accumulation of emissions in a shrinking nocturnal inversion combined with the morning emissions increase and inversion breakup, followed by vertical mixing and chemical loss during the day. The three groups vary in terms of reactivity, but show similar morning to midday change; the change is likely to be mainly dilution during the day. BTEX and pentanes concentration have decreased over the years shown, while C_2-C_4 hydrocarbons seem less consistent in annual change. Isoprene has a distinctly different diurnal pattern, with a modest morning increase in concentration followed by depletion, then a strong peak in the late afternoon–evening. Hypothetically, annual diurnal change in isoprene concentrations appears to reflect variations in June–July meteorological influence combined with oxidation chemistry rather than a systematic decline over the years. Comparison of the diurnal change in isoprene concentration with OC diurnal change (Fig. 15) suggests no direct or parallel link between midday OC associated with SOC production. Data taken at a rural mixed deciduous and evergreen forest site in western Alabama (Kinterbish State Park) could be similar to CTR for biogenic NMOC concentrations. A comparison between isoprene concentrations at YRK and 1990 concentrations at Kinterbish (Goldan et al., 1995) is shown in Supplement Fig. S19, along with Kinterbish α-pinene concentrations. The Kinterbish pattern is similar at night and morning through midday, but displays a weaker afternoon–evening peak compared with YRK. The α-pinene pattern shows a morning peak, followed by

decrease from oxidation and dilution, but is much lower in concentration (ppbv) than isoprene. Interpretation of this diurnal pattern could add perspective on oxidation chemistry and SOC formation.

4   Summary

Inspection of long-term data in the SEARCH region and specifically at CTR indicates that the experiments of summer 2013 generally represent aerometric conditions within the range of those in the last decade, although some parameters were lower relative to previous years. Meteorologically, the summer 2013 data at CTR were biased towards a range of conditions that was marginally wetter and cooler, with lower solar radiation, than in most previous years. Chemically, air quality at CTR in 2013 exhibited a mix of natural and anthropogenic influences, but the magnitude of the anthropogenic component was significantly lower than during the earlier years of the last decade. This result is not anomalous, since emission reductions during the past decade or more reflect regulatory actions intended to lower emissions permanently. The implications of observed changes are uncertain as to whether the ambient response to emission reductions results in slowing reaction rates due to reduced reactant concentrations, or in changes in the relative importance of the hundreds of photochemical reactions involved. This aspect of the change in the southeastern air chemistry needs to be investigated in detail, and SOAS will assist in achieving this understanding. The current conditions are likely to foretell the future conditions, which perhaps will increasingly return to a quasi-natural state as anthropogenic emissions continue to decline.

The 1 June–15 July period of 2013 displayed pollution concentrations ranging from clean air to conditions of substantial intrusion of pollution over the region with evident plumes from urban or point sources. Tracking trends of trace gases indicates important reductions in ambient concentrations since 2000, resulting from regional reductions of CO, SO_2, NO_x, and NMOC emissions as indicated by statistically significant regressions of ambient concentrations against emissions. The emission reductions also

reduced extreme ground-level O_3 concentrations, but not at the rate seen in precursor reductions. Fine particle concentrations have declined since 2000, with declines in concentrations of SO_4 and both EC and OC. There is enough NH_3 in the air to effectively neutralize the average acidity of rural SO_4 and pNO_3, but the summer tends to contain less NH_4 neutralized SO_4 than winter. Average acidic SO_4 has remained approximately the same since 2000; stoichiometrically, SO_4 is present as an ammonium salt, and is approximately neutralized as letovicite or bisulfate in summer. Water-soluble (inorganic) sulfur as sulfate appears to account for almost all ($\lesssim 95\%$) the total S in particles. Gas and particle concentrations tend to be lower along the Gulf Coast compared with inland. There are also urban-rural differences in air quality, with stronger gradients associated with primary pollutants in contrast to secondary species, although weaker secondary species gradients do exist.

Evidence from the long-term record and source apportionment suggests that much of the OC is modern in origin at CTR, but OC in total derives in part from primary sources, including biomass burning and vehicle transportation. This result needs to be accounted for in apportionment of the SOC fraction. Evidence from Zheng et al. (2002a, b) and Blanchard et al. (2008), for example, suggests that the majority of the regional annual or seasonal average OC can be accounted for from primary sources.

A major focus of the SOAS experiments was to evaluate the mechanisms for SOC enhancement through interaction of biogenic emissions with anthropogenic pollution. While it is clear that various SOC formation mechanisms are active (as measured with the chemical tracers), the magnitude of the OC enhancement and when it occurs are in question. SEARCH data coupled with trends in anthropogenic emissions provide the ability to test various hypotheses over an extended time period. The detailed chemical species measurements from the SOAS experiments, combined with the constraints of the long-term SEARCH observations, provide an important framework to add a perspective on how, when and where SOC occurs in the southeastern US.

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Table 1. Linear regression trends models relating 1996–2011 annual average ambient concentrations (ppbv for CO, NO_y, NO_z, NMOC, and O_3; $\mu g\, m^{-3}$ for SO_2, SO_4, EC, OC) to annual, regional[a] chemical emissions (MMT yr^{-1}.). Statistically significant ($p < 0.05$) results are indicated by **bold-face** p values.[b]

Model	N (yrs)	Variance (r^2)	p value (slope)	p value (intercept)
BHM CO = 74.08 ($\pm$13.38) $\times$ (CO emissions) – 69.31 ($\pm$89.13)	11	0.773	**0.0004**	0.426
CTR CO = 12.21 ($\pm$4.90) $\times$ (CO emissions) + 92.14 ($\pm$32.74)	16	0.307	**0.0258**	**0.0138**
Rural SO_2 = 5.276 ($\pm$0.433) $\times$ (SO_2 emissions) – 0.333 ($\pm$0.424)	18	0.903	**< 0.0001**	0.443
Network SO_4 = 2.424 ($\pm$0.271) $\times$ (SO_2 emissions) + 1.356 ($\pm$0.250)	14	0.870	**< 0.0001**	**0.0002**
Rural NO_y = 3.287 ($\pm$0.372) $\times$ (NO_x emissions) – 0.65 ($\pm$0.534)	16	0.848	**< 0.0001**	0.904
Rural NO_z = 1.359 ($\pm$0.368) $\times$ (NO_x emissions) – 0.246 ($\pm$0.493)	13	0.554	**0.0035**	0.628
JST NMOC = 3144.9 ($\pm$523.2) $\times$ (VOC emissions[c]) – 37.2 ($\pm$44.8)	11	0.801	**0.0002**	0.428
Rural O_3 = 9.772 ($\pm$2.315) $\times$ (NO_x emissions) + 37.48 ($\pm$3.327)	16	0.560	**0.0009**	**< 0.0001**
Rural O_3 = 16.299 ($\pm$5839) $\times$ (VOC emissions) + 32.78 ($\pm$6.643)	16	0.358	**0.0144**	**0.0002**
Rural EC = 19.509 ($\pm$4.727) $\times$ (EC emissions) – 0.077 ($\pm$0.154)	14	0.587	**0.0014**	0.624
Rural EC = 25.921 ($\pm$7.136) $\times$ (EC emissions[d]) + 0.085 ($\pm$0.131)	14	0.524	**0.0034**	0.527
Rural OC = 29.411 ($\pm$18.772) $\times$ (OC emissions) – 0.0623 ($\pm$2.277)	14	0.170	0.143	0.789
Rural OC = 207.48 ($\pm$51.40) $\times$ (OC emissions[d]) + 1.171 ($\pm$0.477)	14	0.576	**0.0016**	**0.022**
BHM EC = 73.41 ($\pm$14.297) $\times$ (EC emissions) – 0.622 ($\pm$0.461)	13	0.706	**0.0003**	0.204
BHM EC = 97.293 ($\pm$21.750) $\times$ (EC emissions[d]) – 0.019 ($\pm$0.396)	13	0.645	**0.0009**	0.963
BHM OC = 85.099 ($\pm$37.142) $\times$ (OC emissions) – 5.978 ($\pm$4.494)	13	0.323	**0.0427**	0.210
BHM OC = 491.399 ($\pm$91.910) $\times$ (OC emissions[d]) + 0.164 ($\pm$0.791)	13	0.722	**0.0002**	0.840

[a] Total annual emissions from Alabama, Georgia, Mississippi, and northwest Florida covering 1996–2011.

[b] The p value is a measure of statistical significance, defined as the probability of obtaining a nonzero result as large (small) or larger (smaller) than observed under the null hypothesis (i.e., when the true parameter value is zero).

[c] Georgia on-road mobile source VOC emissions.

[d] Mobile-source emissions.

Table 2. Mean concentrations by inland and coastal sites determined for 1999–2002 and 2009–2012. $PM_{2.5}$ and $PM_{10–2.5}$ mass and species concentrations are means of daily measurements (24 h filter-based samples). O_3 measurements are means of peak daily 8 h maxima. Concentrations of gases are means of days determined from hourly data. Means were determined by year, and the yearly means were then averaged.

Species	Inland Sites				Coastal Sites			
	1999–02		2009–12		1999–02		2009–12	
	CTR	BHM[a]	CTR	BHM[a]	OAK[b]	GFP[b]	OAK[b, c]	GFP[b]
$PM_{2.5}$ ($\mu g\,m^{-3}$)								
Mass	14.17	20.62	8.89	11.88	12.77	12.15	9.61	8.58
SO_4	4.16	4.95	2.20	2.66	3.66	3.75	2.33	2.31
NO_3	0.38	1.00	0.29	0.50	0.35	0.44	0.33	0.36
NH_4	1.32	1.83	0.73	0.96	1.11	1.23	0.74	0.75
EC	0.58	2.05	0.63	1.04	0.52	0.74	0.36	0.43
OM^f	4.70	7.32	3.48	3.96	4.24	3.97	2.65	2.75
MMO	0.36	0.97	0.41	0.92	0.45	0.48	0.67	0.59
$PM_{10–2.5}$ ($\mu g\,m^{-3}$)[c]								
Mass	5.62	13.60	5.01	12.19	NA	NA	6.23	8.26
SO_4	0.21	0.29	0.18	0.34	NA	NA	0.21	0.31
NO_3	0.40	0.46	0.37	0.48	NA	NA	0.46	0.69
NH_4	0.05	0.02	0.03	0.004	NA	NA	0.02	0.07
MMO	1.38	4.47	1.24	4.10	NA	NA	1.76	2.04
Gases (ppbv)								
O_3	36.97	23.27	32.93	24.74	37.05	31.81	33.15	32.96
CO	182.3	502.3	164.7	296.4	169.8	270.3	138.7	179.3
SO_2	2.02	4.87	0.76	2.44	1.65	2.31	0.73	1.17
NO	0.43	19.97	0.15	7.54	0.21	3.63	0.09	1.10
NO_2^d	2.76	14.37	1.51	12.03	1.41	NA	1.02	4.55
NO_y	5.04	38.16	2.72	21.21	3.37	11.91	1.89	6.46
NO_z	1.76	5.98	1.19	2.04	1.42	NA	0.77	0.89
NH_3^e	NA	NA	0.32	2.16	NA	NA	0.31	0.77

[a] Gas measurements at BHM began in 2000.
[b] $PM_{10–2.5}$ measurements at GFP and OAK start in 2003.
[c] Measurements after 2010 not available.
[d] NO_2 measurements commenced 1999–2002.
[e] NH_3 measurements commenced in 2004 as 24 h filter-based measurements; hourly measurements began in 2011.
[f] The SEARCH database adopts the value of OM/OC of 1.4.

Table A1. Glossary.

Experiments and Measurement Programs	
ASACA	Assessment of Spatial Aerosol Composition in Atlanta (1999–. . .)
CASTNET	(Interagency) Clean Air Status and Trends Network (1991–. . .)
CSN	(USEPA) Chemical Speciation Network (1999–. . .)
IMPROVE	Interagency Monitoring of Protected Visual Environments (1985–. . .)
PAMS	(USEPA) Photochemical Assessment Monitoring Station, measuring NMOC, and sometimes NO_y and O_3 (1998–. . .)
SAS	Southern Atmosphere Study (summer 2013)
SEARCH	Southeastern Aerosol Research and Characterization Network (1998–. . .)
SOS	Southern Oxidant Study (1992–1999)
SOAS	Southern Oxidant and Aerosol Study (1 June–15 July 2013)
Carbon Chemical Terms	
EC	Elemental Carbon–Refractory, insoluble, chemically inert, light-absorbing carbon, operationally defined by measurement protocol (SEARCH filter samples utilize CSN/IMPROVE thermal optical reflectance method)
IEPOX	Isoprene epoxydiol, a product of isoprene oxidation
LAC	Light Absorbing Carbon – Operationally defined concentration using light absorbance as an estimate of black (as elemental) carbon
NMOC	Non-methane organic carbon, a part of VOCs
OC	Organic carbon made up of organic species directly from sources (primary organic carbon–POC) and secondary organic carbon (SOC) from chemical reactions of volatile organic species in the atmosphere, including photochemically induced oxidation products
OM	(Particle) Organic Matter– defined as $x \times$ OC, where "x" is an empirical constant ranging from ~ 1.4 to ~ 2.3. SEARCH data are reported with $x = 1.4$
OVOC	Oxygenated volatile organic compounds, including alcohols, aldehydes, ketones and acids
TC	Total carbon normally without the carbonate carbon component
VOC	Volatile organic compounds
Other Terms	
EGU	Electrical Generating Unit – power plant, frequently coal fired in the Southeast
GAM	Generalized (statistical) Additive Model
MMO	Major metal oxides (defined in SEARCH data as the sum of Al_2O_3, SiO_2, K_2O, CaO, TiO_2, and Fe_2O_3)
NEI	(USEPA) National Emissions Inventory
NIS	Non-inorganic sulfate; e.g., sulfate esters, methane sulfonate, sulfite salts
pNO$_3$	Particulate nitrate, often assumed to be mainly NH_4NO_3
RH	Relative humidity
SR	Solar radiation
WSSO4	Water-soluble sulfate from filter extractions with water solvent, or direct particle sample dissolution

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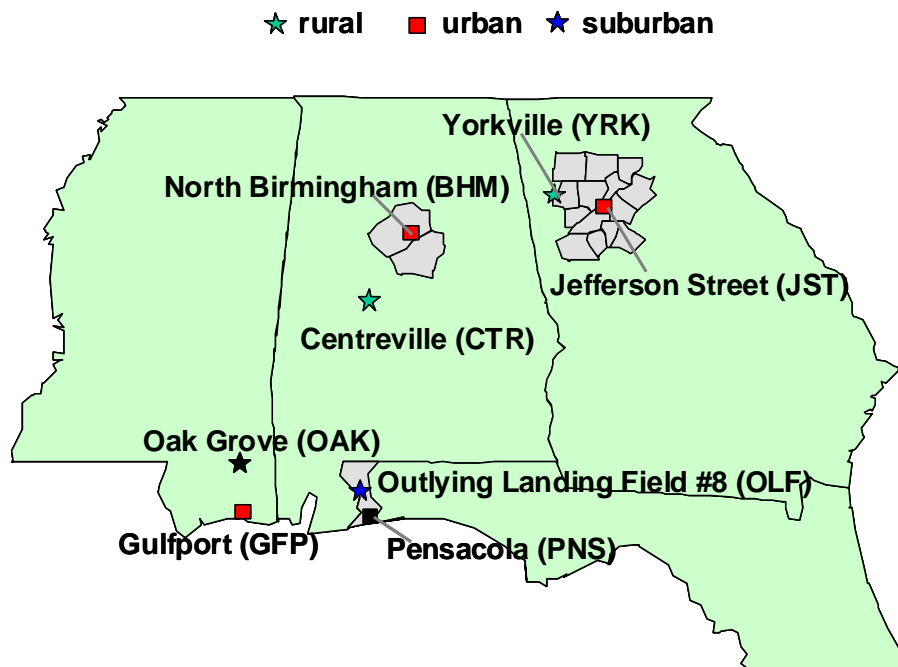
**Figure 1.** Geographical locations of the SEARCH monitoring sites and the nominal region of influence for the site measurements. PNS, OAK, GFP were retired after 2009, 2010, 2012, respectively.
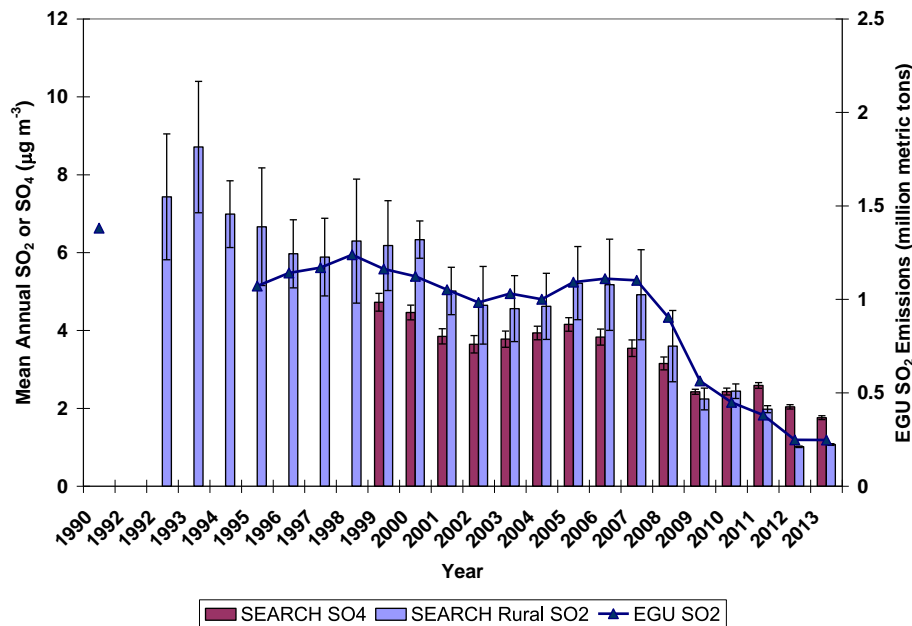
Figure 2. Mean annual SO$_4$ concentrations (all SEARCH sites) and SO$_2$ concentrations (rural SEARCH sites – CTR, OAK, YRK) compared with emissions of SO$_2$ from EGUs located in Alabama, Georgia, northwest Florida, and Mississippi vs. year. Uncertainties are one standard error of the intersite means. EGU emissions are updated from Blanchard et al. (2013b).

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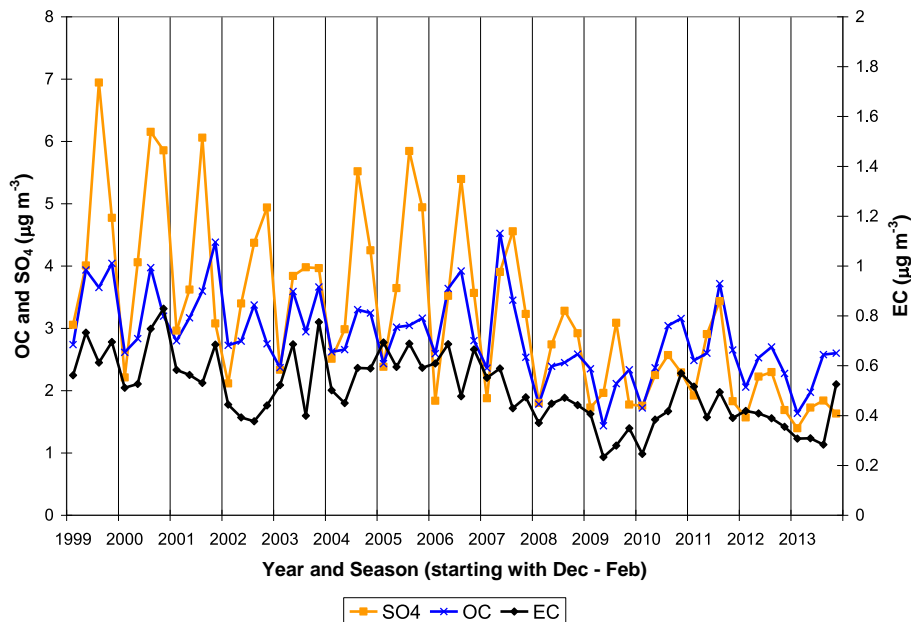
Figure 3. Mean seasonal concentrations of SO$_4$, OC, and EC at CTR. Seasons are by calendar month (1) January–March, (2) April–June, (3) July–September, (4) October–December Vertical divisions are calendar year between Q4 and Q1. OC and EC tend track one another and trends are downward at approximately the same annual rate, while SO4 shows are sharper decrease until 2008. OC tends to have winter minima, but OC maxima vary between Q2–Q4.
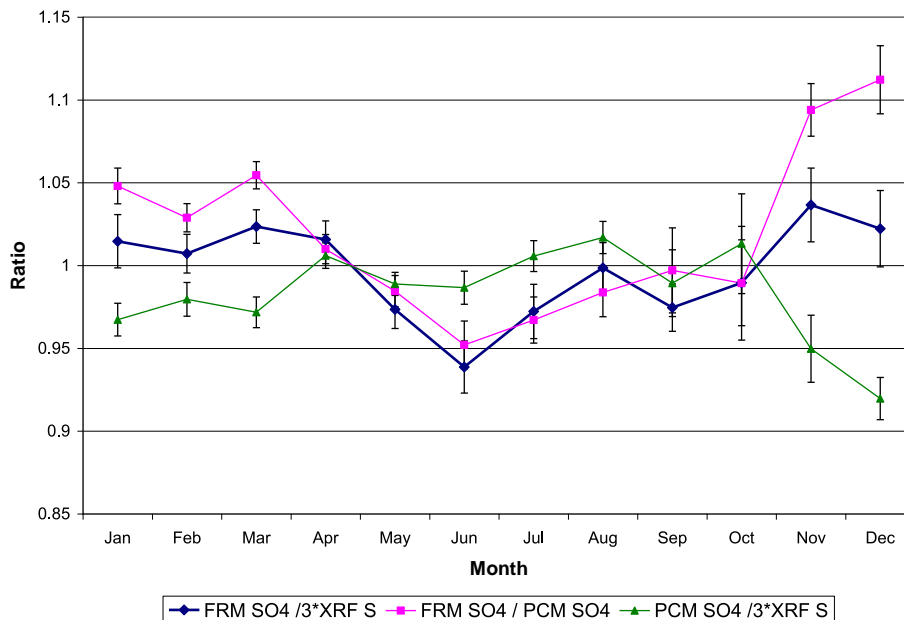
Figure 4. Comparison of federal reference method (FRM) SO$_4$, FRM x-ray fluorescence (XRF) S (multiplied by 3 to represent SO$_4$), and ARA-SEARCH sampler (PCM1) SO$_4$. The data are from JST, 1999 and 2000 (19–54 days per monthly mean). The PCM1 sampler is configured with a denuder to remove SO$_2$ and thereby reduce or eliminate positive artifact, whereas the FRM sampler is not. FRM SO$_4$ measurements at other sites and during other years were too limited for comparison ($n < 4$ values per month except at BHM, where $n = 8$–11 values during 6 months). XRF S measurements are made on FRM filters.
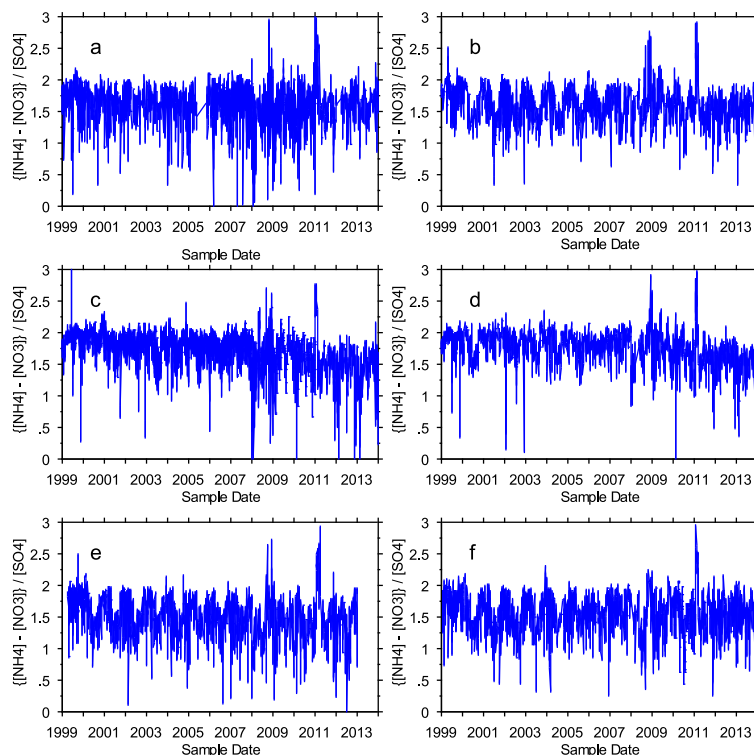
Figure 5. Daily molar ratio of {[NH$_4$]–[NO$_3$]}/{[SO$_4$]} (sulfate neutralization) at **(a)** BHM, **(b)** CTR, **(c)** JST, **(d)** YRK, **(e)** GFP, and **(f)** OLF. The ratios decreased by 0.01–0.03 units yr^{-1} (statistically significant at all sites, $p < 0.0001$) and averaged 1.5 (GFP, OAK) to 1.8 (JST, YRK) over the study period. A seasonal variation in the ratio is seen especially at CTR from 2001–2007, where the ratio is reduced in summer relative to winter.
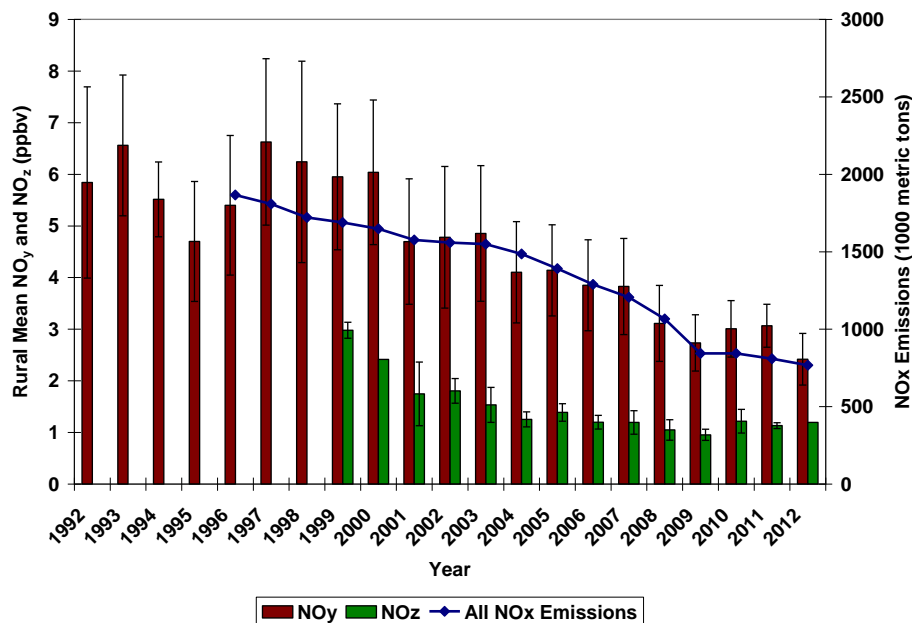
Figure 6. Mean rural NO_y and NO_z concentrations at the three rural SEARCH sites (CTR, OAK, YRK) and emissions of NO_x from all emission sources located in Alabama, Georgia, northwest Florida, and Mississippi vs. year. Uncertainties are one standard error of the intersite means. Emissions are derived from the NEIs and are updated from Blanchard et al. (2013b).
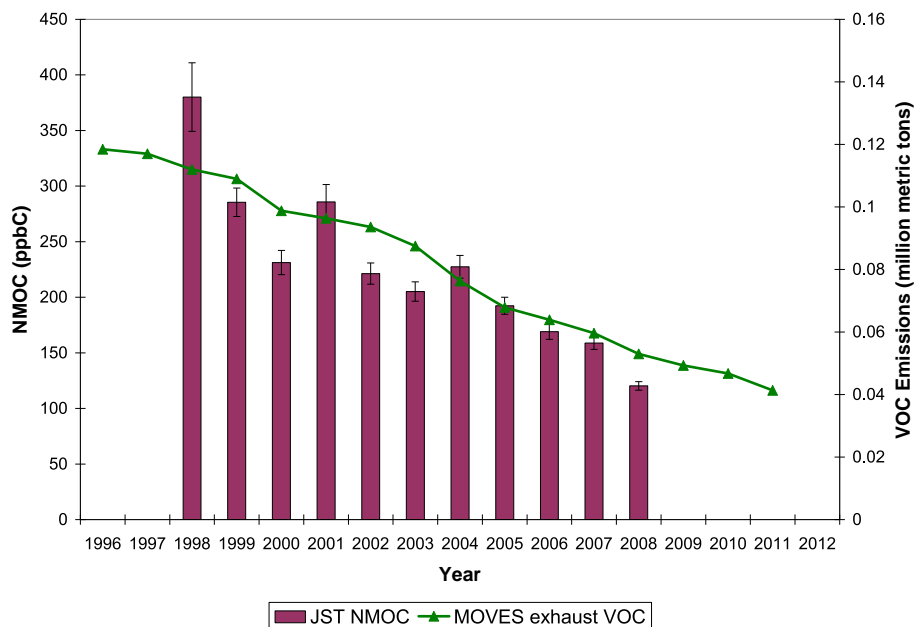
Figure 7. Mean annual NMOC concentrations at JST and emissions of VOC from on-road mobile exhaust within Georgia vs. year. Uncertainties are one standard error of the intersite means. The 1998 NMOC measurements were made from August through December. Emissions are updated from the NEIs, and from Blanchard et al. (2013).

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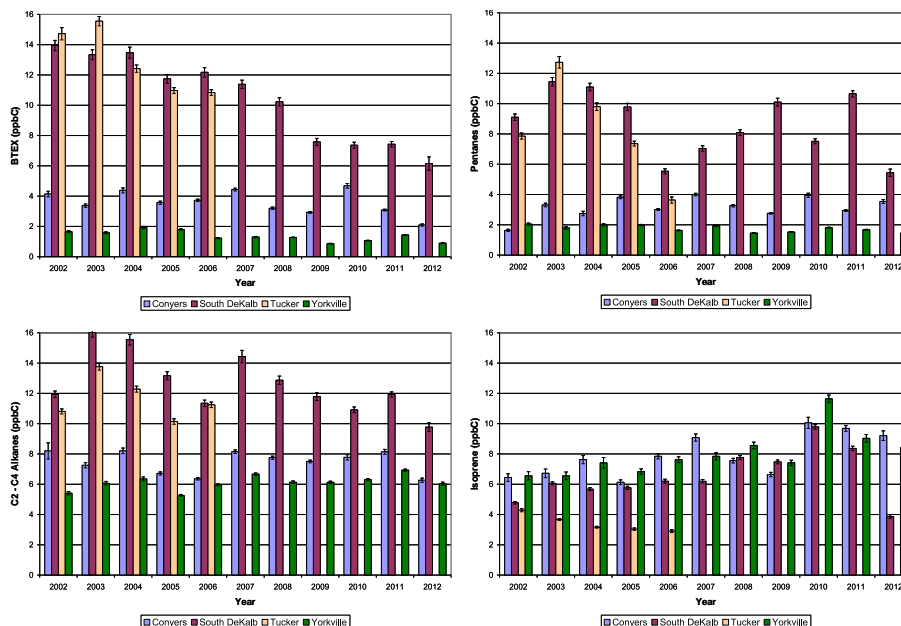
Figure 8. Mean summer (June–August) concentrations of NMOC species at four PAMS sites within the Atlanta metropolitan area. South DeKalb and Tucker are urban sites; YRK is considered an "upwind" non-urban site, while Conyers is a suburban (semirural) "downwind" site.
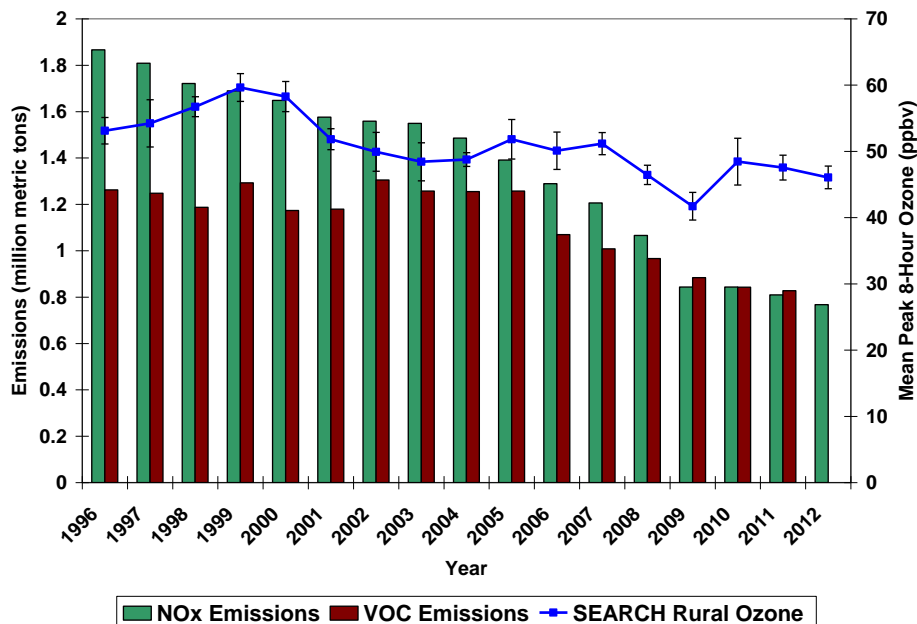
Figure 9. Mean peak 8 h O_3 at rural SEARCH sites during the months of March through October compared with anthropogenic NO_x and VOC emissions in Alabama, Georgia, Mississippi, and northwest Florida. The 2012 NO_x emissions were estimated from 2011 using the 2011 and 2012 CEMS data for EGU emissions.
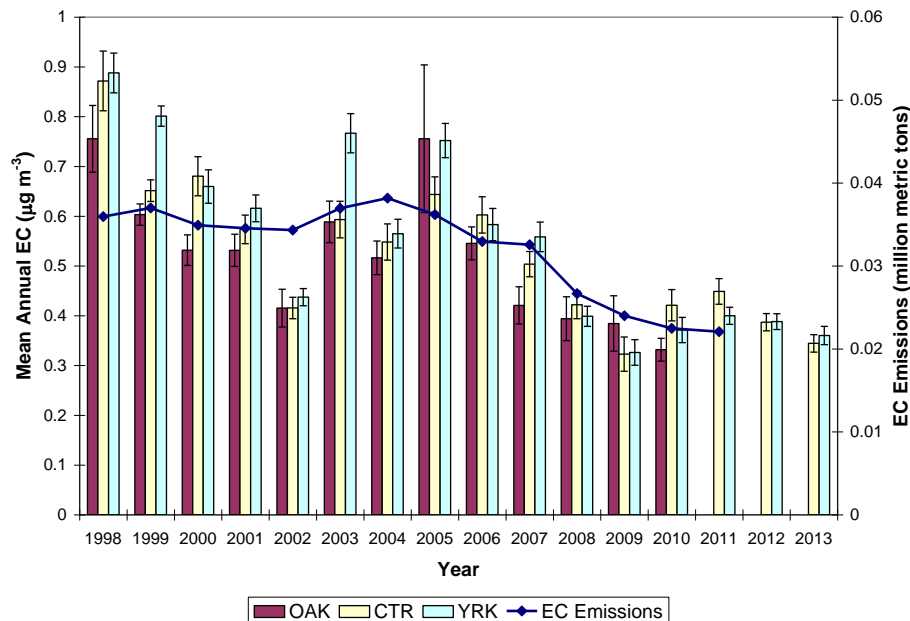
Figure 10. Mean annual EC concentrations at rural SEARCH sites compared with emissions of EC from all emission sources in Alabama, Georgia, Mississippi, and northwest Florida. Emissions data are from Blanchard et al. (2013b).
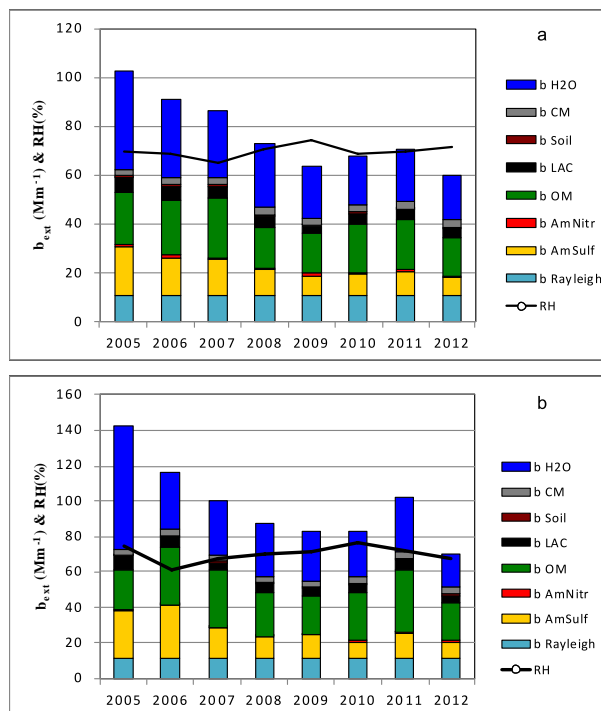
Figure 11. (a) Mean annual light extinction computed from daily species concentrations at CTR calculated using the new IMPROVE algorithm. **(b)** Mean light extinction computed from daily species concentrations at CTR during 1 June–15 July of each year. The aerosol components include ammonium salts, OM, light absorbing carbon (LAC), soil dust, coarse material (CM) and water. The black line in each panel shows the average measured RH during each period. RH dependence was computed using the IMPROVE f(RH) formula with hourly RH measurements at each site. Effects of water in particles, associated with SO_4 and NO_3, are shown separately as the bH$_2$O term. (See also Fig. S10).
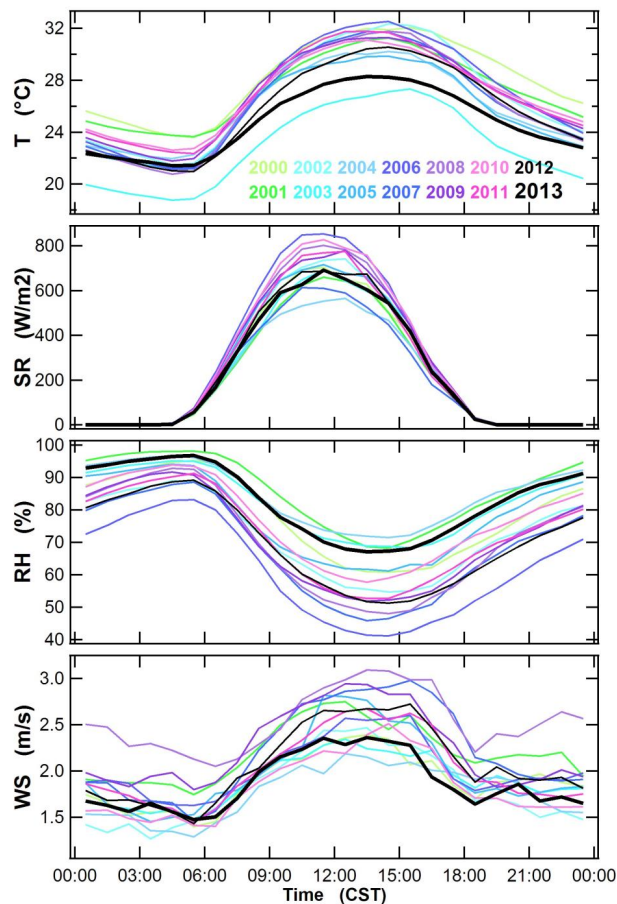
Figure 12. Mean diurnal hourly (CST) temperature (*T*), solar radiation (SR), relative humidity (RH), and wind speed (WS) at CTR from 1 June through 15 July each year.

CTR-ARA 45-Day Period June 1 - July 15

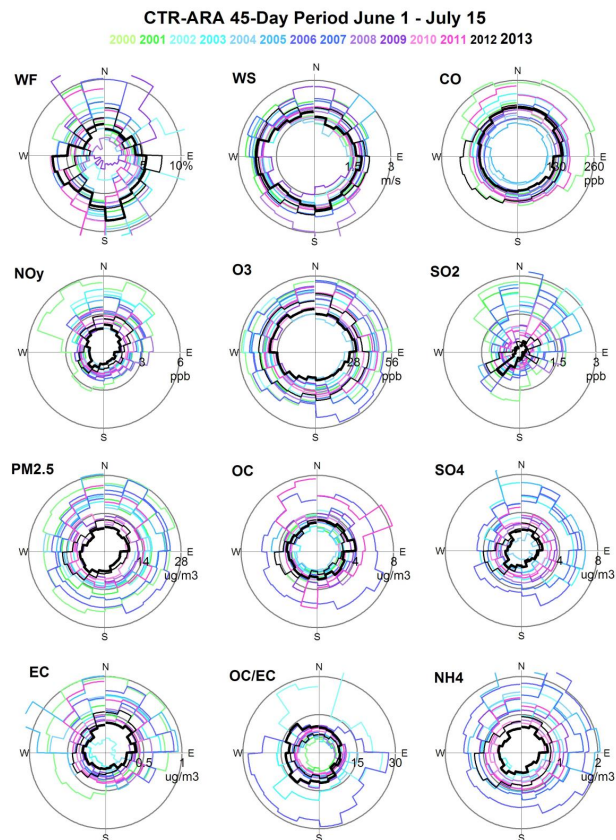2000 2001 2002 2003 2004 2005 2006 2007 2008 2009 2010 2011 2012 2013

Figure 13. Mean directional wind speed frequency and direction, trace gas concentrations, and concentrations of $PM_{2.5}$ mass, EC, OC, SO_4, NH_4 and NH_4/SO_4 at CTR during the SOAS period in 1 June–15 July 2013.
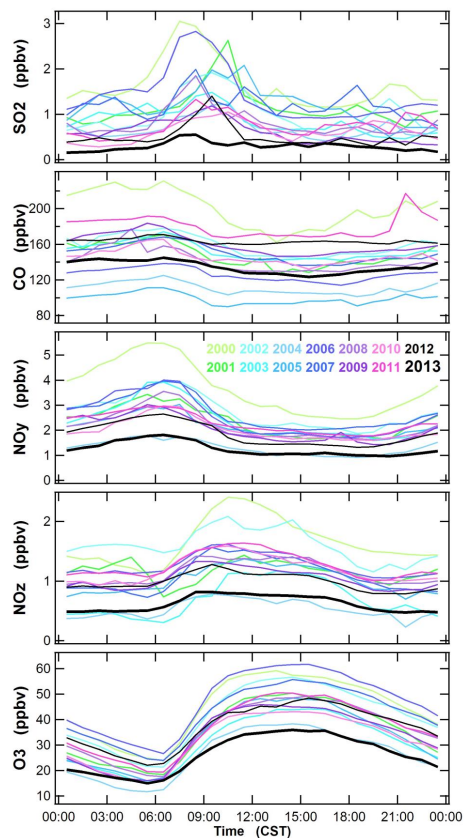
Figure 14. Mean diurnal concentrations of trace gases SO_2, NO_y, NO_z, and O_3 at CTR from 1 June through 15 July each year.
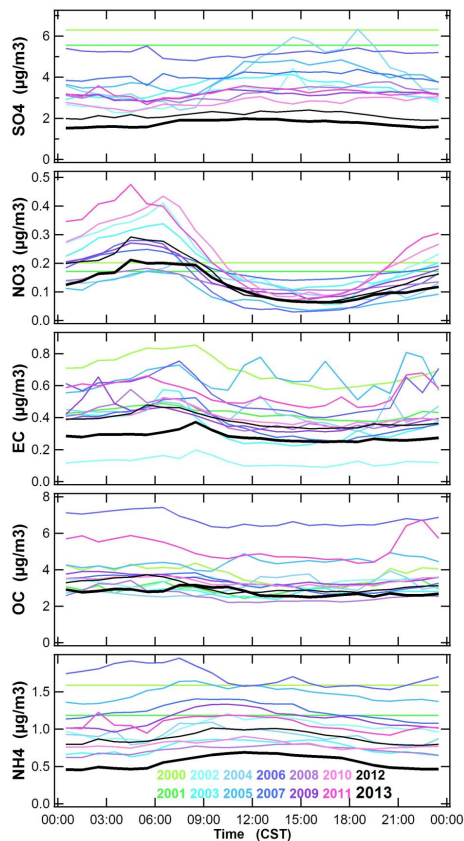
Figure 15. Mean diurnal concentrations of $PM_{2.5}$ SO_4, pNO_3, EC, OC and NH_4 at CTR from 1 June through 15 July each year. 2000–01. SO_4, pNO_3, and NH_4 are 24 h values.