#### Chemical Climatology of the Southeastern United States, 1999 - 2013 1 G. M. Hidy<sup>1</sup>, C. L. Blanchard<sup>1</sup>, K. Baumann<sup>2</sup>, E. Edgerton<sup>2</sup>, S. Tanenbaum<sup>1</sup>, S. Shaw<sup>3</sup>, E. 2 Knipping<sup>3</sup>, I. Tombach<sup>4</sup>, J. Jansen<sup>5</sup>, and J. Walters<sup>5</sup> 3 4 <sup>1</sup>Envair, Albany, CA and Placitas, NM, USA 5 <sup>2</sup>Atmospheric Research and Analysis, Cary, NC, USA 6 <sup>3</sup>Environmental Sector, Electric Power Research Institute, Palo Alto, CA, USA 7 <sup>4</sup>Environmental Consultant, Camarillo, CA, USA 8 9 <sup>5</sup>Research and Environmental Affairs Department, Southern Company Services, Inc., 10 Birmingham, AL, USA 11 12 Correspondence to: G. M. Hidy (dhidy113@comcast.net) 13 14 Abstract 15

16 A series of experiments (the Southern Oxidant and Aerosol Study-SOAS) took place in central 17 Alabama in June-July, 2013 as part of the broader Southern Atmosphere Study (SAS). These 18 projects were aimed at studying oxidant photochemistry and formation and impacts of aerosols at 19 a detailed process level in a location where high biogenic organic vapor emissions interact with 20 anthropogenic emissions, and the atmospheric chemistry occurs in a subtropical climate in North 21 America. The majority of the ground-based experiments were located at the Southeastern Aerosol Research and Characterization (SEARCH) Centreville (CTR) site near Brent, Alabama, 22 23 where extensive, unique aerometric measurements of meteorology, trace gases and particles have 24 been made from the early 1990s through 2013. The SEARCH network data permits a 25 characterization of temporal and spatial context of the SOAS findings. Our earlier analyses of 26 emissions and air quality trends are extended through 2013 to provide a perspective for 27 continued decline in ambient concentrations, and the implications of these changes to regional 28 sulfur oxide, nitrogen-ozone and carbon chemistry. The narrative supports the SAS program in 29 terms of long-term average chemistry (chemical climatology) and short-term comparisons of early summer average spatial variability across the southeastern US at high temporal (hourly) 30 31 resolution. The long-term measurements show that the SOAS experiments took place during the 32 second wettest and coolest year in the 2000-2013 period, with lower than average solar radiation. 33 The pollution levels at CTR and other SEARCH sites were the lowest since full measurements began in 1999. Changes in anthropogenic gas and particle emissions between 1999 and 2013, 34

35 account for the decline in pollutant concentrations at the monitoring sites in the region. The data

36 provide an opportunity to contrast SOAS results with temporally and spatially variable

37 conditions in support for the development of tests for the robustness of SOAS findings.

38

### 39 **1. Introduction**

40

An important element of atmospheric science is the reconciliation of the results of short-term 41 field campaigns with long-term measurements. Such comparisons are used to estimate the extent 42 to which the results from special studies apply to other times, different locations, or under 43 44 different aerometric conditions. Short-term campaigns for studying atmospheric processes are amenable to detailed observations of complex physicochemical processes. While it is impractical 45 46 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) 47 campaign was part of the Southern Atmosphere Study (SAS) held in the period of 1 June -15 48 49 July 2013 (EPA, 2014a; UCAR, 2014). SAS encompassed several major intensive field 50 campaigns, of which SOAS was one. The campaigns involved a number of research groups in 51 order to inform a series of coordinated research questions, which included the following: 1) the 52 amounts, variations, and controlling processes for biogenic fluxes of organic carbon and nitrogen, 2) aerosol composition, secondary aerosol formation processes, associated driving 53 54 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 55 56 nitrogen compounds, and 7) mercury emissions, transformation, and fate. A key recurring theme 57 of all the SAS research was to investigate how interactions of biogenic and anthropogenic 58 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). 59

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 Atmospheric Research and Analysis (ARA) [2014]), 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), 2014; EPRI, 2013). Our approach extends through 2013 earlier analyses of trends (Blanchard et al., 2013 a, b,

c) ending in 2010-2011. In addition to extending the earlier relationships for annual emissions 66 with ambient concentrations of gases and particles, we add statistically significant linear 67 68 relationships between ambient concentrations and emissions for 1999-2013. Also included are 69 several new analyses and trends estimates for the SOAS early summer period, including aspects 70 of the changes in concentrations of primary pollutants compared with secondary species. We first consider the climate of the southeastern United States in which the rural Centreville site (CTR) is 71 72 located. This description is followed by a summary of pollutant emission trends in the region, 73 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 74 75 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 76 77 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. 78

79

### 80 **1.1 The Infrastructure and Climate of the Southeast**

81

The southeastern US is characterized by a warm, moist, subtropical climate, with relatively 82 83 isolated urban communities surrounded by agricultural areas and forests in hilly terrain. 84 Anthropogenic activities in the region are known to emit volatile organic compounds (VOCs), 85 CO, SO<sub>x</sub>, NO<sub>x</sub>, NH<sub>3</sub>, 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 86 87 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 88 89 pollution (e.g., Irving, 1991; Ingram et al., 2013). Climatologically, summers are warm and 90 humid, with occasional thunderstorms associated with continental frontal systems passing 91 through the United States. Winter conditions are cooler, with occasional freezing and isolated 92 snow or ice storms inland, but generally milder conditions along the northern coast of the Gulf of 93 Mexico. The region also is known for its extreme weather conditions where drought occurs, 94 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., 95 96 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).

100

### 101 **1.2 Long-term Observations**

102

103 While multiple ground level monitoring sites were part of SOAS, including several in central 104 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 105 network site (CTR). The SEARCH network (Fig. 1) began in 1992 with three sites (CTR, Oak 106 107 Grove [OAK], and Yorkville [YRK]) as part of the Southern Oxidant Study (SOS) measuring  $O_3$ ,  $NO_v$  (oxidized nitrogen species, including  $NO_x$  [NO + NO<sub>2</sub>], HNO<sub>3</sub>, peroxyacetyl nitrate 108 109 (PAN), 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 110 expanded to eight beginning in 1998 with the addition of discrete and continuous aerosol mass 111 112 and composition instrumentation (Supplement Table S1). Selected sites, including CTR, have involved measurement methods development and deployed additional instrumentation over time 113 114 (e.g., e.g., Solomon et al., 2003; Hansen et al, 2003, 2006; Edgerton et al., 2005; Edgerton et al., 2006; Edgerton et al., 2007; Hatch et al., 2011; Budisulistiorini et al., 2013). The SEARCH sites 115 116 include continuous or semi-continuous measurements of indicators of pollutant emissions, 117 reactants in the atmosphere, and products of chemistry. The basic, long-term measurements for 118 gases, including CO, NO<sub>v</sub>, SO<sub>2</sub>, O<sub>3</sub>, HNO<sub>3</sub> and NH<sub>3</sub>, are listed in Supplement Table S1. At the Atlanta, Georgia site, Jefferson St. (JST), 24-hour canister samples for determination of 119 120 nonmethane organic compounds (NMOC) and oxygenated volatile organic compounds (OVOC) 121 (subsets of VOC) were obtained from 1999-2008. These speciated NMOC observations 122 complement measurements from four PAMS sites (Photochemical Assessment Monitoring 123 Stations [http://www.epa.gov/ttn/amtic/pamsdata.html) in the Atlanta metropolitan area (Tucker, 124 South DeKalb, Convers, and Yorkville, co-located with the YRK SEARCH site). The SEARCH 125 gas and meteorological measurements are supplemented with ambient particle sampling for measurement of mass concentration and composition of  $<\sim PM_{2.5}$  range and PM<sub>10</sub>-PM<sub>2.5</sub>, and 126 127 optical extinction (ambient and dry; e.g., Hansen et al., 2003, 2006; Edgerton et al., 2005, 2006).

128 In addition to the long-term measurements, SEARCH has hosted a number of studies supporting

129 methods development and urban epidemiology. The data have been used for understanding

130 ambient composition and chemistry, and a variety of analyses including characterization of

131 trends (publications using SEARCH data for such purposes are found in

136

132 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),

134 Marmur et al. (2006, 2009), Pun and Seigneur (2008), Pun et al. (2008), and Tesche et al. (2008).

135 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

137 conditions. A number of other monitoring sites for  $O_3$ ,  $NO_v$ , and particulate matter are located in

the region, including those of IMPROVE, CSN, ASACA and CASTNET (Table A1), and those

139 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 140 141 surrounded by mixed deciduous-evergreen forest including the Talladega National Forest a few kilometers to the south and west. Blanchard et al. (2013a) have discussed the representativeness 142 143 of air chemistry at CTR. Support for this conclusion also is included later in this paper based on regional aerometric data and its relative uniformity in azimuthal direction of concentration 144 145 variation. 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 146 147 VOCs and as detritus from vegetation. CTR is approximately 80 km SSW of the Birmingham, 148 Alabama metropolitan area. The site is known to be exposed occasionally to pollution from 149 Birmingham, Tuscaloosa (~45km WNW), and Montgomery (~120 km SE), along with major 150 vehicle traffic routes and certain large point sources in the region, including power plants, pulp 151 and paper mills, and metal processing (e.g., Birmingham) indicated, for example, in Supplement 152 Table S2. For regional gas and particle emissions, see Supplement Figure S2 and the discussion 153 in Blanchard et al., 2013c). The Southeast also experiences a substantial amount of biomass burning (Wade et al., 2000; Haines et al., 2001). Overall, the CTR aerometric conditions 154 155 represent relatively low gas and aerosol concentrations typical of the rural Southeast from 156 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 157 158 exposure to sustained diluted air pollution (e.g., Goldan et al., 1995, 2000; SAMI, 2002). This

159 regime of low, annual-average regional concentrations of monitored pollutants tends to approach 160 nominal background concentrations characteristic of the eastern North American continent, e.g., 161 estimated for different gases and particles, for example, by Seinfeld and Pandis (1998) for NO<sub>x</sub>, Hidy and Blanchard (2005) for PM<sub>2.5</sub>, and Lefohn et al. (2014) for O<sub>3</sub>. The presence of 162 anthropogenic pollution in the Southeast combined with large amounts of natural biogenic 163 emissions yields the potential for a regional air chemistry that has elevated ozone levels, partially 164 165 driven by isoprene from vegetation and anthropogenic NMOC (e.g., Chameides et al., 1988; Chameides and Cowling, 1995; Meagher et al., 1998; SOS, 2014). Associated with the regional 166 photochemistry are various species, including sulfur oxides, reactive nitrogen, VOC and the 167 "secondary" pollutants, inorganic SO<sub>4</sub>, (particle) pNO<sub>3</sub>, O<sub>3</sub>, and secondary organic compounds. 168 169 The Southern Oxidant Study (SOS), beginning in 1988, is of particular interest for 170 elucidating ozone chemistry in the Southeast. This study involved several years of  $O_3$  and 171 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  $O_3$ 172 173 concentrations, affected by precursor emissions distributions, active photochemistry, and 174 meteorological influences. The accumulation of O<sub>3</sub> in the region depends on an interplay of urban plumes, elevated regional concentrations, and point-source plumes. SOS confirmed the 175 176 hypothesis of Chameides et al. (1988), showing the importance of isoprene and the (regional) NO<sub>x</sub> sensitivity of O<sub>3</sub> production. Observation-based O<sub>3</sub> modeling matured from the SOS 177 178 experience, and the nature of  $O_3$  production efficiency using the  $O_3/NO_2$  (or  $O_3/NO_2$ ) ratio was 179 proposed (e.g., Solomon et al., 2000). The role of southeastern meteorology, including multiple 180 scale transport winds horizontally dispersing pollution and vertical mixing, was observed. Also of interest were the observations showing that winds repeatedly arising at night in the boundary 181 182 layer were potentially potentially result in transport of  $O_3$ . The SOS experience served as basis for characterizing the long-term trends in chemical climatology of oxidants in the Southeast, and 183 184 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 185 186 Southeast, but both urban and regional concentrations of O<sub>3</sub> and its precursors have declined 187 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). 188

189 Scientists recognized by the 1960s that secondary organic carbon (SOC) was present in 190 atmospheric aerosols both naturally and from anthropogenic VOC oxidation (e.g., Went, 1960; 191 O'Brien et al., 1975; Grosjean and Friedlander, 1980). Regional and urban SOC in the Southeast 192 was expected, given the presence of isoprene and terpenes as precursors, as well as 193 anthropogenic >C<sub>7</sub> VOCs. Lim and Turpin (2002), Zheng et al. (2002a, b), Saylor et al. (2006), 194 Ding et al. (2008), and Blanchard et al. (2008, 2013a) reported estimates of SOC at SEARCH 195 sites using different methods, all of which suggest that secondary organic carbon, SOC (vs. 196 primary organic carbon, POC) is the smaller fraction of annual-average OC in the SEARCH 197 region.

198 Theories linking oxidant- $O_3$  chemistry with reactions forming SOC are summarized in 199 Seinfeld and Pandis (1998) based on hypothesized mechanisms mainly for  $>C_7$  hydrocarbons 200 (especially C=C containing compounds), and smog chamber experiments. In the 1990s, 201 advanced laboratory experiments showed that lower carbon-number VOCs, including isoprene, 202 could produce aerosols. Hallquist et al. (2009) reviewed the emerging homogeneous and 203 heterogeneous chemical mechanisms and caveats relating to volatility or emitted and aging 204 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., 205 206 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 207 208 the goals of the SOAS experiments.

209

# 210 2. Indicators and Trends in Chemical Climatology

211

# 212 **2.1. Gas and Particle Emissions**

213

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., 2012; 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<sub>3</sub>, and biogenic NMOC. These methodological changes are 220 incompletely documented, which makes interpretation of differences difficult to follow (e.g.,

- Xing et al., 2012; 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 the Supplement Fig. S2. Annual emissions from 223 224 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 225 226 emissions of essentially all anthropogenic species of interest have decreased or remained nearly 227 constant since 2000. Between 1999 and 2013, SO<sub>2</sub> emissions decreased by 75% (Fig. S2a),  $NO_x$ emissions decreased by ~57% (Fig. S2b), and anthropogenic VOC emissions declined by ~ 32% 228 (Supplement Fig. S2c). Whereas NH<sub>3</sub> emissions have remained roughly constant during this 229 230 period (13% decrease--Supplement Fig. S2d), CO emissions decreased by 39% (Supplement Fig. S2e). Fine particle emissions decreased by 7% (Supplement Figure S2f), and primary OC and EC 231 emissions decreased by 0.3% and 36%, respectively (Figures S2g and S2h in the Supplement). 232
- 233

#### 234 2.2 Role of Meteorology

235

Once present in the atmosphere, constituents are dispersed by meteorological processes, and 236 237 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 238 239 chemicals, including those produced in the atmosphere. This knowledge is imbedded in source-240 based air quality models that estimate spatial and temporal concentration distributions from 241 sources (e.g., Seinfeld and Pandis, 1998; McMurry et al., 2004). While emissions of precursors are important, meteorology controls a major fraction of O<sub>3</sub> and SO<sub>4</sub> variability in multi-spatial 242 243 studies from the 1970s through the 1990s (e.g., Rao et al., 1997; Hidy 1994). Analysis of 244 measurements shows relationships with meteorology independent of modeling. Relevant examples for the study of meteorological influences on secondary species include sulfate (SO<sub>4</sub>) 245 and O<sub>3</sub> (e.g., Hidy, 1994; Chameides and Cowling 1995; Meagher et al., 1998; Hidy, 2000; 246 247 Blanchard et al., 2010b; 2014a). Hidy (1994) summarized the key 1978-1980 findings of 248 multiple spatial and temporal scale meteorology in the eastern U.S. that affect  $SO_4$  and  $O_3$ 249 concentrations. Rao et al. (1997) discuss the importance of synoptic scale processes in affecting 250 ground level concentrations at temporal and spatial scales of 1-2 days and ~600 km in the

251 Southeast. The SOS investigators describe meteorology and the multiscale O<sub>3</sub> climatology in the

252 Southeast; Hidy (2000) summarized the role of meteorology in modulating O<sub>3</sub> chemistry, and

Blanchard et al. (2010b, 2013a, b, 2014a) described pollutant species in the light of

254 meteorological parameters in the SEARCH region.

255 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). 256 257 Using principal component analysis, Henry (e.g. Hidy, 1994, Chap. 5) showed that 258 meteorological factors, primarily light winds, temperature, and humidity, accounted for much of 259 the sulfate variability in the East during 1977-1978. As a part of SOS, Vukovich (1994, 1998) 260 found that meteorological factors, including temperature, humidity and winds, accounted for much of the variability in O<sub>3</sub> concentrations in the Southeast based on data from 1980-1991. SOS 261 experiments in the Atlanta, Georgia (1991-1992) and Nashville, Tennessee areas (1994-1995; 262 1999) confirmed the strong influence of meteorological factors, especially temperature, on daily 263 O<sub>3</sub> maxima (e.g., Banta et al., 2002; Frost et al., 1998; White et al., 2002). 264

265 A recent analysis of summer rural and urban mean O<sub>3</sub> concentrations using Camalier et 266 al.'s (2007) generalized additive model (GAM) aimed to quantify statistically the impact of meteorology on O<sub>3</sub> formation in recent years (Blanchard et al., 2010b). The results indicated that 267 268 meteorological factors accounted for  $\sim$ 70% of the variability in daily peak 8-hour O<sub>3</sub> concentrations over the 1999-2007 timeframe. Application of this method to 2002-2011 data 269 from multiple sites confirmed this influence (Blanchard et al., 2013b; 2014a). Temperature and 270 271 relative humidity (RH) were the strongest factors influencing high  $O_3$  concentrations (solar 272 radiation correlated with RH and was a factor when RH was excluded). Other meteorological 273 factors potentially important to  $O_3$  concentrations include light winds or alternatively transport 274 distances <200km, signifying air mass stagnation with slow moving synoptic weather systems over the Southeast. 275

276

#### 277 2.3. Ambient Concentration Trends

278

279 A conventional chemical climatology uses certain "macro" indicators for representing ambient

280 chemistry at the ground (SO<sub>2</sub>, NO<sub>y</sub>, NMOC, CO, O<sub>3</sub> and particle mass and component

concentration). The following discussion of these chemical indicators extends beyond 1999-2010

to 2013 the recent downward trends in ambient concentration trends analyses of Blanchard et al.(2013b).

284

#### 285 **2.3.1. Sulfur Oxides**

286

Historically, evolution of atmospheric conditions in the Southeast involved major urban 287 288 expansion superimposed on a base of agriculture and silviculture. This evolution resulted in a 289 sulfur dioxide (SO<sub>2</sub>)-rich atmosphere inland from the Gulf of Mexico through the early 1990s (e.g., Irving, 1991; Hidy, 1994). After this time, SO<sub>2</sub> emissions and ambient concentrations 290 declined dramatically, both regionally and in cities such as Birmingham and Atlanta. A regional 291 292 decline after 2000 is shown for SO<sub>2</sub> emissions and for annual-average ambient SO<sub>2</sub> and SO<sub>4</sub> concentrations in Figure 2 (see also Figs. S2a and S3 in the Supplement). Regional ambient SO<sub>2</sub> 293 concentrations follow the emissions throughout this period, and are consistent with emissions 294 295 and ambient concentration changes over a longer period of time documented in other studies 296 (e.g., pre-1990s, Irving, 1991; post-1990, Xing et al., 2012). SO<sub>2</sub> emissions from electrical generating units (EGUs) represented 76% of total SO<sub>2</sub> emissions, on average, between 1999 and 297 2013. SO<sub>4</sub> tracks the SO<sub>2</sub> emission reductions (Supplement Fig. S2a). Statistically significant 298 linear relations between annual SO<sub>2</sub> emissions and ambient SO<sub>2</sub> and SO<sub>4</sub> concentrations are 299 indicated in Table 1. The SO<sub>2</sub> intercept is not statistically significant, while the statistically 300 significant SO<sub>4</sub> intercept is ~1  $\mu$ g/m<sup>3</sup>. We identify the SO<sub>4</sub> intercept with a continental 301 302 background similar to that found to the west at this latitude (e.g. Hidy and Blanchard, 2005). 303 Seasonal averages of SO<sub>4</sub> are included in Fig. S3. An example of seasonally averaged changes for SO<sub>4</sub> is shown in Figure 3 relative to changes in organic and elemental carbon (OC 304 305 and EC). The concentrations of SO<sub>4</sub> in CTR are maximum in summer and minimum in winter over a fifteen-year period, with a decline in seasonal amplitude after 2007. This is consistent 306 307 with the known sulfur oxidation chemistry involving temperature, oxidant production and elevated moisture content in summer. The seasonal amplitude in SO<sub>4</sub> is greater than that of the 308 309 carbon components, which correlate during the last three years. Unlike SO<sub>4</sub>, which almost always 310 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), 311 312 except for 2009. The OC concentration tends to rise in spring (Q2) with isoprene and terpene

emissions and temperature dependent reaction potentially involving SO<sub>4</sub>. But the continued OC
and EC increase to summer (Q3) is inconsistent from year to year, sometimes occurring in the
fall.

316 The presence of organic sulfur compounds hypothetically is a factor in SOC formation as 317 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 318 319 (e.g., Novakov, 1972; Hoffman et al., 1980) that particle S can include species other than SO<sub>4</sub> as 320 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 321 322 component (WSSO4) measured by ion chromatography. This difference could reflect NIS 323 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 324 for the period 1999-2000 is shown in Fig. 4. The comparison between XRF and WSSO4 in this 325 urban area suggests small differences between the measures, in the range of -6 to +4% of total 326 sulfur as NIS, depending on season. The months with highest apparent contribution were May 327 328 through September. If the differencing is an indicator of NIS, its S fraction in particles is small 329 relative to inorganic sulfate, even in summer. Given the uncertainty in sampling and 330 measurement expected from a differencing method (see also Supplement Table S3), the presence of NIS is not definitive for detecting small mass fractions of NIS in particles; however, the mass 331 332 of organic sulfur particles would be a larger fraction of OC than of sulfate.

333 Recent studies of SOC formation from biogenic NMOC suggest that condensed material 334 is facilitated with acid nuclei (e.g., Hallquist et al., 2009). Since sulfate is a major contributor to 335 particle acidity, the degree of sulfate neutralization can be used as a qualitative surrogate for 336 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 337 338 evidence of acid catalyzed SOC formation from intercomparison of filter-based SO<sub>4</sub> and OC 339 under varying conditions. However, the Lin et al. (2013) plume study of chemistry in high vs. 340 low SO<sub>2</sub> and NH<sub>3</sub> conditions indicated a small enhancement in isoprene epoxydiol (IEPOX) 341 related tracers in high SO<sub>2</sub> conditions.

342 Analysis of the SEARCH particle data, including  $NH_4$ ,  $SO_4$ , and  $pNO_3$ , indicates that, 343 stoichiometrically, sulfate can be interpreted, on average, as a mixture that lies between

344  $(NH_4)_2SO_4$  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 345 346 neutralization ranging from ammonium sulfate, and bisulfate to (rarely) sulfuric acid. Analysis of 347 the data by year from 2000-2013 (Fig. 5) suggests that acidic SO<sub>4</sub> neutralization has not changed appreciably over this period. Since neutralization has not changed, but sulfate concentrations 348 have declined, the hydrogen ion concentrations associated with SO<sub>4</sub> would have decreased. This 349 350 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 reactants (as indicated in 351 experiments of Nguyen et al., 2013). 352

353

### 354 2.3.2. Nitrogen Oxides, NMOC and Ozone

355

The nitrogen oxides and VOC are important elements of the oxidant photochemistry cycle in the 356 357 troposphere, and are components involved in aerosol particle chemistry. Because of its 358 importance,  $O_3$  and its precursors have been studied extensively in the Southeast in major 359 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<sub>3</sub> production and 360 361 atmospheric transport were investigated under the O<sub>3</sub> precursor conditions at that time. The SEARCH urban-rural site pairs are analogous to the 1994-1995 Nashville study, covering similar 362 363 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 364 365 1990s conditions, with higher O<sub>3</sub> and precursor concentrations than seen since 2000 in the SEARCH region. NO and NO<sub>v</sub> have been measured at SEARCH sites since 1992; NO<sub>2</sub> has been 366 367 measured at some SEARCH sites since 1992 and at all sites since 2002. NMOC was measured at 368 JST through 2008, and is supplemented by the PAMS observations, including from the non-369 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 370 371 VOC emissions, including NMOC, deriving from transportation, industrial, and commercial 372 sources, are superimposed as a small fraction on a much larger regional emissions component of natural sources (see Supplement Fig. S2c). In Table 1, linear regression models indicate 373

statistically significant responses of ambient NO<sub>y</sub> and NMOC concentrations to decreasing NO<sub>x</sub>
 and (anthropogenic) VOC emissions, respectively, without statistically significant intercepts.

376 The SEARCH regional annual NO<sub>x</sub> emissions are shown along with rural annual-average 377 NO<sub>v</sub> concentrations in Fig. 6. Reductions in ambient NO<sub>v</sub> levels tracked the NO<sub>x</sub> emission reductions between 2000 and 2013. The trends in CO emissions for transportation (Supplement 378 379 Figure S2e) have a similar pattern to NO<sub>x</sub> emissions (Fig. S2b in the Supplement). Ambient CO 380 concentrations have decreased at both urban and rural sites in the SEARCH region, with 381 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 382 associated with a regional or larger continental background. Such a "background" was not found 383 384 for SO<sub>2</sub> or NO<sub>v</sub>. This is supported by the linear model for ambient CO and emissions in Table 1, where the CTR relationship has an intercept of ~ 100 ppby; the Birmingham data (BHM) show a 385 strong local total CO emissions relationship without a statistically significant intercept. 386

Emissions of VOC are indicated in Supplement Fig. S2c; the anthropogenic component is 387 388 superimposed on a large natural component such that the decline in anthropogenic VOC 389 emissions is a small increment of the total. Decreases in rural ambient NMOC are not well 390 documented, but the urban-nonurban contrast is established with the PAMS and Atlanta-JST 391 data. The annual averages of 24-hour average NMOC at JST are shown with Georgia motor vehicle emissions in Figure 7. The decline in urban NMOC is similar to the on-road VOC 392 393 emissions reduction-as expected from a principal urban source, motor vehicles; NMOC trends 394 and OH reactivity are discussed, for example, in Blanchard et al. (2010a). Evaluation of trends in 395 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 396 397 of the important contributors to the JST OH reactivity was isoprene, and in summer at the 398 nonurban Yorkville and Convers sites where it contributed half of the estimated reactivity 399 (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

405 possibly exhibiting still lower anthropogenic species concentrations relative to a nominally 406 similar level of natural NMOC. Trends in the summer PAMS data (Fig. 8) are considered for 407 selected species having measurements that appear robust (few values below detection limits; no 408 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 409 410 (representing biogenic species). The concentrations of BTEX have decreased over the years at 411 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 412 concentrations of the anthropogenic groups are substantially lower at YRK, about 60 km WNW 413 414 "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 415 416 has not been explained, but could be related to changes in biogenic emissions and chemistry in response to decreasing O<sub>3</sub> concentrations (e.g., Sharkey et al., 2008) since they don't appear to 417 be consistent with changes in T and RH (e.g., Supplement Fig. S13 for a six-week period in early 418 summer). 419

420 Ozone (with  $NO_2$  and  $NO_2$ ) can be used as an indicator of the oxidation state of the air. 421 Average 8-hour maximum O<sub>3</sub> concentrations in the SEARCH region have declined along with 422 decreasing emissions of its precursors, NO<sub>x</sub> and NMOC (e.g., Fig. 9 and Fig. S2 in the Supplement). Linear regression results for decreasing O<sub>3</sub> concentrations as a function of 423 424 decreasing NO<sub>x</sub> and (anthropogenic) VOC emissions are shown in Table 1. The O<sub>3</sub> decrease is 425 less than a 1:1 proportionality with the precursor emission reductions, as indicated by the 426 presence of intercept terms that are a large fraction of ambient O<sub>3</sub> concentrations. The intercepts of ~29-37 ppbv are similar to background levels projected for the Southeast by Lefohn et al. 427 428 (2014). The O<sub>3</sub> proportionality with its precursors would not necessarily be expected due to the 429 nonlinear photochemistry involved, but given the substantial reduction in precursor emissions a 430 relatively small change in ozone of about 1%/yr has been observed.

431 Rural  $NO_z$  ( $NO_y - NO_x$ , a photochemical reaction product indicator) concentrations have 432 tended to level out since 2005, as indicated in Figure 6, paralleling  $O_3$  concentrations. The linear 433  $NO_z$  relationship with  $NO_x$  emissions is statistically significant (Table 1) with a variance higher 434 than for other gases, and without a statistically significant intercept. Ozone concentrations vary 435 with meteorological conditions, which need to be accounted for in long-term averages. Camalier

436 et al. (2007) have developed a statistical approach (GAM) employing meteorological variables to 437 adjust mean summer  $O_3$  concentrations locally and regionally, which has been adopted by EPA 438 for inspecting O<sub>3</sub> trends (e.g. EPA, 2013). We have extended the GAM method to use air quality 439 variables as well to improve the model for O<sub>3</sub> concentrations in the SEARCH region (Blanchard 440 et al., 2014a). Evidence from JST compared with YRK indicates that Atlanta has frequent periods of NMOC-sensitive O<sub>3</sub> formation, but the regional O<sub>3</sub> formation continues to be NO<sub>x</sub>-441 sensitive as found earlier in the SOS studies, including the Atlanta and Nashville areas (e.g. 442 Blanchard et al., 2010b; Chameides et al., 1988; Chameides and Cowling, 1995; [Meagher et al., 443 1998 considered urban Nashville in transition between NO<sub>x</sub> and NMOC sensitive]). 444 445 Evidence for  $O_3$  as an oxidant indicator derives from comparing diurnal  $O_3$ concentrations with OH and HO<sub>2</sub> data. For example, at a suburban site 8 km NE of downtown 446 447 Nashville, OH and HO<sub>2</sub> 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 448 al., 2003). From the data taken in the New York City area, OH concentrations empirically are 449 450 roughly proportional to  $O_3$  concentrations during the day (e.g., Supplement Fig. S4). If this 451 urban-suburban pattern applies to rural conditions in the Southeast, one could expect to see a decline in daytime OH concentrations between 2000 and 2013. This assumption is tempered by 452 453 recent evidence for the regeneration of OH from isoprene reactions yielding an excess of OH from chemical model calculations (e.g. Fuchs et al., 2013). The morning rise in  $O_3$ 454 455 concentrations at the ground also corroborates the potential importance of air mass transport with 456 down-mixing of  $O_3$  from a residual (upper boundary) layer during the break-up of the nocturnal 457 inversion layer 2-3 hours after sunrise (Baumann et al., 2000). As a part of the analysis of the SOAS data, a close look at relationships between OH, HO<sub>2</sub>, O<sub>3</sub> and VOCs would be of interest 458 459 not only for SOC formation, but also for distinguishing rural from urban O<sub>3</sub> photochemistry. 460

100

#### 461 **2.3.3. Aerosol Particles**

462

463 Suspended particles and their origins are a key element of the SOAS experiments. The SO<sub>4</sub>

464 component was discussed above with SO<sub>2</sub>. Trends in regional and CTR particle mass

465 concentration and composition are shown in Supplement Figure S5. Mass concentrations of fine

466 particles  $(PM_{2.5})$  have decreased with primary emissions and secondary components  $(SO_4 \text{ and }$ 

467 carbon). Sulfate has decreased in fine particles relative to EC and OC;  $NH_4$  has not decreased as 468 much, and  $pNO_3$  decreased, even though increases in  $pNO_3$  concentrations potentially could 469 have occurred as declining SO<sub>4</sub> made an increasing fraction of NH<sub>3</sub> available for reaction with HNO<sub>3</sub> (Blanchard et al., 2007). The major metal oxides (MMO) represent a small fraction of 470 471 fine particle mass. Retained water (associated with species such as SO<sub>4</sub>, and represented as one of the unmeasured components within "other") is relatively large. As shown above in Fig. 3, 472 473 SO<sub>4</sub>, EC, and OC display somewhat different seasonal variations. Regional OC is identified with primary sources such as vehicle transportation and biomass burning (e.g., Lee et al., 2010; 474 Zhang et al., 2010). Biomass burning is believed to be a significant portion of  $PM_{2.5}$ 475 476 concentrations especially in the rural Southeast. Various methods have been used to separate 477 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; 478 479 regression, carbon mass balance, Blanchard et al., 2008; Blanchard et al., 2011; chemical composition particle and gases, Pachon et al., 2010; semi-empirical-air quality models, Yu et al., 480 481 2007). While these methods provide insight into the two components of OC, they do not yield a 482 consistent quantitative picture of the fractions of each. The mean fraction of SOC estimated by 483 different methods varies from  $\sim 20\%$  to > 50% depending on the time of year data were obtained, 484 and the method used.

The trends in rural annual average EC concentrations compared with EC emissions are 485 486 shown in Fig. 10. At the rural SEARCH sites, ambient EC decreases over the decade from 2000, 487 and tracks the EC emission decline occurring between 2005 and 2013. EC concentrations 488 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 489 490 rural SEARCH sites on an annual basis (Supplement Fig. S7). These and other results indicate 491 that POC is a major part of average OC concentrations (e.g., Blanchard et al., 2008; Zheng et al., 492 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 versus mobile source OC emissions are each significant, but neither the

slope nor the intercept for regressions of rural ambient OC versus 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.

504 Birmingham EC and OC regression models are included in Table 1 for comparison with 505 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 506 507 emissions show a much stronger annual rate of decline than the rural cases do, without 508 statistically significant intercepts. Regression models (not shown) for EC and OC in Atlanta 509 (JST) are similar to those found for BHM. The linkages between motor-vehicle OC emissions 510 and ambient OC are more evident at BHM and JST than at CTR because the higher motor 511 vehicle emission density within the urban areas results in a stronger signal that is more readily observed within the variability associated with meteorology and with year-to-year variations in 512 513 biomass burning on small spatial scales (e.g., ~10 - 100 km).

514 From source apportionment, wildfires and prescribed burns are a major factor in OC and 515 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 and POC derive from vehicle 516 517 transportation emissions and biomass burning (Supplement Fig. S2g and h; Blanchard et al., 518 2013c). Over the period from 2002-2013, annual wildfires and prescribed burning are shown in 519 Figure S8. There is substantial variability in fires reported yearly and between states (e.g., 520 Larkin et al., 2013). The prescribed burns in each of the states in the SEARCH regime are much 521 more frequent 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 522 523 EPA, the Georgia fire season is in late winter (Jan-Mar) while the Alabama season is apparently 524 later, mainly in May- June; the information on which these temporal profiles were based is not 525 documented. The implications of the temporal differences are unclear for prescribed-burn EC 526 and POC contributions relative to annual or seasonal ambient averages.

527 The SEARCH data have also given insight into the urban-rural contrasts in ambient EC 528 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<sub>4</sub> and OC has a regional character, with SO<sub>4</sub> having a small increment and OC a larger increment associated with the urban emissions (Blanchard et al., 2013a).

536 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 537 538 the inland pair, CTR-BHM, for particles and gases. Interestingly, mean O<sub>3</sub> concentrations are 539 higher at CTR than BHM. The urban-rural contrast is weaker for the coastal pair, OAK and 540 Gulfport, Mississippi (GLF). The secondary species tend to have weaker urban-rural gradients than the primary species. The data suggest the regional character for  $SO_4$  (also NH<sub>4</sub>) and  $O_3$ , 541 while other species have lower mean concentrations along the coast than inland. The conditions 542 543 along the Gulf Coast show lower concentrations, consistent with smaller cities, fewer major 544 point sources along the coast than further inland, and mesoscale meteorological effects 545 associated with marine conditions. Seasonal similarities and differences are shown in Table S4.

546

#### 547 2.3.4. Aerosol Light Extinction

548

549 Ground level estimates of light extinction have been made at the SEARCH sites between 1999 550 and present. Extinction apportionment gives additional insight into the role of chemical 551 components including retained water. Extinction has tended to decrease over the 2000-2013 period, as expected from the decline in fine particle concentrations. A time series of observations 552 for  $b_{\text{ext}}$  at CTR is shown in Supplement Fig. S9, including the dry light scattering component and 553 554 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 555 556 using a weighting relationship with particle composition, including Rayleigh scattering and also 557 water through a hygroscopicity relationship with RH (Pitchford et al., 2007). On a dry basis, major contributors to "dry" extinction coefficient include SO<sub>4</sub> and organic matter (OM as 1.8 558 559 OC) at the SEARCH sites, including CTR. Water content, shown separately in Fig. 11, based on

560	hygroscopicity of SO <sub>4</sub> and NO <sub>3</sub> , is a major component of extinction at the average RH seen
561	annually in CTR. Hygroscopicity of OM is not included; the inorganic component accounts for
562	most of the water retention. This result is consistent with findings from other studies, including
563	those in the Shenandoah, Virginia region of the Southeast (e.g., Malm et al., 2000) and in the
564	Great Smoky Mountains (Lowenthal et al., 2009), and also with laboratory studies (e.g., Brooks,
565	et al., 2004). The black carbon component (light absorbing carbon or LAC) represents a
566	relatively minor portion of the extinction coefficient annually, while the contribution of OM is
567	larger than ammonium sulfate. For comparison, the contributions to the extinction coefficient
568	based on chemical constituents without separation of water from $SO_4$ and $NO_3$ is given in
569	Supplement Fig. S10.
570	
571	3. Representativeness of 2013
572	
573	The previous section provides a long-term context of air quality changes in the SEARCH
574	domain. For the representativeness of the 2013 summer experiments, we turn to the long-term
575	ambient data associated with the period of June 1 to July 15. The discussion includes
576	consideration of the representativeness of meteorological conditions as well as the ambient
577	chemistry at CTR.
578	
579	3.1. Diurnal Emission Characteristics
580	
581	The annual emission trends derived from the NEIs provide no information about short- term
582	emission patterns. Two major contributors to regional, diurnal emissions relevant to the SOAS
583	experiments are $SO_2$ and $NO_x$ from EGUs, and $NO_x$ and NMOC from transportation. Natural
584	emissions for isoprene and terpenes are also of interest. The June-July diurnal EGU $\mathrm{SO}_2$ and $\mathrm{NO}_x$
585	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
- 587 Figure S12 for comparison with the EGU pattern. The EGU emissions of  $SO_2$  and  $NO_x$  show a
- <sup>588</sup> "common" increase in daytime emissions, rising about 0600 h through the daytime followed by a
- 589 decrease in evening after 1800 h (with stated exceptions, all data are given in local standard time
- 590 [LST]). The annual trends in reduction in emissions across the states are consistent with the

annual changes for  $SO_2$  and  $NO_x$  in Figure S2. The average diurnal changes in the on-road motor

- 592 vehicle emissions (NO<sub>x</sub> and NMOC) show an increase around 0600 h with morning urban
- 593 commutes, with steady levels thereafter with a rise in traffic, followed by a decrease around
- 594 1700. As indicated in the figure, there is a weekday-weekend difference in emission timing.

595 Natural VOC emissions of isoprene are influenced by rising and declining temperature 596 and solar radiation, with a rise at ~0600 h in summer, modulated by  $O_3$  concentrations (e.g. 597 Sharkey et al., 2008). Terpene emissions are mainly temperature dependent and tend to rise at 598 0600 h, before decreasing somewhat during midday and increasing again in the evening 599 (Supplement Fig. S19; e.g., Guenther et al.,1993). NO<sub>x</sub> emissions from soil emanations vary with 500 temperature and soil moisture, with less-known average diurnal character; lightning-derived NO<sub>x</sub>

601 production is obviously intermittent depending on stormy conditions.

602

#### 603 **3.2. Meteorological Conditions**

604

605 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 Supplement Fig. S13 for 1 June

to 15 July 2013. The period generally is characterized by light winds (air mass stagnation),

609 warm daytime temperatures, high relative humidity, and reduced solar radiation relative to other

610 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.

612 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).

615 Conditions for elevated pollution involve large-scale, multiday periods of light winds, 616 high SR and high RH, with limited nocturnal vertical mixing in a temperature inversion in the 617 lower boundary layer. In the morning the inversion tends to break up, permitting increased 618 vertical mixing with pollution aloft reaching the ground. This is followed in the evening by re-619 formation of the inversion layer suppressing mixing. Occasional winds aloft, in the boundary 620 layer, develop around the high pressure regime creating conditions for dispersion of pollution 621 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.

627

### 628 **3.3. Chemical Characterization**

629

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.

635 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 636 637 2013; instead westerly winds occurred more frequently with higher wind speeds than usual. The pollution roses suggest that SO<sub>2</sub> has some directionality that varies from year to year during the 638 639 early summer, with a distinct source influencing the site from the southwest during this period. NO<sub>v</sub>, CO, and EC show less directionality but broad enhancements in northern sectors, pointing 640 641 to urban (traffic) influence from Birmingham and Tuscaloosa. O<sub>3</sub>, PM<sub>2.5</sub>, SO<sub>4</sub>, NH<sub>4</sub>, and OC show more regional character, indicated by near-symmetrical concentration distributions with 642 643 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 644 645 from the west and south in association with low EC, while OC/EC ratios are lower from the 646 north and east. These differences suggest that urban sources influence CTR from the northern 647 and eastern sectors, but non-urban sources (including biomass burning and secondary material) 648 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
potentially different wind directions. Examples during SOAS include an urban plume (June 4<sup>th</sup>,
just before a biomass burn); power plant plume (26 June from the SW); open burning (June 4<sup>th</sup>)

and a dust intrusion from air transported over the Atlantic Ocean (9 June or 23 of June ).
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 656 morning when the convective boundary layer develops rapidly and mixing down from air in the 657 residual layer occurs. Sporadically, this residual layer contains emissions from a power plant 658 659 plume high in SO<sub>2</sub> 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 660 frequency of occurrence decreased over the years. NO<sub>v</sub> concentrations, in contrast, and similar to 661 CO, show a broad morning peak around 0600 h CST associated with accumulation of local 662 (traffic) emissions in a shrinking nocturnal inversion layer, which breaks up after sunrise and 663 dilutes into the convective boundary layer. The level of midday NO<sub>v</sub>, as well as its morning 664 amplitude, decreased over the years, reaching a minimum in 2013. Ozone shows the well-known 665 666 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 667 668 layer during morning break-up of the inversion layer (e.g., Zhang and Rao, 1999). If OH and HO<sub>2</sub> concentrations follow a diurnal change (Martinez et al., 2003) similar to suburban 669 Nashville, a maximum in SOC-OC concentration could be expected near midday. The midday 670 O<sub>3</sub> maxima decrease at CTR over the years. Unlike a purely local development, the midday peak 671 672 shows an extended decrease in ozone concentration into the late evening hours. The principal component of NO<sub>v</sub> is NO<sub>2</sub> (e.g., Supplement Figure S16). NO<sub>z</sub> follows a post-NO<sub>2</sub> diurnal 673 674 pattern with a daytime elevation and a maximum just before 0900 h (local time, LT). The average NO<sub>v</sub> levels at CTR are low, < 1 ppbv, with higher concentrations peaking at  $\sim 2$  ppbv in 675 676 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 677 678 nocturnal inversion layer. A nitrogen oxide mass balance is shown Figure S16. The composite diurnal composition indicates that NO<sub>v</sub> is dominated at night mainly by NO<sub>2</sub>, with NO<sub>z</sub> (sum of 679 680 pNO<sub>3</sub>, HNO<sub>3</sub>, alkyl nitrates [AN] and peroxalkylnitrates [PN]) prevailing during the day, 681 wherein  $pNO_3$  contributes very little. The measurements indicated in the NO<sub>y</sub> mass balance nearly reach mass closure with only a minor fraction unidentified. 682

683 In contrast to  $SO_2$  concentrations, which peak in the morning and evening at CTR, sulfate 684 shows a weak midday to afternoon-evening enhancement (Fig. 15), with declining overall 685 concentrations since 2000. The reactive species concentrations display a character consistent 686 with recent lower hourly reaction rates associated with lower SO<sub>2</sub> and OH concentrations 687 compared with earlier years. The diurnal EC and OC concentrations over the years have settled 688 into low levels slightly enhanced around 0900 h  $\rightarrow$  corresponding to a time similar to NO<sub>y</sub>, thus 689 possibly associated with the same sources such as a local traffic increase. The weak diurnal OC 690 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 691 692 during the day. Periods prior to 2013 show an apparent spiky character of EC concentrations, 693 possibly identified with local yard waste or trash burning, and less associate with the previously-694 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 695 696 larger (Lee et al., 2005) in the forests of the Southeast, including Alabama. In 2013, the 697 Alabama Forestry Commission issued 14,137 burn permits for over one million acres, the largest 698 total burn area since 2010 (B. Elliott, personal communication, 2014). Prescribed burning is 699 regulated differently by state, making the NEI estimates of emissions for this source highly 700 uncertain. Satellite observations are used to locate burns, but they do not reliably identify small 701 burn areas below dense forest canopies.

702 The importance of aerosol water content in SOC reaction chemistry is hypothesized in 703 Shen et al. (2013) and Carlton and Turpin (2013). A sample diurnal pattern of liquid water 704 suggested in the difference between dry particle light scattering and ambient particle scattering is 705 seen in Figure S17. A maximum water uptake is at night with the highest RH, while the aerosol 706 tends to lose water systematically with equilibration to lower midday RH. While ample water is 707 present in the aerosol particles during the day, they are much wetter on average at night. The 708 retained water in particles 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 709 710 of the aerosol at morning to midday, which would indicate release of SOC from nocturnal 711 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

714 the basic SEARCH observations, a long-term record of summer concentrations found at YRK 715 can be compared qualitatively with results taken at a rural sites in the Southeast (Supplement 716 Table S5) at locations relevant to SOS, including CTR (e.g., SOS studies of Goldan et al., 1995; 717 Hagerman et al., 1997; Riemer et al., 1998). The data cited in Table S5 indicate the importance 718 of isoprene as a reactive species in the southeastern rural environment. The data suggest a varied 719 but persistent regional presence of anthropogenic NMOC. In each of the locations, anthropogenic 720 NMOC is mixed with the natural NMOC. These data suggest that the production of SOC in the 721 rural sites may be dominated by natural NMOC, but the formation chemistry is complicated by low concentrations of anthropogenic species. 722

Fig. S18 in the Supplement shows the diurnal changes at YRK in several NMOC groups: 723  $C_2$ - $C_4$ , BTEX, pentanes, and isoprene. The first three groups show a concentration peak in the 724 morning followed by a decrease through midday, with "recovery" of concentrations during the 725 night. As noted earlier, this pattern is interpreted to be associated with the accumulation of 726 emissions in a shrinking nocturnal inversion combined with the morning emissions increase and 727 728 inversion breakup, followed by vertical mixing and chemical loss during the day. The four 729 groups vary in terms of reactivity, but show similar morning to midday change; the change is 730 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 731 732 has a distinctly different diurnal pattern, with a modest morning increase in concentration 733 followed by depletion, then a strong peak in the late afternoon-evening. Hypothetically, annual 734 diurnal change in isoprene concentrations appears to reflect variations in June-July 735 meteorological influence combined with oxidation chemistry rather than a systematic trendover the years. Comparison of the diurnal change in isoprene concentration with OC diurnal change 736 737 (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 738 739 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 740 741 shown in Supplement Fig. S19, along with Kinterbish  $\alpha$ -pinene concentrations. The Kinterbish 742 pattern is similar at night and morning through midday, but displays a weaker afternoon-evening 743 peak compared with YRK. The  $\alpha$ -pinene pattern shows a morning peak, followed by decrease

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

746

#### 747 **4. Summary**

748

Inspection of long-term data in the SEARCH region and specifically at CTR indicates that the 749 750 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. 751 Meteorologically, the early summer 2013 data at CTR were biased towards a range of conditions 752 753 that was marginally wetter and cooler, with lower solar radiation, than in most previous years. 754 Chemically, air quality at CTR in 2013 exhibited a mix of natural and anthropogenic influences, 755 but the magnitude of the anthropogenic component was significantly lower than during the earlier years of the last decade or more. The decline in ambient concentrations of gases and 756 757 particles is not anomalous, since emission reductions after 1999, extending beyond 2010-2011 758 through 2013 reflect regulatory actions intended to lower emissions permanently. The 759 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 760 761 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 762 763 assist in achieving this understanding. The current conditions are likely to foretell the future 764 conditions, which perhaps will increasingly return to a quasi-natural state as anthropogenic 765 emissions continue to decline.

The 1 June - 15 July period of 2013 displayed a range of pollution concentrations ranging 766 767 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 768 769 reductions in ambient concentrations since 2000, resulting from regional reductions of CO,  $SO_2$ , NO<sub>x</sub>, and NMOC emissions as indicated by statistically significant regressions of ambient 770 771 concentrations against emissions. The emission reductions also reduced extreme ground-level O<sub>3</sub> 772 concentrations, but not at the rate seen in precursor reductions. Fine particle concentrations have 773 declined since 2000, with declines in concentrations of SO<sub>4</sub> and both EC and OC. There is 774 enough  $NH_3$  in the air to effectively neutralize the average acidity of rural SO<sub>4</sub> and pNO<sub>3</sub>, 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 (>~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.

788 A major focus of the SOAS experiments was to evaluate the mechanisms for SOC 789 enhancement through interaction of biogenic emissions with anthropogenic pollution. While it is 790 clear that various SOC formation mechanisms are active (as measured with the chemical tracers), 791 the magnitude of the OC enhancement and when it occurs are in question. SEARCH data 792 coupled with trends in anthropogenic emissions provide the ability to test various hypotheses 793 over an extended time period. The detailed chemical species measurements from the SOAS 794 experiments, combined with the constraints of the long-term SEARCH observations, provide an 795 important framework to add a perspective on how, when and where SOC occurs in the 796 southeastern US.

797

Supplementary material related to this article is available online at: doi:10.5194/acpd-14-12014-supplement.

800

Acknowledgements. Funding for the SEARCH network has come from Southern Company
 Services and the Electric Power Research Institute. We are indebted to these sponsors for
 providing the resources for achieving this unique long-term measurement program.

805

### 807 **References**

- 808
- 809 Atmospheric Research and Analysis (ARA): Home, Public Data Archive, available at
- 810 http://www.atmospheric-research.com/studies/SEARCH/index.html (last access: 12 August
- 811 2014), 2014
- 812 Banta, R., Senff, C. Nielsen-Gammon, J., Darby, L., Ryerson, T., White, A., Trainer, M.,
- 813 McNider, R., Valente, J., Mayer, S., Alvarez, R., Hardesty, M. Parrish, D., and Fehsenfeld, F.:
- 814 Daytime buildup and nighttime transport of urban ozone in the boundary layer during a
- stagnation episode, J. Geophys. Res.-Atmos., 103, 22,519-22,544, 1998.
- Baumann, K., Williams, E., Angevine, W., Roberts, J., Norton, R., Frost, G., Fehsenfeld, F.,
- 817 Spingston, S., Bertman, S. and Hartsell, B.: Ozone production and transport near Nashville,
- 818 Tennessee: results from 1994 study at New Hendersonville, J. Geophys. Res.-Atmos., 105,
- 819 9137-9153, 2000.
- 820
- Blanchard, C., Tanenbaum, S., and Hidy, G.M.: Effects of sulfur dioxide and oxides of nitrogen
  emission reductions on fine particulate matter mass concentrations: regional comparisons, J. Air
  Waste Manage. Assoc., 57, 1337-1350, 2007.
- 823 824
- Blanchard, C., Hidy, G. M., Tanenbaum, S., Edgerton, E., Hartsell, B., and Jansen, J.: Carbon in
  Southeastern Aerosol Particles: Empirical estimates of secondary organic aerosol formation,
- 827 Atmos. Environ., 42, 6710-6720, 2008.
- 828
- Blanchard, C., Tanenbaum, S., Hidy, G.M., Rasmussen, R., and Watkins, R.: 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,
  2010a.
- 833
- Blanchard, C.L., Tanenbaum, S., and Hidy, G.M.: 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, 2010b.
- 837
- 838 Blanchard, C., Tanenbaum, S., and Hidy, G.M. 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, 2011.
- 841
- Blanchard, C., Hidy, G.M., Tanenbaum, S., Edgerton, E., and Hartsell, B.: The southeastern
- aerosol research and characterization (SEARCH) study: spatial variations and chemical
  climatology, 1999-2010, J. Air Waste Manage. Assoc., 63, 260-275, 2013a.
- 845
- Blanchard, C., Hidy, G., Tanenbaum, S., Edgerton, E., and Hartsell, B.: The southeastern aerosol
- research and characterization (SEARCH) study: temporal trends in the PM and gas
- concentrations and composition, 1999-2010, J. Air Waste Manage. Assoc., 63, 247-259, 2013b.
- 849

- Blanchard, C., Tanenbaum, S., and Hidy, G. M.: Source attribution of trends in air pollutant
- 851 concentrations in the Southeastern Aerosol Research and Characterization (SEARCH), Environ.
- 852 Sci. Technol., 47, 13,536-13,545,dx.doi.org/10.1021/es402876s, 2013c.
- 853
- Blanchard, C. L., Tanenbaum, S., and Hidy, G.M. : Ozone in the southeastern United States: an
- 855 observation-based model using measurements from the Southeastern Aerosol Research and
- 856 Characterization (SEARCH) network, Atmos. Environ., 48, 192-200,
- 857 dx.doi.org:10.1016/j.atmos.env.2014.02.006, 2014a.
- 858
- Blanchard, C. L., Chow, J., Edgerton, E., Watson, J.G., Hidy, G. M., and Shaw, S.: Organic
- aerosols in the southeastern United States: speciated particulate carbon measurements from the
   SEARCH network, 2006-2010, Atmos. Environ.95, 327-333,
- 862 dx.doi.org/10.1016/j.atmosenv.2014.06.050, 2014b.
- 863
- Brooks, S., deMott, P., and Kreidenweis, S.: Water uptake by particles containing humic
- materials and mixtures of humic materials with ammonium sulfate, Atmos. Environ., 38, 1859-1868, 2004.
- 867 Budisulistiorini, S., Canagarratna, M., Croteau, P., Marth, W., Baumann, K., Edgerton, E., Shaw,
- 868 S., Knipping, E., Worsnop, D., Jayne, J., Gold, A., and Surratt, J., Turpin, B., Guenther, A.,
- Cohen, R., Shepson, P., Shaw, S., Wiedimyer, G., Surratt, J., Wennberg, P., and Pierce, J.: Real-
- time continuous characterization of secondary organic aerosol deriving from isoprene epoxydiols
- 871 in downtown Atlanta, Georgia, using the Aerodyne aerosol chemical speciation monitor,
- 872 Environ. Sci. Technol., 47, 5686-5694, 2013.
- 873
- Camalier, L., Cox, W., and Dolwick, P.: The effects of meteorology and their use in assessing
  ozone trends. Atmos. Environ., 41, 7127-7137, 2007.
- 876 Carlton A., and Turpin, B.: Particle partitioning potential of organic compounds is highest in the
- Eastern US and driven by anthropogenic water. Atmos. Chem. Phys., 13, 10,203-10,2142, 2013.
- 879 Carlton, A., Goldstein, A., Jiminez, J., Pinde, R., deGouw, J., Turpin, B., Guenther, A., Cohen,
- 880 R., Shepson, P., Shaw, S., Wiedimeyer, C., Surratt, J., Wennberg, P., and Pierce, J.: The
- 881 Southern Oxidant and Aerosol Study (design rationale),
- http://climate.env.sci.rutgers.edu/SOAS\_SOAS\_White \_Paper\_final.pdf (last access 15 Jan.
   2014), 2013.
- 884
- Chameides, W., Lindsay, R., Richardson, J., and Kiang, C. : The role of biogenic hydrocarbons in urban photochemical smog: Atlanta as a case study, Science, 24, 1473-1475, 1988.
- 887
- 888 Chameides, W., and Cowling, E. : The State of the Southern Oxidant Study: Policy Relevant
- Findings in O<sub>3</sub> Pollution Research, 1988-1994, Rep. Southern Oxidant Study. North Carolina
- 890 State University, Raleigh, N.C., 1995.
- 891
- <sup>892</sup> Ding, X., Zheng, N.M. Edgerton, E. Jansen, J., and Wang, X.: Contemporary or fossil origin:
- split of estimated seconary organic carbon in the southeastern United States, Environ. Sci.
- 894 Technol.,42, 9122-9128, 2008.

- 896 Edgerton, E., Hartsell, B., Saylor, R., Jansen and, J., Hansen, D.A., and Hidy, G.: The 897 Southeastern Aerosol Research and Characterization Study: Part 2-filter based measurements of 898 PM<sub>2.5</sub> and PM <sub>coarse</sub> mass and composition, J. Air Waste Manage. Assoc., 55, 1427-1442, 2005. 899 900 Edgerton, E., Hartsell, B., Saylor, R., Jansen, J., Hansen, D.A., and Hidy, G.: The Southeastern 901 Aerosol Research and Characterization Study: Part 3- Continuous measurements of PM<sub>2.5</sub> mass 902 and composition, J. Air Waste Manage. Assoc., 56, 1325-1341, 2006. 903 904 Edgerton, E., Saylor, R., Hartsell, B., Jansen, J., and Hansen, D.A.: Ammonia and ammonium measurements from the Southeastern U.S. 2007, Atmos. Environ. ,4, 3339-3351, 2007. 905 906 907 Electric Power Research Institute (EPRI): The Southeastern Aerosol Research and 908 Characterization (SEARCH) Network, Report 1023331, EPRI, Palo Alto, CA, 2013. 909 910 Environmental Protection Agency (EPA): Nonmethane Organic Compound (NMOC) and 911 Speciated Non Methane Organic Compound (SNMOC) Monitoring Program, EPA-454/R-99-912 053, EPA, Research Triangle Park, NC, available at: http://www.epa.gov/ttn/amtic/filges/ambient/criteria/reldocs/r-99-053.pdf (last access: 4 913 914 December 2013), 1999. 915 916 Environmental Protection Agency (EPA): Trends in Ozone Adjusted for Weather Conditions. http://www.epa.gov/airtrends/weather.html, last access: 10 Sept. 2013. 917 918 919 Environmental Protection Agency (EPA): http://blog.epa.gov/science/tag/southern-atmospherestudy-sas, last access: 11 Nov. 2014a. 920 921 Environmental Protection Agency (EPA): 2011 Based Emissions Modeling Platform, available 922 at http://www.epa.gov/ttn/chief/emch/index.html#2011, last access: 28 February 2014b. 923 924 925 Frost, G., Trainer, M., Allwine, G., Bhr, M., Calvert, J., Cantrell, C., Fehsenfeld, F., Goldan, P., 926 Herwehe, J., Hubler, G., Kustler, W., Martin, R., McMillen, R., Montzka, S., Norton, R., Parrish, D., Ridley, B., Shetter, R., Walega, J., Watkins, B., Westberg, H., and Williams, E. : 927 928 Photochemical ozone production in the rural southeastern United States during the 1990 Rural 929 Oxidants in Southern Environments (ROSE) program, J. Geophys. Res.-Atmos., 103, 22, 491-930 22,508, 1998. 931 932 Froyd, K., Murphy, S., Murphy, D., deGouw, J., Eddinger, M., and Wennburg, P.: Contribution 933 of isosprene-derived organosulfates to free tropopsheric aerosol mass, Proc. Natl. Acad. Sci. 934 U.S., 107, 21,360-21,365, 2010. 935 936 Fuchs, H., Hofzumahaus, A., Rohrer, F., Bohn, B., Brauers, T., Dorn, H., Haseler, R., Holland, 937 F., Kaminski, M., Li, X., Lu, K., Nehr, S. Tilmann, R., Wegener, R., and Wahner, A.: Experimental evidence for efficient hydroxyl radical regeneration in isoprene oxidation, Nature 938
- 939 Geoscience., 6,1023-1025, 2013.

- 940
- Gao, S., Surratt, J., Knipping, E., Edgerton, E., Shahgholi, A., and Seinfeld, J.: Characterization
  of polar organic components in fine aerosols in the Southeastern United States: Identity, origin
  and evolution, J. Geophys. Res.-Atmos. ,111, D14314, 2006.
- 944
- Goldan, P., Kuster, W., Fehsenfeld, F., and Montzka, S.: Hydrocarbon measurements in the
  southeastern United States: The rural oxidants in the southern environment (ROSE) program
  1000, L. Caarburg, Page, Atmage, 100, 25, 045, 25, 062, 1005
- 947 1990, J. Geophys. Res.-Atmos., 100, 25,945-25,963, 1995.
- 948
  949 Goldan, P., Parrish, D., Kuster, W., Trainer, M., McKeen, S., Holloway, J., Jobson, B., Sueper,
  950 F., and Fehsenfeld, F.: Airborne measurments of isoprene, CO and anthropogenic hydrocarbon
  951 and their implications, J. Geophys. Res.-Atmos., 105, 9091-9105, 2000.
- 952
- 953 Grosjean, D., and Friedlander, S.: Formation of Organic Aerosols from Cyclic Olefins and
- Diolefins, in: The Character and Origins of Smog Aerosols, edited by Hidy, G. M., Mueller,
- P.K., Grosjean, D., Appel, B., and Wesolowski, J., Wiley Interscience, NY,434-476, 1980.
- 956
- Guenther, A., Zimmerman, P., Harley, P., Manson, R., and Fall, R.: Isoprene and monoterpene
  emision rate variability: Model evaluations and sensitivity analyses, J. Geophys. Res.-Atmos.,
  98, 12,609-12,617, 1993.
- 960
- Hagerman, L., Aneja, V., and Lonneman, W.: Characterization of non-methane hydrocarbons in
  the rural southeast United States. 1997, Atmos. Environ., 31, 4017-4038, 1997.
- Haines, T.K., Busby, R., and Cleaves, D.: Prescribed burning in the South: Trends, purpose and
  barriers, So. J. Appl. Forestry, 25, 149-153, 2007.
- 966
- Hallquist, M., Wenger, J., Baltensberger, U., Rudich, Y., Simpson, D. Claeys, M., Dommen, J.,
- Donahue, N., George, C., Goldstein, A., Hamilton, J., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M., Jimenez, J., Kiendler-Scharr, A., Maenhaut, J., Szmigielski, R., and Wildt,
- J.: The formation, properties and impact of secondary organic aerosol: current and emerging
- 971 issues, Atmos. Chem. Phys., 9, 5155-5236, doi:10.5194/acp-9-5155-2009,2009.
- 972
- Hansen, D.A., Edgerton, E., Hartsell, B., Jansen, J., Hidy, G., Kandaswamy, K., and Blanchard,
- 974 C.: The Southeastern Aerosol Research and Characterization study (SEARCH): 1. Overview, J.
- 975 Air Waste Manage. Assoc., 53, 1460-1471, 2003.
- 976
- Hansen, D. A., Edgerton, E., Hartsell, B., Jansen, J., Burge, H., Koutrakis, P., Rogers, C.,
- 978 Suh, C., Chow, J., Zielinska, B., McMurry, P., Mulholland, J., Russell, A., and Rasmussen,
- R.: Air quality measurements for the aerosol research and inhalation epidemiology study, J. Air
  Waste Manage. Assoc., 56, 1445-1458, 2006.
- Hatch, L., Creaman, J., Ault, A., Surratt, J., Chan, J., Seinfeld, J., Edgerton, E., Su, Y., and
- 982 Prather, K. : Measurments of isoprene-derived organosulfates in ambient aerosols by aerosol
- time of flight mass spectrometery Part 1: Single particle atmospheric observaions in Atlanta,
- 984 Environ. Sci. Technol., 45, 5105-5111, 2011.
- 985

- 986 Hidy, G. M.: Atmospheric Sulfur and Nitrogen Oxides: Eastern North American Source-
- 987 Receptor Relationships, Academic Press, San Diego, CA, 1994.
- Hidy, G. M.: Ozone process insights from field experiments. Part 1. Overview, Atmos. Environ.,
  34, 2001-2022, 2000.
- 990
- Hidy, G. M.: Worldwide aerosol chemistry: from hemispheric distributions to megacity sources,
  J. Air Waste Manage. Assoc., 59, 770-789, 2009.
- 993
- Hidy, G. M., and Blanchard, C. L.: The North American background aerosol and global aerosol
  variation, J. Air Waste Manage. Assoc., 55, 1585-1599, 2005.
- Hoffman, M., Waldman, J., Munger, J., and Jacob, D.: 1986. The chemistry and physics of acid
  fog, clouds and haze aerosol, in: Aerosols: Research, Risk Assessment and Control Strategies,
  edited by Lee, S., Schneider, T., Grant, L. and Verkerk, J., Lewis Publishers, Inc., Ann Arbor,
  MI, 121-150, 1986.
- 1001
- Hunt, S.: Southern Atmosphere Study (SAS): Research Partnership Advancing the Science of
  Organic Aerosols, Air, Climate and Energy Research Program, U. S. Environmental Protection
  Agency, Research Triangle Park, N.C., 2013.
- 1005
- Ingram, K., Dow, K., Carter, L., and Anderson, J., eds.: Climate in the Southeastern United
  States: Variability, Change, Impacts and Vulnerability, Island Press, Washington, DC, 2013.
- Irving, P.,ed.: Acidic Deposition: State of Science and Technology.1. Emissions, Atmospheric
   Processes and Deposition, National Acid Precipitation Program, Washington, DC,1991.
- 1011
- Kleindienst, J., Lowandowski, M., Offenberg, J., Edney, E., Jaoui, M., Zheng, M., Ding, X., and
  Edgerton, E.: Contribution of primary and secondary sources to organic aerosols at SEARCH
  network sites, J. Air Waste Manage. Assoc., 60, 1388-1399, 2010.
- 1014
- Larkin, N., Raffuse, S., and Strand, T.: Wildfire emissions, carbon, and climate: U.S. emissions
  inventories, Forest Ecol. and Manage., 317, 61-69, dx.doi.org/10/1016/j. foreco. 2013.09.012,
  2013.
- 1010
- Lee, S., Baumann, K., Schauer, J., Sheesley, R., Naeher, L. Meinardi, S., Blake, D., Edgerton,
  E., Russell, A., and Clements, M.: Gaseous and particulate emissions from prescribed burning in
  Georgia, Environ. Sci. Technol., 39, 9049–9056, 2005.
- 1023
- Lee, S., Liu, Wand, Y., Russell, A., and Edgerton, E.: Source apportionment of PM<sub>2.5</sub>:
- 1025 Comparing PMF and CMB results for four ambient monitoring sites in the southeastern United 1026 States, Atmos. Environ., 42, 4126-4137, 2010.
- 1027 1028 Lefohn, A., Emert, C., Shadwick, D., Wernli, H., Jung, J., and Oltmans, S: Estimates of
- background surface ozone concentrations in the United States based on model-derived source
- apportionment. Atmos. Environ., 47, 275-288,doi.10.1016/j. atmosenv.2013.11.033, 2014.
- 1031

- Lim, H., and Turpin, B.: Origins of primary and secondary organic aerosol in Atlanta: results of
  time-resolved measurements during the Atlanta supersite experiment, Environ. Sci. Technol. ,36,
  4489-4496, 2002.
- 1035

- Lin, Y.-H., Knipping, E. Edgerton, E., Shaw, S., and Surratt, J.: Investigating the influences of SO<sub>2</sub> and NH<sub>3</sub> levels on isoprene-derived secondary organic aerosol formation using conditional sampling approaches, Atmos. Chem. Phys., 13, 8457-8470, 2013.
- 1040 Lowenthal, D., Zielinska, B., Mason, B., Samy, S., Samburova, V., Collins, D., Spencer, C.,
- 1041 Taylor, J., Allen, J., and Kumar, N.: Aerosol characterization studies at Great Smoky Mountains
- 1042 National Park, summer 2006, J. Geophys. Res.-Atmos., 114, doi/10.1029/2008JD011274, 2009.
  1043
- Malm, W., Day, D., and Kreidenweis, S.: Light scattering characteristics of aerosols at ambient
  and as a function of relative humidity: Part II-A comparison of measured scattering and aerosol
  concentrations using statistical models, J. Air Waste Manage. Assoc., 50, 701-709, 2000.
- 1047
- 1048 Marmur, A., Park, S. K., Mulholland, J. A., Tolbert, P. E., and Russell, A.G.: Source
- 1049 apportionment of PM2.5 in the southeastern United States using receptor and emissions based 1050 models: conceptual differences and implications for time-series health studies,
- 1051 Atmos. Environ., 40, 2533-2551, 2006.
- 1052
- 1053 Marmur, A, Liu, W., Wang, Y., Russell, A. G., and Edgerton, E.S.: Evaluation of model
- 1054 simulated atmospheric constituents with observations in the factor projected space: CMAQ
- simulations of SEARCH measurements, Atmos. Environ., 43, 1839–1849, 2009.
- 1056
- 1057 Martinez, M., Harder, H., Kovacs, T., Simpas, J., Bassis, J., Lesher, R., Brune, W., Frost, G.,
- 1058 Williams, E., Stroud, C., Jobson, B., Roberts, J., Hall, S., Shetter, R., Wert, B. Fried, A., Alicke,
- 1059 B., Stutz, J., Young, V., White, A., and Zamara, R.: OH and HO2 concentrations, sources and
- 1060 loss rates during the Southern Oxidants Study in Nashville, Tennessee, summer 1999, J.
- 1061 Geophys. Res-Atmos., 108, 4617, doi.10.1029/2003JD003551, 2003.
- 1062
- McMurry, P., Shepherd, M., and Vickery, J., eds.: Particulate Matter Science for Policy Makers,
  Cambridge University Press, Cambridge, UK, 283-319, 2004.
- 1065
- 1066 McNider, R., W. Norris, A. Song, R. Clymer, S. Gupta, Banta, R., Zamara, R., and White, A.:
- 1067 Meteorological conditions during the 1995 Southern Oxidants Study Nashville Middle
- 1068 Tennesssee Field Intensive, J. Geophys. Res.-Atmos., 103, 22, 225-22, 243, 1998.
- 1069
- 1070 Meagher, J., Cowling, E., Fehsenfeld, F., and Parkhurst, W.: Ozone formation and transport in
- southeasterm United States: Overview of the SOS Nashville/Middle Tennessee Study, J.
  Geophys.Res.-Atmos., 103, 22,213-22,223, 1998.
- 1073
- 1074 Morris, R. E., McNally, D. E., Tesche, T. W., Tonnesen, G., Boylan, J. W., and Brewer, P.:
- 1075 Preliminary evaluation of the community multiscale air quality model for 2002 over

1076 the southeastern United States, J. Air Waste Manage. Assoc., 55, 1694-1708, 2005. 1077 1078 National Atmospheric and Oceanic Administration (NOAA). : Southeast Nexus (SENEX): 1079 Studying the Interactions between Natural and Anthropogenic Emissions at the Nexus of Air 1080 Quality and Climate Change, NOAA, Boulder, CO, available at: 1081 http://www.esrl.noaa.gov/csd/projects/senex/ (last access: November 20, 2013), 2013. 1082 1083 Nguyen, T., Coggon, M., Bates, K., Zhang, X., Schwantes, R. H., Schilling, K. A., Loza, C.L., 1084 Flagan, R.C., Wennberg, P.O., and Seinfeld, J.H.: Organic aerosol formation from the reactive uptake of isoprene epoxidiols (IEPOX) onto non-acidified and inorganic seeds, Atm. Chem. 1085 1086 Phys. Discuss., 13, 27,677-27,716, 2013. 1087 1088 Novakov, T., Mueller, P., Alcocer, A., and Otvos, J.: 1972. Chemical composition of Pasadena 1089 aerosol by particle size and time of day: III Chemical states of nitrogen and sulfur by 1090 photoelectron spectroscopy, in: Aerosols and Atmospheric Chemistry, edited by Hidy. G. M. 1091 Academic Press, New York, 285-294, 1972. 1092 1093 O'Brien, R., Crabtree, J., Holmes, J., Hoggan, M., and Bockian, A.: Formation of photochemical 1094 aerosol from hydrocarbons: atmospheric analysis, Environ. Sci. Technol., 9, 577-582, 1975. 1095 1096 Pachon, J.E., Balachandran, S., Hu, Y., Weber, R.J., Mulholland, J.A., and Russell, A.G.: 1097 Comparison of SOC estimates and uncertainties from aerosol chemical composition and gas 1098 phase data in Atlanta, Atmos. Environ., 44, 3907-3914, 2010. 1099 1100 Peterson, T., Karl., T., Kossin, J., Kunkel, K., Lawrimore, J., McMahon, J., Vose, R., and Yin, 1101 X.: Changes in weather and climate extremes: State of knowledge relevant to air and water quality in the United States, J. Air Waste Manage. Assoc., 64, 184-197, 2014. 1102 1103 1104 Pitchford, M., Malm, W., Schichtel, B., Kumar, N., Lowenthal, D., and Hand, J.: Revised algorithm for estimating light extinction from IMPROVE particle speciation data, J. Air Waste 1105 1106 Manage. Assoc., 57, 1326-1336, 2007. 1107 1108 Pun, B.K., Seigneur, C.: Organic aerosol spatial/temporal patterns: perspectives of measurements and model, Environ. Sci. Technol., 42, 7287–7293, 2008. 1109 1110 1111 Pun, B.; Seigneur, C., Bailey, E., Gautney, L., Douglas, S., Haney, J., and Kumar, N.: Response of atmospheric particulate matter to changes in precursor emissions: A comparison of 1112 three air quality models, Environ. Sci. Technol., 42, 831-837, 2008. 1113 1114 1115 Rao, S.T., Zurbenko, I., Neagu, R., Porter, P., Ku, J., and Henry, R.: Space and Time Scales in Ambient Ozone Data, Bull. Amer. Meteorol. Soc., 78, 2153-2166, 1997. 1116 1117 Ren, X., Harde, H., Martinez, M., Lesher, R., Oliger, A., Simpas, J., Brune, W., Schwab, J., 1118 Demerjian, K., He, Y., Zhou, X., and Gao, H.: OH and HO2 chemistry in the urban atmosphere 1119 1120 of New York City, Atmos. Environ., 37,3639-3651, 2003. 1121

1122	Riemer, D., Pos, W., Milne, P., Farmer, C., Zika, R., Apel, E., Olszyna, K., Kleindienst, T.,
1123	Lonneman, w., Bertman, S., Snepson, P., and Starn, T.: Observations of nonmethane
1124	Instead States L. Coordina Dec. Atmos. 102, 28, 111, 28, 128, 1008
1125	United States, J. Geophys. ResAtmos., 105, 28,111-28,128, 1998.
1120	Shadrey T. Wiharley A. and Danahya A. Jaannana amiggiona from planta, why and have?
112/	Sharkey, 1., wiberiey, A., and Dononue, A.: isoprene emissions from plants: why and now?
1128	Ann. Bot., 10, 5-18, 2008.
1129	Soular D. Educator E. and Hartsell, D. Lincor reconcion techniques for use in the EC tracer
1130	saylor, R., Edgerton, E., she Hartsen, B.: Linear regression techniques for use in the EC tracer
1131	method of secondary organic aerosof estimation. Atmos. Environ.,40, 7540-7550, 2000.
1132	Sainfold I and Dandia S. Atmospheric Chemistry and Dhysical From Air Dollytion to Climate
1133	Change Wiley Interscience, New York 1008
1134	Change, whey interscience, New Tork, 1998.
1135	Shar V. Theo V. Chan Z. and Usena D. Hatana anna santiana of valatile anomia
1130	Shen, X., Zhao, Y., Chen, Z., and Huang, D.: Helerogeneous reactions of volatile organic
113/	compounds in the atmosphere, Atmos. Environ., 68, 297-514, 2015.
1138	Salaman D. Cardina E. Hila and C. M. Frances, C. Campanian affaits (if a final frame
1139	Solomon, P., Cowling, E., Hidy, and G. M., Furness, C.: Comparison of scientific findings from
1140	major ozone field studies in North America and Europe, Atmos. Environ. ,54, 1885-1920, 2000.
1141	
1142	Solomon, P., Chameides, W., Weber, R., Middlebrook, A., Kiang, C., Russell, A., Butler, A.,
1143	Turpin, B., Mikel, D., Scheffe, R., Cowling, E., Edgerton, E., St. John, J., Jansen, J., McMurry,
1144	P., Hering, S., and Bahadori, T.: Overview of the 1999 Atlanta supersite project, J.
1145	Geophys.ResAtmos., 108, 8413, doi:10.1029/2001JD001458, 2003.
1146	Conthem Annalastic Menutain Inditistas (CAMI), Einst Denart and Commune and Calls to
114/	Southern Appaiachian Mountain Infiliative (SAMI): Final Report and Summary, available at:
1148	www.metro4-Sesarm.org/pubs/SAMI_final reportsummary_Report 0802.pdf, 2012.
1149	Southorn Oridante Study (SOS) 1088 2002; Climatele su of Orone and Orone Programmer
1150	southern Oxidants Study (SOS) 1988-2003: Chimatology of Ozone and Ozone Precursors,
1151	available at: www.iicsu.edu/sos/ii.iitiii, last access 15 January 2014, 2014.
1152	Sumatt I Knell I Kleindingt T Edney E Cleave M Semesshien A No N Offenberg I
1155	Suffatt, J., Kfoll, J., Kleindinst, T., Ediley, E., Claeys, M., Sofoosinali, A., Ng, N., Offenberg, J.,
1154	Lewandowski, M., Jaoui, M., Flagan, K., and Seinield, J.: Evidence of organosultates in
1155	secondary organic aerosol, Environ. Sci. Technol., 41, 517-527, 2007.
1150	Takahama S. C. Davidson and Dandia S. Samioantinuous massurements of anomic carbon
115/	Takanama, S., C. Davidson, and Pandis, S.: Semicontinuous measurements of organic carbon
1158	and actuary during the Philsburgh Air Quanty Study: Implications for actu-cataryzed organic
1159	aerosor formation, Environ. Sci. Technol.,40, 2191-2199, 2000.
1160	Tannan D. Olamma K. Education E. Kninning E. and Show S. Saanshing for evidence of
1101	Tanner, R., Olszyna, K., Edgerton, E., Knipping, E., and Snaw, S.: Searching for evidence of
1102	Atmos Environ 42, 2440, 2444, 2000
1103	Aunos. Environ., 45, 5440-5444, 2009.
1164	Taraha T. W. Mamia D. Tannagan C. MaNaller D. Davian J. and Drawing D.
1105	resche, 1. w., Morris, K., Tonnesen, G., Mcinally, D., Boylan, J., and Brewer, P.:
1100	UNIAQ/CAIVIX annual 2002 performance evaluation over the eastern US, Atmos.

1167 Environ., 40, 4906-4919, 2006.

- 1168
- 1169 University Corporation for Atmospheric Research (UCAR):
- 1170 <u>https://www.eol.ucar.edu/field\_projects/sas</u>,last access 29 April 2014).
- 1171
- 1172 Vukovich, F.: Boundary layer ozone variations in the eastern United States and their association
- with meteorological variations: long-term variations, J. Geophys. Res. -Atmos., 99, 16, 839-16,850, 1994.
- 1175
- 1176 Vukovich, F.: Aspects of subregional variations in the SOS region, Atmos. Environ., 32, 3881-1177 3889, 1998.
- 1178
- 1179 Wade, D.D., Brock, C., Brose, P., Grace, J., Hoch, G., and Patterson, G.: Fire in eastern
- 1180 ecosystems, edited by Brown, J. and Smith, J-K., Wildland Fire in Ecosystems: Effects of Fire
- on Flora, Rep. RMRS-GTR-42, US Forest Service, Rocky Mountain Research Station, Ogden,
   UT, 2000.
- 1182 C
- 1184 Went, F.: Organic matter in the atmosphere and its prossible relation to petroleum formation,
- 1185 Proc. Natl. Acad. Sci,. U. S., 46, 212-221, 1960.
- 1186
- 1187 White, A., Templeman, B., Angevine, W., Zamora, R., King, W., Russell, C., Banta, R., Brewer,
- 1188 W. and Olszayna, K.: Regional contrast in morning transitions observed during the 1999
- Southern Oxidants Study Nashville/Middle Tennessee Intensive, J. Geophys. Res.-Atmos., 107,
  doi:10.1029/2001JD002036, 2002.
- 1191
- Xing, J. Pleim, J., Mathur, R., Poulliot, G., Hogrefe, C., Gan, C.-M., and Wei, C.: Historical
  gaseous and primary aerosol emissions in the United States from 1990-2010, Atmos. Phys.
  Chem. Discuss., 12, 30,327-30,369, 2012.
- 1195
- Yu, S., Bhave, P. V., Dennis, R. L., and Mathur, R.: Seasonal and regional variations of primary
  and secondary organic aerosols over the continental United States: semi-empirical estimates and
  model evaluation, Environ. Sci. Technol., 41, 4690-4697, 2007.
- 1199
- Zhang, J., and Rao, S.: The role of vertical mixing in the temporal evolution of ground-level
  ozone concentrations, J. Appl. Meteorol., 38, 1674-1691, 1999.
- Zhang, X., Hecobian, A., Zheng, M., Frank, N and Weber, R.: Biomass burning impact on
  PM2.5 over the southeastern US during 2007: integrating chemically speciated FRM filter
  measurements, MODIS fire counts and PMF analysis, Atmos. Chem. Phys., 10, 6839-6853,
  2010.
- 1206 1207
- 1208 Zhang, Y., Pun, B., Wu, S. Y., Vijayaraghavan, K., and Seigneur, C.: Application and
- evaluation of two air quality models for particulate matter for a southeastern US
  episode, J. Air Waste Manage. Assoc., 54, 1478-1493, 2004.
- 1211
- 1212 Zheng. M., Cass, G., J. Schauer, and Edgerton, E.: Source apportionment of PM2.5 in the
- 1213 southeastern United States using solvent extractable organic compounds, Environ. Sci.

- 1214 Technol. , 36, 2361-2371, 2002a.
- 1216 Zheng, M., Cass, G. R., Schauer, J. J., and Edgerton, E.: Source apportionment of PM<sub>2.5</sub> in the
- 1217 southeastern United States using solvent-extractable organic compounds as tracers. Environ. Sci.
- 1218 Technol., 36, 2361-2371, 2002b.

#### 1224 List of Tables and Figures

1225

- 1226 Table 1. Linear regression trends models relating 1996 2013 annual average ambient concentrations
- 1227 (ppbv for CO, NO<sub>y</sub>, NO<sub>z</sub>, NMOC, and O<sub>3</sub>;  $\mu$ g/m<sup>3</sup> for SO<sub>2</sub>, SO<sub>4</sub>, EC, OC) to annual, regional<sup>a</sup> chemical
- 1228 emissions (MMT/yr.). Statistically significant (p < 0.05) results are indicated by **bold-face** p values.<sup>b</sup>

Model	Ν	Variance	p value	p value
	(yrs)	$(r^{2})$	(slope)	(inter-
	-		_	cept)
BHM CO = 81.10 (± 12.87)*(CO emissions) – 75.38 (± 71.56)	13	0.783	<0.0001	0.315
BHM CO = $80.00 (\pm 10.96)$ *(CO emissions <sup>d</sup> ) + 123.45 (± 35.21)	13	0.829	<0.0001	0.005
CTR CO = $11.06 (\pm 4.28)$ *(CO emissions) + $105.83 (\pm 25.83)$	18	0.295	0.0199	0.0008
CTR CO = $10.80 (\pm 4.11)^*$ (CO emissions <sup>d</sup> ) + $133.23 (\pm 15.25)$	18	0.302	0.0182	<0.0001
Rural SO <sub>2</sub> = $4.109 (\pm 0.195) * (SO_2 \text{ emissions}) - 0.455 (\pm 0.239)$	18	0.965	<0.0001	0.075
Rural SO <sub>4</sub> = $2.102 (\pm 0.158)$ *(SO <sub>2</sub> emissions) + $1.061 (\pm 0.181)$	15	0.932	<0.0001	<0.0001
Network SO <sub>4</sub> = $2.052 (\pm 0.153)^*$ (SO <sub>2</sub> emissions) + $1.157 (\pm 0.175)$	15	0.933	<0.0001	<0.0001
Rural NO <sub>y</sub> = $3.170 (\pm 0.313)^*$ (NO <sub>x</sub> emissions) + 0.113 ( $\pm 0.432$ )	18	0.865	<0.0001	0.797
Rural NO <sub>z</sub> = $1.178 (\pm 0.306)$ *(NO <sub>x</sub> emissions) + 0.015 (± 0.392)	15	0.533	0.002	0.969
JST NMOC = $3144.9 (\pm 523.2)^{*}$ (VOC emissions <sup>c</sup> ) - $37.2 (\pm 44.8)$	11	0.801	0.0002	0.428
Rural $O_3 = 10.093 (\pm 1.868)^* (NO_x \text{ emissions}) + 36.978 (\pm 2.582)$	18	0.646	<0.0001	<0.0001
Rural $O_3 = 19.667 (\pm 5.259) * (VOC \text{ emissions}) + 28.652 (\pm 5.880)$	18	0.466	0.0018	0.0002
Rural EC = $21.937 (\pm 4.434)$ *(EC emissions) – $0.171 (\pm 0.143)$	16	0.636	0.0002	0.251
Rural EC = $23.381 (\pm 5.539)$ *(EC emissions <sup>d</sup> ) + 0.125 (± 0.098)	16	0.560	0.0009	0.222
Rural OC = $13.177 (\pm 34.212)$ *(OC emissions) + $1.227 (\pm 4.227)$	16	0.010	0.706	0.776
Rural OC = $209.55 (\pm 39.99)^*(OC \text{ emissions}^d) + 1.133 (\pm 0.337)$	16	0.662	0.0001	0.005
BHM EC = $87.79 (\pm 14.031)$ *(EC emissions) - $1.162 (\pm 0.448)$	15	0.751	<0.0001	0.022
BHM EC = $95.073 (\pm 17.163)^*$ (EC emissions <sup>d</sup> ) - 0.013 (± 0.303)	15	0.702	<0.0001	0.967
BHM OC = $3.584 (\pm 77.580)^{*}$ (OC emissions) + $3.641 (\pm 9.579)$	15	0.013	0.964	0.710
BHM OC = $501.45 (\pm 75.16)^{*}$ (OC emissions <sup>d</sup> ) + 0.018 (± 0.627)	15	0.774	<0.0001	0.977

<sup>a</sup>Total annual emissions from Alabama, Georgia, Mississippi, and northwest Florida covering 1996 –

1230 2013 (including emissions from biomass burning but excluding emissions from vegetation and soils)
 1231 <sup>b</sup>The p value is a measure of statistical significance, defined as the probability of obtaining a nonzero
 1232 result as large (small) or larger (smaller) than observed under the null hypothesis (i.e., when the true

1232 parameter value is zero)

- <sup>1234</sup> <sup>c</sup>Georgia on-road mobile source VOC emissions
- <sup>d</sup>Mobile-source emissions
- 1236

1237

- 1238
- 1239

1240

1241

- 1242
- 1243
- 1244 1245

1248	Table 2. Mean conce	trations by inland and coastal sites determined for 1999-2002 and 2009-	
1240	2012 DM and DM	mass and snaping concentrations are masned of daily massymemory (2)	1

1249 2012.  $PM_{2.5}$  and  $PM_{10-2.5}$  mass and species concentrations are means of daily measurements (24-

1250 hour filter-based samples). O<sub>3</sub> measurements are means of peak daily 8-hour maxima.

1251 Concentrations of gases are means of days determined from hourly data. Means were determined 1252 by year, and the yearly means were then averaged.

1253

	Inland Sites				Coastal Sites			
	<u>199</u>	<u>1999-02</u> <u>2009-12</u>		1999-02		2009-12		
Species	CTR	<b>BHM</b> <sup>a</sup>	CTR	BHM <sup>a</sup>	OAK <sup>b</sup>	<b>GFP</b> <sup>b</sup>	OAK <sup>bc</sup>	<b>GFP</b> <sup>b</sup>
PM <sub>2.5</sub> (µg	m <sup>-3</sup> )							
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 <sub>3</sub>	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 <sub>10-2.5</sub> (	$ug m^{-3})^{c}$							
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 <sub>3</sub>	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 (pp	bv)							
$O_3$	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 <sub>v</sub>	5.04	38.16	2.72	21.21	3.37	11.91	1.89	6.46
NOz	1.76	5.98	1.19	2.04	1.42	NA	0.77	0.89
NH <sub>3</sub> <sup>e</sup>	NA	NA	0.32	2.16	NA	NA	0.31	0.77

<sup>a</sup>Gas measurements at BHM began in 2000. <sup>b</sup>PM<sub>10-2.5</sub> measurements at GFP and OAK start in 2003.

1255 <sup>c</sup>Measurements after 2010 not available.

<sup>d</sup>NO<sub>2</sub> measurements commenced 1999-2002

<sup>e</sup>NH<sub>3</sub> measurements commenced in 2004 as 24 hour filter based measurements; hourly measurements began in
 2011.

<sup>f</sup>The SEARCH database adopts the convention OM/OC = 1.4.

1260

1261

1262

1263

1264

1265

- 1267
- 1268 Table A1 Glossary
- 1269

### 1270 Experiments and Measurement Programs

- 1271 ASACA Assessment of Spatial Aerosol Composition in Atlanta (1999–...)
- 1272 CASTNET (Interagency) Clean Air Status and Trends Network (1991–...)
- 1273 CSN (USEPA) Chemical Speciation Network (1999–...)
- 1274 IMPROVE Interagency Monitoring of Protected Visual Environments (1985–...)
- 1275 PAMS (USEPA) Photochemical Assessment Monitoring Station, measuring NMOC, and sometimes NOy
- 1276 and O<sub>3</sub> (1998-...) SAS Southern Atmosphere Study (summer 2013)
- 1277 SEARCH Southeastern Aerosol Research and Characterization Network (1998–...)
- 1278 SOS Southern Oxidant Study (1992–1999)
- 1279 SOAS Southern Oxidant and Aerosol Study (1 June–15 July 2013)

# 1280 Carbon Chemical Terms

- 1281 EC Elemental Carbon–Refractory, insoluble, chemically inert, light-absorbing carbon, operationally
- 1282 defined by measurement protocol (SEARCH filter samples utilize CSN/IMPROVE thermal optical
- 1283 reflectance method) IEPOX Isoprene epoxydiol, a product of isoprene oxidation
- 1284 LAC Light Absorbing Carbon Operationally defined concentration using light absorbance as an
- 1285 estimate black (as elemental) carbon
- 1286 NMOC Non-methane organic carbon, a part of VOCs
- 1287 OC Organic carbon made up of organic species directly from sources (primary organic carbon–POC) and
- 1288 secondary organic carbon (SOC) from chemical reactions of volatile organic species in the
- 1289 atmosphere, including photochemically induced oxidation products
- 1290 OM (Particle) Organic Matter– defined as  $x \times OC$ , where "x" is an empirical constant ranging from  $2 \sim 1.4$
- 1291 to ~2.3. SEARCH data are reported with x = 1.4 by convention
- 1292 OVOC Oxygenated volatile organic compounds, including alcohols, aldehydes, ketones and acids
- 1293 TC Total carbon normally without the carbonate carbon component
- 1294 VOC Volatile organic compounds

# 1295 Other Terms

- 1296 EGU Electrical Generating Unit power plant, frequently coal fired in the Southeast
- 1297 GAM Generalized (statistical) Additive Model
- 1298 MMO Major metal oxides (defined in SEARCH data as the sum of Al2O3, SiO2, K2O, CaO, TiO2, and
- 1299 Fe2O3)
- 1300 NEI (USEPA) US National Emissions Inventory
- 1301 NIS Non-inorganic sulfate; e.g., sulfate esters, methane sulfonate, sulfite salts
- 1302 *p*NO3 Particulate nitrate, often assumed to be mainly NH<sub>4</sub>NO<sub>3</sub>
- 1303 RH Relative humidity
- 1304 SR Solar radiation
- 1305 WSSO<sub>4</sub> Water-soluble sulfate from filter extractions with water solvent, or direct particle sample
- 1306 dissolution
- 1307
- 1308
- 1309
- 1310
- 1311













5. Daily molar ratio of { [NH<sub>4</sub>] – [NO<sub>3</sub>] } / [SO<sub>4</sub>] } (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<sup>-1</sup> (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.</p>





- Mean rural NO<sub>y</sub> and NO<sub>z</sub> concentrations at the three rural SEARCH sites (CT OAK, YRK) and emissions of NO<sub>x</sub> 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. (2013c).





- 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. (2013c).







9.	Mean peak 8-hour O <sub>3</sub> at rural SEARCH sites during the months of March
	through October compared with anthropogenic NO <sub>x</sub> and VOC emissions in
	Alabama, Georgia, Mississippi, and northwest Florida. The 2012-2013 NO <sub>x</sub>
	emissions were estimated from 2011 using the 2011 and 2012-2013 CEMS data
	for EGU emissions.



- 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 extension using the method of Blanchard et al. (2013c).





1725 12. Mean diurnal hourly (CST) temperature (T), solar radiation (SR), relative humidity (RH) and
1726 wind speed (WS) at CTR from 1 June through 15 July each year, 2000-2013.
1727



1732 13.Comparison between average 2000-2012 and the SOAS period in 1 June 1- 15 July 2013
1733 for directional wind speed frequency and direction, trace gas concentrations, and
1734 concentrations of PM<sub>2.5</sub> mass, EC, OC, SO<sub>4</sub>, NH<sub>4</sub> and OC/EC at CTR.



14. Mean diurnal concentrations of trace gases SO<sub>2</sub>, NO<sub>y</sub>, NO<sub>z</sub>, and O<sub>3</sub> at CTR from 1 June
 through15 July each year.



1825 15. Mean diurnal concentrations of PM<sub>2.5</sub> SO<sub>4</sub>, *p*NO<sub>3</sub>, EC, OC and NH<sub>4</sub> at CTR from 1 June
through 15 July each year. For 2000-2001, SO<sub>4</sub>, NO<sub>3</sub>, and NH<sub>4</sub> are 24-hour values.
1827
1828