Chemical Climatology of the Southeastern United States, 1999 - 2013

G. M. Hidy[1], C. L. Blanchard[1], K. Baumann[2], E. Edgerton[2], S. Tanenbaum[1], S. Shaw[3], E. Knipping[3], I. Tombach[4], J. Jansen[5], and J. Walters[5]

[1]Envair, Albany, CA and Placitas, NM, USA
[2]Atmospheric Research and Analysis, Cary, NC, USA
[3]Environmental Sector, Electric Power Research Institute, Palo Alto, CA, USA
[4]Environmental Consultant, Camarillo, CA, USA
[5]Research and Environmental Affairs Department, Southern Company Services, Inc., Birmingham, AL, USA

Correspondence to: G. M. Hidy (dhidy113@comcast.net)

Abstract

A series of experiments (the Southern Oxidant and Aerosol Study-SOAS) took place in central Alabama in June-July, 2013 as part of the broader Southern Atmosphere Study (SAS). These projects were aimed at studying oxidant photochemistry and formation and impacts of aerosols at a detailed process level in a location where high biogenic organic vapor emissions interact with anthropogenic emissions, and the atmospheric chemistry occurs in a subtropical climate in North America. The majority of the ground-based experiments were located at the Southeastern Aerosol Research and Characterization (SEARCH) Centreville (CTR) site near Brent, Alabama, where extensive, unique aerometric measurements of meteorology, trace gases and particles have been made from the early 1990s through 2013. The SEARCH network data permits a characterization of temporal and spatial context of the SOAS findings. Our earlier analyses of emissions and air quality trends are extended through 2013 to provide a perspective for continued decline in ambient concentrations, and the implications of these changes to regional sulfur oxide, nitrogen-ozone and carbon chemistry. The narrative supports the SAS program in 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) resolution. The long-term measurements show that the SOAS experiments took place during the second wettest and coolest year in the 2000-2013 period, with lower than average solar radiation. 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,

account for the decline in pollutant concentrations at the monitoring sites in the region. The data provide an opportunity to contrast SOAS results with temporally and spatially variable conditions in support for the development of tests for the robustness of SOAS findings.

1. Introduction

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

This paper provides a context for, and an assessment of, the representativeness of the SOAS experimental period using long-term surface data, excluding mercury (mercury data are available for some sites in 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,

66 c) ending in 2010-2011. In addition to extending the earlier relationships for annual emissions

67 with ambient concentrations of gases and particles, we add statistically significant linear

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

71 consider the climate of the southeastern United States in which the rural Centreville site (CTR) is

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.

74 The post-1999 trends in concentrations of key natural and pollutant species at CTR and the

75 region are presented, with consideration of contrasts between rural and urban conditions, and

76 between inland and coastal conditions. Finally, we discuss the long-term context and

77 representativeness of the SOAS-SAS experiments from 1 June to 15 July 2013. The narrative is

78 supported with additional tables and figures in the Supplement.

79

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

81

82 The southeastern US is characterized by a warm, moist, subtropical climate, with relatively

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_x, NO_x, NH_3, and particles, including organic carbon (OC) and black (elemental) carbon

86 (EC) (see Table A1 Glossary; e.g., SAMI, 2002; Ingram et al., 2013). The urban areas and the

87 larger southeastern region have experienced a growth in population, transportation, and industry,

88 resulting in increased air pollution since the 1960s, followed by post-1990s reductions in

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

95 the Atlantic Ocean and the Gulf of Mexico penetrate inland on occasion (e.g., Peterson et al.,

96 2014). Extended summer periods of light winds and air mass stagnation are prevalent, leading to

97   accumulation of pollution (e.g., McNider et al., 1998). The region is exposed to smoke from wild

98   and prescribed fires, as well as intrusions of transported dust and other pollution from North

99   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

105 Carolina, by number the most measurements were made at the Centreville, Alabama SEARCH

106 network site (CTR). The SEARCH network (Fig. 1) began in 1992 with three sites (CTR, Oak

107 Grove [OAK], and Yorkville [YRK]) as part of the Southern Oxidant Study (SOS) measuring

108 O_3, NO_y (oxidized nitrogen species, including NO_x [NO + NO_2], HNO_3, peroxyacetyl nitrate,

109 other nitrogen oxide gases, and particulate nitrate [$p$$NO_3$]), other trace gases and meteorological

110 variables (e.g., Chameides and Cowling, 1995; SOS, 2014). The sites were expanded to eight

111 beginning in 1998 with the addition of discrete and continuous aerosol mass and composition

112 instrumentation (Supplement Table S1). Selected sites, including CTR, have involved

113 measurement methods development and deployed additional instrumentation over time (e.g.,

114 e.g., Solomon et al., 2003; Hansen et al, 2003, 2006; Edgerton et al., 2005; Edgerton et al., 2006;

115 Edgerton et al., 2007; Hatch et al., 2011; Budisulistiorini et al., 2013). The SEARCH sites

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_y, SO_2, O_3, HNO_3 and NH_3, are listed in Supplement Table S1. At the

119 Atlanta, Georgia site, Jefferson St. (JST), 24-hour canister samples for determination of

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, Conyers, and Yorkville, co-located with the YRK SEARCH site). The SEARCH

125 gas and meteorological measurements are supplemented with ambient particle sampling for

126 measurement of mass concentration and composition of <~$PM_{2.5}$ range and PM_{10}-$PM_{2.5}$, and

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

132   http://www.atmosphericresearch.com/studies/SEARCH.index.html). SEARCH data also have

133   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-

136   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_y, and particulate matter are located in

138   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).

140   CTR is believed to be a regionally representative location in an agricultural area

141   surrounded by mixed deciduous-evergreen forest including the Talladega National Forest a few

142   kilometers to the south and west. Blanchard et al. (2013a) have discussed the representativeness

143   of air chemistry at CTR. Support for this conclusion also is included later in this paper based on

144   regional aerometric data and its relative uniformity in azimuthal direction of concentration

145   variation. The region, represented by Alabama, Georgia, Mississippi, and northwestern Florida,

146   is of particular interest in that relatively large quantities of natural biogenic emissions occur as

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

154   burning (Wade et al., 2000; Haines et al., 2001). Overall, the CTR aerometric conditions

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

157   Mexico (Blanchard et al., 2013a). In the Southeast, essentially all rural areas experience

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_x,

162 Hidy and Blanchard (2005) for $PM_{2.5}$, and Lefohn et al. (2014) for O_3. The presence of

163 anthropogenic pollution in the Southeast combined with large amounts of natural biogenic

164 emissions yields the potential for a regional air chemistry that has elevated ozone levels, partially

165 driven by isoprene from vegetation and anthropogenic NMOC (e.g., Chameides et al., 1988;

166 Chameides and Cowling, 1995; Meagher et al., 1998; SOS, 2014). Associated with the regional

167 photochemistry are various species, including sulfur oxides, reactive nitrogen, VOC and the

168 "secondary" pollutants, inorganic SO_4, (particle) pNO_3, O_3, and secondary organic compounds.

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,

172 2014). The SOS provided evidence of the regional and urban character of summer O_3

173 concentrations, affected by precursor emissions distributions, active photochemistry, and

174 meteorological influences. The accumulation of O_3 in the region depends on an interplay of

175 urban plumes, elevated regional concentrations, and point-source plumes. SOS confirmed the

176 hypothesis of Chameides et al. (1988), showing the importance of isoprene and the (regional)

177 NO_x sensitivity of O_3 production. Observation-based O_3 modeling matured from the SOS

178 experience, and the nature of O_3 production efficiency using the O_3/NO_z (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

181 of interest were the observations showing that winds repeatedly arising at night in the boundary

182 layer were potentially potentially result in transport of O_3. The SOS experience served as basis

183 for characterizing the long-term trends in chemical climatology of oxidants in the Southeast, and

184 catalyzed in part interest in the aerosol component of southeastern pollution. As discussed

185 below, the aerometric conditions for O_3 accumulation currently remain the same in the

186 Southeast, but both urban and regional concentrations of O_3 and its precursors have declined

187 since the mid-1990s. Recent information about O_3 and precursor chemistry is derived from the

188 SEARCH studies (e.g., Blanchard et al., 2010a, b; 2011).

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 $>C_7$ 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.,

205   Carlton and Turpin, 2013) and organo-sulfates and other tracers with SOC production (e.g.,

206   Takahama et al., 2006; Gao et al., 2006; Surratt et al., 2007; Froyd et al., 2010; Kleindienst et al.,

207   2010; Budisulistiorini et al., 2013). Elucidation of these mechanisms is an important element of

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

214   The principal resource for post-2000 emissions and their trends in the SEARCH region is EPA's

215   National Emissions Inventory (NEI). The NEI is formally revised and updated every three years,

216   but its estimates have been extrapolated on an annual basis (e.g. Xing et al., 2012; Blanchard et

217   al., 2013c). Revision and extrapolation since the 1990s have involved intermittent changes in

218   emission modeling, revised interpretation of emission testing, and addition of major fugitive

219   sources such as open burning, NH_3, and biogenic NMOC. These methodological changes are

220 incompletely documented, which makes interpretation of differences difficult to follow (e.g.,

221 Xing et al., 2012; Blanchard et al., 2013c). In any case, the NEI provides a starting point for

222 interpretation of changes in ambient air chemistry in response to annual emission changes.

223 Annual trends in the region are given in the Supplement Fig. S2. Annual emissions from

224 the states of Alabama, Georgia, Mississippi, and the 12 western counties of Florida are adopted

225 for comparison with ambient data (Supplement Fig. S2). Analysis of the NEI data indicates that

226 emissions of essentially all anthropogenic species of interest have decreased or remained nearly

227 constant since 2000. Between 1999 and 2013, SO_2 emissions decreased by 75 (Fig. S2a), NO_x

228 emissions decreased by ~57% (Fig. S2b), and anthropogenic VOC emissions declined by ~ 32%

229 (Supplement Fig. S2c). Whereas NH_3 emissions have remained roughly constant during this

230 period (13% decrease--Supplement Fig. S2d), CO emissions decreased by 39% (Supplement Fig.

231 S2e). Fine particle emissions decreased by 7% (Supplement Figure S2f), and primary OC and EC

232 emissions decreased by 0.3% and 36%, respectively (Figures S2g and S2h in the Supplement).

233

234 **2.2 Role of Meteorology**

235

236 Once present in the atmosphere, constituents are dispersed by meteorological processes, and

237 react chemically with one another, with varying temperature, humidity, and oxidant levels. It is

238 widely known that meteorological factors have a strong influence on ambient concentrations of

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

242 are important, meteorology controls a major fraction of O_3 and SO_4 variability in multi-spatial

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

245 examples for the study of meteorological influences on secondary species include sulfate (SO_4)

246 and O_3 (e.g., Hidy, 1994; Chameides and Cowling 1995; Meagher et al., 1998; Hidy, 2000;

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_3 climatology in the

252   Southeast; Hidy (2000) summarized the role of meteorology in modulating O_3 chemistry, and

253   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,

256   Virginia and North Carolina, was explored extensively in the 1980s, as reviewed by Hidy (1994).

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

261   much of the variability in O_3 concentrations in the Southeast based on data from 1980-1991. SOS

262   experiments in the Atlanta, Georgia (1991-1992) and Nashville, Tennessee areas (1994-1995;

263   1999) confirmed the strong influence of meteorological factors, especially temperature, on daily

264   O_3 maxima (e.g., Banta et al., 2002; Frost et al., 1998; White et al., 2002).

265   A recent analysis of summer rural and urban mean O_3 concentrations using Camalier et

266   al.'s (2007) generalized additive model (GAM) aimed to quantify statistically the impact of

267   meteorology on O_3 formation in recent years (Blanchard et al., 2010b). The results indicated that

268   meteorological factors accounted for ~70% of the variability in daily peak 8-hour O_3

269   concentrations over the 1999-2007 timeframe. Application of this method to 2002-2011 data

270   from multiple sites confirmed this influence (Blanchard et al., 2013b; 2014a). Temperature and

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

275   over the Southeast.

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_2, NO_y, NMOC, CO, O_3 and particle mass and component

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

282   to 2013 the recent downward trends in ambient concentration trends analyses of Blanchard et al.

283   (2013b).

2.3.1. Sulfur Oxides

285

286   Historically, evolution of atmospheric conditions in the Southeast involved major urban

287   expansion superimposed on a base of agriculture and silviculture. This evolution resulted in a

288   sulfur dioxide (SO_2)-rich atmosphere inland from the Gulf of Mexico through the early 1990s

289   (e.g., Irving, 1991; Hidy, 1994). After this time, SO_2 emissions and ambient concentrations

290   declined dramatically, both regionally and in cities such as Birmingham and Atlanta. A regional

291   decline after 2000 is shown for SO_2 emissions and for annual-average ambient SO_2 and SO_4

292   concentrations in Figure 2 (see also Figs. S2a and S3 in the Supplement). Regional ambient SO_2

293   concentrations follow the emissions throughout this period, and are consistent with emissions

294   and ambient concentration changes over a longer period of time documented in other studies

295   (e.g., pre-1990s, Irving, 1991; post-1990, Xing et al., 2012). SO_2 emissions from electrical

296   generating units (EGUs) represented 76% of total SO_2 emissions, on average, between 1999 and

297   2013. SO_4 tracks the SO_2 emission reductions (Supplement Fig. S2a). Statistically significant

298   linear relations between annual SO_2 emissions and ambient SO_2 and SO_4 concentrations are

299   indicated in Table 1. The SO_2 intercept is not statistically significant, while the statistically

300   significant SO_4 intercept is ~1 µg/m^3. We identify the SO_4 intercept with a continental

301   background similar to that found to the west at this latitude (e.g. Hidy and Blanchard, 2005).

302   Seasonal averages of SO_4 are included in Fig. S3. An example of seasonally averaged

303   changes for SO_4 is shown in Figure 3 relative to changes in organic and elemental carbon (OC

304   and EC). The concentrations of SO_4 in CTR are maximum in summer and minimum in winter

305   over a fifteen-year period, with a decline in seasonal amplitude after 2007. This is consistent

306   with the known sulfur oxidation chemistry involving temperature, oxidant production and

307   elevated moisture content in summer. The seasonal amplitude in SO_4 is greater than that of the

308   carbon components, which correlate during the last three years. Unlike SO_4, which almost always

309   peaks in summer (Q3), mean EC and OC concentrations do not show a consistent peak season,

310   varying from spring (Q2) to fall (Q4) quarters. A consistent minimum occurs in winter (Q1),

311   except for 2009. The OC concentration tends to rise in spring (Q2) with isoprene and terpene

312   emissions and temperature dependent reaction potentially involving SO_4. But the continued OC

313   and EC increase to summer (Q3) is inconsistent from year to year, sometimes occurring in the
314   fall.

315   The presence of organic sulfur compounds hypothetically is a factor in SOC formation as
316   postulated, for example, by Surratt et al. (2007). An upper estimate can be made of the mass of
317   sulfur bound in such compounds through differencing methods. It is known from historic studies
318   (e.g., Novakov, 1972; Hoffman et al., 1980) that particle S can include species other than SO_4 as
319   acid, ammonium or other salts. The fraction of non-(inorganic) sulfate (NIS) component can be
320   estimated by comparing sulfur measured by x-ray fluorescence (XRF) and the water-soluble
321   component (WSSO4) measured by ion chromatography. This difference could reflect NIS
322   compounds such as sulfite salts, methane sulfonate, or other organo-sulfur compounds, including
323   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   through September. If the differencing is an indicator of NIS, its S fraction in particles is small
328   relative to inorganic sulfate, even in summer. Given the uncertainty in sampling and
329   measurement expected from a differencing method (see also Supplement Table S3), the presence
330   of NIS is not definitive for detecting small mass fractions of NIS in particles; however, the mass
331   of organic sulfur particles would be a larger fraction of OC than of sulfate.

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

341   Analysis of the SEARCH particle data, including NH_4, SO_4, and pNO$_3$, indicates that,
342   stoichiometrically, sulfate can be interpreted, on average, as a mixture that lies between
343    $(NH_4)_2SO_4$ and NH_4HSO_4 (e.g., letovicite), both in urban and rural locations. Even though the

344　average sulfate neutralization is equivalent to letovicite, there are excursions in daily values of

345　neutralization ranging from ammonium sulfate, and bisulfate to (rarely) sulfuric acid. Analysis of

346　the data by year from 2000-2013 (Fig. 5) suggests that acidic SO_4 neutralization has not changed

347　appreciably over this period. Since neutralization has not changed, but sulfate concentrations

348　have declined, the hydrogen ion concentrations associated with SO_4 would have decreased. This

349　trend suggests that acid-promoted reactions of biogenic NMOC could be present, but potentially

350　have changed with SO_4 concentrations unless other nucleophiles act as reactants (as indicated in

351　experiments of Nguyen et al., 2013).

352

353　**2.3.2. Nitrogen Oxides, NMOC and Ozone**

354

355　The nitrogen oxides and VOC are important elements of the oxidant photochemistry cycle in the

356　troposphere, and are components involved in aerosol particle chemistry. Because of its

357　importance, O_3 and its precursors have been studied extensively in the Southeast in major

358　programs, including the SOS campaign in the Atlanta, Georgia and Nashville, Tennessee areas in

359　the 1990s (e.g. Meagher et al., 1998). The urban-rural contrasts for O_3 production and

360　atmospheric transport were investigated under the O_3 precursor conditions at that time. The

361　SEARCH urban-rural site pairs are analogous to the 1994-1995 Nashville study, covering similar

362　regional conditions inland, but distinctly different along the Gulf Coast. Thus, the Nashville

363　study, combined with longer-term SOS measurements, yield insight into oxidant chemistry for

364　1990s conditions, with higher O_3 and precursor concentrations than seen since 2000 in the

365　SEARCH region. NO and NO_y have been measured at SEARCH sites since 1992; NO_2 has been

366　measured at some SEARCH sites since 1992 and at all sites since 2002. NMOC was measured at

367　JST through 2008, and is supplemented by the PAMS observations, including from the non-

368　urban site at YRK. The sources of nitrogen oxides are mainly combustion, from transportation,

369　EGUs, and to a lesser extent, industrial, commercial and residential sources. Anthropogenic

370　VOC emissions, including NMOC, deriving from transportation, industrial, and commercial

371　sources, are superimposed as a small fraction on a much larger regional emissions component of

372　natural sources (see Supplement Fig. S2c). In Table 1, linear regression models indicate

373　statistically significant responses of ambient NO_y and NMOC concentrations to decreasing NO_x

374　and (anthropogenic) VOC emissions, respectively, without statistically significant intercepts.

375   The SEARCH regional annual NO_x emissions are shown along with rural annual-average

376   NO_y concentrations in Fig. 6. Reductions in ambient NO_y levels tracked the NO_x emission

377   reductions between 2000 and 2013. The trends in CO emissions for transportation (Supplement

378   Figure S2e) have a similar pattern to NO_x emissions (Fig. S2b in the Supplement). Ambient CO

379   concentrations have decreased at both urban and rural sites in the SEARCH region, with

380   statistically significant linear relationships to CO emissions (Table 1). Blanchard et al (2013b)

381   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   for SO_2 or NO_y. This is supported by the linear model for ambient CO and emissions in Table 1,

384   where the CTR relationship has an intercept of ~ 100 ppbv; 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   superimposed on a large natural component such that the decline in anthropogenic VOC

388   emissions is a small increment of the total. Decreases in rural ambient NMOC are not well

389   documented, but the urban-nonurban contrast is established with the PAMS and Atlanta-JST

390   data. The annual averages of 24-hour average NMOC at JST are shown with Georgia motor

391   vehicle emissions in Figure 7. The decline in urban NMOC is similar to the on-road VOC

392   emissions reduction—as expected from a principal urban source, motor vehicles; NMOC trends

393   and OH reactivity are discussed, for example, in Blanchard et al. (2010a). Evaluation of trends in

394   NMOC at JST indicates that mean concentrations of anthropogenic species decreased between

395   1999 and 2007; however, the average OH reactivity of the NMOCs decreased less, if at all. One

396   of the important contributors to the JST OH reactivity was isoprene, and in summer at the

397   nonurban Yorkville and Conyers sites where it contributed half of the estimated reactivity

398   (Blanchard et al., 2010a). The dominant NMOC in the oxidant cycle at CTR is isoprene.

399   In the absence of long-term NMOC data at CTR, we rely on the PAMS data in the

400   Atlanta area for potential qualitative indications of ambient NMOC characteristics or trends. The

401   contrasting speciated NMOC data in summer from the PAMS sites in Atlanta and the site at

402   YRK indicate the magnitudes of the decreases in species concentrations with distance from the

403   urban area. The YRK concentrations are expected to be similar to those at CTR, with CTR

404   possibly exhibiting still lower anthropogenic species concentrations relative to a nominally

405   similar level of natural NMOC. Trends in the summer PAMS data (Fig. 8) are considered for

406   selected species having measurements that appear robust (few values below detection limits; no

407   obvious extreme outliers). These species include the anthropogenic groups of C_2-C_4 compounds,

408   aromatics as benzene, toluene, ethyl benzene, and xylenes (BTEX), pentanes, and isoprene

409   (representing biogenic species). The concentrations of BTEX have decreased over the years at

410   the Atlanta urban sites but not at the non-urban sites (YRK and Conyers). Mean urban pentane

411   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   "upwind" from Atlanta, while isoprene tends to be larger in concentration away from the city,

414   and slightly increasing by year. The reason for this seasonal increase in isoprene concentration

415   has not been explained, but could be related to changes in biogenic emissions and chemistry in

416   response to decreasing O_3 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 in early

418   summer period).

419   Ozone (with NO_2 and NO_z) can be used as an indicator of the oxidation state of the air.

420   Average 8-hour maximum O_3 concentrations in the SEARCH region have declined along with

421   decreasing emissions of its precursors, NO_x and NMOC (e.g., Fig. 9 and Fig. S2 in the

422   Supplement). Linear regression results for decreasing O_3 concentrations as a function of

423   decreasing NO_x and (anthropogenic) VOC emissions are shown in Table 1. The O_3 decrease is

424   less than a 1:1 proportionality with the precursor emission reductions, as indicated by the

425   presence of intercept terms that are a large fraction of ambient O_3 concentrations. The intercepts

426   of ~29-37 ppbv are similar to background levels projected for the Southeast by Lefohn et al.

427   (2014). The O_3 proportionality with its precursors would not necessarily be expected due to the

428   nonlinear photochemistry involved, but given the substantial reduction in precursor emissions a

429   relatively small change in ozone of about 1%/yr has been observed.

430   Rural NO_z ($NO_y - NO_x$, a photochemical reaction product indicator) concentrations have

431   tended to level out since 2005, as indicated in Figure 6, paralleling O_3 concentrations. The linear

432   NO_z relationship with NO_x emissions is statistically significant (Table 1) with a variance higher

433   than for other gases, and without a statistically significant intercept. Ozone concentrations vary

434   with meteorological conditions, which need to be accounted for in long-term averages. Camalier

435   et al. (2007) have developed a statistical approach (GAM) employing meteorological variables to

436   adjust mean summer O_3 concentrations locally and regionally, which has been adopted by EPA

437 for inspecting O_3 trends (e.g. EPA, 2013). We have extended the GAM method to use air quality

438 variables as well to improve the model for O_3 concentrations in the SEARCH region (Blanchard

439 et al., 2014a). Evidence from JST compared with YRK indicates that Atlanta has frequent

440 periods of NMOC-sensitive O_3 formation, but the regional O_3 formation continues to be NO_x-

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_x and NMOC sensitive]).

444   Evidence for O_3 as an oxidant indicator derives from comparing diurnal O_3

445 concentrations with OH and HO_2 data. For example, at a suburban site 8 km NE of downtown

446 Nashville, OH and HO_2 observations tracked the diurnal buildup and decline of O_3 (Martinez et

447 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 roughly proportional to O_3 concentrations during the day (e.g., Supplement Fig. S4). If this

450 urban-suburban pattern applies to rural conditions in the Southeast, one could expect to see a

451 decline in daytime OH concentrations between 2000 and 2013. This assumption is tempered by

452 recent evidence for the regeneration of OH from isoprene reactions yielding an excess of OH

453 from chemical model calculations (e.g. Fuchs et al., 2013). The morning rise in O_3

454 concentrations at the ground also corroborates the potential importance of air mass transport with

455 down-mixing of O_3 from a residual (upper boundary) layer during the break-up of the nocturnal

456 inversion layer 2-3 hours after sunrise (Baumann et al., 2000). As a part of the analysis of the

457 SOAS data, a close look at relationships between OH, HO_2, O_3 and VOCs would be of interest

458 not only for SOC formation, but also for distinguishing rural from urban O_3 photochemistry.

459

460 **2.3.3. Aerosol Particles**

461

462 Suspended particles and their origins are a key element of the SOAS experiments. The SO_4

463 component was discussed above with SO_2. Trends in regional and CTR particle mass

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

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

466 carbon). Sulfate has decreased in fine particles relative to EC and OC; NH_4 has not decreased as

467 much, and $p$$NO_3$ decreased, even though increases in $p$$NO_3$ concentrations potentially could

468   have occurred as declining SO_4 made an increasing fraction of NH_3 available for reaction with

469   HNO_3 (Blanchard et al., 2007). The major metal oxides (MMO) represent a small fraction of

470   fine particle mass. Retained water (associated with species such as SO_4, and represented as one

471   of the unmeasured components within "other") is relatively large. As shown above in Fig. 3,

472   SO_4, EC, and OC display somewhat different seasonal variations. Regional OC is identified with

473   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   concentrations especially in the rural Southeast. Various methods have been used to separate

476   secondary (SOC) from primary (POC) (e.g., OC/EC ratio method, Lim and Turpin, 2002, Saylor

477   et al., 2006; organic tracer-chemical mass balance, Zheng et al. 2002a, b; Ding et al., 2008;

478   regression, carbon mass balance, Blanchard et al., 2008; Blanchard et al., 2011; chemical

479   composition particle and gases, Pachon et al., 2010; semi-empirical-air quality models, Yu et al.,

480   2007). While these methods provide insight into the two components of OC, they do not yield a

481   consistent quantitative picture of the fractions of each. The mean fraction of SOC estimated by

482   different methods varies from ~20% to >50% depending on the time of year data were obtained,

483   and the method used.

484   The trends in rural annual average EC concentrations compared with EC emissions are

485   shown in Fig. 10. At the rural SEARCH sites, ambient EC decreases over the decade from 2000,

486   and tracks the EC emission decline occurring between 2005 and 2013. EC concentrations

487   declined approximately coinciding with declining mobile source emissions (Fig. S6 in the

488   Supplement). Mean OC concentrations followed similar trends as mean EC at both urban and

489   rural SEARCH sites on an annual basis (Supplement Fig. S7). These and other results indicate

490   that POC is a major part of average OC concentrations (e.g., Blanchard et al., 2008; Zheng et al.,

491   2002a,b; Blanchard et al., 2013c, 2014b).

492   Linear regression models for relating decreases in rural EC and OC concentrations to

493   decreasing emissions are shown in Table 1. Included are relationships between ambient

494   concentrations with total EC and OC emissions and with mobile-source EC and OC emissions.

495   The slopes for total and mobile EC are significant, but the intercepts are not. The slope and

496   intercept for ambient OC versus mobile source OC emissions are each significant, but neither the

497   slope nor the intercept for regressions of rural ambient OC versus total OC emissions is

498   significant. Mobile OC comprises less than 10% of the total POC emissions in the region

499 (Blanchard et al., 2013c), but SOC derived from mobile VOC emissions could augment the

500 mobile POC contributions; OC derived from a combination of motor-vehicle emissions of POC

501 and of low-volatility VOC potentially represents a large enough fraction for the changes in

502 mobile-source emissions to be detectable at CTR.

503 Birmingham EC and OC regression models are included in Table 1 for comparison with

504 the rural case. This urban case is dominated by motor vehicle and industrial carbon emissions.

505 The models for EC and OC vs. annual regional total carbon emissions and motor vehicle

506 emissions show a much stronger annual rate of decline than the rural cases do, without

507 statistically significant intercepts. Regression models (not shown) for EC and OC in Atlanta

508 (JST) are similar to those found for BHM. The linkages between motor-vehicle OC emissions

509 and ambient OC are more evident at BHM and JST than at CTR because the higher motor

510 vehicle emission density within the urban areas results in a stronger signal that is more readily

511 observed within the variability associated with meteorology and with year-to-year variations in

512 biomass burning on small spatial scales (e.g., ~10 - 100 km).

513 From source apportionment, wildfires and prescribed burns are a major factor in OC and

514 EC concentrations in the SEARCH region, including at CTR (e.g. Blanchard et al. 2013c). The

515 post-2005 NEIs indicate that the major contributors to EC and POC derive from vehicle

516 transportation emissions and biomass burning (Supplement Fig. S2g and h; Blanchard et al.,

517 2013c). Over the period from 2002-2013, annual wildfires and prescribed burning are shown in

518 Figure S8. There is substantial variability in fires reported yearly and between states (e.g.,

519 Larkin et al., 2013). The prescribed burns in each of the states in the SEARCH regime are much

520 more frequent than the wildfires over this period. EPA (2014b) has tabulated major seasonal

521 differences by state in occurrence of fires for use in the preparation of the NEI. According to

522 EPA, the Georgia fire season is in late winter (Jan-Mar) while the Alabama season is apparently

523 later, mainly in May- June; the information on which these temporal profiles were based is not

524 documented. The implications of the temporal differences are unclear for prescribed-burn EC

525 and POC contributions relative to annual or seasonal ambient averages.

526 The SEARCH data have also given insight into the urban-rural contrasts in ambient EC

527 and OC. For example, carbon isotope analysis has indicated that most of the total carbon--TC

528 (OC + EC) at CTR is modern carbon compared with nearby Birmingham, which has a major

529 fraction of fossil carbon (e.g., Blanchard et al., 2008). The modern carbon fraction can be

530   derived from primary emissions of smoke from fires, cooking, or from detritus and/or secondary

531   atmospheric reactions of VOC. The secondary component of modern carbon comes from a host

532   of potential biogenic reactions. The urban-rural contrasts between BHM and CTR indicate a

533   large fraction of SO_4 and OC has a regional character, with SO_4 having a small increment and

534   OC a larger increment associated with the urban emissions (Blanchard et al., 2013a).

535   Urban and rural contrasts are readily seen in Table 2, illustrating differences for the urban

536   and rural pairs, and between inland and coastal sites. Strong urban-rural differences are found in

537   the inland pair, CTR-BHM, for particles and gases. Interestingly, mean O_3 concentrations are

538   higher at CTR than BHM. The urban-rural contrast is weaker for the coastal pair, OAK and

539   Gulfport, Mississippi (GLF). The secondary species tend to have weaker urban-rural gradients

540   than the primary species. The data suggest the regional character for SO_4 (also NH_4) and O_3,

541   while other species have lower mean concentrations along the coast than inland. The conditions

542   along the Gulf Coast show lower concentrations, consistent with smaller cities, fewer major

543   point sources along the coast than further inland, and mesoscale meteorological effects

544   associated with marine conditions. Seasonal similarities and differences are shown in Table S4.

545

546   **2.3.4. Aerosol Light Extinction**

547

548   Ground level estimates of light extinction have been made at the SEARCH sites between 1999

549   and present. Extinction apportionment gives additional insight into the role of chemical

550   components including retained water. Extinction has tended to decrease over the 2000-2013

551   period, as expected from the decline in fine particle concentrations. A time series of observations

552   for b_{ext} at CTR is shown in Supplement Fig. S9, including the dry light scattering component and

553   the absorption component. The bulk of the extinction is from light scattering. Figure 11 shows a

554   trend in combined fine and coarse particle (PM_{10}) contributions to light extinction coefficient

555   using a weighting relationship with particle composition, including Rayleigh scattering and also

556   water through a hygroscopicity relationship with RH (Pitchford et al., 2007). On a dry basis,

557   major contributors to "dry" extinction coefficient include SO_4 and organic matter (OM as 1.8

558   OC) at the SEARCH sites, including CTR. Water content, shown separately in Fig. 11, based on

559   hygroscopicity of SO_4 and NO_3, is a major component of extinction at the average RH seen

560   annually in CTR. Hygroscopicity of OM is not included; the inorganic component accounts for

561   most of the water retention. This result is consistent with findings from other studies, including

562   those in the Shenandoah, Virginia region of the Southeast (e.g., Malm et al., 2000) and in the

563   Great Smoky Mountains (Lowenthal et al., 2009), and also with laboratory studies (e.g., Brooks,

564   et al., 2004). The black carbon component (light absorbing carbon or LAC) represents a

565   relatively minor portion of the extinction coefficient annually, while the contribution of OM is

566   larger than ammonium sulfate. For comparison, the contributions to the extinction coefficient

567   based on chemical constituents without separation of water from SO_4 and NO_3 is given in

568   Supplement Fig. S10.

569

570   3. **Representativeness of 2013**

571

572   The previous section provides a long-term context of air quality changes in the SEARCH

573   domain.   For the representativeness of the 2013 summer experiments, we turn to the long-term

574   ambient data associated with the period of June 1 to July 15. The discussion includes

575   consideration of the representativeness of meteorological conditions as well as the ambient

576   chemistry at CTR.

577

578   **3.1. Diurnal Emission Characteristics**

579

580   The annual emission trends derived from the NEIs provide no information about short- term

581   emission patterns. Two major contributors to regional, diurnal emissions relevant to the SOAS

582   experiments are SO_2 and NO_x from EGUs, and NO_x and NMOC from transportation. Natural

583   emissions for isoprene and terpenes are also of interest. The June-July diurnal EGU SO_2 and NO_x

584   emissions for Georgia, Alabama, and Mississippi are shown in Supplement Fig. S11. A national

585   average transportation emission pattern applied to NO_x and NMOCs is shown in Supplement

586   Figure S12 for comparison with the EGU pattern. The EGU emissions of SO_2 and NO_x show a

587   "common" increase in daytime emissions, rising about 0600 h through the daytime followed by a

588   decrease in evening after 1800 h (with stated exceptions, all data are given in local standard time

589   [LST]). The annual trends in reduction in emissions across the states are consistent with the

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

591   vehicle emissions (NO_x and NMOC) show an increase around 0600 h with morning urban

592 commutes, with steady levels thereafter with a rise in traffic, followed by a decrease around

593 1700. As indicated in the figure, there is a weekday-weekend difference in emission timing.

594 Natural VOC emissions of isoprene are influenced by rising and declining temperature

595 and solar radiation, with a rise at ~0600 h in summer, modulated by O_3 concentrations (e.g.

596 Sharkey et al., 2008). Terpene emissions are mainly temperature dependent and tend to rise at

597 0600 h, before decreasing somewhat during midday and increasing again in the evening

598 (Supplement Fig. S19; e.g., Guenther et al.,1993). NO_x emissions from soil emanations vary

599 with temperature and soil moisture, with less-known average diurnal character; lightning-derived

600 NO_x production is obviously intermittent depending on stormy conditions.

601

602 **3.2. Meteorological Conditions**

603

604 Surface meteorological conditions are described in terms of box plots of the CTR data,

605 directional pollution roses and diurnal plots of parameter variation. Box plots of wind speed,

606 temperature, relative humidity and solar radiation are shown in Supplement Fig. S13 for 1 June

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

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

609 years. Comparison of the box plots by year indicates that the period in 2013 was moist and cool

610 relative to previous years, with slightly less solar radiation compared with earlier years.

611 Meteorological conditions favorable to regional pollution episodes around CTR in current years

612 are analogous to those found in the SOS Nashville experiment (McNider et al., 2002; Banta et

613 al., 2002) and identified for the SEARCH region (Blanchard et al., 2013a).

614 Conditions for elevated pollution involve large-scale, multiday periods of light winds,

615 high SR and high RH, with limited nocturnal vertical mixing in a temperature inversion in the

616 lower boundary layer. In the morning the inversion tends to break up, permitting increased

617 vertical mixing with pollution aloft reaching the ground. This is followed in the evening by re-

618 formation of the inversion layer suppressing mixing. Occasional winds aloft, in the boundary

619 layer, develop around the high pressure regime creating conditions for dispersion of pollution

620 across the region, accompanied by decreases in ground level concentrations and concentrations

621 aloft. The diurnal changes in summer EGU and transportation emissions, as well as natural VOC

622 emissions tend to parallel changes associated with vertical mixing and changes in inversion

20

623   conditions, providing increased daytime reactants. The morning increases tend to "fuel" the

624   photochemistry of oxidants and SOC formation even with daytime dilution, while reducing

625   nocturnal chemical reaction rates.

626

627   **3.3. Chemical Characterization**

628

629   Box plots of trace gas and particle composition in Supplement Figs. S14 and S15 indicate the

630   downward trend in pollutants at CTR in June-July, consistent with the trends in annual averages

631   and emissions in the region discussed above. In some years the range of concentrations is large

632   relative to the mean, but in recent years the range, based on the 25th and 75th percentiles,

633   appears to have decreased along with the mean values.

634   Pollution-wind direction roses for the 1 June – 15 July 2013 period are indicated in

635   Fig.13. Wind speed and frequency are also shown, indicating that northerly winds were rare in

636   2013; instead westerly winds occurred more frequently with higher wind speeds than usual. The

637   pollution roses suggest that SO_2 has some directionality that varies from year to year during the

638   early summer, with a distinct source influencing the site from the southwest during this period.

639   NO_y, CO, and EC show less directionality but broad enhancements in northern sectors, pointing

640   to urban (traffic) influence from Birmingham and Tuscaloosa. O_3, $PM_{2.5}$, SO_4, NH_4, and OC

641   show more regional character, indicated by near-symmetrical concentration distributions with

642   direction. The OC/EC ratio has a distinct directional relationship. Although elevated EC derives

643   mainly from the BHM and Tuscaloosa (northern) directions, OC/EC ratios show larger values

644   from the west and south in association with low EC, while OC/EC ratios are lower from the

645   north and east. These differences suggest that urban sources influence CTR from the northern

646   and eastern sectors, but non-urban sources (including biomass burning and secondary material)

647   are strongest from the southwest.

648   The time series and pollution roses indicate that the SOAS experiment observations

649   include a range of conditions in which pollutants were seen at CTR in varying amounts and from

650   potentially different wind directions. Examples during SOAS include an urban plume (June 4th,

651   just before a biomass burn); power plant plume (26 June from the SW); open burning (June 4th)

652   and a dust intrusion from air transported over the Atlantic Ocean (9 June or 23 June).

653 Examination of the air chemistry during these events compared with "non-event" days could

654 provide key indicators of SOC formation in different polluted air conditions.

655   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 plume high in SO_2 emissions being mixed to the ground. The nature of this occurrence causes the

659 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_y 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_y, as well as its morning

664 amplitude, decreased over the years, reaching a minimum in 2013. Ozone shows the well-known

665 concentration variation with a sharp increase in the morning followed by a midday peak in

666 response to combined precursor concentration increases and down-mixing from the residual

667 layer during morning break-up of the inversion layer (e.g., Zhang and Rao, 1999). If OH and

668 HO_2 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_3 maxima decrease at CTR over the years. Unlike a purely local development, the midday peak

671 shows an extended decrease in ozone concentration into the late evening hours. The principal

672 component of NO_y is NO_2 (e.g., Supplement Figure S16). NO_z follows a post-NO_2 diurnal

673 pattern with a daytime elevation and a maximum just before 0900 h (local time, LT). The

674 average NO_y levels at CTR are low, $<\sim 1$ ppbv, with higher concentrations peaking at ~2 ppbv in

675 the morning; the origins of these concentration levels may be local emissions of anthropogenic

676 (most likely mobile) sources and naturally from soil exhalations that accumulate in a shrinking

677 nocturnal inversion layer. A nitrogen oxide mass balance is shown Figure S16. The composite

678 diurnal composition indicates that NO_y is dominated at night mainly by NO_2, with NO_z (sum of

679 pNO_3, HNO_3, alkyl nitrates [AN] and peroxalkylnitrates [PN]) prevailing during the day,

680 wherein pNO_3 contributes very little. The measurements indicated in the NO_y mass balance

681 nearly reach mass closure with only a minor fraction unidentified.

682   In contrast to SO_2 concentrations, which peak in the morning and evening at CTR, sulfate

683 shows a weak midday to afternoon-evening enhancement (Fig. 15), with declining overall

22

684 concentrations since 2000. The reactive species concentrations display a character consistent

685 with recent lower hourly reaction rates associated with lower SO_2 and OH concentrations

686 compared with earlier years. The diurnal EC and OC concentrations over the years have settled

687 into low levels slightly enhanced around 0900 h -- corresponding to a time similar to NO_y, thus

688 possibly associated with the same sources such as a local traffic increase. The weak diurnal OC

689 concentration pattern does not indicate a strong daylight driven component with rapid rise in

690 oxidant concentrations, but does not rule out the potential for SOC formation at night, as well as

691 during the day. Periods prior to 2013 show an apparent spiky character of EC concentrations,

692 possibly identified with local yard waste or trash burning, and less associate with the previously-

693 discussed regional biomass burning (e.g. prescribed fires for forest management). Prescribed

694 burning is a ubiquitous, widespread source for OC and EC with OC/EC emission ratios of 14 or

695 larger (Lee et al., 2005) in the forests of the Southeast, including Alabama. In 2013, the

696 Alabama Forestry Commission issued 14,137 burn permits for over one million acres, the largest

697 total burn area since 2010 (B. Elliott, personal communication, 2014). Prescribed burning is

698 regulated differently by state, making the NEI estimates of emissions for this source highly

699 uncertain. Satellite observations are used to locate burns, but they do not reliably identify small

700 burn areas below dense forest canopies.

701 The importance of aerosol water content in SOC reaction chemistry is hypothesized in

702 Shen et al. (2013) and Carlton and Turpin (2013). A sample diurnal pattern of liquid water

703 suggested in the difference between dry particle light scattering and ambient particle scattering is

704 seen in Figure S17. A maximum water uptake is at night with the highest RH, while the aerosol

705 tends to lose water systematically with equilibration to lower midday RH. While ample water is

706 present in the aerosol particles during the day, they are much wetter on average at night. The

707 retained water in particles provides for an opportunity for both gas and aqueous phase oxidation

708 reactions of NMOC to take place in the CTR environment. OC does not increase with drying out

709 of the aerosol at morning to midday, which would indicate release of SOC from nocturnal

710 reaction products.

711 Diurnal variations in NMOC concentrations are important for characterizing a portion of

712 the potential for SOC production at CTR. While NMOC data were not obtained at CTR as part of

713 the basic SEARCH observations, a long-term record of summer concentrations found at YRK

714 can be compared qualitatively with results taken at a rural sites in the Southeast (Supplement

715   Table S5) at locations relevant to SOS, including CTR (e.g., SOS studies of Goldan et al., 1995;

716   Hagerman et al., 1997; Riemer et al., 1998). The data cited in Table S5 indicate the importance

717   of isoprene as a reactive species in the southeastern rural environment. The data suggest a varied

718   but persistent regional presence of anthropogenic NMOC. In each of the locations, anthropogenic

719   NMOC is mixed with the natural NMOC. These data suggest that the production of SOC in the

720   rural sites may be dominated by natural NMOC, but the formation chemistry is complicated by

721   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   inversion breakup, followed by vertical mixing and chemical loss during the day. The four

728   groups vary in terms of reactivity, but show similar morning to midday change; the change is

729   likely to be mainly dilution during the day. BTEX and pentanes concentration have decreased

730   over the years shown, while C_2-C_4 hydrocarbons seem less consistent in annual change. Isoprene

731   has a distinctly different diurnal pattern, with a modest morning increase in concentration

732   followed by depletion, then a strong peak in the late afternoon-evening. Hypothetically, annual

733   diurnal change in isoprene concentrations appears to reflect variations in June-July

734   meteorological influence combined with oxidation chemistry rather than a systematic trendover

735   the years. Comparison of the diurnal change in isoprene concentration with OC diurnal change

736   (Fig. 15) suggests no direct or parallel link between midday OC associated with SOC production.

737   Data taken at a rural mixed deciduous and evergreen forest site in western Alabama (Kinterbish

738   State Park) could be similar to CTR for biogenic NMOC concentrations. A comparison between

739   isoprene concentrations at YRK and 1990 concentrations at Kinterbish (Goldan et al., 1995) is

740   shown in Supplement Fig. S19, along with Kinterbish α-pinene concentrations. The Kinterbish

741   pattern is similar at night and morning through midday, but displays a weaker afternoon-evening

742   peak compared with YRK. The α-pinene pattern shows a morning peak, followed by decrease

743   from oxidation and dilution, but is much lower in concentration than isoprene. Interpretation of

744   this diurnal pattern could add perspective on oxidation chemistry and SOC formation.

745

746 **4. Summary**

747

748 Inspection of long-term data in the SEARCH region and specifically at CTR indicates that the

749 experiments of summer 2013 generally represent aerometric conditions within the range of those

750 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 that was marginally wetter and cooler, with lower solar radiation, than in most previous years.

753 Chemically, air quality at CTR in 2013 exhibited a mix of natural and anthropogenic influences,

754 but the magnitude of the anthropogenic component was significantly lower than during the

755 earlier years of the last decade or more. The decline in ambient concentrations of gases and

756 particles is not anomalous, since emission reductions after 1999, extending beyond 2010-2011

757 through 2013 reflect regulatory actions intended to lower emissions permanently. The

758 implications of observed changes are uncertain as to whether the ambient response to emission

759 reductions results in slowing reaction rates due to reduced reactant concentrations, or in changes

760 in the relative importance of the hundreds of photochemical reactions involved. This aspect of

761 the change in the southeastern air chemistry needs to be investigated in detail, and SOAS will

762 assist in achieving this understanding. The current conditions are likely to foretell the future

763 conditions, which perhaps will increasingly return to a quasi-natural state as anthropogenic

764 emissions continue to decline.

765 　　　　The 1 June - 15 July period of 2013 displayed a range of pollution concentrations ranging

766 from clean air to conditions of substantial intrusion of pollution over the region with evident

767 plumes from urban or point sources. Tracking trends of trace gases indicates important

768 reductions in ambient concentrations since 2000, resulting from regional reductions of CO, SO_2,

769 NO_x, and NMOC emissions as indicated by statistically significant regressions of ambient

770 concentrations against emissions. The emission reductions also reduced extreme ground-level O_3

771 concentrations, but not at the rate seen in precursor reductions. Fine particle concentrations have

772 declined since 2000, with declines in concentrations of SO_4 and both EC and OC. There is

773 enough NH_3 in the air to effectively neutralize the average acidity of rural SO_4 and pNO_3, but the

774 summer tends to contain less NH_4 neutralized SO_4 than winter. Average acidic SO_4 has remained

775 approximately the same since 2000; stoichiometrically, SO_4 is present as an ammonium salt, and

776 is approximately neutralized as letovicite or bisulfate in summer. Water-soluble (inorganic)

777   sulfur as sulfate appears to account for almost all (>~95%) the total S in particles. Gas and

778   particle concentrations tend to be lower along the Gulf Coast compared with inland. There are

779   also urban-rural differences in air quality, with stronger gradients associated with primary

780   pollutants in contrast to secondary species, although weaker secondary species gradients do exist.

781   Evidence from the long-term record and source apportionment suggests that much of the

782   OC is modern in origin at CTR, but OC in total derives in part from primary sources, including

783   biomass burning and vehicle transportation. This result needs to be accounted for in

784   apportionment of the SOC fraction. Evidence from Zheng et al. (2002a, b) and Blanchard et al.

785   (2008), for example, suggests that the majority of the regional annual or seasonal average OC

786   can be accounted for from primary sources.

787   A major focus of the SOAS experiments was to evaluate the mechanisms for SOC

788   enhancement through interaction of biogenic emissions with anthropogenic pollution. While it is

789   clear that various SOC formation mechanisms are active (as measured with the chemical tracers),

790   the magnitude of the OC enhancement and when it occurs are in question. SEARCH data

791   coupled with trends in anthropogenic emissions provide the ability to test various hypotheses

792   over an extended time period. The detailed chemical species measurements from the SOAS

793   experiments, combined with the constraints of the long-term SEARCH observations, provide an

794   important framework to add a perspective on how, when and where SOC occurs in the

795   southeastern US.

796

797   **Supplementary material related to this article is available online at: doi:10.5194/acpd-14-1-**

798   **2014-supplement.**

799

803

804

805

References

Atmospheric Research and Analysis (ARA): Home, Public Data Archive, available at http//www.atmospheric-research.com/studies/SEARCH/index.html (last access: 12 August 2014), 2014

Banta, R., Senff, C. Nielsen-Gammon, J., Darby, L., Ryerson, T., White, A., Trainer, M., McNider, R., Valente, J., Mayer, S., Alvarez, R., Hardesty, M. Parrish, D., and Fehsenfeld, F.: 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., Spingston, S., Bertman, S. and Hartsell, B.: Ozone production and transport near Nashville, Tennessee: results from 1994 study at New Hendersonville, J. Geophys. Res.-Atmos., 105, 9137-9153, 2000.

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.

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, Atmos. Environ., 42, 6710-6720, 2008.

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.

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.

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.

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.

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
850   concentrations in the Southeastern Aerosol Research and Characterization (SEARCH), Environ.
851   Sci. Technol., 47, 13,536-13,545,dx.doi.org/10.1021/es402876s, 2013c.

852

853   Blanchard, C. L.,Tanenbaum, S., and Hidy, G.M. : Ozone in the southeastern United States: an
854   observation-based model using measurements from the Southeastern Aerosol Research and
855   Characterization (SEARCH) network, Atmos. Environ., 48, 192-200,
856   dx.doi.org:10.1016/j.atmos.env.2014.02.006, 2014a.

857

858   Blanchard, C. L., Chow, J., Edgerton, E., Watson, J.G., Hidy, G. M., and Shaw, S.: Organic
859   aerosols in the southeastern United States: speciated particulate carbon measurements from the
860   SEARCH network, 2006-2010, Atmos. Environ.95, 327-333,
861   dx.doi.org/10.1016/j.atmosenv.2014.06.050 , 2014b.

862

863   Brooks, S., deMott, P., and Kreidenweis, S.: Water uptake by particles containing humic
864   materials and mixtures of humic materials with ammonium sulfate, Atmos. Environ., 38, 1859-
865   1868, 2004.

866   Budisulistiorini, S., Canagarratna, M., Croteau, P., Marth, W., Baumann, K., Edgerton, E., Shaw,
867   S., Knipping, E., Worsnop, D., Jayne, J., Gold, A., and Surratt, J., Turpin, B., Guenther, A.,
868   Cohen, R., Shepson, P., Shaw, S., Wiedimyer, G., Surratt, J., Wennberg, P., and Pierce, J.: Real-
869   time continuous characterization of secondary organic aerosol deriving from isoprene epoxydiols
870   in downtown Atlanta, Georgia, using the Aerodyne aerosol chemical speciation monitor,
871   Environ. Sci. Technol., 47, 5686-5694, 2013.

872

873   Camalier, L., Cox, W., and Dolwick, P.: The effects of meteorology and their use in assessing
874   ozone trends. Atmos. Environ., 41, 7127-7137, 2007.

875   Carlton A. , and Turpin, B.: Particle partitioning potential of organic compounds is highest in the
876   Eastern US and driven by anthropogenic water. Atmos. Chem. Phys., 13, 10,203-10,2142 , 2013.

877

878   Carlton, A., Goldstein, A., Jiminez, J., Pinde, R., deGouw, J., Turpin, B., Guenther, A., Cohen,
879   R., Shepson, P., Shaw, S., Wiedimeyer, C., Surratt, J., Wennberg, P., and Pierce, J.: The
880   Southern Oxidant and Aerosol Study (design rationale),
881   http://climate.env.sci.rutgers.edu/SOAS_SOAS_White_Paper_final.pdf (last access 15 Jan.
882   2014), 2013.

883

884   Chameides,W., Lindsay, R., Richardson, J., and Kiang, C. : The role of biogenic hydrocarbons
885   in urban photochemical smog: Atlanta as a case study, Science , 24, 1473-1475, 1988.

886

887   Chameides, W., and Cowling, E. : The State of the Southern Oxidant Study: Policy Relevant
888   Findings in O_3 Pollution Research, 1988-1994, Rep. Southern Oxidant Study, North Carolina
889   State University, Raleigh, N.C., 1995.

890

891   Ding, X., Zheng, N.M. Edgerton, E. Jansen, J., and Wang, X.: Contemporary or fossil origin:
892   split of estimated seconary organic carbon in the southeastern United States, Environ. Sci.
893   Technol.,42, 9122-9128, 2008.

894
895 Edgerton, E., Hartsell, B., Saylor, R., Jansen and, J., Hansen, D.A., and Hidy, G.: The
896 Southeastern Aerosol Research and Characterization Study: Part 2-filter based measurements of
897 $PM_{2.5}$ and PM $_{coarse}$ mass and composition, J. Air Waste Manage. Assoc., 55, 1427-1442, 2005.
898
899 Edgerton, E., Hartsell, B., Saylor, R., Jansen, J., Hansen, D.A., and Hidy, G.: The Southeastern
900 Aerosol Research and Characterization Study: Part 3- Continuous measurements of $PM_{2.5}$ mass
901 and composition, J. Air Waste Manage. Assoc., 56, 1325-1341, 2006.
902
903 Edgerton, E., Saylor, R., Hartsell, B., Jansen, J., and Hansen, D.A.: Ammonia and ammonium
904 measurements from the Southeastern U.S. 2007, Atmos. Environ. ,4, 3339-3351, 2007.
905
906 Electric Power Research Institute (EPRI): The Southeastern Aerosol Research and
907 Characterization (SEARCH) Network, Report 1023331, EPRI, Palo Alto, CA, 2013.
908
909 Environmental Protection Agency (EPA): Nonmethane Organic Compound (NMOC) and
910 Speciated Non Methane Organic Compound (SNMOC) Monitoring Program, EPA-454/R-99-
911 053, EPA, Research Triangle Park , NC, available at:
912 http://www.epa.gov/ttn/amtic/filges/ambient/criteria/reldocs/r-99-053.pdf (last access: 4
913 December 2013), 1999.
914
915 Environmental Protection Agency (EPA): Trends in Ozone Adjusted for Weather Conditions.
916 http://www.epa.gov/airtrends/weather.html, last access: 10 Sept. 2013.
917
918 Environmental Protection Agency (EPA): http://blog.epa.gov/science/tag/southern-atmosphere-
919 study-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 Frost, G., Trainer, M., Allwine, G., Bhr, M., Calvert, J., Cantrell, C., Fehsenfeld, F., Goldan, P.,
925 Herwehe, J., Hubler, G., Kustler, W., Martin, R., McMillen, R., Montzka, S., Norton, R., Parrish,
926 D., Ridley, B., Shetter, R., Walega, J., Watkins, B., Westberg, H., and Williams, E. :
927 Photochemical ozone production in the rural southeastern United States during the 1990 Rural
928 Oxidants in Southern Environments (ROSE) program, J. Geophys. Res.-Atmos.,103, 22,491-
929 22,508, 1998.
930
931 Froyd, K., Murphy, S., Murphy, D., deGouw, J., Eddinger, M., and Wennburg, P.: Contribution
932 of isoprene-derived organosulfates to free tropopsheric aerosol mass, Proc. Natl. Acad. Sci.
933 U.S., 107, 21,360-21,365, 2010.
934
935 Fuchs, H., Hofzumahaus, A., Rohrer, F., Bohn, B., Brauers, T., Dorn, H., Haseler, R., Holland,
936 F., Kaminski, M., Li, X., Lu, K., Nehr, S. Tilmann, R., Wegener, R., and Wahner, A.:
937 Experimental evidence for efficient hydroxyl radical regeneration in isoprene oxidation, Nature
938 Geoscience., 6,1023-1025, 2013 .

939

940 Gao, S., Surratt, J., Knipping, E., Edgerton, E., Shahgholi, A., and Seinfeld, J.: Characterization
941 of polar organic components in fine aerosols in the Southeastern United States: Identity, origin
942 and evolution, J. Geophys. Res.-Atmos. ,111, D14314, 2006.

943

944 Goldan, P., Kuster, W., Fehsenfeld, F., and Montzka, S.: Hydrocarbon measurements in the
945 southeastern United States: The rural oxidants in the southern environment (ROSE) program
946 1990, J. Geophys. Res.-Atmos., 100, 25,945-25,963, 1995.

947

948 Goldan, P., Parrish, D., Kuster, W., Trainer, M., McKeen, S., Holloway, J., Jobson, B., Sueper,
949 F., and Fehsenfeld, F.: Airborne measurments of isoprene, CO and anthropogenic hydrocarbon
950 and their implications, J. Geophys. Res.-Atmos., 105, 9091-9105, 2000.

951

952 Grosjean, D., and Friedlander, S.: Formation of Organic Aerosols from Cyclic Olefins and
953 Diolefins, in: The Character and Origins of Smog Aerosols, edited by Hidy, G. M., Mueller,
954 P.K., Grosjean, D., Appel, B. , and Wesolowski, J., Wiley Interscience, NY,434-476, 1980.

955

956 Guenther, A., Zimmerman, P., Harley, P., Manson, R., and Fall, R.: Isoprene and monoterpene
957 emision rate variability: Model evaluations and sensitivity analyses, J. Geophys. Res.-Atmos.,
958 98, 12,609-12,617, 1993.

959

960 Hagerman, L., Aneja, V., and Lonneman, W.: Characterization of non-methane hydrocarbons in
961 the rural southeast United States. 1997, Atmos. Environ., 31, 4017-4038, 1997.

962

963 Haines, T.K., Busby, R., and Cleaves, D.: Prescribed burning in the South: Trends, purpose and
964 barriers, So. J. Appl. Forestry, 25, 149-153, 2007.

965

966 Hallquist, M., Wenger, J., Baltensberger, U., Rudich, Y., Simpson, D. Claeys, M., Dommen, J.,
967 Donahue, N., George, C., Goldstein, A., Hamilton, J., Herrmann, H., Hoffmann, T., Iinuma, Y.,
968 Jang, M., Jenkin, M., Jimenez, J., Kiendler-Scharr, A., Maenhaut, J., Szmigielski, R., and Wildt,
969 J.: The formation, properties and impact of secondary organic aerosol: current and emerging
970 issues, Atmos. Chem. Phys., 9, 5155-5236, doi:10.5194/acp-9-5155-2009,2009.

971

972 Hansen, D.A., Edgerton, E., Hartsell, B., Jansen, J., Hidy, G., Kandaswamy, K., and Blanchard,
973 C.: The Southeastern Aerosol Research and Characterization study (SEARCH): 1. Overview, J.
974 Air Waste Manage. Assoc., 53,1460-1471, 2003.

975

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

980 Hatch, L., Creaman, J., Ault, A., Surratt, J., Chan, J., Seinfeld, J., Edgerton, E., Su, Y., and
981 Prather, K. : Measurments of isoprene-derived organosulfates in ambient aerosols by aerosol
982 time of flight mass spectrometery Part 1: Single particle atmospheric observaions in Atlanta,
983 Environ. Sci. Technol., 45, 5105-5111, 2011.

984

985   Hidy, G. M.: Atmospheric Sulfur and Nitrogen Oxides: Eastern North American Source-
986   Receptor Relationships, Academic Press, San Diego, CA, 1994.

987   Hidy, G. M.: Ozone process insights from field expeiments. Part 1. Overview, Atmos. Environ.,
988   34, 2001-2022, 2000.
989
990   Hidy, G. M.: Worldwide aerosol chemistry: from hemispheric distributions to megacity sources,
991   J. Air Waste Manage. Assoc., 59, 770-789, 2009.
992
993   Hidy, G. M., and Blanchard, C. L.: The North American background aerosol and global aerosol
994   variation, J. Air Waste Manage. Assoc., 55, 1585-1599, 2005.
995
996   Hoffman, M., Waldman, J., Munger, J., and Jacob, D.: 1986. The chemistry and physics of acid
997   fog, clouds and haze aerosol, in: Aerosols: Research, Risk Assessment and Control Strategies,
998   edited by Lee, S., Schneider, T., Grant, L. and Verkerk , J., Lewis Publishers, Inc., Ann Arbor,
999   MI, 121-150, 1986.
1000
1001   Hunt, S.: Southern Atmosphere Study (SAS): Research Partnership Advancing the Science of
1002   Organic Aerosols, Air, Climate and Energy Research Program, U. S. Environmental Protection
1003   Agency, Research Triangle Park, N.C., 2013.
1004
1005   Ingram, K., Dow, K., Carter, L., and Anderson, J., eds.: Climate in the Southeastern United
1006   States: Variability, Change, Impacts and Vulnerability, Island Press, Washington, DC, 2013.
1007
1008   Irving, P.,ed.: Acidic Deposition: State of Science and Technology.1. Emissions, Atmospheric
1009   Processes and Deposition, National Acid Precipitation Program, Washington, DC,1991.
1010
1011   Kleindienst, J., Lowandowski, M., Offenberg, J., Edney, E., Jaoui, M., Zheng, M., Ding, X., and
1012   Edgerton, E.: Contribution of primary and secondary sources to organic aerosols at SEARCH
1013   network sites, J. Air Waste Manage. Assoc., 60, 1388-1399, 2010.
1014
1015   Larkin, N., Raffuse, S., and Strand, T.: Wildfire emissions, carbon, and climate: U.S. emissions
1016   inventories, Forest Ecol. and Manage., 317, 61-69, dx.doi.org/10/1016/j. foreco. 2013.09.012,
1017   2013.
1018
1019   Lee, S., Baumann, K., Schauer, J., Sheesley, R., Naeher, L. Meinardi, S., Blake, D., Edgerton,
1020   E., Russell, A., and Clements, M.: Gaseous and particulate emissions from prescribed burning in
1021   Georgia, Environ. Sci. Technol., 39, 9049–9056, 2005.
1022
1023   Lee, S., Liu, Wand, Y., Russell, A., and Edgerton, E.: Source apportionment of $PM_{2.5}$:
1024   Comparing PMF and CMB results for four ambient monitoring sites in the southeastern United
1025   States, Atmos. Environ., 42, 4126-4137, 2010.
1026
1027   Lefohn, A., Emert, C., Shadwick, D., Wernli, H., Jung, J., and Oltmans, S: Estimates of
1028   background surface ozone concentrations in the United States based on model-derived source
1029   apportionment. Atmos. Environ., 47, 275-288,doi.10.1016/j. atmosenv.2013.11.033, 2014.
1030

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.

Lin, Y.-H., Knipping, E. Edgerton, E., Shaw, S., and Surratt, J.: Investigating the influences of SO_2 and NH_3 levels on isoprene-derived secondary organic aerosol formation using conditional sampling approaches, Atmos. Chem. Phys., 13, 8457-8470, 2013.

Lowenthal, D., Zielinska, B., Mason, B., Samy, S., Samburova, V., Collins, D., Spencer, C., Taylor, J., Allen, J., and Kumar, N.: Aerosol characterization studies at Great Smoky Mountains National Park, summer 2006, J. Geophys. Res.-Atmos., 114, doi/10.1029/2008JD011274, 2009.

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.

Marmur, A., Park, S. K., Mulholland, J. A., Tolbert, P. E., and Russell, A.G.: Source apportionment of PM2.5 in the southeastern United States using receptor and emissions based models: conceptual differences and implications for time-series health studies, Atmos. Environ., 40, 2533-2551, 2006.

Marmur, A, Liu, W., Wang, Y., Russell, A. G., and Edgerton, E.S.: Evaluation of model simulated atmospheric constituents with observations in the factor projected space: CMAQ simulations of SEARCH measurements, Atmos. Environ., 43, 1839–1849, 2009.

Martinez, M., Harder, H., Kovacs, T., Simpas, J., Bassis, J., Lesher, R., Brune, W., Frost, G., Williams, E., Stroud, C., Jobson, B., Roberts, J., Hall, S., Shetter, R., Wert, B. Fried, A., Alicke, B., Stutz, J., Young, V., White, A., and Zamara, R.: OH and HO2 concentrations, sources and loss rates during the Southern Oxidants Study in Nashville, Tennessee, summer 1999, J. Geophys. Res-Atmos.., 108, 4617, doi.10.1029/2003JD003551, 2003.

McMurry, P., Shepherd, M., and Vickery, J., eds.: Particulate Matter Science for Policy Makers, Cambridge University Press, Cambridge, UK, 283-319, 2004.

McNider, R., W. Norris, A. Song, R. Clymer, S. Gupta, Banta, R., Zamara, R., and White, A.: Meteorological conditions during the 1995 Southern Oxidants Study Nashville Middle Tennesssee Field Intensive, J. Geophys. Res.-Atmos.,103, 22,225-22,243, 1998.

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.

Morris, R. E., McNally, D. E., Tesche, T. W., Tonnesen, G., Boylan, J. W., and Brewer, P.: Preliminary evaluation of the community multiscale air quality model for 2002 over

1075 the southeastern United States, J. Air Waste Manage. Assoc.*, 55*, 1694-1708, 2005.
1076
1077 National Atmospheric and Oceanic Administration (NOAA). : Southeast Nexus (SENEX):
1078 Studying the Interactions between Natural and Anthropogenic Emissions at the Nexus of Air
1079 Quality and Climate Change, NOAA , Boulder, CO, available at:
1080 http://www.esrl.noaa.gov/csd/projects/senex/ (last access: November 20, 2013),, 2013.
1081
1082 Nguyen, T., Coggon, M., Bates, K., Zhang, X. , Schwantes, R. H., Schilling, K. A., Loza, C.L.,
1083 Flagan, R.C., Wennberg, P.O. , and Seinfeld, J.H.: Organic aerosol formation from the reactive
1084 uptake of isoprene epoxidiols (IEPOX) onto non-acidified and inorganic seeds, Atm. Chem.
1085 Phys. Discuss.*, 13, 27,677-27,716, 2013.
1086
1087 Novakov, T., Mueller, P., Alcocer, A., and Otvos, J.: 1972. Chemical composition of Pasadena
1088 aerosol by particle size and time of day: III Chemical states of nitrogen and sulfur by
1089 photoelectron spectroscopy, in: Aerosols and Atmospheric Chemistry, edited by Hidy. G. M.
1090 Academic Press, New York, 285-294, 1972.
1091
1092 O'Brien, R., Crabtree, J., Holmes, J., Hoggan, M., and Bockian, A.: Formation of photochemical
1093 aerosol from hydrocarbons: atmospheric analysis, Environ. Sci. Technol., 9, 577-582, 1975.
1094
1095 Pachon, J.E., Balachandran, S., Hu, Y., Weber, R.J., Mulholland, J.A., and Russell, A.G.:
1096 Comparison of SOC estimates and uncertainties from aerosol chemical composition and gas
1097 phase data in Atlanta, Atmos. Environ., 44, 3907-3914, 2010.
1098
1099 Peterson, T., Karl., T., Kossin, J., Kunkel, K., Lawrimore, J., McMahon, J., Vose, R., and Yin,
1100 X.: Changes in weather and climate extremes: State of knowledge relevant to air and water
1101 quality in the United States, J. Air Waste Manage. Assoc., 64, 184-197, 2014*.
1102
1103 Pitchford, M., Malm, W., Schichtel, B., Kumar, N., Lowenthal, D. , and Hand, J. : Revised
1104 algorithm for estimating light extinction from IMPROVE particle speciation data, J. Air Waste
1105 Manage. Assoc., 57, 1326-1336, 2007.
1106
1107 Pun, B.K., Seigneur, C.: Organic aerosol spatial/temporal patterns: perspectives of
1108 measurements and model, Environ. Sci. Technol., 42, 7287–7293, 2008.
1109
1110 Pun, B.; Seigneur, C., Bailey, E., Gautney, L., Douglas, S., Haney, J., and Kumar, N.:
1111 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 Rao, S.T., Zurbenko, I., Neagu, R., Porter, P., Ku, J., and Henry, R.: Space and Time Scales in
1115 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 of New York City, Atmos. Environ. , 37,3639-3651, 2003.
1120

1121   Riemer, D., Pos, W., Milne, P., Farmer, C., Zika, R., Apel, E., Olszyna, K., Kleindienst, T.,
1122   Lonneman, W., Bertman, S., Shepson, P., and Starn, T.: Observations of nonmethane
1123   hydrocarbons and oxygenated volatile organic compounds at a rural site in the southeastern
1124   United States, J. Geophys. Res.-Atmos., 103, 28,111-28,128, 1998.

1126   Sharkey, T., Wiberley, A., and Donohue, A.: Isoprene emissions from plants: why and how?
1127   Ann. Bot., 10, 5-18, 2008.

1129   Saylor, R., Edgerton, E., snd Hartsell, B.: Linear regression techniques for use in the EC tracer
1130   method of secondary organic aerosol estimation. Atmos. Environ.,40, 7546-7556, 2006.

1132   Seinfeld, J., and Pandis, S.: Atmospheric Chemistry and Physics: From Air Pollution to Climate
1133   Change, Wiley Interscience, New York,1998.

1135   Shen, X., Zhao, Y., Chen, Z., and Huang, D.: Heterogeneous reactions of volatile organic
1136   compounds in the atmosphere, Atmos. Environ., 68, 297-314, 2013.

1138   Solomon, P., Cowling, E., Hidy, and G. M., Furness, C.: Comparison of scientific findings from
1139   major ozone field studies in North America and Europe, Atmos. Environ. ,34, 1885-1920, 2000.

1141   Solomon, P., Chameides, W., Weber, R., Middlebrook, A., Kiang, C., Russell, A., Butler, A.,
1142   Turpin, B., Mikel, D., Scheffe, R., Cowling, E., Edgerton, E., St. John, J., Jansen, J., McMurry,
1143   P., Hering, S., and Bahadori, T. : Overview of the 1999 Atlanta supersite project, J.
1144   Geophys.Res.-Atmos., 108, 8413, doi:10.1029/2001JD001458, 2003.

1146   Southern Appalachian Mountain Intitiatve (SAMI): Final Report and Summary, avaliable at:
1147   www.metro4-Sesarm.org/pubs/SAMI_final reportsummary_Report 0802.pdf, 2012.

1149   Southern Oxidants Study (SOS) 1988-2003: Climatology of Ozone and Ozone Precursors,
1150   available at: www.ncsu.edu/sos/ii.html, last access 15 January 2014, 2014.

1152   Surratt, J., Kroll, J., Kleindinst, T., Edney, E., Claeys, M., Sorooshian, A., Ng, N., Offenberg, J.,
1153   Lewandowski, M., Jaoui, M., Flagan, R., and Seinfeld, J.: Evidence of organosulfates in
1154   secondary organic aerosol, Environ. Sci. Technol., 41, 517-527, 2007.

1156   Takahama, S., C. Davidson, and Pandis, S.: Semicontinuous measurements of organic carbon
1157   and acidity during the Pittsburgh Air Quality Study: implications for acid-catalyzed organic
1158   aerosol formation, Environ. Sci. Technol.,40, 2191-2199, 2006.

1160   Tanner, R., Olszyna, K., Edgerton, E., Knipping, E., and Shaw, S.: Searching for evidence of
1161   acid-catalyzed enhancement of secondary organic aerosol formation using ambient aerosol data,
1162   Atmos. Environ. , 43, 3440-3444, 2009.

1164   Tesche, T. W., Morris, R., Tonnesen, G., McNally, D., Boylan, J., and Brewer, P.:
1165   CMAQ/CAMx annual 2002 performance evaluation over the eastern US, Atmos.
1166   Environ., 40, 4906-4919, 2006.

1167

1168 University Corporation for Atmospheric Research (UCAR):
1169 https://www.eol.ucar.edu/field_projects/sas,last access 29 April 2014).

1170

1171 Vukovich, F.: Boundary layer ozone variations in the eastern United States and their association
1172 with meteorological variations: long-term variations, J. Geophys. Res. -Atmos., 99, 16, 839-
1173 16,850, 1994.

1174

1175 Vukovich, F.: Aspects of subregional variations in the SOS region, Atmos. Environ., 32, 3881-
1176 3889, 1998.

1177

1178 Wade, D.D., Brock, C., Brose, P., Grace, J., Hoch, G., and Patterson, G.: Fire in eastern
1179 ecosystems, edited by Brown, J. and Smith, J-K. , Wildland Fire in Ecosystems: Effects of Fire
1180 on Flora, Rep. RMRS-GTR-42, US Forest Service, Rocky Mountain Research Station, Ogden,
1181 UT, 2000.

1182

1183 Went, F.: Organic matter in the atmosphere and its prossible relation to petroleum formation,
1184 Proc. Natl. Acad. Sci,. U. S., 46, 212-221, 1960.

1185

1186 White, A., Templeman, B., Angevine, W., Zamora, R., King, W., Russell, C., Banta, R., Brewer,
1187 W. and Olszayna, K.: Regional contrast in morning transitions observed during the 1999
1188 Southern Oxidants Study Nashville/Middle Tennessee Intensive, J. Geophys. Res.-Atmos., 107,
1189 doi:10.1029/2001JD002036, 2002.

1190

1191 Xing, J. Pleim, J., Mathur, R., Poulliot, G., Hogrefe, C., Gan, C.-M., and Wei, C.: Historical
1192 gaseous and primary aerosol emissions in the United States from 1990-2010, Atmos. Phys.
1193 Chem. Discuss., 12, 30,327-30,369, 2012.

1194

1195 Yu, S., Bhave, P. V., Dennis, R. L., and Mathur, R.: Seasonal and regional variations of primary
1196 and secondary organic aerosols over the continental United States: semi-empirical estimates and
1197 model evaluation, Environ. Sci. Technol., 41, 4690-4697, 2007.

1198

1199 Zhang, J., and Rao, S.: The role of vertical mixing in the temporal evolution of ground-level
1200 ozone concentrations, J. Appl. Meteorol., 38, 1674-1691, 1999.

1201

1202 Zhang, X., Hecobian, A., Zheng, M., Frank, N and Weber, R.: Biomass burning impact on
1203 PM2.5 over the southeastern US during 2007: integrating chemically speciated FRM filter
1204 measurements, MODIS fire counts and PMF analysis, Atmos. Chem. Phys., 10, 6839-6853,
1205 2010.

1206

1207 Zhang, Y., Pun, B., Wu, S. Y., Vijayaraghavan, K., and Seigneur, C.: Application and
1208 evaluation of two air quality models for particulate matter for a southeastern US
1209 episode, J. Air Waste Manage. Assoc., 54, 1478-1493, 2004.

1210

1211 Zheng. M., Cass, G., J. Schauer, and Edgerton, E.: Source apportionment of PM2.5 in the
1212 southeastern United States using solvent extractable organic compounds, Environ. Sci.

1213   Technol. , 36, 2361-2371, 2002a.

1214

1215   Zheng, M., Cass, G. R., Schauer, J. J., and Edgerton, E.: Source apportionment of $PM_{2.5}$ in the

1216   southeastern United States using solvent-extractable organic compounds as tracers. Environ. Sci.

1217   Technol., 36, 2361-2371, 2002b.

1218

1219

1220

1221

1222

Model	N (yrs)	Variance (r^2)	p value (slope)	p value (inter-cept)
BHM CO = 81.10 ($\pm$ 12.87)*(CO emissions) – 75.38 ($\pm$ 71.56)	13	0.783	**<0.0001**	0.315
BHM CO = 80.00 ($\pm$ 10.96)*(CO emissions[d]) + 123.45 ($\pm$ 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[d]) + 133.23 ($\pm$ 15.25)	18	0.302	**0.0182**	**<0.0001**
Rural SO_2 = 4.109 ($\pm$ 0.195)*(SO_2 emissions) – 0.455 ($\pm$ 0.239)	18	0.965	**<0.0001**	0.075
Rural SO_4 = 2.102 ($\pm$ 0.158)*(SO_2 emissions) + 1.061 ($\pm$ 0.181)	15	0.932	**<0.0001**	**<0.0001**
Network SO_4 = 2.052 ($\pm$ 0.153)*(SO_2 emissions) + 1.157 ($\pm$ 0.175)	15	0.933	**<0.0001**	**<0.0001**
Rural NO_y = 3.170 ($\pm$ 0. 313)* (NO_x emissions) + 0. 113 ($\pm$ 0.432)	18	0.865	**<0.0001**	0.797
Rural NO_z = 1.178 ($\pm$ 0.306)*(NO_x emissions) + 0.015 ($\pm$ 0.392)	15	0.533	**0.002**	0.969
JST NMOC = 3144.9 ($\pm$ 523.2)*(VOC emissions[c]) – 37.2 ($\pm$ 44.8)	11	0.801	**0.0002**	0.428
Rural O_3 = 10.093 ($\pm$ 1.868)* (NO_x emissions) + 36.978 ($\pm$ 2.582)	18	0.646	**<0.0001**	**<0.0001**
Rural O_3 = 19.667 ($\pm$ 5.259)*(VOC 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[d]) + 0.125 ($\pm$ 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$39.99)*(OC emissions[d]) + 1.133 ($\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[d]) – 0.013 ($\pm$ 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[d]) + 0.018 ($\pm$ 0.627)	15	0.774	**<0.0001**	0.977

[a]Total annual emissions from Alabama, Georgia, Mississippi, and northwest Florida covering 1996 – 2013 (including emissions from biomass burning but excluding emissions from vegetation and soils)

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

[c]Georgia on-road mobile source VOC emissions

[d]Mobile-source emissions

1246
1247 Table 2. Mean concentrations by inland and coastal sites determined for 1999-2002 and 2009-
1248 2012. $PM_{2.5}$ and $PM_{10-2.5}$ mass and species concentrations are means of daily measurements (24-
1249 hour filter-based samples). O_3 measurements are means of peak daily 8-hour maxima.
1250 Concentrations of gases are means of days determined from hourly data. Means were determined
1251 by year, and the yearly means were then averaged.
1252

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

1253 [a]Gas measurements at BHM began in 2000. [b]$PM_{10-2.5}$ measurements at GFP and OAK start in 2003.
1254 [c]Measurements after 2010 not available.
1255 [d]NO_2 measurements commenced 1999-2002
1256 [e]NH_3 measurements commenced in 2004 as 24 hour filter based measurements; hourly   measurements began in
1257 2011.
1258 [f]The SEARCH database adopts the convention OM/OC = 1.4.
1259
1260
1261
1262
1263
1264
1265

1266

1267   Table A1 Glossary

1268

1269   **Experiments and Measurement Programs**
1270   ASACA Assessment of Spatial Aerosol Composition in Atlanta (1999–. . .)
1271   CASTNET (Interagency) Clean Air Status and Trends Network (1991–. . .)
1272   CSN (USEPA) Chemical Speciation Network (1999–. . .)
1273   IMPROVE Interagency Monitoring of Protected Visual Environments (1985–. . .)
1274   PAMS (USEPA) Photochemical Assessment Monitoring Station, measuring NMOC, and sometimes NOy
1275   and O_3 (1998-…)SAS Southern Atmosphere Study (summer 2013)
1276   SEARCH Southeastern Aerosol Research and Characterization Network (1998–. . .)
1277   SOS Southern Oxidant Study (1992–1999)
1278   SOAS Southern Oxidant and Aerosol Study (1 June–15 July 2013)
1279   **Carbon Chemical Terms**
1280   EC Elemental Carbon–Refractory, insoluble, chemically inert, light-absorbing carbon, operationally
1281   defined by measurement protocol (SEARCH filter samples utilize CSN/IMPROVE thermal optical
1282   reflectance method)IEPOX Isoprene epoxydiol, a product of isoprene oxidation
1283   LAC Light Absorbing Carbon – Operationally defined concentration using light absorbance as an
1284   estimate black (as elemental) carbon
1285   NMOC Non-methane organic carbon, a part of VOCs
1286   OC Organic carbon made up of organic species directly from sources (primary organic carbon–POC) and
1287   secondary organic carbon (SOC) from chemical reactions of volatile organic species in the
1288   atmosphere,including photochemically induced oxidation products
1289   OM (Particle) Organic Matter– defined as $x \times OC$, where "x" is an empirical constant ranging from _ ~1.4
1290   to ~2.3 SEARCH data are reported with $x = 1.4$ by convention
1291   OVOC Oxygenated volatile organic compounds, including alcohols, aldehydes, ketones and acids
1292   TC Total carbon normally without the carbonate carbon component
1293   VOC Volatile organic compounds
1294   **Other Terms**
1295   EGU Electrical Generating Unit – power plant, frequently coal fired in the Southeast
1296   GAM Generalized (statistical) Additive Model
1297   MMO Major metal oxides (defined in SEARCH data as the sum of Al2O3, SiO2, K2O, CaO, TiO2, and
1298   Fe2O3)
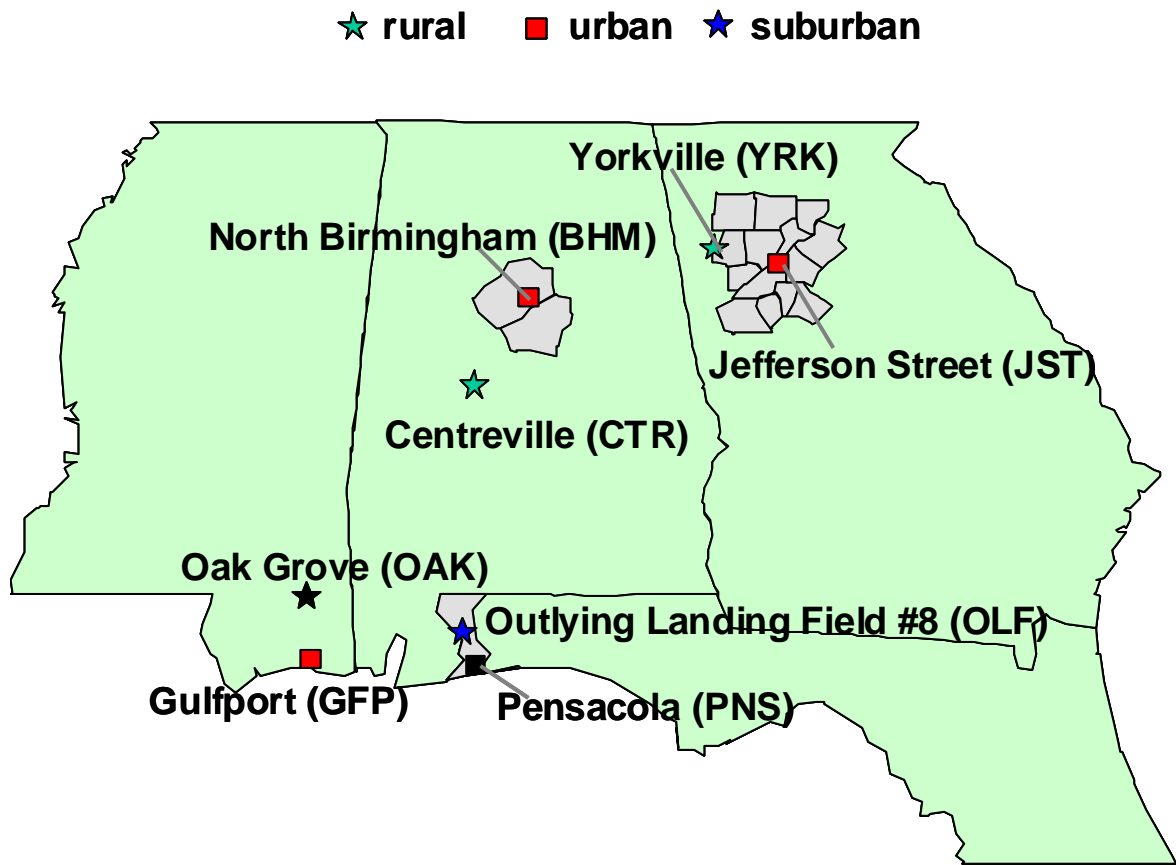1299   NEI (USEPA) US National Emissions Inventory
1300   NIS Non-inorganic sulfate; e.g., sulfate esters, methane sulfonate, sulfite salts
1301 pNO3 Particulate nitrate, often assumed to be mainly NH_4NO_3
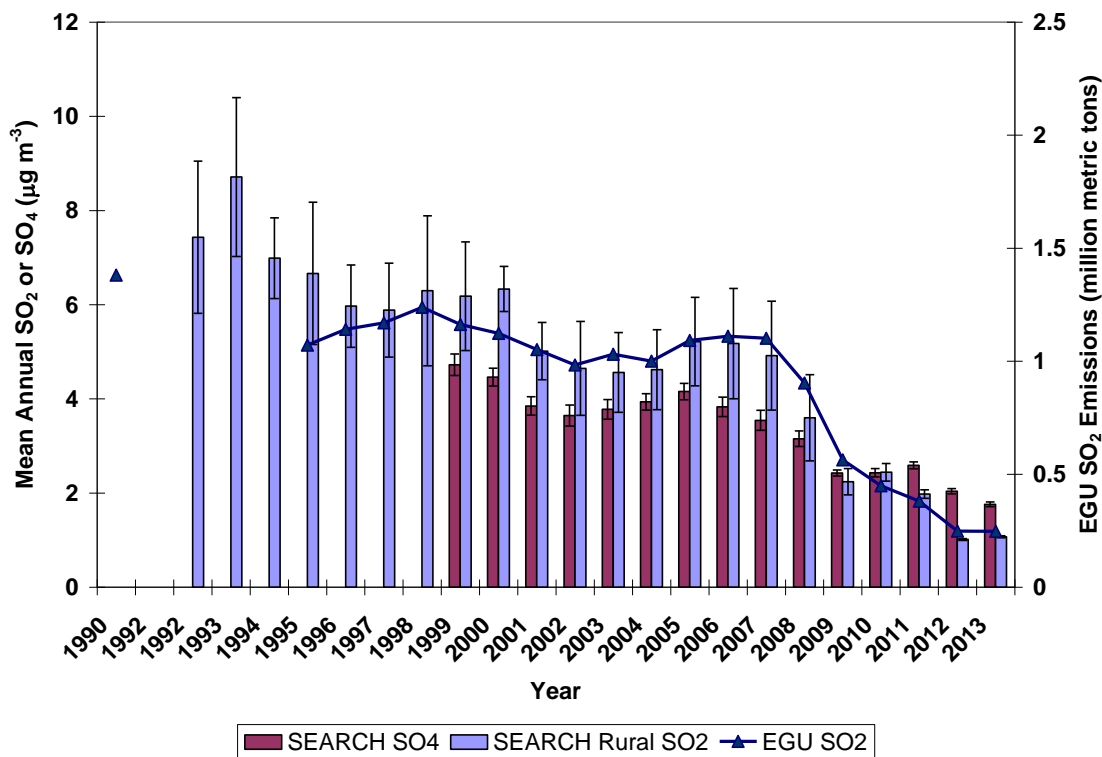1302   RH Relative humidity
1303   SR Solar radiation
1304 $WSSO_4$ Water-soluble sulfate from filter extractions with water solvent, or direct particle sample
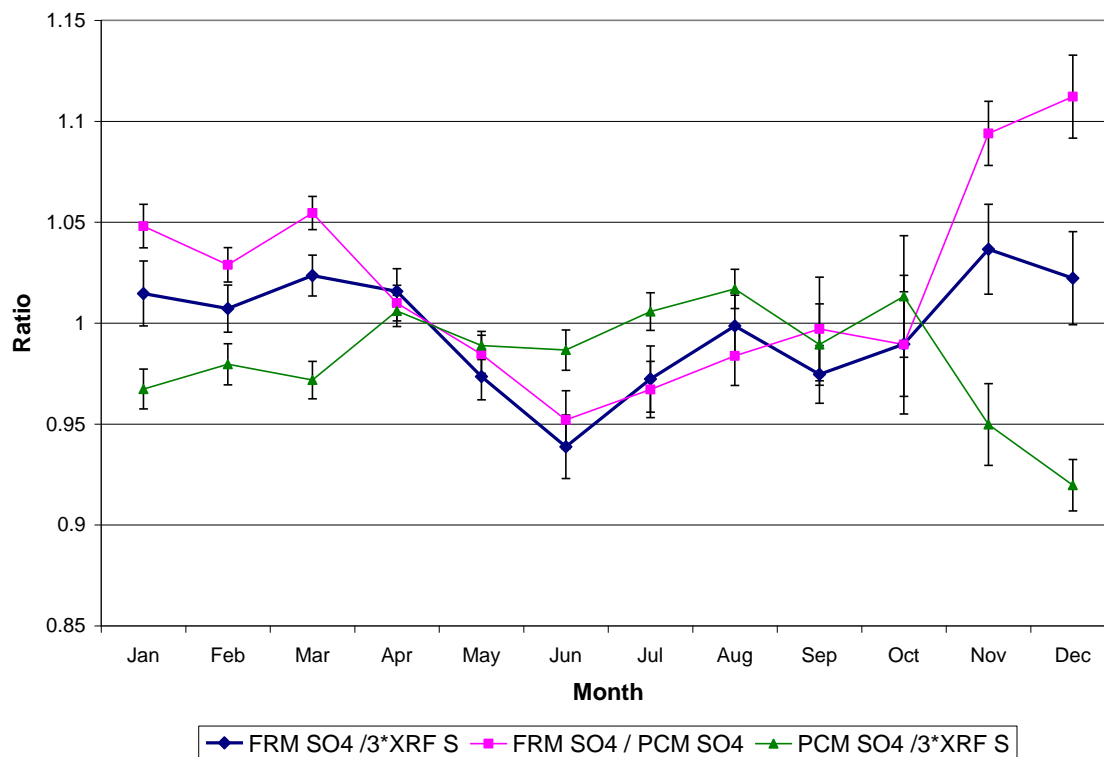1305   dissolution

1306

1307

1308

1309

1310

1311
1312
1313
1314
1315
1316
1317
1318
1319
1320
1321
1322
1323
1324
1325
1326
1327
1328
1329
1330
1331
1332
1333
1334
1335
1336
1337
1338
1339
1340
1341
1342
1343
1344
1345
1346
1347
1348
1349
1350
1351
1352
1353

★ rural   ■ urban   ★ suburban

Yorkville (YRK)

North Birmingham (BHM)

Jefferson Street (JST)

Centreville (CTR)

Oak Grove (OAK)

Outlying Landing Field #8 (OLF)

Gulfport (GFP)   Pensacola (PNS)

1. Geographical locations of the SEARCH monitoring sites and the nominal region of influence for the site measurements. PNS, OAK, GFP were retired after 2009, 2010, 2012, respectively. The grey areas in the figure represent the counties corresponding to the urban metropolitan areas of Birmingham, Atlanta and Pensacola, Florida.

1354
1355
1356
1357
1358
1359
1360
1361
1362
1363
1364
1365
1366
1367
1368
1369
1370
1371
1372
1373
1374
1375
1376
1377
1378

2. Mean annual SO_4 concentrations (all SEARCH sites) and SO_2 concentrations (rural SEARCH sites – CTR, OAK, YRK) compared with emissions of SO_2 from EGUs located in Alabama, Georgia, northwest Florida, and Mississippi vs. year. Uncertainties are one standard error of the intersite means. EGU emissions are updated from Blanchard et al. (2013c).

1384
1385
1386
1387
1388
1389
1390
1391
1392
1393
1394
1395
1396
1397
1398
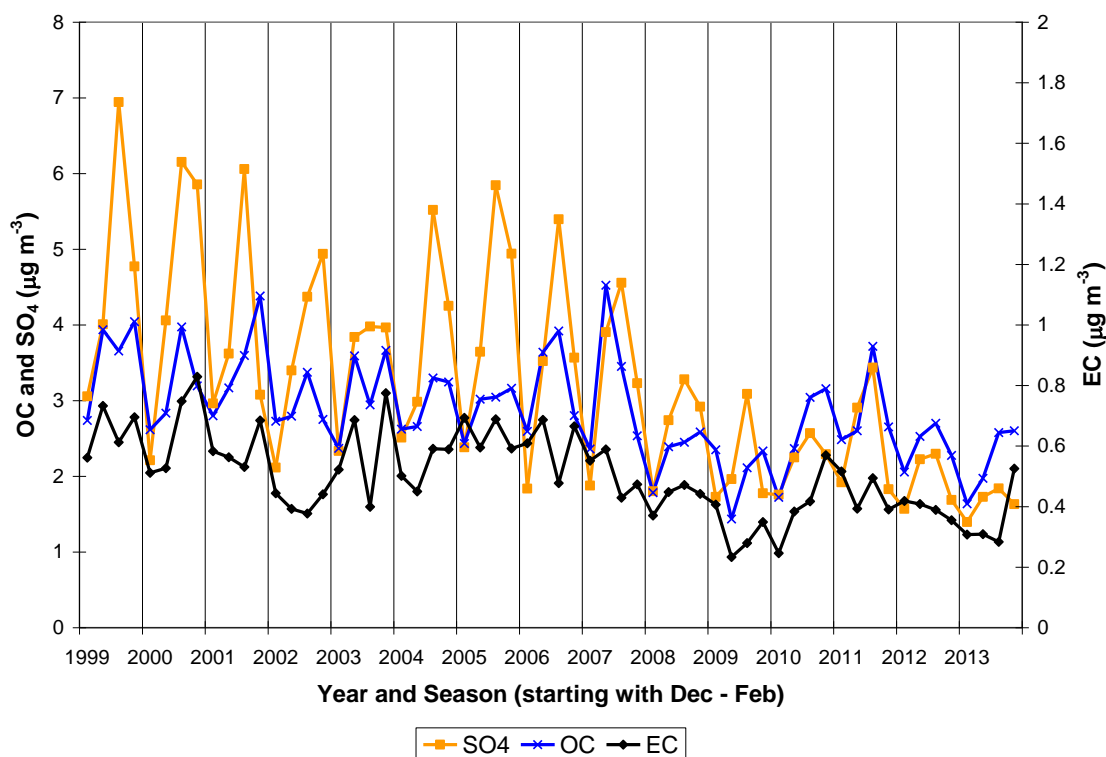
3. Mean seasonal concentrations of SO$_4$, OC, and EC at CTR. Seasons are by calendar month (1) Jan-Mar), (2) April-June), (3) July-Sept., (4) Oct.-Dec. Vertical divisions are calendar year between Q4 and Q1. OC and EC tend track one another and trends are downward at approximately the same annual rate, while SO4 shows a sharper decrease until 2008. OC tends to have winter minima, but OC maxima vary between Q2-Q4.

1442
1443
1444
1445
1446
1447
1448
1449
1450
1451
1452
1453
1454
1455
1456
1457
1458
1459
1460
1461
1462
1463
1464
1465
1466
1467
1468
1469
1470
1471
1472
1473
1474
1475
1476
1477
1478
1479
1480
1481
1482

4. Comparison of the US federal reference method (FRM) SO$_4$, FRM x-ray fluorescence S (multiplied by 3 to represent SO$_4$), and ARA-SEARCH sampler (PCM1) SO$_4$. The data are from JST, 1999 and 2000 (19 – 54 days per monthly mean). The PCM1 sampler is configured with a denuder to remove SO$_2$ and thereby reduce or eliminate positive artifact, whereas the FRM sampler is not. FRM SO$_4$ measurements at other sites and during other years were too limited for comparison (n < 4 values per month except at BHM, where n = 8 – 11 values during 6 months). XRF S measurements are made on FRM filters.

1483
1484
1485
1486
1487
1488
1489
1490
1491
1492
1493
1494
1495
1496
1497
1498
1499
1500
1501
1502
1503
1504
1505
1506
1507
1508
1509
1510
1511
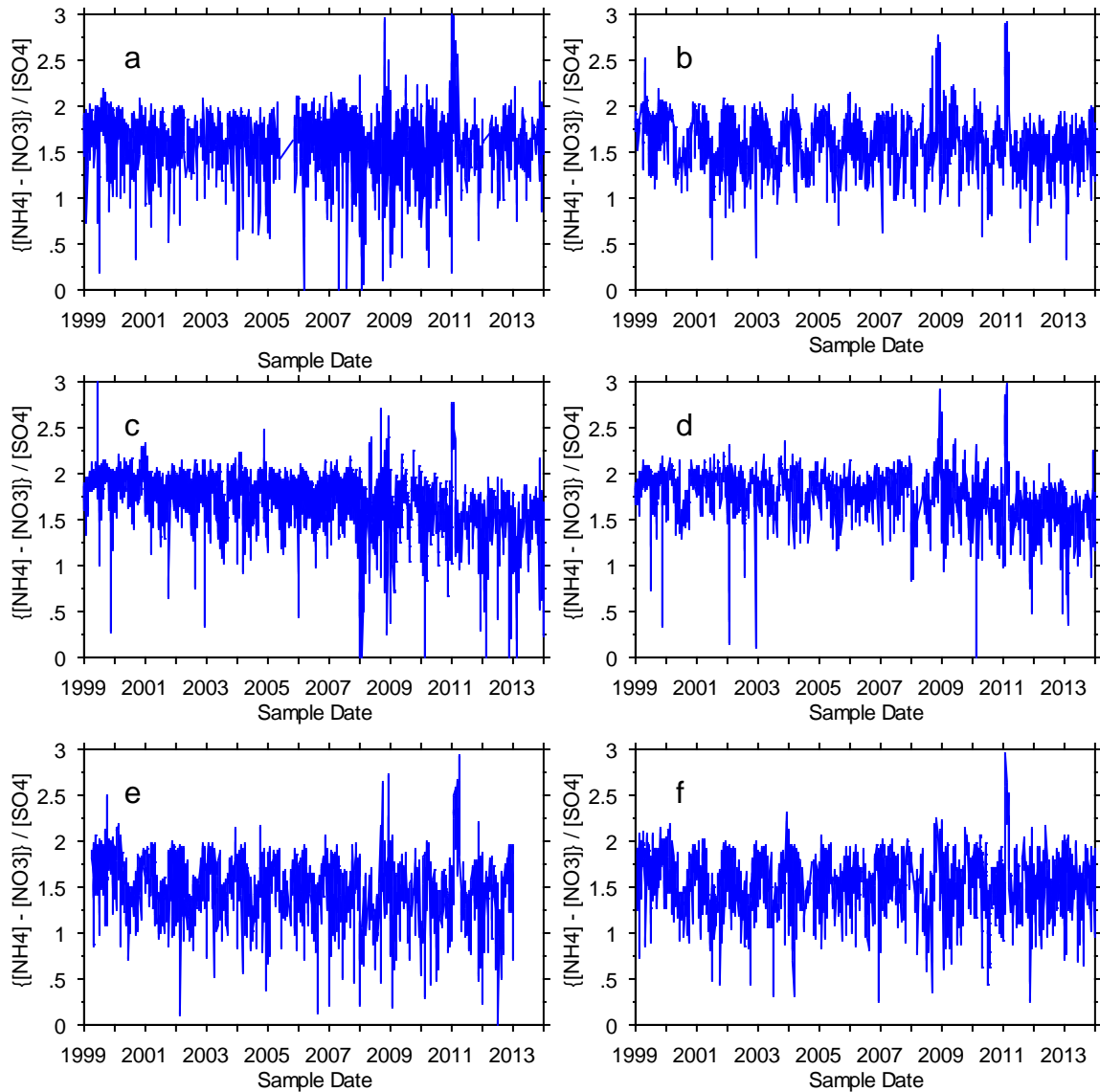
1512   5. Daily molar ratio of { [NH$_4$] – [NO$_3$] } / [SO$_4$] } (sulfate neutralization) at (a)
1513   BHM, (b) CTR, (c) JST, (d) YRK, (e) GFP, and (f) OLF. The ratios decreased
1514   by 0.01 - 0.03 units yr^{-1} (statistically significant at all sites, $p < 0.0001$) and
1515   averaged 1.5 (GFP, OAK) to 1.8 (JST, YRK) over the study period. A seasonal
1516   variation in the ratio is seen especially at CTR from 2001-2007, where the ratio
1517   is reduced in summer relative to winter.

1518
1519
1520
1521
1522

44

1523
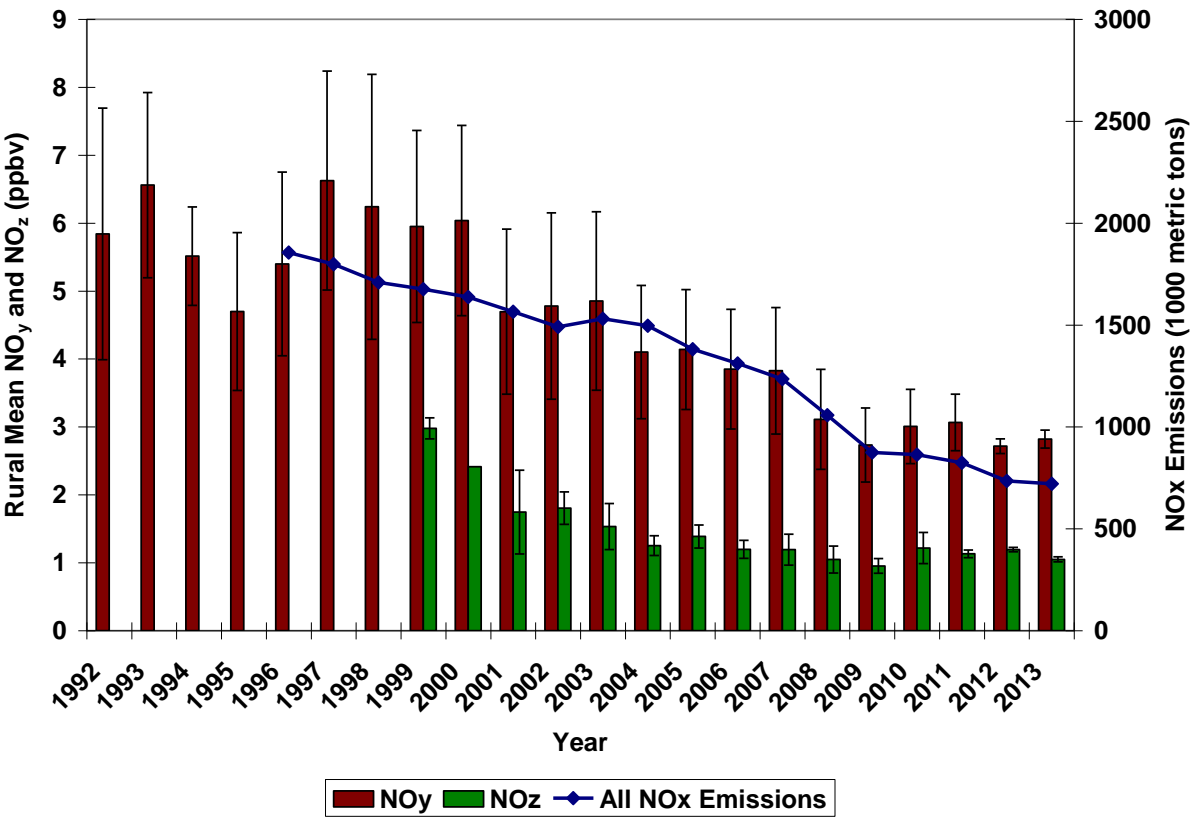
1524
1525
1526
1527
1528
1529   6. Mean rural NO_y and NO_z concentrations at the three rural SEARCH sites (CTR,
1530   OAK, YRK) and emissions of NO_x from all emission sources located in
1531   Alabama, Georgia, northwest Florida, and Mississippi vs. year. Uncertainties
1532   are one standard error of the intersite means. Emissions are derived from the
1533   NEIs and are updated from Blanchard et al. (2013c).
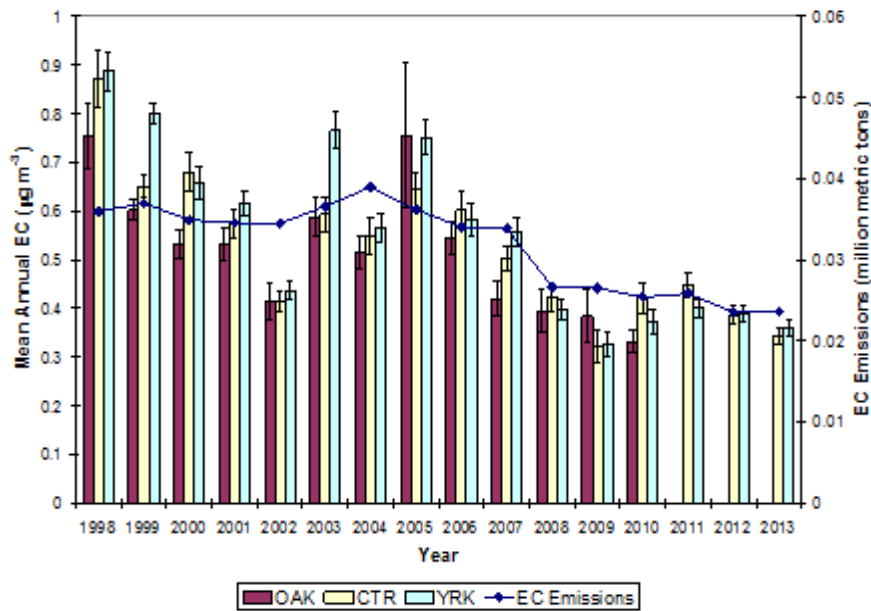
1534
1535
1536
1537
1538
1539
1540
1541
1542
1543
1544
1545

1546
1547
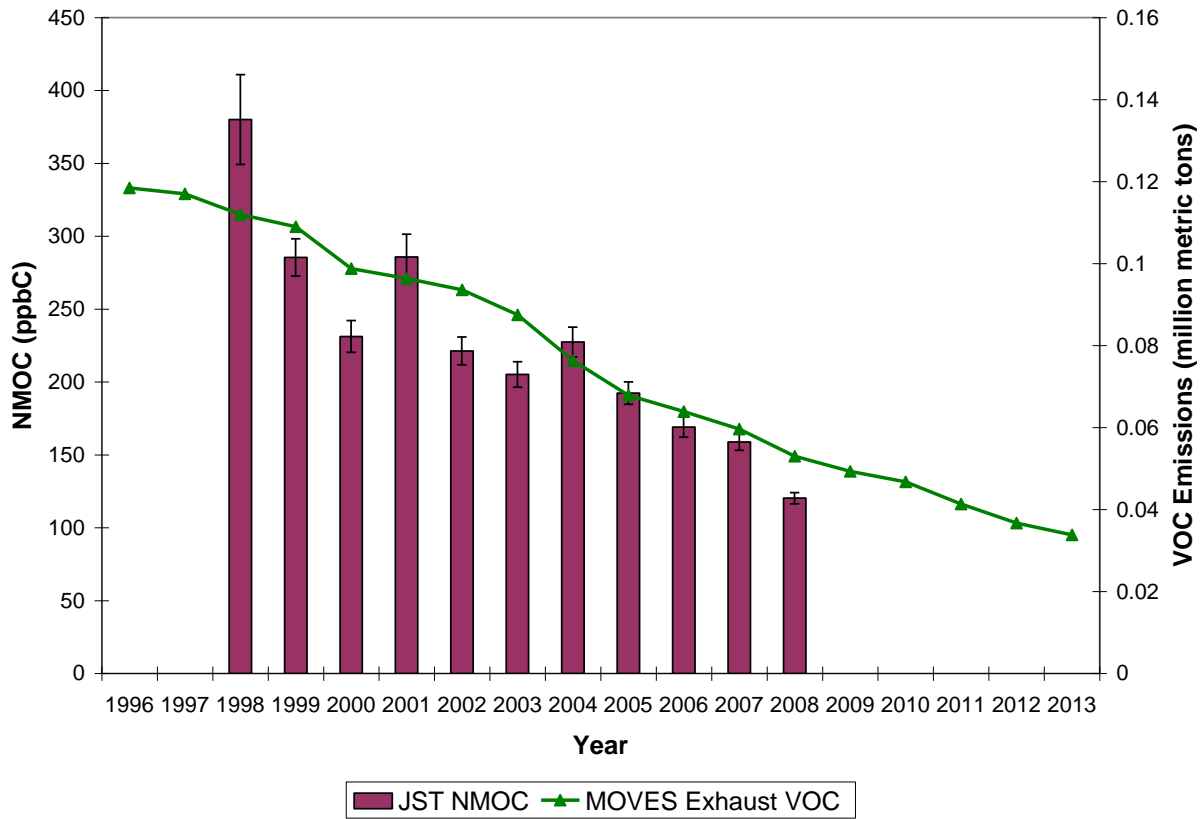
1548
1549
1550
1551
1552
1553   7.   Mean annual NMOC concentrations at JST and emissions of VOC from on-road
1554   mobile exhaust within Georgia vs. year. Uncertainties are one standard error of
1555   the intersite means. The 1998 NMOC measurements were made from August
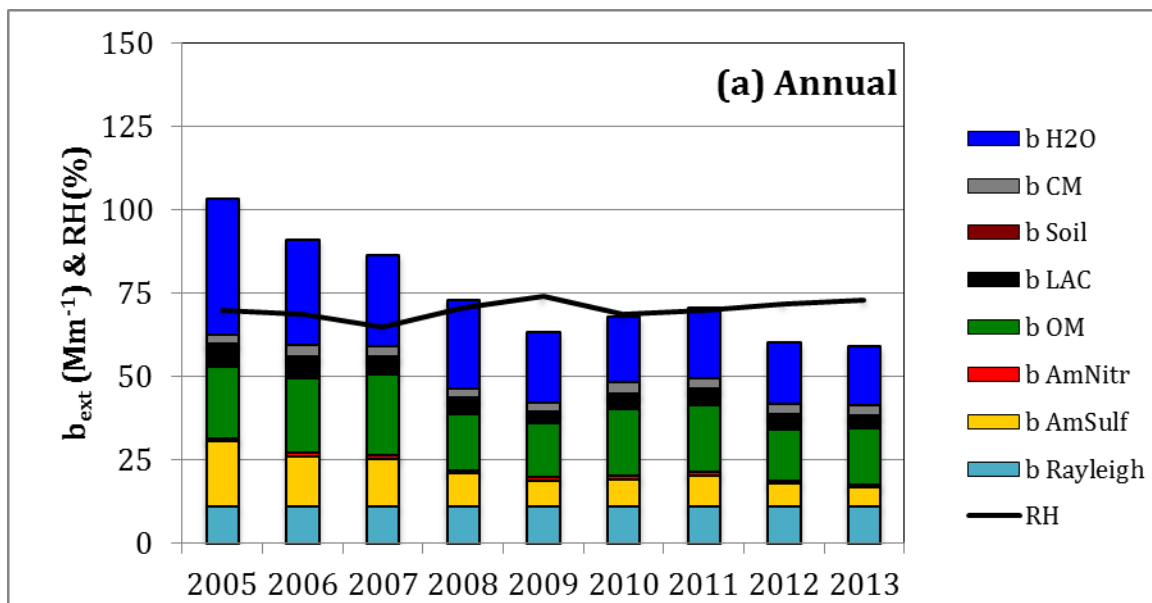1556   through December. Emissions are updated from the NEIs, and from Blanchard
1557   et al. (2013c).

1558
1559
1560
1561
1562
1563
1564
1565
1566
1567
1568
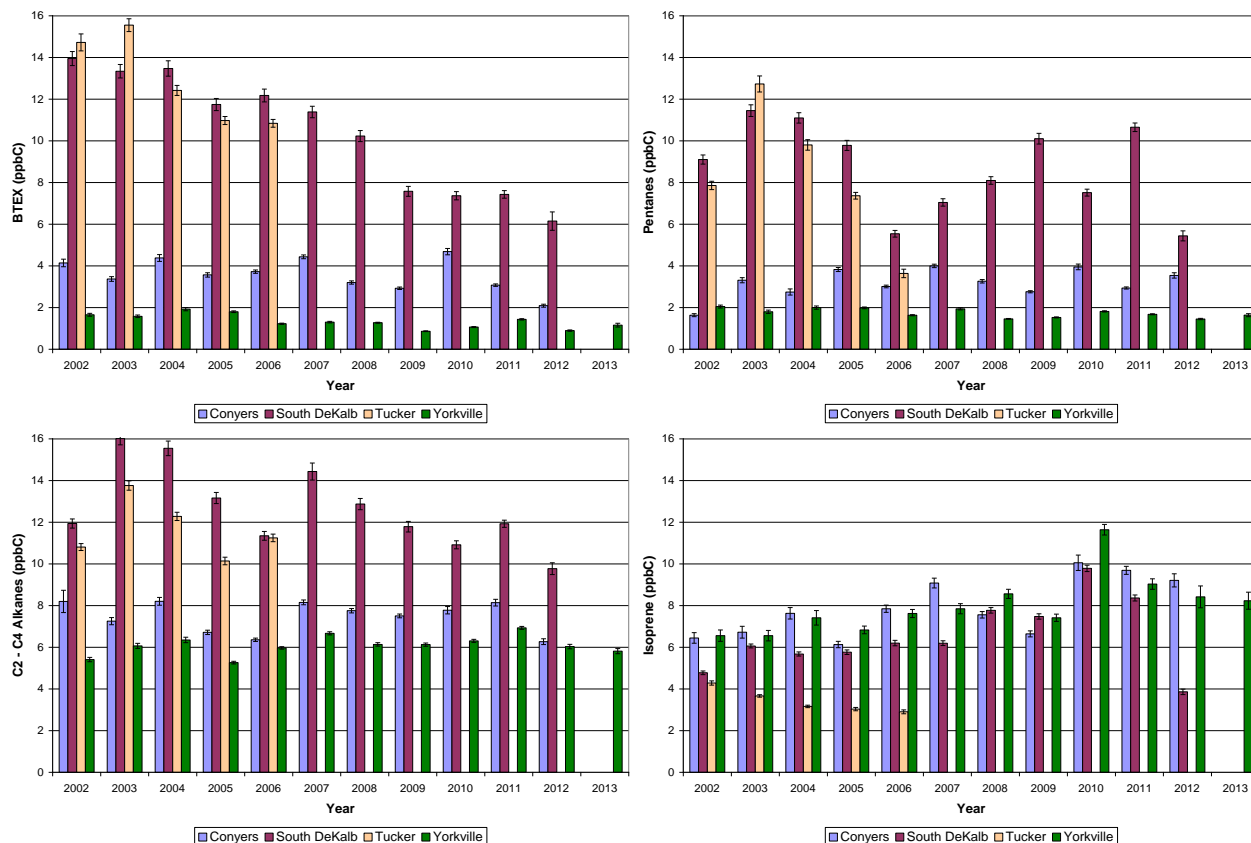
8. Mean summer (June – August) concentrations of NMOC species at four PAMS sites within the Atlanta metropolitan area. South DeKalb and Tucker are urban sites; YRK is considered an "upwind" non-urban site, while Conyers is a suburban (semirural) "downwind" site. (Note: 2012 only July data are available; 2013 only YRK July data are available).
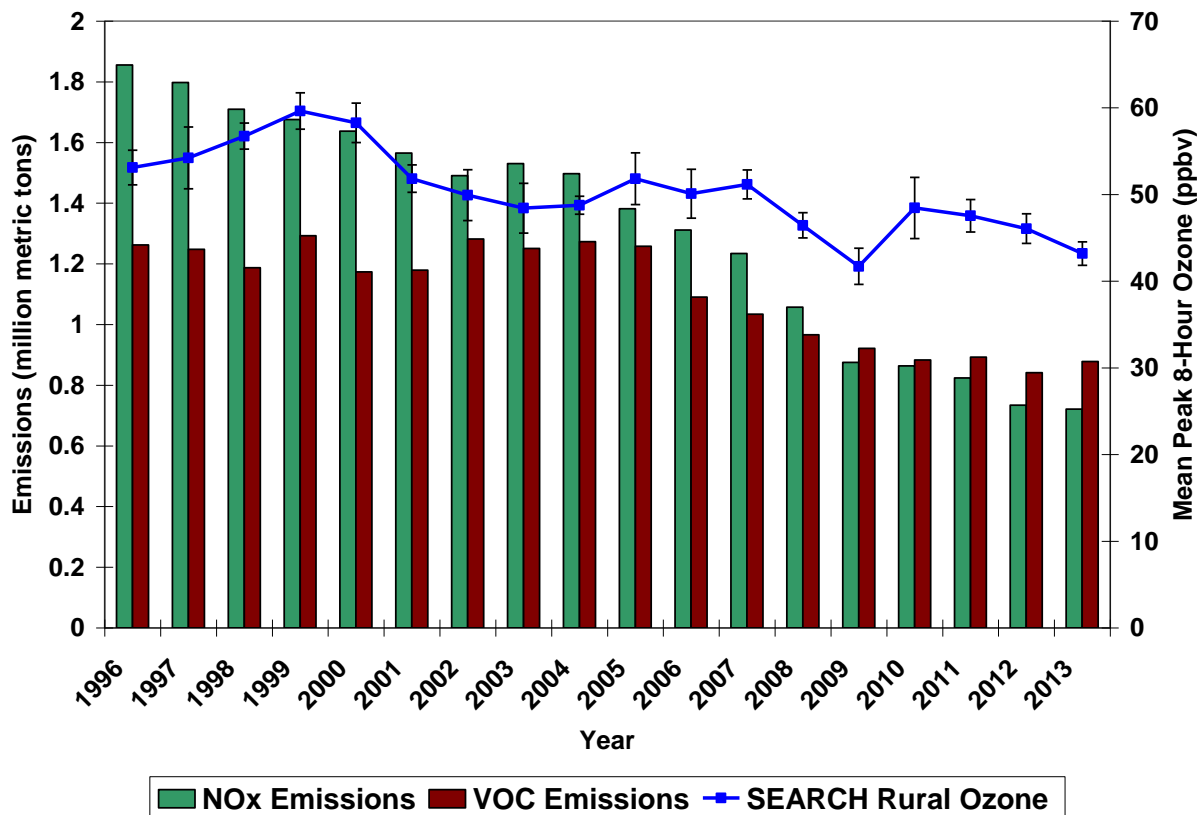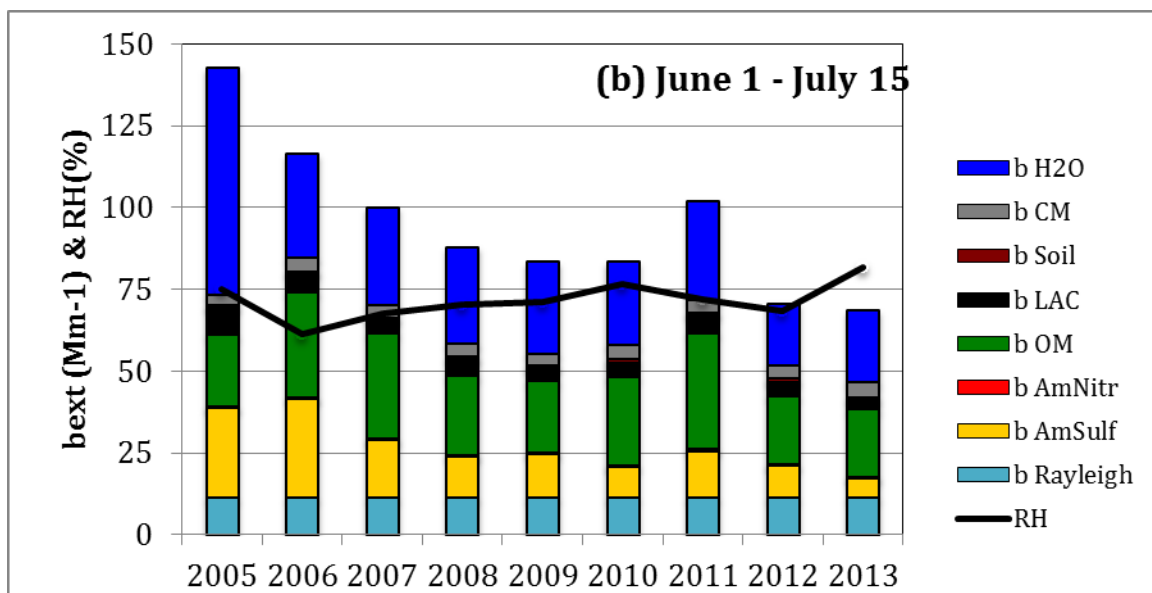
9. Mean peak 8-hour O_3 at rural SEARCH sites during the months of March through October compared with anthropogenic NO_x and VOC emissions in Alabama, Georgia, Mississippi, and northwest Florida. The 2012-2013 NO_x emissions were estimated from 2011 using the 2011 and 2012-2013 CEMS data for EGU emissions.

1614
1615
1616
1617
1618
1619
1620
1621

1622
1623
1624
1625
1626
1627
1628
1629
1630
1631
1632
1633
1634

1635

1636

1637
1638
1639 10. Mean annual EC concentrations at rural SEARCH sites compared with emissions of EC
1640   from all emission sources in Alabama, Georgia, Mississippi, and northwest Florida.
1641   Emissions data are from extension using the method of Blanchard et al. (2013c).
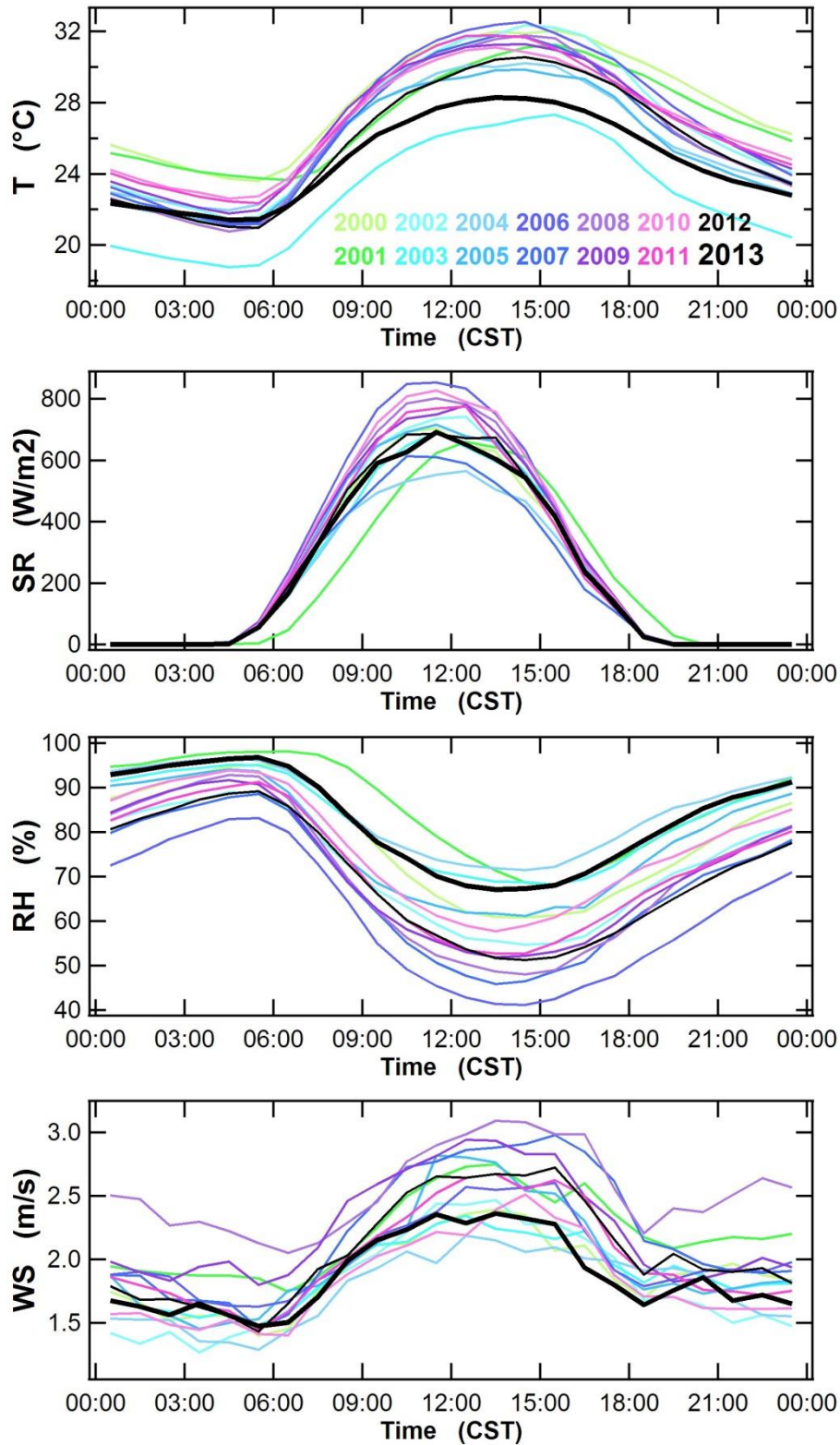
1642
1643
1644
1645
1646
1647
1648
1649
1650
1651
1652
1653
1654
1655
1656
1657
1658
1659
1660
1661
1662
1663

1664
1665   a.
1666

1667
1668   b.
1669
1670   11. Mean annual light extinction computed from daily species concentrations at CTR calculated using the new
1671   IMPROVE algorithm. (b) Mean light extinction computed from daily species concentrations at CTR during
1672   June 1-July 15 of each year. The aerosol components include ammonium salts, OM (=1.8OC), light
1673   absorbing carbon (LAC), soil dust, coarse material (CM) and water. The black line shows the measured RH
1674   averaged over different periods represented in the two panel of the figure. RH dependence was computed
1675   using the new IMPROVE f(RH) formula with hourly RH measurements at each site. Effects of water in
1676   particles, associated with SO_4 and NO_3, are shown separately as the b_{H20} term (See also Figure S10).
1677
1678
1679
1680
1681

1682
1683
1684
1685
1686
1687
1688
1689
1690
1691
1692
1693
1694
1695
1696
1697
1698
1699
1700
1701
1702
1703
1704
1705
1706
1707
1708
1709
1710
1711
1712
1713
1714
1715
1716
1717
1718
1719
1720
1721
1722
1723
1724
1725 12. Mean diurnal hourly (CST) temperature (T), solar radiation (SR), relative humidity (RH) and
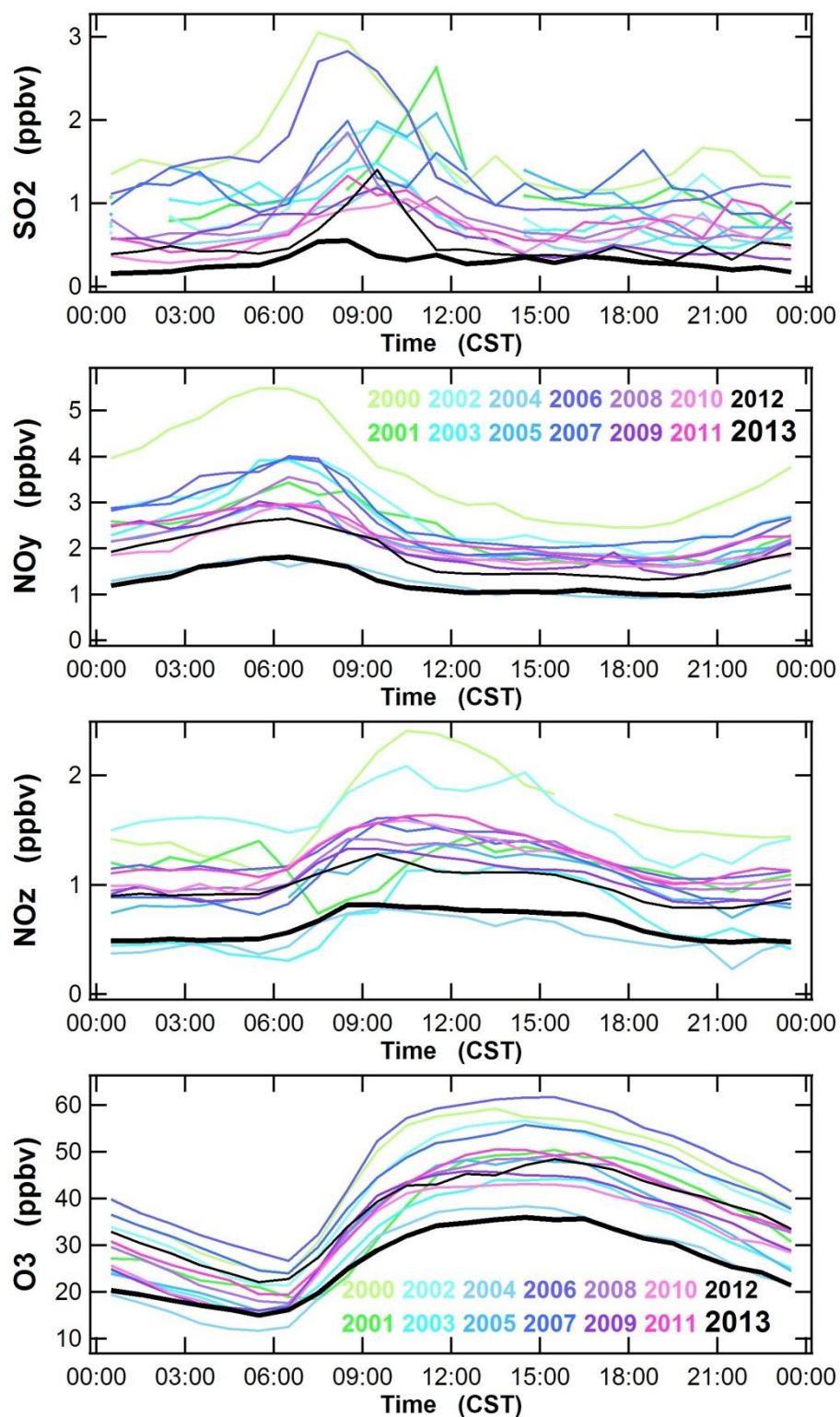1726 wind speed (WS) at CTR from 1 June through 15 July each year, 2000-2013.
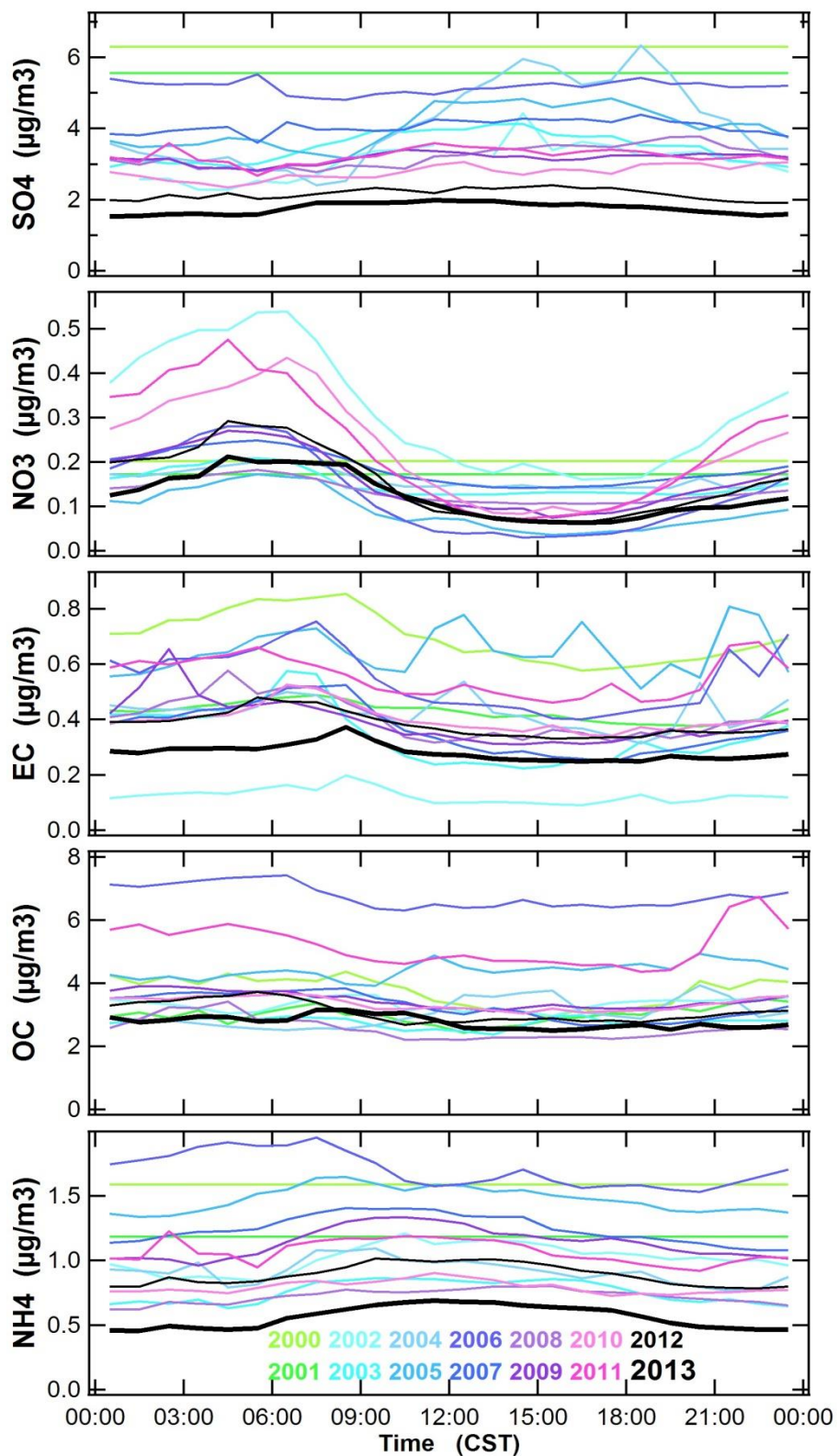1727

1728
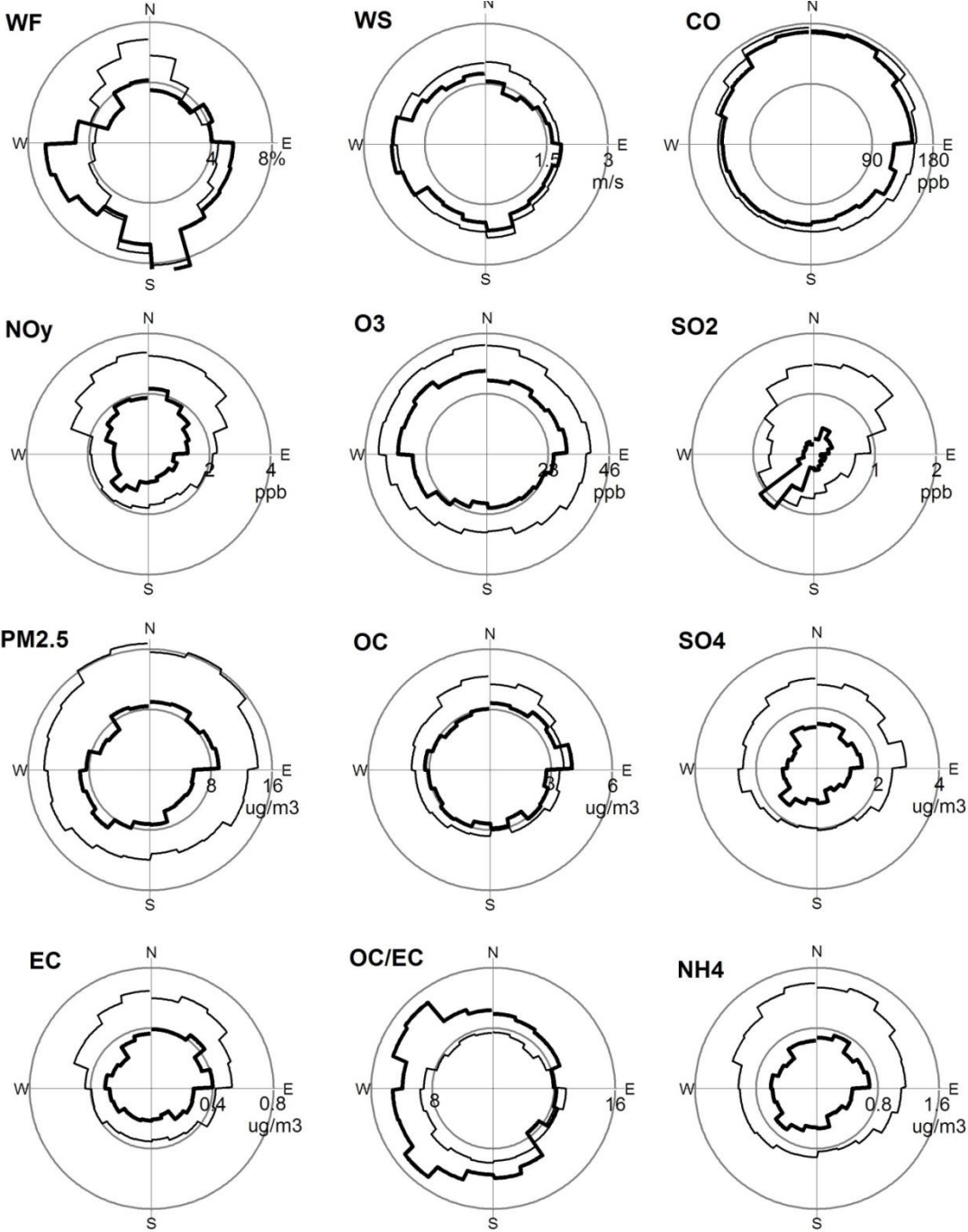
1729
1730
1731

13. Comparison between average 2000-2012 and the SOAS period in 1 June 1- 15 July 2013 for directional wind speed frequency and direction, trace gas concentrations, and concentrations of $PM_{2.5}$ mass, EC, OC, SO_4, NH_4 and OC/EC at CTR.

1735
1736

14. Mean diurnal concentrations of trace gases SO_2, NO_y, NO_z, and O_3 at CTR from June 1
    through July 15 each year.

15. Mean diurnal concentrations of PM$_{2.5}$ SO$_4$, pNO$_3$, EC, OC and NH$_4$ at CTR from 1 June through 15 July 15 each year. For 2000-2001, SO$_4$, NO$_3$, and NH$_4$ are 24-hour values.

54

1829
1830
1831
1832
1833
1834
1835