

# Southeast Atmosphere Studies: learning from model-observation syntheses

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## 43 **Abstract**

44 Concentrations of atmospheric trace species in the United States have changed dramatically over  
45 the past several decades in response to pollution control strategies, shifts in domestic energy policy  
46 and economics, and economic development (and resulting emission changes) elsewhere in the  
47 world. Reliable projections of the future atmosphere require models to not only accurately describe  
48 current atmospheric concentrations; but to do so by representing chemical, physical and biological  
49 processes with conceptual and quantitative fidelity. Only through incorporation of the processes  
50 controlling emissions and chemical mechanisms that represent the key transformations among  
51 reactive molecules can models reliably project the impacts of future policy, energy, and climate  
52 scenarios. Efforts to properly identify and implement the fundamental and controlling mechanisms  
53 in atmospheric models benefit from intensive observation periods (IOPs), during which co-located  
54 measurements of diverse, speciated chemicals in both the gas and condensed phases are obtained.  
55 The Southeast Atmosphere Studies (SAS, including SENEX, SOAS, NOMADSS and SEAC4RS)  
56 conducted during the summer of 2013, provided an unprecedented opportunity for the atmospheric  
57 modeling community to come together to evaluate, diagnose, and improve the representation of  
58 fundamental climate and air quality processes in models of varying temporal and spatial scales.

59 This paper is aimed to discuss progress in evaluating, diagnosing, and improving air quality and  
60 climate modeling using comparisons to SAS observations as a guide to thinking about  
61 improvements to mechanisms and parameterizations in models. The effort focused primarily on  
62 model representation of fundamental atmospheric processes that are essential to the formation of  
63 ozone, secondary organic aerosols (SOA) and other trace species in the troposphere, with the  
64 ultimate goal of understanding the radiative impacts of these species in the Southeast and  
65 elsewhere. Here we address questions surrounding four key themes: gas phase chemistry, aerosol  
66 chemistry, regional climate and chemistry interactions, and natural and anthropogenic emissions.  
67 We expect this review to serve as a guidance for future modeling efforts.

## 68 **1. Introduction**

69 The Southeast US has been studied extensively because it includes both intense emissions of  
70 biogenic VOC and has multiple large sources of anthropogenic emissions (e.g. Chameides et al.,  
71 1988; Trainer et al., 1987). An improved understanding of ozone photochemistry in this region has  
72 subsequently led to effective ozone control strategies (Council, 1991). In 1990s, a number of  
73 aircraft and ground field campaigns were conducted to study ozone photochemistry in the  
74 Southeast US (Cowling et al., 2000, 1998; McNider et al., 1998; Hübler et al., 1998; Meagher et  
75 al., 1998; Martinez et al., 2003; Roberts et al., 2002; Stroud et al., 2001). Aggressive regulatory  
76 efforts over the past decade have substantially decreased  $\text{NO}_x$  in this region (e.g. Russell et al.,  
77 2012). This decrease is changing the factors that control the  $\text{NO}_x$  lifetime and offers an opportunity  
78 to study mechanisms of emission from ecosystems in the region in different chemical regimes. The  
79 decrease in  $\text{NO}_x$  is also shifting the regime of  $\text{HO}_x$  chemistry from one where the primary reaction  
80 partner for  $\text{HO}_2$  and  $\text{RO}_2$  was  $\text{NO}$  to one where isomerization,  $\text{RO}_2 + \text{HO}_2$  and  $\text{HO}_2 + \text{HO}_2$  are  
81 more important. The Southeast Atmosphere Studies (SAS, including SENEX, SOAS, NOMADSS  
82 and SEAC4RS), was designed to study the atmospheric chemistry of the region in the context of  
83 changing anthropogenic emissions.

84 Observational experiments in the Southeastern U.S. during SAS (Southeast Atmosphere Studies)  
85 2013 (SOAS, SENEX, SEAC4RS, NOMADSS) provide a wealth of new insights into the  
86 composition of the atmosphere. Results allow researchers to explore the chemical degradation of

87 biogenic organic molecules over a range of concentrations of ambient nitrogen oxide  
88 concentrations during day and night, and the ensuing consequences for ozone, aerosol and radiative  
89 properties of the atmosphere. The experiment was large and collaborative, and included  
90 coordinated measurements at multiple surface sites and, among several aircraft, with many  
91 flyovers of the surface sites and a wide suite of available remote sensing from space based  
92 instruments. A comprehensive array of instruments at each site/aircraft tracked most of the key  
93 atmospheric observables. Direct tracking of oxidative pathways was made possible by including  
94 gas phase measurements of parent molecules and many of the first- and second-generation  
95 daughter molecules. For the first time, many of the daughter molecules were also tracked into the  
96 aerosol phase. These observations provided an important context for both the characterization of  
97 new instruments and new methods by interpreting measurements from more established  
98 instruments. In parallel with these field measurements, several laboratory experiments used the  
99 same instrumentation to provide insights into the chemical mechanisms of oxidation and  
100 instrument performance under field conditions. Overviews of the entire project and many of the  
101 subprojects have been presented elsewhere (Carlton et al., 2017; Warneke et al., 2016; Toon et al.,  
102 2016). Analyses of the observations have ranged from those that focus on the observations alone  
103 to those that primarily describe model simulations of the region. In this review we focus on the  
104 intersection of these two approaches, which is on analyses of observations that specifically test  
105 and inform the construction of 3-D chemical weather models. Our evaluations are focused on the  
106 Southeast data set, although we assert that the lessons learned are global.

## 107 **2. Gas-phase Chemistry**

### 108 **2.1 Background**

109 Global and regional models tend to significantly overestimate summertime surface ozone over the  
110 Southeastern US (Fiore et al., 2009; Murazaki and Hess, 2006; Yu et al., 2010; Yu et al., 2007;  
111 Lin et al., 2008; Rasmussen et al., 2012), posing a challenge for air quality management in this  
112 region and elsewhere. It remains unclear whether this model bias in summertime surface ozone is  
113 mainly due to the chemical processes (e.g. HO<sub>x</sub> recycling, isoprene nitrate chemistry,  
114 heterogeneous reactions, nighttime chemistry), physical processes (e.g. dry deposition, boundary  
115 layer processes) or emissions. Fiore et al. (2005) suggested that this problem might be due to  
116 incorrect representation of isoprene sources and chemistry. Measured deposition rates for isoprene  
117 oxidation products appear to be higher than current model values (Nguyen et al., 2015a; Karl et  
118 al., 2010). In the meantime, the understanding of isoprene oxidation chemistry has been evolving  
119 rapidly in the past decade (Crounse et al., 2011; Peeters et al., 2014; Peeters et al., 2009), as a  
120 result conclusions drawn from models using older chemical mechanism may not be correct.

121 A large debate surrounds our understanding of hydroxyl radical (OH) and hydroperoxy radical  
122 (HO<sub>2</sub>) concentrations in the presence of isoprene. Traditional mechanisms assume that isoprene  
123 oxidation suppresses OH concentrations in low-NO<sub>x</sub> conditions via the formation of organic  
124 hydroxyperoxides (Jacob and Wofsy, 1988). However, observations show higher-than-expected  
125 OH concentrations in isoprene-rich environments without corresponding enhancements in HO<sub>2</sub> or  
126 RO<sub>2</sub> (Tan et al., 2001; Carslaw et al., 2001; Lelieveld et al., 2008; Hofzumahaus et al., 2009; Ren  
127 et al., 2008; Pugh et al., 2010; Thornton et al., 2002; Stone et al., 2010), suggesting a gap in current  
128 understanding of isoprene oxidation. On the other hand, an interference has been discovered to  
129 affect some of these OH instruments (Mao et al., 2012; Novelli et al., 2014; Feiner et al., 2016).

130 Measurements of higher than expected OH in the presence of isoprene spurred renewed interest in  
131 issues related to the products of the HO<sub>2</sub> + RO<sub>2</sub> reactions. Thornton et al. (2002) and Hasson et al.  
132 (2004) had pointed out that if this reaction does not terminate the radical chain it would change  
133 the behavior of HO<sub>x</sub> radicals at low NO<sub>x</sub>. Several specific case of the HO<sub>2</sub> + RO<sub>2</sub> reactions were  
134 shown to have an OH product (Hasson et al., 2004; Jenkin et al., 2007; Dillon and Crowley, 2008).  
135 Peeters et al. (2009; 2014) identified a new path for OH regeneration through unimolecular  
136 isomerization of isoprene hydroxyperoxy radicals. This pathway was confirmed by laboratory  
137 measurements of its rate (Crouse et al., 2011; Teng et al., 2017). A key feature of the SAS  
138 experiments was that the NO<sub>x</sub> concentrations spanned a range that resulted in measurements where  
139 the three major fates of isoprene peroxy radicals (reaction with NO, HO<sub>2</sub> or isomerization) were  
140 sampled at different times and locations.

141 Another major consequence of isoprene oxidation is the production of isoprene nitrates, formed  
142 from RO<sub>2</sub>+NO reaction in the isoprene degradation chain during daytime and by addition of NO<sub>3</sub>  
143 to the double bonds in isoprene or isoprene daughters at night. Different treatments of these  
144 reactions in models including the yield and subsequent fate of daytime isoprene nitrates, cause as  
145 much as 20% variations in global ozone production rate and ozone burden among different models  
146 (Ito et al., 2009; Horowitz et al., 2007; Perring et al., 2009a; Wu et al., 2007; Fiore et al., 2005;  
147 Paulot et al., 2012). Large variations mainly stem from different yield of isoprene nitrates (Wu et  
148 al., 2007) and the NO<sub>x</sub> recycling ratio of these isoprene nitrates (Ito et al., 2009; Paulot et al., 2012).  
149 Recent laboratory data indicates the yield of first generation isoprene nitrates is in the range of 9%  
150 to 14% (Giacopelli et al., 2005; Patchen et al., 2007; Paulot et al., 2009a; Lockwood et al., 2010;  
151 Sprengnether et al., 2002; Xiong et al., 2015; Teng et al., 2015), which is much higher than the 4%  
152 that was in favor as recently as 2007 (Horowitz et al., 2007). The subsequent fate of these isoprene  
153 nitrates includes oxidation by OH, NO<sub>3</sub> and O<sub>3</sub> (Lockwood et al., 2010; Paulot et al., 2009a; Lee  
154 et al., 2014), photolysis (Müller et al., 2014), and hydrolysis. Synthesis of models and SAS  
155 observations suggest an important role for hydrolysis as expected based on the laboratory  
156 measurements (Romer et al., 2016; Fisher et al., 2016; Wolfe et al., 2015).

157 The SAS observations also provide measurements that guide our thinking about the role of NO<sub>3</sub>  
158 chemistry and its representation in models, especially as it contributes to oxidation of biogenic  
159 volatile organic compounds (BVOC) at night (Warneke et al., 2004; Brown et al., 2009; Aldener  
160 et al., 2006; Ng et al., 2008; Ng et al., 2017; Edwards et al., 2017). During SAS, these reactions  
161 were a substantial sink of NO<sub>x</sub> in addition to their role in oxidation of BVOC. To a large extent  
162 this is due to the high yield of carbonyl nitrates (65%-85%) from the isoprene + NO<sub>3</sub> oxidation  
163 (Perring et al., 2009b; Rollins et al., 2009; Rollins et al., 2012; Kwan et al., 2012; Schwantes et al.,  
164 2015). Models that incorporate this chemistry (Xie et al., 2013; Horowitz et al., 2007; von  
165 Kuhlmann et al., 2004; Mao et al., 2013), indicate that the isoprene+NO<sub>3</sub> reaction contributes more  
166 than 50% of the total isoprene nitrate production and that the reaction is thus a major pathway for  
167 nighttime NO<sub>x</sub> removal. The fate of products from isoprene+NO<sub>3</sub> and to what extent they return  
168 NO<sub>x</sub> remains a subject of discussion and thus an opportunity for exploration with models that  
169 might guide our thinking about a plausible range of product molecules (Perring et al., 2009b;  
170 Müller et al., 2014; Schwantes et al., 2015).

171 Compared to isoprene, the oxidation mechanism of monoterpene has received much less attention  
172 partly due to lack of laboratory and field data. In contrast to isoprene, a significant portion of  
173 terpenes emissions being released at night. Browne et al. (2014) showed that monoterpene  
174 oxidation is a major sink of NO<sub>x</sub> in the Arctic. The high yield of organic nitrates and the low vapor

175 pressure and high solubility of monoterpene organic nitrates results in strong coupling of gas phase  
176 mechanisms to predictions of SOA in a model. For example, the reaction of terpenes+NO<sub>3</sub>  
177 provides a large source of SOA as inferred (Ng et al., 2017). These aerosol organic nitrates can be  
178 either a permanent or temporary NO<sub>x</sub> sink depending on their precursors as well as ambient  
179 humidity (Nah et al., 2016b; Boyd et al., 2015; Lee et al., 2016a; Romer et al., 2016). Some of  
180 monoterpene organic nitrates may be susceptible to rapid hydrolysis/photolysis in aerosol phase  
181 (thus not detected as aerosol nitrates), leading to an underestimate of its contribution to SOA mass  
182 (Rindelaub et al., 2015; Rindelaub et al., 2016).

## 183 **2.2 Major relevant findings**

184 A major focus of the SAS study was to study the daytime and nighttime oxidative chemistry of  
185 isoprene and to compare the observations against models representing the ideas outlined above.  
186 Over the range of the fate of the isoprene RO<sub>2</sub> radical, isomerization was important and the reaction  
187 partners were mostly NO and HO<sub>2</sub> during the day and a mix of NO<sub>3</sub>, RO<sub>2</sub> and HO<sub>2</sub> at night. The  
188 field measurements were closely partnered with laboratory chamber experiments (Nguyen et al.,  
189 2014b) which enhanced our understanding of oxidation mechanisms and provided increased  
190 confidence in our understanding of the measurements of isoprene oxidation products. We  
191 summarize these major relevant findings here:

192 (1) Radical simulation: Combining traditional laser-induced fluorescence with a chemical removal  
193 method that mitigates potential OH measurement artifacts, Feiner et al. (2016) found that their  
194 tower-based measurements of OH and HO<sub>2</sub> during SOAS show no evidence for dramatically  
195 higher OH than current chemistry predicts in an environment with high BVOCs and low NO<sub>x</sub>.  
196 Instead, they are consistent with the most up-to-date isoprene chemical mechanism. Their  
197 measurements are also in agreement with co-located OH measurements by another technique,  
198 chemical ionization mass spectrometry (CIMS)(Sanchez et al., 2017). Romer et al. (2016) found  
199 that the lifetime of NO<sub>x</sub> was consistent with these OH observations and that the major source of  
200 HNO<sub>3</sub> was isoprene nitrate hydrolysis. Their conclusions would be inconsistent with dramatically  
201 higher OH levels, which would imply much more rapid isoprene nitrate production than observed.  
202 Other ratios of parent and daughter molecules and chemical lifetimes are also sensitive to OH and  
203 these should be explored for additional confirmation or refutation of ideas about OH production at  
204 low NO<sub>x</sub>.

205 Isoprene vertical flux divergence in the atmospheric boundary layer over the SOAS site and similar  
206 forest locations was quantified by Kaser et al. (2015) during the NSF/NCAR C-130 aircraft flights  
207 and used to estimate daytime boundary layer average OH concentrations of 2.8 to  
208  $6.6 \times 10^6$  molecules cm<sup>-3</sup>. These values, which are based on chemical budget closure, agree to within  
209 20% of directly-observed OH on the same aircraft. After accounting for the impact of chemical  
210 segregation, Kaser et al. (2015) found that current chemistry schemes can adequately predict OH  
211 concentrations in high isoprene regimes. This is also consistent with the comparison between  
212 measured and modeled OH reactivity on a ground site during SOAS, which show excellent  
213 agreement above the canopy of an isoprene-dominated forest (Kaiser et al., 2016).

214 (2) Isoprene oxidation mechanism: Recent refinements in our understanding of the early  
215 generations of isoprene degradation have stemmed from a synergy of laboratory, field, and  
216 modeling efforts. Laboratory work has provided constraints on the production and fate of a wide  
217 range of intermediates and end products, including organic nitrates (Teng et al., 2015; Xiong et al.,  
218 2015; Lee et al., 2014; Müller et al., 2014), the isoprene RO<sub>2</sub> (Teng et al., 2017), IEPOX (St. Clair

219 et al., 2015; Bates et al., 2014; Bates et al., 2016), MVK (Praske et al., 2015), and MACR (Crounse  
220 et al., 2012). These experiments have been guided and/or corroborated by analyses of field  
221 observations of total and speciated alkyl nitrates (Romer et al., 2016; Nguyen et al., 2015a; Xiong  
222 et al., 2015; Lee et al., 2016a), IEPOX/ISOPOOH (Nguyen et al., 2015a), glyoxal (Min et al.,  
223 2016), HCHO (Wolfe et al., 2016), OH reactivity (Kaiser et al., 2016), and airborne fluxes (Wolfe  
224 et al., 2015). Recent modeling studies have incorporated these mechanisms to some extent and  
225 showed success on reproducing temporal and spatial variations of these compounds (Su et al., 2016;  
226 Fisher et al., 2016; Travis et al., 2016; Zhu et al., 2016; Li et al., 2017; Li et al., 2016), as  
227 summarized in Table 1. Continued efforts are needed to reduce newfound mechanistic complexity  
228 for inclusion in regional and global models.

229 (3) Oxidized VOC: Large uncertainties remain on the production of smaller oxidation products.  
230 Several modeling studies indicate an underestimate of HCHO from isoprene oxidation in current  
231 mechanisms (Wolfe et al., 2016; Li et al., 2016; Marvin et al., 2017). Current chemical mechanisms  
232 differ greatly on the yield of glyoxal from isoprene oxidation (Li et al., 2016; Chan Miller et al.,  
233 2017). The observations indicate that the ratio of glyoxal to HCHO is 2%, independent of NO<sub>x</sub>  
234 (Kaiser et al., 2015), and this ratio is reproduced, at least to some extent, in two modeling studies  
235 (Li et al., 2016; Chan Miller et al., 2017). Confirmation of such a ratio is a useful indicator as these  
236 molecules are also measured from space and both are short-lived and tightly coupled to oxidation  
237 chemistry. Widespread ambient confirmation of the ratio is difficult because of large biases in  
238 satellite glyoxal quantification (Chan Miller et al., 2017).

239 For the case of the major daughter products methylvinylketone (MVK) and methacrolein (MACR),  
240 lab experiments have confirmed that ambient measurements reported to be MVK and MACR, by  
241 instruments with metal inlets including gas chromatography (GC) and proton transfer reaction-  
242 mass spectrometry (PTR-MS), are more accurately thought of as a sum of MVK, MACR and  
243 isoprene hydroperoxides that react on metal and are converted to MVK and MACR (Rivera - Rios  
244 et al., 2014; Liu et al., 2013).

245 (4) Organic Nitrates: The assumed lifetime and subsequent fate of organic nitrates can profoundly  
246 influence NO<sub>x</sub> levels across urban-rural gradients (Browne and Cohen, 2012; Mao et al., 2013),  
247 affecting oxidant levels and formation of secondary organic aerosol (SOA). Field observations  
248 during SAS suggest a short (2-3 hr) lifetime of total and isoprene/terpene organic nitrates (Wolfe  
249 et al., 2015; Romer et al., 2016; Fisher et al., 2016; Lee et al., 2016a). One possible explanation is  
250 aerosol uptake of these organic nitrates followed by rapid hydrolysis as confirmed in laboratory  
251 experiments (Hu et al., 2011; Darer et al., 2011; Rindelaub et al., 2016; Rindelaub et al., 2015;  
252 Jacobs et al., 2014; Bean and Hildebrandt Ruiz, 2016), although the hydrolysis rate varies greatly  
253 with the structure of nitrate and aerosol acidity (Hu et al., 2011; Rindelaub et al., 2016; Boyd et  
254 al., 2017; Boyd et al., 2015).

255 (5) Nighttime Chemistry: The SAS studies examined nighttime BVOC oxidation in both the  
256 nocturnal boundary layer (NBL) and the residual layer (RL). Measurements at the SOAS ground  
257 site provided a wealth of detailed information on nighttime oxidation processes in the NBL via  
258 state of the art instrumentation to constrain the major oxidants, BVOCs and gas and aerosol phase  
259 products (Ayres et al., 2015; Xu et al., 2015b; Lee et al., 2016a). A major focus of these efforts  
260 was to understand the influence of nitrate radical (NO<sub>3</sub>) oxidation as a source of secondary organic  
261 aerosol. These results are reviewed in Section 3.2.3 below, and show that organic nitrates from  
262 reactions of NO<sub>3</sub> with monoterpenes are an important SOA source in the NBL. Reactions of  
263 monoterpenes dominate nighttime chemistry near the surface due to their temperature (but not

264 sunlight) dependent emissions and their accumulation to higher concentration in the relatively  
265 shallow NBL.

266 Nighttime flights of the NOAA P-3 probed the composition of the overlying RL and the rates of  
267 nighttime oxidation processes there. In contrast to the NBL, isoprene dominates the composition  
268 of BVOCs in the RL, with mixing ratios over Alabama on one research flight demonstrating a  
269 nighttime average near 1 ppbv. Monoterpene mixing ratios were more than an order of  
270 magnitude lower. Consumption of isoprene by  $O_3$  and  $NO_3$  was shown to depend on the sunset  
271 ratio of  $NO_x$  to isoprene, with  $NO_3$  reaction dominating at ratios above approximately 0.5 and  $O_3$   
272 reaction dominant at lower ratios. Overall,  $O_3$  and  $NO_3$  contributed approximately equally to RL  
273 isoprene oxidation in the 2013 study. This observation, combined with recent trends in  $NO_x$   
274 emissions, suggests that RL nighttime chemistry in the southeast U.S. is currently in transition  
275 from a  $NO_x$  dominated past to an  $O_3$  dominated future, a condition more representative of the pre-  
276 industrial past. The implications of this trend for understanding organic nitrates and secondary  
277 organic aerosol should be considered in models of the influence of changing  $NO_x$  emissions on  
278 BVOC oxidation (Edwards et al., 2017).

279 (6) HONO: The community's confusion about sources of HONO was not resolved by SAS.  
280 Airborne observations over water from the NCAR C130 suggest that conversion of  $HNO_3$  to  
281 HONO and  $NO_x$  via photolysis of particulate nitrate in the marine boundary layer is important (Ye  
282 et al., 2016). A separate study using NOAA WP-3D observations indicates that HONO mixing  
283 ratios in the background terrestrial boundary layer are consistent with established photochemistry  
284 (Neuman et al., 2016). Persistent uncertainties regarding the potential for measurement artifacts  
285 continue to hamper efforts to resolve outstanding questions about putative novel HONO sources.

286 (7) Higher-order terpenes: Monoterpene and sesquiterpene chemistry requires continued  
287 investigation. Initial studies indicate that monoterpene oxidation can be an important sink of  $NO_x$   
288 and an important source of aerosol precursors (Lee et al., 2016a; Ayres et al., 2015). Additional  
289 analysis is needed to understand the role of monoterpenes. We note that because our understanding  
290 of isoprene chemistry has been changing so rapidly and because the role of isoprene sets the stage  
291 for evaluating the role of monoterpenes, we are now in a much better position to evaluate the role  
292 of monoterpene chemistry.

### 293 **2.3 Model recommendations**

294 Based upon the improved understanding outlined above, we make the following recommendations  
295 for the future modeling efforts:

296 (1) Measurements and modeling effort on OH show no indication of a need for empirical tuning  
297 factors to represent OH chemistry in the rural Southeast US. Detailed mechanisms based on recent  
298 laboratory chamber studies (mostly at Caltech) and theoretical studies (Leuven) for isoprene result  
299 in predicted OH that is in reasonable agreement with observations (Figure 1). Condensed  
300 mechanisms that approximate the detailed ones are expected to do the same. Whatever mechanism  
301 is used, a key diagnostic identified are parent-daughter molecular relationships such as  $NO_2/HNO_3$   
302 or MVK/isoprene. Models calculations should emphasize opportunities for observations of such  
303 ratios as an independent measure of the effect of OH on the atmosphere.

304 (2) The chemistry of isoprene should be treated in more detail than most other molecules. We  
305 recommend that there should be explicit chemistry through the first and second generation of  
306 isoprene oxidation, to better illustrate the role of isoprene in ozone production, OH budget and  
307 SOA production. No other species should be lumped with isoprene or its daughters. Even for

308 climate models that cannot afford this level of complexity, a reduced mechanism of isoprene  
309 oxidation should be generated for a wide range of conditions.

310 (3)  $\text{NO}_3$  chemistry is an important element of VOC oxidation,  $\text{NO}_x$  removal and aerosol production.  
311  $\text{NO}_3$  chemistry should be included in models that do not explicitly take it into account, both as a  
312 loss process of VOCs and  $\text{NO}_x$  and as a source of aerosols.

313 (4) The largest  $\text{NO}_x$  and BVOC emissions are not collocated, as one is mainly from mobile sources  
314 and power plants and the other one is mainly from forests (Yu et al., 2016; Travis et al., 2016). As  
315 a result, model resolution can impact predicted concentrations of trace species. Different model  
316 resolutions may lead to as much as 15% differences at the tails of the  $\text{NO}_x$  and HCHO  
317 distribution—less so for  $\text{O}_3$  (Yu et al., 2016; Valin et al., 2016). Depending on the research  
318 question models should evaluate the need to resolve this last 15% which requires a horizontal  
319 resolution of order 12 km or less.

## 320 **2.4 Key model diagnostics**

321 We identified a number of key diagnostics that should probably be evaluated before a model is  
322 used to pursue more interesting new questions. These include:

323 (1)  $\text{NO}_x$  concentrations from *in situ* and satellite observations. Models that do not predict the  
324 correct magnitude of  $\text{NO}_x$  should produce the wrong OH,  $\text{O}_3$ , and parent:daughter VOC ratios (e.g.  
325 Isoprene: Isoprene + IEPOX, Isoprene : MACR + MVK). At the low  $\text{NO}_x$  characteristic of the  
326 Southeast U.S. these errors are approximately linear—that is, a 15% error in  $\text{NO}_x$  should  
327 correspond to a 15% error in OH, isoprene and other related species. Given the difficulty in  
328 predicting  $\text{NO}_x$  to this tolerance, caution should be taken not to over interpret model predictions.

329 (2) HCHO from space based observations is emerging as a useful diagnostic of model oxidation  
330 chemistry (Valin et al., 2016).

331 (3) A significant fraction of isoprene remains at sunset and is available for oxidation via  $\text{O}_3$  or  $\text{NO}_3$   
332 at night. Analysis of nighttime isoprene and its oxidation products in the RL in the northeast U.S.  
333 in 2004 suggested this fraction to be 20% (Brown et al. 2009). Preliminary analysis from SENEX  
334 suggested a similar fraction, although the analysis depends on the emission inventory for isoprene,  
335 and would be 10-12% if isoprene emissions were computed from MEGAN (see Section 4.2 for the  
336 difference between BEIS and MEGAN). This fact might be a useful diagnostic of boundary layer  
337 dynamics and nighttime chemistry in models. The overnight fate of this isoprene depends strongly  
338 on available  $\text{NO}_x$  (see above). More exploration of the model prediction of the products of  $\text{NO}_3$  +  
339 isoprene and additional observations of those molecules will provide insight into best practices for  
340 using it as a diagnostic of specific model processes.

341 (4)  $\text{O}_3$  and aerosol concentrations and trends over decades and contrasts between weekdays and  
342 weekends across the Southeast remain a valuable diagnostic of model performance, especially as  
343 coupled to trends in  $\text{NO}_x$  on those same time scales.

## 344 **2.5 Open questions**

345 There are many open questions related to gas phase chemistry. Here we highlight a few that we  
346 believe are best addressed by the community of experimentalists and modelers working together  
347 (there were many other open questions that we think could be addressed by individual investigators  
348 pursuing modeling or experiments on their own).



349 (1) The sources and sinks of NO<sub>x</sub> are not well constrained in rural areas that cover most of  
350 Southeast U.S. As anthropogenic combustion related emissions experience further decline, what  
351 do we expect to happen to NO<sub>x</sub>? What observations would test those predictions?

352 (2) As we are reaching consensus on a mechanism for isoprene oxidation, the role of monoterpene  
353 and sesquiterpene oxidation is becoming a larger fraction of remaining uncertainty. Strategies for  
354 exploring and establishing oxidation mechanisms for these molecules and for understanding the  
355 level of detail needed in comprehensive and reduced mechanisms are needed.

356 (3β) Air quality modeling efforts have long been most interested in conditions that are not of top  
357 priority to meteorological researchers—e.g. stagnation. In addition to a better understanding of  
358 horizontal flows in stagnant conditions these experiments highlighted the need for a deeper  
359 understanding of the links between chemical mixing and boundary layer dynamics in day and night.  
360 A number of new chemical observations have been identified in the Southeast US data sets.  
361 Combined approaches using models and these observations to guide our thinking about PBL  
362 dynamics are needed.

### 363 **3. Organic aerosol**

#### 364 **3.1 Background**

365 Improving the representation of organic aerosol (OA) is a critical need for models applied to the  
366 Southeast. Current air quality and chemistry-climate models produce a very wide range of organic  
367 aerosol mass concentrations, with predicted concentrations spread over 1-2 orders-of-magnitude  
368 in free troposphere (Tsigaridis et al., 2014). Secondary OA (SOA) has traditionally been modeled  
369 by partitioning of semivolatile species between the gas and aerosol phase (Odum et al., 1996;  
370 Chung and Seinfeld, 2002; Farina et al., 2010), but very large uncertainties remain on the detailed  
371 formulations implemented in models (Spracklen et al., 2011; Heald et al., 2011; Tsigaridis et al.,  
372 2014). In particular, the recent identification of substantial losses of semivolatile and intermediate  
373 volatility species to Teflon chamber walls (Matsunaga and Ziemann, 2010; Zhang et al., 2014;  
374 Krechmer et al., 2016; Nah et al., 2016a) necessitate a re-evaluation of the gas-phase SOA yields  
375 used in models which has yet to be comprehensively performed. Models have difficulties to  
376 reproduce the mass loading of OA in both urban and rural areas, although order-of-magnitude  
377 underestimates have only been observed consistently for urban pollution (e.g. Volkamer et al.,  
378 2006; Hayes et al., 2015). Furthermore, current OA algorithms often rely on highly parameterized  
379 empirical fits to laboratory data that may not capture the role of oxidant (OH vs O<sub>3</sub> vs NO<sub>3</sub>) or  
380 peroxy radical fate. The peroxy radical fate for historical experiments in particular, may be biased  
381 compared to the ambient atmosphere where peroxy radical lifetimes are longer and autoxidation  
382 can be important.

383 Recent laboratory, field and model studies suggest that a significant fraction of SOA is formed in  
384 aqueous phase cloud droplets and aerosols, following gas-phase oxidation to produce soluble  
385 species (Sorooshian et al., 2007; Fu et al., 2008; Myriokefalitakis et al., 2011; Carlton et al., 2008;  
386 Tan et al., 2012; Ervens et al., 2011; Volkamer et al., 2009). This is also consistent with the strong  
387 correlation between OA and aerosol liquid water in the Southeast US over the past decade (Nguyen  
388 et al., 2015b). A number of gas-phase VOC oxidation products have been recognized as important  
389 precursors for aqueous production of SOA, including epoxides (Pye et al., 2013; Nguyen et al.,  
390 2014a; Surratt et al., 2010) and glyoxal (Liggio et al., 2005; Woo and McNeill, 2015; McNeill et  
391 al., 2012). Aerosol uptake of these oxygenated VOCs can be further complicated by aerosol acidity  
392 and composition (Pye et al., 2013; Paulot et al., 2009b; Nguyen et al., 2014a; Marais et al., 2016).

393 While a significant portion of ambient OA has been attributed to various source classes and  
394 precursors (e.g. BBOA from biomass burning, IEPOX-SOA from isoprene epoxydiols or IEPOX,  
395 and less-oxidized oxygenated OA, LO-OOA from monoterpenes), a large portion of ambient OA  
396 (e.g. more-oxidized oxygenated OA, MO-OOA) remains unapportioned. This portion lacks  
397 detailed chemical characterization or source attribution, so further investigation is warranted (Xu  
398 et al., 2015b; Xu et al., 2015a). A diversity of modeling approaches, including direct scaling with  
399 emissions, reactive uptake of gaseous species, and gas-aerosol partitioning etc., is encouraged to  
400 provide insight into OA processes, while trying to make use of all available experimental  
401 constraints to evaluate the models.

## 402 **3.2 Major relevant findings**

403 A number of modeling groups will be interested in modeling aerosol for the Southeast Atmosphere  
404 Study (SAS) across a variety of spatial and temporal scales. Different studies will be able to  
405 support different levels of detail appropriate for their application. Detailed box model  
406 representations can serve to confirm or refute mechanisms and, eventually, be condensed for  
407 application at larger scales such as those in chemical transport or global climate models. In the  
408 following sections, we highlight areas of organic aerosol that should be represented.

### 409 **3.2.1 Partitioning theory and phases**

410 No large kinetic limitations to partitioning are observed in the southeast and partitioning according  
411 to vapor pressure is active on short timescales (Lopez-Hilfiker et al., 2016). The higher relative  
412 humidity in this region, which results in fast diffusion in isoprene-SOA containing particles (Song  
413 et al., 2015), may be at least partially responsible for this behavior. In some instances (e.g. for key  
414 IEPOX-SOA species), observations indicate that detected OA species are significantly less volatile  
415 than their structure indicates, likely due to thermal decomposition of their accretion products or  
416 inorganic-organic adducts in instruments (Lopez-Hilfiker et al., 2016; Hu et al., 2016; Isaacman-  
417 VanWertz et al., 2016; Stark et al., 2017).

418 Further research is needed regarding the role of organic partitioning into OA versus water and this  
419 can be evaluated using field data. If both processes occur in parallel in the atmosphere, vapor  
420 pressure dependent partitioning to OA may occur along with aqueous processing without  
421 significant double counting or duplication in models. However, due to the high relative humidity  
422 (average RH is 74%, see Weber et al. (2016)) and degree of oxygenation of organic compounds  
423 (OM/OC is 1.9-2.25, see below) in the southeast US atmosphere, inorganic-rich and organic-rich  
424 phases may not be distinct (You et al., 2013) and more advanced partitioning algorithms  
425 accounting for a mixed inorganic-organic-water phase may be needed (Pye et al., 2017a; Pye et  
426 al., 2017b).

427 Phase separation can be predicted based on determining a separation relative humidity (SRH),  
428 which is a function of degree of oxygenation and inorganic constituent identity (You et al., 2013),  
429 and comparing to the ambient relative humidity. For  $RH < SRH$ , phase separation occurs. Pye et al.  
430 (2017a), predicted phase separation into organic-rich and electrolyte-rich phases occurs 70% of  
431 the time during SOAS at CTR with a higher frequency during the day due to lower RH.

### 432 **3.2.2 Primary organic aerosol**

433 Primary organic aerosol concentrations are expected to be small in the Southeast outside urban  
434 areas and we make no major recommendation for how to model them. Modelers should be aware  
435 that a fraction of primary organic aerosol (POA) based on the EPA National Emission Inventory  
436 (NEI) is semivolatile (Robinson et al., 2007). However, not all POA is thought to be semivolatile

437 – for example, OA from sources such as soil are included in the NEI. Modeled POA may already  
438 include some oxidized POA (OPOA) (if the models include heterogeneous oxidation (as in CMAQ  
439 (Simon and Bhawe, 2012)), or hydrophilic conversion (as in GEOS-Chem (Park et al., 2003))).  
440 Thus care should be exercised in evaluating model species such as POA with Aerosol Mass  
441 Spectrometer (AMS) Positive Matrix Factorization (PMF) factors such as hydrocarbon-like OA  
442 (HOA). For semivolatile POA treatments, mismatches between POA inventories and  
443 semivolatile/intermediate volatility organic compounds (S/IVOCs) needs to be carefully  
444 considered. Comparisons of model inventory versus ambient ratios of POA/ $\Delta$ CO, POA/black  
445 carbon (BC), or POA/ $\text{NO}_x$  can be used to indicate whether or not POA emissions are excessive  
446 (De Gouw and Jimenez, 2009). As these ratios can be affected by errors in the denominator species,  
447 it is important to also evaluate those carefully against observations. For models with limited POA  
448 information, the ratio of organic matter to organic carbon (OM/OC) should be adjusted to reflect  
449 the highly oxidized nature of ambient OA (as mass is transferred from hydrophobic/hydrophilic  
450 concentrations for example). The OM/OC ratio of bulk ambient OA in the Southeast US is 1.9-  
451 2.25 as measured during summer 2013 (Kim et al., 2015; Pye et al., 2017a).

452 A biomass burning PMF factor (BBOA) was observed during SOAS and likely has a higher impact  
453 on brown carbon (BrC) than its contribution to OA mass would suggest, although overall BrC  
454 concentrations were very small (Washenfelder et al., 2015). Net SOA mass added via  
455 photochemical processing of biomass burning emissions is thought to be modest, relative to the  
456 high POA emissions (Cubison et al., 2011; Jolleys et al., 2012; Shrivastava et al., 2017).

### 457 **3.2.3 Particle-phase organic nitrates**

458 Organic nitrates, primarily from monoterpene reactions with the nitrate radical, have been  
459 recognized as an important source of OA in the southeast, contributing from 5 to 12% in Southeast  
460 US in summer (Xu et al., 2015a; Ayres et al., 2015; Pye et al., 2015; Xu et al., 2015b; Lee et al.,  
461 2016a). In fact, this number could be an underestimate if some of these organic nitrates are  
462 susceptible to hydrolysis or photodegradation, and thus are not detected as nitrates. We have high  
463 confidence that models should include SOA formation from nitrate radical oxidation of  
464 monoterpenes. Sesquiterpenes and isoprene may also contribute OA through nitrate radical  
465 oxidation, but the contribution is expected to be smaller (Pye et al., 2015; Fisher et al., 2016). A  
466 number of options exist for representing this type of aerosol including fixed yields, Odum 2-  
467 product parameterizations, volatility basis set (VBS) representations (Boyd et al., 2015), and  
468 explicit partitioning/uptake of organic nitrates (Pye et al., 2015; Fisher et al., 2016).

469 Detailed modeling studies can provide additional insight into the interactions between  
470 monoterpene nitrate SOA and gas-phase chemistry, as well as the fates of specific organic nitrates.  
471 Explicit formation and treatment of organic nitrates, yields of which are parent hydrocarbon  
472 specific, can take into account hydrolysis of particle-phase organic nitrate (ON). The hydrolysis  
473 should depend on the relative amounts of primary, secondary, and tertiary nitrates which are  
474 produced in different abundances in photooxidation vs. nitrate radical oxidation (Boyd et al., 2015;  
475 Boyd et al., 2017). Hydrolysis may also depend on the level of acidity and presence of double  
476 bonds in the organic nitrate (Jacobs et al., 2014; Rindelaub et al., 2016). In addition to hydrolysis,  
477 particle organic nitrates could photolyze and release  $\text{NO}_x$  or serve as a  $\text{NO}_x$  sink through deposition  
478 (Nah et al., 2016b).

479 Formation of organic nitrates should also be considered in the context of emerging evidence for  
480 the role of autoxidation, especially in the monoterpene system (Ehn et al., 2014). Autoxidation has  
481 been shown to occur in both photooxidation and ozonolysis of monoterpenes (Jokinen et al., 2015)

482 and leads to highly oxidized species including organic nitrates (Lee et al., 2016a; Nah et al., 2016b),  
483 many of which are low volatility. While some empirical representations (e.g. VBS or Odum 2-  
484 product) of monoterpene SOA may capture these species, autoxidation products may be very  
485 susceptible to chamber wall loss (Zhang et al., 2014; Krechmer et al., 2016) and missing from  
486 SOA parameterizations. The role of autoxidation in forming SOA in the southeastern US  
487 atmosphere remains to be determined. In this regard, future laboratory studies should carefully  
488 constrain the peroxy radical reaction channels (e.g. Schwantes et al., 2015; Boyd et al., 2015) and  
489 be conducted under regimes that are representative of ambient environments where the peroxy  
490 radical lifetimes can vary.

### 491 **3.2.4 Isoprene epoxydiol (IEPOX) SOA**

492 Due to the abundance of observations in the Southeastern atmosphere (Budisulistiorini et al., 2016;  
493 Hu et al., 2015b; Xu et al., 2015a; Xu et al., 2015b; Xu et al., 2016; Hu et al., 2016), similarity  
494 between laboratory and field IEPOX-SOA determined by PMF analysis, and availability of model  
495 parameterizations to predict IEPOX-SOA (Pye et al., 2013; Woo and McNeill, 2015; Marais et al.,  
496 2016; Budisulistiorini et al., 2017; Sareen et al., 2017), we have high confidence that IEPOX-SOA  
497 should be included in models. D'Ambro et al. (2017) predicts IEPOX will be the major precursor  
498 to SOA under low-NO<sub>x</sub> conditions when peroxy radical lifetimes are atmospherically relevant,  
499 which has not always been the case in older experiments. However, a number of parameters needed  
500 to predict IEPOX-SOA are uncertain and different modeling approaches, as well as the use of all  
501 available experimental constraints, could be beneficial. The mechanism of IEPOX-SOA formation  
502 involves gas-phase reactions followed by aqueous processing which can occur either in aerosols  
503 or cloud droplets, although the acid-catalyzed initiation step of the epoxide ring opening favors SE  
504 USA aerosol conditions and makes this process less efficient in cloud water. This mechanism could  
505 be represented as heterogeneous reaction with a reactive uptake coefficient or more explicit  
506 partitioning and particle reaction (Table 1).

507 The correlation of IEPOX-SOA with sulfate (Xu et al., 2015a; Xu et al., 2016; Hu et al., 2015b)  
508 can serve as a useful model evaluation technique as underestimates in sulfate could lead to  
509 underestimates in IEPOX-SOA in models (Figure 2). Current pathways for IEPOX-SOA  
510 formation (Eddingsaas et al., 2010) involve acidity in aqueous solutions (Kuwata et al., 2015), but  
511 several studies suggest that IEPOX-SOA is not correlated well with aerosol acidity or aerosol  
512 water (Budisulistiorini et al., 2017; Xu et al., 2015a). Ion balances or other simple measures of  
513 aerosol acidity are likely inadequate to characterize particle acidity and thermodynamic models  
514 such as ISORROPIA II or AIM are more appropriate for modeling IEPOX-SOA (Guo et al., 2015;  
515 Weber et al., 2016). Currently, different observational datasets indicate different nominal ratios of  
516 ammonium to sulfate (Pye et al., 2017b), so it needs to be kept in mind that some measurements  
517 report only inorganic sulfate (e.g. ion chromatography) while others report total (inorganic +  
518 organic) sulfate (e.g. AMS). A modeling study suggested that ammonia uptake might be limited  
519 by organics, thus affecting acidity (Kim et al., 2015; Silvern et al., 2017).

520 SAS observations also provide estimates of some components of IEPOX-SOA including 2-  
521 methyltetrols and IEPOX-organosulfates (Budisulistiorini et al., 2015; Hu et al., 2015b). For  
522 modeling applications focusing on IEPOX-SOA, additional speciation of IEPOX-SOA (into  
523 tetrols, organosulfates, etc.) and oligomerization and volatility can be treated. Treating the  
524 monomers (e.g. 2-methyltetrols) explicitly with their molecular properties will likely lead to  
525 excessive volatility of the IEPOX-SOA (Lopez-Hilfiker et al., 2016; Hu et al., 2016; Isaacman-  
526 VanWertz et al., 2016; Stark et al., 2017).

### 527 **3.2.5 Glyoxal SOA**

528 New information on glyoxal SOA is emerging in this area but its importance in the Southeast  
529 remains unclear. Glyoxal has been suspected to be the dominant aqueous SOA source under high-  
530  $\text{NO}_x$  ( $\text{RO}_2 + \text{NO}$ ) oxidation conditions (McNeill et al., 2012) and the Southeast has a mix of high-  
531  $\text{NO}_x$  and low- $\text{NO}_x$  ( $\text{RO}_2 + \text{HO}_2$ ) conditions (Travis et al., 2016). In addition, abundant isoprene  
532 emissions can lead to substantial glyoxal concentrations. Modeling for the southeastern U.S.  
533 indicates significant SOA can form from glyoxal (Marais et al., 2016; Pye et al., 2015; Knote et  
534 al., 2014; Li et al., 2016; Chan Miller et al., 2017). Implementation in models may require  
535 modifications to the gas-phase chemistry to specifically track glyoxal which may be lumped with  
536 other aldehydes (e.g. in CB05). Recent model studies do not find that a large SOA source from  
537 glyoxal is required to match observations, but more field measurements and laboratory studies,  
538 especially of the yield from isoprene oxidation and the aerosol uptake coefficient, are required to  
539 constrain the process.

### 540 **3.2.6 Cloud SOA**

541 Results from SOAS and SEAC4RS indicate only a modest enhancement of OA due to cloud  
542 processing over the SE US, which was not statistically significant (Wagner et al., 2015). In addition,  
543 epoxide reactions in cloud droplets are predicted to lead to minor amounts of SOA due to the pH  
544 dependence of IEPOX hydrolysis (Fahey et al., 2017; McNeill, 2015).

### 545 **3.2.7 SOA from Anthropogenic Emissions**

546 While the rural southeast is assumed to be dominated by SOA from biogenic precursors (which  
547 may be influenced by anthropogenic pollution) as a result of high modern carbon (Hidy et al.,  
548 2014), SOA from anthropogenic VOCs is known to play a role from fossil carbon measurements  
549 (~18% at Centerville) (Kim et al., 2015), but it is not directly apportioned otherwise. We note that  
550 since ~50% of urban POA and 30% of urban SOA is non-fossil (Zotter et al., 2014; Hayes et al.,  
551 2015), an urban fraction of ~28% for the SOAS site is consistent with observations (Kim et al.,  
552 2015). This source is as large as most of the other individual sources discussed in this section, and  
553 should not be neglected in modeling studies. A simple parameterization based on CO emissions  
554 (Hayes et al., 2015) may be adequate for incorporating this source in modeling studies and has  
555 shown good results for the Southeast US (Kim et al., 2015), but care should be taken to evaluate  
556 the CO emissions when using it.

### 557 **3.2.8 Surface network observations of organic aerosols**

558 We list several caveats for the process of comparing model results to surface network observations.  
559 OC measurements from IMPROVE surface sites may be biased low in the summer due to  
560 evaporation of organic aerosols during the sample collection and handling (Kim et al., 2015). On  
561 the other hand, SEARCH measurements agree well with research community instruments in  
562 Centerville site, such as AMS. Therefore the SEARCH data should be considered as the reference.

563 Decreases in mass concentrations of particulate sulfate and nitrate over the past decades is  
564 consistent with environmental policy targeting their gas phase precursors, namely  $\text{SO}_x$  and  $\text{NO}_x$   
565 emissions. Reductions in particulate organic carbon in the southeastern U.S. over the past decade  
566 (Blanchard et al., 2016; Blanchard et al., 2013) are more difficult to reconcile because in the  
567 summertime it is predominantly modern and there is no control policy aimed at reducing biogenic  
568 VOCs. Decreased  $\text{SO}_x$  (Kim et al., 2015; Xu et al., 2015b; Blanchard et al., 2013) and  $\text{NO}_x$   
569 emissions modulate the amount of organic aerosol formation through the gas phase impacts

570 described above, and impacts on the absorbing medium amount (Nguyen et al., 2015b; Attwood  
571 et al., 2014) and chemical composition.

572 In addition to sources and sinks of OA, attention should also be paid to the role of dry deposition  
573 of gases in determining mass loadings, as this process can have a large impact on model predictions  
574 and is very poorly constrained (Glasius and Goldstein, 2016; Knote et al., 2015).

### 575 **3.2.8 Climate relevant properties**

576 A motivating goal of the southeast studies was to examine PM mass measurements at the surface  
577 and satellite-measured AOD, to facilitate improved prediction of the total aerosol loading. Aerosol  
578 mass aloft contributes to AOD (Wagner et al., 2015), and this complicates the relationship to  
579 surface concentrations. Relative humidity, vertical structure of the daytime PBL, and aerosol liquid  
580 water (not measured by surface networks) influences remotely sensed AOD (Brock et al., 2016a;  
581 Brock et al., 2016b; Kim et al., 2015; Nguyen et al., 2016). AOD is also complicated by aerosol  
582 composition. Attwood et al. (2014) finds that the steeper decrease in sulfate aerosol relative to  
583 organic from 2001 to 2013, has changed the hygroscopicity of SE US aerosol, leading to lower  
584 aerosol liquid water and thus lower optical extinction and AOD.

### 585 **3.3 Model recommendations**

586 Based upon the improved understanding outlined above, we make the following recommendations  
587 for the future modeling efforts:

588 (1) There is high confidence that a pathway of SOA formation from isoprene epoxydiol (IEPOX)  
589 should be included in models. However, since many of the parameters needed to predict IEPOX-  
590 SOA are uncertain, further mechanistic studies are needed to address these uncertainties.

591 (2) There is high confidence that models should include SOA formation from nitrate radical  
592 oxidation of monoterpenes (with or without explicit nitrate functionality). Sesquiterpenes and  
593 isoprene may also contribute SOA through nitrate radical oxidation, but the contribution is  
594 expected to be smaller.

595 (3) More field measurements and laboratory studies, especially of the yield from isoprene  
596 oxidation and the aerosol uptake coefficient, are required to constrain the importance of glyoxal  
597 SOA.

598 (4) There is high confidence that models should predict SOA from urban emissions with a  
599 parameterization that results in realistic concentrations. The non-fossil fraction of urban POA and  
600 SOA needs to be taken into account when interpreting modern carbon measurements.

601 (5) Current SOA modeling efforts should be coupled with an up-to-date gas-phase chemistry, to  
602 provide realistic concentrations for several important SOA precursors, including IEPOX, glyoxal,  
603 organic nitrates etc.

### 604 **3.4 Open questions**

605 A number of open questions remain that would benefit from modeling studies:

606 (1) What is the role of particle-phase organic nitrates in removing or recycling  $\text{NO}_x$  from the  
607 system?

608 (2) How much detail do models need to represent in terms of types of organic nitrate (ON)?

609 (3) What are the formation mechanisms of highly oxygenated organics?

610 (4) What anthropogenic sources of SOA are models missing?

611 (5) What climate-relevant aerosol properties are needed in models? What are the controls over  
612 the presence and lifetime of condensed liquid water? What model and observational diagnostics  
613 serve as tests of our understanding?

614 (6) What is the role of clouds in forming and processing organic aerosols?

## 615 **4. Emissions**

### 616 **4.1 Background**

617 Emission inventories are a critical input to atmospheric models, and reliable inventories are needed  
618 to design cost-effective strategies that control air pollution. For example, in the 1970s and 1980s,  
619 emission control strategies implemented under the Clean Air Act emphasized the control of  
620 anthropogenic VOC emissions over NO<sub>x</sub> (National Research Council, 2004). Despite large order  
621 of magnitude reductions in anthropogenic VOC emissions (Warneke et al., 2012), abatement of  
622 O<sub>3</sub> was slow in many regions of the country. In the late 1980s, a large and underrepresented source  
623 of biogenic VOC emissions was identified (Trainer et al., 1987; Abelson, 1988; Chameides et al.,  
624 1988), putting into question the effectiveness of anthropogenic VOC emission control strategies  
625 to mitigate O<sub>3</sub> nationally (Hagerman et al., 1997). Since the mid-1990s, large reductions in NO<sub>x</sub>  
626 emissions have resulted from: (i) controls implemented at power plants (Frost et al., 2006), (ii)  
627 more durable three-way catalytic converters installed on gasoline vehicles (Bishop and Stedman,  
628 2008), and (iii) more effective regulation of diesel NO<sub>x</sub> emissions from heavy-duty trucks  
629 (Yanowitz et al., 2000; McDonald et al., 2012). Emission reductions implemented on combustion  
630 sources, have also been linked to decreases in organic aerosol concentrations observed in both  
631 California (McDonald et al., 2015) and the Southeastern U.S. (Blanchard et al., 2016). Though  
632 substantial progress has been made in improving scientific understanding of the major biogenic  
633 and anthropogenic sources of emissions contributing to air quality problems, some issues remain  
634 in current U.S. inventories and are highlighted below.

635 The Southeast US is a region that has both large natural emissions and anthropogenic emissions.  
636 The accurate knowledge of biogenic emissions is key to understanding many of the processes that  
637 lead to ozone and aerosol formation. Previous studies suggest that MEGANv2.1 can estimate twice  
638 as large isoprene emissions compared with BEIS over the Eastern US (Warneke et al., 2010;  
639 Carlton and Baker, 2011), but most global models using MEGANv2.1 do not show a significant  
640 bias of isoprene over the Southeast US (Mao et al., 2013; Millet et al., 2006). This is likely due to  
641 different landcover data being used in the regional and global applications of MEGAN. Validation  
642 of the various biogenic emission inventories was therefore one of the main science questions for  
643 the SAS studies.

644 The National Emissions Inventory (NEI) developed by U.S. EPA, is an inventory of air pollutants  
645 released every three years, and commonly used in U.S.-based air quality modeling studies. A  
646 recent modeling study reported that NO<sub>x</sub> emissions from mobile source emissions were  
647 overestimated by 51-70% in the Baltimore-Washington, D.C. region (Anderson et al., 2014). Past  
648 studies have also found discrepancies in motor vehicle emission models used by EPA to inform  
649 the NEI (Parrish, 2006; McDonald et al., 2012). Additionally, problems have been identified in  
650 estimates of NO<sub>x</sub>, VOC, and methane emissions from U.S. oil and gas development (Ahmadov et  
651 al., 2015; Pétron et al., 2014; Brandt et al., 2014). Some major oil and gas basins of note are located  
652 in the Southeastern U.S., which were measured by aircraft during the SAS2013 studies. In contrast  
653 to mobile source and oil and gas emissions, power plant emissions of NO<sub>x</sub> and SO<sub>x</sub> are believed

654 to be known with greater certainty since large stationary sources of emissions are continuously  
655 monitored. In addition to biogenic emission inventories, the datasets collected by the SAS2013  
656 studies have provided an opportunity to assess the accuracy of anthropogenic emissions and their  
657 impacts on atmospheric chemistry.

658 The topic of model resolution, which involves the relationship between emissions and chemistry,  
659 is also key to interpreting model-observation comparisons. Regional-scale air quality models can  
660 be simulated at very high horizontal resolutions (e.g., 1 km and finer) (Joe et al., 2014); however,  
661 typically they are run at coarser resolutions, such as at 12 km by 12 km (e.g., continental U.S.)(Gan  
662 et al., 2016) or 4 km by 4 km (e.g., urban scale) (Kim et al., 2016b). The horizontal resolution of  
663 global chemistry models has significantly improved, with nesting being performed at horizontal  
664 resolutions as fine as  $0.25^{\circ} \times 0.3125^{\circ}$  degree (Travis et al., 2016). Coarse model resolutions can  
665 complicate evaluations with high spatial and temporal-resolution measurements (e.g., from aircraft)  
666 of chemical constituents undergoing fast chemistry (e.g., isoprene, OH) (Kaser et al., 2015). Sharp  
667 concentration gradients are observable from space for species with relatively short atmospheric  
668 lifetimes (e.g., nitrogen dioxide, formaldehyde, and glyoxal), and potentially provide insights into  
669 the role of natural and anthropogenic emissions on air quality (Duncan et al., 2010; Russell et al.,  
670 2012; Lei et al., 2014). Lastly, some emission sources are described by large emission intensities  
671 (e.g., power plants and biomass burning), which result in elevated concentrations of emitted  
672 species downwind. A coarse model will artificially dilute these high emission fluxes (e.g.,  $\text{NO}_x$   
673 and  $\text{SO}_x$ ) over a wider area, which could alter the chemical regime by which ozone (Ryerson et al.,  
674 1998; Ryerson et al., 2001) and secondary aerosols (Xu et al., 2015a) form.

## 675 **4.2 Major relevant findings**

### 676 **4.2.1 Biogenic emissions**

677 Isoprene emissions measured by the NOAA P3, using the mixed boundary layer budget method,  
678 and NCAR/NSF C-130 and NASA DC-8 aircraft using direct eddy covariance flux measurements  
679 were within the wide range of observations reported by previous studies. The two methods of  
680 estimating isoprene emissions agreed within their uncertainties (Yu et al., 2017). Solar radiation  
681 and temperature measured by the aircraft along the flight tracks and available from regional model  
682 and assimilations (e.g., WRF, NLDAS-2) enabled estimation of emissions using models including  
683 BEIS3.12, BEIS3.13, MEGAN2.0, MEGAN2.1 with default landcover, MEGAN2.1 with revised  
684 landcover, and MEGAN3. Isoprene emissions are highly sensitive to solar radiation and  
685 temperature and biases in the values used to drive emission models can result in errors exceeding  
686 40% and complicating efforts to evaluate biogenic emission models. As has previously been noted  
687 in the southeastern US, MEGAN2.1 predicted isoprene emissions in the Southeast US were about  
688 twice as high as BEIS3.13. The measurements fall between the two models and are within the  
689 model and measurement uncertainties (Warneke et al. 2010). Isoprene mixing ratios were modeled  
690 with a) WRF-Chem using BEIS and with b) CAMx using MEGAN and the results were consistent  
691 with the measurement-inventory comparison: WRF-Chem was biased low and CAMx biased high  
692 (Warneke et al., in preparation).

693 Landcover characteristics including Leaf Area Index (LAI) and tree species composition data are  
694 also critical driving variables for BEIS and MEGAN isoprene and monoterpene emission estimates.  
695 Airborne flux measurements agreed well with MEGAN2.1 for landscapes dominated by  
696 southeastern oaks, which are high isoprene emitting tree species, but landscapes that had an  
697 overstory of non-emitters, with the high isoprene emitters in the understory, showed emissions  
698 lower than expected by the model. The isoprene emission factor was linearly correlated with the



699 high isoprene emitter plant species fraction in the landcover data set. This may indicate a need for  
700 models to include canopy vertical heterogeneity of the isoprene emitting fraction (Yu et al., 2017).

701 A simplification used in current biogenic emission models including BEIS3.13, BEIS3.6, and  
702 MEGAN2.1 is that all high isoprene emitting species are assigned the same isoprene emission  
703 factor. For example, all North American species of *Quercus* (oak), *Liquidambar* (sweetgum),  
704 *Nyssa* (tupelo), *Platanus* (sycamore), *Salix* (willow), *Robinia* (locust) and *Populus* (poplar and  
705 aspen) are assigned a single value based on the average of an extensive set of enclosure  
706 measurements conducted in North Carolina, California and Oregon in the 1990s (Geron et al.,  
707 2001). Earlier studies had reported isoprene emission factors for these tree species that ranged  
708 over more than an order of magnitude (Benjamin et al., 1996). Geron et al. (2001) showed that by  
709 following specific measurement protocols, including leaf cuvettes with environmental controls and  
710 ancillary physiological measurements such as photosynthesis, the variability dropped from over  
711 an order of magnitude to about a factor of 3. They concluded that this remaining variability was  
712 due at least as much to growth conditions as to species differences and so recommended that a  
713 single isoprene emission factor be used for all of these species. Recent aircraft flux measurements  
714 (Misztal et al., 2016; Yu et al., 2017) indicate that there is at least a factor of two difference in the  
715 isoprene emission factors of these species. This could be due to a genetic difference in emission  
716 capacity and/or differences in canopy structure. The aircraft measurements indicate that sweetgum  
717 and tupelo emission factors are similar to the value used in BEIS3.13 and BEIS3.6 while the  
718 California oak emission factor is similar to that used in MEGAN2.1. The aircraft based estimate  
719 of southeastern oak emission factors falls between the BEIS3.6 and MEGAN2.1 values. As a result,  
720 aircraft flux measurements in the southeastern US are higher than BEIS3.13/BEIS3.6 and lower  
721 than MEGAN2.1. The MEGAN3 emission factor processor provides an approach for synthesizing  
722 available emission factor data and can be used to account for the emission rate variability observed  
723 by these aircraft flux studies (Guenther et al., in preparation).

724 Modeling monoterpene emissions is even more challenging than isoprene emissions for reasons  
725 that include multiple emission processes (e.g., both light dependent and light independent  
726 emissions), stress-induced emission capability present in many plant species but not always  
727 expressed, and the potential for enclosure measurements to dramatically overestimate emissions  
728 due to release of monoterpenes from damaged storage pools. The eddy covariance flux  
729 measurements on the NCAR/NSF C130 are similar to the values estimated by MEGAN2.1 for  
730 needle leaf forests, considered to be high emission regions, but are higher than the modeled  
731 monoterpene emissions from other landscapes (Yu et al., 2017). They conclude that unaccounted  
732 processes, such as floral and stress emissions, or sources such as non-tree vegetation may be  
733 responsible for the unexpectedly high monoterpene emissions observed by the aircraft.

734 During the experiment direct observations of fluxes for a variety of species from large aircraft  
735 were conducted, enabling a first direct estimate of fluxes over a regional domain (Wolfe et al.,  
736 2015; Yuan et al., 2015; Kaser et al., 2015). These data have the potential for enabling analyses of  
737 strengths and weaknesses of current emission and deposition schemes and their implementation  
738 within chemical transport models. Vertical flux profiles also contain information on the chemical  
739 production and loss rates, providing a new observational constraint on the processes controlling  
740 reactive gas budgets. An LES model was used to simulate isoprene,  $\text{NO}_x$  and their variability in  
741 the boundary layer. The results showed good agreement between the measurements and the model.  
742 The atmospheric variability of isoprene, the altitude profile in the boundary layer of isoprene and  
743  $\text{NO}_x$  mixing ratios and fluxes were well reproduced in the model, which was used to validate the

744 eddy covariance and mixed boundary layer methods of estimating isoprene fluxes (Kim et al.,  
745 2016a; Wolfe et al., 2015).

#### 746 **4.2.2 Anthropogenic emissions**

747 Travis et al. (2016) utilizing the GEOS-Chem model report that NO<sub>x</sub> emissions are significantly  
748 overestimated by the NEI 2011, and suggest that mobile source and industrial emissions of NO<sub>x</sub>  
749 need to be lowered by 30-60% to be consistent with aircraft measurements collected over the  
750 Southeastern U.S. during the SEAC4RS Study. These results are consistent with modeling studies  
751 performed during the DISCOVER-AQ field campaign, which also found that the NEI 2011  
752 overestimated NO<sub>x</sub> emissions (Anderson et al., 2014; Souri et al., 2016). However, a later study  
753 by Li et al. (2017) utilizing the AM3 model during the SENEX Study suggests that overestimates  
754 in NEI 2011 NO<sub>x</sub> emissions may be smaller than reported in the Travis et al. study (~14% vs. 30-  
755 60%). McDonald et al. (in preparation) using WRF-Chem, found mobile source emissions in the  
756 NEI 2011 to be overestimated by ~50% and a factor of 2.2 for NO<sub>x</sub> and CO, respectively, when  
757 evaluated with SENEX aircraft measurements. Due to rapidly declining trends in vehicle emissions  
758 (McDonald et al., 2013; McDonald et al., 2012), some of the emissions overestimate was attributed  
759 to utilizing a 2011 inventory in 2013 model simulations. However, roadside measurements of  
760 vehicular exhaust also suggest systematic overestimates in emission factors used by EPA's vehicle  
761 emissions model (MOVES), likely contributing to the consistent reporting to date of overestimated  
762 mobile source NO<sub>x</sub> emissions (Anderson et al., 2014; Souri et al., 2016; Travis et al., 2016). When  
763 NO<sub>x</sub> emissions were reduced from mobile sources by this amount, model predictions of O<sub>3</sub> over  
764 the Southeastern U.S. were improved both for mean concentrations and O<sub>3</sub> extreme days  
765 (McDonald et al., in preparation), consistent with modeling by Li et al. (2017) demonstrating the  
766 sensitivity of O<sub>3</sub> to NO<sub>x</sub> emissions in the Southeastern U.S. over the 2004-2013 timespan.

767 Along with other aircraft field campaigns and tall tower measurements in the Upper Midwest, data  
768 from the SENEX Study was used to assess anthropogenic emissions of VOCs in the NEI and a  
769 global inventory (RETRO). Hu et al. (2015a) found that RETRO consistently overestimates U.S.  
770 emissions of C6-C8 aromatic compounds, by factors of 2 - 4.5; the NEI 2008 overestimates toluene  
771 by a factor of 3, but is consistent with top-down emission estimates for benzene and C8 aromatics.  
772 The study also suggests that East Asian emissions are an increasingly important source of benzene  
773 concentrations over the U.S., highlighting the importance of long-range transport on U.S. air  
774 quality as domestic sources of emissions decline (Warneke et al., 2012).

775 Two studies have quantified top-down emissions of oil and gas operations, derived from aircraft  
776 measurements for VOCs and methane from SENEX P-3 data (Peischl et al., 2015; Yuan et al.,  
777 2015). The oil and gas regions measured during SENEX account for half of the U.S. shale gas  
778 production, and loss rates of methane to the atmosphere relative to production were typically lower  
779 than prior assessments (Peischl et al., 2015). Yuan et al. (2015) explored the utility of eddy-  
780 covariance flux measurements on SENEX and NOMADDS aircraft campaigns, and showed that  
781 methane emissions were disproportionately from a subset of higher emitting oil and gas facilities.  
782 Strong correlations were also found between methane and benzene, indicating that VOCs are also  
783 emitted in oil and gas extraction. High wintertime O<sub>3</sub> has been found in the Uinta Basin, UT  
784 (Ahmadov et al., 2015; Edwards et al., 2014), though it is unclear at this time how significant oil  
785 and gas emissions of VOCs could be in an isoprene-rich source region on tropospheric O<sub>3</sub>  
786 formation. Future atmospheric modeling efforts of oil and gas emissions are needed.

787 During the SENEX and SEAC4RS studies, research aircraft measured agricultural fires over the  
788 Southeast. Liu et al. (2016) reported emission factors of trace gases, which were consistent with  
789 prior literature. In general, the authors' found emissions of SO<sub>2</sub>, NO<sub>x</sub>, and CO from agricultural  
790 fires to be small relative to mobile sources (<10%). However, within fire plumes, rapid O<sub>3</sub>  
791 formation was observed, indicating potential air quality impacts on downwind communities. To  
792 represent the impact of biomass burning, air quality models need improved treatments of initial  
793 VOC and NO<sub>x</sub> emissions and near source chemistry. Sub-grid parameterizations, based on detailed  
794 models like the Aerosol Simulation Program (ASP) (Alvarado and Prinn, 2009) and which  
795 incorporates gas-phase chemistry, inorganic and organic aerosol thermodynamics, and evolution  
796 of aerosol size distribution and optical properties, could improve coarse model representations of  
797 chemistry near biomass burning plumes. Zarzana et al. (2017) investigated enhancements of  
798 glyoxal and methylglyoxal relative to CO from agricultural fires, and report that global models  
799 may overestimate biomass burning emissions of glyoxal by a factor of 4. This highlights large  
800 uncertainties and variability in fire emissions, and a need for additional observational constraints  
801 on inventories and models.

### 802 **4.3 Model Recommendations and Future Work**

803 (1) In the Southeast US isoprene emissions are so large that they influence most atmospheric  
804 chemistry processes. Users of model simulations using the different isoprene inventories have to  
805 be aware of the differences. For example, OH and isoprene concentrations are anti-correlated (Kim  
806 et al 2015) and model simulations using BEIS will potentially have higher OH than simulations  
807 using MEGAN and chemistry will proceed at different rates. In addition, modeled products from  
808 isoprene oxidation in the gas and particle phase will be different. Isoprene derived SOA or  
809 secondary CO in the Southeast US can vary by a factor two between the two inventories.

810 (2) For future work, BEIS3.6 is now available and needs to be evaluated using the methods  
811 described here.

812 (3) MEGAN3 emission factor processor can be used to synthesize the available emission factor  
813 estimates from SAS and other studies. A beta version of the MEGAN3 emission factor processor  
814 and MEGAN3 model processes is available and should be evaluated.

815 (4) A revised NO<sub>x</sub> emissions inventory is needed to improve air quality models for O<sub>3</sub>, especially  
816 in the Southeast U.S. where O<sub>3</sub> is sensitive to changes in NO<sub>x</sub> emissions. Anthropogenic emissions  
817 of NO<sub>x</sub> in the NEI 2011 may be overestimated by 14-60% in the Southeastern U.S. during the  
818 SAS2013 study time period (Travis et al., 2016; Li et al., 2017).

## 819 **5. Chemistry-Climate Interactions**

### 820 **5.1 Background**

821 Interactions between atmospheric chemistry and climate over the southeastern United States are  
822 not well quantified. The dense vegetation and warm temperatures over the Southeast result in  
823 large emissions of isoprene and other biogenic species. These emissions, together with  
824 anthropogenic emissions, lead to annual mean aerosol optical depths (AODs) of nearly 0.2, with a  
825 peak in summer (Goldstein et al., 2009). The climate impacts of US aerosol trends in the Southeast  
826 due to changing anthropogenic emissions is under debate (e.g. Leibensperger et al., 2012a, b; Yu  
827 et al., 2014). Climate change can, in turn, influence surface air quality, but even the sign of the  
828 effect is unknown in the Southeast (Weaver et al., 2009). Part of this uncertainty has to do with  
829 complexities in the mechanism of isoprene oxidation, the details of which are still emerging from

830 laboratory experiments and field campaigns (Liao et al., 2015; Fisher et al., 2016; Marais et al.,  
831 2016). In addition, the influence of day-to-day weather on surface ozone and particulate matter  
832 (PM<sub>2.5</sub>) has not been fully quantified, and climate models simulate different regional climate  
833 responses. Resolving these uncertainties is important, as climate change in the coming decades  
834 may impose a “climate penalty” on surface air quality in the Southeast and elsewhere (Fiore et al.,  
835 2015).

## 836 **5.2 Key science issues and recent advances.**

837 We describe recent advances in four areas related to chemistry-climate interactions in the  
838 Southeast.

### 839 **5.2.1. Seasonality and trends in aerosol loading in the Southeast**

840 Using satellite data, Goldstein et al. (2009) diagnosed summertime enhancements in AOD of 0.18  
841 over the Southeast, relative to winter, and hypothesized that secondary organic aerosol from  
842 biogenic emissions accounts for this enhancement. Goldstein et al. (2009) further estimated a  
843 regional surface cooling of  $-0.4 \text{ W m}^{-2}$  in response to annual mean AOD over the Southeast. These  
844 findings seemed at first at odds with surface PM<sub>2.5</sub> measurements, which reveal little seasonal  
845 enhancement in summer. Using SEAC4RS measurements and GEOS-Chem, Kim et al. (2015)  
846 determined that the relatively flat seasonality in surface PM<sub>2.5</sub> can be traced to the deeper boundary  
847 layer in summer, which dilutes surface concentrations.

848 In response to emission controls, aerosol loading over the Southeast has declined in recent decades.  
849 For example, wet deposition fluxes of sulfate decreased by as much as ~50% from the 1980s to  
850 2010 (Leibensperger et al., 2012a). Over the 2003-2013 time period, surface concentrations of  
851 sulfate PM<sub>2.5</sub> declined by 60%. Organic aerosol (OA) also declined by 60% even though most OA  
852 appears to be biogenic and there is no indication of a decrease in anthropogenic sources (Kim et  
853 al., 2015). Model results suggest that the observed decline in OA may be tied to the decrease in  
854 sulfate, since OA formation from biogenic isoprene depends on aerosol water content and acidity  
855 (Marais et al., 2016; Marais et al., 2017). Consistent with these surface trends, 550-nm AOD at  
856 AERONET sites across the Southeast has also decreased, with trends of  $-4.1\% \text{ a}^{-1}$  from 2001-2013  
857 (Attwood et al., 2014). Xing et al. (2015a) reported a roughly -4% decrease in remotely sensed  
858 AOD across the eastern United States, as measured by the Moderate Resolution Imaging and  
859 Spectroradiometer (MODIS) on board Terra and Aqua. These large declines could potentially have  
860 had a substantial impact on regional climate, both through aerosol-radiation interactions and  
861 aerosol-cloud interactions.

### 862 **5.2.2. Contribution of aerosol trends to the U.S. “warming hole.”**

863 Even as global mean temperatures rose over the 20th century in response to increasing greenhouse  
864 gases, significant cooling occurred over the central and southeastern United States. This cooling,  
865 referred to as the U.S. warming hole (Pan et al., 2004), has been quantified in several ways. For  
866 example, Figure 3 shows that annual mean temperatures across the Southeast decreased by ~1 °C  
867 during the 1930-1990 timeframe (Capparelli et al., 2013). A different temperature metric, the 20-  
868 year annual return value for the hot tail of daily maximum temperatures, decreased by 2 °C from  
869 1950 to 2007 (Grotjahn et al., 2016). Over a similar time frame, Portmann et al. (2009) diagnosed  
870 declines in maximum daily temperatures in the Southeast of 2-4 °C per decade, with peak declines  
871 in May-June, and linked these temperature trends with regions of high climatological precipitation.  
872 Since the early 2000s, the cooling trend has appeared to reverse (Meehl et al., 2015).

873 The causes of the U.S. warming hole are not clear. Most freely running climate models  
874 participating in the Coupled Model Intercomparison Project (CMIP5) cannot capture the observed  
875 20th century temperature trends over the Southeast (Knutson et al., 2013; Kumar et al., 2013;  
876 Sheffield et al., 2013); this failure likely arises from either model deficiency or natural variability  
877 not included in the simulations. Indeed, several studies have argued that naturally occurring  
878 oscillations in sea surface temperatures (SSTs) influenced the large-scale cooling in the Southeast  
879 (Robinson et al., 2002; Kunkel et al., 2006; Meehl et al., 2012; Weaver, 2013; Mascioli et al.,  
880 2017). Kumar et al. (2013), for example, linked the June-July-August indices of the Atlantic  
881 Multidecadal Oscillation (AMO) to annual mean temperatures across the eastern U.S. for the 1901-  
882 2004 period. Mauget and Cordero (2014), however, pointed out inconsistencies in these two time  
883 series, with the AMO index sometimes lagging temperature changes. A recent study has argued  
884 that the transition of the Interdecadal Pacific Oscillation (IPO) phase from positive to negative in  
885 the late 1990s may have triggered a reversal of the warming hole trend (Meehl et al., 2015).

886 The cool period in the Southeast coincided with heavy aerosol loading over the region, and several  
887 studies have suggested that trends in aerosol forcing may have also played a role in driving the  
888 U.S. warming hole. For example, Leibensperger et al. (2012a, 2012b) found that the regional  
889 radiative forcing from anthropogenic aerosols led to a strong regional climate response, cooling  
890 the central and eastern US by 0.5-1.0 °C from 1970-1990 (Figure 3), with the strongest effects on  
891 maximum daytime temperatures in summer and autumn. In that study, the spatial mismatch  
892 between maximum aerosol loading and maximum cooling could be partly explained by aerosol  
893 outflow cooling the North Atlantic, which strengthened the Bermuda High and increased the flow  
894 of moist air into the south-central United States. Another model study diagnosed positive  
895 feedbacks between aerosol loading, soil moisture, and low cloud cover that may amplify the local  
896 response to aerosol trends (Mickley et al., 2012). The strength of such positive feedbacks may vary  
897 regionally, yielding different sensitivities in surface temperature to aerosol forcing.

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902 the central and eastern US by 0.5-1.0 °C from 1970-1990 (Figure 3), with the strongest effects on  
903 maximum daytime temperatures in summer and autumn. In that study, the spatial mismatch  
904 between maximum aerosol loading and maximum cooling could be partly explained by aerosol  
905 outflow cooling the North Atlantic, which strengthened the Bermuda High and increased the flow  
906 of moist air into the south-central United States. Another model study diagnosed positive  
907 feedbacks between aerosol loading, soil moisture, and low cloud cover that may amplify the local  
908 response to aerosol trends in the eastern U.S., including the Southeast (Mickley et al., 2012). The  
909 strength of such positive feedbacks may vary regionally, yielding different sensitivities in surface  
910 temperature to aerosol forcing. More recent modelling studies, however, have generated  
911 conflicting results regarding the role of aerosols in driving the warming hole. For example, the  
912 model study of Mascioli et al. (2016) reported little sensitivity in Southeast surface temperatures  
913 to external forcings such as anthropogenic aerosols or even greenhouse gases. In contrast,  
914 Banerjee et al. (2017) found that as much of 50% of the observed 1950-1975 summertime cooling  
915 trend in the Southeast could be explained by increasing aerosols. Examining multi-model output,  
916 Mascioli et al. (2017) concluded that aerosols accounted for just 17% of this cooling trend in

917 summer. These contrasting model results point to the challenges in modeling climate feedbacks,  
918 such as those involving cloud cover or soil moisture.

919 These early model studies have been accompanied by more observationally based efforts to link  
920 trends in surface temperature to aerosol loading. A key first step is to determine whether changes  
921 in surface solar radiation are related to changes in aerosol loading. Measurements from the Surface  
922 Radiation network (SURFRAD) reveal increases of  $+0.4 \text{ Wm}^{-2} \text{ a}^{-1}$  in total surface solar radiation  
923 across the East during 1995-2010 (Gan et al., 2014). An attempt to reproduce the trend in total  
924 surface radiation with a regional chemistry-climate model found a reasonable match with  
925 observations over the East when aerosol-radiation interactions were included (Xing et al., 2015a).  
926 Most of the observed increase in surface solar radiation, however, appears due to increasing diffuse  
927 radiation, at odds with the decline in AOD, which should instead increase direct radiation (Gan et  
928 al., 2015; Gan et al., 2014). Using satellite data and assimilated meteorology, Yu et al. (2014)  
929 showed that trends in spatially averaged AOD and cloud optical depth declined over the 2000-  
930 2011 time period over the eastern US, while daily maximum temperatures and shortwave cloud  
931 forcing increased. These opposing trends suggest that aerosol-cloud interactions may have  
932 influenced the observed  $\sim 1 \text{ }^\circ\text{C}$  warming trend in the Southeast over this ten-year time period, with  
933 the decline in anthropogenic aerosols driving a decrease in cloud cover and a rise in surface  
934 temperatures. Yu et al. (2014) confirmed this hypothesis using a chemistry-climate model. In  
935 contrast, the observational study of Tosca et al. (2017), which also relied on satellite AOD, pointed  
936 to aerosol-radiation interactions as the driver of surface temperature trends in the Southeast.  
937 Analysis of ground-based observations in Mississippi, however, found little covariability between  
938 AOD and clear-sky solar radiation at the surface, casting doubt on the importance of aerosol-  
939 radiation interactions in driving the observed cooling in this region (Cusworth et al., 2017).

940 Continued improvements of  $\text{PM}_{2.5}$  air quality in the Southeast may further influence regional  
941 climate. Lee et al. (2016b) projected a warming of about  $+0.5 \text{ Wm}^{-2}$  over the eastern U.S.,  
942 including the Southeast, over the 2000-2030 timeframe due to anticipated improvements in air  
943 quality and the associated reduction in AOD. Xing et al. (2015b) have pointed out that an  
944 overlooked beneficial effect of aerosol reduction is increased ventilation of surface air, a positive  
945 feedback that leads to further decline in surface  $\text{PM}_{2.5}$  concentrations. The feedback arises from  
946 changes in the temperature profile, with warmer temperatures at the surface and cooler  
947 temperatures aloft, which together enhance atmospheric instability and ventilation as aerosol  
948 induced cooling is reduced. The feedback may lead to unexpected health benefits of clearing  $\text{PM}_{2.5}$   
949 pollution (Xing et al., 2016).

### 950 **5.2.3. Influence of meteorology on surface air quality in the Southeast**

951 Pollution episodes in the southeastern United States are correlated with high temperatures, low  
952 wind speeds, clear skies, and stagnant weather (Camalier et al., 2007; Jacob and Winner, 2009).  
953 The spatial extent of the Bermuda High also plays a role in modulating air quality in the Southeast  
954 (Zhu and Liang, 2013).

955 Fu et al. (2015) used models and observations to examine the sensitivity of August surface ozone  
956 in the Southeast to temperature variability during 1988-2011. This study finds that warmer  
957 temperatures enhance ozone by increasing biogenic emissions and accelerating photochemical  
958 reaction rates. However, variability in ozone advection into the region may also explain much of  
959 the variability of surface ozone, with possibly increased advection occurring during the positive  
960 phase of the Atlantic Multidecadal Oscillation (AMO). Applying empirical orthogonal functions  
961 (EOF) analysis to observed ozone, Shen et al. (2015) determined that the sensitivity of surface

962 ozone in the Southeast can be quantified by the behavior of the west edge of the Bermuda High.  
963 Specifically, for those summers when the average position of the west edge is located west of  
964  $\sim 85.4^\circ$  W, a westward shift in the Bermuda High west edge increases ozone in the southeast by 1  
965 ppbv  $\text{deg}^{-1}$  in longitude. For all summers, a northward shift in the Bermuda High west edge  
966 increases ozone over the entire eastern United States by 1-2 ppbv  $\text{deg}^{-1}$  in latitude.

967 The influence of meteorology on  $\text{PM}_{2.5}$  in the Southeast is not well quantified. Tai et al. (2010)  
968 found that observed sulfate and OC concentrations increase with increasing temperature across the  
969 region due to faster oxidation rates and the association of warm temperatures with stagnation and  
970 biogenic and fire emissions. Nitrate  $\text{PM}_{2.5}$ , however, becomes more volatile at higher temperatures  
971 and decreases with temperature. Using local meteorology, however, Tai et al. (2010) could explain  
972 only about 20-30% of  $\text{PM}_{2.5}$  daily variability in the Southeast. Both Thishan Dharshana et al. (2010)  
973 and Tai et al. (2012b) diagnosed a relatively weak effect of synoptic scale weather systems on  
974  $\text{PM}_{2.5}$  air quality in the Southeast, especially in the deep South. Shen et al. (2017), however,  
975 extended the statistical studies of Tai et al. (2012a, b) by taking into account not just the local  
976 influences of meteorology on  $\text{PM}_{2.5}$  air quality but also the relationships between local  $\text{PM}_{2.5}$  and  
977 meteorological variables in the surrounding region. These authors developed a statistical model  
978 that explains 30-50% of  $\text{PM}_{2.5}$  monthly variability in the Southeast. Shen et al. (2017) further  
979 reported that many atmospheric chemistry models may underestimate or even fail to capture the  
980 strongly positive sensitivity of monthly mean  $\text{PM}_{2.5}$  to surface temperature in the eastern United  
981 States, including the Southeast, in summer. In GEOS-Chem, this underestimate can be traced to  
982 the overly strong tendency of modeled low cloud cover to decrease as temperatures rise (Shen et  
983 al., 2017).

#### 984 **5.2.4. Effects of future climate change on Southeast air quality**

985 Emissions of U.S. pollution precursors are expected to decline in coming decades (Lamarque et  
986 al., 2013; Fiore et al., 2015), which may offset any potential climate penalty. Background ozone,  
987 however, may increase due to increasing methane (West et al., 2012). A major challenge in  
988 quantifying the future trends in surface air quality is our lack of knowledge in temperature-  
989 dependent isoprene emissions and photochemistry (Achakulwisut et al., 2015).

990 Using a regional chemistry-climate model, Gonzalez-Abraham et al. (2015) found that daily  
991 maximum 8 h average (MDA8) ozone concentrations in the Southeast would likely increase by 3-  
992 6 ppbv by the 2050s due solely to climate change and land use change. Changes in anthropogenic  
993 emissions of ozone precursors such as methane could further enhance MDA8 ozone in the  
994 Southeast by 1-2 ppbv. Rieder et al. (2015), however, determined that large areas of the Southeast  
995 would experience little change in surface ozone by the 2050s, but that study neglected the influence  
996 of warming temperatures on biogenic emissions. Shen et al. (2016) developed a statistical model  
997 using extreme value theory to estimate the 2000–2050 changes in ozone episodes across the United  
998 States. Assuming constant anthropogenic emissions at the present level, they found an average  
999 annual increase in ozone episodes of 2.3 d ( $>75$  ppbv) across the United States by the 2050s, but  
1000 relatively little change in the Southeast. In fact, a key result of this work is the relative insensitivity  
1001 of ozone episodes to temperature in the Southeast. However, Zhang and Wang (2016) have  
1002 suggested that warmer and drier conditions in the Southeast future atmosphere could extend the  
1003 ozone season, leading to ozone episodes in October.

1004 Model studies differ on the effects of future climate change on  $\text{PM}_{2.5}$  in the Southeast. Tai et al.  
1005 (2012a) and Tai et al. (2012b) analyzed trends in meteorological modes from an ensemble of  
1006 climate models and found only modest changes in annual mean  $\text{PM}_{2.5}$  ( $\pm 0.4 \mu\text{g m}^{-3}$ ) by the 2050s

1007 in the Southeast, relative to the present-day. Using a single chemistry-climate model, Day and  
1008 Pandis (2015) calculated significant increases of  $\sim 3.6 \mu\text{g m}^{-3}$  in July mean  $\text{PM}_{2.5}$  along the Gulf  
1009 coast by the 2050s and attributed these increases to a combination of decreased rain-out, reduced  
1010 ventilation, and increased biogenic emissions. Building on the statistical model of Tai et al.  
1011 (2012a,b), Shen et al. (2017) found that  $\text{PM}_{2.5}$  concentrations in the Southeast could increase by  
1012  $0.5\text{-}1.0 \mu\text{g m}^{-3}$  by 2050 on an annual basis, and as much as  $2.0\text{-}3.0 \mu\text{g m}^{-3}$  in summer, assuming  
1013 anthropogenic emissions remained at present-day levels. These authors found that the driver for  
1014 these increases was rising surface temperature, which influences both biogenic emissions and the  
1015 rate of sulfate production.

### 1016 **5.3. Open questions**

1017 Unresolved issues in chemistry-climate interactions in the Southeast include the following:

1018 1. What is the impact of aerosols on regional climate of the Southeast? What role do feedbacks  
1019 play, including feedbacks involving cloud cover, soil moisture, and boundary layer height? Did  
1020 land use changes play a role in the Southeast warming hole? How will changing aerosol  
1021 composition affect regional climate? Can we reconcile observed trends in insolation and aerosols?  
1022 Can we use observed weekly cycles in temperature or precipitation to probe possible aerosol  
1023 effects on regional climate (Forster and Solomon, 2003; Bell et al., 2008; Bäumer et al., 2008;  
1024 Daniel et al., 2012)?

1025 2. What caused the U.S. warming hole? Is the observed cooling over the Southeast partly due to  
1026 natural variability of North Atlantic SSTs? Do aerosol changes induce changes the North Atlantic  
1027 SSTs that feedback on the Southeast U.S.? Has the warming hole ended and made the central and  
1028 southeastern United States more vulnerable to high temperatures and drought?

1029 3. What limits model skill in simulating the variability of surface pollution in the Southeast? Can  
1030 we capture the observed effects of the Bermuda High or the AMO on surface air quality?

1031 4. How will air quality in the Southeast change in the future? Do current model weaknesses in  
1032 simulating present-day ozone and  $\text{PM}_{2.5}$  daily or seasonal variability limit our confidence in future  
1033 projections?

### 1034 **5.4. Model recommendations**

1035 We recommend the following approaches for studies involving chemistry-climate interactions in  
1036 the southeastern U.S.

1037 1. Take advantage of findings from the 2013 measurement campaigns.

1038 For aerosol, such findings include information on composition, hygroscopicity, lifetime, aerosol-  
1039 cloud interactions, optical properties, and the mechanism of SOA formation. Modelers should also  
1040 take advantage of new information on isoprene emission flux and oxidation mechanisms.

1041 2. Link 2013 results with findings from previous measurement campaigns and with long-term in  
1042 situ and satellite data.

1043 3. Work to apply best practices, including standard statistical tests, to chemistry-climate studies.

1044 Modelers need to consider the statistical significance of observed trends and perform ensemble  
1045 simulations for robust statistics. The auto-correlation of the variables under investigation should  
1046 be examined. Comparison of observed trends with samples of internal climate variability from



1047 model control runs, as in (Knutson et al., 2013), may be a useful approach, and modelers should  
1048 acknowledge that observations may represent an outlier of unforced variability.

1049 4. Benchmark chemistry-climate models in a way that is useful for chemistry-climate studies.

1050 For the Southeast, modelers should consider testing the following model properties:

1051 (1) Sensitivity of surface air quality to synoptic weather systems, including the westward extent  
1052 of Bermuda High and cold front frequency.

1053 (2) Sensitivity of surface air quality to local meteorological variables and isoprene emissions  
1054 on a range of temporal scales.

1055 (3) Sensitivity of soil moisture and cloud cover to changing meteorology and the consequences  
1056 for regional climate and air quality.

## 1057 **6. Summary**

1058 The primary purpose of this work is to improve model representation of fundamental processes  
1059 over Southeast US. We summarize the modeling recommendations here:

1060 **Gas-phase chemistry** (1) Up-to-date “standard” chemical mechanisms represent OH chemistry  
1061 well over the observed range of NO<sub>x</sub> concentrations. Detailed mechanisms based on recent  
1062 laboratory chamber studies (mostly at Caltech) and theoretical studies (Leuven) for isoprene  
1063 chemistry result in predicted OH that is in reasonable agreement with observations. Condensed  
1064 mechanisms that approximate these details are expected to do the same. (2) Given the large  
1065 emissions and high chemical reactivity of isoprene, its chemistry should be treated fairly explicitly,  
1066 including more detail than for most other hydrocarbons. (3) NO<sub>3</sub> chemistry contributes  
1067 significantly to both VOC oxidation and aerosol production. (4) The regions of peak NO<sub>x</sub> and  
1068 BVOC emissions are not collocated. As a result, the model resolution can impact the predictions.

1069 **Organic Aerosol** (1) There is high confidence that a pathway of SOA formation from isoprene  
1070 epoxydiol (IEPOX) should be included in models. However, since many of the parameters needed  
1071 to predict IEPOX-SOA are uncertain, further mechanistic studies are needed to address these  
1072 uncertainties. (2) There is high confidence that models should include SOA formation from nitrate  
1073 radical oxidation of monoterpenes (with or without explicit nitrate functionality). Sesquiterpenes  
1074 and isoprene may also contribute SOA through nitrate radical oxidation, but the contribution is  
1075 expected to be smaller. (3) More field measurements and laboratory studies, especially of the yield  
1076 from isoprene oxidation and the aerosol uptake coefficient, are required to constrain the  
1077 importance of glyoxal SOA. (4) There is high confidence that models should include SOA from  
1078 urban emissions with a parameterization that results in realistic concentrations.

1079 **Natural and anthropogenic emissions** (1) Biogenic emissions from BEIS are generally lower,  
1080 and those from MEGAN generally higher, than from measurements for all campaigns. (2)  
1081 Observations confirm a rapid decrease of ozone precursor emissions over past few decades. Thus,  
1082 use of the correct scaling of anthropogenic emissions for a particular year is important for accurate  
1083 simulations. (3) National Emissions Inventory (NEI) 2011 likely overestimates NO<sub>x</sub> emissions in  
1084 the study area from mobile sources that use fuel-based estimates.

1085 **Climate and chemistry interactions** (1) Annual mean temperatures during the 1930-1990  
1086 timeframe decreased by ~1°C over the central and southeastern United States. Several studies have  
1087 argued that patterns of sea surface temperatures in the North Atlantic may have caused this large-  
1088 scale cooling. Trends in aerosol forcing may have also played a role. (2) Pollution episodes in the

1089 southeastern United States are correlated with high temperatures, low wind speeds, clear skies,  
1090 and stagnant weather. Surface air quality over Southeast US may be to some extent modulated by  
1091 large-scale circulations, such the Bermuda High or Atlantic Multi-decadal Oscillation (AMO).

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## 1108 **7. Glossary of Acronyms**

1109 **AM3:** The atmospheric component of the GFDL coupled climate model CM3.  
1110 **AMS:** Aerosol Mass Spectrometer  
1111 **AMO:** Atlantic Multi-decadal Oscillation  
1112 **AOD:** aerosol optical depth  
1113 **BBOA:** Biomass burning OA  
1114 **BEIS:** Biogenic Emission Inventory System  
1115 **BVOC:** Biogenic Volatile Organic Compounds  
1116 **CAMx:** Comprehensive Air Quality Model with Extensions  
1117 **CEMS:** Continuous emission monitoring systems  
1118 **CMAQ:** Community Multi-scale Air Quality Model  
1119 **CSN:** Chemical Speciation Monitoring Network  
1120 **EF:** Emission Factor  
1121 **FIXCIT:** A laboratory experiment focused on isoprene oxidation chemistry and the instruments  
1122 we took to the field to understand that chemistry  
1123 **HOA:** Hydrocarbon-like OA  
1124 **IEPOX:** Isoprene epoxydiol  
1125 **IMPROVE:** Interagency Monitoring of Protected Visual Environments visibility monitoring  
1126 network  
1127 **LAI:** Leaf Area Index  
1128 **LES:** Large-eddy simulation  
1129 **LO-OOA:** Less-oxidized oxygenated OA  
1130 **MACR:** Methacrolein  
1131 **MEGAN:** Model of Emissions of Gases and Aerosols from Nature  
1132 **MO-OOA:** More-oxidized oxygenated OA

1133 **MVK:** Methyl vinyl ketone  
1134 **NEI:** National Emissions Inventory  
1135 **NOAA:** National Oceanic and Atmospheric Administration  
1136 **NOMADSS:** Nitrogen, Oxidants, Mercury and Aerosol Distributions, Sources and Sinks aircraft  
1137 campaign, took place during Jun-Jul 2013 with the NSF/NCAR C-130 aircraft.  
1138 **OA:** Organic aerosol  
1139 **OC:** Organic carbon  
1140 **OM:** Organic matter  
1141 **OMI:** Ozone Monitoring Instrument  
1142 **PAN:** Peroxy Acetyl Nitrate  
1143 **PFT:** Plant Functional Type  
1144 **PMF:** Positive Matrix Factorization  
1145 **POA:** primary organic aerosol  
1146 **RGF:** Ratio of Glyoxal to Formaldehyde  
1147 **SAS:** Southeast Atmosphere Studies  
1148 **SCIPUFF:** Second Order Closure Integrated Puff Model  
1149 **SEAC4RS:** Studies of Emissions, Atmospheric Composition, Clouds and Climate Coupling by  
1150 Regional Surveys aircraft campaign, took place during Aug-Sept 2013 with NASA DC-8 and  
1151 ER-2 aircraft  
1152 **SEARCH:** Southeastern Aerosol Research and Characterization Network  
1153 **SENEX:** SouthEast NEXus of air quality and climate campaign  
1154 **S/IVOCs:** Semivolatile/intermediate volatility organic compounds  
1155 **SOA:** Secondary Organic Aerosols  
1156 **SOAS:** the Southern Oxidant and Aerosol Study ground-based campaign, took place during Jun-  
1157 Jul 2013 near Brent, Alabama.  
1158 **SURFRAD:** Surface Radiation Budget Network  
1159 **VBS:** volatility basis set (VBS)  
1160 **WRF-Chem:** Weather Research and Forecasting with Chemistry model  
1161

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2302 Table 1 A subset of model evaluations for SAS observations (till 2017)

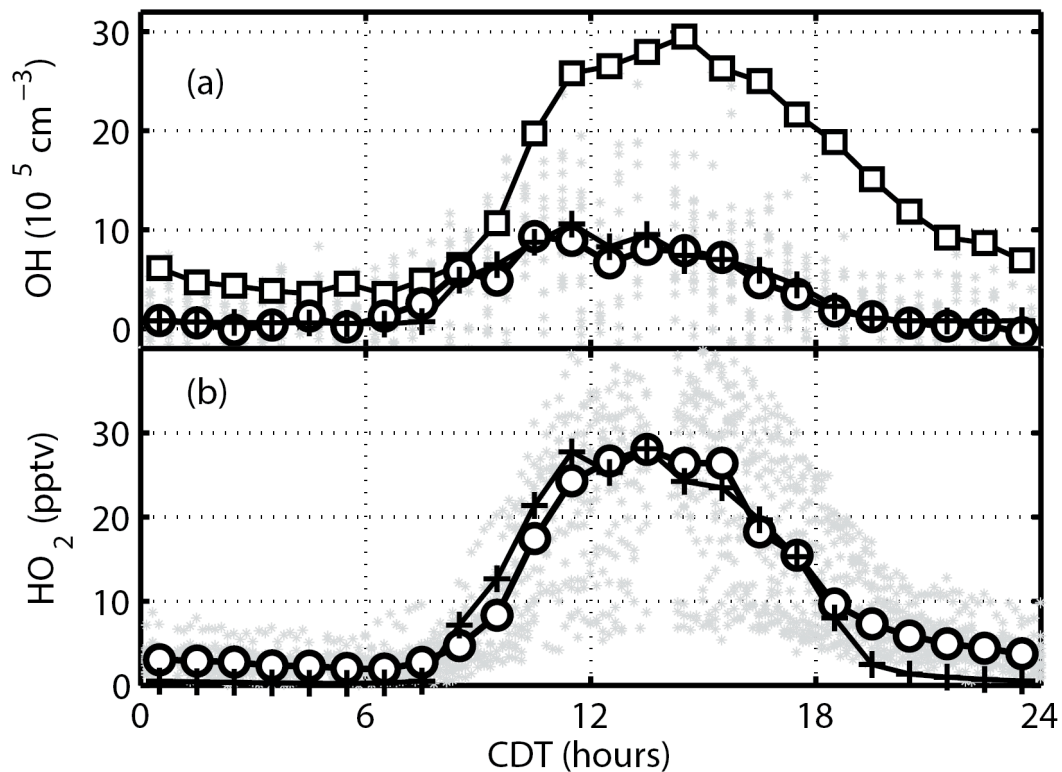
Model name	Model -type	References	Targeted species	Major findings
F0AM	0-D	Feiner et al. (2016)	OH, HO <sub>2</sub> , OH reactivity	Measured and modeled OH agree well.
Box model	0-D	Lee et al. (2016a)	Speciated organic nitrates	Particle-phase organic nitrates are an important component in organic aerosols, but could have a short particle-phase lifetime.
F0AM	0-D	Wolfe et al. (2016)	HCHO	Current models accurately represent early-generation HCHO production from isoprene but under-predict a persistent background HCHO source.
F0AM	0-D	Kaiser et al. (2016)	OH reactivity	Missing OH reactivity is small.
F0AM	0-D	Marvin et al. (2017)	HCHO	Model HCHO-isoprene relationships are mechanism-dependent. Condensed mechanisms (esp. CB6r2) can perform as well as explicit ones with some modifications.
ISORROPIA	0-D	Weber et al. (2016); Guo et al. (2015)	Aerosol Acidity	Submicron aerosols are highly acidic in Southeast US.
MXLCH	1-D	Su et al. (2016)	Isoprene, HCHO, MVK, MACR, organic nitrates, OH, HO <sub>2</sub>	Diurnal evolution of O <sub>3</sub> is dominated by entrainment. Diurnal evolution of isoprene oxidation products are sensitive to NO:HO <sub>2</sub> ratio.
GEOS-Chem	3-D	Fisher et al. (2016)	Organic nitrates	Updated isoprene chemistry, new monoterpene chemistry, and particle uptake of RONO <sub>2</sub> . RONO <sub>2</sub> production accounts for 20% of the net regional NO <sub>x</sub> sink in the Southeast in summer.
GEOS-Chem	3-D	Travis et al. (2016)	NO <sub>x</sub> , ozone	NEI NO <sub>x</sub> emissions from mobile and industrial sources reduced by 30–60%. The model is still biased high by 6-

				14 ppb relative to observed surface ozone.
GEOS-Chem	3-D	Zhu et al. (2016)	HCHO	GEOS-Chem used as a common intercomparison platform among HCHO aircraft observations and satellite datasets of column HCHO. The model shows no bias against aircraft observations.
GEOS-Chem	3-D	Kim et al. (2015)	Organic and inorganic aerosols	GEOS-Chem used as a common platform to interpret observations of different aerosol variables across the Southeast. Surface PM <sub>2.5</sub> shows far less summer-to-winter decrease than AOD.
GEOS-Chem	3-D	Chan Miller et al. (2017)	Glyoxal, HCHO	New chemical mechanism for glyoxal formation from isoprene. Observed glyoxal and HCHO over the Southeast are tightly correlated and provide redundant proxies of isoprene emissions.
GEOS-Chem	3-D	Marais et al. (2016)	IEPOX, organic aerosols	New aqueous-phase mechanism for isoprene SOA formation. Reducing SO <sub>2</sub> emissions in the model decreases both sulfate and SOA by similar magnitudes.
GEOS-Chem	3-D	Silvern et al. (2017)	Aerosol acidity	Sulfate aerosols may be coated by organic material, preventing NH <sub>3</sub> uptake.
GFDL AM3	3-D	Li et al. (2016)	Glyoxal, HCHO	Gas-phase production of glyoxal from isoprene oxidation represents a large uncertainty in quantifying its contribution to SOA.
GFDL AM3	3-D	Li et al. (2017)	Organic nitrates, ozone	Reactive oxidized nitrogen species, including NO <sub>x</sub> , PAN and HNO <sub>3</sub> decline proportionally with decreasing NO <sub>x</sub> emissions in Southeast U.
CMAQ	3-D	Pye et al. (2015)	Terpene nitrates	Monoterpene + NO <sub>3</sub> reactions responsible for significant NO <sub>x</sub> -dependent SOA.

				Magnitude of SOA dependent on assumptions regarding hydrolysis.
Box model with CMAQ/Simple-GAMMA algorithms	0-D	Budisulistiorini et al. (2017); Budisulistiorini et al. (2015)	IEPOX, SOA	Sulfate, through its influence on particle size (volume) and rate of particle-phase reaction (acidity), controls IEPOX uptake at LRK.
CMAQ	3-D	Pye et al. (2017a)	Aerosol liquid water, water soluble organic carbon(WSOC)	Aerosol water requires accurate organic aerosol predictions as models considering only water associated with inorganic ions will underestimate aerosol water. Gas-phase WSOC, including IEPOX+glyoxal+methylglyoxal, is abundant in models.
CMAQ	3-D	Fahey et al. (2017)	Cloud-mediated organic aerosol	Cloud-processing of IEPOX increased cloud-mediated SOA by a modest amount (11 to 18% at the surface in the eastern US)
CMAQ	3-D	Murphy et al. (2017)	Organic aerosol from combustions sources	CTR organic aerosol predictions are not very sensitive to assumptions (volatility, oxidation) for combustion-derived organic aerosol.
CMAQ	3-D	Baker and Woody (2017)	Ozone, PM2.5	Single-source impacts of a coal fired power plant, including the contribution to secondary pollutants, can be estimated from a 3-D CTM.
AIOMFAC, CMAQ	0-D/3-D	Pye et al. (2017b)	Inorganic aerosol, semivolatile species	Thermodynamic models are consistent with SEARCH and MARGA measured ammonium sulfate at CTR. Organic-inorganic interactions can cause small decreases in acidity and increased partitioning to the particle for organic species with O:C>0.6.
WRF-Chem	3-D	McDonald et al. (in preparation)	NO <sub>x</sub> , CO, Ozone	Mobile source NO <sub>x</sub> and CO emissions overestimated by 50% and factor of 2.2, respectively. Model surface O <sub>3</sub>

				improves with reduced mobile source NO <sub>x</sub> emissions.
NCAR LES	3-D	Kim et al. (2016)	Isoprene, OH	Turbulence impacts isoprene-OH reactivity, and effect depends on NO <sub>x</sub> abundance.

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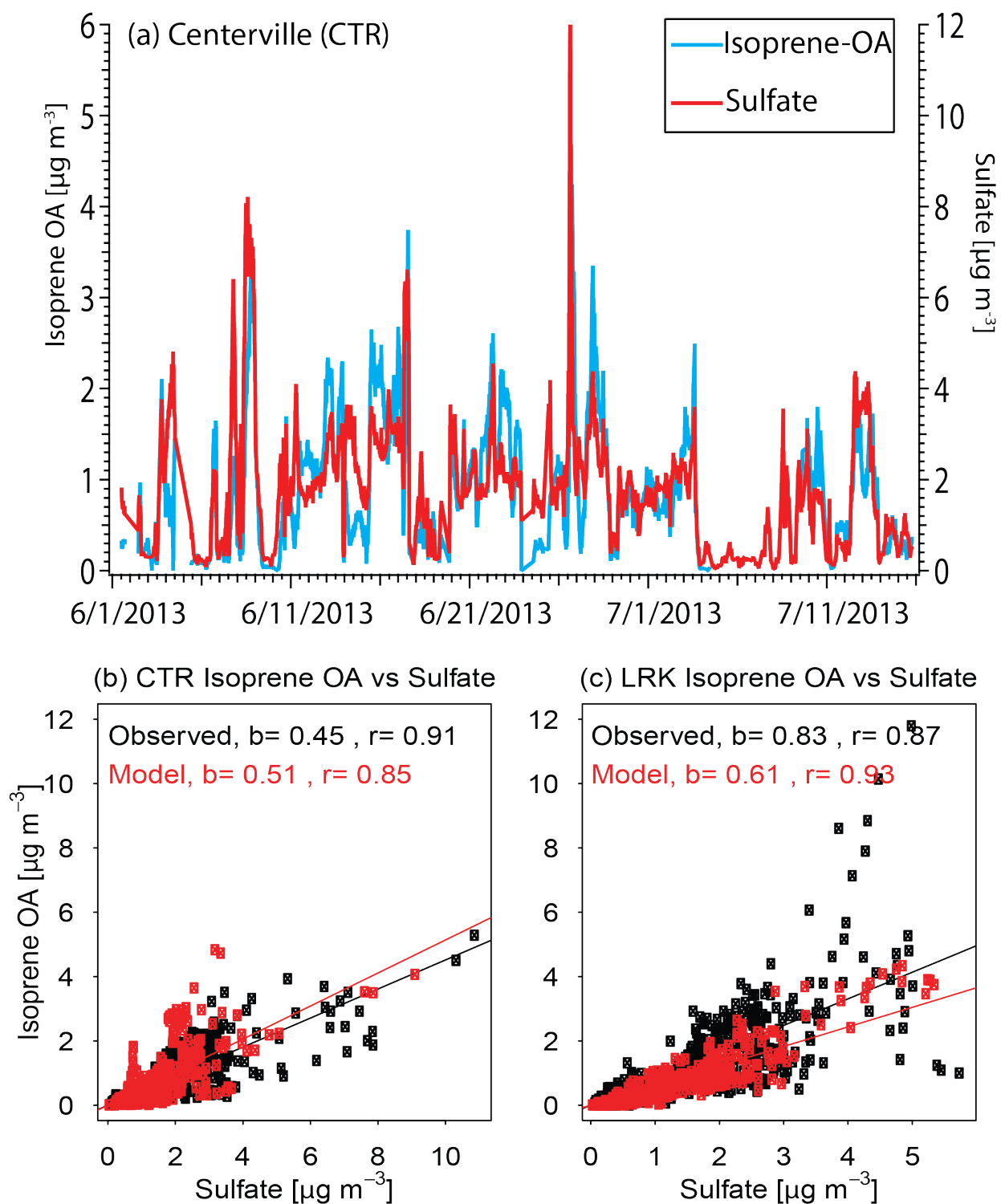


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2307 Figure 1 Diel variation of measured and modeled OH/HO<sub>2</sub> during SOAS (Feiner et al., 2016). In  
 2308 panel (a), measured OH by a traditional laser induced fluorescence technique is shown in squares  
 2309 and by a new chemical scavenger method is shown in circles. The latter one is considered as the  
 2310 “true” ambient OH. Simulated OH from a photochemical box model with Master Chemical  
 2311 Mechanism (MCM) v3.3.1 is shown in pluses. In panel (b), measured HO<sub>2</sub> is shown in circles and  
 2312 modeled HO<sub>2</sub> is shown in pluses. For both panels, gray dots are individual 10-minute  
 2313 measurements.

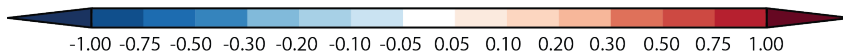
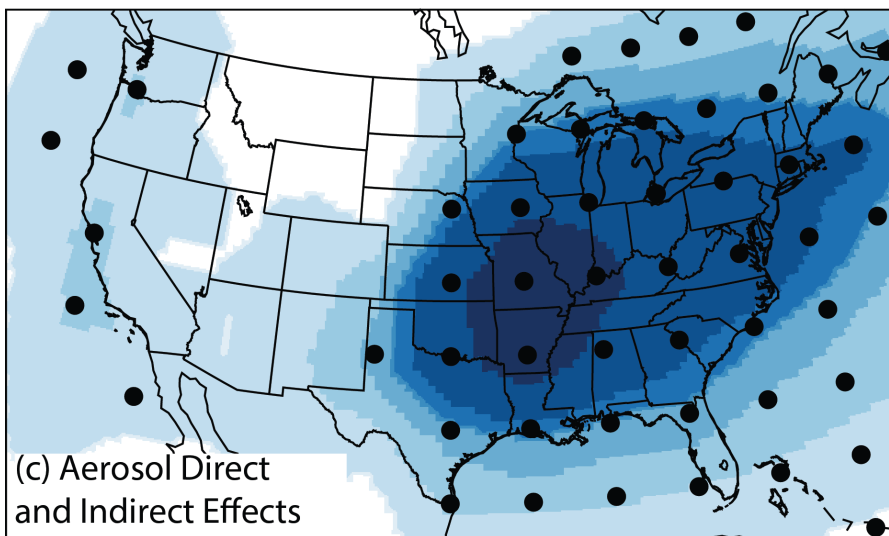
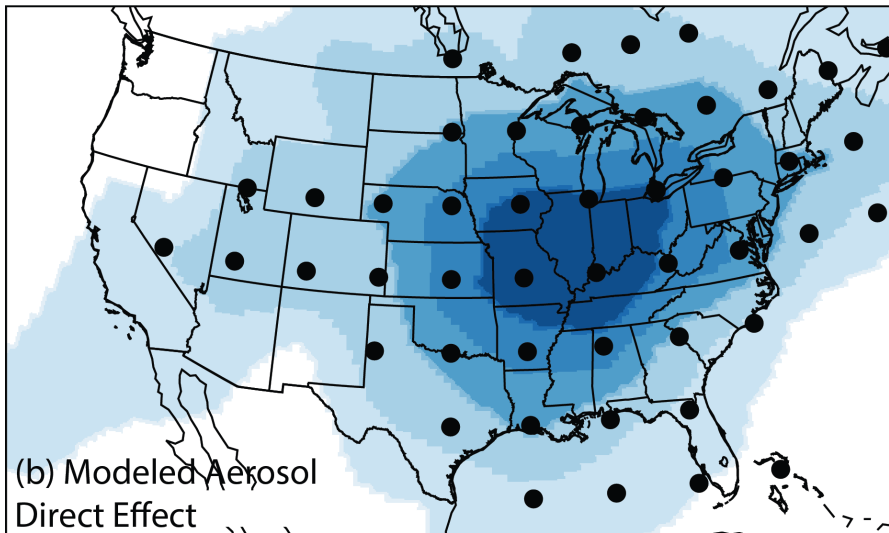
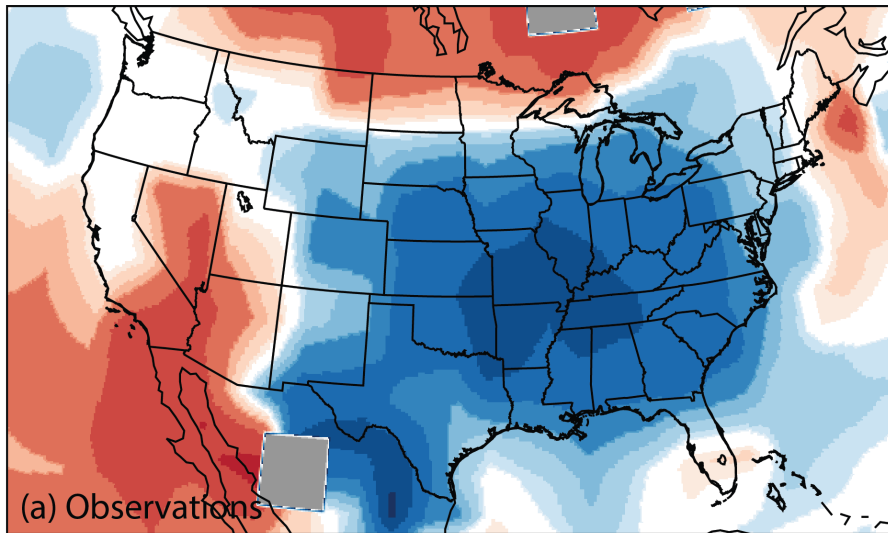
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2318 Figure 2. Time series and correlation between Isoprene OA and sulfate during SOAS (Pye et al.,  
2319 2016; Xu et al., 2015). Panel (a) shows the time series of both Isoprene OA and sulfate at  
2320 Centerville site during SOAS. Panel (b) and (c) shows the correlation plot between Isoprene OA

2321 and sulfate from both measurements and model results at two sites (Centreville and Little Rock)  
2322 during SOAS.  
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2325 Figure 3 Observed difference in surface air temperature between 1930 and 1990 (a) and modeled  
2326 effect of US anthropogenic aerosol sources on surface air temperatures for the 1970–1990 period  
2327 when US aerosol loading was at its peak (b and c) (Leibensperger et al., 2012a). Observations are  
2328 from the NASA GISS Surface Temperature Analysis (GISTEMP;  
2329 <http://data.giss.nasa.gov/gistemp/>). Model values represent the mean difference between 5-  
2330 member ensemble GCM simulations including vs. excluding US anthropogenic aerosol sources,  
2331 and considering the aerosol direct only (b) and the sum of direct and indirect effects (c). In (b) and  
2332 (c), dots indicate differences significant at the 95th percentile.  
2333