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Discussions

Southeast Atmosphere Studies: learning from model-observation syntheses

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Abstract

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

In the summer of 2015 a group of experimentalists and modelers convened at the NOAA Geophysical Fluid Dynamics Laboratory (GFDL), to discuss use of SAS observations to evaluate, diagnose, and improve air quality and climate modeling over the Southeast US. The effort focused primarily on model representation of fundamental atmospheric processes that are essential to the formation of ozone, secondary organic aerosols (SOA) and other trace species in the troposphere over the Southeastern US, with the ultimate goal of understanding the radiative impacts of these species in the Southeast and elsewhere. The workshop addressed questions surrounding four key themes: gas phase chemistry, aerosol chemistry, regional climate and chemistry interactions, and natural and anthropogenic emissions. This paper serves as a summary from this meeting and more importantly, as guidance for future modeling efforts.

1. Introduction

Observational experiments in the Southeastern U.S. during SAS (Southeast Atmosphere Studies) 2013 (SOAS, SENEX, SEAC4RS, NOMADSS) provide a wealth of new insights into the composition of the atmosphere. Results allow researchers to explore the chemical degradation of biogenic organic molecules over a range of concentrations of ambient nitrogen oxide concentrations during day and night, and the ensuing consequences for ozone, aerosol and radiative properties of the atmosphere. The experiment was large and collaborative, and included coordinated measurements at multiple surface sites and, among several aircraft, with many flyovers of the surface sites and a wide suite of available remote sensing from space based instruments. A comprehensive array of instruments at each site/aircraft tracked most of the key atmospheric observables. Direct tracking of oxidative pathways was made possible by including gas phase measurements of parent molecules and many of the first- and second-generation daughter molecules. For the first time, many of the daughter molecules were also tracked into the aerosol phase. These observations provided an important context for both the characterization of new instruments and new methods by interpreting measurements from more established instruments. In parallel with these field measurements, several laboratory experiments used the same instrumentation to provide insights into the chemical mechanisms of oxidation and instrument performance under field conditions. Overviews of the entire project and many of the subprojects have been presented elsewhere (Carlton et al., 2016, The Southeast Atmosphere Studies (SAS): coordinated investigation and discovery to answer critical questions about fundamental atmospheric processes submitted; Toon et al., 2016; Warneke et al., 2016). Analyses of the observations have ranged from those that focus on the observations alone to those that primarily describe model simulations of the region. In this workshop we focused on the intersection of these two approaches, which is on analyses of observations that specifically test and inform the construction of 3-D chemical weather models. Our evaluations are focused on the Southeast data set, although we assert that the lessons learned are global.

2. Gas-phase Chemistry

2.1 Background

Global and regional models tend to significantly overestimate summertime surface ozone over the Southeastern US (Fiore et al., 2009; Lin et al., 2008; Murazaki and Hess, 2006; Rasmussen et al., 2012; Yu et al., 2010; Yu et al., 2007), posing a challenge for air quality management in this region and elsewhere. It remains unclear whether this model bias in summertime surface ozone is mainly due to the chemical processes (HO_x, isoprene nitrate chemistry, heterogeneous reactions, nighttime chemistry) or physical processes (dry deposition, boundary layer processes). Fiore et al. (2005) suggested that this problem might be due to incorrect representation of isoprene sources and chemistry. Measured deposition rates for isoprene oxidation products appear to be higher than current model values (Karl et al., 2010; Nguyen et al., 2015a). In the meantime, the understanding of isoprene oxidation chemistry has been evolving rapidly in the past decade (Crounse et al., 2011; Peeters et al., 2014).

A large debate surrounds our understanding of hydroxyl radical (OH) and HO_2 concentrations in the presence of isoprene. Traditional mechanisms assume that isoprene oxidation suppresses OH concentrations in low-NO_x conditions via the formation of organic hydroxyperoxides (Jacob and Wofsy, 1988). However, some recent observations show higher-than-expected OH concentrations in isoprene-rich environments without corresponding enhancements in HO_2 or RO_2 (Carslaw et al., 2001; Hofzumahaus et al., 2009; Lelieveld et al., 2008; Pugh et al., 2010; Ren et al., 2008; Stone et al., 2010; Tan et al., 2001; Thornton et al., 2002). On the other hand, an interference has been discovered to affect some OH instruments (Mao et al., 2012; Novelli et al., 2014).

Measurements of higher than expected OH in the presence of isoprene spurred renewed interest in issues related to the products of the HO_2 + RO_2 reaction. Thornton et al. (2002) and Hasson et al. (2004) had pointed out that if this reaction does not terminate the radical chain it would change the behavior of HO_x radicals at low NO_x. Several specific case of the RO_2+HO_2 reaction were shown to have an OH product (Dillon and Crowley, 2008; Hasson et al., 2004; Jenkin et al., 2007). Peeters et al. (Peeters et al., 2014; Peeters et al., 2009) identified a new path for OH regeneration through unimolecular isomerization of isoprene hydroxyperoxy radicals. This pathway was confirmed by laboratory measurements of its rate (Crounse et al., 2011). A key feature of the SAS experiments was that the NO_x concentrations spanned a range that resulted in measurements where the three major fates of isoprene peroxy radicals (reaction with NO, HO_2 or isomerization) were sampled at different times and locations.

Another major consequence of isoprene oxidation is the production of isoprene nitrates, formed from RO_2+NO reaction in the isoprene degradation chain. Different treatments of this reaction causes large variations of global and regional ozone budget among different models (Fiore et al., 2005; Horowitz et al., 2007; Ito et al., 2009; Perring et al., 2009a; Wu et al., 2007). Recent laboratory data indicates the yield of first generation isoprene nitrates is in the range of 10% to 14% (Giacopelli et al., 2005; Lockwood et al., 2010; Patchen et al., 2007; Paulot et al., 2009a; Sprengnether et al., 2002; Teng et al., 2015; Xiong et al., 2015), which is much higher than 4% suggested by a global model study (Horowitz et al., 2007). The subsequent fate of these isoprene nitrates includes oxidation by OH, NO_3 and O_3 (Lee et al., 2014; Lockwood et al., 2010; Paulot et al., 2009a), photolysis (Müller et al., 2014), and hydrolysis. Synthesis of models and SAS observations suggest an important role for hydrolysis as expected based on the laboratory measurements (Fisher et al., 2016; Romer et al., 2016; Wolfe et al., 2015).

The SAS observations also provide measurements that guide our thinking about the role of NO_3 chemistry, especially as it contributes to oxidation of biogenic volatile organic compounds (BVOC) at night (Aldener et al., 2006; Brown et al., 2009; Ng et al., 2008; Warneke et al., 2004). During SAS, these reactions were a substantial sink of NO_x in addition to their role in oxidation of BVOC. To a large extent this is due to the high yield of carbonyl nitrates (65%-85%) from the isoprene + NO_3 oxidation (Kwan et al., 2012; Perring et al., 2009b; Rollins et al., 2012; Rollins et al., 2009; Schwantes et al., 2015). Models that incorporate this chemistry (Horowitz et al., 2007; Mao et al., 2013; von Kuhlmann et al., 2004; Xie et al., 2012), indicate that the isoprene+NO_3 reaction contributes more than 50% of the total isoprene nitrate production and that the reaction is thus both a major pathway for isoprene removal and for NO_x removal. The fate of products from isoprene+NO_3 and to what extent they return NO_x remains a subject of discussion and thus an opportunity for exploration with models that might guide our thinking about a plausible range of product molecules (Müller et al., 2014; Perring et al., 2009b).

2.2 Preliminary findings

A major focus of the SAS study was to study the daytime and nighttime oxidative chemistry of isoprene and to compare the observations against models representing the ideas outlined above. Over the range of the fate of the isoprene RO_2 radical, the reaction partners were mostly NO and HO_2 during the day and a mix of NO_3, RO_2 and HO_2 at night. The field measurements were closely partnered with laboratory chamber experiments (Nguyen et al., 2014) which enhanced our understanding of oxidation mechanisms and provided increased confidence in our understanding of the measurements of isoprene oxidation products. For the case of the major daughter products methylvinylketone (MVK) and methacrolein (MACR), the lab experiments showed that many instruments have been detecting isoprene hydroperoxides and reporting them as MVK and MACR (Liu et al., 2013; Rivera - Rios et al., 2014). There are also extensive day and night measurements of monoterpene and sesquiterpene chemistry.

As anthropogenic emissions decrease, the concentrations of NO_x in the southeast US are dropping (Russell et al., 2012b). This decrease is changing the factors that control the NO_x lifetime and offers an opportunity to study mechanisms of emission from ecosystems in the region in different chemical regimes. The decrease in NO_x is also shifting the regime of HO_x chemistry from one where the primary reaction partner for HO_2 and RO_2 was NO to one where RO_2 + HO_2 and HO_2 + HO_2 are more important. These experiments were optimally timed to observe that transition as often the relative contributions of both types of chemistry were important. In contrast, field experiments conducted a decade ago were dominated by NO_x chemistry.

The observations from these studies provide a variety of constraints on OH, HO_2, and RO_2. Both direct measurements of these radical species with multiple methods and measurements of a variety of parent and daughter molecules (e.g. isoprene and isoprene hydroperoxides) were made. Questions about the chemical controls over these radicals under conditions of high isoprene concentrations and a range of NO_x levels can be addressed more clearly than ever before.

The role of NO_3 chemistry was specifically targeted by the NOAA nighttime aircraft flights and is evident in the surface measurements. The observations reinforce the idea that NO_3 oxidation of BVOC is an important source of organic aerosol and raise new questions about the lifetime and products of the aerosol nitrate. The role of vertical mixing in leaving BVOC in the residual layer emerged as a key issue for describing the regional scale effects of this chemistry.

To address the above questions, some of the key results highlighted at the workshop were:

(1) There is no evidence during SAS for dramatically higher OH at low NO_x than current chemistry predicts. Both direct measurements of OH and the ratios of parent to daughter molecules support this conclusion (Feiner et al., 2016).

(2) The experiments included direct measurements of 1st and 2nd generation isoprene oxidation products originating from OH, O_3 and NO_3 chemistry. The measurements support detailed mechanistic, kinetic and computational research to establish a comprehensive isoprene oxidation mechanism. There are many observations that are central to improved understanding of the detailed mechanisms, especially the recognition of the inadvertent detection of hydroperoxides as ketones and aldehydes by many of the instruments used in this experiment and in many prior ones. Many recent laboratory experiments provide constraints on comprehensive chemical mechanisms and thus guidance on key elements of reduced mechanisms, including constraints on organic nitrates (Lee et al., 2014; Müller et al., 2014; Teng et al., 2015; Xiong et al., 2015), IEPOX (Bates et al., 2014; Bates et al., 2016; St. Clair et al., 2015) and the fate of MVK (Praske et al., 2015) and MACR (Crounse et al., 2012).

(3) Several lines of evidence arguing for a short (~2hr) lifetime of total and isoprene organic nitrates are emerging from the analysis. This short lifetime affects our understanding of the lifetime of NO_x and the spatial pattern of transported NO_x and the resulting oxidation rates by OH, O_3, and NO_3, and the composition of secondary organic aerosol (SOA) (Fisher et al., 2016; Romer et al., 2016; Wolfe et al., 2015).

(4) The observations indicate that the ratio of glyoxal to HCHO is 2%, independent of NO_x (Kaiser et al., 2015). This is a useful indicator as these molecules are also measured from space and both

are short lived and tightly coupled to oxidation chemistry. This will also help compare ground measurements to those measured from space.

(5) We observe strong links between specific isoprene oxidation products (glyoxal and IEPOX) and SOA and have identified markers for these mechanisms in SOA (see next section).

(6) During the experiment direct observations of fluxes for a variety of species from large aircraft are conducted, enabling reports over a larger domain (Kaser et al., 2015; Wolfe et al., 2015; Yuan et al., 2015). This provides potential for analysis of strengths and weaknesses of current emission and deposition schemes and their implementation within chemical transport models. Vertical flux profiles also contain information on the chemical production and loss rates, providing a new observational constraint on the processes controlling reactive gas budgets.

(7) Several instruments observe that organic nitrates are an important component of ambient OA (~5-12% in SE US in summer) (Kiendler-Scharr et al., 2016; Lee et al., 2016a; Xu et al., 2015a; Xu et al., 2015b). Recent laboratory experiments suggest that aerosol organic nitrates can be either a permanent or temporary NO_x sink depending on their precursors as well as ambient humidity (Boyd et al., 2015; Lee et al., 2016a; Nah et al., 2016b).

2.3 Model recommendations

Based upon these preliminary findings, we make the following recommendations for the future modeling efforts:

(1) There is no evidence from these studies of a need for empirical tuning factors to represent OH chemistry at any NO_x concentration sampled in the rural Southeast. Detailed mechanisms based on recent laboratory chamber studies (mostly at Caltech) and theoretical studies (Leuven) for isoprene result in predicted OH that is in reasonable agreement with observations (Figure 1). Condensed mechanisms that approximate the detailed ones are expected to do the same. Whatever mechanism is used, a key diagnostic identified are parent-daughter molecular relationships. Models calculations should emphasize opportunities for observations of such ratios as an independent measure of the effect of OH on the atmosphere.

(2) The chemistry of isoprene should be treated in more detail than most other molecules. We recommend that there be explicit chemistry through the first and second generation of isoprene oxidation. No other species should be lumped with isoprene or its daughters.

(3) NO_3 chemistry is an important element of both VOC oxidation and aerosol production.

(4) The largest NO_x and BVOC emissions are not collocated. As a result model resolution can impact predicted concentrations of trace species. Resolution is especially important for the 15% or so at the tails of the NO_x and HCHO distribution—less so for O_3 (Yu et al., 2016). Depending on the research question models should evaluate the need to resolve this last 15% which probably requires a horizontal resolution of order 12 km or less.

2.4 Key model diagnostics

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

1) NO_x concentrations from *in situ* and satellite observations. Models that do not predict the correct magnitude of NO_x should produce the wrong OH, O_3, and parent:daughter VOC ratios (e.g. Isoprene: Isoprene + IEPOX, Isoprene : MACR + MVK). At the low NO_x characteristic of the Southeast U.S. these errors are approximately linear—that is, a 15% error in NO_x should correspond to a 15% error in OH, in isoprene, etc. Given the difficulty in predicting NO_x to this tolerance, caution should be taken not to over interpret model predictions.
2) H_2CO from space based observations is emerging as a useful diagnostic of model oxidation chemistry (Valin et al., 2016).
3) A significant fraction (estimated to be on the order of 20% of emissions) of isoprene remains at sunset and is oxidized by NO_3 at night. This fact might be an useful diagnostic of boundary layer dynamics and daytime chemistry in models. More exploration of the model prediction of the products of NO_3 + isoprene and additional observations of those molecules will provide insight into best practices for using it as a diagnostic of specific model processes.
4) O_3 and aerosol concentrations and trends over decades and contrasts between weekdays and weekends across the Southeast remain a valuable diagnostic of model performance; especially as coupled to trends in NO_x on those same time scales.

2.5 Open questions

The workshop identified a few open questions that are best addressed by the community of experimentalists and modelers working together (there were many open questions that are best addressed by individual investigators and we do not summarize those here).

1) The sources and sinks of NO_x are not well constrained in rural areas that cover most of Southeast U.S. As anthropogenic combustion related emissions experience further decline what do we expect to happen to NO_x? What observations would test those predictions?
2) Now that we are reaching consensus on a mechanism for isoprene oxidation, the role of monoterpene and sesquiterpene oxidation is becoming a larger fraction of remaining uncertainty. Strategies for exploring and establishing oxidation mechanisms for these molecules and for understanding the level of detail needed in comprehensive and reduced mechanisms are needed.
3) Water in aerosol (and cloud) is identified as an important control over gas-phase concentrations. What are the controls over the presence and lifetime of condensed liquid water? What model and observational diagnostics serve as tests of our understanding?
4) Air quality models have long been most interested in conditions that are not of top priority to meteorological researchers—e.g. stagnation. In addition to a better understanding of horizontal flows in stagnant conditions these experiments highlighted the need for a deeper understanding of the links between chemical mixing and boundary layer dynamics in day

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and night. A number of new chemical observations have been identified in the Southeast US data sets. Combined approaches using models and these observations to guide our thinking about PBL dynamics are needed.

3. Organic aerosol

3.1 Background and preliminary results

Improving the representation of organic aerosol (OA) is a critical need for models applied to the Southeast. Current air quality and chemistry-climate models produce a very wide range of organic aerosol mass concentrations, with predicted concentrations spread over 1-2 orders-of-magnitude in free troposphere (Tsigaridis et al., 2014). Secondary OA (SOA) has traditionally been modeled by partitioning of semivolatile species between the gas and aerosol phase (Chung and Seinfeld, 2002; Farina et al., 2010; Odum et al., 1996), but very large uncertainties remain on the detailed formulations implemented in models (Heald et al., 2011; Spracklen et al., 2011; Tsigaridis et al., 2014). In particular, the recent identification of substantial losses of semivolatile and intermediate volatility species to Teflon chamber walls (Krechmer et al., 2016; Matsunaga and Ziemann, 2010; Nah et al., 2016a; Zhang et al., 2014) necessitate a re-evaluation of the gas-phase SOA yields used in models which has yet to be comprehensively performed. In addition, recent laboratory, field and model studies suggest that a significant fraction of SOA is formed in aqueous phase cloud droplets and aerosols, following gas-phase oxidation to produce soluble species (Carlton et al., 2008; Ervens et al., 2011; Fu et al., 2008; Myriokefalitakis et al., 2011; Sorooshian et al., 2007; Tan et al., 2012; Volkamer et al., 2009). This is also consistent with the strong correlation between OA and aerosol liquid water in the Southeast US over the past decade (Nguyen et al., 2015b). A number of gas-phase VOC oxidation products have been recognized as important precursors for aqueous production of SOA, including epoxides (Nguyen et al., 2013; Pye et al., 2013; Surratt et al., 2010), and glyoxal (Liggio et al., 2005; McNeill et al., 2012; Woo and McNeill, 2015). Aerosol uptake of these oxygenated VOCs can be further complicated by aerosol acidity and composition (Marais et al., 2016; Nguyen et al., 2013; Paulot et al., 2009b; Pye et al., 2013). Results from SOAS and SEAC4RS indicate only a modest enhancement of OA due to cloud processing over the SE US, which was not statistically significant (Wagner et al., 2015).

While a significant portion of ambient OA has been attributed to various source classes and precursors (e.g. BBOA from biomass burning, IEPOX-SOA from isoprene epoxydiols or IEPOX, and less-oxidized oxygenated OA, LO-OOA from monoterpenes), a large portion of ambient OA (e.g. more-oxidized oxygenated OA, MO-OOA) remains unapportioned. This portion lacks detailed chemical characterization or source attribution, so further investigation is warranted (Xu et al., 2015a; Xu et al., 2015b). A diversity of modeling approaches is encouraged to provide insight into OA processes, while trying to make use of all available experimental constraints to evaluate the models.

3.2 Model recommendations

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

3.2.1 Partitioning theory and phases

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

Further research is needed regarding the role of organic partitioning into OA versus water and this can be evaluated using field data. If both processes occur in parallel in the atmosphere, vapor pressure dependent partitioning may occur along with aqueous processing without significant double counting or duplication in models. However, due to the high relative humidity and degree of oxygenation of organic compounds in the southeast US atmosphere, inorganic-rich and organic-rich phases may not be distinct (You et al., 2013) and more advanced partitioning algorithms accounting for a mixed inorganic-organic-water phase may be needed (Pye et al., 2016).

Only one study evaluated the potential impact of SOA formation in clouds in the SE US during 2013, and found a small and not statistically significant effect (Wagner et al., 2015).

3.2.2 Primary organic aerosol

Primary organic aerosol concentrations are expected to be small in the Southeast outside urban areas and we make no major recommendation for how to model them. Modelers should be aware that a fraction of primary organic aerosol (POA) based on the EPA National Emission Inventory (NEI) is semivolatile (Robinson et al., 2007). However, not all POA is thought to be semivolatile – for example, OA from sources such as soil are included in the NEI. Modeled POA may already include some oxidized POA (OPOA) (if the models include heterogeneous oxidation (as in CMAQ (Simon and Bhave, 2012)), or hydrophilic conversion (as in GEOS-Chem (Park et al., 2003))). Thus model POA is not directly equal to Aerosol Mass Spectrometer (AMS) Positive Matrix Factorization (PMF) factors such as hydrocarbon-like OA (HOA). For semivolatile POA treatments, mismatches between POA inventories and semivolatile/intermediate volatility organic compounds (S/IVOCs) needs to be carefully considered. Comparisons of model inventory versus ambient ratios of POA/ΔCO, POA/black carbon (BC), or POA/NO_x can be used to indicate whether or not POA emissions are excessive (De Gouw and Jimenez, 2009). As these ratios can be affected by errors in the denominator species, it is important to also evaluate those carefully against observations. For models with limited POA information, the ratio of organic matter to organic carbon (OM/OC) should be adjusted to reflect the highly oxidized nature of ambient OA (as mass is transferred from hydrophobic/hydrophilic concentrations for example). The OM/OC ratio of bulk ambient OA in the Southeast US is 1.9-2.25 as measured during summer 2013 (Kim et al., 2015; Pye et al., 2016).

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

3.2.3 Particle-phase organic nitrates

Organic nitrates, primarily from monoterpene reactions with the nitrate radical, have been recognized as an important source of OA in the southeast, contributing from 5 to 12% in Southeast US in summer (Ayres et al., 2015; Lee et al., 2016a; Pye et al., 2015; Xu et al., 2015a; Xu et al., 2015b). We have high confidence that models should include SOA formation from nitrate radical oxidation of monoterpenes. Sesquiterpenes and isoprene may also contribute OA through nitrate radical oxidation, but the contribution is expected to be smaller (Fisher et al., 2016; Pye et al., 2015). A number of options exist for representing this type of aerosol including fixed yields, Odum 2-product parameterizations, volatility basis set (VBS) representations (Boyd et al., 2015), and explicit partitioning/uptake of organic nitrates (Fisher et al., 2016; Pye et al., 2015).

Detailed modeling studies can provide additional insight into the interactions between monoterpene nitrate SOA and gas-phase chemistry, as well as the fates of specific organic nitrates. Explicit formation and treatment of organic nitrates, yields of which are parent hydrocarbon specific, can take into account hydrolysis of particle-phase organic nitrate (ON). The hydrolysis should depend on the relative amounts of primary, secondary, and tertiary nitrates which are produced in different abundances in photooxidation vs. nitrate radical oxidation (Boyd et al., 2015).

Hydrolysis may also depend on the level of acidity and presence of double bonds in the organic nitrate (Jacobs et al., 2014). In addition to hydrolysis, particle organic nitrates could photolyze and release NO_x or serve as a NO_x sink through deposition (Nah et al., 2016b).

3.2.4 Isoprene epoxydiol (IEPOX) SOA

Due to the abundance of observations in the Southeastern atmosphere (Budisulistiorini et al., 2015a; Hu et al., 2015; Xu et al., 2015a; Xu et al., 2016; Xu et al., 2015b), similarity between laboratory and field IEPOX-SOA determined by PMF analysis, and availability of model parameterizations to predict IEPOX-SOA (Marais et al., 2016; Pye et al., 2013; Woo and McNeill, 2015), we have high confidence that IEPOX-SOA should be included in models. However, a number of parameters needed to predict IEPOX-SOA are uncertain and different modeling approaches, as well as the use of all available experimental constraints, could be beneficial. The mechanism of IEPOX-SOA formation is likely aqueous processing which can occur either in aerosols or cloud droplets. This mechanism could be represented as heterogeneous reaction with a reactive uptake coefficient or more explicit partitioning and particle reaction.

The correlation of IEPOX-SOA with sulfate (Hu et al., 2015; Xu et al., 2015a; Xu et al., 2016) can serve as a useful model evaluation technique as underestimates in sulfate could lead to underestimates in IEPOX-SOA in models (Figure 2). Current pathways for IEPOX-OA formation (Eddingsaas et al., 2010) involve acidity. Ion balances or other simple measures of aerosol acidity are likely inadequate to characterize particle acidity and thermodynamic models such as

ISORROPIA II or AIM are more appropriate for modeling IEPOX-SOA (Guo et al., 2015; Weber et al., 2016). Ammonia uptake might be limited by organics thus affecting acidity (Kim et al., 2015).

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

3.2.5 Glyoxal SOA

New information on glyoxal SOA is emerging in this area but its importance in the Southeast remain unclear. Glyoxal has been suspected to be the dominant aqueous SOA source under high-NO_x (RO_2 + NO) oxidation conditions (McNeill et al., 2012) and the Southeast has a mix of high-NO_x and low-NO_x (RO_2 + HO_2) conditions (Travis et al., 2016). In addition, abundant isoprene emissions can lead to substantial glyoxal concentrations. Modeling for the southeastern U.S. indicates significant SOA can form from glyoxal (Knote et al., 2014; Li et al., 2016; Marais et al., 2016; Pye et al., 2015). Implementation in models may require modifications to the gas-phase chemistry to specifically track glyoxal which may be lumped with other aldehydes (e.g. in CB05). We cannot assert that this pathway should be universally included in all southeastern modeling applications. However, future modeling studies, when compared with measurements, can help understand the role of aerosol uptake and glyoxal yield from isoprene.

3.2.6 SOA from Anthropogenic Emissions

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

3.2.7 Surface network observations of organic aerosols

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

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

3.2.8 Climate relevant properties

The first goal of studies examining the implications of southeast PM on AOD should be to predict the total mass loading of aerosol correctly. AOD is not directly proportional to the surface concentrations due to changes in PBL (Kim et al., 2015). Representing aerosol water is also important for climate applications.

3.3 Open questions

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

- What is the role of particle-phase organic nitrates in removing or recycling NO_x from the system?
- How much detail do models need to represent in terms of types of organic nitrate (ON)?
- What are the formation mechanisms of highly oxygenated organics?
- What anthropogenic sources of SOA are models missing?
- What interactions with aerosol- and cloud-water are needed in models?
- What is the role of clouds in forming and processing organic aerosols?

4. Emission inventories

4.1 Background

Emission inventories are a critical input to atmospheric models, and reliable inventories are needed to design cost-effective strategies that control air pollution. For example, in the 1970s and 1980s, emission control strategies implemented under the Clean Air Act emphasized the control of anthropogenic VOC emissions over NO_x (National Research Council, 2004). Despite large order of magnitude reductions in anthropogenic VOC emissions (Warneke et al., 2012), abatement of O_3 was slow in many regions of the country. In the late 1980s, a large and underrepresented source of biogenic VOC emissions was identified (Abelson, 1988; Chameides et al., 1988; Trainer et al., 1987), putting into question the effectiveness of anthropogenic VOC emission control strategies to mitigate O_3 nationally (Hagerman et al., 1997). Since the mid-1990s, large reductions in NO_x emissions have resulted from: (i) controls implemented at power plants (Frost et al., 2006), (ii) more durable three-way catalytic converters installed on gasoline vehicles (Bishop and Stedman, 2008), and (iii) more effective regulation of diesel NO_x emissions from heavy-duty trucks (McDonald et al., 2012; Yanowitz et al., 2000). Emission reductions implemented on combustion sources, have also been linked to decreases in organic aerosol concentrations observed in both California (McDonald et al., 2015) and the Southeastern U.S. (Blanchard et al., 2016). Though a lot of progress has been made in improving scientific understanding of the major biogenic and anthropogenic sources of emissions contributing to air quality problems, some issues remain in current U.S. inventories and are highlighted below.

The Southeast US is a region that has both the highest natural emissions and large anthropogenic emissions. The accurate knowledge of biogenic emissions is key to understanding many of the processes that lead to ozone and aerosol formation. Previous studies suggest that MEGAN can produce twice as much isoprene compared with BEIS over the Eastern US (Carlton and Baker, 2011; Warneke et al., 2010), but most global models using MEGAN do not show a significant bias of isoprene over the Southeast US (Mao et al., 2013; Millet et al., 2006). Validation of the various biogenic emission inventories was therefore one of the main science questions for the SAS2013 studies. *Which of the most commonly used isoprene emission inventories represents the magnitude and the location the best?*

The National Emissions Inventory (NEI) developed by U.S. EPA, is an inventory of air pollutants released every three years, and commonly used in U.S.-based air quality modeling studies. A recent modeling study reported that NO_x emissions from mobile source emissions were overestimated by 51-70% in the Baltimore-Washington, D.C. region (Anderson et al., 2014) Past studies have also found discrepancies in motor vehicle emission models used by EPA to inform the NEI (McDonald et al., 2012; Parrish, 2006). Additionally, problems have been identified in estimates of NO_x, VOC, and methane emissions from U.S. oil and gas development (Ahmadov et al., 2015; Brandt et al., 2014; Pétron et al., 2014). Some major oil and gas basins of note are located in the Southeastern U.S., which were measured by aircraft during the SAS2013 studies. In contrast to mobile source and oil and gas emissions, power plant emissions of NO_x and SO_x are believed to be known with greater certainty since large stationary sources of emissions are continuously monitored. In addition to biogenic emission inventories, the datasets collected by the SAS2013 studies have provided an opportunity to assess the accuracy of anthropogenic emissions and their impacts on atmospheric chemistry. *How are O_3 concentrations affected by uncertainties in NO_x and VOC emissions for key anthropogenic sectors in bottom-up emission inventories?*

The topic of model resolution, which involves the relationship between emissions and chemistry, was also of great interest at the SAS workshop. Regional-scale air quality models can be simulated at very high horizontal resolutions (e.g., 1 km and finer) (Joe et al., 2014); however, typically they are run at coarser resolutions, such as at 12 km by 12 km (e.g., continental U.S.)(Gan et al., 2016) or 4 km by 4 km (e.g., urban scale) (Kim et al., 2016b). The horizontal resolution of global chemistry models has significantly improved, with nesting being performed at horizontal resolutions as fine as ~0.25 degree (Travis et al., 2016). Coarse model resolutions can complicate evaluations with high spatial and temporal-resolution measurements (e.g., from aircraft) of chemical constituents undergoing fast chemistry (e.g., isoprene, OH) (Kaser et al., 2015). Sharp concentration gradients are observable from space for species with relatively short atmospheric lifetimes (e.g., nitrogen dioxide, formaldehyde, and glyoxal), and potentially provide insights into the role of natural and anthropogenic emissions on air quality (Duncan et al., 2010; Lei et al., 2014; Russell et al., 2012a). Lastly, some emission sources are described by large emission intensities (e.g., power plants and biomass burning), which result in elevated concentrations of emitted species downwind. A coarse model will artificially dilute these high emission fluxes (e.g., NO_x and SO_x) over a wider area, which could alter the chemical regime by which ozone (Ryerson et al., 1998; Ryerson et al., 2001) and secondary aerosols (Xu et al., 2015a) form.

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4.2 Preliminary Findings

Isoprene emissions were measured onboard of the NOAA P3 and NCAR/NSF C-130 aircraft using the mixed boundary layer method and eddy covariance flux measurements. The two methods of estimating isoprene emissions agreed within their uncertainties. In addition, isoprene emissions were estimated along the flight tracks from emission inventories (BEIS3.12, BEIS3.13, MEGAN2.0, MEGAN2.1, and MEGAN_v2015) with meteorological data measured on the aircraft as input. The measurements and inventory estimates were compared and showed that on average BEIS was lower than the measurements and MEGAN was higher than the measurements. MEGAN predicted isoprene emissions in the Southeast US were about twice as high as BEIS. Isoprene mixing ratios were modeled with a) WRF-Chem using BEIS and with b) CAMx using MEGAN and the results were consistent with the measurement-inventory comparison: WRF-Chem was biased low and CAMx biased high. (Warneke et al., in preparation)

Landcover characteristics including Leaf Area Index (LAI) and tree species composition data are critical driving variables for MEGAN isoprene and monoterpene emission factors. The isoprene and monoterpene emission factors were estimated using the airborne flux measurements. It was found that the isoprene emission factors agreed well with MEGAN2.1 for landscapes dominated by high isoprene emitting species, but landscapes that had the high isoprene emitters in the understory showed emissions lower than expected by the model. The isoprene emission factor was linear correlated with the high isoprene emitter plant species fraction in the landscape data set. This shows the need for models to include canopy vertical heterogeneity of the isoprene emitting fraction (Yu et al., in preparation).

The LES model was used to simulate isoprene, NO_x and their variability in the boundary layer. The results showed good agreement between the measurements and the model. The atmospheric variability of isoprene, the altitude profile in the boundary layer of isoprene and NO_x mixing ratios and fluxes were well reproduced in the model, which was used to validate the eddy covariance and mixed boundary layer methods of estimating isoprene fluxes (Kim et al., 2016a; Wolfe et al., 2015).

To investigate potential causes of previous discrepancies and the usefulness of RGF (Ratio of Glyoxal and Formaldehyde) measurements of CHOCHO and HCHO were presented over the Southeast US from SENEX2013 and compared with OMI (Ozone Monitoring Instrument) satellite retrievals. High time-resolution flight measurements show that high RGF is associated with monoterpene emissions, low RGF is associated with isoprene oxidation, and emissions associated with oil and gas production can lead to small-scale variation in regional RGF. During the summertime in the Southeast US, RGF is not a reliable diagnostic of anthropogenic VOC emissions, as HCHO and CHOCHO production are dominated by isoprene oxidation. The results show that a new CHOCHO retrieval algorithm reduces the previous disagreement between satellite and in situ RGF observations. As the absolute values and trends in RGF observed during SENEX are largely reproduced by OMI observations, the conclusion is that satellite- based observations of RGF can be used alongside knowledge of land use as a global diagnostic of dominant hydrocarbon speciation (Kaiser et al., 2015).

To investigate mobile source emissions, a fuel-based approach to estimating NO_x emissions was presented. Engine activity was grounded in fuel use data, and emission factors were estimated from *in situ* roadway measurements. Compared to the fuel-based inventory, the NEI overestimated NO_x emissions by ~50% and ~20% from mobile sources and all anthropogenic sources, respectively, in the Southeast. When NO_x emissions in the NEI were replaced with the fuel-based inventory, and simulated in a chemical transport model for the SENEX Study, modeling biases of O_3 were reduced in the Southeastern U.S. by up to 4 ppbv (McDonald et al., in preparation). The overestimate in NO_x emissions is consistent with another modeling study performed during the SEAC4RS Study, which found that NO_x emissions in the NEI were overestimated by 50% nationally and in the Southeast (Travis et al., 2016). When NO_x emissions were reduced by this amount, model predictions of O_3 over the Southeastern U.S. were also significantly improved.

A couple studies have quantified top-down emissions of oil and gas operations, derived from aircraft measurements for VOCs and methane from SENEX P-3 data (Peischl et al., 2015; Yuan et al., 2015). Modeling studies are underway to determine the extent to which air quality is impacted from oil and gas emissions.

The SCICHEM Plume Model, fed with meteorological data from the WRF model and emissions from CEMS, was compared to NOAA P-3 aircraft data downwind of a coal-fired power plant. The model under-predicted peak plume concentrations by a factor of 2 for SO_2 and NO_y at 8 km downwind, though results improved further downwind. More research is needed to determine whether these under-predictions are related to chemistry, transport, or emissions.

To represent the impact of biomass burning, air quality models need improved treatments of initial VOC and NO_x emissions and near source chemistry. Sub-grid parameterizations, based on detailed models like the Aerosol Simulation Program (ASP) (Alvarado and Prinn, 2009) and which incorporates gas-phase chemistry, inorganic and organic aerosol thermodynamics, and evolution of aerosol size distribution and optical properties, could improve coarse model representations of chemistry near biomass burning plumes.

4.3 Model Recommendations and Future Work

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

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

(3) MEGAN emission factors could be updated with the linear relationship to the isoprene emitter fraction that might come available as a result of the SAS work and should be evaluated.

(4) A revised NO_x emissions inventory is needed to improve air quality models for O_3, especially in the Southeast U.S. where O_3 is sensitive to changes in NO_x emissions. Anthropogenic emissions of NO_x in the NEI 2011 may be overestimated by 20-50% in the Southeastern U.S. during the SAS2013 study time period.

5. Chemistry-Climate Interactions

5.1 Background

Interactions between atmospheric chemistry and climate over the southeastern United States are not well quantified. The dense vegetation and warm temperatures over the Southeast result in large emissions of isoprene and other biogenic species. These emissions, together with anthropogenic emissions, lead to annual mean aerosol optical depths (AODs) of nearly 0.2, with a peak in summer (Goldstein et al., 2009). The climate impacts of US aerosol trends in the Southeast due to changing anthropogenic emissions is under debate (Leibensperger et al., 2012a, b; Yu et al., 2014). Climate change can, in turn, influence surface air quality, but even the sign of the effect is unknown in the Southeast (Weaver et al., 2009). Part of this uncertainty has to do with complexities in the mechanism of isoprene oxidation, the details of which are still emerging from laboratory experiments and field campaigns (Fisher et al., 2016; Liao et al., 2015; Marais et al., 2016). In addition, the influence of day-to-day weather on surface ozone and particulate matter (PM2.5) has not been fully quantified, and climate models simulate different regional climate responses. Resolving these uncertainties is important, as climate change in the coming decades may impose a "climate penalty" on surface air quality in the Southeast and elsewhere (Fiore et al., 2015).

5.2 Key science issues and recent advances.

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

5.2.1. Seasonality and trends in aerosol loading in the Southeast

Using satellite data, Goldstein et al. (2009) diagnosed summertime enhancements in AOD of 0.18 over the Southeast, relative to winter, and hypothesized that secondary organic aerosol from biogenic emissions accounts for this enhancement. Goldstein et al. (2009) further estimated a regional surface cooling of -0.4 Wm-2 in response to annual mean AOD over the Southeast. These findings seemed at first at odds with surface PM2.5 measurements, which reveal little seasonal enhancement in summer. Using SEAC4RS measurements and GEOS-Chem, Kim et al. (2015) determined that the relatively flat seasonality in surface PM2.5 can be traced to the deeper boundary layer in summer, which dilutes surface concentrations.

In response to emission controls, aerosol loading over the Southeast has declined in recent decades. For example, wet deposition fluxes of sulfate decreased by as much as ~50% from the 1980s to 2010 (Leibensperger et al., 2012b). Over the 2003-2013 time period, surface concentrations of sulfate PM2.5 declined by 60% and organic aerosol (OA) also declined by 60% even though most OA appears to be biogenic and there is no indication of a decrease in anthropogenic sources (Kim et al., 2015). Model results suggest that the observed decline in OA may be tied to the decrease in sulfate, since OA formation from biogenic isoprene depends on aerosol water content and acidity (Marais et al., 2016). Consistent with these surface trends, 550-nm AOD at AERONET sites across the Southeast has also decreased, with trends of -4.1% a-1 from 2001-2013 (Attwood et al., 2014). Xing et al. (2015a) reported a roughly -4% decrease in remotely sensed AOD across the eastern United States, as measured by Aqua on board the Moderate Resolution Imaging and Spectroradiometer (MODIS). These large decreases could potentially have had a substantial impact on regional climate, both through aerosol-radiation interactions and aerosol-cloud interactions.

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

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

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

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

These early model studies have been followed by more observationally based efforts to link trends in surface temperature to aerosol loading. A key first step is to determine whether changes in surface solar radiation are related to changes in aerosol loading. Measurements from the Surface

Radiation network (SURFRAD) reveal increases of +0.4 Wm^{-2} a^{-1} in total surface solar radiation across the East during 1995-2010 (Gan et al., 2014). An attempt to reproduce the trend in total surface radiation with a regional chemistry-climate model found a reasonable match with observations over the East when aerosol-radiation interactions were included (Xing et al., 2015a). Most of the observed increase in surface solar radiation, however, appears due to increasing diffuse radiation, at odds with the decline in AOD, which should instead increase direct radiation (Gan et al., 2014; Gan et al., 2015). Using satellite data and assimilated meteorology, Yu et al. (2014) showed that trends in spatially averaged AOD and cloud optical depth declined over the 2000-2011 time period over the eastern US, while daily maximum temperatures and shortwave cloud forcing increased. These opposing trends suggest that aerosol-cloud interactions may have influenced the observed ~1 °C warming trend in the Southeast over this ten-year time period, with the decline in anthropogenic aerosols driving a decrease in cloud cover and a rise in surface temperatures. Yu et al. (2014) confirmed this hypothesis using a chemistry-climate model.

In contrast to Leibensperger et al. (2012a) and Yu et al. (2014), the model study of Mascioli et al. (2016) reported little sensitivity in Southeast surface temperatures to external forcings such as anthropogenic aerosols or even greenhouse gases. For example, trends in anthropogenic aerosols in this model had no impact on surface temperature in the Southeast from 1860 to 2005, at least as quantified by the metric *TXx*, the maximum of the daily maximum temperature over a 30-year time period. It is not clear what accounts for the differences in sensitivity to changing aerosols among the different models. Uncertainties in aerosol-cloud interactions, soil moisture feedbacks, and aerosol optical properties all likely contribute to the modeled discrepancies.

Continued improvements of PM2.5 air quality in the Southeast may further influence regional climate. Lee et al. (2016b) projected a warming of about +0.5 Wm^{-2} over the eastern U.S., including the Southeast, over the 2000-2030 timeframe due to anticipated improvements in air quality and the associated reduction in AOD. Xing et al. (2015b) have pointed out that an overlooked beneficial effect of aerosol reduction is increased ventilation of surface air, a positive feedback that leads to further decline in surface PM2.5 concentrations. The feedback arises from changes in the temperature profile, with warmer temperatures at the surface and cooler temperatures aloft, which together enhance atmospheric instability and ventilation as aerosol induced cooling is reduced. The feedback may lead to unexpected health benefits of clearing PM2.5 pollution (Xing et al., 2016).

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

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

Fu et al. (2015) used models and observations to examine the sensitivity of August surface ozone in the Southeast to temperature variability during 1988-2011. This study finds that warmer temperatures enhance ozone by increasing biogenic emissions and accelerating photochemical reaction rates. However, variability in ozone advection into the region may also explain much of the variability of surface ozone, with possibly increased advection occurring during the positive phase of the Atlantic Multidecadal Oscillation (AMO). Applying empirical orthogonal functions (EOF) analysis to observed ozone, Shen et al. (2015) determined that the sensitivity of surface ozone in the Southeast can be quantified by the behavior of the west edge of the Bermuda High. Specifically, for those summers when the average position of the west edge is located west of ~85.4° W, a westward shift in the Bermuda High west edge increases ozone in the southeast by 1 ppbv deg^{-1} in longitude. For all summers, a northward shift in the Bermuda High west edge increases ozone over the entire eastern United States by 1-2 ppbv deg^{-1} in latitude.

The influence of meteorology on $PM_{2.5}$ in the Southeast is not well quantified. Tai et al. (2010) found that observed sulfate and OC concentrations increase with increasing temperature across the region due to faster oxidation rates and the association of warm temperatures with stagnation and biogenic and fire emissions. Nitrate $PM_{2.5}$, however, becomes more volatile at higher temperatures and decreases with temperature. Using local meteorology, however, Tai et al. (2010) could explain only about 20-30% of $PM_{2.5}$ daily variability in the Southeast. Both Thishan Dharshana et al. (2010) and Tai et al. (2012b) diagnosed a relatively weak effect of synoptic scale weather systems on $PM_{2.5}$ air quality in the Southeast, especially in the deep South, where such systems explained less than 20% of the variability.

5.2.4. Effects of future climate change on Southeast air quality

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

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

Model studies differ on the effects of future climate change on $PM_{2.5}$ in the Southeast. Tai et al. (2012a) and Tai et al. (2012b) analyzed trends in meteorological modes from an ensemble of climate models and found only modest changes in annual mean $PM_{2.5}$ ($\pm 0.4\ \mu g\ m^{-3}$) by the 2050s in the Southeast, relative to the present-day. Using a single chemistry-climate model, Day and Pandis (2015) calculated significant increases of ~ 3.6 $\mu g\ m^{-3}$ in July mean $PM_{2.5}$ along the Gulf

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coast by the 2050s and attributed these increases to a combination of decreased rain-out, reduced ventilation, and increased biogenic emissions.

5.3. Open questions

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

1. What is the impact of aerosols on regional climate of the Southeast? What role do feedbacks play, including feedbacks involving cloud cover, soil moisture, and boundary layer height? How will changing aerosol composition affect regional climate? Can we use observed weekly cycles in temperature or precipitation to probe possible aerosol effects on regional climate (Bäumer et al., 2008; Bell et al., 2008; Daniel et al., 2012; Forster and Solomon, 2003)?

2. What caused the U.S. warming hole? Is the observed cooling over the Southeast partly due to natural variability of North Atlantic SSTs? Has the warming hole ended and made the central and southeastern United States more vulnerable to high temperatures and drought?

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

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

5.4. Model recommendations

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

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

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

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

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

Modelers need to consider the statistical significance of observed trends and perform ensemble simulations for robust statistics. The auto-correlation of the variables under investigation should be examined. Comparison of observed trends with samples of internal climate variability from model control runs, as in (Knutson et al., 2013), may be a useful approach, and modelers should acknowledge that observations may represent an outlier of unforced variability.

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

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

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- Sensitivity of surface air quality to synoptic weather systems, including the westward extent of Bermuda High and cold front frequency
- Sensitivity of surface air quality to local meteorological variables and isoprene emissions on a range of temporal scales.
- Sensitivity of soil moisture and cloud cover to changing meteorology and the consequences for regional climate and air quality.

6. Summary

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

Gas-phase chemistry (1) Up-to-date "standard" chemical mechanisms represent OH chemistry well over the observed range of NO_x concentrations. Detailed mechanisms based on recent laboratory chamber studies (mostly at Caltech) and theoretical studies (Leuven) for isoprene chemistry result in predicted OH that is in reasonable agreement with observations. Condensed mechanisms that approximate these details are expected to do the same. (2) Given the large emissions and high chemical reactivity of isoprene, its chemistry should be treated fairly explicitly, including more detail than for most other hydrocarbons. (3) NO_3 chemistry contributes significantly to both VOC oxidation and aerosol production. (4) The regions of peak NO_x and BVOC emissions are not collocated. As a result, the model resolution can impact the predictions.

Organic Aerosol (1) There is high confidence that a pathway of SOA formation from isoprene epoxydiol (IEPOX) should be included in models. However, since many of the parameters needed to predict IEPOX-SOA are uncertain, further mechanistic studies are needed to address these uncertainties. (2) There is high confidence that models should include SOA formation from nitrate radical oxidation of monoterpenes (with or without explicit nitrate functionality). Sesquiterpenes and isoprene may also contribute SOA through nitrate radical oxidation, but the contribution is expected to be smaller. (3) Models can help determine how important glyoxal (produced from isoprene, as well as from anthropogenic VOCs) is as a SOA precursor. (4) There is high confidence that models should predict SOA from urban emissions with a parameterization that results in realistic concentrations.

Natural and anthropogenic emissions (1) Biogenic emissions from BEIS are generally lower and those from MEGAN, generally higher than from measurements for all campaigns. (2) Observations confirm a rapid decrease of ozone precursor emissions over past few decades. Thus, use of the correct scaling of anthropogenic emissions for a particular year is important for accurate simulations. (3) National Emissions Inventory (NEI) 2011 likely overestimates NO_x emissions in the study area from mobile sources that use fuel-based estimates.

Regional climate and chemistry interactions (1) Annual mean temperatures during the 1930-1990 timeframe decreased by ~1°C over the central and southeastern United States. Several studies have argued that patterns of sea surface temperatures in the North Atlantic may have caused this large-scale cooling. Trends in aerosol forcing may have also played a role. (2) Pollution episodes in the southeastern United States are correlated with high temperatures, low wind speeds, clear skies, and stagnant weather. Surface air quality over Southeast US may be to some extent modulated by large-scale circulations, such the Bermuda High or Atlantic Multi-decadal Oscillation (AMO).

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7. Glossary of Acronyms

AM3: The atmospheric component of the GFDL coupled climate model CM3.

AMS: Aerosol Mass Spectrometer

AMO: Atlantic Multi-decadal Oscillation

AOD: aerosol optical depth

BBOA: Biomass burning OA

BEIS: Biogenic Emission Inventory System

BVOC: Biogenic Volatile Organic Compounds

CAMx: Comprehensive Air Quality Model with Extensions

CEMS: Continuous emission monitoring systems

CMAQ: Community Multi-scale Air Quality Model

CSN: Chemical Speciation Monitoring Network

EF: Emission Factor

FIXCIT: A laboratory experiment focused on isoprene oxidation chemistry and the instruments we took to the field to understand that chemistry

HOA: Hydrocarbon-like OA

IEPOX: Isoprene epoxydiol

IMPROVE: Interagency Monitoring of Protected Visual Environments visibility monitoring network

LAI: Leaf Area Index

LES: Large-eddy simulation

LO-OOA: Less-oxidized oxygenated OA

MACR: Methacrolein

MEGAN: Model of Emissions of Gases and Aerosols from Nature

MO-OOA: More-oxidized oxygenated OA

MVK: Methyl vinyl ketone

NEI: National Emissions Inventory

NOAA: National Oceanic and Atmospheric Administration

NOMADSS: Nitrogen, Oxidants, Mercury and Aerosol Distributions, Sources and Sinks aircraft campaign, took place during Jun-Jul 2013 with the NSF/NCAR C-130 aircraft.

OA: Organic aerosol

OC: Organic carbon

OM: Organic matter

OMI: Ozone Monitoring Instrument

PAN: Peroxy Acetyl Nitrate

PFT: Plant Functional Type

PMF: Positive Matrix Factorization

POA: primary organic aerosol

RGF: Ratio of Glyoxal to Formaldehyde

SAS: Southeast Atmosphere Studies

SCIPUFF: Second Order Closure Integrated Puff Model

SEAC4RS: Studies of Emissions, Atmospheric Composition, Clouds and Climate Coupling by Regional Surveys aircraft campaign, took place during Aug-Sept 2013 with NASA DC-8 and ER-2 aircraft

SEARCH: Southeastern Aerosol Research and Characterization Network

SENEX: SouthEast NEXus of air quality and climate campaign

S/IVOCs: Semivolatile/intermediate volatility organic compounds

SOA: Secondary Organic Aerosols

SOAS: the Southern Oxidant and Aerosol Study ground-based campaign, took place during Jun-Jul 2013 near Brent, Alabama.

SURFRAD: Surface Radiation Budget Network

VBS: volatility basis set (VBS)

WRF-Chem: Weather Research and Forecasting with Chemistry model

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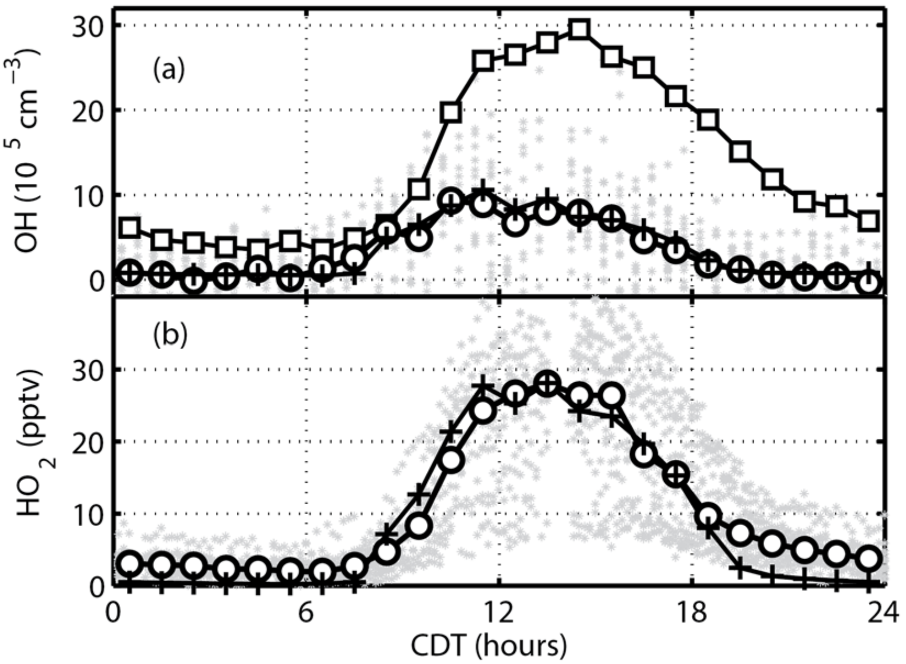

Figure 1 Diel variation of measured and modeled OH/HO_2 during SOAS (Feiner et al., 2016). In panel (a), measured OH by a traditional laser induced fluorescence technique is shown in squares and by a new chemical scavenger method is shown in circles. The latter one is considered as the "true" ambient OH. Simulated OH from a photochemical box model with Master Chemical Mechanism (MCM) v3.3.1 is shown in pluses. In panel (b), measured HO_2 is shown in circles and modeled HO_2 is shown in pluses. For both panels, gray dots are individual 10-minute measurements.

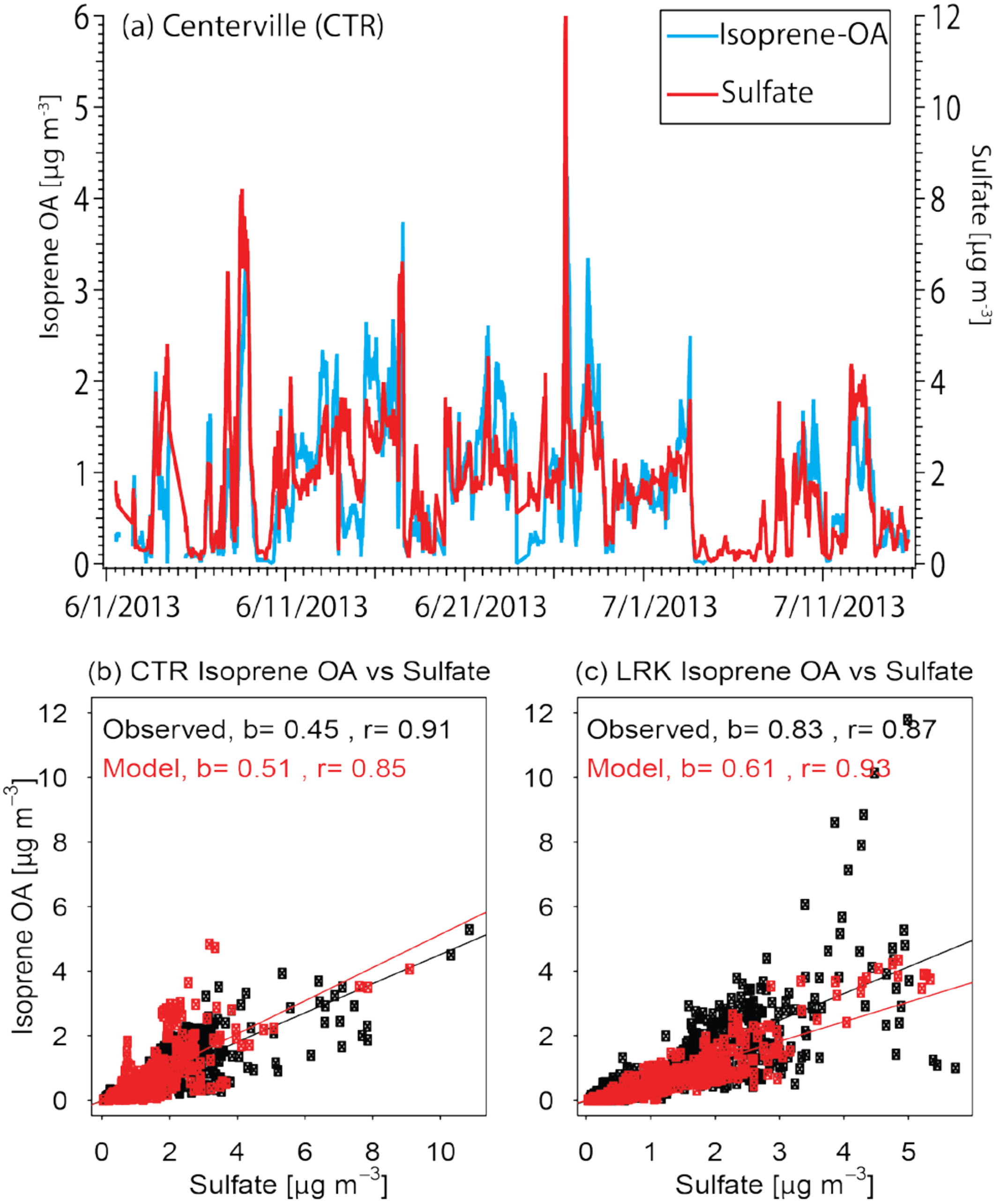

Figure 2. Time series and correlation between Isoprene OA and sulfate during SOAS (Pye et al., 2016; Xu et al., 2015). Panel (a) shows the time series of both Isoprene OA and sulfate at

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Centreville site during SOAS. Panel (b) and (c) shows the correlation plot between Isoprene OA and sulfate from both measurements and model results at two sites (Centreville and Little Rock) during SOAS.

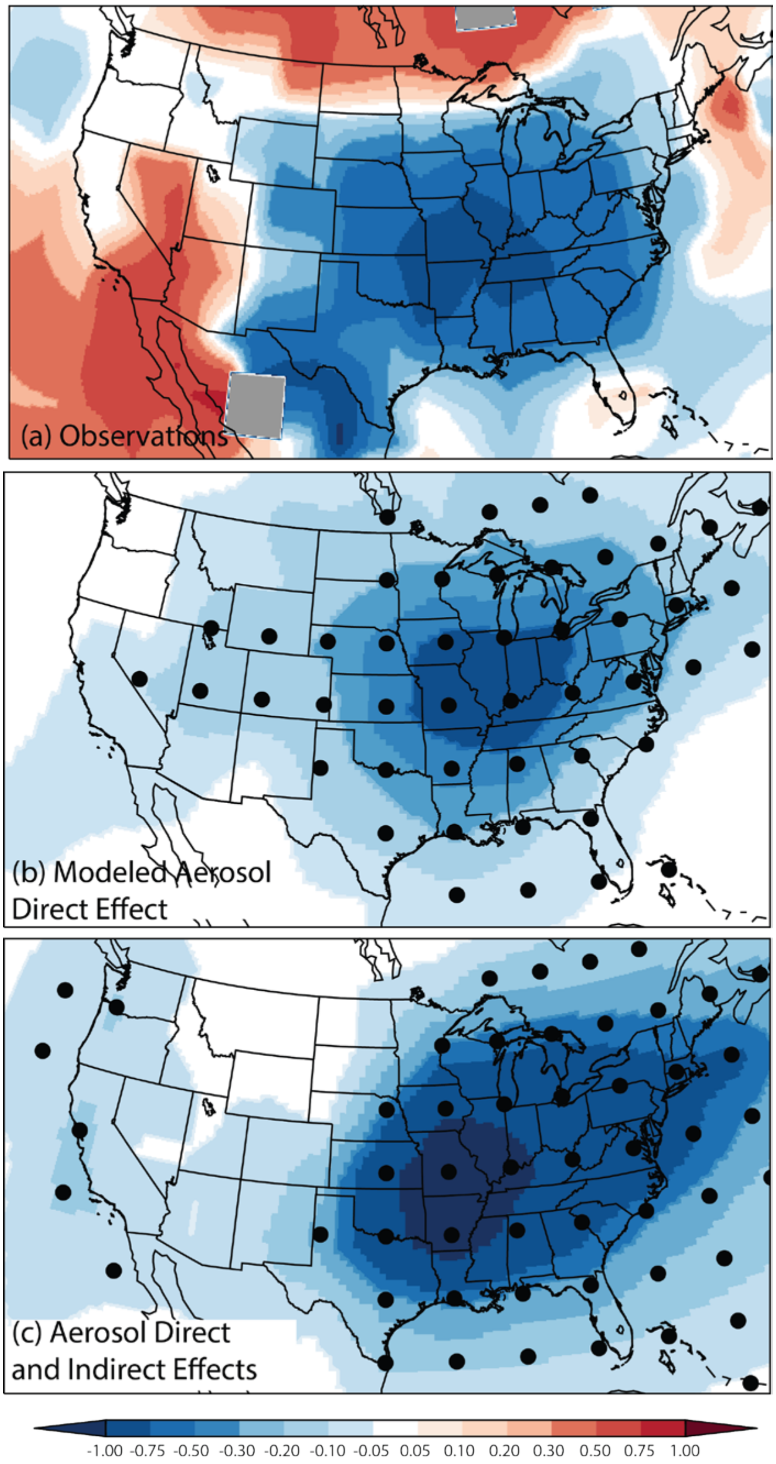
(a) Observations
(b) Modeled Aerosol Direct Effect
(c) Aerosol Direct and Indirect Effects
-1.00
-0.75
-0.50
-0.30
-0.20
-0.10
-0.05
0.05
0.10
0.20
0.30
0.50
0.75
1.00

Figure 3 Observed difference in surface air temperature between 1930 and 1990 (a) and modeled effect of US anthropogenic aerosol sources on surface air temperatures for the 1970–1990 period when US aerosol loading was at its peak (b and c) (Leibensperger et al., 2012a). Observations are from the NASA GISS Surface Temperature Analysis (GISTEMP; http://data.giss.nasa.gov/gistemp/). Model values represent the mean difference between 5-member ensemble GCM simulations including vs. excluding US anthropogenic aerosol sources, and considering the aerosol direct only (b) and the sum of direct and indirect effects (c). In (b) and (c), dots indicate differences significant at the 95th percentile.