

The Southern Oxidant and Aerosol Study (SOAS):

Measuring and modeling at the interface of air quality and climate change to understand biosphere-atmosphere interactions

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OVERVIEW

The Southeastern U.S. has been a focus area in classic and historic atmospheric field studies. Natural emissions of organic compounds (e.g., isoprene and monoterpenes) in the Southeast are high, rivaling rates in tropical areas. The location is ideal to study biogenic-anthropogenic interactions (Figure 1), due to the proximity of natural emissions with a variety of anthropogenic pollution sources. In the past decade, there has been a remarkable decrease in combustion related NO_x emissions, resulting in significant changes in the chemistry of organic oxidation.

The Southern Oxidant Study (SOS) spanned nearly a decade (the 1990s), involving several sites around Nashville, TN, Atlanta, GA and other locations. The Southeastern Aerosol and Visibility Study (SEAVS) took place in 1995 in the Great Smoky Mountains National Park. During the 20⁺ years since these intensive field studies, our understanding of biosphere-atmosphere interactions and the subsequent influences on atmospheric oxidant chemistry and aerosol formation has dramatically improved. We now have specific knowledge of first and second generation products of isoprene photooxidation and have the beginnings of a mechanistic understanding of isoprene oxidation and secondary organic aerosol formation from isoprene, monoterpenes and sesquiterpenes. Analytical instrumentation for laboratory and *in situ* measurements are vastly improved, not only in temporal resolution, but in the spectrum of measurable compounds. It is now possible to explicitly quantify a variety of gas and aerosol phase species in near real time, such as: glyoxal, alkyl nitrates, epoxides, [•]RO₂ radicals and

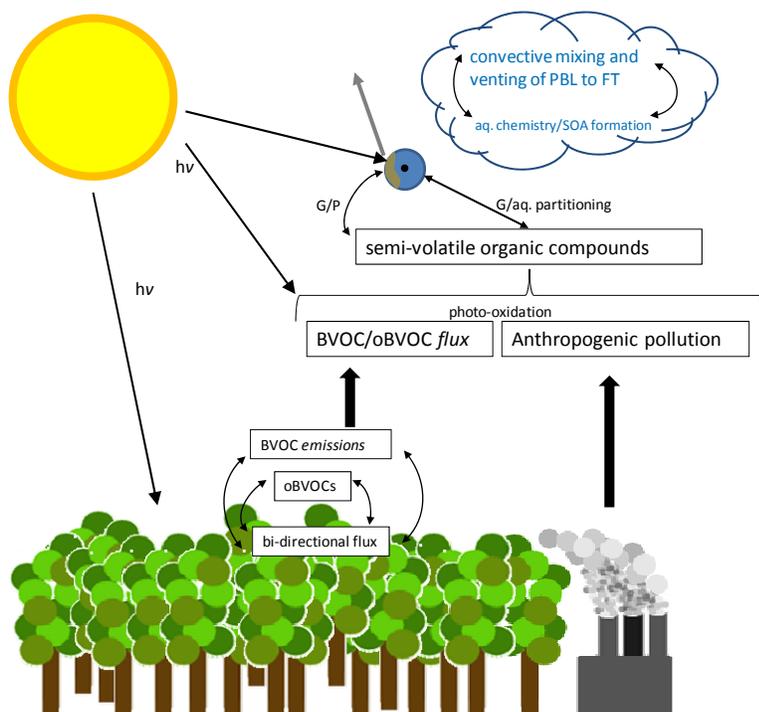


Figure 1. Biogenic emissions and anthropogenic pollution interact and affect atmospheric photo-oxidation chemistry and subsequently air quality and climate.

compounds, and secondary organic aerosol tracers specific to VOC precursor. Satellite based sensors are recording changes in NO_x associated with reduced emissions from electric generating units with remarkable fidelity. The experimental advances make this an opportune moment to build on the history of experiments in the Southeast to address pressing scientific questions in our field, hence the Southern Oxidant and Aerosol Study (SOAS).

The Southeast has not warmed like other regions of the U.S. in

response to global climate change^[1,2] (Figure 2). The anomaly may arise for a variety of reasons. A recent hypothesis is that the climate anomaly may be due to the radiative effects of aerosols derived from biogenic volatile organic compounds (BVOCs)^[1,2]. To understand the causal relationships resulting in this trend, as a community we must ask: 1) What sources and processes control the fate of biogenic compounds in anthropogenically-influenced environments? 2) What are the climate-relevant properties and air quality impacts?

Though widely acknowledged to occur, the degree to which man-made pollution alters biogenic emissions, fluxes and their ultimate fate remains poorly understood. Conventional wisdom during the SOS study regarding biogenic emissions was that BVOCs, namely isoprene, react in the atmosphere to increase O₃ while decreasing OH^[3]. However, twenty years later, current models still cannot adequately describe oxidant concentrations in biogenically-dominated areas^[2] and the daytime oxidation pathways are still uncertain and hotly debated^[4-6]. A better understanding of BVOC oxidation, including nighttime isoprene nitrate formation is essential to understand oxidant production (e.g., ozone, OH), the fate of reactive nitrogen, and the formation of particulate matter (PM).

Until recently, biogenic contributions to the PM burden were thought to arise largely from gas phase terpene oxidation with minor contribution from plant debris (e.g., cuticular waxes)^[7]. Recently isoprene has been shown to contribute to regional secondary organic aerosol (SOA), through gas-phase and multiphase processes. Further, interactions between biogenic and anthropogenic emissions have been demonstrated to affect BVOC oxidation pathways, products and ultimately fate in the atmosphere. Chemical tracers of BVOC contributions to SOA have been measured in a variety of environments^[8-12], including the Southeast U.S.^[13] and the free troposphere^[14]. Yet, adequate process- and regional-level understandings of the coupled effects among BVOCs, and the atmosphere's oxidative capacity and aerosol burden remain elusive.

These critical gaps in our knowledge cannot be addressed in isolation. A coordinated, comprehensive effort is needed to simultaneously advance our understanding of emissions, atmosphere-biosphere exchange, chemistry, aerosol processes, and climate change. An experiment bringing the state-of-the-art capabilities of our community has the potential to produce a substantial leap in our understanding. We propose that as a community we focus

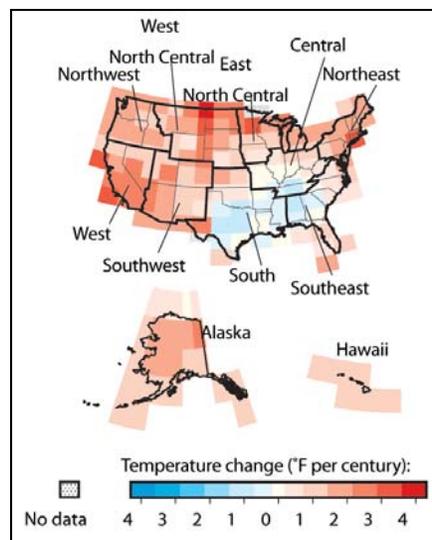


Figure 2. Annual mean temperature anomalies 1901-2005. Figure courtesy of [U.S. EPA](#), data courtesy [NOAA's National Climatic Data Center](#).

our varied talents to answer the following science questions. Regional and global models, as well as satellite information indicate the Southeastern US is a good “laboratory” in which to address them.

SCIENCE QUESTIONS

1. What are the magnitudes, variations, and controlling processes for biosphere-atmosphere fluxes of oxidants and reactive carbon and nitrogen across spatial scales relevant to air quality and climate?

Related science sub-questions:

- What are the critical and most sensitive uncertainties for biogenic emissions?
- How can we account for biogenically-emitted carbon through understanding fluxes, deposition and emissions?
- What processes control the bi-directional fluxes of oxidized and reduced nitrogen and low molecular weight oxygenated VOC (aldehydes and organic acids)?
- How does the atmosphere control and influence what plants and soils emit, and what escapes forest canopies?

Biogenic VOC (BVOC) and NO emissions are significant and in some regions dominate over anthropogenic sources^[15]. Biogenic emissions and the uptake of ozone are among the dominant processes controlling tropospheric O₃ and particulate matter (PM) in the southeastern U.S. and yet these processes are poorly constrained^[16], in part due to a lack of consistent and widespread measurements. Estimates of terrestrial biogenic emissions, such as those from MEGAN or BEIS models, are based on the same general modeling framework but isoprene emissions for the same time and location can differ between the models by a factor of 2^[17] and emissions of oVOCs diverge even more^[18]. Accurate prediction of changes in air quality and climate in the southeastern U.S. require a better understanding of the processes controlling biosphere-atmosphere exchange. This includes quantification of within-canopy processes that include leaf-level emission and uptake, within canopy chemical transformations, and transport.

2. What are the chemical and physical processes that control the oxidation of BVOC? How do anthropogenic emissions alter the distribution of the BVOC oxidation products, and what are the implications for the formation of ozone, reactive nitrogen, and aerosol precursors?

Related Science sub-questions:

- During the day and the night, what is the mechanism for BVOC oxidation and how is it mediated by levels of NO_x?
- How do these BVOC reactions impact the photochemical production and loss of ozone, [•]OH, NO_y species, and aerosol?
- Which of these oxidation products lead to the formation of secondary organic aerosol?

Historically, our goal in understanding the oxidation of BVOC was to determine the processes that lead to the formation of ozone and serve as a sink for $\cdot\text{OH}$. However, the oxidation of BVOC also plays an important role in the recycling of $\cdot\text{OH}$ and formation of secondary organic aerosol and the fate of reactive nitrogen. Understanding these phenomena requires a new, more comprehensive understanding of the BVOC oxidation. Recent laboratory and theoretical studies have elucidated some of the reactions controlling the oxidation of BVOC including the formation of alkyl and multifunctional nitrates^[19, 20], epoxides^[21], HO_x reformation^[5, 6, 22], and organic aerosol formation^[20, 23, 24]. While these advances bring us tantalizingly closer, our understanding of BVOC oxidation photo-chemical cascade is not sufficient to explain the observed production and loss of ozone, $\cdot\text{OH}$, NO_y , and semi-volatile compounds that form SOA. Anthropogenic emissions, especially NO_x , substantially alters the oxidation process and the production of SOA precursors. Understanding the gas phase oxidation kinetics, pathways and products will enable a more comprehensive understanding of the processes that lead to SOA formation. This serves as the foundation for the next science question.

3. To what extent do anthropogenic influences impact biogenic SOA formation?

Related science sub-questions:

- Is there measurable atmospheric evidence of anthropogenic influence/contribution to SOA derived from BVOC precursors? Can we quantify a NO_x influence? An acidity influence? How are these influences confounded by relative humidity?
- What is the influence of anthropogenic pollution on the spatial and vertical distribution of biogenic oxidation products?
- Which of these oxidation products lead to the formation of secondary organic aerosol?
- Which of these oxidation products are the most important for surface air quality?
- Which of these oxidation products are the most important for climate?

The term “biogenic” SOA can be misleading. There is compelling evidence to suggest that anthropogenic pollution can affect the formation of SOA from BVOC precursors. Anthropogenic oxidants and condensation sites contribute substantially to biogenic SOA formation^[25]. Additionally there are potential SO_2 /acidity effects that facilitate mass formation^[26] and aerosol H_2O uptake. In rainforests, the lowest NO_x , isoprene-dominated terrestrial environments in the world, aerosol concentrations are usually below $1 \mu\text{g m}^{-3}$ ^[27]. In the southeast U.S., where biogenic emissions are also very high, anthropogenic (e.g., NO_x , SO_2) pollution routinely mixes with BVOCs and organic aerosol concentrations are much higher. Laboratory evidence indicates a difference in the isoprene SOA yield depending on “high” or “low” NO_x conditions^[28]. Field measurements of chemically-characterized products suggest evidence of the low NO_x pathway with observation of epoxydiols^[29] and the high NO_x pathway with observation of methyltetrols^[13]. Increased aerosol acidity, often a consequence of anthropogenic SO_2 emissions, may also affect SOA production from BVOCs^[30,31]. Regional scale air quality modeling suggests that a large fraction (~50%) of biogenic SOA in the Southeastern U.S. only forms when

there is sufficient anthropogenic pollution to facilitate formation^[25]. Despite large advances in the characterization and modeling of SOA, large discrepancies between measurements and predictions persist. These discrepancies may arise, in part, due to the failure of most models to include multiphase organic chemistry (Question 4), or properly represent regional emissions (Question 1) or incomplete gas phase chemical mechanisms (Question 2).

4. How does aqueous chemistry and cloud processing of BVOCs and related aerosols influence atmospheric SOA?

Related science sub-questions:

- Is there evidence of SOA formation through aqueous chemistry in the atmosphere, e.g., does ground-level particulate organic carbon concentrations increase with increasing aerosol liquid water content? Is it enhanced above, compared to below clouds?
- Are there tracers of “aqueous” SOA, similar to hydroxymethanesulfonate (HMS), that are traceable to (B)VOC precursor(s)?
- What are the most important precursors of “aqueous” SOA?
- Does cloud processing alter the vertical profile of particulate carbon?
- How substantial a contributor is aqueous SOA to ground level organic aerosol concentrations?

Smog chamber studies of SOA formation have focused on gas phase chemistry and partitioning into particulate organic matter at low relative humidity (RH). However, in many locations, including the southeastern US, photochemically active periods are accompanied by high RH. Globally, water is the most abundant component of PM_{2.5}. Its presence in aerosols undoubtedly affects SOA formation in ways that are only beginning to be considered. It has been hypothesized that chemistry in atmospheric waters (i.e., in clouds and wet aerosols) is a substantial source of SOA. Many atmospherically-abundant organic compounds (e.g., acetic acid, glyoxal, methylglyoxal, acetone, glycolaldehyde, phenols) are water soluble and react readily with OH radical in controlled laboratory experiments to form low volatility products. Thus, these compounds are expected to form secondary aerosol. A limited number of aircraft and ground-based field measurements provide evidence for this process: 1) demonstrating that aerosols are enriched in oxalate above, compared to below clouds, and 2) that ground-level concentrations of SOA tracers increase dramatically when aerosol liquid water content is high. However, we do not yet know what the most important precursors are, or the magnitude of the contribution of this pathway to SOA. Additionally, field data are needed to test and refine chemical transport models that are currently incorporating versions of this chemistry.

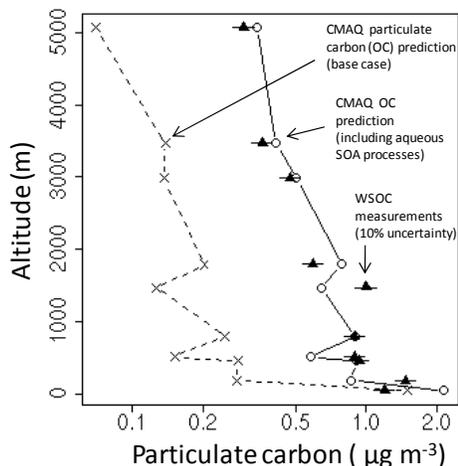


Figure 3. CMAQ-predicted vertical profile of organic carbon with and without organic multiphase chemistry.

Further, the vertical profile of the short-lived climate forcer (SLCF) particulate carbon is not well simulated in atmospheric models and this contributes to uncertainty in forcing calculations and climate projections^[32]. Recent field measurements show that isoprene-derived compounds contribute to organic aerosol in the free troposphere^[14]. Changes in emissions, SOA partitioning parameters, (among other efforts) do not improve model-predicted vertical profiles^[33], but inclusion of aqueous phase organic chemistry (e.g., cloud processing of VOCs) does^[34]. Many of the aqueous phase products of cloud processing are known to produce light-absorbing “brown carbon”(e.g., [35]). The production of optically-active brown carbon, in particular, aloft has important implications for climate (Question 5).

5. What are the climate-relevant properties of biogenic aerosol (VOC of biogenic origin)?

Related Science sub-questions:

- What is the impact of aerosol of biogenic origin on the regional radiation budget?
- What is the impact of aerosol of biogenic origin on cloud properties and lifetime?
- How do biogenic SOA and biogenic VOCs impact new particle formation?
- How does biogenic SOA contribute to the growth of ultrafine particles to Cloud Condensation Nuclei (CCN) sizes?
- How does the chemical composition of biogenic SOA affect CCN activity?

Global temperatures have increased over the past 100 years, yet these increases have not been uniform. The southeastern US has, in fact, cooled over this period. This could be a result of changing global circulation patterns, increased forest cover, or trends in aerosol radiative forcing^[1] and clouds. BVOCs can affect radiative forcing through direct and indirect pathways

by altering aerosol number and CCN concentrations. The magnitude (and sign) of their impact is unclear.

Biogenic SOA has been shown to contribute greatly to the growth of ultrafine particles in northern Boreal forested regions in Finland and Canada^[36]. However, aerosol growth depends greatly on the properties of the gas phase biogenic precursors^[37], which may be different in the Southeastern US compared to the northern Boreal forests. For example, the isoprene:terpene ratio is much higher in the Southeastern US compared to Boreal forests. Furthermore, SOA has recently been shown to directly contribute to new-particle formation^[38]. Therefore, SOA can grow ultrafine particles to CCN sizes and contribute to the creation of the ultrafine particles. On the other hand, biogenic

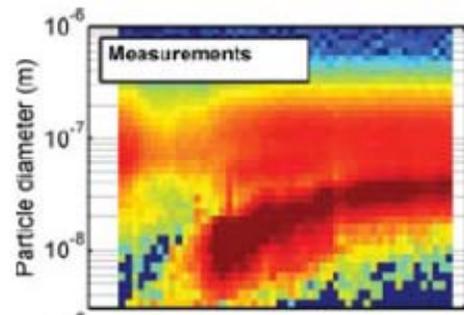


Figure 4. Sulfuric acid is insufficient to explain new particle formation and evolution of the aerosol size distribution in Boreal forests. BVOC products provide a plausible explanation. (Figure adapted from Riipinen et al., (2011)).

VOCs consume atmospheric oxidants, altering oxidant concentrations and subsequently the rate of SO₂ oxidation to form sulfuric acid, another precursor critical for new-particle formation. An additional uncertainty concerning BVOCs is their CCN activity (the moles of solute per organic aerosol mass). The CCN activity depends greatly on the organic aerosol source as well as age in the atmosphere^[39].

PRELIMINARY STUDY DESIGN

To answer the SOAS science questions identified above, we recommend five experimental platforms. First, laboratory atmospheric chamber experiments are needed to elucidate the mechanism by which biogenic compounds are oxidized and form aerosol. While laboratory experiments allow control over confounding factors, there are atmospherically relevant conditions that are difficult to replicate in chambers – especially high humidity and low NO_x concentrations prevalent in the Southeastern US. Accordingly, the second experimental platform is a comprehensive field site that includes measurements of emissions, in-canopy and surface deposition fluxes, chemically speciated gases and aerosols, and meteorological conditions. This surface site should be located such that it experiences times of high anthropogenic influence and times relatively free of pollution (in the sense of reaching NO_x that is high enough to modulate whether RO₂ reacts with HO₂ or NO significantly). Thirdly, to understand the interactions between these aerosols and clouds, measurements of speciated gases, aerosols, and cloud hydrometer properties from an aircraft platform are critical. Fourth, space-based remote-sensing observations and aircraft-based flux measurements are needed to understand emissions across the region. Fifth, regional chemistry-climate models are needed to integrate the knowledge gained from each of the process studies described above in order to quantify the impact of anthropogenic pollution on biogenic organic carbon.

Laboratory chamber experiments:

Environmental chamber studies performed before and after the field campaign are needed to (1) establish consistency between the field instrumentation (e.g. evaluate calibration and interferences); (2) enhance optimization of the operations of the instrumentation; (3) test hypotheses that arise from analysis of the field campaign. For (1) and (2), we will create in the laboratory stable and consistent aerosol and gas phase mixtures that allow careful comparisons of the data from the field instrumentation. These mixtures will be prepared using methods and equipment that have been carefully developed and characterized over the last decade. In addition, a series of experiments following the oxidation of the central biogenic components of the southeast US will be performed under oxidative conditions that match those expected in

the ambient atmosphere (e.g. Crouse et al., 2011 [40]). These experiments will be designed to provide guidance for optimizing the operations of instruments and platforms during the field campaign. Finally, we anticipate a follow up study using the environmental chamber approximately one year after the field campaign to test hypotheses that arise from ongoing analyses of the field data.

Comprehensive field site:

While the laboratory study described above helps elucidate the mechanism of BVOC oxidation, field measurements are needed to examine the interactions between atmospheric chemistry, meteorology, anthropogenic emissions, and atmosphere-biosphere exchange. The measurement strategy must be comprehensive in order to discern these interactions. This includes the capability to

1. Quantify the emissions and bi-direction surface flux of biogenic and reactive nitrogen compounds.
2. Observe the photo-chemical cascade of compounds that comprise the primary, secondary, and later-stage oxidation products of biogenic VOCs.
3. Characterize the chemical composition of aerosols with enough specificity to determine which biogenic VOC they originated from
4. Measure the transport of these species within the canopy and venting to the troposphere.
5. Perform all of these measurements in a location that experiences a range of anthropogenic influence, with enough time-resolution to differentiate the varying levels of anthropogenic influence.

Fortunately, new measurement techniques are capable of greatly improved chemical specificity and time-resolution. For understanding the atmospheric chemistry, these techniques can observe the intermediate compounds that make up the photo-chemical cascade of BVOC oxidation. High temporal resolution can characterize the rapid photo-chemistry and chemical fluxes within a forest canopy. Also, these techniques provide unprecedented capabilities to resolve the chemical differences within narrow, anthropogenic plumes.

Is it possible to find a field site in the Southeast US that experiences a range of anthropogenic influences? To answer this question, we mine the history of measurements. In Table 1, we have identified five criteria necessary for supporting the science questions. Based on previous and ongoing measurements, we have selected five candidate sites, listed in Table 2. All of these sites are situated in areas dominated by biogenic emissions, yet influenced by anthropogenic

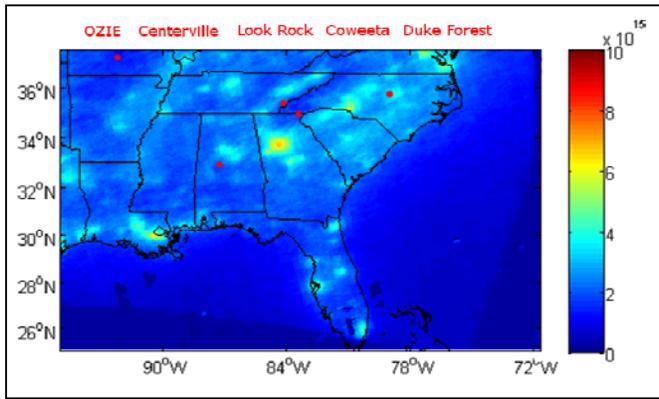


Figure 5: NO_2 column density from OMI averaged for summer of 2010, derived using techniques described in Russell et al. (2010). Candidate surface sites are shown as red dots and labeled from left to right.

range of oxidation and aerosol acidity conditions that are conducive to the formation of biogenic aerosol. The Coweeta and OZIE sites are rarely influenced by anthropogenic emissions, while the Duke Forest site is too dominated by anthropogenic emissions. This is clearly visible in the NO_2 column density plot in Figure 5, where the Duke Forest site is surrounded by high NO_2 levels, while the Coweeta and OZIE sites are surrounded by low NO_2 levels. The Look Rock and Centerville sites are bordered both by areas of high and low NO_2 concentrations, providing the contrast needed to understand the impact of anthropogenic emissions. Figures 7 and 8 show the range of NO_x conditions previously measured at these two sites.

pollution. Figure 5 shows the location of the candidate sites, overlaid on summer 2010 average NO_2 column density measurements from a satellite-based sensor (OMI)^[41], while Figure 6 shows the isoprene emission intensity.

After examining the history of measurements at these sites, the Look Rock and Centerville sites are most promising. These two sites experience a

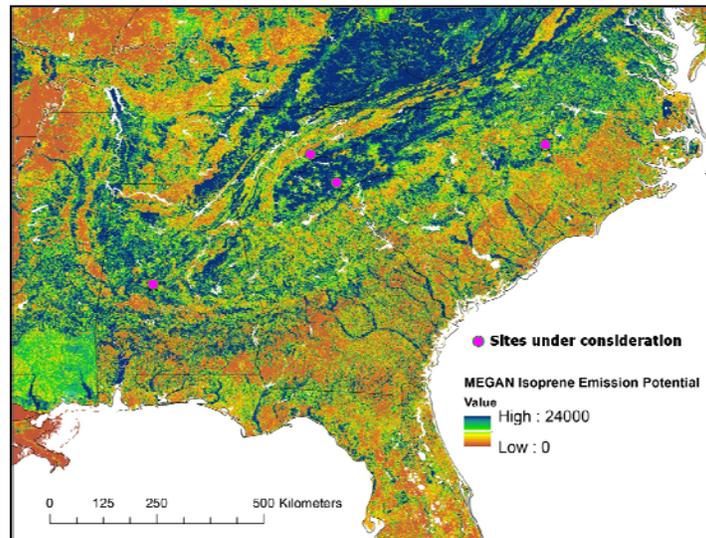


Figure 6: Model estimate of the isoprene emission potential and measurement sites under consideration. From left to right, Centerville, Look Rock, Coweeta, and Duke Forest. All sites have high levels of local isoprene emissions.

Table 1: Criteria for selecting surface sites to answer the SOAS science questions.

Criteria for selecting a surface measurement site		Look Rock, TN	Centerville, AL	Coweeta, NC	Duke Forest, NC	OZIE, MO
Primary Priorities	Site with strong contrast, where at times we observe largely biogenic air masses and at times we observe biogenic air masses that have been influenced by a range of NO _x emissions	YES	YES	NO	NO	NO
	Minor influence of wildfires	YES	YES	YES	YES	YES
Secondary Priorities	Range of aerosol acidity conditions, due to a range of SO ₂ and sulfate levels	YES	YES	NO	NO	NO
	To reduce confounding variables, air masses with high ammonia should be distinct from SO ₂ and NO _x influenced air masses.	YES	YES	YES	YES	YES
	To isolate isoprene chemistry, high isoprene : terpene emission ratio	YES	YES	YES	NO	YES

Table 2: Surface sites under consideration for SOAS that hosted previous field campaigns.

Site	Description	Latitude	Longitude	Altitude (m)
OZIE	Ft. Leonard Wood, MO: a rural site in the OZIE field campaign during 1998	37.631	-92.154	262
Centerville	A rural site that is part of the SEARCH monitoring network	32.90289	-87.24968	126
Look Rock	A site run in collaboration with National Park Service and the Tennessee Valley Authority	35.63314	-83.94185	802
Coweeta	A long term ecological site, measurements are currently being collected at this remote forest site	35.00	-83.50	900
Duke Forest	Part of this forest was dedicated to CO ₂ fertilization experiments; measurements are currently being collected at this forest site surrounded by sub-urban development	35.978175	-79.09419	110

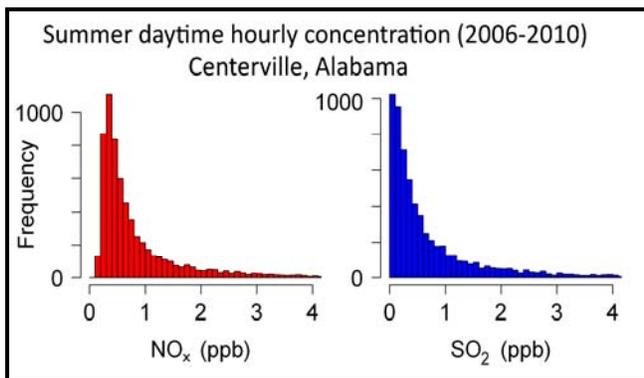


Figure 7: Range of summertime NO_x and SO₂ concentrations at Centerville, AL monitoring site from 2006 – 2010.

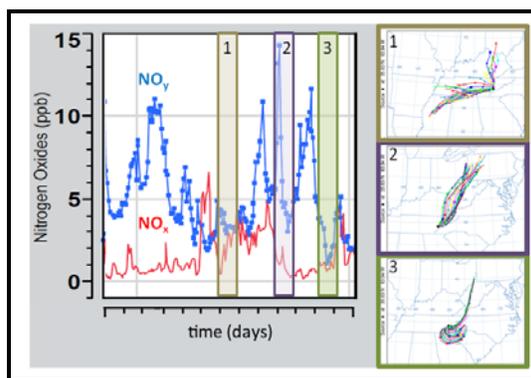


Figure 8: Back trajectories, NO_x and NO_y measurements at Look Rock, TN. On day (1), fresh NO_x emissions are transported from local sources. On day (2), aged NO_y is transported from distant sources. On day (3), low NO_x levels are observed in air masses from an unpolluted area.

Table 3. Measurements Critical to Answering Science Questions

Parameter to be measured / process to be modeled	Ques. 1	Ques. 2	Ques. 3	Ques. 4	Ques. 5	Comments
meteorology	1	1	1	1	1	Met tower
Photolysis frequencies	1	1	1	2	1	radiometer
BL height and structure	1	1	3	1	2	LIDAR, SODAR, releasesondes or ceilometer
Clouds	3	3	3	1*	1*	Physical (e.g., LWC) and optical (e.g., AOD) presence/absence and degree
Non-fossil carbon fraction	1	1	1	2*	3	
Reactivity by compound class	1	1	1	2*	3	Measurements at times scales ≤ BL mixing
Eddy co-variance*	1	1	1	2	3	
Carbon accounting & balance	1	1	1	2*	2	
Daytime atmospheric oxidants	1	1	1	2*	3	Measurements at time scales ≤ chemical lifetimes
Night time atmos. oxidants	1	1	1	2*	3	Measurements at time scales ≤ chemical lifetimes
O ₃	2	1	1	3	3	
OH-reactivity	1	1	1	2	3	Measurements at time scales ≤ chemical lifetimes
HO _x	1	1	1	2	3	
Speciated NO _y	2	1	1	3	3	
Speciated SOA tracers	3	1	1	2	3	
Aerosol size distribution	3	3	1	1	1	
Aerosol single scattering albedo, optical depth	3	2	2	2	1	
CCN activity	3	3	3	1*	1*	
Canopy scale modeling	1	1	3	3	3	Determine critical & sensitive processes/parameters for net flux
Regional scale modeling	2	2	1	1	1	Evaluation of AQ measurements, regional climate signals

**Aircraft measurements are critical; Priority: 1=must, 2=important, 3=useful*

Aerosols, radiative properties, and clouds measured from aircraft:

The laboratory chamber experiments and instrumented surface site will provide great insight into science questions 1 – 3. Questions 4 and 5 address interactions between aerosols, their light absorbing properties throughout the troposphere, and clouds. An aircraft platform is critical to the necessary measurements required for Questions 4 and 5. Flight plans and transects will consist of mid-boundary layer and free troposphere (above cloud top) altitudes. Specific flights will be designated “cloudy air” flight plans with transects 1) below cloud base, 2) within cloud layer and 3) above cloud top. These capabilities are required to answer the science questions:

1. Observe the photo-chemical cascade of compounds that comprise the primary, secondary, and later-stage oxidation products of biogenic VOCs as well as tracer compounds that are indicative of aqueous-phase processing.
2. Characterize the chemical composition of aerosols with enough specificity to determine which biogenic VOC they originated from
3. Simultaneous measurement of the physical properties relevant for cloud condensation nuclei: hygroscopicity and size distribution
4. Distinguish the light-scattering and light-absorbing properties of organic aerosols
5. Perform all of these measurements in air-masses that have and have not been recently influenced by clouds
6. Perform all of these measurements in air-masses that have and have not been recently influenced by an anthropogenic plume

Aircraft-based flux estimates:

The magnitude and spatial-temporal distribution of biosphere-atmosphere chemical fluxes is highly uncertain and their impact on atmospheric oxidants and aerosol is considered important but not well known. The successful demonstration of airborne eddy covariance techniques for measuring fluxes of VOC^[42], NO^[43] and ozone^[44] provides a promising approach for characterizing chemical fluxes on scales relevant for regional production and loss of ozone and aerosol. These observations are also valuable for understanding and constraining the atmospheric cycling and fate of organics, HO_x, and NO_x (e.g., [45], [43]). In addition, recent advances in constraining regional scale emissions with satellite data products promise to improve biogenic emission estimates of terpenoids^[46], NO^[47] and methanol^[48]. However, these efforts are limited by the lack of suitable observations for quantitatively representing the processes linking surface emissions to satellite data products. The proposed SOAS airborne flux experiment will directly address Science Question 1.

Specific objectives for the airborne flux experiment include:

- Directly quantify isoprene, isoprene oxidation products, monoterpene, methanol and NO fluxes across spatial scales relevant for regional models and use the results to understand and reconcile current discrepancies among and between “bottom-up” and “top-down” emission estimates.
- Use isoprene, ozone and NO_x vertical flux divergence and concentration measurements to constrain •OH concentrations, ozone reactivity, and HO_x/NO_x/organics cycling and fate in low and high pollution regimes.
- Compare satellite data products, model estimates and in-situ observations of formaldehyde, glyoxal and methanol concentration distributions and relate to measured primary BVOC emissions in low and high pollution regimes.

Integrating our understanding with regional chemistry-climate models:

Each of the measurements described above are critically important for understanding emissions, atmospheric chemistry, aerosol physics, and climate-relevant impacts of aerosols. Regional-scale, chemistry-climate models integrate these individual processes in order to understand their interaction across the continent at fine horizontal spatial scales (4km). Modeling experiments, when constrained with observations, can quantitatively answer the over-arching science question of this effort – what is the effect of anthropogenic influence on biogenic aerosol, and what are the implications for climate change? The fifth component of SOAS is to learn from the field and laboratory measurements, incorporate these advancements into state-of-science chemistry-climate models, and then apply the models to understand the interactions between anthropogenic pollution, biogenic processes, and climate change.

Robust scientific findings depend on a community of modeling approaches. To support this goal, the emission, meteorology, boundary-condition, and land cover inputs needed to drive the chemistry-climate models will be generated and made available to any interested groups. Common datasets will facilitate the comparison of modeling approaches and speed the development of parameterizations that are true to the observations.

EXPECTED OUTCOMES

While the Southeastern US will serve as our laboratory, these outcomes are relevant across the globe at the interface of human activity and biogenic emissions.

1. Develop methods and directly measure biogenic fluxes across a large geographic region using aircraft-based flux techniques.
2. Elucidate the reaction pathways that control oxidation of biogenic volatile organic carbon and determine the impact of anthropogenic emissions on these reaction pathways.

3. Discover the links between biogenic oxidation, anthropogenic influences, and the formation of secondary organic aerosol.
4. Determine the importance of relative humidity, aerosol water, and clouds to the formation, aging, lifetime, and radiative properties of aerosol.
5. Observe the role of biogenic aerosol in contributing to cloud condensation nuclei.
6. Use chemistry-climate models to extend our findings to the rest of the world by quantifying regional and global impacts of anthropogenic pollution on biogenic oxidation, aerosol formation, and radiative effects.

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