

Abstracts of Proposals for the SOAS 2013 Field Experiment

Shared with the purpose of motivating collaborations and cross-pollination

Version 9, contains proposals sent to Jose by 11-March-13

To add further abstracts or project summaries or report any errors on Jose's part,
pls email him at jlj.colorado@gmail.com

NSF - Brune - Resolving issues of OH measurements and oxidation chemistry in forest environments - Abstract

Understanding atmospheric oxidation chemistry is critical for establishing the links between atmospheric composition, air quality, and climate change. Hydroxyl (OH) is the atmosphere's primary oxidant. Comparisons of measurements and models provide evidence that OH and hydroperoxyl (HO₂) chemistry is generally understood in clean, remote environments, but less well understood in cities when nitrogen oxide (NO_x) levels are high. Other evidence indicates that OH is most poorly understood in low-NO_x, high biogenic VOC (BVOC) environments, particularly forests where measured OH has greatly exceeded modeled OH by a factor of 2 to 10, well beyond the typical $\pm 30\%$ 2σ uncertainties.

These forest environments are challenging the models, for which new oxidation mechanisms are being designed, and the measurements, which can have interferences and be near their detection limits. A previously suspected interference was recently confirmed for the combination of O₃, OH, and alkenes in our laser-based Ground-based Hydrogen Oxides Sensor (GTHOS) by adding the ability to detect OH by chemical removal of OH (called OHchem) to our usual method wavelength modulation on and off an OH spectral line (called OHwave). Laboratory tests demonstrate that OHchem is the real OH for GTHOS.

We propose to contribute measurements of OHchem, OHwave, HO₂, alkene-based RO₂, and OH reactivity to a multi-investigator study that will provide a consistent picture of the isoprene oxidation mechanism, demonstrate that OHchem is the real OH, and determine if the GTHOS OH interference is caused by an atmospherically relevant intermediate species. We also propose to find the reason that GTHOS appears to be much more sensitive to this O₃/OH/alkene interference than other OH-measuring instruments and to reduce that sensitivity if the interference is not atmospherically relevant. These goals of this two-year study will be accomplished primarily by participating with other groups who are proposing separately in a Focused Isoprene-chemistry eXperiment (FIX), which has a month-long laboratory environmental chamber component, a field component as part of the Secondary Organic Aerosol Study, and a second laboratory environmental chamber component. Pre-FIX and post-FIX analysis, laboratory, modeling, and instrument characterization studies are also proposed.

Intrinsic merit

This effort will result in a more certain understanding of isoprene oxidation chemistry and greater confidence in the OH and HO₂ measurements from GTHOS and perhaps other OH measuring instruments. Both are important for improving the understanding of atmospheric oxidation processes and the BVOC mechanisms that are being included in regional and global chemical transport models.

Broader impacts

An undergraduate and a graduate student will be trained by participating in all aspects of the research. During the summer period, we will mentor several high school students from under-represented groups in a research project related to these studies as part of a Penn State program that includes classes and research. The results of this research will lead to improved oxidation mechanisms in the models that are used for regional and for global air quality, thus providing guidance to policy makers.

EPA-STAR (Early Career): Anthropogenic influence on biogenic VOC oxidation: the role of NO_x pollution in secondary organic aerosol production in the Southeast U.S.

FON: Anthropogenic Influences on Organic Aerosol Formation and Regional Climate Implications, Early Career, EPA-G2012-STAR-D2

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Project period & location: Apr. 1, 2013-Mar. 31, 2016; Reed College, Portland, OR; SOAS field campaign in the southeastern U.S.; NOAA ESRL and University of Colorado (Boulder, CO)

(1) Nitrogen oxides, through their interactions with volatile organic compounds (VOCs), NH₃, OH, and other gas-phase species, exert important controls on the lifetime and fate of atmospheric VOCs and the formation of secondary aerosol. During the night, the NO₃ radical is an important oxidant, reacting rapidly with unsaturated VOCs, many of which are biogenic in origin (BVOC), to produce organic nitrates and other oxidized VOCs, some of which lead to the formation of secondary organic aerosol (SOA). We hypothesize that this NO₃-BVOC reaction pathway will be important at and above the SOAS campaign ground site, which is situated in a relatively polluted region where BVOC comprise essentially all of VOC reactivity toward NO₃. NO₃-BVOC SOA formation has been the subject of a few experiments in large environmental chambers; however, quantitative demonstration of these processes in the ambient atmosphere is practically non-existent. Field verification of the competitive role of inorganic nitrate chemistry also remains incomplete. Our objective is to measure the reactive N budget and fate of oxidized nitrogen in and above the forest canopy at the SOAS flux tower in Centreville, AL, a site with large BVOC emissions that are representative of those across the southeastern U.S.

(2) At the Southern Oxidant and Aerosol Study (SOAS), we propose to measure oxides of nitrogen (NO_y): NO₃ radical, N₂O₅, and NO₂, (using cavity ringdown and chemiluminescence) at several heights, coordinated with aircraft vertical profile measurements of the same species (SENEX) and with other groups' measurements of VOCs, RONO₂, ROONO₂, and HNO₃, to get a complete picture of the NO_y budget in and above the forest canopy, with special focus on the fate of the reactive NO₃ radical. We will also measure gas- and aerosol-phase HNO₃, NH₃, NH₄⁺ and NO₃⁻ using ion chromatography. We will assess maximum potential aerosol mass (PAM) using a flow reactor to which we add a known amount of NO₃. After analysis of the field data, we will conduct a chamber experiment collaboration in Boulder simulating ambient and NO₃ PAM chemistry, to verify field-observed relationships and assess the predictive capacity of the PAM flow reactor.

(3) This proposal targets EPA STAR call "Anthropogenic Influences on Organic Aerosol Formation and Regional Climate Implications," particularly addressing the stated goals of achieving improvements in understanding (a) the influence of anthropogenic pollution on SOA formation from BVOCs, and (b) role of NO_x in the oxidation of isoprene and the formation of SOA. NO₃-initiated chemistry is either not included or treated in a highly simplified form in air quality models, impeding decision-makers' ability to accurately predict the downstream effects of e.g. NO_x emissions reductions in forested regions. The proposed project seeks to improve this predictive ability with consequential improvements in risk assessment related to emissions policies.

The Role of Oxidation of BVOCs in SOA Production in the Southeastern U.S.

Steve Bertman (Western Michigan University), Kerri Pratt (Purdue University), Paul Shepson (Purdue University), John Seeley (Oakland University), Tim Starn (West Chester University of Pennsylvania)

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Project Summary

Objectives: We are proposing to conduct a key set of measurements of ambient concentrations of a wide array of atmospheric volatile organic compounds and photoproducts as part of the Southern Oxidant & Aerosol Study (SOAS) during the summer of 2013. The overarching goal is to enable better understanding of interactions between the biosphere and the anthroposphere in the production of atmospheric organic nitrates and secondary organic aerosols. These interactions will be further investigated using 1-D and CMAQ models, as well as off-line aerosol chemistry measurements.

Experimental Approach: On-line field measurements will be made with complementary instruments: 1) a new custom-designed 2D-GC instrument capable of obtaining automated hourly measurements of speciated anthropogenic and biogenic VOCs and oxidation products, including organic nitrates, 2) a CIMS instrument that is capable of measuring organic nitrates within classes, including total isoprene nitrates, and other important SOA precursors such as N₂O₅, 3) PAN compounds by GC-ECD. In addition, 4) aerosol filter sampling will be utilized for off-line FTIR and LC-ESI-MS measurements of various oxidation products in the particle-phase. One-dimensional and regional air quality (CMAQ) modeling will be used to probe organic nitrate and SOA production, with comparisons to field measurements of the individual precursors.

Expected Results: We plan to test three key hypotheses: 1) organic nitrates are important aerosol precursors in the southeastern U.S.; 2) NO₃ - BVOC reactions are an important organic nitrate production route, even for daytime; and 3) the relative contributions of anthropogenic and biogenic SOA production in the southeastern U.S. can be determined, to a first order, using speciated VOC data, measured/calculated oxidant concentrations, and laboratory rate constants and aerosol yields. The relative importance of individual VOCs and oxidants will be tested using our 1-D modeling approach, and reaction of NO₃ with isoprene will be added to CMAQ as a SOA production pathway to evaluate its significance in the southeastern U.S. This effort will also support a range of specific questions posed by SOAS, including uncertainties in the distribution and drivers of VOC and BVOC emissions, the roles of specific individual VOCs and BVOCs in SOA production, and the role of organic nitrates and nighttime chemistry in the production of SOA. Pursuit of these goals will yield a better understanding of the interactions between the atmosphere and the biosphere. This will allow more effective strategies for management of pollution sources and natural areas that ensure protection of environmental and human health. We also aim to provide undergraduate students with meaningful experiences conducting hypothesis-driven field research.

Supplemental Keywords: RONO₂, GCxGC, NO₃, atmosphere, ozone, ecological effects, particulates, nitrogen oxides, oxidation, environmental chemistry

Proposal Title: Measurements of Amines during the SOAS Field Campaign

PI: Shanhu Lee, Kent State University

Intellectual Merit: We propose to make ground-based measurements of amines with a fast-time response chemical ionization mass spectrometer (CIMS) during the 2013 Southern Oxidants and Aerosol Study (SOAS) to investigate the effects of amines on secondary aerosol formation processes. The southeastern U.S. has a unique atmospheric environment favorable for secondary aerosol formation with abundant volatile organic compounds (VOCs) emitted from biogenic and anthropogenic sources, combined with high concentrations of atmospheric oxidants, and thus is an ideal location to study secondary aerosol formation processes. Amines are ubiquitous in the atmosphere. Atmospheric observations have shown that they are commonly present in aerosol particles. Amines can contribute to secondary organic aerosol (SOA) formation, either via condensation of amine oxidation products or by formation of salts with acidic aerosols. Amines can also participate in aqueous phase reactions for SOA formation during cloud processing. Organic amine base compounds can affect the aerosol acidity, a key chemical condition for SOA formation from biogenic VOCs. Organic base compounds react with acidic aerosols to form salts, thereby contributing to aerosol solidification to affect the aerosol phase, a likely factor to explain long-standing discrepancies between model-predicted and atmospherically-measured SOA concentrations. In addition, amines are important precursors for new particle formation and participate in growth of nanoparticles, another important pathway to form secondary aerosols in the atmosphere. Amines and their oxidation products have adverse health effects and directly impact air quality. However, at present, measurements of gas-phase amines especially in biogenic environments in the southeastern U.S. are critically lacking.

Objective. Based on the measured amine concentrations by our group (likely Centerville, Alabama), together with aerosol chemical composition analysis and other key chemical trace measurements, we will investigate the roles that organic amine base compounds play in secondary aerosol formation processes in the biogenic environment with or without the influence of anthropogenic emissions.

Approach. We will deploy our newly-developed chemical ionization mass spectrometer (CIMS) to make fast-time response detection of atmospherically-relevant amines and ammonia, simultaneously. We are currently one of only three research groups in the world that can measure atmospheric trace amines with fast-time response. This CIMS measurement can add a significant instrument capability to the SOAS field campaign by providing the chemical trace information crucial to study SOA and new particle formation processes.

Total and speciated Hg at SOAS/SEARCH Alabama site and cross-calibrations with an HgBr₂ source

Dan Jaffe, Lynne Gratz and Crystal McClure
University of Washington Bothell

Goals:

1. Provide calibrated Total Hg data at the SOAS/SEARCH site to use in the NAAMEX-NOMADSS analyses;
2. Use the data to examine anthropogenic sources in the Southeastern US;
3. Compare ground based observations with the C-130 aircraft using the same methodology;
4. Examine the response of a Tekran speciation system to HgBr₂. This data can then be used to better understand all Tekran speciation data in the Atmospheric Mercury Network (AMNet) and elsewhere;

The UWB group will provide the measurement system for THg and the calibrated HgBr₂ source. Eric Edgerton's group (SEARCH) will make measurements of speciated Hg using the standard Tekran 2537/1130/1135 system. At present the Tekran system is not calibrated for HgX₂ compounds, and yet the system has known interferences. We will carry out regular calibrations of both the UWB THg system and the Edgerton 2537/1130/1135 system using our calibrated HgBr₂ permeation tubes. This is similar to experiments that we carried out during the recent RAMIX inter-comparison (Reno, NV, August-September 2011). Calibrations with HgBr₂ will be done manually (in order to minimize wall loss) at least 3 times per week on both systems. We have found that manual calibrations are the most reliable for HgBr₂ since the material can be delivered with no change in the flow path. Between calibrations, the HgBr₂ will be fully scrubbed using a charcoal canister with a pre-filter.

Our preference for carrying out this work is at the Centreville, AL SOAS site. However, if for some reason this site is not suitable, or if the speciated Hg measurements are not available there, we will conduct this work at the Birmingham, AL SEARCH (E. Edgerton, personal communication). The figure on the next page shows our required instrument layout.

Please let me know any questions.

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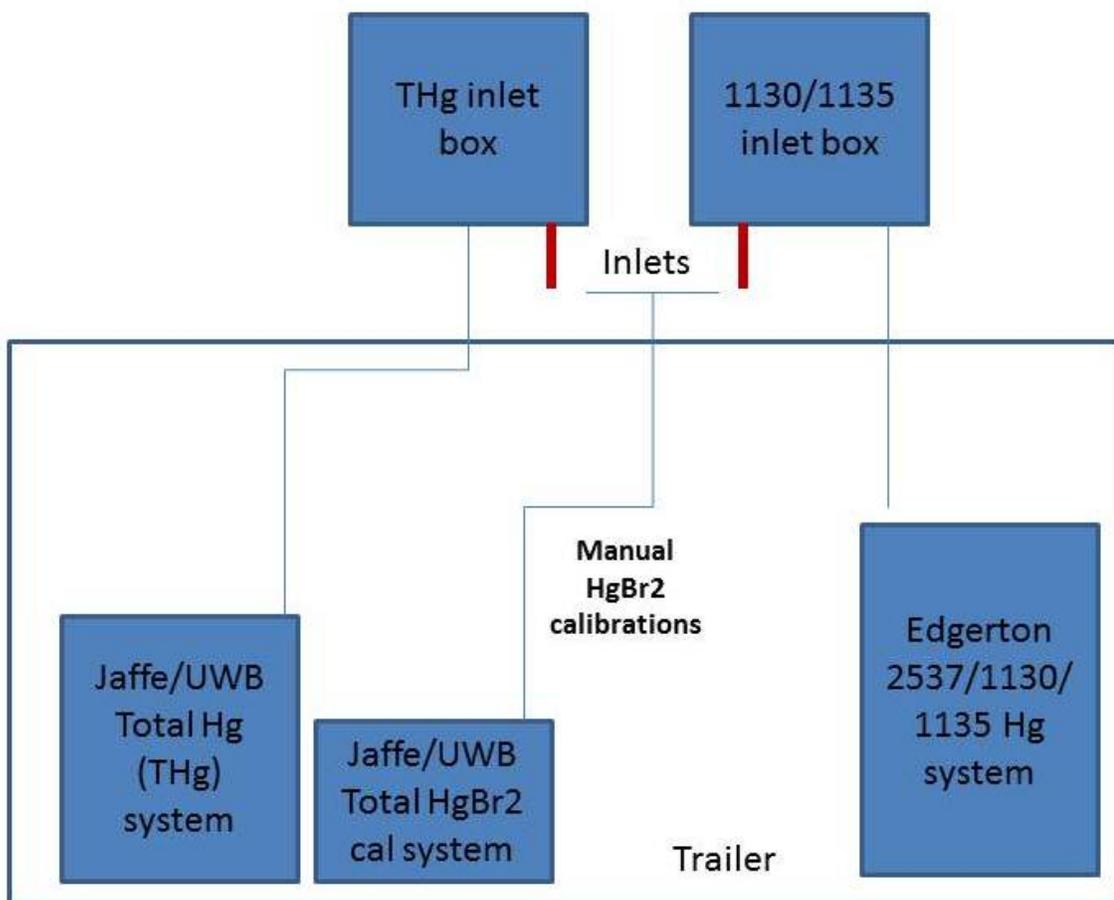


Figure 1. Arrangement of instrumentation and inlets for SOAS Hg experiment.

Abstract

a. Funding Opportunity Title and Number: Anthropogenic Influences on Organic Aerosol Formation and Regional Climate Implications, Early Career, EPA-G2012-STAR-D2

b. Project Title: **Impacts of Anthropogenic Emissions in the Southeastern U.S. on Heterogeneous Chemistry of Isoprene-Derived Epoxides Leading to Secondary Organic Aerosol Formation**

c. Investigator: Dr. Jason D. Surratt, Assistant Professor

d. Institution: University of North Carolina at Chapel Hill (UNC-CH)

e. Project Period and Location: October 1, 2012 to September 30, 2015 at UNC-CH

g. Project Summary:

Objectives – The underlying hypothesis of this study is that anthropogenic emissions enhance isoprene SOA formation through the heterogeneous chemistry of isoprene-derived epoxides (see Figure 1 below), possibly leading to light-absorbing SOA in the southeastern U.S. The specific objectives to evaluate this hypothesis include: (1) Leveraging our ongoing Look Rock, TN, field site during the community-led Southern Oxidant & Aerosol Study (SOAS) in summer 2013 to evaluate how isoprene SOA formation chemistry varies between regional and urban influenced air masses; (2) Evaluate the effects of relative humidity, aerosol acidity, and seed aerosol type on the heterogeneous chemistry of isoprene-derived epoxides leading to SOA and how this might yield light-absorbing aerosol constituents (i.e., brown carbon); (3) Evaluate gaseous yields of epoxides from isoprene oxidation under varying initial levels of nitric oxide.

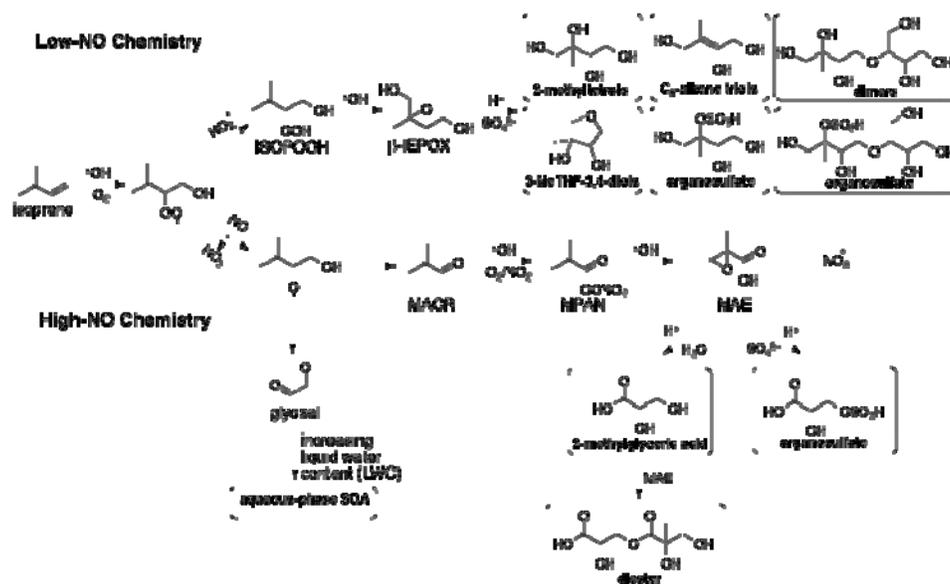


Figure 1. Proposed chemical mechanism leading to isoprene SOA formation under initially low- and high-NO levels. IEPOX = isoprene epoxydiols; MAE = methacrylic acid epoxide (or 2-methyl-oxirane-2-carboxylic acid)

Approach – We will directly couple our capability in synthetic organic chemistry with our involvement in the SOAS field campaign and our pre- and post-campaign UNC smog chamber studies. We have established synthetic routes for the isoprene-derived epoxides and their selected SOA products. These key chemicals will be provided for advanced mass spectrometry techniques, such as a chemical ionization high-resolution time-of-flight mass spectrometry (CI-

HR-TOFMS) and an aerosol chemical speciation monitor (ACSM), that will be utilized to quantitatively measure in real-time the gas- and aerosol-phase constituents related to isoprene oxidation. Furthermore, we will chemically characterize PM_{2.5} samples collected onto filters during the SOAS campaign and from our smog chamber studies for known isoprene SOA tracers using gas chromatography/mass spectrometry (GC/MS) and ultra performance liquid chromatography/electrospray ionization high-resolution mass spectrometry (UPLC/ESI-HR-MS). UPLC-diode array detection (DAD) will also be used to detect and characterize brown carbon (or light-absorbing) aerosol constituents.

Expected Results – The proposed activities will yield the formulation of parameterizations that can be incorporated into SOA models that will lead to improvement in the ability to simulate isoprene SOA formation in the southeastern U. S. Specific results include: (1) characterization of reaction pathways that control the oxidation of isoprene in the southeastern U. S. and quantitative assessment of the impact of anthropogenic emissions on these pathways; (2) discover the links between isoprene oxidation, anthropogenic influences, and formation of isoprene-derived SOA; (3) determine the importance of RH, aerosol water content, pre-existing PM, and aerosol acidity on isoprene SOA formation enhanced by anthropogenic emissions; and (4) characterization of isoprene-derived SOA constituents leading to light-absorbing brown carbon. These results will provide improvements that are essential so that air quality models can be used with increased confidence in predicting organic PM_{2.5}.

h. Supplemental Keywords: atmosphere, particulates, environmental chemistry, biogenic volatile organic compounds, terpenes

Collaborative Proposal Atmospheric mixed phase chemistry for improved climate predictions: field measurements and modeling of the Southern Oxidant and Aerosol Study

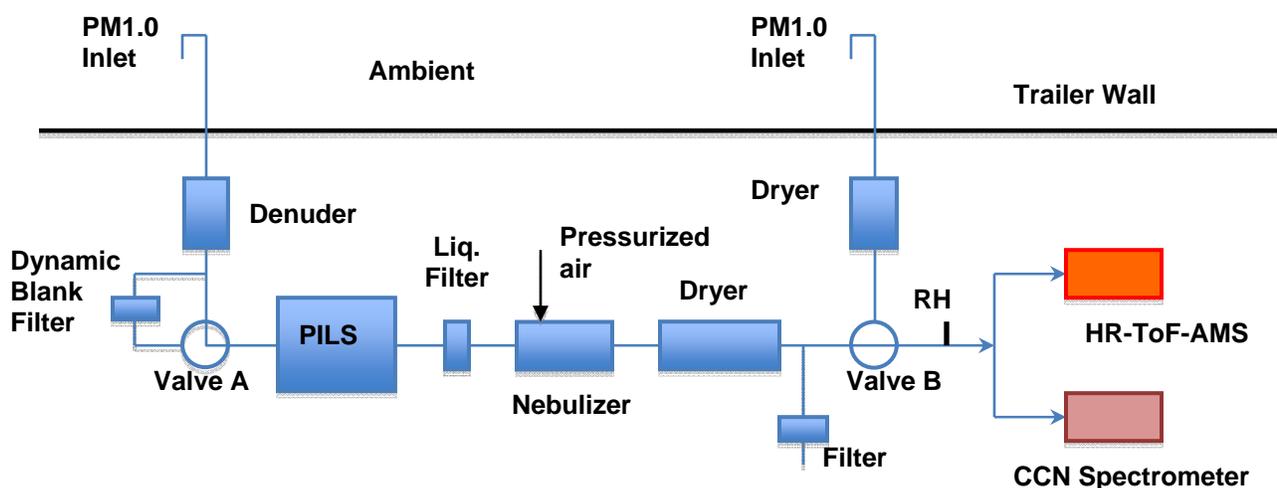
A.G. Carlton, Department of Environmental Science, Rutgers University

R.J. Weber, A. Nenes, N.L. Ng, Georgia Institute of Technology

Objectives: 1.) Develop an instrument and carry out novel semi-continuous measurements of SOA composition that will include identifying the fraction of total SOA from biogenic and anthropogenic VOCs and to quantify the extent of anthropogenically modulated SOA in the SE USA. 2.) Determine the CCN activation properties of primary organic aerosol (POA) and the water-soluble SOA separately 3.) Quantitatively characterize the chemical composition of the ambient aerosol using complimentary methods and include measurements of ambient H_2O_{ptcl} and particle pH (pH_{ptcl}) to allow robust comparisons between measured H_2O_{ptcl} and pH_{ptcl} and predictions. 4.) Develop parameterizations that relate optical and water uptake properties with H_2O_{ptcl} , pH_{ptcl} , SOA mass and composition.

Approach: 1.) Since WSOC is an overwhelming fraction of SOA in the SE (Fig. 1) an instrument for exclusive measurement of WSOC composition will be developed by coupling a Particle-Into-Liquid Sampler and Aerosol Mass Spectrometer (PILS-AMS). AMS mass spectra, along with other high time resolution data, (NO_x, CO, EC, VOCs, air mass origins) will be combined to investigate the extent of anthropogenic SOA (ASOA) and biogenic SOA (BSOA) to overall SOA mass. 2.) PILS-AMS will also be coupled to a CCN counter to investigate the CCN properties of WSOC isolated from POA 3.) A suite of online instruments will be deployed to comprehensively measure aerosol chemical composition (Table 1) to provide supporting data for the project objectives. In addition, measurements will be made of H_2O_{ptcl} via two techniques: a temperature and humidity controlled H-TDMA system^[13] and ambient and dry nephelometers. Aerosol pH will be measured using minimally extracted aliquots and a flat-surface transistor probe^[14]. Thermodynamic models (e.g., ISORROPIA II and E-AIM) coupled with our aerosol composition measurements will be compared to measured and predicted LWC and pH. 4.) CTM simulations with the 2-way coupled WRF-CMAQ model will evaluate predictions of organic aerosol, H_2O_{ptcl} , pH_{ptcl} .

Expected Results: Quantitatively determine the extent of biogenic/anthropogenic VOCs on SOA with high temporal resolution Quantitatively understand the link between organic water-soluble fraction, oxidation state, subsaturated water uptake and CCN activity. Characterize the ambient particle pH and liquid water in the Southeast, and test the ability of models to predict particle H_2O_{ptcl} and pH_{ptcl} . These unique data will allow investigation of the conditions and processes leading to various forms of SOA and will enhance climate predictions through a more robust understanding of atmospheric multiphase chemistry, their climate-relevant properties and an improved understanding of biosphere-atmosphere interactions.



Title: Organic aerosol formation in the humid, photochemically-active Southeastern US: SOAS experiments and simulations

Funding Opportunity: Anthropogenic Influences on Organic Aerosol Formation and Regional Climate Implications FON#: EPA-G2012-STAR-D1

PI: Barbara Turpin, Rutgers University; 848-932-3625; turpin@envsci.rutgers.edu

Co-I: Ann Marie Carlton, Rutgers University; 848-932-5778; carlton@envsci.rutgers.edu

Institution: Rutgers, The State University of New Jersey, New Brunswick, NJ 08901

Objectives: Water is the most abundant fine particulate matter species in the eastern US, and yet its impact on ambient secondary organic aerosol formation is poorly understood. This proposal makes use of aqueous OH radical oxidation experiments conducted with ambient samples and evaluation of intermediate model products to improve mechanistic linkages between emissions and secondary organic species (gases and aerosol) in the humid, photochemically-active eastern United States. The proposed research is designed to be an integral part of the Southern Oxidant and Aerosol Study (SOAS), a collaborative field campaign taking place in a southeastern location influenced by biogenic emissions and with varying impacts from anthropogenic sources. We expect this work to ultimately lead to the development of more effective air quality management through models that better capture critical atmospheric processes. *We hypothesize* that chemistry that takes place in atmospheric waters has a substantial impact on the formation and properties of organic aerosol (note: we expect that gas-phase chemistry followed by aqueous chemistry will form SOA which is more hygroscopic and has higher O:C ratios). Gas phase photochemical reactions fragment and oxidize organic emissions, leading to the abundant formation of small, polar compounds (e.g., acetic acid, glyoxal, methylglyoxal, glycolaldehyde, acetone) that readily partition into cloud, fog and aerosol waters. Subsequent reactions in the aqueous phase can form low volatility products (e.g., organic acid salts, oligomers) that remain in the particle phase even after water evaporation. Thus, in an environment where photochemistry and abundant liquid water coexist, gas followed by aqueous chemistry could be the predominant source of secondary organic aerosol (SOA). The SOAS campaign is an ideal opportunity to test this.

Approach: We will 1) compare predicted and measured aerosol water concentrations during the SOAS campaign; 2) predict concentrations of total and selected water soluble gases for comparison with SOAS measurements and to link to ambient aqueous photooxidation experiments; 3) conduct ambient aqueous photooxidation experiments using water soluble gases scrubbed from the ambient air during the SOAS campaign and model reaction kinetics in these experiments. This will enable us to evaluate the degree to which aqueous photooxidation is captured by current aqueous chemistry models and identify key precursors and products of aqueous chemistry leading to SOA formation, 4) collaborate broadly to address SOAS science goals.

Expected Results – Outputs and Outcomes: A better understanding of SOA formation, properties and behavior in the humid eastern U.S. including dependence on anthropogenic emissions. More accurate air quality prediction enabling more accurate air quality management. Scientific insights communicated via peer-reviewed publications and other means. Supplemental Keywords: ambient air, environmental chemistry, fine particles, PM_{2.5}

Collaborative Research – Investigation of the Effects of Anthropogenic-Biogenic Interactions on SOA Formation

PIs – J.L. Jimenez, D.A. Day, Univ. of Colorado-Boulder, Doug Worsnop – Aerodyne Research
Intellectual Merit: Secondary organic aerosols (SOA) comprise a major fraction of submicron aerosols, which play a critical but poorly understood role on climate forcing, human health, visibility, and acid deposition. These effects depend on aerosol composition, size, and spatio-temporal distribution. Over the last decade large gaps have been identified between SOA models and measurements. Several possible explanations have been proposed that can close the gaps and even result in too much SOA in models; however, the information content of past field experiments has been insufficient to clarify the key sources and factors that control SOA in ambient air. Recent evidence strongly suggests that a large fraction of global SOA is formed through synergistic effects between biogenic volatile organic compounds (BVOC) and anthropogenic pollution, however the key precursors and pathways remain unclear.

The goal of this collaborative proposal is to investigate the composition, sources, and pollution-dependence of SOA formation in the Southeast US, which is thought to be a hot spot of anthropogenic/biogenic interactions. We will participate in the Southern Oxidant & Aerosol Study (SOAS) at the forested Supersite in Centreville, AL, in the southeastern United States in summer 2013. This site experiences substantial biogenic VOC (monoterpenes and isoprene) concentrations and widely varying anthropogenic influence (e.g. NO_x , SO_2), making it an ideal location for these scientific questions. We will investigate three key aspects of this system: 1) The sources of the submicron OA and organic gases present at the site will be investigated through factor analysis of High-Resolution Time-of-Flight Aerosol Mass Spectrometry (HR-ToF-AMS) data, combined with modern/fossil carbon measurements on filter samples (for total, elemental, organic, and water-soluble carbon), and with molecular markers and factor analysis of two state-of-the-art speciation instruments: a Chemical-Ionization High-Resolution ToFMS coupled to a Micro-Orifice Volatilization Impactor (MOVI-HRToF-CIMS) and an Aerodyne High-Resolution ToFMS alternating between an atmospheric pressure interface (API-ToF) for analyzing ambient ion concentration and composition and an atmospheric pressure nitrate chemical ionization source (NO_3^- -API-ToF-CIMS) to quantify the concentration and composition of highly oxidized organic gases. 2) The potential of airmasses to form SOA will be investigated in real-time with two Potential Aerosol Mass (PAM) flow reactors by continuously exposing ambient air to varying concentrations of OH, O_3 , or NO_3 radical; their output will be analyzed by the real-time instruments. In addition, the potential for SOA aging via water-phase chemistry will be explored by aging filter samples in water with added H_2O_2 . 3) The volatility of the OA and organic gases will be investigated with several complementary techniques: a thermal denuder (TD) in front of the AMS, and both thermograms and gas/aerosol ratios from the MOVI-HRToF-CIMS. These analyses will be stratified as a function of BVOC, RH, and pollution (NO , NO_2 , SO_2 , acidity, NO_3) conditions, in order to identify key precursors and factors controlling SOA formation in this site and region. We will also conduct selected experiments in a large environmental chamber and perform computer modeling to support the interpretation of the field measurements. The proposing groups are leading the development and application of these advanced mass spectrometric and flow reactor techniques and are uniquely qualified to perform this research. These measurements and analyses, combined with the large suite of aerosol, gas, and meteorological measurements and modeling efforts conducted by other groups, will allow placing much firmer constraints on anthropogenic-biogenic SOA formation.

Broader Impacts: Understanding the chemistry and atmospheric processes that control SOA formation and the persistent gaps between SOA observations and models is a critical step toward predicting how this important atmospheric constituent may act as a climate forcing agent, affect air quality and change under future climates, anthropogenic and biogenic emission patterns, and land uses. The improved understanding will help guide prediction capabilities that are critical for managing the climate and health impacts of SOA. This project will also provide training for two graduate students and one postdoc with state-of-the-art instrumentation as part of a world-class collaborative experiment, which will provide an intense and highly motivating learning environment.

SOAS 2013: Characterization of oxidized volatile organic compounds with chemical ionization mass spectrometry

Principal investigator: Paul O. Wennberg (Caltech)

Instrument operators: Tran B. Nguyen, Alex Teng, Jason M. St. Clair, John D. Crounse.

The temperate forests of Southeastern USA are dominant emitters of isoprene (C₅H₈), the most abundant non-methane hydrocarbon in the atmosphere. Isoprene and its oxidation products contribute a significant fraction of the loss of oxidants (especially the hydroxyl radical, OH) in forested environments [1-3]. In addition, isoprene and other biogenically produced alkenes are known to contribute to the organic aerosol budget in this region. Furthermore, investigating isoprene chemistry in the Southeastern USA is important for the understanding the budgets of oxidants, volatile compounds, and aerosol distribution in other large regions of the globe where isoprene emissions dominate the atmospheric flux of reduced carbon.

We use chemical ionization mass spectrometry (CIMS) for the sensitive characterization of oxidized volatile organic compounds (OVOC) from the atmospheric reactions of isoprene and other biogenically-derived compounds. This method is specific with respect to acids, peroxides, and multifunctional compounds [4], enabling the quantification of key tracers for HO_x and NO_x reactivity and aerosol precursors. For example, CIMS has high sensitivity for organic acids and nitrates, indicative of high-NO_x chemistry, and hydroperoxides and epoxydiols, indicative of low-NO_x chemistry.

We will deploy two CIMS instruments at the SOAS ground site: a time-of-flight (ToF) and triple-quadrupole (TripleQ) CIMS. The ToF CIMS couples high time resolution with selective ion chemistry. We plan to use the ToF CIMS to estimate fluxes of select isoprene oxidation products using the eddy covariance technique. For some OVOC, these measurements will be the first determinations of their deposition characteristics. The TripleQ CIMS will be used for the elucidation of isobaric or interference-prone OVOC via collision-induced dissociation [5, 6]. Examples of OVOC that can be uniquely resolved by the TripleQ CIMS include glycolaldehyde, acetic acid, methylhydroperoxide (MHP), isoprene hydroxyhydroperoxides (ISOPOOH), and isoprene epoxydiols (IEPOX). An example of the utility of the CIMS method is the chemical speciation and quantification of organic nitrates at Bearpex 2009 [7]. The total signals of organic nitrates detected by the TripleQ CIMS was consistent with the sum of alkyl nitrates observed by thermal dissociation laser-induced fluorescence (TD-LIF, UC Berkeley), essentially closing the budget for organic nitrates at Bearpex. Tightly-correlated time profiles of isoprene, measured by proton transfer ionization ToF mass spectrometry (PTR-ToF-MS, NCAR), with ISOPOOH from DC3 2012 (unpublished) suggest that laboratory-determined rates and yields for these compounds are dependable. Similar comparisons may be done at SOAS, and we welcome collaborations by SOAS investigators. Further information and a list of previous campaigns can be found on our group website [8].

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Project Title: Novel Measurements of Volatility- and Polarity-Separated Organic Aerosol Composition and Associated Hygroscopicity to Investigate the Influence of Mixed Anthropogenic-Biogenic Emissions on Atmospheric Aging Processes.

Investigator: Brent Williams (PI); brentw@seas.wustl.edu; Washington University in St. Louis
Project Summary

Objectives: Coupling of anthropogenic and biogenic emissions and subsequent atmospheric aging processes are hypothesized to be the leading single contribution to global organic aerosol (OA) mass concentrations, and is also perhaps the least understood single contribution to OA. Improved understanding of this coupling is a high priority topic in the field of atmospheric chemistry in order to determine mitigation strategies for OA control, a pollutant that alters climate and causes detrimental health effects. The primary objective of this proposed work is to better characterize the controlling factors in enhanced secondary organic aerosol (SOA) formation from combined anthropogenic and biogenic emission sources through innovative laboratory and field studies using novel instrumentation.

Experimental Approach: The proposed project consists of four key components: 1) Development of new instrumentation to obtain new insights on the inherent complex chemistry and composition of SOA formation and evolution, 2) Deployment to a large field study (Southern Oxidant & Aerosol Study), 3) Controlled laboratory studies using a custom emissions/combustion chamber, a flow-tube Potential Aerosol Mass (PAM) reaction chamber, and a large suite of chemical and physical measurement systems, and 4) A second field study (East St. Louis) which incorporates key lessons from the initial field study and extensive laboratory studies to perform in-field controlled oxidation experiments (utilizing the PAM reaction chamber) to test the sensitivity of ambient SOA formation and transformation to perturbations in oxidation intensity and precursor composition. Both proposed field studies have the advantage of being in regions of mixed biogenic and anthropogenic emissions, and are at locations with sufficient infrastructure and supporting measurements. The infrastructure for proposed laboratory measurements already exists in the PI's laboratory, so will require limited setup time and cost. The proposed instrument development is focused on two measurement methods: 1) Volatility and Polarity Separator (VAPS) for *in-situ*, high time-resolution, volatility- and polarity-separated OA composition, and 2) a modified Hygroscopicity – Tandem Differential Mobility Analyzer (HTDMA) for measurement of particle hygroscopicity, particle volatility, and size-dependent oxidation effects.

Expected Results: Through the proposed study, novel measurements of compositional and hygroscopic changes during SOA formation and transformation under various mixtures of biogenic- anthropogenic sources will be observed: 1) under unperturbed conditions, allowing meteorology to deliver various emission mixtures (SOAS), 2) in a laboratory setting, with complete control over oxidant levels, emission types, specific particle coatings, etc., and 3) with ambient emissions of gases/particles, but having the option to perturb the oxidation level, or add specific biogenic or anthropogenic gases/particles to the photochemical reaction mixture (East St. Louis). This study design will lead to many new insights on the formation processes and atmospheric transformations of SOA produced from mixed biogenic-anthropogenic emissions, and the associated potential for climate interactions.

ABSTRACT

a. Funding Opportunity Title and Number: Anthropogenic Influences on Organic Aerosol Formation and Regional Climate Implications, EPA-G2012-STAR-D1

b. Project Title: Using Particle Functional Group Composition to Identify and Quantify the Effects of Anthropogenic Emissions on Biogenic Secondary Organic Aerosol

c. PI: Lynn M. Russell; University of California, San Diego; lmrussell@ucsd.edu

Co-PI: Paul J. Ziemann; University of California, Riverside; paul.ziemann@ucr.edu

d. Institution: University of California, San Diego, CA

e. Project Period and Location: 01/01/2013 to 12/31/2015; University of California, San Diego, CA

f. Project Cost: \$400,000

g. Project Summary:

1. Objectives: The proposed research project combines ambient measurements and environmental chamber experiments on organic aerosols to identify and quantify the effects of anthropogenic inorganic and organic emissions on biogenic secondary organic aerosol (bSOA) formed in the Southern Oxidants and Aerosol Study (SOAS) in Summer 2013.

2. Approach: The overall objective of the project will be met by completing the following tasks: (1) identify and quantify the organic functional group (OFG) compositions and infrared spectroscopic features of bSOA in samples collected as part of SOAS, (2) determine the effects of NO_x, SO_x, and anthropogenic VOCs on the characteristic functional group and spectroscopic features of bSOA formed from reactions of biogenic volatile organic compounds (bVOC), and on the SOA yields, and (3) interpret the functional group compositions and infrared spectroscopic features of SOAS organic aerosol samples using results of laboratory experiments and ambient measurements of other relevant aerosol and gas properties in order to identify and quantify the contributions of biogenic and anthropogenic emissions to SOA formed during the study.

3. Expected Results: The expected results of this project are: (1) Improved chemical characterization of biogenic SOA in the southeastern US, (2) Improved quantification of biogenic SOA in the southeastern US, (3) Improved understanding of the effects of pollutants on biogenic SOA composition and yield, and (4) Improved understanding of the reactions that control biogenic SOA composition and yield.

h. Supplemental Keywords: fine particles, PM_{2.5}, isoprene, nitrogen oxides, oxidation, mass spectrometry.

Size-resolved nanoparticle composition during SOAS in the Southeastern U.S.

Jim Smith and Mike Lawler (National Center for Atmospheric Research and Univ. of Eastern Finland, Kuopio)
jimsmith@ucar.edu, mlawler@ucar.edu

Motivation:

The formation and subsequent growth of nanometer-scale particles in the atmosphere may be a significant contributor to total particle and cloud condensation nucleus (CCN) concentrations, with potential impacts on human health, regional weather, and global climate. However, the compounds responsible for the formation and growth of small particles are not well-characterized, making it difficult to estimate the actual impact of these processes or predict how they may change in the future. Knowing the molecular makeup of nanoparticles provides clues about the precursor species that led to the particles' formation.

The SOAS experiment provides the opportunity to look at small particles in the context of a range of observations of potential precursor species, including hydrocarbons, organic nitrates, speciated odd nitrogen, amines, and sulfuric acid.

Experimental Approach:

We will make size-resolved chemical composition measurements of 10-30 nm particles using the TOF-TDCIMS (time-of-flight thermal desorption chemical ionization mass spectrometer). The instrument is capable of measuring a variety of organic and inorganic species, in some cases providing full molecular information. Particle composition during new particle formation events will be compared with background and plume particle composition to isolate species that contribute to rapid particle growth. We will compare the observed particulate compounds to gas phase observations to find likely precursors.

Expected Results:

We expect our observations to address these questions:

1. How do recently formed particles differ in composition from background aerosol?
2. What precursor species are likely involved in nanoparticle growth in this environment?
3. How do different oxidants (NO₃, OH) affect nanoparticle composition?

ABSTRACT

EPA Funding Opportunity Title and Number: Anthropogenic Influences on Organic Aerosol Formation and Regional Climate Implications, EPA-G2012-STAR-D1

Title: Emission, Fate, and Contribution of Biogenic Volatile Organic Compounds to Organic Aerosol Formation in the Presence of Anthropogenic Pollution: Measurements and Modeling during SOAS

Multiple PI application. Contact PI: John E. Mak (john.mak@stonybrook.edu)

Additional PIs: Allen H. Goldstein (ahg@berkeley.edu), Alex Guenther (guenther@ucar.edu)

Institutions: Stony Brook Univ., NY; Univ. of California, Berkeley, CA; NCAR, Boulder CO.

Project Period: March 1 2013-Feb 28 2015

Project Location: Alabama **Project Cost:** \$399,964

Objectives of Study: The overall goals of this project are to quantify biogenic Volatile Organic Compound (VOC) emissions and VOC deposition to terrestrial ecosystems, characterize VOC atmospheric oxidation, and understand the impact of anthropogenic pollution on secondary organic aerosol (SOA) formation. Specific objectives include: constrain and understand biogenic VOC (BVOC) emission, oxidation and deposition processes; elucidate SOA formation pathways under polluted and clean conditions; evaluate contributions of biogenic and anthropogenic VOC emissions to regional SOA; search for previously unidentified/unmeasured semivolatile organics (SVOC); investigate the impacts of urban/rural emission patterns on climate.

Experimental approach: Tower based vertical gradient, eddy covariance flux, cartridge relaxed eddy accumulation (REA) flux, and aircraft based vertical gradient and cartridge REA flux measurements, will be used to quantify temporal and spatial variations in BVOC emissions and atmospheric oxidation, and VOC deposition. VOC measurements from the tower and aircraft will use proton transfer reaction time-of-flight mass spectrometers (PTR-TOFMS) to measure emission and deposition of most of the VOC species that have a major role in SOA production. Additional speciated VOC measurements (monoterpenes and alkanes) will be done with REA samples analyzed by gas chromatography with mass spectrometer and flame ionization detectors. Observations will be used to evaluate and improve the Model of Emissions of Gases and Aerosols from Nature (MEGAN) and the WRF-Chem model. WRF-Chem will then be used for a series of model simulations to investigate the impact and influence of anthropogenic and BVOCs on secondary organic aerosol formation in the Southeastern U.S. Data from the proposed measurements will be critical to analysis by the overall SOAS research team in determining anthropogenic influences on organic aerosol formation and regional climate implications.

Expected results: The primary deliverable products will be measurements of VOC emission and deposition on spatial and temporal scales that are optimal for evaluating and improving regional models. Outcomes will include approaches for quantifying VOC emission uncertainties and identifying missing VOC emission sources that can be utilized by regulatory agencies and the scientific community. The proposed work will also improve understanding of the processes controlling BVOC emission and VOC deposition variations that will lead to improved emission and deposition representations in models. The proposed work directly addresses the solicitation by addressing how anthropogenic emissions influence the oxidation pathway of BVOCs and the subsequent formation of SOA. The overall benefit of this project will be improving regional VOC emission and SOA simulations that enable the development of regulatory control strategies that will enhance efforts to improve and maintain clean air.

Supplemental keywords: BEIS, isoprene, biogenic VOC oxidation products, deposition

The physical phase and phase changes of SOA particles under anthropogenic influences

PI: Annele Virtanen, annele.virtanen@uef.fi

University of Eastern Finland, Kuopio, Finland

Background & Goal: According to our recent results published in Nature (Virtanen et al., 2010), atmospheric SOA particles formed in boreal forest can be amorphous solid in their physical state at least several hours after their formation. Our recent laboratory study shows also, that SOA from anthropogenic precursors can be amorphous solid in their physical phase (Saukko et al., 2012a). The amorphous solid state provokes a rethinking of SOA processes as it may influence the partitioning of semi-volatile compounds, reduce the rate of heterogeneous chemical reactions, affect the particles' ability to accommodate water and act as a cloud condensation or ice nuclei, and change their atmospheric lifetime. In this project, we will study the physical phase and humidity induced phase transitions during the Southern Oxidant & Aerosol Study (SOAS) campaign 2013. The location of the SOAS campaign site is ideal to study biogenic-anthropogenic interactions, due to the proximity of natural emissions with a variety of anthropogenic pollution sources and offers significantly different measurement environment compared to the boreal areas, hence greatly increasing the global significance of the results gained in this study.

Methodology: To study the physical phase of the particles, we'll investigate the mechanical bounce properties of the particles knowing, that liquid particles don't bounce in the impaction process, while solid particles do. We will utilize the improved version of the measurement system described in detail in Saukko et al. (2012b). The new system consists of a micro-orifice impactor operating in pressure range close to ambient values, and a polished steel substrate. Size-selected aerosol (the size range of the system is 80-200 nm) is guided through the impactor stage and the particle number concentration is measured up- and down-stream of the impactor. The method is conceptually similar to that used by Virtanen et al. (2010), but the optical detection of particles employed here removes the effect of charge transfer processes. We will also study the humidity induced phase transitions, by adjusting the relative humidity of the sample air from RH 20% to RH 90%. Our measurement system will be combined with the PAM –reactor during the campaign.

Expected results: We will find out the physical phase of atmospheric SOA particles in the environment where anthropogenic emissions play a role in the formation and aging processes. The results will significantly increase our understanding on the formation, fate, atmospheric processes, and climatic implications of SOA particles influenced by anthropogenic emissions.

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Funding Opportunity and Number: EPA-G2012-STAR-D2-Anthropogenic Influences on Organic Aerosol Formation and Regional Climate Implications

Title: Understanding regional oxidation capacity by comprehensive observations to constrain hydroxyl radical sources and sinks during the Southern Oxidant Aerosol Study (SOAS)

Principal Investigator: Saewung Kim (saewungk@uci.edu),

Institutions: University of California, Irvine

Objectives: The overall goal of this project is to improve our understanding of oxidation capacity in the Southeastern U.S. region where biogenic volatile organic compounds (BVOCs) play a significant role in regional photochemistry to produce photochemical ozone and secondary organic aerosols (SOA) with different anthropogenic pollution influences (especially, NO_x). Our specific objectives include:

- Providing high-resolution datasets of OH, HO₂+RO₂, H₂SO₄, NO_x, and OH reactivity to the SOAS study participants and the entire scientific community.
- Constraining OH sources including photolytic and recycling sources and OH chemical sinks by measurements
- Understanding HO_x budget and implications for SOA production by comparing measured OH ([OH]_{MEA}), measurement constrained steady-state model calculated OH ([OH]_{SS}) and University of Washington Chemical Mechanism (UWCM), which embedded the near-explicit chemical mechanism (MCM 3.2) calculated OH ([OH]_{UWCM}) to assess our current HO_x and SOA modeling capacity in isoprene rich environments for various NO_x levels.

Approach: deploy 1) a chemical ionization mass spectrometry system for OH/HO₂+RO₂/H₂SO₄, 2) an OH reactivity measurement system with a comparative reactivity method, and 3) a cavity ring-down spectroscopy system for NO_x measurements for Southern Oxidant & Aerosol Study (SOAS). These measurements are a critical addition to the SOAS campaign comprehensive measurement suite that will provide constraints for radical and SOA sources and sinks for the highly constrained steady-state model and box-model calculations.

Expected Results: The proposed field measurements and data analysis will provide an important constraint to understand oxidation capacity in the Southeastern U.S. that determines SOA and photochemical ozone formation. Unexpectedly high levels of OH determining oxidation capacity have been consistently reported in high isoprene environments. Therefore, the comprehensive dataset from this proposed study is needed to seamlessly constrain OH sources and sinks and improve our understanding of OH primary production and recycling mechanisms in the Southeastern U.S. These outcomes, eventually, will improve modeling capability to predict SOA and photochemical ozone in the Southeastern U.S. region.

Supplemental keywords: ambient air, tropospheric OH, SOA, observation, Southeast

EPA STAR (Early Career): Sources and Radiative Properties of Organosulfates in the Atmosphere

PI: Elizabeth A. Stone, Ph.D. (betsy-stone@uiowa.edu),
Chemistry Department, University of Iowa, Iowa City, IA 52242

Objectives: In this proposal, field measurements are designed to understand how secondary organic aerosol (SOA) forms in mixtures of biogenic and anthropogenic emissions and laboratory studies are proposed to evaluate its impacts on climate. The proposed study focuses on organosulfates that are significant components of ambient aerosol and unique to SOA formed under acidic conditions. *Field-based measurements of organosulfates will be used to test the hypothesis that anthropogenic sulfur dioxide emissions impact SOA formation. Laboratory studies will further test the hypothesis that organosulfates are climate forcing agents.* The primary objectives of the proposed work are to: 1) Identify the anthropogenic and biogenic emission sources and atmospheric conditions that lead to organosulfate and SOA formation. 2) Evaluate the direct and indirect radiative properties of organosulfates, including their light absorption, hygroscopicity, and cloud condensation nuclei activity.

The proposed study will improve the understanding of SOA formation, advance the analytical tools to study particulate matter, provide the first measurements of the climatically-relevant properties of organosulfates, and make significant contributions to the upcoming Southern Oxidant & Aerosol Study (SOAS).

Experimental Approach: To allow for organosulfate quantification in ambient aerosol, a novel set of biogenic organosulfate molecules will be generated using targeted organic synthesis. With these standards, we propose to further develop analytical methodology for organosulfate detection using liquid chromatography and tandem mass spectrometry for the separation, identification, and quantification (Stone et al., 2012). Validated methodology will be applied to fine particulate matter collected in the Southeastern United States during the SOAS field campaign. Complementary chemical analysis will include measurements of organic carbon, sulfate and other inorganic ions, organic molecular markers for primary aerosol sources, and SOA tracers (Stone et al., 2010; Stone et al., 2007; Stone et al., 2008). Receptor-based source apportionment techniques will be applied to evaluate the sources of organic aerosol, SOA, and organosulfates (EPA, 2008). The direct and indirect radiative forcing properties of organosulfates will be evaluated with physical measurements of ultraviolet and visible light absorption, hygroscopicity, and cloud condensation nuclei activity (Gibson et al., 2006; Hatch et al., 2009).

Expected Results: It is expected that these studies will provide mechanistic insight to how SOA forms under acidic conditions and how it impacts direct and indirect radiative forcing. We also expect that understanding the chemical and physical properties of SOA will lead to future advancements in the predictive capabilities of air quality and climate models.

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Title: AEROSOL OPTICAL PROPERTIES AND BIOGENIC SOA: EFFECT ON HYGROSCOPIC PROPERTIES AND LIGHT ABSORPTION

Investigators: PI: A.Khlystov; Co-PIs: R.Subramanian, and V.Aneja

Institution: Research Triangle Institute, Research Triangle Park, NC; North Carolina State University, Raleigh, NC

PROJECT SUMMARY

Objectives: Secondary organic aerosol (SOA) from biogenic sources is a major contributor to the global aerosol burden. It is estimated to have a profound effect on regional and global climate. There is strong evidence that biogenic SOA can influence optical properties of ambient aerosol by altering its hygroscopicity and contributing to light absorption directly via formation of brown carbon and indirectly by enhancing light absorption by black carbon (“lensing effect”). The magnitude of these effects remains highly uncertain. It was suggested that organo-nitrogen (ON) compounds are the substances responsible for formation of brown carbon in biogenic SOA. No evidence exists yet for such a link in ambient aerosol. *The goal of this project is to provide comprehensive characterization of optical properties of anthropogenically-influenced biogenic SOA, its contribution to aerosol hygroscopicity and light absorption via formation of brown carbon and “lensing” effect, and investigate the link between ON and brown carbon.*

Approach: A set of state-of-the-art instruments will be deployed during two field campaigns, one at the SEARCH site near Centerville, AL during the SOAS campaign in summer 2013, the other at Duke Forest site near Chapel Hill, NC in summer 2014. The two sites are strongly influenced by biogenic sources, but are different in their proximity to anthropogenic sources. Measurements will include aerosol light absorption and scattering at two wavelengths (405 nm and 532 nm); black carbon mass and its mixing state; light absorption spectra by water-soluble aerosol; ON, water soluble organic carbon and the main ionic species in the aerosol. Light absorption and scattering will be measured for both temperature- and humidity-conditioned aerosols, which will help determine absorption enhancement due to the “lensing” effect and the humidity dependence of aerosol light scattering as a function of biogenic SOA, respectively. Measurement of the Ångstrom Absorption Exponent over the two wavelengths, evaluation of the relative lensing effect at these two wavelengths, and light absorption properties of water-soluble aerosol will help reduce uncertainty in determining brown carbon. The amount of brown carbon will then be compared to the amount of ON to test the proposed link between the two.

Expected results: This study will provide a comprehensive characterization of optical properties of biogenic SOA and their sensitivity to anthropogenic influence. Several parameters critical for climate modeling, such as absorption cross-section, single scattering albedo and sensitivity to RH, will be measured. The measurements will also provide an indirect test of brown carbon formation mechanisms proposed in smog chamber studies. One graduate student will be trained during the project. The results of the study will be widely disseminated via publications in peer-reviewed publications and presentations at professional conferences.

Supplemental keywords: tropospheric aerosol, organics, climate change.

Project Title: Contribution of Biogenic Volatile Organic Compounds to Organic Aerosol Formation in the Presence and Absence of Anthropogenic Pollution

PI: Allen Goldstein, University of California Berkeley

Project Summary Two closely related field studies are planned to elucidate the role of biogenic volatile organic compound (BVOC) emissions in atmospheric chemistry and climate, and to understand how the transformation and fate of BVOC is altered by the presence of anthropogenic pollution sources. Planned for the southeastern US in 2013 (Southern Oxidant and Aerosol Study - SOAS) and the Amazon region around Manaus, Brazil, in 2014 (GOAMAZON), these studies are designed to comprehensively examine how BVOC emissions and their interaction with anthropogenic pollution (i.e., black carbon, nitrogen oxides and sulfur dioxide) alter the atmosphere's oxidative capacity, influence secondary aerosol formation, atmospheric composition and, ultimately, affect the earth's radiation balance and climate. We propose detailed speciated measurements of semivolatile organic matter, including both vapor and particle phases, including in-situ hourly observations with our Semi-Volatile Thermal desorption Aerosol Gas chromatograph (SVTAG) instrument and off-line filter analysis using multidimensional GC with both electron impact and vacuum ultraviolet ionization coupled to high mass resolution time-of-flight mass spectrometry (GCxGC/HR-VUV, EI-TOFMS). We will focus on measurements of a suite of chemicals that have recently been identified as major tracers for BVOC oxidation in both polluted and clean environments, but which have not been measurable in-situ with hourly time resolution up to now. Coupled with other co-located measurements, these data will be used to understand BVOC emission, oxidation, and particle formation pathways at the molecular level, to understand how these pathways change when influenced by anthropogenic sources, and their importance for the atmospheric budget of aerosols and the earth's radiation balance on regional scales. Doing these measurements during both the SOAS 2013 and GOAMAZON 2014 campaigns will allow a critical comparison between BVOC oxidation mechanisms occurring in polluted versus clean environments. Both study regions have high BVOC emission, but one has high aerosol loading and large regional cooling due to aerosols (SOAS) and the other has low aerosol loading but is rapidly developing and undergoing substantial land use change leading to increasing anthropogenic emissions (GOAMAZON). Developing a better understanding of the formation and transformation of SOA is the primary goal of this proposal. Until very recently, it was not possible to measure hourly speciated organic chemical composition of aerosols with in-situ instrumentation, limiting investigations of SOA formation and aerosol source contributions. We have now developed that capability in collaboration with Aerosol Dynamics Inc., and propose employing it to study the contributions and interactions of biogenic and anthropogenic emissions to SOA processes.

Intellectual Merit The results of our proposed research will be time-resolved data defining the chemical composition of organic aerosols in two distinct environments, the southeast US and the Amazon rainforest downwind of Manaus, and laboratory measurements of aerosol and gas phase products from isoprene and terpene photooxidation. The combined data set will be examined to assess differences in the reaction pathways for SOA formation from BVOC in the presence and absence of anthropogenic influence. Accurate in-situ measurements of biogenic VOC emissions and their oxidation products in both the gas and particle phase are crucial for our understanding of the fate of BVOC emissions and how they are oxidized to form SOA in both polluted and pristine environments.

Broader Impacts This research will provide important new constraints for models predicting the formation and distribution of SOA, models that estimate the effects of VOC emissions on regional air quality and global climate, and models predicting the interaction of biogenic VOC emissions with climate change and increasing anthropogenic influence. Multiple collaborative research efforts during the SOAS 2013 and GOAMAZON 2014 will be made possible or enhanced through support of this proposal. PhD students and postdoctoral researchers will be trained through this research, and undergraduates will gain experience through their involvement. Research methodologies and results developed through this project will be integrated into classroom teaching by Professor Goldstein. Additionally, GOAMAZON will include educational opportunities for students in Brazil during the field campaign.

Project title: Getting organic aerosol volatility right: measurements of equilibrium and kinetic phase partitioning properties to improve atmospheric models

PI: Andrew Grieshop, NCSU; **Co-PI:** Andrey Khlystov, RTI

Measurements of aerosol volatility: The main experimental setup consists of 4 sampling lines (See Fig. 1). Each line will have a dedicated SMPS to measure aerosol size evolution. In addition, an Aerosol Chemical Speciation Monitor (Aerodyne ACSM) will be used to help constrain the effect of temperature

on chemical composition of the aerosol. The ACSM will be switching between different lines. Inverse modeling will be used to fit volatility basis set (VBS) parameters: effective saturation concentrations (C^*), enthalpies of vaporization and evaporation coefficients. Data from the cooled line at constant temperature (5 C will be used to constrain condensation of more volatile aerosol components in conjunction with the heated lines for estimation of volatility parameters.

(Note: Use of the cooled line is still uncertain pending feasibility tests prior to the campaign).

Expected results and outputs include: volatility basis set-based distributions for ambient aerosols dominated by secondary organic aerosol from biogenic precursors generated under differing levels of anthropogenic influence;

measurements of low-volatility organic vapors in equilibrium with aerosols; data and parameterizations describing the volatility of organic species associated with new particle formation events and condensational growth of existing aerosols under varying meteorological conditions; estimates for the temperature-dependence of partitioning; new data on constraints to mass-transfer in aerosol partitioning; development and field testing of new techniques to measure the equilibrium and kinetics of organic aerosol phase partitioning.

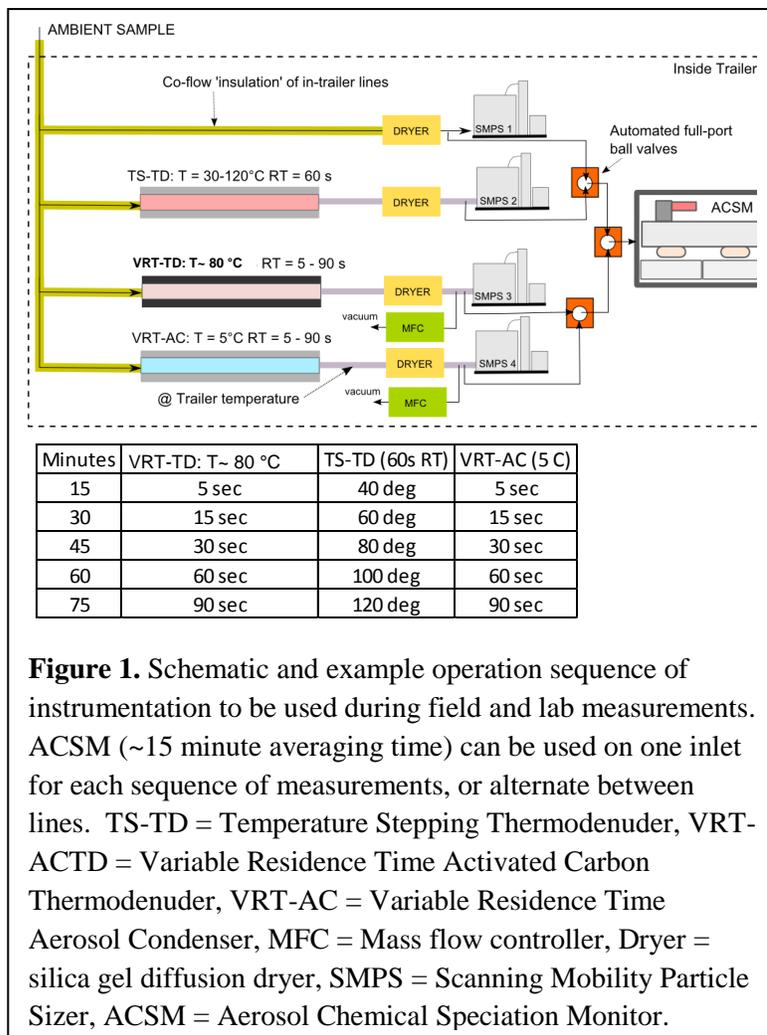


Figure 1. Schematic and example operation sequence of instrumentation to be used during field and lab measurements. ACSM (~15 minute averaging time) can be used on one inlet for each sequence of measurements, or alternate between lines. TS-TD = Temperature Stepping Thermodenuder, VRT-ACTD = Variable Residence Time Activated Carbon Thermodenuder, VRT-AC = Variable Residence Time Aerosol Condenser, MFC = Mass flow controller, Dryer = silica gel diffusion dryer, SMPS = Scanning Mobility Particle Sizer, ACSM = Aerosol Chemical Speciation Monitor.

Project title: Collaborative Research: Sensitivity of gas and aqueous phase production of secondary organic aerosol to chemical and environmental perturbations

PIs: Don Collins, Texas A&M University; Robert Griffin, Rice University

Intellectual Merit Characterization of ambient aerosol and novel chamber based experiments will be combined to address critical questions concerning the formation of secondary organic aerosol (SOA) during two sequential field campaigns: first as participants in the Southern Oxidant and Aerosol Study (SOAS) near Centreville, Alabama during the summer of 2013 and then in an independent investigation at a site in southeastern Texas during the summer of 2014. The major scientific objectives are:

1. To characterize the ambient aerosol at each site in order to investigate the processes and sources that lead to observed concentrations and properties;
2. To relate these processes and sources to anthropogenic and biogenic activity;
3. To investigate *in situ* the sensitivity of secondary aerosol processes, specifically those involving biogenic SOA, to anthropogenic factors such as enhanced oxidant or NO_x concentration, the presence of acidic seed aerosols, etc.;
4. To investigate *in situ* the sensitivity of secondary aerosol processes, specifically those involving biogenic SOA, to physical parameters such as aerosol liquid water content (related to relative humidity (RH)), the presence of cloud water, etc.; and
5. To investigate the reversibility of SOA formation at each site and relate the findings to the level of anthropogenic influence.

The first pair of objectives will be achieved by measurements made using an ensemble of analytical aerosol instrumentation including a high resolution, time-of-flight aerosol mass spectrometer, a particle-into-liquid sampler integrated with ion chromatography, a scanning mobility particle sizer, a humidified tandem differential mobility analyzer, and a cloud condensation nuclei counter. This instrumentation will also be employed to address the remaining objectives by supporting the experiments using the recently developed captive aerosol growth and evolution (CAGE) chamber system. That system consists of two parallel environmental chambers in which injected particles are exposed to conditions closely mirroring those outside. Experiments addressing the third objective will involve perturbing the gas- or aerosol-phase in one chamber in a manner reflective of that resulting from increased anthropogenic influence. The CAGE system also supports perturbations of RH and cloud formation, enabling experiments addressing the fourth objective. Finally, removing semi-volatile species from the chambers at the end of many of the experiments will test the reversibility of gas-particle partitioning and address the final science objective.

Broader Impacts The expected results from this project will address several aspects of the role of changing aerosol precursors on climate. The direct measurement of sensitivities of SOA production rate and properties to various perturbations superimposed on ambient conditions will provide a convenient way to test chemical mechanisms used in a variety of models. Beyond the scientific goals, however, the proposed project is intended to have broader benefits for the participants, the scientific community, and for the education provided by the hosting universities. This project will involve undergraduate and graduate students, research staff and faculty, creating an invaluable environment for student development and exposure to research and collaborative practices. The proposed project will provide excellent opportunities for integrating research and teaching, a regular activity of both PIs. Further, it will facilitate their ongoing commitment to increasing the role of underrepresented groups in science and engineering. Broad benefits for the scientific community will proceed from the participation in collaborative research, the SOAS campaign, and in the standard forums for disseminating scientific results. These activities will enhance the impact and visibility of new findings and new methods (especially the CAGE system), help forge new ties for future endeavors and form habits of collaboration in participating students.

NCAR ACD ACCORD NOMADSS/SOAS activities

Alex Guenther (NOMADSS/SOAS co-PI), Peter Harley, Andrew Turnipseed, Jim Greenberg, Roger Seco, Lisa Kaser, Wenzhang Fang, Junfeng Liu, Andy Weinheimer, Eric Apel, Becky Hornbrook, Alan Hills, Deedee Montzka, Teresa Campos, Frank Flocke, Sam Hall, Geoff Tyndall, Jim Smith, John Ortega, Louisa Emmons, Mary Barth, Christoph Knote, Alma Hodzic, Xiaoyan Jiang, Christine Wiedinmyer

1. C130 measurements

Objectives:

Direct quantification of VOC, ozone and NO_x surface fluxes; investigate processes controlling surface fluxes; reconcile differences between “bottom-up” and “top-down” flux estimates; indirect estimate of OH concentrations; ; better understanding of HO_x/NO_x/ozone/organics/aerosol distributions, sources and sinks.

Measurements: VOC (PTRMS, Fast GCMS), NO, NO₂, O₃, CO, CO₂, actinic flux, SMPS

2. ISFS flux tower and ISS boundary layer sounding measurements

Objectives:

Quantify and understand the bi-direction flux and vertical structure of VOC, NO, NO₂, O₃, CO₂, H₂O, and energy within and above a southeastern US broadleaf forest canopy.

Quantify and understand boundary layer height and vertical structure and characterize dynamics and transport throughout the boundary layer.

Measurements:

NCAR/ACD: VOC (PTRMS, GCMS), NO, NO₂, O₃

NCAR/EOL: canopy turbulence, CO₂, H₂O, energy; boundary layer structure (wind, temperature, humidity) using LIDAR, SODAR, wind profiler, release sondes.

3. SEARCH site measurements

Objectives:

Provide observations to support the SOAS research team

Measurements:

PTRMS for U. Colorado (Jimenez) PAM study

PTR-TOFMS for UC Berkeley (Goldstein) BVOC flux study.

HO_x-CIMS for UC Irvine (Kim) HO_x study

NO, SMPS, SO₂ for core gas and particle characterization

4. Modeling: Chemical tracer forecasts and emissions

WRF-chem simulations during and after the experiment

Assess emissions inventories (biogenic anthropogenic, fires, etc.) and coordinate use by various groups

Provide real-time WRF-FLEXPART forecasts, showing projected anthropogenic, biogenic, and fire plume locations

MOZART tracers for influence of continental-scale sources (e.g., western fires, Ohio Valley power plants, etc.)

Title: Broadband field measurements of optical extinction by biogenic aerosols in the ultraviolet spectral region

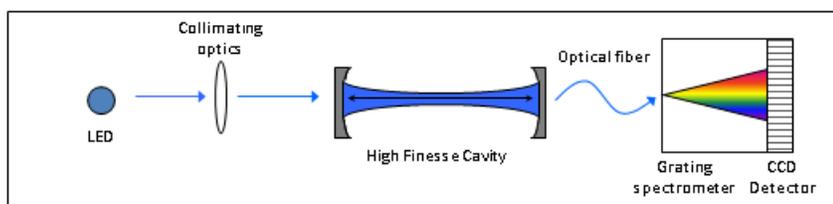
Investigators: Rebecca Washenfelder, Alexis Attwood, Steve Brown

University of Colorado and NOAA, Boulder, CO

rebecca.washenfelder@noaa.gov , alexis.attwood@noaa.gov, steven.s.brown@noaa.gov

Objectives: Aerosols influence the Earth's radiative budget by scattering and absorbing incoming solar radiation. The optical properties of aerosols vary as a function of wavelength, but few measurements have reported the wavelength dependence of aerosol extinction cross-sections and complex refractive indices. In particular, brown carbon aerosols, which include secondary organic and biomass burning aerosols, have wavelength-dependent absorption that increases toward the ultraviolet spectral region. We plan to measure aerosol optical extinction and aerosol extinction cross-sections as a function of wavelength to quantify the radiative properties of these aerosols.

Approach: Broadband cavity enhanced spectroscopy is a sensitive and accurate technique for measuring optical extinction. We have recently demonstrated measurements of aerosol extinction cross-sections in the laboratory, and used these to determine complex refractive indices as a function of wavelength (representing the absorption and scattering by aerosol particles), using cavity enhanced spectroscopy [Washenfelder, 2013]. The instrument requires a broadband light source, optical cavity, and multichannel detector:



During CalNex 2010, we used a similar analytical approach to measure glyoxal and nitrous acid [Washenfelder, 2011; Young, 2012]. We have modified our existing field instrument to measure aerosol optical extinction in the 360 – 420 nm wavelength region. By combining the measurement of aerosol optical extinction with a condensation particle counter (CPC) and a differential mobility analyzer (DMA), we will calculate aerosol optical cross-sections and refractive indices.

Expected Results: The Southeastern U.S. has high emissions of biogenic alkenes, including isoprene and monoterpenes, that have been shown to contribute to secondary organic aerosol. Understanding the climate-relevant properties of biogenic aerosols is an important question. We are interested in quantifying the impact of biogenic aerosol on the regional radiative budget. Further, we hope to examine how aqueous chemistry and cloud processing may affect the aerosols that are formed, and their optical properties.

Relevant papers:

Washenfelder R. A., C. J. Young, S. S. Brown, et al. The glyoxal budget and its contribution to organic aerosol for Los Angeles, California during CalNex 2010. *J. Geophys. Res.*, 2011.

Young, C. J., R. A. Washenfelder, J. M. Roberts, et al. Vertically resolved measurements of nighttime radical reservoirs in Los Angeles and their contribution to the urban radical budget. *Env. Sci. Tech.*, 2012

R. A. Washenfelder, J. M. Flores, C. A. Brock, S. S. Brown, and Y. Rudich, 2013, Broadband measurements of aerosol extinction in the ultraviolet spectral region. *Atmos. Meas. Tech. Discuss.*, 2013. <http://www.atmos-meas-tech-discuss.net/6/113/2013/amtd-6-113-2013.html>

Frank Keutsch – Wisconsin – SOAS

B. Project Summary: Aerosol and ozone (O_3) affect human health, the environment, and climate. Oxidation of volatile organic compounds (VOCs), in particular via the hydroxyl radical (OH), the most important atmospheric oxidant, is directly coupled to formation of O_3 and secondary organic aerosol (SOA), an important component of ambient aerosol. We propose comprehensive laboratory and field studies focused on improving the understanding of the processes controlling OH and isoprene, the most important volatile organic compound, especially in rural (low-NO) environments, and use of oxidation product (flux) measurements for an analysis of potentially missing BVOCs. We will also study the anthropogenic impact on biogenic VOC (BVOC) oxidation and resulting SOA formation.

The proposed project addresses the following questions: 1) How well do current mechanisms represent VOC oxidation, especially for isoprene, and in particular under low-NO conditions? 2) How well do current mechanisms/models represent OH photochemistry in view of recent findings of potential measurement interferences? 3) What are the dominant mechanisms of anthropogenic influence on rural VOC oxidation and resulting O_3 and SOA formation? 4) How well do current models represent surface/atmosphere exchange processes?

To address these questions and study the processes outline above, we will combine advanced synthetic organic chemistry of key isoprene oxidation products with collaborative, mechanistic gas-phase and SOA laboratory studies, during the Focused Isoprene-chemistry eXperiment (FIX). This will provide an improved framework for analyzing collaborative field-measurements that combine existing support and instrument advances. The field work focuses on the Southern Oxidant and Aerosol Study (SOAS) in the SE-US for investigation of HOx, isoprene photochemistry and anthropogenic impact.

Frank Keutsch – Wisconsin - SENEX

Assessing anthropogenic impact on secondary pollutant formation in the South-Eastern US via airborne formaldehyde measurements

Objectives:

The primary objective of the proposed work is to improve our mechanistic understanding of the anthropogenic influence on processes transforming primary emissions into secondary pollutants, especially ozone and secondary organic aerosol (SOA), and to constrain the temporal and spatial scales of this anthropogenic impact in the SE-US. Specifically, airborne measurements of formaldehyde, in conjunction with a full suite of chemical and meteorological observations, will be used to evaluate the impact of anthropogenic volatile organic carbon (VOC) and nitrogen oxide (NO_x) emissions on ozone and SOA production efficiency at the urban-rural interface. Analysis will focus on quantifying the degree of fragmentation versus functionalization, and the related extent of chain terminating reactions during the photochemical lifecycle of biogenic and anthropogenic VOCs. These factors determine the relative ozone production rates and mass of reactive carbon in the gas and condensed phases. We will evaluate how synergistic and competitive mechanisms interact to influence SOA loadings and optical properties. Formaldehyde measurements will also enable improved isoprene emission models that can then be used as a reference for isoprene inferred from formaldehyde via satellite retrievals, which are critical to regional models of air quality.

Experimental Approach:

Formaldehyde measurements will be obtained on the NOAA P3 during the Southern Oxidant and Aerosol Study (SOAS) as part of the simultaneous NOAA Southeast Nexus (SENEX) campaign. We will deploy a custom-built instrument utilizing fiber-laser induced fluorescence for measurement of formaldehyde, a technique developed by the Keutsch research group at UW-Madison that has unparalleled sensitivity and provides high-time resolution data. The data will be used in conjunction with the large suite of other measurements on the NOAA P3 in a comprehensive analysis that makes use of ratios of oxidation products and primary emissions to dissect the complex gas-phase photochemistry under varying anthropogenic influence. Measurements, especially those of oxidation product ratios, will be analyzed using 0-D and 1-D chemical box models to evaluate and improve our understanding of current gas-phase mechanisms. Observations will also be used to quantify the temporal and spatial scale of anthropogenic influence at this site and to provide constraints on regional emissions of isoprene, which will lead to improved regional chemical transport models.

Expected Results:

This project will provide a critical, publically available formaldehyde dataset during the SOAS campaign. The major expected result will be an improved understanding of the influence of anthropogenic VOC and NO_x emissions on secondary pollutant concentrations and properties in a rural setting. Findings will be framed in the context of the competitive processes of fragmentation versus functionalization during gas-phase photochemical VOC oxidation, allowing results to be generalized across a range of mechanistic scales. Furthermore, it is anticipated that acquired data will be applied to reduce uncertainties in isoprene emission models. Together, these results will improve mechanisms of ozone and SOA production in air quality models. Overall, the project will provide better tools for evaluating strategies to mitigate the anthropogenic influence on air quality, climate, and human health.

Organic functional group and trace metal concentrations During the 4-wk campaign, we will collect particles on Teflon filters for with both PM₁ (4-6 hr) and PM_{2.5} (24 hr) cyclones. All filters will be analyzed by FTIR to quantify organic functional group concentrations (Russell et al., 2009; Takahama et al., 2012), and selected filters will be analyzed by X-Ray Fluorescence (Schneider, 1989) to compare and validate ongoing IMPROVE sampling protocols (Gilardoni et al., 2007; Liu et al., 2009; Russell et al., 2009).

Post-processing and analysis. Analysis will include factor analysis and clustering of infrared spectra, backtrajectory analysis, and correlations with elemental composition to identify mixture classes for source apportionment of OM (e.g., Russell et al., 2009).

Instrument S-S3. *Contact: Satoshi Takahama (satoshi.takahama@epfl.ch) and Lynn Russell (lmrussell@ucsd.edu).* Funding source: Swiss NSF (Takahama); US EPA (Russell).

PI Satoshi Takahama (EPFL) at the SEARCH CTR Supersite

Inorganic ion concentrations (gas+particle phases). Further targeting the characterization of PM₁, we will measure inorganic ion composition and their associated gas-phase concentrations with an URG Corporatoin Ambient Ion Monitor (AIM) (Markovic et al., 2012) (or equivalent) at 5-30 minute time resolution.

Measurement of volatility and hygroscopicity. To relate particle-phase composition measurements to metrics of volatility and hygroscopicity, we will collaborate with Andrey Khlystov (RTI) and Andy Grieshop (NCSU) who will deploy a thermomuder and condenser coupled with a Scanning Mobility Particle Sizer (SMPS), which will be operated in parallel with the chemical composition measurements. We will also use an instrument similar to the Dry-Ambient Aerosol Size Spectrometer (DAASS; Stanier et al., 2004) to measure the water content of bulk PM₁ aerosols, and collaborate with Ann Marie Carlton (Rutgers University) and Markus Petters (NCSU) who will deploy a Humidified Tandem Differential Mobility Analyzer (HTDMA) for measurements of size-resolved water uptake.

Post-processing and analysis. Analysis will include evaluation of activity coefficient models that relate condensed-phase composition to predictions of water activity and saturation vapor pressures (e.g., E-AIM, <http://www.aim.env.uea.ac.uk/aim/aim.php>; AIOMFAC, <http://www.aiomfac.caltech.edu/>).

Instruments S-A1, S-A3. *Contact: Satoshi Takahama (satoshi.takahama@epfl.ch).* Funding source: Swiss NSF (Takahama).

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Observation of HCHO and NO₂ vertical profiles using MAX-DOAS

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Goals:

1. Observation of HCHO, NO₂, and aerosol extinction vertical profiles at the SEARCH site during SOAS;
2. Validate airborne MAX-DOAS system on the NSF C-130 in the framework of the NOMADSS project;
3. Investigate HCHO profiles over a forested area, comparison with other flux measurements.

Method:

Multi-Axis (MAX) Differential Optical Absorption Spectroscopy (Platt and Stutz, 2008) measures trace gas absorptions in scattered solar light. The MAX-DOAS system measures scattered sunlight at various elevations angles, from 1° above the horizon to the zenith. The change in elevation angle leads to a variation of the tropospheric absorption path length and thus the optical densities of the absorbers. A DOAS analysis (Pikelnaya et al., 2007) will be used to determine slant column densities (SCD) of NO₂, HCHO, and O₄ (to measure aerosol extinction) and their uncertainties. The elevation dependent SCDs will be further analyzed using a radiative transfer model (VLIDORT) and an optimal estimation inversion method to derive vertical profiles with a vertical resolution of ~250m in the lowest 1.5 km of the atmosphere. Interpretation will be achieved through direct comparison with the NSF C-130 data and a 1D chemistry and transport model.

Instrument Description:

The UCLA MAX-DOAS instrument consists of three main components: 1) Telescope, containing light-collecting assembly in weatherproofed enclosure; 2) Temperature-controlled enclosure for the spectrometer; 3) Enclosure for electronics containing all electronic components for temperature control and industrial computer for data acquisition and storage. The MAX-DOAS telescope has to be placed outdoors with a clear line of sight towards the horizon. The preferred viewing direction, if possible, would be towards the main tower site. Electronics enclosure needs to be indoors and spectrometer enclosure can be indoors or outdoors. All cables and fiber connecting three elements together are 5m-long (~16ft) and therefore can be arranged up to 5m away from each other. In order to fasten the MAX-DOAS telescope to a mast or platform in the field, an adapter will be designed once placement location for the instrument is selected. Figure 1 shows schematic layout of these components and a photo of the telescope and spectrometer enclosure. Table 1 lists dimensions, weight and requirements for the UCLA MAX-DOAS instrument.

Table 1. MAX-DOAS components description, and requirements.

Component	Dimensions (WxLxH), in	Weight, lb	Requirements	Notes
Telescope	4 x 20 x 6	10	Outdoors	Fiber to the Spectrometer Enclosure – 5m (16.40ft) Cabling to the Electronics Enclosure – 5m
Spectrometer Enclosure	17.5 x 20 x 10	40	Outdoors or indoors	Cabling to the Electronics Enclosure – 5m
Electronics Enclosure	17.5 x 20 x 7	20	Indoors Requires one 115V AC outlet. Maximum power consumption – 300 W. Internet connection for remote access.	

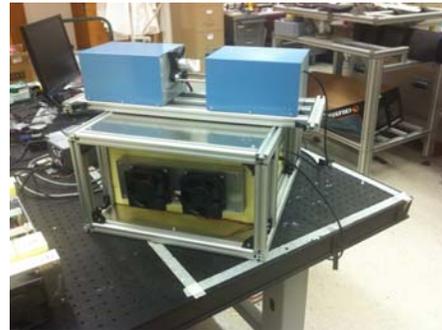


Figure 1. Schematic and photograph of UCLA MAX-DOAS instrument. Main components of the system are numbered as following: 1 – MAX-DOAS telescope assembly; 2 – Temperature-controlled spectrometer enclosure; 3 – Electronics enclosure. Drawing is not to scale.

References:

1. Platt, U. and J. Stutz, *Differential Optical Absorption Spectroscopy: Principles and Applications*, Springer Verlag, Heidelberg, ISBN 978-3540211938, 597pp, 2008.
2. Pikel'naya O., Hurlock S. H., Trick S., and J. Stutz, Intercomparison of multi-axis and long-path differential optical absorption spectroscopy measurements in the marine boundary layer, *J. Geophys. Res.*, 112, D10S01, doi:10.1029/2006JD007727, 2007.

Delphine Farmer – Colorado State Univ.

Project Summary “Organic acid concentrations and fluxes over a Southeastern forest during the Southern Oxidant and Aerosol Study (SOAS)”

Intellectual Merit. One of the key gaps in our understanding of how atmospheric chemistry impacts air quality and climate is the role of the biosphere in affecting the composition of the atmosphere – both in terms of an emission source for volatile organic compounds (VOCs), and as a surface for deposition of volatile and semi-volatile species. These VOCs are oxidized in a photochemical cascade, in which multiple generations of organic products can be produced, each with varying lifetimes, vapor pressures, and acidities – thus affecting O₃ production, secondary organic aerosol (SOA) formation and ecosystem processes differently. The biosphere potentially acts as both a source and a sink for oxidized VOCs, complicating our interpretation of biosphere-atmosphere interactions. One suite of biogenic VOC oxidation products are the organic acids, which have varying VOC precursors and potential primary biogenic emission sources, and may serve as tracers of biogenic VOC oxidation. However, understanding their biosphere-atmosphere exchange is necessary for interpreting their sources, sinks, and role in the atmosphere’s photochemical cascade of organic compounds.

The primary objectives of this proposal are: (1) To investigate the potential of organic acids to act as tracers of biogenic VOC oxidation chemistry by quantifying gas-phase concentrations of four key organic acids (formic acid, acrylic acid, methacrylic acid, pyruvic acid) using gas-phase organic acids using high resolution chemical ionization time-of-flight mass spectrometry (HR-CIMS), and (2) To better constrain the magnitude, variation and controlling process of biosphere-atmosphere exchange of organic acids by quantifying ecosystem-scale fluxes of the four target organic acids. These measurements will be made over a Southeastern US forest as part of the Southeastern Oxidant and Aerosol Study (SOAS) in the summer of 2013. The Southeastern US is a significant source of isoprene and other biogenic VOCs, as observed in VOC and particle concentrations, and is thus an excellent site for studying organic acids and their ecosystem-scale fluxes.

The intellectual merit of the research includes the significant advancement of knowledge by: (1) developing the capability of measuring eddy covariance fluxes of organic acids using HR-CIMS, (2) addressing key needs of the SOAS project by making a unique set of concentration and flux measurements of organic acids over a forest, which will be invaluable to model development of canopy exchange processes, regional air quality and climate, and (3) determining whether organic acids can be used as tracers of biogenic VOC oxidation.

The Broader Impacts of the research are at least 5-fold: (1) The teaching and training of graduate students, (2) Enhance infrastructure for research by expanding networks between the PI’s group and scientists at other institutions and national labs, (3) Improved understanding of biogenic VOC oxidation and biosphere-atmosphere exchange of organic acids, which is essential for accurate modeling of air quality and climate on local, regional and global scales, and (4) Broad dissemination of the research and observations through publications and presentations to the scientific and local (high school, undergraduate, graduate students) community.

Title: Development and evaluation of an improved parameterization for SOA from biogenic hydrocarbons

PI: Havala Pye and Rob Pinder, EPA AMAD

Background

Isoprene is the most abundant non-methane hydrocarbon emitted into earth's atmosphere and significantly contributes to ambient organic aerosol in locations such as the southeast United States. CMAQ parameterizes isoprene SOA based on initial reaction with OH leading to two semivolatile (Odum type) products followed by oligomerization and enhancement under conditions of strong acidity [Carlton *et al.*, 2010]. Laboratory and ambient work indicates secondary organic aerosol (SOA) from isoprene involves multigenerational gas-phase chemistry subject to biogenic and anthropogenic influences, and isoprene epoxydiols have been identified as precursors to SOA under low-NO_x conditions. In addition, isoprene reaction with NO₃ can form SOA, a pathway not currently parameterized in CMAQ.

Approach

The regional chemical transport model CMAQ v5.01 with SAPRC07 chemistry has recently been extended to allow for the prediction of later generation isoprene products such as isoprene epoxydiols [Xie *et al.*, 2012]. In addition, an SOA precursor formed under high-NO_x conditions from the oxidation of MPAN has been added to CMAQ [Lin *et al.*, submitted]. In this work, additional pathways will be added to CMAQ v5.01 with extended SAPRC07 [Lin *et al.*] to allow later generation isoprene products (epoxides, etc) to form SOA. The formulation will include a more mechanistic dependence of SOA on particle phase composition (water, acidity, sulfate, etc), and we plan to provide predictions of isoprene derived organosulfates, organonitrates, methyl tetrols, and oligomers (dimers only) in the aerosol phase for the Southeast U.S. We also hope to perform a targeted model evaluation against ambient observations which should allow for examination of anthropogenic influences (acidity, NO_x) on biogenic SOA and a refinement of the initial model parameterization.

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Xie, Y., F. Paulot, W. P. L. Carter, C. G. Nolte, D. J. Luecken, W. T. Hutzell, P. O. Wennberg, R. C. Cohen, and R. W. Pinder (2012), Understanding the impact of recent advances in isoprene photooxidation on simulations of regional air quality, *Atmos. Chem. Phys. Discuss.*(12), 27173-27218.

PI: Jesse Kroll, MIT

This proposed work involves the deployment of a novel instrument for measuring intermediate-volatility organic compounds (IVOCs) and semivolatile organic compounds (SVOCs) during the Southern Oxidant and Aerosol Study (SOAS) in summer 2013. IVOCs and SVOCs are thought to be crucial species in the formation and evolution of secondary organic aerosol – a major research focus of SOAS – but are very poorly constrained, since they are not routinely measured by available techniques. We have recently developed an instrument for the quantitative, real-time measurement of such compounds, which utilizes pre-concentration, temperature-programmed desorption, and mass spectrometric detection of organics. The use of a temperature ramp and high-resolution mass spectrometry allow for the measurement of organic volatility and carbon oxidation state, respectively. Deployment of this instrument to the SOAS ground field site will close a major gap in the measurement of organic species. By combining measurements from this instrument with those from other instruments at the site, we will be able to describe the full distribution of all organic species present, in terms of both their volatility and their key chemical properties. Such measurements are crucial for meeting several of the SOAS science objectives, including understanding the fluxes and oxidation of biogenic carbon, and the influences of anthropogenic emissions on biogenic aerosol.

SEARCH Centreville Enhancements for SOAS

Southeastern Aerosol Research and Characterization (SEARCH) Network, a collaboration of Atmospheric Research & Analysis (ARA), Southern Company, and the Electric Power Research Institute (EPRI) Stephanie Shaw (sshaw@epri.com) and Karsten Baumann (kbaumann@atmospheric-research.com)

Objectives: SEARCH will be enhancing the current measurement suite (see separate abstract) during the SOAS campaign to include additional instrumentation and data products in order to support the activities of other researchers and fill in data gaps, as well as to test the performance of novel instruments for chemical concentrations, deposition fluxes, and meteorological parameters. Additionally, analysis will be performed to provide temporal and spatial context for the interpretation of the CTR-located and Look Rock-located research activities.

Activities:

1. New measurements will be added to enhance the existing suite at CTR:
 - a. TPAN & TON analysis, to attempt mass closure as a large portion of NO_y is NO_z in summer in the Southeast,
 - b. Continuous NH₃ to compare with denuder NH₃ across the SEARCH network,
 - c. Optek nephelometers at CTR and Birmingham (BHM), the urban pair to CTR, for light extinction,
 - d. Jenoptik CHM15k ceilometer for mixed layer depth, including working with the manufacturer to develop of algorithm to provide desired parameters in a more automated manner,
 - e. Trace element analysis of filter PM by ICPMS, and
 - f. Dynamically-controlled chambers for dry-deposition flux measurements of SO₂, NH₃ and HNO₃ which will inform losses of important chemicals in the lower atmosphere and test feasibility of new low-cost flux chamber design
2. Data Products and Resources:
 - a. Provision of routine suite of SEARCH data to all investigators at accelerated rates during campaign for use in day-to-day operation/planning
 - b. Public access and some support for use of FirstLight (the SEARCH data management program) by campaign researchers
3. Additional measurements at satellite SOAS sites:
 - a. 4 high-volume samplers for detailed characterization of SOA and/or SOA tracers at CTR, BHM and Look Rock, and
 - b. Modified TEKRAN for Hg measurements at BHM to compare across sites and to evaluate potential instrument bias
4. Research and Analysis
 - a. Analysis of the temporal representativeness of CTR during SOAS as compared to historical values and trends
 - b. Analysis of the spatial representativeness of CTR during SOAS in the context of the other SEARCH sites and Look Rock Monitoring Station across the Southeast US
 - c. Trends analysis of historical data across the southeastern US covered by the SEARCH network
 - d. Trends analysis of historical data collected at the Look Rock, TN, SOAS site
 - e. Analysis of the temporal and spatial representativeness of Look Rock during SOAS
 - f. Modeling and analysis of particle nucleation within power plant plumes, with evaluation using aircraft plume transect data

Current Measurement Suite Available at the SEARCH Centreville Ground Site for SOAS

Southeastern Aerosol Research and Characterization (SEARCH) Network, a collaboration of Atmospheric Research & Analysis (ARA), Southern Company, and the Electric Power Research Institute (EPRI) Stephanie Shaw (sshaw@epri.com) and Karsten Baumann (kbaumann@atmospheric-research.com)

Objectives: SEARCH is a comprehensive, multi-pollutant network addressing scientific and regulatory questions on O₃ and its precursors, PM mass and composition, mercury speciation and deposition, wet deposition of acidity and nutrients, and atmospheric visibility. Since establishment in early 1990s as part of the Southern Oxidants Study SCION network, individual sites have served as platforms for long-term investigations of air quality health effects and short-term campaigns to address key questions on the chemistry and physics of atmosphere. SEARCH has deployed continuous methods in order to measure and understand rapid processes governing PM_{2.5} and co-pollutant emissions, formation, fate, transport and deposition. Novel instrumentation and new model development has been tested at SEARCH sites. SEARCH data has been extensively used for air quality model evaluation on local & global scales.

Approach: SEARCH was created as a highly instrumented set of urban-rural site pairs in AL, FL, GA & MS

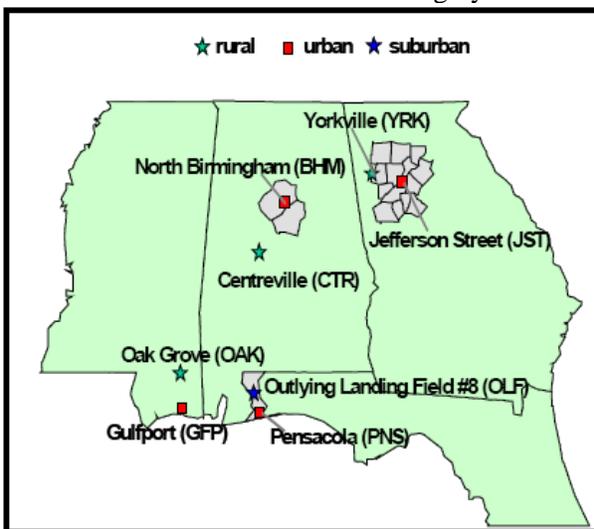


Figure 1. SEARCH Network. PNS retired 01/01/10. OAK retired 01/01/11. GFP retired 01/01/12.

Expected Results:

SEARCH data (<http://www.atmospheric-research.com/studies/SEARCH/>) have been the basis of almost 200 peer-reviewed scientific publications. SEARCH has provided an ambient air data set with minimal sample adjustment and of sufficient breadth of measured variables, geographical diversity & extent, frequency of measurement, & duration of measurement such that:

- long-term spatial and temporal trends of PM, mercury, and oxidant climatology for the region have been established,
- coarse and fine PM concentrations as well as the gaseous, particulate and aqueous forms of mercury have been distinguished,
- chemical constituents of PM and their physical states have been characterized and associations among precursor and product materials in the atmosphere are determined, allowing hypotheses regarding pollutant sources to be tested,
- insights have been gained into aerosol formation mechanisms,
- differences between airborne materials in coastal vs. inland, and rural vs. urban areas have been documented, and
- biases in measurement methods, such as use of a single Teflon filter in the Federal Reference Method for PM_{2.5}, have been characterized.

Table 1: Current Measurement Suite at SEARCH Centreville Site

Variable	Z (magl)	Analyzer/Sensor	Time Resolution (min)
WS/WD	10	RMYoung 81000 sonic	5
T/RH/BP	9	Paroscientific Met4A	5
T/RH	2	Vaisala	5
PAR	2	Licor	5
precipitation	2	ETI-NOAH IV	5
aerosol/cloud layers	50-15,000	JenOptik CHM 15k	5
O3	10	Thermo 49i	5
CO	10	Thermo 48i	5
SO2	10	Thermo 43i	5
NO	10	Thermo 42i	5
NO2	10	photolysis/Thermo 49i	5
HNO3	10	continuous denuder diff/Thermo 42i	5
NOy	10	cat. reduction/Thermo 42i	5
NH3	5	continuous denuder diff/Thermo 42i	5
Total PANs	5	thermophotolytic/Thermo 42i	5
Total Alkyl Nitrates	5	thermophotolytic/Thermo 42i	5
Continuous PM2.5 Mass	5	TEOM	5
Continuous PM2.5 SO4	5	cat. reduction/Thermo 43i	5
Continuous PM2.5 NO3	5	cat. reduction/Thermo 42i	5
Continuous PM2.5 NH4	5	cat. oxidation/Thermo 42i	5
Continuous PM2.5 TC/EC	5	Sunset	5
dry Babs (550 nm)	5	Radiance Research M903	5
dry Bsp	5	Magee 2ch. Aeth	5
ambient Bsp	5	Optec NGN-2a	5
Discrete PM2.5 Mass	5	filter/gravimetry	1440, daily
Discrete PM2.5 ions	5	filter/IC	1440, daily
Discrete PM2.5 major/minor elements	5	filter/XRF	1440, daily
Discrete PM2.5 water-soluble metals	5	filter/ICPMS	1440, daily
Discrete PM2.5 OC/EC	5	filter/TOR	1440, 1 in 3
Discrete PM10 Mass	5	filter/gravimetry	1440, 1 in 3
Discrete PM10 ions	5	filter/IC	1440, 1 in 3
Discrete PM10 major/minor elements	5	filter/XRF	1440, 1 in 3
Discrete PM10 water-soluble metals	5	filter/ICPMS	1440, 1 in 3
wet deposition ions	2	bucket/IC	10080
wet deposition total-Hg	2	glass btl./CVAAS	10080
wet deposition trace elements	2	poly btl./ICPMS	10080

Title: Development and evaluation of an improved parameterization for SOA from biogenic hydrocarbons

PI: Havala Pye and Rob Pinder, EPA AMAD

Background

Isoprene is the most abundant non-methane hydrocarbon emitted into earth's atmosphere and significantly contributes to ambient organic aerosol in locations such as the southeast United States. CMAQ parameterizes isoprene SOA based on initial reaction with OH leading to two semivolatile (Odum type) products followed by oligomerization and enhancement under conditions of strong acidity [Carlton *et al.*, 2010]. Laboratory and ambient work indicates secondary organic aerosol (SOA) from isoprene involves multigenerational gas-phase chemistry subject to biogenic and anthropogenic influences, and isoprene epoxydiols have been identified as precursors to SOA under low-NO_x conditions. In addition, isoprene reaction with NO₃ can form SOA, a pathway not currently parameterized in CMAQ.

Approach

The regional chemical transport model CMAQ v5.01 with SAPRC07 chemistry has recently been extended to allow for the prediction of later generation isoprene products such as isoprene epoxydiols [Xie *et al.*, 2012]. In addition, an SOA precursor formed under high-NO_x conditions from the oxidation of MPAN has been added to CMAQ [Lin *et al.*, submitted]. In this work, additional pathways will be added to CMAQ v5.01 with extended SAPRC07 [Lin *et al.*] to allow later generation isoprene products (epoxides, etc) to form SOA. The formulation will include a more mechanistic dependence of SOA on particle phase composition (water, acidity, sulfate, etc), and we plan to provide predictions of isoprene derived organosulfates, organonitrates, methyl tetrols, and oligomers (dimers only) in the aerosol phase for the Southeast U.S. We also hope to perform a targeted model evaluation against ambient observations which should allow for examination of anthropogenic influences (acidity, NO_x) on biogenic SOA and a refinement of the initial model parameterization.

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NCAR Integrated Soundings Systems support for SOAS

William Brown NCAR / EOL

Introduction: NCAR’s Earth Observing Lab (EOL) will be bring a Integrated Sounding System (ISS) to SOAS as part of an NSF Lower Atmosphere Observing Facilities (LAOF) facility request (Guenther et.al.). The ISS will include a variety of instruments to characterize the boundary layer in the SOAS area. The instruments include remote sensing systems (e.g., wind profilers, lidar, sodar) and soundings. The instruments will be split between two sites: a former NWS site approximately 1km from the SEARCH site, and about 20km to the south at the AABC fish ponds approximately 1km from the flux site.

Instrument	Make/Model	Characteristics	Site
Radiosonde Soundings	Vaisala RS92 GPS radiosondes	T, RH, P & winds to the tropopause	NWS
Radar wind profiler	Vaisala/Radian LAP-3000 + RASS	Winds from ~ 150m up to ~ 3-4 km, Tv from 150m to ~ 0.5-0.8 km	NWS
Ceilometer	Vaisala CL-31	Cloud base to ~ 8km & (aerosol) backscatter	NWS
Met tower	(Various)	10m winds, 2m T, RH, P, solar vis & ir, rain	NWS
Sodar	Metek DSDPA 90-24 with RASS	Winds from 40m up to 200-300m, Tv from 40m up ~ 150m	AABC
Lidar	Leosphere windcube 200S	Scanning Doppler lidar, winds and (aerosol) backscatter to ~ 2-4 km	AABC
Basic met	Vaisala WXT 520	T, RH, P, wind, rain	AABC

Table 1: Summary of the ISS instruments and their proposed locations for SOAS.

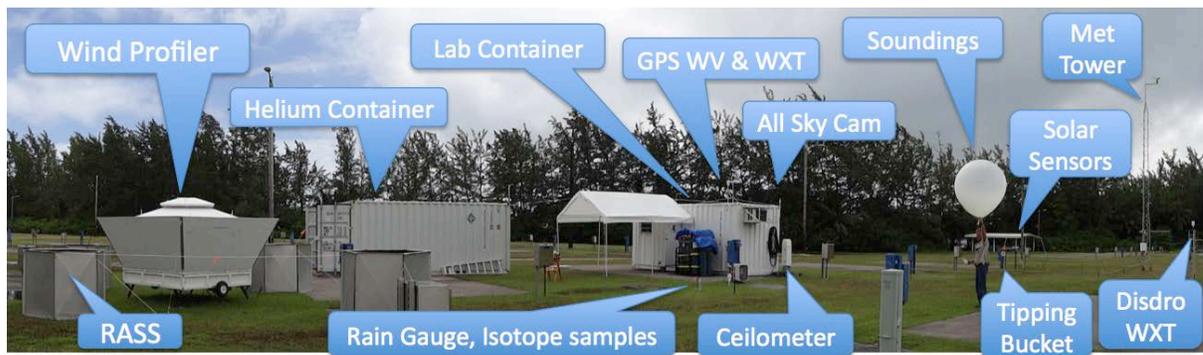


Fig 1: Typical ISS site. For SOAS a different mix of instruments will be deployed & split between 2 sites. (Photo of ISS site at Diego Garcia BIOT for DYNAMO).

Soundings : Soundings will be launched from the former NWS site, approximately 1km from the SEARCH site. Vaisala RS92 GPS radiosondes will be used on a 200g Helium filled balloon, recording full thermodynamic and winds data to the

tropopause. Data is recorded on a specialist GAUS (GPS Advanced Upper-air Sounding) receiving system that enables raw data to be collected at 1 Hz, corresponding to 5 – 10 meters resolution. Soundings will be released twice daily at 10am and 4pm. On four intensive observation days, additional soundings will be launched every 2 – 3 hours.

Radar Wind Profiler : The LAP3000 profiler is a vertically pointing 915 MHz radar that measures the wind from about 150m up to 3 or 4 km altitude (in 60m steps). The radar can also be used to monitor the depth of the daytime convective boundary layer. It uses radar reflections from humidity gradients and turbulence, and will provide a wind profile every 15 to 30 minutes. The profiler will be equipped with RASS (Radio Acoustic Sounding System) for measuring virtual temperature. RASS uses a loud source to generate vertically propagating sound waves that are tracked by the radar. An approximate virtual temperature profile is estimated from the propagation speed from about 150m up to around 500 - 800m. The system is sensitive to clutter and radio interference. RASS operations may be curtailed due to noise. The system will be sited at the former NWS site.

Sodar-RASS: A mini Doppler sodar will be sited at the AABC to monitor the lower boundary layer. The system is a Metek DSDPA 90-24 system, which uses 2 kHz acoustic pulses to measure winds from about 40m up to 200 - 300 m (about 20m steps). It also has RASS add-on which gives virtual temperature from about 40m up to 100 - 200m. The RASS also uses a 915MHz radar so has to be located at least a few miles from the radar wind profiler.

LIDAR : A Leosphere Windcube 200S Doppler lidar is proposed for the AABC site to monitor the boundary layer. The system is has full 3-D scanning capability and is capable of monitoring flow, turbulence and boundary layer structure out to a range of 2 – 4 km. At the AABC site, the system would be positioned around 1 km from the flux tower and scanned past the tower to extend spatially extend wind and turbulence measurements from the tower. In addition to winds, the system reports backscatter reflectivity, which is related to aerosol concentration. Being uncalibrated, the system can't measure absolute aerosol levels, but can be used to observe the spatial variation in the aerosol backscatter field.

Ceilometer: The ceilometer is a Vaisala CL-31, a vertically point low power lidar used for measuring cloud base height. In high aerosol areas, a vertical profile of backscatter intensity is reported, which can (with caveats) be used to estimate boundary layer depth and structure. This system will be sited at the NWS site.

Measurements of Organic aerosol species and semivolatile compounds at the SEARCH ground site during the SOAS Field Campaign

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Funding: Electric Power Research Institute grant (pending), Marie Curie Fellowship (FP7-PEOPLE-2011-IIF)

Summary:

We propose to conduct ground-based measurements of a wide range of organic aerosol species and semivolatile organic compounds (SVOCs) during Southern Oxidant & Aerosol Study (SOAS) campaign in summer 2013. The study will allow better quantification of BVOCs oxidation products that are capable of partitioning into the particle phase. The campaign site is highly impacted by Biogenic Volatile Organic Compounds (BVOCs) with occasionally influenced by anthropogenic pollution. With the proposed measurements, we will be able to measure the impact of anthropogenic pollution on semivolatile BVOC oxidation products on both, the quantity and the chemical composition. The quantification of semivolatile organic compounds and organic aerosol species from SOAS will give valuable insights into sources and processing of Secondary Organic Aerosols (SOAs) that will be used to provide realistic parameterizations for use in regional and global climate models.

Approach:

We will deploy thermal-desorption proton-transfer-reaction mass-spectrometer (TD-PTR-MS) at the SEARCH ground site, Centreville, AL for *in-situ* semivolatile gas phase and aerosol measurements. Organic species will be detected with a commercial PTR-TOF 8000 instrument (Ionicon Inc., Austria). The TD-PTR-MS consists of sampling units for aerosols and semivolatile gas phase compounds. Humidified aerosols will be collected on an impactor and thermally desorbed for analysis. Semivolatile gas phase compounds will be collected on a 3-stage denuder system and thermally desorbed sequentially and stepwise for analysis. The measurements will be run on a fully automated cycle at a time resolution of 90 minutes.

Expected results:

It is expected that several hundreds aerosol species and semivolatile organic compounds will be identified with our instrumental set-up. We also expect our measurements to address these SOAS science questions:

- (1) How do anthropogenic emissions alter the distribution of the BVOC oxidation products?

- (2) To what extent do anthropogenic pollutions impact on biogenic SOA formation?
- (3) How do aqueous chemistry and cloud processing of BVOCs and related aerosols influence atmospheric SOA?

Steve Oncley & Steve Semmer – NCAR ISFS

NCAR/EOL/ISFS will support the SOAS goals by measuring turbulent fluxes in and just above a mixed deciduous/coniferous forest. A 50m tower will be erected inside a 30m-high forest canopy with 8 levels of direct eddy-covariance measurements of momentum, sensible, and latent heat fluxes. Six of these levels also will have carbon dioxide flux measurements and 4 will have turbulent pressure fluctuation sensors. In combination with fast-response BVOC measurements, eddy-covariance fluxes of these species also will be measured directly, along with gradients of these species within the canopy. In addition, 4-component radiometers will be deployed above and below the forest canopy to determine the radiative heating/cooling of the canopy and soil heating/cooling also will be measured to complete the surface energy balance. Photosynthetically-active radiation (PAR) and will be measured at 5 levels in, and just above, the canopy to characterize light interception. Other measurements will include rain rate, cloudiness, and leaf temperature. These observations will be combined with remote-sensing measurements made by NCAR/EOL/ISS of wind, temperature, and aerosol backscatter to characterize the dynamics of the entire atmospheric boundary layer above the forest.

Tuukka Petaja, Univ. of Helsinki

UHEL & Aerodyne will deploy Particle Size Magnifier (PSM, Vanhanen et al. 2011, AST) and Neutral and Air Ion Spectrometer (NAIS, Manninen et al. 2009) during SOAS. Our scientific aim will be to determine neutral and ion cluster concentrations in this high-isoprene environment. Furthermore, we characterize the new particle formation events (formation rate J1 and growth rate GR, Kulmala et al. 2012) during the experiments and explore the connections of the freshly formed nanoparticles with trace gas concentrations. Our instruments are operated in concert with CI-API-TOF (Jokinen et al. 2011) and CI-IMS-API-TOF (Aerodyne, UHEL) to simultaneously characterize the physical and chemical properties of nanoclusters. The particular interest is the role of isoprene and other organic vapors, as well as sulfuric acid, to aerosol dynamics.

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Sources, Sinks, and Chemical Transformations of Nitrogen Oxides

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Understanding the chemical and physical transformations of nitrogen oxides within forest canopies is crucial as these processes impact air quality, climate, and nitrogen partitioning on regional and global scales. Our research aims to better constrain the uptake and emission of NO_x from plants, as well as the formation rates, yield, and fate of the reaction products of NO_x with biogenic volatile organic compounds (BVOCs). In a recent series of studies, we have explored the biosphere-atmosphere exchange of NO_x (Min 2012, Min PhD thesis, Wolfe 2012), as well as contribution of organic nitrates to the reactive nitrogen budget using gas and aerosol-phase measurements and chemical transport models (Beaver 2009, Browne 2011, Browne 2013, Day 2008, Rollins 2012). Here we plan several linked research activities building on this work and incorporating observations from the Southern Oxidant Aerosol Study (SOAS) in Centreville, Alabama, a site characteristic of the Southeastern United States where chemistry is heavily influenced by both BVOC emissions and NO_x transported from urban areas. Specifically, we plan to:

- 1) Make observations of gas-phase NO , NO_2 , total peroxy nitrates (RO_2NO_2), total alkyl nitrates (RONO_2), and HNO_3 , as well as aerosol-phase RONO_2 at the SOAS field site using our home-built thermal dissociation laser-induced fluorescence (TD-LIF) and chemiluminescence instruments.
- 2) Compare canopy scale and regional models of N abundance and speciation to assess the role of emissions, deposition, and chemistry driven by BVOC in setting the large scale and local balance of N in the southeast U.S.
- 3) Continue a suite of synthetic and chamber experiments in both pairwise and larger collaborations with Caltech focusing on the role of RONO_2 in BVOC oxidation. These will include synthesis of isoprene nitrates and studies of their reactivity.
- 4) Investigate uptake and emission of NO_x and higher oxides of N from plant canopies using model systems in the laboratory.
- 5) Support related investigations by SOAS collaborators using our measurements, in particular those of Fry & Brown on NO_3 Chemistry, Russell & Jimenez on aerosol-phase RONO_2 , Thornton on peroxy nitrate chemistry, and other investigators interested in comparison of new techniques for nitrogen oxide measurement.

Speciated measurements of VOC using GC-MS at the Southern Oxidant and Aerosol Study Centreville Search tower site

PIs: Allen Goldstein, UC-Berkeley and Joost de Gouw, NOAA

The driving scientific questions posed for the Southern Oxidant and Aerosol Study (SOAS) are:

- 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?

In order to answer these questions it is critical to have measurements of a wide range of chemical species that define the emissions and the chemical transformation processes of biogenic compounds and the degree to which these processes are influenced by anthropogenic emissions. Extensive measurements of both biogenic and anthropogenic primary and secondary volatile organic compounds (VOC) are key to understanding these processes and the importance of different emission sources in the region.

We propose to make speciated measurements of VOC during SOAS using an automated in-situ gas chromatograph with a quadrupole mass spectrometer (GC-MS) developed at the National Oceanic and Atmospheric Administration (NOAA). This instrument has been widely used in the field and provides 30 minute time resolution. Measured compounds will include the major primary biogenic and anthropogenic VOCs in the range of 2 to 10 carbon atoms. Specific target compounds include: speciated monoterpenes, isoprene, methylvinylketone (MVK), methacrolein (MACR), C2 to C10 alkanes, C2 to C5 alkenes, C6 to C9 aromatics, C2 to C4 oxygenated VOCs (OVOC) (e.g. alcohols and ketones), halogenated VOCs, alkyl nitrates, DMS and acetonitrile. Some of the compounds we measure will simultaneously be measured with higher time resolution by PTRTOFMS (e.g. OVOCs, MVK+MACR, total monoterpenes), but our GC-MS measurements have the critical advantage of separately measuring isomers (MVK vs MACR, speciated instead of total monoterpenes, etc).

Our main objectives include characterizing the biogenic and anthropogenic VOC emissions influencing air masses in the region as a function of time, identification of emission source profiles, and providing core data to a wide range of collaborative analyses that will focus on the fate of primary VOCs and their role in ozone and aerosol formation and regional photochemistry. For example, our measurements will help define the relative importance of biogenic versus anthropogenic sources of VOC in the region. Specifically, Isoprene is known to be the dominant biogenic emission in the region and its oxidation products are thought to provide a dominant contribution to regional secondary organic aerosol (SOA). Our measurements of isoprene, MVK, and MACR will be key to defining the first part of the process for this contribution, while collaborators will be measuring many of the known oxidation products further down the pathway towards the incorporation of isoprene into SOA. Measured VOC's will be used as tracers to understand the origin of the air mass, including markers for biogenic emissions, biomass burning, and a variety of types of anthropogenic emissions. Measured VOCs will also be useful as a photochemical clock to estimate the age of the air mass from the ratio of reactive species originating from the same source region.

Project Title: Ozone Reactivity of Biogenic Volatile Organic Compound Emissions

PI: Detlev Helmig, Univ. of Colorado-Boulder (detlev.helmig@colorado.edu)

Co-PI: Alex Guenther, NCAR (guenther@ucar.edu)

PROJECT SUMMARY

Research Hypothesis: We hypothesize that the total ozone reactivity of trace gases emitted from vegetation foliage is larger than what can be accounted for by currently identifiable emissions, and that this reactivity varies significantly between vegetation species and follows distinct diurnal and seasonal cycles.

Objectives: The objective of this project is to further develop a new tool for BVOC reactivity studies and to apply it in research on BVOC emissions. The following particular activities are planned. 1) Further Refine and Characterize Ozone Reactivity Experiment, 2) Determine the Ozone Reactivity of BVOC Emissions from Vegetation Species and Its Dependence on Environmental Conditions including Stress 3) Determine the Portion of the Ozone Reactivity that can be accounted for by Identified Emissions 4) Compare and evaluate ozone and OH Reactivity in Emissions 5) Evaluate representativeness of BVOC + O₃ rate constants for use in O₃ + BVOC removal rate calculation, 6) Evaluate Findings from these Studies with Model Representations of VOC Chemistry and Ozone Fluxes in the Forest Atmosphere.

Experimental Approach: Figure 1 depicts a cartoon figure of the basic principle of the experiment. Building on our experience in emissions studies and high accuracy ozone concentration and gradient measurements, we designed a new experiment which allows determination of the reactivity of BVOC emitted from vegetation with ozone directly. Identification and quantification of emissions from the same experiment with common analytical tools then allows for characterizing the fraction of ozone reactivity that cannot be accounted for by identified compounds. This experimental approach investigates vegetation species on an individual basis, and therefore allows deciphering how individual plants contribute to the missing reactivity. By screening the dominant vegetation at a particular site, estimates of missing reactivity can be developed for the whole ecosystem.

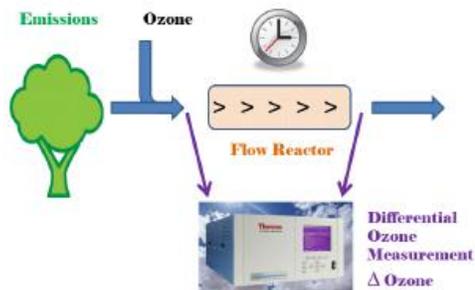


Figure 1
Schematic of the ozone reactivity experiment.

Expected Results: The ozone reactivity results from the different vegetation species will allow assessment of which vegetation types and ecosystem exhibit large reactivity in their emissions. Results are anticipated to shed new light onto the interpretation of the above referenced previous studies that have reported on missing reactivities in forest environments. Findings will provide a new means for evaluation of recent publications on this topic that were based on above canopy ozone flux measurements. Results from the enclosure studies on different tree species will help direct future research campaigns to sites where this effect is most apparent. Ultimately, the outcome from this work will be beneficial for modelers who are working on improving description of photochemical radical chemistry in the forest atmosphere.

Anthropogenic Influences on Biogenic Contributions to Secondary Organic Aerosols.

John H Offenberg, US EPA / National Exposure Research Laboratory, RTP, NC

Objectives: Field measurements will be performed to better understand secondary organic aerosol (SOA) formation from biogenic precursors in the presence of anthropogenic oxidants (e.g. NO_x, SO_x).

Field measurements of organic tracer compounds will be used to evaluate impacts of anthropogenic emissions on contributions to SOA formation. This work will help improve the understanding of SOA formation through the Southern Oxidant & Aerosol Study (SOAS).

Experimental Approach: In order to estimate contributions of several biogenic and anthropogenic precursor hydrocarbons to secondary organic aerosol (SOA) formation, previously developed tracer compounds (e.g. Kleindienst et al. 2007; Offenberg et al., 2007; Joui et al., 2012; Kleindienst et al., 2012) will be measured in ambient PM_{2.5}. Precursor specific estimates of SOA contributions will be estimated by applying laboratory based mass fractions to the measured tracer concentrations. Complementary chemical analyses will include measurements of Organic and Elemental Carbon, and radiocarbon content (¹⁴C expressed as fraction modern).

In addition to the above analysis to be performed in central Alabama, we will perform these, and additional measurements, in parallel in Research Triangle Park, NC.

Anticipated Results: It is expected that these studies may improve understanding of how SOA forms under various anthropogenically impacted (e.g. acidic aerosol) conditions. We also expect that understanding the chemical and physical characteristics of SOA will lead to future advancements in the predictive capabilities of air quality models.