

## CHARACTERIZING THE FORMATION OF SECONDARY ORGANIC AEROSOLS

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**Statement of Problem:** Formation of secondary organic aerosols (SOA) is important because they contribute significant particle mass in urban and rural areas. SOA are derived from volatile and semi-volatile hydrocarbon emitted from the biosphere, fuels and their combustion products from mobile sources, and operations concerned with oil and gas exploration and production. SOA and their precursors influence atmospheric processes at the urban, regional, and global scales and potentially affect visibility, ozone chemistry, ambient PM-2.5 (particle mass having diameters of 2.5 microns or less) concentrations, actinic flux, global climate, and human health. SOA are postulated to be an important particle source in the Central Rocky region, in the South, Northeast, and West. SOA form when organic vapors emitted into the atmosphere are oxidized to produce less volatile products, which then partition between the gas and particle phase. SOA production from a given volatile organic compound (VOC) depends on: (1) the abundance and reactivity of the given VOC compound; (2) the abundance of radicals in the atmosphere; (3) the nature of its reaction pathways; (4) the volatility and gas-to-particle partitioning properties of its products; (5) the ambient aerosol mass concentration; (6) temperature; (7) relative humidity; and (8) light intensity. Research concerning SOA formation from hydrocarbon emissions is sparse, and primarily consists of controlled experiments in laboratory smog chamber experiments. Clearly, an understanding of the reaction pathways, kinetics, and aerosol-forming behavior of hydrocarbon emissions from biogenic, mobile, and industrial sources is important to develop and benchmark models for particle formation. Modeling SOA formation is important for understanding air quality issues and for source apportionment; however, describing SOA formation is one of the most challenging aspects of building robust models to predict (aerosol) PM concentrations, visibility, and ozone concentrations. The contribution of SOA to particle mass in rural areas where oil and gas exploration and production occur is not well characterized because of the enhanced role of biogenic emissions in SOA formation. There is a need to improve our scientific understanding of the chemistry and physics of SOA formation to build more robust models for particles, visibility, and ozone. These models must be representative of actual atmospheric conditions, which involve the transport and transformation of emissions over urban and regional scales. In response to this need, we are conducting experimental, analytical, and modeling research whose **objective is to investigate SOA formation under actual field conditions to establish a rich data set that will be analyzed to characterize SOA formation from hydrocarbon emissions from a number of sources, at the regional scale.** The understanding of SOA derived from these studies will contribute to model development and model benchmarking.

**Application and Benefits of Research to Industry:** SOA and their precursors influence atmospheric processes at the urban, regional, and global scales and impact visibility, ozone chemistry, ambient PM-2.5 concentrations, actinic flux, global climate, and human health. SOA are postulated to be an important particle source in the Central Rocky region, in the South, Northeast, and West. In the Central Rocky region, in Wyoming and Colorado, and in the Gulf of Mexico area, SOAs contribute to regional haze in Class I areas. These are regions where considerable oil and gas exploration and production occur. Models for particle formation in these regions are especially poor because of the enhanced role of biogenics in SOA formation; hence visibility and visibility change cannot be modeled to detect signals of the size required by the rule. In addition, implementation of the regional haze rule in areas near Class I areas where oil and gas exploration and production are occurring requires that conditions commensurate with natural background be identified. This will require determining the contributions of biogenic emissions to the formation of secondary organic aerosols. Contributions of natural sources to ozone chemistry, PM chemistry, and visibility also have significant implications for the choice and extent of controls for anthropogenic emissions required to achieve National Ambient Air Quality Standards and to conform to rules associated with air quality-related values, like the regional haze rule for visibility. Species, which are involved in SOA production, are often simultaneously involved in ozone chemistry. It is crucial that we understand key steps in the formation of SOA and ozone in order that control design results in benefits (reductions) in both pollutants of concern rather than a benefit (reduction) in one and a disbenefit (enhancement) in the other. Sound science is needed to support cost-effective, beneficial control strategies. This research is strongly leveraged by prior and current support for Professor Allen Goldstein of the University of California Berkeley from CARB, the University of California, and the NSF. Prior support from LBNL-Laboratory Directed Research and Development Funds was used to demonstrate proof of the research concept to study particle formation. **Why DOE should support project:** It is the energy and transportation industries that are most frequently regulated to comply with most air quality regulations. Energy and energy security are at the heart of the DOE mission, and as a result they provide technical support to oil and gas in the exploration for and production of fuels. The DOE is a third party that is independent with high credibility. With this unique position DOE can serve in an intermediate position between regulatory agencies and industry, and it can do this without bias by supplying strong science upon which control decisions can be based.

**Tasks and Contributions of the Research Team:** The sets of experiments being conducted are aerosol characterization studies in the ambient environment of the foothills of the Sierra Nevada Mountains in California at the University of California's Blodgett Forest Research Station. Emissions there are from an aged air parcel from a more distant urban area with refineries, from a nearby urban area, and from the ambient biogenic emissions at the experiment location. Meteorological data and trace gas fluxes are measured approximately 5 to 6 meters above the average tree height and at four heights throughout the canopy. Instruments are accessed with a 12-m walk-up tower. The California Air Resources Board (CARB) has supported and the National Science Foundation (NSF) currently

supports measurement and analysis of ambient gas phase concentrations of NO<sub>x</sub> and hydrocarbons. Winds at this site are terrain-driven, blowing up-slope from the southwest during the day and down-slope from the northeast at night. Winds from the southwest travel through the Sacramento Valley and consist of both anthropogenic and biogenic emissions, whereas winds from the northeast travel across the western slope of the Sierra Nevada and mainly carry biogenic emissions. Measurements of meteorology, black carbon, carbon monoxide, and other trace gases are used to indicate the extent to which air masses are impacted by anthropogenic sources. Aerosol properties including chemical composition, size distributions, optical properties, and total number density are measured. The appearance of large concentrations of particles of approximately 20 nm diameter indicates local formation and growth of SOA. Instrumentation placed in the field includes a condensation particle counter, a nephelometer, an aethalometer, and a scanning electrical mobility spectrometer. The gas phase and particle data are collected in real time, continuously over a substantial period involving seasons and years to characterize the role of atmospheric variability, source variability, aging of air parcels, and the ambient environment especially local meteorology, on the SOA processes. These measurements, conducted using the atmosphere as a laboratory, offer the advantage of having all reactants present in realistic concentrations and reducing the role of artificial surfaces that often plague traditional smog chamber experiments. The data set provides critical information necessary for the identification of chemical pathways by which emitted organic vapors form secondary organic aerosol particles. The data are being used to determine how aerosol mass yields derived in the field from atmospheric studies differ from those derived from smog chambers for anthropogenic and biogenic precursor VOC compounds. Approaches that are being pursued for data analysis are the traditional statistical analyses, including time series analysis, principal component and/or factor analysis to determine the dependence of particle loading characteristics on measured gas phase composition and meteorology. Follow-on modeling activities will involve contributing to the formulation and data needs associated with model building and the benchmarking of models of varying levels of complexity that are used to estimate particle concentrations. The research consists of the following five integrated tasks: **Task I: Review and assess SOA models to identify areas of impact with experiment:** We continue to review new advances in the theories associated with SOA formation (e.g., chemical kinetic modeling) that are used to explain SOA formation from reactive and condensable gases, relevant experiments associated with SOA formation, and the various modeling approaches currently being pursued to describe SOA formation from gas phase precursors. Particular attention is given to the data needs of the models and approximations that underlie them. The modules associated with CMAQ are of particular interest because of their prominence in the regional haze debate. **Task II: Plan and preparation for field measurements:** Instrumentation needs have been addressed; instruments have been modified, especially with respect to particle size resolution and time resolution needs of the measurements. Instruments have been rendered field worthy, interfaced with data collection facilities, and deployed successfully in the field for 2002 and 2003. **Task III: Conduct experimental campaign in summer/fall 2002 and 2003:** These field intensive campaigns have been conducted and were interfaced with the field studies of investigators supported by CARB and NSF. **Task IV: Analyze data from field experiments:** Data analysis is being pursued within the context of three subtasks: 1) The first is to bring the very rich data set to Levels I and II. 2) Second, data analysis will be conducted without the organic data, and this includes evaluating correlations among the various types of particle data and between particle data and meteorological variables. This approach allows us to make progress before the organic data are analyzed and available to us. It will also allow us to examine issues of variability introduced by the meteorology. 3) Third, data analysis will be conducted that includes the organic data that involves statistical analysis of the particle, gas phase, and the meteorological data in concert. Approaches that are being pursued during data analysis are enumerated above. Intensive analysis is being performed on a number of interesting days or episodes to derive mechanistic information. We are determining how the SOA yield varies with meteorological parameters that affect the emissions, transport, and transformations of the precursor organics and the gas-to-particle conversion. Follow-on modeling activities will involve building and benchmarking models of varying levels of complexity. Additional modeling research to be pursued will involve working with other investigators, who are building SOA models from first principles by modeling the relevant aerosol physics and chemistry. **Task V: Technology Transfer:** Considerable technology transfer has and will be conducted as part of this research by informing the scientific, regulatory, and industrial communities of our research results.

**Critical Decision Points:** Failure to have reliable data on the gas phase measurements.

**Calendar Year 3 Beginning May 2004.**

**Milestones:** 1) Complete Level 1 and Level II data analyses for 2003 data set. 2) Conduct extensive data analysis for 2003 data set using statistical approaches, and methodology determined in Year 2. 3) Continue, with the results of data analysis of 2002 and 2003 data sets to critique existing models of SOA formation. 4) Use results to suggest best approach for modeling SOAs, especially for the purpose of visibility modeling.

**Deliverables:** Paper describing research to be submitted for publication and to DOE as a report, 2004. Paper presented at a scientific meeting, 2004. Paper examining reliability of model in light of conducted field program submitted for publication and to DOE, 2005. Bimonthly progress reports.

Throughout study considerable technology transfer: Appropriate presentations at Technical Meetings and to Regulatory and other Federal and State Agencies. Papers in the refereed scientific literature.

## Progress for Calendar Year 1. Beginning May 2003

**Milestones:** 1) Revise experimental plan based on analyses of Year 1 data. 2) Conduct 2002 spring/summer/fall experimental intensives. 3) Complete Level I and Level II data analyses for the 2002 data set. 4) Conduct data analysis using statistical approaches. 5) Initiate using results of data analysis to critique existing models of SOA formation paying particular attention to partitioning theories and simplification approaches used for visibility modeling.

**Deliverables:** Data set for the first set of field intensives that were completed by November 30, 2002. Report on first year research submitted to DOE. Paper describing research is submitted for publication and to DOE as a report. Paper presented at a scientific meeting. Bi-monthly progress reports.

### Task I: Review and assess SOA models to identify areas of impact with experiment

We continued to review various studies concerned with SOA formation. This includes studies of new advances in partitioning theory, chemical kinetics of reactive organic compounds, thermodynamics of condensed phase organics, smog chamber experiments, and modeling studies of SOA formation. There has been considerable research using smog chambers devoted to finding yields for particular organic gases or mixtures of organic gases. The amount of SOA formed from a particular reactive organic compound, ROG, is the fractional mass yield. The semi-empirical yield formulae derived from smog chamber experiments where conditions are well controlled are not suitable for predictively modeling the more complex SOA systems found in the atmosphere. The inability to model atmospheric SOAs is due to not being able to represent meteorological variability, and not having sufficient thermodynamic and kinetic understanding and data. There have been recent attempts to model SOA yields from smog chamber studies for prototypical compounds like alpha-pinene using theoretically derived partitioning data, rather detailed chemical kinetics, and some empirically derived stoichiometric coefficients. Results from these efforts are encouraging. Other efforts have attempted to improve the description of SOA formation in more complex photochemical models. In these efforts, there has been considerable aggregation of first principle data into highly lumped surrogates. Although promising, the data requirements are substantial, and suitable data may not be available for areas close to Class I areas. From our survey to date, it appears that our unique coupling of gas and particulate measurements along with meteorological measurements will allow us to focus on the gas-to-particle conversion processes at a level that has not been previously pursued.

### Task II: Plan and prepare for field measurements

Protocols developed during the 2002 field studies were also used in 2003. New this year was the addition of filter measurements that are providing measures of the concentration of particulate sulfate, nitrate, black and organic carbon present in the atmosphere. This information is crucial for describing the gas-to-particle partitioning of the VOCs. The physical properties of the aerosols at the site were measured using several instruments. The optical properties of the aerosol were measured using an aethelometer and an integrating nephelometer. An integrated measure of the number concentration of aerosols was provided by a condensation particle counter. Particle size distributions at the site were measured using a scanning electrical mobility analyzer providing size distributions between 10 and 400 nm. Instruments were rendered field ready in the early summer of 2003.

### Task III: Conduct experimental campaign in summer/fall 2003

Data were collected between June 23 and present. All instruments were fully operational for the period 8/6 until 11/19/2003. Concentrations of a larger set of VOC species were also measured during 2003. During the summer we have observed a number of days where the formation of nuclei-mode particles occurred. We captured a few episodes where emissions from local and remote forest fires affected our site. These data will help characterize the transport and fate of forest fires emissions and their effect upon local particle loading and visibility.

### Task IV: Analyze data from field experiments

The 2002 data set is at Level I and Level II, except for removing the signal to an on site diesel. Systematically and defensibly removing the black carbon signal from the on site diesel generator has proven to be quite difficult, and was recently solved. Time series analysis of the VOC concentrations for various species has revealed patterns that allow us to distinguish the impacts of biogenic and anthropogenic emissions on SOA formation. Correlations have been evaluated between particle size and mass and meteorological variables using the 2002 data. Afternoon formation of small nuclei mode particles (<20nm) occurred on many days. These formation events were anti-correlated with temperature. Lifetime estimates of the small particles indicate that they are formed in the forest either from a combination of biogenic processing of anthropogenic air mass or solely by biogenic reactions. Formation events have been observed both in the presence and absence of high aerosol loading. In contrast, observations by other investigators at other locations have suggested that particle formation events are preceded by a period of relatively particle-free air. Under circumstances of substantial growth, particles having diameters less than 50 nm can increase to as much as 10% of the ambient aerosol volume. Based upon the estimated mass of particles less than 50 nm and the mass of ambient monoterpenes, it is possible that the small particle mass could consist entirely of the oxidation products of biogenic compounds.

**Deliverables:** Presentation at meetings: Melissa Lunden, Douglas Black, Nancy Brown, Anita Lee, Gunar Schade, and Allen Goldstein. "Fine Particle Formation and Processing in a California Pine Forest." American Association of Aerosol Research, October 2003. A report describing the work conducted in Year I is being edited, and will be submitted to DOE before the February review. Bimonthly reports have been submitted.