

FINAL REPORT

DE-SC0011791: ORG AREO BOREAL FOREST

Sources, compositions and properties of newly formed and regional organic aerosol in a boreal forest during the Biogenic Aerosol: Effects on Clouds and Climate Campaign

Publications citing DE-SC0011791 research, June 2014-June 2017

Major goals of the project

The major goals of this project were to make unique measurements, as part of the DOE sponsored Biogenic Aerosol Effects on Clouds and Climate (BAECC) campaign, of the volatility and molecular composition of organic aerosol, as well as gas-phase concentrations of oxygenated organic compounds that interact and affect organic aerosol. In addition, we aimed to conduct a similar set of measurements as part of a collaborative set of environmental simulation chamber experiments at PNNL, the aim of which was to simulate the atmospheric oxidation of key biogenic volatile organic compounds (BVOC) and study the associated formation and evolution of secondary organic aerosol (SOA). The target BVOC were a set of monoterpenes, isoprene, and related intermediates such as IEPOX. The ultimate goal of such measurements are to develop a more detailed mechanistic understanding of the sensitivity of SOA mass formation and lifetime to precursor and environmental conditions. Molecular composition and direct volatility measurements provide robust tracers of chemical processing and properties. As such, meeting these goals will allow for stronger constraints on the types of processes and their fundamental descriptions needed to simulate aerosol particle number and size, and cloud nucleating ability in regional and global earth system models.

Major accomplishments towards these goals

We have largely met our goals set out above. We processed nearly a terabyte worth of observations obtained during the BAECC campaign, and we carried out a comprehensive set of collaborative laboratory experiments using the PNNL environmental simulation chambers to study SOA formation from monoterpene and isoprene. The experiments involved 10 PIs from a range of national and international academic institutions and DOE laboratories. In addition, 7 graduate students, 4 postdoctoral fellows, and at least 3 undergraduates participated in the experiments and data analysis.

We have published more than 8 peer-reviewed manuscripts utilizing results obtained as a result of the above activities. These publications, discussed in more detail below, connect the measured composition and volatility of SOA in controlled settings to that observed in the field to provide detailed constraints on its sources and processing needed to describe the SOA life cycle. We also demonstrated new instrumental methods and the dynamic cycling of organic compounds between the atmosphere and biosphere.

The laboratory experiment matrix was dense and produced a rich set of process level information that we continue to mine for interpreting observations made as part of the Hi-SCALE and BAECC campaigns. We studied SOA formation and properties for 5 different precursors evolving under 32 different atmospheric conditions using 5 different mass spectrometers, 3 different aerosol sizing instruments, and 4 standard trace gas instruments. In short, our monoterpene oxidation experiments successfully replicated typical spectra we observe for regional background organic aerosol and gas composition as measured during BAECC.

Opportunities provided for training and professional development

This project directly involved the training and professional development of 3 postdoctoral fellows (2 male, 1 female), 2 graduate students (1 male, 1 female), and 2 undergraduate students (1 male, 1 female). These are just the personnel in my group that have worked on this project directly, but the collaboration this project inspired at PNNL involved an even wider array of students and postdocs. The opportunities for training and professional development taken by these students involved experiment design and logistical planning, state-of-the-art instrumentation and method development, data analysis methodologies, instrument control and data analysis software development, scientific discussions and group presentations.

Dissemination of results: Peer-reviewed publications

Below I highlight publications resulting from this project and provide a summary of the key results for each.

Mohr, Claudia, Joel A. Thornton, Felipe D. Lopez-Hilfiker, Arto Heitto, Anna Lutz, Mattias Hallquist, Emma L. D'Ambro, Matti P. Rissanen, Liqing Hao, Siegfried Schobesberger, Markku Kulmala, Roy L. Mauldin III, Ulla Makkonen, Mikko Sipilä, Tuukka Petäjä, (2017), Taina Yli-Juuti Molecular identification of the organic vapors driving atmospheric nanoparticle growth rates, for Nature submission 2017

It is estimated that about half of atmospheric cloud condensation nuclei (CCN) are particles formed in the atmosphere via nucleation. Growth of these newly formed particles limits CCN production. Understanding particle growth is thus fundamental for accurate estimations of future climate scenarios, as these are largely limited by uncertainties in aerosol-cloud interactions. The role of extremely low volatile organic compounds (ELVOC), many of them highly oxygenated molecules (HOM) formed via autoxidation, in early (< 5 nm) particle production has been solidified in the field and in the laboratory⁴⁻⁵. It was suggested based on laboratory data that the growth from 5 to 50 nm is driven by compounds of less low volatility (LVOC)⁵, but molecular identities have not been confirmed to date, and quantitative data are missing. Furthermore, the mechanisms for gas-to-particle conversion of these species are not known⁶. Here we present the first ever ambient observations on molecular basis of the “missing” molecular contribution for particle growth. We show that these molecules can quantitatively explain particle growth and evaporation, bringing the understanding of nanoparticle growth from 1 to 50 nm to closure. Our results further indicate that the gas-to-particle conversion processes are reversible upon heating of the sample, and thus that gas-phase mechanisms dominate over particle-phase reactions for the formation of OVOC in this environment and on these timescales. This work represents a fundamental step forward in the characterization of atmospheric particle growth.

Mohr, Claudia, Felipe D. Lopez-Hilfiker, Taina Yli-Juuti, Arto Heitto, Anna Lutz, Mattias Hallquist, Emma L. D'Ambro, Matti P. Rissanen, Liqing Hao, Siegfried Schobesberger, Markku Kulmala, Roy L. Mauldin III, Ulla Makkonen, Mikko Sipilä, Tuukka Petäjä, Joel A. Thornton, (2017), Ambient observations of dimers from terpene oxidation in the gas-phase: implications for new particle formation and growth, *Geo. Phys. Research Letters*, 44, 2958-2966, doi:10.1002/2017GL072718.

We present ambient observations of dimeric monoterpene oxidation products ($C_{16-20}H_{y}O_{6-9}$) in gas and particle phases in the boreal forest in Finland in spring 2013 and 2014, detected with a chemical ionization mass spectrometer with a filter inlet for gases and aerosols employing acetate and iodide as reagent ions. These are among the first online dual-phase observations of such dimers in the atmosphere. Estimated saturation concentrations of 10^{-15} to $10^{-6} \mu\text{g m}^{-3}$ (based on observed thermal desorptions and group-contribution methods) and measured gas-phase concentrations of 10^{-3} to $10^{-2} \mu\text{g m}^{-3}$ ($\sim 10^6$ – 10^7 molecules cm^{-3}) corroborate a gas-phase formation mechanism. Regular new particle formation (NPF) events allowed insights into the potential role dimers may play for atmospheric NPF and growth. The observationally constrained Model for Acid-Base chemistry in NANoparticle Growth indicates a contribution of $\sim 5\%$ to early stage particle growth from the ~ 60 gaseous dimer compounds.

Lopez-Hilfiker, Felipe D. , Siddarth Iyer , Claudia Mohr , Ben H. Lee, Emma L. D'Ambro, Theo Kurtén , and Joel A. Thornton, (2016), Constraining the sensitivity of iodide adduct chemical ionization mass spectrometry to multifunctional organic molecules using the collision limit and thermodynamic stability of iodide ion adducts, *Atmos. Meas. Tech.*, 9, 1505–1512, 2016, doi:10.5194/amt-9-1505-2016.

The sensitivity of a chemical ionization mass spectrometer (ions formed per number density of analytes) is fundamentally limited by the collision frequency between reagent ions and analytes, known as the collision limit, the ion–molecule reaction time, and the transmission efficiency of product ions to the detector. We use the response of a time-of-flight chemical ionization mass spectrometer (ToF-CIMS) to N_2O_5 , known to react with iodide at the collision limit, to constrain the combined effects of ion–molecule reaction time, which is strongly influenced by mixing and ion losses in the ion–molecule reaction drift tube. A mass spectrometric voltage scanning procedure elucidates the relative binding energies of the ion adducts, which influence the transmission efficiency of molecular ions through the electric fields within the vacuum chamber. Together, this information provides a critical constraint on the sensitivity of a ToF-CIMS towards a wide suite of routinely detected multifunctional organic molecules for which no calibration standards exist. We describe the scanning procedure and collision limit determination, and we show results from the application of these constraints to the measurement of organic aerosol composition at two different field locations.

Schobesberger S., Lopez-Hilfiker F. D., Taipale D., Millet D. B., D'Ambro E. L., Rantala P., Mammarella I., Zhou P., Wolfe G. M., Lee B. H., Boy M., Thornton J. A. (2016), High upward fluxes of formic acid from a boreal forest canopy, *Geophys. Res. Lett.*, 43, 9342–9351 (2016), 10.1002/2016GL069599.

Eddy covariance fluxes of formic acid, HCOOH , were measured over a boreal forest canopy in spring/summer 2014. The HCOOH fluxes were bidirectional but mostly upward during daytime, in contrast to studies elsewhere that reported mostly downward fluxes. Downward flux episodes were explained well by modeled dry deposition rates. The sum of net observed flux and modeled dry

deposition yields an upward “gross flux” of HCOOH, which could not be quantitatively explained by literature estimates of direct vegetative/soil emissions nor by efficient chemical production from other volatile organic compounds, suggesting missing or greatly underestimated HCOOH sources in the boreal ecosystem. We implemented a vegetative HCOOH source into the GEOS-Chem chemical transport model to match our derived gross flux and evaluated the updated model against airborne and spaceborne observations. Model biases in the boundary layer were substantially reduced based on this revised treatment, but biases in the free troposphere remain unexplained.

Lee, B. H., C. Mohr, F. D. Lopez-Hilfiker, A. Lutz, M. Hallquist, L. Lee, P. Romer, R. C. Cohen, S. Iyer, T. Kurten, W. Hu, D. A. Day, P. Campuzano-Jost, J. L. Jimenez, L. Xu, N. L. Ng, H. Guo, R. J. Weber, R. J. Wild, S. S. Brown, A. Koss, J. de Gouw, K. Olson, A. H. Goldstein, R. Seco, S. Kim, K. McAvey, P. B. Shepson, T. Starn, K. Baumann, E. S. Edgerton, J. Liu, J. E. Shilling, D. O. Miller, W. Brune, S. Schobesberger, E. L. D’Ambro, and **J. A. Thornton**, (2016), Highly functionalized organic nitrates in the southeast United States: Contribution to secondary organic aerosol and reactive nitrogen budgets, *Proceedings of the National Academy of Sciences of the United States of America*, 113(6), 1516-1521, doi: 10.1073/pnas.1508108113.

Speciated particle-phase organic nitrates (pONs) were quantified using online chemical ionization MS during June and July of 2013 in rural Alabama as part of the Southern Oxidant and Aerosol Study. A large fraction of pONs is highly functionalized, possessing between six and eight oxygen atoms within each carbon number group, and is not the common first generation alkyl nitrates previously reported. Using calibrations for isoprene hydroxynitrates and the measured molecular compositions, we estimate that pONs account for 3% and 8% of total submicrometer organic aerosol mass, on average, during the day and night, respectively. Each of the isoprene- and monoterpenes-derived groups exhibited a strong diel trend consistent with the emission patterns of likely biogenic hydrocarbon precursors. An observationally constrained diel box model can replicate the observed pON assuming that pONs (i) are produced in the gas phase and rapidly establish gas–particle equilibrium and (ii) have a short particle-phase lifetime (~2–4 h). Such dynamic behavior has significant implications for the production and phase partitioning of pONs, organic aerosol mass, and reactive nitrogen speciation in a forested environment.

Liu, J., D’Ambro, E.L., Lee, B.H., Lopez-Hilfiker, F.D., Zaveri, R.A., Rivera-Rios, J.C, Keutsch, F.N., Iyer, S., Kurten, T., Zhang, Z., Gold, A., Surratt, J.D., Shilling, J.E., Thornton, J.A., (2016), Efficient isoprene secondary organic aerosol formation from a non-IEPOX pathway, *Environ. Sci. Technol.*, DOI:10.1021/acs.est.6b01872, 2016.

With a large global emission rate and high reactivity, isoprene has a profound effect upon atmospheric chemistry and composition. The atmospheric pathways by which isoprene converts to secondary organic aerosol (SOA) and how anthropogenic pollutants such as nitrogen oxides and sulfur affect this process are subjects of intense research because particles affect Earth’s climate and local air quality. In the absence of both nitrogen oxides and reactive aqueous seed particles, we measure SOA mass yields from isoprene photochemical oxidation of up to 15%, which are factors of 2 or more higher than those typically used in coupled chemistry climate models. SOA yield is initially constant with the addition of

increasing amounts of nitric oxide (NO) but then sharply decreases for input concentrations above 50 ppbv. Online measurements of aerosol molecular composition show that the fate of second-generation RO₂ radicals is key to understanding the efficient SOA formation and the NO_x-dependent yields described here and in the literature. These insights allow for improved quantitative estimates of SOA formation in the preindustrial atmosphere and in biogenic-rich regions with limited anthropogenic impacts and suggest that a more-complex representation of NO_x-dependent SOA yields may be important in models.

*D'Ambro, Emma L.; Lee, Ben H.; Liu, Jiumeng; Shilling, John E.; Gaston, Cassandra J.; Lopez-Hilfiker, Felipe D.; Schobesberger, Siegfried; Zaveri, Rahul A.; Mohr, Claudia; Lutz, Anna; Zhang, Zhenfa; Gold, Avram; Surratt, Jason D.; Rivera-Rios, Jean C.; Keutsch, Frank N.; Thornton, Joel A., (2017), Molecular composition and volatility of isoprene photochemical oxidation secondary organic aerosol under low- and high-NO_x conditions, *Atmos. Chem. Phys.*, 17, 159–174, 2017 doi:10.5194/acp-17-159-2017.*

We present measurements of secondary organic aerosol (SOA) formation from isoprene photochemical oxidation in an environmental simulation chamber at a variety of oxidant conditions and using dry neutral seed particles to suppress acid-catalyzed multiphase chemistry. A high-resolution time-of-flight chemical ionization mass spectrometer (HR-ToF-CIMS) utilizing iodide-adduct ionization coupled to the Filter Inlet for Gases and Aerosols (FIGAERO) allowed for simultaneous online sampling of the gas and particle composition. Under high-HO₂ and low-NO conditions, highly oxygenated (O : C ≥ 1) C₅ compounds were major components (~ 50 %) of SOA. The SOA composition and effective volatility evolved both as a function of time and as a function of input NO concentrations. Organic nitrates increased in both the gas and particle phases as input NO increased, but the dominant non-nitrate particle-phase components monotonically decreased. We use comparisons of measured and predicted gas-particle partitioning of individual components to assess the validity of literature-based group contribution methods for estimating saturation vapor concentrations. While there is evidence for equilibrium partitioning being achieved on the chamber residence timescale (5.2 h) for some individual components, significant errors in group contribution methods are revealed. In addition, > 30 % of the SOA mass, detected as low-molecular-weight semi-volatile compounds, cannot be reconciled with equilibrium partitioning. These compounds desorb from the FIGAERO at unexpectedly high temperatures given their molecular composition, which is indicative of thermal decomposition of effectively lower-volatility components such as larger molecular weight oligomers.

*D'Ambro, E.L., Møller, K.H., Lopez-Hilfiker, F.D., Schobesberger, S., Liu, J., Shilling, J.E., Kjærsgaard, H.G., Thornton, J.A., (2017), Isomerization of second generation isoprene peroxy radicals: epoxide formation and implications for secondary organic aerosol yields. *Environ. Sci. Technol.* DOI: 10.1021/acs.est.7b00460, 2017.*

We report chamber measurements of secondary organic aerosol (SOA) formation from isoprene photochemical oxidation, in which radical concentrations were systematically varied and the molecular composition of semi- to low-volatility gases and SOA were measured online. Using a detailed chemical kinetics box model, we find that to explain the behavior of low-volatility products and SOA mass yields relative to input H₂O₂ concentrations, the second-generation dihydroxy hydroperoxy peroxy radical (C₅H₁₁O₆·) must undergo an intramolecular H-shift with a net forward rate constant of order 0.1 s⁻¹ or higher. This finding is consistent with quantum chemical calculations that suggest a net forward rate

constant of 0.3–0.9 s⁻¹. Furthermore, these calculations suggest that the dominant product of this isomerization is a dihydroxy hydroperoxy epoxide (C₅H₁₀O₅), which is expected to have a saturation vapor pressure ~2 orders of magnitude higher, as determined by group-contribution calculations, than the dihydroxy dihydroperoxide, ISOP(OOH)₂(C₅H₁₂O₆), a major product of the peroxy radical reacting with HO₂. These results provide strong constraints on the likely volatility distribution of isoprene oxidation products under atmospheric conditions and, thus, on the importance of nonreactive gas-particle partitioning of isoprene oxidation products as an SOA source.

Rissanen, M. P., T. Kurten, M. Sipila, **J. A. Thornton**, O. Kausiala, O. Garmash, H. G. Kjaergaard, T. Petaja, D. R. Worsnop, M. Ehn, and M. Kulmala (2015), Effects of Chemical Complexity on the Autoxidation Mechanisms of Endocyclic Alkene Ozonolysis Products: From Methylcyclohexenes toward Understanding alpha-Pinene, *J. Phys. Chem. A*, 119(19), 4633-4650, doi: 10.1021/jp510966g.

Formation of highly oxidized, multifunctional products in the ozonolysis of three endocyclic alkenes, 1-methylcyclohexene, 4-methylcyclohexene, and α -pinene, was investigated using a chemical ionization atmospheric pressure interface time-of-flight (CI-API-TOF) mass spectrometer with a nitrate ion (NO₃⁻) based ionization scheme. The experiments were performed in borosilicate glass flow tube reactors at room temperature (T = 293 ± 3 K) and at ambient pressure. An ensemble of oxidized monomer and dimer products was detected, with elemental compositions obtained from the high-resolution mass spectra. The monomer product distributions have O/C ratios from 0.8 to 1.6 and can be explained with an autocatalytic oxidation mechanism (=autoxidation) where the oxygen-centered peroxy radical (RO₂) intermediates internally rearrange by intramolecular hydrogen shift reactions, enabling more oxygen molecules to attach to the carbon backbone. Dimer distributions are proposed to form by homogeneous peroxy radical recombination and cross combination reactions. These conclusions were supported by experiments where H atoms were exchanged to D atoms by addition of D₂O to the carrier gas flow. Methylcyclohexenes were observed to autoxidize in accordance with our previous work on cyclohexene, whereas in α -pinene ozonolysis different mechanistic steps are needed to explain the products observed.

Dissemination of results: Presentations at Conferences and other Institutions

Thornton, J.A. October 2017, *invited plenary lecture*, "Towards a Molecular Understanding of Biogenic Secondary Organic Aerosol", **American Association for Aerosol Research Annual Conference**

Thornton, J.A. January 2016, *invited lecture*, "Forests, Humans, and Atmospheric Aerosol Particles", **University of California, Irvine**, Department of Chemistry seminar series

Thornton, J.A. December 2015, *invited lecture*, "Applications of online high resolution time of flight chemical ionization mass spectrometry (HRTof-CIMS): opportunities and challenges for aircraft measurements, atmosphere-ecosystem exchange, and organic aerosol composition", AGU Fall Meeting, San Francisco, CA

Thornton, J.A. October 2015, *invited lecture*, "On the volatility of IEPOX derived SOA," **American Association for Aerosol Research Annual Meeting**, Minneapolis, MN

Thornton, J.A. August 2015, *invited lecture*, "Highly Functionalized Organic Nitrates: Implications for SOA and Reactive Nitrogen Cycling," **American Chemical Society Fall Meeting**, Boston, MA

Thornton, J.A. April 2015, *invited lecture*, “Forests, Humans, and Atmospheric Aerosol Particles”, **Colorado State University**, Department of Chemistry seminar series

Thornton, J.A. August 2014, *invited lecture*, “Nitrogen oxides in high biogenic voc environments: implications for NO_x removal and SOA formation,” **American Chemical Society Annual Meeting**, San Francisco

Thornton, J.A. August 2014, *invited lecture*, “Detection of extremely low volatility organic compounds in the gas-phase: implications for cloud condensation nuclei and secondary organic aerosol,” **American Chemical Society Annual Meeting**, San Francisco

Thornton, J.A. July 2014, *invited lecture*, “Attack of the Peroxides: ELVOC and the Saving Grace of IEPOX”, **Telluride Science Research Conference Organic Aerosol meeting**

Thornton, J.A. May 2014, *invited lecture*, “Detection of extremely low volatility organic compounds in the gas-phase: implications for cloud condensation nuclei and secondary organic aerosol”, **EMSL Aerosol Initiative Science Meeting, PNNL**

D'Ambro, ‘From tree emissions to particles, an oxidative journey’, Le Moyne College (Syracuse, NY) April 7, 2017.

D'Ambro, ‘Mechanistic Insights into non-IEPOX isoprene SOA formation’, AGU (San Francisco, CA) Dec 14, 2016.

Schobesberger, ‘High Upward Fluxes of Formic Acid from a Boreal Forest’, AGU Fall Meeting, San Francisco, 2016.

D'Ambro, ‘Measurements and modeling of isoprene photooxidation products: the role of oligomeric material and particle phase reactions’, AAAR (Portland, OR) Oct 6, 2016.

D'Ambro, ‘Online measurements and modeling of isoprene photo-oxidation products: insights from the laboratory and SOAS field campaign’, poster, AGU Fall Meeting Dec. 16 2015, San Francisco CA.

D'Ambro, ‘Forests, humans, and aerosol particles (oh my!)’, UW Atmospheric chemistry and physics seminar (Seattle, WA) Nov 16 2015.

Mohr, ‘Identification, quantification, and volatility of compounds in the gas and particle phase during new particle formation events’, EAC, Milano, Italy, 09 11 2015.

Mohr, ‘Investigating the chemical composition of sub-100 nm particles with chemical ionization mass spectrometry’, UFP-5, Brussels, Belgium, 05 04 2015.

Mohr, ‘Chemical composition of organic compounds in gases and particles measured in a boreal forest using chemical ionization mass spectrometry’, IAC, Busan, Korea, 08 30 2014.

Mohr, ‘Simultaneous gas and particle phase measurements using a chemical ionization HRTof-MS’, IMSC, Geneva, Switzerland, 08 25 2014.

Mohr, 'Carboxylic acids in the atmosphere: A new inlet for simultaneous gas and particle phase measurements', AAAR, Portland, Oregon, 10 03 2013.

Mohr, 'FIGAERO (Filter Inlet for Gases and Aerosols)', Aerodyne Users Meeting, Prague, Czech Republic, 09 08 2013.

Mohr, 'Secondary Organic Aerosol in Forested Environments', Seminar, University of Gothenburg, Sweden, 09 13 2012.

Partners:

John Shilling at PNNL

Other Collaborators:

U Helsinki, UNC, Concordia, Brookhaven, UC Davis, Portland State University/UC Riverside

Impact on principle discipline

Our results from this project have already begun to impact the SOA modeling community. U. Helsinki modelers are working to reproduce our observations of SOA composition and gas-phase precursors using 1-D canopy-chemistry model with aerosol microphysics. Manish Shrivastava is incorporating our findings on isoprene SOA formation developed from SOAFEE and related chamber experiments we conducted with J. Shilling into a WRF-Chem regional model applied to the Go-AMAZON campaign. In addition, our findings about IEPOX derived SOA are influencing how best to incorporate that SOA source into models now that some of the complexity of the products has been resolved by our measurements.

Impact on other disciplines

I do not have direct knowledge, but I can imagine these findings will also influence the air quality modeling community as aerosol formation and sources are important to resolve for regulatory purposes.

Impact on human resources

See above related to opportunities for training and professional development.

Impact on infrastructure

None

Impact on technology transfer

Our development of high resolution time of flight chemical ionization mass spectrometry as part of this grant has led to several insights into best practices which we have shared with the associated user groups around the world and published in open-access journals such as Atmospheric Measurement Techniques.