

Sources, Composition, and Properties of Newly Formed and Regional Organic Aerosol in a Boreal Forest during the Biogenic Aerosol: Effects on Clouds and Climate Field Campaign Report

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May 2016



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Executive Summary

The Thornton Laboratory participated in the U.S. Department of Energy (DOE) Atmospheric Radiation Measurement (ARM) Climate Research Facility's Biogenic Aerosol Effects on Clouds and Climate (BAECC) campaign in Finland by deploying our mass spectrometer. We then participated in environmental simulation chamber studies at Pacific Northwest National Laboratory (PNNL). Thereafter, we analyzed the results as demonstrated in the several presentations and publications. The field campaign and initial environmental chamber studies are described below.

Acronyms and Abbreviations

ARM	Atmospheric Radiation Measurement Climate Research Facility
ASR	Atmospheric System Research Program
BAECC	Biogenic Aerosol Effects on Clouds and Climate
DOE	U.S. Department of Energy
FIGAERO	Filter Inlet for Gases and AEROsols
HR-ToF-CIMS	High-Resolution Time-of-Flight Chemical Ionization Mass Spectrometer
SMEAR II	Station for Measuring Ecosystem–Atmosphere Relations II

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1.0 BAECC Results

The University of Washington (Principal Investigator Thornton) deployed a Filter Inlet for Gases and AEROSols (FIGAERO) coupled to a High-Resolution Time of Flight Chemical Ionization Mass Spectrometer (HR-ToF-CIMS) operating in iodide-adduct ionization. The FIGAERO HR-ToF-CIMS instrument was deployed at the top of the new 30-m measurement tower at the Station for Measuring Ecosystem–Atmosphere Relations II (SMEAR II) field station at Hyytiälä, Finland, from April 15 to June 5, 2015. The instrument ran nearly continuously for the entire deployment period in its own weatherproof box at the edge of the tower platform, thereby requiring only a 1-m-long inlet to extend beyond the influence of the tower into the prevailing wind direction.

The FIGAERO HR-ToF-CIMS allows in situ measurements of the compositions of both gases and particles, with a specificity toward oxygenated organic compounds, though a few select inorganic compounds (e.g., HNO_3 , H_2SO_4 , halogens, etc.) are also measured. The major scientific objectives for deployment of the University of Washington's FIGAERO HR-ToF-CIMS during BAECC were as follows:

1. Characterize the molecular composition and volatility of submicron aerosol particles as a function of time of day and season to constrain the predominant source types and aging mechanisms controlling organic aerosol mass (e.g., monoterpene oxidation, isoprene oxidation, NO_x -influenced, sulfate-influenced, etc.).
2. Compare molecular composition and volatility of submicron particles measured during the growth phase of new particle formation events to the mean background composition and volatility determined outside of events to provide a means for assessing how the mechanisms of local and regional aerosol formation and growth might be different from those sustaining the background organic aerosol mass.
3. Simultaneously, and without loss of capability for objectives 1 and 2, measure gas-phase composition at high time resolution and collocated with a sonic anemometer to quantify the flux of potential aerosol mass forming compounds to/from the surface, which is a key aspect of three-dimensional chemistry-climate models that remains poorly constrained.

Preliminary results suggest that these objectives were met successfully. Data processing and quality control activities continue, but are almost complete, and analysis of the observations now is underway. The initial analysis of molecular composition and volatility measurements suggest that a large contribution of organic aerosol mass is derived from monoterpene oxidation, with an extremely low volatility, containing compounds consistent with both accretion (dimers, trimers, etc.) and functionalization of monomers with oxygen ($\text{O/C} > 0.7$).

In Figure 1, an example of FIGAERO HR-ToF-CIMS data is shown from an almost 24-hour period during a new particle formation and growth event. During the event, particles less than 10 nm in size appear, and grow over the course 12 hours up to 40 to 60 nm. The FIGAERO HR-ToF-CIMS measures several classes of organic components that increase in abundance in correlation with the increase in particle mass carried by the small growing particles (middle panel). The components that show the most pronounced changes that correlate with growing particles have very low volatilities (see below), such as monomers having $\text{O/C} \sim 0.7$ or higher, or larger molecular compounds such as dimers having compositions ranging from C_{18} to C_{20} .

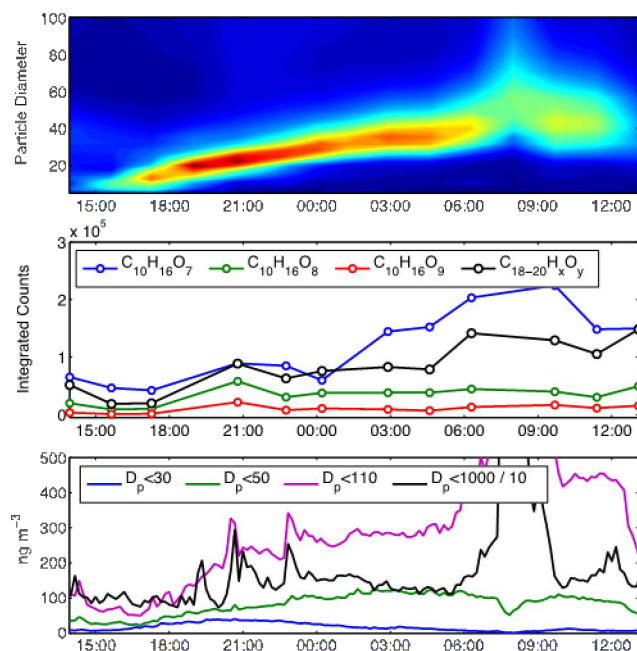


Figure 1. New particle formation and growth event during the BAECC campaign. The particle number diameter distributions are shown versus time of day in spring 2015 (top), specific molecular components measured by the FIGAERO HR-ToF-CIMS in the submicron aerosol particles are shown for the same time period (middle), and particle mass concentrations in different size bins are shown in the lower panel. The FIGAERO HR-ToF-CIMS shows that certain components (e.g., $C_{10}H_{16}O_7$) increase in abundance during the event correlated with the growing particles (50 to 100 nm).

The absolute abundance of the compounds shown in Figure 1 is uncertain, because specific calibration standards are lacking; however, using reasonable estimates of calibration coefficients, the absolute abundance likely is 10 ng/m³ or possibly higher, of order 5 to 10% of the mass growth below 100 nm. These compounds are merely a small subset of those measured, suggesting that it might be possible to explain the composition of a significant portion of the mass growth during such events, which is a piece of the puzzle that has been missing in studies of new particle formation and growth. As a result, these events (we sampled through about half a dozen) will form a central part of our ongoing analysis.

With each measurement of particle composition, the signal of a compound during the temperature programmed thermal desorption, known as a thermogram, provides insight into the volatility distribution of particle components. Previously, we connected the desorption temperature at which the signal of a detected compound reaches a maximum to its sublimation enthalpy. In this context, the thermograms obtained during a new particle event suggest that the growing particles begin at an extremely low volatility state, and by the end of the event, the contribution of higher-volatility compounds has become more significant. That said, even at the end of the event, the bulk of the mass we detect with FIGAERO HR-ToF-CIMS is associated with volatilities much lower than any mechanistic-based model is currently able to predict, but consistent with an important role for both formation of extremely low-volatility organic compounds in the gas phase and potentially accretion reactions within the particle phase.

Figure 2 shows the blank corrected thermograms of a subset of compounds detected in the particle phase during a new particle formation and growth event, similar to that shown above. We sum the signals of all

compounds containing 18 to 20 carbons that desorb. At the start of the growth event, the total concentrations are low, as evidenced by the area under the blue thermogram, but in subsequent desorptions, the total area grows consistent with the growing particle population. As the growth event continues, there is a shift in the temperature at which the desorbing mass in this subset reaches a maximum. The shift is from higher temperatures (later times on the x-axis) early in the event, to lower temperatures later in the event, which is consistent with the early contributions to this subset being of extremely low volatility and a higher volatility fraction growing relatively more as the population ages. These unique insights provide constraints on the mechanisms controlling the formation of particle mass, at least in this subset, and thus provide guidance to how best to model these events. A working hypothesis consistent with this data is provided below.

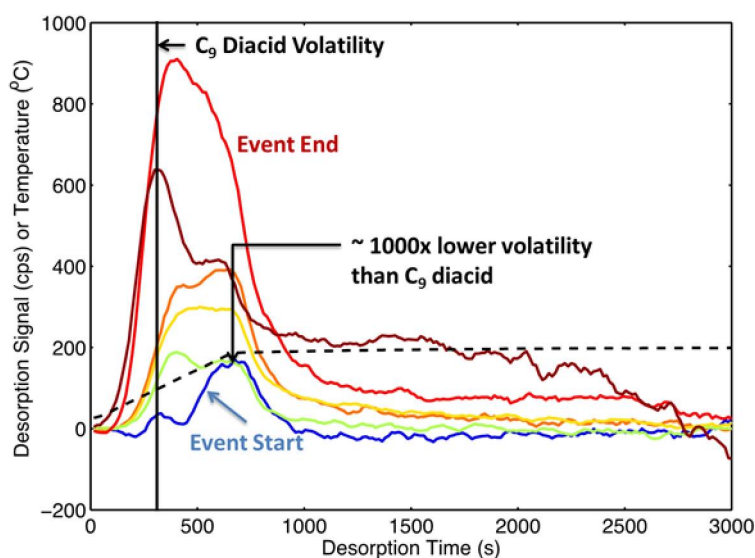


Figure 2. Thermograms of the sum of C18 to C20 compounds are shown as signal versus desorption time (solid lines). The desorption temperature during the ramp and soak is shown as a dashed line. At the start of the event, total concentrations (proportion to area under the thermogram) are low, but the majority of the mass desorbs at higher temperature (later times), consistent with having a saturation vapor concentration orders of magnitude lower than a common monoterpene oxidation product. As the event progresses, the total mass of C18 to C20 compounds increases, consistent with the overall growth of the ambient particle population, and both extremely low-volatility compounds and higher-volatility components increase in abundance.

Early in the event, extremely low-volatility compounds such as highly oxygenated dimers (C18 to C20 compounds with more than eight oxygens) produced in the gas phase condense to the nascent particles, and the presence of these compounds in the particle phase then supports partitioning of less volatile compounds and accretion reactions that lead to less oxygenated dimers (C18 to C20 with five oxygens). Given that this class of compounds alone explains ~ 5 to 10% of the mass growth between 30 and 75 nm, these measurements likely explain a significant fraction of the source of new particle growth.

The results discussed above are focused on specific components of particles during growth events. While these events occur frequently during the spring in Hyytiälä and the components highlighted contribute significant mass concentration, we also are interested in the average composition of the background

aerosol and how that relates to composition during growth events. Figure 3 shows a broader characterization of FIGAERO HR-ToF-CIMS measured particle composition, organized into carbon number groups: C4 to C5, C8 to C10, C18 to C20, and those carbon number groups that also contain nitrogen in the form of an organic nitrate. In the top panel, the time series of these groups is shown for more than 4 weeks during spring as a stacked area plot. Absolute concentrations have not been calculated because calibration data is still being analyzed, but the maxima of the sum of all the components shown correspond to approximately 1 to 5 ug/m^3 , which is between 50 to 100% of total organic aerosol mass measured by an Aerodyne HTToF-AMS.

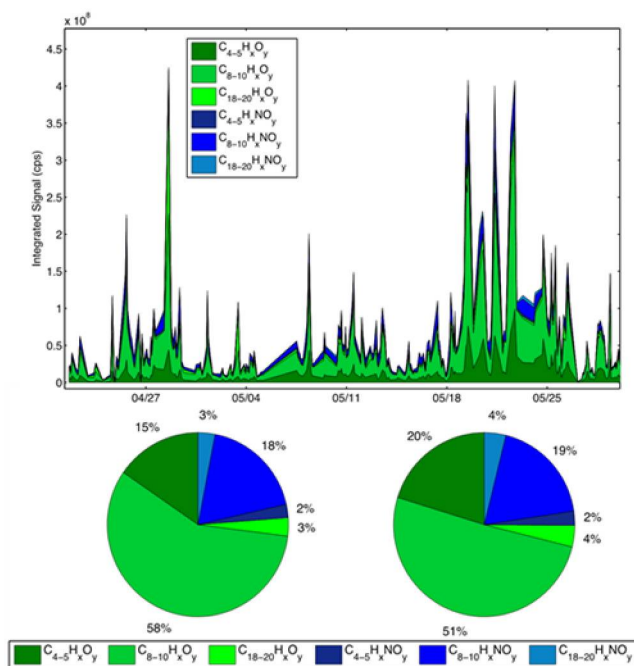


Figure 3. Time series (top) and pie charts of FIGAERO HR-ToF-CIMS determined composition. In the top panel, the signal proportional to absolute mass concentrations is shown for different carbon number bins for more than four weeks of the campaign. The maxima in this panel correspond to of order 1 to 5 ug/m^3 . The distribution of mass in these carbon number bins (pie charts) is approximate, and the specific contribution of the organic nitrates could be larger by a factor of two.

The carbon number bins shown in Figure 3 are chosen to represent contributions from condensation or partitioning of predominant oxidation products from the major biogenic volatile organic carbon precursors such as monoterpenes (C8 to C10), isoprene and/or methyl butene-1-ol (MBO) (C4 to C5), and tracers of either gas- or particle-phase accretion reactions (C18 to C20) involving these biogenic precursor oxidation products. The nitrates are, on the one hand, a tracer of anthropogenic influence, given that globally most NO_x now arises from anthropogenic emissions, but also nitrates can be a tracer of different types of chemistry: that is, chemistry driven by daytime photochemistry or by nighttime chemistry involving ozonolysis or oxidation by the nitrate radical. In the top panel, it is clear that monoterpene oxidation products tend to dominate the fraction of mass characterized by the FIGAERO HR-ToF-CIMS, which is consistent with the biogenic emissions distribution upwind of the measurement site during the spring. However, as spring progresses, there is a noticeable enhancement in the contribution of C4 to C5 compounds, likely because of the onset of isoprene emissions as plants leaf out and temperatures increase.

Overall, a rather consistent composition appears to dominate the background, with large contributions from monoterpene oxidation products, “dimers” indicating particle-phase chemistry, and organic nitrates, suggesting an important role for anthropogenic influence even in this rural site location. An important caveat to the last point is that natural soil emissions of NO_x may constitute the dominant source of NO_x that leads to nitrates at this site. We will be assessing this aspect as our analysis progresses.

In summary, the BAECC deployment of the FIGAERO HR-ToF-CIMS was successful in all aspects. We are embarking on an analysis that will provide unprecedented constraints on the emissions and chemical processes that drive the contribution of organic material to the growth of new particles and to the regional background aerosol during the spring. These insights will be able to put constraints on mechanisms capable of being incorporated into large-scale chemistry-climate models, which is an outcome goal for future work on this project.

2.0 Future Planned Activities

During 2015, the Thornton Laboratory will continue to analyze the mass spectrometer data from the BAECC campaign and will draft papers for publication, while conducting another chamber experiment at PNNL. As proposed, we are following up our participation in BAECC with a controlled environmental simulation chamber study of the chemical processes that we hypothesize are important in the formation and growth of new particles to cloud condensation nuclei active sizes in the Finnish boreal forest. We have leveraged the interest of several collaborators in this particular study to accomplish one of the most comprehensive characterizations of chamber chemical conditions to date. Collaborators and their contributions to the study are listed below. These capabilities are being provided at no additional cost to the DOE Atmospheric System Research (ASR) program. Given the use of the PNNL chamber and the lead Principal Investigators, Thornton and Shilling, using DOE funds, the state-of-the-art scientific outcomes possible with this combination of collaborators without additional costs will surely bring significant recognition to the DOE ASR program. Experiments will begin June 1, and will continue at differing levels of intensity through July 31.

3.0 Publications, Presentations, and other Products

We have two papers submitted or in preparation on FIGAERO applications to chambers and monoterpene oxidation, where DOE ASR as a source of funding is/will be acknowledged.

Lopez-Hilfiker, FD, C Mohr, M Ehn, F Rubach, E Kleist, J Wildt, TF Mentel, A Carrasquillo, K Daumit, J Hunter, JH Kroll, D Worsnop, and JA Thornton. 2015. “Phase partitioning and volatility of secondary organic aerosol components formed from α -pinene ozonolysis and OH oxidation: the importance of accretion products and other low volatility compounds.” *Atmospheric Chemistry and Physics* 15: 7765-7776, [doi:10.5194/acp-15-7765-2015](https://doi.org/10.5194/acp-15-7765-2015).

Liu, J, BH Lee, E D'Ambro, FD Lopez-Hilfiker, R Zaveri, JE Shilling, and JA Thornton. “Unexpectedly efficient secondary organic aerosol formation from isoprene photo-oxidation” In preparation for submission April, 2015.

Lee, BH, C Mohr, FD Lopez-Hilfiker, A Lutz, M Hallquist, L Lee, P Romer, RC Cohen S Iyer, T Kurten, W Hu, DA Day, P Campuzano-Jost, JL Jimenez, L Xu, NL Ng, H Guo, RJ Weber, RJ Wild, SS Brown, A

Koss, J de Gouw, K Olson, AH Goldstein, R Seco, S Kim, K McAvey, PB Shepson, T Starn, K Baumann, ES Edgerton, J Liu, JE Shilling, DO Miller, W Brune, S Schobesberger, EL D'Ambro, and JA Thornton. "Highly functionalized particle-phase organic nitrates observed in the Southeastern United States: contribution to secondary organic aerosol and reactive nitrogen budgets." 2015. *Proceedings of the National Academy of Sciences of the United States of America* 113(6): 1516-1521, [doi:10.1073/pnas.1508108113](https://doi.org/10.1073/pnas.1508108113).

Following are citations for oral presentations regarding data taken by our instrument, where DOE ASR was cited as a funding source. Students and postdoctoral fellows as lead presenter are underlined.

Lee, BH. 2014. "Atmosphere-biosphere-climate interactions: enhanced conversion of forest emissions to aerosols." NOAA Summer Institute, July 2014, Steamboat, Colorado.

Thornton, et al, "Attack of the Peroxides: From the ELVOC empire to the saving grace of IEPOX", Telluride Science Research Conference, August 2014.

Lee, BH. 2014. "Insights into NO₃-driven alkyl nitrate formation from SENEX & SOAS." Southeast Atmosphere Study Data Workshop, March 31-April 2, 2014, National Center for Atmospheric Research, Boulder, Colorado.

Lopez-Hilfiker, FD, et al. 2014. "Volatility and composition of submicron organic aerosol: Insights from the Figaero-TOF-CIMS." SOAS Science Team, December 2014.

Thornton, et al, "Extremely Low Volatility Organic Compounds from Monoterpene Oxidation: Implications for New Particle Formation and Growth", American Chemical Society, August 2014.

Thornton, et al, "RO₂ isomerization and the formation of extremely low volatility organic compounds from monoterpene oxidation: Implications for new particle formation and growth." Atmospheric Chemical Mechanisms Conference, December 10, 2014, University of California-Davis, Davis, California.

Lee, BH. 2015. "How does pollution influence the biosphere-chemistry-climate relationship?" Undergraduate Seminar for Education Outreach, University of Richmond, February 2015, Richmond, Virginia.

Following are citations for posters presentations regarding data taken by our instrument, with acknowledgement to the DOE ASR program (FIGAERO HR-ToF-CIMS development):

Whybrew, L (undergraduate research assistant). 2014. "Seasonal variations and regional sources of ultrafine particulate matter at a semi-rural site on the Olympic Peninsula." Poster presented at the AAAR Meeting, October 20-24, 2014, Orlando, Florida.

Lopez-Hilfiker, FD. 2014. "FIGAERO-TOF-CIMS: Speciated organics in the gas and particle phase." Poster presented at the Goldschmidt Conference, June 8-13, 2014 Sacramento, California.

Additional people who worked on this research activity are identified below:

Lee, BH (postdoctoral fellow). Partial support by NOAA Climate and Global Change Postdoctoral Fellowship. Focus area: aerosol composition using FIGAERO.

Schobesberger, S (postdoctoral fellow). Full support (2 months so far). Focus area: analyzing fluxes of gases measured during BAECC.

Goldberger, L (postgraduate student). Full support (7 months so far). Focus area: constructing a complement to FIGAERO HR-ToF-CIMS to measure total particulate organic carbon during PNNL studies.

D'Ambro, E (postgraduate student). Partial support from the National Science Foundation. Focus area: support for IEPOX chemistry, needed to constrain and compare to photochemistry studied at PNNL for this project.

Lopez-Hilfiker, F (postgraduate student). Partial support (6 months). Focus area: deployed FIGAERO during BAECC; analyzing data in this report. Other time is on an unrelated National Science Foundation project.

Whybrew, L (undergraduate student). No fiscal support, obtained fellowship.



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