

**DOE ASR Final Report on “Connecting Organic Aerosol Climate-Relevant Properties to
Chemical Mechanisms of Sources and Processing”**

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Final Scientific/Technical Report

Executive Summary

The research conducted on this project aimed to improve our understanding of secondary organic aerosol (SOA) formation in the atmosphere, and how the properties of the SOA impact climate through its size, phase state, and optical properties. The research involved developing and improving methods to provide online measurements of the molecular composition of SOA under atmospherically relevant conditions and to apply this technology to controlled simulation chamber experiments and field measurements. The goal of this project was to demonstrate that the use of molecular composition information to mechanistically connect source apportionment and climate properties can improve the physical basis for simulation of SOA formation and properties in climate models. The project started with an evaluation of the existing Micro-Orifice Volatilization Impactor (MOVI) coupled to a high resolution time of flight mass spectrometer using chemical ionization (HR-ToF-CIMS) developed as part of a DOE SBIR project. We used this technology in a field campaign (ClearLo) and as part of chamber experiments producing SOA from monoterpenes and other compounds. While clearly providing new insights, the tests under controlled conditions allowed us to develop a much improved method that used Teflon filters instead of inertial impaction, which suffers from poor coverage of the relevant size ranges and particle bounce. The new approach that we developed, known as the FIGAERO, was then applied to chamber studies as well as a related field campaign as originally planned for this project.

The FIGAERO HR-ToF-CIMS is not inexpensive, but it is very powerful. Aerodyne Research Inc is now marketing and selling the FIGAERO, having distributed 8 around the world, with another 5 – 10 on order or proposed, largely because of the scientific demonstration we provided as part of this project. The science we have completed with the FIGAERO is high impact. We have quantified molecular components of “brown carbon” (light absorbing SOA), and identified new mechanisms for the formation of SOA from both monoterpenes and isoprene. We have also demonstrated that the volatility of monoterpene derived SOA is far lower than current model parameterizations would estimate – thereby changing the inferred atmospheric lifetime and thus abundance. The science that will now come from its widespread use, regardless of funding source, will be entirely because this project provided the demonstration of its capabilities. No other funding agency contributed to the development or application of the FIGAERO, and thus, the DOE’s Atmospheric Systems Research program will be solely responsible for advancing the scientific capabilities of an entire field of atmospheric research.

Accomplishments

From the original proposal, the goals of the project were:

- 1) identification of chemical (mass spectral) fingerprints associated with specific sources, processing regimes, or aerosol optical and cloud nucleating properties that can be utilized in future field or laboratory studies, and*

2) *multi-dimensional molecular-level constraints on the gas and particle phase chemical mechanisms describing organic aerosol evolution for use in regional and global models.*

In general, we successfully met the objectives for this project. Starting with the proof-of-concept instrument for measurements of molecular composition of organic aerosol that we had developed at the time of the proposal, MOVI HR-ToF-CIMS, we arrived at a highly capable and robust technology that is now being purchased by groups around the world. The new technology, known as a “Filter Inlet for Gases and AEROSol”, FIGAERO, coupled to a high resolution time of flight mass spectrometer using chemical ionization, has allowed us to study the organic aerosol composition in chamber studies and field campaigns with sources of organic aerosol ranging from monoterpene and isoprene oxidation, biomass burning, and fossil fuels.

As a result of accomplishing this technique development, we have generated mass spectral fingerprints for the following organic aerosol systems:

1. monoterpene ozonolysis (Julich, UW, MIT chambers)
2. monoterpene oxidation by OH (Julich and MIT chambers)
3. isoprene oxidation by OH with/without NO_x (PNNL chambers)
4. wintertime biofuel/biomass burning aerosol in the UK (ClearfLo campaign)
5. wintertime biofuel/biomass burning aerosol WA (not DOE funded)
6. springtime organic aerosol in the boreal forest of Finland (BAECC campaign)
7. C₁₀ alkanes and JP10 – a new formula for jet fuel (MIT chambers)

These molecular fingerprints are now stored as “peak lists”, described in publications (both published and forthcoming) and have been shared with other groups for further analyses of aerosols measured in other regions. These include MIT, CU Boulder, PNNL, University of Helsinki, and Gothenburg University.

A second major accomplishment is the use of the thermal desorption profiles (molecular composition as a function of temperature) inherent to the FIGAERO technique to constrain the volatility of organic aerosol components. The volatility of organic aerosol determines its response to atmospheric aging by gas-phase chemical processing and to dilution due to atmospheric mixing processes. It is such a crucial aspect of modeling organic aerosol, there is now wide-spread use and development of a “volatility basis set” for modeling the formation and transport of organic aerosol in large scale chemistry/climate earth system models. Our work on this project demonstrated that the FIGAERO provides a uniquely quantitative constraint on the volatility of organic aerosol. Using this method we have shown that at least 50% of SOA mass formed from during monoterpene ozonolysis is of extremely low volatility – 4 orders of magnitude lower than any current parameterization would predict. Current parameterizations are indirect estimates and therefore subject to large error, and these errors can propagate into the inference of other organic aerosol properties such as phase state and/or viscosity. Our observations, described in a paper to be submitted shortly (draft sent to Ashley Williamson), will likely open up a whole new area of investigation – the origins of this

extremely low volatility organic aerosol which appears to involve oligomeric or other large molecular weight and highly oxygenated compounds.

A third major accomplishment was the finding that gas-phase oxidation chemistry and produce extremely low volatility organic compounds promptly in the gas-phase. This project provided the ability to establish important international collaborations, namely with the University of Helsinki. Our collaboration with them on chamber experiments at Julich Research Center in Germany was motivated by the idea that by focusing on elucidating the molecular composition of both gas and particle phase organics using HR-ToF-CIMS, we would develop a much more comprehensive understanding of the mechanisms driving SOA formation that can then be used to parameterize new particle formation and growth in climate models. These chamber experiments provided the setting for using the FIGAERO to assess particle volatility described above, and for our study of the gas-phase chemistry leading to SOA. The finding that extremely low volatility organic vapors are formed promptly in the gas-phase and could explain new particle growth rates in the boreal forest was published in *Nature*.

Project Activities

As noted above, the key hypothesis guiding the work on this project was:

Elucidating the molecular composition of both gas and particle phase organics using HR-ToF-CIMS will reveal the mechanisms driving SOA formation and its climate relevant properties, such as, its contribution to new particle formation, volatility (lifetime), hygroscopicity (cloud nucleating ability), and light absorption (optical properties). These insights will then provide guidance on how to simulate aerosol-climate effects within climate models.

This project then had as its primary goal to provide the necessary tests of this hypothesis. In order to accomplish this goal, we chose to conduct chamber studies and field measurements under a range of conditions to demonstrate that the HR-ToF-CIMS, with an inlet to separately analyze gases and particles, provided unique molecular information for as many organic aerosol source types feasible with the funding and time available. As I (the PI) have limited chamber facilities at UW, I established collaborations with the Julich Research Center (T. Mentel and Mikael Ehn), Jesse Kroll at MIT, and John Shilling at PNNL. I also took part in the ClearLo campaign in collaboration with Aerodyne Research, an exploratory campaign that served as a model for the DOE BAEECC campaign in the boreal forest of Finland, and ultimately the BAEECC campaign.

Because of the synergy between our collaborative project with Aerodyne to participate originally in GVAX, but ultimately in ClearLo, there was overlap in the activities between those the two projects. For this particular project, however, we were focused on testing the above hypothesis under a range of conditions, not just the ClearLo campaign.

Perhaps the most significant problem encountered during the project occurred early on, with the first tests of the proto-type apparatus on the MIT chamber. While the MOVI-CIMS approach seemed to work fairly well during ClearfLo, where the conditions were relatively clean (especially in the gas-phase) due to the prevalence of fairly well aged air masses impacting the site, on a chamber, where typically high concentrations of reactants are used and fast changes in particle size distributions occur, the MOVI suffered from significant artifacts. In particular, we were unable to cleanly separate gas and particle chemical analysis because the high gas concentrations contaminated the particle signals due to adsorption to the particle collector, and the often high concentration of small particles contaminated the gas-phase measurement because they were too small to be inertially sampled. While the situation was likely not as dire in the atmosphere, the issue of particle bounce is always present in inertial impaction methods, and so the combination of issues led us to come up with a new strategy.

As part of the tests done on the MIT chamber, we found that Teflon filters passed a majority of gas-phase organics (even highly oxygenated ones) with minimal adsorption, while collecting 99% of particles of any size. We therefore used these results to develop the Filter Inlet for Gases and Particles (FIGAERO). We designed a prototype within months of the MIT chamber experiments, and deployed the prototype during the collaborative experiments at Julich Research Center. We found that the prototype was highly correlated with the Aerosol Mass Spectrometer measurements of organic and inorganic aerosol components (Figure 1). This level of correlation and even portion of organic aerosol mass explained by molecular level composition measurements was unprecedented.

These results gave us confidence that the FIGAERO HR-ToF-CIMS was going to be suitable for meeting our primary goals. We published a description of the FIGAERO HR-ToF-CIMS in *Atmospheric Measurement Techniques*.

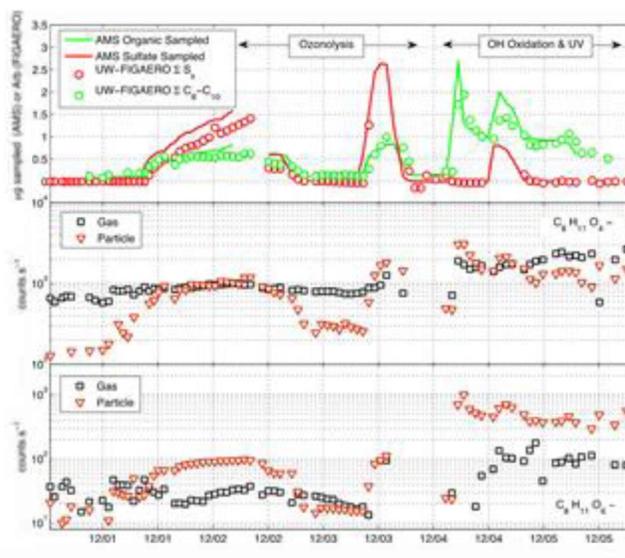


Figure 1. Time series of FIGAERO HR-ToF-CIMS and AMS aerosol particle quantities (top) during the Julich chamber experiment. Middle and bottom panels show time series for specific molecular tracers in the gas and particle phases.

As part of the experiments studying monoterpene oxidation as a source of SOA in the Julich chamber facility, the FIGAERO HR-ToF-CIMS measurements provided the opportunity to assess the volatility of organic aerosol and test equilibrium partitioning theory which assumes that compounds partition to the particle phase based on their concentration relative to their saturation vapor pressures (Raoult's Law). By examining the molecularly resolved thermograms and directly measured gas and particle phase

concentrations of a suite of molecular components, we found that as a whole, the organic aerosol was much lower than current parameterizations would predict, and that in order to explain the measured partitioning much of the organic aerosol material must be oligomeric and undergoing thermal decomposition during our thermal desorption analysis (Figure 2). These findings have very significant implications for how models should treat monoterpene SOA. Assuming, as many models do, that monoterpene is mostly semi-volatile is inaccurate – our direct measurement shows it to be several orders of magnitude less volatile than such parameterizations would predict (Figure 3). This specific set of results is in manuscript form, about to be submitted for publication in *Atmospheric Chemistry and Physics*.

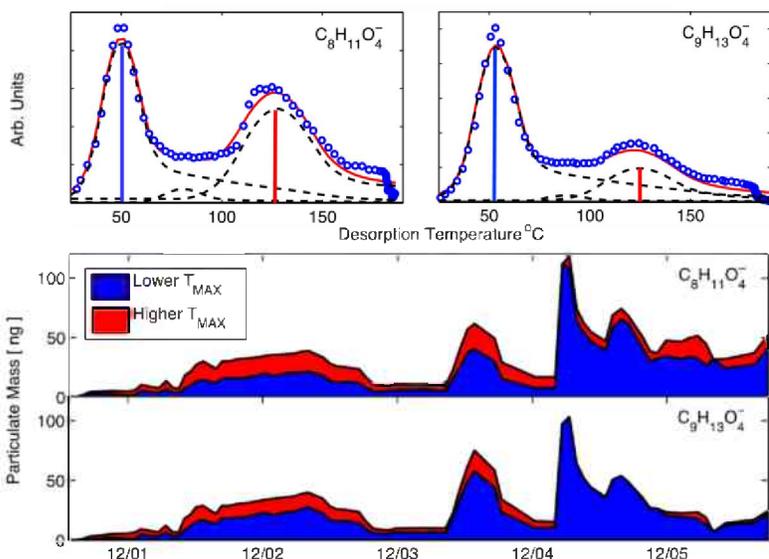


Figure 2. Thermal desorption profiles (top) for two different molecular tracers. The multi-modes suggest very low volatility compounds are decomposing at high desorption temperatures into the measured tracers. The lower panel shows the time series of the higher (blue) and lower (red) volatility components.

It should be noted that the field measurements largely support this picture, especially those obtained in the boreal forest of Finland. The data are still being processed, and not yet in final form, but we are using the opportunity to participate in the BAECC campaign on a follow-on grant from the DOE to pursue this aspect of organic aerosol from monoterpenes.

At the end of the award period, we also participated in what were meant to be exploratory measurements in collaboration with John Shilling at PNNL in order to demonstrate that the FIGAERO HR-ToF-CIMS measures different chemical properties for aerosol formed from isoprene compared to monoterpenes. This work resulted in some rather surprising results and the likelihood of a very high profile paper that we are currently drafting. The main result is that we have identified, with the

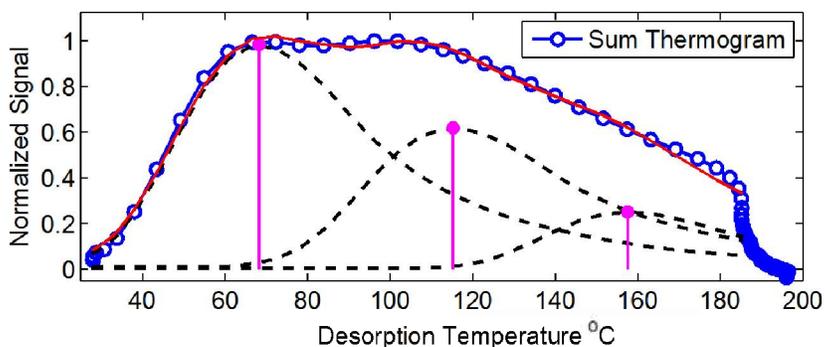


Figure 3. The sum thermogram - all signal measured with the FIGAERO at each temperature during the desorption - is fit by three broad components, each representing a different class of volatility. At low desorption temperature is the semi-volatile component (as most commonly assumed), but this is only ~ 50% of the measured mass, the other half of the desorption signal occurs at temperatures corresponding to 3 or 4 orders of magnitude lower volatility.

FIGAERO HR-ToF-CIMS the key reaction product from isoprene that is responsible for generating ~ 25 – 50% of the SOA. Moreover, the overall SOA yield tracks exactly the yield of this compound, a di-hydroxy di-hydroperoxide ($C_5H_{12}O_6$), in response to various perturbations, such as changing oxidants and NO_x concentrations. The elucidation of this chemistry will provide clear guidance for modeling SOA formation from the most significant biogenic VOC – isoprene.

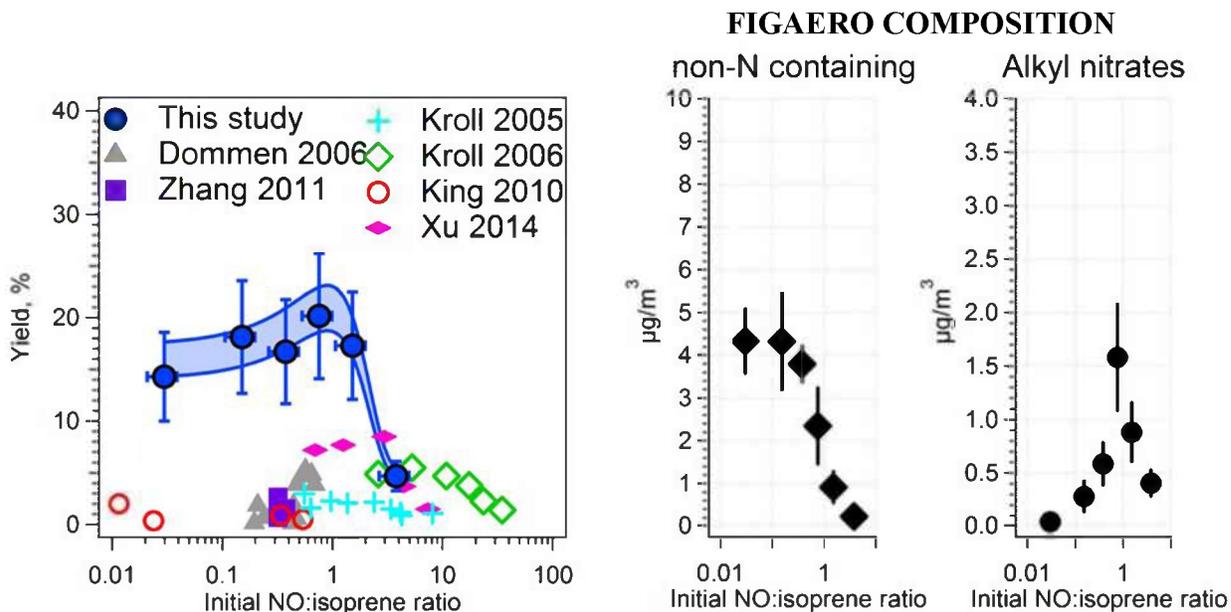


Figure 4. SOA yield from isoprene as a function of NO_x (right), FIGAERO measured particle phase $C_5H_{12}O_6$ and other non-nitrates (middle) as well as particle-phase alkyl nitrates (right), as a function of NO_x . We are following upon this finding with continued collaborations with John Shilling as part of our current DOE award centered around BAEC in which we plan to study contributions of monoterpenes and isoprene under conditions of the boreal forest to aerosol formation and growth.

As noted above, the synergy of two simultaneous awards (this one and one for the ClearLo campaign which was the GVAX replacement), was useful in that we were able to use our understanding of the MOVI deployed during ClearLo to extract meaningful data on the contribution of nitrogen containing compounds to “brown carbon”. I won’t discuss this aspect here as it was more relevant to the other project, but that activity was influenced by all the activities described above.

Products

We have produced several peer-reviewed publications, with two more near submission (drafts sent to Ashley Williamson), that were made possible with funding from this project or resulted from collaborations established as part of this project. We have also given several invited or contributed conference presentations based data gathered as part of this project. These are listed below. † refers to student or postdoctoral fellow mentored by J. A. Thornton and supported by this project at some point.

- Ehn, M., **J. A. Thornton**, E. Kleist, M. Sipila, H. Junninen, I. Pullinen, M. Springer, F. Rubach, R. Tillmann, B. Lee[†], F. Lopez-Hilfiker[†], S. Andres, I.-H. Acir, M. Rissanen, T. Jokinen, S. Schobesberger, J. Kangasluoma, J. Kontkanen, T. Nieminen, T. Kurten, L. B. Nielsen, S. Jorgensen, H. G. Kjaergaard, M. Canagaratna, M. D. Maso, T. Berndt, T. Petaja, A. Wahner, V.-M. Kerminen, M. Kulmala, D. R. Worsnop, J. Wildt, and T. F. Mentel (2014), A large source of low-volatility secondary organic aerosol, *Nature*, 506(7489), 476-479.
- Kulmala, M., T. Petäjä, M. Ehn, **J. Thornton**, M. Sipilä, D. R. Worsnop, and V.-M. Kerminen (2014), Chemistry of Atmospheric Nucleation: On the Recent Advances on Precursor Characterization and Atmospheric Cluster Composition in Connection with Atmospheric New Particle Formation, *Annu. Rev. Phys. Chem.*, 65(1).
- Lopez-Hilfiker[†], F. D., C. Mohr[†], M. Ehn, F. Rubach, E. Kleist, J. Wildt, T. F. Mentel, A. Lutz, M. Hallquist, D. Worsnop, and **J. A. Thornton** (2014), A novel method for online analysis of gas and particle composition: description and evaluation of a Filter Inlet for Gases and AEROSols (FIGAERO), *Atmos. Meas. Tech.*, 7(4), 983-1001.
- Yatavelli, R. L. N., H. Stark, S. L. Thompson, J. R. Kimmel, M. J. Cubison, D. A. Day, P. Campuzano-Jost, B. B. Palm, A. Hodzic, **J. A. Thornton**, J. T. Jayne, D. R. Worsnop, and J. L. Jimenez (2014), Semicontinuous measurements of gas-particle partitioning of organic acids in a ponderosa pine forest using a MOVI-HRToF-CIMS, *Atmos. Chem. Phys.*, 14(3), 1527-1546.
- Sipilä, M., T. Jokinen, T. Berndt, S. Richters, R. Makkonen, N. M. Donahue, R. L. Mauldin Iii, T. Kurtén, P. Paasonen, N. Sarnela, M. Ehn, H. Junninen, M. P. Rissanen, **J. Thornton**, F. Stratmann, H. Herrmann, D. R. Worsnop, M. Kulmala, V. M. Kerminen, and T. Petäjä (2014), Reactivity of stabilized Criegee intermediates (sCIs) from isoprene and monoterpene ozonolysis toward SO₂ and organic acids, *Atmos. Chem. Phys.*, 14(22), 12143-12153.
- Rissanen, M. P., T. Kurtén, M. Sipilä, **J. A. Thornton**, J. Kangasluoma, N. Sarnela, H. Junninen, S. Jørgensen, S. Schallhart, M. K. Kajos, R. Taipale, M. Springer, T. F. Mentel, T. Ruuskanen, T. Petäjä, D. R. Worsnop, H. G. Kjaergaard, and M. Ehn (2014), The Formation of Highly Oxidized Multifunctional Products in the Ozonolysis of Cyclohexene, *J. Am. Chem. Soc.*, 136(44), 15596-15606.
- Mohr[†], C., F. D. Lopez-Hilfiker[†], P. Zotter, A. S. H. Prevot, L. Xu, N. L. Ng, S. C. Herndon, L. R. Williams, J. P. Franklin, M. S. Zahniser, D. R. Worsnop, W. B. Knighton, A. C. Aiken, K. J. Gorkowski, M. K. Dubey, J. D. Allan, and **J. A. Thornton** (2013), Contribution of Nitrated Phenols to Wood Burning Brown Carbon Light Absorption in Detling, United Kingdom during Winter Time, *ES&T*, 47(12), 6316-6324.
- Craven, J. S., L. D. Yee, N. L. Ng, M. R. Canagaratna, C. L. Loza, K. A. Schilling, R. L. N. Yatavelli[†], **J. A. Thornton**, P. J. Ziemann, R. C. Flagan, and J. H. Seinfeld (2012), Analysis of secondary organic aerosol formation and aging using positive matrix factorization of high-

resolution aerosol mass spectra: application to the dodecane low-NO_x system, *Atmos. Chem. Phys.*, 12(24), 11795-11817.

Yatavelli[†], R. L. N., F. Lopez-Hilfiker[†], J. D. Wargo[†], J. R. Kimmel, M. J. Cubison, T. H. Bertram, J. L. Jimenez, M. Gonin, D. R. Worsnop, and **J. A. Thornton** (2012), A Chemical Ionization High-Resolution Time-of-Flight Mass Spectrometer Coupled to a Micro Orifice Volatilization Impactor (MOVI-HRToF-CIMS) for Analysis of Gas and Particle-Phase Organic Species, *Aerosol Sci. Technol.*, 46(12), 1313-1327.

Perhaps the most significant product has been a well characterized method for measuring the composition and abundance of a wide suite of particle and gas-phase organics, the FIGAERO HR-ToF-CIMS. This technology is unique in that it allows insights about volatility and chemical composition to be obtained simultaneously, for compounds which are so highly oxygenated and of too low volatility to be analyzed by methods relying on gas-chromatography. This methodology has been described in the literature (Lopez-Hilfiker, AMT 2014), and is now being sold to several institutions via Aerodyne Research.

Finally, we have amassed a significant data set of molecular fingerprints that can be used by future deployments of the FIGAERO by other groups as a basis for comparing and constraining the sources and properties of organic aerosol. We are currently creating a database of mass spectral peak lists which can be shared through SQL database technology.