



A Report from the University of Vermont Transportation Research Center

Atmospheric Oxidative Chemistry of Organic Particulate Emissions from Fuel Combustion

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Atmospheric Oxidative Chemistry of Organic Particulate Emissions from Fuel Combustion

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Disclaimer

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Introduction

Construction and characterization of the University of Vermont Environmental Chamber (UVMEC) were completed in this last phase of the project. The primary function of the UVMEC is to enable tropospheric particulate formation and aging studies to be performed on environmentally relevant timescales. Proxies for anthropogenic- and biogenic-derived secondary organic aerosol were the focus of the past year's research, wherein volatilization, oxidation and condensation processes of these proxies was examined.

The UVMEC is now coupled to a novel instrument, near infrared (NIR) laser desorption/ionization (LDI) aerosol mass spectrometer (AMS), developed in the Petrucci group.¹ In our last progress report, we described the results of our research to measure the physical and chemical characteristics of the chamber, including wall loss kinetics of gases and particles. Since completion of the characterization work, we have conducted detailed chemical investigations of two biogenic aerosol precursors, α -pinene and limonene, with ozone as the primary oxidant.

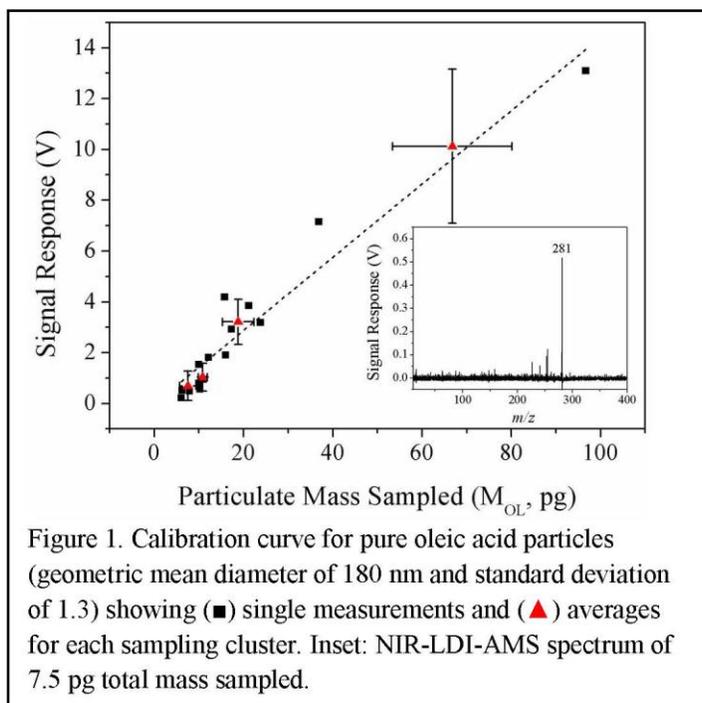
Research Methods

The experimental system has been designed to permit the generation and measurement of low-level (sub ppmv) oxidants inside the reaction chamber. The UVMEC's current configuration is an 8 m³ (8000 L) cube supported by an aluminum frame. A custom, particle-free air system has been designed to include silica gel, activated carbon, and HEPA filters to prevent contamination due to water vapor, volatile organics and background particles, respectively. Numerous ports are positioned around the chamber for introducing gaseous oxidants, water vapor, volatile organics (including parent nitrogen-containing organics and fuel proxies) and seed aerosol. Instruments coupled to the chamber include an ozone generator (OL80A/DLS, OzoneLab, Burton, BC, Canada), and an ozone monitor (Ozomat MP D-7400, Anseros GmbH, Tubingen, Germany), and several different methods of aerosol generation. Particle distributions and concentrations are continuously measured with a scanning mobility particle sizer (SMPS 3936, TSI Inc., Shoreview, MN) operating at 0.4 L/min.

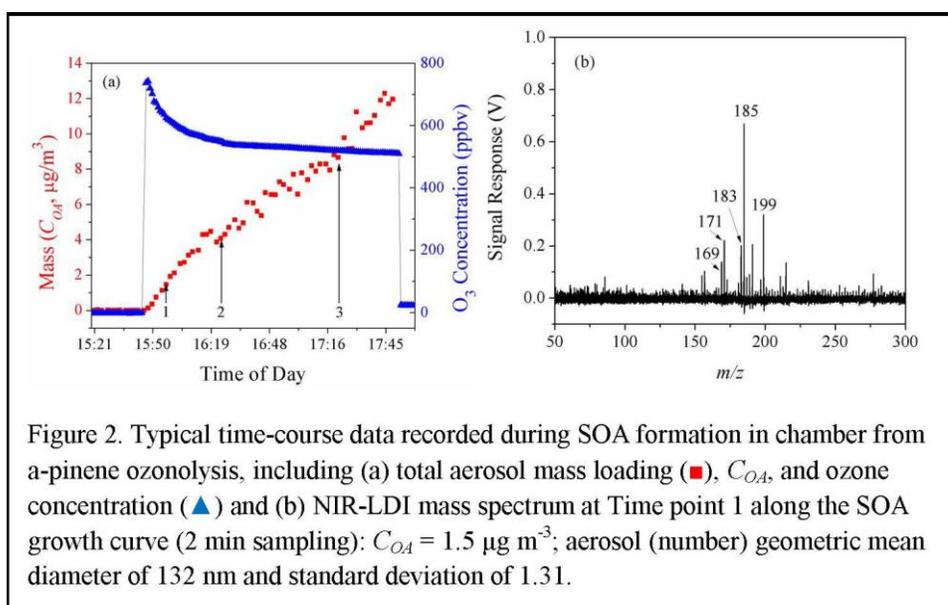
The dedicated aerosol mass spectrometer provides the bulk of the chemical information gained during chamber experiments. The new NIR-LDI-AMS system has an improved sensitivity (over the photoelectron resonance capture AMS reported in previous reports) of approximately 1000-fold, permitting measurements at atmospherically relevant aerosol mass loadings (COA). The NIR-LDI-AMS permits chemical analysis of aerosols at loadings as low as 1 $\mu\text{g m}^{-3}$ with a time resolution of less than one minute. Furthermore, aerosol measurements are now augmented with gas phase measurements of precursor concentrations and volatile and semi-volatile chemical products, bringing us a step closer to achieving carbon mass balance.

Results and Discussion

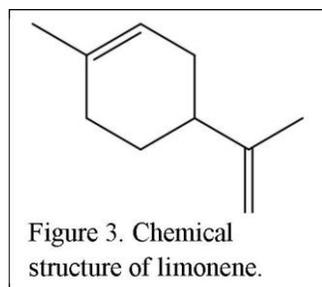
A detailed description of the NIR-LDI-AMS, as well as operating characteristics and performance, is given in a recent publication.¹ Briefly, using oleic acid aerosol (generated by homogeneous nucleation) as a model system, we measured a limit of detection of 0.14 μg total sampled mass (Figure 1), an improvement of over to orders of magnitude compared to existing instruments.



We also demonstrated the ability of the NIR-LDI-AMS to measure secondary organic aerosol (Figure 2) at atmospherically relevant levels below $10 \mu\text{g m}^{-3}$ with a two minute time resolution.



Using this research infrastructure, we were able to make the first measurements to demonstrate the stepwise oxidation of an aerosol precursor, delineating the initial oxidation step (leading to low volatility products that nucleated to aerosol particles) from secondary, heterogeneous oxidation of the particle phase. This work focused on limonene (Figure 3), a doubly unsaturated terpene commonly emitted by terrestrial vegetation.



Limonene is especially interesting (from a chemical perspective) because of the dramatically different ozonolysis rates of the two double bonds: 30 times greater rate for the endocyclic double bond. Details of this research were published recently.² Briefly, we were able to show conclusively that oxidation of limonene occurred in two steps, with initial oxidation of the endocyclic double bond leading to particle formation, followed by subsequent *heterogeneous* oxidation of the remaining (exocyclic) double bond. From aerosol mass spectra (Figure 4), we were able to monitor the evolution of “two-step” ozonolysis products ($201 m/z$ and $187 m/z$ in Figure 5) relative to initial oxidation products from oxidation of the endocyclic double bond only ($199 m/z$ in Figure 5).

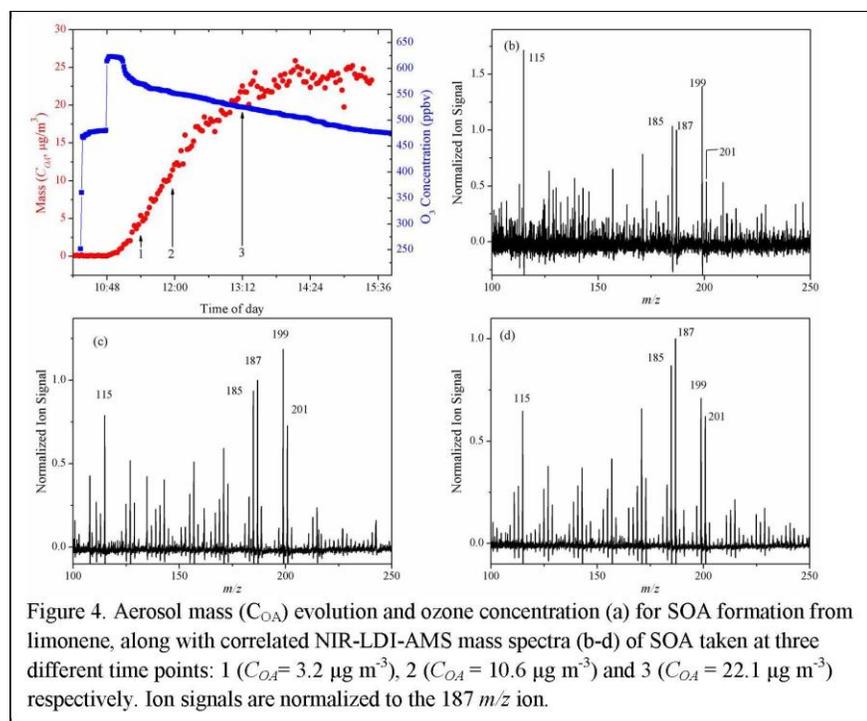
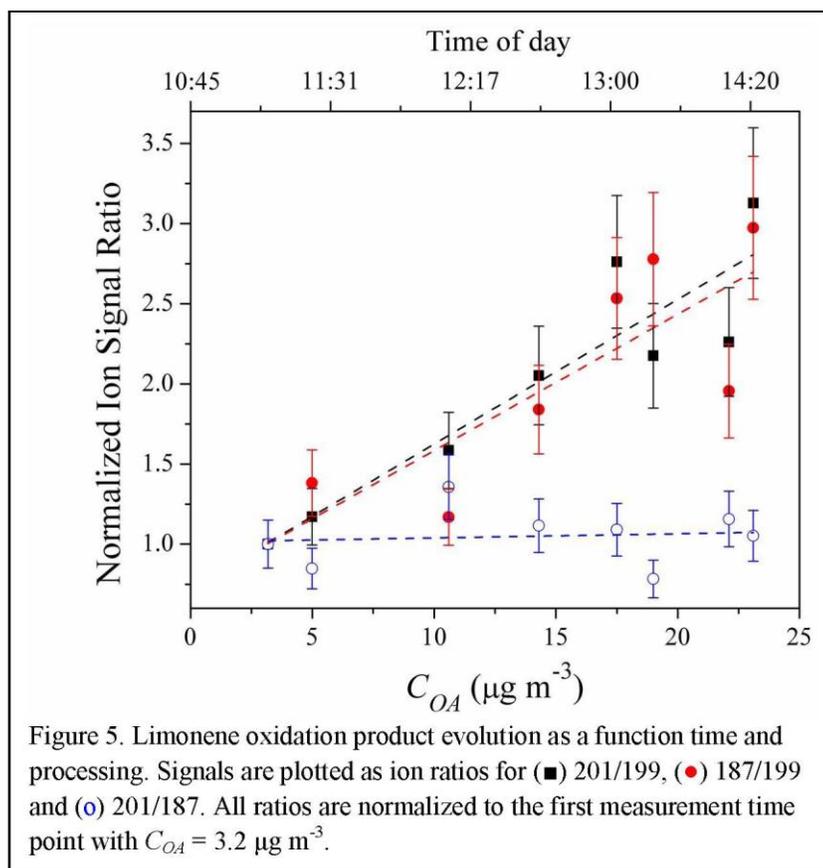


Figure 4. Aerosol mass (C_{OA}) evolution and ozone concentration (a) for SOA formation from limonene, along with correlated NIR-LDI-AMS mass spectra (b-d) of SOA taken at three different time points: 1 ($C_{OA} = 3.2 \mu\text{g m}^{-3}$), 2 ($C_{OA} = 10.6 \mu\text{g m}^{-3}$) and 3 ($C_{OA} = 22.1 \mu\text{g m}^{-3}$) respectively. Ion signals are normalized to the $187 m/z$ ion.



Conclusions

An environmental chamber has been constructed and characterized for the study of atmospheric reactions of volatile compounds. To present, the research has focused on the formation of aerosol from ozonolysis of biogenically derived precursors, such as pinene, limonene and isoprene. Work is in progress to extend this work to fuel derived precursors, such as toluene, xylene and pyrroles, which are likely to be only moderately reactive with ozone, requiring we modify our experimental conditions to employ hydroxyl radical as the primary oxidant. The ultimate challenge will be to study and understand aerosol formation from mixed biogenic-anthropogenic systems and the subsequent atmospheric (chemical) fate of the resulting aerosol. *Personnel and Deliverables:*

Funding for this project has contributed significantly to enhancing the research infrastructure at UVM. Furthermore, this project has contributed directly to the training of several graduate and undergraduate students (including three women) and was instrumental in acquiring an independent researcher grant from the National Science Foundation.

Results from this project have contributed to three peer-reviewed publications¹⁻³ and three presentations⁴⁻⁶ at scientific meetings.

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