Direct Observations of the Formation of Isoprene-derived SOA in Ambient Cloud Droplets

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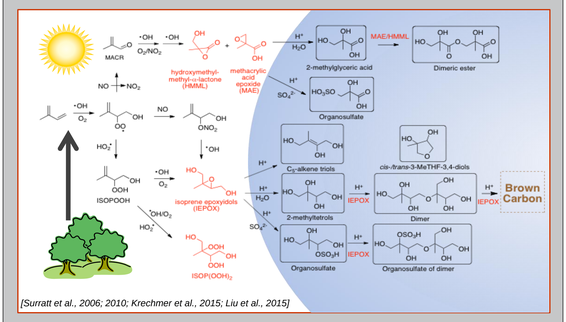
Multiphase Chemistry of Isoprene-Derived Oxidation Products

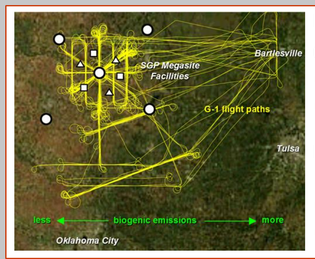
- Isoprene is the most abundant non-methane biogenic VOC
- Reactive uptake of isomeric isoprene epoxydiols (IEPOX) in the presence of sulfate particles is shown to be the dominant source of isoprene-derived SOA
- The rates and yields of IEPOX-SOA formation reactions depend on aerosol acidity, sulfate concentration, water content, and the presence of other organics
- Very few studies focused on chemistry in cloud droplets



[Surratt et al., 2006; 2010; Krechmer et al., 2015; Liu et al., 2015]

HI-SCALE Field Campaign

- Data acquired during Holistic Interactions of Shallow Clouds, Aerosols, and Land-Ecosystems campaign provide direct evidence for IEPOX-SOA formation in cloud droplets



Phase 1:

04/24-05/20, 2016

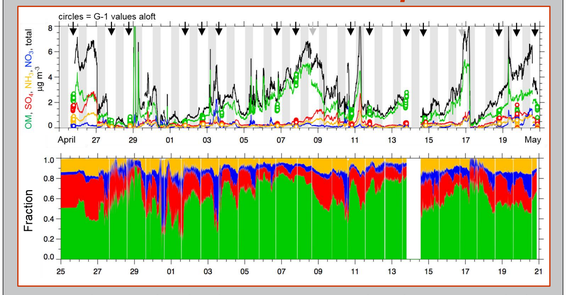
- 17 flights, 57.8 hrs total
- 9 in clouds, 6.5 hrs

Phase 2:

08/28-09/23, 2016

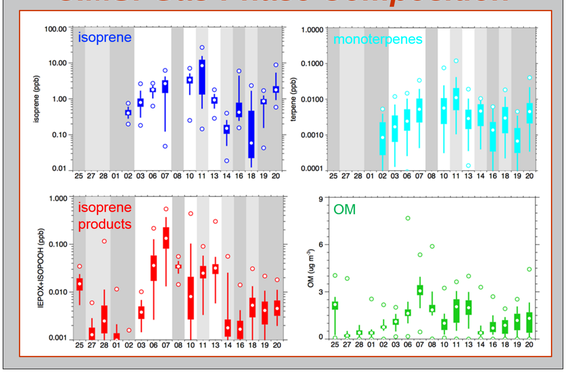
- 21 flights, 47.8 hrs total
- 9 in clouds, 1.1 hrs

AMS: Bulk Aerosol Composition



- Organics are the dominate component, but there are periods where inorganics represent more than 50% of total mass

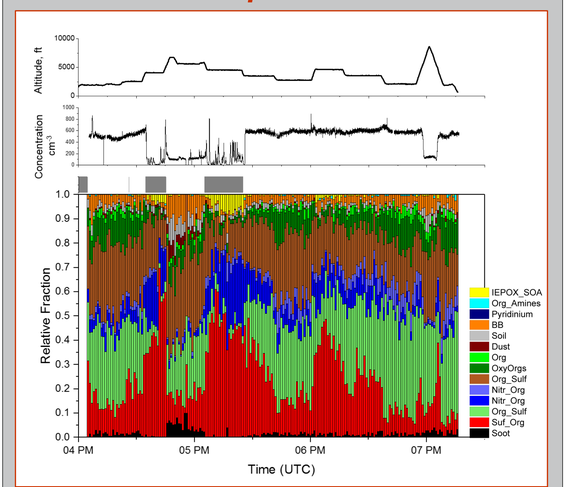
CIMS: Gas-Phase Composition



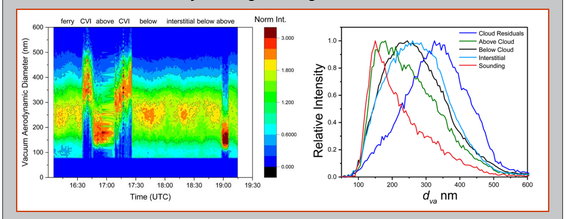
miniSPLAT: Size and Composition of Individual Aerosol Particles

- Sampling rate: size ~5000 p/sec, composition ~20 p/sec)
- Refractory and non-refractory fractions in each particle
- Number concentrations (1 sec, particles, d>85 nm)
- Size distributions (d_{va}) (~1 min)
- Sampled through Isokinetic and CVI inlets

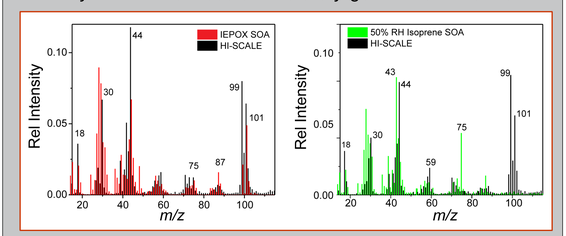
April 25



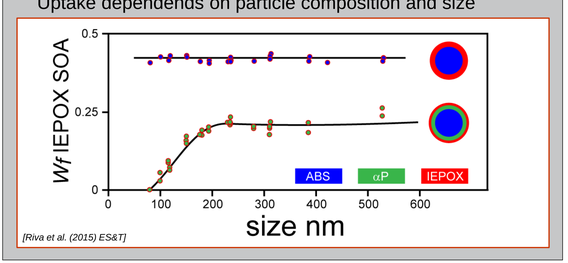
- Aerosol compositions, size distributions, and number concentrations vary during the flight



- Droplet residuals were significantly larger than particles sampled outside the cloud
- Cloud droplet residuals were comprised of individual particles with high relative fractions of sulfate and nitrate and significant fraction of particles with mass spectra that are nearly identical to those of laboratory-generated IEPOX-SOA



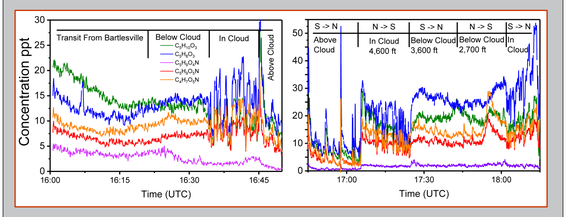
- Previously we demonstrated that IEPOX uptake by pure sulfate particles is a volume-controlled process
- Acidity enhances IEPOX-SOA formation rates
- Thin α-pinene SOA (αP) coatings greatly hinders IEPOX reactive uptake by ammonium bisulfate (ABS) particles. Uptake dependends on particle composition and size



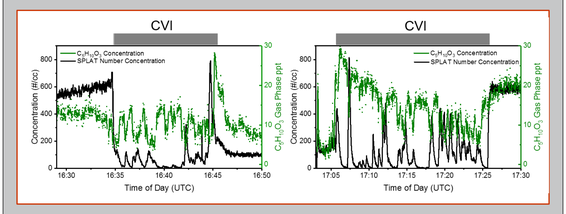
[Riva et al. (2015) ES&T]

CIMS: Isoprene Oxidation Products

- Concentrations of isoprene oxidation products (e.g. $C_5H_{10}O_3$ - ISOPOOH / IEPOX) are nearly constant below the cloud
- Concentrations of isoprene oxidation products (e.g. $C_5H_{10}O_3$ - ISOPOOH / IEPOX) vary greatly within the cloud

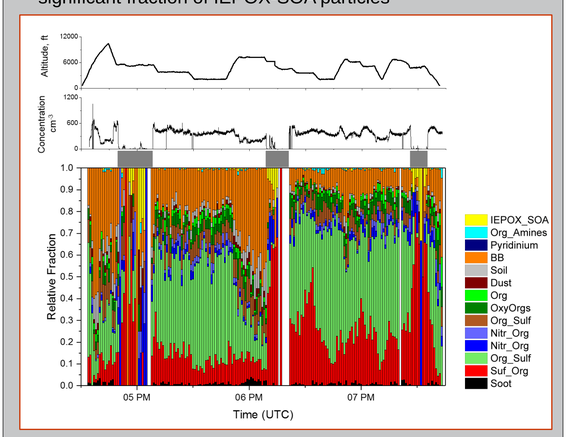


- $C_5H_{10}O_3$ - ISOPOOH / IEPOX concentration measured by CIMS is anti-correlated with number concentrations of droplet residuals behind the CVI measured by miniSPLAT



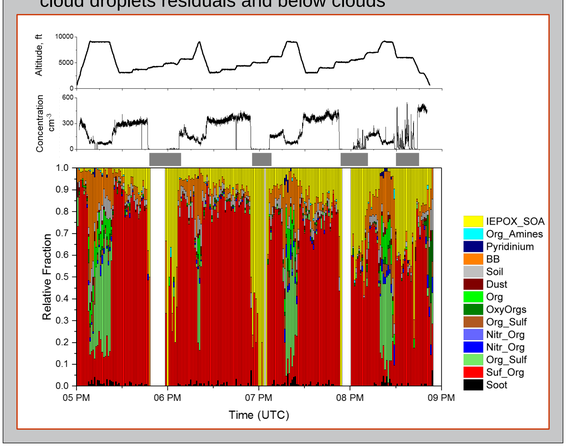
May 11, 2016

- Similar to the observations on April 25, cloud droplet residuals characterized on May 11 were larger than particles sampled outside the cloud and comprised of individual particles with high relative fractions of sulfate and nitrate and significant fraction of IEPOX-SOA particles

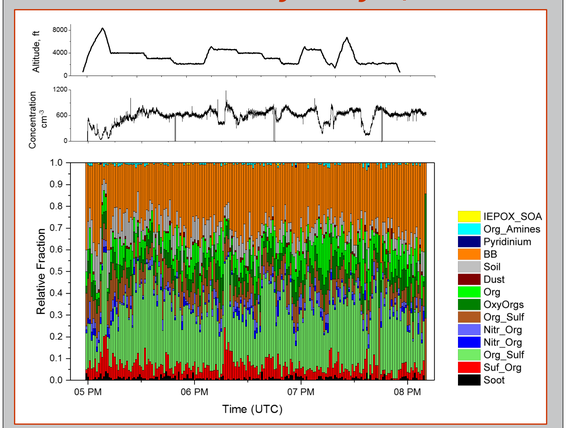


May 18, 2016

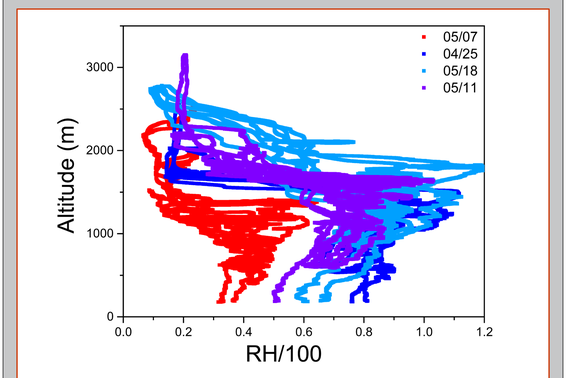
- Large fraction of IEPOX-SOA particles were observed in cloud droplets residuals and below clouds



Cloud-free Day: May 7, 2016



- CIMS measurements indicate very high concentrations of isoprene oxidation products. Concentration of $C_5H_{10}O_3$ (ISOPOOH / IEPOX) reached over 500 ppt
- Measurements by miniSPLAT point to large fraction of biomass burning aerosol and particles composed of organic mixed with small amounts of sulfate
- Most importantly, under these low RH conditions IEPOX-SOA formation ***was not*** observed in sulfate-dominated particles



Summary

- Data acquired during HI-SCALE field campaign provide direct evidence for IEPOX-SOA formation in cloud droplets
- We find that the composition and size distribution of cloud droplet residuals were markedly different than that of aerosol particles sampled outside the cloud
- Cloud droplet residuals were larger, contained high relative fractions of sulfate and nitrate and significant fraction of particles with mass spectra that are nearly identical to those of laboratory-generated IEPOX-SOA particles
- The observed cloud-induced formation of IEPOX-SOA was accompanied by simultaneous decrease in measured concentrations of IEPOX and other gas-phase isoprene photooxidation products
- We show that aqueous aerosol/cloud phase provides a medium for reactive uptake of isoprene photooxidation products, and in particular, isomeric isoprene epoxydiols (IEPOX), with reaction rates and yields being dependent on aerosol acidity, water content, sulfate concentration, and organic coatings
- Combined cloud, aerosol, and gas-phase measurements are used to develop and evaluate model treatments of aqueous-phase isoprene SOA formation

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