Processing of Biogenic Organics from the Surface to the Clouds

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EMSL

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

NSF

SOAS Aircraft Effort:

- Characterize CO_2, CH_4, O_3, H_2O vertical profiles
- **Compare atmospheric particle & cloud water organic molecular composition to gain insights into in-cloud aqueous-phase reaction pathways**

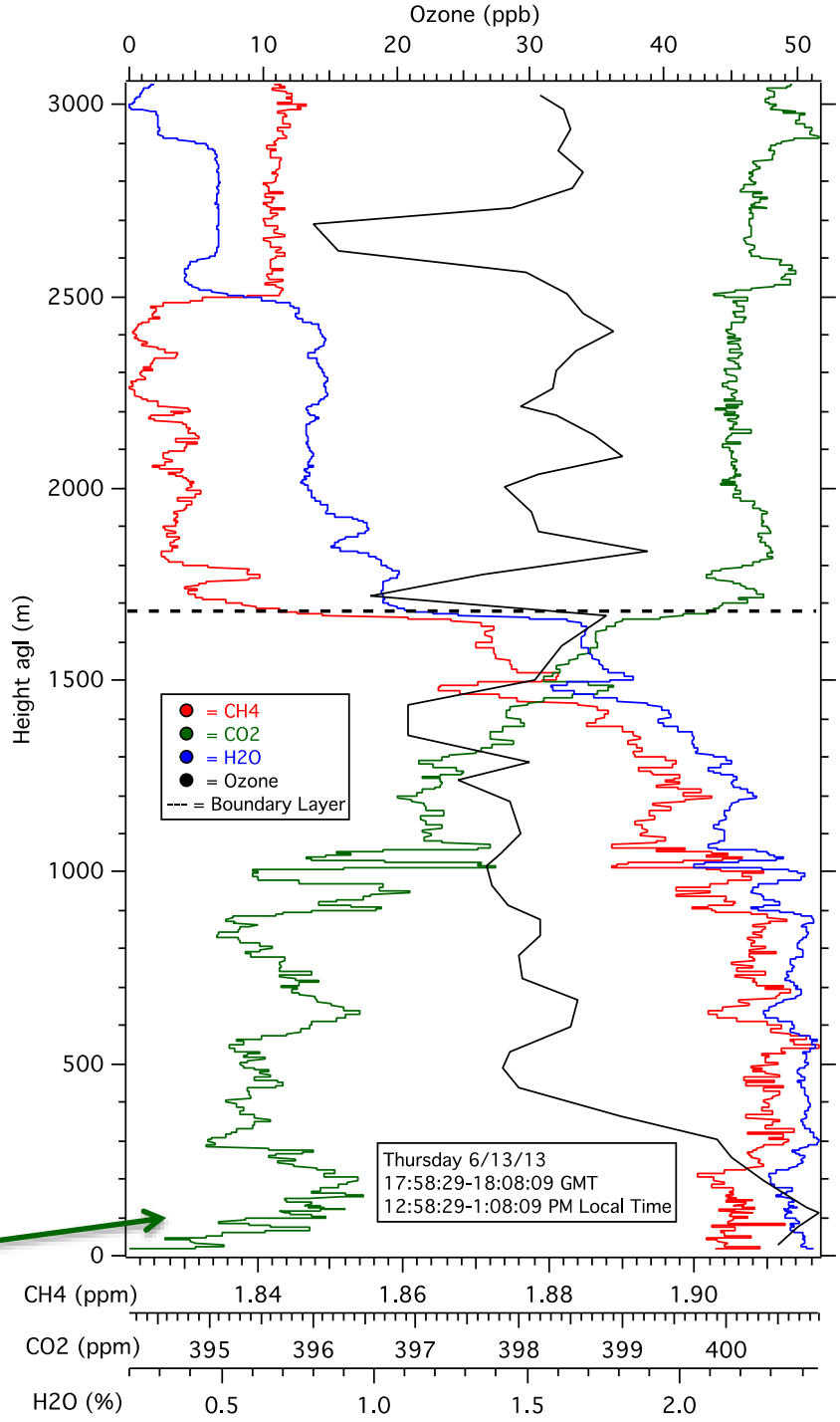
SOAS Centerville Ground Efforts:

- Isoprene nitrate (including lab studies, **Xiong et al., 2015, *ACP***), PAN and MPAN, speciated monoterpene concentrations
- Single-particle morphology & chemical composition (CCSEM-EDX and Raman microspectroscopy)
- Organic molecular composition (nano-DESI-MS)
- Vegetation survey

Clear Sky Vertical Profiles

- CO_2, CH_4, H_2O
- O_3
- Temperature, turbulence parameters

Decreased CO_2 over forest



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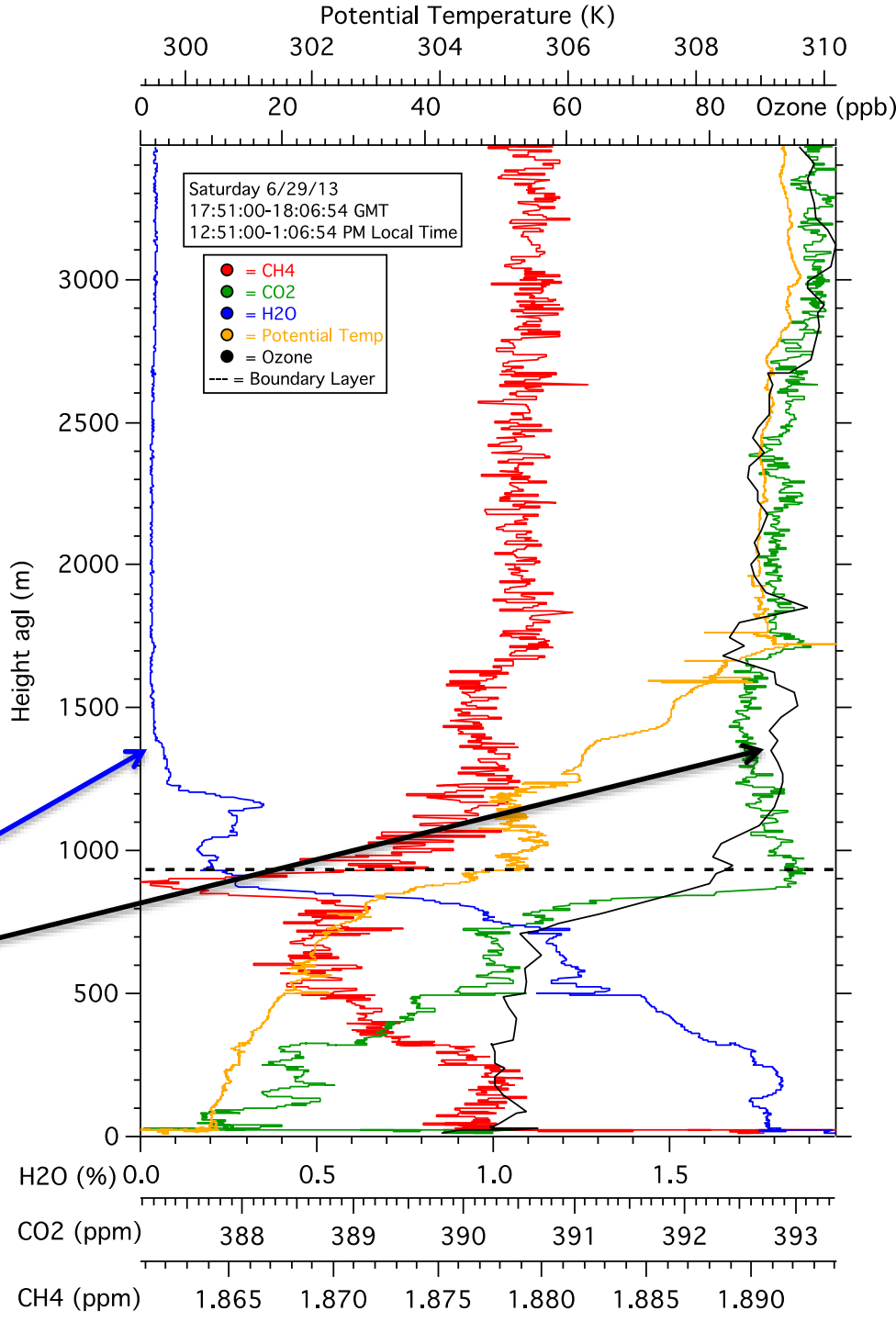
June 29, 2013 - Case of Stratospheric Intrusion



Very low H_2O

High O_3

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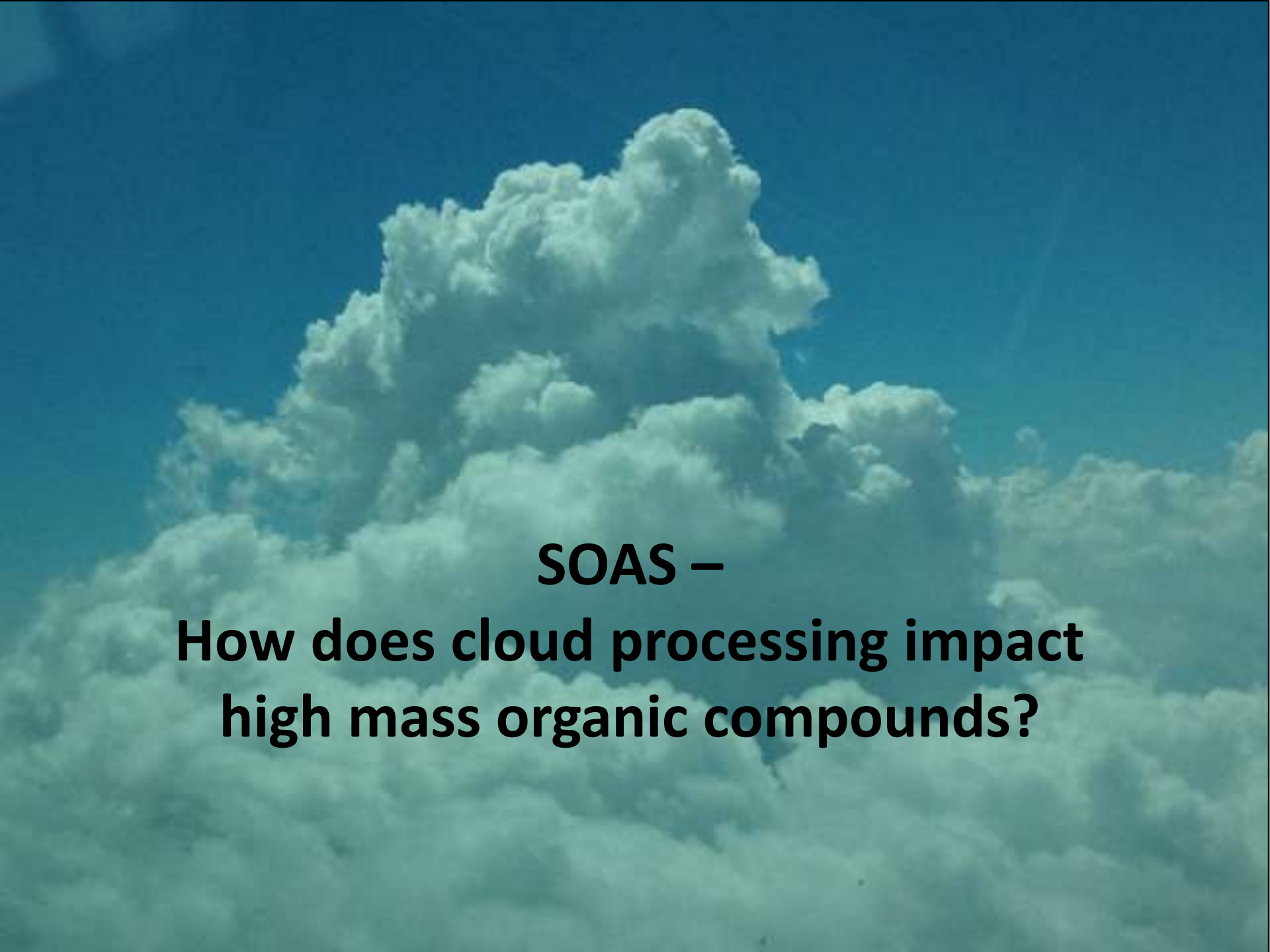
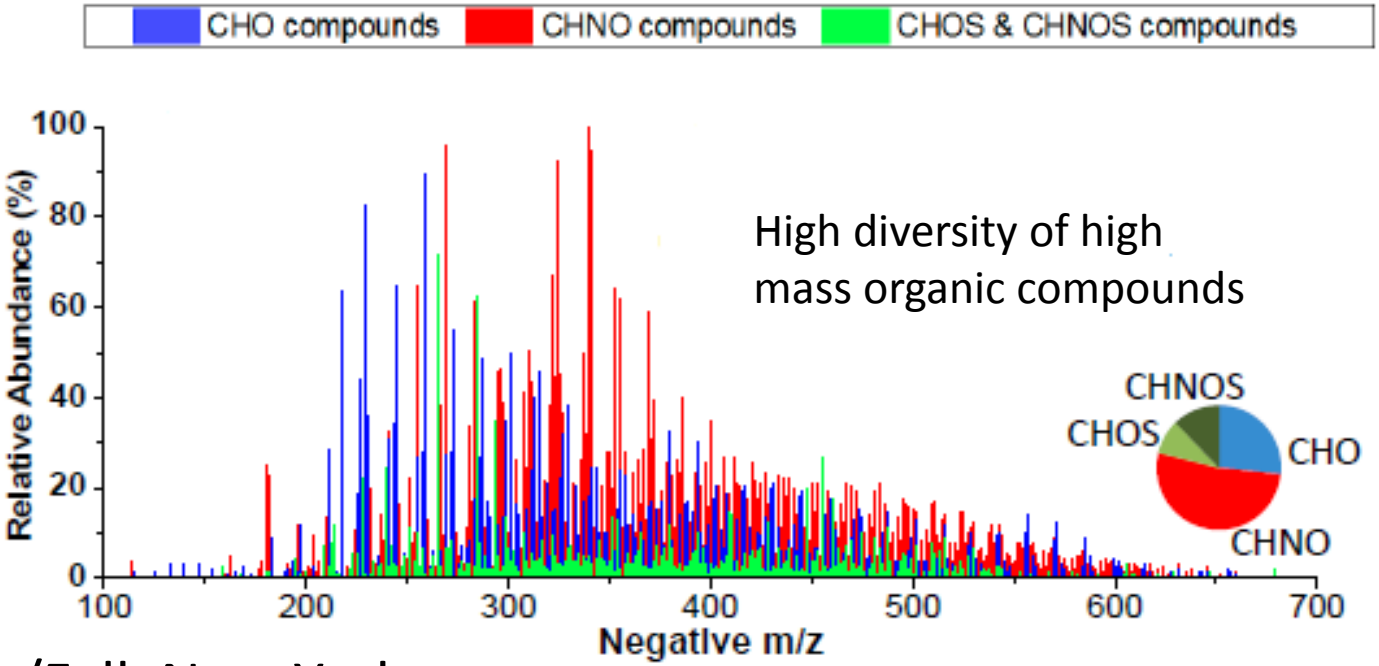

SOAS –
How does cloud processing impact
high mass organic compounds?

Few Cloud Water Measurements of Individual High Mass Organic Compounds Exist

- Fall, Germany – Feng and Möller 2004, *J. Atmos. Chem.*
- Summer/Fall, Germany – Van Pinxteren and Herrman 2007, *J. Chromat. A*
- Winter, Colorado – Samy et al. 2010, *Atmos. Environ.*
- **Summer, Missouri – Pratt et al. 2013, *Atmos. Environ.***
- Winter, Colorado – Zhao et al. 2013, *ACP*

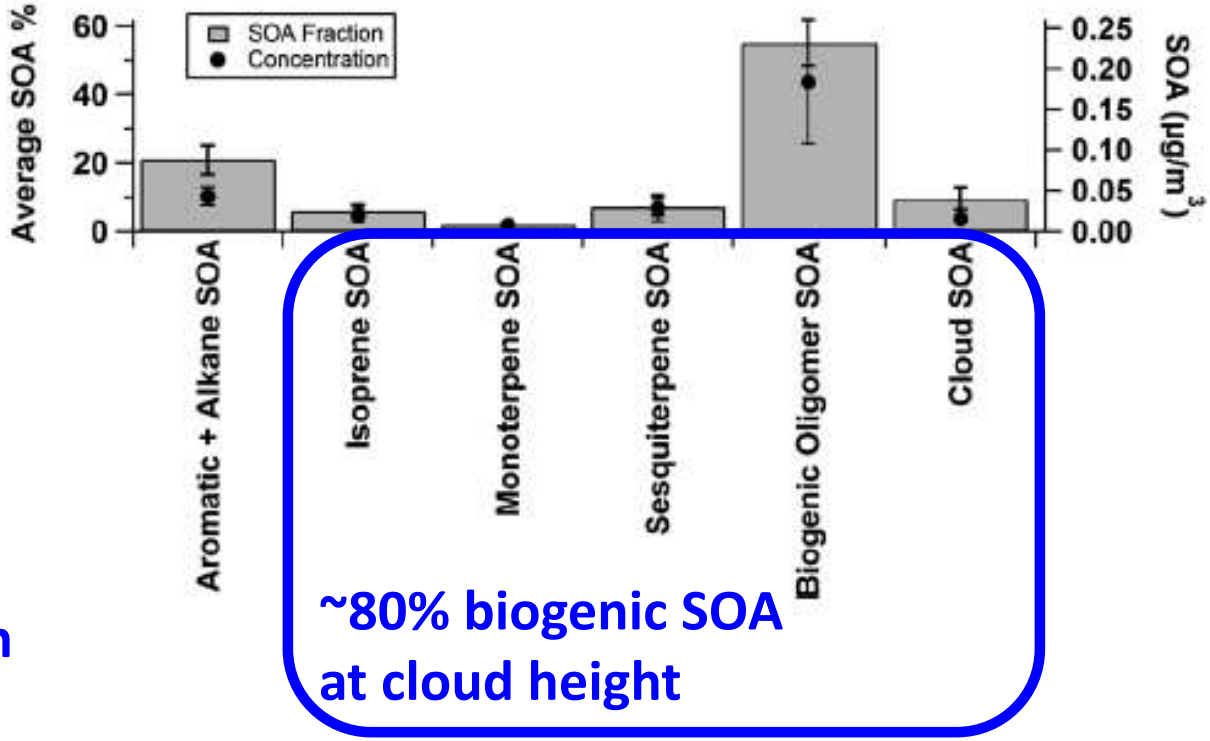


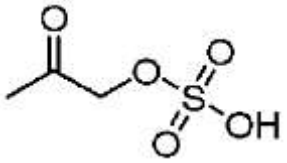
- Summer/Fall, New York – Sagona et al 2014, *J. Chromatogr. A*

Previous EPA STAR Grants: Biogenic VOC Influence on Cloud Water

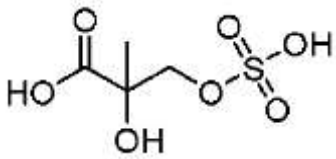
Pratt et al. 2013, *Atmos. Environ.*
*EPA STAR: G2007-STAR-E1 & 83504101

- Cloud water collection & ESI-MS analysis
- CMAQ simulations for cloud sampling altitude in July over the Missouri Ozarks (high isoprene emissions)
- **Detection of isoprene-derived organosulfates in cloud water:**

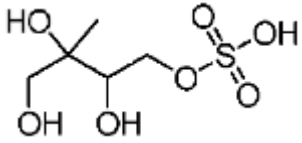




m/z 153



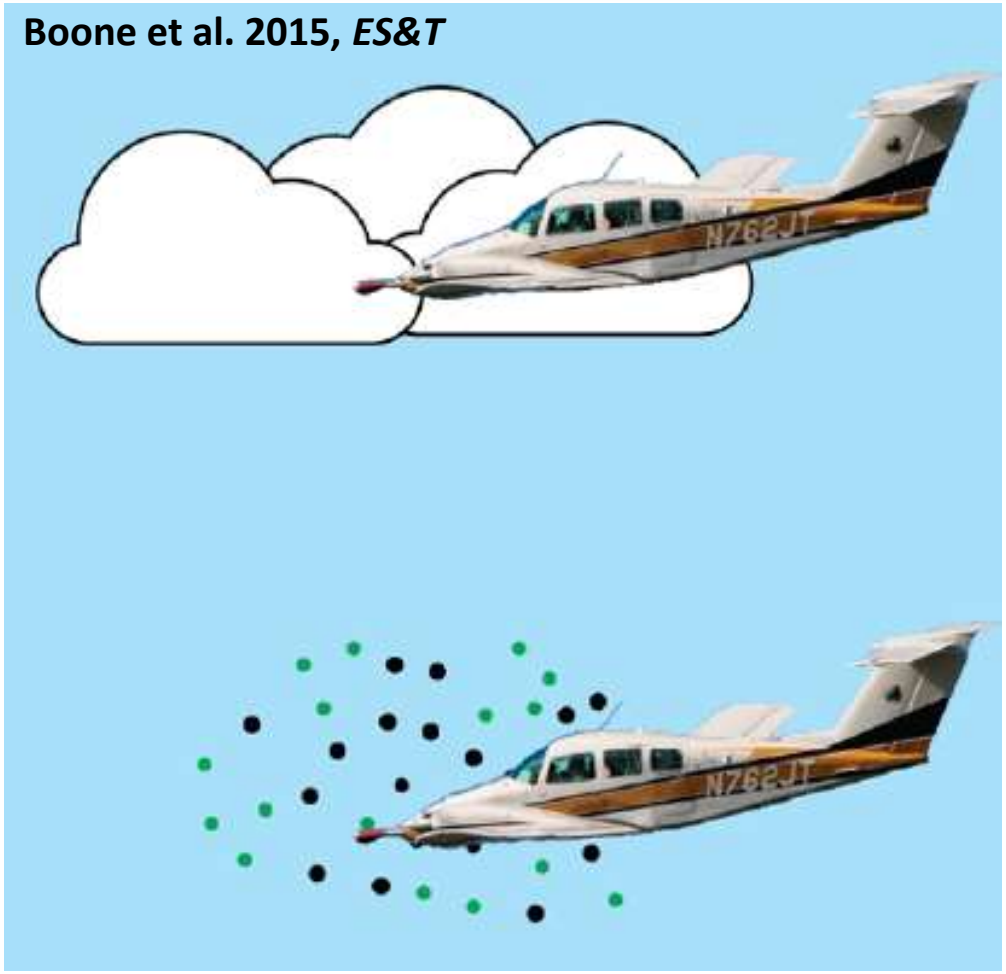
m/z 199



m/z 215

- All proposed structures (Surratt et al. 2007, *ES&T*) are primary organosulfates that are resistant to hydrolysis (Darer et al. 2011, *ES&T*).

Focus: Aerosol & Cloud Sampling



Step 2: Cloud water sampling at ~1.8-2.0 km asl (middle/upper sections of developing cumulus clouds)

Step 1: Below-cloud particle sampling at ~1-1.2 km asl

- June 10, 13, & 27 flights with particle + cloud water sampling
- Moderate → very high convective instability (boundary layer influence)

Aircraft-based Sample Collection

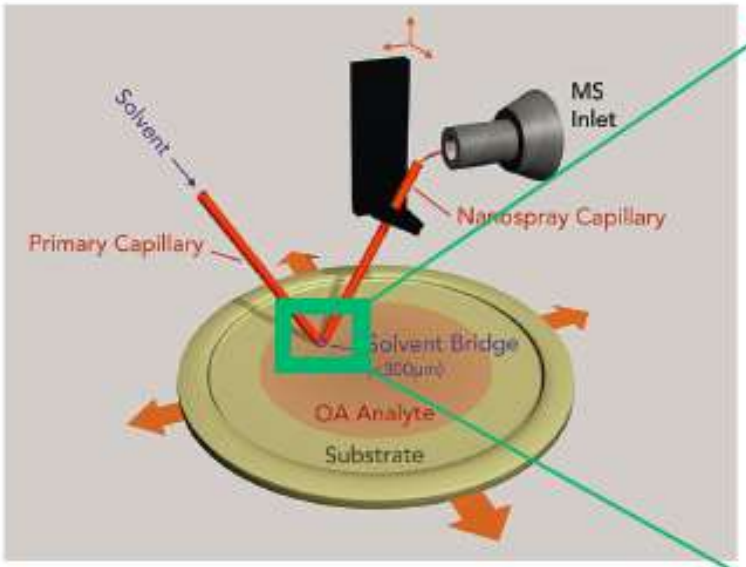
- ***Below-cloud particle* collection**
  - ~30-45 min of sampling onto Al foil using a rotating drum impactor (Bateman et al. 2009, *PCCP*)
  - Analyzed particles from Stage 2 (0.34-1.2 µm) – expected to have activated to form cloud droplets
  - Estimated ~20 ng of organic material collected

- ***Cloud water* collection**
  - ~30-45 min of sampling using a modified Mohnen slotted rod cloud water collector (Huebert et al. 1988, *J. Atmos. Chem.*)
  - Cloud droplet 50% cut-point of ~5.5 µm (Kim & Boatman 1992, *J. Atmos. Ocean Technol.*)
  - Typically ~5 mL of cloud water collected

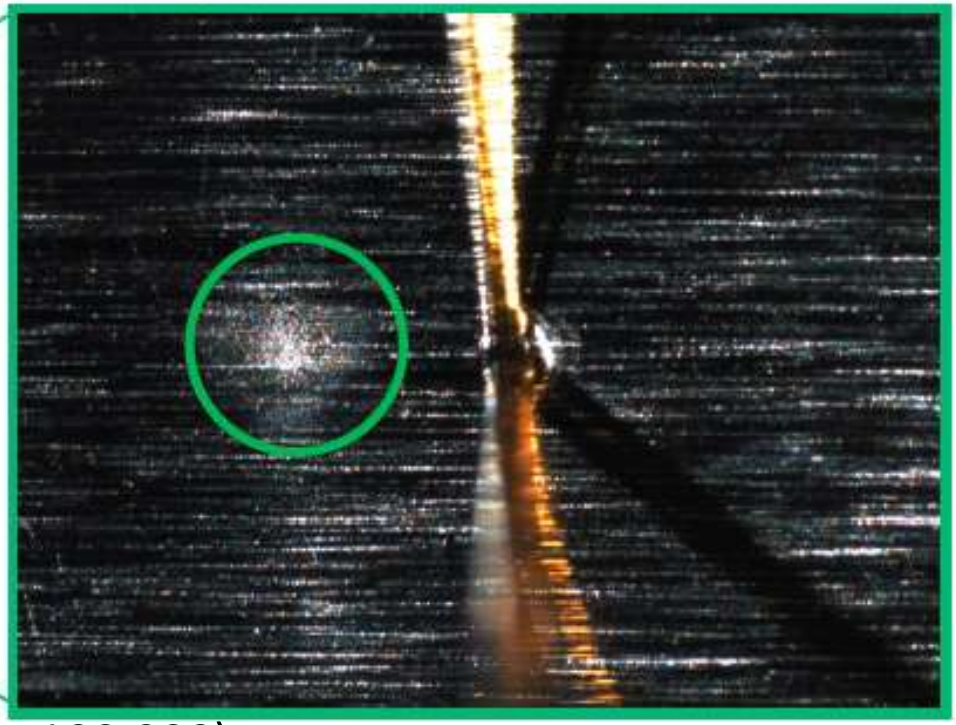
cloud water collector

Mass Spectrometry Analysis

- Cloud water: Direct injection electrospray ionization (ESI), following acetonitrile addition (70% by volume)
- Atmospheric particles: Nanospray desorption electrospray ionization (nano-DESI) using acetonitrile/water (70/30, by volume) as the solvent

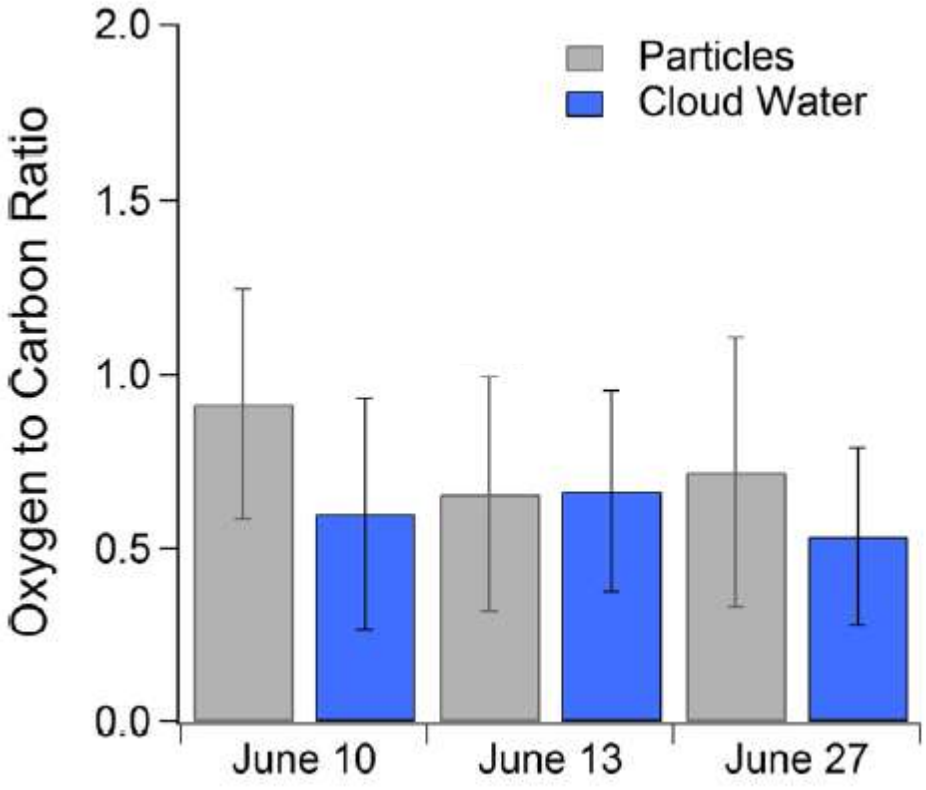


Roach et al. 2010, *Analytical Chem*.



- Orbitrap mass spectrometry (R = 100,000)
  - Negative ion mode; *m/z* 150-1000 (focus on *m/z* <400); Kendrick mass defect analysis used to assign peaks

No Change in Bulk O:C of High Mass Organics Observed with Cloud Processing

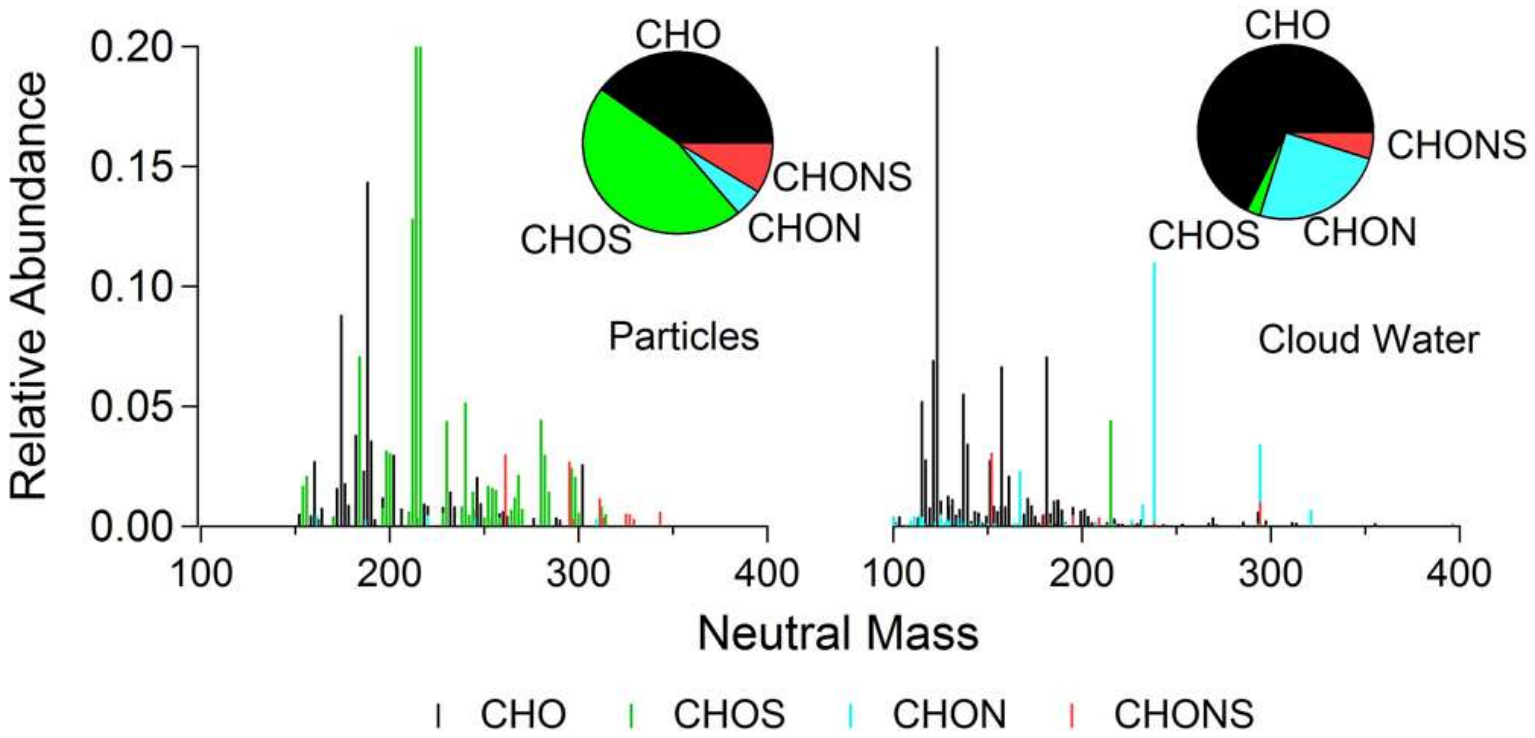


Boone et al. 2015, *ES&T*

- Expected organic compounds in cloud water to have a higher O:C ratio based on many bulk aqueous photochemistry lab studies (Ervens et al. 2011, *ACP*)
- However, no O:C ratio change in recent biogenic SOA aqueous photochemistry studies (Nguyen et al. 2012, *ACP*; Romonosky et al. 2014, *JPCA*)

Below-Cloud Aerosol vs. Cloud Water

Example Mass Spectra



General Trends:

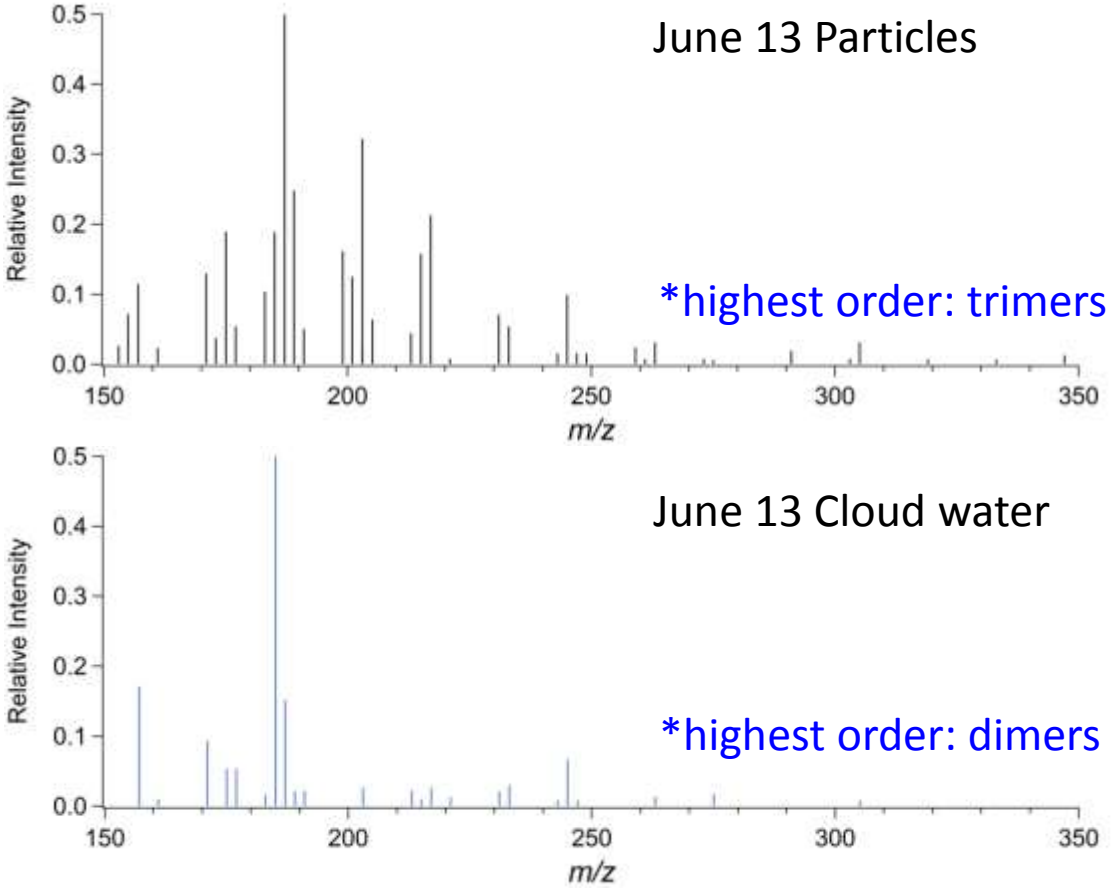
- Significant decreases in CHOS & increases in CHON (number) from particles → cloud water
- Decreasing overall molecular masses from particles → cloud water

Boone et al. 2015, *ES&T*

Fragmentation of Isoprene SOA Oligomers in Cloud Water

2-methylglyceric acid (2MGA) oligomers (Surratt et al. 2006, *JPCA*)
& glycoaldehyde oligomers (Nguyen et al. 2011, *ACP*)

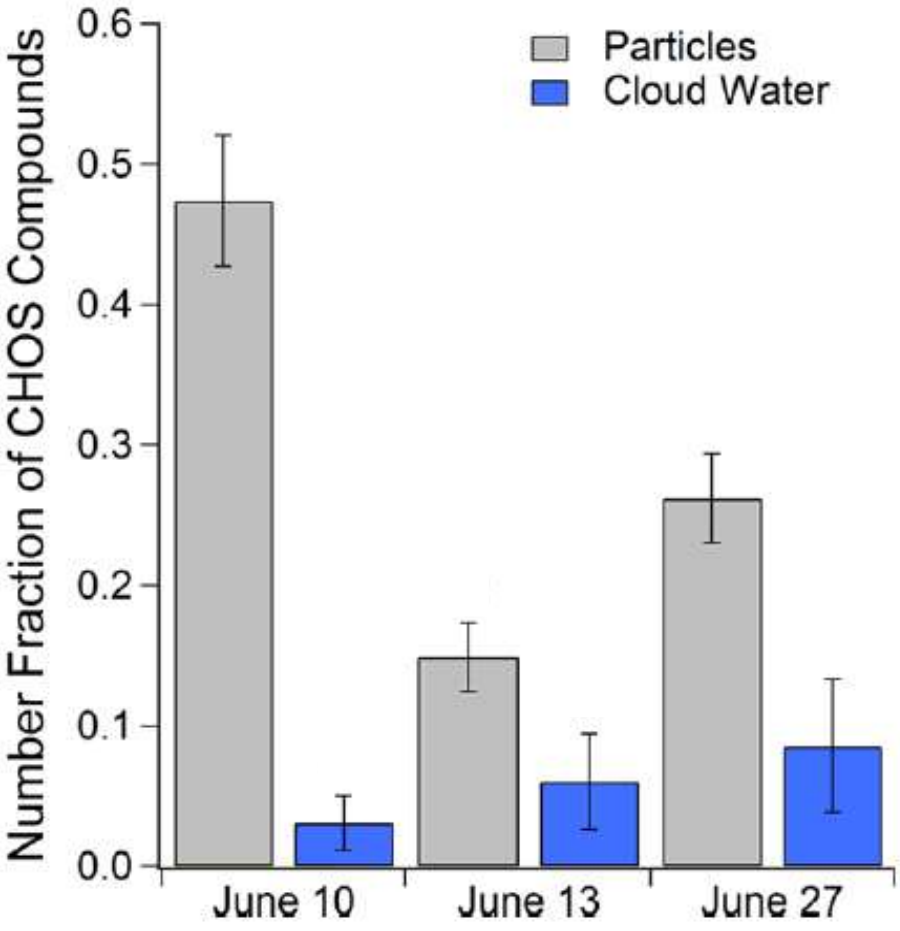
- 2MGA oligomers enhanced in particle-phase under lower RH (Nguyen et al. 2011, *ACP*; Zhang et al. 2011, *ACP*)
- 2MGA oligomers previously suggested to be observed in cloud water (Pratt et al. 2013, *AE*)

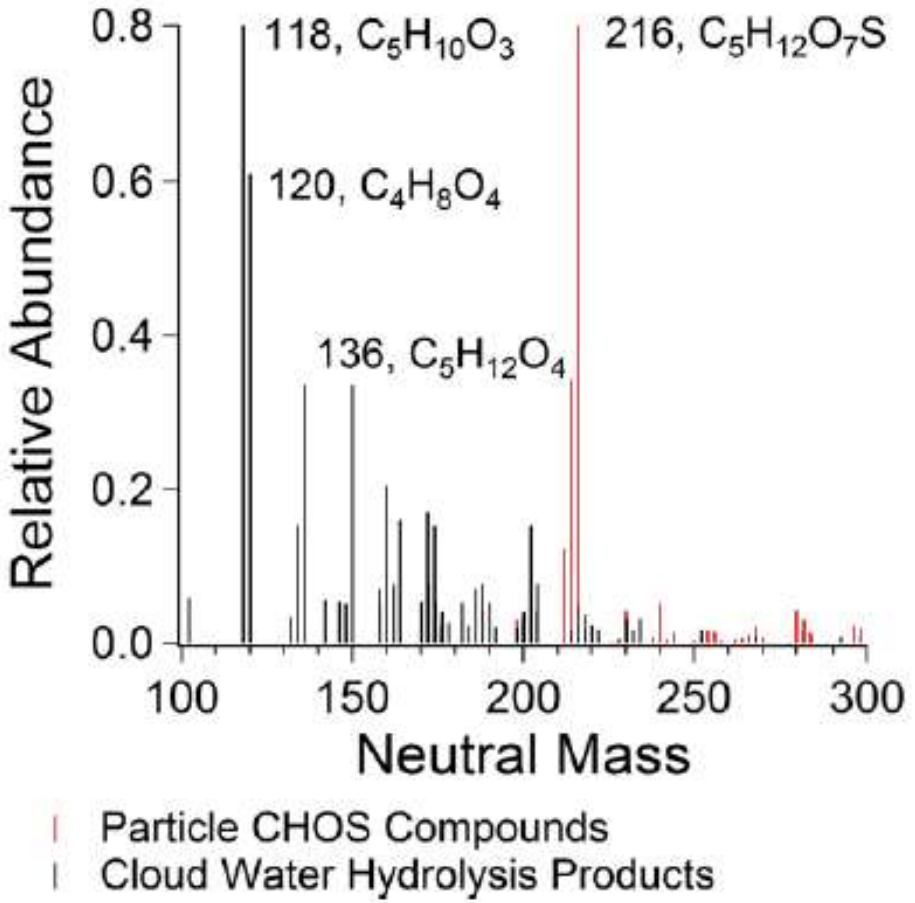


Reconstructed mass spectra

Boone et al. 2015, *ES&T*

In-Cloud Hydrolysis of Organosulfates



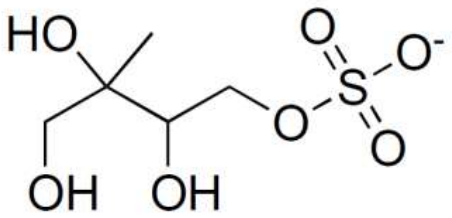


- $ROSO_3H + H_2O \leftrightarrow ROH + H_2SO_4$
- ~70% of CHOS compounds had corresponding hydrolysis product CHO formulas in the cloud water

Boone et al. 2015, *ES&T*

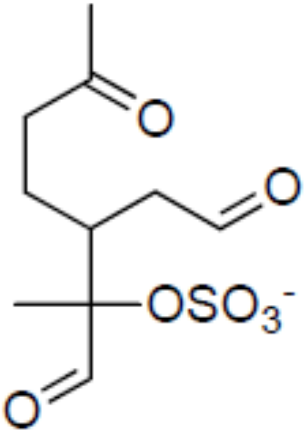
Most Abundant Organosulfates

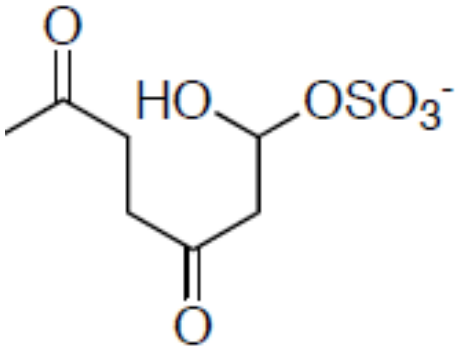
Across all particle-phase samples:



- *m/z* 211 ($C_5H_7O_7S^-$), 213 ($C_5H_9O_7S^-$), 215 ($C_5H_{11}O_7S^-$)
- Attributed to isoprene oxidation
- Particle samples by number: 30-50% of identified organosulfates attributed to isoprene oxidation, with the remaining identified organosulfates corresponding to monoterpene oxidation.
- Particle samples by intensity: >90% from isoprene oxidation

Other abundant organosulfates:
limonene oxidation products



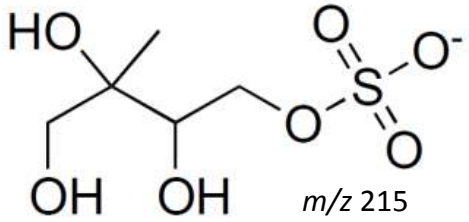


Boone et al. 2015, *ES&T*

Surratt et al. 2008, *JPCA*

Primary Organosulfates

- Only abundant organosulfate observed in cloud water (also observed in particles):

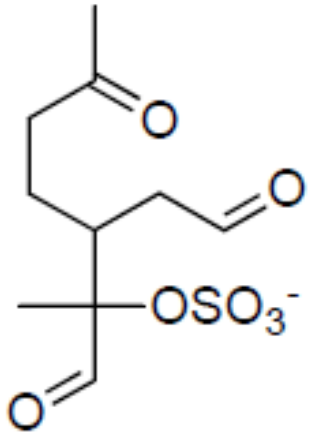


m/z 215

- Primary isoprene-derived organosulfate
- Hydrolysis lifetime >2500 h (Darer et al. 2011, *ES&T*)
- Previously measured in cloud water (Pratt et al. 2013, *Atmos. Environ.*)

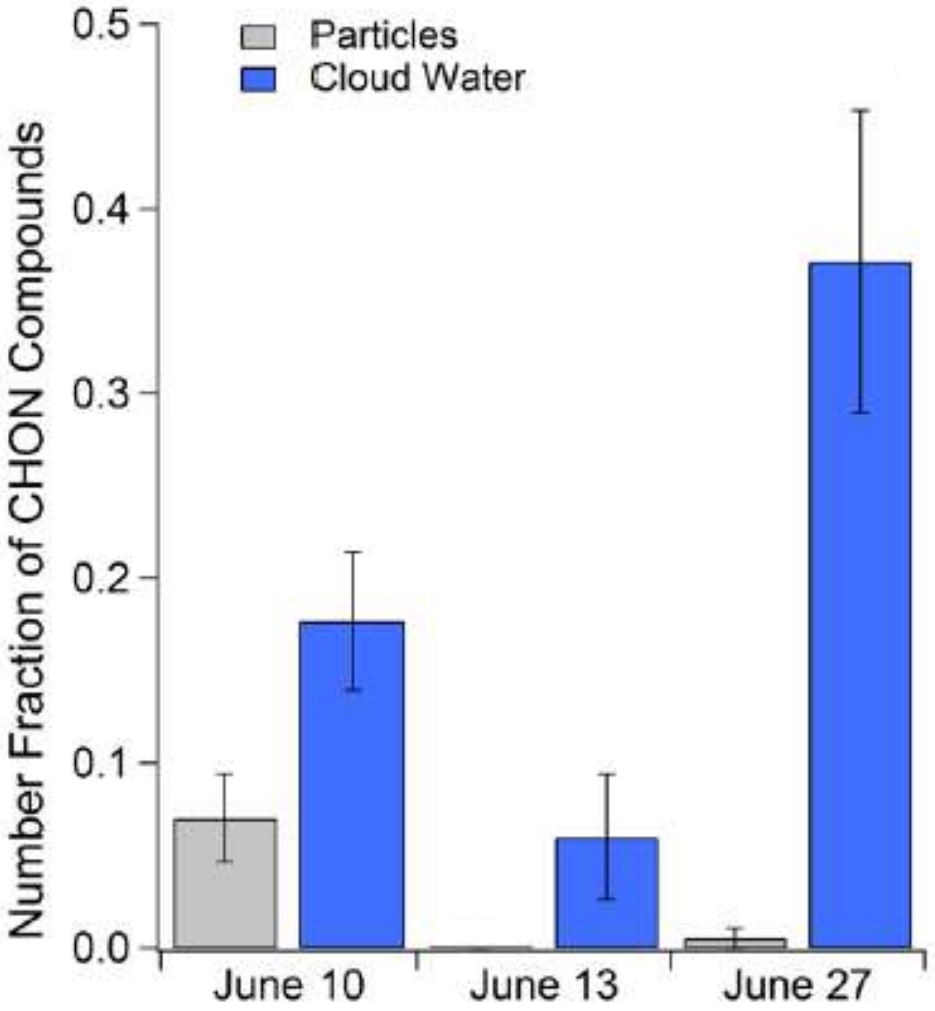
Tertiary Organosulfates

- Considering all proposed organosulfates with structures identified based on comparisons to lab studies:
  - 50-86% particle-phase organosulfates had tertiary functionality.
  - Shorter hydrolysis lifetimes of ~20-460 h at neutral pH, shorter in acidic cloudwater (Darer et al. 2011, *ES&T*)
  - Only 12% of these tertiary organosulfates were observed in cloud water.



Boone et al. 2015, *ES&T*

Formation of CHON Compounds

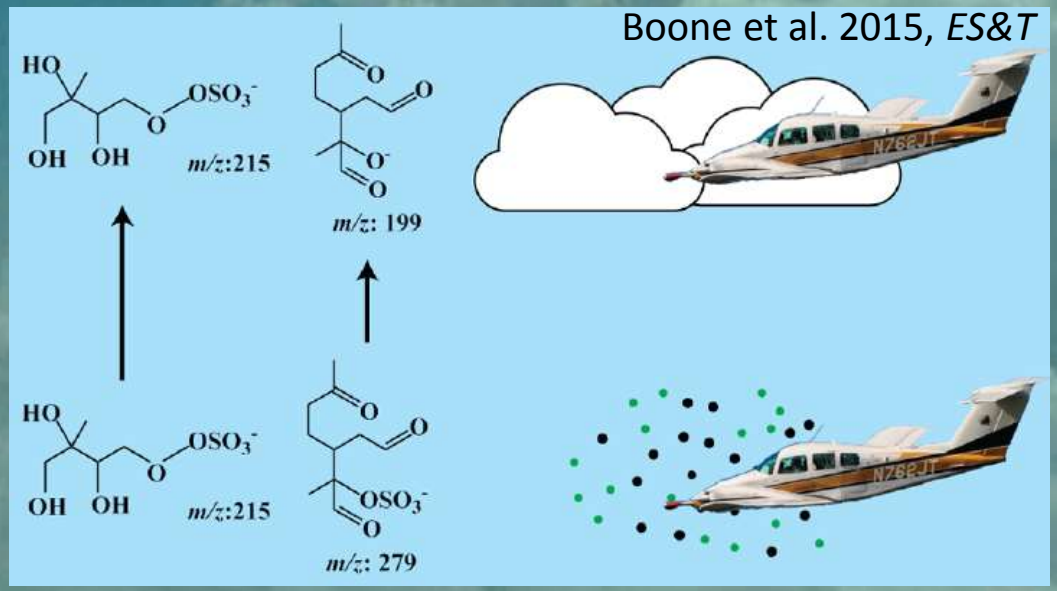


- On average, ~4x more CHON compounds detected in cloud water
- Average N:C ratio increased from 0.03 for particles to 0.14 for cloud water (0.3 for CHON compounds in cloud water)
- Not organonitrates, ~50% expected to have aromatic structures (chromophores)
- Formation mechanism? More lab studies needed!

Boone et al. 2015, *ES&T*

Aqueous Processing of Atmospheric Organic Particles in Cloud Droplets

- Significant influence of BVOC oxidation products during convective cloud events during SOAS
- No overall trend in O:C ratio with cloud processing
- In-cloud fragmentation of isoprene oxidation oligomers
- Hydrolysis of tertiary organosulfates in cloud droplets



- Formation of CHON compounds
- Additional measurements of high molecular weight compounds in atmospheric particles and cloud droplets are needed to assess cloud processing pathways!