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Combining Offline and Online AMS Analysis to Understand Aqueous Processing of Aerosols

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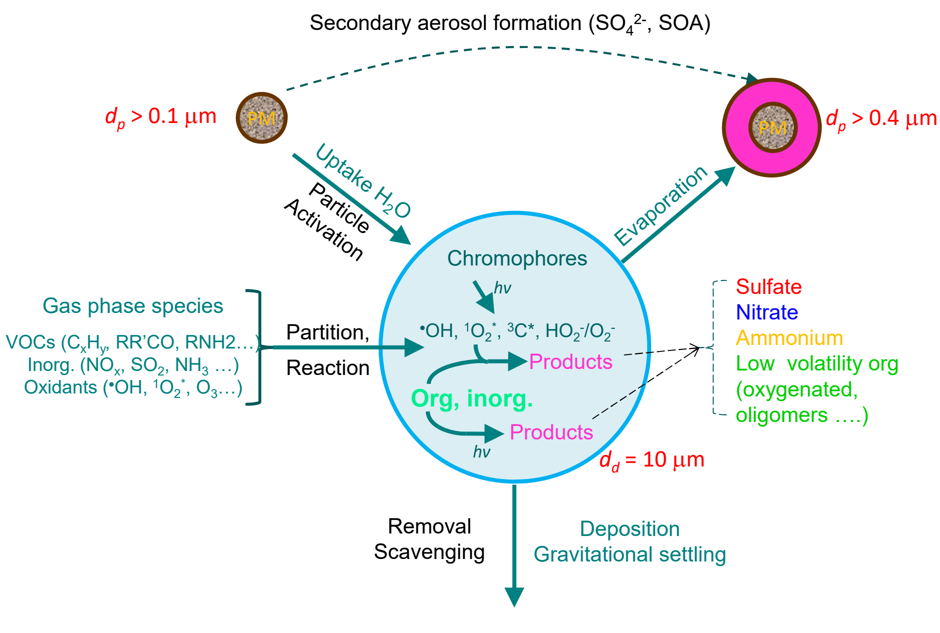
Cloud Processing of Aerosol



Why Study Aq. Processing of Aerosol?

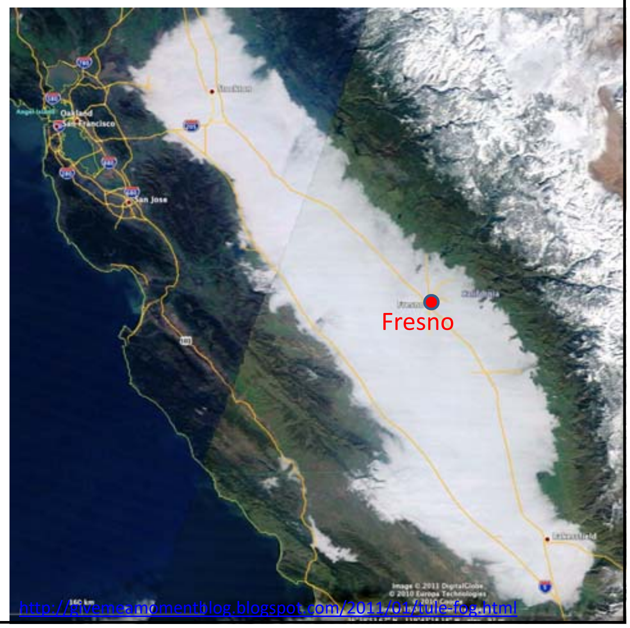
- Aq. processes
  - Influence aerosol comp, size distribution
  - Influence aerosol properties (optical, hygroscopic and microphysical)
  - Formation of surface-active and light-absorbing organic species can affect cloud properties.
- SOA formed through aqueous reactions (aqSOA) is poorly understood, although aqSOA is likely different than gasSOA:
  - Different reaction pathways
    - →different SOA composition
    - →Different hygroscopic and optical properties

Ambient and Laboratory Studies to Investigate Aq-Processes and Their Effects on Aerosols

- Field study of fog chemistry and influence of fog processing on aerosol Chemistry during winter in CA
  - Examine in-cloud formation and processing of aqSOA by comparing interstitial aerosol and cloud/fog water compositions and their evolution characteristics.
  - Compare aerosol composition and properties observed during cloudy/foggy conditions vs. those observed during clear conditions immediately before or after the presence of clouds/fogs to gain insights into how aqueous processing affects aerosol properties.
- Laboratory study aqSOA formation from phenolic compounds under cloud- and fog-drop conditions
  - Quantify kinetics and *SOA yields*
  - *C*haracterize SOA reaction products and photochemical evolution
  - Ambient Particle Characterization and Photochemistry

Study of Fog and Aerosol Chemistry in CA

- Regional nighttime fogs during winter in the Central Valley (CV) of California
- Rapid surface cooling at <u>night</u> due to radiation loss of heat
- Calm, stable met. conditions, suitable for studying aerosol processing.
- Near ground process, easy to access

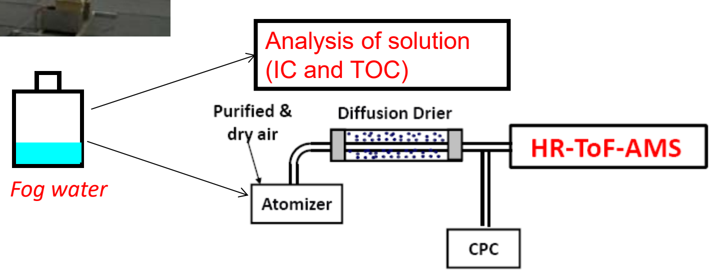


Ambient Aerosol Sampling

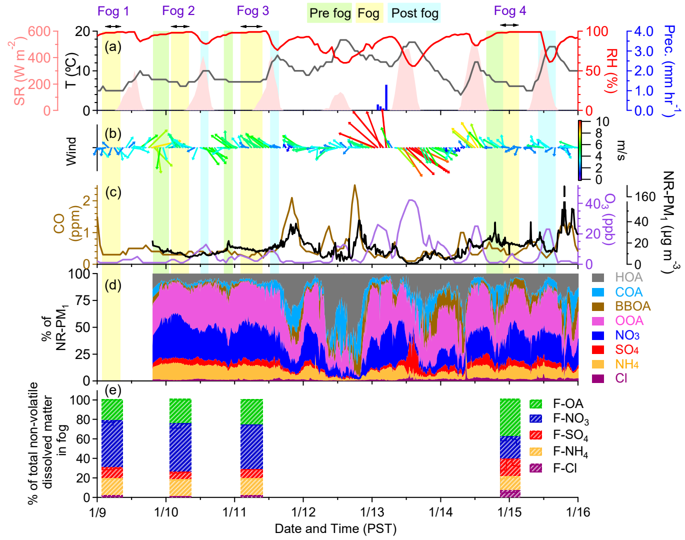
- In situ measurements with HR-ToF-AMS

Fog Sampling and Analysis

- Samples were collected with a Caltech Active Strand Cloud water Collector (CASCC)
- Droplets > 3.5 μm (50% efficiency) were collected
- Fog sampled analyzed using HR-ToF-AMS, Ion Chromatographs (IC), and TOC analyzer

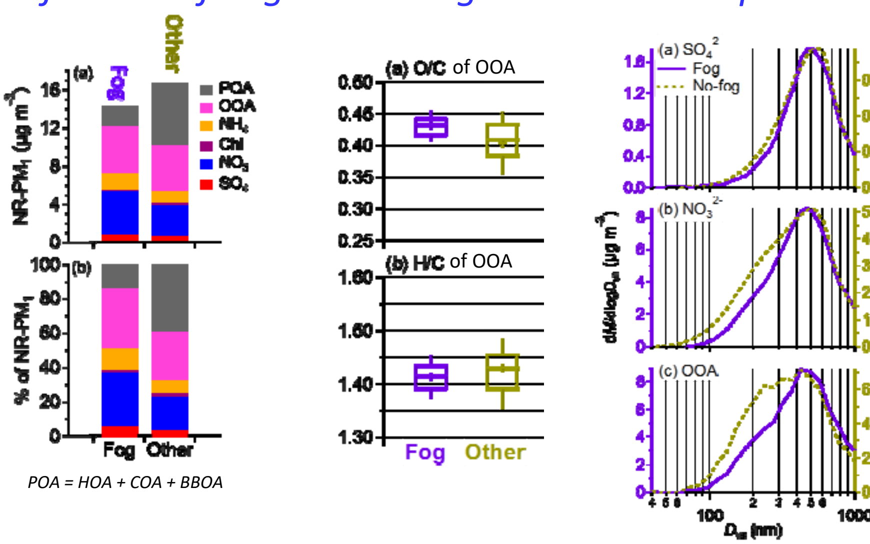


Observation of Fog & Aerosol in Fresno



- Calm wind condition persisted throughout fog events, as well as during the periods representing immediately before and after fog episodes.

Influence of Fog Processing on Aerosol Properties

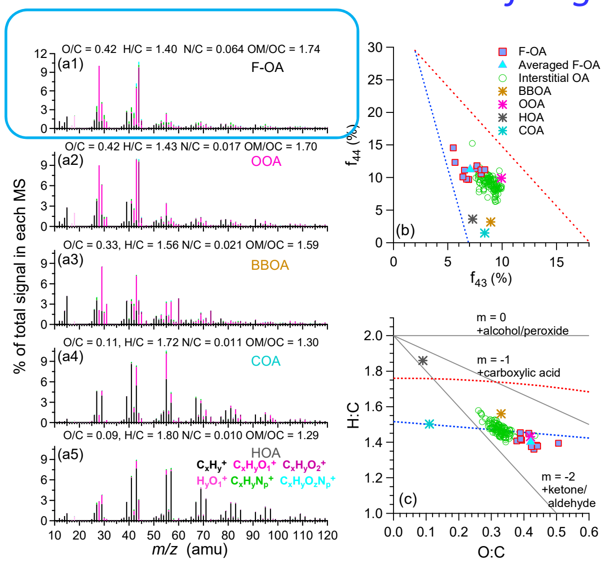


POA = HOA + COA + BBOA

Ge et al., Environ. Chem. 2012

- All secondary aerosol species increased during fog
- Sulfate is formed efficiently in fog water, increase of nitrate is mainly due to partitioning

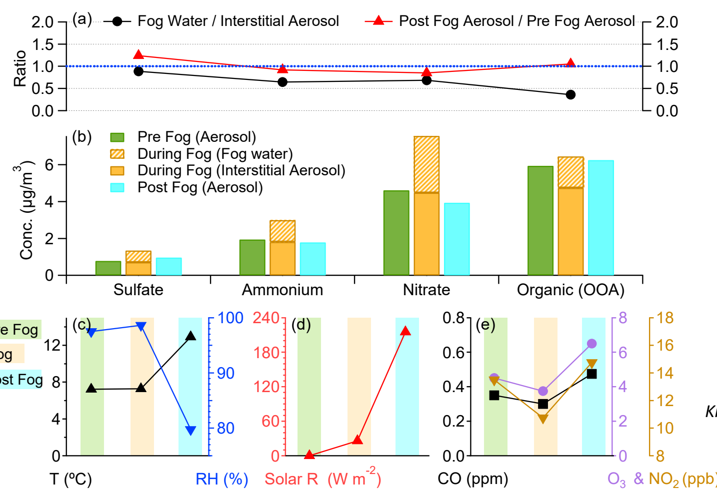
Chemical Characteristics of Fog Organics



Kim et al., ES&T, submitted
Ng et al., ACP, 2010

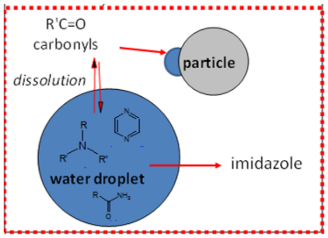
- F-OA is chemically more similar to OOA than to POA components
- F-OA appears to be more enriched of carboxylic acids and organic nitrogen compounds than OOA

Evidence for aqSOA Formation in Fog

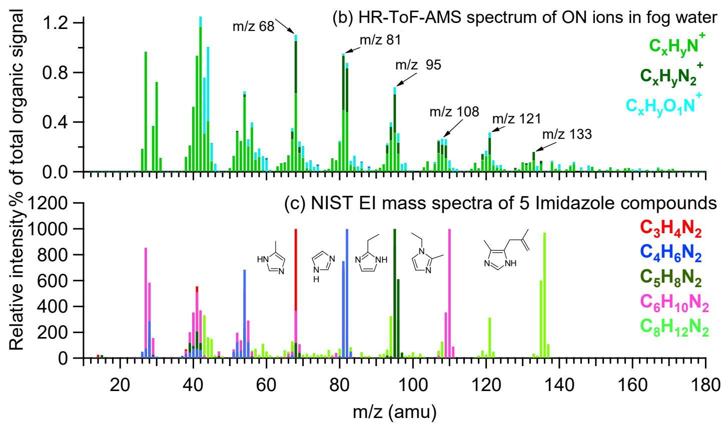


Kim et al., ES&T, submitted

- Calm wind condition persisted throughout the fog event, as well as during the periods representing immediately before and after fog episodes.
- Secondary species (Nitrate , Sulfate, OOA) are all enhanced during humid period→ Aqueous phase reaction influence to the formation of secondary organic and inorganic species.
- Sulfate is formed efficiently in fog water, increase of nitrate is mainly due to partitioning
- Part of the reduction of aerosol loading after fog may be due to depositional losses.

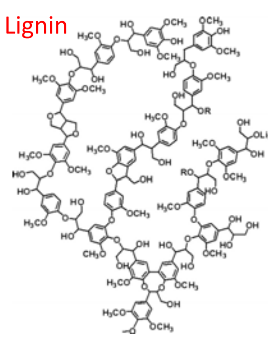


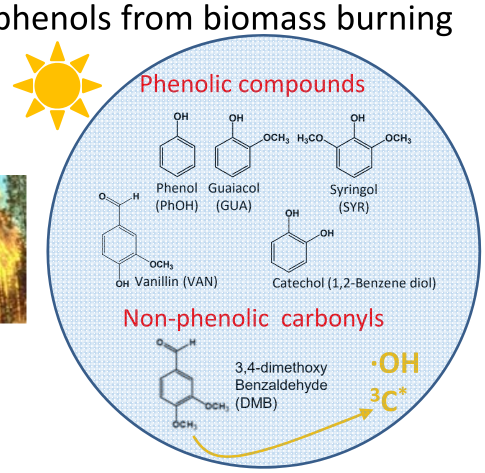
Carbonyl (R-C=O, glyoxal) + ammonia/amine(aq) → imidazole
(*De Hann et al., 2009; Galloway et al., 2009; Liggio et al., 2005; Trainic et al., 2011*)



Investigate AqSOA formation from Phenolic Compounds

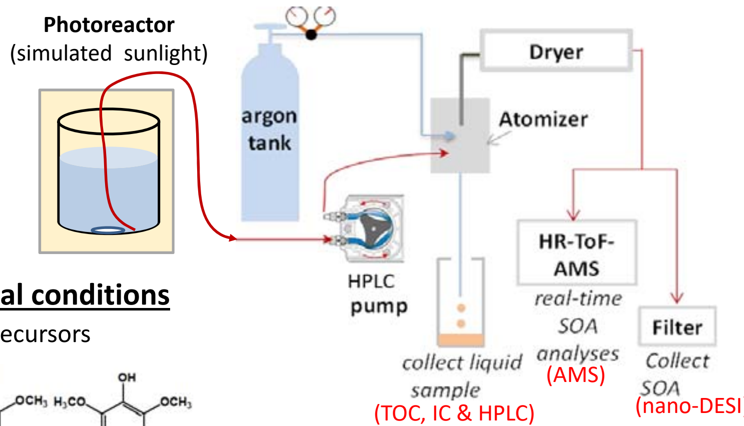
- Large emissions of gaseous phenols from biomass burning





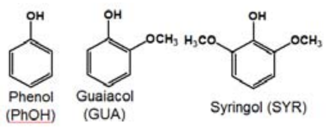
- High Henry's Law constant → partition into aq. phases
- Aqueous phenols are rapidly oxidized by a variety of mechanisms: hν, ·OH, $^3C^*$ (triplet excited states of OC)

Experimental Setup



Experimental conditions

- Phenolic precursors

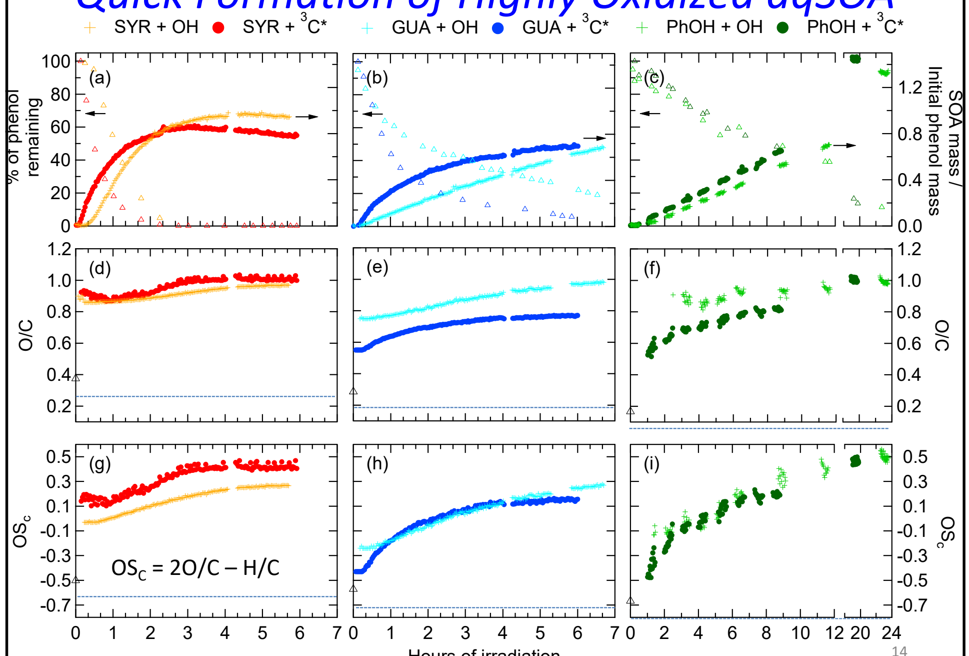


- $[\text{phenols}]_{\text{initial}}$ = 100 µM in H_2O
- Oxidant:
  1. 100 µM H_2O_2
  2. 5µM 3,4-DMB ($^3C^*$)

Analytical techniques

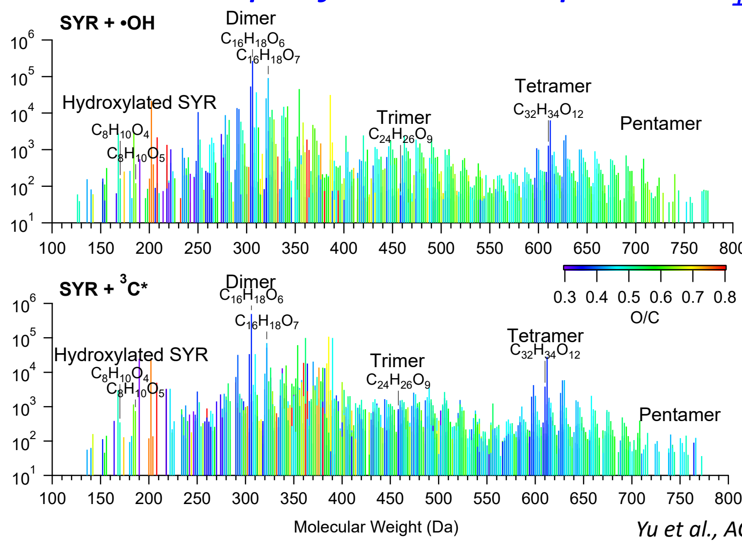
- HR-ToF-AMS: SOA **bulk comp.**, O/C, OS_C
- TOC: total organic carbon in soln.
- Nano-DESI MS: SOA **molecular comp.**
- IC: small acids in soln.
- HPLC : phenol conc.

Quick Formation of Highly Oxidized aqSOA



Yu et al., ACP, 2016

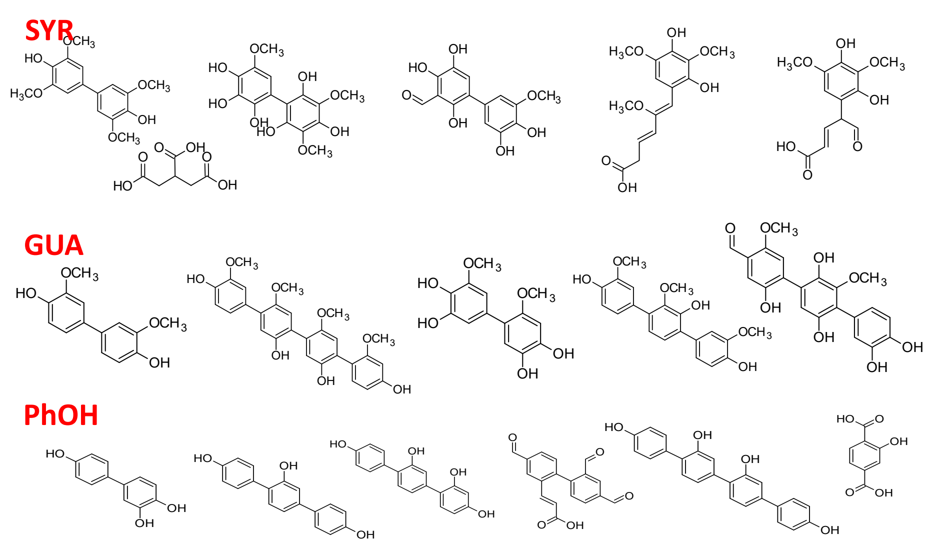
Molecular Comp. of Phenolic aqSOA at $t_{1/2}$



Yu et al., ACP, 2014

- Hundreds of SOA species, generally more oxidized than precursor.
- Oligomers (up to hexamers) and derivatives

Examples of Most Abundant Molecules

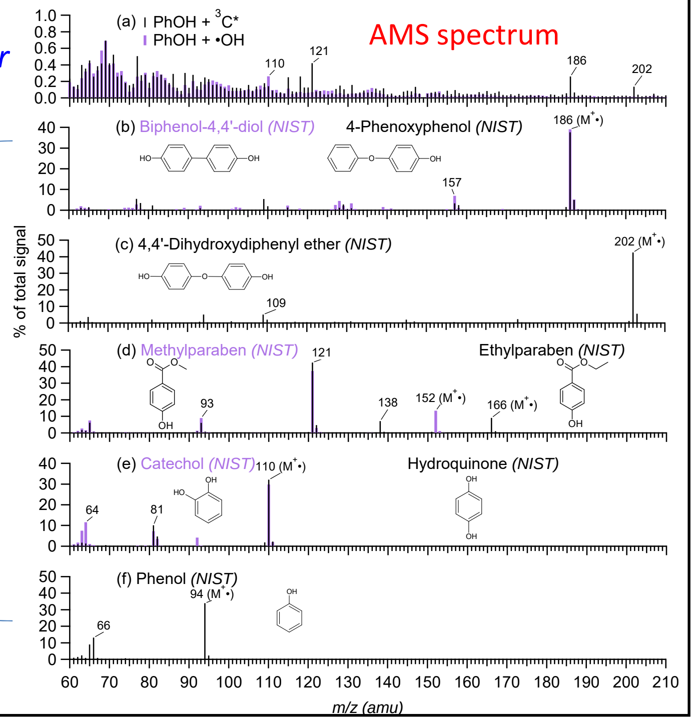


Yu et al., ACP, 2014

Oligomers, functionalized monomer and oligomers with carbonyl, carboxyl, and hydroxyl groups, demethoxylated aromatic species, ring opening species

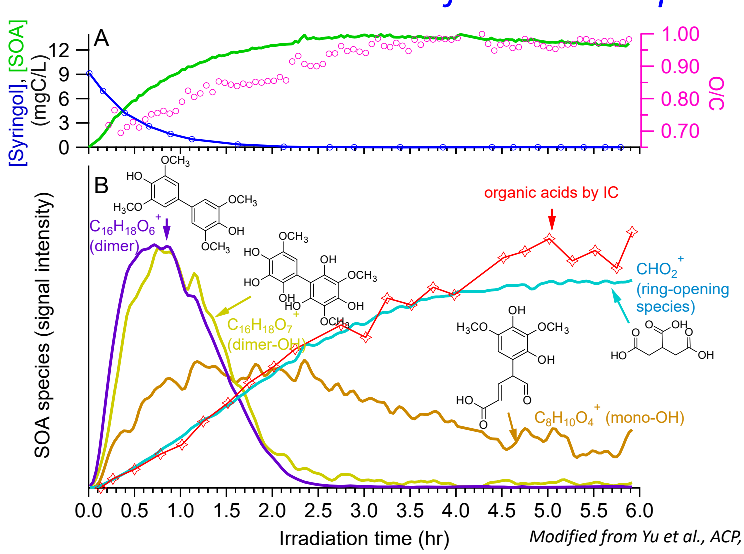
Identification of AMS tracer ions for phenolic aqSOA

NIST spectra



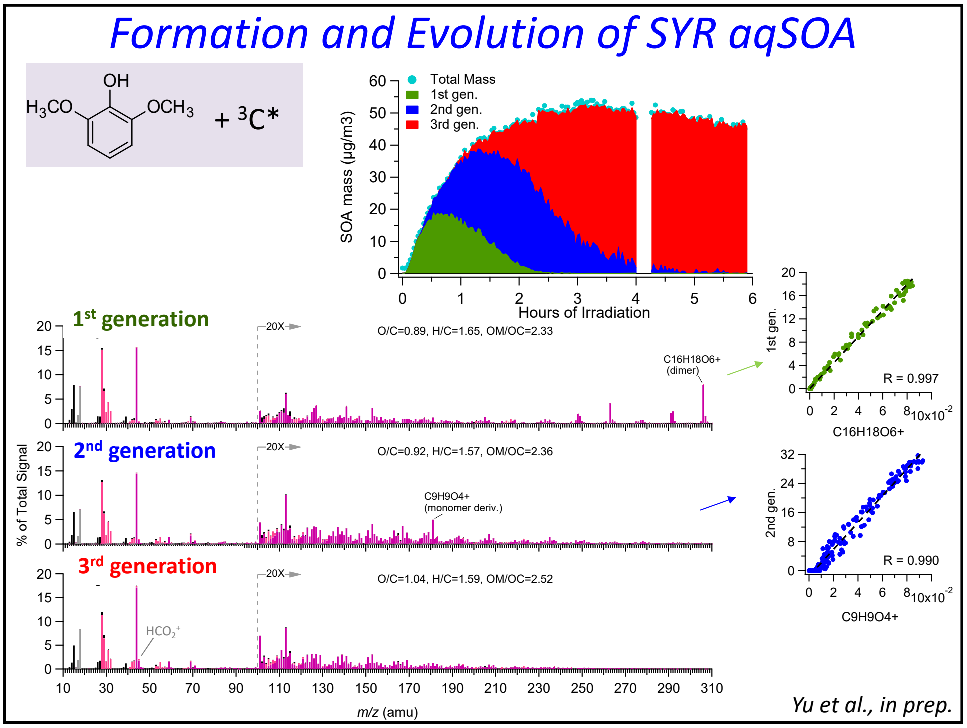
Sun et al., ACP, 2010

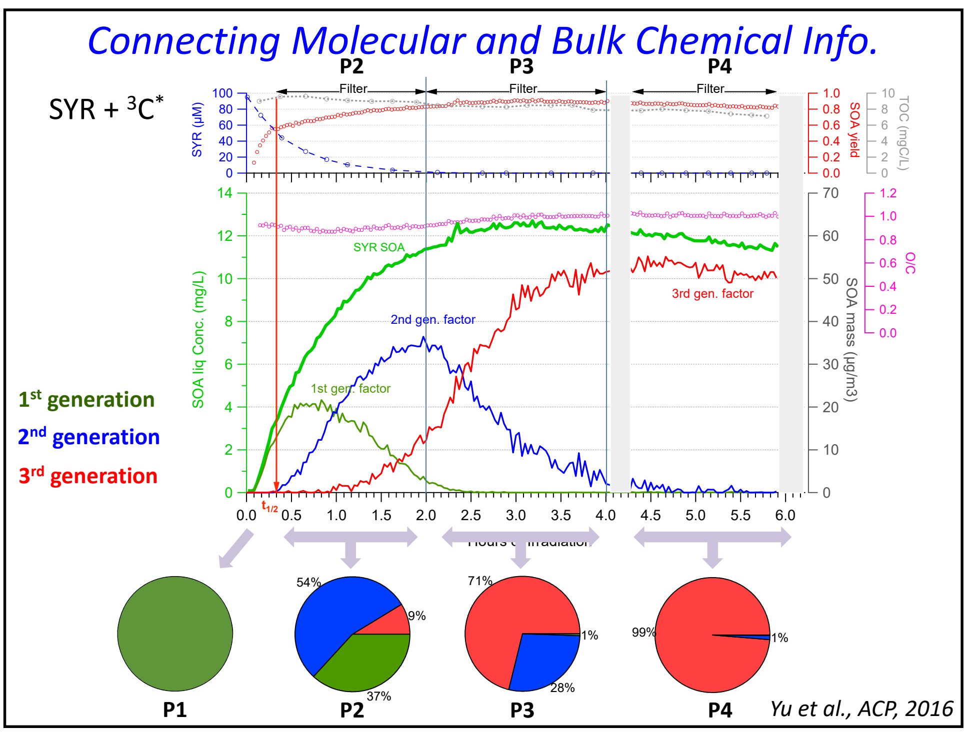
Formation and Evolution of Phenolic aqSOA



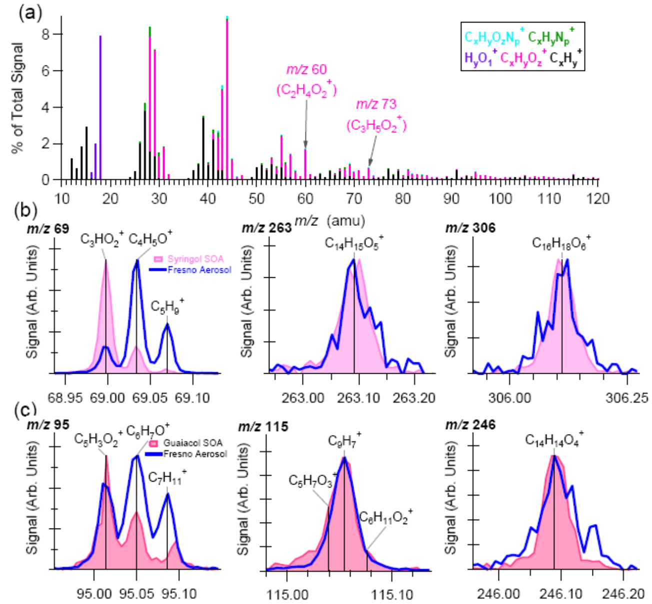
Modified from Yu et al., ACP, 2014, 2016

- Similar behaviors for different phenols aq reactions.
- Formation of a variety of functionalized aromatic and ring-opening products with high O/C
- Varying importance of oligomerization, functionalization, and fragmentation throughout rxn.


Formation and Evolution of SYR aqSOA
+ ^{3}C*
Total Mass
1st gen.
2nd gen.
3rd gen.
SOA mass (µg/m3)
Hours of Irradiation
1st generation
2nd generation
3rd generation
O/C=0.89, H/C=1.65, OM/OC=2.33
O/C=0.92, H/C=1.57, OM/OC=2.36
O/C=1.04, H/C=1.59, OM/OC=2.52
C16H18O6+ (dimer)
C9H9O4+ (monomer deriv.)
HCO2+
20X
% of Total Signal
m/z (amu)
R = 0.997
R = 0.990
C16H18O6+
C9H9O4+
Yu et al., in prep.


Connecting Molecular and Bulk Chemical Info.
SYR + ^{3}C*
P2
P3
P4
Filter
SYR (µM)
SOA yield
TOC (mgC/L)
SYR SOA
2nd gen. factor
1st gen. factor
3rd gen. factor
SOA liq Conc. (mg/L)
SOA mass (µg/m3)
O/C
1st generation
2nd generation
3rd generation
54%
9%
37%
71%
1%
28%
99%
1%
P1
P2
P3
P4
Yu et al., ACP, 2016

Observation of Phenolic aqSOA in Fresno PM



Sun et al., ACP, 2010

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Sonya Collier Shan Zhou

Collaborators

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EMSL
Pacific Northwest NATIONAL LABORATORY

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