Measurements of *in-situ* SOA Formation and Chemistry Using an Oxidation Flow Reactor

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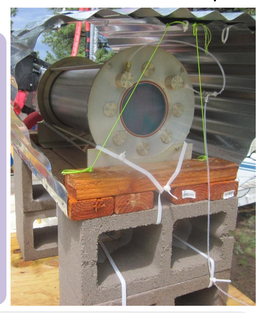
Take Home Points

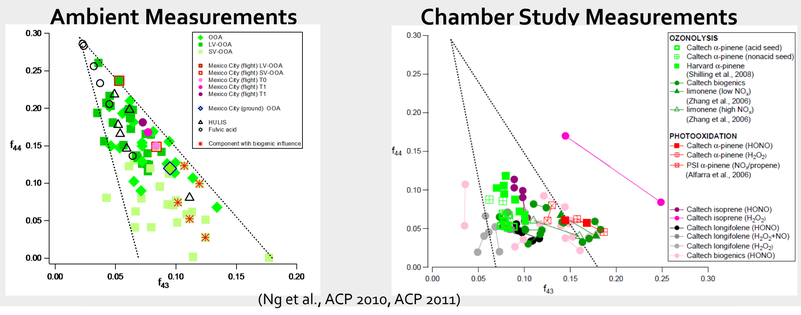
- Flow reactor oxidation appears to approximately reproduce and extend atmospheric oxidation processes
- SOA formation correlates with ambient VOC concentrations
- Oxidation of ambient air in a flow reactor produces approximately a factor of 10 more SOA than predicted from traditional VOC precursors, suggesting another source of SOA such as unmeasured oxidation products of VOCs



Motivation: Secondary Organic Aerosols (SOA)

- Organic aerosols (OA) have significant effects on climate, air quality, and human health, but OA formation and aging in the atmosphere is poorly understood
- Chamber studies:
  - Cannot sample ambient air in near real-time
  - Have difficulty producing OA as oxidized as in the atmosphere, e.g., as shown by the mass spectrometric tracers f_{44} (→ aged OA) vs. f_{43} (→ fresh OA) below
- A new method is needed to study OA formation and aging

Ambient Measurements | **Chamber Study Measurements**



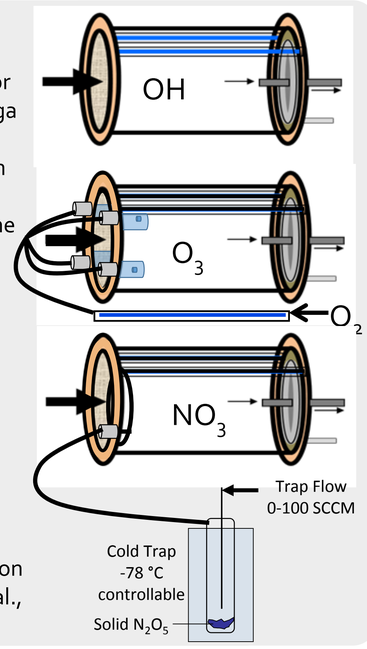
(Ng et al., ACP 2010, ACP 2011)

Method: Oxidation Flow Reactor

- 13 L Potential Aerosol Mass (PAM) oxidation flow reactor (Kang et al., 2007; Kang et al., 2011; Li et al., 2013; Ortega et al., 2013)
- Higher degree of oxidant exposures than chambers with reduced wall effects
- Oxidant concentrations in the reactor are elevated in one of four ways:

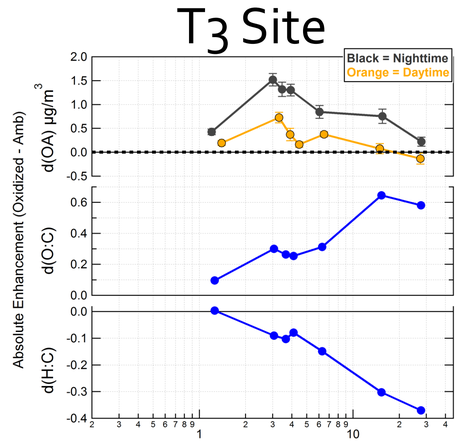
$OH_{185+254}$:	$O_2 + h\nu\,(185nm) \rightarrow O_3$
	$O_3 + h\nu\,(254nm) + H_2O \rightarrow\rightarrow 2\,OH$
	$H_2O + h\nu\,(185nm) \rightarrow OH$
OH_{254}:	Inject $O_3 + h\nu\,(254nm) + H_2O \rightarrow\rightarrow 2\,OH$
O_3:	Inject O_3
NO_3:	Inject $N_2O_5 \rightarrow NO_2 + NO_3$

- Aerosols and gases formed in the flow reactor are analyzed using an Aerodyne HR-ToF-AMS, SMPS, and PTR-TOFMS, etc.
- Photochemically-processed aerosols show SOA formation, oxidation, hygroscopicity, and cloud activation similar to the atmosphere (Kang et al., 2011; Lambe et al., 2011)

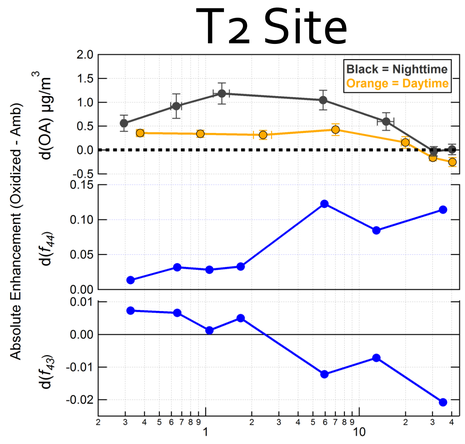


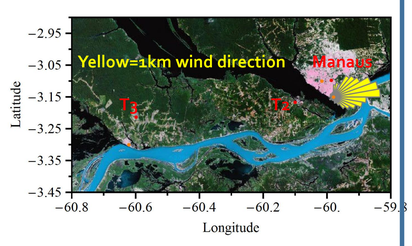
GoAMAZON2014- Wet Season (Feb-Mar)

T3 Site



T2 Site



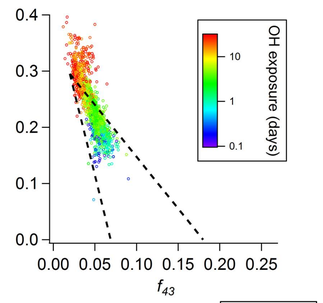


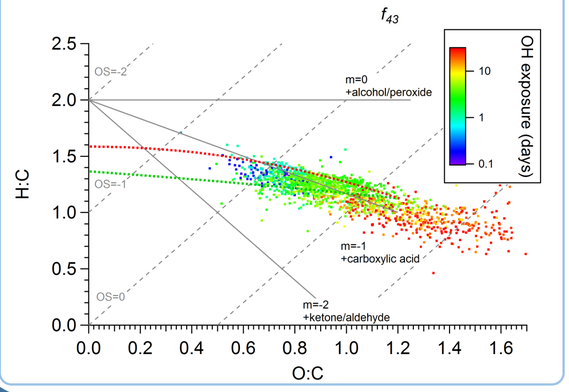
- Manaus is a city of 2 million people surrounded by forest
- T2 site is across the Rio Negro from Manaus; T3 site is ~70km downwind

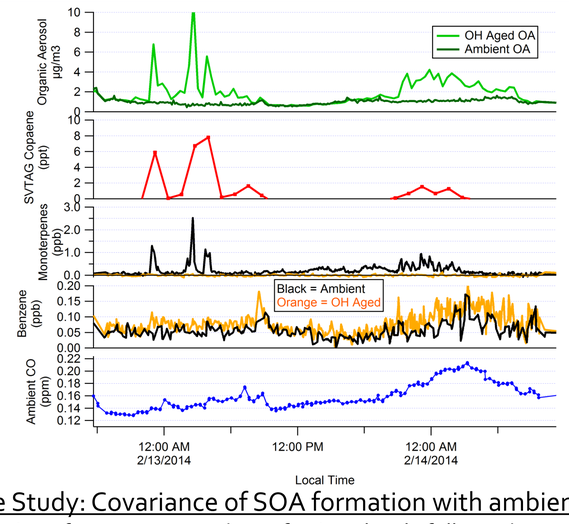
OH Oxidation of ambient air in an OFR

- Organic aerosol is formed via functionalization/condensation of organic gases, with maximum aerosol formation occurring from approx. 1-4 days of equivalent atmospheric aging
- More SOA formation in the flow reactor at night (~1.5μg/m³) than during the day (~0.5μg/m³), likely due to diurnal changes in the concentration of organic gases
- Aerosol mass formed from <1 day equiv. aging shows a similar level of oxidation to preexisting ambient aerosol.
- At high OH exposures, fragmentation/evaporation leads to loss of mass and highly oxidized SOA
- Despite being closer to Manaus, the amount of SOA formed on average at the T2 site was similar to the T3 site. However, specific events where Manaus plume is transported from T2 to T3 need to be investigated in more detail

T3 level of oxidation





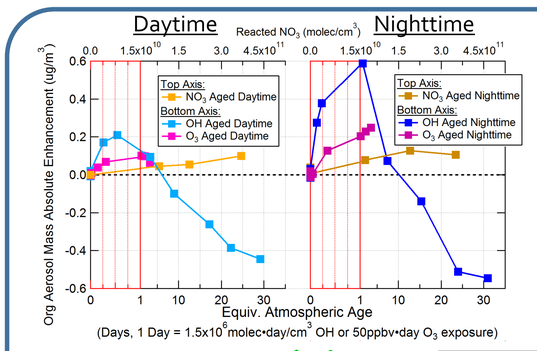


T3 Case Study: Covariance of SOA formation with ambient gases

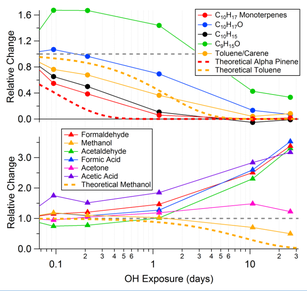
- SOA formation after approx. 3-4 days of aging closely follows the availability of precursor gases
- However, the amount of SOA formed in the reactor is more than the predicted aerosol yield from measured VOCs, suggesting that aerosol is being formed from other gases (e.g., unmeasured oxidation products of VOCs)

BEACHON-RoMBAS 2011

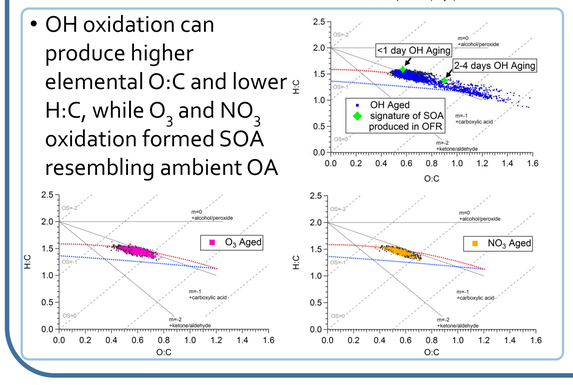
- Pine forest in rural Colorado, USA
- OH, O_3, and NO_3 oxidation experiments

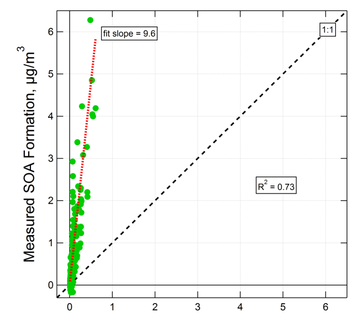


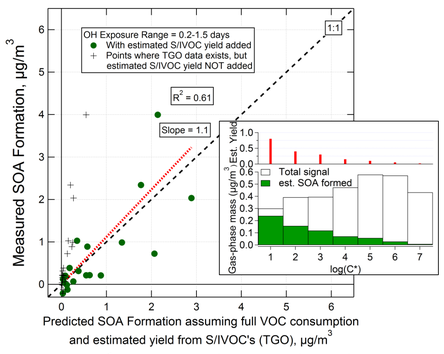
- OH oxidation led to larger enhancement than O_3 or NO_3 ox.
- OA enhancement was largest at night, corresponding to the highest monoterpene concentrations



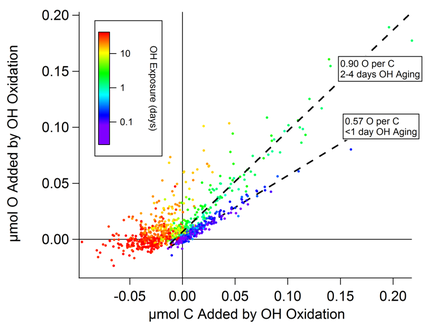
- OH oxidation can produce higher elemental O:C and lower H:C, while O_3 and NO_3 oxidation formed SOA resembling ambient OA

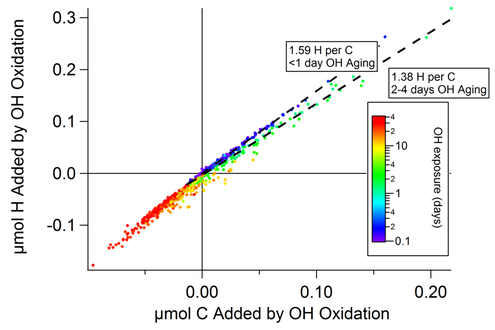






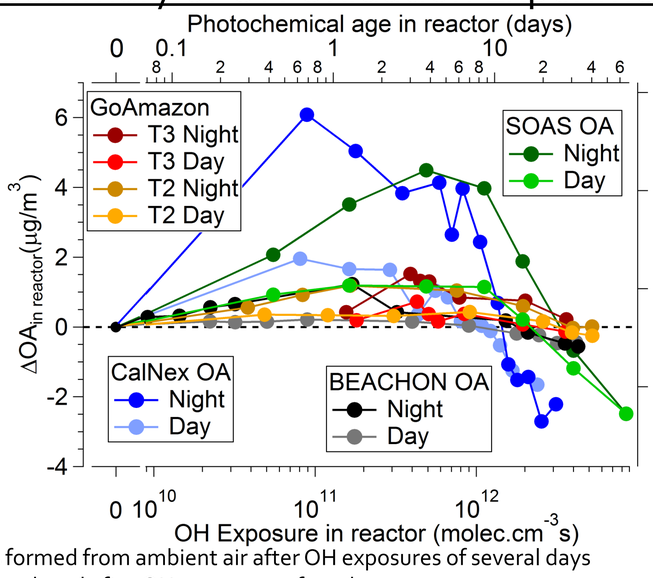
- 0.2-1.5 days OH oxidation led to approx. 10 times more SOA formation than predicted assuming all significant VOCs are reacted away (MT, SQT, toluene)
- Assigning estimated yields to unidentified gas-phase organic mass with log(C*)=1-7 can bring SOA formation into agreement with predictions, but further studies are needed to validate this result





- The O:C and H:C ratios of the mass added by OH exposures of <1 day are similar to the ratios measured in ambient aerosol

Summary of OH Oxidation Experiments



- OA is formed from ambient air after OH exposures of several days
- OA is reduced after OH exposures of weeks
- OA formation potential in a flow reactor is higher at night than during the day, likely due to changes in ambient gas concentrations
- CalNex (urban) and SOAS (regional pollution/forest) show highest OA formation potential, while GoAmazon (forest, downwind of Manaus) and BEACHON (rural pine forest) show less OA formation potential

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