

Measurements of SOA formation potential, chemical evolution, and gas-particle partitioning

Objective: Measure SOA concentrations, formation potential, chemical composition and evolution, gas-particle partitioning; compare to models and develop parameterizations applicable to regional and global modeling.

Climate Relevant SOA Property(s) Investigated:

- Chemically-speciated mass concentrations and size distributions (in situ, potential) ("*climate-relevant properties*")
- O/C, elemental ratios, oxidation state, functional groups (*process-relevant properties*)
- Gas-particle partitioning thermodynamic and kinetics (*process-relevant properties*)

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Collaborators: Jim Smith, Alma Hodzic (NCAR), Julie Fry (Reed), Steve Brown (NOAA), Joel Thornton (UW), Doug Worsnop, John Jayne, Joel Kimmel (Aerodyne Research, Inc.), Mike Cubison (Tofwerk AG), Joost de Gouw & Rui Li (NOAA), GoAmazon14 collaborators (Wang, Martin, Alexander, Guenther...)

Summary of progress:

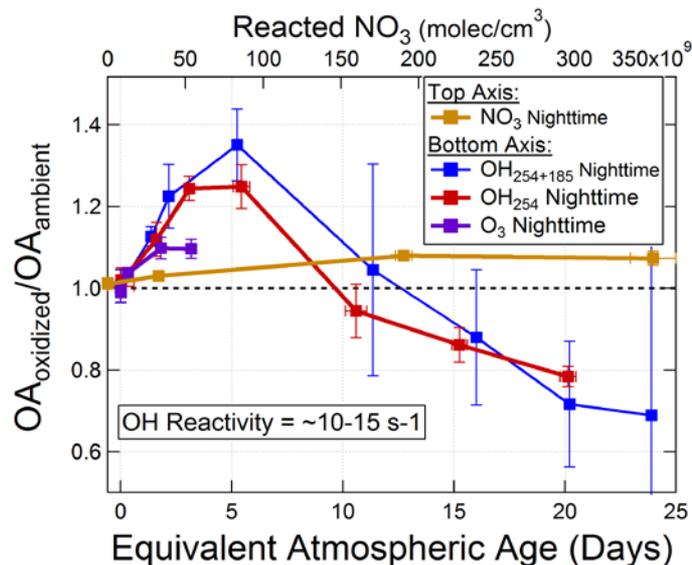
- Collected measurements of potential SOA formation and chemical evolution from major atmospheric oxidants in diverse environments and from sources in the laboratory. Typically for field observations of OH-driven chemistry, net SOA production is observed for the first few days of atmospheric equivalent aging, after which further oxidation results in loss of mass demonstrating the competing effects of functionalization/condensation vs. fragmentation/evaporation; whereas the degree of oxidation continues to increase. Organic nitrate SOA production was observed from NO₃ radical oxidation. Using, in part, our laboratory-measured yields and measured VOCs, modeled SOA mass is consistently underestimated compared to observations in the field and BB chamber. For BB, the amount of SOA formed was positively correlated with initial POA. At an urban site, SOA production followed concentrations of more reactive VOC. Crude oil evaporates showed that VOC with volatilities of $C^* = 10^5 - 10^6 \mu\text{g m}^{-3}$ contributed the majority of SOA mass formed.
- Developed new analytical methods to extract, distill, and interpret chemical properties from extremely complex HR CIMS spectra. Bulk gas-phase acids were observed to be composed of smaller, more oxidized molecules than in the particle phase with oxidation state showing a functional dependence on carbon #.
- Compared in-situ gas-particle partitioning of speciated/bulk organic acids to absorptive partitioning models. Carbon # and oxygen content are good predictors; re-partitioning appears to occur on timescales of hours.

Challenges or needed resources/collaborators: ARM support and collaborative measurements (Wang, Martin, Alexander, etc) during GoAmazon, support for measurements in other regions, the laboratory (e.g. partitioning studies), modeling.

Oxidation Flow Reactor Results

Examples from measurements in a pine forest

SOA Mass

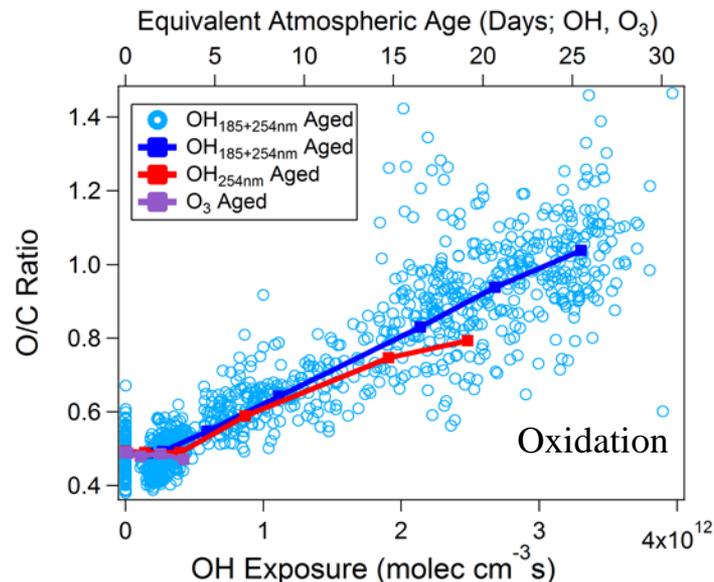


- SOA formation from oxidation of VOCs by 3 main oxidants (OH, O₃, & NO₃) in pine forest.
- All oxidants produce SOA (OH the most)
- High OH exposures result in destruction (fragmentation/evaporation) of preexisting OA.



Aerosol Concentration,
Scattering, CCN

SOA Composition

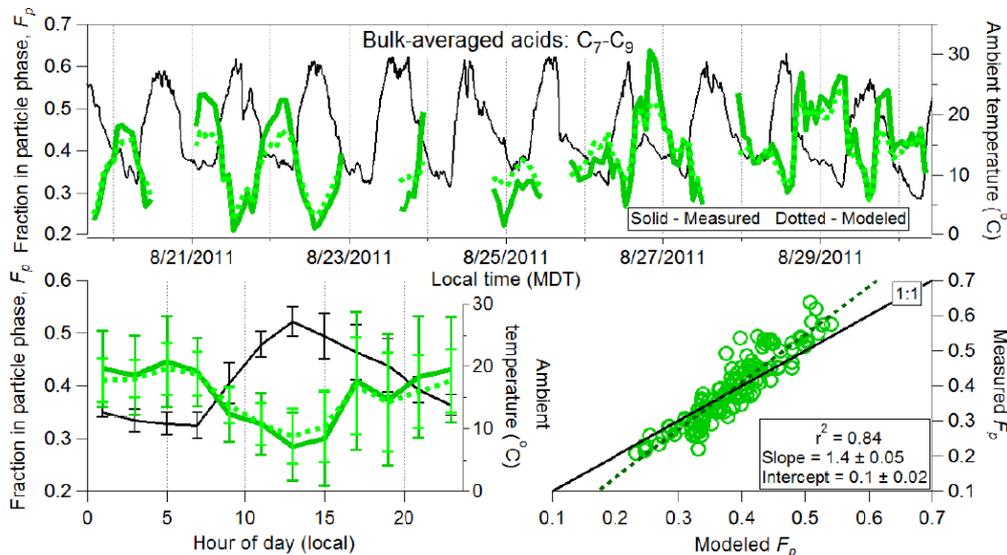
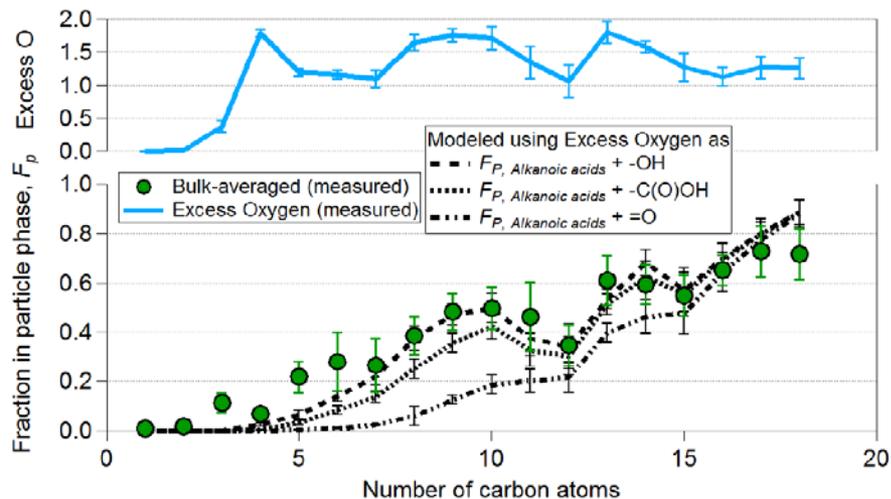


- At low exposures oxidation is constant (likely due to adding similar SOA to ambient), after which it continues to increase to the highest exposures.
- Other locations and sources show similar results.



Hygroscopicity, $K_{org} \rightarrow$ CCN
(Massoli et al., 2010, Mei, Wang et al., 2013)

Gas-Particle Partitioning: Organic Acids



- Carbon # and oxygen content are good predictors for gas-particle partitioning (F_p).
- Hydroxyl addition (to organic acid) is the most consistent avg. functionalization based on model/measurement comparison.

- Observed F_p follows diurnal temperature swings, suggesting these acids were re-establishing gas-particle equilibrium on short timescales of < 1-2 hrs.
- Good agreement between model and measurements for many acids.



SOA Mass, Sources
Sensitivity to T, OA loading