

SOA: Potential in Ambient Air at GoAmazon & Partitioning Quantification in a Chamber

University of Colorado Boulder, J.L. Jimenez^{1,2}, B.B. Palm^{1,2}, J. Krechmer^{1,2}, X. Liu^{1,2}, S.S. de Sá³, P. Campuzano-Jost^{1,2}, D.A. Day^{1,2}, W. Hu^{1,2}, D. Pagonis^{1,2}, P. Ziemann^{1,2}, Y. Liu³, R. Seco⁴, J.H. Park⁵, S. Sjostedt⁴, A. Guenther⁴, S. Kim⁴, J. Brito⁷, F. Wurm⁷, P. Artaxo⁷, L. Yee⁸, G. Isaacman⁸, A. Goldstein⁸, R. Wernis⁸, R. Souza⁹, A.O. Manzi¹⁰, O. Vega¹¹, J. Tota¹², M.K. Newburn¹³, M.L. Alexander¹³, S. Springston¹⁴, S. Martin³, W.H. Brune¹⁵

¹CIRES and ²Dept. of Chemistry, Univ. of Colorado, Boulder; ³Harvard University, Cambridge, MA; ⁴University of California, Irvine; ⁵National Center for Atmospheric Research, Boulder, CO; ⁶Pacific Northwest National Laboratory (PNNL), Richland, WA; ⁷University of São Paulo, Brazil; ⁸University of California, Berkeley; ⁹University of the State of Amazonas, Manaus, Brazil; ¹⁰National Institute of Amazonian Research, Manaus, Brazil; ¹¹Instituto de Pesquisas Energeticas e Nucleares, Cidade Universitaria, São Paulo, Brazil; ¹²Universidade Federal do Oeste do Pará, Santarém, Brazil; ¹³EMSL, PNNL, Richland, WA; ¹⁴Brookhaven National Laboratory; ¹⁵Penn State Univ.



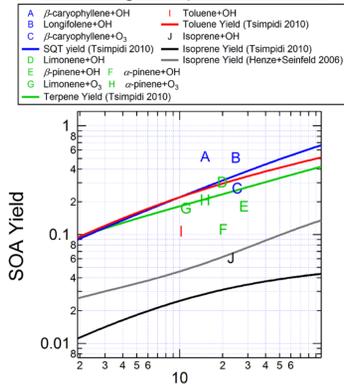
Conclusions

- OFR approx. reproduces and extends atmospheric oxidation
- Yields: standard addition to ambient are similar to chambers**
- SOA formation correlates with ambient VOC concentrations
- Oxidation of ambient air produces **x2-10 more SOA than predicted** from traditional VOC precursors, suggesting another source such as unmeasured oxidation products of VOCs
- Multilinear regression suggests that **partially oxidized biogenic gases were the largest contributors** during both seasons
- Biomass burning precursors more important in the dry season

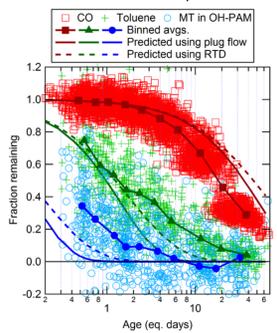
Motivation: SOA Sources, Aging, and Lifetime

- Secondary Organic Aerosols (SOA) have significant effects on climate, air quality, and human health, but its sources, formation and aging in the atmosphere is poorly understood
- Chamber studies:
 - Cannot study ambient air in near real-time
 - Have difficulty producing OA as oxidized as in the atmosphere
- A new method is used to study OA formation and aging in real-time → oxidation flow reactor
 - Allows studying real-time variations of SOA-forming potential in the field

Measuring SOA yields in an OFR



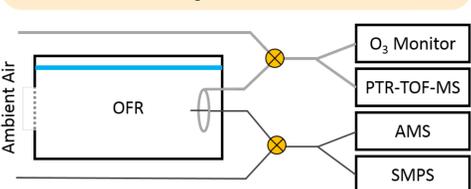
- Several VOCs injected into the OFR under ambient conditions → SOA yields were consistent with published chamber yields



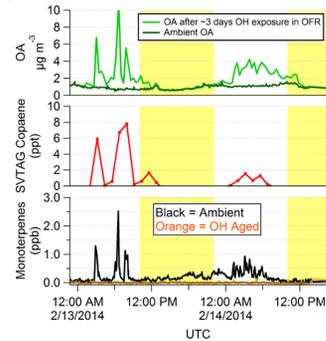
- Measured decay of ambient VOCs and injected CO verifies that modeled OH exposure is accurate within approx. a factor of 2-3 (consistent w/ Li et al. 2010, Peng et al. 2015)

Method: Oxidation Flow Reactor

- 13 L Potential Aerosol Mass (PAM) oxidation flow reactor (Kang et al., 2007; 2011; Lambe et al., 2011; 2012; Li et al., 2013; 2015; Ortega et al., 2013; 2015; Palm et al., 2016, 2017; Peng et al., 2015; 2016; 2017)
- Larger range of oxidant exposures than chambers with reduced wall effects
- Oxidant concentrations in the reactor are elevated in one of several ways:
 - OFR185: $O_2 + hv(185nm) \rightarrow O_3$
 $O_3 + hv(254nm) + H_2O \rightarrow 2 OH$
 $H_2O + hv(185nm) \rightarrow OH$
 - OFR254: Inject $O_3 + hv(254nm) + H_2O \rightarrow 2 OH$
 - O₃ OFR: Inject O₃
- Aerosols and gases formed in the reactor are analyzed w/ HR-ToF-AMS, SMPS, and PTR-TOF-MS, CCN, etc.
- Photochemically-processed aerosols show SOA formation, oxidation, hygroscopicity, and cloud activation similar to the atmosphere (e.g., Kang et al., 2011; Lambe et al., 2011)
- A model has been developed and verified to correct for losses of condensable gases in the OFR (Palm et al. 2016)

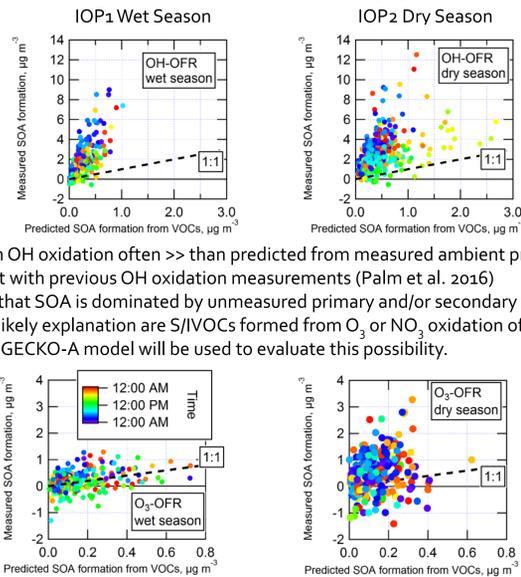


Case Study: Covariance of SOA Formation with Ambient VOCs



- SOA formation after approx. 3 days of OH aging follows the availability of biogenic precursor gases
- Substantially higher SOA potential at night

SOA Formed from Ambient Air Compared to Amount Predicted from VOCs in GoAmazon

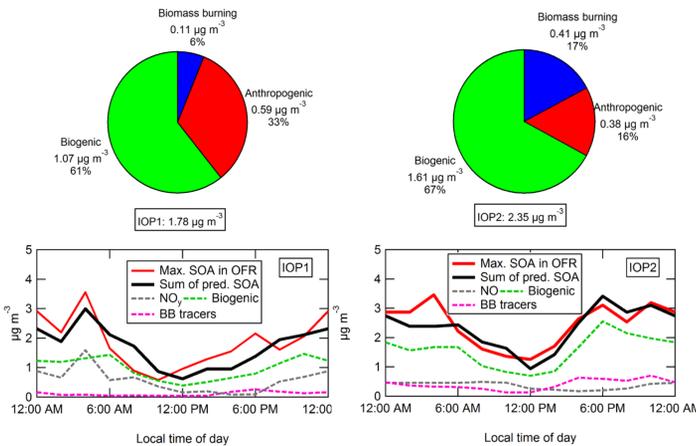


- SOA from OH oxidation often >> than predicted from measured ambient precursors
- Consistent with previous OH oxidation measurements (Palm et al. 2016)
- Suggests that SOA is dominated by unmeasured primary and/or secondary S/IVOCs. The most likely explanation are S/IVOCs formed from O₃ or NO₂ oxidation of VOCs at night. The GECKO-A model will be used to evaluate this possibility.

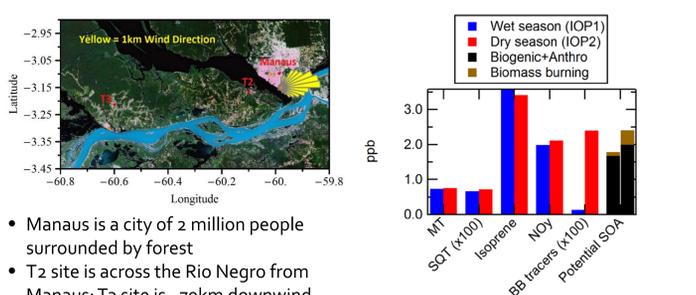
- SOA from O₃ oxidation is consistent with amount predicted from ambient VOCs
- Suggests that ambient S/IVOCs are reactive towards OH but not O₃ (no C=C left).
- Consistent with similar O₃ oxidation experiments in Colorado forest (Palm et al. 2017)

Estimating Source Contributions to Ambient SOA-forming Gases (VOCs+S/IVOCs) Using Multilinear Regression Analysis – Preliminary Results

- Multilinear regression of SOA formation in OFR vs. tracers for anthropogenic (NO_y), biogenic (MT+SQT+isoprene, run as multiple separate tracers), and biomass burning (vanillin + vanillic acid + syringol + guaicol) source types
- Biogenics is the largest contributor, with anthropogenic similar on both seasons.
- BB gases are more important in dry season, as expected

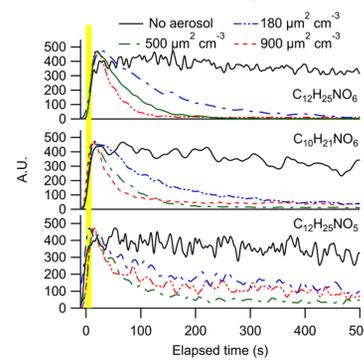


- Stability of results is consistent with consistent levels of precursors in both seasons
- Modest increase in SOA Potential between the seasons is consistent with modest impact of biomass burning on SOA (e.g. Cubison et al., 2011)



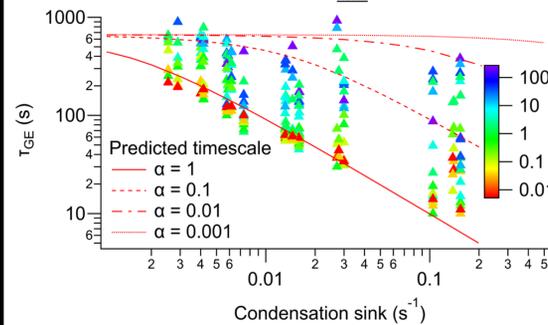
- Manaus is a city of 2 million people surrounded by forest
- T2 site is across the Rio Negro from Manaus; T3 site is ~70km downwind

Condensable Gases Partitioning vs. Seed Surface Area



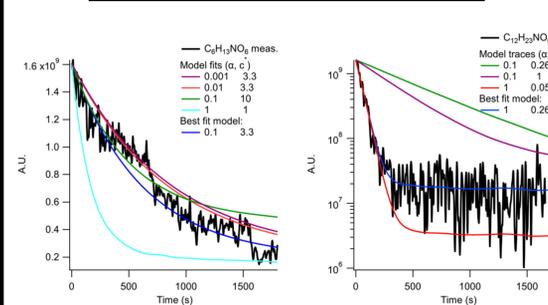
- Wall loss timescale (no aerosol) measured at ~1000 s (consistent with Ziemann, Donahue results; Krechmer et al., 2016)
- Can directly measure the strong gas loss timescale dependence on aerosol surface area

Timescales (τ_{GWP})



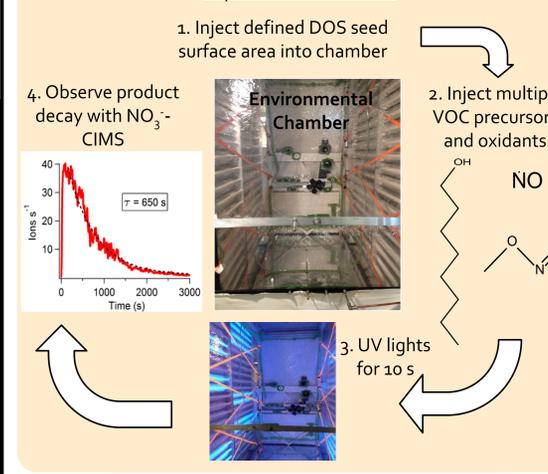
- Equilibrium time scales for each gas-phase compound at different seed aerosol condensational sink values
- Combined gas loss timescales consistent with model predictions
- α ~ 1 for the lowest volatility compounds
- α < 1 for more volatile species
- Compounds are colored according to SIMPOL-estimated c*

How well does the model constrain α and c*?



- Kinetic box model is used to fit α (dependent on rate of initial decay: kinetics) and c* (dependent on ending equilibrium concentration: thermodynamics)
- Low volatility compounds (right panel above) have very well constrained α
- Higher volatility compounds (left panel above) have α < 1, but harder to quantify at < 0.1 from single experiments
- Combining results of multiple experiments reduces uncertainty
- Results are robust against uncertainties on C_{wall}

Experimental Method



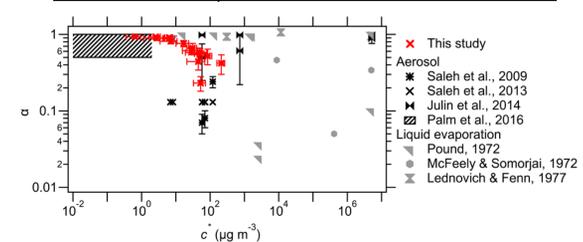
Conclusions

- Quantification of fundamental SOA formation processes in a Teflon chamber is possible using fast-product-burst method**
- Simple chemical system rapidly produces low-volatility gas products taken up by liquid OA seed and chamber walls
- Clear differences in kinetics vs. OA seed amounts allow us to separate and quantify the influence of wall and particle uptake
- We reproduce gas- and aerosol-phases w/ kinetic box model
- Aerosol mass accommodation coefficient (α): average ~0.6, near 1 for low-volatility species, decreases as c* increases**
- The experimentally-constrained model framework can be used to derive a correction factor (Φ~1.4) for SOA mass yields due to vapor losses to walls as a function of species properties.
- Experiments underway or planned for solid and viscous seeds
- Model suggests no difference in yields between batch and continuous-flow chambers

Motivation: GPP laboratory experiments

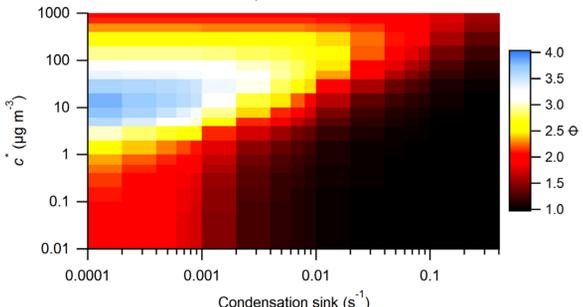
- Gas-particle partitioning (GPP) is a process that describes gas-phase species uptake into particles depending on equilibrium
- Most aerosol models use gas-particle equilibrium partitioning theory as default treatment of gas-aerosol transfer, despite questions about its validity and applicability
- Remaining questions about how gas-phase wall losses affect SOA yields

Measurement of α, the mass accommodation coefficient



- This has been a remarkably difficult parameter to quantify, with some literature studies proposing or using α = 0.001
- Average for all compounds α ~ 0.6
- On the same range as values measured in several previous studies of liquid droplets or aerosols
- Points from are averages for each compound across multiple experiments
- Error bars are standard error of the mean

Wall-loss SOA yield correction model



- Matrix providing an aerosol mass yield correction factor (Φ) for SOA formation from single condensable gas w/ given c* and CS
- Factors for each VBS bin can be derived and applied
- Assumes that SVOC production is rapid
- Does not account for oligomerization, or heterogeneous particle-phase chemistry (but it can be used as a component of a more complex model that includes those processes)

Model set-up

