Urban Atmospheric Chemistry

State of current science, critical open questions, and possible future directions

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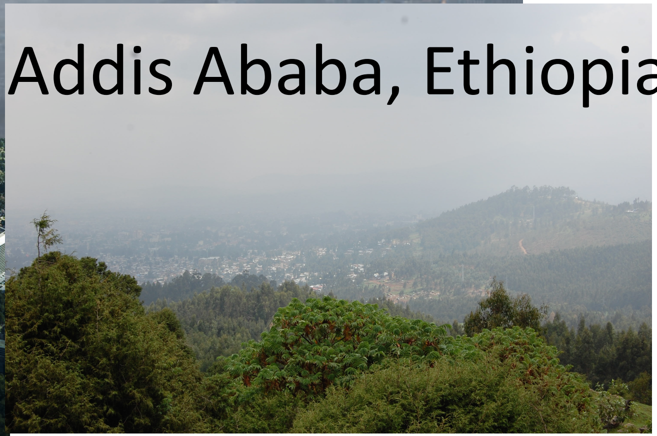
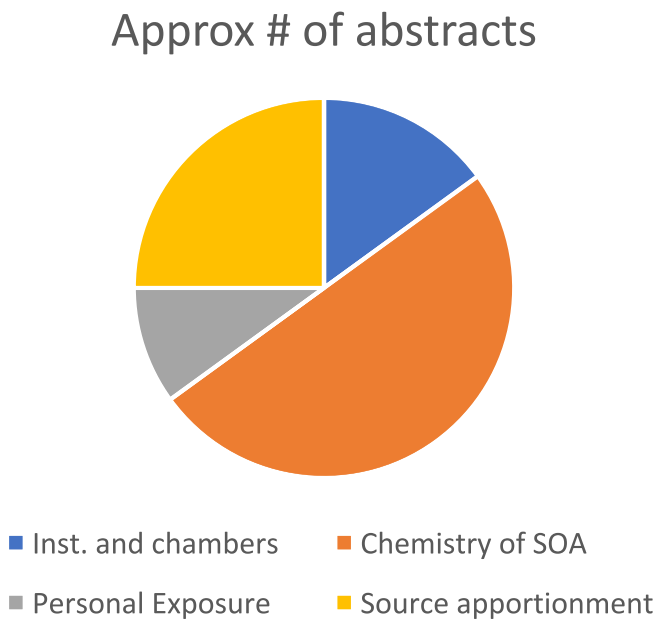
What does “urban” mean to us?



Umbrella topics (from recent NSF awards and 2017 AAAR abstracts)

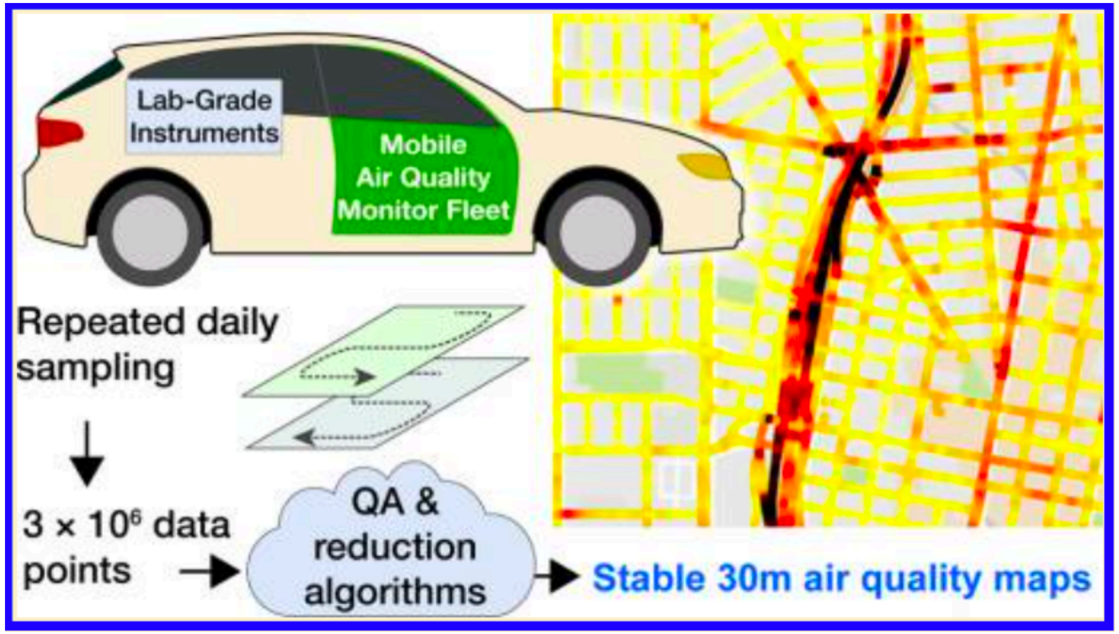
- **Personal exposure** (low cost sensors, increased spatiotemporal resolution, toxicity, and urban design)
- **Source apportionment methods** (PMF, ME-2, and friends)
- **Developments in instrumentation and chambers** (continuous flow reactors, SP-AMS, EESI-TOF, and TD-CAPS as well as vapor wall-loss corrections for chamber expts and remote sensing)
- **Chemistry of SOA** (meas-model comparisons, role of oxidants, role of particle viscosity and volatility, role of nitrogen, nighttime chemistry, non-vehicular VOCs, heterogeneous chemistry & partitioning, aerosol pH, and extreme air pollution events, and much more)



Low-cost sensors review, Lewis, von Schneidemesser, and Peltier 2018

State of science and current questions in

Personal Exposure

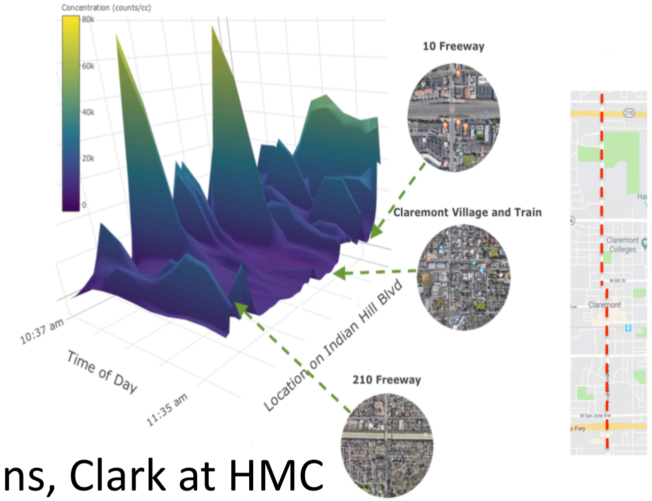


Google streetview cars, Apte et al., 2017, ES&T

Figure 1. A range of typical low-cost sensor components, example measurement compounds, and approximate cost

ARIsense

Aerodyne Research

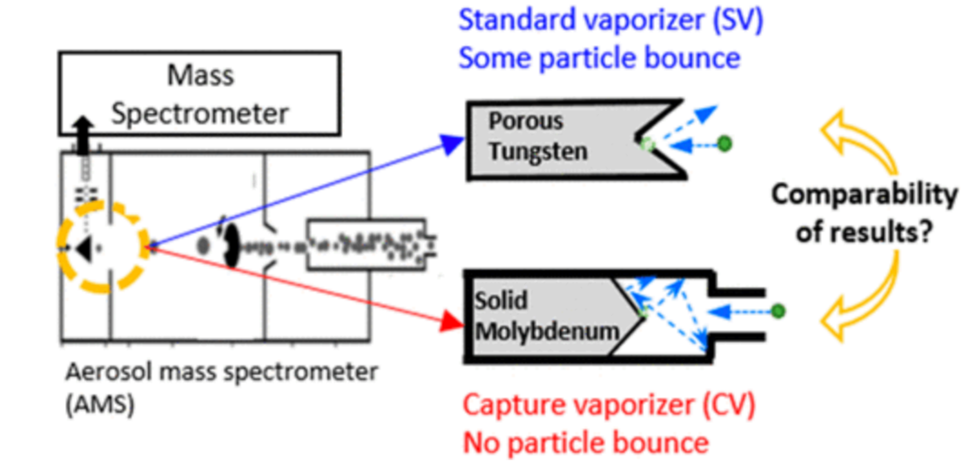


Casar, Hawkins, Clark at HMC

Citizen science vs mobile labs with research grade instrumentation

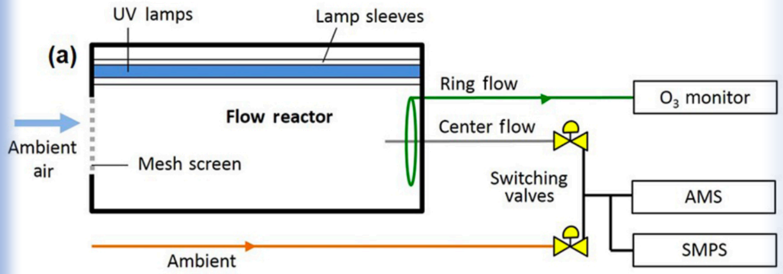
State of science and current questions in

Instrumentation, techniques, and chambers

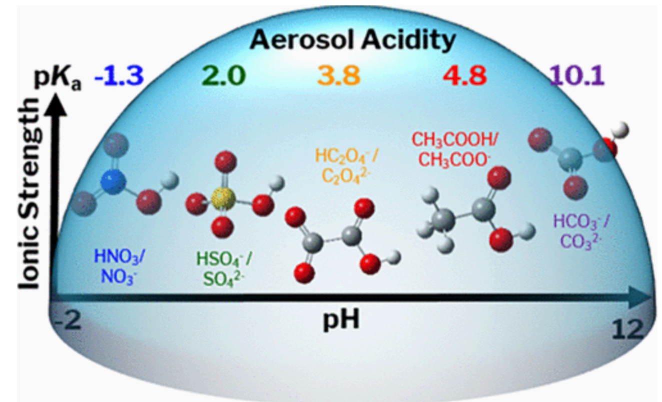


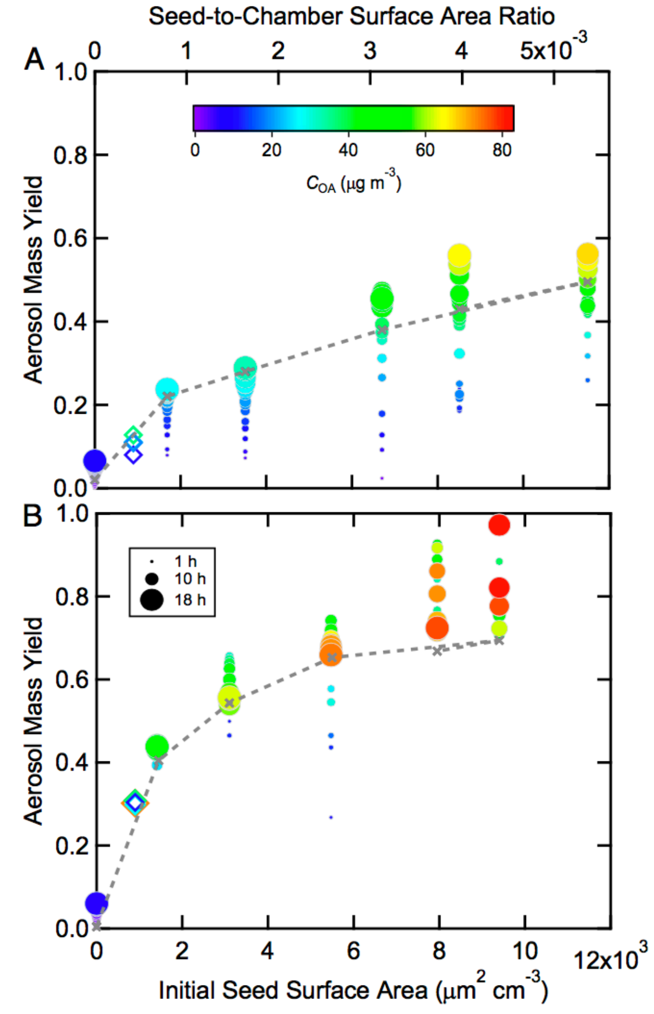
INCREASED COLLECTION EFFICIENCY
Hu et al., 2018, Earth & Space Chemistry

PAM OFR with stepped aging,
Ortega et al., 2016



MORE ACCURATE pH
Craig et al., 2017, J Phys Chem





VAPOR WALL LOSS CORRECTION
Zhang et al., 2014, PNAS

State of science and current questions in

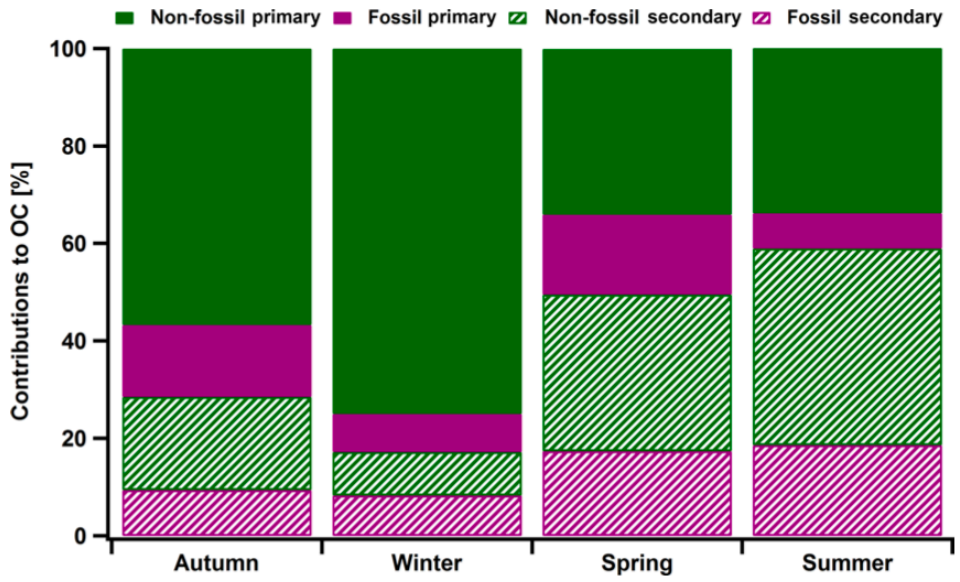
Instrumentation, techniques, and chambers

- Extractive electrospray ionization ToF mass spec for online soft ionization (2017 Zurich study, PSI, 2017 AAAR)
- HRToF-ESCIMS for improved sensitivity to groups of SOA precursors without a radioactive source (Univ of Washington, 2017 AAAR)
- Thermal dissociation CAPS for alkyl nitrates and peroxy nitrates (Deployed in Atlanta, from Georgia Tech)

State of science and current questions in

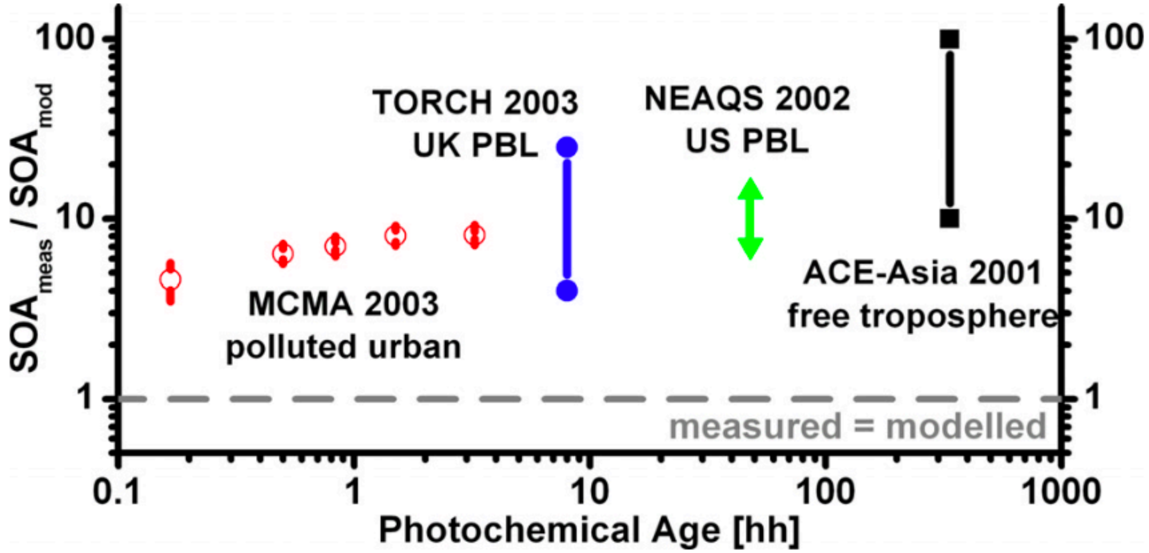
Source Apportionment: PCA, CMB, unconstrained PMF, or ME-2+PMF

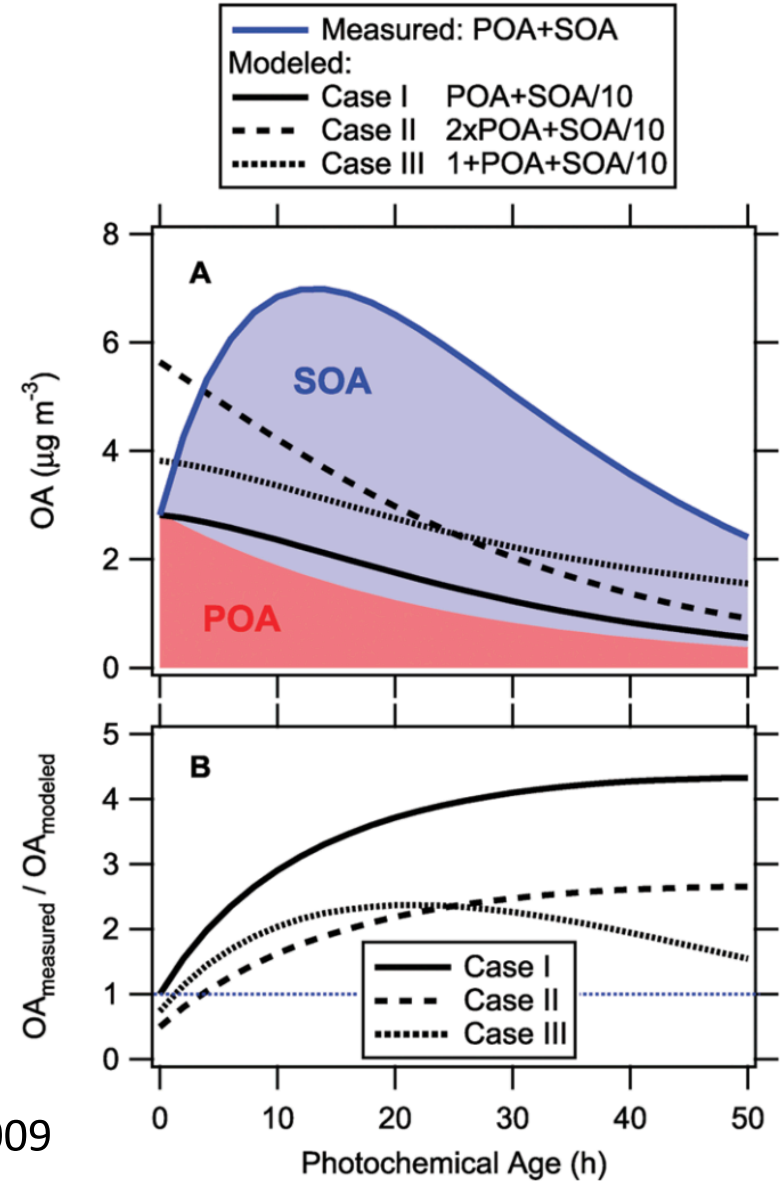
- We can constrain PMF model output with target profiles (multi-linear engine, ME-2, Paatero 1999, Canonaco et al., 2013)
- Consider using short time-span (e.g. seasons) for ME-2 analysis to achieve better model output because *profiles may change* between seasons (Reyes-Villegas et al., 2016)
- Couple ME-2 on offline AMS data with ^{14}C to constrain O:C from fossil and modern carbon sources (OC_{fossil} vs $OC_{nonfossil}$), Vlachou et al., 2018



Secondary organic aerosol formation from anthropogenic air pollution: Rapid and higher than expected

Rainer Volkamer,[1,2] Jose L. Jimenez,[3] Federico San Martini,[1,4] Katja Dzepina,[3] Qi Zhang,[3,5] Dara Salcedo,[6] Luisa T. Molina,[1,7] Douglas R. Worsnop,[8] and Mario J. Molina[1,2]

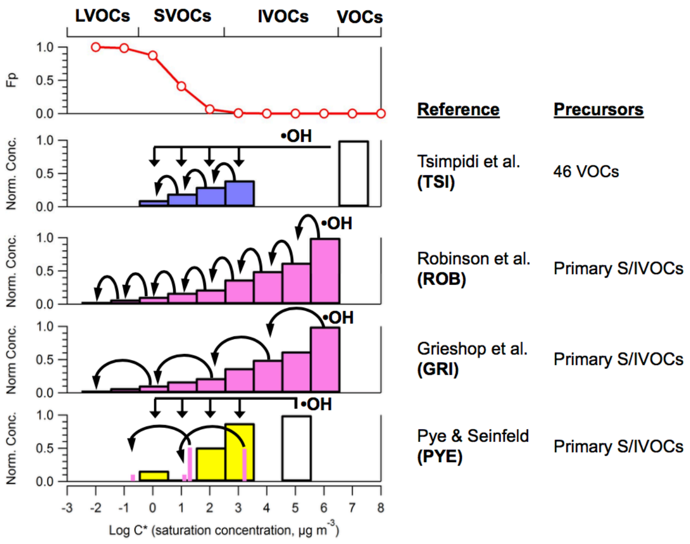


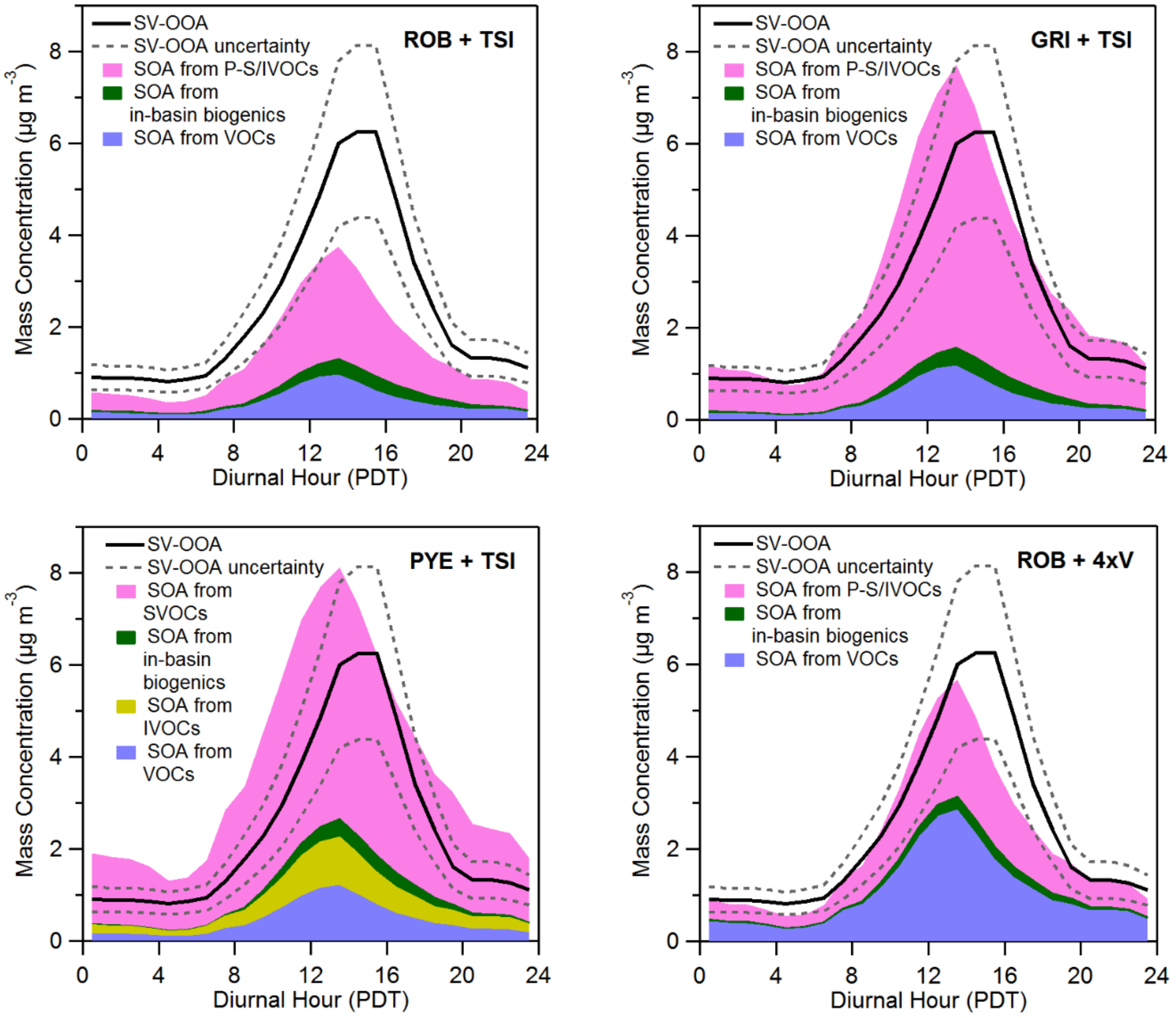


de Gouw and Jimenez, ES&T 2009

SOA Measurements vs models

- The models underpredict SOA under <1 day aging (even w/ higher chamber yields and multi-gen oxidation).
- Must include P-SVOCs and IVOCs.
- But the model then overpredicts SOA at >1 days (when SIMPLE is best).

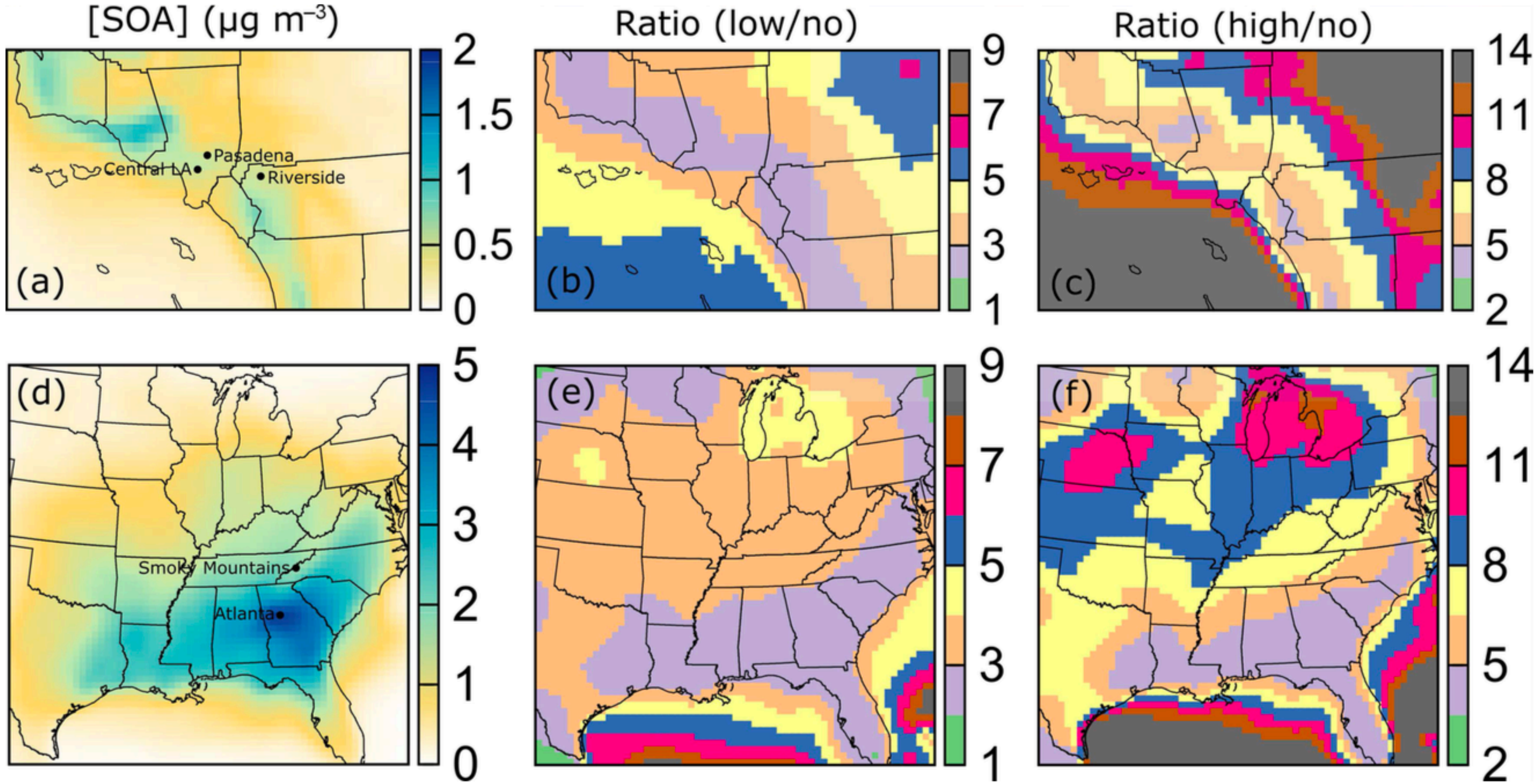




Hayes et al., 2015, ACP

SOA Measurements vs models

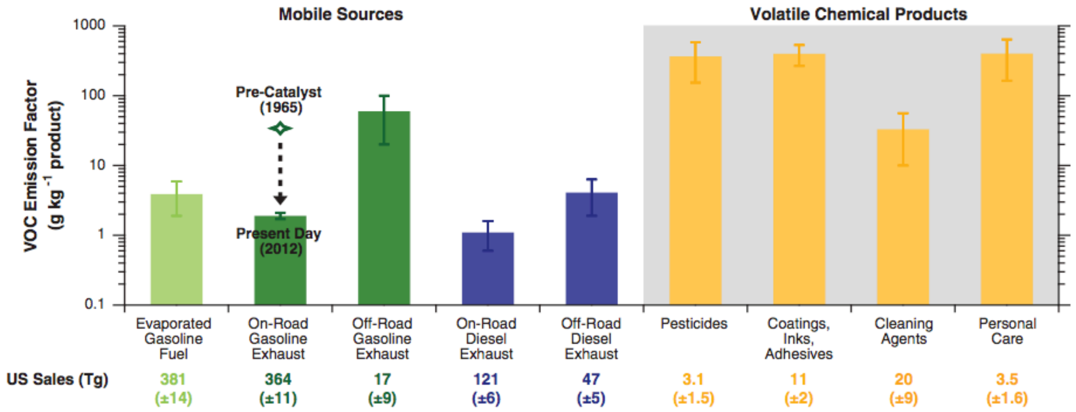
- More explicit correction for vapor wall losses (contrast with scaling in previous model comparison)
- Not including semi-volatile POA or IVOCs

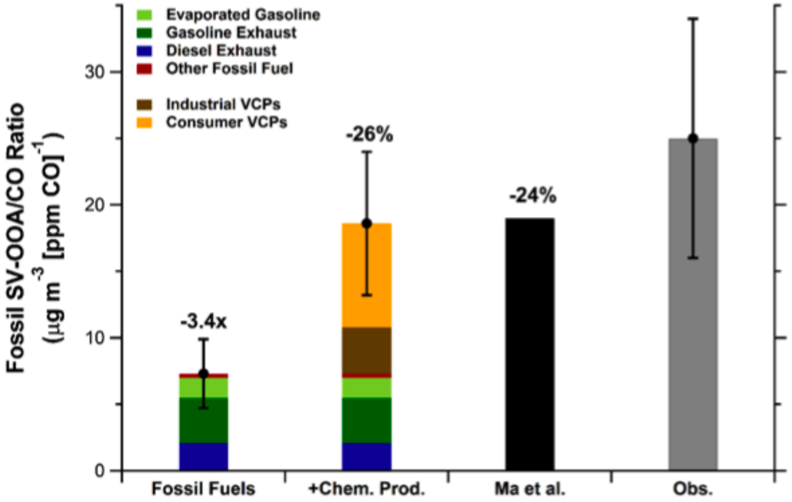


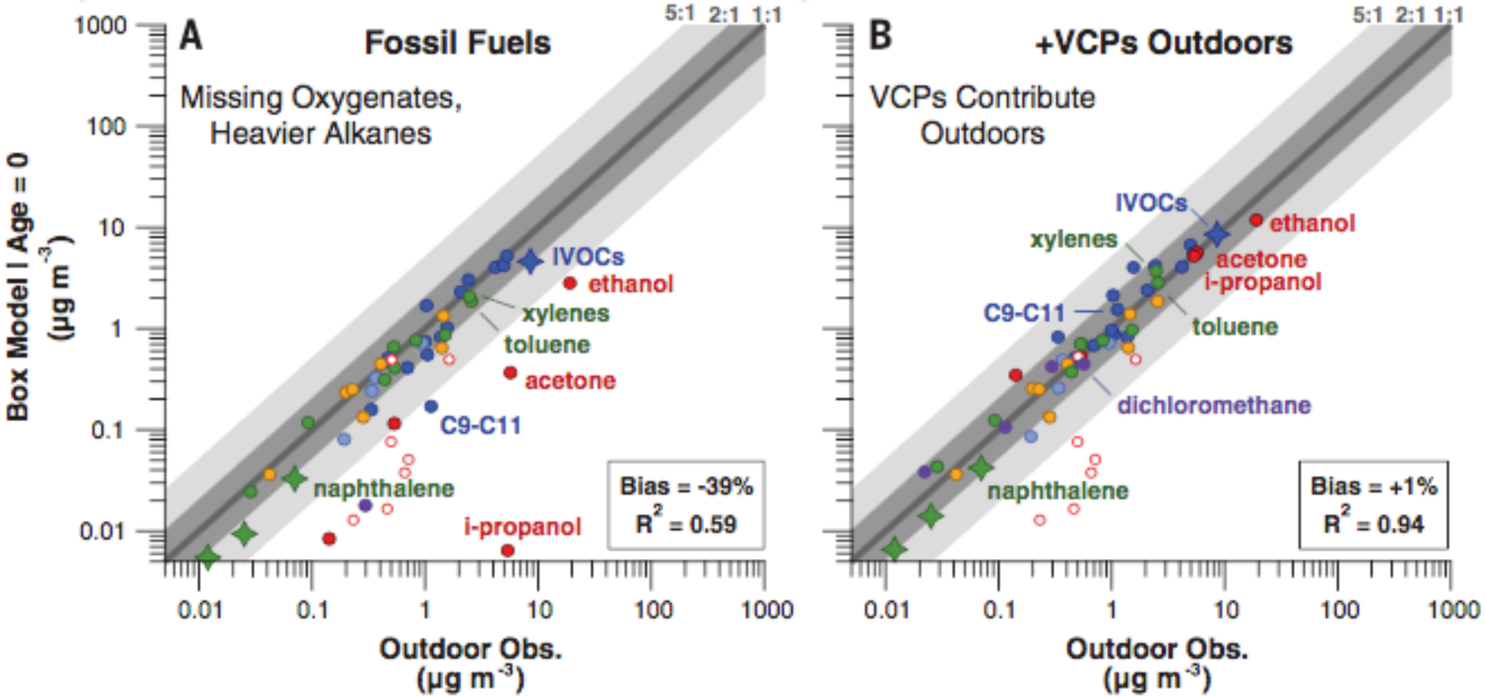
Cappa et al., 2016, ACP

SOA Measurements vs models

- Are volatile chemical products the "next big thing" in urban SOA chemistry?





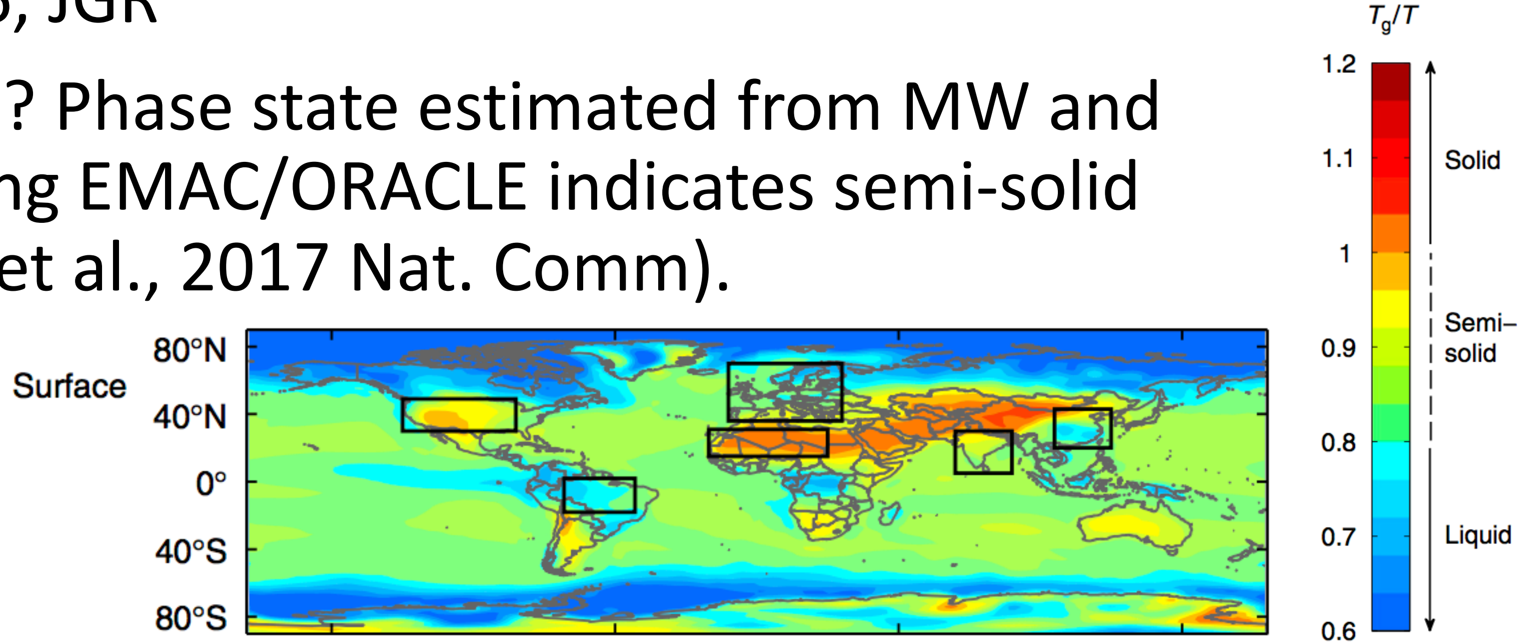


McDonald et al., 2018, Science

State of science and current questions in

Chemistry of SOA

- When do models get HO_x right? And when do they over/under predict? (And what does that tell us about the missing VOCs or reactions?) Griffith et al., 2016, JGR
- Where and when is SOA liquid? Phase state estimated from MW and O:C, and modeled globally using EMAC/ORACLE indicates semi-solid in dry mid-latitudes (Shiraiwa et al., 2017 Nat. Comm).



- Can nighttime chemistry predict the next day's SOA loading? OFR in CalNex indicates maybe(Ortega et al., 2016).

Urban SOA and ozone reduction

- If reduction is the goal, should we limit VCPs? (McDonald 2018) Maybe only aldehydes and alcohols? (de Gouw 2018)
- Or be concerned that NO_x is getting too low relative to gasoline-vehicle derived VOCs for further SOA reduction? (Zhao 2017 and Warneke 2013)
- How does the chemistry/toxicity of low NO_x SOA differ? (since NO_x is predicted to continue dropping w/ stricter emissions standards)
- What role does long range transport play in western and eastern US? In Europe?
- What is in store for places like Beijing, where ozone may increase as PM is initially reduced?

Additional possible topics for discussion

- Urban forested areas and the role of biogenic emissions in urban areas (Bonn 2017 Journal Cleaner Production)
- Cold, dark SOA formation (urban polar regions)
- Urban "street canyons" and urban design
- Trace metals and SOA formation (catalysis)
- Chemistry of aromatics in SOA formation
- Role of condensed water in SOA formation (clouds, fog, aerosol water)
- Unintended consequences (cool roofs and ozone, PM reduction in China linked to increase in ozone)
- Exposure to air pollution indoors in urban environments (both low and high NO_x)
- Coatings on BC in urban environments (Chemistry/Climate)
- Role of ammonia in SOA, brown carbon
- Extreme air pollution events driven by a combination of chemistry and meteorology.

Take Aways

- We learned a lot from CalNex and continue to do so
- LA SOA is important, but what about urban areas in a) humid climates, b) biogenically-influenced regions, c) much higher NO_x conditions, d) places with different P-S/IVOCS?
- We'll find what we are looking for - Do we need another CalNex/SENEX, to target volatile chemical product SOA instead of vehicular SOA? If so, when and where? Developed vs developing megacities? Biogenically influenced vs not?
- We probably need more chamber studies to quantify SOA yields from VOCs specific to VCPs and cooking and to quantify species-specific wall losses
- Is improved SOA model/measurement agreement to date for the RIGHT reasons? (e.g. wall loss corrections, including P-S/IVOCS, multi-step aging, fragmentation loss)
- How can we learn more about particle-phase oxidation processes so that O:C and total SOA can be modeled correctly?

SOA Measurements vs models

- Hayes 2015 https://www.atmos-chem-phys.net/15/5773/2015/acp-15-5773-2015.html
- Ma 2017 https://www.atmos-chem-phys.net/17/9237/2017/
- Robinson 2007 http://science.sciencemag.org/content/315/5816/1259
- Ortega 2016 https://www.atmos-chem-phys.net/16/7411/2016/acp-16-7411-2016.html
- Cappa 2016 https://www.atmos-chem-phys.net/16/3041/2016/acp-16-3041-2016.html
- De Gouw 2018 https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1002/2017JD027976
- Griffith 2016 https://agupubs.onlinelibrary.wiley.com/doi/full/10.1002/2015JD024358
- Volkamer 2006 models underestimated SOA (is this about glyoxal? Likely)
- Zhao 2017 http://www.pnas.org/content/114/27/6984.short
- Jathar 2014 http://www.pnas.org/content/111/29/10473.short
- Dzepina 2011