Simulation of semi-explicit mechanisms of SOA formation from glyoxal in a 3D model

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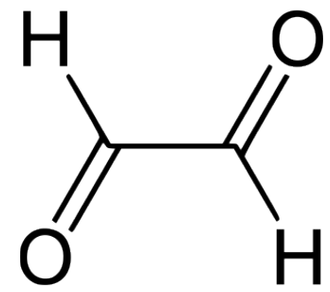
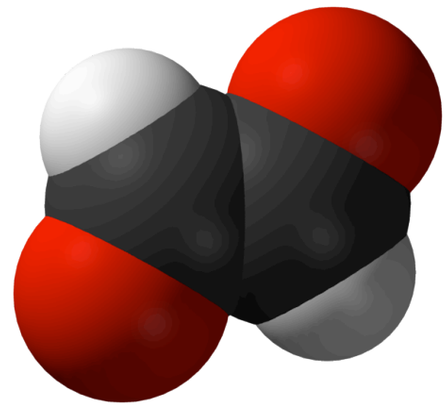
[10)]Indiana University, Bloomington, Indiana, USA
[10)]Department of Environmental Toxicology, University of California, Davis, USA

NCAR



http://en.wikipedia.org/wiki/Glyoxal



Glyoxal

- occurs in the atmosphere at **sub-ppbv levels**
- **anthropogenic and biogenic sources**
- **highly soluble**
- reversible and irreversible **SOA formation observed in laboratory studies**
- modeling studies found mass contributions of **15% of SOA in Mexico City, 0-4% in LA**

a novel pathway for multiphase SOA formation?

WRF-Chem 3.4.1 setup

2 weeks in June 2010 (CalNex, CARES meas. campaigns)

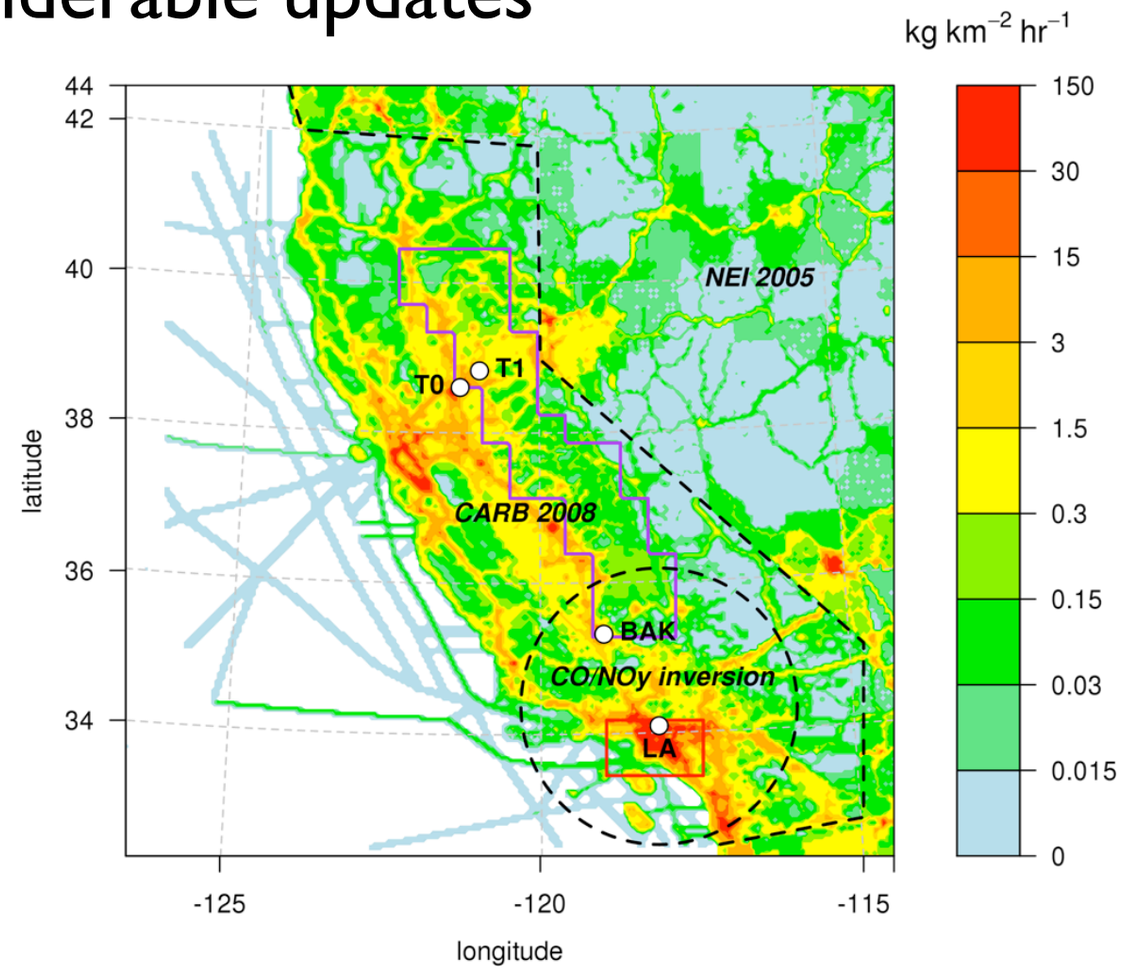
4 km horiz. res., 40 vertical levels

IC/BC: GFS (meteorology) / MOZART (chemistry)
emissions: NEI 2005 + CARB 2008 + considerable updates

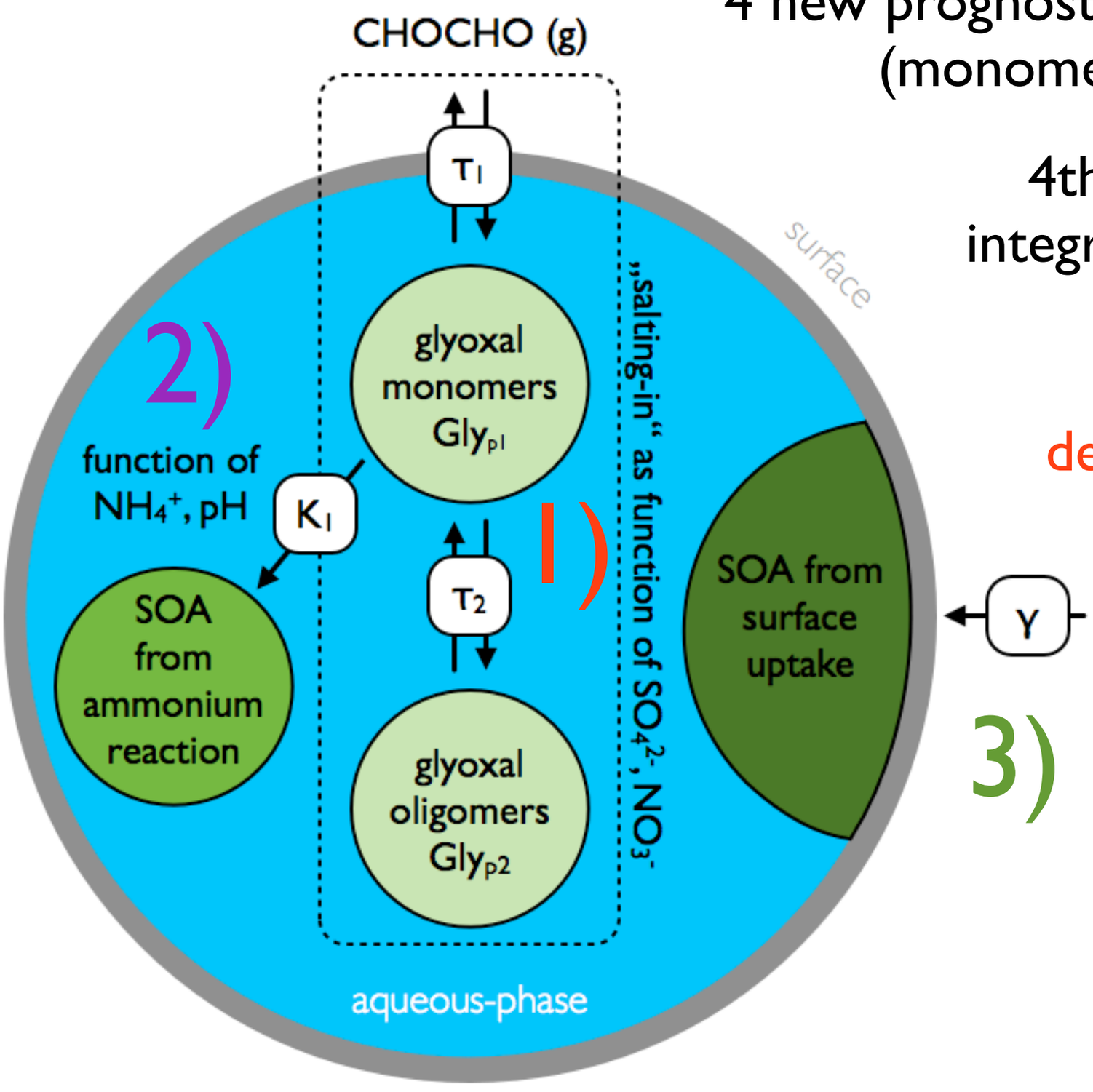
MOZART gas-phase chemistry
(Emmons et al., GMD, 2010)

+ more explicit aromatics scheme
+ ethyne chemistry
+ updated isoprene oxidation
+ HONO photolysis

MOSAIC 4-bin aerosol scheme with
simplified traditional SOA formation
(Zaveri et al., JGR, 2008; Hodzic and Jimenez, GMD, 2011)



Implementation in WRF-Chem



4 new prognostic components in each size bin (monomers, oligomers, volume, surface)

4th-order Runge-Kutta numerical integration each chemistry timestep

1) gas-liquid partitioning dependent on salt concentration

2) volume pathway

3) surface uptake

based on

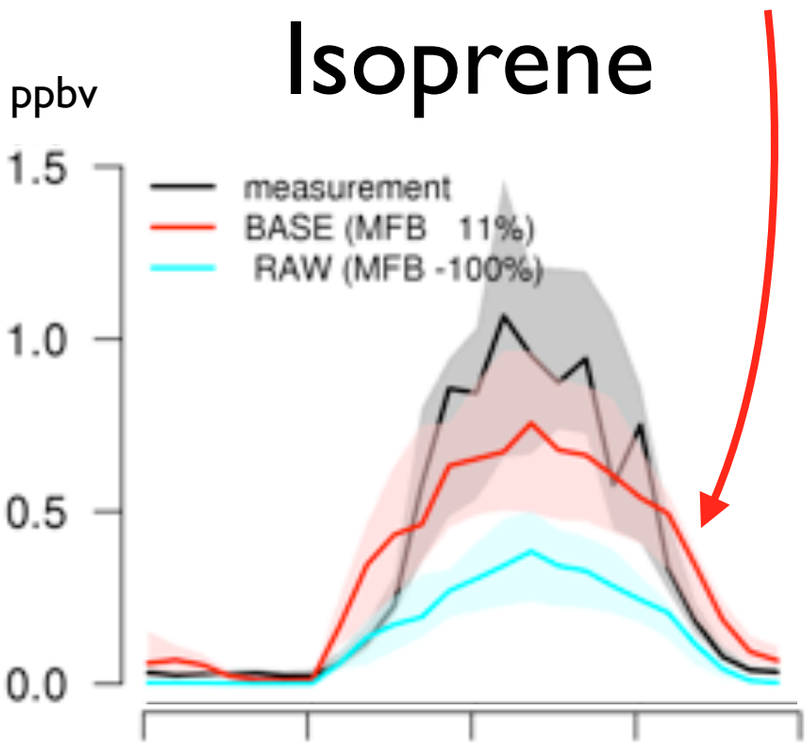
Noziere et al., J. Phys. Chem. A, 2008

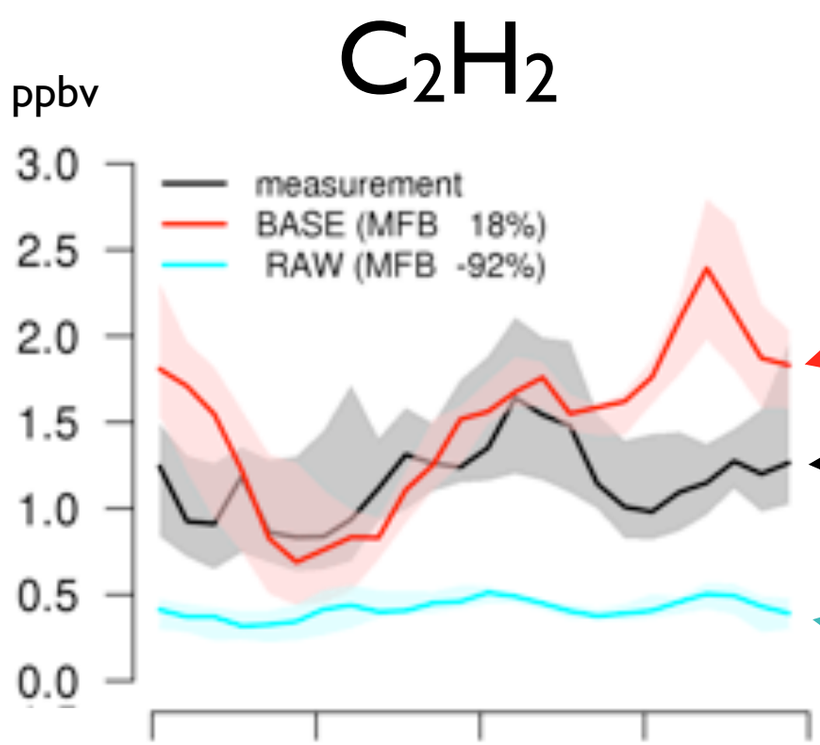
Ervens and Volkamer, ACP, 2010

Kampf et al., ES&T, 2013

Precursors in Pasadena

MEGAN over urban areas x 2.5

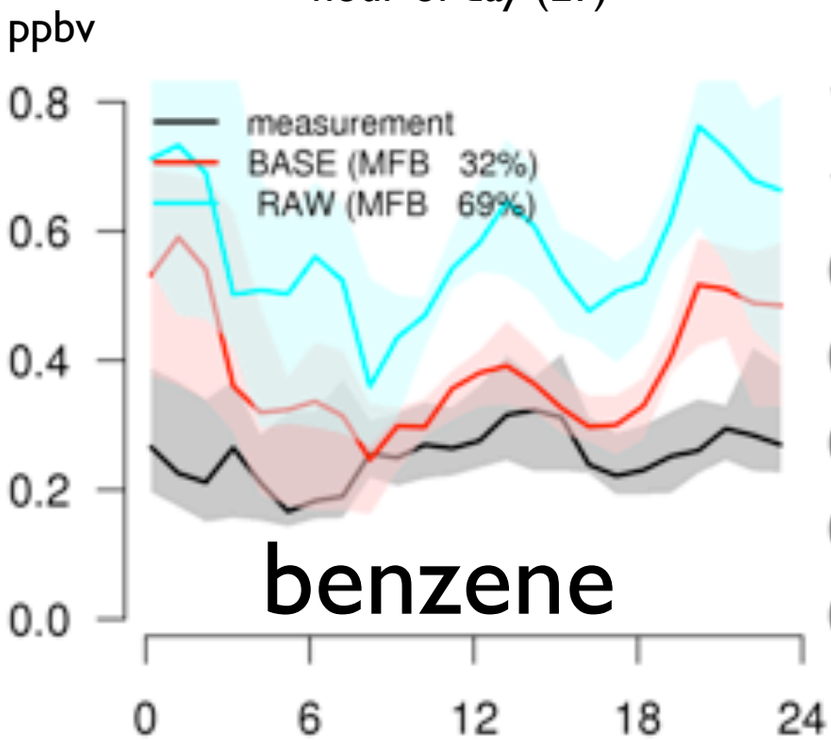


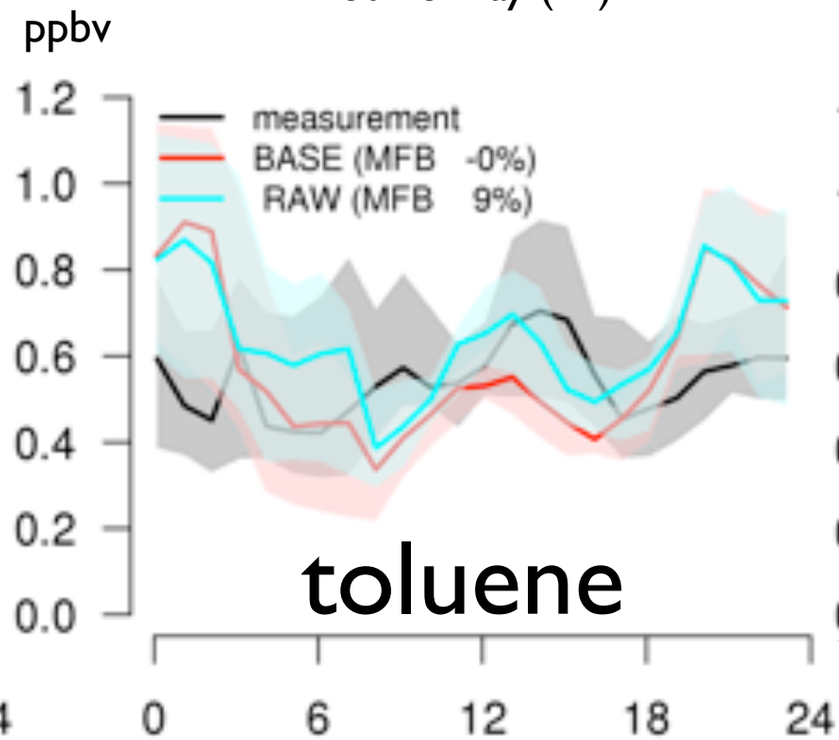


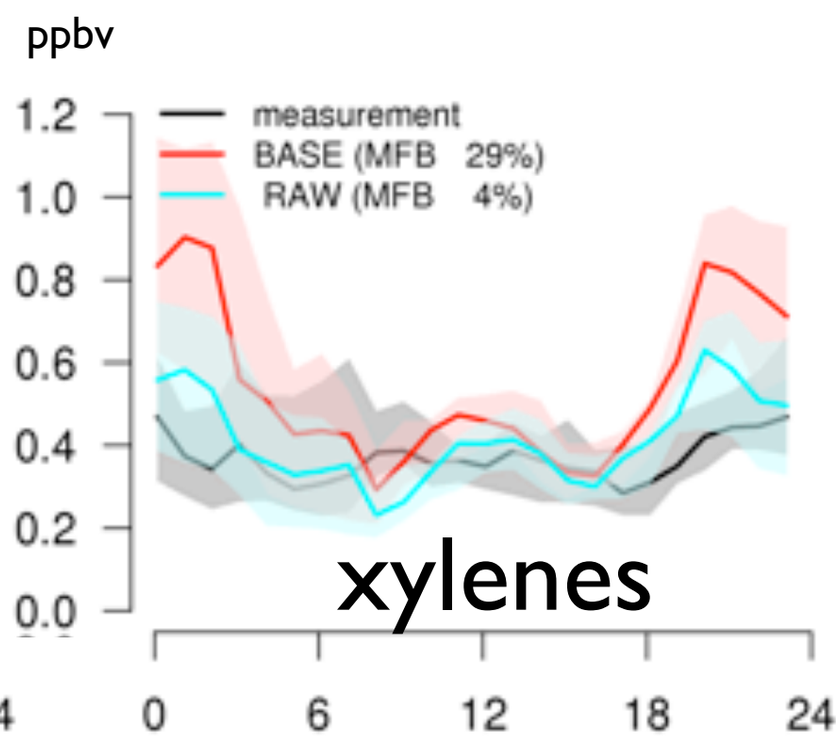
updated emissions

measurements

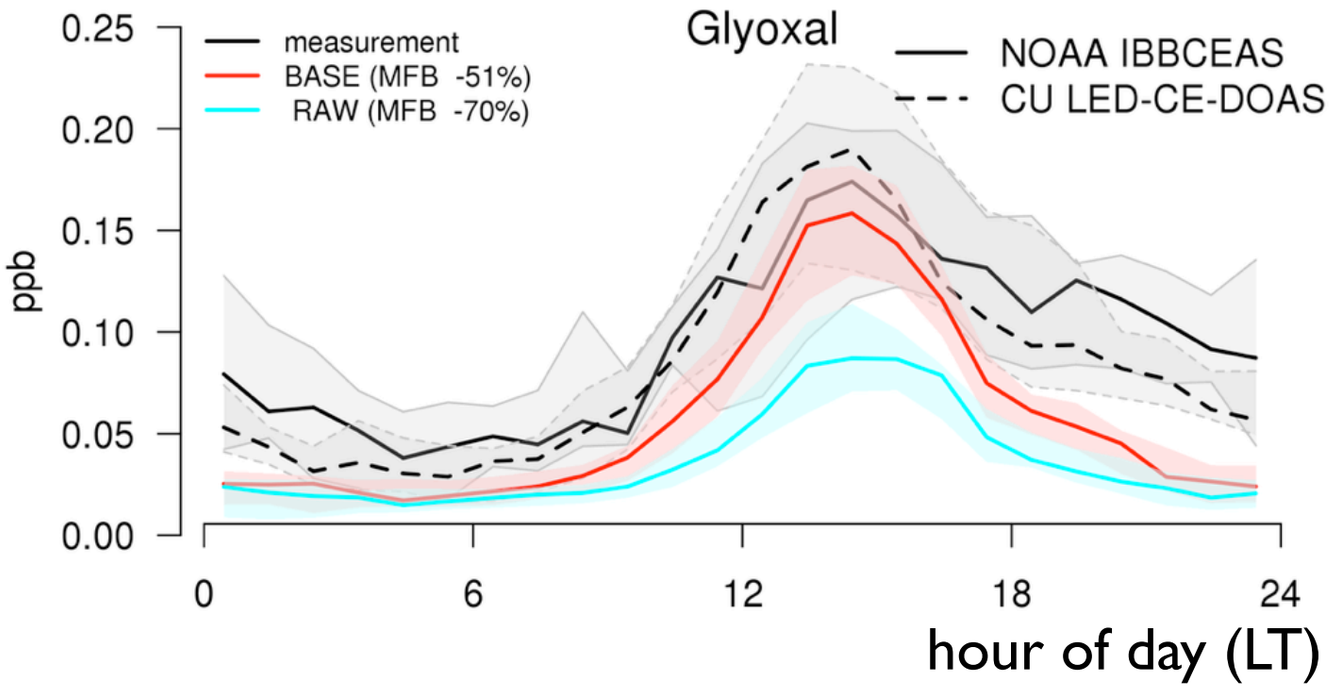
CARB/NEI inventory







GC-MS measurements by de Gouw, Gilman, Kuster (NOAA)



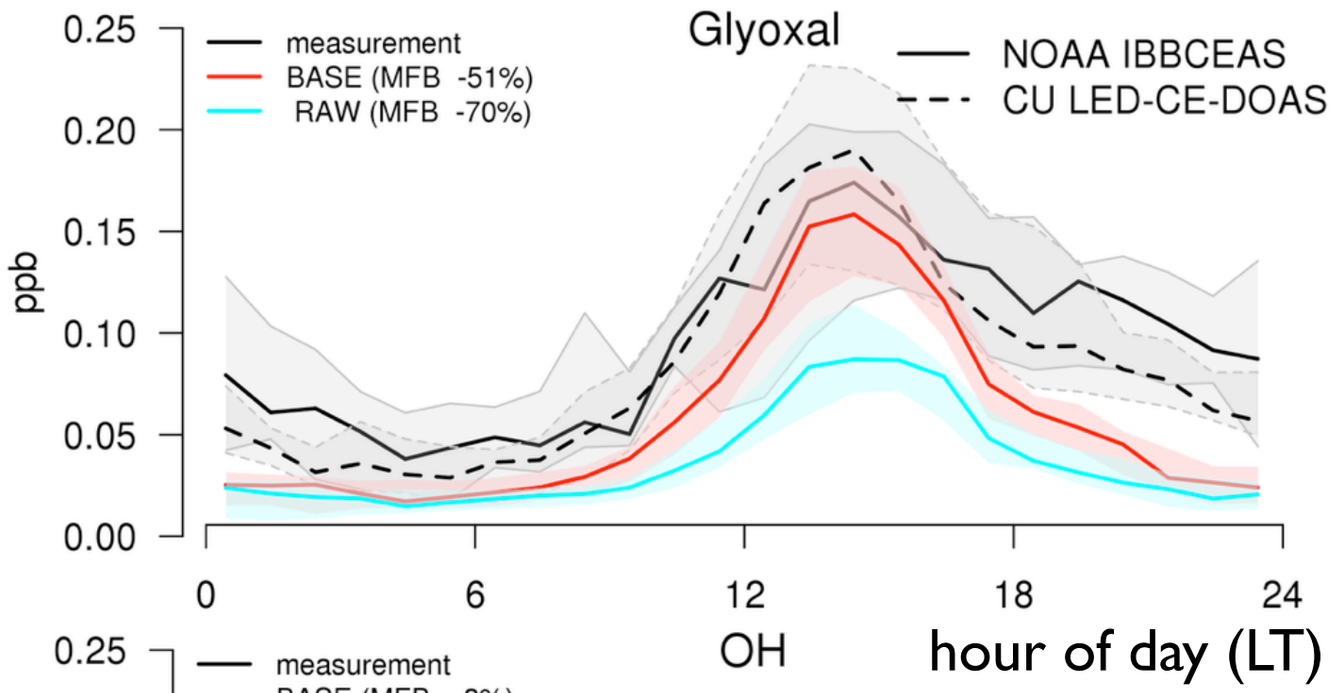
Glyoxal concentrations

Pasadena ground site

measurements by

Washenfelder, Young, Brown (NOAA)

Thalman, Waxman, Volkamer (CU Boulder)



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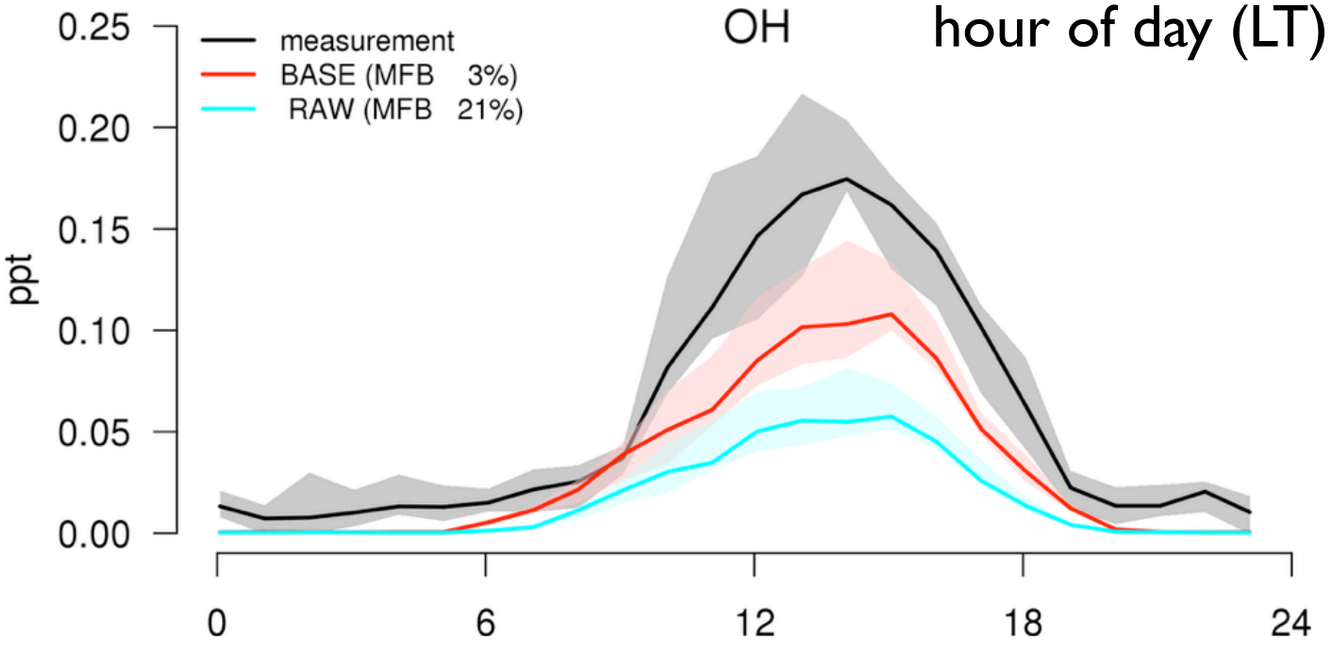
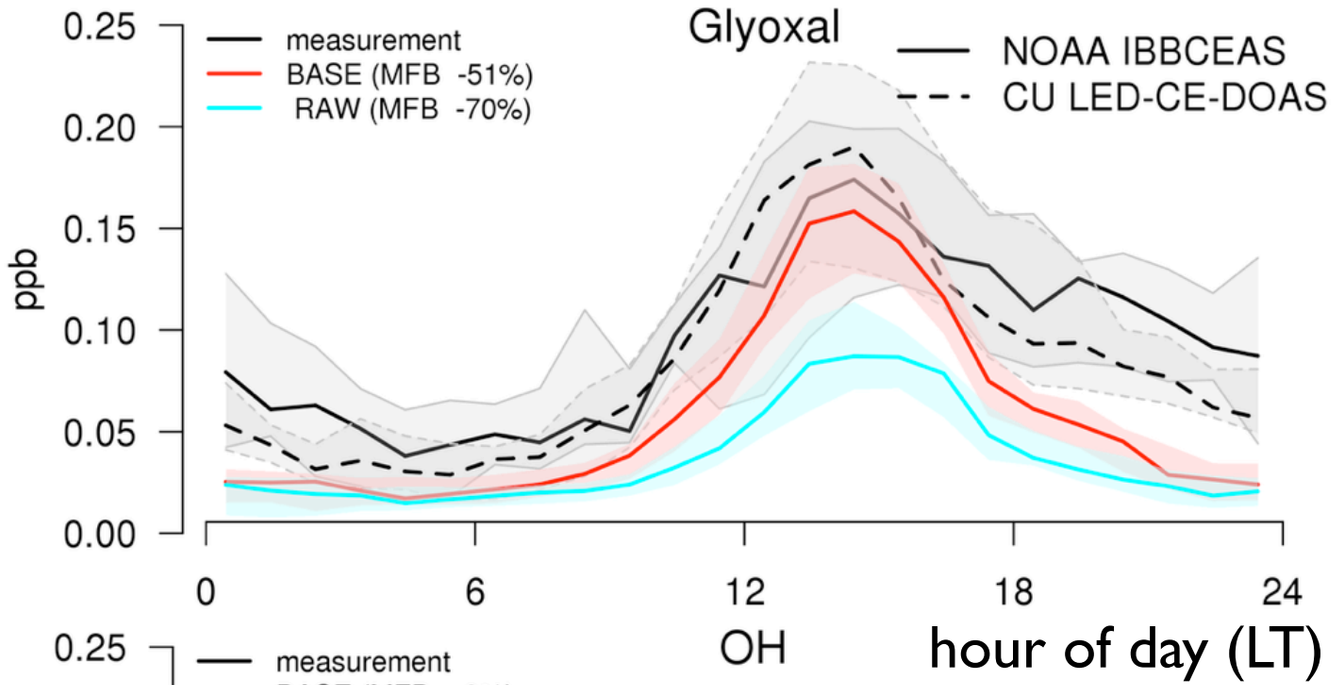


OH sink

Pasadena ground site

measurements by
Dusanter, Griffith, Hansen, Stevens (U Indiana)



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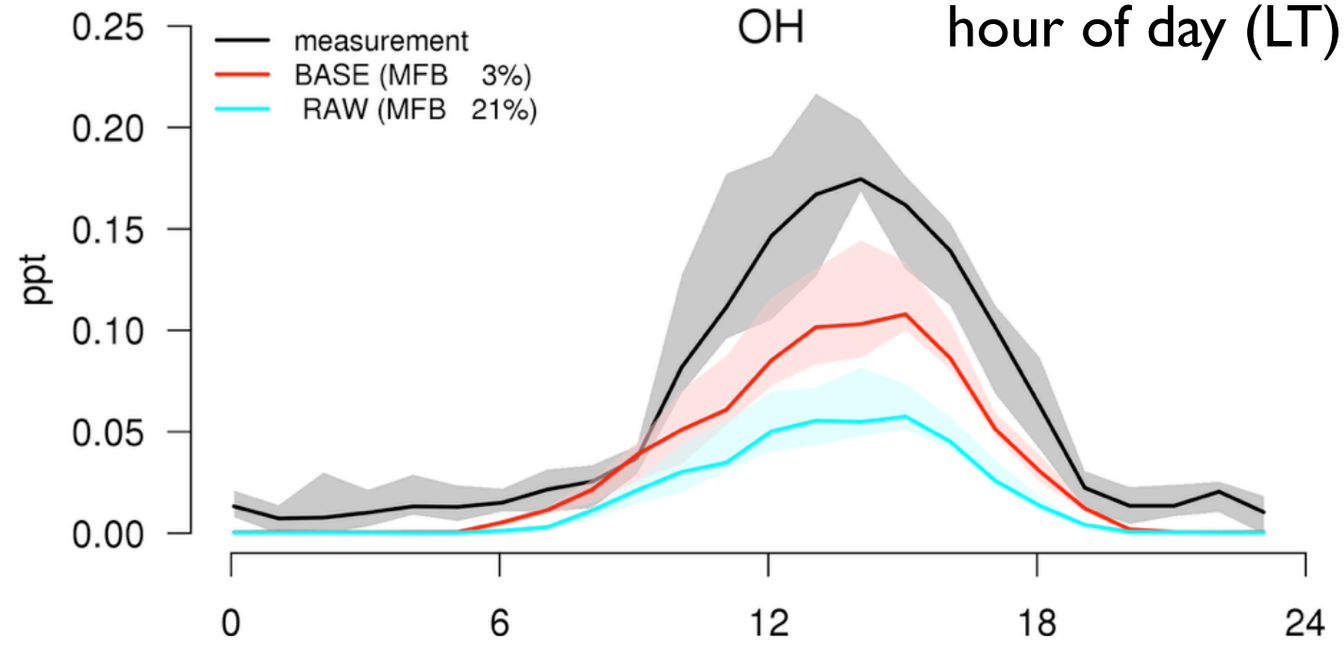

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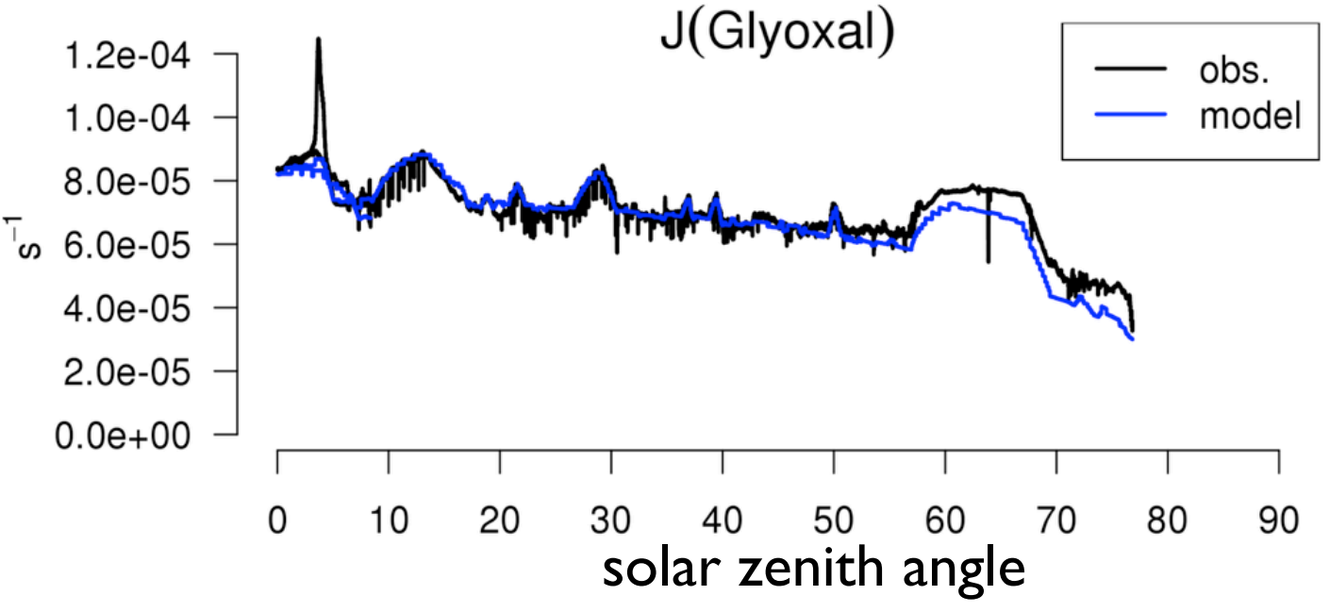


Photolysis sink

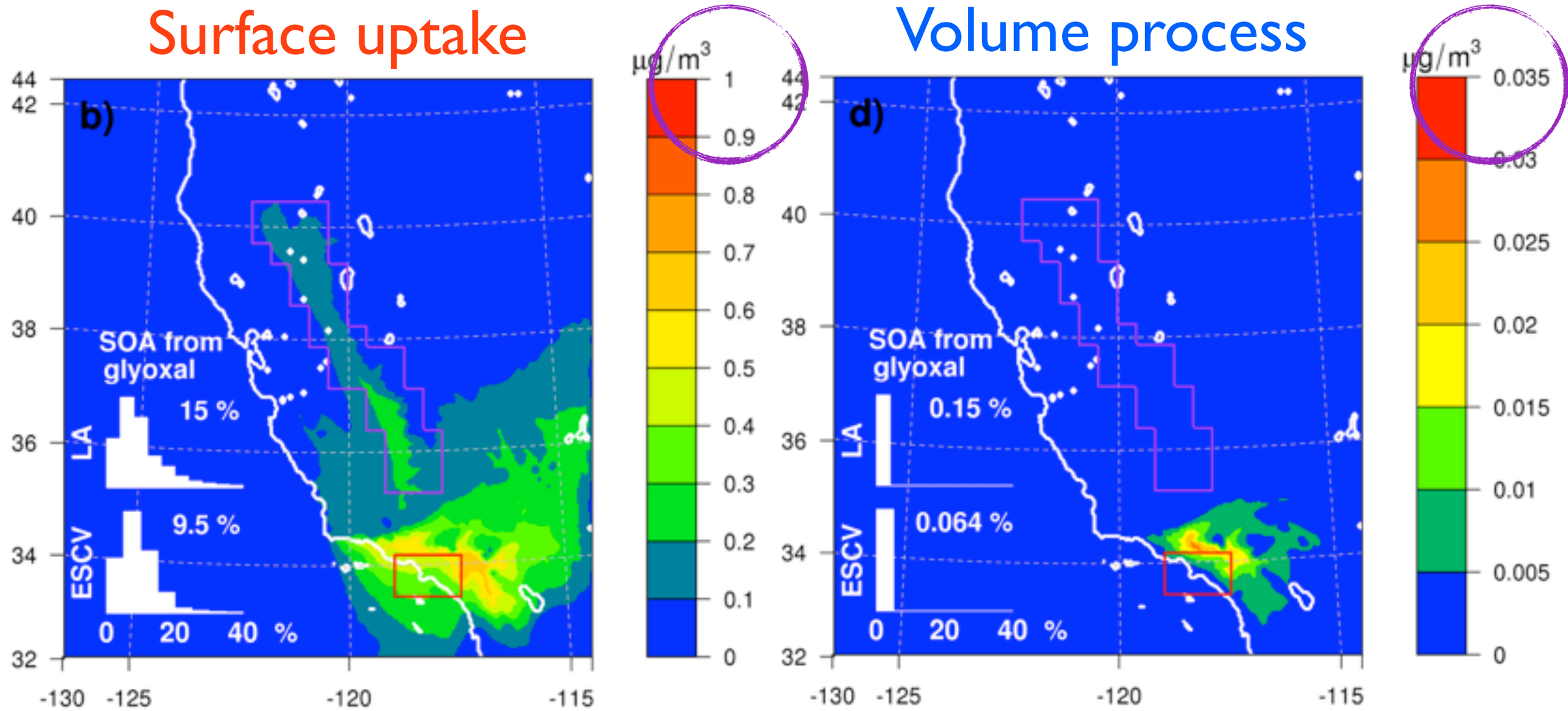
NOAA P3 flight on 06/14

measurements by Harald Stark

SOA contribution from glyoxal

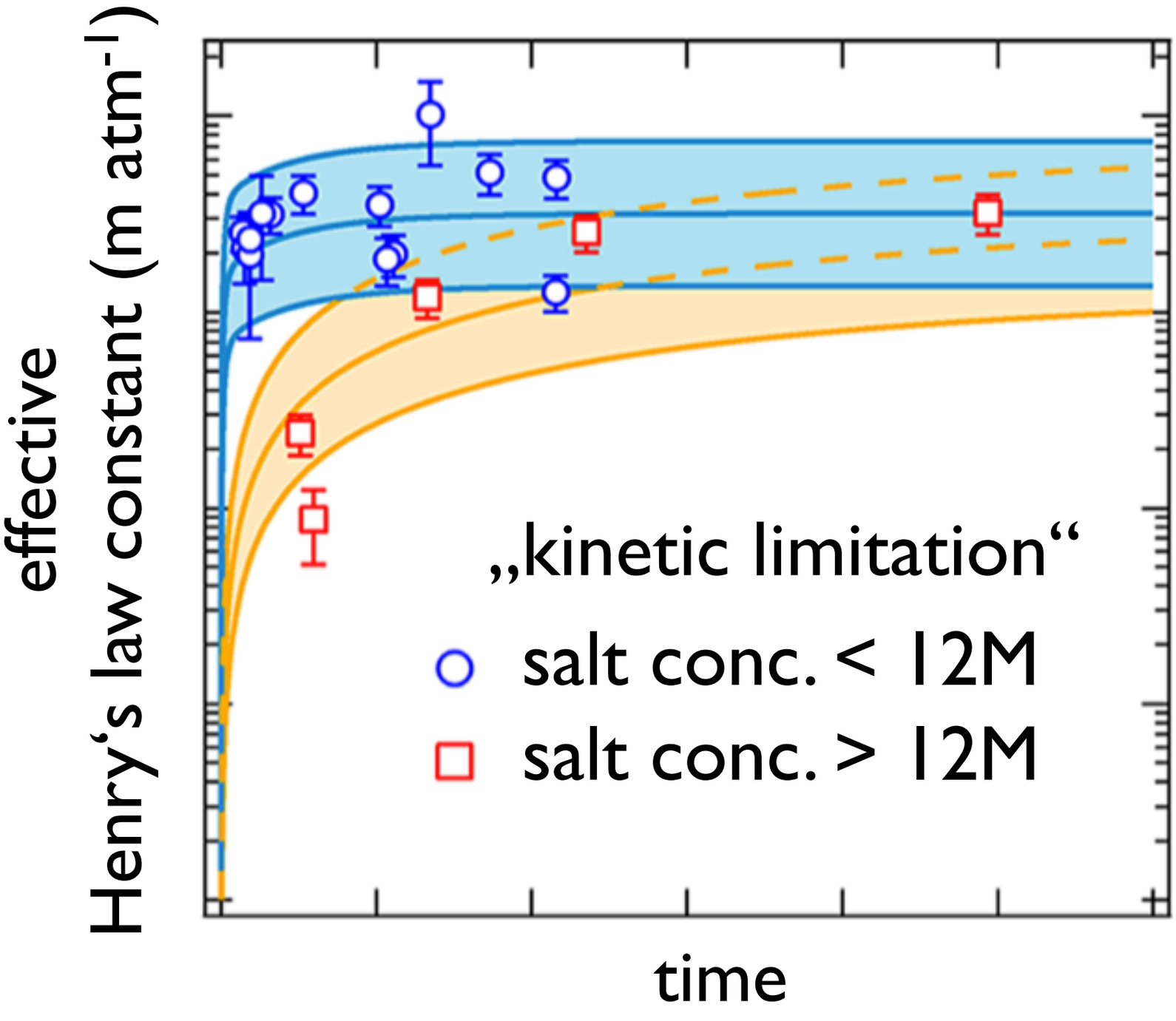
Surface uptake

Volume process



with a simple **surface uptake** parameterization, glyoxal adds **15% to SOA mass** in the LA basin, with a **volume process** only **0.15%**.

Why isn‘t there more SOA through the volume pathway?



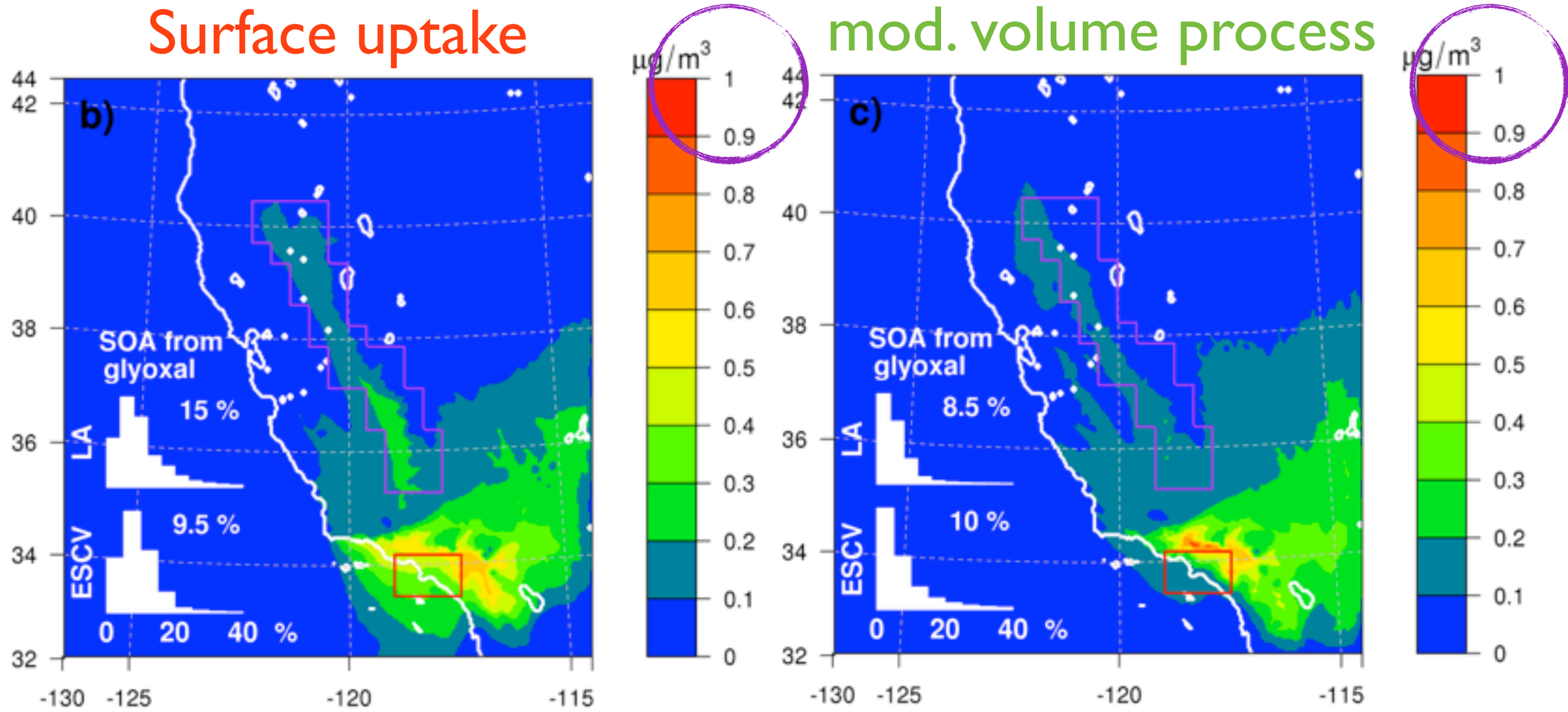
at high salt concentrations, supply of glyoxal to aerosol is limiting SOA production

figure adapted from Kampf et al., ES&T, 2013 and strongly simplified

SOA contribution from glyoxal

Surface uptake

mod. volume process

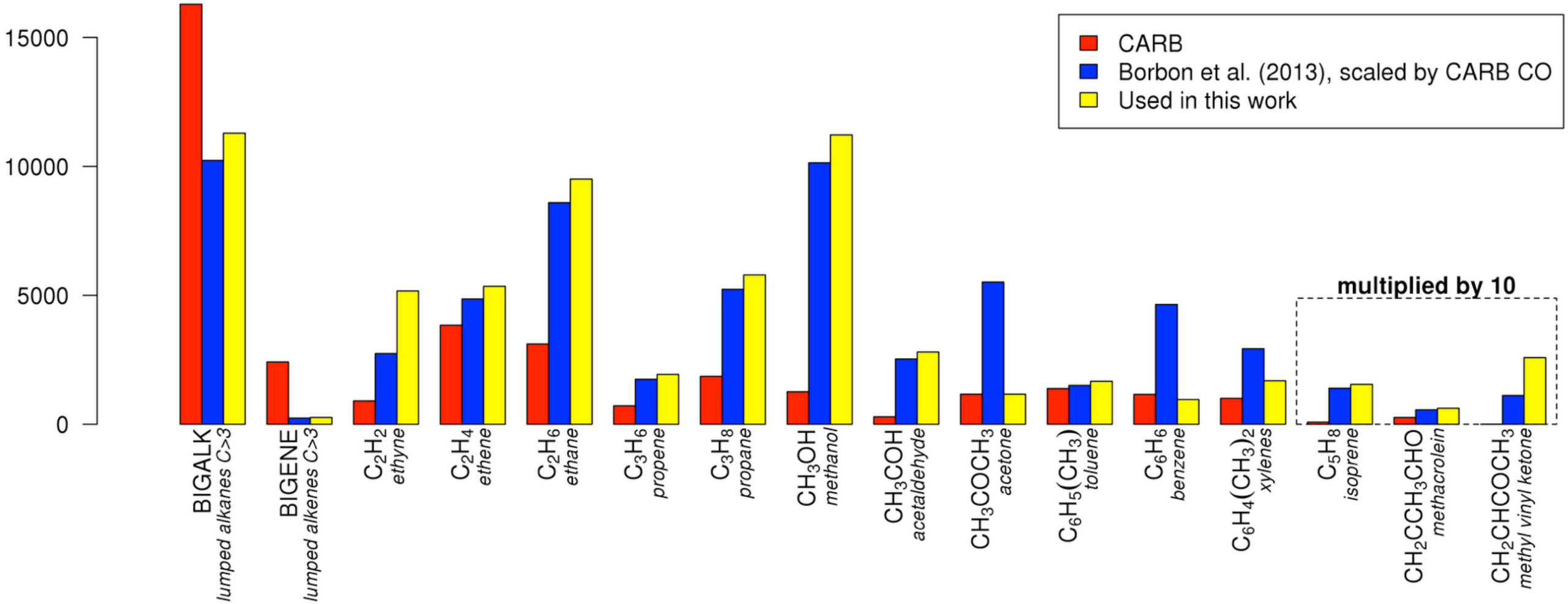


without kinetic limitation the **volume process contributes 8.5%** to SOA mass in LA basin.

Conclusions

- SOA formation from glyoxal investigated on the regional scale with WRF-Chem
- Parameterizations ranging from very simple to detailed methods
- **LA basin is hotspot for SOA formation from glyoxal** in all parameterizations
- contributions of **0.15 to 15% of total SOA mass** in LA basin, depending on parameterization chosen
- **limiting for volume pathway** production **is** a kinetic limitation in the **gas to liquid-phase transfer**

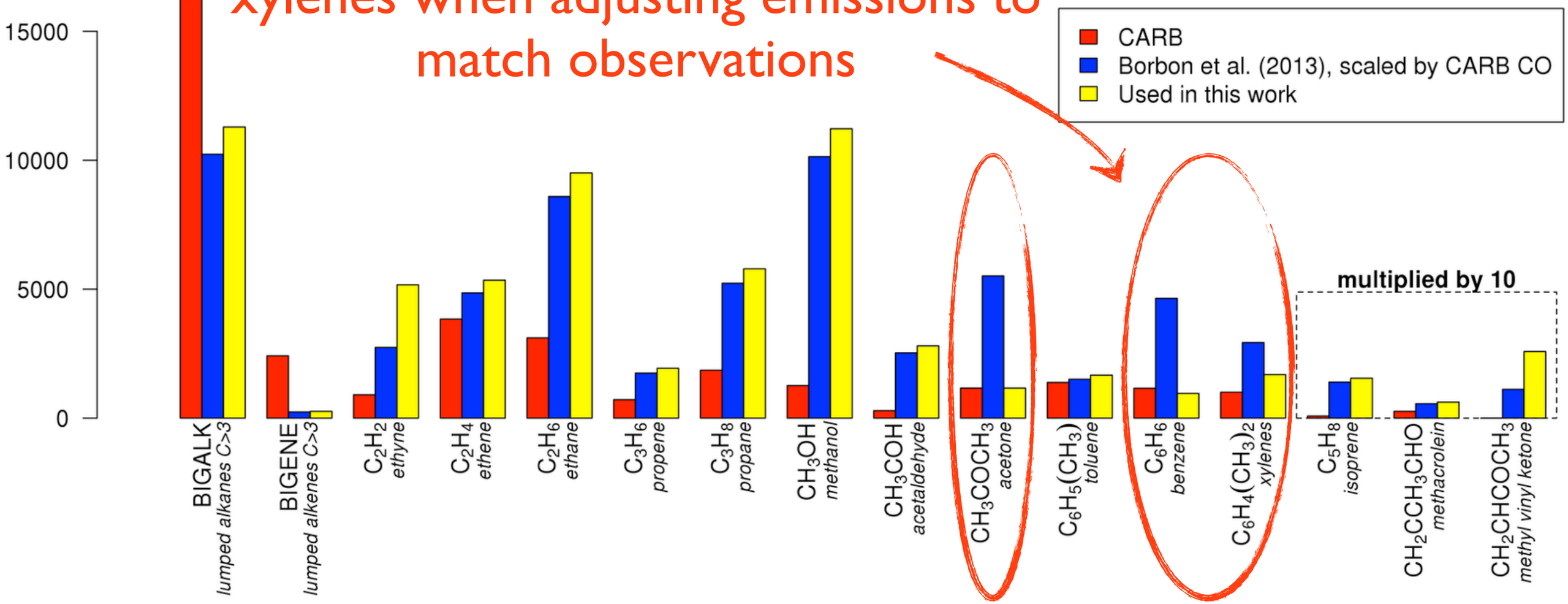
Emissions



Large discrepancies in speciated anthropogenic VOC emissions between inventories (CARB, NEI) and inversion-based approach (Borbon et al., JGR, 2013)

Emissions

but: inventory seems more reasonable for acetone, benzene and xylenes when adjusting emissions to match observations



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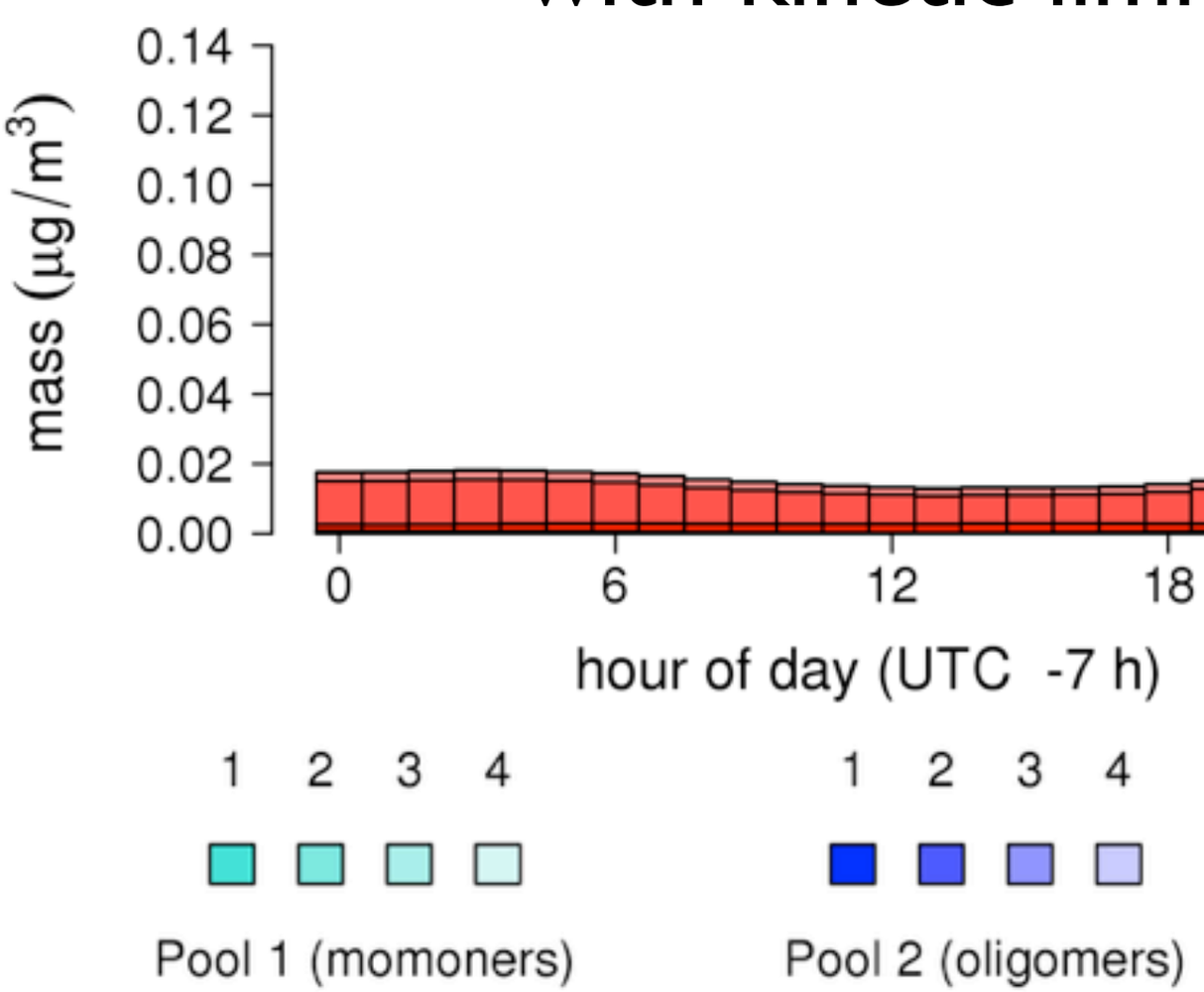
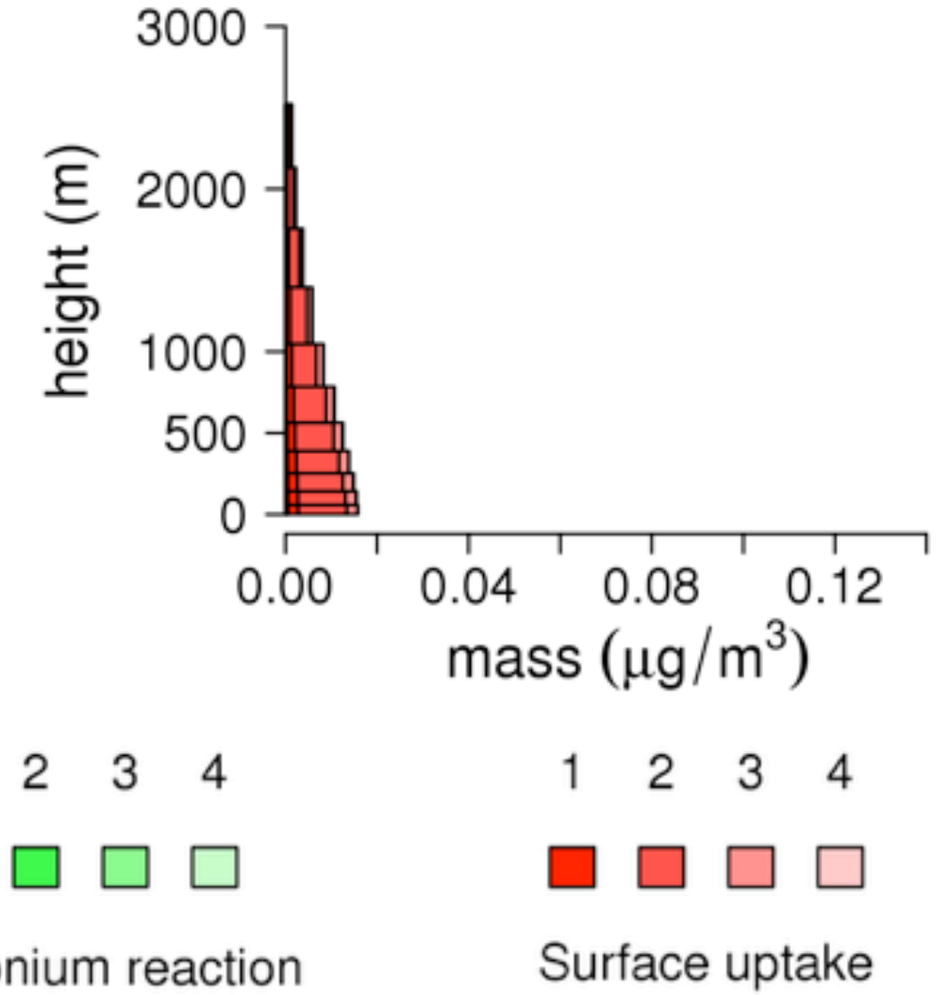
Reversible vs. irreversible processes

with kinetic limit





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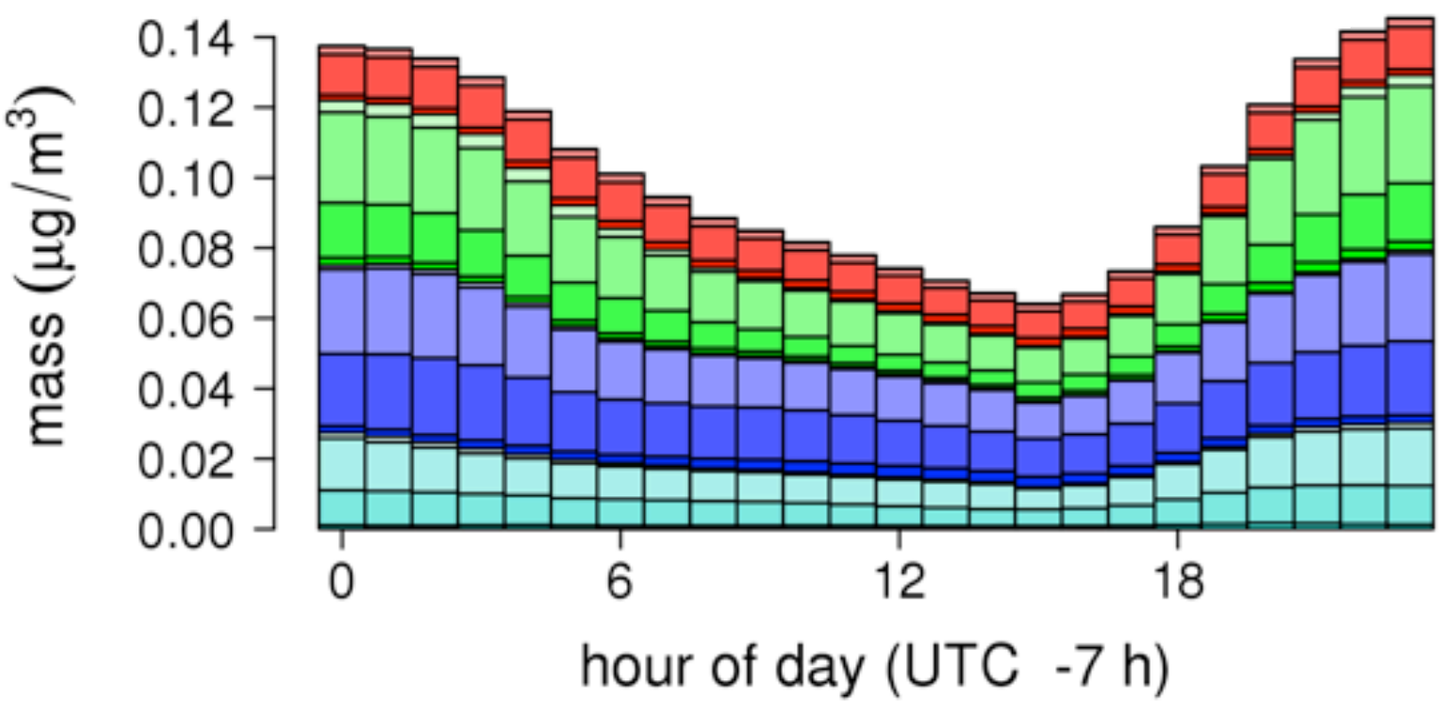

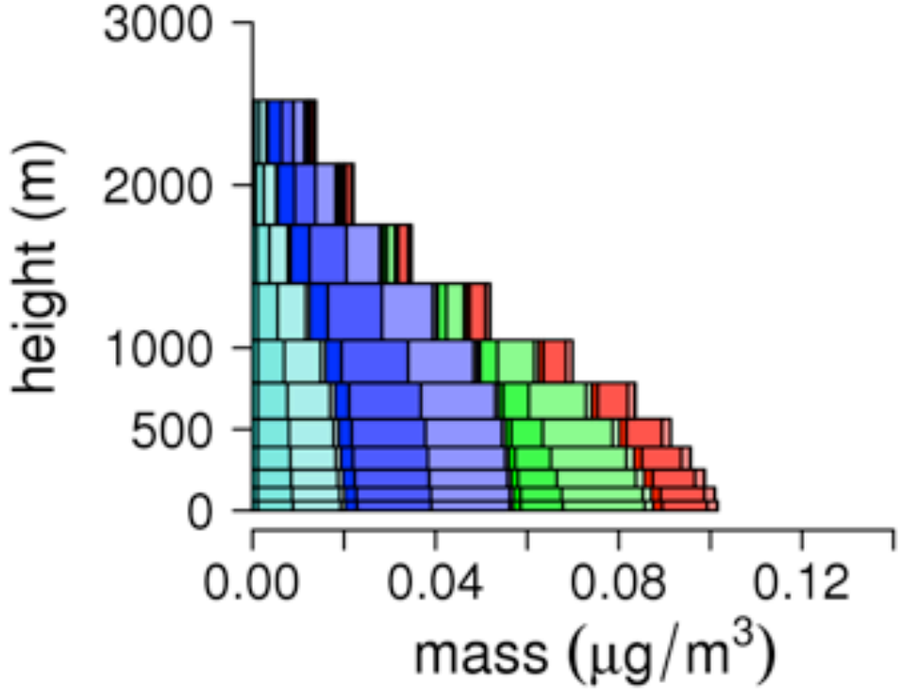

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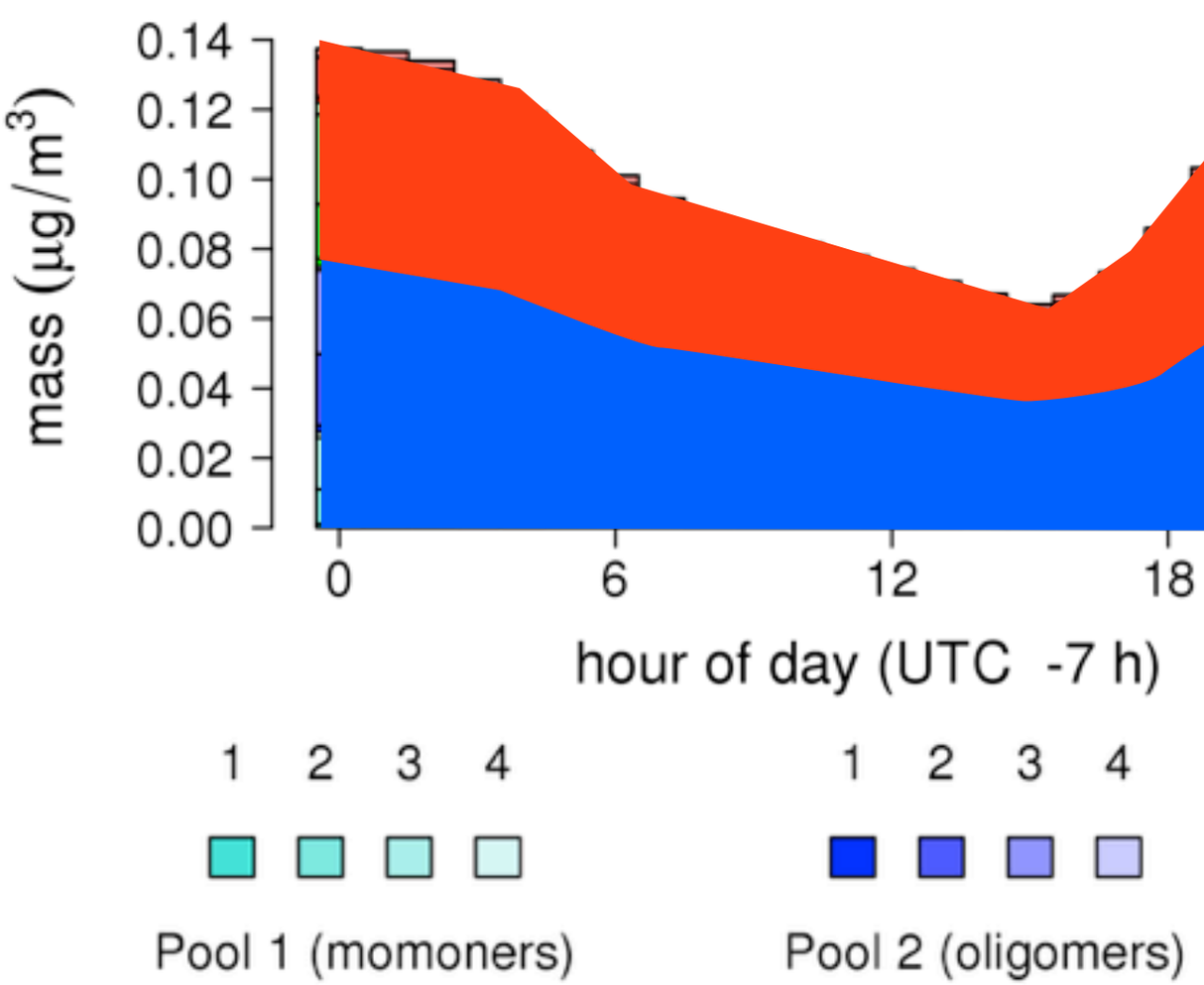

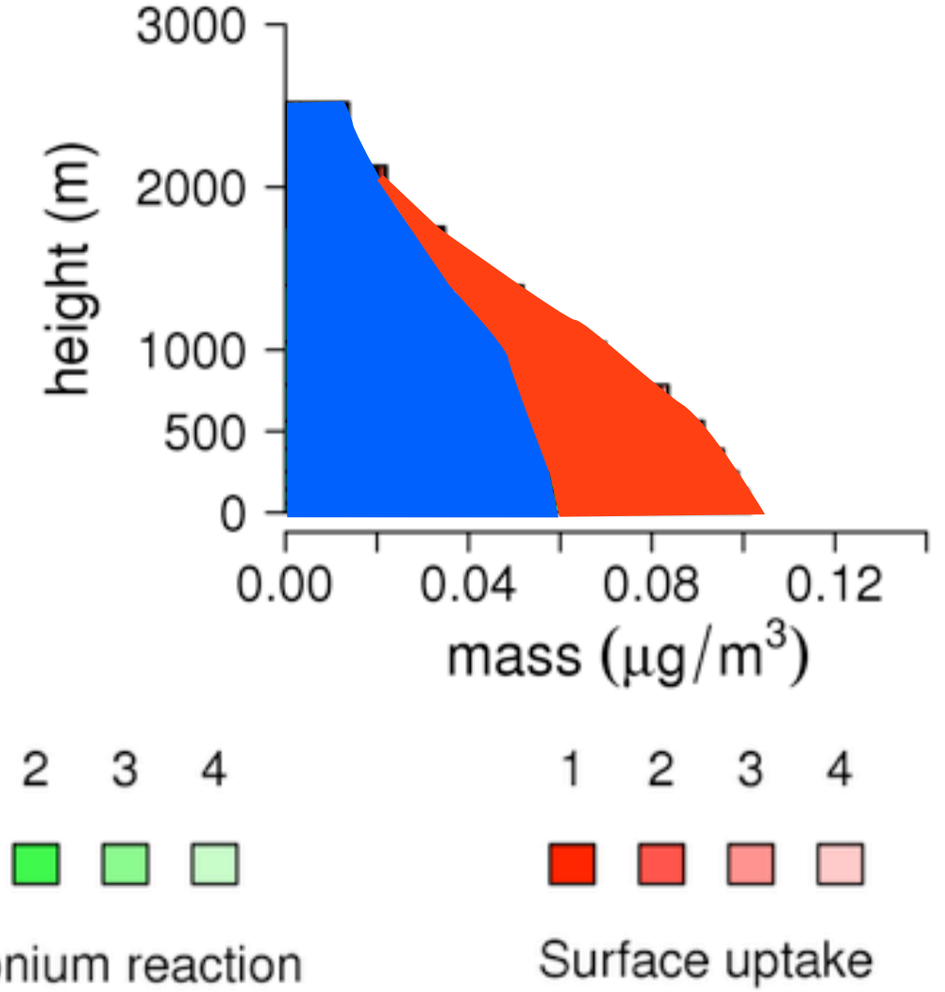

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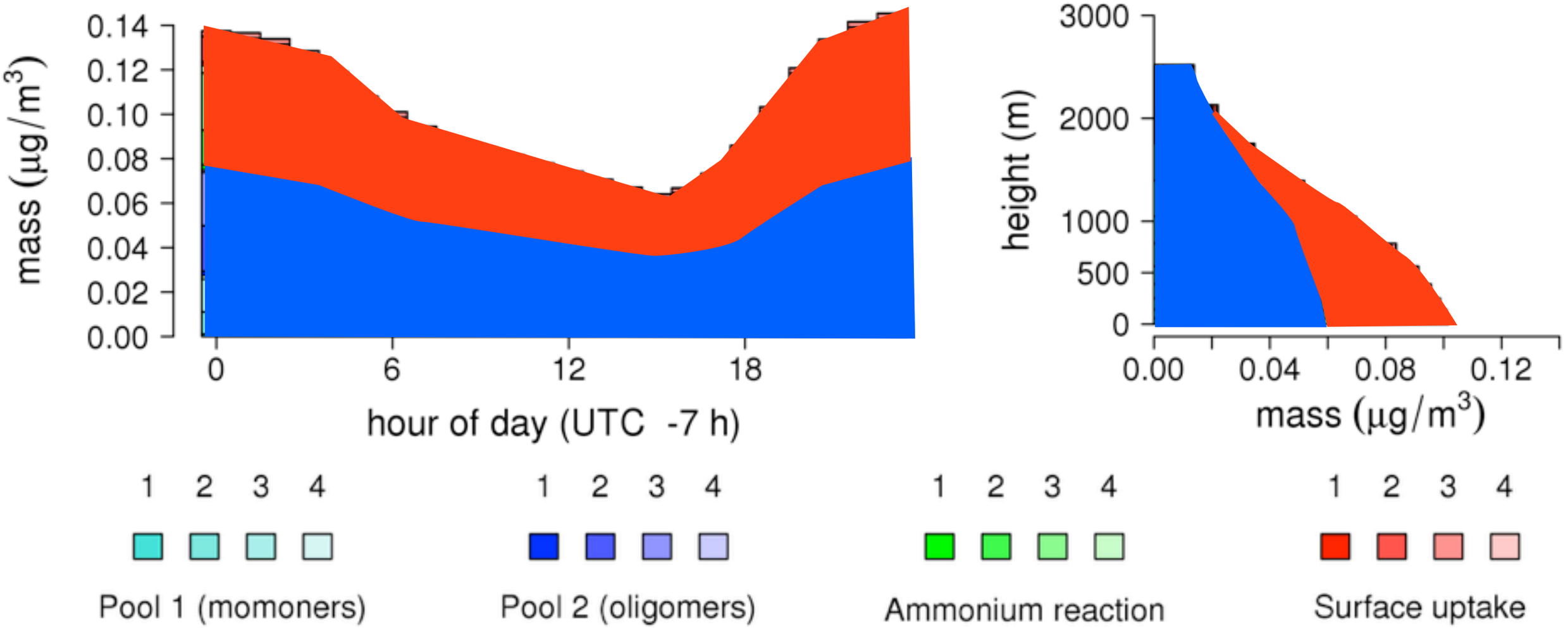
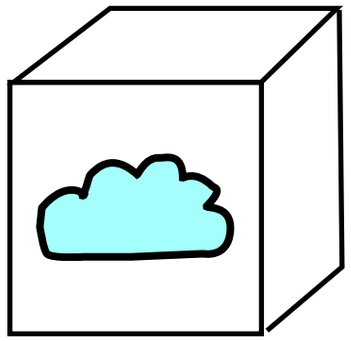


IF the kinetic limitation is not real (e.g. measurement artefact), then reversible formation (monomers, oligomerization) contributes > 50% to SOA from glyoxal

SOA formation from glyoxal

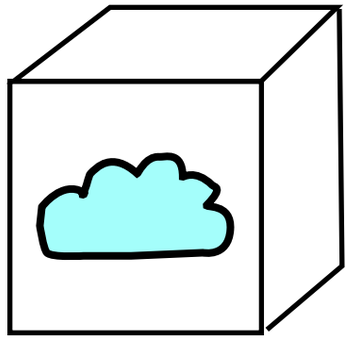


Smog chamber study

(Kampf et al., ES&T, 2013)

„salting-in“: dissolved salts in aerosol water increase K_H by 3 orders of magnitude

SOA formation from glyoxal



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Laboratory study

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„glyoxal + NH^{-}_{4} → SOA“ as function of ammonium activity and aerosol pH

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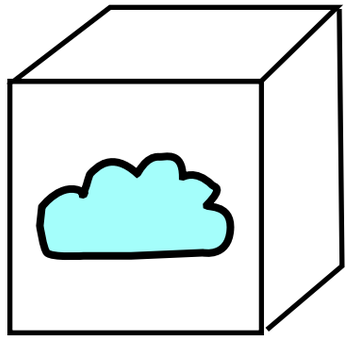

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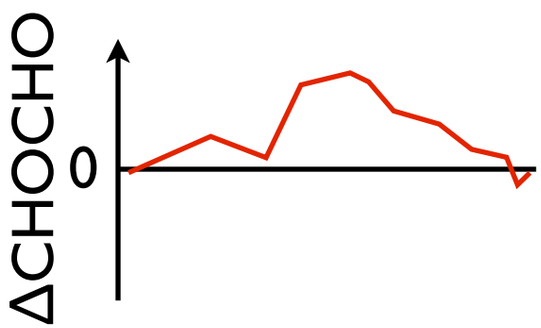


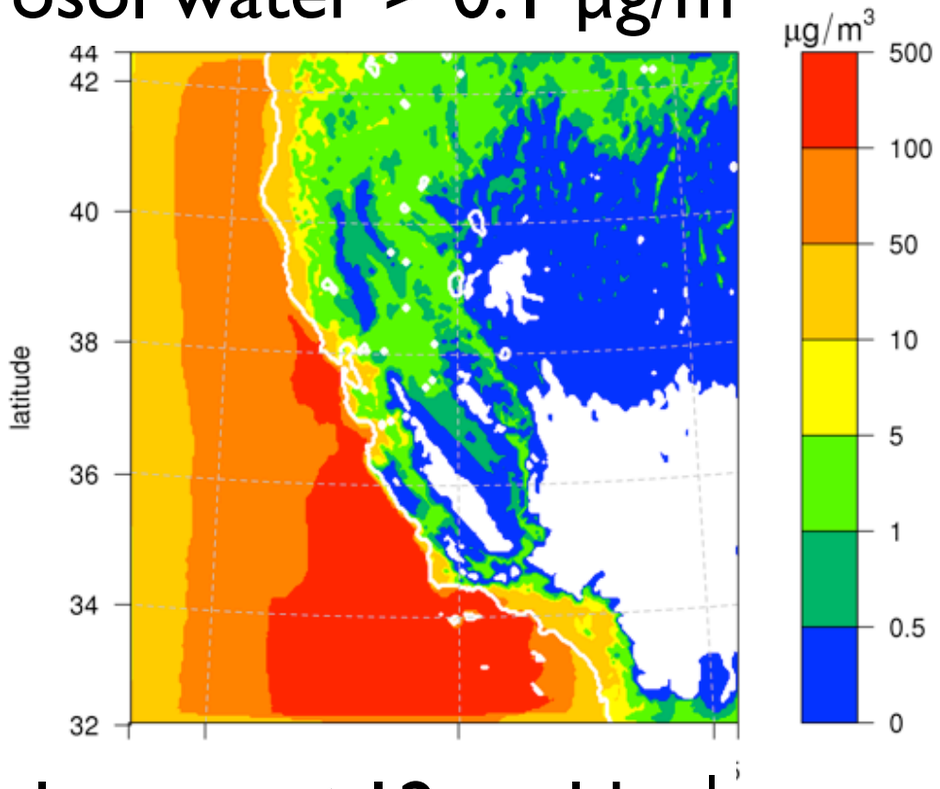
Model+measurement imbalance studies

(Volkamer et al., GRL, 2007, Washenfelder et al., JGR, 2011)

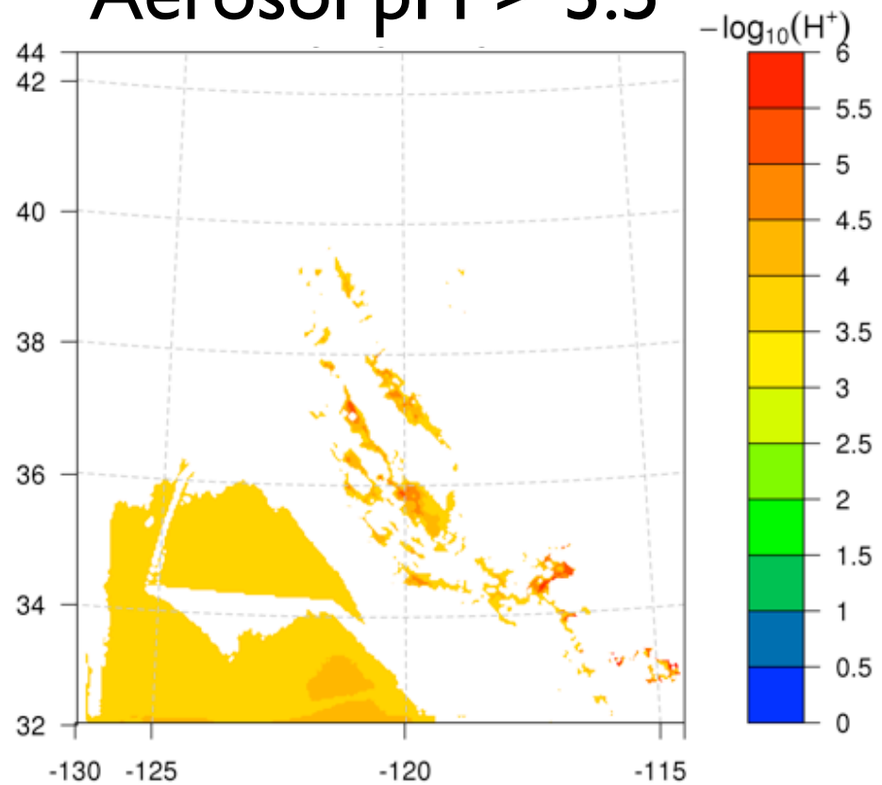
surface uptake with γ~1e-3

Favorable environment for volume process

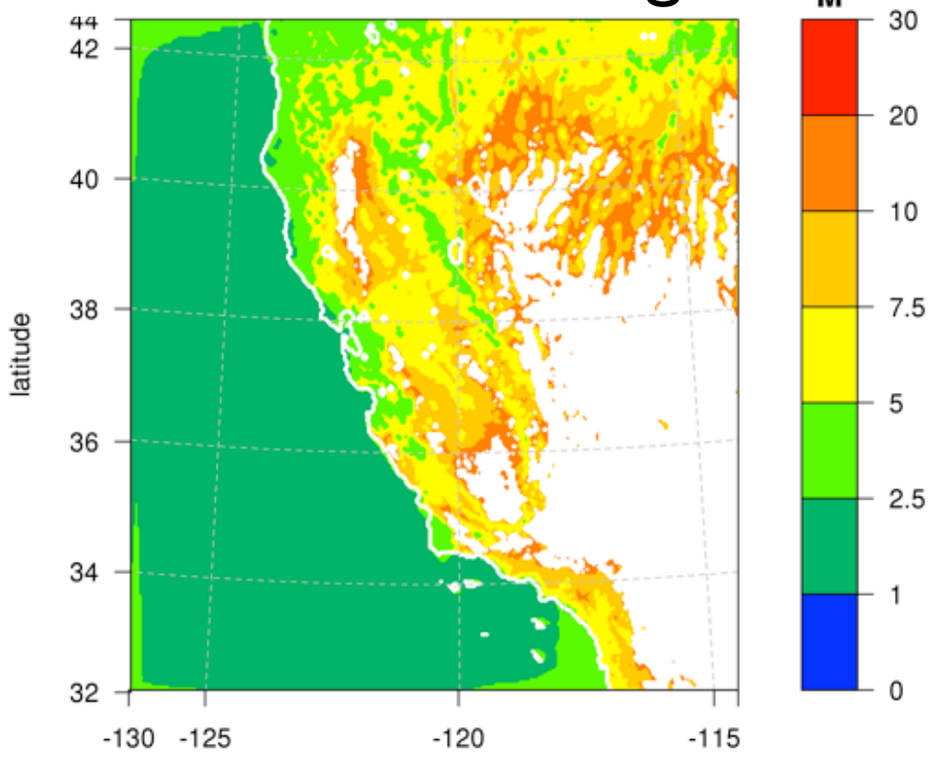
Aerosol water > 0.1 μg/m^3

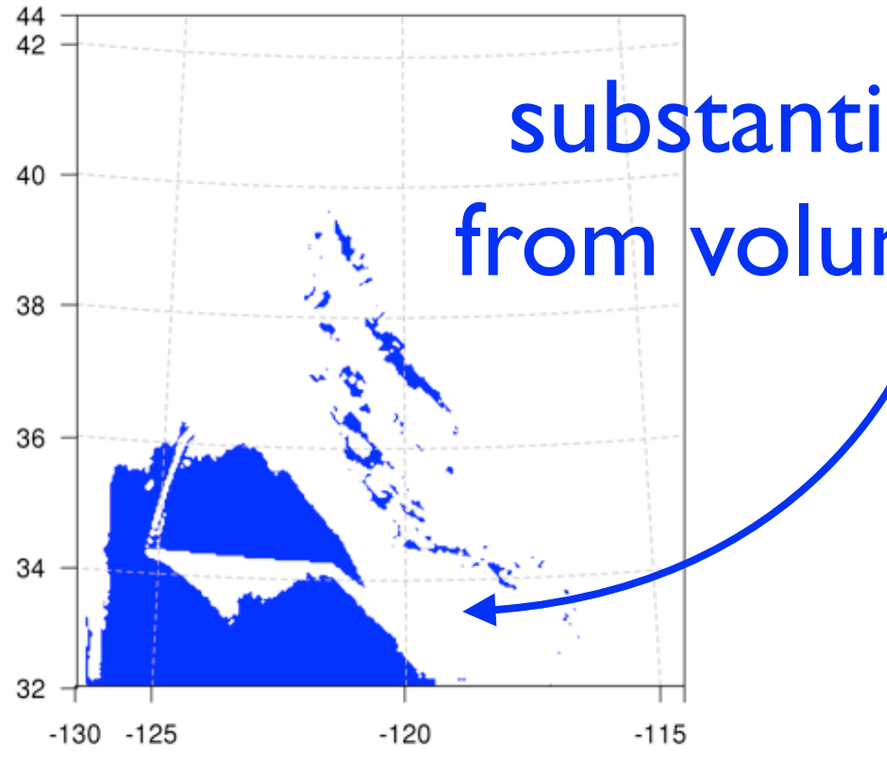


Aerosol pH > 3.5



salt conc. < 12 mol kg^{-1}





substantial contrib.
from volume process