

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

Christoph Knote¹⁾, Alma Hodzic¹⁾, Jose L. Jimenez^{2,3)}, Rainer Volkamer^{2,3)}, Sunil Baidar^{2,3)}, Jerome Brioude^{3,5)}, Jerome Fast⁴⁾, Jessica B. Gilman^{3,5)}, Allen Goldstein⁹⁾, Joost de Gouw^{3,5)}, Patrick Hayes^{2,3)}, B. Tom Jobson⁶⁾, W. Berk Knighton⁷⁾, William C. Kuster^{3,5)}, Hilke Oetjen⁸⁾, John Orlando¹⁾, Chen Song⁴⁾, Harald Stark^{3,5)}, Philip S. Stevens¹⁰⁾, Ryan Thalman^{2,3)}, Geoff Tyndall¹⁾, Carsten Warneke^{3,5)}, Rebecca Washenfelder^{3,5)}, Eleanor Waxman^{2,3)}, Qi Zhang¹¹⁾

¹⁾ Atmospheric Chemistry Division, National Center for Atmospheric Research, Boulder, USA

²⁾ Department of Chemistry and Biochemistry, University of Colorado, Boulder, USA

³⁾ CIRES, University of Colorado, Boulder, USA

⁴⁾ Pacific Northwest National Laboratory, Richland, Washington, USA

⁵⁾ Chemical Sciences Division, NOAA Earth System Research Laboratory, Boulder, USA

⁶⁾ Department of Civil and Environmental Engineering, Washington State University, Pullman, WA 99164, USA

⁷⁾ Montana State University, Bozeman, MT 59717, USA

⁸⁾ UCLA/JPL Joint Institute for Regional Earth System Science and Engineering (JIFRESSE), Los Angeles, CA 90095, USA

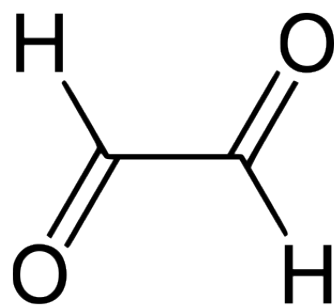
⁹⁾ Dept. of Civil & Environmental Engineering, University of California, Berkeley, USA

¹⁰⁾ Indiana University, Bloomington, Indiana, USA

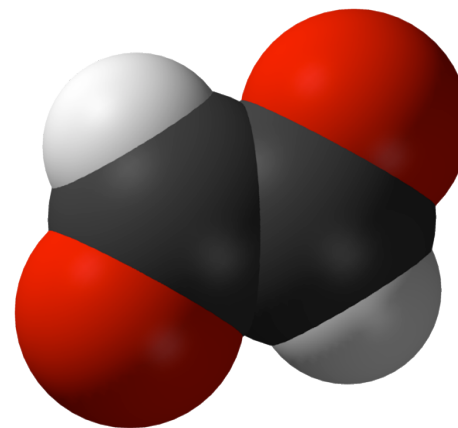
¹¹⁾ Department of Environmental Toxicology, University of California, Davis, USA



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)

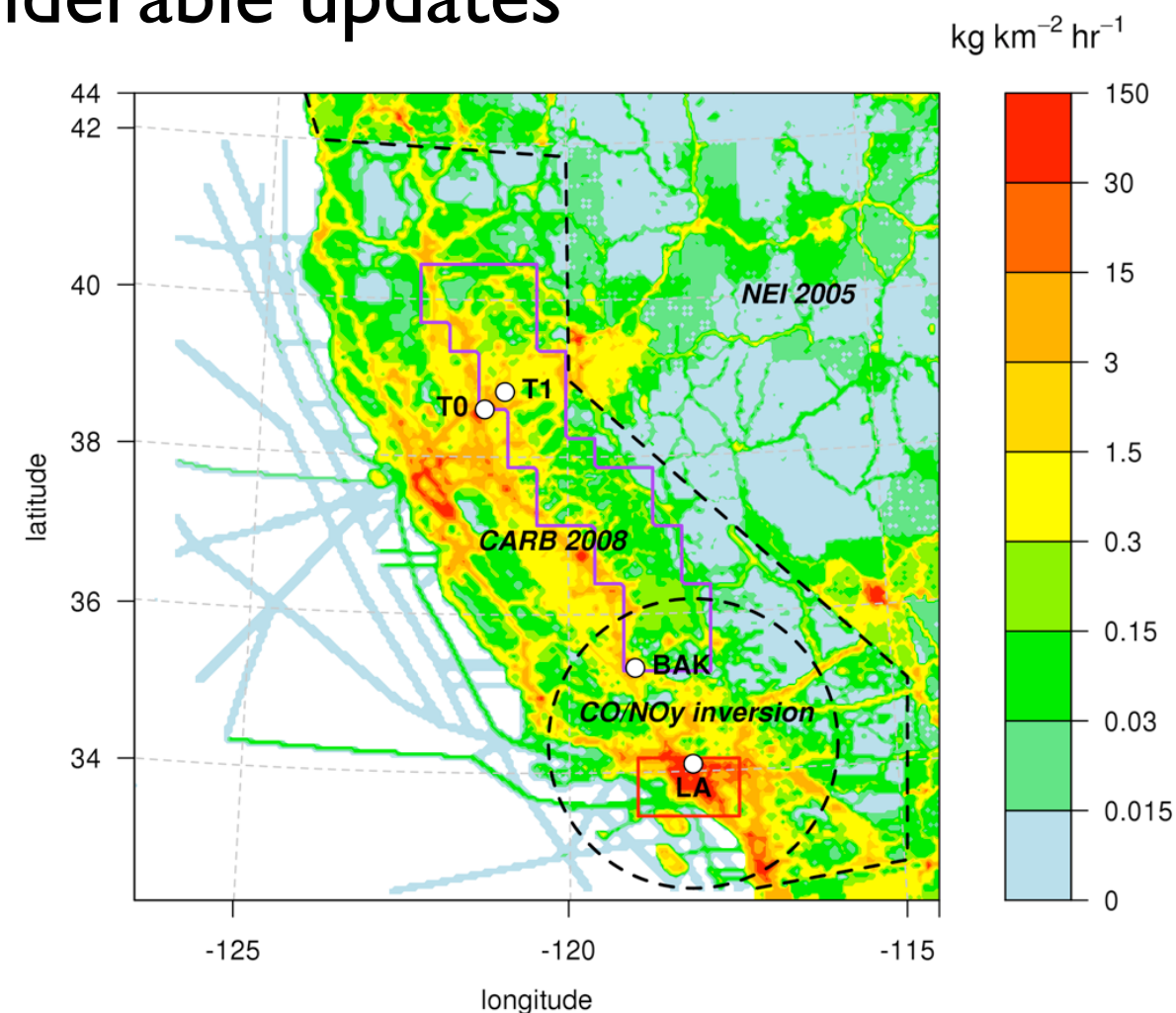
emissions: NEI 2005 + CARB 2008 + considerable updates

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

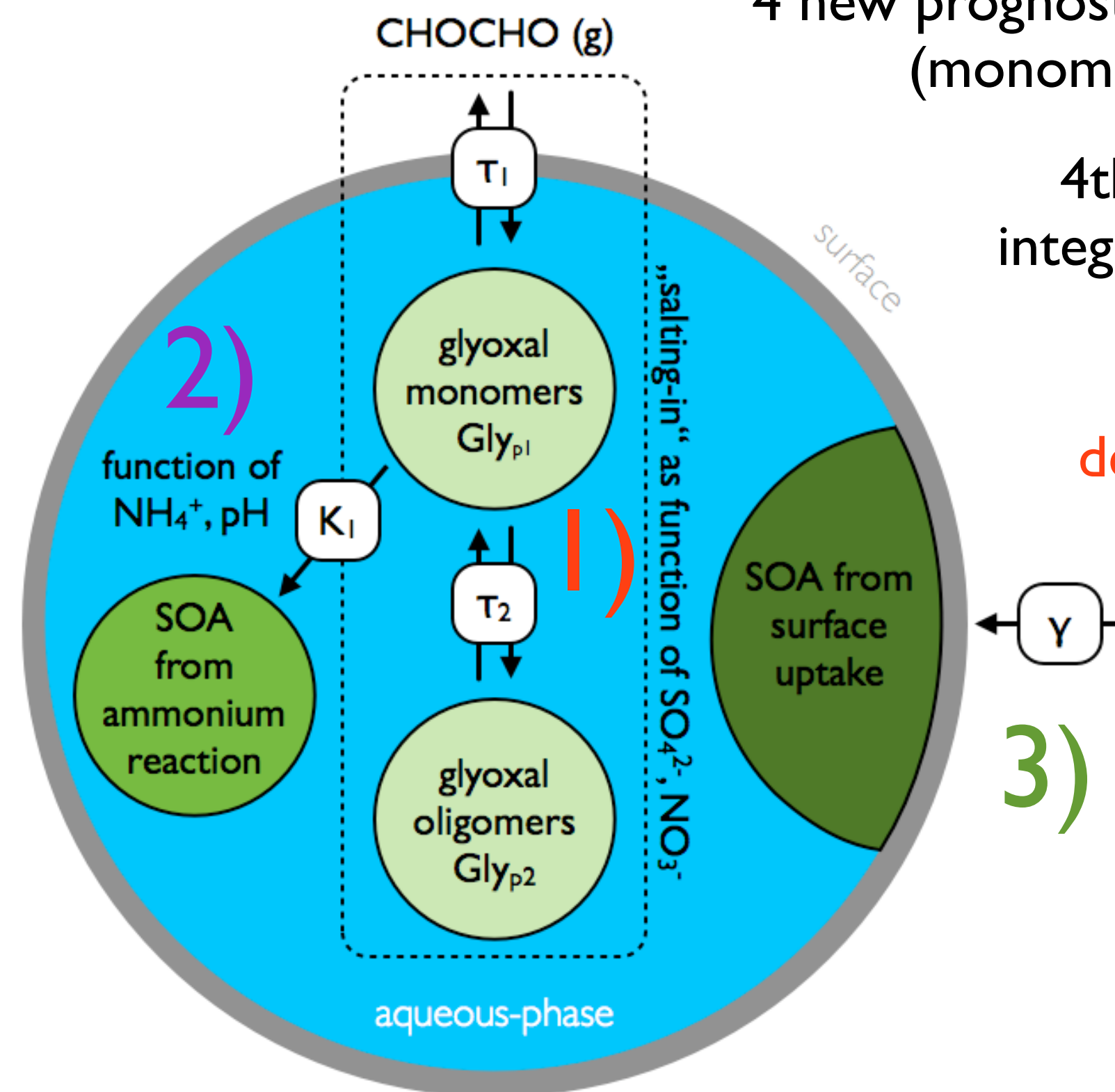
3) surface uptake

based on

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

Ervens and Volkamer, ACP, 2010

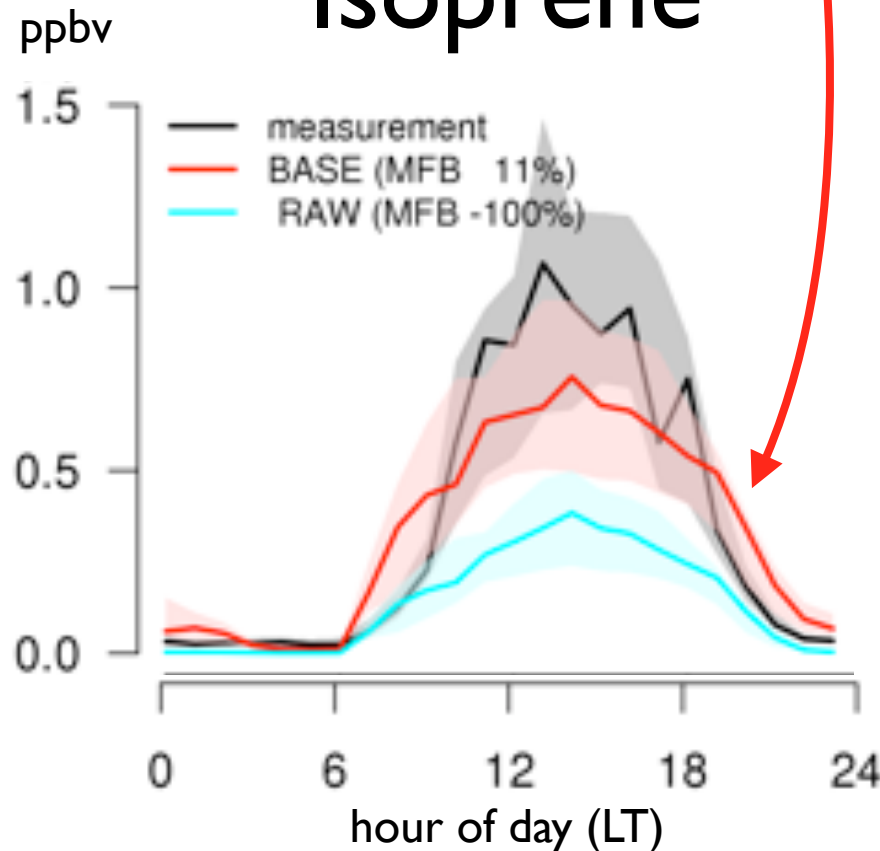
Kampf et al., ES&T, 2013



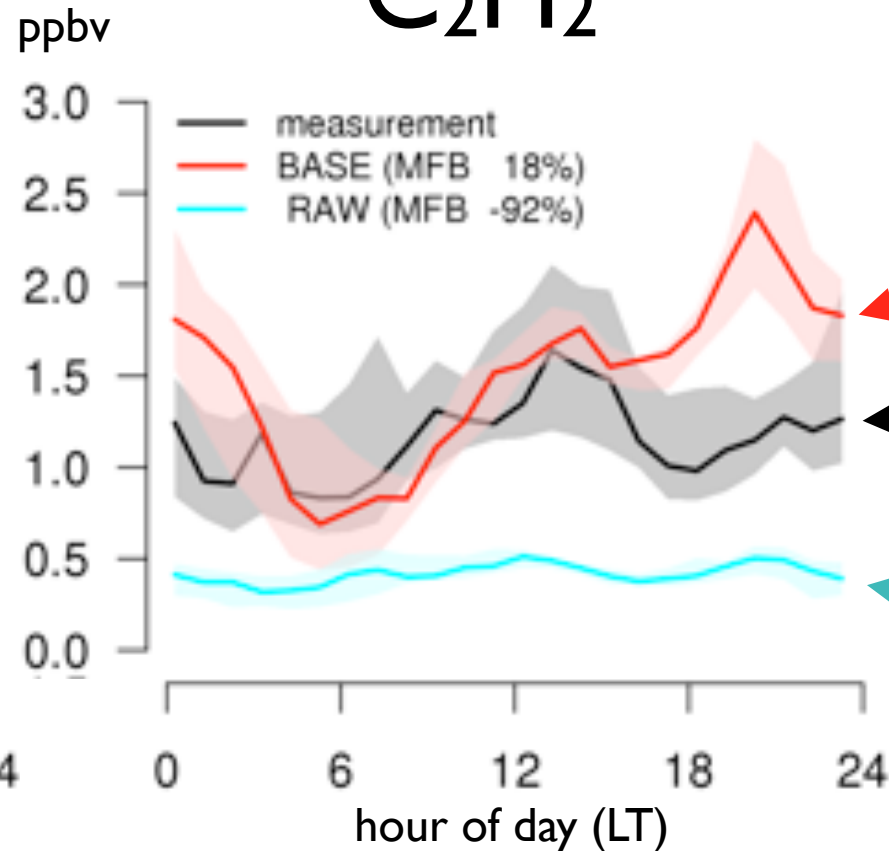
MEGAN over urban areas x 2.5

Precursors in Pasadena

Isoprene



C₂H₂

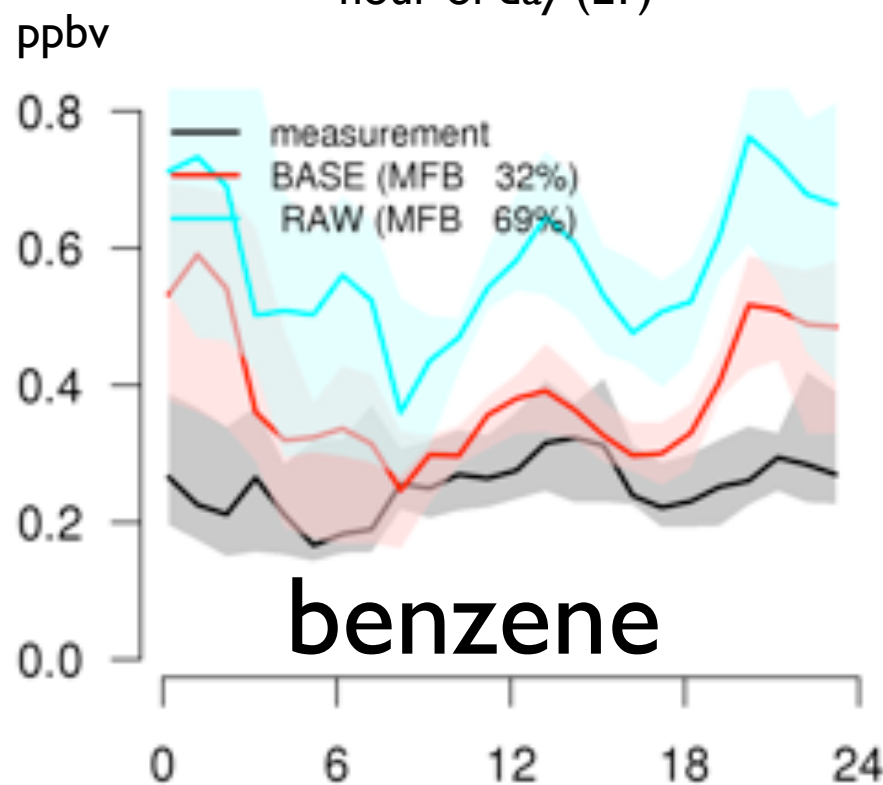


updated emissions

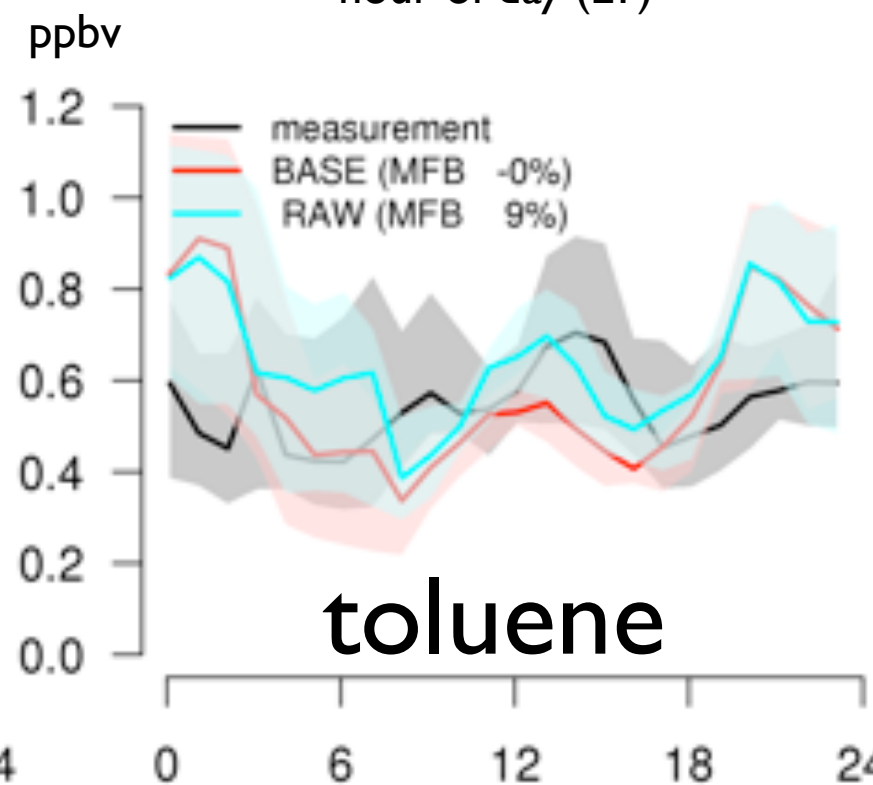
measurements

CARB/NEI inventory

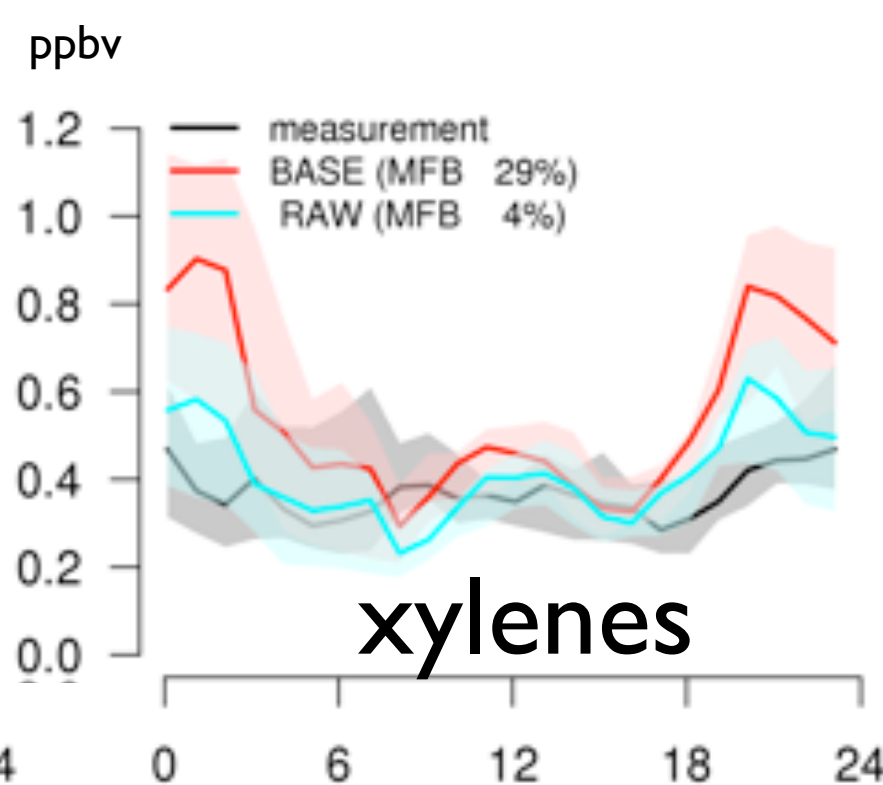
benzene



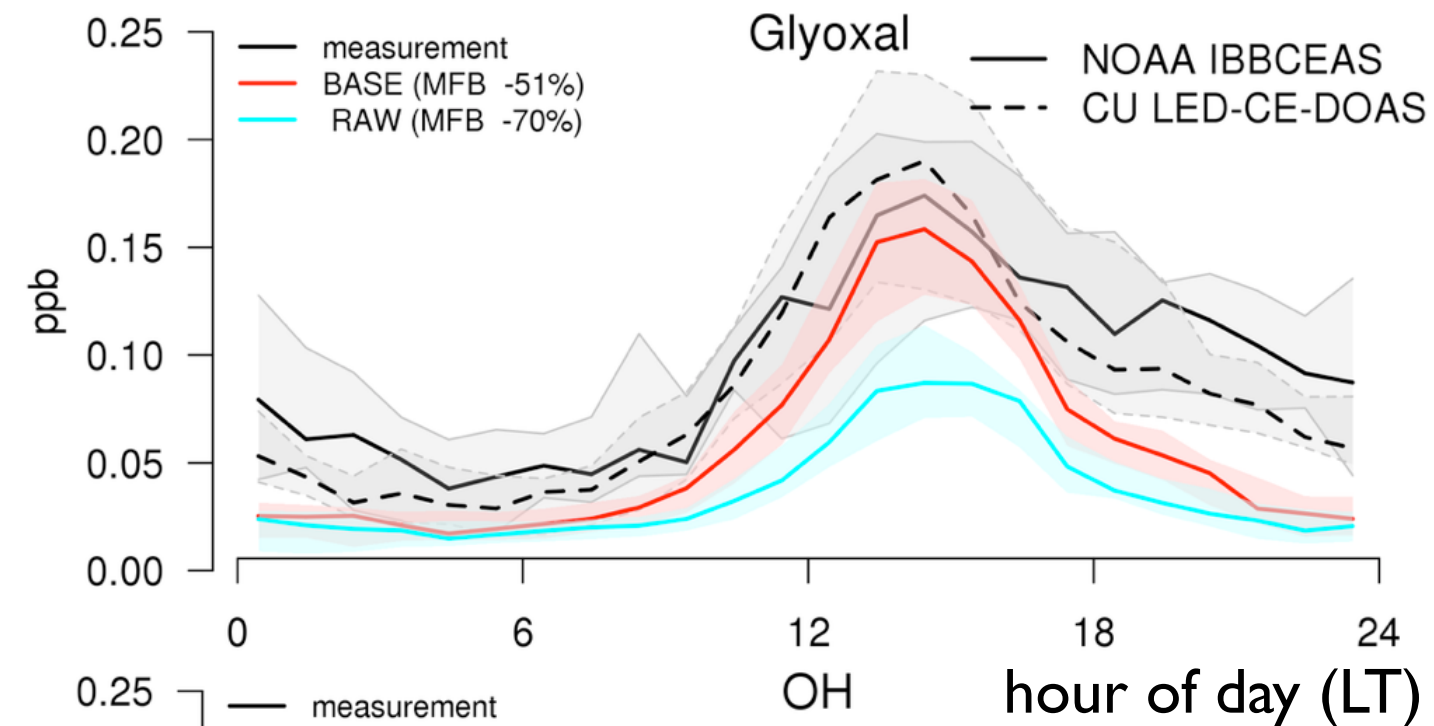
toluene



xylene



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



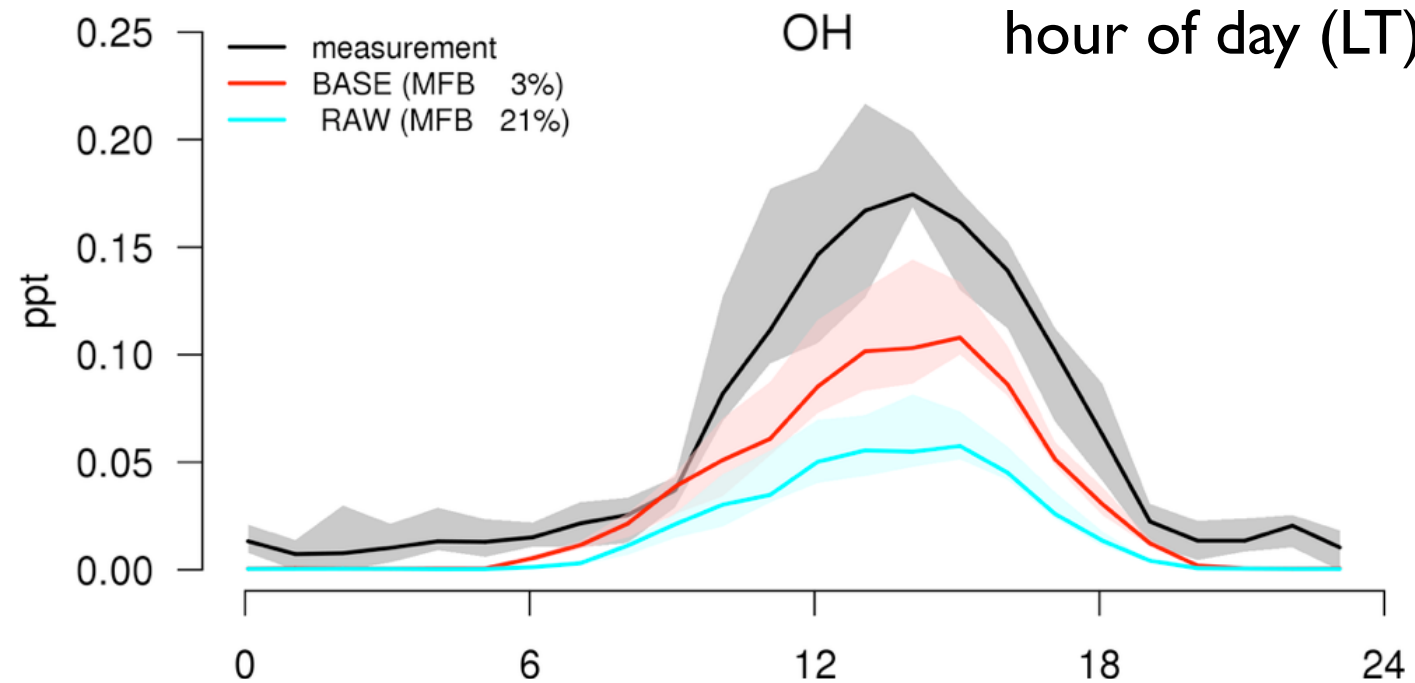
Glyoxal concentrations

Pasadena ground site

measurements by

Washenfelter, Young, Brown (NOAA)

Thalman, Waxman, Volkamer (CU Boulder)

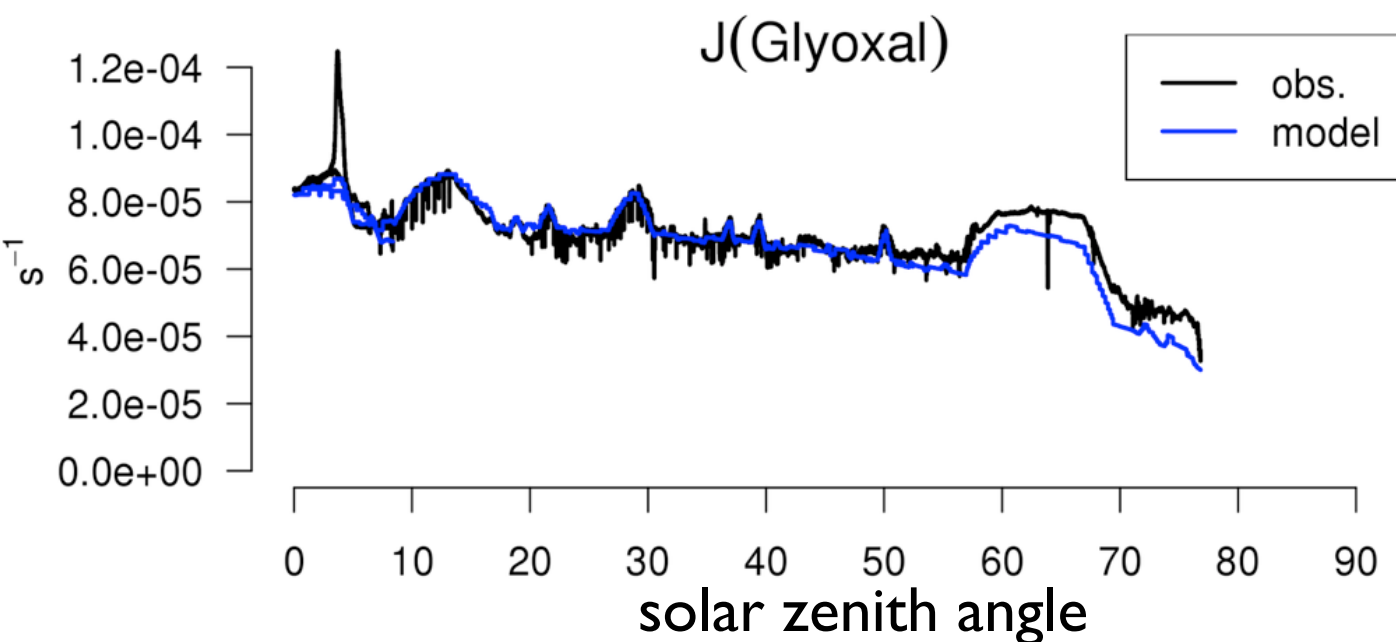


OH sink

Pasadena ground site

measurements by

Dusanter, Griffith, Hansen, Stevens (U Indiana)



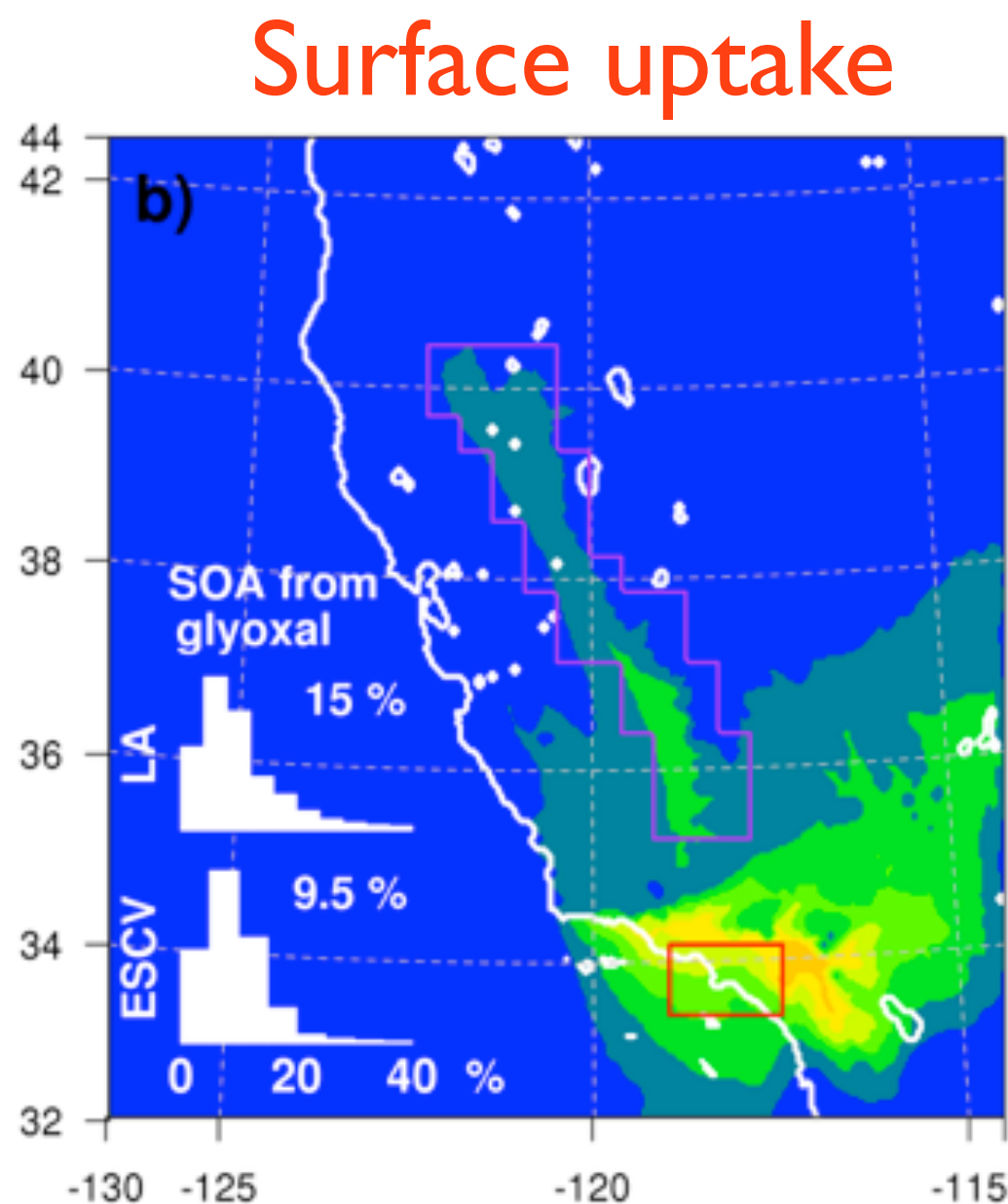
Photolysis sink

NOAA P3 flight on 06/14

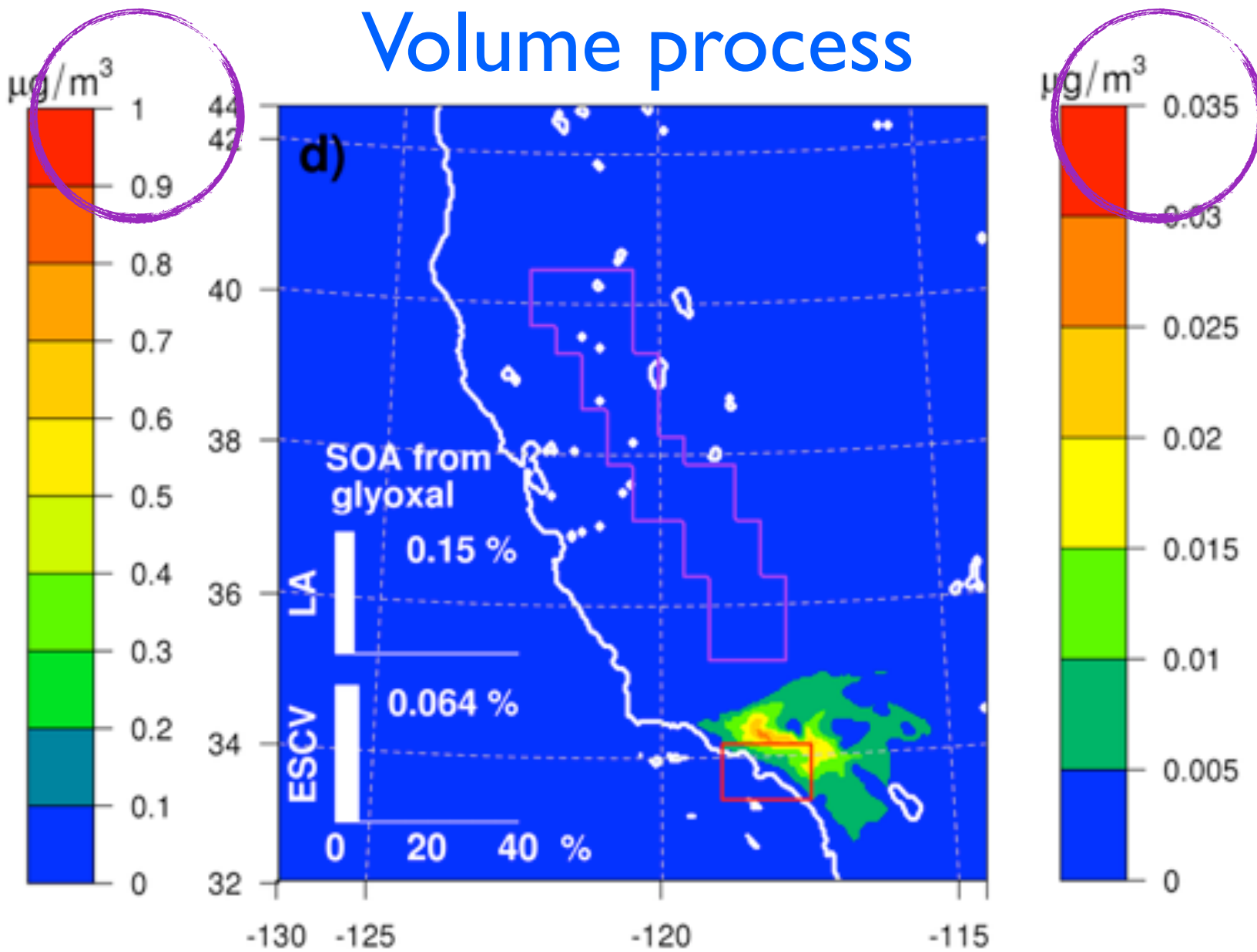
measurements by Harald Stark

SOA contribution from glyoxal

Surface uptake

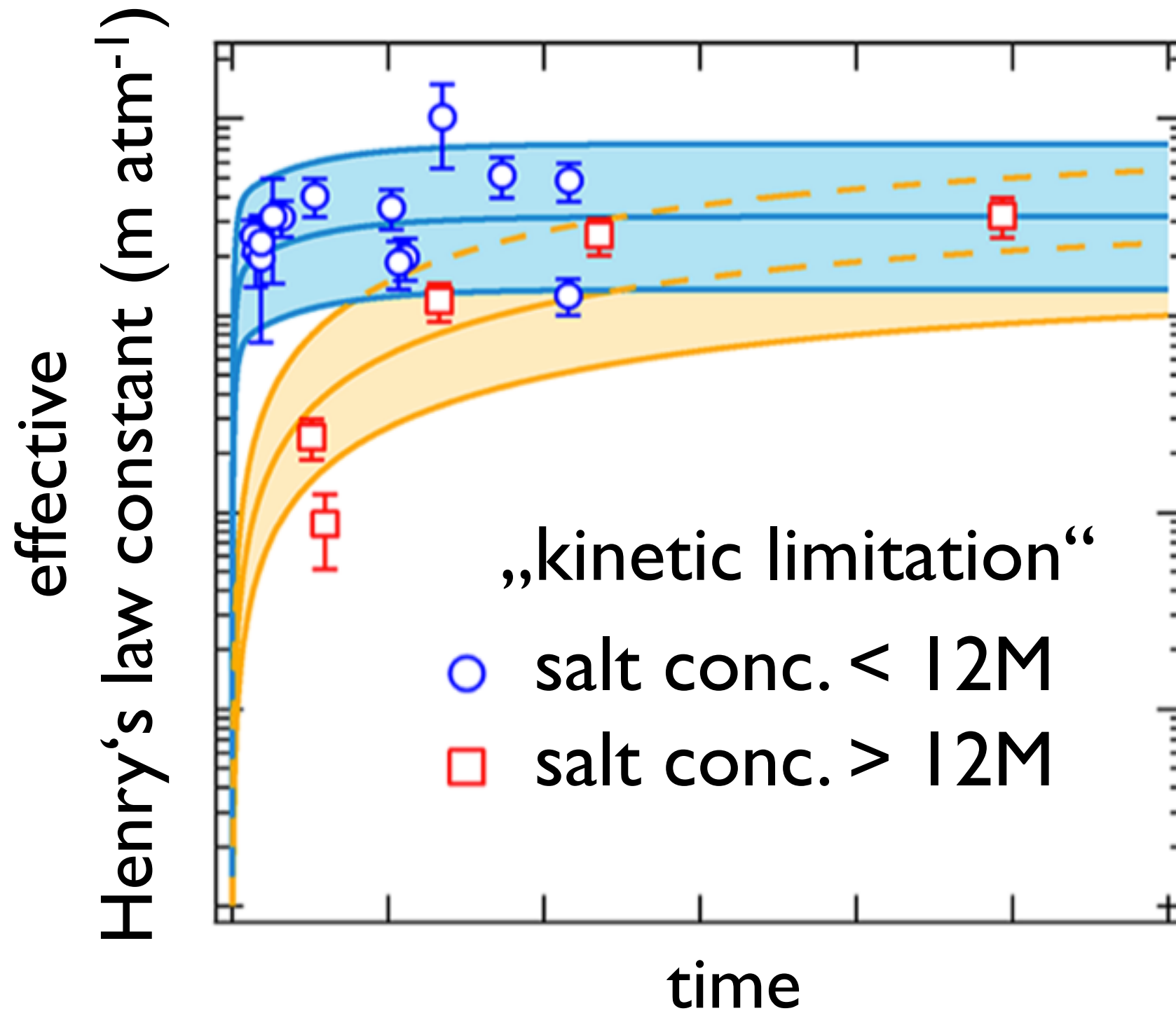


Volume process



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?



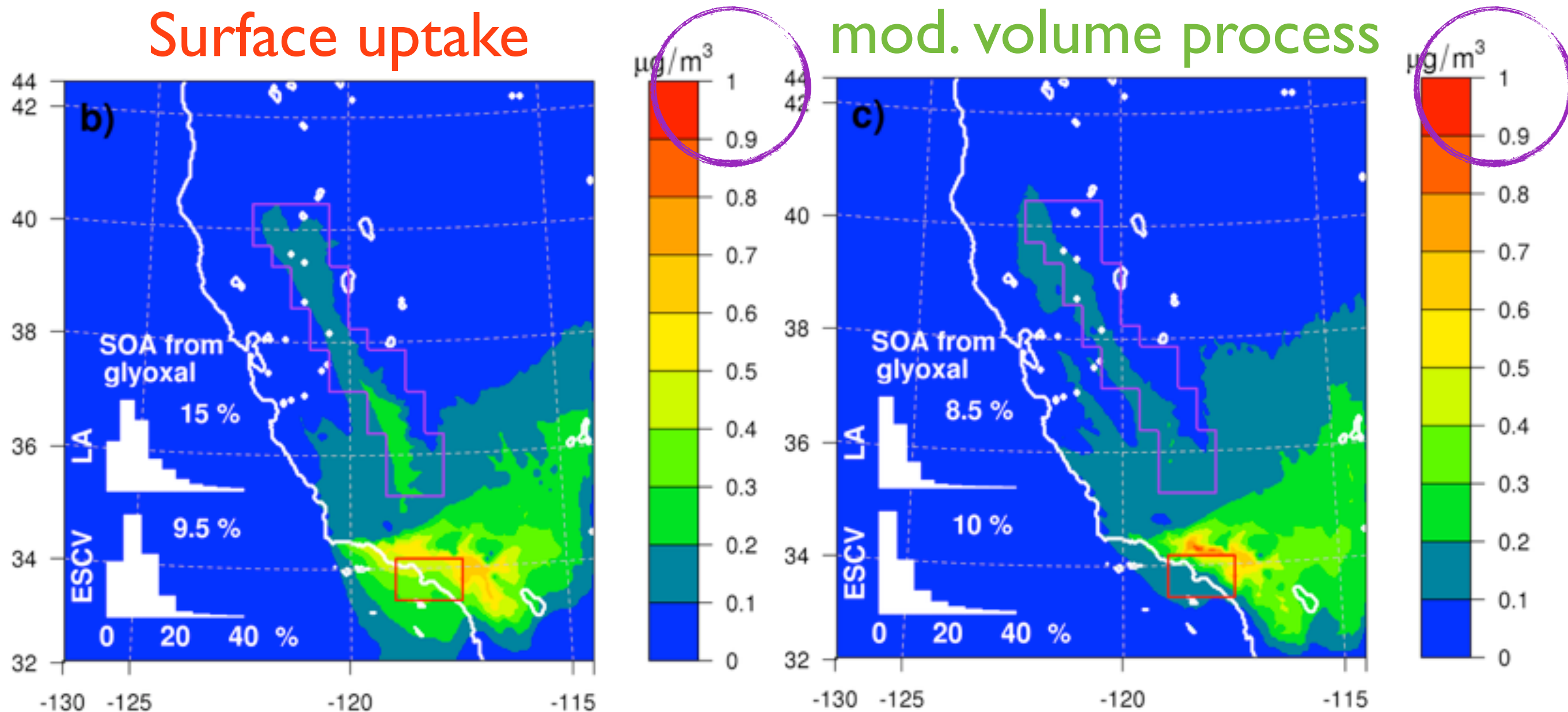
at high salt concentrations, supply of glyoxal to aerosol is limiting SOA production

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**