



Evaluation of CMAQ SOA during CALNEX with Consideration of Volatility Space

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For additional model details see [Kelly et al. Poster](#)

CMAQ exhibits a persistent negative bias in OA mass prediction.
Community consensus that it is a consequence of 2^o processes.

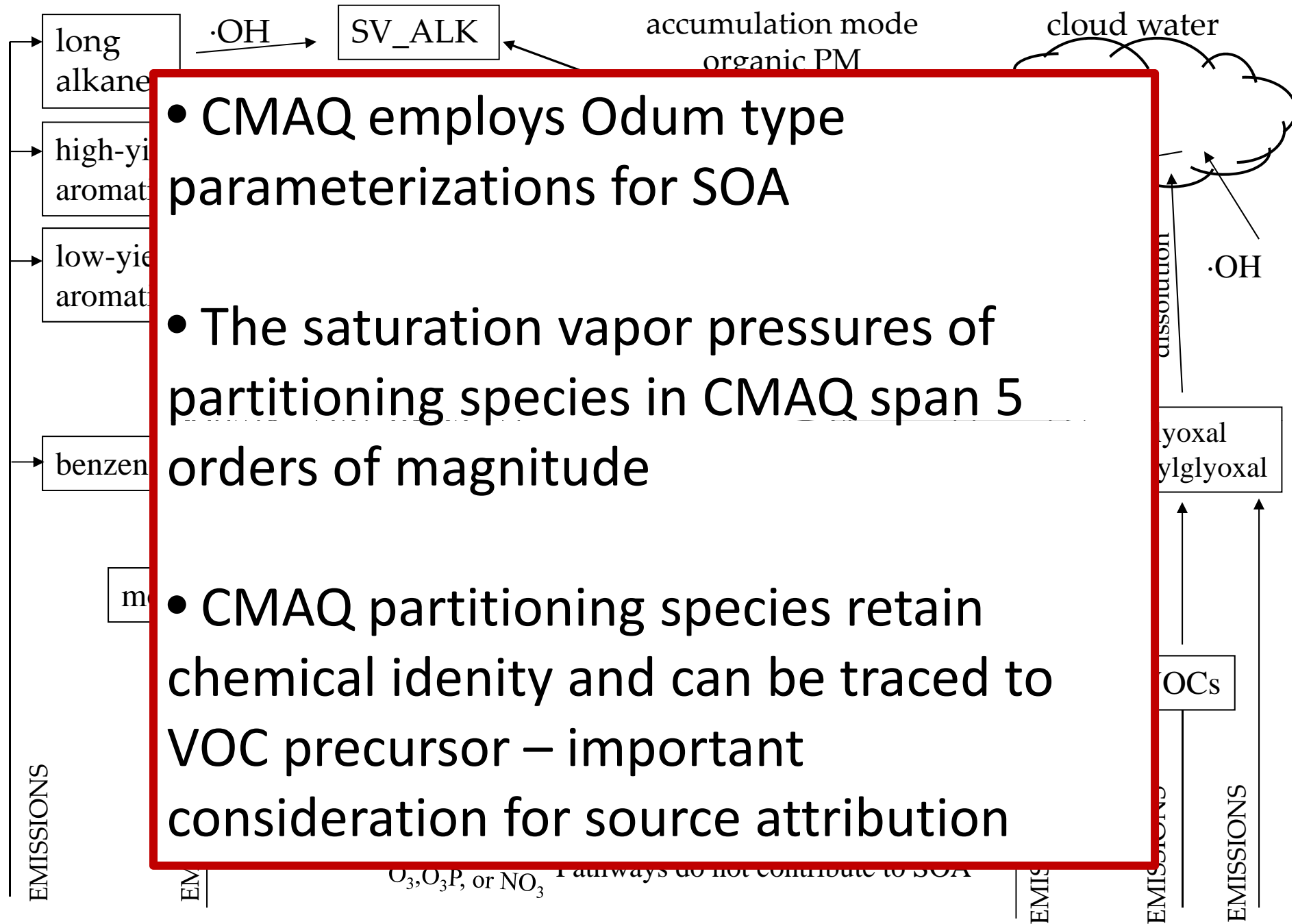
Missing VOCs? More SV products?

Possibly, but even when precursors are perfectly known (e.g., Parikh et al., (2010)) models still fail.

Missing Processes?

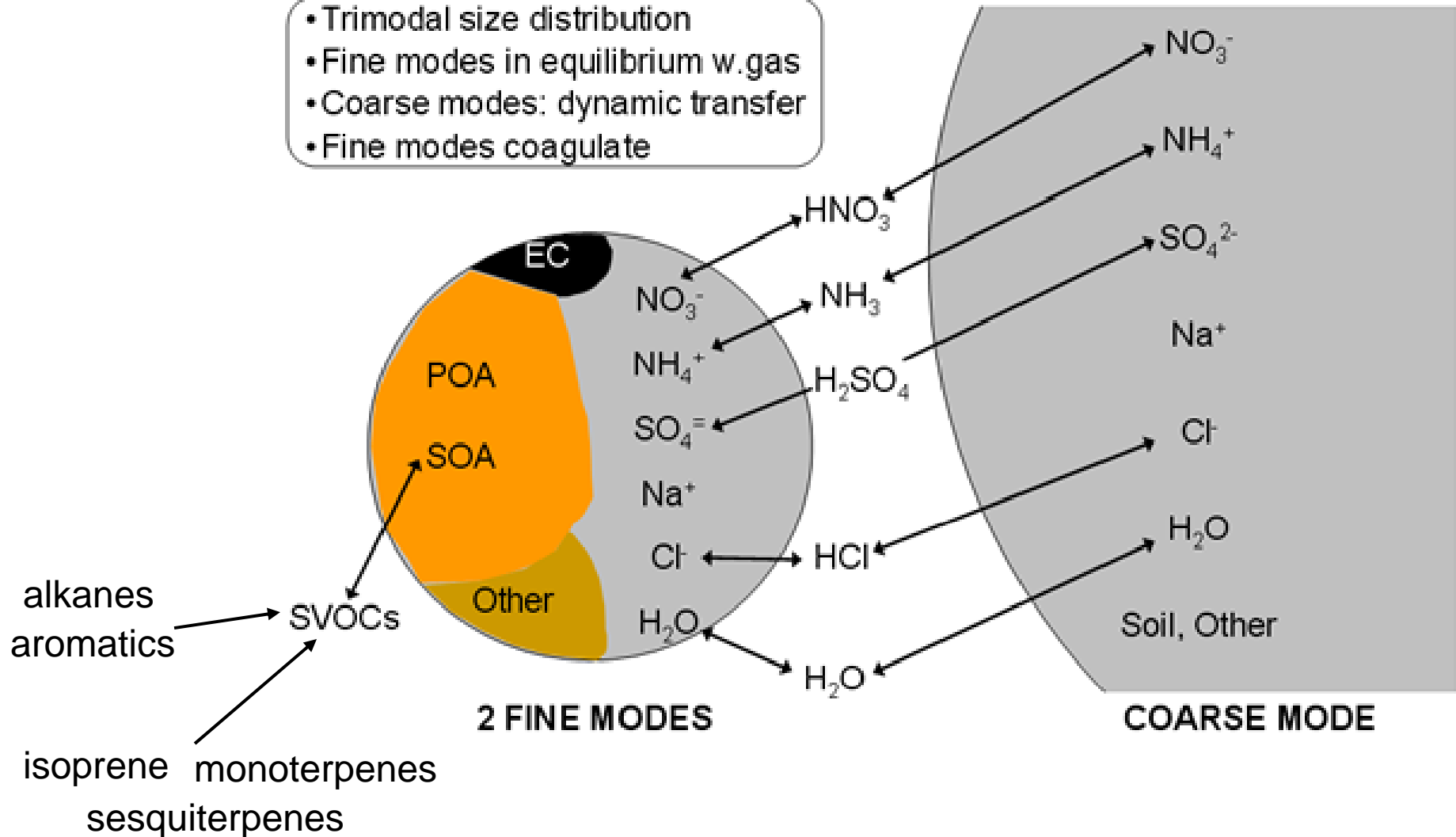
Application of theory needs expanding: “Like” into “Like” means polar organic compounds into polar solvents (**water**) (Parikh et al., 2010; Wayne et al., 2010; Pankow and Barsanti, 2009)

Total carbon comparisons are insufficient to guide *effective* mechanism development. Evaluation of *theory* and *chemical tracers* is critical.



- CMAQ employs Odum type parameterizations for SOA
- The saturation vapor pressures of partitioning species in CMAQ span 5 orders of magnitude
- CMAQ partitioning species retain chemical identity and can be traced to VOC precursor – important consideration for source attribution

- Trimodal size distribution
- Fine modes in equilibrium w. gas
- Coarse modes: dynamic transfer
- Fine modes coagulate



$$K_{P,i} = \frac{C_{aer,i}}{C_{gas,i} TPM} = \frac{1}{p^{\circ}_{L,i}} \left[\underbrace{\frac{N_s a_{TSP} T e^{(Q-Q_v/RT)}}{1600}}_{\text{surface adsorption}} + \underbrace{\frac{f_{om} 760RT}{MW_{om} \zeta_i 10^6}}_{\text{organic-phase absorption}} \right]$$

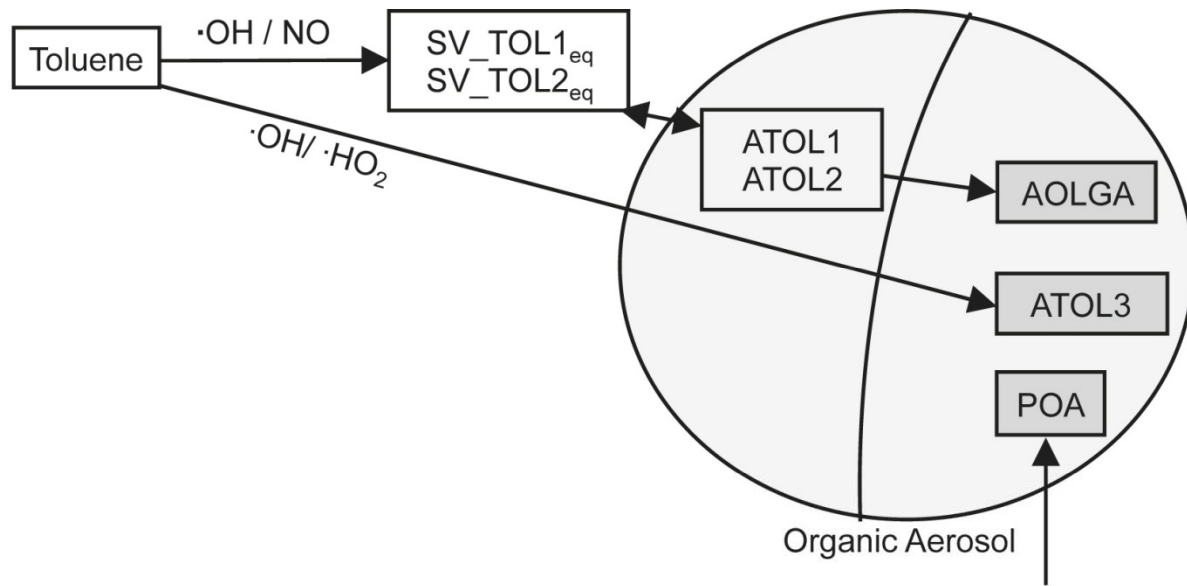
$$K_{om,i} = \frac{C_{aer,i}}{C_{gas,i} M_o} = \frac{760RT}{p^{\circ}_{L,i} MW_{om} \zeta_i 10^6}$$

Expressed partitioning behavior of each compound as a function of **temperature** and **organic-phase composition**

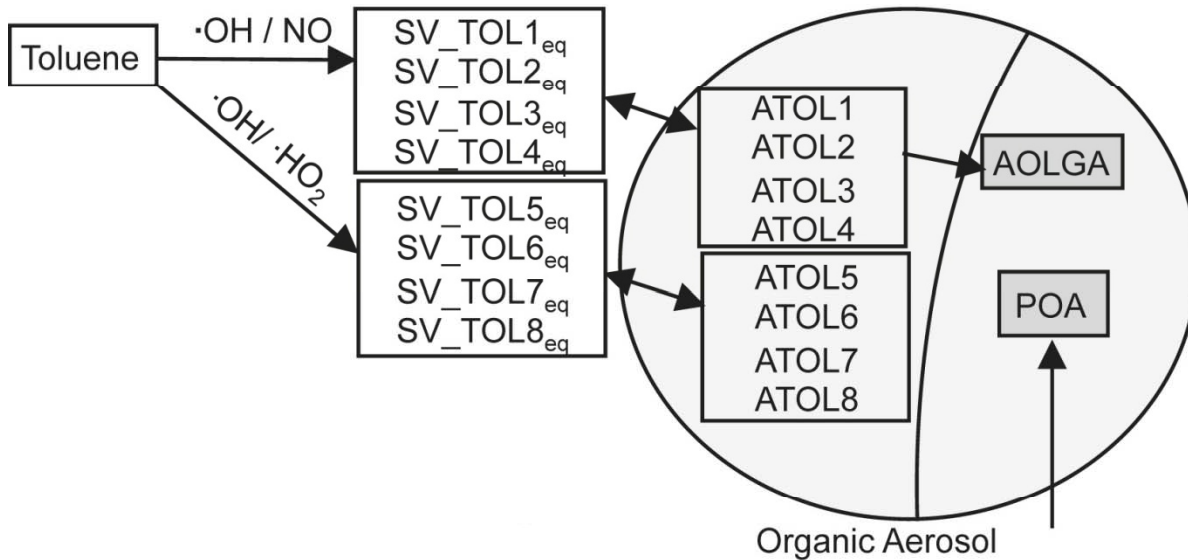
M_o is the organic-phase mass concentration

Notation differs slightly from primary reference

- Ref: Pankow, *Atmos. Env.* (1994)
- Slide courtesy of P. Bhawe



Odum type 2 product
Ng et al. (2007)

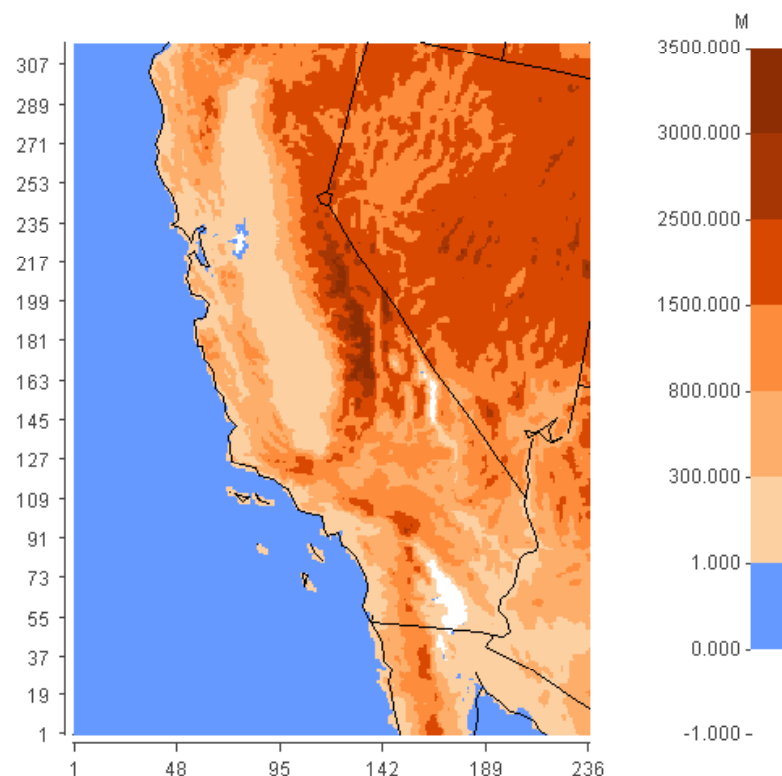


Volatility basis set
Hildebrandt et al., (2009)

Parikh et al., *AE*, 2011

CMAQ and GEOS-Chem have multiphase (heterogeneous) SOA processes

- May-July 1, 2010 episode
- CMAQ v4.7.1 (N2a)
- CB05 & AERO5
- WRF v3.2 (MCIP v3.6)
- BEIS v3.14
- WRF 2 m temperature and WRF shortwave downward radiation
- 2005v2 NEI anthropogenic emissions for U.S.
- Mexico emissions based on 1999 inventory (Mexico a minimal influence during CalNex).



- Horizontal grid cell size = 4 km
- NX = 236, NY = 317
- Lambert projection centered at (-97,40) with true latitudes 33 and 45
- Domain origin (-2416 km, -832 km)

For additional model details see [Kelly et al. Poster](#)

Missing gaps in CMAQ's SOA volatility distribution when CB05 is employed.

Organic mass "aging" (VOC → SV_VOC → SV_OA → LV_OA)

assumptions need some re-visiting

- # of carbons in SV species ≠ to parent VOC
- assigned OM:OC ratios should be calculated for individual, representative chemicals

Chemical SOA tracers are underpredicted for all measurable species at 2 CA locations: urban and rural

- Some chemical identity is lost during oligomerization
- Tracers are not conservative or OM:OC is not constant from chamber to field
- Gas phase VOC/SV_VOC precursors mixing ratios are not correct,

- James Kelly
- Rich Mason
- Laura Reynolds, Allan Beidler, James Beidler, Chris Allen