

New model developments of SOA formation in the aqueous phase

Chemical processes in cloud droplets vs aqueous particles

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SOA formation in the aqueous phase (aqSOA)

...of cloud droplets

Parameterization of SOA formation from glyoxal

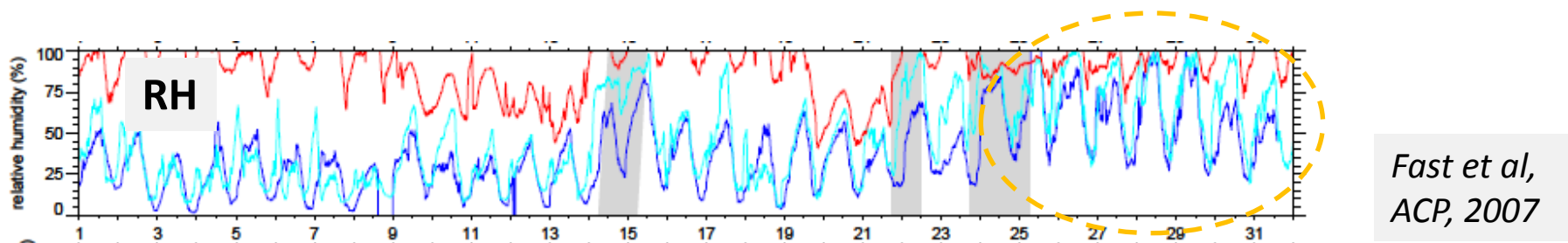
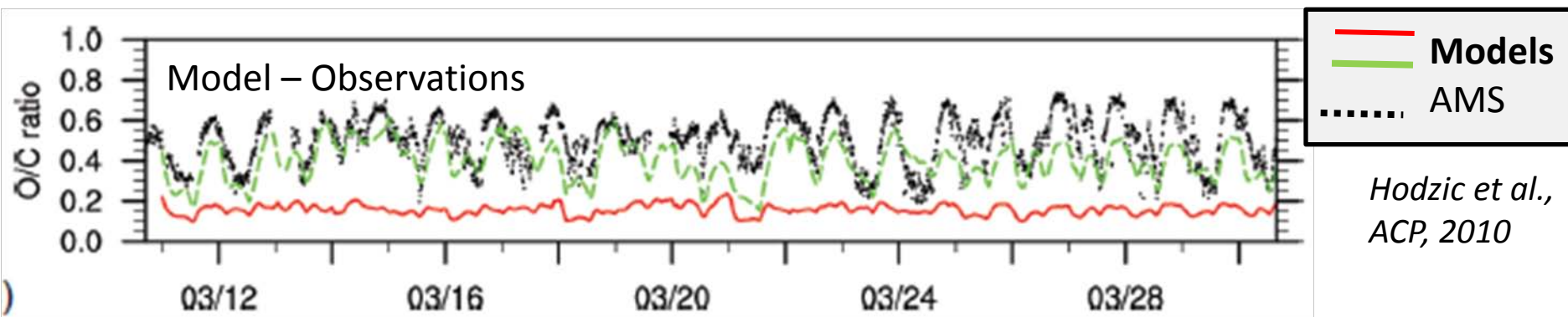
...of aqueous (deliquesced) particles

- Derivation of individual rate constants based on lab studies
- Quantifying differences to cloud chemistry

First model studies

Comparison of cloud- and particle-SOA

Evidence in current models of 'missing SOA'



Correlation of highly oxidized aerosol (O/C) and RH!

'Traditional SOA'
 $0.02 < O/C < 0.8$

aqSOA from glyoxal

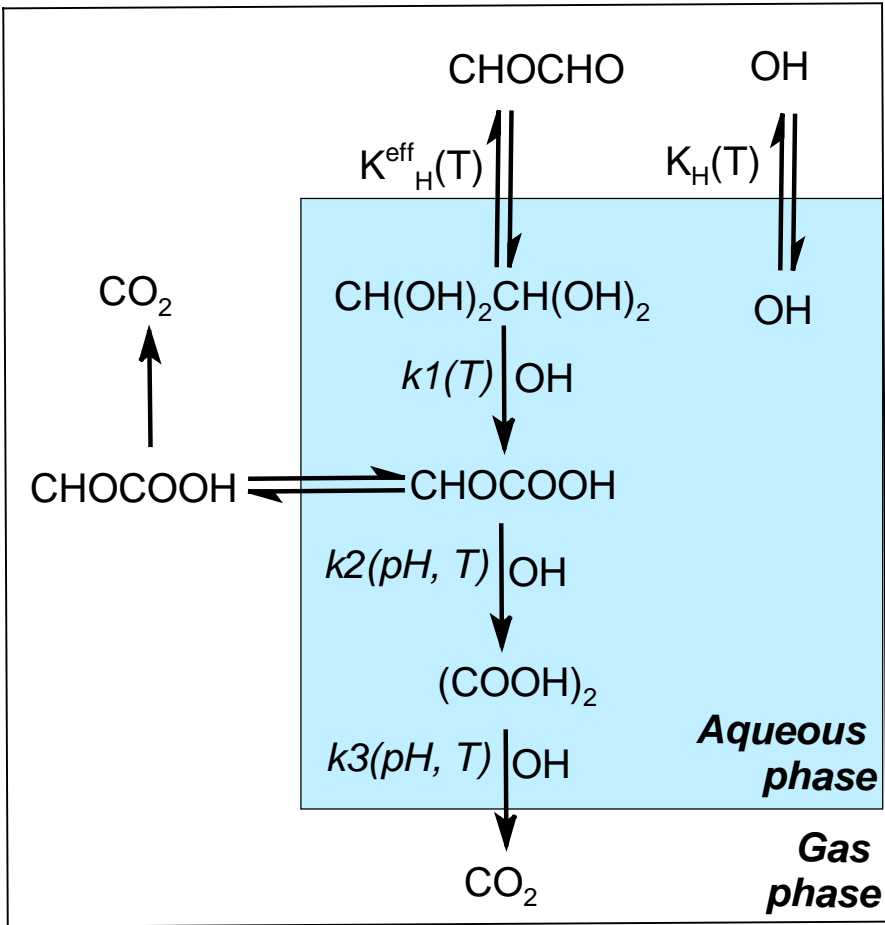
$1 < O/C < 2$

aqSOA from methylglyoxal

$0.4 < O/C < 1$

I. Cloud chemistry

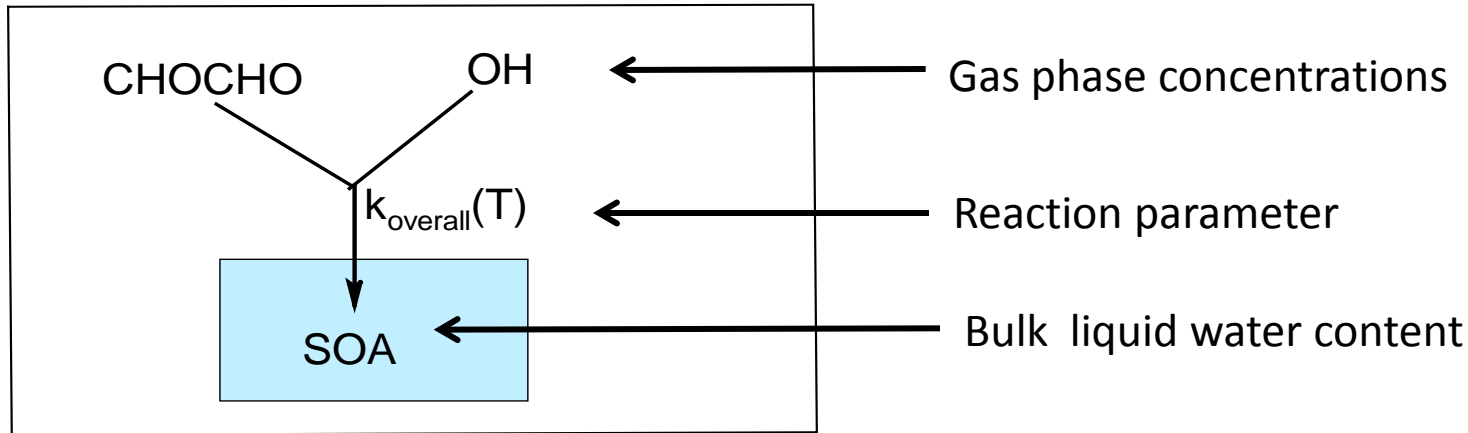
Liquid water content	$\sim 0.1-1 \text{ g m}^{-3}$
Lifetime of cloud droplet	$\sim \text{minutes}$
Solute concentration	$\mu\text{M} - \text{mM}$



O/C
1
1-2
1.5-2
2

- Oxidation by OH
- Acid formation
- Formation and loss are pH dependent
- T and pH dependencies for all rate constants are known

Simplification of cloud chemistry: aqSOA formation from glyoxal



$$\frac{d[\text{SOA}]}{dt} = k_{\text{overall}} \cdot [\text{Gly}]_{\text{gas}} \cdot [\text{OH}]_{\text{gas}} \cdot \text{LWC} \cdot \text{Factor}$$

‘Theory’

Factor: - Deviation from thermodynamic equilibrium $[\text{Gly}]_{\text{aq}} = K_{\text{H}}^{\text{Gly}} \cdot [\text{Gly}]_{\text{gas}}$
 $[\text{OH}]_{\text{aq}} = K_{\text{H}}^{\text{Gly}} \cdot [\text{OH}]_{\text{gas}}$

- Loss processes Oxalic acid/Oxalate + OH \rightarrow CO₂

How to derive the empirical 'factor' ?

~100,000 box model simulations using 'detailed cloud chemistry'

$$0.01 \text{ ppb} \leq [\text{Gly}]_{\text{gas}} \leq 1 \text{ ppb}$$

$$10^4 \text{ cm}^{-3} \leq [\text{OH}]_{\text{gas}} \leq 7 \cdot 10^6 \text{ cm}^{-3}$$

$$0.01 \text{ g m}^{-3} \leq \text{LWC} \leq 1.5 \text{ g m}^{-3}$$

$$275 \text{ K} \leq T \leq 300 \text{ K}$$

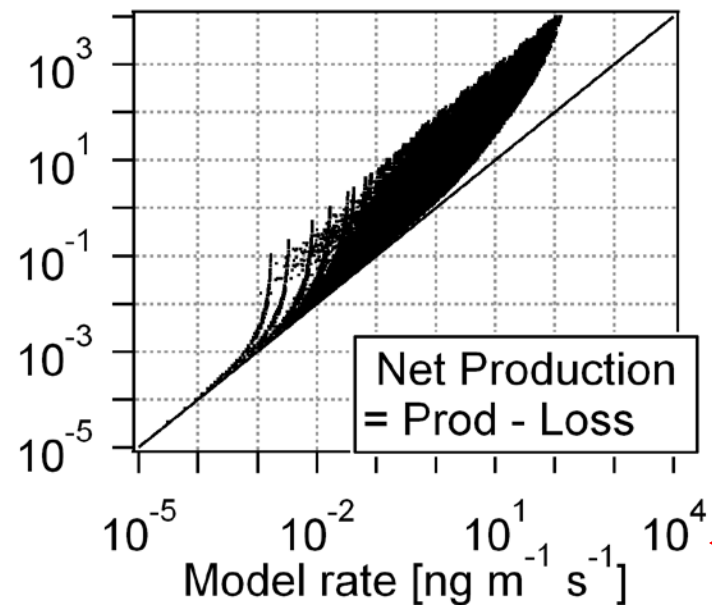
$$2 \leq \text{pH} \leq 6.5$$

'Model rate'

$$\frac{d[\text{SOA}]}{dt} \quad \frac{\text{ng}}{\text{m}^3 \text{ s}}$$

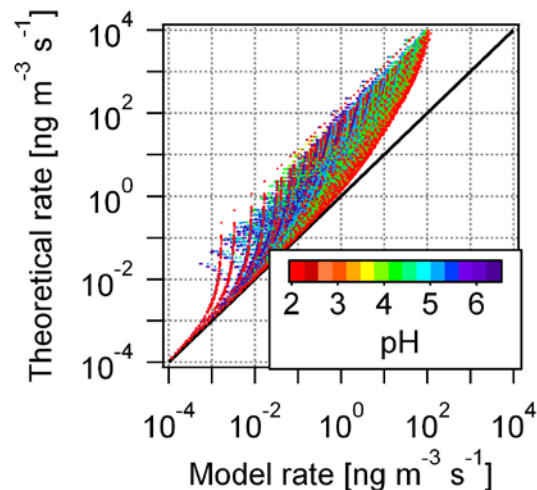
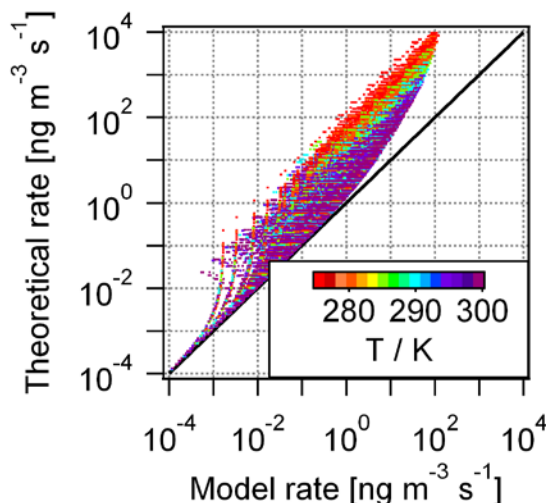
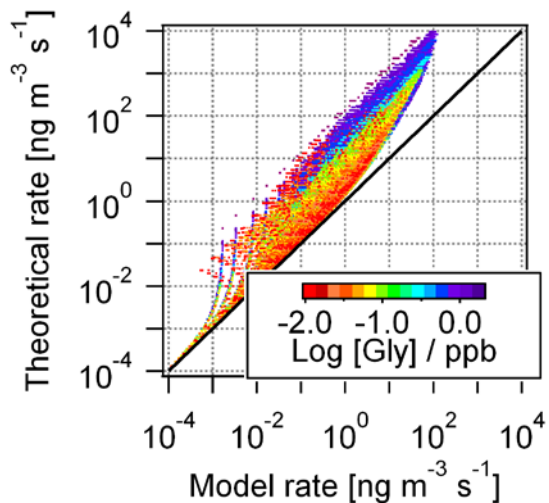
$$\underbrace{k_{\text{overall}}(T)}_{k_{\text{OH}}^{\text{aq}} \cdot K_{\text{H}}^{\text{Gly}} \cdot K_{\text{H}}^{\text{OH}}} \cdot [\text{Gly}]_{\text{gas}} \cdot [\text{OH}]_{\text{gas}} \cdot \text{LWC}$$

Theoretical rate [$\text{ng m}^{-3} \text{ s}^{-1}$]



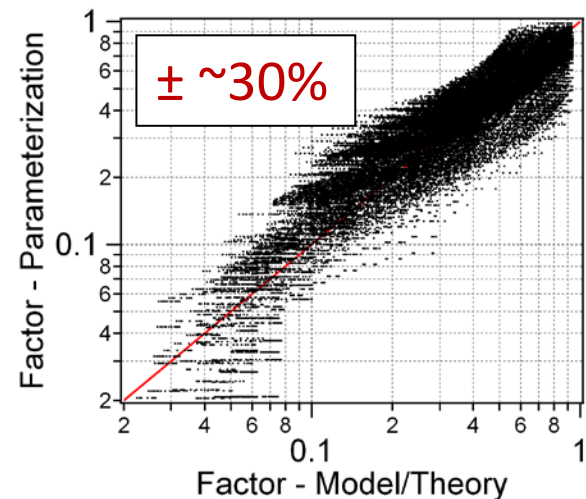
Net Production = Prod - Loss

Resulting parameterization



Deviation from 'ideal behavior' (1:1) scales with

- glyoxal concentration
 - temperature (K_H)
 - pH (oxalate loss)
- } OH consumption
 $\Rightarrow \neq [\text{OH}]_{\text{aq}} (\text{equil})$

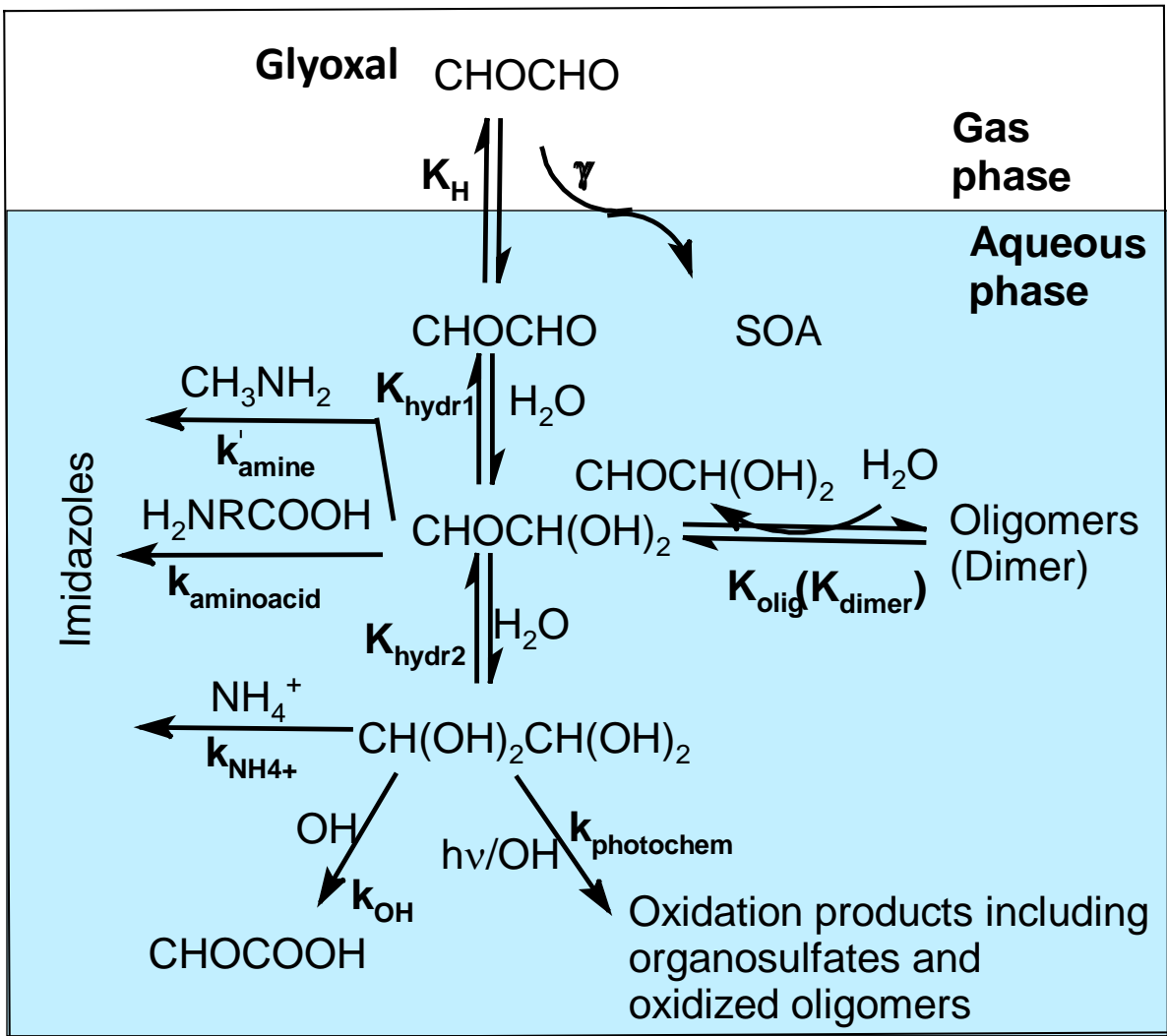


$$\text{Factor} = a_1 + a_2 [y(\text{pH}) + A(\text{pH}) \cdot \exp(C(\text{pH}) \cdot [\text{Gly}]_{\text{gas}})] + a_3 \cdot T + a_4 [\text{Gly}]_{\text{gas}}$$

Coefficients: $a_1, a_2, a_3, a_4, y(\text{pH}), A(\text{pH}), C(\text{pH})$

II. SOA formation in aqueous particles

LWC $\sim 10^{-6} - 10^{-4} \text{ g m}^{-3}$
 Particle lifetime \sim days
 Solute concentration \sim M



Complex mechanism:

- Surface and bulk processes
- Reversible and irreversible
- Photochemistry/ dark chemistry
- Solute (activity) dependent
- Oligomerization (Products?)

Quantifying chemical differences between cloud and particle chemistry

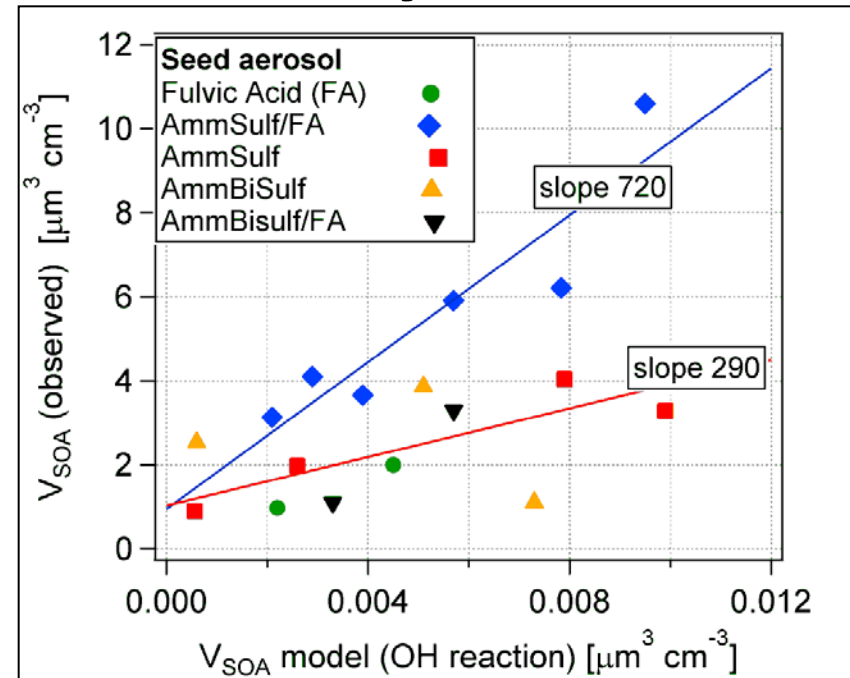
Laboratory studies

Glyoxal uptake on aqueous aerosol (different seed composition), in the presence of OH/hv

Volkamer et al., ACP, 2009

Model studies

Simulations of chamber conditions
Assumed 'cloud chemistry'



Ervens and Volkamer, ACP, 2010

Cloud chemistry reaction scheme underestimates photochemical SOA formation **by more than two orders of magnitude!**

Additional photochemical process(es)

Glyoxal \rightarrow SOA with $0.8 \text{ s}^{-1} < k_{\text{photochem}} < 7 \text{ s}^{-1}$

can account for the discrepancy

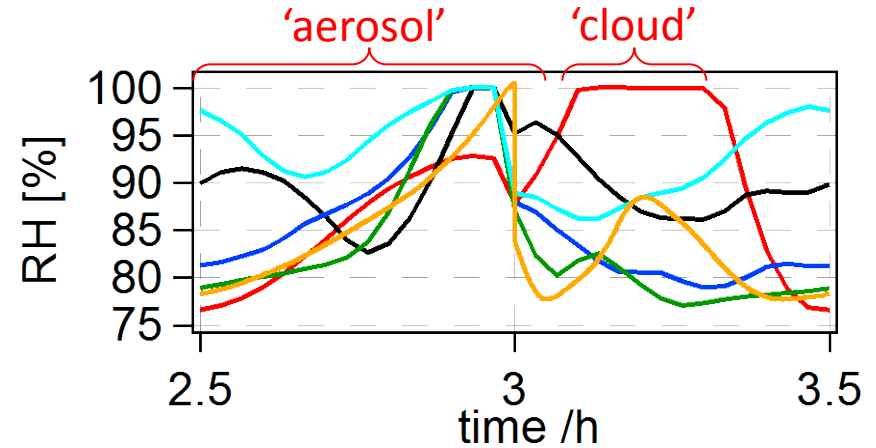
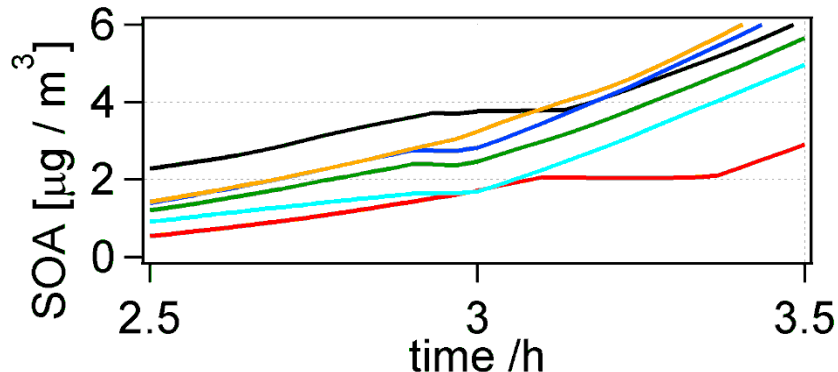
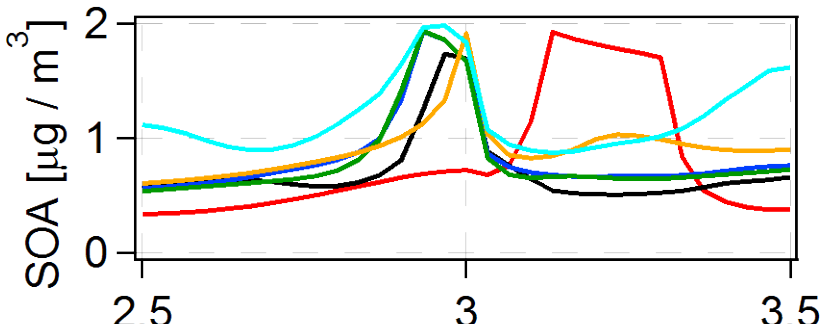
$k_{\text{photochem}} = f(\text{particle composition, hygroscopicity})$

Model simulations: Cloud vs particle SOA

Parcel model

Prescribed RH, liquid water content, temperature, pressure...

Model results: 2.5 h < time < 3.5 h



Cloud SOA

(oxalic, glyoxylic, glycolic, pyruvic acid):

- $\sim 1 \mu\text{g} \text{m}^{-3}$ after 3 hours (f(LWC, time))
- Sink: Oxidation and evaporation

Particle SOA

Oligomers, org. N-compounds

Steady increase (no sink – correct?)

- Several $\mu\text{g} \text{m}^{-3}$ after a few hours

SOA formation in clouds and aqueous particles about equally efficient

Conclusions

- Aqueous phase chemistry is important for the SOA budget (mass, O/C)
 - Cloud droplets/ aqueous particles = different aqueous phases
-

Parameterization of **in-cloud aqSOA formation** as $f([\text{Gly}]_{\text{gas}}, \text{pH}, T)$

Kinetic data for **particle-aqSOA** based on laboratory studies

- Application of process model (e.g., MCMA-2003; CARES; CalNex...)
 - Lab studies to extent parameter space (pH, seed, species...)
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SOA formation from glyoxal in cloud droplets and particles might yield **similar amounts of highly oxidized aqSOA mass** (O/C > 1)