RUTGERS
THE STATE UNIVERSITY OF NEW JERSEY

Improved prediction of the vertical profile of atmospheric black carbon: development and evaluation of WRF-CMAQ

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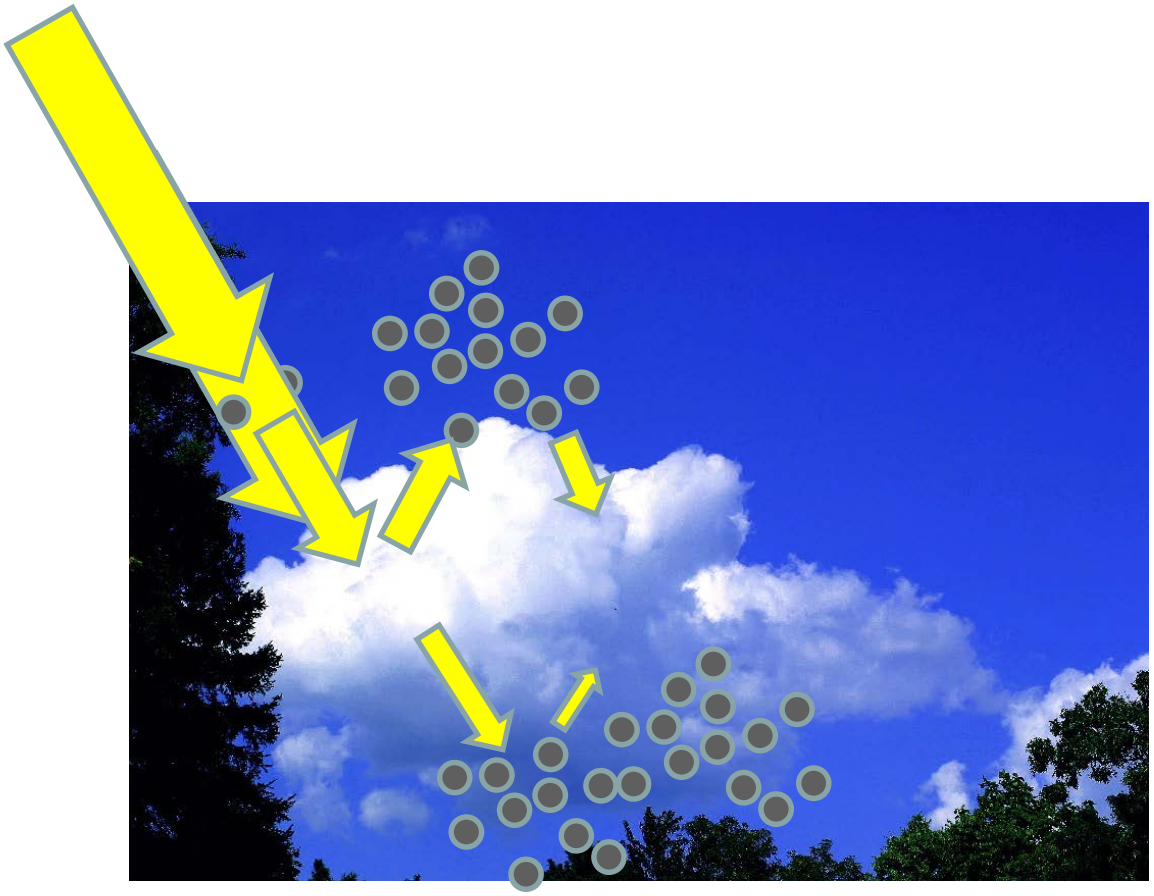
CAA is most successful US bill **EVER**

Bush Administration OMB estimated Benefit to cost ratio is $30:$1, 2nd place bill is $2:$1

Credit: Chester Higgins, Jr. 1973

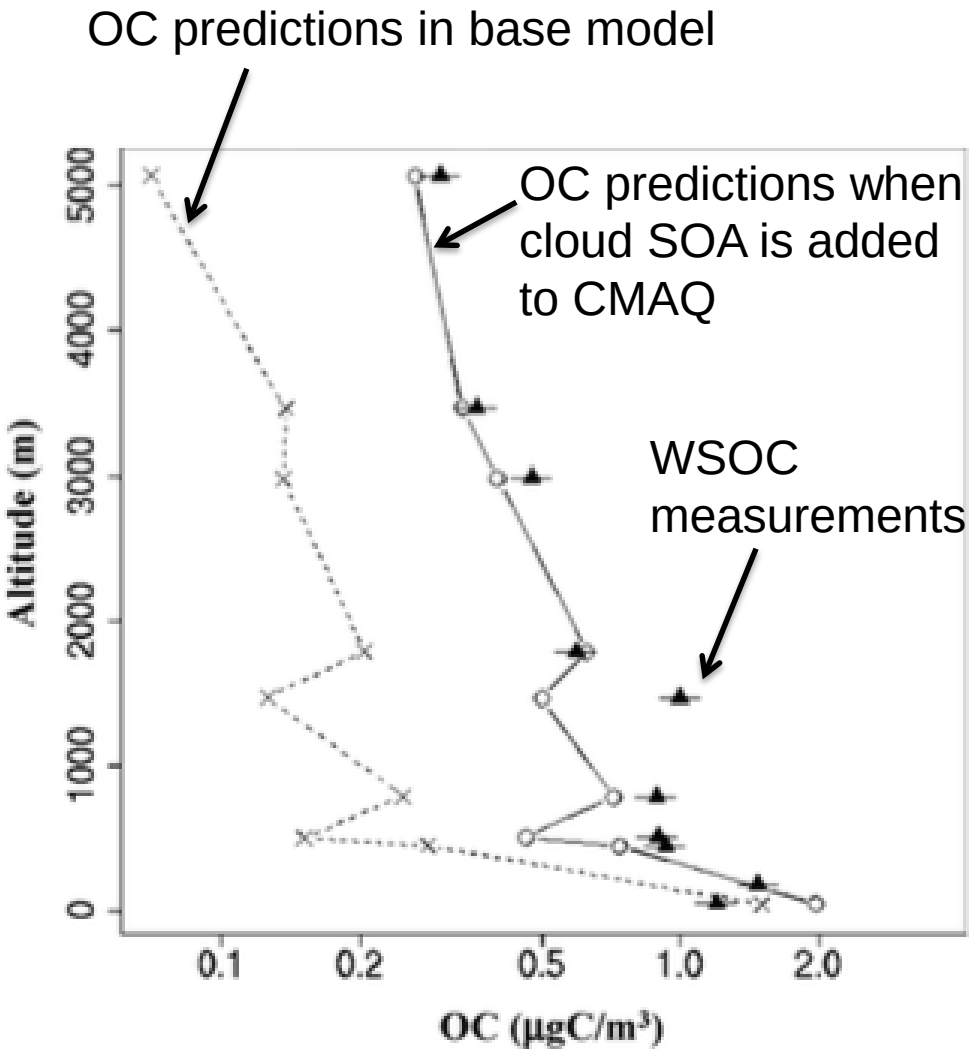
http://magictouchimaging.com/gwbridge.html

Vertical profile: motivation to get it right



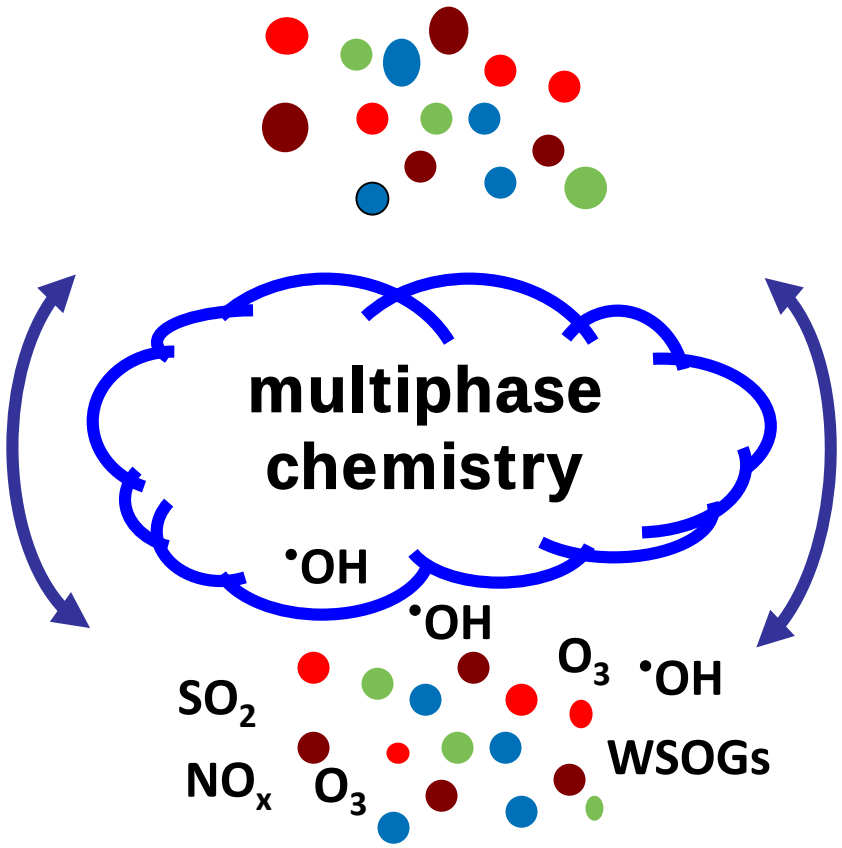
Aloft aerosols above clouds scatter diffuse backscatter and are subject to less removal processes

Simple organic cloud chemistry changes vertical profile



Carlton et al., *ES&T*, 2008

Cloud Processing

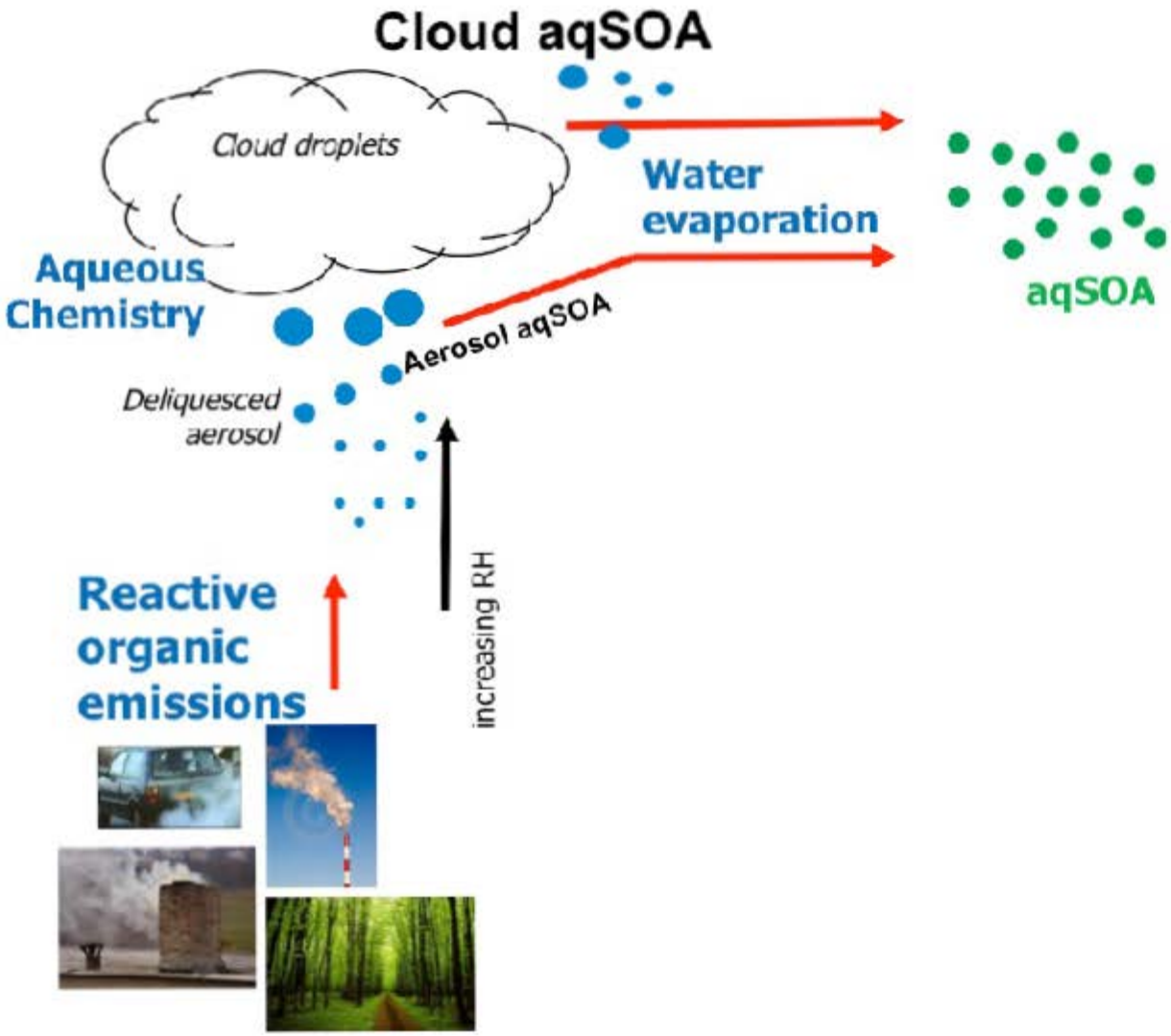


vertical redistribution of trace species

Δ in aerosol population GMD (droplet mode)

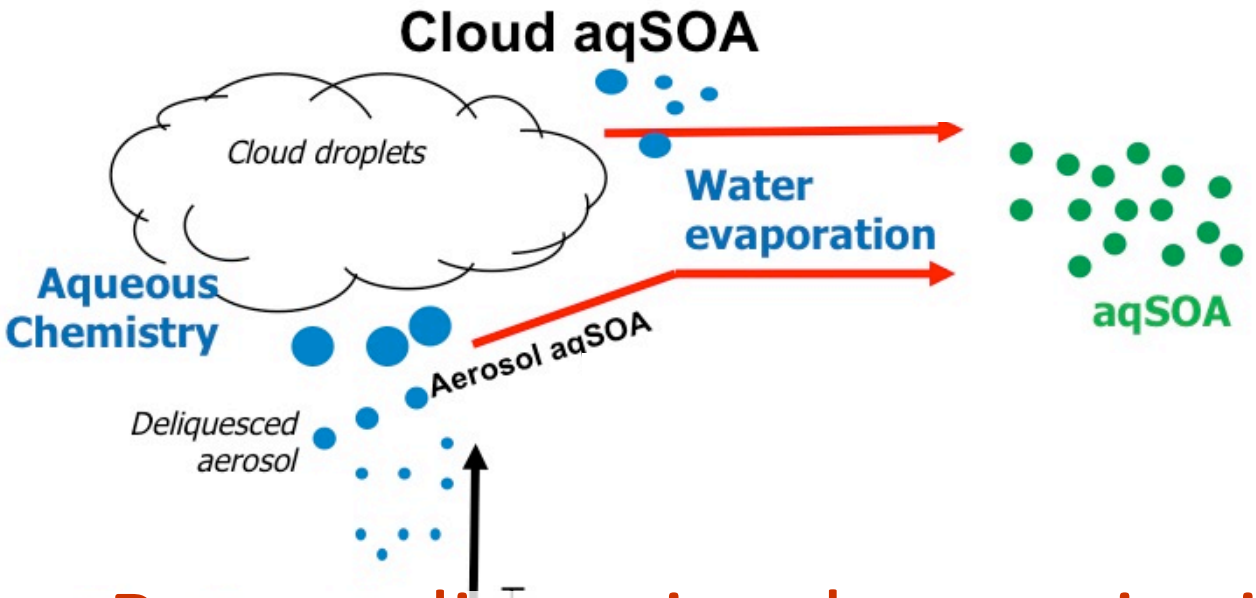
oxidation chemistry

Atmosphere is a Continuum



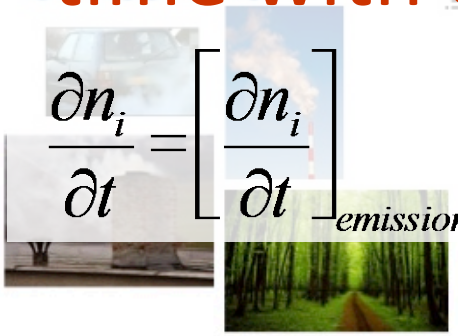
Adapted from Ervens et al., 2011

Atmosphere is a Continuum



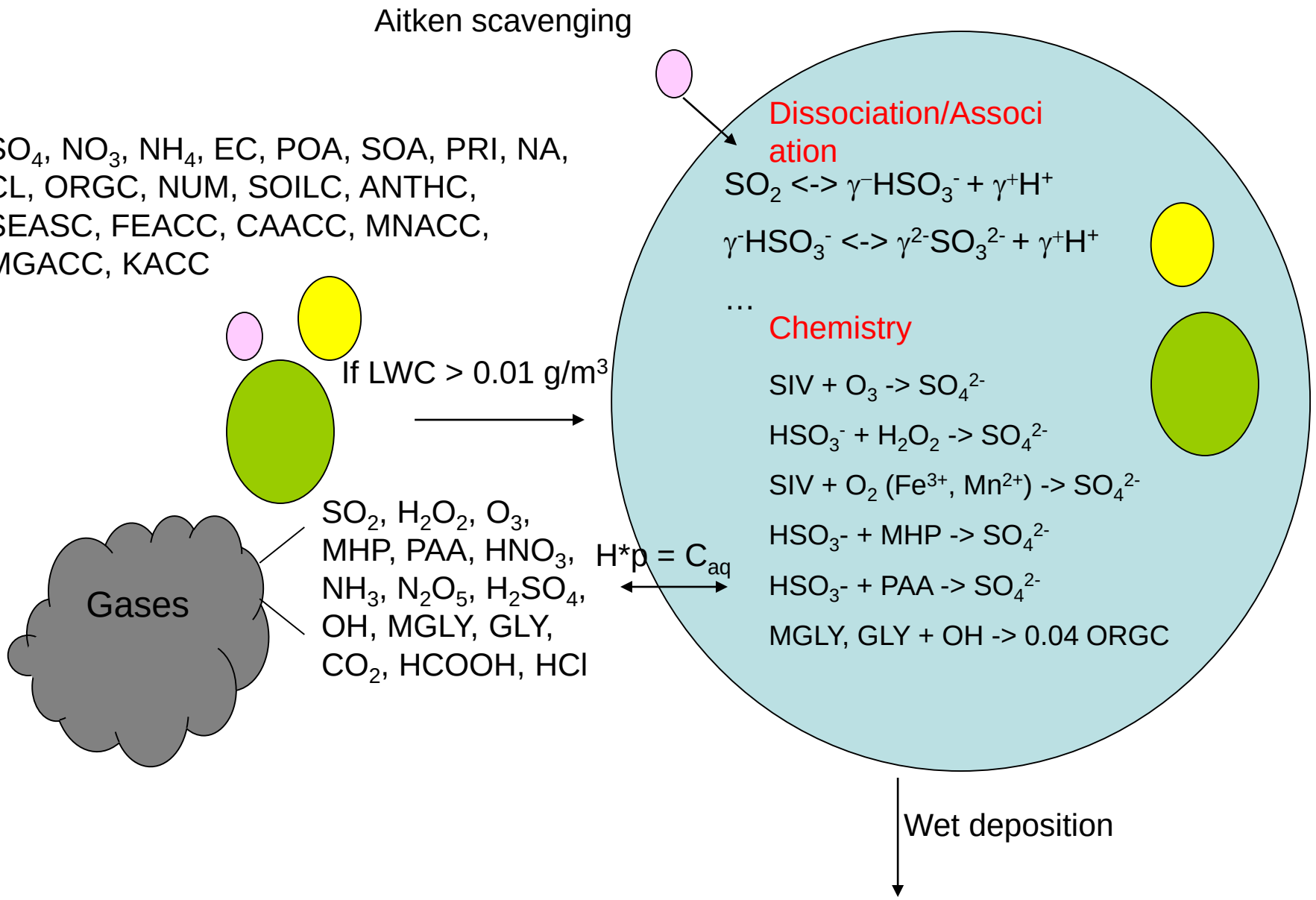
But we discretize the continuity equation in time with operator splitting

$$\frac{\partial n_i}{\partial t} = \left[\frac{\partial n_i}{\partial t}\right]_{emissions} + \left[\frac{\partial n_i}{\partial t}\right]_{gaschemistry} + \left[\frac{\partial n_i}{\partial t}\right]_{partitioing} + \left[\frac{\partial n_i}{\partial t}\right]_{AQchemistry} + \ldots$$

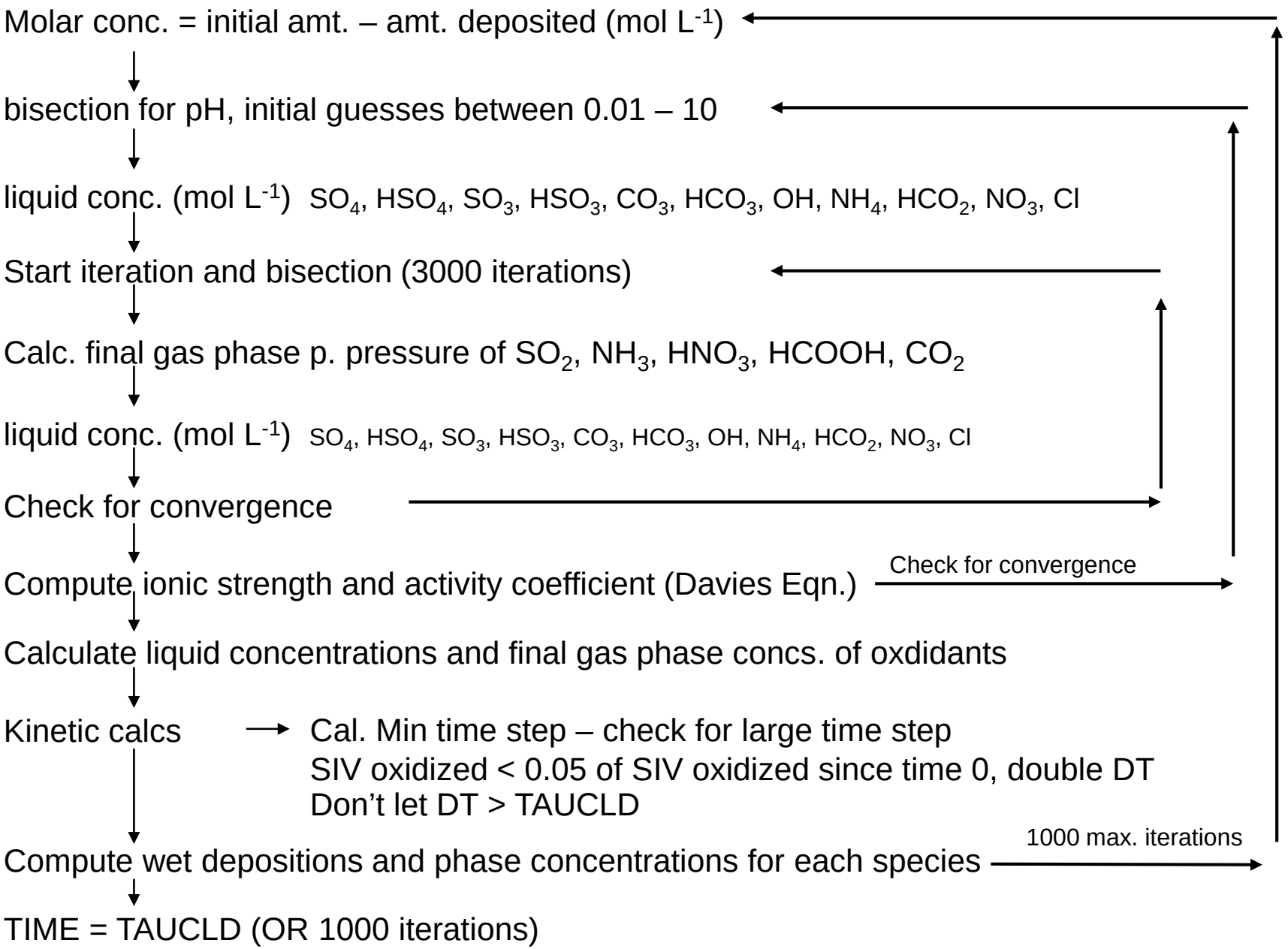


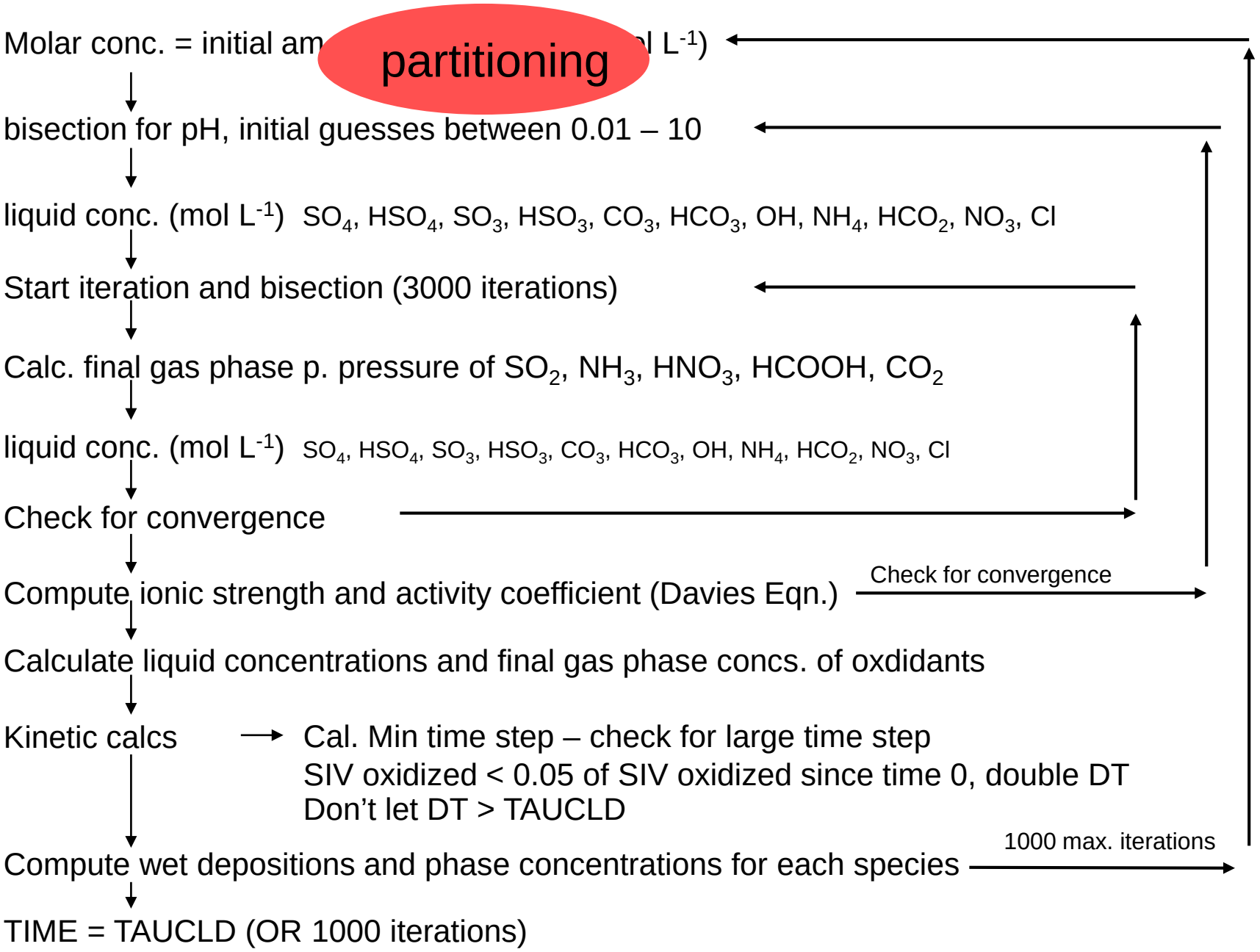
Adapted from Ervens et al., 2011

Aqueous Chemistry in CMAQ: AQCHEM



*Based on original RADM model (Chang et al., 1987; and Walcek and Taylor, 1986)


Molar conc. = initial amt. – amt. deposited (mol L^{-1})
bisection for pH, initial guesses between 0.01 – 10
liquid conc. (mol L^{-1}) SO_4, HSO_4, SO_3, HSO_3, CO_3, HCO_3, OH, NH_4, HCO_2, NO_3, Cl
Start iteration and bisection (3000 iterations)
Calc. final gas phase p. pressure of SO_2, NH_3, HNO_3, HCOOH, CO_2
liquid conc. (mol L^{-1}) SO_4, HSO_4, SO_3, HSO_3, CO_3, HCO_3, OH, NH_4, HCO_2, NO_3, Cl
Check for convergence
Check for convergence
Compute ionic strength and activity coefficient (Davies Eqn.)
Calculate liquid concentrations and final gas phase concs. of oxdidants
Kinetic calcs
Cal. Min time step – check for large time step
SIV oxidized < 0.05 of SIV oxidized since time 0, double DT
Don't let DT > TAUCLD
1000 max. iterations
Compute wet depositions and phase concentrations for each species
TIME = TAUCLD (OR 1000 iterations)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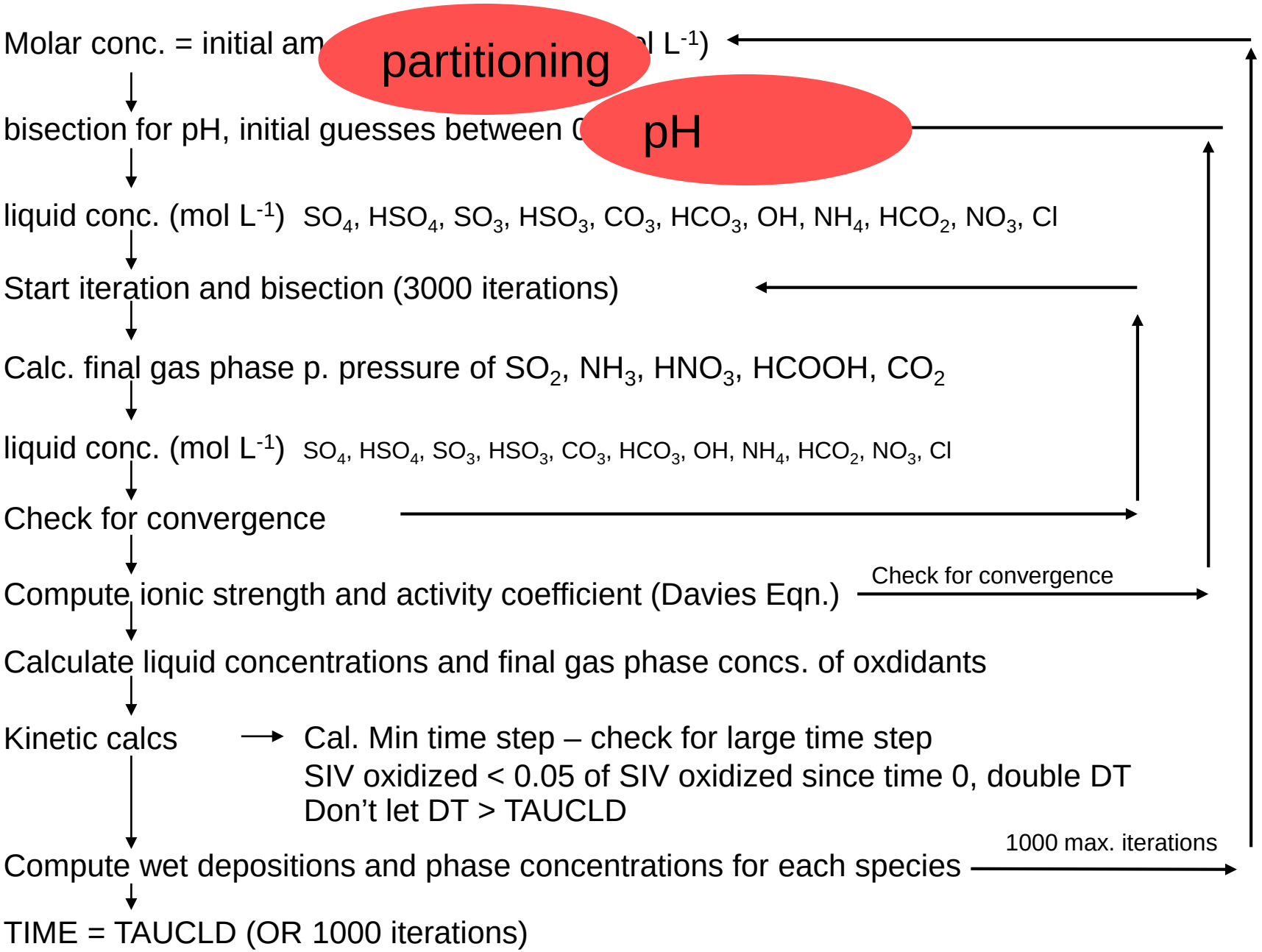
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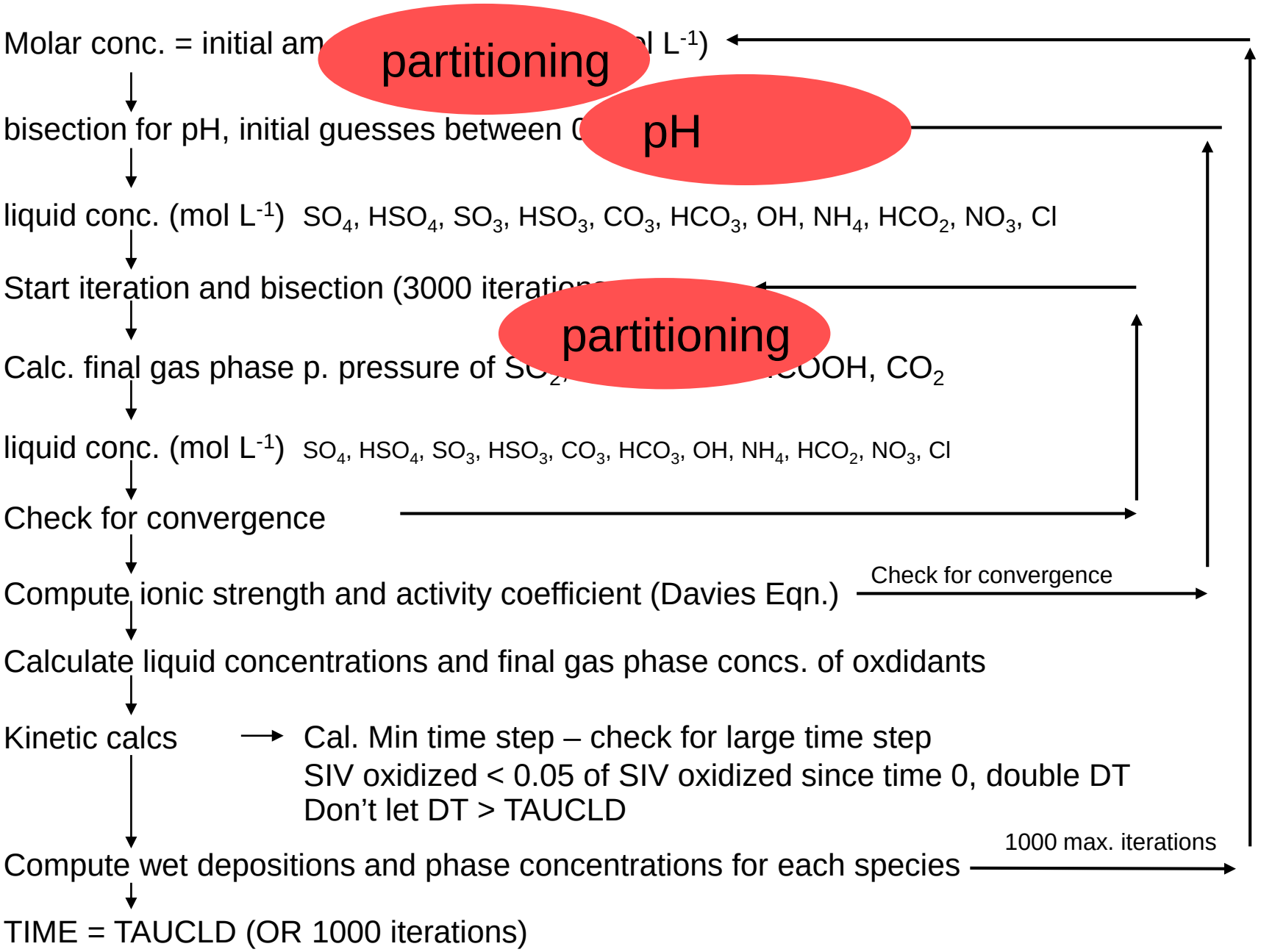
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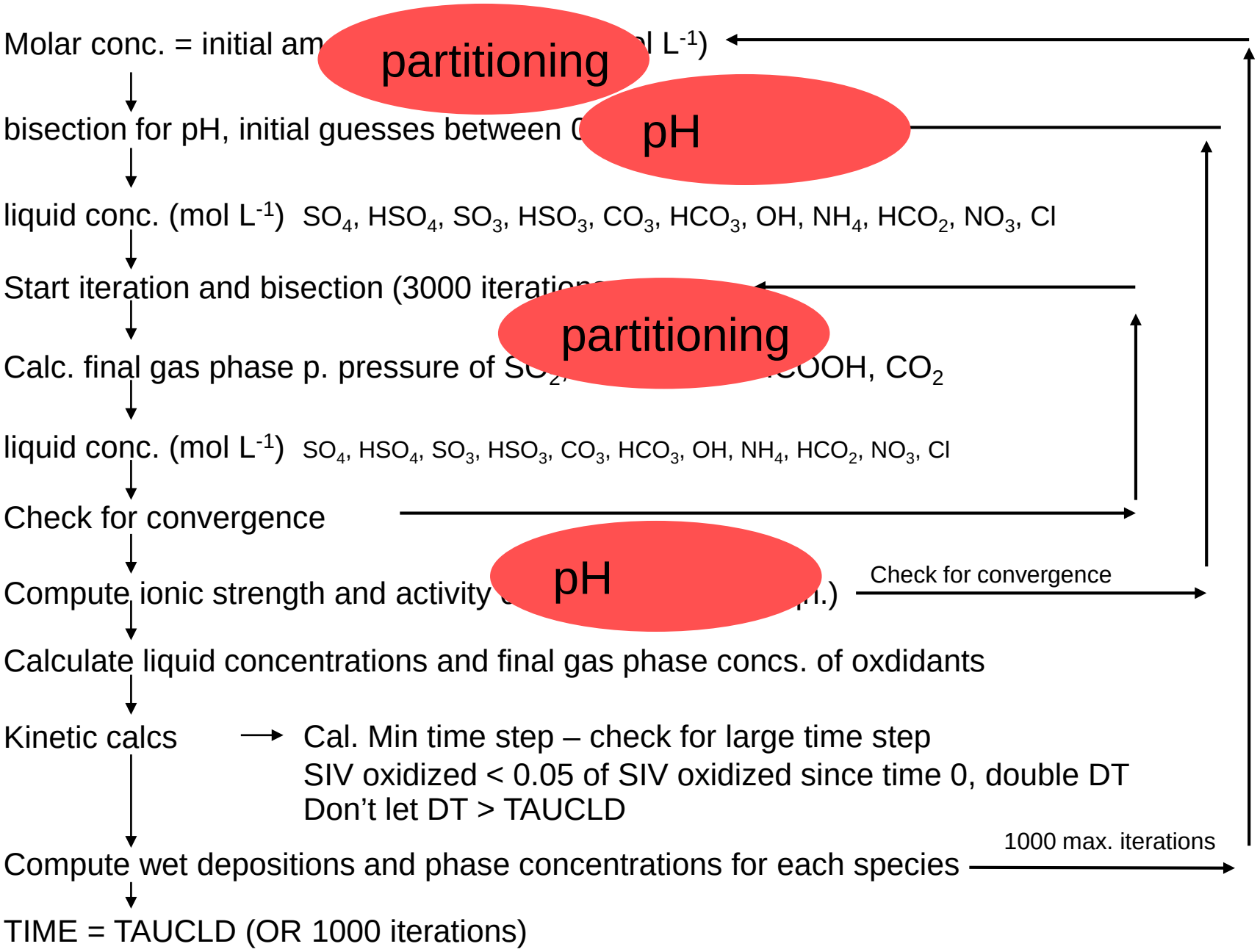
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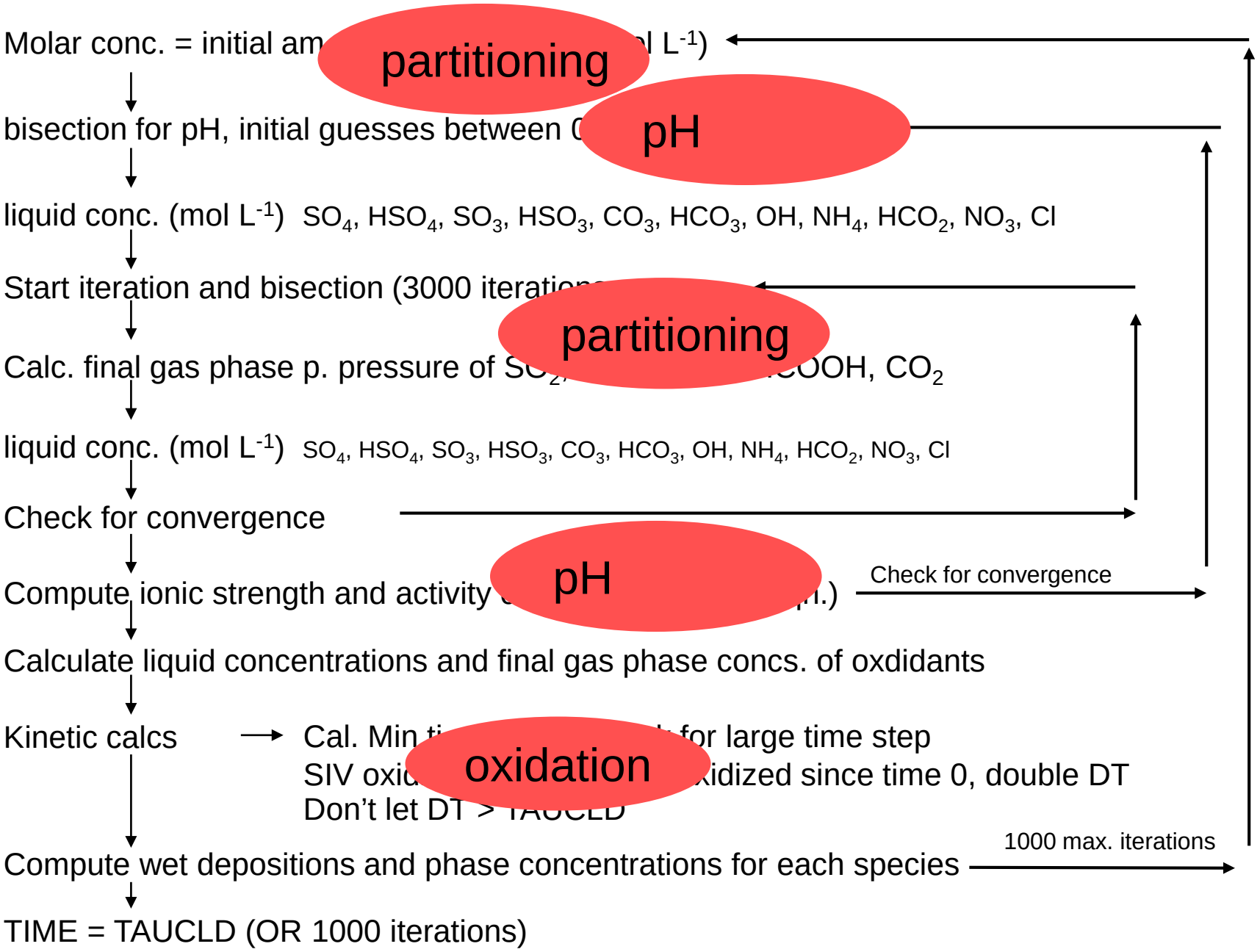
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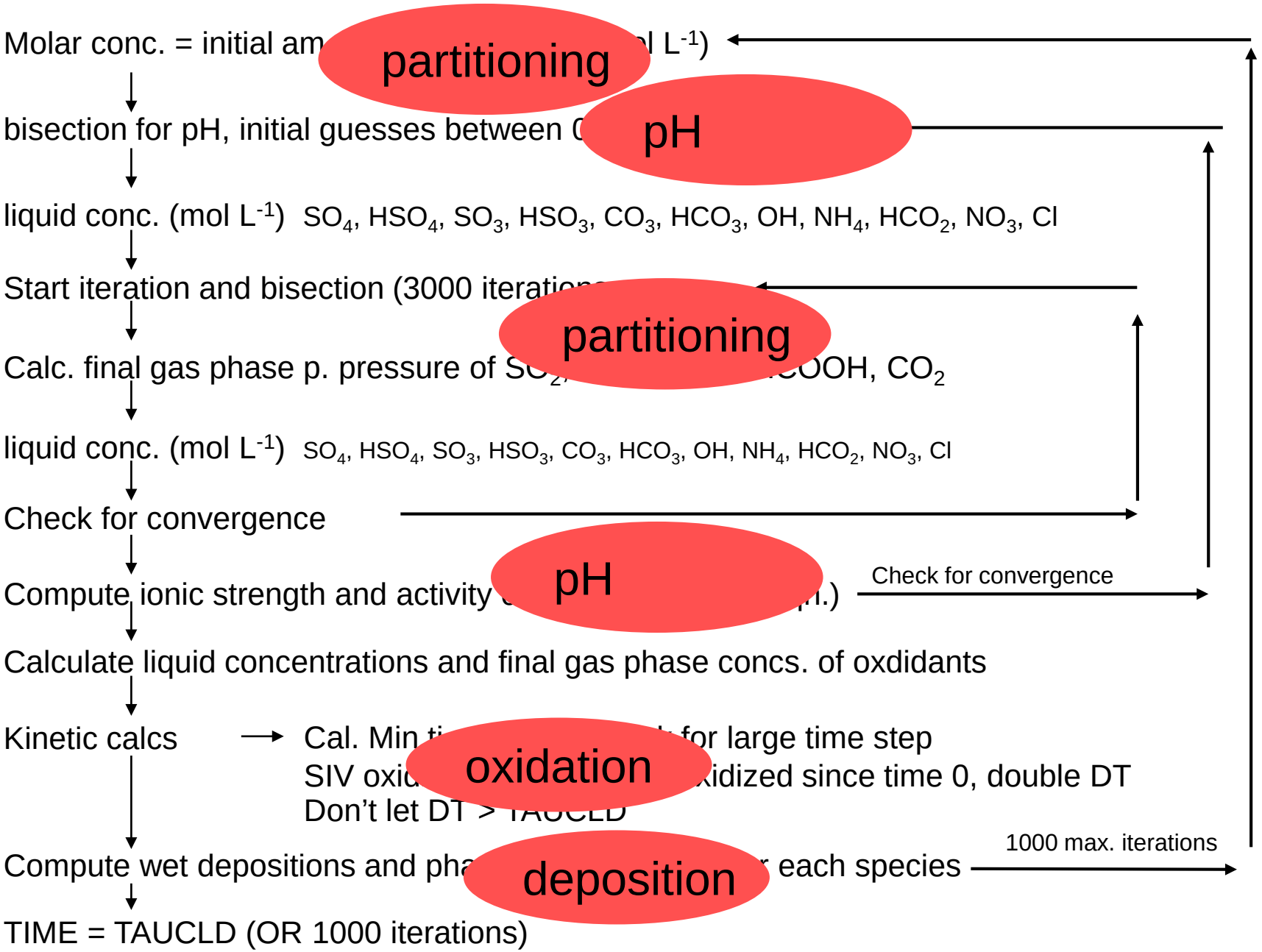
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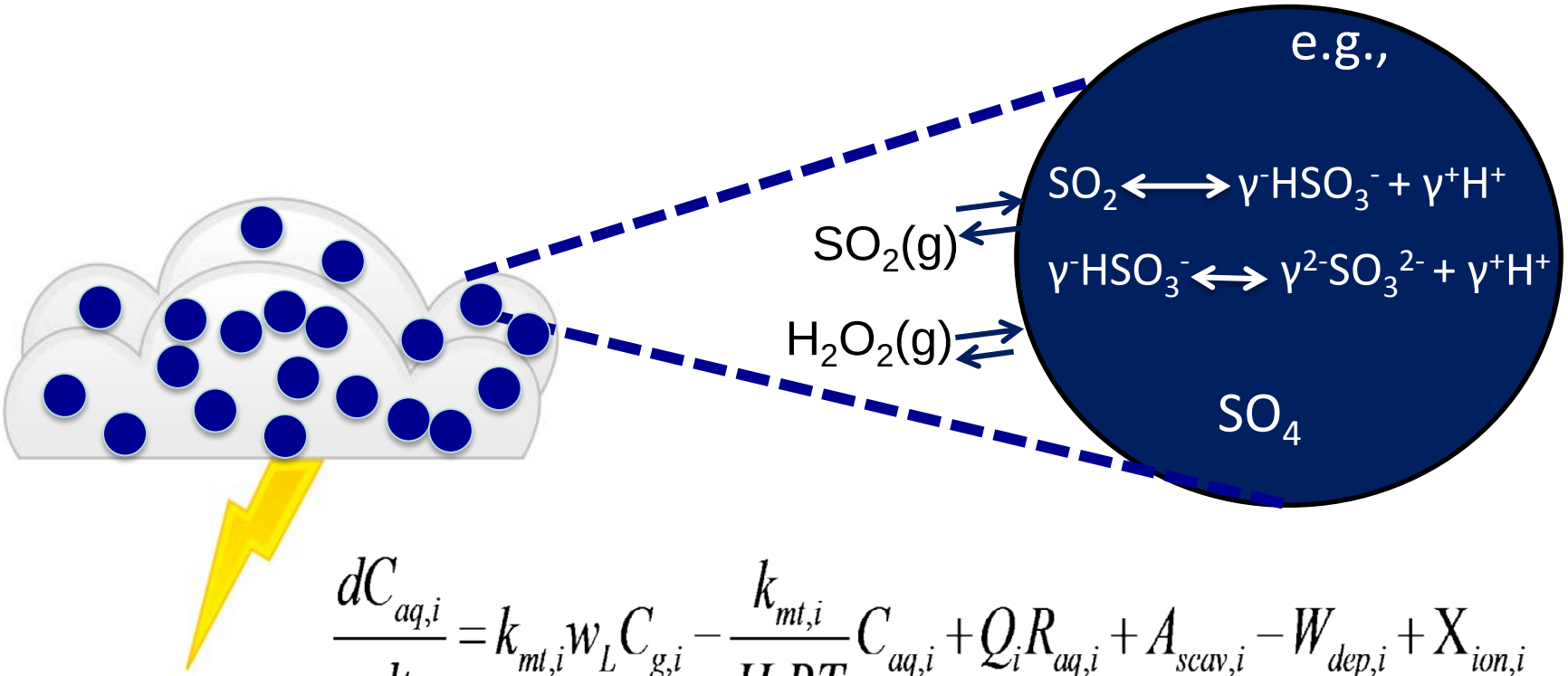
AQchem with Rosenbrock solver and kinetic mass transfer: AQCHEM-KMT



$$\frac{dC_{aq,i}}{dt} = k_{mt,i} w_L C_{g,i} - \frac{k_{mt,i}}{H_i RT} C_{aq,i} + Q_i R_{aq,i} + A_{scav,i} - W_{dep,i} + X_{ion,i}$$

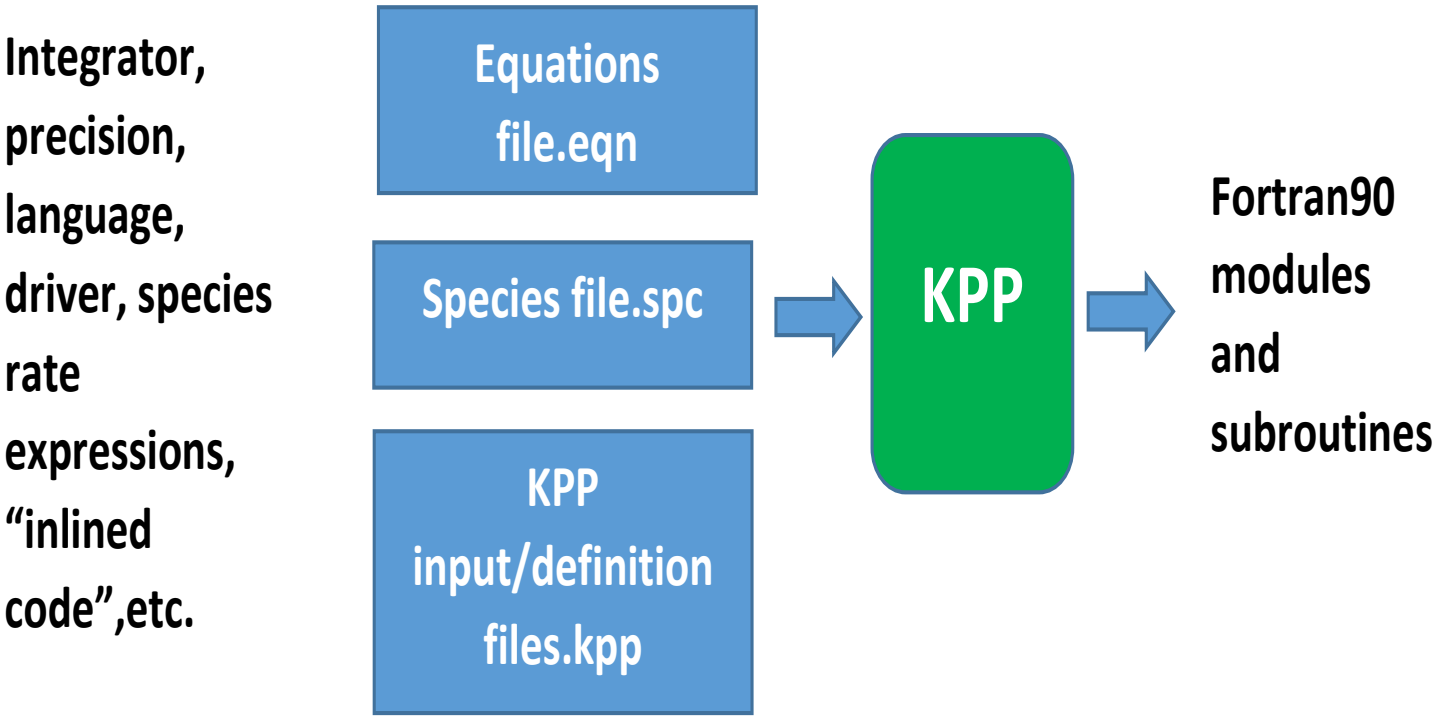
$$\frac{dC_{g,i}}{dt} = -k_{mt,i} w_L C_{g,i} + \frac{k_{mt,i}}{H_i RT} C_{aq,i} \qquad \frac{dC_{aero,i}}{dt} = -A_{scav,i}$$

$$k_{mt} = \left(\frac{R_d^2}{3D_g} + \frac{4R_d}{3\alpha\upsilon}\right)^{-1} \qquad \upsilon = \left(\frac{8RT}{\pi MW}\right)^{1/2}$$

interfacial processes by Schwartz (1986)

Kinetic PreProcessor (KPP)*

translates chemical mechanism (e.g., species, Rxns, rate coefficients) to Fortran90 • exploits **Jacobian sparsity** • modularity allows "easy" incorporation of new chemical mechanisms and/or solvers • can generate the tangent linear or **adjoint**



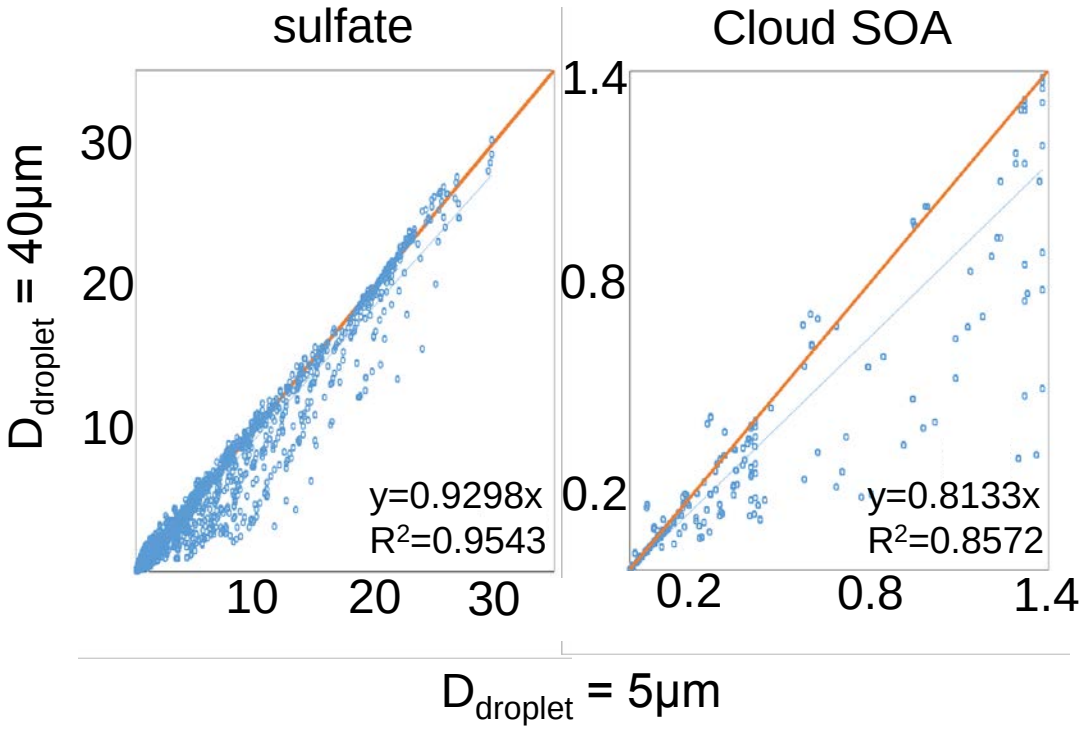
V. Damian, A. Sandu, M. Damian, F. Potra, and G.R. Carmichael, ``The Kinetic PreProcessor KPP -- A Software Environment for Solving Chemical Kinetics", Computers and Chemical Engineering, 26(11), 1567-1579, 2002.

Modeled processes and rate coefficients

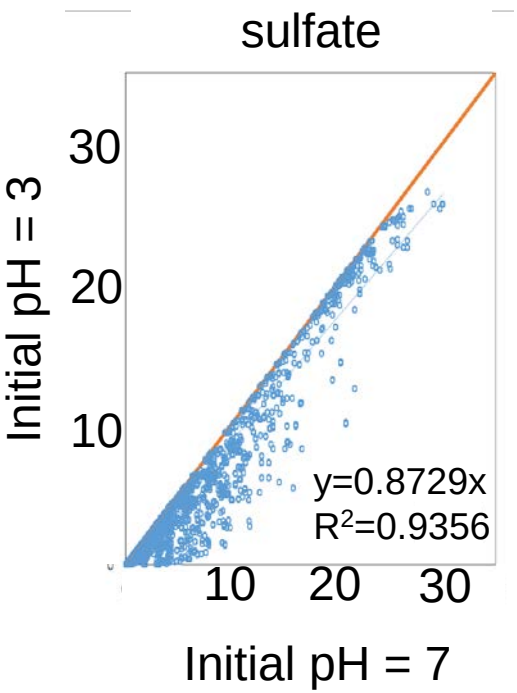
Process	Equations	Rate coefficients	Other information
Gas-Liquid phase transfer	$C_{g,i} \xrightarrow{k_f} C_{aq,i}$	$k_f = k_{mt} w_L$	$k_{mt}(s^{-1}\frac{vol_{air}}{vol_{aq}}) = \left(\frac{a^2}{3D_g} + \frac{4a}{3\bar{\upsilon}\alpha}\right)^{-1}$
Liquid-Gas phase transfer	$C_{aq,i} \xrightarrow{k_b} C_{g,i}$	$k_b = \frac{k_{mt}}{H_{T,i} RT}$	
Dissociation	$C_{aq,i} \xrightarrow{k_f} C_{aq,i}^{-1} + H^+$	k_b = literature value, independent of T $k_f = Keq_{i,T} k_b$	$Keq_{i,T} = Keq_{i,Tref}\left[\frac{-\Delta H_a}{R}\left(\left(\frac{1}{T}\right) - \left(\frac{1}{Tref}\right)\right)\right]$ Activity coefficients are rolled into the forward and backward rates as appropriate
Association	$C_{aq,i}^{-1} + H^+ \xrightarrow{k_b} C_{aq,i}$		
Aitken scavenging	$C_{aer,i,akn} \xrightarrow{\alpha} C_{aq,i}$	α	α is the attachment rate for interstitial aerosols (an input to AQCHEM)
Wet deposition	$C_{aq,i} \xrightarrow{Wdep} C_{WD,i}$	$Wdep = \frac{1}{\tau_{wash}}$	$\tau_{wash}(\text{sec}) = \frac{WT_{AVG} \times CTHK \times 3600.d0}{PRCRATE}, 0.d0$
Chemical kinetics	$C_{aq,1} + C_{aq,2} \xrightarrow{k_{rxn}} C_{aq,3}$	k_{rxn}	Complex rate coefficients that are set according to 5.0.2 base mechanism

Impact of droplet diameter and initial pH

DIAMETER EFFECTS



pH_0 EFFECT

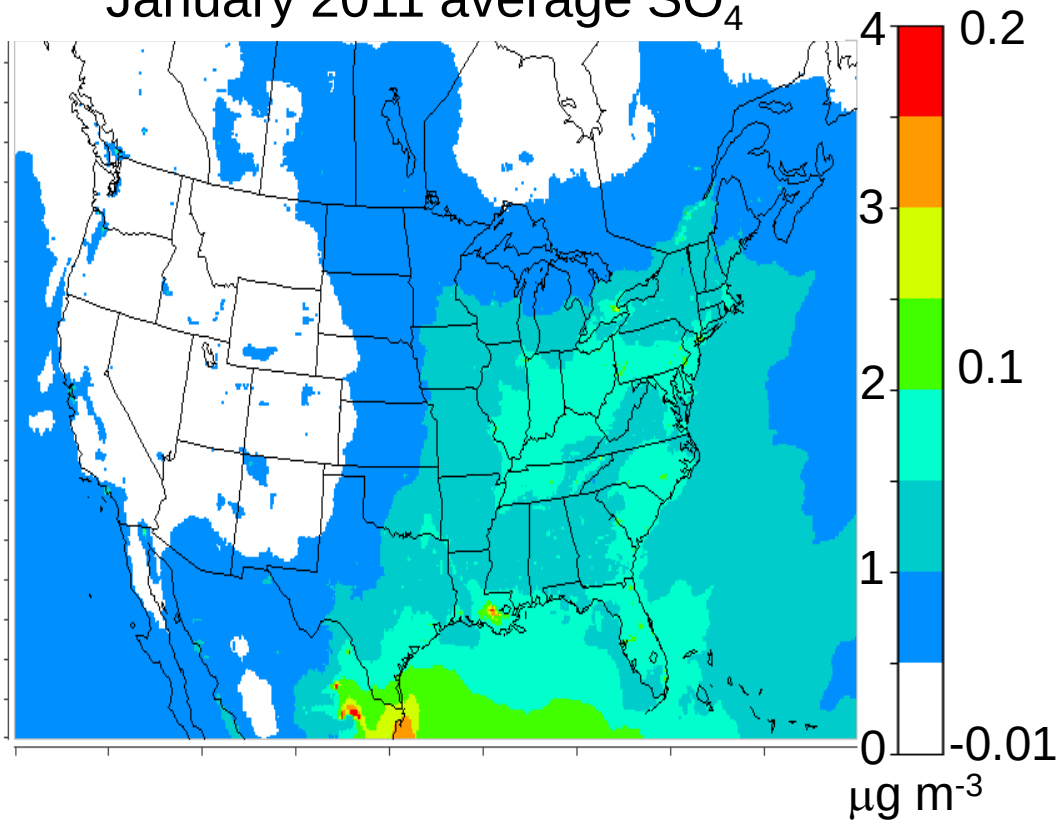


Cloud droplet size changes k_{mt} and impacts SO_4 and SOA_{cloud}

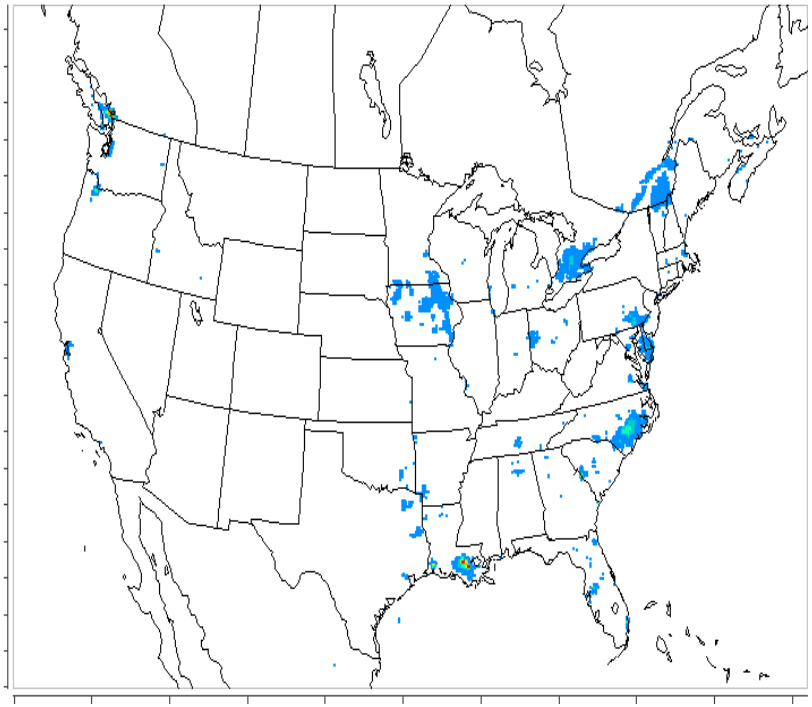
Suggests continued development of linkages between microphysics (e.g., effective cloud droplet radius, activated aerosol fraction) and aqueous phase chemistry is needed

Impacts of AQCHEM-KMT in CMAQ

January 2011 average SO_4



Jan. 2011 average SO_4 difference



Typically < 10% (max: 16%) Δ in **monthly average surface** SO_4

Hourly differences can be more substantial: max. $\Delta SO_{4,hr}$ = 16 μg/m^3

Explicit Oxidation Mechanism

Current SOA reactions in CMAQ

GLY + OH → 0.04 * ORGC	$k_1 = 3.0E10\ M^{-1}\ s^{-1}$
MGLY + OH → 0.04 * ORGC	$k_1 = 3.0E10\ M^{-1}\ s^{-1}$

Explicit reactions in new box model

GCOL + OH → GCOLAC + H_2O + HO_2	$k_1 = 5.0E8\ M^{-1}\ s^{-1}$
GCOL + OH → GLY + HO_2	$k_1 = 1.0E9\ M^{-1}\ s^{-1}$
GCOLAC + OH → $GLYAC^-$ + H^+ + HO_2	$k_1 = 6.0E8\ M^{-1}\ s^{-1}$
$GCOLAC^-$ + OH → $GLYAC^-$ + HO_2	$k_1 = 8.6E8\ M^{-1}\ s^{-1}$
GLY + OH → GLYAC + HO_2	$k_1 = 1.1E9 * EXP(-1516/RT)\ M^{-1}\ s^{-1}$
GLYAC + OH → OXLAC + H_2O + HO_2	$k_1 = 1.5E8\ M^{-1}\ s^{-1}$
$GLYAC^-$ + OH → $OXLAC^-$ + H_2O + HO_2	$k_1 = 1.2E9\ M^{-1}\ s^{-1}$
OXLAC + 2 OH → 2 CO_2 + 2 H_2O	$k_1 = 1.4E6\ M^{-1}\ s^{-1}$
$OXLAC^-$ + OH → CO_2 + CO_2^- + 2 H_2O	$k_1 = 4.7E7\ M^{-1}\ s^{-1}$
$OXLAC^{2-}$ + OH → CO_2 + CO_2^- + OH^-	$k_1 = 7.7E6\ M^{-1}\ s^{-1}$
MGLY + OH → 0.92 $PYRAC^-$ + 0.08 $GLYAC^-$ + HO_2 + H_2O	$k_1 = 7.0E8\ M^{-1}\ s^{-1}$
PYRAC + OH → CH_3CO_2H + CO_2 + HO_2	$k_1 = 6.0E7\ M^{-1}\ s^{-1}$
$PYRAC^-$ + OH → $CH_3CO_2^-$ + CO_2 + HO_2	$k_1 = 6.0E7\ M^{-1}\ s^{-1}$
CH_3CO_2H + OH → 0.85 GLYAC + 0.15 CH_2OHYD	$k_1 = 1.6E7\ M^{-1}\ s^{-1}$
$CH_3CO_2^-$ + OH → 0.85 $GLYAC^-$ + 0.15 CH_2OHYD	$k_1 = 8.5E7\ M^{-1}\ s^{-1}$
CH_2OHYD + OH → HCOOH + H_2O + HO_2	$k_1 = 1.1E9 * EXP(-1020/RT)\ M^{-1}\ s^{-1}$
HCOOH + OH → H_2O + HO_2	$k_1 = 1.2E8 * EXP(-990/RT)\ M^{-1}\ s^{-1}$

GCOL – glycolaldehyde

GCOLAC – glycolic acid

GLY – glyoxal

GLYAC – glyoxylic acid

OXLAC – oxalic acid

MGLY – methylglyoxal

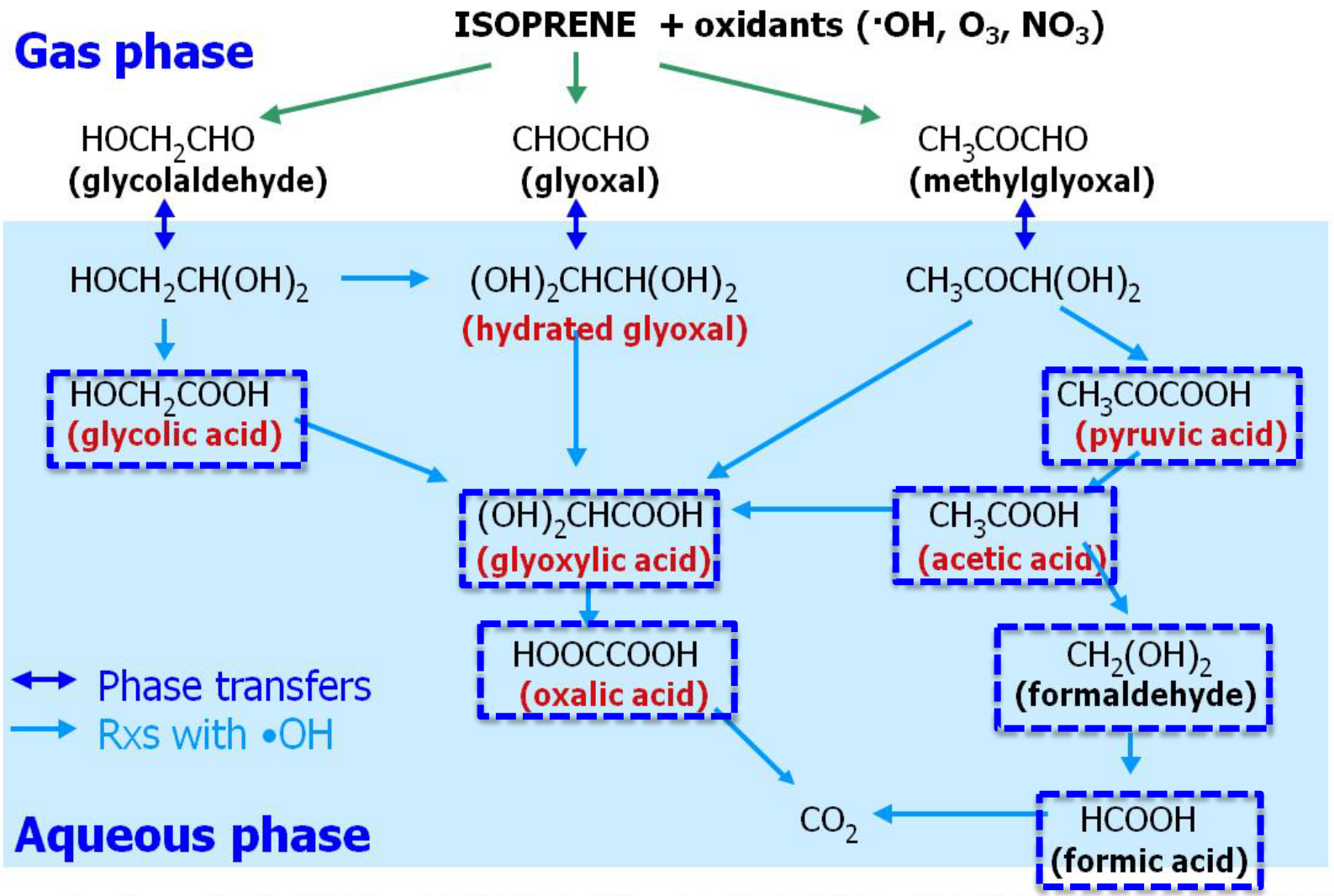
PYRAC – pyruvic acid

CH_3CO_2H – acetic acid

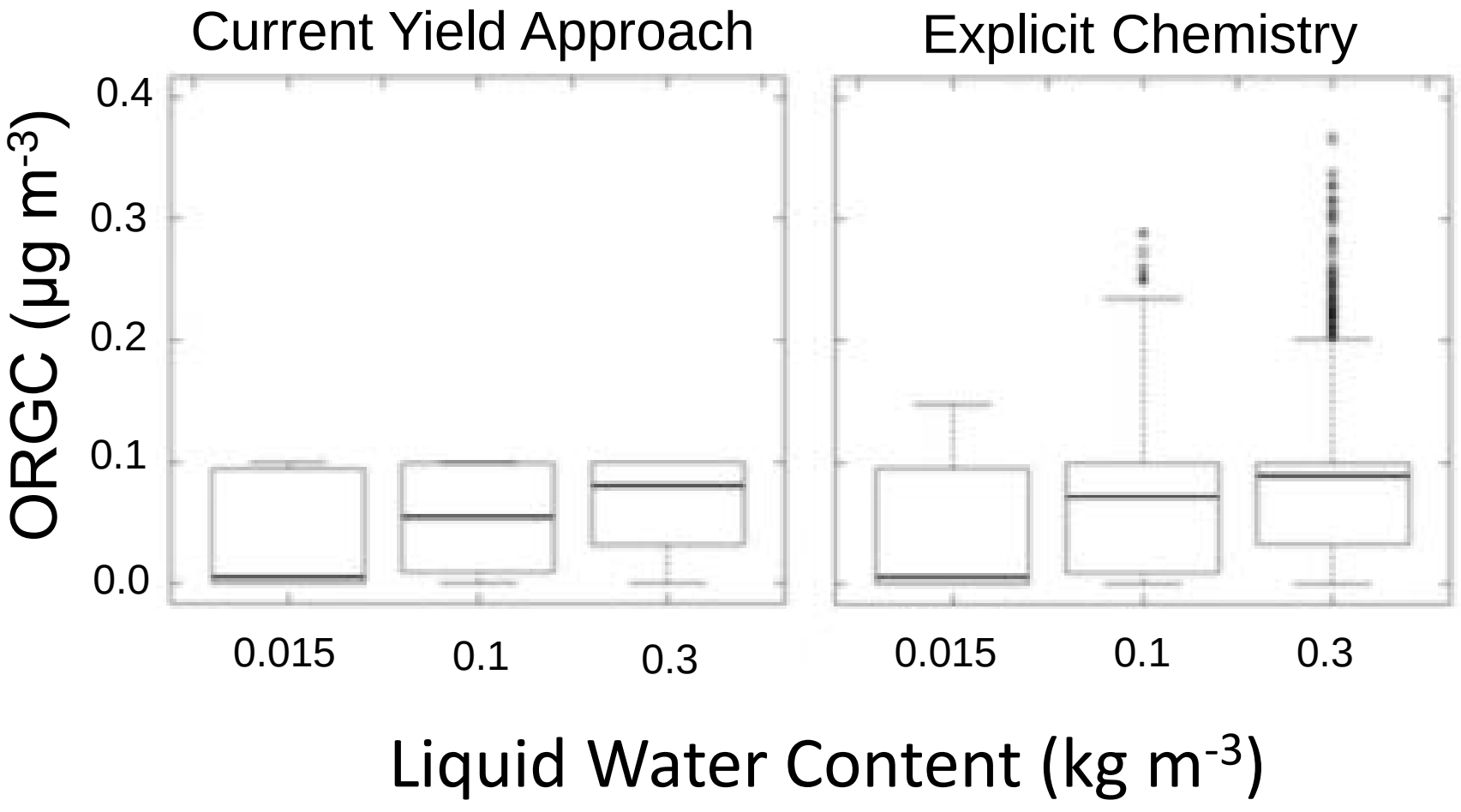
CH_2OHYD – hydrated formaldehyde

Explicit aqueous organic chemistry

Introduces pH dependence to SOA_{cld}



Carlton *GRL* 2006, *AE* 2007; Altieri *EST* 2006, *AE* 2008; Perri *AE* 2009

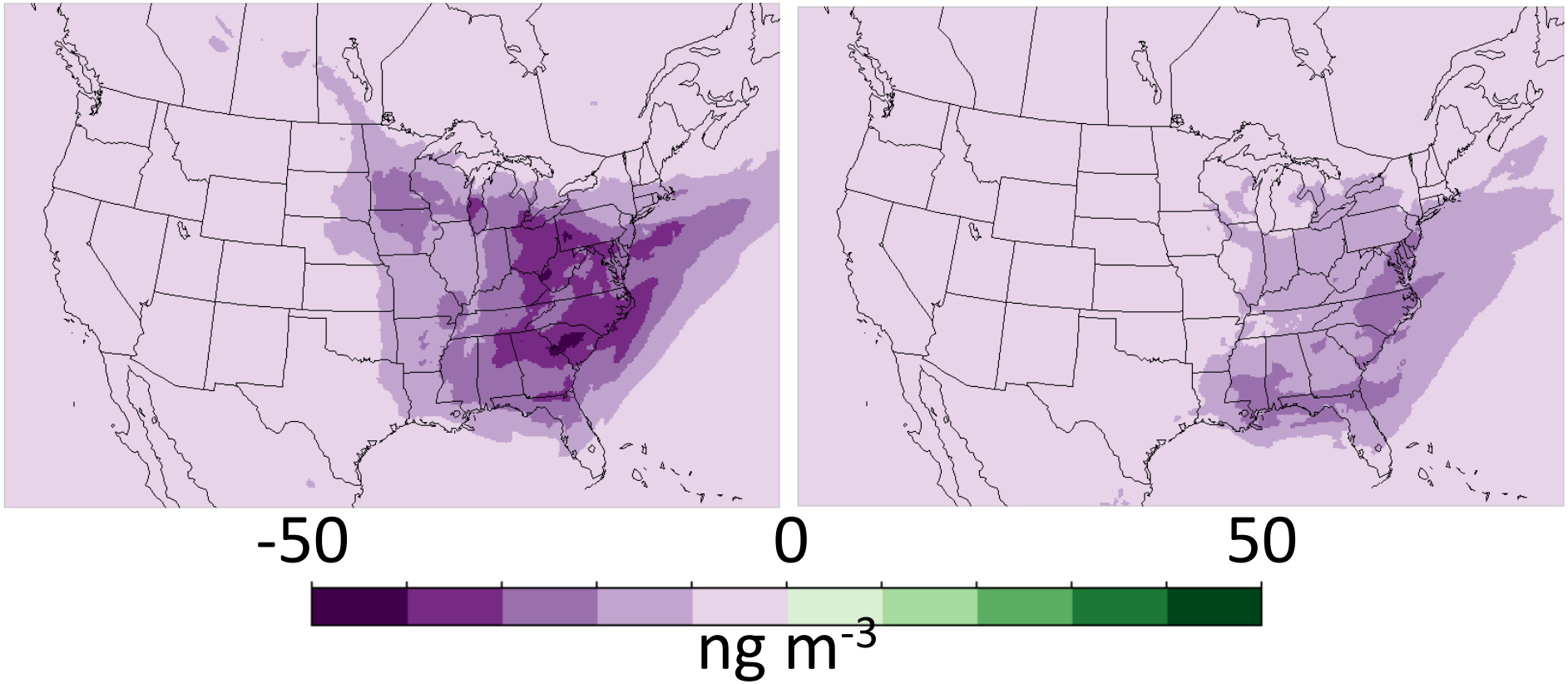


Explicit chemistry does not perturb the averages, but **increases variability** in cloud SOA predictions

Average SOA_{cloud}

surface

800 mb



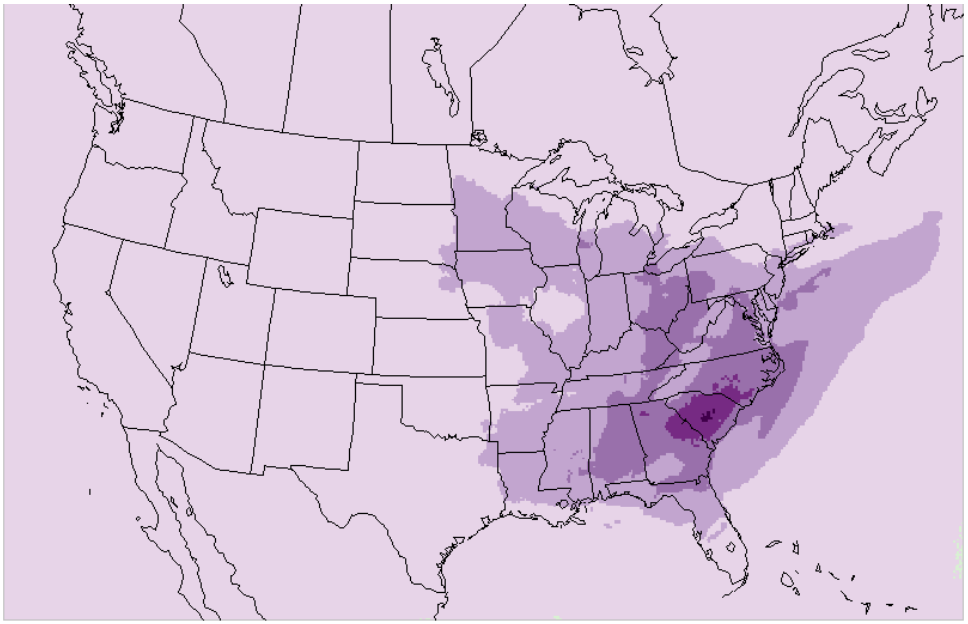
AQChem-KMT KPP CMAQ simulations:
explicit GLY, MGLY oxidation – psuedo 1st order approximation

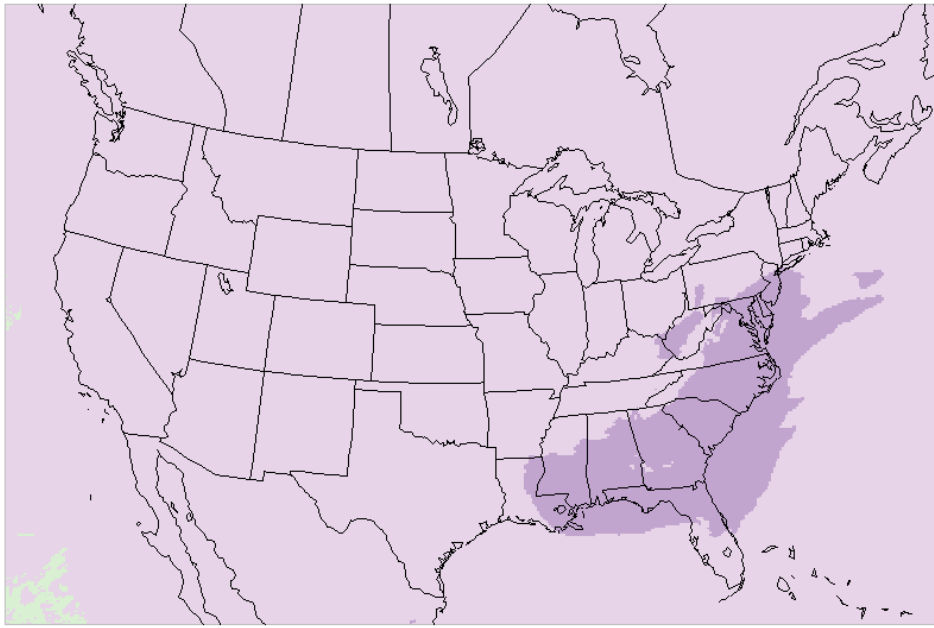
10 day average during July 2013

Average Total SOA

surface

800 mb





-0.1 0 0.1

µg m^{-3}

AQChem-KMT KPP CMAQ simulations:
explicit GLY, MGLY oxidation – psuedo 1st order approximation

10 day average during July 2013

Conclusions and Future Directions

New solver for aqueous chemistry implemented in CMAQ, available through CMAS

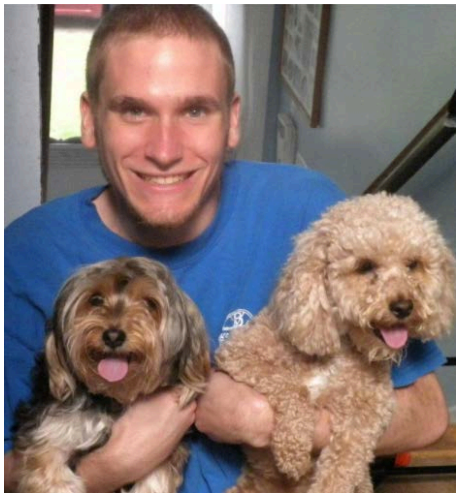
Droplet size dependent chemistry changes **SO_4** and **cloud SOA** production **amounts** and **variability**

Explicit Chemistry for organic species changes average cloud SOA values at the **surface** and **aloft and introduces a pH dependence**

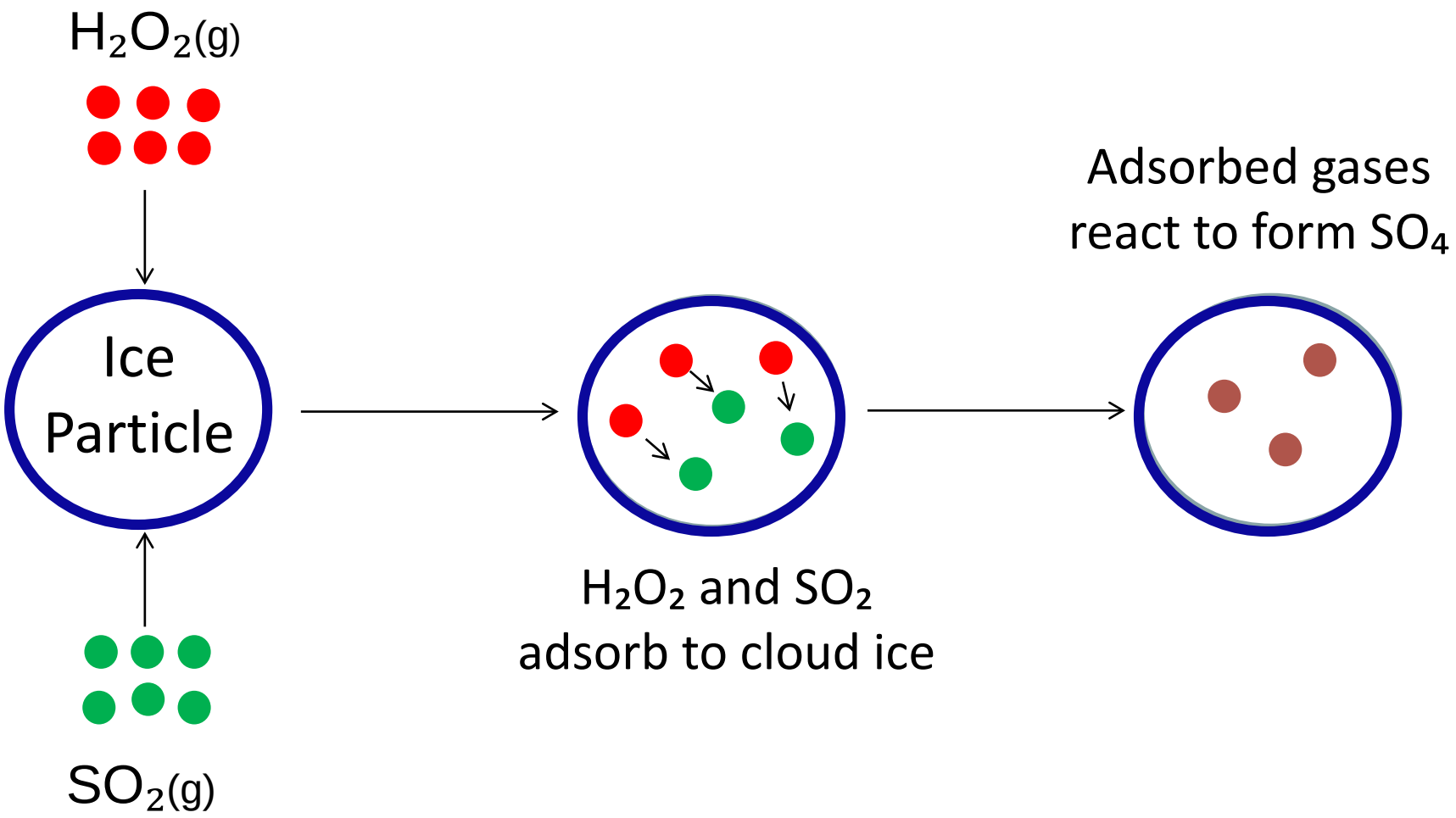
Explicit calculation of the adjoint for cloud chemistry is now possible.

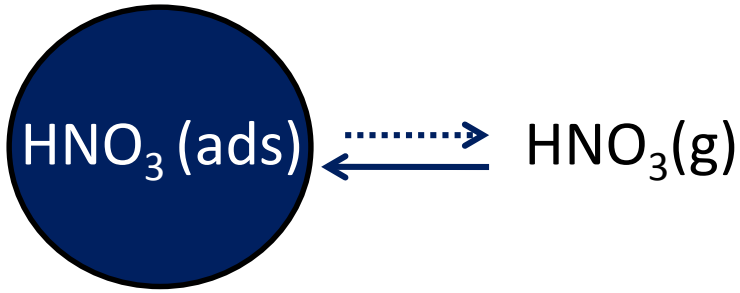
From CMAQ subroutine ***scavwdep.F***:

C... NOTE: for now, scavenging coefficients are computed for only
C... the liquid water content, not on the total water content
C... therefore, no ice phase scavenging is considered at this
C... time, but it should be added in the future!

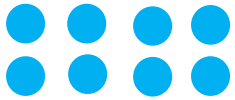


Ice chemistry





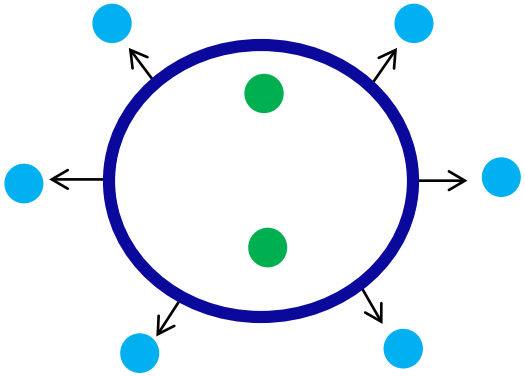
$HNO_{3(g)}$

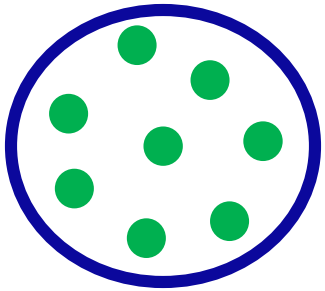


Ice Particle

HNO_3 adsorbs to surface of the Ice

25% Partitioning Case



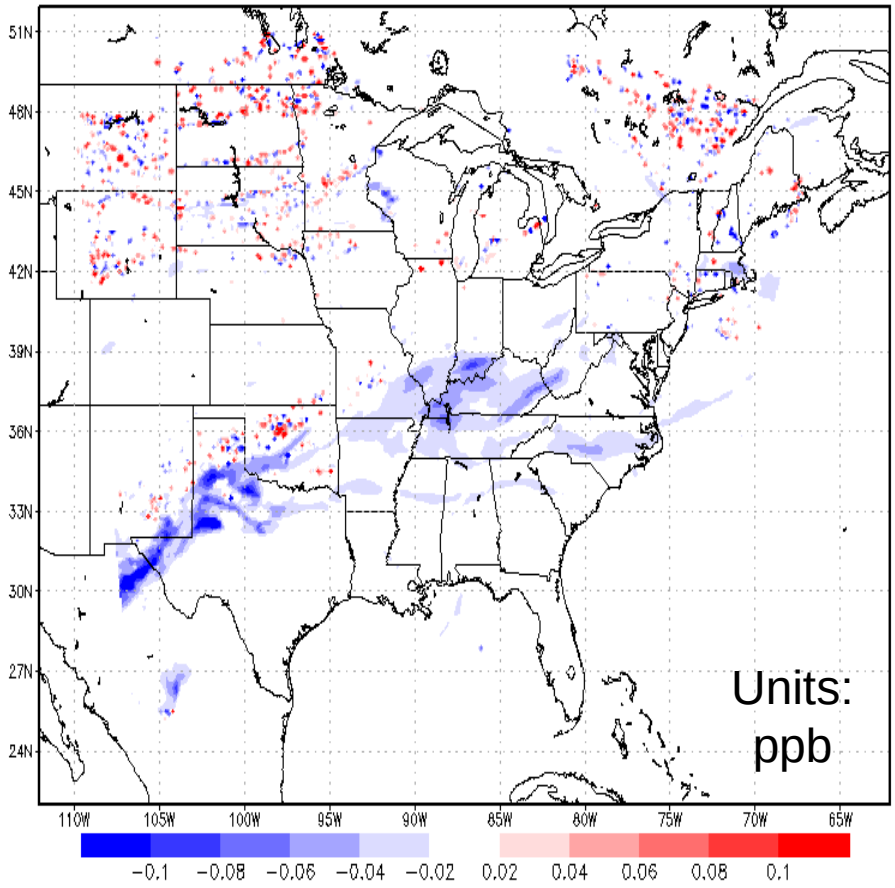


100% Partitioning Case

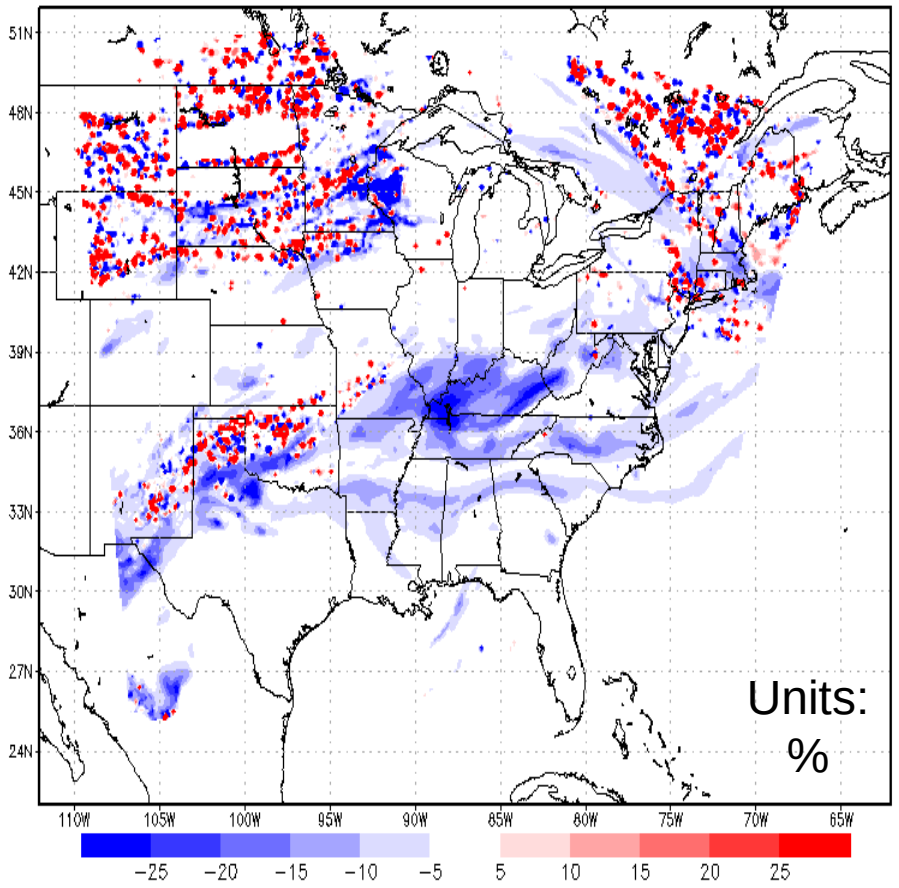
Differences in Gas Phase HNO_3

Differences in gas phase HNO_3 concentrations between 100% partitioning case and LNO_x case at 400 mb for 0Z on August 12th.

a) Absolute Differences



b) Percent Differences

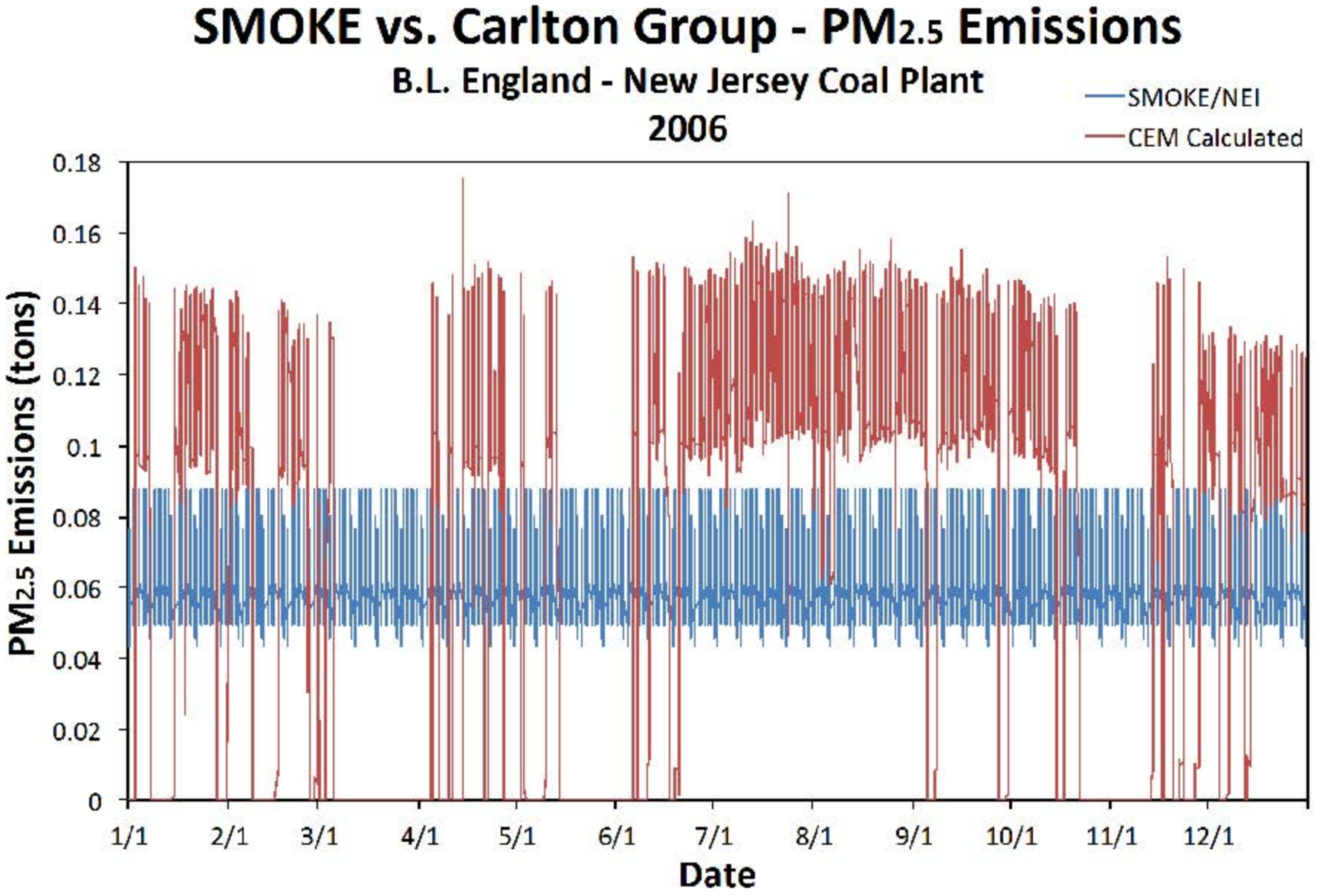


Maximum decreases in gas phase HNO_3 were near 0.10 ppb or 25%

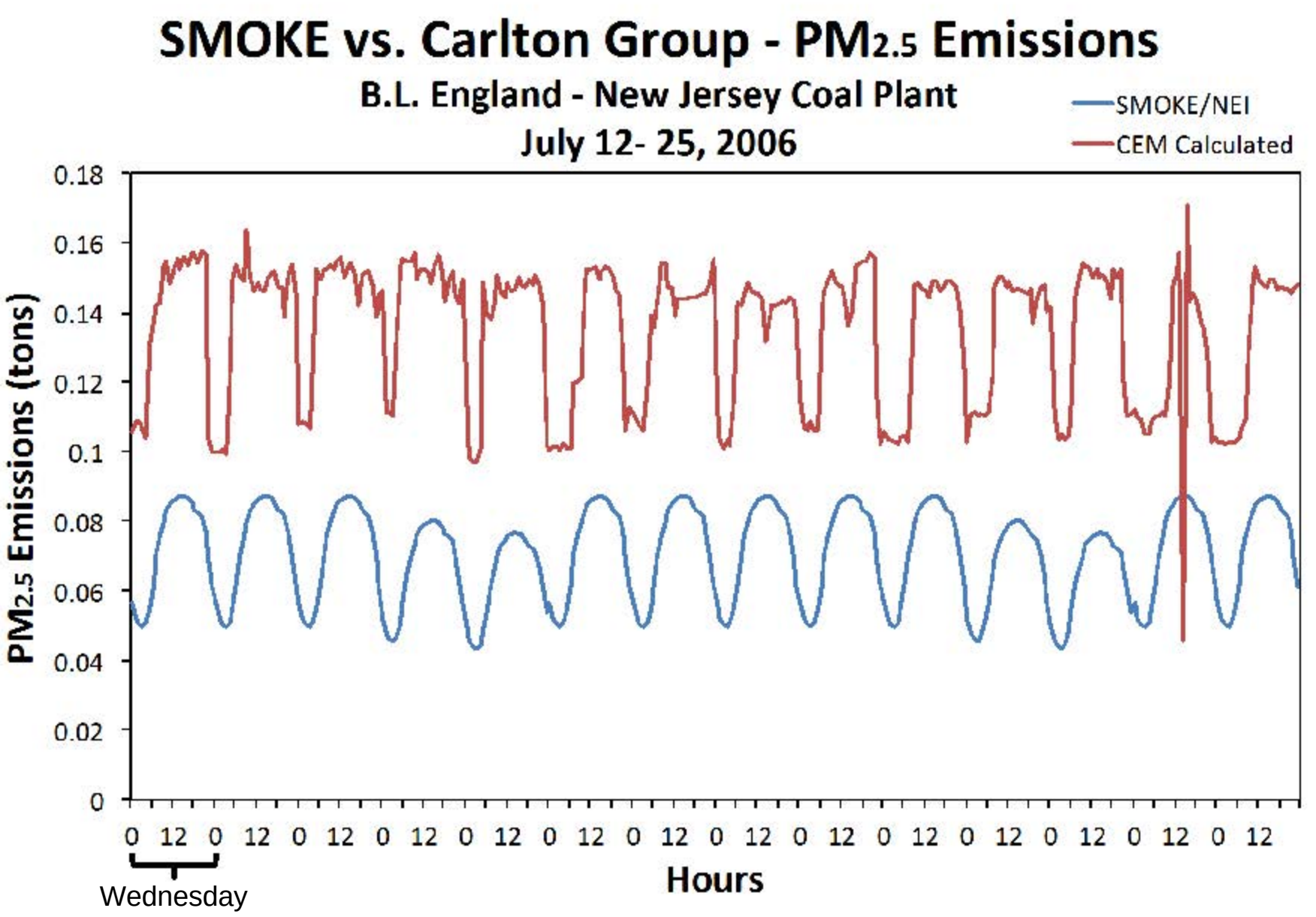
Conclusions

- HNO_3 partitioning to ice is an important process in the atmosphere
  - Decreases in gas phase HNO_3 were as high as 25%
  - This resulted in decreases in NO_x and HONO near 10%
  - Increases in particulate nitrate mass were as high as 0.15 μg/m³
- Very little sulfate formed on ice: the reaction as implemented did not change predictions

BC inspired emissions



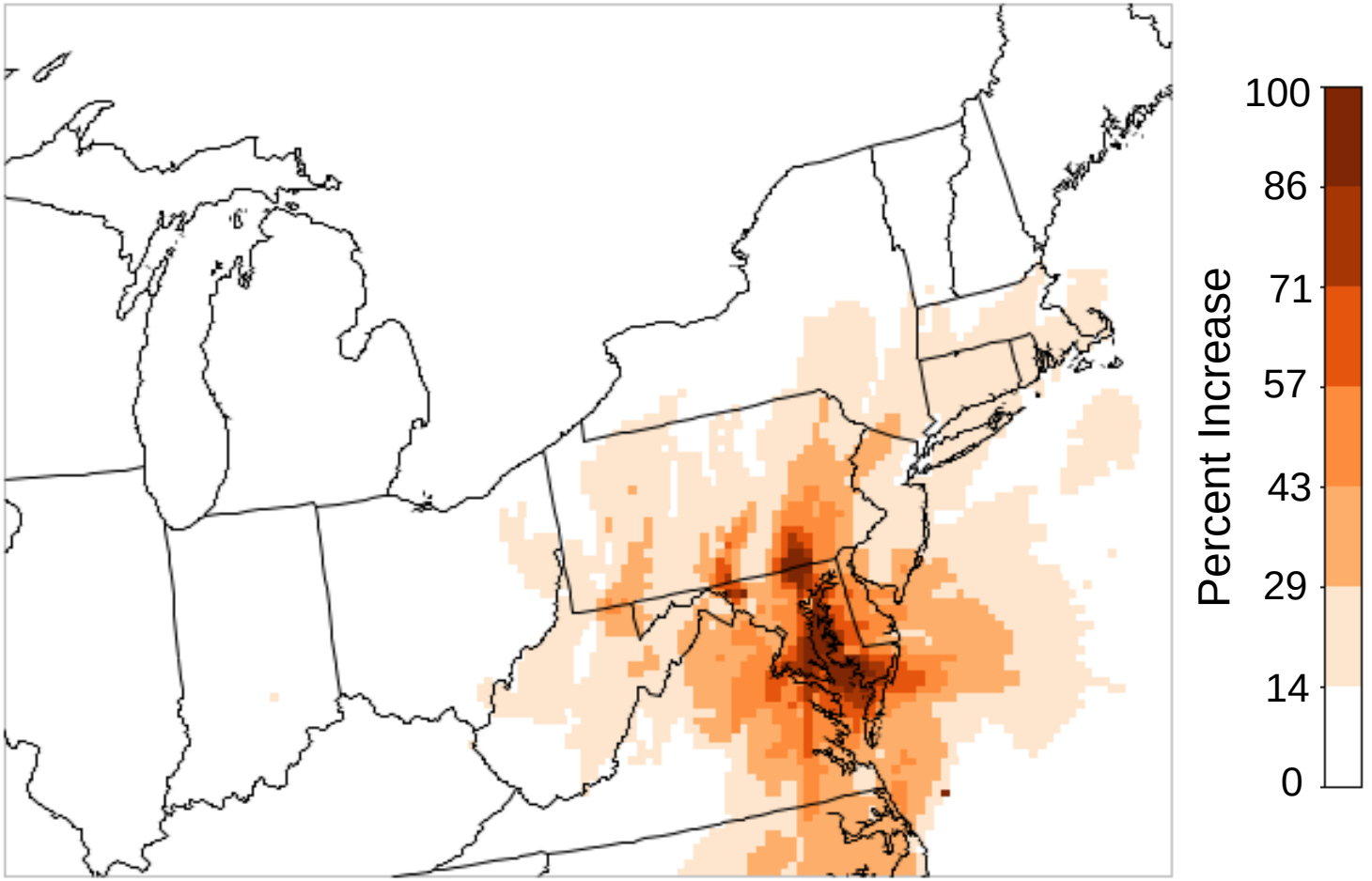
SUMMER COMPARISON



CMAQ RESULTS

Ambient $PM_{2.5}$ Maximum Increase

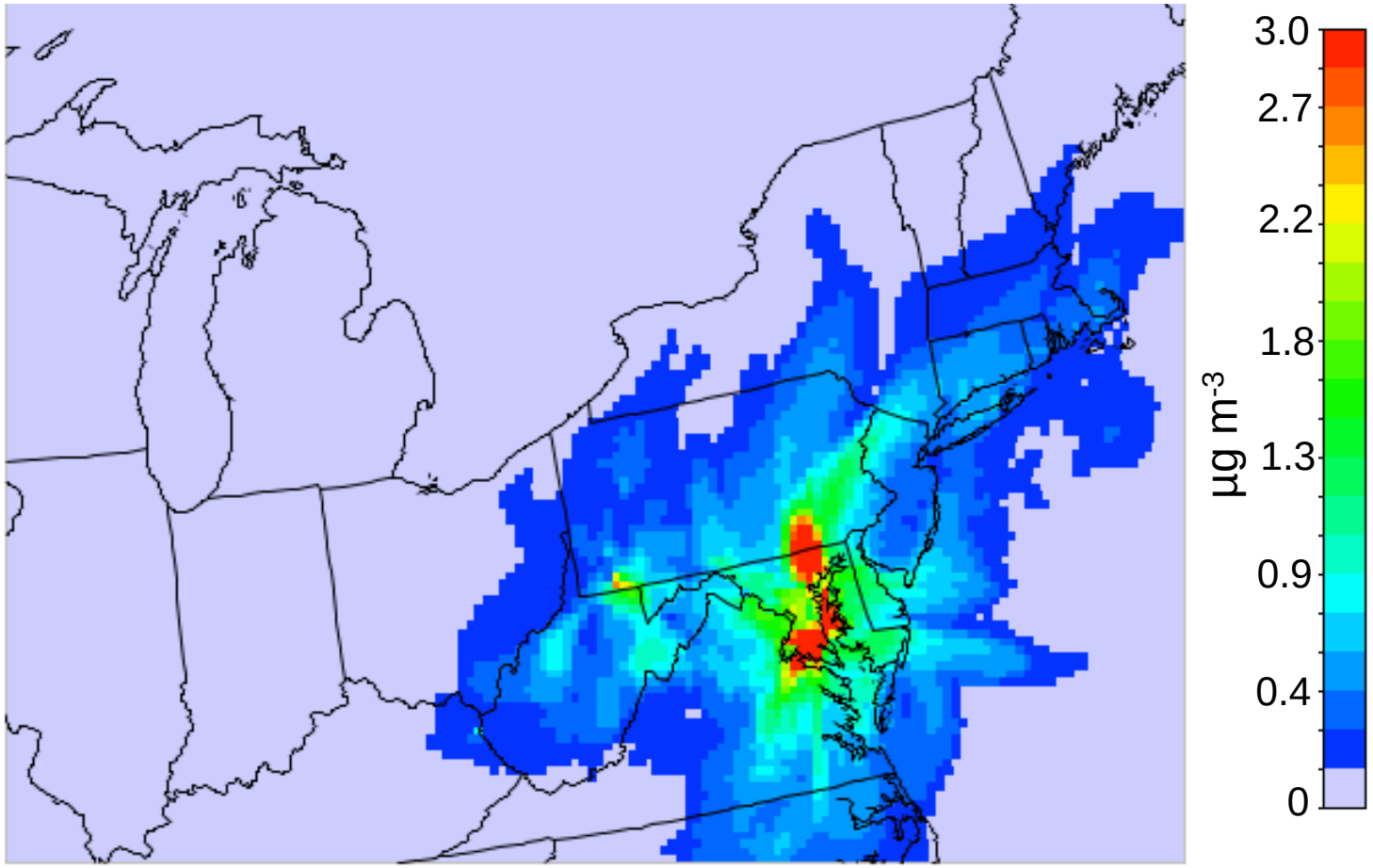
July 12, 2006 – July 25, 2006



Maximum increases of >100% at some sites

Ambient $PM_{2.5}$ Maximum Increase

July 12, 2006 – July 25, 2006



Maximum Increase > 6 µg m^{-3} → 40% of annual standard

Conclusions:

$PM_{2.5}$ emissions increase up to 500% during heat waves compared to base case SMOKE calculated emissions

Up to 2x ambient $PM_{2.5}$ mass concentrations during heat wave when emissions are re-temporalized

Robust inclusion of 520 unmatched CEMs and plants with multiple fuels and evaluating findings.

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