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THE STATE UNIVERSITY
OF NEW JERSEY

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

Annmarie G. Carlton

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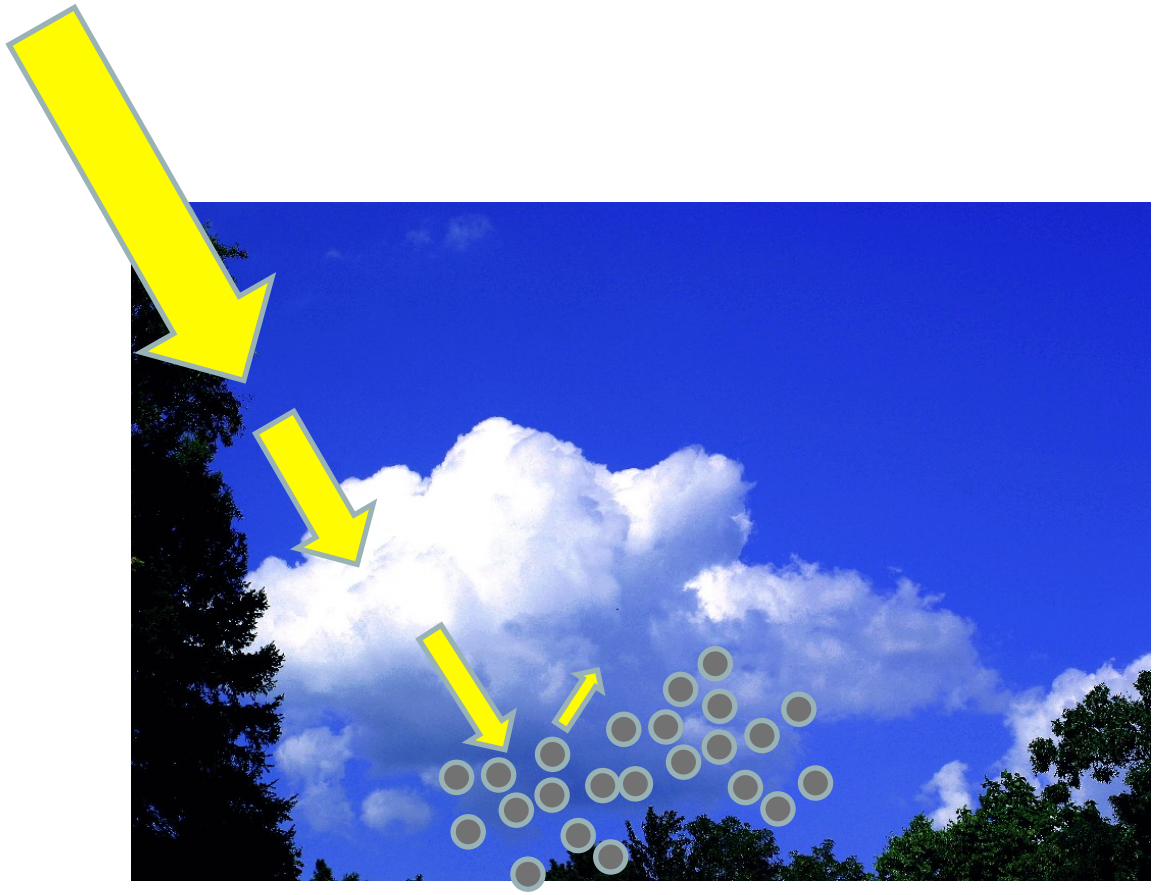
Critical Importance of Vertical profile



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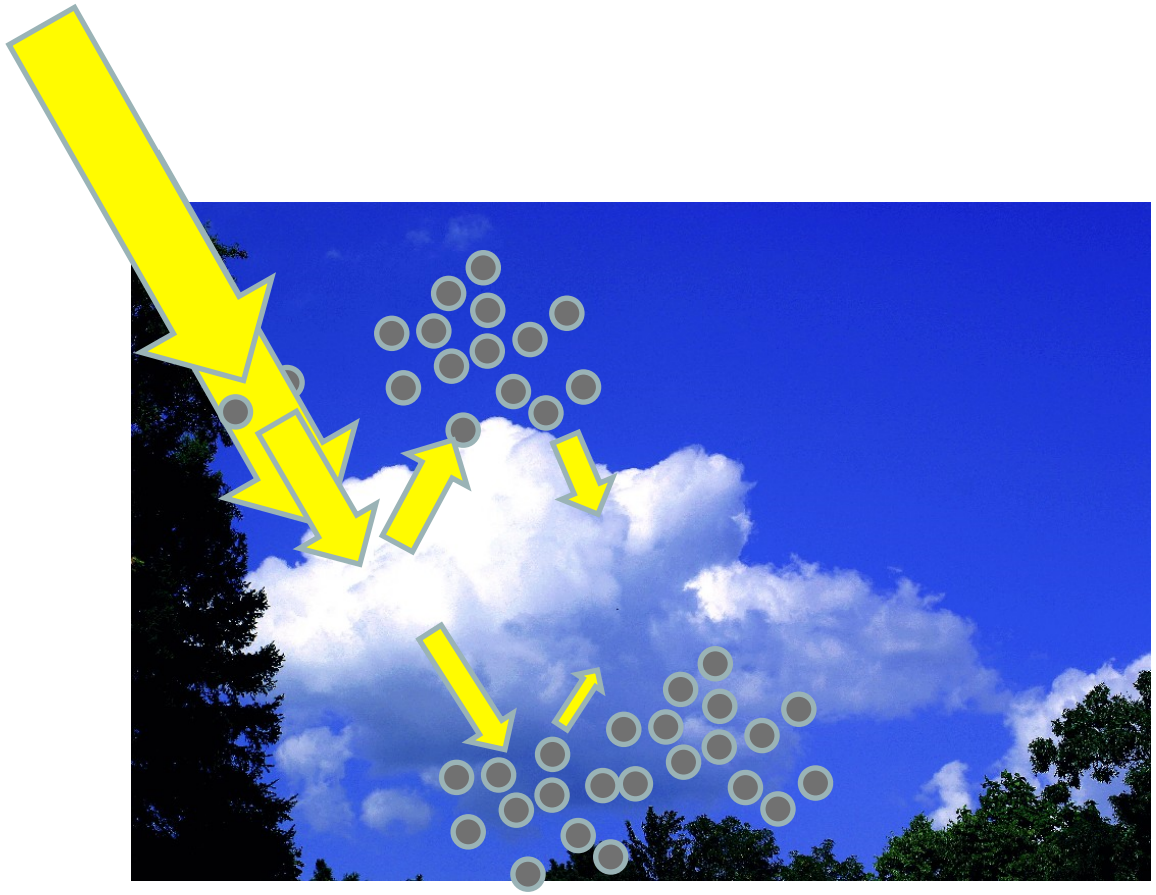
Critical Importance of Vertical profile



aerosols above clouds: diffuse backscatter, less removal processes

OC 2nd largest contributor to AOD

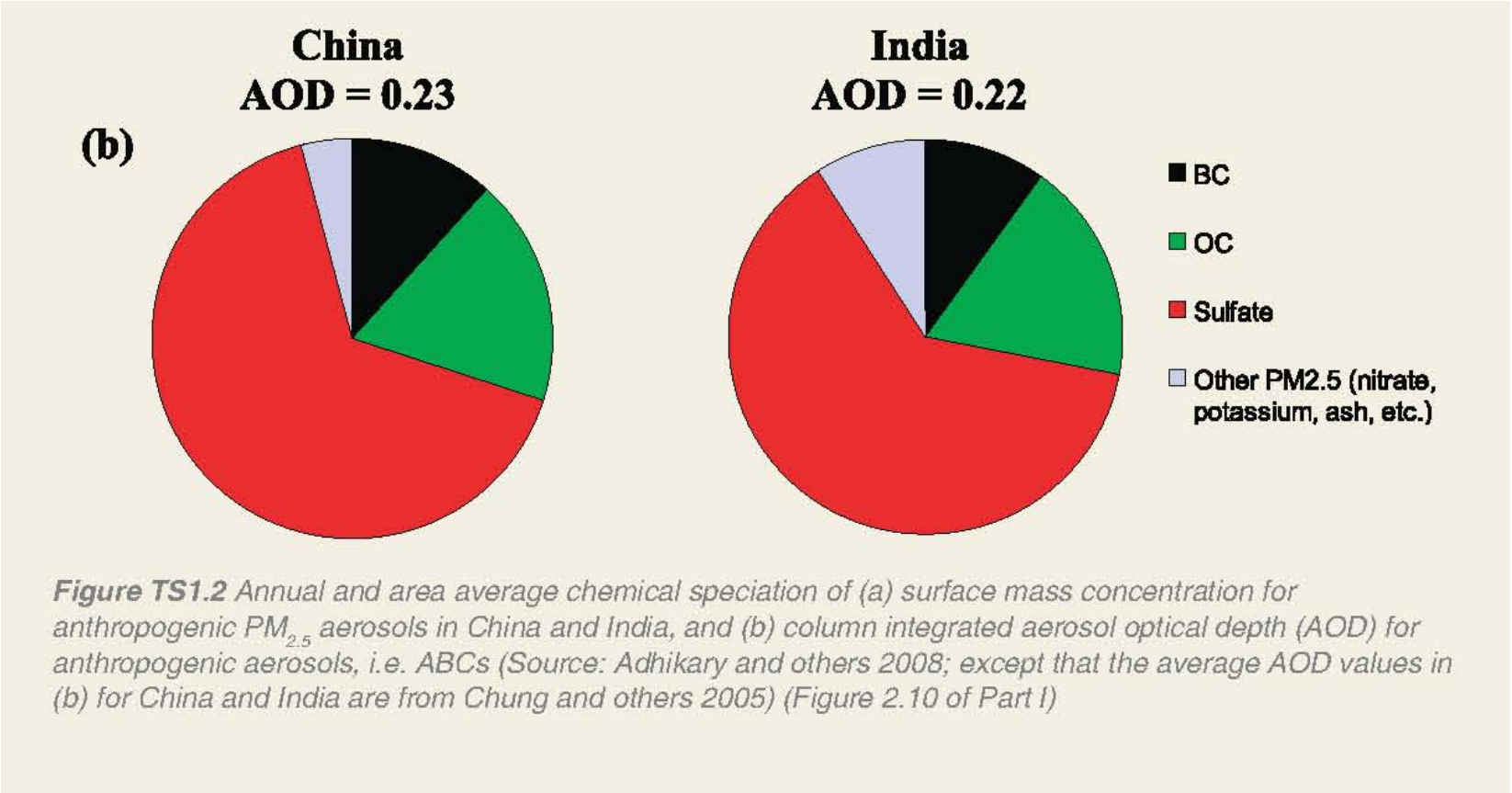


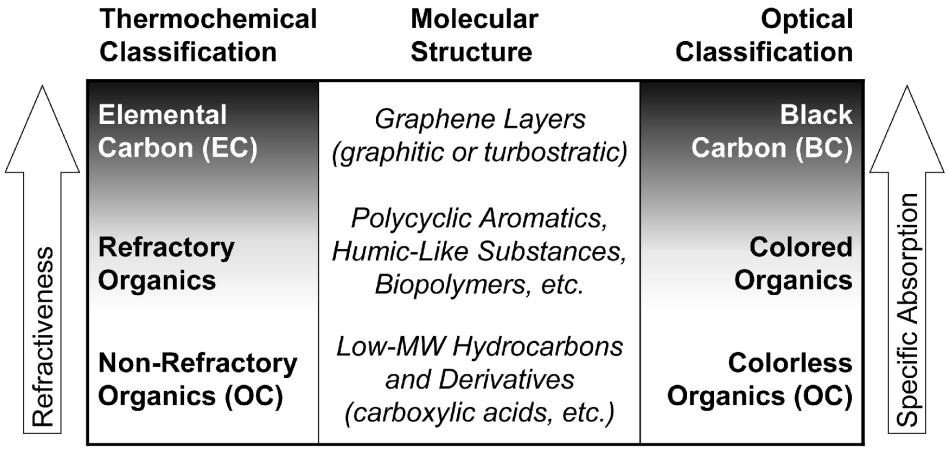
Figure TS1.2 Annual and area average chemical speciation of (a) surface mass concentration for anthropogenic $PM_{2.5}$ aerosols in China and India, and (b) column integrated aerosol optical depth (AOD) for anthropogenic aerosols, i.e. ABCs (Source: Adhikary and others 2008; except that the average AOD values in (b) for China and India are from Chung and others 2005) (Figure 2.10 of Part I)

Sulfate > organic “brown” carbon > black carbon > nitrate and others

UNEP, Atmospheric Brown Clouds, Regional Assessment Report (2008)

BC Definition

"**Brownish**" color of ABCs assumed to arise *via* absorption by BC particles.



Separation based on single wavelength measurements (adapted from Pöschl, 2003).

Black Carbon: colloquially means "soot", highly light-absorbing carbon

Elemental Carbon: chemically refers to thermally-refractory pure carbon with a graphitic structure

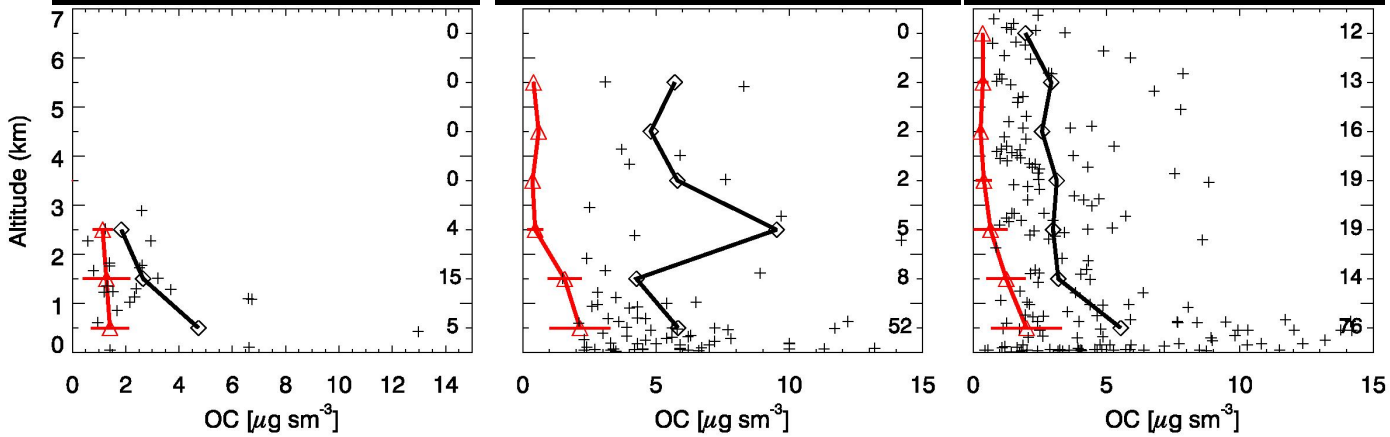
In CMAQ, Black Carbon contains elemental carbon and organic carbon, both absorbs and scatters UV and visible radiation

ambiguity and arbitrariness to the separation of "BC" from organic or "**brown**"

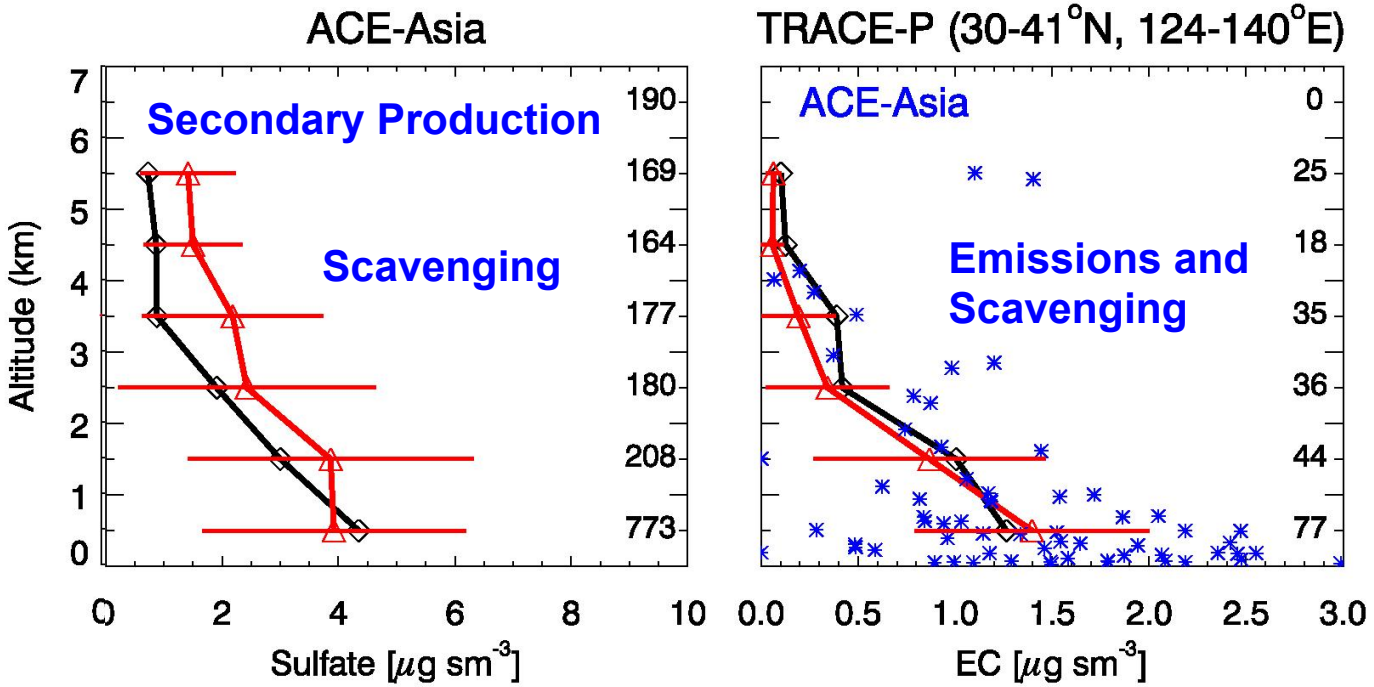
black dilutes to **gray** not **brown**

ACE-ASIA: FIRST OC AEROSOL MEASUREMENTS IN THE FREE TROPOSPHERE (Spring 2001)

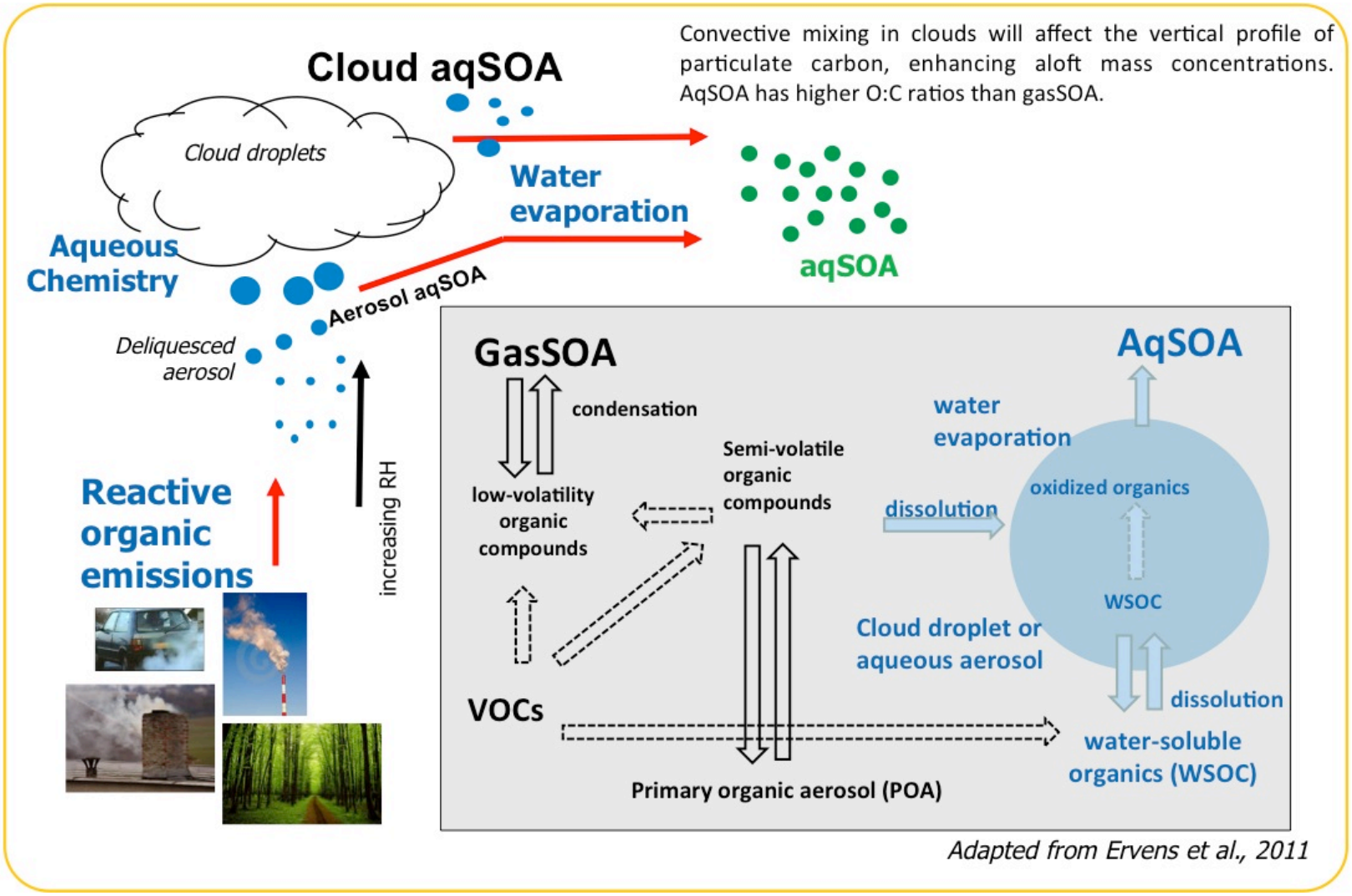
[Mader et al., 2002] [Huebert et al., 2003] [Maria et al., 2003] [Heald et al., 2005]



Vertical profile of **OC** is more like **SO_4** (produced in **clouds**) than **Elemental Carbon** (surface emissions)



Mean Observations
Mean Simulation
\+ Observations



Aqueous lab experiments with methylglyoxal form low volatility brown material. Figure courtesy of V.F. McNeill, Columbia

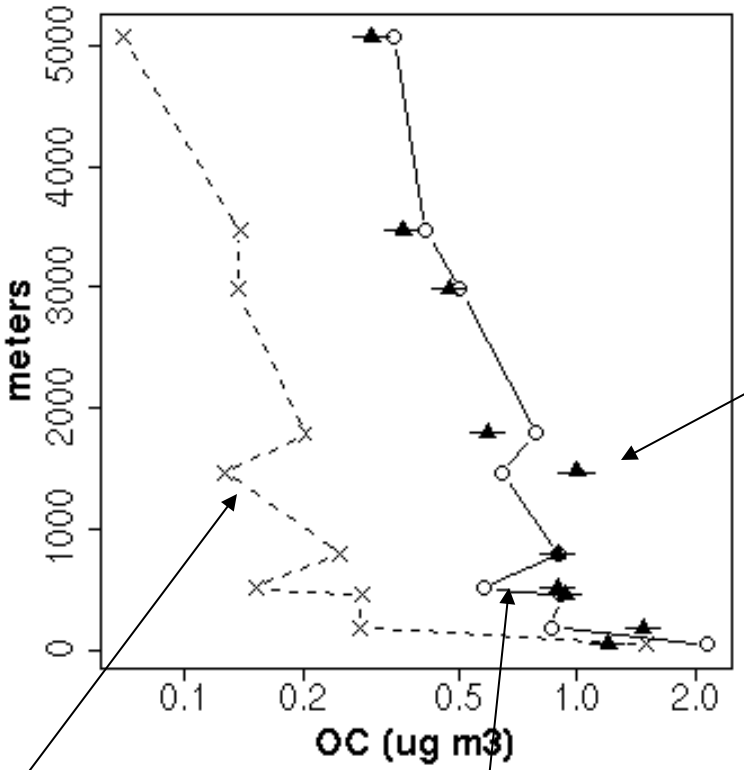
ICARTT cloud experiment: Vertical Profile of particulate carbon

1st order approximation of aqueous phase organic chemistry improves model performance aloft.

Clouds are areas of convective mixing.

Organic chemistry improves the vertical profile of particulate carbon.

Other efforts do not change the aloft predictions (only surface mass)



ICARTT
PILS WSOC meas.

Base CMAQ

CMAQ w/ SOA_{cloud}

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

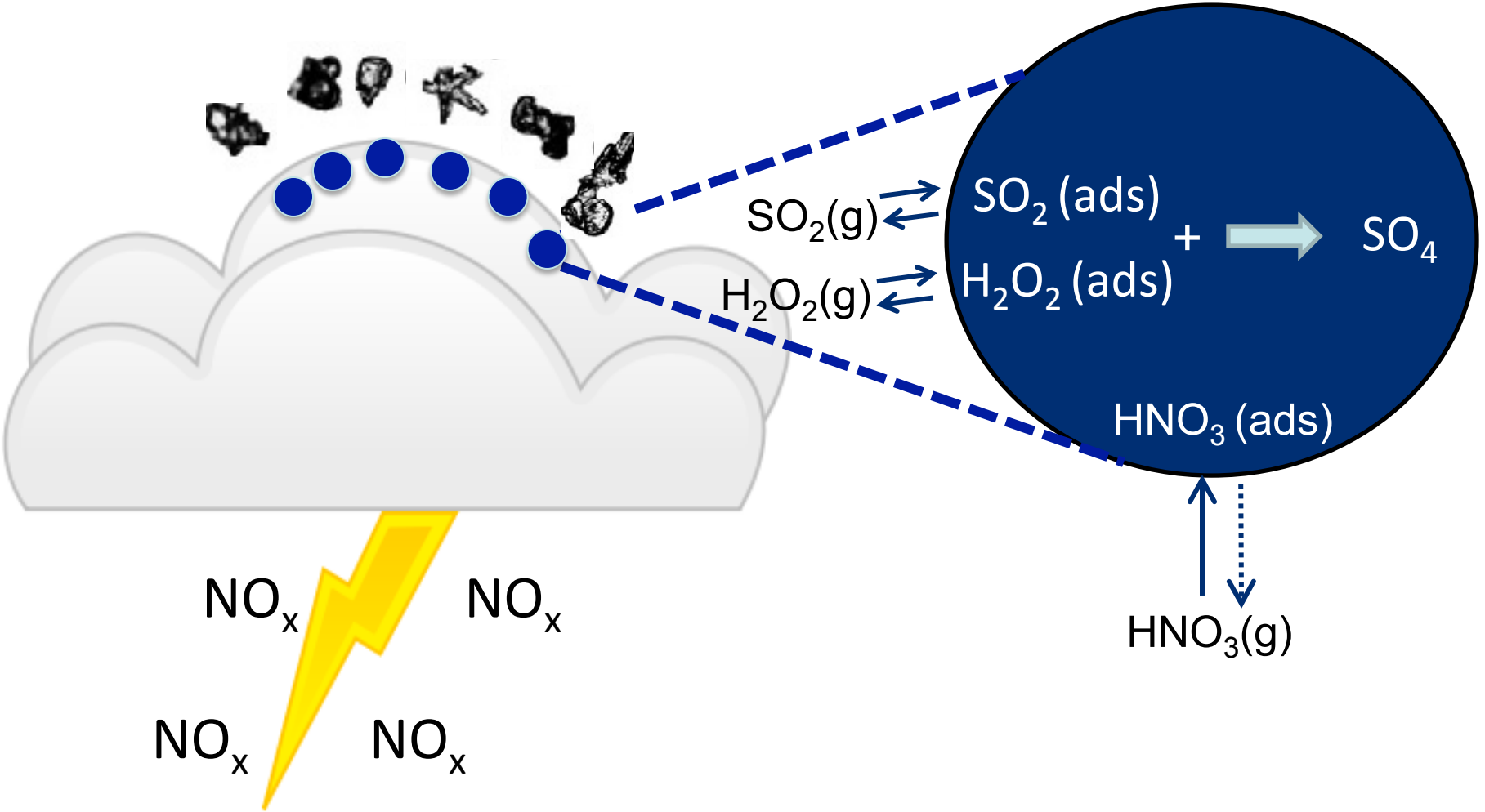
What we proposed

1.) Develop **condensed phase mechanisms** suitable for CTMs that produce optically active **aerosol aloft**

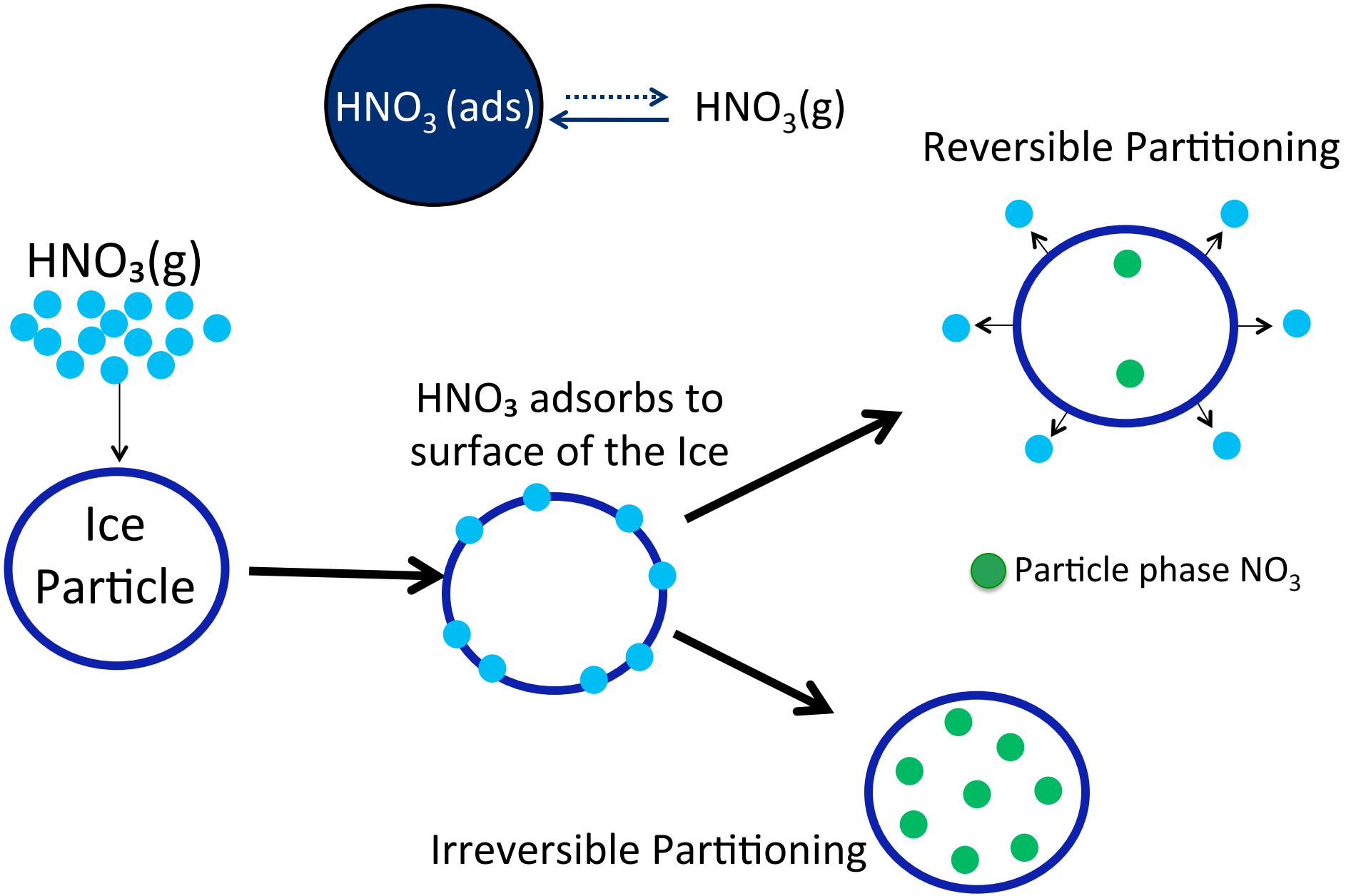
2.) Identify conditions, precursors and sources that have the **largest impact** on brown carbon predictions

3.) Incorporate new mechanism(s) into WRF-CMAQ and evaluate impacts.

ICE chemistry 1) partitioning to cloud ice by SO_2, H_2O_2, HNO_3; 2) ice phase SO_2 →SO_4 chemistry; 3) explore the sensitivity in aloft nitrate mass concentrations regarding debate over reversibility of HNO_3 partitioning

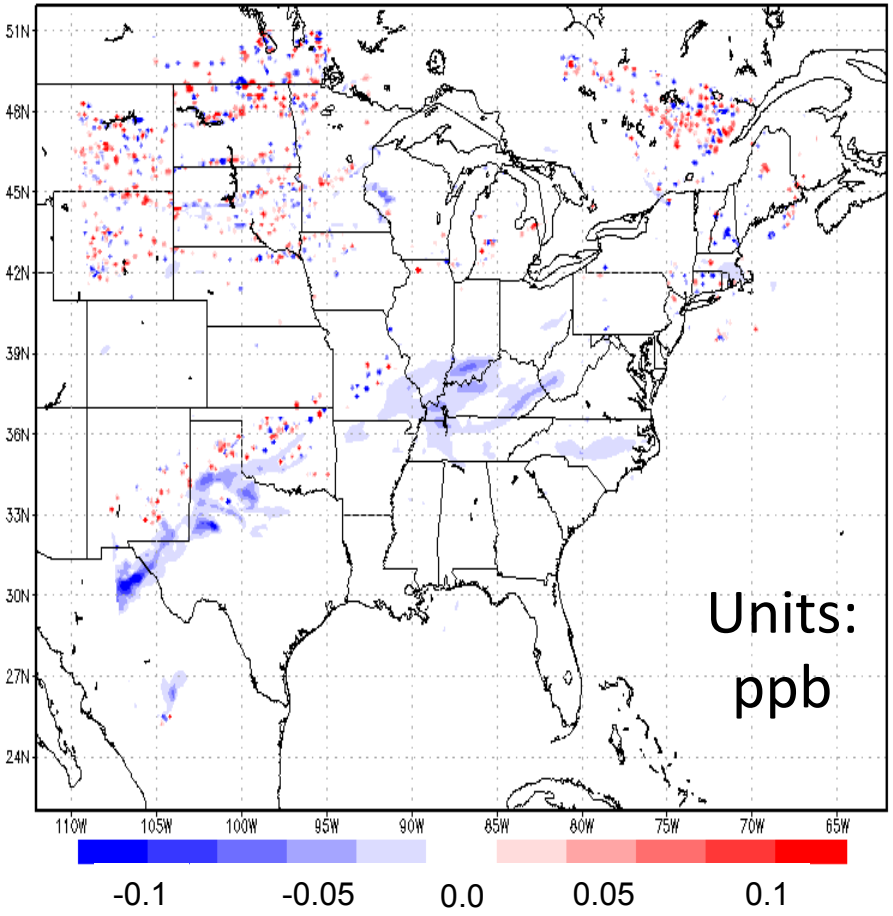


HNO_3 adsorption to ice and explore sensitivity to debate in the literature regarding reversibility

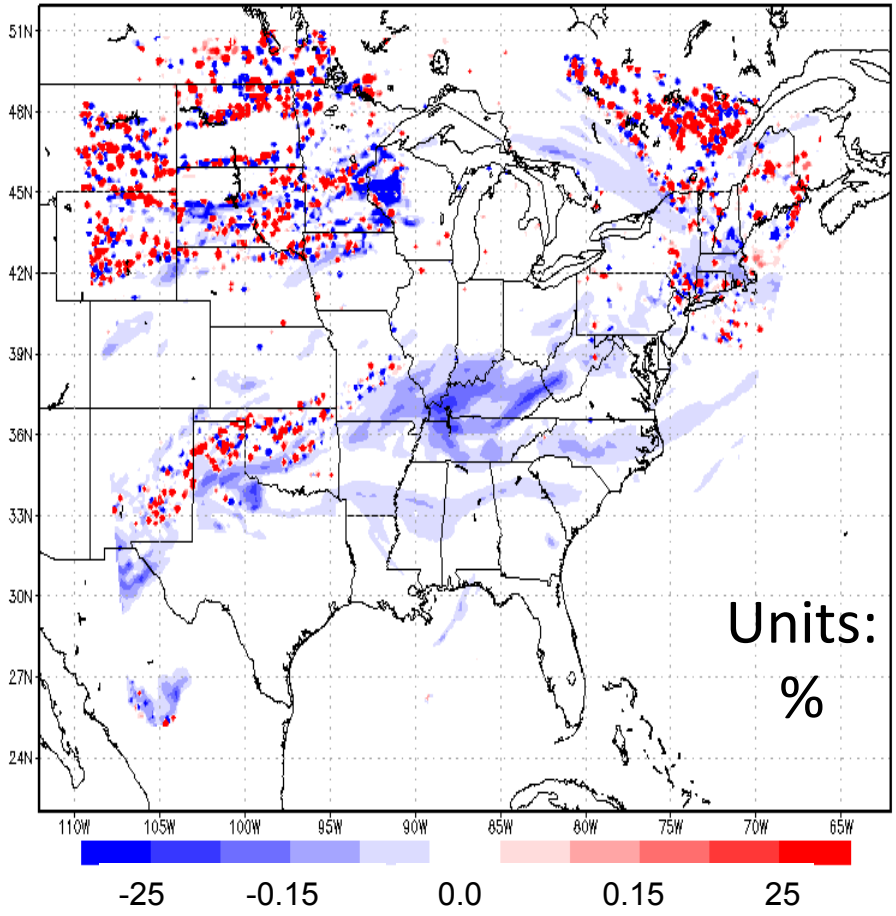


[HNO_3(g)] differences between base case and reversible partitioning

Absolute Differences

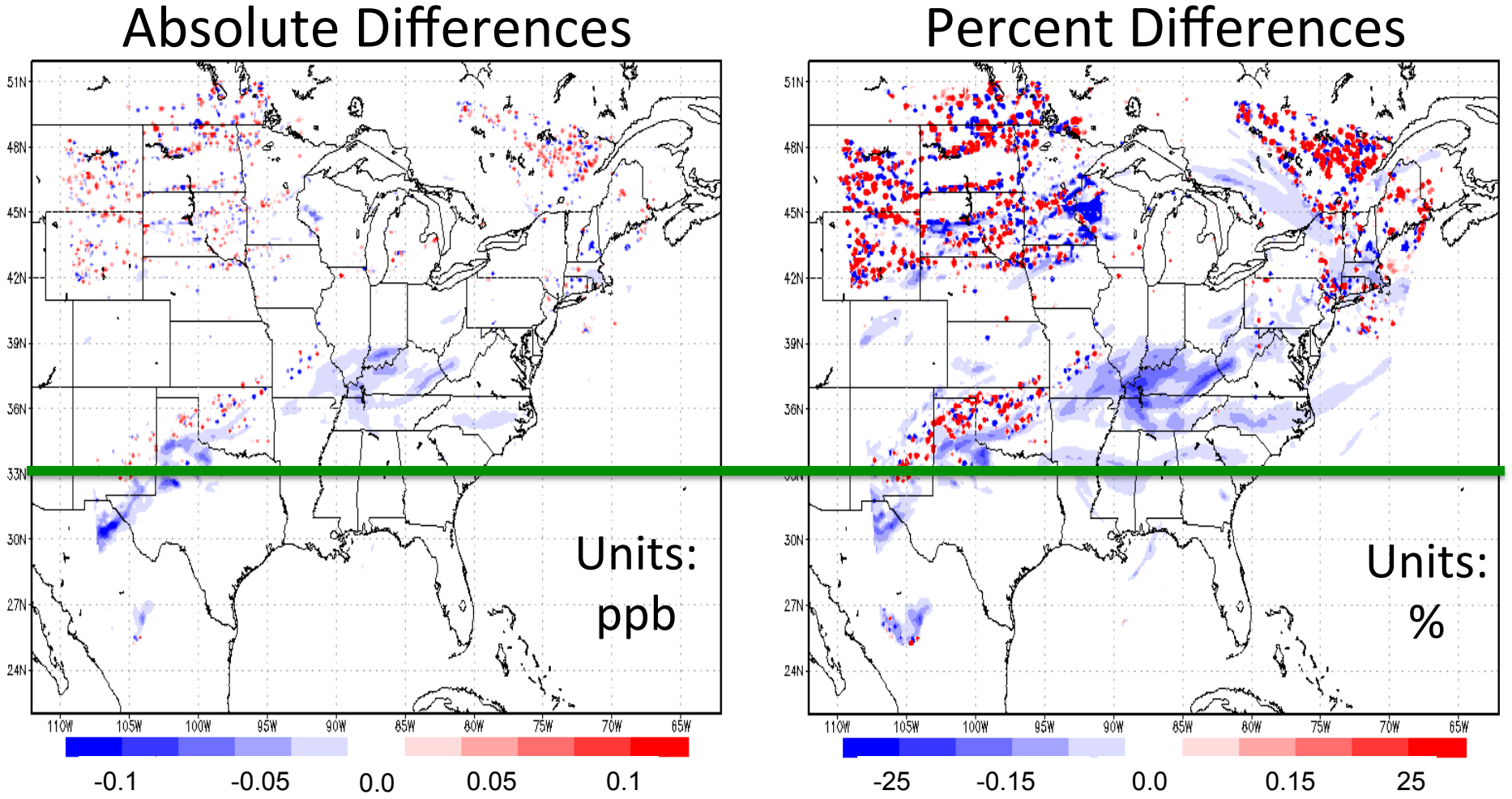


Percent Differences



Changes in HNO_3(g) were less in magnitude and smaller in spatial extent compared to 100% partitioning case. Plots at 400 mb for 0Z on August 12th.

[HNO_3(g)] differences between base case and reversible partitioning



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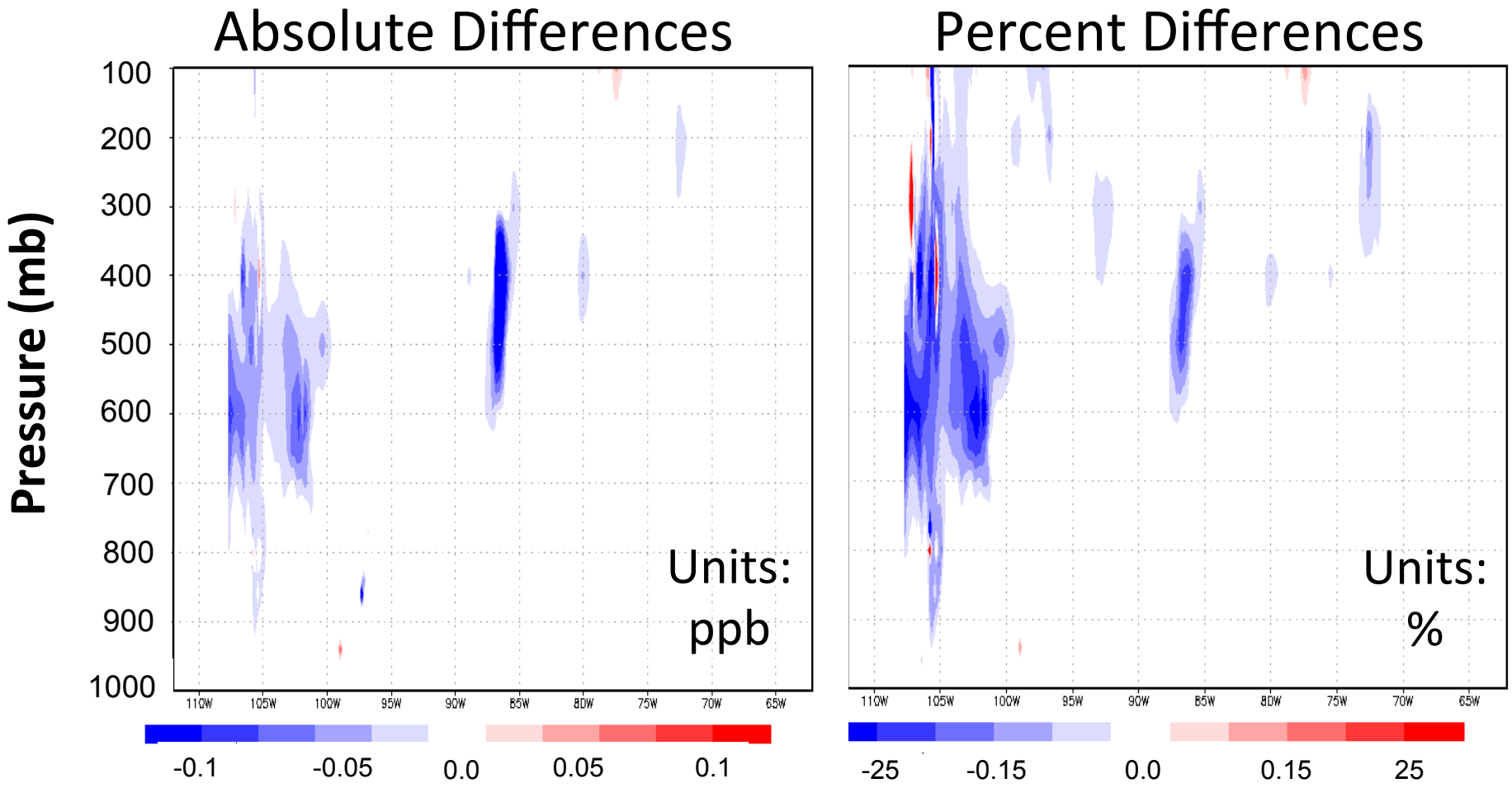
$[HNO_3(g)]$ differences between base case and 100% partitioning

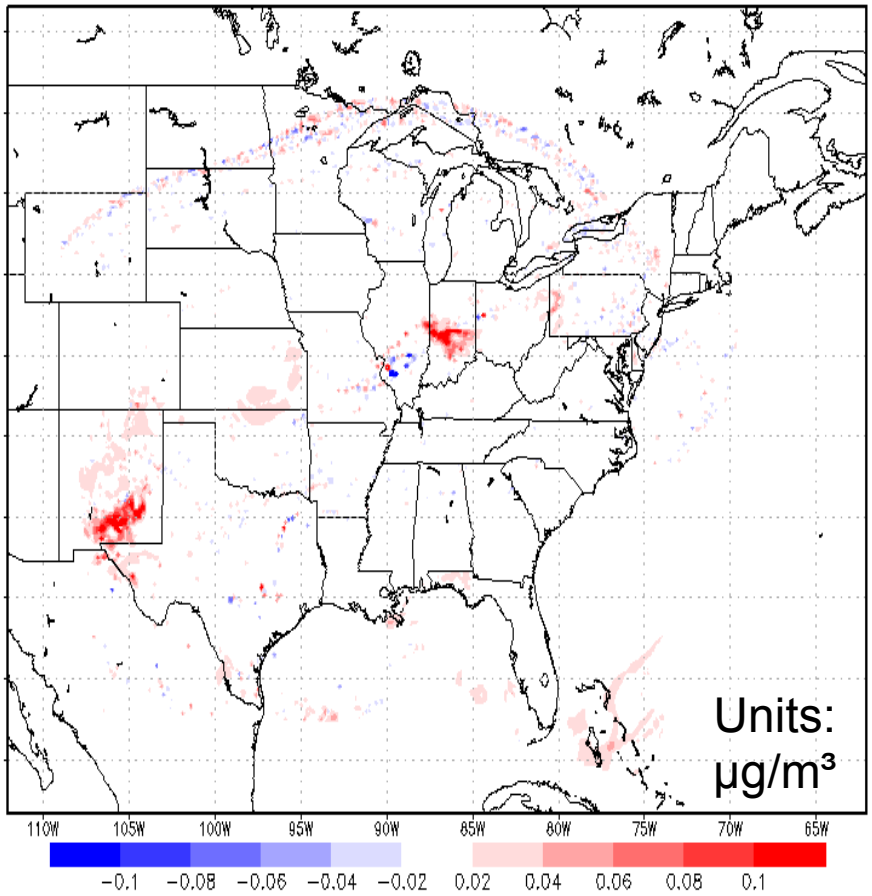


Large changes in $[HNO_3(g)]$ were seen from 300 mb to 650 mb

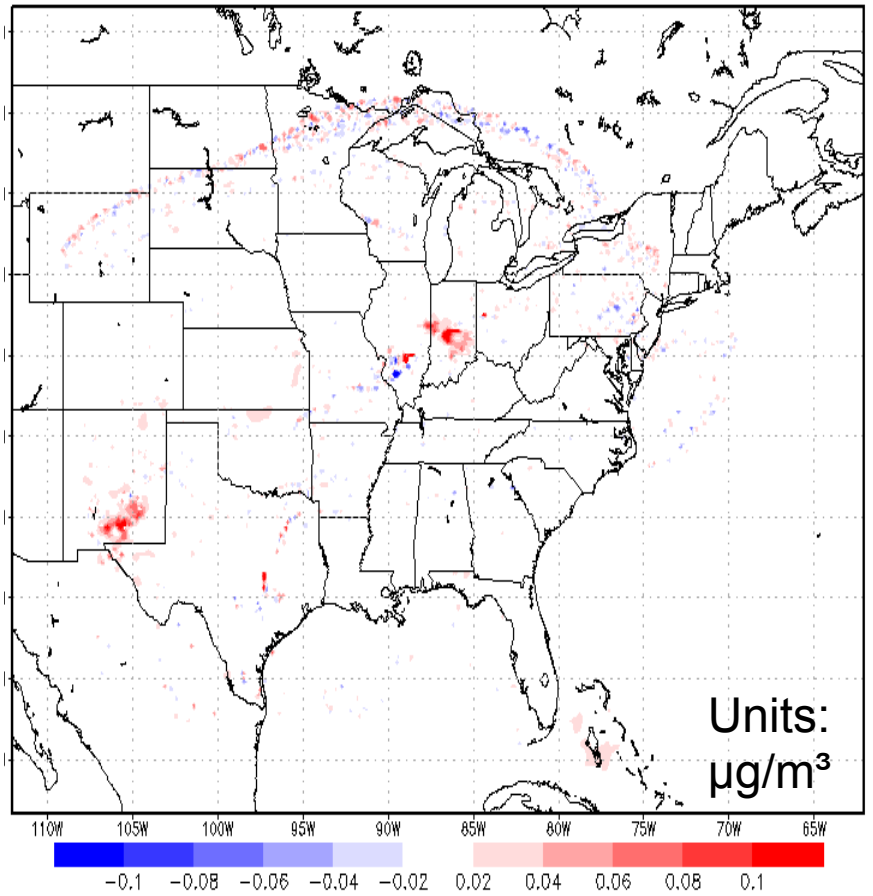
for latitude of 33°N at 10Z on August 23rd

Difference in **accumulation mode [NO_3] when ice chemistry is included** at **100 mb** for 0Z on August 12th. Maximum differences > 0.10 μg m^{-3}

Irreversible Partitioning Case



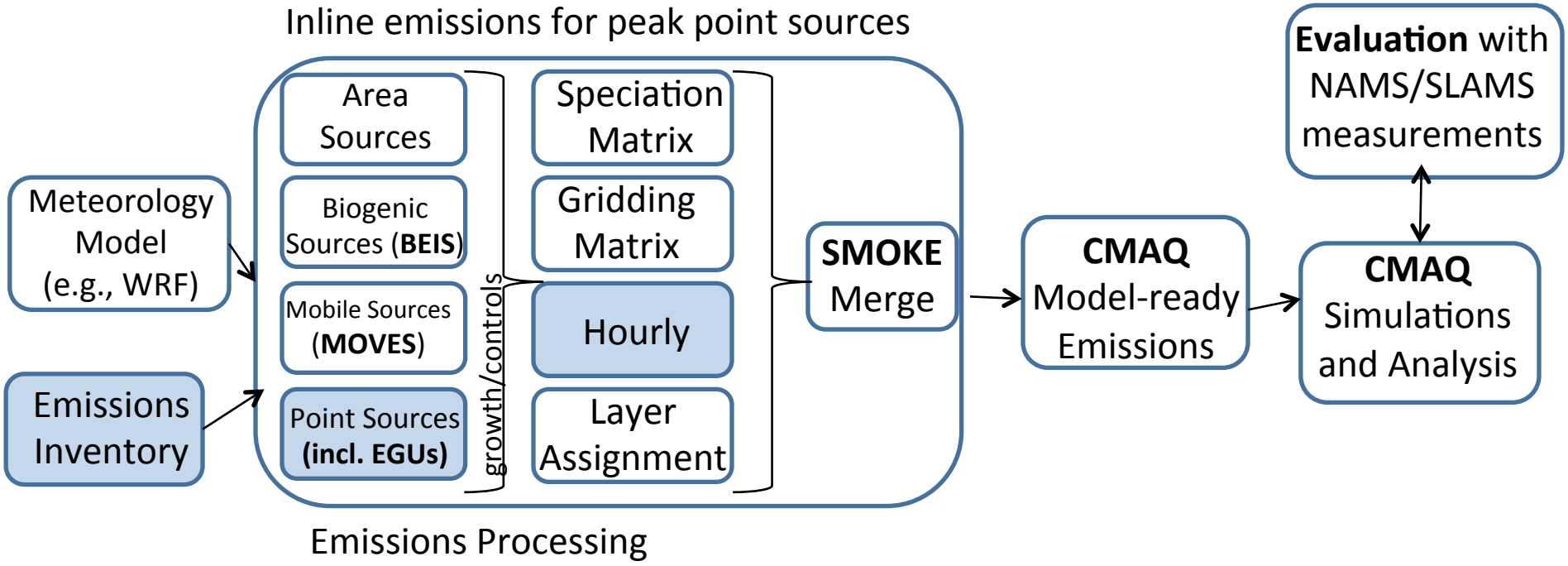
Reversible Partitioning Case



Marmo et al., *AE*, (2013): The modified CMAQ subroutines are available for sharing!

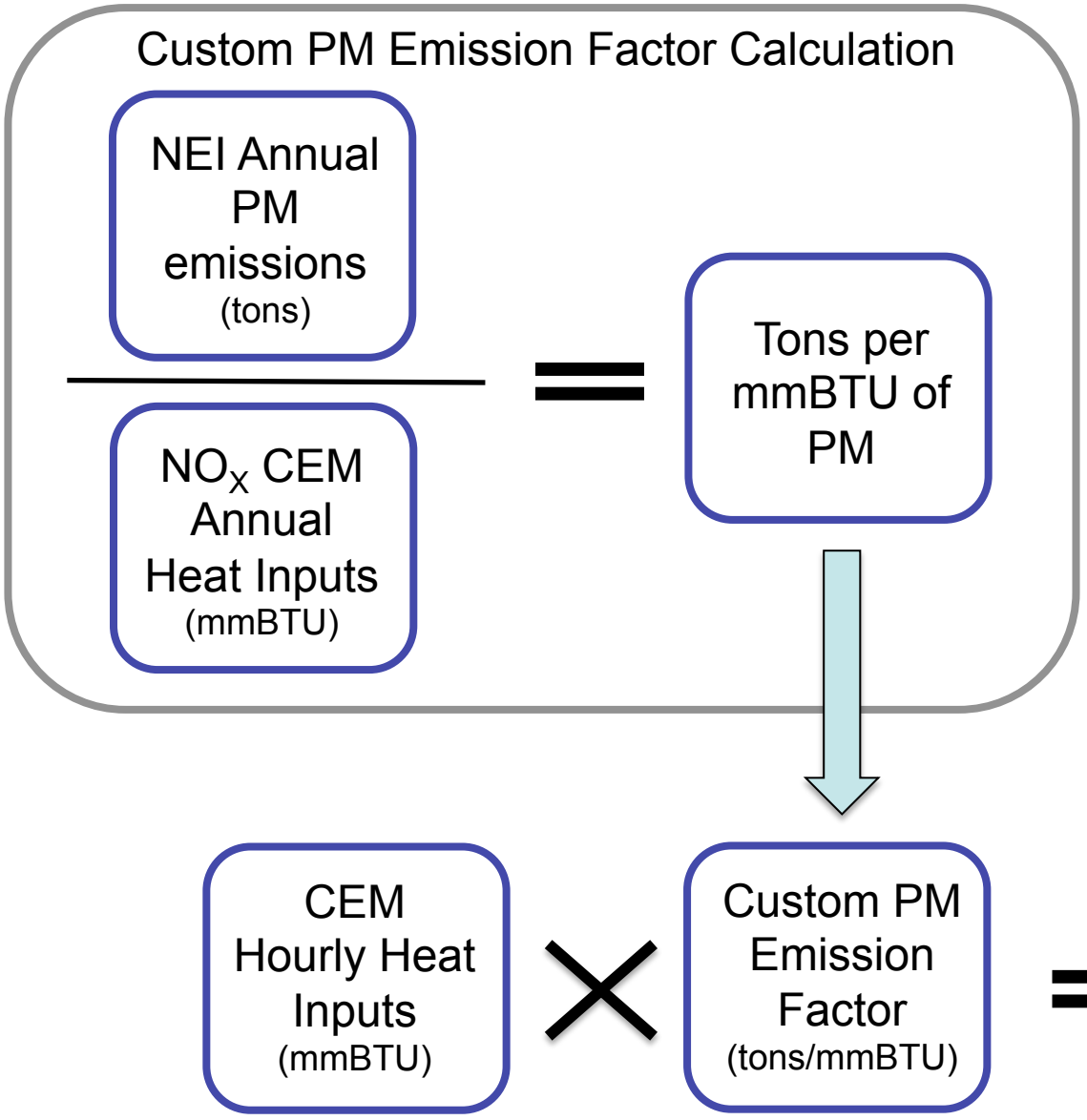
EC emissions

Assessing primary EC/OC emission sources: mobile, residential, meat cooking and electricity largest sources in NJ



Hourly temporal assignment based on *a priori* calculations to describe typical conditions designed and reflect annual average/total.

Temporalization of PM emissions

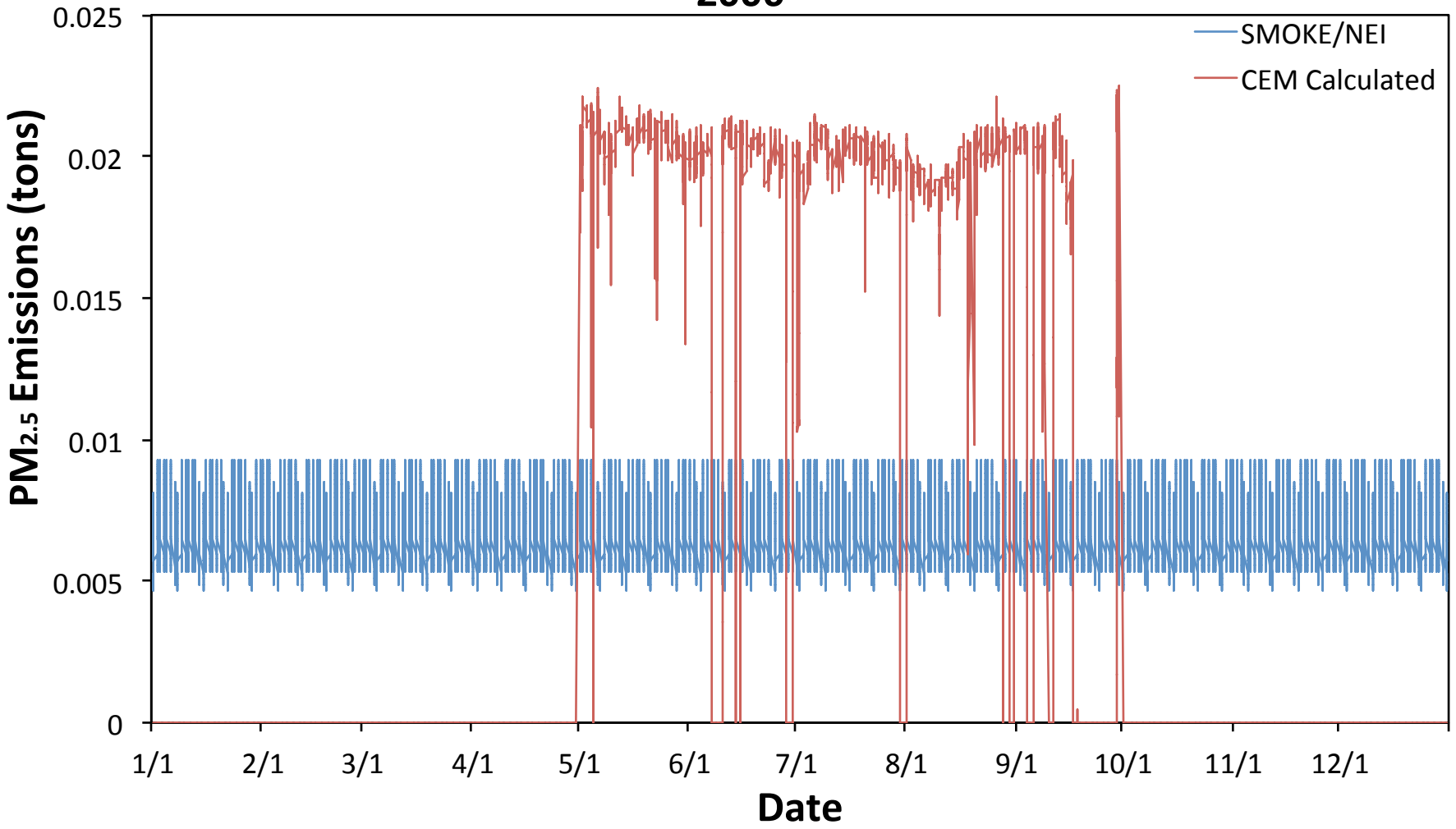


Actual measured emission data is not used for point sources with CEMs when "ORIS" ID number is not reported with annual NEI total.

SMOKE vs. Carlton Group - $PM_{2.5}$ Emissions

AES Beaver Plant - Pennsylvania Coal Plant

2006



Intermediate Load Facility

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Modeled EGU plants in PJM energy sector July 12 –25, 2006:

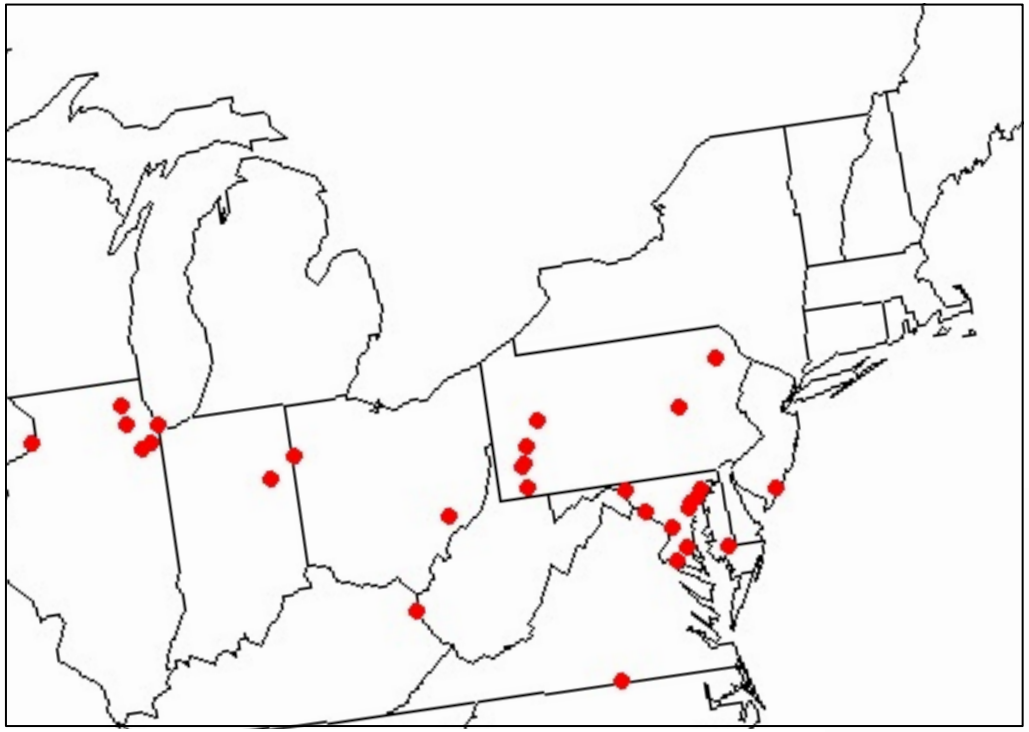
Major heat wave over entire continental US. Record temperatures (high and low)

1450 units in PJM
(including renewables and nuclear)

910 units have CEMS

390 units EIA/ORIS matches between the NEI and CEM

138 modeled (Primary SCCs)



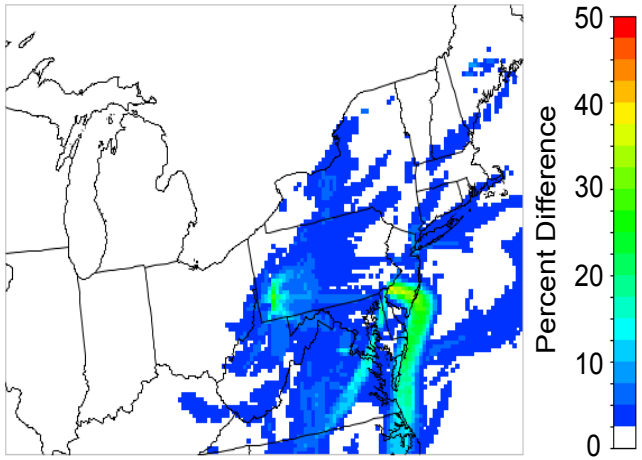
"crosswalk" used to match facilities is available upon request!

- CMAQv4.7
- CB05-TU
- BEISv3.14
- WRFv3

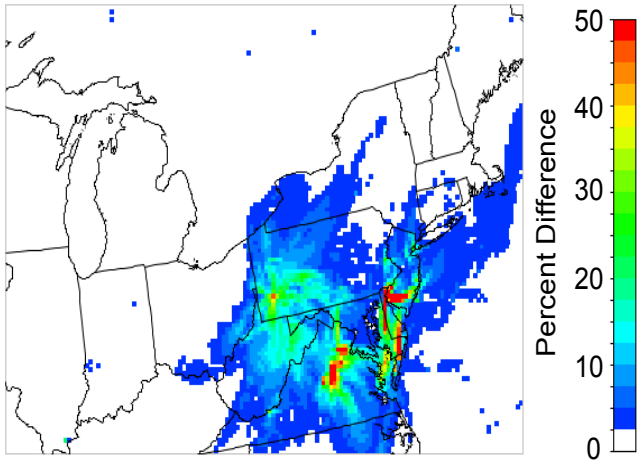
- 12km x 12km
- 34 layers to 50mb
- 2005 NEIv4.2
- SMOKEv3.5

[EC] differences at the surface and aloft (800mb)

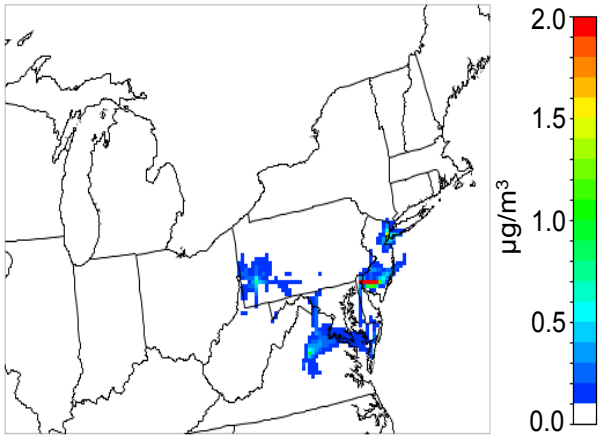
Surface [EC] (%)



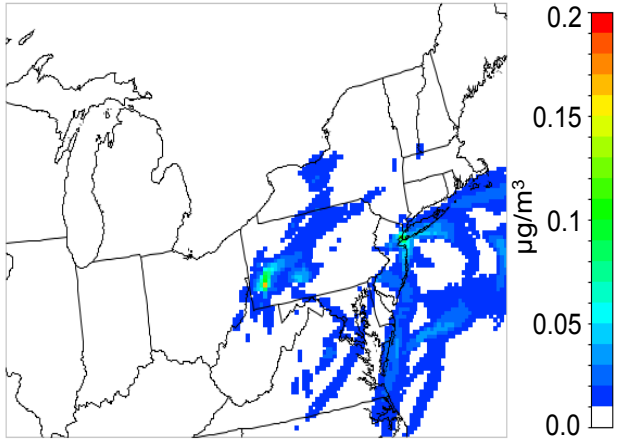
Aloft 800 mb [EC] (%)



Surface [EC] (μg m^{-3})



Aloft 800 mb [EC] (μg m^{-3})



Farkas et al., *ES&T*, In Review

Developing and implementing more robust representation of organic aqueous chemistry

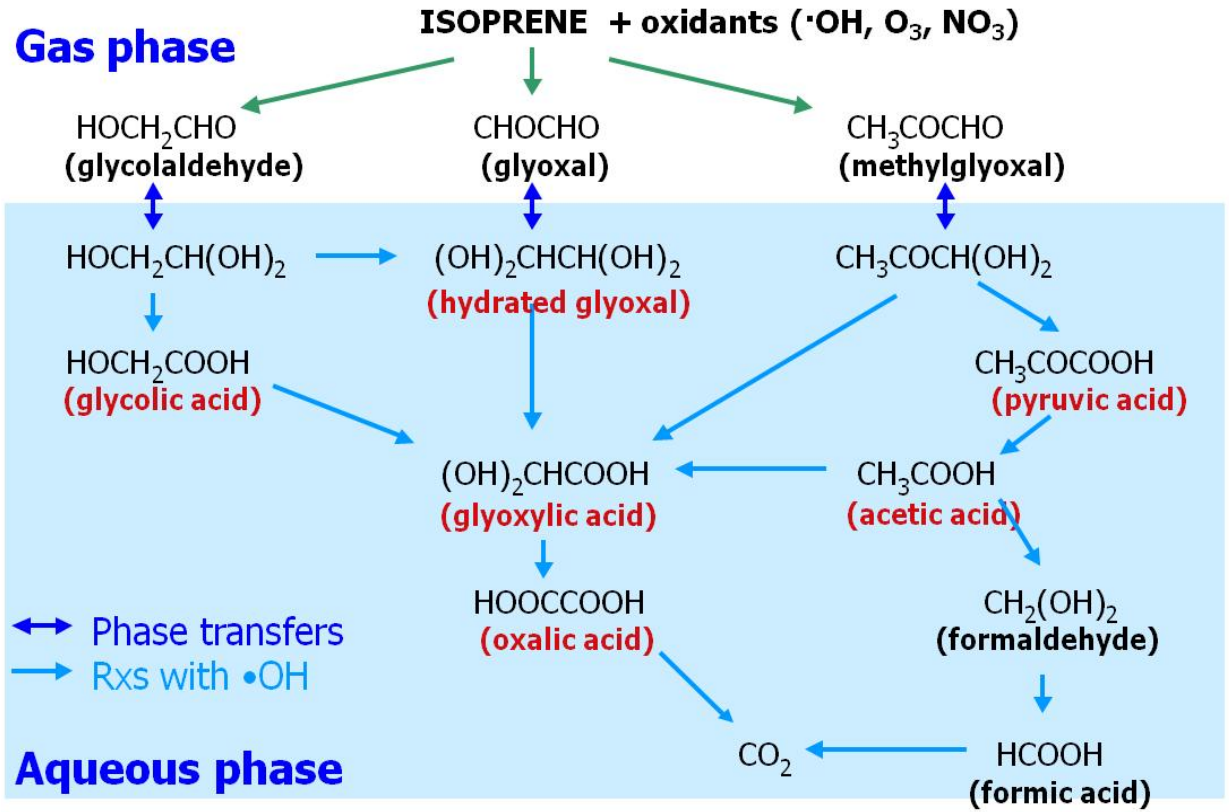
Identify the most important water-soluble gas phase precursors and controlling factors for cloud-produced OA.

Develop expanded and efficient new chemical mechanism

Develop new solver technique – collaboration with Kathleen Fahey and Bill Hutzell

Early Implementation of aqueous organic chemistry

Lab experiments verify



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

1st attempt at CTM implementation

glyoxal + OH → "cloud SOA"

methylglyoxal + OH → "cloud SOA"

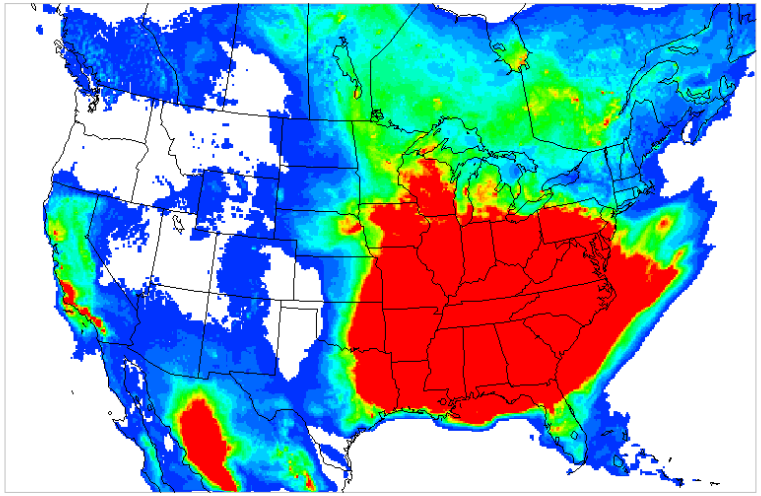
Highest Potential Water-soluble Gases

Abundance	WSOM potential
MEK	Glyoxal
Acetaldehyde	Methylglyoxal
Acetic acid	Acetic acid
Formaldehyde	Formaldehyde
Methanol	Acetaldehyde
Acetone	Acetone
Methylglyoxal	MEK
Glyoxal	Methanol
MVK	MVK
Methacrolein	Methacrolein

$$C_J(aq) = H_J RTLC_J(g)$$

Highest Potential Water-soluble Gases

IEPOX

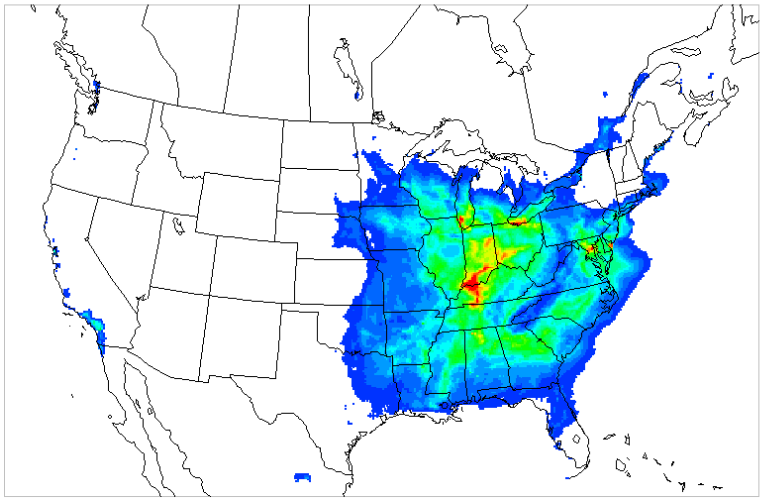


$$C_J(aq) = H_J RTLC_J(g)$$

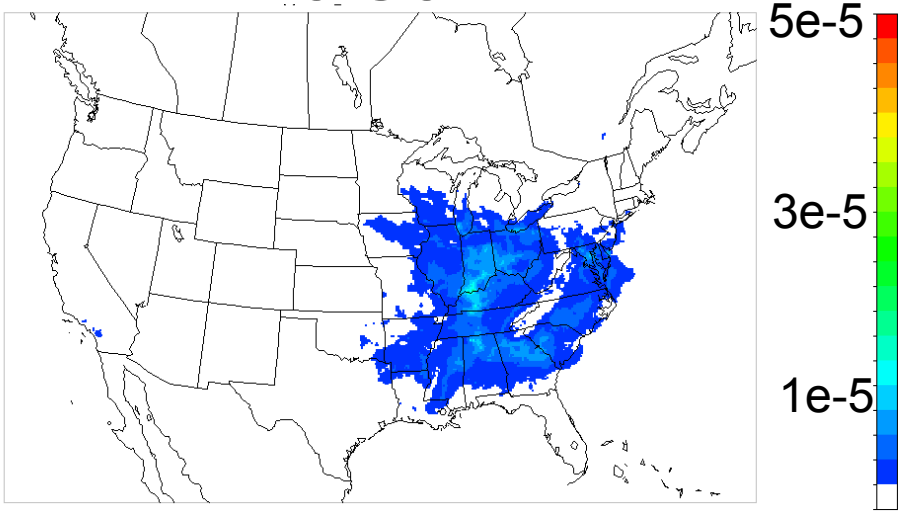
IEPOX is predicted to be dominant SOA component, consistent with very recent measurements

Karambelas et al., *ES&T Letters*, 2014.

Glyoxal



Methylglyoxal



WRF-CMAQ modeling

Modeling 10 days of the SOAS campaign (12km x 12km CONUS) AERONET measurements at SOAS site

1.) Base case, CMAQv5.01

1a.) added heterogeneous IEPOX chemistry (Pye et al., *ES&T*, 2013)

1b.) expanding aqueous chemical mechanism to include ammonium-organic reactions

1c.) Liquid water uncertainty analysis (Liu, Horowitz, Carlton et al., *ACP*, 2013)

2.) KPP (RODAS3 solver) for same aq. chemical mechanism in base model with CB05 gas phase chemical mechanism collaboration with EPA: K. Fahey, B. Hutzell

Droplet dependent kinetic partitioning, droplet size is consistent with WRF predictions/meteorology assumptions.

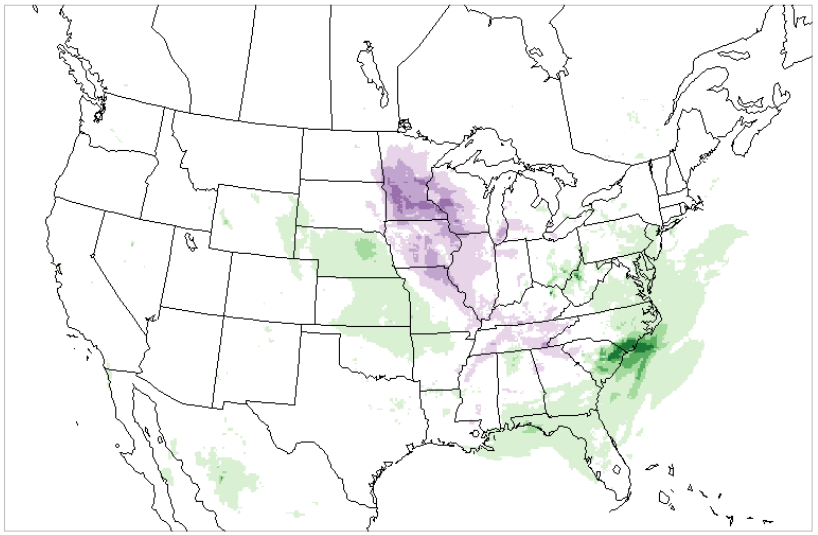
2a.) SAPRC07 gas phase chemical mechanism

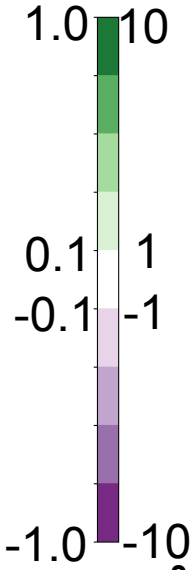
2b.) More explicit aq. chemical mechanism with SAPRC07

including glycoaldehyde as a precursor, explicit carboxylic acids

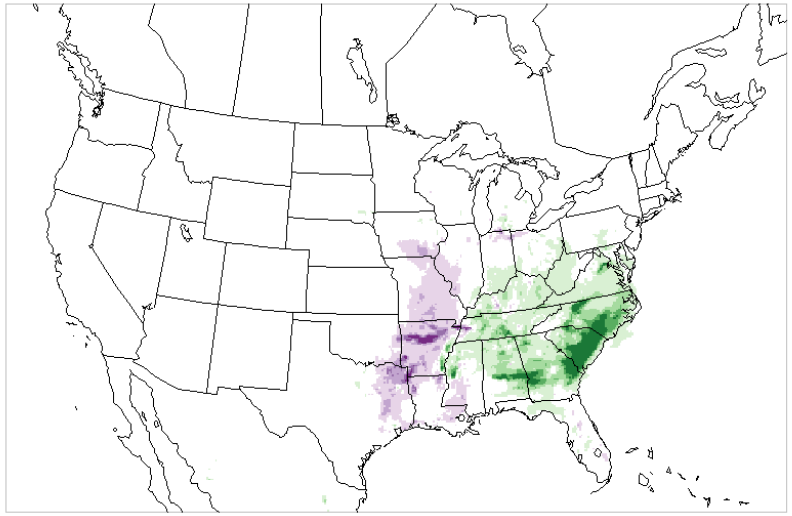
RUTGERS NH_4-organic reactions added to CMAQv5.01

Surface aqSOA

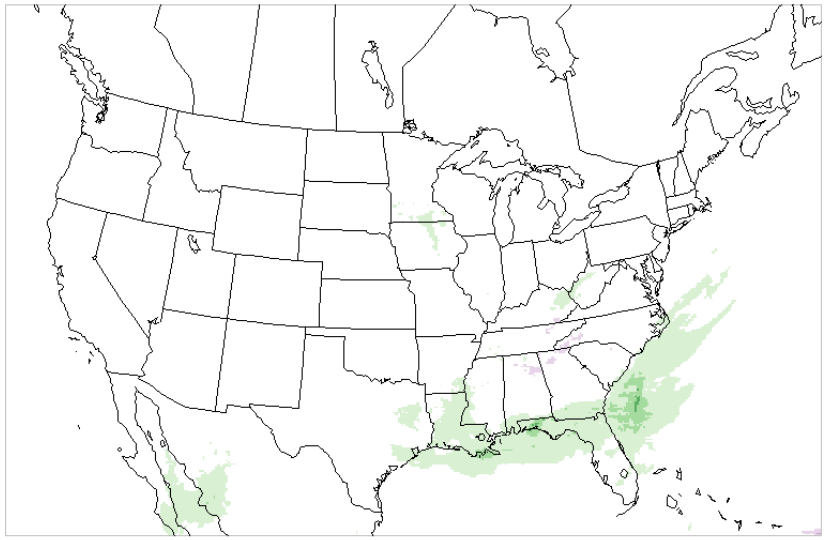


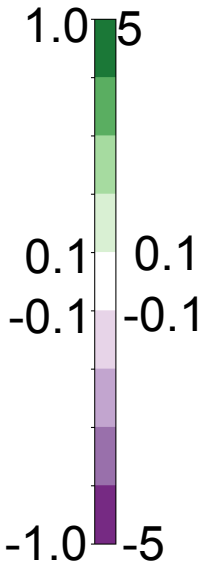


Surface Total SOA

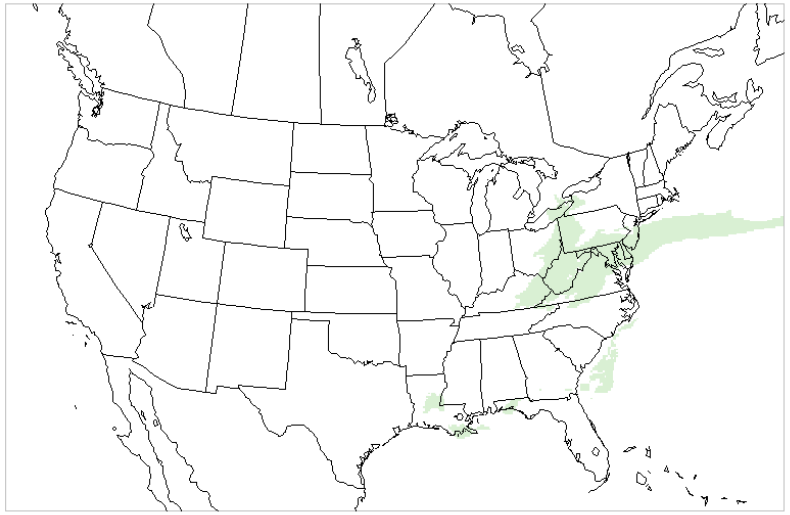


Aloft (800mb) aqSOA

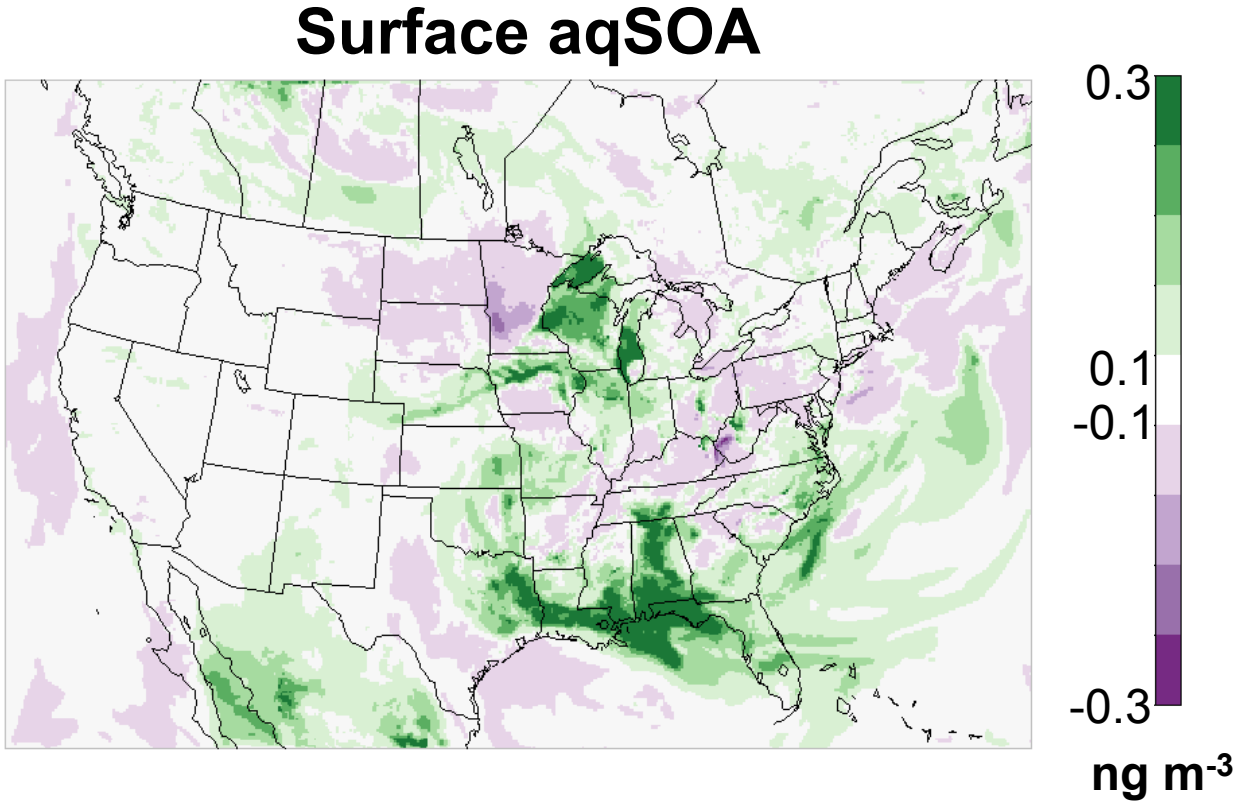




Aloft (800mb) Tot SOA



Liquid water content (+40%)



He, Liu, Horowitz, Carlton et al., *ACP*, (2013) found that in a global model that for a given organic cloud chemical mechanism, liquid water content was the most sensitive parameter

New Solver

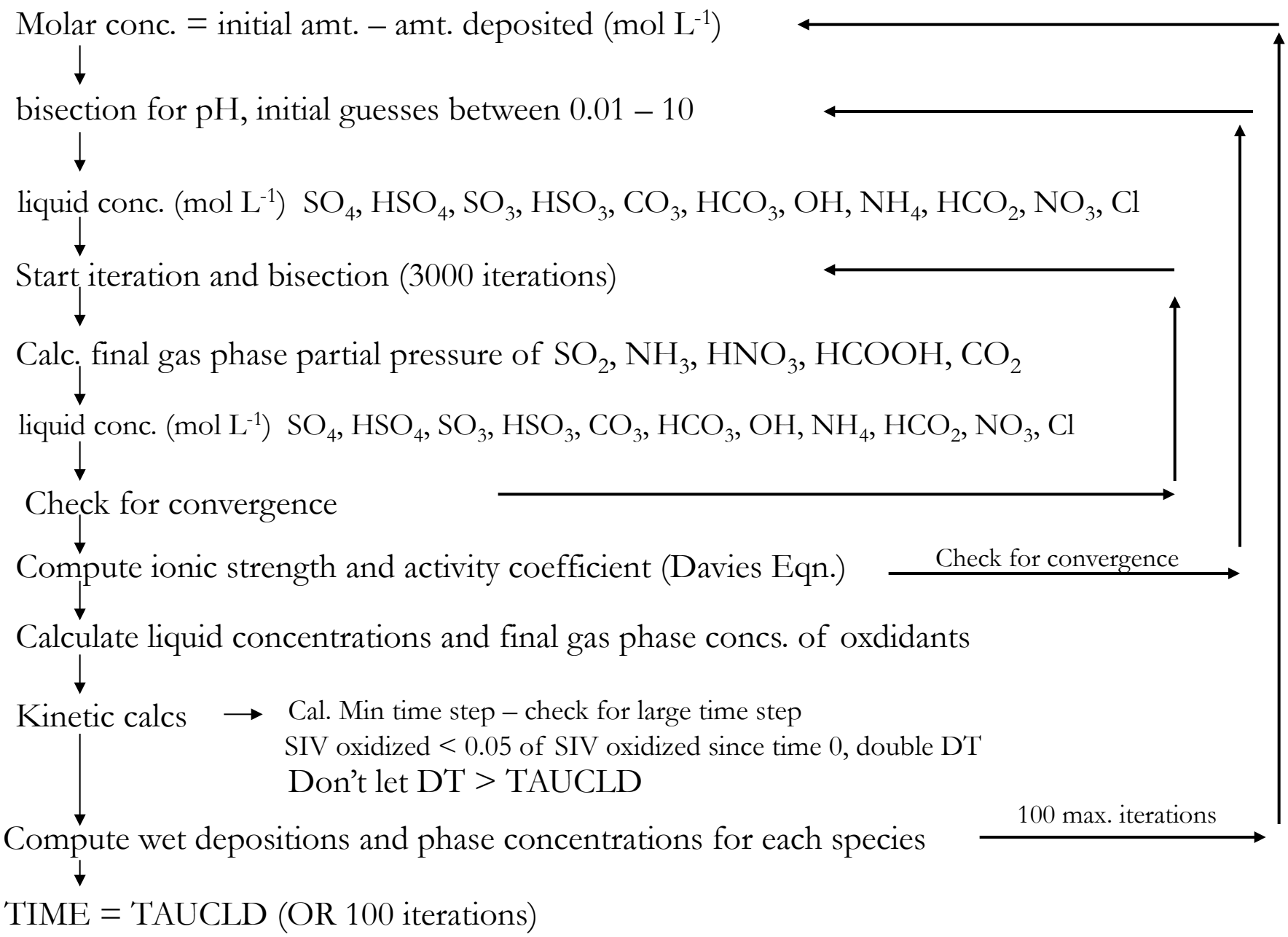
Atmospheric aqueous phase chemistry is more complex than typical model mechanisms

Current CMAQ aqueous chemistry module does not easily expanded

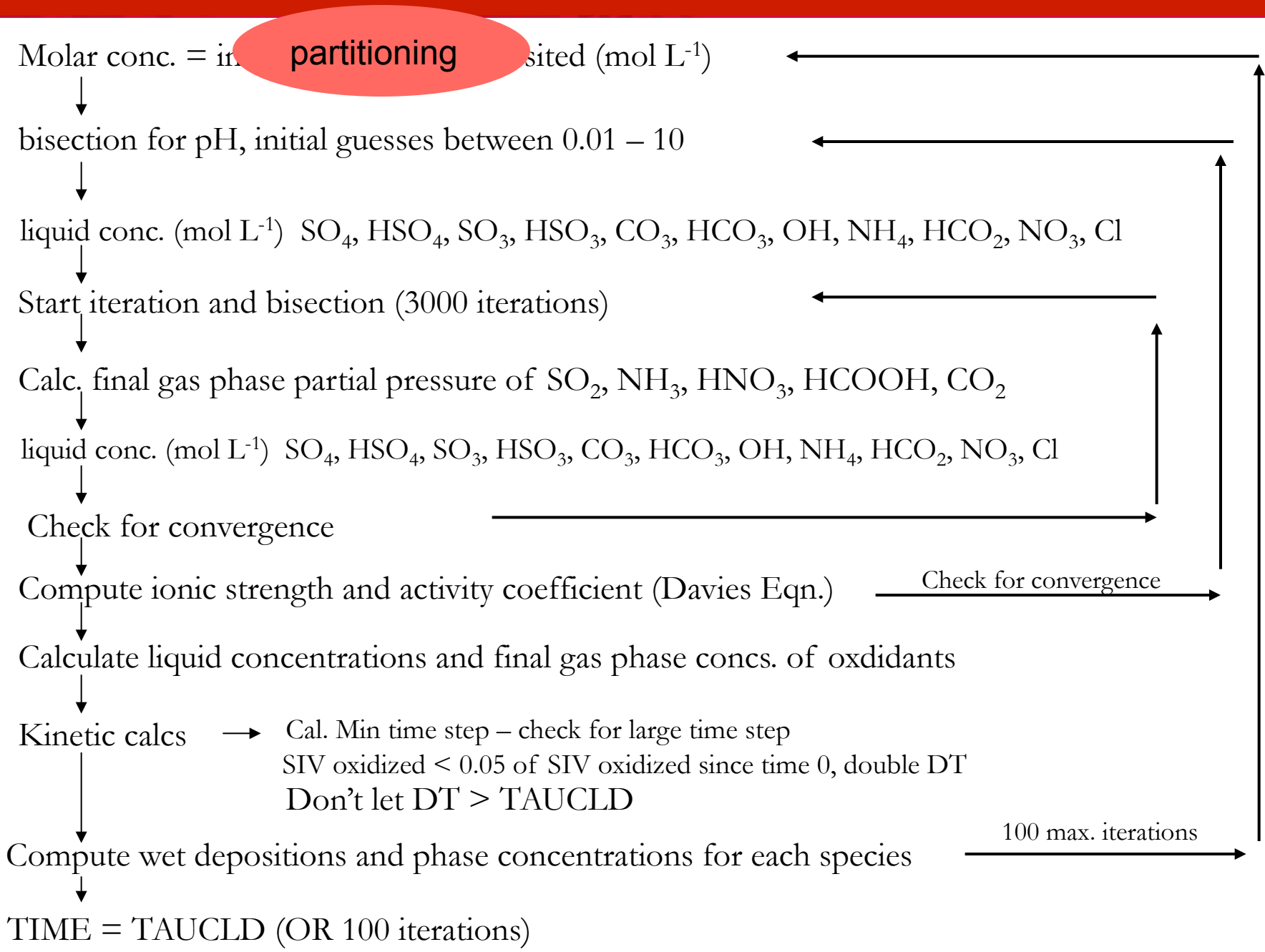
- Forward Euler solver for oxidation and bisection method for pH
- (note: linear convergence for bisection method)
- Stiffness induced by wide dynamic range of the system

RODAS3 solver in KPP is a good candidate for solving atmospheric aqueous chemistry (Sandu et al., 1997; Djouad et al., 2002)

CMAQ Aqueous Chemistry Map (*aqchem.F*)



CMAQ Aqueous Chemistry Map (*aqchem.F*)



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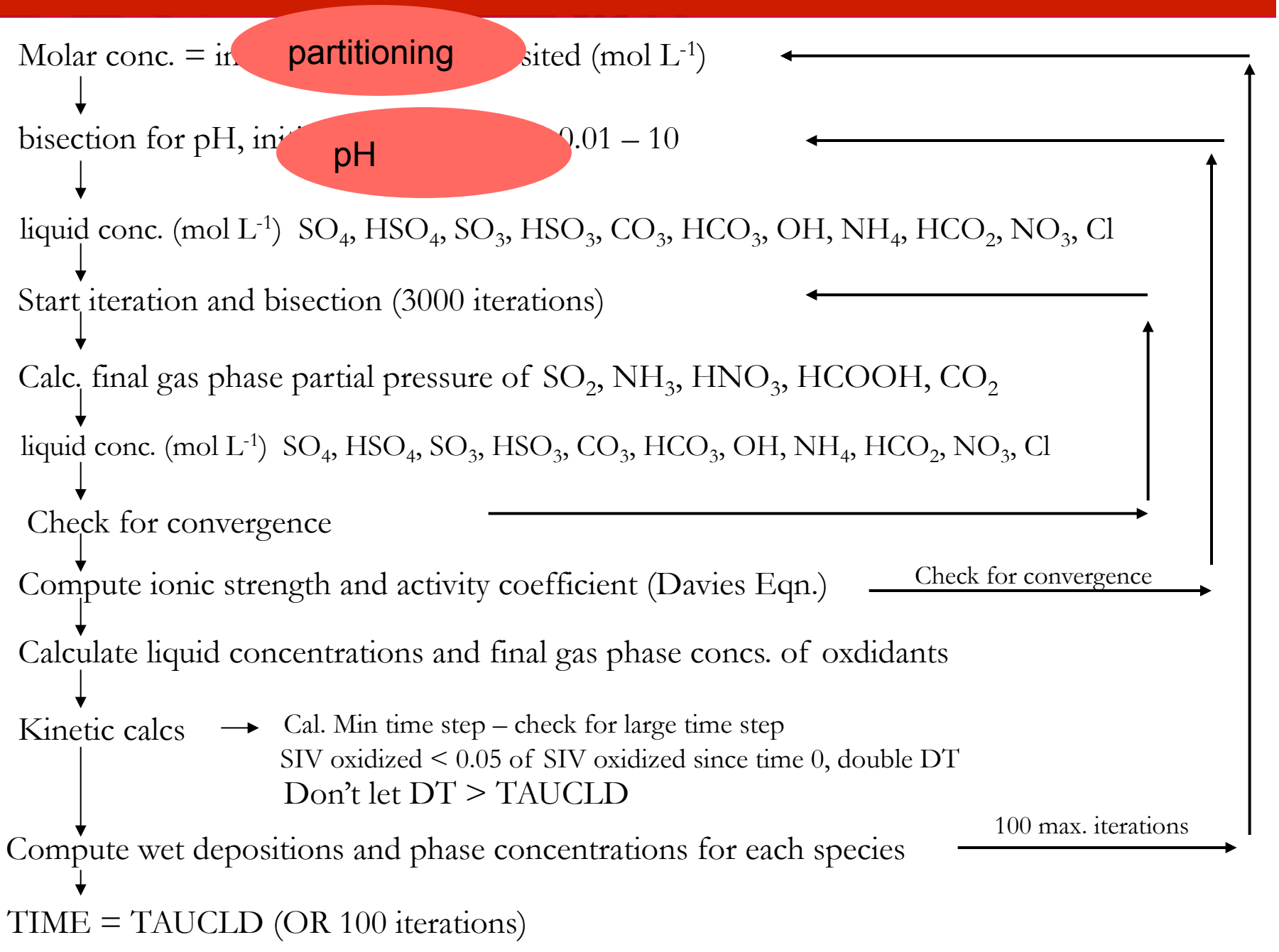

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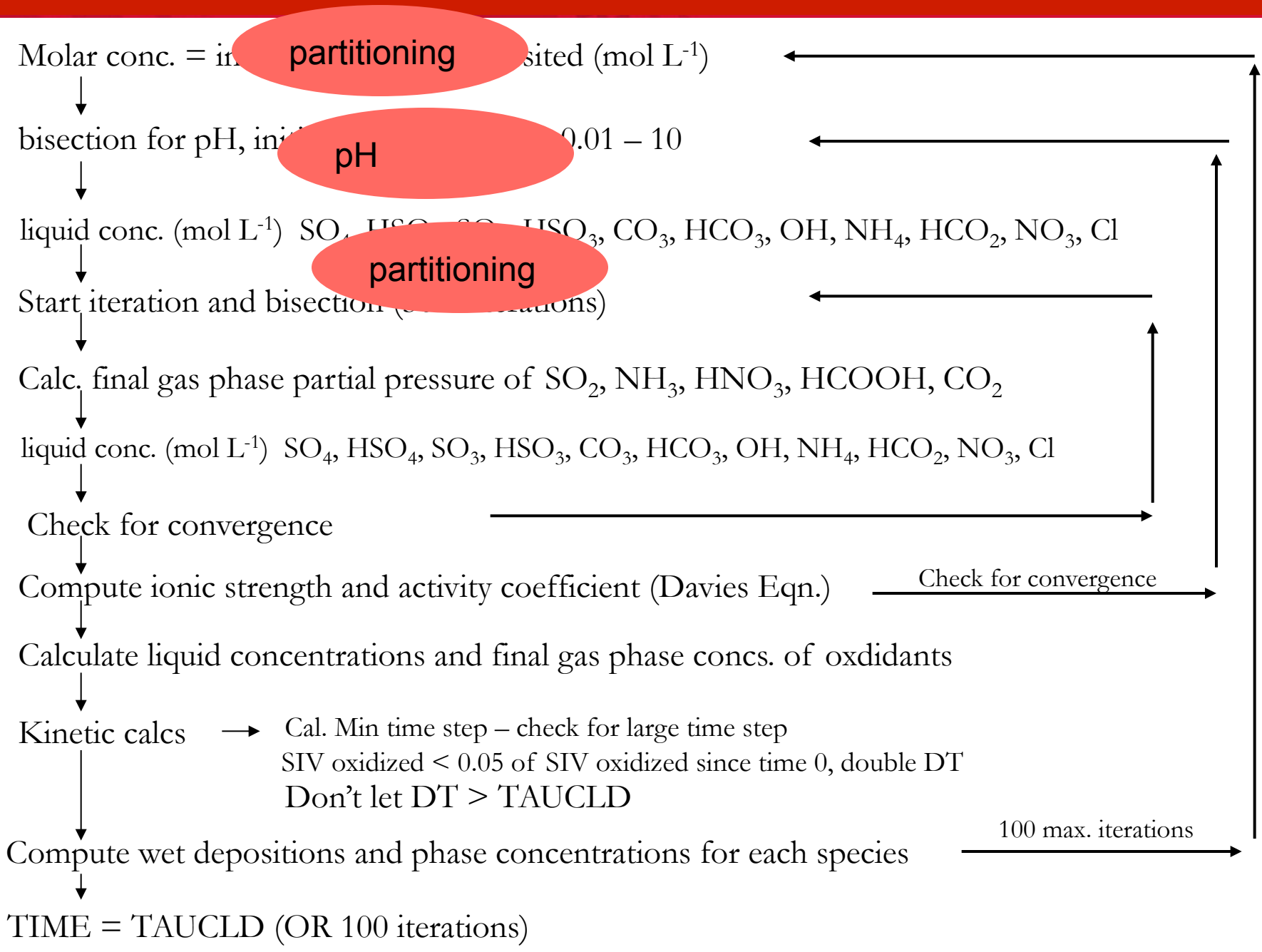

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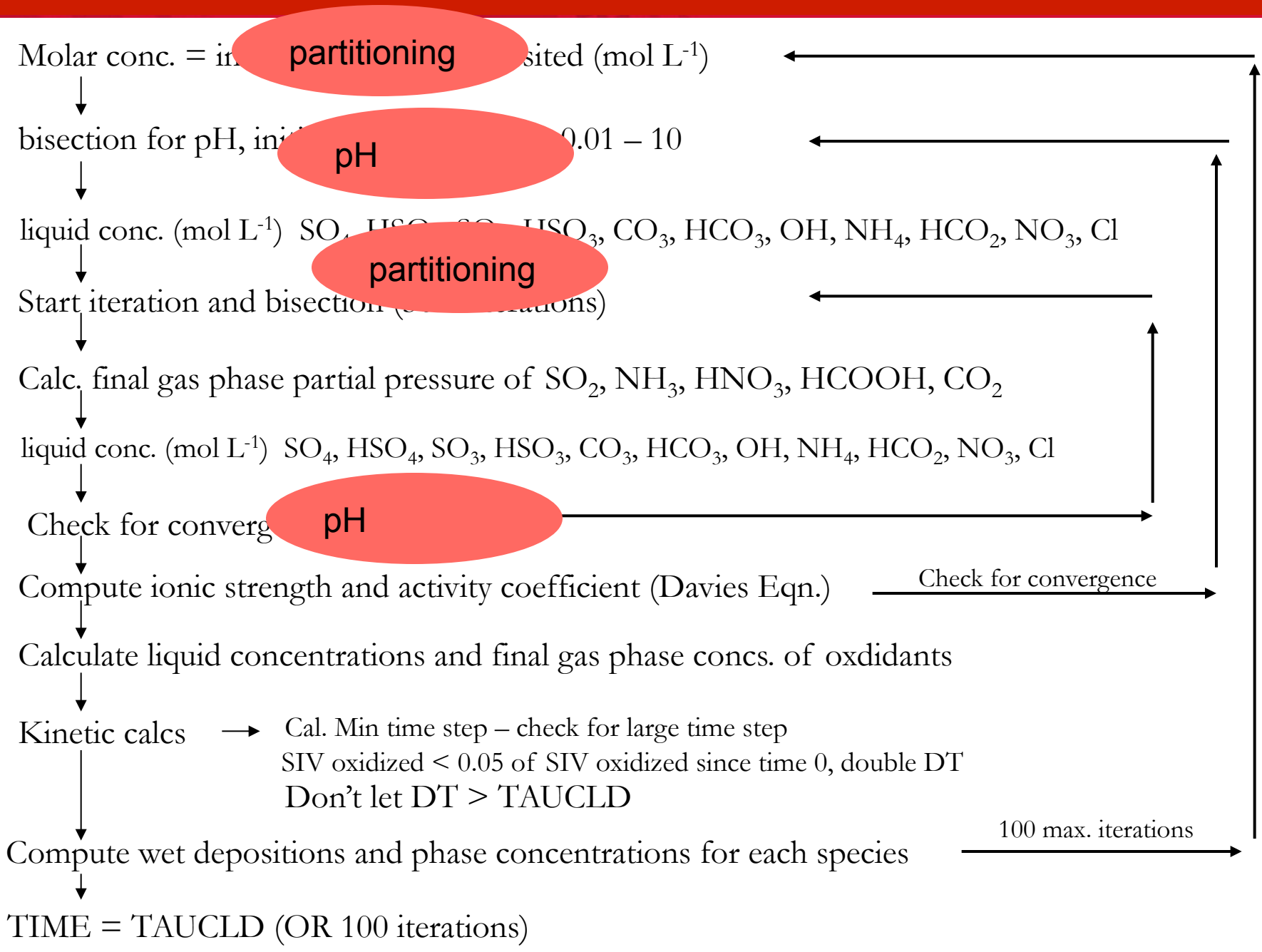
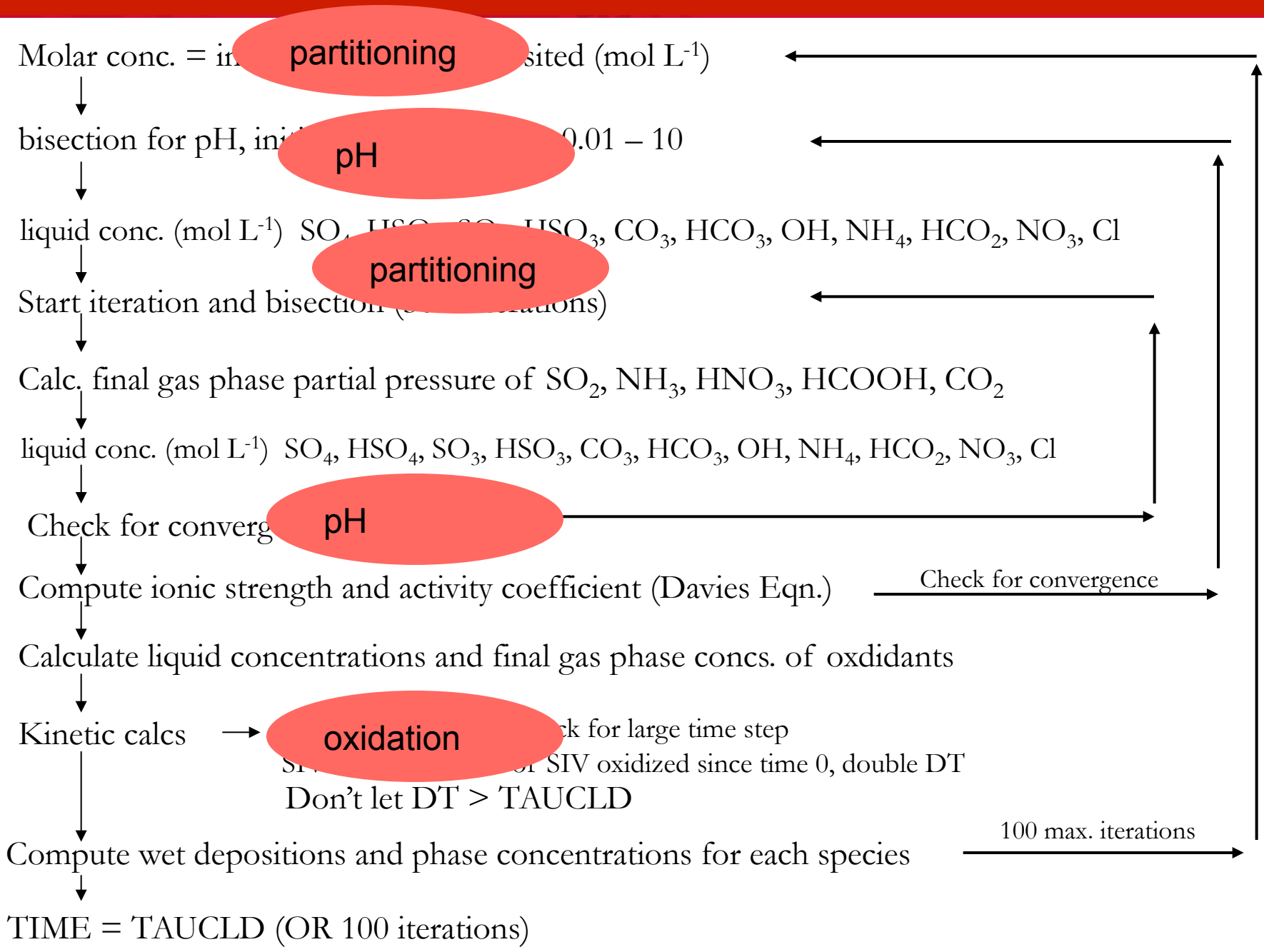
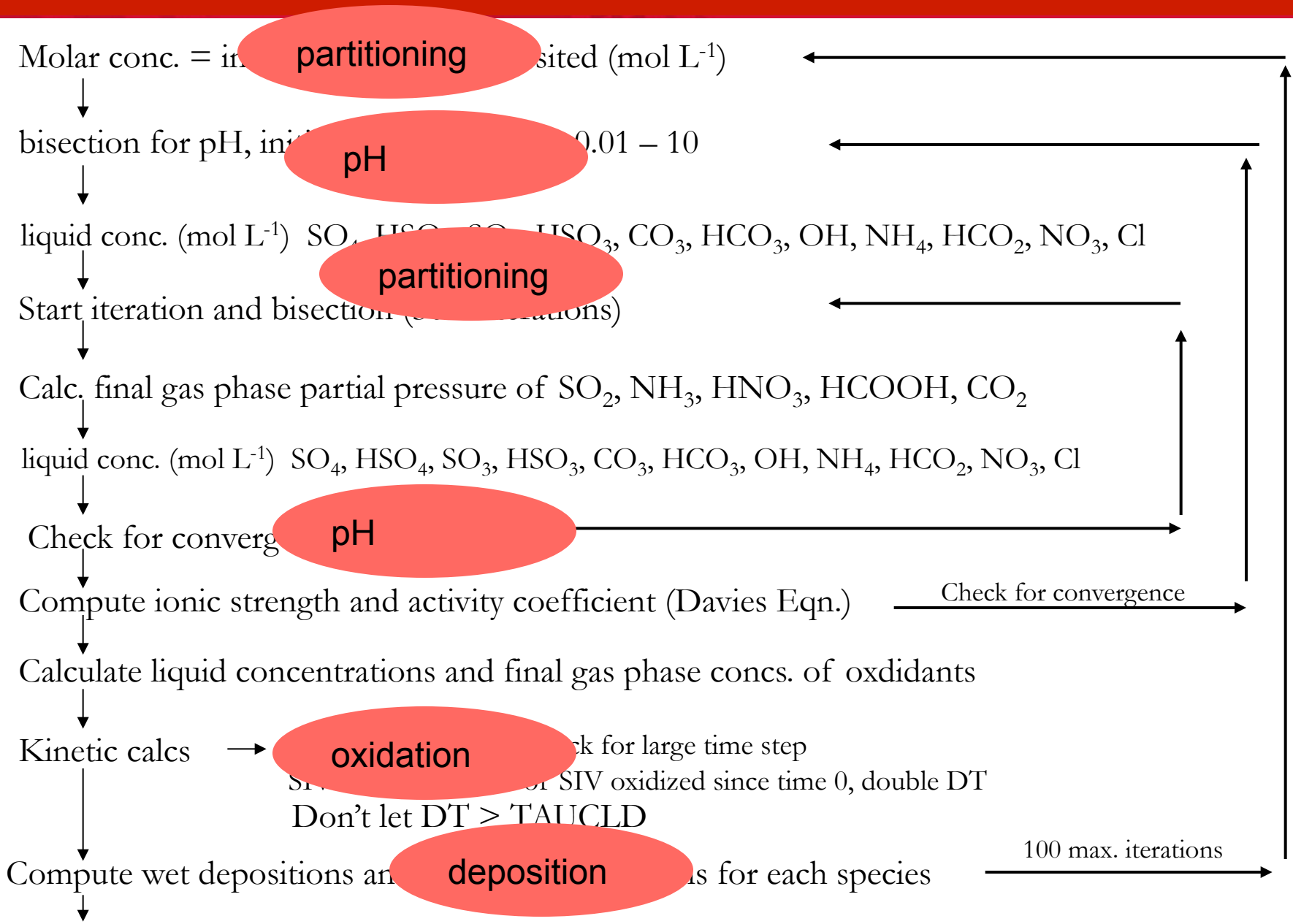


CMAQ Aqueous Chemistry Map (*aqchem.F*)



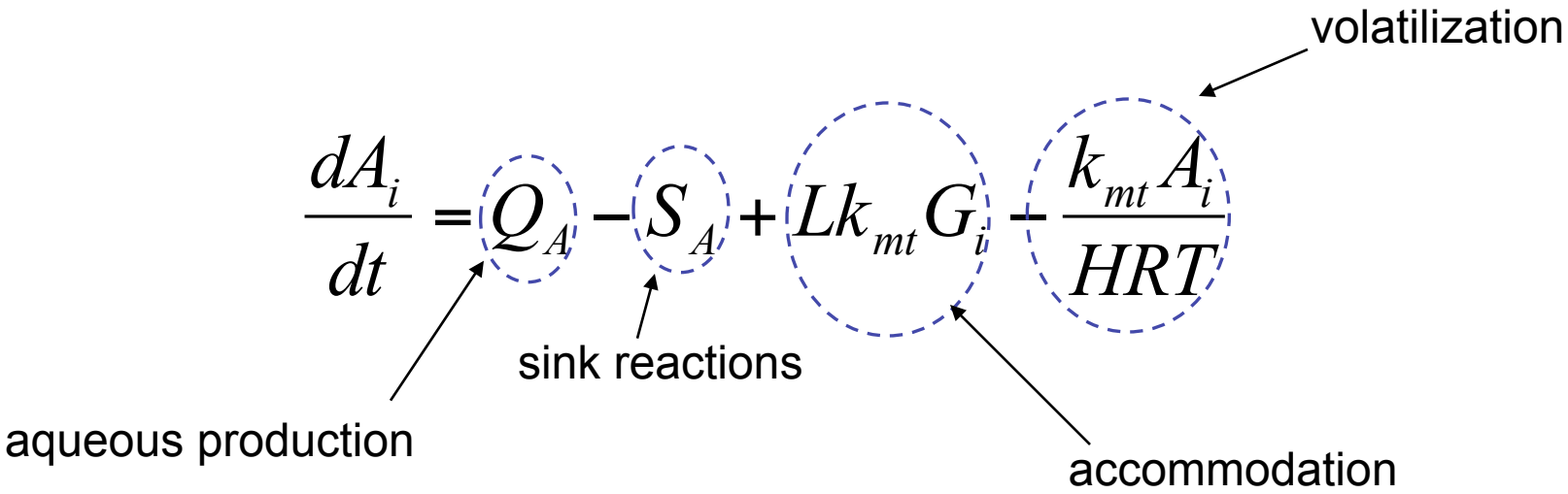
CMAQ Aqueous Chemistry Map (*aqchem.F*)



Reduction in Operator Splitting

$A_i(g) \rightarrow A_i(aq)$

$A_i(aq) = H_A p_A$ Theoretical maximum



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

interfacial processes by Schwartz (1986)

Partitioning Assumptions

Comparison of cloud-produced sulfate when SO_2 partitions according to Henry's Law to "bulk" cloud water vs. kinetic mass transfer to monodisperse droplet population.

Current approach in CMAQ

	Bulk chemistry (no droplets)	5 µm droplets	10 µm droplets	20 µm droplets
Predicted sulfate (µg m^{-3})	3.5	2.3	2.1	2.0

Note: surface level cloud-produced sulfate. Averaged values for the continental U.S.

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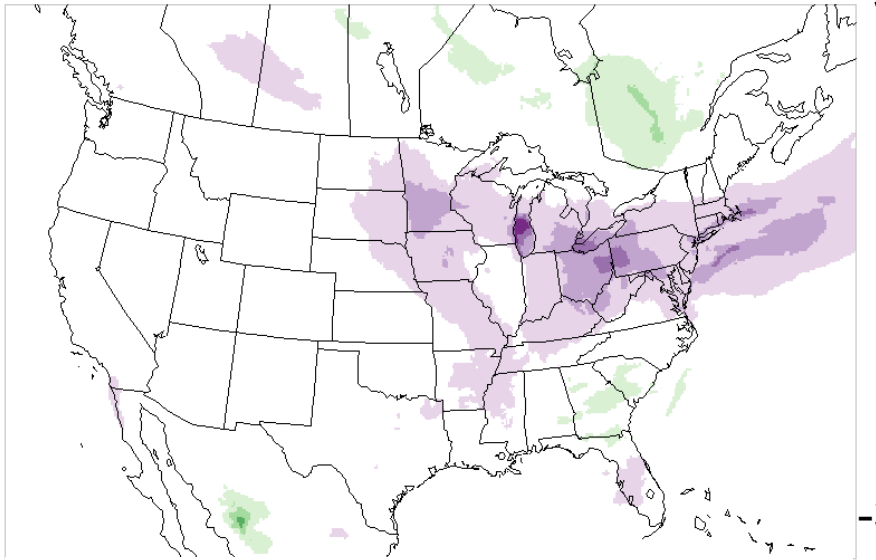
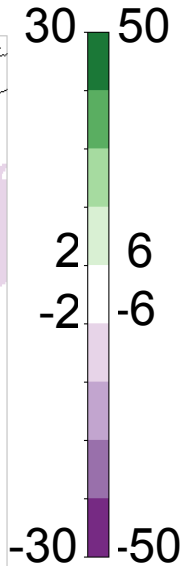
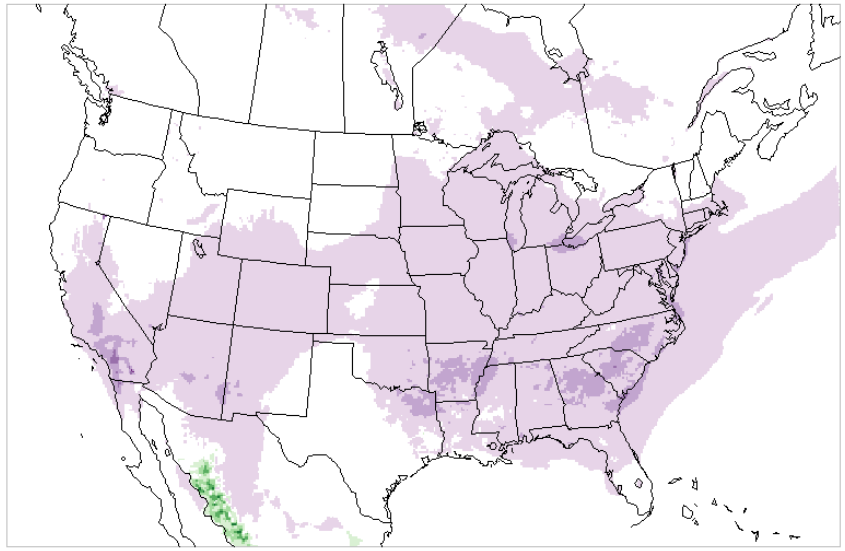
KPP vs. Base CMAQv5.01

Surface aqSOA

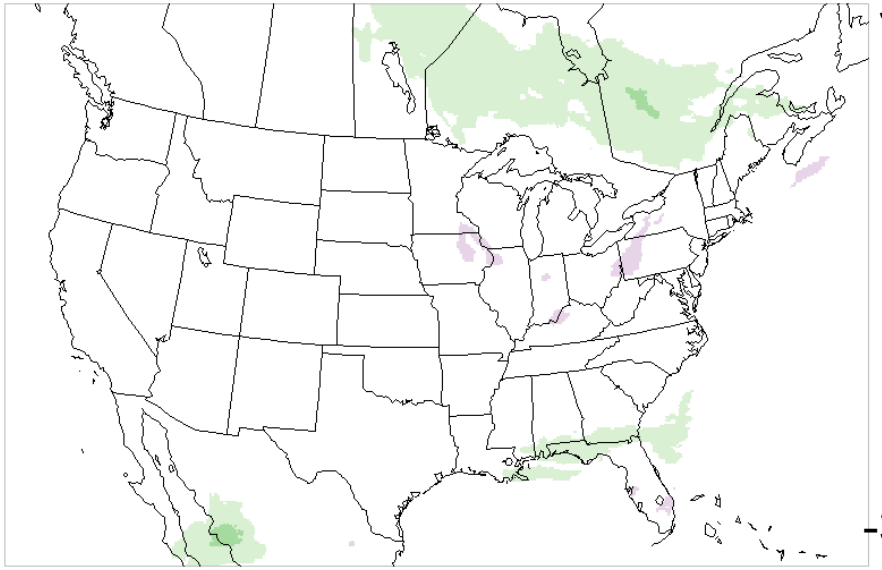




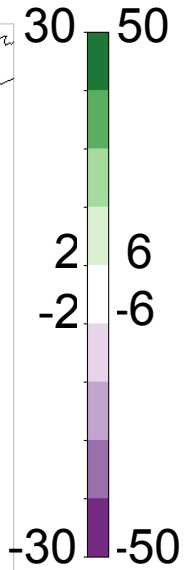
Surface Total SOA



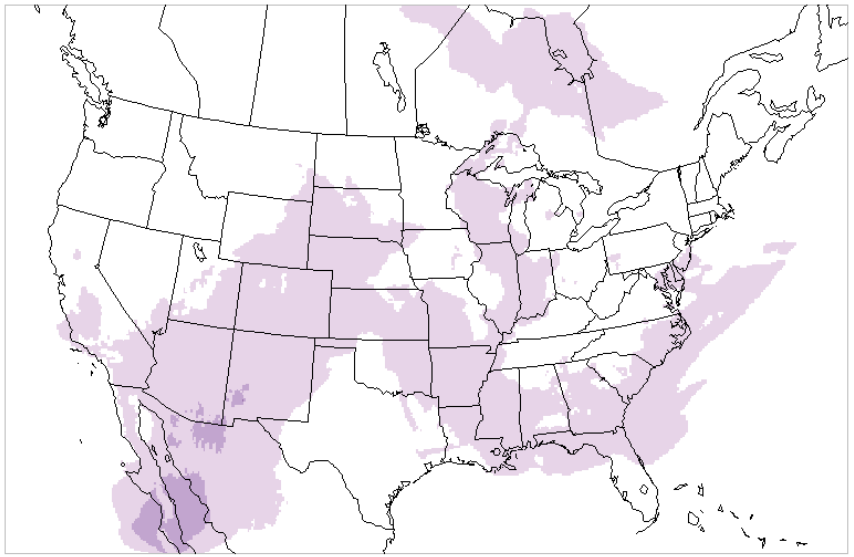
Aloft (800mb) aqSOA



ng m^{-3}



Aloft (800mb) Tot SOA



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Future Directions (~9 months)

Continued refinement of EC/OC emissions from electricity sector

- behind the meter, other peak demand generation

Continued refinement and validation of aqueous chemical mechanisms: SOAS data

- in particular AERONET measurements
- assign refractive properties
- investigate vertical profile sensitivities

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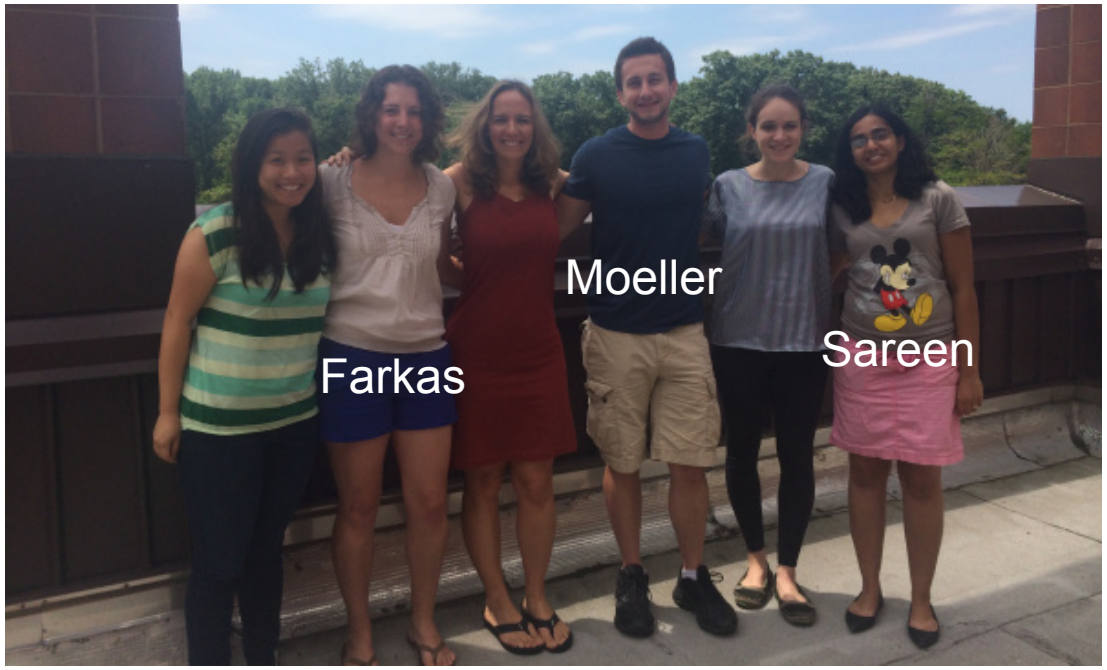
Acknowledgements

EPA STAR Program

- John Dawson, Sherri Hunt, Wil Wilson

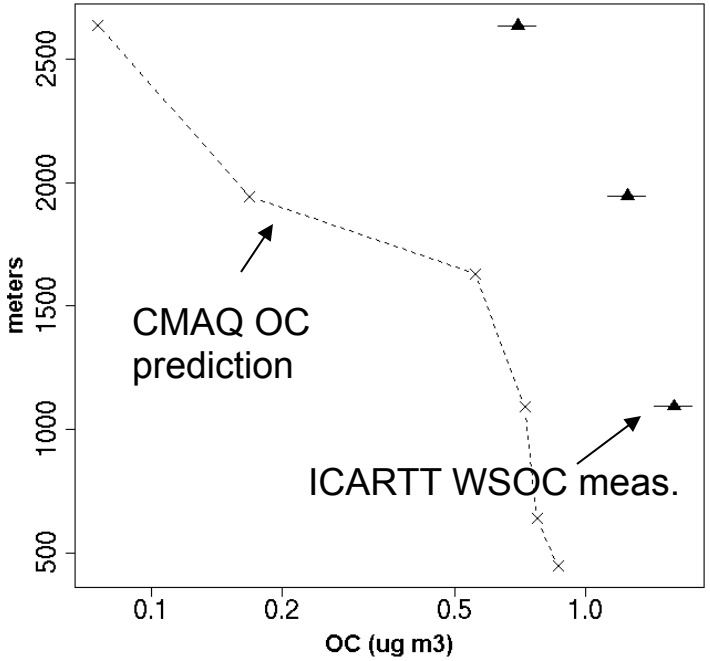
All the CMAQ and SMOKE model developers

Group Members: Brian Marmo, Neha Sareen, Caroline Farkas, Michael Moeller, Neha Sareen, Eleana Little

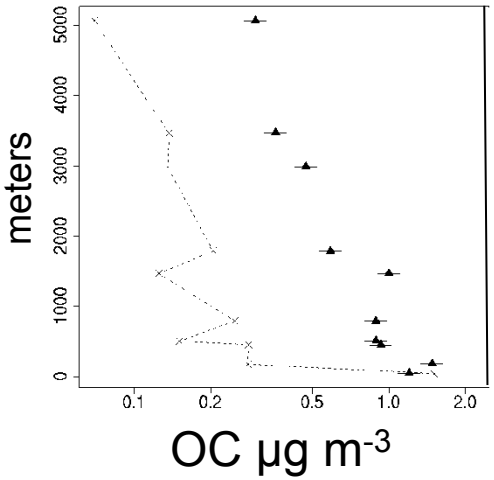


CMAQ & ICARTT (summer 2004)

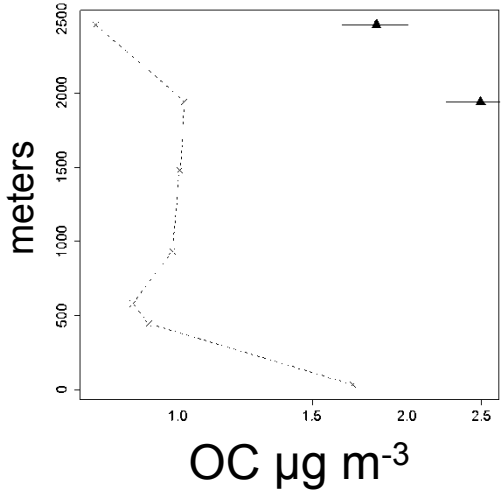
Aug. 3 – new england



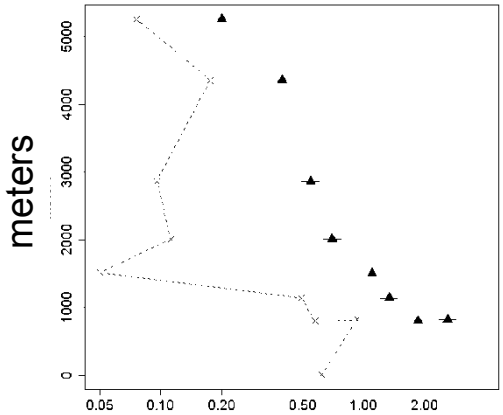
Aug. 14, 2004 - clouds



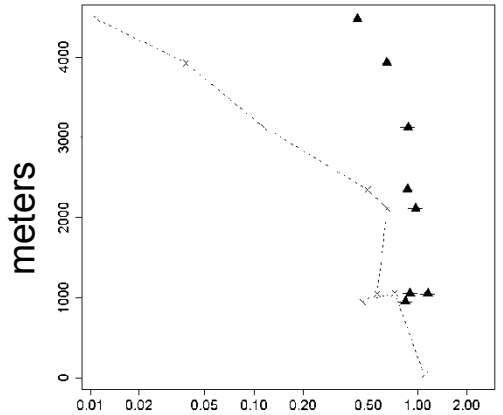
Aug. 11 – NYC plume



Aug. 15
transit to FL via Atlanta



Aug. 6
Ohio Valley power plants



WSOC measurements by Rodney Weber

RUTGERS Multiphase chemistry: ignored at our peril

Atmospheric models have 100s of gas phase reactions, and ~5 aqueous phase reactions (often a trick to get gas phase concentrations right)

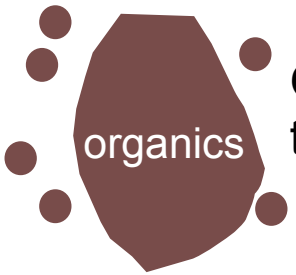
Catalytic properties of water ignored → Chapman cycle insufficient to describe stratospheric ozone

Aqueous phase SO_2 oxidation → acid rain problem, unable to develop effective control strategies.

Heterogeneous chemistry on polar stratospheric clouds discovered → finally we completely understand the ozone hole.

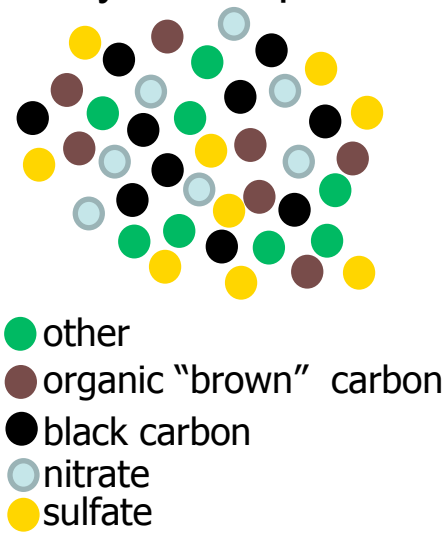
Hypothesis: insufficient representation of multiphase organic chemistry leads to incorrect vertical profiles of particulate carbon in atmospheric models. This hinders development of effective strategies for air quality and climate.

Particle models



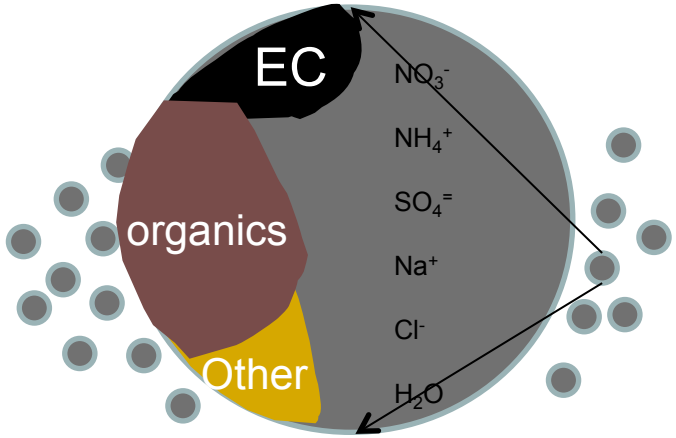
Organics: can be primary (emitted) or secondary (formed in the atmosphere)

externally-mixed particle model



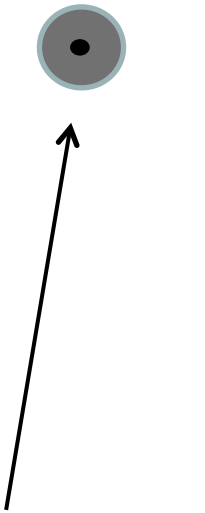
global climate models

internally-mixed particle model



regional-scale air quality models

hybrid



how BC is most often observed in the atmosphere

In climate models, BC only absorbing species (historically).