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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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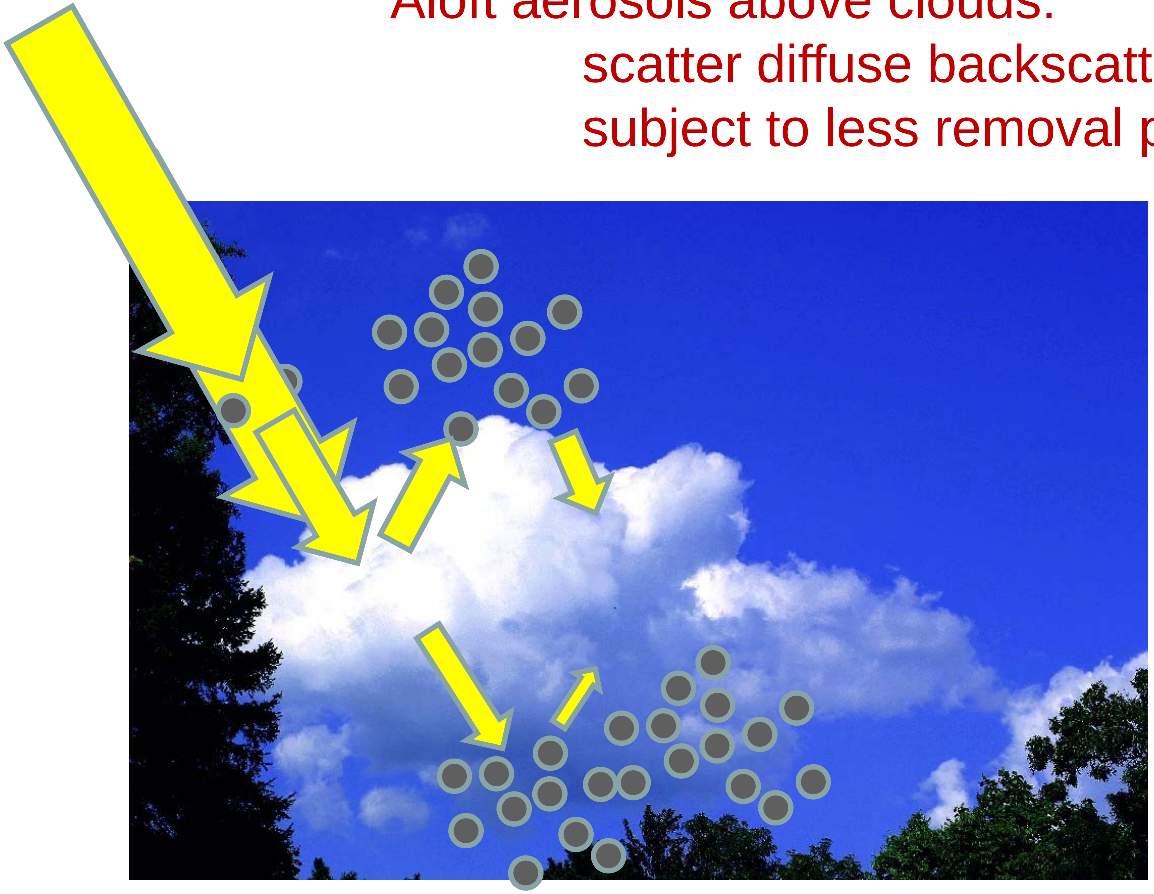
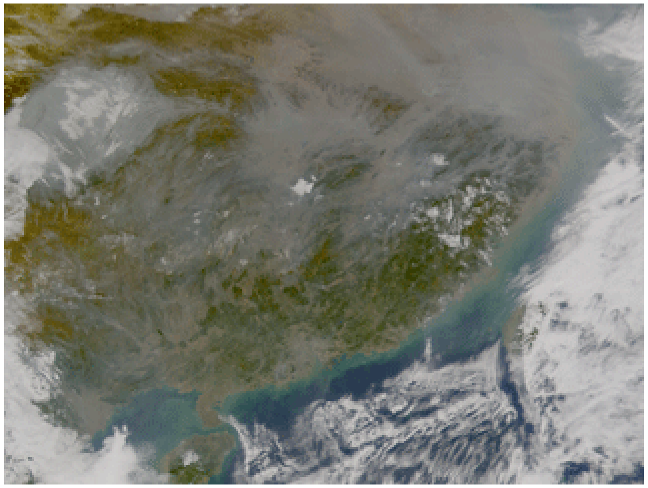
Vertical profile: motivation to get it right

Aloft aerosols above clouds:
- scatter diffuse backscatter
- subject to less removal processes



RUTGERS The ABCs of climate change and long-range pollution transport



1999: NASA scientists announce a giant, atmospheric "brown cloud“ that forms over South Asia and the Indian Ocean has intercontinental reach.

Atmospheric Brown Clouds (ABCs)
collection of submicrometer aerosols, including black carbon (BC) and other chemical constituents (e.g., sulfate, organics).

These aerosols are called **“Short-Lived Climate Forcers” (SLCFs)** because their atmospheric lifetime (~days-weeks) is much shorter than for CO_2 (100^+ years).

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ABC Constituents Contribute to Scattering

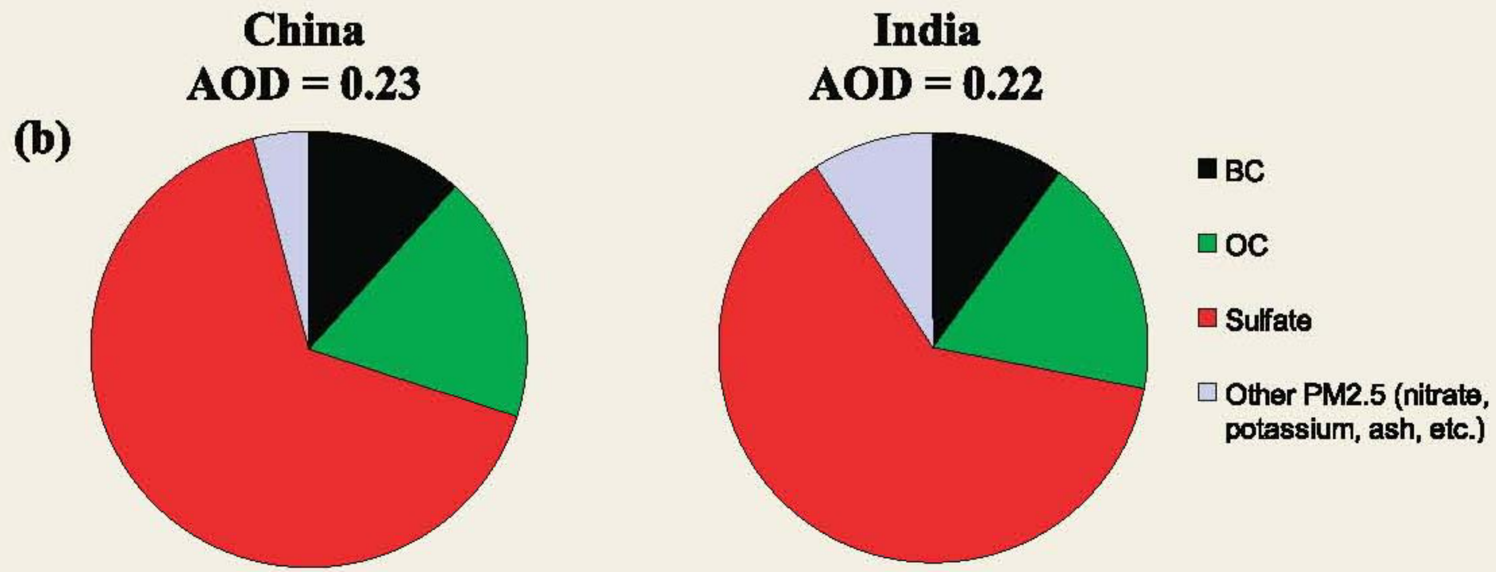


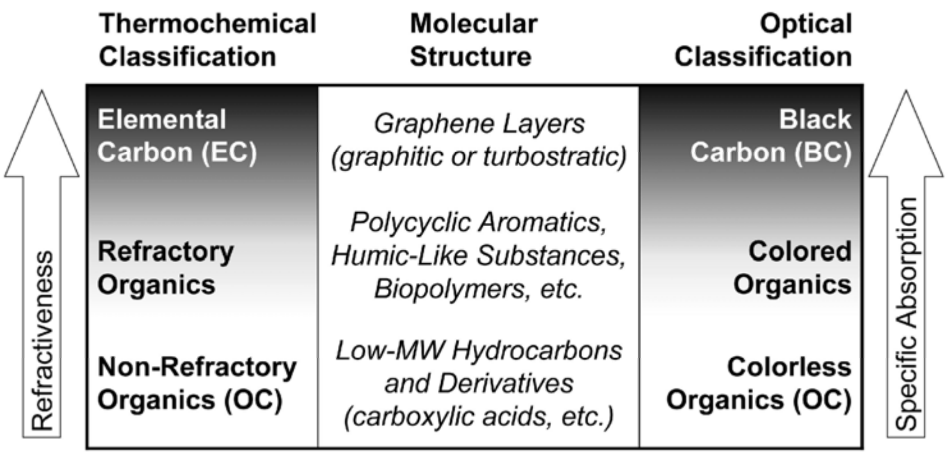
Figure TS1.2 *Annual and area average chemical speciation of (a) surface mass concentration for anthropogenic $PM_{2.5}$ aerosols in China and India, and (b) column integrated aerosol optical depth (AOD) for anthropogenic aerosols, i.e. ABCs (Source: Adhikary and others 2008; except that the average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

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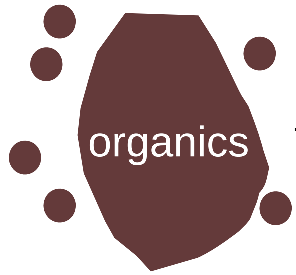
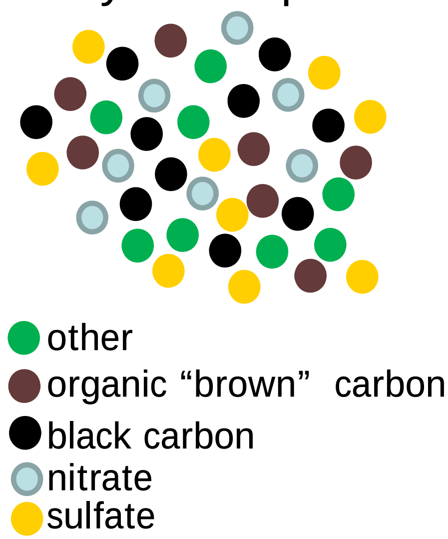
Particle models



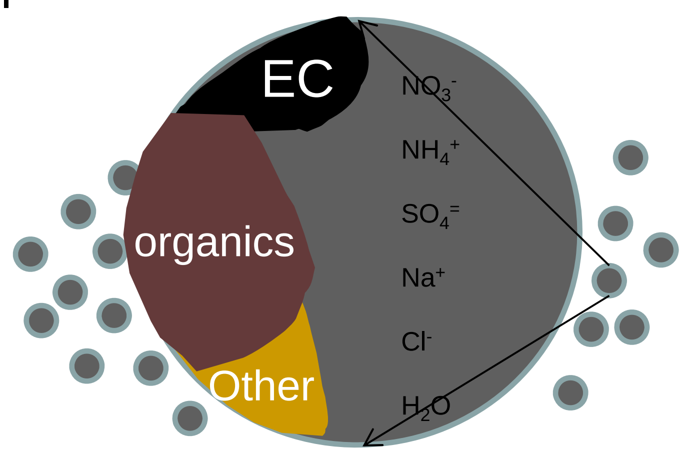
Organics: can be primary (emitted) or secondary (formed in the atmosphere)

externally-mixed particle model



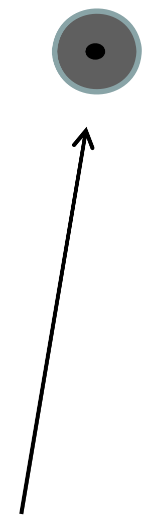
global climate models

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).

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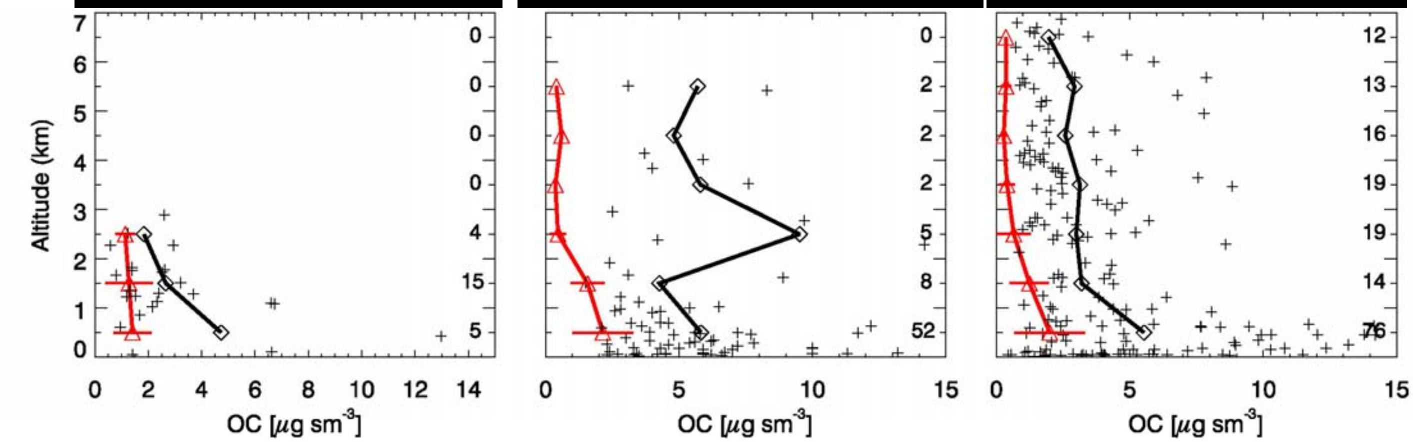
ACE-ASIA: FIRST OC AEROSOL MEASUREMENTS IN THE FREE TROPOSPHERE (Spring 2001)

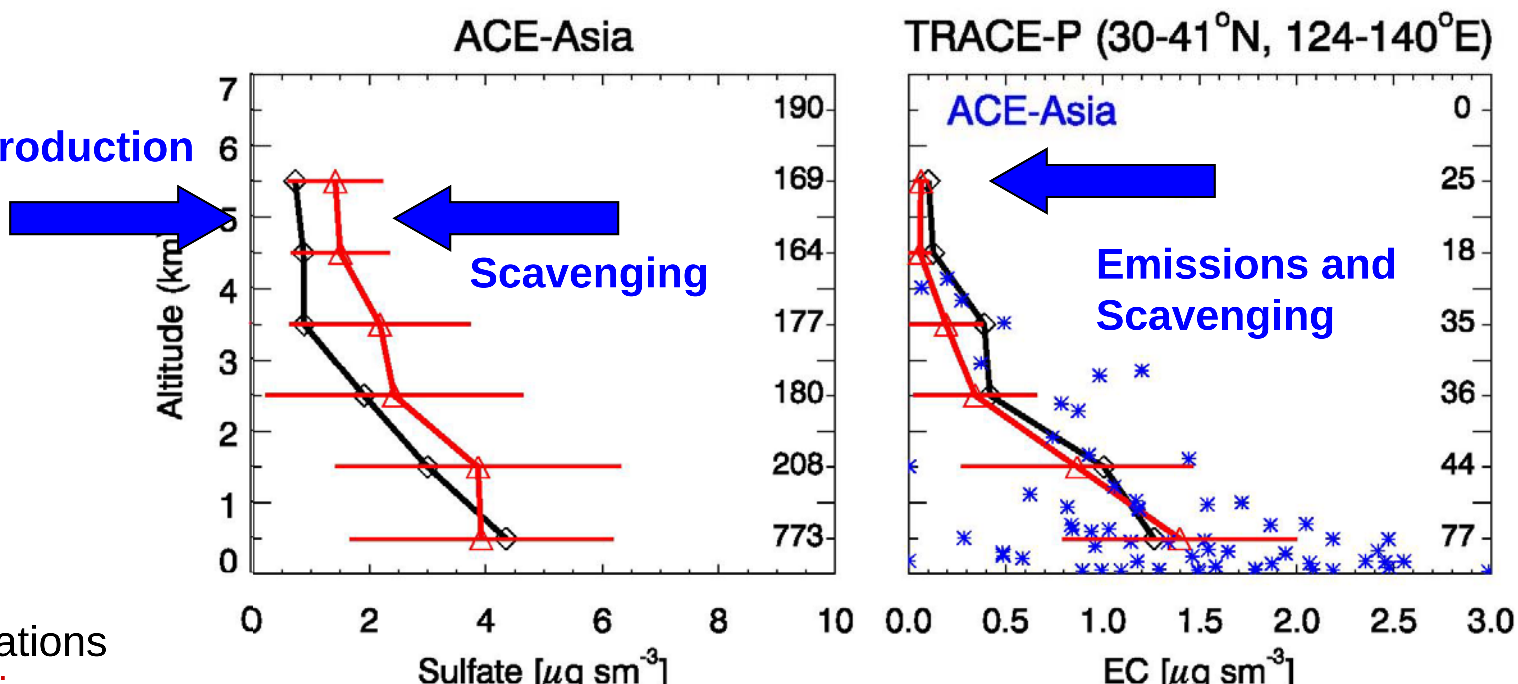
[Mader et al., 2002] [Huebert et al., 2003] [Maria et al., 2003]



$f_{OC/aer}$:
~50% (surface)
~80% (aloft)

[Heald et al., 2005]

Secondary Production



— Mean Observations
— Mean Simulation
+ Observations

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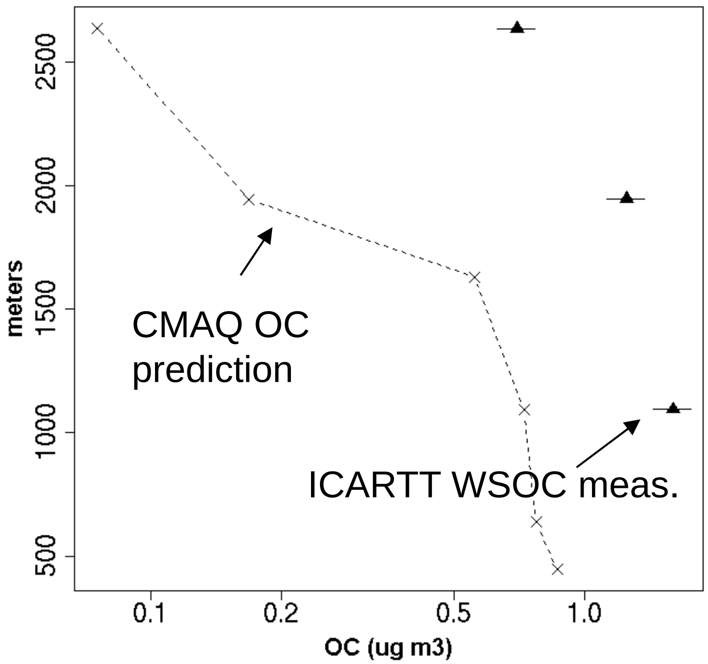
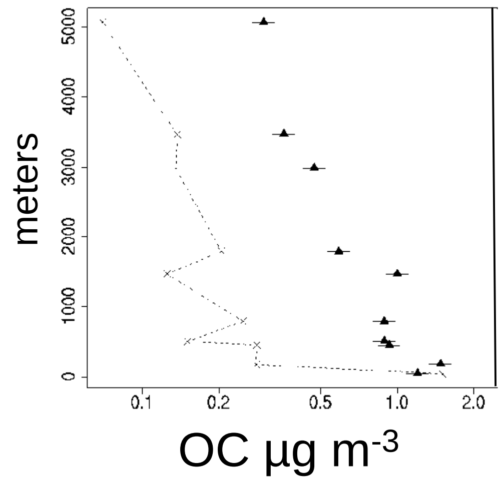
CMAQ & ICARTT (summer 2004)

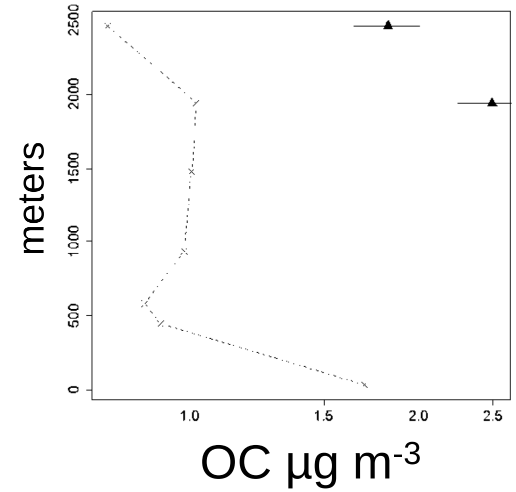
Aug. 3 – new england



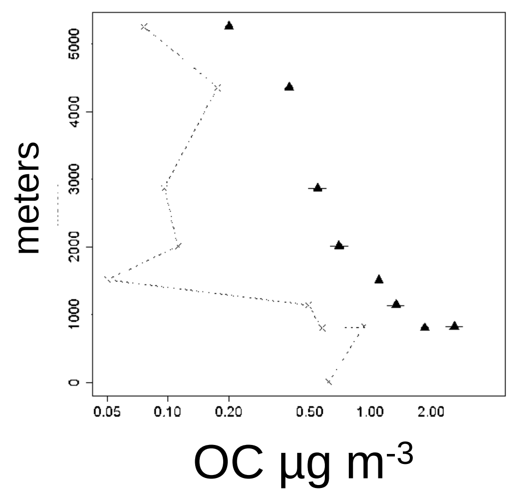
Aug. 14, 2004 - clouds



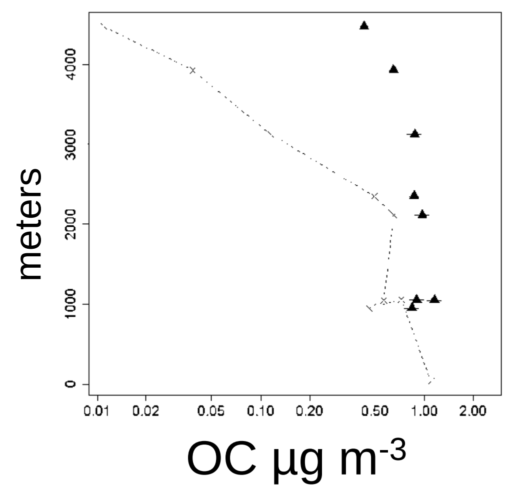
Aug. 11 – NYC plume



Aug. 15
transit to FL via Atlanta



Aug. 6
Ohio Valley power plants



WSOC measurements by Rodney Weber

Photooxidation Experiments Typically Carried Out in Dry Conditions

Kroll et al., (2006) RH < 10%
Ng et al., (2007) RH ~ 5%
Kleindienst et al., (2009) < 3%
Presto et al., (2010) RH < 20%

An 80 m^3 2 mil Teflon bag used in the study of aerosol dynamics (p. 257-8).

Friedlander, *Smoke Dust and Haze,* 1977

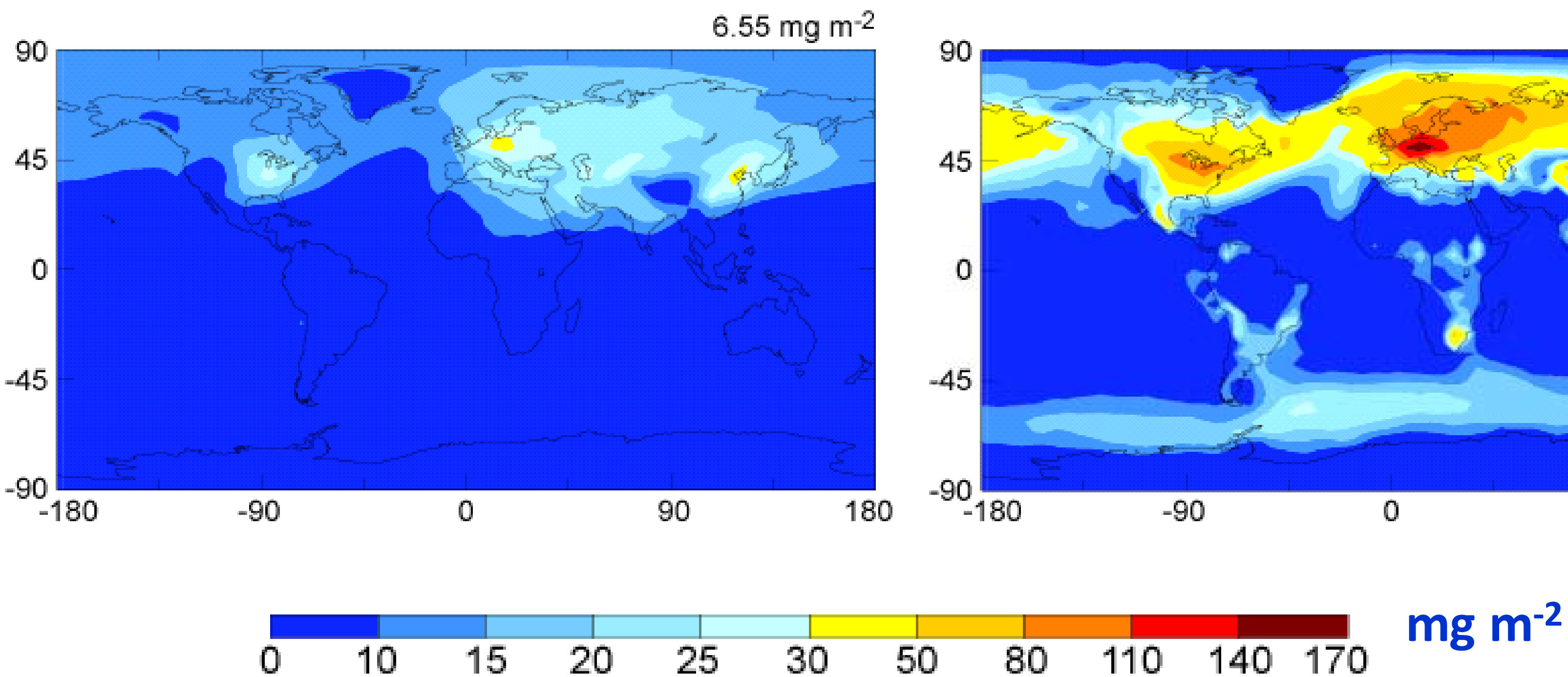
Clouds cover ~60% of the Earth's Surface

MODIS blue marble project

Particle phase liquid water dominates aerosol mass

Dry sulfate/nitrate/ammonium aerosols

Water associated with sulfate/nitrate/ammonium aerosols



Aerosol water is 2-3 times dry particle mass

Liao and Seinfeld (2005)

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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

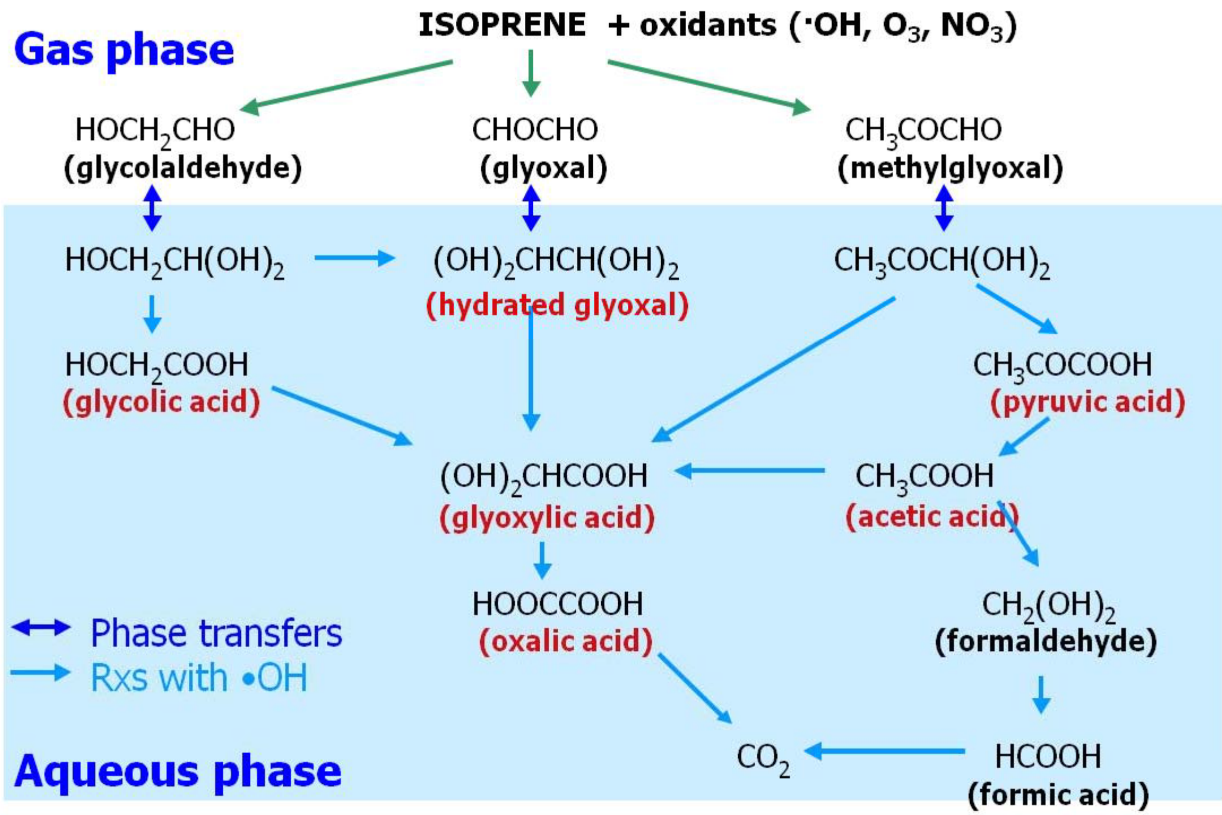
Aqueous phase SO_2 oxidation → acid rain problem, unable to develop effective control strategies.

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.

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"

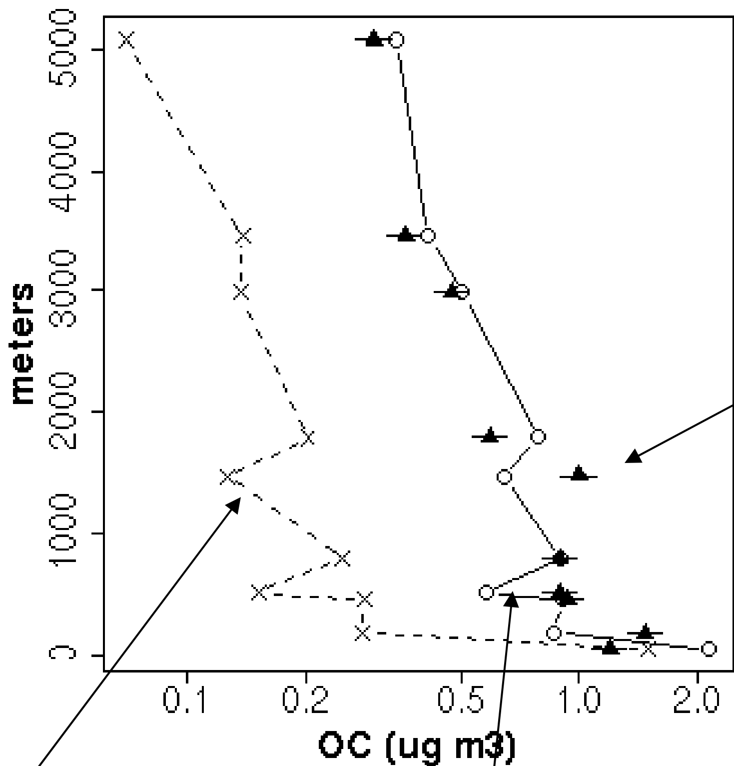
ICARTT cloud experiment: Vertical Profile of absorbing particulate carbon

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., 2008

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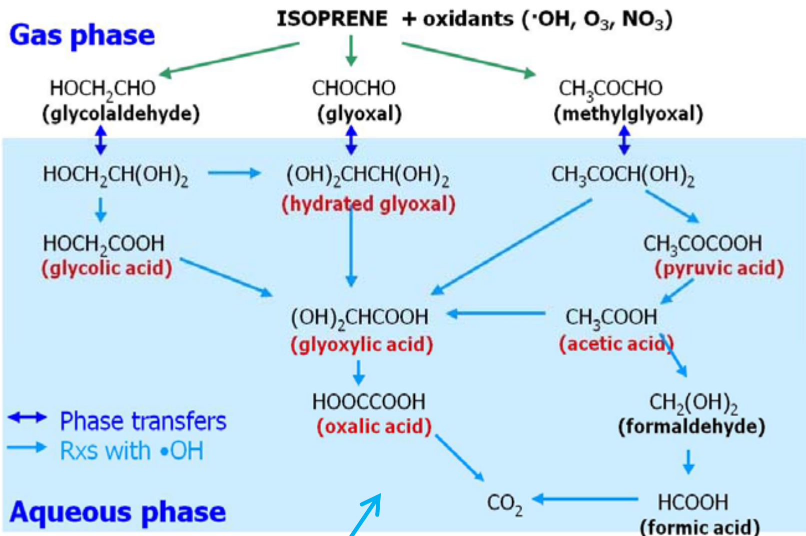
Where to go from here

Lab experiments verify

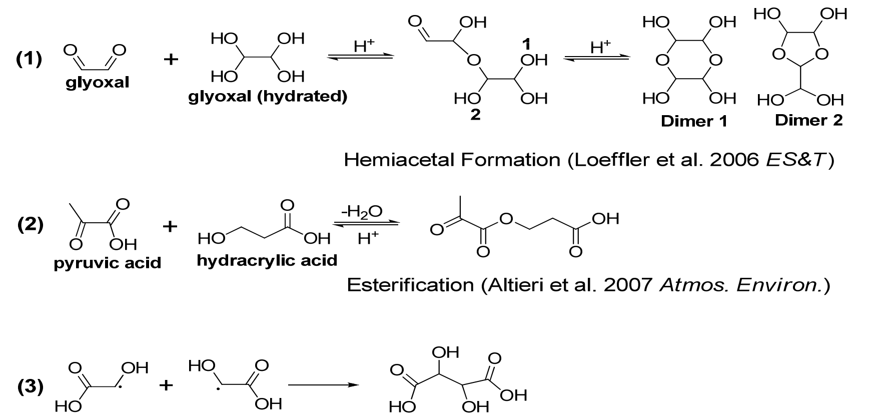


Methacrolein

organosulfates

amines

Glyoxal-methylgloxal cross reactions

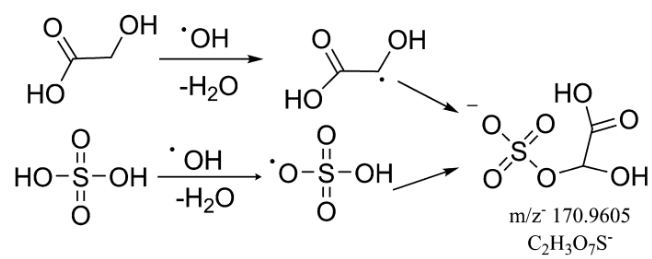


Hemiacetal Formation (Loeffler et al. 2006 *ES&T*)

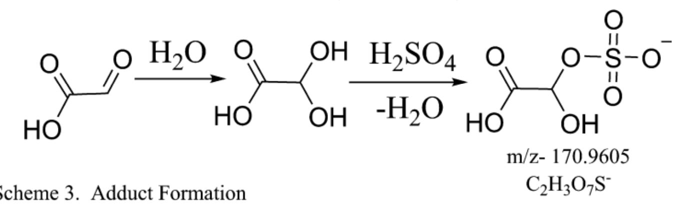
Esterification (Altieri et al. 2007 *Atmos. Environ.*)

Radical-radical reaction Lim et al. 2010 *Atmos. Chem. Phys.*

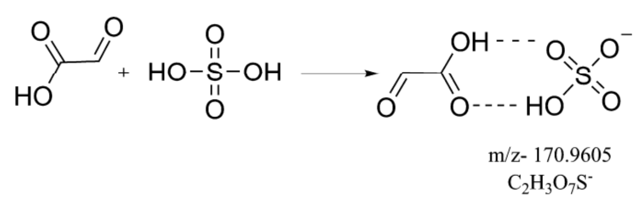
Scheme 1. Radical-Radical Mechanism



Scheme 2. Formation via Condensation (Esterification)



Scheme 3. Adduct Formation



CMAQ Aqueous Chemistry Map (*aqchem.F*)

Molar conc. = in **partitioning** sited (mol L^{-1})

↓

bisection for pH, ini **pH** 0.01 – 10

↓

liquid conc. (mol L^{-1}) SO_4, HSO **partitioning** SO HSO$_3$, CO_3, HCO_3, OH, NH_4, HCO_2, NO_3, Cl

↓

Start iteration and bisectio ions)

↓

Calc. final gas phase partial 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 converg **pH**

↓

Compute ionic strength and activity coefficient (Davies Eqn.) — Check for convergence →

↓

Calculate liquid concentrations and final gas phase concs. of oxdidants

↓

Kinetic calcs → **oxidation** ck for large time step

S SIV oxidized since time 0, double DT

Don't let DT > TAUCLD

↓

Compute wet depositions an **deposition** s for each species — 100 max. iterations →

↓

TIME = TAUCLD (OR 100 iterations)

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Objectives and Current Approaches

1.) Improved Prediction of the Vertical Profile of Particulate Carbon (black and brown)

2 new aqueous phase mechanisms:

- consistent with CB05 and SAPRC07A (e.g., explicit species)
- benchmark with an explicit (>400 oxidation reactions) developed from laboratory experiments

--*$[SO_4]_{accum}$ and $[AORGC]_{accum}$ within 10% of the explicit predictions

Robust solver for aqchem.F

- continued development of ROS3 solver in 3-dimensional simulations
- testing of partitioning and droplet size assumptions
- investigating coupling of gas and aqueous chemistry oxidation chemistry

2.) Investigation of the effects of improved prediction of particulate carbon vertical profile

- 2 way coupled WRF-CMAQ model simulations with and without expanded organic mechanism

Current Mechanism

- $H_2O_2 + S(IV) \rightarrow S(VI)$
- $MHP + S(IV) \rightarrow S(VI)$
- $PAA + S(IV) \rightarrow S(VI)$
- $O_3 + S(IV) \rightarrow S(VI)$
- $O_2 + S(IV) \xrightarrow{\text{Mn, Fe}} S(VI)$
- (M)GLY + OH → cloud SOA

Partitioning Assumptions

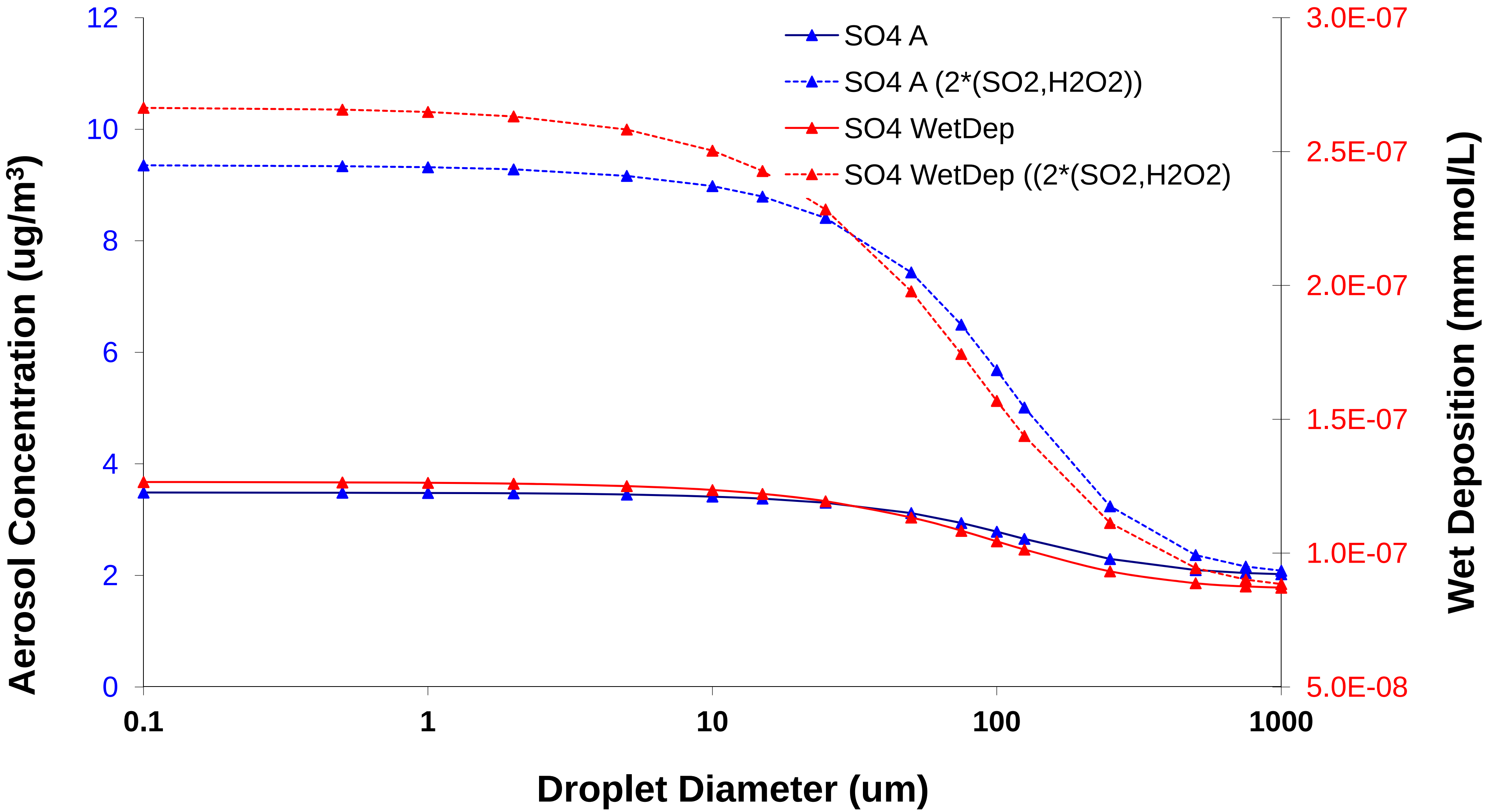
Comparison of cloud-produced sulfate when SO_2 partitions according to Henry's Law to "bulk" cloud water vs. kinetic mass transfer to monodisperse droplet population.

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.

Droplet size sensitivities for individual reactions



SIV Mechanism Upgrades

SIV + O_3:

pH ≥ 2.7

discontinuities in the SIV oxidation chemistry create a stiff system

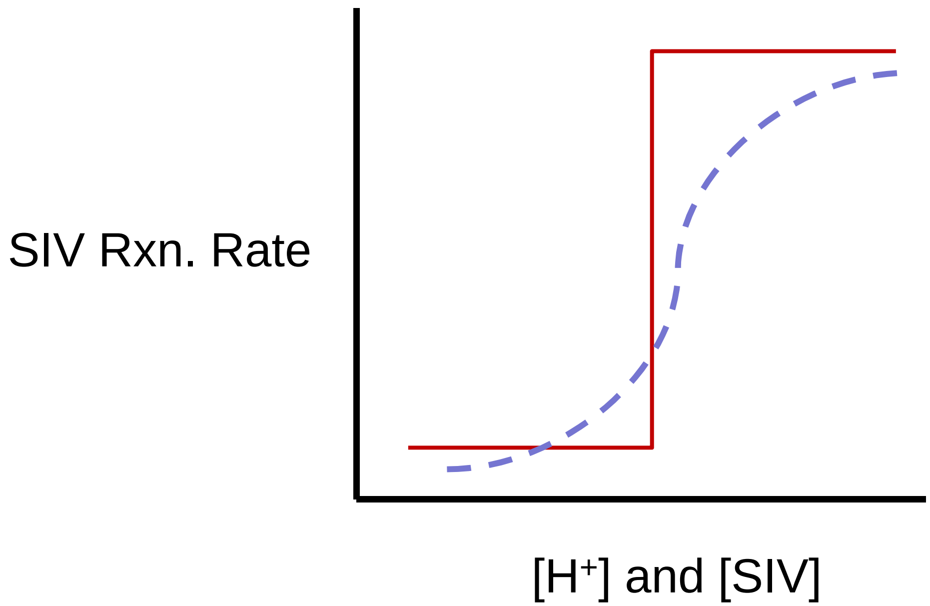
SIV + O_2 (catalyzed by transition metals):

pH ≥ 4.0 & [SIV] ≤ 1.0E^{-5}

pH ≥ 4.0 & [SIV] > 1.0E^{-5}

pH < 4.0 & [SIV] ≤ 1.0E^{-5}

pH < 4.0 & [SIV] > 1.0E^{-5}



New formulations in CMAQv5

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Cloud Ice

- Cloud Ice mixing ratios can be highest in summer

- Added HNO_3, H_2O_2 and SO_2 partitioning to cloud ice
  - $H_2O_2 + SO_2 \rightarrow H2SO_4$

- We observe changes in the spatial distributions nitrogen and sulfur compounds when cloud ice is substantial
  - What will happen if carbon species partition to ice?

To improve the vertical profile of particulate carbon in CMAQ this year we will:

- Expansion of aqueous phase chemical mechanism focused on sulfate and organic species
- Testing, understanding and revising current model assumptions and approaches
- Develop and apply robust solver

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Acknowledgements

- EPA STAR Program
  - John Dawson for organizing this meeting
- All the CMAQ model developers
- Partha Bhattacharjee, Brian Marmo and Neha Sareen