

Atmospheric Acidity and the Role of Clouds on Air Quality

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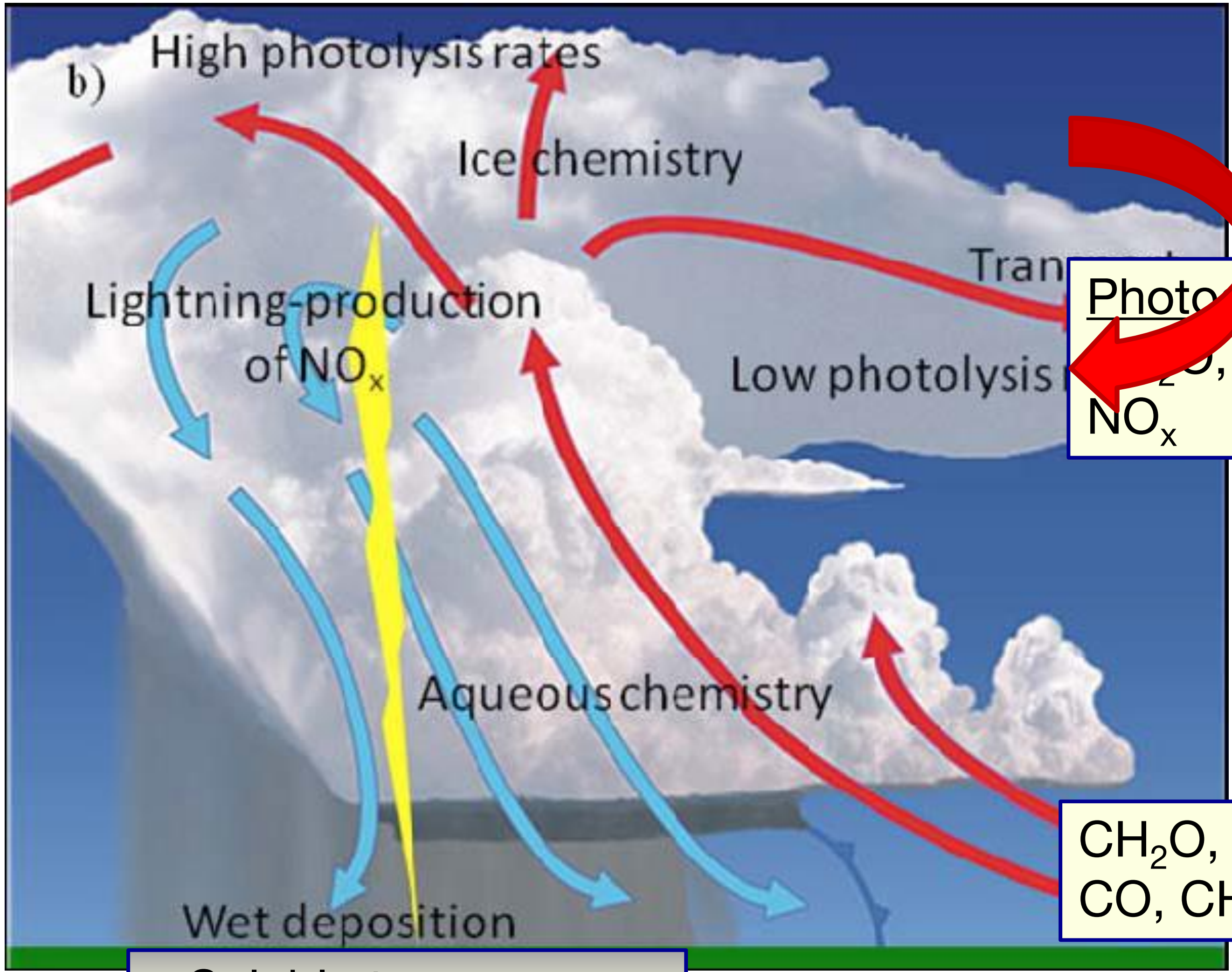
Thunderstorm Processing of Trace Gases



- Stratospheric air can be brought into the upper troposphere and wrap around anvil

Photochemically-active plumes
CH_2O, H_2O_2, CH_3OOH, CO, CH_4, VOCs, NO_x → O_3 in UT where O_3 is a GHG

CH_2O, H_2O_2, CH_3OOH, CO, CH_4, VOCs, NO_x, O_3

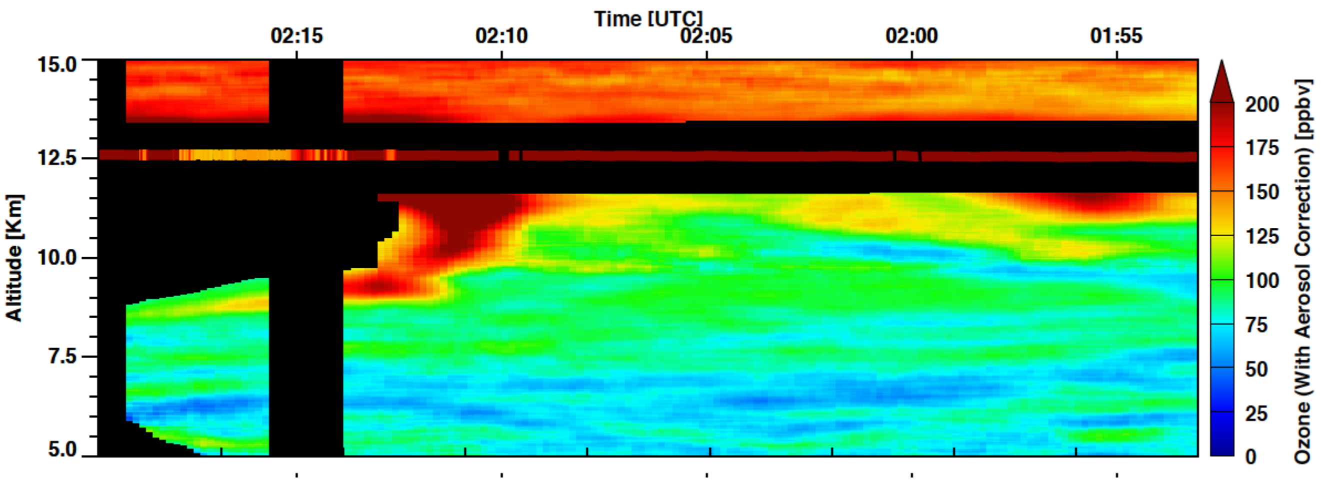
Soluble trace gases

CH_2O = formaldehyde
H_2O_2 = hydrogen peroxide
NO_x = nitrogen oxides = NO + NO_2
VOCs = volatile organic compounds
CH_3OOH = methyl hydrogen peroxide
CH_4 = methane

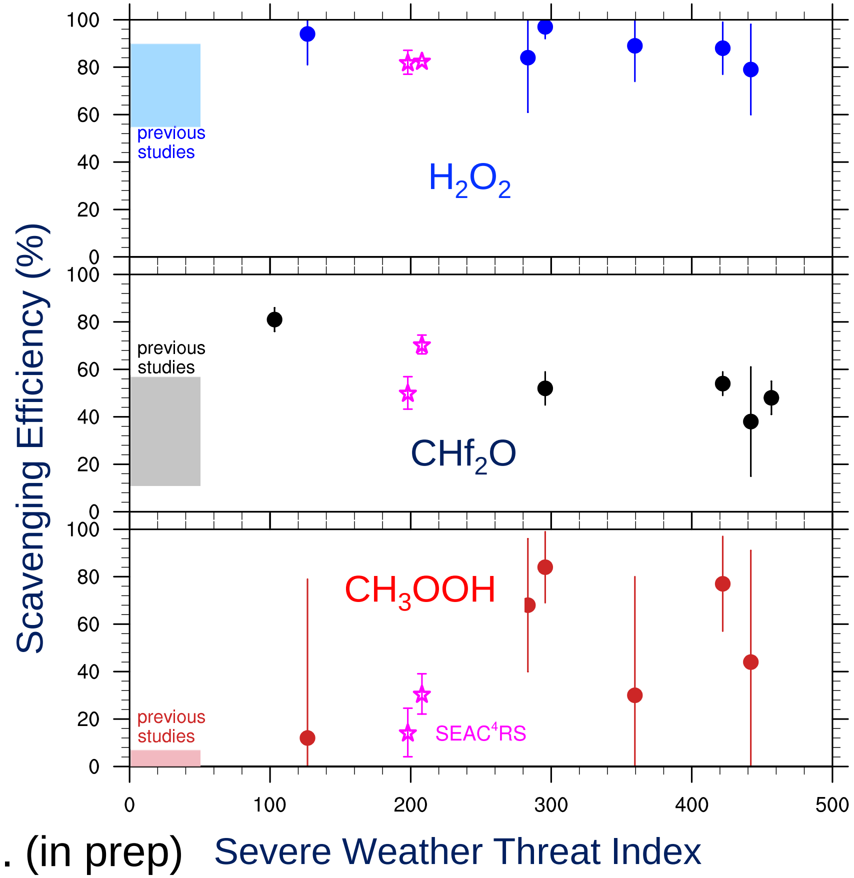
Thunderstorm Processing of Trace Gases

2012 Deep Convective Clouds and Chemistry (DC3) Field Campaign

- Convective transport: cloud-ice physics can affect scavenging of soluble gases
- Lightning is a challenge to predict using empirical fits to various storm characteristics
- Lightning-NO_x predictions are likely uncertain because its production can depend on other characteristics like flash size
- 5-20 ppbv/day of O_3 produced in convective outflows
- Frequently found stratospheric O_3 in upper troposphere



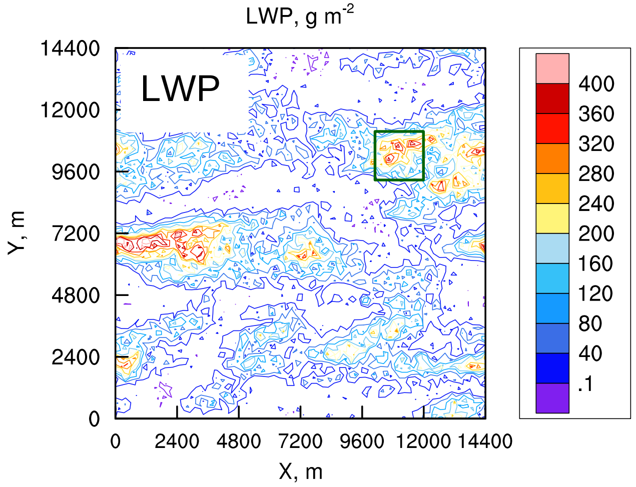
Pan et al. (2014) *GRL* ; Phoenix et al. *(in prep)*

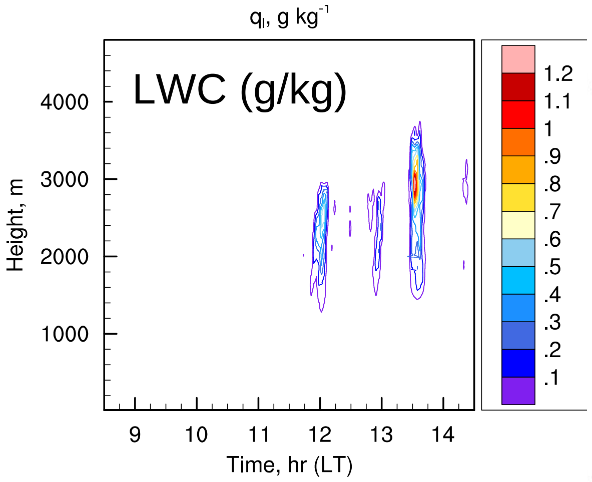


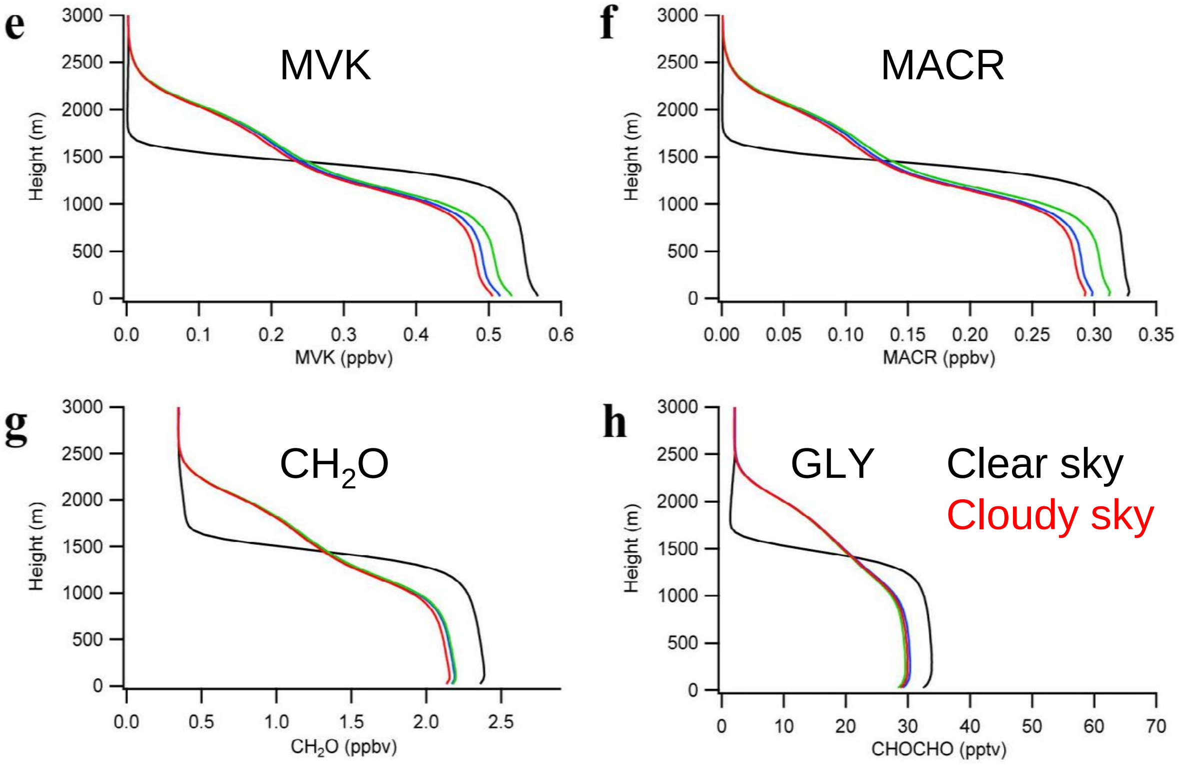
Cuchiara et al. (in prep)

Effect of Clouds on Tropospheric Composition

- Fair-weather cumulus clouds – vent the boundary layer, but are also venues for aqueous-phase chemistry



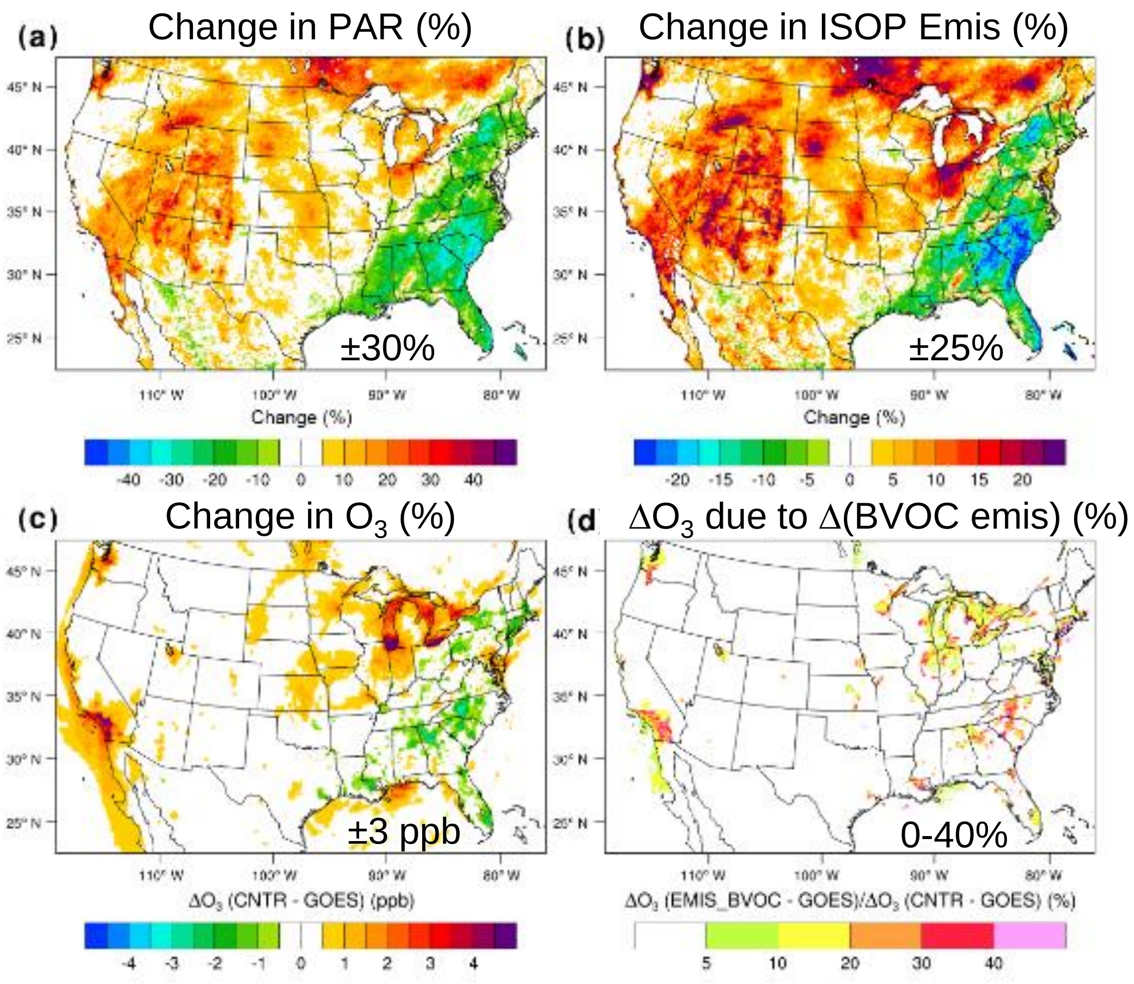




Large eddy simulation results from Kim et al. (2012) JGR

Clouds affect ozone

- Poor predictions in clouds, and therefore radiation, can cause ozone biases



Ryu et al. (2018) *ACP ;* WRF-Chem model results

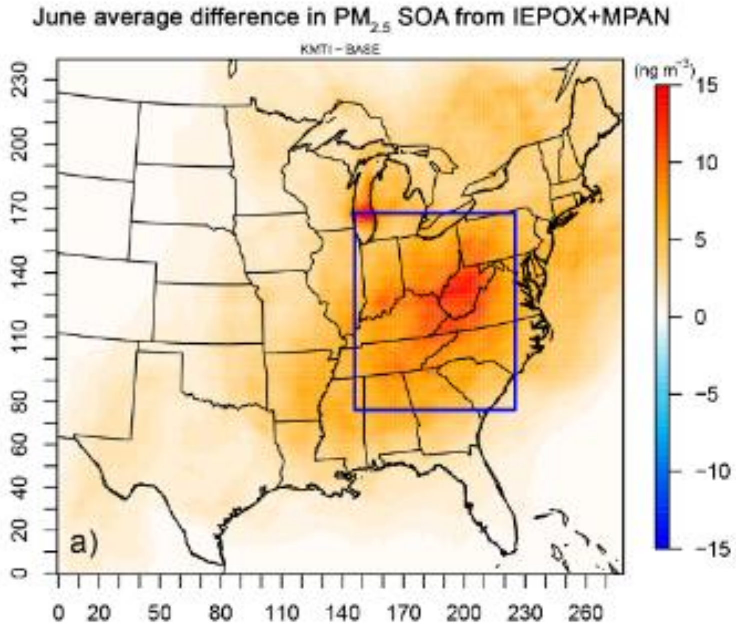
Compare WRF-Chem results with cloud fields corrected with GOES satellite data to control forecast

- WRF-Chem predicts 55% of clouds in right locations, and underpredicts cloud optical depth
- Averaged 1-5 ppbv difference in summertime, surface ozone (MDA8 O3; ~40% of MDA8 O3 bias)
- Mostly from cloud scattering effects on photolysis rates; small effect from BVOC emissions

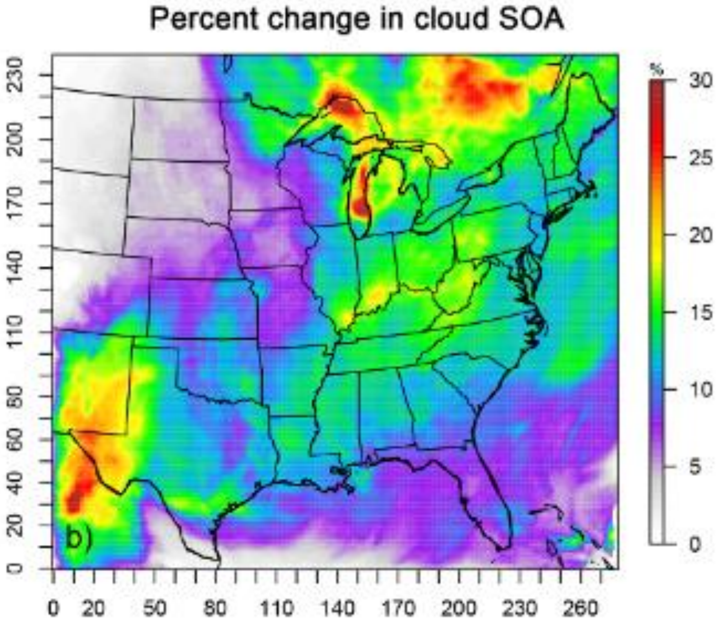
Clouds affect secondary organic aerosol abundance

- Aqueous-phase chemistry of carbonyls produce more SOA

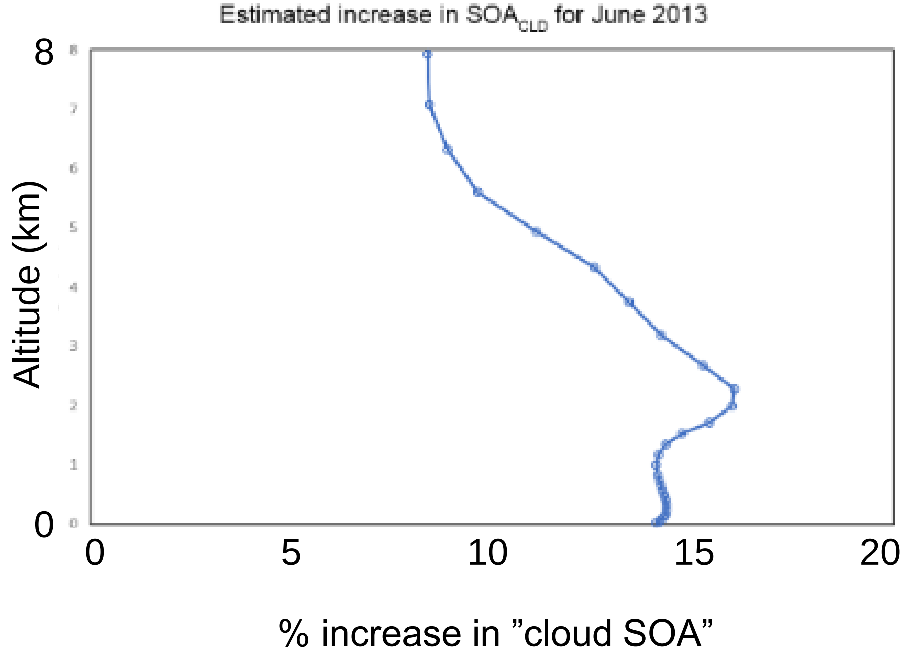
Increase of up to 15 ng/m3 SOA
from cloud processing of carbonyls



Up to 30% increase of “cloud SOA”
at surface



Vertical profile of “cloud SOA”
increase for blue box



Fahey et al. (2017) *GMD*
CMAQ model results

Aqueous-phase Sulfur Chemistry is a Major Source of Sulfate Aerosols

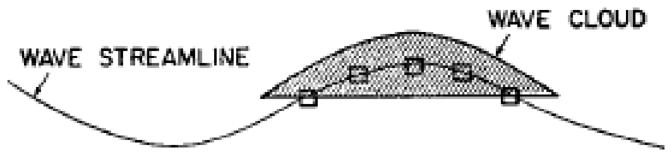


FIG. 1. Schematic diagram of cloud model. The squares indicate the successive locations of the cloud parcel followed in the computations.

From Easter and Hobbs, 1974

Wave clouds used to investigate sulfur chemistry in clouds (Hegg and Hobbs, 1981, 1982)

→ Increased acidity of cloud drops and rain impacting the environment

→ Effects on climate

Acidity of rain, clouds, and aerosols have important impacts

- Aqueous-phase chemistry depends on pH of drops or aerosols
- Health Impacts of Aerosol Acidity
- Ecosystem Impacts: Acid Rain
- Acidity affects global nutrient cycles

How well do we predict the acidity of cloud water and aerosols?

The State of Acidity in Atmospheric Particles in Clouds

- Review article in preparation led by Havala Pye (EPA) and Thanos Nenes (EPFL) – focus on aerosol and cloud pH
  - Definition of pH
  - Proxies for aerosol pH and assessment of their capabilities
  - Aqueous-phase chemistry – effects of pH and effects on pH
  - Observations of aerosol and cloud water pH
  - Chemistry transport model predictions of aerosol and cloud water pH

- ➢ Motivated the work presented today
- ➢ How well do chemistry transport models predict pH?
  - ➢ WRF-Chem cloud water pH and aerosol pH
  - ➢ CAM-Chem cloud water pH

pH is a metric of acidity

pH = -log10 [H⁺]

$$[H^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] + [HSO_3^-] + 2[SO_3^{2-}] + 2[SO_4^{2-}] + [NO_3^-] - [NH_4^+]$$

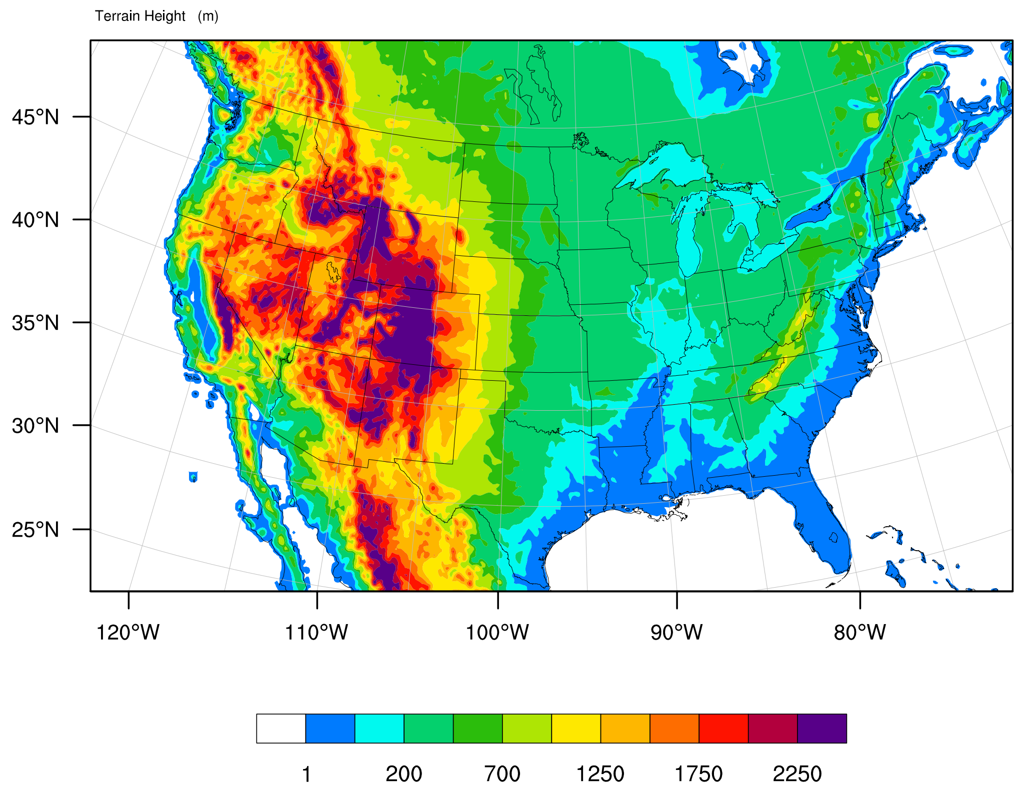
H_2O CO_2 SO_2 CCN HNO_3 NH_3

Other components may contribute: Na^+, Cl^-, K^+, Ca^{2+}, Mg^{2+}, Fe^{3+}, Mn^{2+}

sea salt, BB, dust

BB = biomass burning

WRF Configuration



Weather Research and Forecasting Model

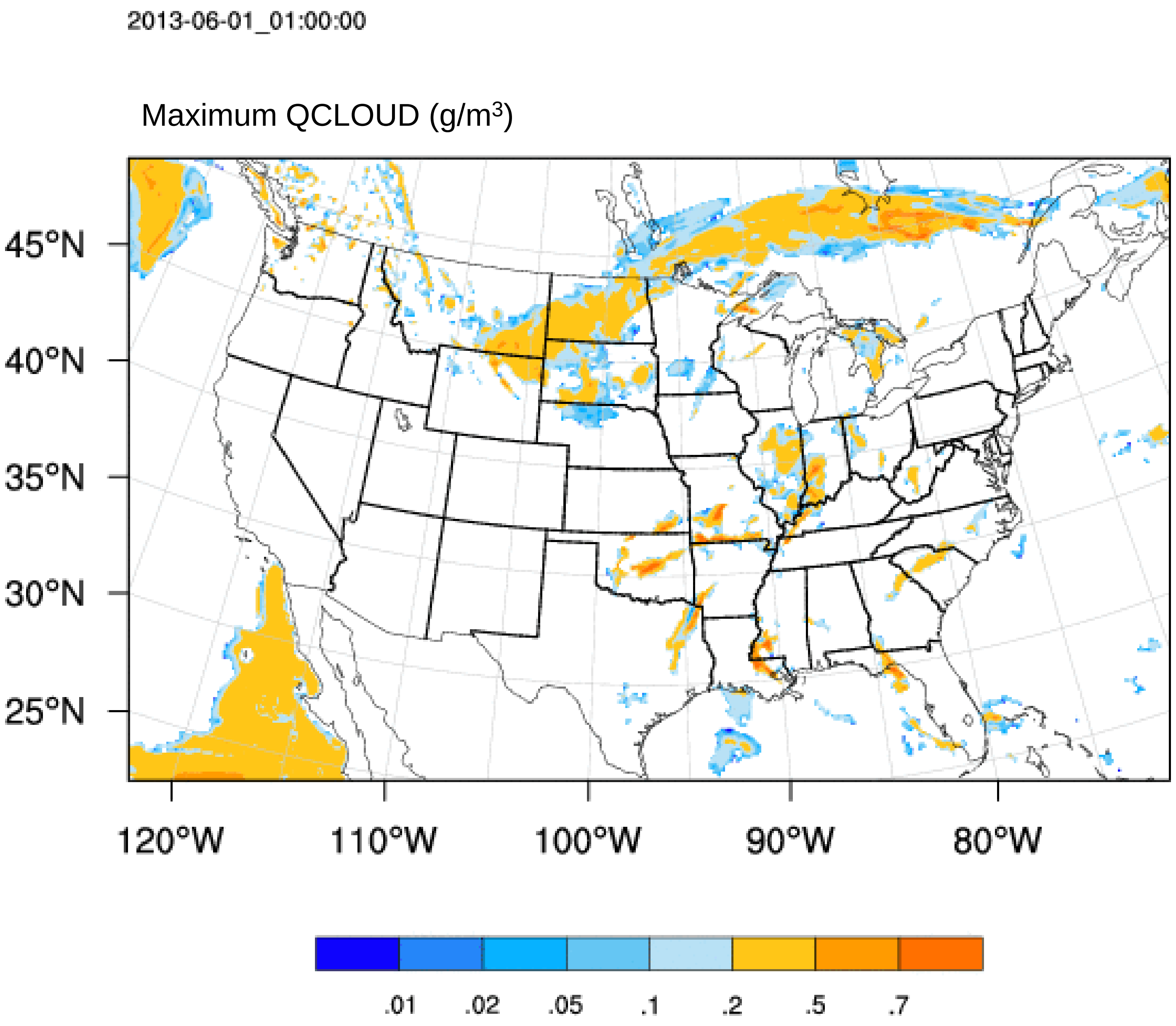
Continental US domain

- Δx = 12 km, 40 vertical levels to 50 hPa
- Cloud physics: Morrison 2-moment
- Radiation: RRTMG (short and longwave)
- PBL parameterization: MYJ
- Convective parameterization: Grell-Freitas
- Surface: Noah Land model

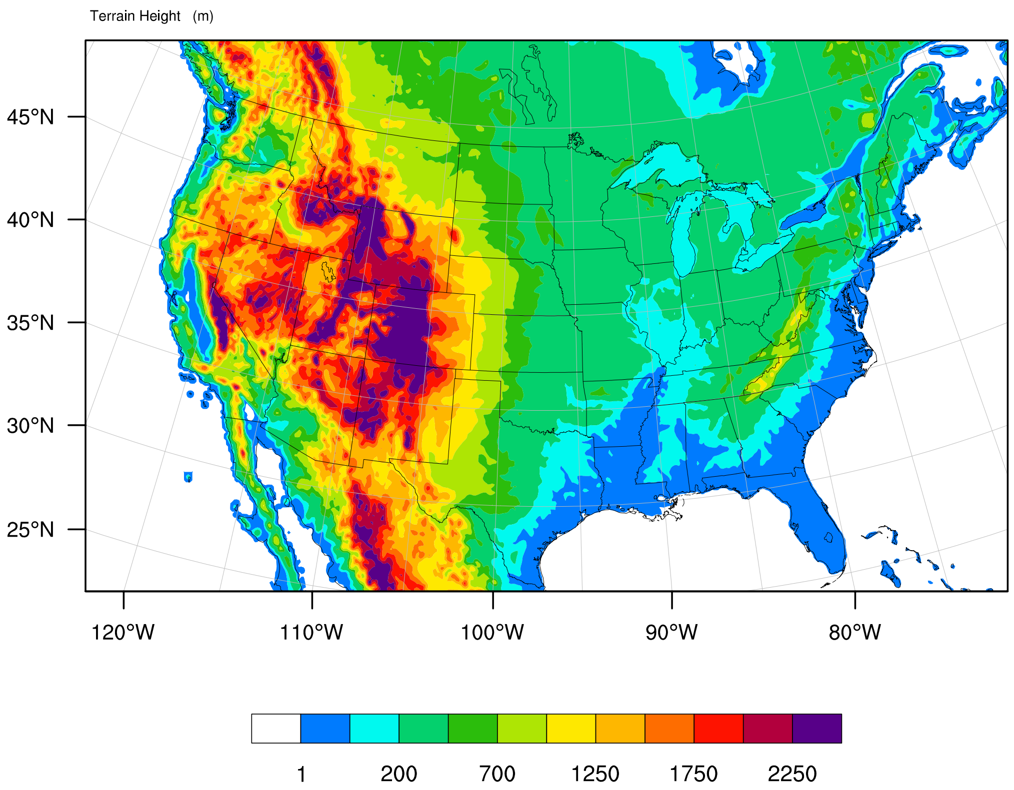
- NAM initial/boundary conditions
- No data assimilation or nudging

Two week simulation: June 1-14, 2013

Active period of clouds except in SW US



WRF Chemistry Configuration



- MOZART gas chemistry
- MOSAIC 4-bin aerosol scheme
  - Multi-component Equilibrium thermodynamic Solver: sulfate – nitrate – ammonium
  - Aerosol water determined (ZSR method)
- Secondary Organic Aerosol formed via a volatility basis set (VBS) approach
- Cloud water chemistry based on Fahey and Pandis (2001)
  - Sulfate production
  - Simple organic chemistry (formaldehyde)
  - Non-reactive uptake of HNO_3, NH_3, and other trace gases

WRF-Chem Calculation of Acidity

Cloud water pH:

$$[H^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] + [HSO_3^-] + 2[SO_3^{2-}] + 2[SO_4^{2-}] + [NO_3^-] - [NH_4^+]$$

H_2O CO_2 SO_2 CCN HNO_3 NH_3

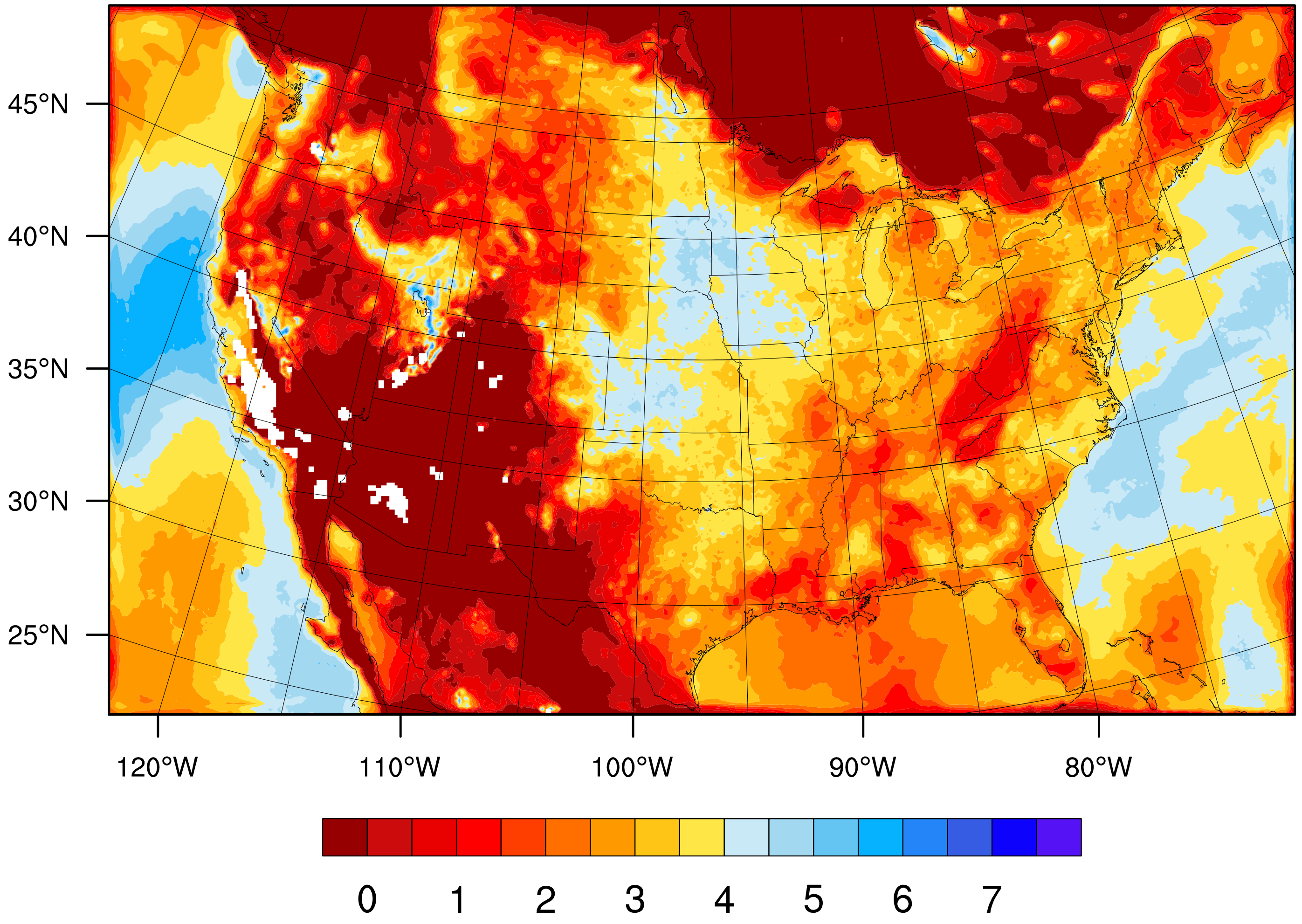
Aerosol pH:

$$[H^+] = [OH^-] + 2[SO_4^{2-}] + [MSA^-] + [NO_3^-] + [Cl^-] + [HCO_3^-] + 2[CO_3^{2-}] - [NH_4^+] – [Na^+] – 2[Ca^{2+}]$$

- Aerosol pH calculated for each size bin
- What's missing? Organic acids
- MOZART gas chemistry does not include HCl → sulfate cannot displace chloride in sea salt

Average pH of fine mode aerosol (d<2.5μm)

LWC-weighted average pH for 14-day time period of surface aerosols



- Aerosol pH much lower than cloud water pH
- Highest pH values in Central U.S. (agricultural influence) and over ocean (sea salt)
- *Note* model is *not* representing well composition of aerosol over ocean because sulfate is not displacing chloride (no HCl in MOZART gas-phase mechanism

$$[H^+] = [OH^-] + 2[SO_4^{2-}] + [MSA^-] + [NO_3^-] + [Cl^-] + [HCO_3^-] + 2[CO_3^{2-}] - [NH_4^+] - [Na^+] - 2[Ca^{2+}]$$

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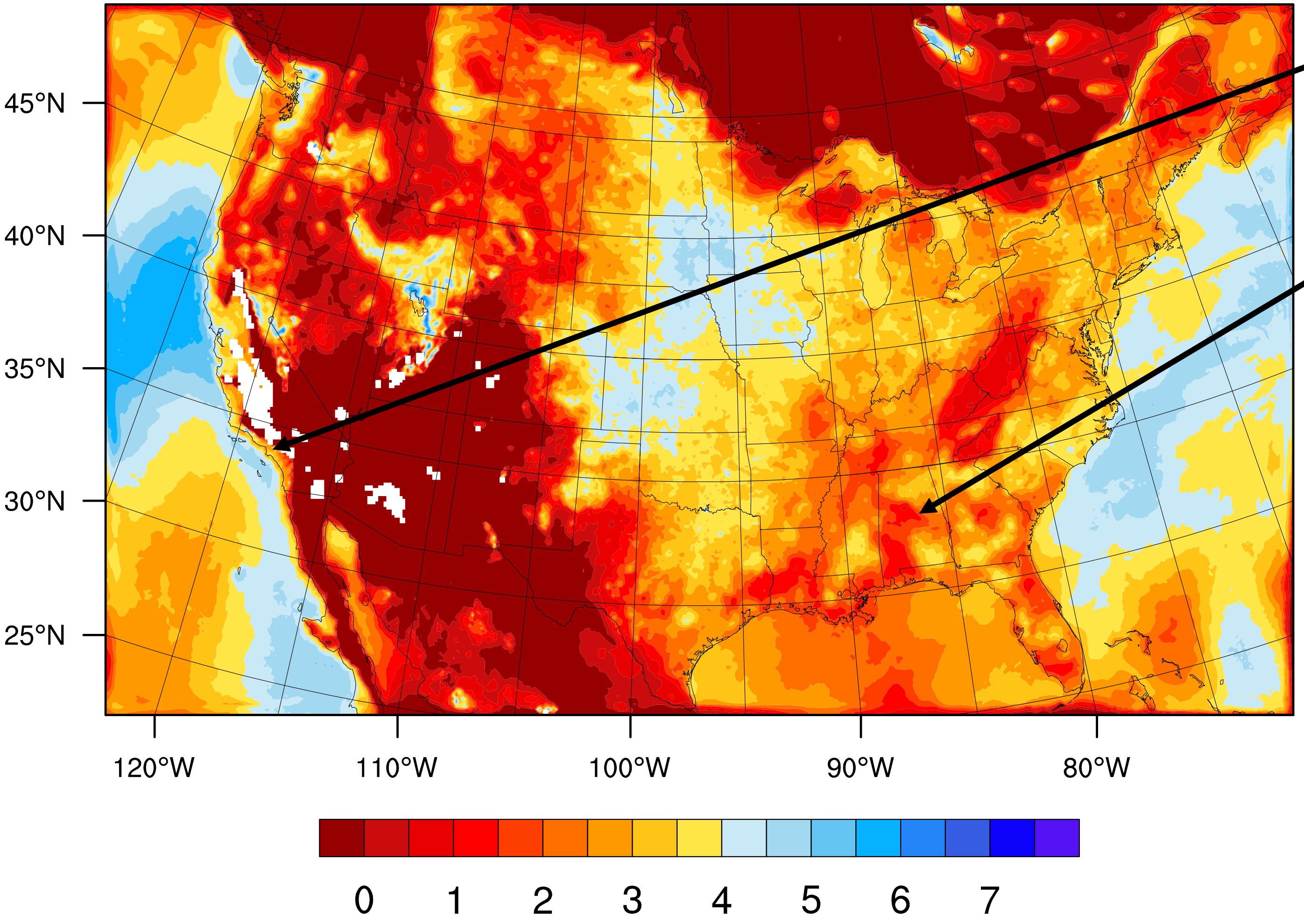


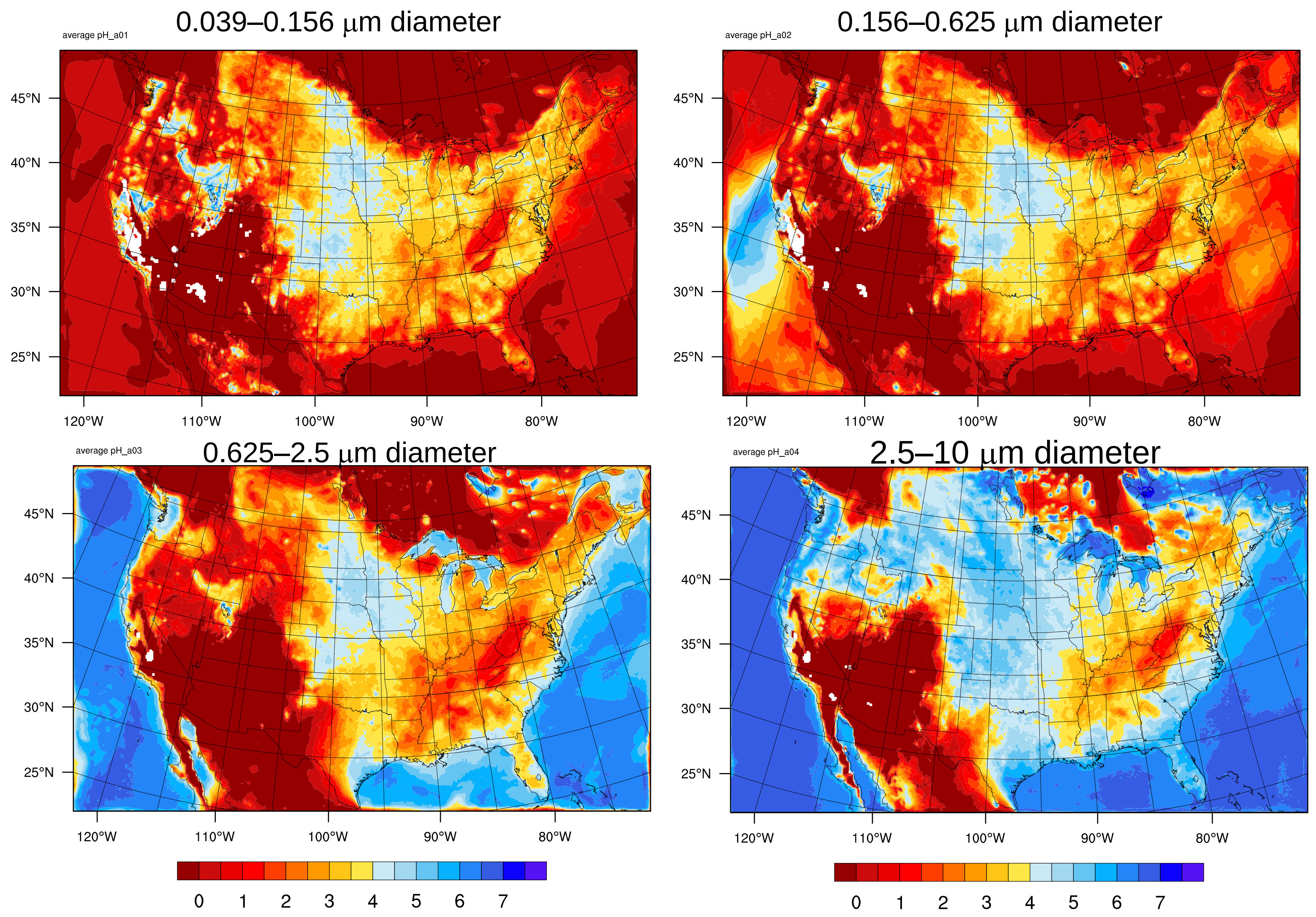
- 2.7 ± 0.3 at Pasadena, CA (Guo et al., 2017)
- 3.4 WRF-Chem
- 0.9 ± 0.6 at Centreville, AL (Guo et al., 2015)
- 1.5 WRF-Chem

➢ Fairly good agreement (within 0.5 pH unit)

➢ Measurements over long periods of time would be useful

$$[H^+] = [OH^-] + 2[SO_4^{2-}] + [MSA^-] + [NO_3^-] + [Cl^-] + [HCO_3^-] + 2[CO_3^{2-}] - [NH_4^+] - [Na^+] - 2[Ca^{2+}]$$

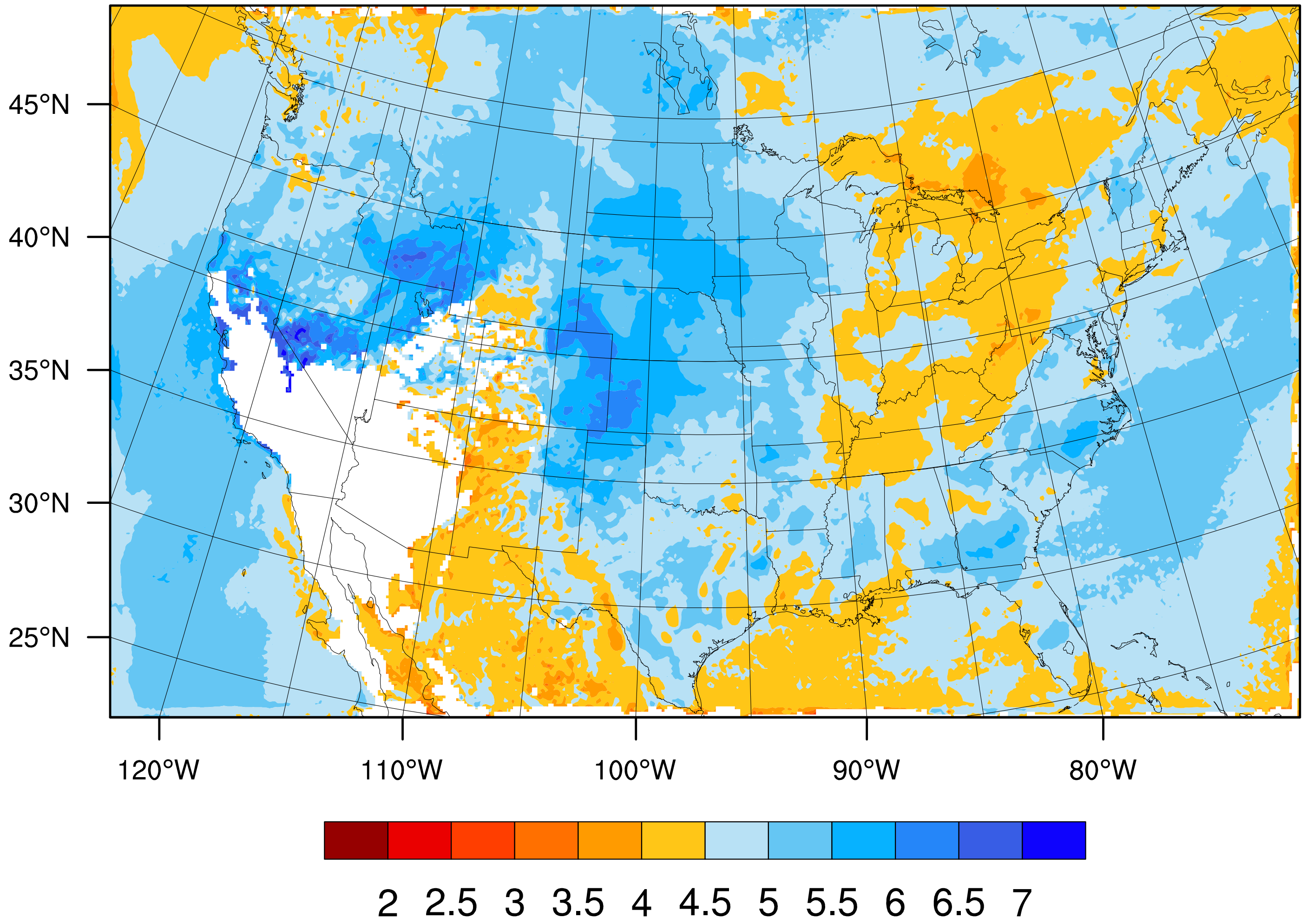
Average aerosol pH as a function of size



- Aerosol pH increases with size
- Very acidic aerosol in/near desert regions, but WRF-Chem includes only Ca^{2+} in pH calculation
- Need to investigate whether non-volatile cations, e.g. Fe^{3+}, Mn^{2+}, and other cations related to dust contribute to pH

Average pH of cloud water

LWC-weighted average pH for vertical column and 14-day time period



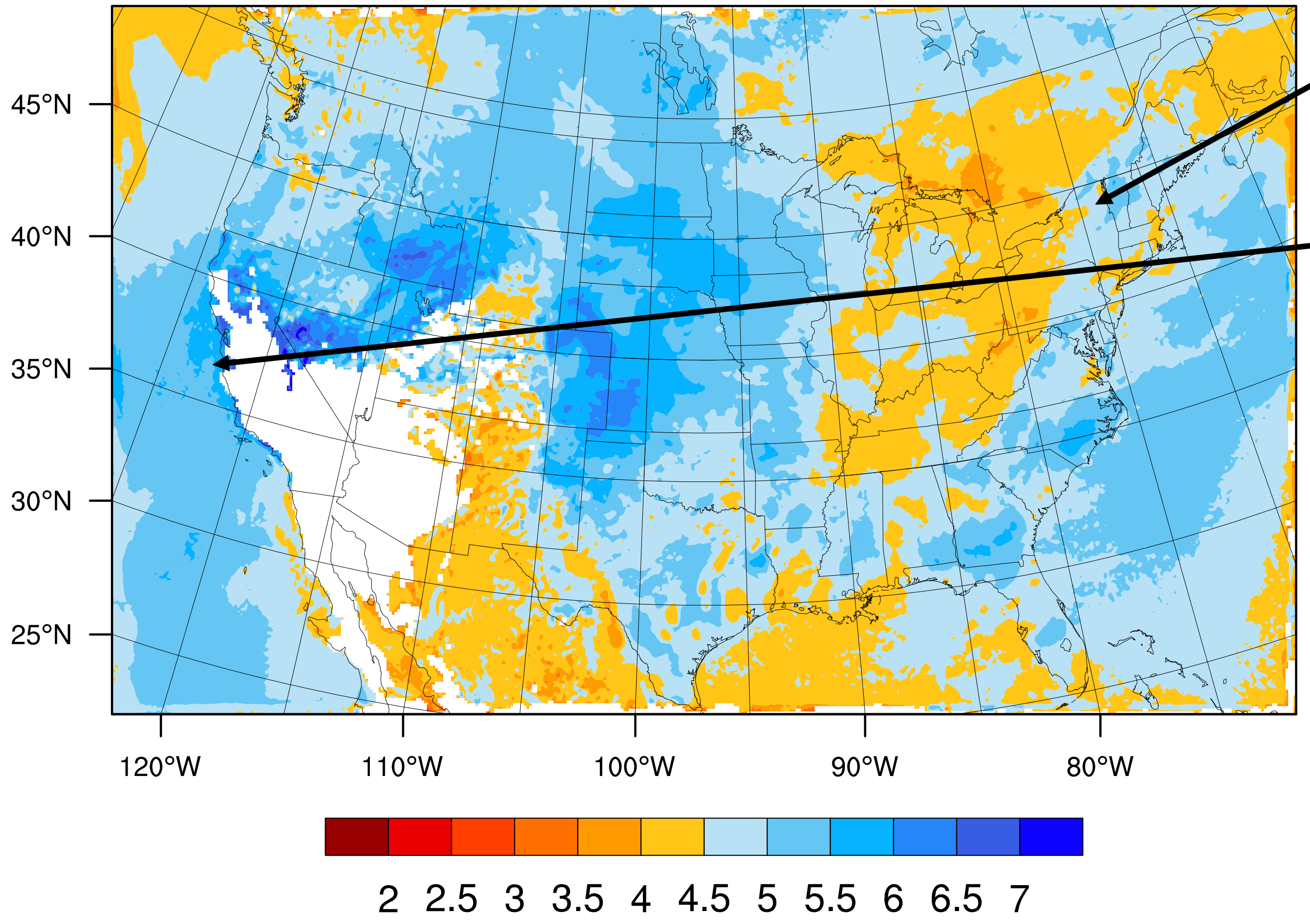
WRF-Chem Results

- pH < 4.5 in Ohio River Valley, Great Lakes region – sulfate contribution
- pH > 6 in agricultural regions – ammonium contribution

$$[H^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] + [HSO_3^-] + 2[SO_3^{2-}] + 2[SO_4^{2-}] + [NO_3^-] - [NH_4^+]$$

Average pH of cloud water

LWC-weighted average pH for vertical column and 14-day time period



4.8 at Whiteface Mtn Observatory (Schwab et al., 2016)

4.6 WRF-Chem

4.4 off coast of California, E-PEACE and NICE (MacDonald et al., 2018)

5.5 WRF-Chem

- Fairly good agreement, but more direct comparisons needed
- More measurements would be useful in regions where there are gradients (e.g., Central Plains to Midwest)

$$[H^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] + [HSO_3^-] + 2[SO_3^{2-}] + 2[SO_4^{2-}] + [NO_3^-] - [NH_4^+]$$

CAM Chemistry Configuration

Community Atmosphere Model with chemistry

Global model

- Δx = 0.9° x 1.25°, 56 vertical levels to 35 km
- CAM6 physics
- Meteorology driven by GEOS

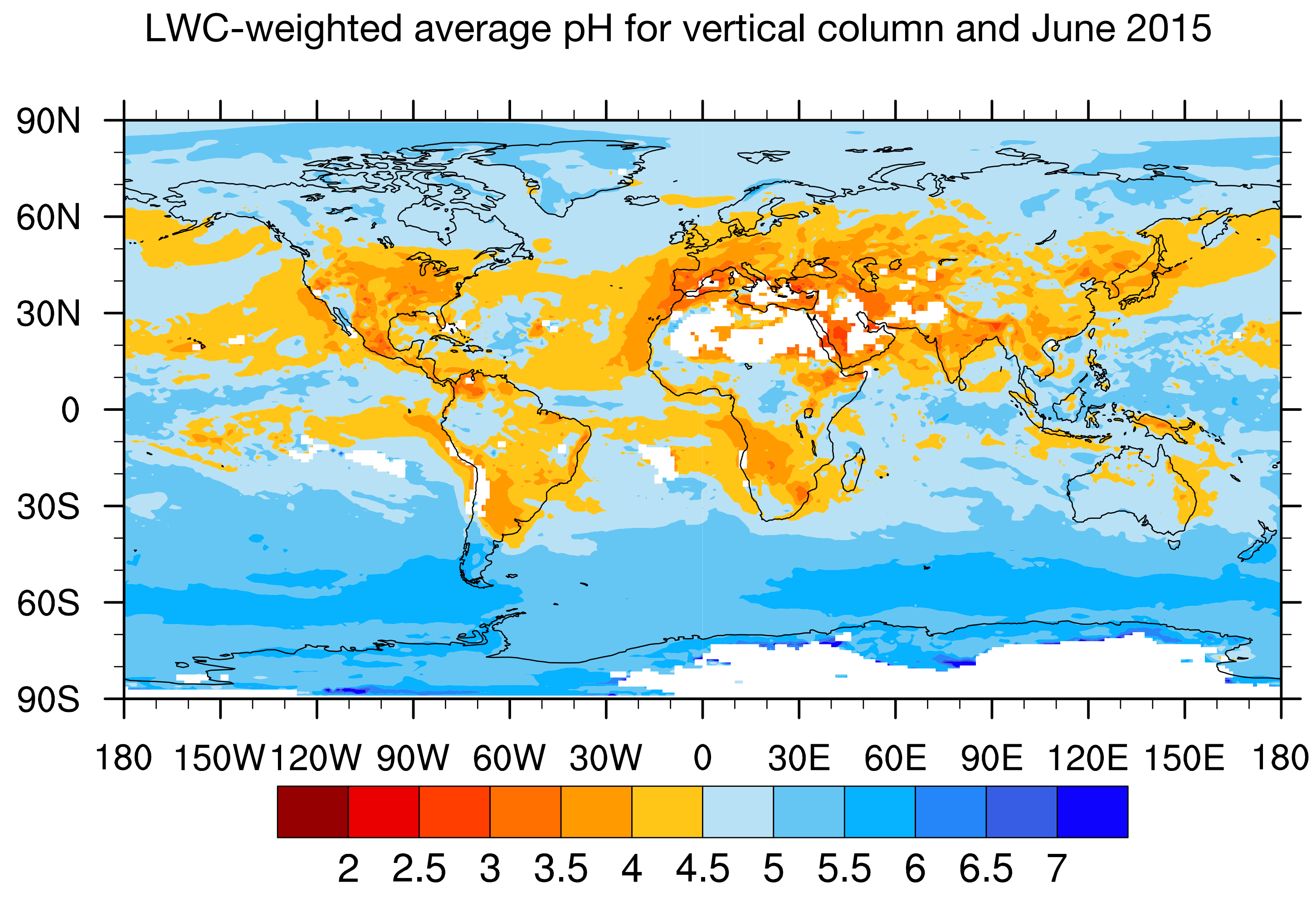
One-month simulation: June 1-30, 2015

MOZART T1 gas chemistry

Modal Aerosol Model (MAM4)

Simple sulfur aqueous chemistry

Average pH of cloud water

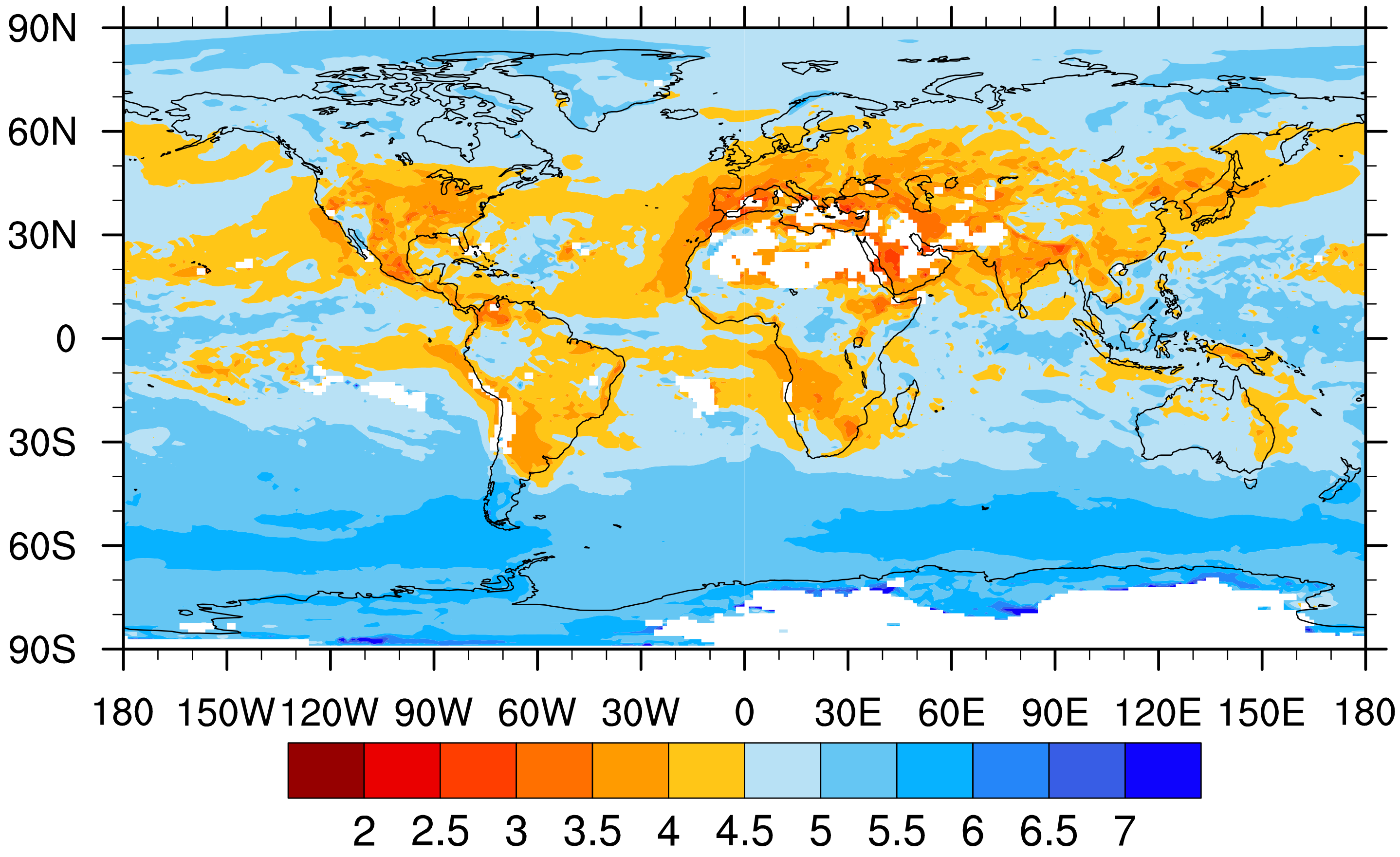


- More acidic in industrial regions
- Least acidic in polar regions, Southern Ocean

$$[H^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] + [HSO_3^-] + 2[SO_3^{2-}] + 2[SO_4^{2-}] + [NO_3^-] - [NH_4^+]$$

Average pH of cloud water

LWC-weighted average pH for vertical column and June 2015



4.9 at Mt. Tai,
4.4 CAM-chem

6.0 Shanghai, China
4.2 CAM-chem

7.6 Egypt ;
5.6 CAM-chem

7.3 Morocco
3.6 CAM-chem

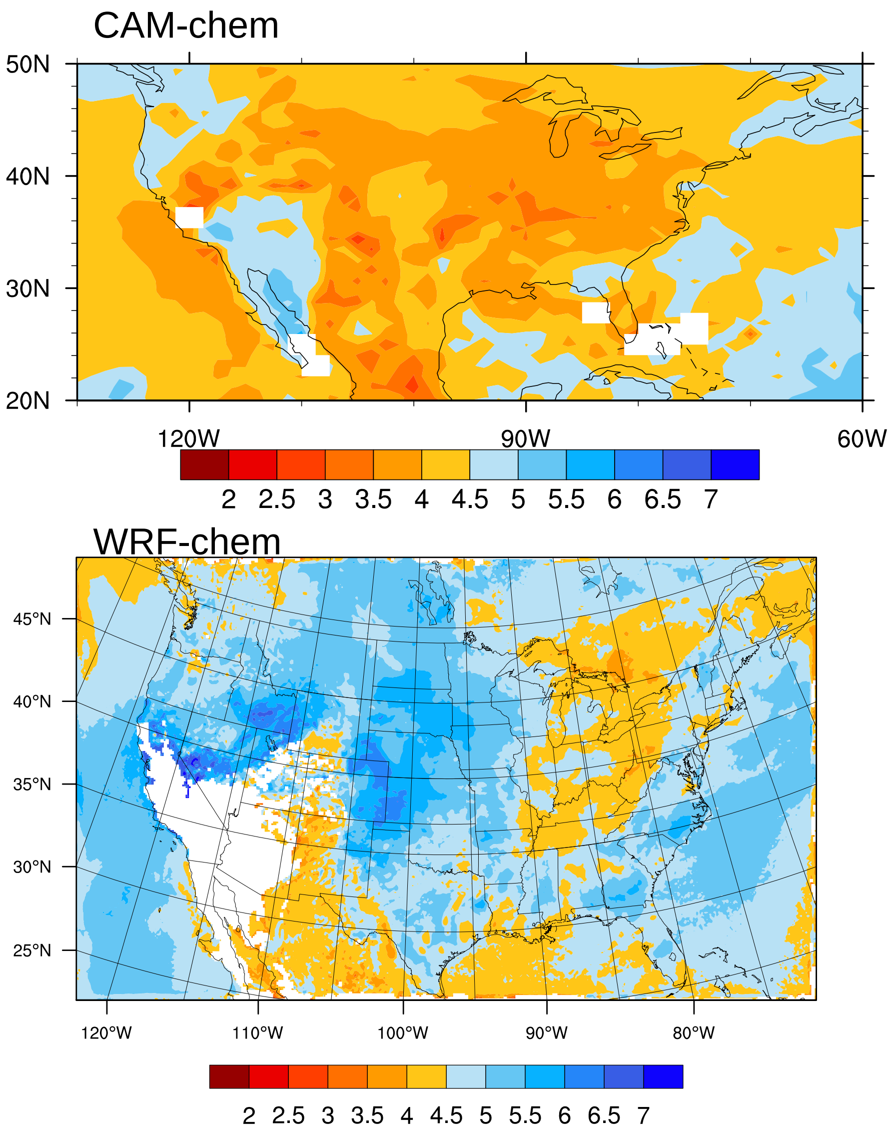
5.6 France ;
4.1 CAM-chem

5.0 Norway
4.6 CAM-chem

- Need to investigate whether non-volatile cations, e.g. Fe^{3+}, Mn^{2+}, and other cations related to dust contribute to cloud water pH

Average pH of cloud water

LWC-weighted average pH for vertical column



- Some similar regional patterns (Ohio River Valley, New Mexico – Colorado)
- Over ocean, WRF-Chem overpredicts pH, CAM-Chem underpredicts pH

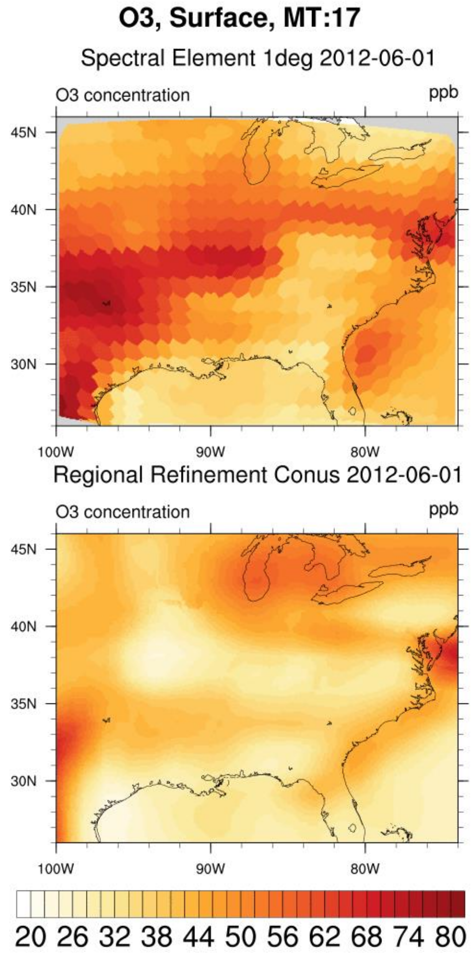
4.8 at Whiteface Mtn Observatory, New York
4.6 WRF-chem
4.2 CAM-chem

4.4 off coast of California, E-PEACE and NICE
5.5 WRF-chem
3.8 CAM-chem

Multiscale Infrastructure for Chemistry and Aerosols (MUSICA)

Developing a new modeling infrastructure to conduct global to regional to local scale simulations of atmospheric chemistry → MUSICA

- Model Independent Chemistry Module allows coupling with any atmosphere model
- Test of CAM-Chem on the spectral element grid mesh with regional refinement is the first realization of MUSICA
  - Linking MICM and MUSICA to the Model for Prediction Across Scales (MPAS) can address non-hydrostatic motions
- MUSICA is being co-developed with the community
  - MUSICA Kickoff Meeting 21-22 May 2019



Courtesy F. Lacey, R. Schwantes, S. Tilmes, N. Davis

Clouds affect air quality and tropospheric composition impacting climate

- Transport, wet deposition, and lightning-NO_x generation
- Modified photolysis rates
- Aqueous-phase chemistry