Prediction of acidity in WRF-Chem

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Why evaluate acidity?

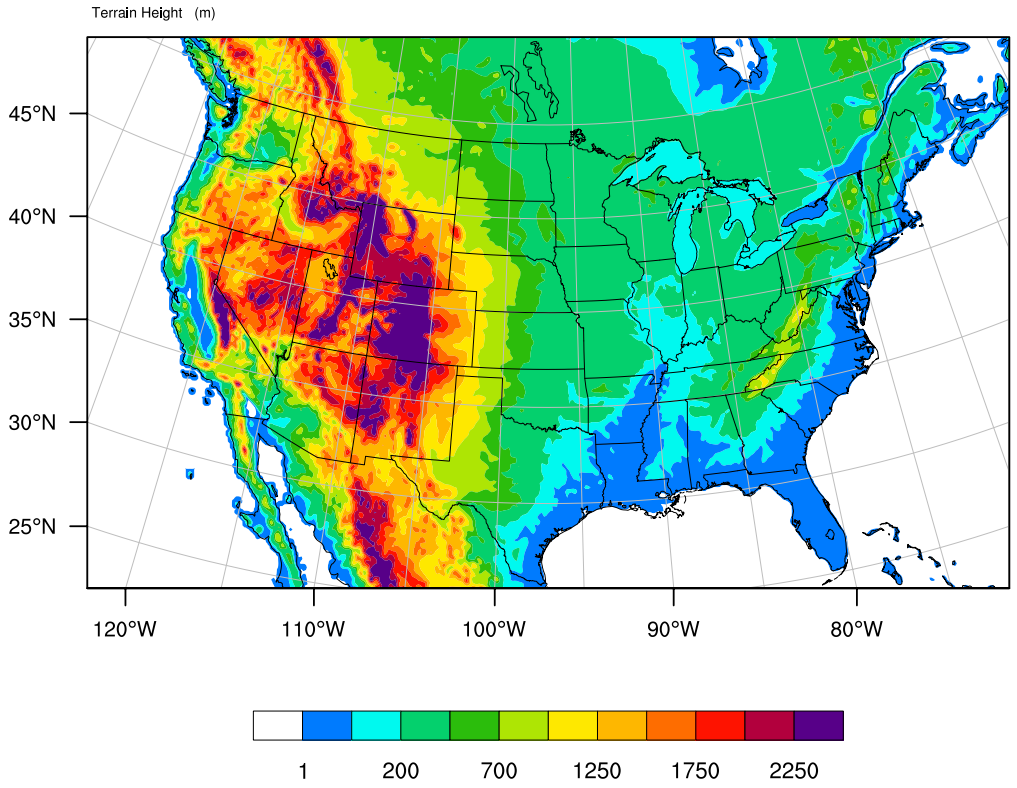
- Acid Rain
- Health Impacts of Aerosol Acidity
- Aqueous-phase chemistry depends on pH of drops or aerosols
- Acidity affects global nutrient cycles

The State of Acidity in Atmospheric Particles in Clouds

- Review article in preparation led by Havala Pye (EPA) and Thanos Nenes (EPFL)
  - 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
- ➢ WRF-Chem cloud water pH and aerosol pH have not been evaluated with observations, or with other models

WRF Configuration



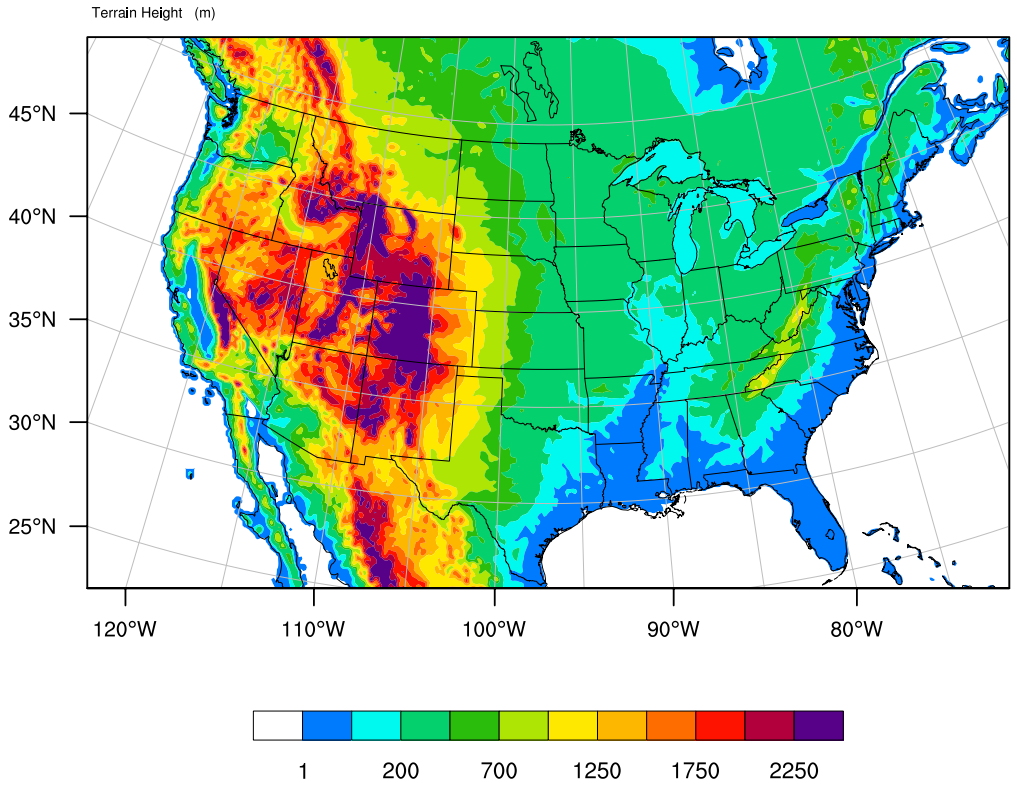
Continental US domain

- Δx = 12 km, 40 vertical levels to 50 hPa
- Cloud physics: Morrison 2-moment
- Radiation: RRTMG (sw and lw)
- PBL parameterization: MYJ
- Convective parameterization: GF
- Surface: Noah

- NAM initial/boundary conditions
- No DA or nudging

Two week simulation: June 1-14, 2013

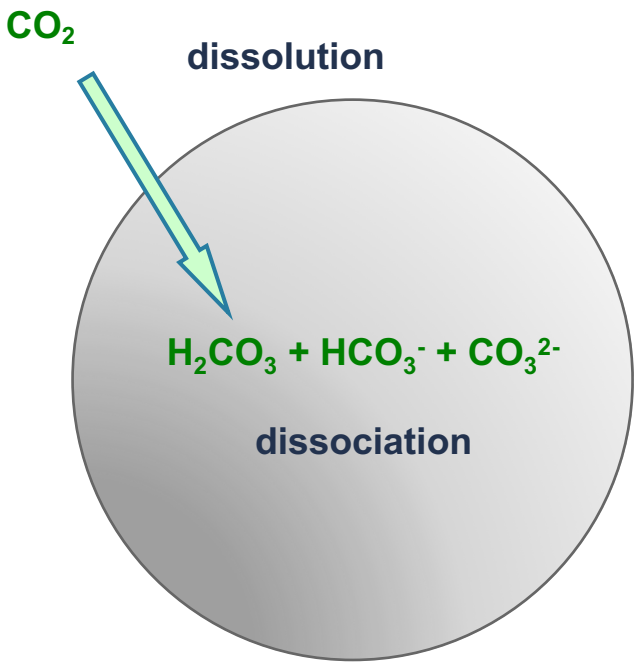
Chemistry Configuration



Chemistry Option 202

- 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

pH is a metric of acidity



Cloud drop

$pH = -\log10\ [H^+]$

$H_2O \leftrightarrow H^+ + OH^-$

CO_2 hydrates to H_2CO_3

$H_2CO_3 \leftrightarrow HCO_3^- + H^+$

$HCO_3^- \leftrightarrow CO_3^{2-} + H^+$

$[H+] = [OH-] + [HCO_3^-] + 2[CO_3^{2-}]$

pH = 5.6

- Cloud water and rain are naturally acidic

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-Chem Calculation of Acidity

Cloud water pH:

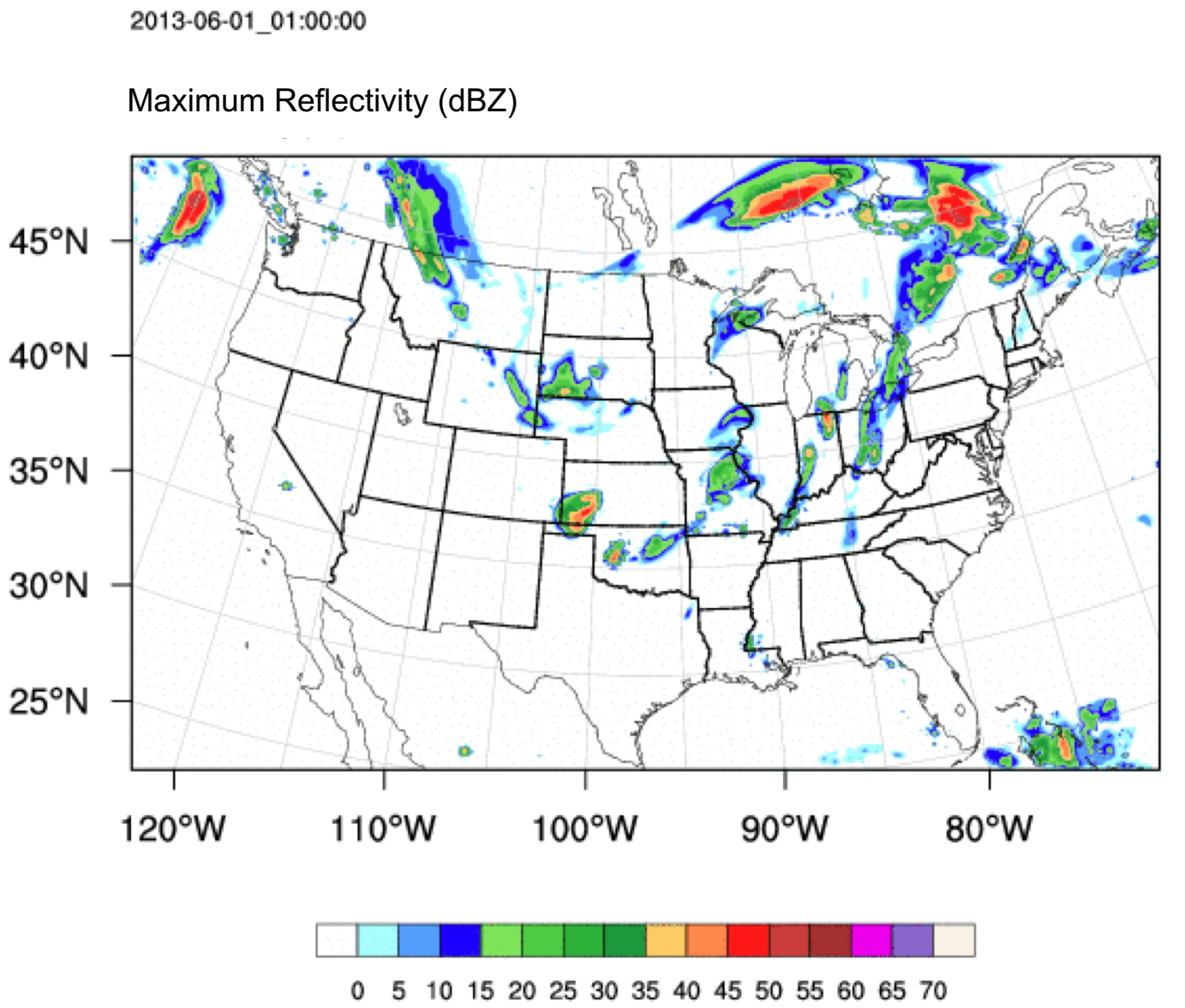
$$[H^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] + [HSO_3^-] + 2[SO_3^{2-}] + 2[SO_4^{2-}] + [NO_3^-] - [NH_4^+]$$

H_2O CO_2 SO_2 CCN HNO_3 NH_3

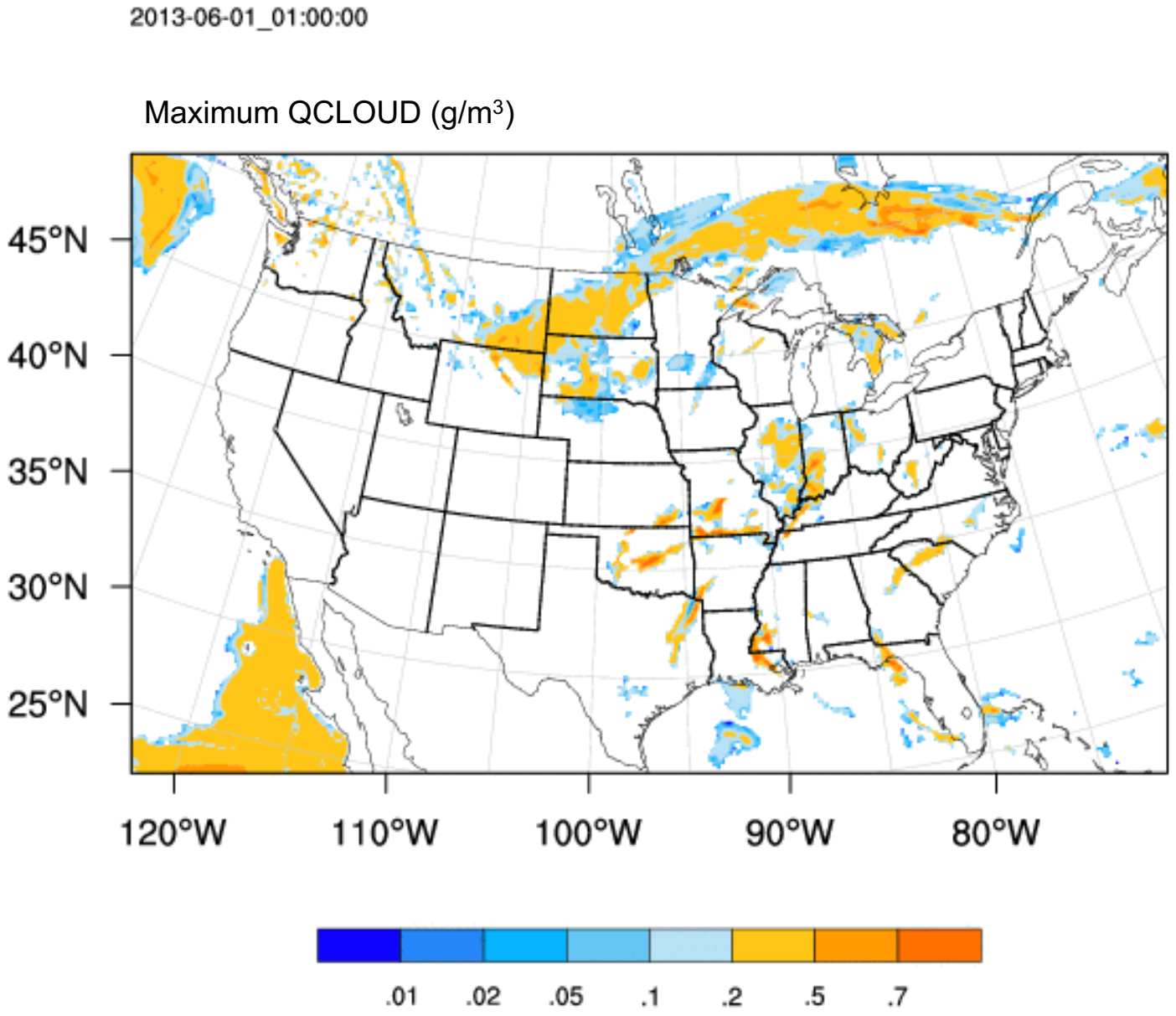
$$[H^+] = [OH^-] + 2[SO_4^{2-}] + [MSA^-] + [NO_3^-] + [Cl^-] + [HCO_3^-] + 2[CO_3^{2-}] - [NH_4^+] - [Na^+] - 2[Ca^{2+}]$$

- 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

Active period of storms

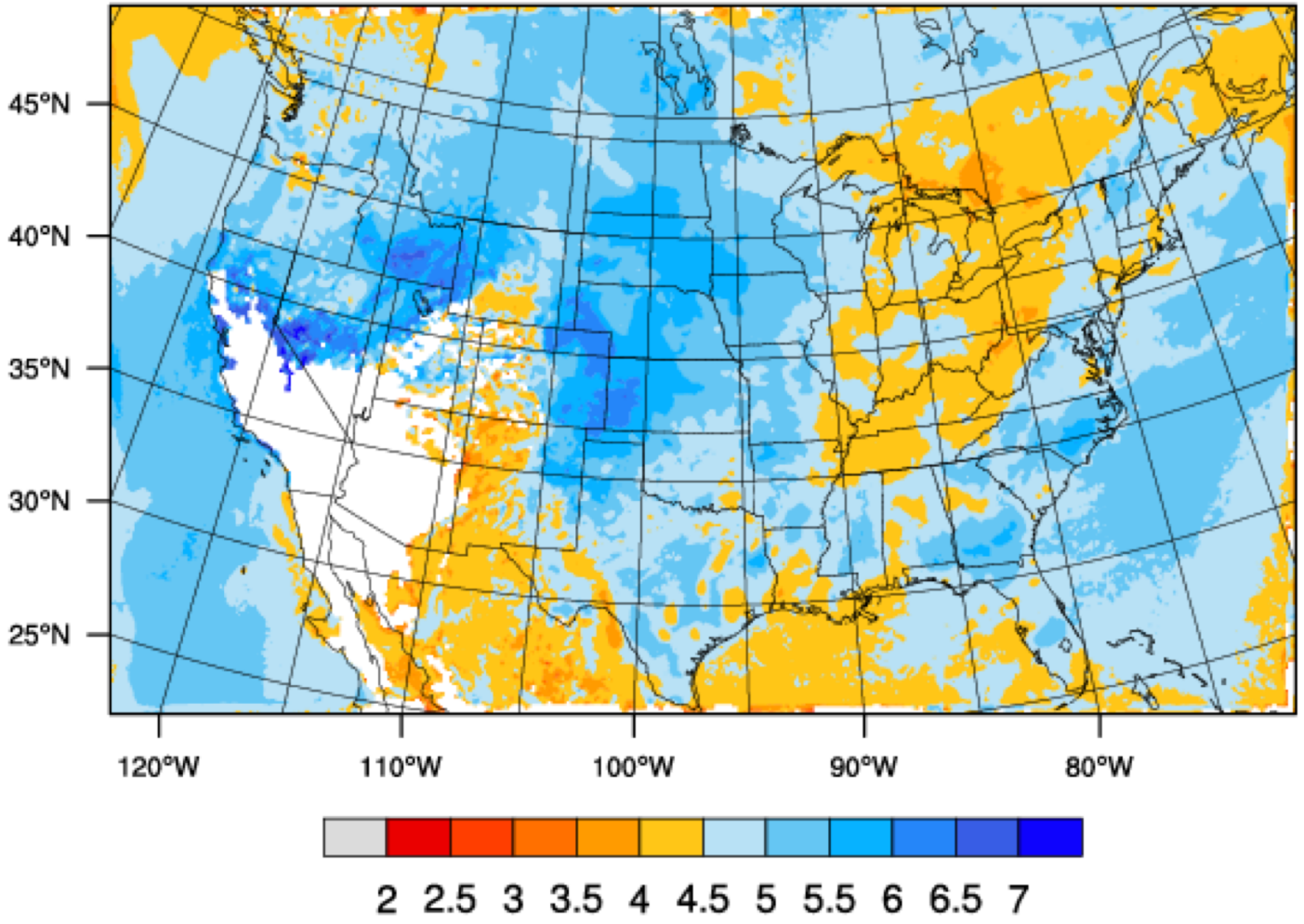


Active period of clouds except in SW US



Average pH of cloud water

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

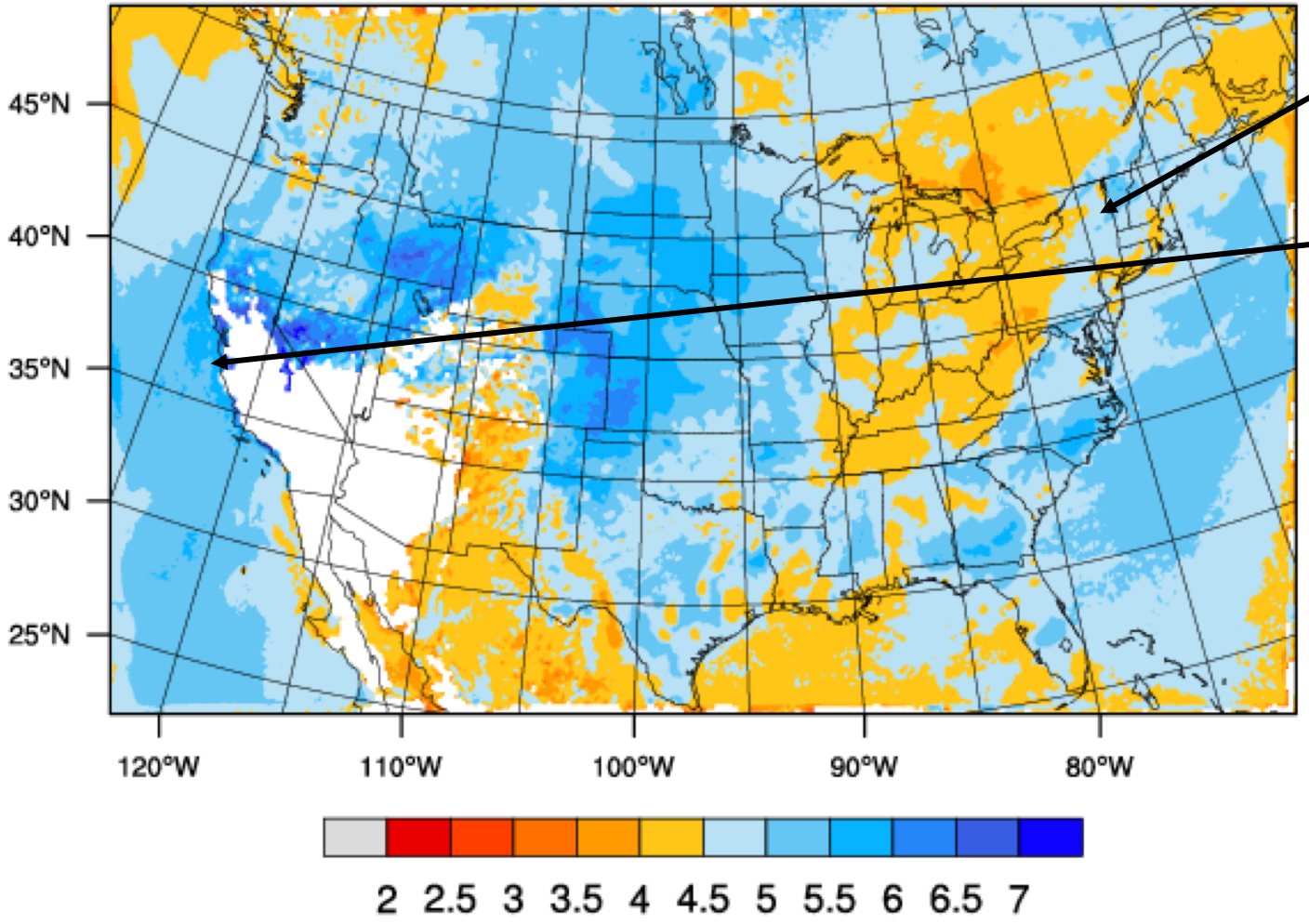


- pH < 4.5 in Ohio River Valley, Great Lakes region – sulfate contribution
- pH > 6 in agricultural regions – ammonium contribution

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

Average pH of cloud water

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



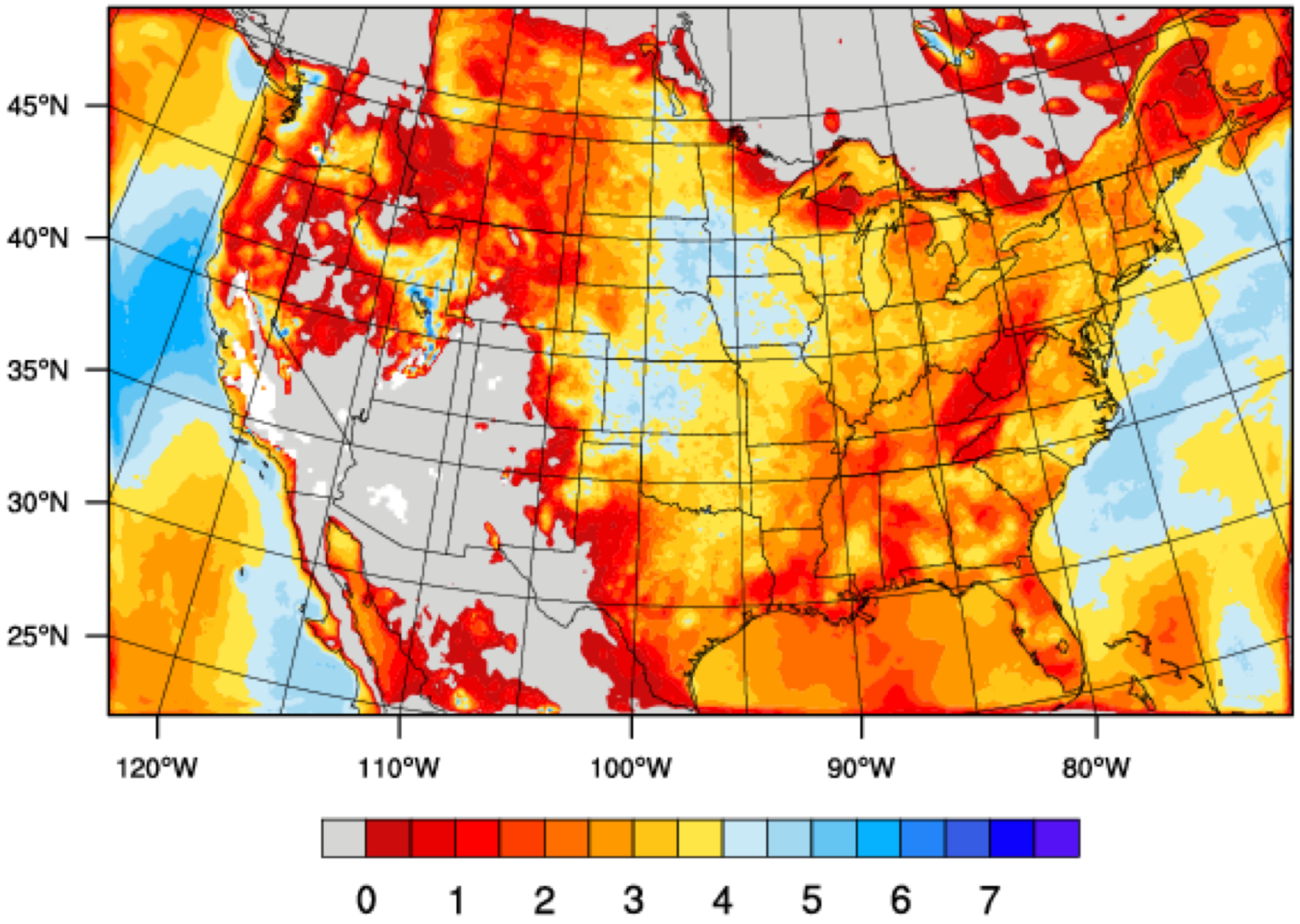
- ~4.7 at Whiteface Mtn Observatory (Schwab et al., 2016)
- ~4.2 off coast of California, E-PEACE and NICE (MacDonald et al., 2018)

- 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)

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

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

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

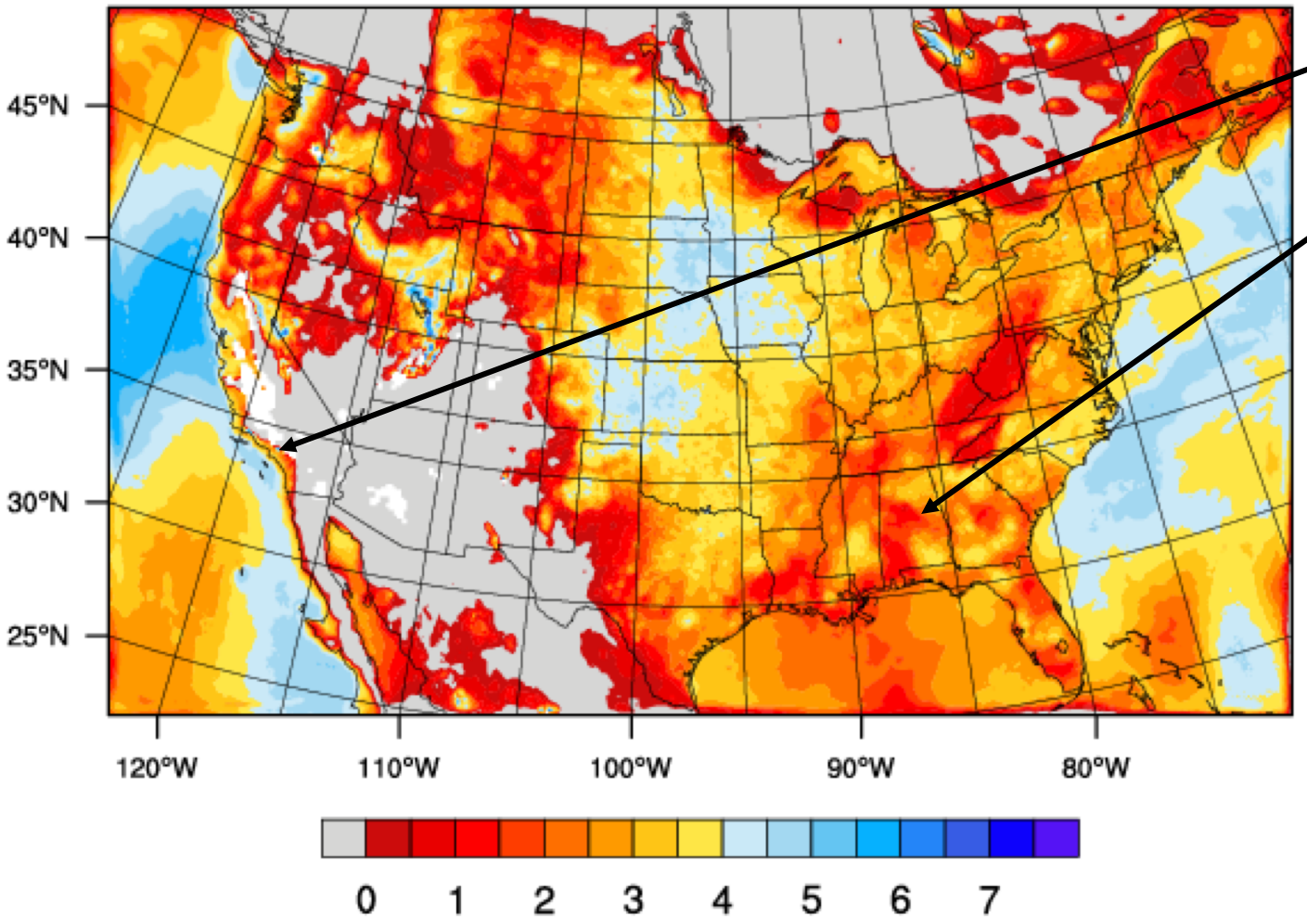


- Aerosol pH much lower than cloud water pH
- Highest pH values in Central U.S. (agricultural influence) and over ocean (sea salt)
- *But* model is *not* representing composition of aerosol over ocean because sulfate is not displacing chloride (no HCl in MOZART gas-phase mechanism

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

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

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

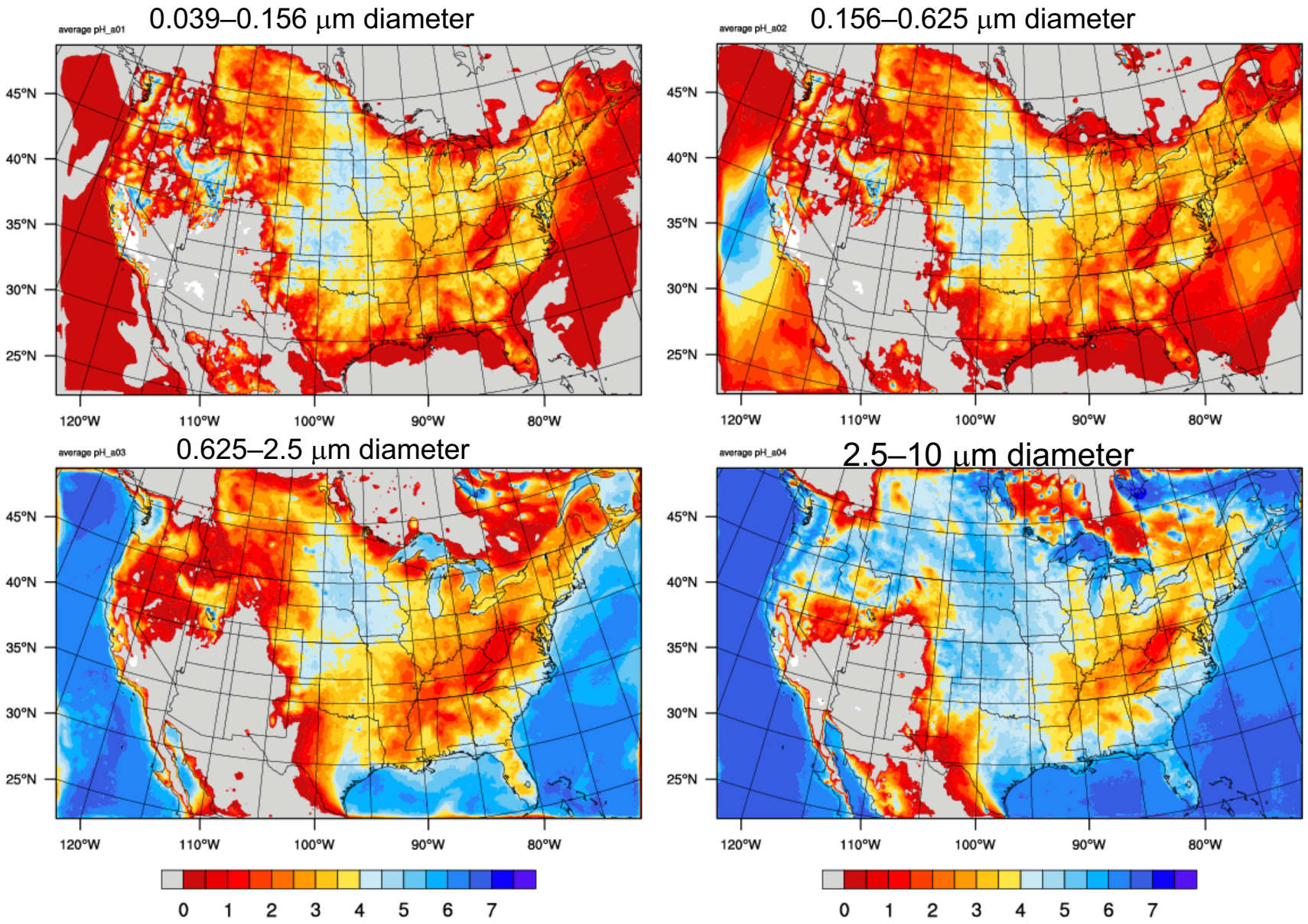


- 2.7 ± 0.3 at Pasadena, CA (Guo et al., 2017)
- 0.9 ± 0.6 at Centreville, AL (Guo et al., 2015)

- Fairly good agreement
- 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

Summary

First time acidity of cloud water and aerosols examined with WRF-Chem

- MOZART gas chemistry with the MOSAIC 4-bin aerosol scheme

- Cloud water pH fairly well predicted for continental US region
- Aerosol pH also fairly well predicted but sparse measurements
- Aerosol pH increases as size of aerosol increases

<u>Needs:</u>

- Account for HCl to represent sulfate displacement of chloride in sea salt aerosols
- Include organic acids in pH calculation
- More measurements, especially in other parts of the world (e.g. semi-arid regions, mix agriculture and urban)
- Account for non-volatile cations such as iron, manganese, etc related to dust