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# Regional impacts of extending inorganic and organic cloud chemistry with AQCHEM-KMT

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## 1. Background

- Many CTMs include only a simple representation of in-cloud chemistry, usually with a focus on a few SO<sub>2</sub> oxidation reactions
- Cloud water can provide a reaction medium for many other species and impact gas phase chemistry in surrounding air by preferentially scavenging more soluble species and altering them through chemistry
- Over the last decade much research has gone into characterizing SOA chemistry in the aqueous phase of cloud droplets and wet aerosols
- CMAQ's AQCHEM-KMT cloud chemistry module is well-suited for incorporating additional chemistry in clouds and investigating its impact on modeled concentrations

## 2. Cloud chemistry updates

**Existing CMAQ cloud chemistry:** AQCHEM-KMT<sup>1</sup> includes S(IV) to S(VI) oxidation via 5 pathways (i.e., H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>, O<sub>2</sub> catalyzed by Fe<sup>3+</sup>/Mn<sup>2+</sup>, CH<sub>3</sub>OOH, CH<sub>3</sub>C(O)OOH) and yield-based SOA formation from glyoxal and methylglyoxal. AQCHEM-KMT1 also includes SOA formation from biogenic epoxides. The Kinetic PreProcessor (KPP)<sup>2</sup> is used to generate the solver and related subroutines to solve a system of ODEs that describe the phase transfer, dissociation, chemical reactions, interstitial aerosol scavenging, and wet deposition for each species.

In this work we add the following reactions to investigate the impacts of additional S, N, O-H chemistry as well as more mechanistic SOA chemistry on select gas and aerosol concentrations for a winter/summer period:

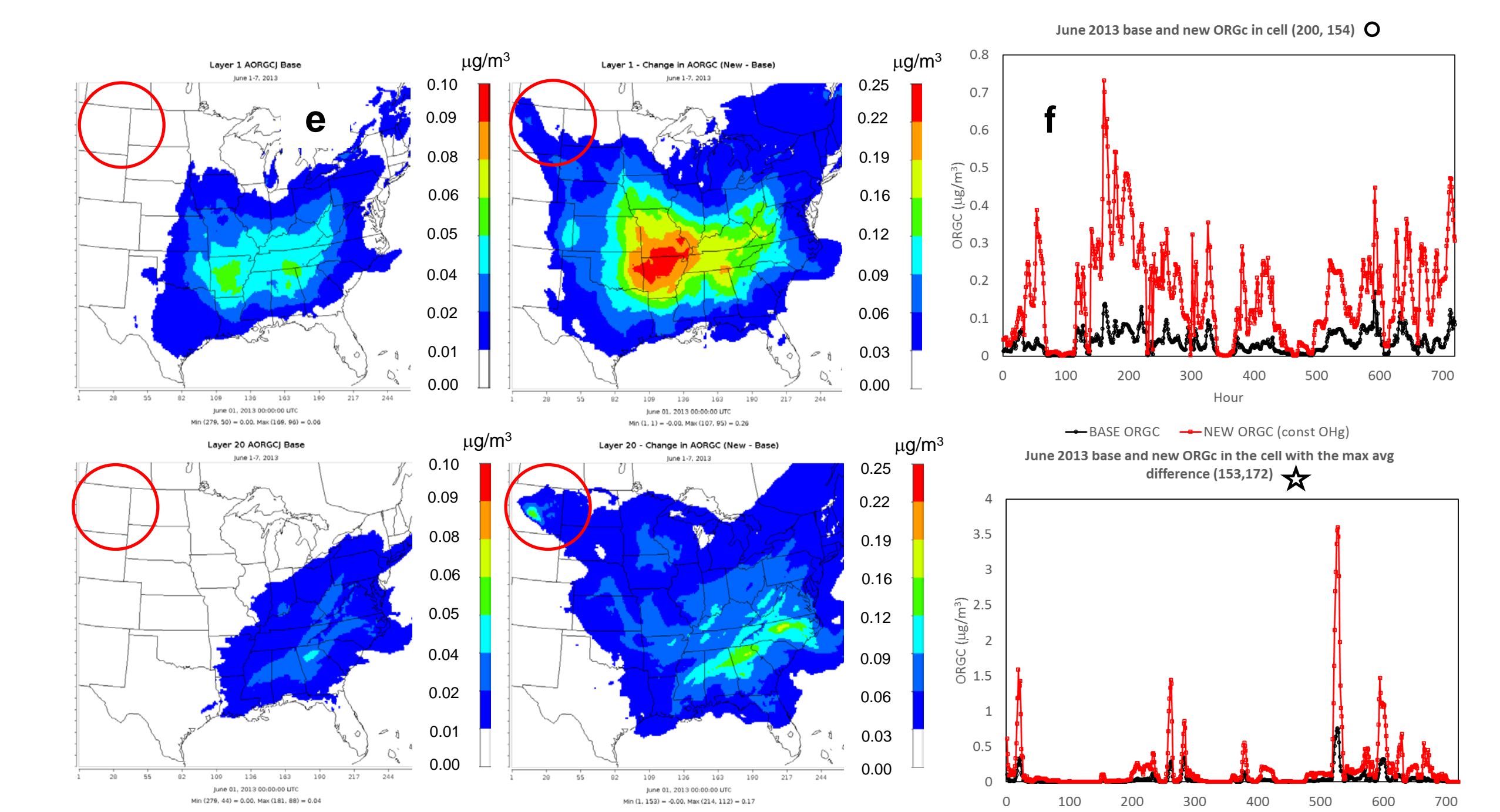
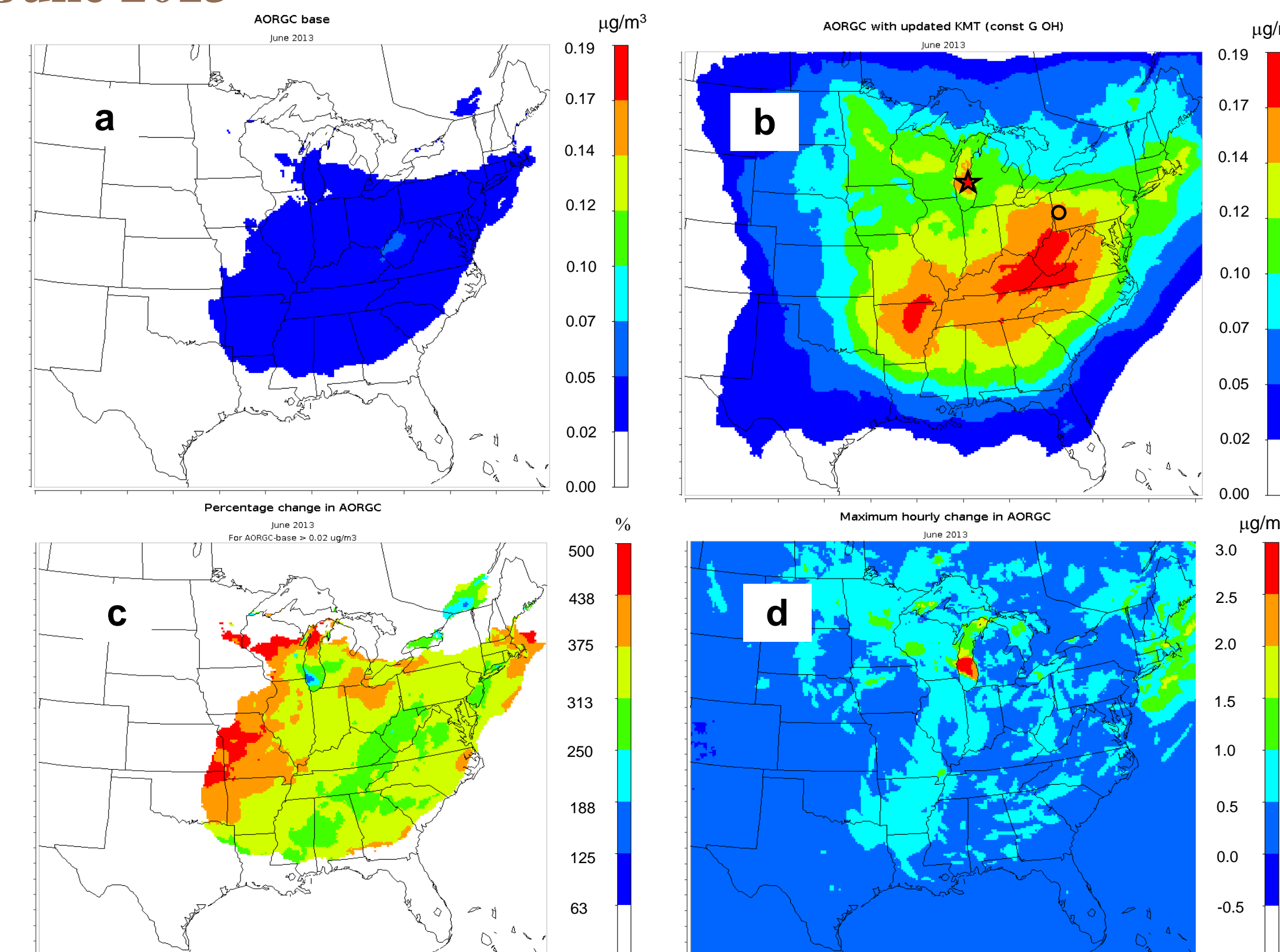


<sup>1</sup>Fahey et al., 2017; <sup>2</sup>Damian et al., 2002; <sup>3</sup>mostly from ReLACS-AQ (Lerliche et al., 2013) unless otherwise noted; <sup>4</sup>max photolysis rates adjusted according to the solar zenith angle, soon to be updated with photolysis rates calculated inline; <sup>5</sup>Warneck, 1999; <sup>6</sup>Lee and Schwartz, 1983; <sup>7</sup>based on Lim et al. (2005) and Tan et al. (2009) and updated by Sareen et al., 2013. Gas phase OH is held constant during the model sync step to minimize errors from solving gas and aqueous phase chemistry separately. Upon droplet evaporation, new organic acids are added to the existing cloud SOA species "AORGC".

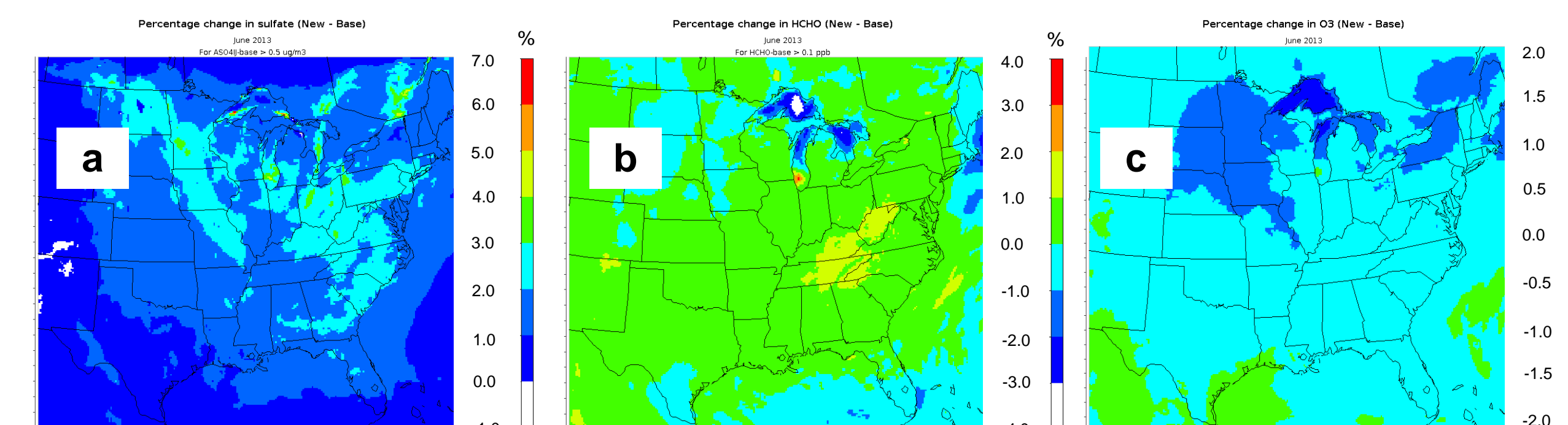
## 3. CMAQ simulations for summer/winter months

	Summer	Winter
CMAQ version	5.2	5.2-beta
Gas phase mechanism	saprc07tic_ae6i_aq	cb05e51_ae6nvPOA_aq
Aqueous chemistry	AQCHEM-KMT1 + all new reactions, removing standard GLY/MGLY+OH parameterization Base case: AQCHEM-KMT1	AQCHEM-KMT + new "inorganic" reactions (i.e., not new in-cloud SOA chemistry). Base case: AQCHEM-KMT
Modeled Period	June 1-30, 2013 (+11 days spinup)	January 1-31, 2011 (+10 days spinup)
Domain	Eastern U.S., 12-km, 35 layers up to 100mb	CONUS, 12-km, 35 layers up to 50 mb

### June 2013

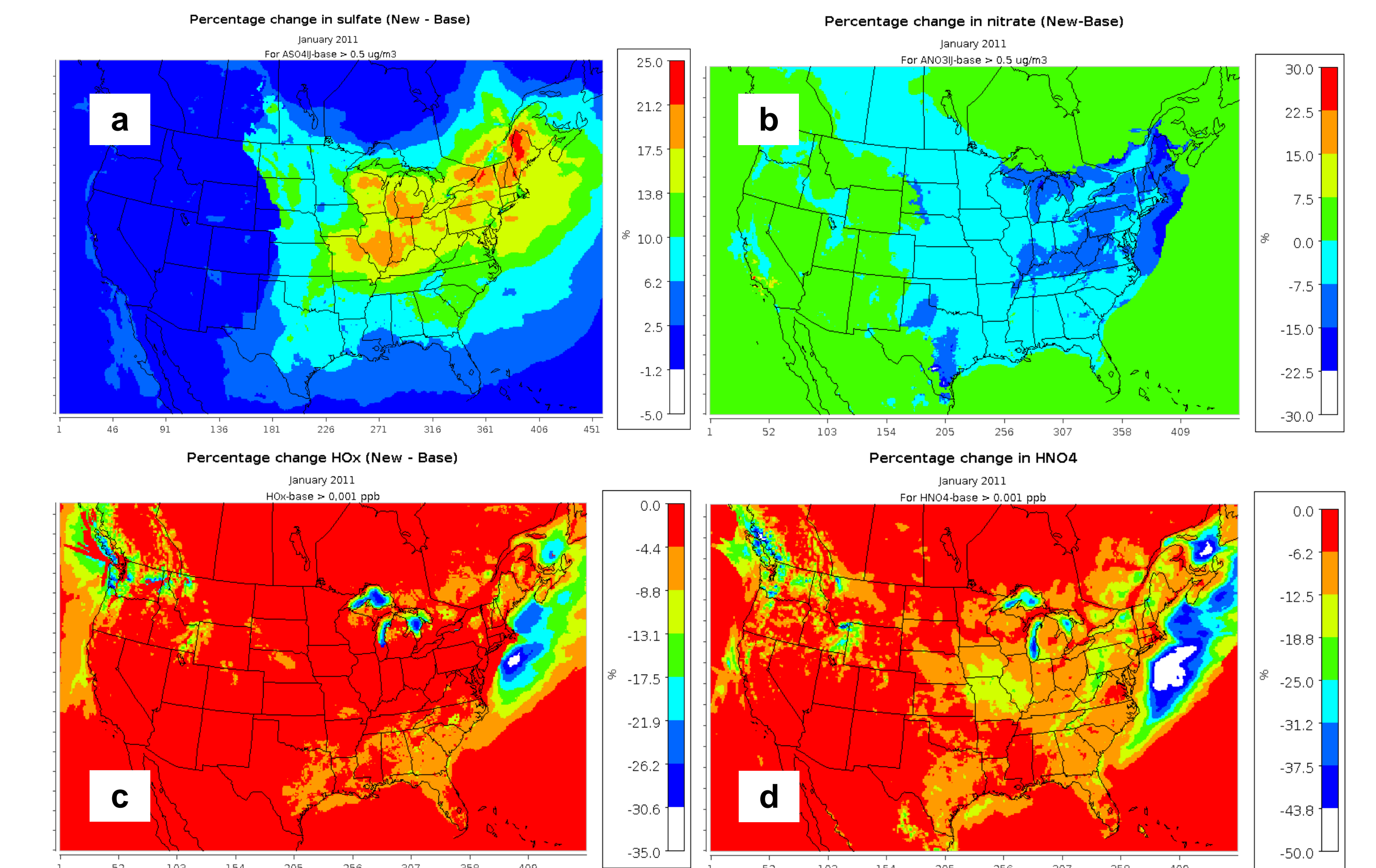


**Figure 1.** June average surface (a) AORGC<sub>base</sub> and (b) AORGC<sub>new</sub>. AORGC is in-cloud SOA formed from GLY, MGLY, (GCOL, CCOOH). (c) % change in AORGC (New-Base); (d) Maximum hourly ΔAORGC (e) (from top left, clockwise) Weekly average (Jun 1-7) surface layer AORGC<sub>base</sub>, surface layer ΔAORGC (New-Base), Layer 20 ΔAORGC (New-Base), and Layer 20 AORGC<sub>base</sub>. (f) time series of base and new AORGC for a cell in western PA (circle in fig 1b) and the cell with max ΔAORGC (star in fig 1b).



**Figure 2.** June average % differences between the updated and base cases for (a) sulfate, (b) HCHO, and (c) O<sub>3</sub>. Monthly average differences are small for these species during June. Maximum hourly differences can be large (7.9 μg/m<sup>3</sup>, 3 ppb, and 17 ppb for sulfate, HCHO, and O<sub>3</sub> respectively), though large differences are limited in area.

### January 2011



**Figure 3.** % change in January average (a) sulfate, (b) nitrate, (c) HOx, and (d) HNO<sub>4</sub> (New - Base). Average O<sub>3</sub>, HCHO, and NOx saw only small impacts over CONUS.

## 4. Summary and ongoing work

CMAQ's AQCHEM-KMT(I) cloud chemistry module was further updated with an expanded mechanism with additional reactions for sulfur, nitrogen, organic, and other species and replacing the simple yield parameterization of in-cloud SOA from (methyl)glyoxal to a mechanistic representation of SOA production from glyoxal, methylglyoxal, glycolaldehyde, and CH<sub>3</sub>COOH. A set of base-case and updated CMAQ simulations were run over the E. US for June 2013 and CONUS for Jan 2011. Base/updated model comparisons showed:

- summer**
  - 300+% increase in surface level "cloud SOA" concentrations
  - Elevated cloud SOA at both the surface and aloft; spatial distributions can differ in part due to additional precursors in the new mechanism
  - Average impacts on sulfate, HCHO, and O<sub>3</sub> are on the order of a few percent or less. Significantly larger impacts can be seen hourly, but those are sporadic and limited in area
- winter**
  - Average sulfate increased up to 25%, with the largest impacts in the Ohio River Valley through the Northeast
  - Average nitrate decreased up to 30% with a similar pattern as sulfate in the eastern half of the domain; nitrate increased up to 30% in parts of SoCal
  - Average HOx saw decreases up to 36% in some areas, with a spatial distribution similar to a combination of the sulfate and HOx changes. HNO<sub>4</sub> has been observed to contribute a significant amount to in-cloud S(IV) conversion in some areas (Ervens, 2015). HNO<sub>4</sub>, NO<sub>2</sub>, and OH contribute to new oxidation pathways for S(IV) in the updated chemistry here.
  - HCHO, and NOx saw only small impacts over CONUS (~2% or less)
  - HNO<sub>4</sub> saw decreases up to ~60% in some areas, with a spatial distribution similar to a combination of the sulfate and HOx changes.

Ongoing tasks include evaluating model results against available data, adding explicit tracking in CMAQ for the organic acids produced in-cloud, and development of a hybrid AQCHEM-KMT+ module that allows for equilibrium or dynamic mass transfer depending on the species/conditions to boost model efficiency.

**References:** Damian et al., 2002, Computers and Chemical Engineering, 26(11), 1567-1579. • Ervens, 2015, Chem. Rev., 115, 4157-4198 • Fahey et al., 2017, Geosci. Mod. Dev., 10, 1587-1605. • Lerliche et al., 2013, Geosci. Mod. Dev., 6, 1275-1298. • Lee and Schwartz, 1983, Precipitation Scavenging, Dry Deposition, and Resuspension, v1 • Lim et al., 2005, Environ. Sci. Technol., 39, 4441-4446. • Sareen et al., 2013, CMAS 2013. • Tan et al., 2009, Env. Sci. Technol. 43, 8105-8112. • Warneck, 1999, Phys. Chem. Chem. Phys., 1, 5471-5483.