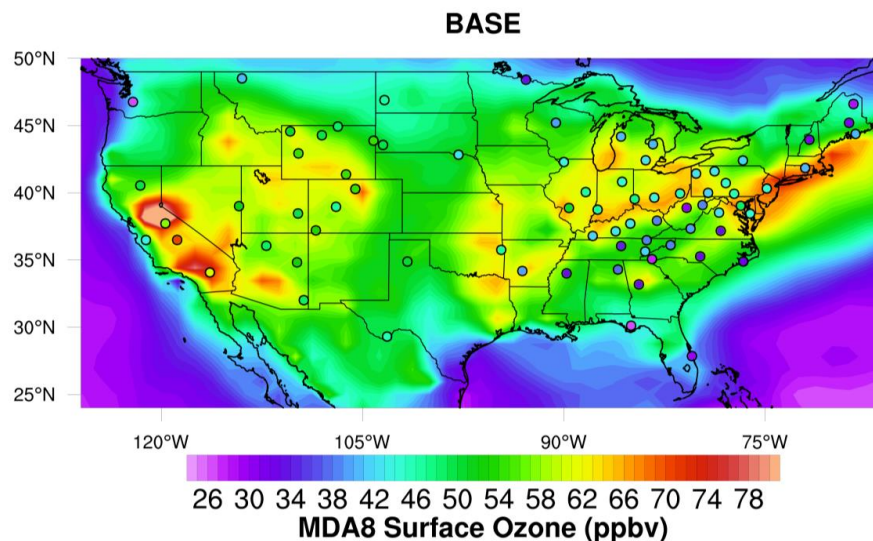


Uncertainties in Isoprene and Terpene Chemistry Impact on Simulated Surface Ozone in the United States

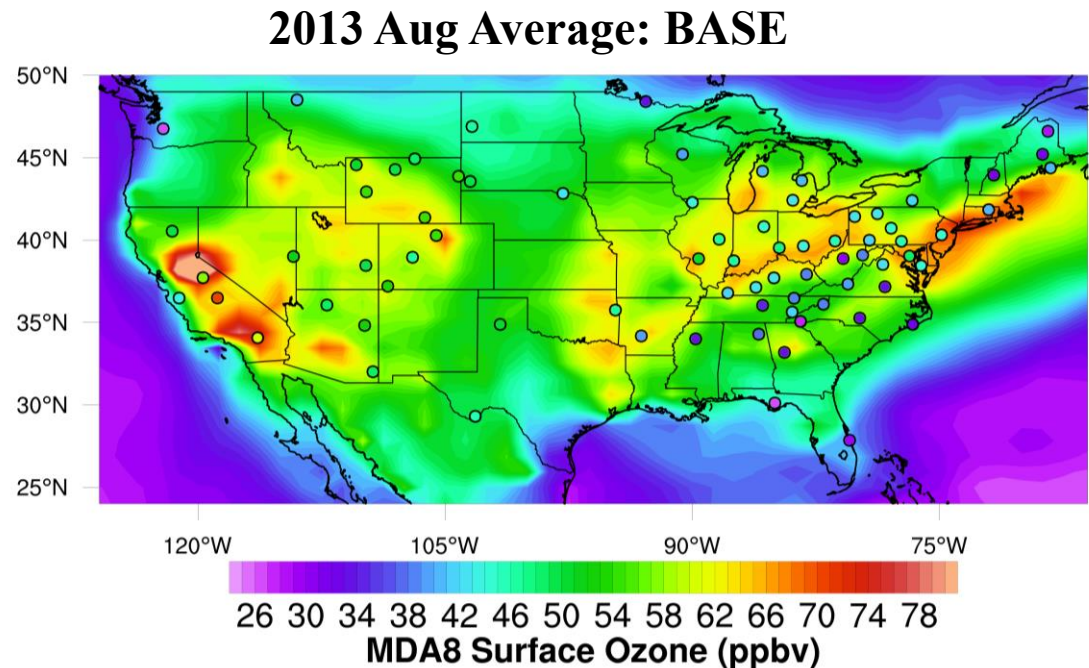
Rebecca (Becky) H. Schwantes, Louisa K. Emmons, John J. Orlando,
Geoffrey S. Tyndall, Simone Tilmes, Mary Barth, Sam Hall, Kirk
Ullmann + SEACR⁴S Science Team

CESM Winter Working Group Meeting 2019



The Problem:

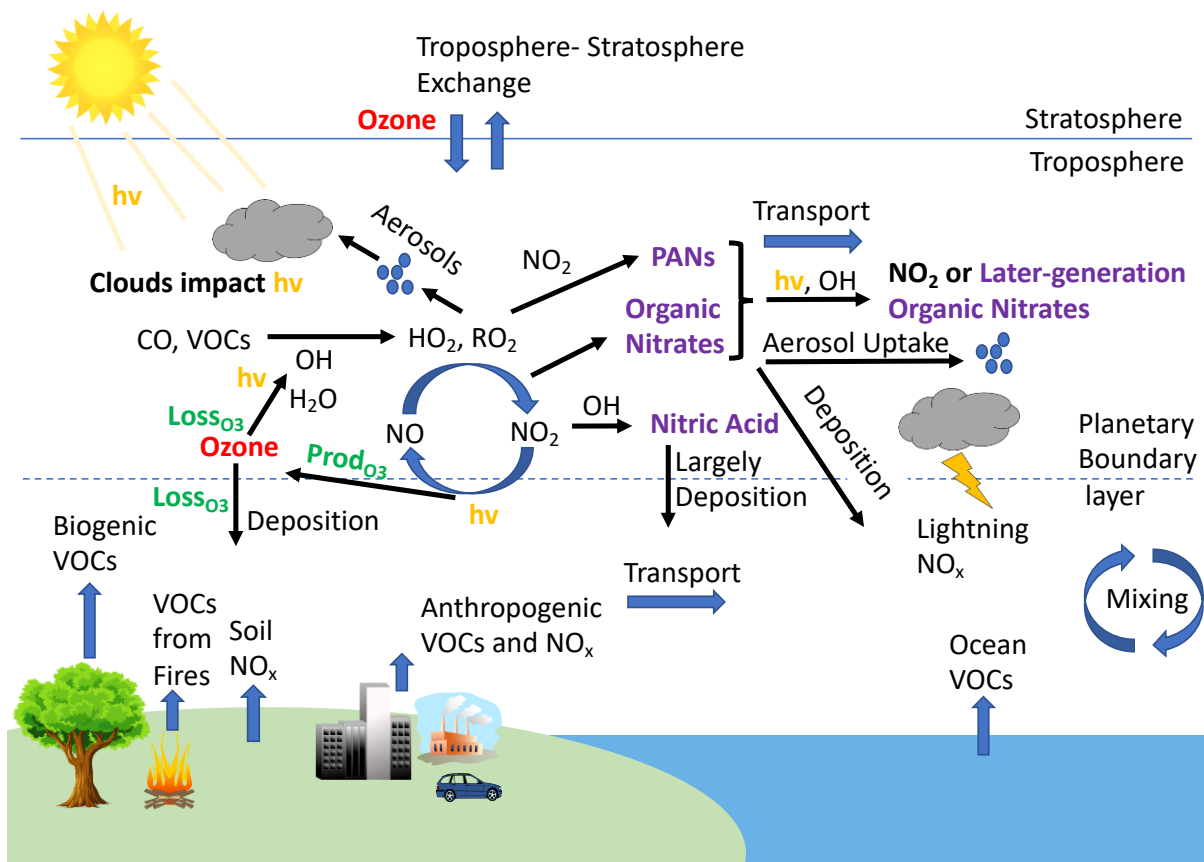
- Ozone is consistently over-predicted in the Southeast U.S. during the summer in CESMTM/CAM-chem.
- The U.S. EPA recently strengthened the ozone standard and new studies suggest ozone more significantly impacts human health than previously thought (e.g., Turner et al. 2016).
- Ozone is a complicated pollutant to simulate as it is not directly emitted and production and loss pathways are non-linear
 - Oxidation Chemistry + Wet/Dry Deposition + Aerosol uptake
 - Emissions of VOCs and NO_x
 - Clouds (i.e. NO₂ photolysis)
 - Dynamics (e.g., planetary boundary layer height/mixing)
 - O₃ deposition



MDA8 = Maximum daily 8 hr average

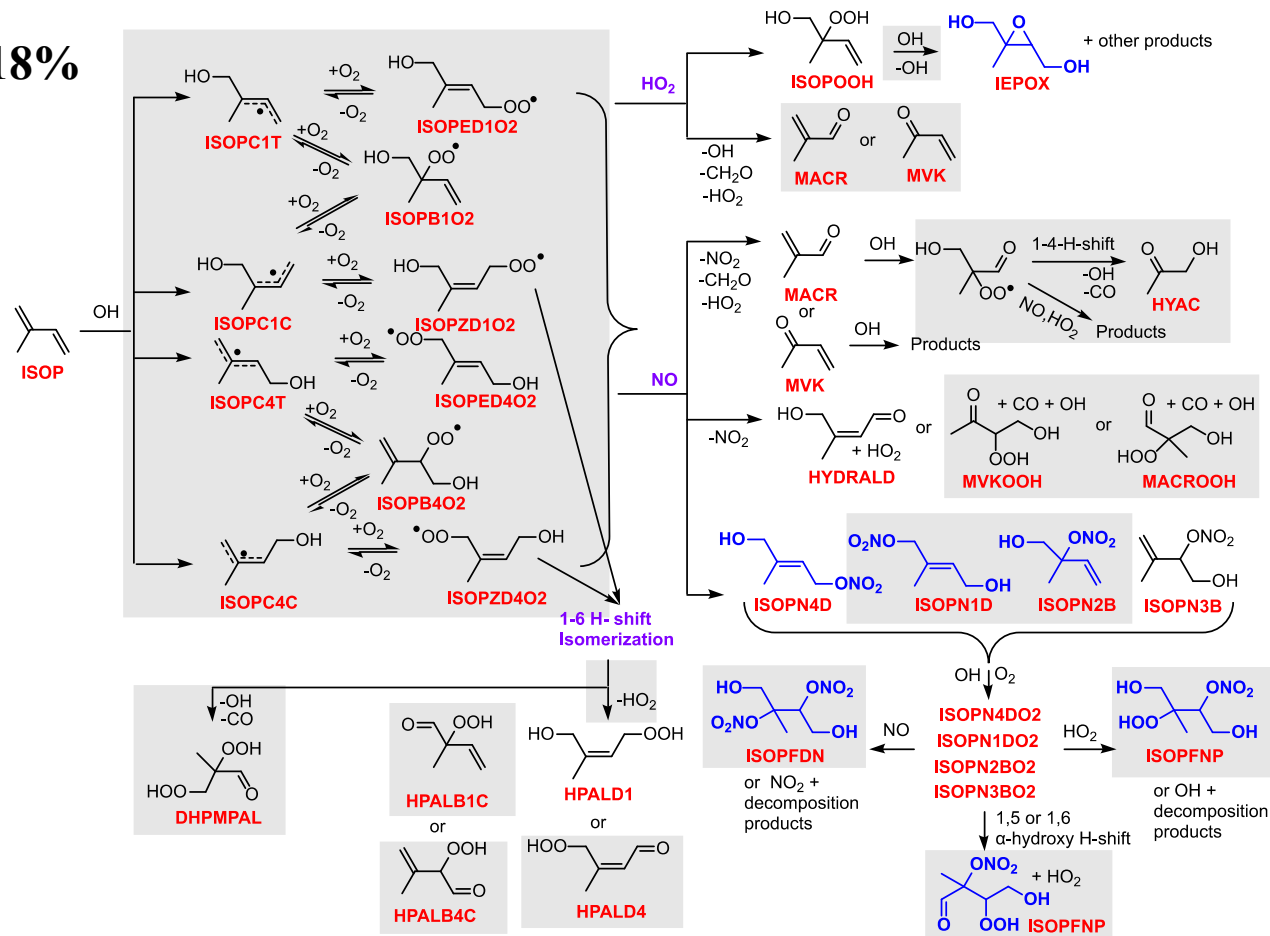
Objectives:

- Use the Community Earth System Model (CESM™)/Community Atmosphere Model (CAM)-Chem to:
 - Update isoprene and terpene chemistry based on experimental results in literature.
 - Evaluate the relative impact of various assumptions and uncertainties in the isoprene and terpene chemical mechanism on simulated surface ozone (O_3).



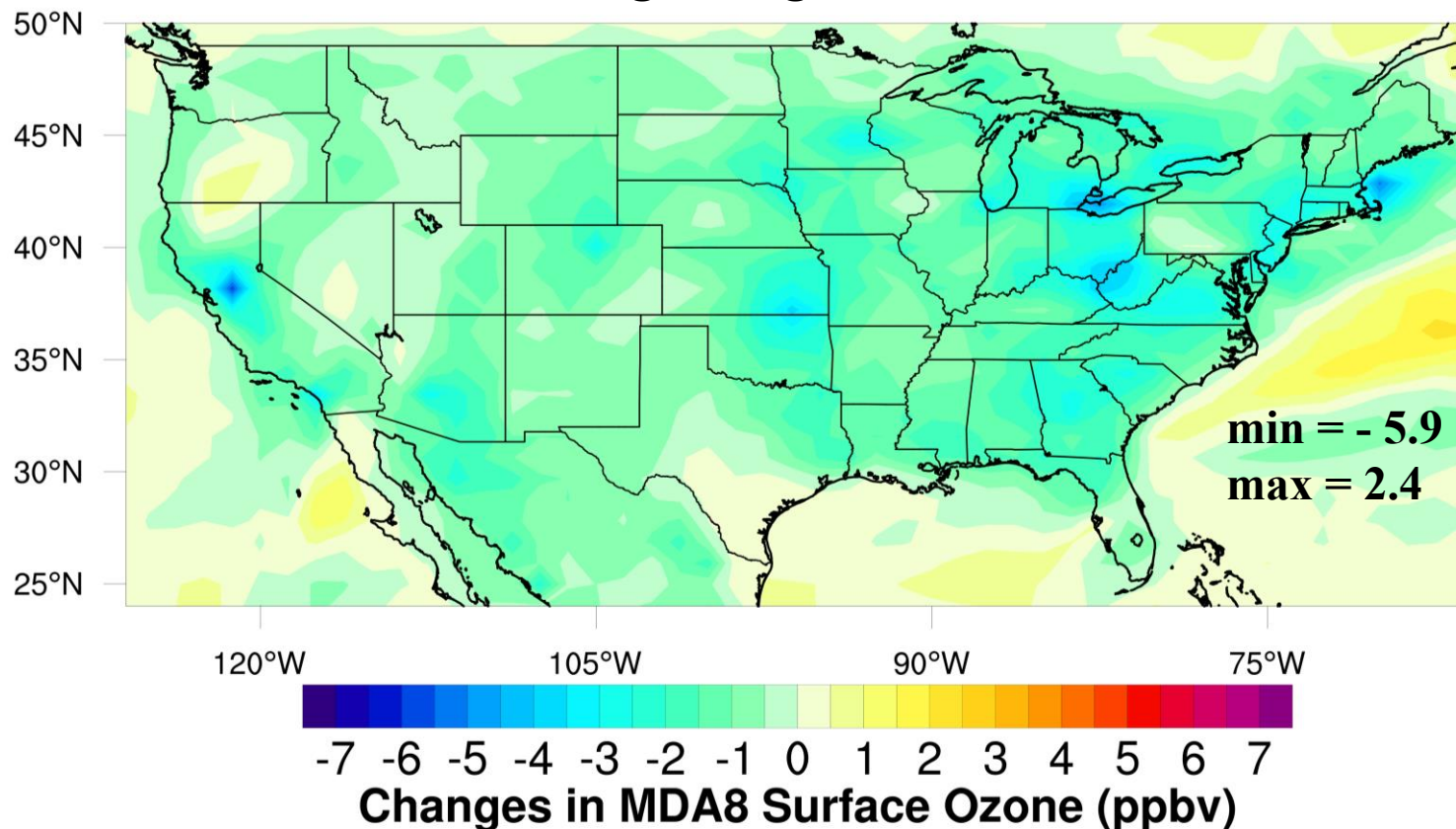
Isoprene Chemistry Updates:

- Updated isoprene chemistry with a specific focus on more completely describing later generation organic nitrate formation and fate.
- Transported species added: **21**
- Non-transported species added: **18**
- Reactions added: **139**
- Increase in run time: **18%**
- For context, the T1 chemical mechanism has 221 species and 528 reactions



Isoprene Chemistry Updates Impact on Surface Ozone:

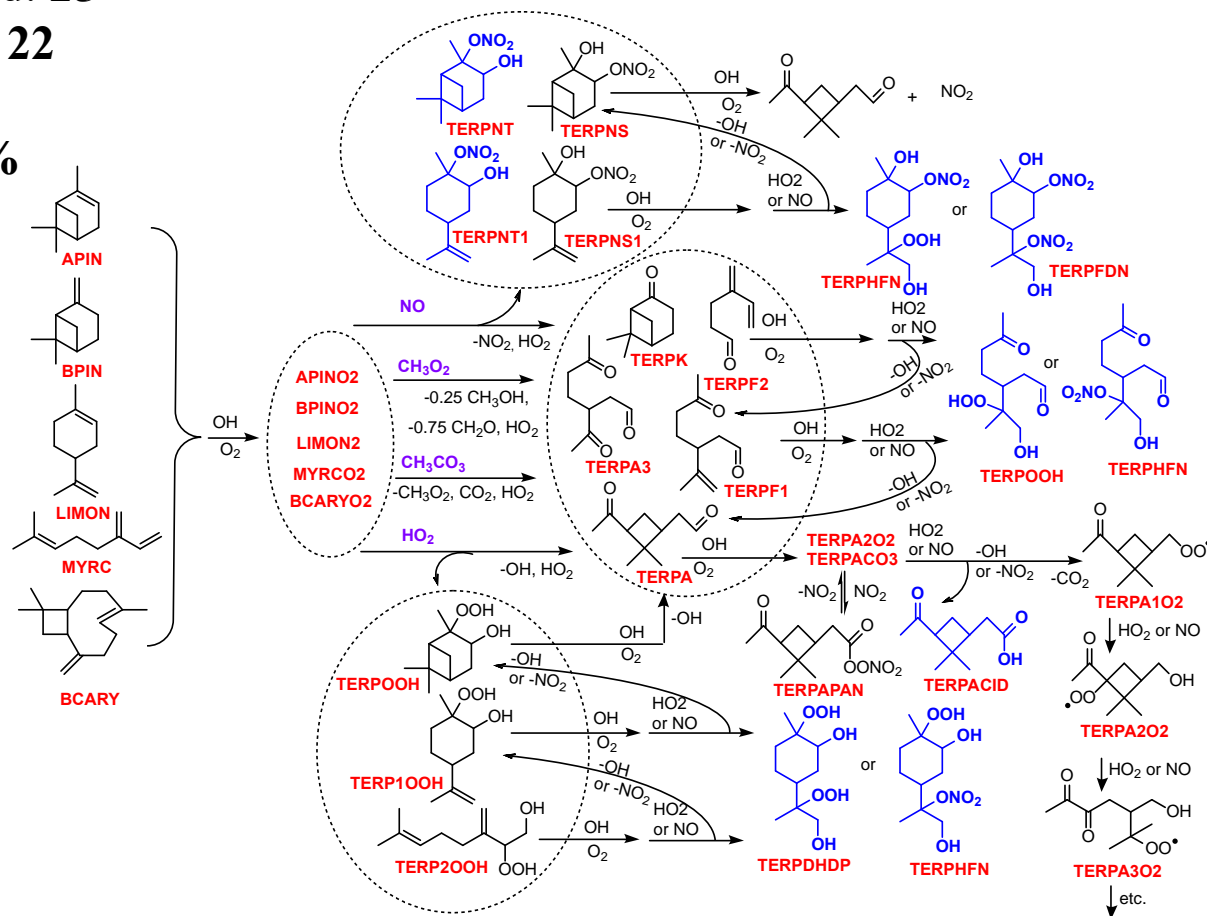
2013 Aug Average: ISOP - BASE



- Isoprene updates overall reduce ozone throughout the U.S. by a couple ppb.

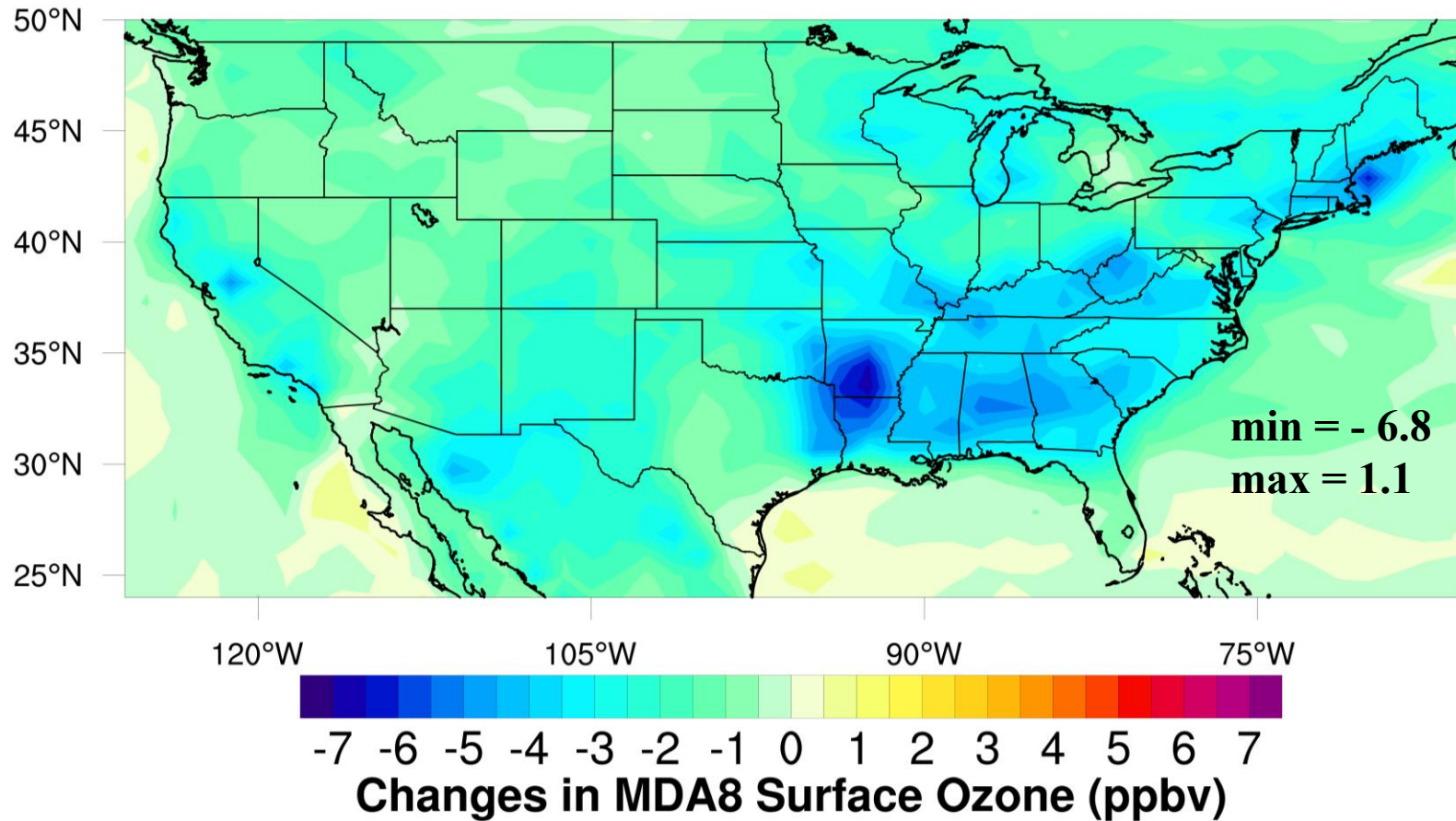
Terpene Chemistry Updates:

- Updated terpene chemistry from 1 to 5 surrogate species with terpenes grouped according to chemical structure. Each surrogate species is oxidized to form different yields of aldehydes/ketones, hydroxy nitrates, and hydroxy hydroperoxides.
- Transported species added: **25**
- Non-transported species: **22**
- Reactions added: **219**
- Increase in run time: **26%**
- For context, the T1 chemical mechanism has 221 species and 528 reactions.
- So both isoprene and terpene chemistry together increase run time by **44%**.



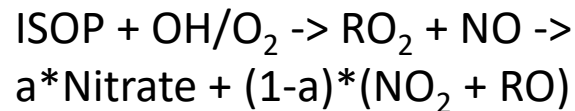
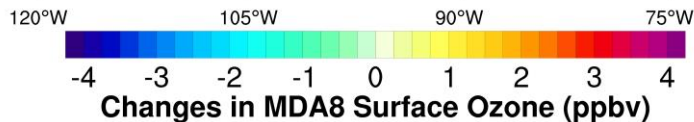
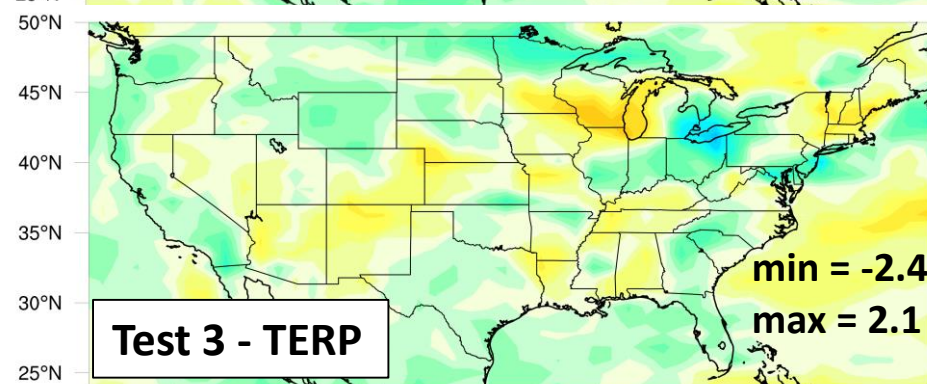
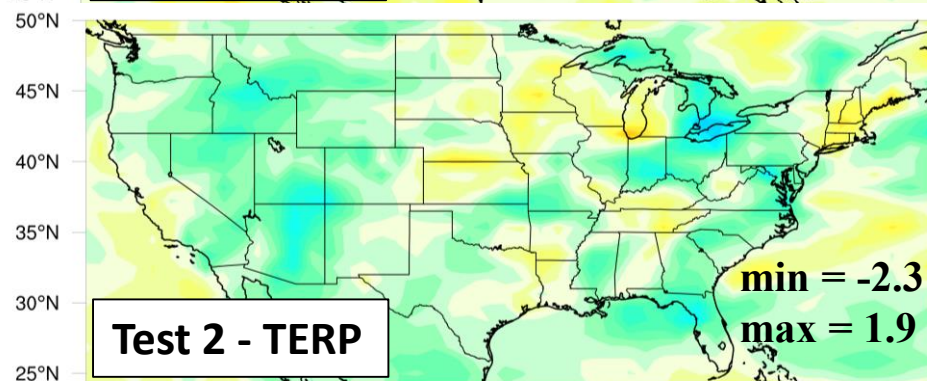
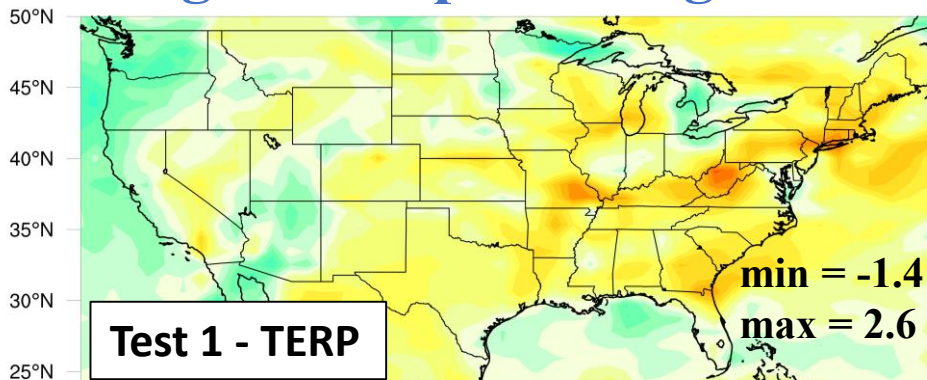
Terpene Chemistry Updates Impact on Surface Ozone:

2013 Aug Average: TERP - BASE

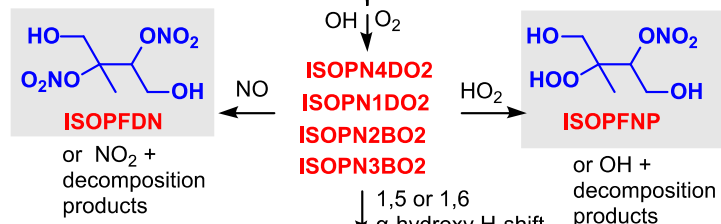
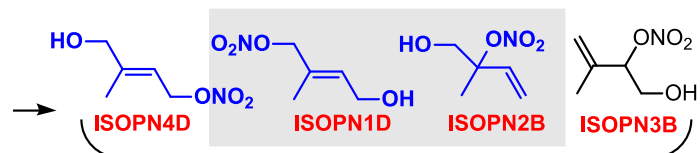


- Terpene updates reduce ozone particularly in the Southeast U.S. and are as important as the isoprene updates even though traditionally they have received less attention.

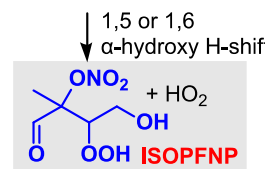
Changes to Isoprene Organic Nitrate Formation:



Test 1: a = 0.13 -> a = 0.09



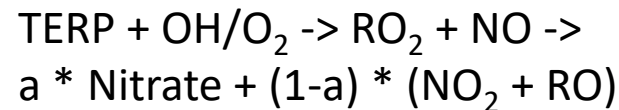
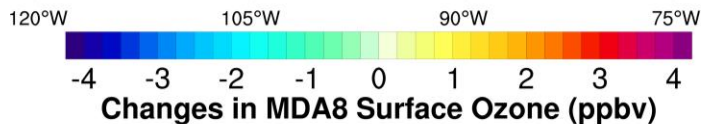
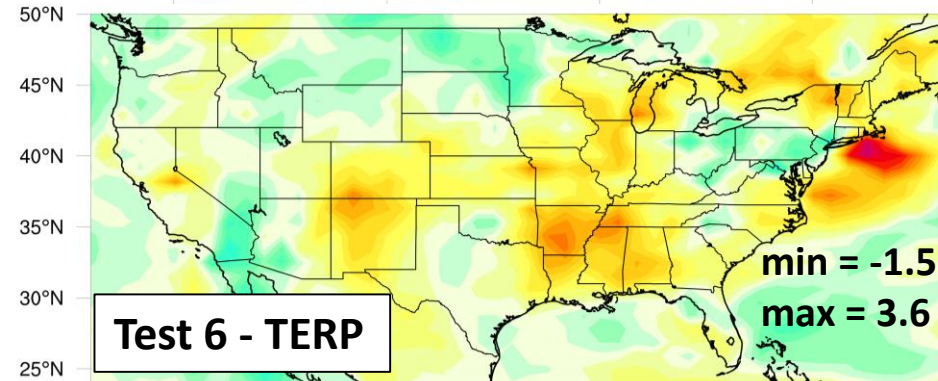
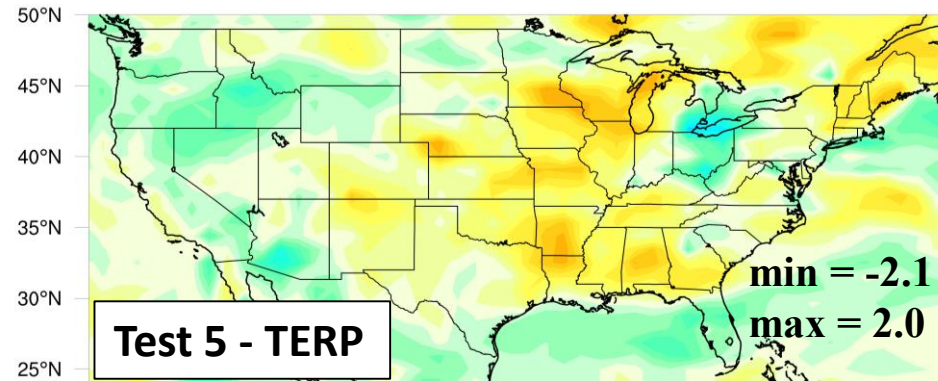
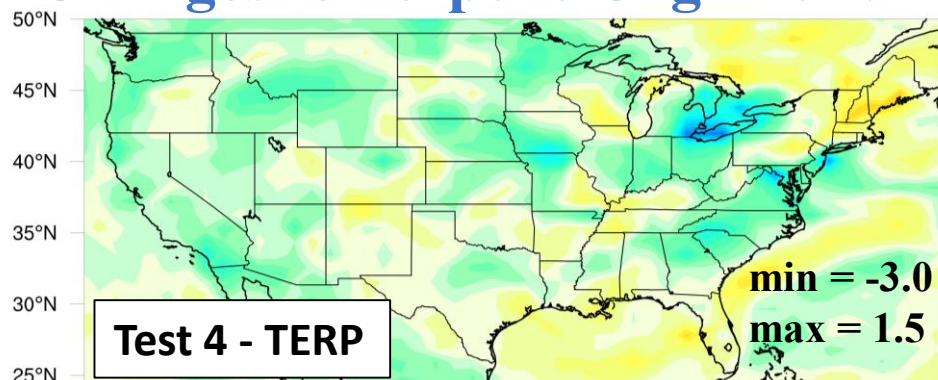
Test 2: a = 0.02-0.2 -> a = 0.3



Test 3: Turn off isomerization channel

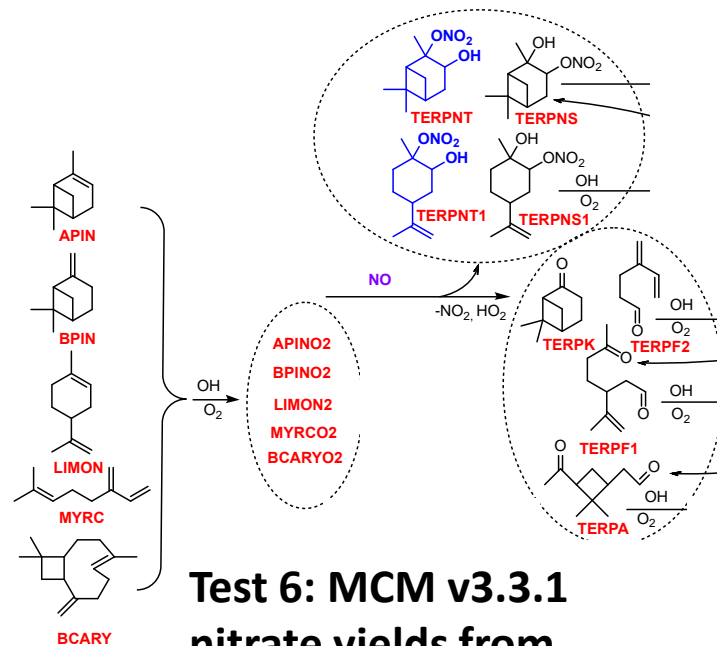
Sensitivity tests based on experimental work: Wennberg et al. 2018, Teng et al. 2017, Xiong et al. 2015, Lee et al. 2014

Changes to Terpene Organic Nitrate Formation:



Test 4: a = 0.23-0.3 -> a = 0.30

Test 5: a = 0.23-0.3 -> a = 0.15



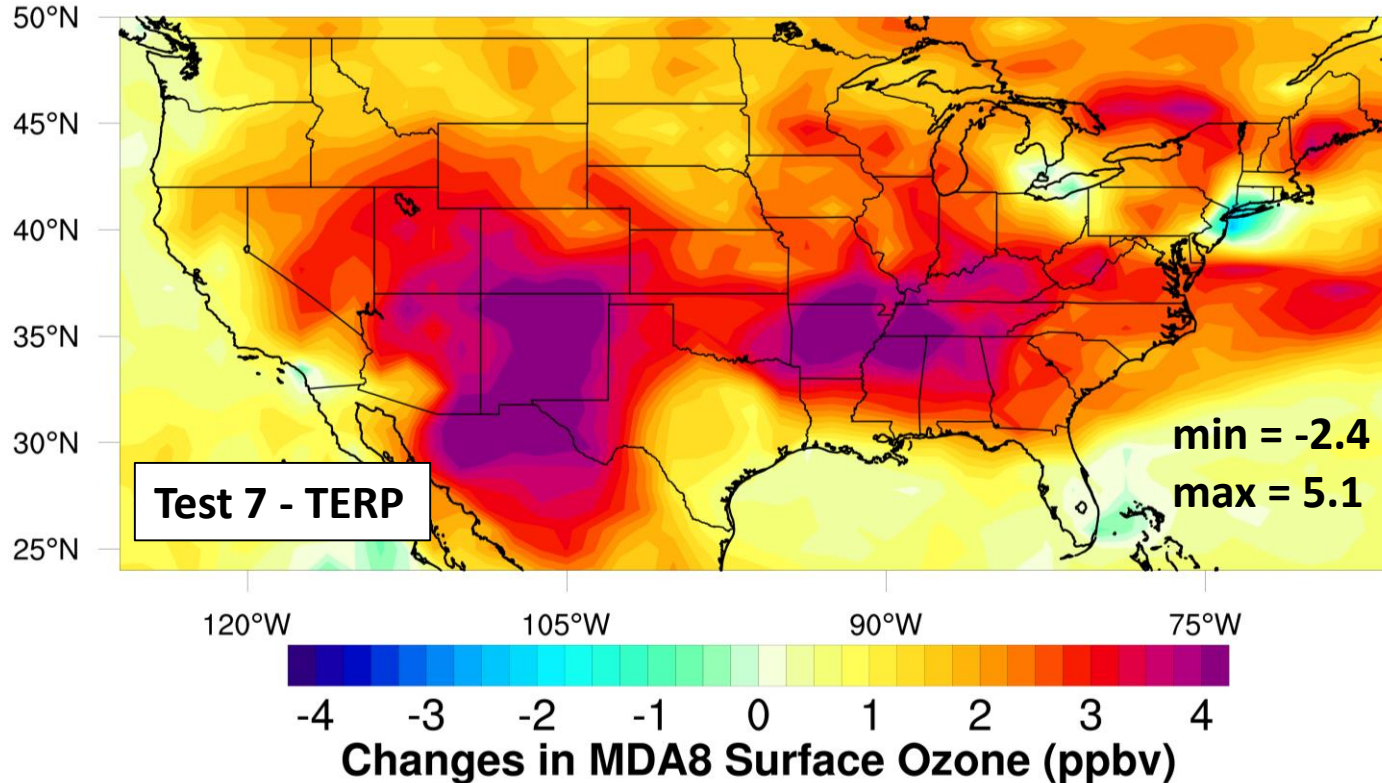
**Test 6: MCM v3.3.1
nitrate yields from
pinonaldehyde oxidation**

Sensitivity tests based on experimental work:
Noziere et al. 1999, Capouet et al. 2004,
Rindelaub et al. 2015, Ruppert et al. 1999,
Orlando and Tyndall 2012, MCM v3.3.1,
Wennberg et al. 2018

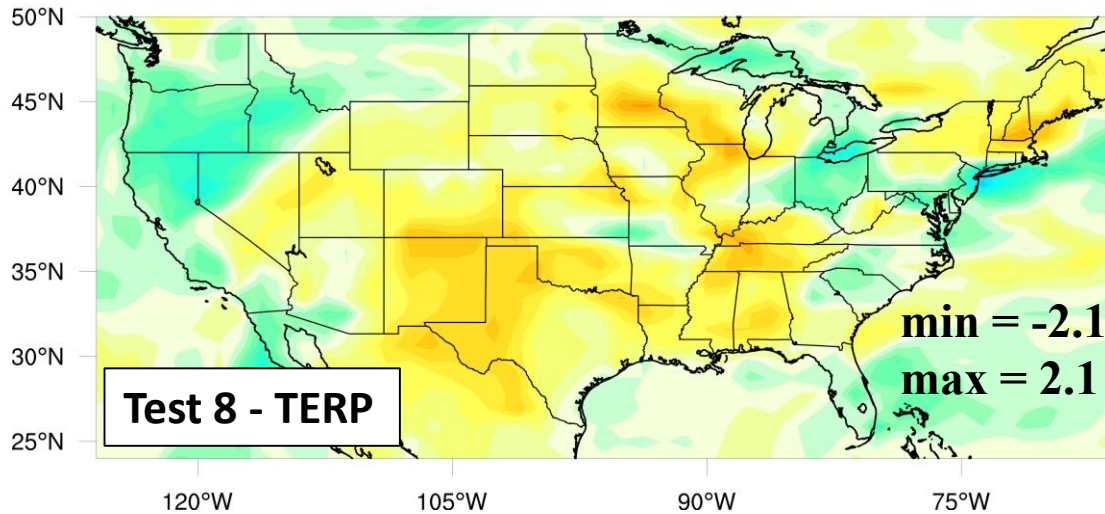
Aerosol Uptake of Isoprene and Terpene Organic Nitrates:

- Current aerosol uptake assumptions:
 - For all tertiary 1st gen isoprene and terpene nitrates, $\gamma = 0.02$ (Wolfe et al. 2015 estimated from field data for total isoprene hydroxy nitrates)
 - For all 2nd and later gen low volatility/highly functionalized organic nitrates from isoprene and terpene oxidation, $\gamma = 0.1$ (Marais et al. 2016, GEOS-chem).

Turn off all organic nitrate aerosol uptake

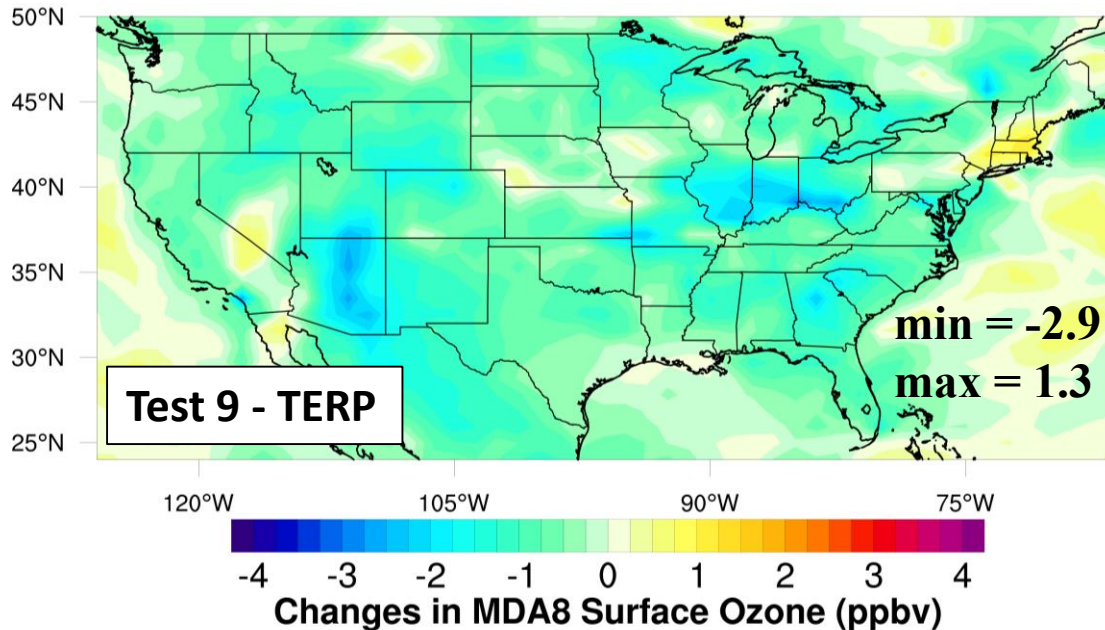


Different Assumptions for Aerosol Uptake of All Organic Nitrates:



Test 8: Fisher et al. 2015 (GEOS-Chem)

- $\gamma = 0.005$ for all isoprene nitrates
- $\gamma = 0.01$ for all terpene nitrates

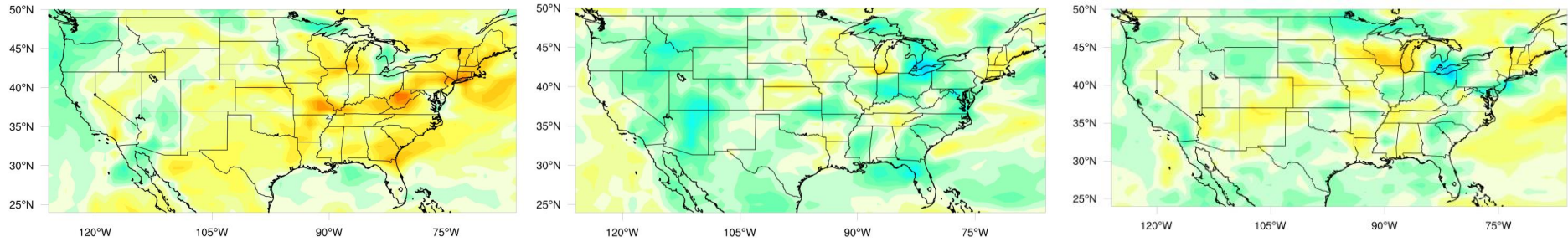


Test 9: Wolfe et al. 2015 and Marais et al. 2016 hybrid

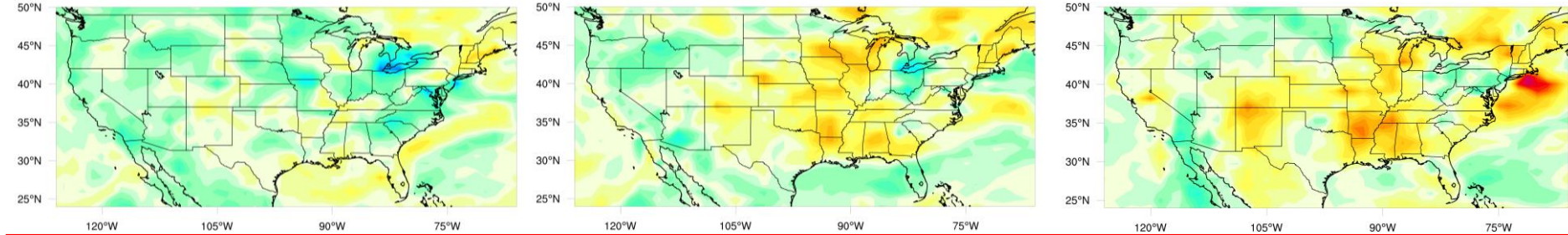
- $\gamma = 0.02$ for all isoprene and terpene 1st gen nitrates
- $\gamma = 0.1$ for all later generation isoprene and terpene low/volatility highly functionalized nitrates

All Together:

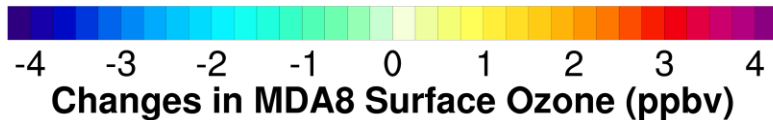
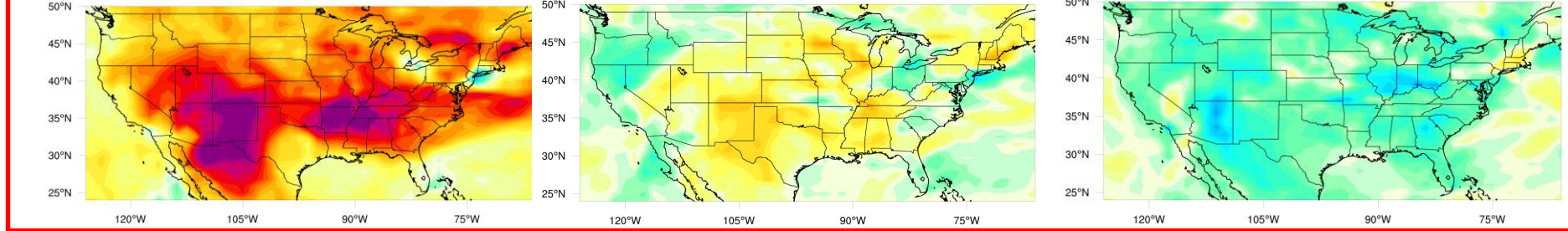
Sensitivity to assumptions for isoprene organic nitrate formation



Sensitivity to assumptions for terpene organic nitrate formation



Sensitivity to assumptions for aerosol uptake

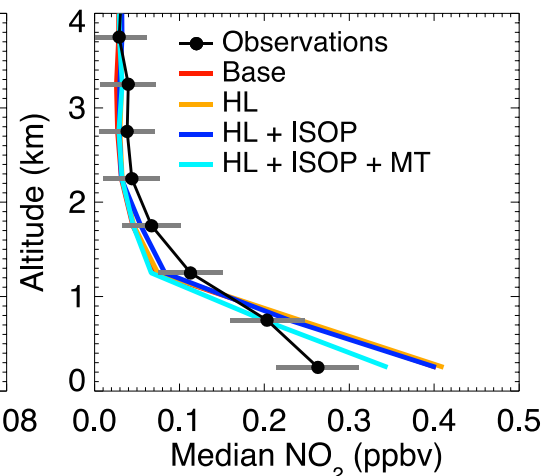
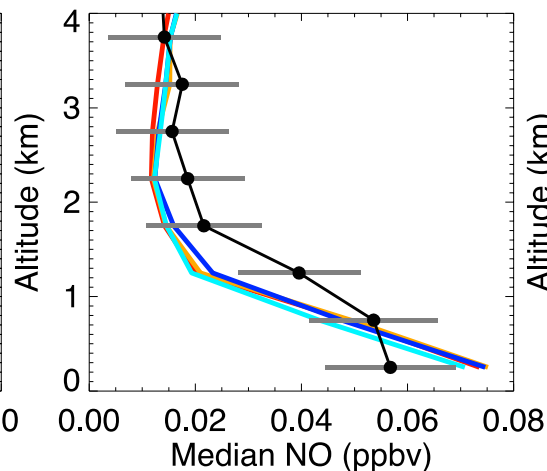
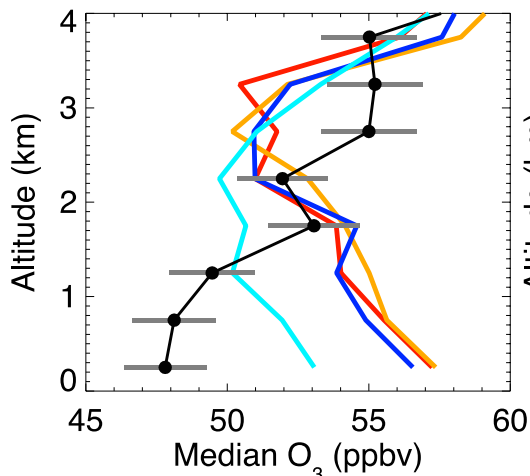


- Uncertainties in organic nitrate aerosol uptake are particularly large and deserve further study

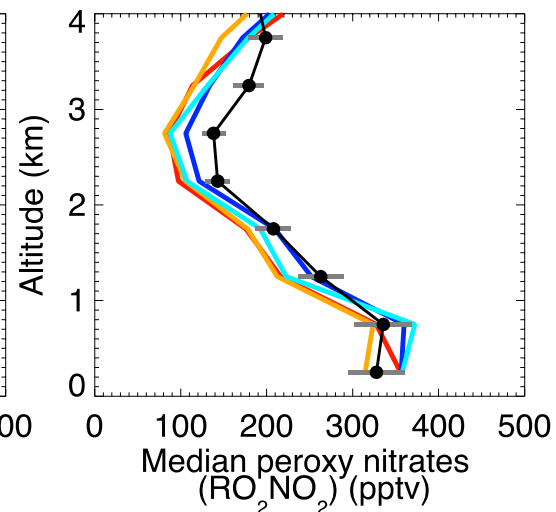
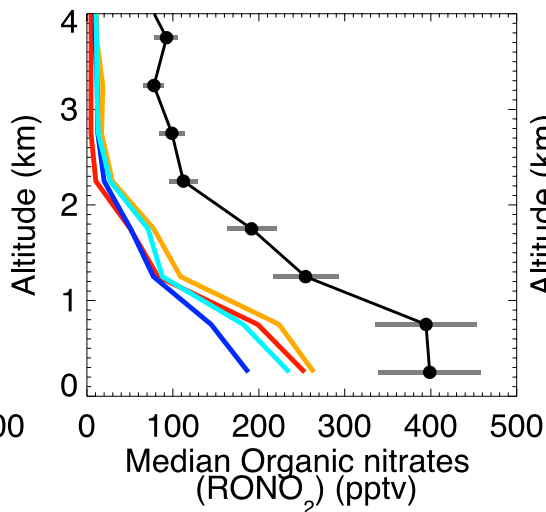
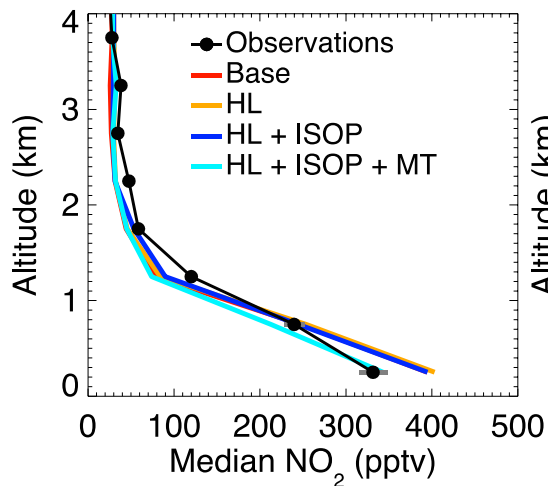
Quick Comparison to SEAC⁴RS Field Campaign:

- The uncertainties tested above are only the known uncertainties in the chemistry for isoprene and terpenes.
- The model is still not perfectly capturing ozone or organic nitrates when compared to SEAC⁴RS field campaign results.

O₃, NO, NO₂, from Thomas Ryerson (NOAA ESRL Chemical Science Division) using chemiluminescence

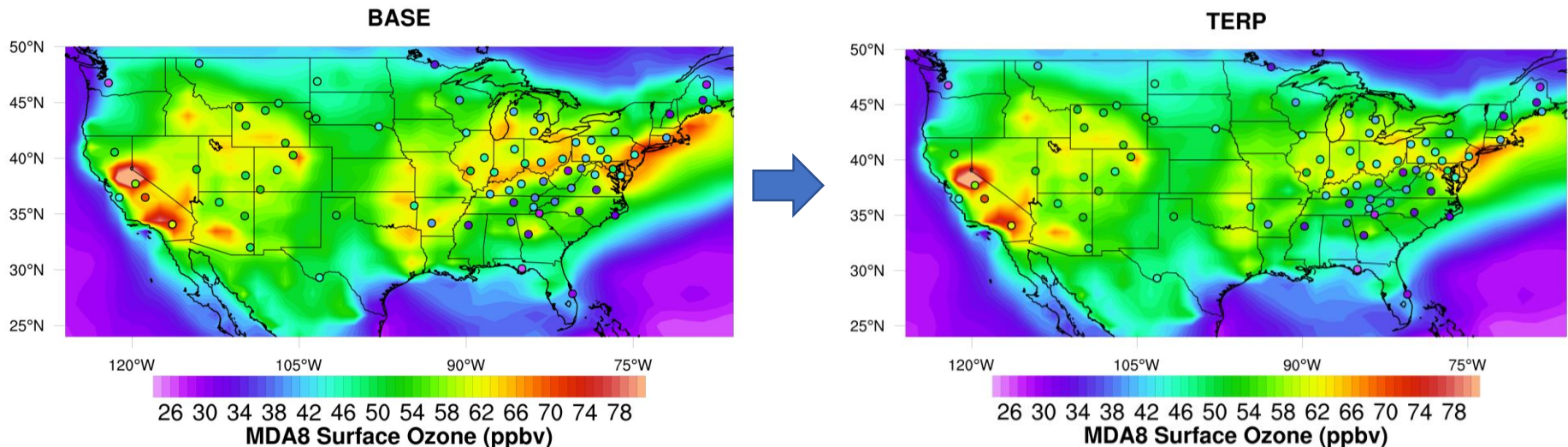


NO₂, alkyl nitrates, and peroxy nitrates from Ronald Cohen (University of California-Berkeley) using the thermal dissociation-laser induced fluorescence.



Conclusions and Future Work:

- Updating and adding more complex isoprene and terpene chemistry has a large impact on simulated surface ozone in CESM™/CAM-chem.
- Terpene oxidation, which has been heavily reduced or ignored in models in the past, is particularly important especially now that isoprene chemistry is more well understood.
- Uncertainties in the aerosol uptake of organic nitrates derived from isoprene and terpene oxidation have a larger impact on simulated surface ozone than uncertainties existing for organic nitrate formation.
- Future work to improve the southeast ozone bias will include further work on emission and resolution improvements.



Acknowledgements:



Contact Info: Becky Schwantes
Email: rschwant@ucar.edu