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AMORE: Automated Model Reduction for Atmospheric Chemical Mechanisms

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Geoscientific Model Development Discussions
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AMORE-Isoprene v1.0: A new reduced mechanism for gas-phase isoprene oxidation

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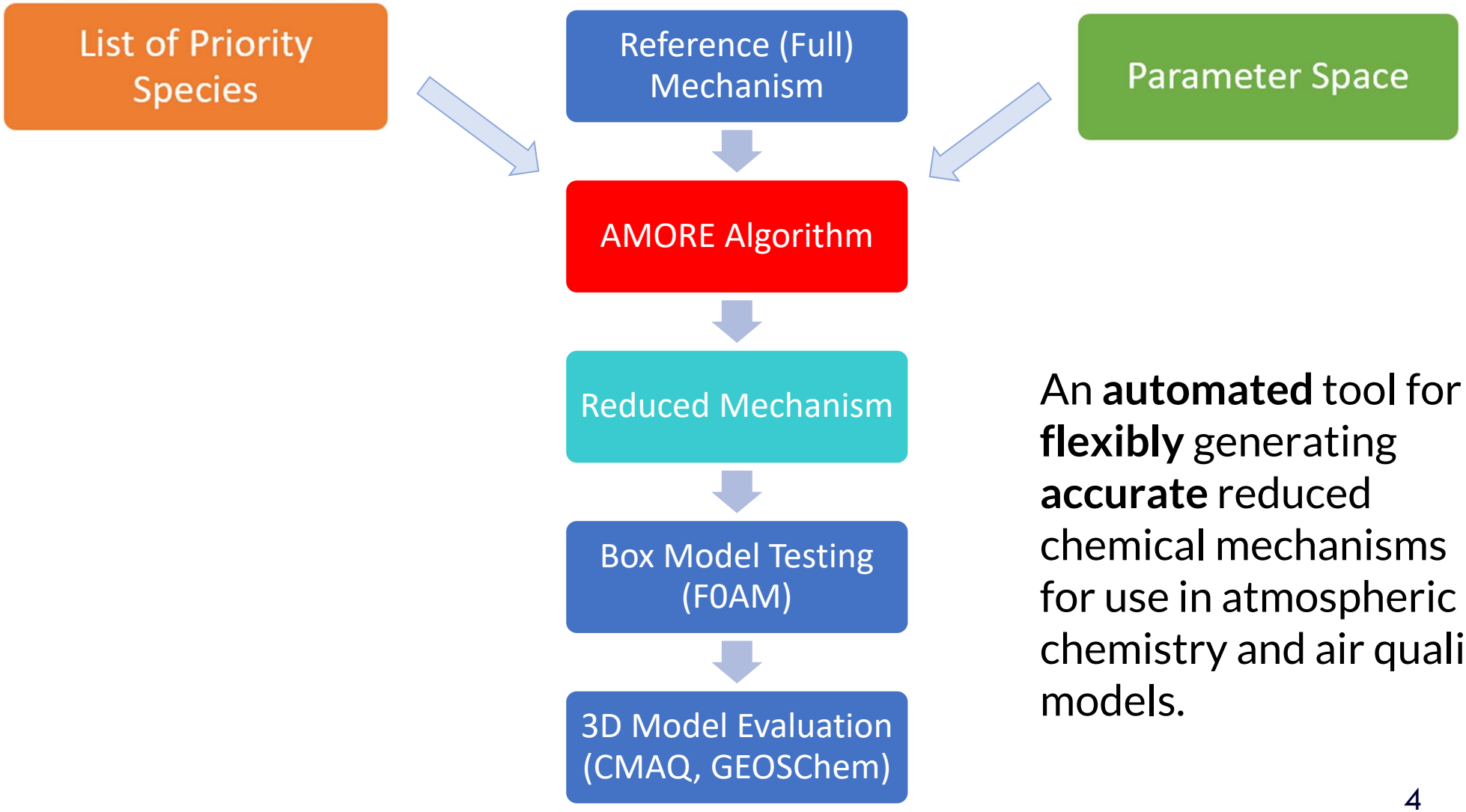
Abstract. Gas-phase oxidation of isoprene by ozone (O_3) and the hydroxyl (OH) and nitrate (NO_3) radicals significantly impacts tropospheric oxidant levels and secondary organic aerosol formation. The most comprehensive and up to date chemical mechanism for isoprene oxidation consists of several hundred species and over 800 reactions. Therefore, the computational expense of including the entire mechanism in large-scale atmospheric chemical transport models is usually prohibitive, and

Challenges of Bridging Scales and Handling Complexity in Atmospheric Chemistry

- Large-scale models used for predictions and decision making should synthesize best current knowledge
- Important phenomena discovered in the lab one particle (or a few molecules) at a time.
- Including new science in models requires work, and in some cases, major changes to the model. Often adds complexity.
- Need (good, fast, not artisanal) **model reduction** to deal with network complexity.
- **Automation** reduces barrier to mechanism updates

AMORE (Atmospheric Chemistry MOdel REduction)



An **automated** tool for **flexibly** generating **accurate** reduced chemical mechanisms for use in atmospheric chemistry and air quality models.

Isoprene oxidation: Model reduction testbed

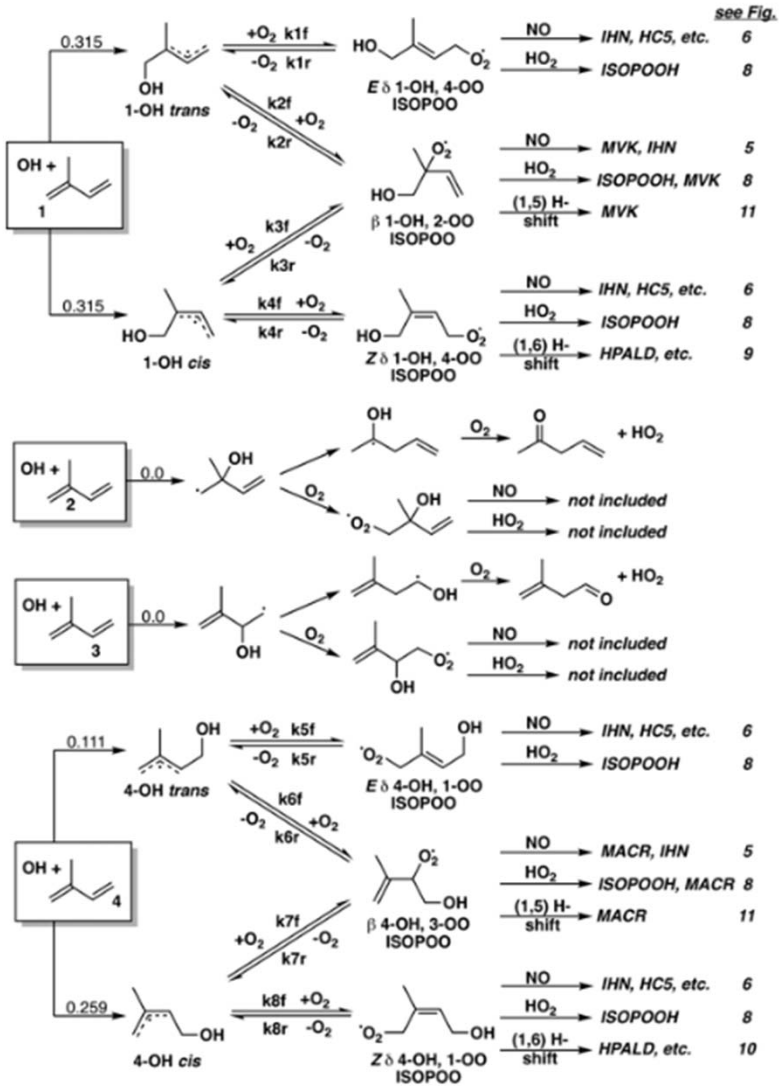
Mechanism	Number of species	Number of reactions	Reference
MCM 3.3.1	602	1926	Jenkin et al. (2015)
Caltech	404	897	Wennberg et al. (2018)
Caltech Reduced Plus	131	220	Wennberg et al. (2018)
RACM2	9	12	Sarwar et al. (2013), Goliff et al. (2013)
CB6r3	10	17	Yarwood et al. (2010); Emery et al. (2015)
AMORE-Isoprene	12	22	This work

The Reference Mechanism

Reference (Full) Mechanism

"Complete" Gas Phase Isoprene Chemistry

- Wennberg 2018: Master compilation of experimental data
- > 400 isoprene-specific species, >800 isoprene-specific reactions
- Woods expanded the Caltech mechanism for this project to include missing downstream chemistry of some species (similar to Bates v5)
- Updated mechanism: 428 species and 1325 reactions



Considerations

- Algorithm should not require too much information besides the full mechanism (equations + rate laws), parameter space, and priority species list

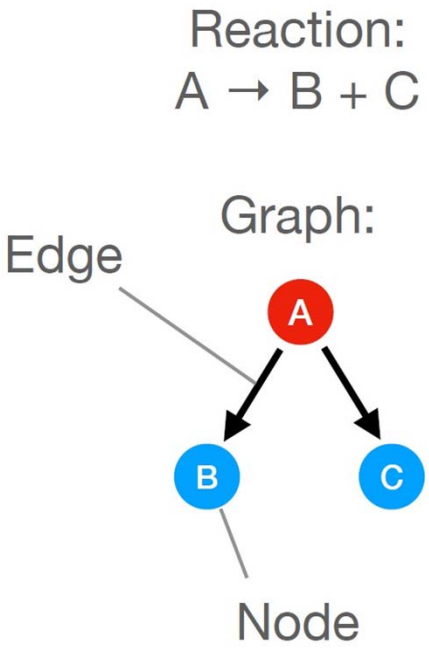
List of Priority Species

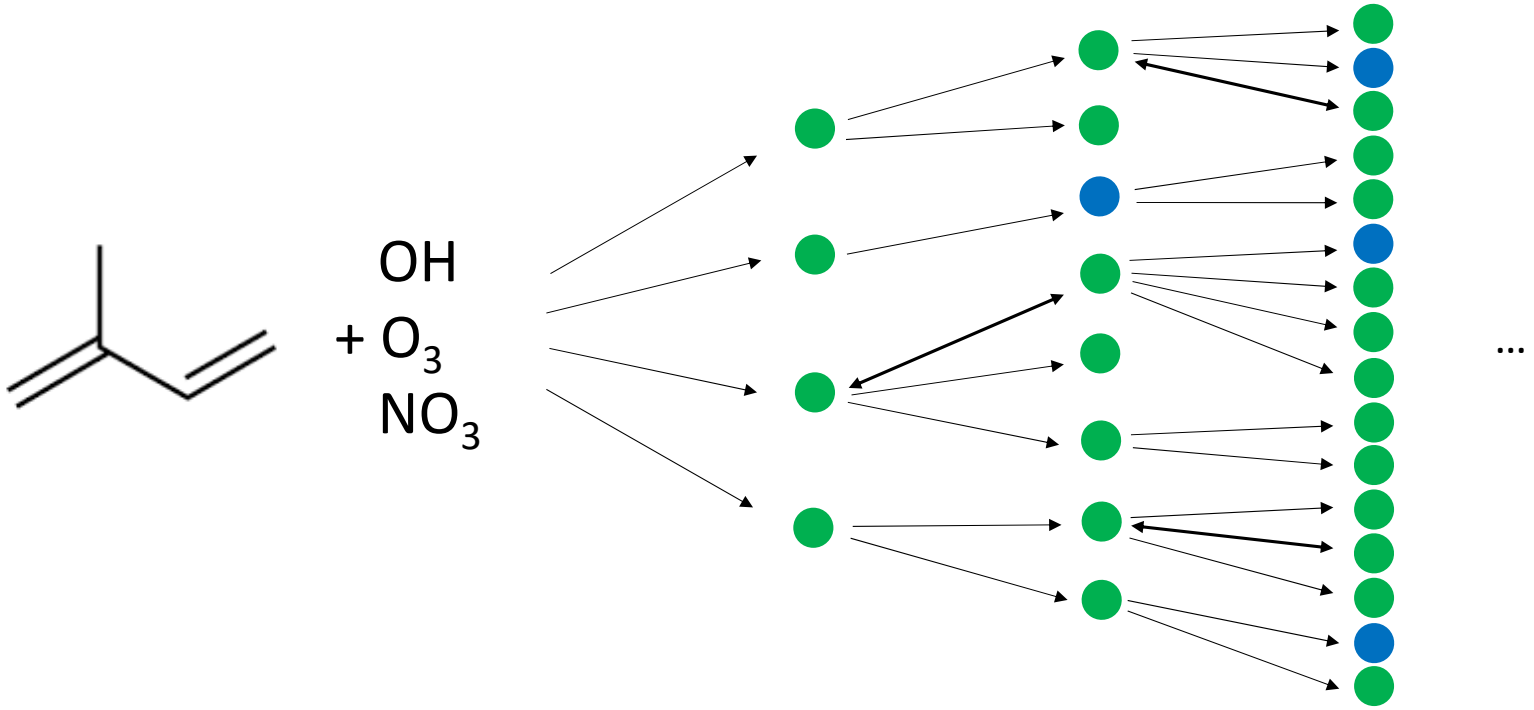
IEPOX (lumped), formaldehyde, Glyoxal, methacrolein, MVK, MGLY, PAN and isoprene nitrates (lumped)

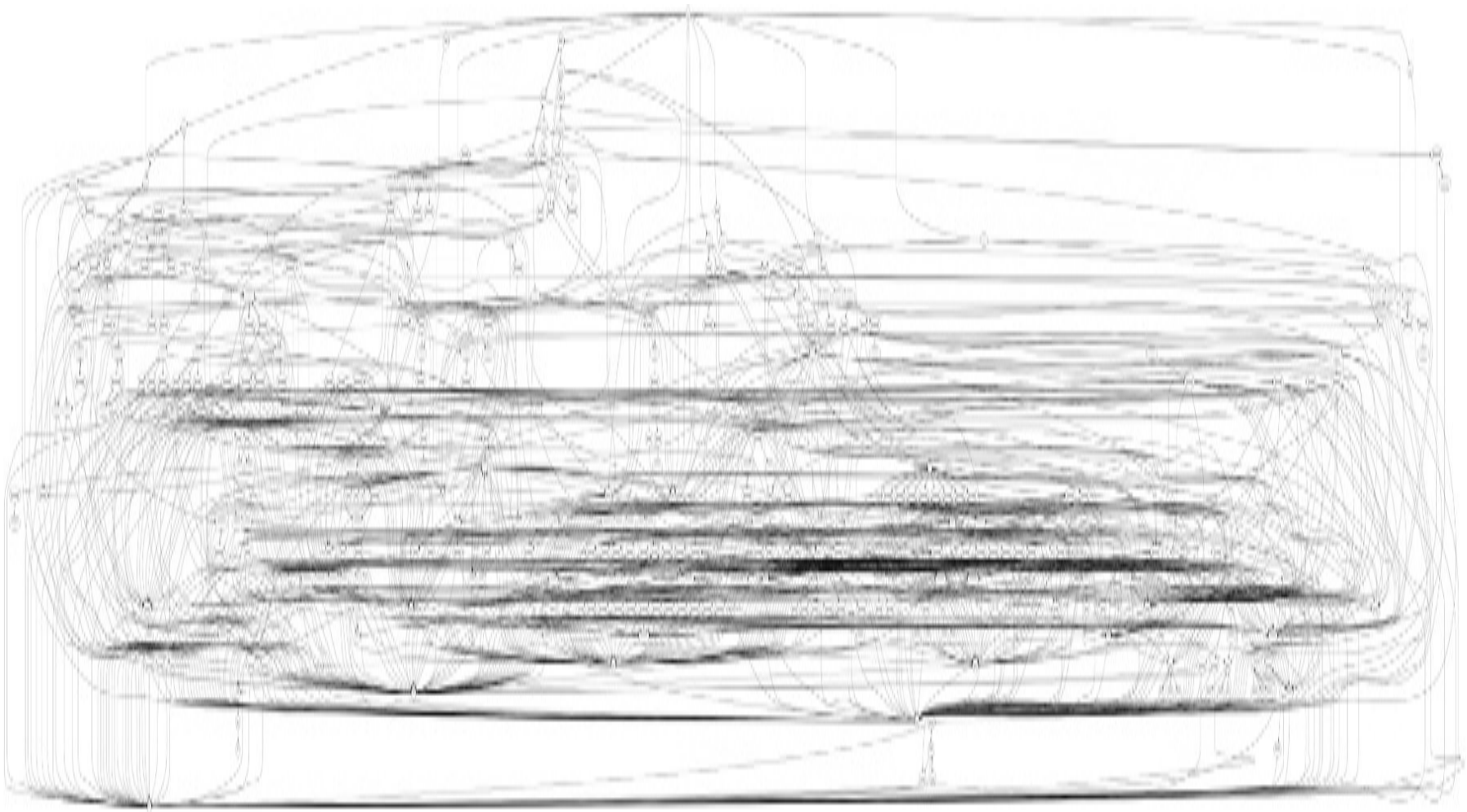
- Algorithm should eventually be generally applicable to other reaction networks
- Target mechanism size similar to currently used mechanisms (e.g., ~10 species and ~20 reactions for isoprene in CMAQ)
- Compare performance to chamber data and field data
- Target accuracy as good as or better than currently used reduced mechanisms

Reduction Algorithm First Attempt: Directed Relation Graph method

- Lessons from combustion literature, graph theory
- Represent chemical mechanism as a *directed relation graph* (C species = nodes, reactions = edges)
- Analyze reaction network and eliminate paths with low flux through them (while protecting priority species)
- Assign weights r_{AB} to each branch (normalized contribution of B to the production rate of A)
- Eliminate branches with r_{AB} below a threshold ε in order of least to most importance to reduce the mechanism

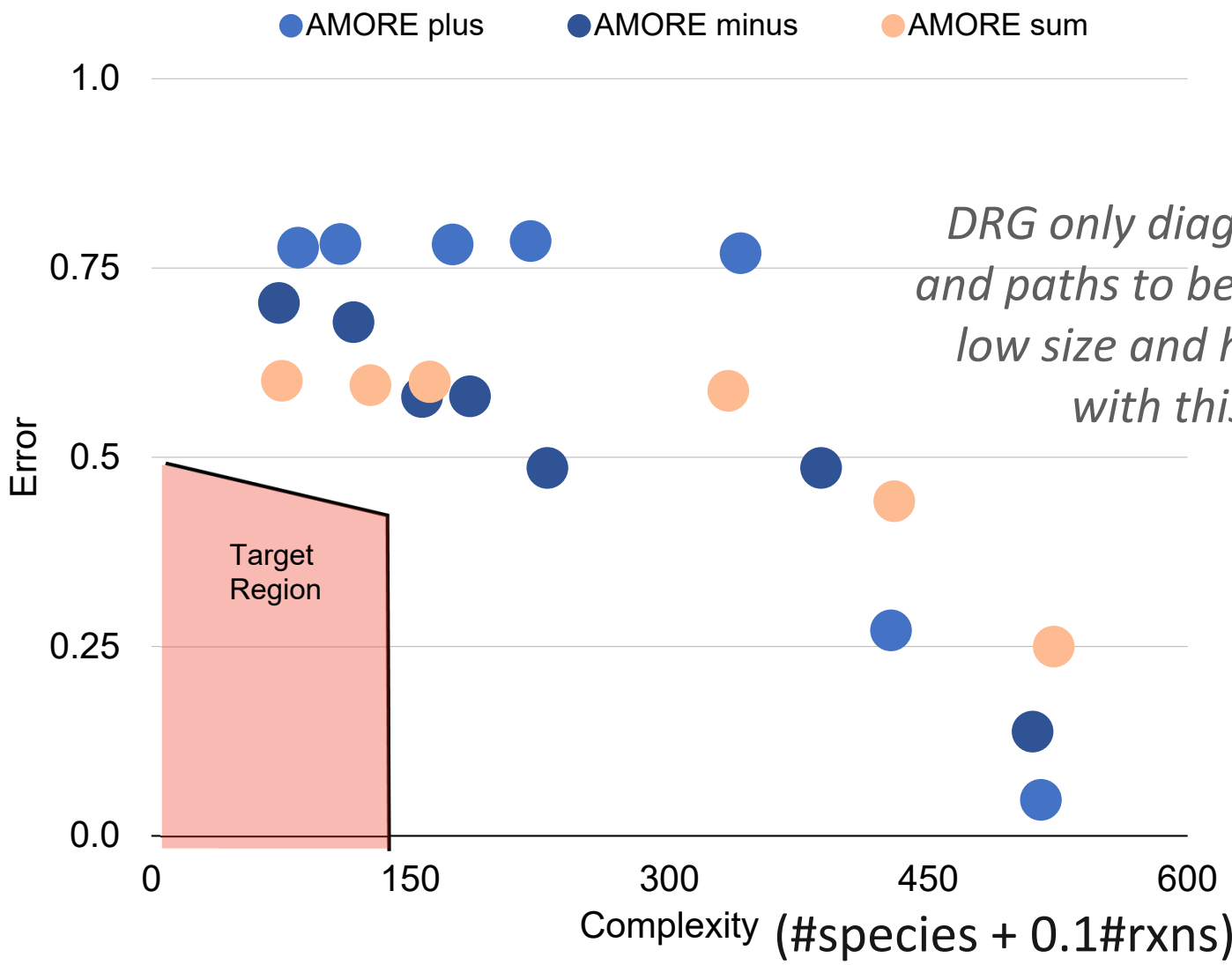



OH
+ O3
NO3
...



Directed Relation Graph Method Preliminary Results

Performance vs. Complexity

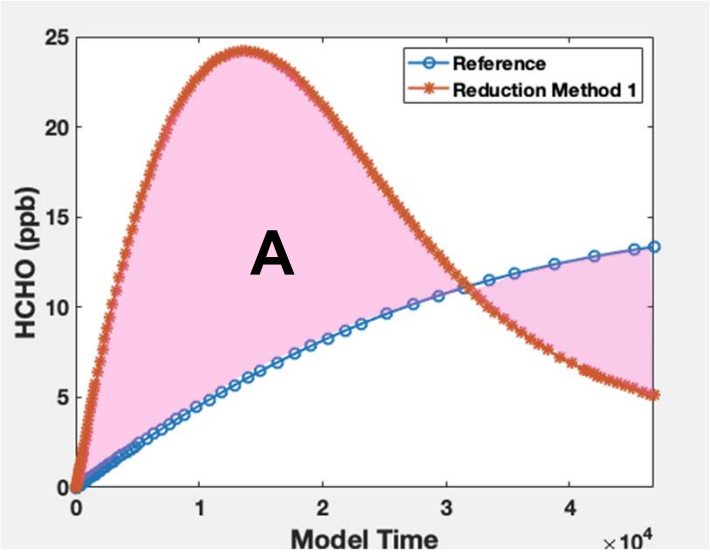


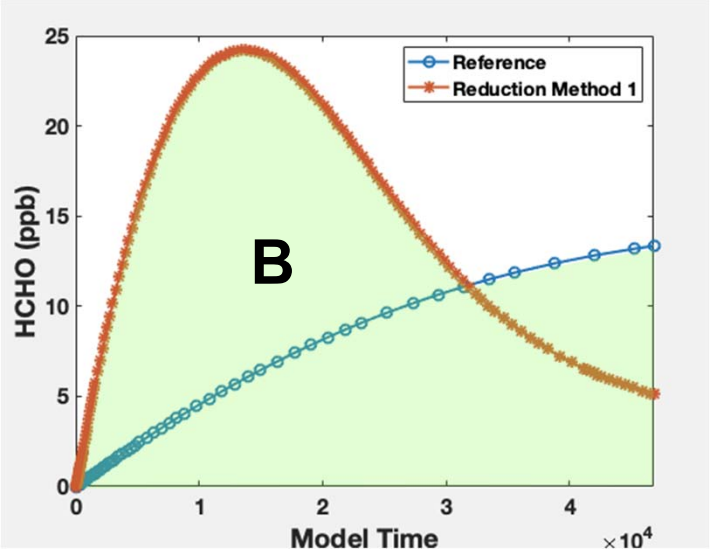
DRG only diagnoses species and paths to be cut – can't get low size and high accuracy with this alone.

Error Metric

Compare species concentration output to data

- Formula:
  - A: integral difference between curves
  - B: envelope of both curves
  - A/B
- Can be averaged between samples and species to obtain overall mechanism performance
- Ranges from 0 to 1





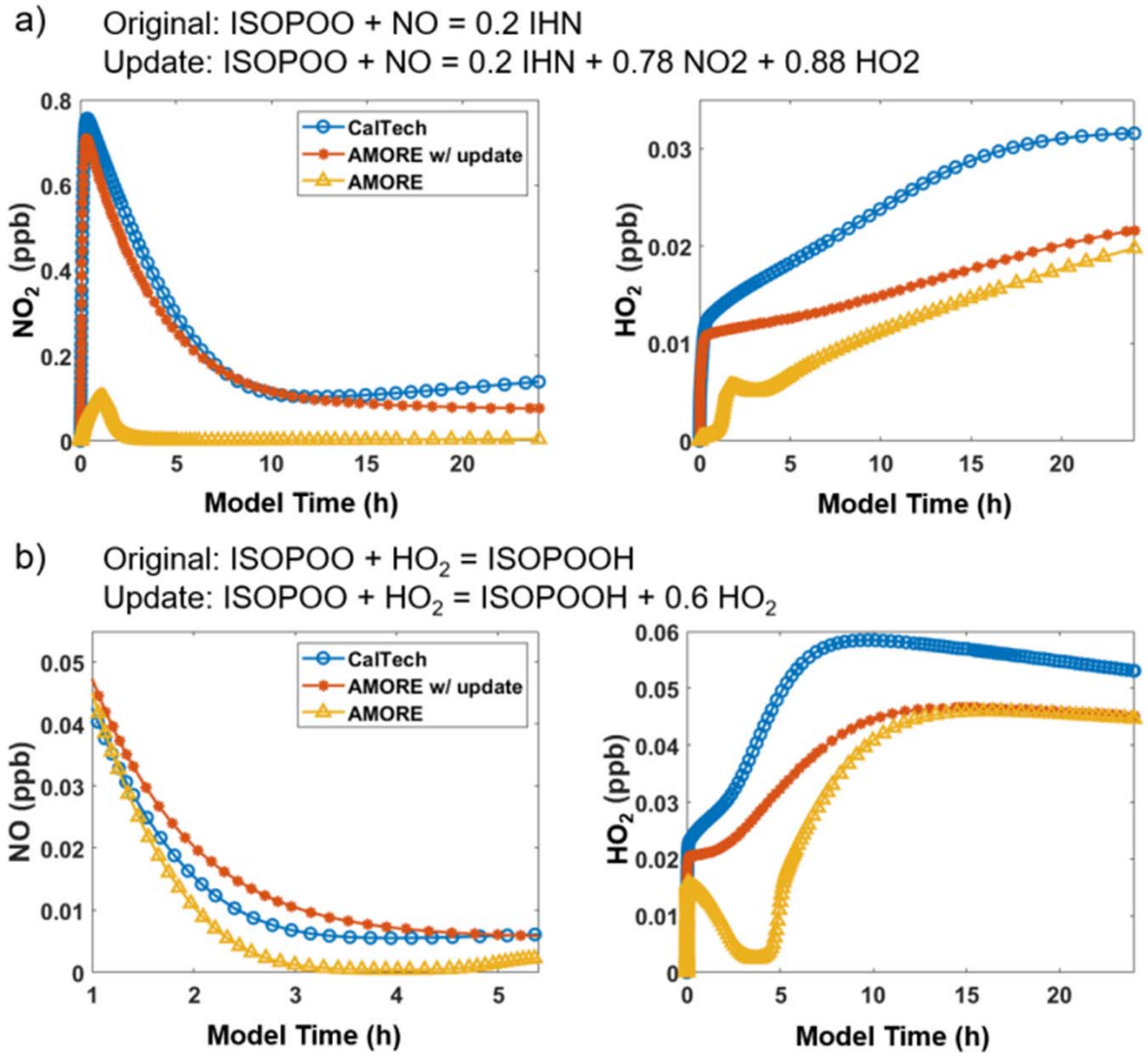
Next attempt: Automated Path-Based Reduction Algorithm

- "Summarize" reaction network in a way that emulates the full mechanism, rather than trimming
- Noting each path has unique dependency on the inputs, analyze sensitivity of the output to each possible path (sequence of reactions) by sampling the input space (OH, NOx, HO_2, etc.)
- Combine most important (sensitive) paths to create the reduced mechanism
- Identify opportunities for grouping species (lumping)

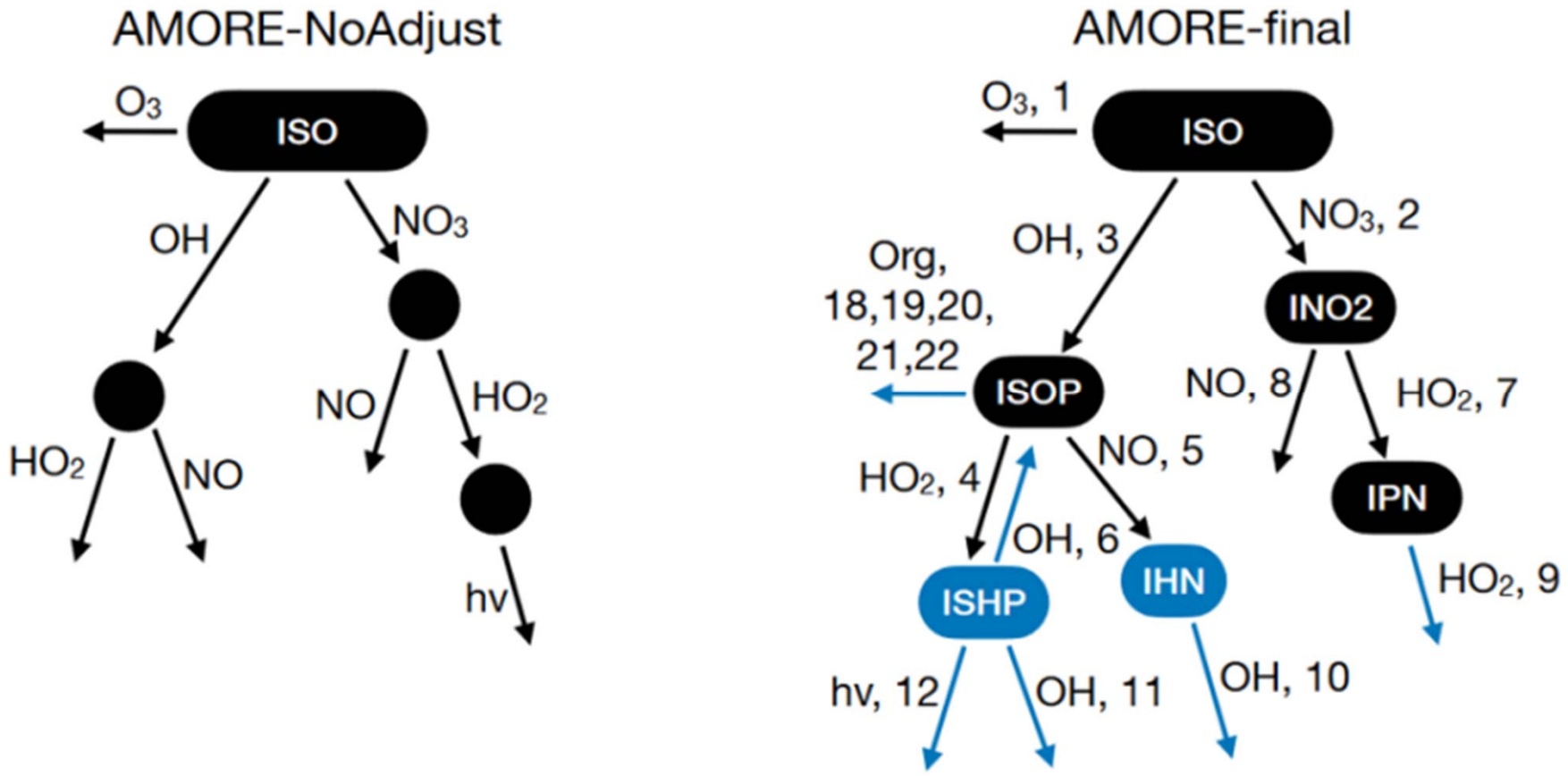
Wiser et al., *GMDD* 2022

Input Cycling Adjustments

Current automated Path-based reduction algorithm missed HO_2 and NOx cycling, needed to manually add



Mechanism Comparison: Before and After Adjustments



AMORE isoprene mechanism

1. ISO + O3 = 0.07*MACR + 0.189*MVK + 0.58*HCHO + 0.25*HO + 0.25*HO2 + 0.58*HCHO + 0.08*MO2 + 0.1*ACO3 + 0.09*H2O2 + 0.1*MACP + 0.461*MACR + 0.14*CO + 0.28*ORA1 + 0.15*OLT # **1.58E-14 @ 2000;**

2. ISO + NO3 = INO2 + 0.3*HCHO + 0.3*NO2 + 0.3*ISON # **2.95E-12 @ 450;**

3. ISO + HO = ISOP + 0.02*MO2 # **2.69E-11 @ -390;**

4. ISOP + HO2 = ISHP + 0.6*HO2 + 0.15*HCHO # **4.5E-13 @ -1300;**

5. ISOP + NO = 0.14*IHN + 0.7*HCHO + 0.44*MVK + 0.88*HO2 + 0.78*NO2 + 0.28*MACR + 0.021*GLY # **2.7E-12 @ -350;**

6. ISHP + HO = ISOP # **4.6E-12 @ -200;**

7. INO2 + HO2 = IPN + HO # **3.14E-14 @ -580;**

8. INO2 + NO = 0.9*HCHO + 0.5*MGLY + 0.8*MVK + 0.5*NO2 + 1*HO2 + 0.2*ISON + 0.1*MO2 # **9.42E-16 @ -580;**

9. IPN + HO2 = 0.8*NO2 + 0.4*HCHO + 0.05*GLY + 0.1*MGLY + 0.4*MACR + 0.8*NO2 + 1*HO2 + 0.94*MVK + 0.2*ISON + 0.1*MO2 # **3.4E-11 @ -390;**

10. IHN + HO = 1*ISON + 1*HO + 0.2*IEPOX # **2.4E-7 @ -580;**

11. ISHP + HO = 0.15*HCHO + 0.05*MGLY + 0.15*MACR + 0.02*GLY + 0.2*MVK + 0.4*NO2 + 0.05*IPC + 0.58*IEPOX + 0.8*HO # **2.97E-11 @ -390;**

12. ISHP = 0.4*HCHO + 0.1*MGLY + 0.06*ACO3 # **1.0/<HCHO_RAD_RACM2>;**

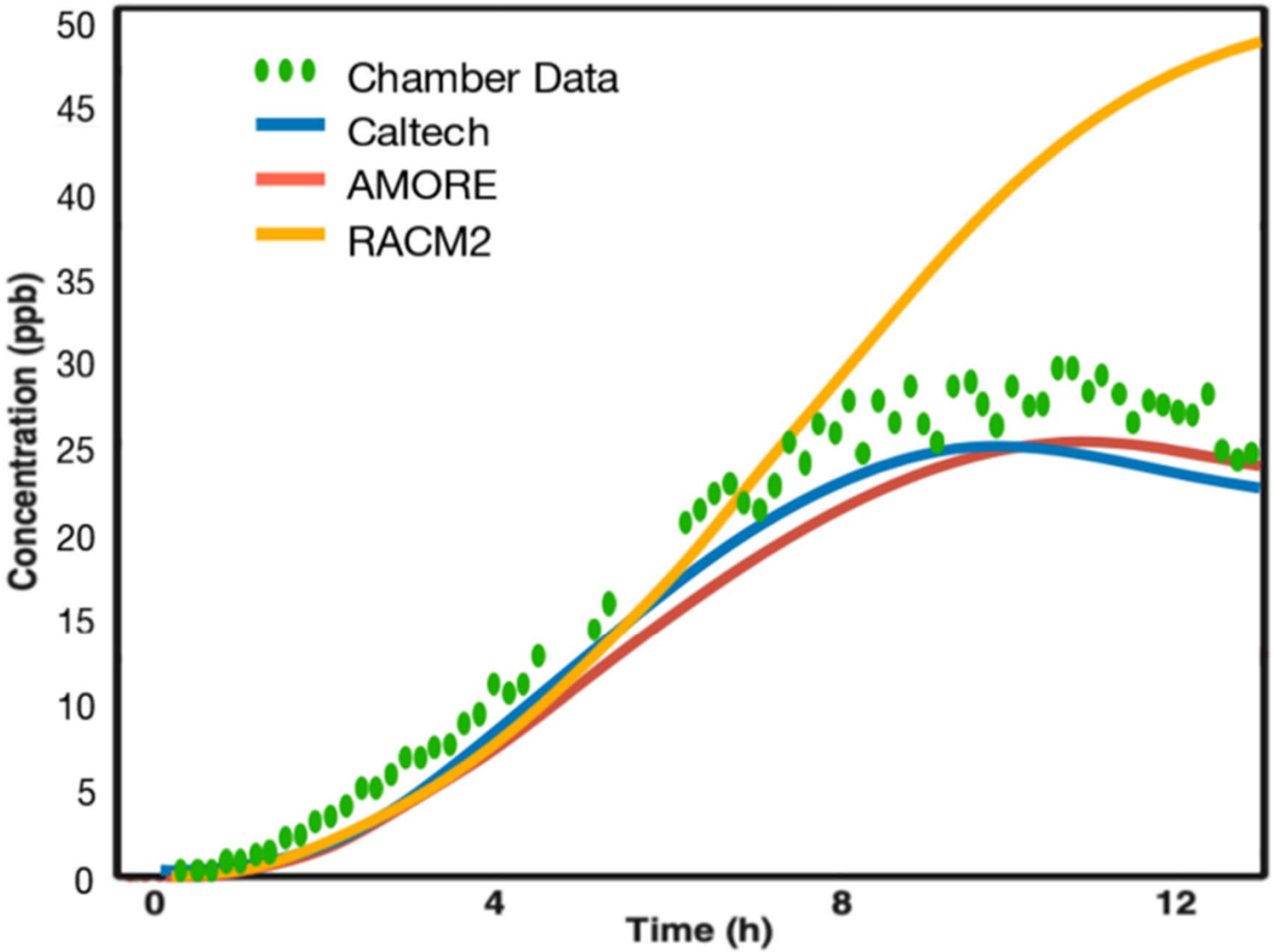
13. IPC + NO = 0.35*NO2 + 0.8*NO # **1.0E-10;**

14. ISON + HO = CO + 0.12*NO2 # **5E-11;**

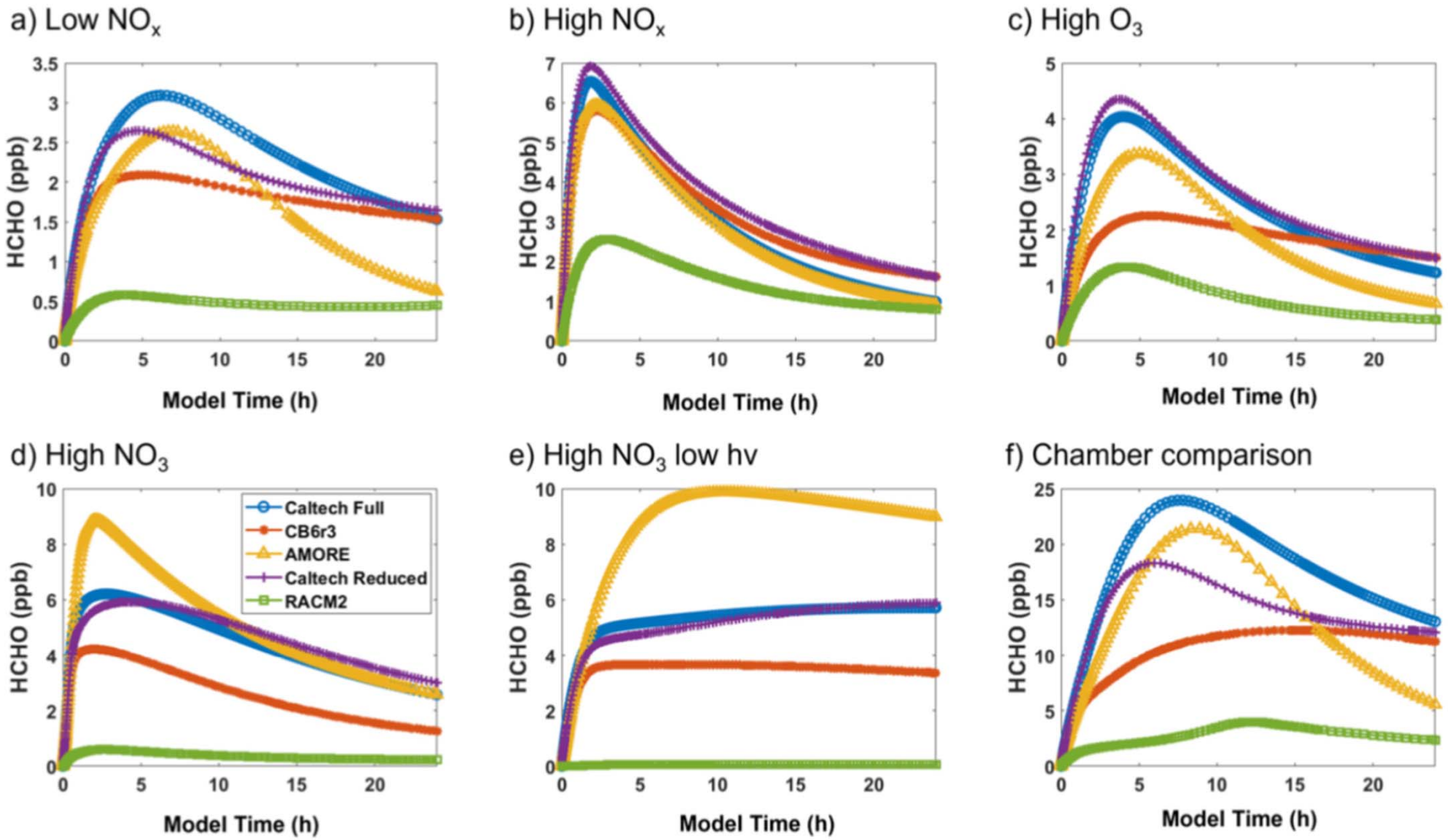
15. ISON + NO3 = CO # **2.0E-14;**

16. IHN = HNO3 # **2.3E-5;**

Box Model Results: IEPOX Chamber Data Comparison

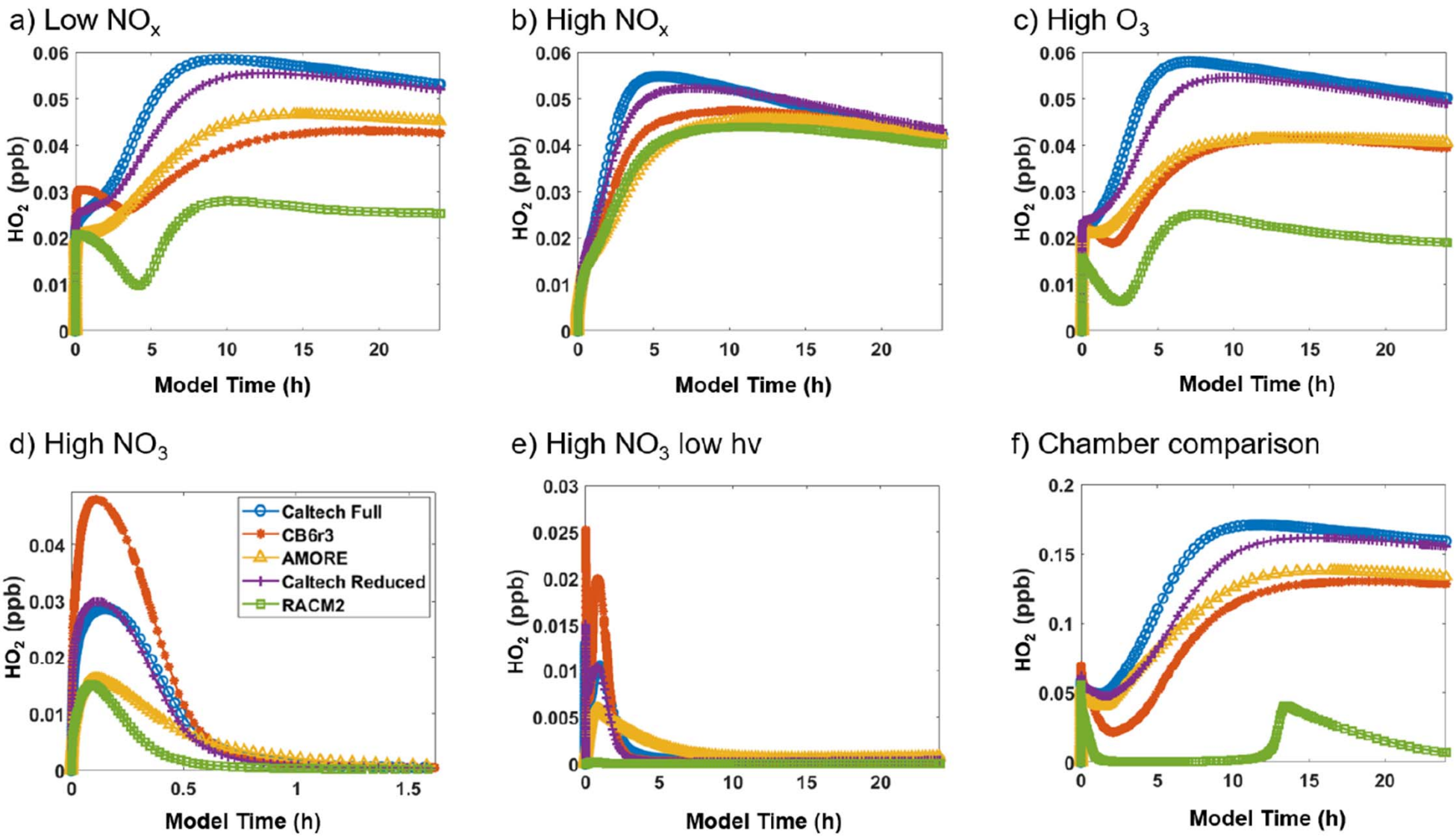


Box Model Results: Formaldehyde



Wiser et al., *GMDD* 2022

Box model Results: HO_2



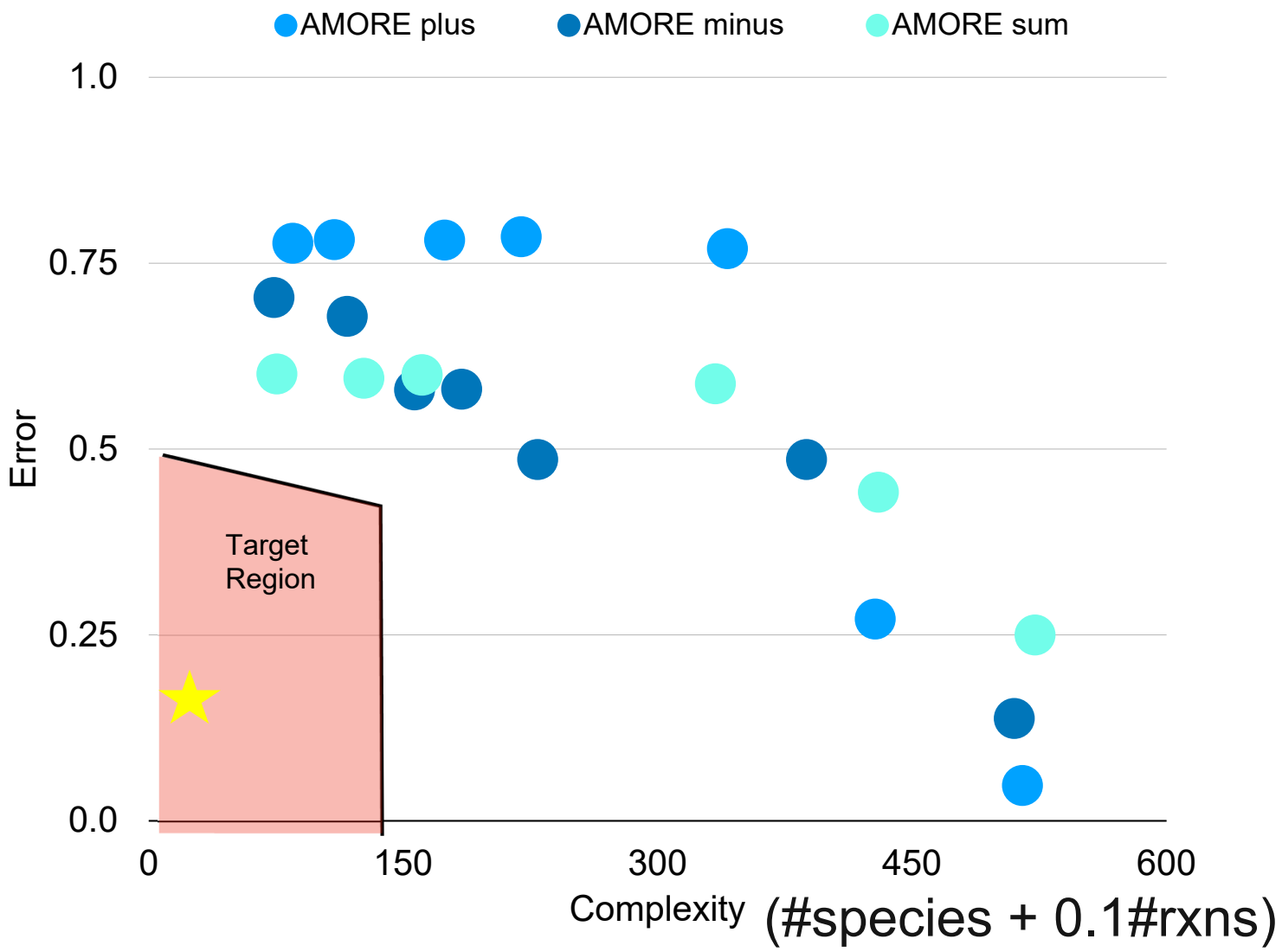
Wiser et al., *GMDD* 2022

Mechanism comparison (Box Model Results)

Mechanism	Species	Reactions	Total Error
AMORE-isoprene	12	22	0.17
Caltech Reduced Plus	131	220	0.13
RACM2	9	12	0.44
Carbon Bond v6 revision 3	10	17	0.30

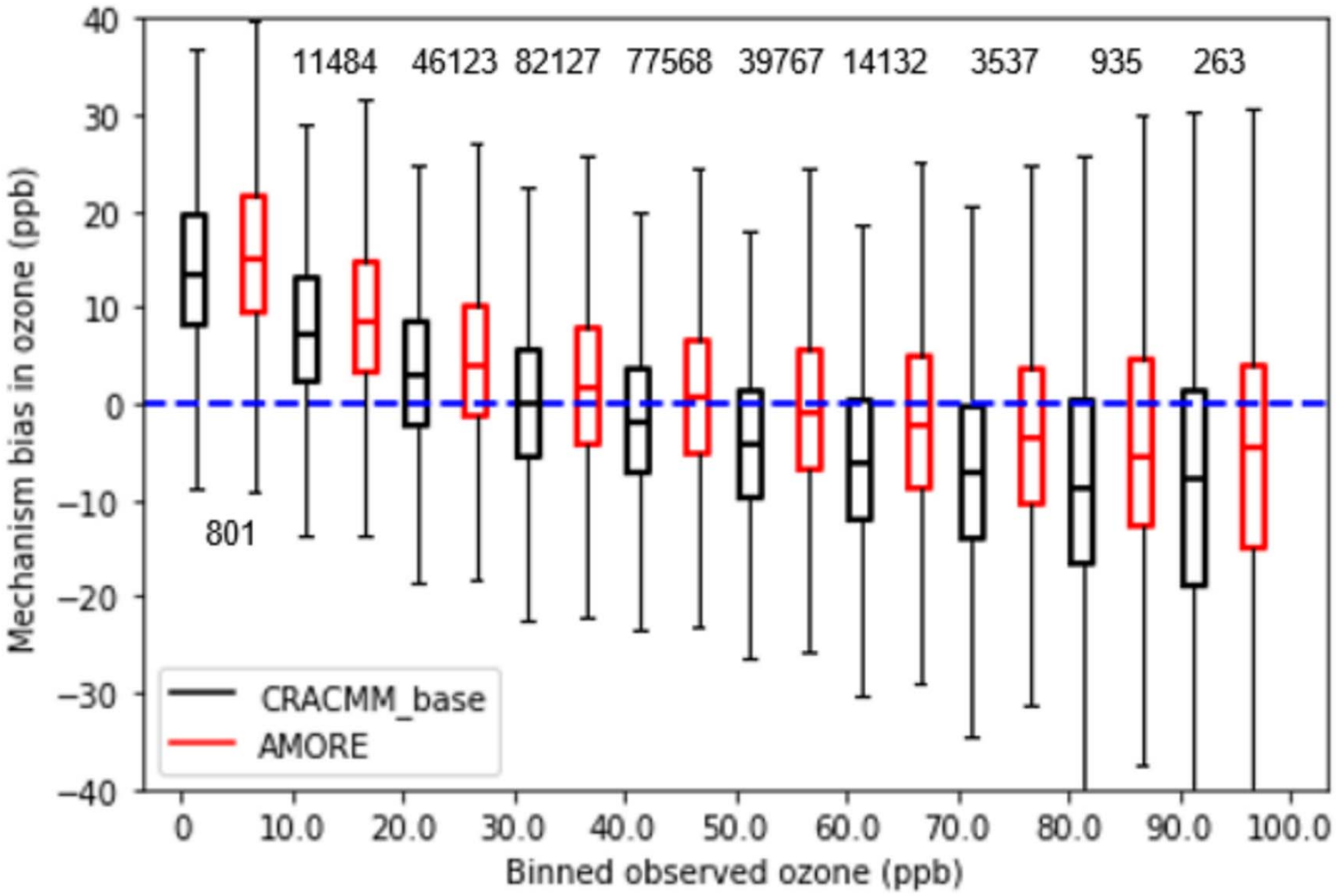
Wiser et al., *GMDD* 2022

Performance vs. Complexity



EPA CMAQ CRACMM-AMORE Testing

O_3 Bias

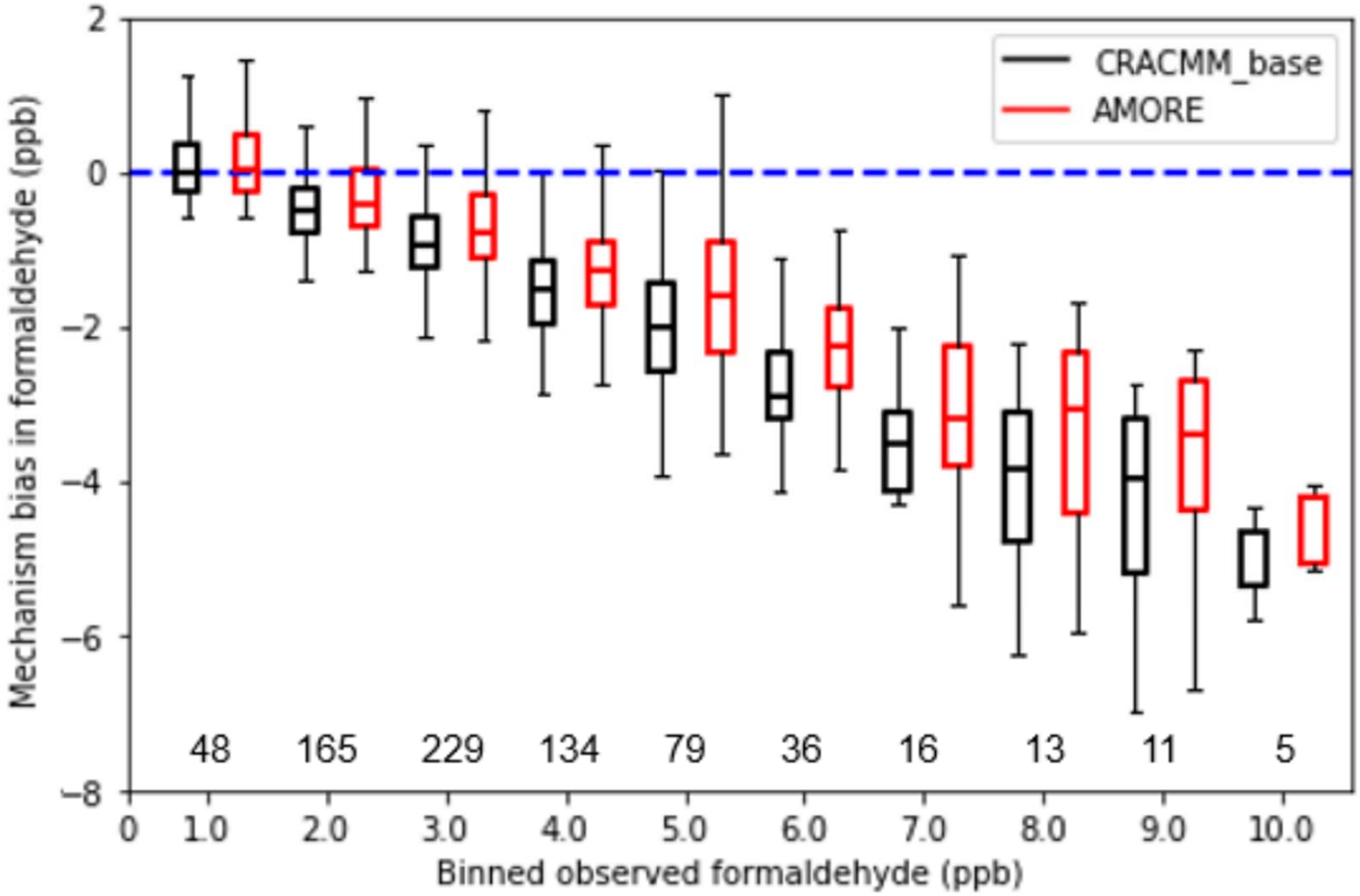


Bryan Place

Wiser et al., *GMDD* 2022

EPA CMAQ CRACMM-AMORE Testing

Formaldehyde Bias



Bryan Place

Wiser et al., *GMDD* 2022

AMORE Isoprene in GEOS-Chem: Mechanism comparison (Box Model Results)

Mechanism	Species	Reactions	Total Error
AMORE-isoprene	12	22	0.17
Caltech Reduced Plus	131	220	0.13
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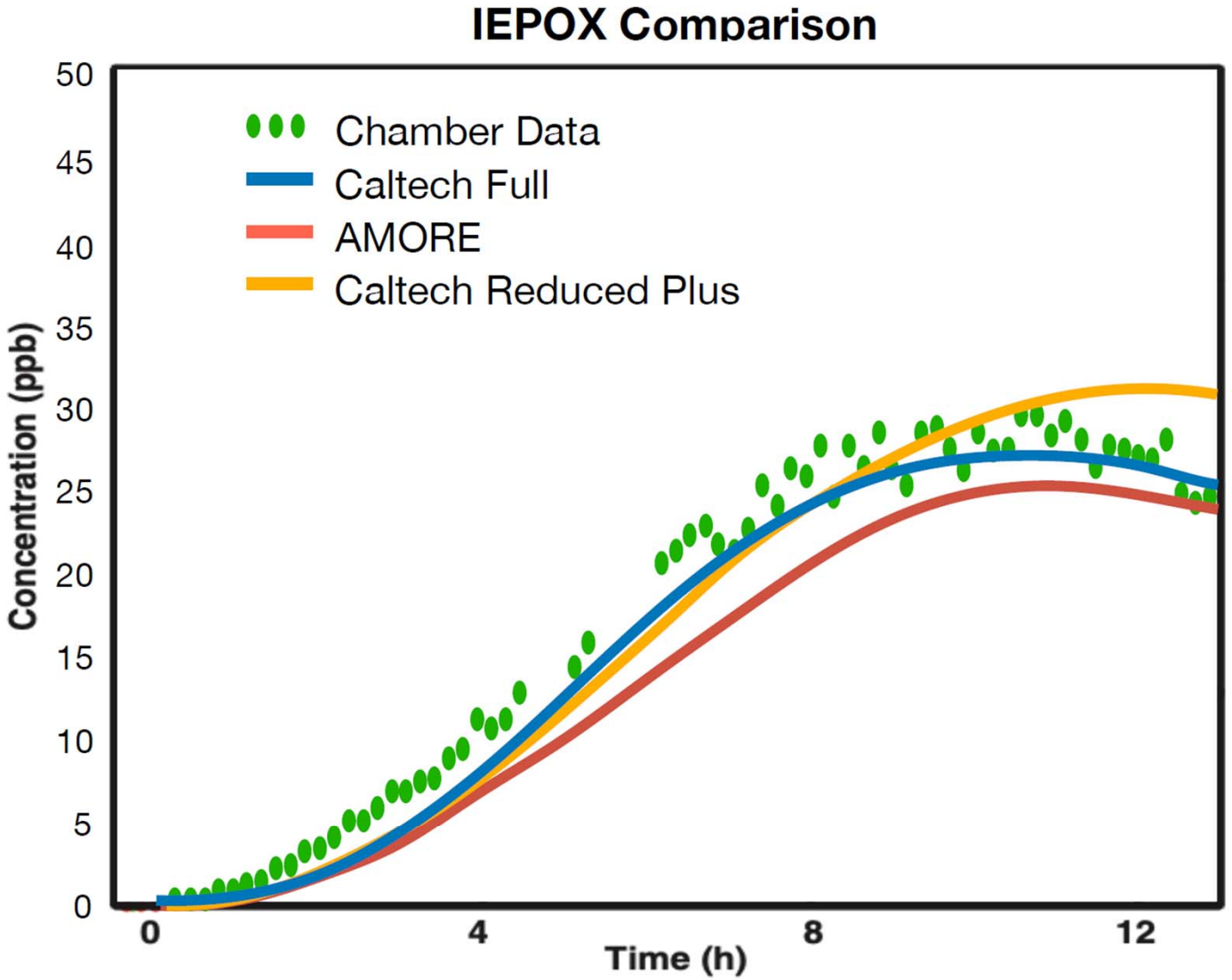
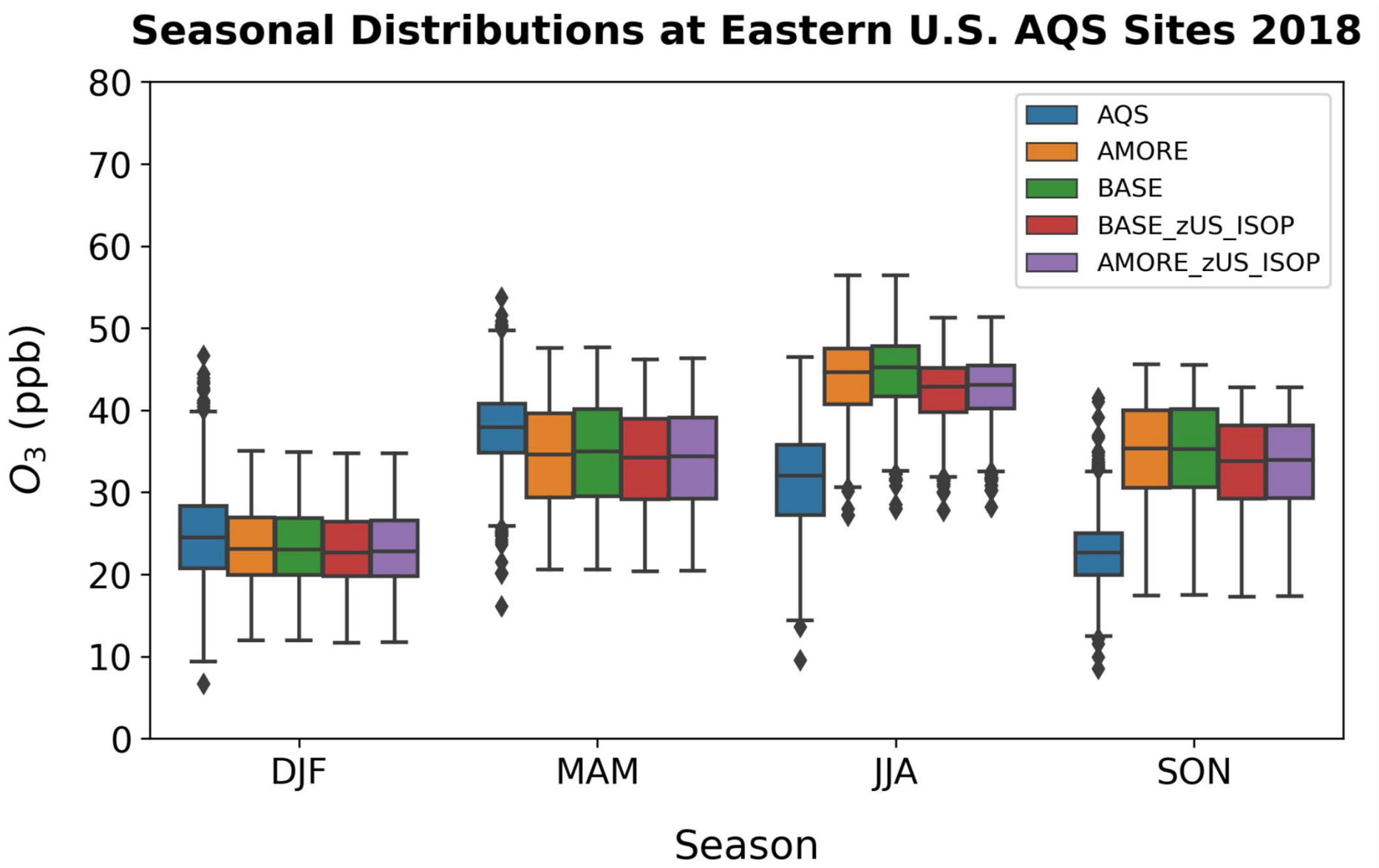
Wiser et al., *GMDD* 2022

Box Model Results: IEPOX Chamber Data Comparison



Init. Isoprene Concentration 92.5 ppb, H2O2 used as OH source init concentration 1660 ppb, H2O2 Photolysis rate constant 2.15e-6, NOx Concentration 1 ppb, green dots are experimental data from Paulot et al, solid lines are F0AM simulations

AMORE isoprene – GEOS Chem Testing



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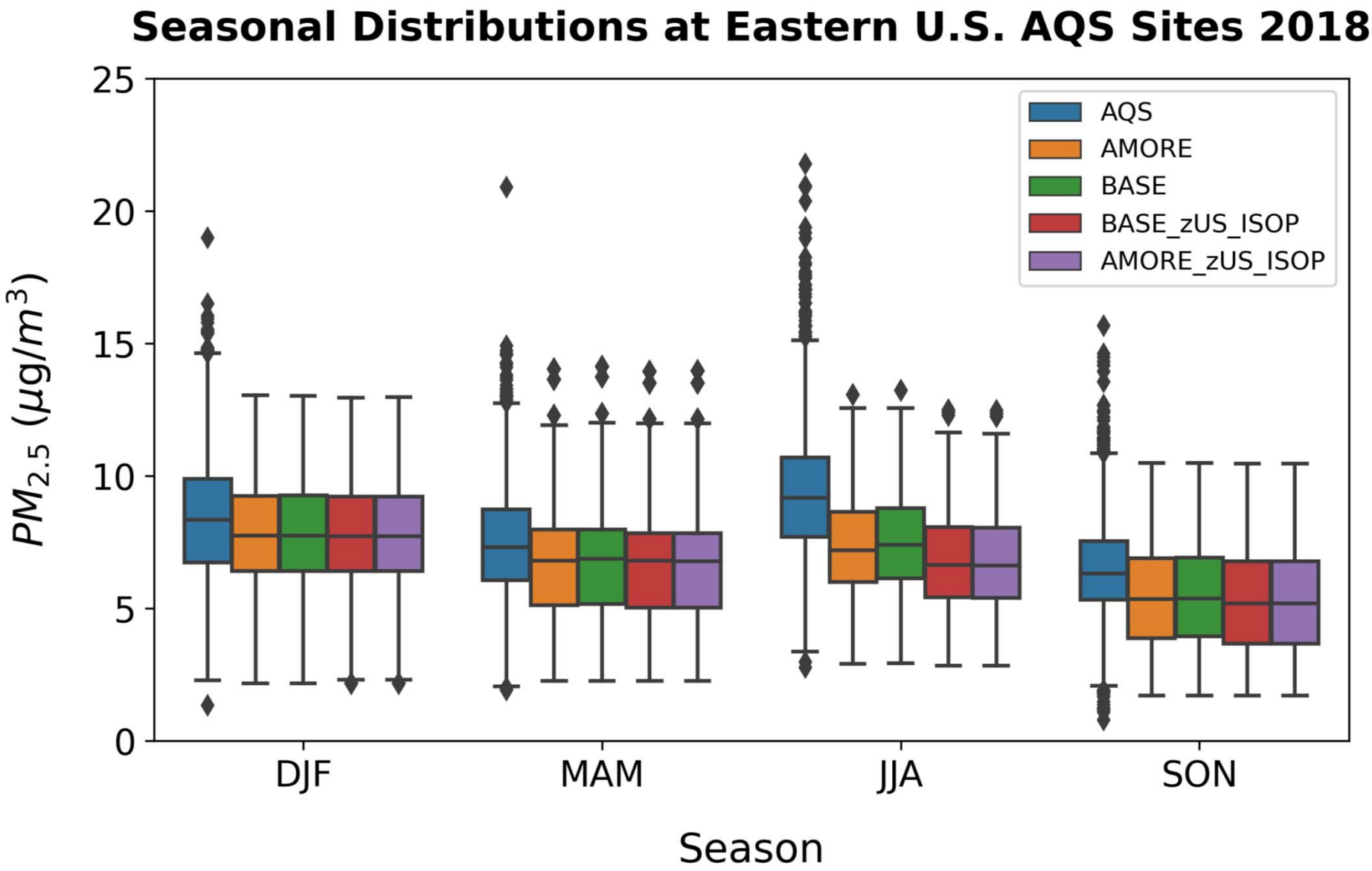
AMORE isoprene – GEOS Chem Testing



Ben Yang

Summary and Next Steps

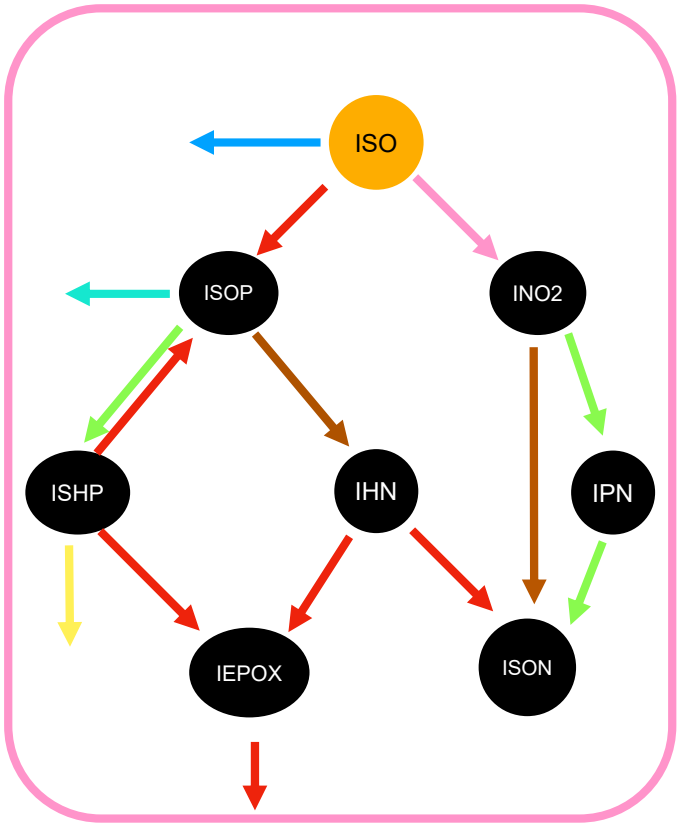
- Automated model reduction is a catalytic tool that reduces barriers for the new science → model update pipeline
- Provides insights into “importance” as well as generating useful reduced mechanisms
- AMORE reduced isoprene mechanism generated using (*mostly*) automated reduction algorithm met targets (small, high accuracy)
- CRACMM1AMORE
- AMORE-isoprene speeds up GEOS-Chem simulations with similar accuracy to base mechanism
- **Next: (more) fully automated algorithm**

Test generalizability to other reaction networks

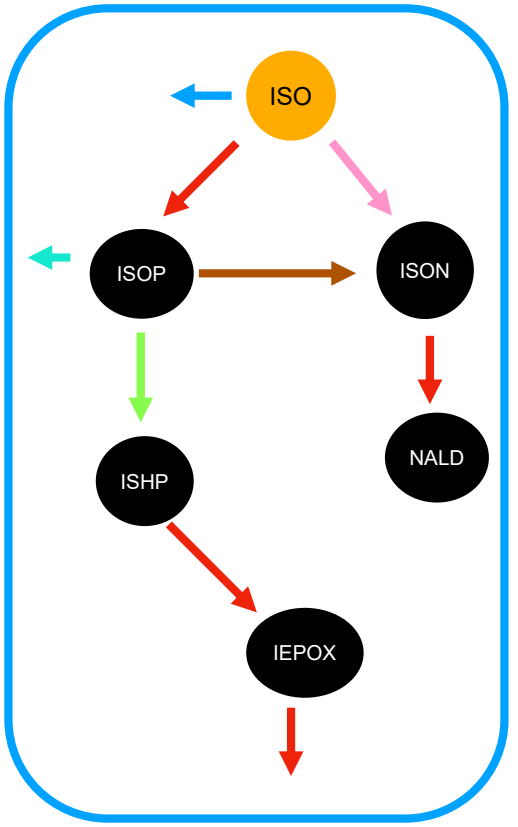

THANK YOU

Mechanism Comparison: AMORE and RACM2

AMORE after manual adjustment



RACM2



OH
HO2
NO3
None
NO
O3
Photolysis
MO2

Our attempts at bridging scales and dealing with complexity and the "importance" paradox

Paradox: How do we evaluate which new processes are "important" enough to include in models until they've been modeled/loop closed with observations?

Physical complexity

- **Process Model: GAMMA** (McNeill et al. 2012…)
- **Lab-to-Environment Modeling** (Sumner et al. 2014, Tsui et al. 2017, 2018, Fankhauser 2019)
- **Parameterizations** (Curry et al. 2019)

Reaction network complexity

- **Simplified Mechanism: simpleGAMMA** (Woo and McNeill 2015, Budisulistiorini et al 2015, 2017, Shrivastava et al 2019)
- **Automated model reduction: AMORE (Wiser et al. 2022)**