Sensitivity of GEOS-Chem to Automated Isoprene Chemical Mechanism Reduction

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1. Introduction

- Biogenic volatile organic compounds, chiefly isoprene, are a significant source of **secondary organic aerosols (SOA) and ozone** in the eastern U.S. during summer.
- The full isoprene oxidation chemical mechanism is highly complex, thus **model reduction** is required for inclusion in large-scale models.
- Even in reduced form, isoprene oxidation is often one of the most **computationally-intensive** components of global 3-D chemical transport models including GEOS-Chem.
- Furthermore, to date, model reduction is generally done by hand, creating a barrier to making updates.
- Our primary goal was to study the **impacts** of incorporating a novel reduced isoprene oxidation mechanism into GEOS-Chem on air pollutants such as $PM_{2.5}$, O_3, NO_2, and formaldehyde.

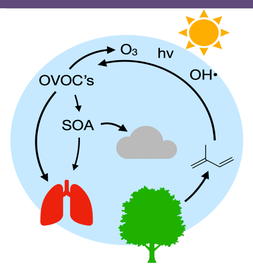
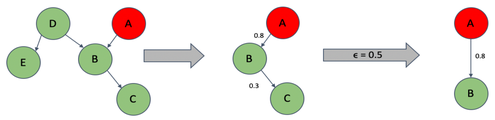


Figure 1. Isoprene is the fuel for atmospheric oxidation by OH, O_3, and NO_3, in the presence of NO_x, that affects air quality.

2. AMORE Method

- Developed the **Automated Model Reduction (AMORE)** algorithm, based on graph theory, with minimal manual adjustment of the output mechanism.
  - AMORE-Isoprene mechanism: **10 species and 23 reactions**
  - Default GEOS-Chem (Caltech Reduced Mini): **52 species and 189 reactions**



$$r_{AB} \equiv \frac{\sum_{i=1,I}|v_{A,i}\omega_i\delta_{Bi}|}{\sum_{i=1,I}|v_{A,i}\omega_i|},$$

$$\delta_{Bi} = \begin{cases} 1 & \text{if the } i\text{th elementary reaction involves species } B, \\ 0 & \text{otherwise.} \end{cases}$$

ω_i = rate of reaction

Figure 2. The chemical mechanism is represented as a directed relation graph with nodes (species) and edges (reactions). Weights r_{AB} are assigned to each edge and eliminated below threshold ϵ.

- Starting from the full mechanism, less important species and reactions were removed, while species in similar reaction pathways were grouped (chemical lumping).
- Steps in the algorithm included yield estimation, path importance, path combination, and path yield addition.
- Performed manual optimization of the mechanism using the F0AM box model with six conditions. Tested in CMAQ, followed by GEOS-Chem.

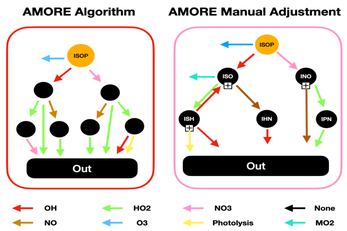


Figure 3. A comparison between the fully algorithmic AMORE mechanism and AMORE with manual updates. In addition, NO_2 chemistry was manually optimized.

3. GEOS-Chem Model Setup and Evaluation

- GEOS-Chem "Classic" v13.3.3, full chemistry, complex SOA (semi-volatile POA) scheme, MERRA-2 meteorology, 2.0 x 2.5° horizontal resolution, 72 vertical levels.
- Replaced default chemical mechanism in **Kinetic PreProcessor (KPP)** v2.3.3 custom description file to create new solver files (Fortran-90 format), which were then compiled in GEOS-Chem.
- Four full-year global simulations (January-December 2018) were run on Columbia's HPC "Ginsburg" on a 32-core node, with monthly output diagnostic files.
  - With AMORE-Isoprene mechanism (**AMORE**): **~13 hours runtime / month simulation**
  - With default mechanism (**BASE**): **~14 hours runtime / month simulation**
  - AMORE and BASE with isoprene emissions zeroed out over the contiguous U.S. (**zUS_ISOP**)
- Used daily observations from **EPA AQS and *IMPROVE sites**, averaged monthly and seasonally, to assess model performance (nearest grid cell to each point observation).
  - $PM_{2.5}$: 667 sites
  - NO_2: 197 sites
  - Formaldehyde: 94 sites
  - O_3: 834 sites
  - Isoprene: 28 sites
  - *Total organic carbon: 54 sites
- Focused on latitude = [24°, 49°] and longitude = [-100°, -66°], a bounding box roughly encompassing the relatively humid, forested, and urbanized "eastern" U.S.

4. Sensitivity Analysis Box Plots

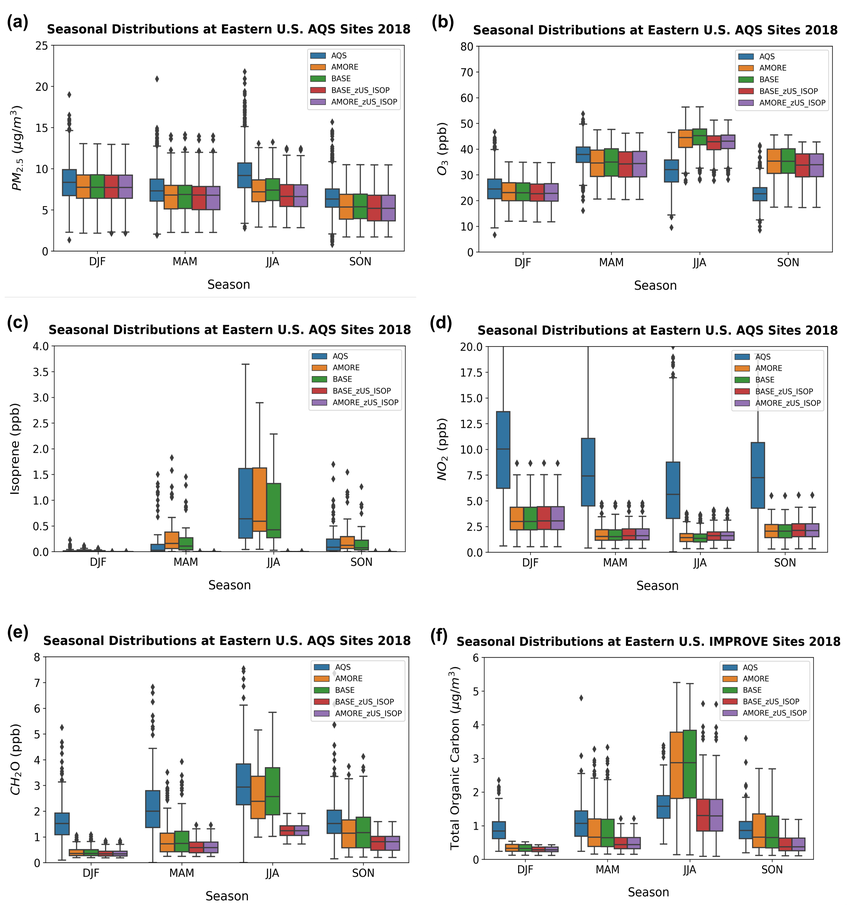


Figure 4. Distributions of $PM_{2.5}$ (**a**), O_3 (**b**), isoprene (**c**), NO_2 (**d**), formaldehyde (**e**), and total organic carbon (**f**) at AQS/IMRROVE sites within the eastern U.S. domain for all GEOS-Chem simulations, grouped by season. Isoprene emissions peak in the summer, slightly elevating simulated $PM_{2.5}$ and O_3 levels, but more significantly increasing formaldehyde and total OC levels. Observed NO_2 is influenced by local or urban (higher) emissions, while modeled NO_2 is averaged (lower) by coarse grid cells.

5. Spatial Results

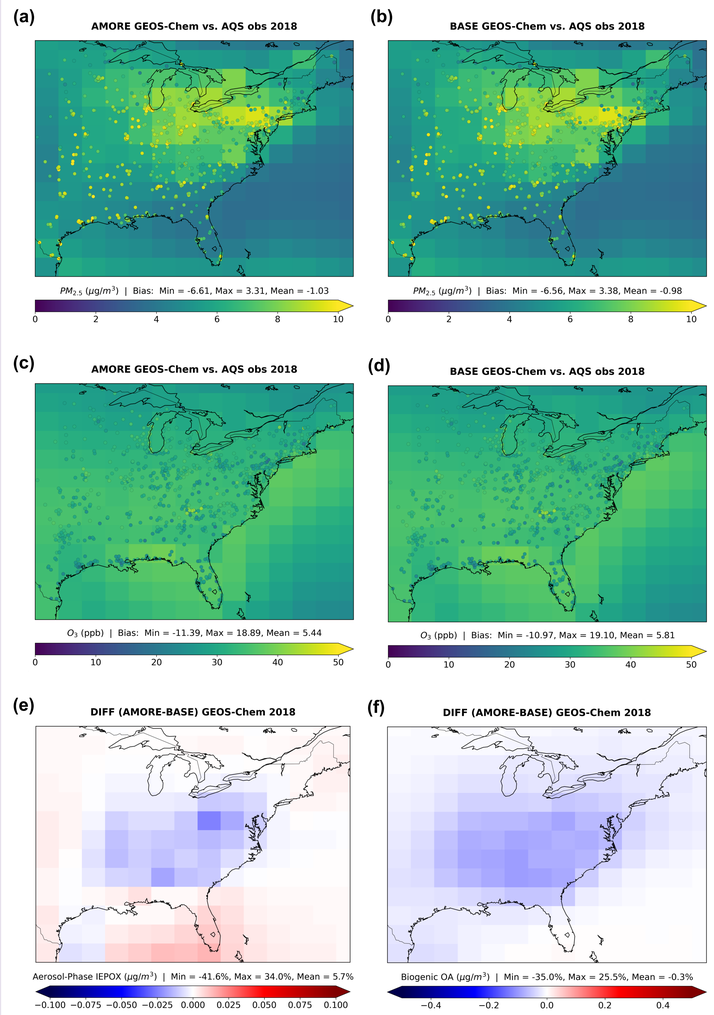


Figure 5. Maps of simulated $PM_{2.5}$ (**a-b**), O_3 (**c-d**), aerosol-phase IEPOX (**e**), and biogenic OA (**f**) averaged over 2018 for the eastern U.S. domain. Dots represent AQS sites, and bias is the modeled minus observed values. $PM_{2.5}$ and O_3 are both slightly lower (mean biases differ by 0.05 μg m^{-3} and 0.37 ppb) in AMORE than BASE, practically the same. Difference plots of aerosol-phase IEPOX and biogenic OA indicate minor reductions in SOA formation in AMORE.

6. Conclusions

- GEOS-Chem can simulate air pollutants with **similar accuracy** using the AMORE-Isoprene mechanism over the default mechanism.
- For some species, including O_3, AMORE even slightly reduced the existing model bias.
- AMORE is **computationally faster** than BASE by ~7% for total model runtime, ~15% for all chemistry, and ~25% for KPP.
- The automated reduction process can **streamline model development**.
- Tests reveal that optimizing chemical cycling of NO_2 is particularly important for isoprene oxidation which affects $PM_{2.5}$ and O_3 via different pathways.
- We aim to eventually make AMORE open source and sufficiently flexible to allow for timely future updates and application to other chemical systems for efficient air quality forecasting, research, and management.

8. Acknowledgements

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7. References

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