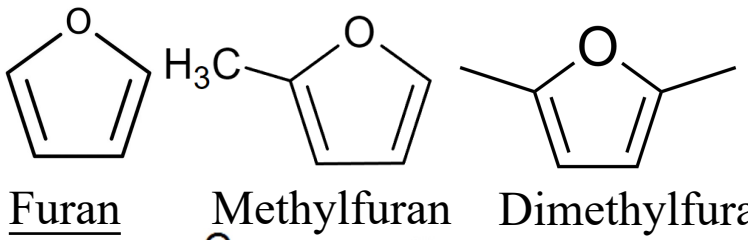
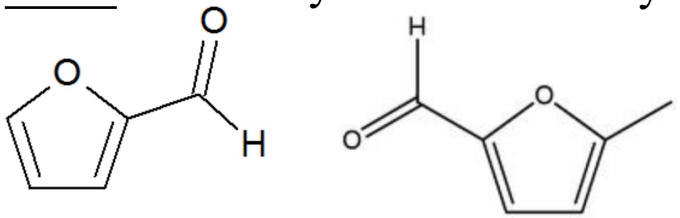
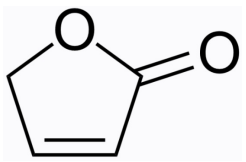
Global chemical impacts of furanoids: model analysis and constraints from in-situ observations

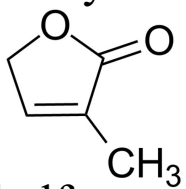


Furan Methylfuran Dimethylfuran



Furfural Methylfurfural





Furanone Methylfuranone

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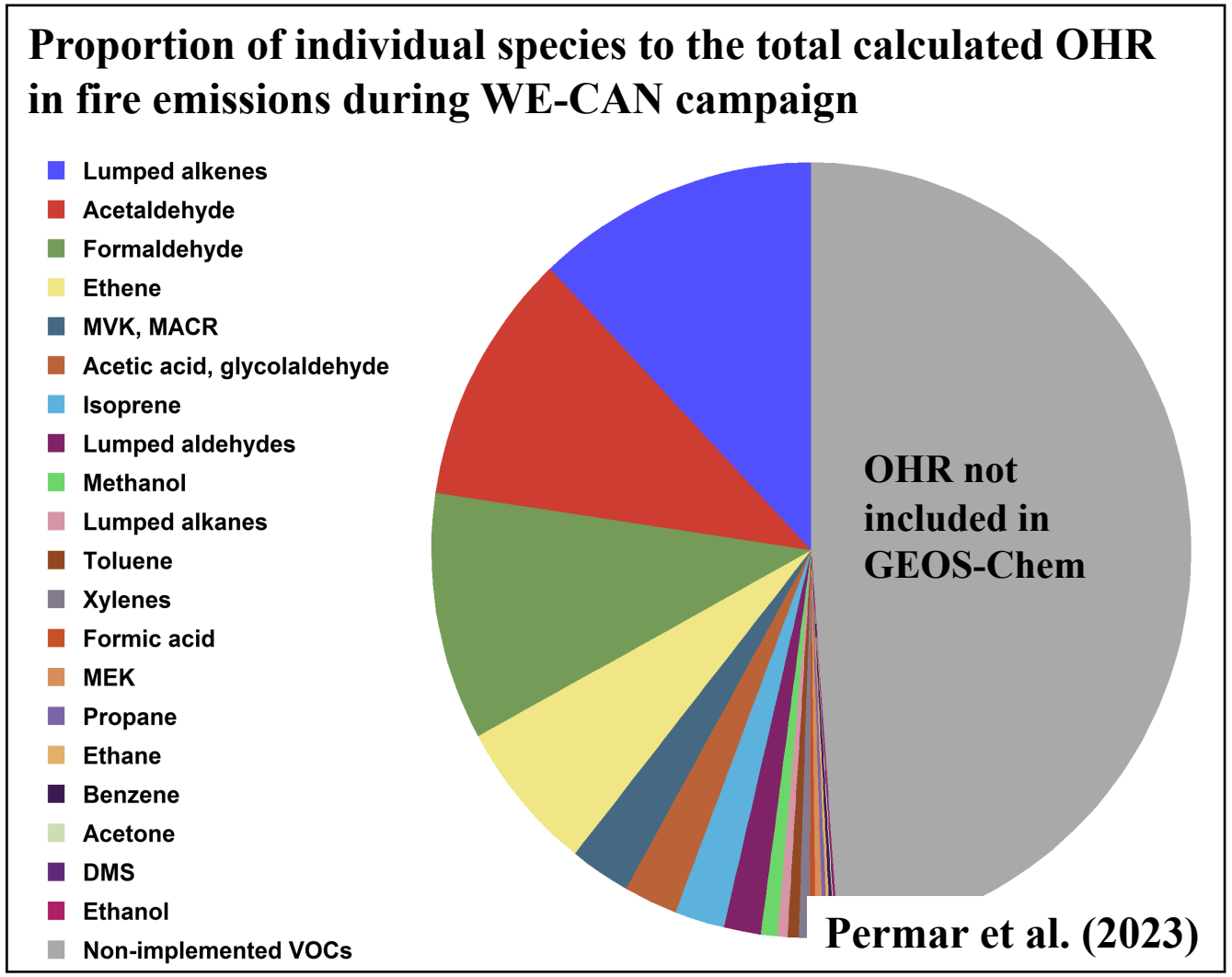
The importance of understanding oxidation of furanoids

OH reactivity (OHR) is used to describe how reactive the species are.



About half of the OH reactivity in fire emissions are not currently included in the GEOS-Chem!

Keywords: OH reactivity, unmodelled, furanoids

The importance of understanding oxidation of furanoids

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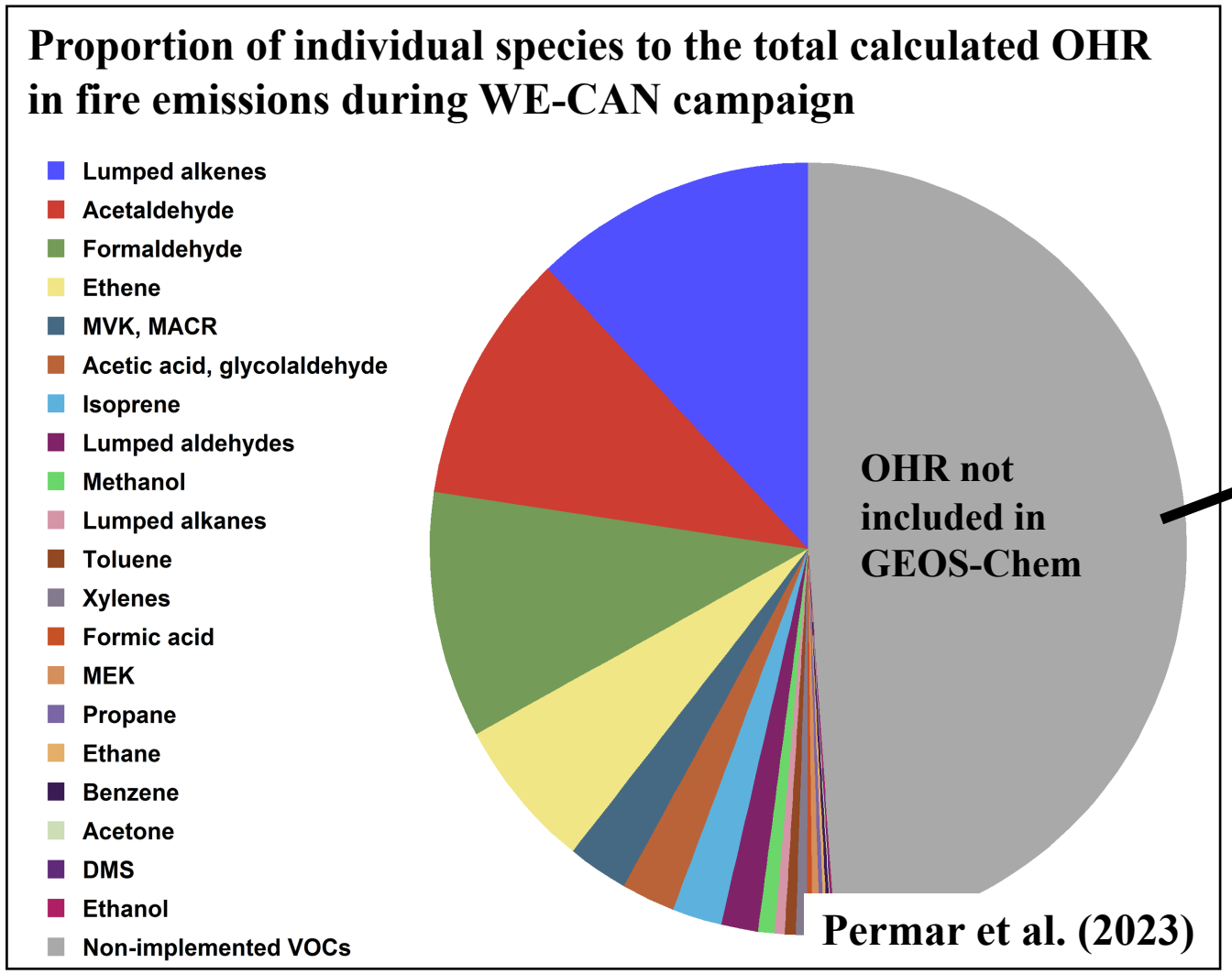
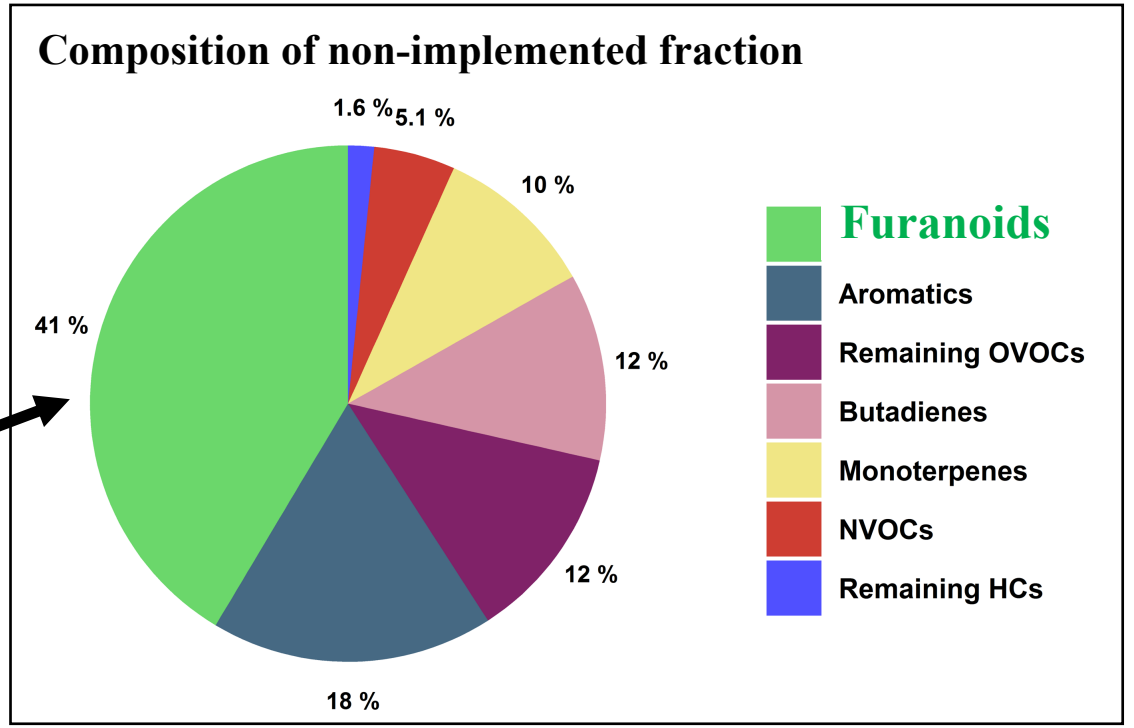


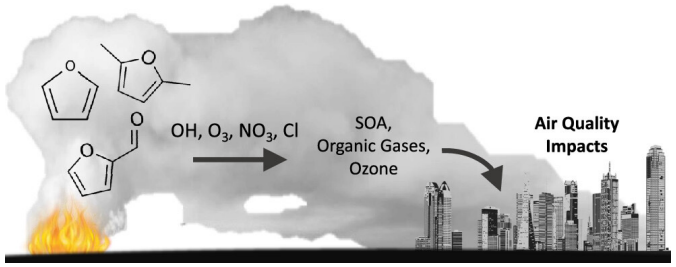


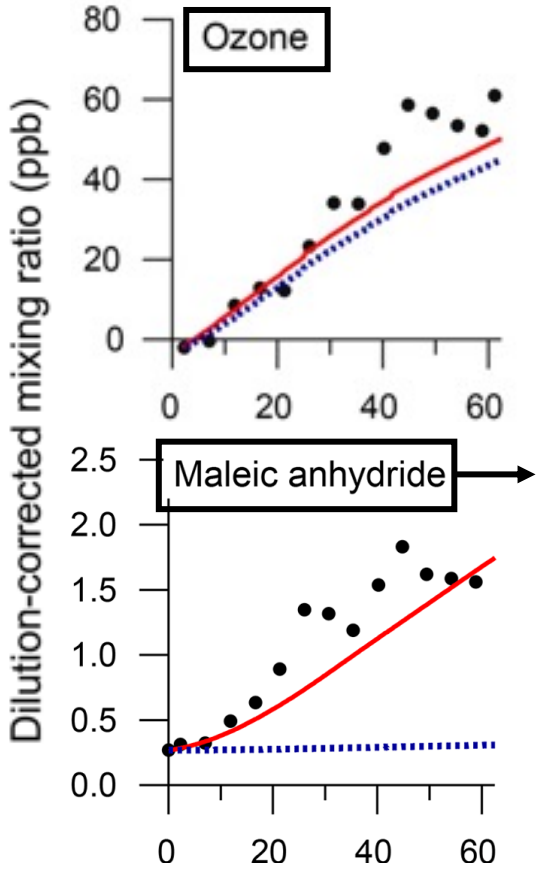
About 40% of unmodelled OH reactivity are from furanoid compounds!

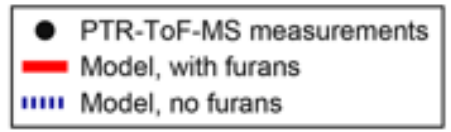
Keywords: OH reactivity, unmodelled, furanoids

The importance of understanding oxidation of furanoids

Furanoids







Coggon et al. (2019)

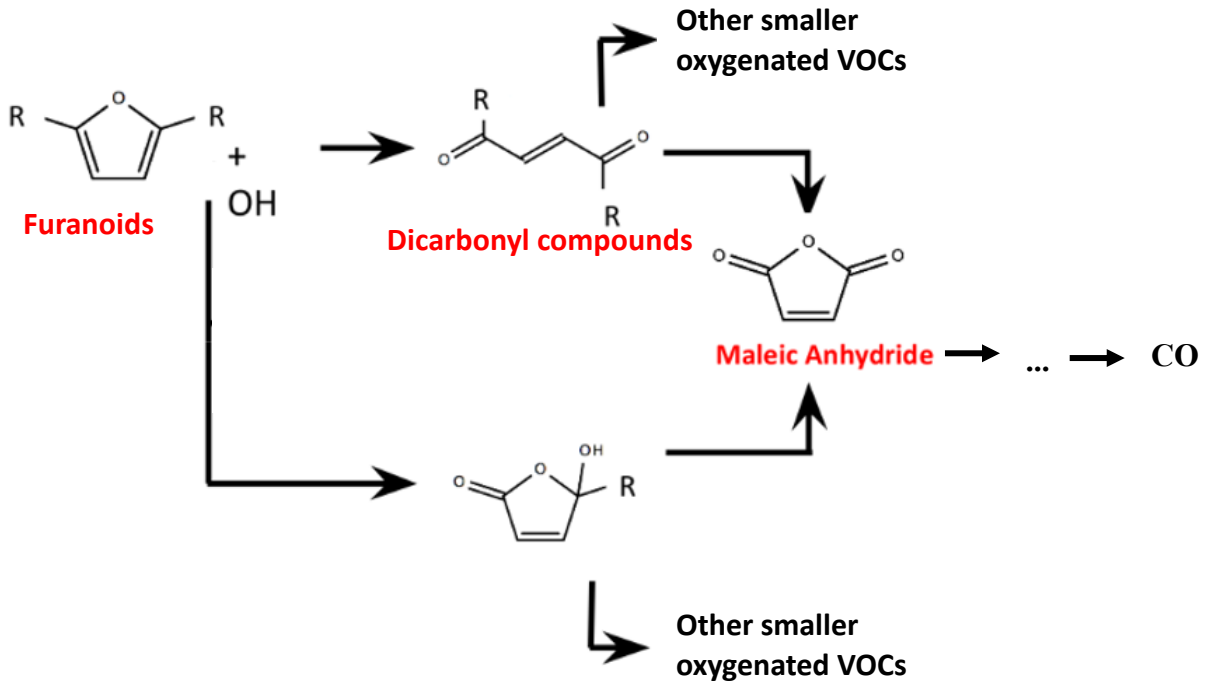
Hazardous air pollutants (HAP)
(e.g., asthma and cancer)

Evaluating OH, O_3, and PAN in Biomass Burning Plumes: Insights from MCM and GEOS-Chem

- Furanoids account for 10% of ozone formation within 1 hours of plume aging.
- The 90% of maleic anhydride (one of HAPs) in smoke plumes are from the furanoids oxidation.
- Also, furanoids are important precursors of PAN-like organic nitrates (Roberts et al., 2022; **Poster C7**).

Reduced mechanism development

Box model validation: focusing on chemical mechanism alone



The furanoid chemistry is fairly straightforward – the reaction of a number of furanoids react with OH, and then form a second-generation product, **maleic anhydride.**

Explicit furanoid mechanism (Coggon et al.):

- 35 species and 300 reactions
- chemistry for seven individual furanoids

↓ **Lumping based on similar chemical structures**

Reduced FA mechanism (+NO_3 and O_3 loss):

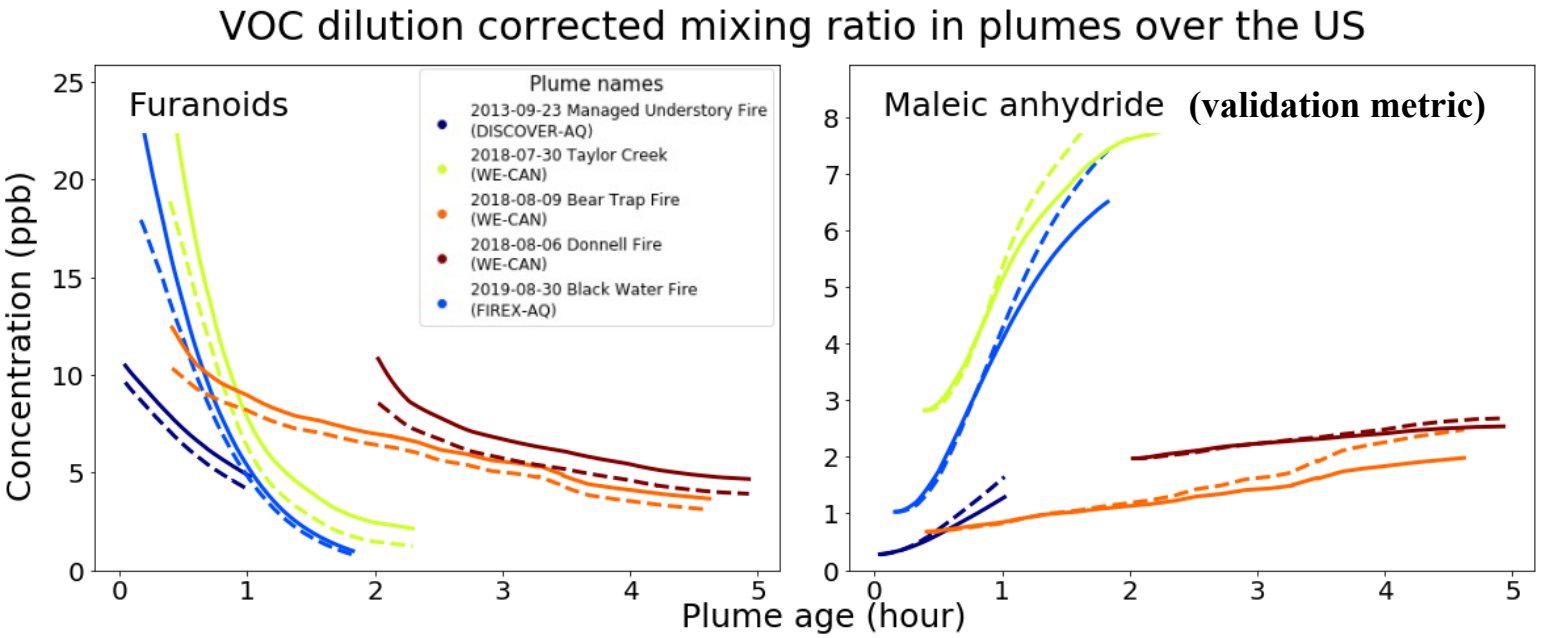
- 14 unique species and 23 unique reactions
- chemistry for three furanoid precursors
- They are lumped furans, lumped furfurals, and lumped furanones

- We developed a reduced furanoid mechanism (FA) to describe the chemistry of seven furanoids using **14 unique species and 23 reactions**.
- When compared to MCM, the FA mechanism can agree with the explicit mechanism within 10% for both furanoids and maleic anhydride, indicating the robustness of the reduced mechanism in furanoid oxidation.

Mechanism validation in a box model

Furanoids

Box model validation: **focusing on chemical mechanism alone**



MCM (explicit): solid lines

FA (reduced): dashed lines

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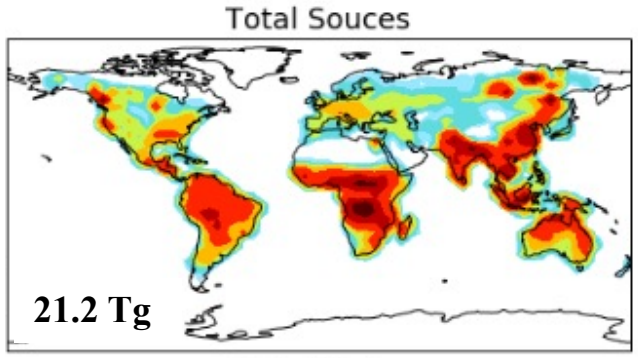
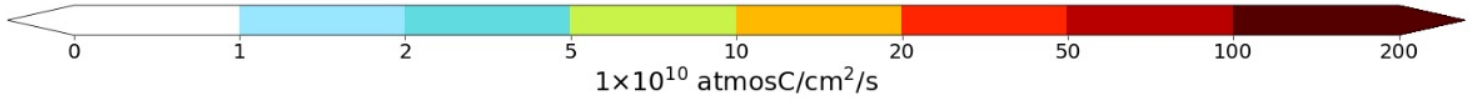
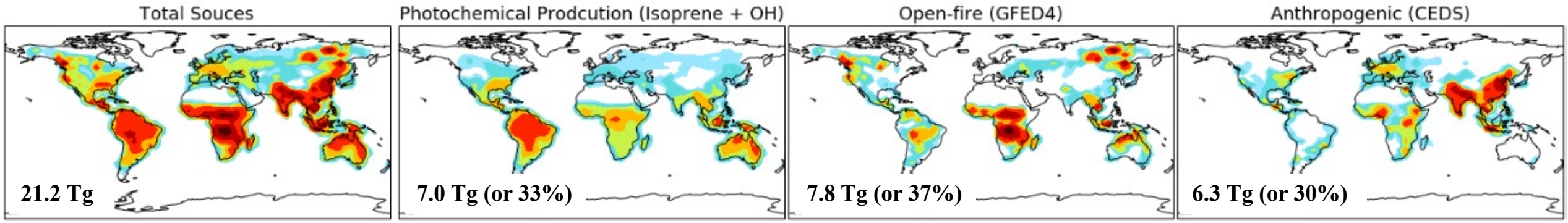
Current understanding of global furanoid sources and sinks



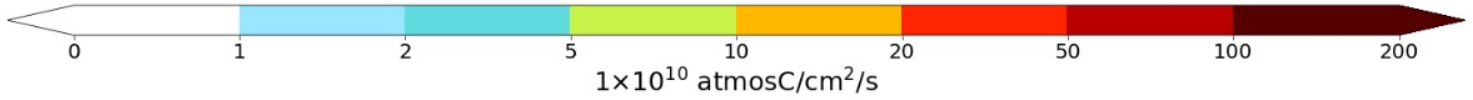


- The global source of furanoids are estimated at **21.2 Tg yr^{-1}**, which **are comparable to** estimation of the total of benzene, toluene, and xylenes (16–26 Tg yr^{-1}).

Current understanding of global furanoid sources and sinks

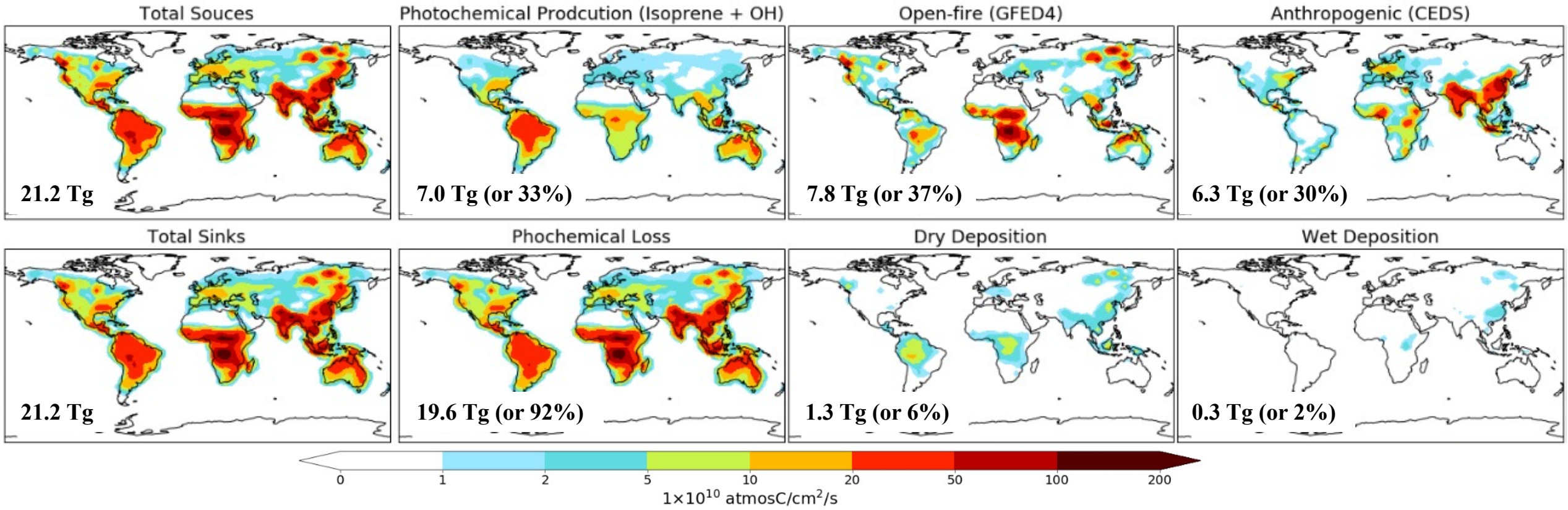


Not just about fire emissions



- The photochemical production are from the **OH oxidation of isoprene** yielding 3-methylfuran.
- The open fire emissions are calculated by **GFED4** with recent compilation of fire emission factors (EFs).
- The anthropogenic emissions are calculated by **CEDS** with updating EFs of **biofuel, trash burning, and traffic emission**.

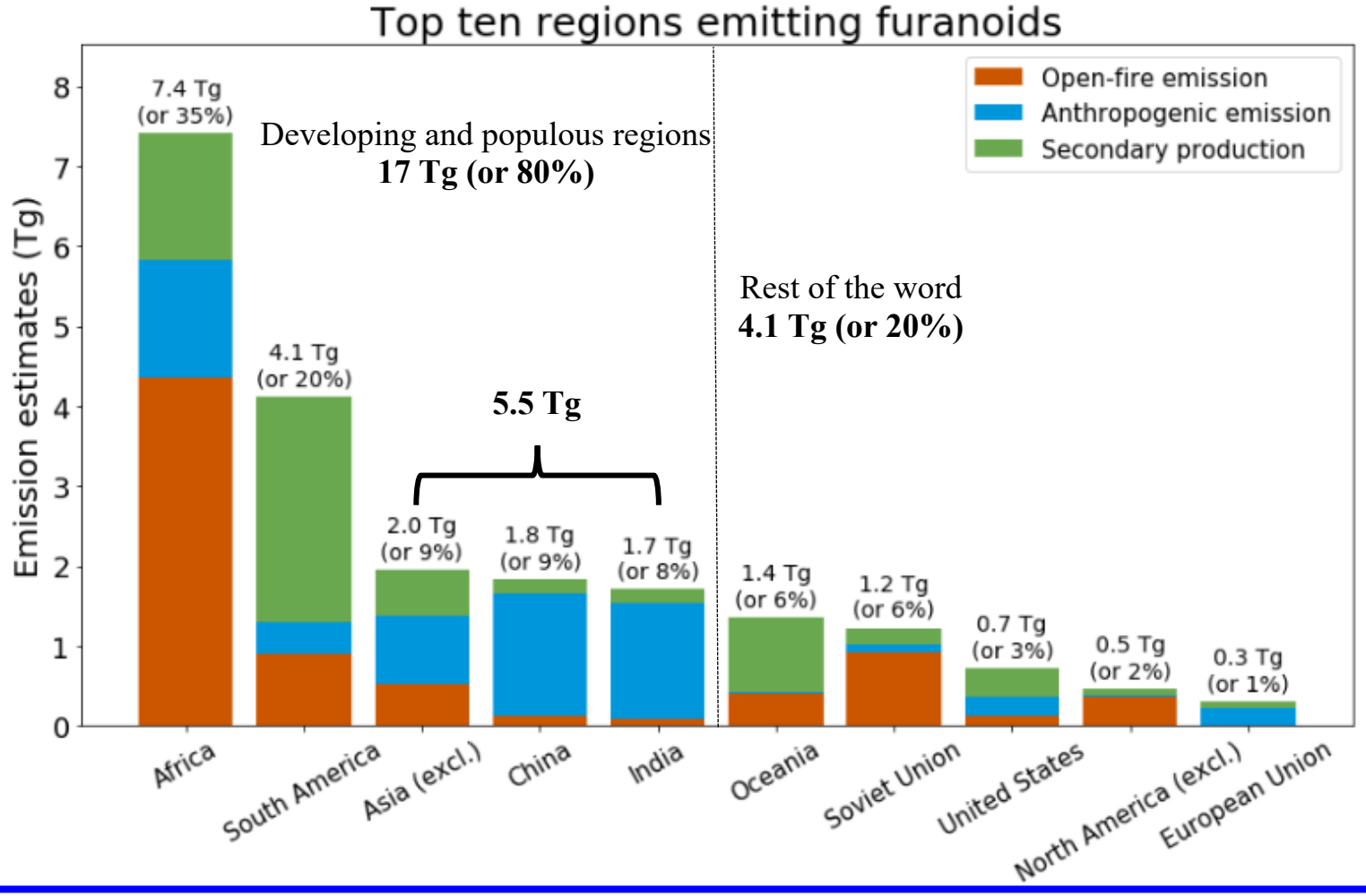
Current understanding of global furanoid sources and sinks



- The 92% of the global source estimates are balanced by photochemical loss paths in the form of gas phase oxidation by **OH (70%), NO_3 (22%), and O_3 (<1%).**

- The remaining 8% of the furanoids source is consumed by dry and wet deposition.

Current understanding of regional furanoid sources

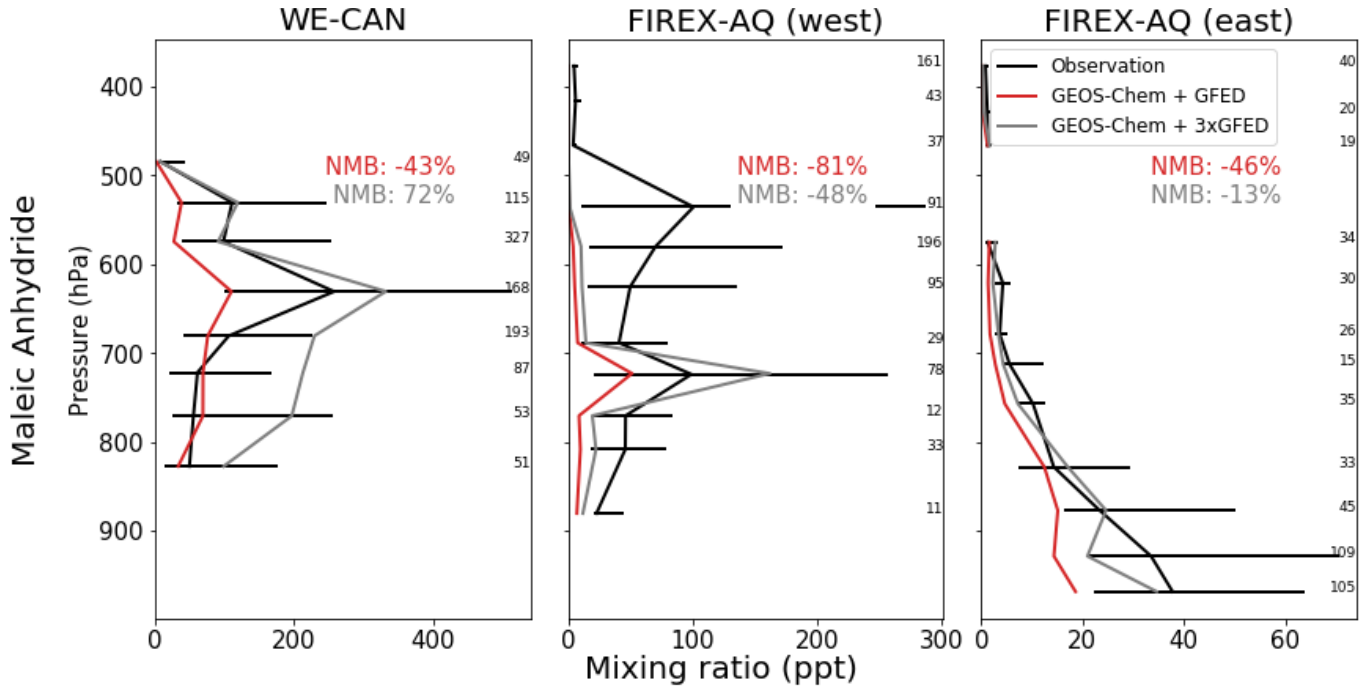


- Furanoid sources are disproportionately high in developing and populous regions.
- In Asia, anthropogenic emissions are the major furanoid contributors. Specifically, China and India are identified as the leading contributors within Asia, responsible for about 65% of the continent's furanoid sources.

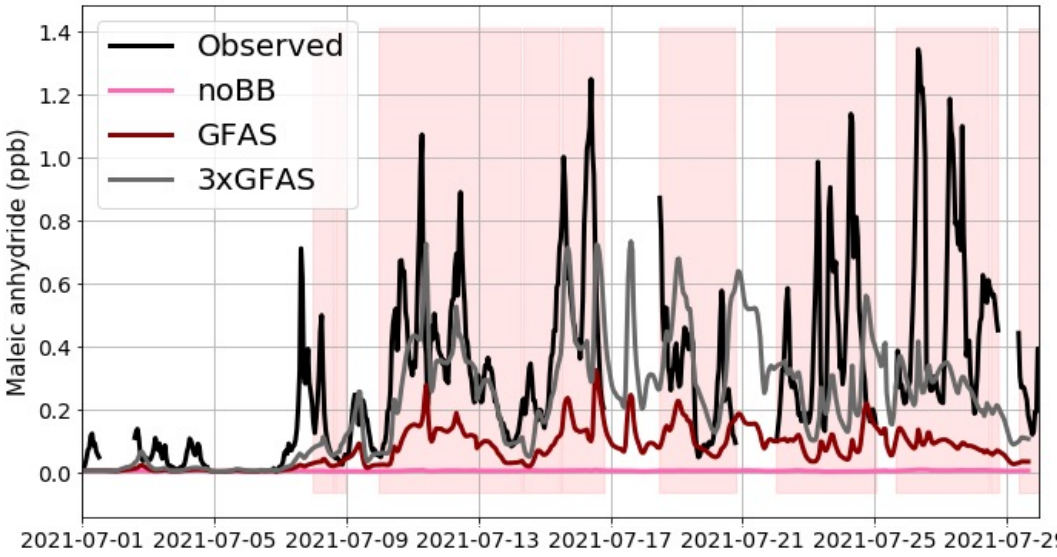
Model evaluation in GEOS-Chem CTM

CTM: emission, chemistry, injections, and sub-grid issues

Median vertical profile during WE-CAN and FIREX-AQ

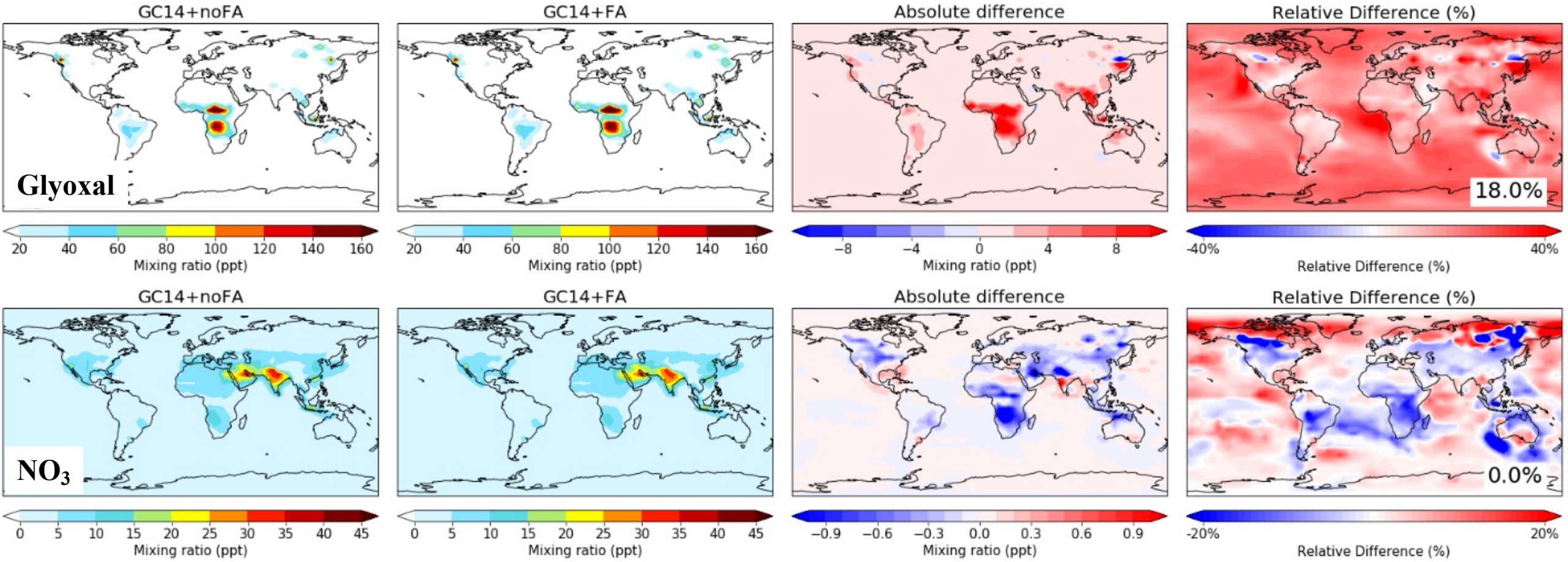


Maleic anhydride ground measurement (Missoula)



- The base model underestimates maleic anhydride by 50-100%, likely due to underestimated fire emissions in fire inventories (Jin et al., 2023).
- Simulations with tripled fire emissions fairly agree observations within instrument uncertainty (50%), **confirming the robustness of the reduced FA mechanism.**

Global chemical impact of furanoids in surface annual mean



- The furanoids and their products are important precursors of OVOCs such as glyoxal, **contributing to ~20% of annual glyoxal abundance globally**.
- Also, **NO_3 is decreased by up to 20%** in source regions, indicating a significant amount of secondary aerosol such as brown carbon is likely produced through furanoids' oxidation (Chen et al., 2022).

Summaries

Conclusions:

- We developed a reduced furanoids mechanism (FA) to describe the chemistry of key furanoids using **14 unique species and 23 unique reactions**.
- We validated the FA mechanism using aircraft and ground measurements, showing that the **FA mechanism can reasonably reproduce the explicit mechanism and observations**.
- Globally, furanoids are estimated at **21.2 Tg per year**, which are comparable to estimation of BTX aromatics. Regionally, furanoids are **disproportionately high in developing and populous regions** driven by anthropogenic emissions (e.g., biofuel usage).
- Sensitivity tests show that furanoids contribute to **20% of glyoxal** abundance globally, and likely **an important source of brown carbon** in source regions.

Future work:

- Summarize the chemical impacts of furanoids on various compounds at both regional and global scale, including ozone, PAN-like nitrates, atmospheric radicals, and smaller OVOCs.

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Keywords:
Furanoids, reduced mechanism, emissions, and chemical impacts