

One-dimensional canopy modeling of biogenic VOCs during the 2016 PROPHET AMOS campaign

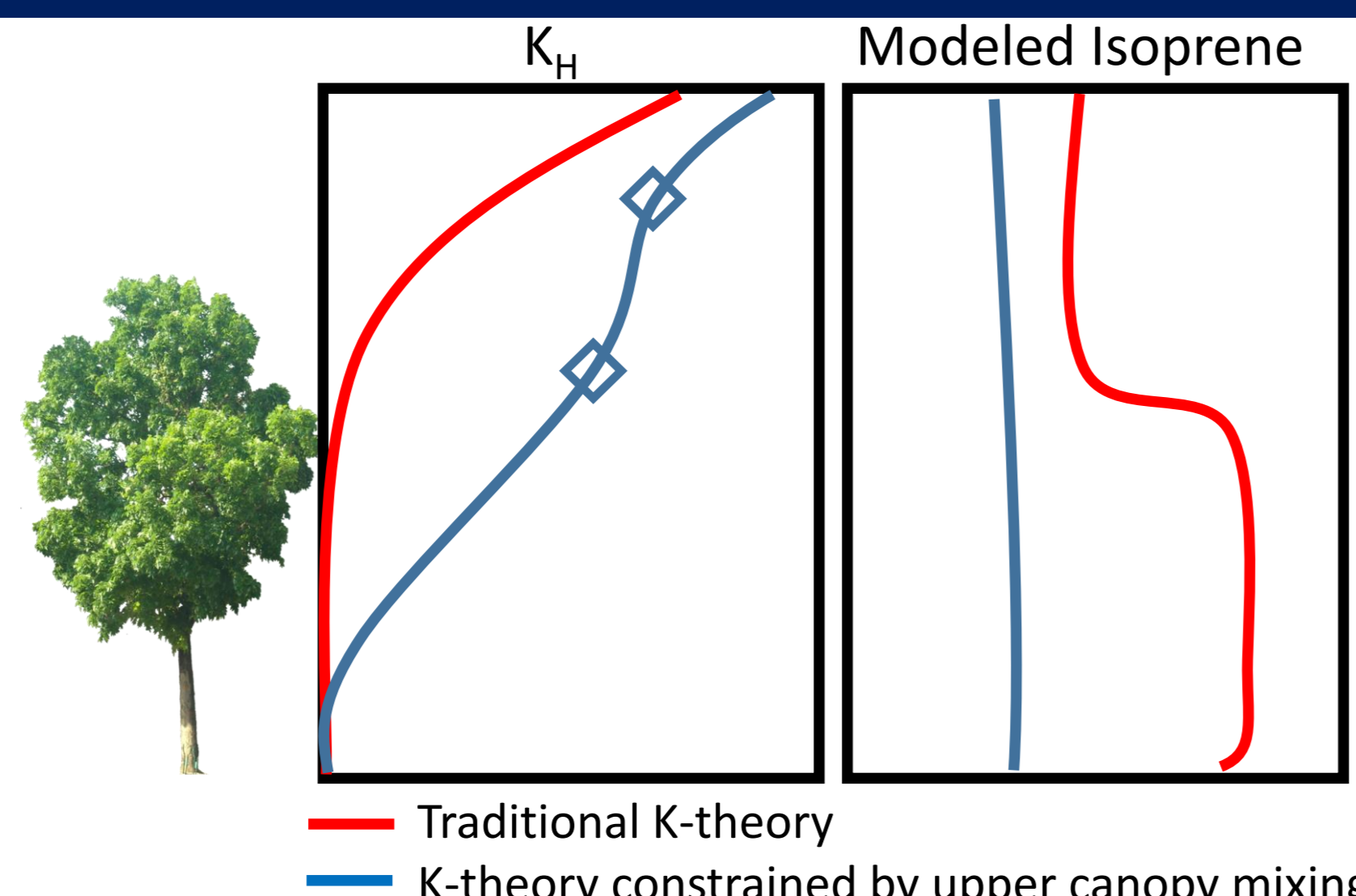
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Motivation

Significant model-measurement discrepancies in biogenic volatile organic compound (BVOC) rich, low NO_x regions point to important gaps in our understanding of gas-phase oxidation in forested environments. Significant underestimates of modelled OH [1] and over estimates of isoprene and oxidation products [2-3] support the idea of missing oxidation pathways [4-5]. In addition to mechanism uncertainties, uncertainties arising from the challenges of modelling turbulence within forest canopies further hinders our ability to evaluate chemical mechanisms. Turbulence is frequently parameterized within the boundary layer following K-theory, where turbulent exchange is a function of eddy diffusivity (K_H). This parametrization has been shown to significantly mischaracterize mixing in forests [6], but it is still widely used because of its simplicity. Bryan et al. found that modifying K-theory with constraints from above canopy and upper canopy sonic anemometers could significantly improve prediction of reactive species in a 1D model [7]. These constraints did not remove model discrepancies entirely and one suggestion for this was that, while mixing at the top of the canopy was well constrained, mixing within the subcanopy (<0.6 x canopy height) was not.

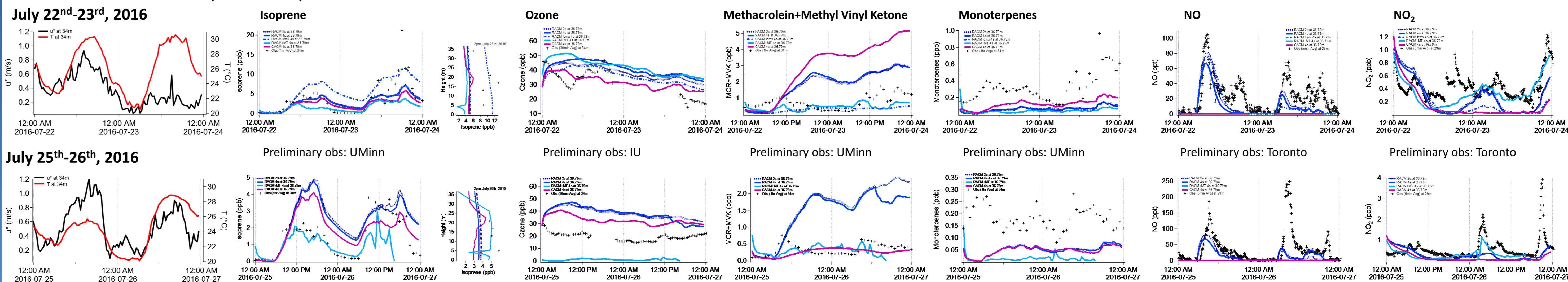


— Traditional K-theory
— K-theory constrained by upper canopy mixing

How well does K-theory modified by upper canopy observations characterize lower canopy mixing? Can we improve BVOC oxidation modelling by adding more observational constraints on subcanopy mixing? Will an improved turbulence representation allow us to better select chemical mechanisms for canopy modelling?

Campaign Time Series: Modelled Results and Preliminary Measurements

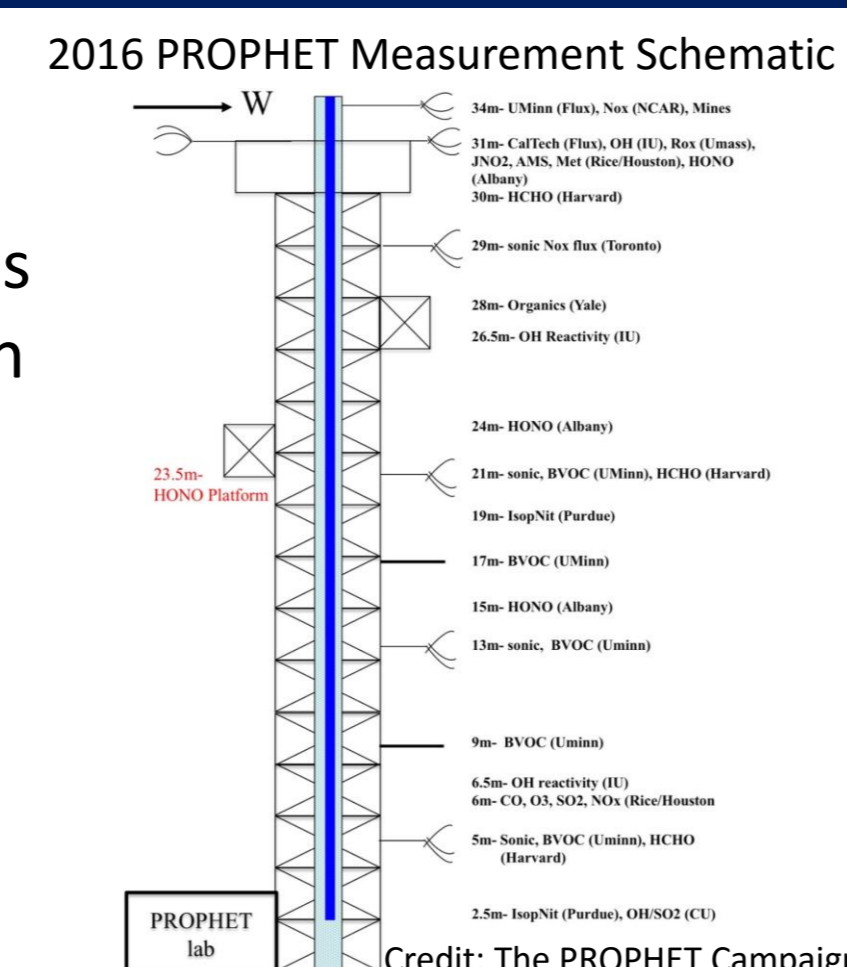
Two modelled 48 hour windows are shown below. July-22nd-23rd is chosen because of the anomalously high isoprene concentrations seen on the 23rd that corresponded with a period of midday atmospheric stability. July 25th-26th is chosen because it was an unstable period with enhanced subcanopy mixing. Both windows were free from precipitation. Preliminary mixing ratio observations have been provided by co-authors.



PROPHET AMOS Campaign: July 1st-31st, 2016

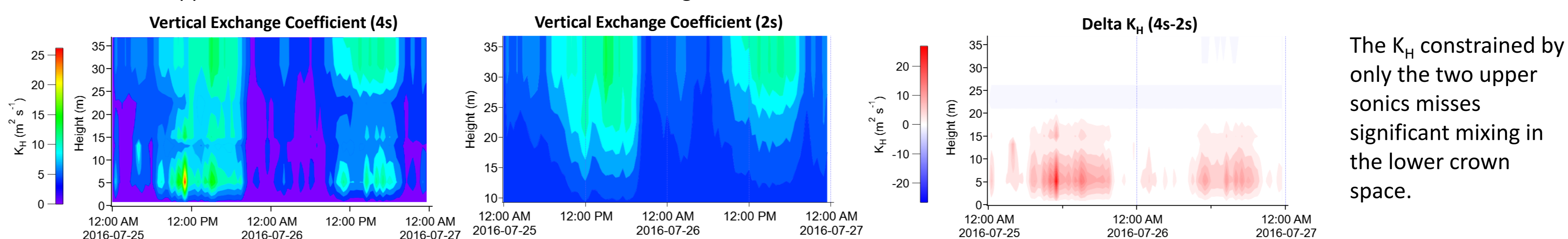
The PROPHET (Program for Research on Oxidants: PHotochemistry, Emissions, and Transport) site consists of a 34m flux tower and laboratory located at the University of Michigan Biological Station (45.5528° N, 84.7839° W) surrounded by a mixed deciduous forest. The 2016 AMOS (Atmospheric Measurements of Oxidants in Summer) campaign took place from July 1st-31st, 2016 to build on measurements of reactive species made during CABINEX in 2009 [7]. Measurements of HO_x, reactive nitrogen species, ozone, BVOCs, and oxygenated products were made this summer and some preliminary observations are included here. See schematic on right for the full campaign measurement list.

Four 3D sonic anemometers were set up at 5m (CSAT3), 13m (CSAT3), 21m (CSAT3), and 29m (81000 RM Young) heights on the tower to constrain mixing in the model.



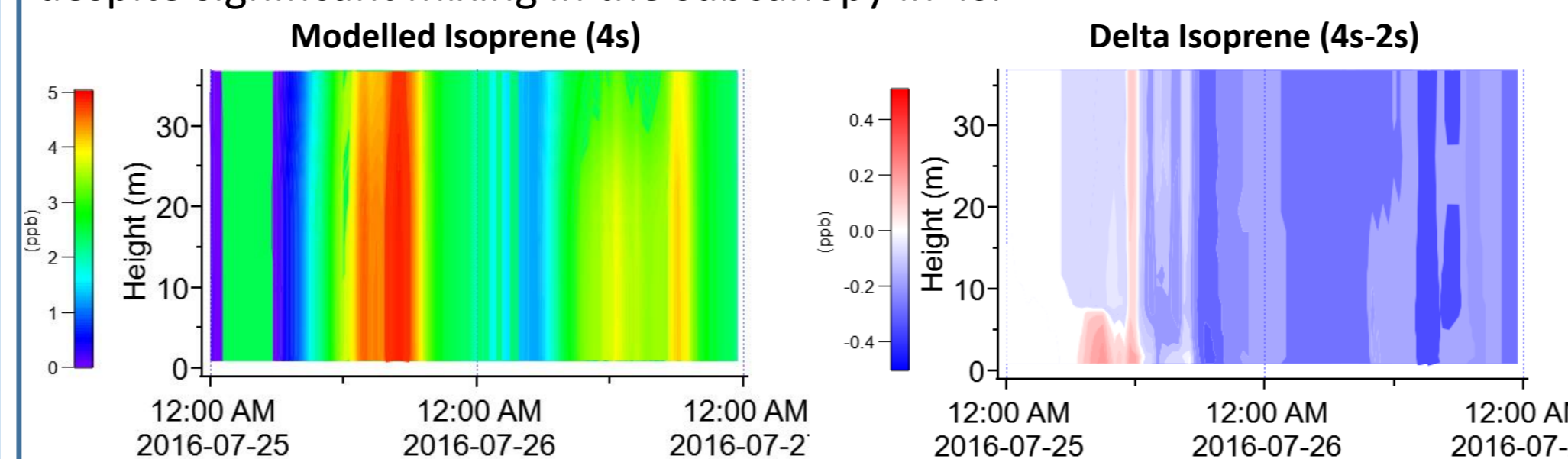
The Role of Lower Canopy Mixing

The 4s and 2s scenarios show small differences in isoprene mixing ratios and vertical structure, even during the July 25-26th window, where significant differences are apparent between the two modelled vertical exchange coefficients.

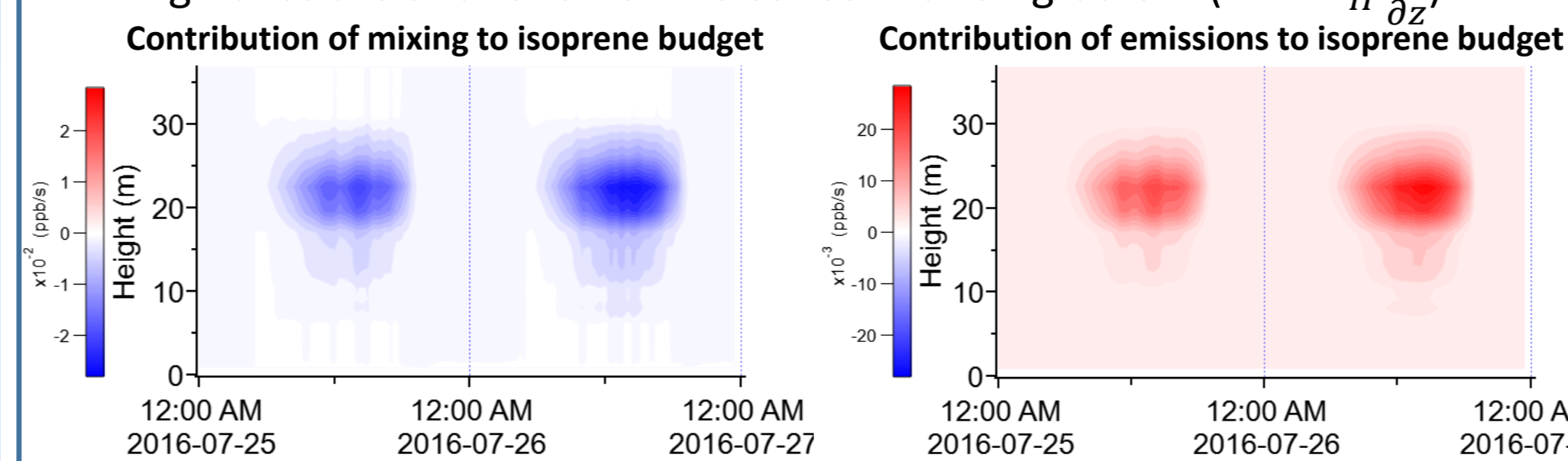


The K_H constrained by only the two upper sonics misses significant mixing in the lower crown space.

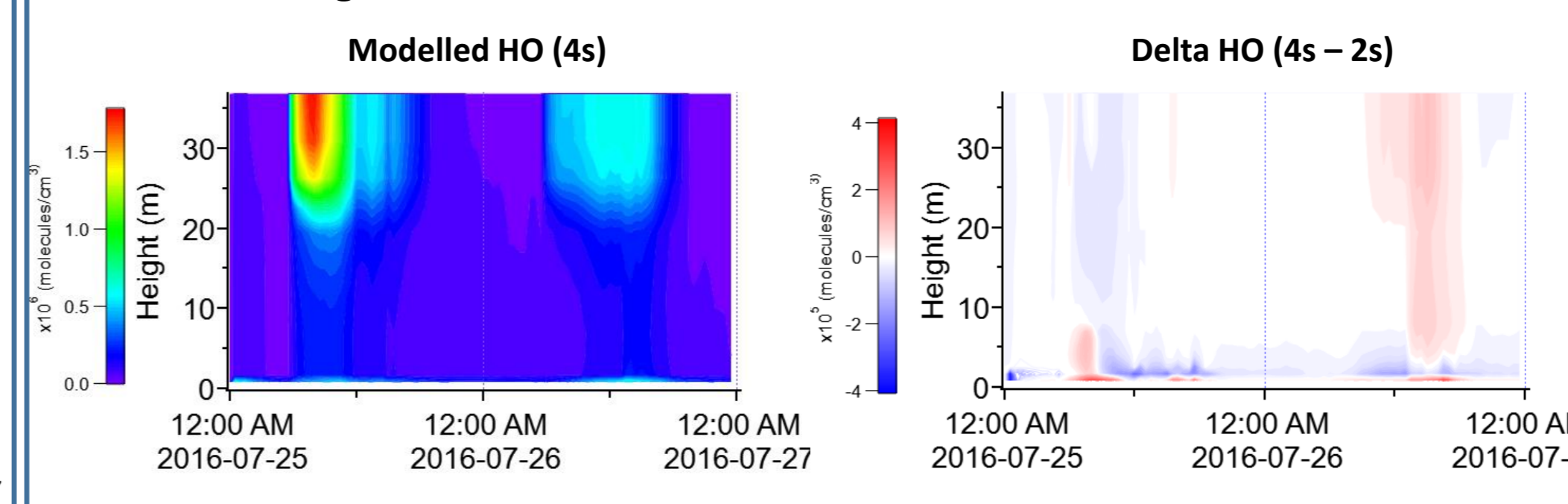
Isoprene is generally well-mixed within the model, and few vertical gradients develop. Differences of up to 10% in isoprene mixing ratio exist between the 4s and 2s simulation. No significant changes to vertical structure develop, despite significant mixing in the subcanopy in 4s.



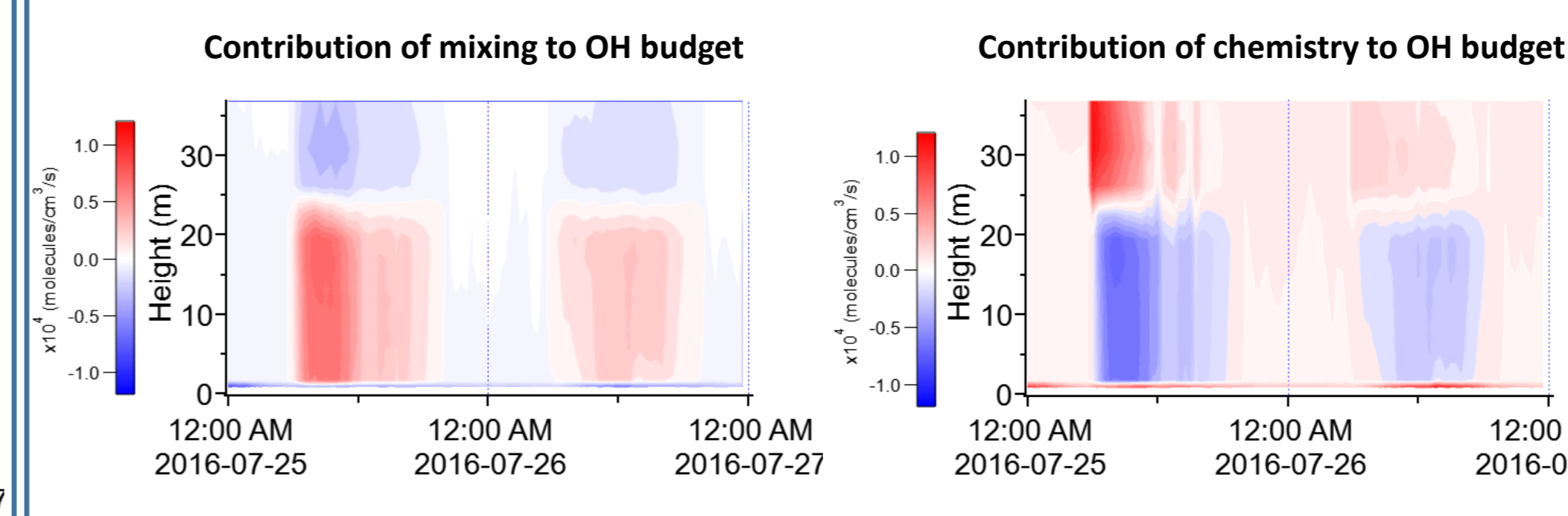
Below, the simulated process tendencies (rate of change out of a layer attributable to a given process) indicate that isoprene mixing ratios are relatively insensitive to turbulent transfer in the lower canopy. Emissions are strongest in the upper canopy, driving stronger mixing tendencies as mixing fluxes are a function of the concentration gradient ($F = K_H \frac{\partial c}{\partial z}$).



OH is a much shorter lived species than isoprene and is not well mixed in the canopy. Changes to subcanopy mixing between the 4s and 2s scenarios impart a 0-200% change on modelled OH concentrations



Unlike isoprene, OH is sensitive to mixing in the lower canopy (<14 m) but the modeled OH concentration is so low in this region that the absolute effect of mixing is minor. Overall, mixing has the same order of magnitude effect on the OH budget as chemical production and loss.



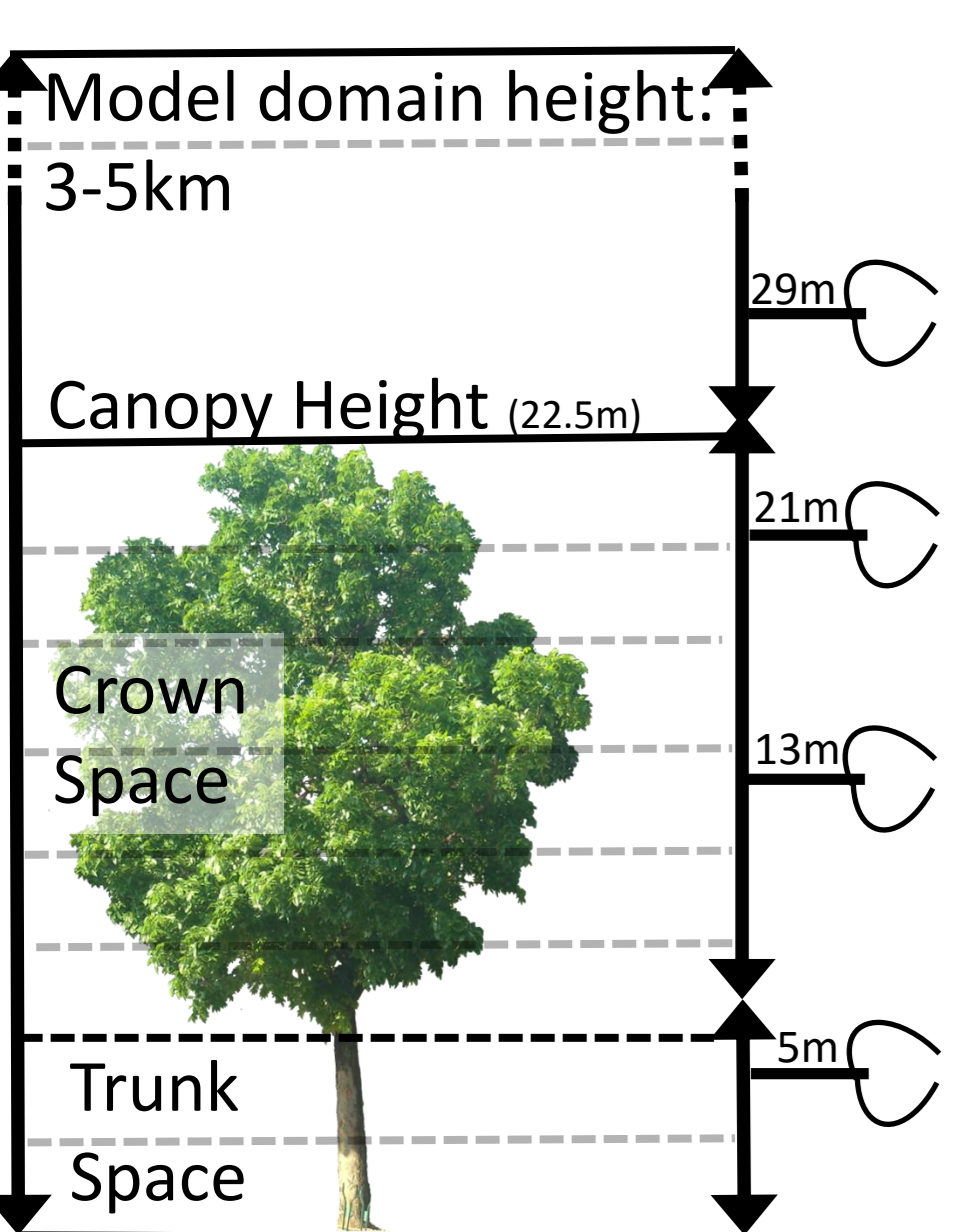
The FORCAST Model

The FORCAST (FORest Canopy Atmosphere Transfer) model [8] is a 1-D column model including atmospheric chemistry and dynamics based on the CACHE canopy exchange model [9] and the CUPID canopy radiative transfer [10]. The model domain is divided into 40 layers where each layer is a box model containing emissions, deposition, advection, turbulence, and chemistry.

Mass fluxes are calculated by solving the continuity equation:

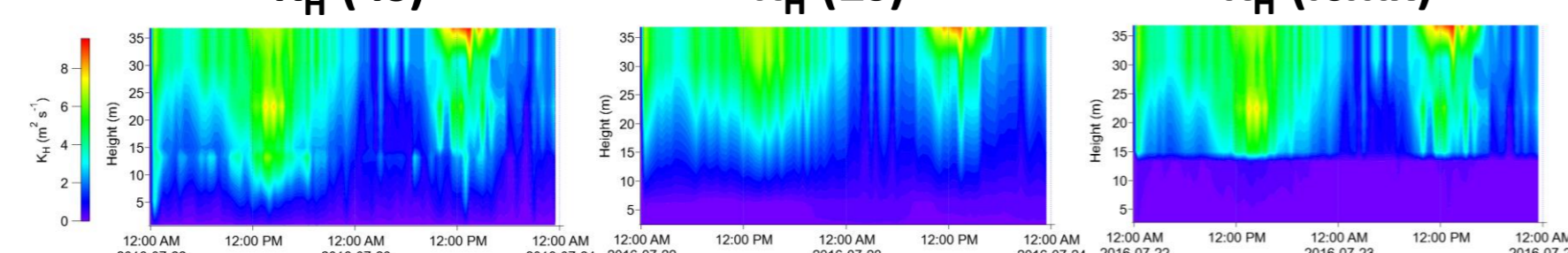
$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial z} \left(K_H \frac{\partial c}{\partial z} \right) + S_c + C$$

Where c is the mixing ratio of the species of interest, K_H is the turbulence exchange coefficient, S_c includes contributions from emissions, deposition, and advection, and C represents chemical production and loss. K_H is calculated based on K-theory [10] modified by the observational constraints provided by the friction velocity and standard deviation of vertical wind speed calculated from the sonic anemometers [7].



Three versions of the mixing scheme are used:

- **4s**: including constraints from all 4 sonic anemometers.
- **2s**: including constraints from only the 29m and 21m sonic anemometers.
- **lcmx**: reduces K_H by a factor of 10 in the trunk and lower crown space to simulate an exceptionally stable canopy.



Three chemical mechanisms are explored:

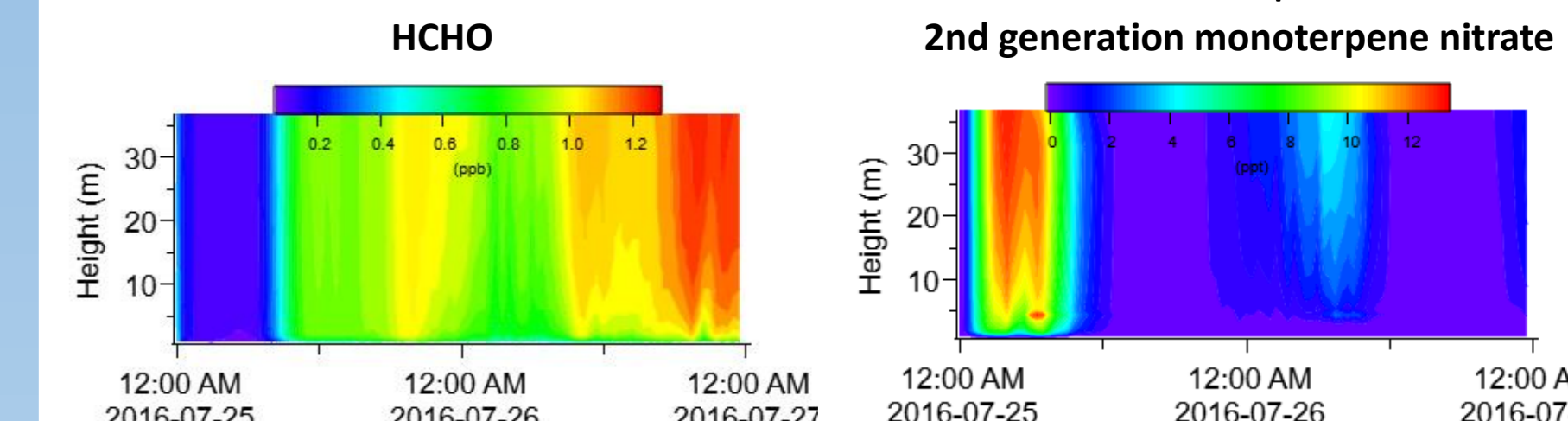
- **RACM**: The Regional Atmospheric Chemistry Mechanism plus Mainz isoprene (84 gas-phase species, 249 reactions) [8,12]
- **RACM+MIT**: RACM plus the updated monoterpene and nitrate chemistry of Browne et al. This mechanism is new to FORCAST and has not been fully evaluated in the model. (139 gas-phase species, 382 reactions) [13]
- **CACM**: The Caltech Atmospheric Chemistry Mechanism (300 gas-phase species, 620 reactions) [14]

Conclusions

- K-theory modified by only upper canopy and above canopy observations underestimates subcanopy mixing.
- Changes to subcanopy mixing consistent with observations can change isoprene mixing ratios by up to 10%, but these changes alone don't increase measurement agreement significantly. When subcanopy mixing is substantially reduced (lcmx), midday isoprene concentrations are elevated by 80-105%. While this improves measured-modeled agreement in the July 23rd simulation, it is inconsistent with micrometeorology and decreases model agreement for other species.
- Selection of chemical mechanism currently introduces the largest variability in modelled output in FORCAST. Each of the three mechanisms exhibit different successes and failures and further work needs to be done to understand what is driving these differences. Constraints to the subcanopy mixing parametrization on its own is not sufficient.

Future Work

When more chemical observations from the campaign become available, we will be able to further examine model performance.



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