

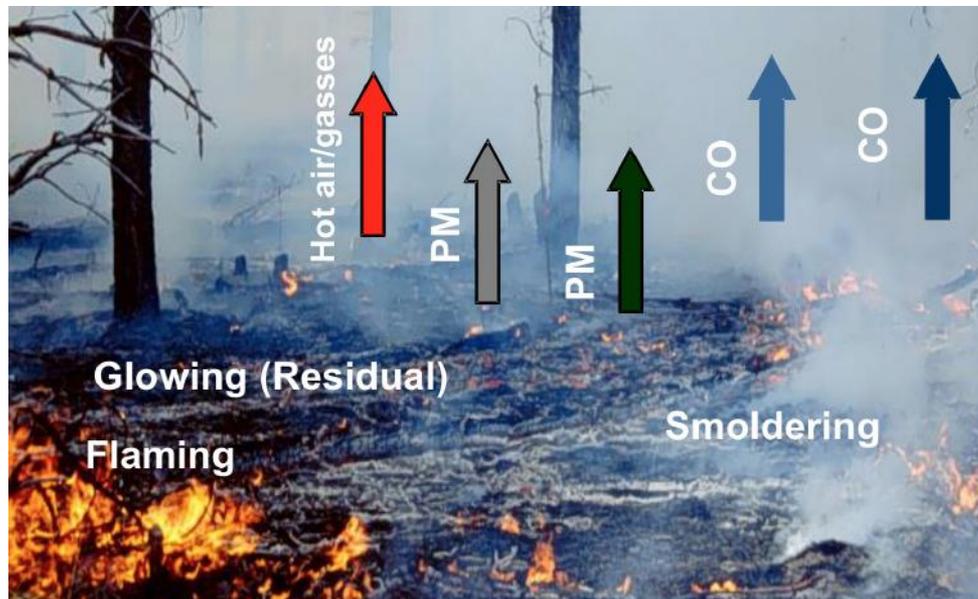
Explicit modeling of $\text{NO}_x\text{-O}_3$ photochemistry in fresh wildfire plumes

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Introduction

- ▶ Wildfire activity in the Western United States causes poor air quality, adverse human health impacts, and substantial economic costs (Jaffe et al., 2008; Kochi et al., 2010; Liu et al., 2015).
- ▶ Fire emissions vary dramatically with fuel type and burning conditions
 - ▶ Includes speciation of VOCs, directly emitted PM_{2.5}, oxidized nitrogen gases
 - ▶ The mixture of gases could produce O₃ downwind

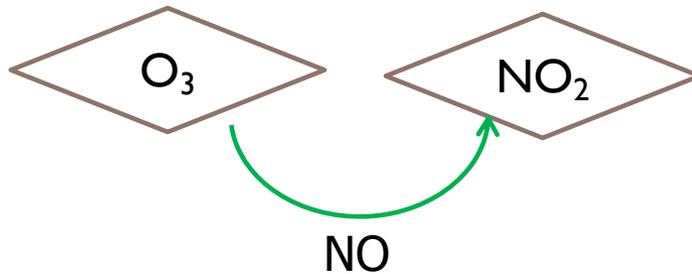
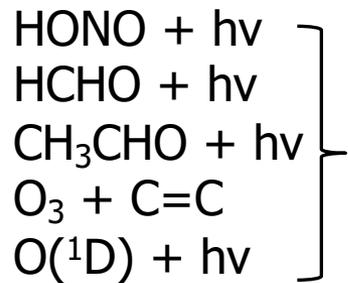


Ottman et al., (2016)

Chemical scheme in fresh fire plumes



Free radical initiators

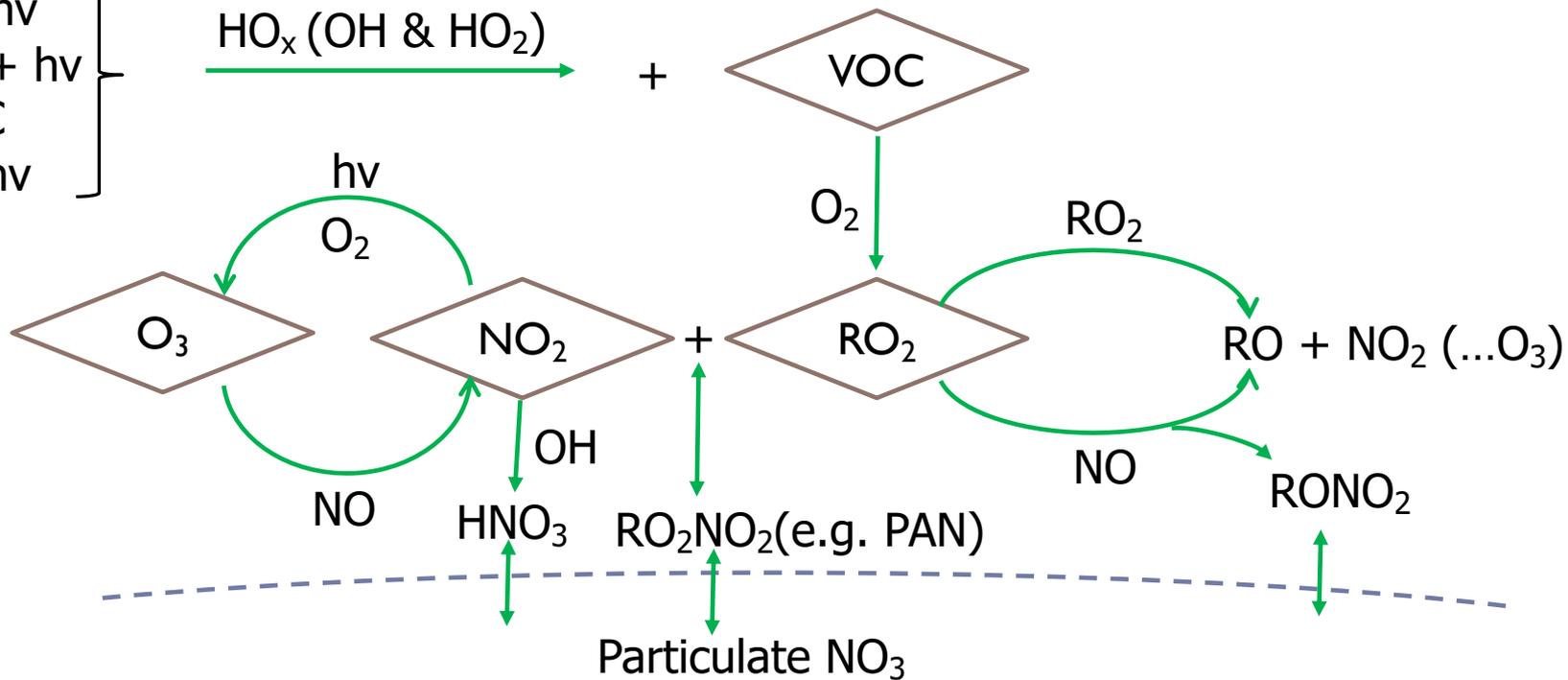


Chemical scheme in fresh fire plumes



Free radical initiators

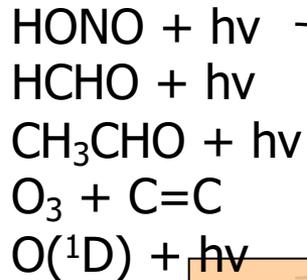
HONO + hv
HCHO + hv
CH₃CHO + hv
O₃ + C=C
O(¹D) + hv



Chemical scheme in fresh fire plumes



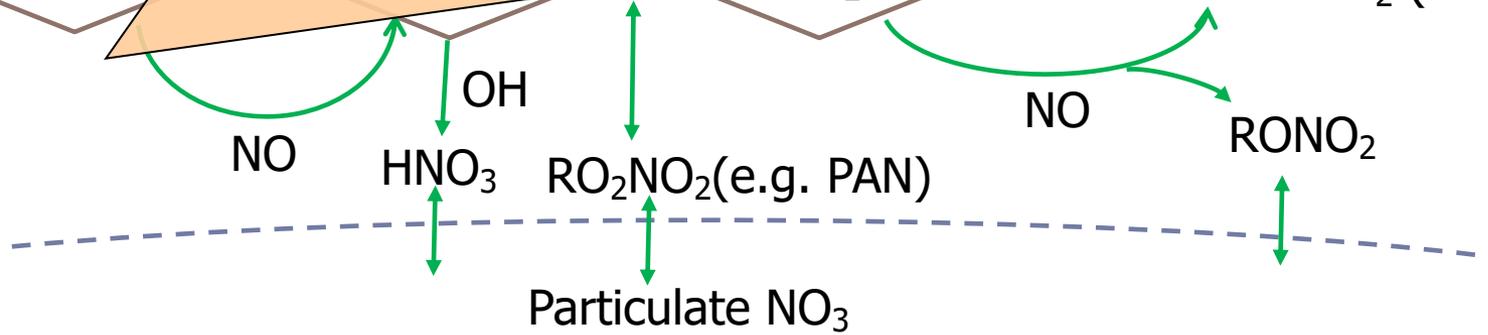
Free radical initiators



+

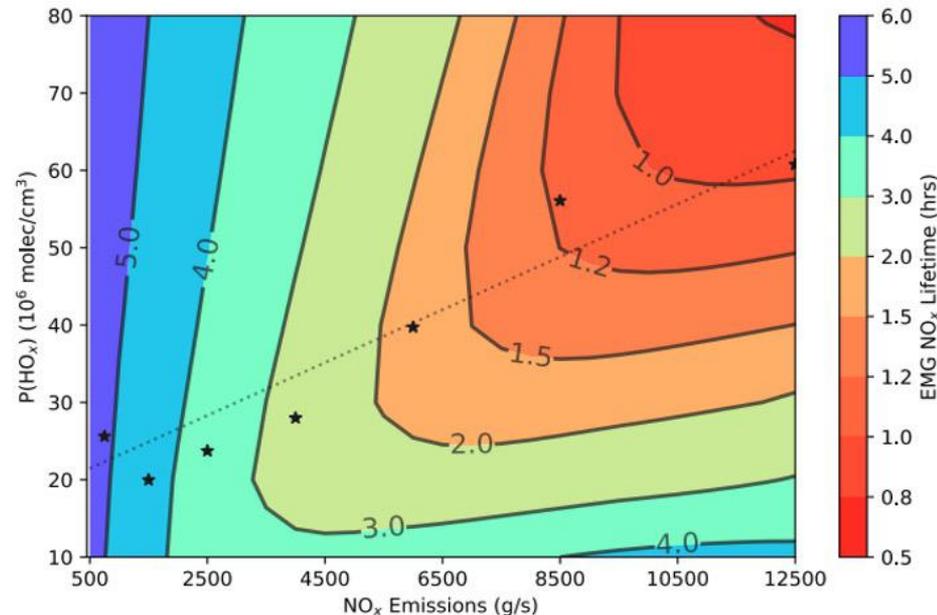


Understanding the fate of NO_x and organics emitted is crucial to quantifying the regional impacts of wildfires.



Factors affecting NO_x fates

- ▶ Alvarado et al. (2010) suggested that higher emission ratios of NO_x in the smoke plumes may lead to higher fractions of PAN formed.
- ▶ Romer et al. (2020) suggested that the loss of NO_x through formation of RONO₂ increases with NO_x emissions.
- ▶ Jin et al. (2021) observed decreasing NO_x lifetime with fire intensity, likely due to the increase in both NO_x abundance and hydroxyl radical production.

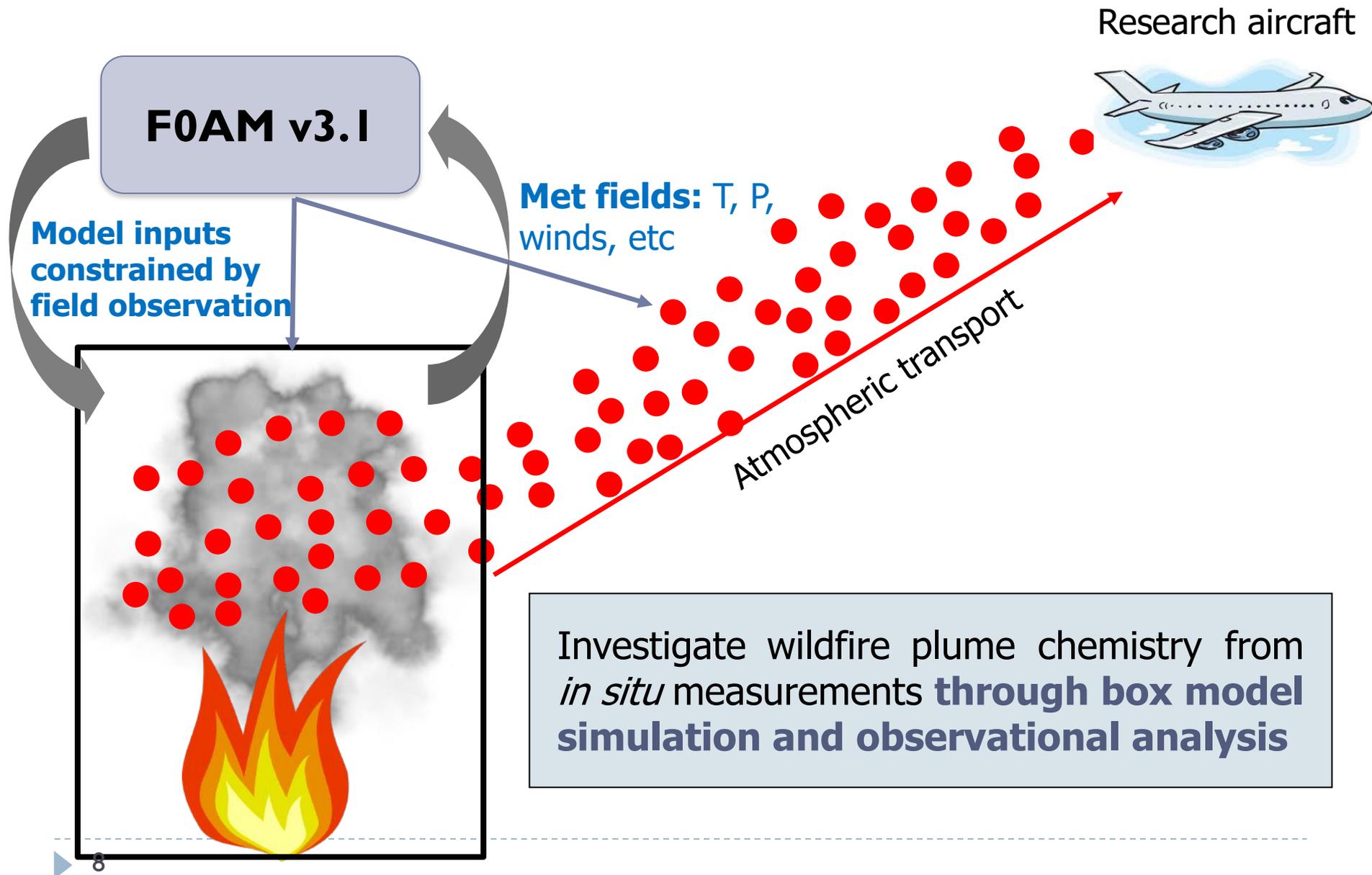


Jin et al., 2021

Outstanding issues on wildfire plume chemistry

- ▶ Large uncertainties in ozone formation, and gap in understanding the main drivers of variabilities across fires
 - ❖ the majority of observations suggest some degree of O₃ production from wildfires (Bertschi and Jaffe, 2005; Morris et al., 2006; Pfister et al., 2006; Jaffe et al., 2008; Buysse et al., 2019).
 - ❖ several studies have found that O₃ is minimally enhanced or even depleted downwind of some biomass burning plumes (Paris et al., 2009; Alvarado et al., 2010).

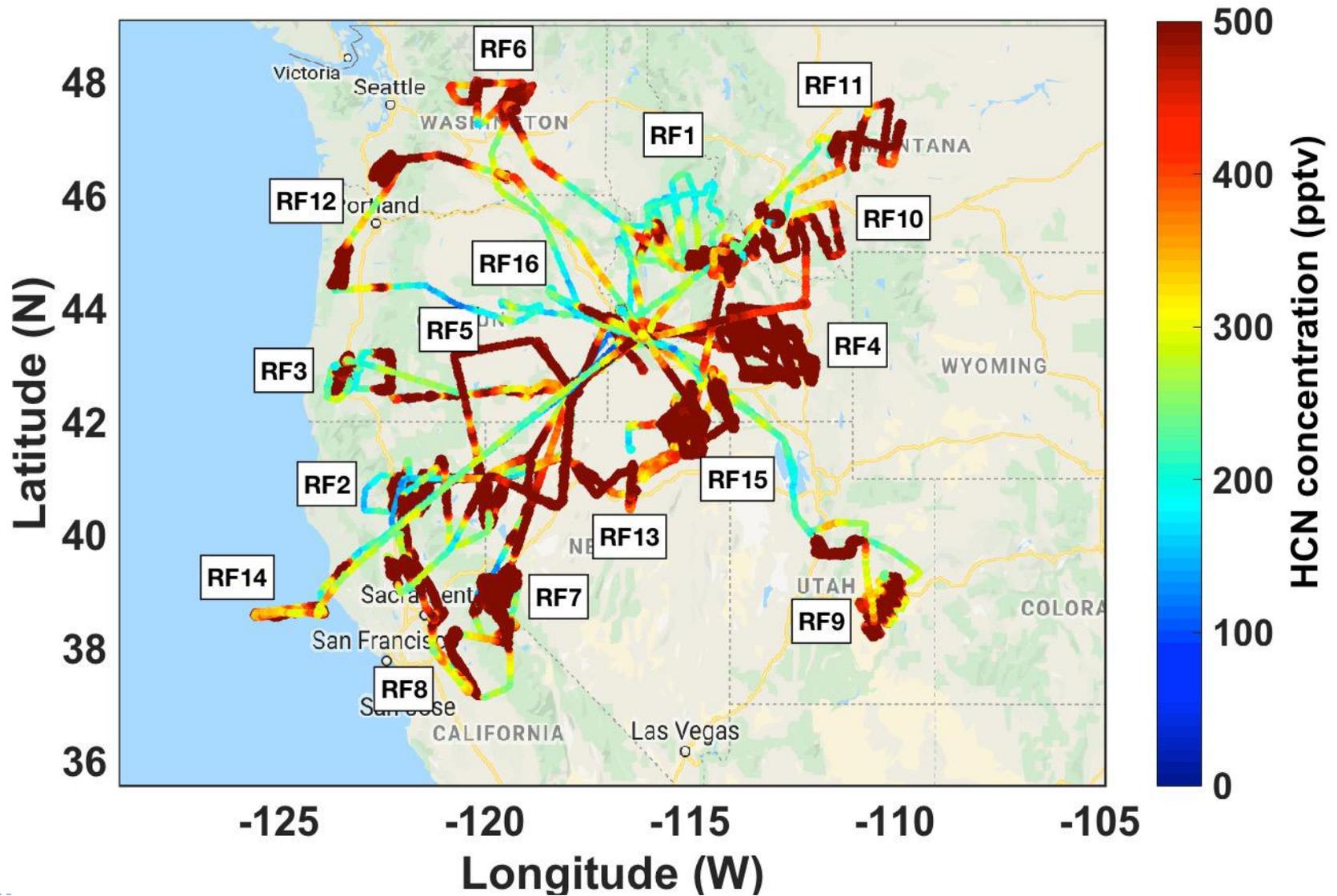
Proposed Approach



Summer 2018 Field Study: Western wildfire Experiment for Cloud chemistry, Aerosol absorption and Nitrogen (WE-CAN)

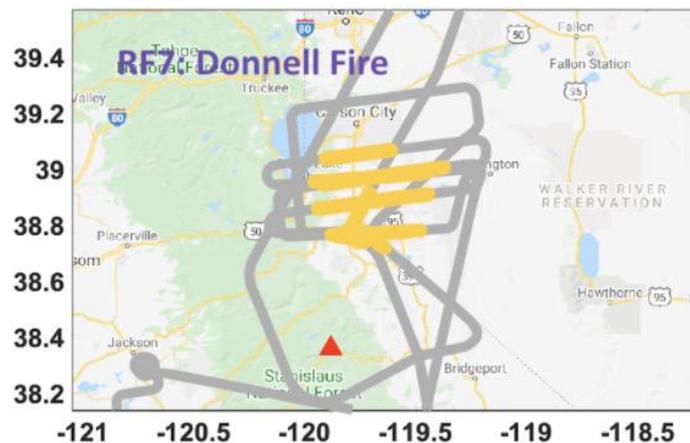
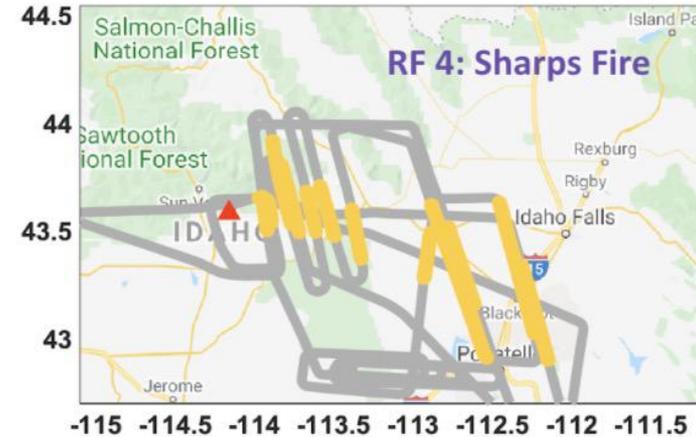
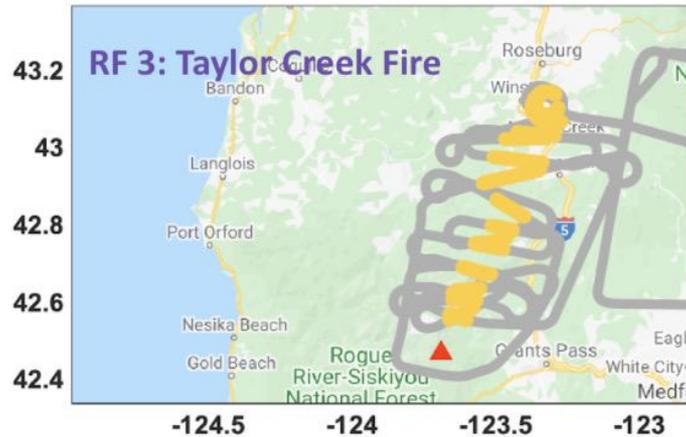


WE-CAN Flight tracks



Pseudo-Lagrangian measurements

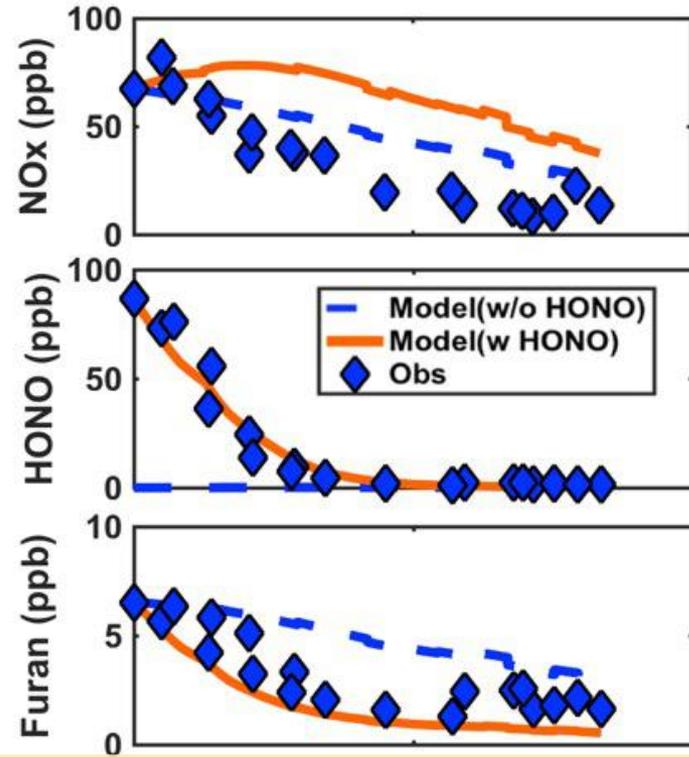
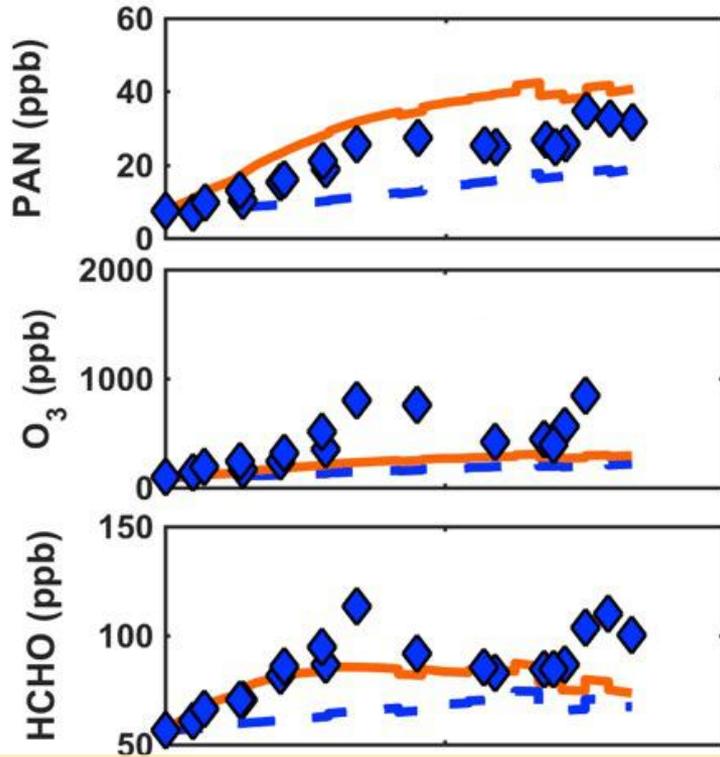
WE-CAN provides a valuable data set for investigating pseudo-Lagrangian plume evolution



Model Setup

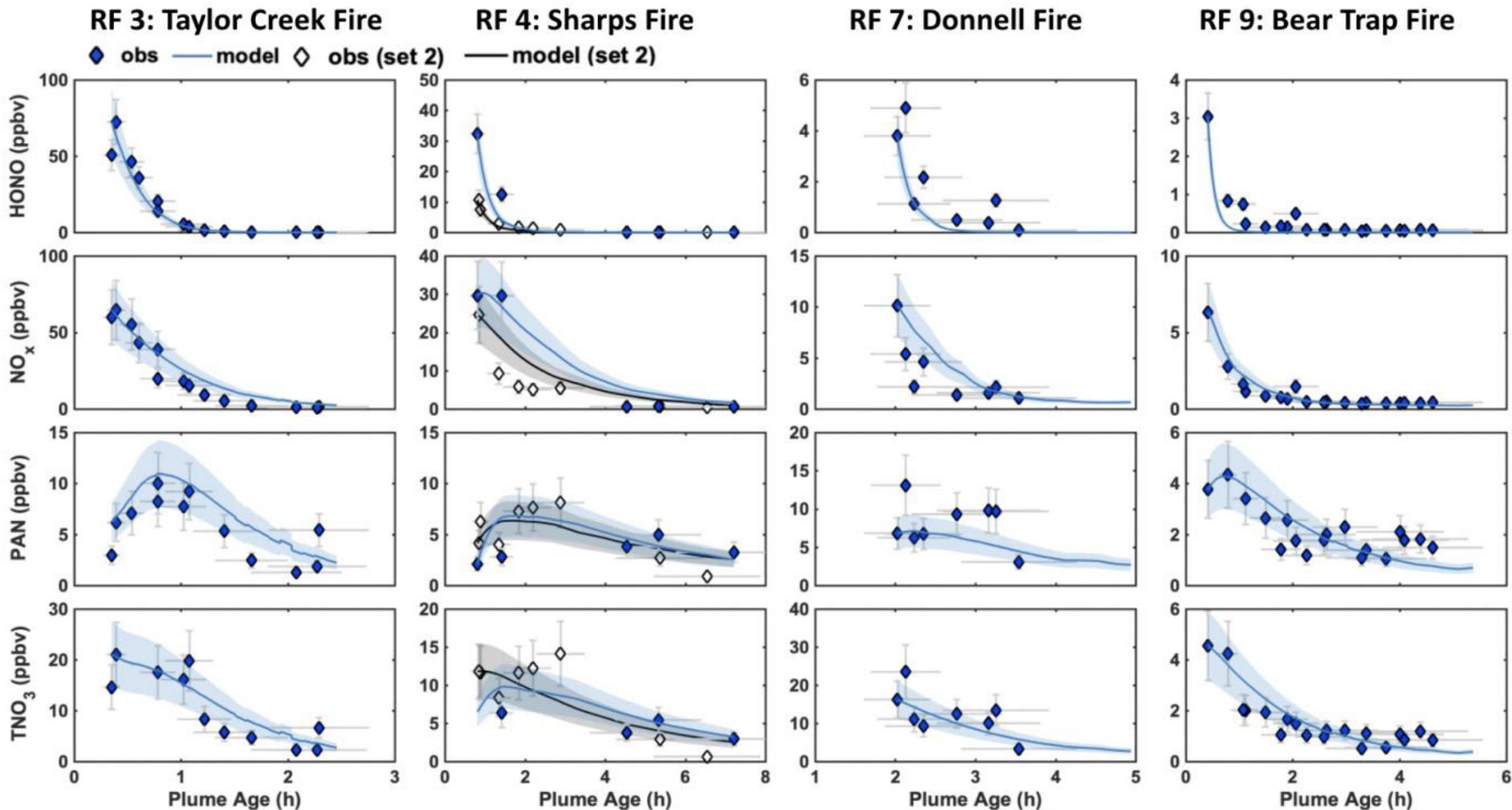
- ▶ The **F**ramework for **0-D** **A**tmospheric **M**odeling (F0AM) (Glenn et al., 2016)
- ▶ Initialized with observations at the freshest plume pass, with concentrations of a few unmeasured species derived from emission inventory.
- ▶ MCM v3.3.1
 - ▶ Furans + OH mechanism from Coggan et al. (2019)
 - ▶ Furans/phenolics/BBVOC + NO₃ mechanism from Decker et al. (2018)
- ▶ the dilution rate was obtained from the measured molar excess mixing ratios of CO (fitting decay of (CO-CO_{bkg}) vs. age)
- ▶ In case we didn't capture the plume core, we normalize both the model output and the observations by CO

Taylor Creek Fire Case Study

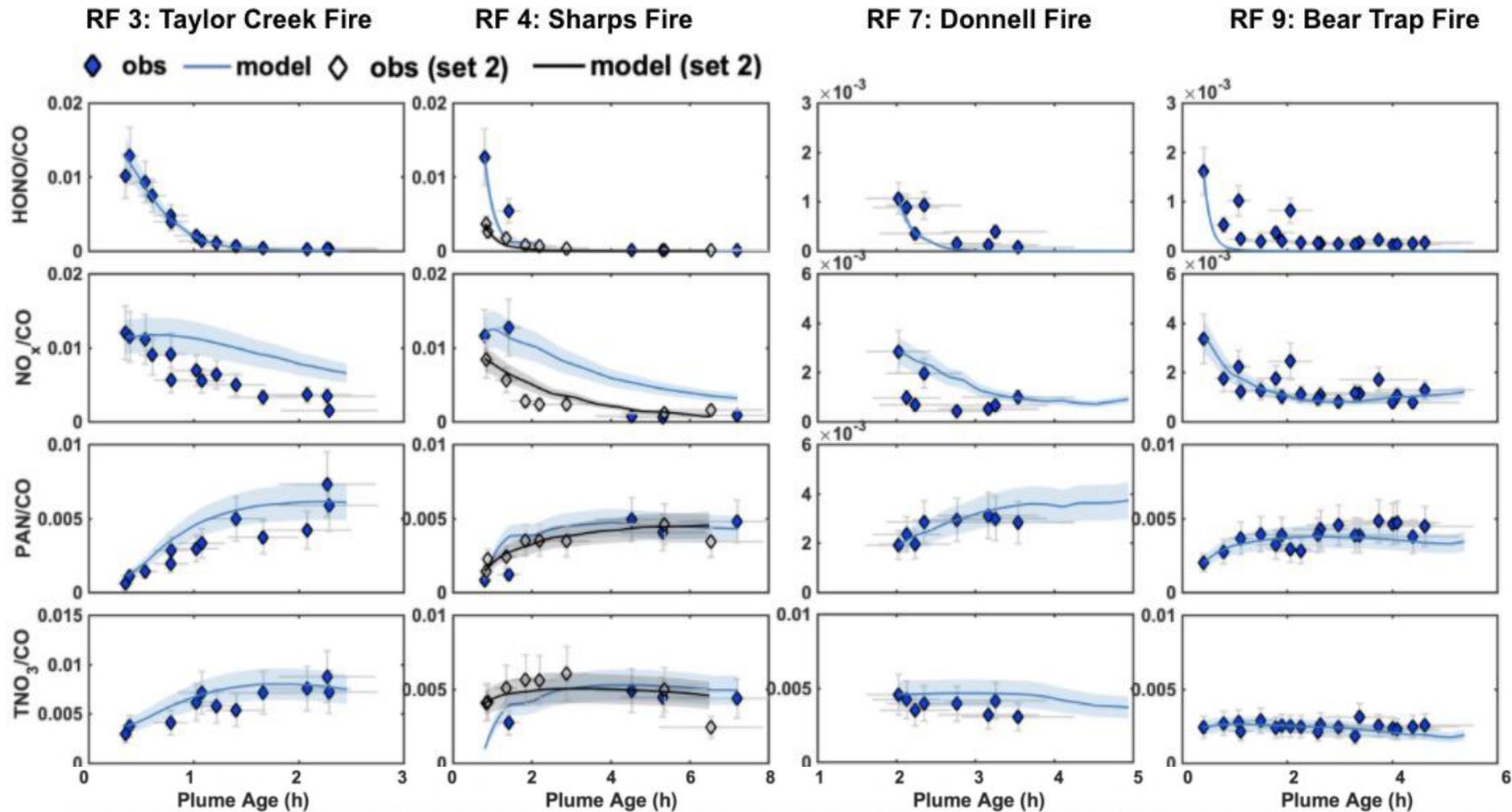


- The addition of initial HONO nearly doubles the modelled nitrate_{tot}
- Omitting the emissions of HONO leads to significantly lower PAN, HCHO, and HNO₃ concentrations.
- The base model underestimates the secondary production of O₃ and loss of NO_x.

Model simulation vs. field observations



Model simulation vs. field observations (CO-normalized)



What drives the model-obs discrepancy in NO_x ?

Model overestimates NO_x



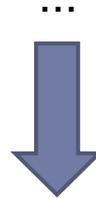
Missing VOC reactivity?

Changing fire emissions?

Differential dilution?



Introduce additional
VOC/ RO_2 into the model

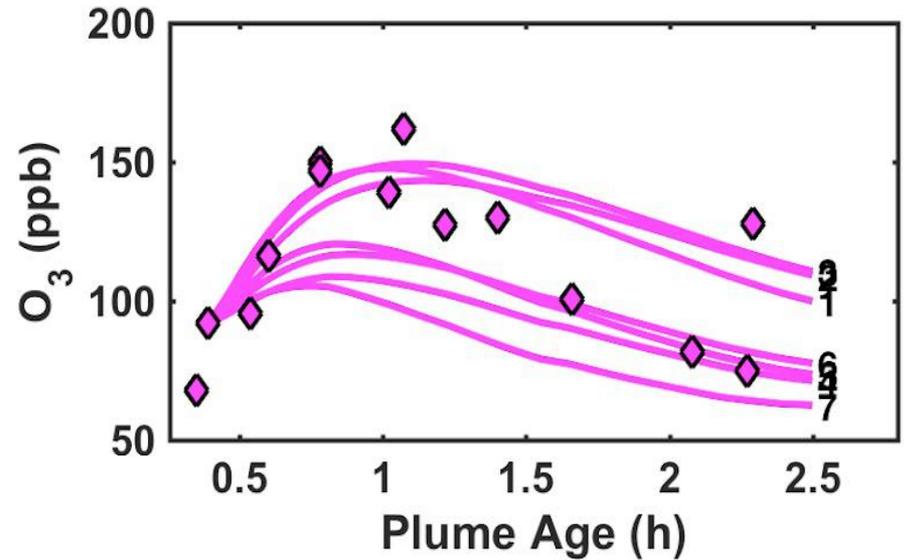
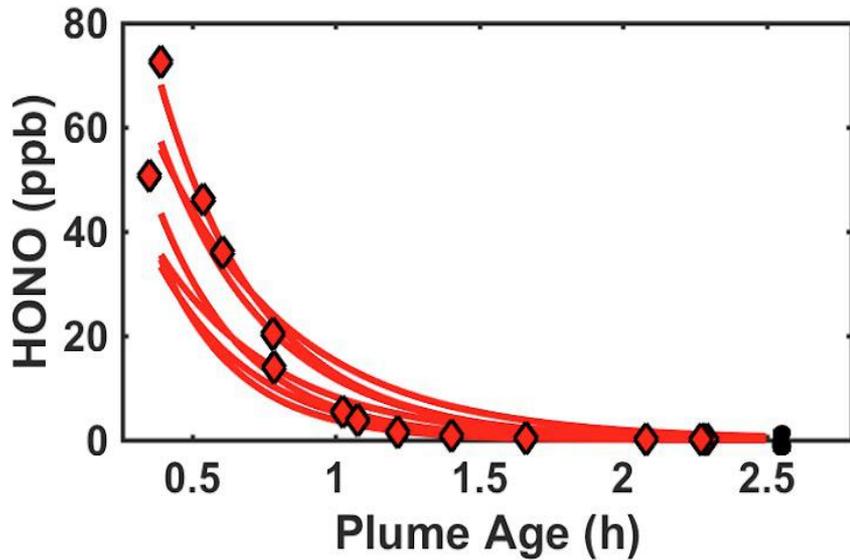
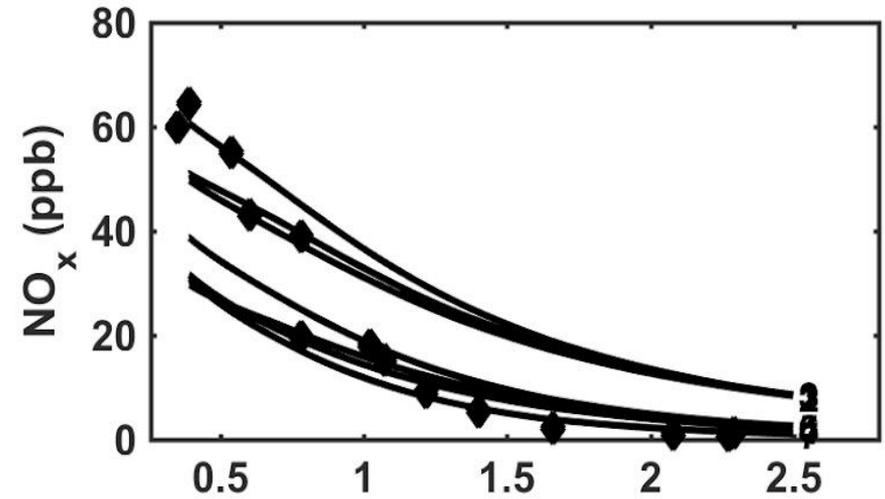
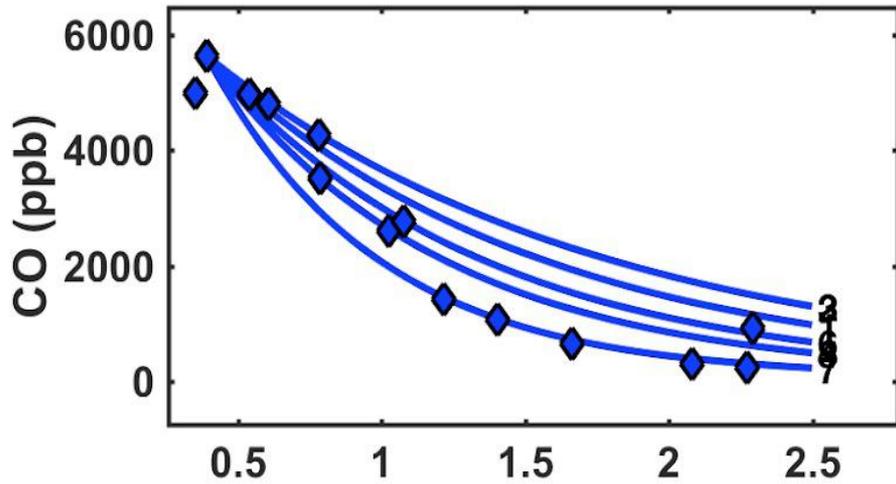


Inspect variations
in MCE and plume
 $\Delta\text{NO}_y/\Delta\text{CO}_2$

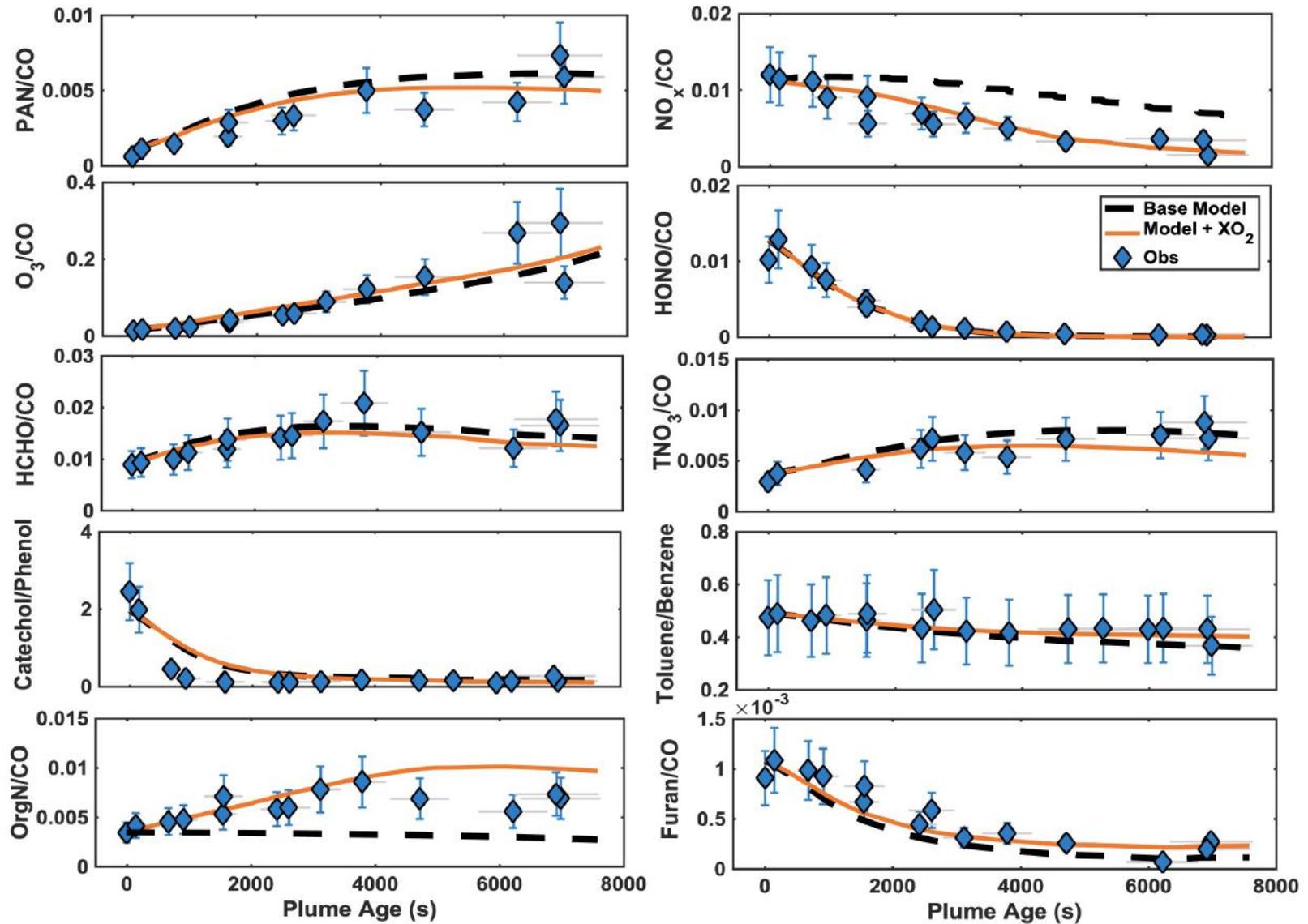


Try varying
dilution rates and
initial conditions

Back-extrapolating Plume Transects

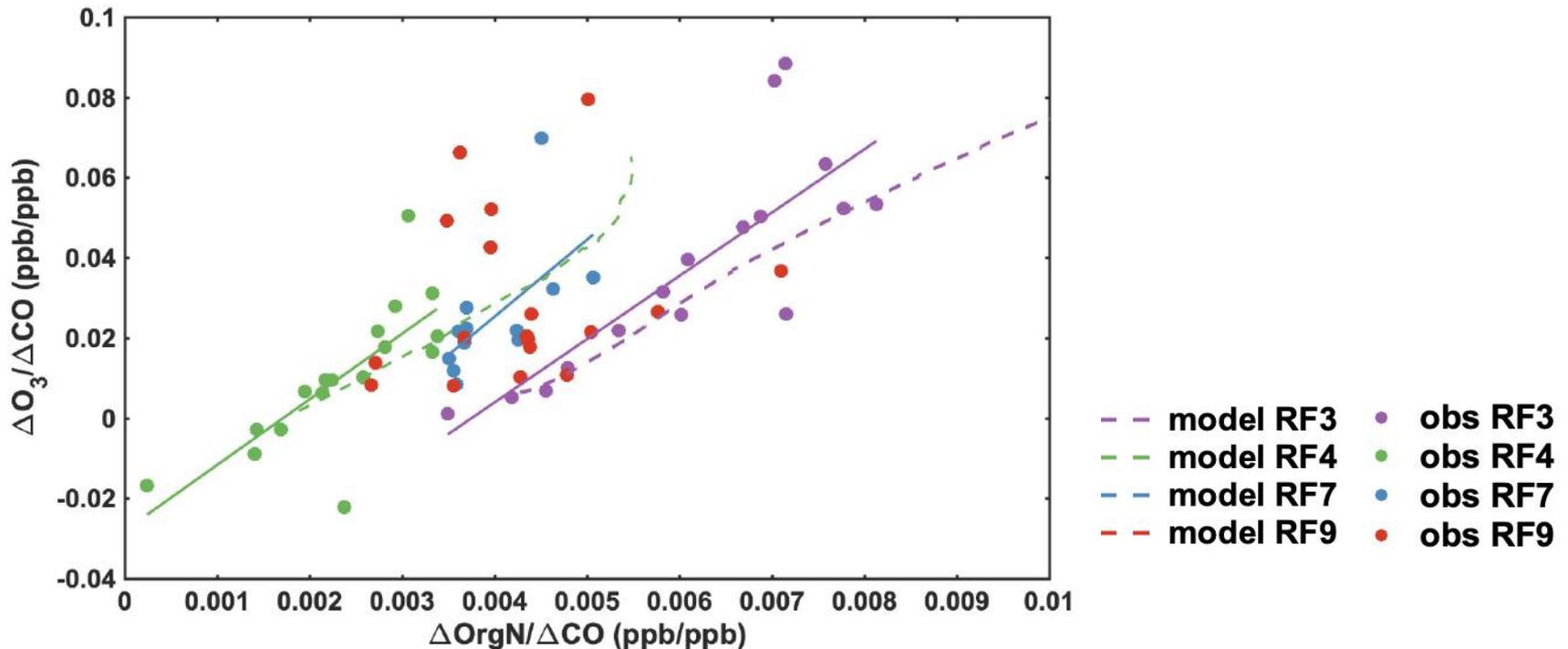


Additional RO₂ helps resolve the NO_x discrepancy



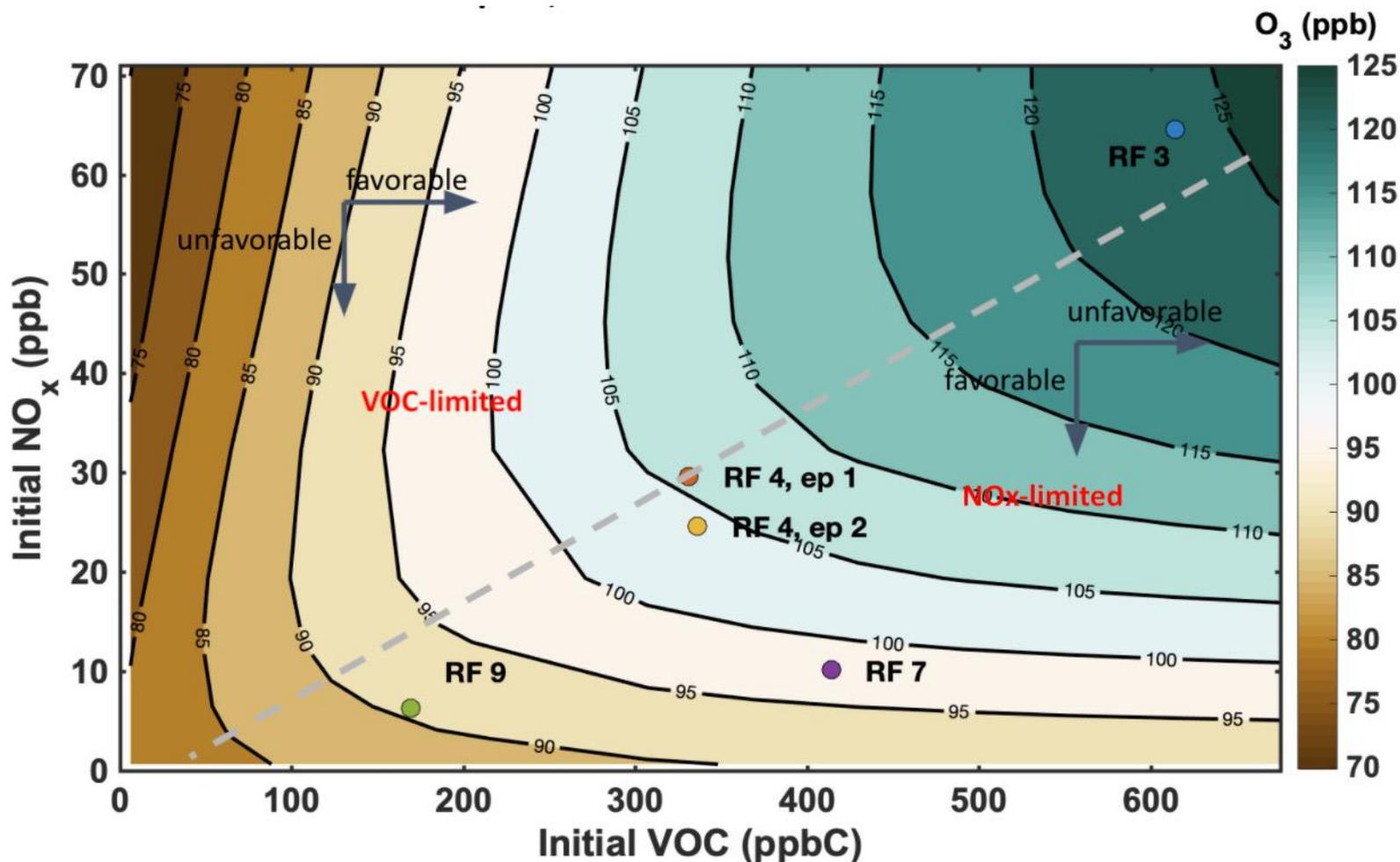
Organic Nitrogen Uncharacterized in the Model

- ▶ This organic nitrogen reservoir is equivalent in magnitude to that of PAN, and thus represents an important fate of NO_x with uncertain impacts on downwind O_3 .



Isopleths: O₃ photochemical scheme

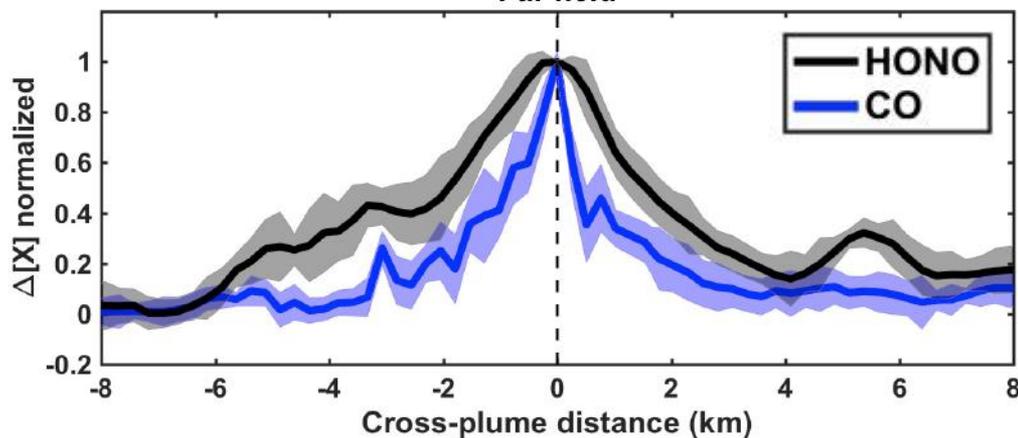
- ▶ RF 3 is VOC-limited regime, while RF 4, 7, 9 are NO_x-limited regime



Take home message

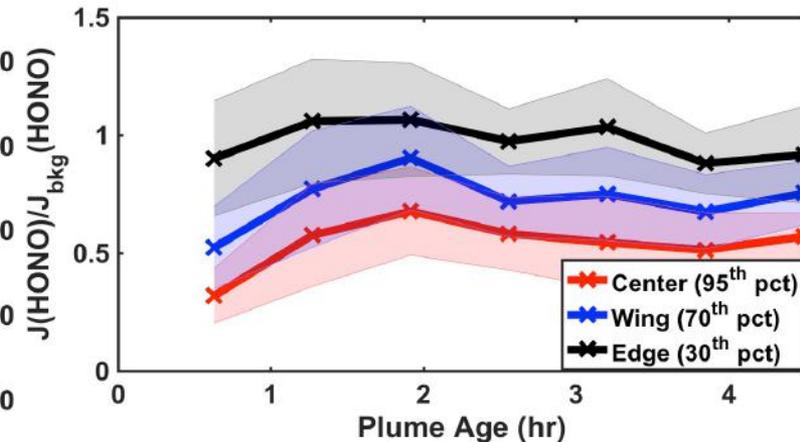
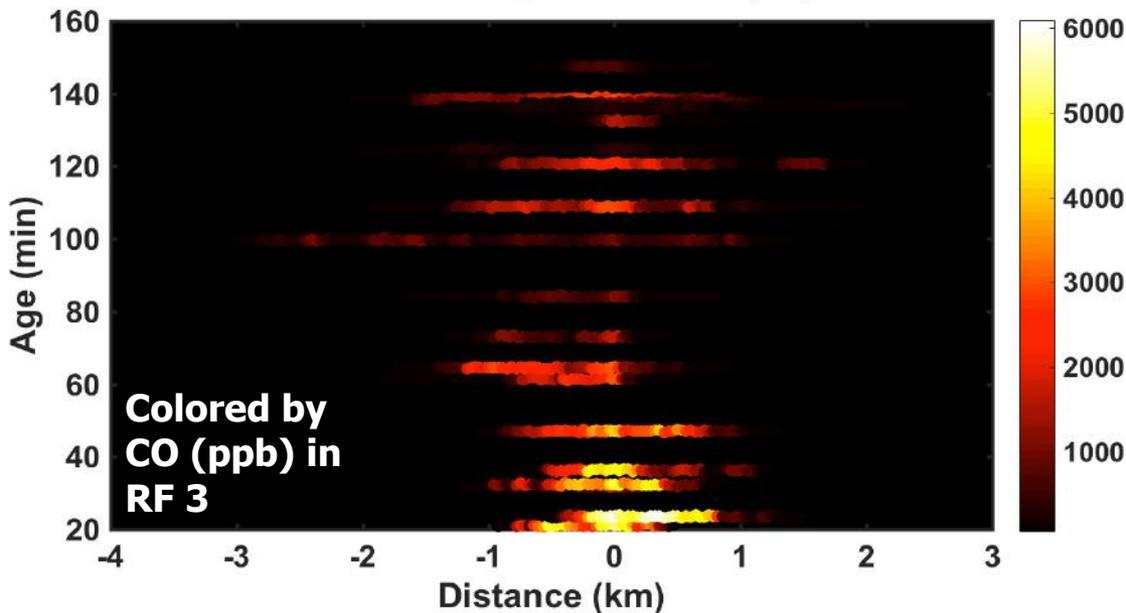
- ▶ Model-observation discrepancy in certain flights hypothesized to result from missing chemical sinks in model mechanisms or non-lagrangian behaviors of the plumes sampled.
- ▶ These could help better understand emissions and photochemical model application for wildfire plumes.

Future Work

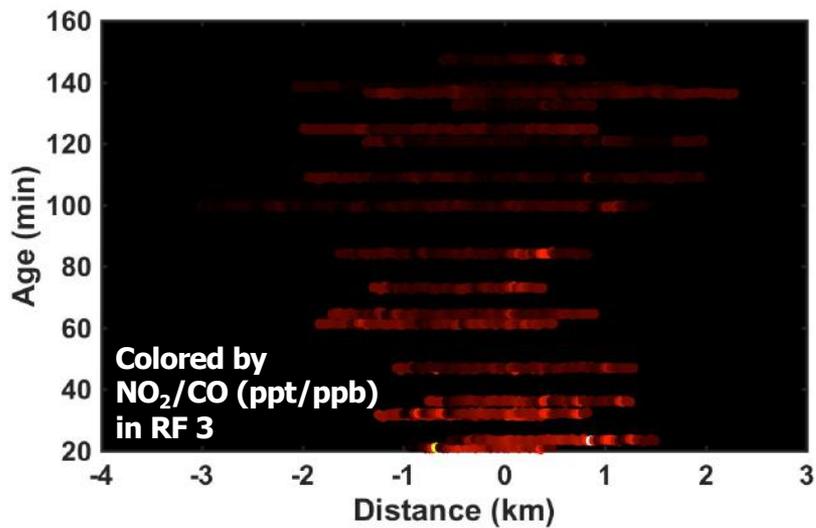
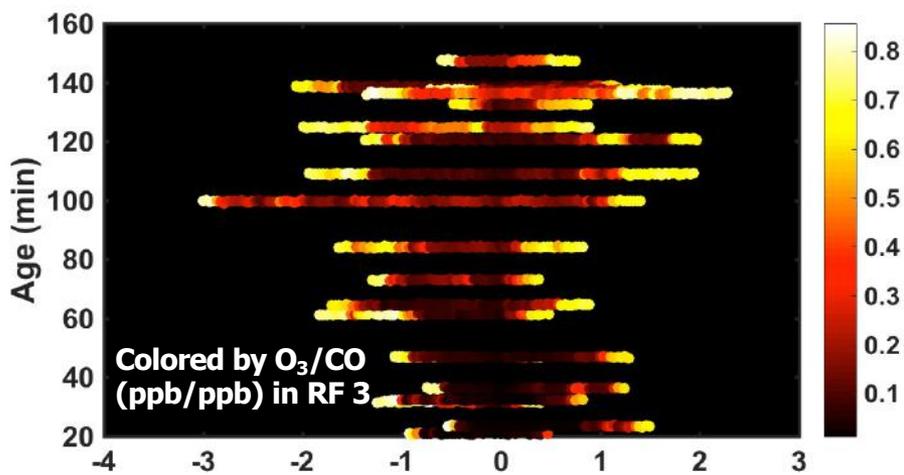


F0AM2D: Two dimensions of evolution

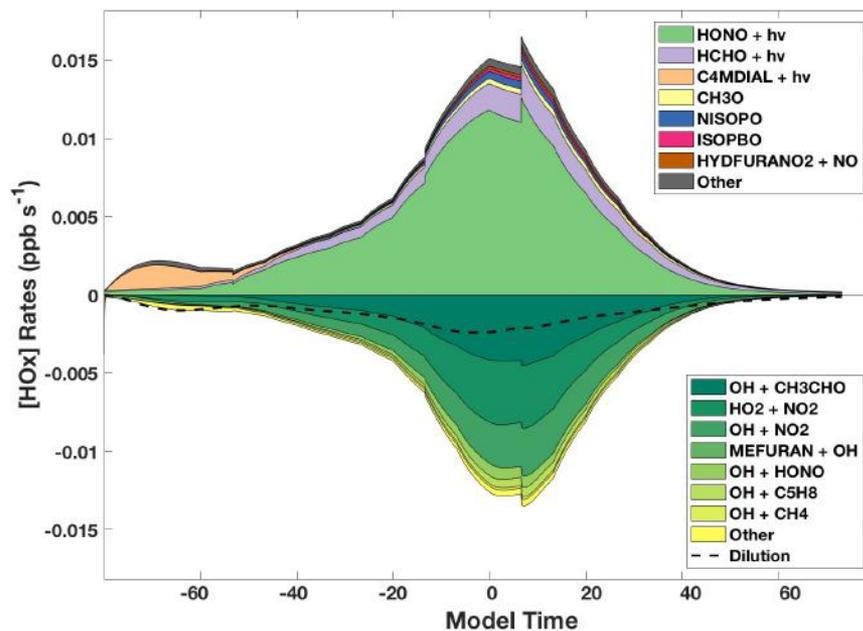
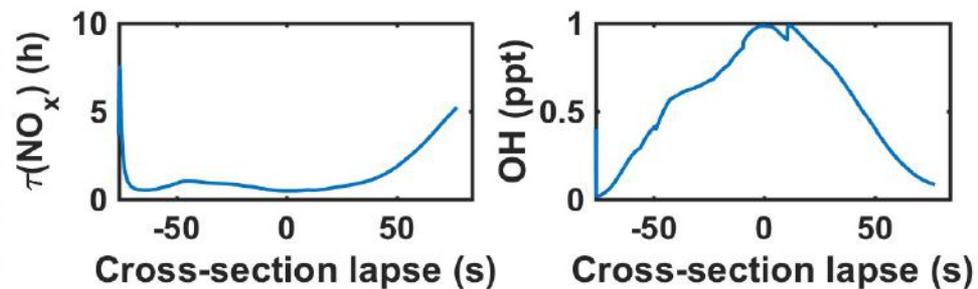
We see different chemistry at different ages AND different positions within a plume!



Future Work



Nonlinear chemistry across a plume



Thank you!

▶ Questions?