



# The chemical fate of particulate sulfur from nighttime oxidation of thiophene

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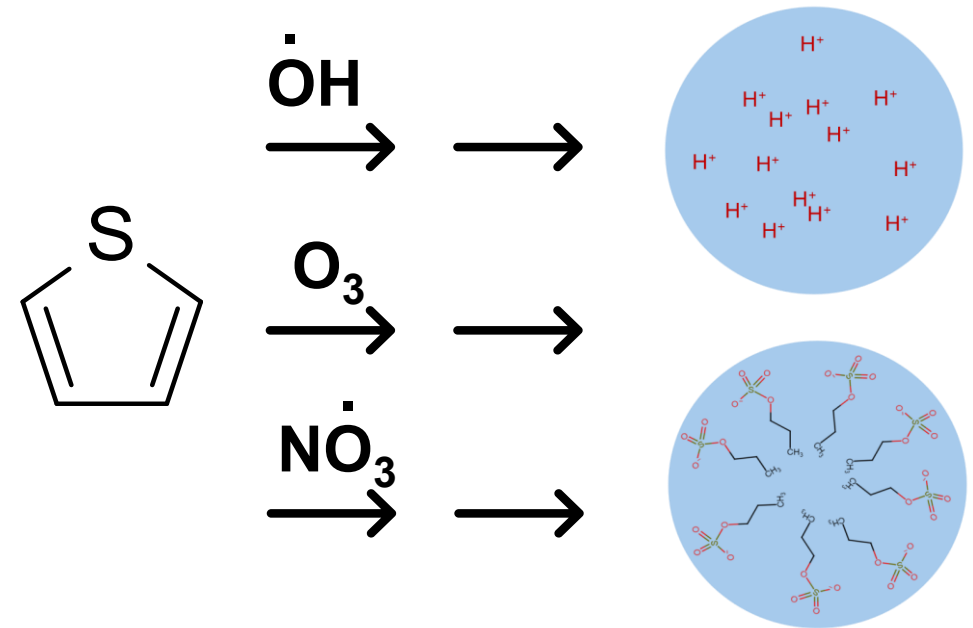
# Atmospheric presence and impact of thiophene

## Reduced organosulfur VOC oxidation

- Oxidized products environmentally impactful
  - $\text{SO}_4^{2-}$  -> Particle/Droplet Acidification
  - Organosulfates/Sulfonates -> Changes in surface tension
- Dimethyl sulfide well studied for its impacts
  - Reduced sulfur compounds of other structures less studied

## Thiophene biomass burning emissions

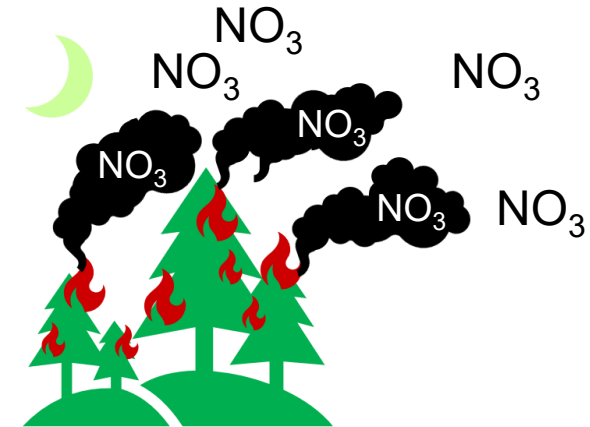
- Koss et al. (2018) - *FIREX*
  - 0.057 ppb Thiophene/ppm CO
- Hatch et al. (2015) - *FLAME-4*
  - $4.6 \times 10^{-3}$  g thiophene/kg ponderosa pine



# Nighttime Oxidation of Biomass Burning VOC

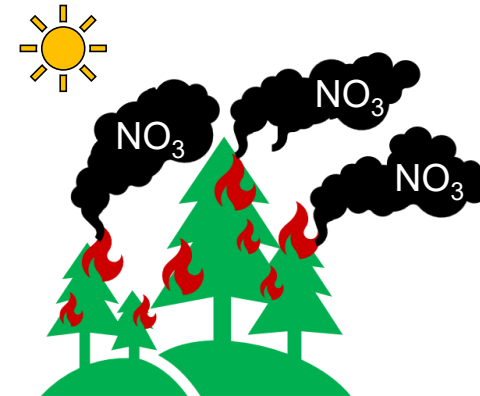
## Nitrate oxidation of thiophene still very understudied

- Oxidation product prediction and observations currently only cover early-generation products
- Many studies focus on kinetics



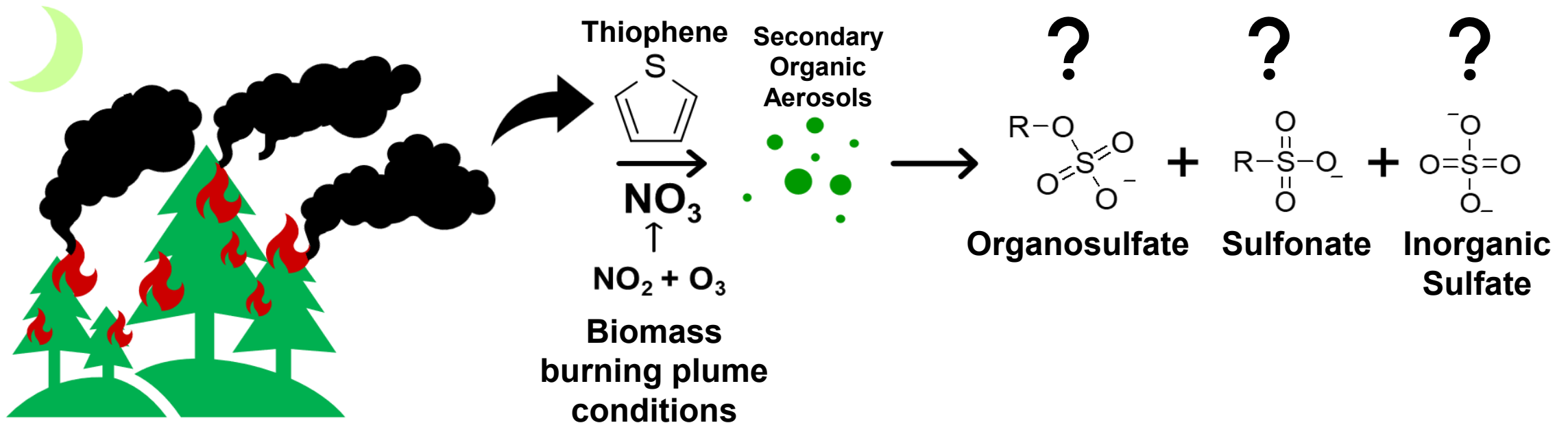
## Underestimation of nitrate radical impact

- Diurnal cycles allow nitrate chemistry to dominate at night
- Decker et al. (2021) showed high VOC reactivity can cause reaction with  $\text{NO}_3$  to dominate during typical daytime hours



# Objective

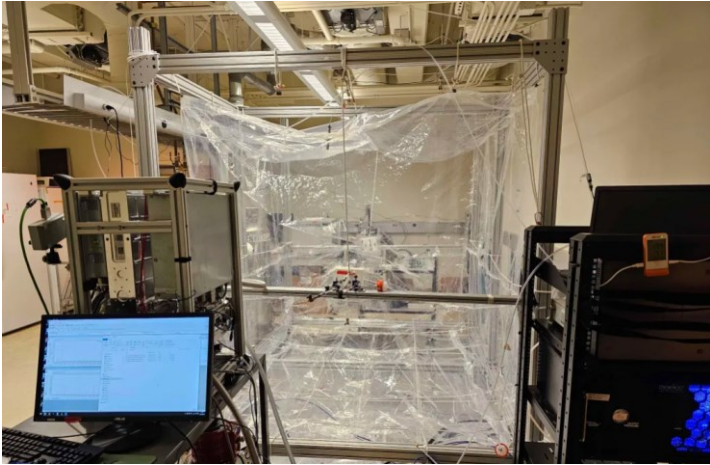
Using thiophene as a model for reduced organosulfur aromatic VOCs, this study investigated the production of particulate-phase inorganic sulfate, organosulfate, and sulfonate products



## Research questions:

- What **relative concentration of sulfur-containing products** are produced under nighttime nitrate-radical driven conditions?
- What major **organosulfate** or **sulfonate products** are produced by nitrate oxidation of reduced organosulfur compounds?

# Experimental Setup



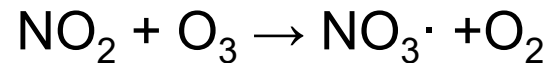
10 m<sup>3</sup> Teflon (PTFE) Chamber

## O<sub>3</sub> - only

O<sub>3</sub>

- Quantification control to ensure ozonolysis isn't dominating

$$[\text{NO}_2]/[\text{O}_3] = 0.1$$



- Conditions observed in biomass plumes by Singh et al.
- ~ 8 ppbv NO<sub>3</sub> predicted by model

## O<sub>3</sub> – free



- Qualification control to differentiate products resulting from NO<sub>3</sub> initiated oxidation

## Online Experiment Monitoring

- O<sub>3</sub> Concentration
- NO<sub>x</sub> Concentration
- Relative Humidity
- Chemical Ionization Mass Spectrometer (Soft Ionization)
- Mini Aerosol Mass Spectrometer (Hard Ionization)

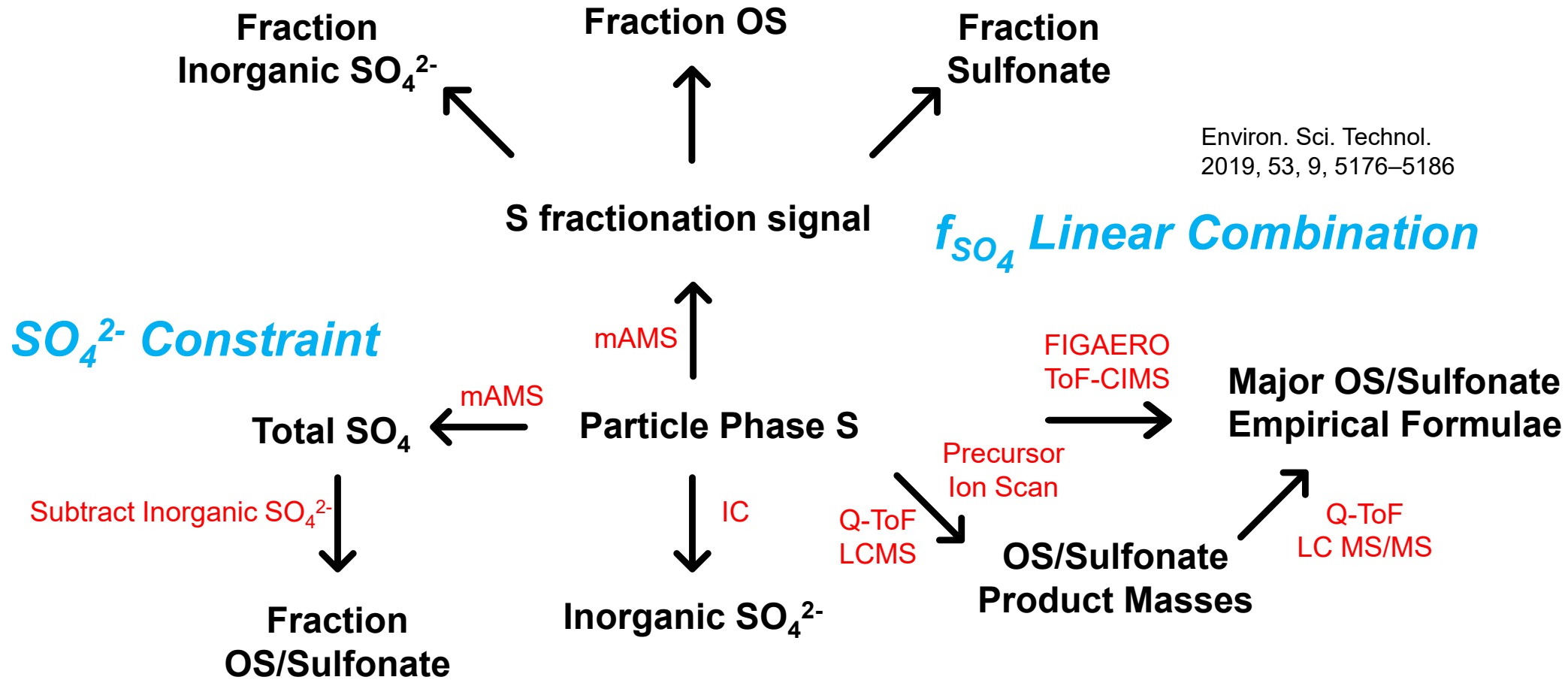
# Analytical Methodology

$$\left(\frac{80}{48}\right)_{observed} = 0.541(f_{SO_4i}) + 0.062(f_{sulfon}) + 0.427(f_{OS})$$

$$\left(\frac{81}{48}\right)_{observed} = 0.316(f_{SO_4i}) + 0.135(f_{sulfon}) + 0.008(f_{OS})$$

$$1 = (f_{SO_4i}) + (f_{sulfon}) + (f_{OS})$$

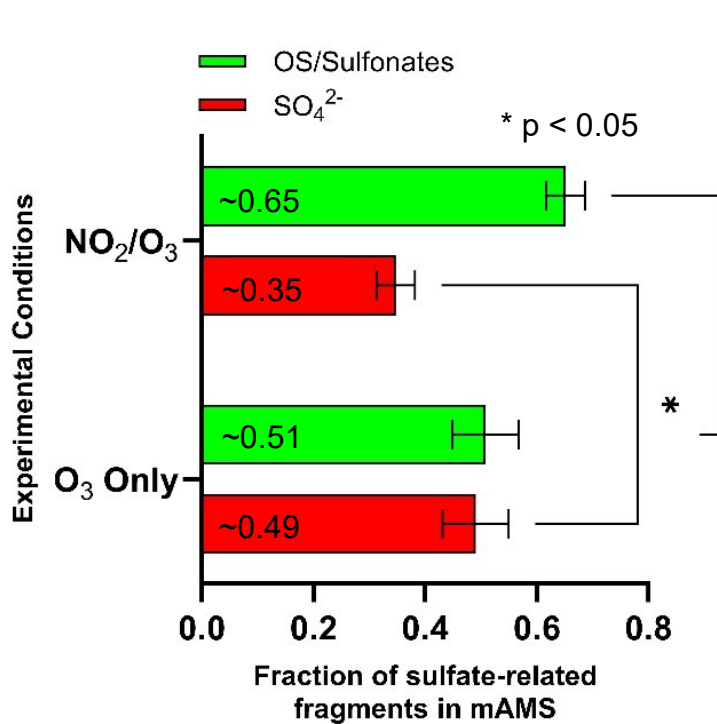
Environ. Sci. Technol.  
2019, 53, 9, 5176–5186



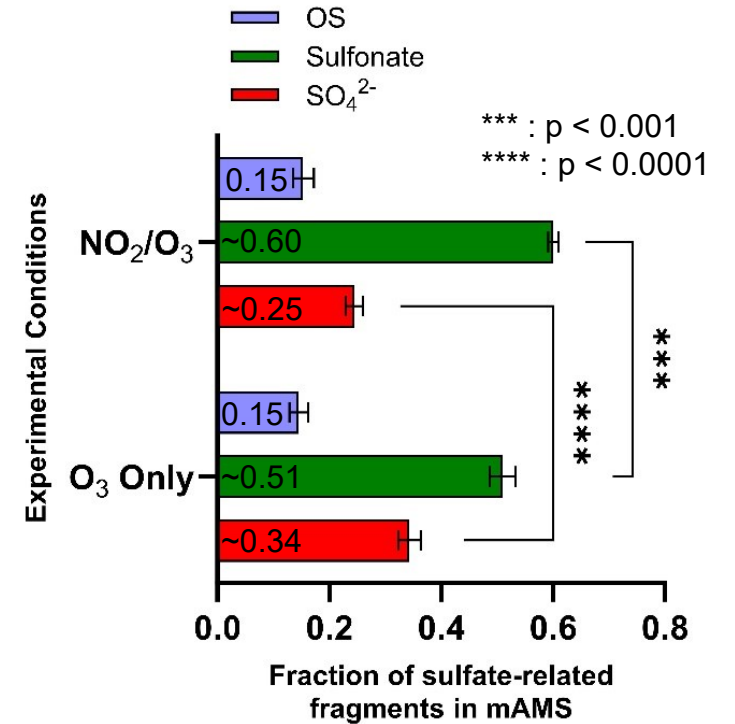
# Sulfur-Containing Product Distribution

## Constraining percentages of sulfur-containing products

- IC was used to constrain  $\text{SO}_4^{2-}$ 
  - Cannot differentiate organic products
- mAMS linear combination used to differentiate between organosulfates and sulfonates
- Trends observed for  $\text{SO}_4^{2-}$  same between the two methods



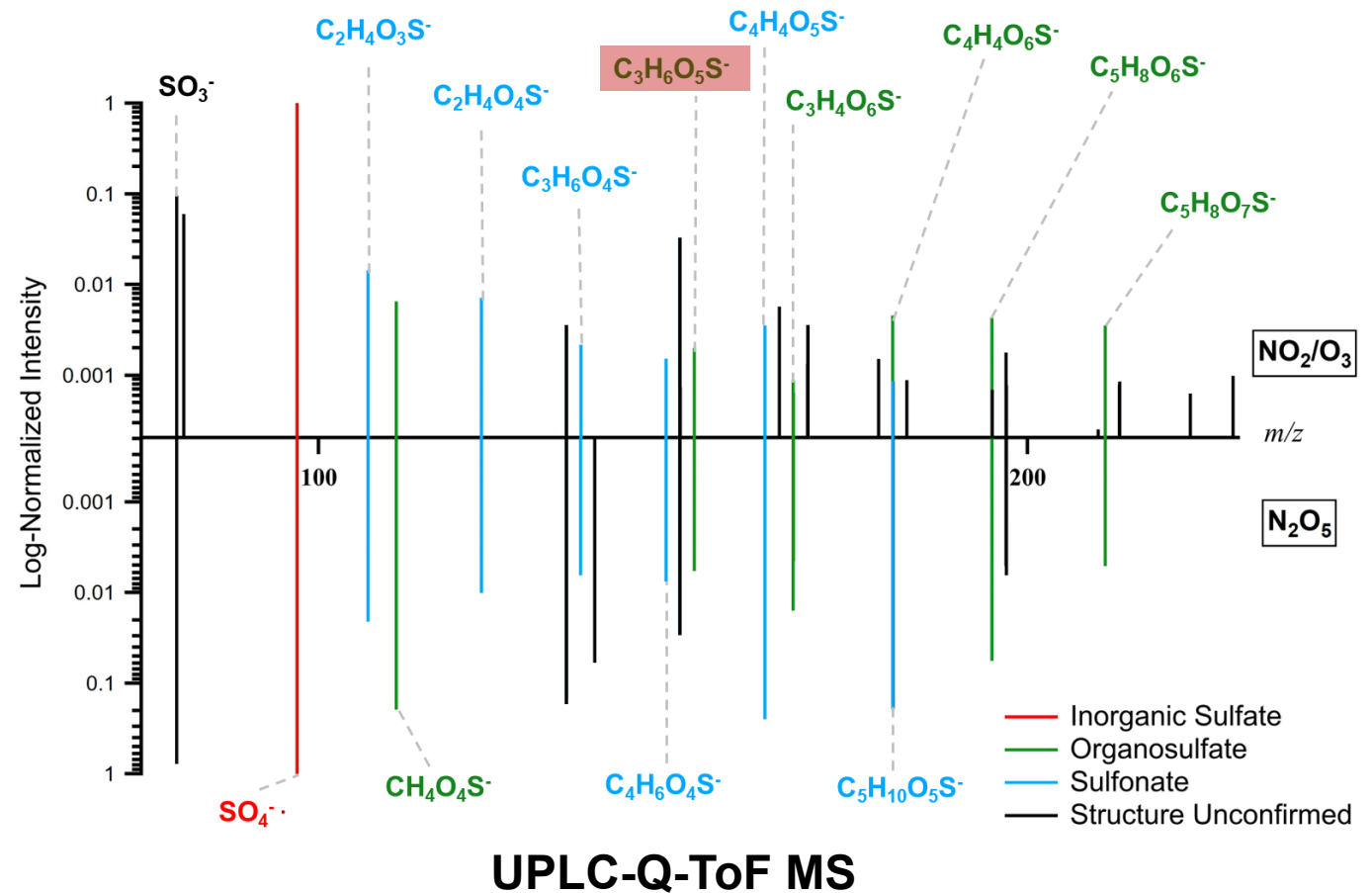
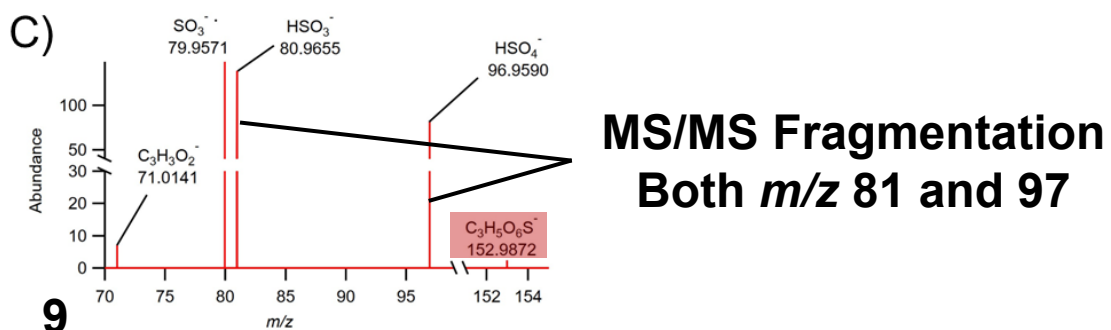
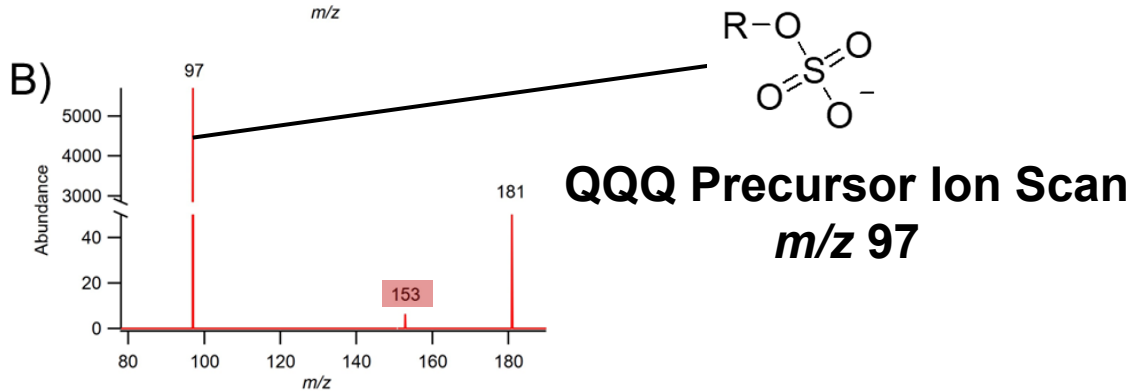
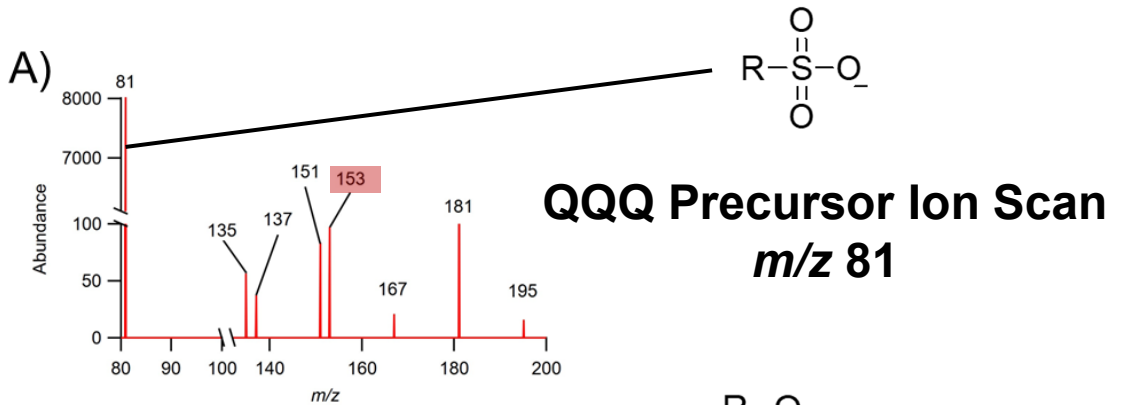
$\text{SO}_4^{2-}$  Constraint



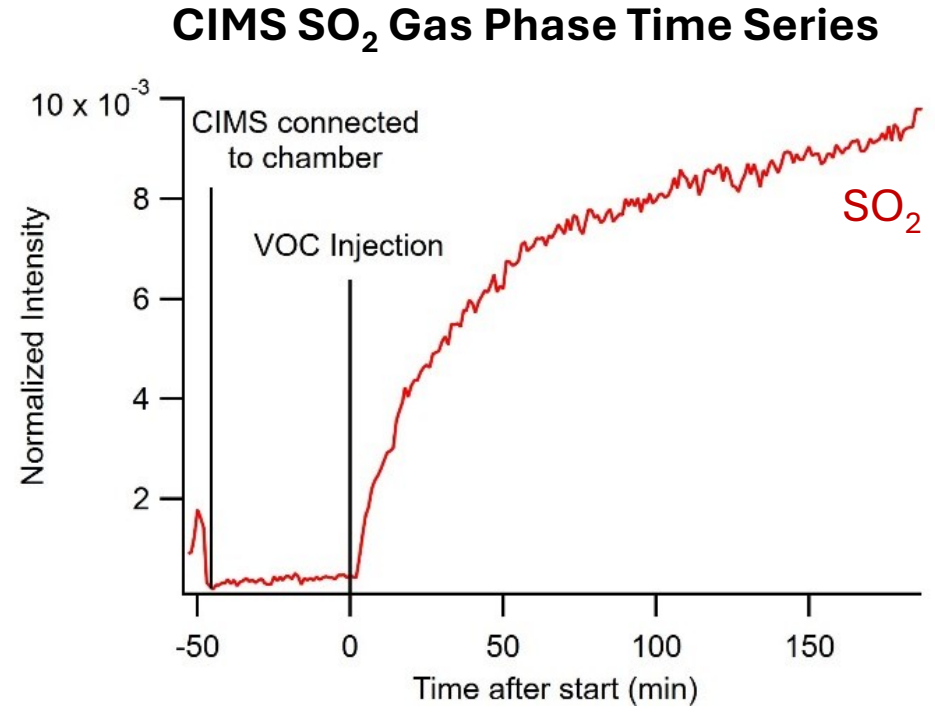
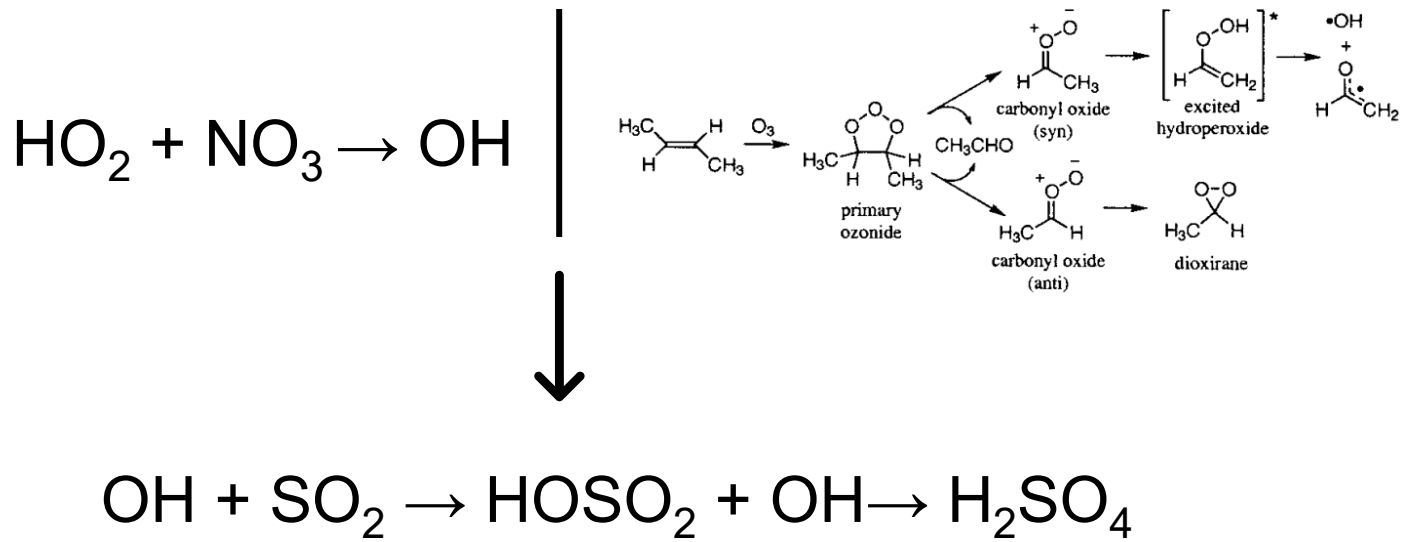
$f_{\text{SO}_4}$  Linear Combination



# OS / Sulfonate LC-MS Identification



# Dark OH production and role in SO<sub>4</sub><sup>2-</sup> formation



- O<sub>3</sub> only experiment performed with 1-butanol**
- Filter analyzed on IC, no inorganic sulfate was detected
  - OH oxidation of SO<sub>2</sub> may be a key mechanism for formation of SO<sub>4</sub><sup>2-</sup>

# Conclusion and takeaways

- Significant amounts of sulfonates, OS, and  $SO_4^{2-}$  are formed through oxidation of reduced aromatic organosulfur VOCs
- Results of this study predict  $1.30 \times 10^{-4}$  g  $SO_4^{2-}$  / kg of ponderosa pine burned during wildfire events.
  - Combined with findings from Jiang et al. (2019) and Hatch et al. (2015).

$$EF_{Thio} \times Y_{SA} \times f_{SO_4} \times f_{inorg} = \frac{\mu g SO_4^{2-}}{kg \text{ fuel burned}}$$

- More competition between oxidants than previously estimated
  - Rate constant of thiophene with  $NO_3$  and  $O_3$ 
    - $NO_3$  reaction ( $k = 3.2 \times 10^{-14}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>), ~8 ppbv
    - $O_3$  reaction ( $k < 6 \times 10^{-20}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>), ~1500 ppbv
  - Production and dark OH radicals



**Thank you for listening**

**Questions?**