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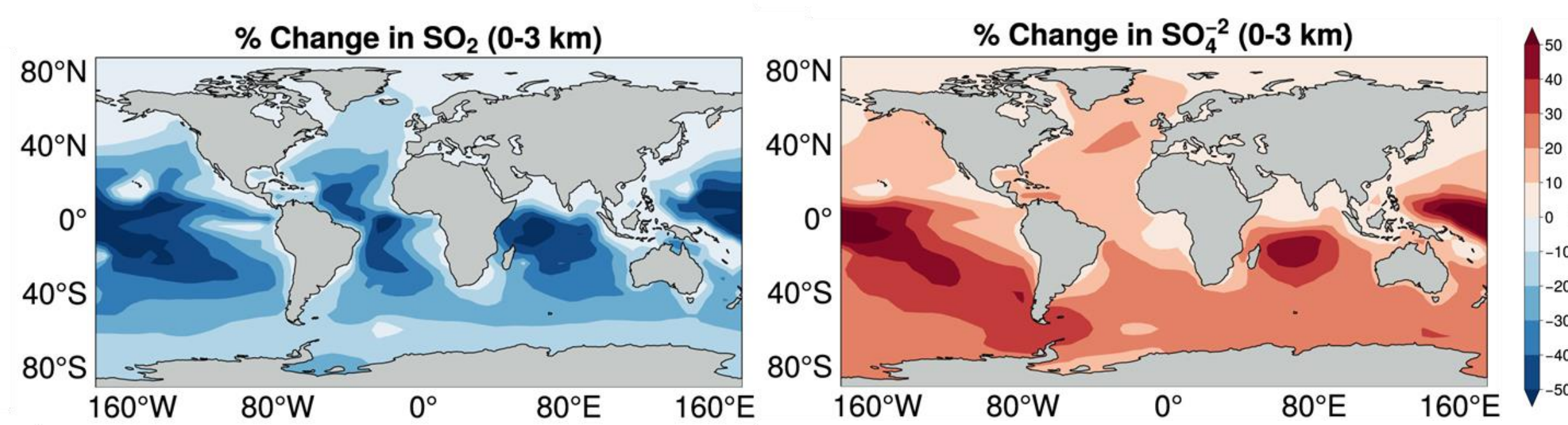
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## Background and Motivation

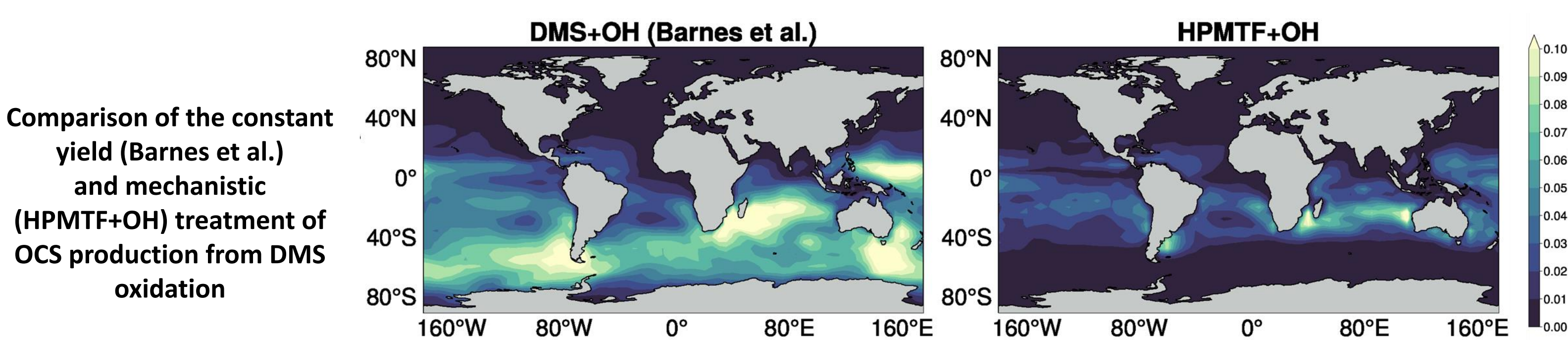
### Oxidation of DMS in the pristine marine environment

- Dimethyl sulfide (DMS) is a major source of reduced sulfur to the atmosphere and a significant source of sulfate aerosol<sup>1</sup>
- Carbonyl sulfide (OCS) is the largest continuous source of sulfate aerosol to the stratosphere<sup>2</sup>
- Hydroperoxymethyl thioformate (HPMTF) is major product of DMS oxidation and has been observed and modeled to be ubiquitous over the marine environment<sup>3</sup>

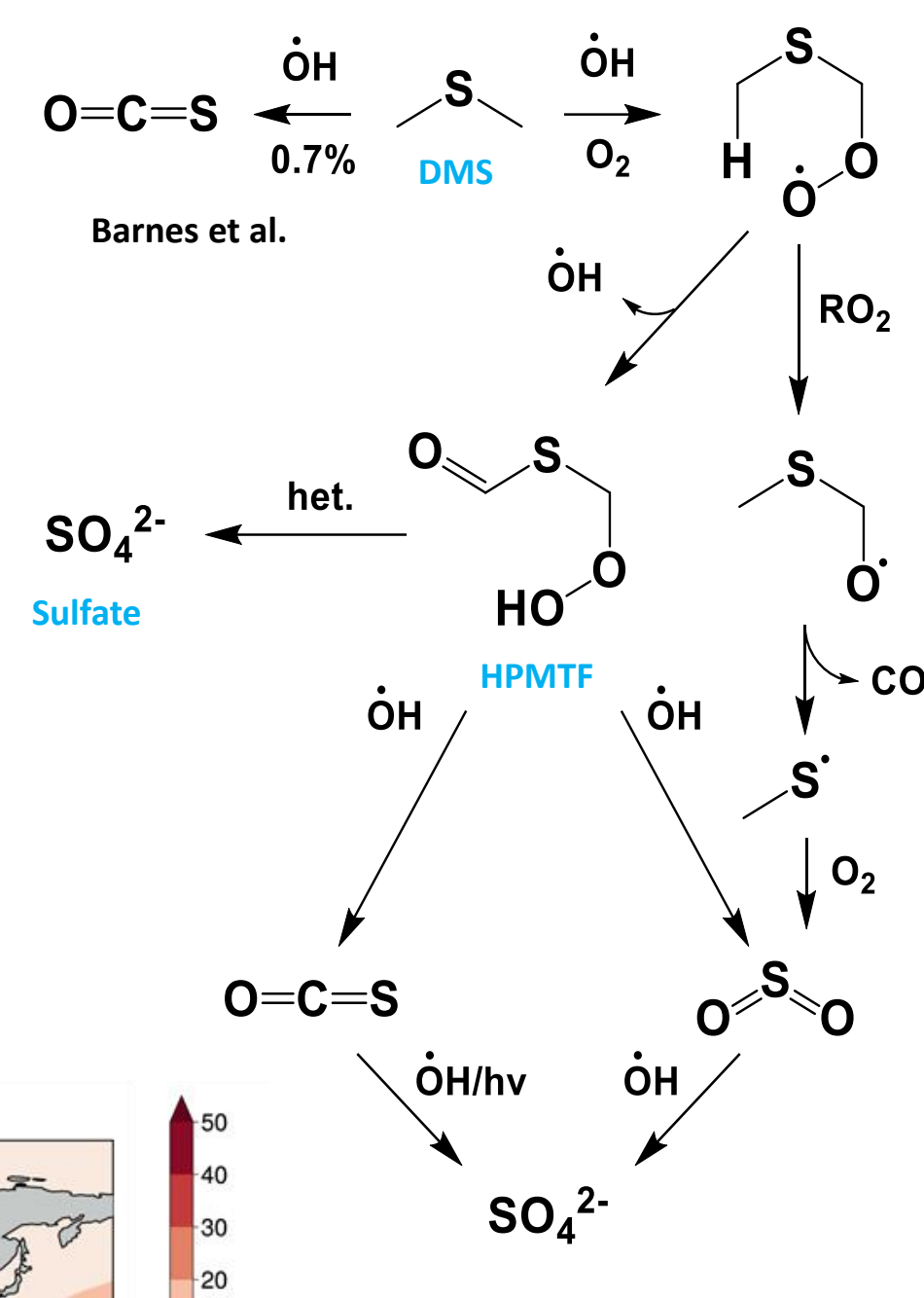
### HPMTF multiphase chemistry controls SO<sub>2</sub> distribution<sup>4</sup>



### HPMTF multiphase chemistry controls OCS distribution<sup>5</sup>



Here, we evaluate the assumption of 100% and 0% conversion to sulfate and OCS from aqueous HPMTF processing through laboratory experiments, respectively.



Change in SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup> as a function of the inclusion of HPMTF cloud loss process within a global climate model

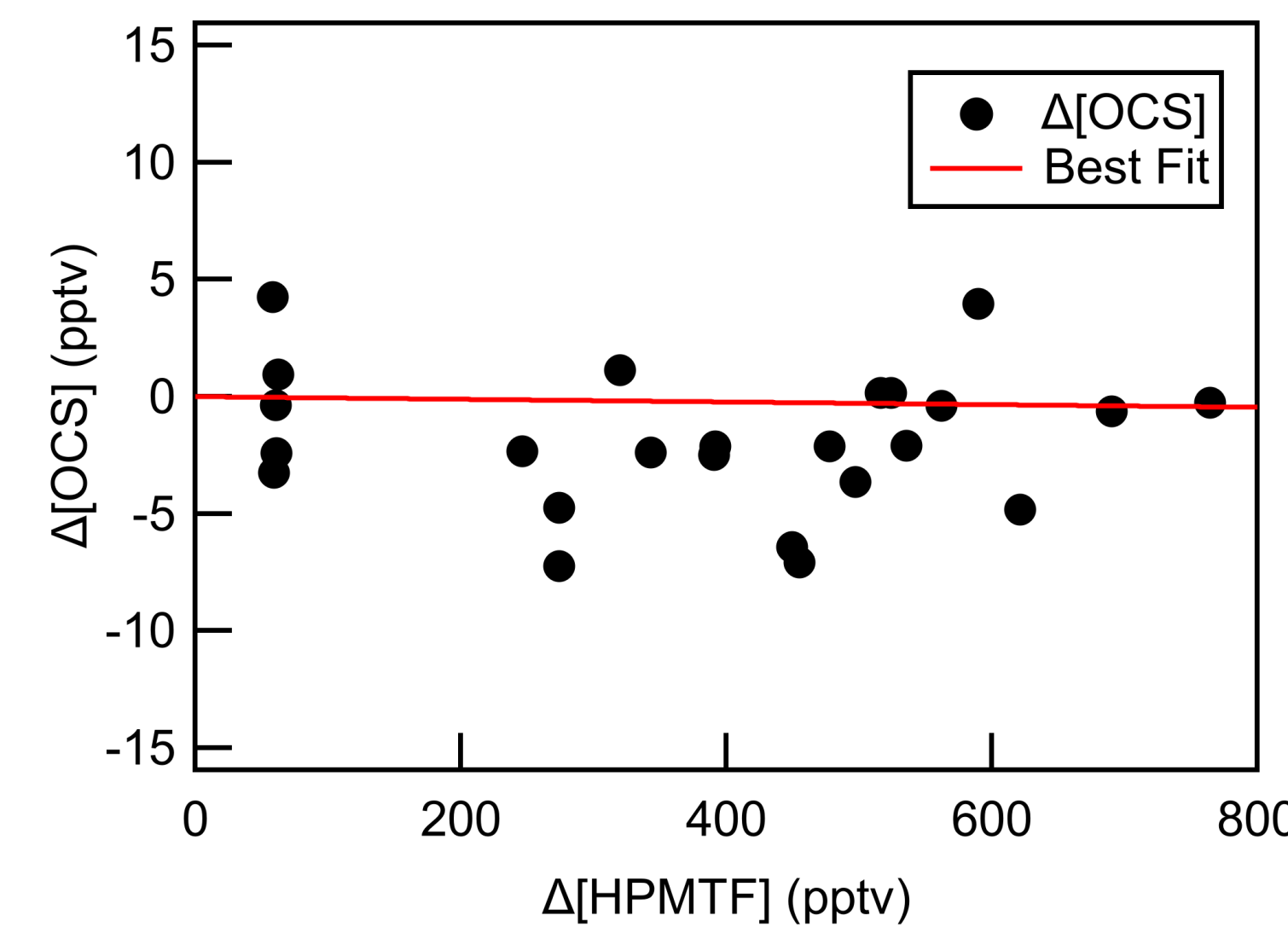
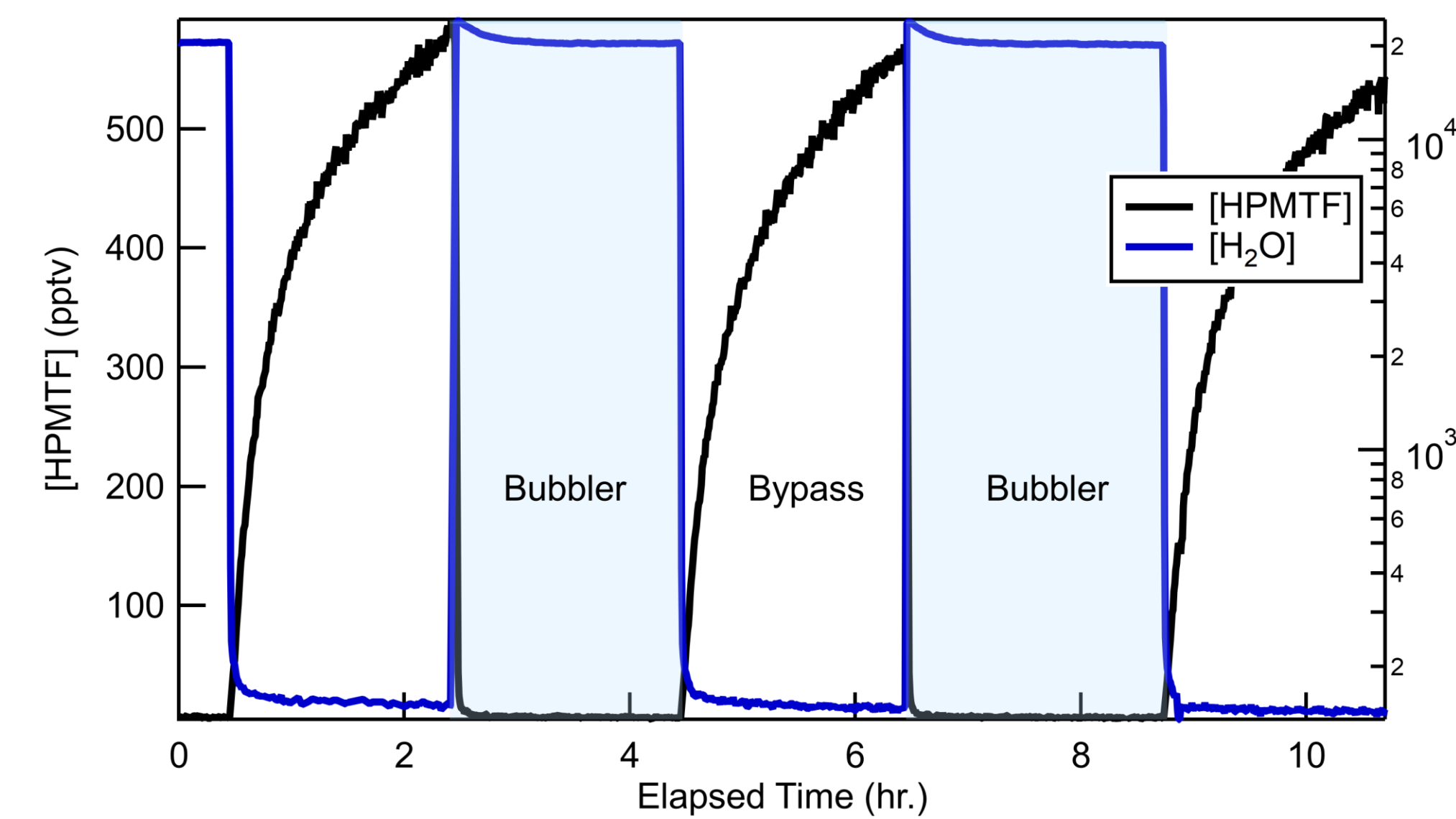
## Results and Discussion

### 1. Production of carbonyl sulfide (OCS) from aqueous processing of HPMTF

- The aqueous processing HPMTF was calculated by varying the concentration of HPMTF in a continuous flow of air through a MilliQ water

Alternate between bypass and bubbler to determine HPMTF exposure

HPMTF is irreversibly lost to the bubbler system



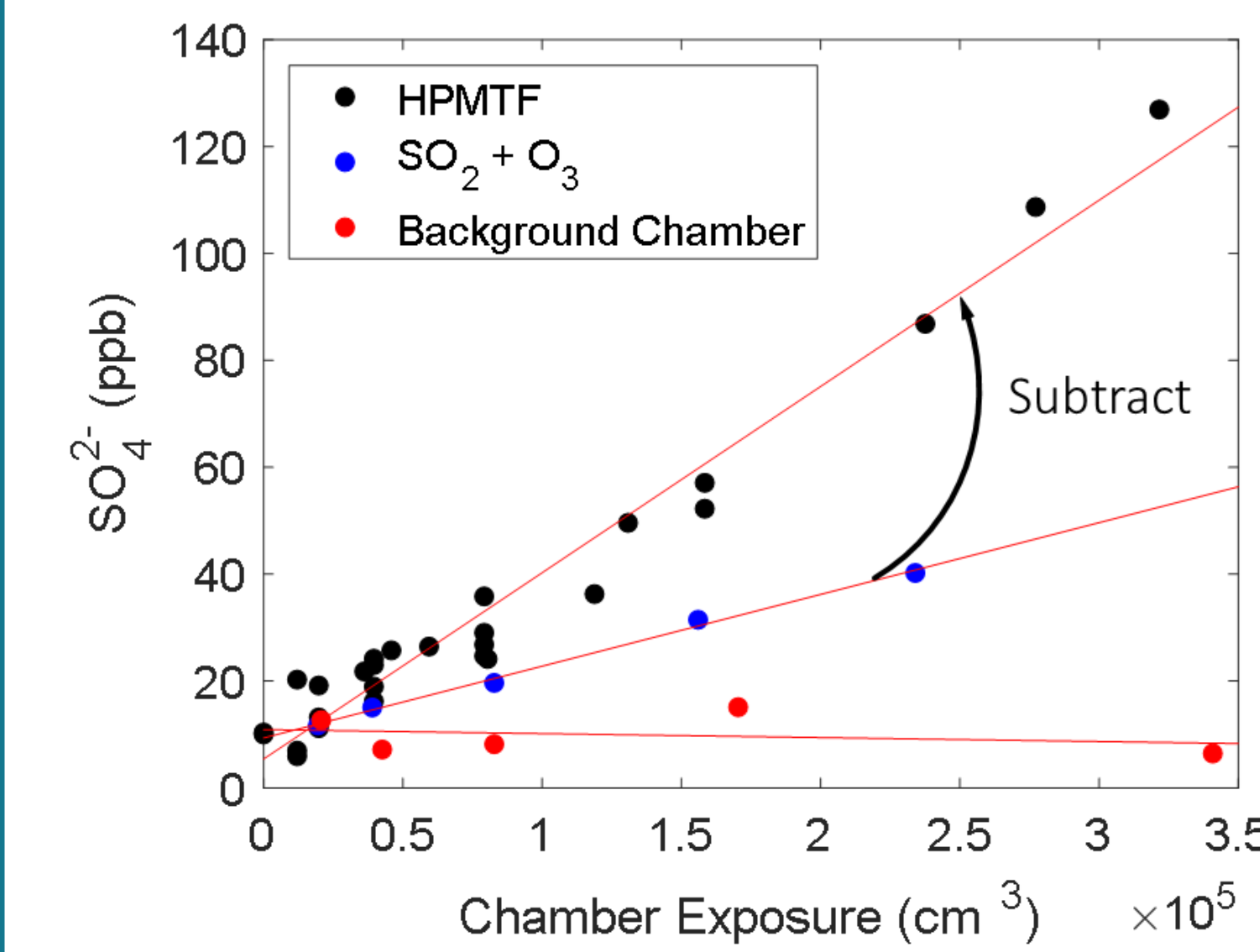
Account for the change in OCS background as a function of water content

<1% yield of OCS from aqueous processing of HPMTF

No observable gaseous production of carbonyl sulfide from the bubbling of HPMTF

### 2. Production of sulfate (SO<sub>4</sub><sup>2-</sup>) from aqueous processing of HPMTF

- The [SO<sub>4</sub><sup>2-</sup>]<sub>aq</sub> was determined using ion chromatography and normalized to a volume of 20 ml to account for increased concentration associated with water loss from bubbling
- A mixture of SO<sub>2</sub> and ozone, held at a concentration equivalent to the chamber flow, (0.86 and 75 ppb, respectively), to isolate the contribution of sulfate formation from non-HPMTF SO<sub>2</sub> multiphase processing.

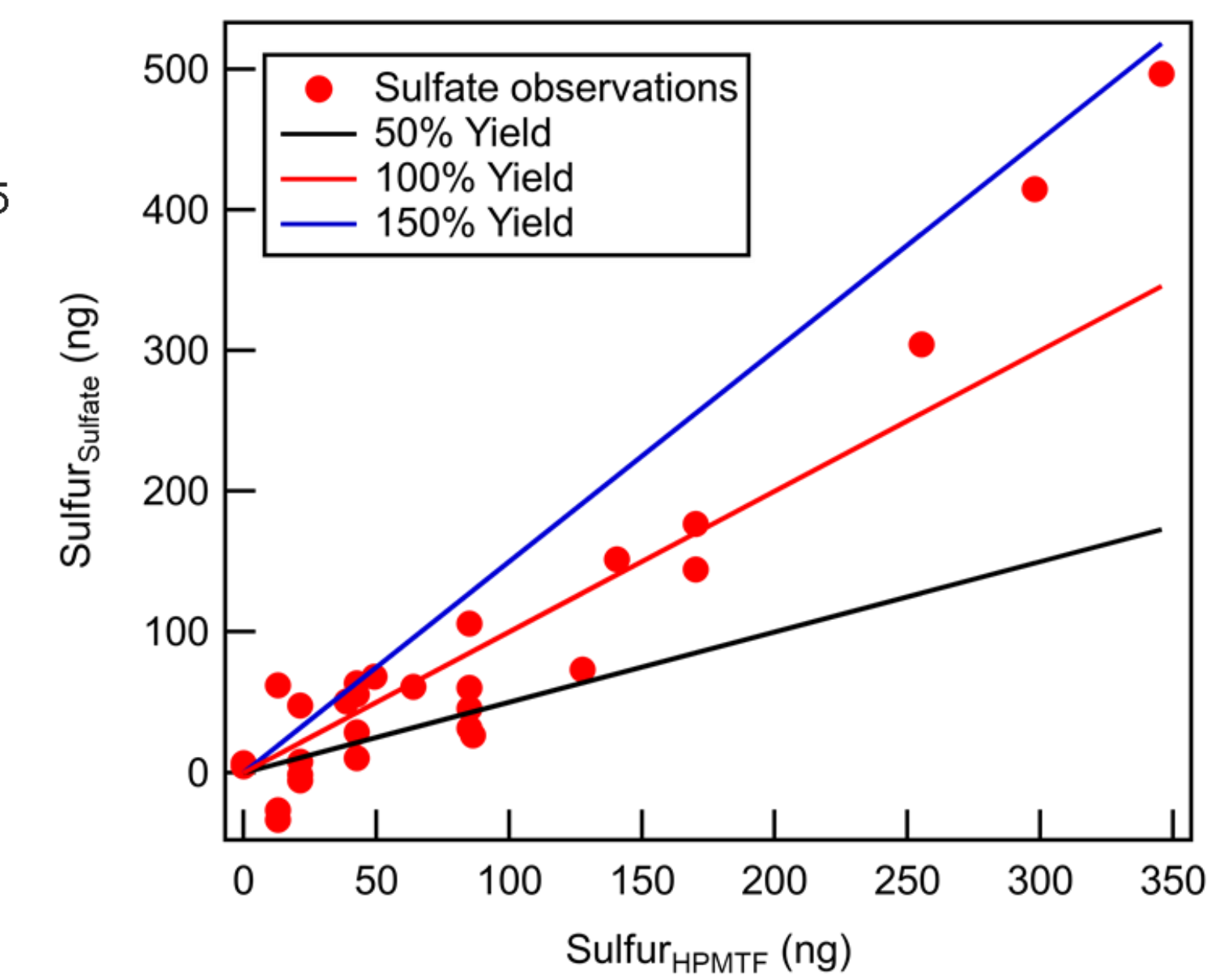


Convert chamber exposure to mass of sulfur utilizing observation of irreversibly lost of HPMTF

100% yield of SO<sub>4</sub><sup>2-</sup> from aqueous processing of HPMTF

Chamber Exposure = Chamber flow rate (cm<sup>3</sup>min<sup>-1</sup>) x Bubbling time (min)

Account for the sulfate formation via the oxidation of dissolved SO<sub>2</sub> with ozone

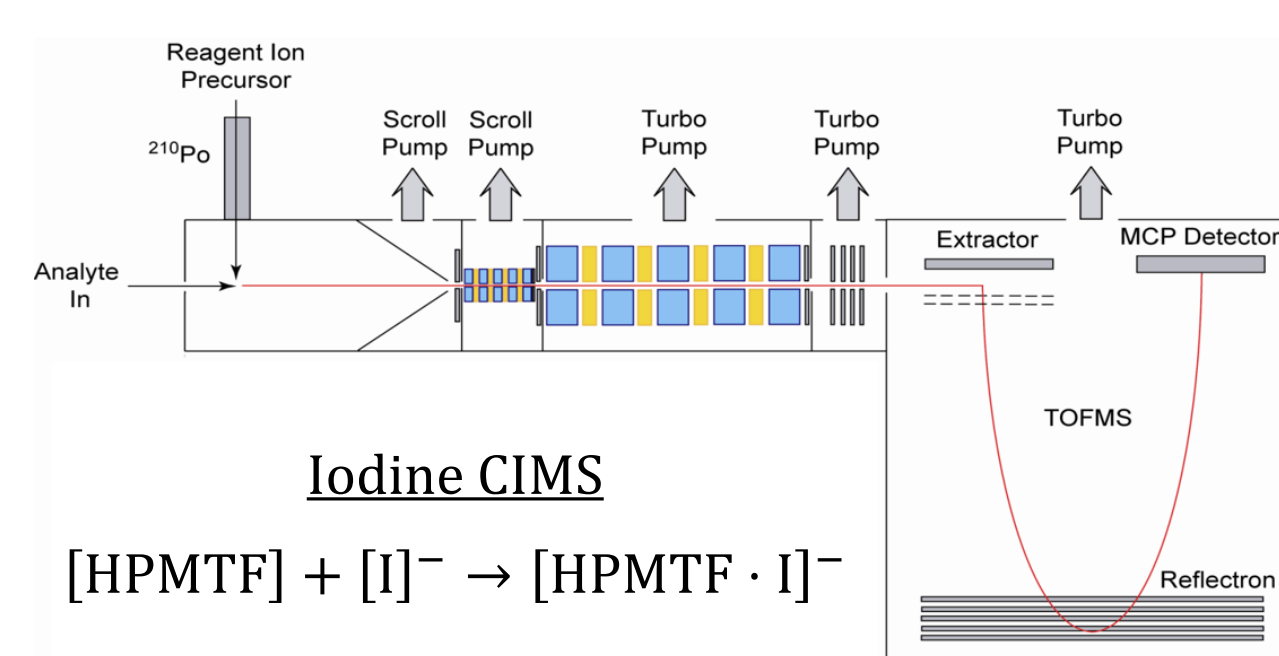


HPMTF goes on to form sulfate under neutral conditions with ozone present

## Methods and Instrumentation

### Chemical Ionization Mass Spectrometry (CIMS)

- A Compact Time of Flight Chemical Ionization Mass spectrometer (C-ToF) was used with iodide anions to detect HPMTF signal<sup>2,6</sup>

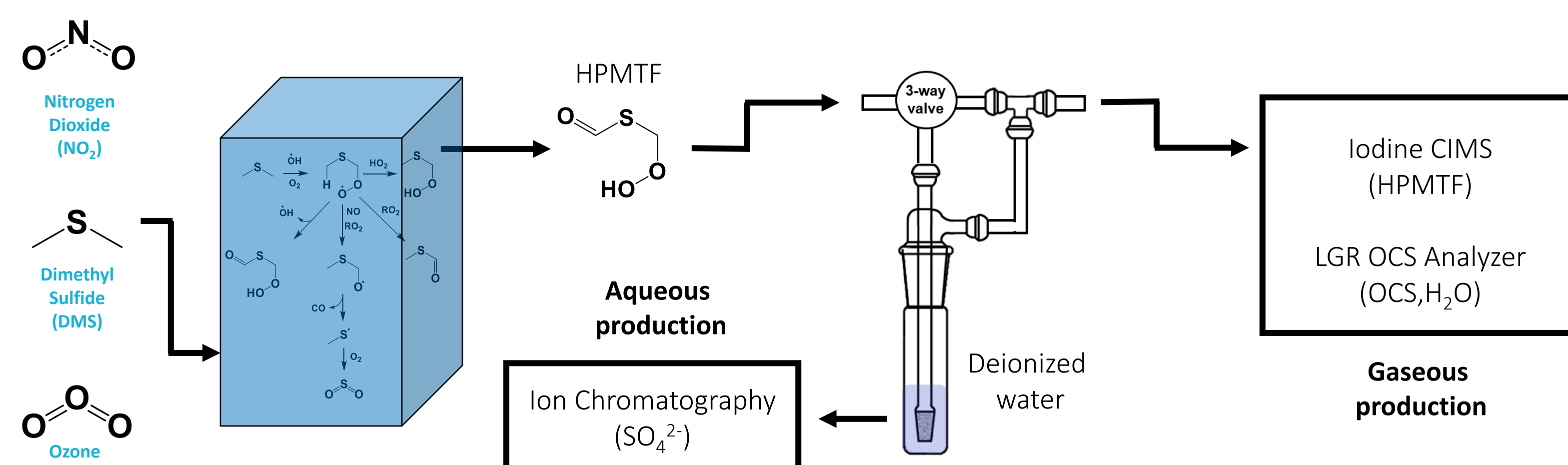


### CASPLASH Experimental Set-up

- Carbonyl sulfide and Sulfate Production from Loss of Aquatically Sequestered HPMTF

- A 0.6 m<sup>3</sup> 3 mil PFA environmental chamber was used to generate a steady state concentration of HPMTF from the oxidation of DMS by the nitrate radical (NO<sub>3</sub>)

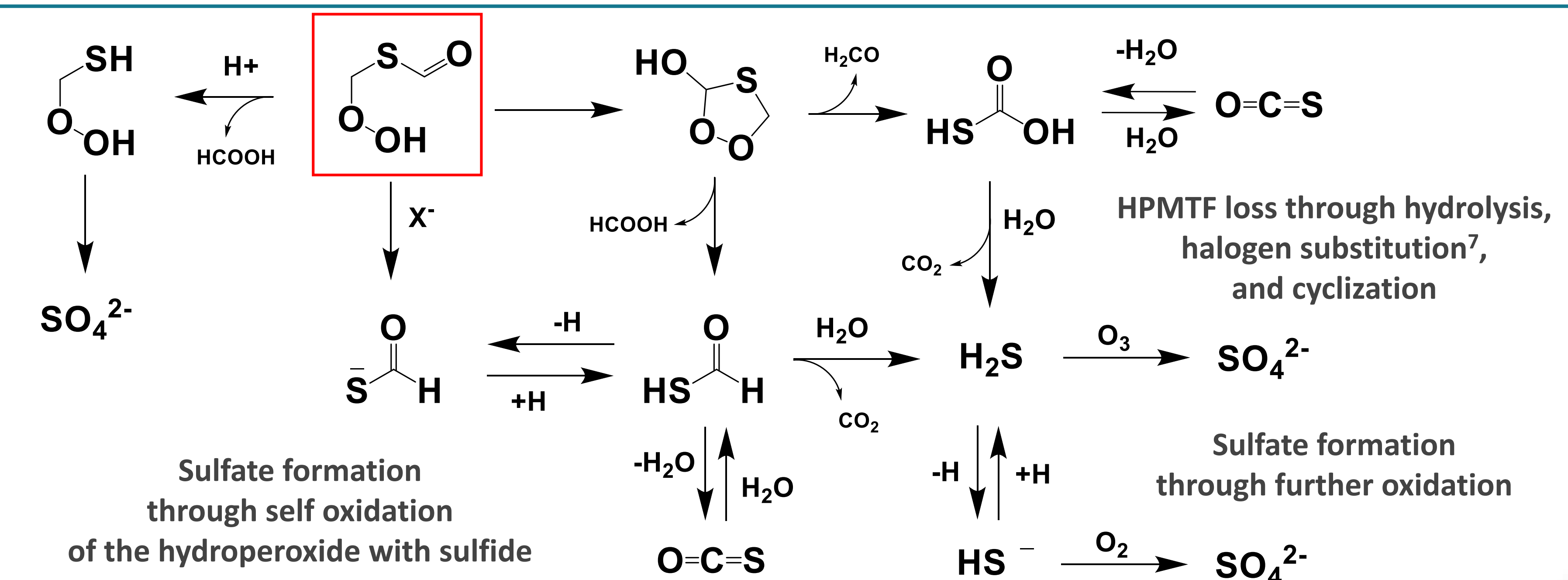
- Sulfate (SO<sub>4</sub><sup>2-</sup>) concentration was determined utilizing Ion chromatography



High sensitivity instruments are used to detect gaseous production of HPMTF and OCS and aqueous production of sulfate (SO<sub>4</sub><sup>2-</sup>)

### 3. Potential mechanisms for aqueous processing of HPMTF

- Carbonyl sulfide or other sulfur related products were not found above detection limits to be emitted from the bubbling of HPMTF
- Multiple routes could exist leading to the formation of sulfate and not OCS from the aqueous processing of HPMTF
- Hydrolysis is assumed to be a dominant loss process for HPMTF either through hydrolysis of the carbonyl or a potential water mediated cyclization to a cyclic peroxy hemiacetal
- The eventual formation of sulfate in the system could be mediated by ozone present in the HPMTF chamber flow as well as the potential for self oxidation of the sulfur atom by the hydroperoxide group



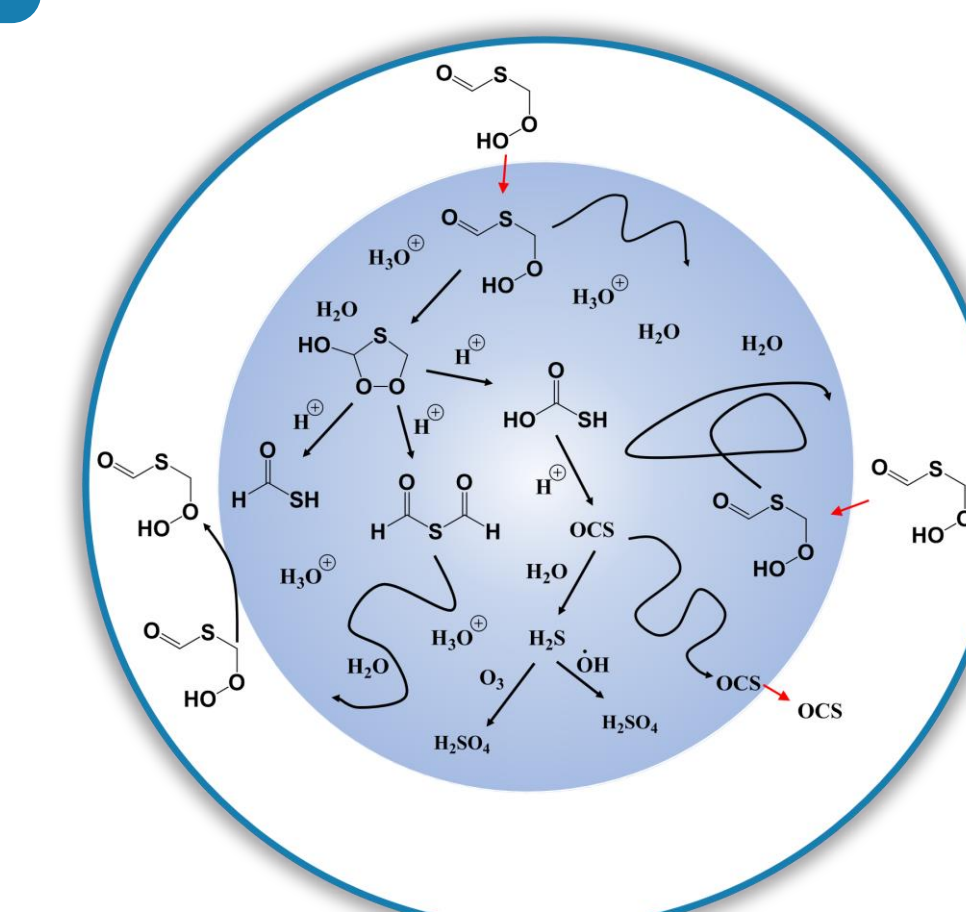
## Conclusions and Future Directions

### HPMTF is efficiently and irreversibly lost to aqueous mediums

- HPMTF was found through experimental observations to ubiquitously form sulfate and not OCS under neutral aqueous conditions

### Environmentally relevant aerosols and aqueous conditions

- Increased heterogeneous loss and oxidation by hydroperoxides (ROOH) and carbonyl (C=O) molecules within acidic and ionic aerosols could lead to differing product distribution than seen here



## Acknowledgements

References: (1) Lana, A. et al. *Global Biogeochem. Cycles* (2011). (2) Crutzen, P. J. *Geophys. Res. Lett.* (1976) (3) Veres, P. R. et al. *Proc. Natl. Acad. Sci.* (2020). (4) Novak, G. A. et al. *Proc. Natl. Acad. Sci.* (2021). (5) Jernigan, C. et al. *Geophys. Res. Lett.* (2022) (6) Bertram, T. H. et al. *Atmos. Meas. Tech.* 4, 1471–1479 (2011). (7) Jernigan, C. et al. *J. Phys. Chem. A* (2022)

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