Observations and Constraints on the Sulfur Budget over the Marine Environment

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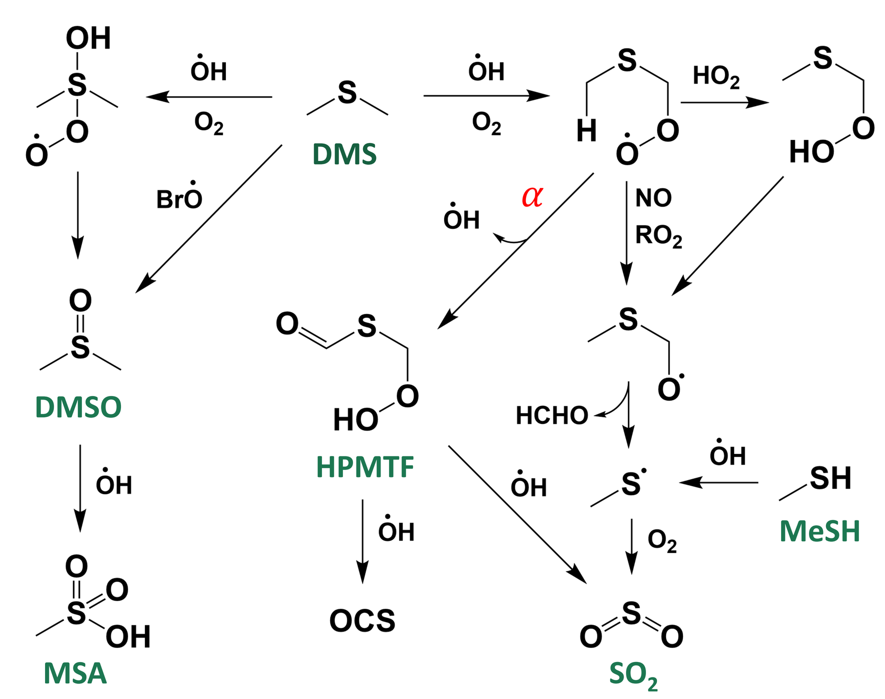
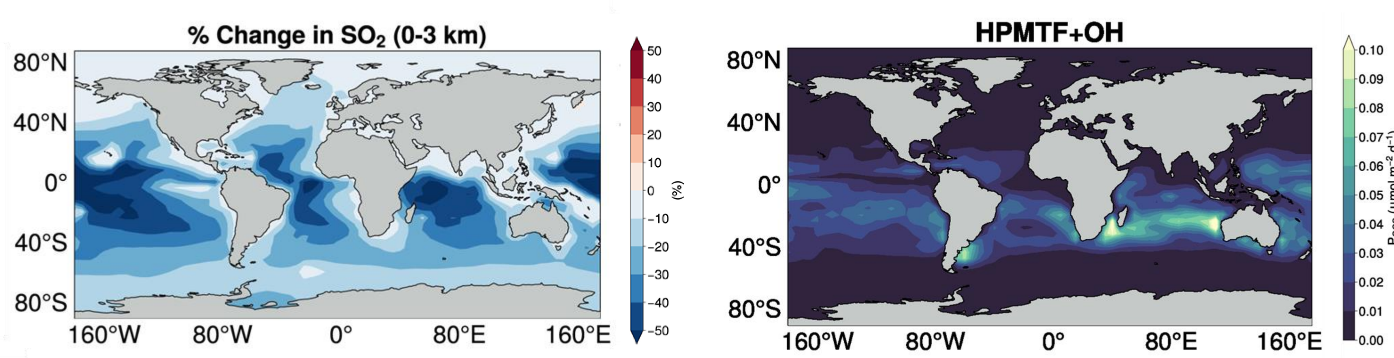
Background and Motivation

Oxidation of DMS

- Dimethyl sulfide (DMS) and methanethiol (MeSH) are important sources of reduced sulfur to the atmosphere and a significant source of sulfate aerosol[1]
- Carbonyl sulfide (OCS) is the largest continuous source of sulfate aerosol to the stratosphere[2]
- Hydroperoxymethyl thioformate (HPMTF) is major product of DMS oxidation and has been observed and modeled to be ubiquitous over the marine environment[3]



HPMTF fate controls SO_2 and OCS distribution[4,5]



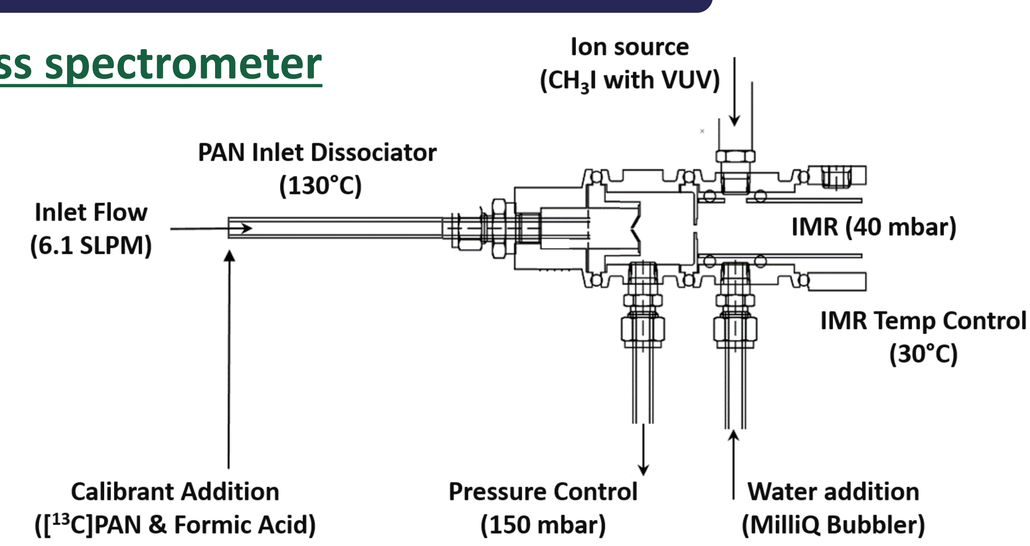
Change in SO_2 and updated OCS production with new HPMTF cloud loss process

Here, we present observations of major sulfur compounds over the pristine marine environment to determine the drivers of sulfur oxidation

Instrumentation and Calibration

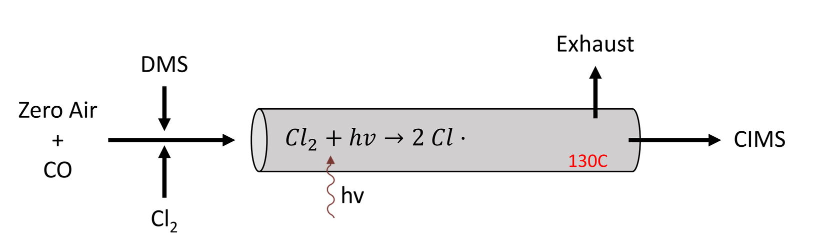
NOAA Chemical Ionization Mass spectrometer

- A temperature of 30°C and cluster ratio ($[I]^-/[I\cdot H_2O]^-$) of 0.55 were held within the Ion Molecule Region (IMR)
- A 130°C inlet was maintained for consistent peroxyacetyl nitrate (PAN) observations and N_2O_5 dissociation
- Formic acid and ^{13}C PAN were added as calibrants



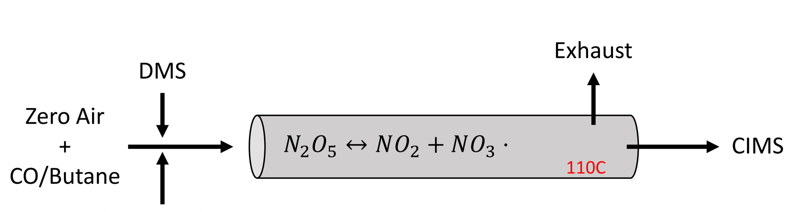
Adapted from *Robinson et al 2022*

Calibration of hydroperoxymethyl thioformate (HPMTF)



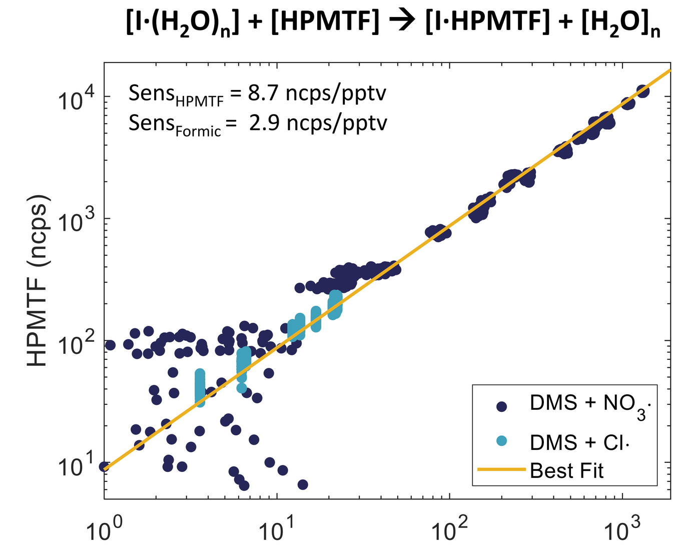
DMS + Cl Assumptions and Parameters:[7]
k_{isom}(373K) = 10 s^{-1}, t_{res} = 0.1 s; $[DMS]_i$ = 1 ppm; $[CO]_i$ = 4%; $[Cl_2]_i$ = 15 ppb
351 nm laser to photolyze Cl_2; Calibrate [Cl] with [$ClNO_2$] in excess [NO_2]

DMS + NO_3 Assumptions and Parameters:
k_{isom}(373K) = 10 s^{-1}, t_{res} = 5 s; $[DMS]_i$ = 1 ppm; $[CO]_i$ = 4%; $[N_2O_5 + NO_3]_i$ = 1.2 ppb
Performed in dark; Calibrate [NO_3] with CRDS



HPMTF Calibration Curve

$[I\cdot(H_2O)_n]^- + [HPMTF] \rightarrow [I\cdot HPMTF]^- + [H_2O]_n$



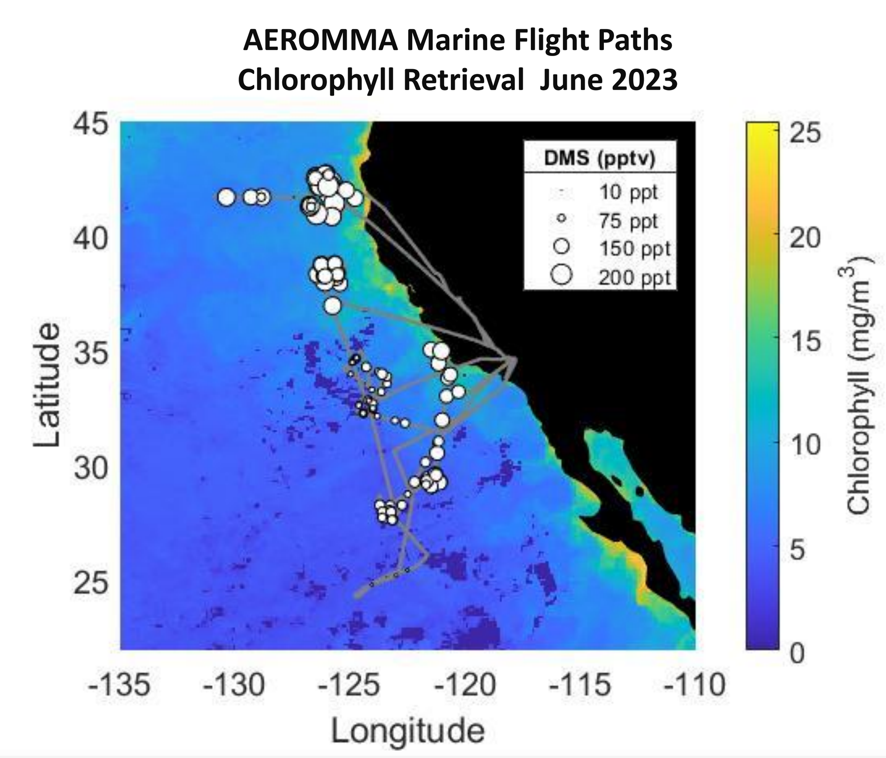
High sensitivity instruments are used to detect gaseous concentration of HPMTF calibrated via multiple different methods

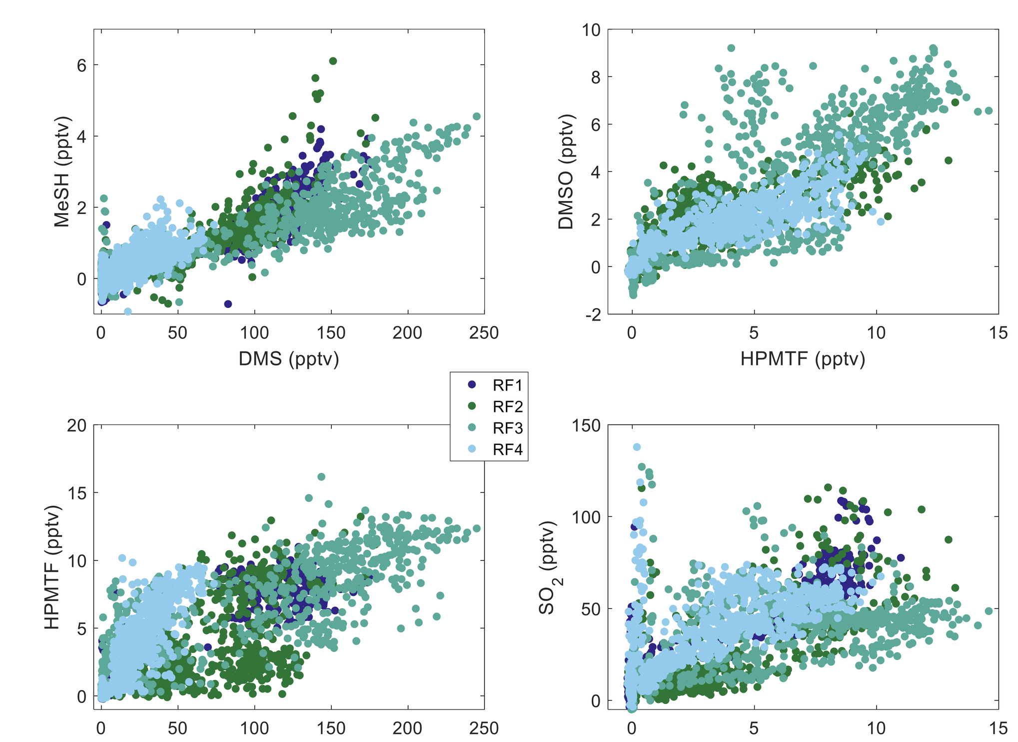
Observations and Atmospheric Constraints

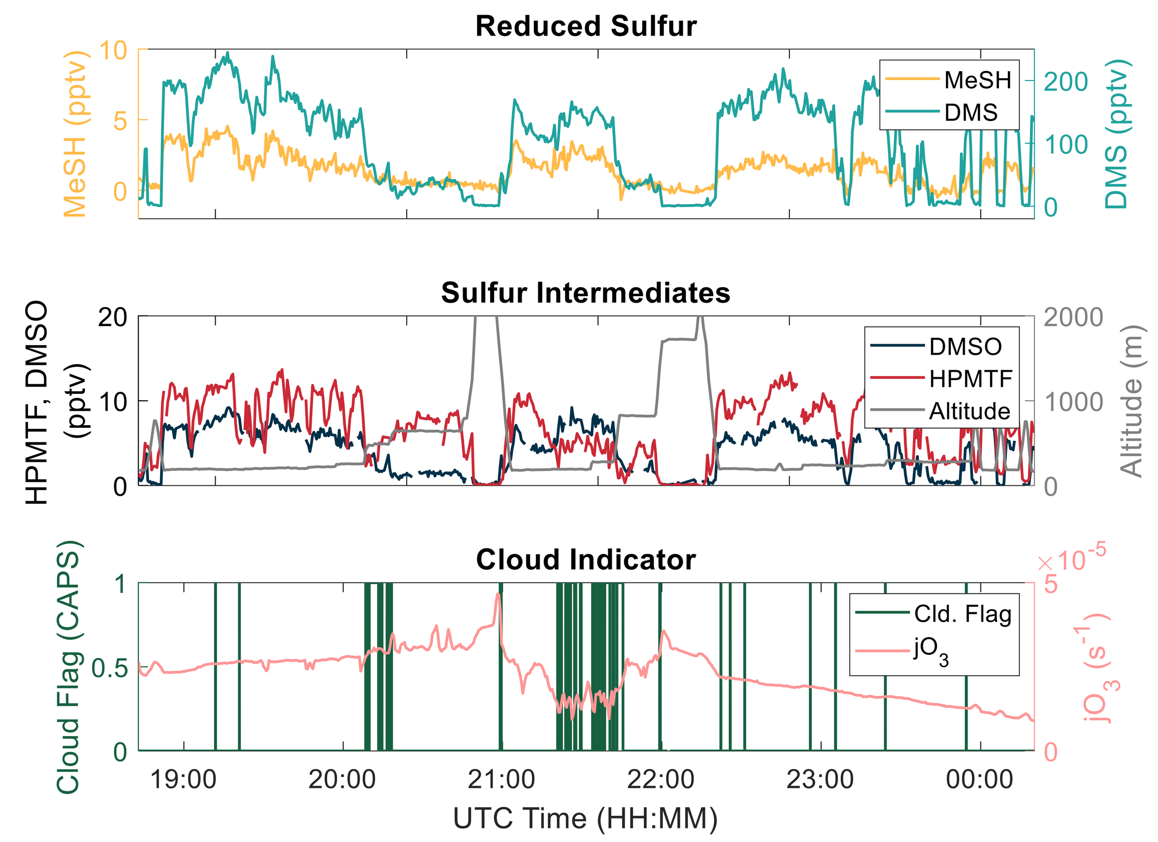
All sulfur presented as 10s averaged data

Atmospheric Emissions and Reactions Observed from Megacities to Marine Areas (AEROMMA) Campaign

Airborne measurements from the NASA DC-8 off the west coast in June 2023

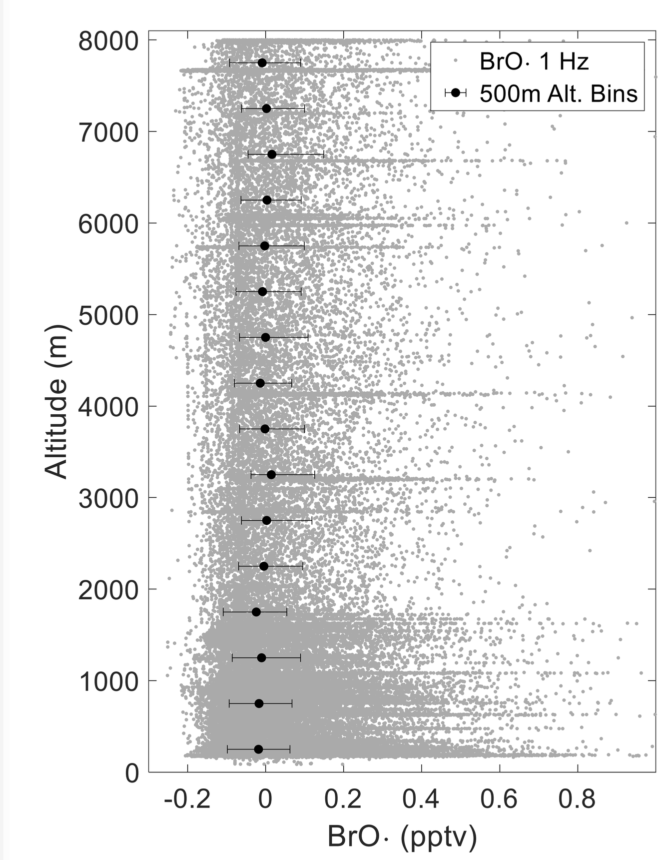






Research Flight 3, June 21, 2023

Marine BrO· Observations



LOD = 0.30 ± 0.1 pptv @ 15 sec

$\tau_{DMS,BrO}$ = 8.3 ± 2 hrs. @ LOD

Minimal BrO· implies minimal DMSO production

HPMTF Steady State Analysis

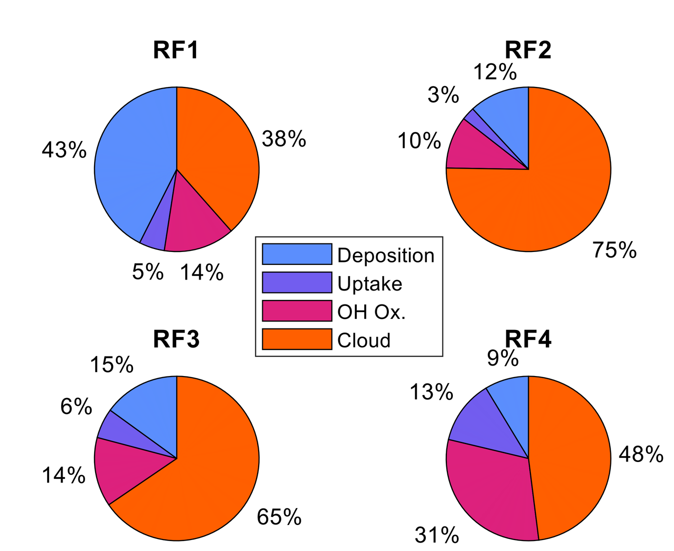
Assume

$\gamma_{HPMTF} = 1.6 \times 10^{-3}$ $\quad k_{DMS+OH(Abs)} = 1.12 \times 10^{-11} \times e^{(-250/T)}$

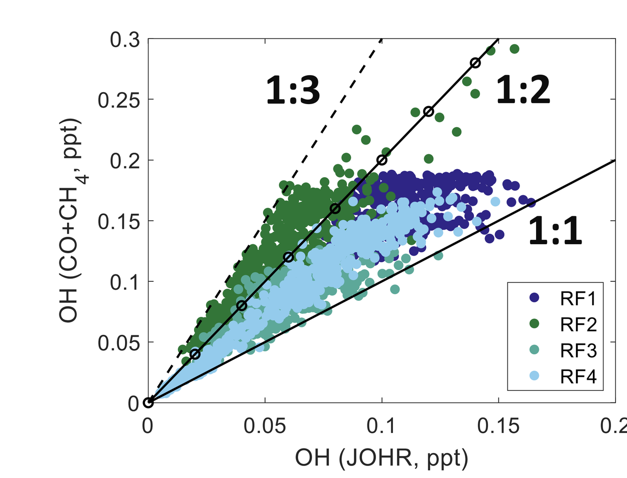
$v_d = f(U_{10})$ (cm s^{-1}) $\quad k_{HPMTF+OH} = 1.4 \times 10^{-11}$ (cm^3 molec.$^{-1}$ s^{-1})

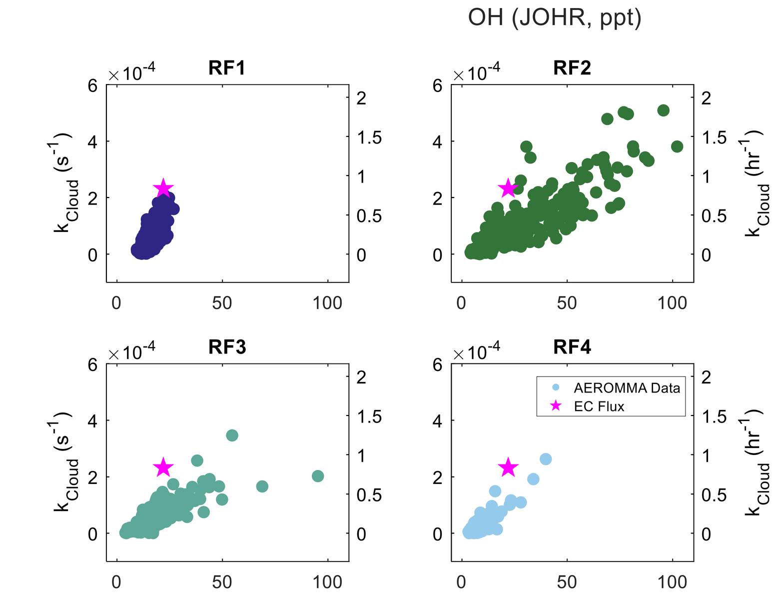
$$\frac{[DMS]}{[HPMTF]} = \frac{\frac{\gamma\omega}{4} S_A + \frac{v_d}{BLH} + k_{cld} + k_{OH}[OH]}{\alpha k_{OH}[OH]}$$

$$[OH] = \frac{f O(1D) \cdot jO_3 \cdot [O_3] \cdot 2 \cdot [H_2O]}{OHR}$$

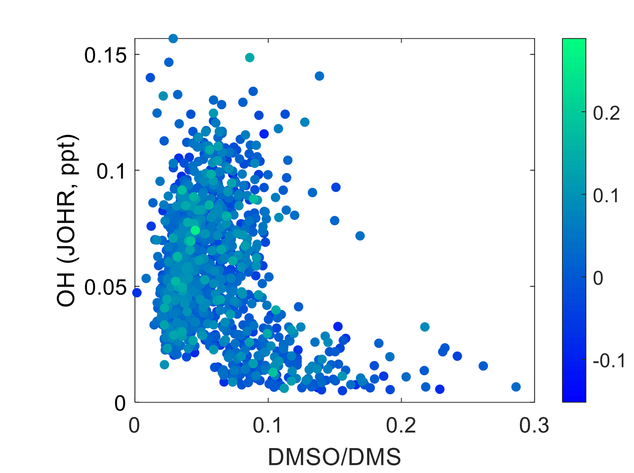


Evaluate Drivers of OH

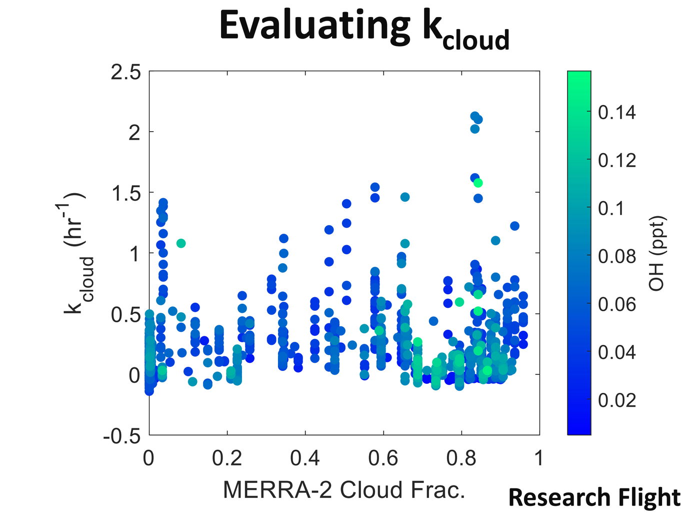




Constrain OH exposure



Evaluating k_{cloud}



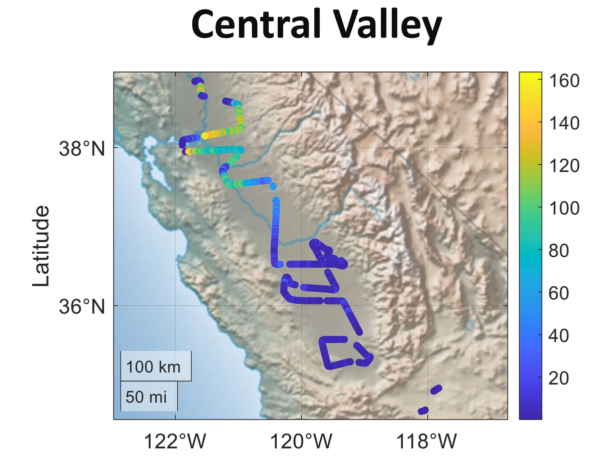
Research Flight 3
June 21, 2023

Calculated k_{cloud} term contributes to a significant fraction of the observed HPMTF loss

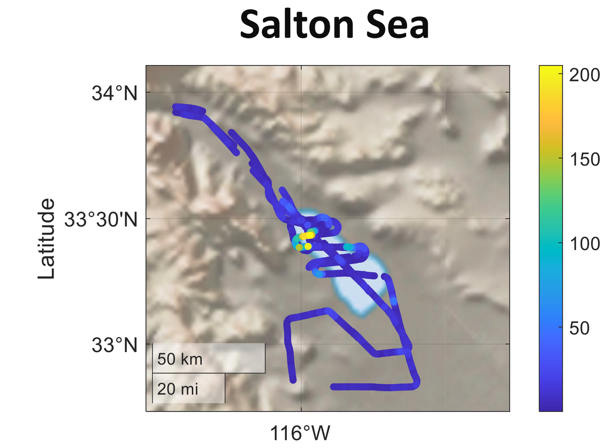
Urban and Terrestrial HPMTF

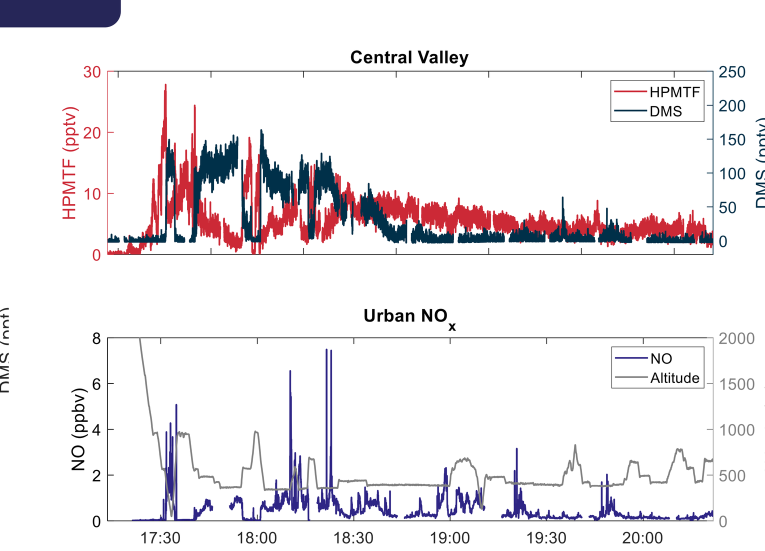
SARP and LA Flights Mix of Urban and Marine Air

Central Valley



Salton Sea





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)Robinson M. et al. *AMT* (2022). (7) Assaf, E. et al *JPCA* (2023).(8) Wolfe, G. M et al. *Geoscientific Model Development* (2016)

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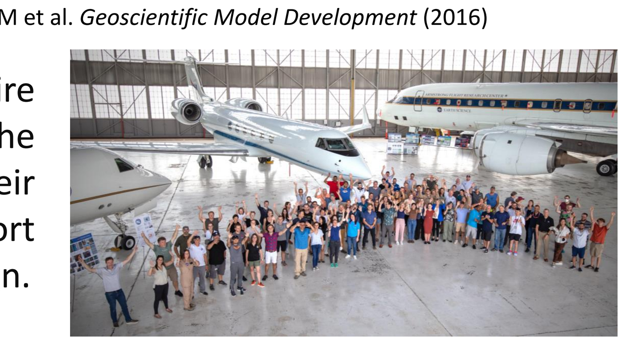

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