Modeling of methyl hydroperoxide observations in urban and remote air over South Korea:

Demonstration of high-NO and low-NO regimes for hydrocarbon oxidation, and inference of atmospheric methanediol

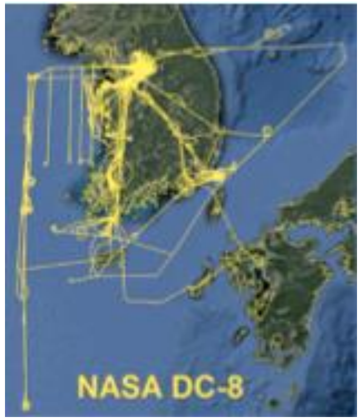
Laura H. Yang

D.J. Jacob, K.H. Bates, H. Lin, H.M. Allen, S.S. Brown,
R. Dang, D.K. Colombi, S. Zhai, R.M. Yantosca,
J.-F. Müller, K.R. Travis, J.F. Brewer, N.L. Ng, J.D. Crounse,
P.O. Wennberg, H. Liao

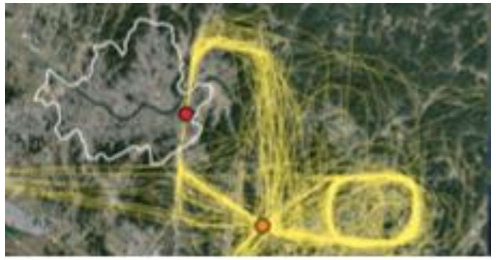
AMS 2025
January 16, 2025

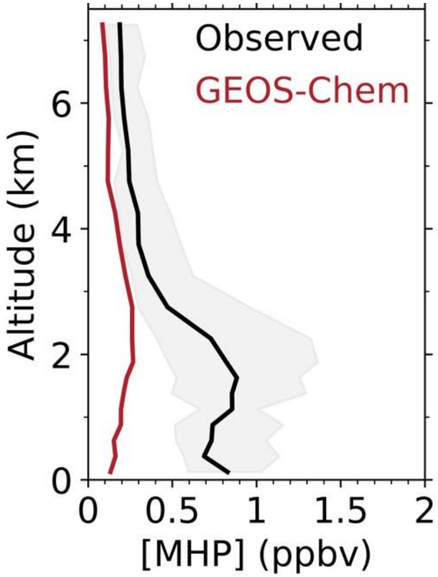
KORUS-AQ provides a detailed characterization of atmospheric chemistry in the polluted planetary boundary layer and the background free troposphere

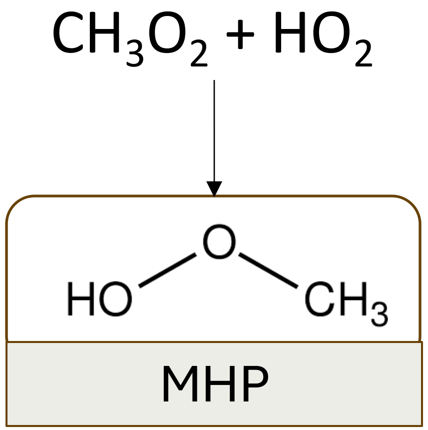
May – June, 2016



- Aircraft observations also provide vertical profiling over the Seoul Metropolitan Area (SMA)
  - Every morning, midday, and afternoon



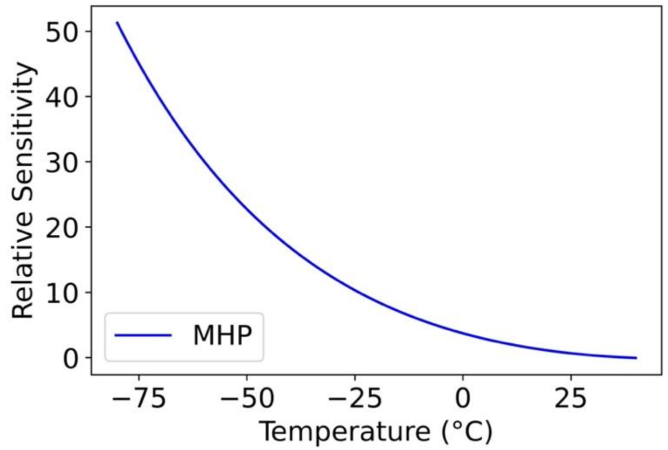


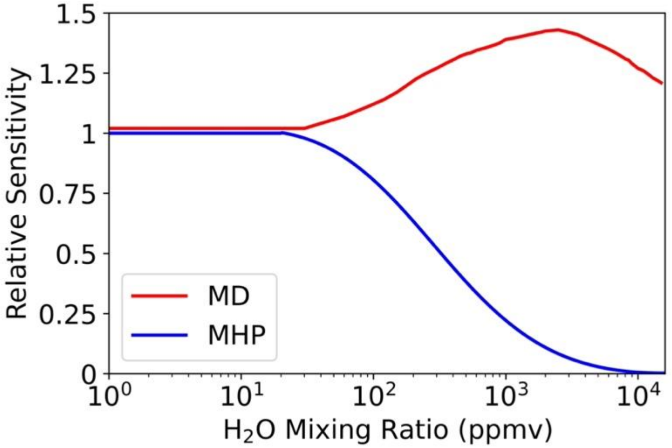


- KORUS-AQ has been used extensively to evaluate & improve GEOS-Chem oxidant and aerosol simulations
  - But GEOS-Chem underestimates MHP by a factor of 5 😲

[Figures from Crawford et al. 2021]

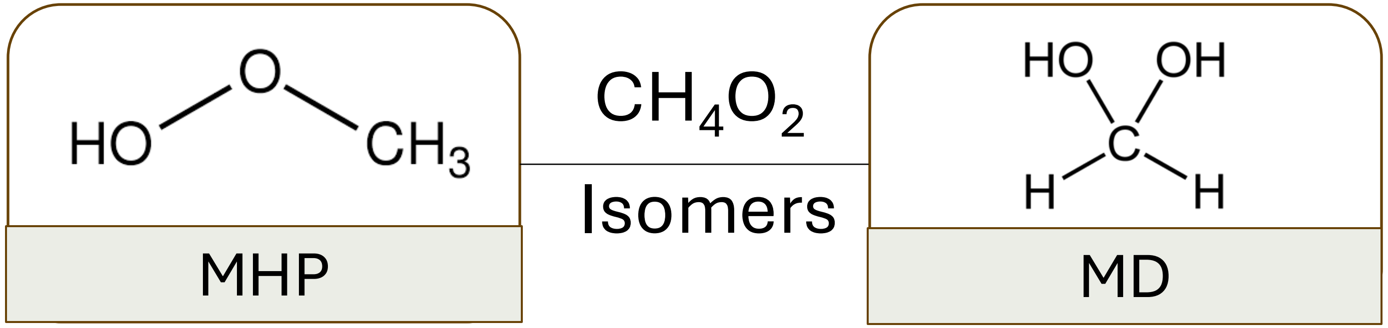
The methyl hydroperoxide (MHP) measurement from CIT-CIMS has positive interference from methanediol (MD)





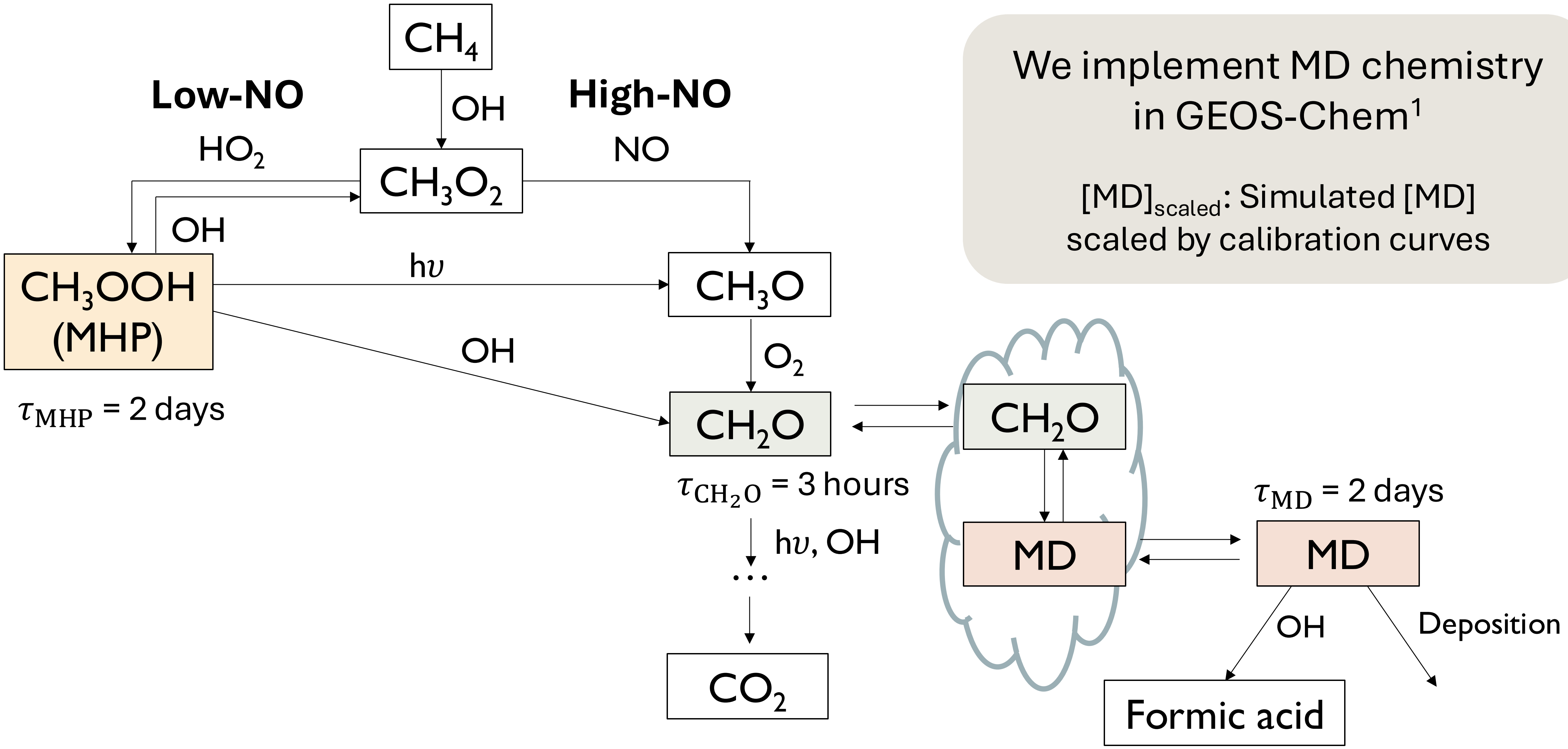
CIT-CIMS instrument's sensitivity to MD and MHP

[Calibration curves from Allen et al. 2021]



- CIT-CIMS instrument's sensitivity to MHP declines rapidly at higher temp. and water mixing ratio
  - MD Interference becomes important
  - Calibration curves are valid up to H_2O mixing ratio of 10^4 ppmv

Overview of MHP and MD chemistry

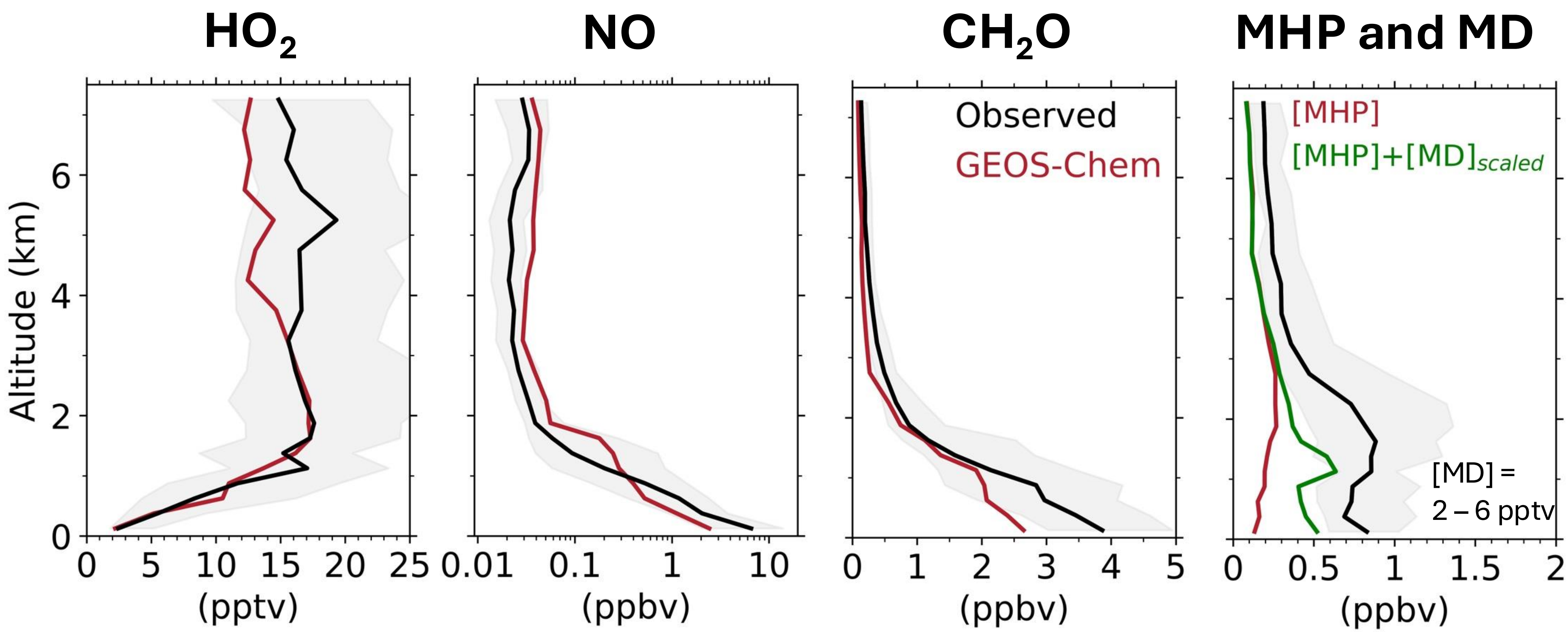


We implement MD chemistry in GEOS-Chem[1]

$[MD]_{scaled}$: Simulated [MD] scaled by calibration curves

[1]Implementation follows Nguyen et al. (2023)

Comparison of median vertical profiles over the SMA during KORUS-AQ

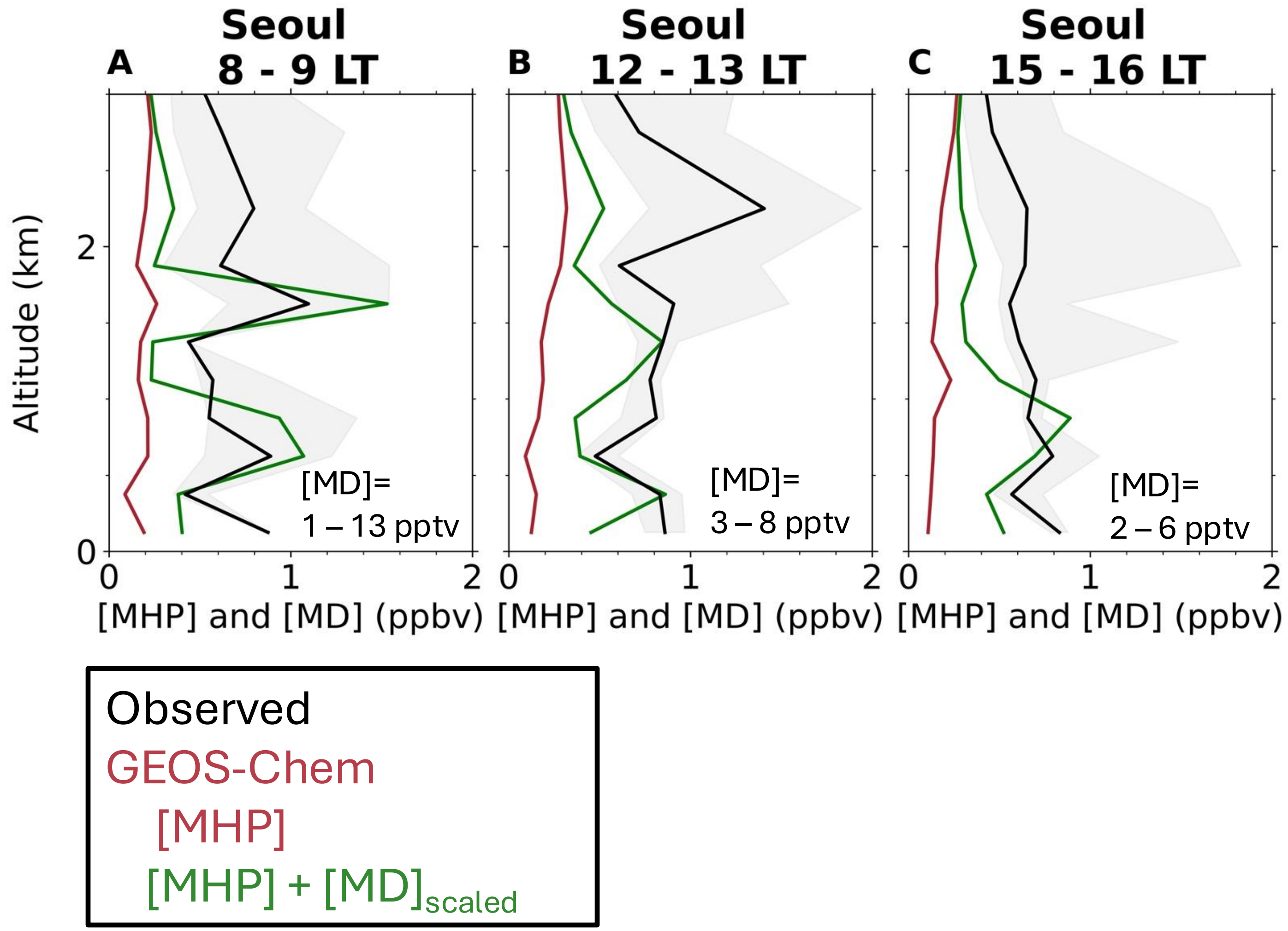


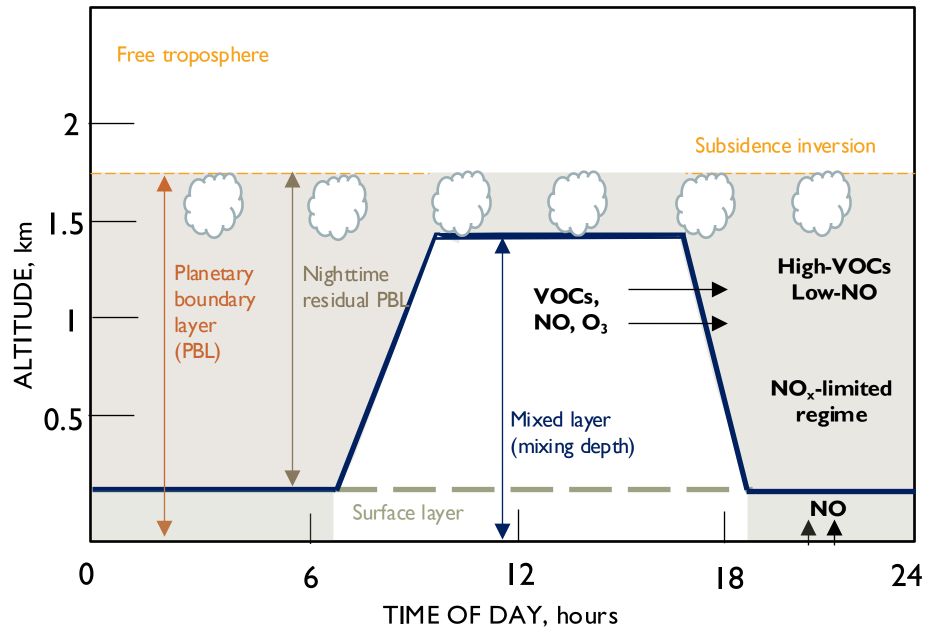
- HO_2 and NO are well simulated
    - Defining the low-NO and high-NO regimes for VOC oxidation
- The high concentration of observed MHP can be explained by the measurement's positive interference from the MD

SMA: Seoul Metropolitan Area

Only used MHP data with [H_2O mixing ratio] < 10^4 ppmv

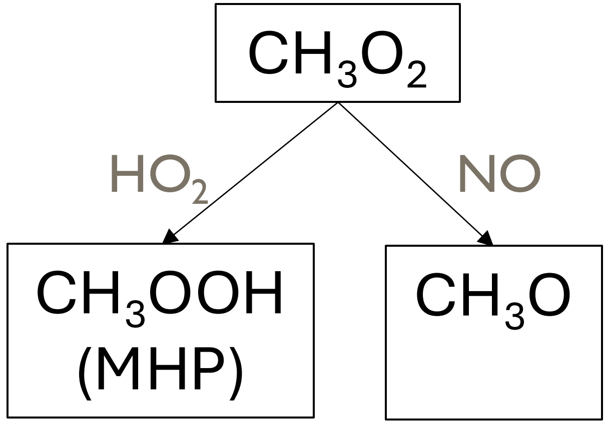
Investigating the variability of MHP and MD in the planetary boundary layer (PBL) using SMA profiles





LT: Local time, only used data with [H_2O mixing ratio] < 10^4 ppmv

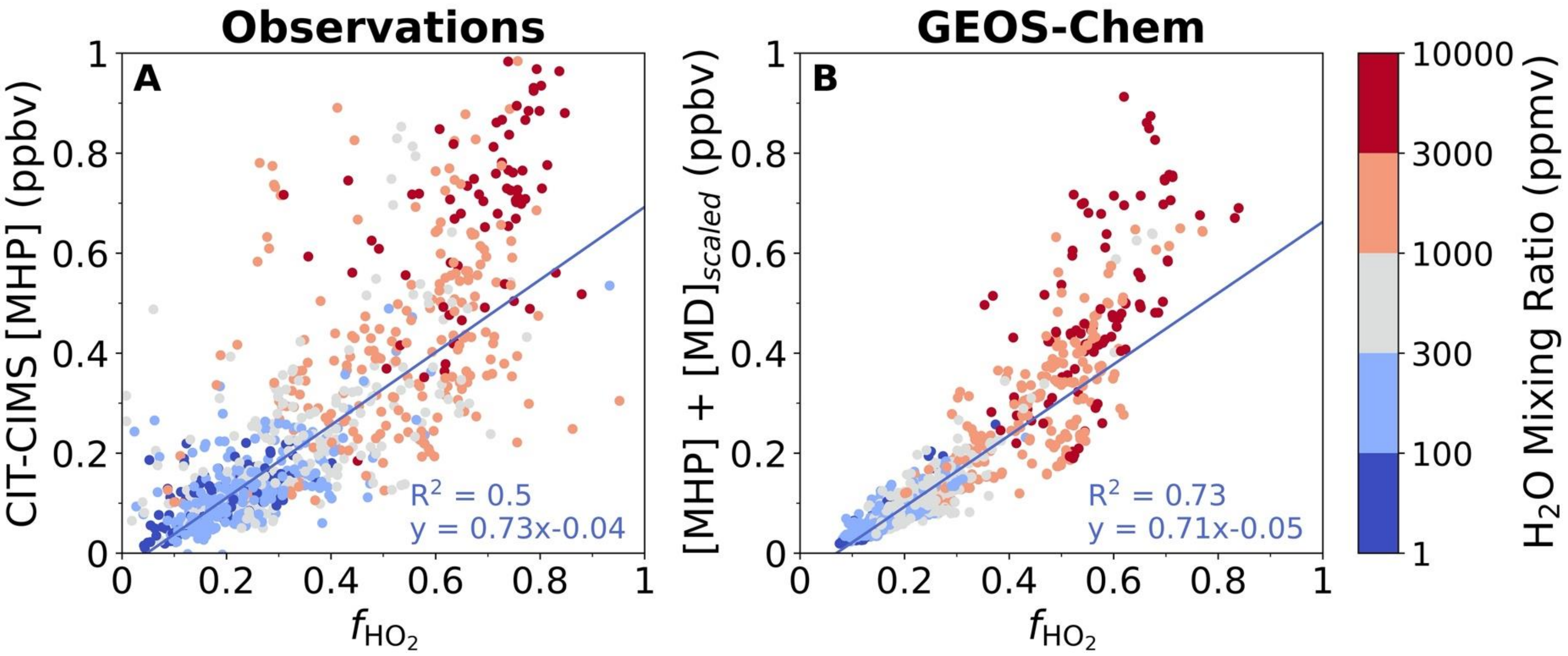
The free tropospheric data confirm our understanding of MHP chemistry & distinct oxidative pathways of VOCs in high- and low-NO regimes



$f_{HO_2} = 1$
Low-NO

$f_{HO_2} = 0$
High-NO

Data from altitude > 4 km



$$f_{HO_2} = \frac{k_{CH_3O_2+HO_2}[HO_2]}{k_{CH_3O_2+NO}[NO] + k_{CH_3O_2+HO_2}[HO_2]}$$

Implications of MD chemistry in GEOS-Chem

Formic acid budget	GEOS-Chem (Base)	GEOS-Chem (with MD chemistry)
Sources (Tg yr^{-1})		
Emissions	9.4	9.4
Photochemical	40.0	44.5
Total	49.4	53.9
Sinks (Tg yr^{-1})		
Deposition	37.5	40.5
Photochemical	10.7	12.1
Total	48.2	52.6
Burden (Tg)	0.48	0.54
Lifeime (days)	3.7	3.8

$$\text{MD} \xrightarrow{\text{OH}} \text{Formic acid}$$

Still underestimates formic acid compared to satellite-based estimates by a factor of 2-5

- The formic acid burden increases by 10% when MD chemistry is included
  - More studies on the sources/sinks of formic acid are needed
- The effects on other species are negligible

Takeaways

KORUS-AQ observations of methyl hydroperoxide in the free troposphere support the current understanding of high-NO and low-NO regimes for the oxidation of VOCs

The observations provide the first evidence of atmospheric methanediol production from the aqueous-phase processing of formaldehyde in clouds

Inclusion of methanediol in the GEOS-Chem model increases the global formic acid source by 10%

The authors acknowledge funding support from the NASA ACCDAM Program and the NSF GRFP.