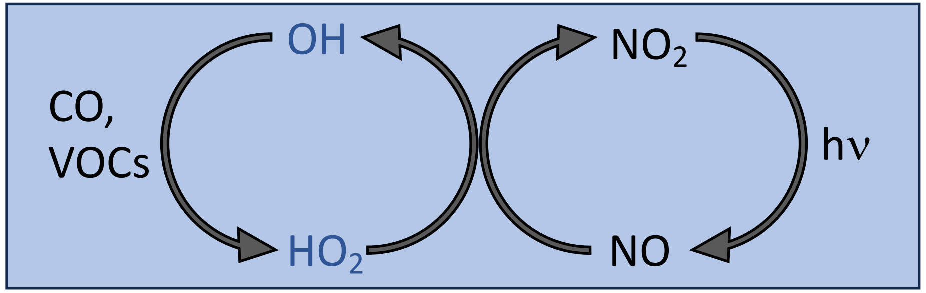
SO_2 and NO_x as secondary aerosol precursors: ACCLIP and SABRE

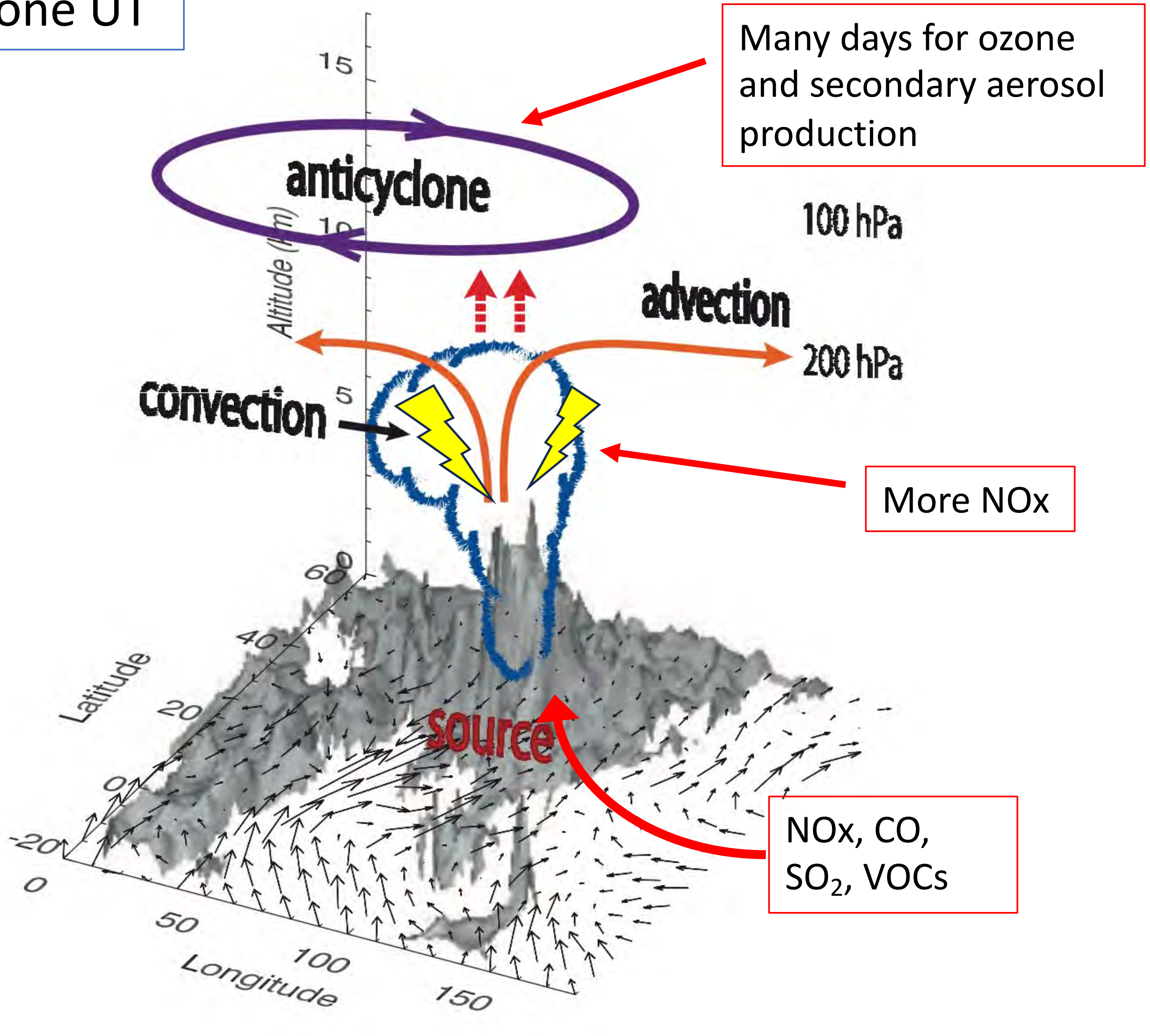
Andrew Rollins, Eleanor Waxman, Gordon Novak, Troy Thornberry, Ru-Shan Gao, Ren Smith, Glenn Wolfe, Elliott Atlas, Paul Bui, Jim Podolske, and the ACCLIP & SABRE Science Teams

Understanding photochemistry and secondary pollutant production in the ASM Anticyclone UT

- Inputs of hydrocarbons, SO_2, NOx, NH_3 allow for enhanced photochemical aerosol production in the UT.
- Convection and cloud formation mostly remove primary aerosols and some soluble gasses, while increasing NOx from lightning.
- In the UT anticyclone, photochemistry (OH) is greatly enhanced by NOx.



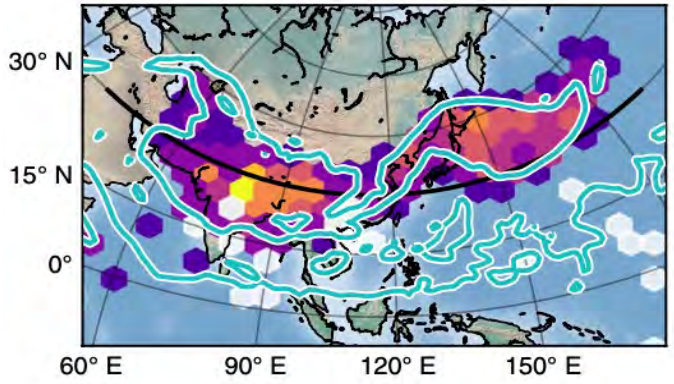
- What is the photochemical regime in the UT ASMA and sensitivity to changes in NO_x and other gasses?
- What is the relative importance of inorganic and organic aerosol precursors? What are the fates of secondary aerosols produced there?



Park et al., 2009

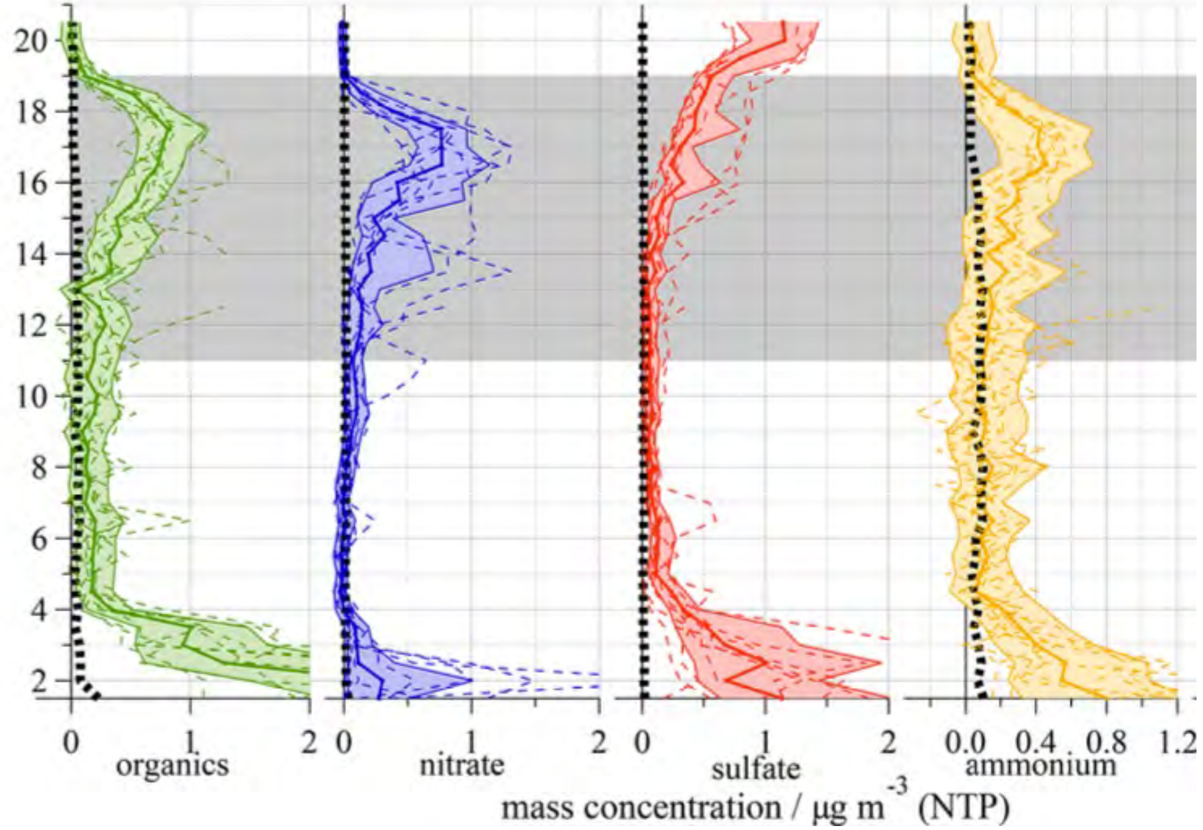
Aerosol composition measurements in the ASMA before ACCLIP

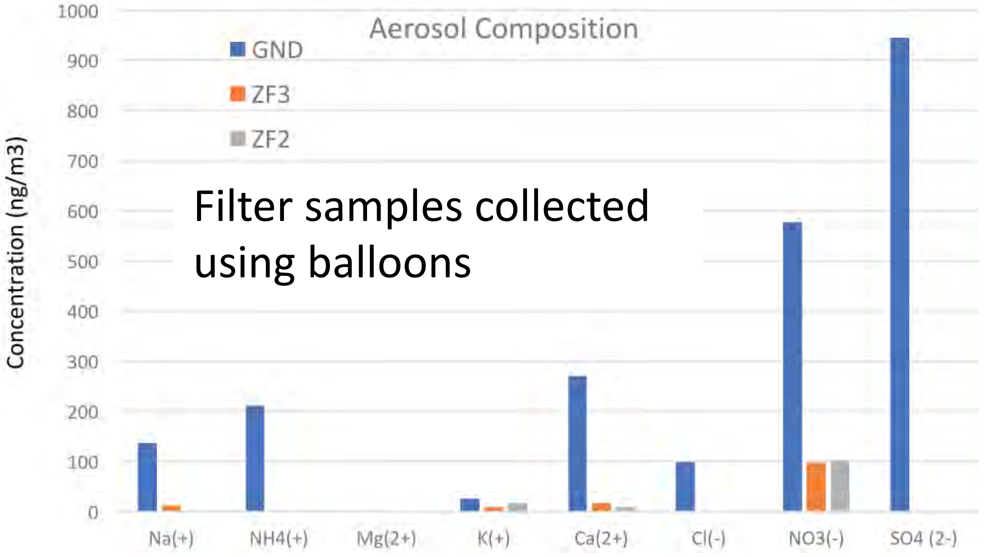
Remote sensing of ammonia and solid nitrate from airborne and satellite instruments.



Summary: There is more nitrate than was expected there, but sulfate and organics are also significant. Overall, the sampling of aerosol chemistry is limited.

In-situ composition measurements from Stratoclim

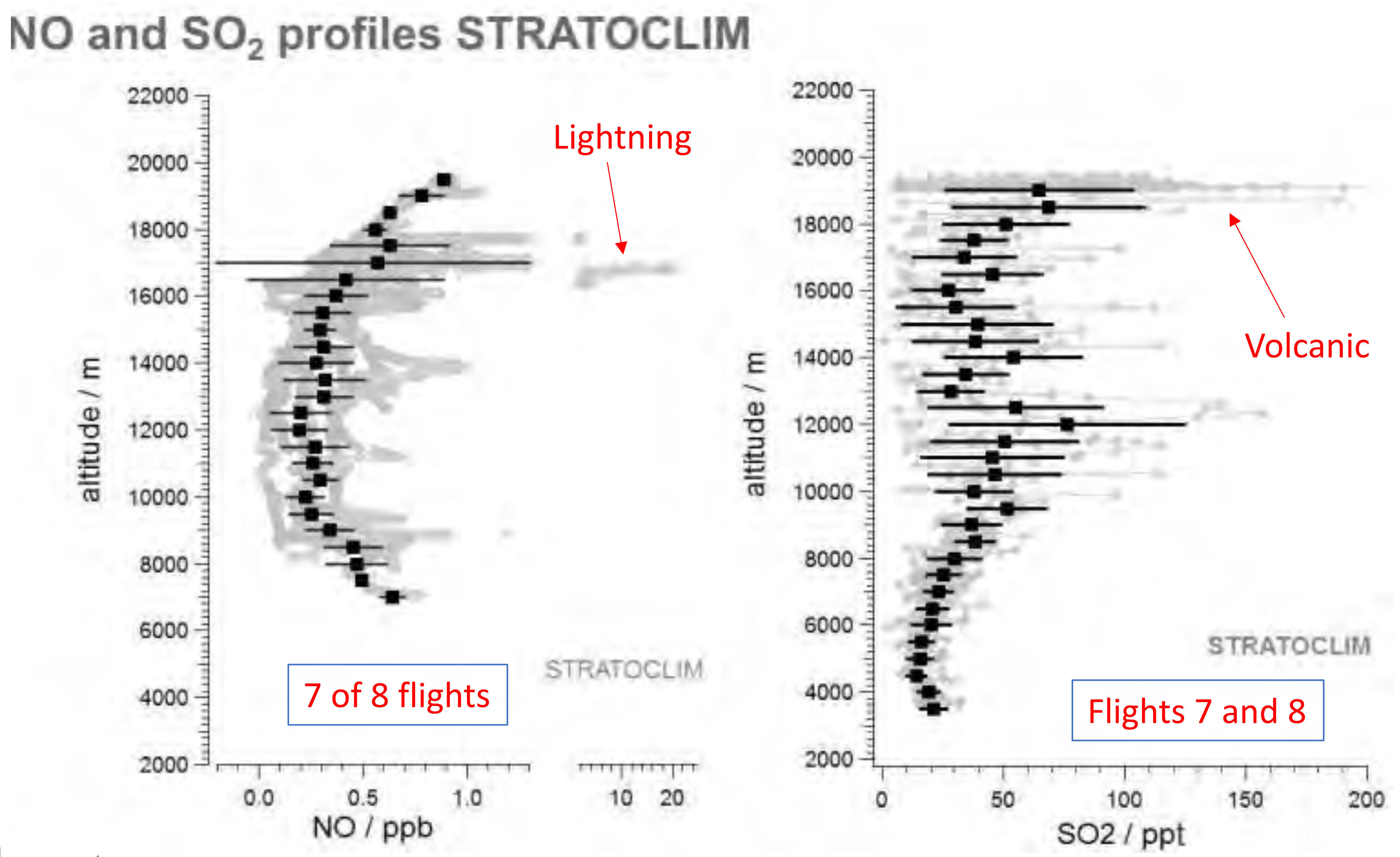


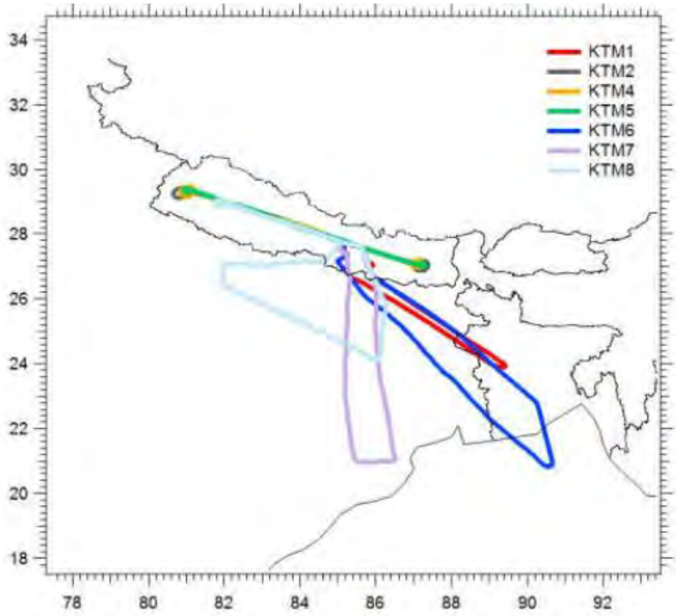


Filter samples collected using balloons

Vernier et al.;Hoepfner et al.,2019; Appel et al., 2022

StratoClim observations of SO_2 and NO





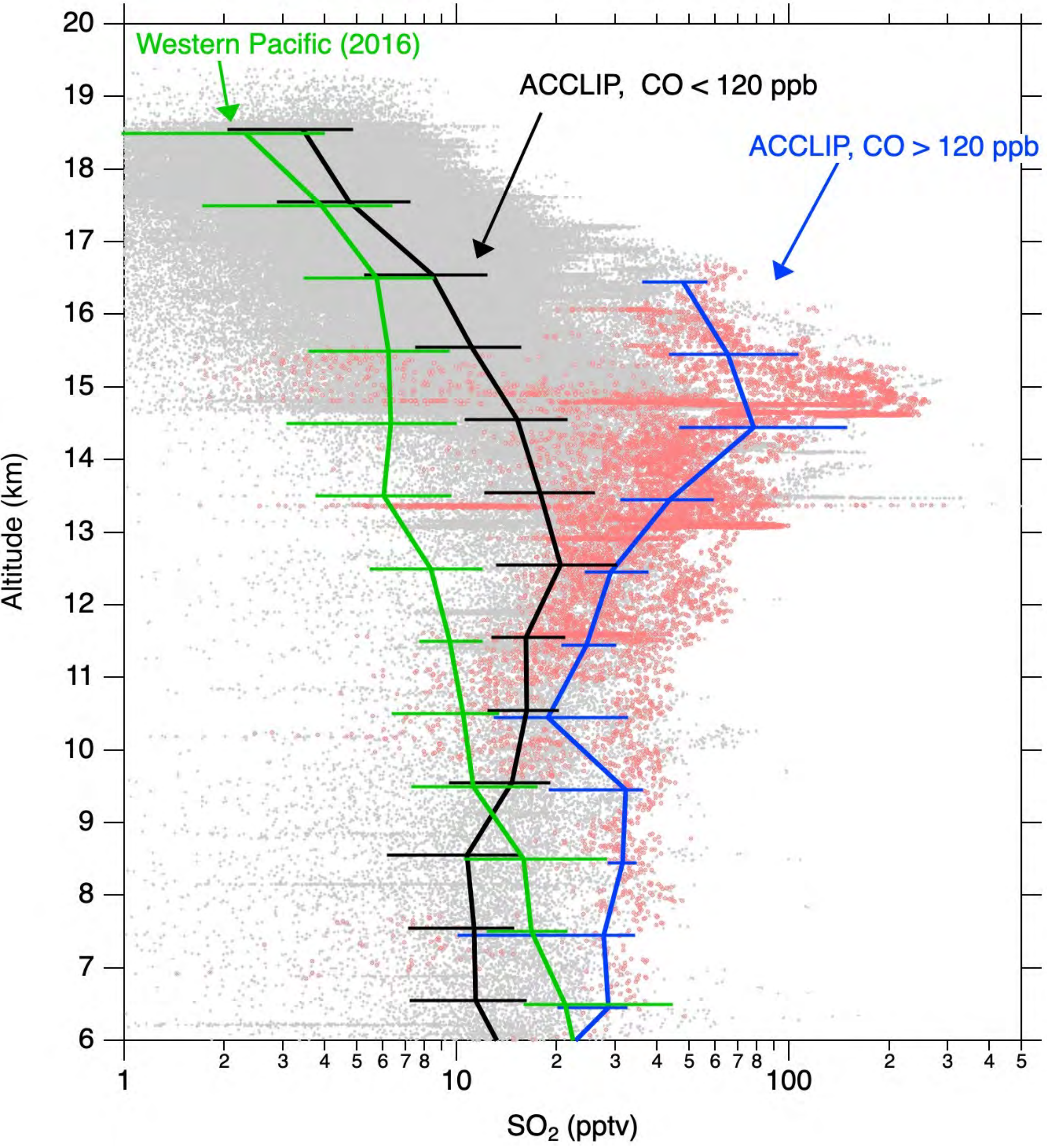
StratoClim

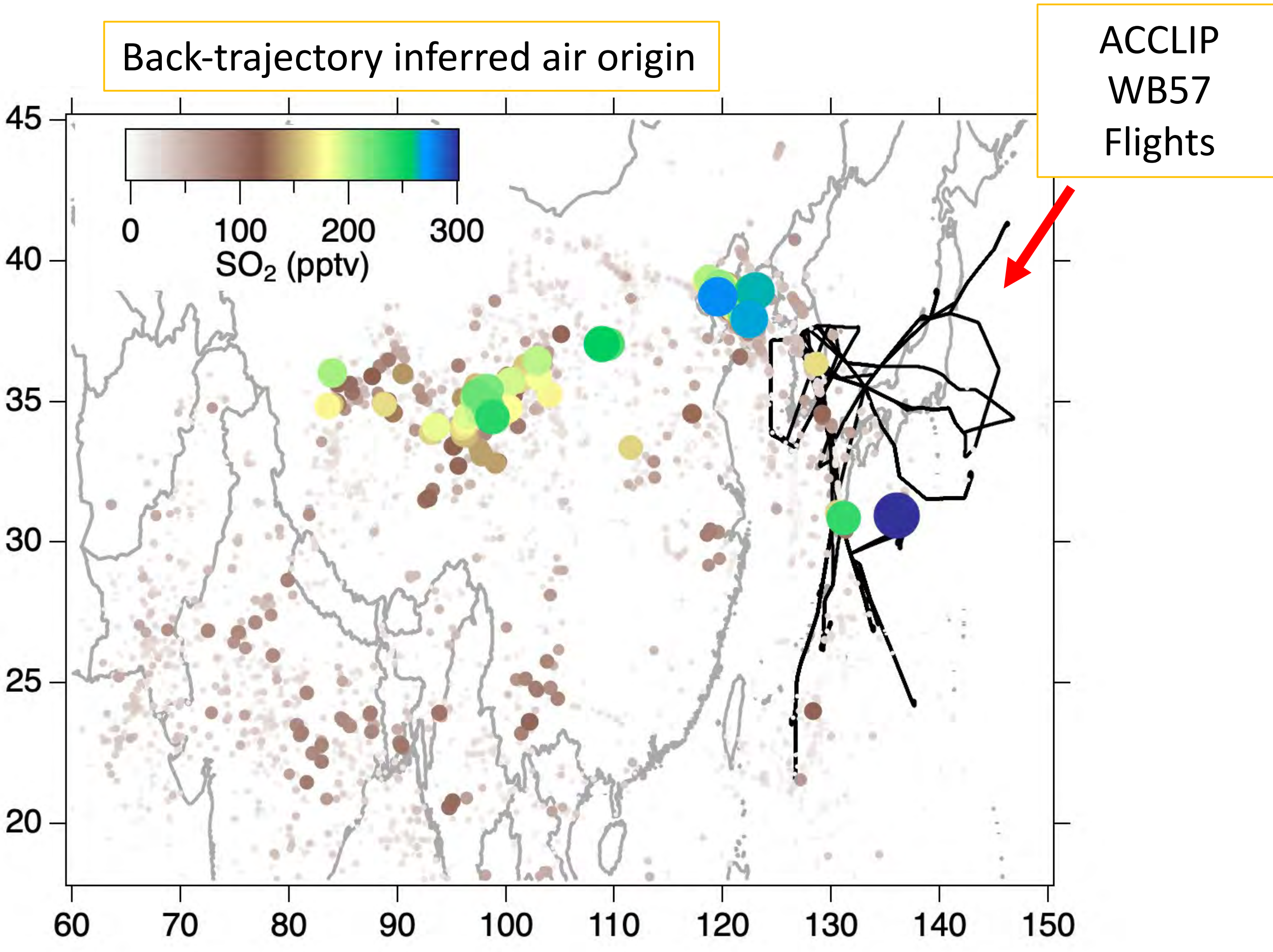
(Schlager, Stratmann, et al., DLR)

DLR

High SO_2 is observed in the outflow and core of the ASMA
Enhanced SO_2 not observed in lower stratosphere

100 ppt SO2 -> ~0.4 µg / sm^3 SO_4





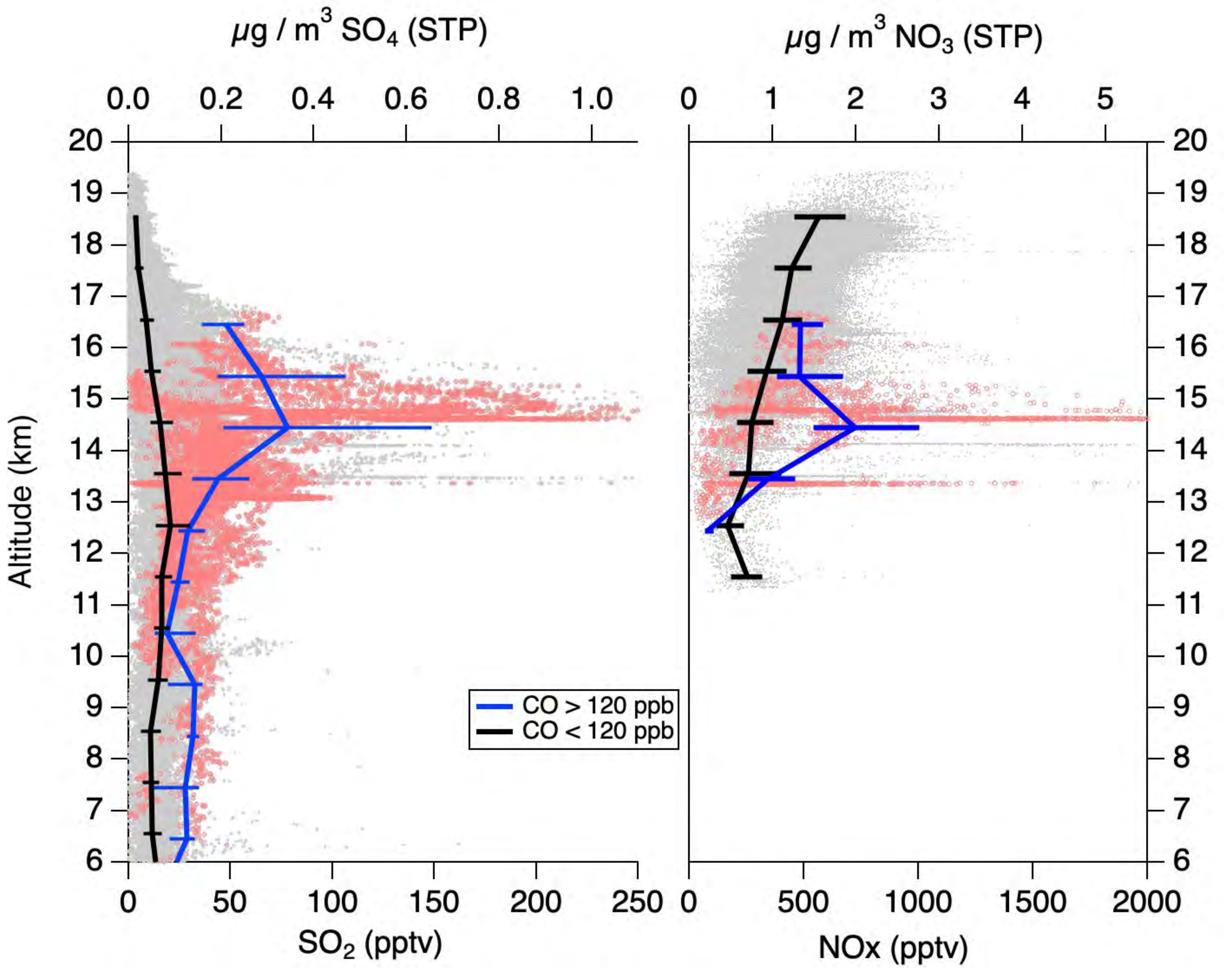
NOx and SO_2 as aerosol precursors

$NO_2 + OH \rightarrow HNO_3$

$HNO_3 + NH_3 \rightarrow NH_4NO_3$ (aerosol)

$SO_2 + OH \rightarrow \rightarrow H_2SO_4$ (condenses rapidly)

- k_{NO2+OH} / k_{SO2+OH} ~ 10, and NOx is mostly NO in the UT, therefore, HNO_3 will form much more quickly than H_2SO_4.
- SO_2 oxidation is much slower in the UT than in the PBL due to lack of aqueous aerosol oxidation.
- Nitrate aerosol formation may be limited by availability of ammonia rather than nitric acid.



Understanding photochemistry in the ASM Anticyclone UT

Calculate HO_x and ozone tendency using detailed chemical box model (F0AM)

- Run model to convergence at aircraft observation.
- Approach validated using HO_x observations from NASA ATom campaign.

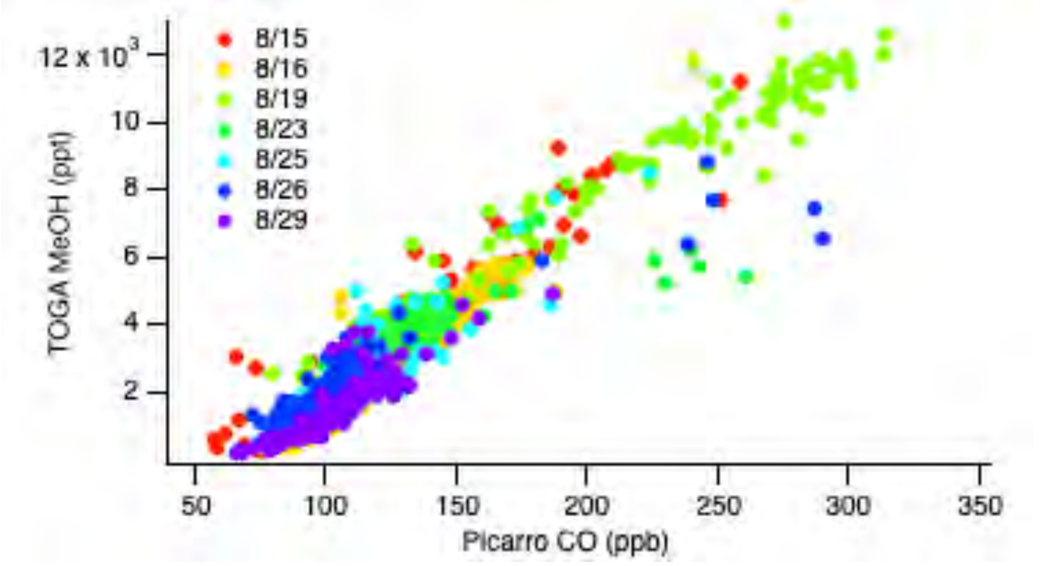
Eleanor Waxman

Ozone tendency:

- $P(O_3) = k_{NO+HO2}[NO][HO_2] + k_{NO+RO2}[NO][RO_2]$
- $L(O_3) = k_{O3+HO2}[O_3][HO_2] + k_{O3+OH}[O_3][OH] + \alpha_{O1D} j_{O1D}[O_3]$

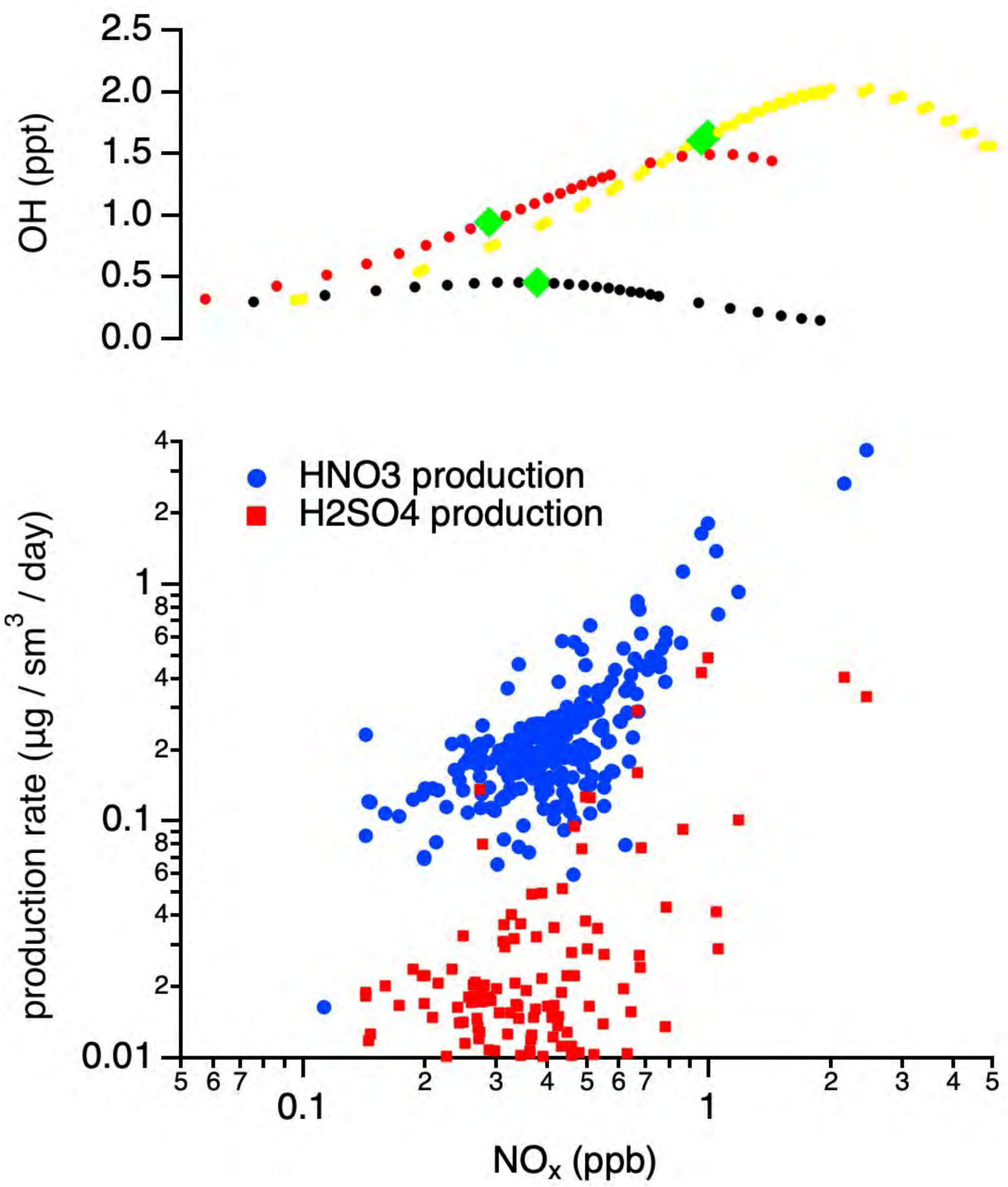
Chemical Observations used for F0AM 0-D box modeling.

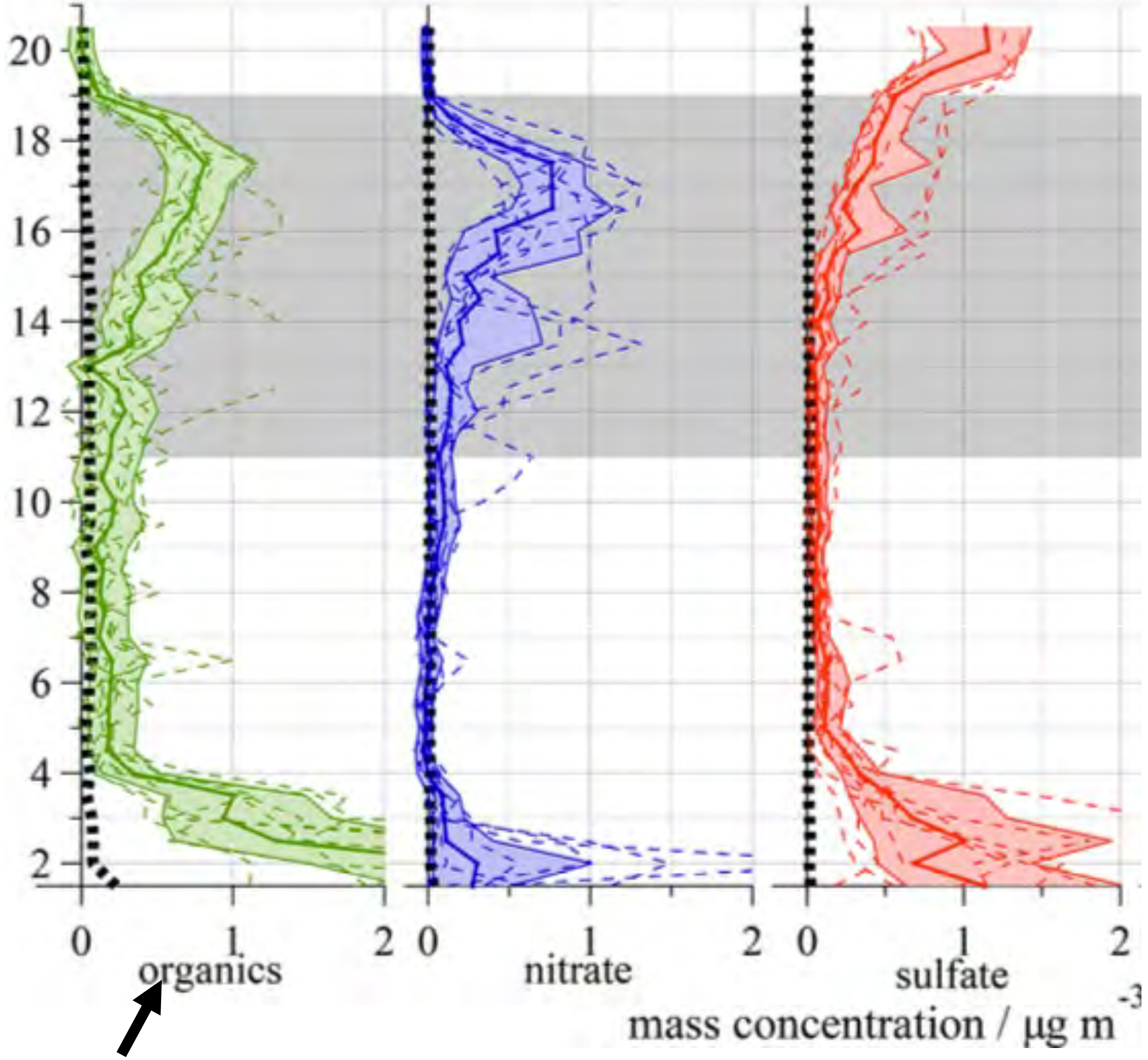
- NO_x, O_3, HCHO, H_2O, CO (NASA WB-57)
- VOCs from WAS (WB-57)
- Methanol, ethanol, acetone: TOGA vs CO correlation (G-V)



What are production rates of nitrate and sulfate?

$NO_2 + OH \rightarrow HNO_3$ ~ **0.30 ug** / sm^3 / day
$SO_2 + OH \rightarrow H_2SO_4$ ~ **0.02 ug** / sm^3 / day



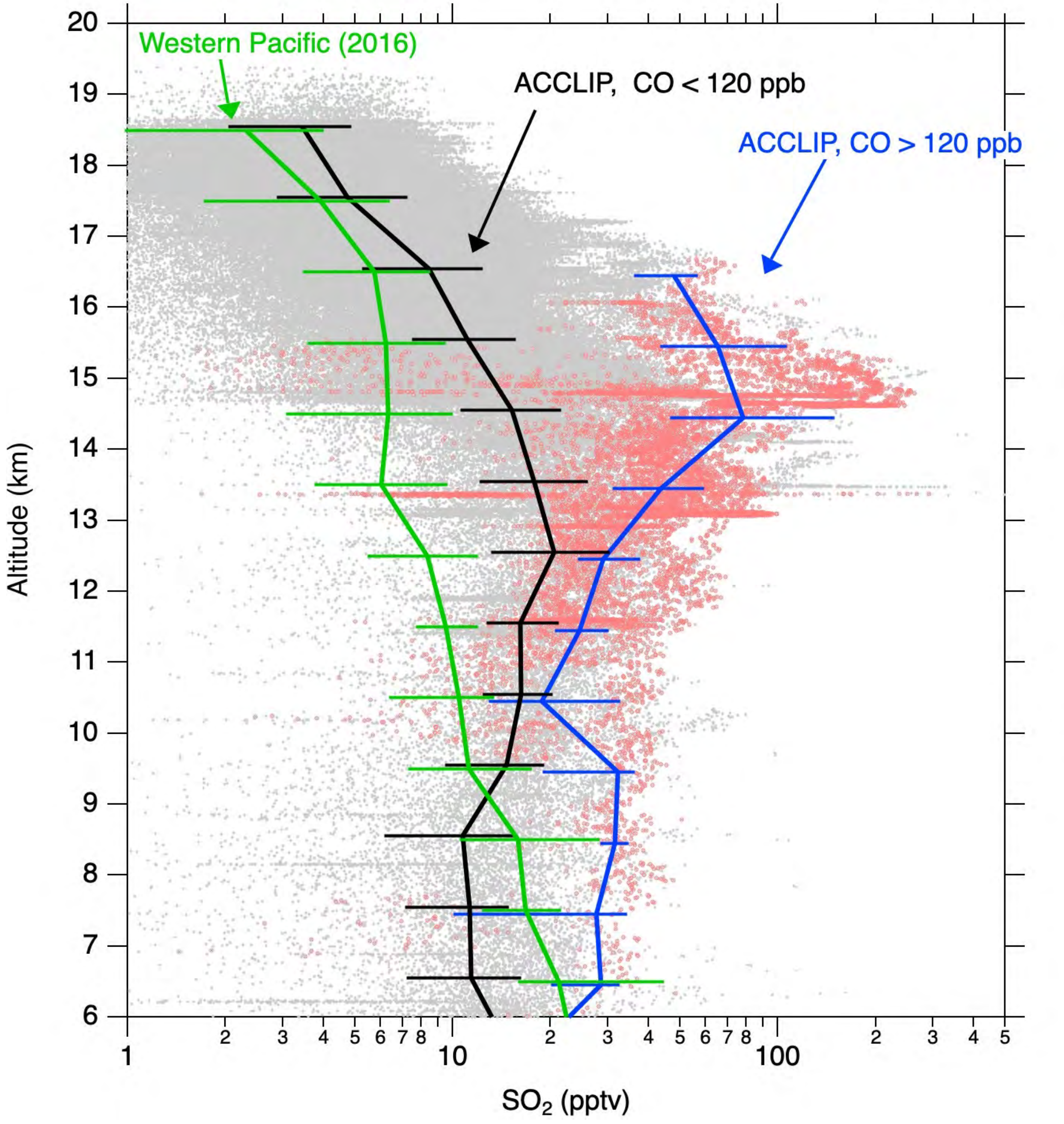


STRATOCLIM aerosol results

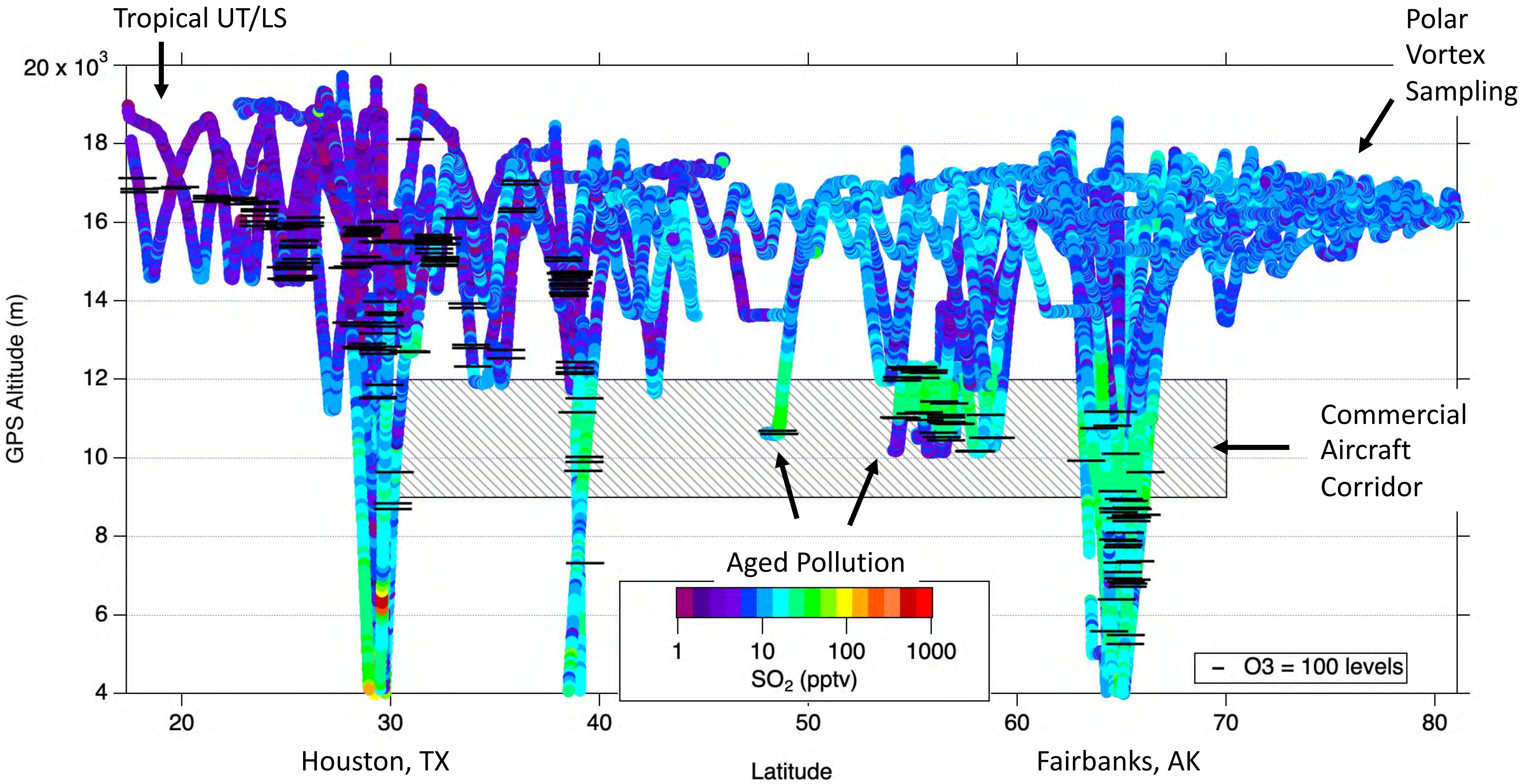
Appel et al., 2022

ACCLIP Summary

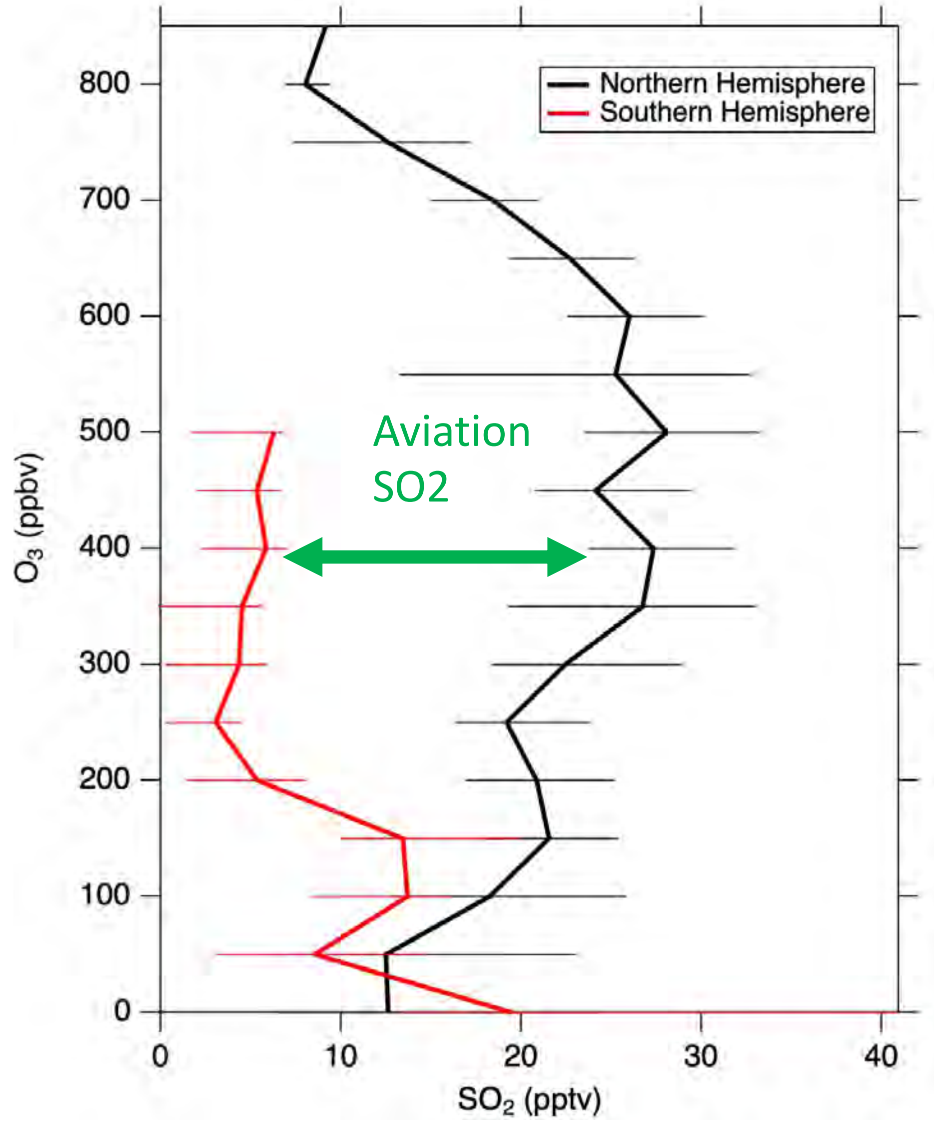
- SO_2 concentrations measured during ACCLIP are highest we have seen in the UT. Impact on LS is not apparent in local SO_2 measurements.
- Observed values of SO_2 in the ASMA is consistent the observations of sulfate on the order of 0.5 μg / m^3 (STP) which is 1/4-1/3 of aerosol mass in the ATAL.
- NOx enhancements are very high and much larger than SO_2. NOx abundance is more than sufficient to produce the observed nitrate, implying ammonia is the limiting factor for nitrate aerosol formation.
- Production of nitrate in the ASMA core is calculated to be on order of 0.3 µg / sm^3 / day, while sulfate production is ~15x slower. This seems to be consistent with the relative concentrations of nitrate and sulfate and observed and shapes of those vertical profiles from STRATOCLIM.

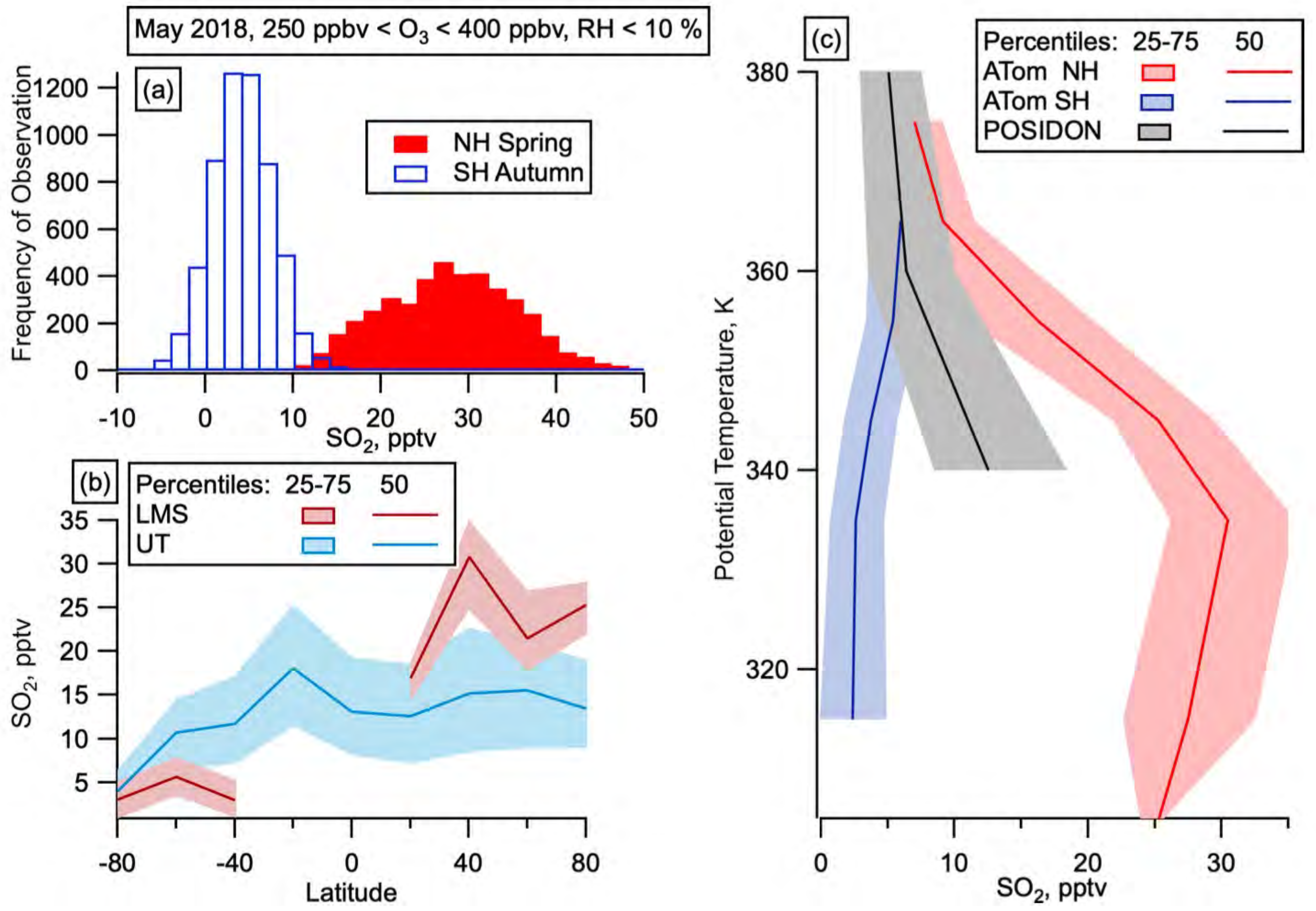


SABRE 2023 SO_2 cross-section



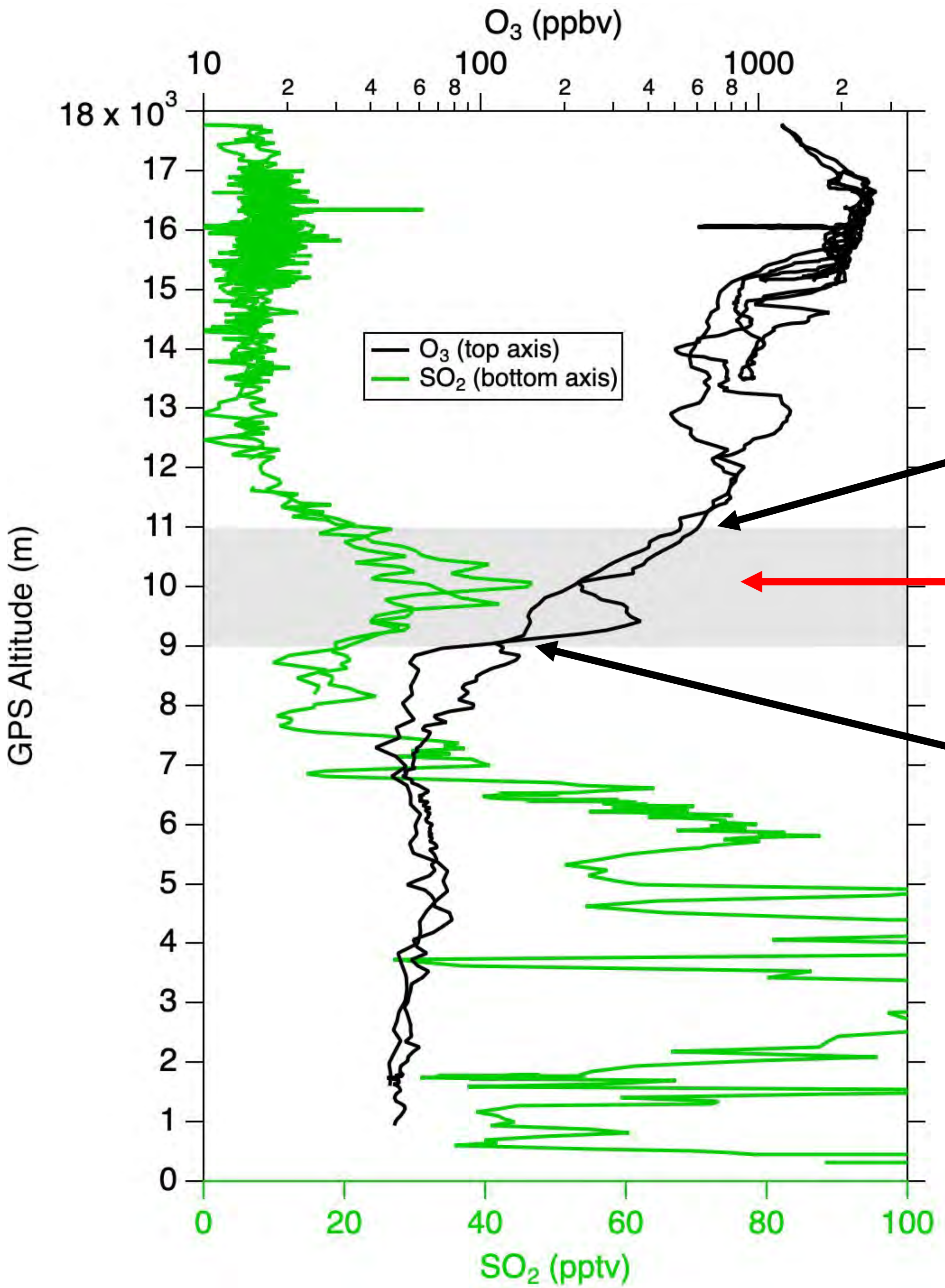
Northern Lower Stratosphere SO_2 enhancement from ATom





Williamson et al., ACP 2021

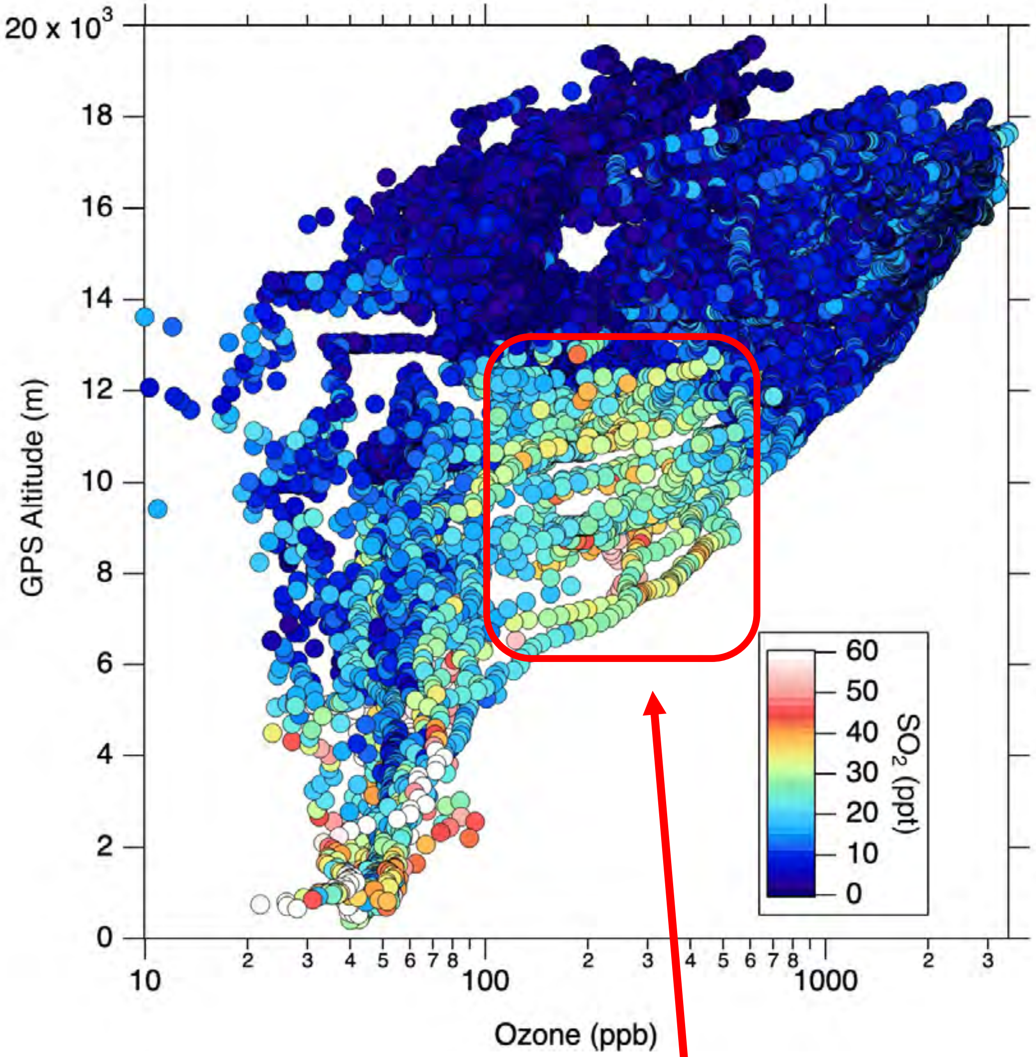
Lower Stratosphere SO_2 layer in air traffic corridor also observed during SABRE



3/11/2023 flight from Fairbanks

- Most profiles in and out of Fairbanks, as well as profiling at lower latitudes frequently revealed an enhanced SO_2 layer there.
- Unusually high-altitude pollution layer above AK somewhat obscured the LS layer.

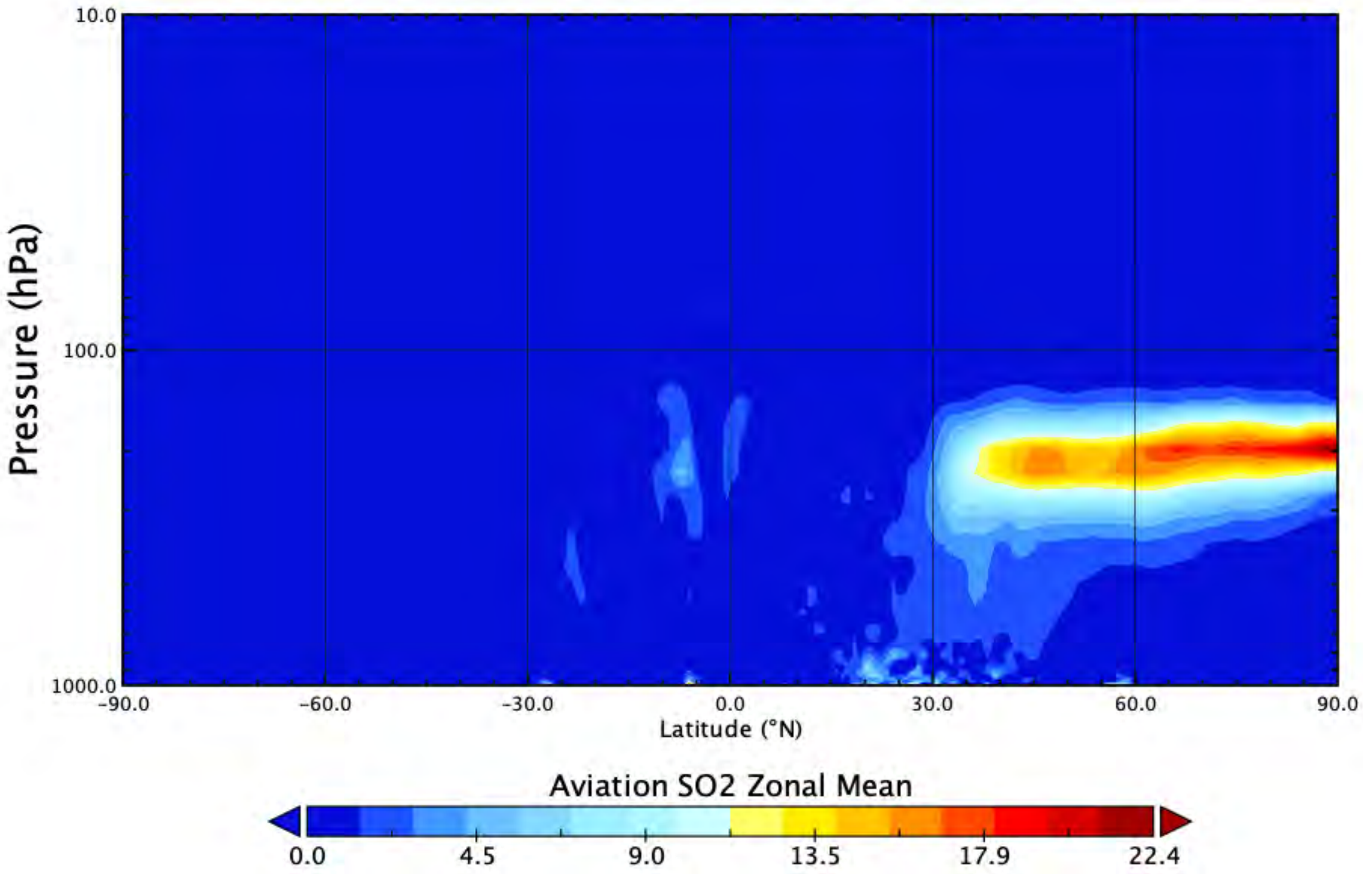
All SABRE Data (TX and AK)



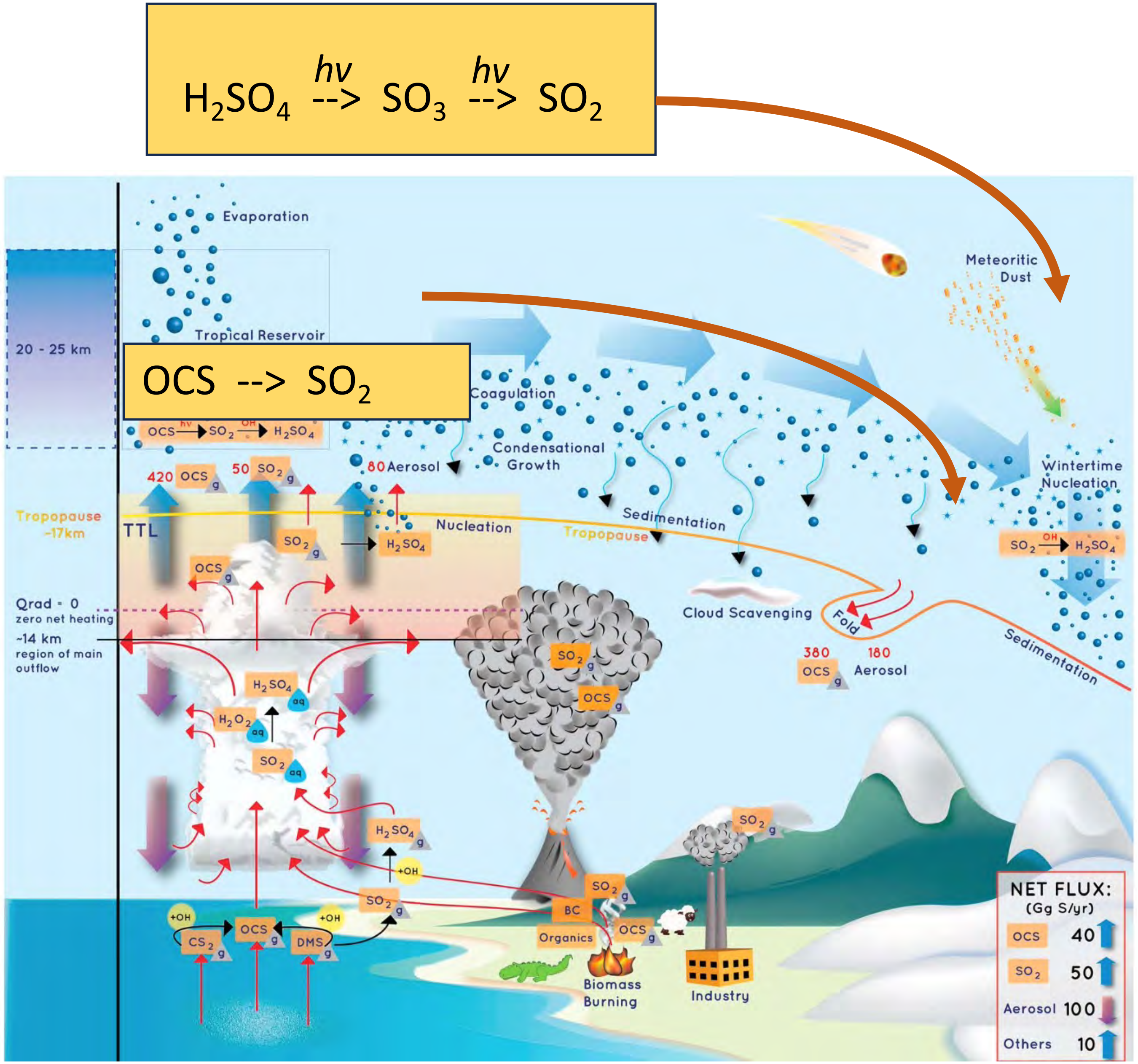
Persistence of SO2 layer

Testing aviation SO2 in CESM2: Run with Aviation SO2 emissions – Run with Aviation emissions off ~ 20 ppt zonal enhancement.

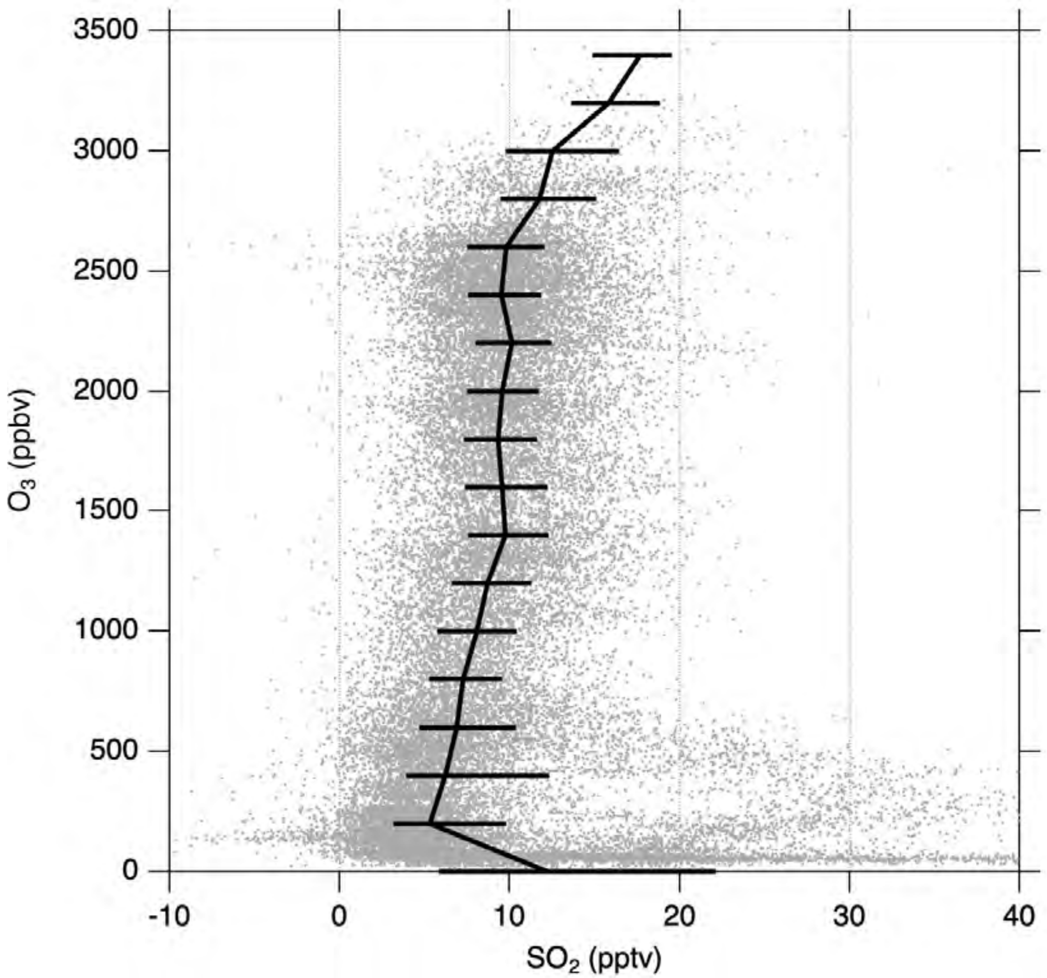
CESM2 run – 1/31/2023



Subtle increase in SO_2 observed in aged air



- SO_2 appears to increase slightly in more aged air.
- This could be explained by sulfuric acid photolysis at > 30 km.
- May contribute to aerosol nucleation in high latitude stratosphere.



SABRE

- SO2 observations show a persistent layer of enhancement in LS the air-traffic corridor, consistent with observations from ATom. SO2 in that region is correlated to nucleation mode aerosol at times.
  - ➢ Can SO2 there explain all aerosol enhancements here or are other species required?

- SO2 appears to increase modestly with age of air, implying a photochemical source of SO_2 from the stratosphere/mesosphere. Such a source has been previously hypothesized through observations suggesting nucleation in the arctic spring, but not directly verified.
  - ➢ TBD on how consistent the magnitude of observed SO_2 is with theory.

- NOy: clear signature of denitrification in the vortex. Preliminary analysis of NOy vs. O3 and NOy vs. N2O show similar reltionships to prior publications (e.g. Fahey, Murphy et al.)
  - ➢ Can we detect changes in NOy vs N2O since 20 years ago or understand physics of denitrification?