OCS Observations at the UTLS during ACCLIP: Highlighting the uncertainty of anthropogenic emissions on the stratospheric sulfur budget

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Carbonyl Sulfide

OCS or COS

- Long Lifetime
  >1 year in Free Troposphere
  ~50 years in Stratosphere
- Most abundant Sulfur species in stratosphere (Usually)
- Fairly uniform global free troposphere MR ~500PPT
- Low water solubility, effective vertical transport in large convective systems
- Direct Radiative Forcing Effect (Longwave Absorption)
- Indirect Radiative Forcing Effect (Sulfate Aerosol Formation)

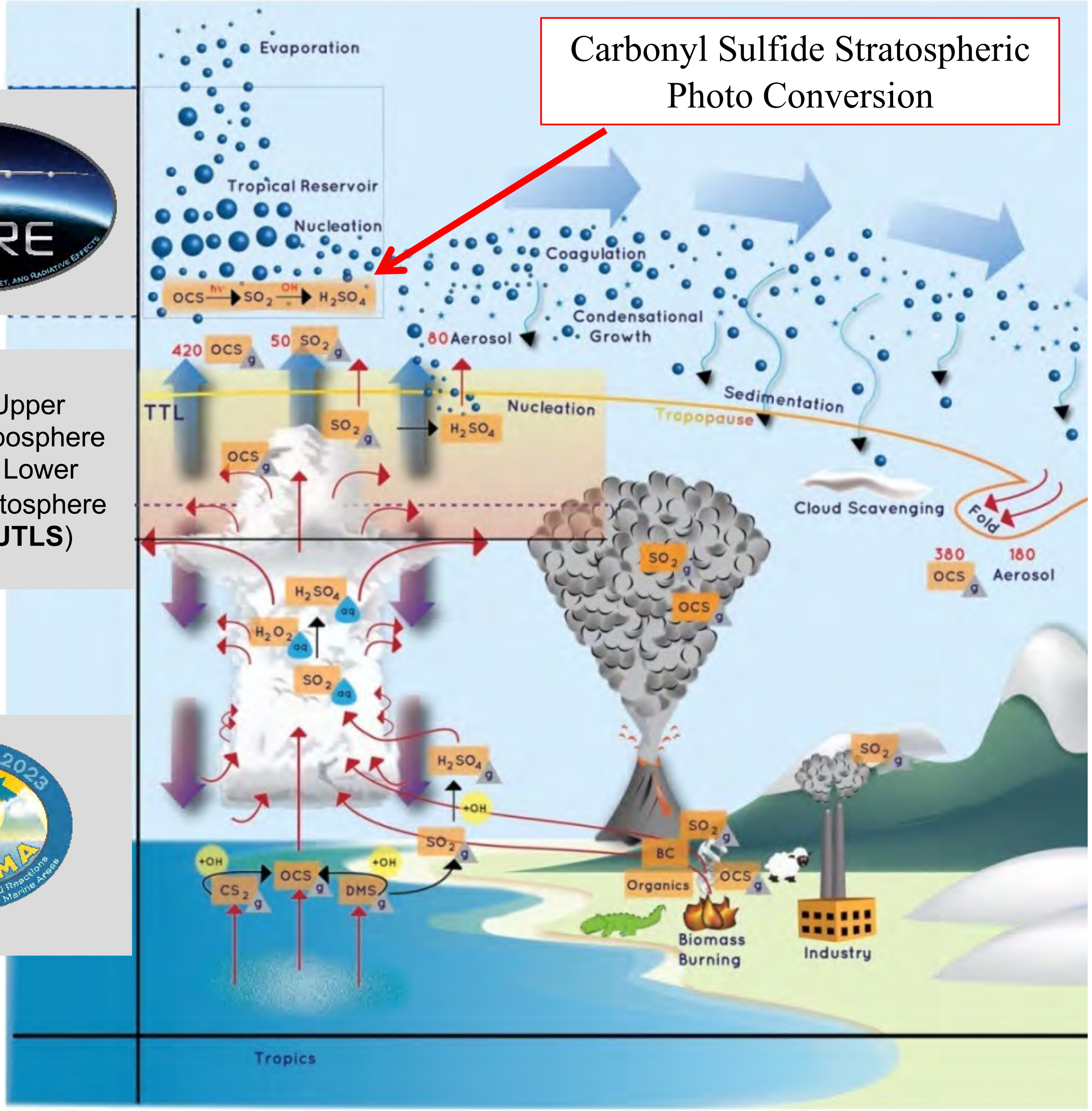
Sources:

- **Primary:** Ocean Surface
- **Secondary:** Biomass Burning
- **Poorly Constrained Anthropogenic Sulfur emissions:** Industrial CS_2, Rayon Production, Coal Combustion, etc.

Sinks:

- **Boundary Layer:** Plant Uptake (photosynthesis proxy)
- **Free Troposphere:** No significant removal mechanism
- **Stratosphere:** Photo Conversion Pathway to Sulfuric Acid/Sulfate Aerosol.

Upper Troposphere & Lower Stratosphere (**UTLS**)



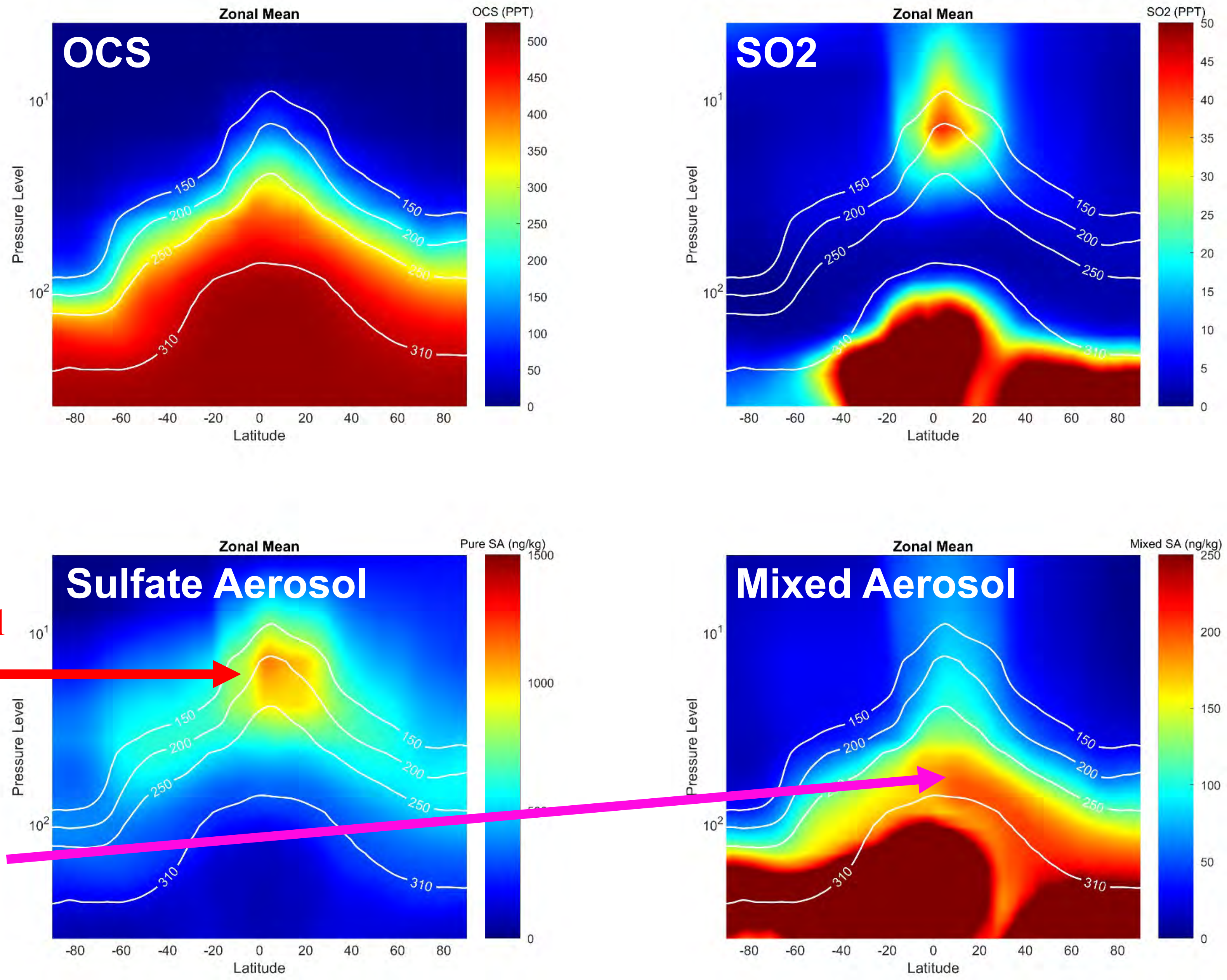
Kremser, Stefanie, et al. "Stratospheric aerosol—Observations, processes, and impact on climate." *Reviews of Geophysics* 54.2 (2016): 278-335.

OCS to Sulfate Conversion: Volcanically Quiescent Period

- Most atmospheric models demonstrate a consistent trend in OCS photolysis in the Tropical Pipe (20S-20N), with a small region of intermediary gas phase SO2 Produced above the equator at ~30km
- Stratospheric SO2 volcanic injections 2018-Present significantly complicate the interpretation of sulfate aerosol formation in the ACCLIP/SABRE period

- Sulfate Aerosol formation in the Tropical pipe is dominated by OCS depletion, Peak Sulfate ~ 1500ng/kg (1PPT OCS ~1ng/kg Sulfur)
- Lower Stratosphere Mixed Aerosol is dominated by Troposphere sourced SO2

CESM Run: 20041101 - 20041201

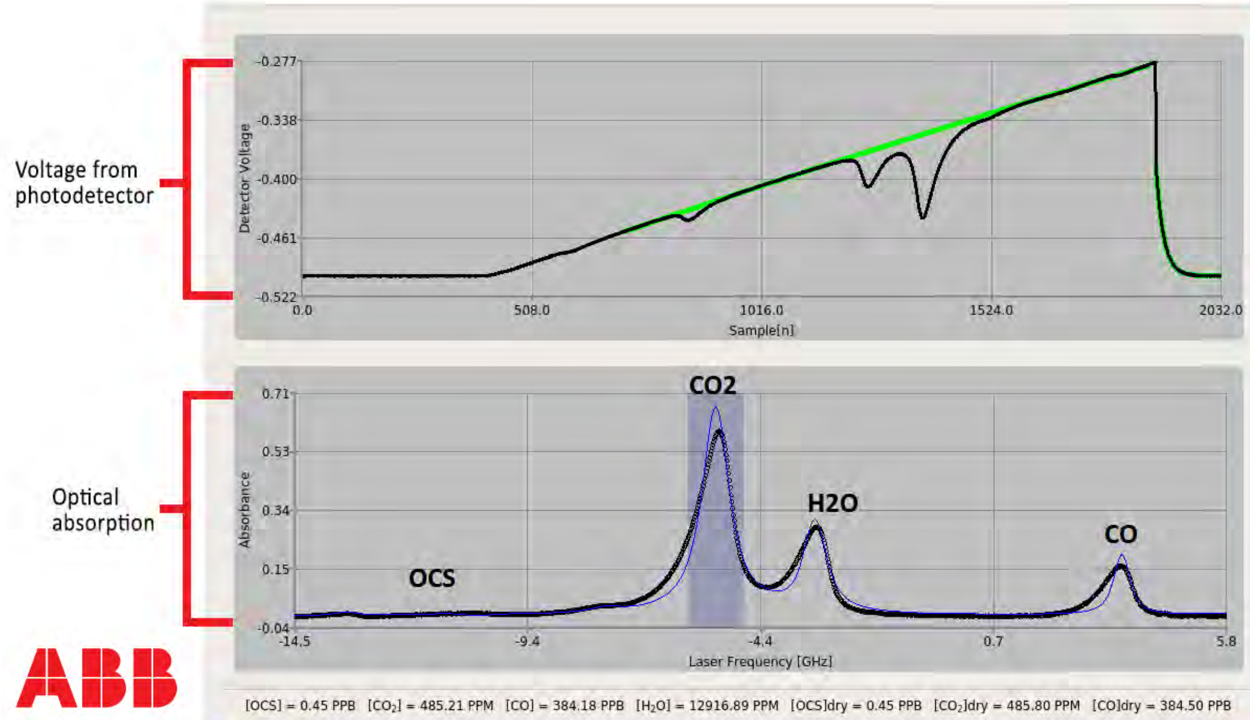


Airborne Spectrometer

Airborne **C**arbonic **O**xides and **S**ulfide Spectrometer (**ACOS**)

Sampled Species:

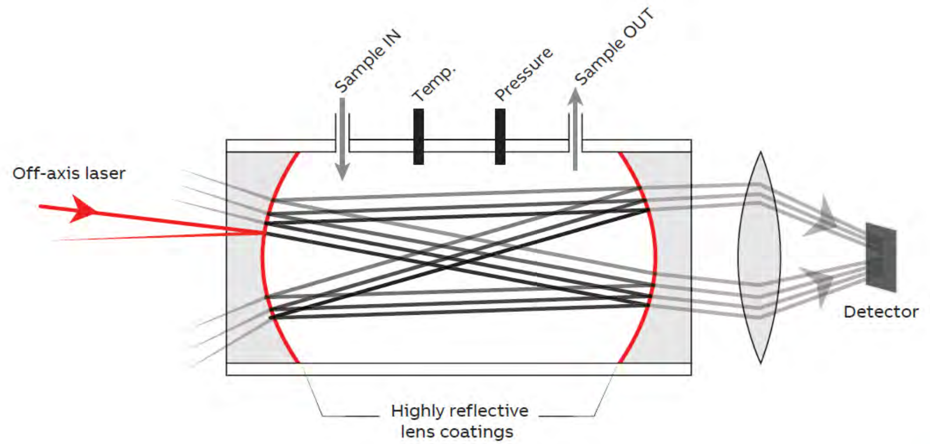
OCS, CO_2, H_2O, **CO**



- ICOS based multi-pass spectrometer
- Scan range 2050-2051cm^{-1}
- Data Archived at 1Hz
- CO Precision (1σ) ~5PPB
- OCS Precision (1σ) ~50PPT

LGR-ICOS Technology

OA-ICOS (Off-Axis Integrated Cavity Output Spectroscopy)



ABB

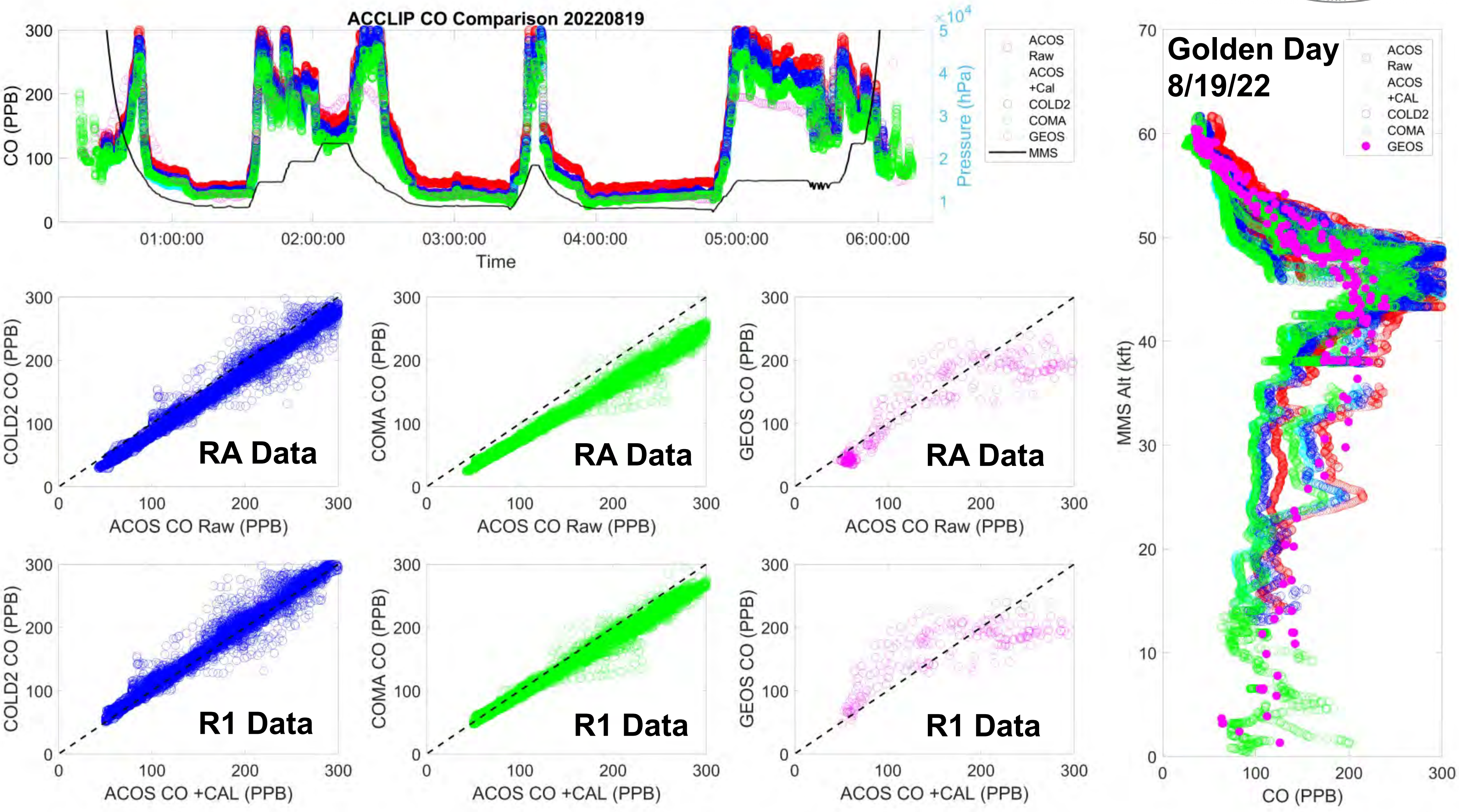
NOAA CHEMICAL SCIENCES LABORATORY

ACCLIP CO Inter-comparison

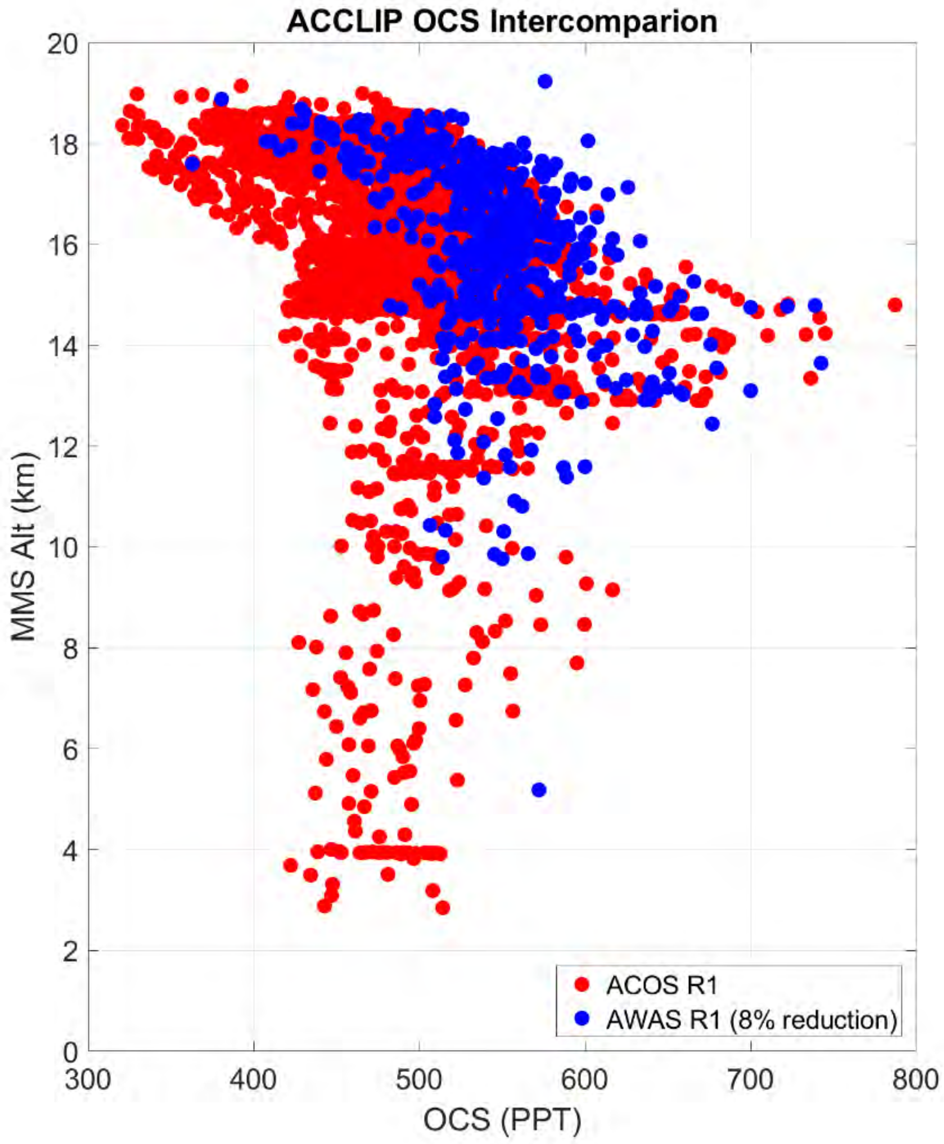
WB57 Simultaneous CO measurements during ACCLIP:

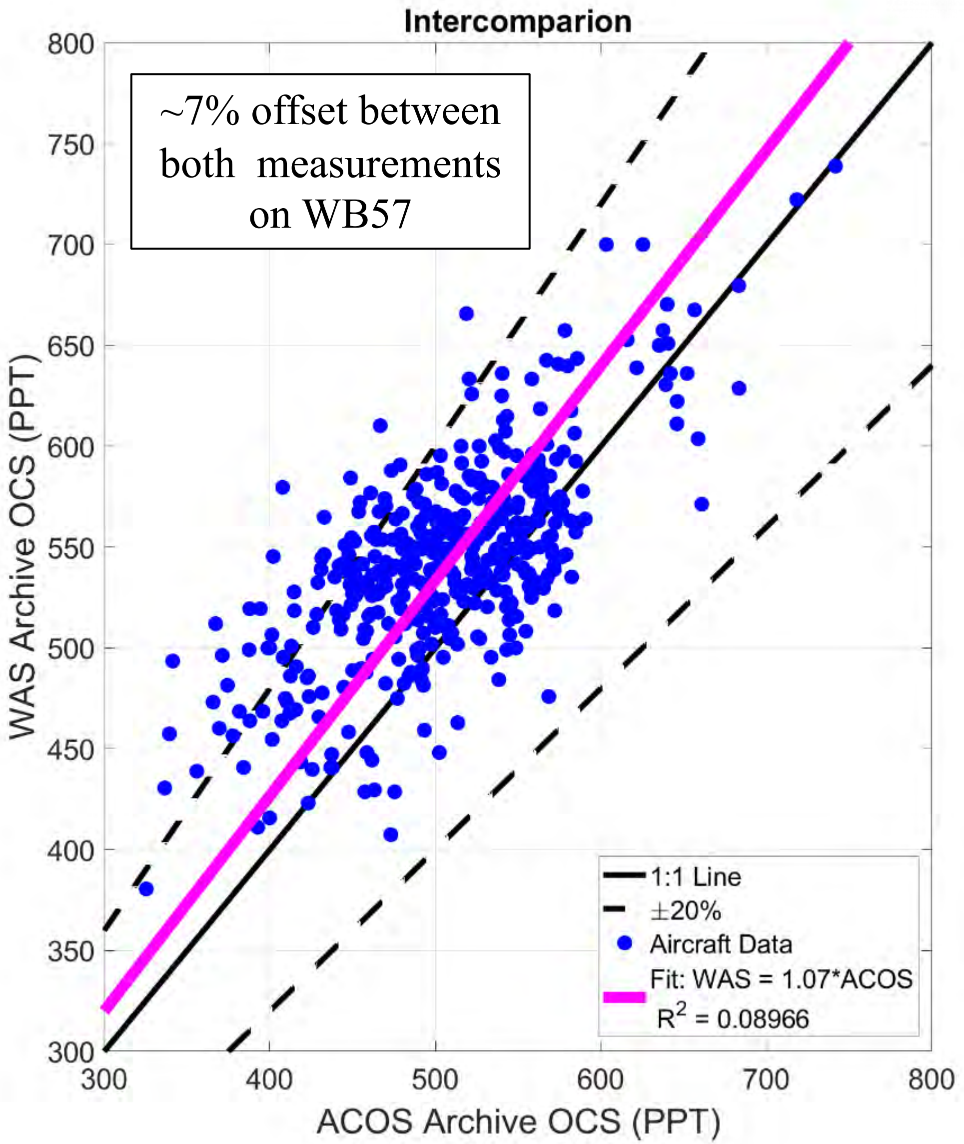
1. ACOS
2. COMA
3. COLD2

- Excellent Temporal Correlation between all three instruments (>0.9)
- ACOS ACCLIP Data Time Synced to COLD2
- Good agreement with GEOS model on most days (8/19 is a bad example)



WB57 OCS Inter-comparison (ACOS & AWAS)



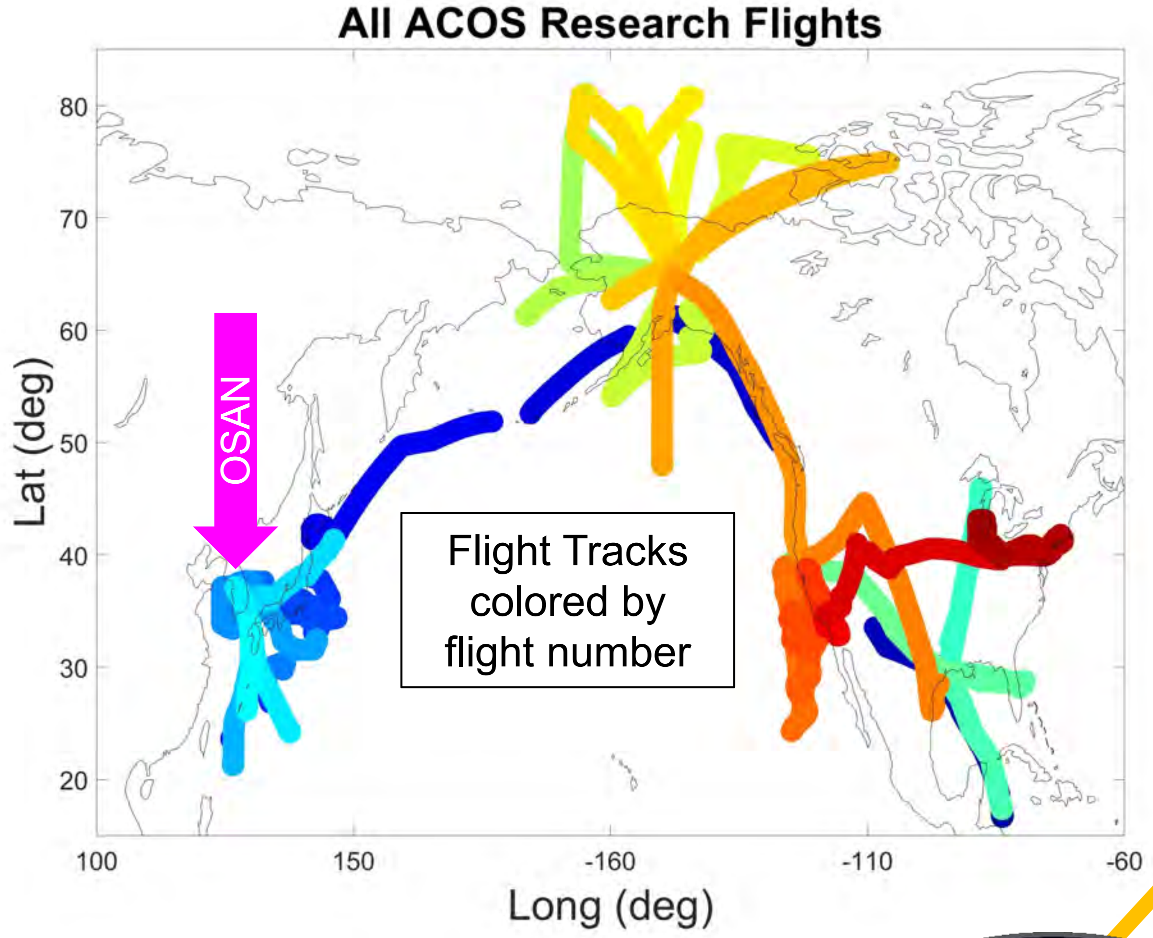


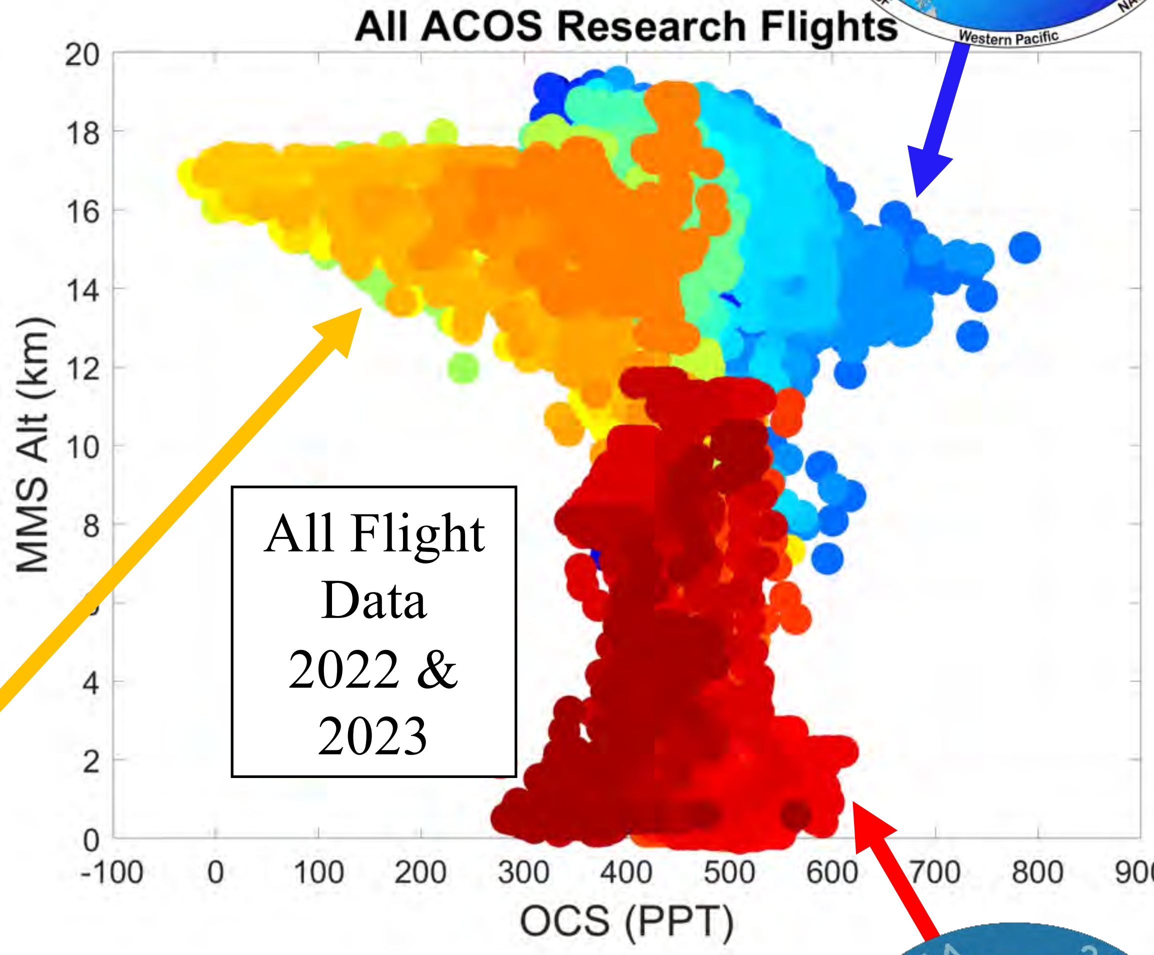
ACOS In-Situ OCS Measurements

54 Research Flights

ACCLIP (WB57):

- OCS enhancement in Upper Troposphere from Anthropogenic Emissions?





SABRE (WB57):

- Depletion of OCS in the stratosphere

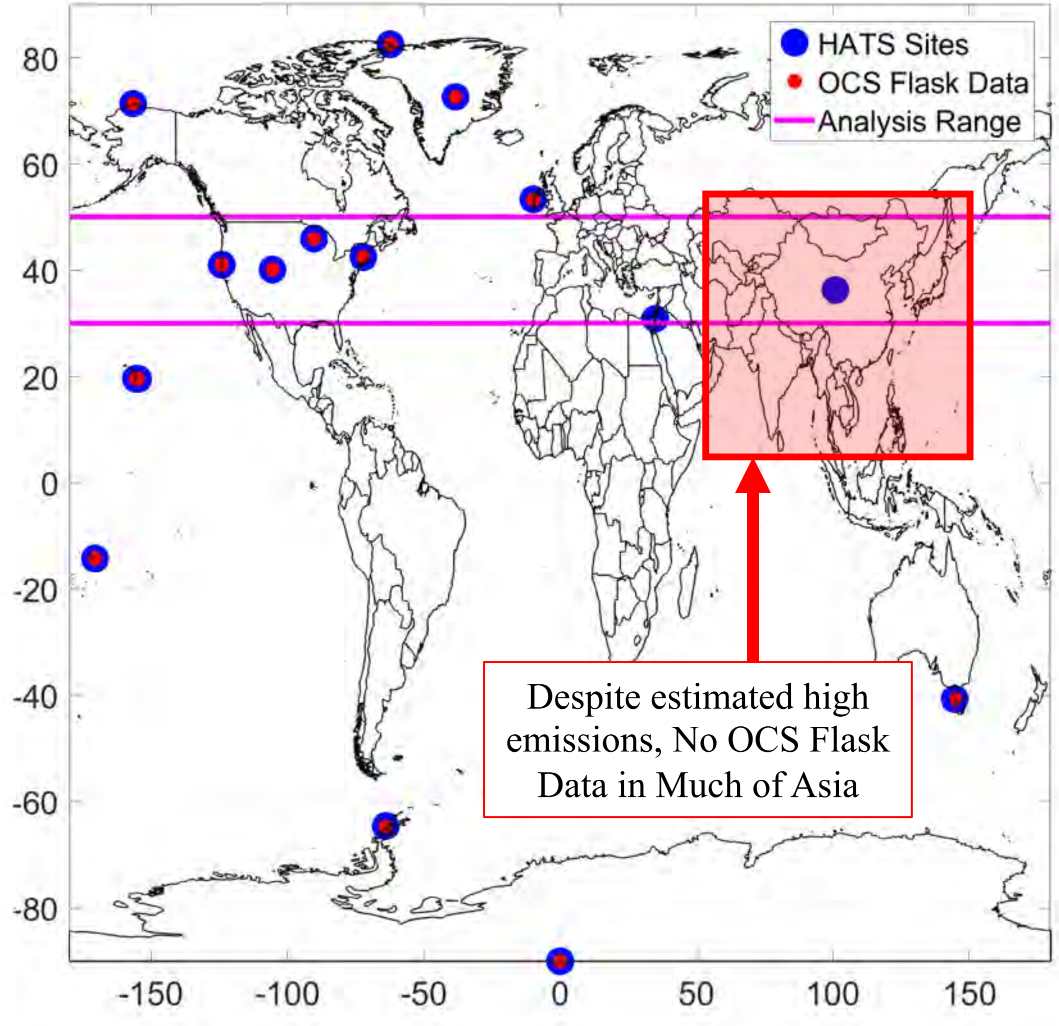
AEROMMA (DC8):

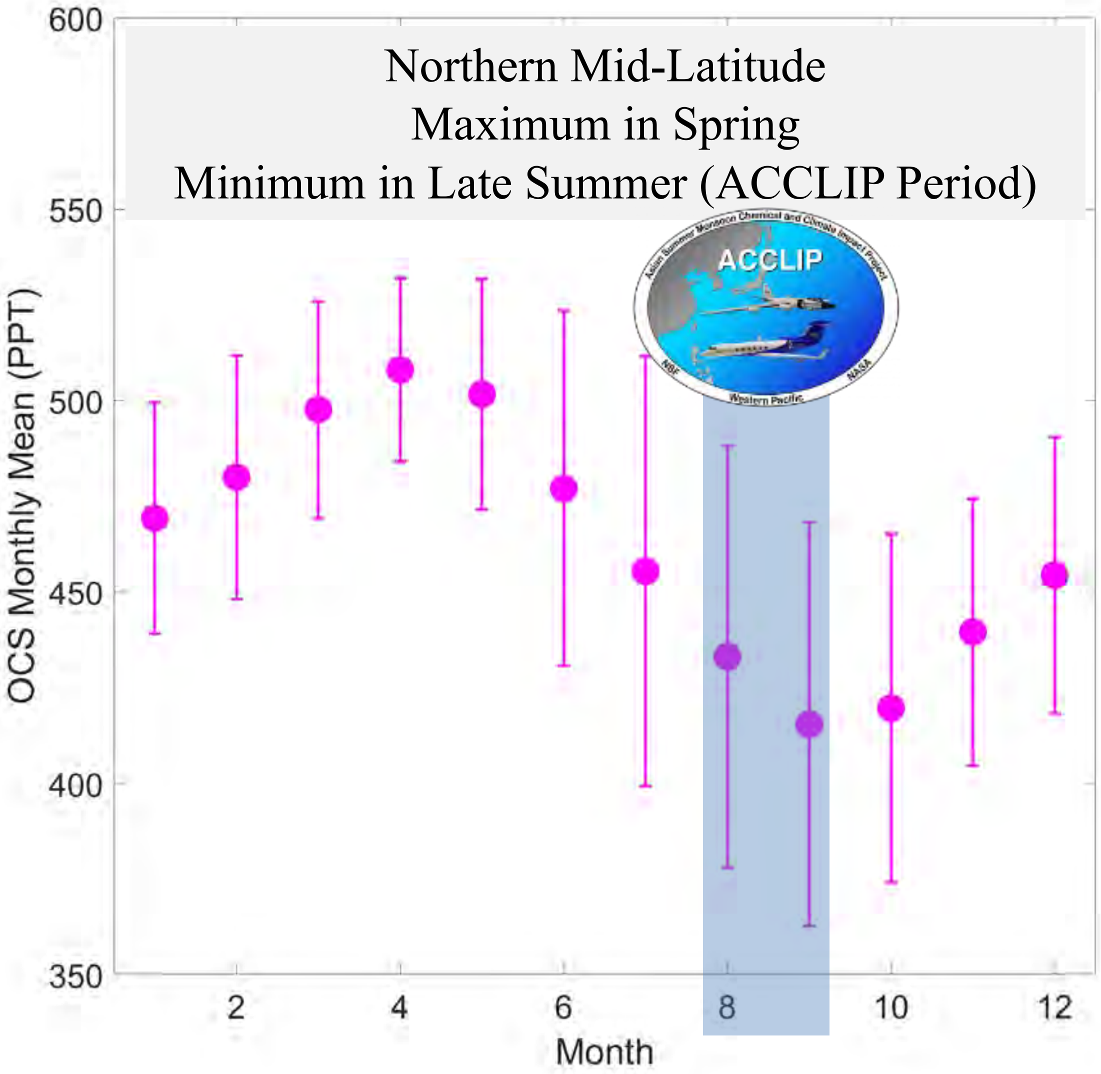
- OCS Emissions in Boundary Layer
- OCS Uptake in Boundary Layer

OCS Boundary Layer Measurements

Global Monitoring Laboratory
Earth System Research Laboratories

- NOAA GML HATS best record of OCS surface concentrations globally
- No long term OCS ground based measurement record in Asia
- ACCLIP Campaign Northern Hemisphere Mid Latitude Summer: Approaching Annual OCS minimum due to max plant uptake





OCS Anthropogenic Emissions Inventory

(2012 Most Recent Period from Campbell Group)

- ~180 GgS/year per Kettle 2002, Montzka 2007 and Berry 2013
- ~400 GgS/year based on 2012 Emissions Estimate from Zumkehr et al 2018
- Cartwright et al 2023 TOMCAT Model run utilizes the higher Anthropogenic emissions from Campbell Group 2012, most models assume mixed OCS boundary condition of 500PPT

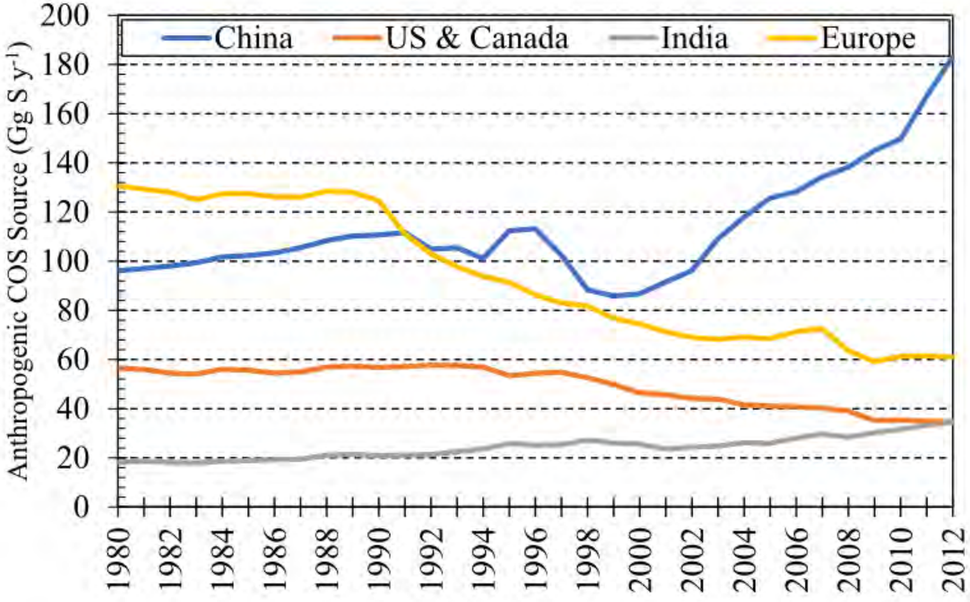
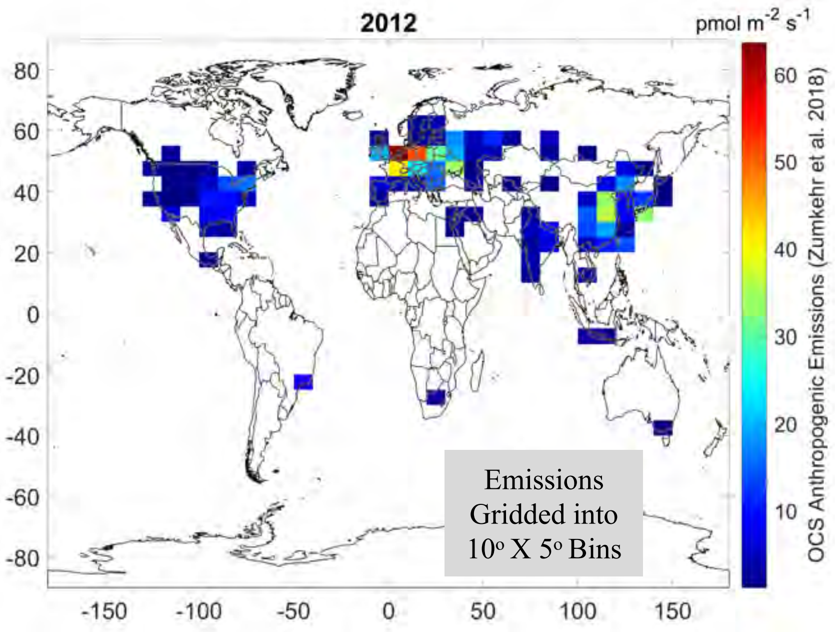
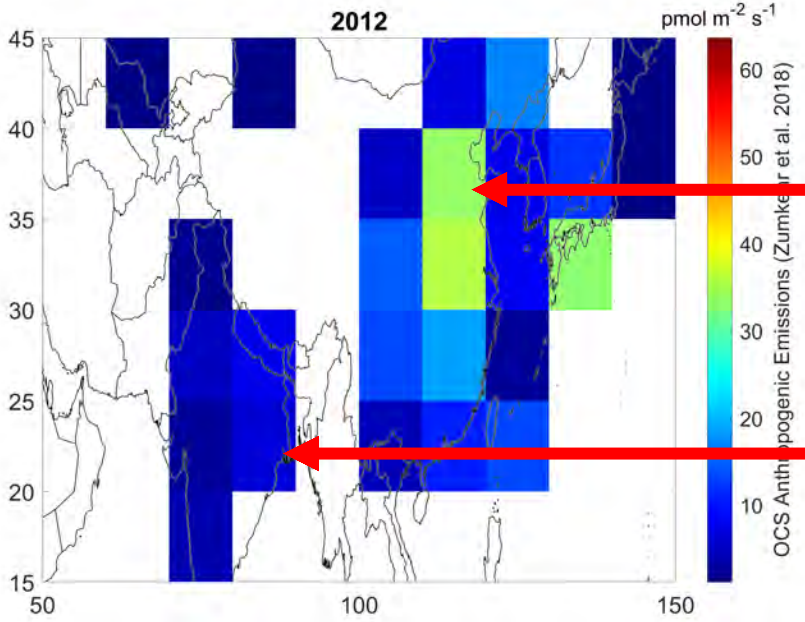


Fig. 3. Time series of the total anthropogenic source of COS (Gg S y^{-1}) from the highest contributing regions.

Zumkehr, Andrew, et al. "Global gridded anthropogenic emissions inventory of carbonyl sulfide." *Atmospheric Environment* 183 (2018): 11-19.

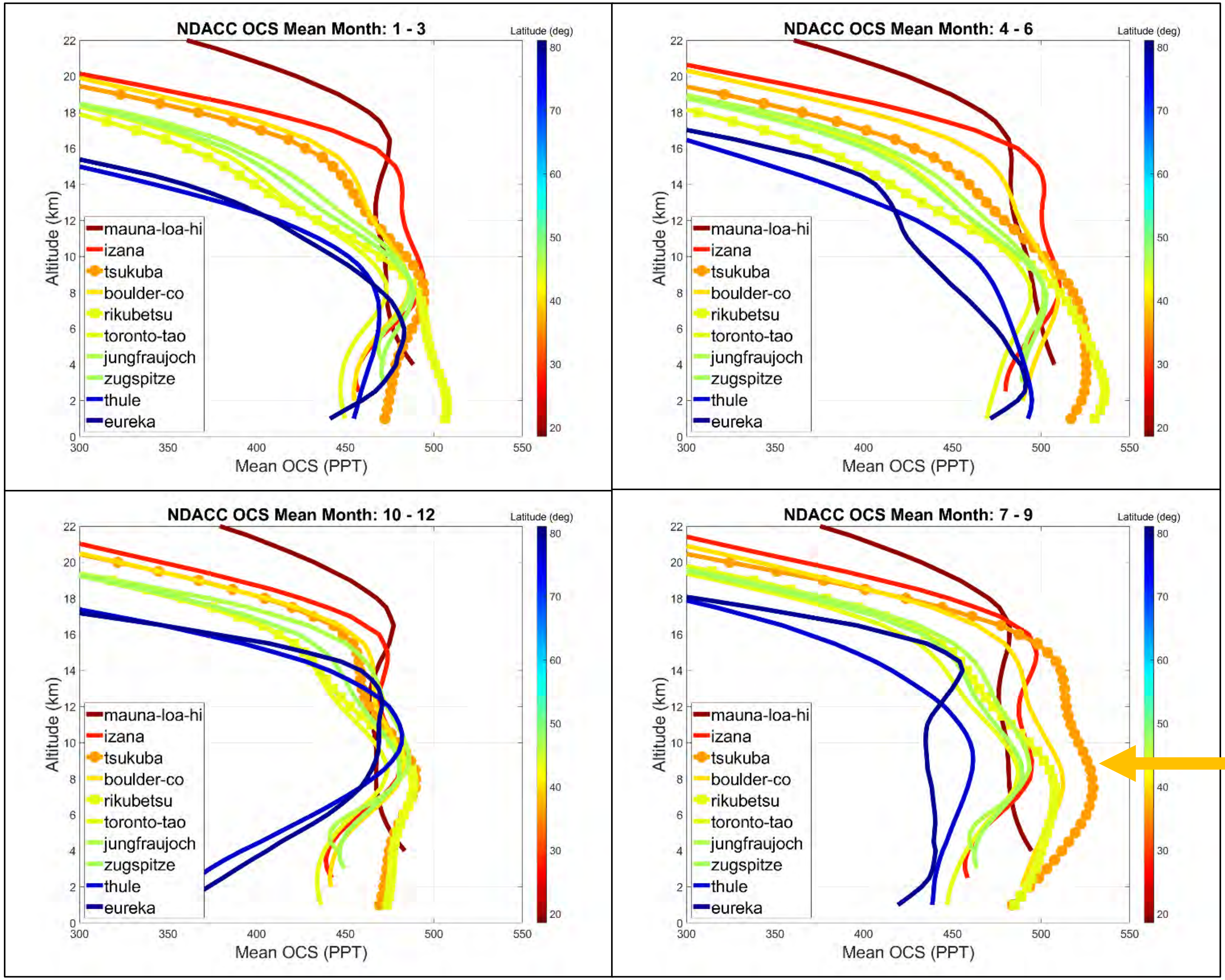




Significant Emissions from Northern China

Lower Estimated Emissions from India

OCS Vertical Profiles: NDACC Remote Sensing



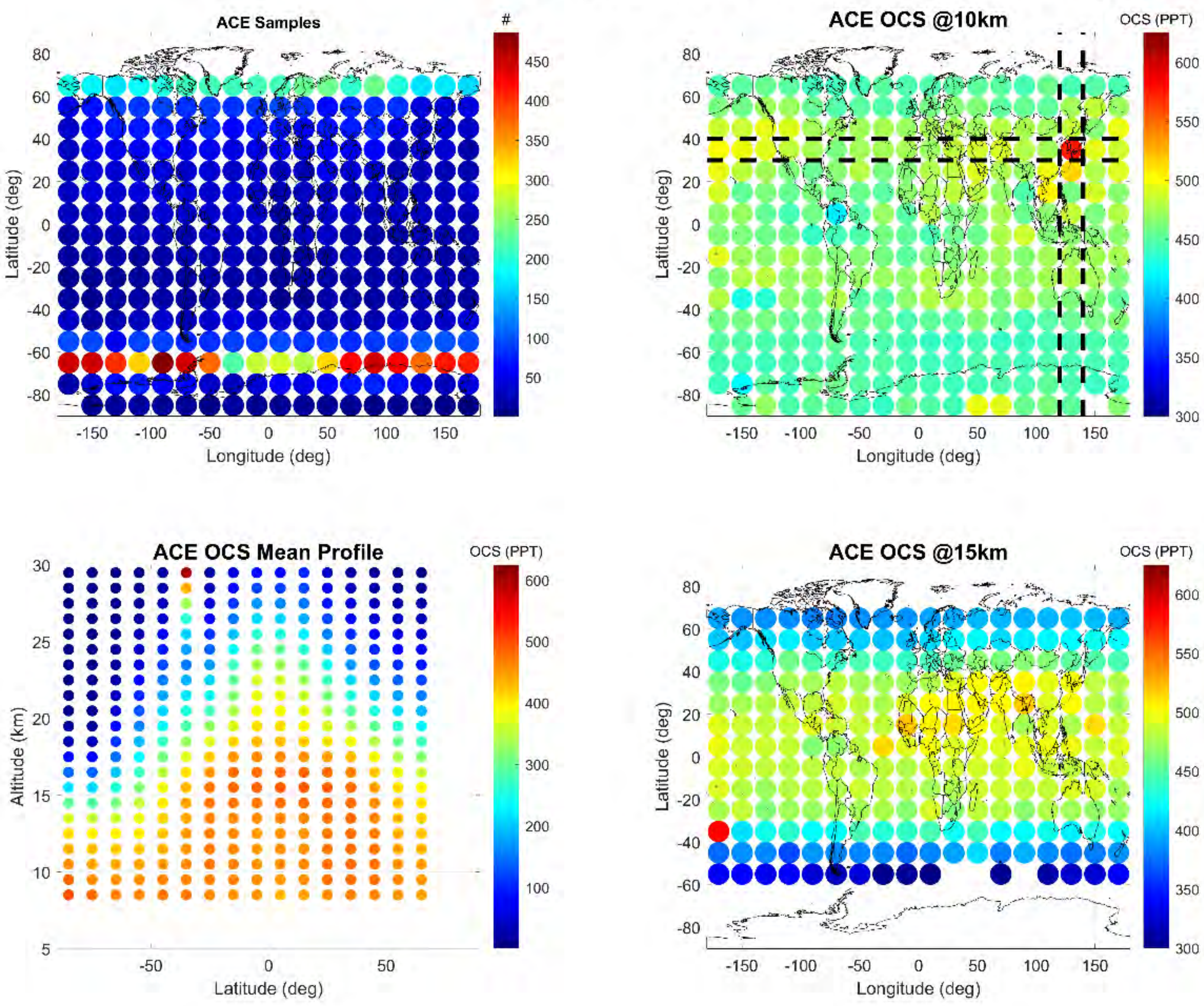
Network for the Detection of Atmospheric Composition Change NDACC

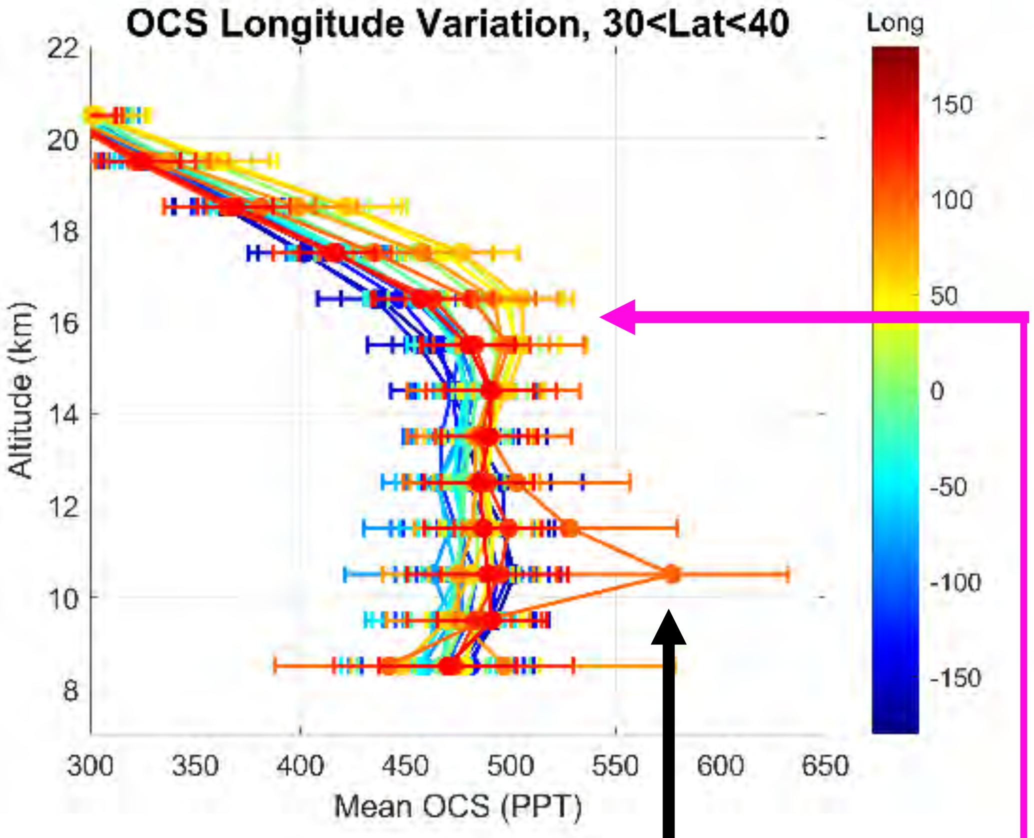
- Despite estimated high emissions, No OCS Vertical Profile Data in Much of Asia
- 2009-2016 increasing OCS mixing ratios from most NDACC sites at all levels of the atmosphere (~1% year), but a slight decreasing trend since 2016 (Hannigan et al 2022)

Highest NH free tropospheric OCS detected at Japan NDACC Tsukuba Site in summer, suggests significant Asian emissions source but sampling in summer months is sparse due to weather conditions

ACE Satellite Data: July-August Period Complete Archive

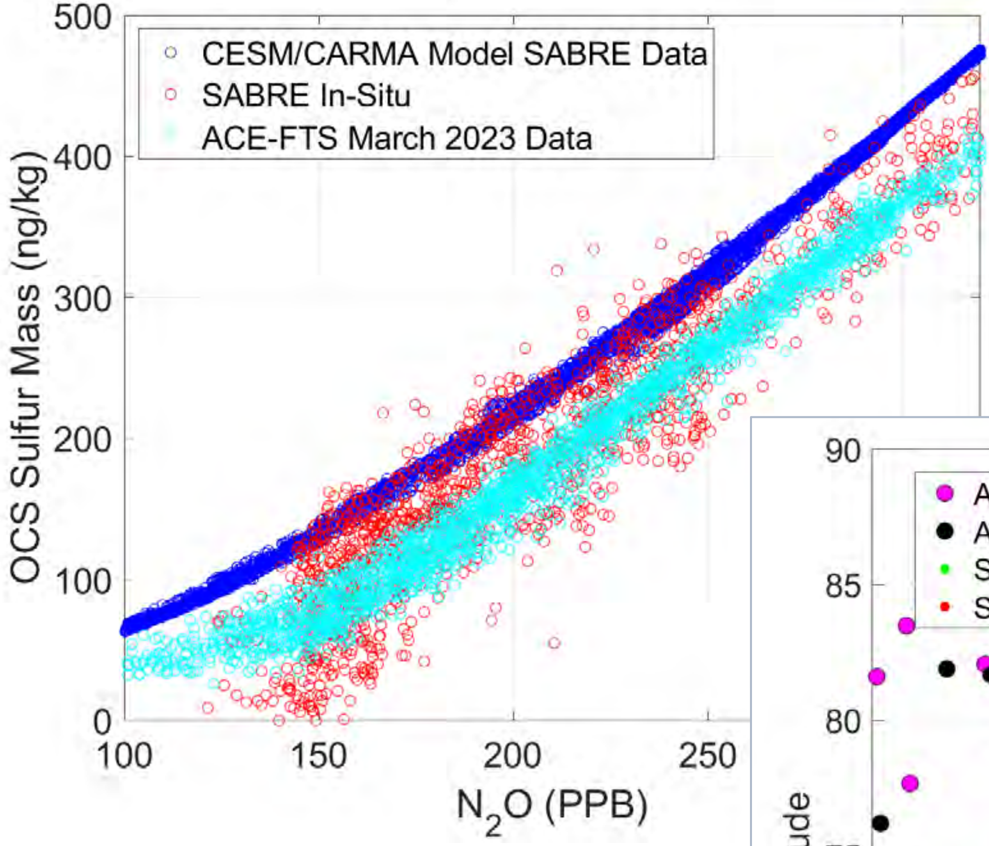
- ACE-FTS V5.2, Currently main OCS satellite sampling platform with 2 decades of data (2004-Present)
- Vertical profiles for many chemical species reported, but very sparse sampling

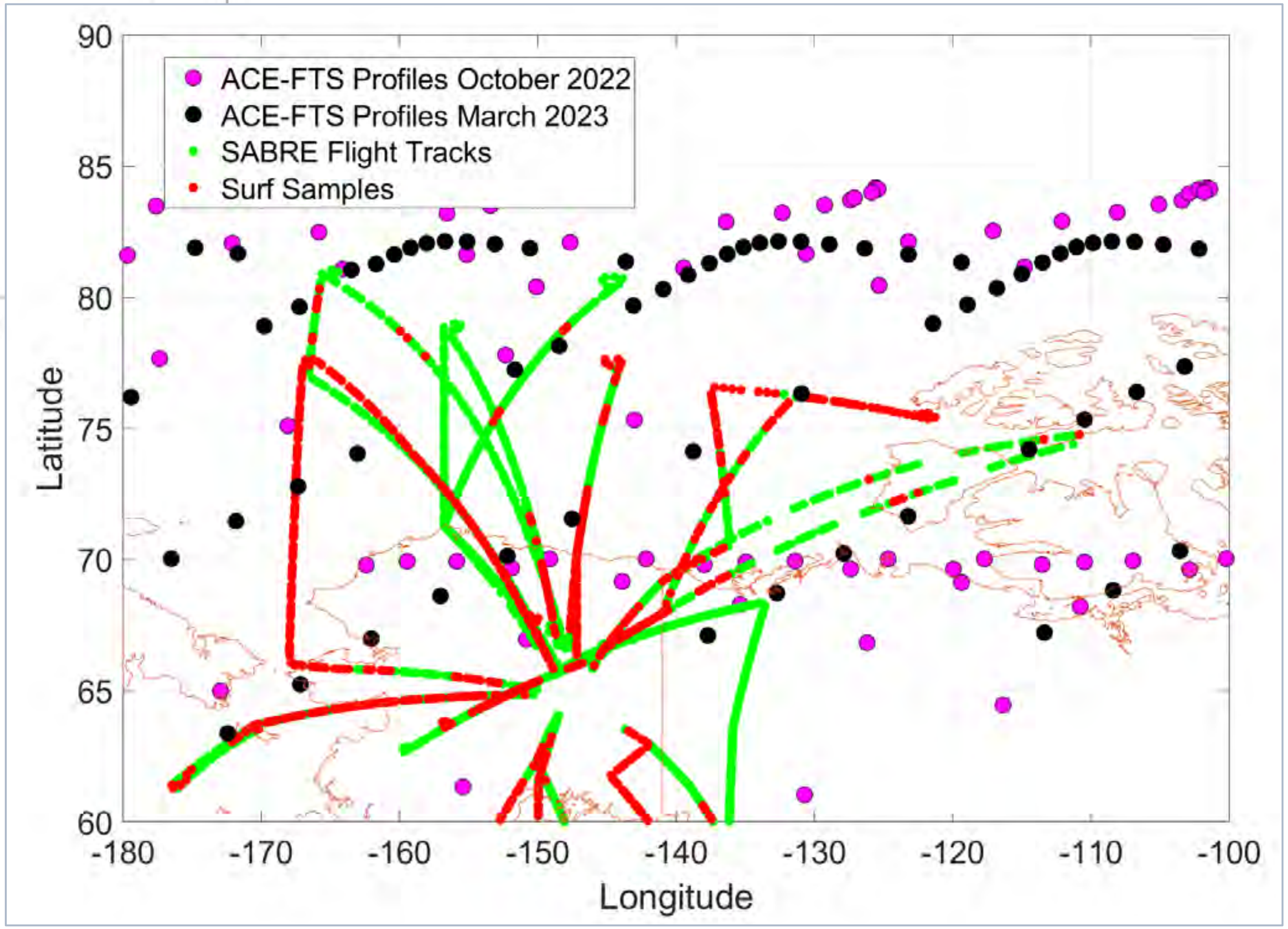




- Largest global OCS concentrations at N. China costal region (ACCLIP Domain)
- Enhanced OCS observed in the ASM region UTLS ~17km (Park et al. 2008)

2023 SABRE Campaign ACE-FTS Comparison



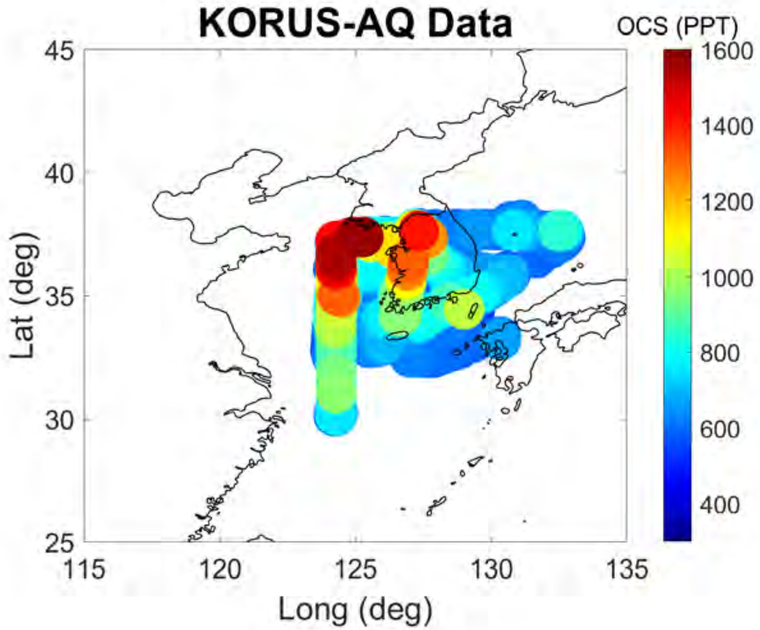


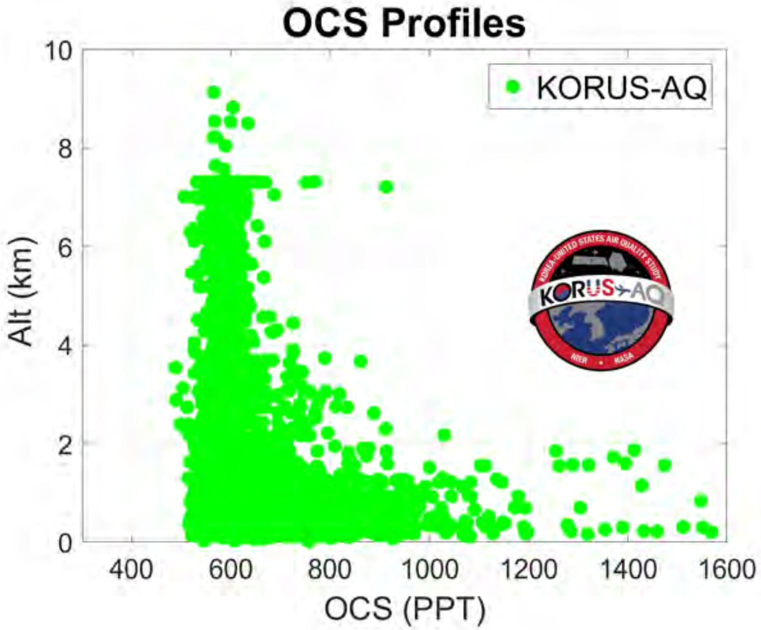
- Excellent agreement between in N2O/OCS relationship between ACOS in-situ and ACE-FTS V5.2 in March 2023 (NH Lat>60)

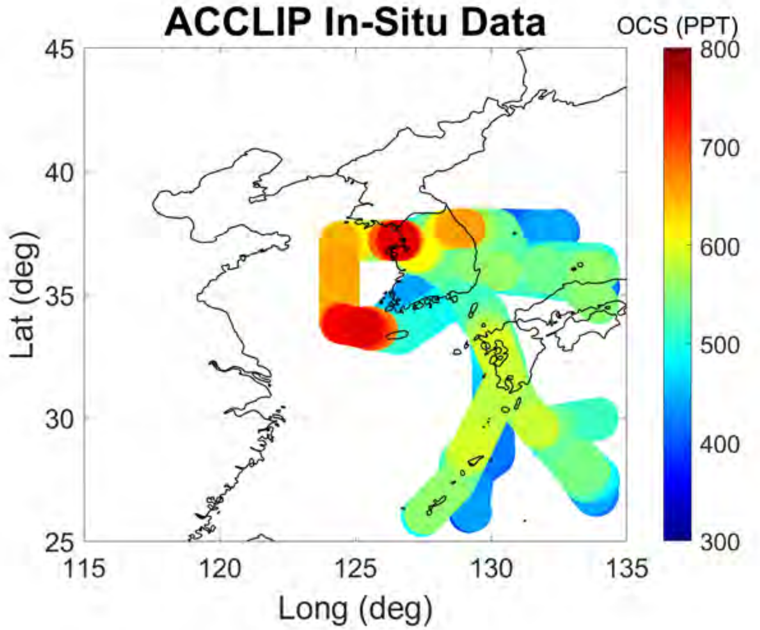
- Low TOP CESM model results show a similar trend in N2O/OCS relationship between ACE-FTS and ACOS In-Situ, but with an ~50PPT offset. Offset likely result of model fixed surface boundary condition.

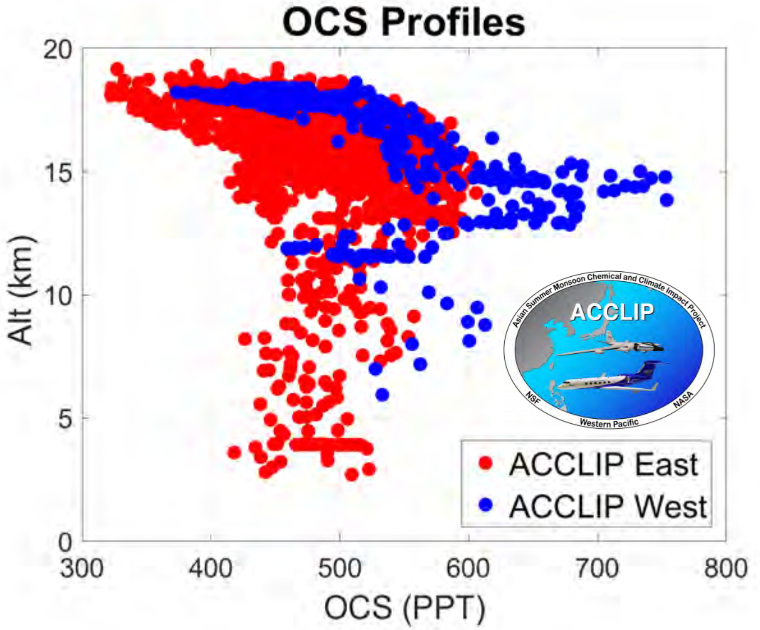
2022 ACCLIP In-Situ UTLS Carbonyl Sulfide Data

- 2016 KORUS-AQ sampling in the Northern Asia Costal Region Boundary Layer & Free Troposphere region during late spring early summer (May-June)
- 2022 ACCLIP sampling of the Northern Asia Costal Region UTLS during summer (August)
- Both campaign indicates the highest Carbonyl Sulfide concentrations in the Yellow Sea corridor
- 2016 KORUS-AQ high OCS concentrations are primarily attributed to anthropogenic emissions from Northern China, in agreement with earlier sampling form the 2002 TRACE-P campaign





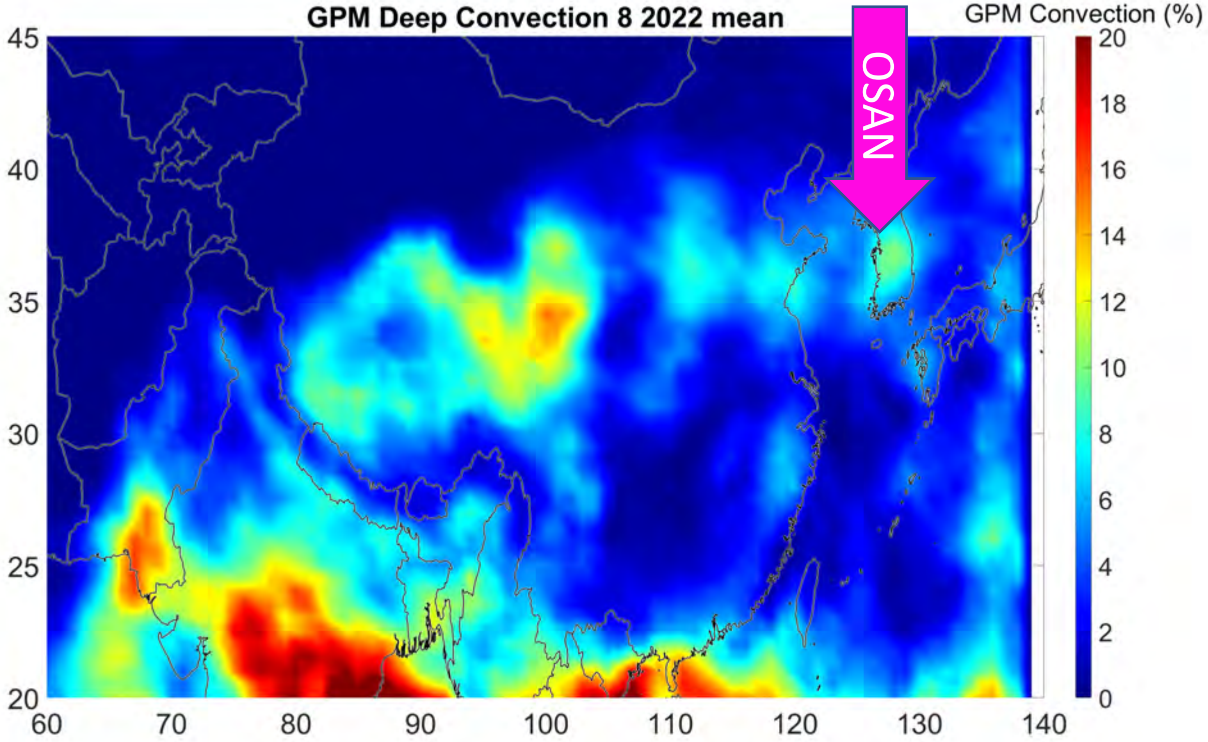


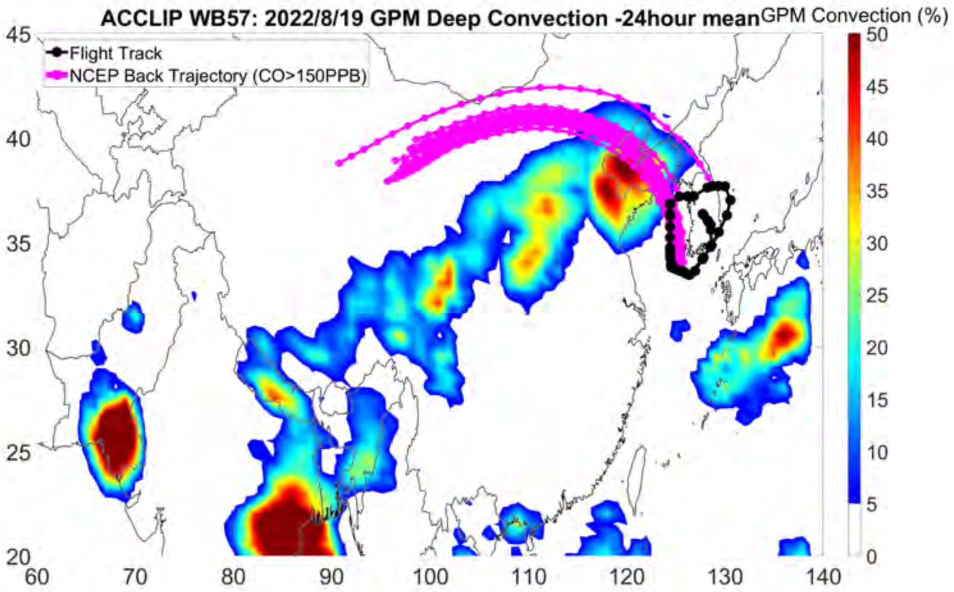


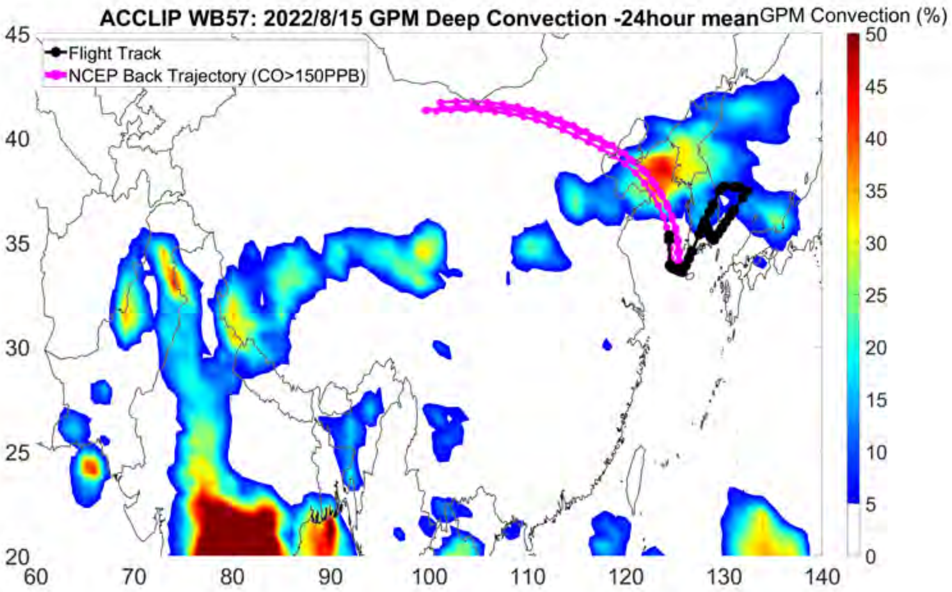
ACCLIP Trajectory Analysis for Convective Influence

- In August 2022 the deep convection distribution (GPM MergeIR Brightness Temperature <235K) indicates relatively minimal strong convective activity in the Chinese costal region

- 24 hour backward trajectories (Hysplit w/NCEP winds) from two specific flights (8/19 & 8/15) indicate that in-situ sampled air parcels with high CO (>150PPB) recently encountered deep convective systems in the Yellow Sea region



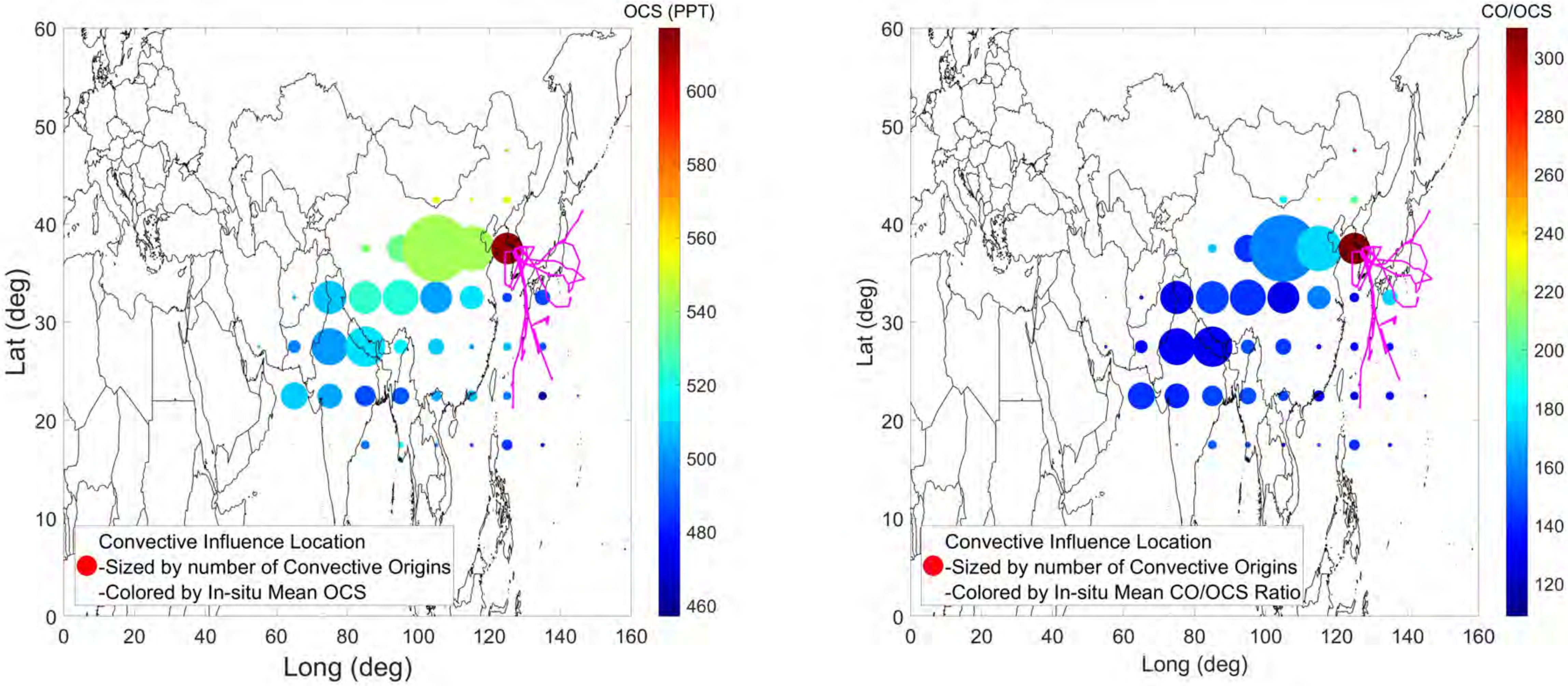




2022 ACCLIP In-Situ data Convective Origins

WB57 Convective Influence Product Courtesy of Ren Smith

- WB57 ACOS OCS data overlaid onto the NCAR convective influence product (two week back trajectories) to isolate source regions for the high altitude in-situ measurements (MAGENTA flight tracks).
- Highest OCS mixing ratios appear to originate from the Yellow Sea region, with estimated time since convection as little as 1-2 days
- High CO/OCS Ratio in the Yellow Sea region indicates fresh anthropogenic emissions due to short CO lifetime (~1 month).

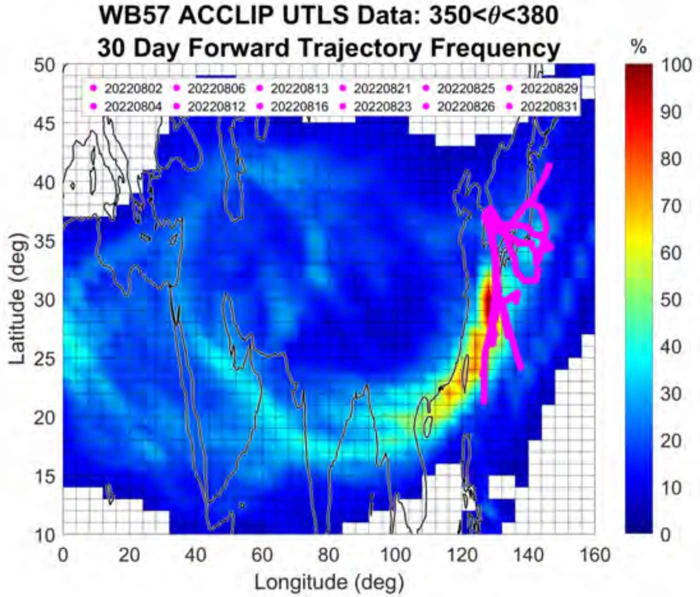


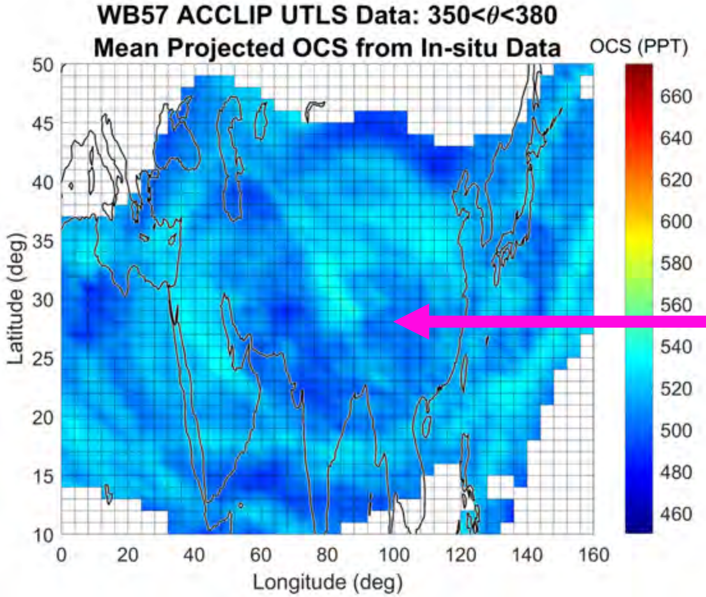
2022 ACCLIP In-Situ data Forward Trajectories

(Courtesy of Ren Smith and Rei Ueyama)

- Enhanced OCS mixing ratio inside the ASM circulation region **~100PPT**

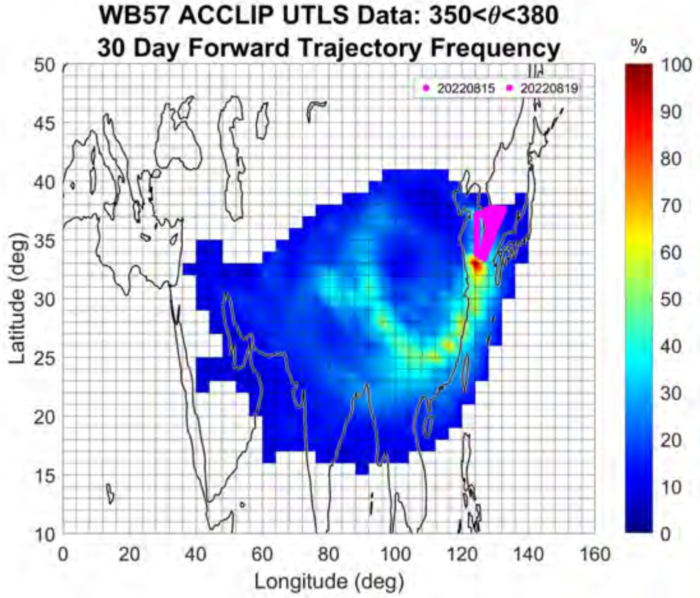
Sampling Outside ASM Region:
Flying East from Osan Flights:
8/02, 8/04, 8/06, 8/12, 8/13, 8/16, 8/21, 8/23, 8/25, 8/26, 8/29, 8/31

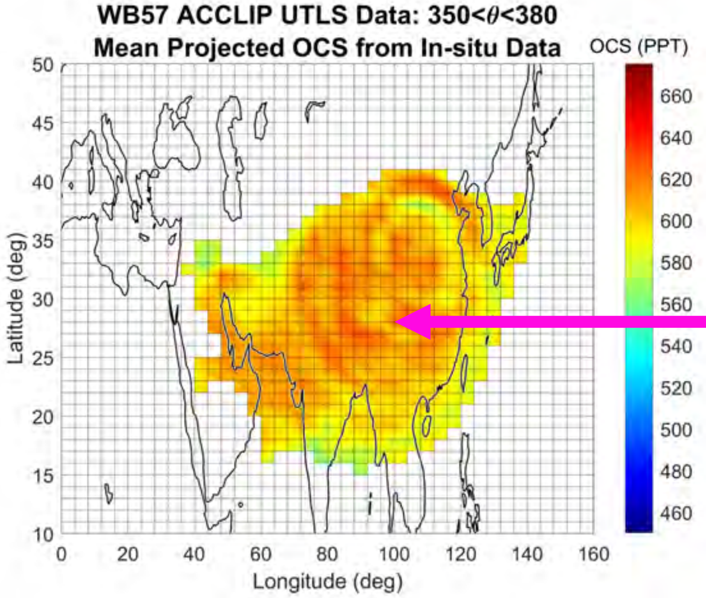




No Enhanced OCS concentrations in ASM Region (Mean ~500PPT)

Sampling Inside ASM Region:
Flying West from Osan Flights:
8/15 & 8/19



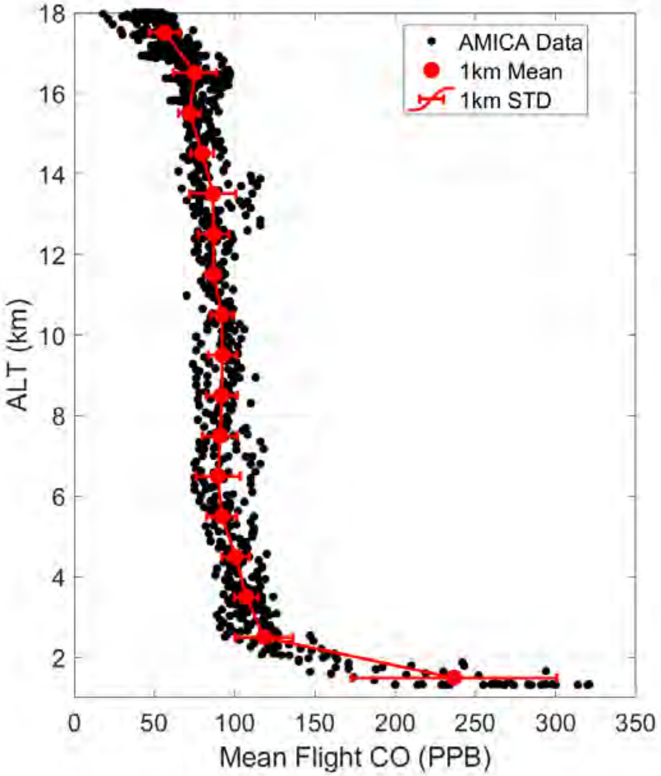


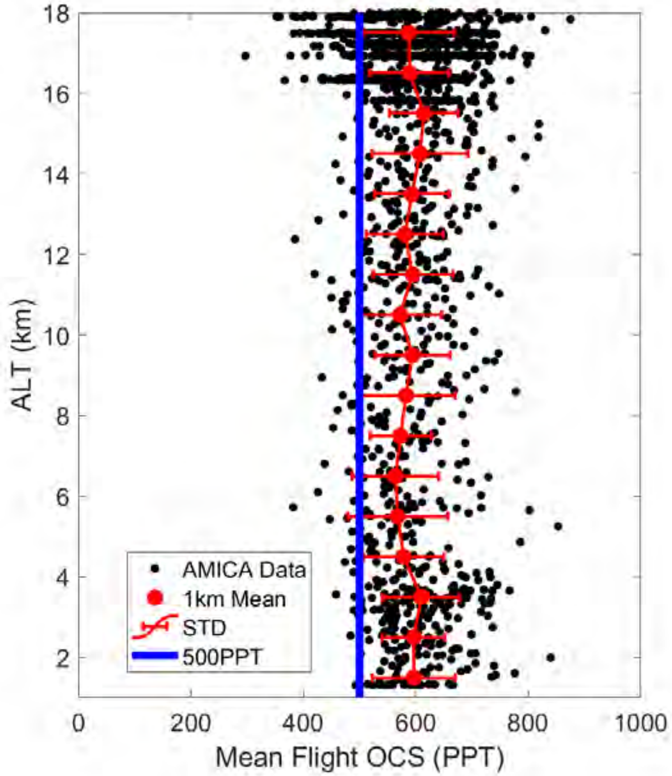
No Enhanced OCS concentrations in ASM Region (Mean ~600PPT)

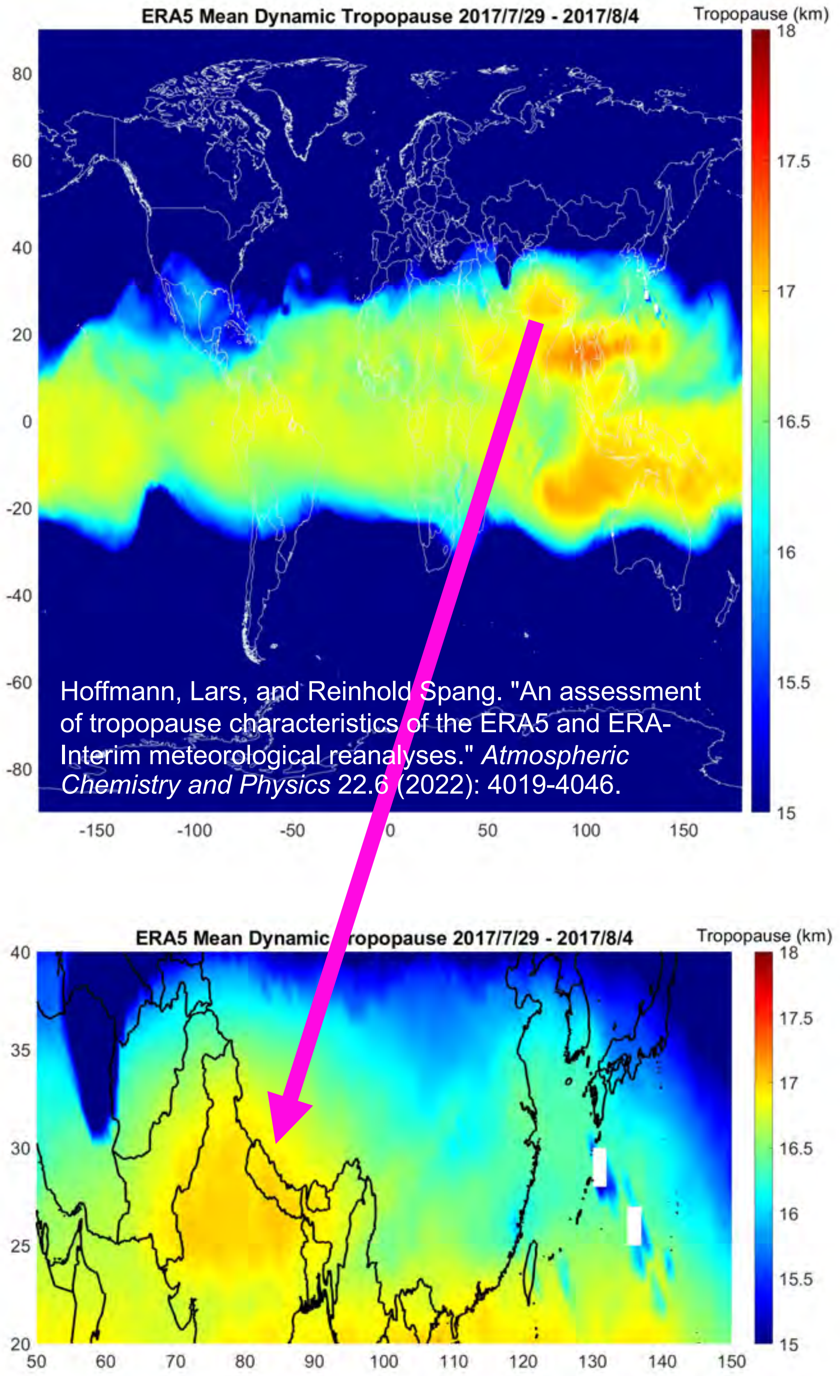
2017 STRATOCLIM Inside ASM

Courtesy of Marc V. Hobe, AMICA PI

- Flight Dates: 7/29, 8/2, 8/4. Entire Flight Paths contained to Nepal Airspace
- Nepal contained within enhanced ASM Tropopause region (Dynamic Tropopause ~17km)
- No significant UT pollution influence as CO is approximately constant with altitude.
- Approximately uniform OCS values (~600PPT) measured throughout tropopause
- High AMICA OCS values (~600PPT troposphere) are not unreasonable compared to ground based sampling in the Kathmandu Valley OCS~660PPT (Islam et al . 2020)

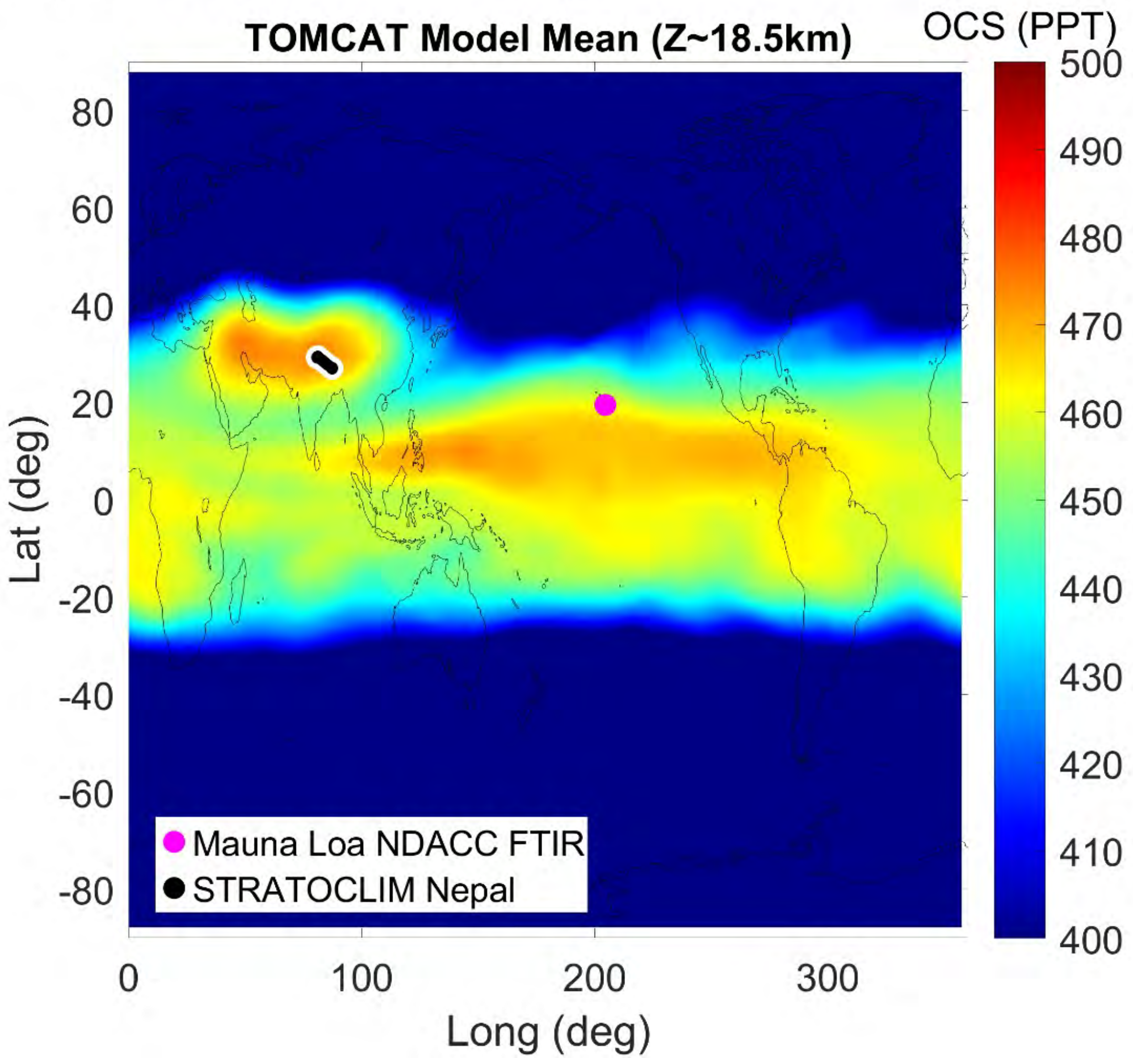


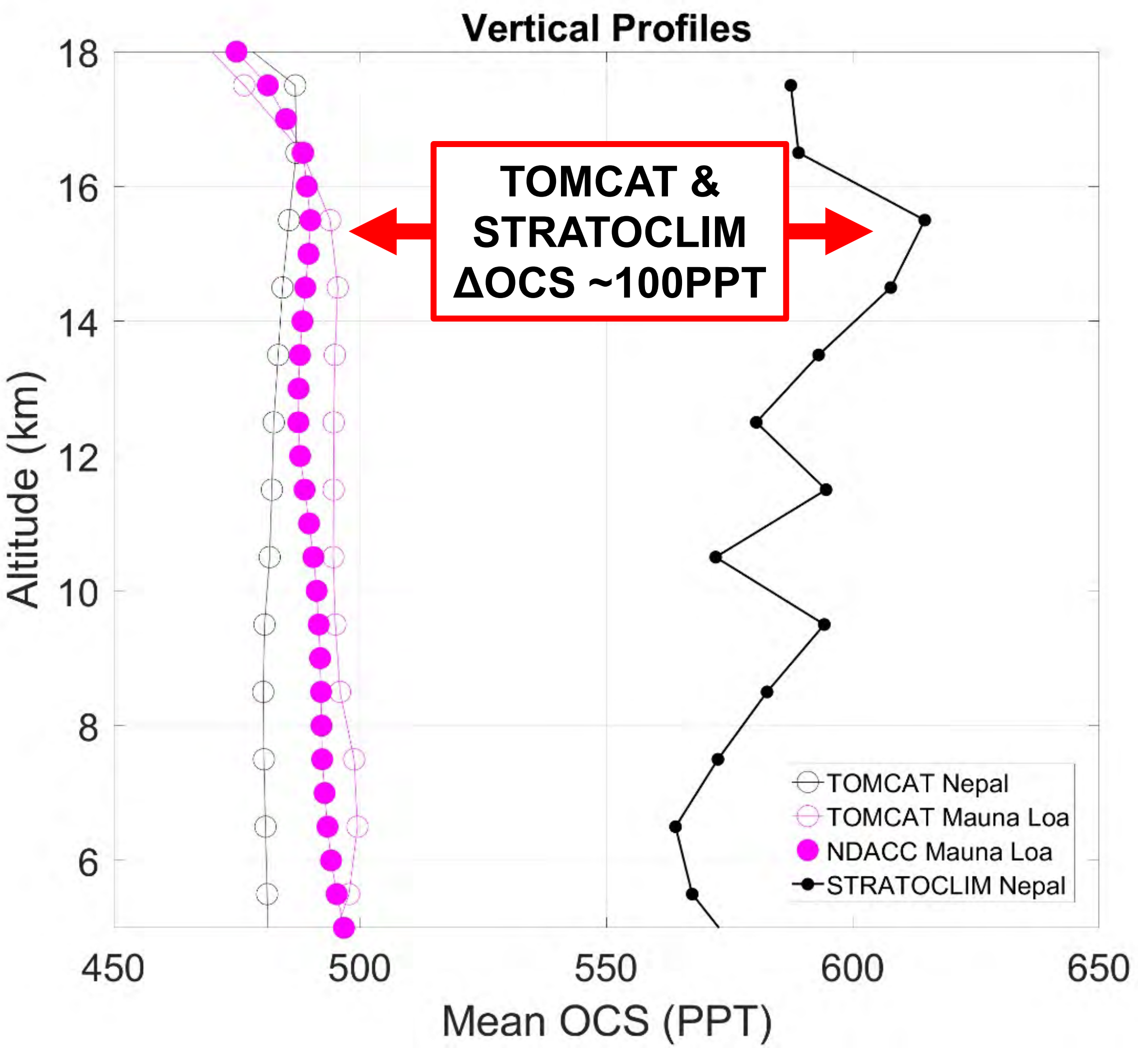




2017 TOMCAT - STRATOCLIM Comparison

- Data from Cartwright et al. 2023 (OCS Emissions + ERA-Interim Vertical Transport)
- TOMCAT produces good agreement in vertical OCS profile at Mauna Loa with NDACC observations
- TOMCAT underestimates ASM OCS vertical profile compared to STRATOCLIM measurements ~20% in UTLS





Missing Carbonyl Sulfide in Global Models

- Tropospheric Modeling of OCS generally agrees with airborne data from the free troposphere, with possible exception of some instances in NH summer
- Ma et al. 2023 compare multiple model runs with ATOM and HIPPO data and notes a missing free troposphere OCS source, possible attribution to anthropogenic emissions

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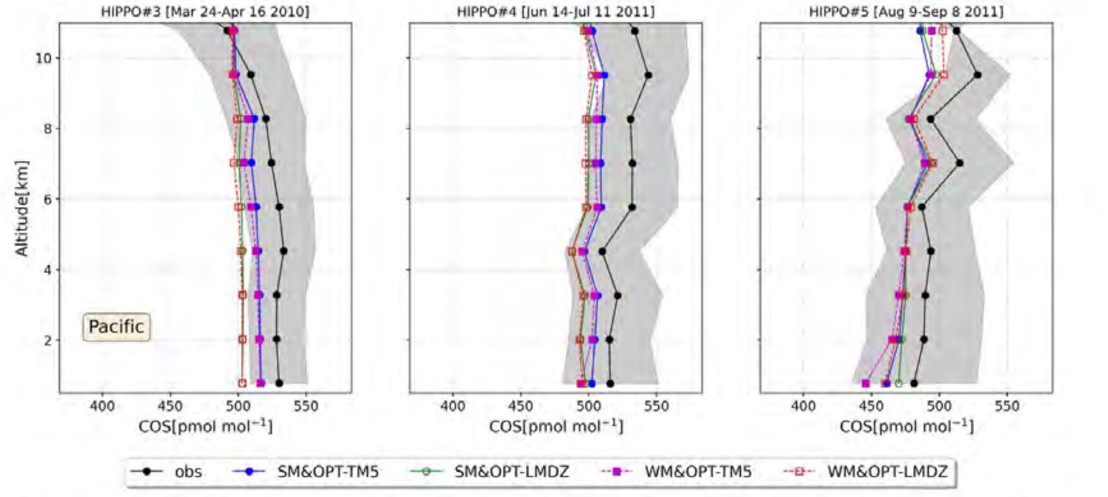

Figure 8. Carbonyl sulfide (COS) Vertical gradient of HIAPER Pole-To-Pole Observations (HIPPO) measurements against model groups over the oceans. The data are averaged over layers of 1.25 km.

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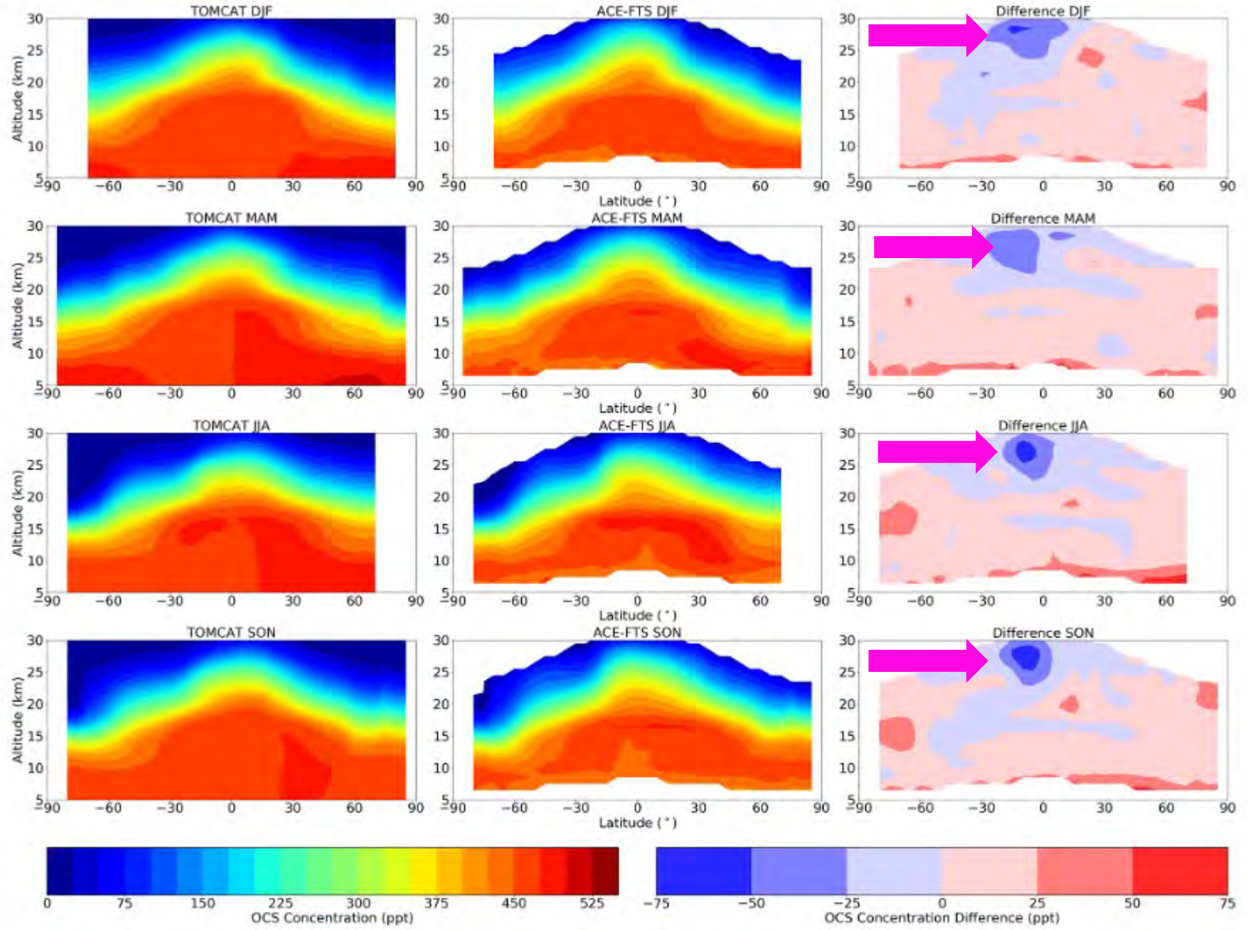


Figure 3. Seasonal zonal mean concentration (mixing ratio) of OCS (ppt) from $TOMCAT_{OCS}$ (left) and ACE (centre) and the difference between the two ($TOMCAT_{OCS}$ minus ACE, right) for the period of 2004 to 2018. $TOMCAT_{OCS}$ and ACE data averaged in 5° latitude bins and over all longitudes.

- TOMCAT Model Run 2005-2014 (Cartwright et al 2023)
- Reasonable agreement in Free Troposphere ($OCS \pm 25PPT$)
- Poorer agreement above 20km where ACE-FTS indicates higher OCS values

Transport to Stratosphere from ASM OCS Injection

- A significant portion of the convection lofted OCS observed during ACCLIP will be transported to the some region of the stratosphere, ~30% efficiency for parcels lifted above 350K (Yan et al 2019)
- ASM air mass fraction in the tropical pipe reaches a maximum of ~5% in approximately 9 months (Ploeger et a. 2017).
- OCS Stratospheric Baseline ~450PPT
- OCS from ASM Parcels ~600PPT
- Estimated 2% enhancement tropical pipe stratospheric OCS concentration as a result of ASM anthropogenic emissions
- 1PPT OCS in Tropical Pipe converts to ~3ng/kg of sulfate aerosol
- Sulfate Aerosol mixing ratio enhancement of more than 20ng/kg result from efficient ASM transport of anthropogenic OCS emissions

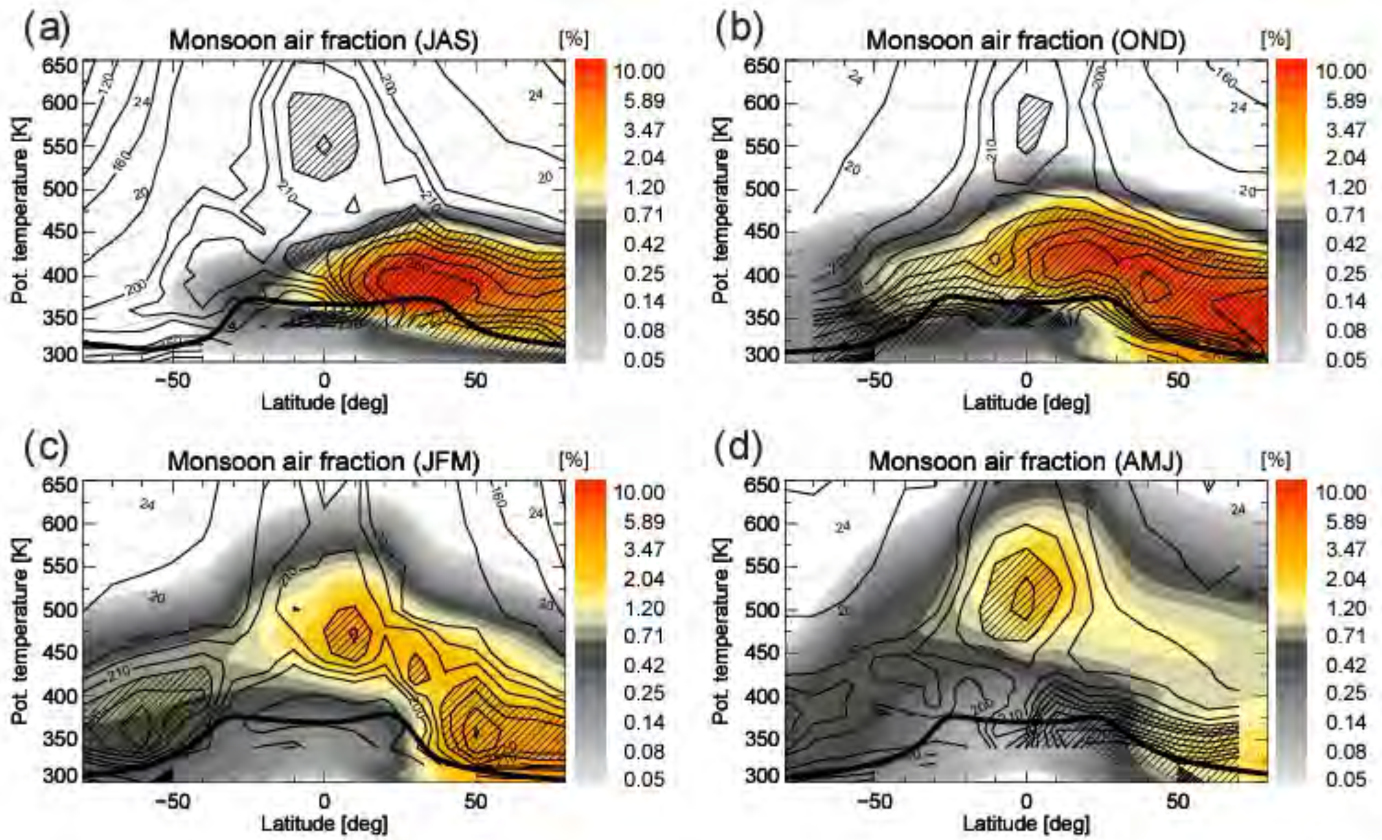
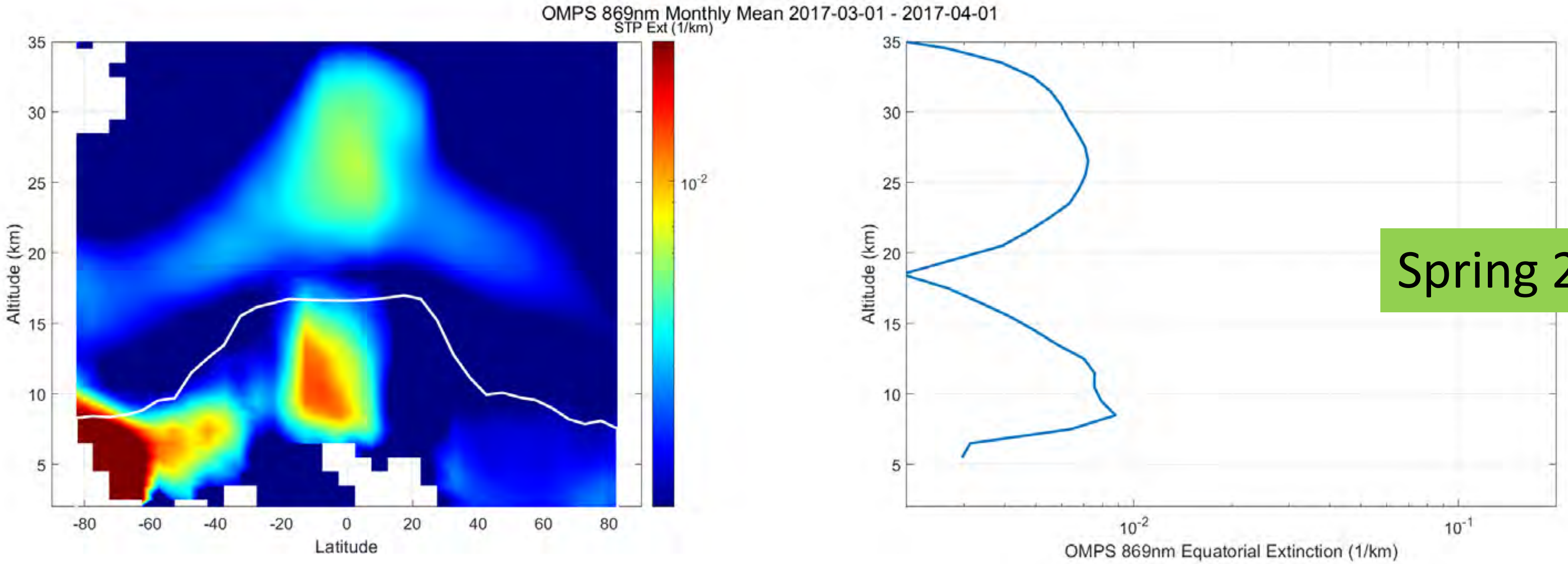


Figure 1. Seasonal evolution of climatological (2010–2013) zonal mean monsoon air mass fraction from CLaMS (color-coded) and HCN from ACE-FTS observations (black contours) during July–September (**a**), October–December (**b**), January–March (**c**), and April–June (**d**). Regions with HCN values above 215 pptv are hatched. The thick black line shows the (WMO) tropopause, and thin black lines show altitude levels (2 km spacing).

Ploeger, Felix, et al. "Quantifying pollution transport from the Asian monsoon anticyclone into the lower stratosphere." *Atmospheric Chemistry and Physics* 17.11 (2017): 7055-7066.

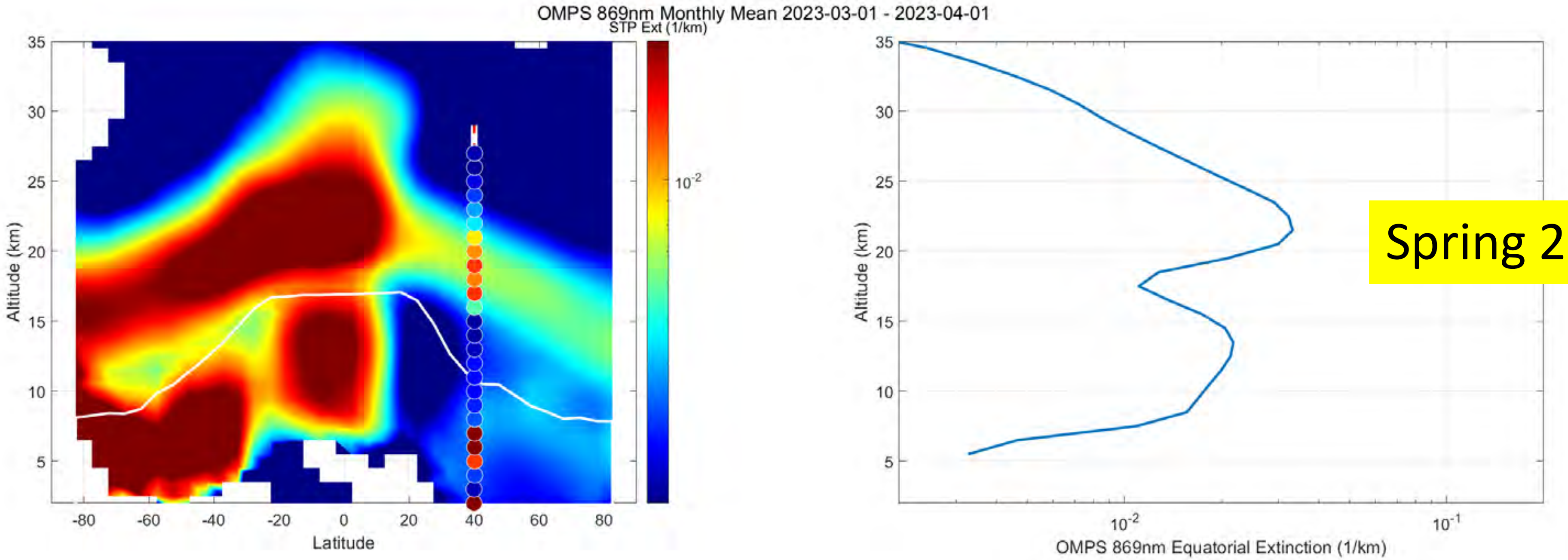
Complicating Factor: Volcanic Aerosol…

- Fairly quiescent stratosphere period in 2017 STRATOCLIM
- Peak in OMPS 869nm extinction around ~27km



Spring 2017

- Highly perturbed stratosphere period in 2022-2023 ACCLIP/SABRE
- Peak in OMPS 869nm extinction around ~22km



Spring 2023

Conclusions

- In-situ measurements of enhanced OCS during the ACCLIP demonstrate efficient transport to the UTLS via deep convection events
- ACCLIP UTLS measurements are consistent with past airborne campaigns (KORUS, TRACE-P) suggesting significant anthropogenic emissions in the Northern China, but a lack of ground based measurements limits our understanding of local sources
- Trajectory analysis and long term satellite data suggest that enhanced UTLS OCS (as much as 20%) will persist in the ASM anticyclone, allowing for stratospheric transport due to long OCS lifetime. These estimates are supported by STRATOCLIM measurements from within the ASM core.
- Current global models appear to underestimate the role the ASM pathway for transport of anthropogenic OCS emissions to the stratosphere, which may have a significant impact on sulfate aerosol formation
- Given the paucity of remote sensing observations, more in-situ measurements are needed to constrain the amount of OCS entering the tropical pipe

NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION NOAA U.S. DEPARTMENT OF COMMERCE

EARTH'S RADIATION BUDGET

CSL NOAA CHEMICAL SCIENCES LABORATORY — Boulder, Colorado USA —

Asian Summer Monsoon Chemical and Climate Impact Project ACCLIP NSF NASA Western Pacific