Reactive Nitrogen in the Global Upper Troposphere: Insights from Historic NASA DC8 Campaigns and GEOS-Chem

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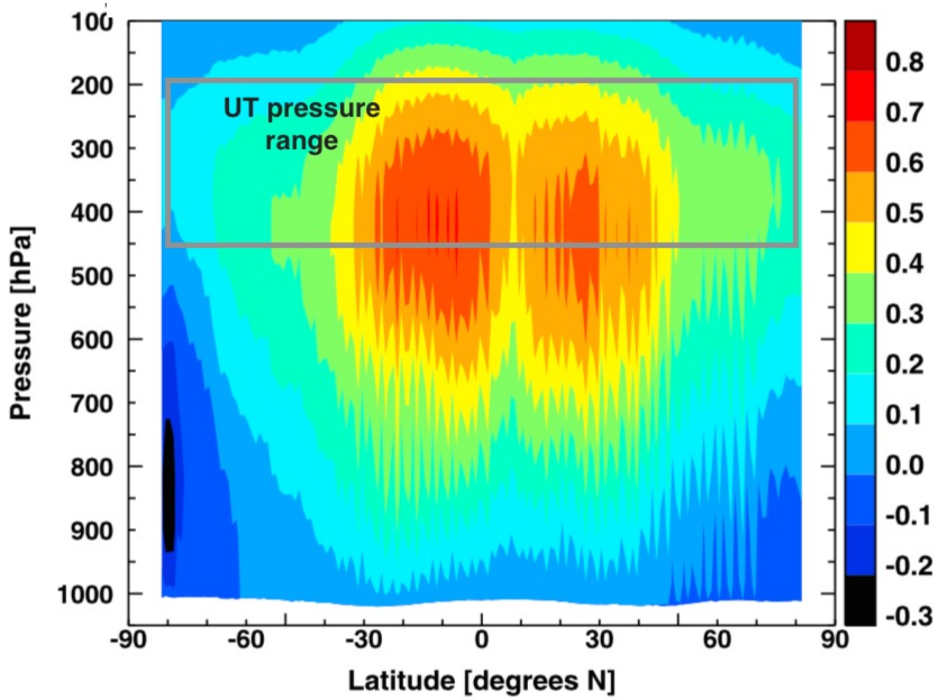
The 2nd GEOS-Chem Europe Meeting   Twitter: @NanaWei_Nevaeh   Figures: https://simpleflying.com/nasa-douglas-dc-8-guide/

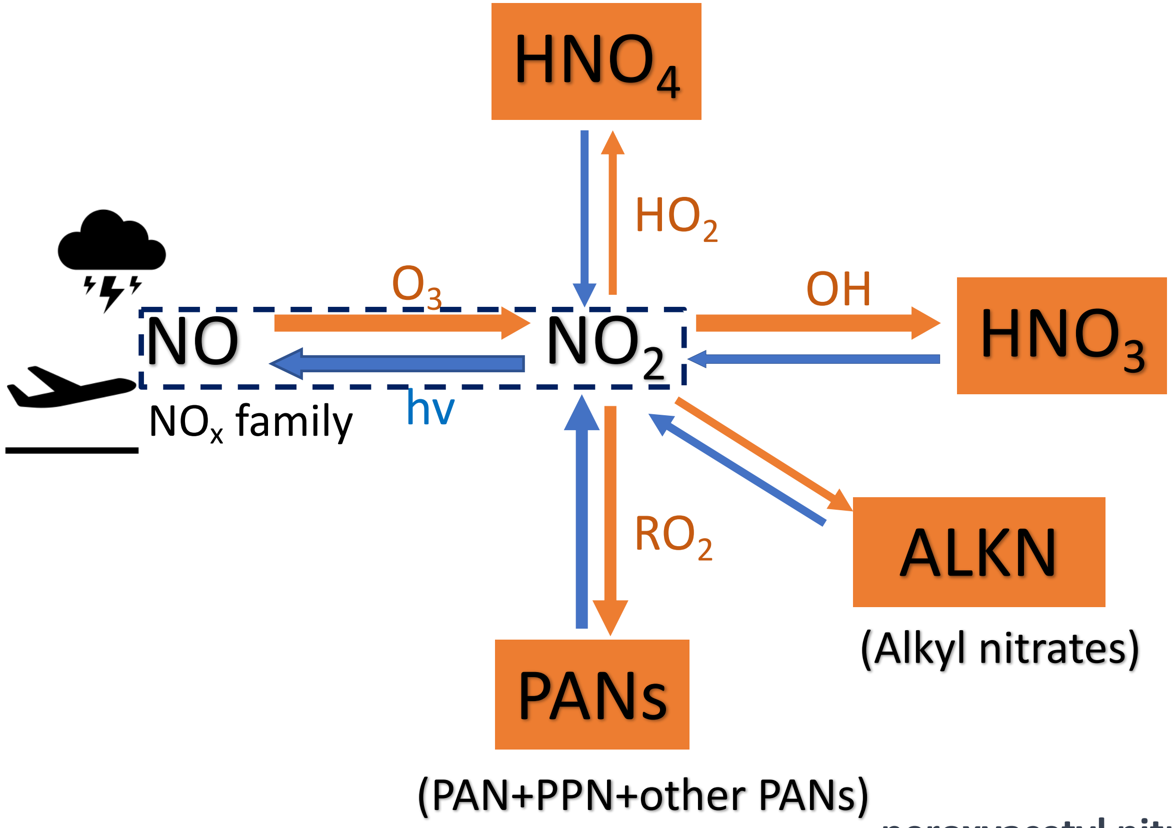
Ozone production in the UT depends critically on the availability of NO_x

Highest ozone production efficiency in the UT
Greatest ozone radiative forcing observed in the UT



The zonal mean distribution of radiative forcing kernels ($mW/m_2/ppbv$) in August 2006. [Aghedo et al., 2011]

NO_y = NO_x + NO_x reservoirs
NO_x limited UT → Ozone and OH



peroxyacetyl nitrate (PAN)

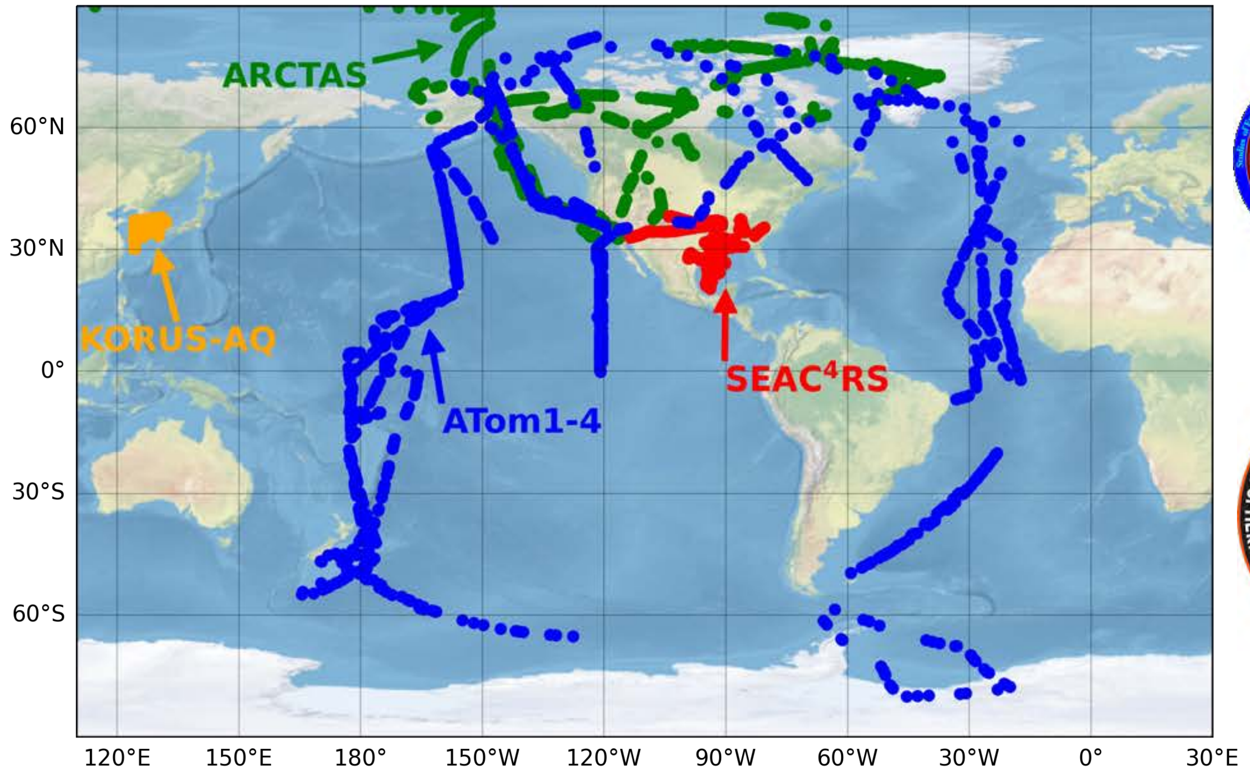
Understanding reactive nitrogen in the UT and diagnosing complete reactive nitrogen budget in models is fundamental to reduce the uncertainties of projections of Ozone and OH.

Historic NASA DC8 campaigns combined to achieve extensive global coverage of the upper troposphere(UT)

The DC8 campaigns extend from ARCTAS in 2008 to ATom from 2016 to 2018.

Pollution transported to Arctic

Air quality in South Korea



Biogenic-anthropogenic interactions

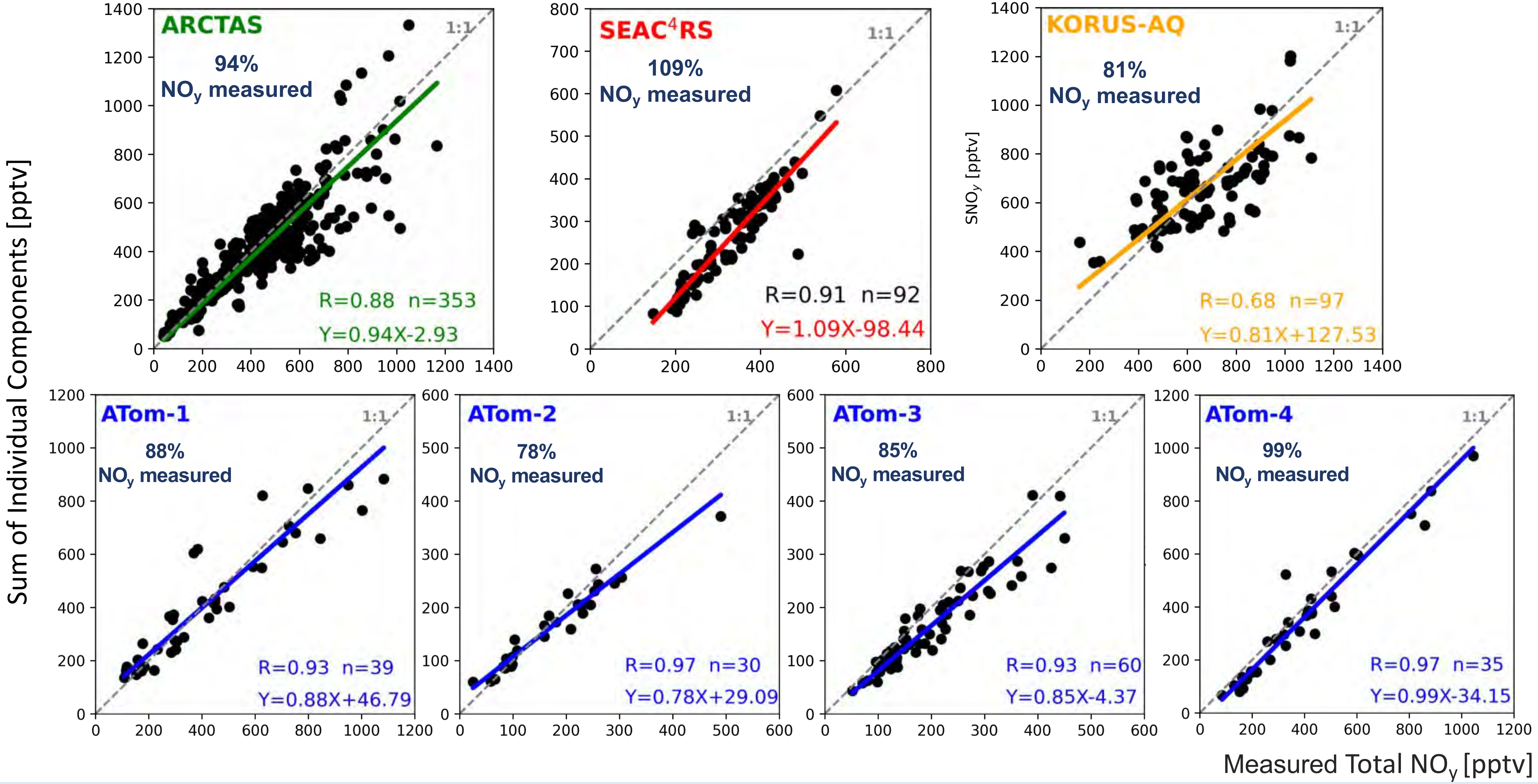
Remote troposphere

- DC8 flight ceiling of ~13 km extending into the UT.
- INTEX-NA, SONEX, DC3 are excluded.
- NO_2 are calculated from: $PSS = \frac{[NO]}{[NO_2]} = \frac{j_{NO_2}}{k_1[O_3] + k_2[HO_2] + k_3[RO_2] + k_4[BrO]}$

We filtered out stratospheric air, fresh injections and plumes, selected daytime for photochemical steady state.

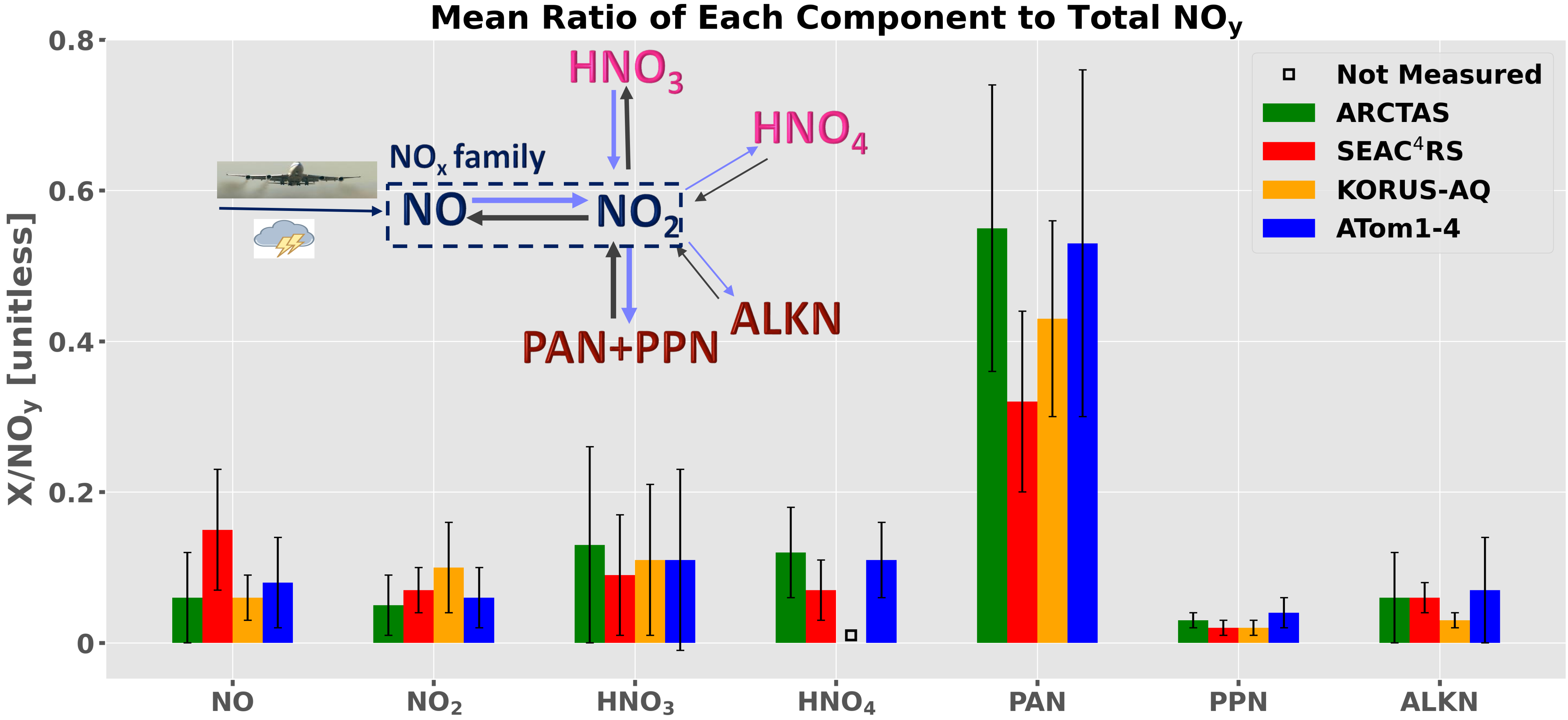
Proportion of UT NO_y measured during DC8 campaigns

Relationship between sum of individual NO_y components ($NO+NO_2+HNO_3+HNO_4$+PANs+ALKN)and total NO_y measured by chemiluminescence



Most of UT NO_y contributed by a handful of species including NO_x, PANs, HNO_3, HNO_4 and alkyl nitrates.

Contribution of dominant individual components to total NO_y

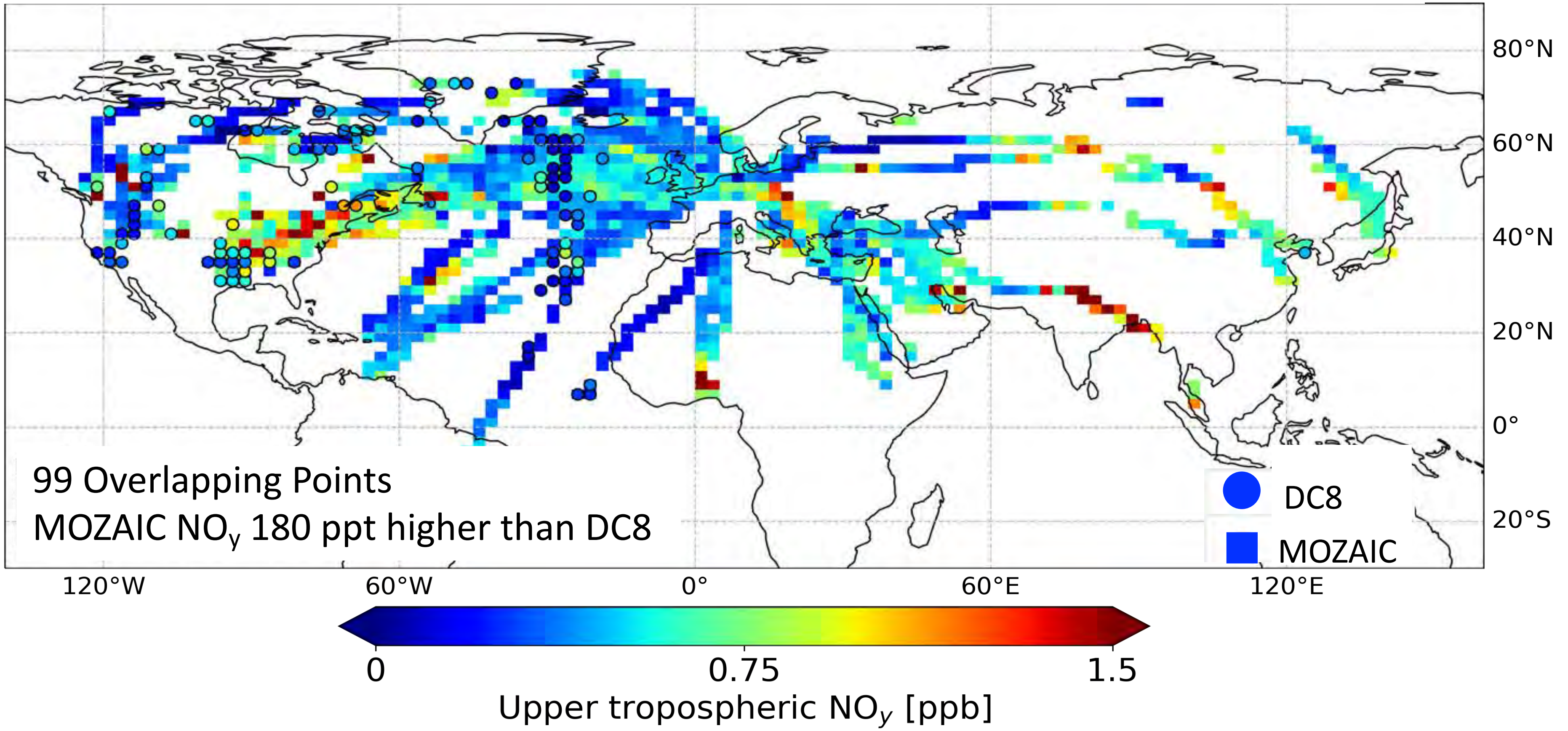


- ➢ PAN dominants NO_y components, varying from 32% - 43% over land to 53%-55% in cold Arctic and remote areas. Following is NO_x, lowest in ARCTAS (11%) and highest in SEAC^{4}RS (23%).
- ➢ HNO_3 makes up 11% of total UT NO_y on average, HNO_4 about 10%, ALKN about 6%, and PPN about 3%.

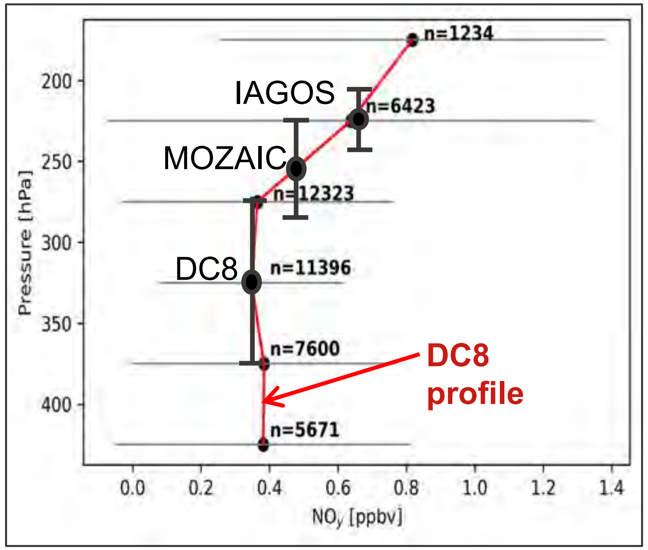
Comparison of short-term DC8 and multiyear commercial aircraft NO_y

We assessed how representative of DC8 UT NO_y to normal condition measured frequently by MOZAIC and IAGOS

Spatial distribution of UT NO_y during DC8 and MOZAIC



Vertical sampling extent of aircraft campaigns



DC8 NO_y averages 0.18 ppb lower than MOZAIC NO_y and 0.23 ppb lower than IAGOS NO_y. This is due to altitude variations and a high bias from HCN conversion in the onboard commercial aircraft instrument.

GEOS-Chem Simulations with Aircraft ObsPack Diagnostic

INPUT

Emissions:
(Lightning,
Aircraft etc.,)

(MERRA-2) meteorology

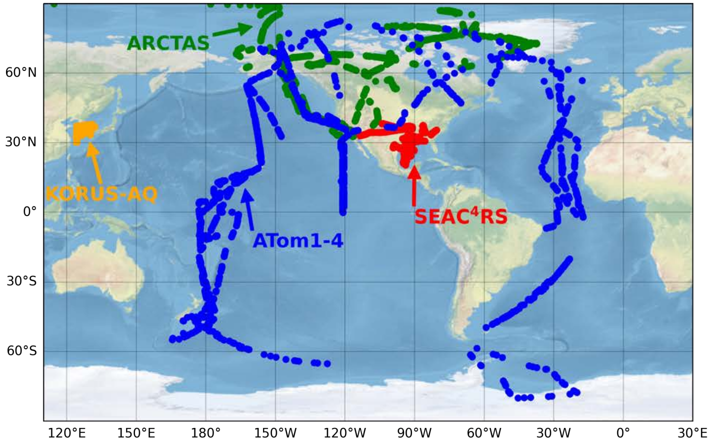
Detailed Chemistry Deposition

ObsPack diagnostic input file

V13.0.2 $2^\circ \times 2.5^\circ$ 47 levels

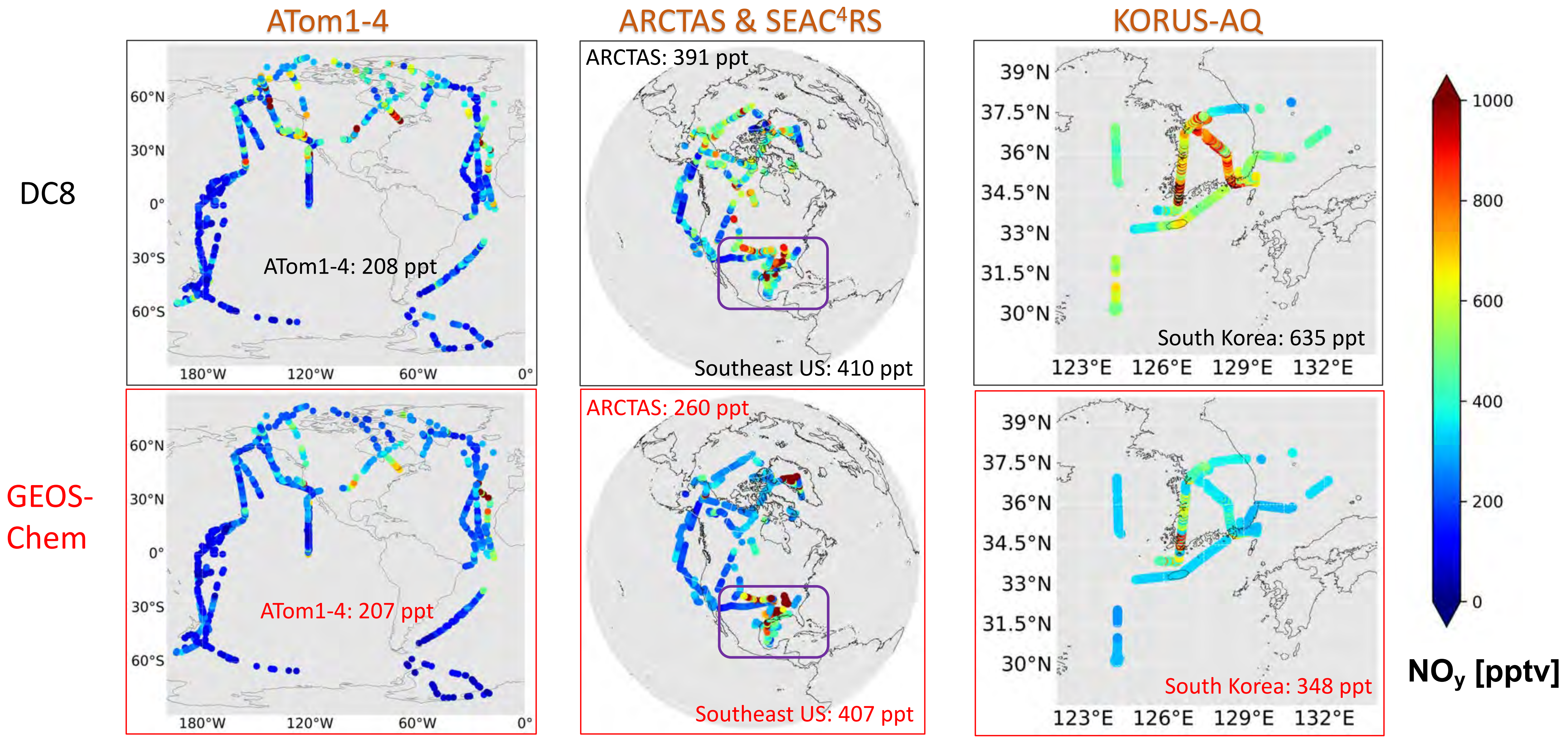
OUTPUT

Concentrations of atmospheric components at the same time and location as the DC8 observations



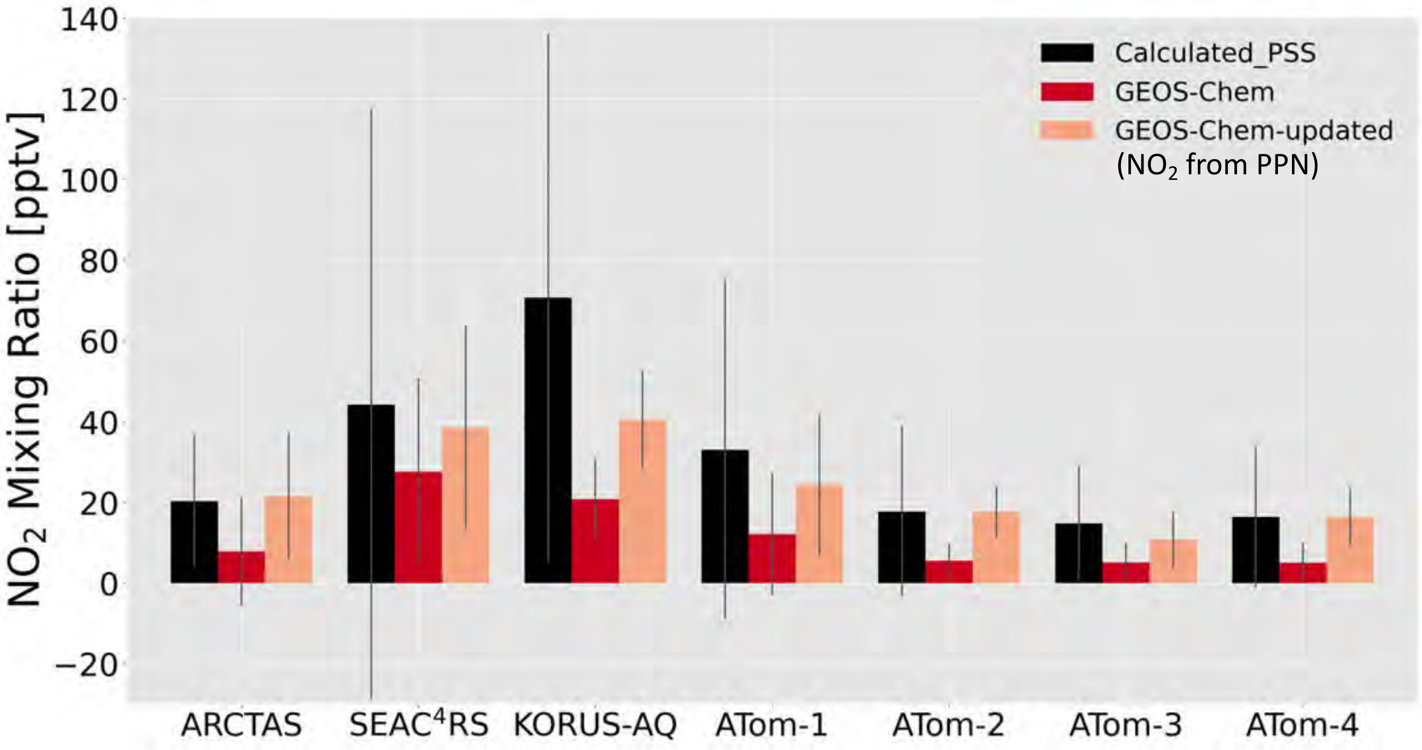
GEOS-Chem model input emissions relevant to the UT include aircraft and lightning emissions. We selected all NO_y components from GEOS-Chem output files and calculated total NO_y concentration.

GEOS-Chem skill at simulating UT total NO_y

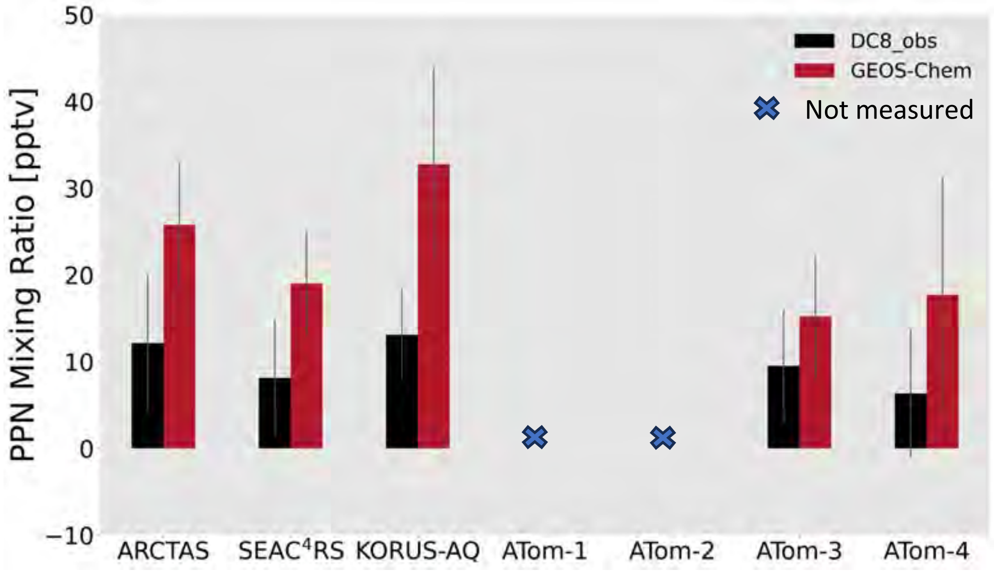


GEOS-Chem can reproduce UT NO_y over remote ocean areas and Southeast US but underestimate UT NO_y over Arctic, Canada during ARCTAS, and South Korea during KORUS-AQ.

GEOS-Chem skills at simulating UT NO_y components



GEOS-Chem overestimates PPN by 6-20 ppt

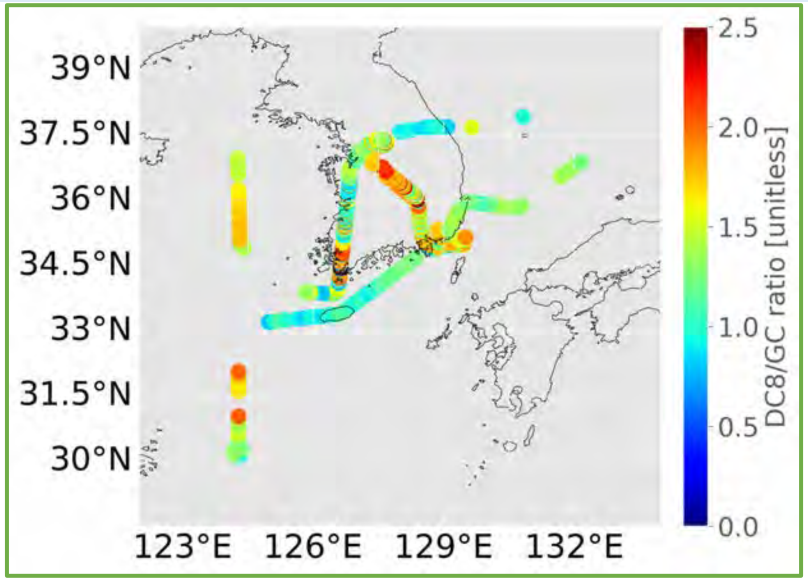


1. GEOS-Chem underestimates NO_2 by 7-50 ppt, as it locks up about 12 ppt NO_2 as PPN that is overestimated in the model due to missing PPN photolysis.

2. Updated GEOS-Chem with PPN photolysis can reduce the NO_2 difference to 4-30 ppt. Preliminary results from GEOS-Chem simulation with nitrate photolysis show that NO_2 increase is negligible in the UT.

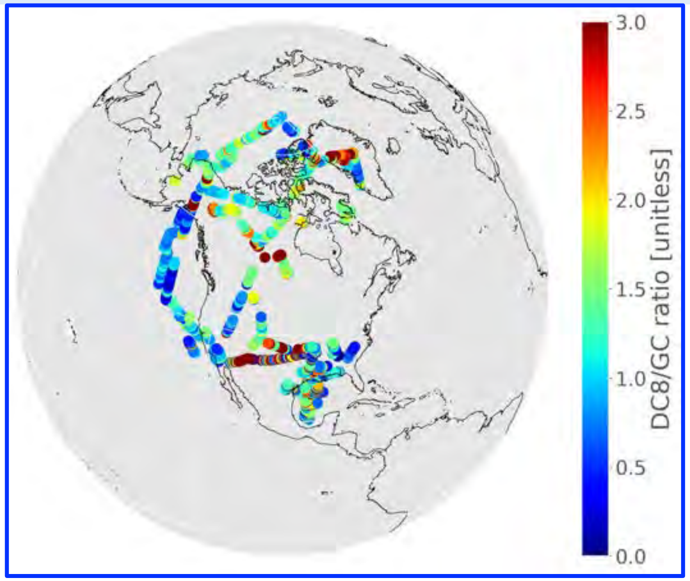
We resolved most of discrepancy of NO_2 with PPN photolysis except (KORUS-AQ) Southeast Asia areas.

GEOS-Chem skill at simulating UT total PANs Species



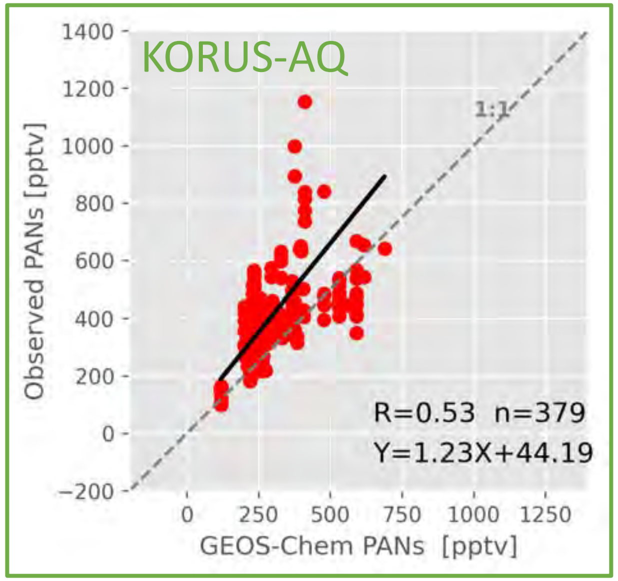
ARCTAS and SEAC^{4}RS:

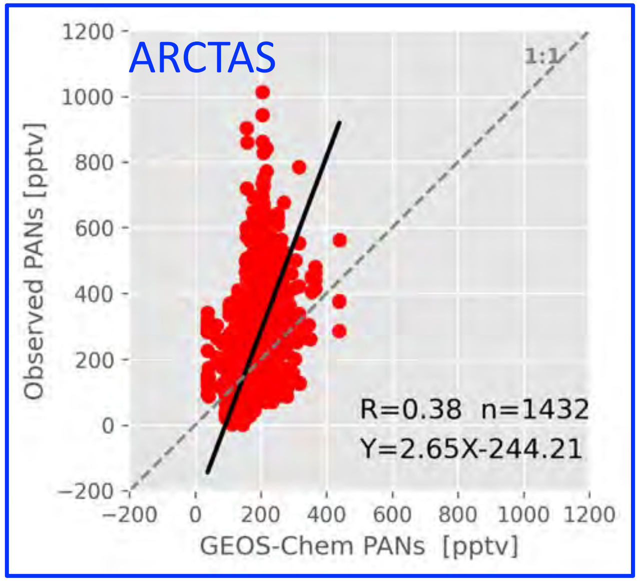
- Total PANs over high latitudes in the North Hemisphere can be as high as 3 times of GEOS-Chem simulation.

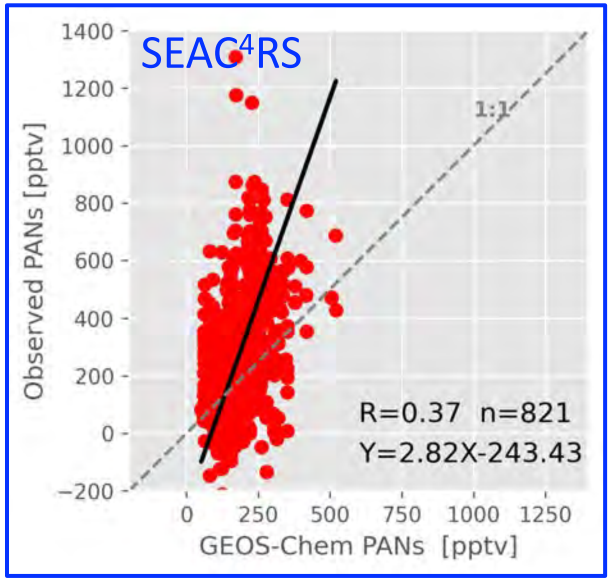


KORUS-AQ:

- Total PANs over South Korea is about 23% higher than GEOS-Chem simulation







GEOS-Chem underestimates total PANs for ARCTAS, SEAC^{4}RS and KORUS-AQ campaigns.

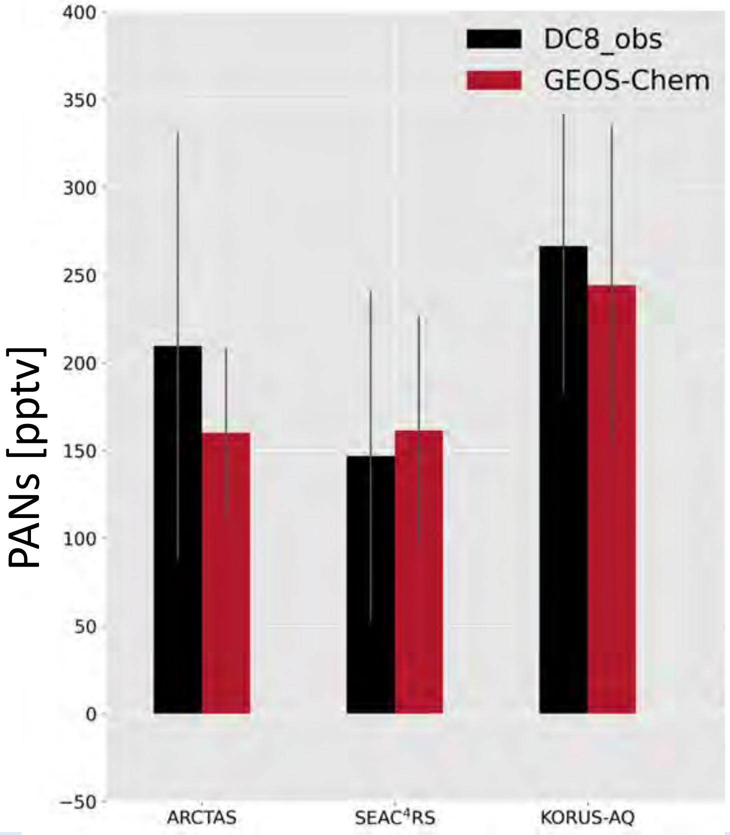
Missing PAN species in GEOS-Chem leads to total PANs underestimation

VOCs ⟹ $MCO_3 + NO_2$

- **PAN** — ARCTAS: 84%, SEAC[4]RS: 57%, KORUS-AQ: 69%
- **PPN** — ARCTAS: 5%, SEAC[4]RS: 3%, KORUS-AQ: 3%
- **APAN** — ARCTAS: 0.4%, SEAC[4]RS: 0.04% KORUS-AQ: 0.2%
- **PiBN** — ARCTAS: 0.2%, SEAC[4]RS: 0.2%
- **PBzN** — KORUS-AQ: 0.1%
- **MPAN** — Estimated from GEOS-Chem: 0.04%
- **Other PANs** — **(Estimated ARCTAS: 10%, SEAC4RS:40%, KORUS-AQ:28%)**

DC8 Total PANs

GEOS-Chem Total PANs: (PAN+PPN+MPAN)



1. GEOS-Chem’s PAN underestimation drives the majority of total PANs discrepancy in ARCTAS (80%), 20% underestimation is from missing PAN species.
2. GEOS-Chem's total PANs underestimation during SEAC[4]RS is mostly due to missing PAN species (100%).
3. In KORUS-AQ, GEOS-Chem's total PANs underestimation results from PAN underestimation(23%), and missing PAN species (77%).

Conclusions

- Most total measured reactive nitrogen in the upper troposphere is from a few individual components(NOx, PANs, HNO_3, HNO_4 and Alkyl nitrates) and PAN dominants NO_y components.
- DC8 UT NO_y consistency with MOZAIC and IAGOS supports the use of single-year observations from DC8 for assessing GEOS-Chem.
- GEOS-Chem underestimates UT NO_x from primary emissions over Southeast Asia.
- GEOS-Chem's underestimation of UT NO_y is associated with its concurrent underestimation of total PANs species.
- This PANs discrepancy is chiefly ascribed to PAN underestimation in the ARCTAS, during SEAC^{4}RS and KORUS-AQ, the primary factor is the absence of certain PAN species within the GEOS-Chem model.
- The absence of PAN species within GEOS-Chem model leads to inaccuracies in understanding NO_x distributions, impacting projections of ozone and OH concentrations.

Any Questions? Please contact Nana Wei (nana.wei.21@ucl.ac.uk) Twitter:@NanaWei_Nevaeh