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Factors Controlling Peroxyacetyl Nitrate (PAN) in Polluted and Remote Atmospheres: Insights from the KORUS-AQ and ATom Campaigns

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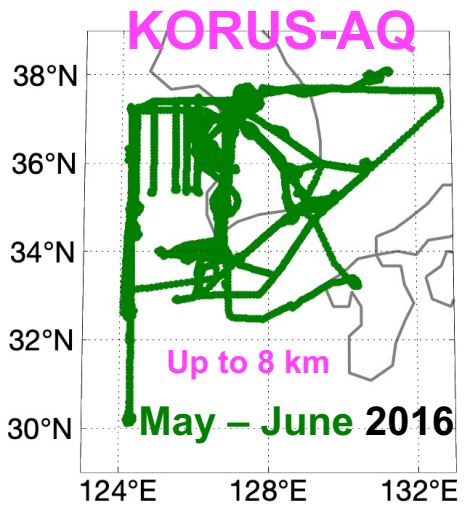
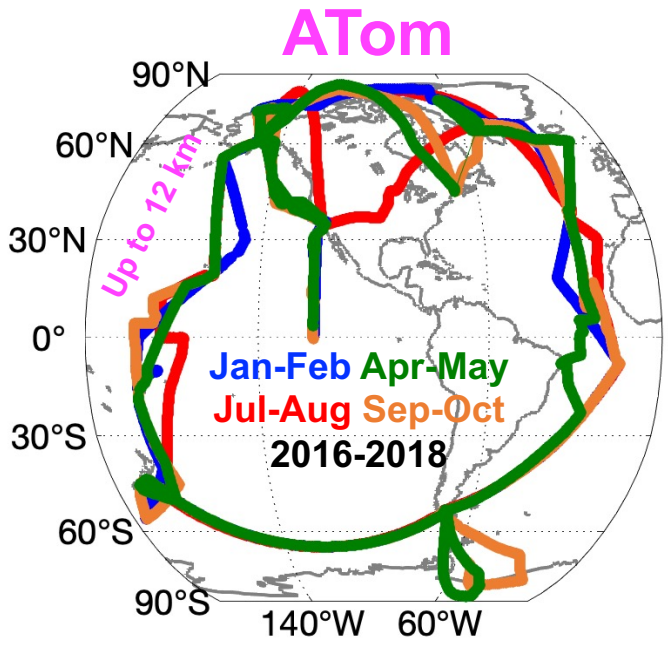
Factors controlling peroxyacetyl nitrate (PAN) in polluted and remote atmospheres: insights from the KORUS-AQ and ATom campaigns



Measurements: PAN, PAA, HO_2, acetaldehyde, acetone, ethanol, ethane, propane, CO, HCN, CH_3CN, etc.



Long-range transport at low temperature → **PAN**

Thermal decomposition during subsidence → **PAN**

$NO_x + CH_3C(O)O_2\cdot \underset{}{\overset{M}{\rightleftharpoons}}$ **PAN**

$\cdot OH/h\nu$

$VOCs \xrightarrow{\cdot OH} OVOCs$

NO_x & VOCs/OVOCs

NO_x & VOCs/OVOCs

VCP VOCs/OVOCs

VOCs/OVOCs

$CH_3C(O)O_2\cdot$ + NO → NO_2 $\underset{}{\overset{h\nu,\ O_2}{\rightleftharpoons}}$ O_3 + NO

$HO_2\cdot$, $RO_2\cdot$, RH ⇄ $\cdot OH$

$CH_3C(O)O_2H \xrightarrow{h\nu} CH_3C(O)O\cdot$

$CH_3O_2\cdot + NO \rightarrow \ldots$

VOCs/OVOCs

Populated regions

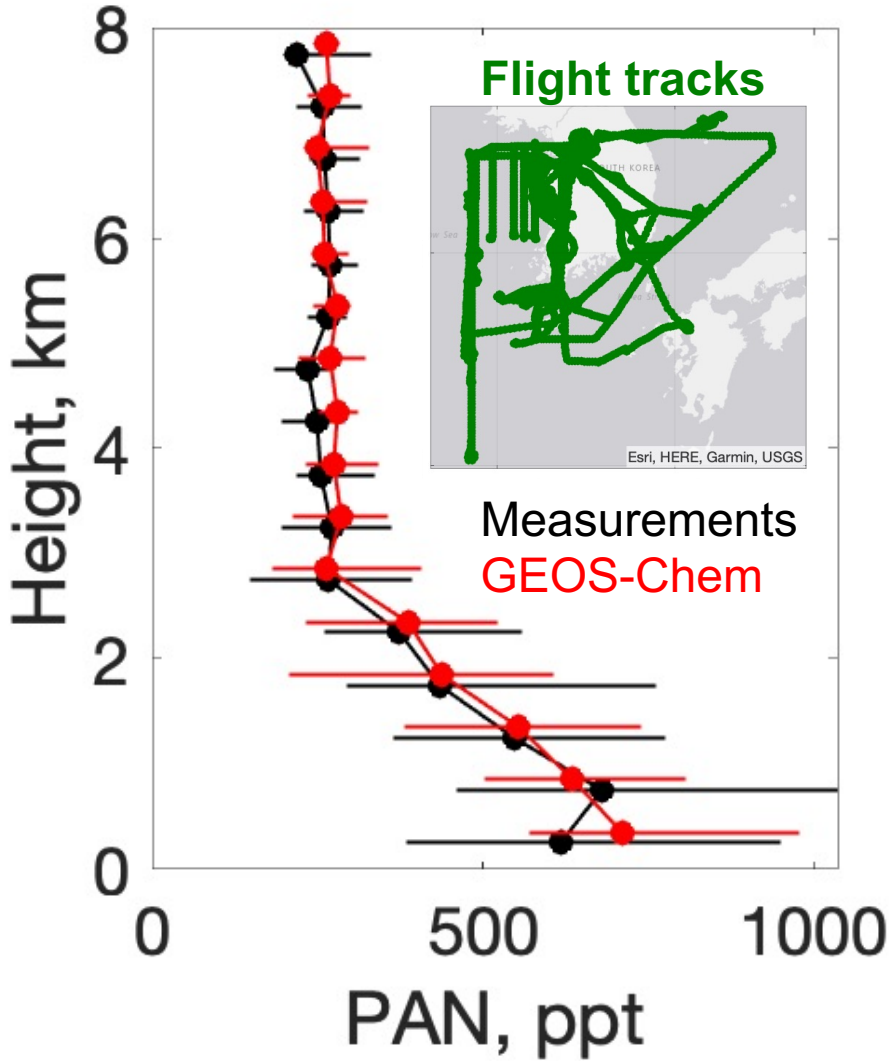
Wildfire and biogenic source regions

Remote atmosphere

GEOS-Chem simulation of KORUS-AQ and ATom	
Recent updates on relevant chemistry schemes	New **isoprene chemistry** by Bates and Jacob (2019); New **aromatic oxidation mechanism** by Bates et al. (2021); **Particle nitrate photolysis** by Shah et al. (in prep). Improved global simulation of PAN.
Meteorology	MERRA-2
Resolution	4° x 5°
Anthropogenic emissions	Global: CEDS (up to 2017), with ethane from Tzompa-Sosa et al., (2016) and propane from Xiao et al., (2008). Asia: KORUSv5 (China excluded); China: MEIC (up to 2017).
Natural emissions	**NO_x** from lightning (Murray et al., 2012) and soil (Hudman et al., 2012); **Biogenic VOCs** from MEGANv2 (Guenther et al., 2012); **Open fire emissions** from GFED4 (van der Werf et al., 2017); and **Sea salt** following Jaegle et al. (2011).

PAN in the PBL during KORUS-AQ is mainly locally produced

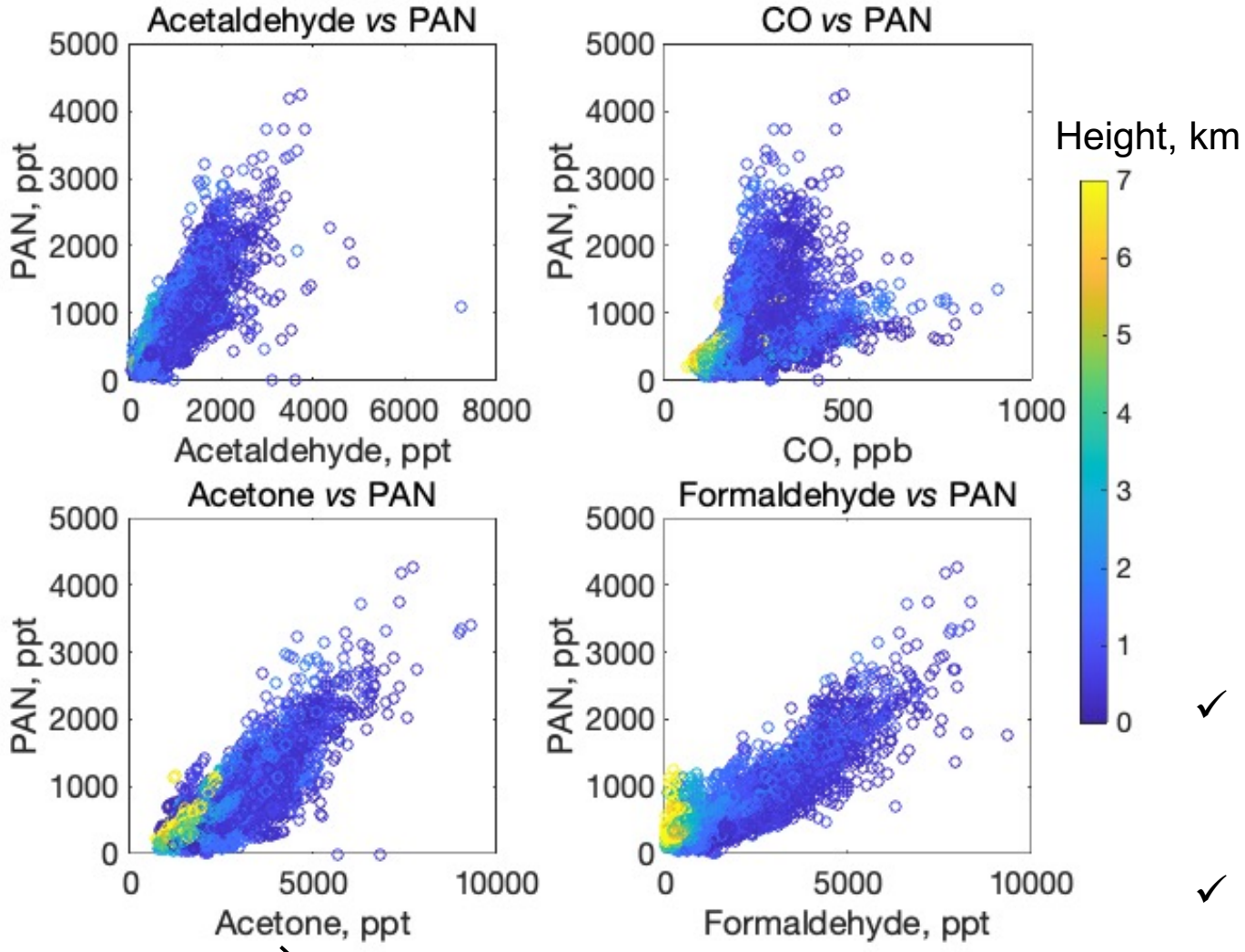
KORUS-AQ median vertical profiles

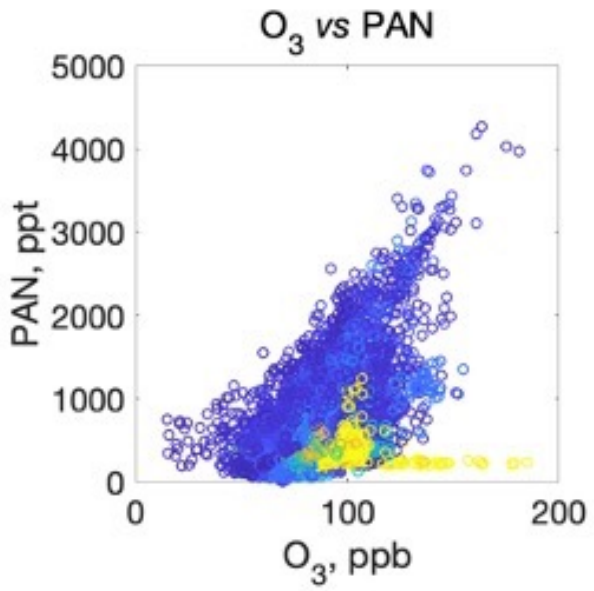


✓ GEOS-Chem reproduces PAN over the Asia Pacific Rim, which gains confidence in its simulation of Asian outflow of PAN.

[Zhai et al., in prep]

Acetaldehyde is the principal immediate precursor for PAN during KORUS-AQ



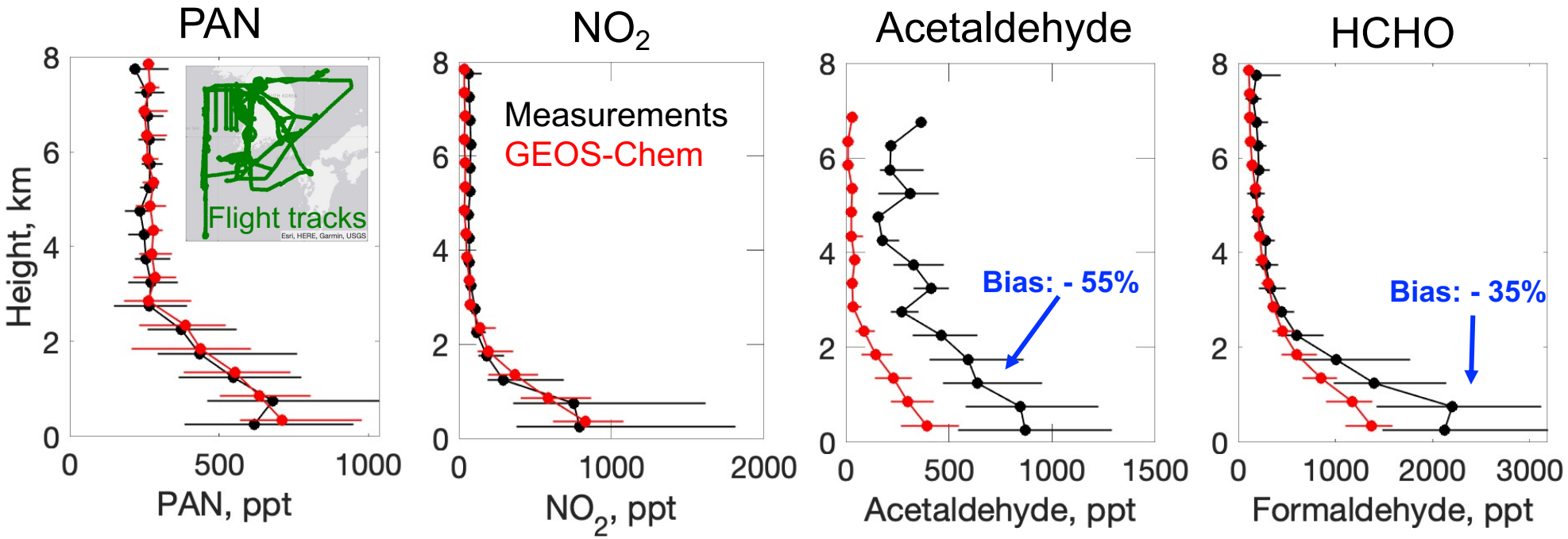


Only important in the most remote regions of the upper troposphere [Fischer et al., 2014].

- ✓ The strong correlation with acetone is due to that PAN and acetone are both products of photochemical VOC oxidation.
- ✓ PAN has high concentration only when O_3 concentration is high, but high O_3 does not necessarily result in high PAN.

[Zhai et al., in prep]

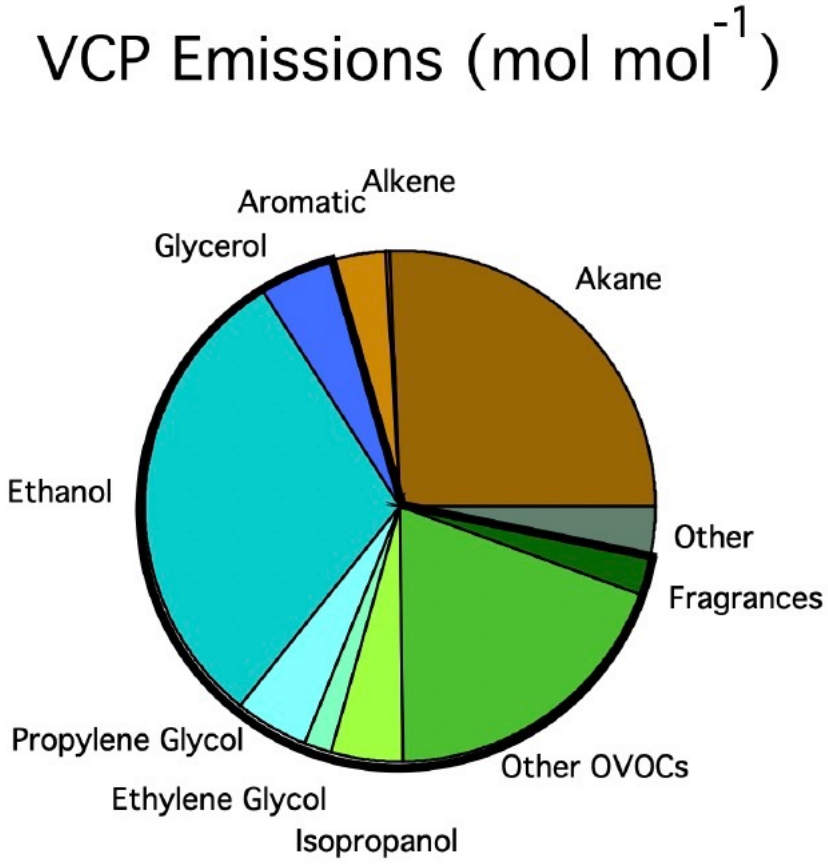
GEOS-Chem reproduces PAN and NO_x however largely underestimates acetaldehyde



✓ The VOC precursors of PAN are largely underestimated.

[Zhai et al., in prep]

Volatile Chemical Product (VCP) emissions could account for a large portion of the missing VOCs

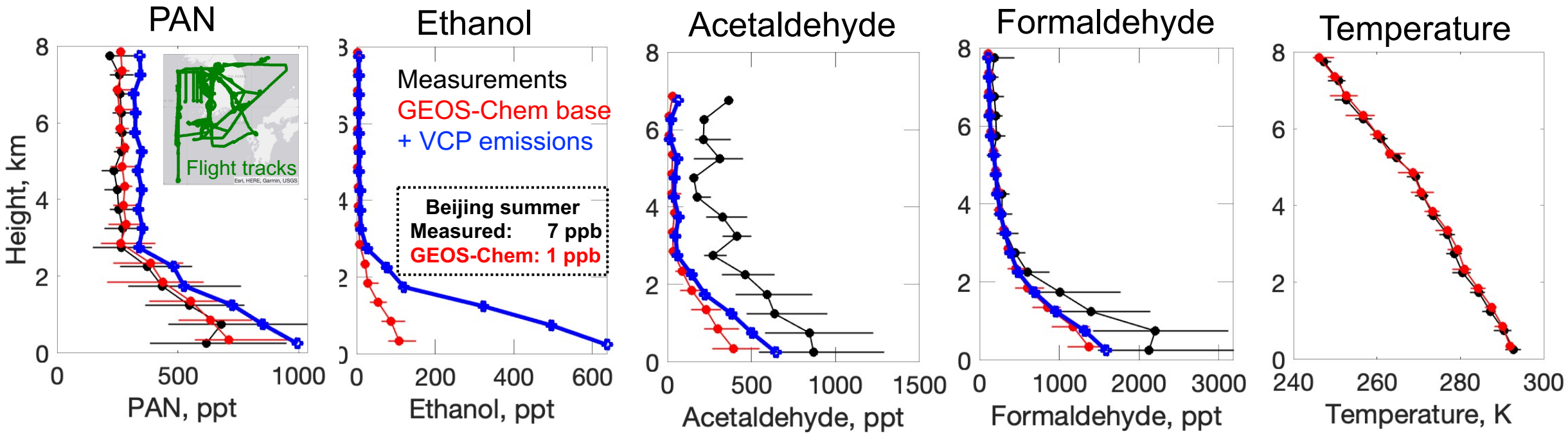


[Coggon et al., 2021]

- ✓ KORUSv5 does not contain VCPs from personal care products, cleaning agents, etc., which accounts for a large portion of VOC emissions in urban environments [McDonald et al., 2018].
- ✓ Alkanes, alkenes, and ethanol are the main precursors for acetaldehyde [Millet et al., 2010].

Kelvin H. Bates introduced into GEOS-Chem global population-scaled VCP ethanol, ethane, propane, lumped >=C4 alkanes, toluene, lumped >=C3 alkenes, limonene, methanol, formaldehyde, acetone, and methyl ethyl ketone following McDonald et al. (2018) and Coggon et al. (2021).

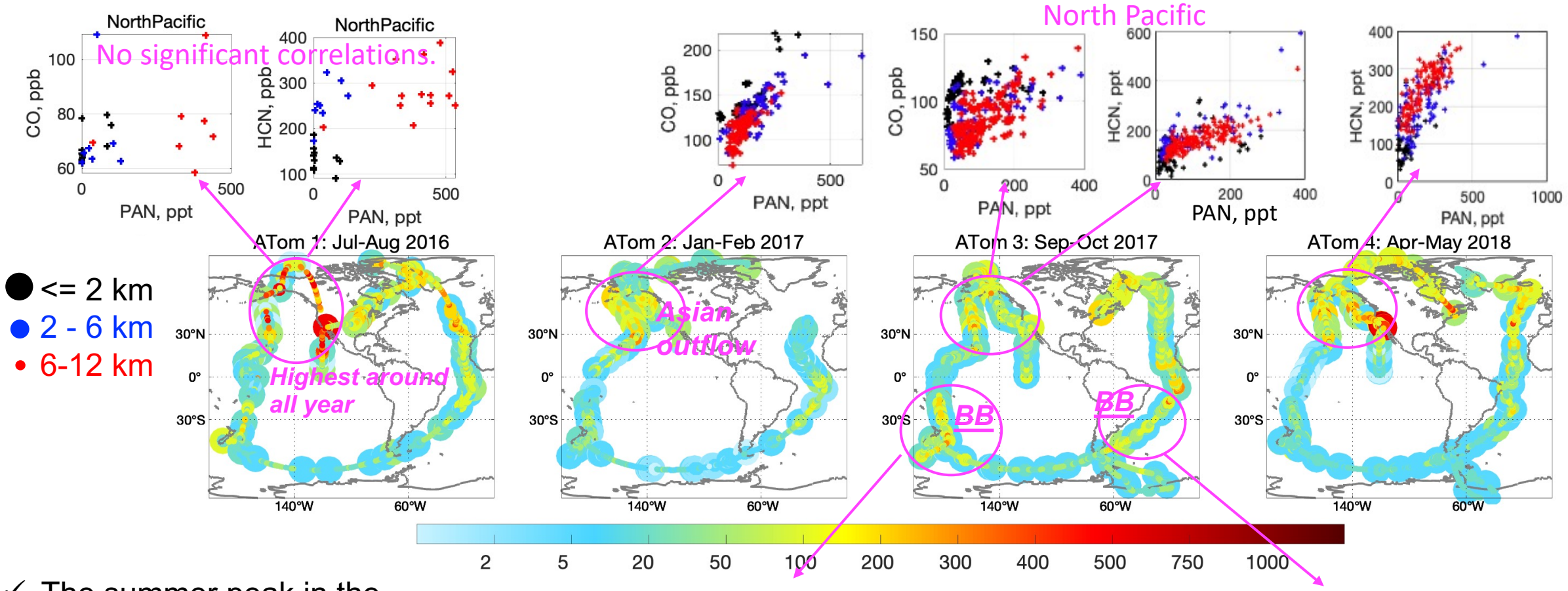
Adding VCP emissions brings GEOS-Chem OVOCs (including acetaldehyde) closer to measurements however leads to PAN overestimate



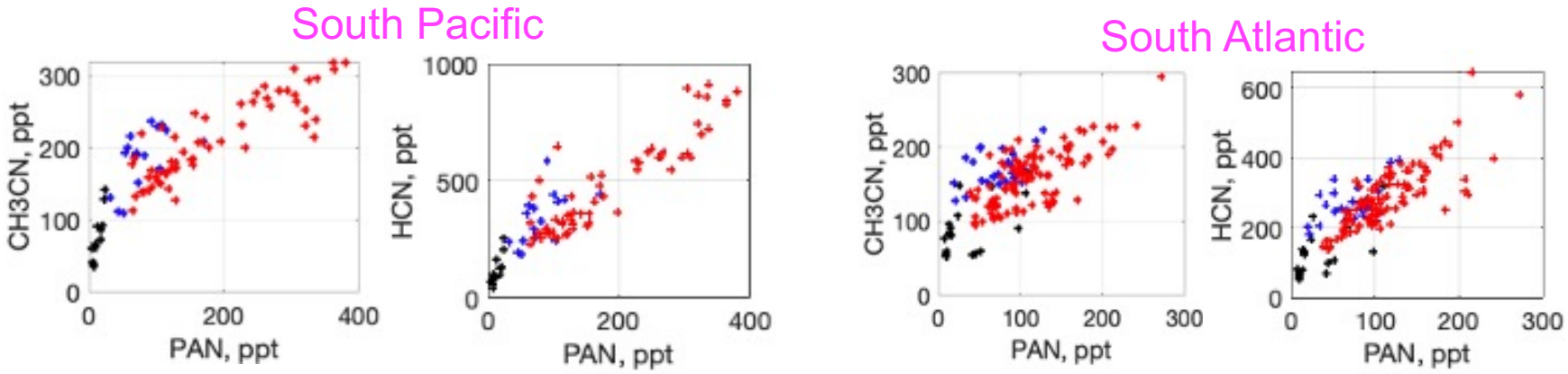
- ✓ No obvious temperature bias exist that could explain the overestimate of PAN.
- ✓ Insufficient dry deposition in the model could be one factor driving PAN overestimate.
- ✓ Uncertainties in chemical kinetics could be another factor for the overestimate of PAN.

[Zhai et al., in prep]

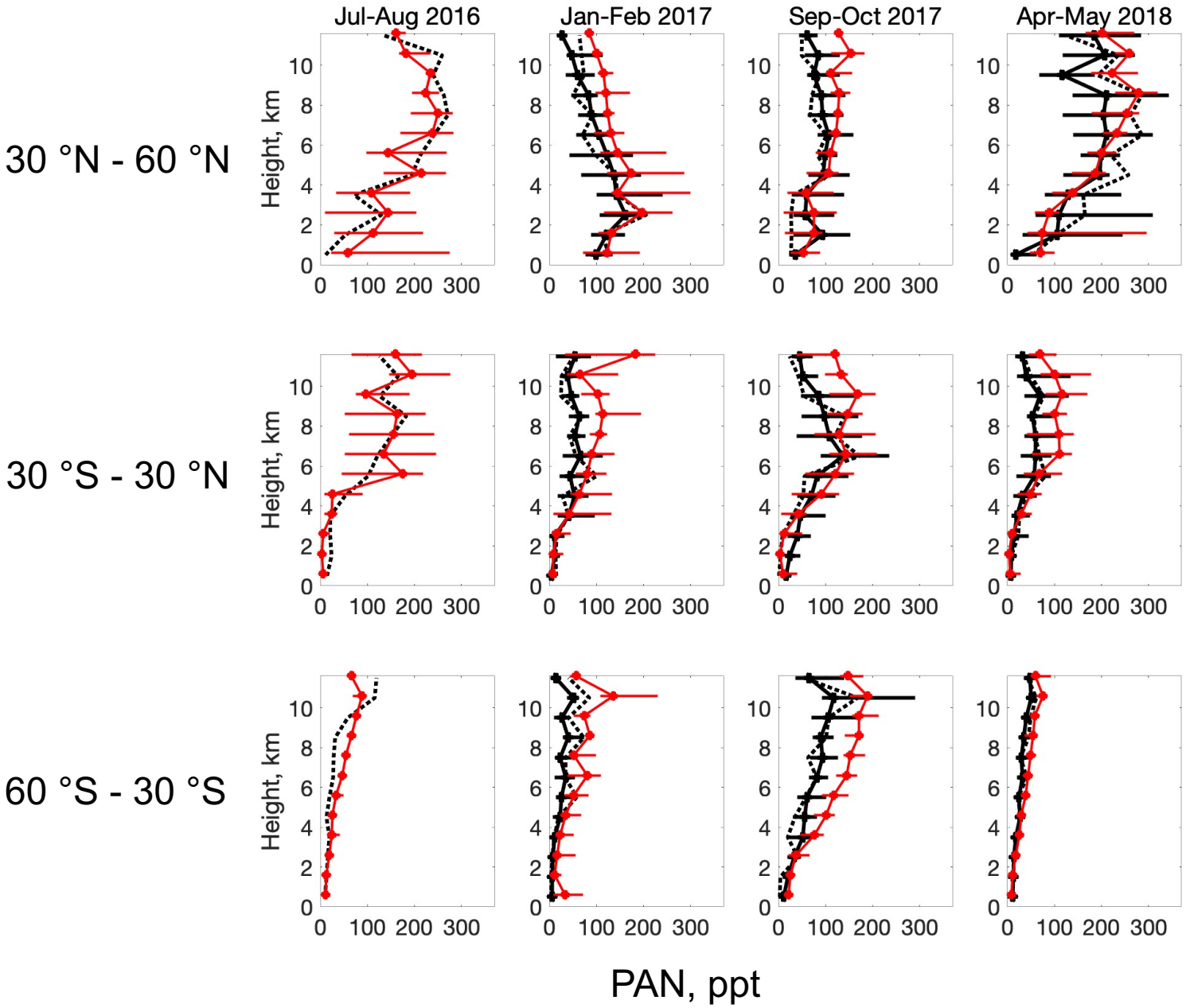
PAN measured during ATom: global distribution, seasonality, and sources



✓ The summer peak in the upper troposphere over the northern hemisphere could be due to strong vertical transport of aged air to the upper troposphere.



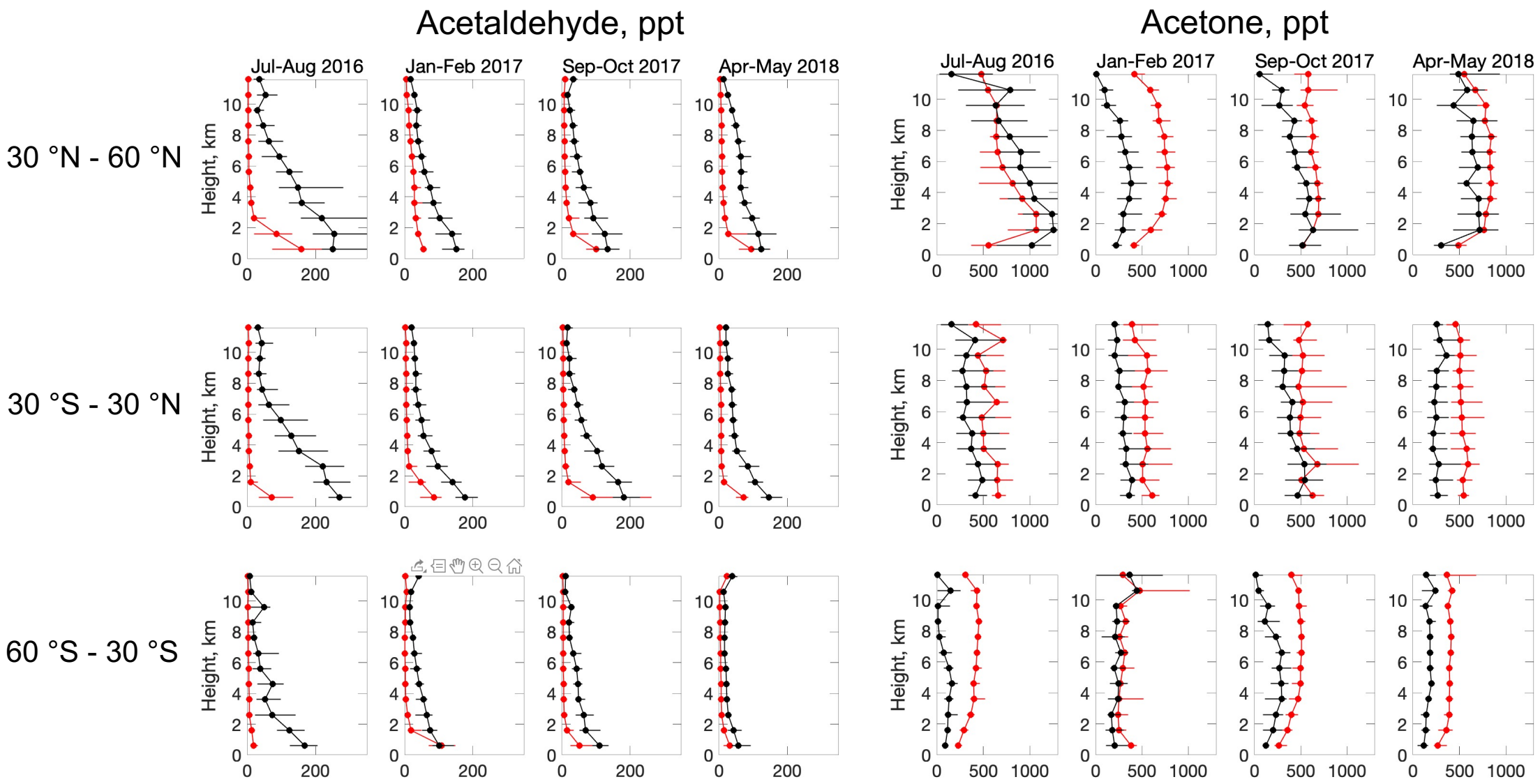
GEOS-Chem reproduces the main features of global PAN



Measurements
Solid: GTCIMS PAN
Dotted: GCECD PAN
GEOS-Chem

✓ GEOS-Chem overestimates free tropospheric PAN over the tropics and the southern hemisphere.

GEOS-Chem underestimates acetaldehyde and overestimates acetone



✓ In the remote free troposphere, the overestimate of acetone could drive the overestimate of PAN.

Conclusions

- ✓ PAN in the planetary boundary layer during KORUS-AQ is mainly locally produced.
- ✓ Acetaldehyde is observed and simulated as an important precursor for PAN during KORUS-AQ.
- ✓ The GEOS-Chem model reproduces ATom PAN however underestimates acetaldehyde and overestimates acetone almost everywhere during ATom.

Further investigations needed:

- Better understanding of model representation of the deposition, formation, and decomposition of PAN.
- Better understanding of the distributions and budgets of the main precursors of PAN (acetaldehyde, acetone, ethanol, etc.).