Consequences of insufficient production of temporary NO_x reservoirs on ozone production in models during KORUS-AQ

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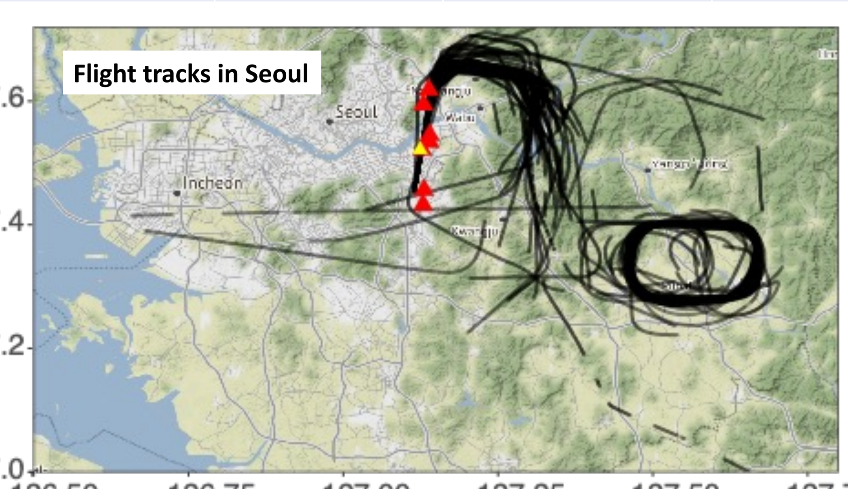
Motivation

The advent of geostationary satellites, starting with GEMS over South Korea, offer the potential for additional insight into urban air quality. In preparation for these satellites, the joint NIER-NASA KORUS-AQ field campaign in 2016 obtained a large dataset for understanding local air quality and the contribution of local emissions to ozone and $PM_{2.5}$ pollution.

- Models partitioned NO_x primarily into inorganic nitrate (HNO_3 + nitrate aerosol) while observations suggest that acyl peroxy nitrates (PNs) should be an important sink.
- Models tended to produce ozone too efficiently, which may be due to insufficient alkyl/multifunctional nitrate (ANs) production.
- Models are unable to simulate the transport of NO_x away from the urban center and its impact on ozone production downwind.

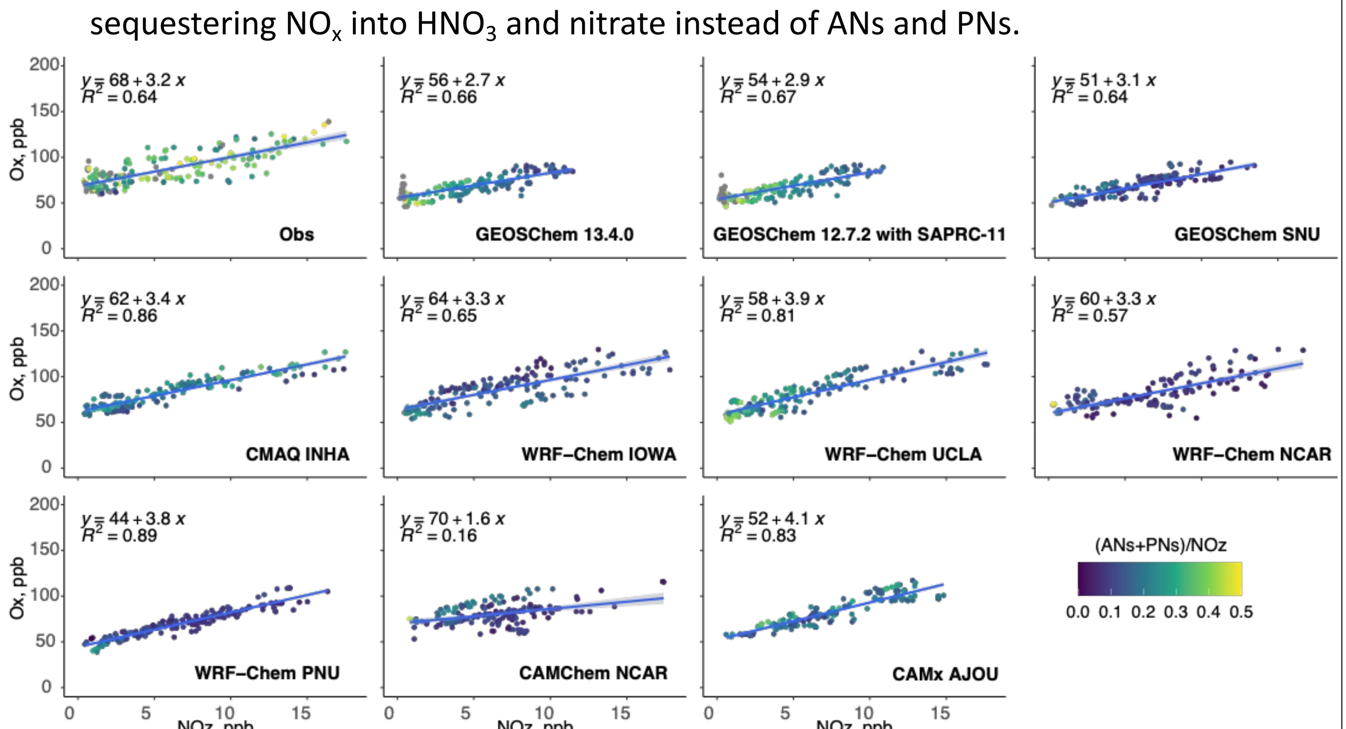
Model	Institution	Resolution	Chemistry	AN yield from aromatics, and isoprene
GEOS-Chem 12.7.2	Travis et al., 2022	0.25°x0.3125°	12.7.2 Tropchem with SAPRC-11 (Yan et al., 2018)	2.7% BENZ, 7.4% TOLU, 9.8% XYLE, 9% ISOP
GEOS-Chem 13.4.0	This study	0.25°x0.3125°	13.4.0 Fullchem	0% BENZ/TOLU/XYLE ~12-15% ISOP
GEOS-Chem v12.7.2	Seoul Natl U.	0.25°x0.3125°	12.7.2 Tropchem	0% BENZ/TOLU/XYLE, 9% ISOP
CAM-Chem	NCAR	0.47°x0.63°	MOZART-T1	0% BENZ/TOLU/XYLE, 8% ISOP
CAMx v6.2	Ajou U.	27x27km	SAPRC99	1.1% ARO1, 0.9% ARO2
WRF-Chem v4.0	NCAR	15x15km	MOZART-4 + updates from Knote et al., 2014	0% BENZ/TOLU/XYLE, 8% ISOP
WRF-Chem v4.0	Pusan Natl U.	27x27km	RACM-ESRL	5% TOLU+BENZ, 5% XYLE/C8 aromatics, 4.6% ISOP
WRF-Chem v3.6.1	U. Of Iowa	4x4km	Pfister et al., 2014	13% paraffinic carbon atoms, 15% ISOP
WRF-Chem v3.6.1	UCLA	4x4km	RACM-ESRL	5% TOLU+BENZ, 5% XYLE/C8 aromatics, 4.6% ISOP
CMAQ v5.0.1	Inha U.	9x9km	CB05-TU	14% from TOLU, 13% from paraffinic carbon atoms, 8.8% ISOP



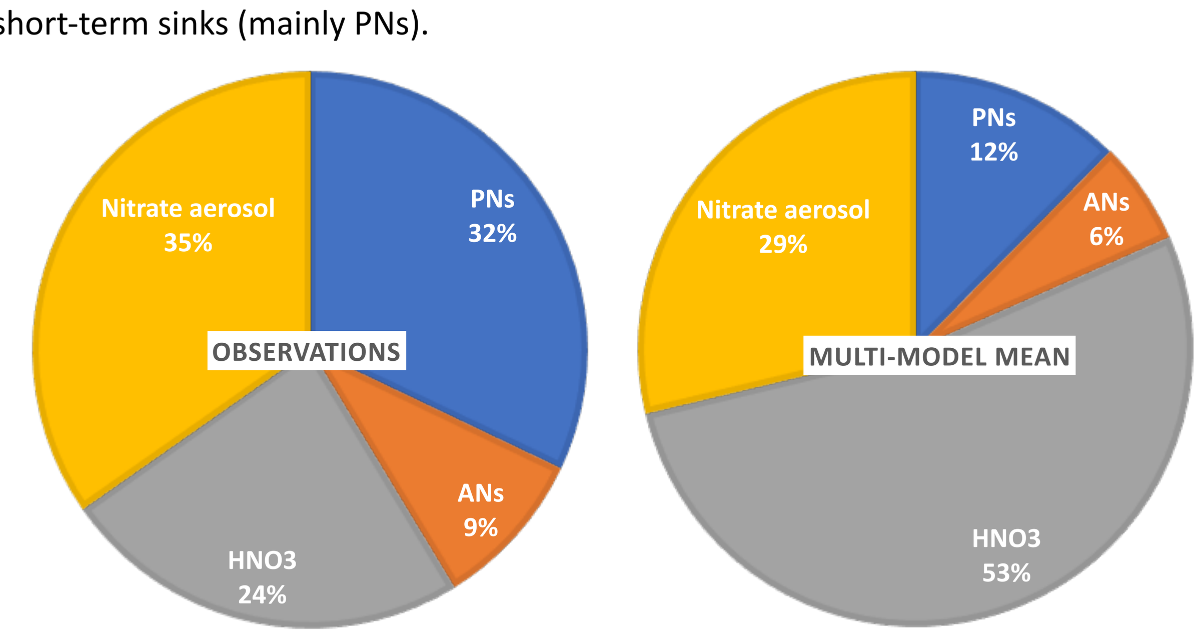
- KORUS-AQ observations are described in Crawford et al. (2021) and available at doi: 10.5067/Suborbital/KORUSAQ/DATA01 and include NO_x, NO_y from NCAR CL PNs and ANs from TDLIF, VOCs from PTR-MS and WAS.

Model comparison of O_x vs. NO_z

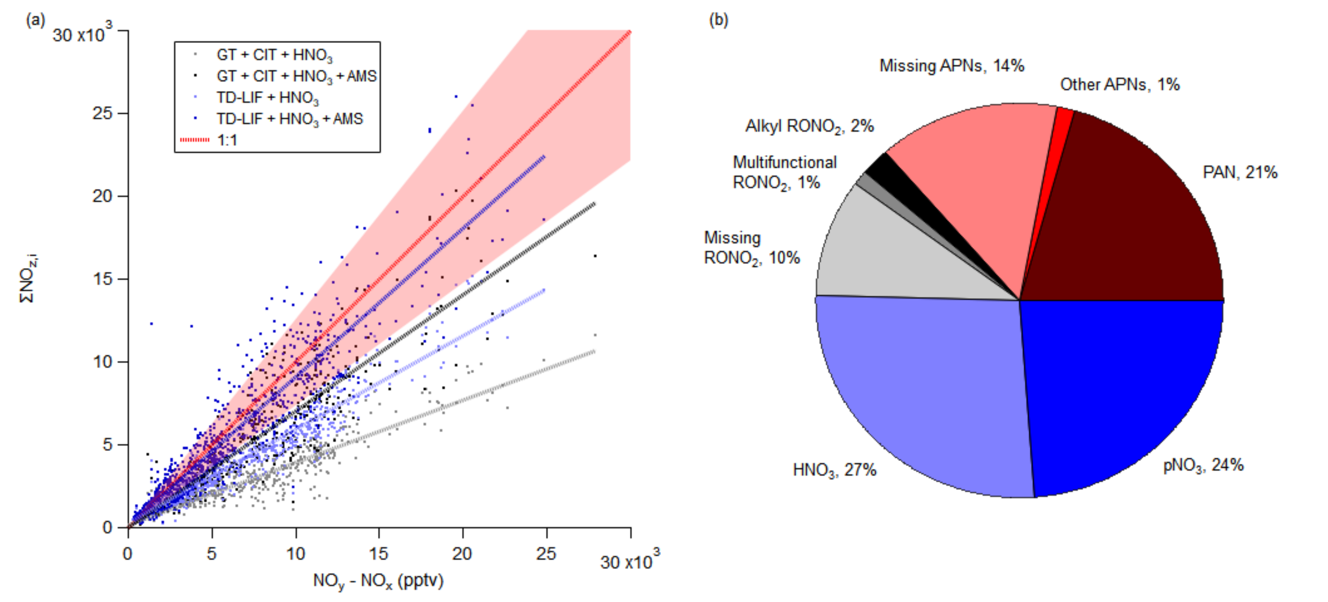
- Most models produce O_x at approximately the right efficiency (~3), but while sequestering NO_x into HNO_3 and nitrate instead of ANs and PNs.



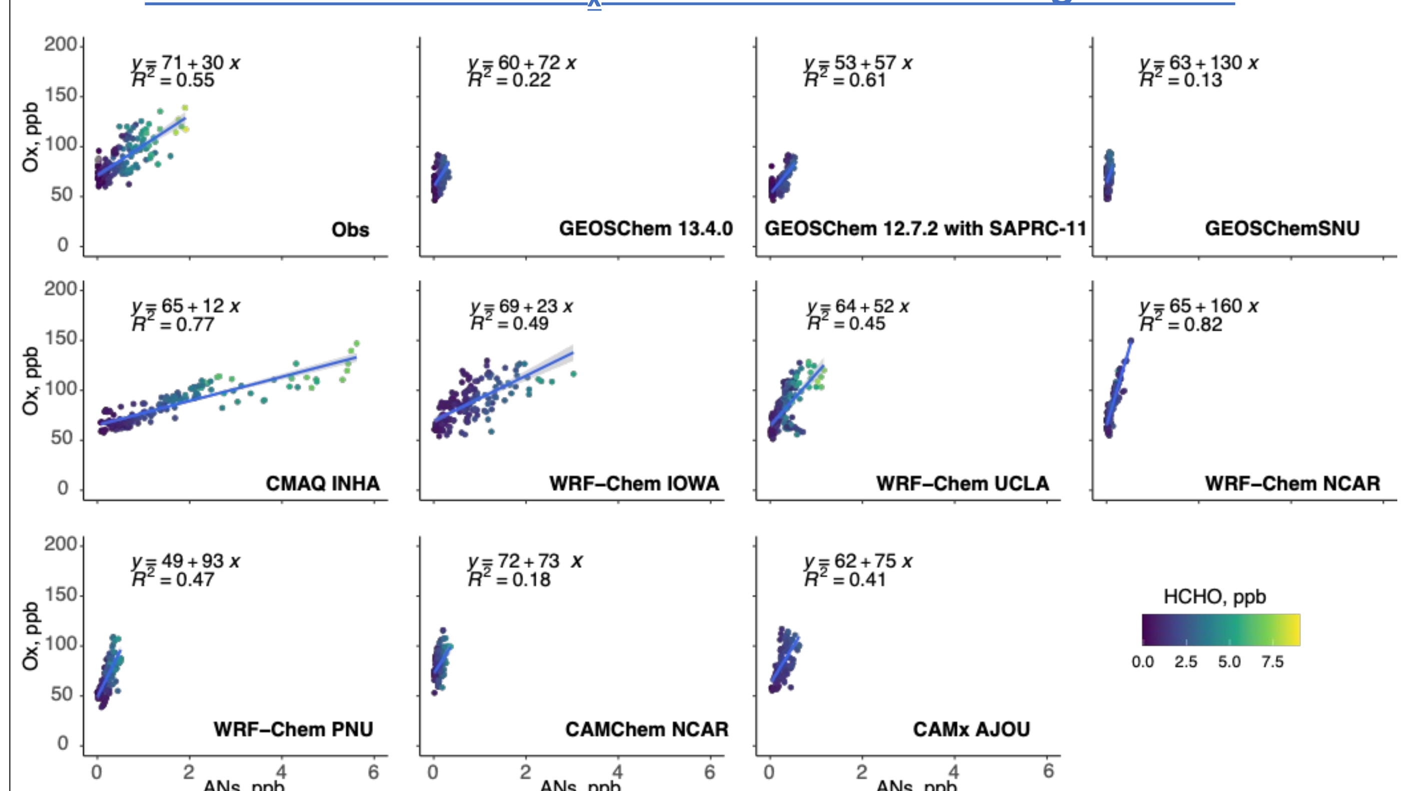
- The model ensemble tends to underestimate the observed PAN and AN fractions with large intermodel variability (Park et al., 2021)
- Models overestimate HNO_3 and underestimate ANs + PNs by a factor of two. The NO_x sequestered in permanent (HNO_3, nitrate, some of ANs) is overestimated compared to short-term sinks (mainly PNs).



Observations of NO_y are consistent with unobserved ANs/PNs



Model simulations of O_x vs. ANs show wide disagreement

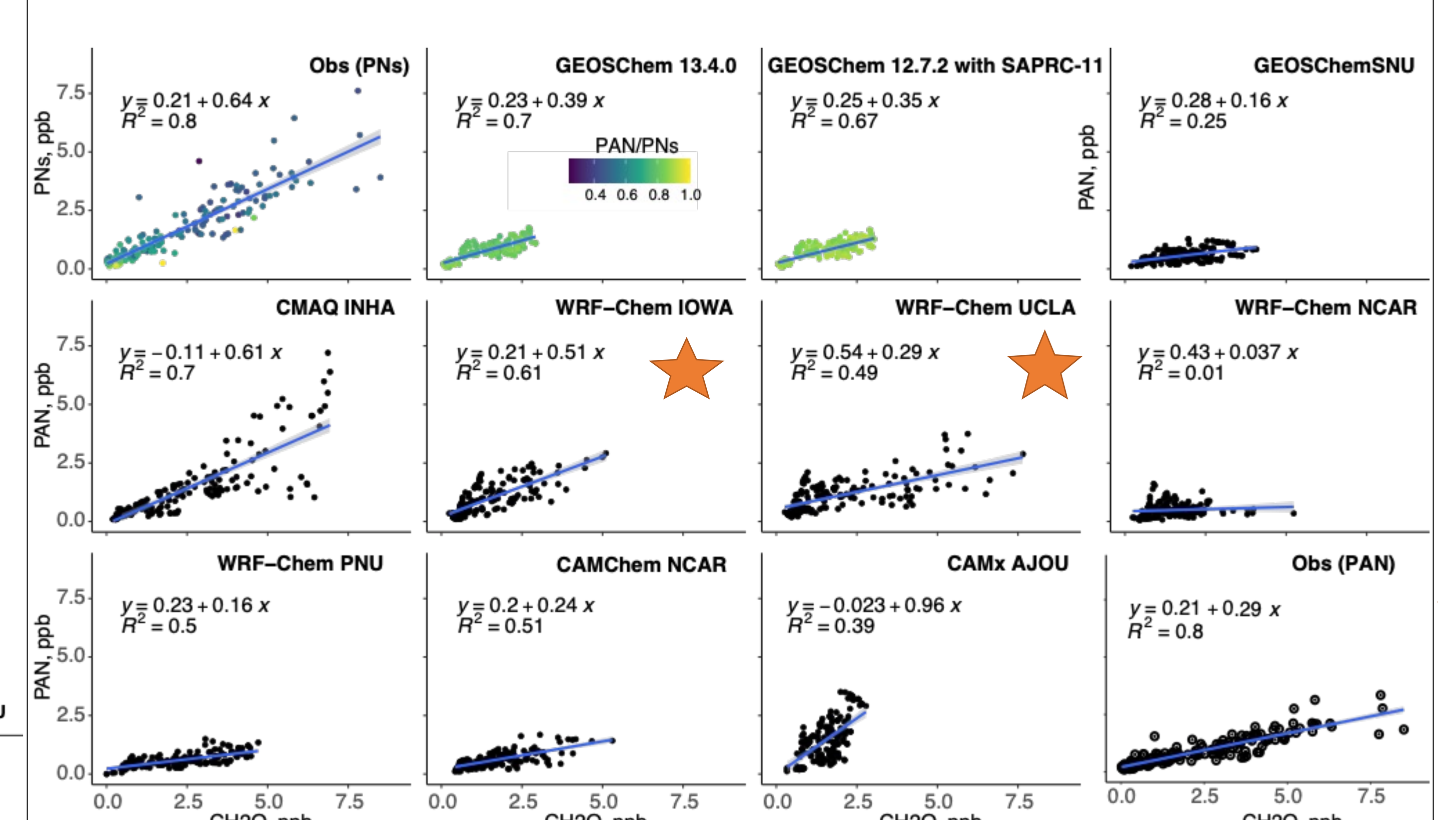


- *Models have very different yields of ANs from aromatic species and isoprene.*
- *The relationship of O_x vs. $RONO_2$ is similar to other urban regions.*

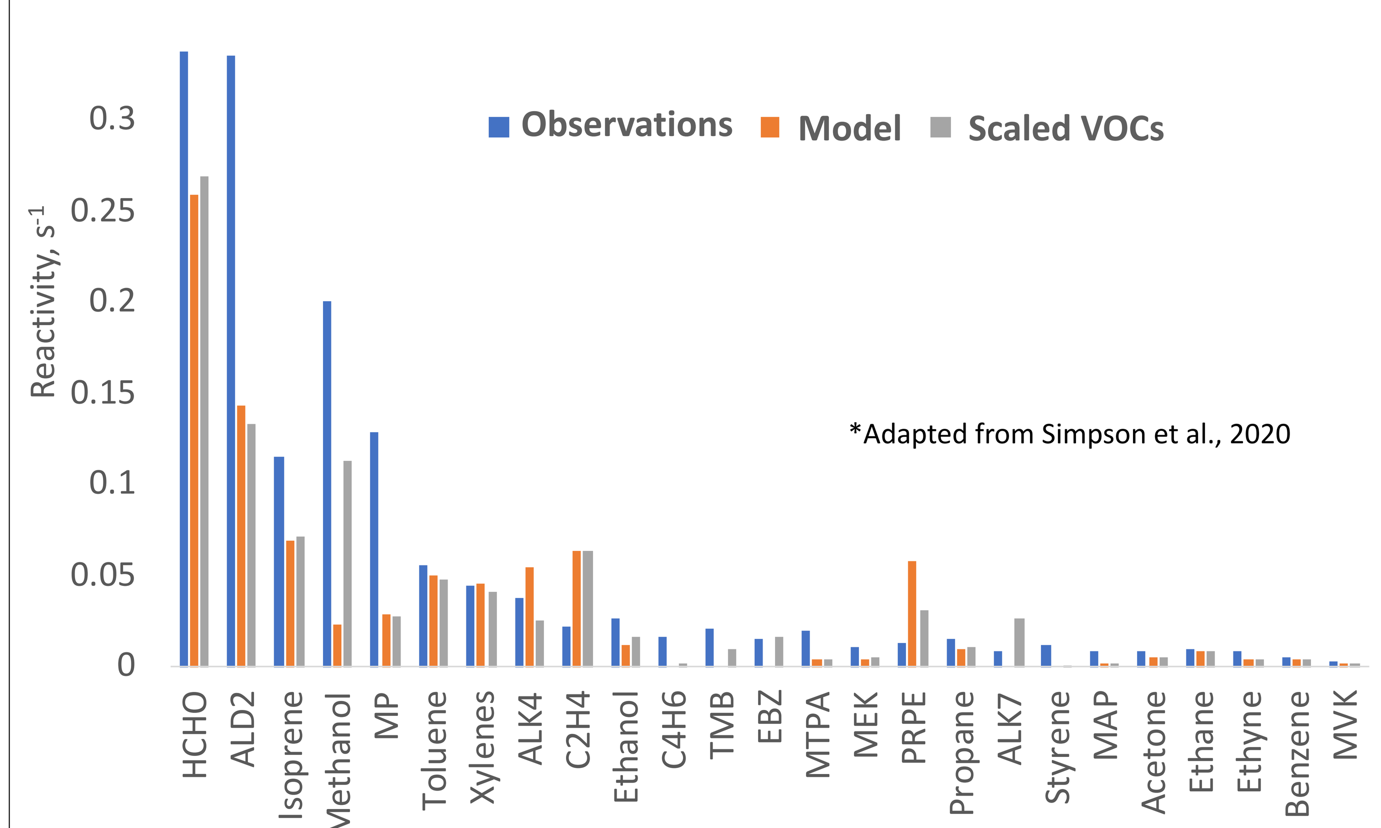
Location	Slope O_x vs $\Sigma RONO_2$	Reference
Seoul	30	This study
Mexico City, Airborne	17	Perring et al., 2009
Mexico City, Ground	27	Farmer et al., 2011
Hong Kong	47	Xiaopu, 2018
Houston	41	Rosen et al., 2004
Denver	13	Kenagy et al., 2020

PAN/PNs decreases in the observations with increasing CH2O

- Models are unable to reproduce the relationship between CH2O and PAN/PNs.



- Observed HCHO can be reproduced in a box model with observed VOCs (Schroeder et al., 2020).
- Model underestimates primary VOC reactivity by ~40% and is missing associated production of secondary species (HCHO, ALD2, etc).
- Base model overestimates alkenes. Improving the model requires increasing most other VOCs by large amounts (almost an order of magnitude for methanol).
- ***Preliminary scaling needs additional refinement based on observations.***



*TMB = trimethylbenzenes, *EBZ = ethylbenzene, *ALK4 = >C4 alkanes, ALK6 = >C6 alkanes

Preliminary GEOS-Chem improvements to AN/PN/VOC simulation

PNs

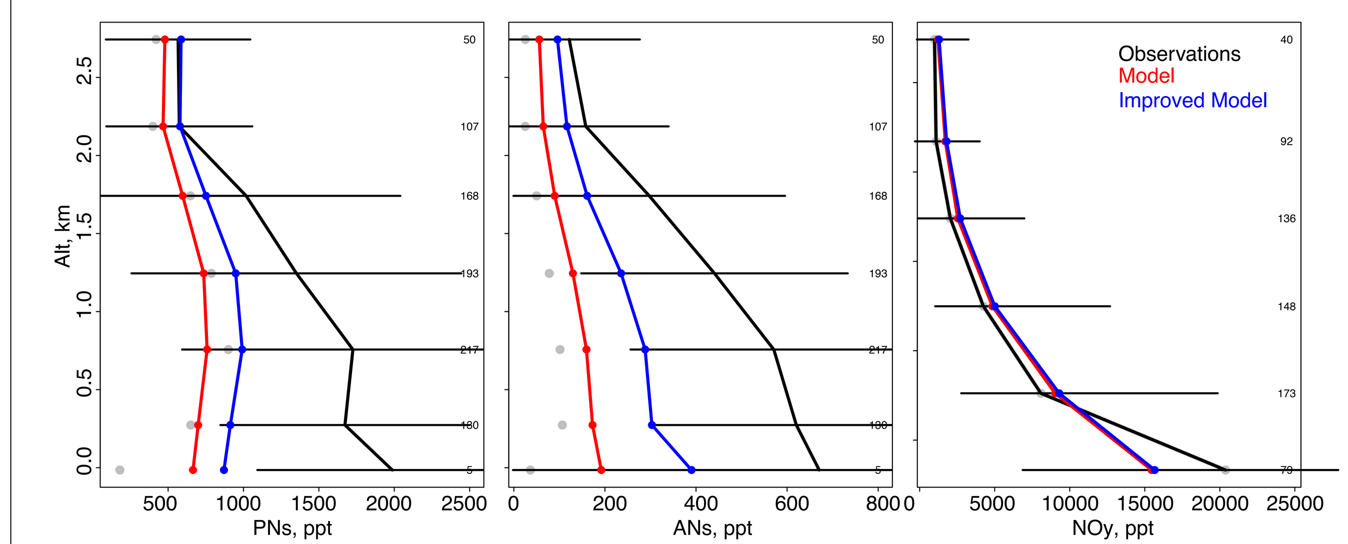
1. 1,3-butadiene (C4H6) chemistry to produce peroxyacryloyl nitrate (APAN) from the MCM.
2. Glycolaldehyde (GLYC) chemistry to produce peroxyhydroxyacetic nitric anhydride (PHAN) from the MCM.

ANs

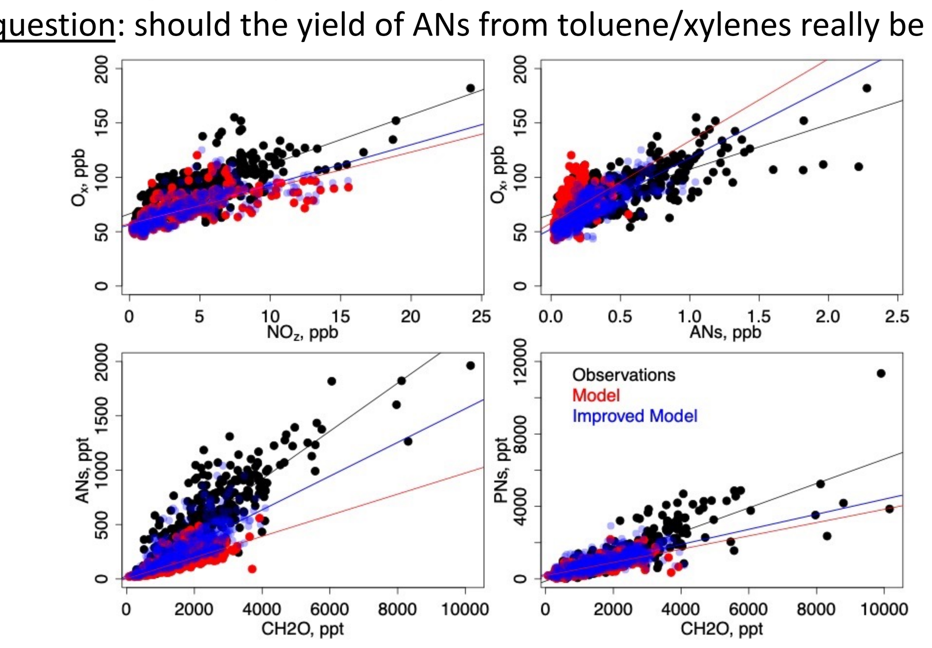
1. >C6 alkane (ALK7) chemistry from Lurmann et al., 1986. Alkyl nitrate (R7N2) yield of 30% (parameterized as heptane).
2. Propene nitrates, 2-oxopropyl nitrate (NOA) and 2-hydroxypropyl nitrate (PROLNO3), from propene + NO3.

Other VOCs

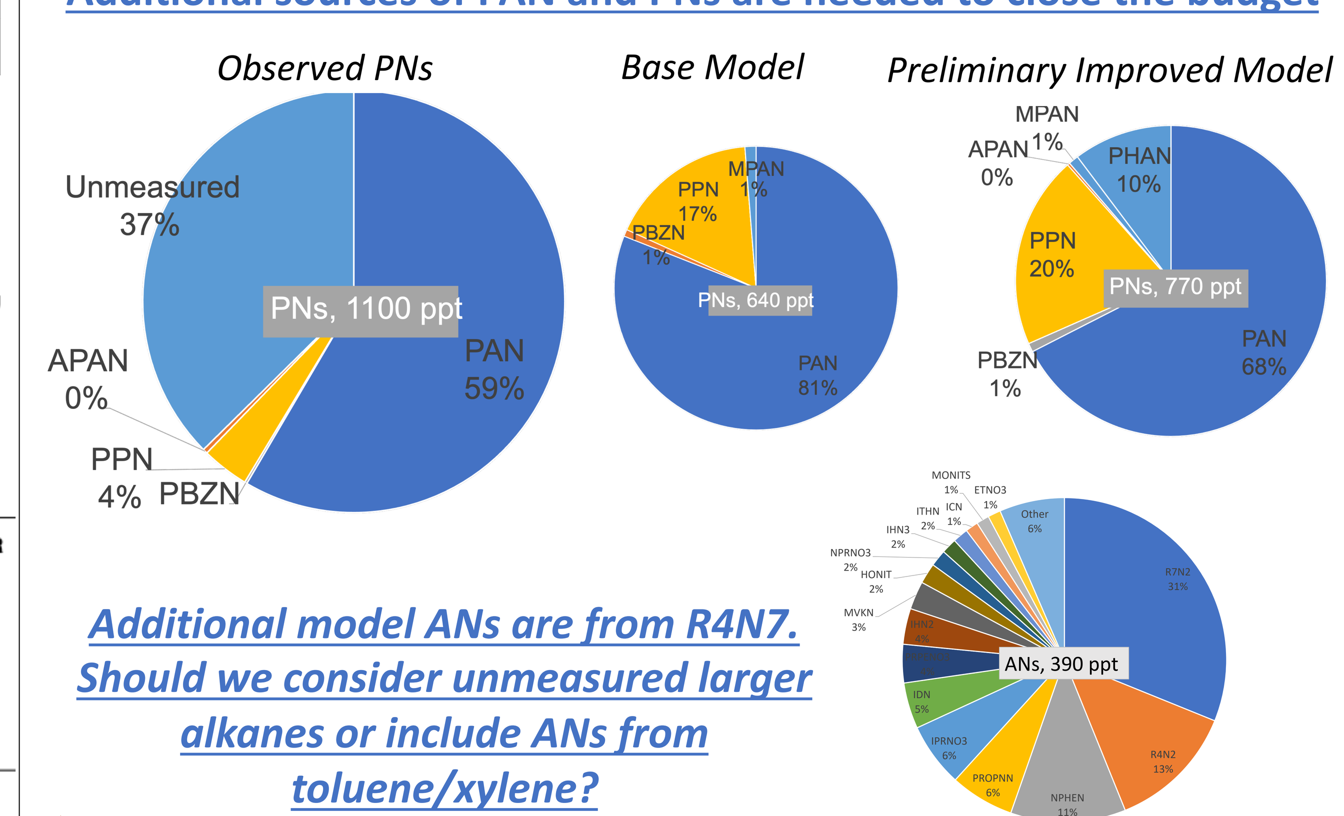
1. Styrene chemistry from the MCM.
2. Ethylbenzene (EBZ) and trimethylbenzene (TMB) chemistry from Bates et al. (2021).



- Very preliminary model improvements improve PNs due to PHAN from GLYC and ANs due to R4N7 from ALK7 but more ANs/PNs are needed.
- F0AM modeling will help us identify additional PNs/ANs.
- Key question: should the yield of ANs from toluene/xylenes really be 0%?



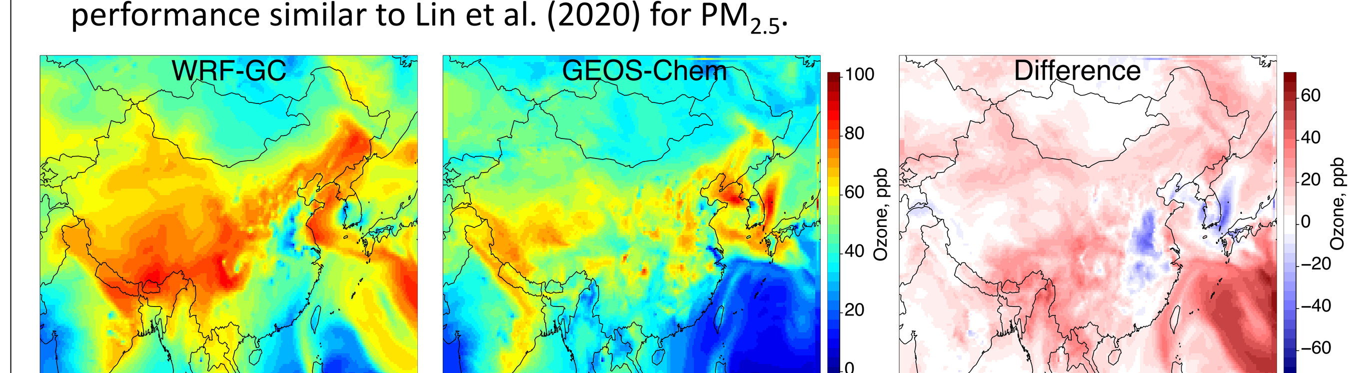
Additional sources of PAN and PNs are needed to close the budget



Additional model ANs are from R4N7. Should we consider unmeasured larger alkanes or include ANs from toluene/xylene?

Higher resolution (~4km) appears necessary to simulate the range of observed CH_2O

- Improved chemistry from GEOS-Chem 13.4.0 will be incorporated into WRF-GC and run at higher spatial resolution (~4km).
- Example comparison day (0.25° X 0.3125°) shows higher ozone in WRF-GC than in GEOS-Chem. Next step is a thorough comparison of WRF-GC vs. GEOS-Chem performance similar to Lin et al. (2020) for $PM_{2.5}$.



**Thanks to Haipeng Lin for helping me get WRF-GC up and running!*

Key takeaways

- Observations of NO_y support the presence of unmeasured PNs/ANs.
- Models vary widely in their simulations PNs and ANs, while producing ozone at the observed rate.
- This degrades confidence in their ability to simulate NO_x transport from the source regions to the surrounding area.

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