Organic nitrates and ozone during SENEX

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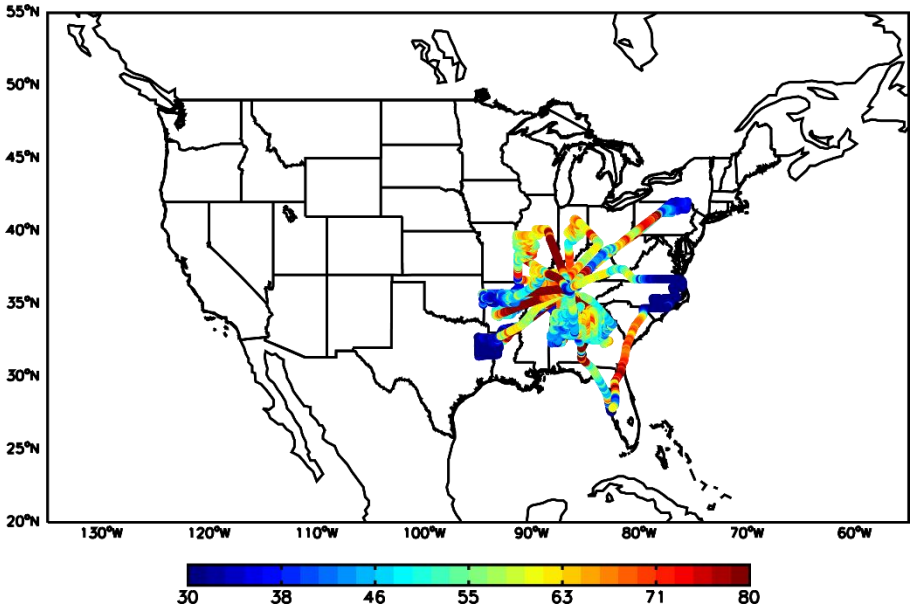
Funding from NOAA CPO

SENEX (NOAA)

June 3rd to July 10th

SENEX (Southeast) flight track

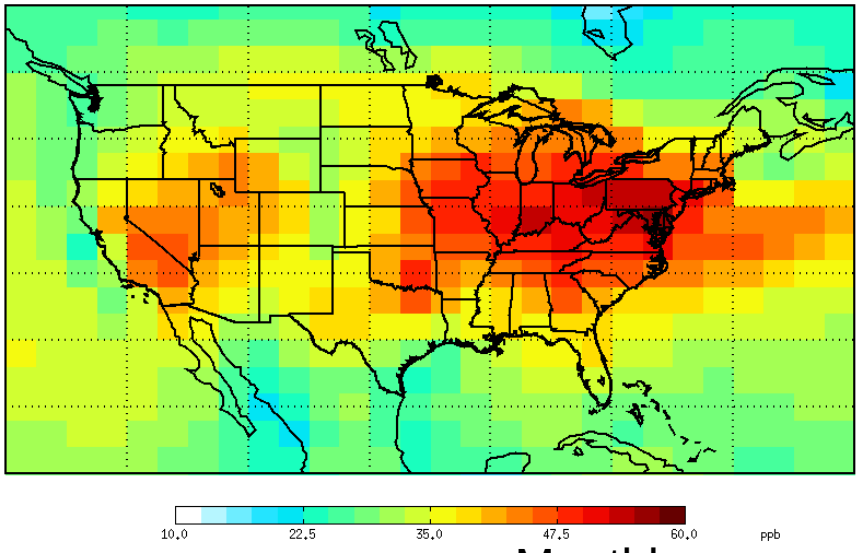


Colored by ozone

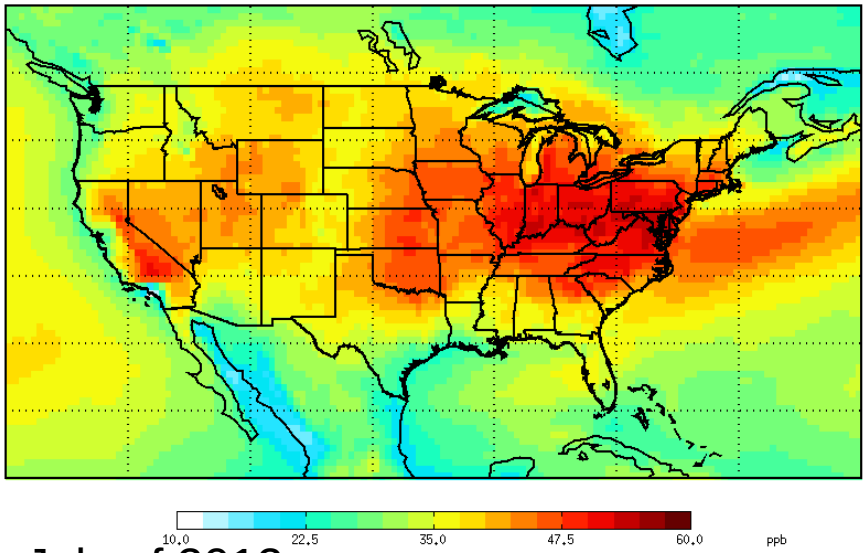
GFDL AM3 model configuration for SENEX

- Fully coupled chemistry-climate model
  - Parameterizes aerosol activation into liquid cloud droplets
  - solves both tropospheric and stratospheric chemistry over the full domain
- Nudging wind with GFS meteorological field
- Global high resolution (50 x 50 km) and coarse resolution (200 x 200 km)
- MEGAN biogenic emissions (process-based emission)
- Anthropogenic emissions use RCP 8.5 scenario (0.5 x 0.5 degree)
- New isoprene chemistry (Mao et al., 2013 JGR)

C48 (200 x 200km)

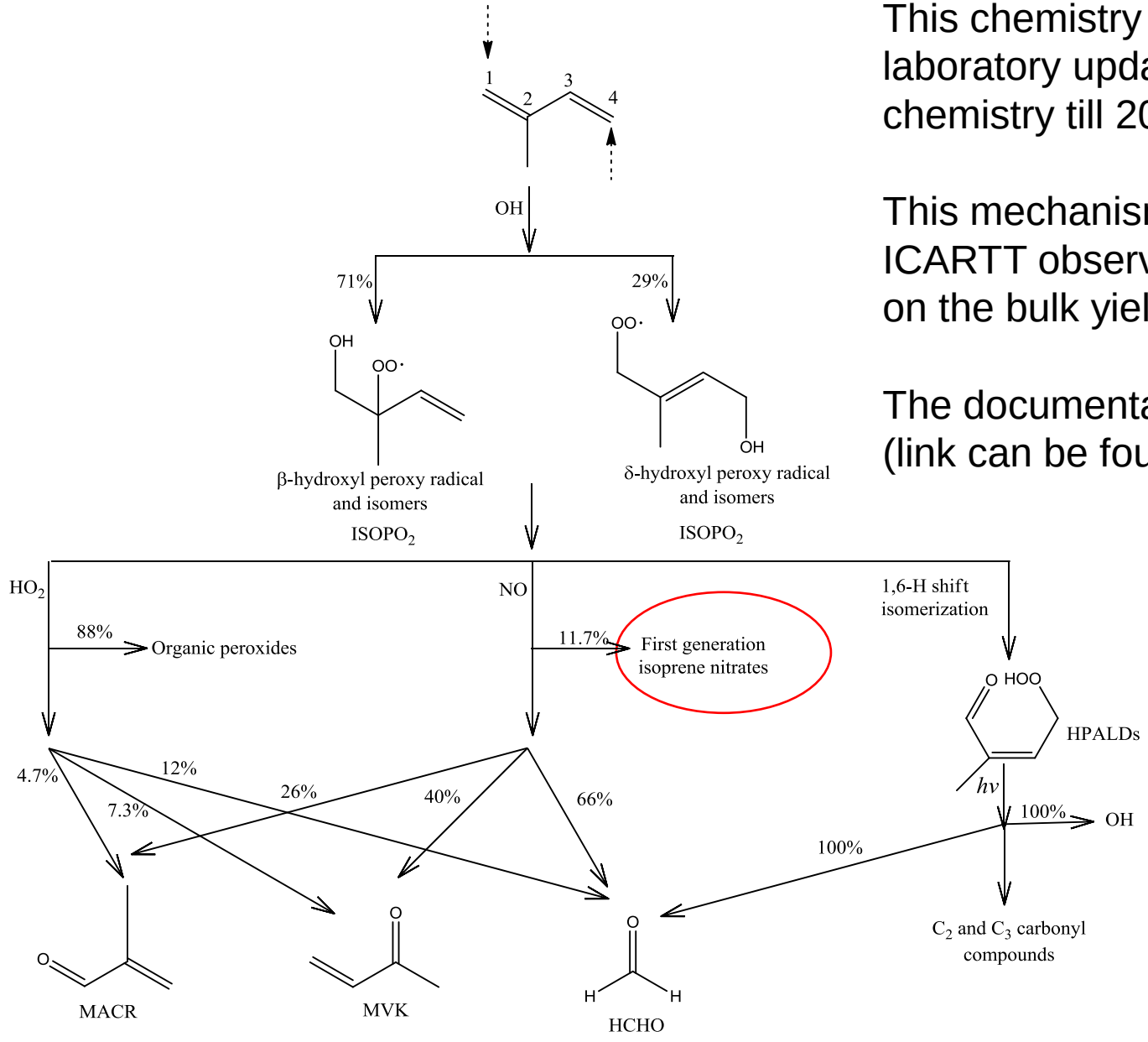


C180 (50 x 50km)



Monthly mean ozone for July of 2012

A new isoprene chemistry for global models



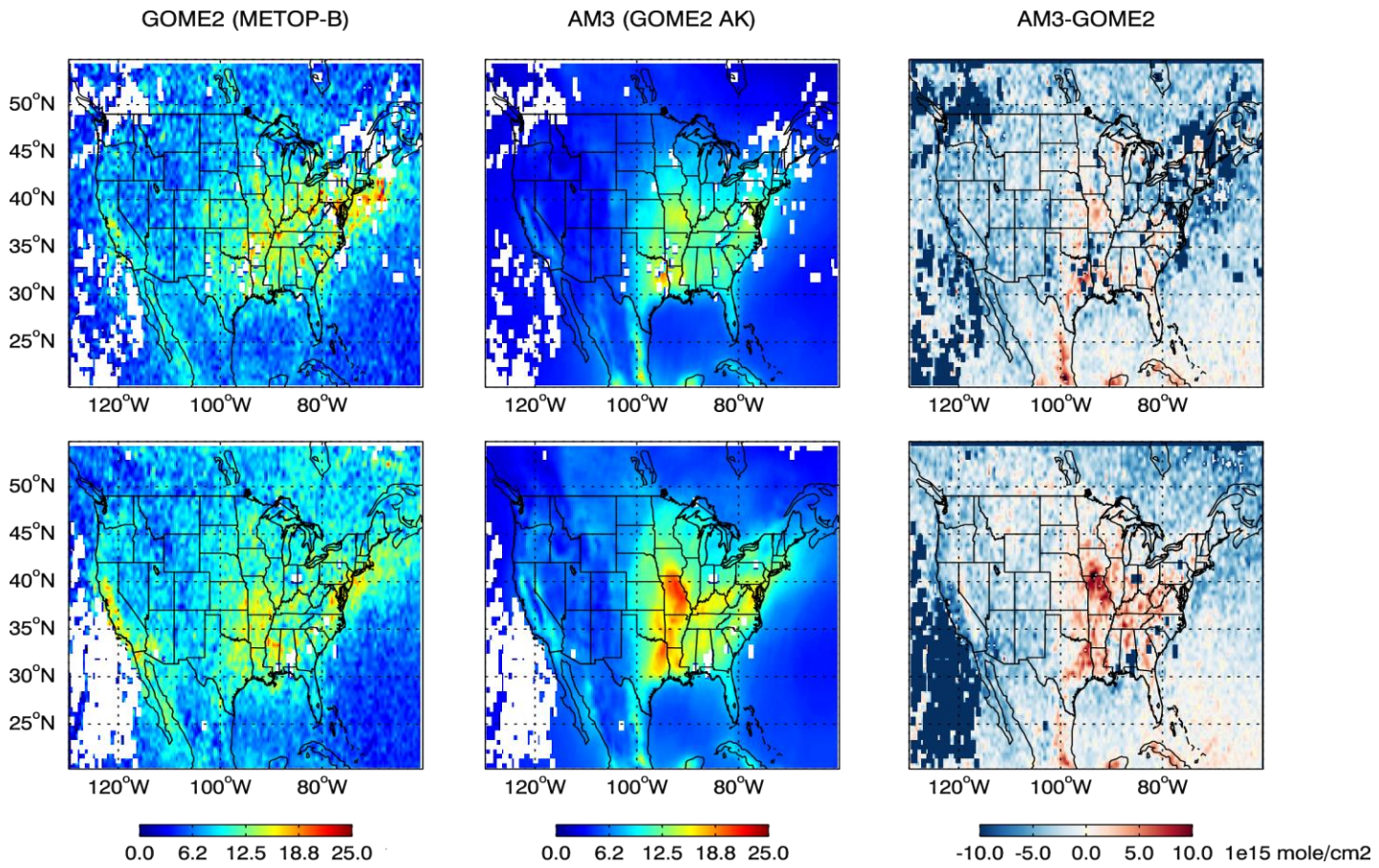
This chemistry includes recent laboratory updates on isoprene chemistry till 2013!

This mechanism was evaluated with ICARTT observations and works great on the bulk yield of organic nitrates!

The documentation is available online (link can be found in my JGR paper).

(Mao et al., 2013, JGR)

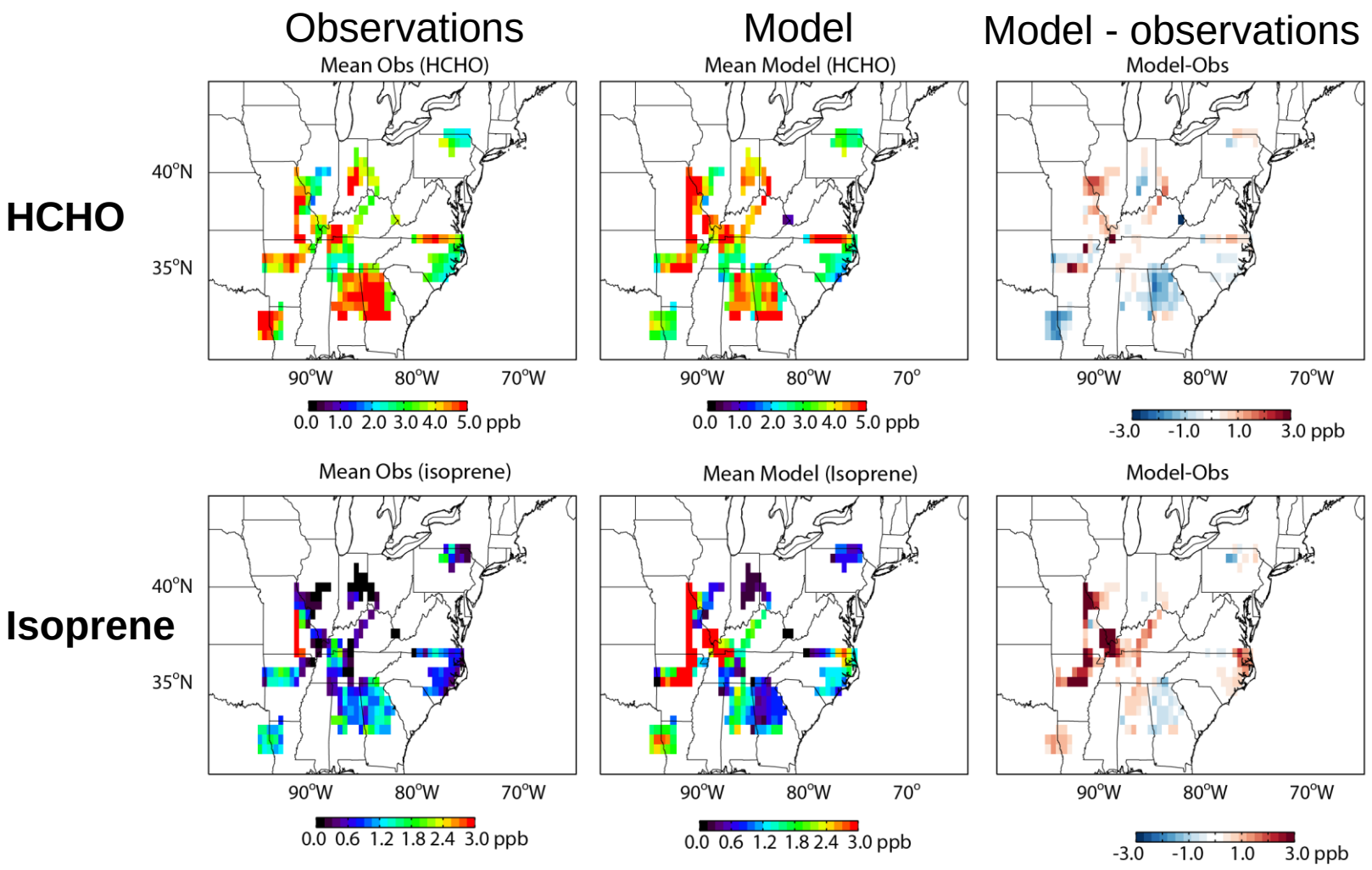
Model compared with GOME-2 HCHO for June and July of 2013



$$\hat{x} = \boldsymbol{A}x + (I - \boldsymbol{A})x_a$$

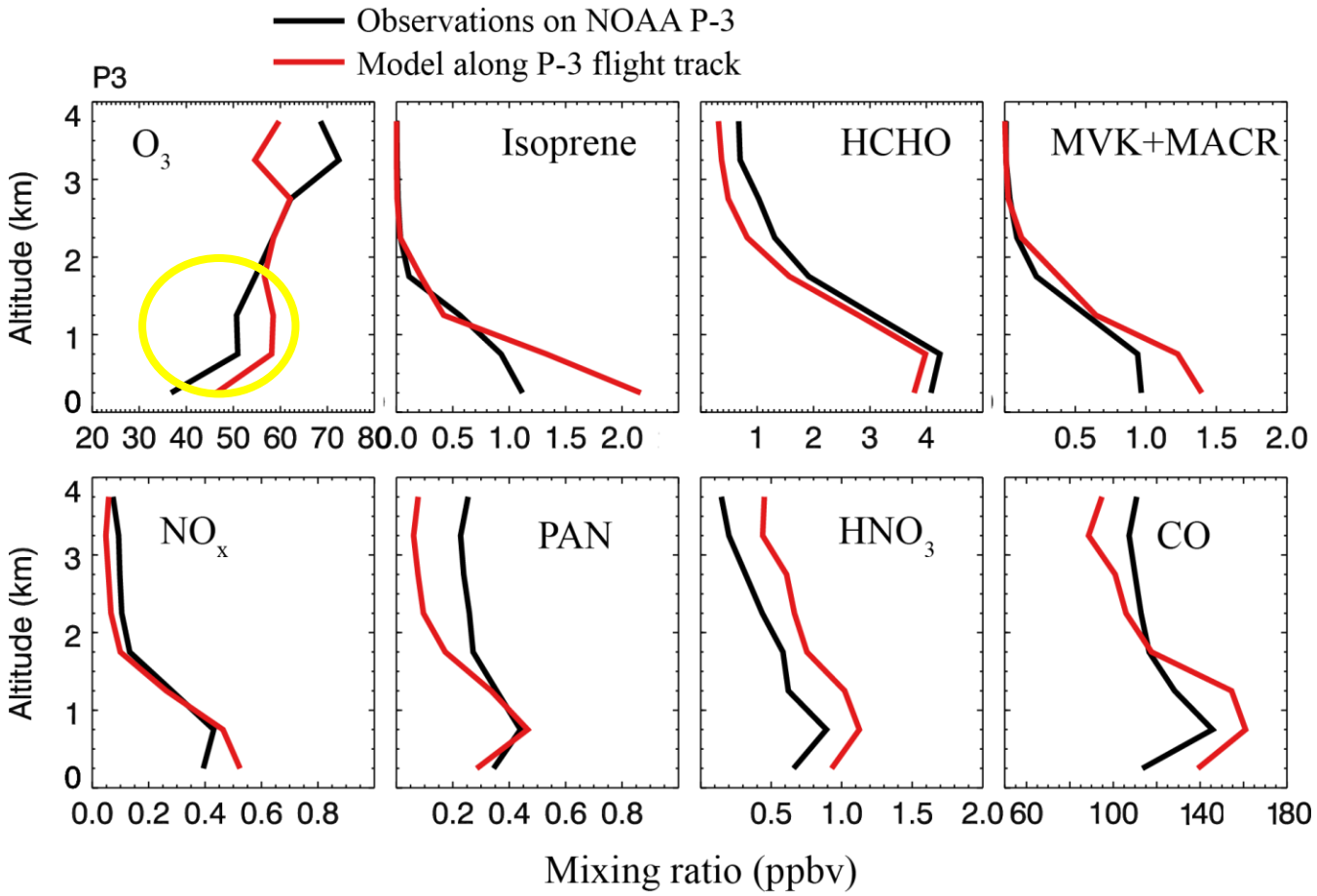
- Model seen by GOME-2 ($\hat{x}$) is calculated by averaging kernels ($\boldsymbol{A}$),a priori profiles (x_a)
- and model vertical profiles (x) (GOME-2 overpass time 9:30 am).
- Model can well reproduce HCHO in June.
- Model tends to overestimate HCHO in July, particularly over the Ozark Plateau.

Model compared with aircraft measurements in boundary layer



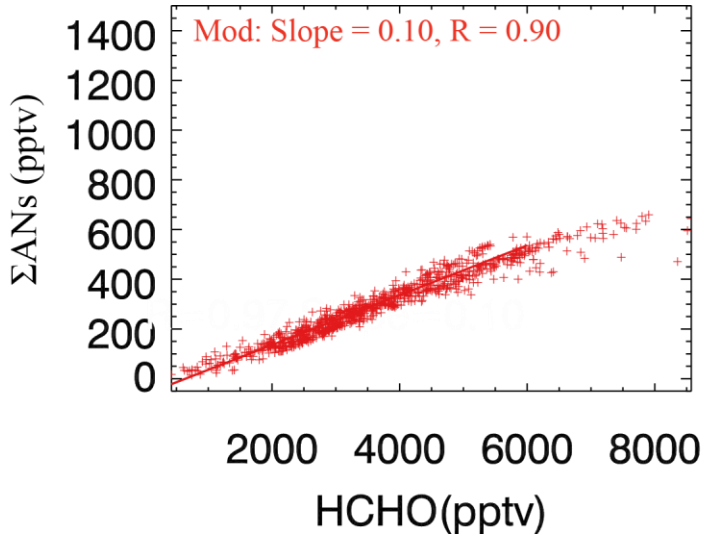
Both aircraft and satellite measurements suggest model overestimate of isoprene emissions over the Ozark Plateau.

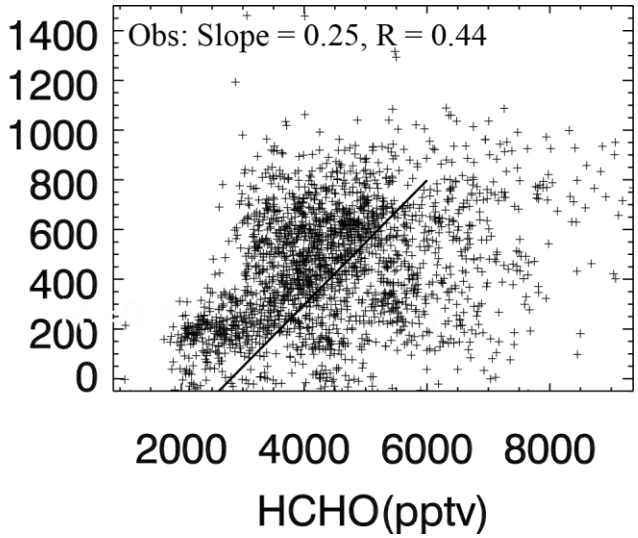
Mean vertical profiles during SENEX



- Plumes have been filtered by NO_x/NO_y<0.4, NO_x<4 ppbv, CH_3CN<225 pptv.
- Model tends to overestimate ozone by 5-10 ppb.
- By including **a high yield of daytime terpene nitrates (27%)**, ozone can be reduced by <1 ppb in boundary layer.
- By including **a high yield of nitrate from terpene + NO_3**, ozone can be reduced by < 1ppb in boundary layer.

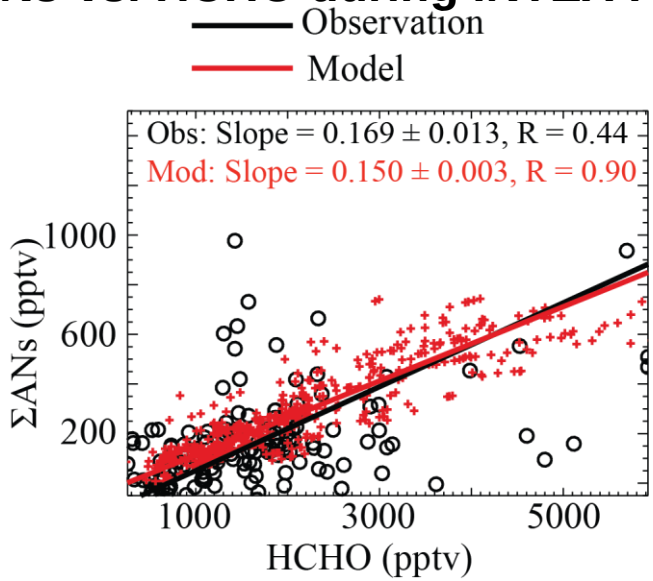
∑ANs vs. HCHO in boundary layer during SENEX





Observed ∑ANs = NO_y – HNO_3 – NO_x – PAN - PPN

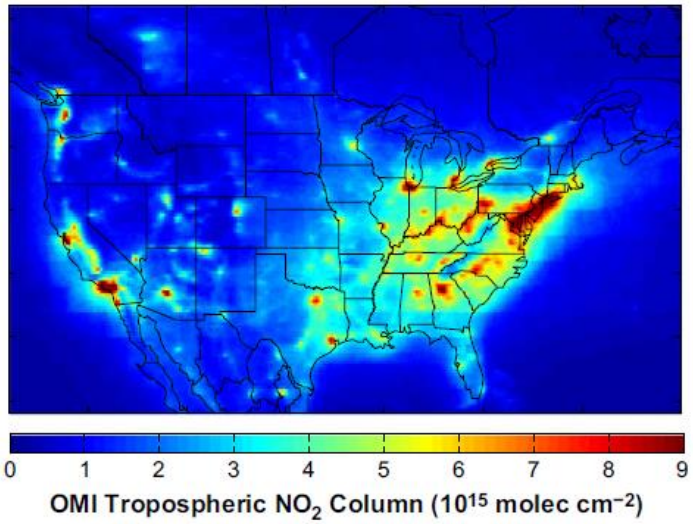
∑ANs vs. HCHO during INTEX-A



This good correlation was also seen during SEAC4RS and well reproduced in the GEOS-Chem model.

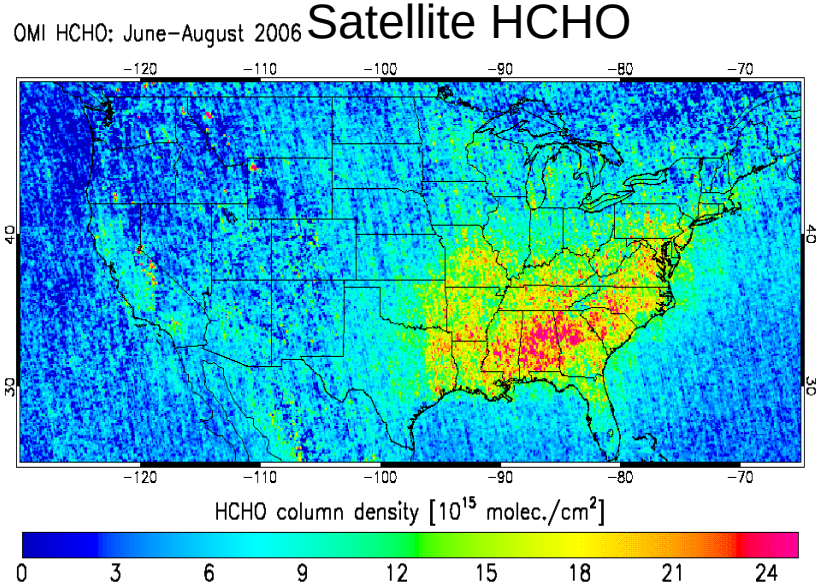
(Mao et al., 2013, JGR)

Satellite NO_2



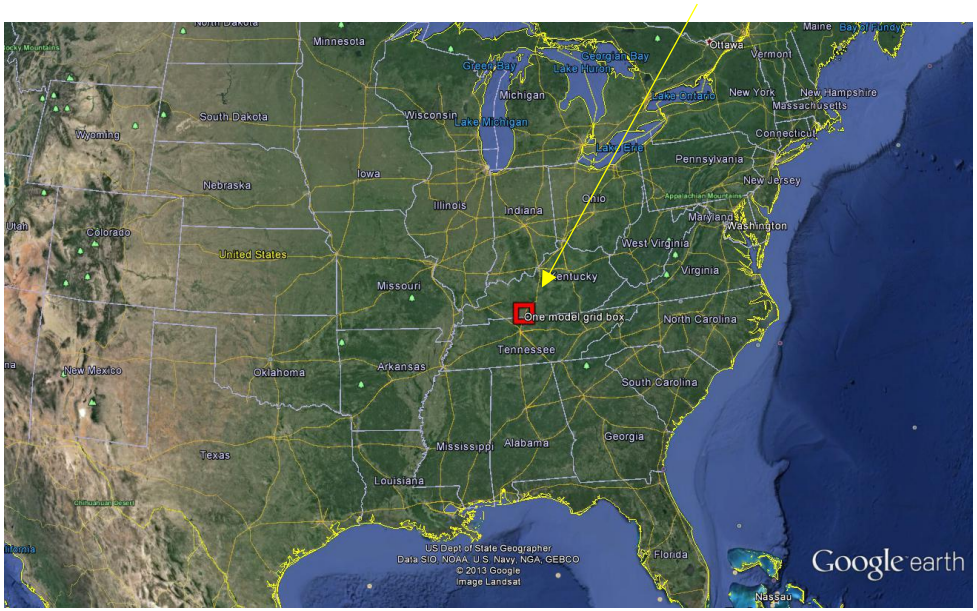
(Martin et al., 2008, AE)

Satellite HCHO

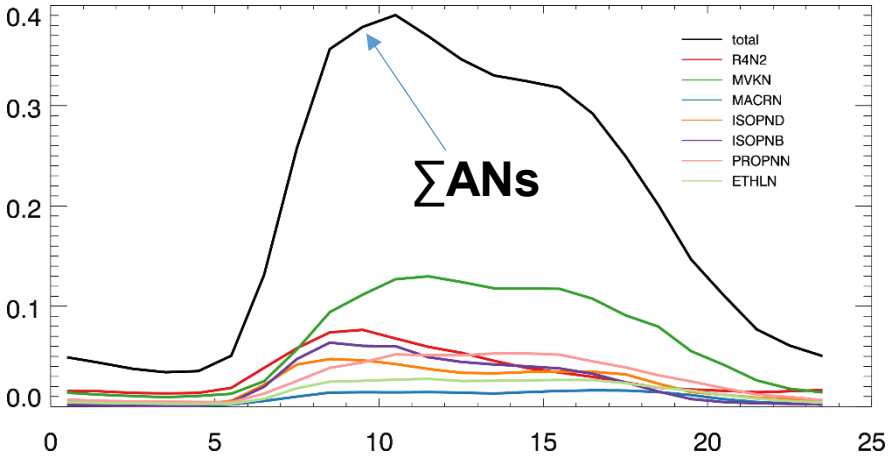


(Millet et al., 2008, JGR)

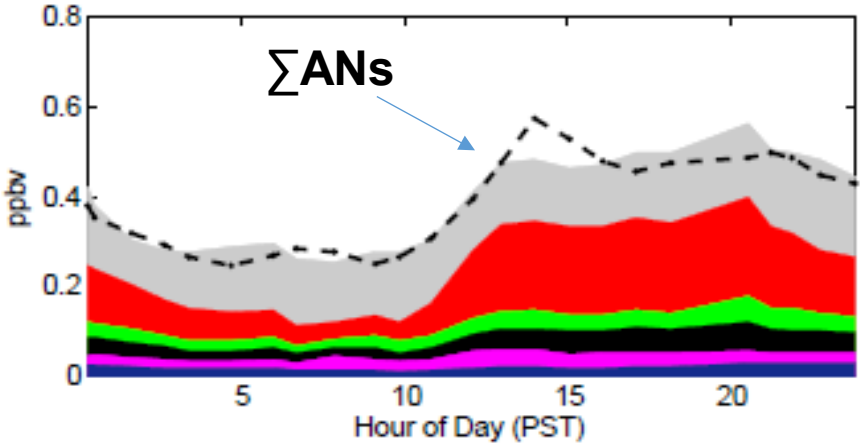
Pick one grid box for diurnal cycle



Diurnal cycle of ANs in AM3 (June average)



Diurnal cycle of measured ANs at Blodgett Forest



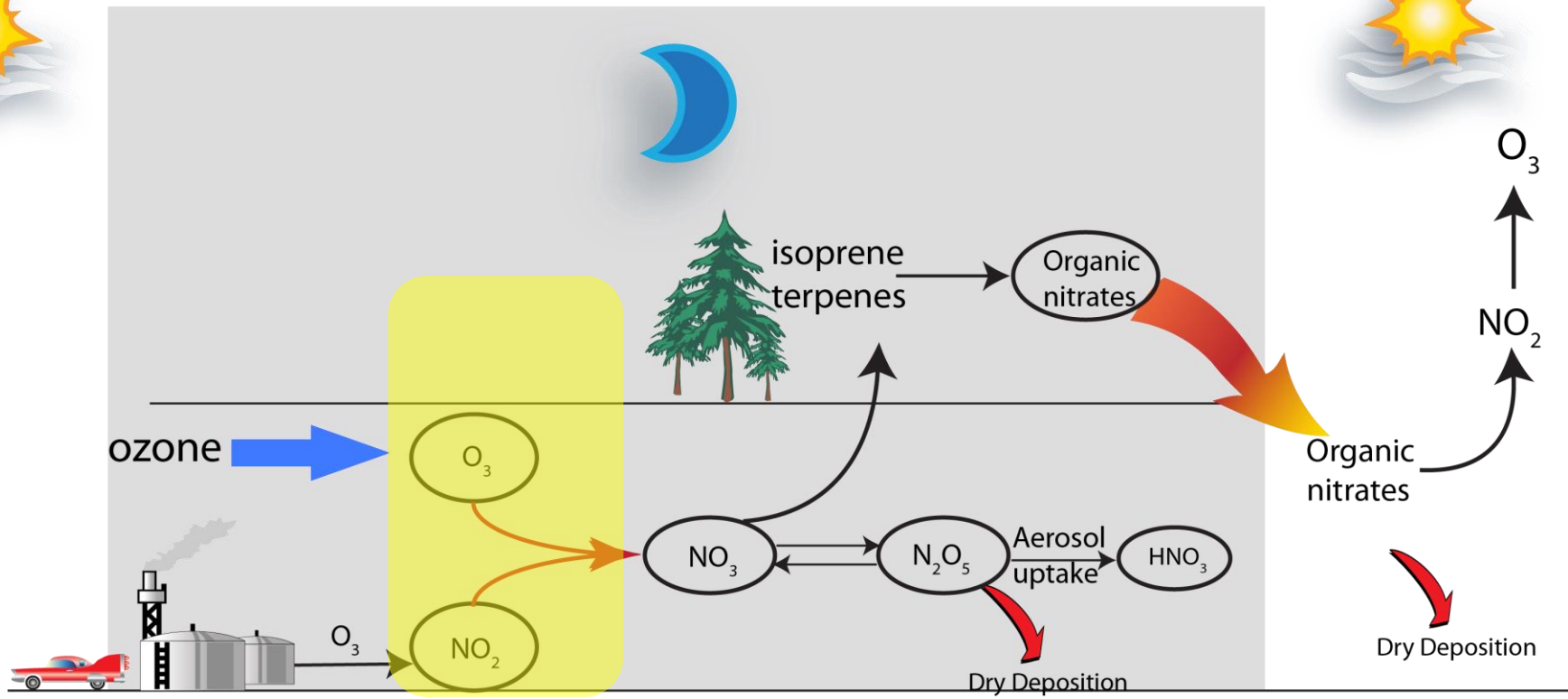
(Beaver et al., 2012, ACP)

The majority of alkyl nitrates appears to be produced during daytime.

The peak is late for Blodgett Forest was because isoprene was emitted upwind and transported to the site after 1-2 hours.

How about the ground measurements during SOAS???

Influence of nighttime NOx chemistry on daytime ozone



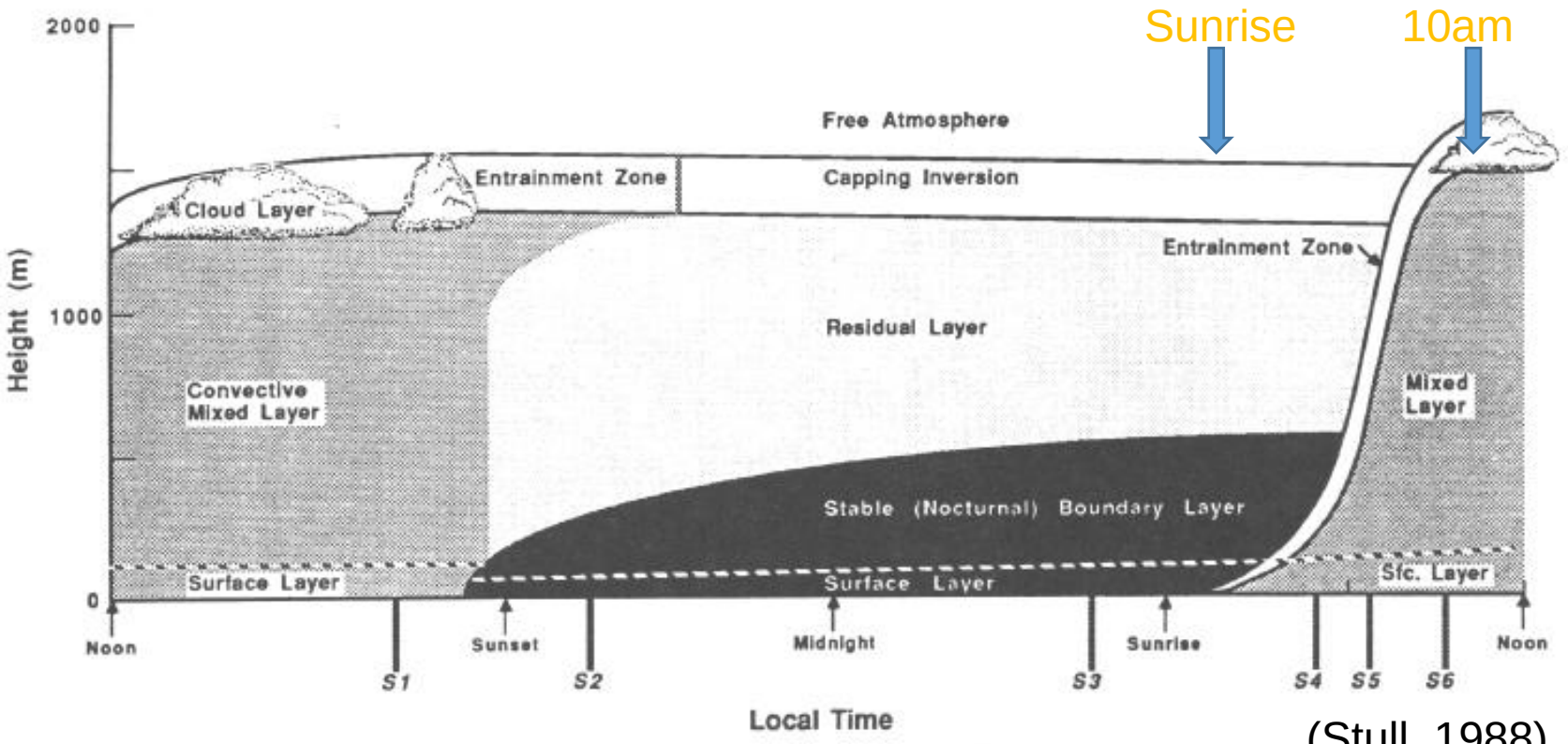
The limiting step is NO_2 + O_3 reaction.

- With 40 ppb of O_3, nighttime NO_x lifetime is about 8 hours.

The production of NO_3 can be mainly considered as a sink for NO_x.

- Organic nitrate yield of isoprene + NO_3 is ~70%>> daytime yield (11.7%)
- Organic nitrate yield of terpenes + NO_3 is 40-50% (Fry et al., 2009,2011, ACP)

Diurnal evolution of the BL

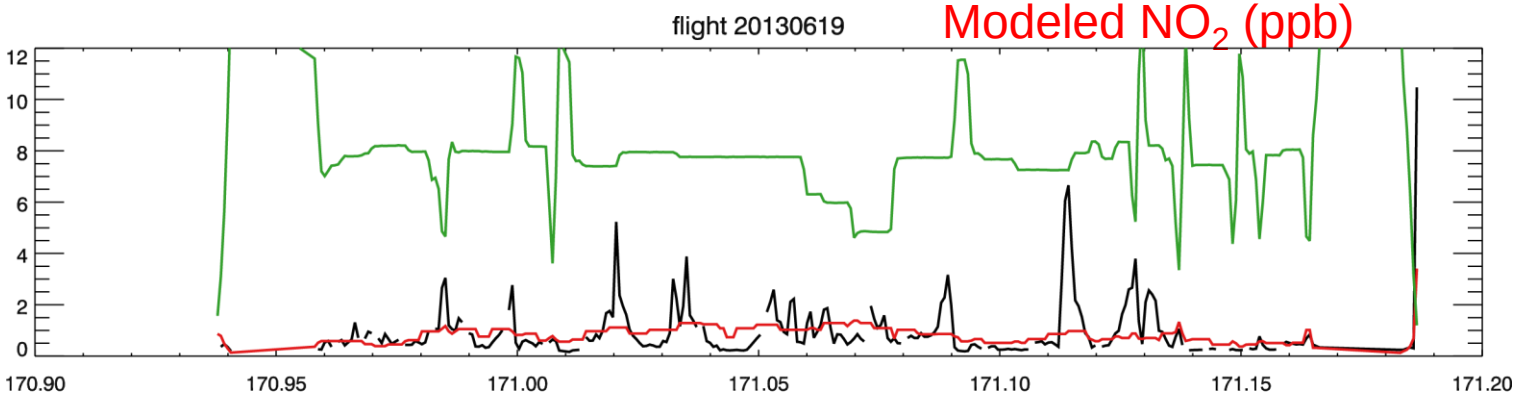


(Stull, 1988)

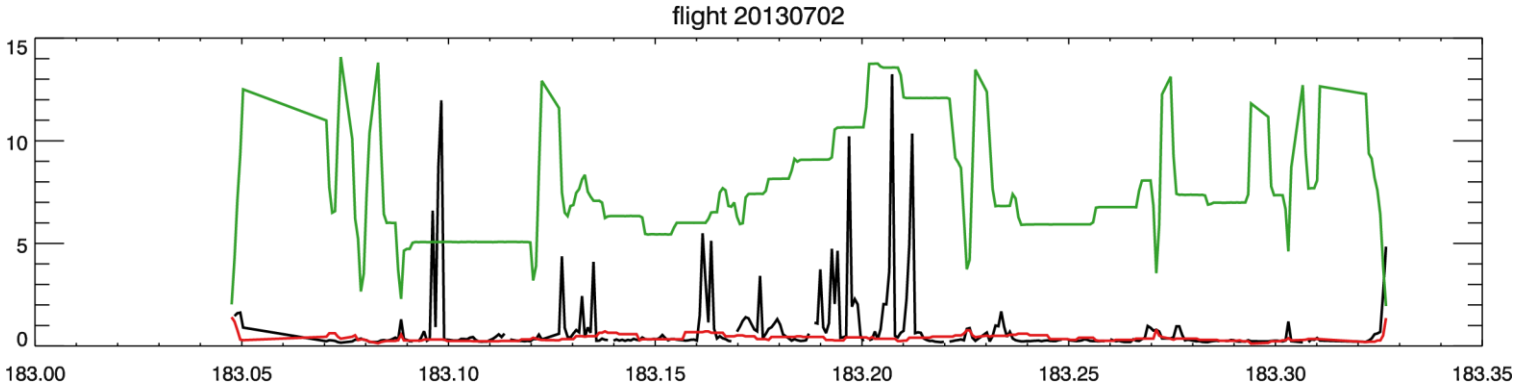
Even after sunrise, it may take a while for residual layer to mix with the surface air (a few hours).

Three night flights

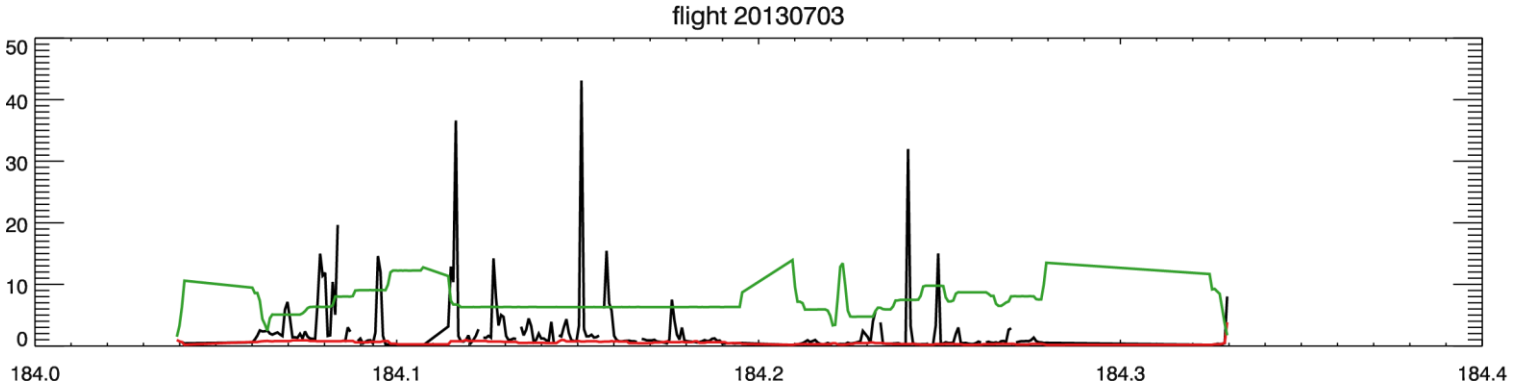
Altitude (m)/100
Measured NO_2 (ppb)
Modeled NO_2 (ppb)



Atlanta



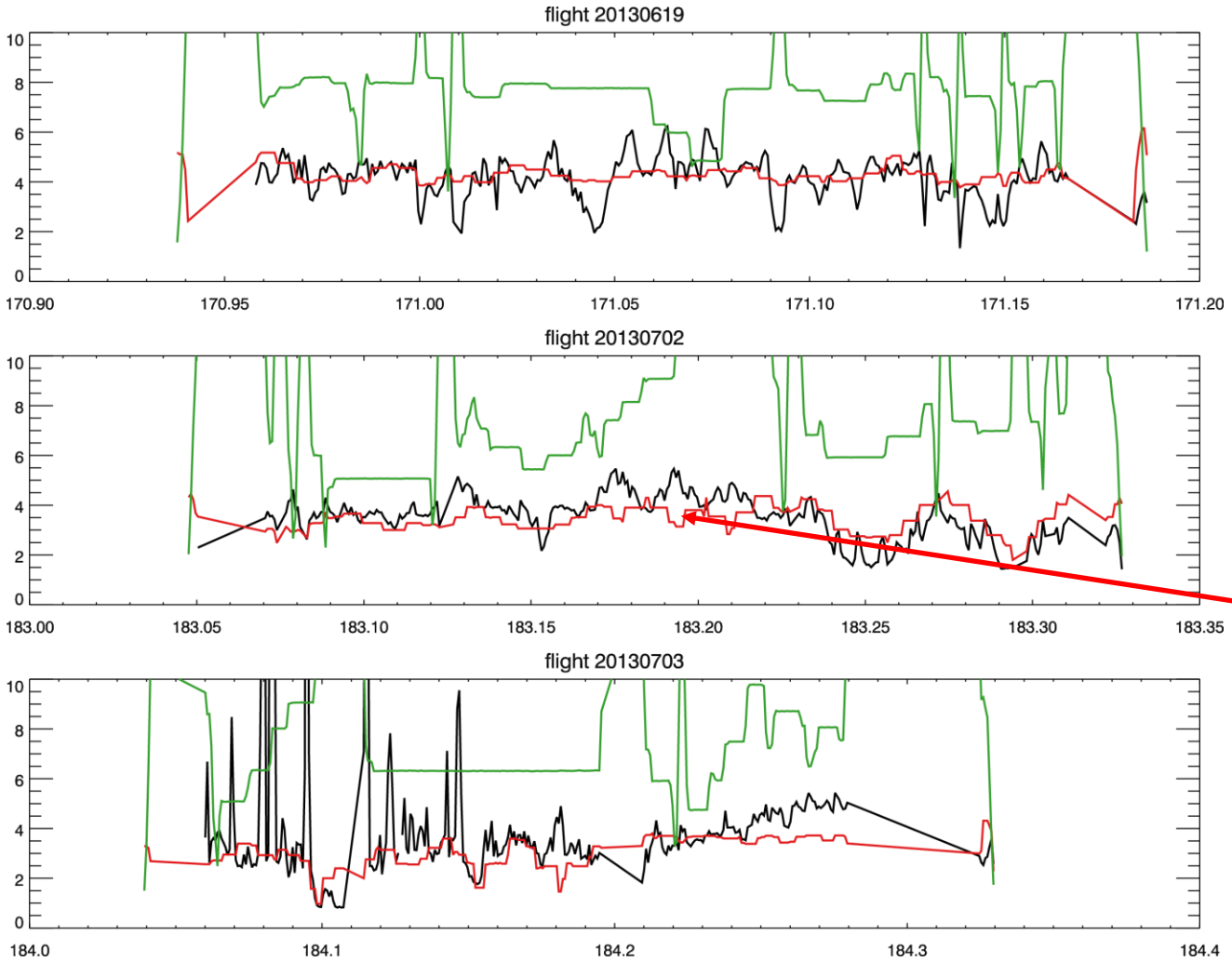
Power plants



Power plants

Most plumes are emitted at 500 – 1000 m (in residual layer).
NO_2 in plume is 10-30 ppbv, not high enough to titrate ozone.

Remarkable feature : Large amount of VOCs remain in residual layer!



Altitude (m)/100
Measured HCHO (ppb)
Modeled HCHO (ppb)

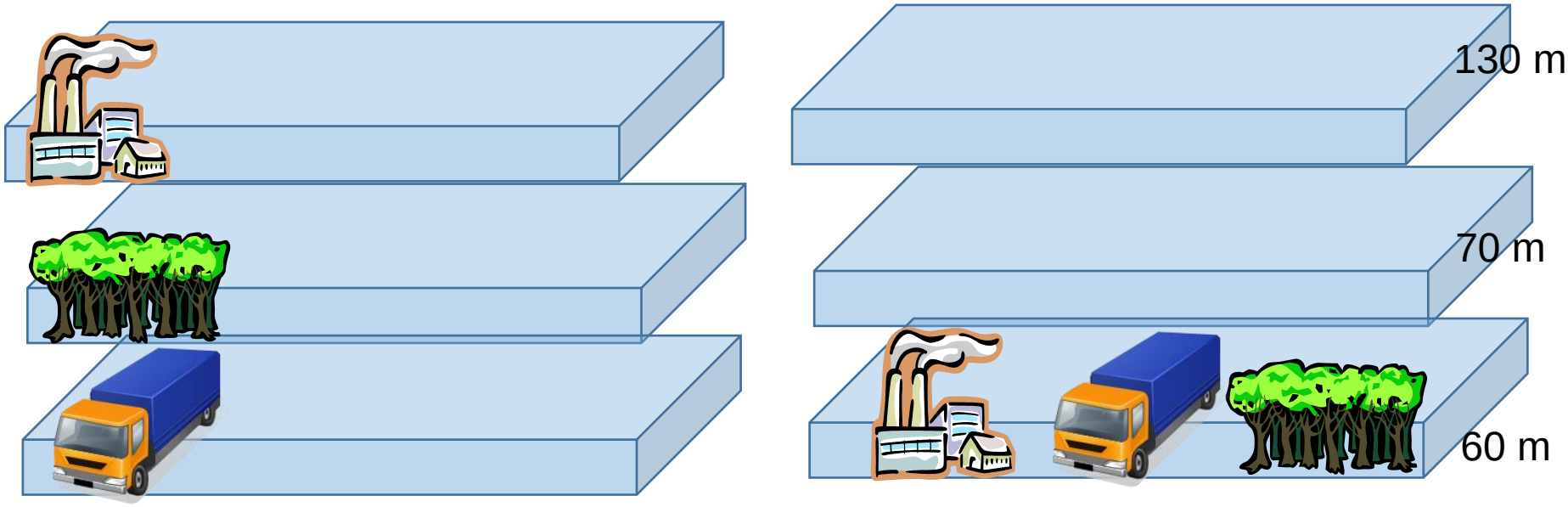
Well mixed HCHO in residual layer.

HCHO is around 4 ppb at different heights, indicating a well mixed residual layer from the last day.
Acetaldehyde is around 1 ppb throughout the night (PAN precursor)
Isoprene (not shown) is about 1-2 ppb in residual layer.

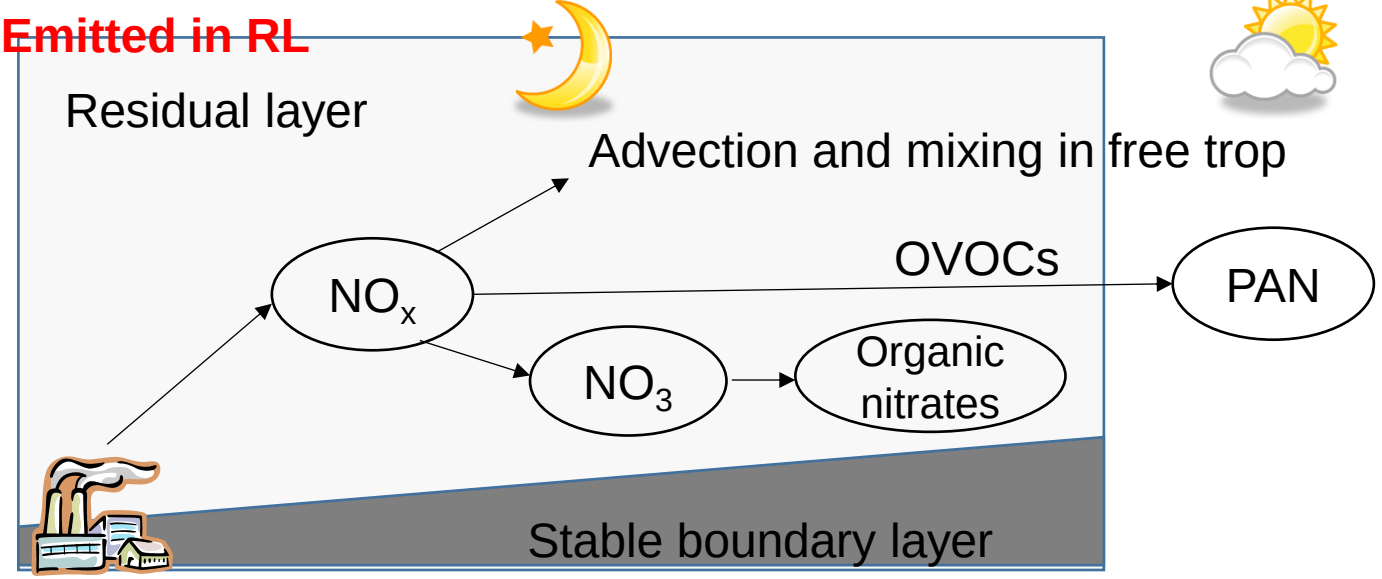
A potential problem in current models for nighttime chemistry

Real world

Model world

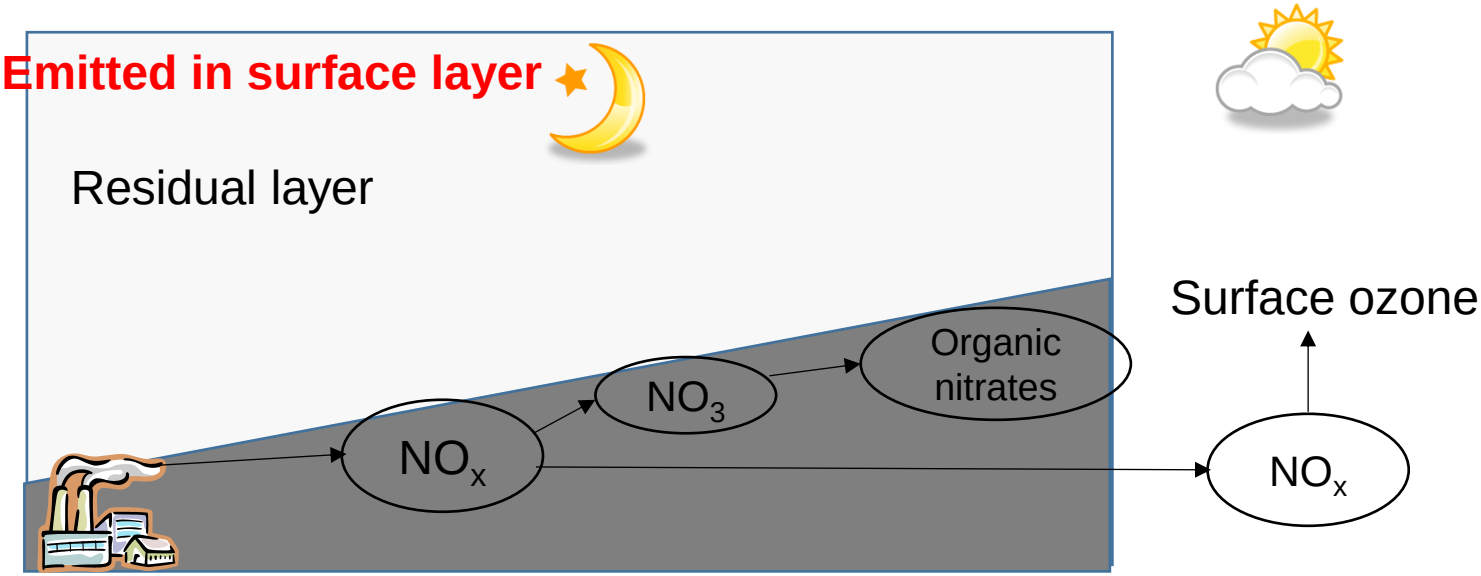


Model assumed well-mixed lowest layer.



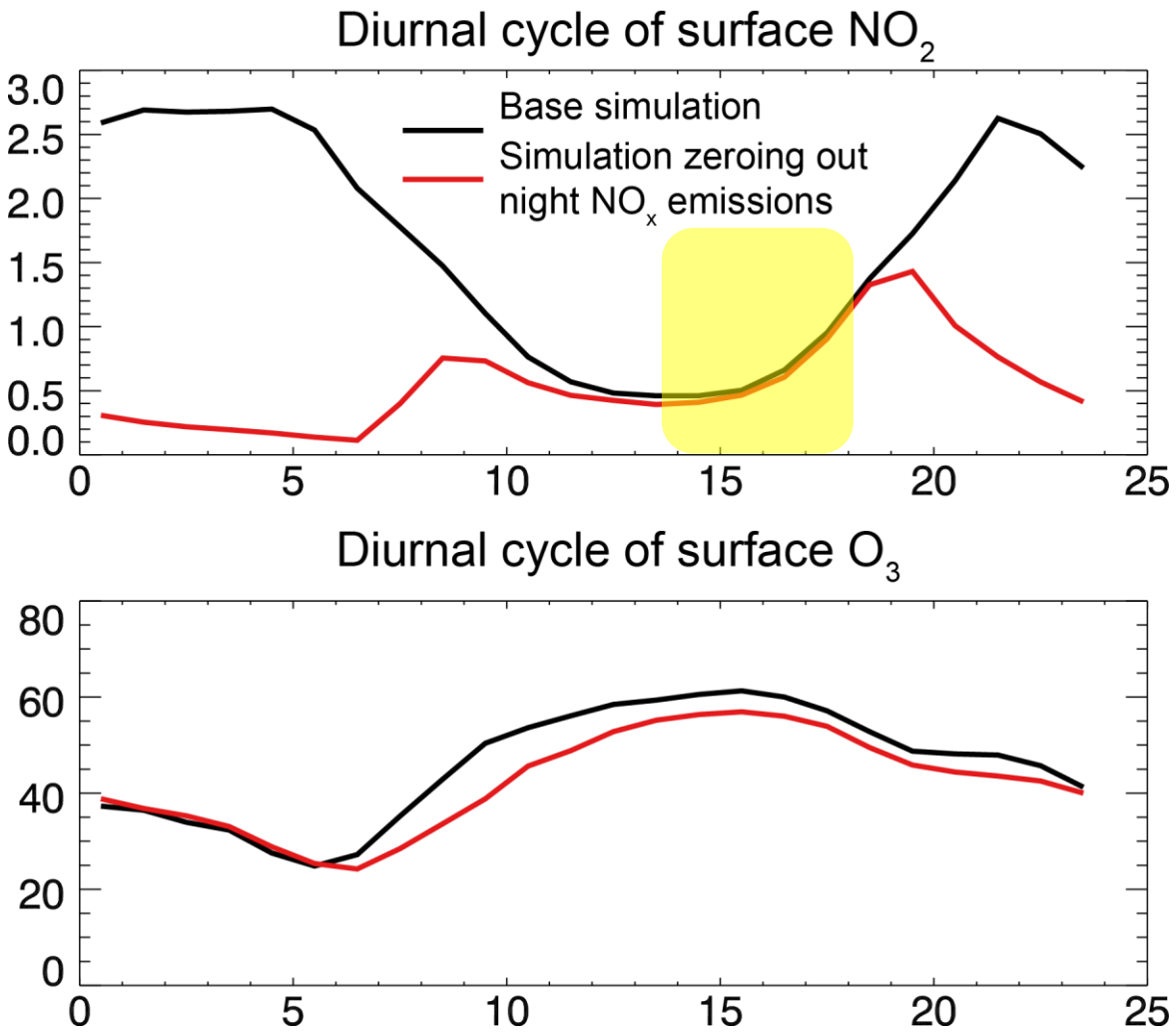
Consistent with Paul Shepson's measurements during SOAS.

Maybe some PAN is being formed at night?



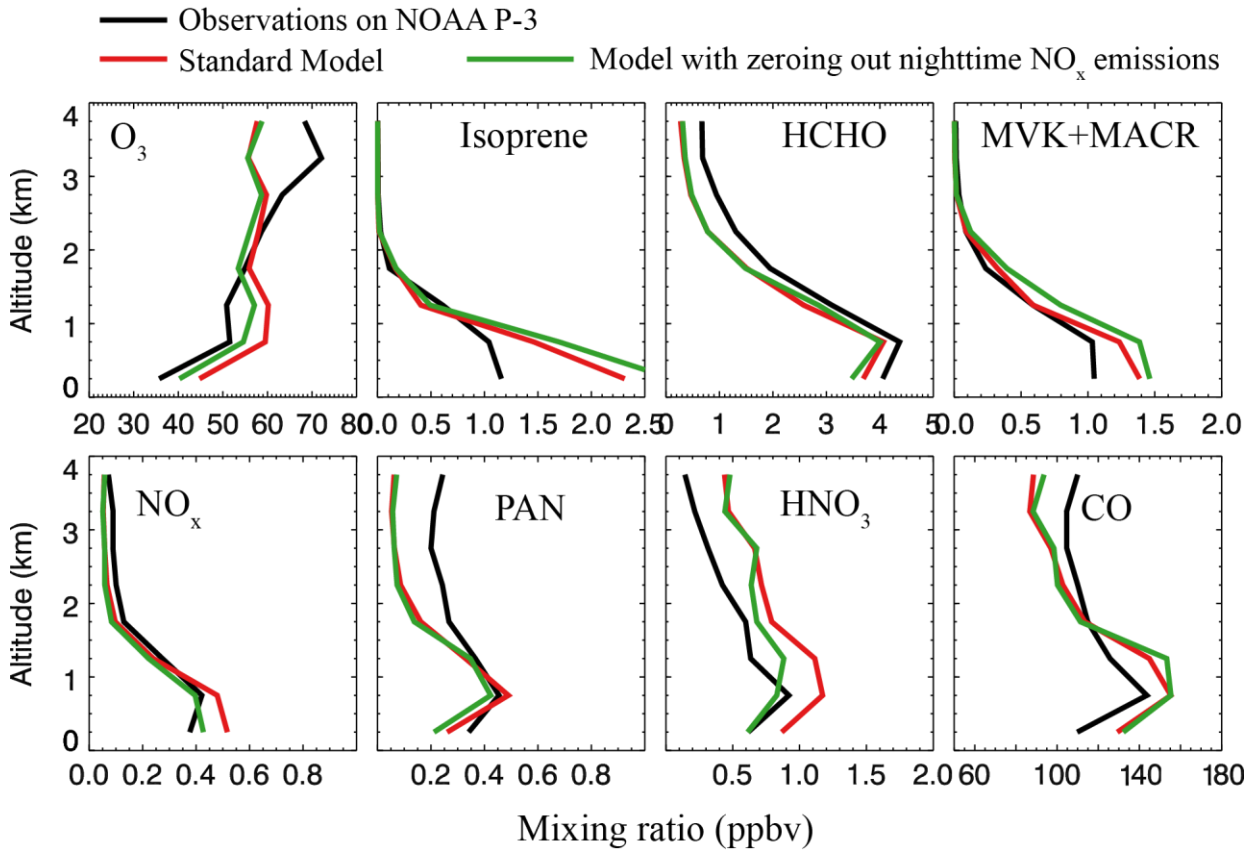
NO_x emitted into the residual layer will:
(1) be oxidized faster through $NO_2 + O_3$ (more ozone),
(2) A lot more isoprene in residual layer to react than surface layer (bigger volume),
(3) contribute less to surface ozone.

We now calculate the upper limit of the effect of vertically resolved nighttime NO_x emissions (assuming all emissions into the residual layer are removed instantly).



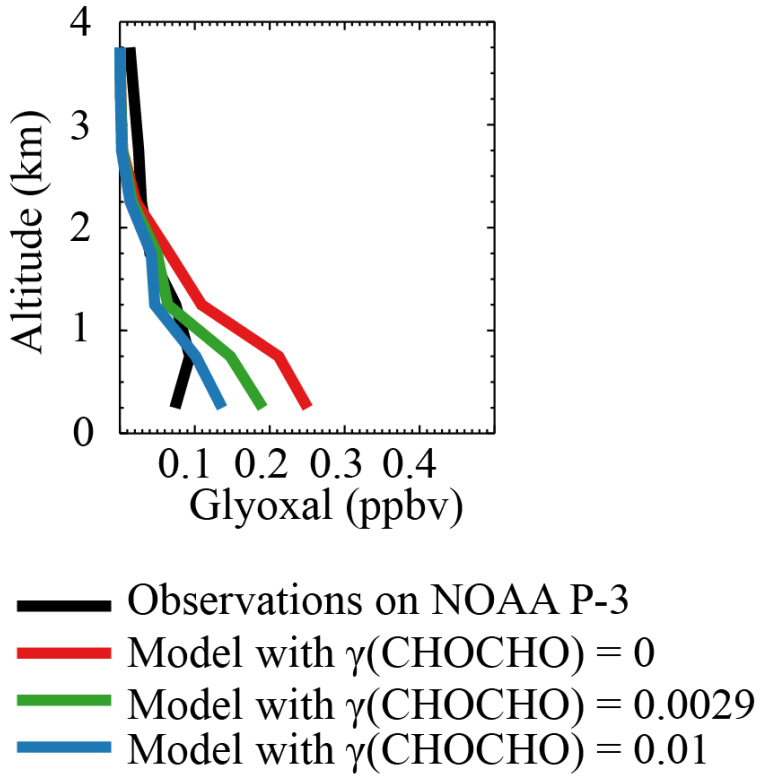
Not much difference on afternoon NOx, where we do most aircraft sampling. But you can see difference on ozone, 5-10 ppb.

Zeroing out nighttime NO_x emission in the model (30% of total anthropogenic NO_x emissions)



- This improves afternoon ozone by 5 ppb in the model.
- If we assume those nighttime NO_x can be converted to PAN, this may also improve PAN simulation.

Our next step on SENEX: SOA modeling



- First in-situ airborne measurements of glyoxal.
- Our chemistry includes the first generation yield of glyoxal.
- γ(CHOCHO) =0.0029 is based on Fu et al. (2008)
- Aerosol uptake may play a key role in determining glyoxal concentrations.
- Need validation on model aerosol surface area.

Conclusion & Future work

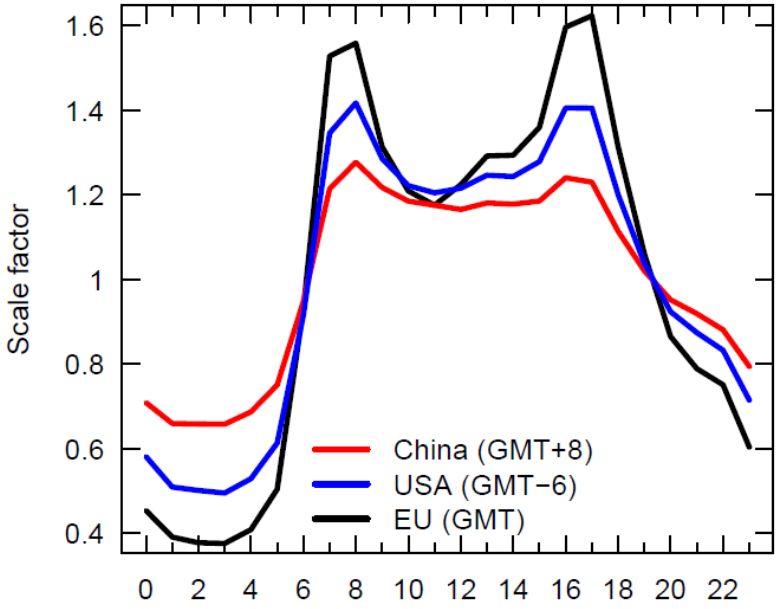
- Nighttime BVOCs oxidation is a sink for NOx
  -- Sink is more efficient for emissions in residual layer (high O_3, VOCs)
  -- But, most models emit NO_x into surface layer (this will introduce ozone bias in the model)
  -- Stack heights from power plants (hundreds of meters) are above lowest model layer (~50m)

Implications for nitrogen export
  -- PANs and alkyl nitrates may be produced more efficient in residual layer.

We need to model the fate of NO_x in the residual layer.

More evidence is needed for this hypoethesis.

Diurnal cycle for NO_x emissions



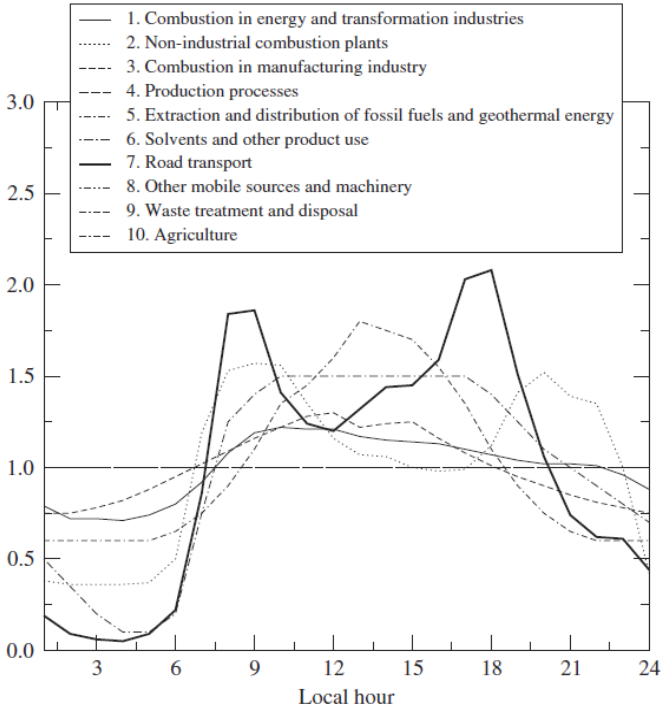


Fig. 3. Emissions hourly factors of the 10 SNAP anthropogenic activities sectors.

(Menut et al., 2012, AE)