

HO_x-NO_x chemistry in the polar spring: comparison with TOPSE2000

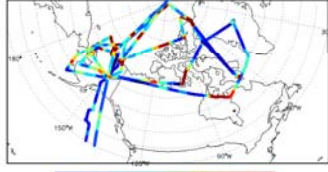
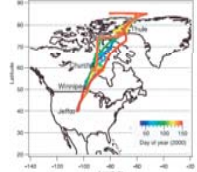
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1. FLIGHT TRACKS

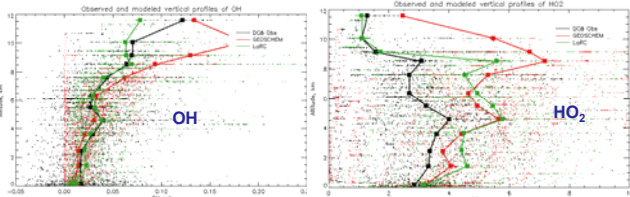
TOPSE(April, 2000, data w/ lat>60)

ARCTAS(Phase I, April 1st-19th)



GEOSCHEM (V8-01-01) :1.2x2.5 resolution; 2.GEOS-5 met field(Quick fix for optical depth); 3. FLAMBE emissions (start from Jan 1st, 2008)
 Box model: NASA LaRC model (constrained by peroxides, HNO₃ and PAN)

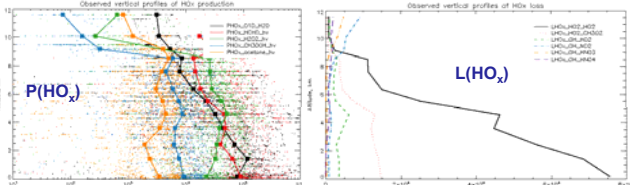
2. HO_x meas/GeosChem/box model (ARCTAS)



Both GeosChem and Box model overpredict HO₂ in the upper troposphere.

HO_x sources include:
 1. O(1D)+hv->2OH(dominate in lower trop)
 2. HCHO+hv->HO₂
 3. H₂O₂+hv->2OH(dominate in upper trop)
 4. CH₃OOH+hv(minor)
 5. Acetone+hv(minor)

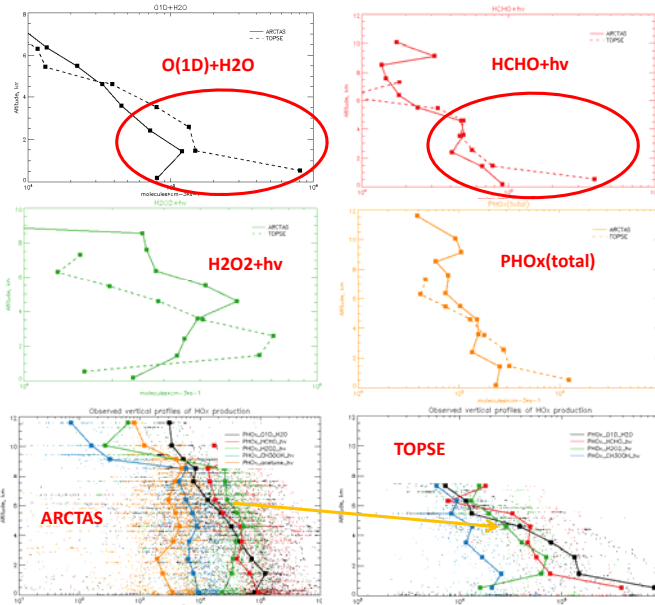
HO_x Loss include:
 1. HO₂+HO₂(dominate)
 2. HO₂+CH₃O₂
 3. OH+HO₂
 4. OH+HNO₃
 5. OH+HNO₄



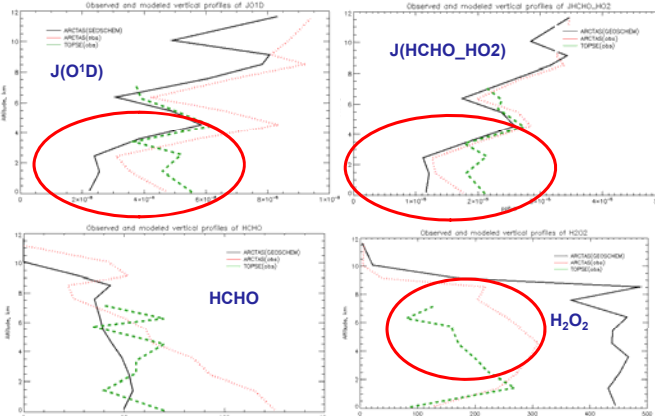
•To increase L(HO₂), we need to either increase measured HO₂ or add extra sinks for HO_x(such as HO₂ uptake) in the calculation.
 •Model sensitivity tests show that increasing NO (or BrO) by 10ppt will not significantly change HO₂ under this condition, but will increase OH level. NO (or BrO) is competing with the main HO_x sink term HO₂+HO₂ thus HO₂ is not very sensitive to NO.

P(HO_x)-L(HO_x)≠0?

3. HO_x budget and reservoirs(ARCTAS vs. TOPSE)

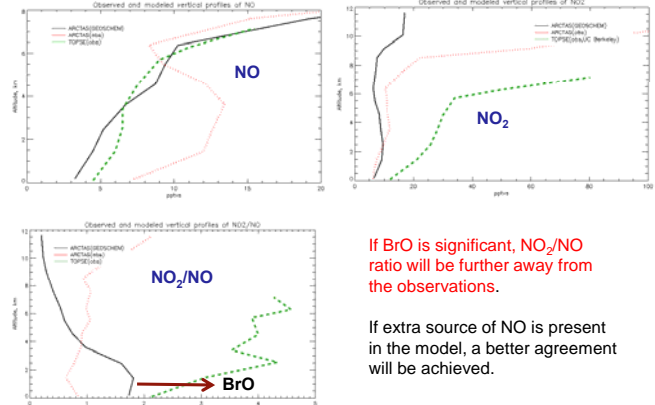


1. TOPSE presented higher oxidation capacity than ARCTAS below 4km(PHO_x is much higher below 4km).
 2. H₂O₂ becomes the major HO_x source in the upper troposphere (UP) during ARCTAS, while HCHO dominates HO_x sources in UP during TOPSE. The main reason is H₂O₂ is much higher during the first phase of ARCTAS than the same period of TOPSE. This needs further investigation.



•J values was much higher below 4km during TOPSE, while they agree well with ARCTAS above 4km.
 •So HCHO has a shorter photochemical lifetime in boundary layer?

4. NO_x cycling (ARCTAS vs. TOPSE)



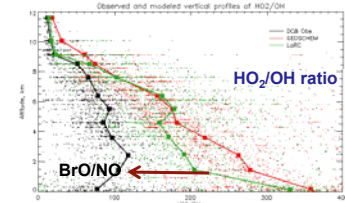
If BrO is significant, NO₂/NO ratio will be further away from the observations.

If extra source of NO is present in the model, a better agreement will be achieved.

$$\frac{NO_2}{NO} = \frac{K_{NO+O_3}[O_3] + K_{NO+HO_2}[HO_2] + K_{NO+RO_2}[RO_2] + K_{NO+BrO}[BrO]}{J_{NO_2}}$$

1. Measured NO during ARCTAS was higher than measured NO during TOPSE.
2. TOPSE NO was closer to the modeled NO during ARCTAS. Not much snow emission of NO during TOPSE?

5. HO_x cycling



$$\frac{[HO_2]}{[OH]} = \frac{\text{Total OH loss rates}}{k_{NO+HO_2}[NO] + k_{O_3+HO_2}[O_3] + k_{BrO+HO_2}[BrO] + P_{OH}(hv)/[HO_2]}$$

where POH(hv)=POH(O1D+H2O)+POH(H2O2+hv)+POH(CH3OOH+hv)

- Extra NO or BrO in the model will make a better agreement between models and obs.
- The box model is constrained by measured NO and shows the similar behavior.
- Two possibilities:1. BrO+HO2-> OH (not good for NO_x cycling) 2. extra sinks:HO2 uptake.

6. Summary

- HO₂ was overpredicted in the box model and chemical transport model.
- Imbalance between P(HO_x) and L(HO_x) indicates extra HO₂ sinks (such as HO₂ uptake to aerosol).
- Compared to TOPSE, H₂O₂ was at a much higher level and became the major HO_x sources in the upper troposphere during ARCTAS.
- During TOPSE, J values was about 2~3 times higher than ARCTAS below 4km and thus provided higher oxidation capacity. This needs further investigation.
- HO_x-NO_x cycling also implies the need of extra HO₂ sinks.