HO_x Observations and Photochemistry during INTEX-NA

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Objective

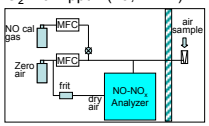
- To understand chemical processes that link pollutant emissions to persistent secondary pollutants;
- To understand HO_x sources and sinks;
- To compare with model calculations and to test our understanding of photochemistry;
- To investigate O_3 budget and its vertical profile.

Experimental

1. *OH, HO_2*

Penn State ATHOS, uncertainty: ±32%; detection limits: OH = 0.01 pptv; HO_2 = 0.1 pptv (2σ, 1 min)

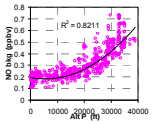
ATHOS inlet

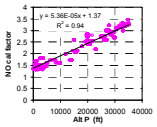


NO sample and calibration

2. *NO*

TEI 42C NO-NO_x analyzer
- NO single mode
- Online NO span and zero check
- Altitude dependence of NO bkg and cal factor



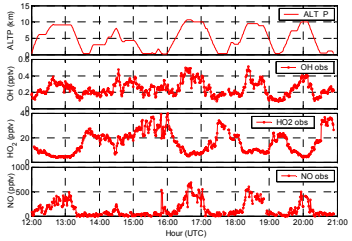


Model Calculation

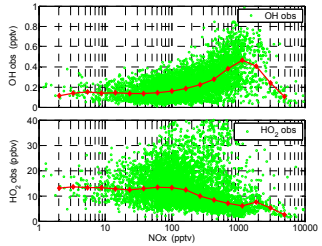
NASA LaRC 0-D photochemical box model with 1-min input data of O_3, CO, NO_2, JNO_2, H_2O, T, P and constrained to H_2O_2, CH_3OOH, HNO_3, and PAN when these measurements are available.

Observation Results

July 22, Flight # 11

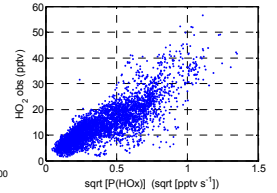


NO_x dependence of observed HO_x



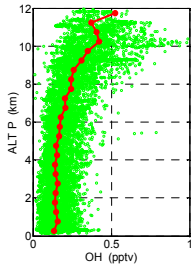
HO_2 – $P(HO_x)$ relationship

Steady State : $P(HO_x) = L(HO_x) \propto [HO_2]^2$
$[HO_2] \propto \text{sqrt}\{P(HOx)\}$

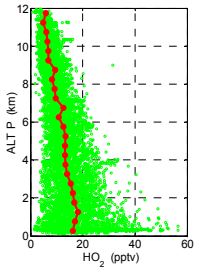


Vertical Profiles

OH ~ ALT

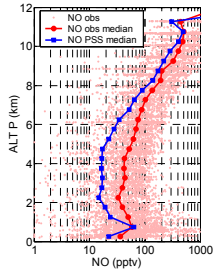


HO_2 ~ ALT

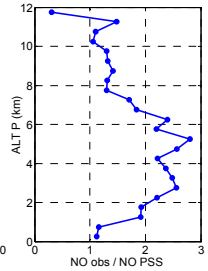


- OH ~ 0.2 pptv between 0-8 km. Above 8 km, it increases with increasing altitude.
- HO_2 decreases with increasing altitude.

NO ~ ALT

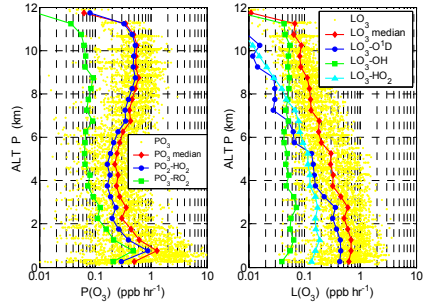


NO_{obs}/NO_{pss} ~ ALT

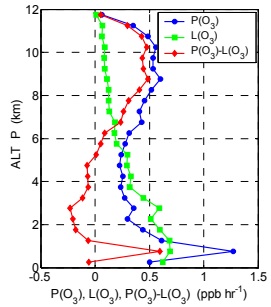


- Obs NO levels are higher than PSS NO values at altitudes between 1 and 7 km.
- NO values between 2-6 km are around the NO detection limit (~50 pptv).

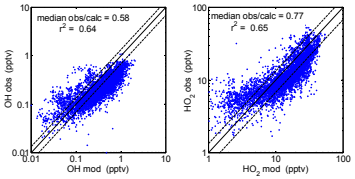
Ozone Budget

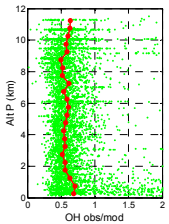


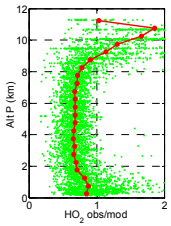
- Main $P(O_3)$: HO_2+NO
- Main $L(O_3)$: O^1D+H_2O (below 5 km), O_3+HO_2/OH (above 5 km)
- Net O_3 loss at altitudes between 1 km and 5 km.
- Net O_3 production above 5 km.



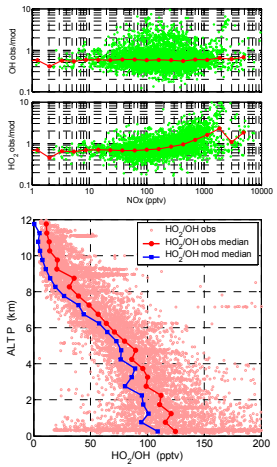
Model Comparison







- On average the model under-predicted OH by a factor of 1.7 and HO_2 by a factor of 1.3.
- Little altitude dependence of observed to modeled OH ratios at all altitudes and HO_2 ratios below 8 km. The model tends to under-predict HO_2 above 9 km.
- Little NO_x dependence of observed to modeled OH ratios at all NO_x levels and HO_2 ratios when NO_x is less than a few hundred pptv. The model tends to under-predict HO_2 at higher NO.
- Modeled HO_2/OH ratios are lower than observed HO_2/OH ratios at all altitudes.



HO_x Budget

OH production and loss

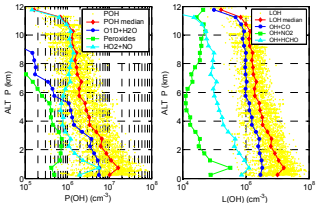
Main P(OH):
O^1D+H_2O (below 5 km)
HO_2+NO (above 5 km)

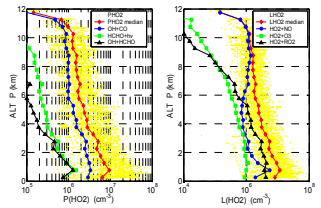
Main L(OH):
OH+CO/VOC

HO_2 production and loss

Main $P(HO_2)$:
OH+CO

Main $L(HO_2)$:
HO_2-RO_2 self-reactions (below 5 km)
HO_2+NO (above 5 km)





Summary

- HO_x and NO data are available on the DC-8 platform.
- Obs. NO levels are higher than PSS NO values at altitudes between 1 and 7 km.
- The model under-predicted OH and HO_2, with a median obs/mod OH ratio of 0.58 and a median obs/mod HO_2 ratio of 0.77, which is very similar to the results during TRACE-P.
- Main P(OH) is O^1D+H_2O (below 5 km) and HO_2+NO (above 5 km). Main L(OH) is OH+CO/VOC.
- Main $P(HO_2)$ is OH+CO. Main $L(HO_2)$ is HO_2 self-reactions (below 5 km) and HO_2+NO (above 5 km).
- There is a net O_3 loss at altitudes between 1 and 5 km.

Acknowledgements

We thank other groups participating in the INTEX mission for the use of their data in this study.