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HO_x Chemistry and Ozone Production during INTEX-B

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Objectives

- To understand chemical processes that link pollutant emissions to persistent secondary pollutants;
- To understand HO_x sources and sinks;
- To test photochemical models and to examine heterogeneous effects of clouds and aerosols and HO_x-NO_x daytime and nighttime chemistry
- To investigate O_3 budget and its vertical profile.

Experimental

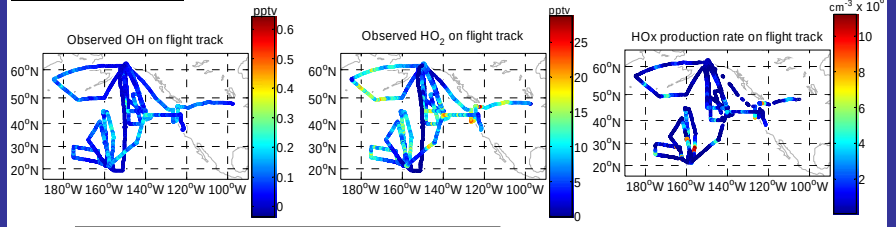
Penn State ATHOS for OH and HO_2 detection using laser-induced fluorescence, uncertainty: ±32%; detection limits: OH = 0.01 pptv; HO_2 = 0.1 pptv (2σ confidence, 1-min integration)

ATHOS inlet ATHOS in DC-8 forward pit

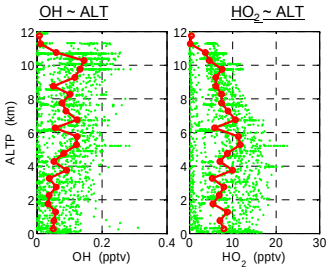
Model Calculation

NASA LaRC 0-D photochemical box model constrained by observed 1-min data of O_3, CO, NO, VOCs, dew point, photolysis frequencies, T, and P. Constrained model results (i.e., the model is constrained to observed H_2O_2, CH_3OOH, HNO_3, and PAN) are used in this study (INTEX-B Phase II only).

Observation Results

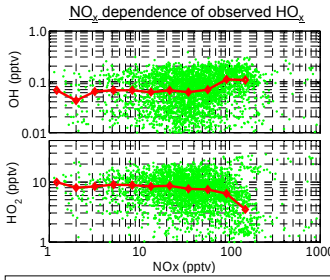


• Higher HO_x levels are due to higher HO_x production rates.



• [OH] gradually increases from 0.05 pptv at 0 km to ~0.15 at 10 km. Above 10 km, it increases as altitude increases.

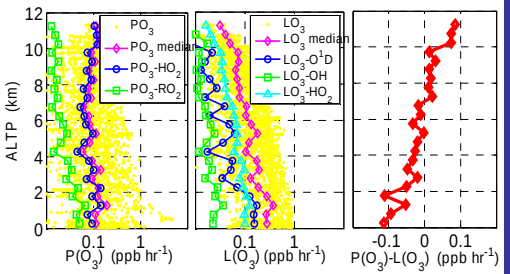
• $[HO_2]$ is about 8 ppt between 0 and 8 km. Above 8 km HO_2 decreases as altitude increases.



• Little NO_x dependence of observe [OH] and $[HO_2]$ when [NOx] is lower than 50 ppt.

• When [NOx] is higher than 50 pptv, [OH] increases and $[HO_2]$ decreases as [NOx] increases.

Instantaneous Ozone Production and Loss

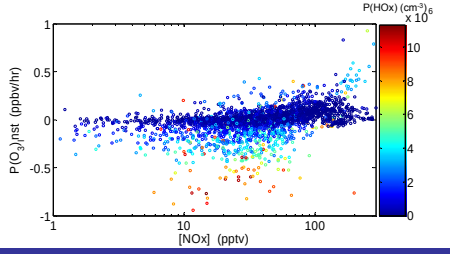


• Main $P(O_3)$: HO_2+NO, depending on NO_x levles and $P(HO_x)$)

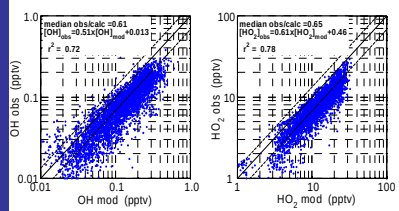
• Main $L(O_3)$: O^1D+H_2O and O_3+HO_2

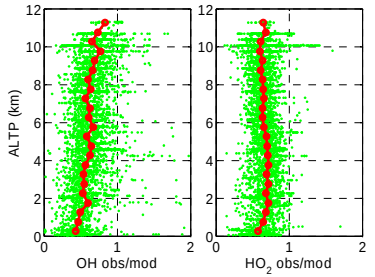
• Net O_3 production above 7 km: 0-0.1 ppb/hr

• Net O_3 loss belos 7 km: 0.1-0 ppb/hr



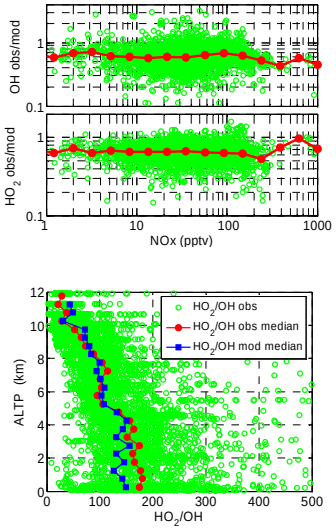
Model Comparison





- On average the model under-predicted OH by a factor of 1.6 and HO_2 by a factor of 1.5, which is significant considering combined observed and modeled uncertainties.
- Little altitude and NO_x dependence of observed-to-modeled OH and HO_2 ratios
- Observed HO_2/OH ratios and modeled HO_2/OH ratios are in good agreement.
- Possible reasons for the discrepancies:

(1) HOx instrument error (calibration)
(2) missing or incorrect chemistry in the model
(3) instrument errors for measurements that are crucial for modeling HO_x
(4) unmeasured atmospheric constituents that strongly influence HO_x.



HO_x Budget

OH production and loss
Main P(OH):
HO_2+NO and $O(^1D)+H_2O$

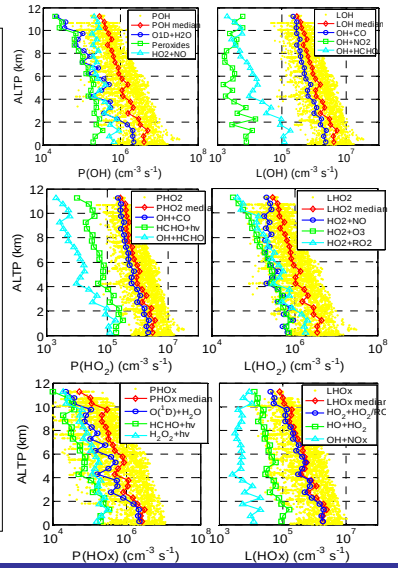
Main L(OH):
OH+CO/VOC

HO_2 production and loss
Main $P(HO_2)$:
OH+CO

Main $L(HO_2)$:
HO_2+NO and HO_2-RO_2

HO_x production and loss
Main P(HOx):
$O(^1D) + H_2O$

Main L(HOx):
HO_2+HO_2/RO_2



Summary

- OH and HO_2 data were collected on the NASA DC-8 during INTEX-B.
- The box model under-predicted both OH and HO_2, with a median obs-to-mod OH ratio of 0.61 and a median obs/mod HO_2 ratio of 0.65, which is similar to the results during INTEX-A, except above 8 km, where the model under-predicted HO_2 during INTEX-A.
- Main P(OH) was HO_2+NO and O^1D+H_2O. Main L(OH) was OH+CO/VOC.
- Main $P(HO_x)$ was $O(^1D)+H_2O$. Main $L(HO_x)$ was HO_2+HO_2 and HO_2+RO_2 reactions.
- Slight net O_3 loss (0.1-0 ppb/hr) below 7 km, and slight net O_3 production (0-0.1 ppb/hr) above 7 km.

Acknowledgements

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