HOx 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 HOx sources and sinks;
• To compare with model calculations and to test our understanding of photochemistry;
• To investigate O3 budget and its vertical profile.

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

2. NO
TEI 42C NO-NOx analyzer
– NO single mode
– Online NO span and zero check
– Altitude dependence of NO bkg and cal factor

Model Calculation
NASA LaRC D-O photochemical box model with 1-min input data of O3, CO, NOx, JNOx, H2O, T, P and constrained to H2O2, CH3OH, HNO3, and PAN when these measurements are available.

Model Comparison
• On average the model under-predicts OH by a factor of 1.7 and HOx by a factor of 1.3.
• Little altitude dependence of observed to modeled OH ratios at all altitudes and HOx ratios below 8 km. The model tends to under-predict HOx above 9 km.
• Little NOx dependence of observed to modeled OH ratios at all NOx levels and HOx ratios when NOx is less than a few hundred pptv. The model tends to under-predict HOx at higher NOx.
• Modeled HO2/NOx ratios are lower than observed HO2/NOx ratios at all altitudes.

Vertical Profiles
• OH = 0.2 pptv between 0-8 km. Above 8 km, it increases with increasing altitude.
• HOx decreases with increasing altitude.

Ozone Budget

• Main P(O3): HOx+NO
• Main L(O3): O3+H2O2 (below 5 km), O2+HO2 (above 5 km)
• Net O3 loss at altitudes between 1 km and 5 km.

Summary
• HOx 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 HOx with a median obs/mod OH ratio of 0.58 and a median obs/mod HOx ratio of 0.77, which is very similar to the results during TRACE-P.
• Main P(O3) is O3+H2O2 (below 5 km) and HOx+NO (above 5 km). Main L(O3) is O3+CO/CO2.
• Main P(HOx) is OH+CO. Main L(HOx) is HO2+RO2 (below 5 km) and HOx+NO (above 5 km).
• There is a net O3 loss at altitudes between 1 and 5 km.

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