HO\textsubscript{x} and NO Observations during INTEX-A

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HO$_x$ and NO measurement techniques

• **OH and HO$_2$ measurements**
  ATHOS — Airborne Tropospheric Hydrogen Oxides Sensor
  – Laser-induced fluorescence (LIF) detection of OH
  – Chemically convert HO$_2$ to OH by HO$_2$+NO followed by the detection of OH with LIF

• **NO measurements**
  TEI 42C NO-NO$_x$ analyzer
  – Chemiluminescence
  – NO single mode
  – Online NO span and zero checks
Data Quality

• Data coverage:
  - OH (1 min) - 97%
  - HO₂ (1 min) - 95%
  - NO (1 min) - 89%

• Typical uncertainties:
  - HOₓ ±32% (2σ)
  - NO ±30% (2σ)

• Detection limits:
  - OH 0.01 pptv
  - HO₂ 0.1 pptv
  - NO 50 ppt
HO$_2$ and OH have good precision – sub-minute resolution will be used to examine variability.
The NO values between 2-6 km are around or below the NO detection limit (~50 pptv).
• Median observed-to-modeled OH ~ 0.6 at all altitudes.
• Median observed-to-modeled HO$_2$ ~ 0.8 up to 8 km.
• Behavior is similar to that in TRACE-P.
• Large observed-to-modeled OH in PBL correlates to isoprene (from Jim Crawford) as seen in forests.
• \( \text{NO}_x \) in INTEX-A is greater than in TRACE-P & PEM TB; CO and \( \text{O}_3 \) are similar in INTEX-A & TRACE-P.
• Observed-to-modeled \( \text{HO}_2/\text{OH} \) is close to 1 below 7 km, but exceeds 2 above \( \sim 9 \) km.
• \( \text{HO}_2/\text{OH} \) deviations appear to be \( \text{NO}_x \) related.
• Observed-to-modeled OH shows little NO\textsubscript{x}-dependence.
• Observed-to-modeled HO\textsubscript{2} grows for NO\textsubscript{x} > few 100 pptv.
• INTEX-A and TRACE-P dependences on NO\textsubscript{x} are similar.
• Observed-to-modeled HO\textsubscript{2} < 1 for NO\textsubscript{x} < few 100 pptv & > 1 for NO\textsubscript{x} > few 100 pptv is usually observed by us and a few others.
\( \text{HO}_2 \text{ versus } (\text{PHO}_x)^{1/2} \)

- \( \text{P(HO}_x) = \text{L(HO}_x) \propto \left[ \text{HO}_2 \right]^2 \), so \( \left[ \text{HO}_2 \right] \propto \sqrt{\text{P(HO}_x)} \).
- Much \( \text{HO}_2 \) variance can be explained by \( \text{P(HO}_x) \).
**HO\textsubscript{x} observed & modeled comparisons**

- Solid line: 1:1; dashed lines: obs. uncertainty ±32%.
- HO\textsubscript{x} comparison similar to that in TRACE-P.
Main $P(OH)$ is $O^1D+H_2O$ (below 5 km) and $HO_2+NO$ (above 5 km).
Main $L(OH)$ is $OH+CO/VOC$. 
Modeled HO$_2$ production and loss

Main P(HO$_2$) is OH+CO.
Main L(HO$_2$) is HO$_2$-RO$_2$ self-reactions (below 5 km) & HO$_2$+NO (above 5 km).
**O₃ budget**

- **Main P(O₃):** HO₂+NO.
- **Main L(O₃):** O¹D+H₂O (< 5 km) & O₃+HO₂/OH (> 5 km).
- **Net O₃ loss** at altitudes between 1 km and 5 km.
Science questions we hope to answer

• General comparisons between observed and modeled HO\textsubscript{x}
  – Were previous observed-to-modeled anomalies also observed in INTEX-A? (e.g., NO\textsubscript{x}-dependence of observed-to-modeled HO\textsubscript{2})
  – Can the HO\textsubscript{x} heterogeneous effects (or lack thereof) be understood?

• High speed photochemistry – one-to-a-few seconds
  – What are the effects of scale on calculating P(O\textsubscript{3}) from HO\textsubscript{2} & NO?
  – Is HO\textsubscript{x} behavior understood in urban, forest-fire, and long-range regionally transported plumes?

• HO\textsubscript{x} behavior in the planetary boundary layer
  – What is the behavior of HO\textsubscript{x} and P(O\textsubscript{3}) and vertical distribution in the boundary layer?
  – Is isoprene chemistry in forested regions adequately understood?

• Collaborations with many others on these & other questions.