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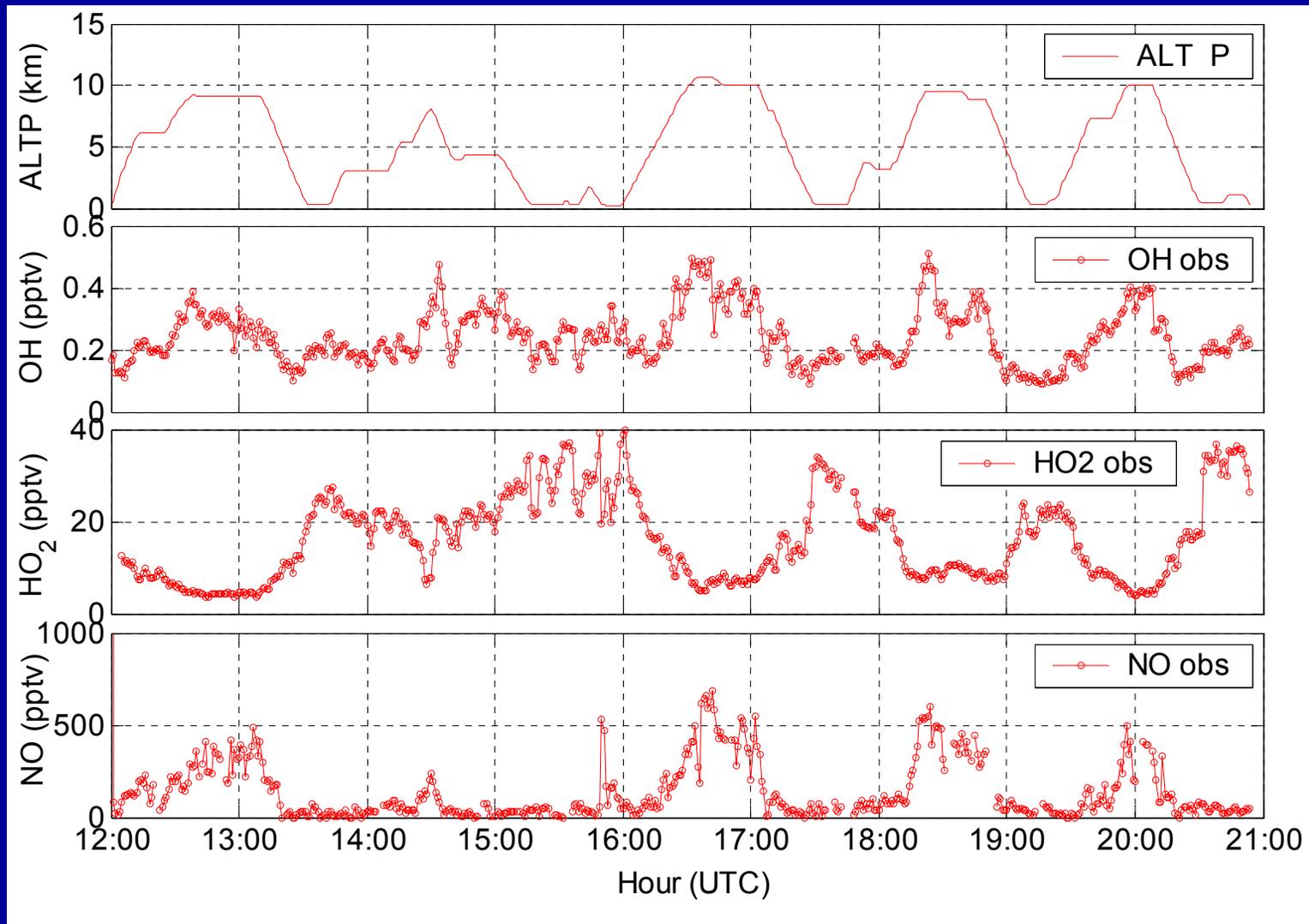
- **NO measurements**
  TEI 42C NO-NO$_x$ analyzer
     – Chemiluminescence
     – NO single mode
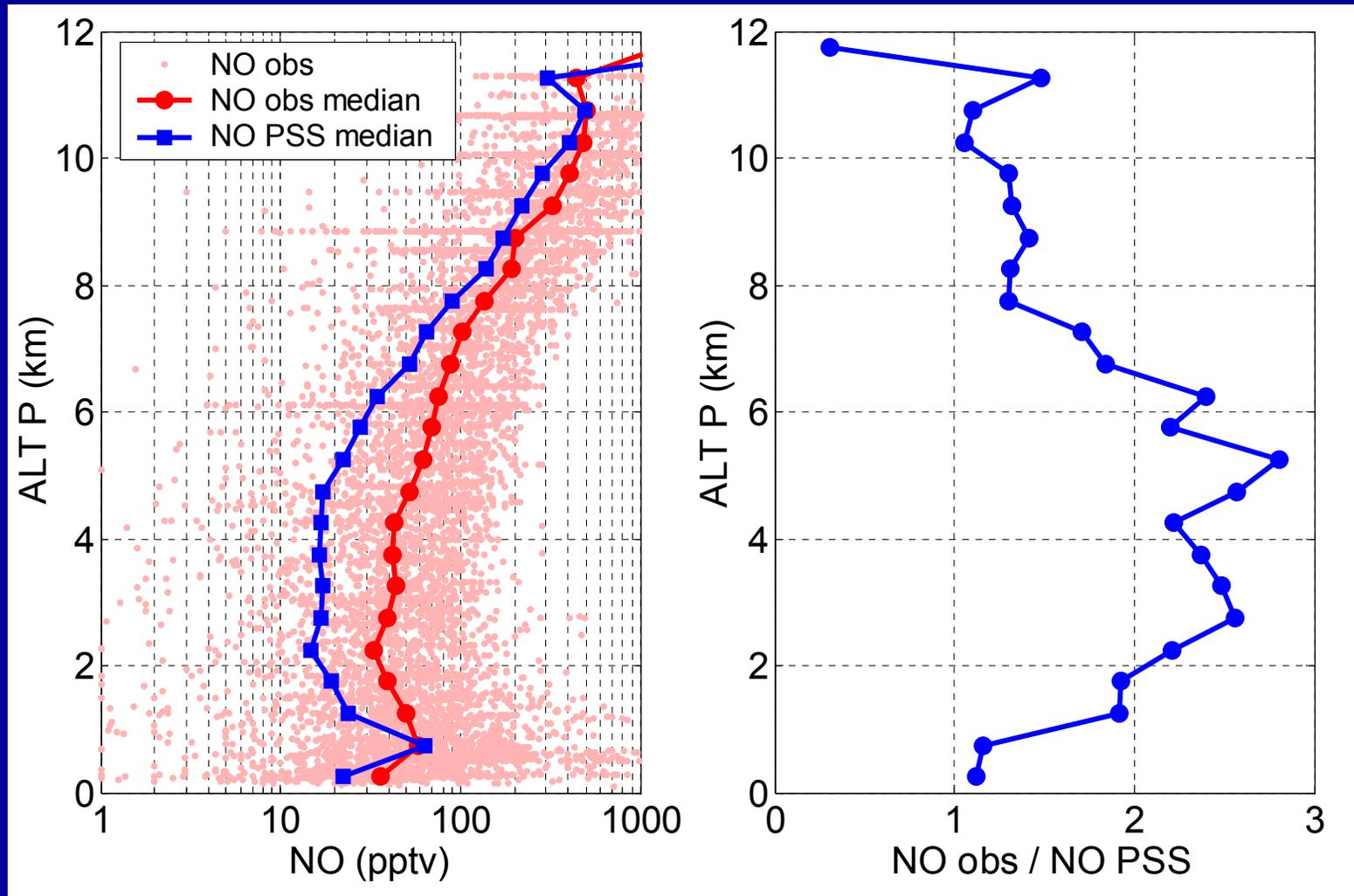   – Online NO span and zero checks

Data Quality

- Data coverage:

$$OH \ (1 \ min) \ - \ 97\%$$
$$HO_2 \ (1 \ min) \ - \ 95\%$$
$$NO \ (1 \ min) \ - \ 89\%$$

- Typical uncertainties:

$$HO_x \ \pm 32\% \ (2\sigma)$$
$$NO \ \pm 30\% \ (2\sigma)$$

- Detection limits:

$$OH \quad 0.01 \ pptv$$
$$HO_2 \quad 0.1 \ pptv$$
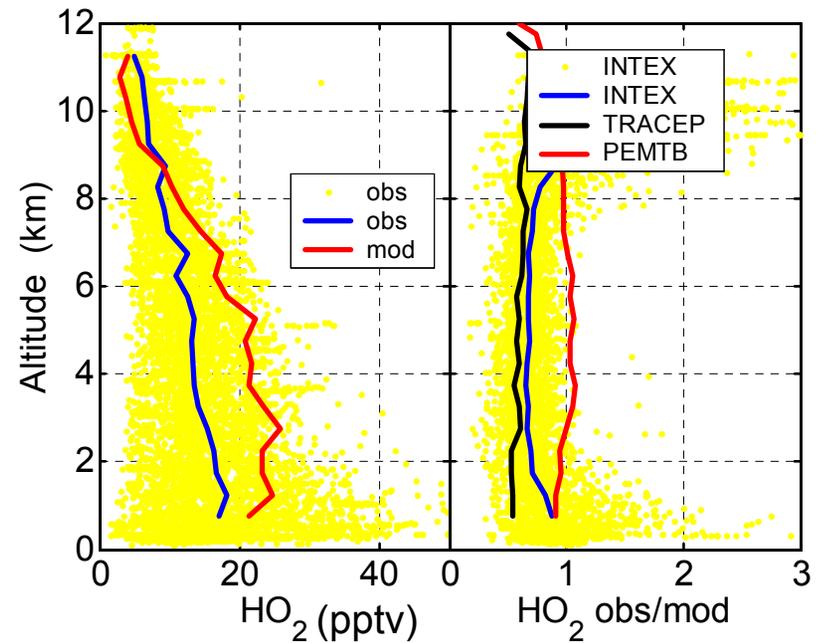$$NO \quad 50 \ ppt$$

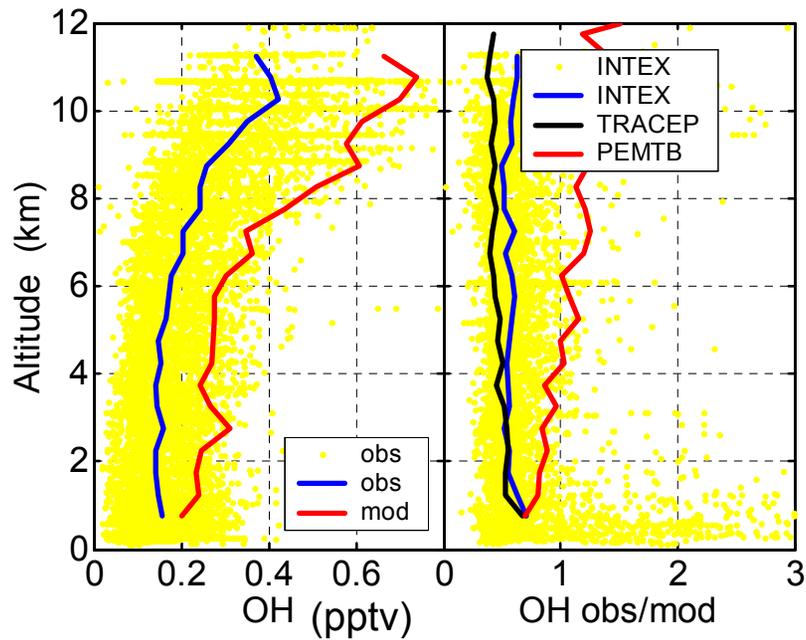# HO$_x$ and NO observations (July 22, Flight 11)

HO$_2$ and OH have good precision – sub-minute resolution will be used to examine variability.
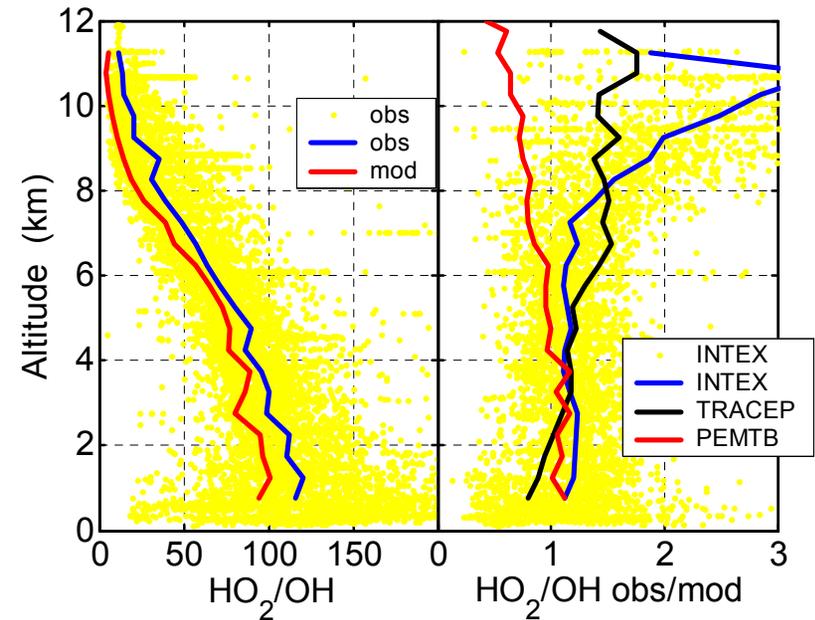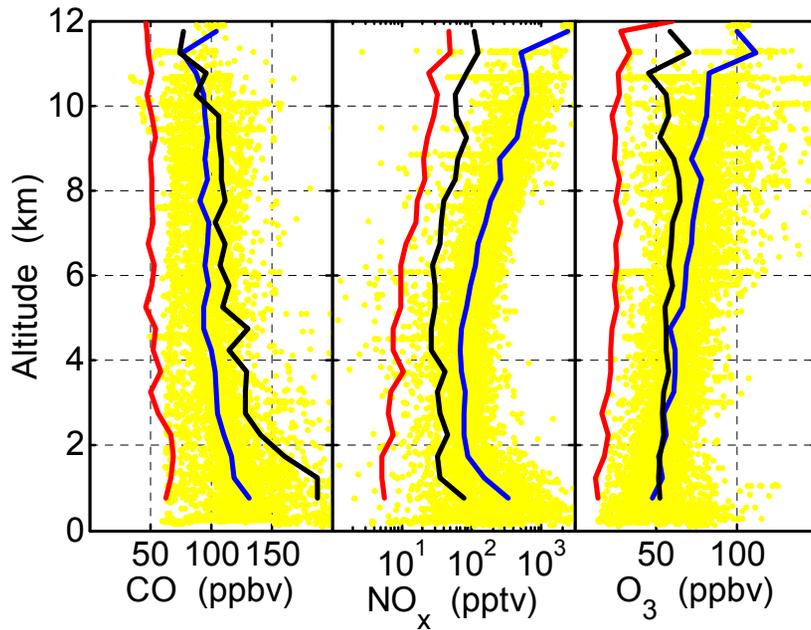
Observed & PSS NO vertical profiles

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.

- NO$_x$ in INTEX-A is greater than in TRACE-P & PEM TB; CO and O$_3$ are similar in INTEX-A & TRACE-P.

- Observed-to-modeled HO$_2$/OH is close to 1 below 7 km, but exceeds 2 above ~9 km.

- HO$_2$/OH deviations appear to be NO$_x$ related.
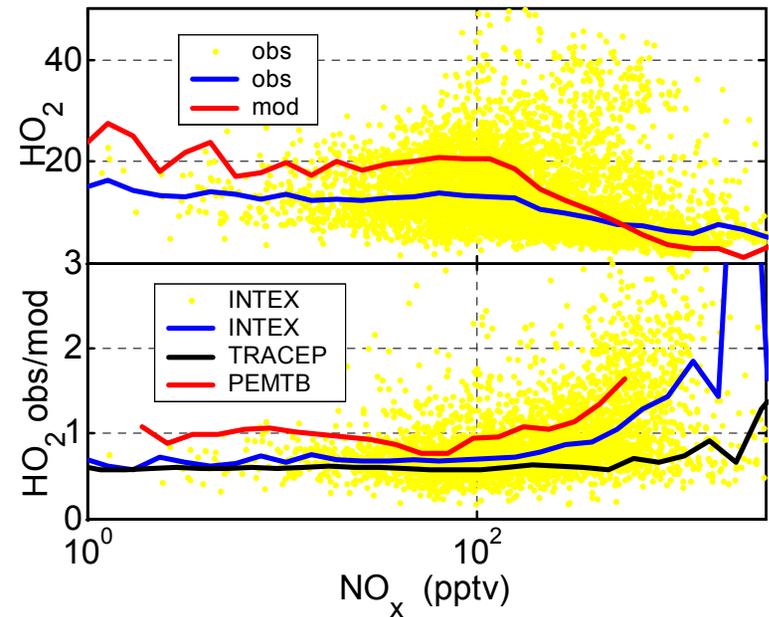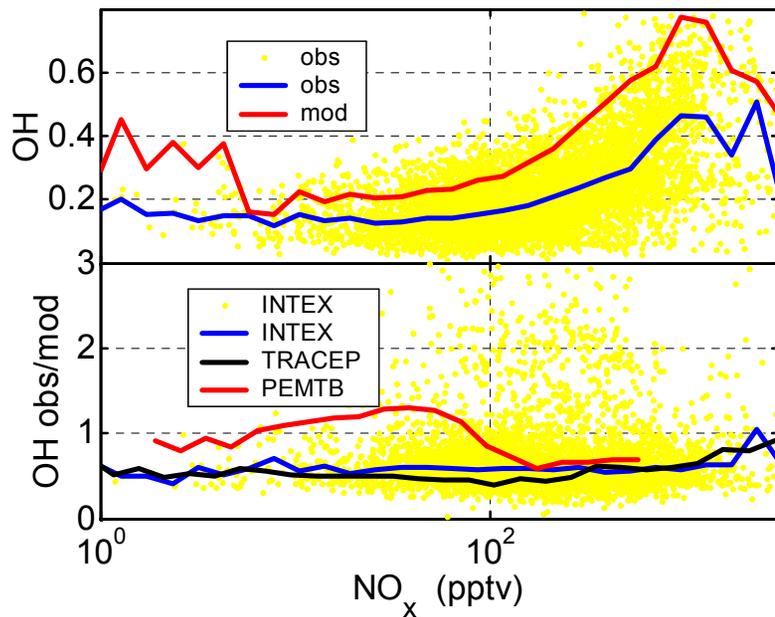
- Observed-to-modeled OH shows little NO_x-dependence.
- Observed-to-modeled HO_2 grows for NO_x > few 100 pptv.
- INTEX-A and TRACE-P dependences on NO_x are similar.
- Observed-to-modeled HO_2 < 1 for NO_x < few 100 pptv & > 1 for NO_x > few 100 pptv is usually observed by us and a few others.

HO$_2$ versus (PHO$_x$)$^{1/2}$
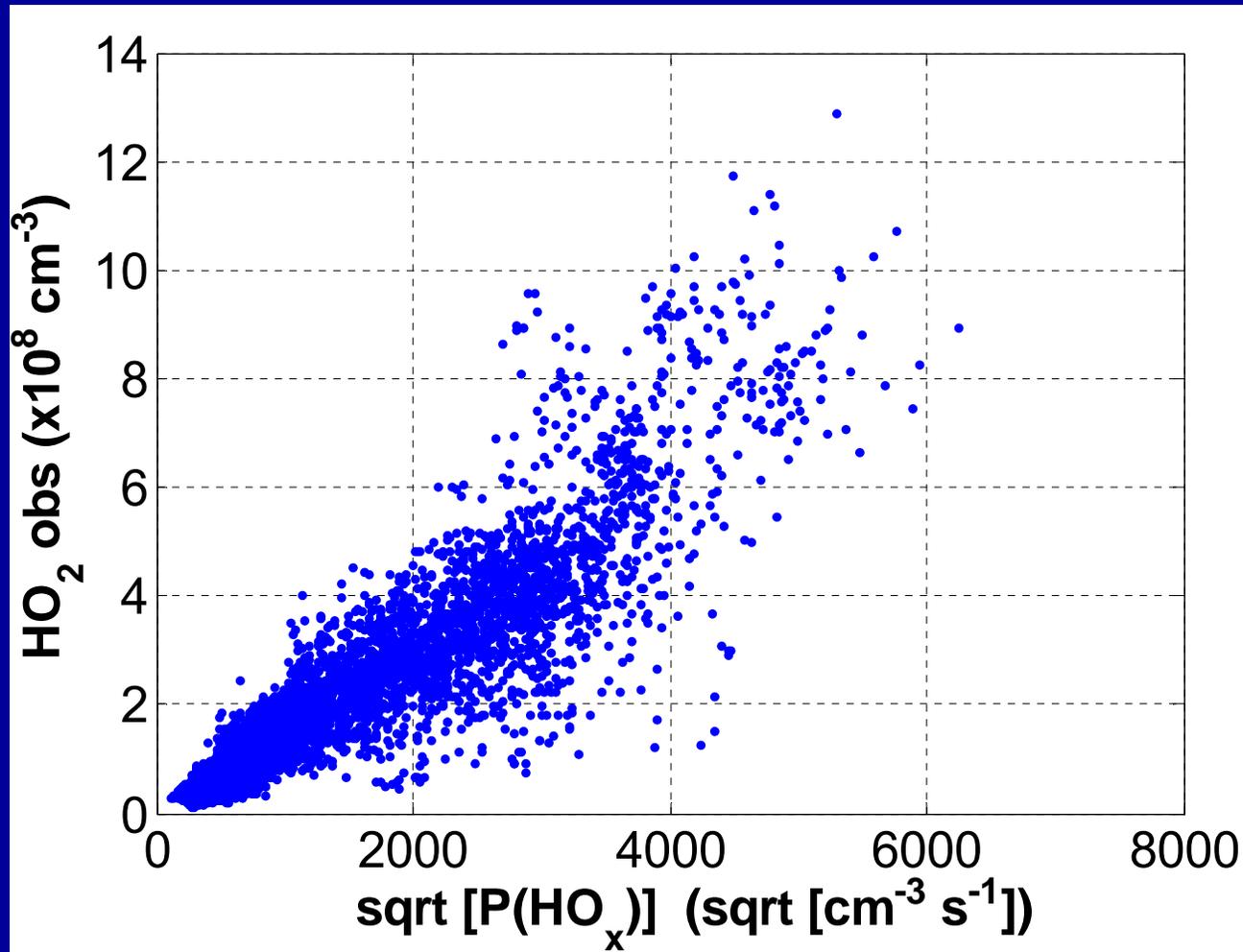
- P(HO$_x$) = L(HO$_x$) $\propto$ [HO$_2$]^2, so [HO$_2$] $\propto$ sqrt {P(HOx)}.
- Much HO$_2$ variance can be explained by P(HO$_x$).
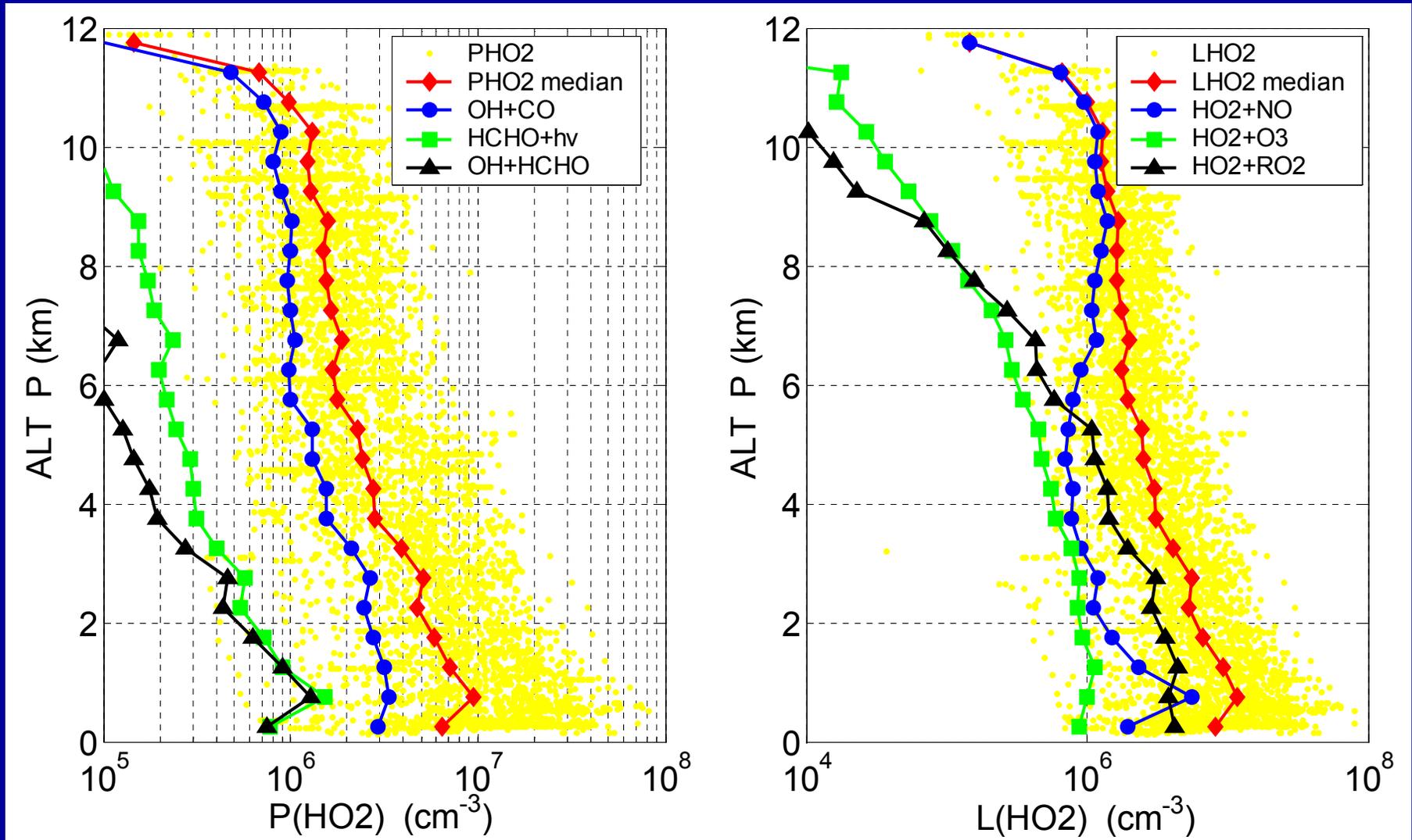
HO$_x$ observed & modeled comparisons
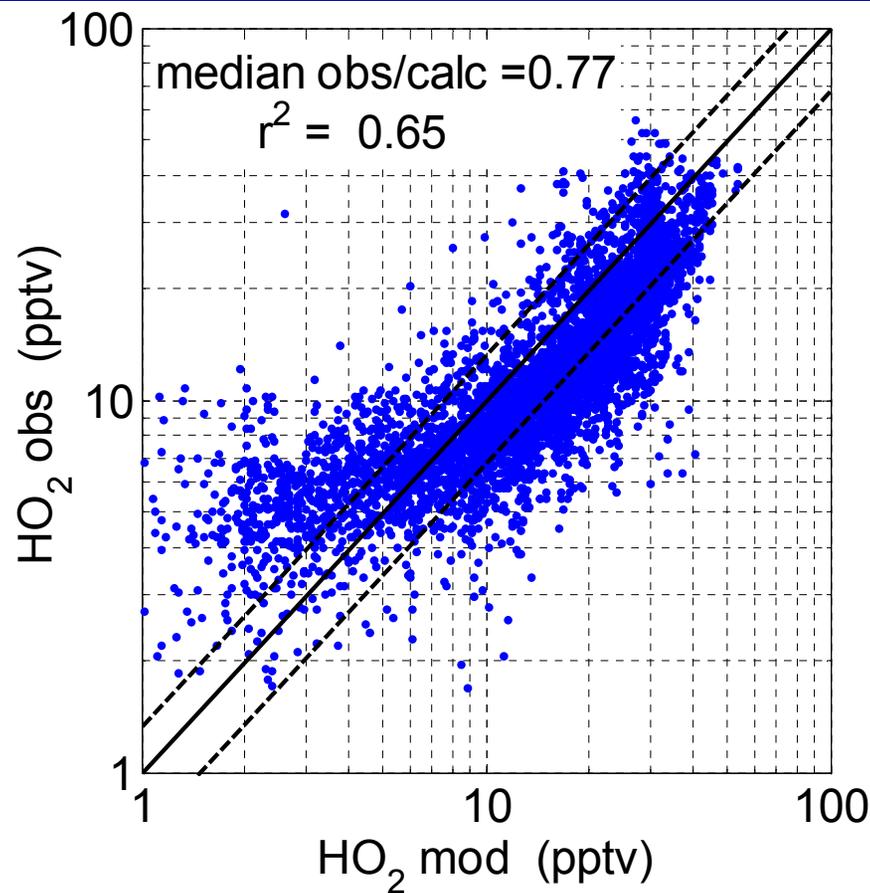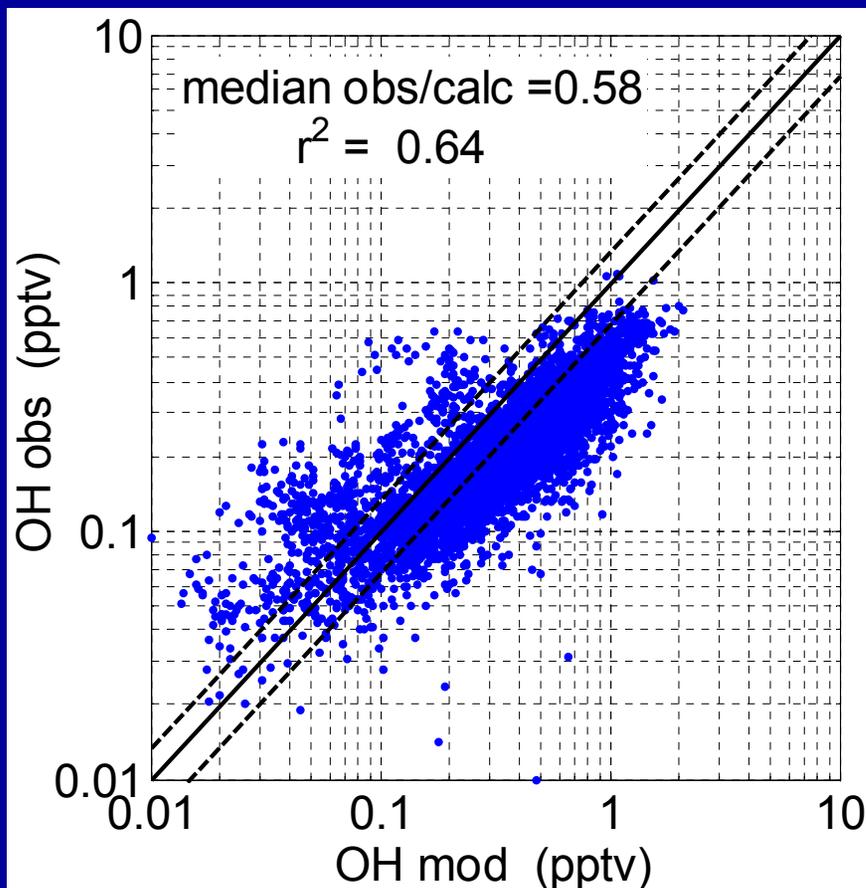
- Solid line: 1:1;   dashed lines: obs. uncertainty ±32%.
- HO$_x$ comparison similar to that in TRACE-P.

Modeled OH production and loss
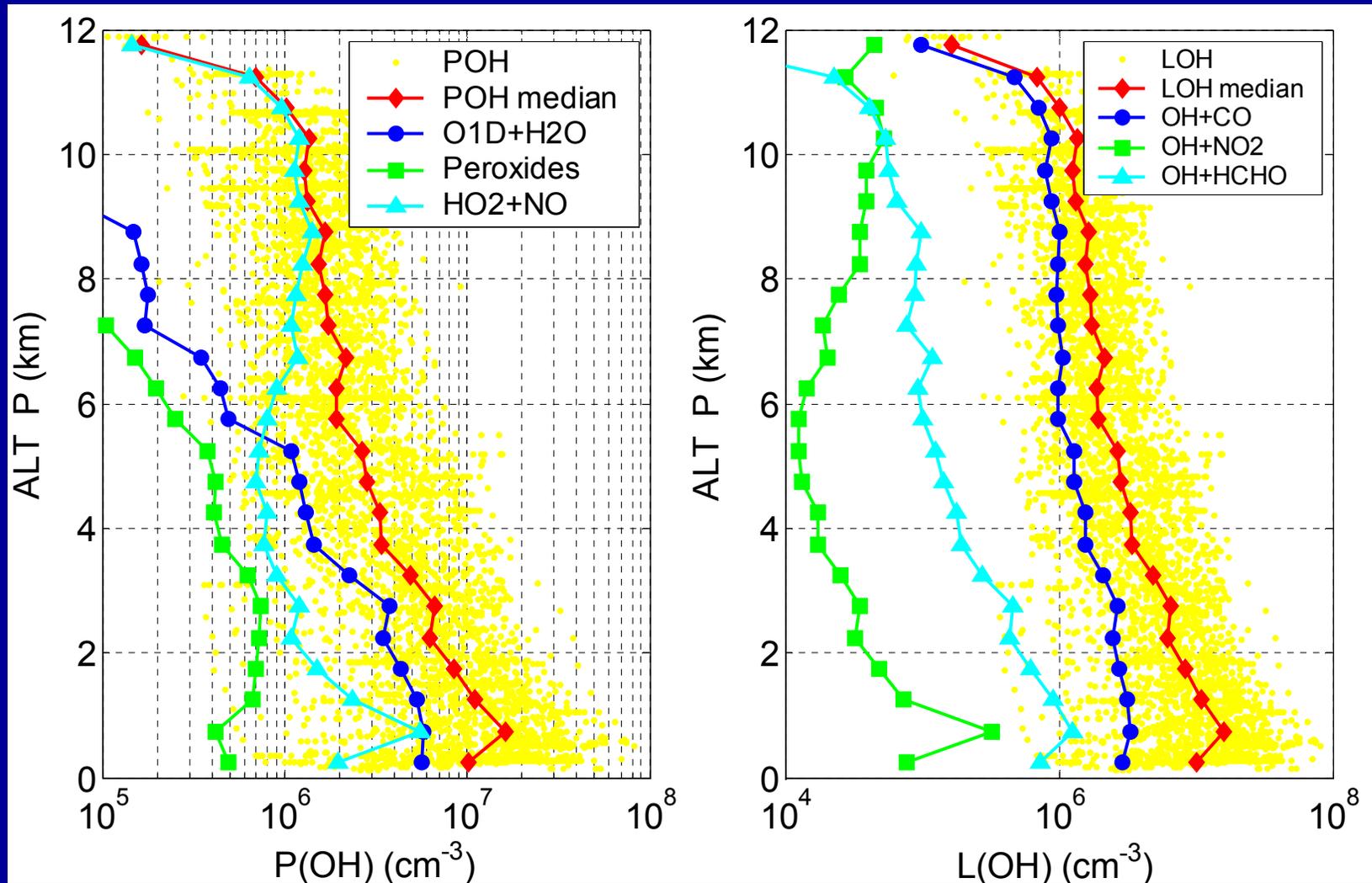
Main P(OH) is O^1D+H_2O (below 5 km) and HO_2+NO (above 5 km).
Main L(OH) is OH+CO/VOC.

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).

O$_3$ budget
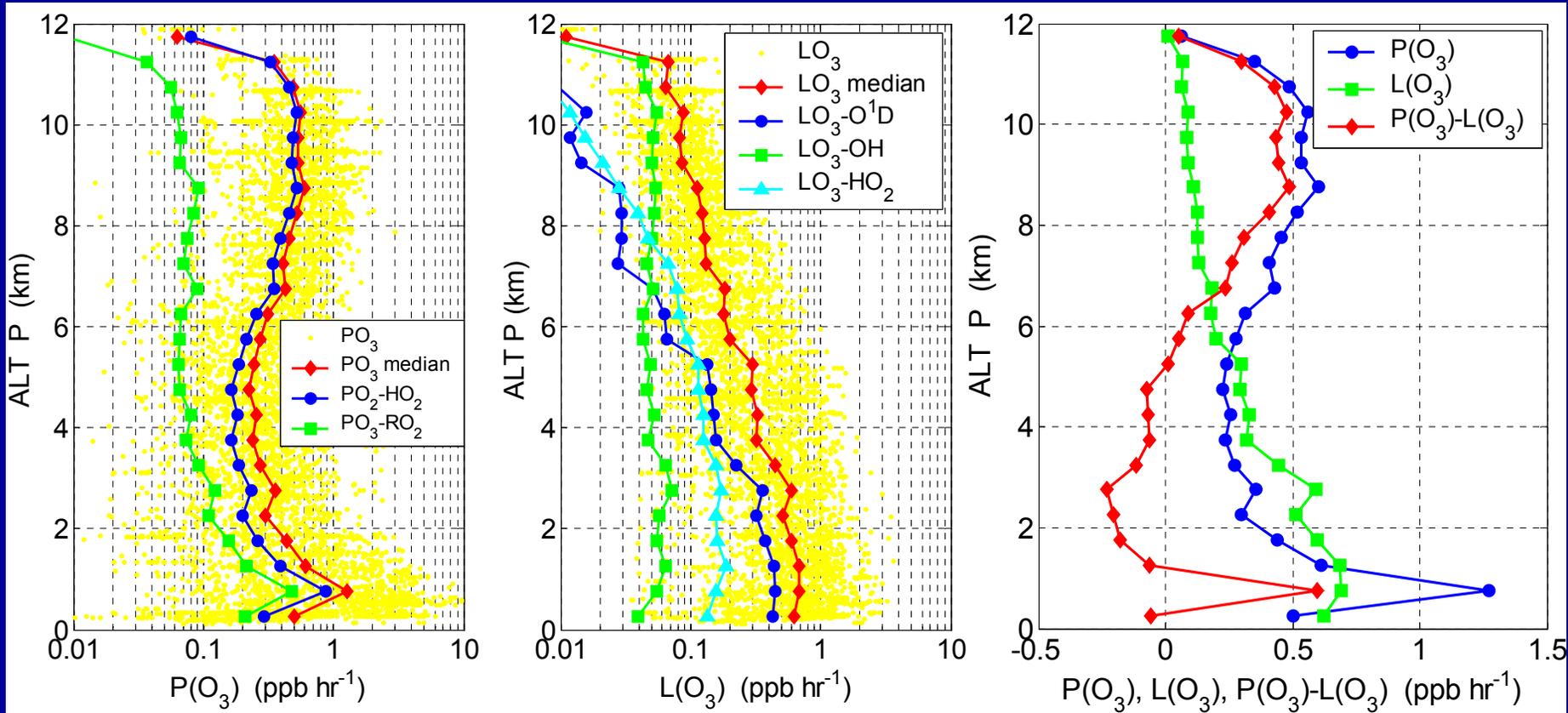
- Main P(O$_3$): HO$_2$+NO.
- Main L(O$_3$): O^{1}D+H$_2$O (< 5 km) & O$_3$+HO$_2$/OH (> 5 km).
- Net O$_3$ loss at altitudes between 1 km and 5 km.

Science questions we hope to answer

- General comparisons between observed and modeled HO_x
  - Were previous observed-to-modeled anomalies also observed in INTEX-A? (e.g., NO_x-dependence of observed-to-modeled HO_2)
  - Can the HO_x heterogeneous effects (or lack thereof) be understood?

- High speed photochemistry – one-to-a-few seconds
  - What are the effects of scale on calculating $P(O_3)$ from HO_2 & NO?
  - Is HO_x behavior understood in urban, forest-fire, and long-range regionally transported plumes?

- HO_x behavior in the planetary boundary layer
  - What is the behavior of HO_x and $P(O_3)$ and vertical distribution in the boundary layer?
  - Is isoprene chemistry in forested regions adequately understood?

- Collaborations with many others on these & other questions.