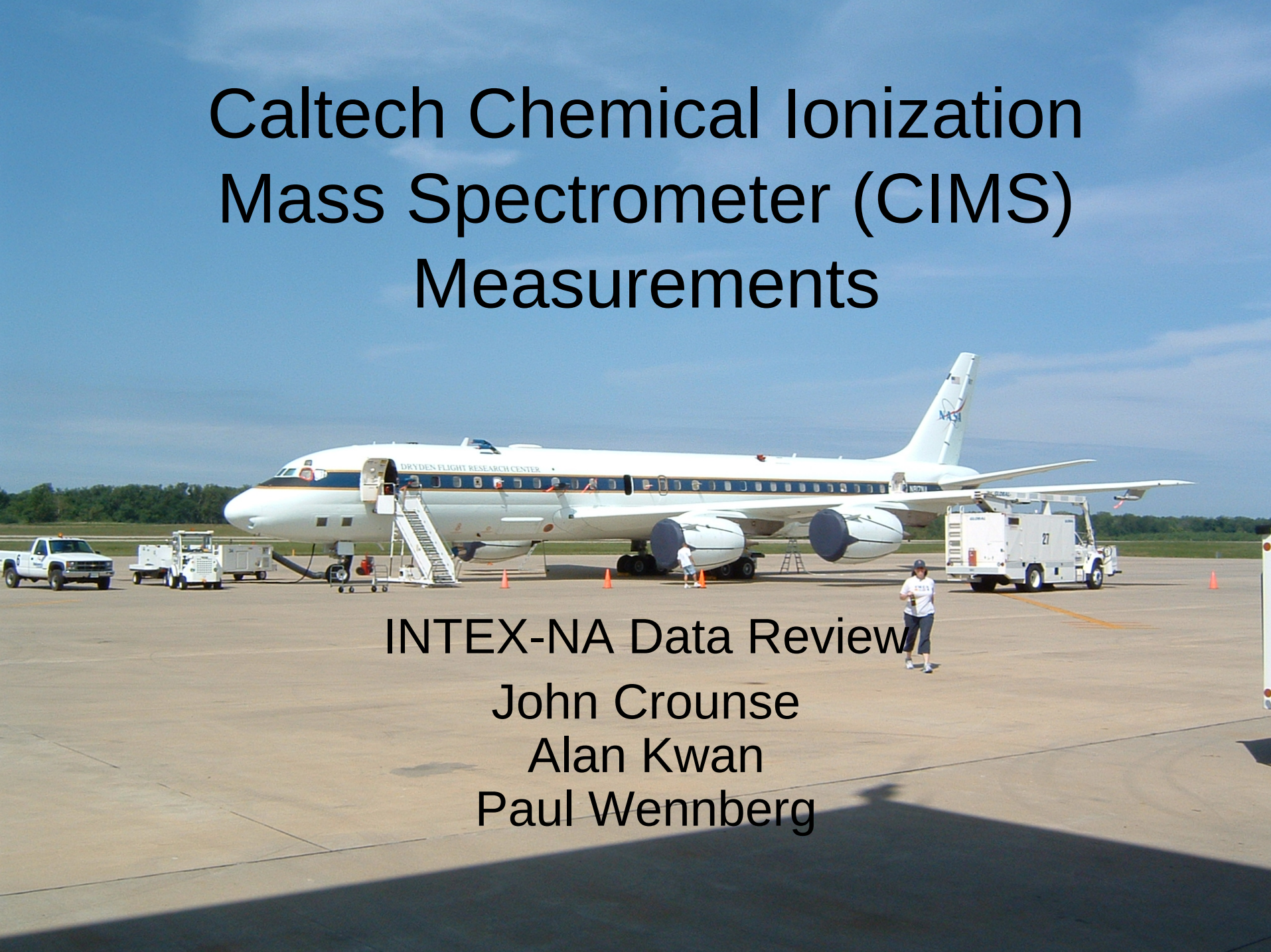
Caltech Chemical Ionization Mass Spectrometer (CIMS) Measurements



INTEX-NA Data Review

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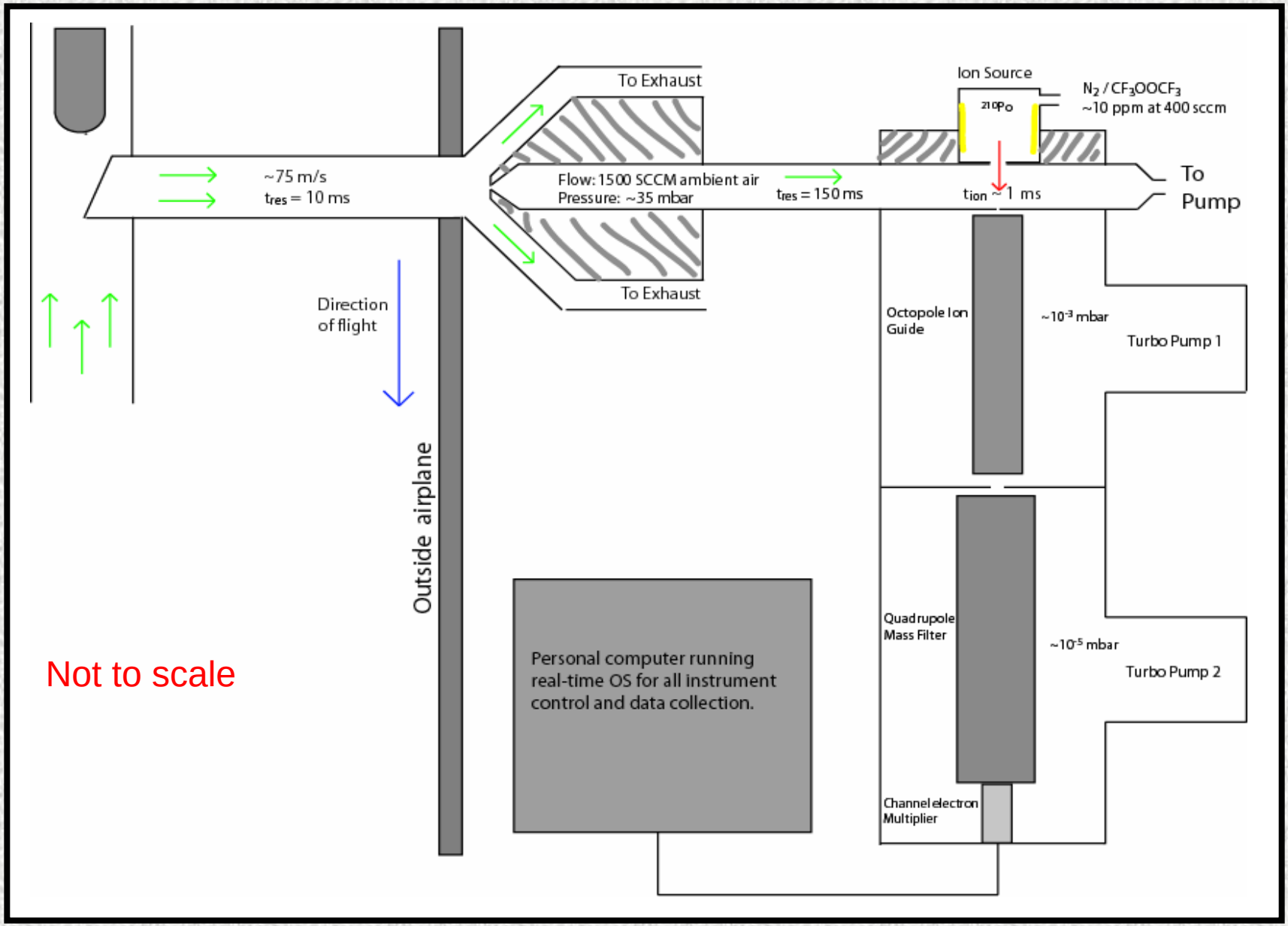
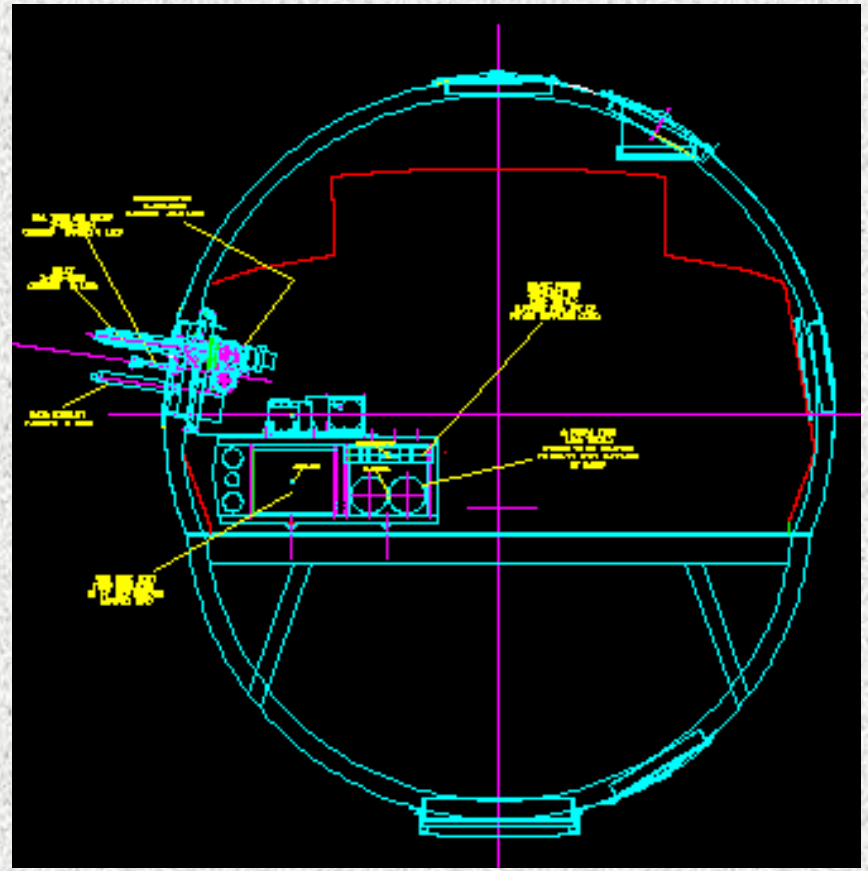
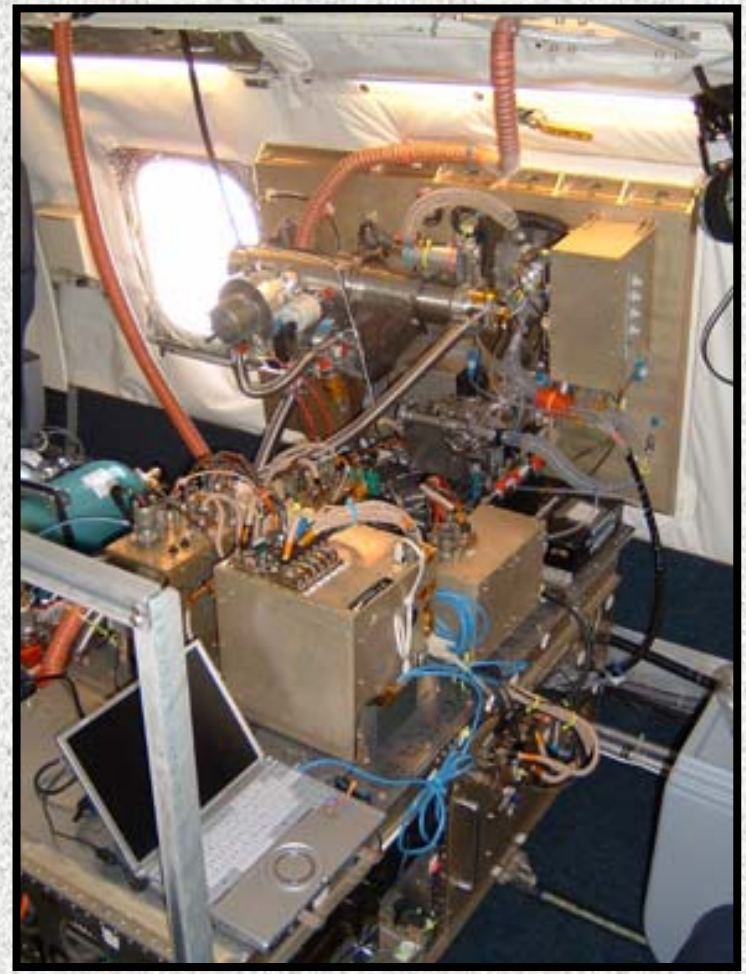
Instrument Block Diagram



CIMS on DC-8





Measurements

- HNO_3 (0.5 s every 5 s)
- H_2O_2 (0.5 s every 5 s)
- Peroxyacetic Acid (PAA, $CH_3C(O)OOH$)
  - (0.5 s every 10 s)
- HCN (Flight #10 onwards)
  - (0.5 s every 10 s)

Calibration

- Online HNO_3 calibration from perm tube held at constant temp.
- Online H_2O_2 calibration from urea-hydrogen peroxide held at constant temperature.
- Calibrations performed every hour.

Data Reduction

Concentration =

cts_signal_ion / cts_reagent_ion / F([H_2O]) * cal_factor

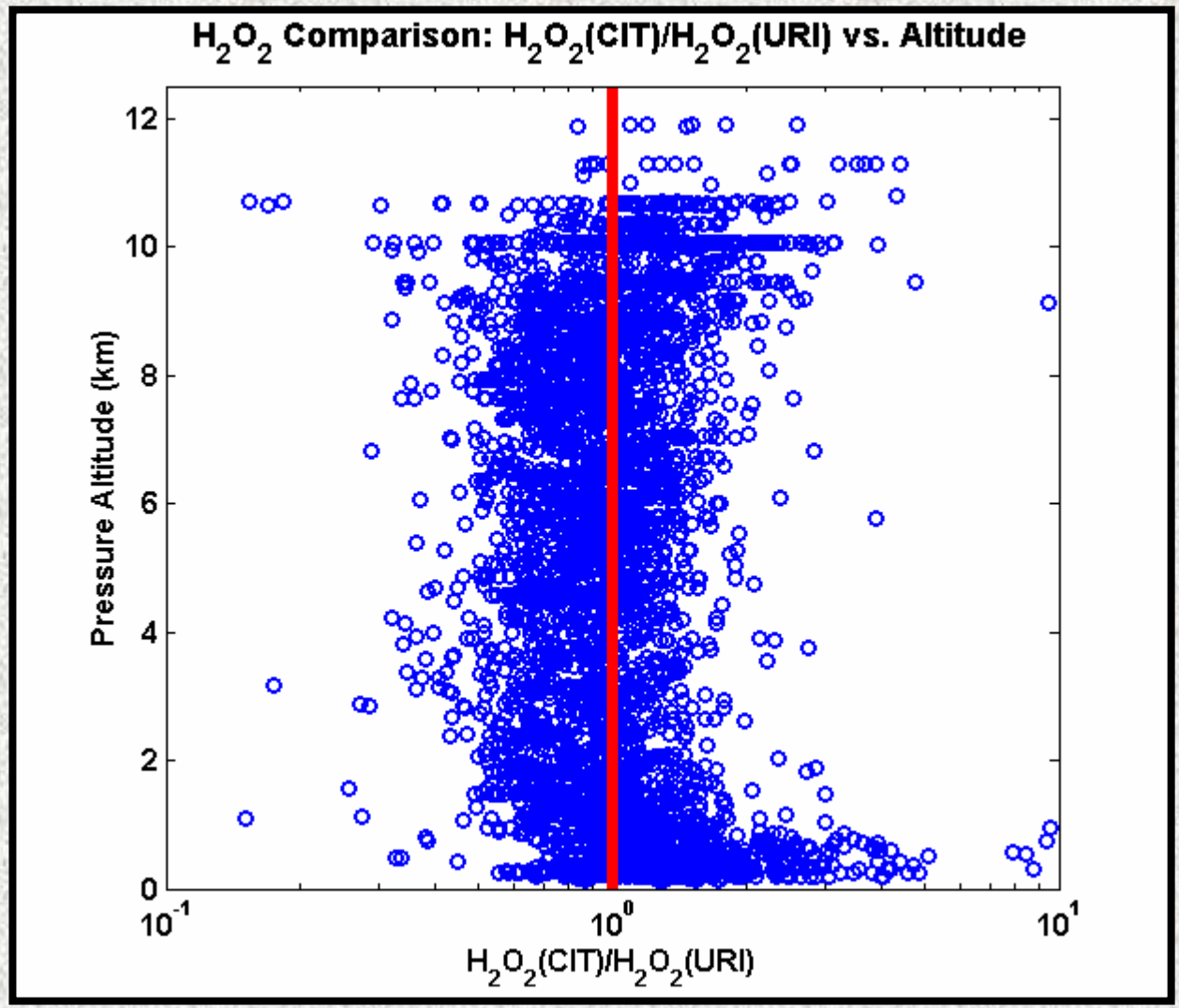
DLH-H_2O was used for ambient water concentrations.

H_2O_2 Measurements

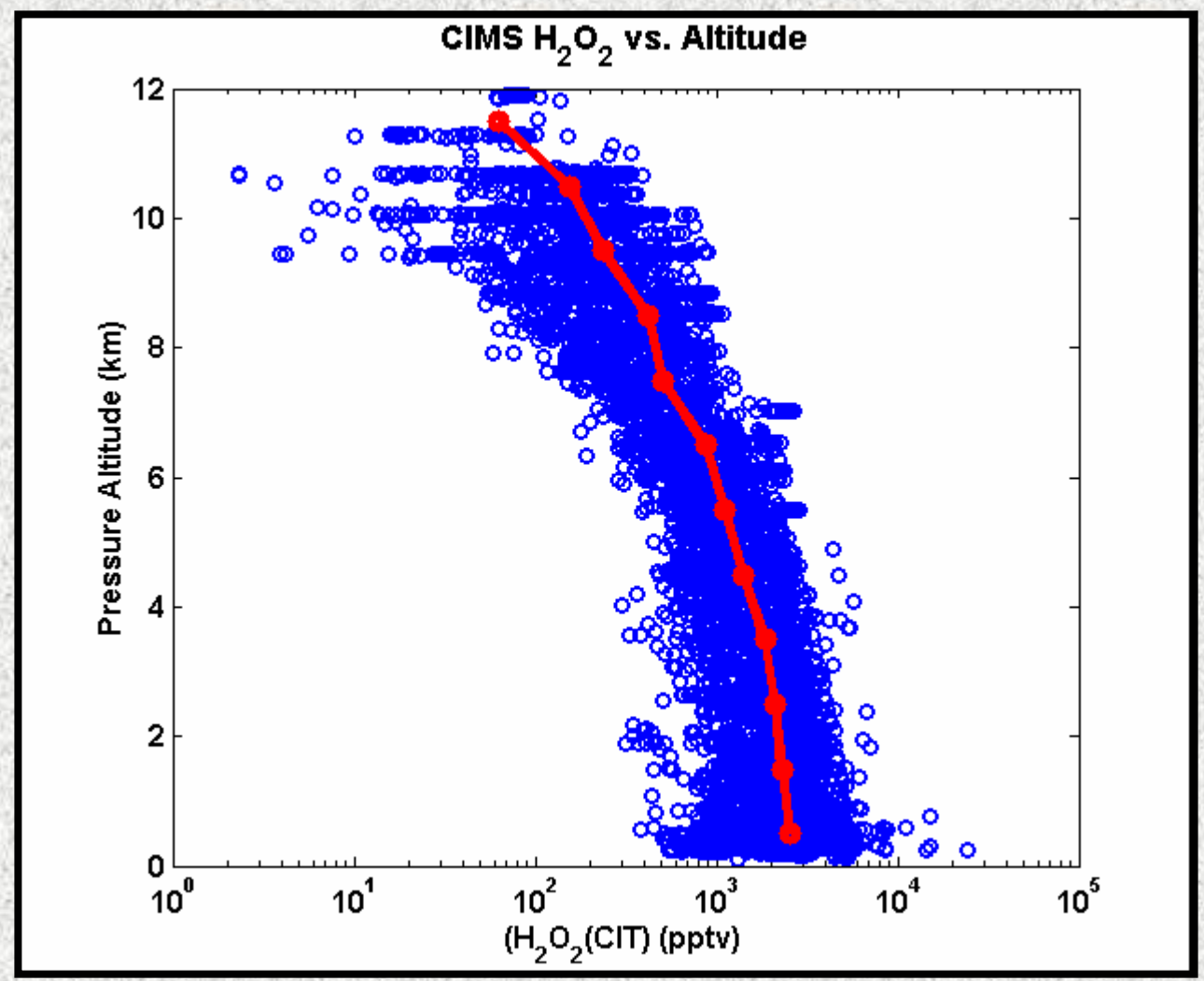
- Compare well with URI HPLC/Fluorescence measurements
- There is an interference at high SO_2 and high H_2O, this only affects a small fraction of measurements.

CIT/URI H_2O_2 Comparison

Median: 0.98
Mean: 1.10



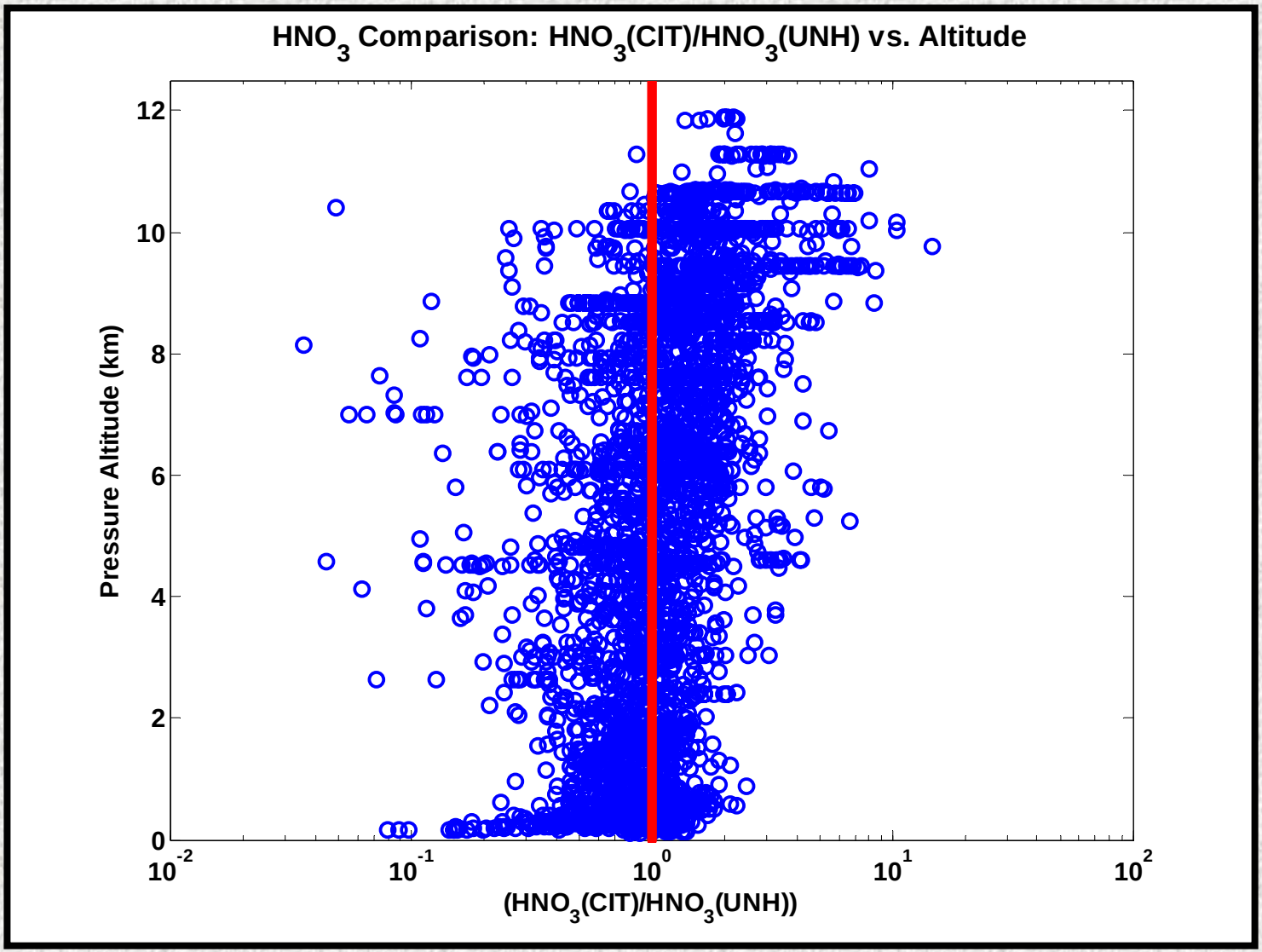
Altitude Profile H_2O_2



HNO_3 Measurements

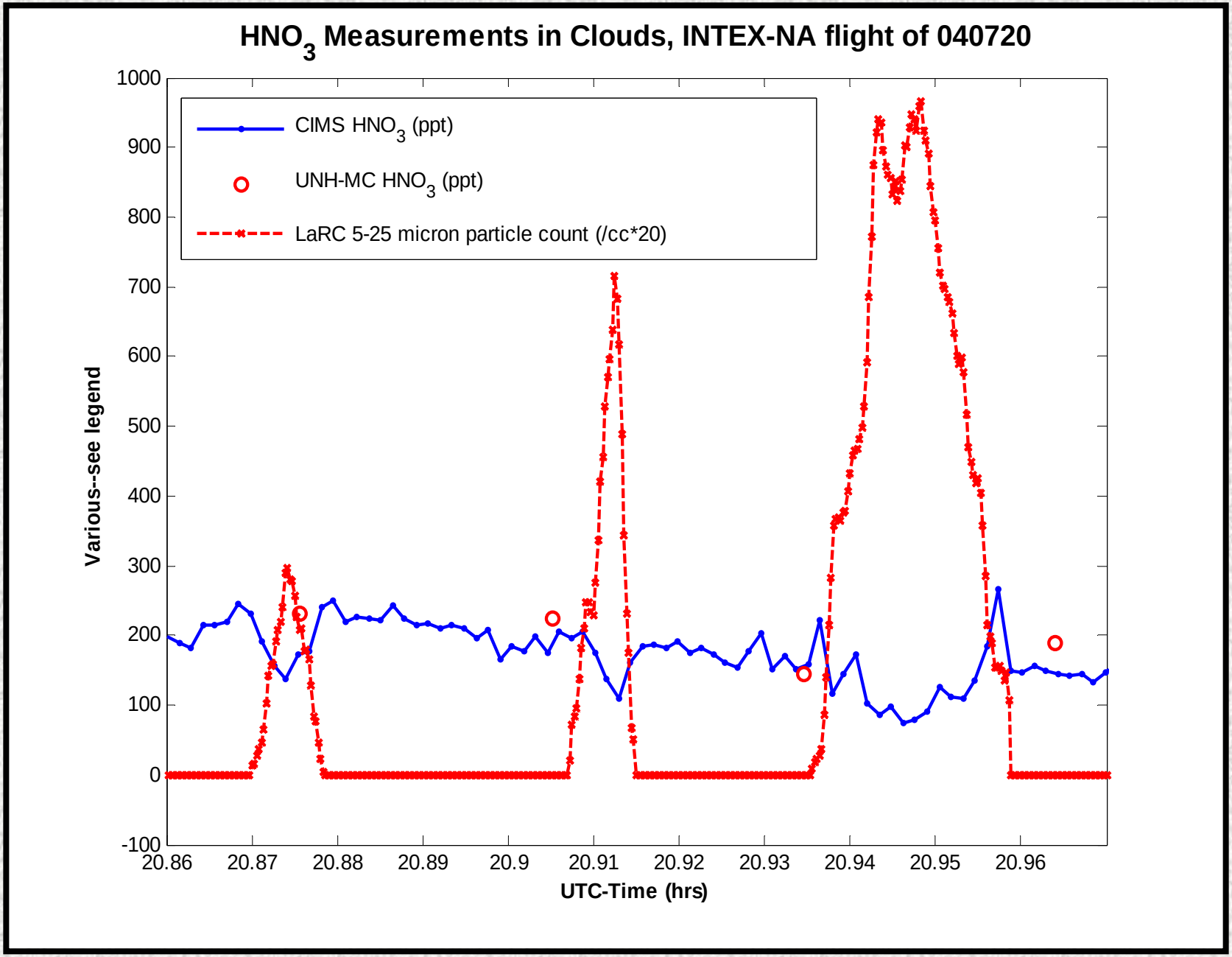
- Compared with UNH well overall but with certain differences: Altitude trend, low altitude trend, biomass burning plumes.

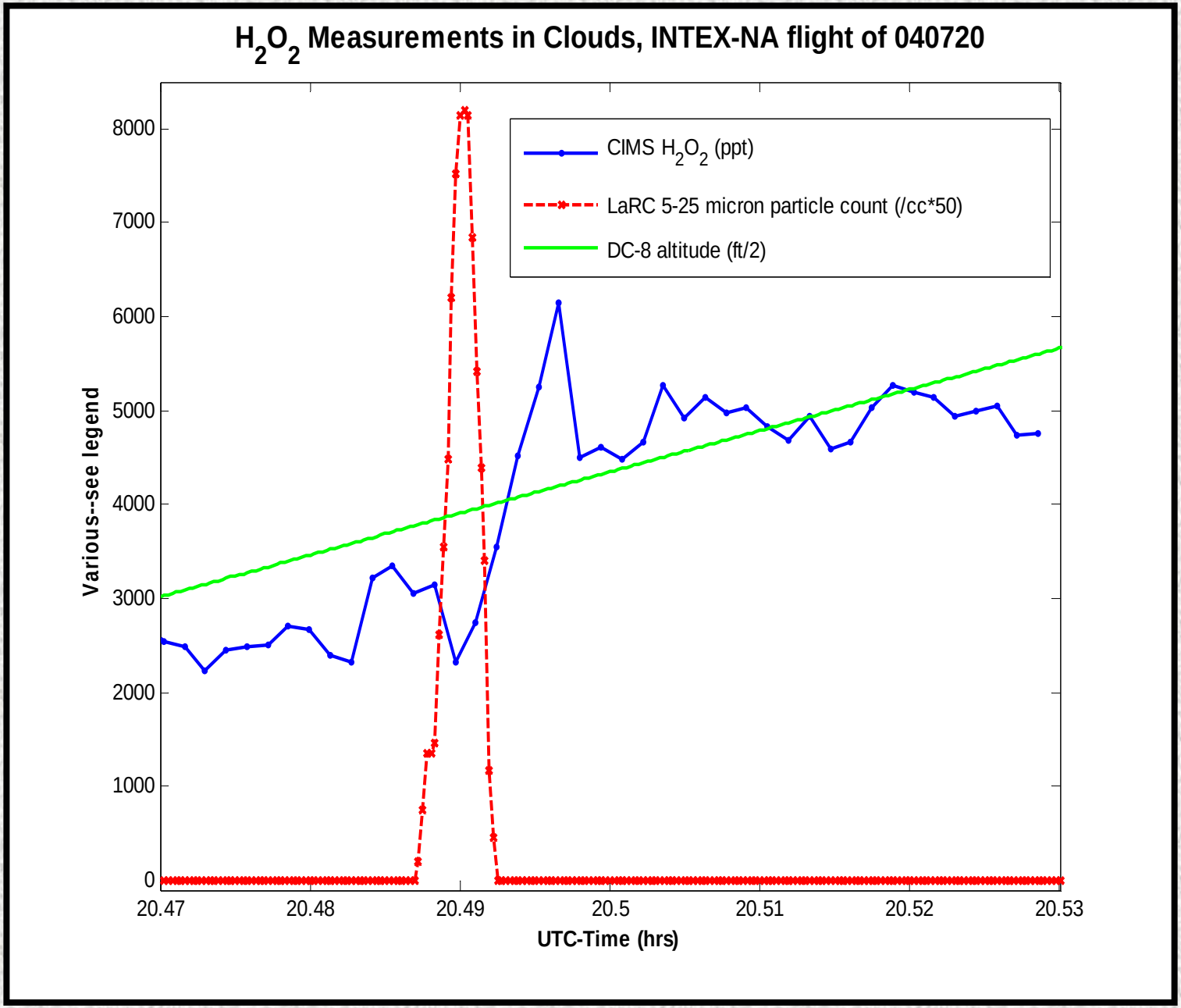
HNO_3 Comparison



Fast HNO_3 and H_2O_2 Measurements

- Interesting data within cloud, and around cloud/clear interfaces.


HNO3 Measurements in Clouds, INTEX-NA flight of 040720
CIMS HNO3 (ppt)
UNH-MC HNO3 (ppt)
LaRC 5-25 micron particle count (/cc*20)
Various--see legend
UTC-Time (hrs)
1000
900
800
700
600
500
400
300
200
100
0
-100
20.86
20.87
20.88
20.89
20.9
20.91
20.92
20.93
20.94
20.95
20.96


H_2O_2 Measurements in Clouds, INTEX-NA flight of 040720
CIMS H_2O_2 (ppt)
LaRC 5-25 micron particle count (/cc*50)
DC-8 altitude (ft/2)
Various--see legend
UTC-Time (hrs)
0
1000
2000
3000
4000
5000
6000
7000
8000
20.47
20.48
20.49
20.5
20.51
20.52
20.53

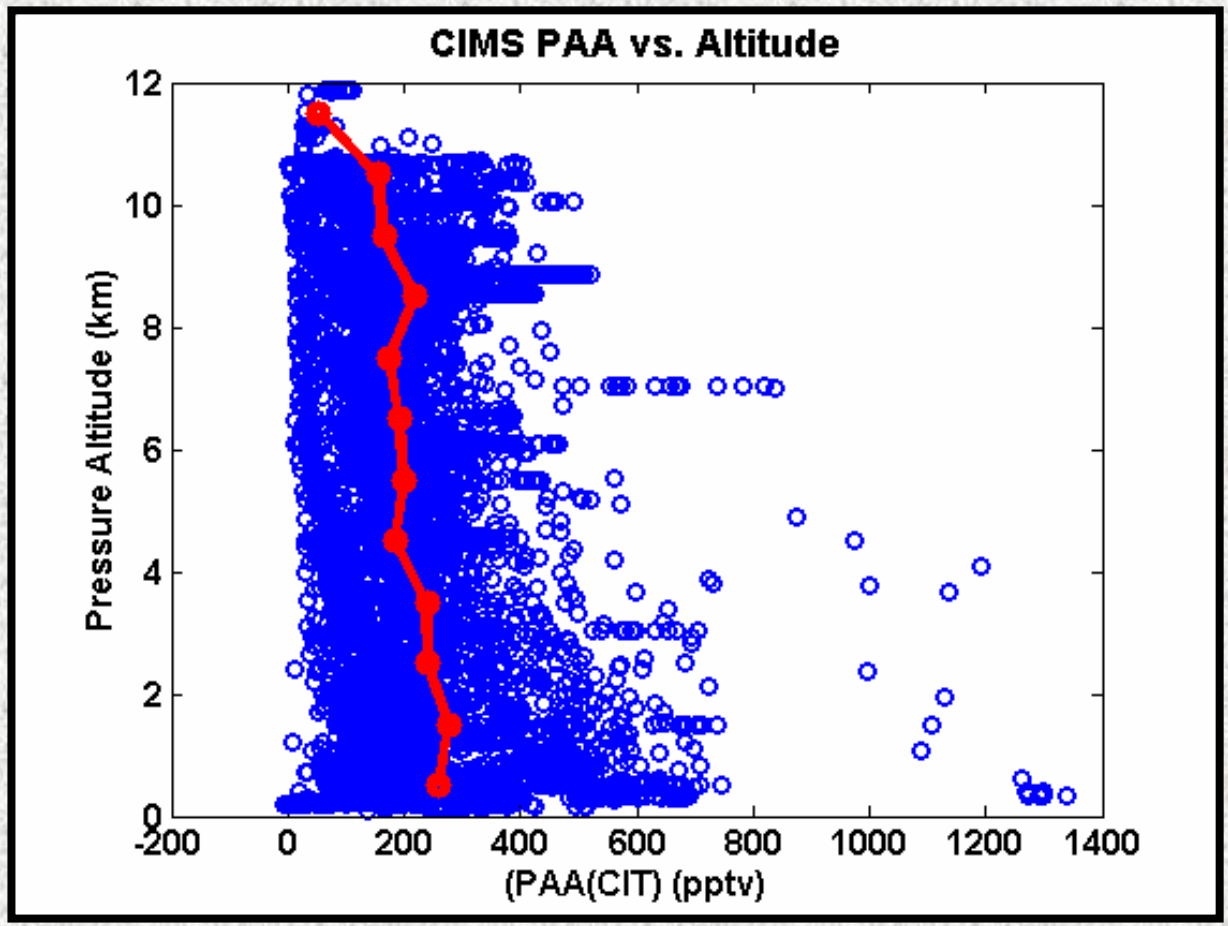
PAA Measurements

- Measured significant amounts of this molecule throughout mission, though it’s abundance was quite variable in space and time.

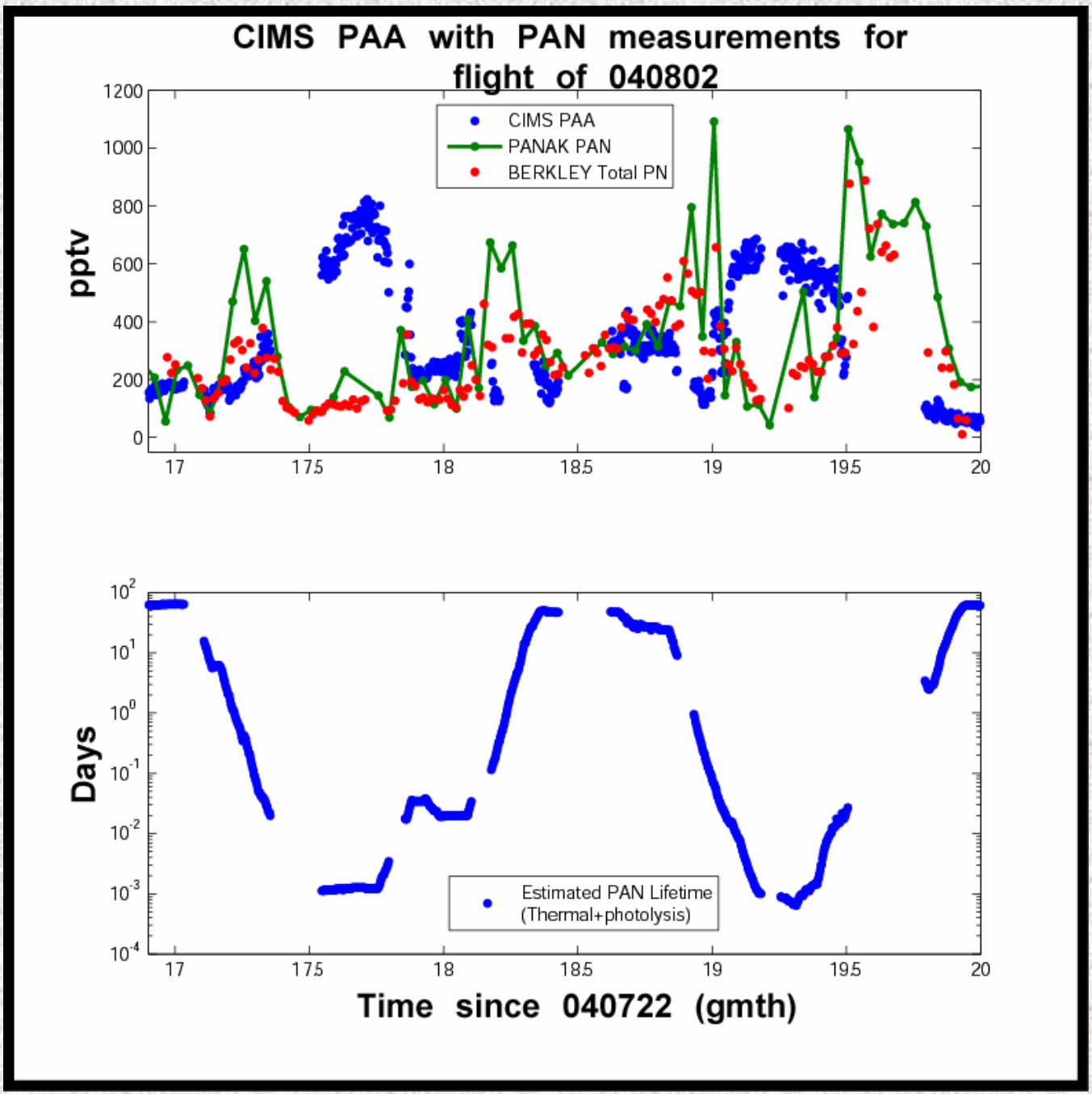
Significant concentrations observed.
Mean:213 pptv
Median: 188 pptv

Falls off weakly with altitude.

Highly variable in space and time.



Does PAA come from the thermal decomposition of PAN ?



PAA Lifetime?

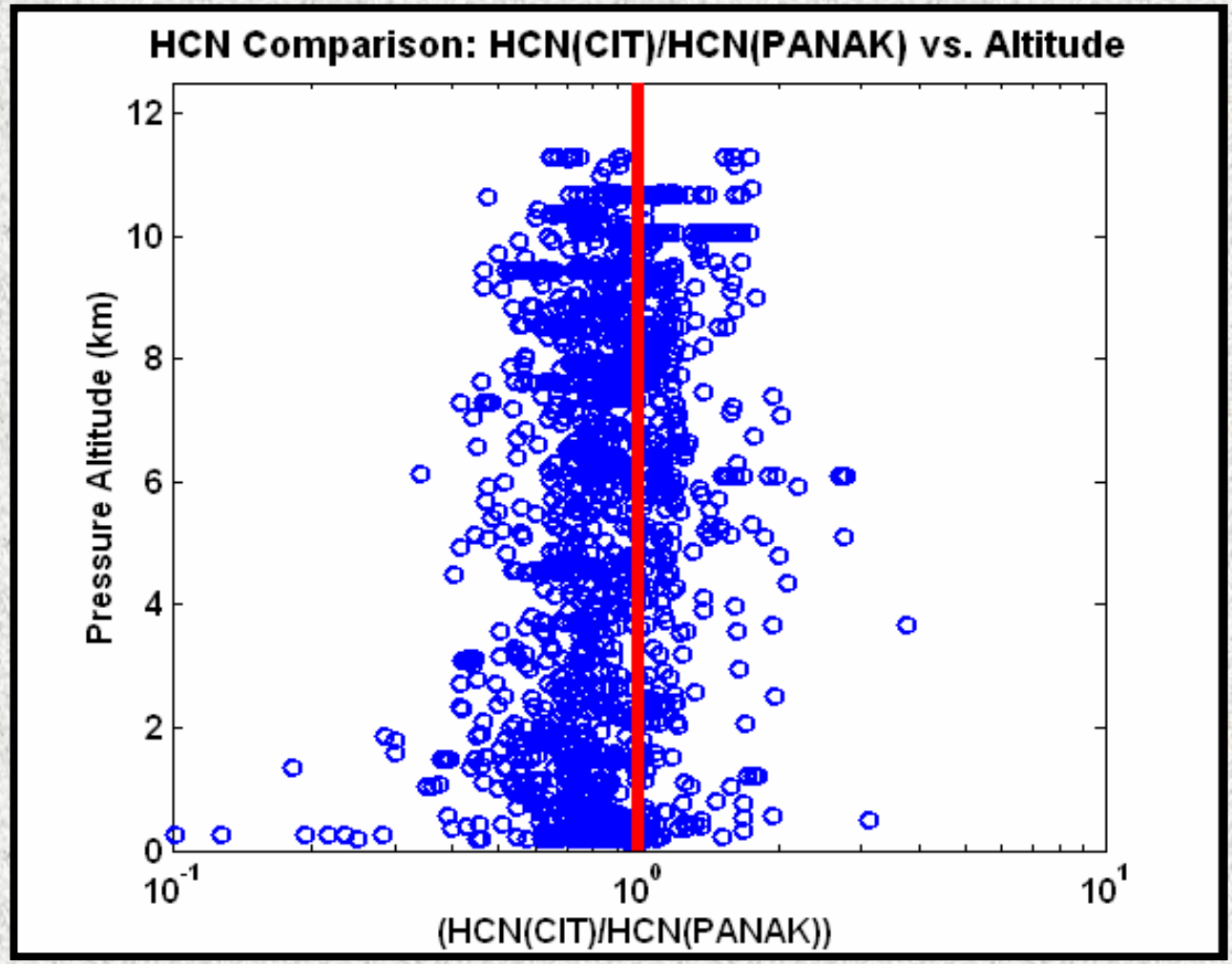
- Atmospheric lifetime??
  - Photolysis: 3-4 weeks → J = $5 \times 10^{-7} s^{-1}$ (Orlando, et. al., 2003)
  - Reaction rate with OH has NOT been measured!!
    - Estimated to be $1\text{-}7 \times 10^{-12}$ from the measured rates of OH with HOOH, and CH_3OOH.
    - This gives lifetime of 2-12 days.

HCN Measurements

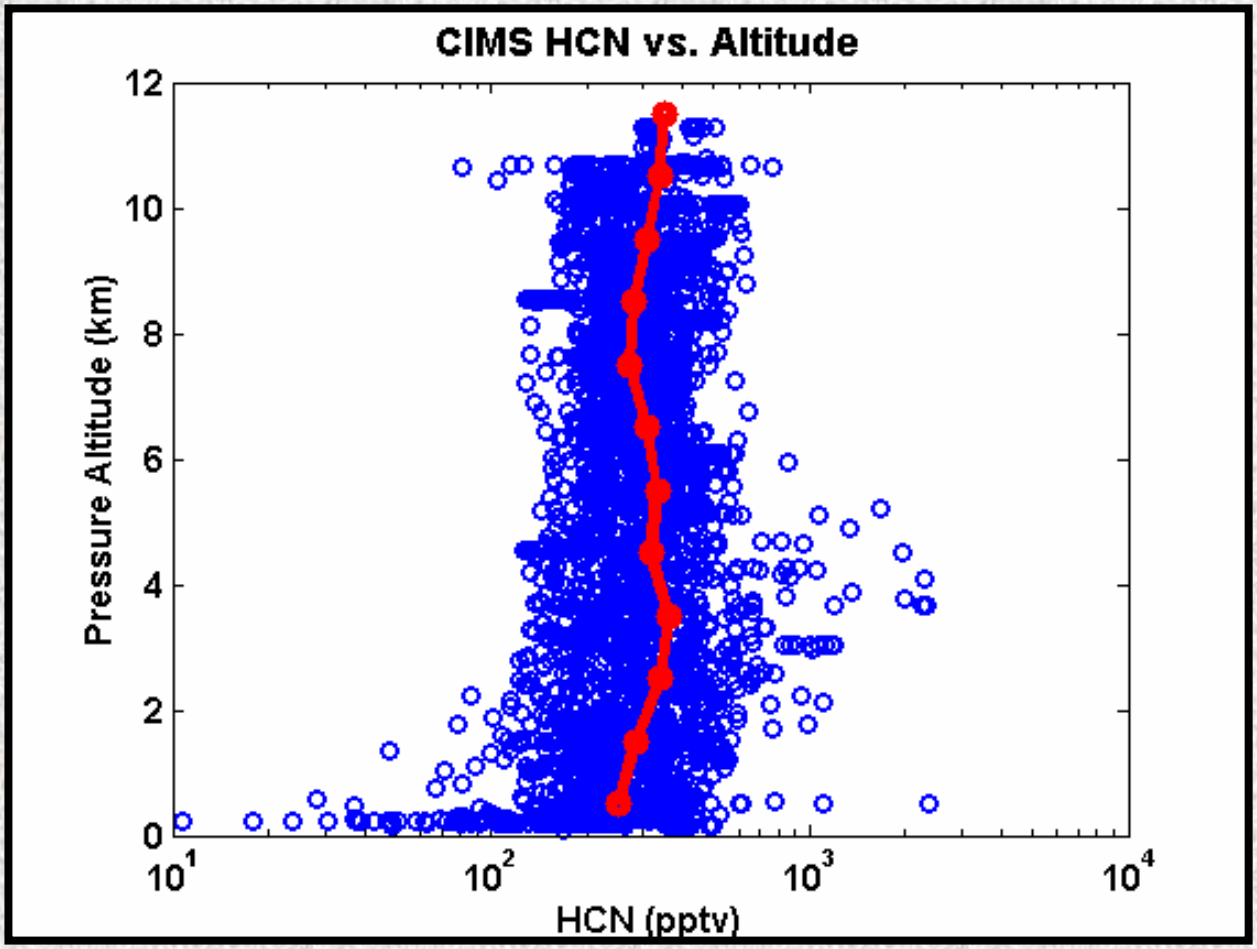
- Fair agreement with PANAK-HCN.
- CIT has high uncertainty at high H_2O mixing ratios as product ion has a water dependent mass analog interference, as well as decreased sensitivity at high H_2O.
- Fast HCN measurements may help understand complex air masses which may be a mixture of biomass burning and anthropogenic pollution.

HCN comparison versus altitude:

Median: 0.88
Mean: 0.98



HCN altitude profile:
Median: 279 pptv
Mean: 302 pptv



Areas of interest

- Understanding atmospheric importance of PAA: sources, sinks, and lifetime.
  - Utilize model to help constrain these
- Measurements of HNO_3 and H_2O_2 in clouds and around cloud/clear interfaces.
- Use of fast HCN measurements to help constrain ‘complicated’ air masses.