DC-8 HNO_3 Comparison

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Instruments

- CIT Chemical Ionization Mass Spectrometer (CIMS)
  - Sample Type: Discrete
  - Sample Time: 0.5 s grab sample every 5 s.

- UNH Mist Chamber
  - Sample Type: Continuous collection
  - Sample Time: ~100 s

Data Merge/Time-base

- The data merge to UNH time-base provided by Crawford et. al. was used for comparing data (mrgUNHMC_dc8_2004xxxx_R0).

- Certain comparison issues may arise during rapidly changing air simply from the fact that the CIT only measures HNO_3 ~10% of the time while UNH measures it 100% of the time.

Main Issues

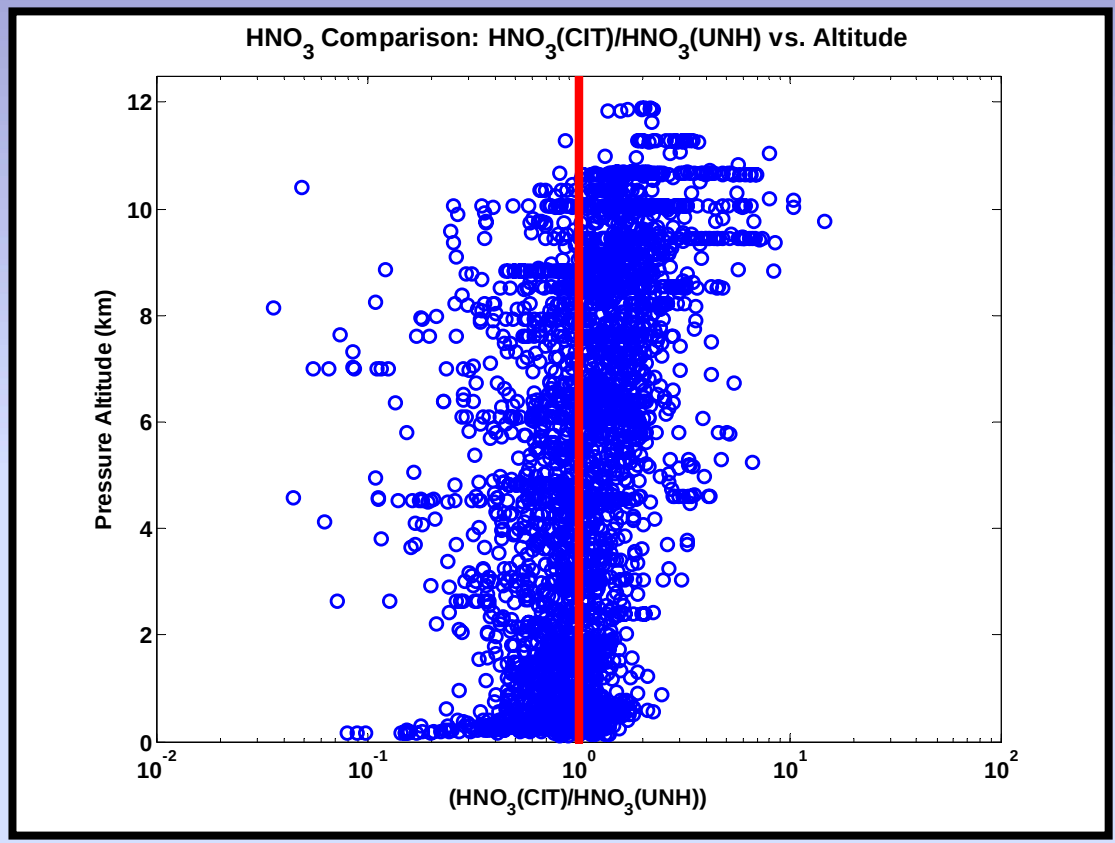
- Apparent altitude trend.
- Low altitude (<1 km), low HNO_3 (<500 pptv) trend.
- Differences in biomass burning and other high pollution plumes.

Altitude Trend

Significant trend of CIT > UNH above 6 km.

By looking at the data on equal-pressure and equal-H_2O surfaces, this appears to actually be a trend with water.

Due to changes in ion chemistry that accompany changing [H_2O], CIT-CIMS must make a [H_2O] dependent correction to the raw ion signal to back out [HNO_3].



CIT Ion Chemistry

- $CF_3O^- + HNO_3 \rightarrow HF{\cdot}NO_3^- + CF_2O$
- $CF_3O^- + H_2O + M \rightarrow CF_3O^-{\cdot}H_2O + M$
- $CF_3O^-{\cdot}H_2O + HNO_3 \rightarrow HF{\cdot}NO_3^- + H_2O$
- $H_2O + HF{\cdot}NO_3^- \rightarrow H_2O{\cdot}NO_3^- + HF$

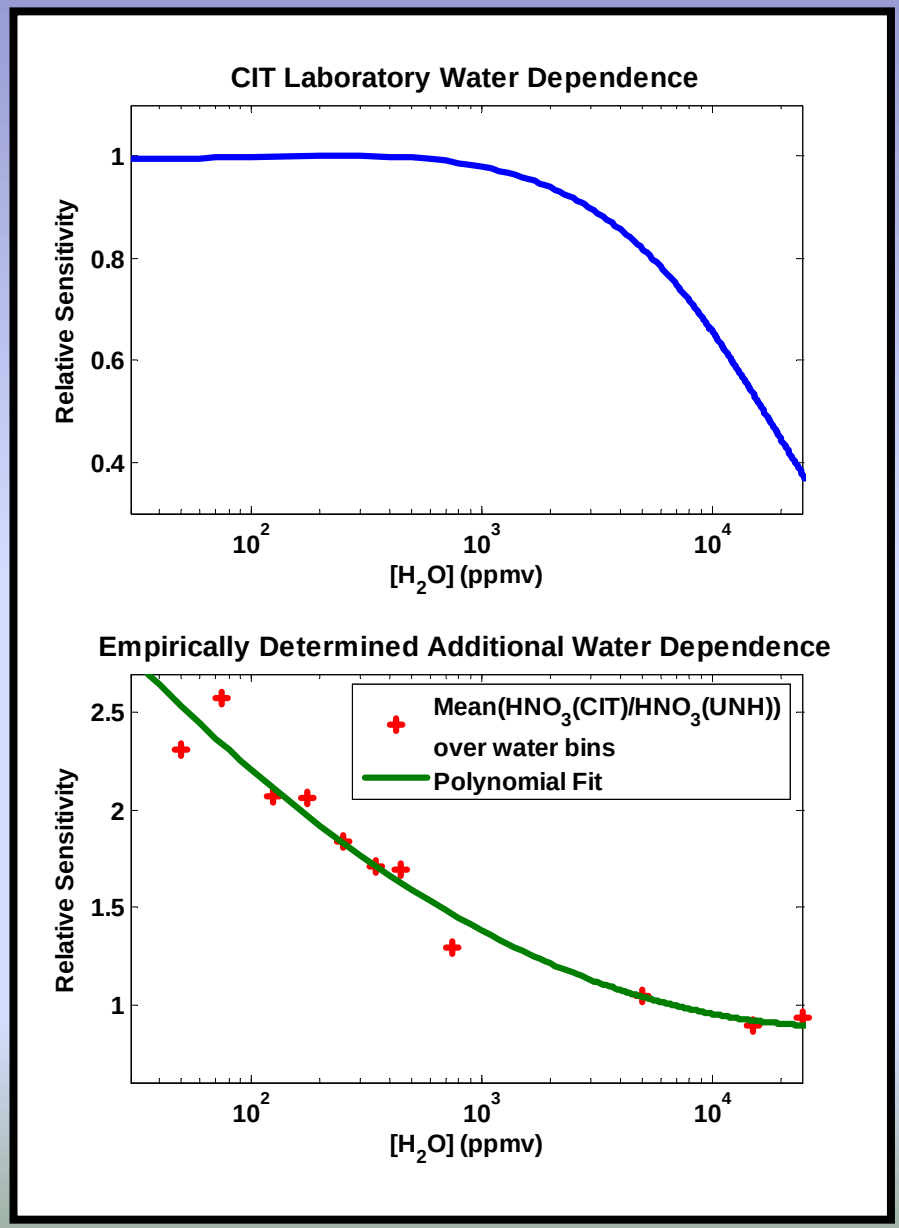
The CIMS water dependent calibration was determined through laboratory experiments.

CIT water dependence

Water dependence measured in laboratory (top panel).

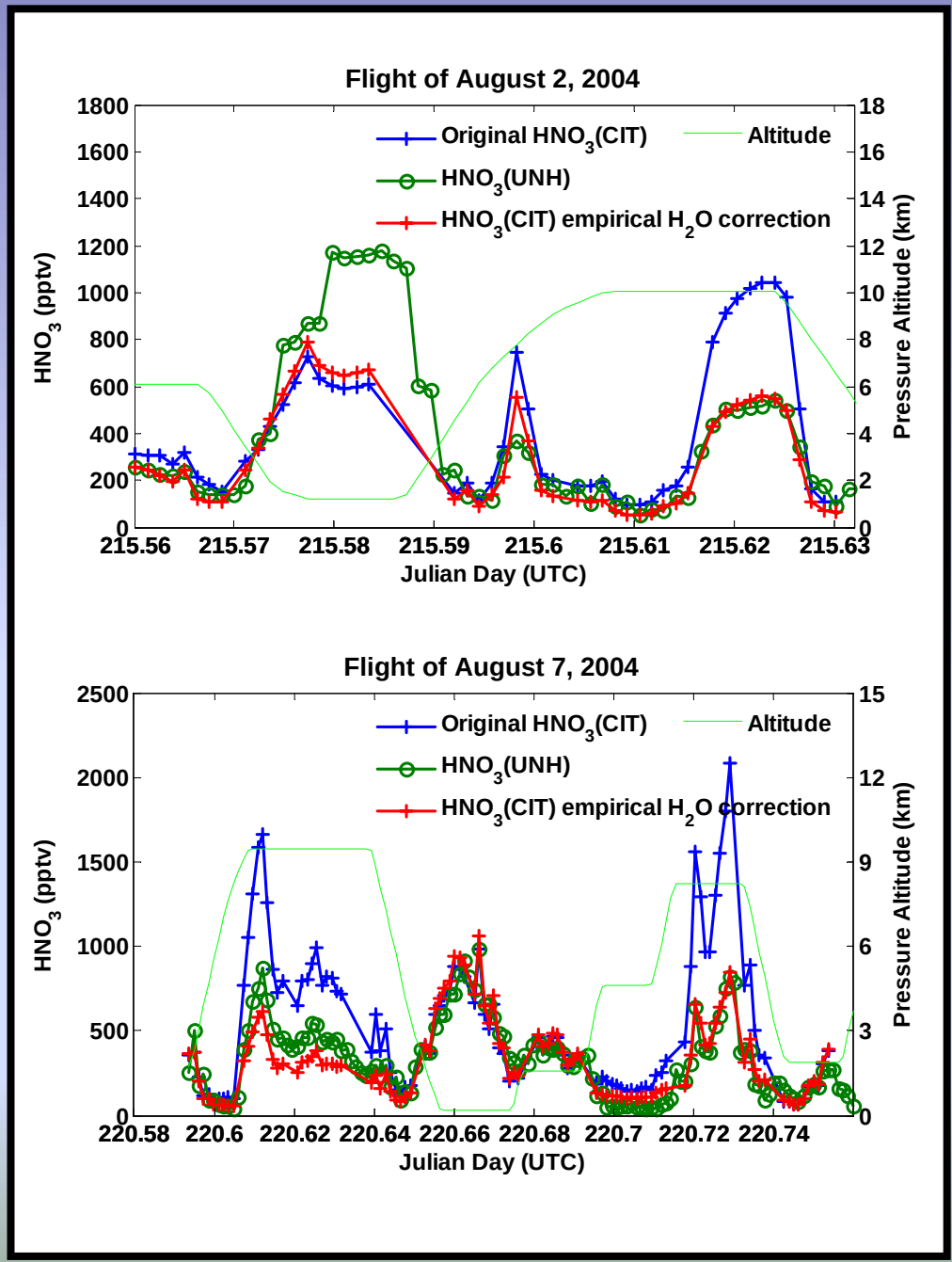
Empirical correction determined from comparison with UNH as function of water (bottom panel). This shows CIT likely in error (>) by a factor ~2 in stratospheric air.

Additional lab work is needed to sort out why our initial relationship was inadequate.



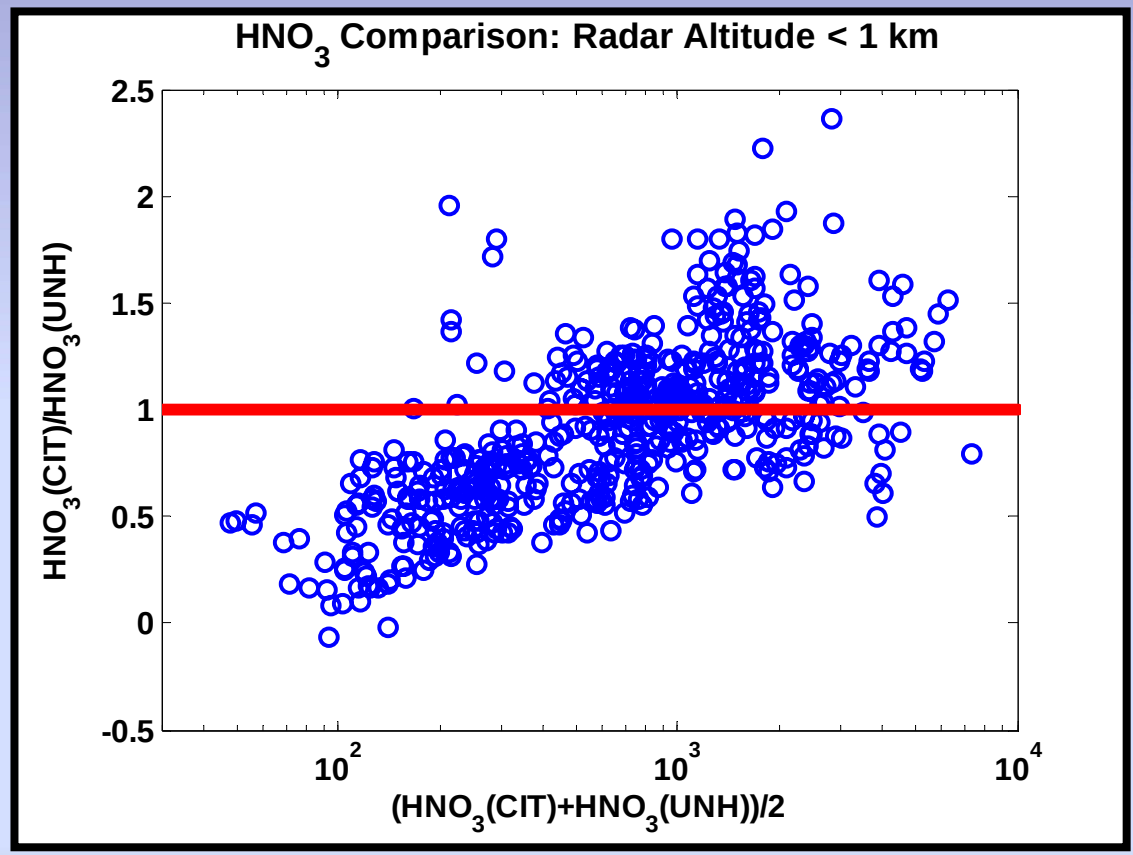
Timelines which show data before and after H_2O correction. The periods in stratospheric air (JD 215.615-215.628 and JD 220.718-220.740) now show very good agreement.

There are still certain flight-to-flight differences that need to be addressed specifically.

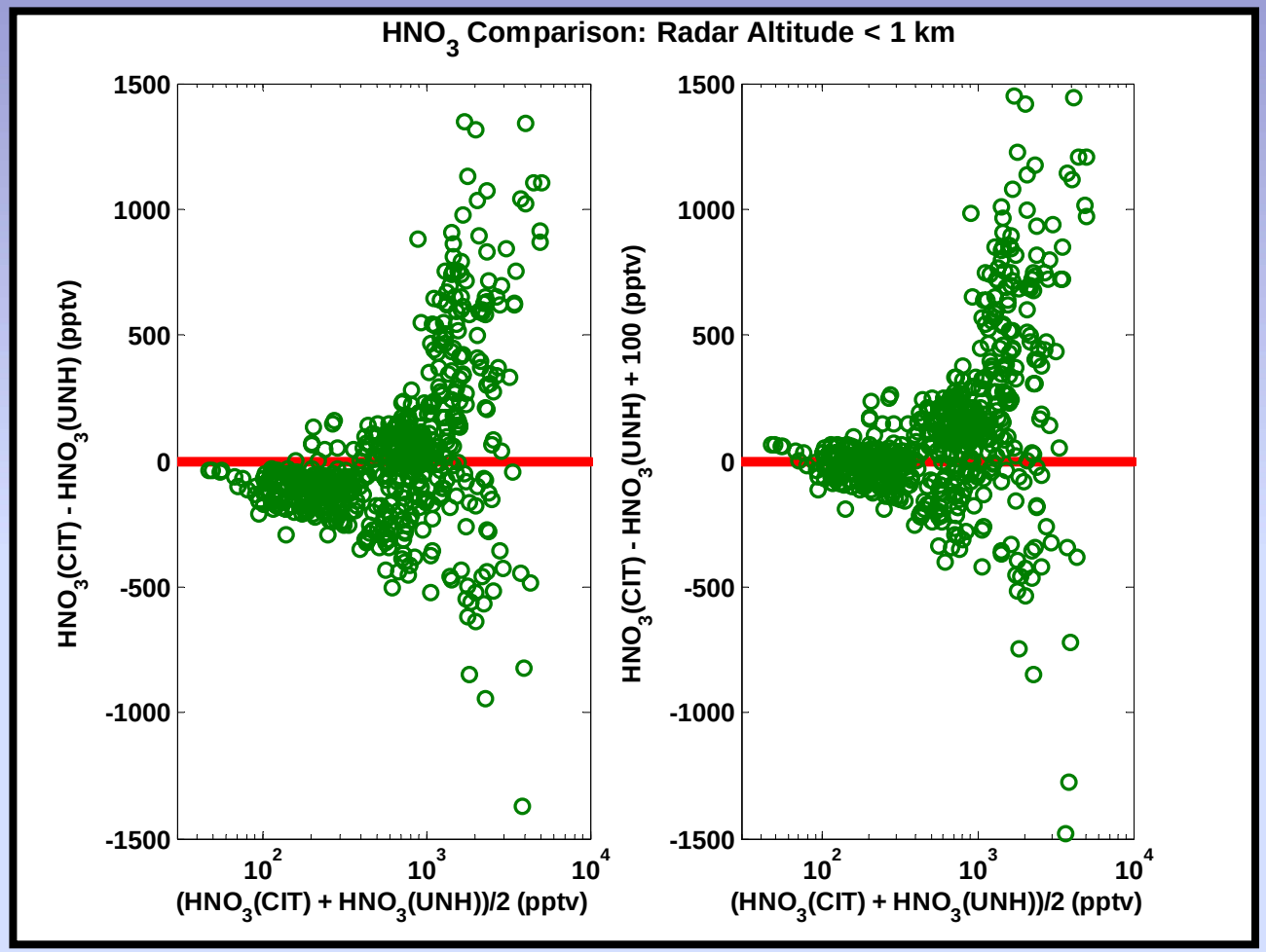


Low altitude, low HNO_3 trend

The data suggest there may by a systematic difference between the instruments at low altitudes.



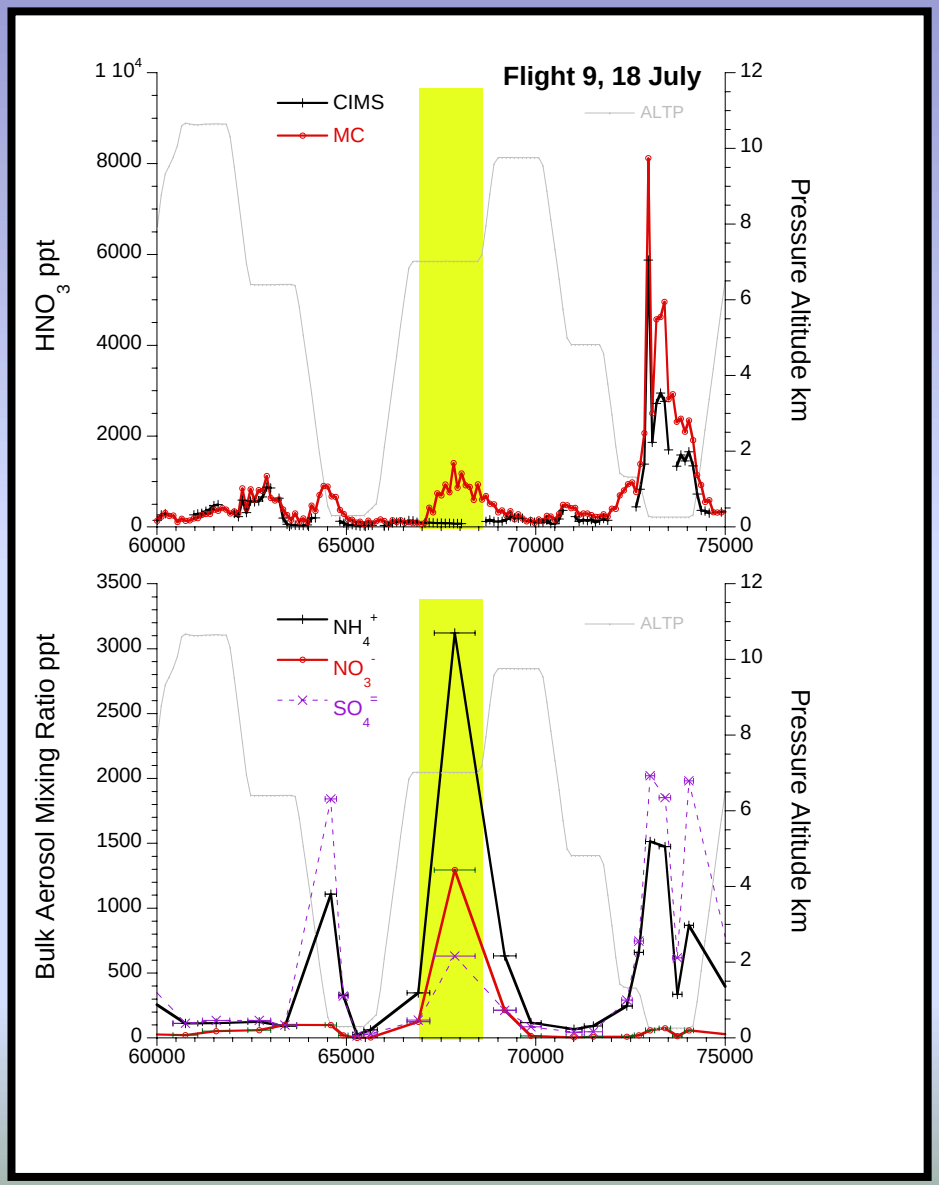
Plotting the difference between CIT and UNH versus the average, shows that most of the trend can be accounted for by inserting ~100 pptv offset between the instrument zeros.



Biomass Burning and other Plumes

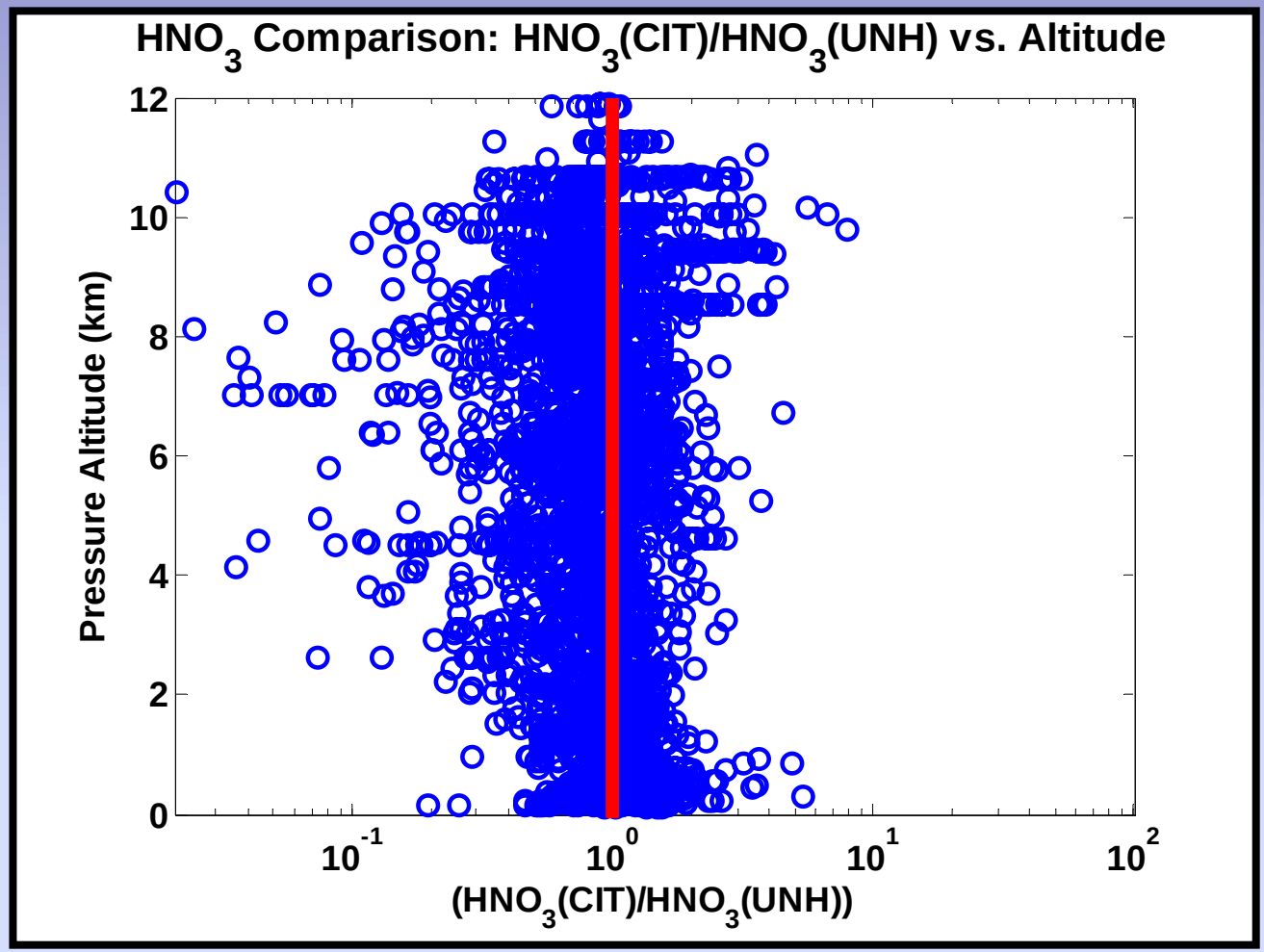
During measurements in biomass burning plumes UNH often measured significantly higher HNO_3 than CIT.

UNH includes fine aerosol NO_3^- (if present) as part of their signal. The suggestion is that NH_4NO_3 fine aerosol in the BB plume accounts for the difference in HNO_3 signals.



Data comparison after correcting CIT by empirical water dependence, and accounting for low altitude trend by imposing offset.

Mean: 0.98
Median: 0.90
N: 3158



Conclusions

- Empirical water correction corrects altitude trend above 8 km.
  - CIT will post revised data set (end of May, 2005) after more laboratory work concerning water dependency.
- Zero offset corrects low altitude, low HNO_3 trend.
- Biomass plumes and other high pollution plumes should be investigated on an individual basis to determine if aerosol NO_3^-, may be influencing the UNH measurement.