Measurements of SO_2 and HO_2NO_2 with a Chemical Ionization Mass Spectrometer During INTEX-A

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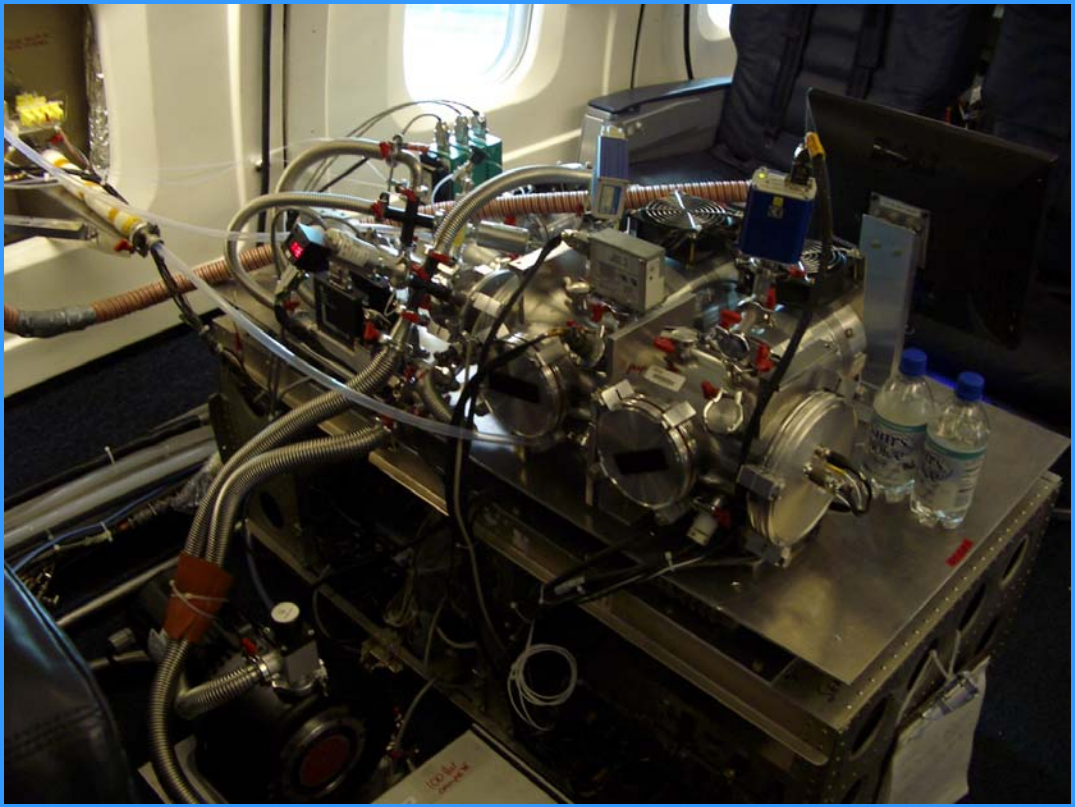
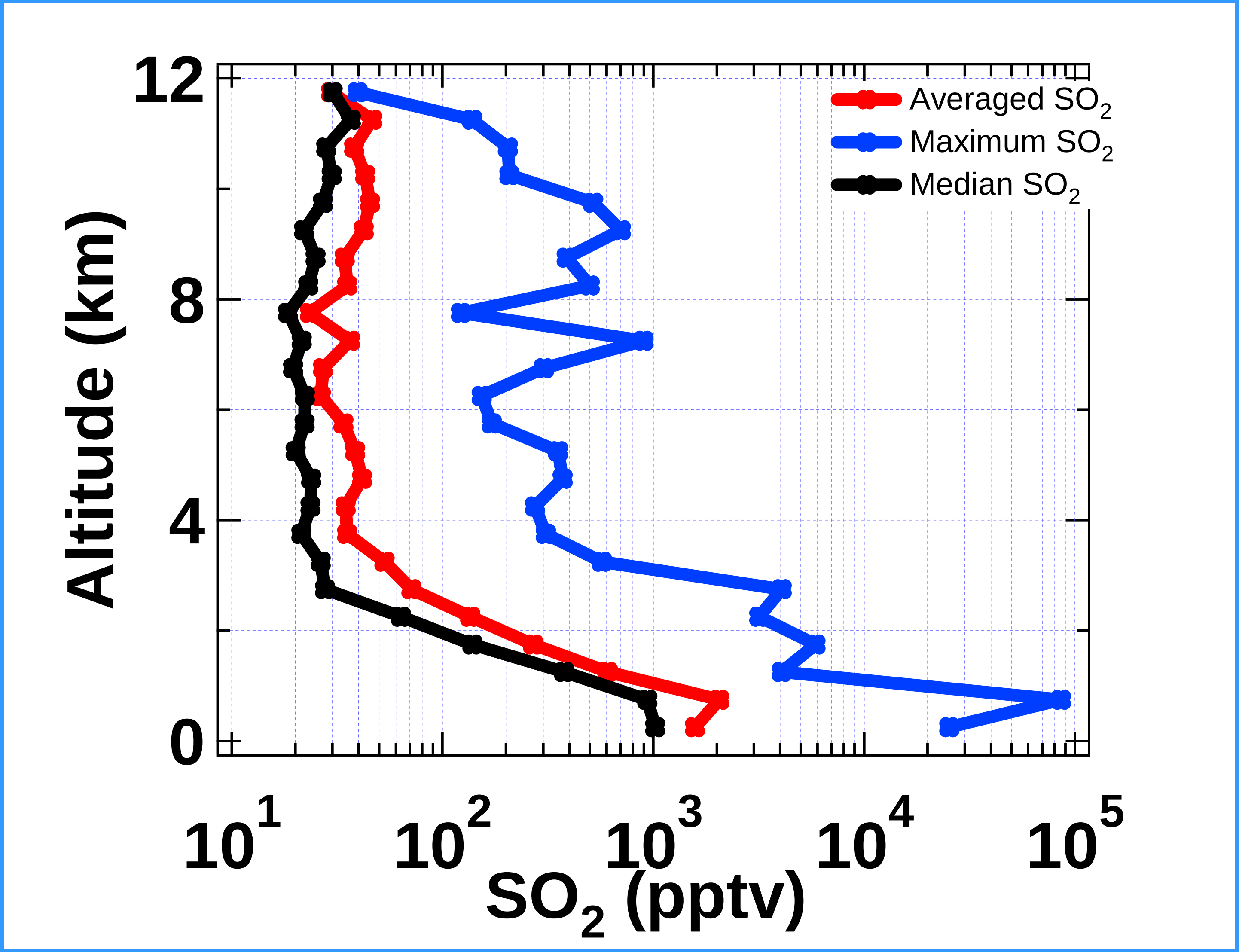
Outline

- SO_2 (brief)
  - Profile
  - Tracing Sources
- HO_2NO_2
  - Properties
  - Steady State Analysis



SO_2 Altitude Profile



HO_2NO_2

Formation

$HO_2 + NO_2 \rightarrow HO_2NO_2$ k_1

Losses

1) Thermal Decomposition – Strong Function of Temperature

$HO_2NO_2 \rightarrow HO_2 + NO_2$ k_{-1}

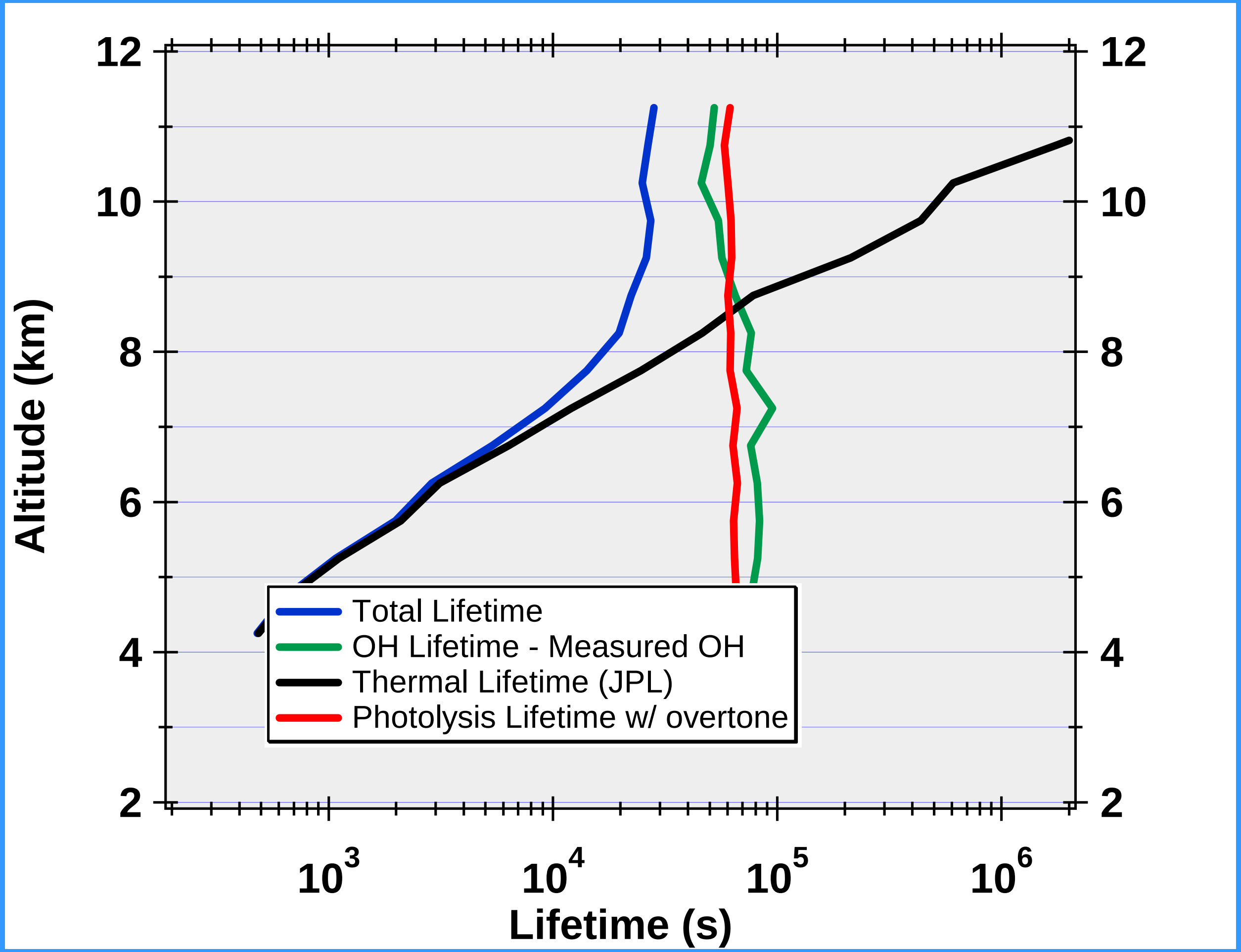
2) Reaction with OH

$OH + HO_2NO_2 \rightarrow H_2O + O_2 + NO_2$ k_2

3) Photolysis – Both UV and IR (overtone) J

$HO_2NO_2 + h\nu \rightarrow HO_x + NO_x$

Altitude Profile of HO_2NO_2 Lifetime for INTEX - A

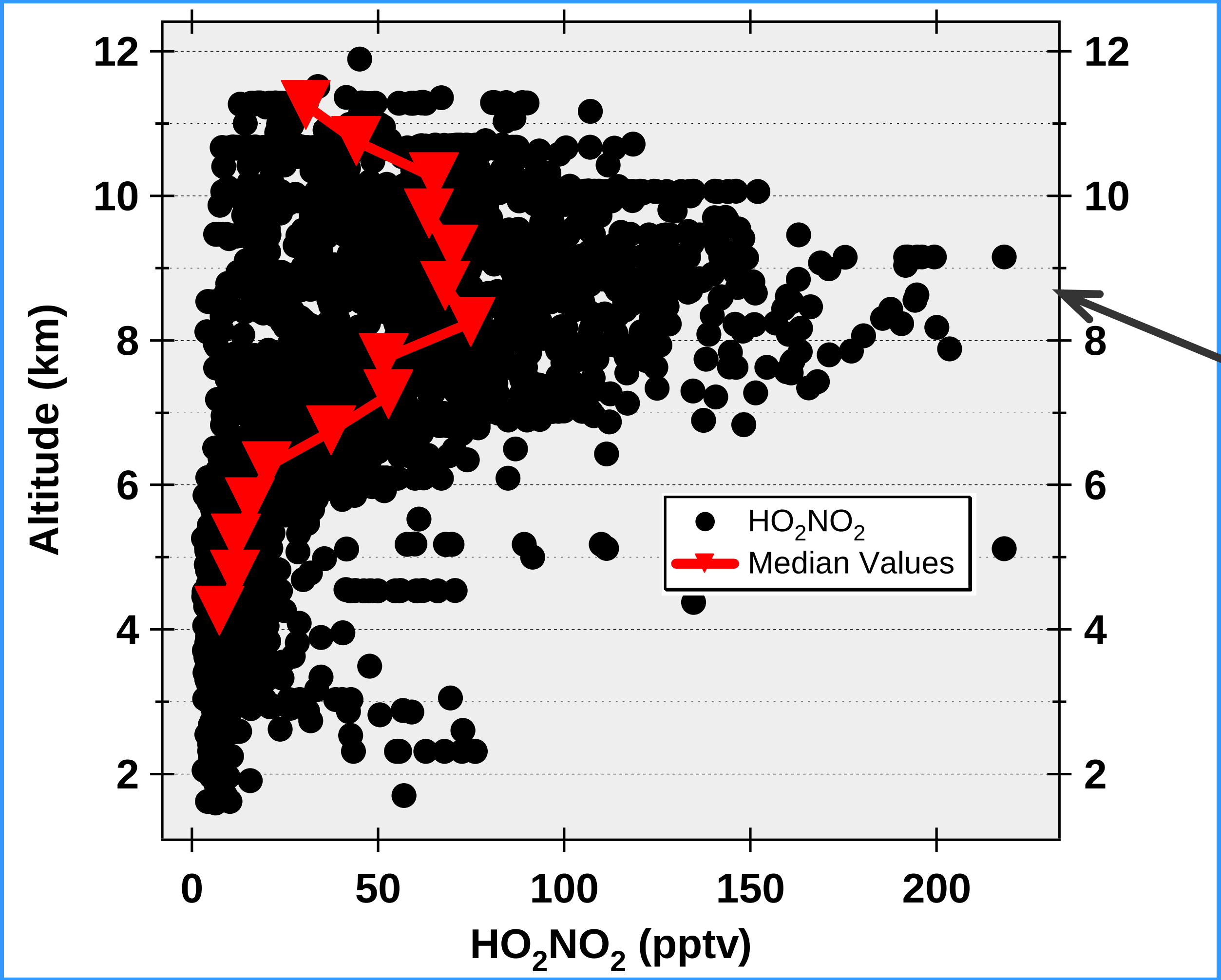


Above 7 km lifetime is dominated by OH and J 6-8 hours

Below 7 km lifetime is dominated by thermal decomp.

< 3 hours

Measured HO_2NO_2 –INTEX-A



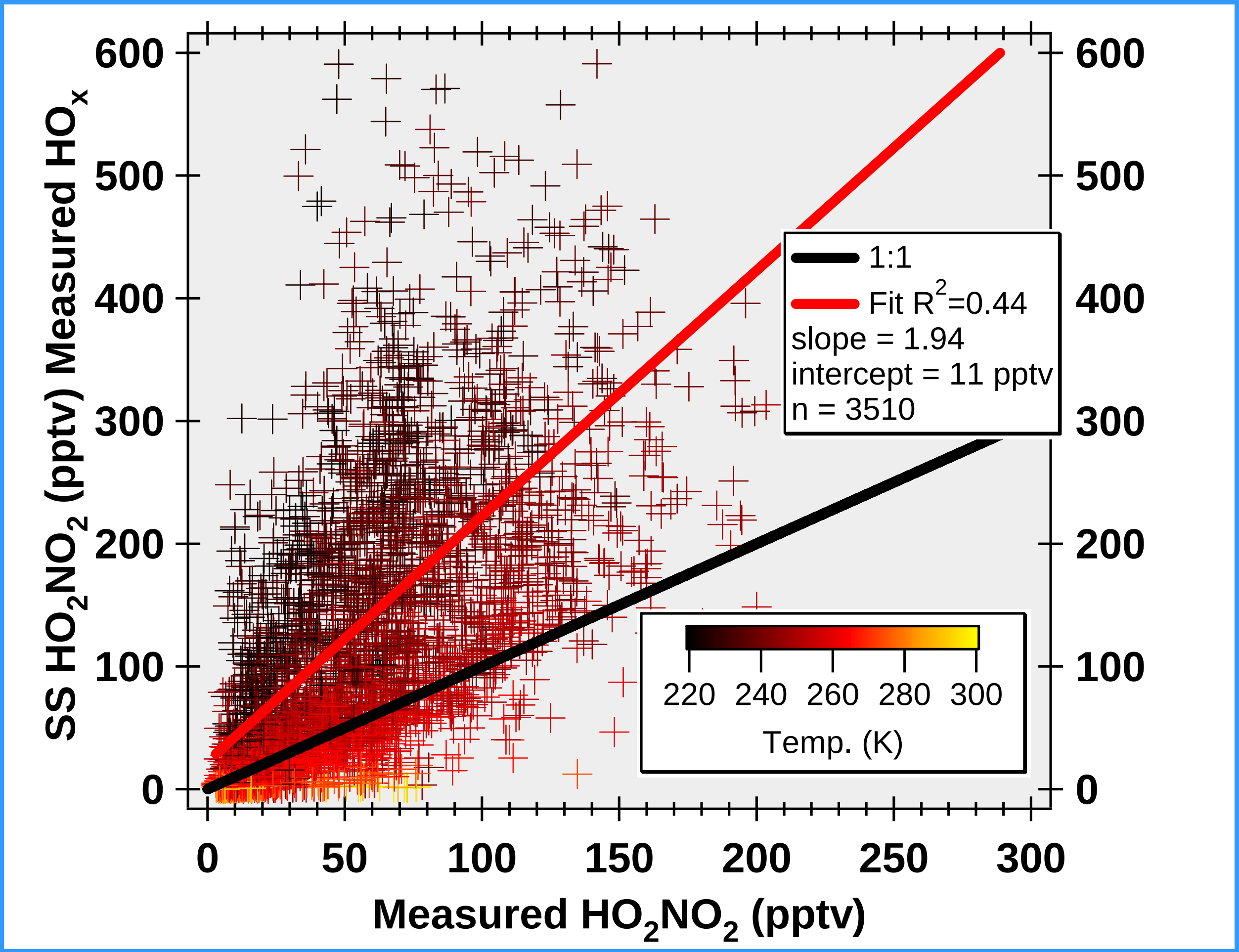
Pernitric peaks at ~9 km with average of 77 pptv

Steady State HO_2NO_2

$$[HO_2NO_2]_{SS} = \frac{k_1[HO_2][NO_2]}{k_{-1} + J + k_2[OH]}$$

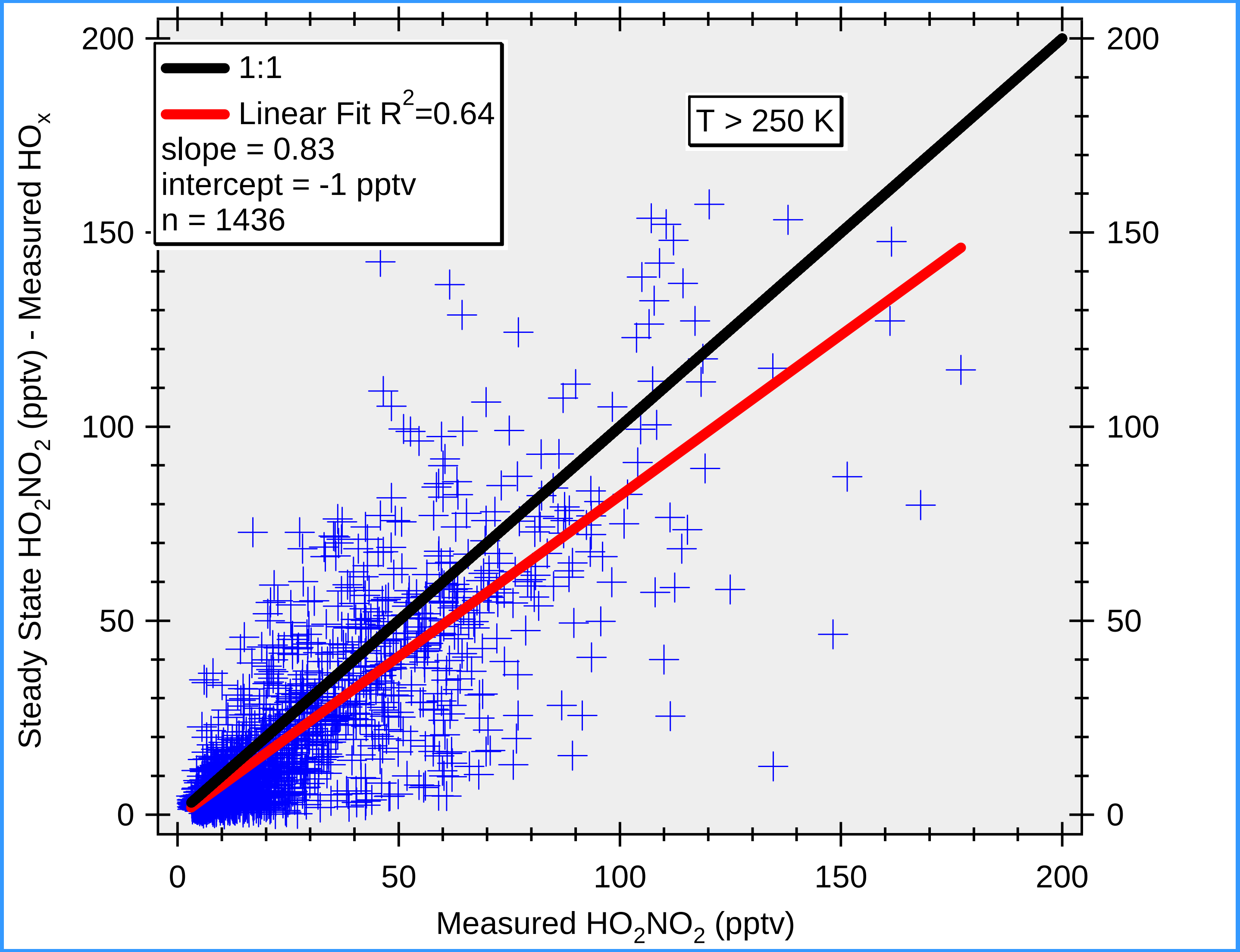
SS approximation should be valid at least at lower altitudes.

SS vs. Measured HO_2NO_2 Measured HO_x – Filtered Data

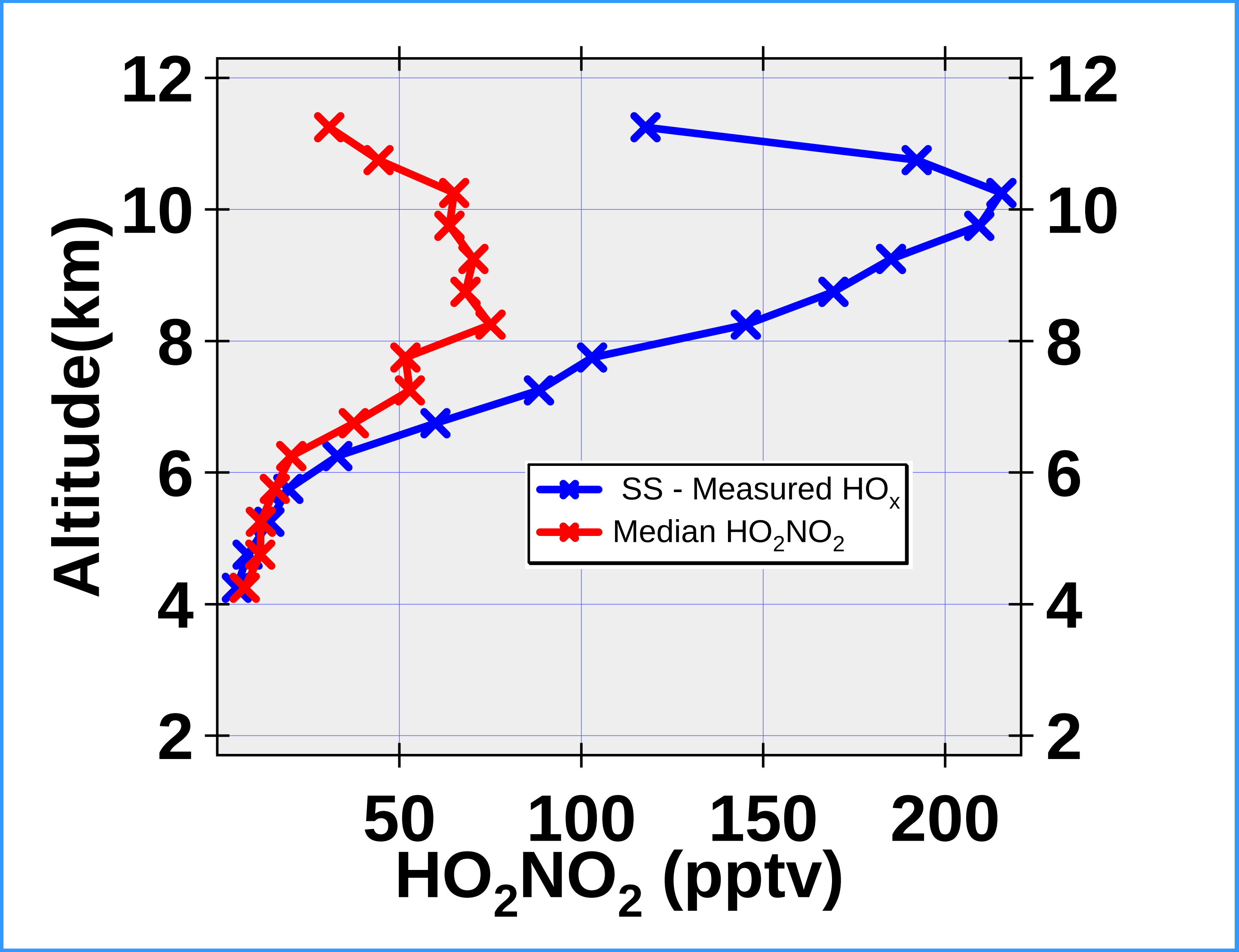


Correlation driven by higher T, low altitude data

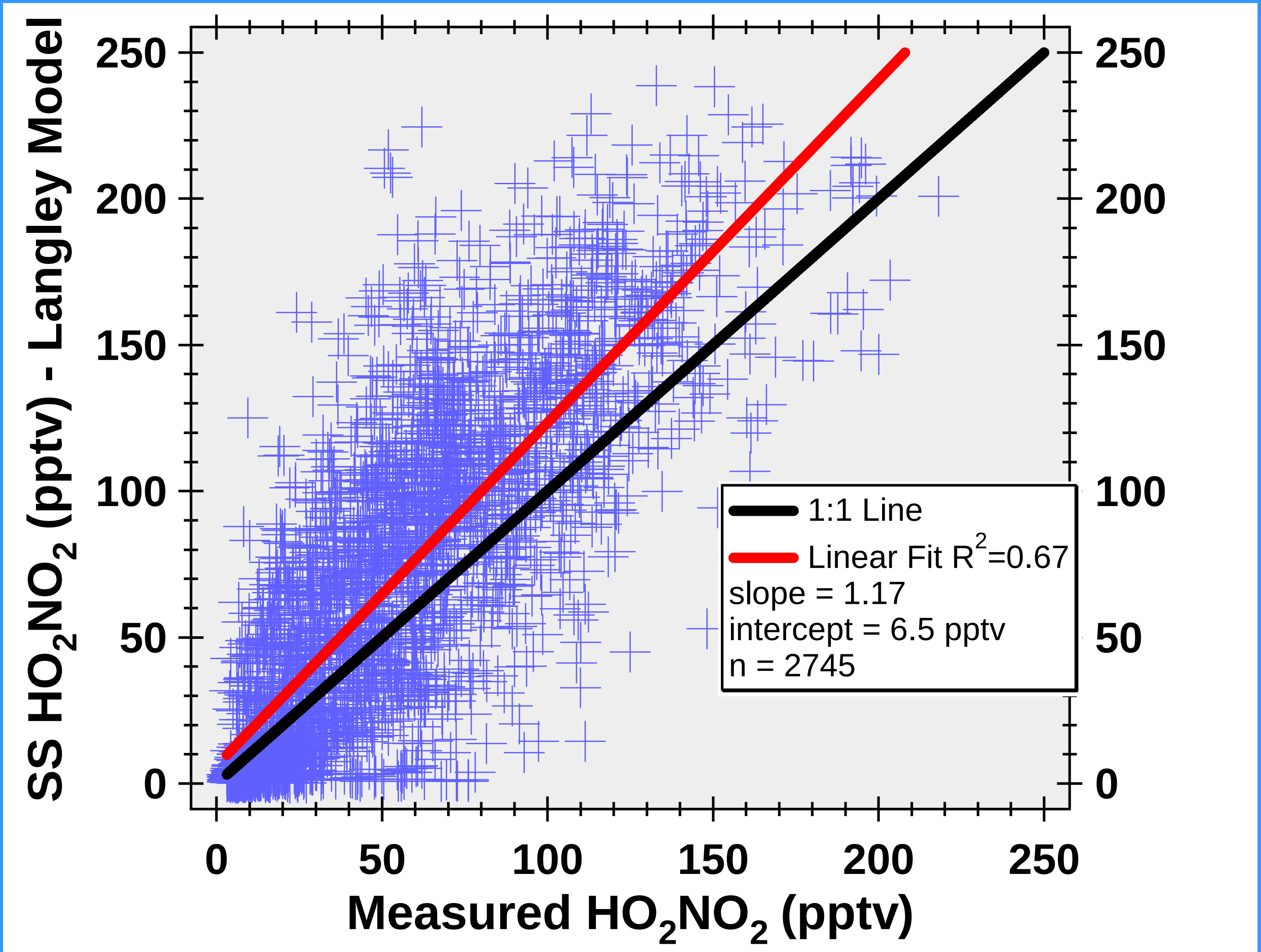
SS – Measured HO_x and T>250 K



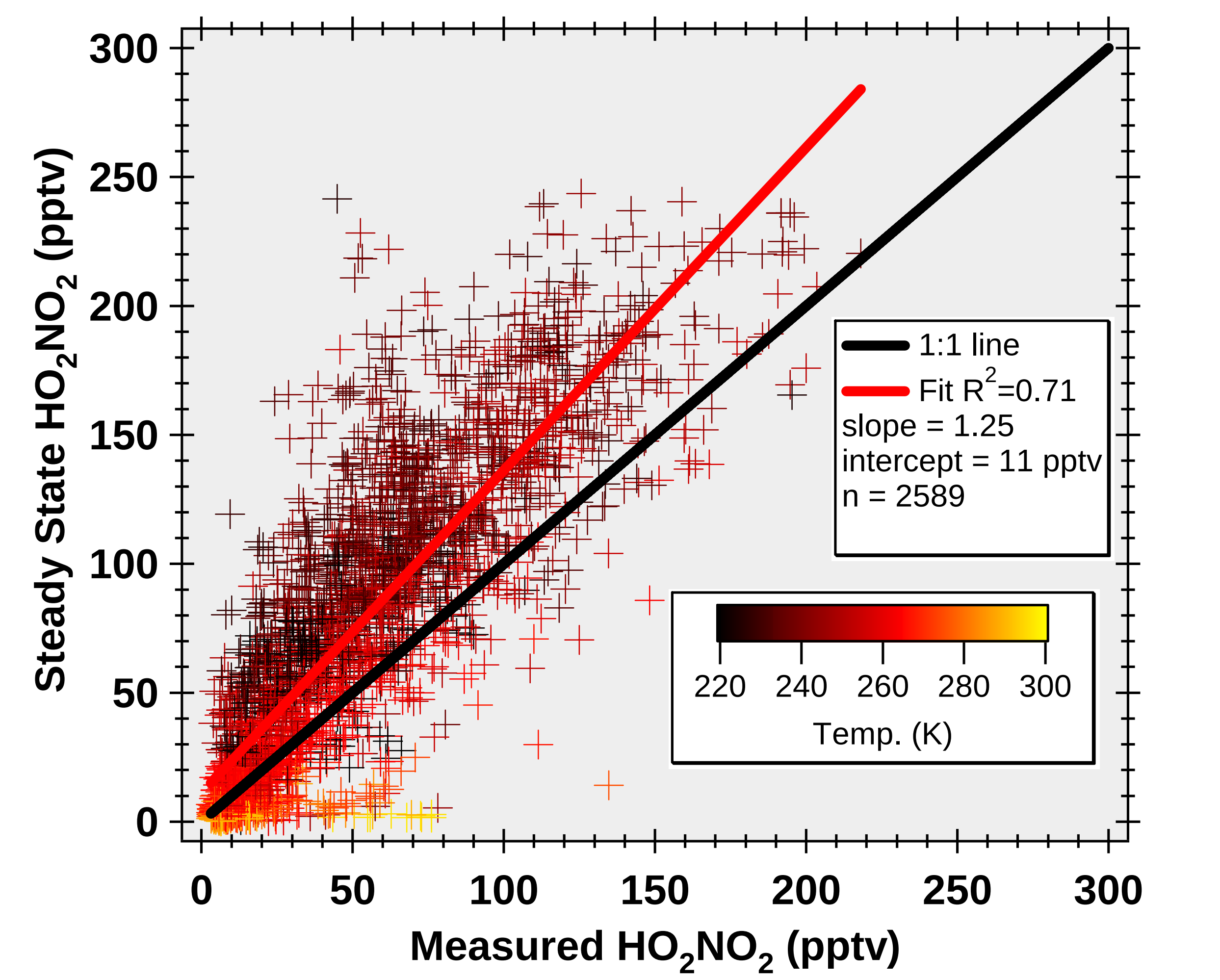
Altitude Profile w/ measured HO_x



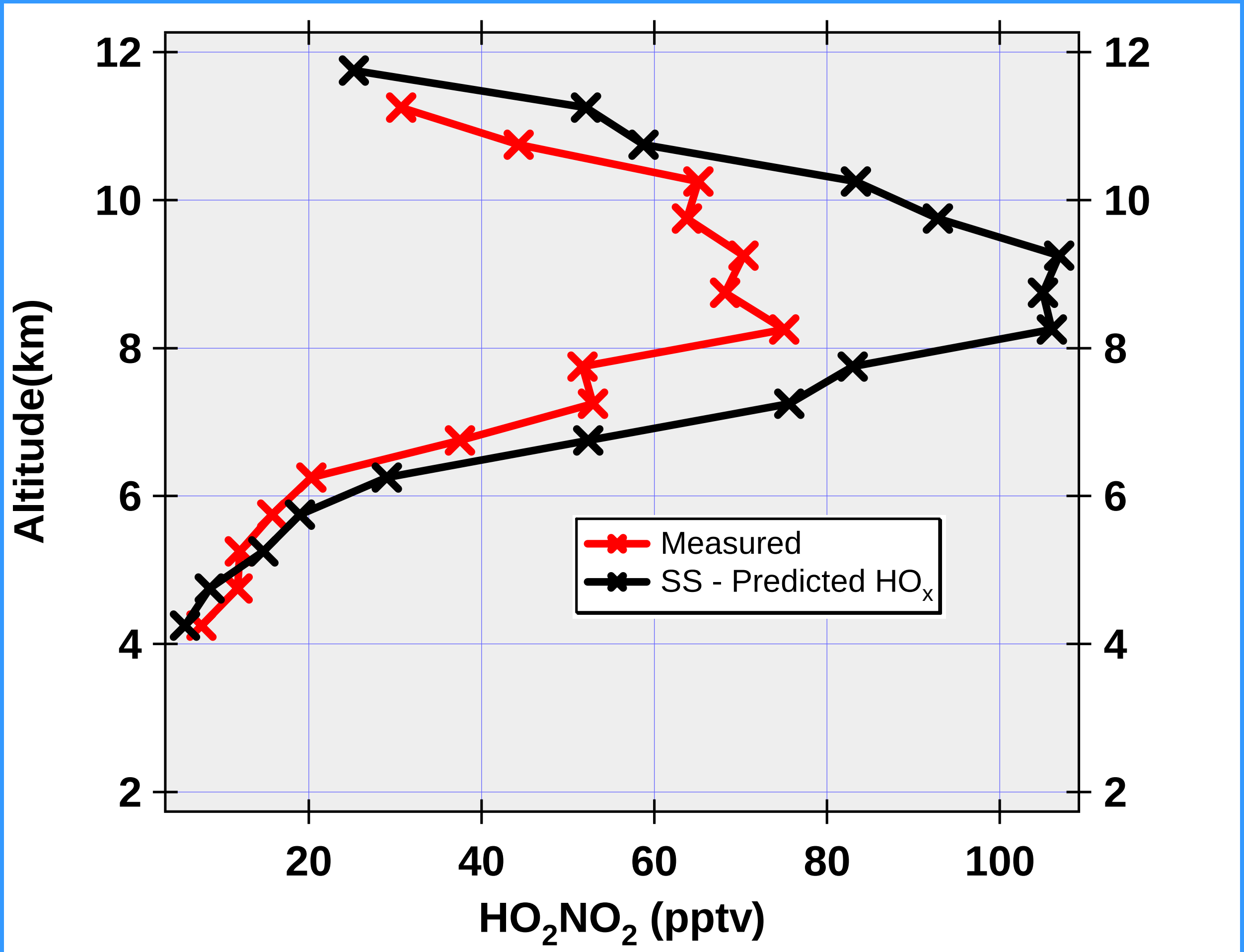
Correlation w/ Langley 24 hour Model



SS vs. Measured HO_2NO_2 Langley Model HO_x – Filtered Data



Altitude Profile w/ Langley Model HO_x



Conclusions

- SO_2 good marker for coal burning, etc. – need help from transport models to analyze
- Pernitric data is consistent with measured HO_x and NO_x at lower altitudes where thermal decomposition dominates
- At all altitudes HO_2NO_2 data is consistent with measured NO_2 and model HO_x.
- HO_2NO_2 is a good test of photochemistry above 8 km. Depends on both HO_2 and OH.
- Other issues to investigate HO_2NO_2 interaction with cirrus cloud, ratio of HO_2NO_2 to HNO_3 as an indicator of air mass age, HO_2NO_2 as a marker for ozone production, evaluate magnitude of HO_2NO_2 as HO_x sink, etc.

Cautions

- J value is not well constrained – Could it be a factor of 2 higher?
- Steady State analysis is certainly imperfect
- All model results based on inferred NO – Impacts HO_2 to OH ratio