

Measurements of PANs at Chebogue Point, 2004

Jim Roberts

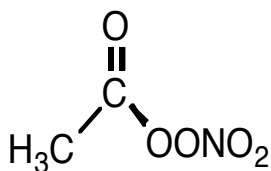
Dylan Millet, Allen Goldstein

Jennifer Murphy, Ron Cohen

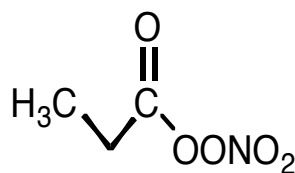
Betsy Andrews, Ellsworth Dutton



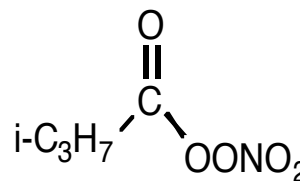
Peroxycarboxylic Nitric Anhydrides, PANs



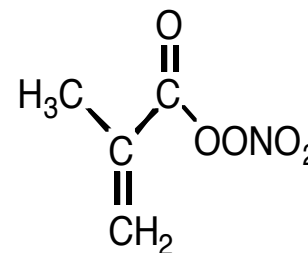
PAN



PPN



PiBN



MPAN

Sources:

• PAN/PPN/PiBN =
Anthropogenic HCs

• PAN/MPAN =
Biogenic HCs

Loss Processes:

• Thermal Decomposition
NO₂/NO Dependent

• PA + H₂O droplets

• MPAN Reaction with OH

Importance:

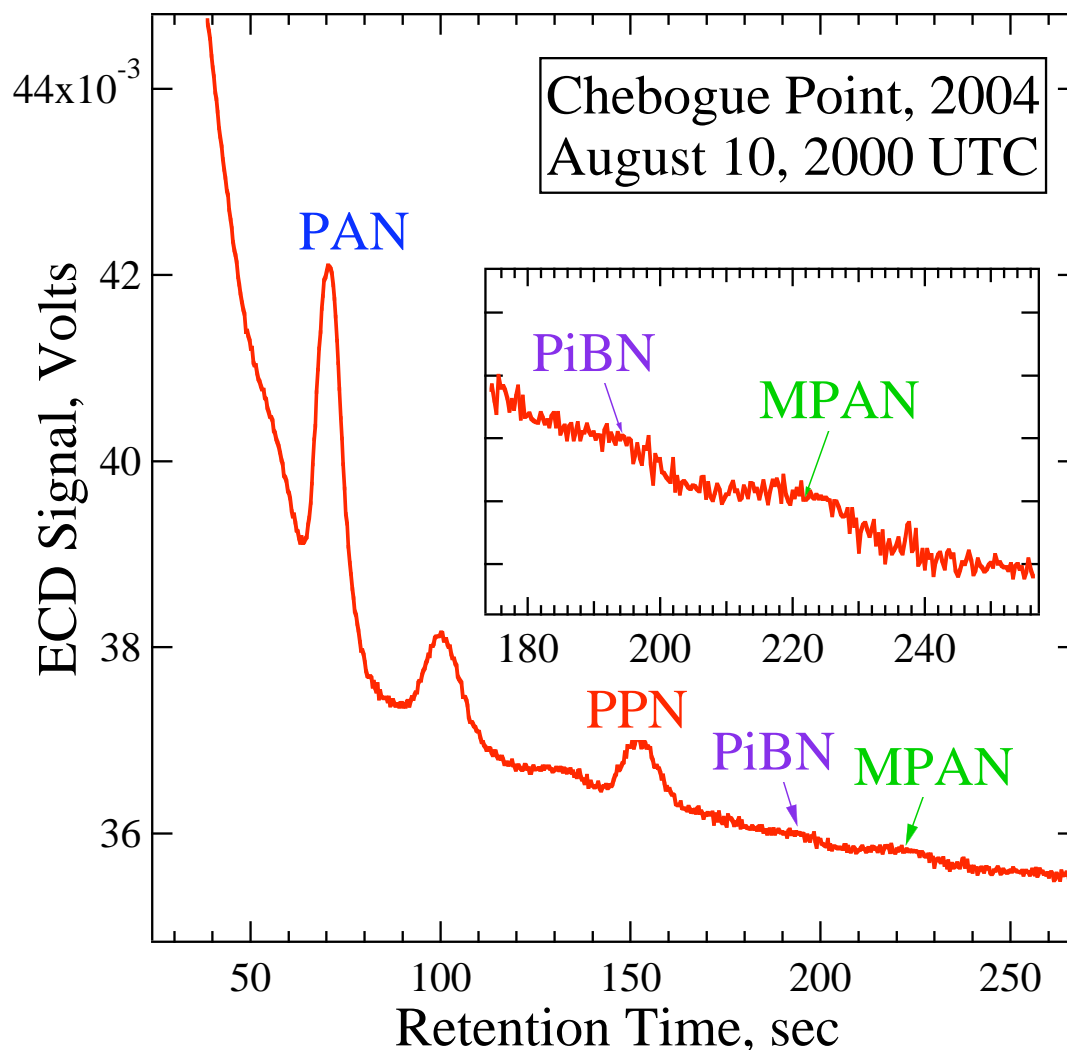
• Good Markers for
VOC-NO_x photochem.

• NO_x Reservoir
Radical production

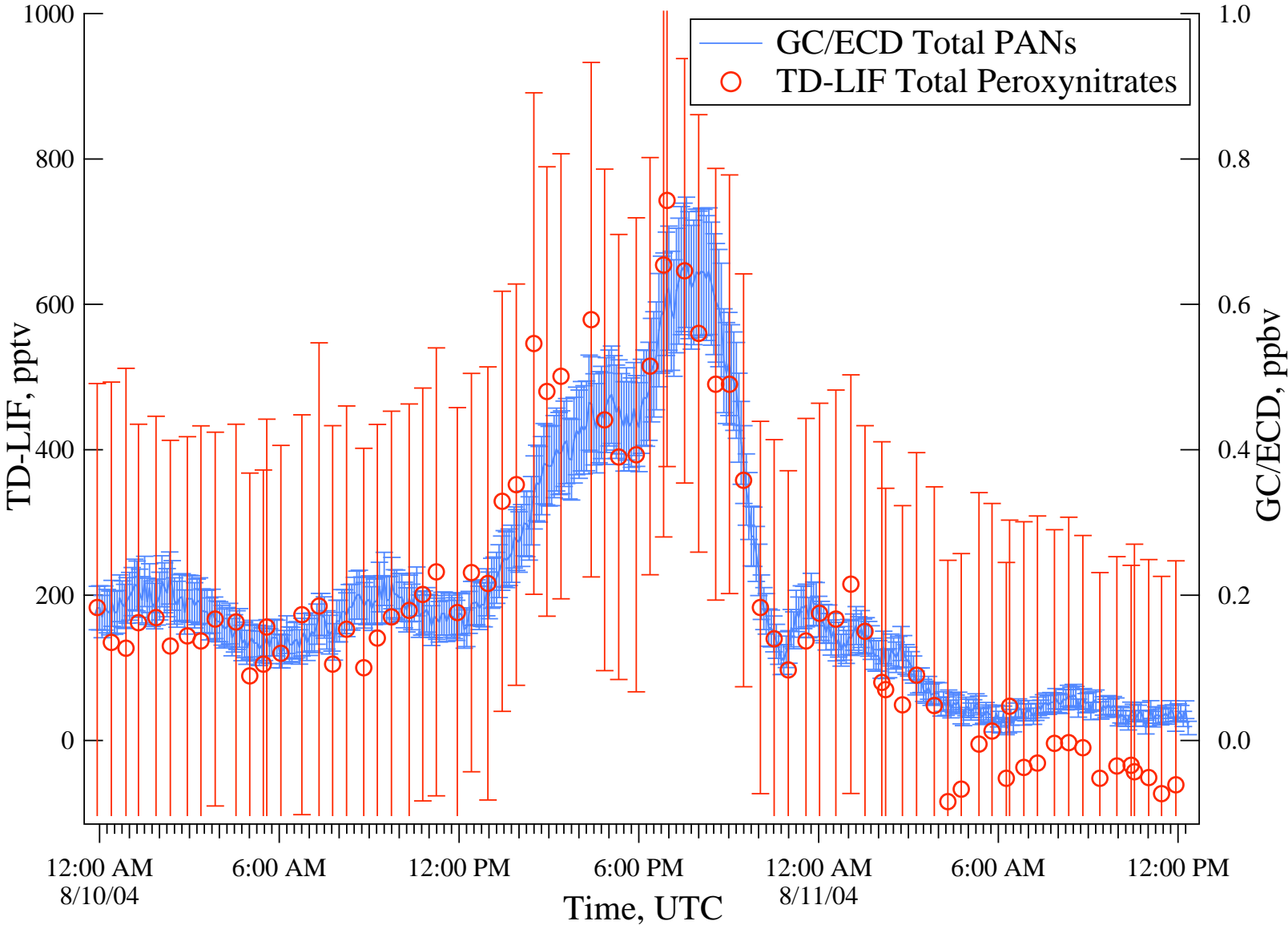
• Transport of NO_x

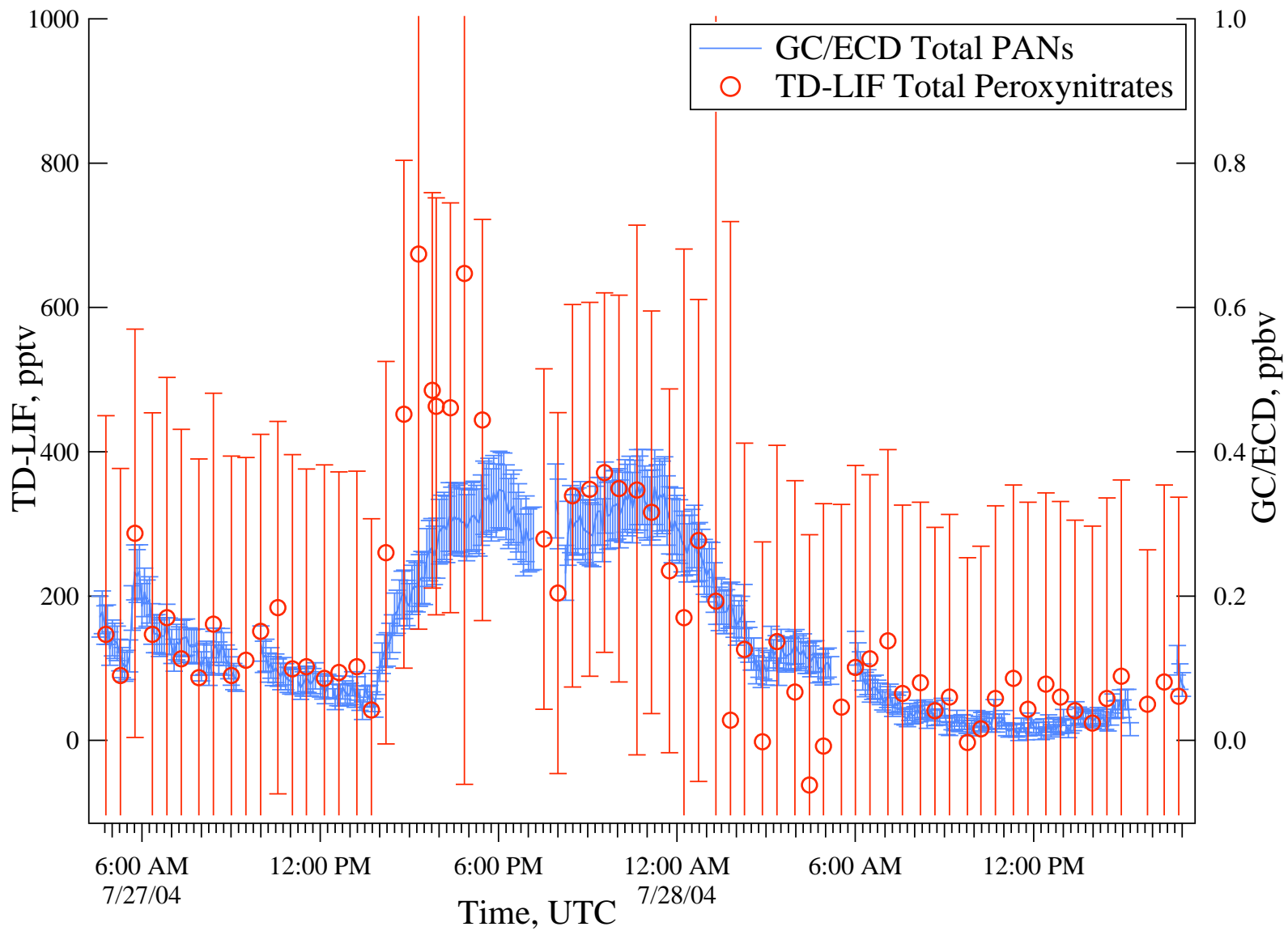
PAN Compounds at Chebogue Point During ICARTT 2004

- **Capillary GC/ECD:**
 - 1 chromatogram every 5 min
- **Detection Limits:**
 - 5-10 pptv depending on compound
- **Calibration:**
 - Acetone photolysis for PAN
 - Relative response factors for others
- **Overall Uncertainties:**
 - $\pm 15\%$ for PAN & PPN
 - $\pm 20\%$ for PiBN & MPAN

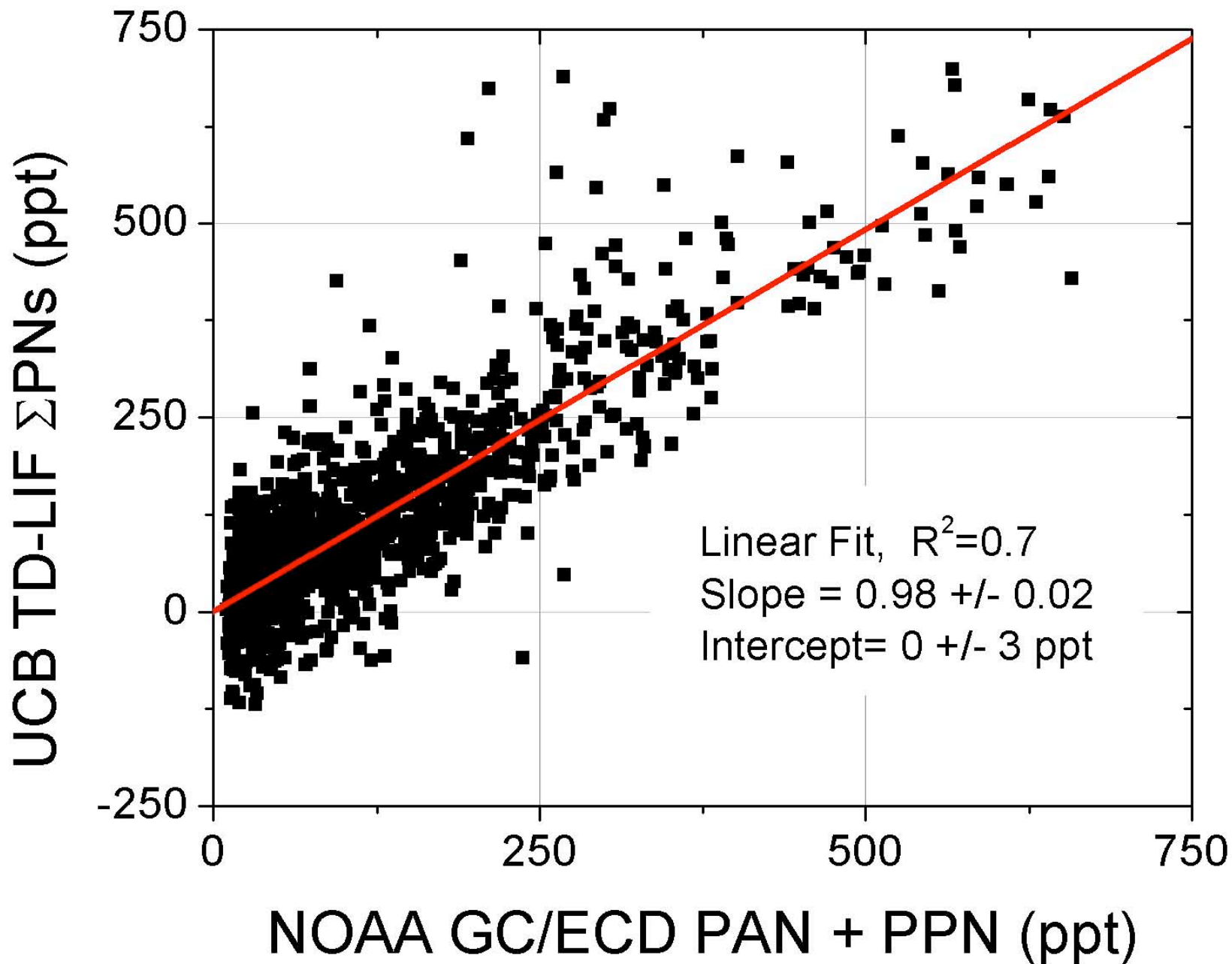


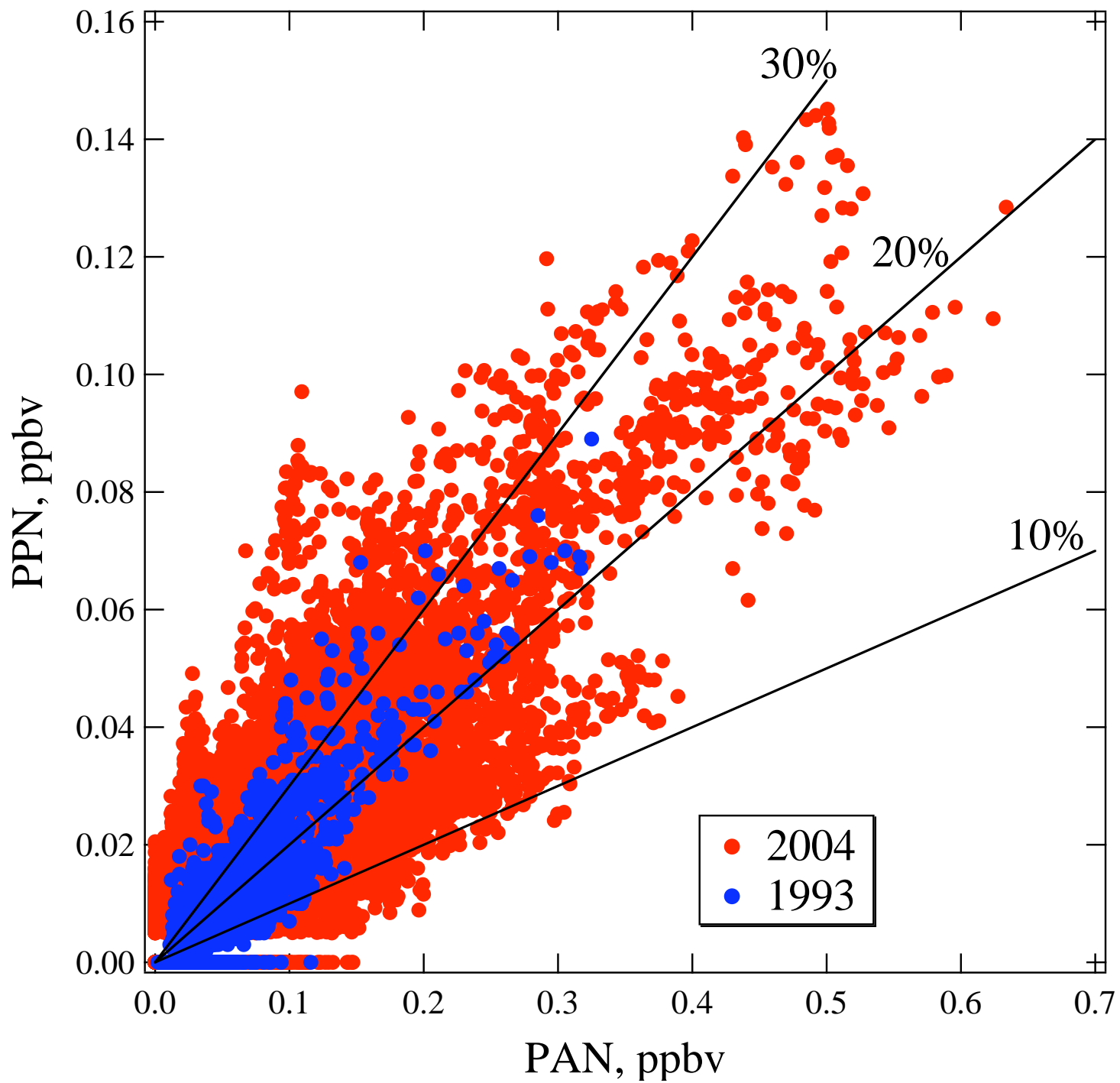
Comparison of GC/ECD and TD-LIF techniques

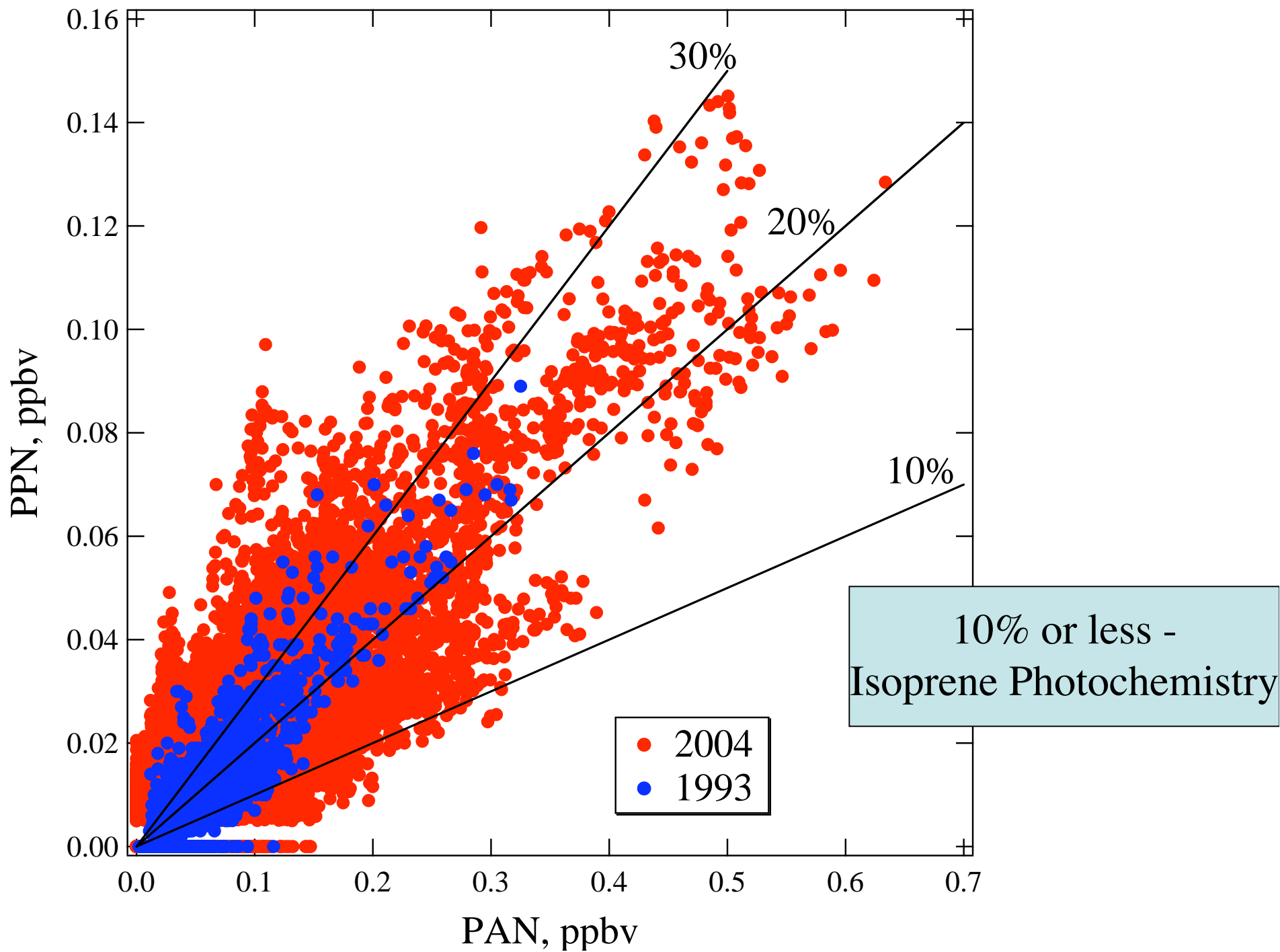


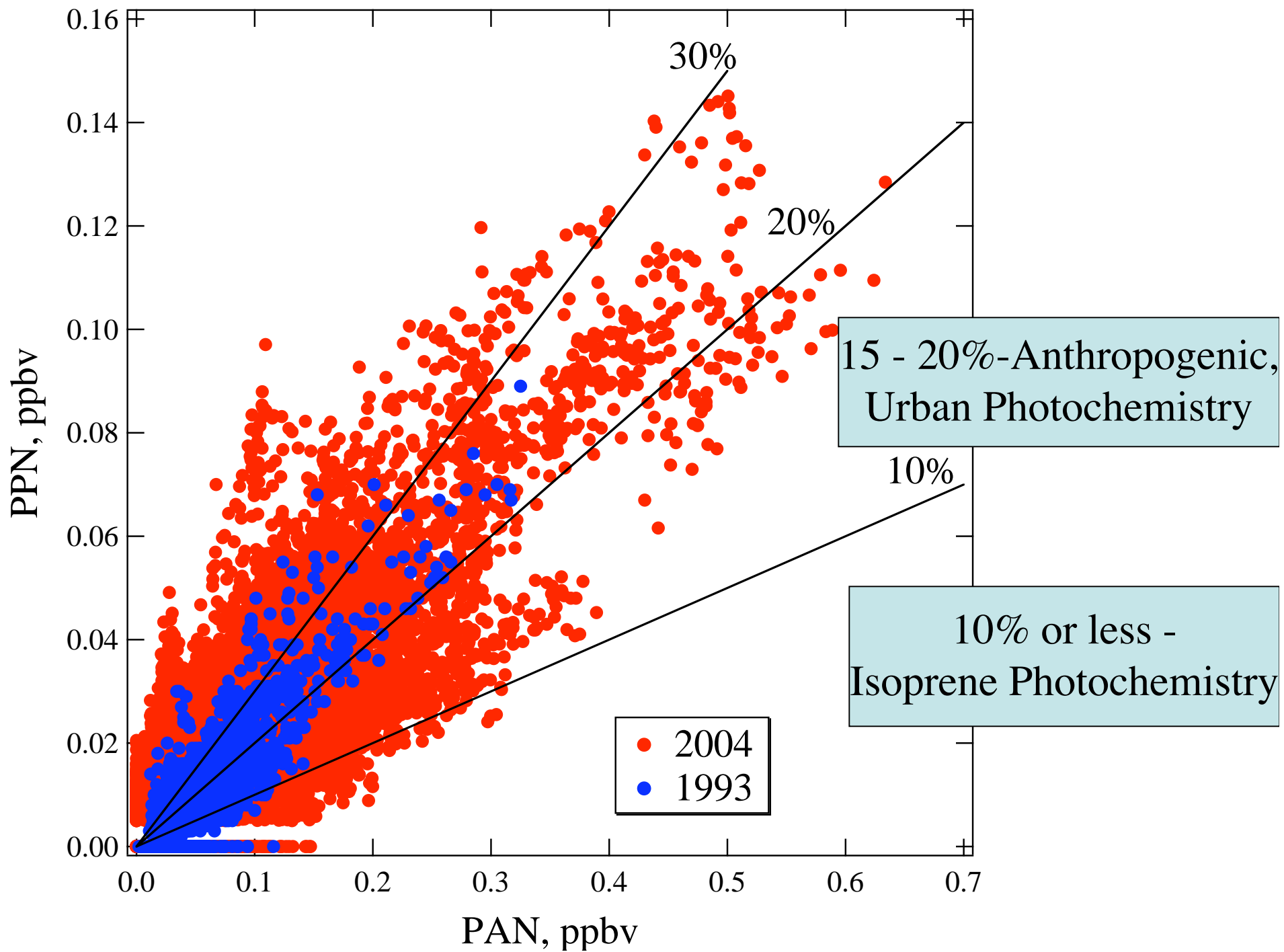


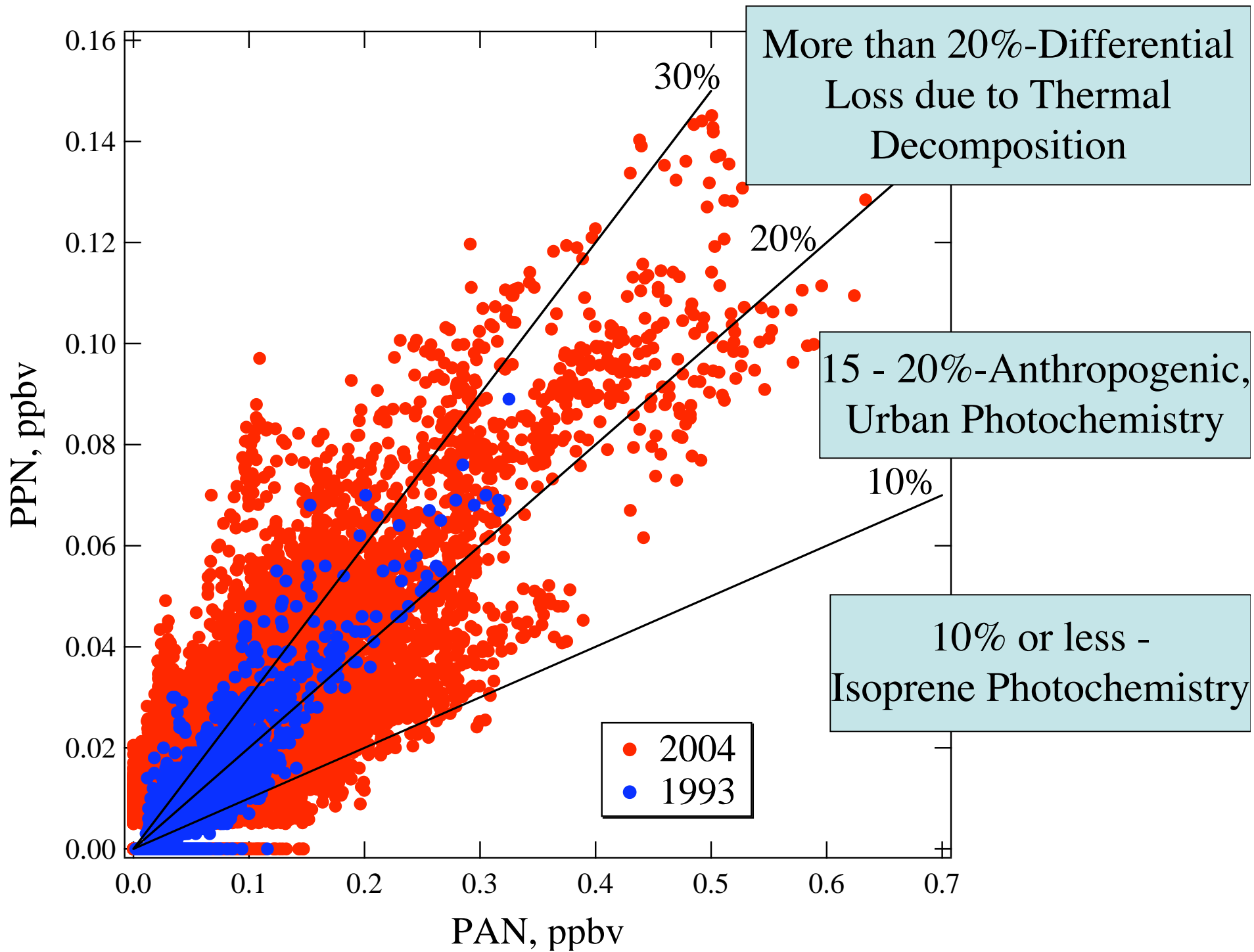
Peroxynitrate Intercomparison (Half Hour Data)

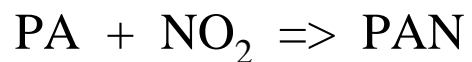
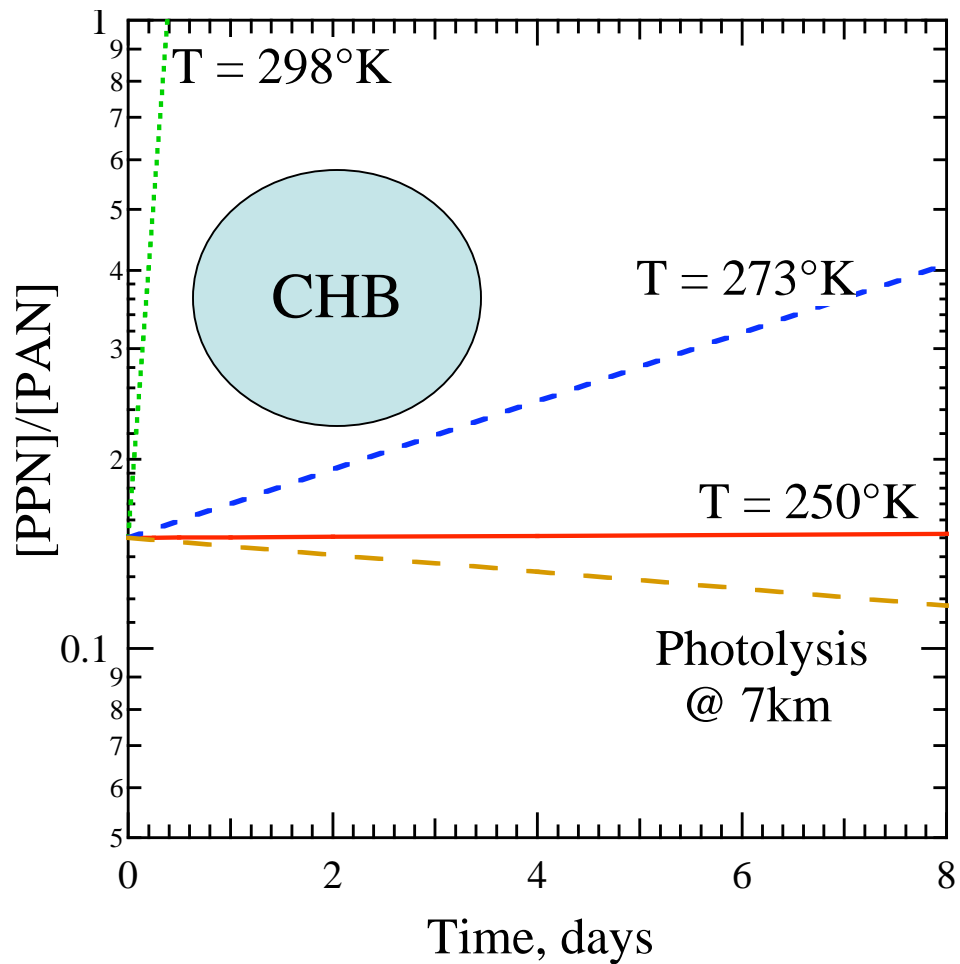






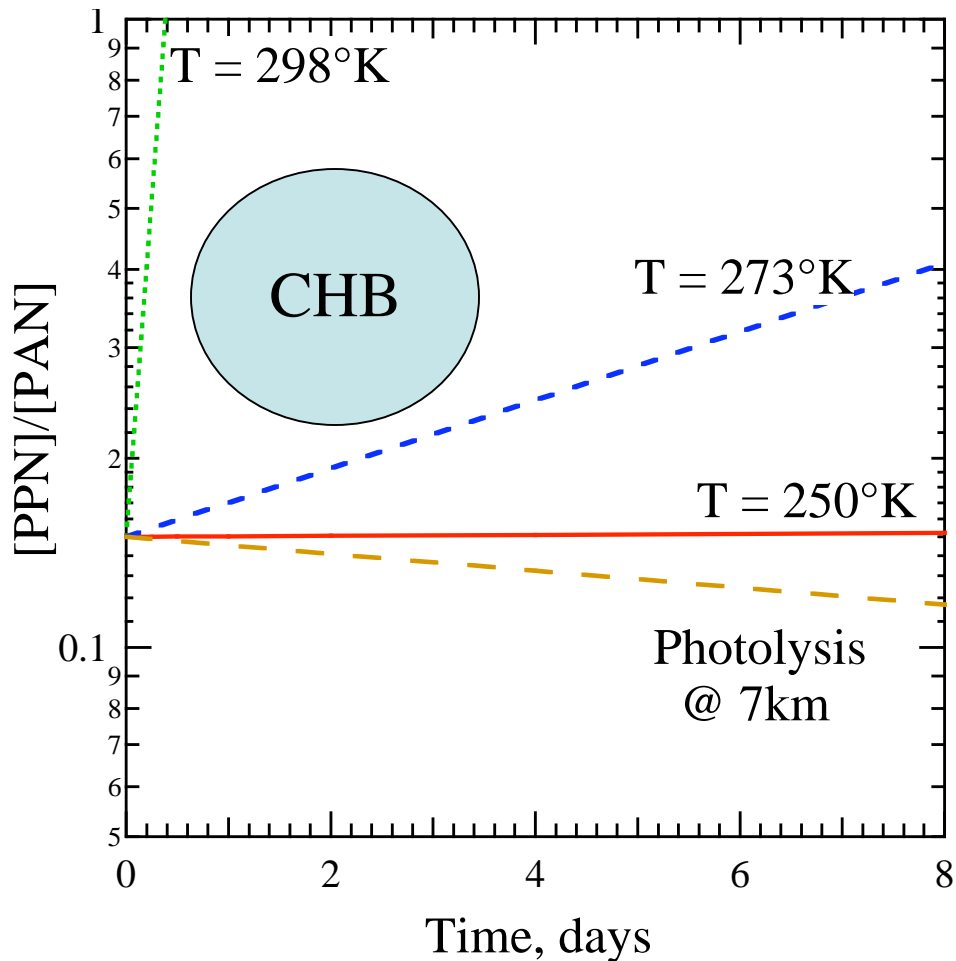




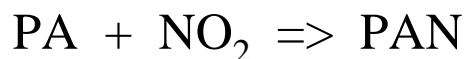


Effective Thermal Decomposition
Correction Factor

$$1 - \left\{ \frac{1}{1 + k_3[\text{NO}]/k_2[\text{NO}_2]} \right\} = 0.1 \text{ to } 0.2$$



If there is sufficient Fog droplet Surface Area such that PA + H₂O can compete with PA + NO₂, then this process will speed up the loss of PAN and therefore the change in PPN/PAN



Effective Thermal Decomposition
Correction Factor

$$1 - \left\{ \frac{1}{1 + k_3[\text{NO}]/k_2[\text{NO}_2]} \right\} = 0.1 \text{ to } 0.2$$

How can we tell if there is Fog Water Processing?

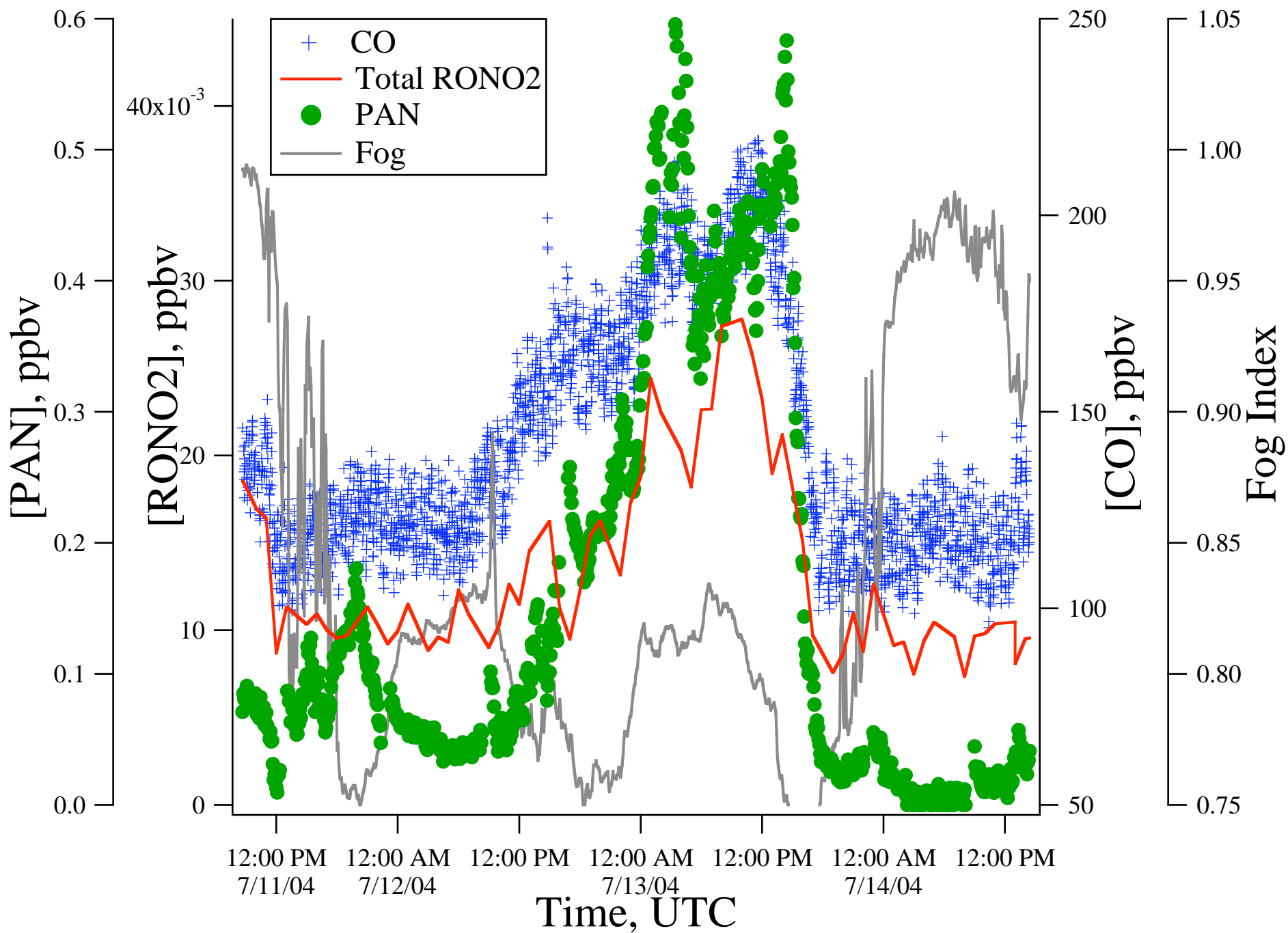
CO, General Tracer of Continental Sources

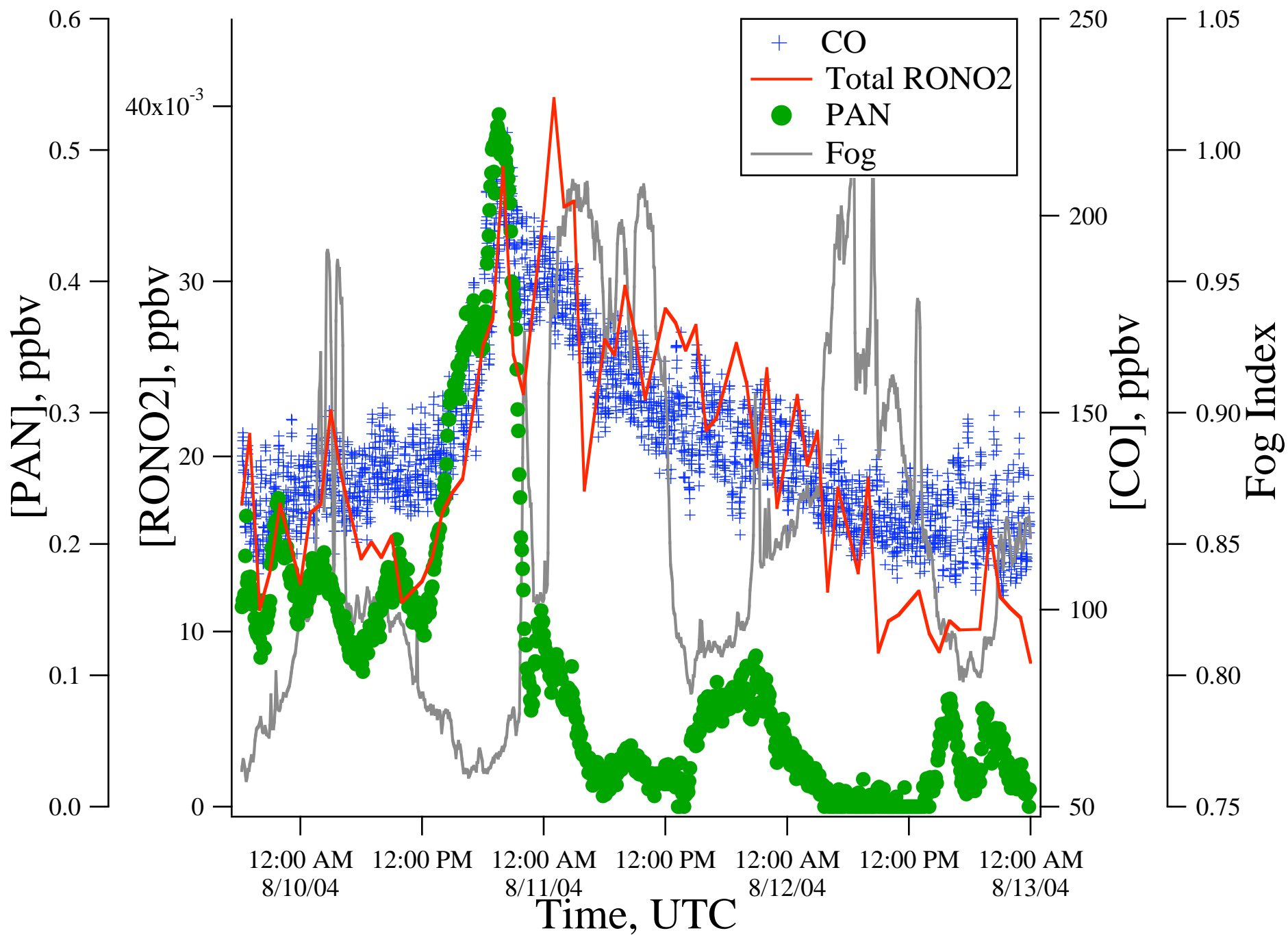
VOC/NO_x Photochemistry -> PAN, RONO₂s

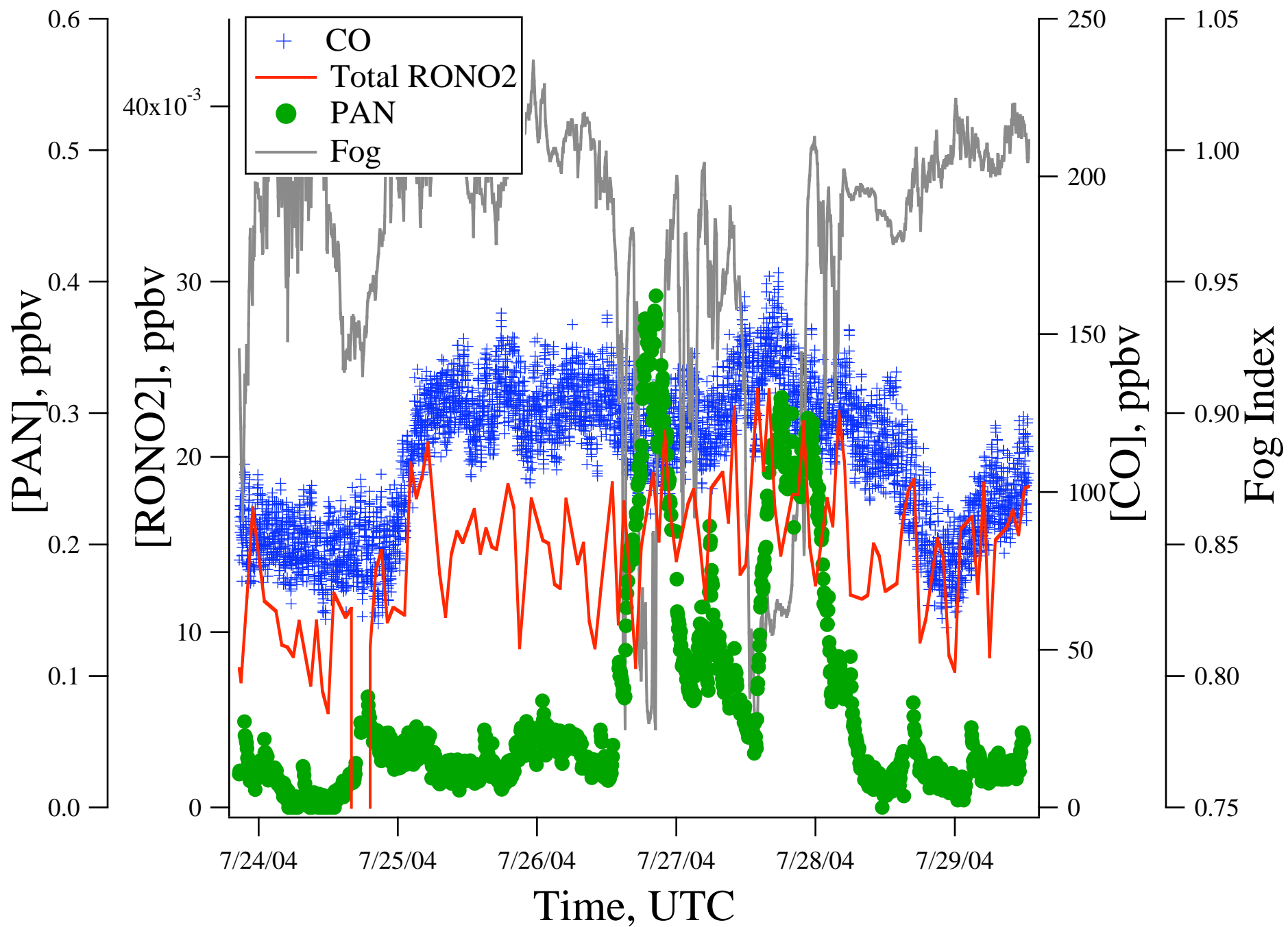
RONO₂s, Thermally Stable, Insoluble in Water

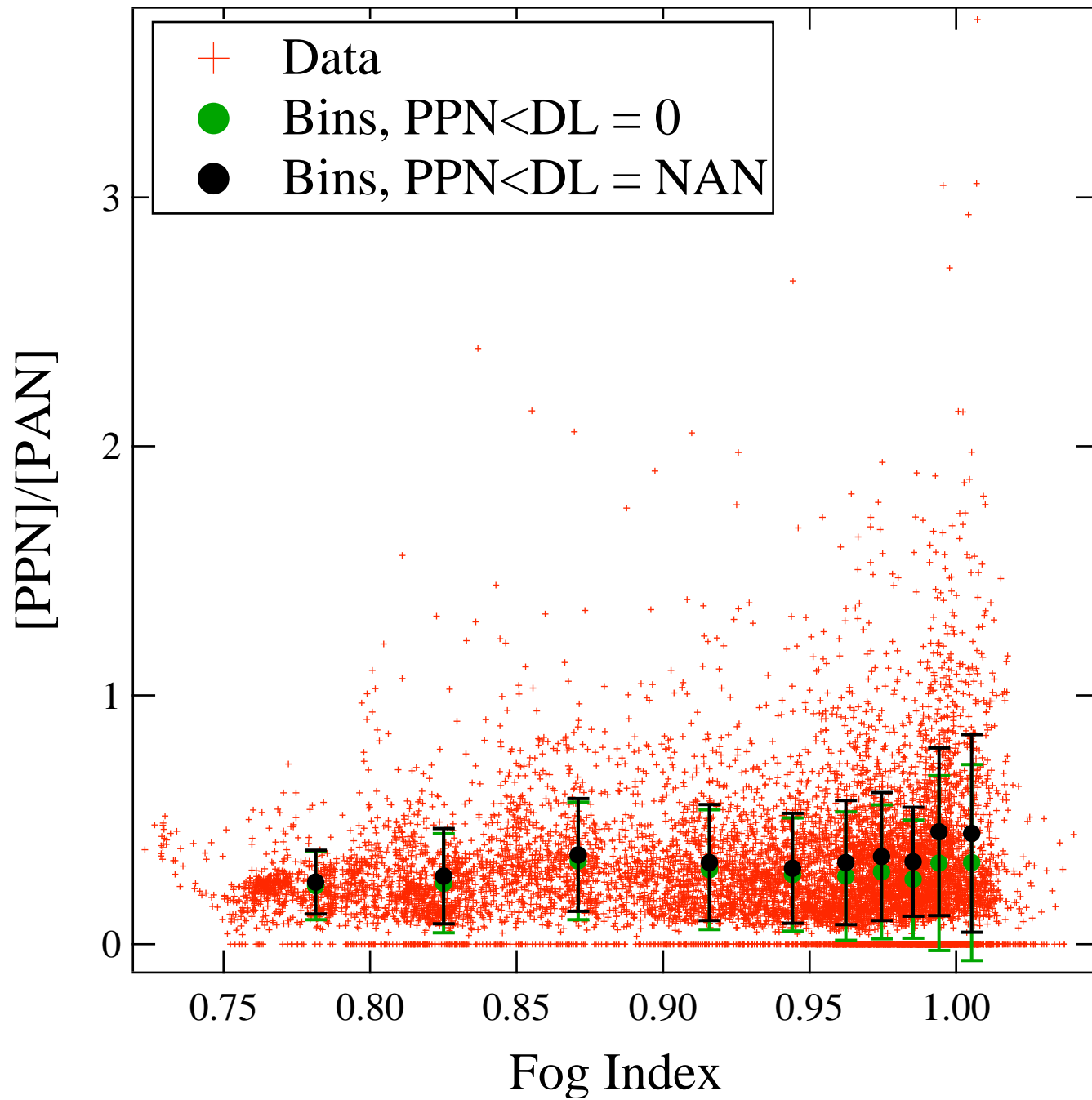
Fog Occurrence and Intensity

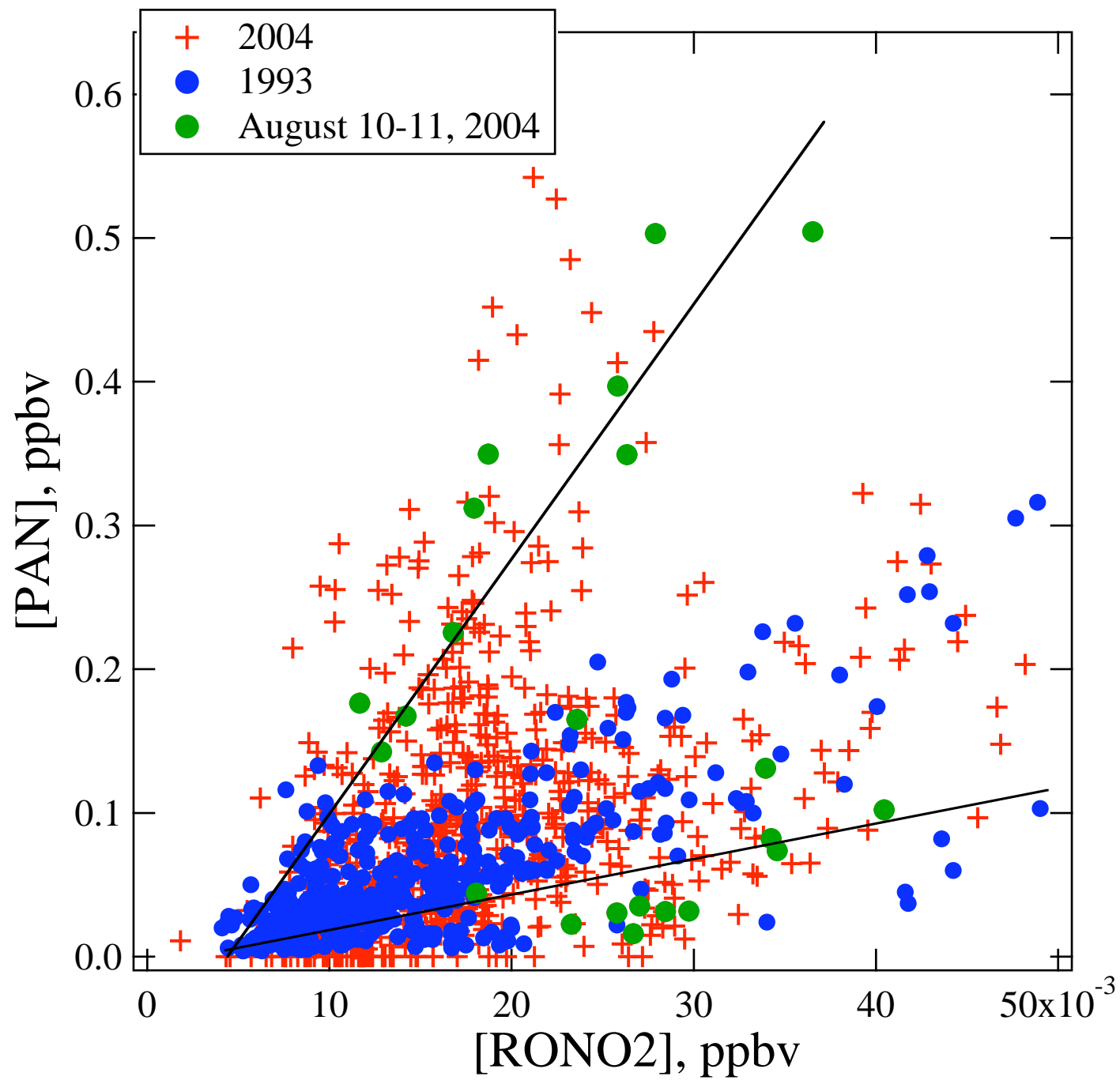
IR radiometer- Up/Down











SUMMARY

PAN and PPN complete, PiBN and MPAN still in the works

PAN and PPN higher in 2004 than in 1993, more impact events

PPN/PAN similar in 2004 and 1993, indicating thermal decomposition losses

Several interesting fog processing events in 2004.

FUTURE WORK

Explore back trajectories to see if timescales are consistent.

Is there a quantitative relationship between PA fog water loss and other processes such as $\text{SO}_2 \rightarrow \text{SO}_4^-$ conversion?

Does PA \rightarrow fog water provide a significant source of HO_x to fog water?