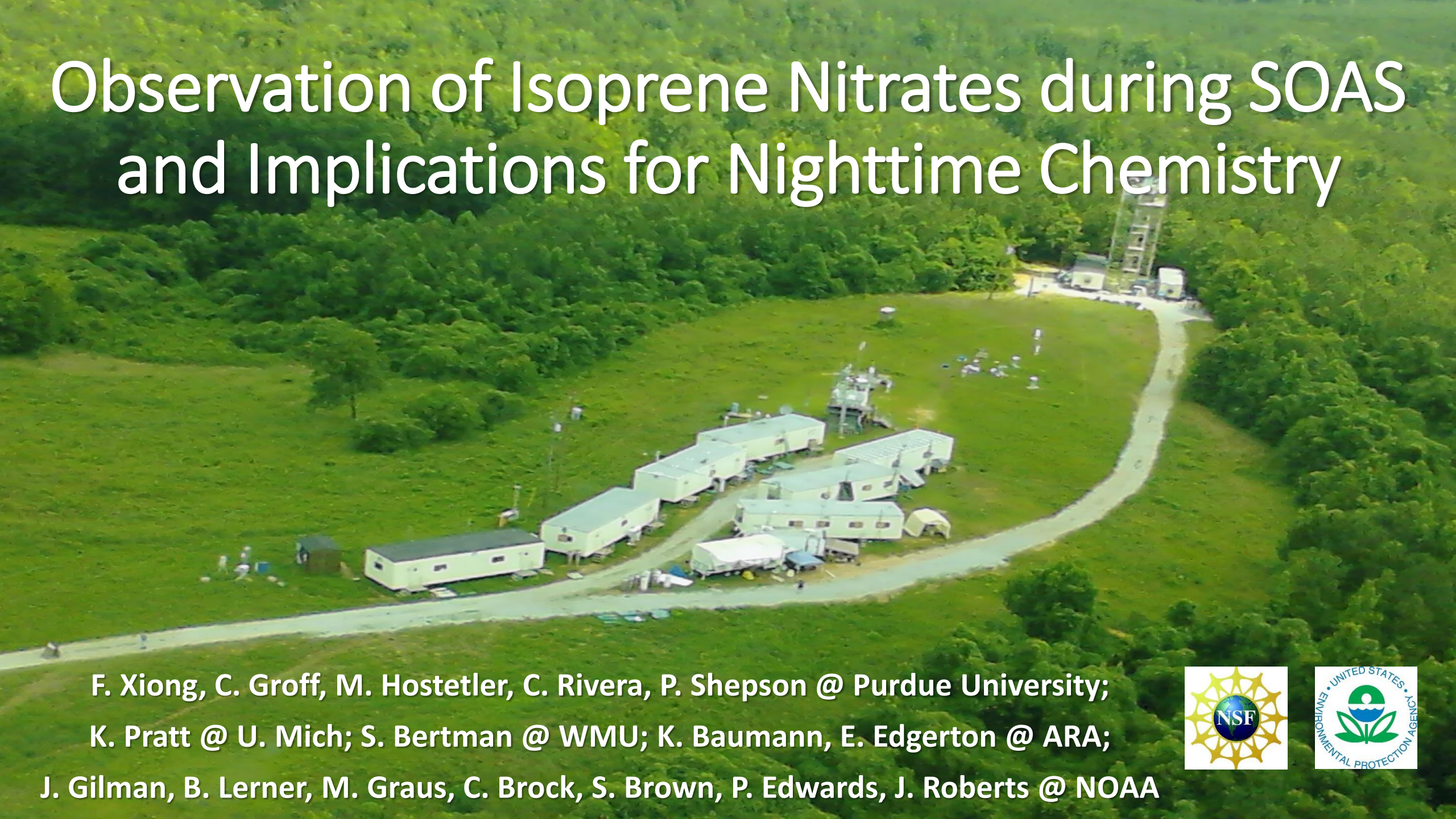


Observation of Isoprene Nitrates during SOAS and Implications for Nighttime Chemistry



F. Xiong, C. Groff, M. Hostetler, C. Rivera, P. Shepson @ Purdue University;
K. Pratt @ U. Mich; S. Bertman @ WMU; K. Baumann, E. Edgerton @ ARA;
J. Gilman, B. Lerner, M. Graus, C. Brock, S. Brown, P. Edwards, J. Roberts @ NOAA

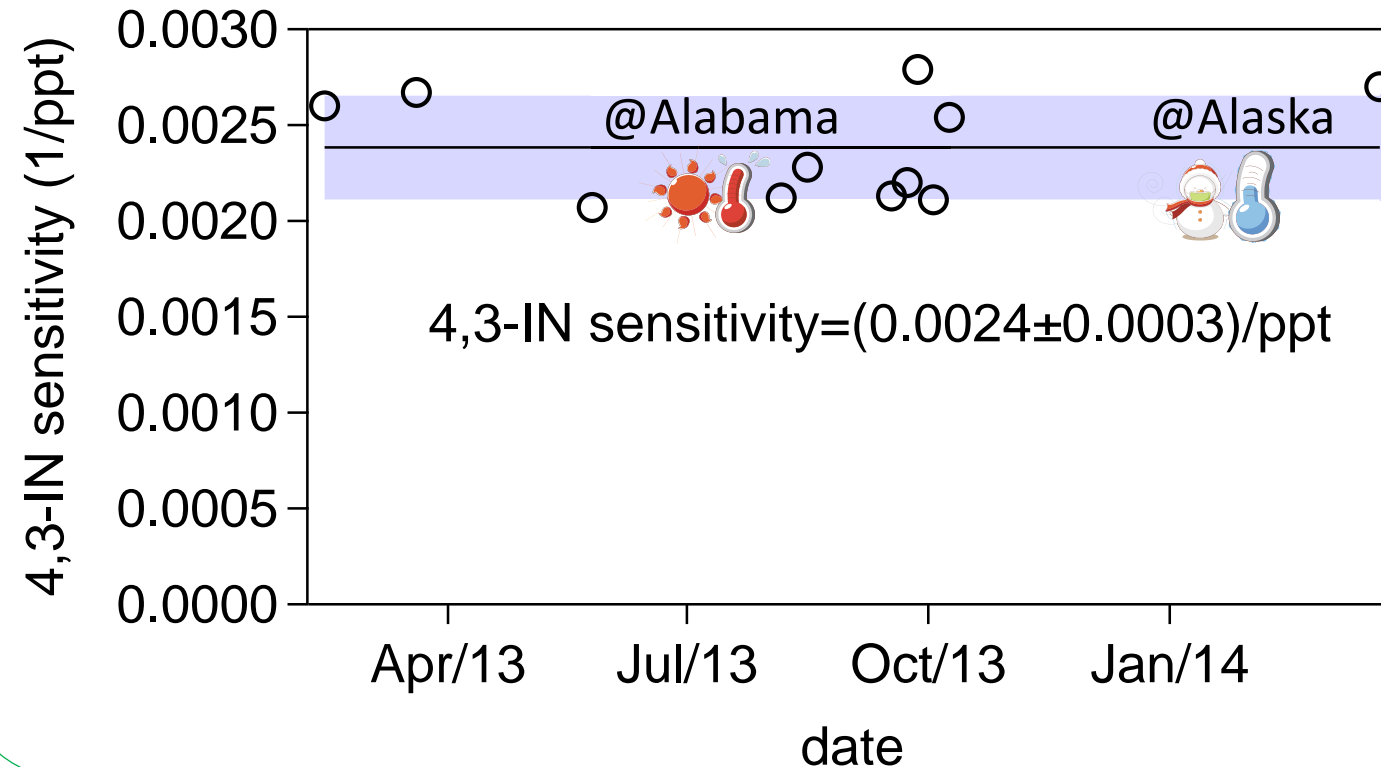
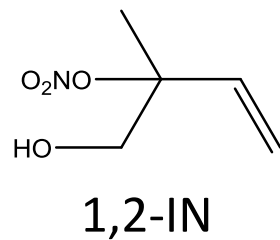
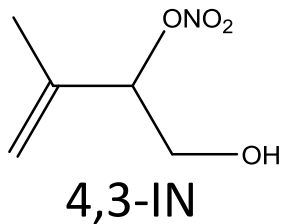


Observation of Isoprene-derived Nitrate Products

- CIMS: $\text{I}^-(\text{H}_2\text{O})_n$ reagent ion; quadrupole mass analyzer
- @ CTR ground site
- 5/26 - 7/11: isoprene-derived nitrates
- 7/11 - 7/15: peroxyacetyl nitrate

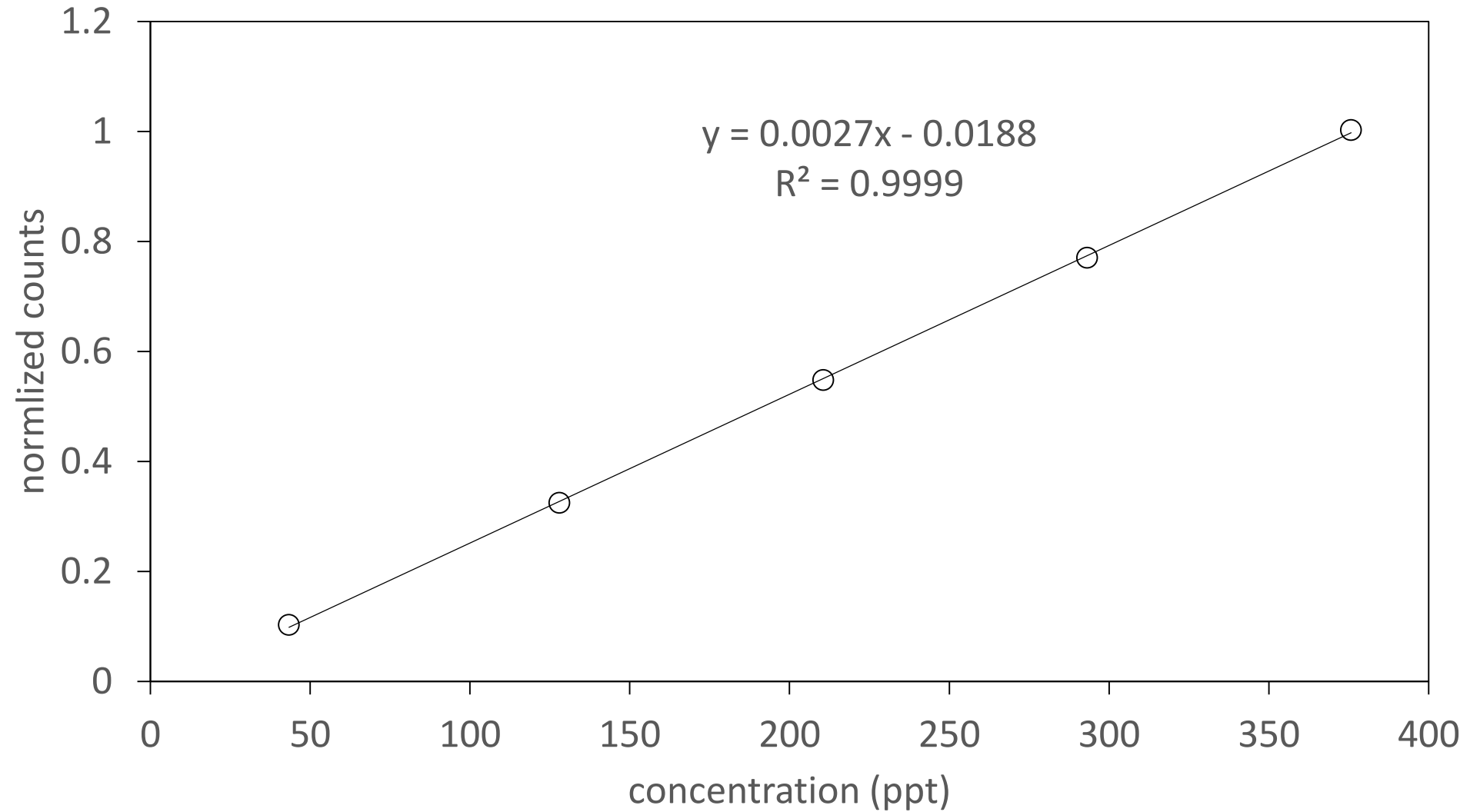
Isoprene Hydroxynitrates (INs) Measurement with CIMS

standard
compound
for calibration

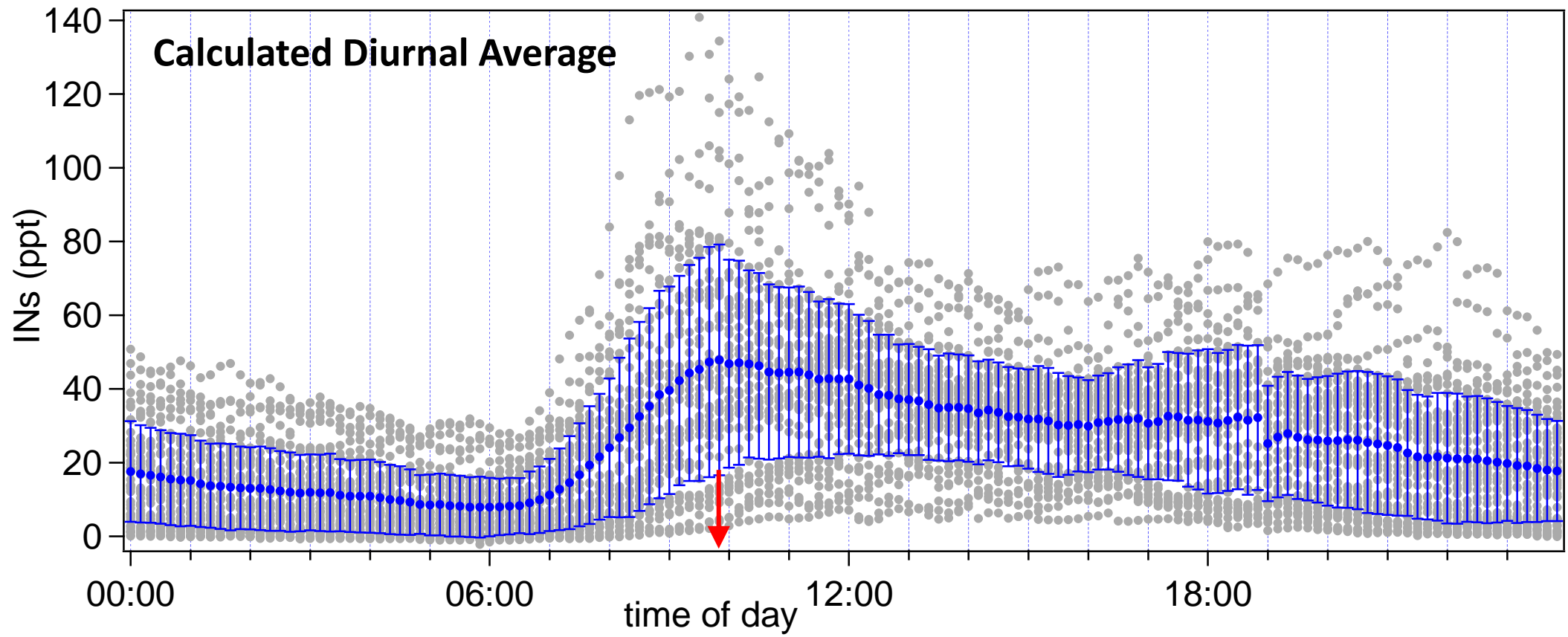
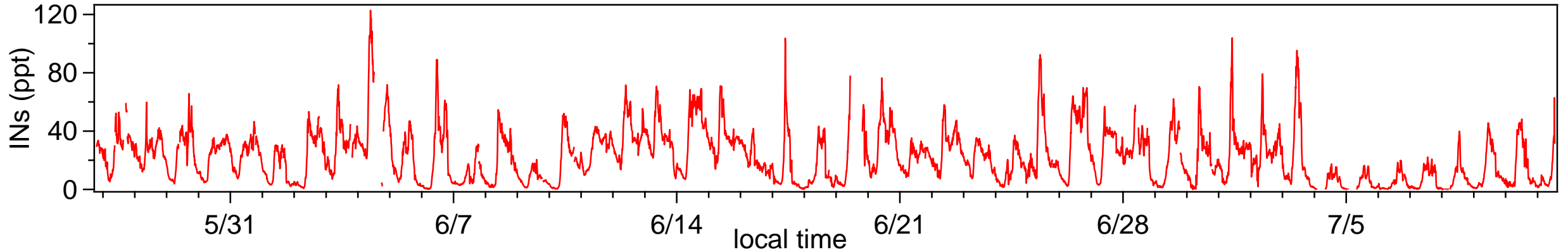


preliminary 1,2-IN sensitivity = 0.0004/ppt (?!)

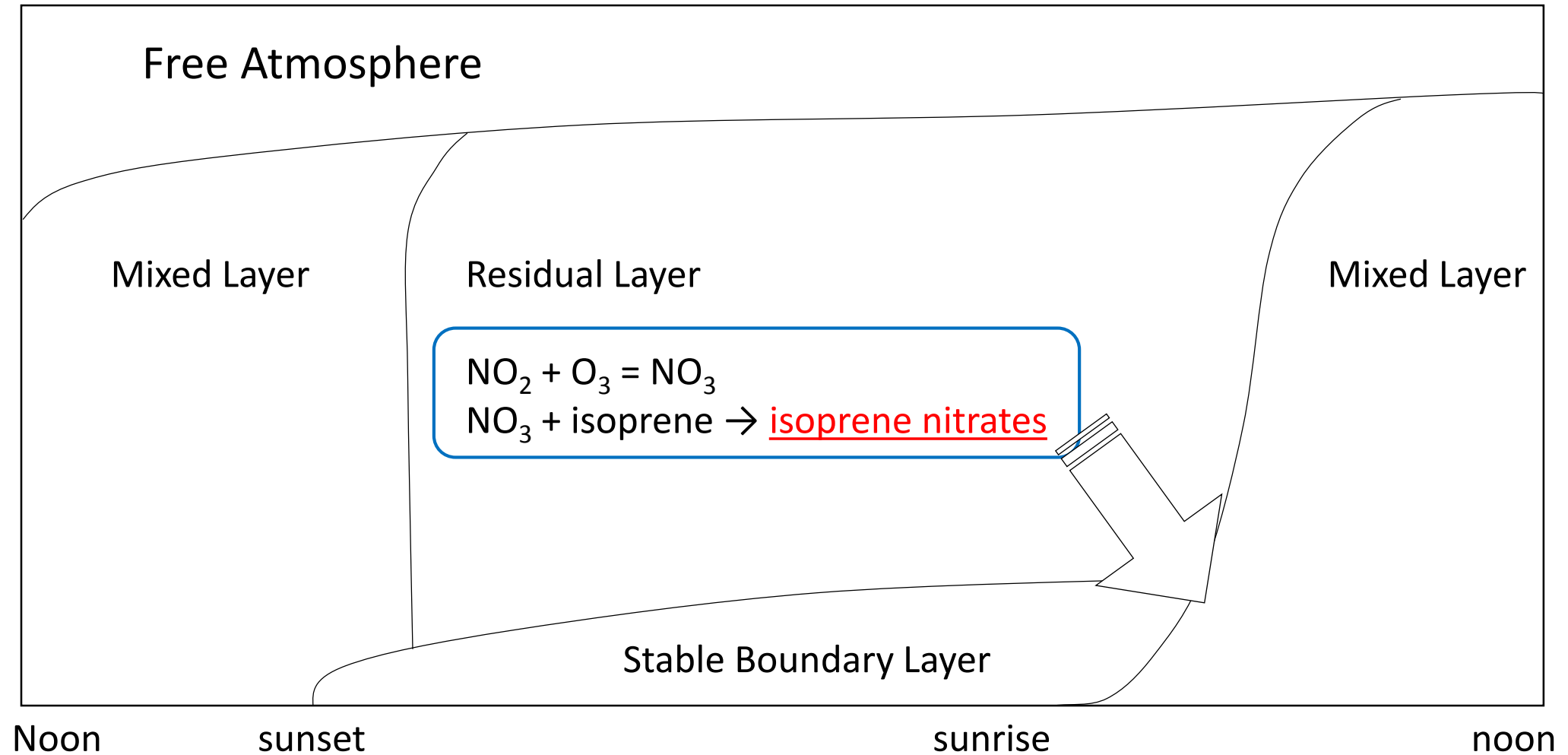
4,3-IN Bag Calibration @ Purdue on 2014-3-22



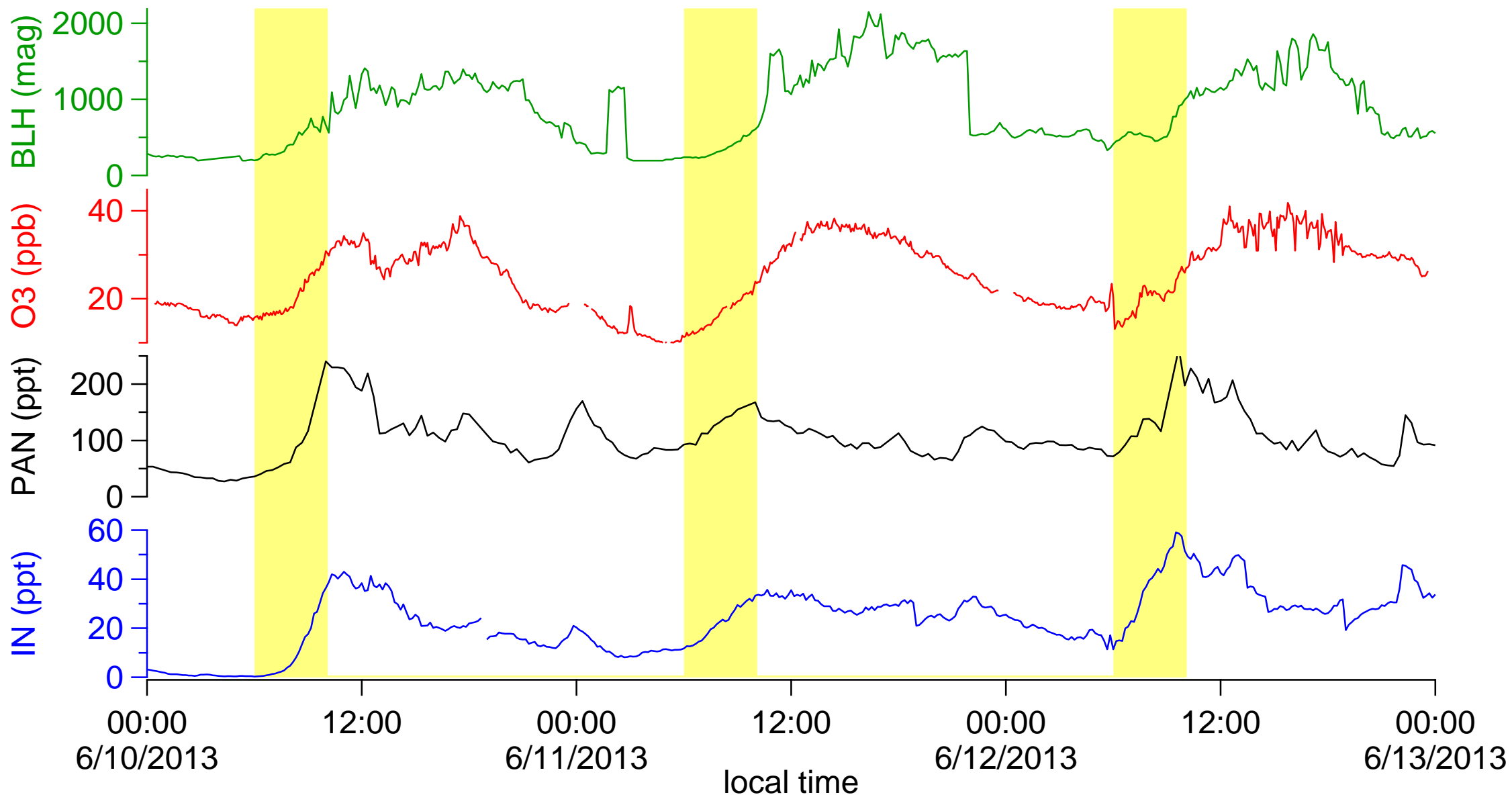
IN Data for the Entire Campaign



Hypothesis: Nighttime Chemistry and Downward Mixing

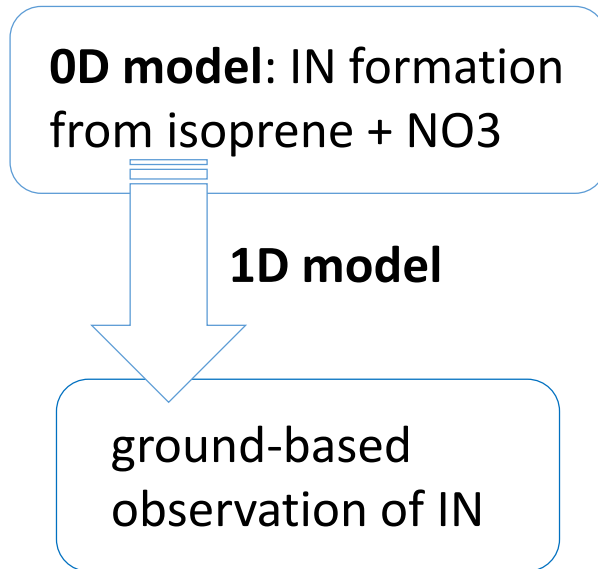


Morning Growth of IN, PAN and O₃



PAN data courtesy of the Bertman Group @ WMU; O₃ and BLH data courtesy of Karsten and Eric @ARA

0D Model: Nighttime Isoprene Nitrate Formation in Residual Layer?



isoprene nitrate formation mechanism in the dark:
NO₃ + isoprene = NISOPO₂
~30% NISOPO₂ + RO₂ → NISOPO (radical propagation)
~70% NISOPO₂ + RO₂ → carbonyl + isoprene nitrates

IN yield from NO₃ + isoprene ~21% (Kwan et al., 2012)

Ongoing 0D model Case Study...

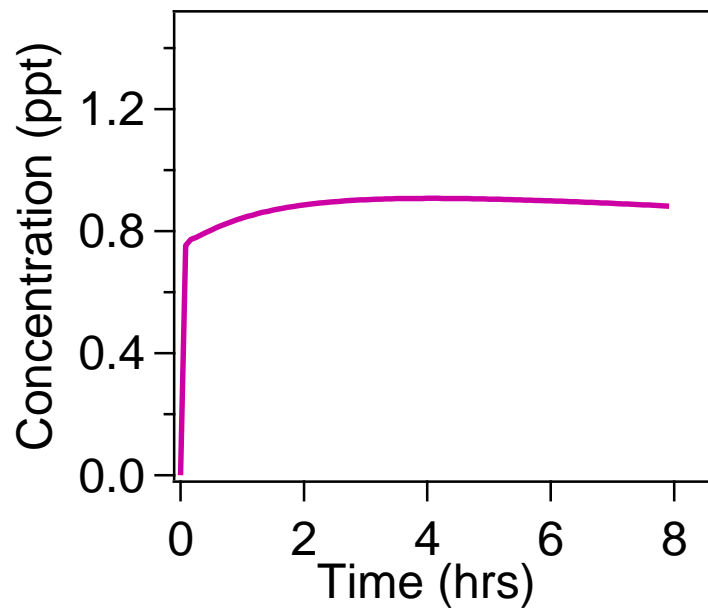
7/1/13 P3 flew over CTR site @ 8pm CDT

initial condition

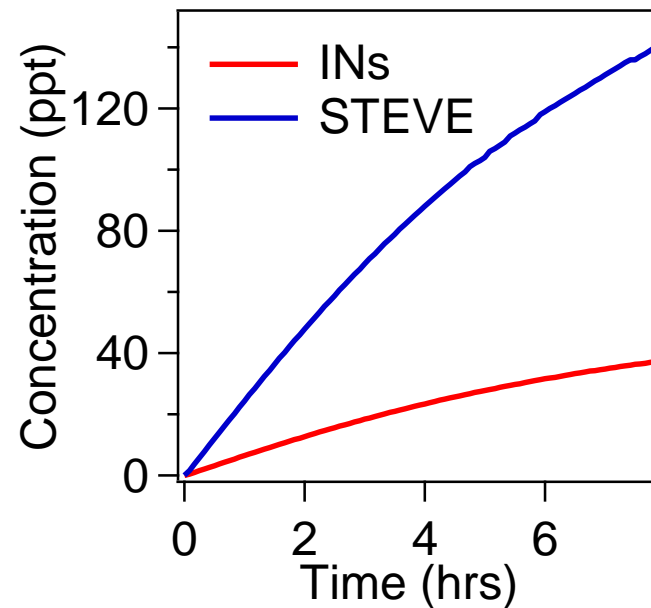
- NO=0.15ppb, NO₂=0.2ppb, O₃= 40ppb
- Isoprene=700ppt, MT=35ppt (44% alpha-pinene, 41% beta-pinene, 15% limonene)
- steady state NO₃ and HO_x will be modeled

Preliminary Model Results and Comparison with Observation

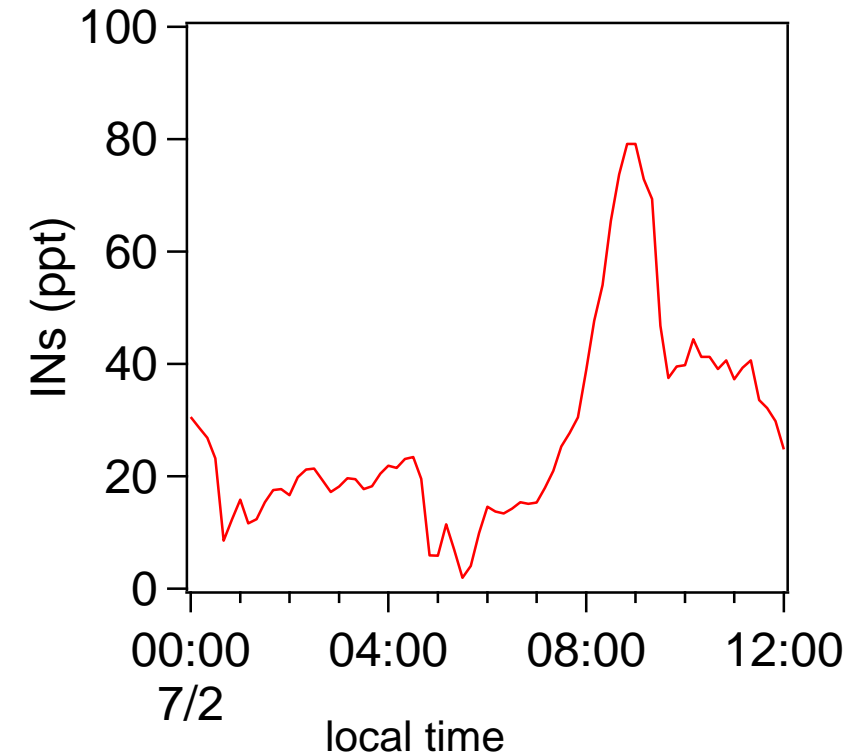
Night Time Steady State NO3



Night Time INs Production



INs Growth in the Morning



Plans and Thoughts

- Determine CIMS sensitivity for different IN isomers
- Determine IN yield from NO_3 + isoprene reaction
- 0D model: estimate nighttime IN formation
- 1D model: nighttime IN formation and vertical IN transport
- Other sources of IN?