NO_y fate in the southeastern U.S.: NO_3-initiated organonitrate production vs. dust uptake of HNO_3

Juliane L. Fry (fry@reed.edu), Benjamin Ayres, Hannah Allen, Danielle Draper

Reed College

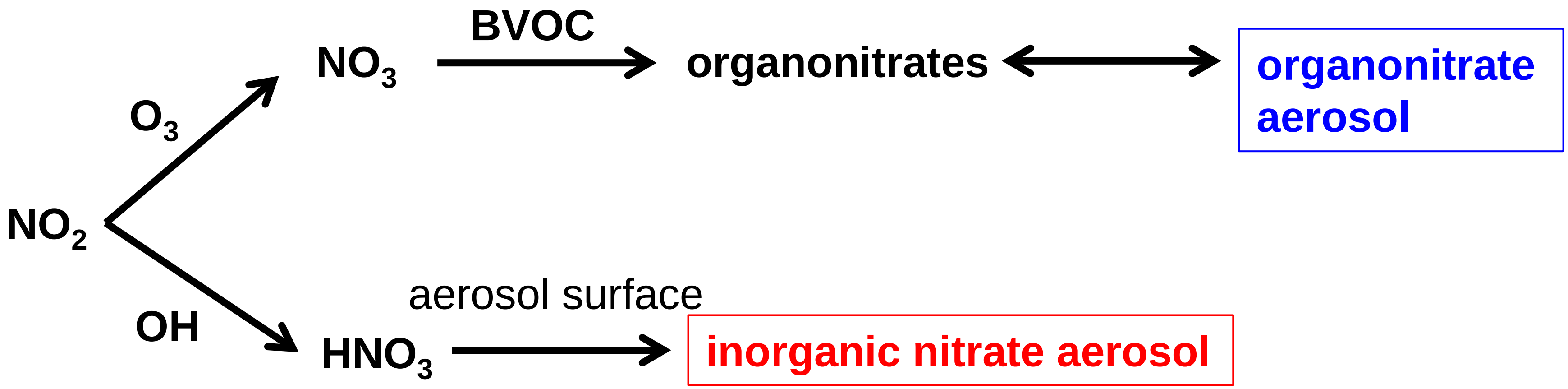
with input/data provided by **many** SOAS friends: Steve Brown, Rob Wild, Abby Koss, Joost de Gouw, Allen Goldstein, Kevin Olson, Karsten Baumann, Eric Edgerton, Weiwei Hu, Brett Palm, Jose Jimenez, Christoph Knote, Ron Cohen, Paul Wooldridge, Kaitlin Duffy, Paul Romer, Joel Thornton, Ben Lee, Andy Ault, Amy Bondy, Paul Shepson, Lizi Xiong

4/1/14 SOAS data meeting

This research is funded by
U.S. EPA - Science To Achieve Results (STAR) Program
Grant # RD-83539901

Goals

What is the fate of anthropogenic NOx in the summertime southeastern U.S.?



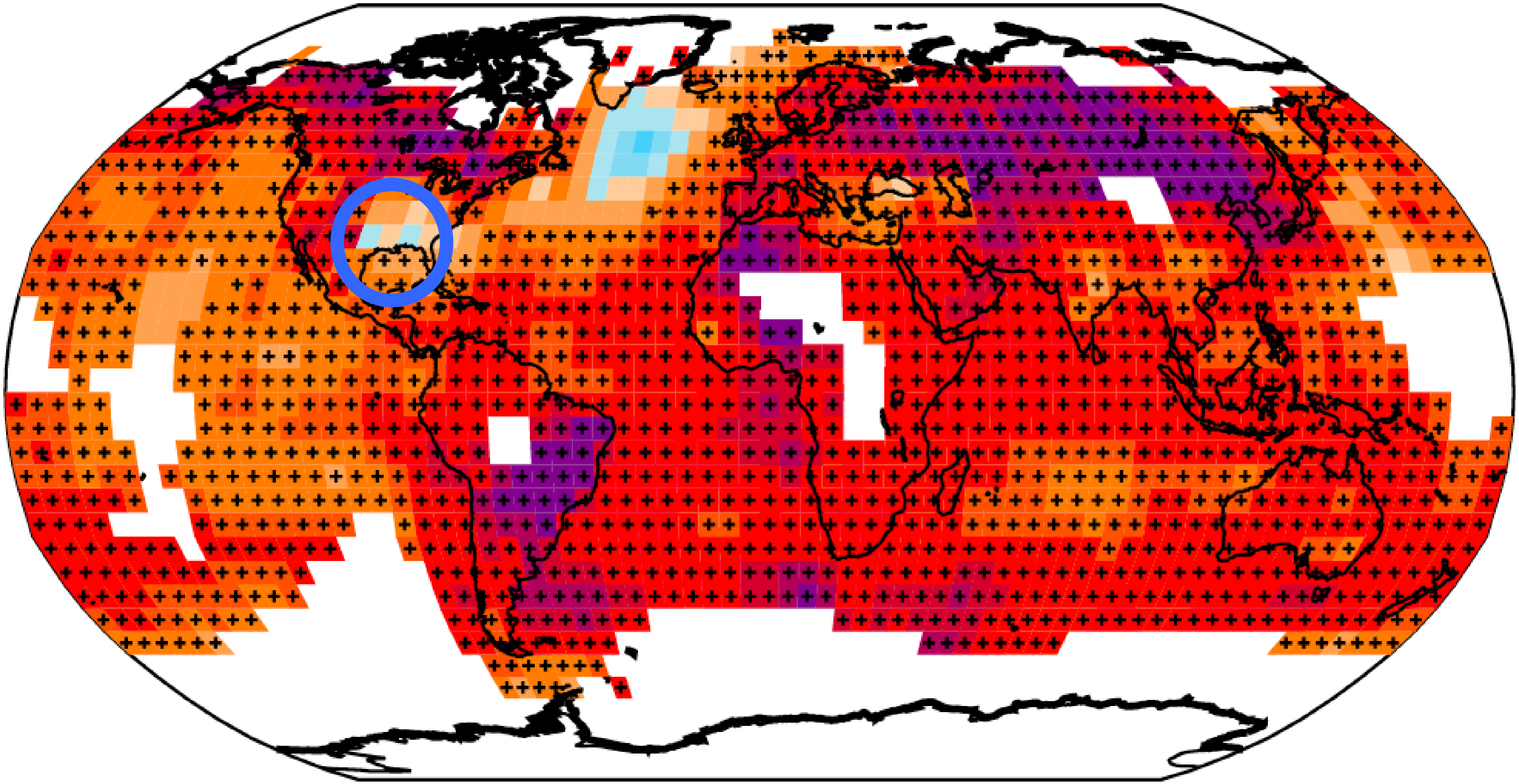
EPA-STAR (Early Career): Anthropogenic influence on biogenic VOC oxidation: the role of NOx pollution in secondary organic aerosol production in the Southeast U.S.

FON: Anthropogenic Influences on Organic Aerosol Formation and Regional Climate Implications, Early Career, EPA-G2012-STAR-D2

PI: Juliane L. Fry, http://academic.reed.edu/chemistry/fry/, fry@reed.edu

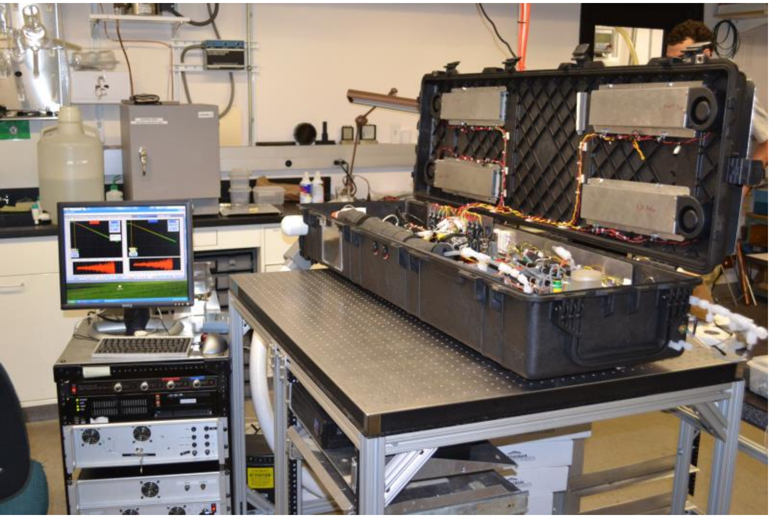
Chemistry Department, Reed College, Portland, OR 97202

Seeking to understand a hole in global warming!



IPCC AR5 2013, WG1 report, Summary for Policymakers Fig. SPM.1

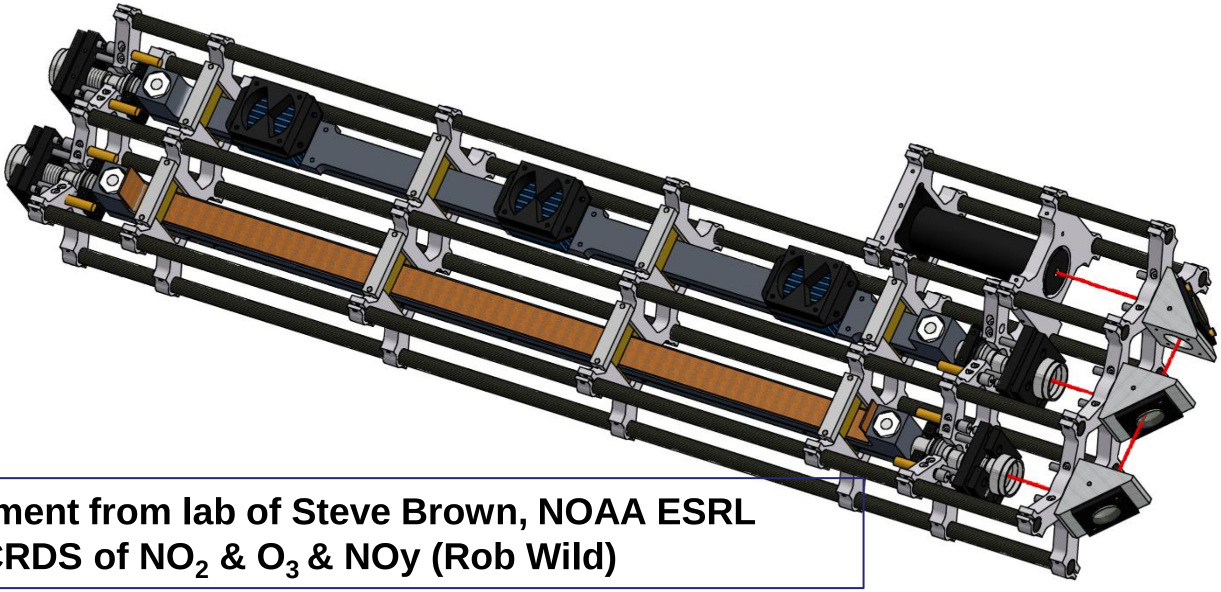
CRDS detection of NO_3/N_2O_5 @ CTR tower



NO_3: 662-nm optical extinction
L.O.D = 0.2 - 3 pptv, 20% Accuracy

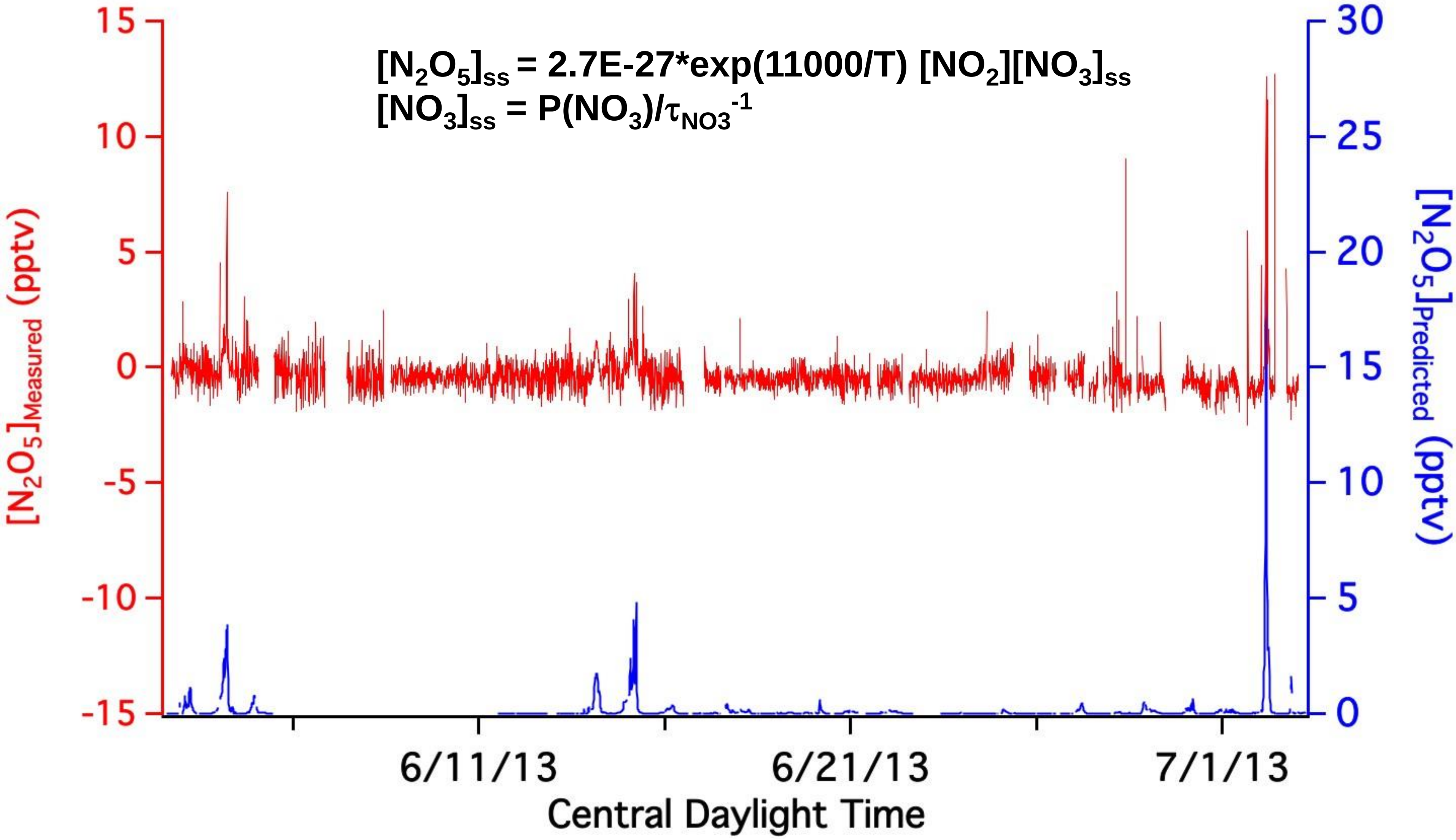
N_2O_5: Thermal conversion + 662-nm
L.O.D. = 0.5 - 3 pptv, 10% Accuracy

Measure first-order decay rate coefficient of light intensity from an optical cavity



Instrument from lab of Steve Brown, NOAA ESRL
Also CRDS of NO_2 & O_3 & NOy (Rob Wild)

CRDS observed [N_2O_5] agrees with steady-state predicted [N_2O_5]; no surprise, losses are efficient!



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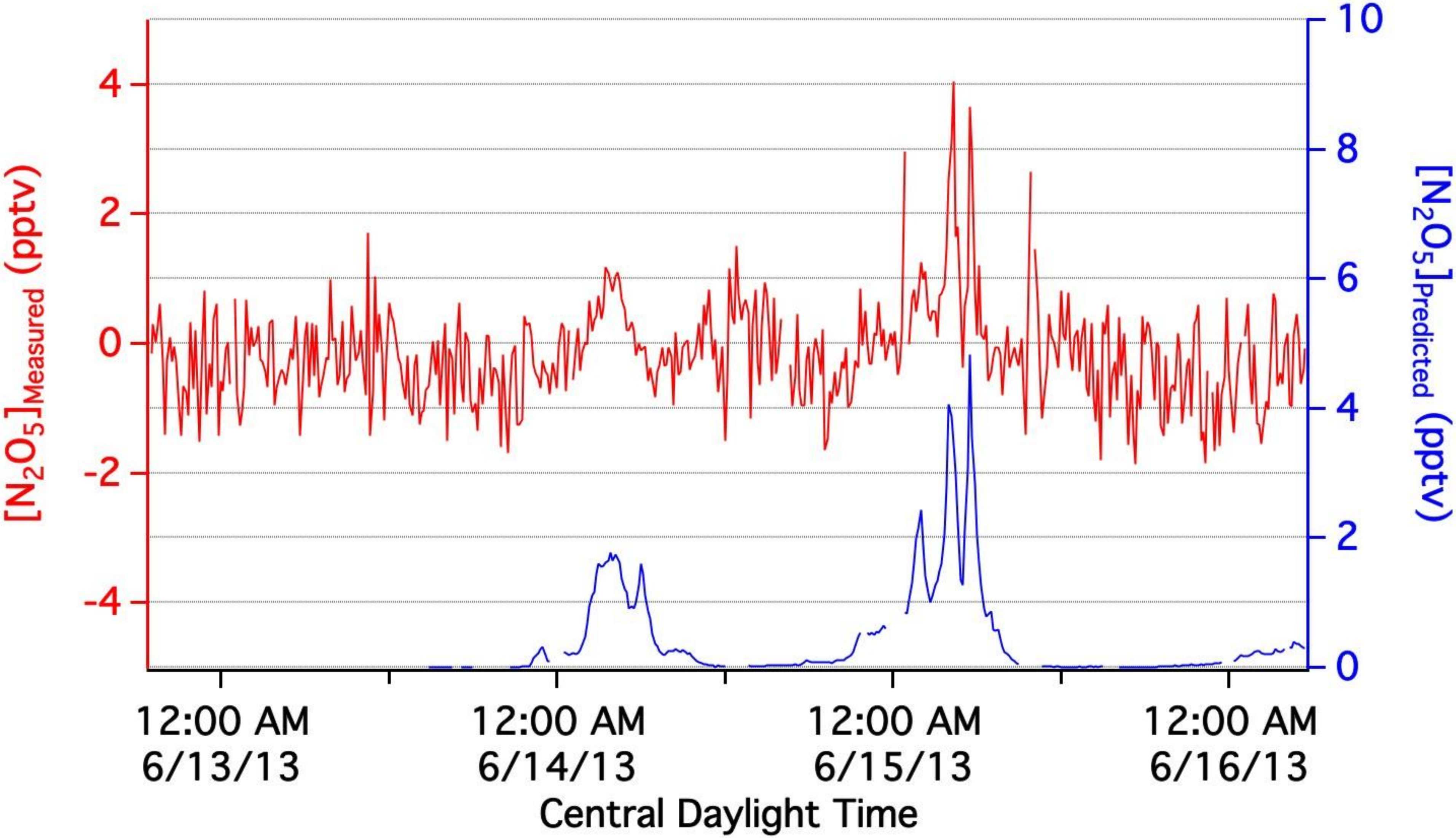
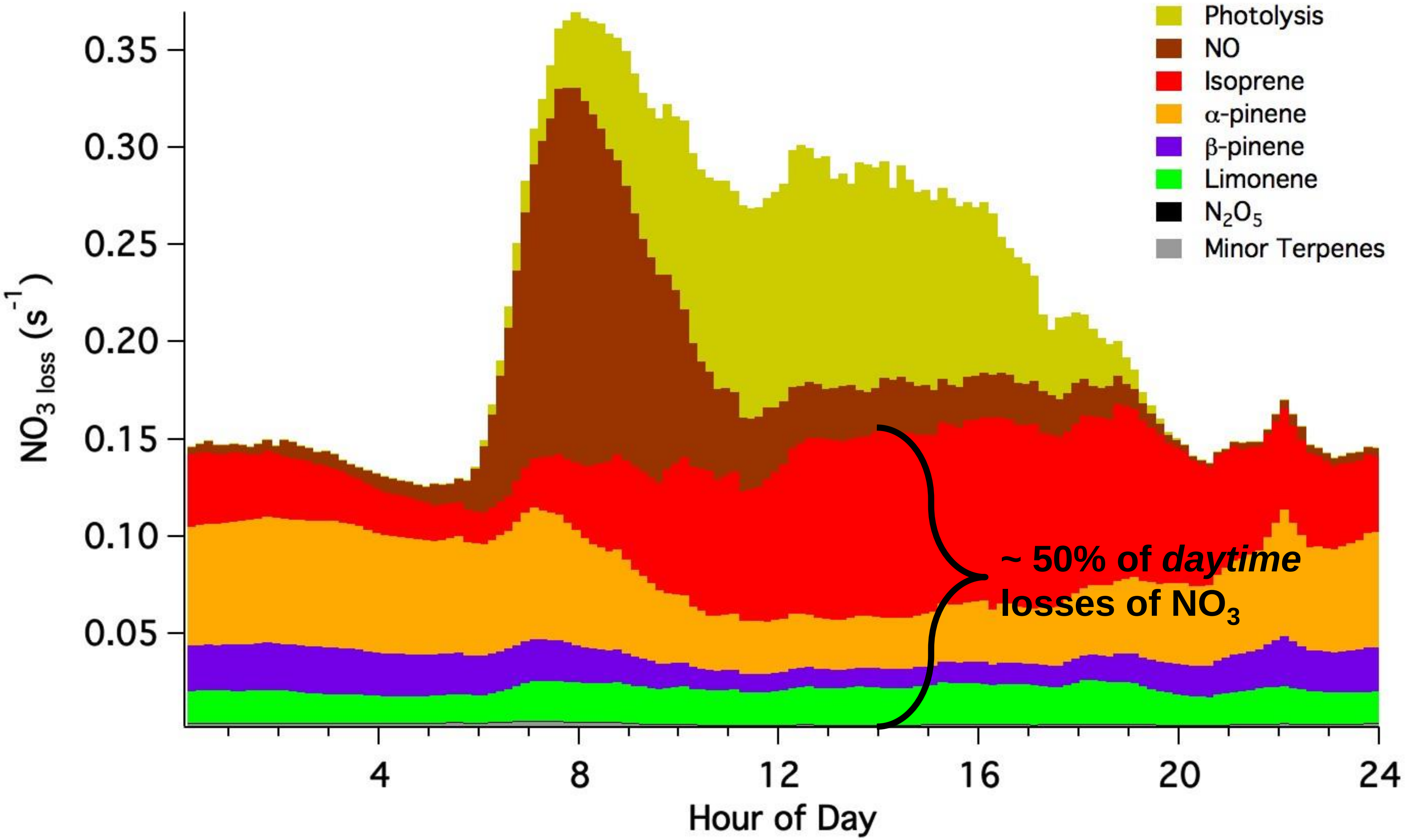
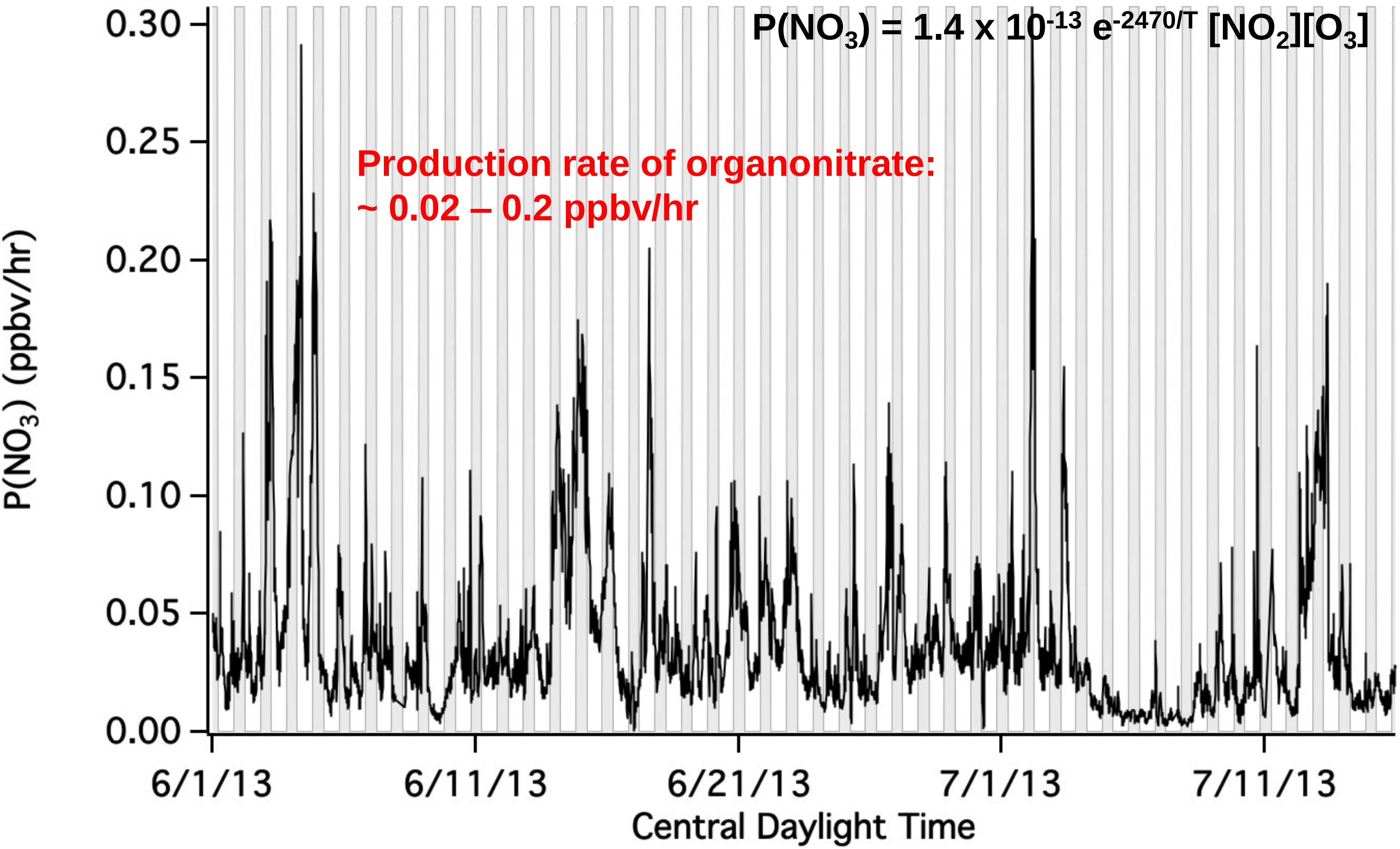


Losses of NO_3/N_2O_5: Substantial fraction to BVOC!

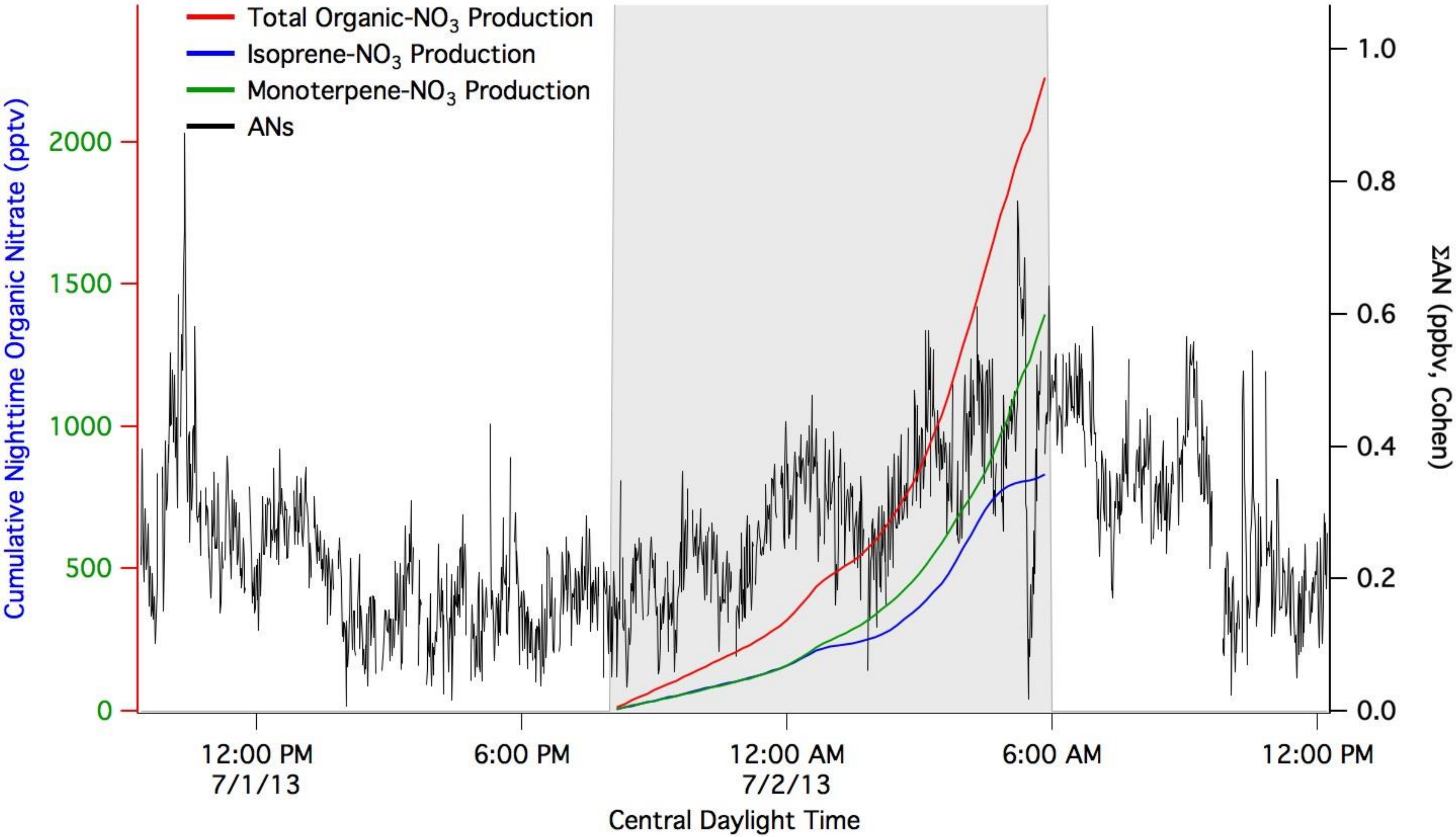


Production rate of nitrate radical supports high organonitrate production



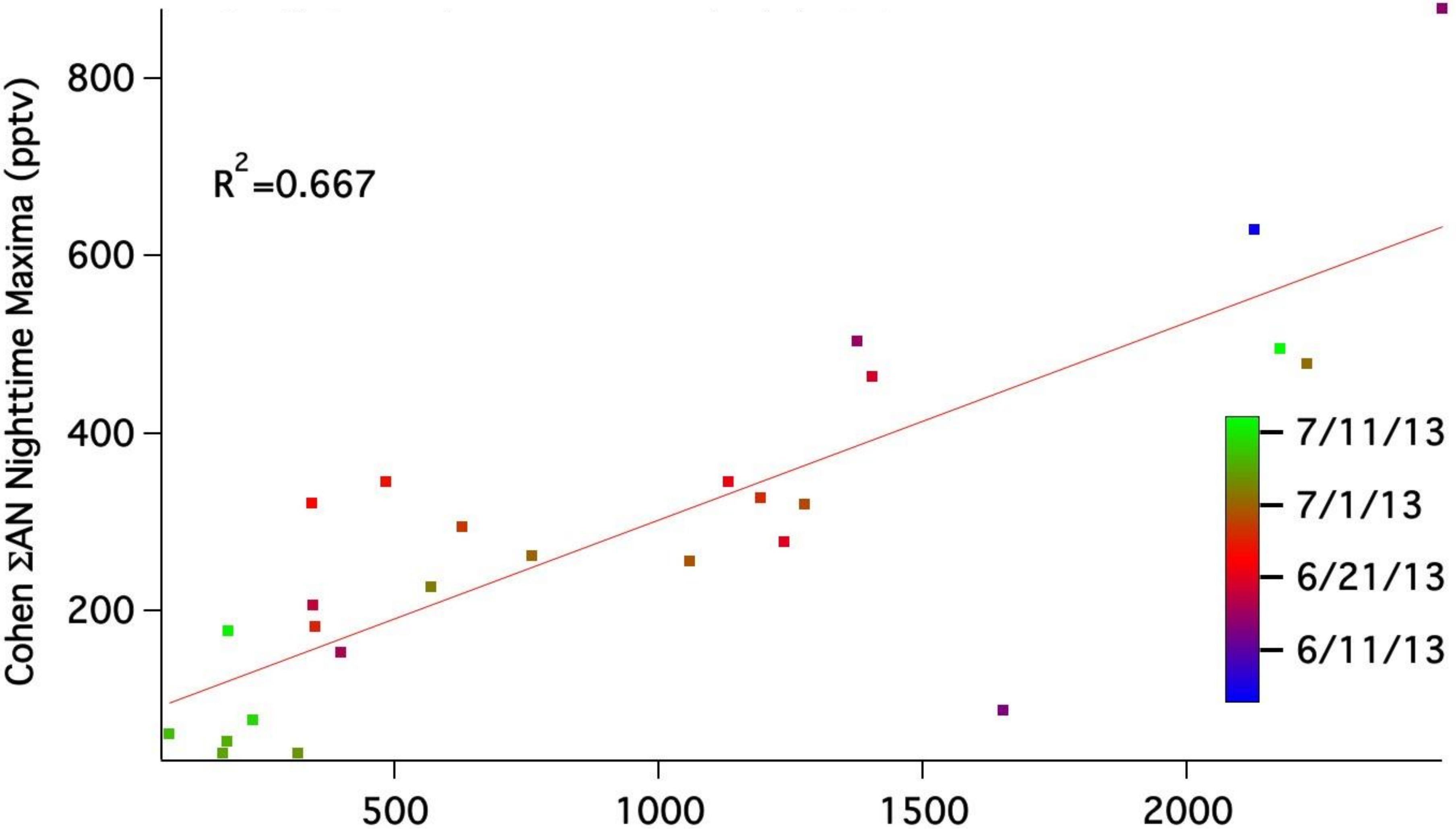
NO_2/O_3 data courtesy Steve Brown group, NOAA

Predictions of organonitrate production



Total ΣANs data courtesy Ron Cohen group, UC Berkeley

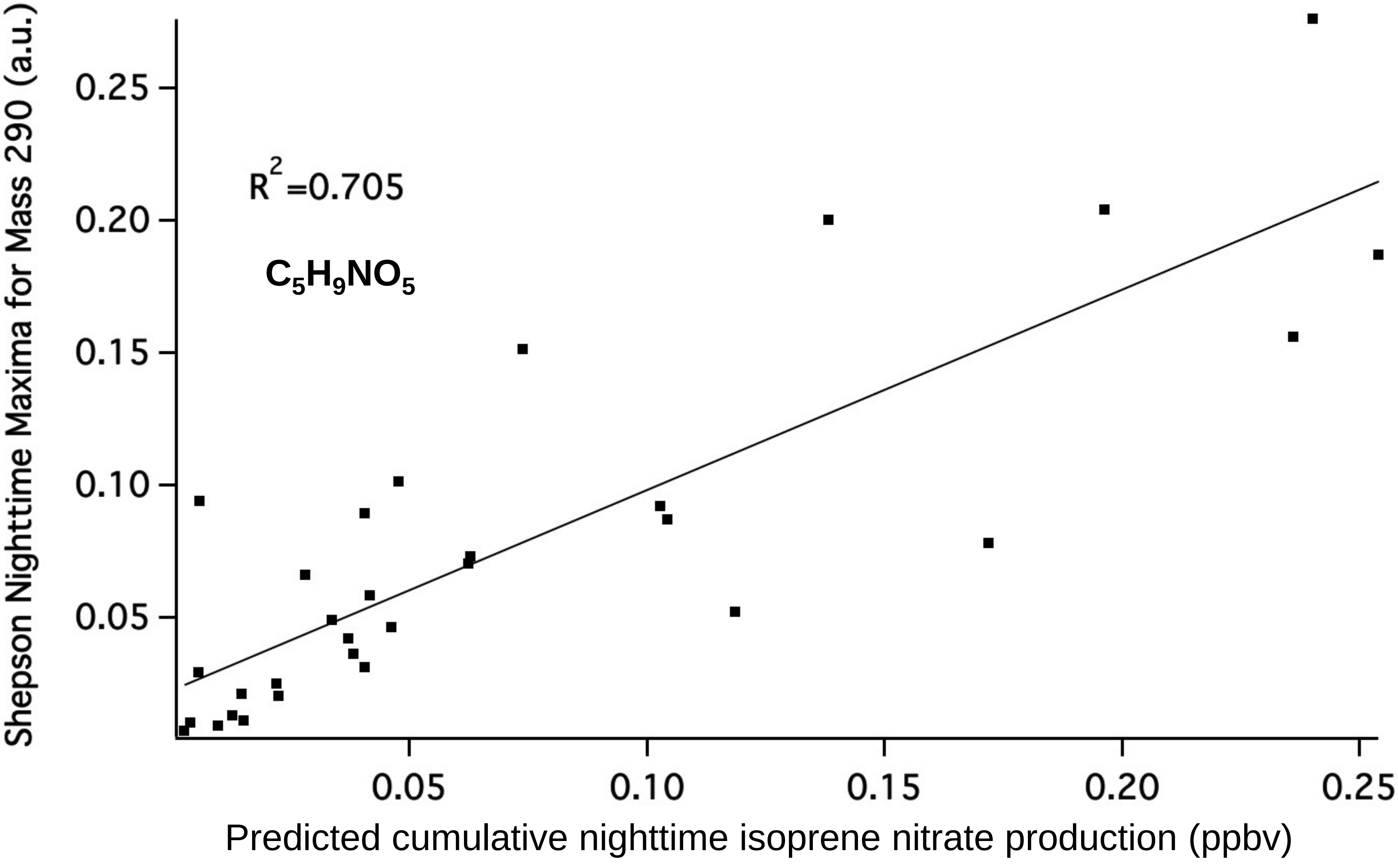
Using $[NO_3]_{ss}$, we can predict total (known) alkyl nitrate production



Predicted cumulative nighttime AN production from NO_3 (isoprene + MTs) (pptv)

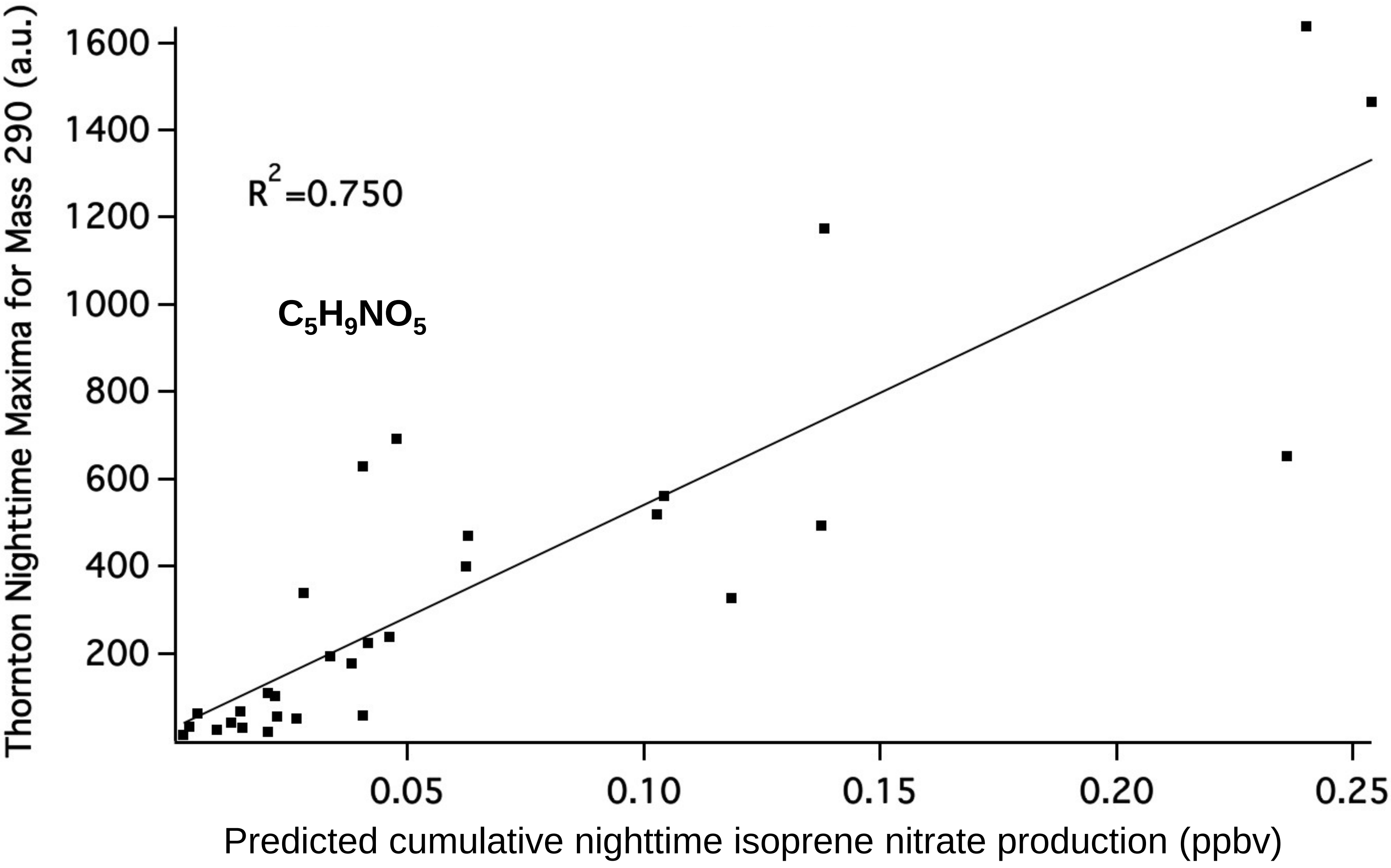
Total ΣANs data courtesy Ron Cohen group, UC Berkeley

Specific BVOC precursors: 1) $C_5H_9NO_5$ isoprene hydroxynitrate appears to be a nighttime NO_3 product



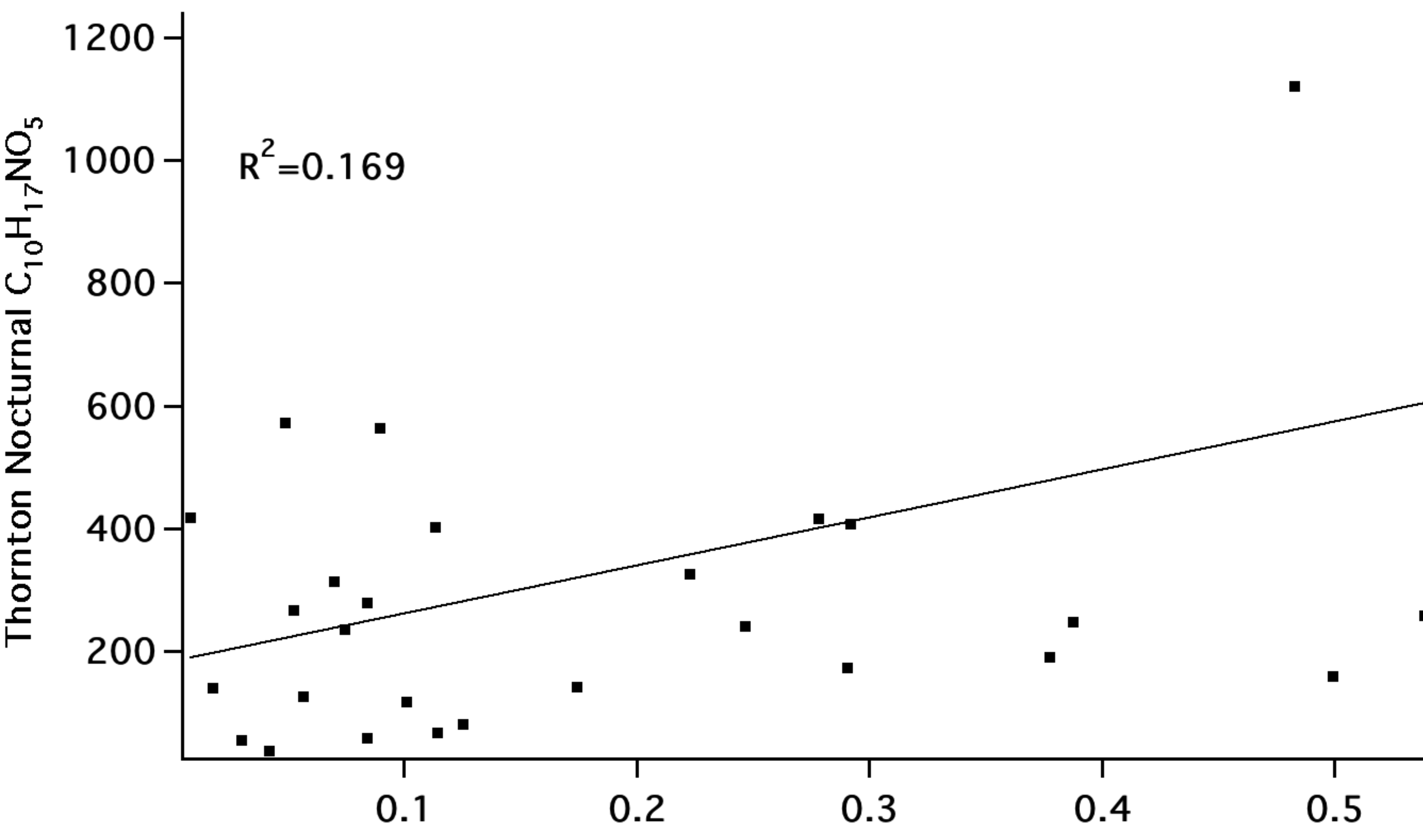
Isoprene nitrate data courtesy Paul Shepson group, Purdue University

Different CIMS dataset, similar correlation



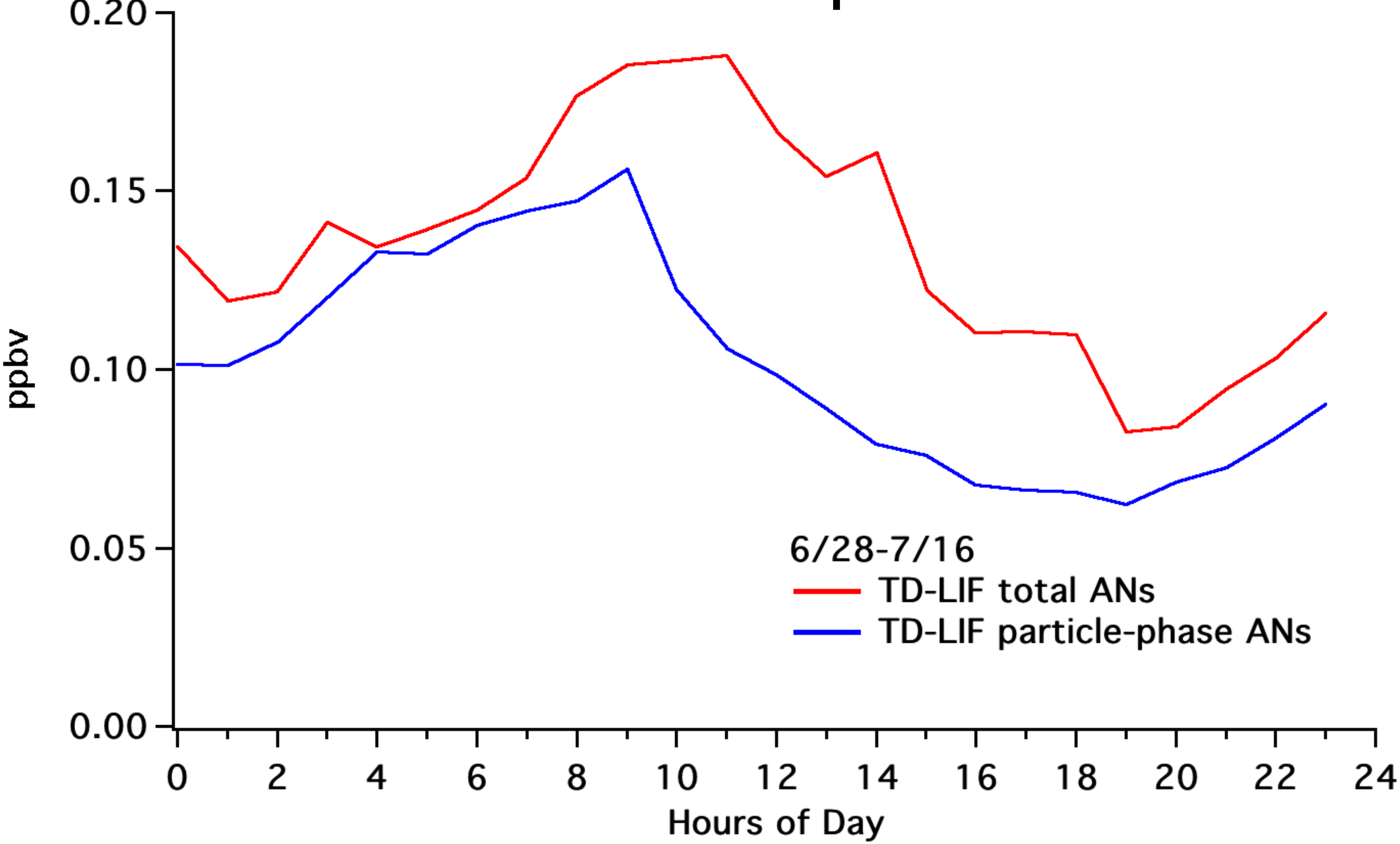
Isoprene nitrate data courtesy Joel Thornton group, University of Washington

Specific BVOC precursors: 2) $C_{10}H_{17}NO_5$ monoterpene hydroxynitrate is ***not*** well predicted by NO_3 source alone!



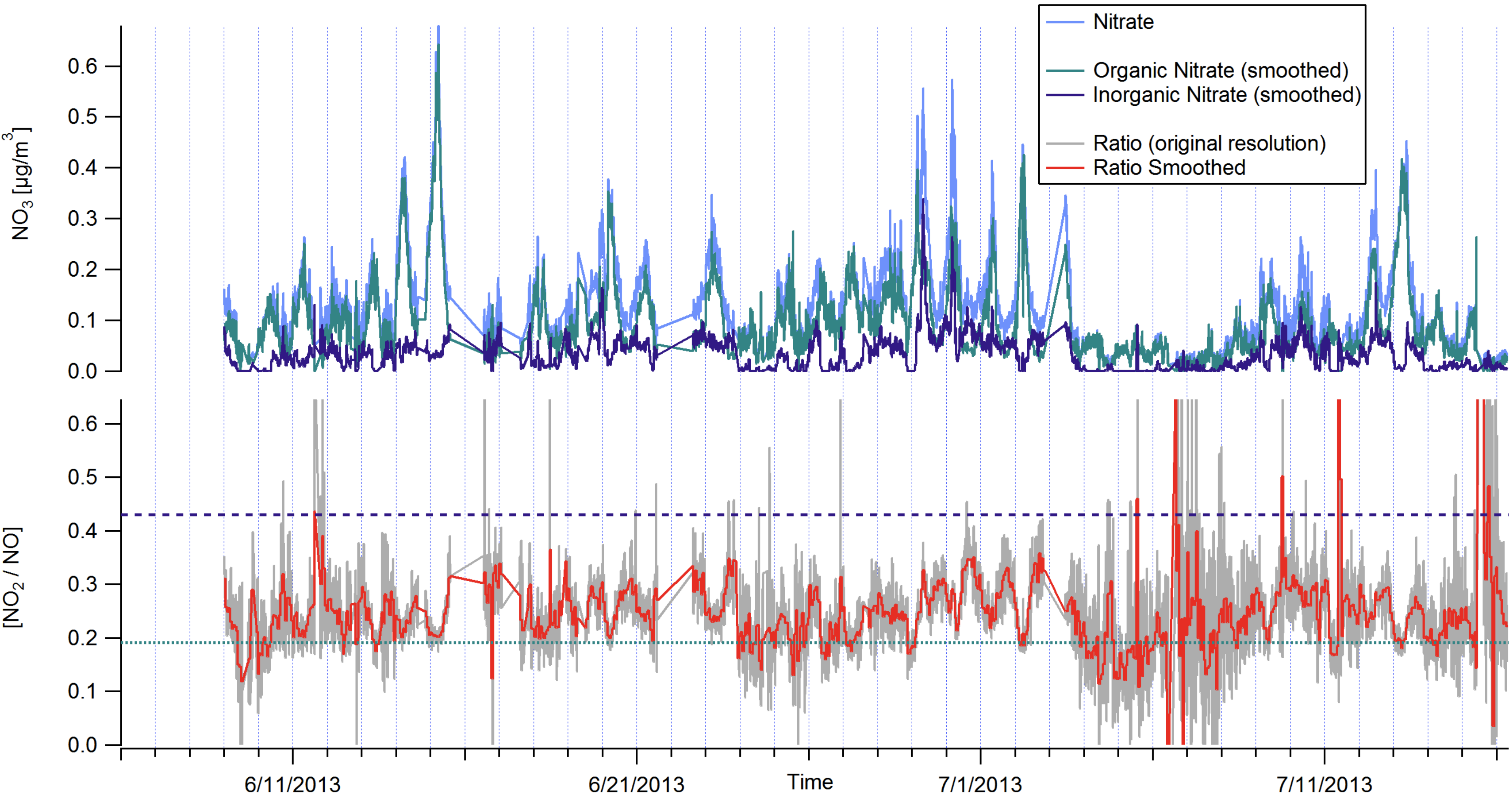
CIMS nitrate data courtesy Joel Thornton group, University of Washington

Majority of $PM_{2.5}$ organic nitrate is in the aerosol phase



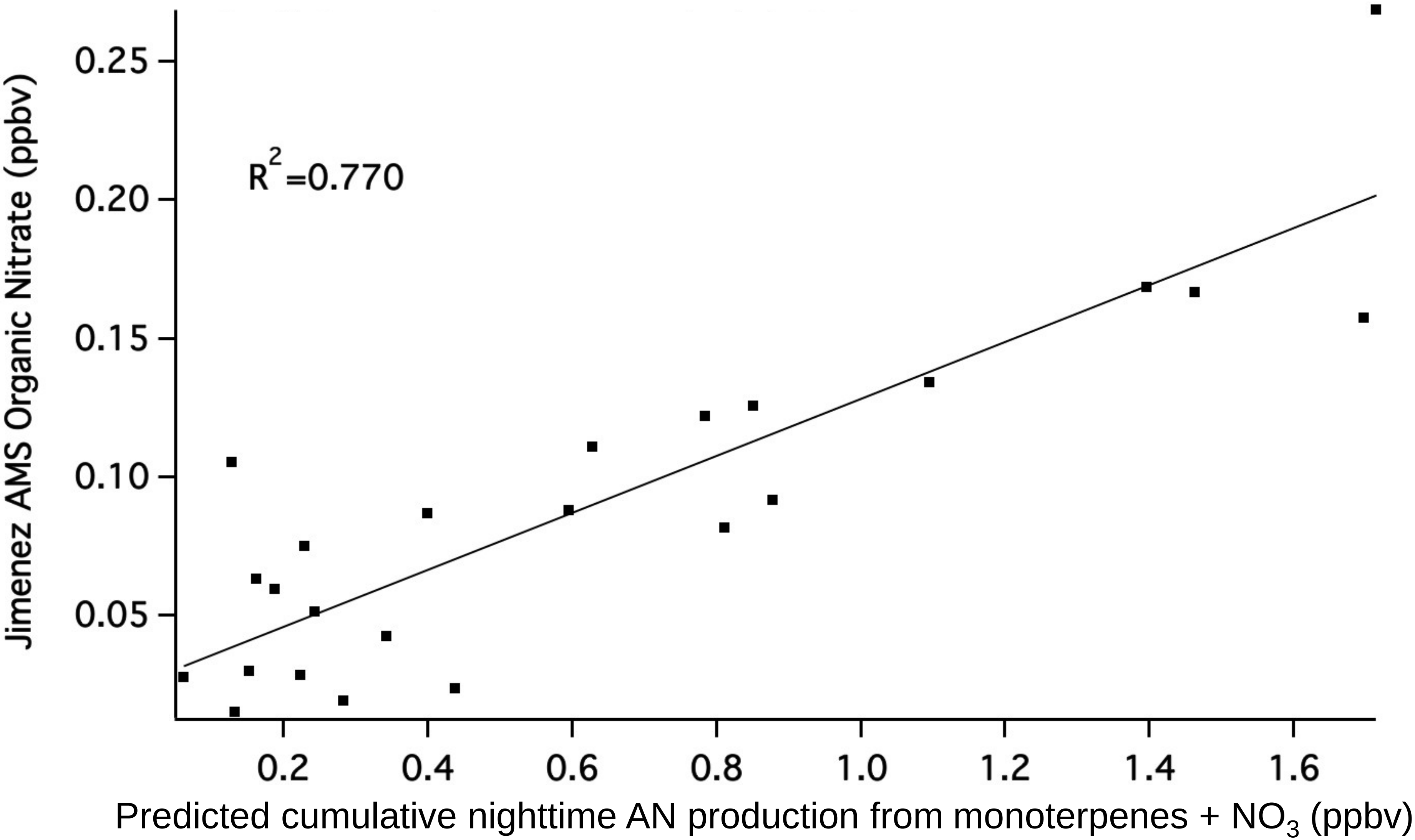
Total ΣANs data courtesy Ron Cohen group, UC Berkeley

Almost all (~85%) AMS-observed (≈PM_1) nitrate is organic nitrate at SOAS

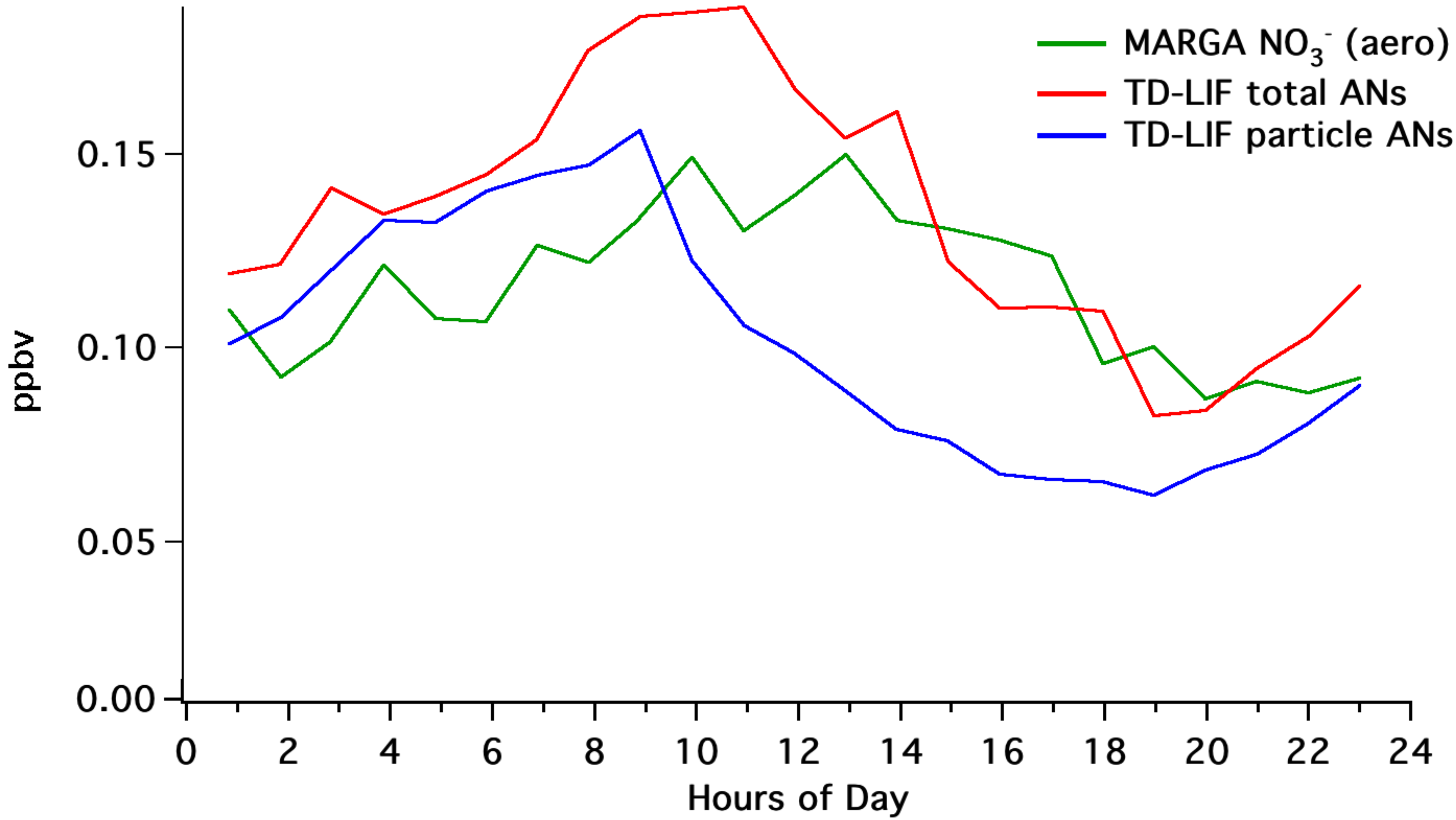


AMS data courtesy Jose Jimenez group, UC Boulder

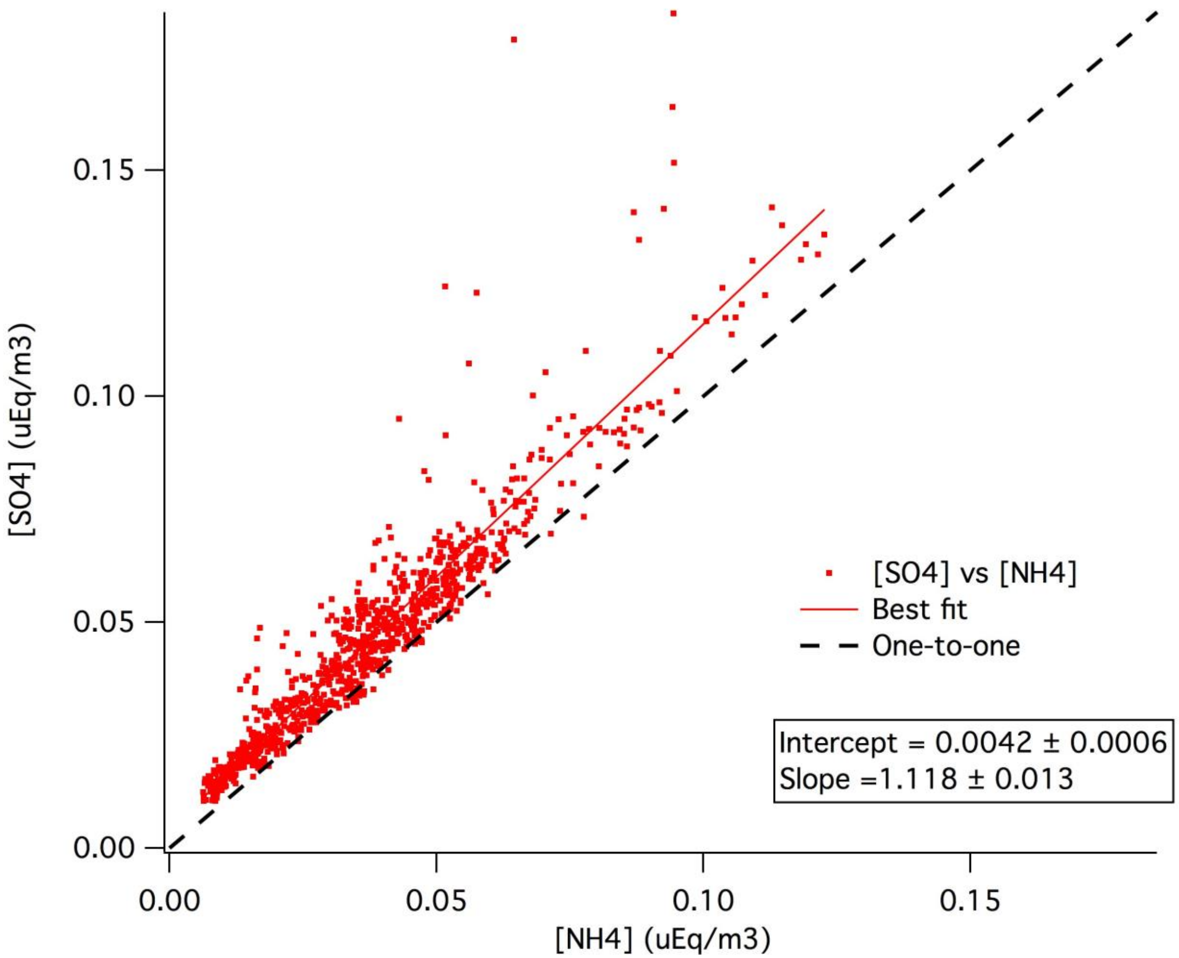
… and is also well-predicted by NO_3 chemistry



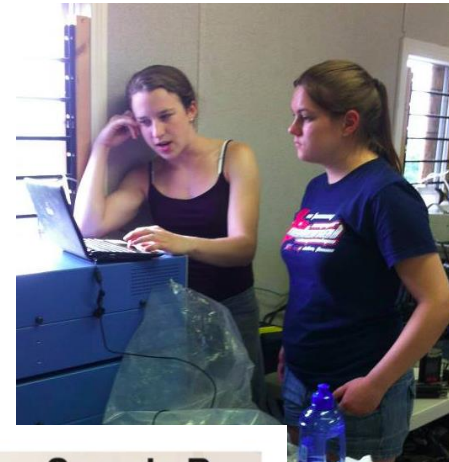
BUT, when we look at the $PM_{2.5}$ aerosol composition, there's often as much <u>inorganic</u> as <u>organic</u> nitrate!



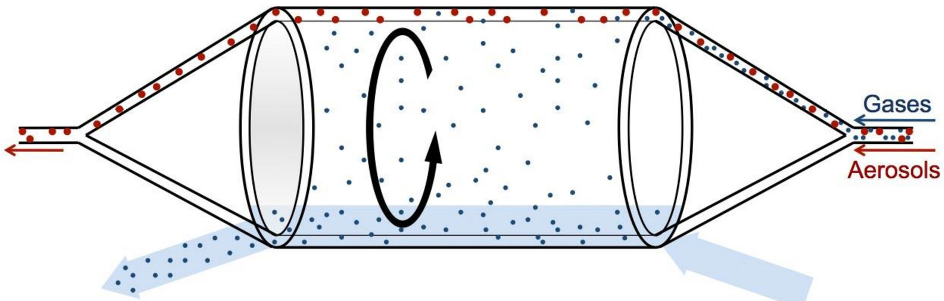
… despite the fact that aerosol is universally acidic!

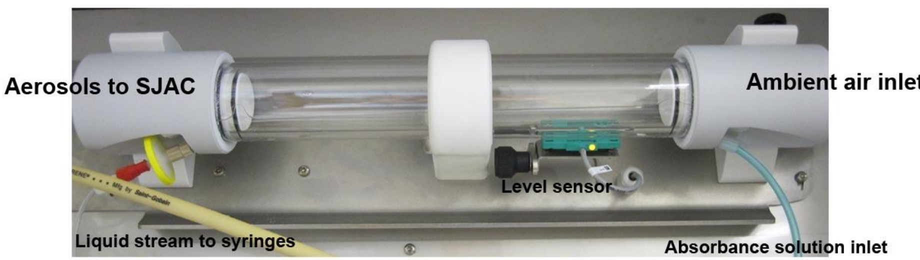


Inorganic aerosol composition was measured by a MARGA: Monitor for AeRosols and Gases (Metrohm Applikon)

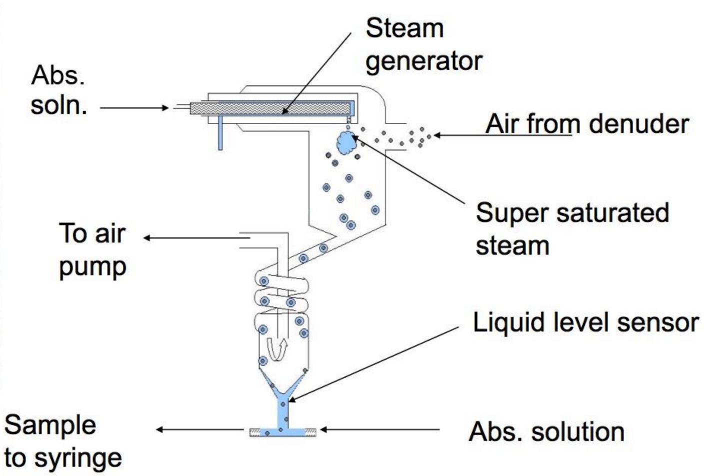


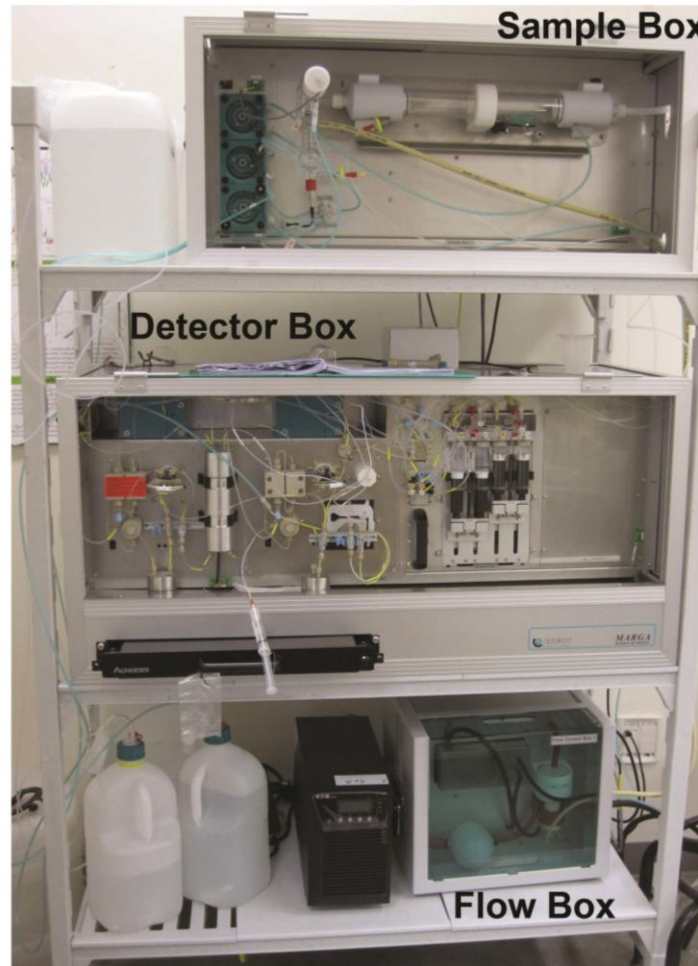
GAS collection:



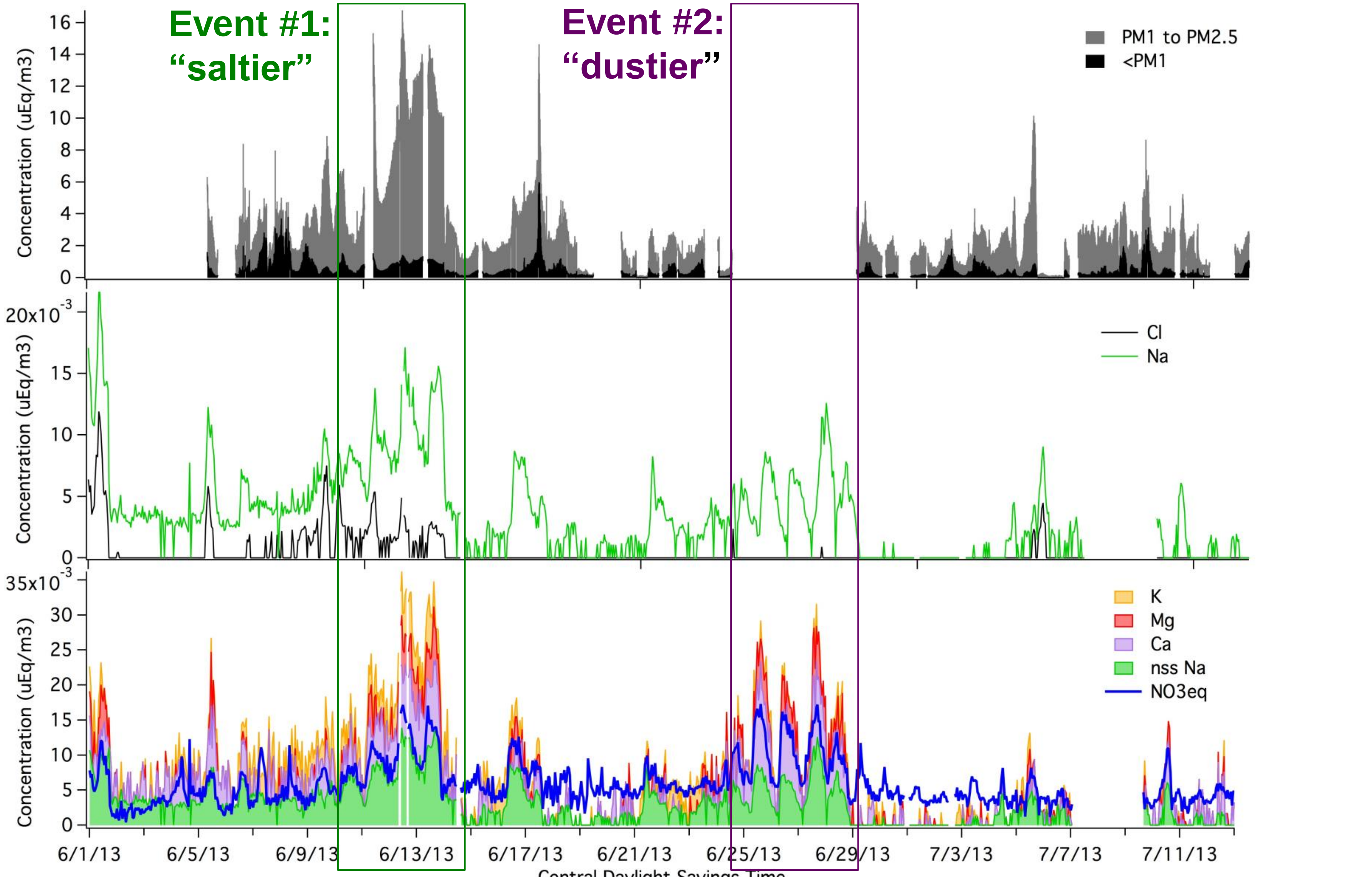


AERO collection:



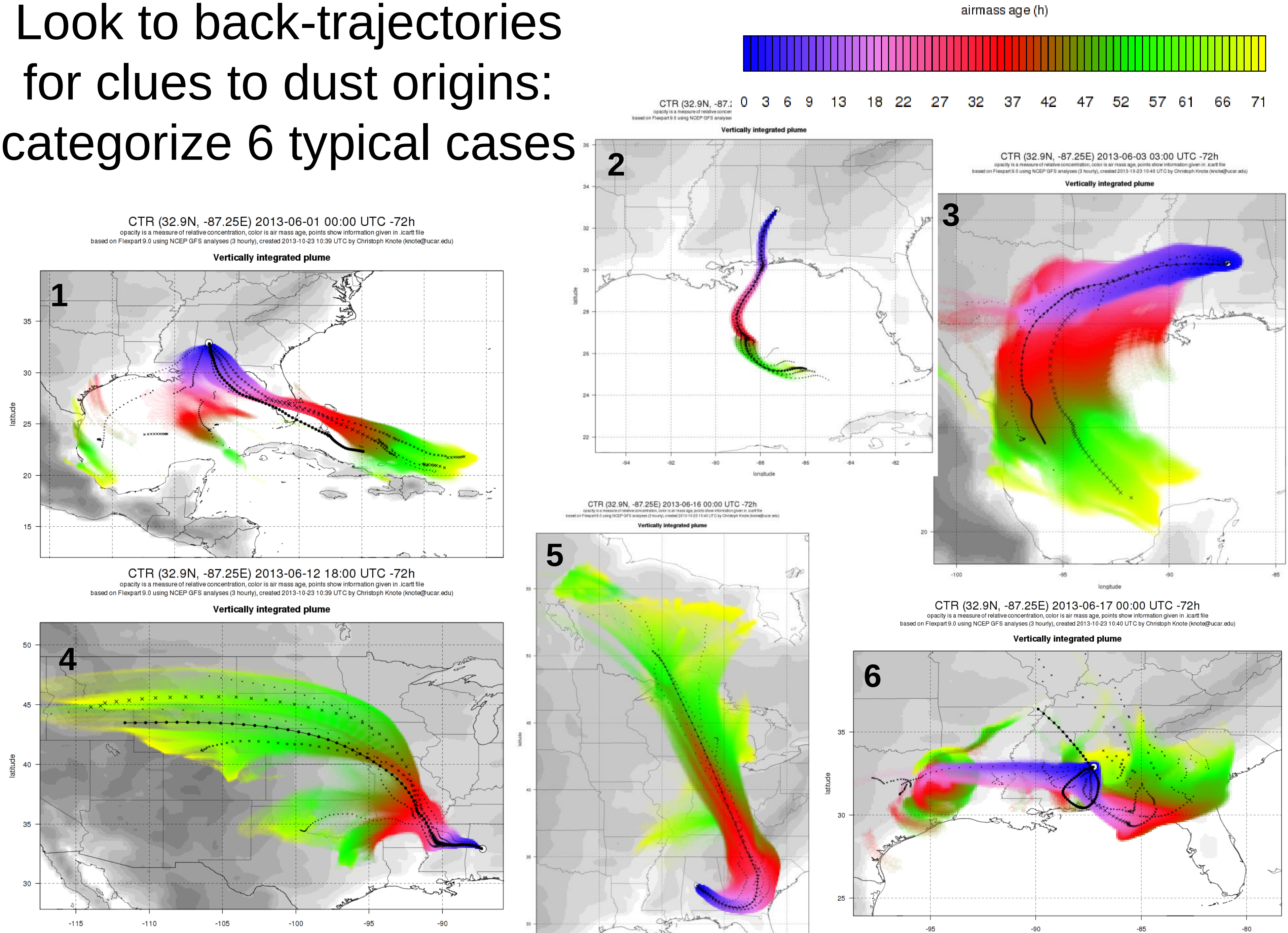


Aerosol inorganic composition shows two clear mineral nitrate events: 6/12-6/14, and 6/25-6/28



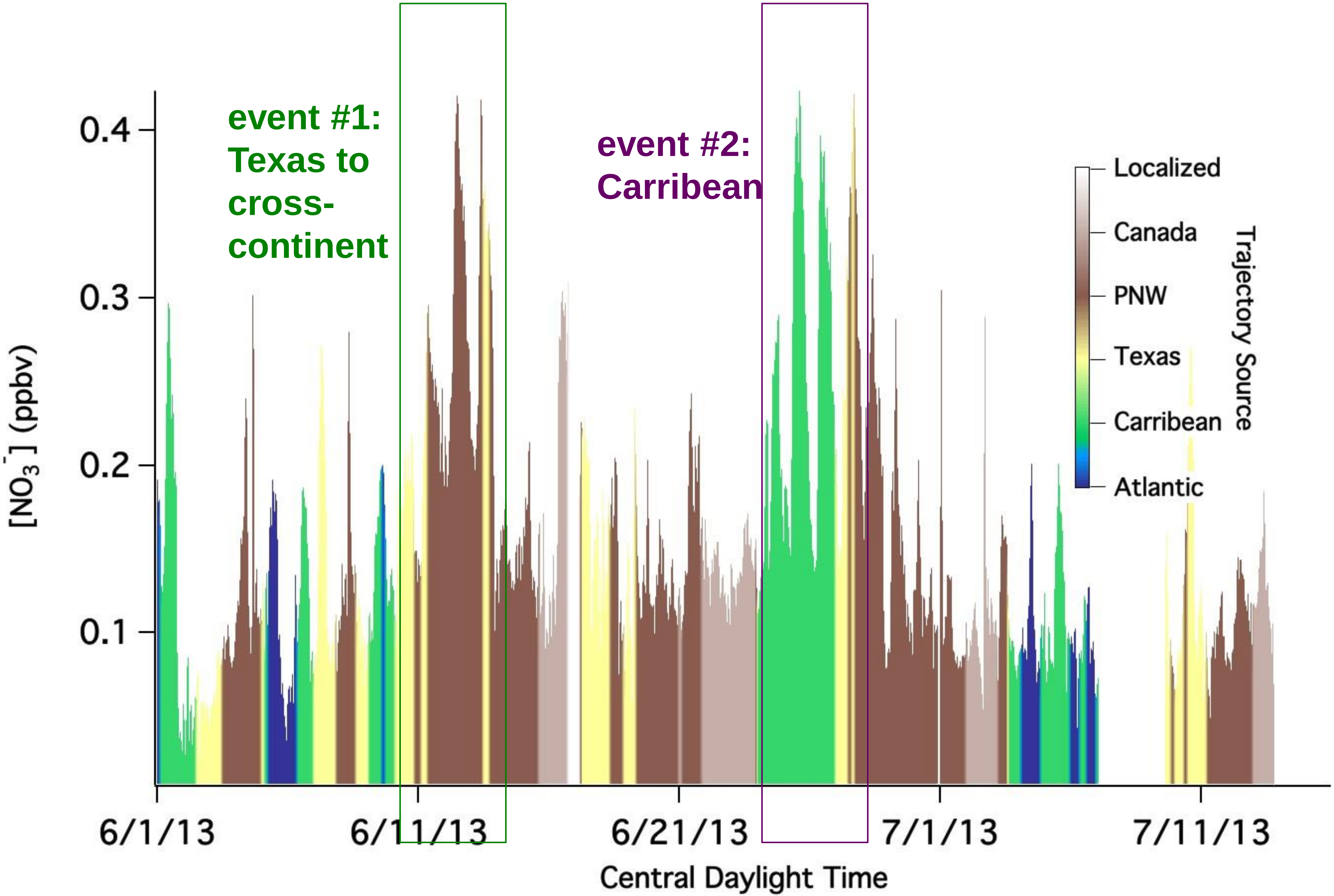
Surface area data courtesy Satoshi Takehama group, EPFL

Look to back-trajectories for clues to dust origins: categorize 6 typical cases

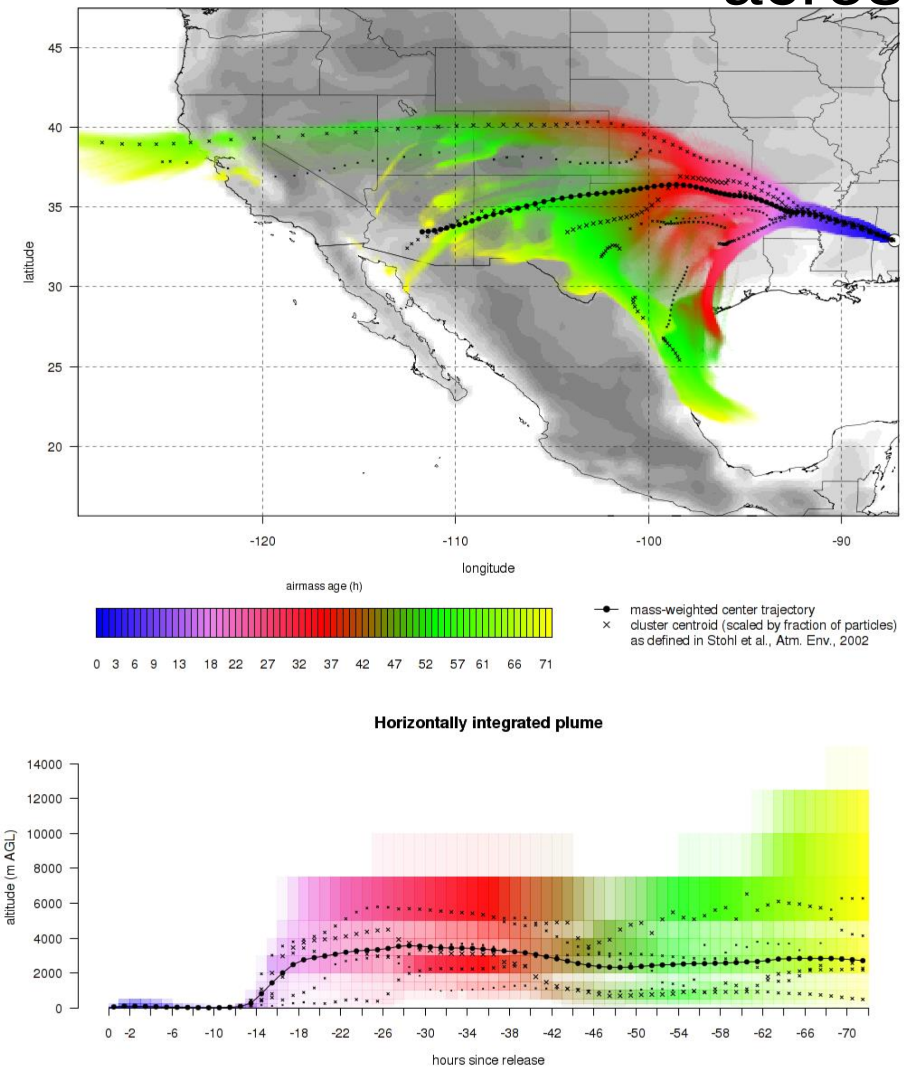


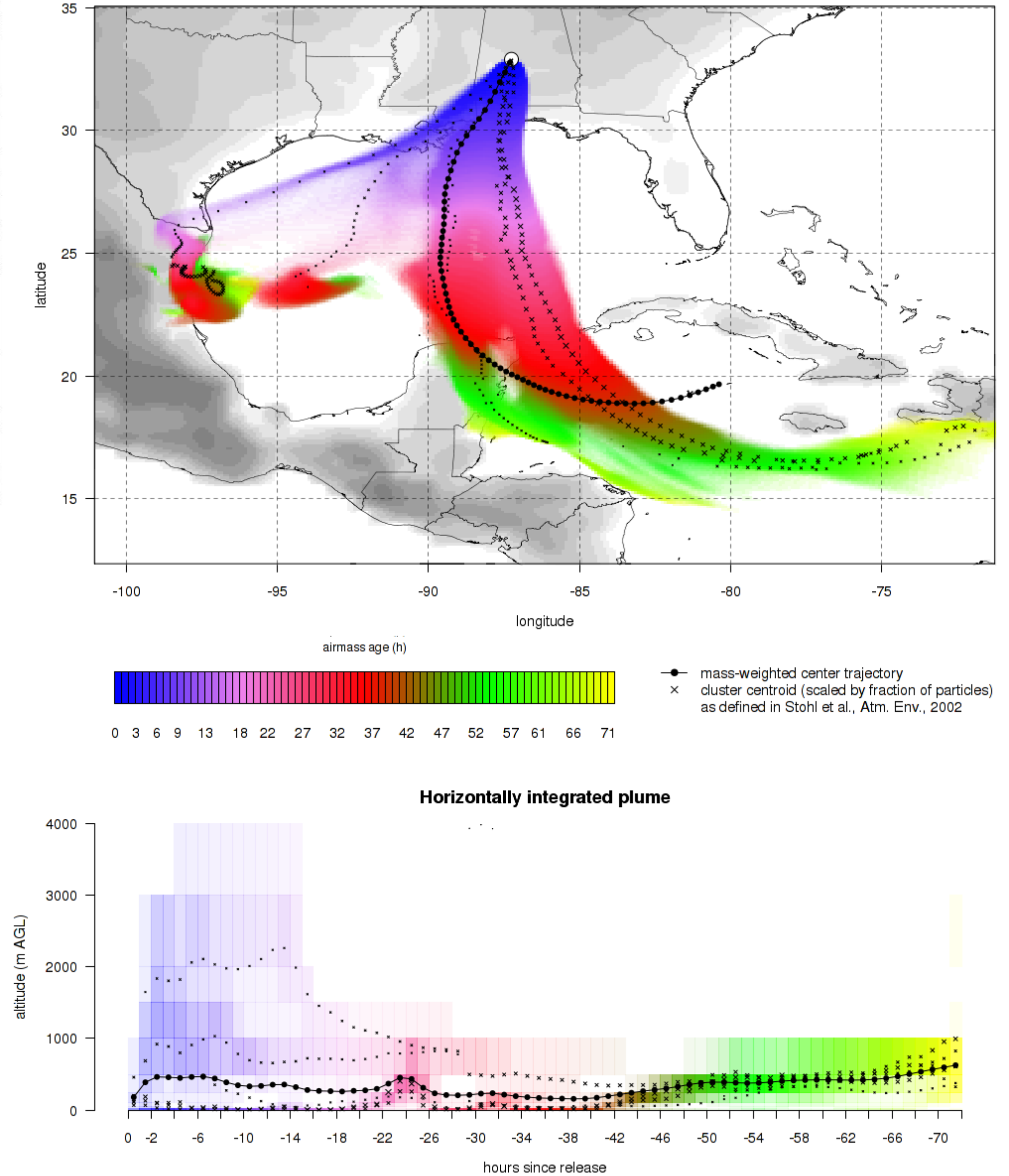
Back-trajectory data courtesy Christoph Knote, NCAR

Classification of dust source regions



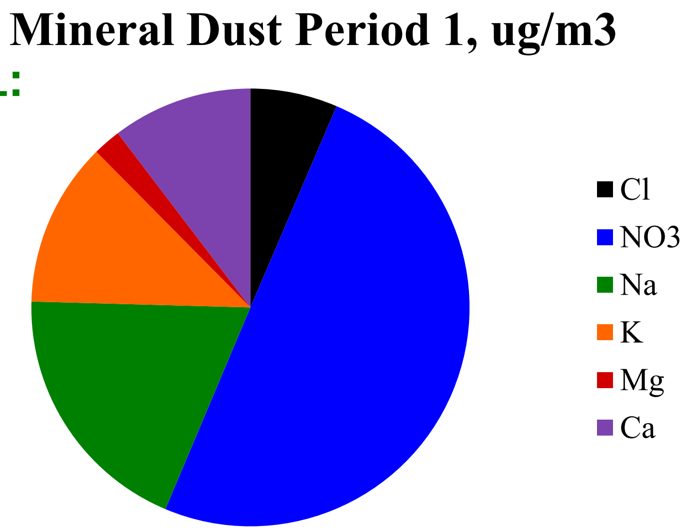
Cross-continent (PNW) trajectories (case 4) descend from aloft; Texas & Caribbean (cases 2&3) come low across the Gulf



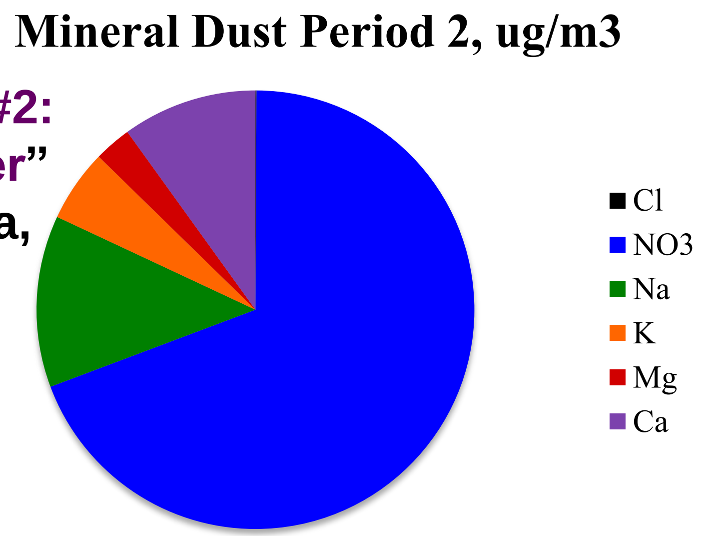


Aerosol inorganic composition shows two clear mineral nitrate events: 6/12-6/14, and 6/25-6/28

Event #1: "saltier"
Na>Ca; more Cl



Event #2: "dustier"
Ca ~ Na, no Cl



Can we use cation ratios to ID dust source?

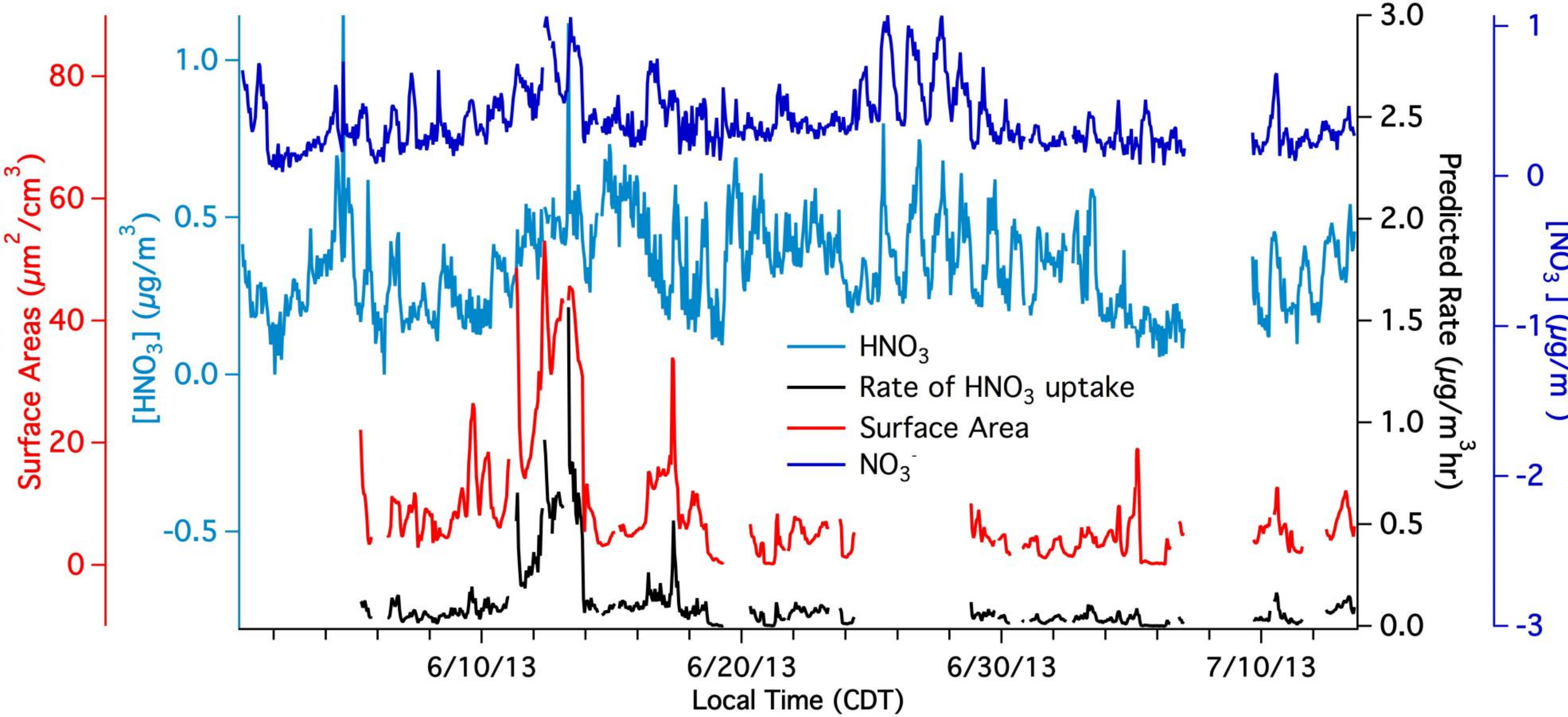
Ca/K: 0.9

Ca/K: 1.9

reference Ca/K's:
Saharan: 3-6
Saudi: 1
China: 40
central Asia: 3
southwestern U.S.: 3
sedimentary rocks: 2

Krueger et al. Atmospheric Environment 38 (2004): 6253-6261; Usher et al, Chem. Rev. 2003, 103, 4883-4939

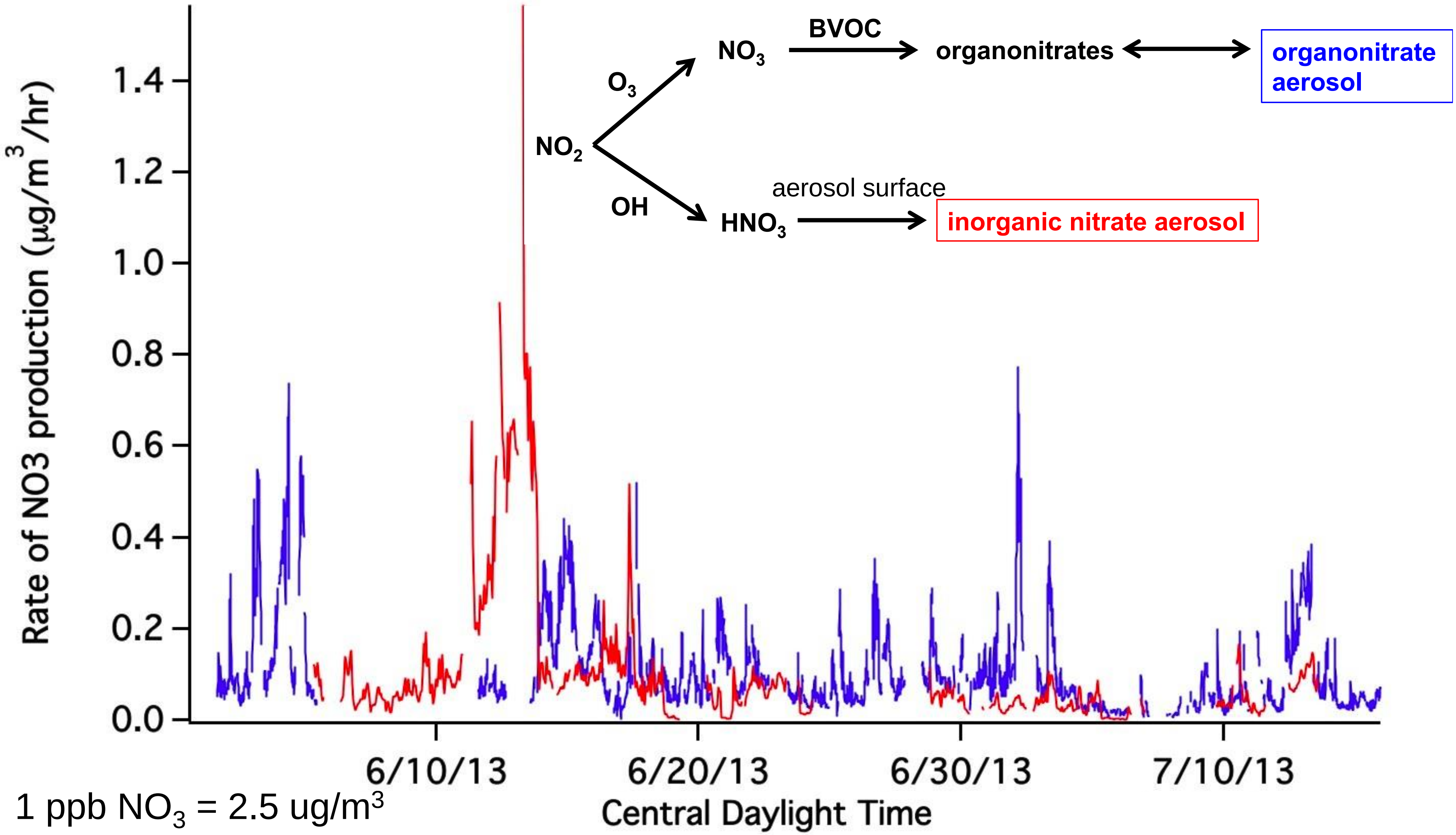
Hypothesis based on high mineral nitrate concentrations: Uptake of HNO_3 onto dust produces coarse-mode inorganic nitrate.



estimated rate based on γ = 0.1

Usher et al., Chem. Rev., 2003, 103, 4883-4939

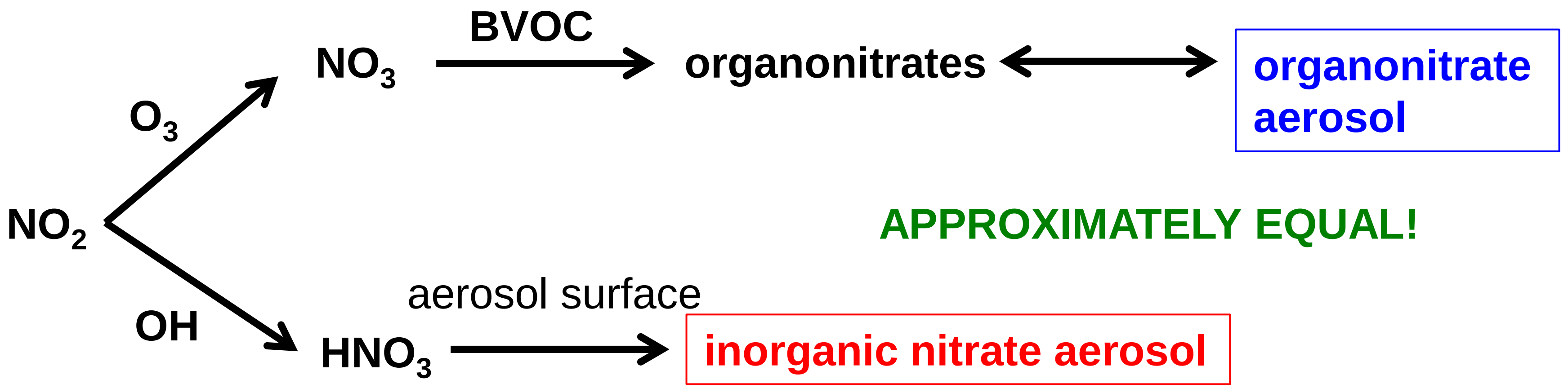
Relative rates of competing NO_2 loss pathways



1 ppb NO_3 = 2.5 ug/m^3

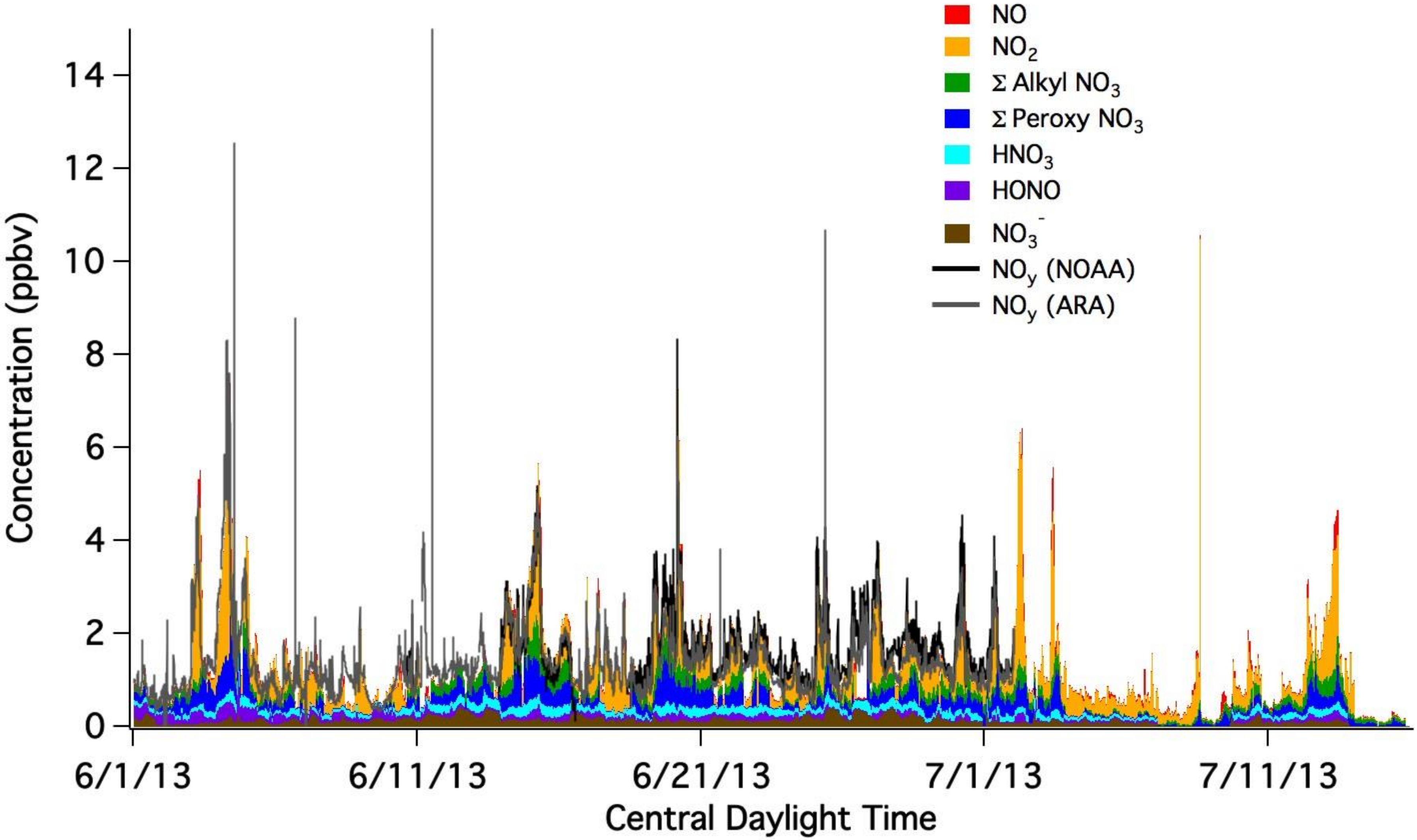
Conclusions

- We're measuring ~ all of NOy
- Surface concentrations of organic/inorganic nitrate aerosol are comparable on average (organic is mostly < PM1, inorganic is mostly >PM_1)
- Campaign avg rate of organonitrate formation: 0.25 ppb hr^{-1}, max 2 ppb hr^{-1} ; mostly NO_3+monoterps
- Campaign avg rate of inorganic nitrate formation: 0.25 ppb hr^{-1}, max 3.8 ppb hr^{-1}; mostly dust events



Thank you!

NOy: closure among instruments



NOy species data courtesy Karsten Baumann, ARA

NOy: closure among instruments