Quantification of Secondary Pollutant Formation Metrics in Southeastern New Hampshire (A51E-0730)

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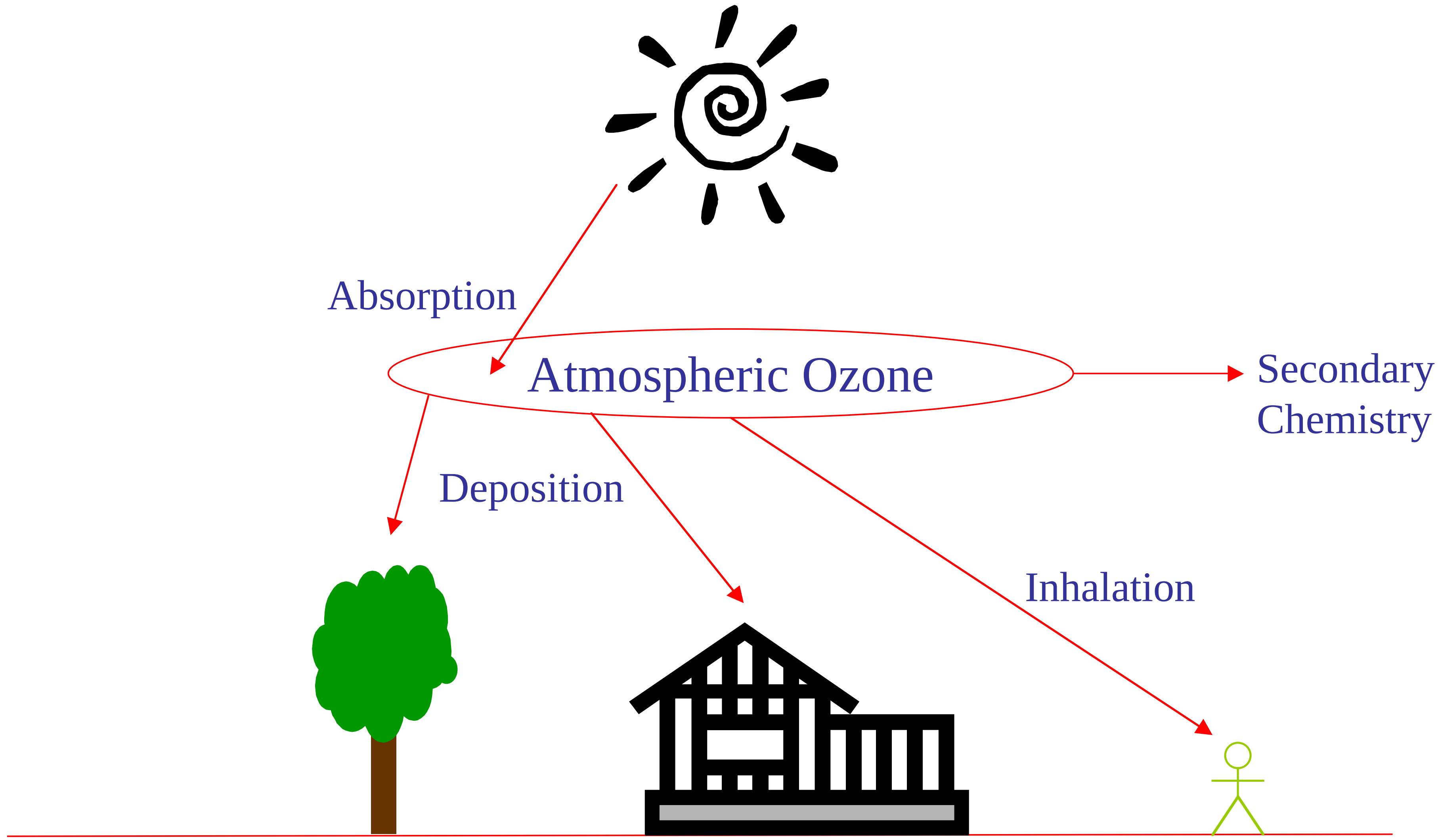
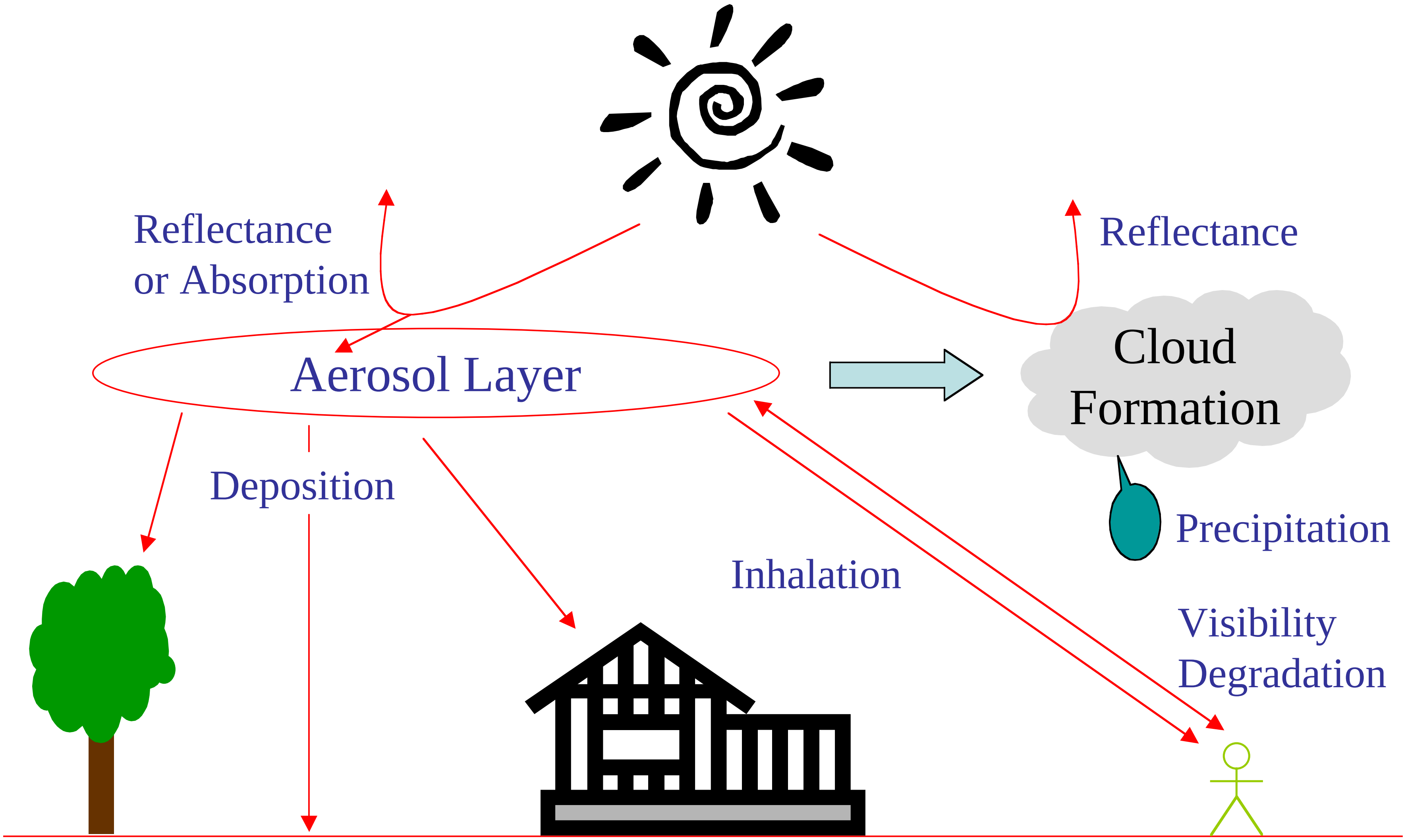
University of New Hampshire   AIRMAP   NOAA

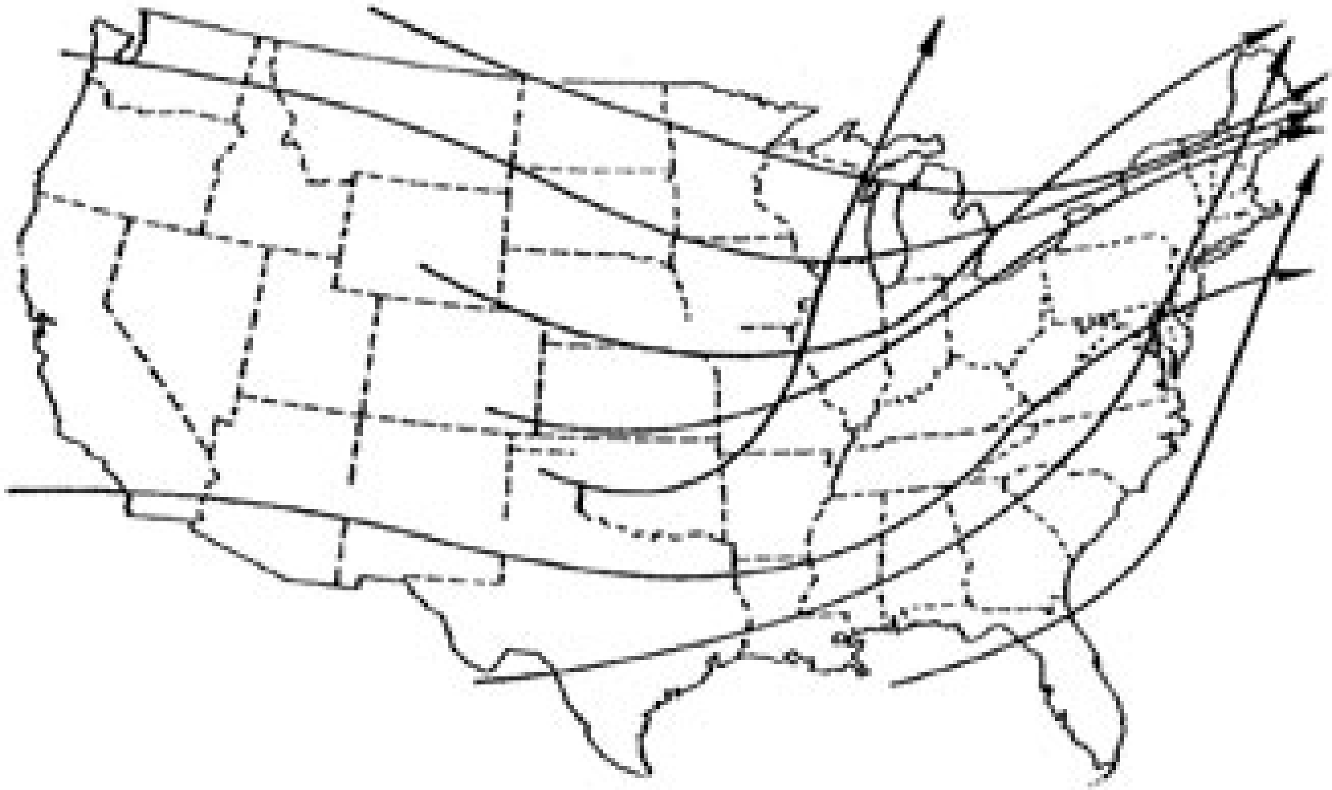
Why Do We Care About Ozone?



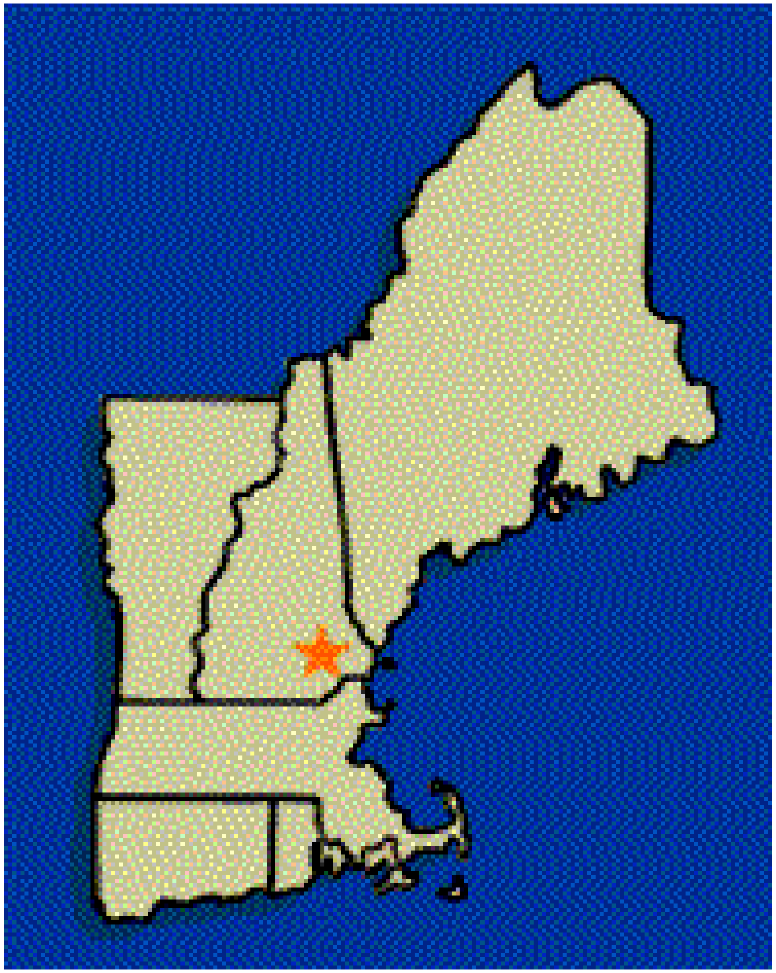
Effects of Tropospheric Aerosols



The Tailpipe of the United States



AIRMAP Thompson Farm Sampling Site



Relevant Data Collected

Particle data (24-hour resolution):

Particle composition (Filters)

Gas-phase data (all 1-minute resolution except *):

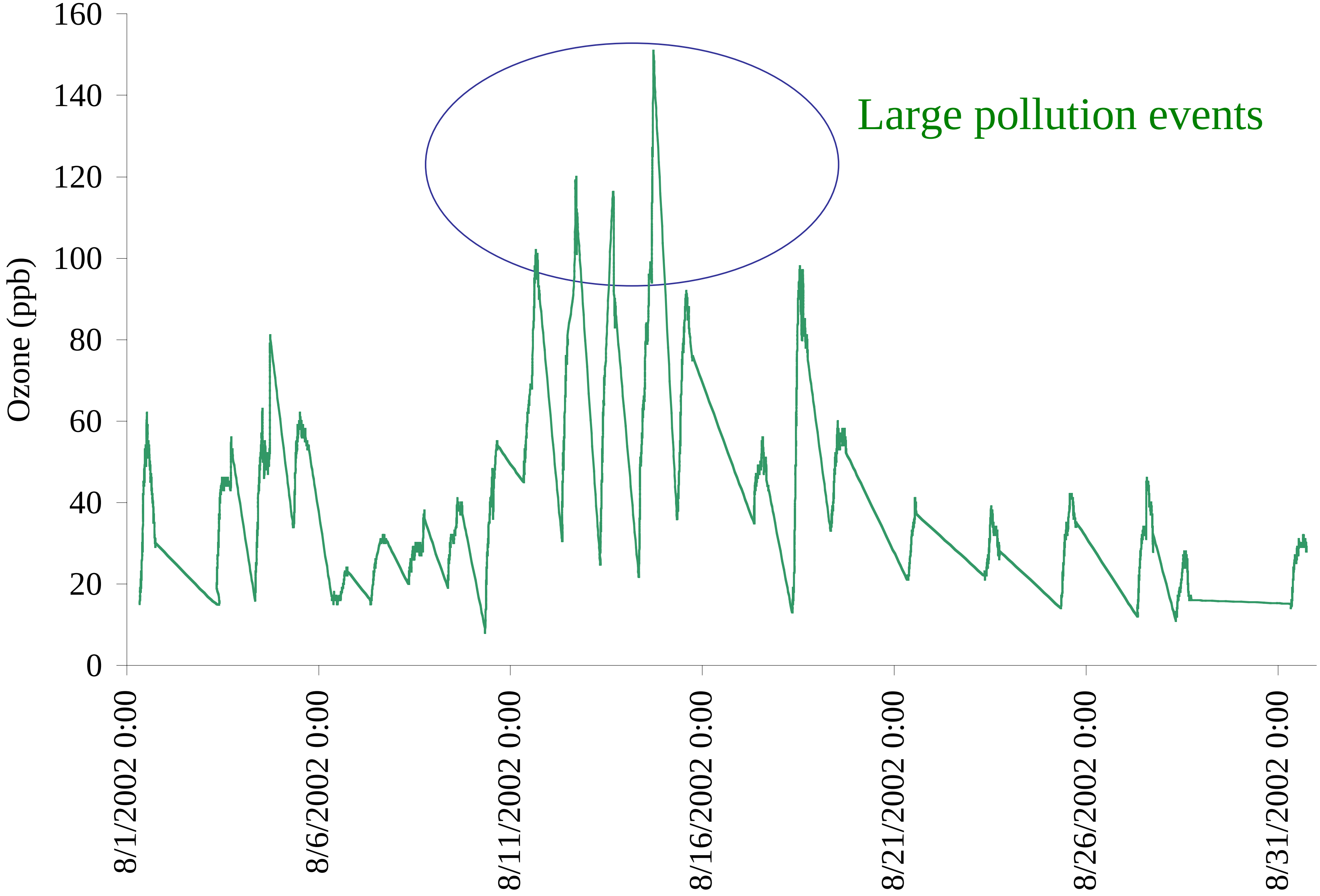
CO (IR Spectroscopy), NO and NO_y (Chemiluminescence), O_3 (UV Spectroscopy), SO_2 (Pulsed Fluorescence); C_2-C_{10} Organics (*Hourly 10-minute averages, Gas Chromatography)

Other data (1-minute resolution):

j_{NO2} (Filter Radiometry)

Meteorological parameters

Example Data: Ozone



Data Reduction

- Data are considered only for August 2002 during the New England Air Quality Study
- Data are not considered from 6PM through 8AM due to lack of strong solar radiation
- Data are ignored if any of the monitors were zeroing, calibrating, or reading values below the detection limit
- Data are removed when the photostationary state was not expected to/did not hold
- Data are averaged to time-scale of VOC measurements (except for regressions)

Ozone Production Rate

- OPR1 = $k_{\mathrm{OH\text{-}CO}}[\mathrm{OH}][\mathrm{CO}] + \quad {}_{i}k_{i,\mathrm{OH}}Y_i[\mathrm{OH}][\mathrm{VOC}]_i$
  - Rate constants from literature as f(T)
  - *Y* estimated from expected VOC degradation pathways
  - Background levels were assumed for higher carbon number VOCs
  - [OH] estimated by a box-version of a gas-phase mechanism for atmospheric chemistry (CACM)
  - ppb hr^{-1}
- OPR2 = $2.0k_{\mathrm{NO\text{-}HO2}}[\mathrm{NO}][\mathrm{HO_2}]$
  - $[\mathrm{HO_2}]$ estimated by CACM

Ozone Production Efficiency

- Regression techniques (give average OPE)
  - O_3 versus NO_y-NO_x (slope = OPE, intercept = background O_3)
  - $[NO_2]$ from photostationary state
  - O_3 versus CO (corrected slope = OPE), gives poor correlation and unrealistic value
  - O_3 versus acetylene (corrected slope = OPE), gives poor correlation and unrealistic value
  - Dimensionless
- OPE = OPR/$L(NO_x)$ (gives temporal resolution)
  - $L(NO_x)$ (rate of loss of NO_x) assumed to be equivalent to the rate of nitric acid formation: $k_{OH\text{-}NO2}[OH][NO_2]$

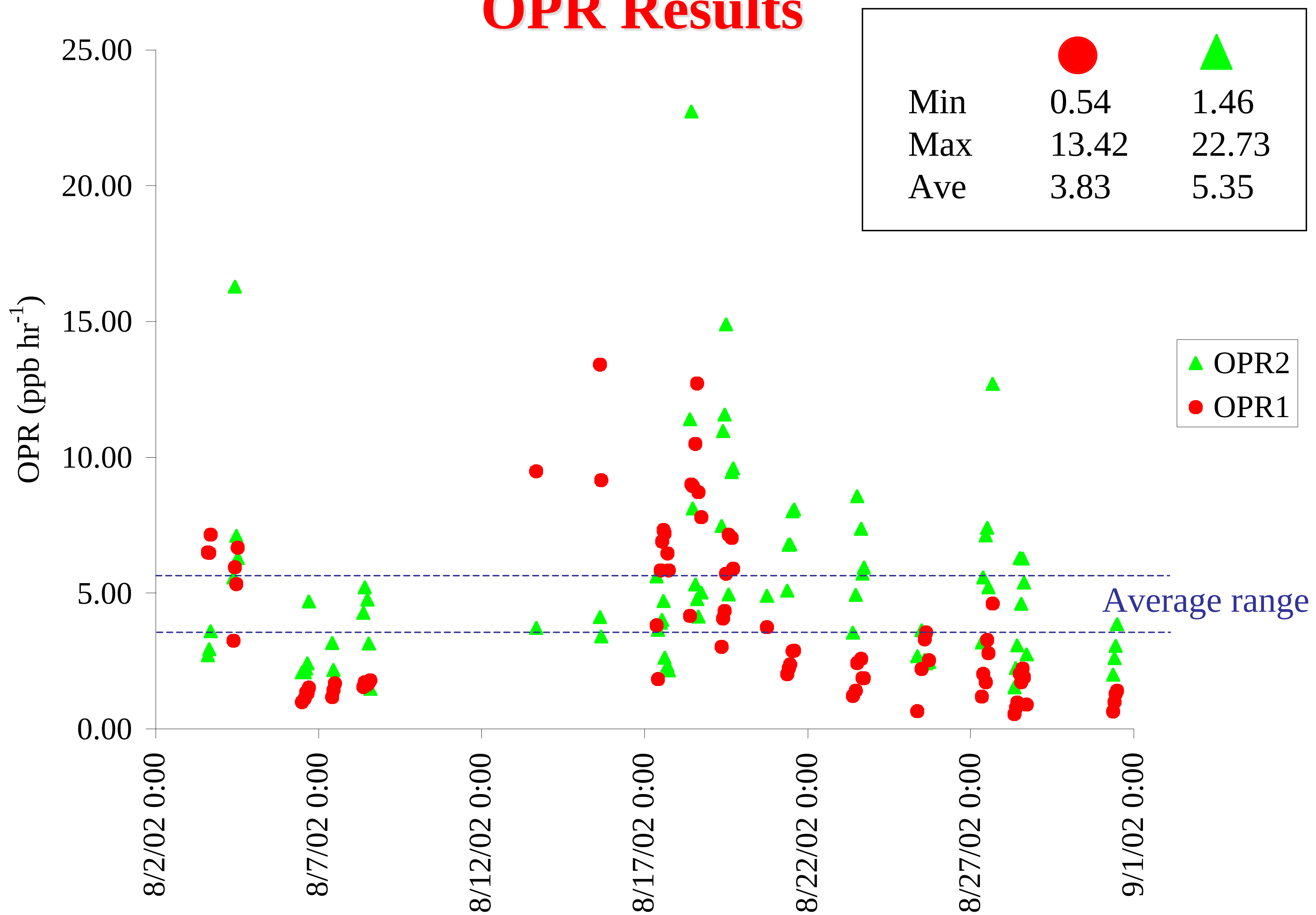
Reactivity

- $R_i = k_{i,\mathrm{OH}}[\mathrm{VOC}]_i$ (also applicable to CO)
  - $R1 = \quad {}_i\, R_i$
  - Equivalent to OPR1/[OH] if $Y \sim 1$ for all VOCs (very close)
  - s^{-1}
- $R2$ = OPR2/[OH]
  - Assumes that $Y \sim 1$ for all VOCs

CACM Overview

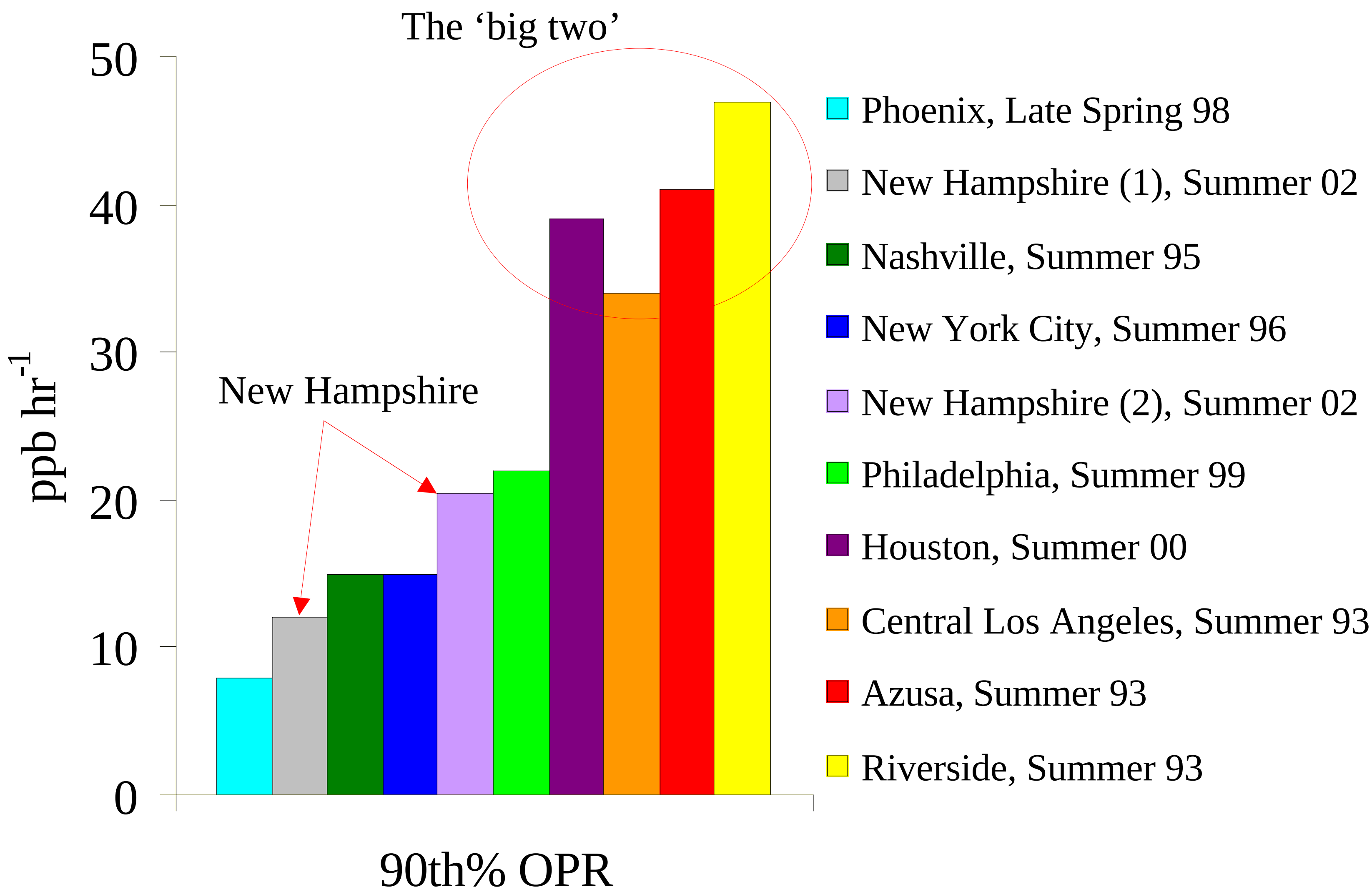
- Total of 361 reactions considered
- Total number of species for which kinetic expressions are solved: 123
- Total number of species for which the pseudo-steady state approximation is made: 68
- Parent VOCs lumped according to structure, functionality, reactivity, and experimental SOA-forming potential

OPR Results



Min 0.54 1.46
Max 13.42 22.73
Ave 3.83 5.35
OPR (ppb hr-1)
25.00
20.00
15.00
10.00
5.00
0.00
OPR2
OPR1
Average range
8/2/02 0:00
8/7/02 0:00
8/12/02 0:00
8/17/02 0:00
8/22/02 0:00
8/27/02 0:00
9/1/02 0:00

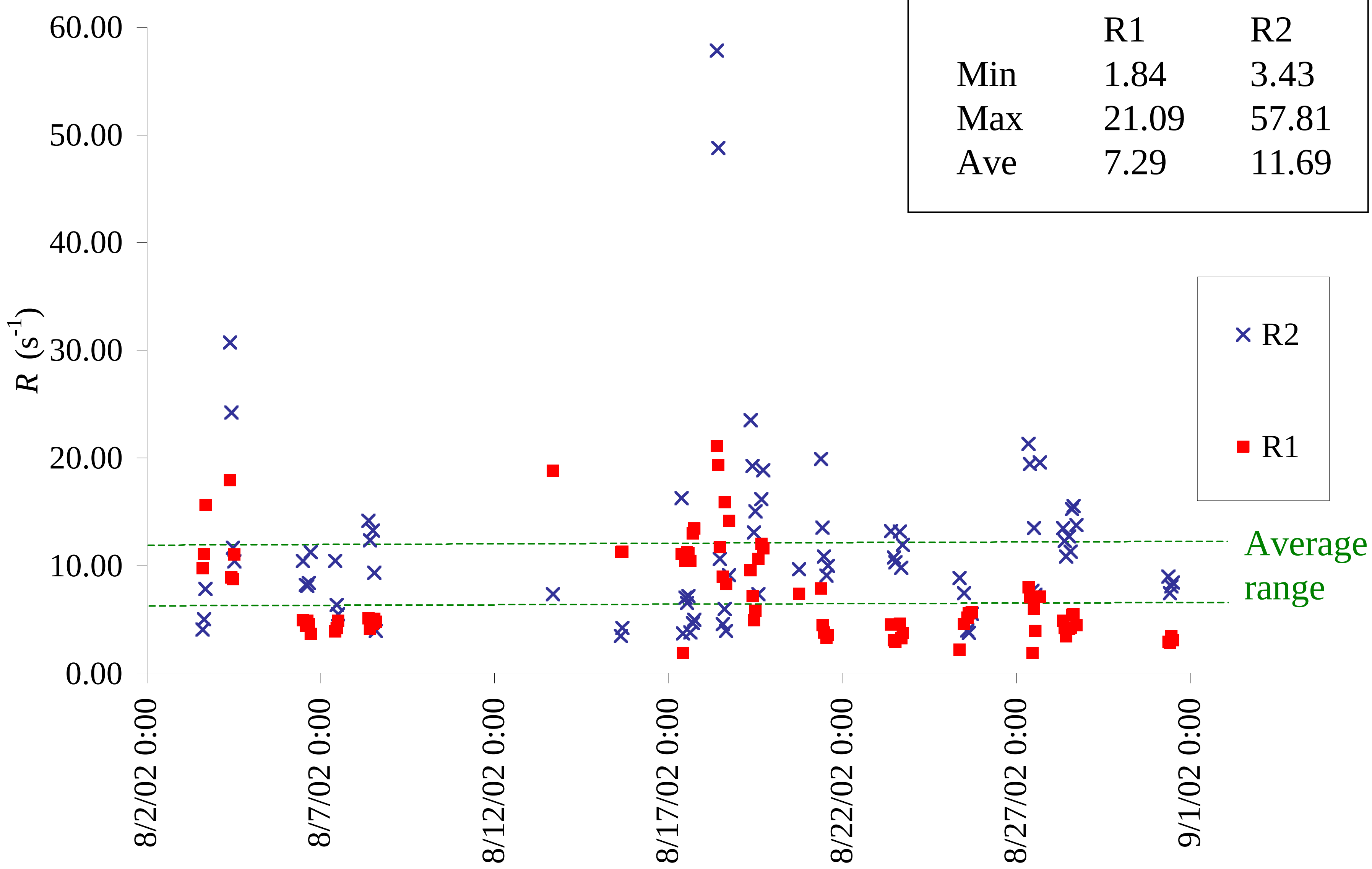
OPR Comparisons



Caveat: Many of the other studies give elevated or vertically averaged values that tend to be lower than surface values

Reactivity Results

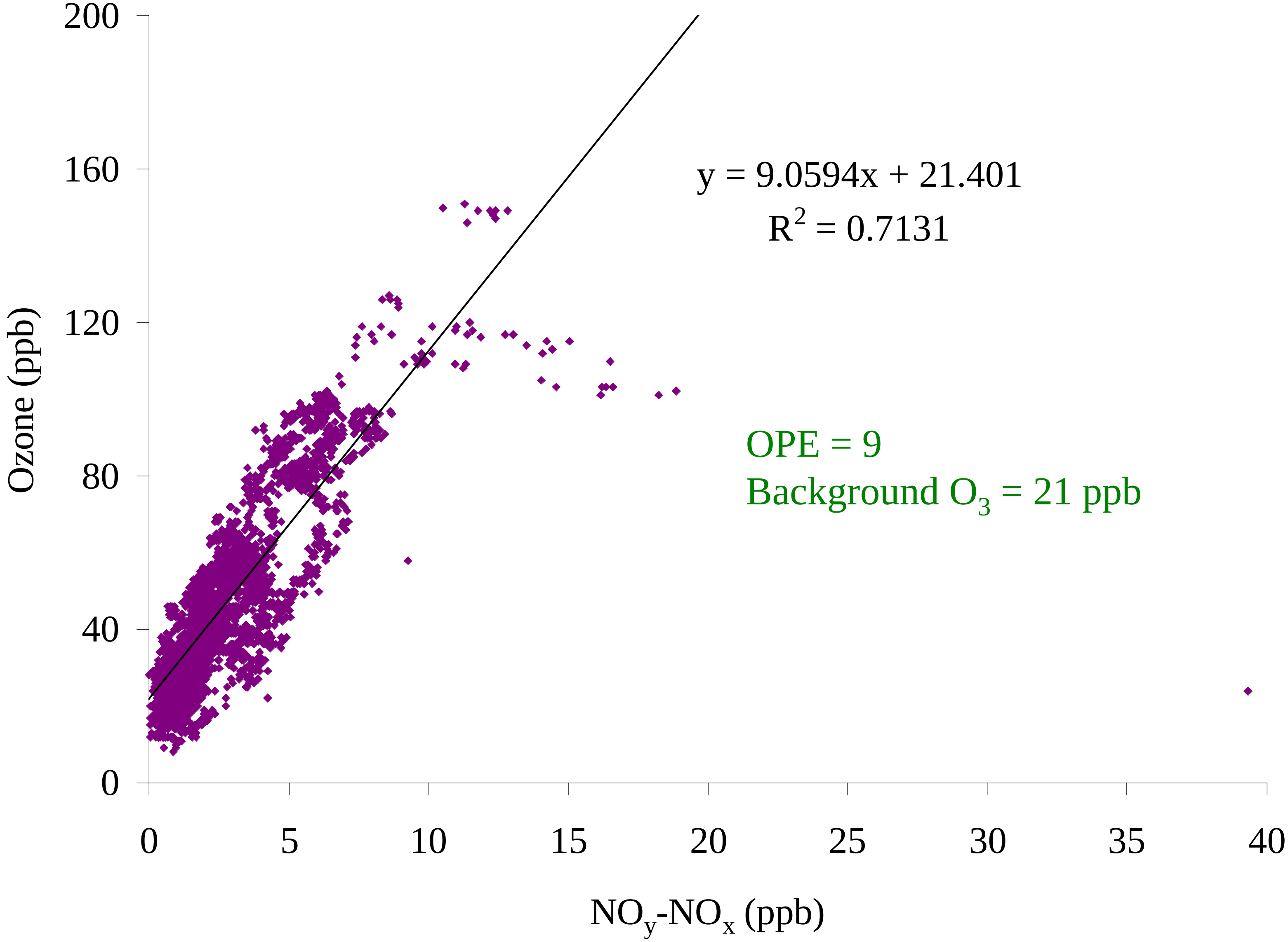
	R1	R2
Min	1.84	3.43
Max	21.09	57.81
Ave	7.29	11.69



Reactivity Comparisons

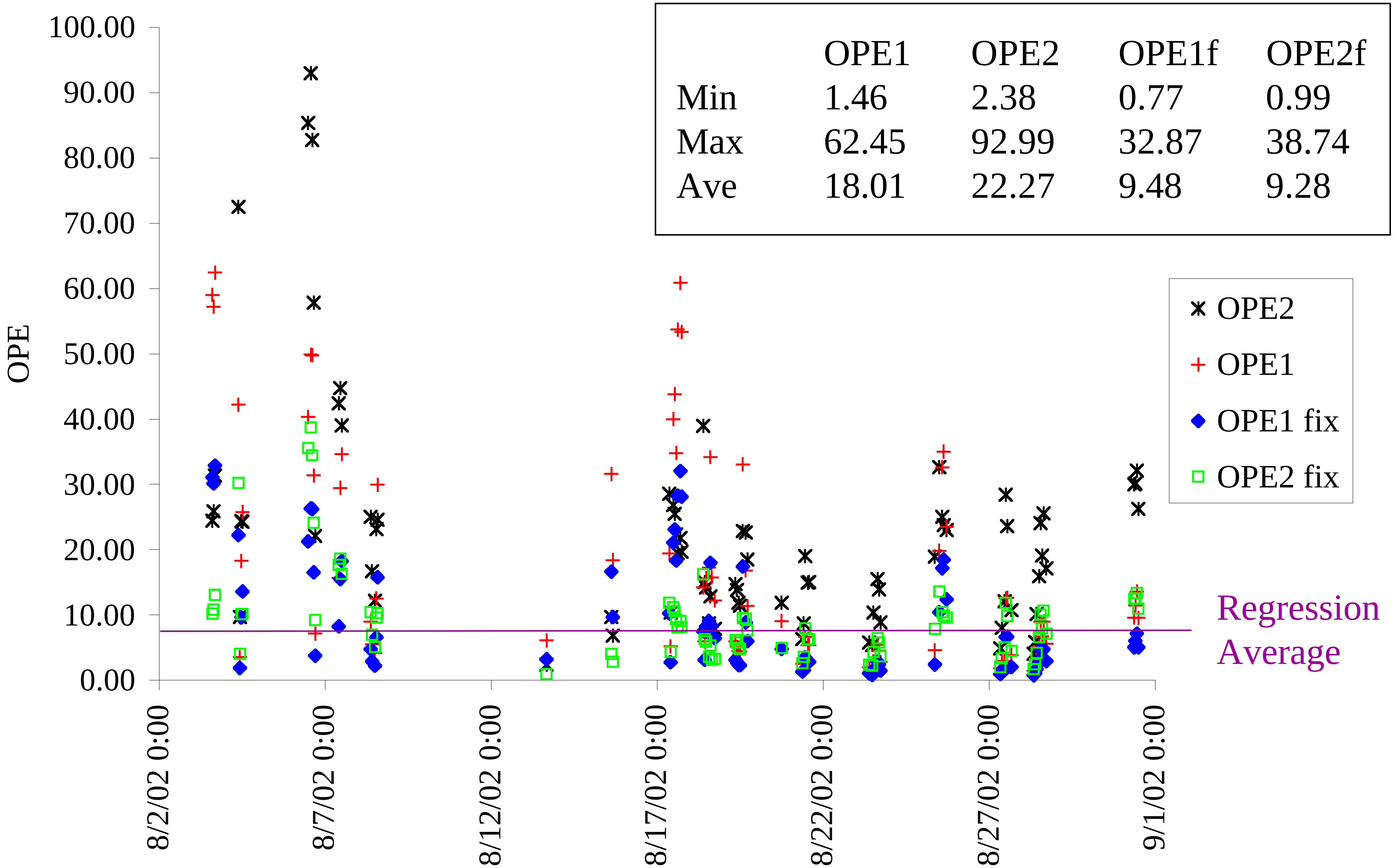
- Overall reactivities in New Hampshire are very low compared to those in these other locations
- In Nashville and NYC, biogenic > anthropogenic (as in New Hampshire)
- In Philadelphia, biogenic ~ anthropogenic
- In Phoenix, anthropogenic > biogenic
- In the SoCAB and Houston, anthropogenic >> biogenic

Average OPE



y = 9.0594x + 21.401
R2 = 0.7131
OPE = 9
Background O3 = 21 ppb
Ozone (ppb)
NOy-NOx (ppb)
0
40
80
120
160
200
0
5
10
15
20
25
30
35
40

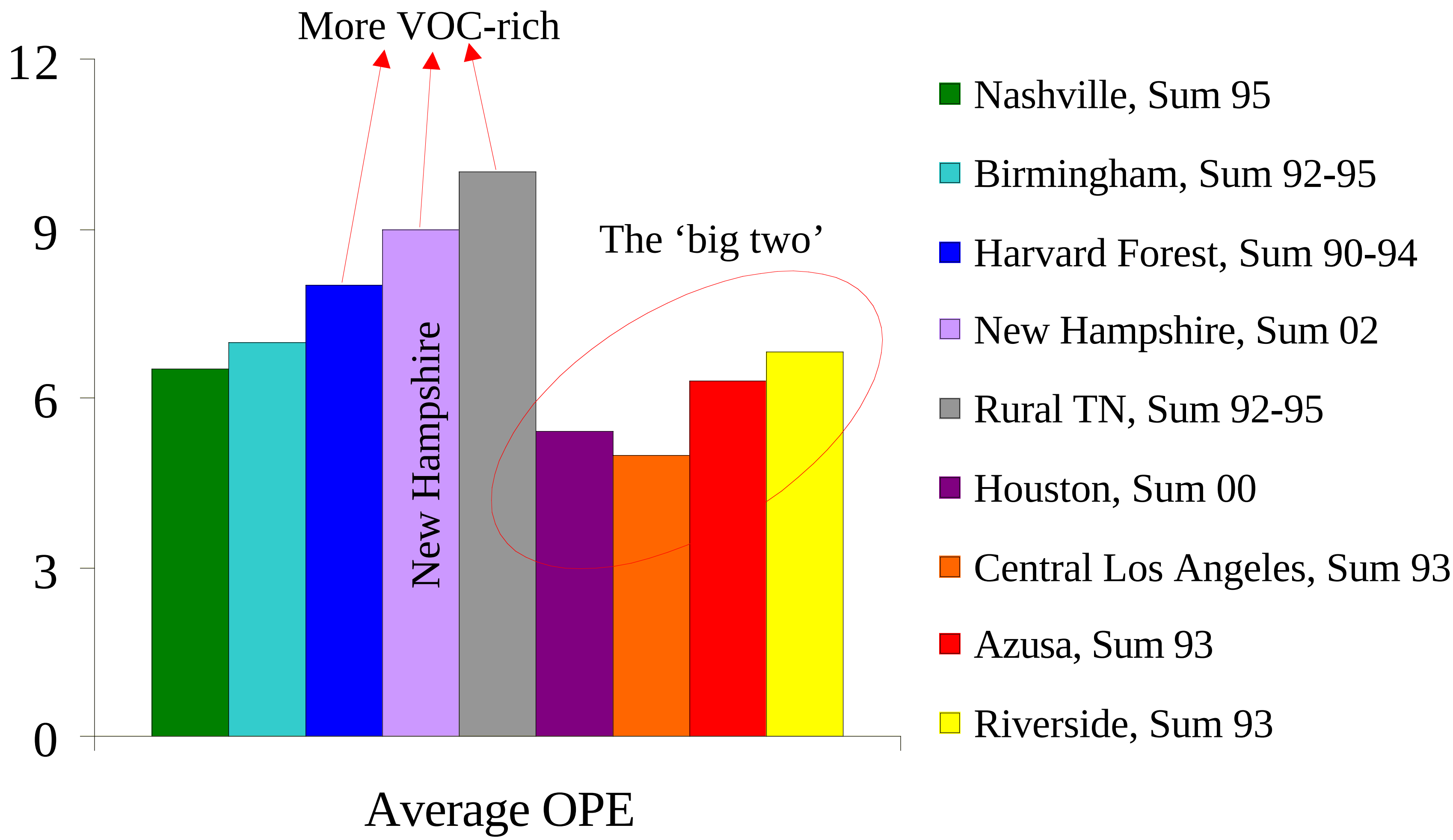
Temporal OPE



	OPE1	OPE2	OPE1f	OPE2f
Min	1.46	2.38	0.77	0.99
Max	62.45	92.99	32.87	38.74
Ave	18.01	22.27	9.48	9.28

Fix: $L(NO_x)$ increased (~x2) so that average OPE was < 9.5

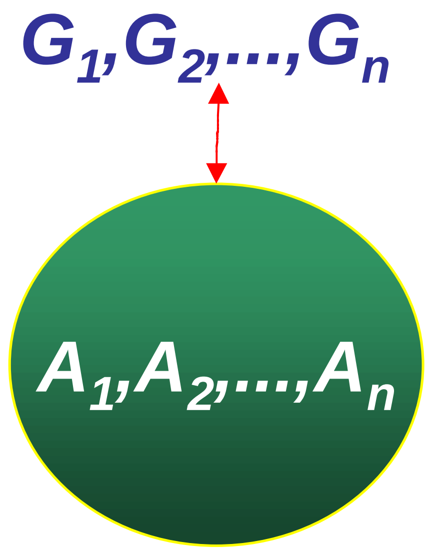
OPE Comparisons



Highest OPEs in less polluted environments

Formation of SOA

VOC + ox → $P_1, P_2, \ldots P_n$



Here, we apply the equivalent of the principle of OPR to estimate SOA production rate

Implications: Visibility reduction, health effects, climate change (direct and indirect effects), etc.

Calculation Methods

CACM Measurements CACM

$$\mathrm{ROG}_i = [\mathrm{ROG}_i]_{t_1}\left(1 \quad \exp\left(\quad \left(k_{\mathrm{OH},i}[\mathrm{OH}] + k_{\mathrm{O_3},i}[\mathrm{O_3}] + k_{\mathrm{NO_3},i}[\mathrm{NO_3}]\right)\left(t_2 \quad t_1\right)\right)\right)$$

Hydrocarbon measurements

Literature values as f(T)

Hydrocarbon measurements

$$Y_i = \frac{\mathrm{SOA}_i}{\mathrm{ROG}_i} = \mathrm{OM} \; _j \; \frac{\text{á}_{ij} K_{ij}}{1 + \mathrm{OM}K_{ij}}$$

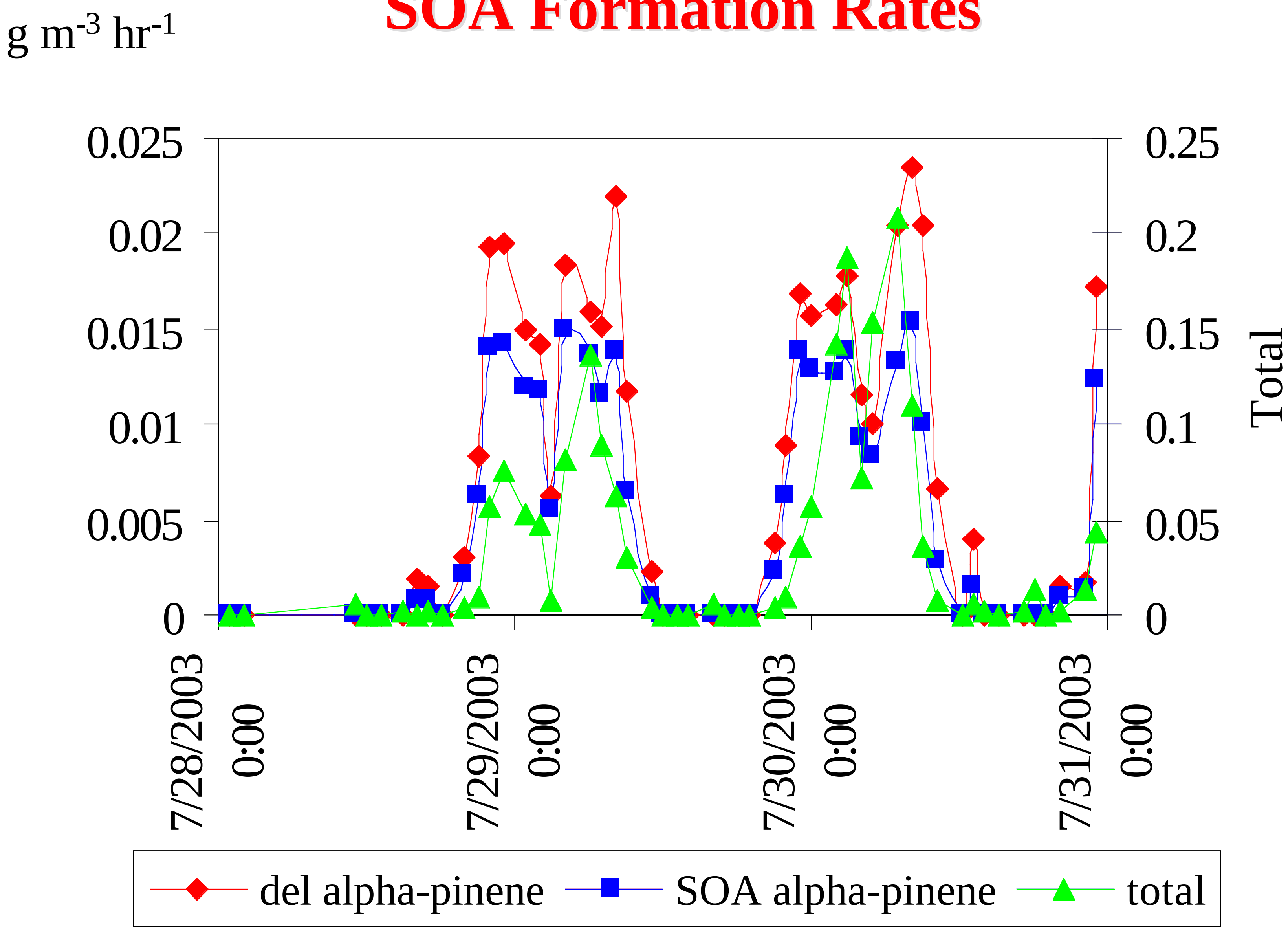
Chamber-derived, corrected for T

Filter samples (analyzed by combustion)

$$\mathrm{SOA_T} = {}_i\; \mathrm{SOA}_i = {}_i\; Y_i \;\; \mathrm{ROG}_i$$

$$\mathrm{SOA\ rate} = \mathrm{SOA_T} / \left(t_2 \quad t_1\right)$$

SOA Formation Rates



Ozone Conclusions/SOA Conclusions/Acknowledgments

- Low OPR
- High OPE (NO_x poor); significant contribution to NO_x loss from route other than nitric acid formation
- Low reactivity dominated by alkenes (biogenic)
- Mixing of aged or O_3-rich air masses probably leads to larger peaks in O_3
- Range of 0.1 to 2.9 g m^{-3} day^{-1} for SOA production rate if OM from filter measurements is varied by a factor of 2 and yield is increased by a factor of 2 (highest rates for monoterpenes)
- If lifetime is ~ 1 day, SOA formed on-site represents 2-59% of total OA and up to 24% of fine PM observed on these dates (remainder: POA or transport)
- NOAA-AIRMAP Cooperative Institute
- UNH Colleagues: Rachel Russo, Barkley Sive, Bob Talbot, and Yong Zhou

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