

Chemical Characteristics of Air Pollution Outflow from North America: Early Insights from Nova Scotia 2004



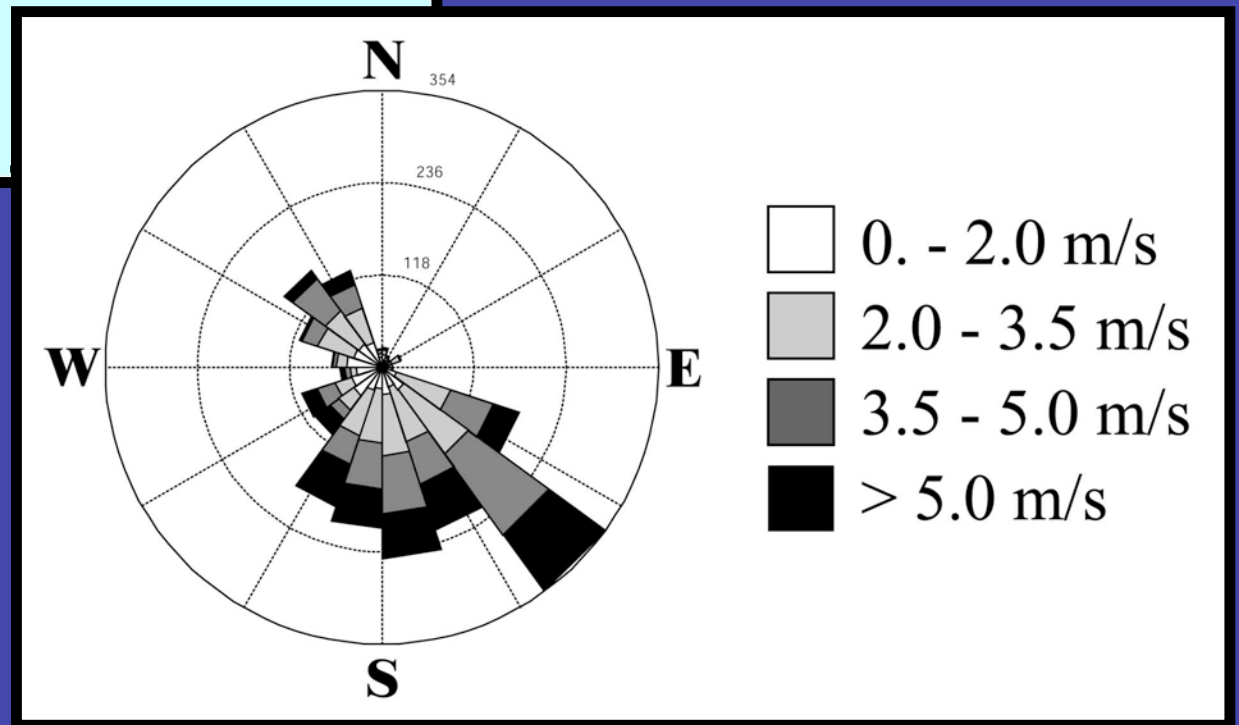
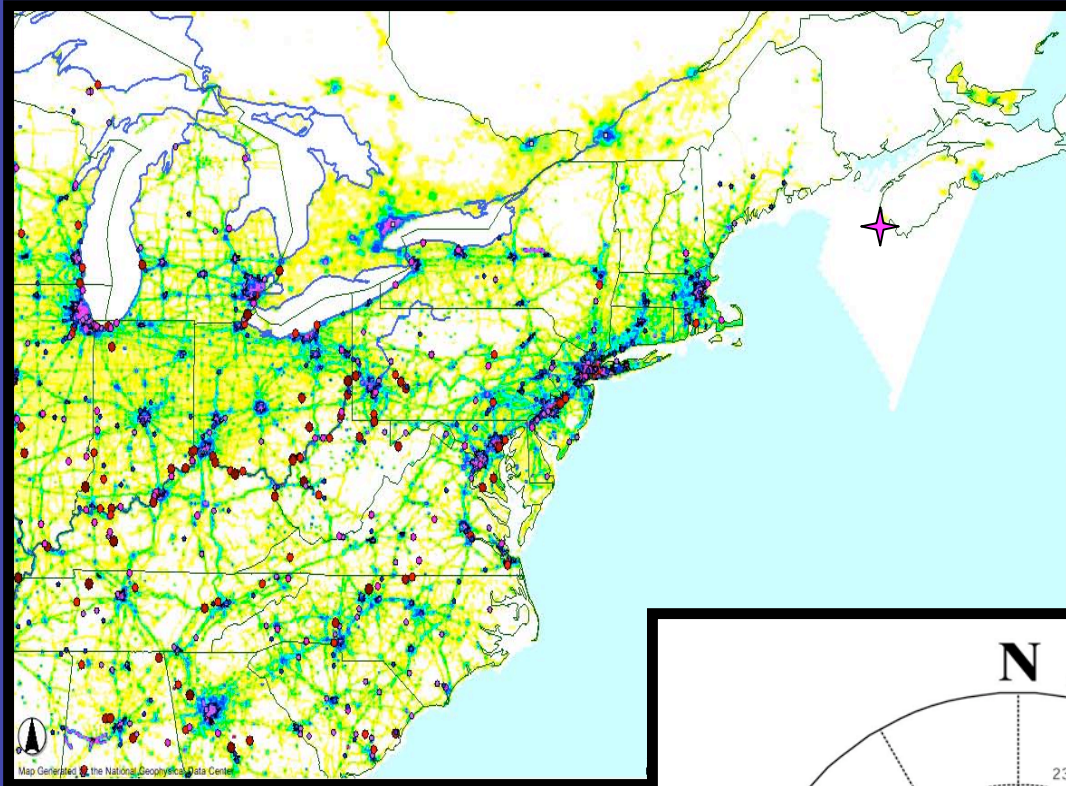
Allen Goldstein

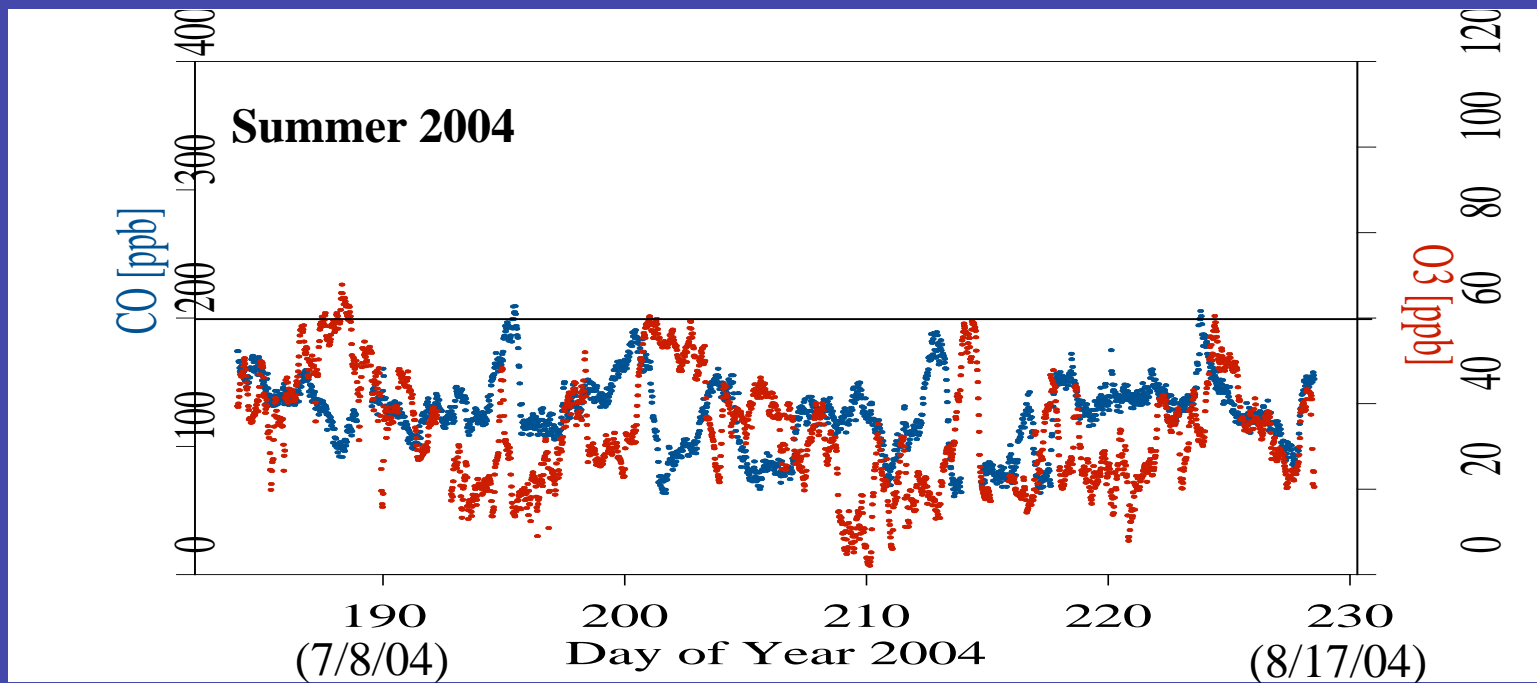
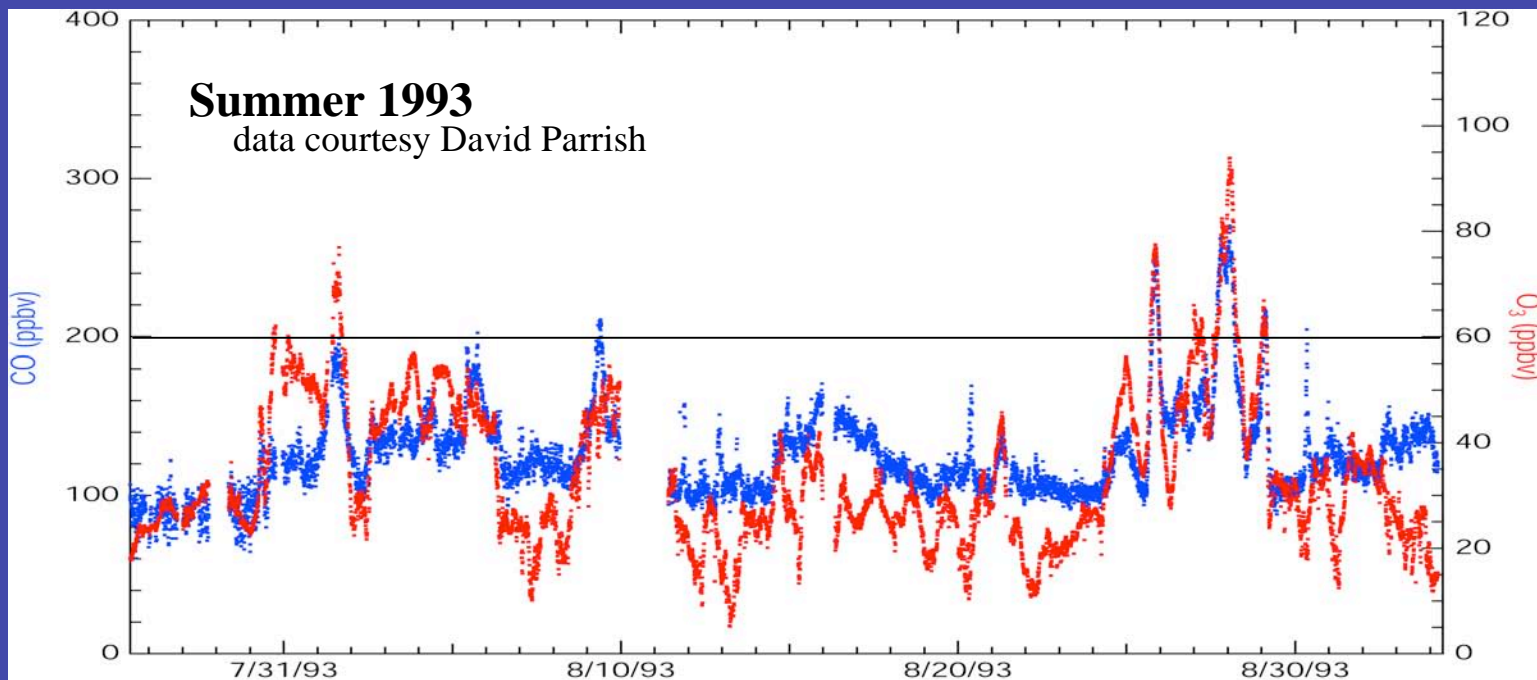
University of California, Berkeley

(MOSTLY PREPARED BY DYLAN MILLET)

Outline

1. Site description & comparison to 1993
2. What were the dominant processes/sources impacting atmospheric composition at CP?
3. What can the combination of VOC/TAG/AMS data tell us about organic aerosol sources & chemistry?
4. What can we say about the composition & chemistry of pollution outflow?





NARE 1993

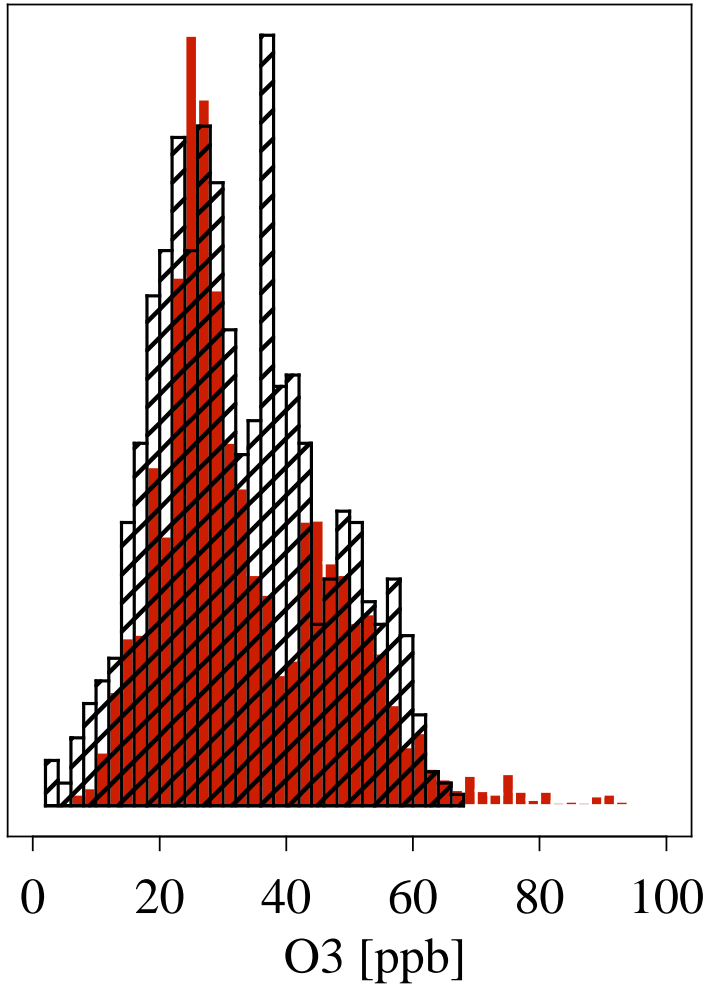
MEAN O3 (PPB): 34 +/- 14 (RANGE: 5-94)

MEDIAN O3 (PPB): 30

ICARTT 2004

MEAN O3 (PPB): 33 +/- 13 (RANGE: 2-68)

MEDIAN O3 (PPB): 31



NARE 1993

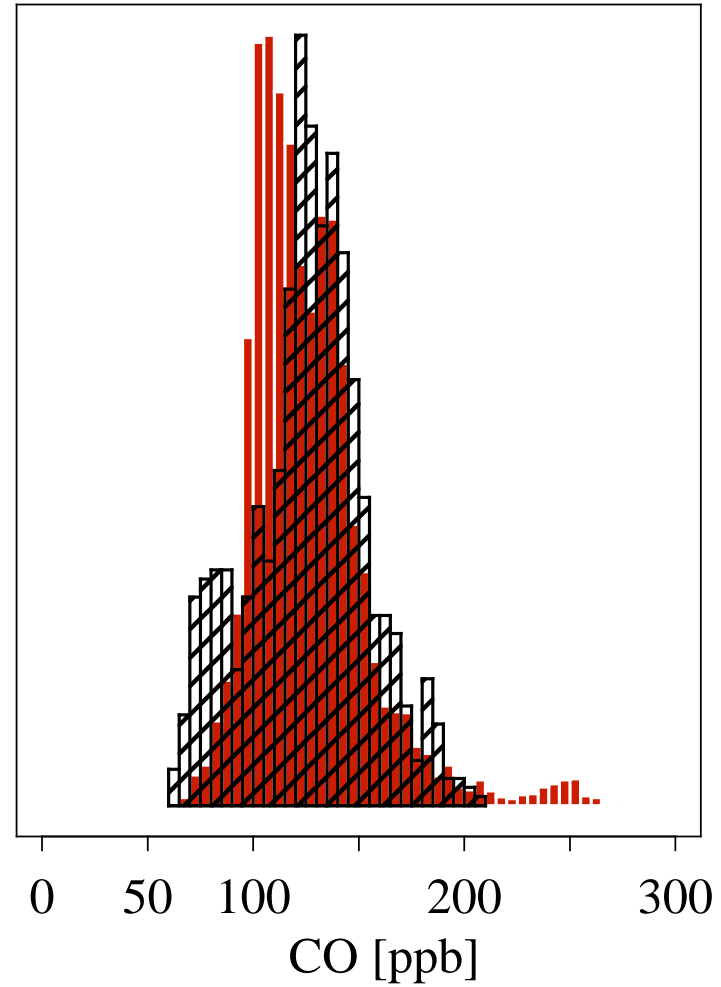
MEAN CO (PPB): 126 +/- 28 (RANGE: 60-270)

MEDIAN CO (PPB): 121

ICARTT 2004

MEAN CO (PPB): 126 +/- 28 (RANGE: 63-206)

MEDIAN CO (PPB): 128



Factor Analysis

F1: US dominated

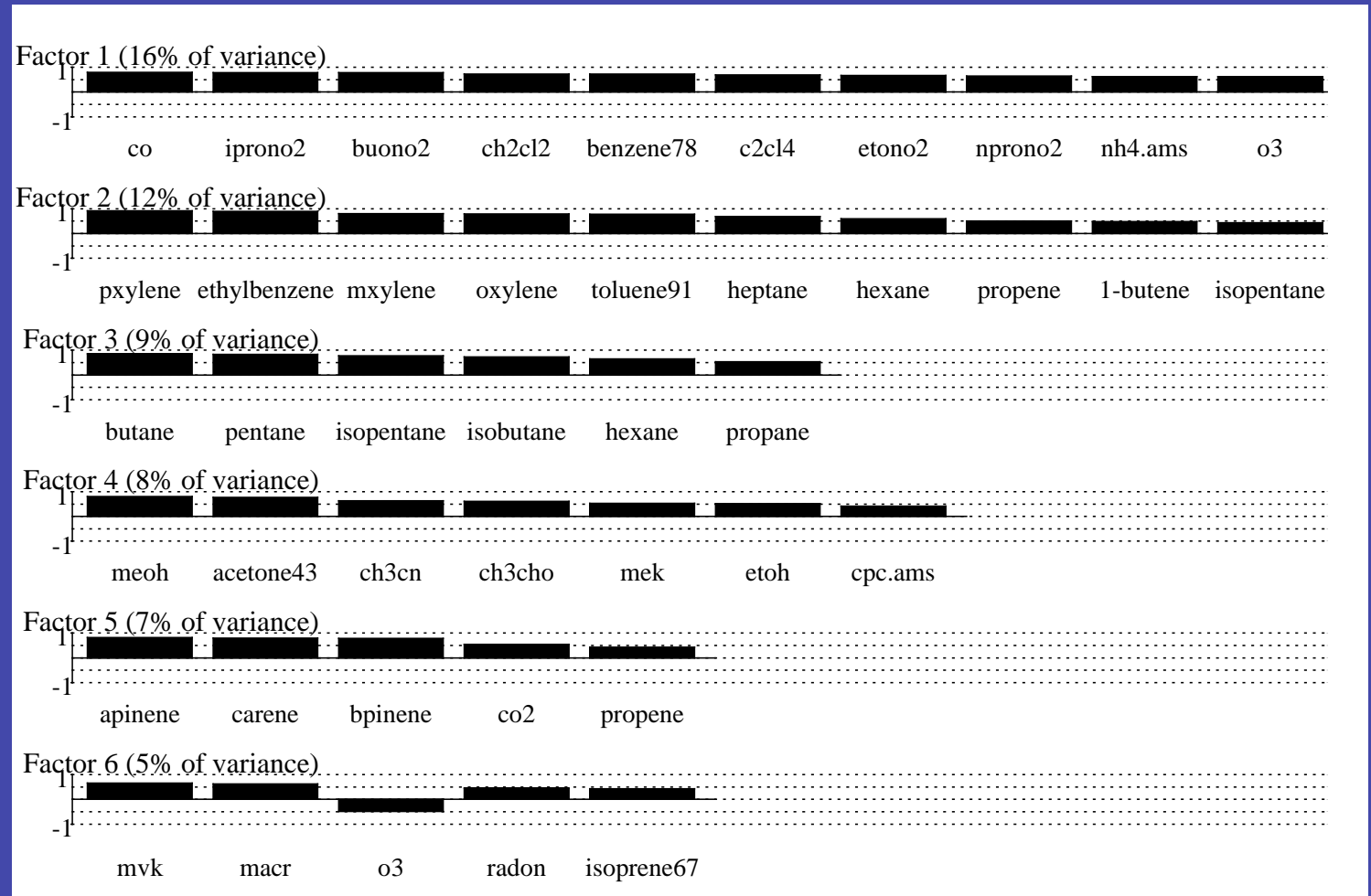
F2: Local combustion

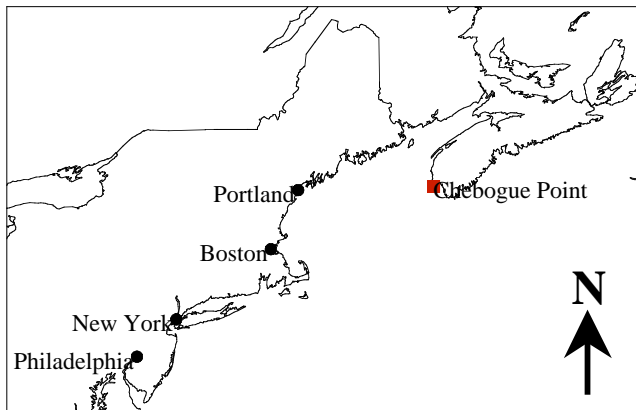
F3: Alkanes

F4: OVOC

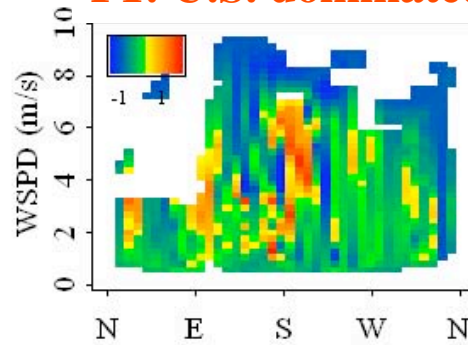
F5: Terpenes

F6: Biogenic OX

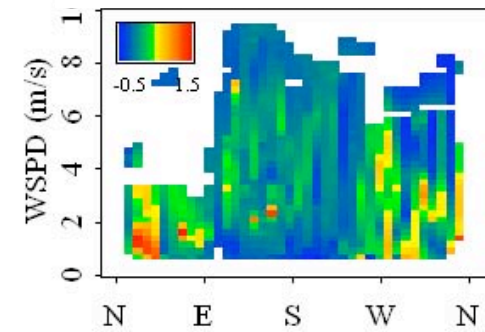




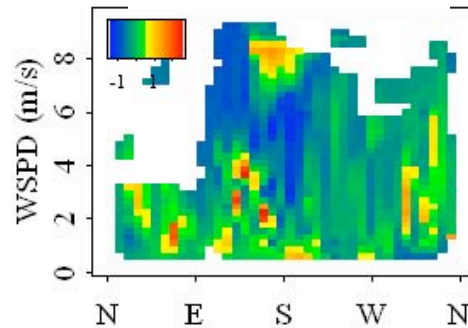
F1: U.S. dominated



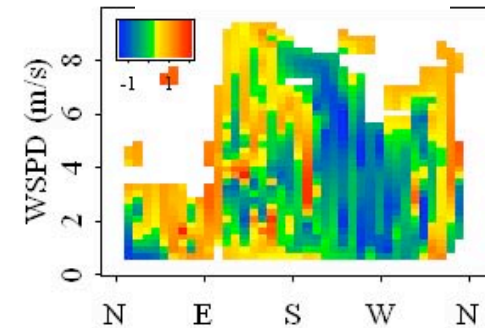
F2: Local combustion



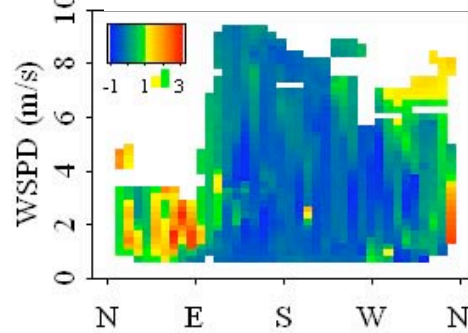
F3: Alkanes



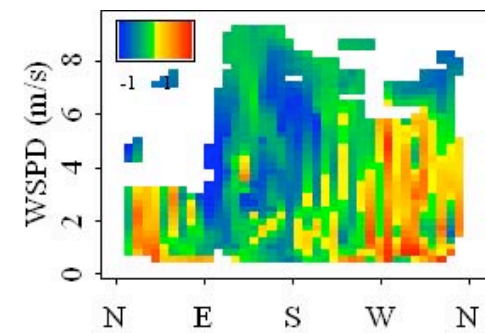
F4: OVOC



F5: Terpenes

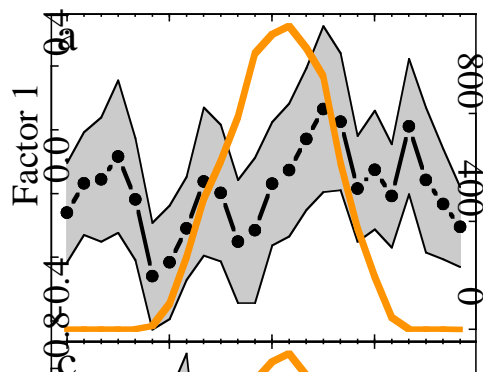


F6: Biogenic OX

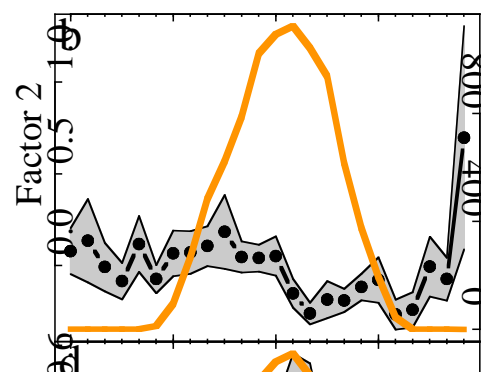


Diurnal Patterns

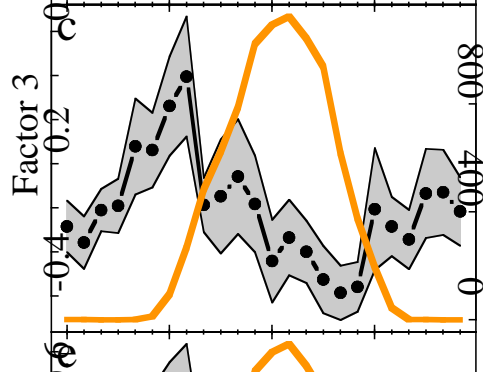
F1: U.S.



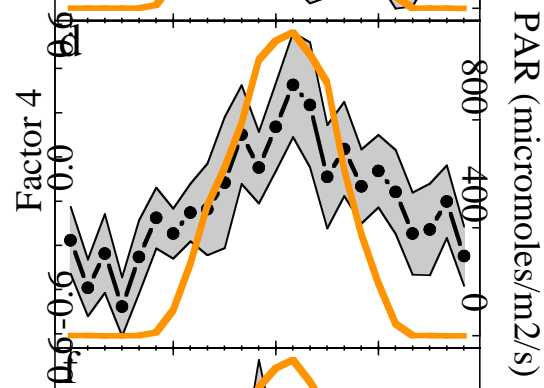
F2: Local combustion



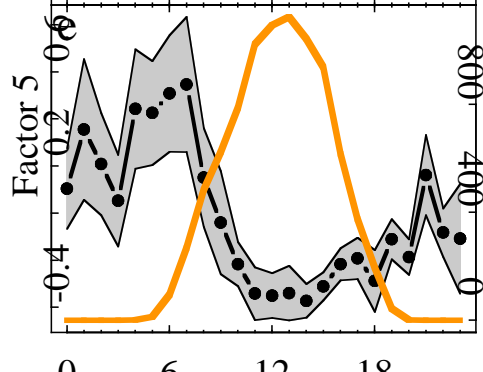
F3: Alkanes



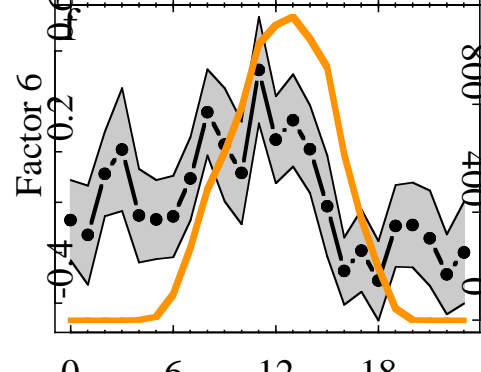
F4: OVOC



F5: Terpenes



F6: Biogenic OX



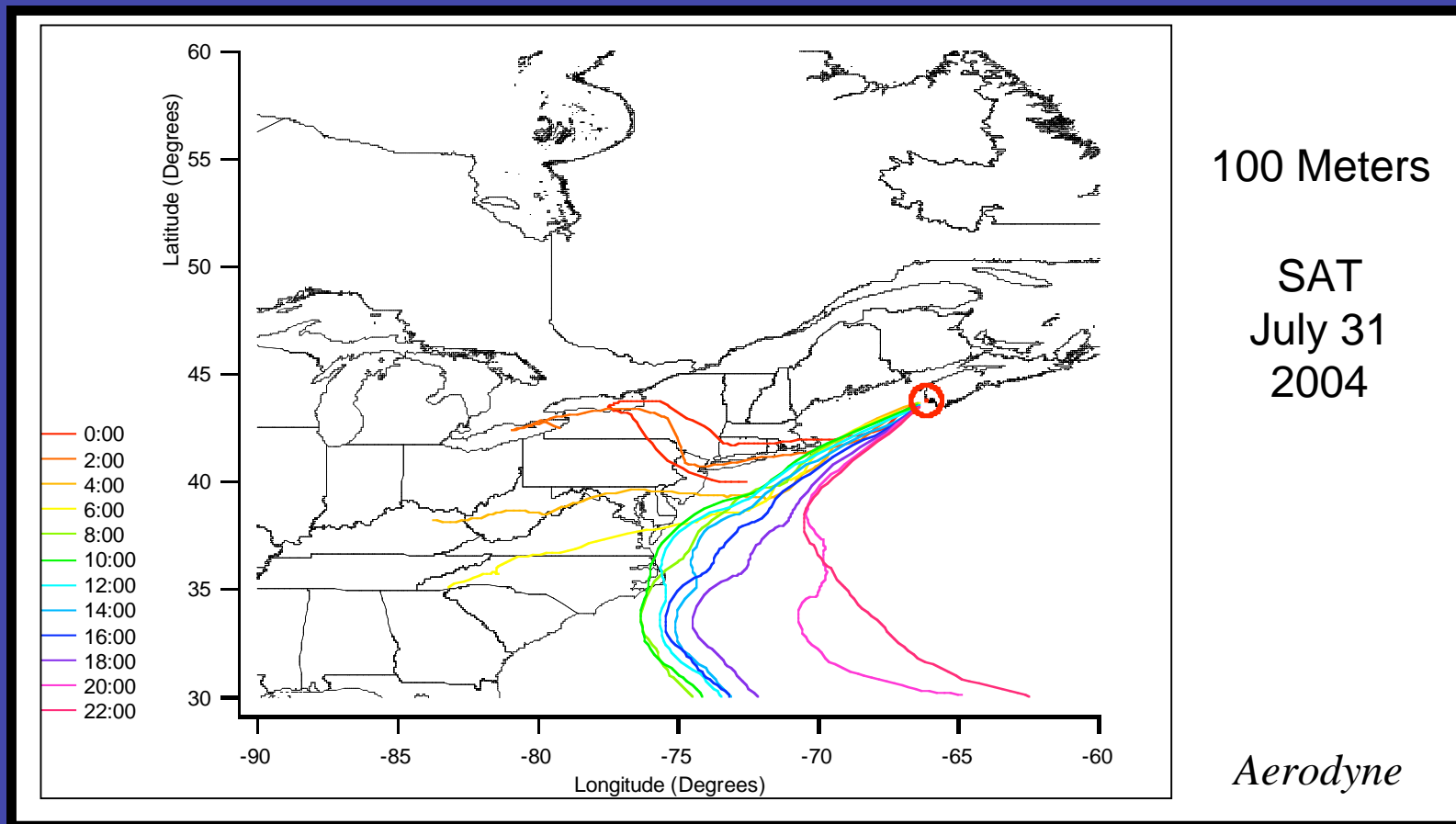
Eastern U.S. Emissions

F1 (U.S.) can be further split:

- F1a: 1^o & 2^o gas-phase & particle phase pollution
- F1b: Very high in particulate SO_4 , NH_4 , OC, and O_3

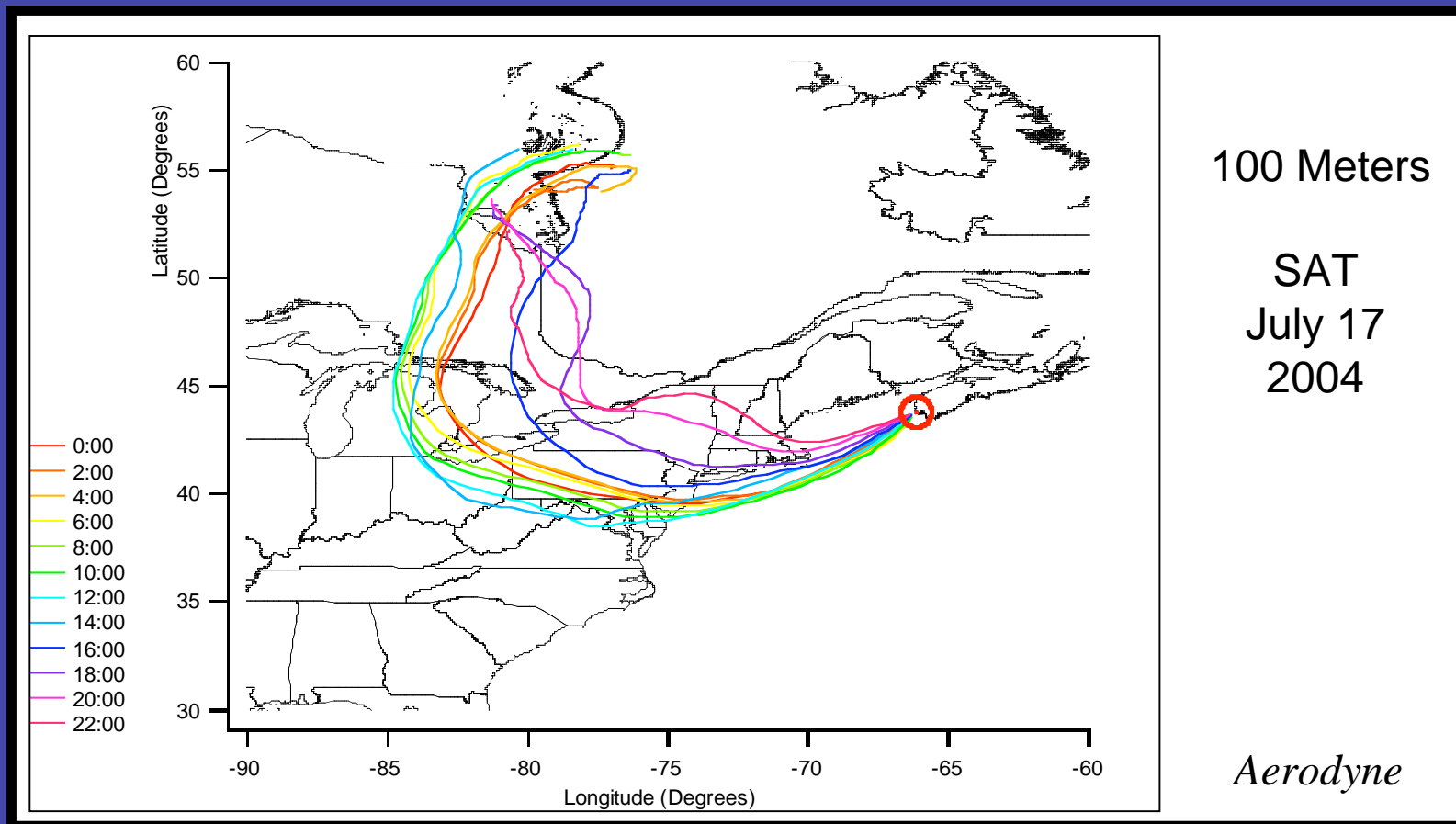
Eastern U.S. Emissions

Example 4d back-trajectory for F1a:



Eastern U.S. Emissions

Example 4d back-trajectory for F1b:



Organic Aerosol Chemical Composition

- Total aerosol OC variability driven by:
 - F1a & F1b (US emissions) (most important)
 - Also F4 (OVOCs) & F6 (Biogenic OX)
- Can we get any more detail?

Online Organic Aerosol Chemical Composition

TAG

(B. Williams, A. Goldstein, S. Hering, N. Kreisberg)

- Individual species provide information on OC source types
 - Insights into OC sources and production mechanisms
- All compounds measured appear highly oxygenated
- Identification and quantification: major challenge when far from sources

Organic Aerosol Chemical Composition

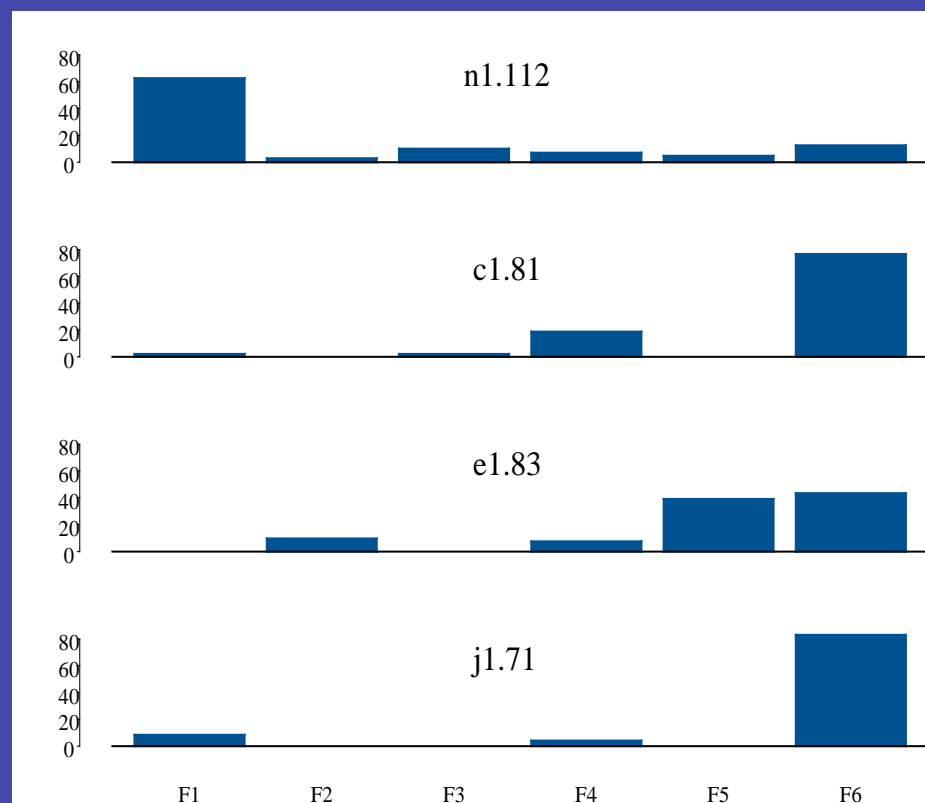
Multiple regression of OC species with 6 factors:

Tentative Compound ID:

1,6-dioxaspiro[4,4]nonane-
2,7-dione ($C_7H_8O_4$) ?

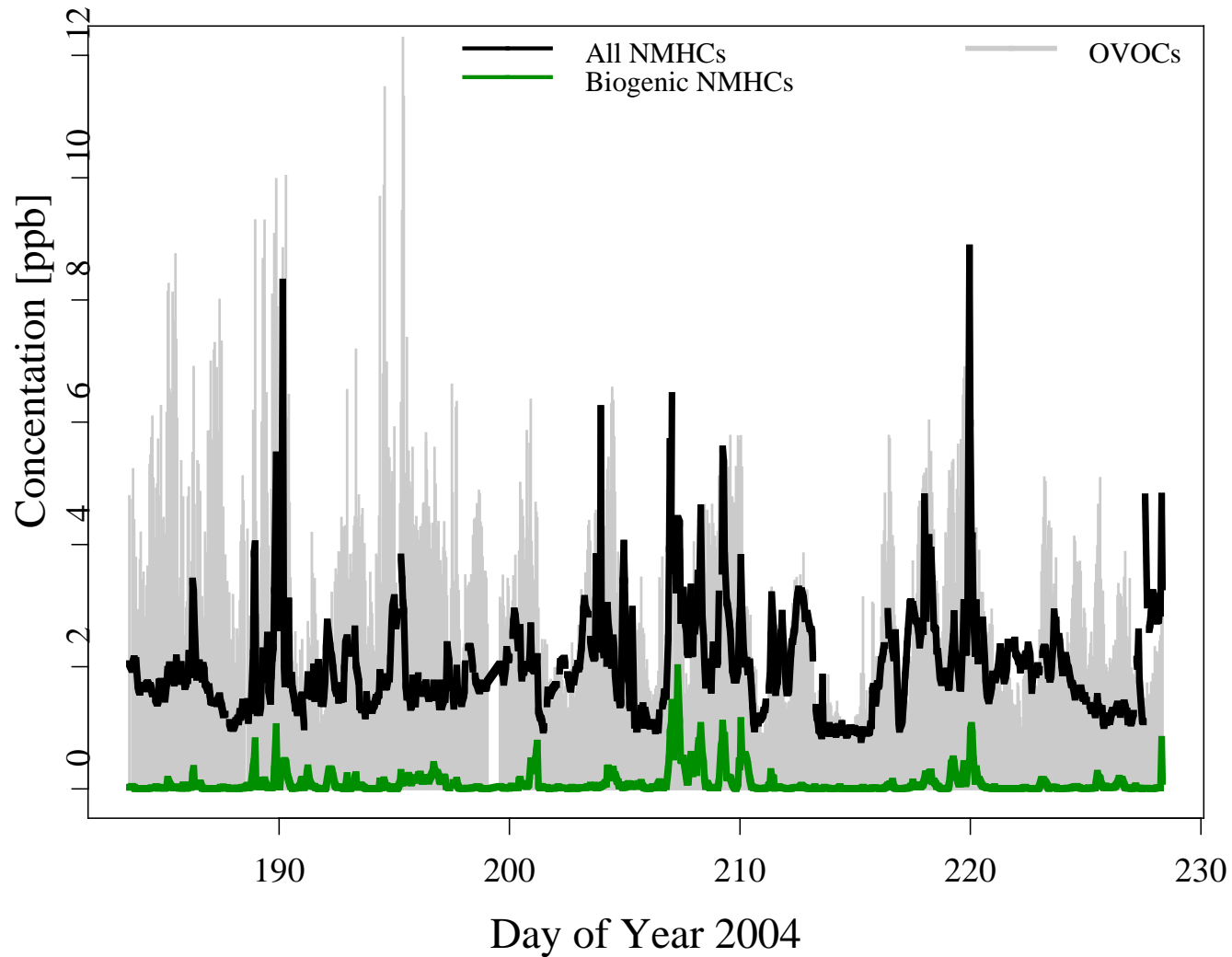
7-anti-methyl-2-oxo-bicyclo[2.2.1]heptane-
7-carboxylic acid ($C_9H_{12}O_3$) ?

2,3-pinenediol ($C_{10}H_{18}O_2$) ?

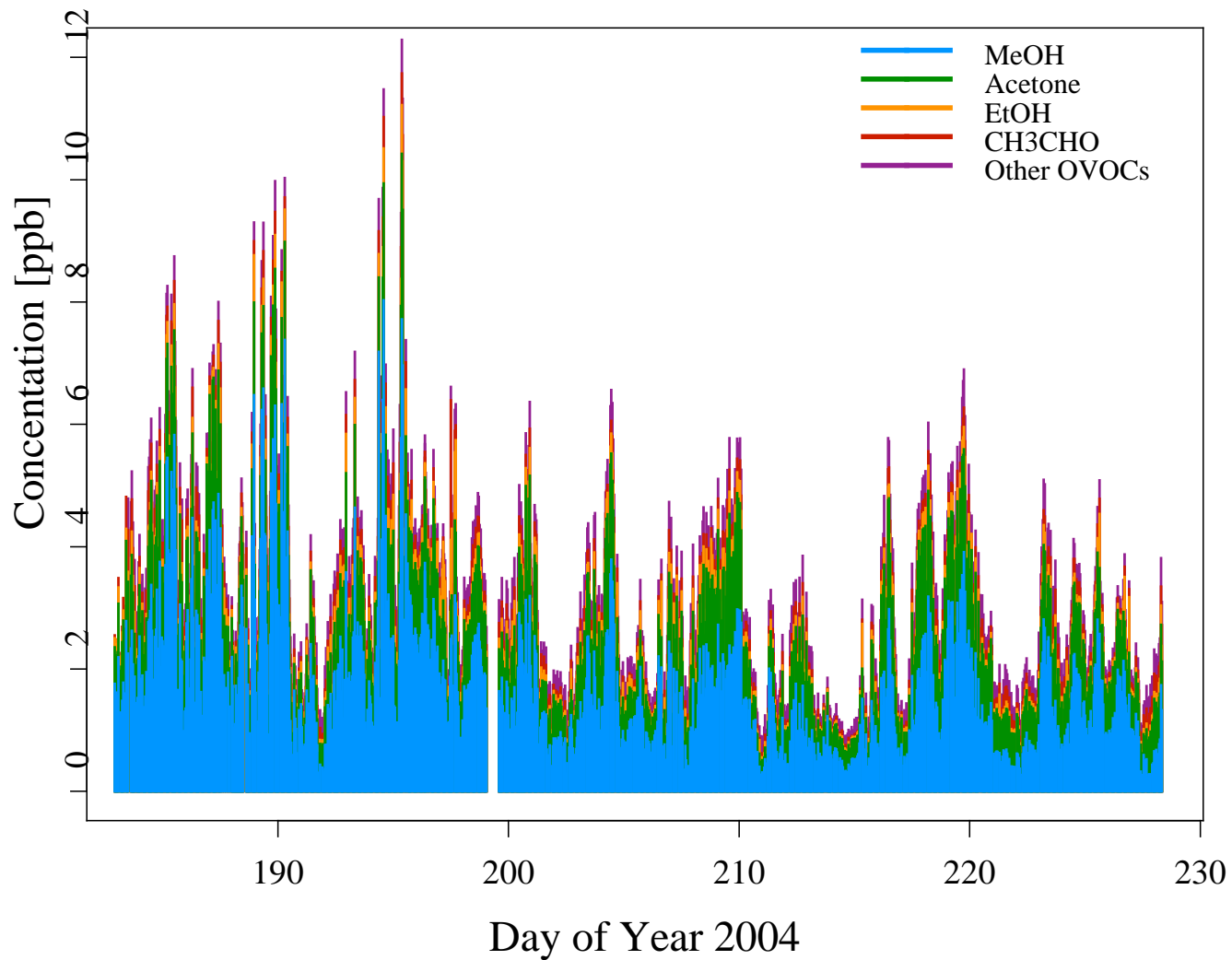


U.S. Alkanes Terpenes
Local comb OVOC Biog OX

VOC concentrations



What About the OVOCs?

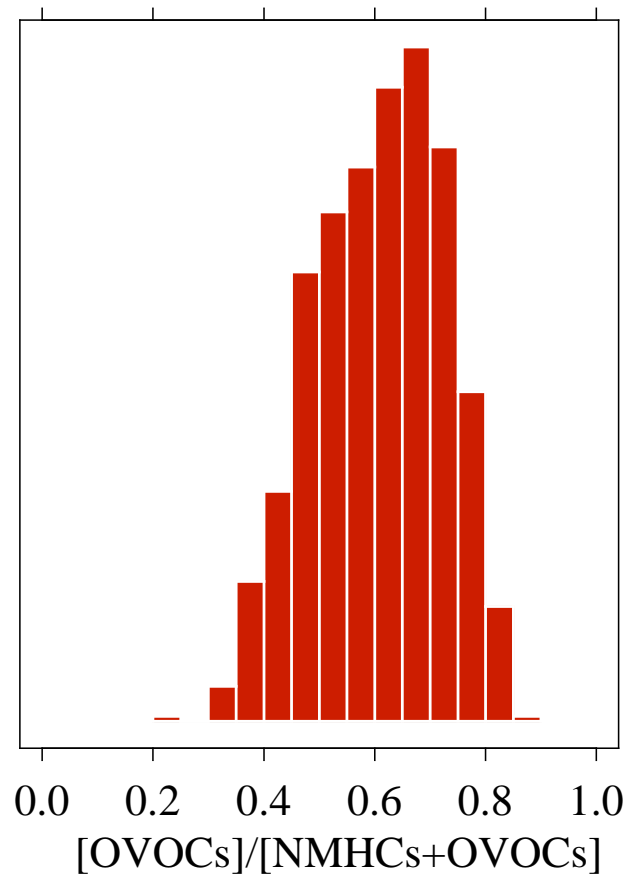
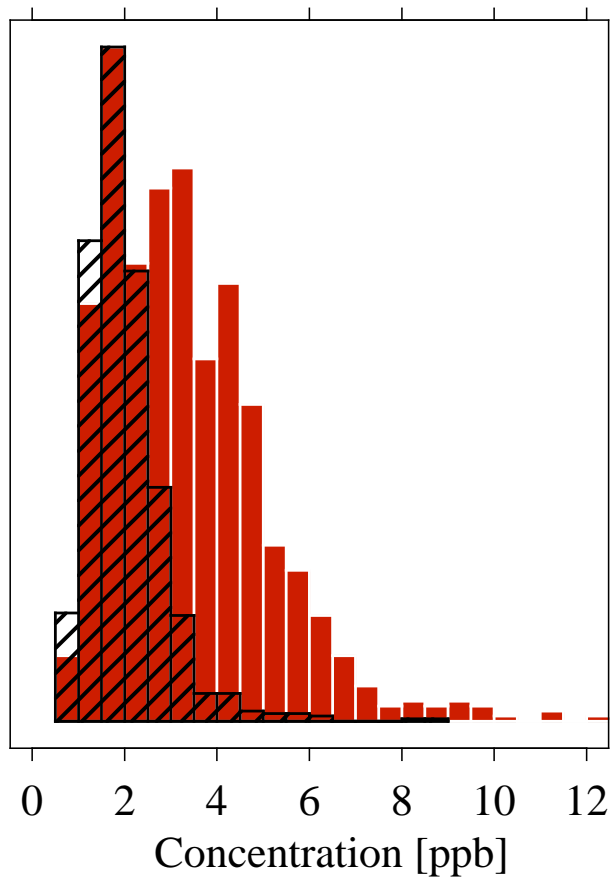


What About the OVOCs?

OVOCs
MEAN [PPB]: 3.35 +/- 1.73

NMHCs
MEAN [PPB]: 2 +/- 0.85

$[\text{OVOCs}]/[\text{NMHCs}+\text{OVOCs}]$
MEAN: 0.61 +/- 0.12

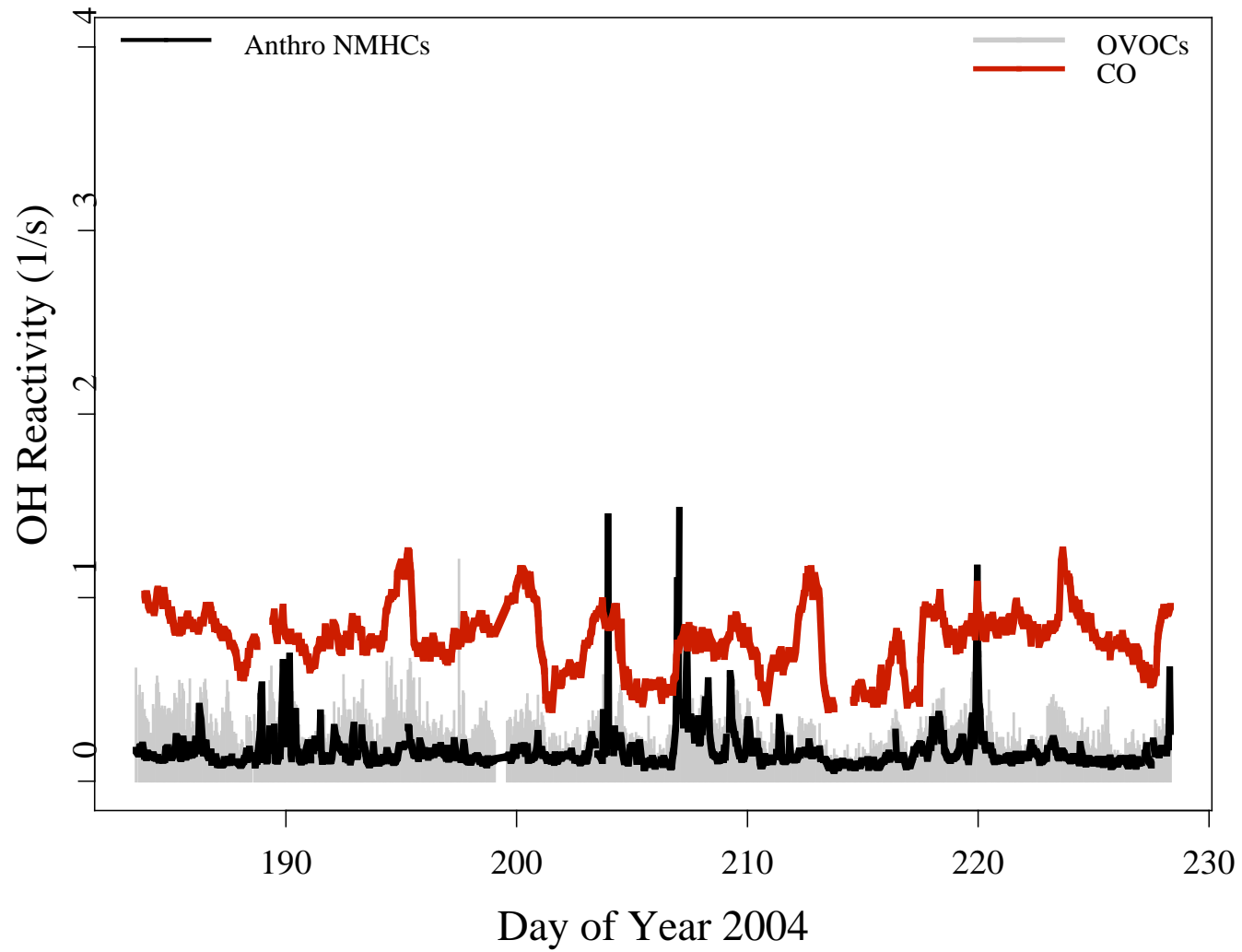


VOC OH Reactivity

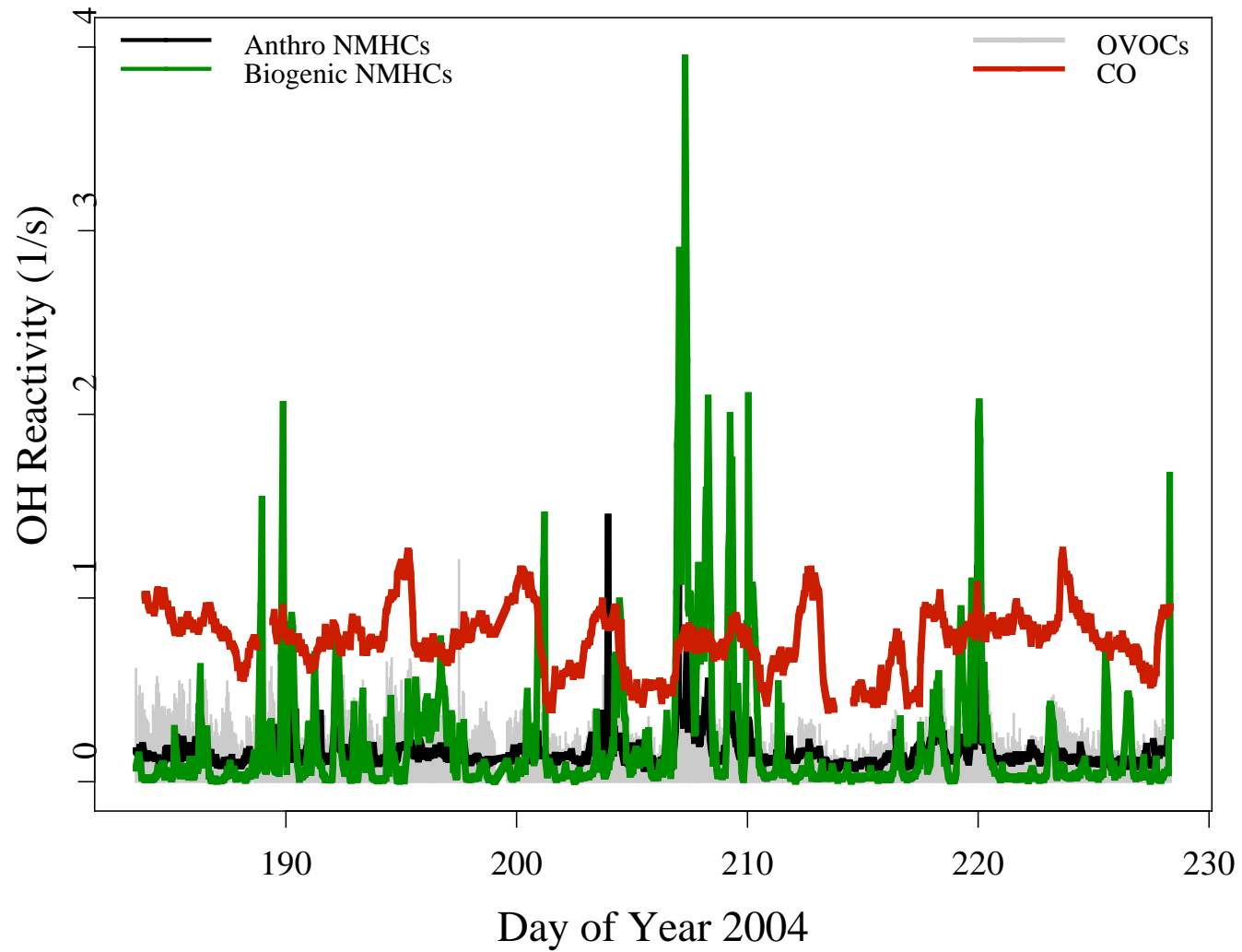
$$L_{\text{OH}} = \sum_i k_i [X_i]$$

- Index of the chemical reactivity of an air mass
- Inverse lifetime of OH wrt reaction with the measured compounds
- What are the dominant VOCs competing for OH radicals?

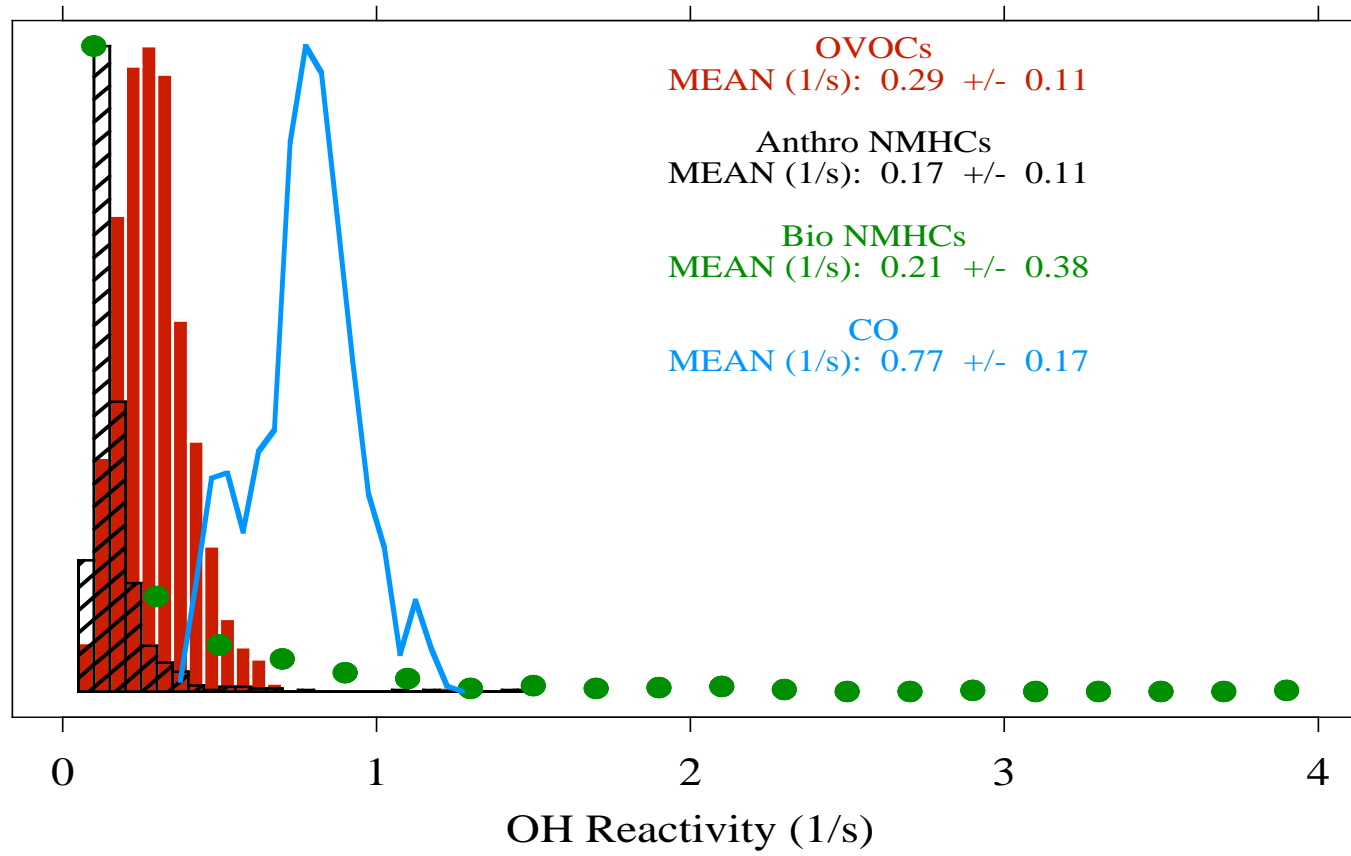
OH Reactivity



OH Reactivity



OH Reactivity

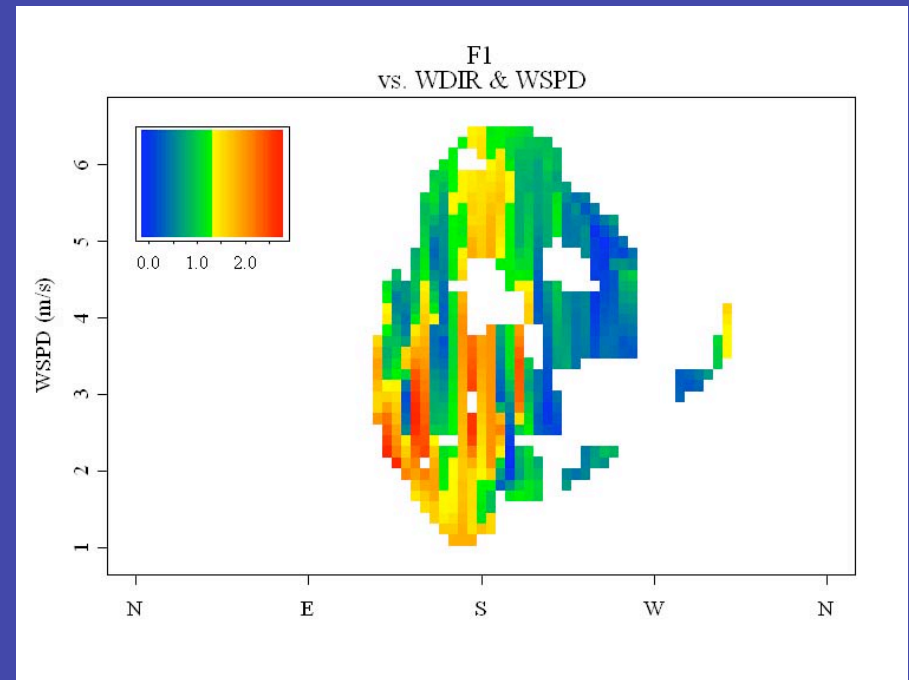


Filtering for NE US emissions

- Use F1 as a filter for NE US outflow
- Choose times when

$$F1 > \sum_{i=2}^6 F_i$$

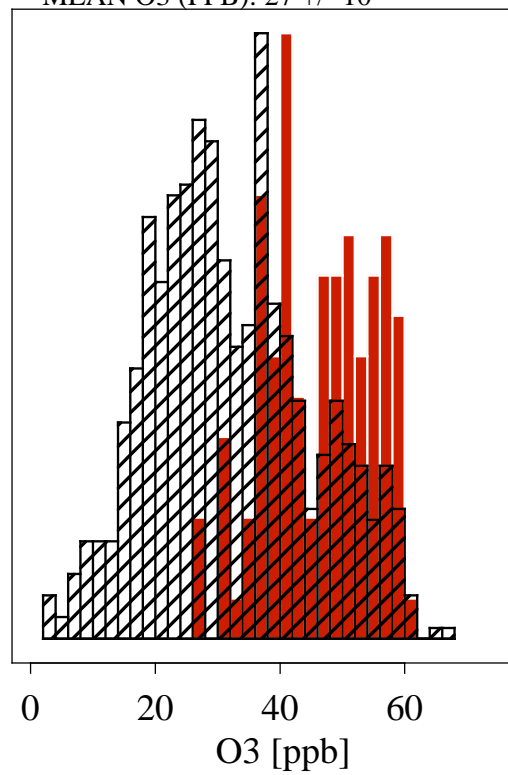
(117 / 899 hours; 13%)



O₃ & CO

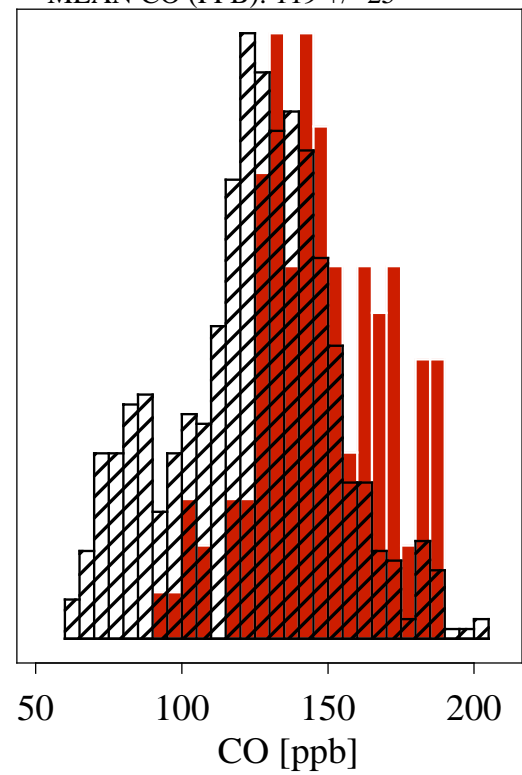
US Outflow
MEAN O3 (PPB): 46 +/- 9

Other
MEAN O3 (PPB): 27 +/- 10



US Outflow
MEAN CO (PPB): 148 +/- 22

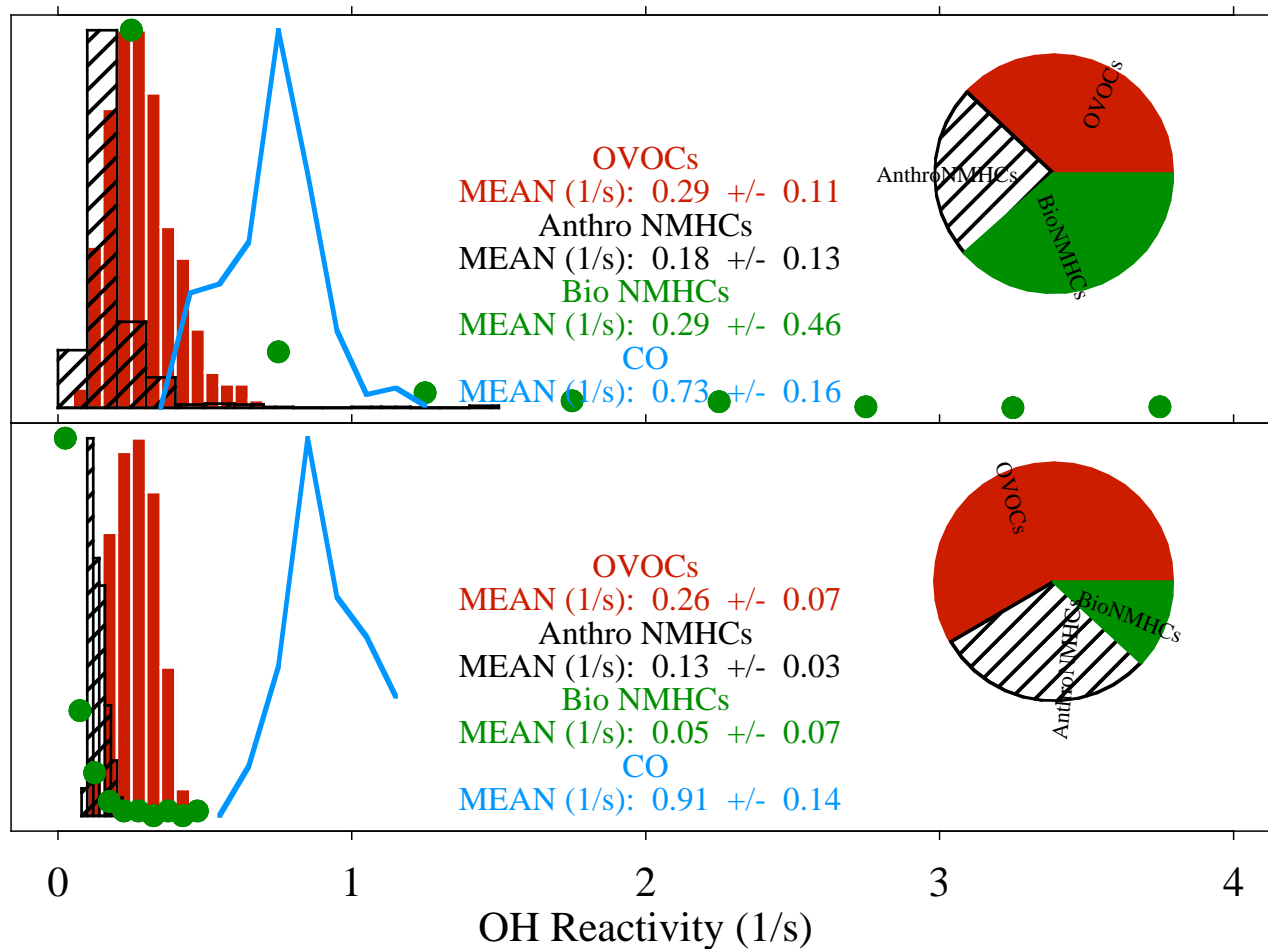
Other
MEAN CO (PPB): 119 +/- 25



VOC OH reactivity

Other
periods

US
outflow



Conclusions & Future Work

Conclusions:

1. CO & O₃ levels similar to 1993
2. FA provides context & means to segregate data
3. Organic aerosol highly oxygenated
 - NE pollution
 - Oxidation of biogenic precursors
4. OVOCs are ~ 2x as important as NMHCs during NE outflow periods

To do:

- Look in detail for evidence of changes in composition & photochemistry since 1993
- Continue investigation of organic carbon budget and chemistry in gas + particle phase

Acknowledgements

Dylan Millet, Brent Williams, Rupert Holzinger, Jen Murphy, Megan McKay (UC Berkeley)

Susanne Hering, Nathan Kreisberg (Aerosol Dynamics)

James Allan, Doug Worsnop, Jose Jimenez (UMIST, Aerodyne, U. Colorado)

Dan Jaffe (UW Bothell)

Funding:

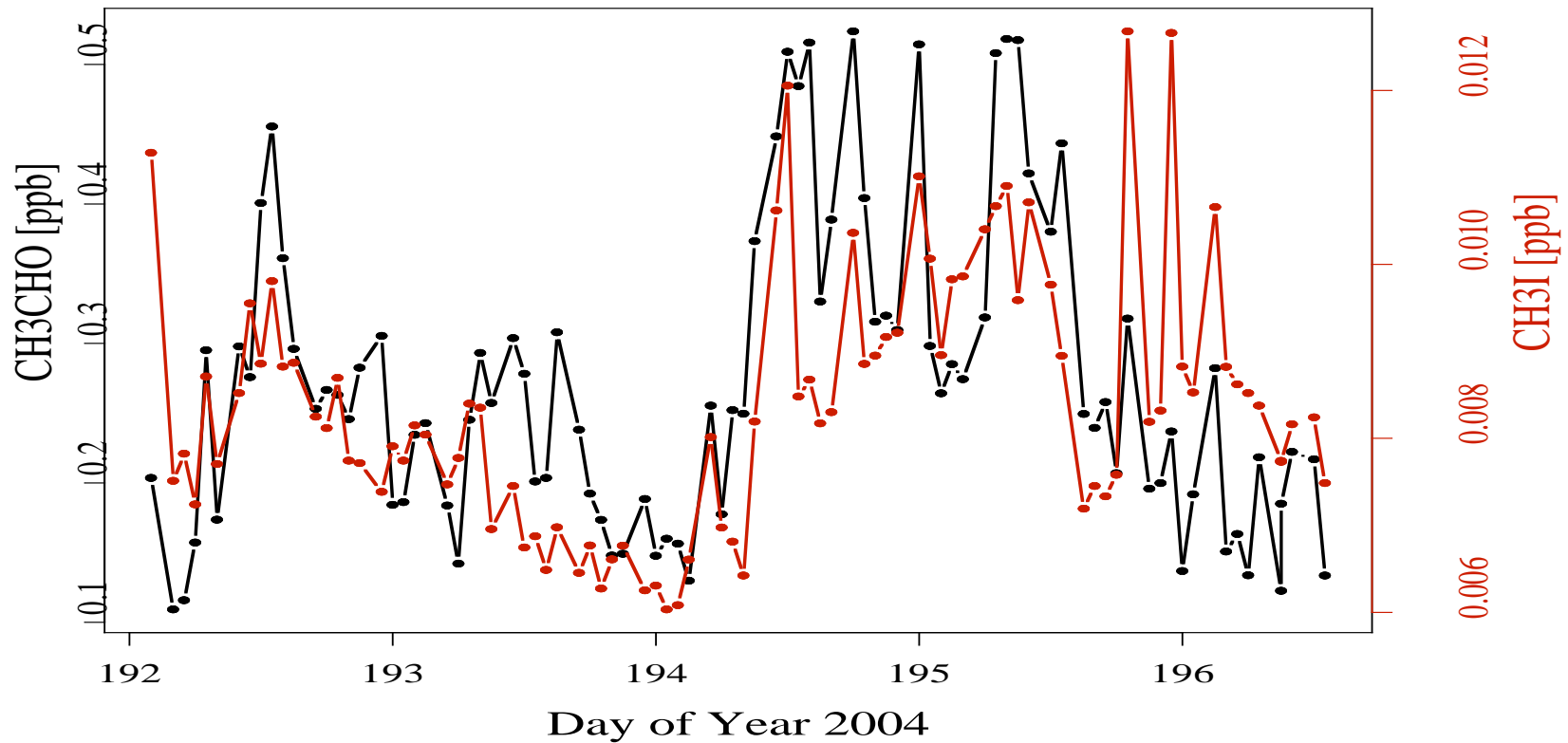
NOAA Office of Global Programs

DOE SBIR Program

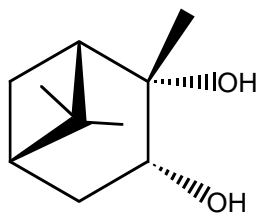
DOE Global Change Education Program

Oceanic OVOC Source?

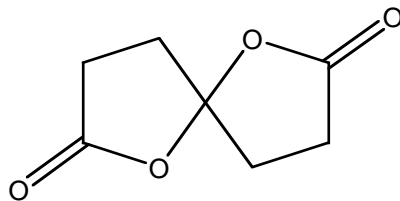
Nothing definitive, but a few hints...



Aerosol OC Composition



j1.71: 2,3-pinenediol



n1.112: 1,6-dioxaspiro[4,4]nonane-2,7-dione