FIREX-AQ Chem Otter Science Meeting

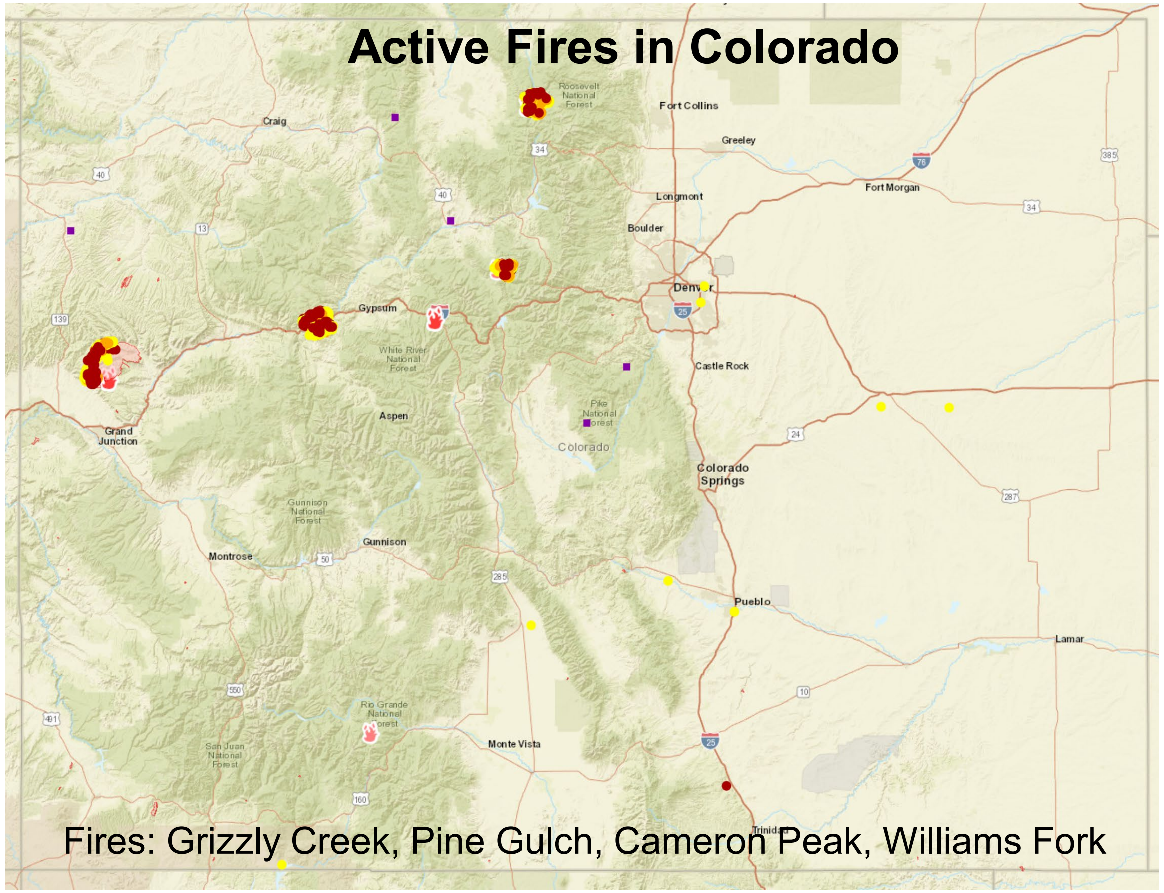
Agenda:

1. Updates: Metadata for plume transects

2. Ale Franchin: Relations between chemical composition and optical properties of BBOA

3. Paul Van Rooy: GCxGC ToF MS:
Terpene measurements made on both ground-based and airborne platforms during FIREX 2019

4. Mike Robinson: Variability and diel dependence of O3-NOx-VOC chemistry in western wildfire plumes: Results from the NOAA Twin Otter



17 August 2020

Metadata for each plume transect

Metadata is organized as an ICARTT file with one row per plume transect.

Category	Metadata
Transect time	Transect_Start_Time, Transect_Stop_Time, Transect_Start_Row, Transect_Stop_Row
Flight information	Transect_Flight_Name, Transect_Flight_Leg, Transect_Plume_Number, Transect_Type
Aircraft location and altitude	Transect_Lat_Midpoint, Transect_Lon_Midpoint, Transect_Alt_Avg, Transect_Alt_Range
Wind speed and direction	Transect_WindSpd_Avg, Transect_WindDir_Avg
Reanalysis plume age	Transect_Reanalysis_Plume_Age, Transect_Reanalysis_Plume_Age_Unc
Average CO and CO_2	Transect_CO_Avg, Transect_CO2_Avg
Fire information	Fire_ID, Fire_Lat, Fire_Lon, Fire_Type
Background times	Background1_Start_Time, Background1_Stop_Time, Background2_Start_Time, Background2_Stop_Time, Background1_Start_Row, Background1_Stop_Row, Background2_Start_Row
Background CO and CO_2	Background1_CO_Avg, Background1_CO2_Avg, Background2_CO_Avg, Background2_CO2_Avg
MCE	MCE_by_Integration, MCE_by_ODR, MCE_by_ODR_r2

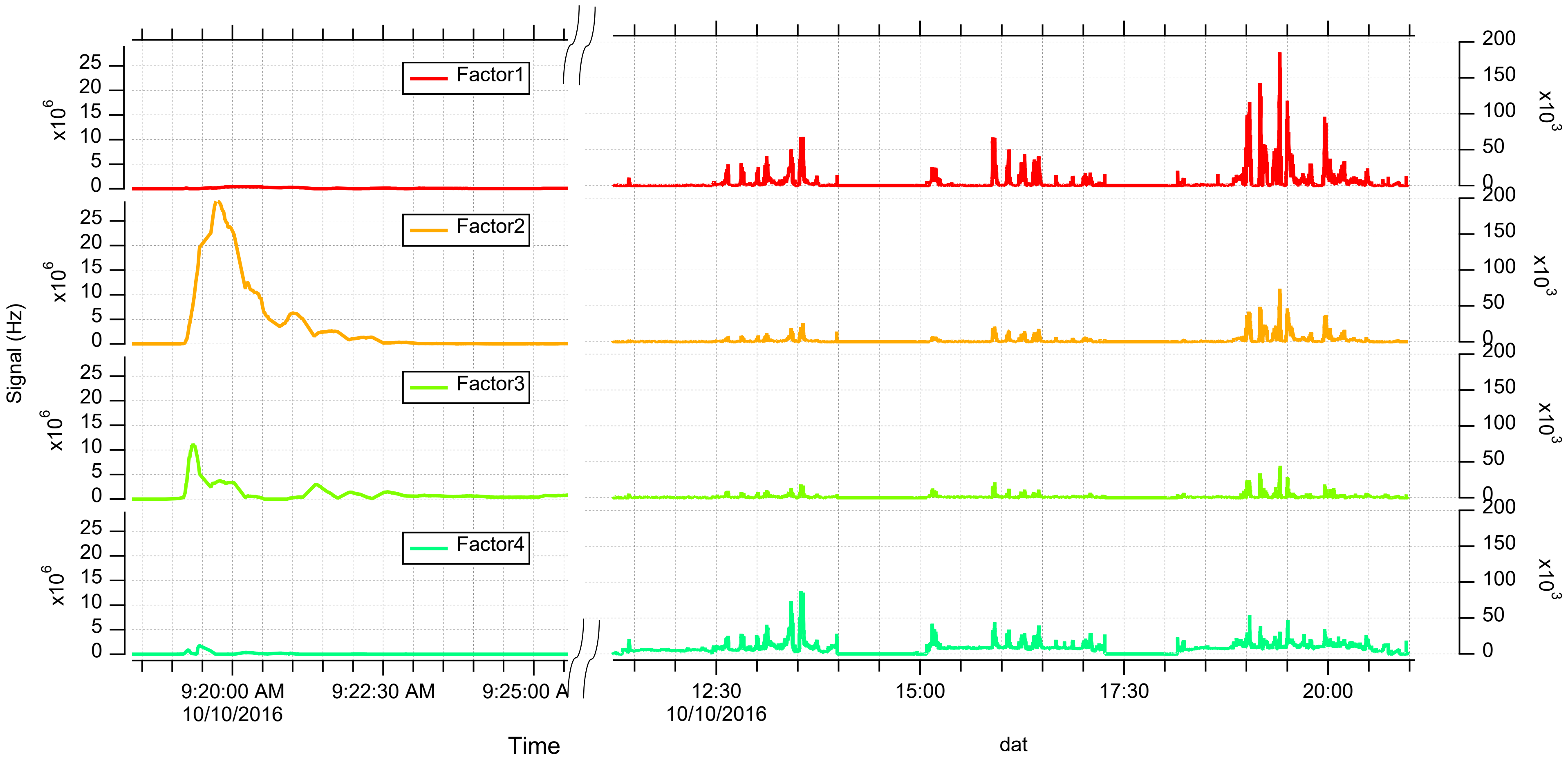
Relations between chemical composition and optical properties of BBOA

Ale Franchin et al.

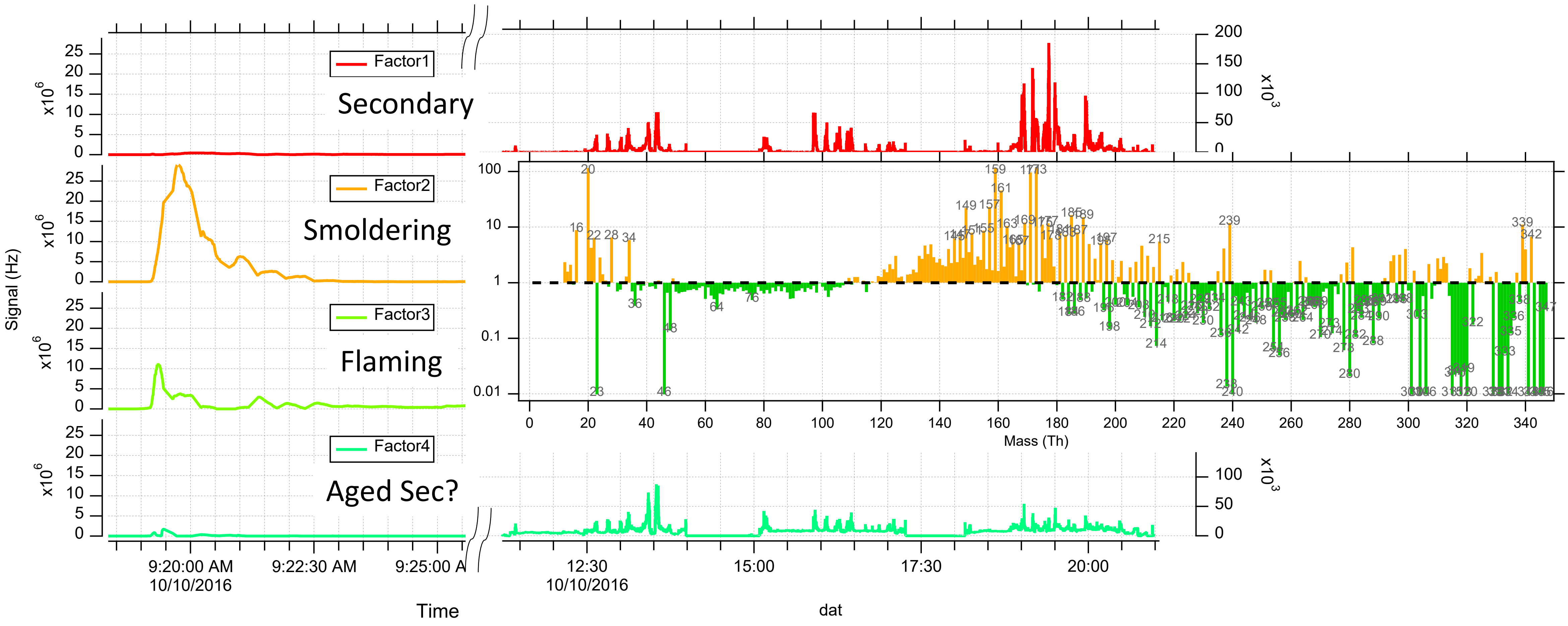
Contrasting daytime vs nighttime and center-plume vs edges

- Is there a chemical signature for absorbing aerosols?
- Is there a difference between day and night, plume age and/or time of day emitted?
- Can we identify flaming, smoldering (and pyrolysis?) and secondary contributions?
- Is there a difference between the plume edges and the plume center?
- Do we see similarities/differences in the altitude profiles?
- Calculate MAC BrC by using CLAP abs and AMS Org
- Investigate fast oxidation within the first tens of minutes

PMF with Fire 15 and RF13 -- flt20200828



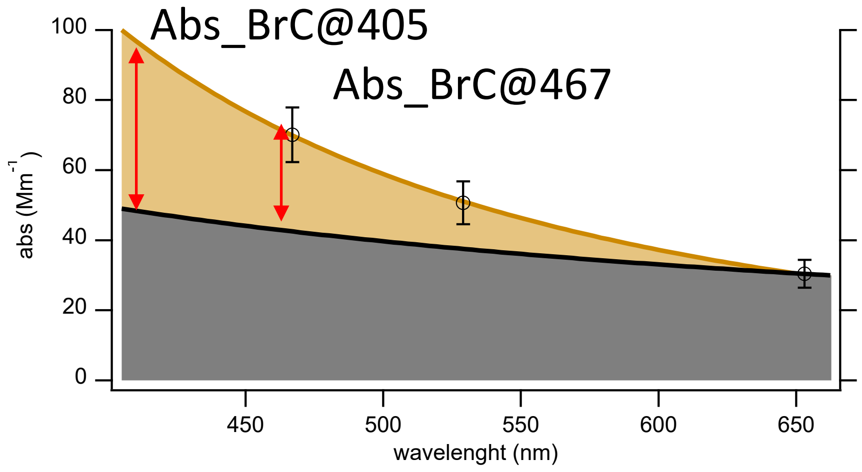
PMF with Fire 15 and RF13 -- flt20200828

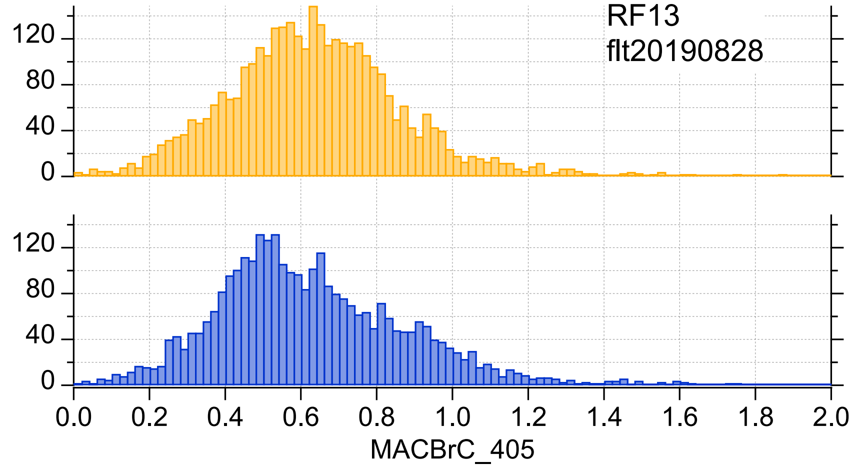


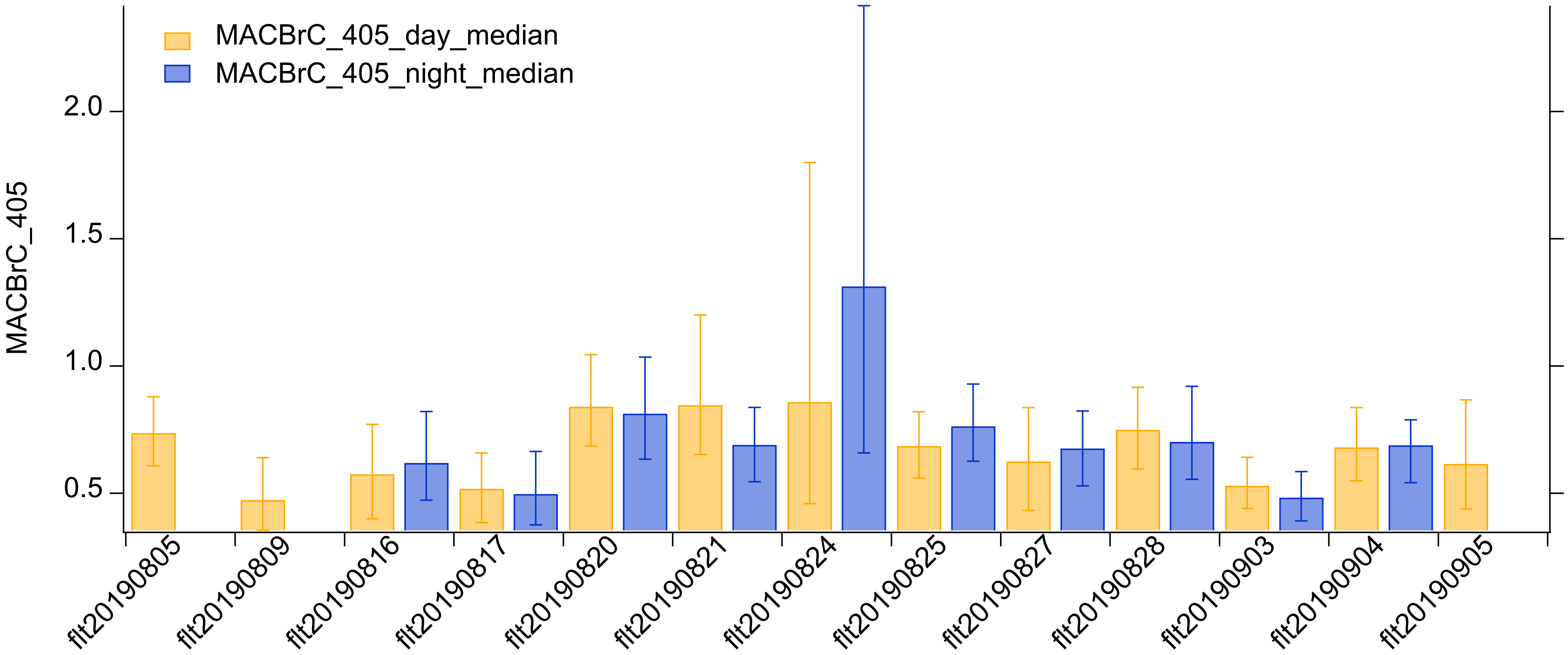
MAC BrC

Assuming that abs@653 is all due to BC

$$MAC = \frac{Abs\_BrC}{Org}$$







GCxGC ToF MS: Terpene measurements made on both ground-based and airborne platforms during FIREX 2019

Paul Van Rooy, Christos Stamatis, Lindsay Hatch, Avi Lavi, Kelley Barsanti

University of California, Riverside

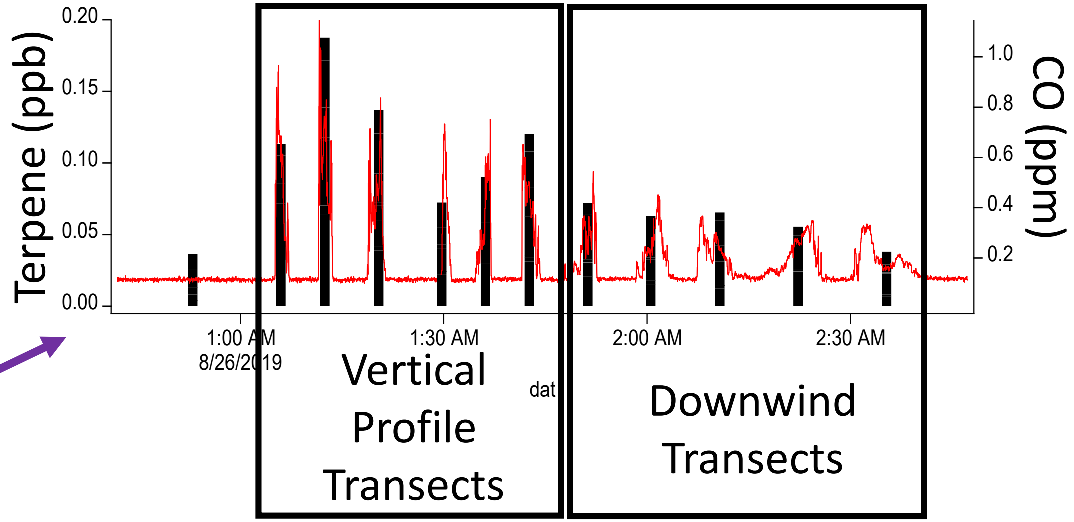
Twin Otter Flight Analysis Overview

Data quality is mixed

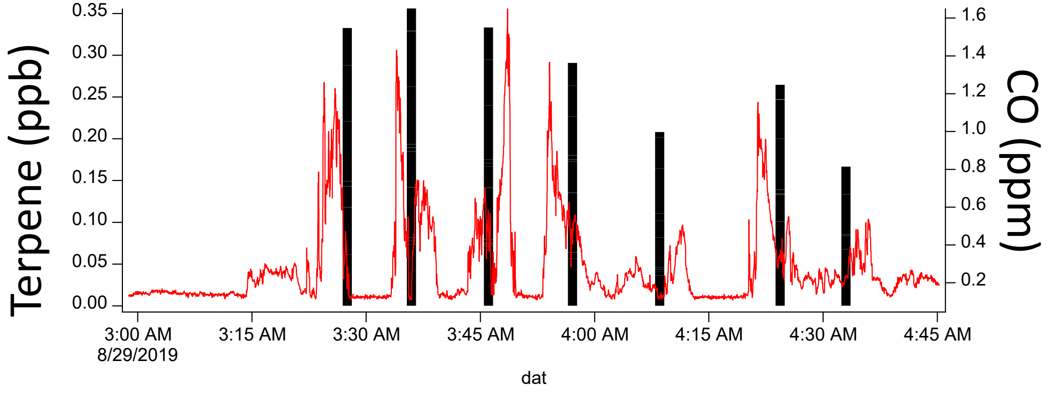
Flights Analyzed
20190816 L2, L3
20190817 L1, L2
20190820 L1, L2, L3
20190821 L1, L2
20190824 L2, L3
20190825 L1, L2, L3
20190827 L1, L2
20190828 L1, L2, L3
20190903 L1, L2, L3
20190904 L1, L2, L3
20190905 L1, L2

Data quality is generally good

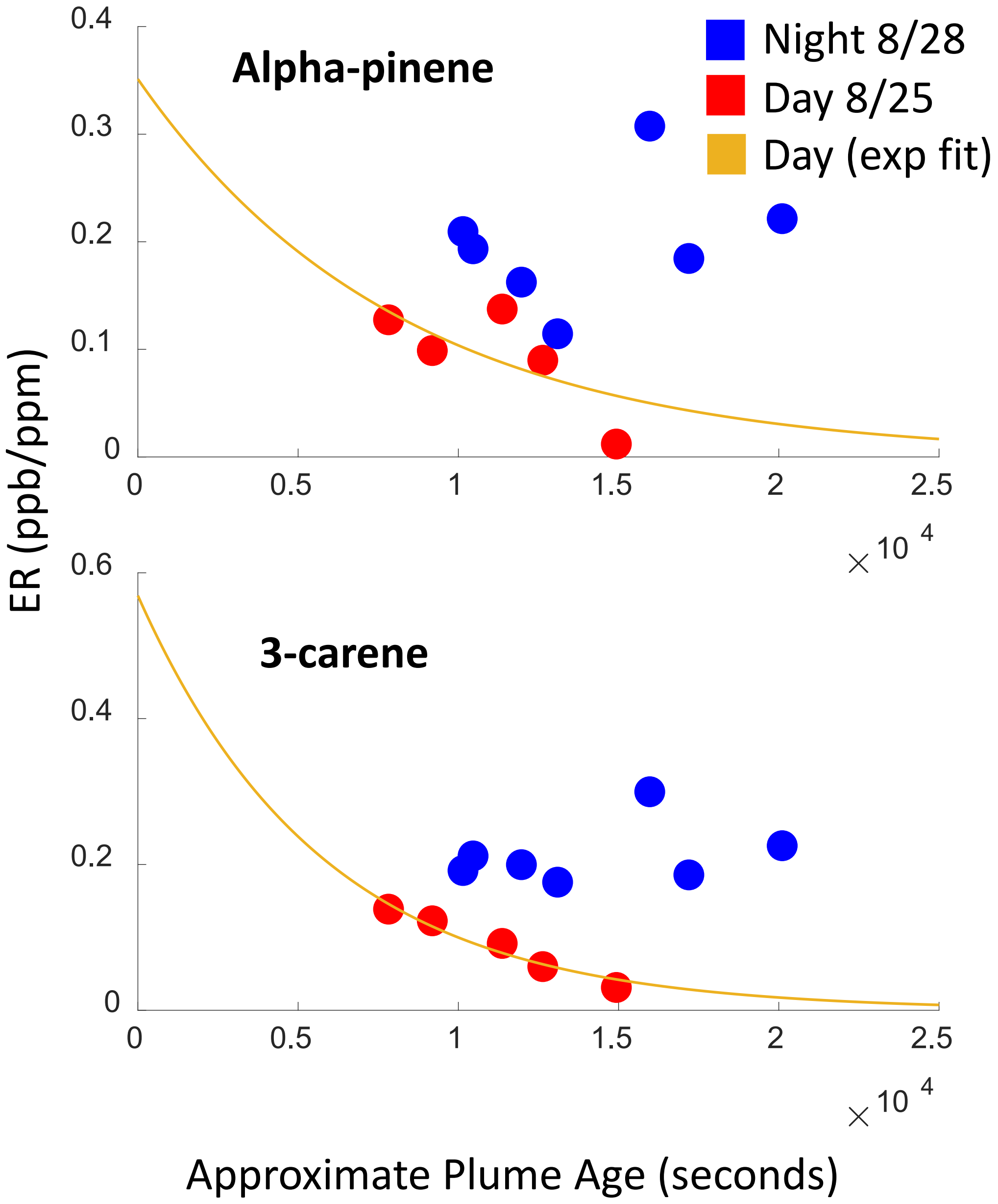
Cow Fire 8/25 Sunset Flight



Cow Fire 8/28 Night Flight



Determining Emission Ratios and Oxidant Concentrations



-Emission ratios (ER), calculated using average transect CO, can be helpful in understanding in plume chemistry

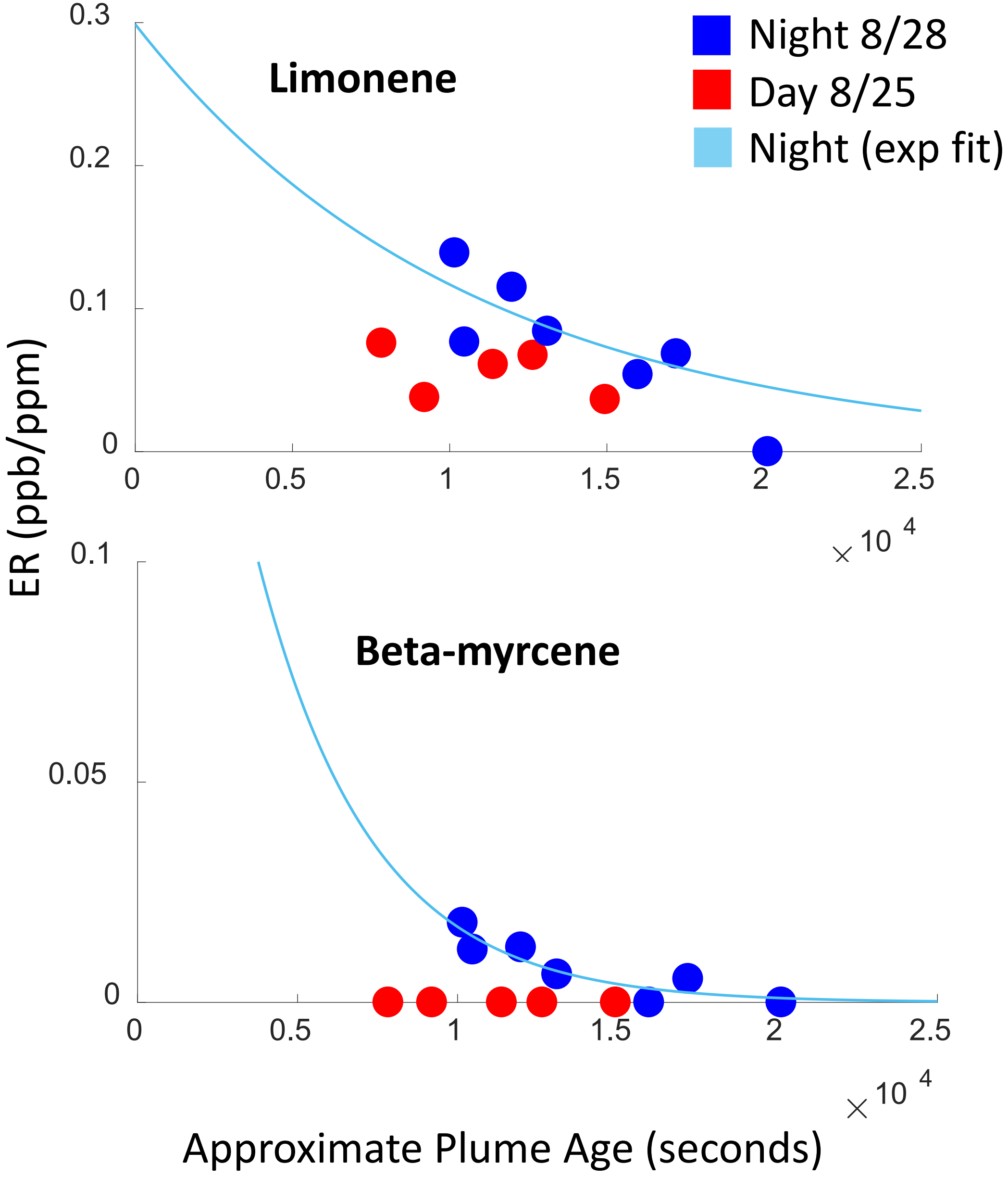
-By fitting an exponential curve to the daytime flight data, we can estimate:
1) ER at time=0
2) OH concentration (if rate constant is known, neglecting ozone)

-NOTE: Plume ages are approximations, NOT the values that were recently shared

A=Ao*exp(-k*OH*t)

Compound	Estimated OH (molecules/cm^3)
Alpha-pinene	2.3x10^6
Beta-pinene	1.7x10^6
Sabinene	7.4*10^5
Beta-phellandrene	6.5*10^5
3-carene	2.0*10^6

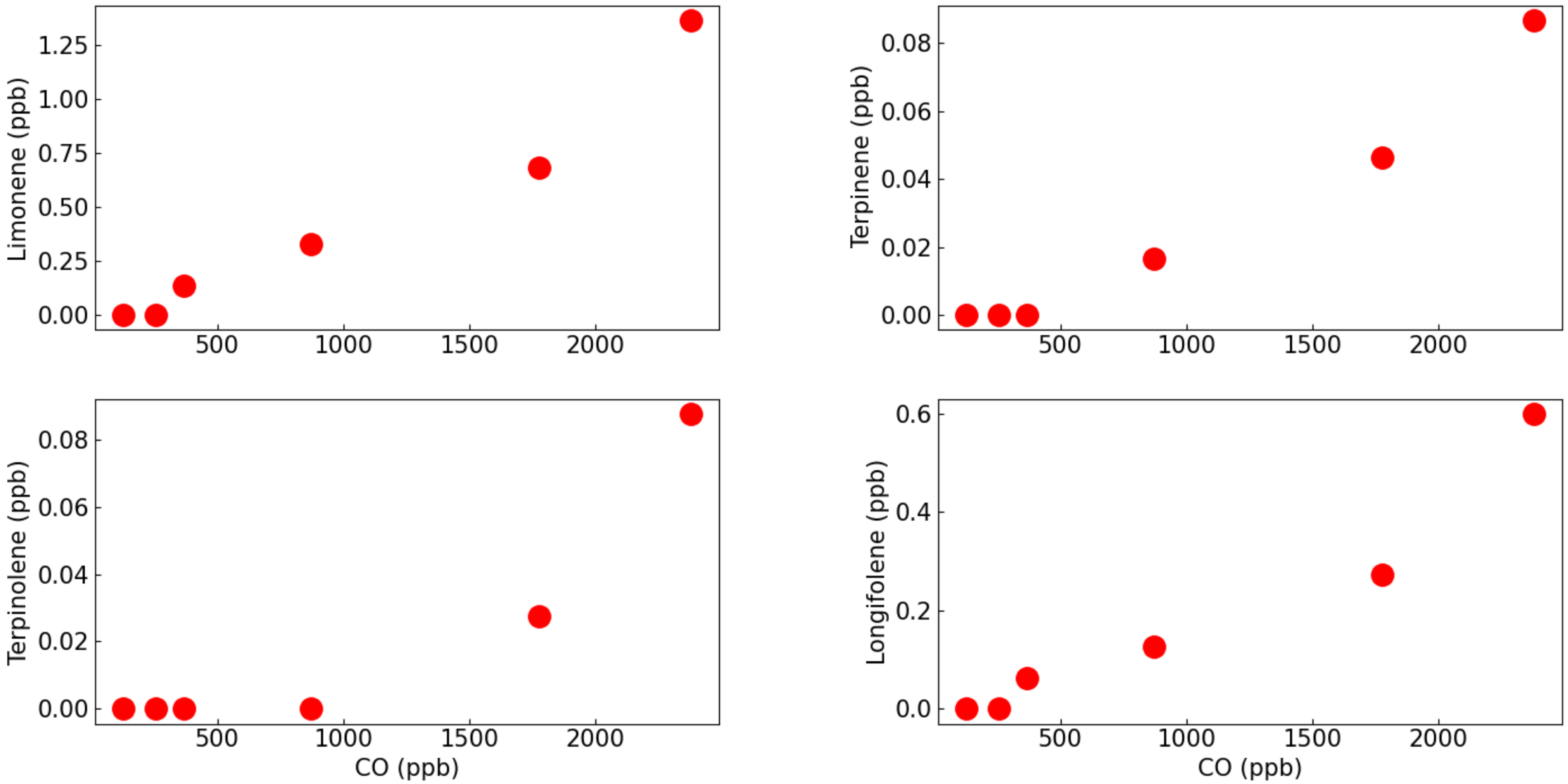
Determining Emission Ratios and Oxidant Concentrations



-This curve fitting method was applied to compounds that showed obvious nighttime decay to estimate average nitrate radical concentration

Compound	Estimated NO3 (molecules/cm^3)
Beta-myrcene	2.4*10^7
2,5 Dimethylfuran	5.5*10^6
Limonene	8.4*10^6
Indene	3.9*10^7

Ground Based in-plume Terpene Measurements (Aerodyne Mobile Lab)



- Terpene emissions trend well with CO
- Ground-based measurements will be compared to airborne measurements

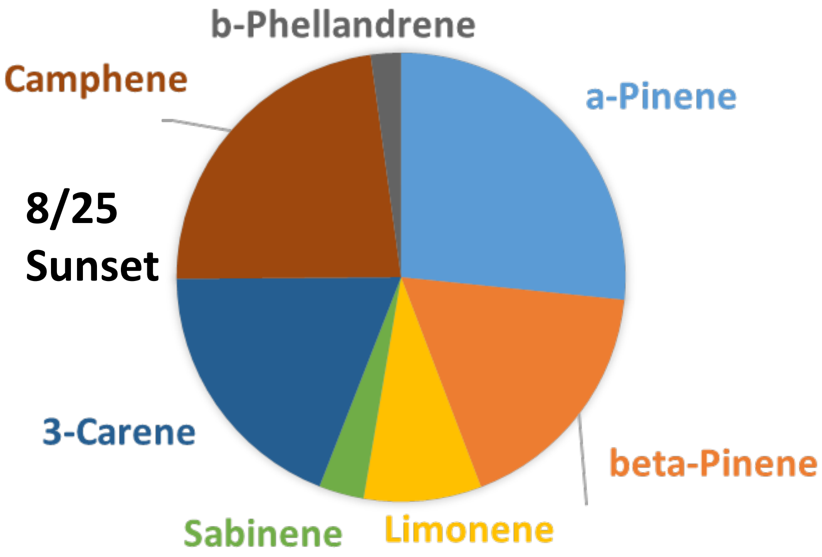
Fires sampled:
Nethker
Castle (Arizona)
Ikes (Arizona)
Cow (Oregon)

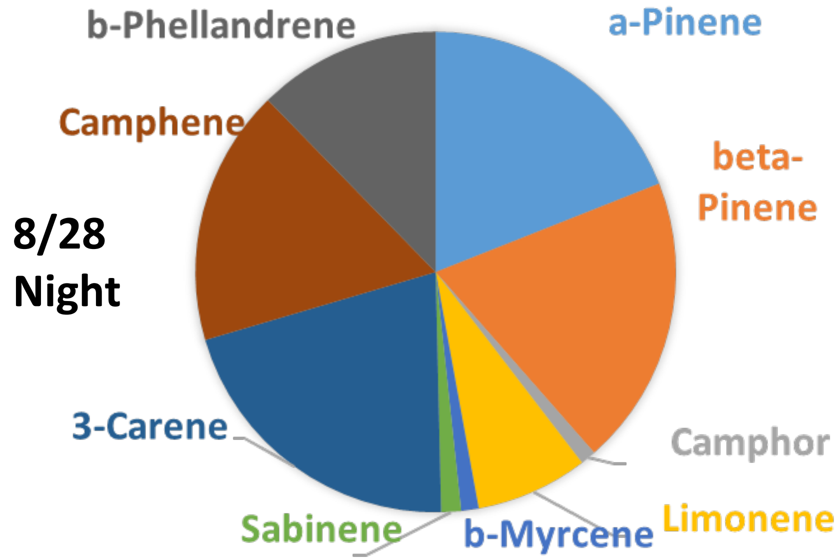
Compound	Airborne ER (Twin Otter, 8/25)	Airborne ER (Akagi et al.)	Ground ER (Aerodyne Mobile Lab)	Ground ER (Akagi et al.)
Alpha-pinene	3.5E-04	1.9E-04 to 2.3E-04	TBD	3.4E-05 to 5.8E-03
Beta-pinene	2.7E-04	6.1E-05 to 1.6E-04	TBD	1.2E-04 to 6.1E-04
Limonene	4.7E-04	1.7E-04 to 6.4E-03	TBD	3.8E-03 to 5E-03
Carene	5.7E-04	1.5E-05 to 3.7E-04	TBD	1.5E-04 to 1.6E-04
Myrcene	4.9E-05	1.5E-05	TBD	9.8E-05
Sabinene	5.2E-05	-	TBD	
Beta-phellandrene	4.9E-05	-	TBD	

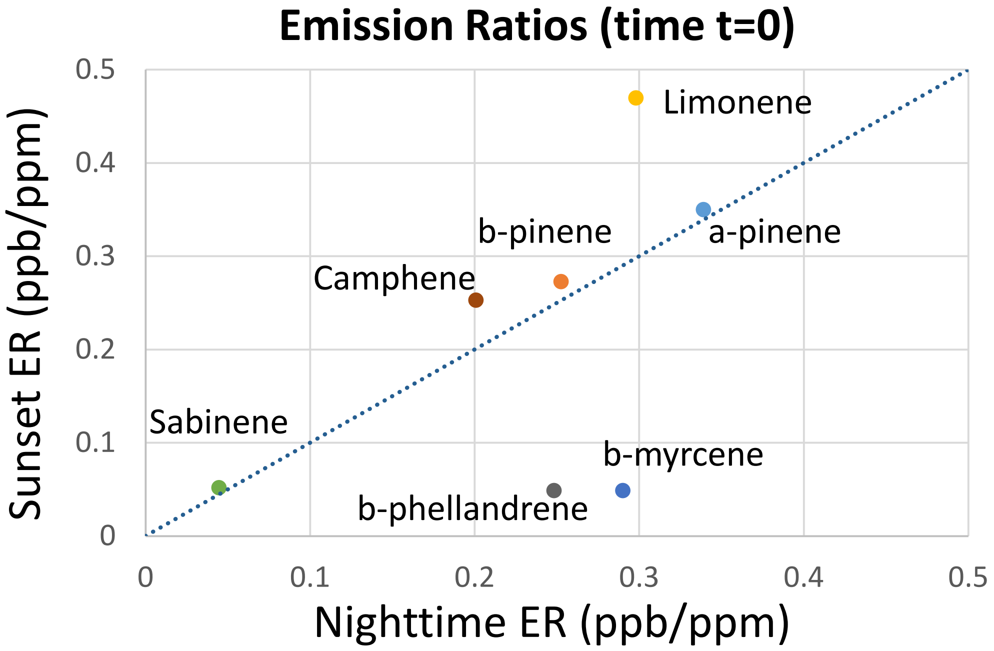
ER in ppbVOC/ppbCO

Terpene Composition Day v Night

Composition at t=3 hrs







-Limonene ER higher during daytime
-B-phellandrene and b-myrcene ERs higher during nighttime
-Could provide insight into how fire activity impacts emissions (day v night)

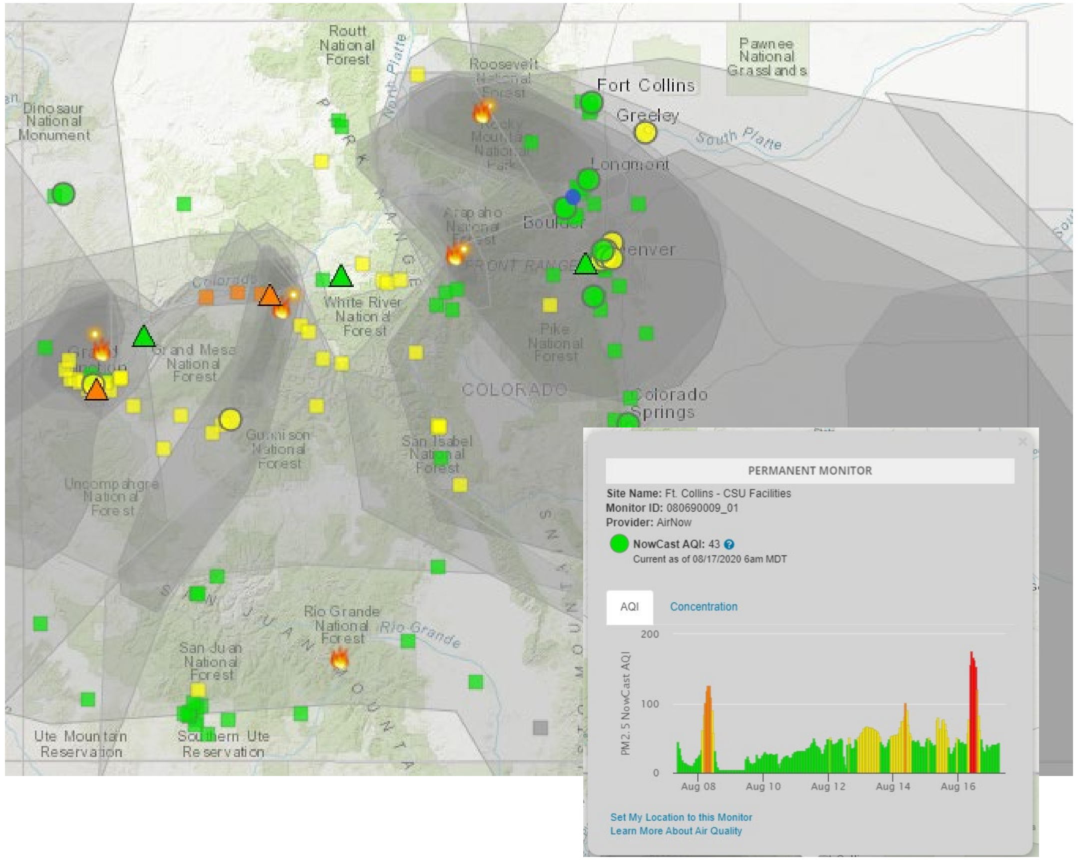
Next Steps:

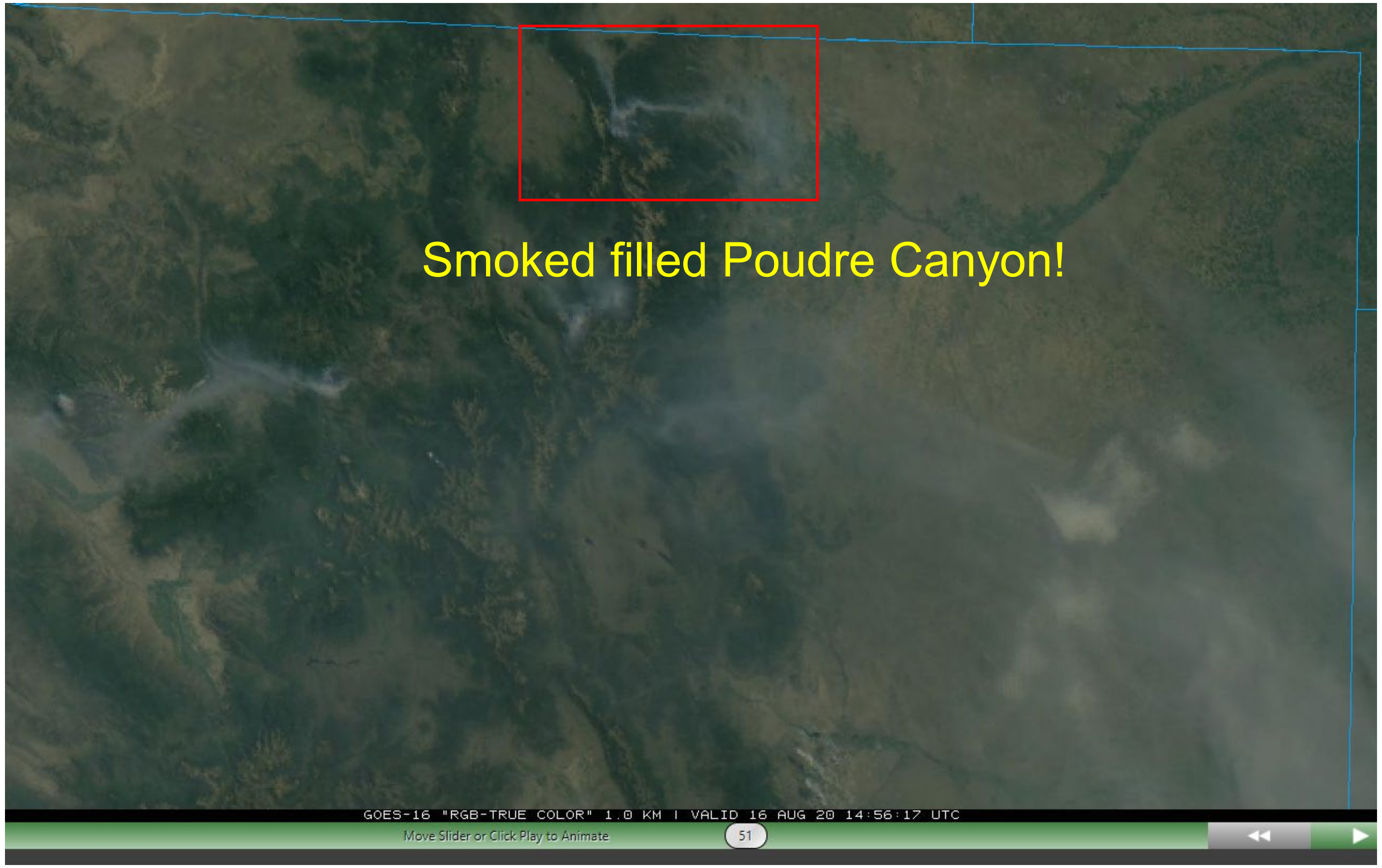
- Continue calculating ERs, taking into account ozone reactivity
- Calculate terpene ERs for ground samples
- Investigate vertical plume distribution and ERs of terpenes
- Distribute terpene mass across plume transect using CIMS signal – provide insight into terpene chemistry across plume transect
- Probe the impact of in plume terpenes on air quality: modeling ozone, SOA, org-nitrate formation
- Apply fuel-based chemical fingerprinting and machine learning techniques to twin otter samples

Variability and diel dependence of O_3-NO_x-VOC chemistry in western wildfire plumes: Results from the NOAA Twin Otter

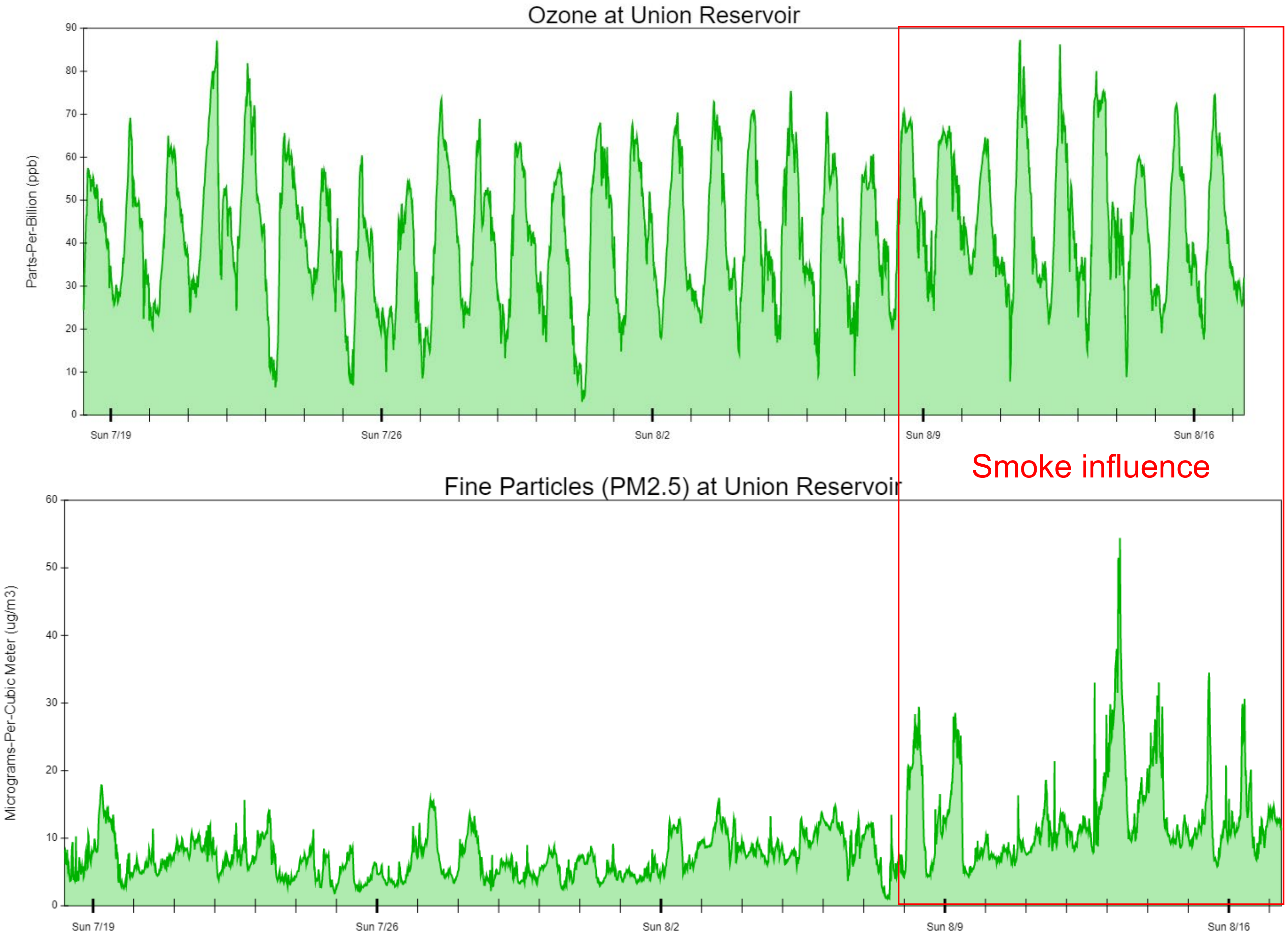
Michael A. Robinson, Zachary Decker, Kelley C. Barsanti, Matthew M. Coggon, Frank Flocke, Carly Fredrickson, Christopher Holmes, Avi Lavi, Denise Monksta, Brett B. Palm, Joel A. Thornton, Geoff Tyndall, Paul Van Rooy, Rebecca H. Schwantes, Andrew Wenhiemer, and Steven S. Brown

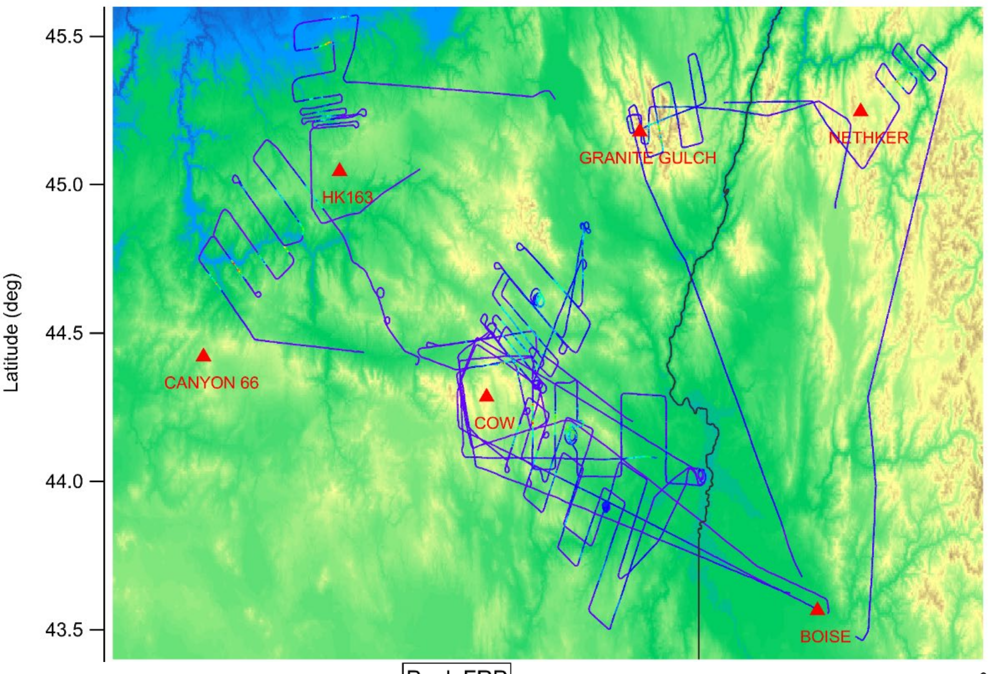
A quick look at the current situation

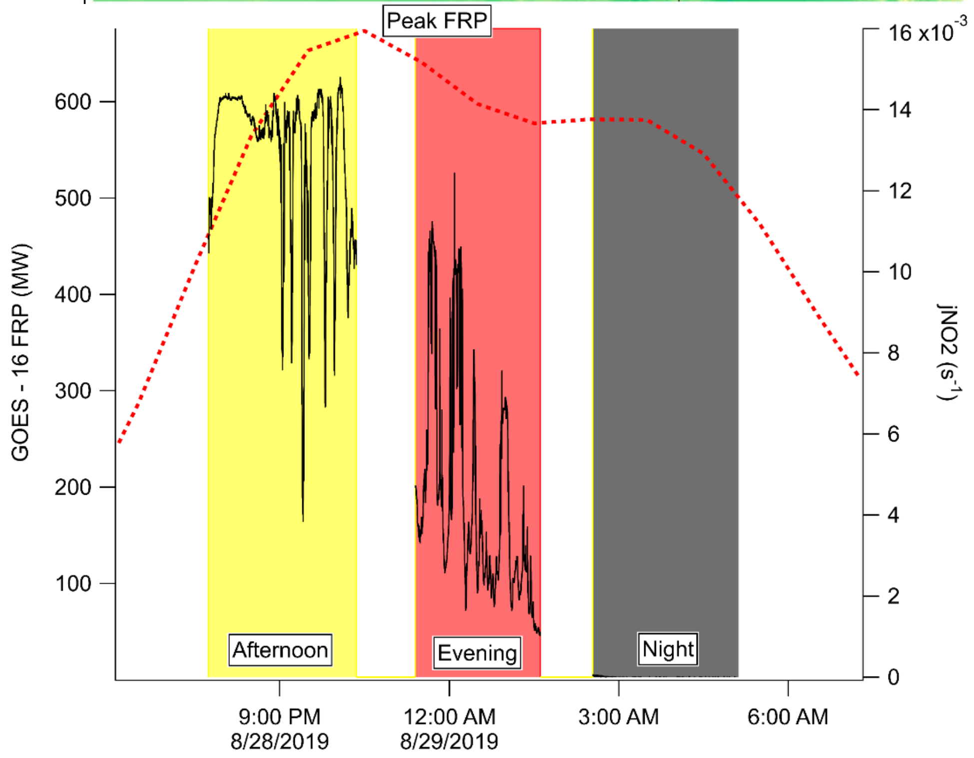




10 active fires in CO this morning.

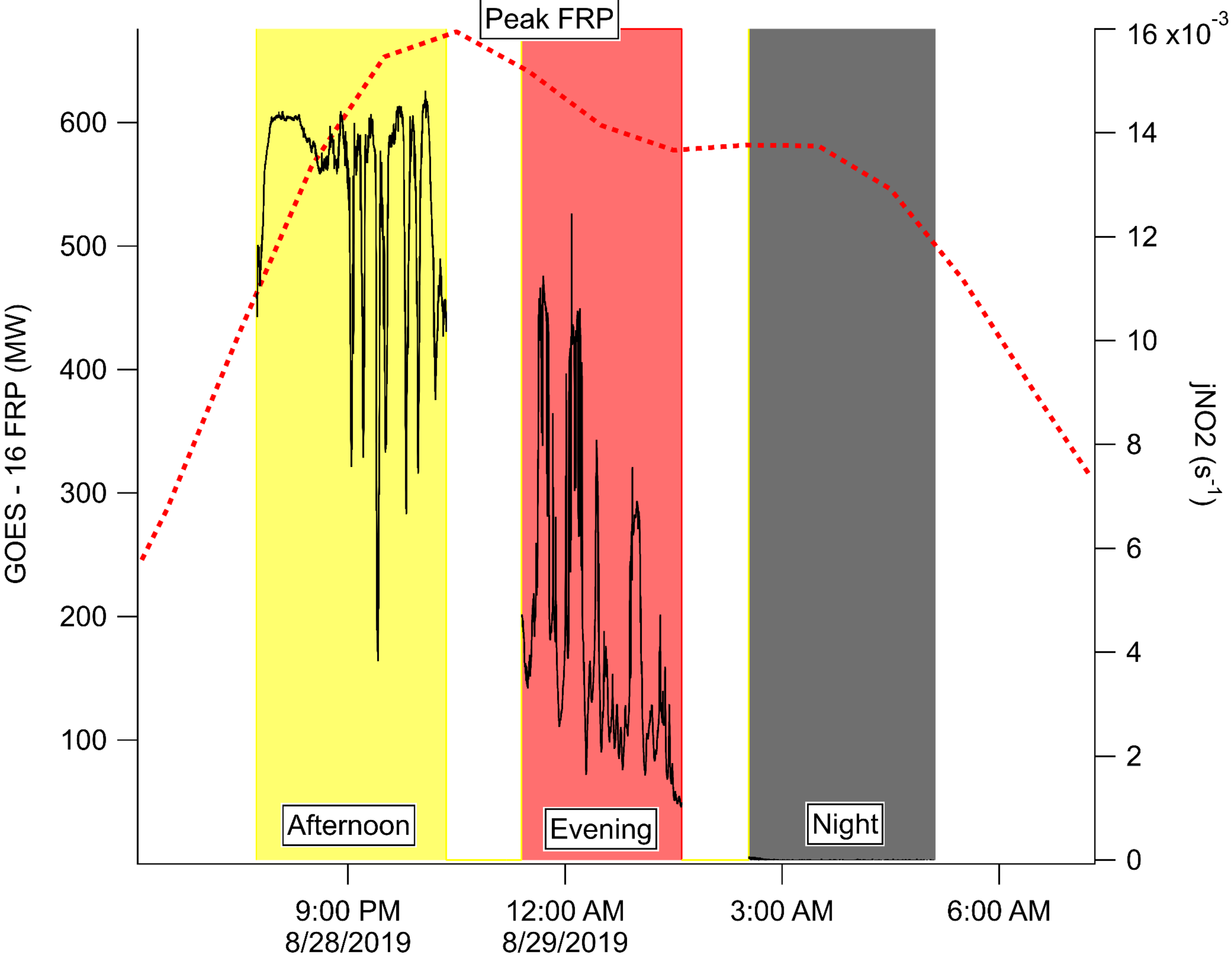

Ozone at Union Reservoir
Parts-Per-Billion (ppb)
90
80
70
60
50
40
30
20
10
0
Sun 7/19
Sun 7/26
Sun 8/2
Sun 8/9
Sun 8/16
Smoke influence
Fine Particles (PM2.5) at Union Reservoir
Micrograms-Per-Cubic Meter (ug/m3)
60
50
40
30
20
10
0
Sun 7/19
Sun 7/26
Sun 8/2
Sun 8/9
Sun 8/16





Chemistry Twin Otter Photochemical Flights

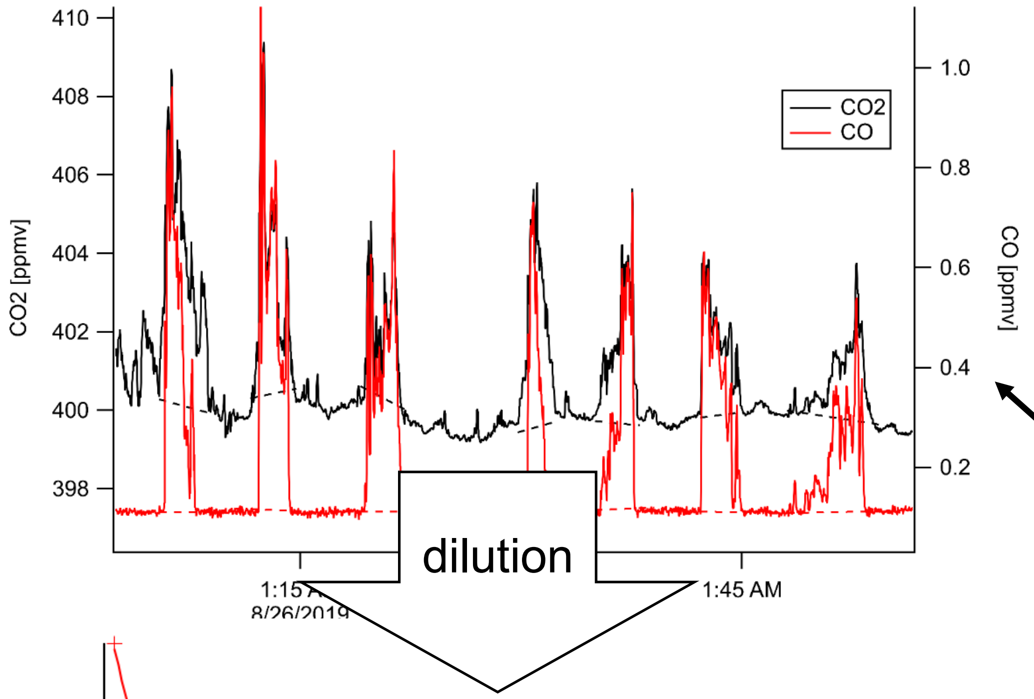
Date	Fire Name	State	Local Time	Lat	Long	Burn Size Acres	Fuel	FRP	No. Trans	Time of Day	Average jNO_2
8/9/19	HK 163	OR	11:58 14:31	45.045	-119.462	2696	PP	n/a	4	Afternoon	0.0123 ± 2.21e-05
8/9/19	Nethker	ID	15:26 17:40	45.245	-115.930	2000	DF PP	241	3	Afternoon	0.0119 ± 3.74e-05
8/16/19	Granite Gulch	OR	15:17 17:40	45.178	-117.427	2000	DF PP	80	3	Afternoon	0.0130 ± 1.38e-05
8/20/19	Little Bear	UT	16:45 19:19	37.589	-112.320	1360	WF GO	206	4	Afternoon	0.00843 ± 2.51e-05
8/21/19	Castle	AZ	18:03 20:47	36.531	-112.228	19368	XT	61	8	Evening	0.00240 ± 2.54e-05
8/25/19	COW 1 COW 2	OR	14:38 17:19 18:12 20:52	44.285	-118.460	1650	SF	92	4 4	Afternoon Evening	0.0130 ± 1.29e-05 0.00454 ± 3.51e-05
8/27/19	COW 3	OR	13:57 16:31	44.285	-118.460	3441	SF	180	2	Afternoon	0.0139 ± 8.80e-06
8/28/19	COW 4	OR	17:24 19:37	44.285	-118.460	3781	SF	643	5	Evening	0.00434 ± 3.02e-05
9/3/19	COW 5 COW 6	OR	13:38 16:20 17:30 19:37	44.285	-118.460	8452	SF	159	5 3	Afternoon Evening	0.0131 ± 1.51e-05 0.00623 ± 3.20e-05
9/4/19	Canyon 66	OR	17:45 19:42	44.420	-120.385	2800	PP	311	4	Evening	0.00725 ± 3.48e-05

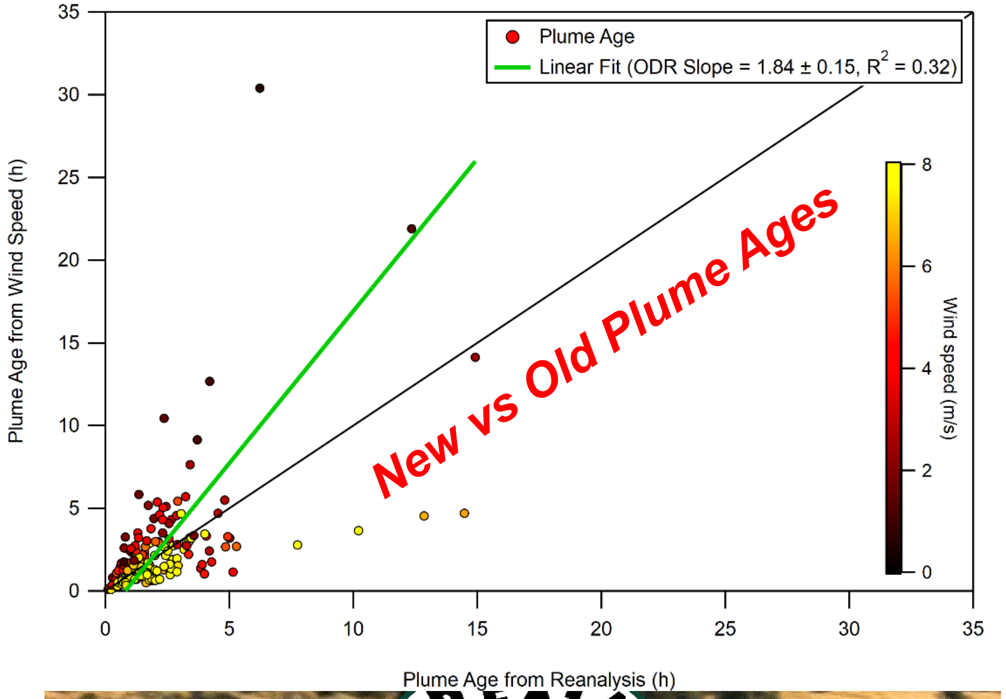


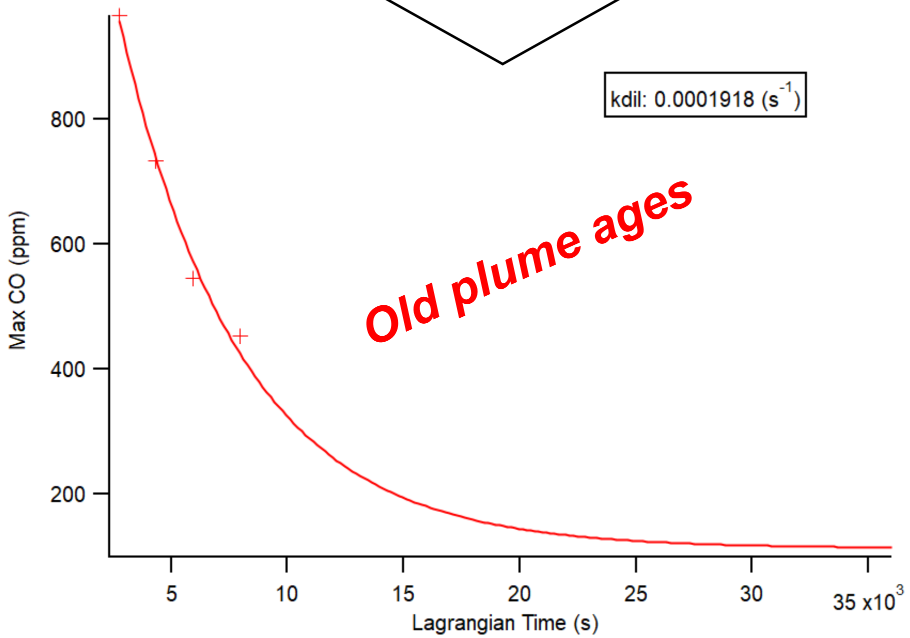
win Otter
cal Flights

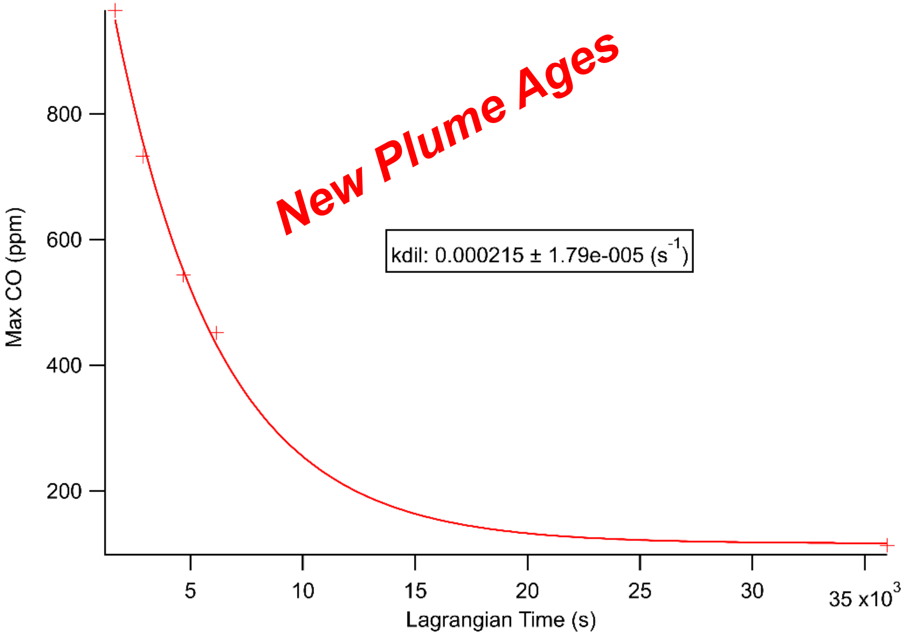
n e es	Fuel	FRP	No. Trans	Time of Day	Average jNO_2
6	PP	n/a	4	Afternoon	0.0123 ± 2.21e-05
0	DF PP	241	3	Afternoon	0.0119 ± 3.74e-05
0	DF PP	80	3	Afternoon	0.0130 ± 1.38e-05
0	WF GO	206	4	Afternoon	0.00843 ± 2.51e-05
68	XT	61	8	Evening	0.00240 ± 2.54e-05
0	SF	92	4 4	Afternoon Evening	0.0130 ± 1.29e-05 0.00454 ± 3.51e-05
1	SF	180	2	Afternoon	0.0139 ± 8.80e-06
1	SF	643	5	Evening	0.00434 ± 3.02e-05
2	SF	159	5 3	Afternoon Evening	0.0131 ± 1.51e-05 0.00623 ± 3.20e-05
0	PP	311	4	Evening	0.00725 ± 3.48e-05

Process Overview - updates







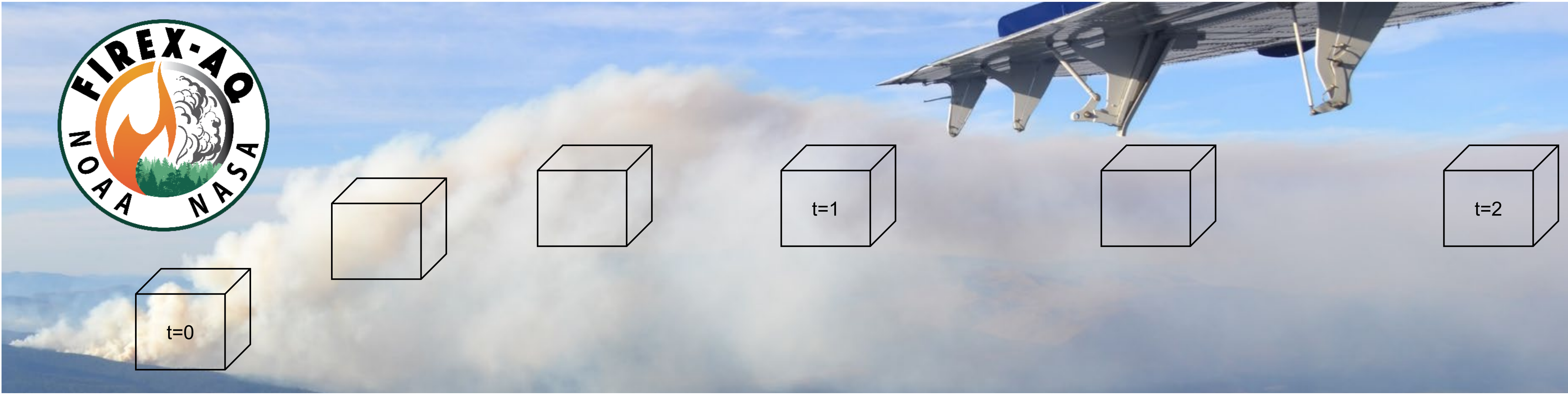


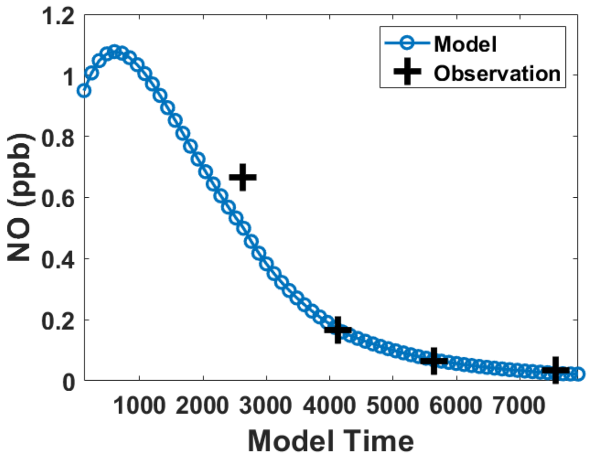
ressure, ~~Winds~~, ***plume ages***

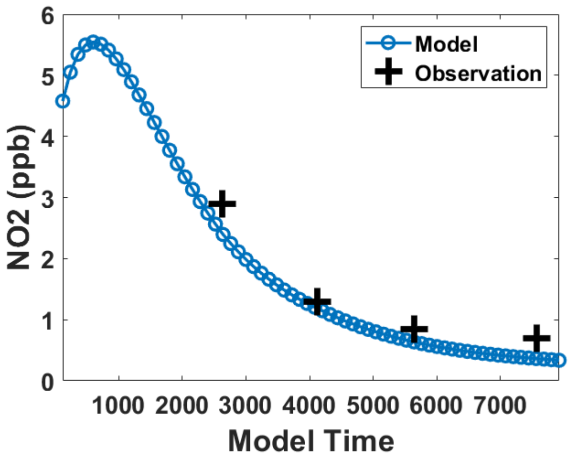
iol, Catechol, Cresol

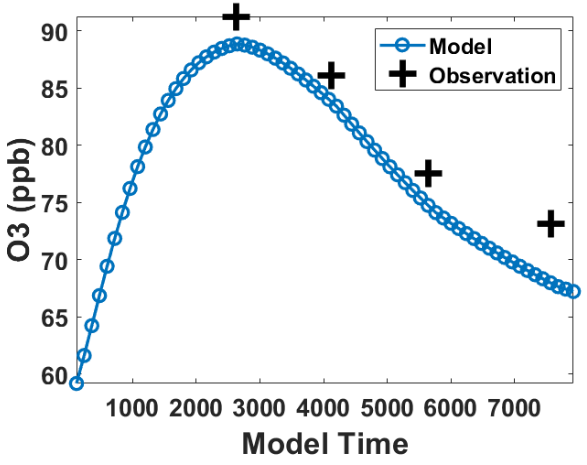
samples

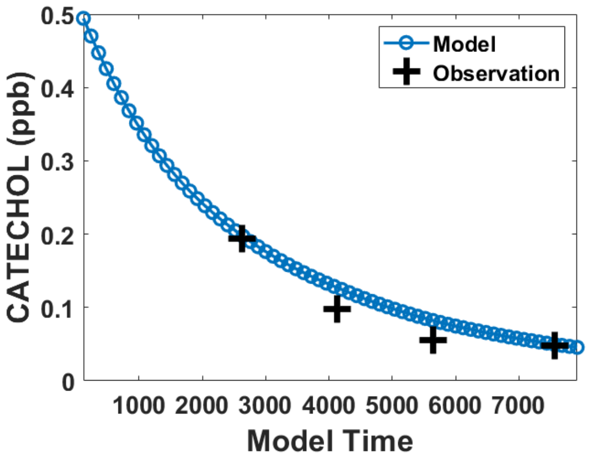
Iterative Box Model – what about t=0?



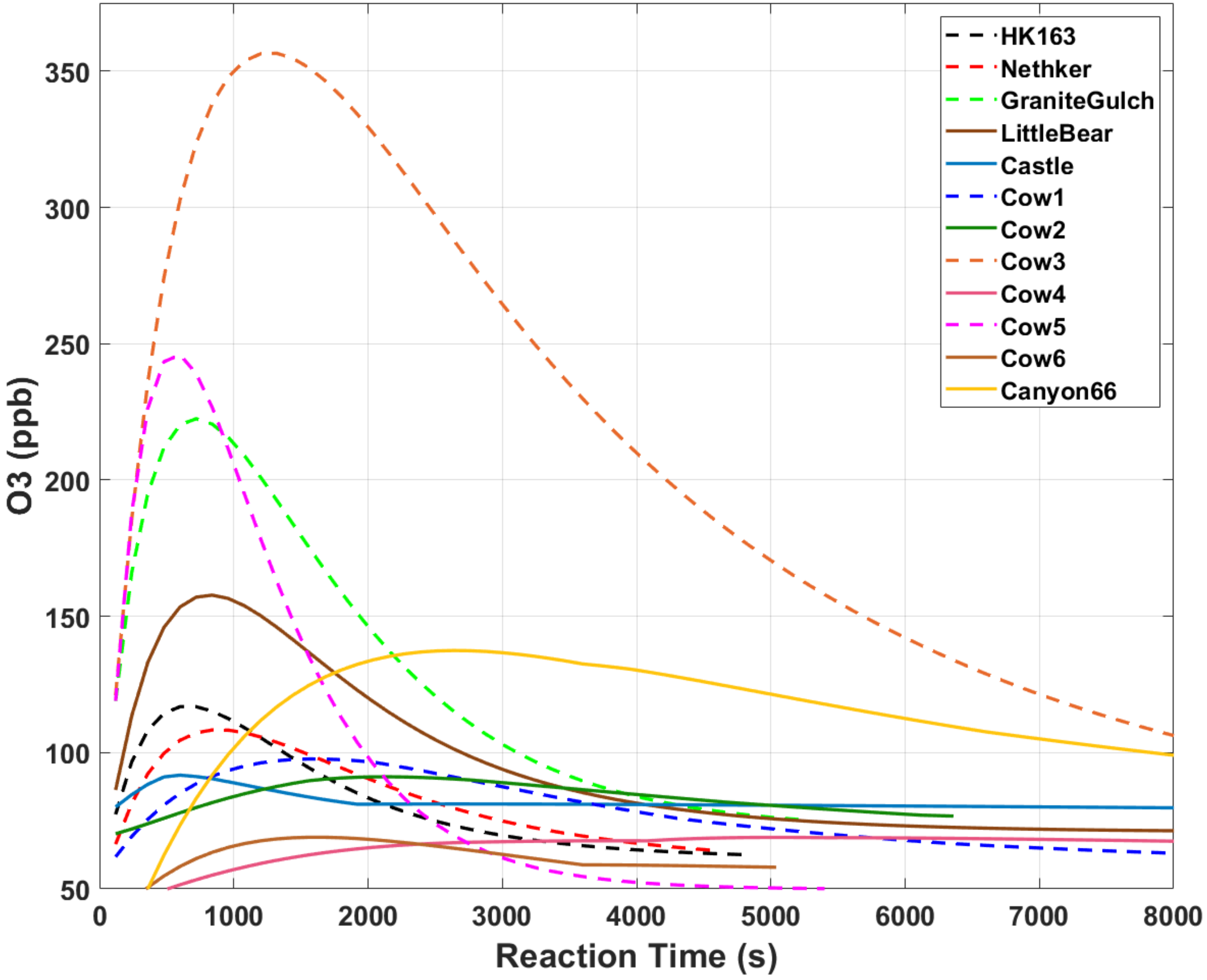






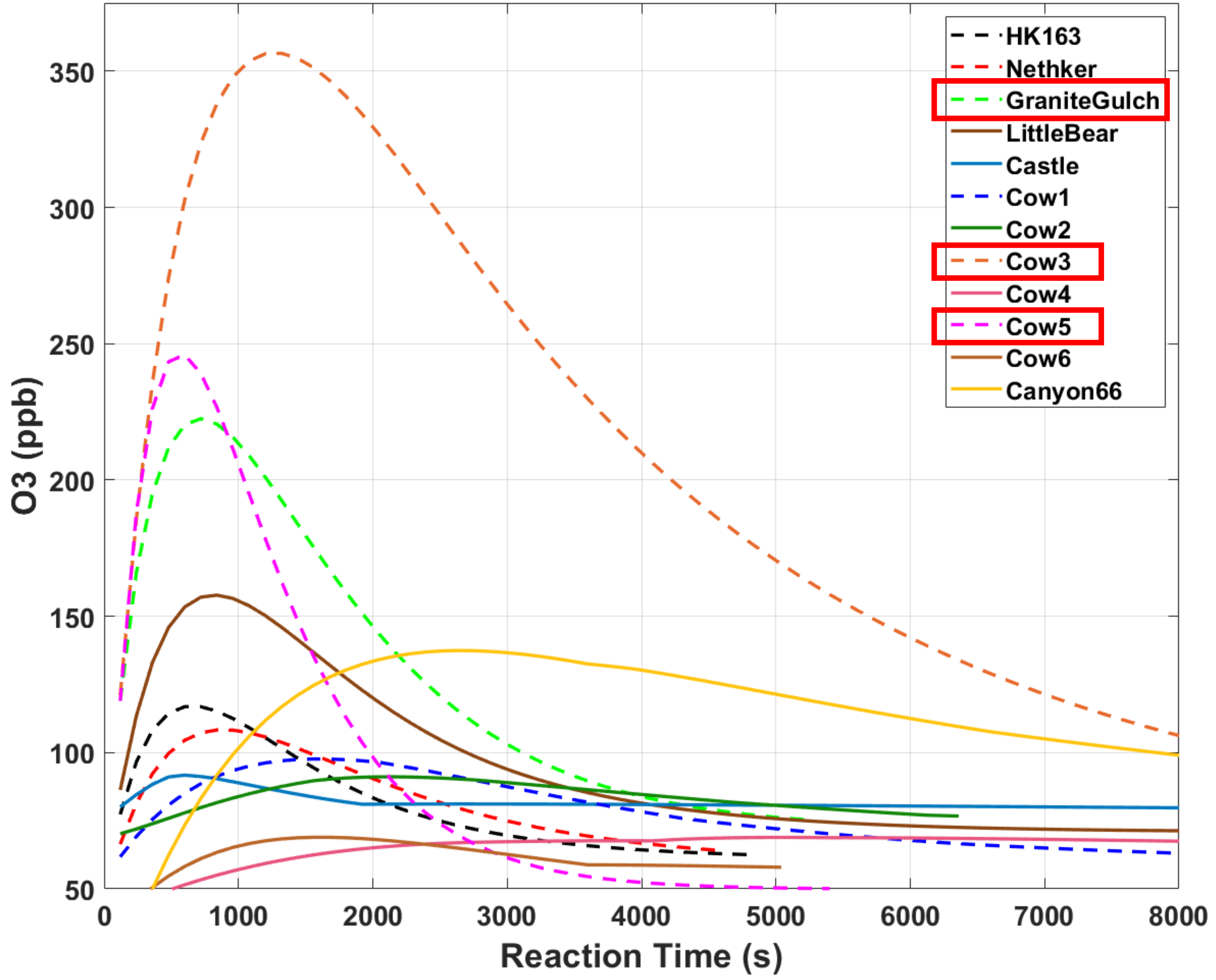


Ozone photochemistry is fast



- Maximum O_3 on average produced within ***24 minutes*** of emission
- Afternoon plumes produced maximum O_3 within ***15 minutes*** of emission
- Evening plumes produced maximum O_3 within ***35 minutes*** of emission

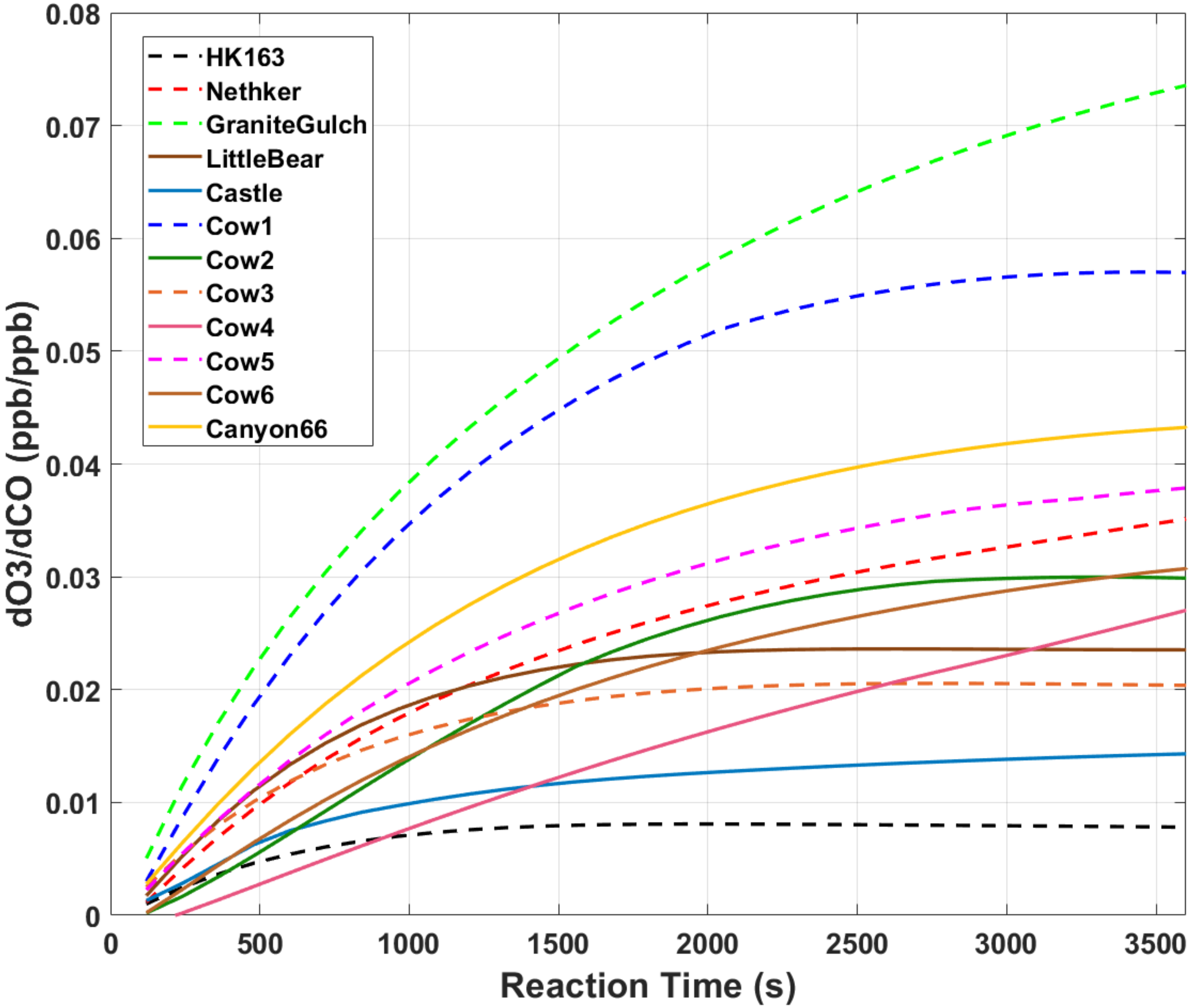
Ozone photochemistry is fast



- Maximum O_3 on average produced within ***24 minutes*** of emission
- Afternoon plumes produced maximum O_3 within ***15 minutes*** of emission
- Evening plumes produced maximum O_3 within ***35 minutes*** of emission

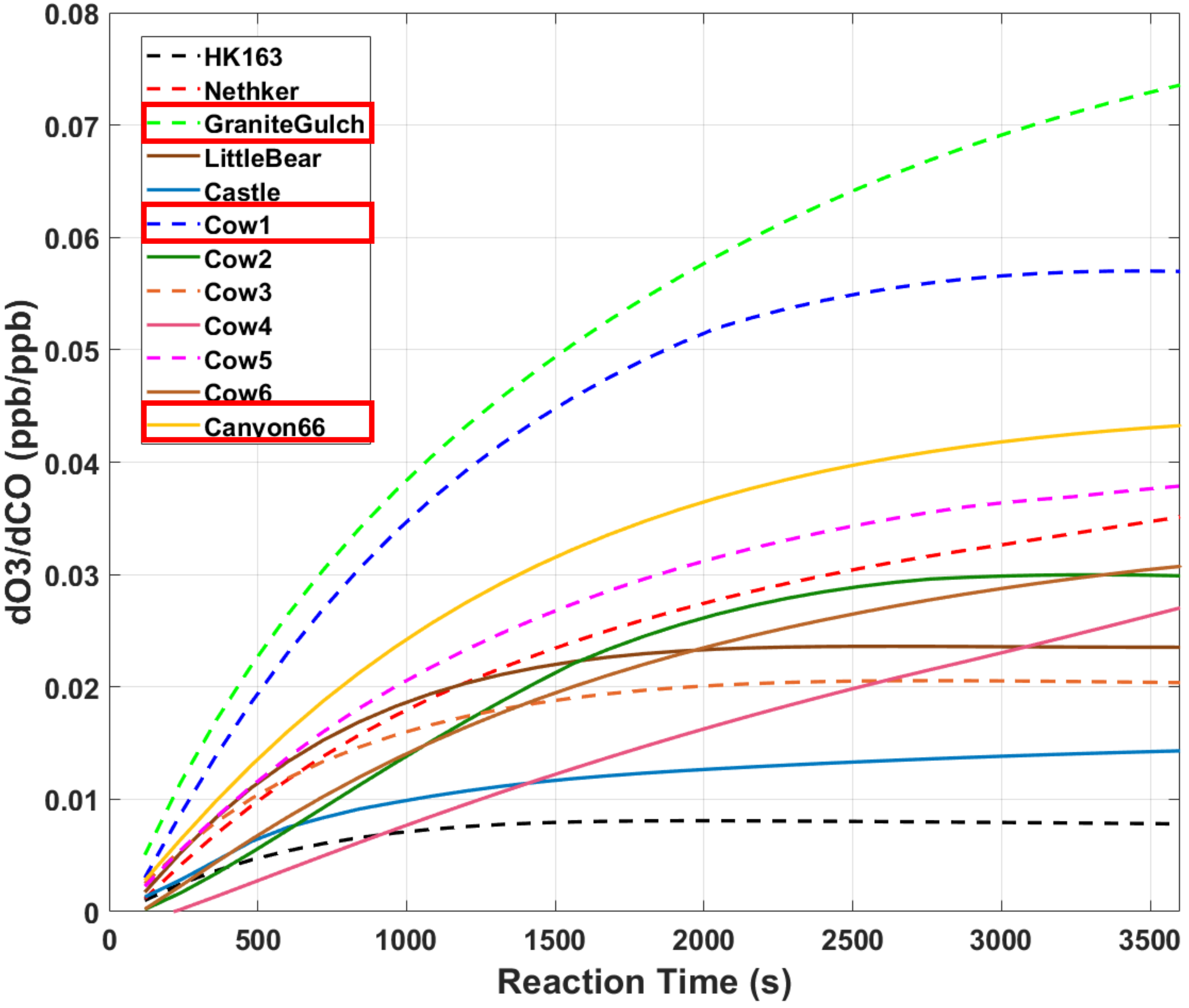
What happens when corrected for dilution?

- Different fires are more chemically productive when correcting for dilution.
- This takes into account any background entrainment of O_3
- Afternoon fires still stand out as highly productive photochemistry

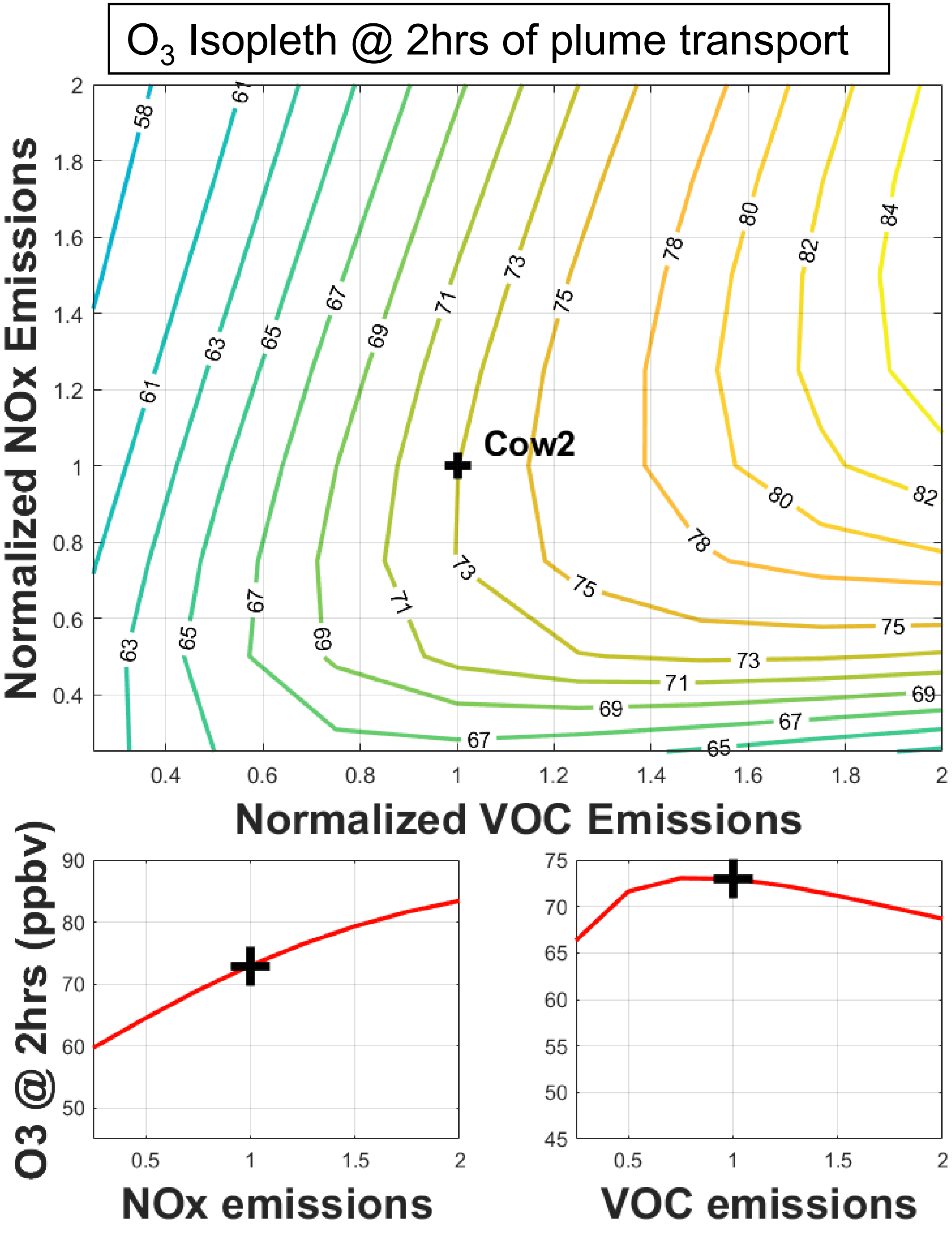


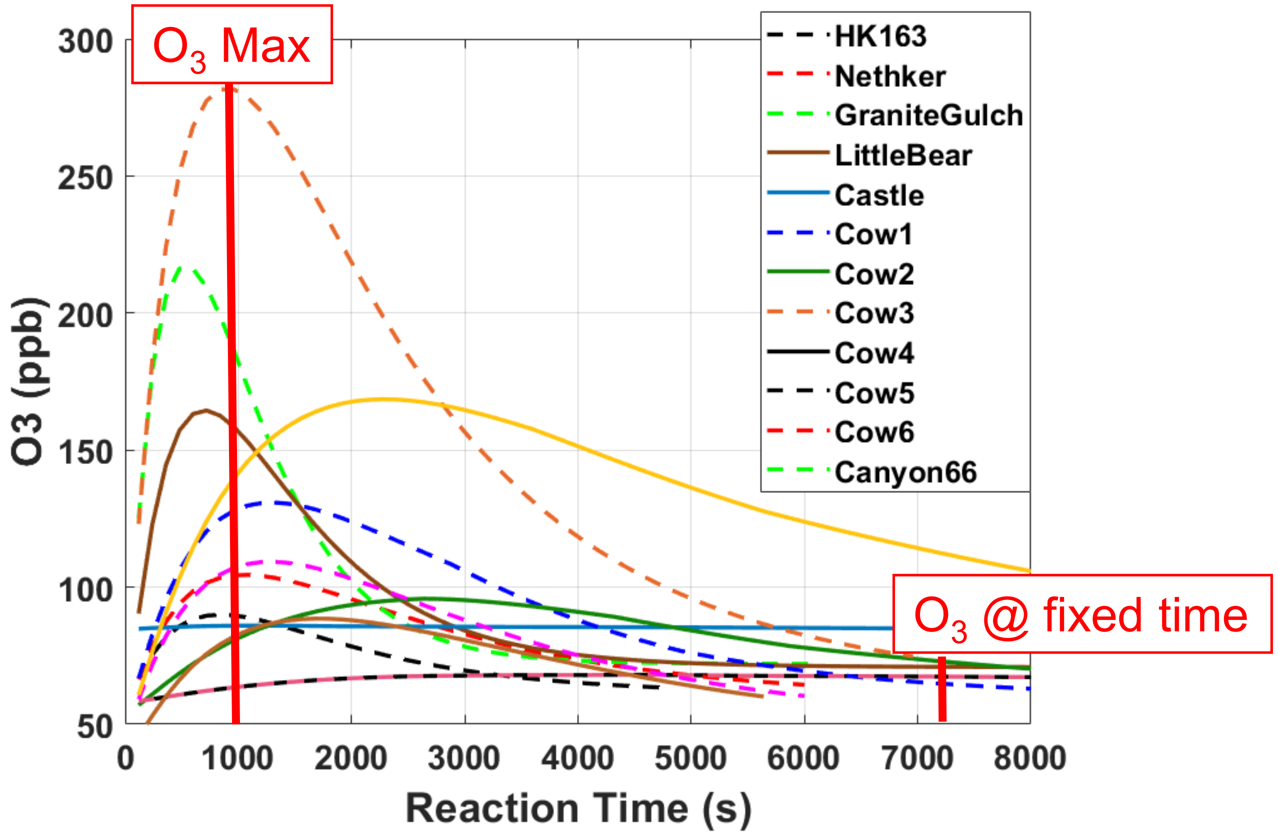
What happens when corrected for dilution?

- Different fires seem more chemically productive then when looking at maximum production
- This takes into account any background entrainment of O_3
- Afternoon fires still stand out as highly productive photochemistry

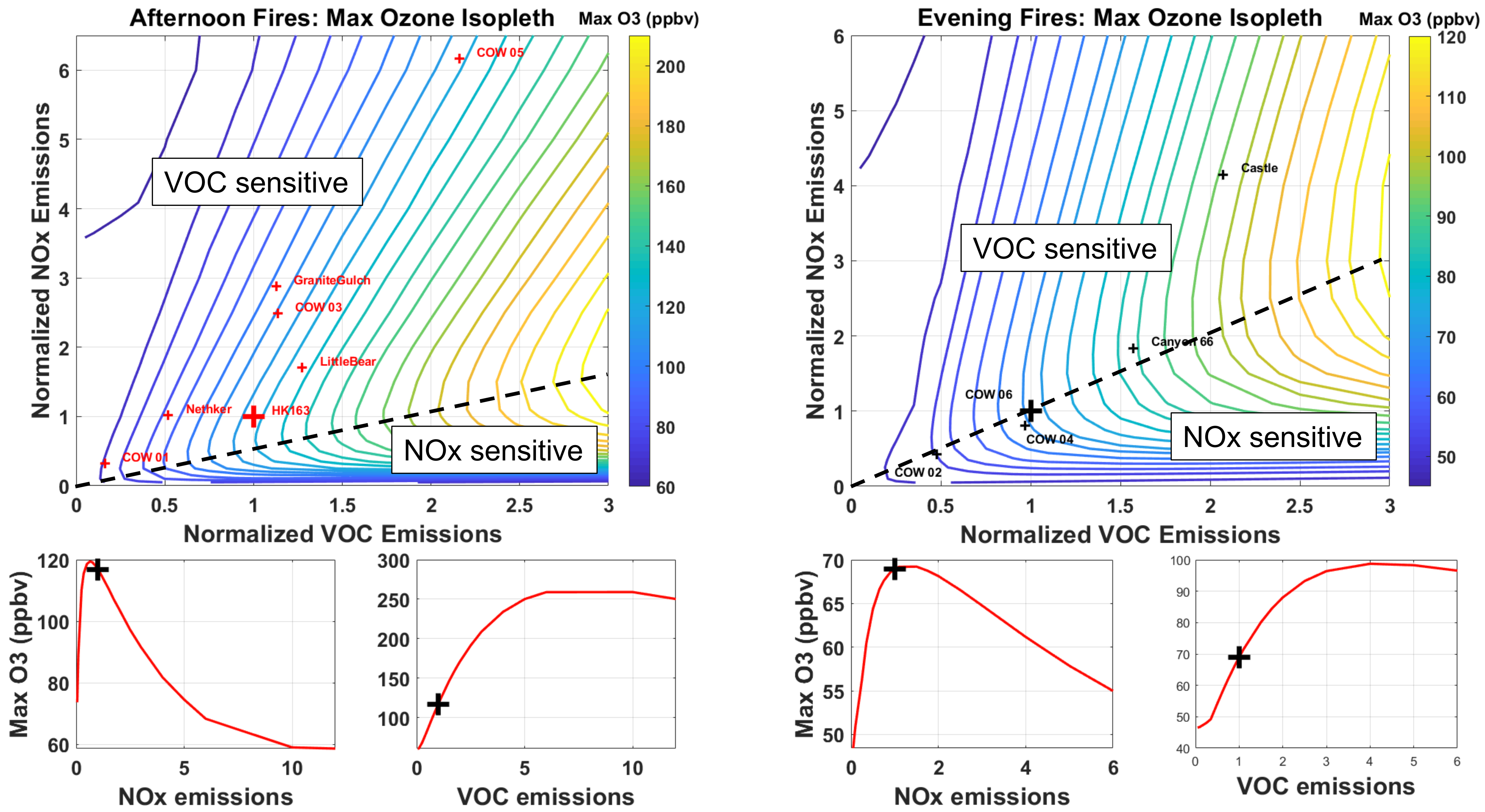


Western wildfires: O_3 isopleth?





- Isopleths are useful tools to understand the chemical domain of western wildfires even though we don't have emission controls like in the urban case



Afternoon Fires: Max Ozone Isopleth
Max O3 (ppbv)
VOC sensitive
NOx sensitive
COW 05
GraniteGulch
COW 03
LittleBear
Nethker
HK163
COW 01
Normalized NOx Emissions
Normalized VOC Emissions
Evening Fires: Max Ozone Isopleth
Max O3 (ppbv)
Castle
Canyon 66
COW 06
COW 04
COW 02
VOC sensitive
NOx sensitive
Normalized NOx Emissions
Normalized VOC Emissions
Max O3 (ppbv)
NOx emissions
VOC emissions
Max O3 (ppbv)
NOx emissions
VOC emissions

L_n/Q – a definition

$$Q = 2k_1[HO_2][HO_2] + 2k_2[HO_2][RO_2] + L_R + L_N$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \quad k_1$$

$$HO_2 + RO_2 \rightarrow ROOH + O_2 \quad k_2$$

L_R:

$$RO2 + R'O_2 \rightarrow$$

$$OH + HO_2 \rightarrow H_2O + O_2$$

L_n:

$$OH + NO_2 \rightarrow HNO_3$$

$$RO_2 + NO \rightarrow RONO_2 + M$$

$$RO_2 + NO_2 \rightarrow PAN$$

$$OH + Phenols \rightarrow \cdots RO' + NO_2 \rightarrow Nitro\ Aromatics$$

GEOPHYSICAL RESEARCH LETTERS, VOL. 24, NO. 18, PAGES 2299-2302, SEPTEMBER 15, 1997

Dependence of ozone production on NO and hydrocarbons in the troposphere

Lawrence I. Kleinman, Peter H. Daum, Jai H. Lee, Yin-Nan Lee, Linda J. Nunnermacker, Stephen R. Springston, and Leonard Newman

Environmental Chemistry Division, Department of Applied Science, Brookhaven National Laboratory, Upton, NY 11973

Judith Weinstein-Lloyd

Chemistry/Physics Department, SUNY/Old Westbury, Old Westbury, NY 11568

Sanford Sillman

Department of Atmospheric, Oceanic, and Space Sciences, University of Michigan, Ann Arbor, MI 48109

When:

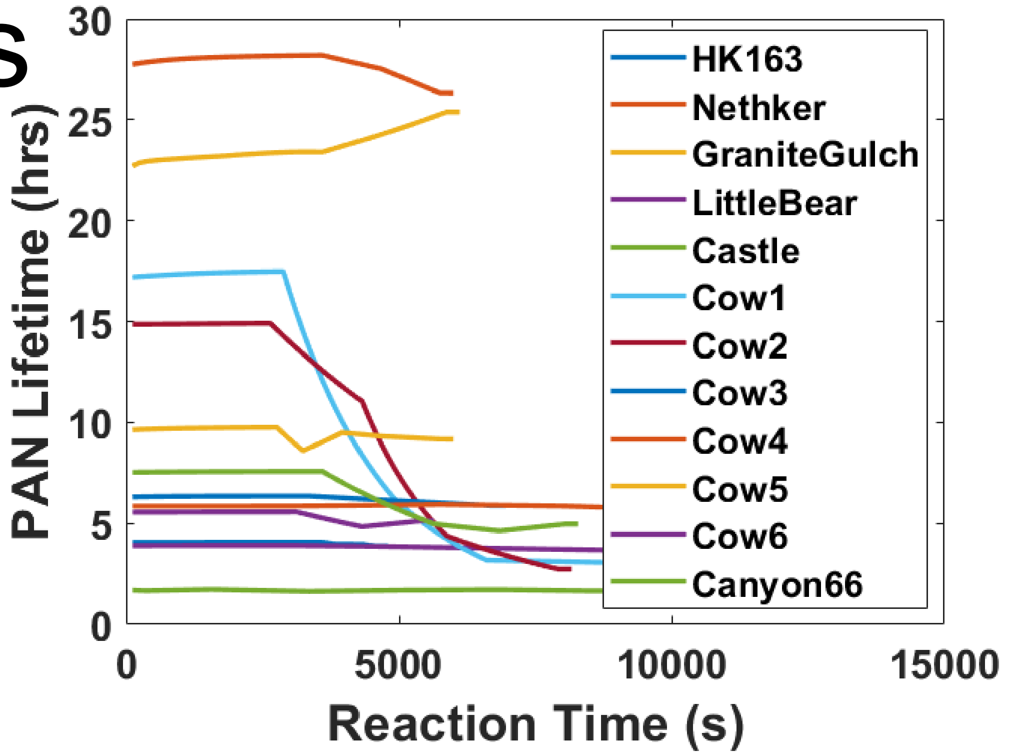
$$Q > L_n$$ NOx sensitive chemistry

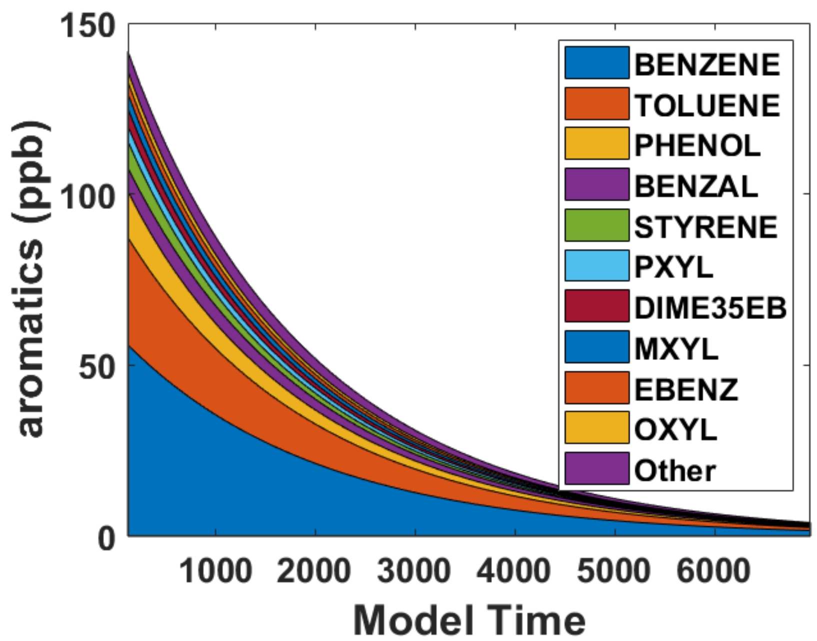
When:

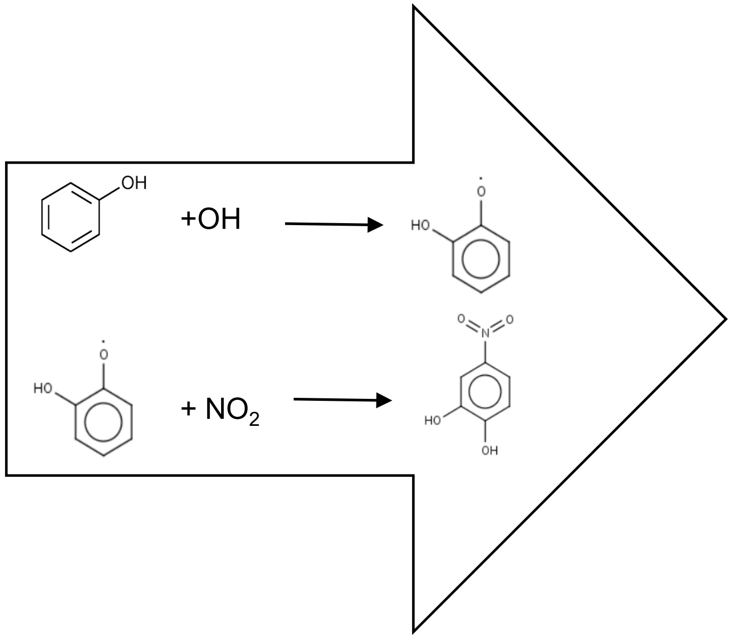
$$Q < L_n$$ VOC sensitive chemistry

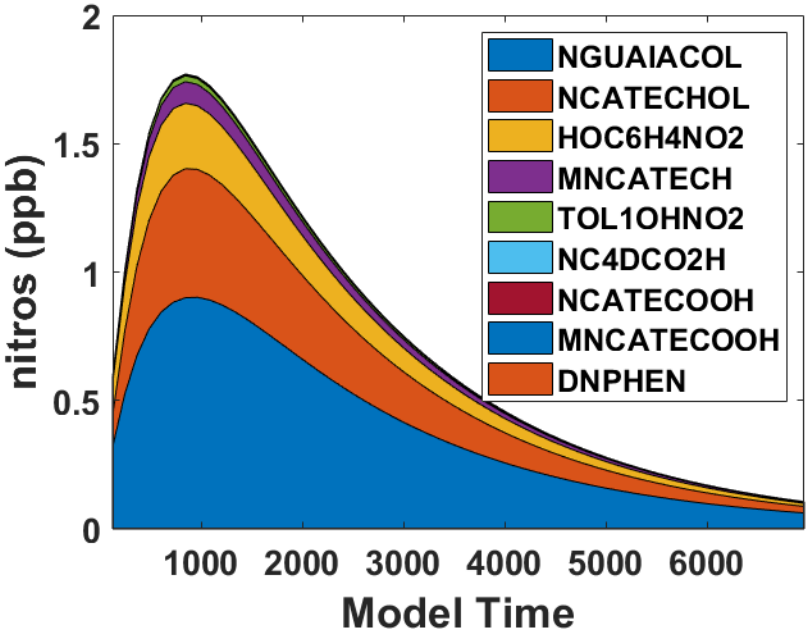
Changes to Ln for BB Plumes

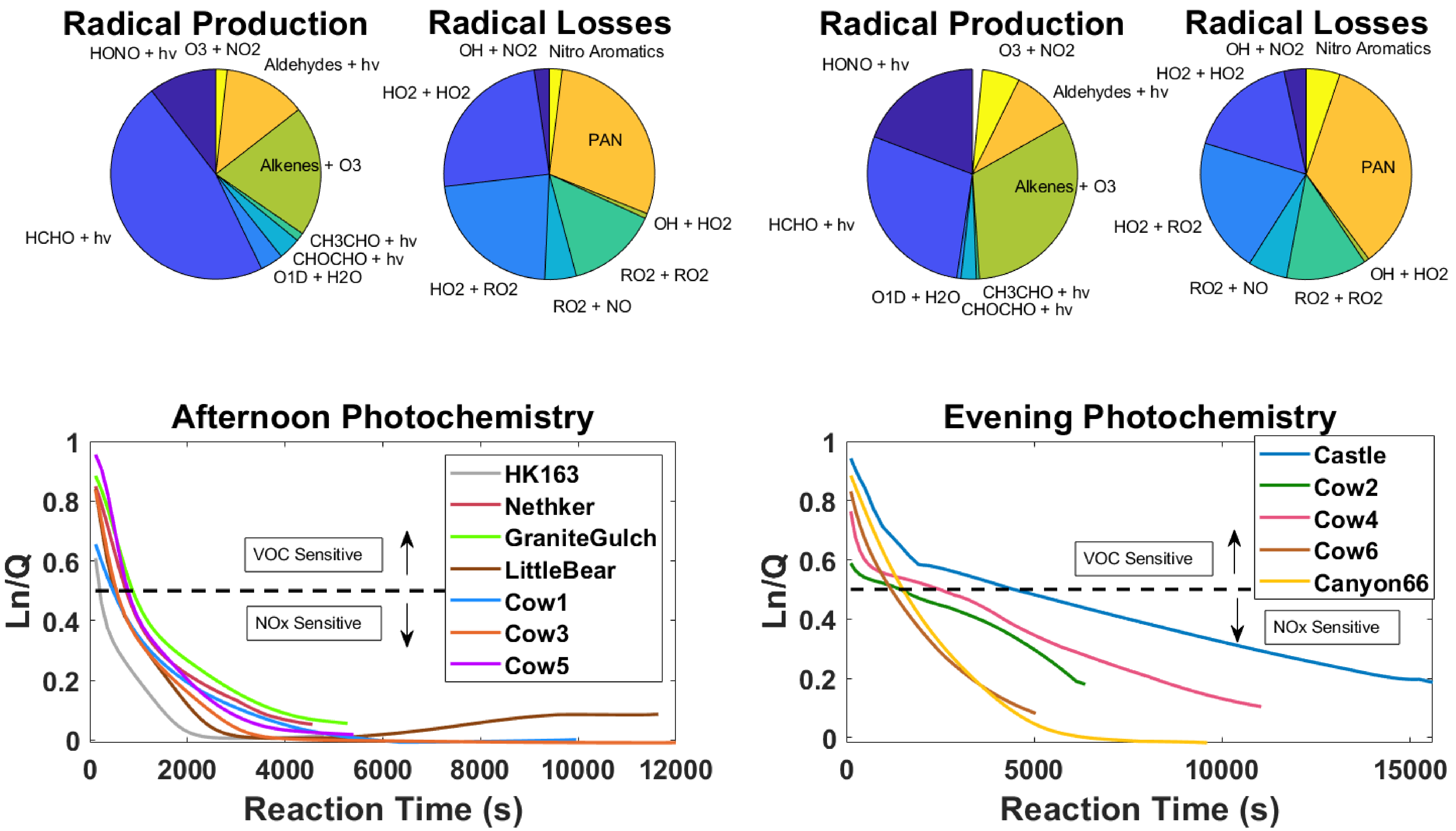
- PAN lifetimes are predicted to be long
  - Wildfire plumes sampled by the TO were relatively cool (2 to 11 degC)
- PAN formation is significant and fast
- Nitro aromatics are predicted to be a significant radical loss mechanism



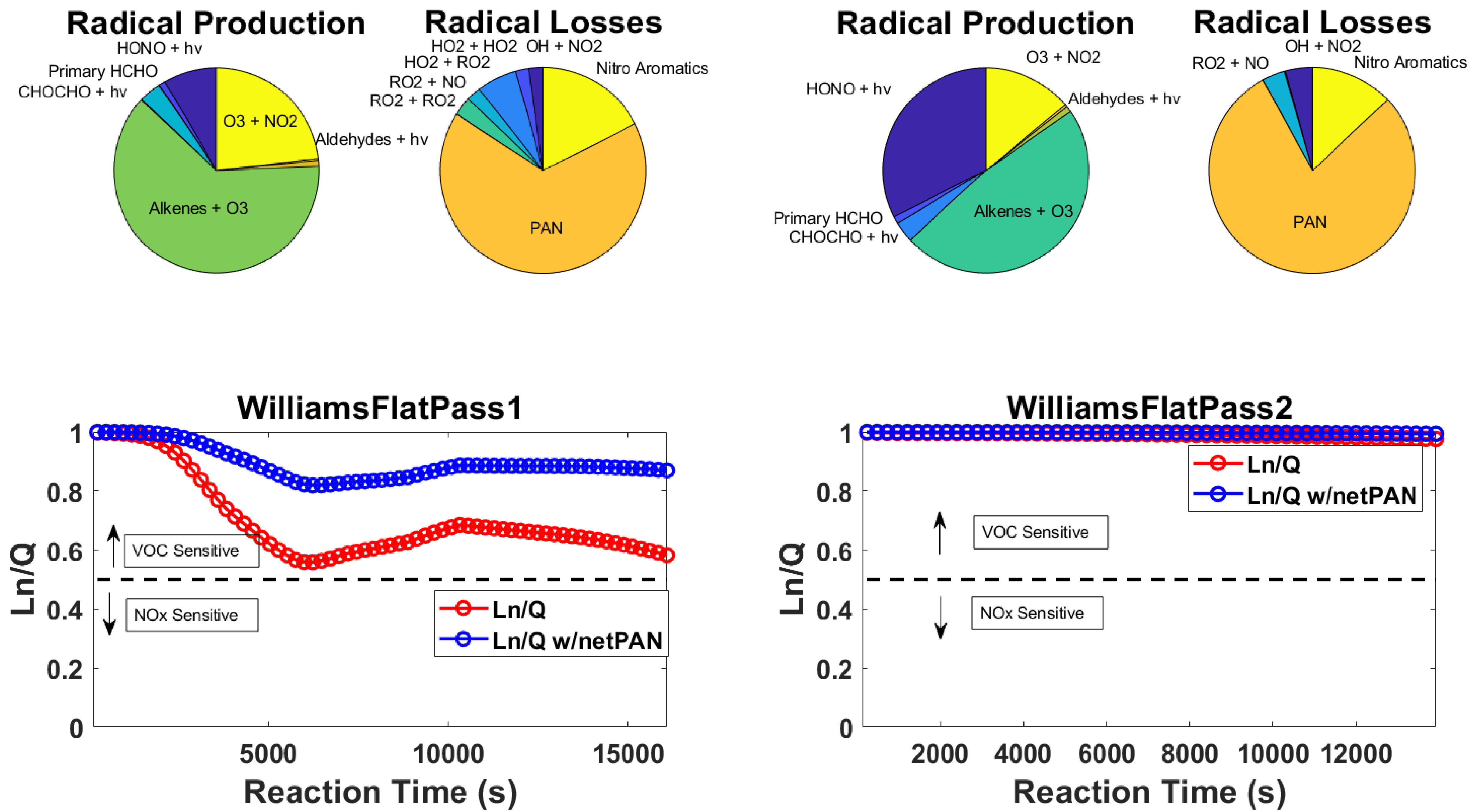






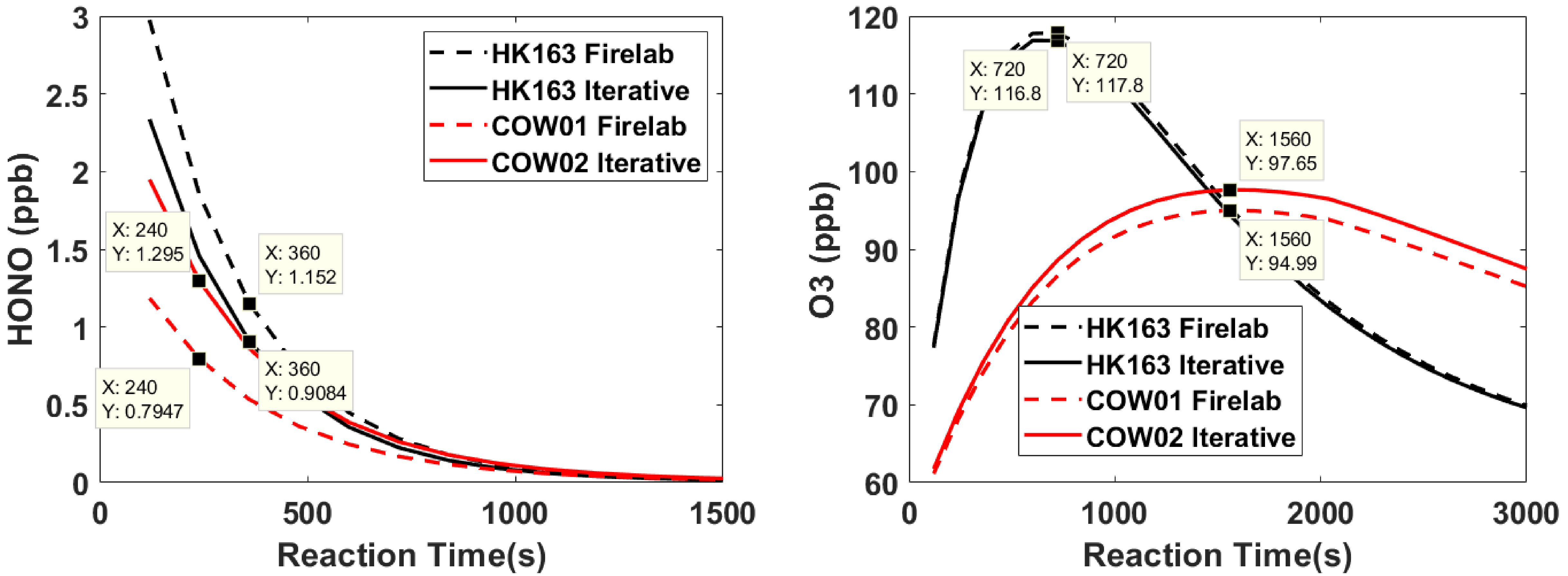


Radical Production
HONO + hv
O3 + NO2
Aldehydes + hv
Alkenes + O3
HCHO + hv
CH3CHO + hv
CHOCHO + hv
O1D + H2O
Radical Losses
OH + NO2
Nitro Aromatics
HO2 + HO2
PAN
OH + HO2
RO2 + RO2
HO2 + RO2
RO2 + NO
Radical Production
HONO + hv
O3 + NO2
Aldehydes + hv
Alkenes + O3
HCHO + hv
O1D + H2O
CH3CHO + hv
CHOCHO + hv
Radical Losses
OH + NO2
Nitro Aromatics
HO2 + HO2
PAN
HO2 + RO2
OH + HO2
RO2 + NO
RO2 + RO2
Afternoon Photochemistry
Ln/Q
Reaction Time (s)
VOC Sensitive
NOx Sensitive
HK163
Nethker
GraniteGulch
LittleBear
Cow1
Cow3
Cow5
Evening Photochemistry
Ln/Q
Reaction Time (s)
VOC Sensitive
NOx Sensitive
Castle
Cow2
Cow4
Cow6
Canyon66



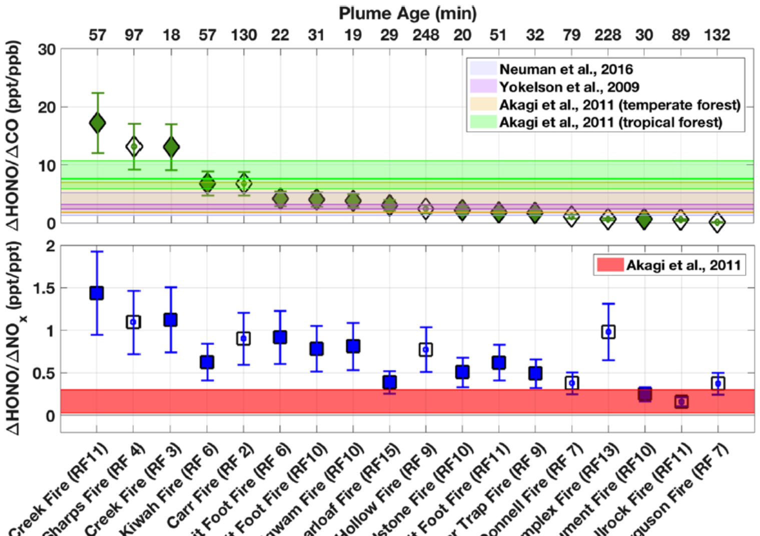
Radical Production
HONO + hv
Primary HCHO
CHOCHO + hv
O3 + NO2
Aldehydes + hv
Alkenes + O3
Radical Losses
HO2 + HO2
OH + NO2
HO2 + RO2
RO2 + NO
RO2 + RO2
Nitro Aromatics
PAN
Radical Production
O3 + NO2
HONO + hv
Aldehydes + hv
Primary HCHO
CHOCHO + hv
Alkenes + O3
Radical Losses
OH + NO2
RO2 + NO
Nitro Aromatics
PAN
WilliamsFlatPass1
Ln/Q
VOC Sensitive
NOx Sensitive
Ln/Q
Ln/Q w/netPAN
Reaction Time (s)
0
0.2
0.4
0.6
0.8
1
5000
10000
15000
WilliamsFlatPass2
Ln/Q
Ln/Q
Ln/Q w/netPAN
VOC Sensitive
NOx Sensitive
Reaction Time (s)
0
0.2
0.4
0.6
0.8
1
2000
4000
6000
8000
10000
12000

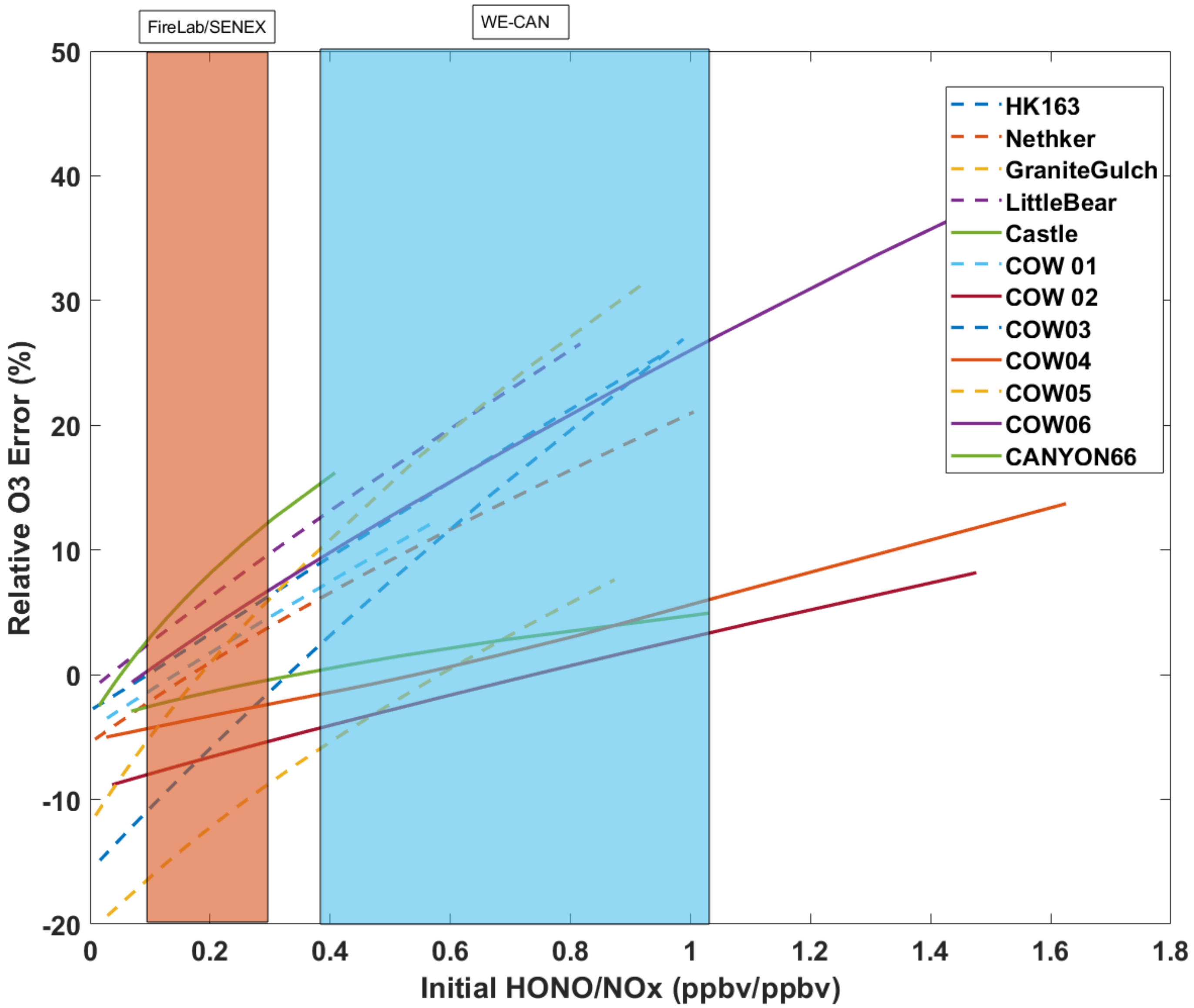
How sensitive are the model runs to initial HONO?



HONO sensitivity tests

- Several ways to constrain HONO:
  - Let the model iterate, this often leads to difficulty solving for O_3 , NO_x, or VOCs
  - Fix HONO/NOx per literature:
    - FireLab (Roberts et al 2020): 0.21 ± 0.13
    - WE-CAN (Peng et al 2020): 0.72 ± 0.34
    - SENEX (Neuman et al 2016): 0.02 – 0.14





A few initial thoughts:

- Afternoon WW plumes produce twice as much O_3 in half the time when compared to evening plumes.
- Radical Production
  - HONO and HCHO make up < 50% of the primary HOx production in both afternoon and evening plumes (vs. ~2% from O1D + H2O)
  - Evening photochemistry reduces photolysis rates, making non photolysis radical sources more significant (Alkene + O_3 & NO_3 radical)
  - pHOx from HONO photolysis is ~2x in evening plumes than in afternoon plumes
  - Initial HONO has an effect of ~25% on downwind O_3 production for most plumes
- Radical Termination
  - PAN formation is often the largest portion of radical termination for both afternoon and evening photochemistry
  - Nitro-aromatics termination reactions are ~2x as high in evening plumes, but still a small portion of the termination budget (~5%).
- Plumes often start VOC sensitive and quickly transition to NOx sensitive downwind. This transition is slower in the evening.

Ongoing work:

- Sensitivity tests:
  - HCHO, dilution, photolysis
- Secondary formation of HONO?
  - Evidence of heterogeneous chemistry?
- Manuscript

Questions?

michael.a.robinson@noaa.gov

Questions?

Next Meeting:
Monday September 14 at 11 am with Felipe Rivera and Zach Decker