DISCOVER-AQ

Statistical Analysis of P3B Data: *Some Initial Results*

Bryan Duncan
Jerry Ziemke
Melanie Follette-Cook
NASA Goddard Space Flight Center, Greenbelt, MD

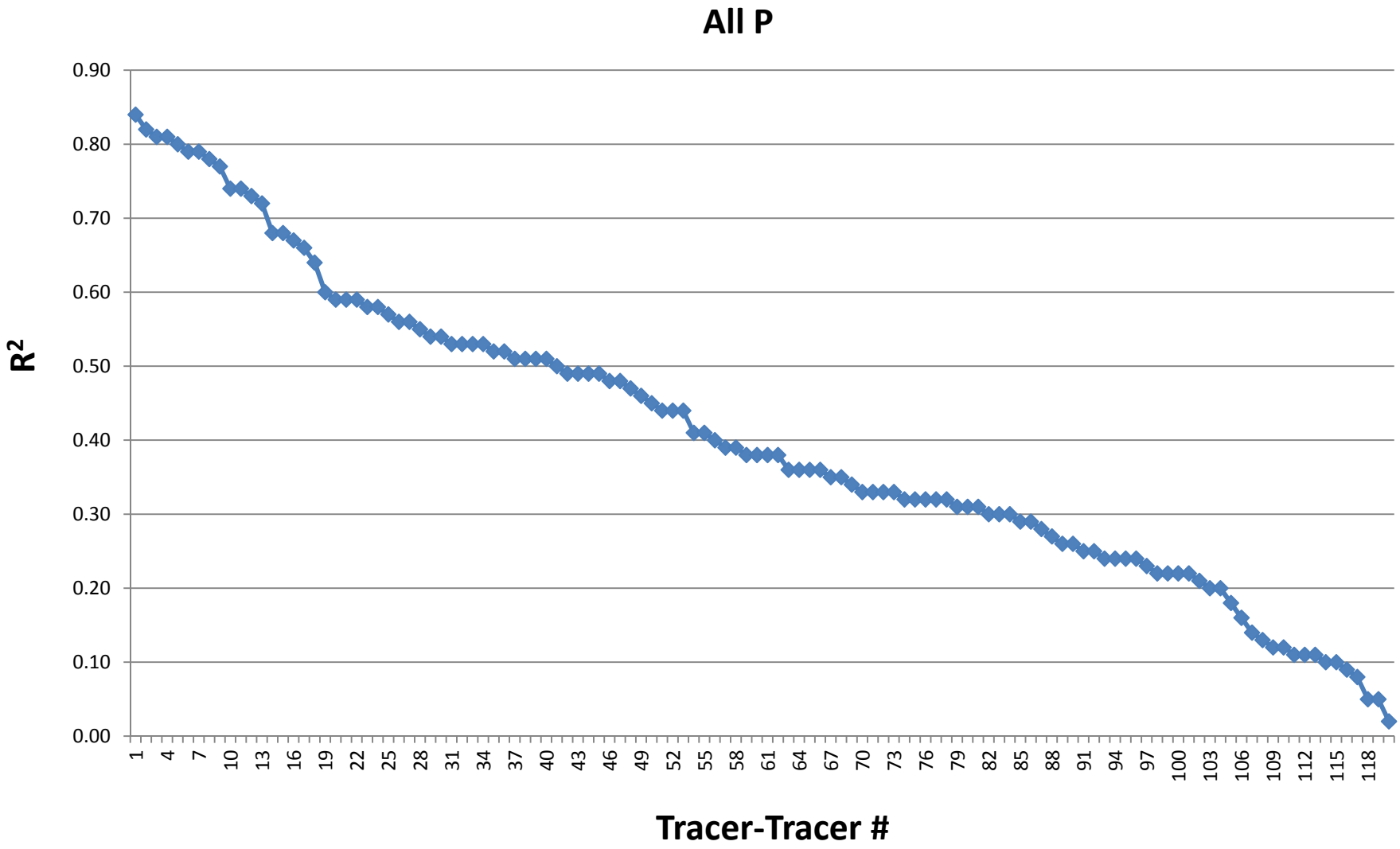
R^2 for Top 25 (of 120)

"Fuzzy" Boundary

Free Troposphere | Boundary Layer | All Data

SPECIES #1	SPECIES #2	< 650 mb	650-750	750-850	850-950	> 950	All P
HCHO (ppb)	Acetaldehye (ppb)	0.18	0.33	0.70	0.78	0.79	0.84
CO (ppb)	Acetaldehye (ppb)	0.34	0.29	0.68	0.78	0.76	0.82
HCHO (ppb)	CO (ppb)	0.03	0.03	0.67	0.77	0.74	0.81
H2O (ppm)	Acetone (ppb)	0.57	0.33	0.76	0.81	0.79	0.81
HCHO (ppb)	MVK MAC (ppb)	0.21	0.43	0.73	0.67	0.72	0.80
HCHO (ppb)	Acetone (ppb)	0.23	0.34	0.58	0.70	0.81	0.79
CO (ppb)	Acetone (ppb)	0.35	0.32	0.64	0.75	0.74	0.79
Acetone (ppb)	Acetaldehye (ppb)	0.33	0.38	0.64	0.74	0.77	0.78
Acetone (ppb)	Methanol (ppb)	0.51	0.45	0.73	0.69	0.65	0.77
CO (ppb)	Methanol (ppb)	0.64	0.61	0.65	0.56	0.47	0.74
H2O (ppm)	HCHO (ppb)	0.39	0.56	0.48	0.57	0.64	0.74
H2O (ppm)	Methanol (ppb)	0.09	0.03	0.60	0.63	0.54	0.73
HCHO (ppb)	Methanol (ppb)	0.05	0.09	0.61	0.54	0.60	0.72
H2O (ppm)	Temperature (K)	0.11	0.06	0.36	0.53	0.48	0.68
NOy (ppb)	NO2 (ppb)	0.01	0.01	0.37	0.56	0.65	0.68
Acetaldehye (ppb)	Methanol (ppb)	0.39	0.28	0.56	0.57	0.56	0.68
CO (ppb)	CH4 (ppb)	0.85	0.78	0.72	0.48	0.29	0.67
H2O (ppm)	CO (ppb)	0.01	0.00	0.41	0.56	0.54	0.66
H2O (ppm)	Relative Humidity (%	0.93	0.93	0.81	0.63	0.60	0.64
H2O (ppm)	Acetaldehye (ppb)	0.26	0.13	0.41	0.52	0.52	0.64
HCHO (ppb)	Temperature (K)	0.01	0.06	0.13	0.39	0.53	0.63
HCHO (ppb)	CH4 (ppb)	0.01	0.01	0.50	0.46	0.23	0.60
Toluene (ppb)	Xylenes (ppb)	-9.99	0.01	0.36	0.45	0.52	0.59
HCHO (ppb)	Peroxynitrates (ppb)	0.13	0.30	0.60	0.49	0.35	0.59

R^2 for All Data : Ordered from High to Low



I expected to see clusters of R^2's but that's not the case.

R^2 for Top 25

SPECIES #1	SPECIES #2	Free Troposphere < 650 mb	Free Troposphere 650-750	Boundary Layer 750-850	Boundary Layer 850-950	Boundary Layer > 950	All Data All P
HCHO (ppb)	Acetaldehye (ppb)	0.18	0.33	0.70	0.78	0.79	0.84
CO (ppb)	Acetaldehye (ppb)	0.34	0.29	0.68	0.78	0.76	0.82
HCHO (ppb)	CO (ppb)	0.03	0.03	0.67	0.77	0.74	0.81
H2O (ppm)	Acetone (ppb)	0.57	0.33	0.76	0.81	0.79	0.81
HCHO (ppb)	MVK MAC (ppb)	0.21	0.43	0.73	0.67	0.72	0.80
HCHO (ppb)	Acetone (ppb)	0.23	0.34	0.58	0.70	0.81	0.79
CO (ppb)	Acetone (ppb)	0.35	0.32	0.64	0.75	0.74	0.79
Acetone (ppb)	Acetaldehye (ppb)	0.33	0.38	0.64	0.74	0.77	0.78
Acetone (ppb)	Methanol (ppb)	0.51	0.45	0.73	0.69	0.65	0.77
CO (ppb)	Methanol (ppb)	0.64	0.61	0.65	0.56	0.47	0.74
H2O (ppm)	HCHO (ppb)	0.39	0.56	0.48	0.57	0.64	0.74
H2O (ppm)	Methanol (ppb)	0.09	0.03	0.60	0.63	0.54	0.73
HCHO (ppb)	Methanol (ppb)	0.05	0.09	0.61	0.54	0.60	0.72
H2O (ppm)	Temperature (K)	0.11	0.06	0.36	0.53	0.48	0.68
NOy (ppb)	NO2 (ppb)	0.01	0.01	0.37	0.56	0.65	0.68
Acetaldehye (ppb)	Methanol (ppb)	0.39	0.28	0.56	0.57	0.56	0.68
CO (ppb)	CH4 (ppb)	0.85	0.78	0.72	0.48	0.29	0.67
H2O (ppm)	CO (ppb)	0.01	0.00	0.41	0.56	0.54	0.66
H2O (ppm)	Relative Humidity (%	0.93	0.93	0.81	0.63	0.60	0.64
H2O (ppm)	Acetaldehye (ppb)	0.26	0.13	0.41	0.52	0.52	0.64
HCHO (ppb)	Temperature (K)	0.01	0.06	0.13	0.39	0.53	0.63
HCHO (ppb)	CH4 (ppb)	0.01	0.01	0.50	0.46	0.23	0.60
Toluene (ppb)	Xylenes (ppb)	-9.99	0.01	0.36	0.45	0.52	0.59
HCHO (ppb)	Peroxynitrates (ppb)	0.13	0.30	0.60	0.49	0.35	0.59

Correlations tend to be highest in well-mixed boundary layer.

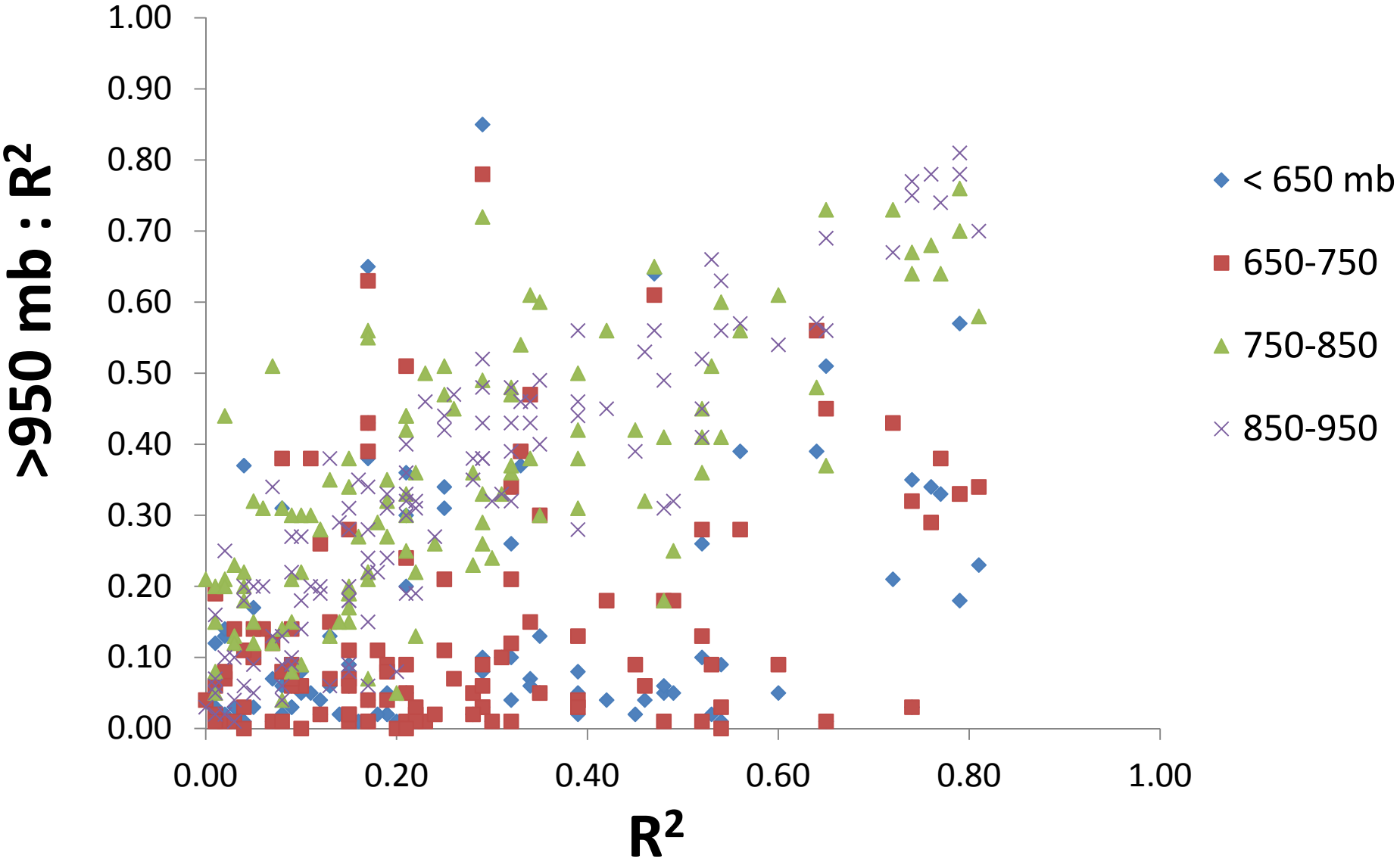
R^2 for Top 25

SPECIES #1	SPECIES #2	Free Troposphere < 650 mb	Free Troposphere 650-750	Boundary Layer 750-850	Boundary Layer 850-950	Boundary Layer > 950	All Data All P
HCHO (ppb)	Acetaldehye (ppb)	0.18	0.33	0.70	0.78	0.79	0.84
CO (ppb)	Acetaldehye (ppb)	0.34	0.29	0.68	0.78	0.76	0.82
HCHO (ppb)	CO (ppb)	0.03	0.03	0.67	0.77	0.74	0.81
H2O (ppm)	Acetone (ppb)	0.57	0.33	0.76	0.81	0.79	0.81
HCHO (ppb)	MVK MAC (ppb)	0.21	0.43	0.73	0.67	0.72	0.80
HCHO (ppb)	Acetone (ppb)	0.23	0.34	0.58	0.70	0.81	0.79
CO (ppb)	Acetone (ppb)	0.35	0.32	0.64	0.75	0.74	0.79
Acetone (ppb)	Acetaldehye (ppb)	0.33	0.38	0.64	0.74	0.77	0.78
Acetone (ppb)	Methanol (ppb)	0.51	0.45	0.73	0.69	0.65	0.77
CO (ppb)	Methanol (ppb)	0.64	0.61	0.65	0.56	0.47	0.74
H2O (ppm)	HCHO (ppb)	0.39	0.56	0.48	0.57	0.64	0.74
H2O (ppm)	Methanol (ppb)	0.09	0.03	0.60	0.63	0.54	0.73
HCHO (ppb)	Methanol (ppb)	0.05	0.09	0.61	0.54	0.60	0.72
H2O (ppm)	Temperature (K)	0.11	0.06	0.36	0.53	0.48	0.68
NOy (ppb)	NO2 (ppb)	0.01	0.01	0.37	0.56	0.65	0.68
Acetaldehye (ppb)	Methanol (ppb)	0.39	0.28	0.56	0.57	0.56	0.68
CO (ppb)	CH4 (ppb)	0.85	0.78	0.72	0.48	0.29	0.67
H2O (ppm)	CO (ppb)	0.01	0.00	0.41	0.56	0.54	0.66
H2O (ppm)	Relative Humidity (%	0.93	0.93	0.81	0.63	0.60	0.64
H2O (ppm)	Acetaldehye (ppb)	0.26	0.13	0.41	0.52	0.52	0.64
HCHO (ppb)	Temperature (K)	0.01	0.06	0.13	0.39	0.53	0.63
HCHO (ppb)	CH4 (ppb)	0.01	0.01	0.50	0.46	0.23	0.60
Toluene (ppb)	Xylenes (ppb)	-9.99	0.01	0.36	0.45	0.52	0.59
HCHO (ppb)	Peroxynitrates (ppb)	0.13	0.30	0.60	0.49	0.35	0.59

Some are high in all levels for a few tracer-tracer correlations. Acetone, methane, methanol and CO are relatively long-lived (days-weeks) & have important biogenic sources.

R^2's for >950mb vs R^2's for P-levels

DAQ Results Relevant for GEO-CAPE Mission Planning



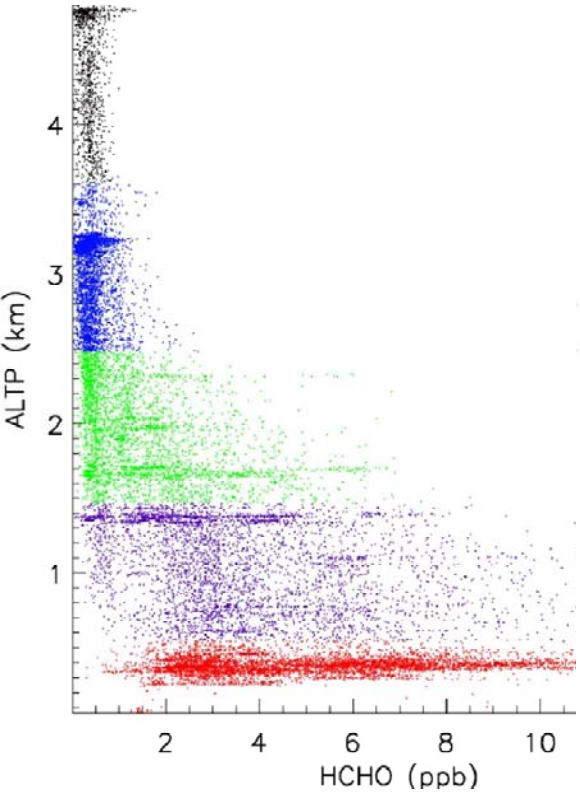
R^2 - A Dynamical Component

SPECIES #1	SPECIES #2	Free Troposphere		Boundary Layer			All Data
		< 650 mb	650-750	750-850	850-950	> 950	All P
H2O (ppm)	ALTP (km)	0.04	0.01	0.10	0.04	0.01	0.53
ALTP (km)	Methanol (ppb)	0.01	0.01	0.14	0.03	0.03	0.49
HCHO (ppb)	ALTP (km)	0.01	0.02	0.14	0.11	0.02	0.47
CO (ppb)	ALTP (km)	0.02	0.01	0.10	0.06	0.00	0.45
HNO3 (ppb)	ALTP (km)	0.03	0.02	0.10	0.04	0.00	0.37
ALTP (km)	MVK MAC (ppb)	0.01	0.02	0.07	0.11	0.01	0.33
Toluene (ppb)	Acetone (ppb)	0.08	0.07	0.15	0.20	0.15	0.33
ALTP (km)	Acetone (ppb)	0.02	0.00	0.08	0.01	0.03	0.33
H2O (ppm)	Toluene (ppb)	0.06	0.06	0.08	0.10	0.09	0.31
H2O (ppm)	Peroxynitrates (ppb)	0.10	0.14	0.12	0.05	0.05	0.30
ALTP (km)	Acetaldehye (ppb)	0.01	0.02	0.06	0.03	0.02	0.30
Xylenes (ppb)	Methanol (ppb)	0.01	0.01	0.12	0.13	0.07	0.25
Peroxynitrates (ppb)	Temperature (K)	0.10	0.13	0.00	0.01	0.02	0.24
H2O (ppm)	NOy (ppb)	0.12	0.06	0.05	0.02	0.01	0.22
Isoprene (ppb)	Methanol (ppb)	0.06	0.07	0.13	0.06	0.13	0.22
Temperature (K)	Relative Humidity (%	0.01	0.00	0.07	0.04	0.01	0.19
Sulfate (ug/m3)	ALTP (km)	0.06	0.04	0.01	0.00	0.03	0.15

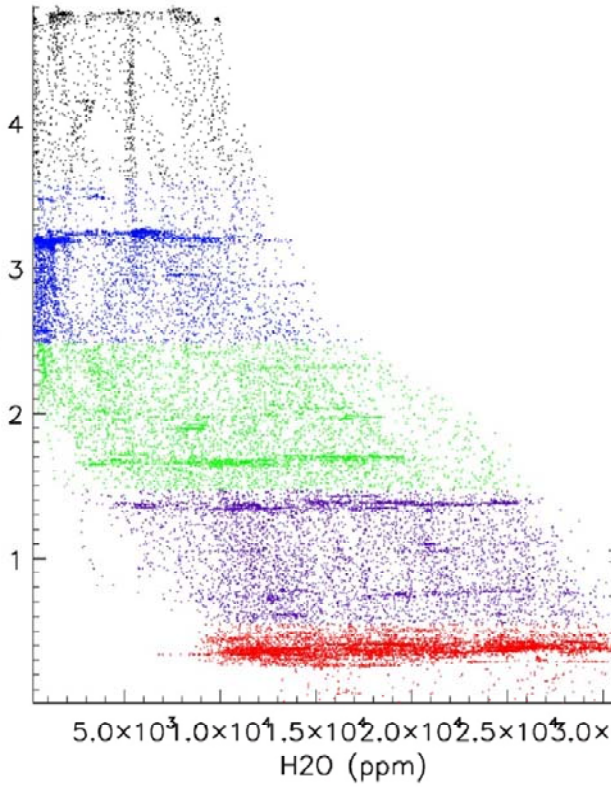
CAUTION: A number of species DO NOT correlate within pressure levels, but DO correlate when all data are used! Using altitude pressure (ALTP) illustrates point.

R^2 - A Dynamical Component – Similar Vertical Distributions

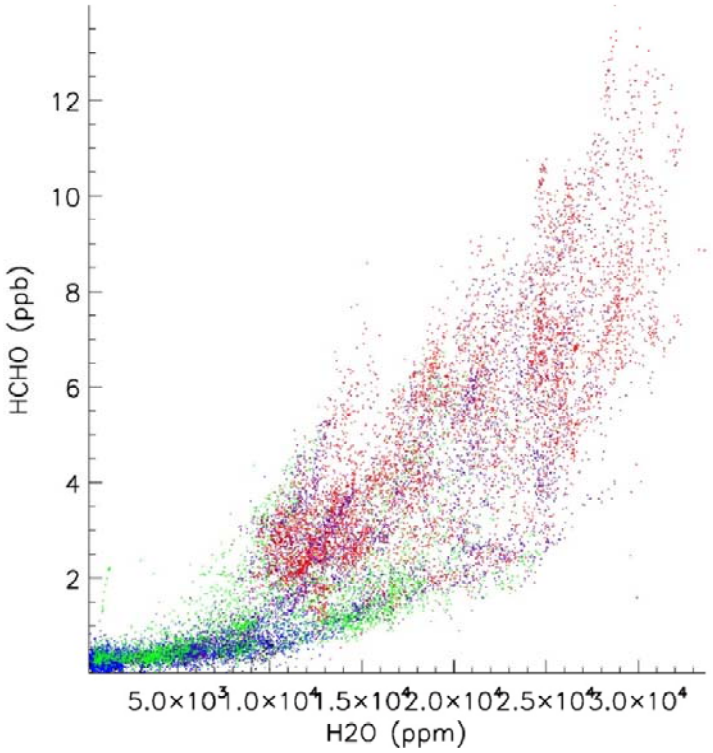
ALTP(km) v HCHO (ppb)



ALTP (km) v H2O (ppm)



HCHO (ppb) v H2O (ppm)



There's a chemical component to R^2 too – more later.

Are biogenic VOCs a bigger player than anthropogenic VOCs for HCHO ?

Short Answer: Biogenics

SPECIES #1	SPECIES #2	Free Troposphere < 650 mb	Free Troposphere 650-750	Boundary Layer 750-850	Boundary Layer 850-950	Boundary Layer > 950	All Data All P
HCHO (ppb)	Acetaldehye (ppb)	0.18	0.33	0.70	0.78	0.79	0.84
CO (ppb)	Acetaldehye (ppb)	0.34	0.29	0.68	0.78	0.76	0.82
HCHO (ppb)	CO (ppb)	0.03	0.03	0.67	0.77	0.74	0.81
H2O (ppm)	Acetone (ppb)	0.57	0.33	0.76	0.81	0.79	0.81
HCHO (ppb)	MVK MAC (ppb)**********	0.21	0.43	0.73	0.67	0.72	0.80
HCHO (ppb)	Acetone (ppb)	0.23	0.34	0.58	0.70	0.81	0.79
CO (ppb)	Acetone (ppb)	0.35	0.32	0.64	0.75	0.74	0.79
Acetone (ppb)	Acetaldehye (ppb)	0.33	0.38	0.64	0.74	0.77	0.78
Acetone (ppb)	Methanol (ppb)	0.51	0.45	0.73	0.69	0.65	0.77
CO (ppb)	Methanol (ppb)	0.64	0.61	0.65	0.56	0.47	0.74
H2O (ppm)	HCHO (ppb)	0.39	0.56	0.48	0.57	0.64	0.74
H2O (ppm)	Methanol (ppb)	0.09	0.03	0.60	0.63	0.54	0.73
HCHO (ppb)	Methanol (ppb)	0.05	0.09	0.61	0.54	0.60	0.72
H2O (ppm)	Temperature (K)	0.11	0.06	0.36	0.53	0.48	0.68
NOy (ppb)	NO2 (ppb)	0.01	0.01	0.37	0.56	0.65	0.68
Acetaldehye (ppb)	Methanol (ppb)	0.39	0.28	0.56	0.57	0.56	0.68
CO (ppb)	CH4 (ppb)	0.85	0.78	0.72	0.48	0.29	0.67
H2O (ppm)	CO (ppb)	0.01	0.00	0.41	0.56	0.54	0.66
H2O (ppm)	Relative Humidity (%	0.93	0.93	0.81	0.63	0.60	0.64
H2O (ppm)	Acetaldehye (ppb)	0.26	0.13	0.41	0.52	0.52	0.64
HCHO (ppb)	Temperature (K)	0.01	0.06	0.13	0.39	0.53	0.63
HCHO (ppb)	CH4 (ppb)	0.01	0.01	0.50	0.46	0.23	0.60
Toluene (ppb)	Xylenes (ppb)**********	-9.99	0.01	0.36	0.45	0.52	0.59
HCHO (ppb)	Peroxynitrates (ppb)	0.13	0.30	0.60	0.49	0.35	0.59

Methyl vinyl ketone & Methacolein (MVK_MAC) – oxidation products of biogenic isoprene

Toluene & Xylenes: traffic tracers (highest Edgwood->Essex & Beltsville->Padonia)

Methanol & Acetone have strong biogenic components to total source.

July 1st, 2011

Multivariate Linear Regression

$z = x*B_x + y*B_y + \text{residual}$

HCHO (ppb) = MVK_MAC (ppb)$*B_x$ + Xylenes (ppt)$*B_y$ + residual

z = HCHO (ppb)
min/max(z) = 0.262267/5.08800
x = MVK_MAC (ppb)
min/max(x) = 0.000500000/1.45700
y =Xylenes (ppt)
min/max(y) = 0.00487799/149.000
points = 716

B_x = 4.87371

B_y = 0.0127763

mean(z) = 2.60141

mean(x)$*B_x$ = 1.92396
2*sigma = 0.227916

mean(y)$*B_y$ = 0.423391
2*sigma = 0.00251175

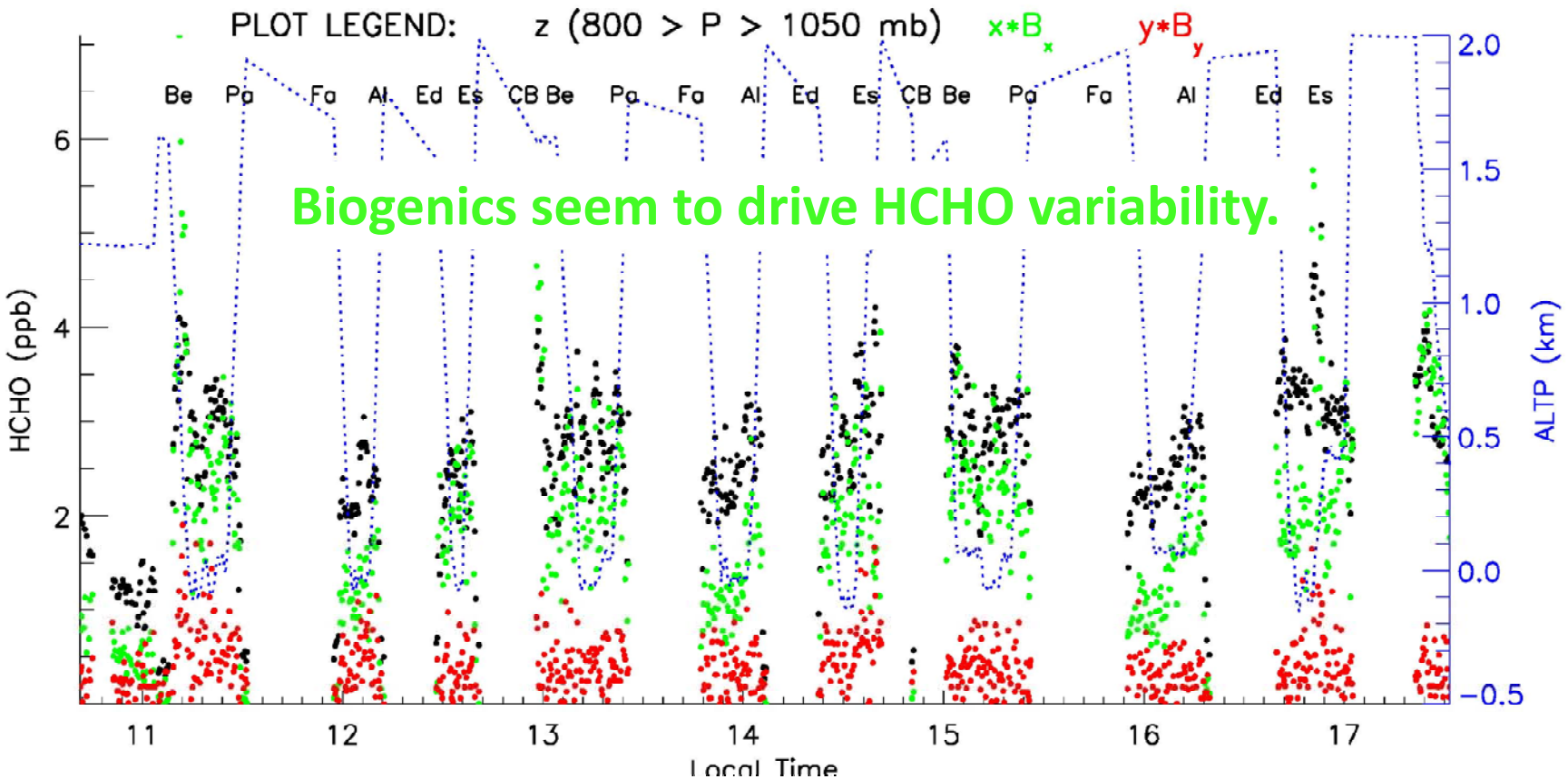
mean(residual) = 0.254056

abs mean(residual) = 0.609169

R^2 (x,z) = 0.603062

R^2 (y,z) = 0.133797

R^2 (x,y) = 0.130784



July 1st, 2011

Multivariate Linear Regression

$z = x*B_x + y*B_y + \text{residual}$

CO (ppb) = MVK_MAC (ppb)$*B_x$ + Xylenes (ppt)$*B_y$ + residual

z = CO (ppb)
min/max(z) = 96.7087/188.001
x = MVK_MAC (ppb)
min/max(x) = 0.000500000/1.45700
y =Xylenes (ppt)
min/max(y) = 0.00487799/170.759
points = 818

B_x = 209.895

B_y = 0.969534

mean(z) = 139.427

mean(x)$*B_x$ = 83.0589
2*sigma = 15.2826

mean(y)$*B_y$ = 32.8788
2*sigma = 0.164836

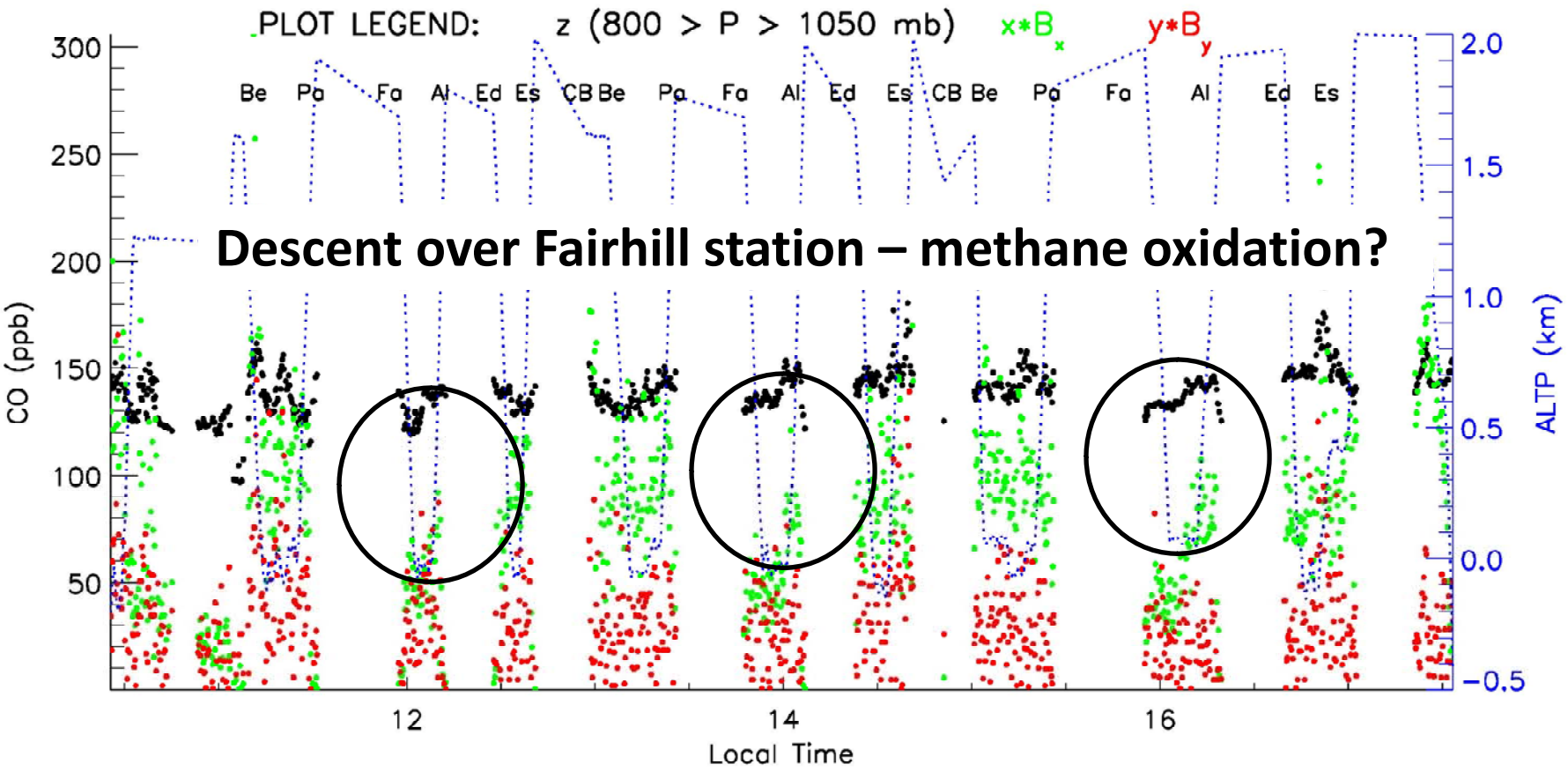
mean(residual) = 23.4894

abs mean(residual) = 44.5517

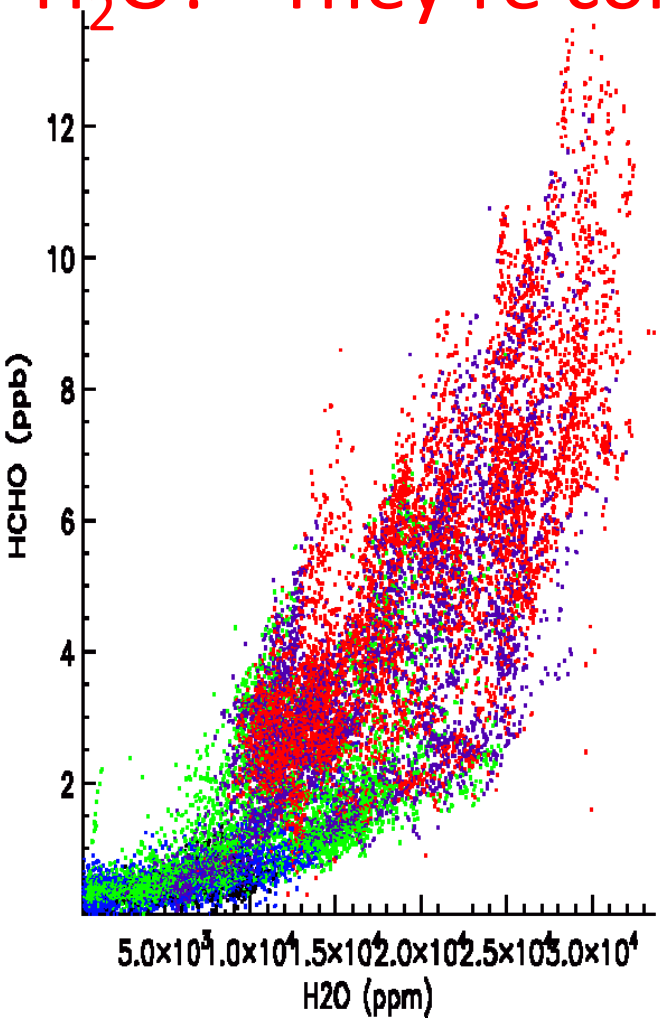
R^2 (x,z) = 0.244574

R^2 (y,z) = 0.133383

R^2 (x,y) = 0.119782



Why are VOC oxidation products so correlated with H_2O? They're correlated within pressure levels too.



$O_3 + hv \rightarrow O^1D + O_2$

$O^1D + H_2O \rightarrow 2OH$

Limiting reagent for radical production?

Will work on this with Jennifer Olson's box model results.

Phoenix's radical production limited by H_2O and low VOC/NO_x (Kleinman et al., 2005), but isn't the DC area real juicy?

How do species vary in different meteorological regimes?

TEMPERATURE IN F:							:PCPN:	SNOW:	WIND				:SUNSHINE: SKY				:PK WND	
1	2	3	4	5	6A	6B	7	8	9	10	11	12	13	14	15	16	17	18
									12Z	AVG	MX	2MIN						
DY	MAX	MIN	AVG	DEP	HDD	CDD	WTR	SNW	DPTH	SPD	SPD	DIR	MIN	PSBL	S-S	WX	SPD	DR
1	89	60	75	0	0	10	0.00	0.0	0	3.0	12	50	M	M	2		21	360
2	93	58	76	1	0	11	0.00	0.0	0	2.8	14	120	M	M	5		18	360
3	93	69	81	6	0	16	0.55	0.0	0	5.8	28	310	M	M	8	13	37	310
4	89	70	80	4	0	15	T	0.0	0	3.3	7	250	M	M	9		14	350
5	93	69	81	5	0	16	0.00	0.0	0	2.9	12	100	M	M	4	18	15	20
6	89	71	80	4	0	15	T	0.0	0	4.0	12	150	M	M	6	18	15	190
7	95	70	83	7	0	18	0.10	0.0	0	5.3	30	360	M	M	4	138	39	10
8	87	71	79	3	0	14	0.83	0.0	0	3.7	22	280	M	M	8	1238	28	280
9	90	68	79	3	0	14	0.00	0.0	0	4.5	14	30	M	M	4	18	20	360
10	90	68	79	3	0	14	0.00	0.0	0	3.4	15	150	M	M	3	1	20	180
11	93	72	83	7	0	18	0.17	0.0	0	8.0	31	270	M	M	4	13	38	270
12	93	74	84	7	0	19	0.00	0.0	0	8.0	17	280	M	M	6		25	270
13	92	72	82	5	0	17	0.26	0.0	0	4.4	15	30	M	M	6	138	21	20
14	83	66	75	-2	0	10	0.00	0.0	0	6.2	16	50	M	M	4	8	24	20
15	83	64	74	-3	0	9	0.00	0.0	0	4.4	13	240	M	M	4		17	230
16	87	60	74	-3	0	9	0.00	0.0	0	5.3	15	220	M	M	3	8	21	220
17	91	68	80	3	0	15	0.00	0.0	0	5.3	13	210	M	M	4		16	190
18	95	70	83	6	0	18	0.00	0.0	0	5.5	14	270	M	M	5		18	270
19	95	74	85	8	0	20	0.16	0.0	0	4.1	16	80	M	M	8	138	24	350
20	93	72	83	6	0	18	0.00	0.0	0	3.8	10	110	M	M	3	18	14	130
21	100	77	89	12	0	24	0.00	0.0	0	4.9	15	240	M	M	3	18	23	220
22	106	81	94	17	0	29	0.00	0.0	0	5.4	16	310	M	M	4	8	22	310
23	102	78	90	13	0	25	0.06	0.0	0	5.3	15	340	M	M	6		21	350
24	98	78	88	11	0	23	0.00	0.0	0	6.5	14	110	M	M	7	18	21	320
25	91	73	82	5	0	17	0.64	0.0	0	4.4	14	340	M	M	7	138	20	310
26	95	72	84	7	0	19	0.00	0.0	0	5.2	14	220	M	M	3	1	22	230
27	90	71	81	4	0	16	0.00	0.0	0	5.0	15	260	M	M	5		22	320
28	91	68	80	3	0	15	T	0.0	0	3.4	9	160	M	M	8		15	250
29	101	77	89	12	0	24	0.00	0.0	0	6.2	21	310	M	M	5	18	30	300
30	96	73	85	8	0	20	0.00	0.0	0	4.8	16	320	M	M	5		23	340
31	98	68	83	7	0	18	0.00	0.0	0	3.9	14	300	M	M	4		21	330

"Typical" Summer Weather
- High temps
- High dewpts
- N & NW winds

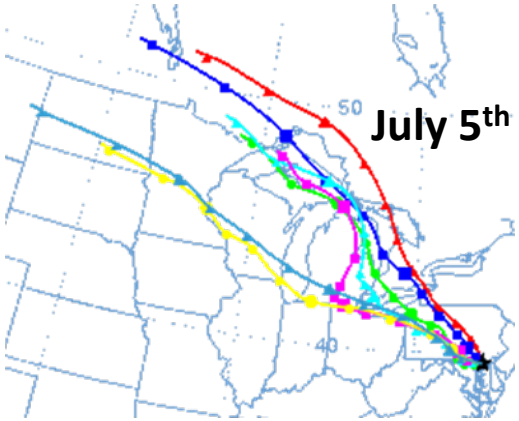
Clean Canadian Air
- Low temps
- Low dewpts
- Northerly winds

Hot Weather
- Very high temps
- Very high dewpts
- Westerly wind component

How do species vary in different meteorological regimes?
Some random observations.

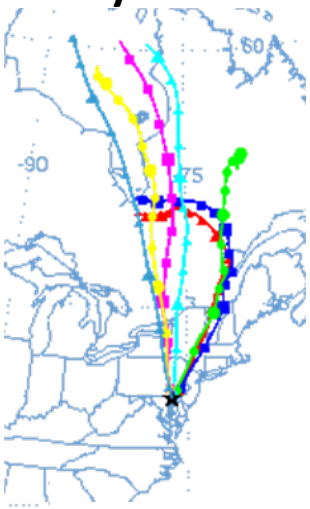
"Typical Summer" Flights (< 14th) – N & NW

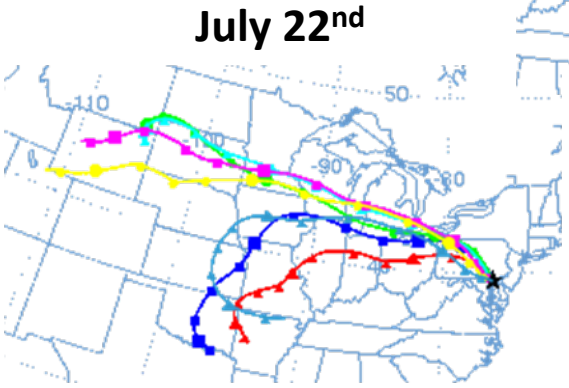
- Overhead ozone column higher than during "hot" flights.



"Clean" Flights (14th & 16th) - N

- Have lowest concentrations of pollutants – no surprise.
- Highest methane recorded (in boundary layer) – wetlands in Canada or local sources?
- Lowest overhead ozone column on one day.

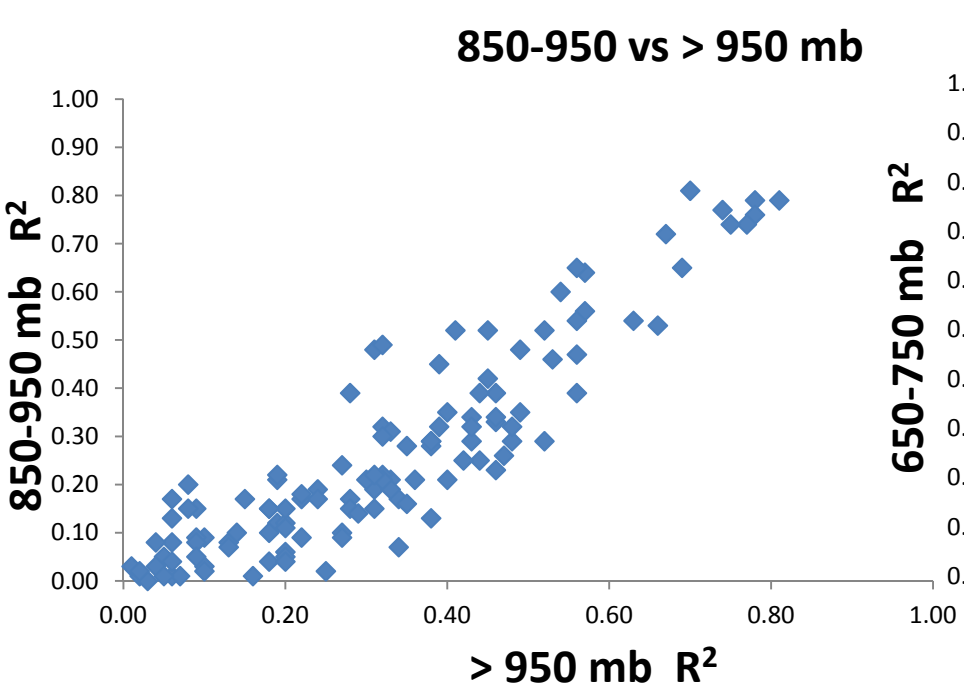


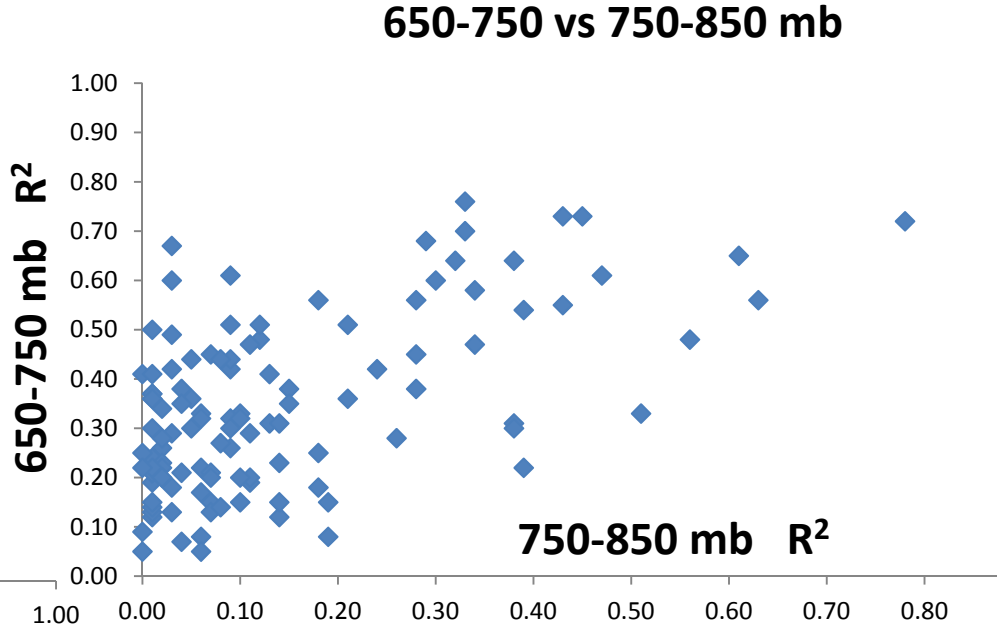


"Hot" Flights (> 16th) – NW & W & SW

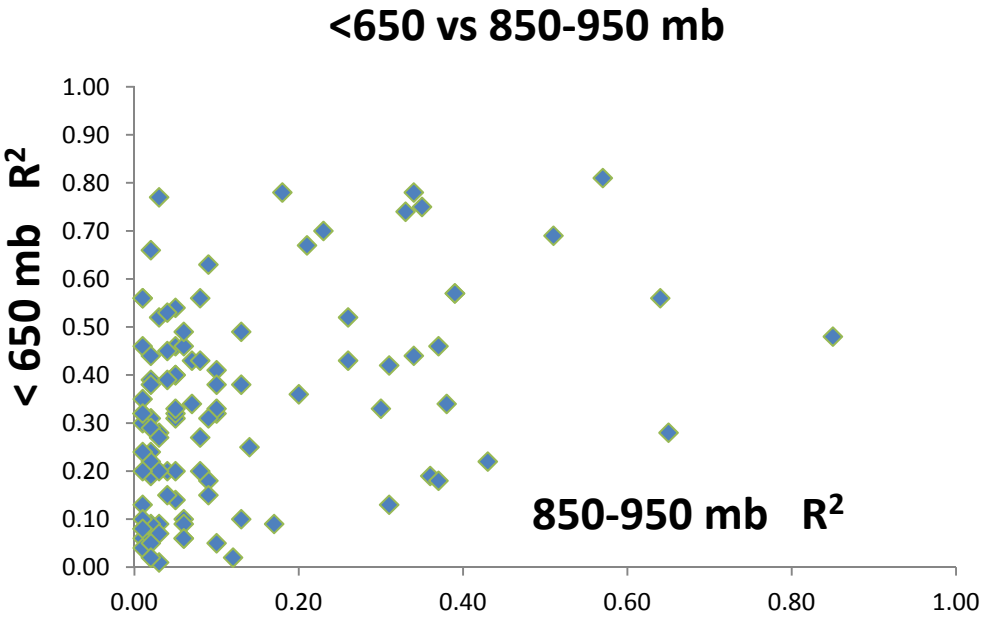
- Dewpoints & temperatures typically highest.
- Generally highest acetone, methanol, sulfates.

Similar results between pressure levels?





Not too much correlation between free tropospheric and boundary layer concentrations.



VOC Species and Emission Types for Select Days at Beltsville and Edgewood MD in July of 2011

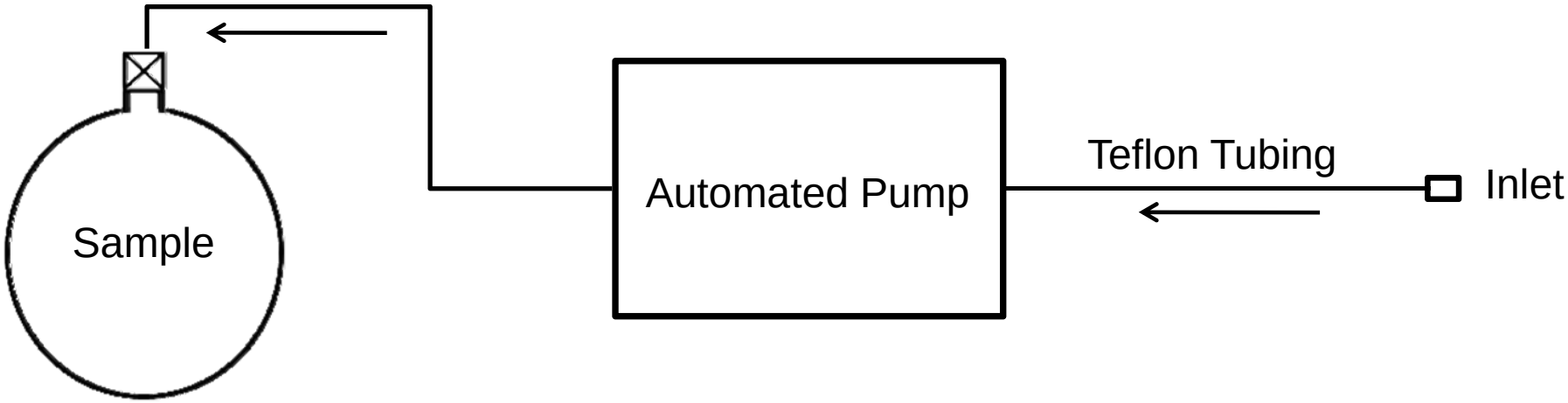
Hannah Halliday

Anne Thompson, Doug Martins, Jose Fuentes

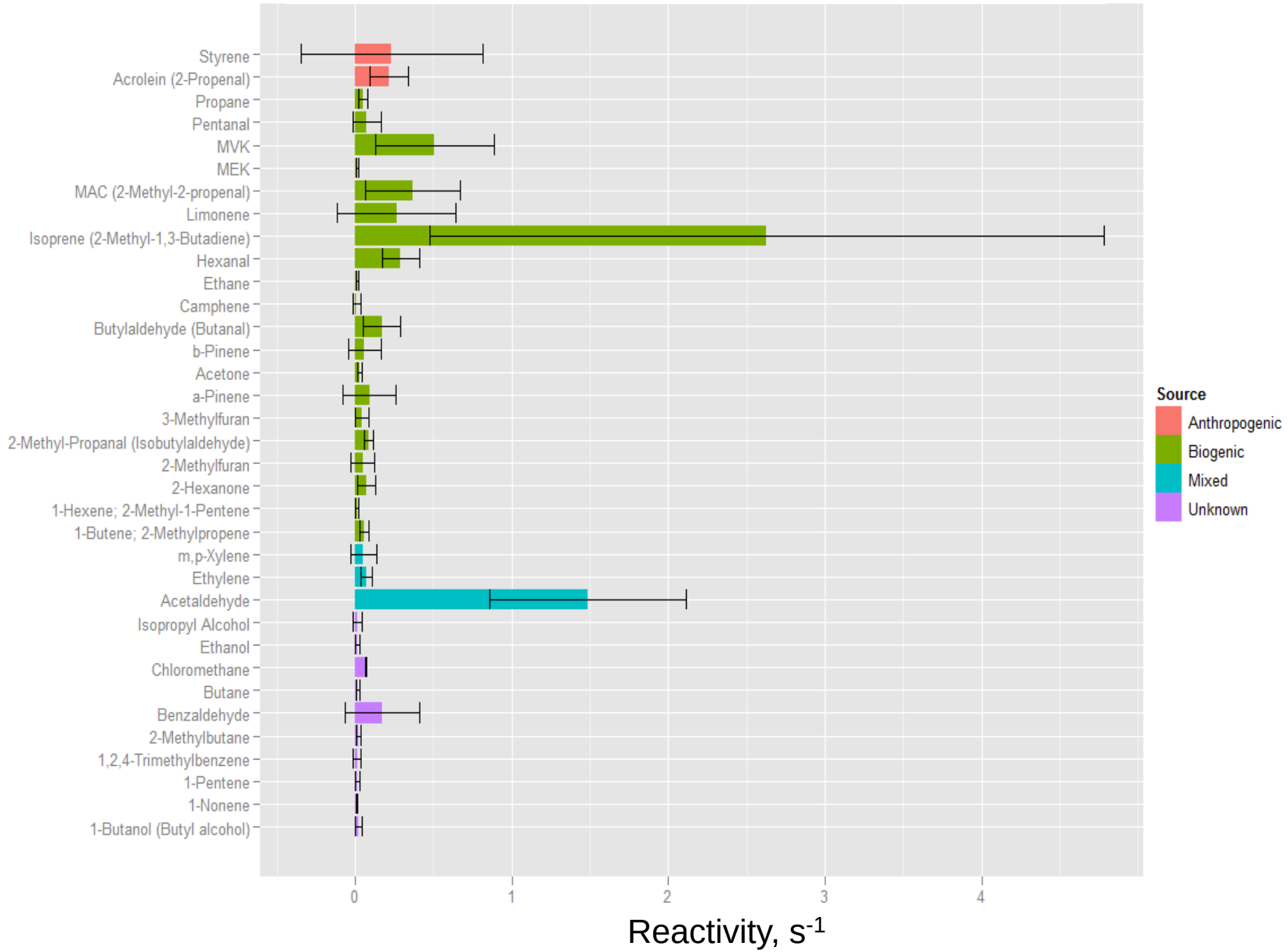
Penn State University

Quick Introduction

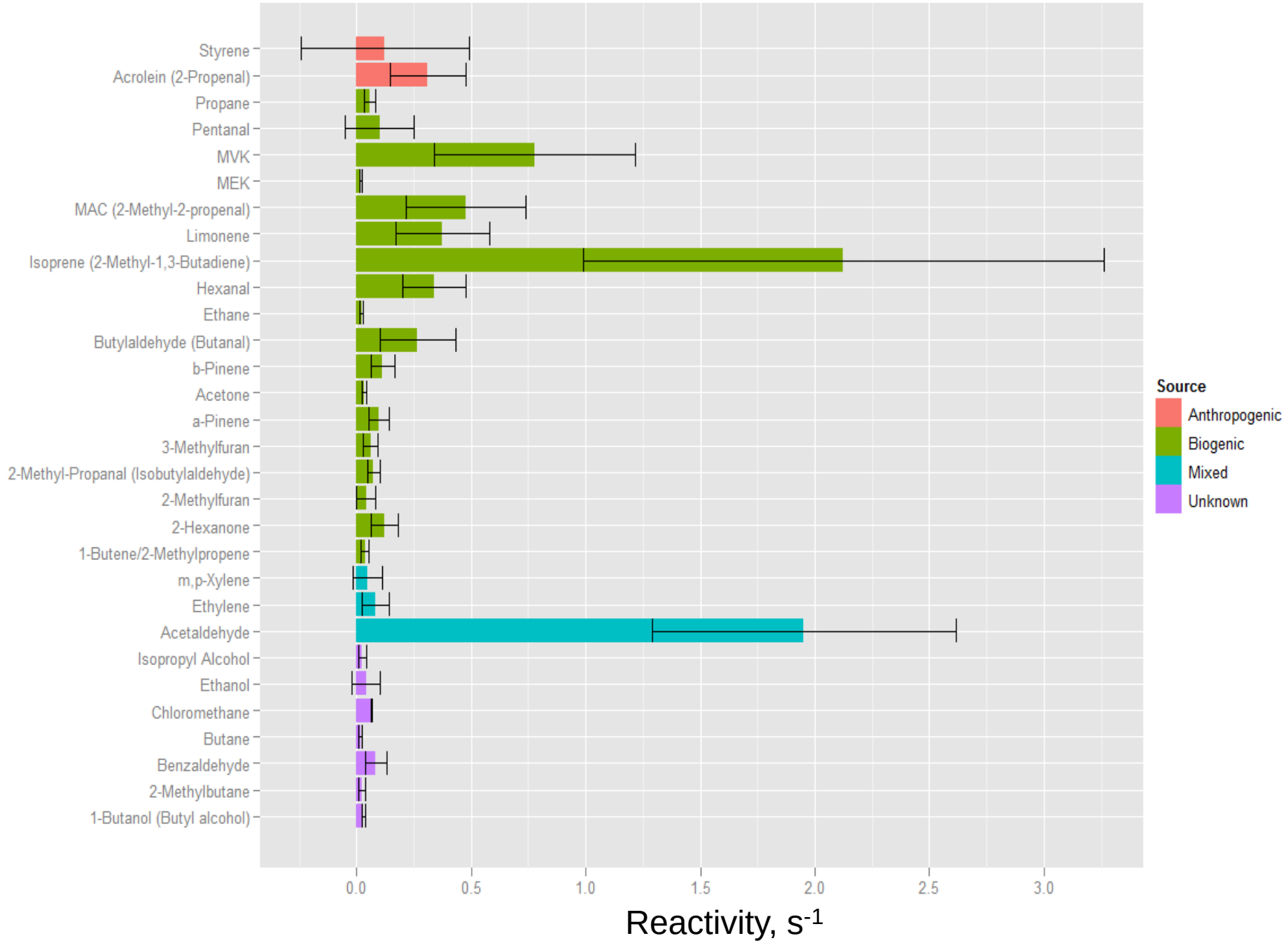
- Reactivity = kOH * [VOC]
- Reactivity Benchmark: 0.01 s-1
- Still a significant reactivity value!



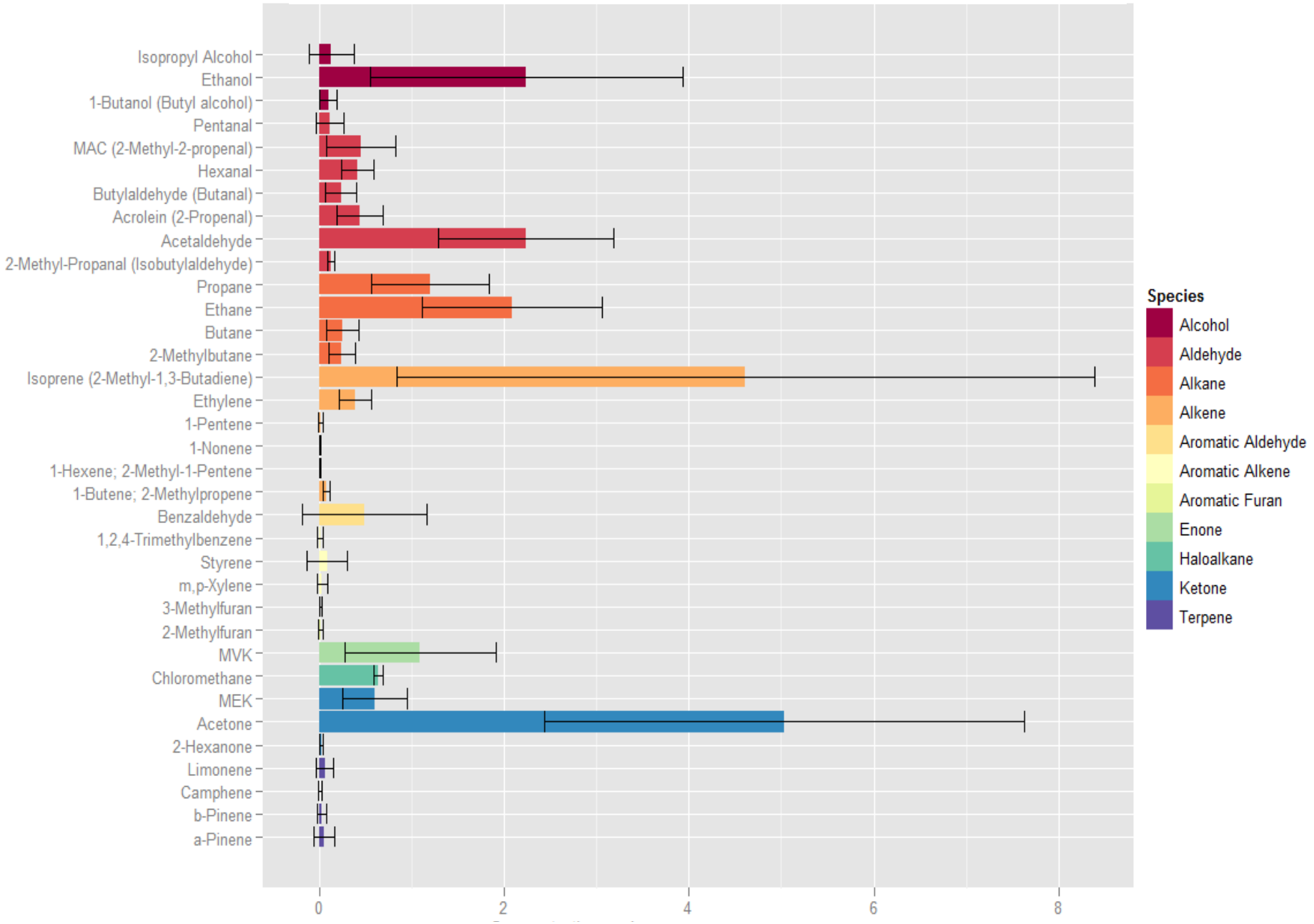
Edgewood MD, OH Reactivity Mean Values



Beltsville MD, OH Reactivity Mean Values

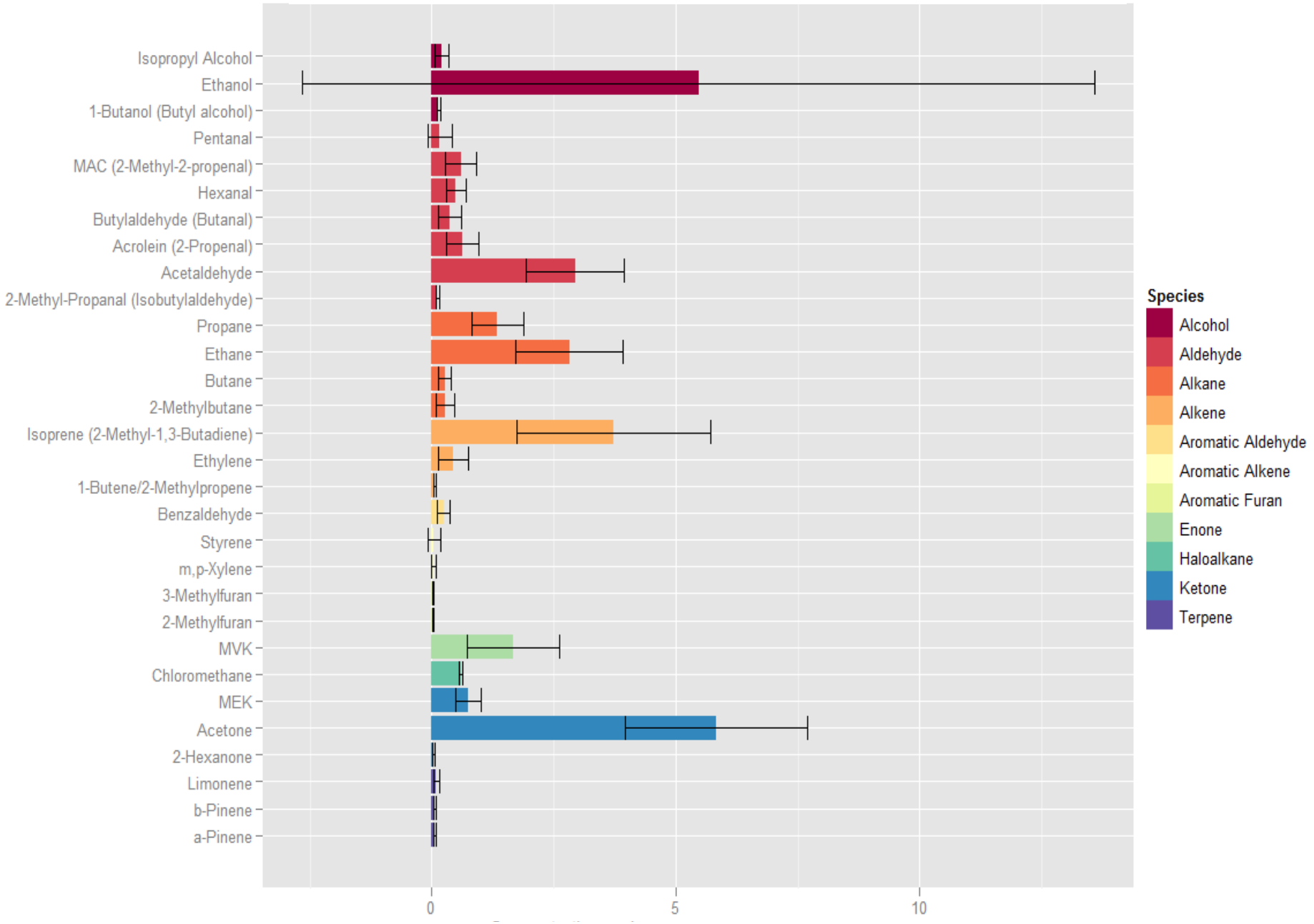


Edgewood MD, Concentration Mean Values



Concentration, ppbv

Beltsville MD, Concentration Mean Values



Concentration, ppbv

Species	Location	Chemical Family
1-Butanol (Butyl alcohol)	Beltsville & Edgewood	Alcohol
1-Butene; 2-Methylpropene		Alkene
2-Hexanone		Ketone
2-Methylbutane		Alkane
2-Methylfuran		Aromatic Furan
3-Methylfuran		Aromatic Furan
Acetaldehyde		Aldehyde
Acetone		Ketone
Acrolein (2-Propenal)		Aldehyde
a-Pinene		Terpene
Benzaldehyde		Aromatic Aldehyde
b-Pinene		Terpene
Butane		Alkane
Butylaldehyde (Butanal)		Aldehyde
Chloromethane		Haloalkane
Ethane		Alkane
Ethanol		Alcohol
Ethylene		Alkene
Hexanal		Aldehyde
Isobutylaldehyde		Aldehyde
Isoprene (2-Methyl-1,3-Butadiene)		Alkene
Isopropyl Alcohol		Alcohol
Limonene		Terpene
m,p-Xylene		Aromatic Alkene
MAC (2-Methyl-2-propenal)		Aldehyde
MEK		Ketone
MVK		Enone
Pentanal		Aldehyde
Propane		Alkane
Styrene		Aromatic Alkene
1,2,4-Trimethylbenzene	Edgewood Only	Aromatic Alkene
1-Hexene; 2-Methyl-1-Pentene		Alkene
1-Nonene		Alkene
1-Pentene		Alkene
Camphene		Terpene

Future Work for this VOC Analysis

- Comparison to aircraft chemical profiles
- Reevaluate reactivity benchmark for better representation of chemistry
- Estimations of the ozone formation reactivity for these significant species
- Wind and advection analysis for sources and characterization of air masses

Box Model Analysis of DISCOVER-AQ data

Jennifer Olson, Alan Fried, Armin Wisthaler, Jim Crawford, Bryan Duncan, +….

We observe a strong correlation between CH_2O and H_2O within given altitude bins. e.g., within boundary layer, increased/decreased concentrations of CH_2O from profile to profile are correlated with increased/decreased values of H_2O.
Correlations of CH_2O also exist with other species: isoprene, temperature, CO, etc.
Focus of this initial work is to untangle the cause of correlations. i.e.,

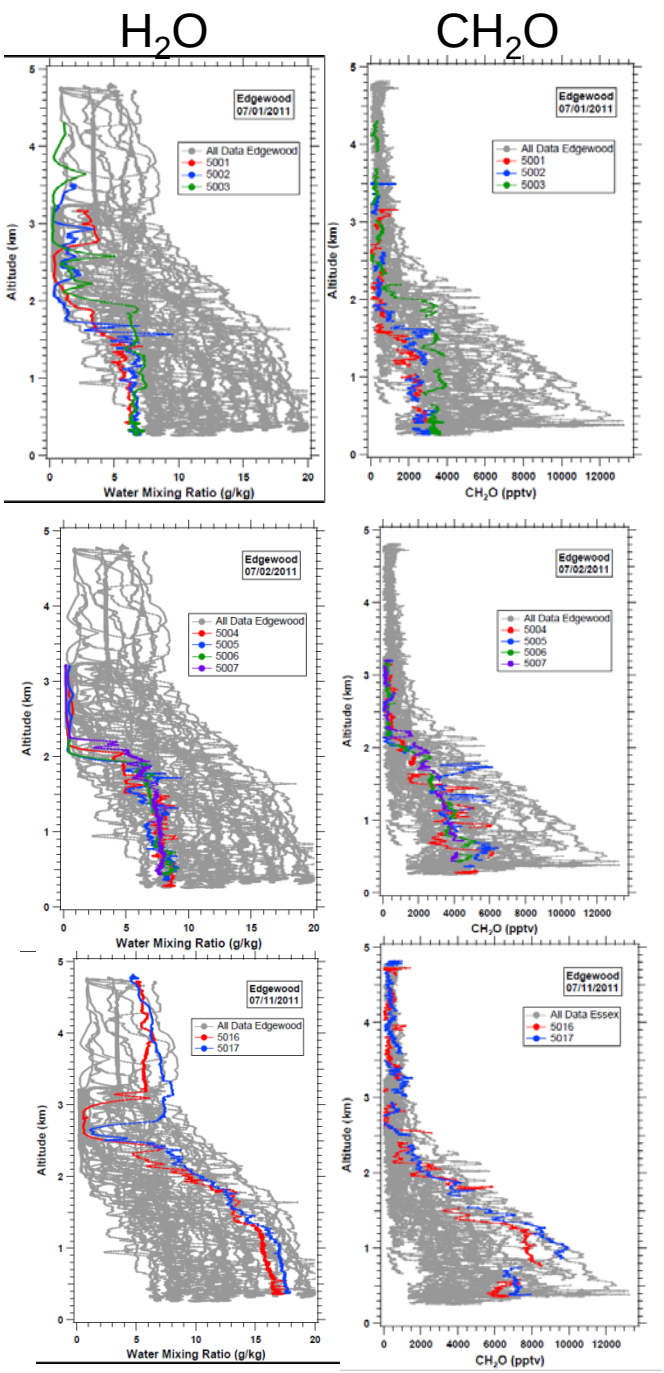
- What drives the variability in CH_2O within flight legs?
- What drives the variability in CH_2O between days?

Precursors? (NMHCs – especially isoprene)
Oxidation rate? (driven by water vapor and O3 photolysis)

- What drives the correlation between CH_2O and CO?

Common sources/precursors?
Is isoprene oxidation a significant source of CO?

Can we assume that near the surface, there is a “baseline” NMHC (isoprene dominant) background that contributes to large temporal scale differences (i.e., day to day) while variability in the oxidation rate (OH primary source from water vapor) is source of smaller temporal scale variability of CH_2O (within flights)?



Examples from selected days at Edgewood.

Low water vapor days correspond to low CH2O days and vice versa.

Next plots show observations of CH2O below 1 km for individual flights (black asterisks, shown in all plots)

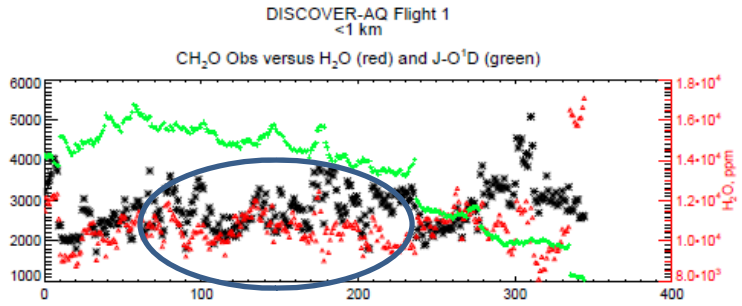
Model was run 3 ways:

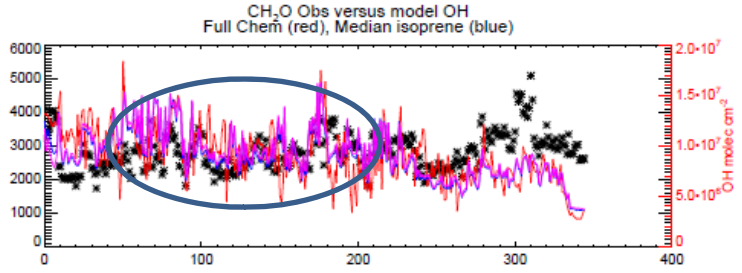
Full chemistry (obs isoprene, aromatics, methanol, acetone, etc.)

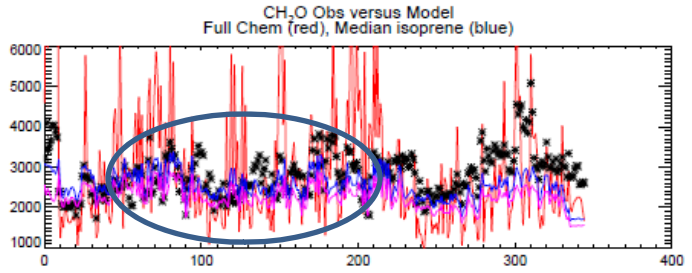
Full chemistry but with wonstant isoprene (median isoprene for flight, plus observed CH4, aromatics, methanol, acetone, etc.)

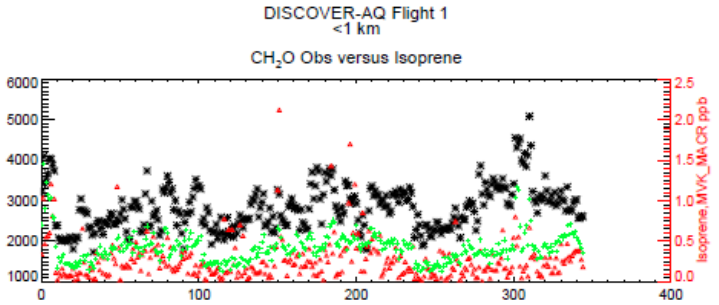
Methane and Constant isoprene ONLY (median isoprene for flight, observed CH4, zero out aromatics, methanol, acetone, etc)

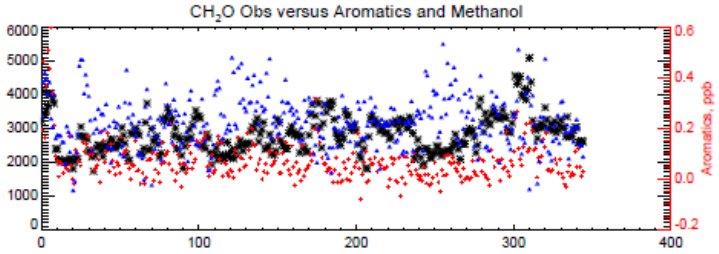
July 1:
CH2O correlated with water vapor and predictions of OH
Variability in predicted CH2O driven by variations in oxidation (OH) of constant background isoprene?



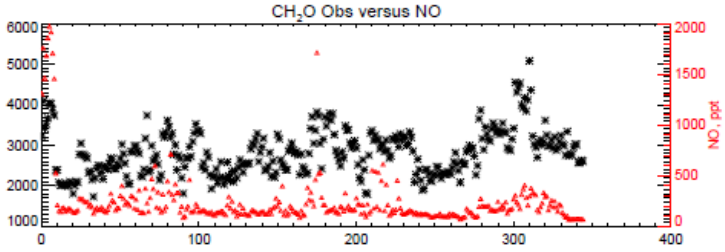




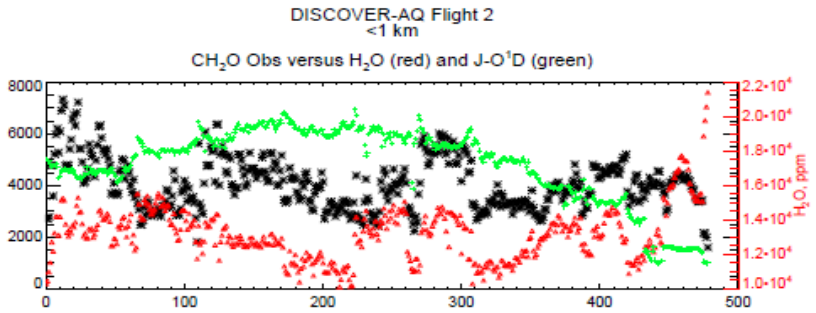


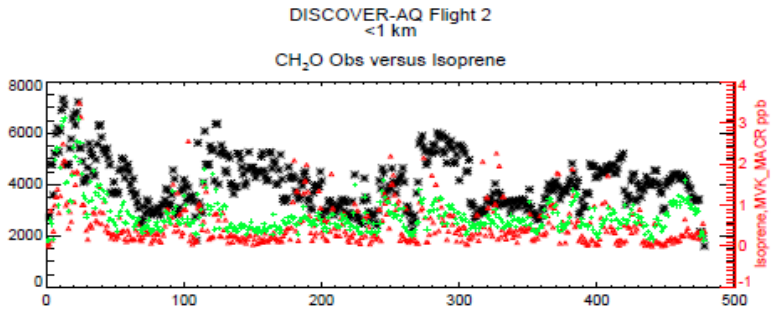


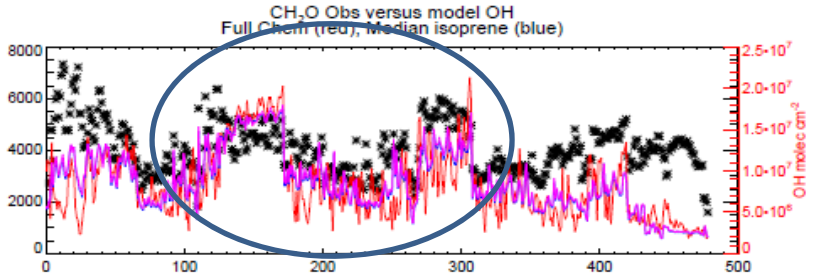
7000
Methanol
0

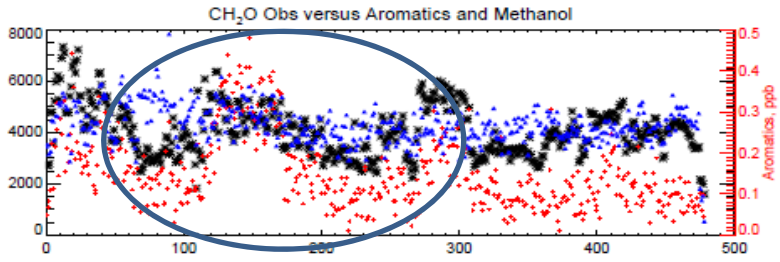


July 2:
CH2O correlates with aromatics and NO
Model runs with constant isoprene and constant isoprene ONLY (no NMHCs, methanol or acetone) suggest OH is driven by primary source and NO
Predicted CH2O variability is then driven by constant level of isoprene and variable oxidation rate (OH)

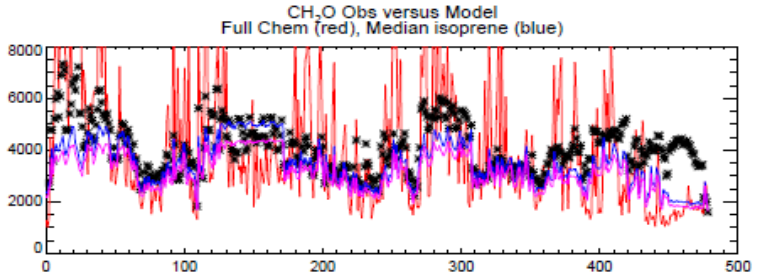


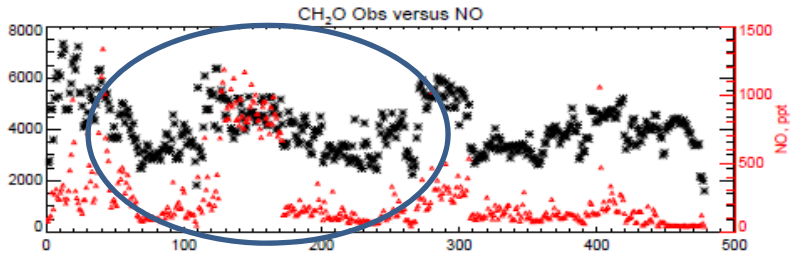




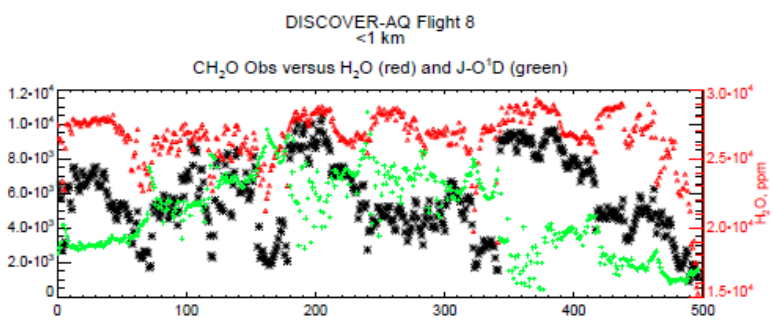


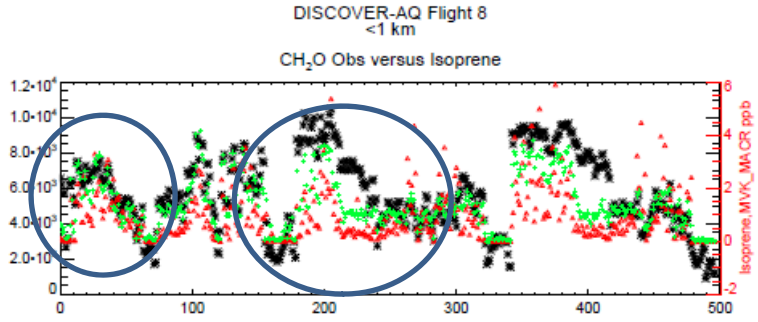
8000
Methanol
2000

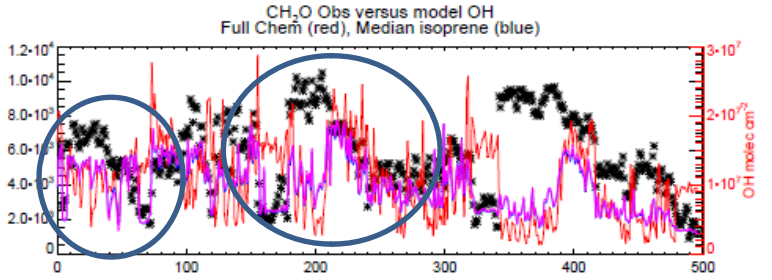


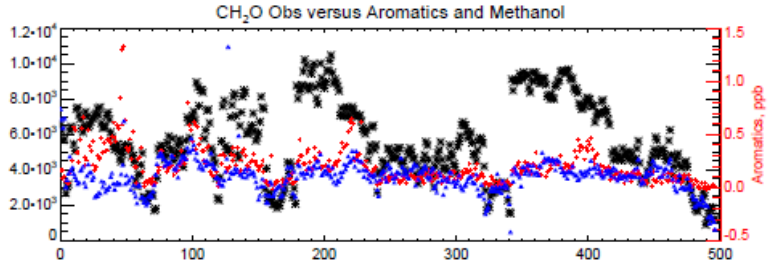


July 20:
CH2O correlated with Isoprene.
NOT with OH, however (high isoprene suppresses OH)
In this case, variability in predicted CH2O is driven by isoprene and MVK+MACR (biogenic) variations (not in variability of oxidation rate)

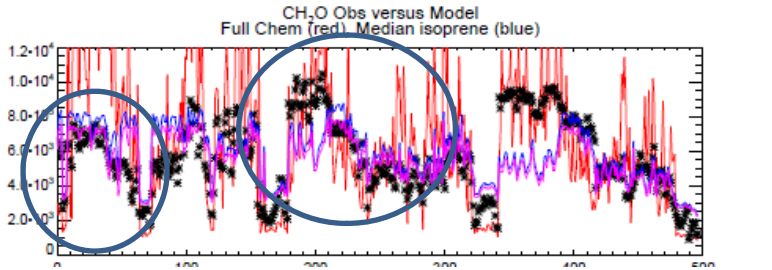


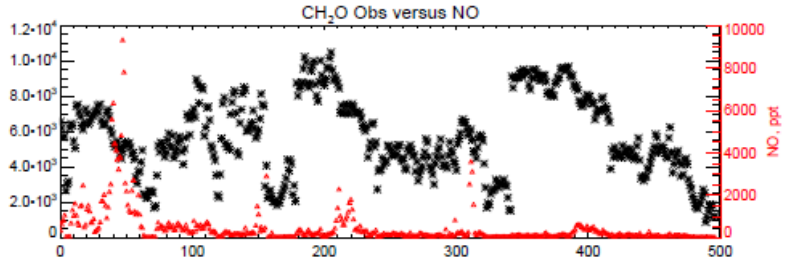


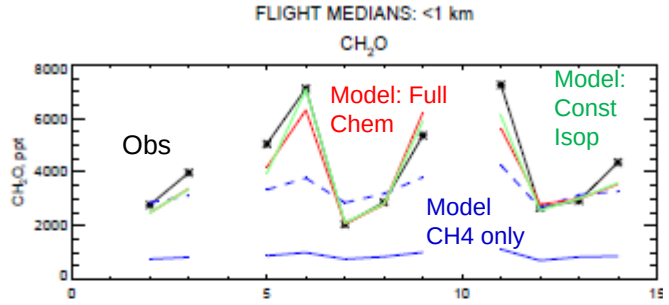


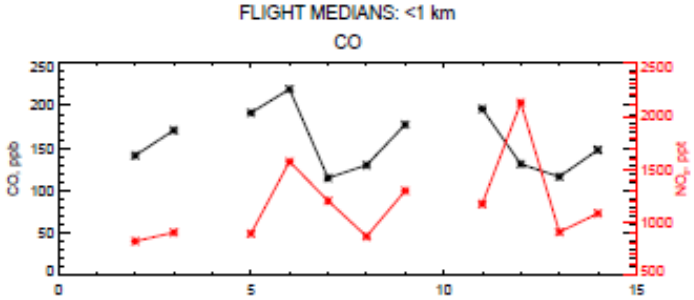


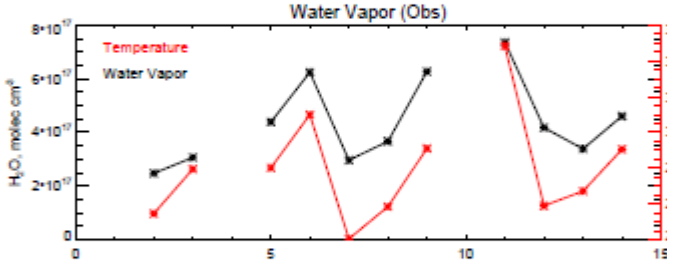
14000
Methanol
2000

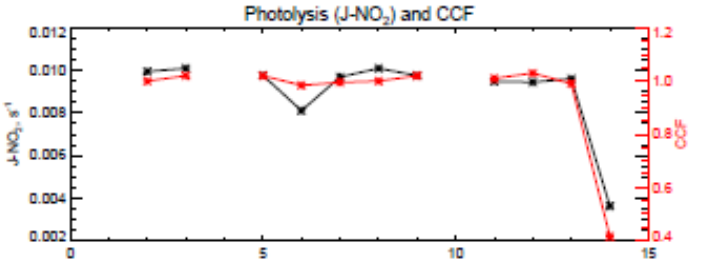


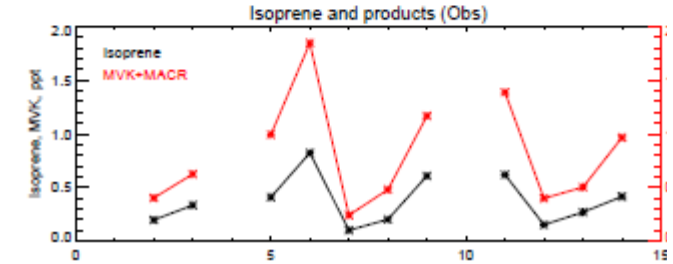


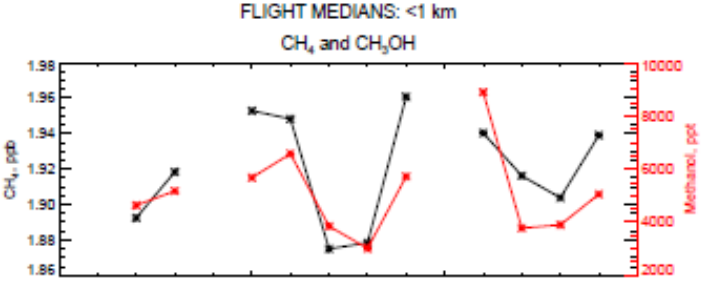

FLIGHT MEDIANS: <1 km
CH2O
Obs
Model: Full Chem
Model: Const Isop
Model CH4 only
CH2O, ppt

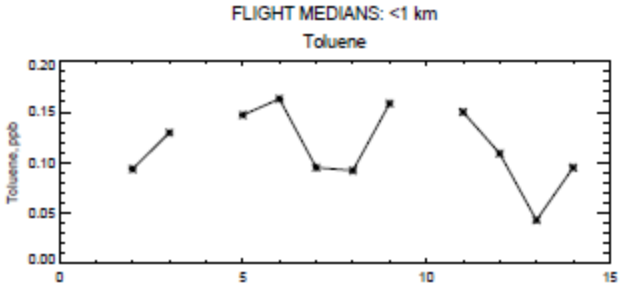

FLIGHT MEDIANS: <1 km
CO
CO, ppb
NOy, ppt


Water Vapor (Obs)
Temperature
Water Vapor
H2O, molec cm-3

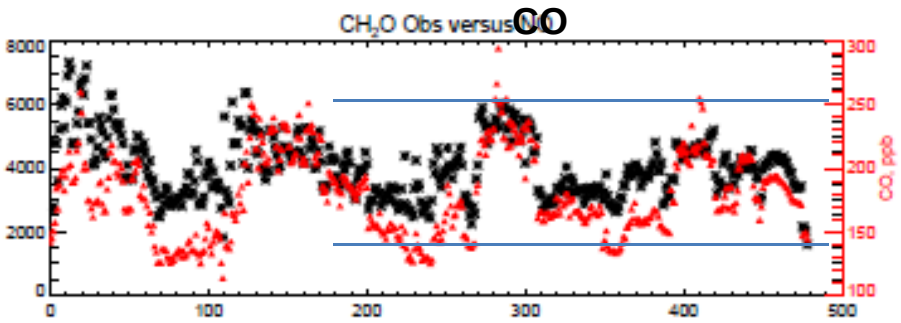

Photolysis (J-NO2) and CCF
J-NO2, s-1
CCF

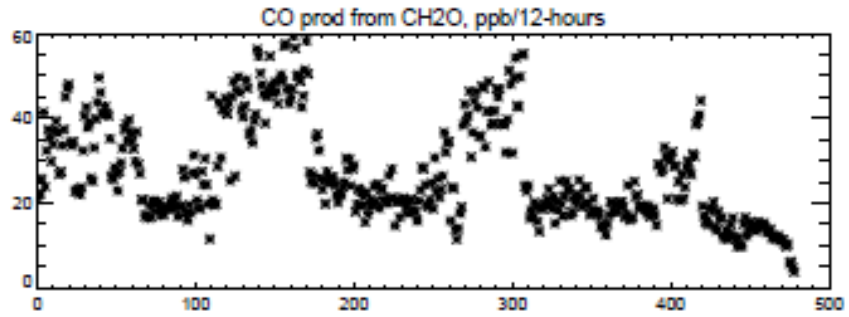

Isoprene and products (Obs)
Isoprene
MVK+MACR
Isoprene, MVK, ppt


FLIGHT MEDIANS: <1 km
CH4 and CH3OH
CH4, ppb
Methanol, ppt


FLIGHT MEDIANS: <1 km
Toluene
Toluene, ppb

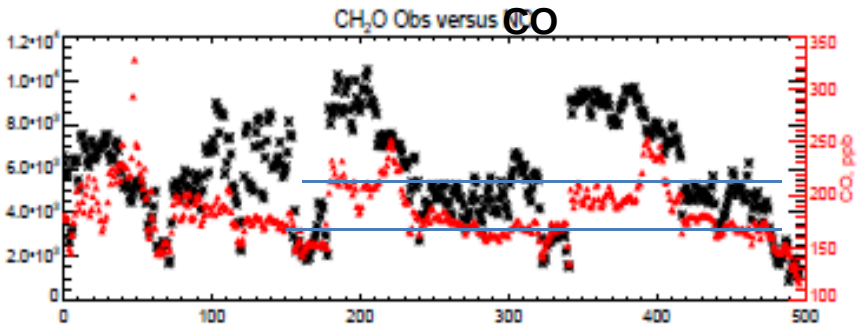
July 2:

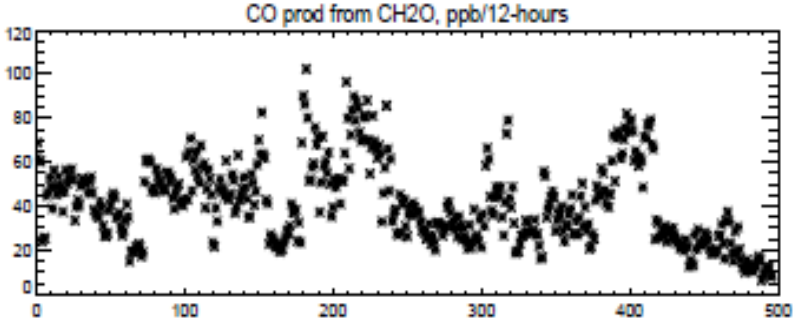




~100 ppb variance in CO
CO production from Isoprene/CH2O < half
Isoprene <1 ppb

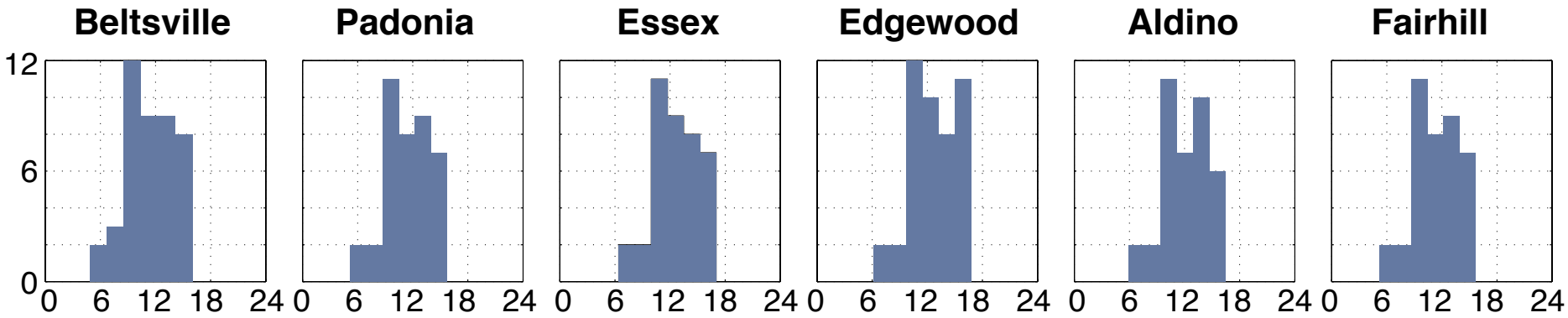
July 20:



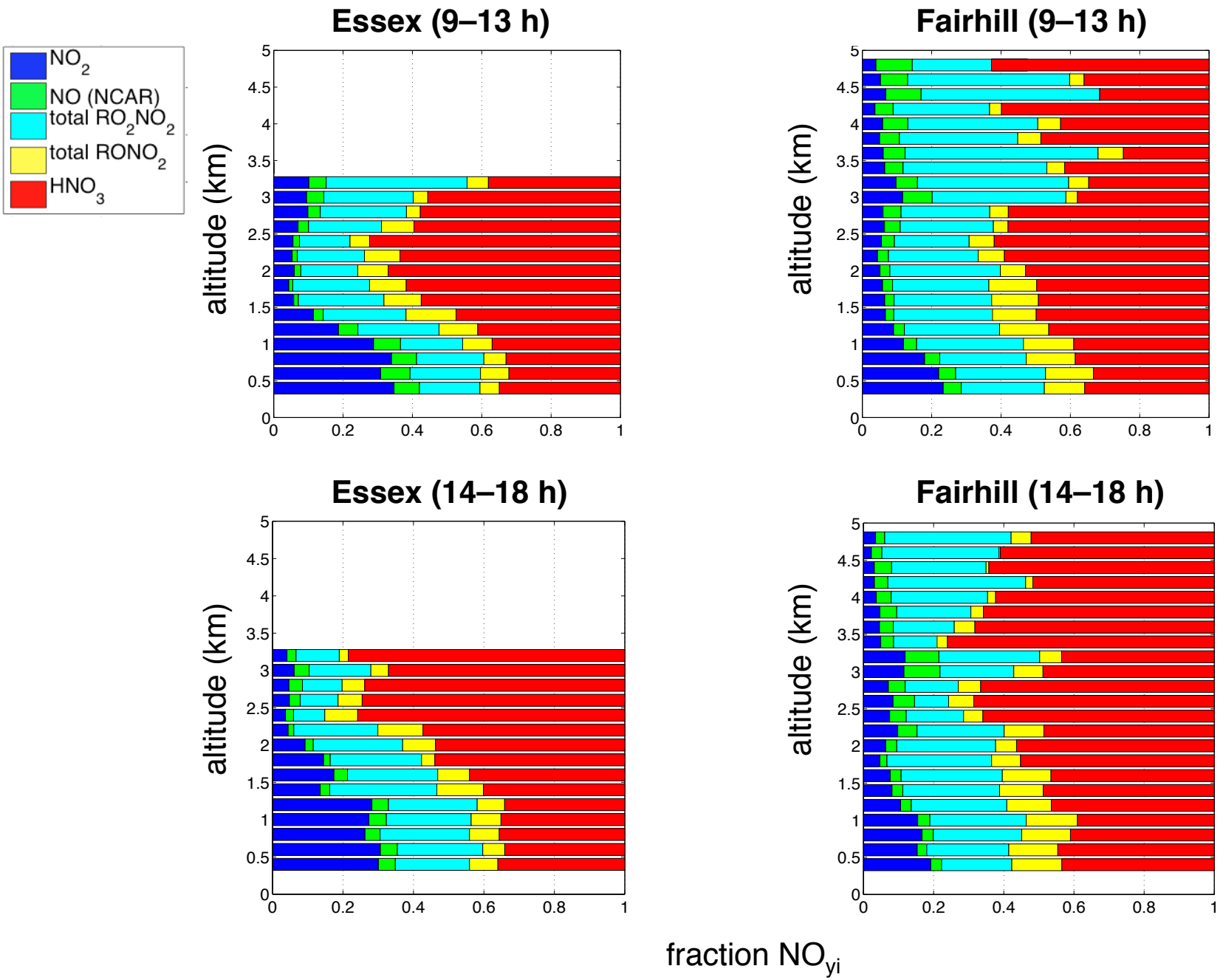


~50 ppb variance in CO
CO production from Isoprene/CH2O might cover this???
Isoprene 1-2 ppb

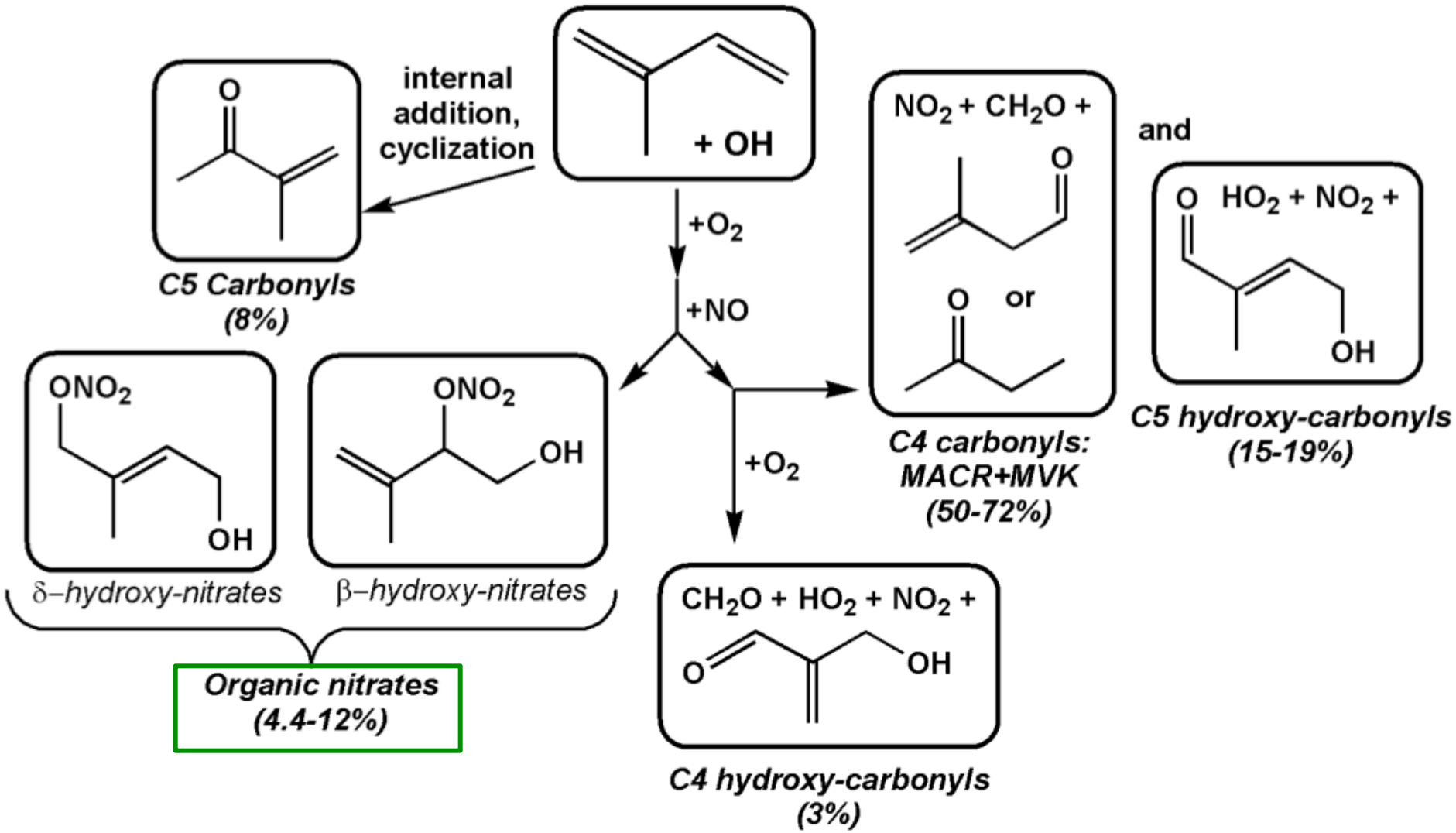
Number of profiles with time of day



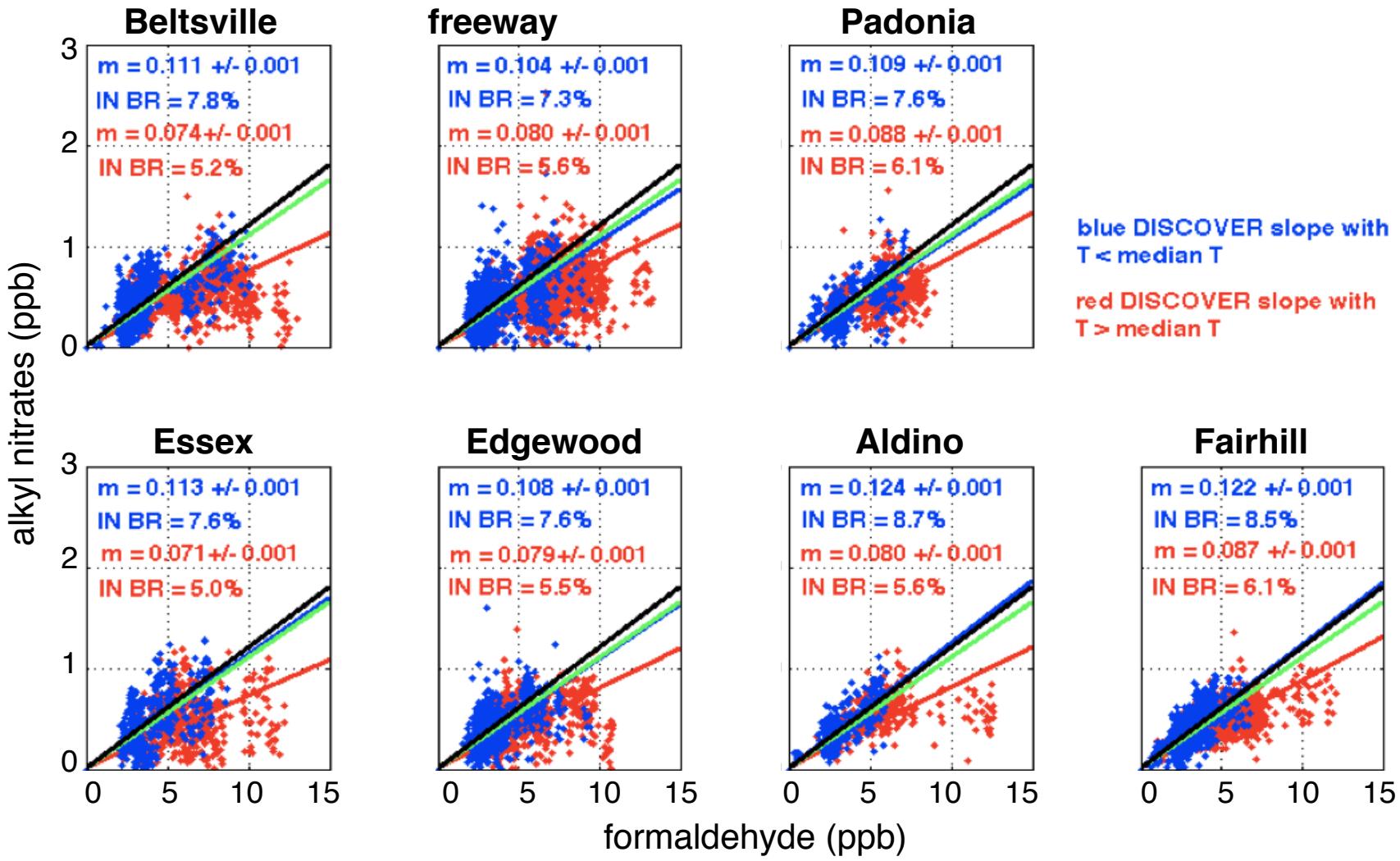
Nitrogen oxide speciation with time of day



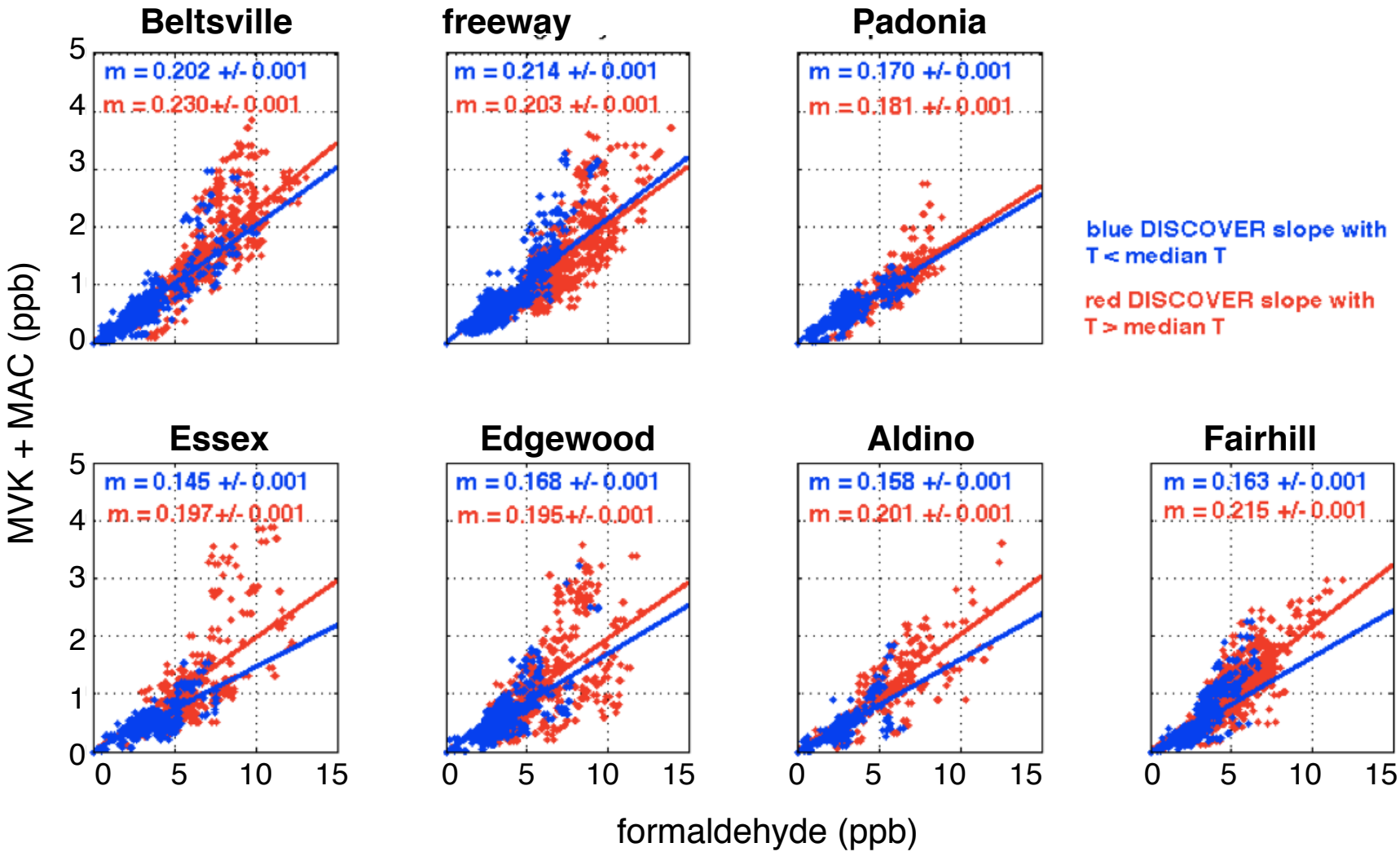
Isoprene oxidation chemistry



Isoprene oxidation chemistry



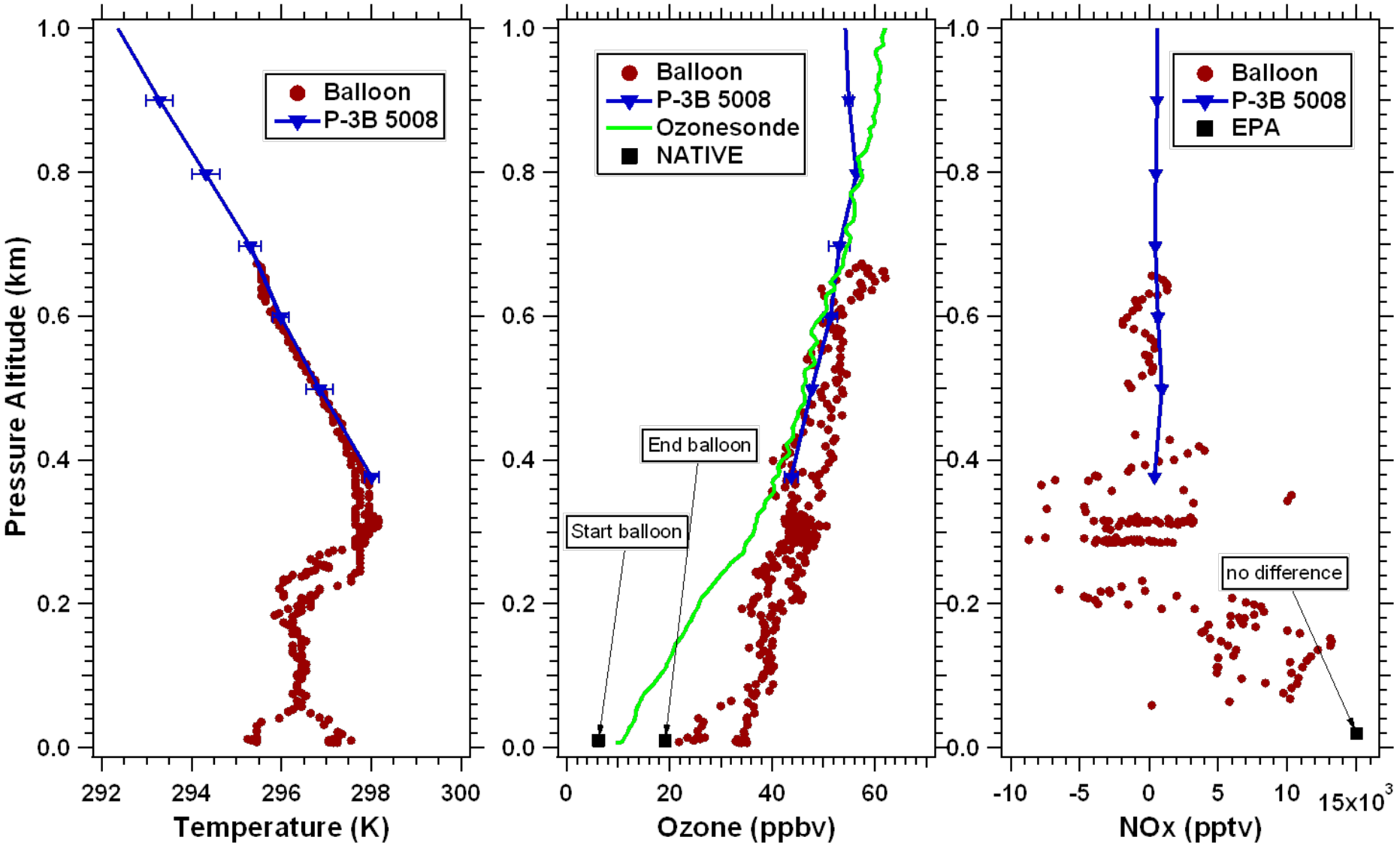
Isoprene oxidation chemistry



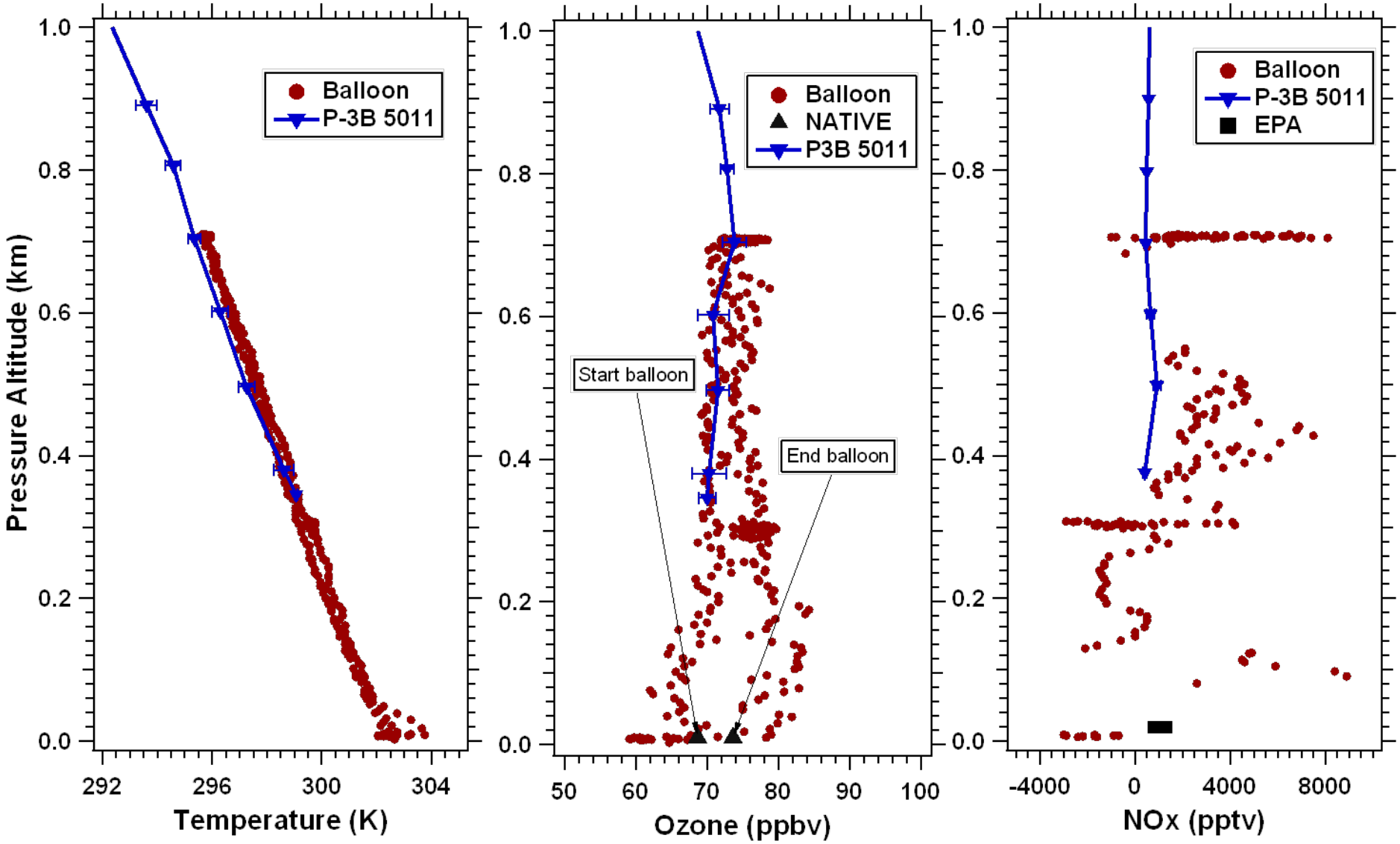
DISCOVER-AQ *in-situ* Vertical Profile Measurements

- Vertical profile measurements consist of P-3B spiral, ozonesonde, surface measurement, and tethered balloon
- Tethered balloon measurement is important to fill the gap between the spiral and surface measurements
- It is important to assess the consistency between all measurements

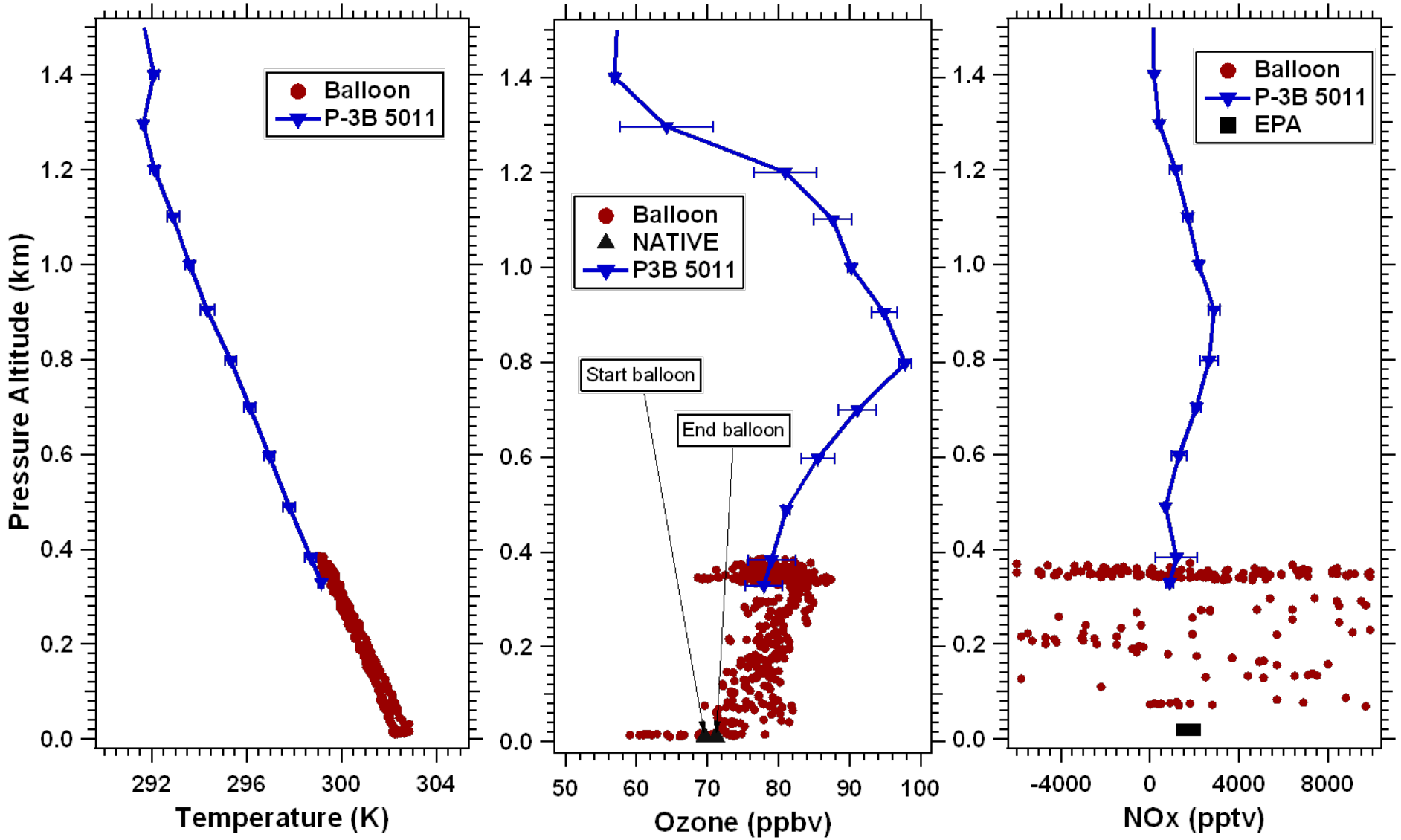
Comparison of Vertical Profiles
Edgewood, 7/5/2011 ~7:20 EDT



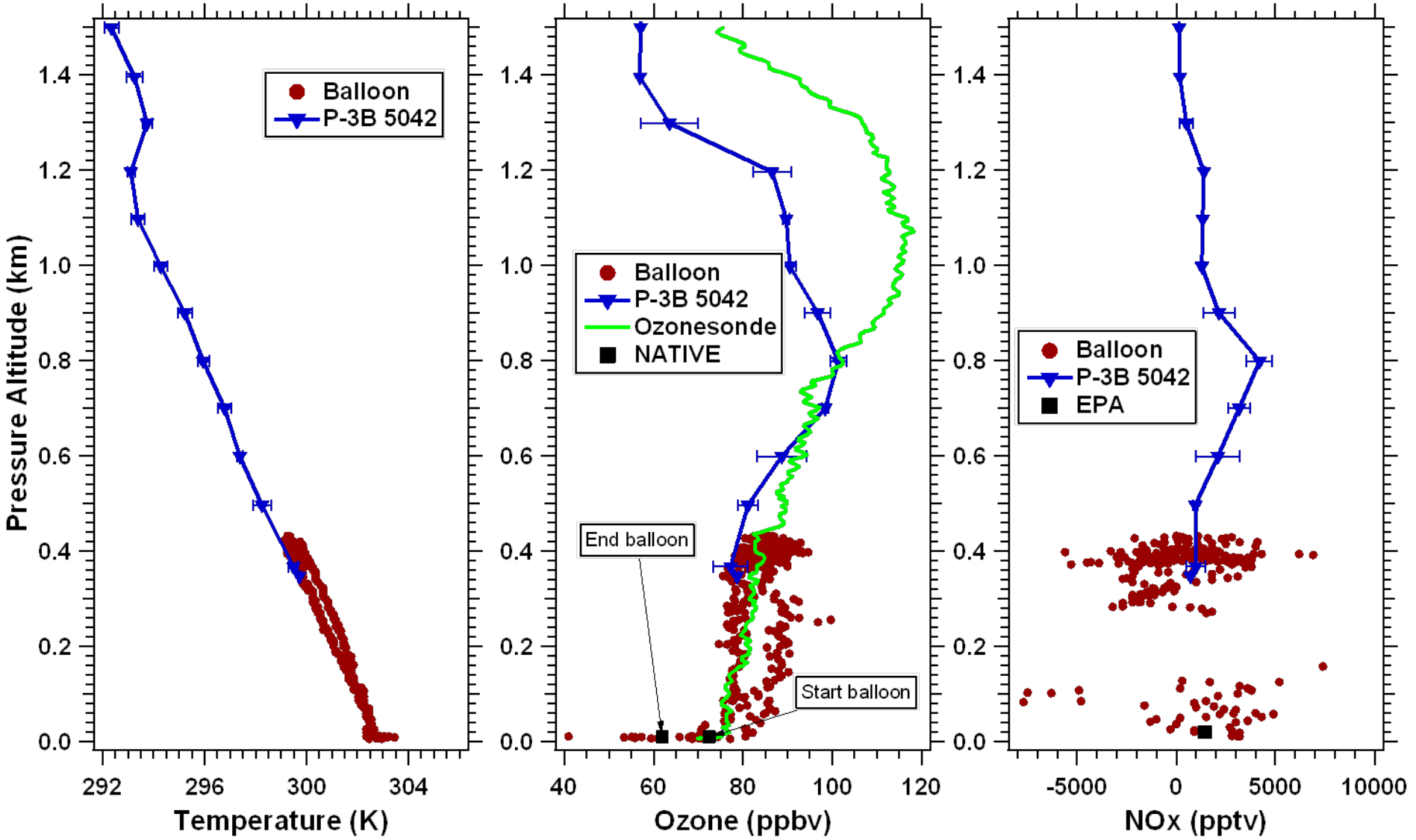
Comparison of Vertical Profiles
Edgewood, 7/5/2011 ~12:30 EDT



Comparison of Vertical Profiles
Edgewood, 7/28/2011 ~14:30 EDT



Comparison of Vertical Profiles
Edgewood, 7/28/2011 ~16:30 EDT



More Work….

- Consistency should be systematically assessed among tethered balloon, P-3B, surface, and ozonesonde measurements
  - Vertical profile comparison
  - Time series comparison of fixed vertical bins
  - Others …

Ozone Profile-Satellite Comparisons, Inferred Processes & Maryland Climatology (2005-2011)

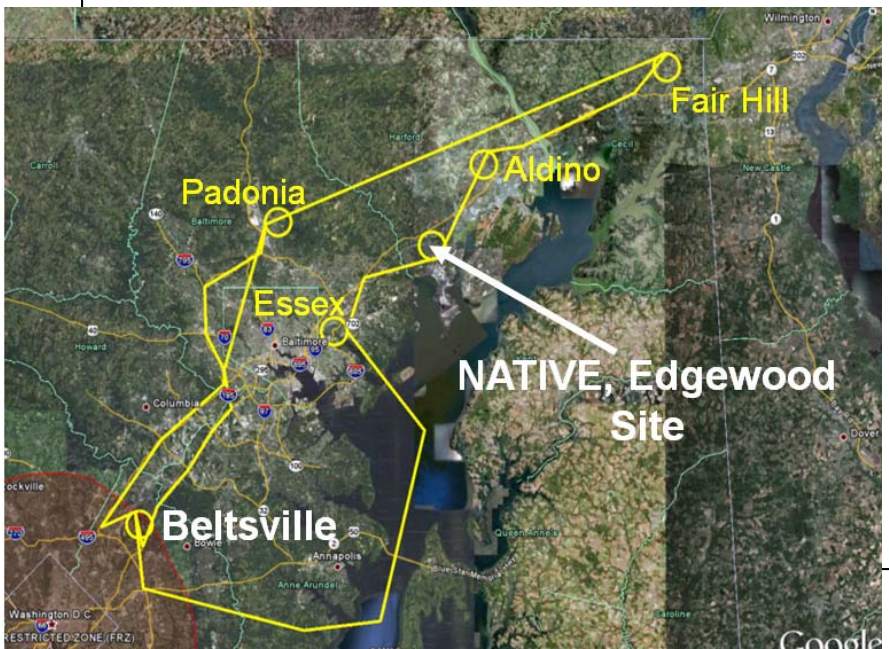
Anne Thompson, PSU; amt16@psu.edu

With: SK Miller, DK Martins, RM Stauffer, JA Bielli, E Joseph, R Clark

Also – Doug Martins. Surface-Air-Satellite-P-3 Comparisons – Statistics, Stability Relations

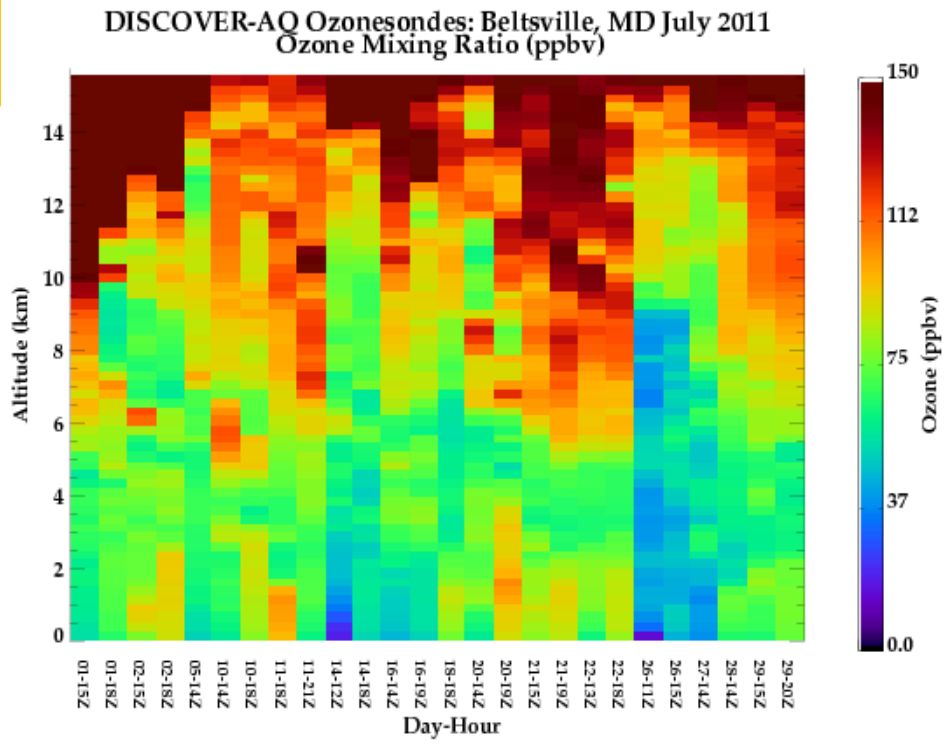
Key DISCOVER-AQ Data Sources

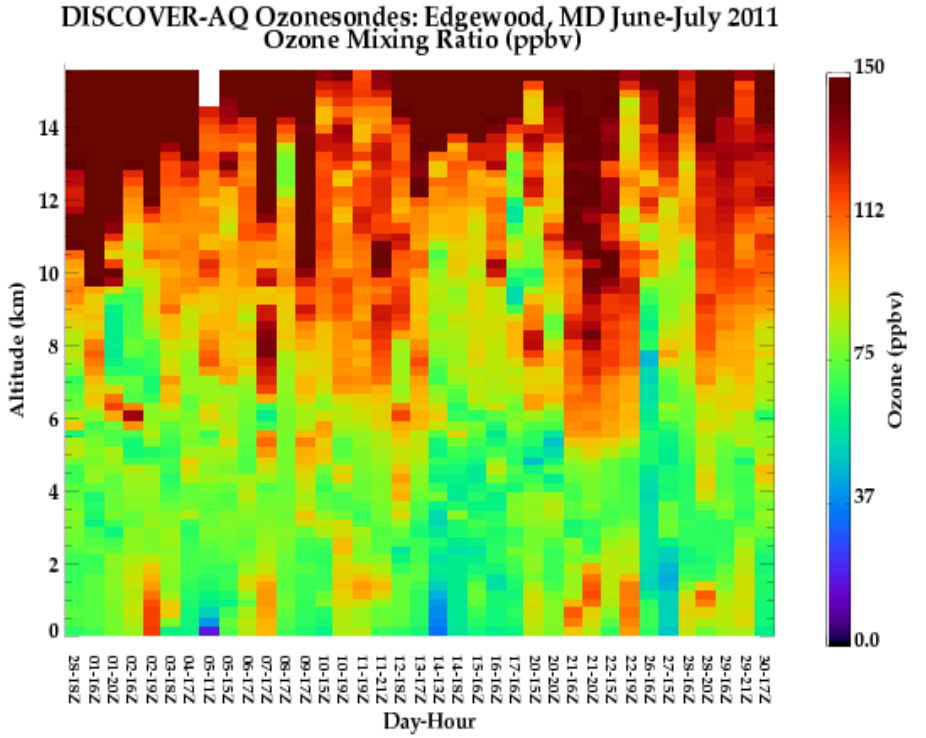
- Soundings at Beltsville, MD (39.0N, 77W), 20 km NE of WDC & Edgewood, MD (39.4N, 76.3W), 30 km NE of Baltimore on Chesapeake Bay
- Instruments @ Edgewood: PSU NATIVE trailer, EPA-LaRC $NO/No_x/NO_2$, MDE ozone monitor, with Pandoras, Cimel, Leosphere, aerosol lidar. 2 km to MU sodar, tethered balloon O_3



Ozonesondes Integrate In-Situ Data, Satellites, Models

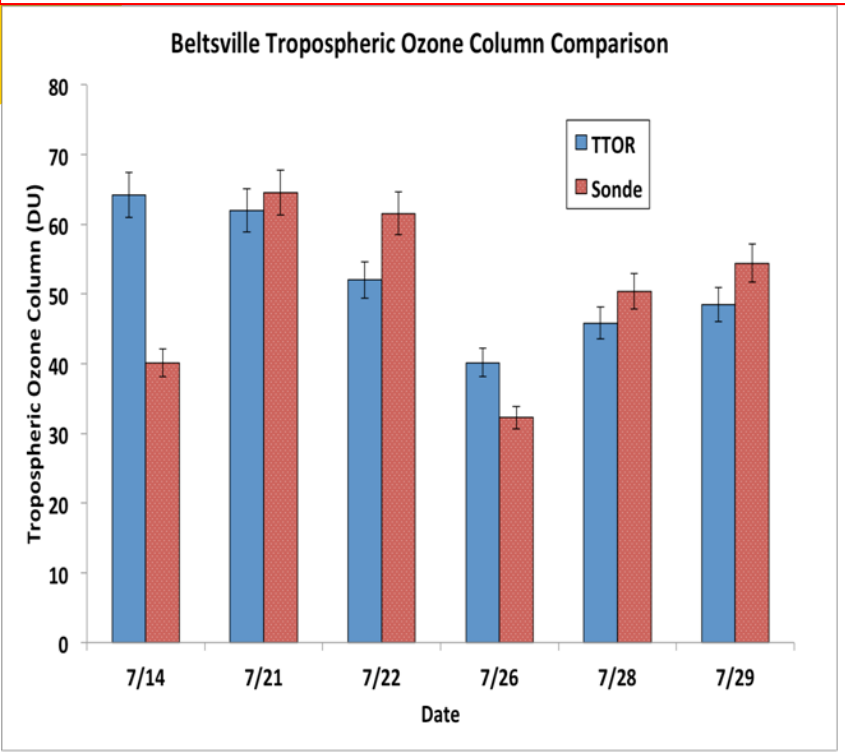
- High vertical resolution (~100 m), consistent sonde location vital to evaluation of satellite algorithms & models
- Two Maryland tropospheric ozone records: Overview, July 2011. Beltsville (58 DU) less ozone than Edgewood (62 DU).

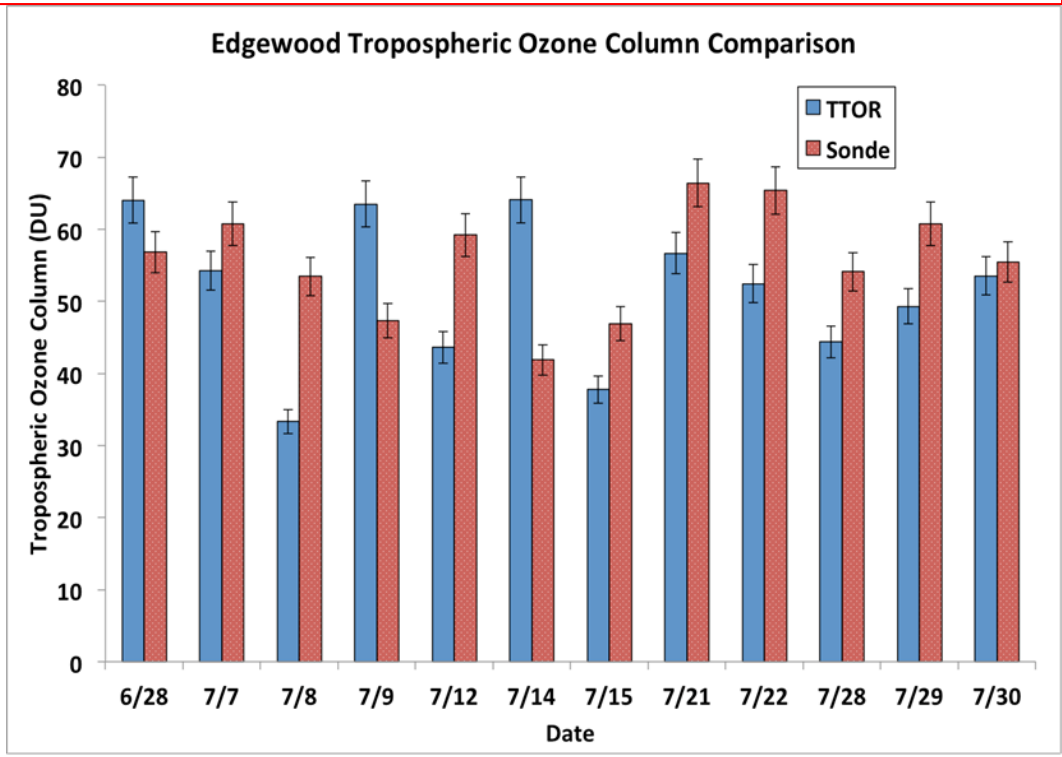




Ozonesondes – TTOR Tropospheric Ozone Comparisons

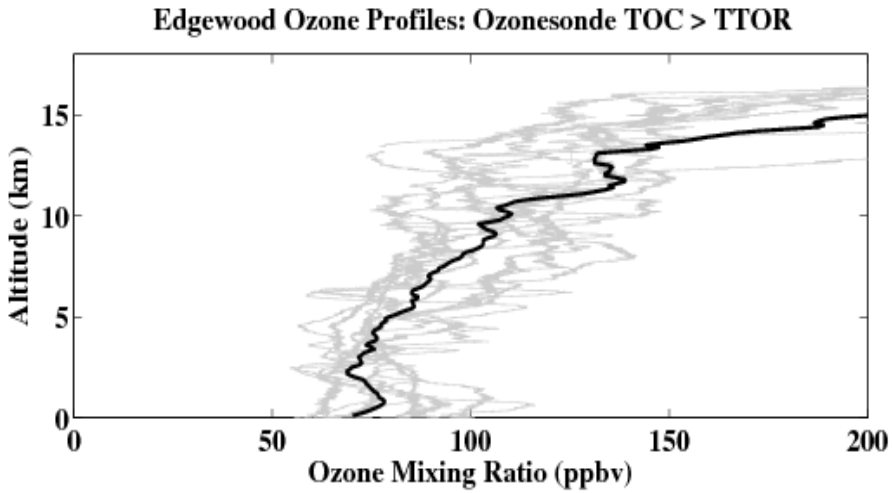
- OMI/MLS TTOR from: ftp://hyperion.gsfc.nasa.gov/pub/aura/tropo3
- Sondes generally greater than TTOR (4 of 6 at Beltsville, 9 of 12 at Edgewood). At Edgewood, 5 of 9 offsets ~ 10 DU (15-20%).

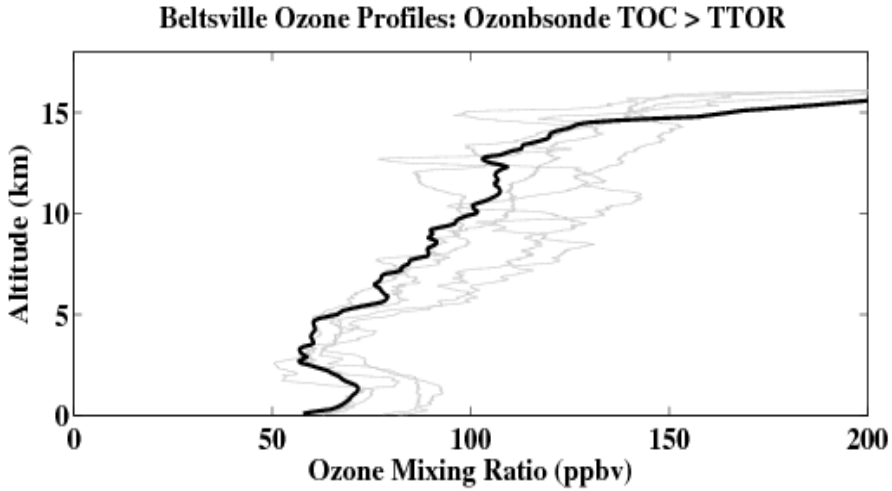




Factors to Consider in Satellite-Sonde Offsets (1)

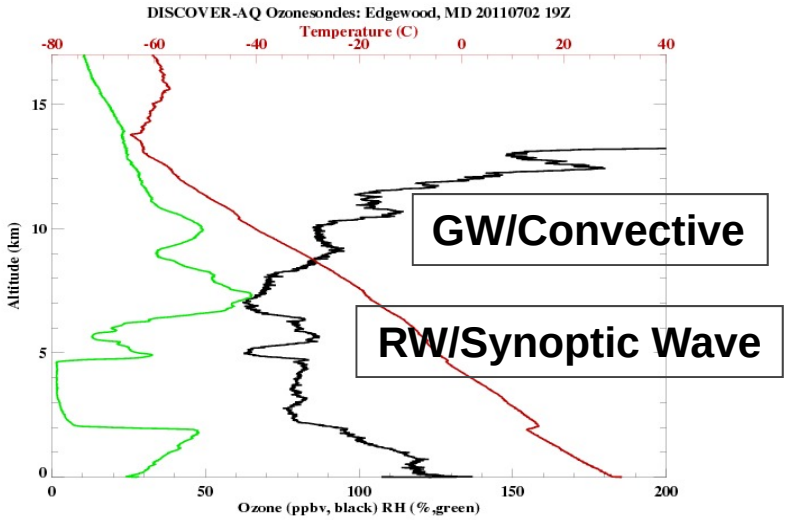
- Ozone distribution within profiles. Is there a pattern?
- Meteorological patterns. Do certain ones imply better or worse agreement?
  - Bay breeze effects @ Edgewood (*Martins et al.*, 2012; ***Stauffer et al.*, Poster**)
  - Air mass types (categories by dry/moist; polar/tropical; *Normile,* 2011)
- Profile segment autocorrelations (***Chatfield et al.*, in review, 2012; Poster**)

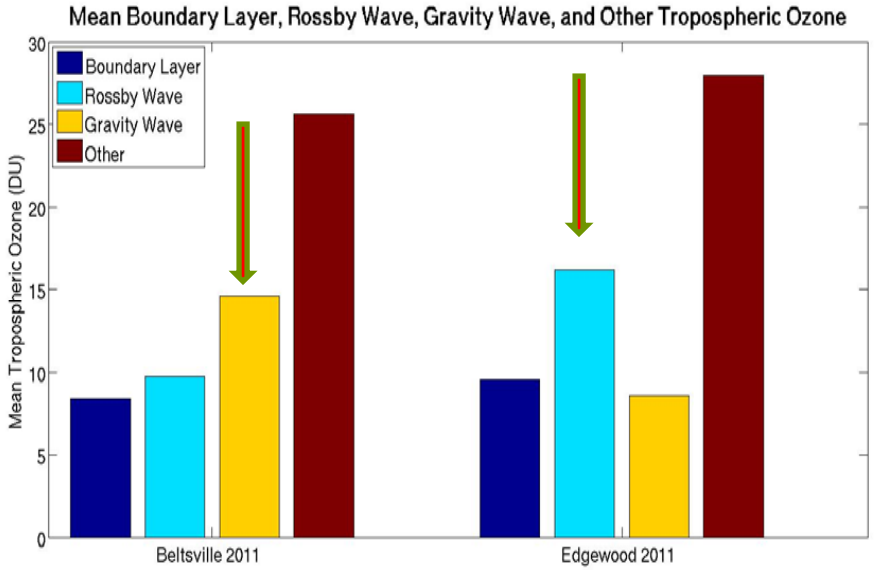




Factors to Consider in Satellite-Sonde Offsets (2)

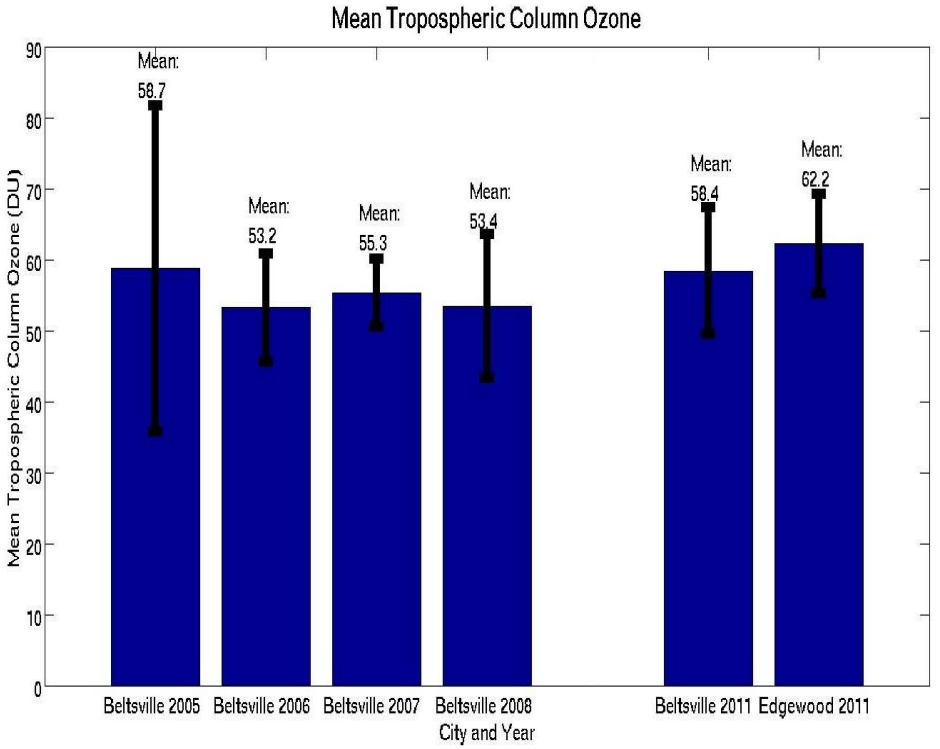
- Laminar budgets (*Thompson et al.,* 2007; 2011) classify influences within each profile.
  - Four terms. BL, AD = imported pollution & "background"
  - "GW" proxy <u>for vertical mixing, more prominent at Beltsville</u>
  - "RW" proxy for advective influences, e.g., bay-breeze pollution<u>, more prevalent at Edgewood</u>
- In progress: compare 2011 ozone with 2004-2010 Beltsville ozonesonde climatology





Moving Forward

- Constellation of repetitive aircraft, sonde, tether & surface observations in DISCOVER-AQ reveal complexities (vertical) & regionally over 10-20 km site separation, land-sea gradients
- Add'l information at Edgewood & Beltsville (flux data, VOC) will allow calculation of ozone formation rates **(H. Halliday Poster; D. Kollonige in progress)**, BL features
- Beltsville sondes (2004-2011) provide multi-year perspective on D-AQ. 2011 fairly high
- **Thanks to: BCCSO (E. Joseph & J. Fuentes) T. Meade at Aberdeen Proving Ground**



EXTRAS

DISCOVER-AQ – Multiple Ozone Profiles for Lowest Troposphere

Mean tether-Sonde ascent

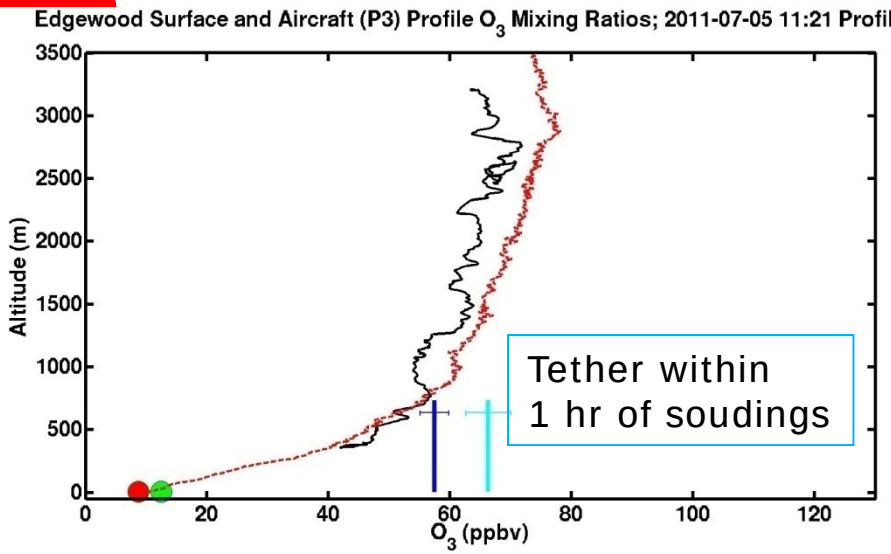
Mean tether-Sonde descent

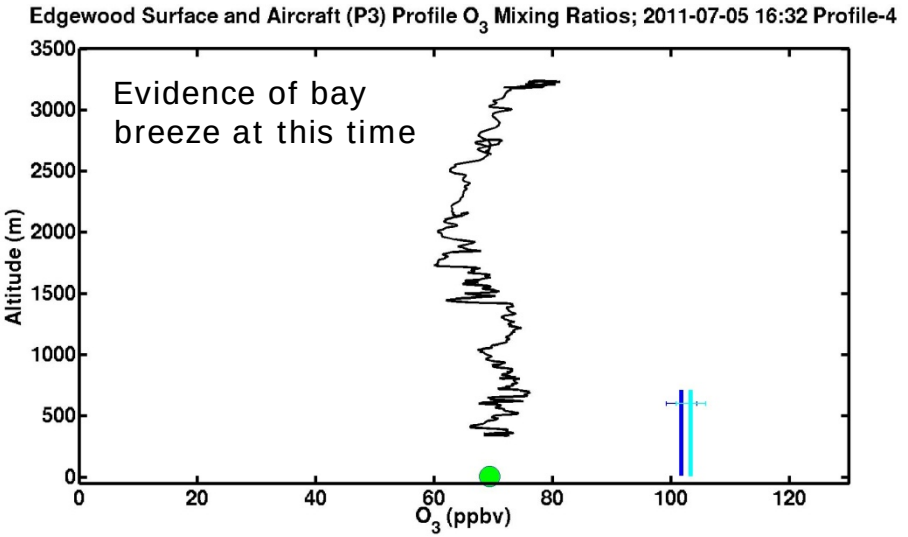
P3 Ozone Profile

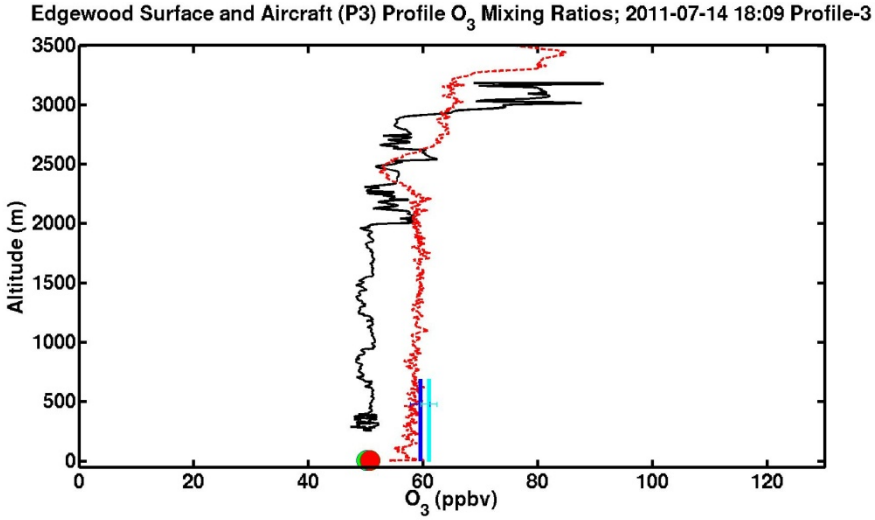
Ozonesonde

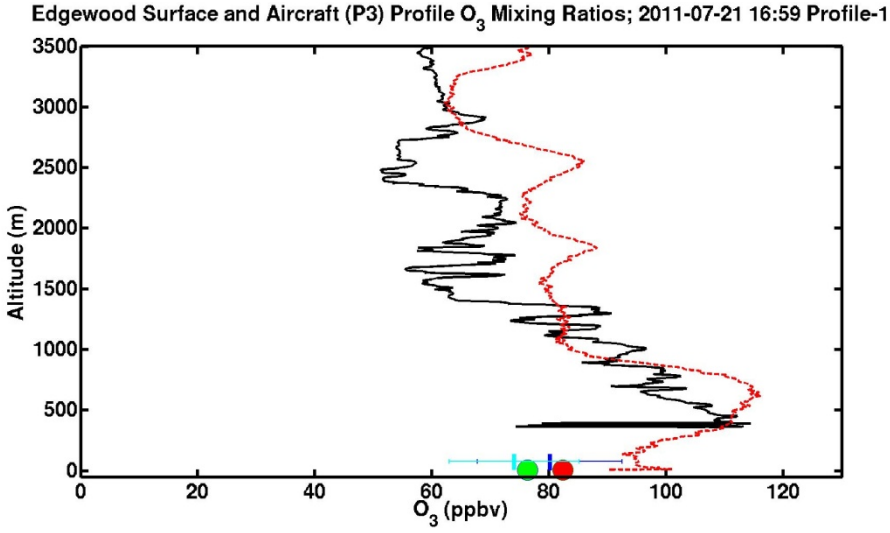
NATIVE/Surface averaged during P3 overpass

NATIVE/Surface 10-min averaged about ozonesonde launch









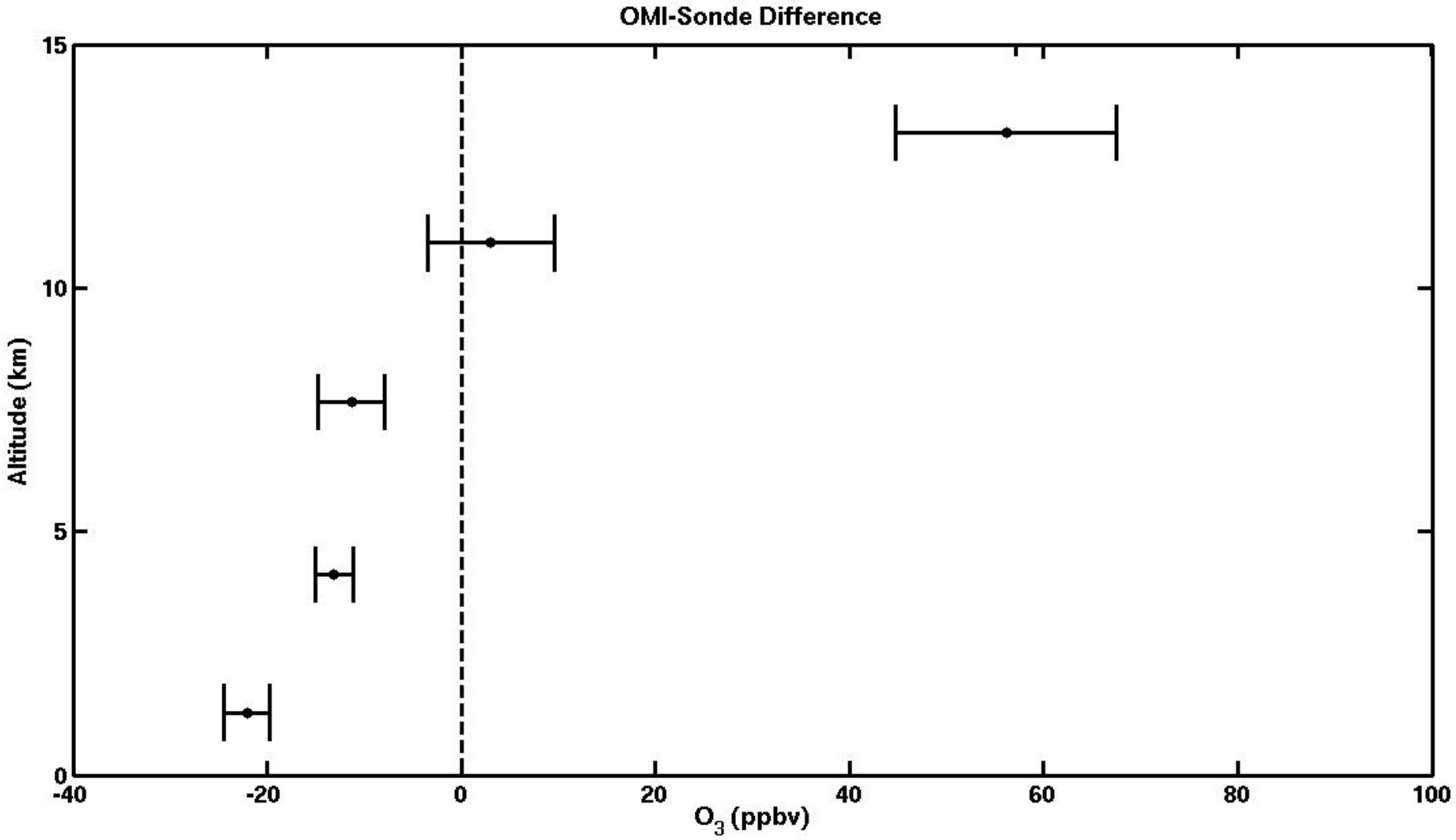
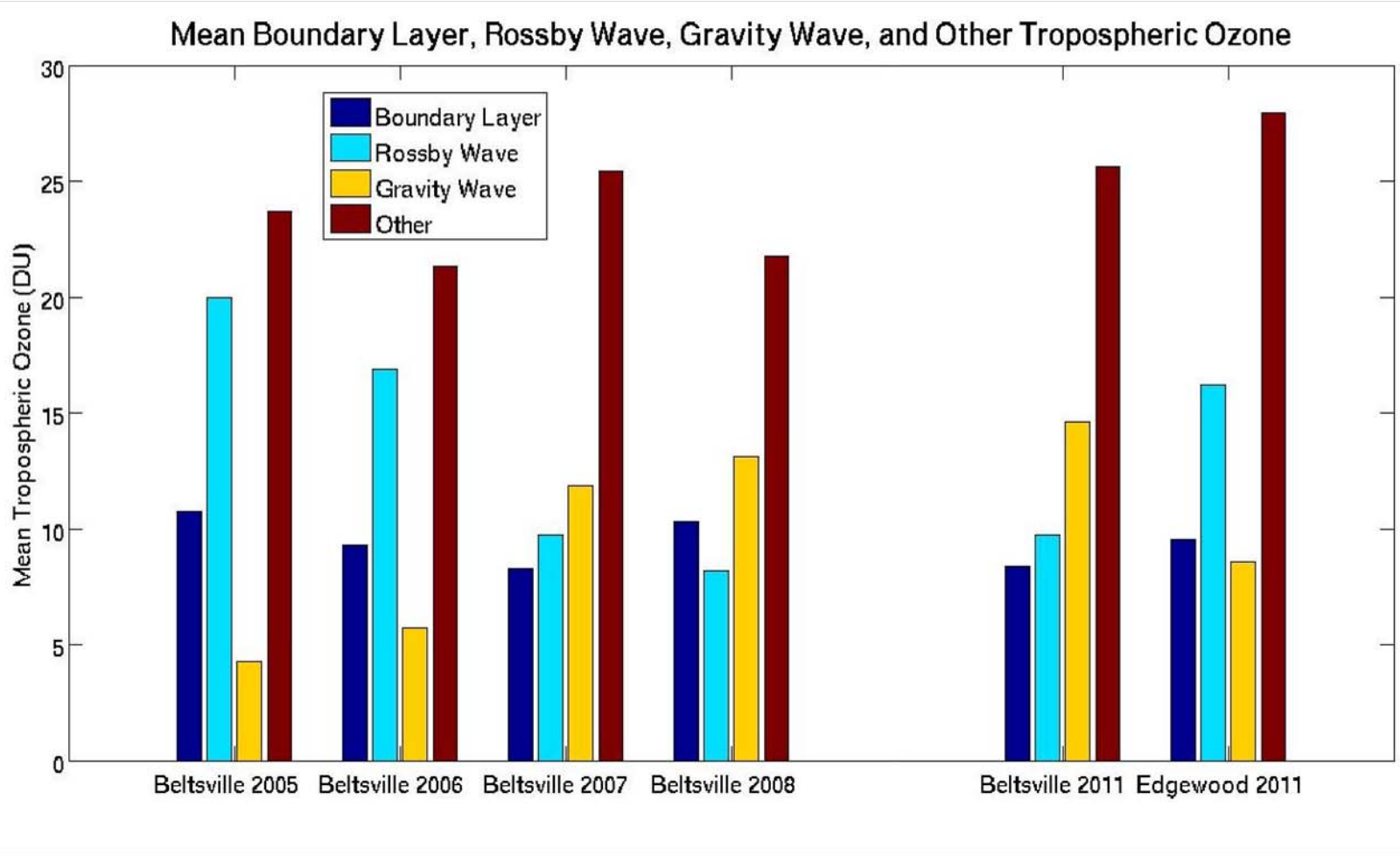
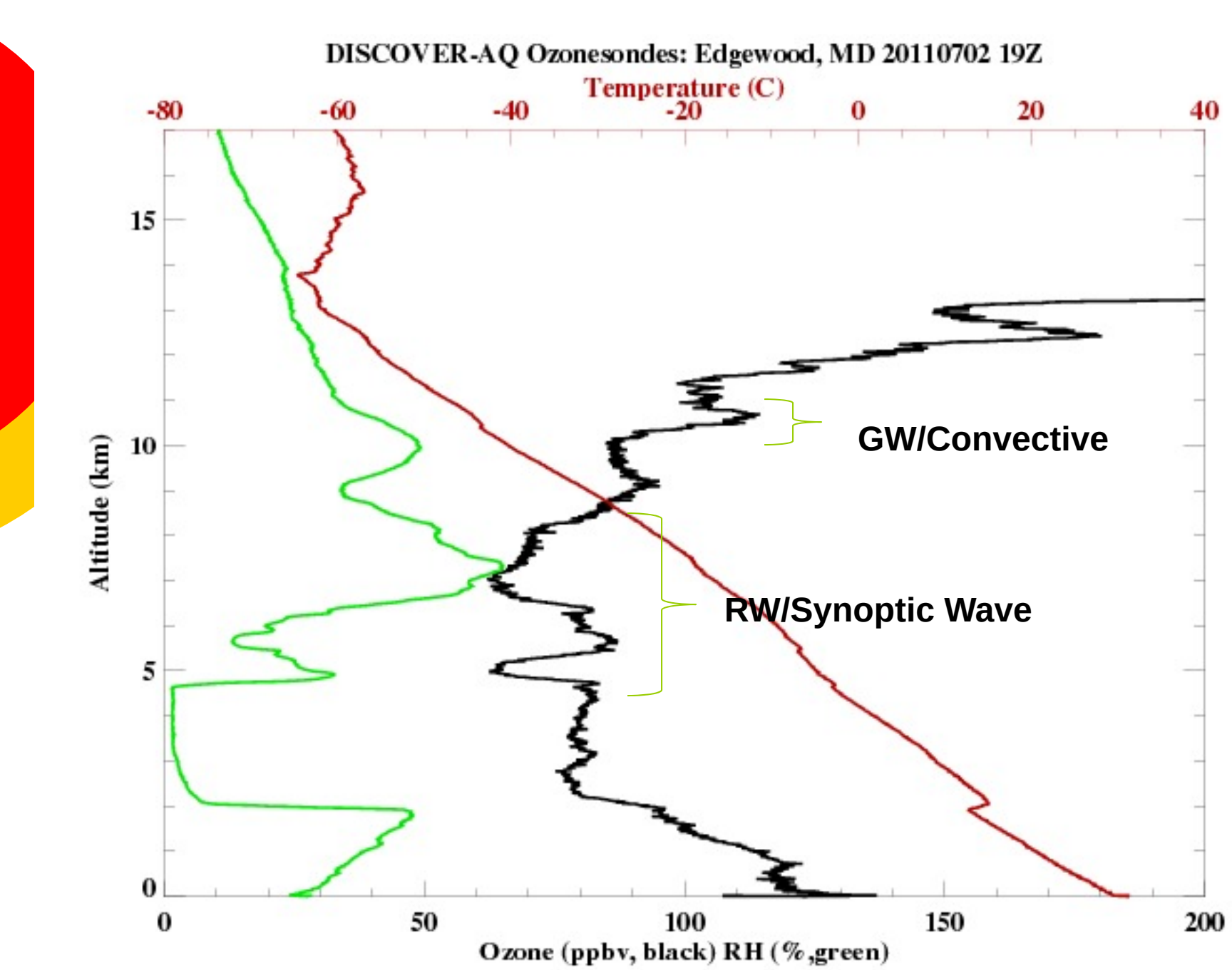


Figure. Comparison of OMI ozone profiles (OMO3PR) and coincident ozonesonde measurements at Edgewood, MD. The satellite profile closest to the ozonesonde launching site was chosen for each day. Ozonesonde measurements were bin-averaged at each satellite vertical layer. Error bars represent one standard deviation of a bootstrap resampling (10,000 points) of each vertical layer mean.

Mean Wave & Boundary Layer Ozone: Beltsville (2005-08) & DISCOVER-AQ



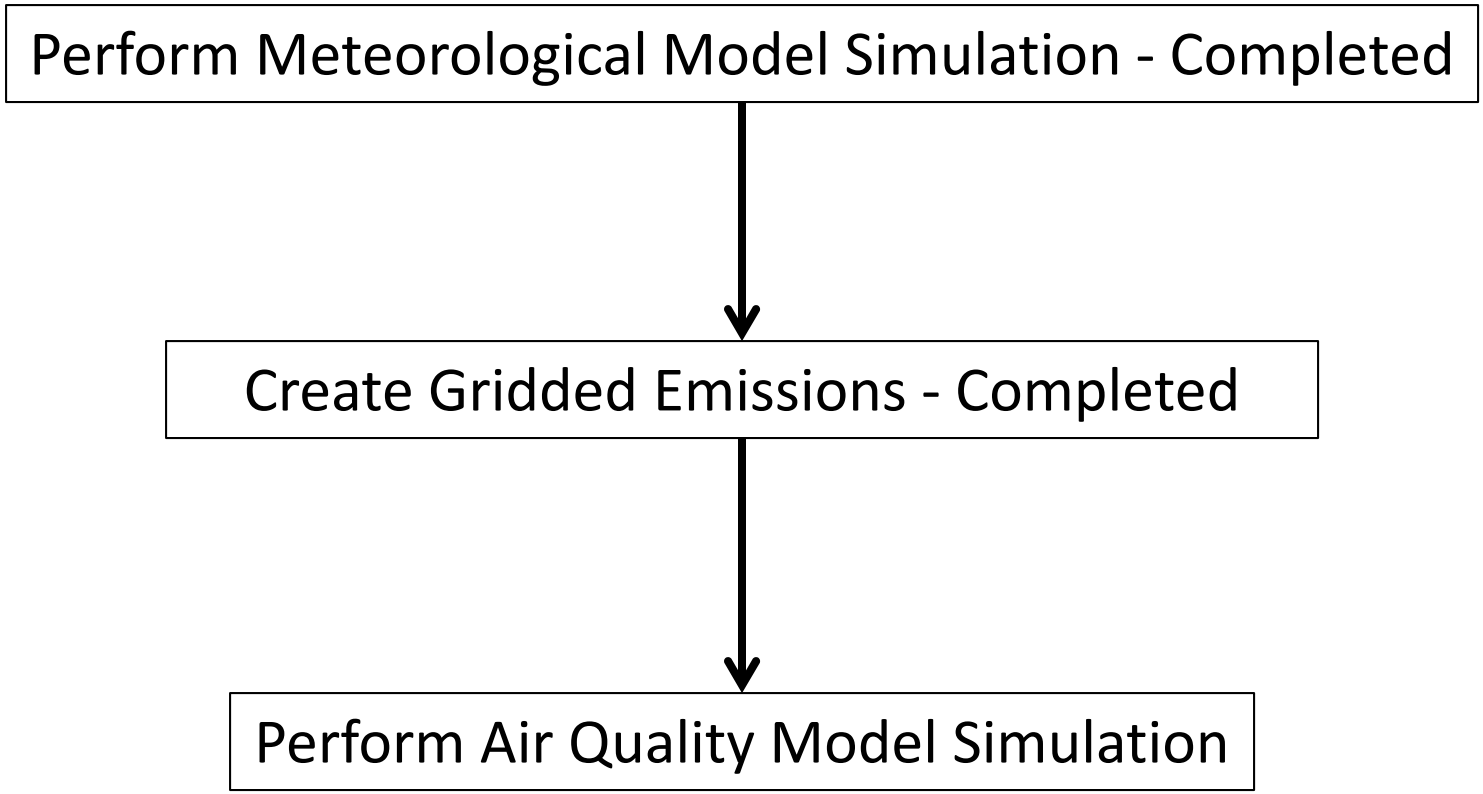

DISCOVER-AQ Ozonesondes: Edgewood, MD 20110702 19Z
Temperature (C)
-80
-60
-40
-20
0
20
40
15
10
5
0
Altitude (km)
GW/Convective
RW/Synoptic Wave
0
50
100
150
200
Ozone (ppbv, black) RH (%,green)

Atmospheric Modeling DISCOVER-AQ Field Campaign

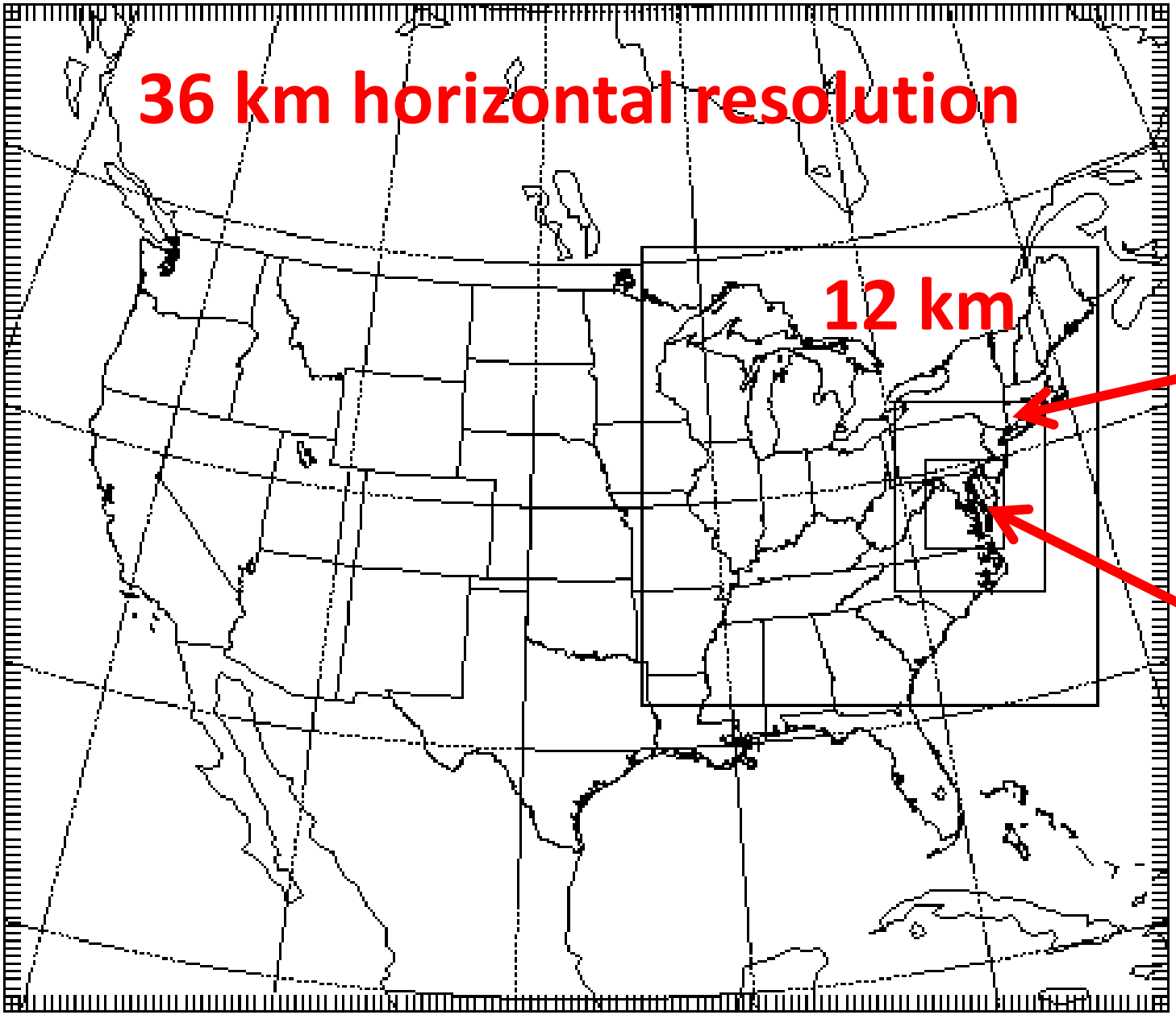
DISCOVER-AQ Science Team Meeting
14-16 February 2012

Chris Loughner (ESSIC UMD / NASA GSFC)
Chinmay Satam (UMD)
Melanie Follette-Cook (MSU / NASA GSFC)
Zhining Tao (USRA / NASA GSFC)
Ken Pickering (NASA GSFC)

WRF-Chem, NU-WRF, and CMAQ Modeling Approach

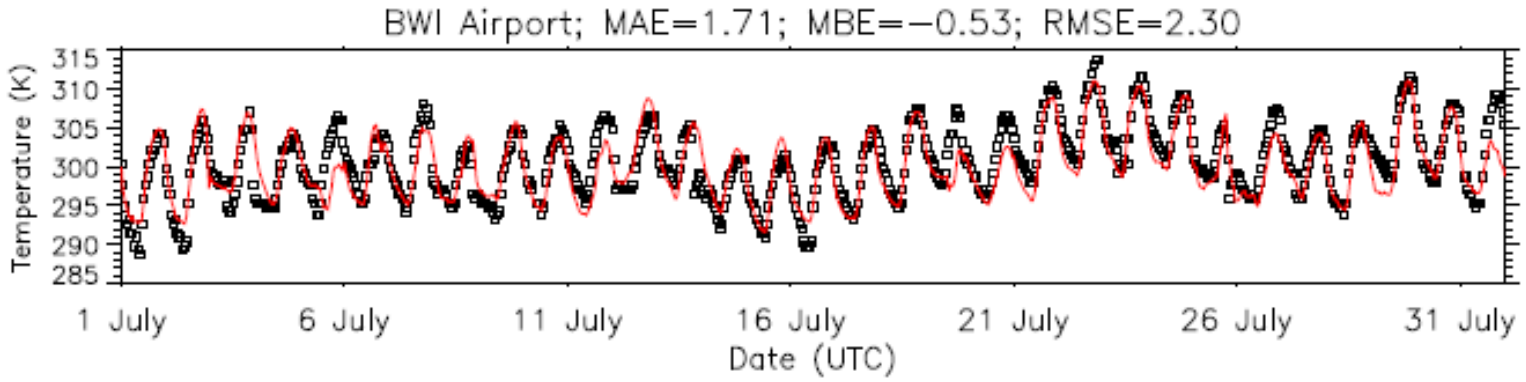


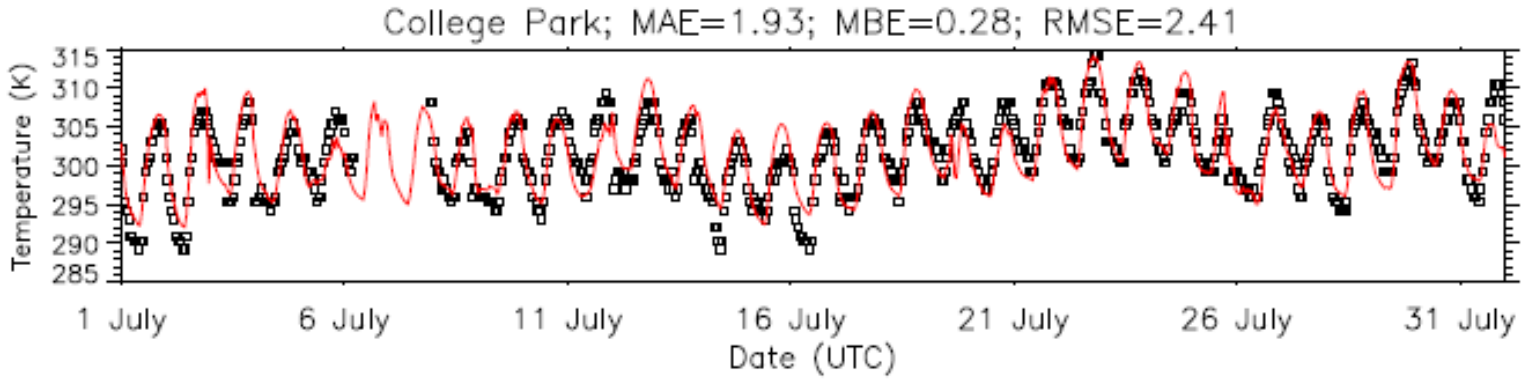
WRF-Chem, NU-WRF, and CMAQ Modeling Domains

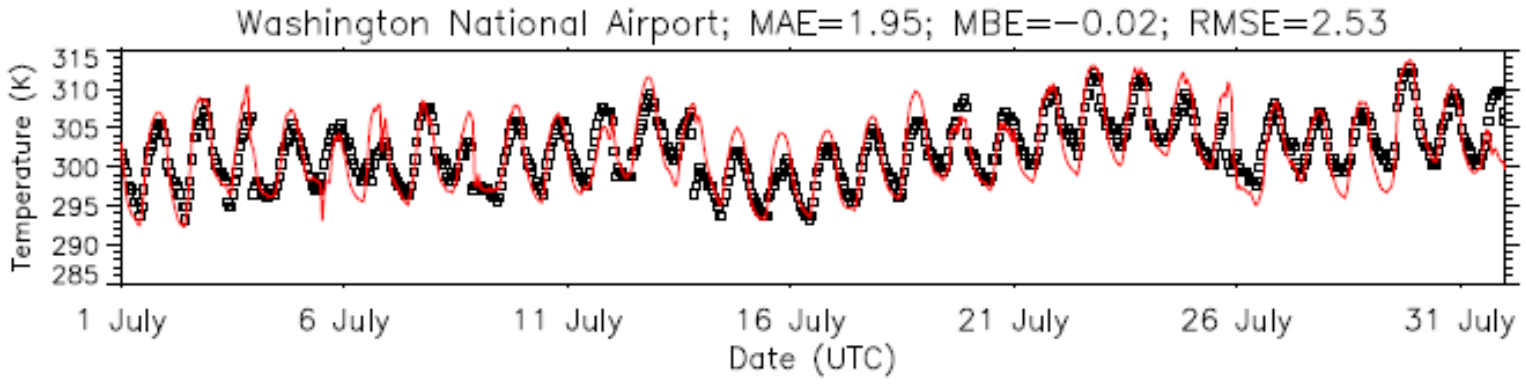


Weather Research and Forecasting (WRF) Model Options	
Time Period	May 24 – August 5, 2011
Re-initialize	Every 3 days except for soil temperature and soil moisture
Length of each run	3.5 days (first 12 hours of each run are discarded)
Initial and Boundary Conditions	NCEP Final Analysis
Radiation	LW: RRTM SW: Goddard
Surface Layer	Pleim-Xiu
Land Surface Model	Pleim-Xiu
Boundary Layer	ACM2
Cumulus	Kain-Fritsch (none for 1.3 km domain)
Microphysics	WSM-6
Nudging	Observational and analysis nudging
Damping	Vertical velocity and gravity waves damped at top of modeling domain

Temperature; red – model (resolution: 1.3km), black – observations
MAE=mean absolute error; MBE=mean bias error; RMSE=root mean square error

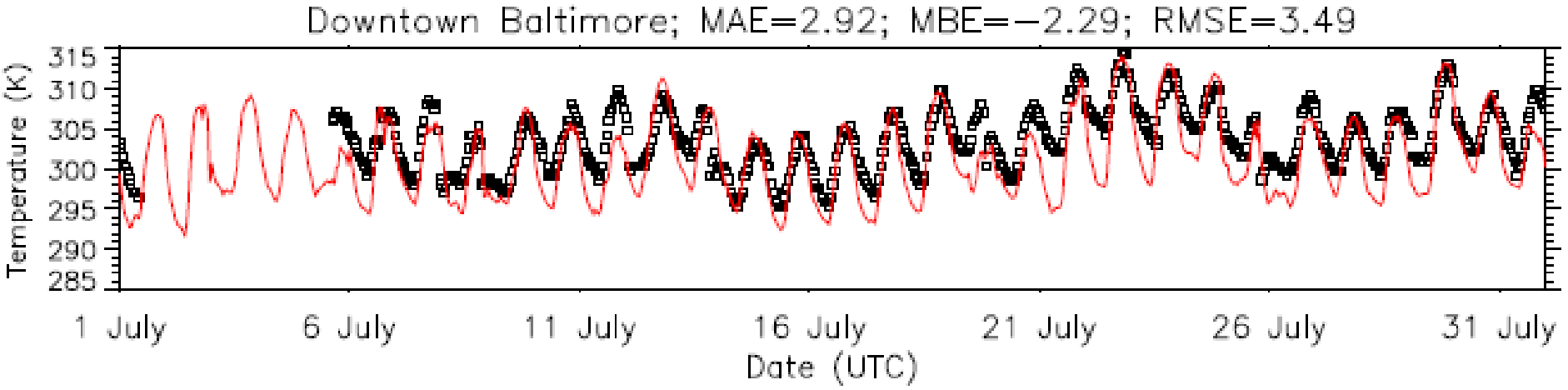






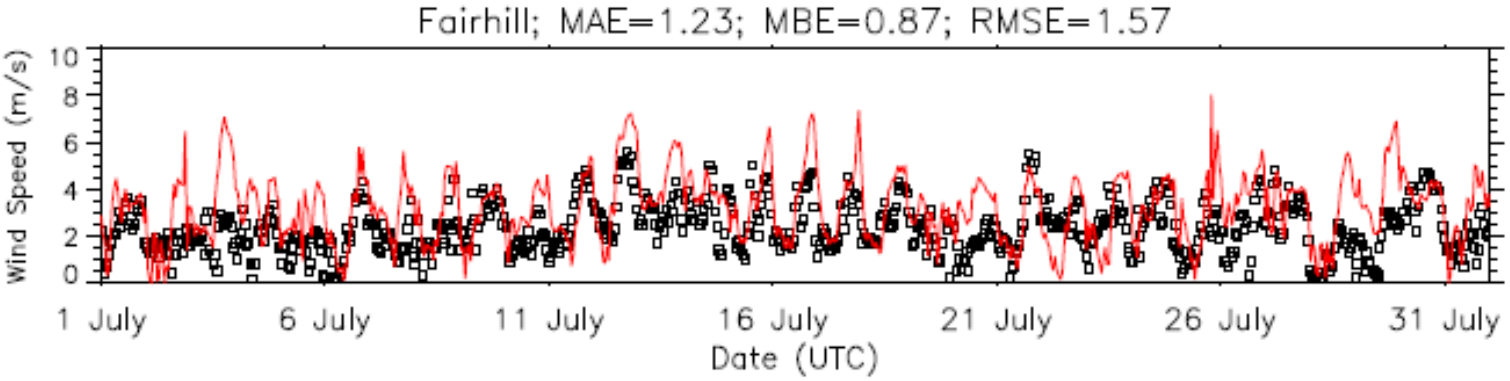
While there are good statistical relationships between the model and observations for the entire month of July as a whole, there are a few days when the model has poor agreement with the observations

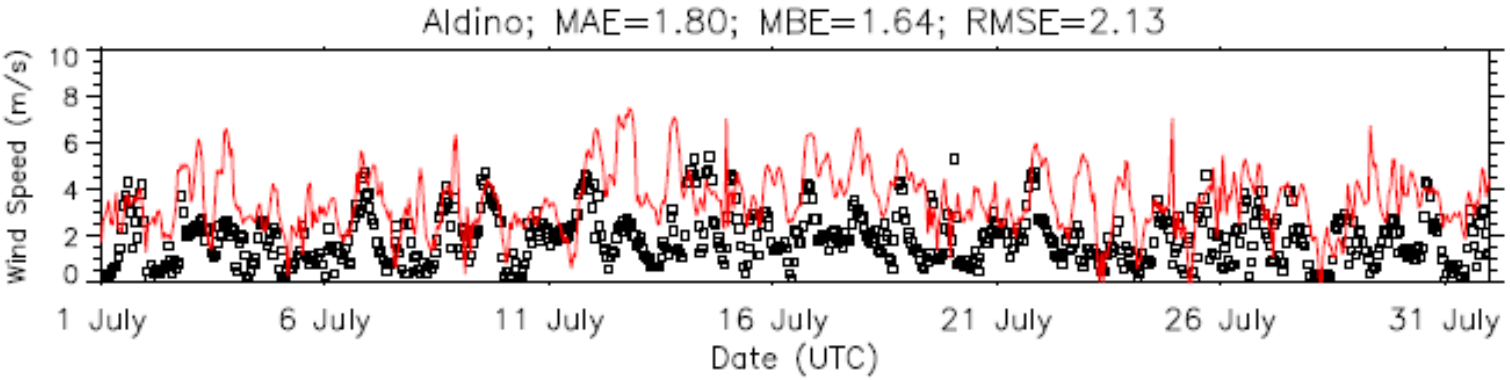
Temperature; red – model (resolution: 1.3km), black – observations
MAE=mean absolute error; MBE=mean bias error; RMSE=root mean square error

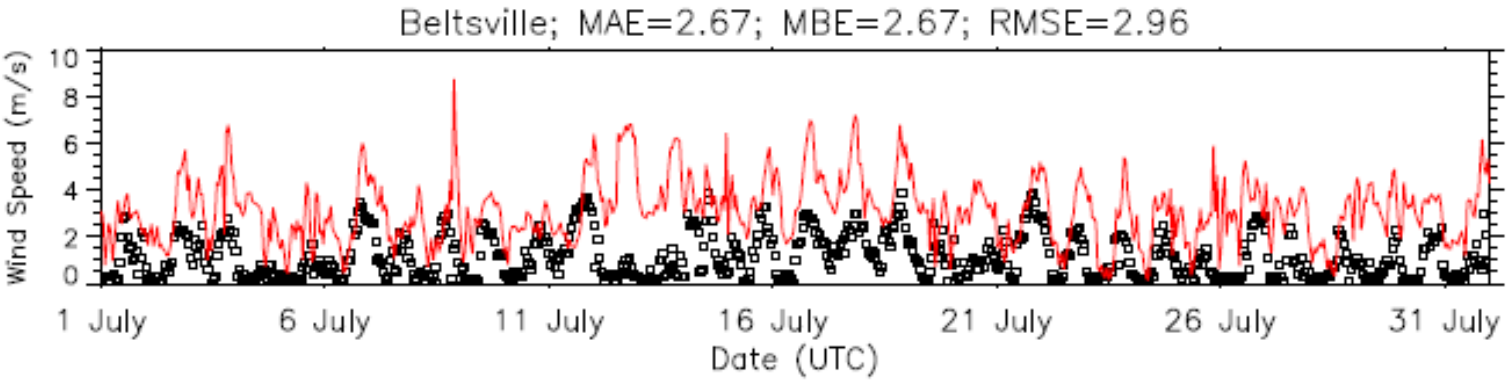


Model performs worse in downtown Baltimore. Model does not accurately represent urban heat island effects.

Wind speed; red – model (resolution: 1.3km), black – observations
MAE=mean absolute error; MBE=mean bias error; RMSE=root mean square error

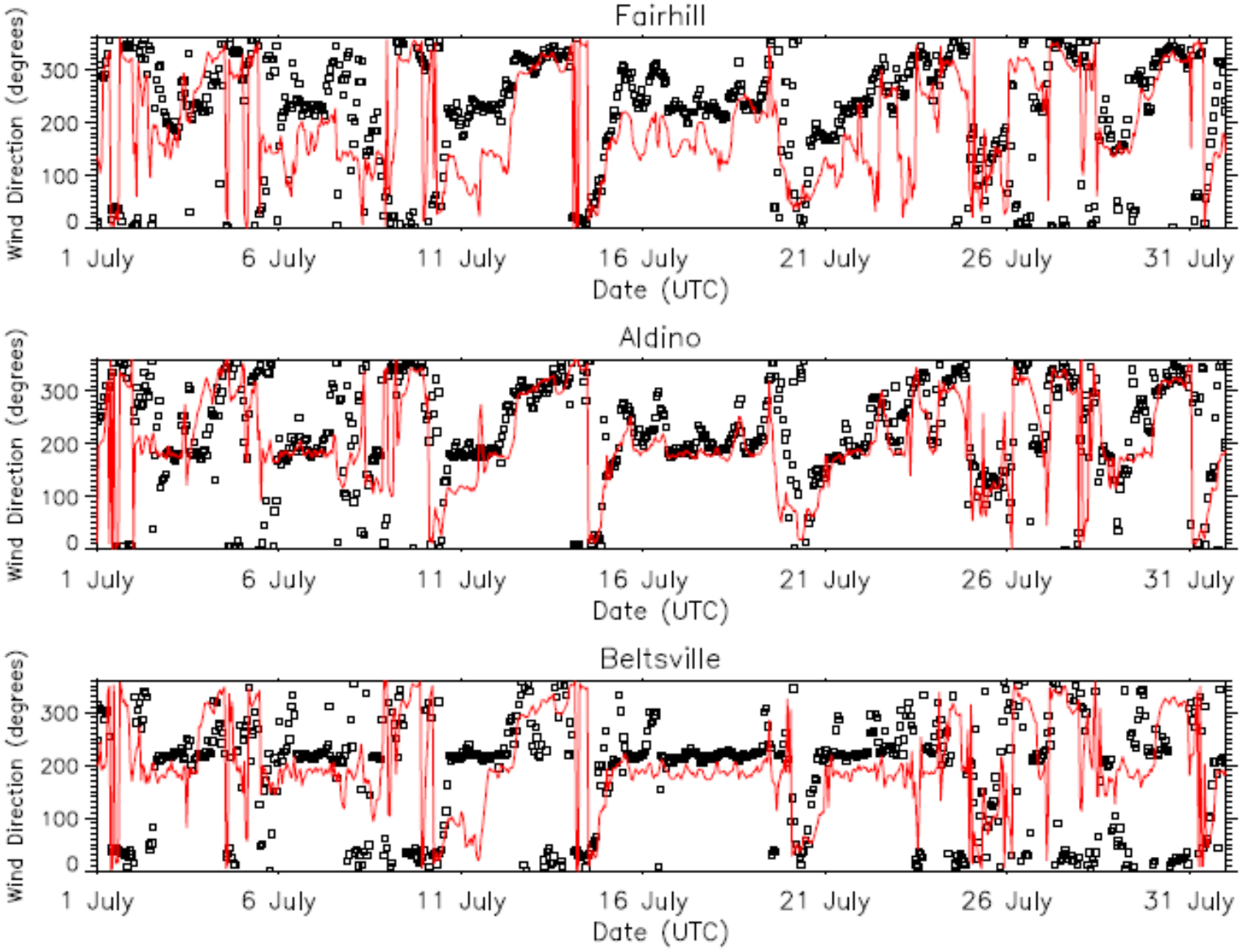






Model wind speed has a high bias compared with observations

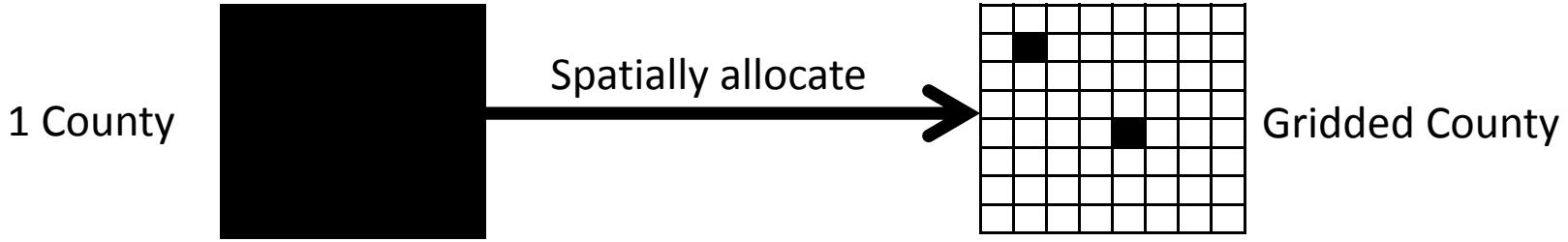
Wind direction; red – model (resolution: 1.3km), black – observations



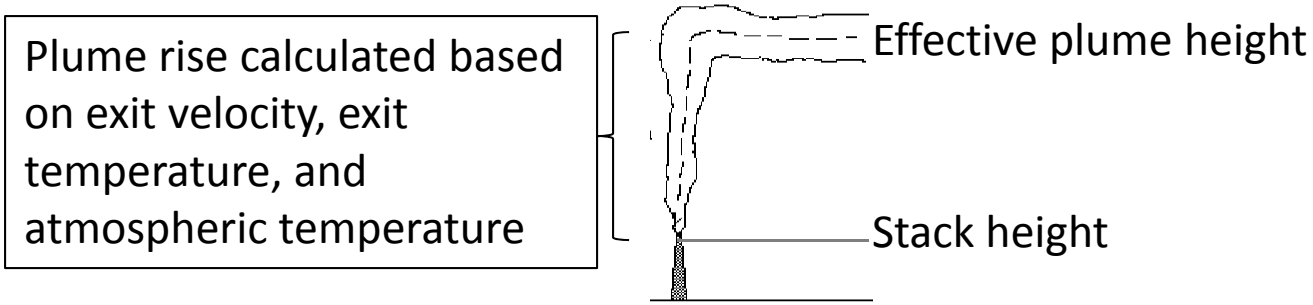
Model wind direction compares reasonably well with observations

Emissions Processing

- Anthropogenic emissions: Projected 2012 emissions based on the 2005 National Emissions Inventory (NEI) processed with SMOKE.
  - Area sources: annual countywide emissions are temporally distributed by time of day, day of week, and season and spatially distributed based on gridded landuse patterns to produce hourly gridded emissions.



  - Point sources: emissions are temporally allocated as described above and spatially distributed in the vertical based on stack height and plume rise.



  - Mobile sources: EPA's Mobile Vehicle Emission Simulator (MOVES) is used to calculate emissions from moving, idling, and parked vehicles based on road type and the distribution of vehicle type, vehicle age, and operating mode (i.e., stop and go or cruising).

Emissions Processing

- Biogenic emissions: Model of Emission of Gases and Aerosols from Nature (MEGAN) calculates biogenic emissions at 1 km^2 resolution and is driven by weather, land cover, and atmospheric chemical composition.

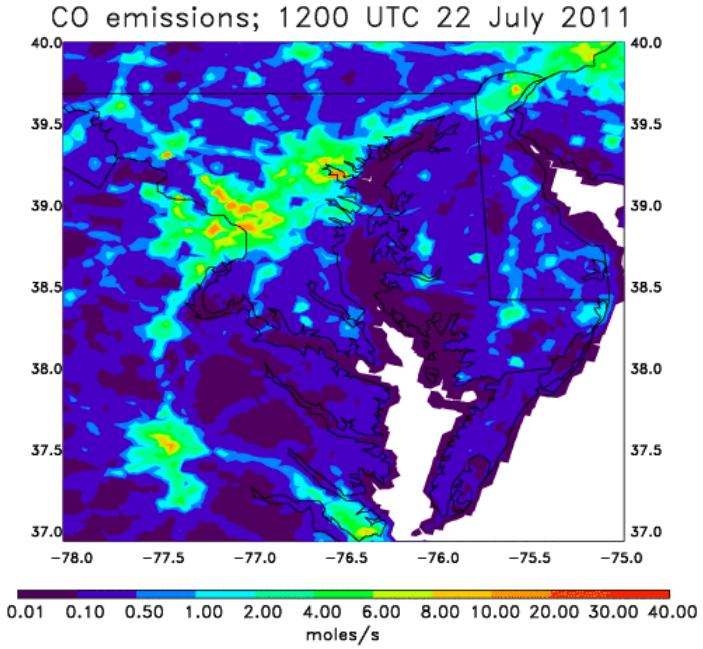
- Biomass burning emissions: Fire Inventory from NCAR version 1.0 (FINNv1) estimates biomass burning emissions with a resolution 1 km^2 based on fire hot spots, area burned, land cover maps, and biomass consumption estimates from MODIS products.

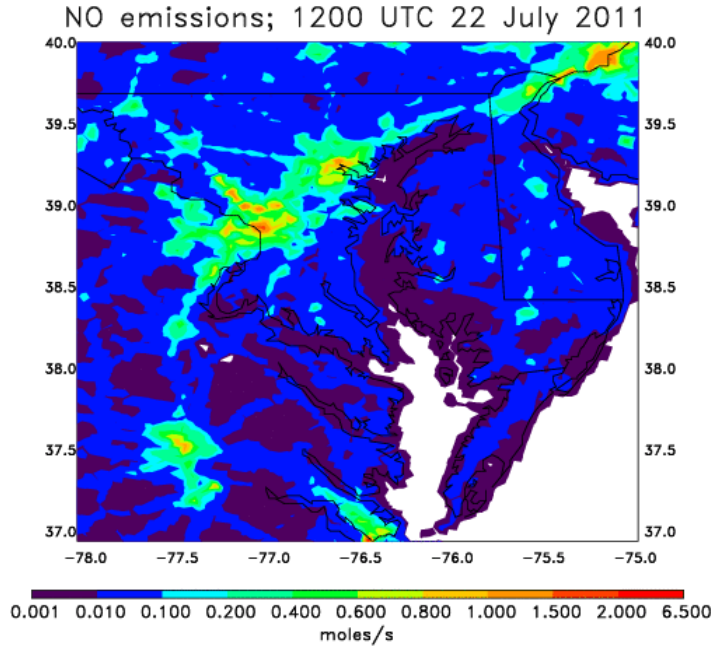
Emissions Version 2

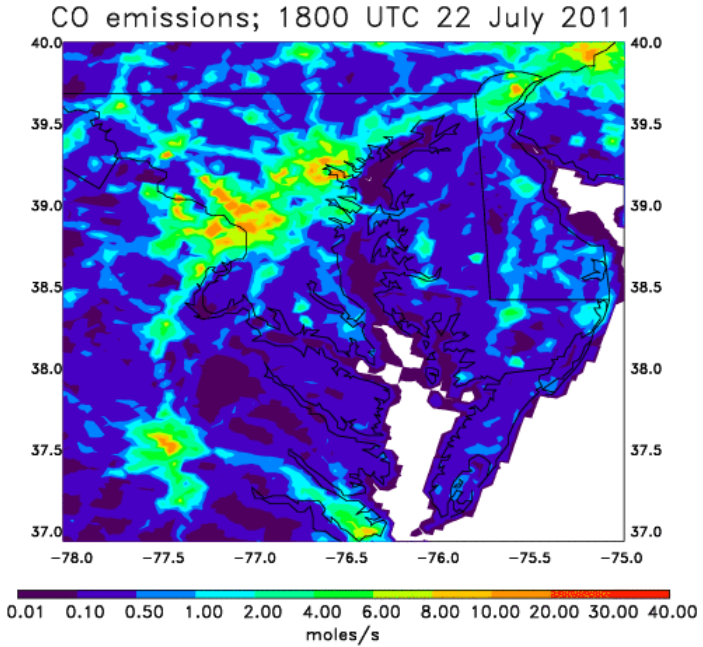
- Point source emissions will be updated with Continuous Emissions Monitoring (CEM) emissions data when available.
  - CEM data: observed emissions datasets from industrial stacks

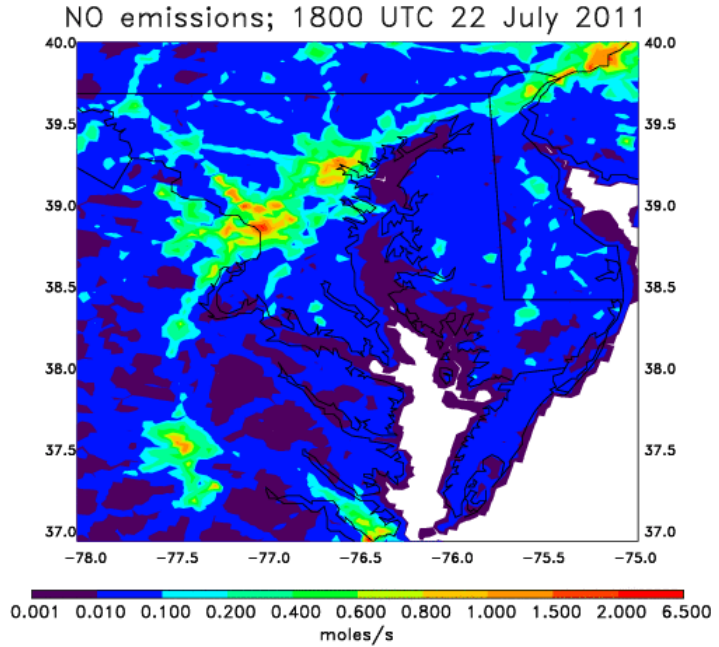
- Mobile emissions will be updated with highway traffic data and used to verify the day of the week patterns in the SMOKE emissions processing system.

4 km anthropogenic CO and NO emissions









Work in progress

Air Quality Model Simulations	
CMAQ	Horizontal Resolution: 36, 12, 4, and 1.3 km Time Period: Late May through July
WRF-chem	Horizontal Resolution: 36, 12, and 4 km Time Period: Late June through July
WRF-chem (NCAR)	Horizontal Resolution: 12 km domain covering the entire continental US Time Period: Late June through July

WRF-Chem Model Output

- Meteorology variables: temperature, pressure, humidity, wind velocity, mixing ratios (water vapor, liquid, ice), precipitation, shortwave and longwave radiation, PBL height, surface energy fluxes, cloud optical thickness
- 53 trace gas species
- 13 aerosol species in 8 size bins
- Additional aerosol information: extinction coefficient, optical thickness, asymmetry parameter, and single scattering albedo at wavelengths of 300, 400, 600, and 999nm

Model Options

WRF-Chem Version 3.3.1	
Chemical Mechanism	CBMZ
Aerosols	MOSAIC 8 bins Direct and indirect effects
Chemical initial and boundary conditions	MOZART CTM
Dry deposition	Wesely
NASA Unified WRF (NU-WRF)	
Chemical Mechanism	RADM2
Aerosols	GOCART Direct and indirect effects
Chemical initial and boundary conditions	MOZART CTM
Dry deposition	Wesely
CMAQ Version 5.0	
Chemical Mechanism	CB05
Aerosols	AE5
Chemical initial and boundary conditions	MOZART CTM
Dry deposition	M3DRY Bi-directional flux of ammonia