Maryland Department of the Environment

Volatile Organic Compounds, Trace Gases, and their Sources over the Chesapeake Bay during OWLETS-2

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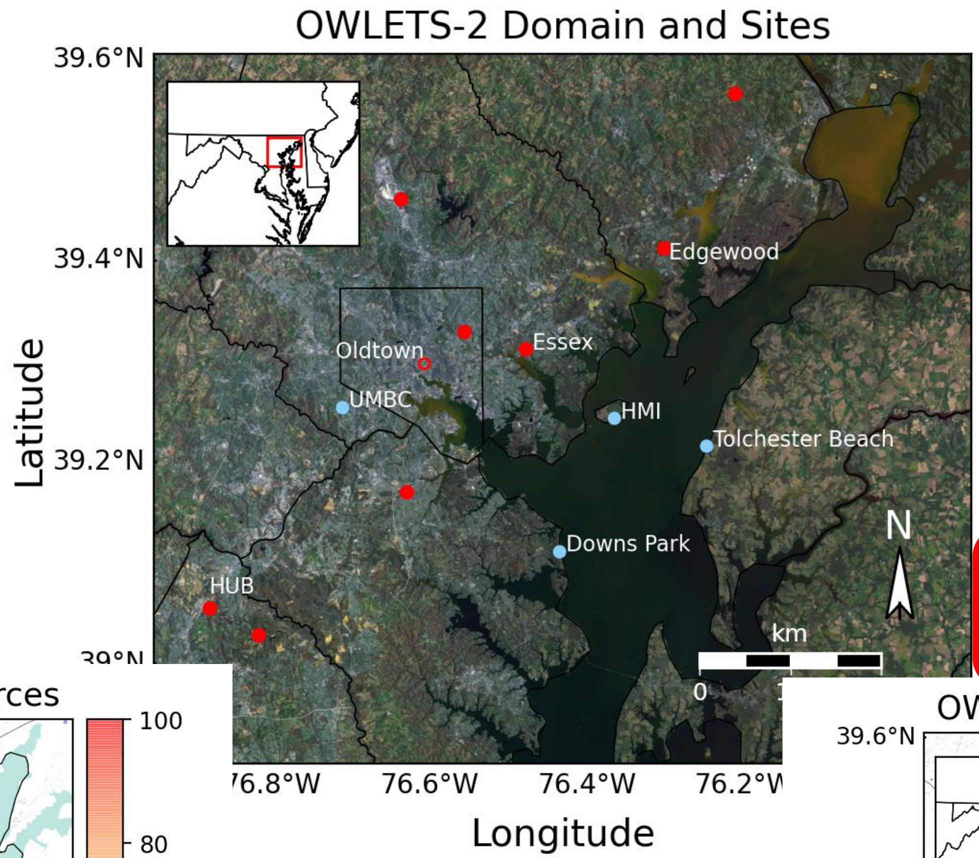
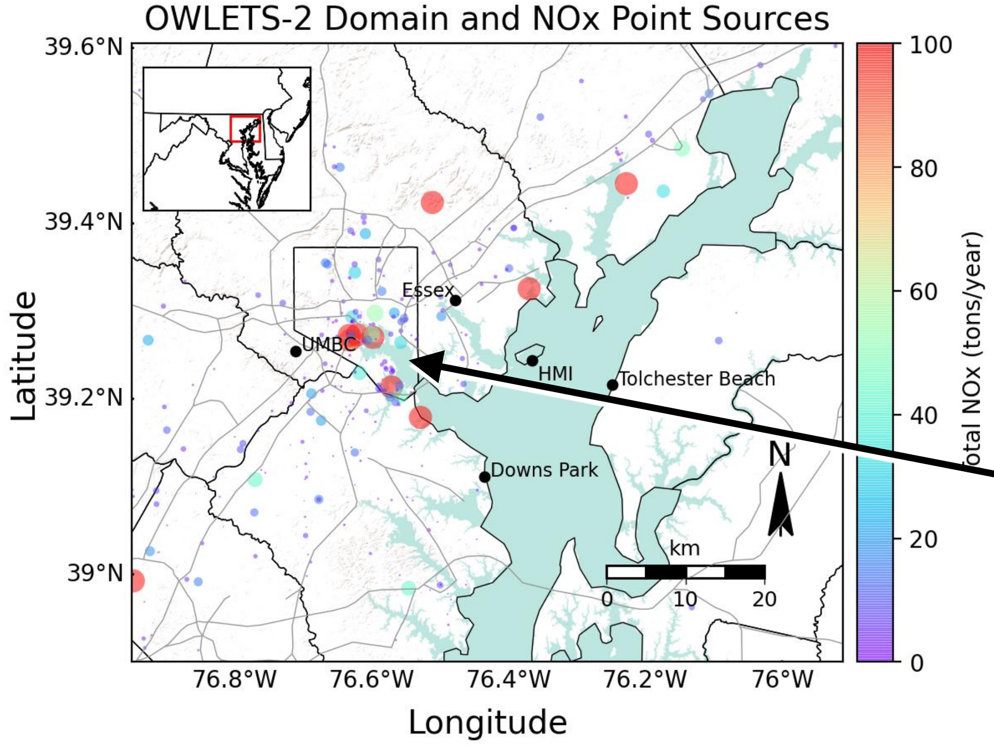
AWMA BW Chapter March 25 Webinar
Air Quality and the Air-Water Interface of the Chesapeake Bay
March 25, 2021

Experimental Domain

- Super sites straddling land-water interface and major NOx and VOC sources
- Extra sites to "enclose" the domain
- Many source sector influences possible, including on-road, non-road, EGU, industry, and biogenics

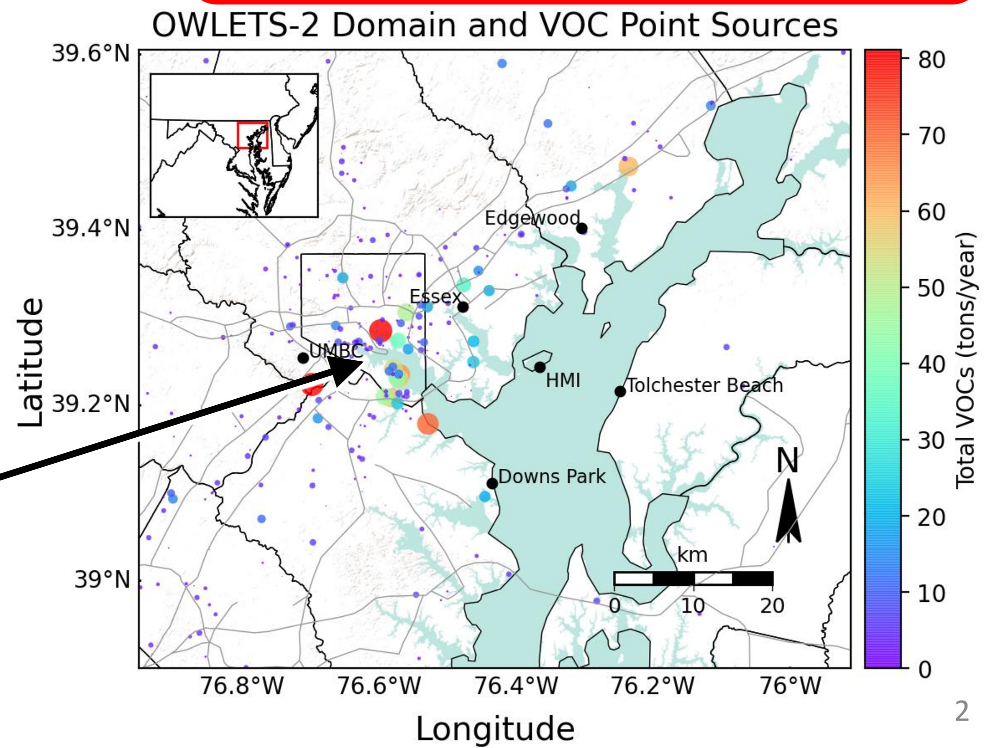


1. What is the spatial and vertical extent of the ozone (and ozone precursors) in and around the Chesapeake Bay?
2. What are the mechanisms (low boundary layer, chemistry, weather) that produce high ozone over the Chesapeake Bay and lead to high ozone at locations on land near the Chesapeake Bay?
3. How much of the ozone (ozone precursors) are a result of local sources (EGUs, mobile, ship, boat, etc) and pollutant transport (westerly, nocturnal low level jet) into Maryland?
4. Why do the photochemical models appear to over predict ozone concentrations in and around the Chesapeake Bay?
5. What source groups and in what locations do policy makers need to focus on to reduce ozone over the Chesapeake Bay?



Area of major NOx and VOC sources between two super sites

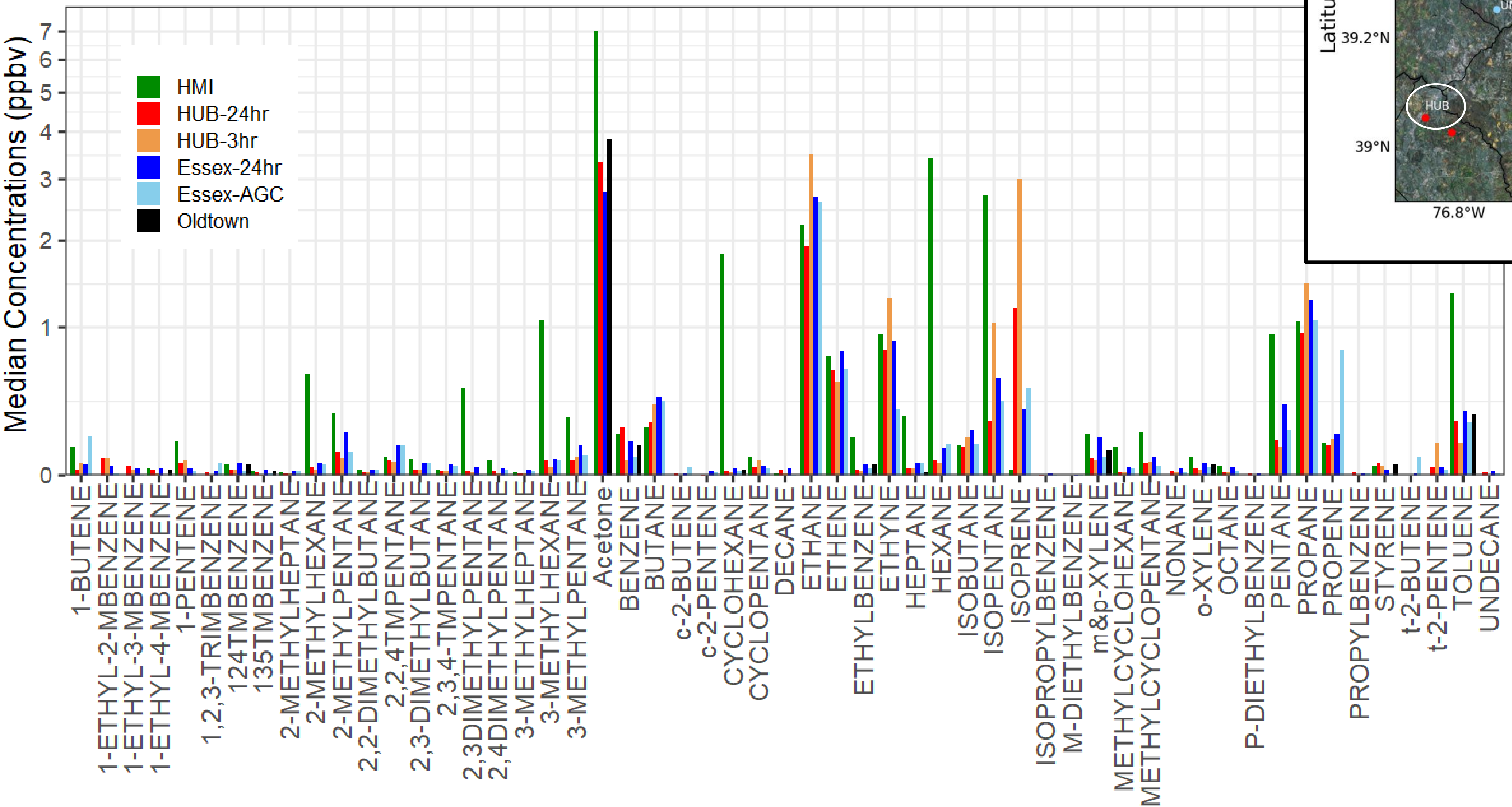
We really need to understand what is happening over the water

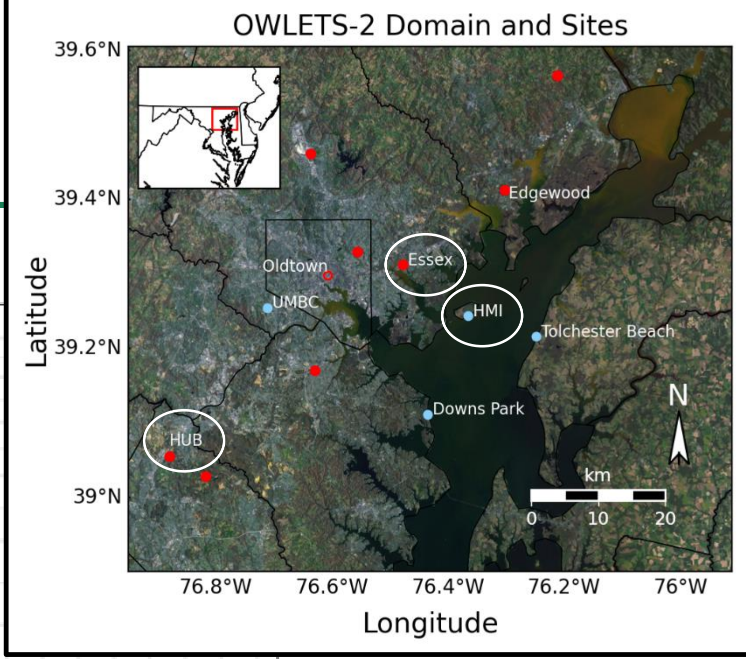


VOC Collection

What did we find?...

Median VOC Concentrations (ppbv) at HMI





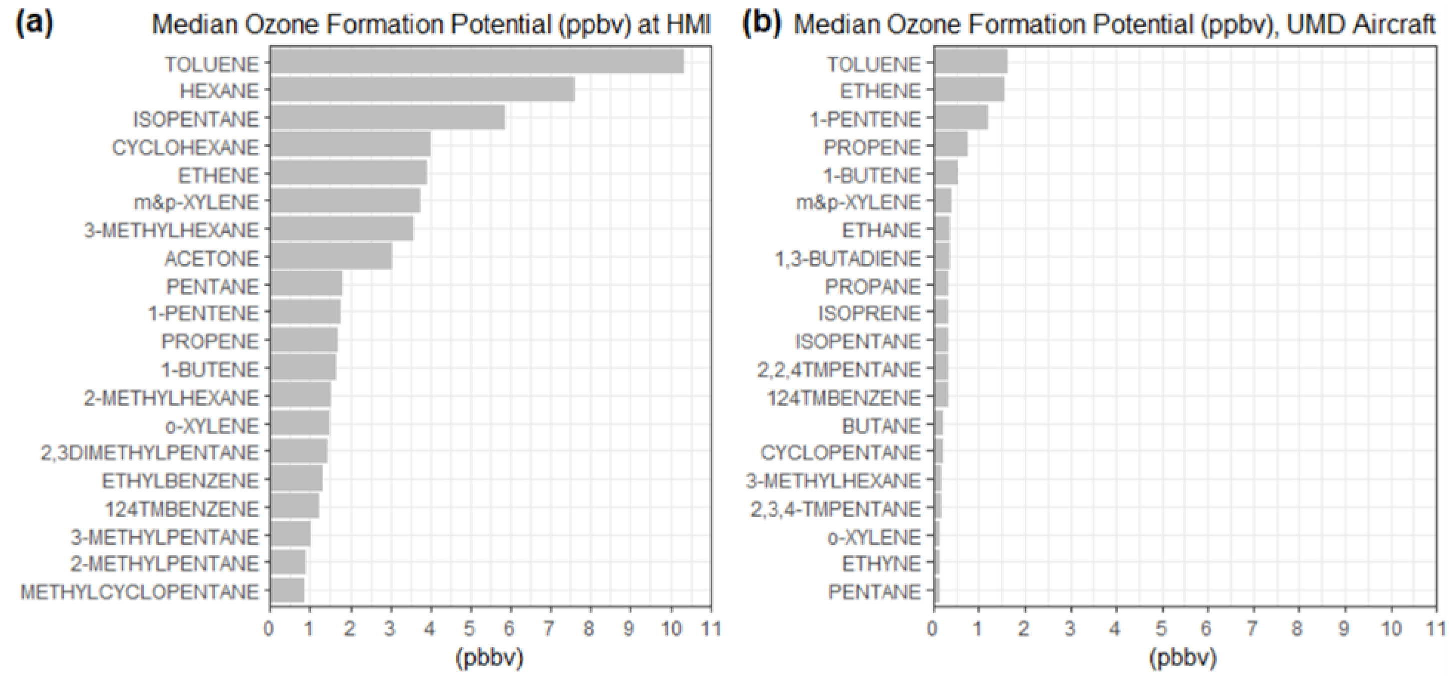
...gasoline

and lots of oxidized VOCs (Acetone)

Concentrations and MIR (Reactivity)

Rank	VOC Name	Mean	Med	Max	Min	Std
1	Acetone	8.20	7.04	36.83	3.58	5.51
2	HEXANE	3.37	3.43	6.78	0.70	1.57
3	ISOPENTANE	4.55	2.70	27.46	0.57	4.96
4	ETHANE	2.69	2.23	5.89	0.78	1.24
5	CYCLOHEXANE	2.52	1.82	8.87	0.68	1.67
6	TOLUENE	1.27	1.35	2.44	0.27	0.64
7	3-METHYLHEXANE	1.22	1.06	3.37	0.23	0.78
8	PROPANE	1.18	1.05	2.37	0.55	0.45
9	ETHYNE	1.20	0.94	3.71	0.50	0.72
10	PENTANE	1.20	0.93	4.67	0.19	1.00
11	ETHENE	0.86	0.75	1.52	0.54	0.27
12	Chloromethane	0.64	0.64	0.79	0.54	0.06
13	2-METHYLHEXANE	0.69	0.61	1.86	0.12	0.45
14	Dichlorodifluoromethane	0.56	0.54	0.67	0.49	0.04
15	2,3-DIMETHYLPENTANE	0.55	0.51	1.35	0.12	0.31
16	2-METHYLPENTANE	0.34	0.33	0.56	0.11	0.12
17	HEPTANE	0.39	0.32	1.07	0.07	0.27
18	3-METHYLPENTANE	0.31	0.31	0.47	0.10	0.09
19	BUTANE	0.33	0.25	1.64	0.03	0.29
20	Trichlorofluoromethane	0.26	0.25	0.32	0.23	0.02

Top 20 individual VOC species by median concentration (ppbv) over all canisters collected during the OWLETS-2 campaign on HMI, 2018. Statistics given are mean, median (Med), Maximum (Max), Minimum (Min), and Standard Deviation (Std) of each compound's concentration. Compounds in all caps were from the PAMS analysis method. Title case was used for compounds from the TO-15 method.



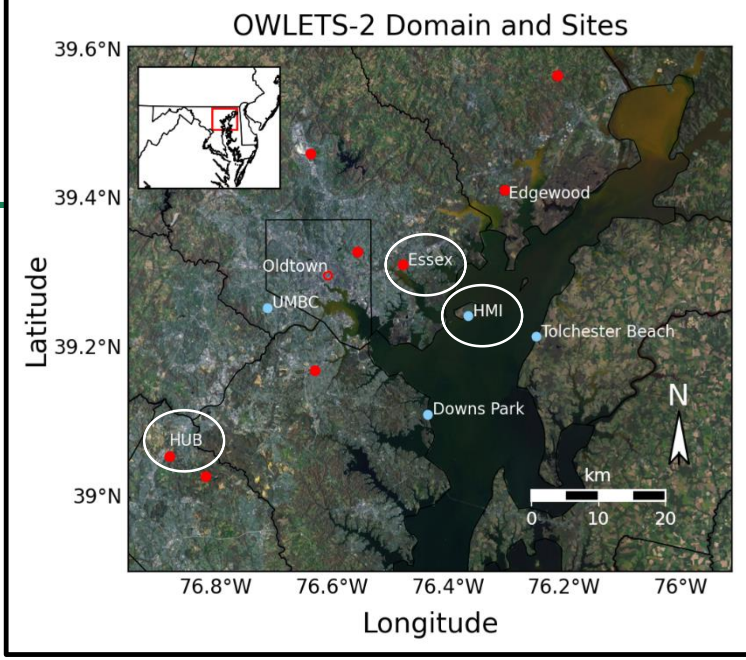
MIR from Carter (2010)

Sample Date	HMI Cans	UMD Cans	DOW	Max 8-hour Ozone [ppbv]
2018-06-08	4	-	Friday	58.00
2018-06-17	4	6 (1)	Sunday	74.00
2018-06-18	4	12 (2)	Monday	61.00
2018-06-19	1	-	Tuesday	46.00
2018-06-24	3	-	Sunday	48.00
2018-06-29	4	9 (2)	Friday	79.00
2018-06-30	4	9 (2)	Saturday	85.00
2018-07-01	5	-	Sunday	79.00
2018-07-02	4	-	Monday	64.00
2018-07-05	1	-	Thursday	27.00

Comparisons by Percentages: HMI to Essex

Rank	VOC	% Diff
1	CYCLOHEXANE	8,800.00
2	2,3-DIMETHYLPENTANE	2,176.47
3	HEXANE	1,755.96
4	3-METHYLHEXANE	1,320.00
5	STYRENE	1,225.00
6	2-METHYLHEXANE	908.33
7	1-ETHYL-4-MBENZENE	825.00
8	ISOPENTANE	712.50
9	1-PENTENE	653.85
10	HEPTANE	442.00
11	ETHYLBENZENE	402.86
12	PENTANE	283.33
13	METHYLCYCLOPENTANE	262.16
14	TOLUENE	244.40
15	ETHYNE	233.33
16	METHYLCYCLOHEXANE	214.71
17	CYCLOPENTANE	189.47
18	3-METHYLPENTANE	150.68
19	2-METHYLPENTANE	131.46
20	1,2,4-TMBENZENE	127.59
21	2,4-DIMETHYLPENTANE	126.09
22	BENZENE	100.00
23	m&p-XYLENE	97.06
24	OCTANE	95.65
25	1,3,5-TMBENZENE	92.86
26	o-XYLENE	80.00

List of VOCs observed at HMI with median concentrations at least 80% greater than observed by the Auto-GC at the nearby land site at Essex, MD during simultaneous campaign observations. The Auto-GC does not detect all TO-15 toxics, making comparisons possible only to PAMS compounds.

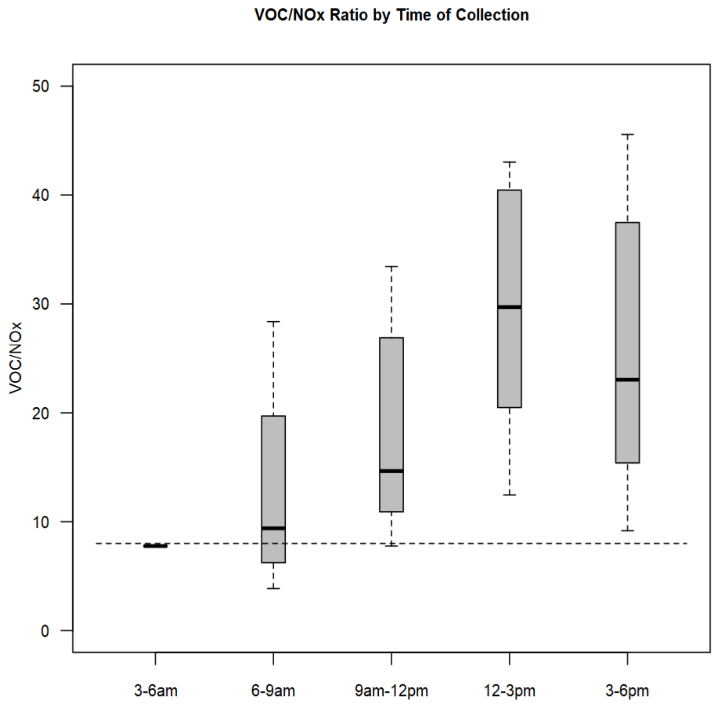


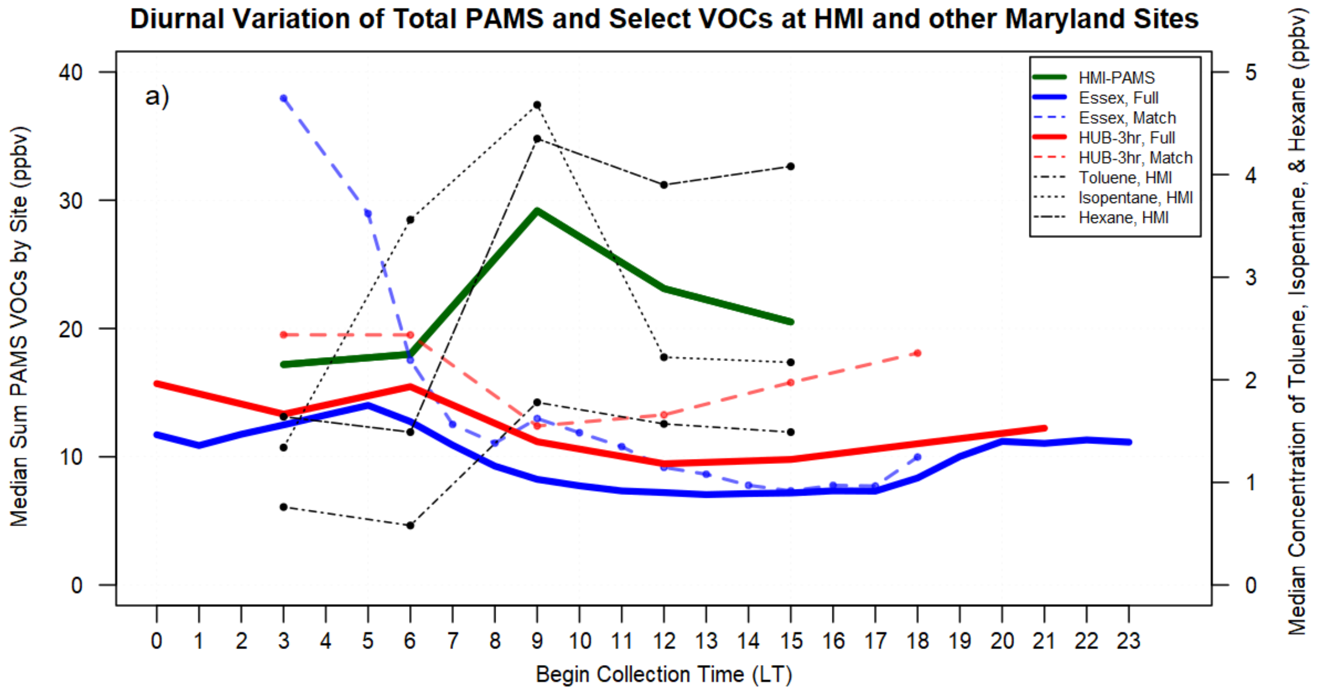
The majority of compounds were greater in concentration at HMI than at Essex DURING SIMULTANEOUS OBSERVATIONS (Auto-GC comparison)

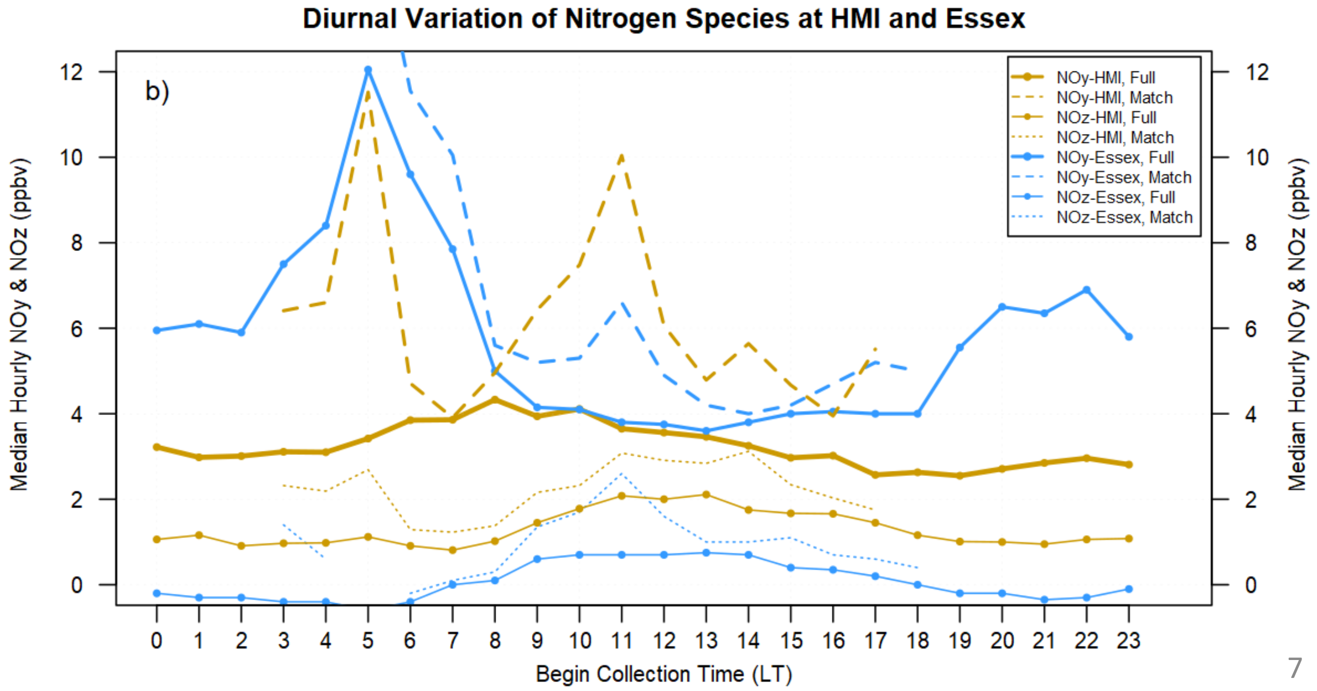
- 32 of 58 compounds greater at HMI than Essex
  - The list of 26 was dominated by C_6-C_9 compounds (21) with four of the remaining five C_5 compounds.
- 24 of 58 compounds less at HMI than Essex
  - 8 were C_9+ compounds
  - Importance of episodic variability of source?

Diurnal Trends

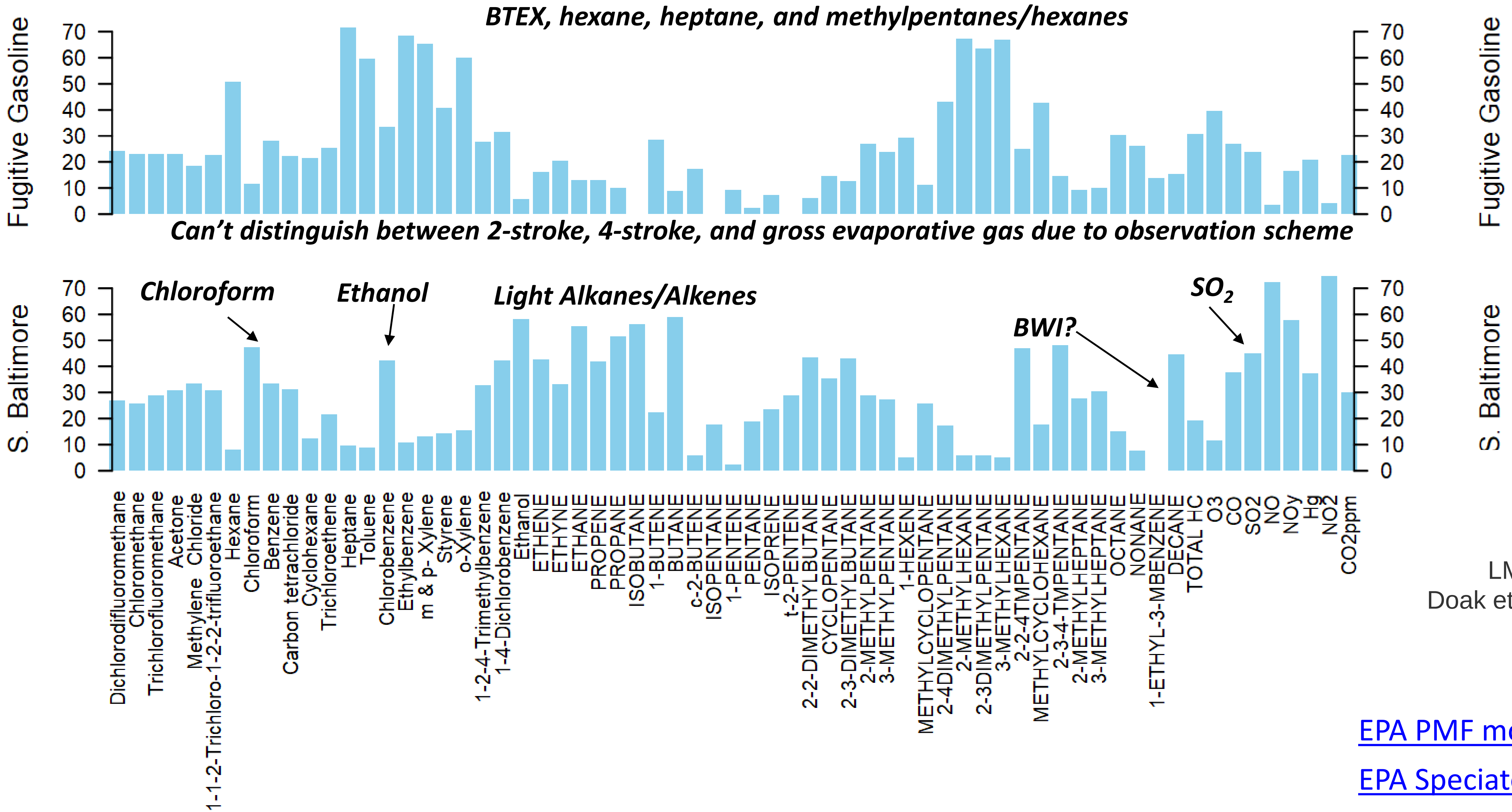
- The northern Chesapeake Bay becomes increasingly NO_x sensitive through midday. Opposite of land.
- There are more NO_x reservoir species (NO_z) over the water than at Essex, even during episodic events,
- There is LESS NO_x over the water than at Essex, except during specific times and events.







Source Profiles at HMI



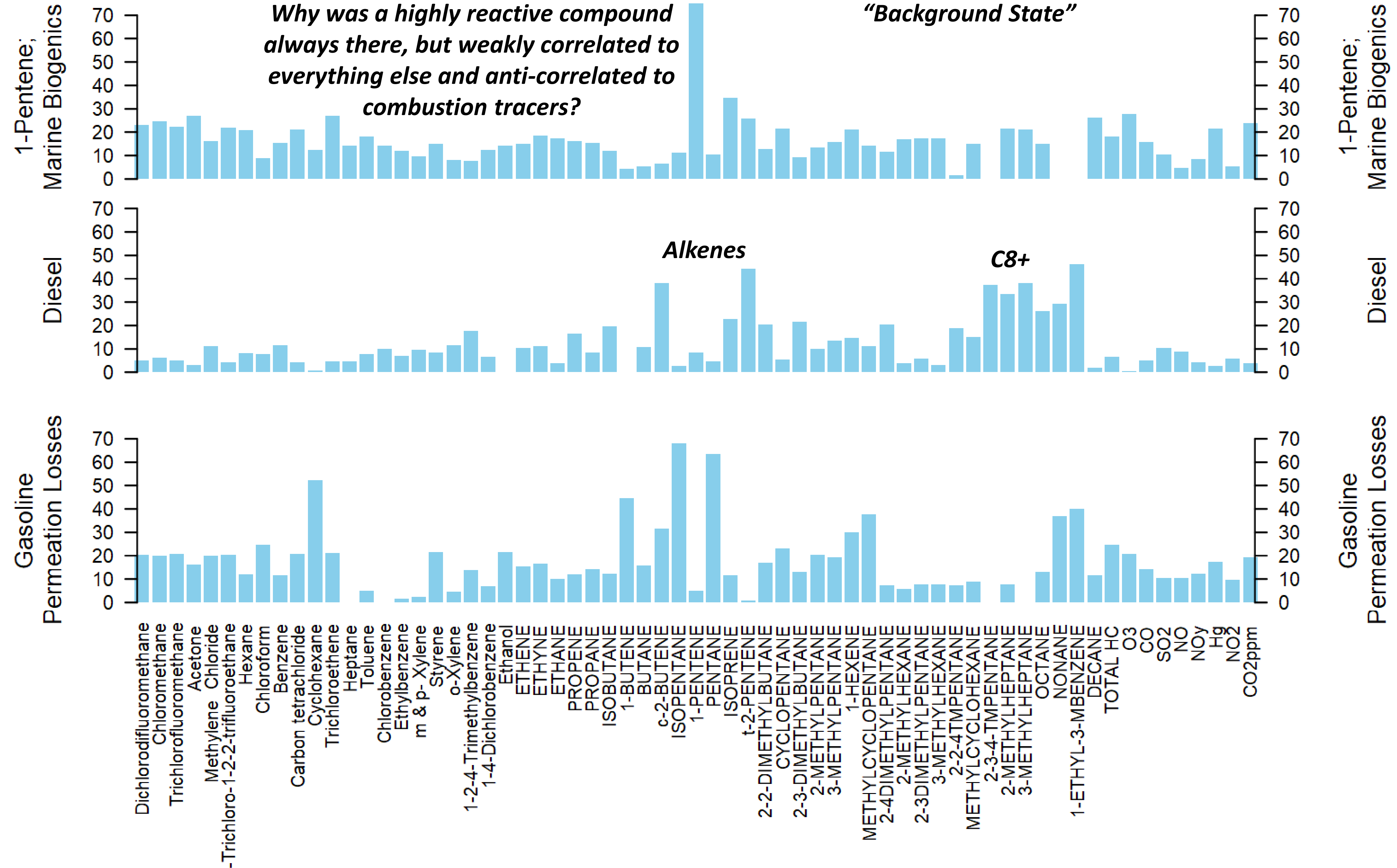
30% of TNMHC

~74% of NOx!! Signal strongest in the morning!

LMOS:
Doak et al. (2021)

[EPA PMF model]

[EPA Speciate]

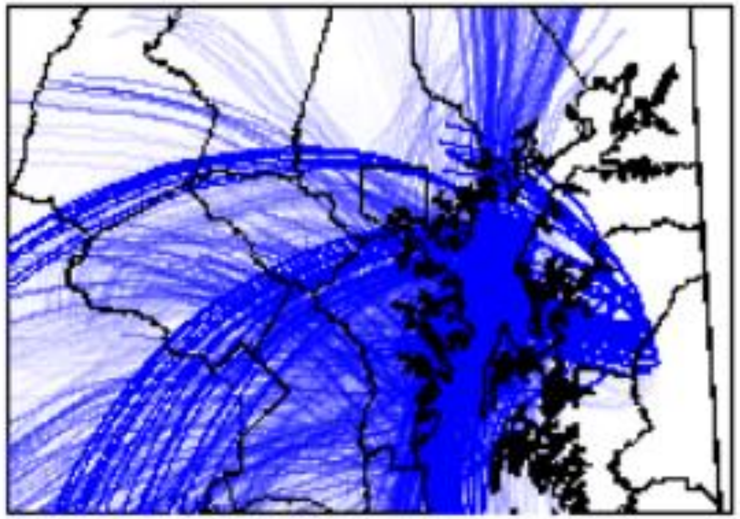


19% of TNMHC

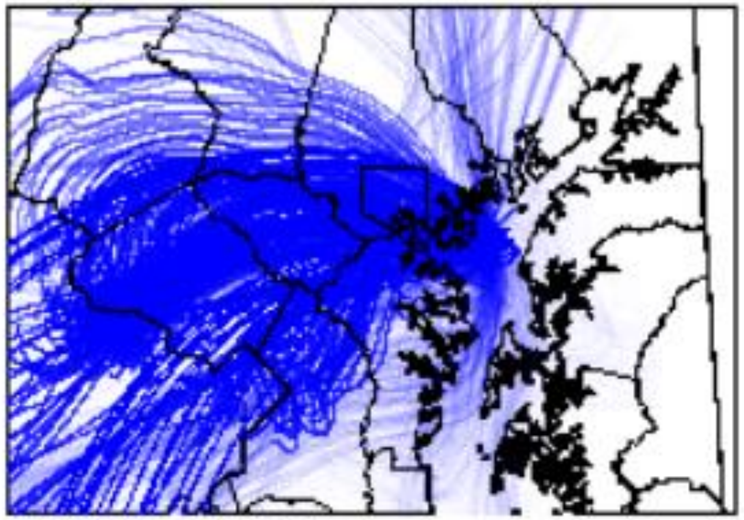
7% of TNMHC

25% of TNMHC

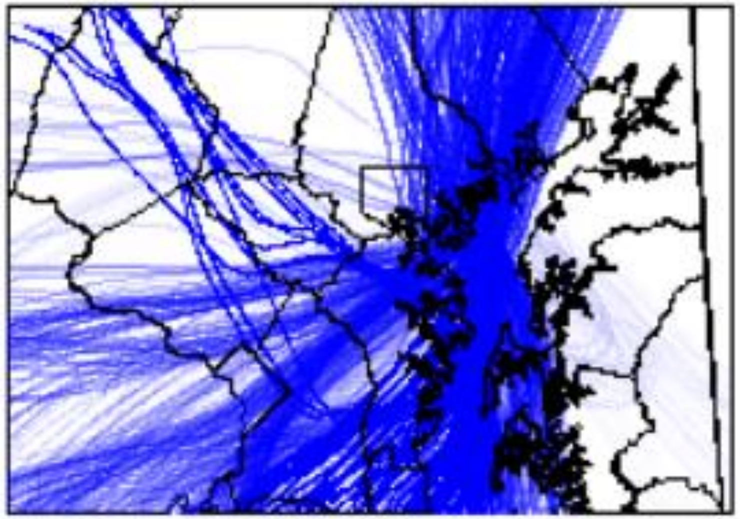
Fugitive Gasoline



S. Baltimore

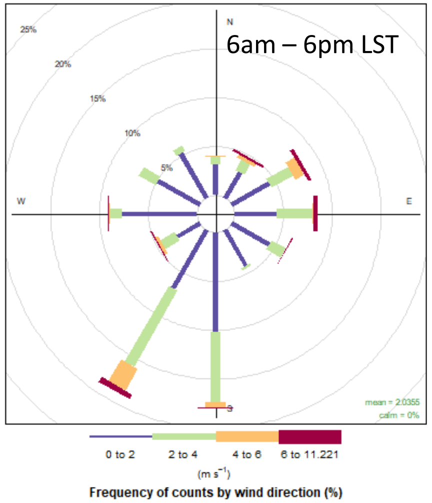


1-Pentene; Marine Biogenics

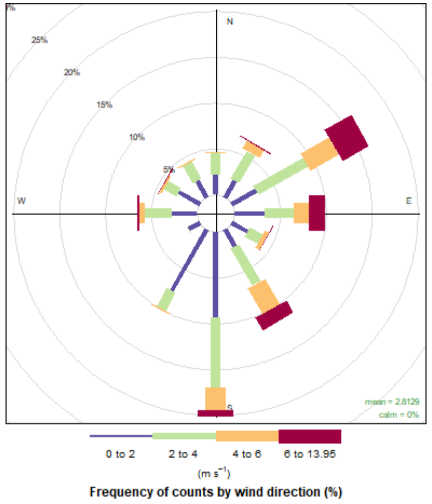


Each sample in PMF has a contribution to each factor. Here, each sample is weighted (cubic) by the greatest concentration of that factor. Those weights are applied to ensemble trajectories, 27 for each hour, 2700 total. Meteorology is from 3km HRRR

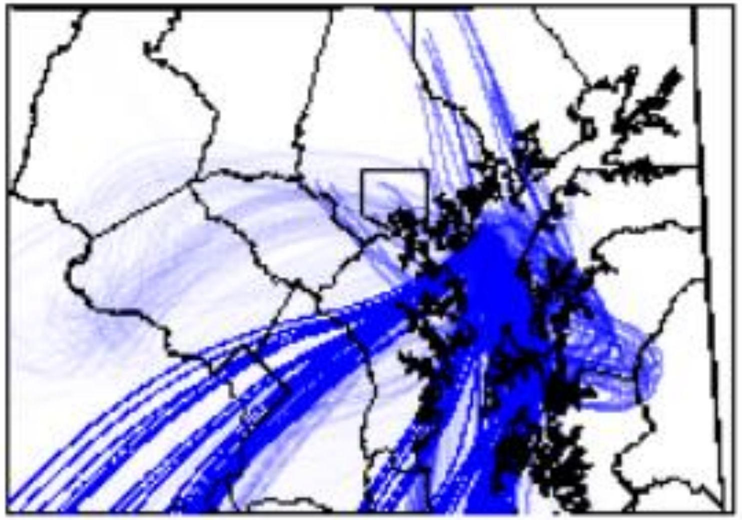
2016-2017



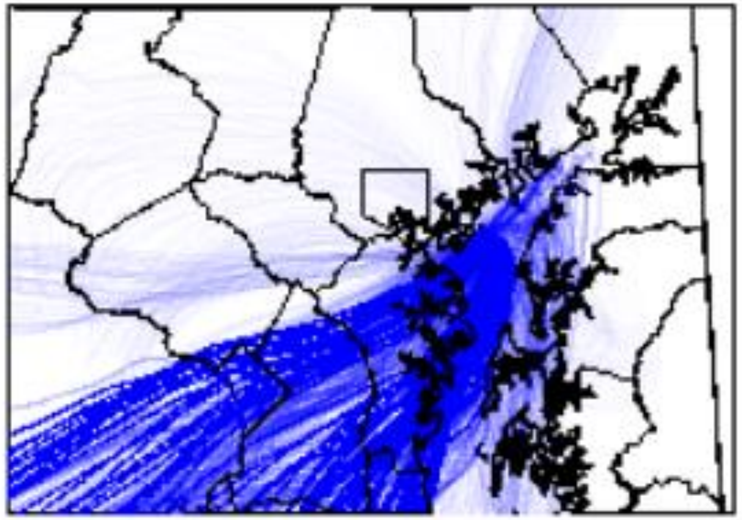
2018



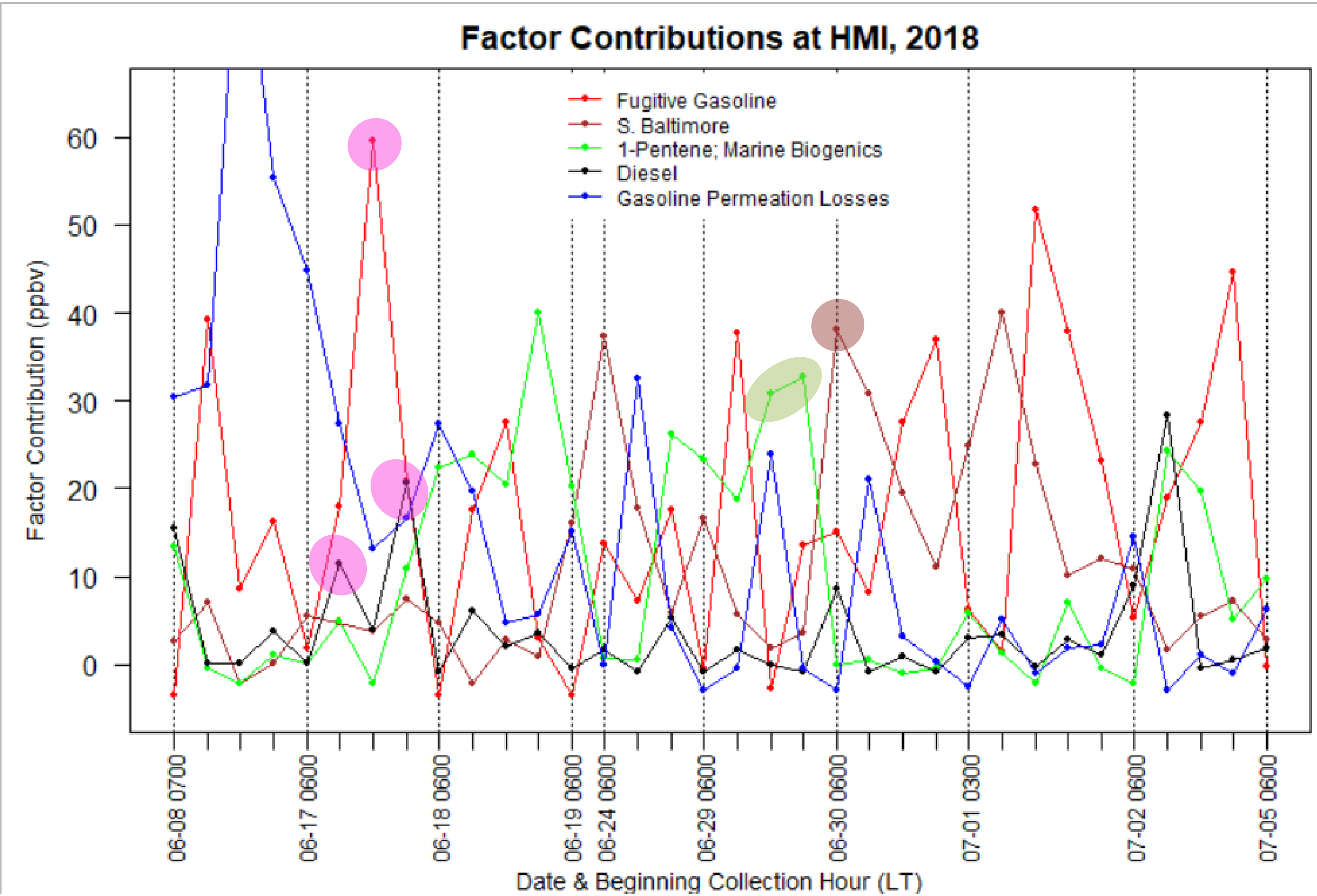
Diesel



Gasoline Permeation Losses



Cases June 17 & 29, 2018



- June 17 – Sunday (Father's Day)
  - Characterized by the 2nd and 4th highest Diesel influence of the campaign.
  - There were 2x as many hoteling hours than average at the Baltimore Port on June 15 (88 hrs), and quick drop to below normal by June 17 (16th:54hrs; 17th:29hrs)
  - Largest fugitive gasoline contribution of the campaign: boats!
- June 29 – Quintessential Bay Breeze Day
  - 1-Pentene influence both before and after ozone surge at HMI; Southerly wind connection (June 18; June 24, June 29)?
  - Also increase in Gasoline, S. Baltimore markers (SO_2, CO_2, NO_y)

Summary

- Gasoline compounds dominate the VOC mass at HMI and the disparity between nearby Essex.
- Reservoir species are greater over the water
- Logistical constraints limit some ability to parse sources (3-hour sampling), however, samples were able to identify recreational boats, diesel influences, Baltimore influences, and potentially a marine biogenic component.
- While recreational boats are strongly influential on VOCs, their ability to create ozone events may be curbed by the imbalance of NO_x.
- Larger NO_x variability from Baltimore than marine locations (hoteling diesels are the exception)

Picture Credit: Will Shuart & Sean Flynn

Questions & Extra Slides

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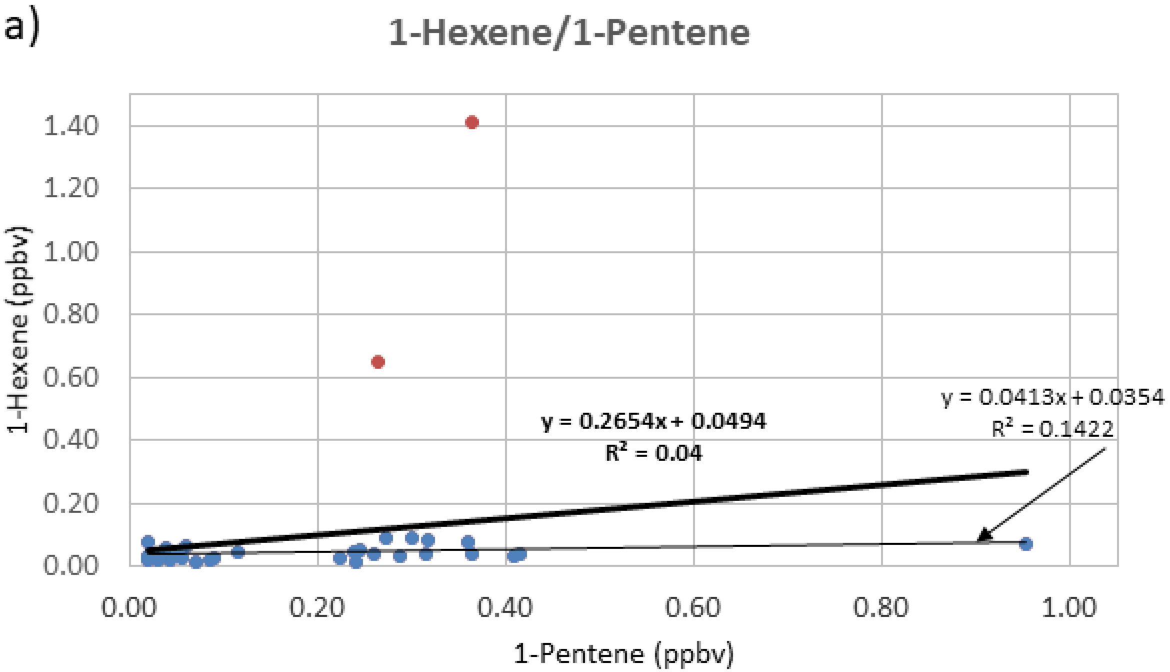
Unpublished work. Do not cite.

Recent publication of similar content from LMOS:
Doak et al. (2021), Characterization of ground-based atmospheric pollution and meteorology sampling stations during the Lake Michigan Ozone Study 2017, Journal of the Air & Waste Management Association, DOI: 10.1080/10962247.2021.1900000

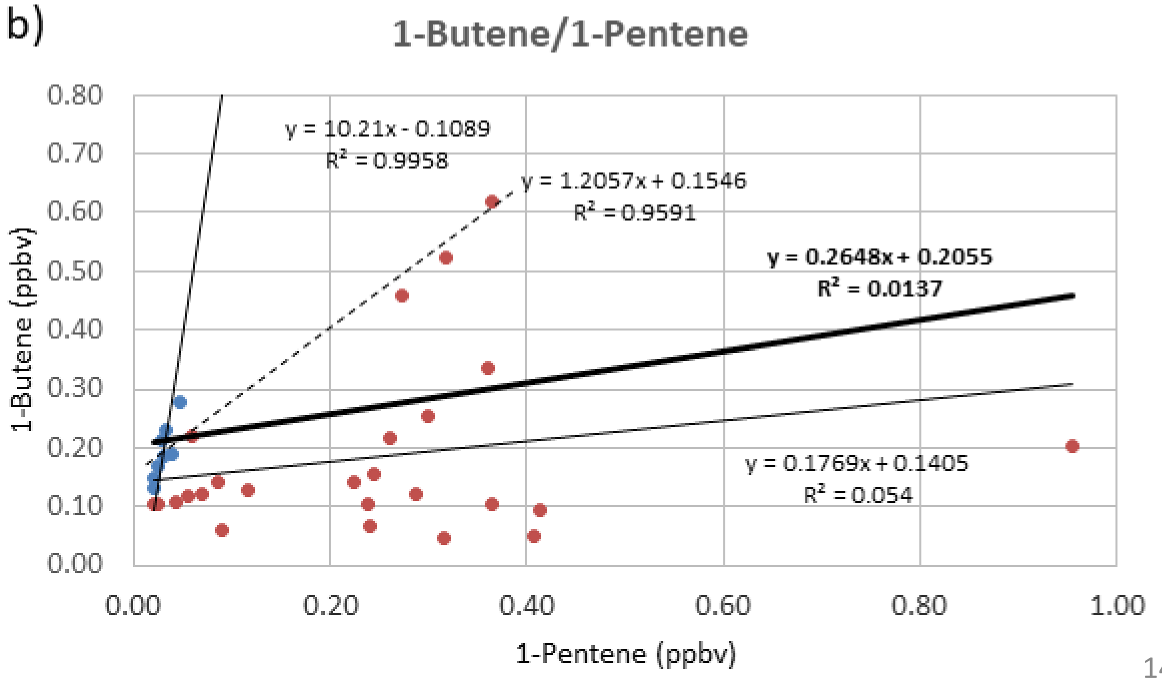
1-Pentene; Marine Biogenics?

a)

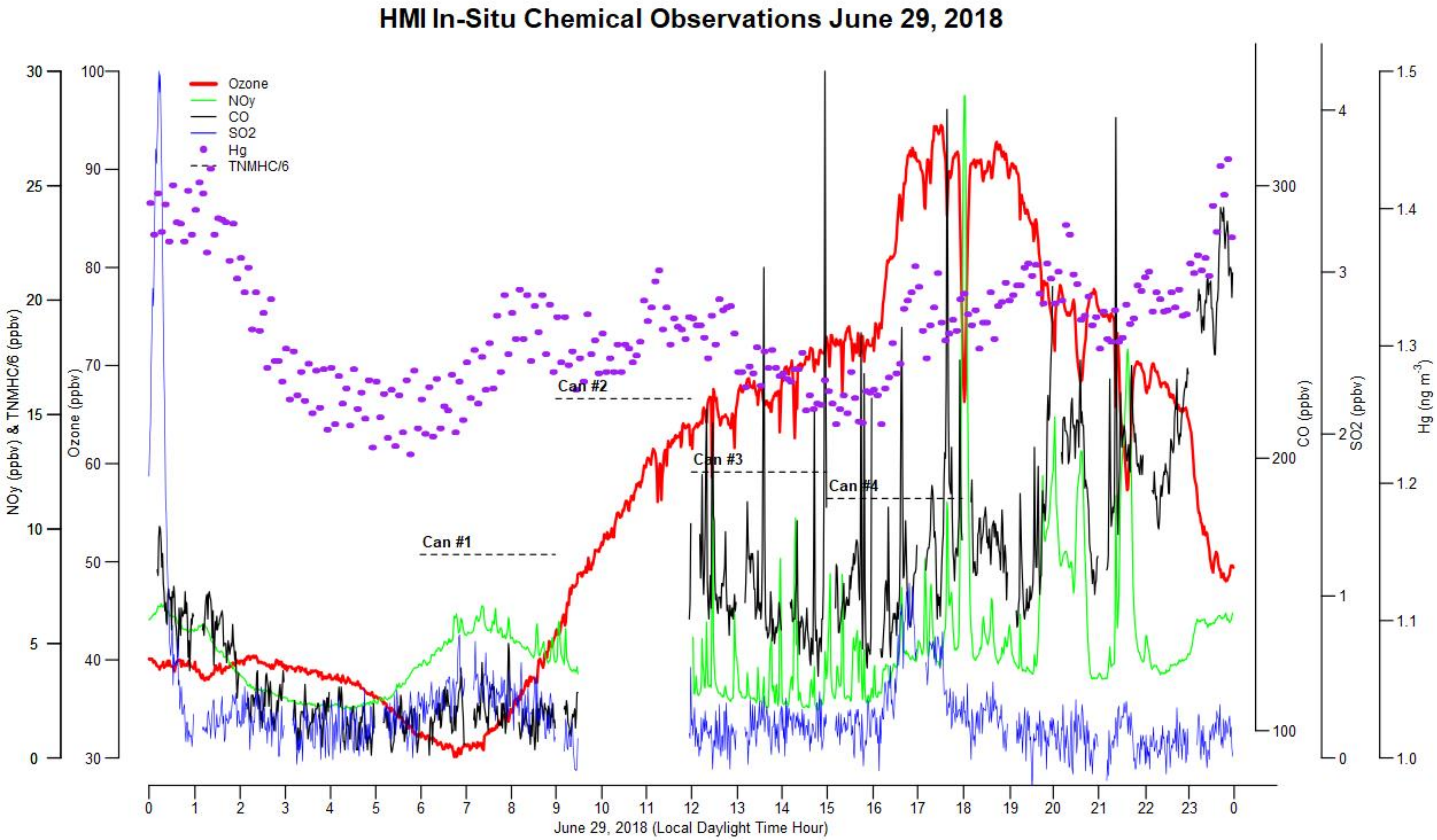


Correlations 1-Pentene: [observed in samples]
1,2,3-TRIMBENZENE (0.50); [3]
1,2-Dichloroethane (0.49); [14]
ISOPROPYLBENZENE (0.43); [3]
c-2-BUTENE (0.41); [11]
Chloromethane (0.41); [28]
t-2-BUTENE (0.40); [3]

b)



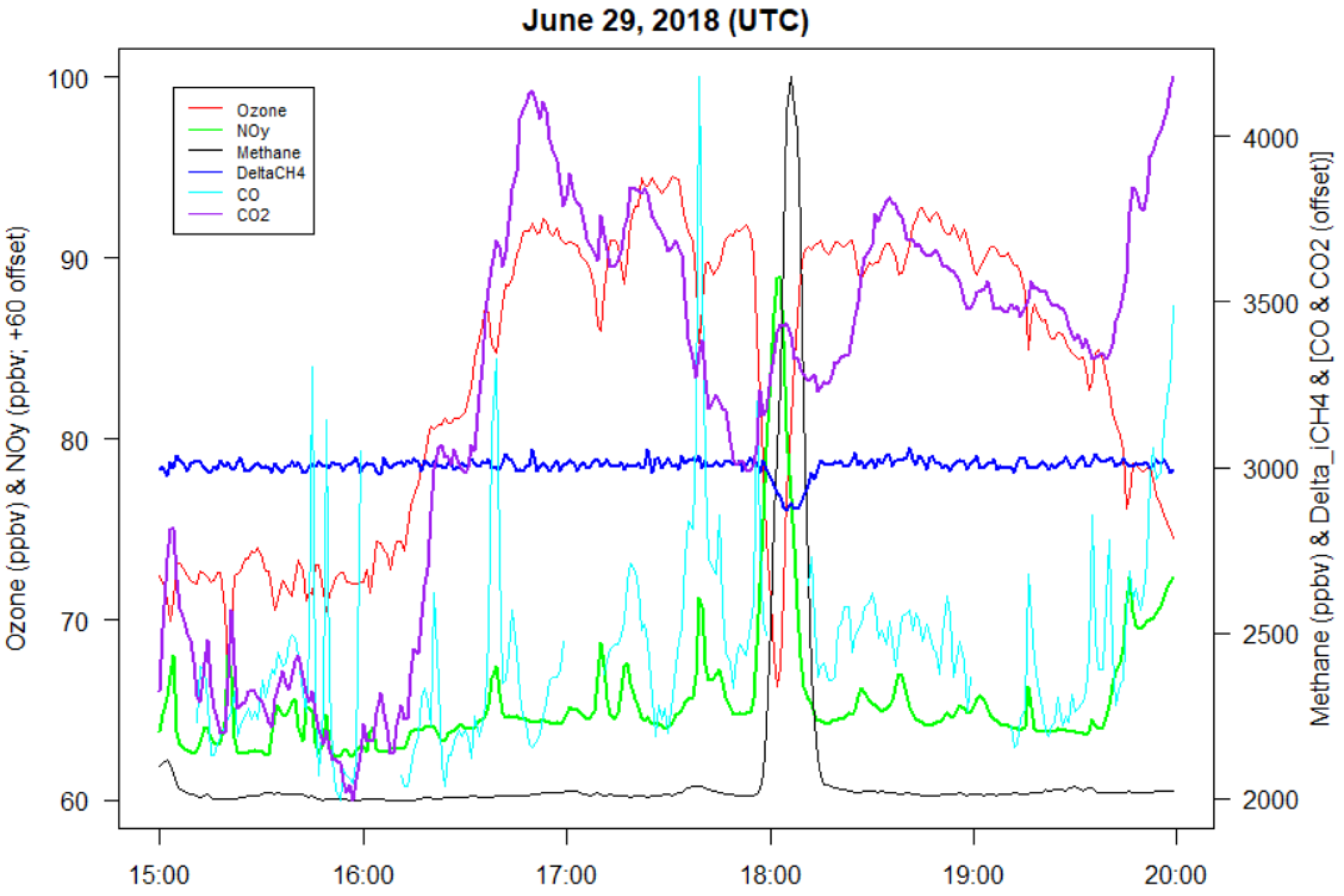
1-hexene to 1-pentene ratio: 0.27 (vehicles: 0.49 ± 0.25);
1-butene to 1-pentene ratio: 0.26 (vehicles: 3.75 ± __);
Jobson et al. (2004).


HMI In-Situ Chemical Observations June 29, 2018
Ozone
NOy
CO
SO2
Hg
TNMHC/6
Can #1
Can #2
Can #3
Can #4
NOy (ppbv) & TNMHC/6 (ppbv)
Ozone (ppbv)
CO (ppbv)
SO2 (ppbv)
Hg (ng m-3)
June 29, 2018 (Local Daylight Time Hour)

Visible Satellite on June 29, 2018

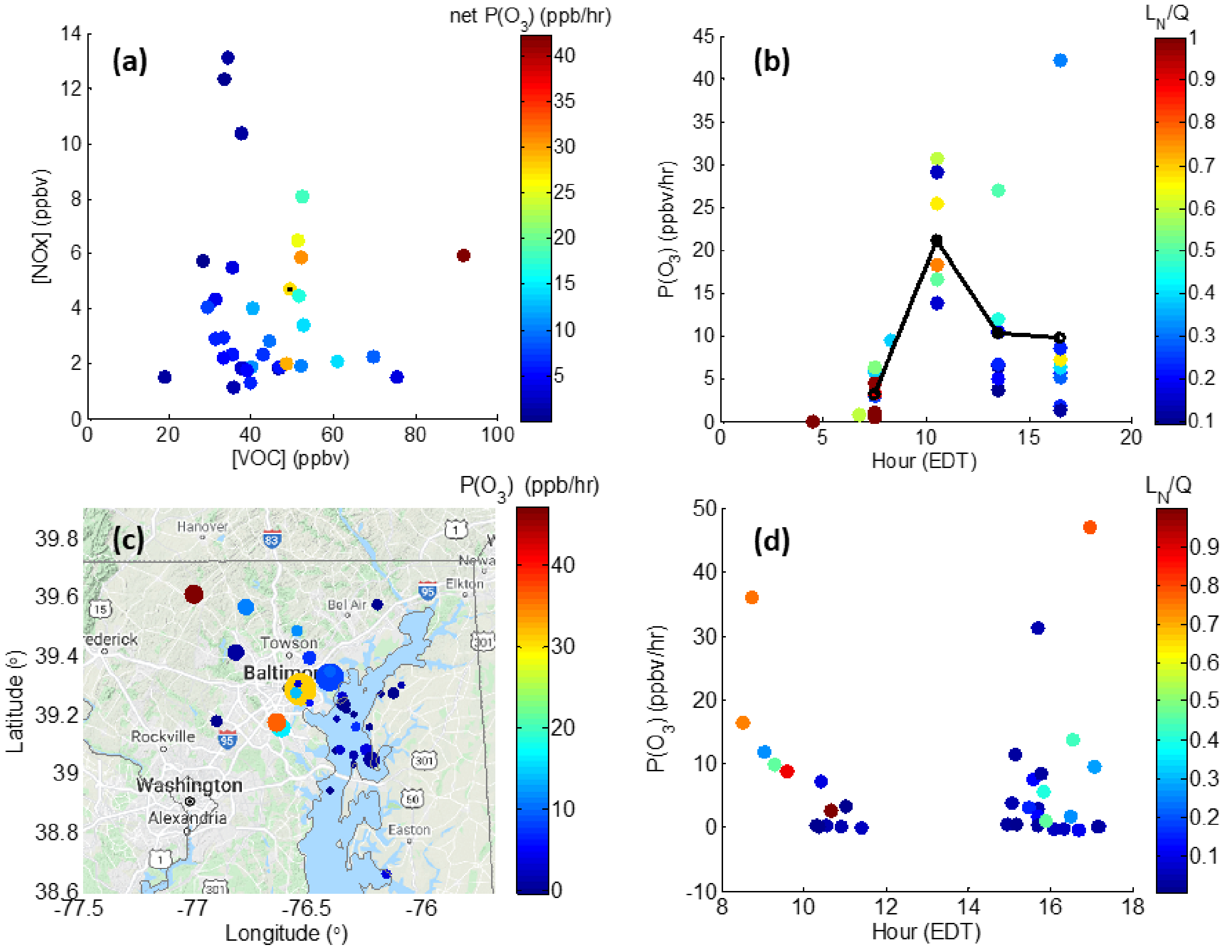
- Bay Breeze Evident
- Note wind direction in cloud field is ~315°
- Northern Chesapeake Bay wind direction was SOUTHERLY
- Can see Bay Breeze move inland north of Annapolis

- We are dropping Baltimore emission into the Bay and moving it northwards.



June 29, 2018 (UTC)
Ozone
NOy
Methane
DeltaCH4
CO
CO2
Ozone (ppbv) & NOy (ppbv; +60 offset)
Methane (ppbv) & Delta_iCH4 & [CO & CO2 (offset)]
100
90
80
70
60
4000
3500
3000
2500
2000
15:00
16:00
17:00
18:00
19:00
20:00

Box Modeling



(a) *Scatter plot of ozone production efficiency (P(O3)) at HMI for all 34 canisters within the box model against concentrations of VOCs and NOx (ppbv).*

(b) *Production efficiency of individual canisters (dots) by time of day (centered in 3-hour time bins), colored by NOx sensitivity. Generally LN/Q > 0.5 is VOC sensitive while LN/Q < 0.5 is NOx sensitive.*

(c) *The spatial distribution of P(O3) (ppb/hr) from 35 VOC canister samples taken by the UMD aircraft over the OWLETS-2 domain*

(d) *the temporal distribution of P(O3) and LN/Q in (d). Circle size in (c) represents total VOC concentrations with the minimum value of 4.2 ppbv and the maximum value of 99.4 ppbv.*