VOCs: Sources and Ozone Formation at Hart-Miller Island

The OWLETS-2 Campaign: 2018
Joel Dreessen, Daniel Orozco
Daniel Gardner, Katie Green

MARAMA Monitoring Meeting
November 20, 2018
Chesapeake Bay Background

Maryland “Water Issues”

• Edgewood’s “Bay Breeze”
• Ozone Forecasts
• Compliance modeling

Forecast 8-hour maximum ozone averages
July 6, 2016 [06z run]

106ppb at HMI

How do we verify any of this?

NOAA Forecast 8-hour maximum ozone averages July 6, 2016 [06z run]

Tim Canty, PhD, UMD
Land-Water Transition:

Median Afternoon Temperature Difference: 9.9°F
Median Morning Temperature Difference: 10.7°F
Bay Temperature in Summer: 70-85°F

0.5-1.5km layer average wind:
12z Radiosondes: 311°
HUB RWPs: 286°

15 tons Nox/day on average!
(When operating)

Bay Surface winds during high ozone:
191.1° [189.5°] @ 4.3kts [3.6kts]

Conceptual Meteorology during High Ozone
Satellite NOx “City” Plume

Tropomi NO₂ (Source: https://scihub.copernicus.eu/)

Average Retrieval 7/1 – 9/15, 2018

TropOMI: Daniel Goldberg; Argonne National Laboratory; GW Univ.
Hysplit Dispersion: Mark Cohen; Air Resources Lab; NOAA

All data is considered preliminary and subject to change
MDE VOC Integrated Grab Samples

Data Collection: Daniel Gardner & Katie Green; MDE
Canisters & Samplers

• Entech 6L Canister
  – Silonite: Inert ceramic interior
  – Kept at vacuum

• Nutech 2701 Sampling Timer
  – Programmable Date & Time
  – Time integrated: 3 hours
Location and Timing

- **Timing**
  - 4 Timers, 3 hour increments
  - 6-9am, 9-12pm, 12-3pm, 3-6pm (EDT)
- **Setup Schedule**
  - Sampling days were “intensive” days as decided during daily call
  - 6am run set up previous day
  - For multiple day events, swapped out can after 9am
OWLETS-2 Campaign Summary: VOCs

Campaign Statistics: Top 20 VOCs [ppbC]

<table>
<thead>
<tr>
<th>Rank</th>
<th>SPECIES</th>
<th>MEAN</th>
<th>MED</th>
<th>MAX</th>
<th>MIN</th>
<th>STD</th>
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<tbody>
<tr>
<td>1</td>
<td>ISOPENTANE</td>
<td>22.75</td>
<td>13.52</td>
<td>137.28</td>
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<td>2</td>
<td>HEXANE</td>
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<td>3</td>
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<td>17.10</td>
<td>1.92</td>
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<td>7</td>
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<td>8</td>
<td>ETHANE</td>
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<td>PROPANE</td>
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<td>11</td>
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<td>7.42</td>
<td>1.01</td>
<td>1.45</td>
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<td>2.01</td>
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<td>1.09</td>
<td>0.54</td>
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<td>15</td>
<td>METHYL-CYCLOPENTANE</td>
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<td>1.33</td>
<td>2.91</td>
<td>0.52</td>
<td>0.56</td>
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<tr>
<td>16</td>
<td>BUTANE</td>
<td>1.31</td>
<td>1.00</td>
<td>6.55</td>
<td>0.12</td>
<td>1.15</td>
</tr>
</tbody>
</table>

Ordered Median VOC [ppbC] Top 5 VOCs by concentration represent 50% of total VOCs measured!

34 Canisters
10 days:
- 7 w/ 4 samples*
- 1 - failure
- 1 w/ 5 samples
- 2 w/ 1 sample
- 3 - hour integrated sampling totaling 99 hours...
- Used 6am – 6pm EDT
- Focused 6am – 6pm EDT
- 1 Canister overnight during an exceedance event

VOC abundance does not necessarily mean excessive ozone production (e.g. methane)

All data is considered preliminary and subject to change.
Top Ozone Formation Potential

1. **Toluene**
2. **N-Hexane**
3. **Isopentane**
4. **Cyclohexane**
5. **3-Methylhexane**
6. **Ethylene**
7. **m,p-Xylene**
8. **N-Pentane**
9. **1-Pentene**
10. **2-Methylhexane**

All Hexanes (in top 20) together: 17.6

All data is considered preliminary and subject to change
Comparing canisters from JJA in 2016-2018 at HUB and ESX and canisters at HMI, 2018

Maybe there is nothing out of the ordinary happening at HMI compared to other PAMS sites?

- 3x as many PAMS target VOCs at HMI than HUB and ESX; During sunlight
- Select species account for majority of difference

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<th>PAMS</th>
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<tr>
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<td>130</td>
</tr>
<tr>
<td>HU-Beltsville (HUB 24-hr)</td>
<td>41</td>
</tr>
<tr>
<td>Essex (ESX 24-hr)</td>
<td>50</td>
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ESSEX AutoGC & HMI Canisters

Apples to Apples comparison – Comparison of exact same hours at HMI and Essex

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<td>Essex (AutoGC)</td>
<td>43</td>
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More VOCs present than either of the other two PAMs sites in Maryland (HU-Beltsville & Essex)

There are specific VOCs which account for the majority of the VOC abundance.
- Hexanes
- Toluene
- Isopentane

Where are they coming from and why are they there?
Airmass Age: VOC Ratios

ESSEX

Avg. May-Sept Canisters vs All HMI Canisters

Hu-BELTSVILLE

All data is considered preliminary and subject to change
ESSEX

- Binned 3-hour averages of the Essex Auto GC were compared with 3-hour HMI canisters

Diurnal patterns showed:
- Toluene and Xylenes were increasingly “fresh” or new emission in the afternoon at HMI.
- Acetylene/Benzene ratio was “fresher” at HMI than at Essex, but the diurnal pattern was similar.
- Propylene/Ethylene ratio suggests an “aged” chemical regime for these pollutants at HMI compared to Essex.

All data is considered preliminary and subject to change.
VOC Diurnal Cycle

VOC diurnal cycle of HMI is **opposite** that over land!

- ~Triple the number of VOCs present in the afternoon over the Chesapeake than at Essex (ESX) or HU-Beltsville (HUB)
- Increase in VOCs during the afternoon at HMI

*Sum VOCs at Essex AutoGC for same days as VOC obs at HMI

#Sum VOCs at HUB for 3-hr canisters from JJA in 2018

$Sum VOCs at HMI using 3-hr canisters

All data is considered preliminary and subject to change.
EPA’s PMF Model

Key Items:
- Evaporative Gas
- Plastics/Rubber
- Industry/Manufacturing

Evap Gas
~20% or more of total

All data is considered preliminary and subject to change.
Location of VOCs – All data, all years
Location of VOCs – 2018
Location of VOCs – 2018 [“VOCs”]

~860 TONS of VOCs / year

~400 TONS of VOCs / year
Location of VOCs – 2018 [“Hexanes”]

~3.9 TONS of Hexane / year
• Individual retrievals of HCHO are noisy

• Long-term averaging of retrievals is robust (over land)

• Some uncertainties in retrieval remain over water, may be spurious

Source TropOMI Averaging:
Dr. Dan Goldberg
Argonne National Laboratory
George Washington University
What comes out of a liquid storage tank is dependent upon atmospheric conditions and frequency and amount of use.

There are more VOC emissions during higher temperatures, and greater use. (2-10x more)
What does this mean?

- NOx controls total ozone; VOCs control rate of ozone formation
- Northern Chesapeake Bay (NCB) is intensely NOx limited (lots of VOCs)
  - Increases in NOx output may quickly result in ozone formation
- Availability of VOCs suggests overnight “chemical” storage of NOx is reasonable for ozone formation the following day.
- Initial analysis implicates evaporative gasoline products stored in Curtis Bay/Fairfield (Southern Baltimore) as the largest contributor to VOC concentrations within the Bay.
- Ozone variability and magnitude in the NCB may be explained by the chemistry of increased & collocated NOx + VOC releases on hot days with northwest flow.
Questions / Discussion / Suggestions
**Ozone Formation Potential**

**Mechanism Reactivity (Maximum Incremental Reactivity)**

\[
C_{j,MIR} = MIR_j \times C_{j,ppbv} \times \frac{m_j}{M}
\]

- \(C_{j,ppbv}\) represents the concentration by volume (ppbv) for species \(j\)
- \(m_j\) is the molecular mass of species \(j\) in the VOCs
- \(M\) represents the molecular mass of Ozone
- \(MIR_j\) is the maximum incremental reactivity*

* \(MIR\) is obtained from Carter (2010).
**Ozone Formation Potential**

**Kinetic Reactivity (Propylene-Equivalent Concentration)**

\[
C_{j,\text{Propy-Equiv}} = C_{j,C} \times \frac{k_{j,OH}}{k_{\text{Propy,OH}}}
\]

- \( j \) represents a species of VOC
- \( C_{j,C} \) represents the carbon atom concentration (ppbC)
- \( k_{j,OH} \) and \( k_{\text{Propy,OH}} \) denote the chemical reaction rate constant of species \( j \) and propylene with OH.

* \( k_{j,OH} \) is obtained from a study by Atkinson and Arey (2003)
VOC Ratios – an age indicator

\[ \text{Age} = \frac{\text{Reactive Species}}{\text{Less Reactive Species}} \]

- Goes away quickly
- Relatively Stable

\[ R = \frac{\text{Xylene}}{\text{Benzene}} \]

- “Fresh” Emissions
- “Aged” Emissions

• Every region and location will have a different ratio based on nearby sources and distance from sources
• We can use “long-term” ratios at HU-Beltsville and Essex to determine the relative age of observations at HMI
• Is the airmass/emissions/chemistry “aged” or “fresh”
P(O₃) Isopleth Diagram during OWLETS-2 & LISTOS

OWLETS-2 summer 2018

LISTOS summer 2018

- Background: P(O₃) isopleth based on mean met & chemical conditions
- Circles: data points with VOC measurements
- Most samples are NOx-sensitive with other samples to be VOC-sensitive
- Controlling both NOx and VOCs to reduce P(O₃)

Xinrong Ren; UMD/NOAA
Net $\text{P}(\text{O}_3)$: Spatial Variation

OWLETS-2 summer 2018
Mean net $\text{P}(\text{O}_3) = 7.1 \text{ ppb/hr}$
(Median = 3.0 ppb/hr)

LISTOS summer 2018
Mean net $\text{P}(\text{O}_3) = 4.0 \text{ ppb/hr}$
(Median = 3.1 ppb/hr)

- Each circle represents the location where we collected VOC sample.
- In general higher $\text{P}(\text{O}_3)$ at sites near emission source regions

Xinrong Ren; UMD/NOAA
P(O_3): Sensitivity to NOx and VOCs

**OWLETS-2 summer 2018**

- In general VOC sensitive near emission sources
- NOx sensitive away from source regions.

**LISTOS summer 2018**

Xinrong Ren; UMD/NOAA
HMI Diurnal VOC Changes [6-9am]

6am-9am Averages

- **Average Concentration**
- **Exceedance Avg**
- **Non-Exceedance Avg**
HMI Diurnal VOC Changes [9am-12pm]
HMI Diurnal VOC Changes [12pm-3pm]

12pm-3pm Averages

- Average Concentration
- Exceedance Avg
- Non-Exceedance Avg

PPBC
Correlation of VOCs

- BENZENE
- TOLUENE
- m.p. XYLENE
- ETHYL BENZENE
- ISOPENTANE
- HEXANE
- CYCLOHEXANE
Correlation of VOCs

Correlations (r) > 0.7

1. **TOLUENE**; 2-3-Dimethylpentane(0.890), 2-Methylhexane(0.888), Ethylbenzene (0.883), Heptane(0.883), M&P-Xylene(0.880), 3-Methylhexane(0.862), Methylcyclohexane (0.827), Hexane(0.819), o-Xylene (0.792), 2-4-Dimethylpentane(0.774)

2. **ISOPENTANE**; Pentane(0.913), Tetrahydrofuran(0.897), Cyclohexane (0.849), METHYLCYCLOPENTANE(0.804), HEXENE (0.773)

3. **N-HEXANE**; Toluene(0.819), METHYLCYCLOHEXANE(0.779), M.P.XYLENE (0.704), 3.METHYLHEXANE (0.706), 2.3DIMETHYLPPENTANE (0.731)

4. **CYCLOHEXANE**; ISOPENTANE (0.848), PAMSHC (0.846), PENTANE(0.827), Tetrahydrofuran (0.765), METHYLCYCLOPENTANE (0.735)
PMF

PRELIMINARY DATA
Percent Source Contributions

Factor Contribution > 0.05 %
- Mixed; Aged; Baltimore; Gasoline, LPG, or car exhaust = 18.92000 (10.9 %)
- Pesticides = 17.23200 (9.9 %)
- Industrial Processes = 5.82990 (3.4 %)
- Mix of solvents or polymer or refrigerant use = 33.22500 (19.2 %)
- Evaporated Gasoline = 33.58500 (19.4 %)
- Mixed; Aged-CarExhaust? = 35.84200 (20.7 %)
- Mixed; Polymer; CarExhaust = 8.31580 (4.8 %)
- Heavy Diesel = 20.47400 (11.8 %)
Factor 1: Baltimore Plume Mix; Evap Gas, Cars, Natural Gas

- MTBE (50%) - Octane booster
- 2 & 3-Methylheptane (>45%) (isomer of Octane)
- Acrolein (60%)
- Butane & Isobutane - LPG

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Factor 2: Fumigants, Pesticides, Nematocides & Chemical intermediates and dry cleaning

Fumigants or Pesticides

Trans-1,3-dichloropropene (95%)
Preplant fumigant and nematicide
Water soluble…….

Dry Cleaning

Because these compounds contain chlorine, it is possible this group hinders ozone production
EPA’s PMF Model

Key Items:
- Evaporative Gas
- Plastics/Rubber
- Industry/Manufacturing

Factor Contribution > 0.05 %
- Coal & CB Industry = 33.91600 (19.6 %)
- Plastic manufacturing, Evap Fuel/BWI? = 10.87600 (6.3 %)
- Biogenic & Agriculture = 7.97650 (4.6 %)
- Heavy Diesel = 11.96800 (6.9 %)
- Evaporative Gas / Coal? = 30.41200 (17.6 %)
- Foam Insulation/Polystyrenes = 12.19000 (7.1 %)
- Mixed; Baltimore Plume / Cars? = 19.05200 (11.0 %)
- ?? Trapp mixture – chemical (WR Grace?) & Evap Gas = 31.51500 (18.2 %)
- Industrial Process = 5.44950 (3.2 %)
- Chemical Manufacturing = 9.46050 (5.5 %)

All data is considered preliminary and subject to change.
VOC Ratios: AutoGC @ Essex vs HMI 2018

3am-6am

6am-9am

9am-12pm

12-3pm

3-6pm

- Acetylene/Benzene
- Toluene/Benzene
- M&P-Xylene/Benzene
- Propene/Ethene
- HMI-A/B
- HMI-T/B
- HMI-X/B
- HMI-P/E

Graphs showing ratios for different time periods.
Do the ratios change based on Exceedance v. Non-Exceedance?

**Daily Acetylene/Benzene Ratio**

**Daily M&P-Xylene/Benzene Ratio**

**Daily Toluene/Benzene Ratio**

**Daily Propene/Ethene Ratio**
Gas cans at HMI

- All vehicles run on diesel except lawn equipment, which was generally not run during the project.

- Evaporative gas was omni-present, making it unlikely a hyper-local source on HMI.