Preliminary VOC source apportionment analysis at Goethals Field, Staten Island

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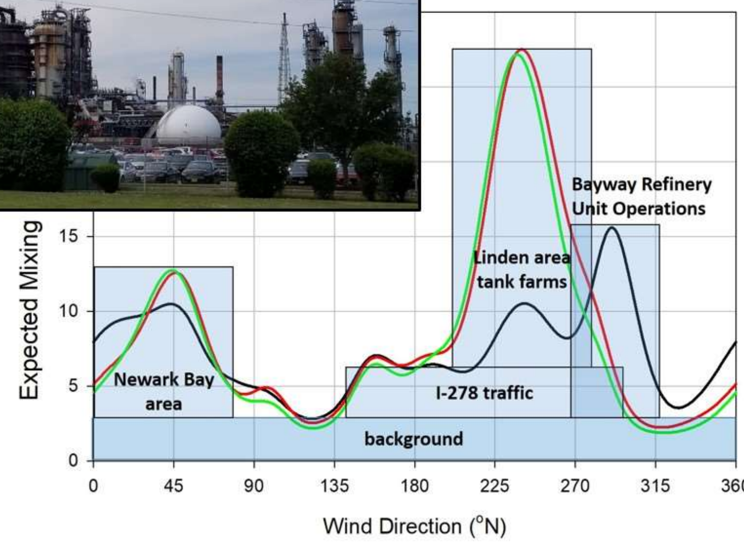
Credit: Phil Degginer / Science photo Library



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NYSERDA Supported

Briefing to NACAA Monitoring Steering Committee

February 2, 2023

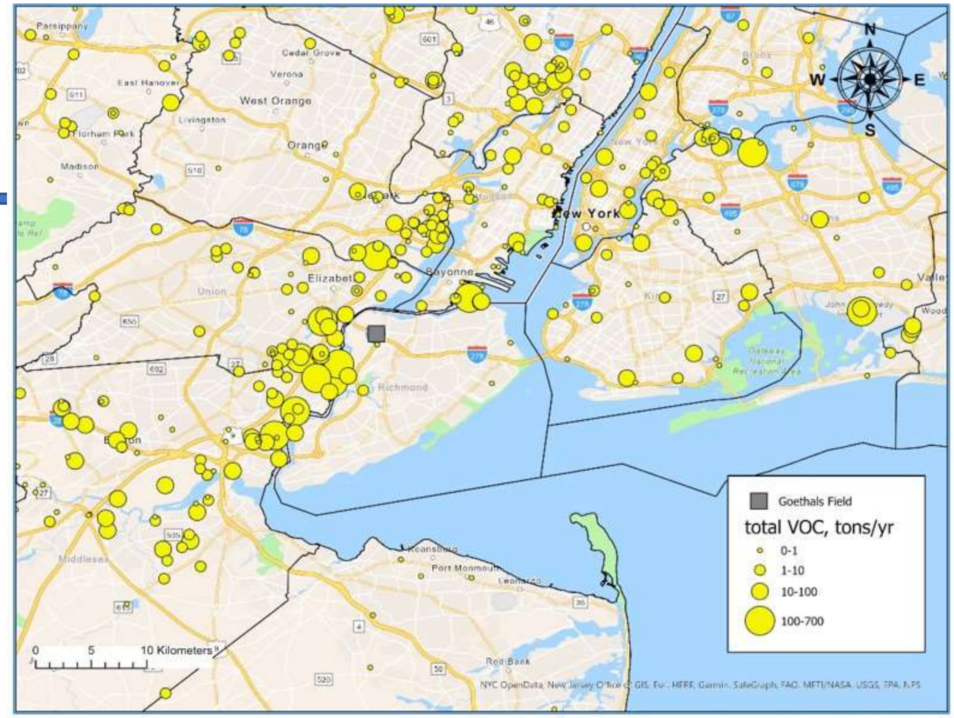
Motivation

- May 2017 aircraft measurements collected over the NYC region by U. Maryland identified propylene as a key reactive VOC species potentially contributing to increased ozone levels in the VOC-sensitive NYC urban core.

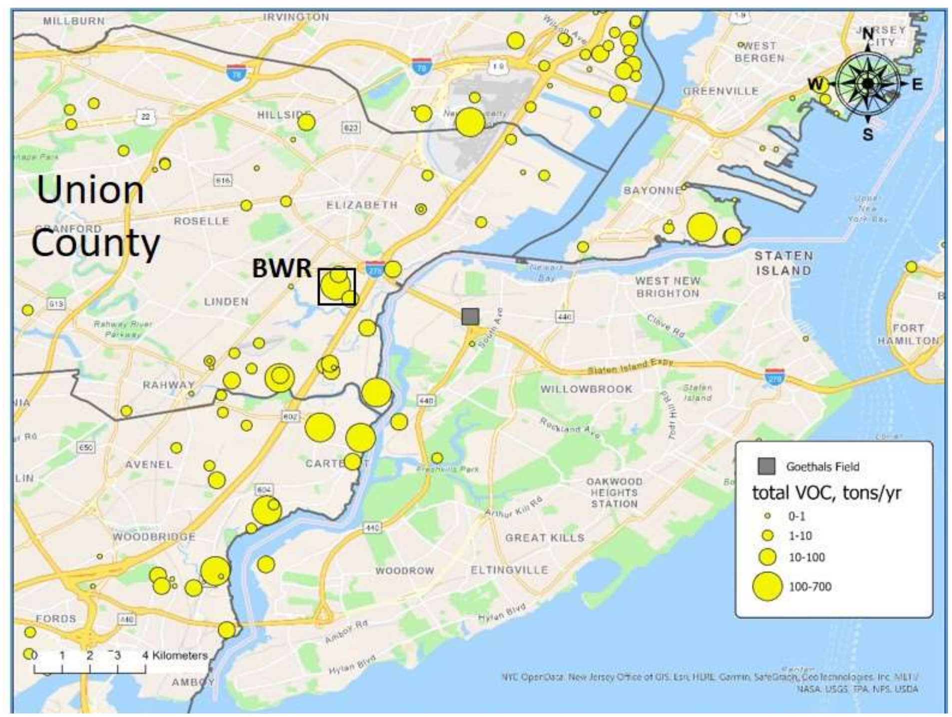
- This special study site was established to try to identify the sources of propylene (and other key VOCs) in the area upwind of NYC

VOC Emissions

2017 National Emissions Inventory (NEI)



- Phillips 66 Bayway Refinery (BWR) estimated to be the 4th largest facilities VOC emissions source in the two-state NY-NJ area



- Several other notable facilities VOC emissions sources nearby

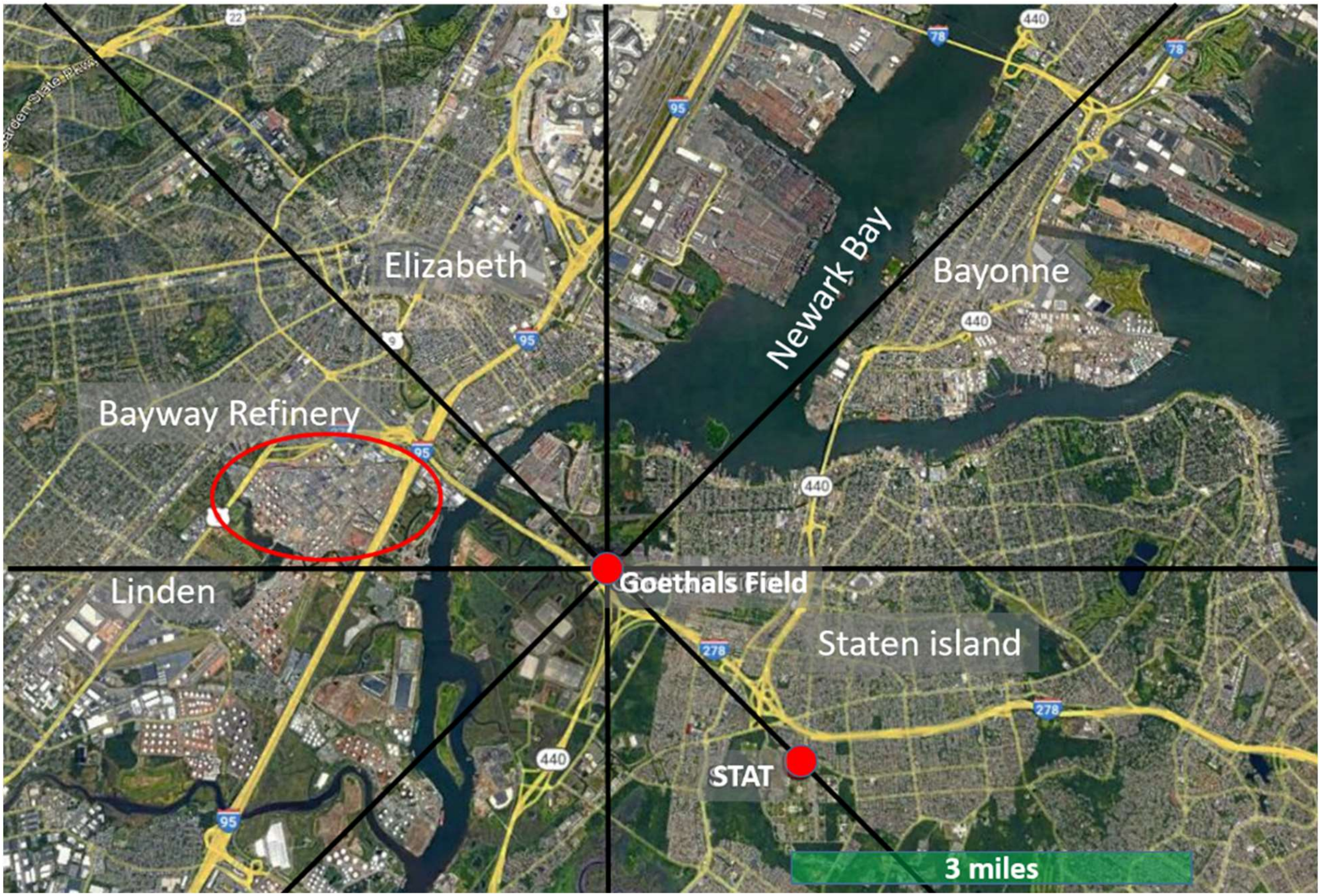
Objectives

- Construct a bottom-up VOC emissions inventory (EI) for the Phillips 66 Bayway Refinery ("Bayway")
- Several key findings, e.g.
    - Zero propylene emissions from the Bayway polypropylene plant
    - SPECIATE and TRI emissions estimates often dramatically different
    - *Not further discussed today*
- Assess VOC emissions from Bayway and other nearby emission sources using a top-down approach (monitoring data)
    - *Today's briefing*

Approach

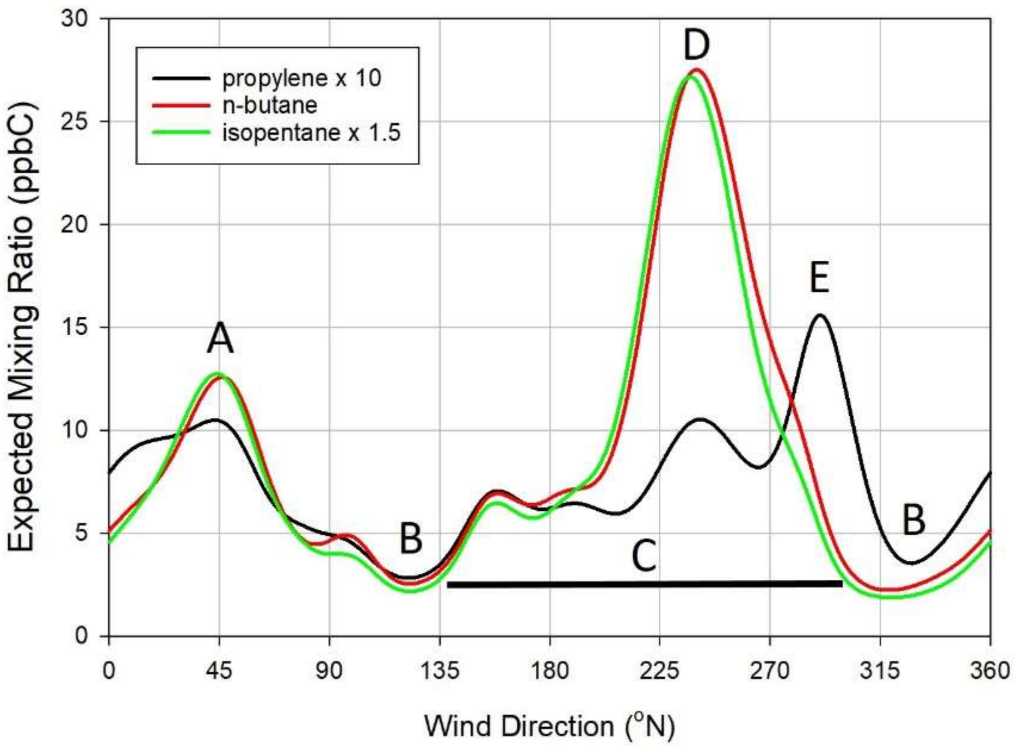
- NYS DEC established a Special Purpose Monitor for hourly speciated VOCs at their Goethals Field site on Staten Island
- Quantified 28 VOCs (subset of full PAMS analyte list)
- Monitoring started December 2021 and will continue through summer 2023 (but not winter 2022/2023)
- While ozone primarily is a summertime issue, conduct a preliminary analysis of data collected through April 2022
- **Use a top-down approach to identify emission sources (or at least source regions)**

Goethals Field Environment

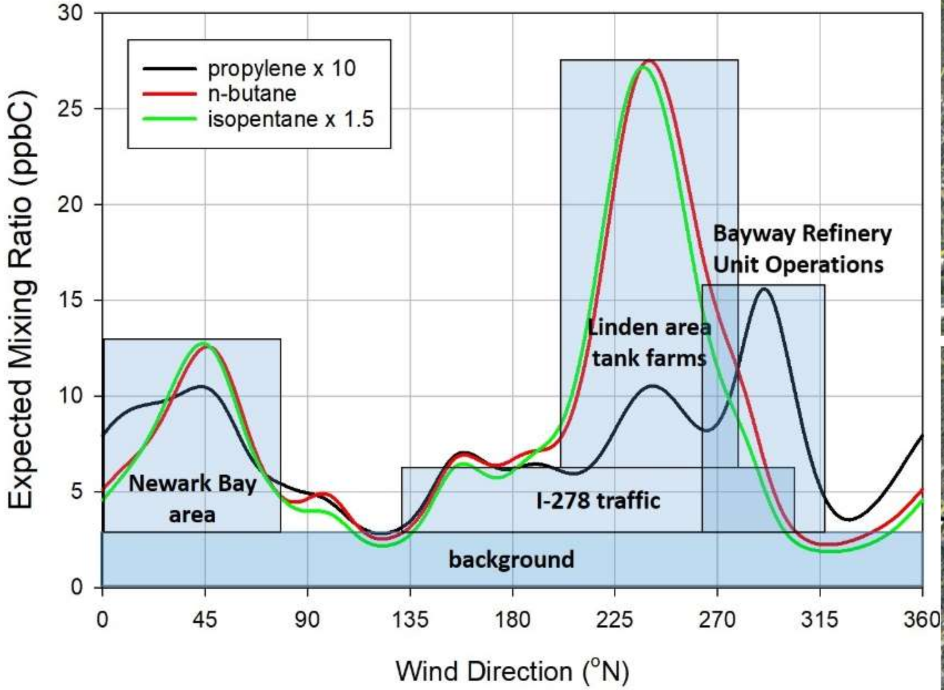


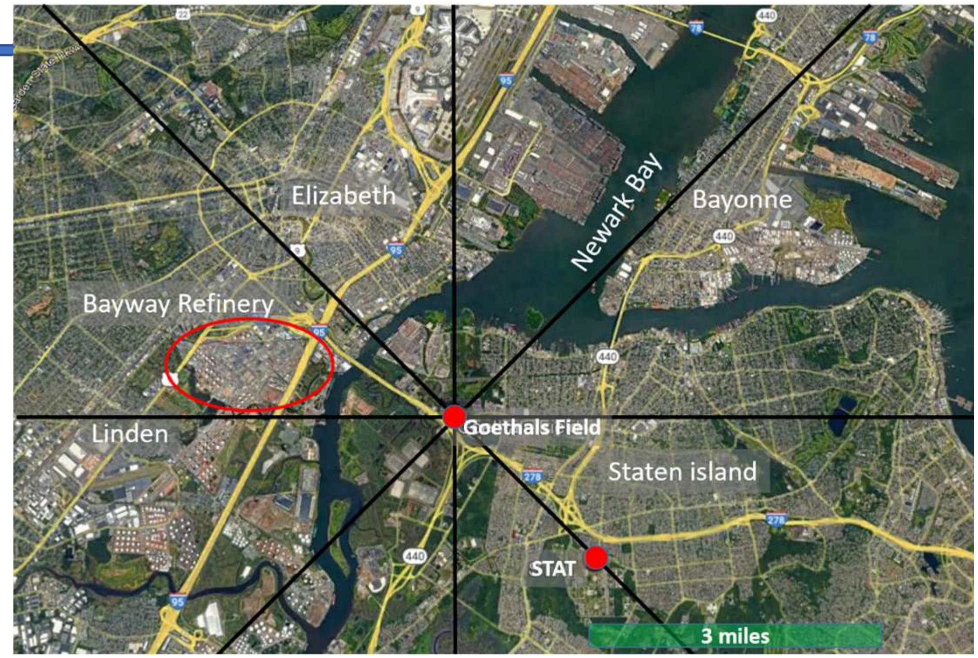
Nonparametric Wind Regression (NPWR)

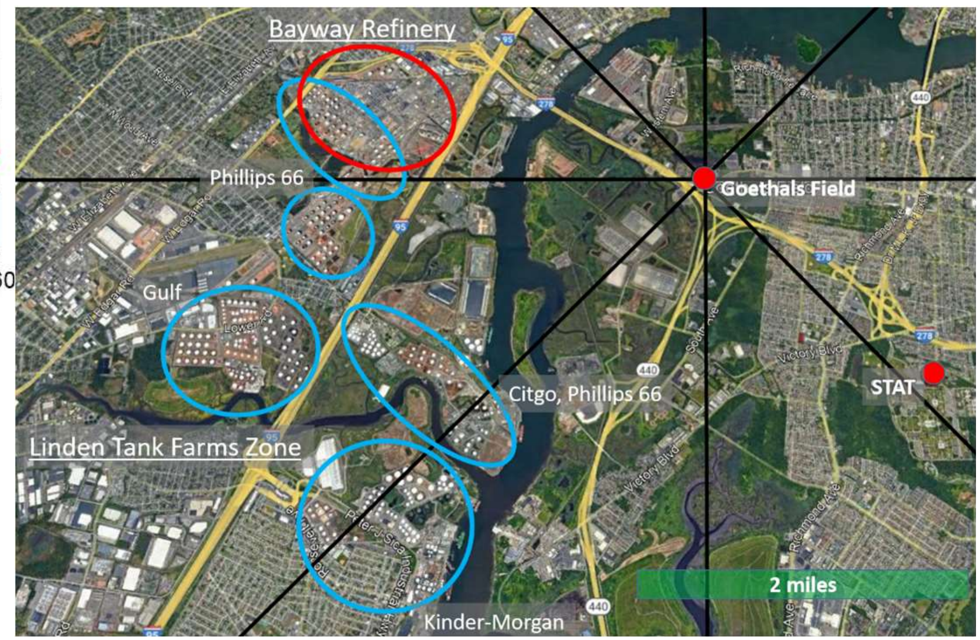
- Essentially a pollution rose but does not require subjectively defining wind direction bins
- Underlying statistical support, although confounded by serial correlation and also varying emission rates
- Better trends detection using Cartesian plot instead of polar plot



Preliminary Conceptual Model

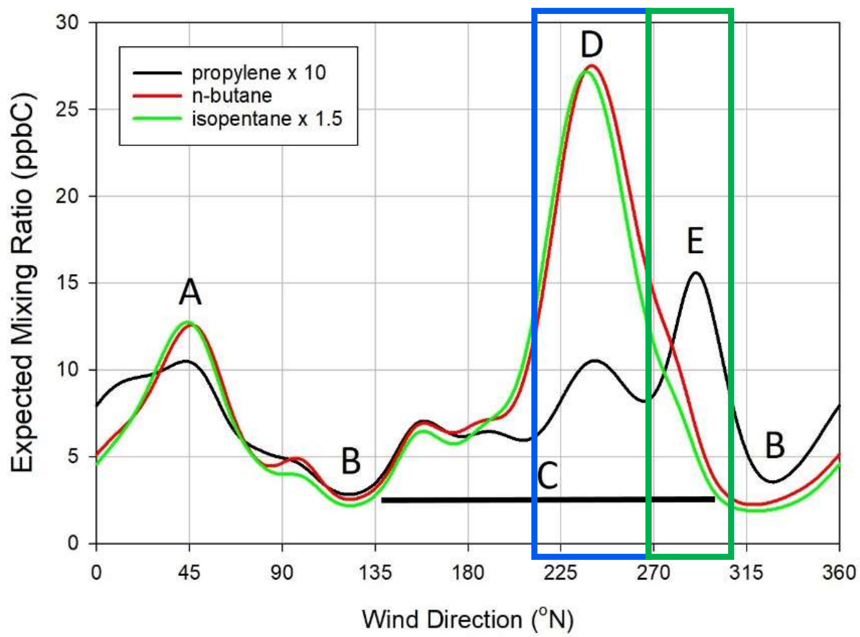




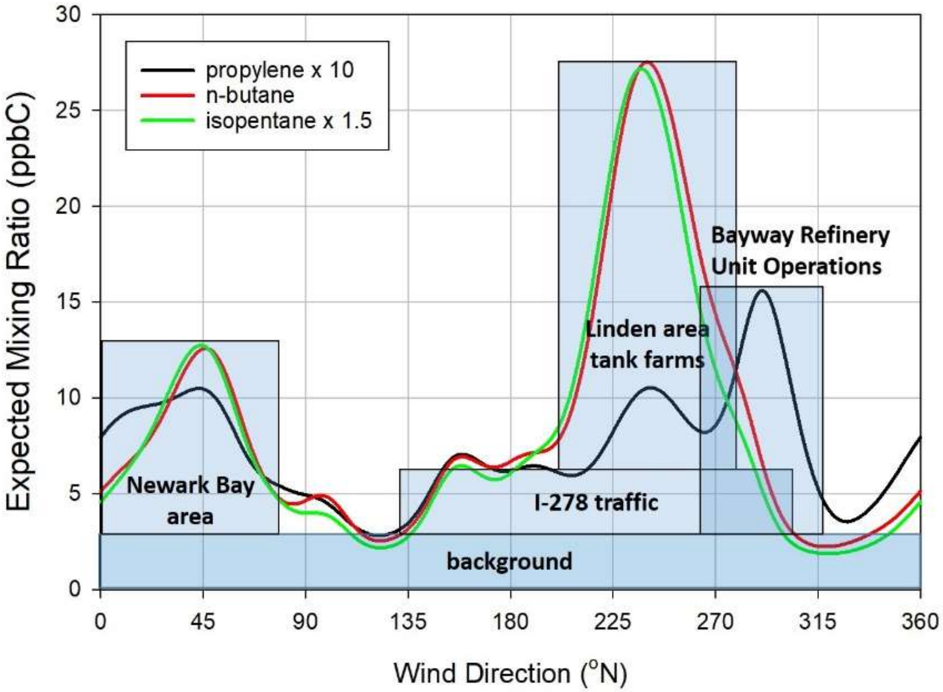


Linden area emissions

Putative emissions zones for the NPWR mixing ratio peaks at ~240° (blue wedge) and ~290° (green wedge) using baseline-adjusted peak widths at ½-height for n-butane and isopentane (240° peak) and propylene (290° peak).

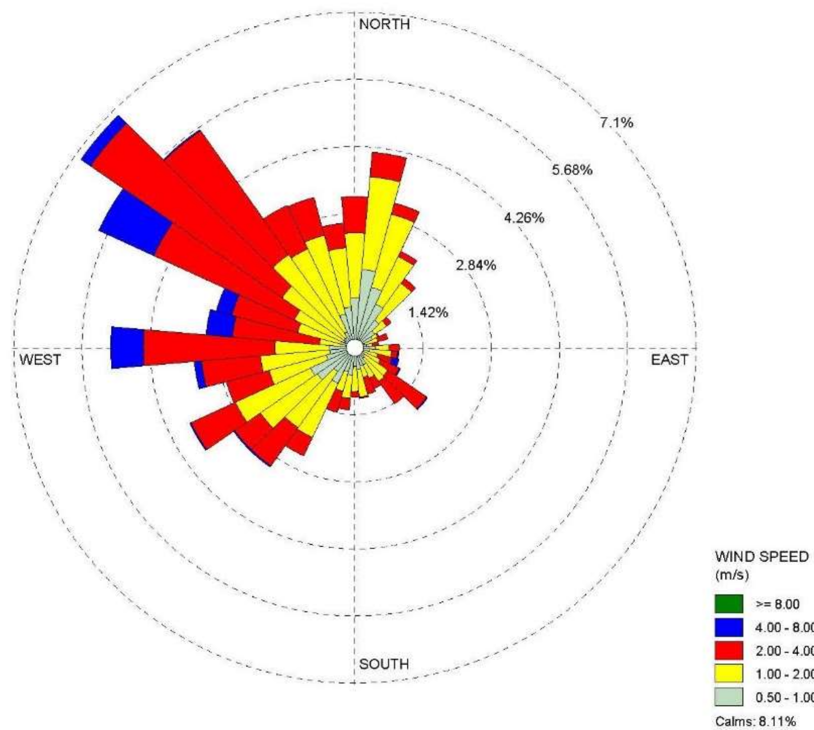


A limitation of the preliminary analysis…



- Summertime winds from the south/southeast might help to clarify traffic contributions
- Additional data for winds from north/northeast might clarify the Newark Bay area contributions

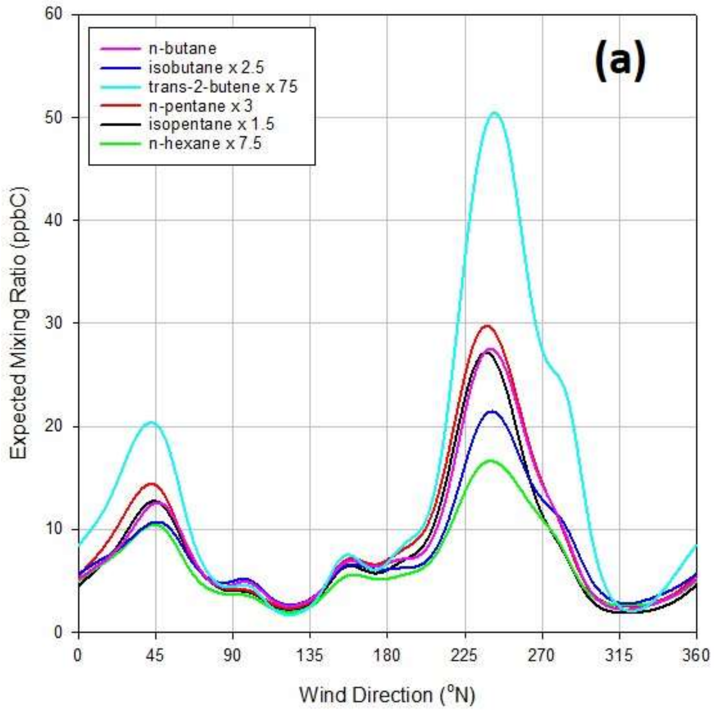
Hourly Wind Rose

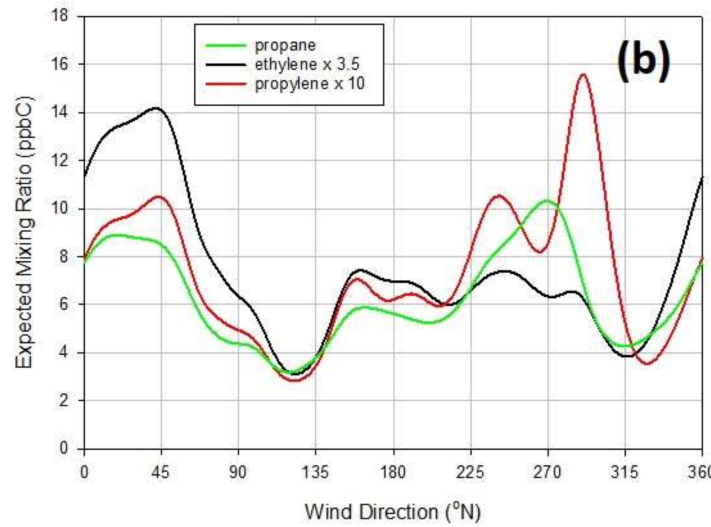


NPWR on additional VOCs

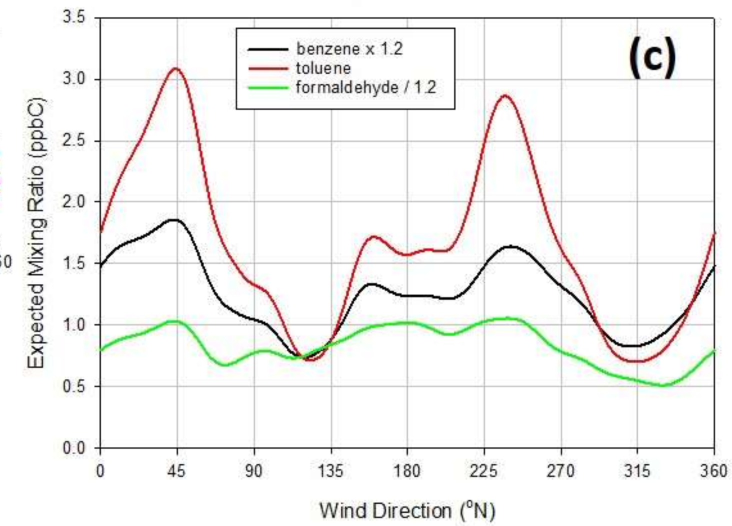
- Provides insights into species covariance

C4+, mostly alkanes





C2-C3

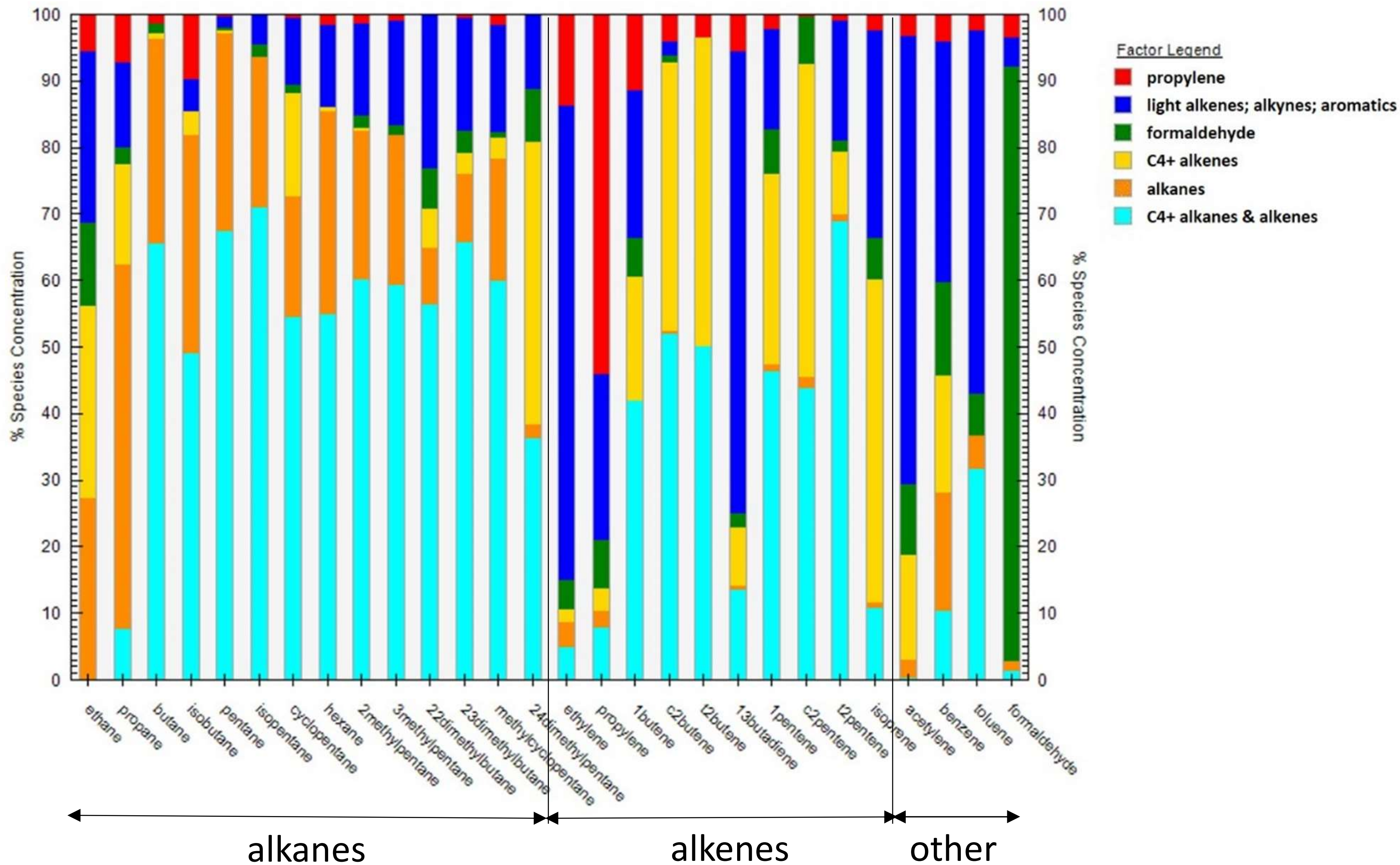


aromatics, HCHO

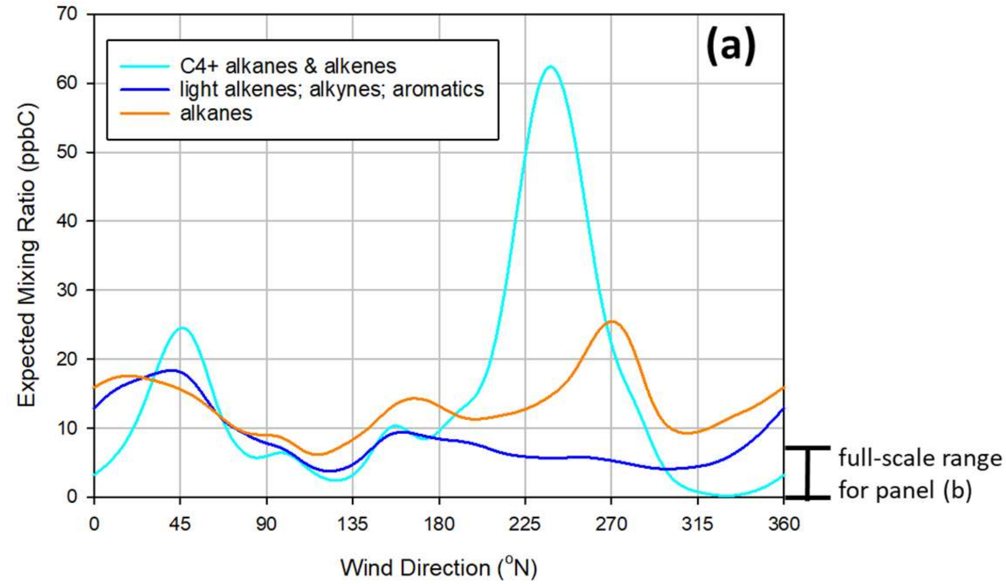
- Conduct this analysis prior to source apportionment modeling

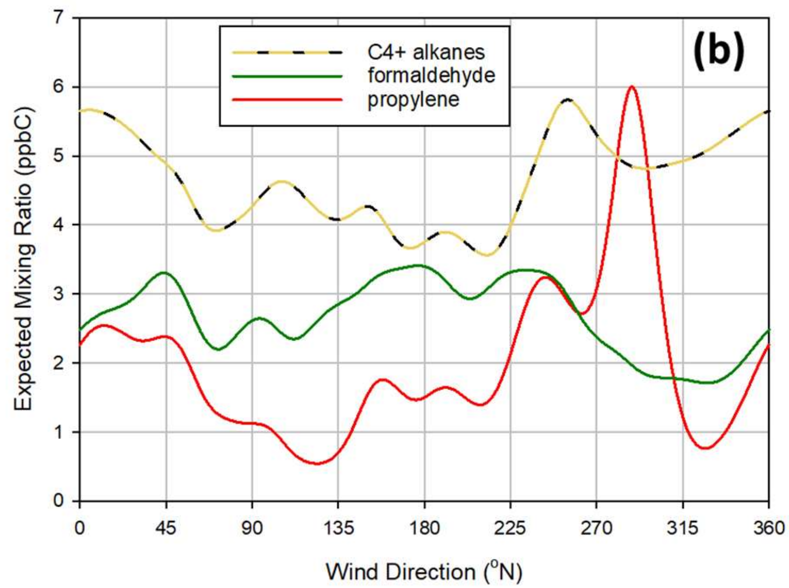
Source Apportionment using Positive Matrix Factorization (PMF)

"fingerprint plot" (distribution of each species across the resolved factors) for six-factor solution



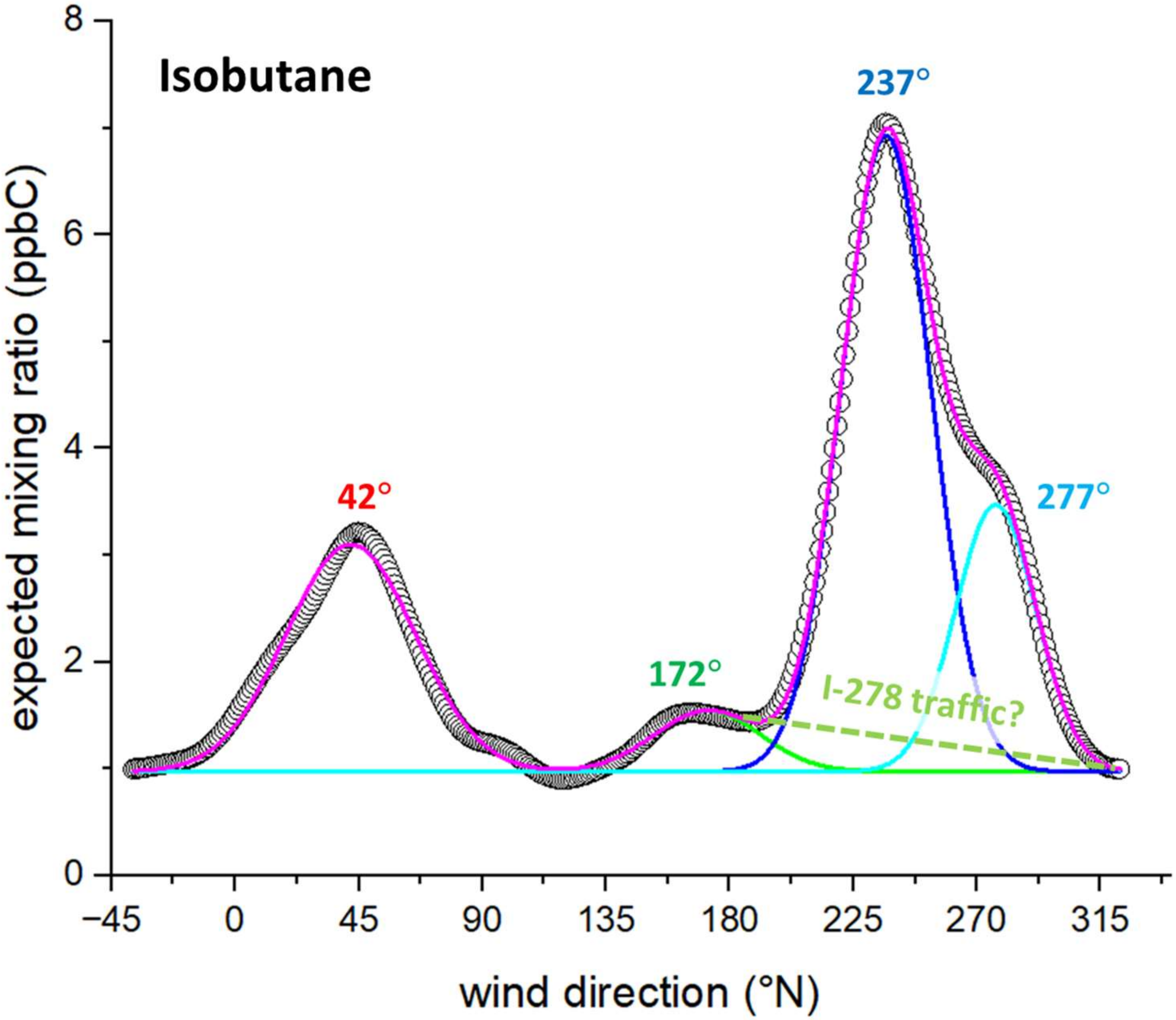
NPWR on the PMF-Resolved Factors



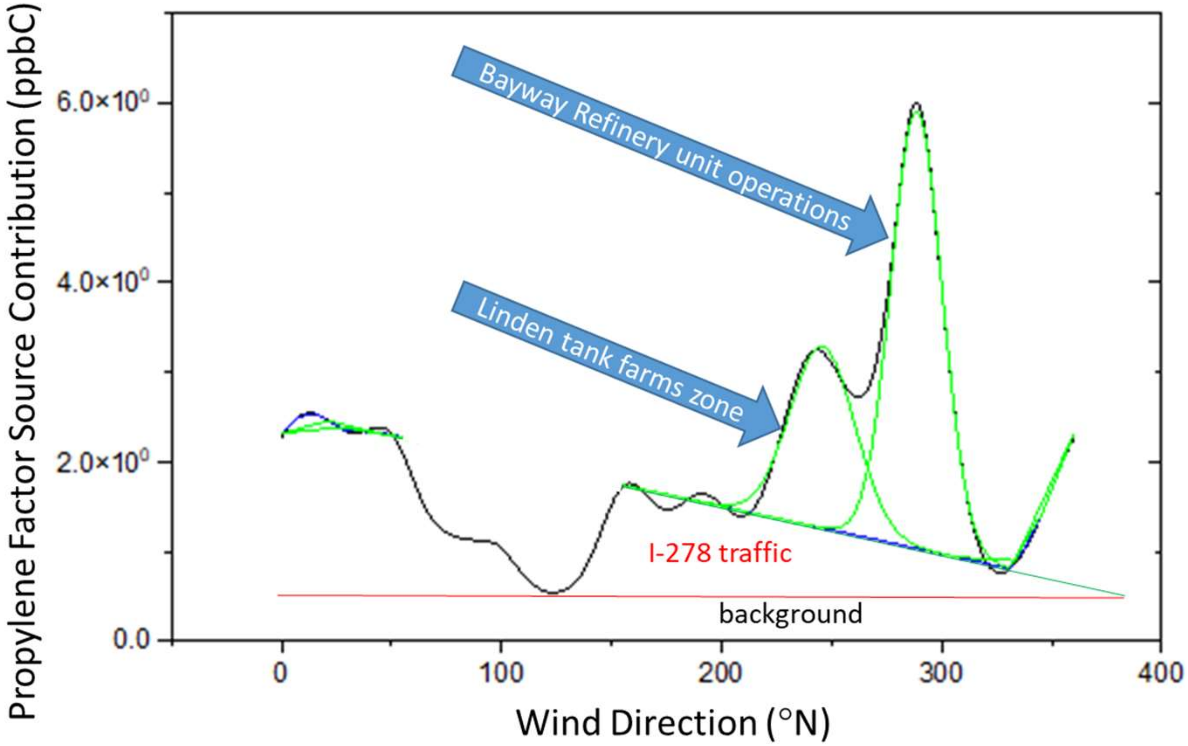


Broadly similar results obtained using another source apportionment model - UNMIX

Quantifying source region impacts



Quantifying source region impacts

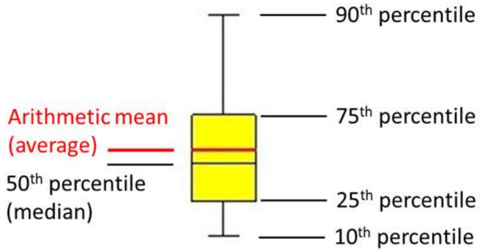


Separation of two NPWR peaks in the PMF-resolved propylene factor

Source	Mixing Ratio (ppbC) Linden tank farm zone, 246°	Mixing Ratio (ppbC) Bayway Refinery unit operations, 289°
Designated Source	1.99 (62%)	4.94 (82%)
I-278 Traffic	0.69 (21%)	0.51 (9%)
Background	0.54 (17%)	0.54 (9%)
FWHM[(1)]	35°	27°

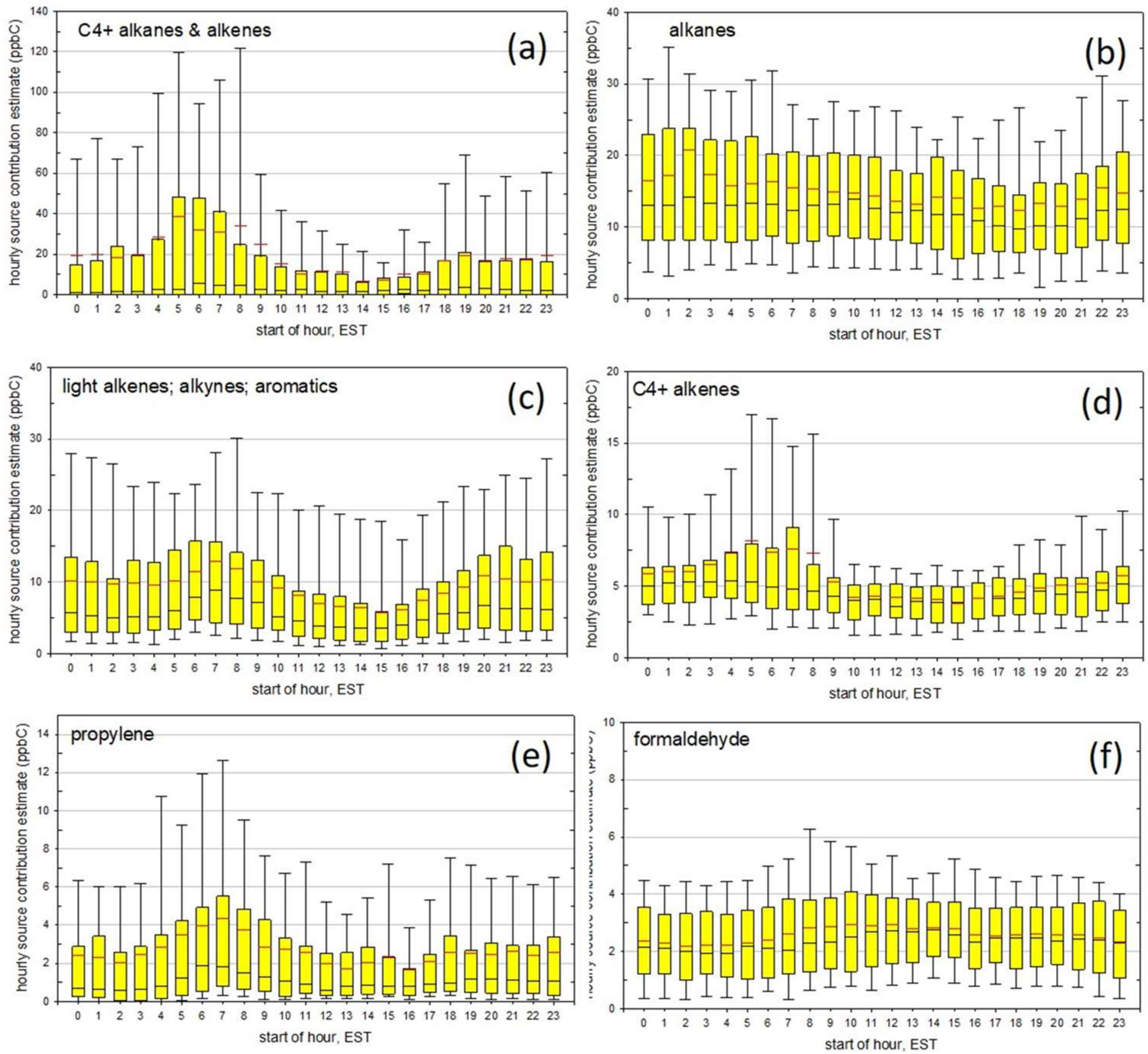
(1) FHWM = full width at half maximum for the Designated Source peak

Diel Profiles for the PMF-Resolved Factors



Looking for two features:

- Diel profile shape
- Gap between mean and median values



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- NYS MesoNet (Jerry Brotzge)

Workflow

- Evaluate VOCs and surface winds data quality and representativeness – *not discussed today*
- Using data for the three VOCs of primary interest, develop a conceptual model for VOC impacts
- Conduct detailed analysis of the complete VOC dataset
- Refine the conceptual model
- Make recommendations for future monitoring and analysis

VOCs of primary interest

Ranked contributors to ozone formation among the 28 reported PAMS Target List compounds; contributions calculated using Maximum Incremental Reactivity (MIR) values. Numbers in parentheses after a compound name correspond to the rank on the other list.

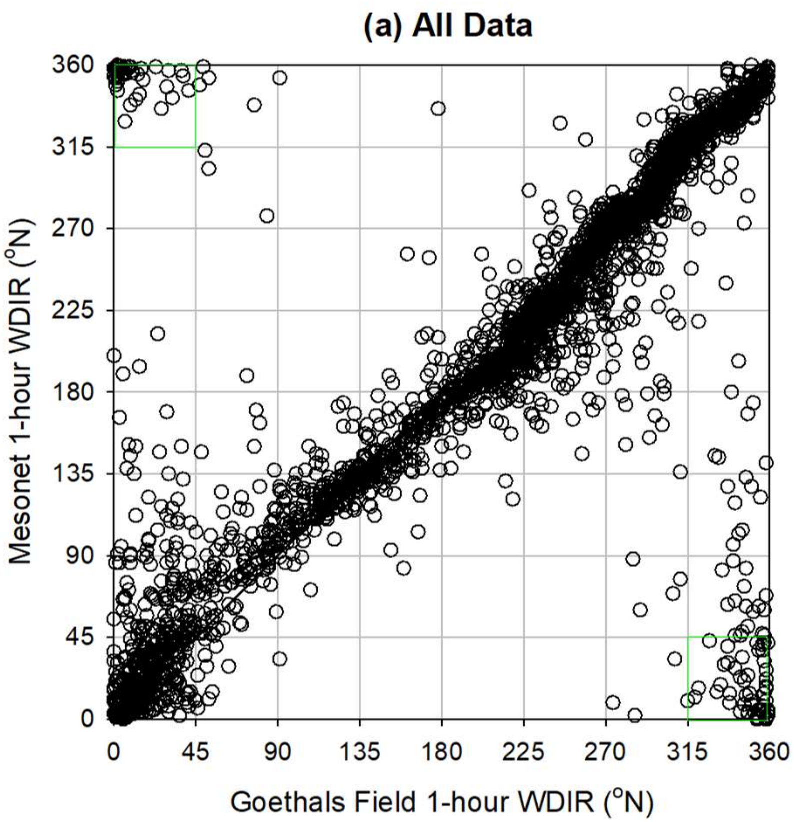
Rank	GF Mixing Ratios[1]	BW Emissions Inventory[2]
1	ethylene	toluene
2	formaldehyde	propylene
3	n-butane	ethylene
4	propylene	benzene (22)
5	isopentane (14)	formaldehyde
6	toluene	n-hexane (15)
7	n-pentane	n-butane
8	isobutane	n-pentane
9	trans-2-butene (21)	propane
10	propane	isobutane

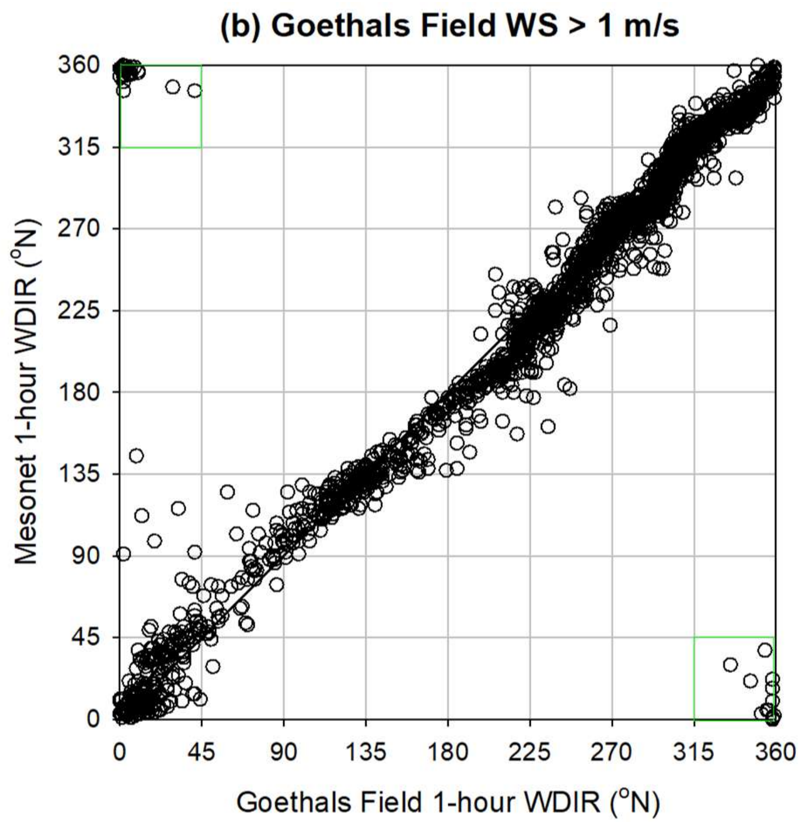
(1) Goethals Field measured mean mixing ratios

(2) Phillips 66 Bayway Refinery 2017 emission inventory

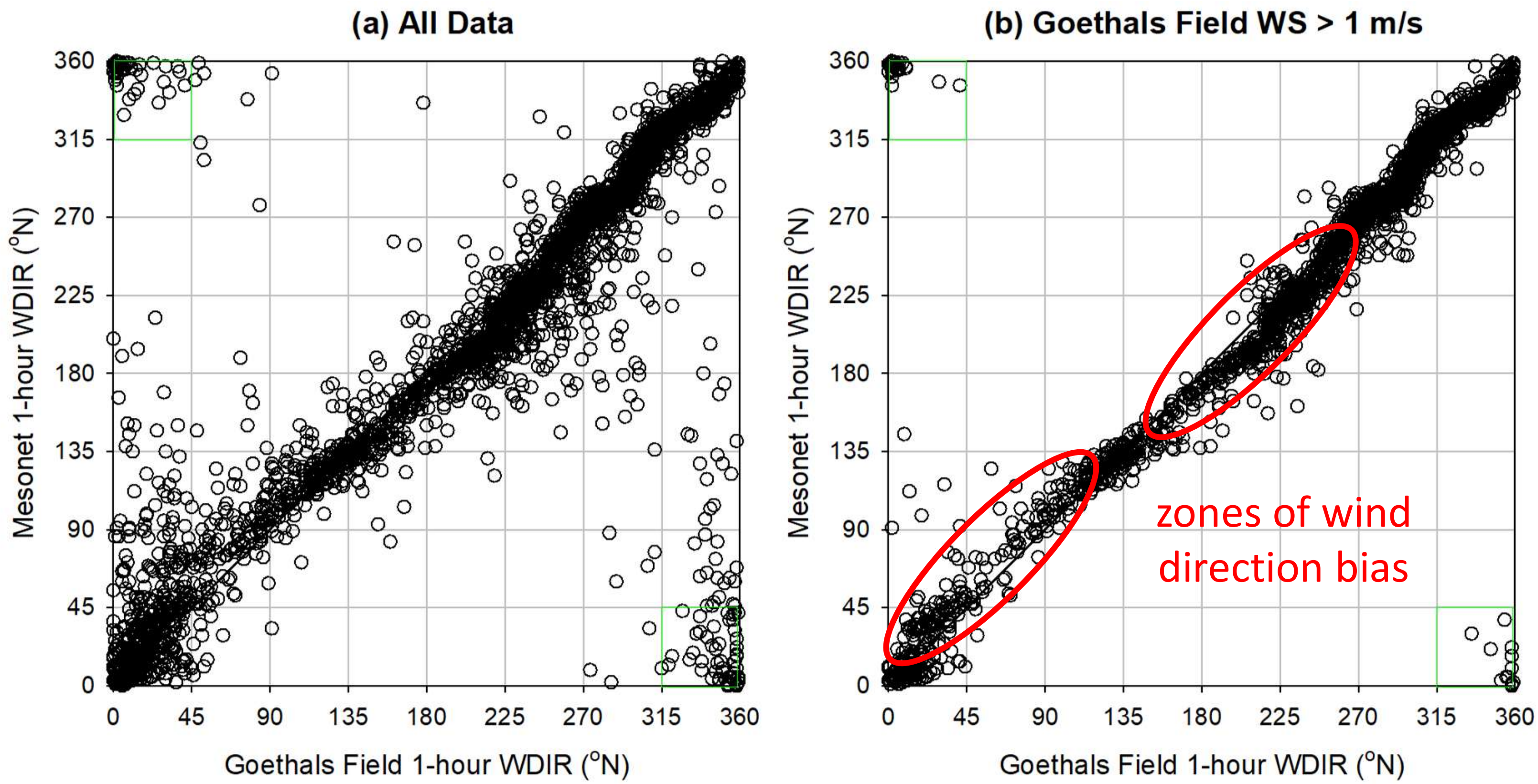
Surface Winds Data

- 10m meteorology tower at Goethals Field (“GF”)
- 10m meteorology tower on the roof of building ~2 miles to the southeast (Mesonet site, station ID “STAT”)





Surface Winds Data



- Wind channeling from Newark Bay?
- Obstructions (trees) affecting the GF measurements?

Recommendations

- Monitor a "unique" tracer for traffic emissions, e.g., CO ☑
- Strive to elucidate impact of Bayway polypropylene plant temporary shut down on observed propylene mixing ratios
- Optimize source apportionment modeling
  - Uncertainties for the source contribution estimates
  - Sensitivity of PMF modeling results to assigned analytical uncertainties
  - Refine the UNMIX modeling (try UNMIX-O model)
- Explore sensitivity of results to the NPWR wind speed threshold
- Construct diel wind roses to examine emissions-meteorological coupling
- Stratify the PMF-resolved factors by wind direction and construct diel profiles and source contribution estimates
- Weight NPWR results by wind direction frequencies to quantify time-averaged source impacts

NPWR Wind Speed Threshold

Run	Winds	WS (m/s)	θ
01	**GF 1°**	**> 1**	**10°**
02	GF 2°	all	10°
03	GF 1°	> 0.5	10°
04	GF 1°	> 1	5°