Briefing on Roxana Air Quality Study (RAQS)

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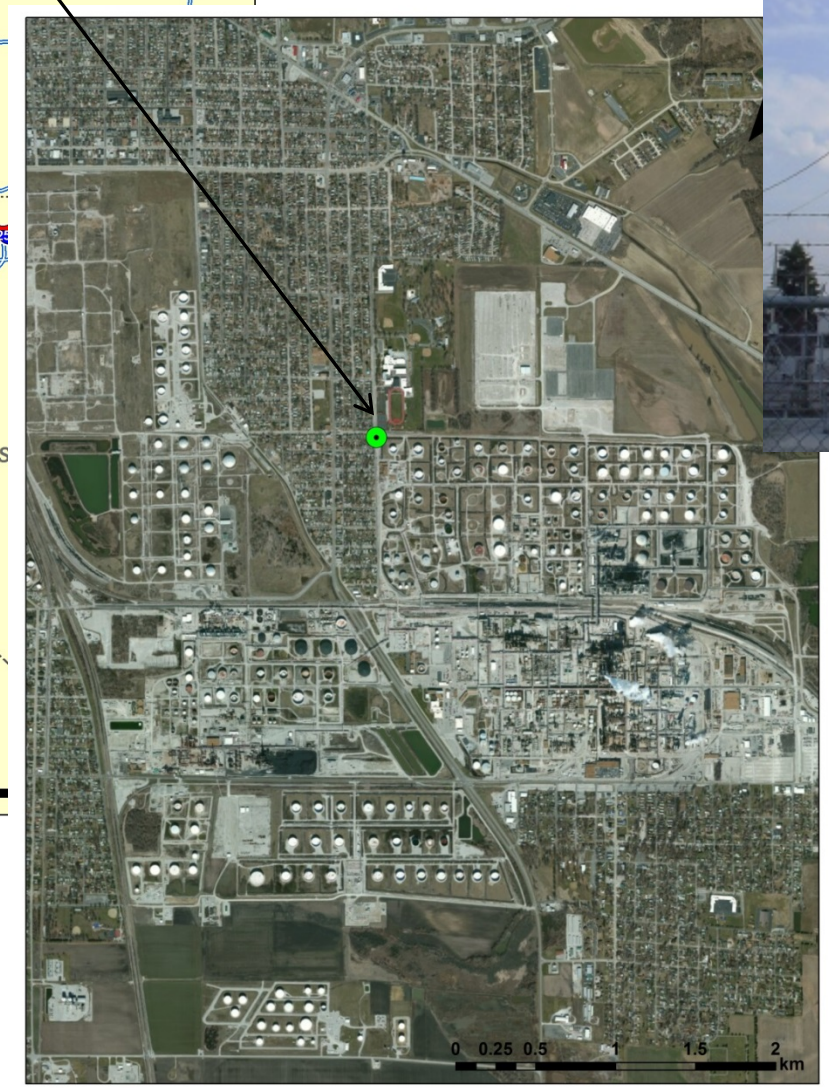
Washington University in St. Louis

Jersey
Calhoun
Madison
St. Charles
St. Louis
St. Louis City
Jefferson
Monroe
0 2.75 5.5


0 0.25 0.5 1 1.5 2
km

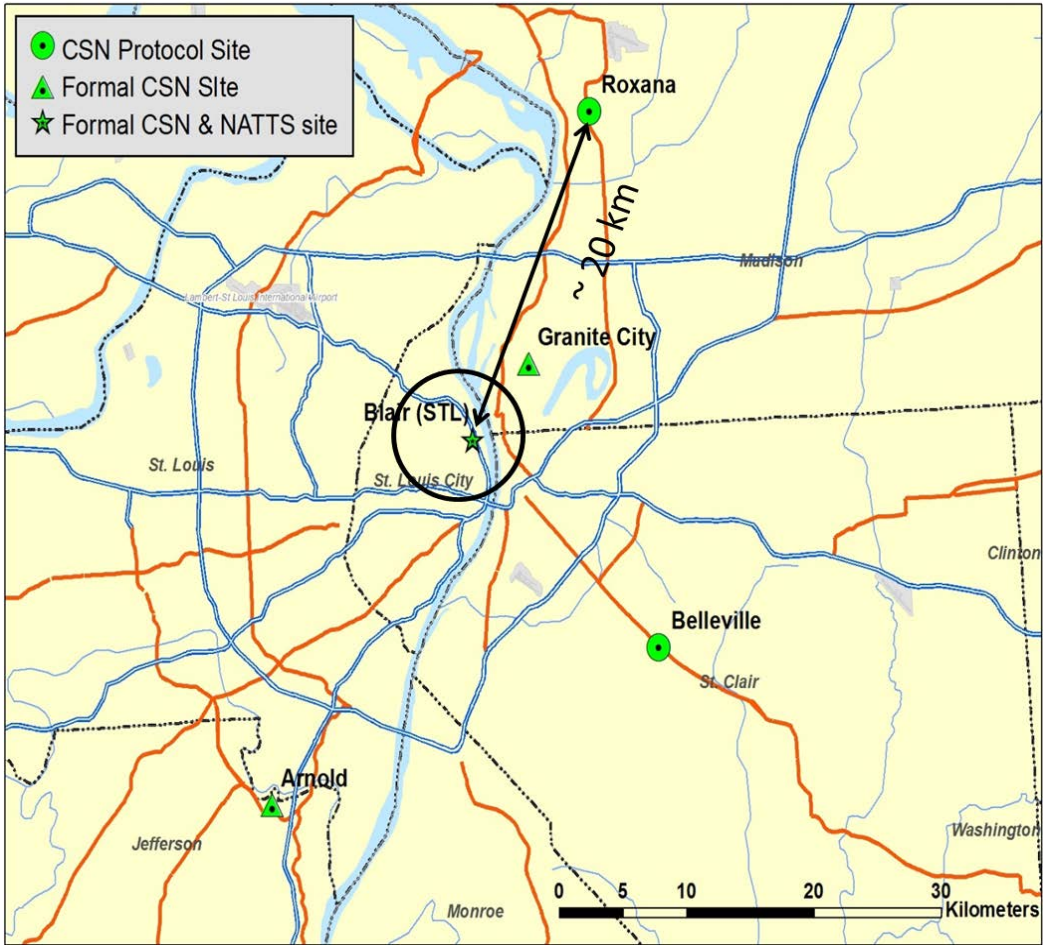
Measurements Summary

Parameter(s)	Frequency	Start Date	Analysis Lab
Air Toxics gases	1-in-6 day	06/08/2012	ERG
$PM_{2.5}$ speciation	1-in-6 day	06/08/2012	RTI
H_2S/SO_2	5-minute	Aug 2010	N/A
Meteorology	5-minute	Sep 2010	N/A

- Air Toxics gases
  - ***58*** Volatile organic compounds (VOCs) and ***13*** carbonyl compounds
  - Methods: EPA TO-15 (VOCs), EPA TO-11A (carbonyls)
  - NATTS protocol and analytical lab
- $PM_{2.5}$ speciation
  - gravimetric mass, **5** water soluble ions, **33** metals and carbon fractions
  - STN (CSN) protocol and analytical lab
  - additional in-house $PM_{2.5}$ speciation for select elements by ICP-MS

RAQS Data in Context

- Compare RAQS data to City of St. Louis Blair Street station data (NATTS site, STN site)
- Both sites could have local influences, so difference represents the minimum local contribution at the higher concentration site



Spatial Variability*: Roxana vs. Blair

HOMOGENEOUS	HETEROGENEOUS	
	Roxana > Blair	*Blair >Roxana*
Carbon tetrasulfide	**Acrolein**	**Acetylene**
1,3,5-Trimethylbenzene	**n-Octane**	**1,3-Butadiene ****
Chloromethane	**Propylene**	**Methyl Isobutyl Ketone**
Dichlorodifluoromethane	**Benzene**	**Dichloromethane**
Trichlorotrifluoroethane	**Ethylbenzene**	**Chloroform**
Dichlorotetrafluoroethane	**m,p-Xylene**	**Trichlorofluoromethane**
Propionaldehyde	**Toluene**	**Valeraldehyde ****
Hexaldehyde	**o-Xylene**	**Crotonaldehyde ****
	1,2,4-Trimethylbenzene	**Acetaldehyde ****
	1,2-Dichloroethane	**Butyraldehyde**
	Benzaldehyde	**Formaldehyde****
	Tolualdehyde **	**Acetone**
		2-Butanone
		Acetonitrile***

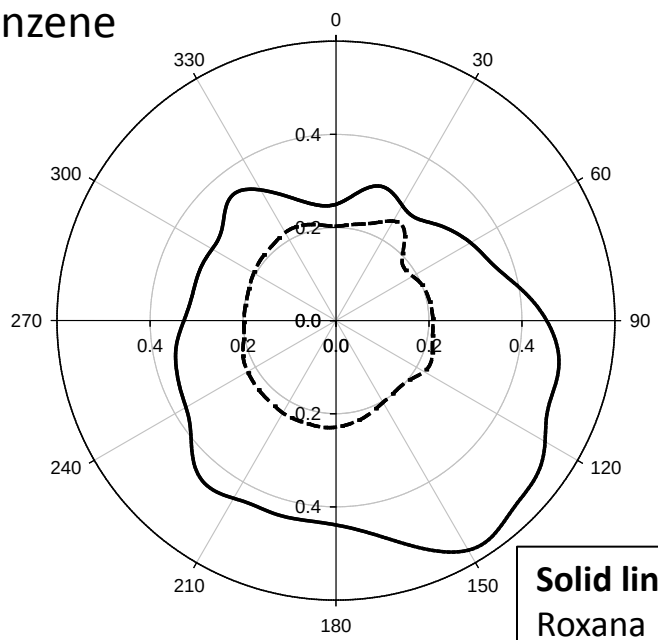
***** Categorization using a Wilcoxon paired signed-rank test on the concentration distributions. Significance at the 95th percent confidence level. Compounds marked with (**) were homogeneous using a Kruskal-Wallis test.

*** Dramatic change in concentration time series. Will confirm with ERG.

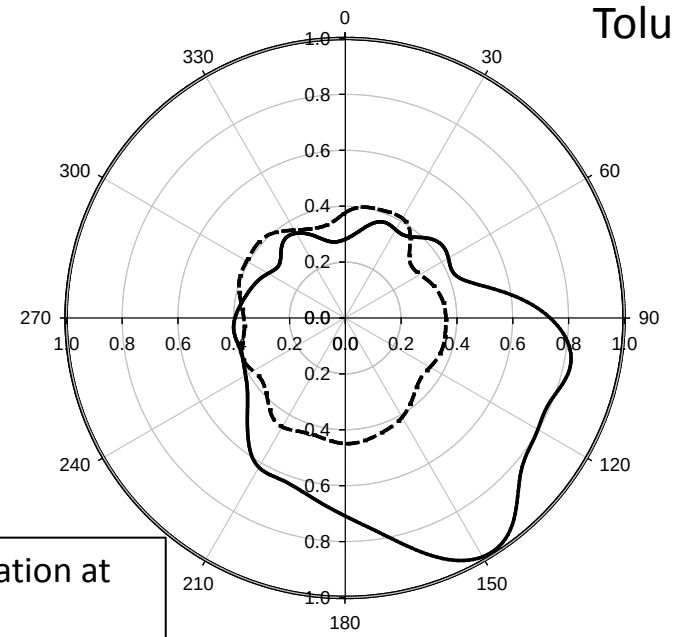
Excludes data collected at Roxana from June 2012 through December 2012 because of measurement artifacts for the carbonyls data

Nonparametric Wind Regression

Benzene

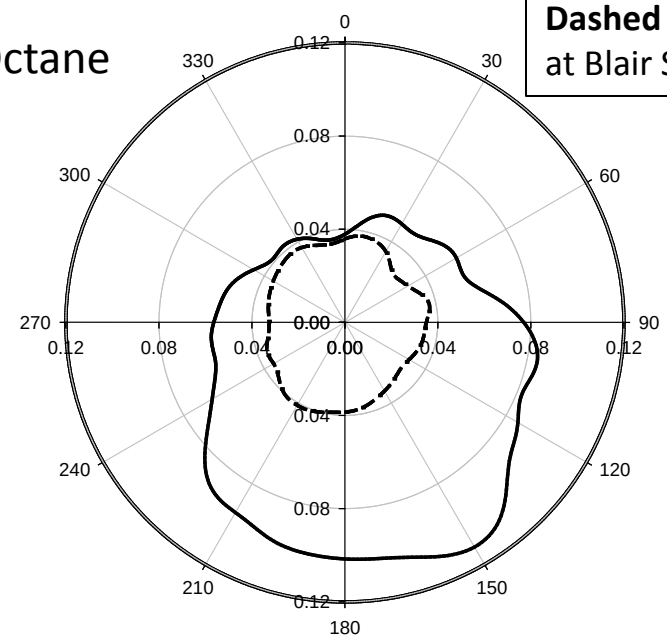


Toluene

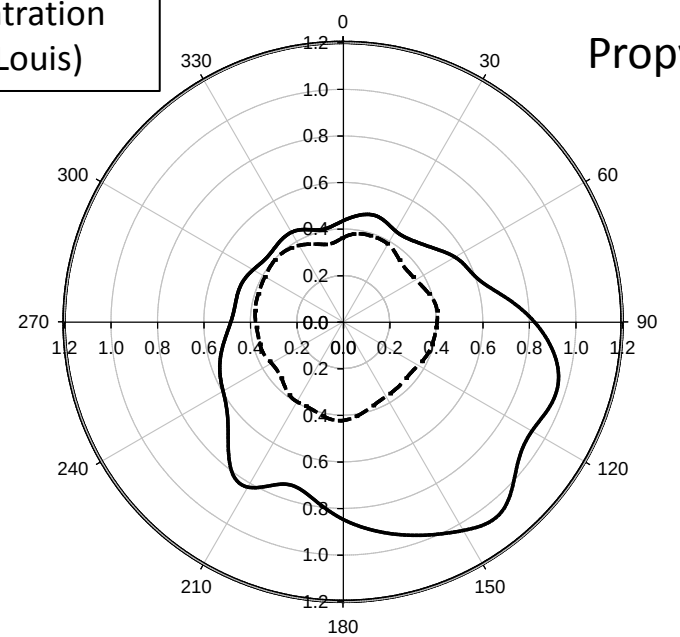


Solid line: expected concentration at Roxana
Dashed line: expected concentration at Blair Street (downtown St. Louis)

n-Octane

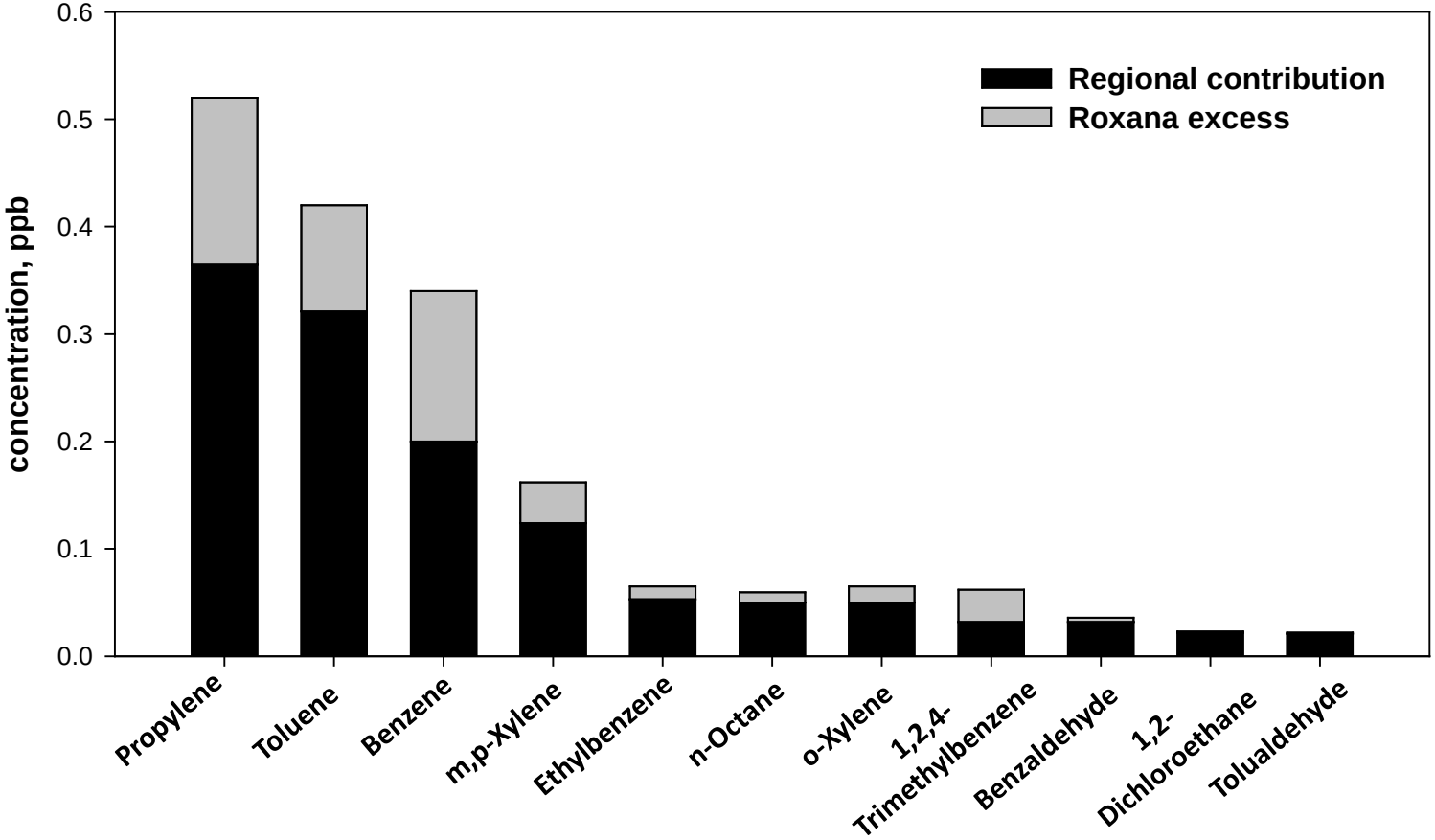


Propylene



Spatial Variability: Roxana vs. Blair

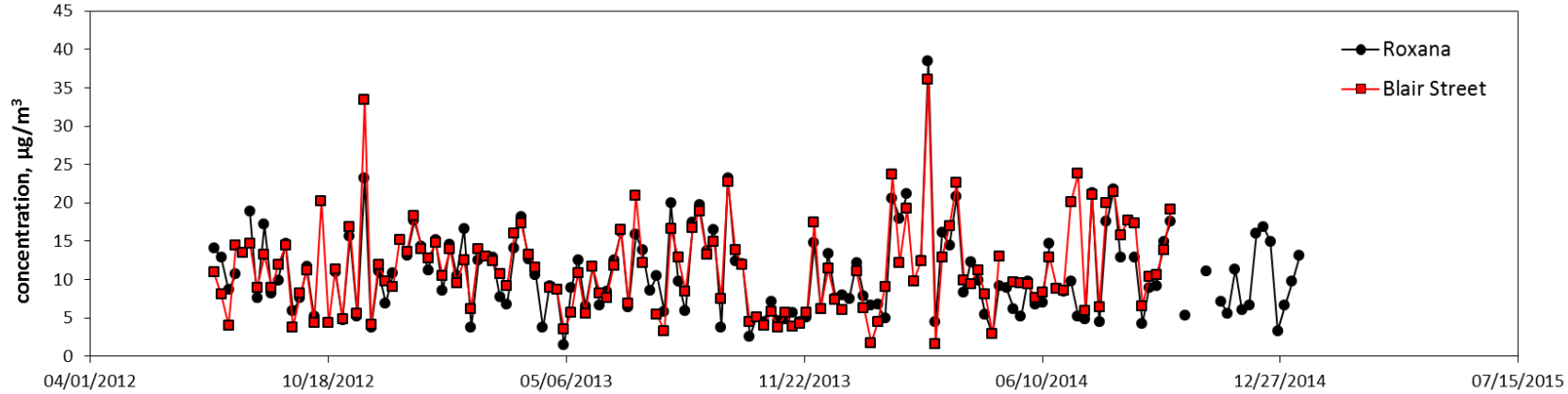
Estimate of local source contribution at Roxana,

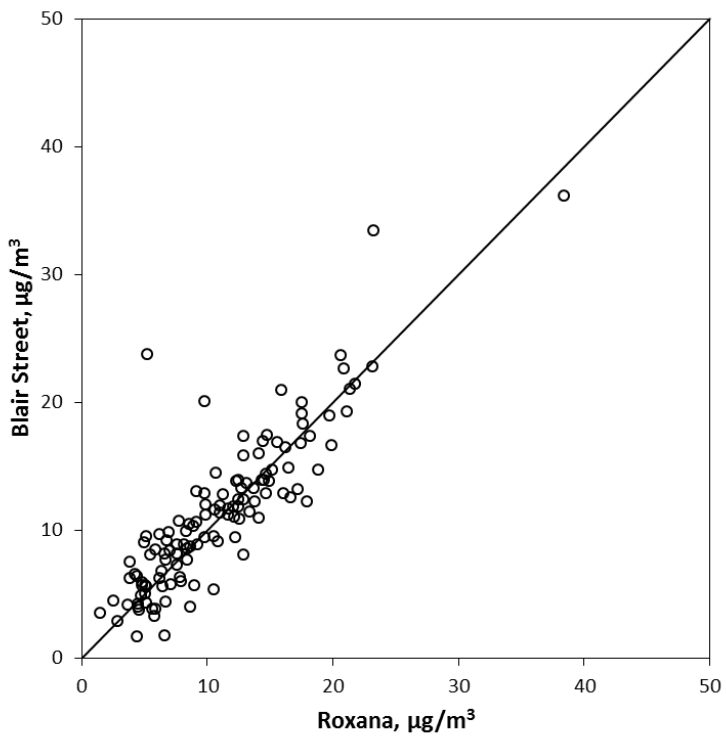


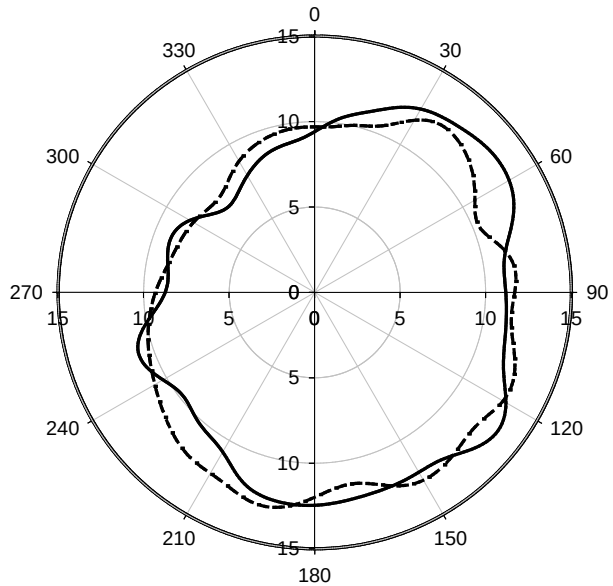
Roxana excess = median of (Roxana minus Blair Street difference distribution)

Regional contribution = median (Roxana) – Roxana excess

$PM_{2.5}$ mass - Roxana







Solid line: Roxana winds
Dashed line: Lambert winds

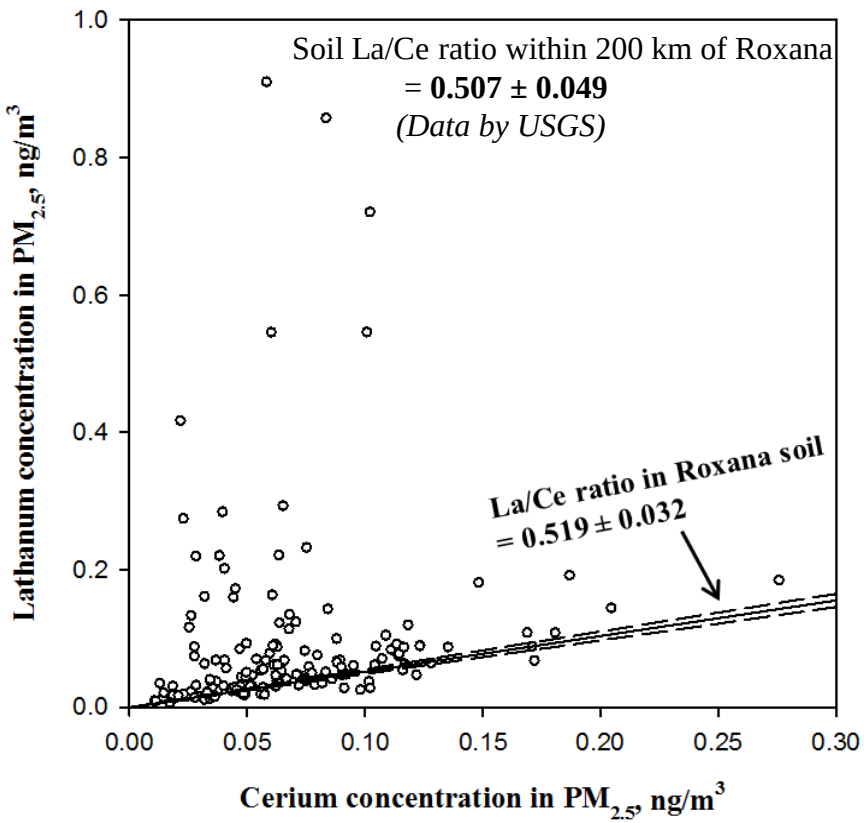
- $PM_{2.5}$ mass is relatively homogeneous in the St. Louis region.
- No directional pattern was observed at Roxana indicating no major sources.

Rare Earth Element (REEs) in $PM_{2.5}$

- REEs (lanthanum and cerium in particular) are enriched in catalysts used in fluidized catalytic crackers (FCC)
- REEs exist in the crustal materials, such as soil and rock
- REEs in the ambient $PM_{2.5}$ could serve as tracers for refinery FCC emissions
  - Method first proposed and demonstrated by the Chellam group at University of Houston
- A manuscript was submitted on the topic to Science of the Total Environment.

Lanthanum and Cerium in $PM_{2.5}$

$PM_{2.5}$ samples (open circles)



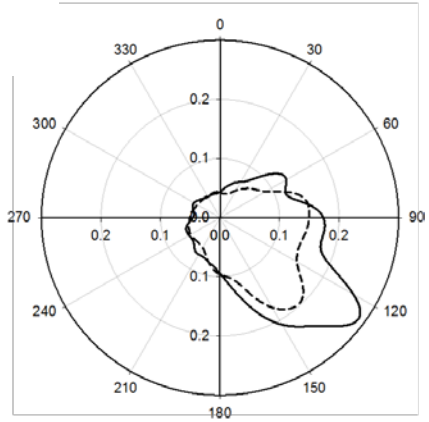
- $PM_{2.5}$ samples collected every 1 in 6 day were analyzed in the lab for Rare Earth Elements (REEs) – La and Ce in particular
- Local soil samples were resuspended and analyzed following the same protocol as $PM_{2.5}$ samples to establish the profiles of REEs in the soil.

- The La/Ce ratios were bounded by the average ratio obtained from local soil at the low edge
- Higher La/Ce ratios indicate mixed sources from local soil and possibly FCC emissions

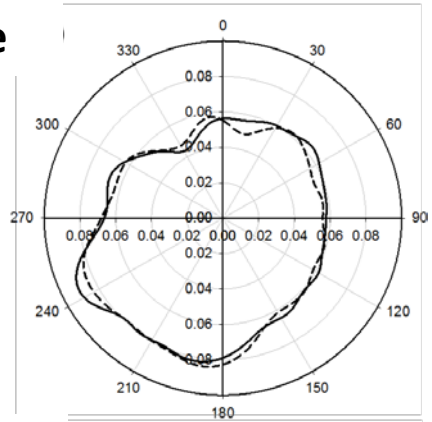
Nonparametric Wind Regression (NWR) on La, Ce and La/Ce

Solid line: Roxana winds
Dashed line: winds at Lambert airport

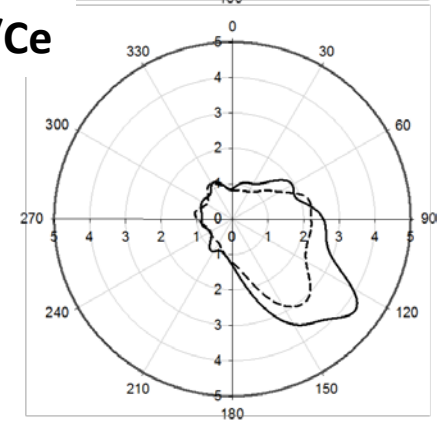
La

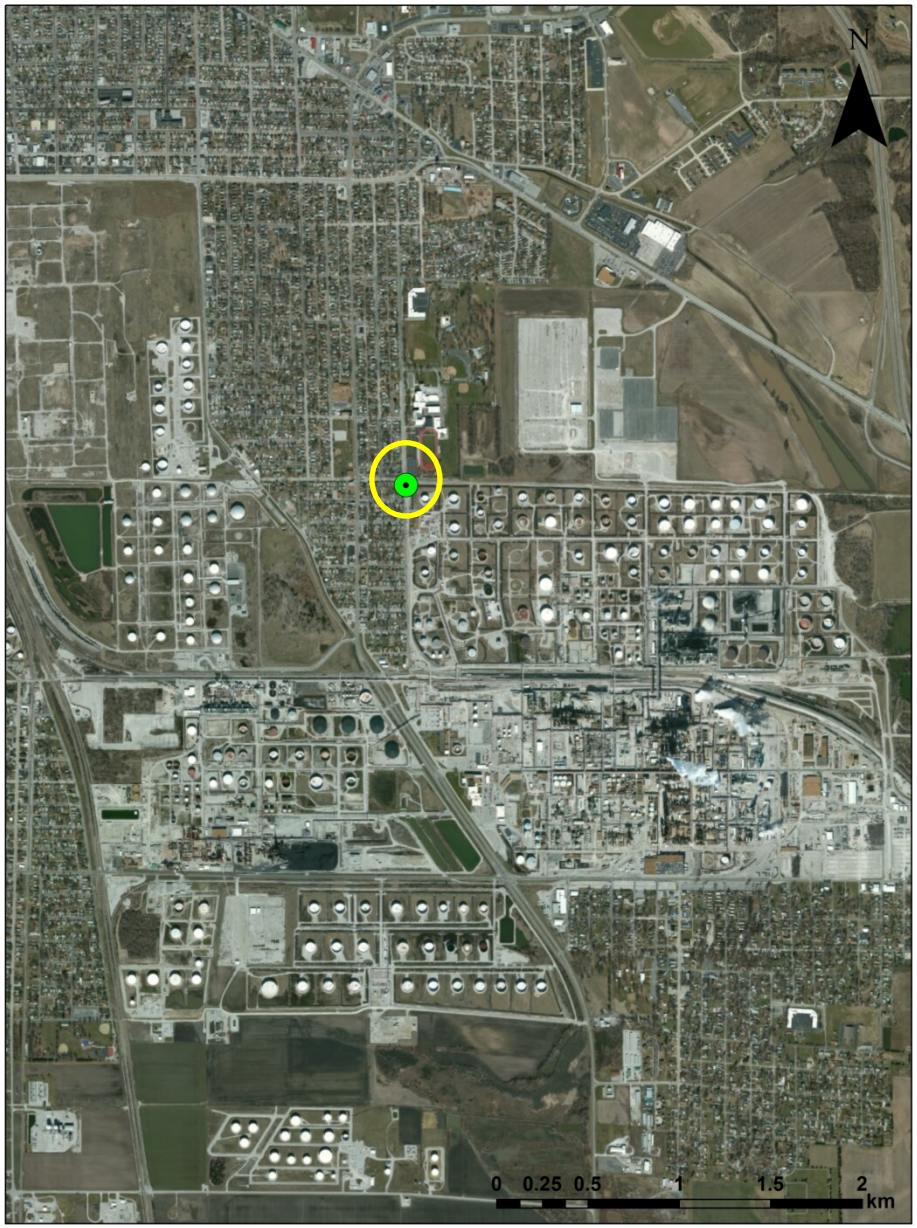


Ce

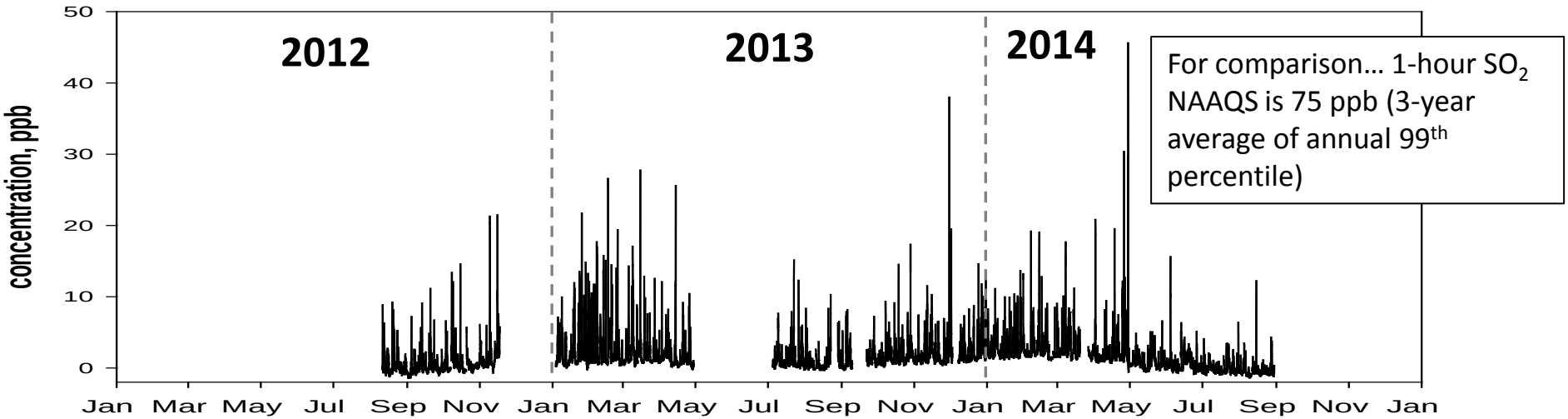


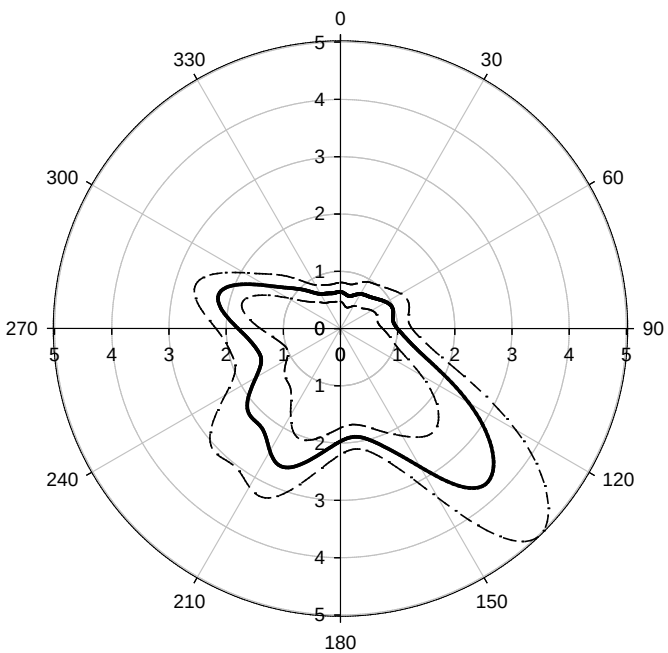
La/Ce





Hourly SO_2 at Roxana





- Nonparametric wind regression analysis indicates contributions from the main operation area (southeast) and the sulfur recovery unit (southwest).

Summary I

Trends for gaseous air toxics compounds…

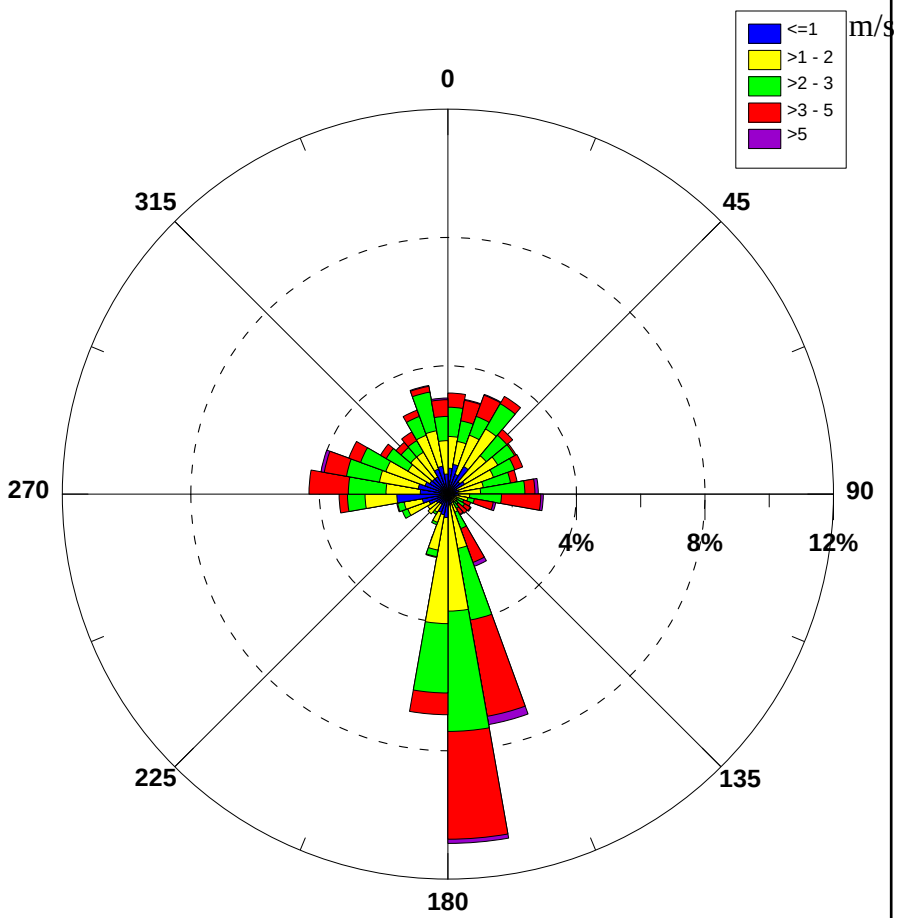
- Modestly elevated concentrations for aromatics and other petroleum related compounds were observed at Roxana compared to Blair Street
- *Assuming Blair concentrations are representative of urban- and larger-scale concentrations*, at Roxana local sources contribute up to 40% of the measured concentration (for those compounds that show higher concentration at Roxana)
- Wind regression results show evidence of aromatics and other petroleum related compounds from the direction of the refinery, not so for other compound classes (aldehydes, halogenated hydrocarbons, etc.)

Summary II

Findings on PM…

- Wind regression shows consistency between high La/Ce ratio periodically observed at Roxana and bearings of refinery unit operations. No exceptional emission events were observed.
- $PM_{2.5}$ shows no significant local source contributions and agrees with the urban and larger-scale contributions.
- SO_2 hourly average concentrations well below the NAAQS standards

Wind rose was created from the meteorological data collected at Roxana on the **sampling days only**



Non parametric wind regression analysis (NWR)

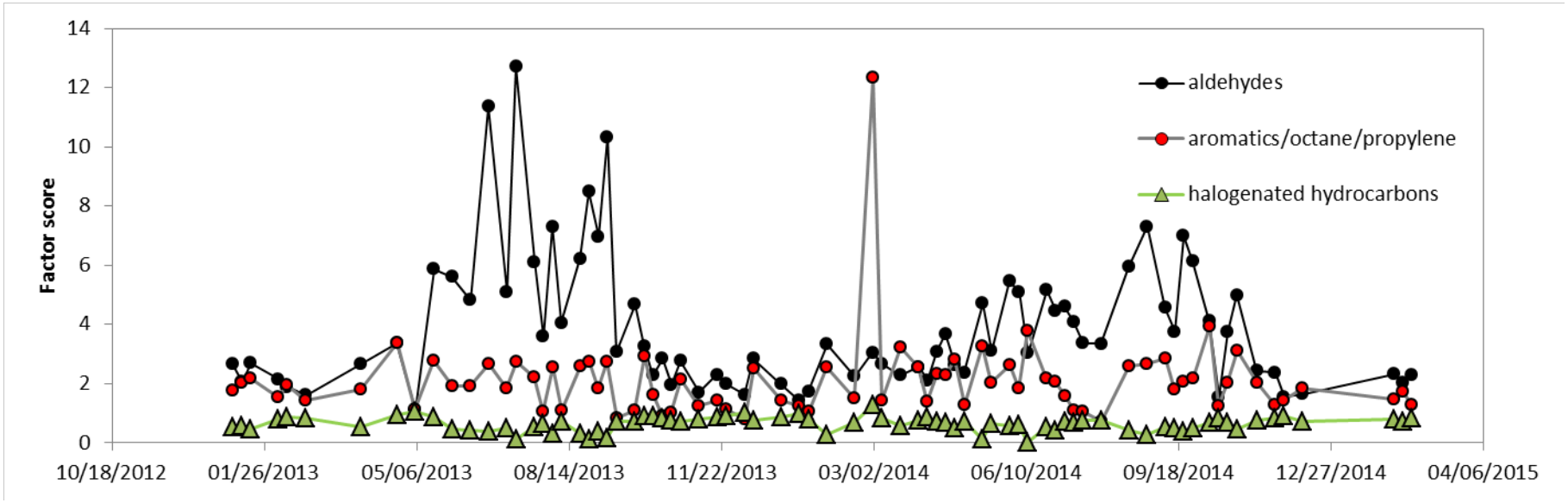
- can identify the bearings of potential emission sources
- calculate the expected concentration at a receptor site based on wind direction data
- use a Gaussian kernel to create a weighted average of concentration for each wind direction window
- Confidence intervals can be used to identify whether the concentration peaks are real for <u>stable emission sources</u>

Principal Component Analysis on Air Toxics Gases at Roxana

Principal component analysis on air toxics data at Roxana suggests four possible categories:

- **aldehydes;**
- **aromatics, n-octane and propylene;**
- **halogentated hydrocarbons; and**
- **mixture**.

Time series of factor scores on four categories identified by PCA

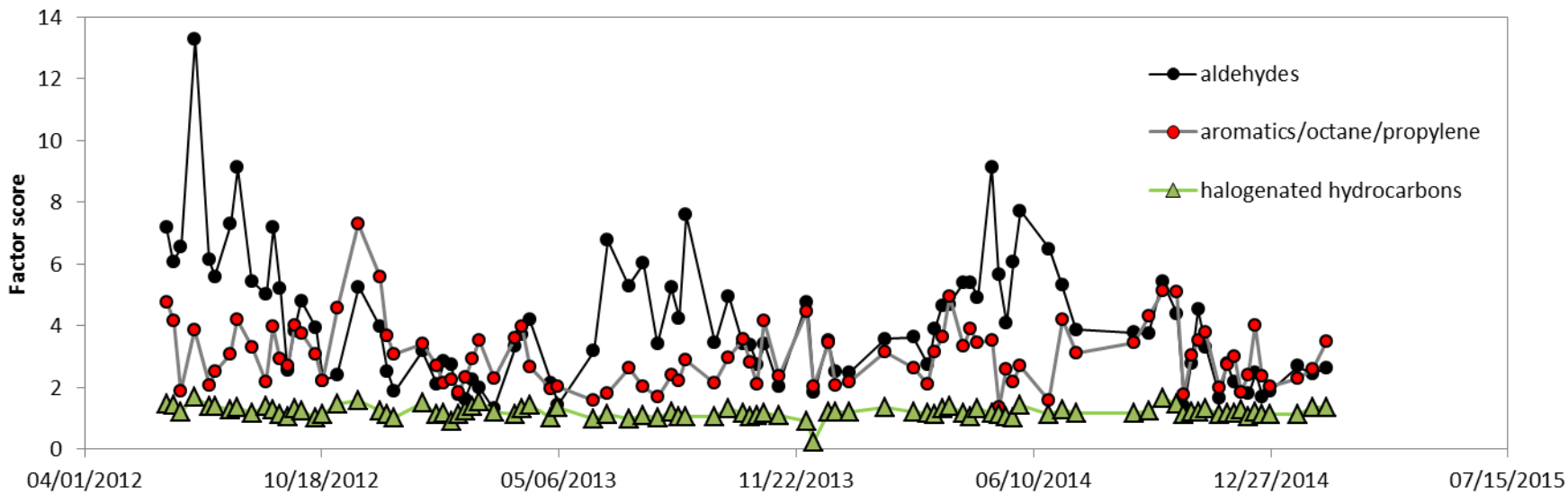


Principal Component Analysis on Air Toxics Gases at Blair Street

Principal component analysis on air toxics data at Blair suggests four possible categories :

- **aldehydes;**
- **aromatics, n-octane and propylene;**
- **halogenated hydrocarbons; and**
- **Mixture.**

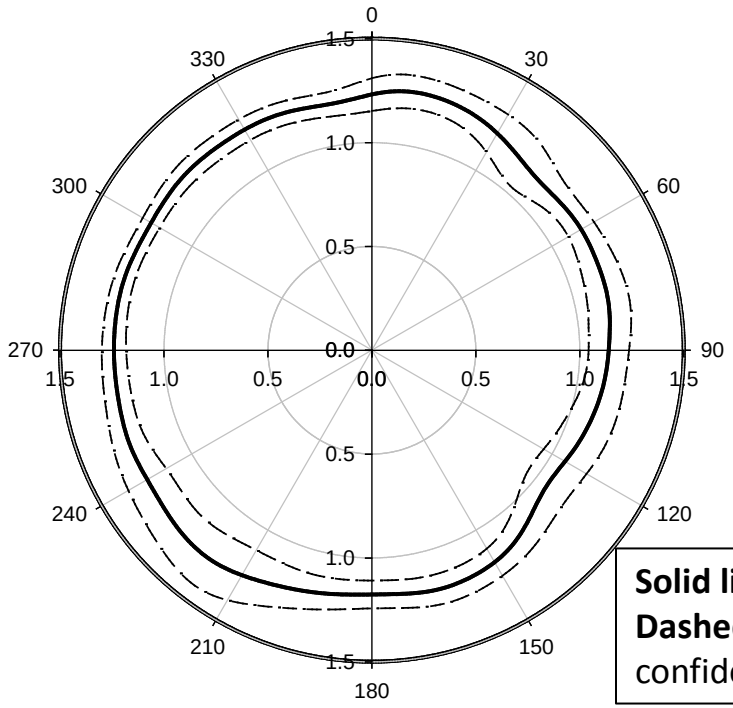
Time series of factor scores on four categories identified by PCA



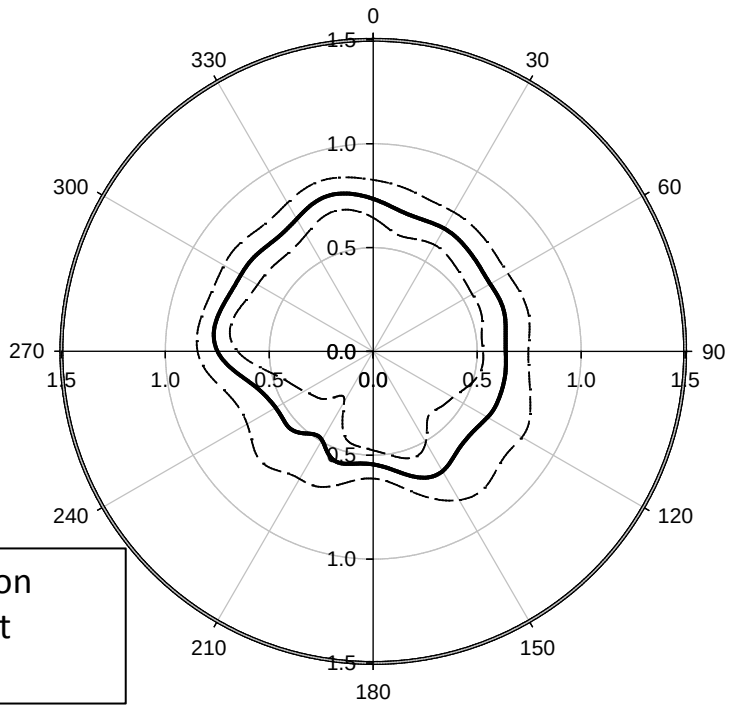
Nonparametric Wind Regression on PCA Scores

halogenated hydrocarbons

Blair



Roxana



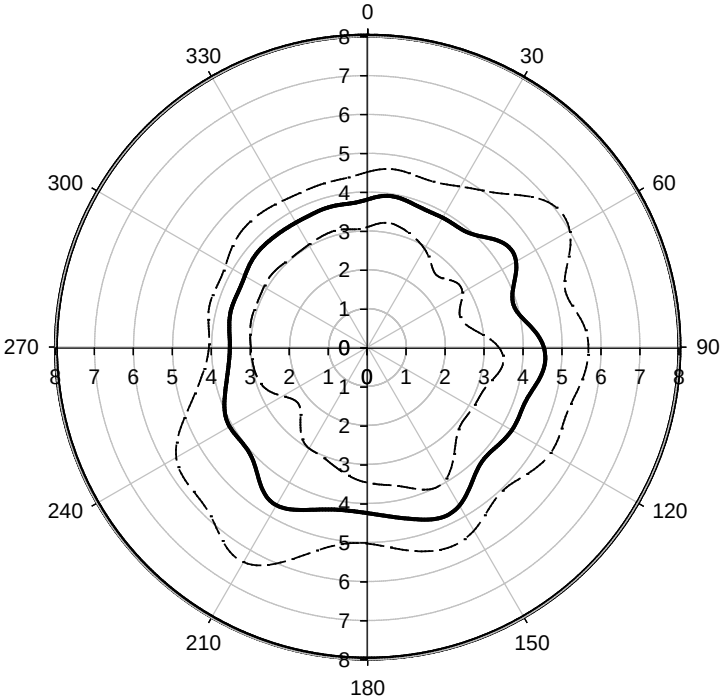
Solid line: expected concentration
Dashed line: 5th and 95th percent confidence intervals

- Similar patterns at Blair and Roxana suggest regional sources dominate
- Lack of directional features support ubiquitous presence of these compounds
- Consistent during the time period of interest

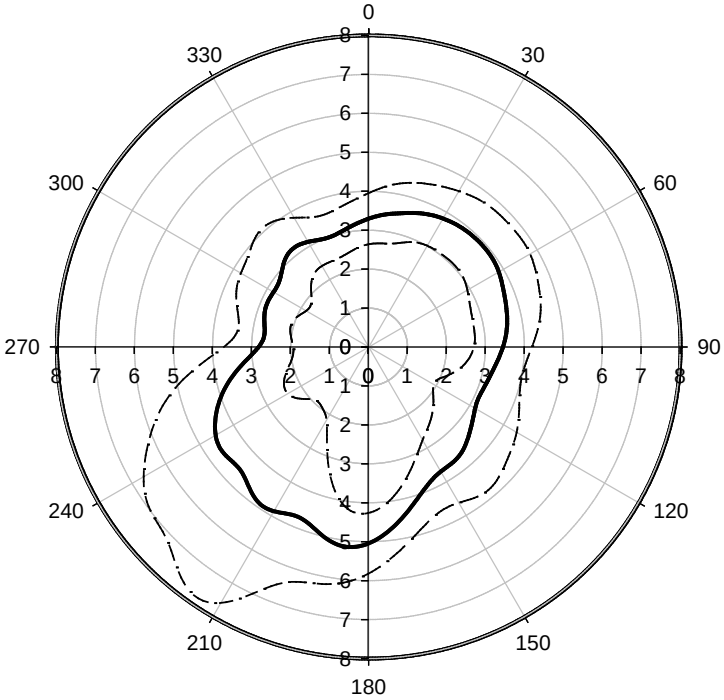
Nonparametric Wind Regression on PCA Scores

aldehydes

Blair



Roxana

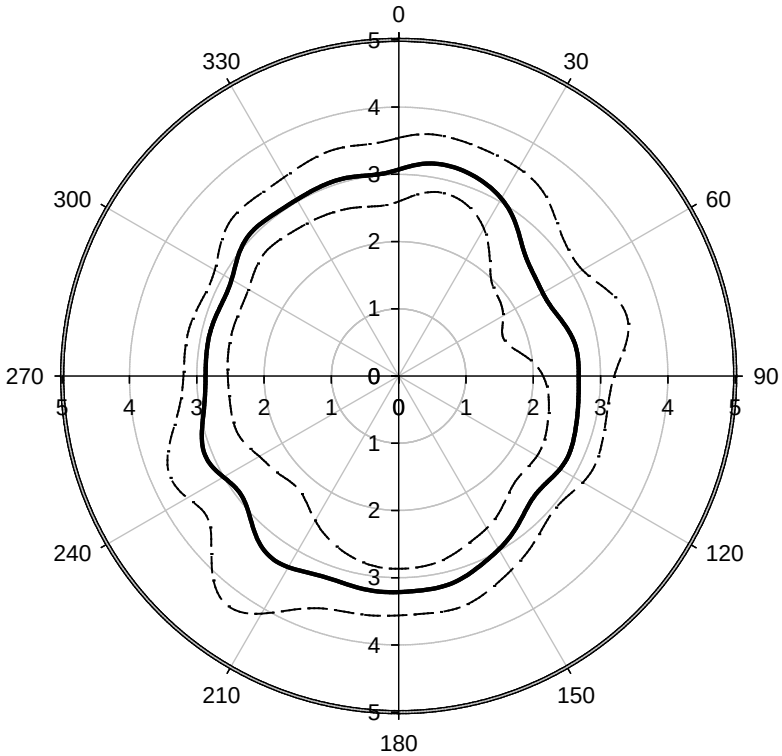


- Pattern shows consistency between the elevated concentrations and southerly wind in the summer

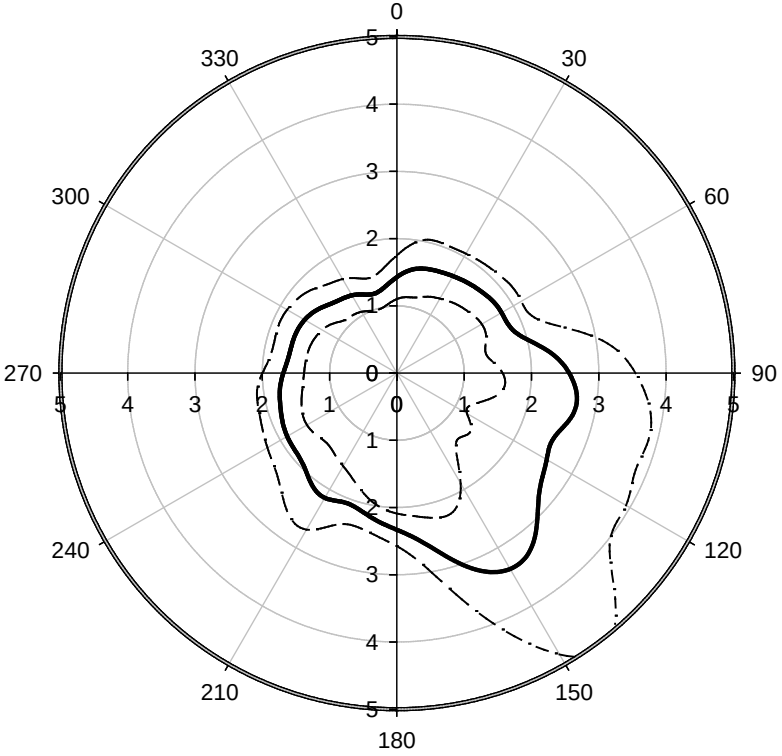
Nonparametric Wind Regression on PCA Scores

aromatics, …

Blair



Roxana



- Patterns consistent with refinery contributions at Roxana.

  No directional pattern observed at Blair Street.