Source Apportionment of VOCs in the Houston, Texas Area

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Introduction

- Frequent ozone exceedences occur in Houston.
- Automated gas chromatographs (auto-GCs) in the Houston area collect hourly VOC data.
  - Data exists for some sites from 1998 to 2001.
  - These data can be used to better understand the spatial and temporal characteristics of VOC precursor concentrations leading to high ozone.

SAM HOUSTON PKWY
LOOP 8
Lake Houston
Aldine
2000
Houston North Wayside C405
HRM-4 Sheldon Rd C604
CROSBY FRWY
2001
Channelview
Channelview
Houston
Houston East C1
HRM Site 3
2001
Baytown C148
2001
HRM-7 Baytown C607
San Jacinto Monument
Baytown
Clinton
98-01
Bayland Park
98-00
98-01
Deer Park
Deer Park C35
Pasadena
La Porte
HRM-8 LaPorte C608
Friendswood
SAM HOUSTON PKWY
LOOP 8
LOOP 8
N
0
10
20 Kilometers
Legend
AGC
AutoGC
THC / Nox
Triggers
Cities
Major roads
Primary road with limited access
Primary road
Secondary and connecting road
Urbanized area
Counties

Key Questions

- Can receptor modeling isolate and identify sources of VOCs using auto-GC data?
- What are the sources of VOCs?
- What are these sources' temporal trends?
- Where are these sources located?
- Is the hydrocarbon composition dominated by mobile or industrial sources?
- What sources have the highest potential for ozone formation?
- What sources are higher in concentration and weight percent on mornings of ozone exceedences?

Positive Matrix Factorization (PMF)

- As a multivariate receptor model, PMF requires the input of data from multiple samples and extracts the source apportionment information from all the sample data simultaneously.
- PMF requires ambient data only – no source profiles.
- Each data point is weighted by specific uncertainty values; this weighting enables the use of data sets that are incomplete due to missing and below-detection data.

Data for PMF

- Hourly data of nearly 60 VOCs available from Clinton Drive for 1998-2001
- Some samples excluded
  - Missing, invalid and suspect samples
  - Samples with abundant compounds reported as 0
  - Samples without TNMOC
- Over 21,000 samples remained for source apportionment
- 39 species used, including Unidentified ppbC

Assumptions/Caveats

- PMF assumes no change in composition between source and receptor.
  - Some VOCs will react away quickly.
  - Clinton Drive is located in an emission-dense area of the Houston Ship Channel, with both industrial and mobile sources nearby, so emissions are generally fresh.
- Uncertainty estimates are important.
- Factors must make physical sense, and should conform to conceptual model of emissions.

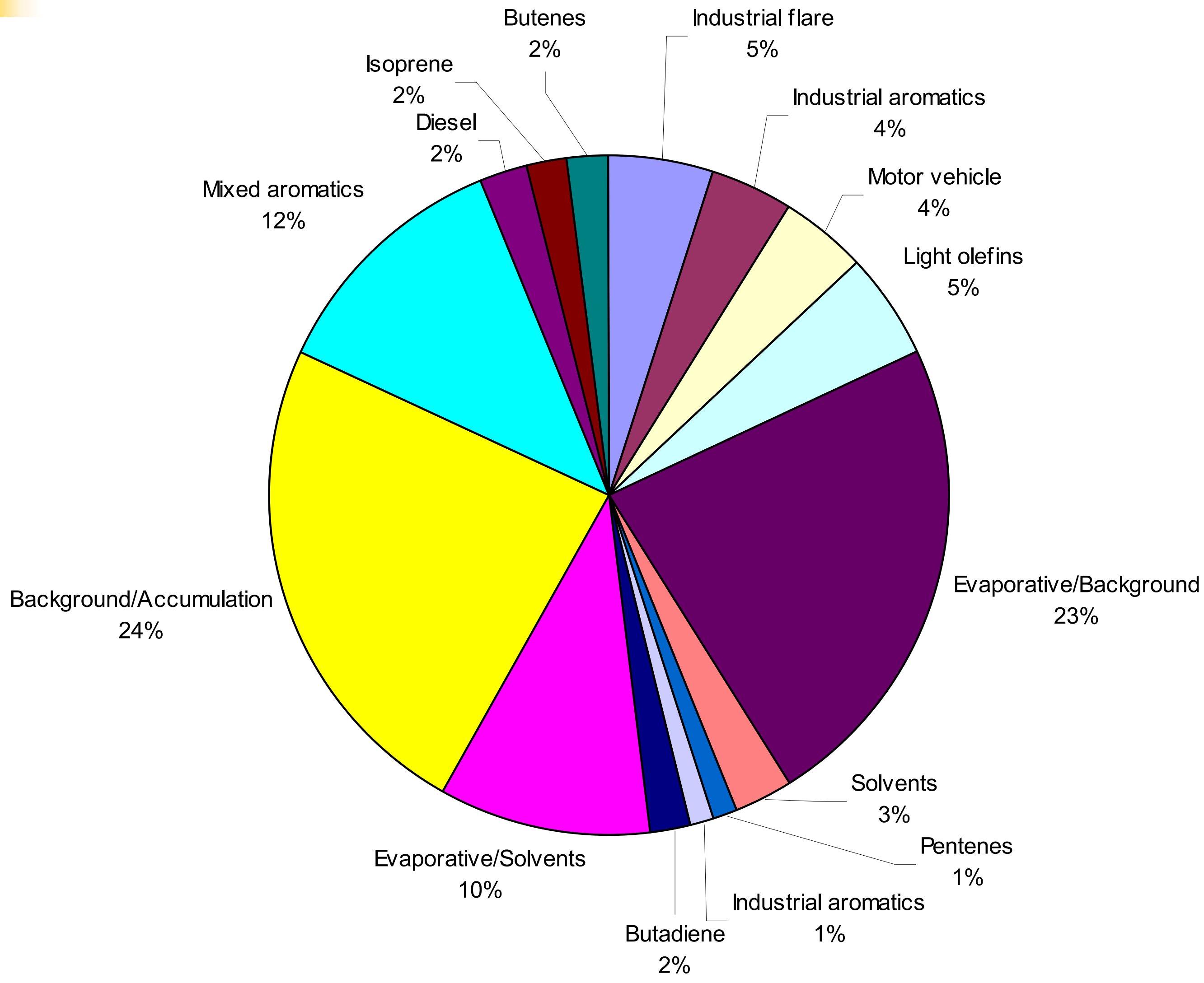
Preliminary Analysis Results

- High concentrations of any VOC can occur during any time of day, week, month, and year.
- Industrial activities appear to be significant to VOC composition.
- VOC concentration and composition depend largely on wind direction.
  - Multiple strong sources in a given direction
  - Suggests a high number of factors may be needed to best characterize emissions

Summary of PMF Results

- 15 factors identified
- Good reconstruction of mass ($r^2 = 0.91$)
- Rotation used ($F_{Peak} = 0.2$)
- Residuals within +/- 3 standard deviations
- No feasible multiple solutions

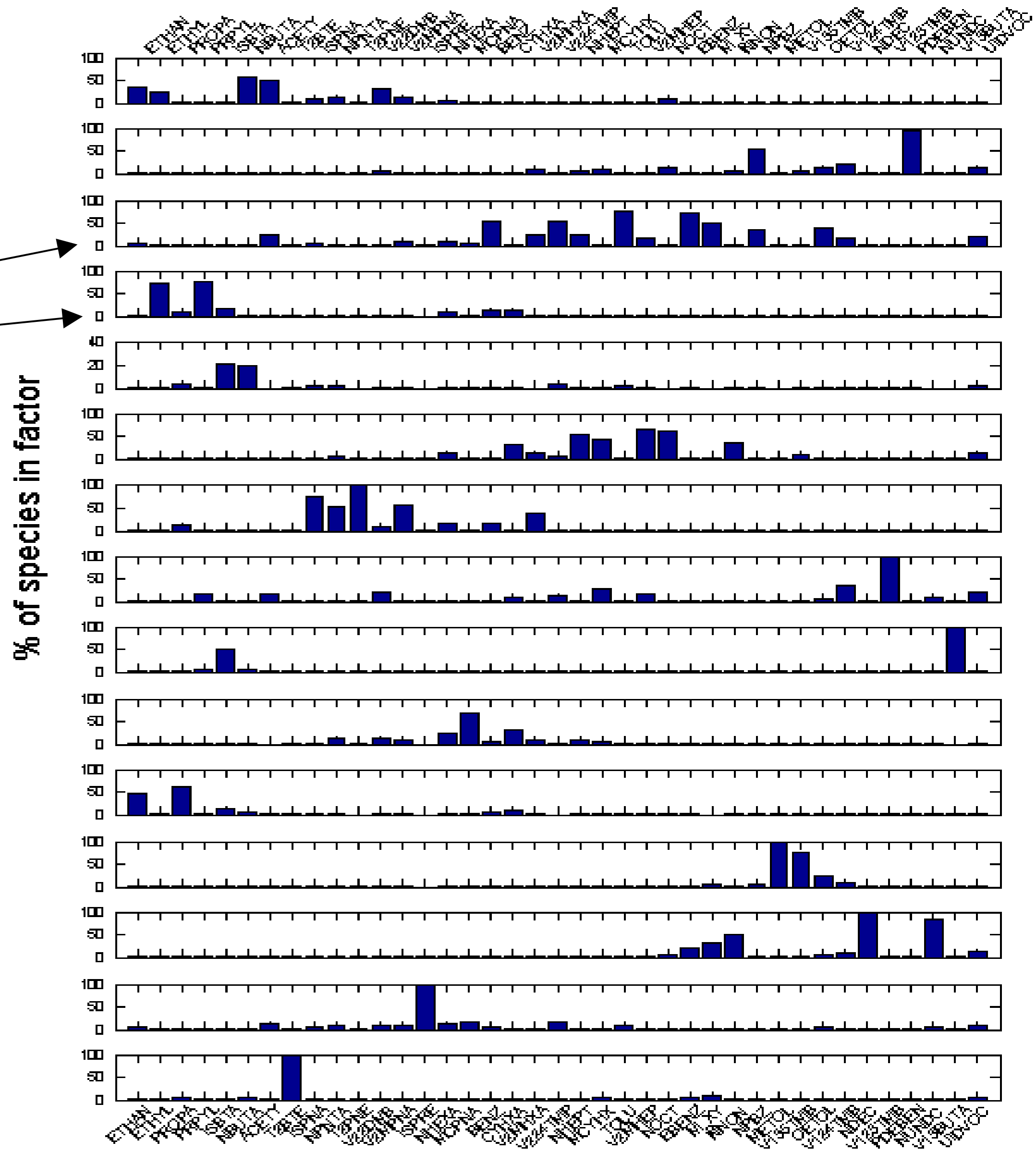
Average VOC Composition



Details of Sources

Factor	Source ID	Significant Species	Wind Direction
1	Industrial flares	Ethane, ethene, n-butane acetylene	E, NW
2	Industrial aromatic hydrocarbons #1	UID, diethylbenzene	S, SW
3	Motor vehicle	Benzene, toluene, acetylene, xylenes	SW, W, NW
4	Industrial light olefins	Ethene, propene	E, S
5	Evaporative emissions/background	Butanes	E, S
6	Solvent use	C6-C9 paraffins	SSE
7	Industrial pentene source	Pentenes	S, ESE
8	Industrial aromatic hydrocarbons #2	UID, trimethylbenzenes	N, E
9	Butadiene sources	1,3-butadiene	S
10	Evaporative emissions/solvents	C5-C7 paraffins	E, SE, S
11	Accumulated emissions and natural gas	Ethane, propane	E, N
12	Heavy aromatic sources	Ethyltoluene	E, N
13	Diesel	C10-C11 alkanes, xylenes	W, N
14	Biogenic with outliers from industry	Isoprene	W, E, S
15	Industrial butene source	Butenes	S

Factor Profiles

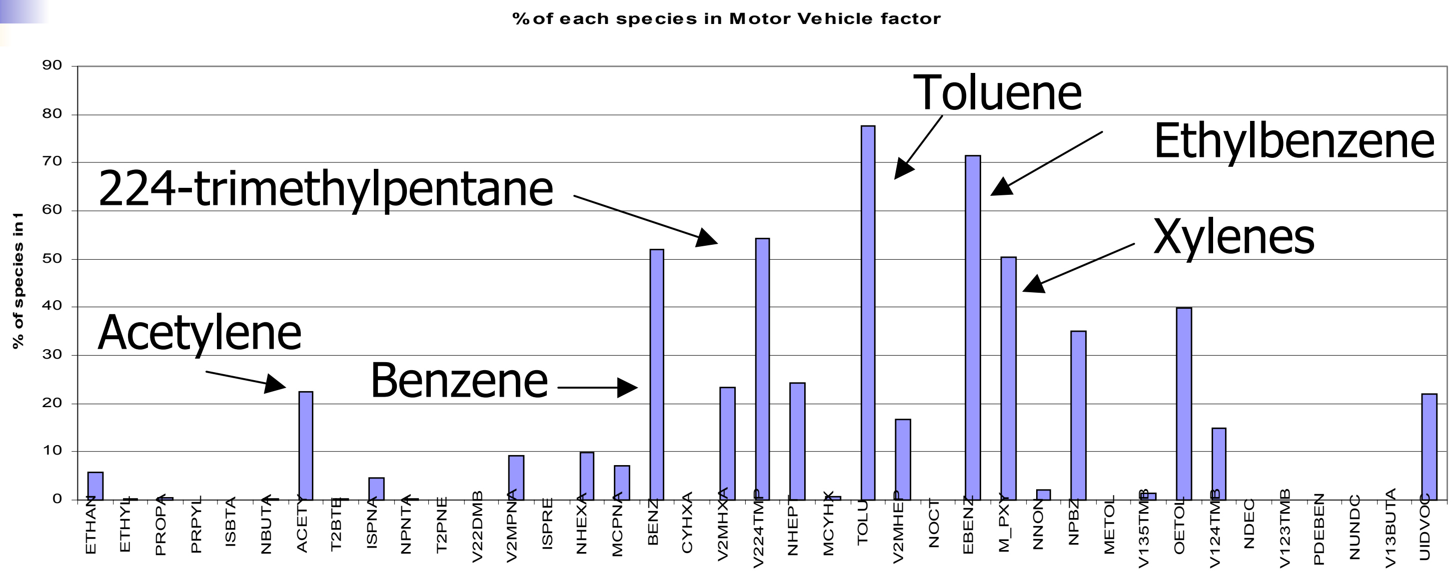


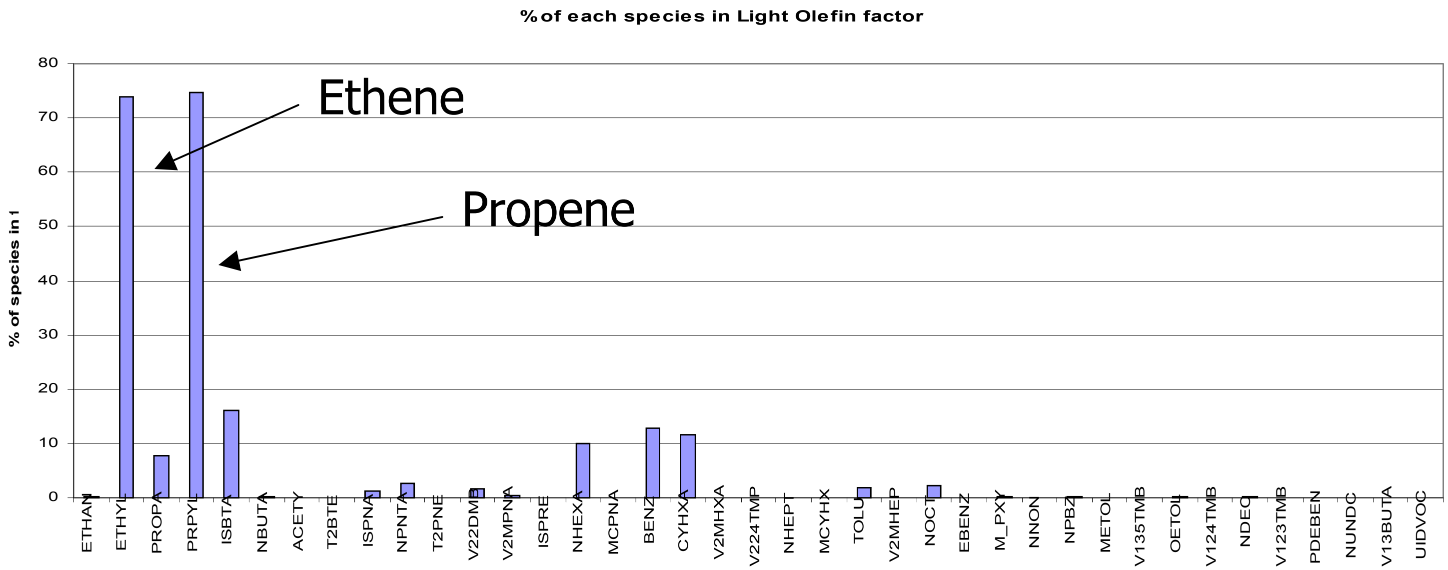
Motor Vehicle

Ethene/Propene

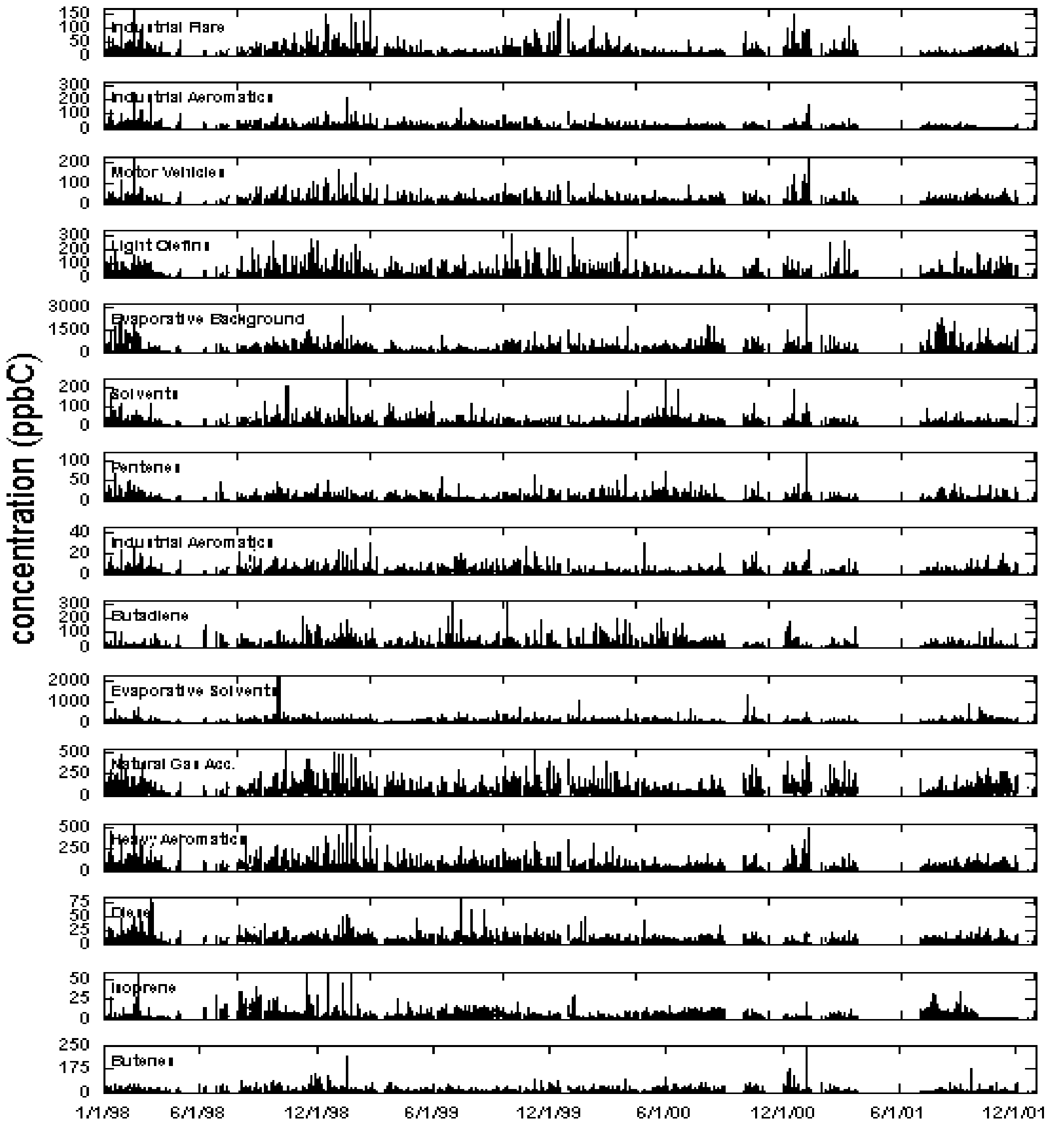
Expanded on next slide

Example Profiles



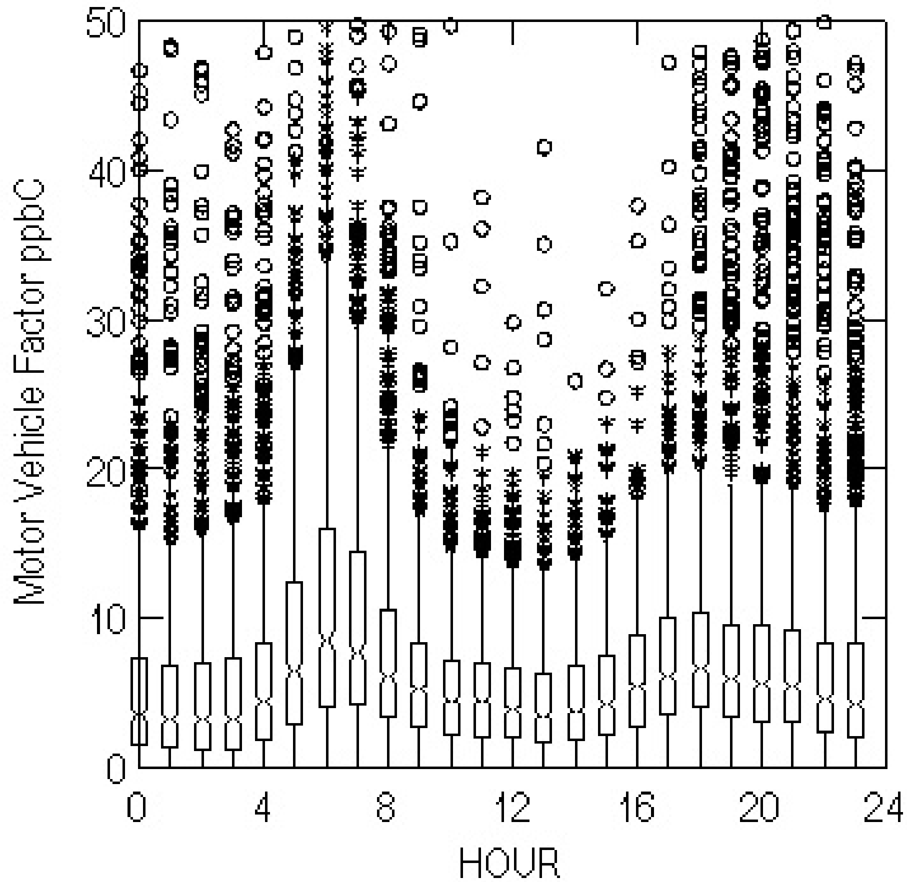


Concentrations of Chemical Species



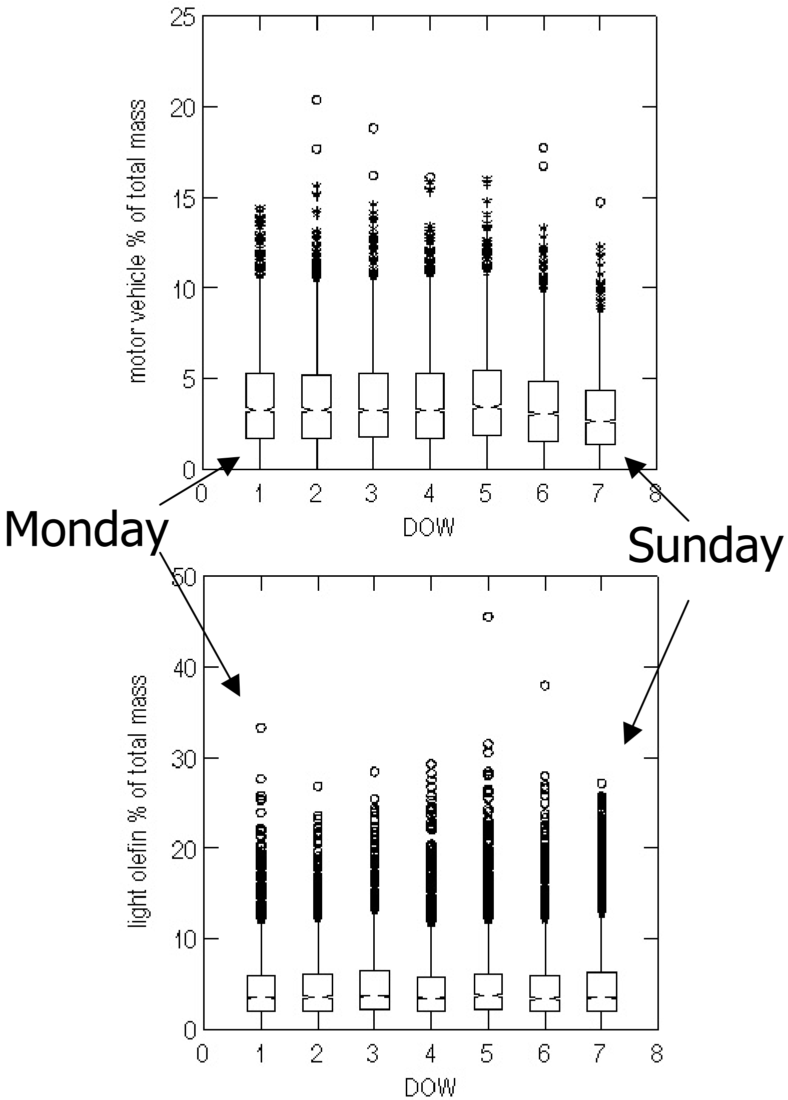
Example of Diurnal Variations

- Overall time series of hourly observations through four years were difficult to analyze.
- Sources were statistically evaluated by time of day, etc.
- Motor vehicle source shows typical diurnal pattern, confirms identification.
- Sources identified as industrial showed no pattern or nighttime accumulation.



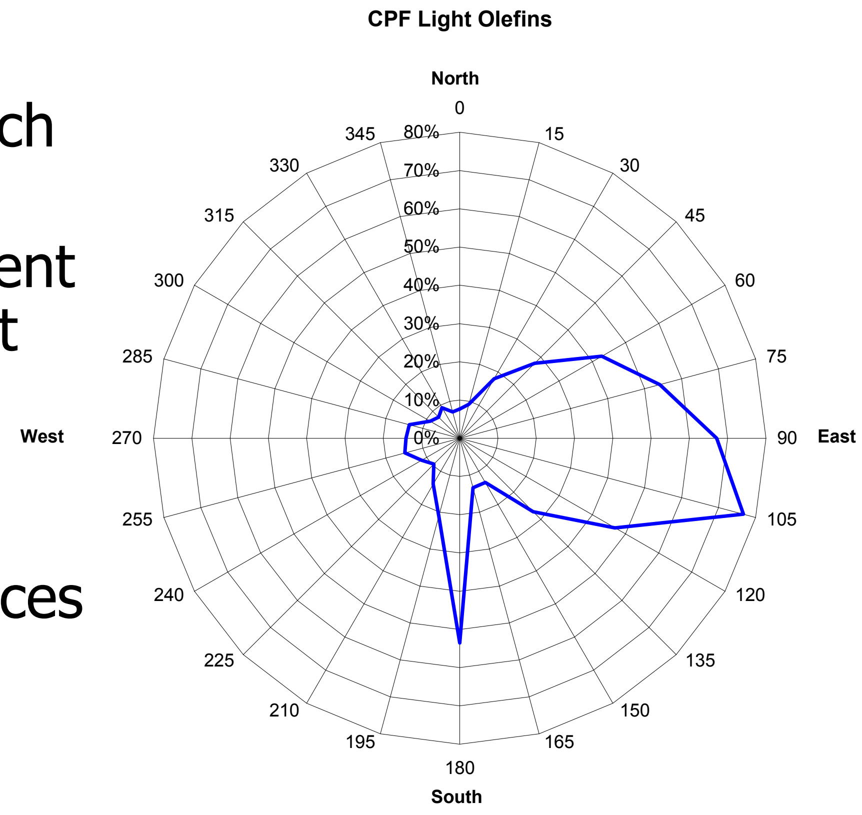
Day-of-week Variations

- Mobile source factors decrease on weekends.
- Light olefin (likely industrial) shows little difference.
- This analysis supports identification of mobile and industrial signatures.



Conditional Probability Function

- CPF[1] was used to identify wind directions where the top 25th percentile concentrations of each source originated.
- Light olefin source was prominent from east and south, consistent with emission inventories in the Houston Ship Channel.
- Other industrial sources show similar results, pointing to sources in the Ship Channel.
- Mobile source factors were highest from W and S, the direction of freeways.

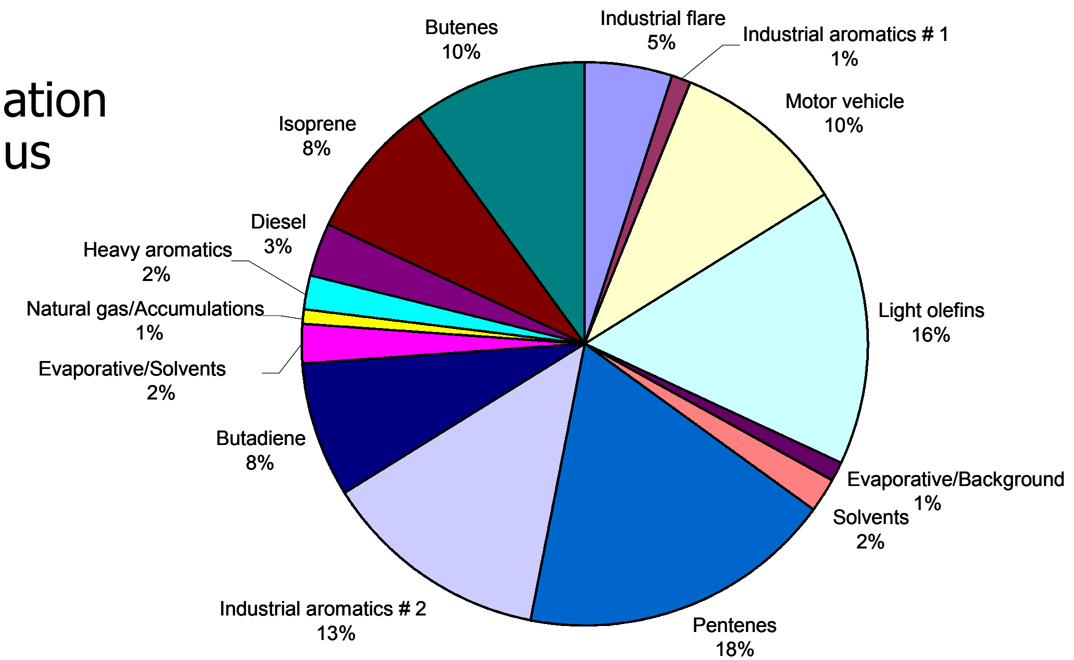


[1] Ashbaugh et al., 1985; Kim et al., 2002

Sources Scaled by MIR Reactivity

- Maximum Incremental Reactivity (MIR)[2] scale was used to assess ozone formation potential of each source.
  - MIR is based on ozone formation potential of hydrocarbons plus their reaction products and is dependent on air mass composition.
- No single source or VOC dominated ozone formation potential.
- Ethene/propene, industrial aromatic, and motor vehicle sources had highest average formation potential.

[2]Carter, 1994; 2001



Source Strength on Ozone Episodes

- Mornings of ozone episodes (O_3 > 125 ppb) were further investigated.
  - Higher concentrations of a source on episode mornings would suggest it is more important to ozone formation.
- Six factors' weight percents were significantly higher (95% CL) on ozone episode days.
  - Industrial aromatics, motor vehicle, heavy aromatics
  - Are these aromatic compounds responsible for high ozone or do they provide a small amount of extra ozone on episode days to add to the high baseline?
  - Are the more reactive species already reacted away before reaching the monitors on episode days?

Conclusions

- PMF identified sources of VOCs from auto-GC data that were consistent with current understanding of VOC emissions in the Houston Ship Channel area.
  - Industrial sources were prominent, showed little weekday-weekend differences, and had highest concentrations in the direction of major sources in the Ship Channel.
  - Mobile sources were identified, decreased significantly on weekends, and were associated with winds in the direction of major freeways.
- Light olefin, industrial aromatic, and motor vehicle sources had the highest ozone formation potential.
- Six factors were higher on mornings of ozone exceedences, though were not the most conducive to ozone formation.

Future Work

- Compare results to other models such as CMB
- Utilize nighttime-only data so reactivity impacts are minimized
- Utilize summer-only data to better characterize sources during ozone exceedences
- Apply PMF to other sites in Houston
- Triangulate sources between sites to see if wind directions match