Reconciliation of VOC and NO_x Emissions Estimates with Ambient Data in the Houston, Texas Region

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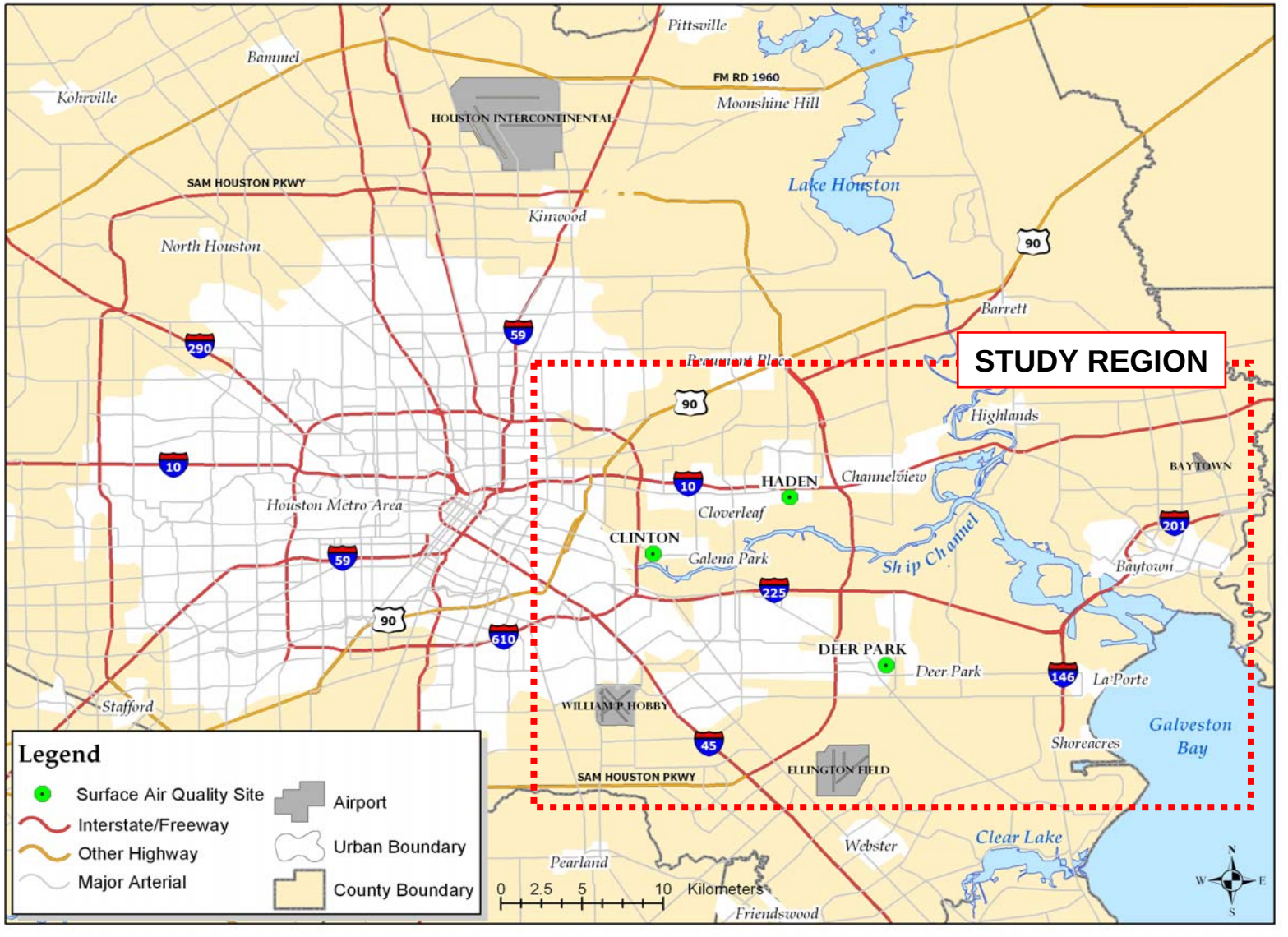
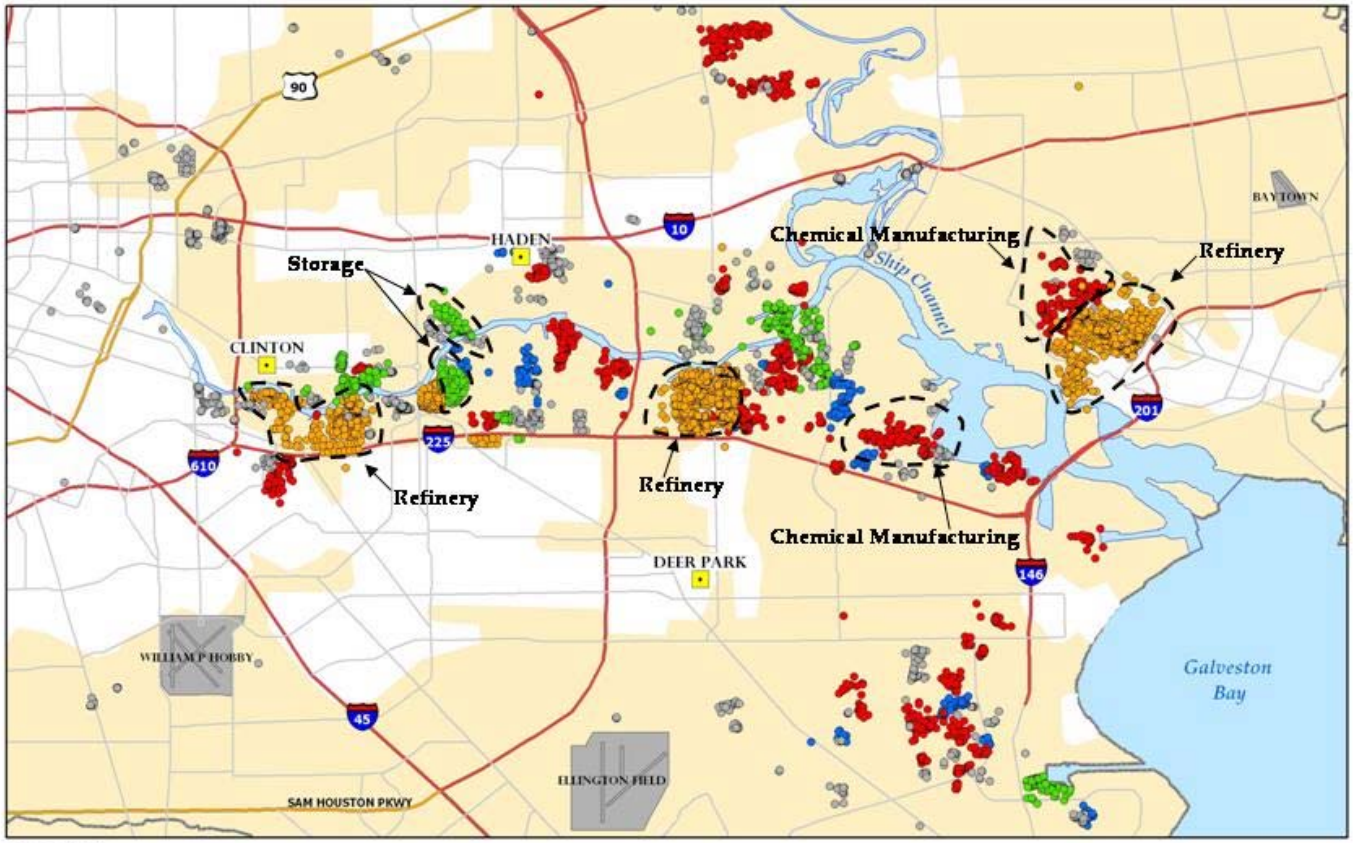
Introduction

- Houston Ship Channel (HSC) is a heavily industrialized area influenced by large emissions sources: petroleum refineries and chemical manufacturing facilities
- VOC emissions from these sources can be difficult to quantify (i.e., flares, fugitive)
- Area and mobile sources are also significant

Map of HSC Region



Point Source Clusters in the HSC Region



Legend

- Surface Air Quality Site

SIC Code

- 2869: Manufacturing industrial organic chemicals
- 2911: Producing gasoline, kerosene, etc, through distillation and processing of crude oil
- 4226: Warehousing and storage of products such as household goods, automobiles, etc.
- 2821: Manufacturing synthetic resins, plastics materials,etc.
- Other

0 2.5 5 Kilometers

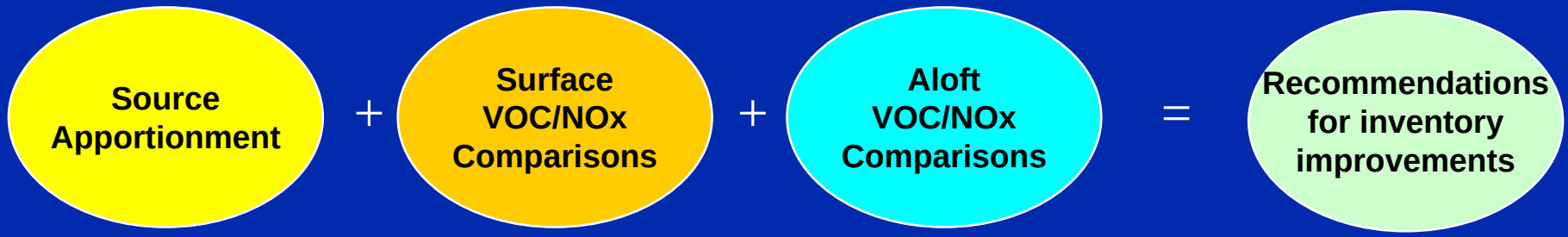
N W E S

Study Objectives

- Explore innovative methods to assess the spatial, temporal, and chemical speciation of the 2000 HSC emission inventory
- Focus on volatile organic compounds (VOC) most likely to contribute to ozone formation (most abundant reactive species): acetaldehyde; formaldehyde; ethylene; propylene; 1,3-butadiene; all butenes (butylenes); isoprene; all pentenes; toluene; all xylenes; all ethyltoluenes; and all trimethylbenzenes
- Make recommendations on possible improvements to the point source inventory

Overview of Approach

- Multi-task effort utilizing surface *and* aircraft data for 2000 and 2001 in the Houston-Galveston area (HGA)
- Three-pronged approach:



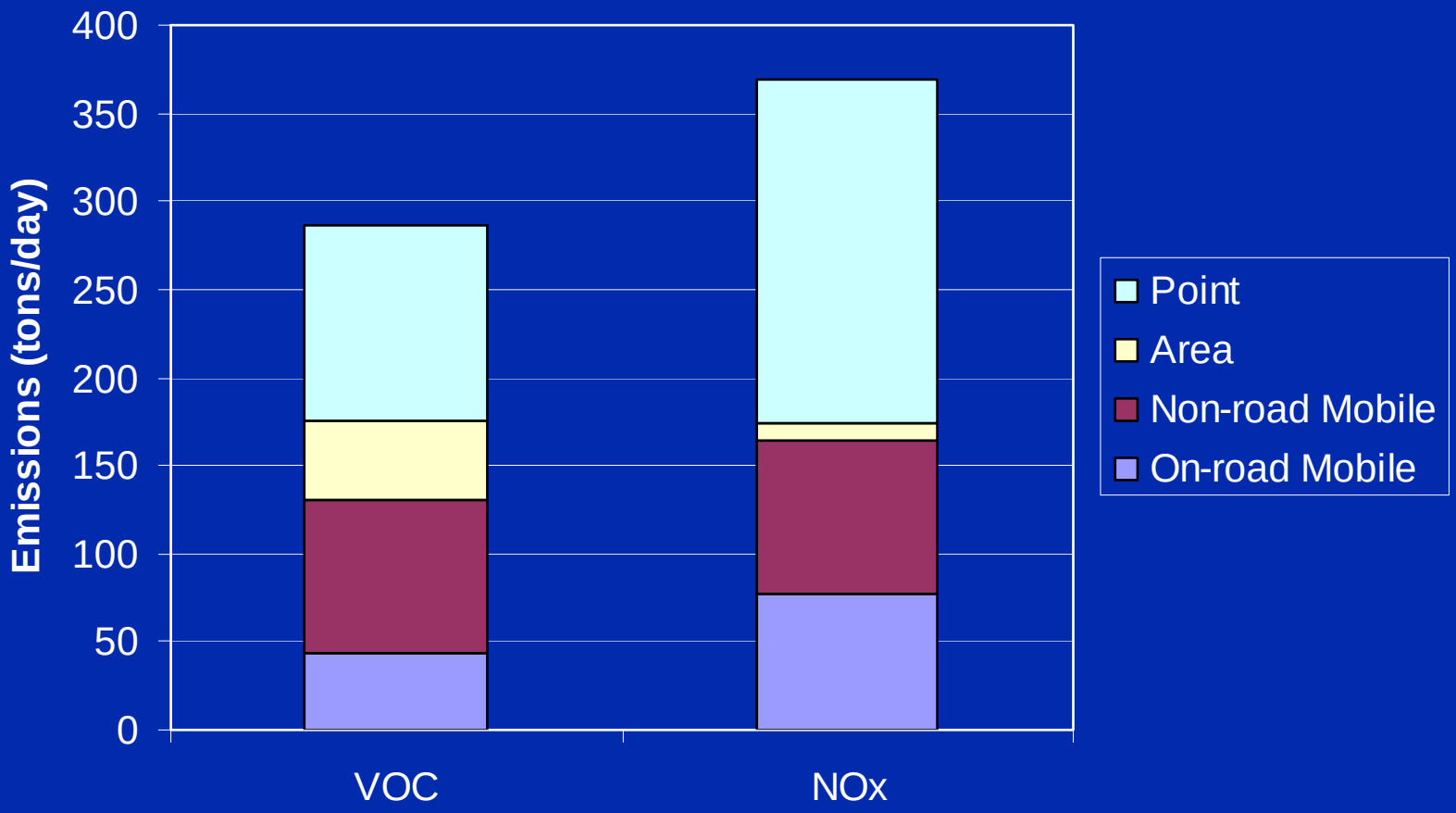
- Data requirements:
  - hourly, gridded, and speciated hydrocarbon and NO_x emission inventory
  - speciated surface hydrocarbon and NO_x data
  - speciated aloft hydrocarbon and NO_x data
  - wind speed and direction data

What Did We Find?

- Total VOC/NO_x ratios underestimated by factors of 2-10
- Most under-representation appears to be from the industrial segment of the inventory
- Olefins and aromatics appear to be underestimated

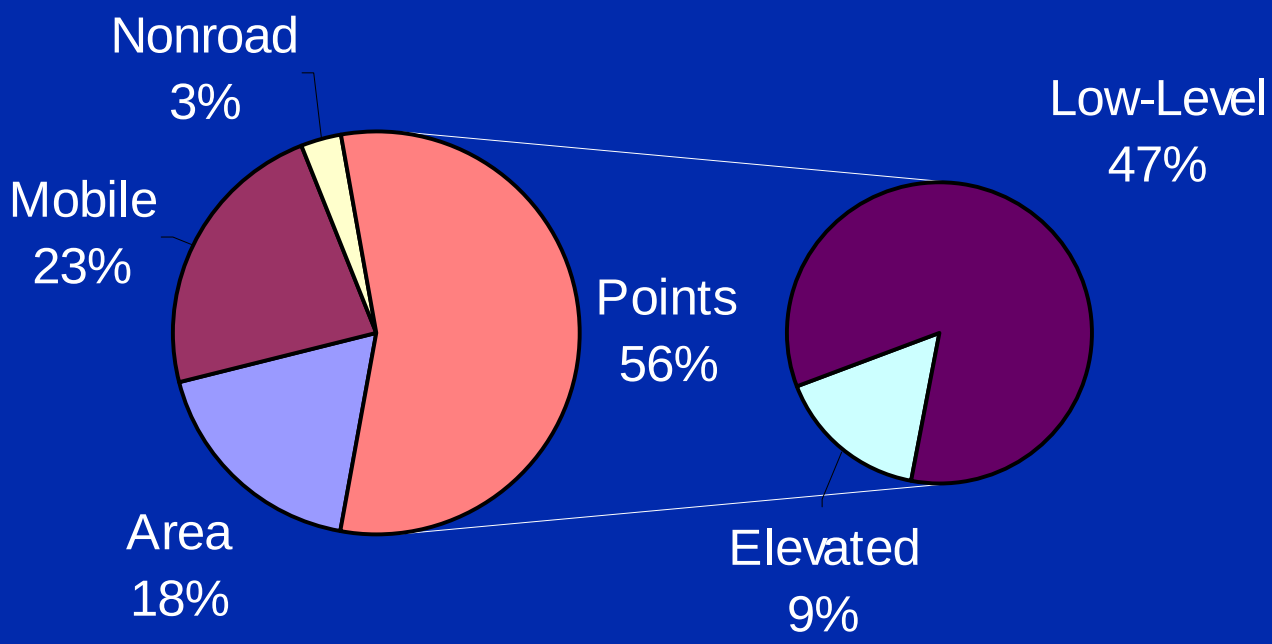
HGA Emission Inventory Summary

Emissions by source category for the HGA region for August 29, 2000



HGA Emission Inventory Summary

Distribution of VOC sources in the region around Clinton Drive for 0500-0600 CST



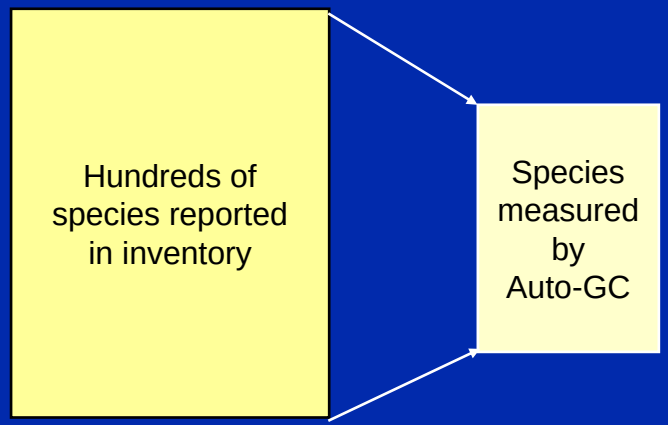
~ 500 km^2 region centered at monitoring site

Top-Down Reconciliation Method (1 of 2)

- Ambient Data
  - Quality-assurance
  - Ambient data segregated by time period to include data for 0500-0900 CDT sampling periods for weekdays (to minimize photochemical reactions and focus on fresh emissions)
- Meteorological Data
  - Determines average wind speeds and predominant wind directions for 0500-0900 CST period
  - Determines the spatial extent of the ratio analyses
  - Identifies the sources that are most likely to impact the ambient monitor

Top-Down Reconciliation Method (2 of 2)

- Emissions Inventory
  - Chemical species in the emission inventory were matched to the ambient data

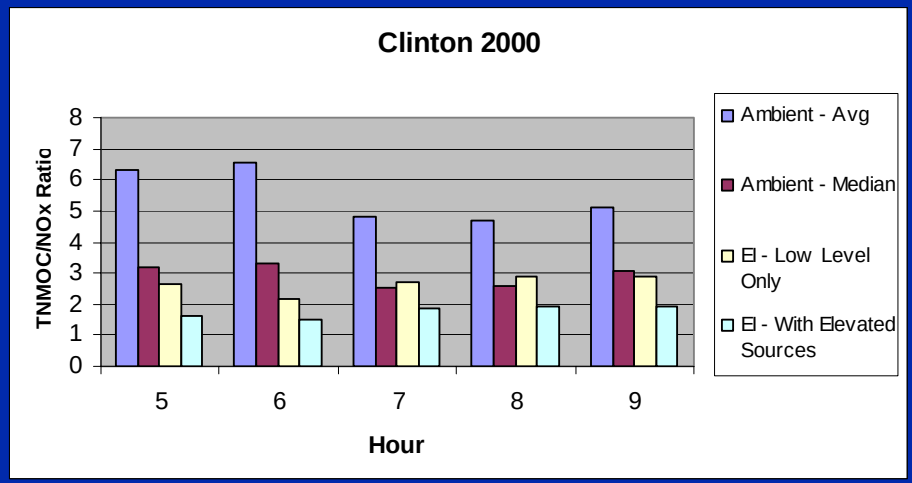


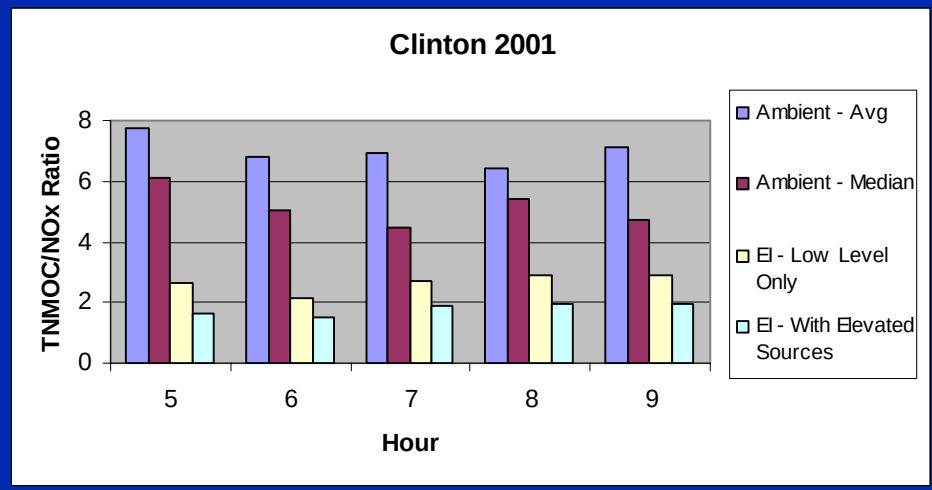
= 60 – 70% mass

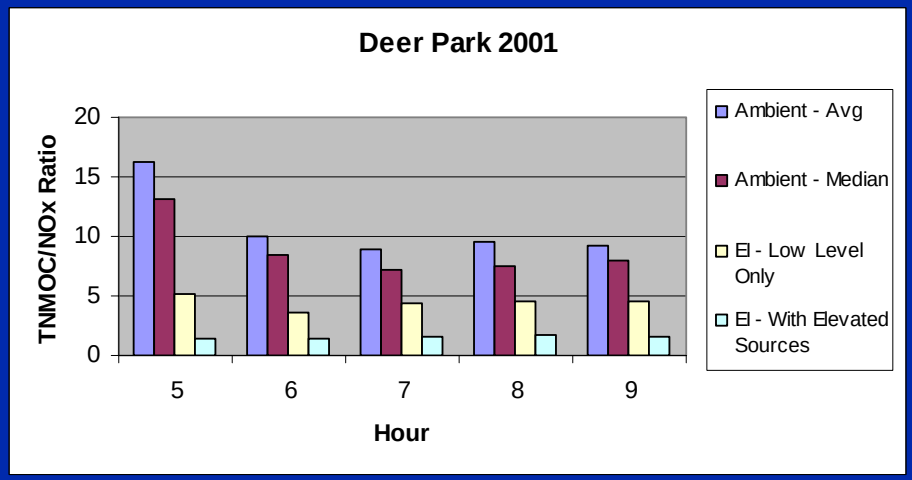
  - Emissions were converted from a mass to a molar basis to compare to the ambient data reported in ppbC

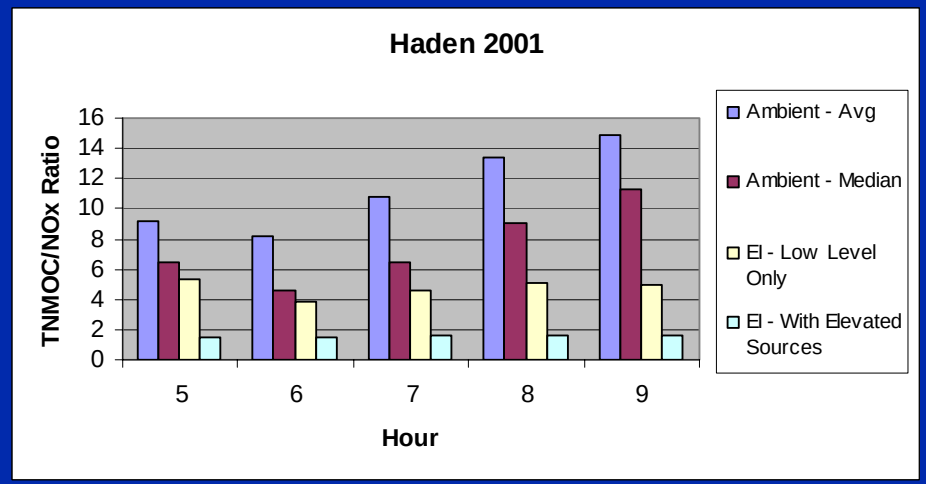
Emission Inventory – Ambient Comparison

Hourly $TNMOC/NO_x$ ratios by site



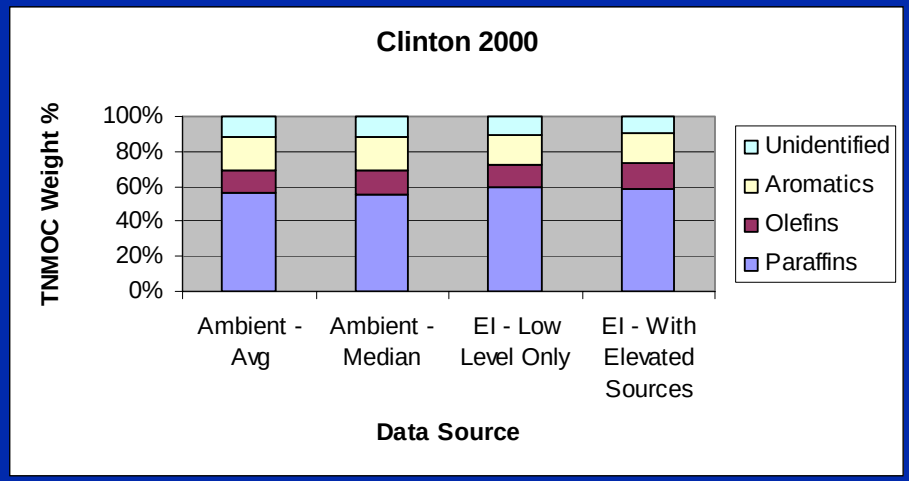


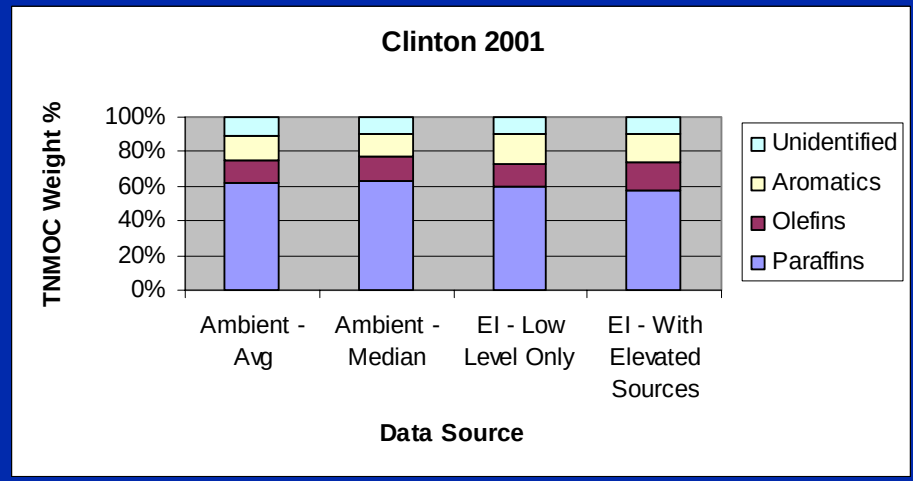


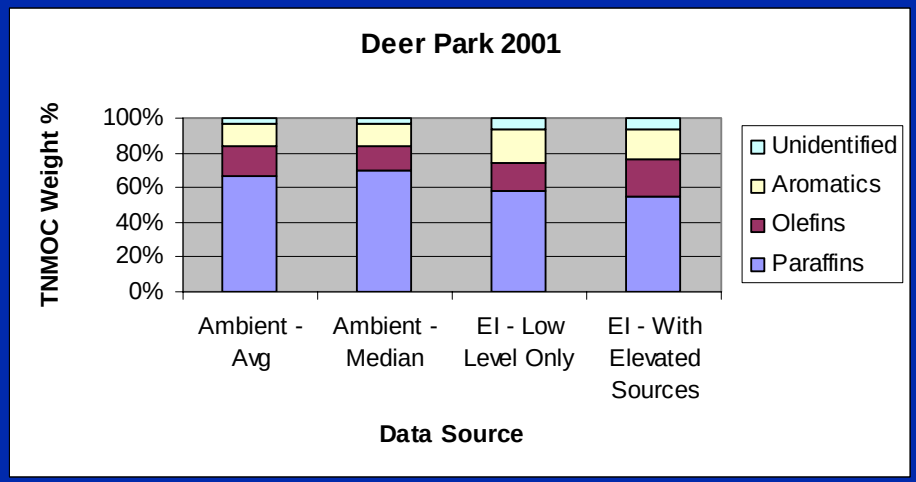


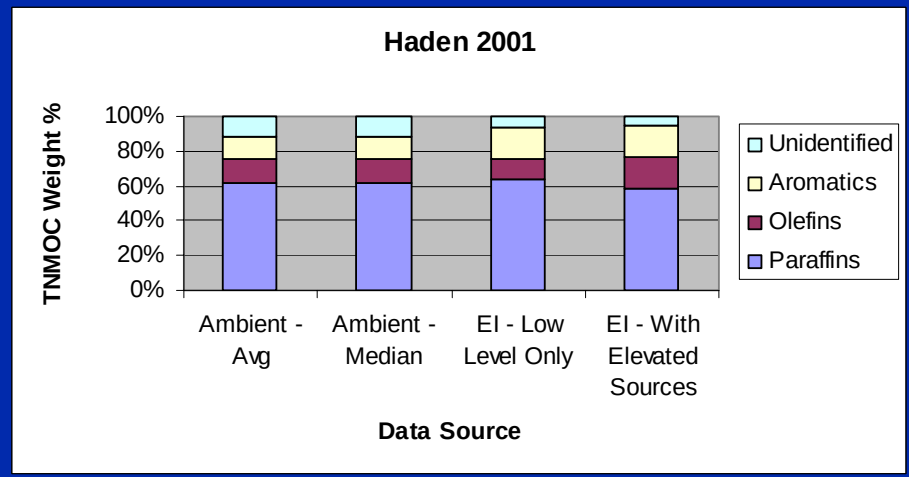
Emission Inventory – Ambient Comparison

Relative composition of species groups by site



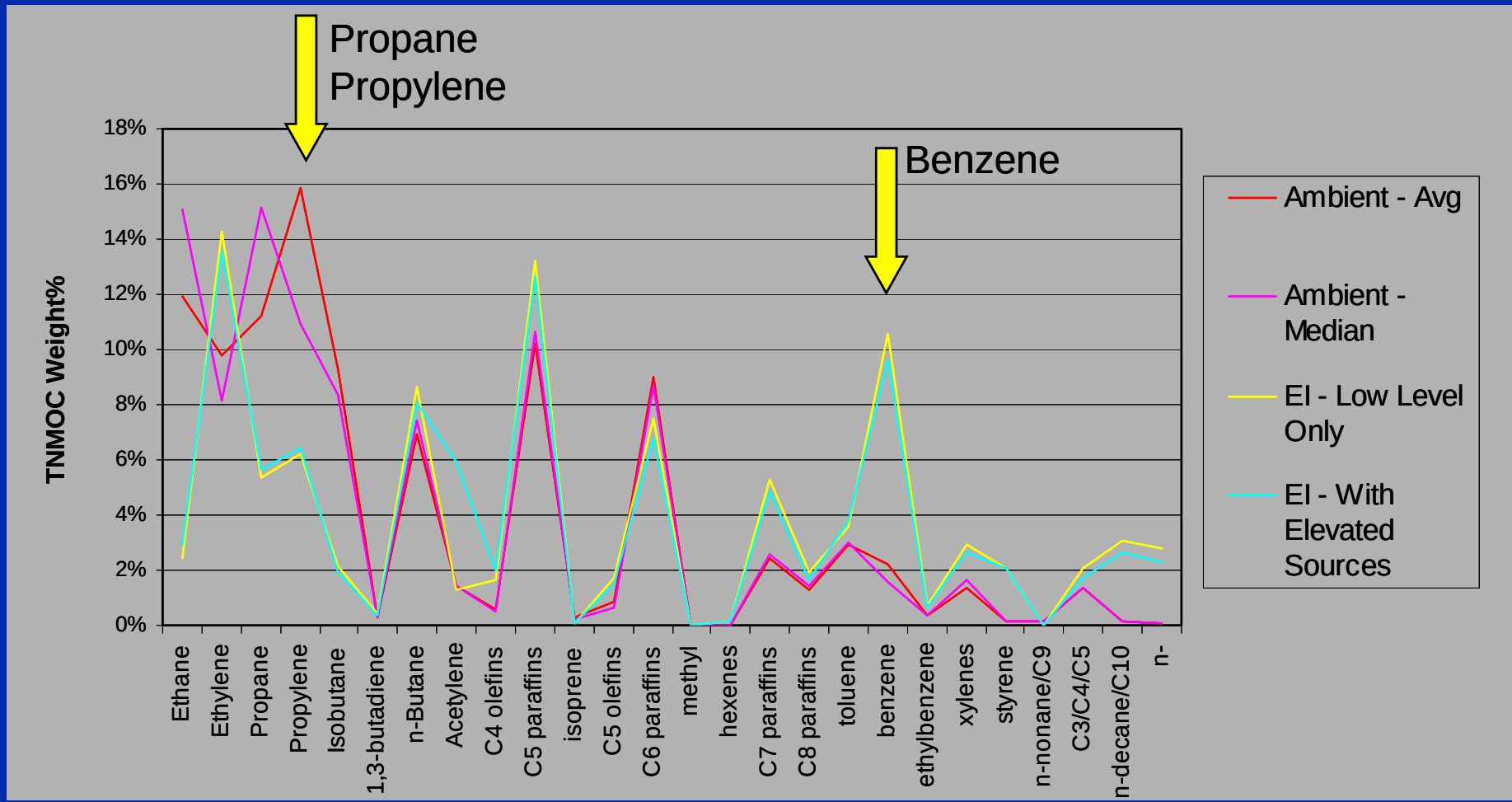






Emission Inventory – Ambient Comparison

Relative species composition for Deer Park (northeast)



Source Apportionment Method

Source apportionment gives another view of ambient data to compare to inventory:

- How are the mix of source types in the ambient data apportioned compared to the inventory?
- What is the magnitude of each source type in ambient data compared to inventory?
- What species in which source type appear to be under- or overestimated in the inventory?
- Can significant sources that are not in inventory be identified and quantified?

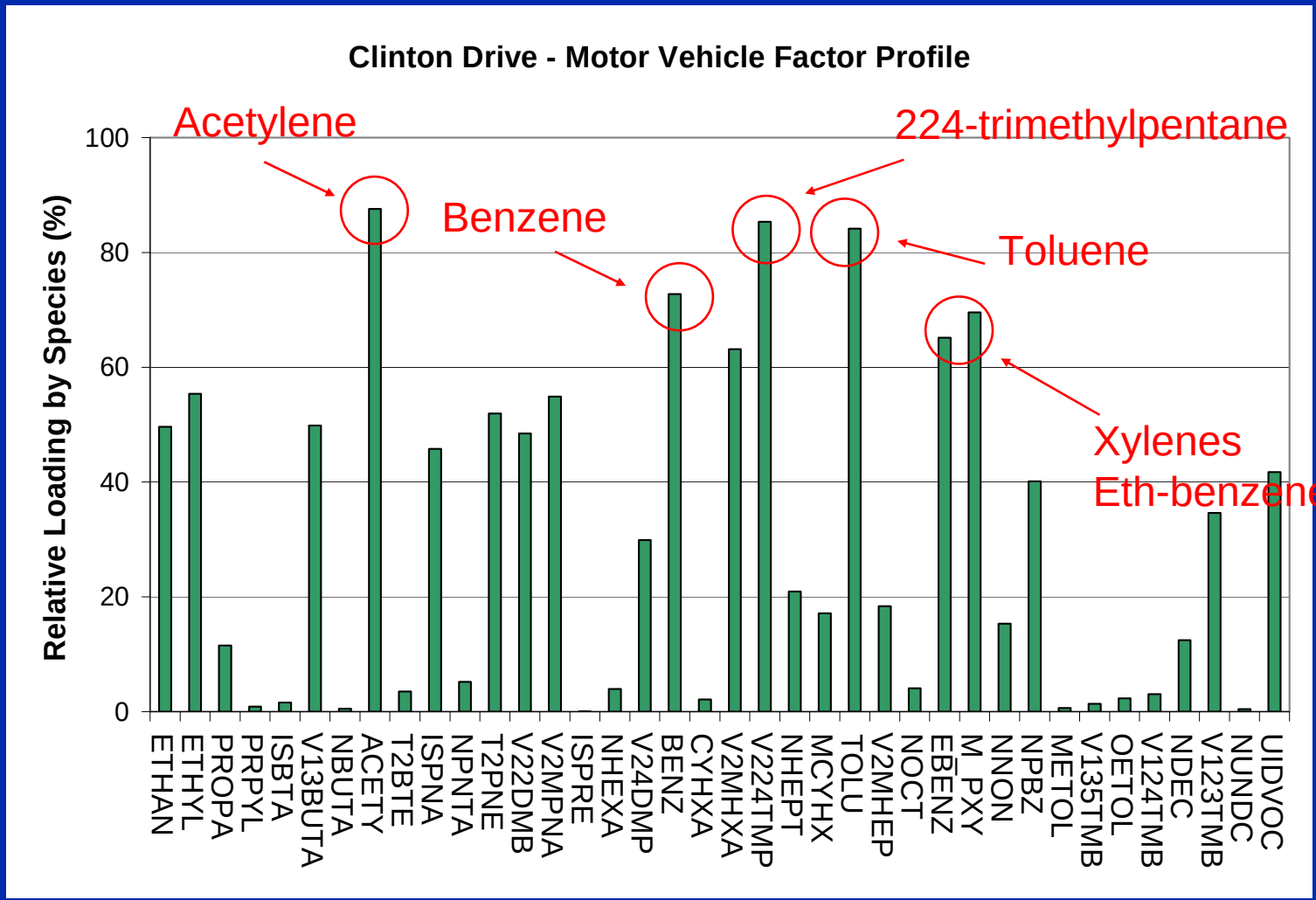
Positive Matrix Factorization (PMF)

- 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 (species x time) – no source profiles.

Source Apportionment Method

- Hourly speciated VOC data for summer 2001 at three sites (>700 samples at each site – larger sample size generally gives better results)
- Only nighttime data used to avoid photochemistry and to focus on fresh industrial emissions (mixing heights are low)
- Analyzed results by wind direction, day of week, hour

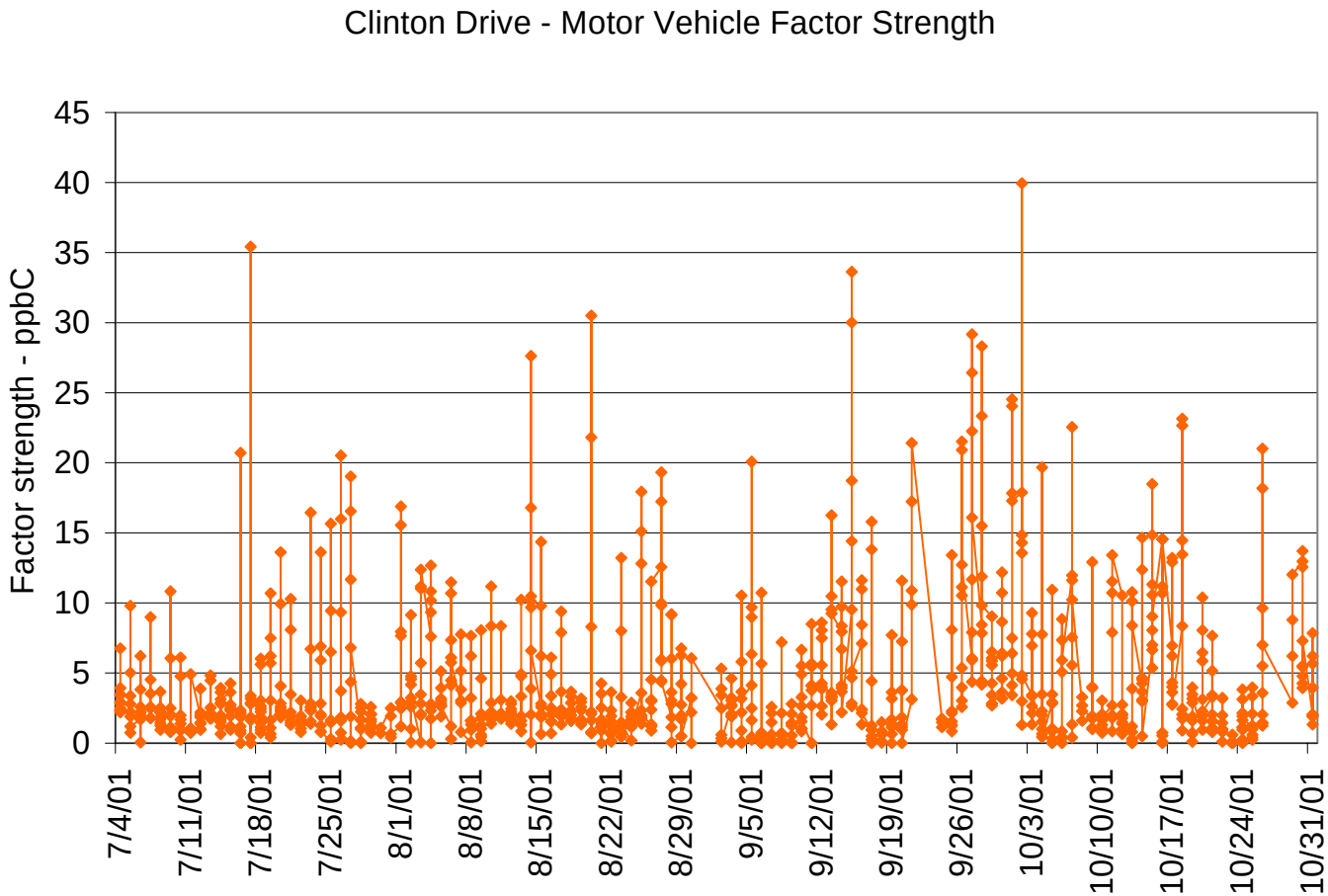
Example PMF-derived Profile – Motor Vehicle



Example Time Series

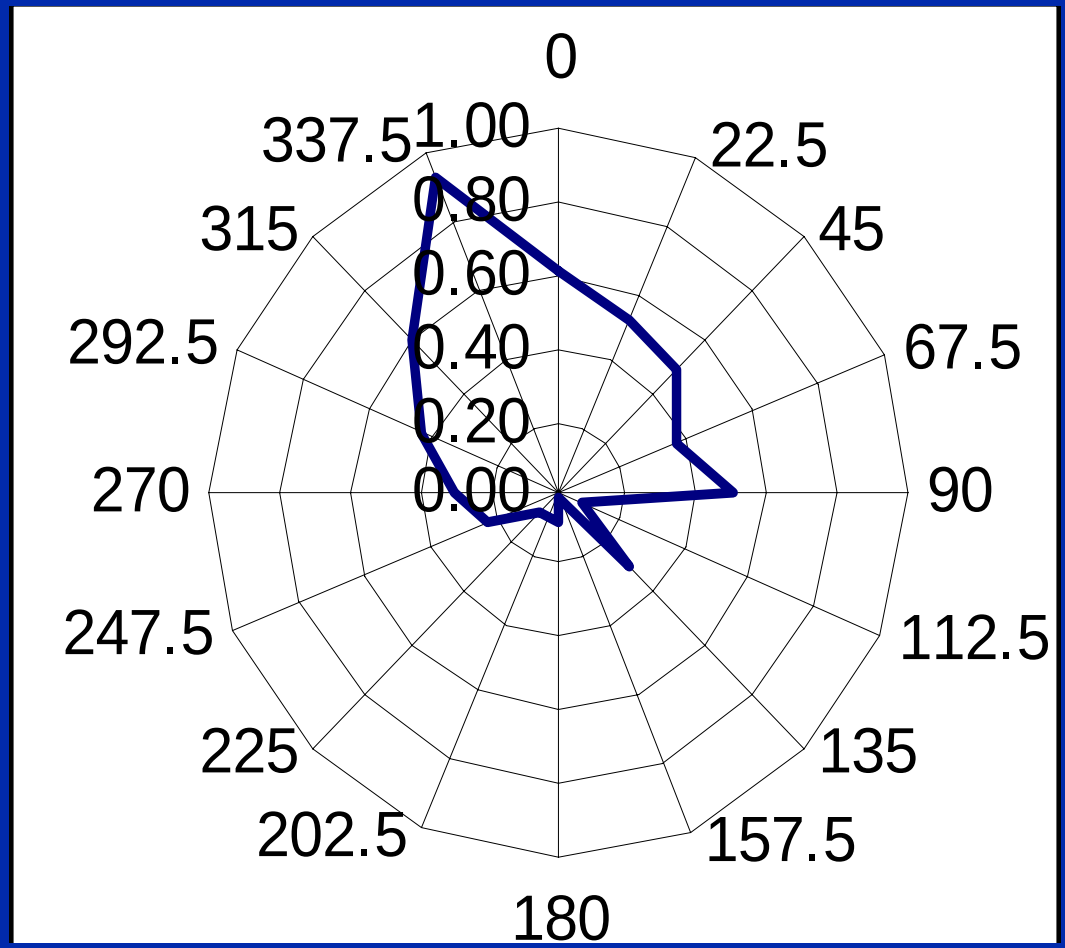
Examine temporal variation in factor:

- Weekday – weekend
- Time of day
- Season
- Similar to inventory?



Wind Direction Analysis

- Use Conditional Probability Function (CPF) to isolate area of influence
- Example: Motor vehicle
- Most influence from freeways to northwest, similar to inventory



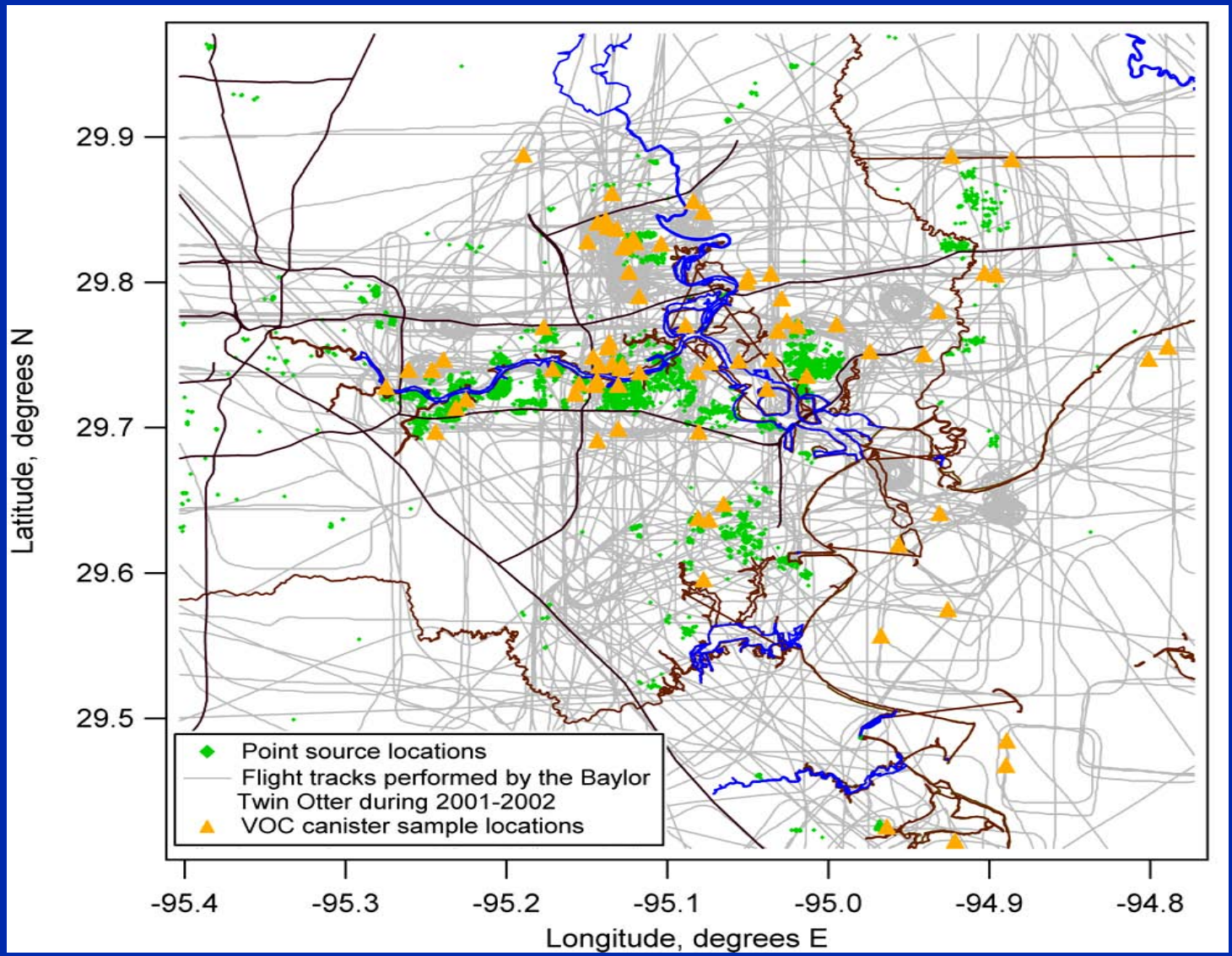
Source Apportionment Results

- Identified and quantified between 7 and 11 factors at each site
- Wind direction analysis results were consistent with spatial distribution of sources in emission inventory
- Composition of VOCs by factor similar to inventory, but some major differences noted:
  - Mobile sources appear to be better represented than industrial sources
  - Propene significantly underestimated at all sites
  - Light olefins underestimated near selected sources

Aircraft Methodology

- Collected VOC canisters within emission plumes
  - NO_x/NO_y ratio analysis to assess the photochemical age to gain a better understanding of the change in the observed VOC/NO_x ratio with photochemical processing time
- Flight data paired with wind direction and VOC results
- Based on spatial examination, a group of point sources were identified as influencing each sample

Aircraft Data Collection



Aircraft Analysis Results

Principal source	Emission Inventory ΣVOC/NO_x	Observed ΣVOC/NO_y	Ratio of observed to expected emissions
Chevron Phillips Chemical Co LP - 0145	Average= 0.588 Std. Deviation=0.004	Average= 14.7 Std. Deviation= 9.0	25.0
The Dow Chemical Co - 0041	Average= 0.131 Std. Deviation= 0.013	Average= 3.8 Std. Deviation= 3.8	29.0
Sterling Chemicals Inc - 0010	Average= 0.865 Std. Deviation=0.000	Average= 7.1 Std. Deviation= 4.2	8.2
Shell Oil Co - 0039	Average=1.123 Std. Deviation= 0.191	Average= 7.2 Std. Deviation= 6.1	6.4
Oil Tanking Houston Inc - 0277	Average= 19.154 Std. Deviation=0.020	Average= 9.8 Std. Deviation=10.7	0.5
Hoechst Celanese Chemical Group, Inc. - 0003	Average= 0.198 Std. Deviation= 0.015	Average= 8.5 Std. Deviation= 7.9	42.9
EXXON MOBIL Chemical Co – 0014	Average=0.896 Std. Deviation=0.340	Average= 8.8 Std. Deviation= 5.1	9.8
Equistar Chemicals LP - 0075	Average=0.782 Std. Deviation= 0.162	Average= 5.2 Std. Deviation= 3.5	6.6
BP Solvay Polyethylene N. America - 0004	Average= 2.548 Std. Deviation=0.937	Average= 6.1 Std. Deviation= 2.7	2.4

Aircraft Analysis Results

- VOC/NO_x ratios appear to be underestimated in the emission inventory by factors ranging from 2 to 43
- Alkenes/NO_x ratios appear to be underestimated by factors ranging from 3 to 64
- Aromatics/NO_x ratios appear to be underestimated by factors ranging from 3 to 20

Integrated Conclusions

- Multiple methods for reconciling the emission inventory were extremely effective and gave good consensus
- Total VOC/NO_x ratios appear to be underestimated by up to an order of magnitude (mostly near industrial sources)
- Olefins appear to be underestimated by a factor of 2 to 5, and by 3 to 64 for a single source
- Aromatics also appear to be underestimated by a factor of 2 to 5 and from 3 to 20 for a single source

Acknowledgments

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- HARC contract managers Dr. Jay Olaguer and Ms. Anne Brun
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