Question D: What distribution of anthropogenic and biogenic emissions of ozone and aerosol precursors can be inferred from observations?

VOC speciation during the morning rush hour

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Overview - Methods

- VOC analysis
- Data selection
- Data analysis
- Comparison with model results

VOC Analysis

- On-line VOC GC
  - Perkin Elmer Clarus 500 & Turbomatrix 650 ATD
  - 40 min sampling time
  - Calibration gases:
    - 73 VOC NCAR standard (200 pptv - 10 ppbv)
    - 30 VOC NPL standard (4 ppbv each)
- Location: Moody Tower (60 m a.g.l.)

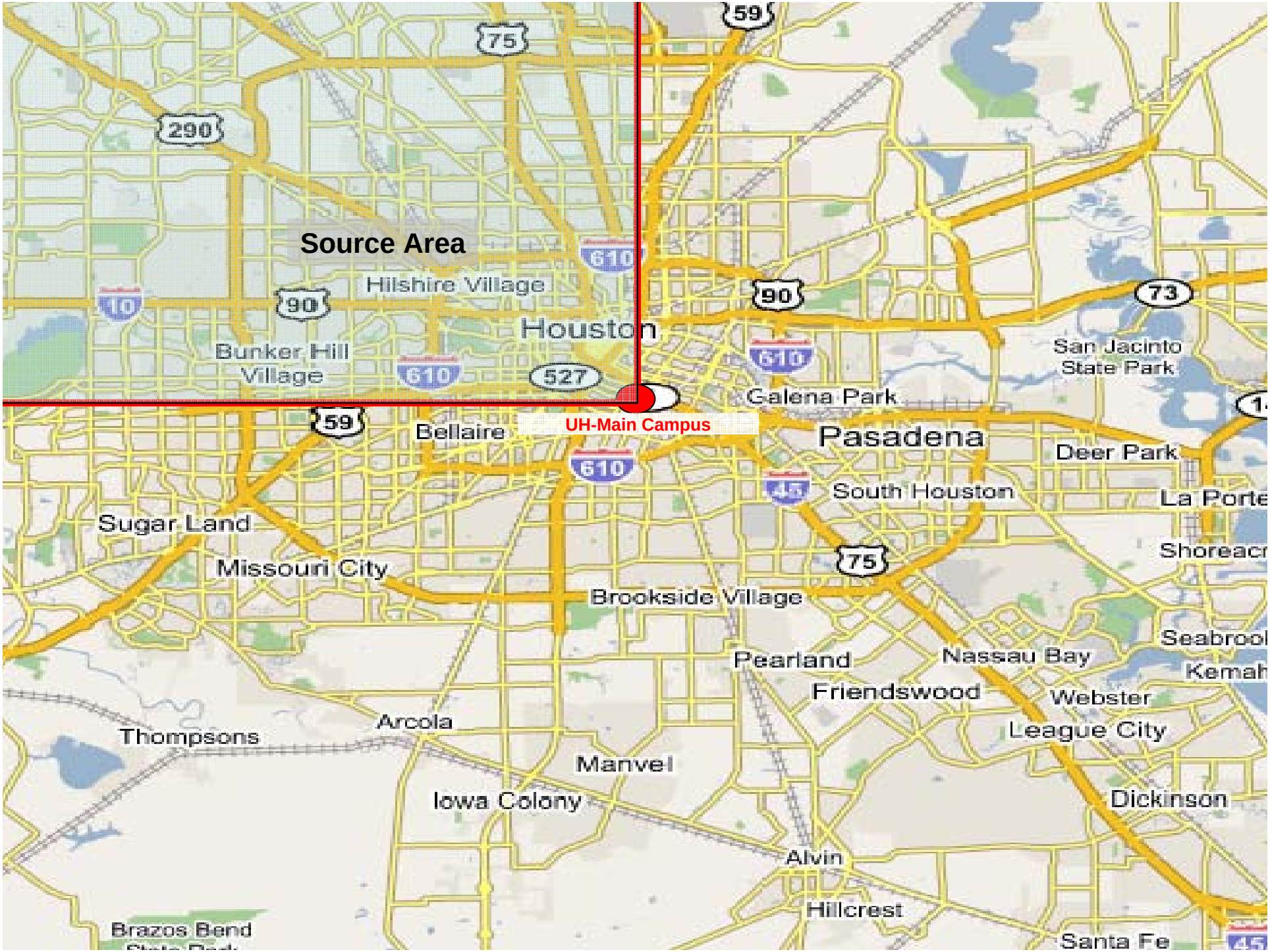
VOC Analysis

- Location:
  Moody Tower
  (60 m a.g.l.)

Data Selection

- Data selection based on:
  - time period: 6-9 am LT
  - type of day: weekday
  - boundary layer height: below 300 m
  - average wind direction in PBL: 270° - 360°
  - std deviation of wind direction: 15°

- Number of data:
  - 3 days: 8/21, 9/12, 9/13
  - 9 samples

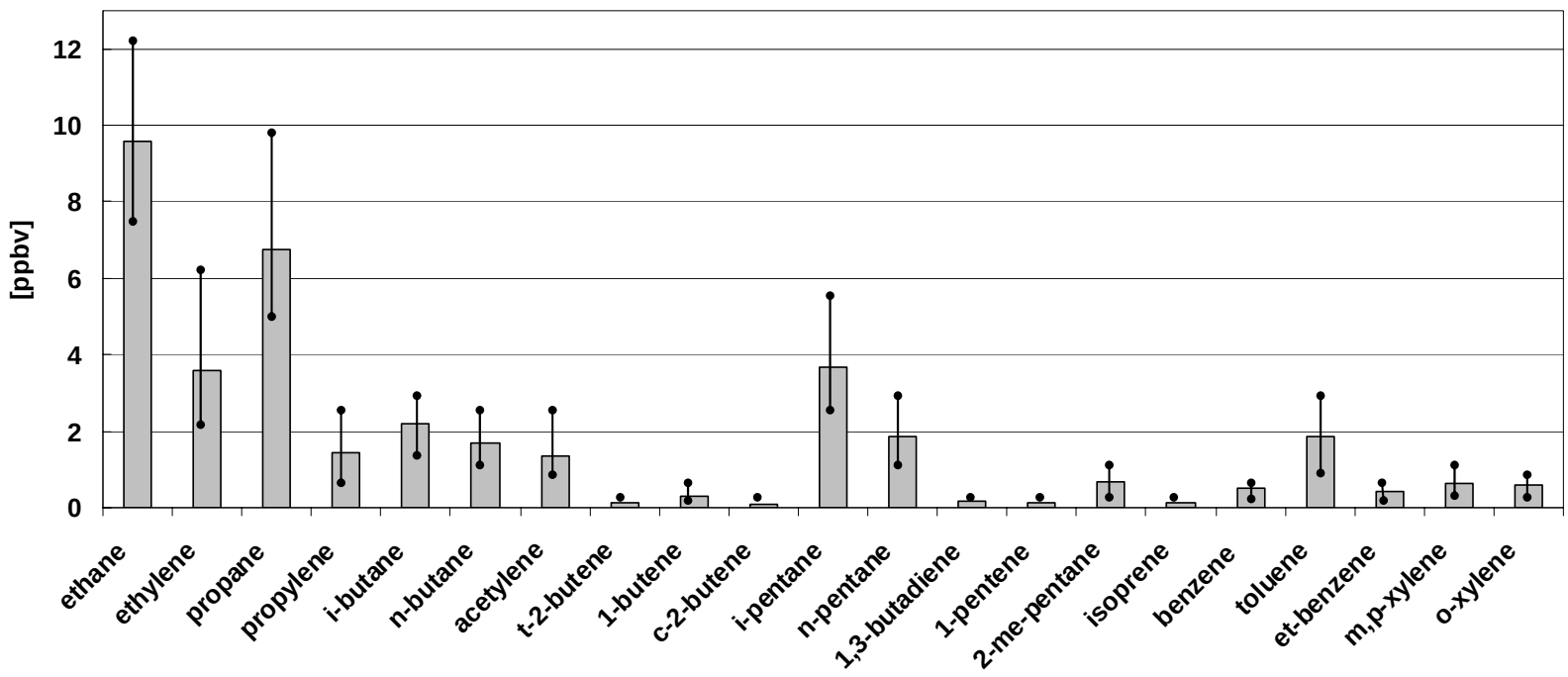

Source Area
UH-Main Campus
Hilshire Village
Houston
Bunker Hill Village
Bellaire
Galena Park
Pasadena
San Jacinto State Park
Deer Park
South Houston
La Porte
Sugar Land
Missouri City
Brookside Village
Pearland
Nassau Bay
Friendswood
Webster
League City
Arcola
Thompsons
Manvel
Iowa Colony
Dickinson
Alvin
Hillcrest
Brazos Bend
Santa Fe
59
75
290
610
90
10
527
73
45

View NNE

View West

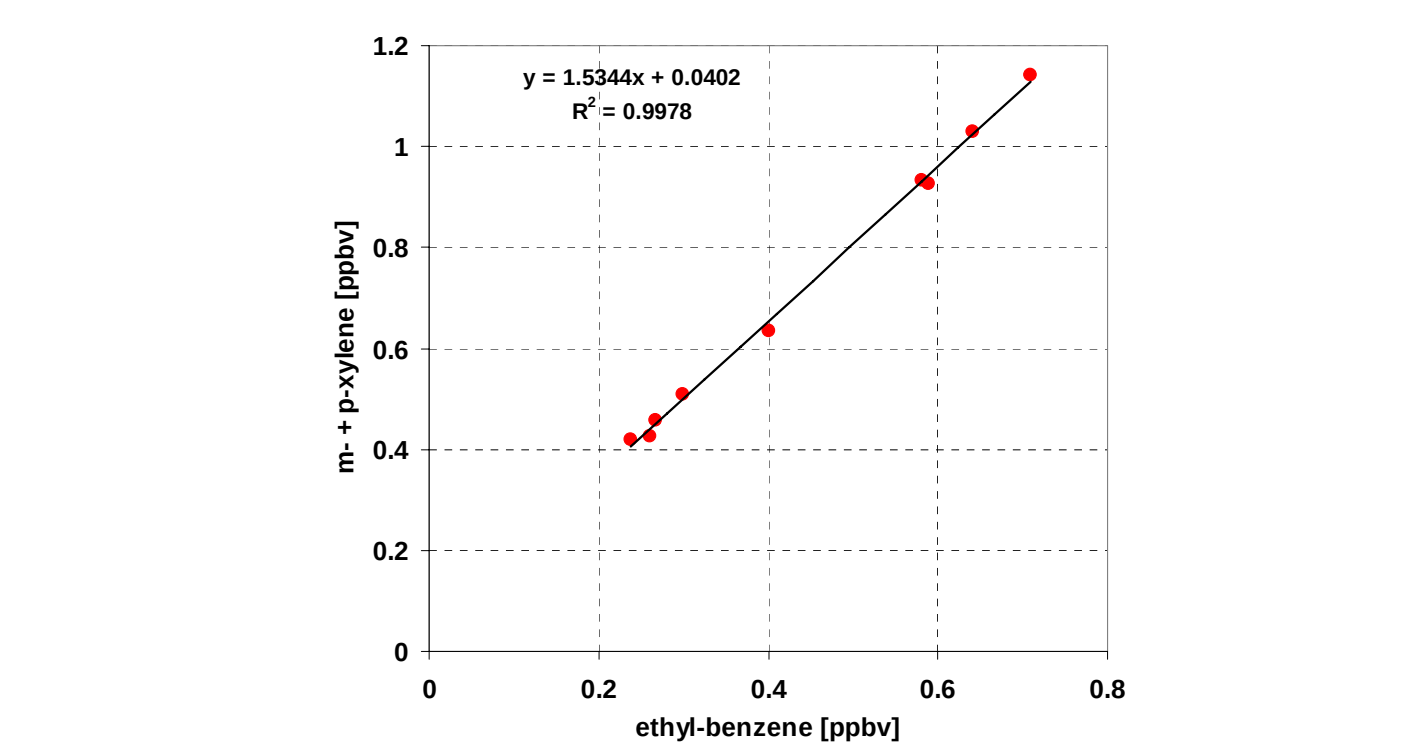
Data Analysis

- VOC composition



Data Analysis

- VOC correlations - aromatics vs aromatics



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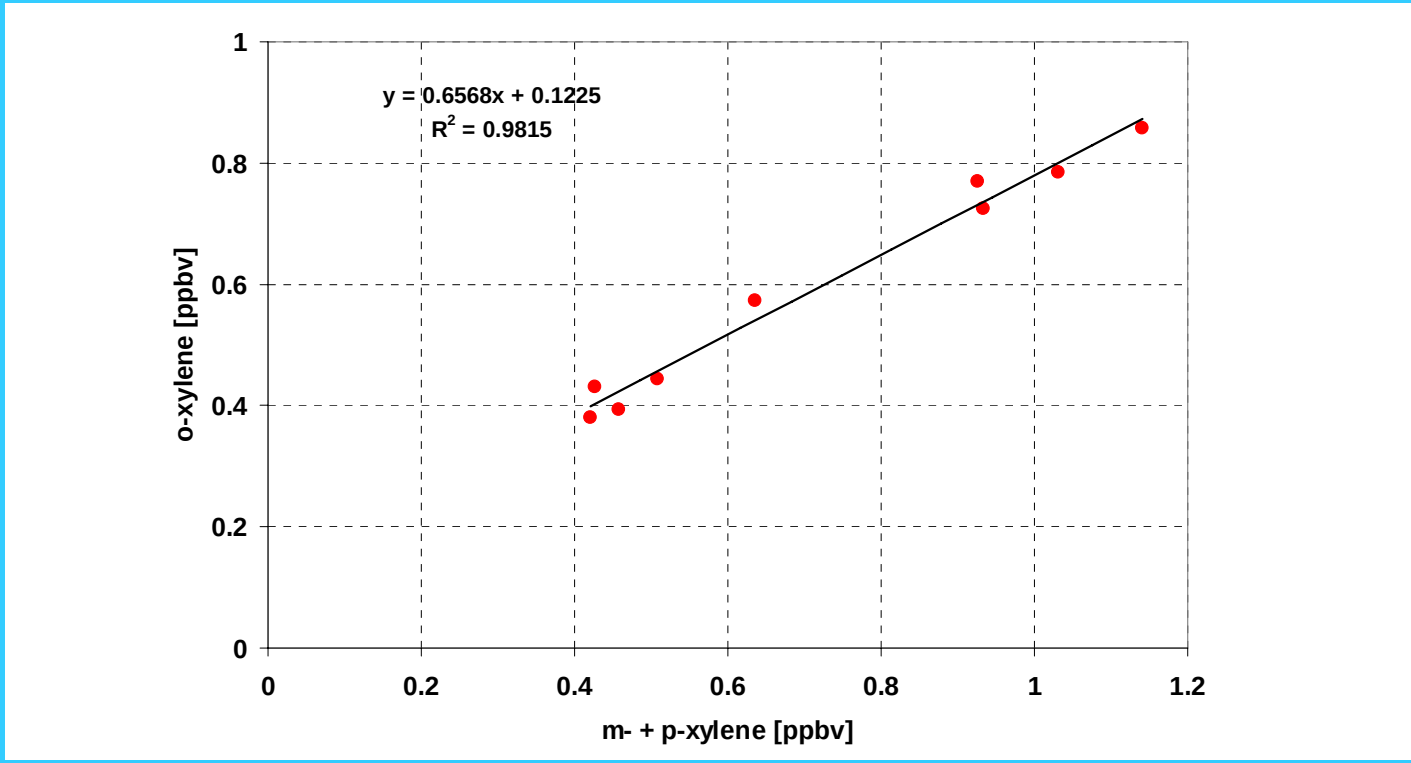

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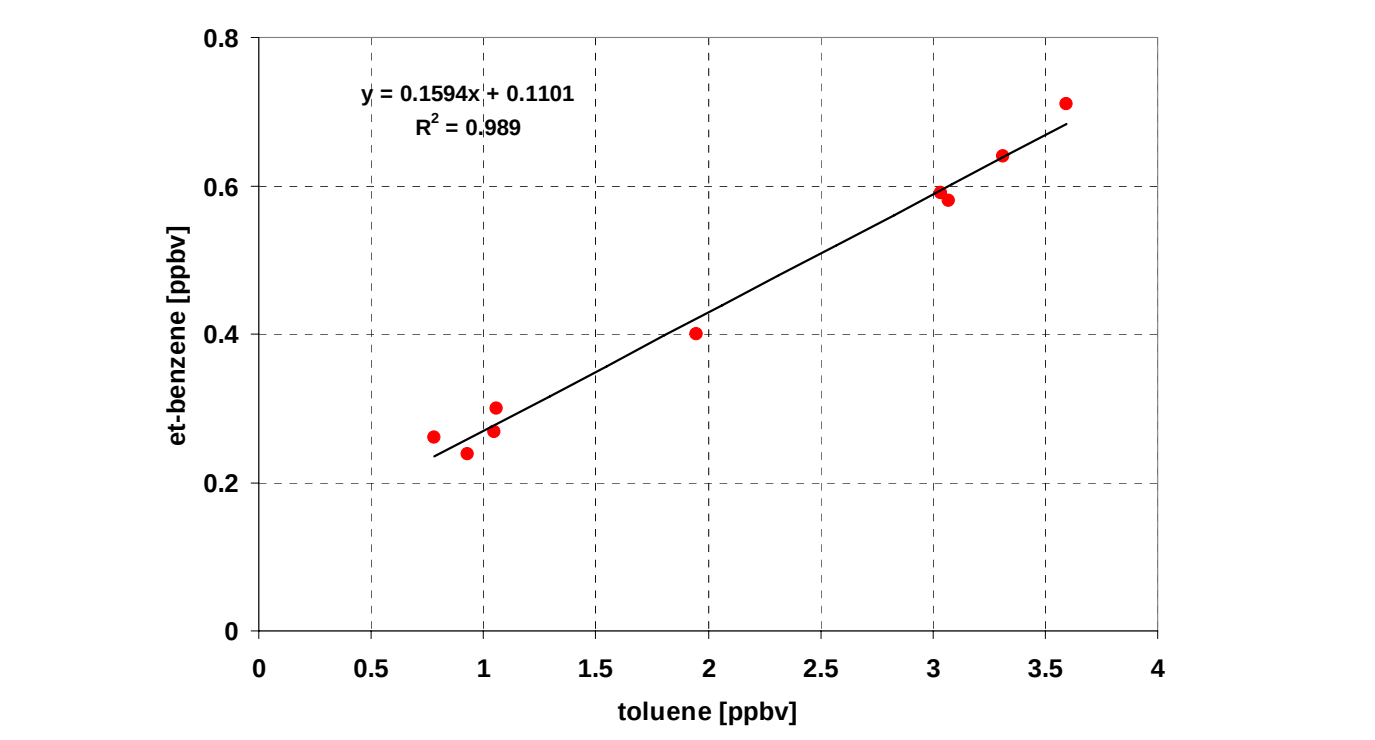

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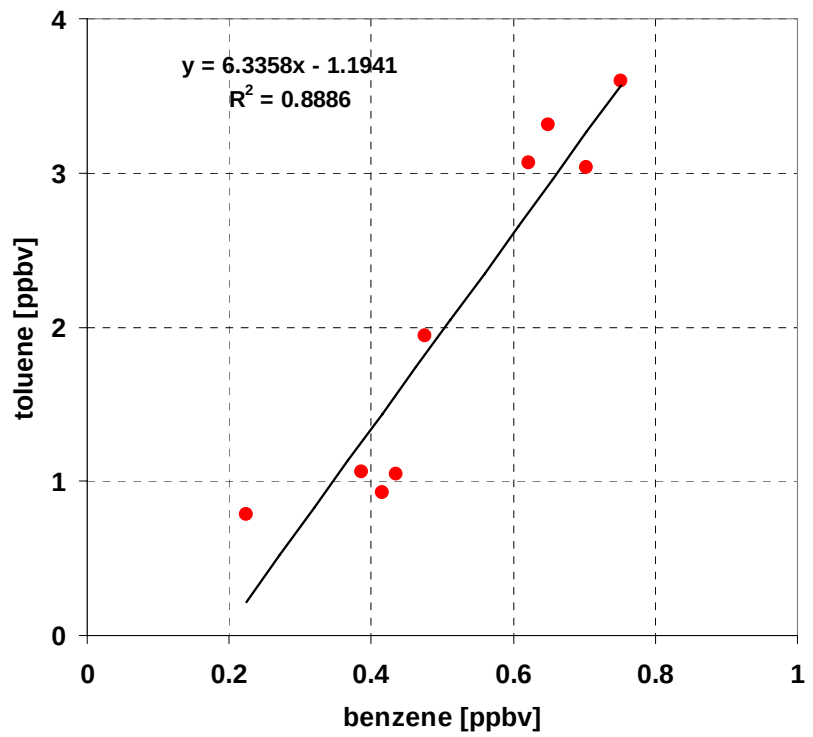
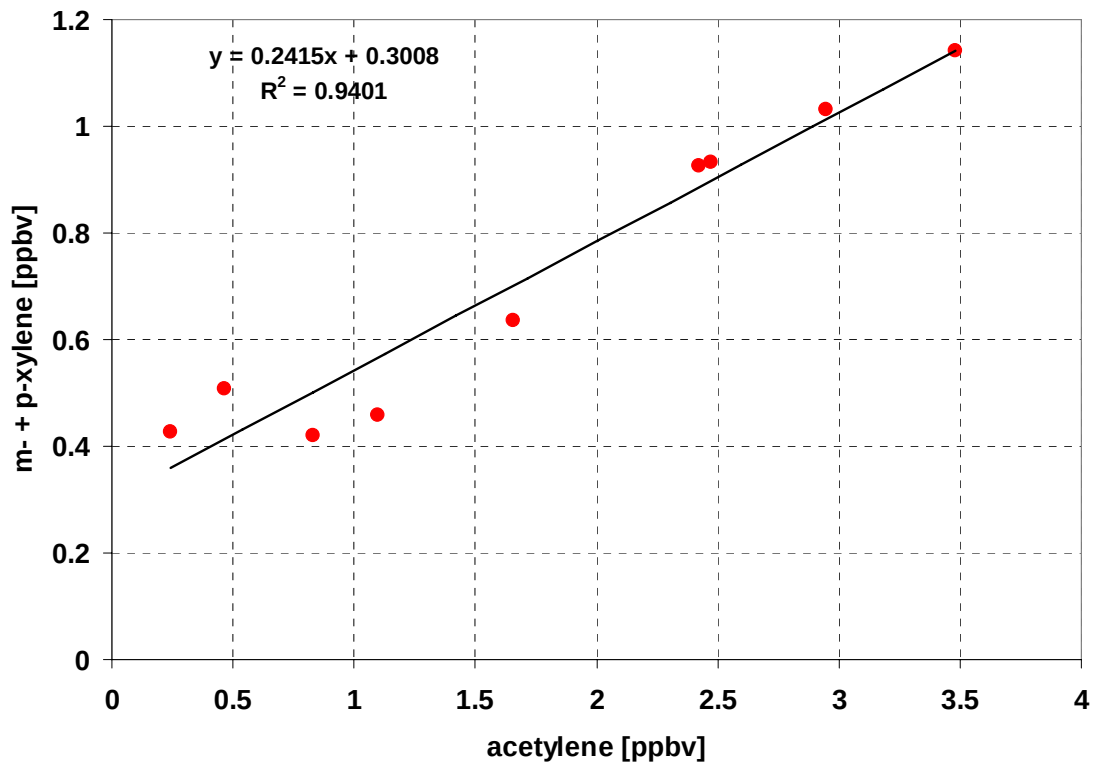


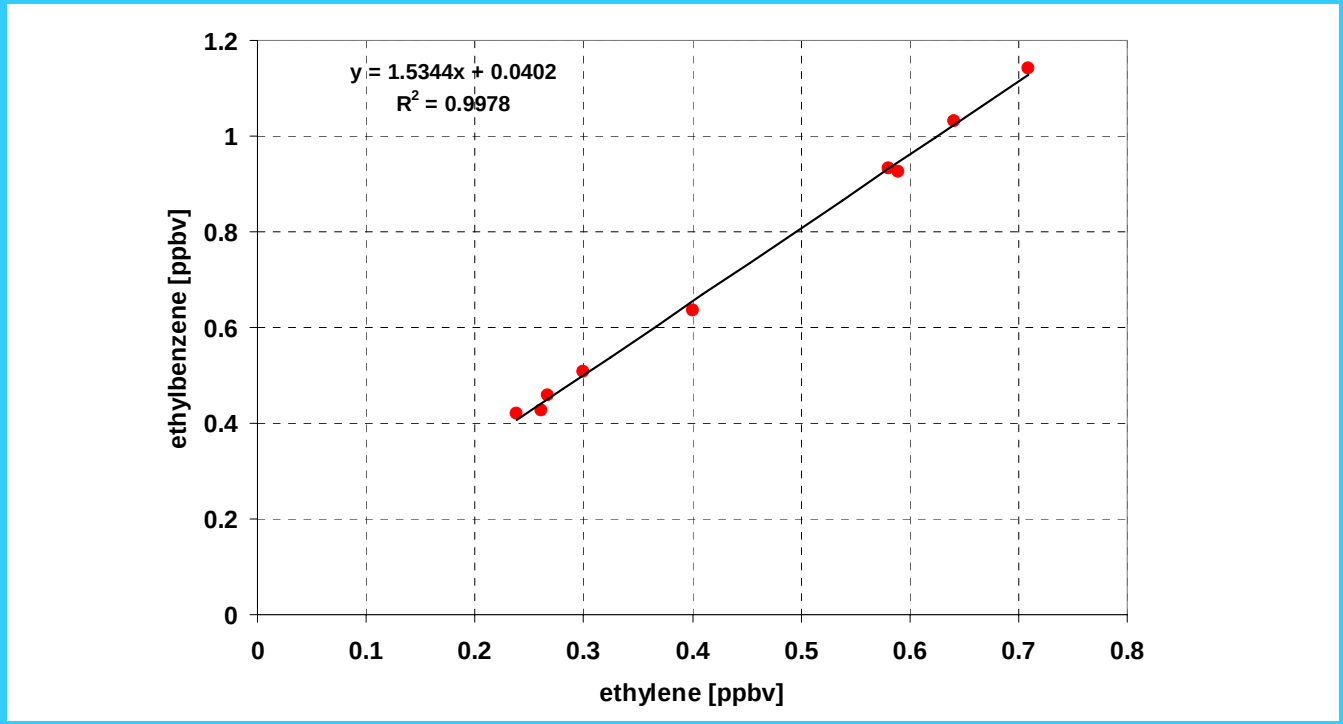
Data Analysis

- VOC correlations - aromatics vs acetylene



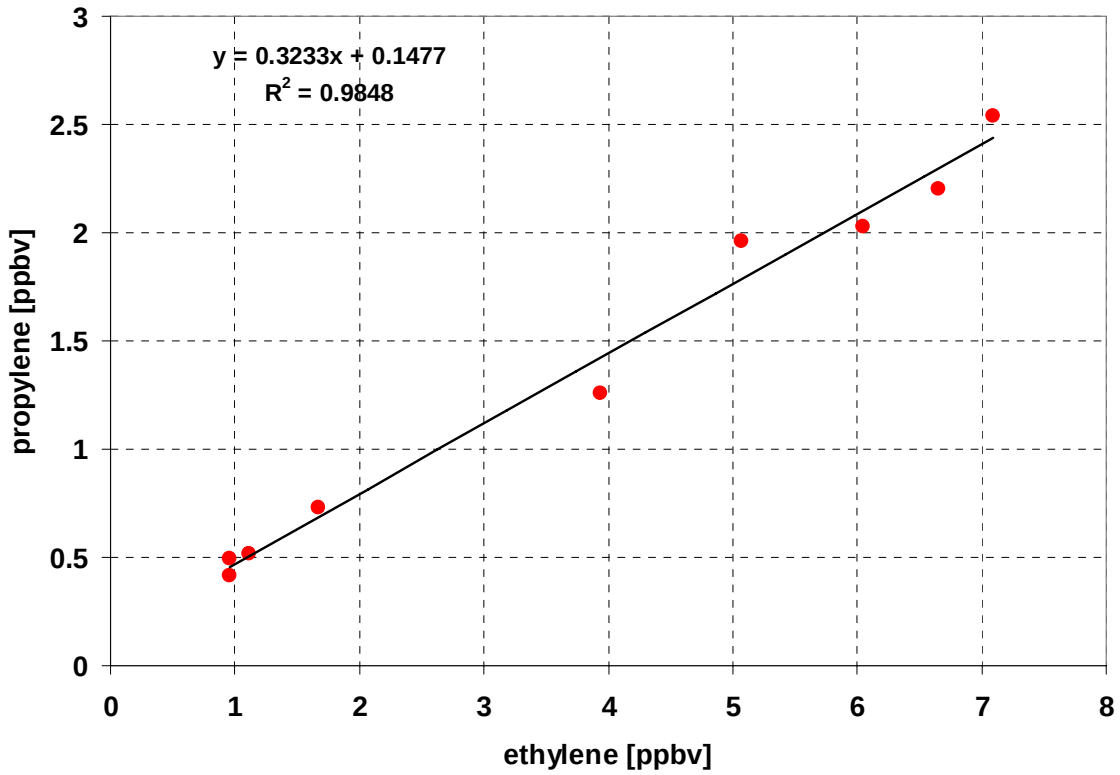
Data Analysis

- VOC correlations - aromatics vs ethylene



Data Analysis

- VOC correlations - propylene vs ethylene



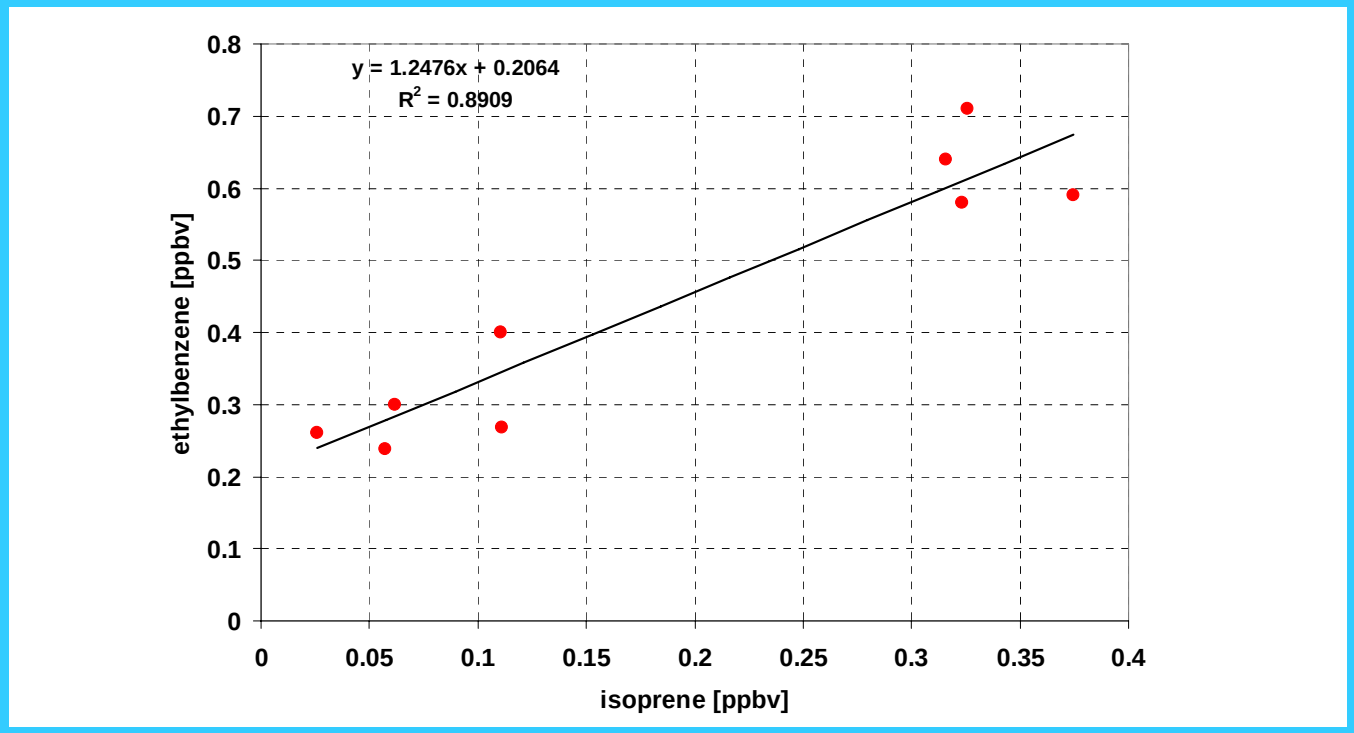
Data Analysis

- 1. Result

  Aromatics, acetylene, ethylene, and propylene highly correlated, most likely related to traffic emissions

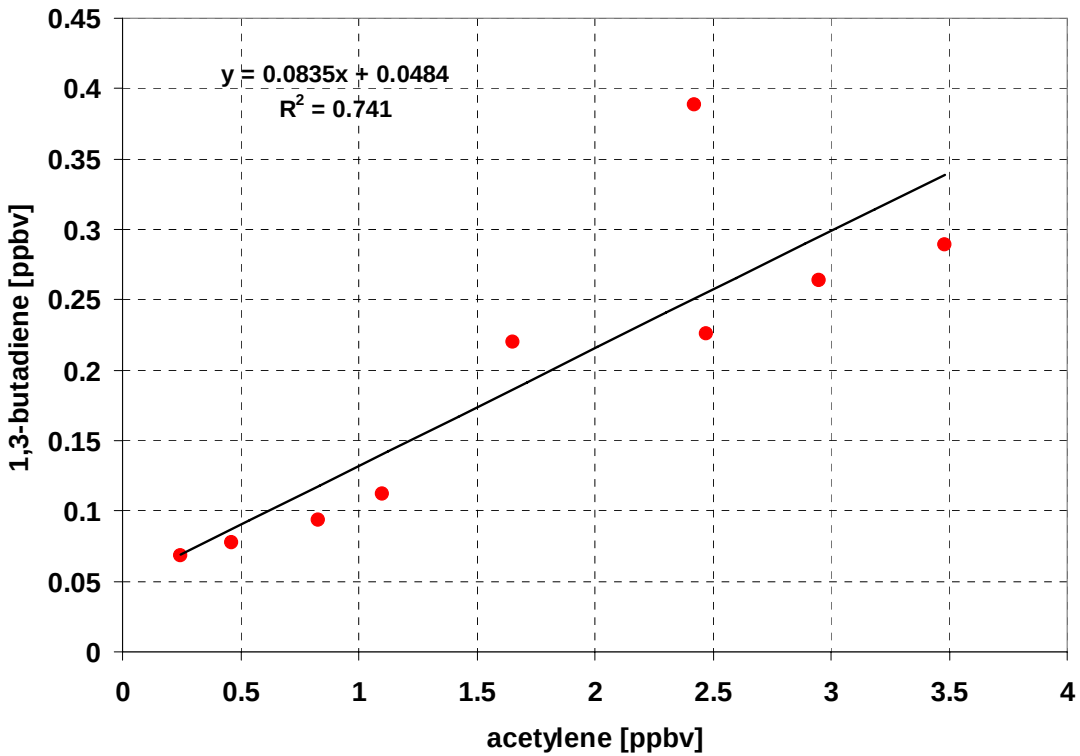
Data Analysis

- VOC correlations - ethylbenzene vs isoprene



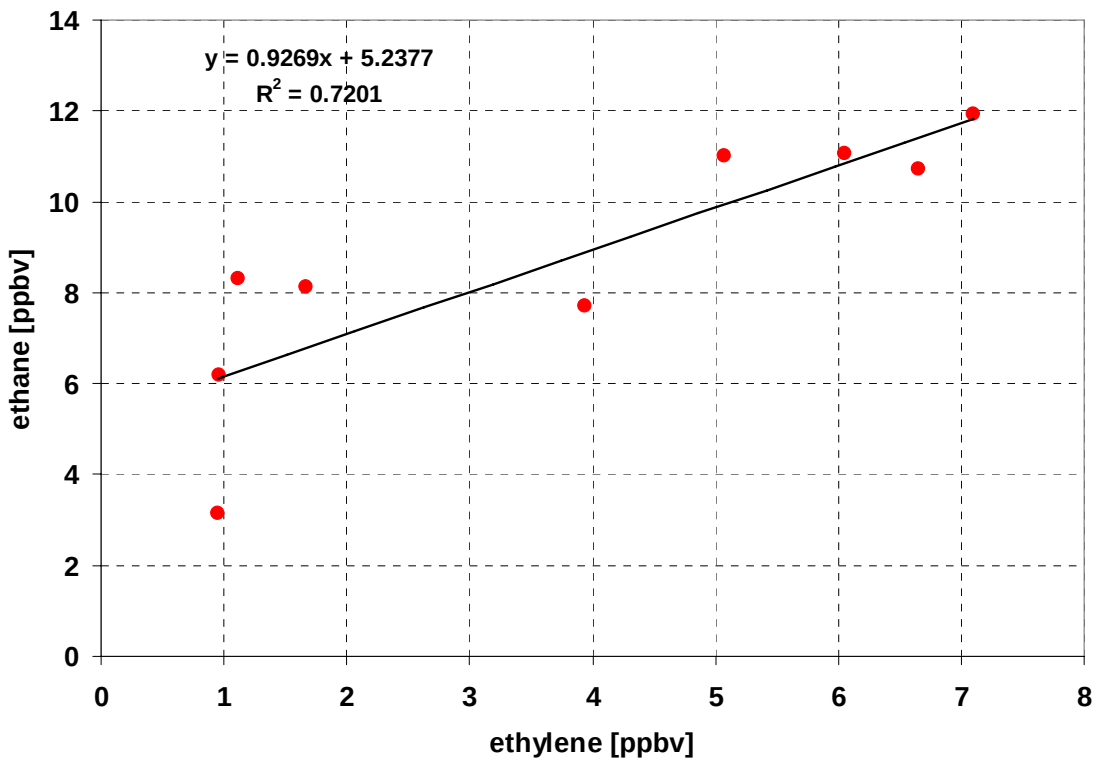
Data Analysis

- VOC correlations - 1,3 butadiene vs acetylene



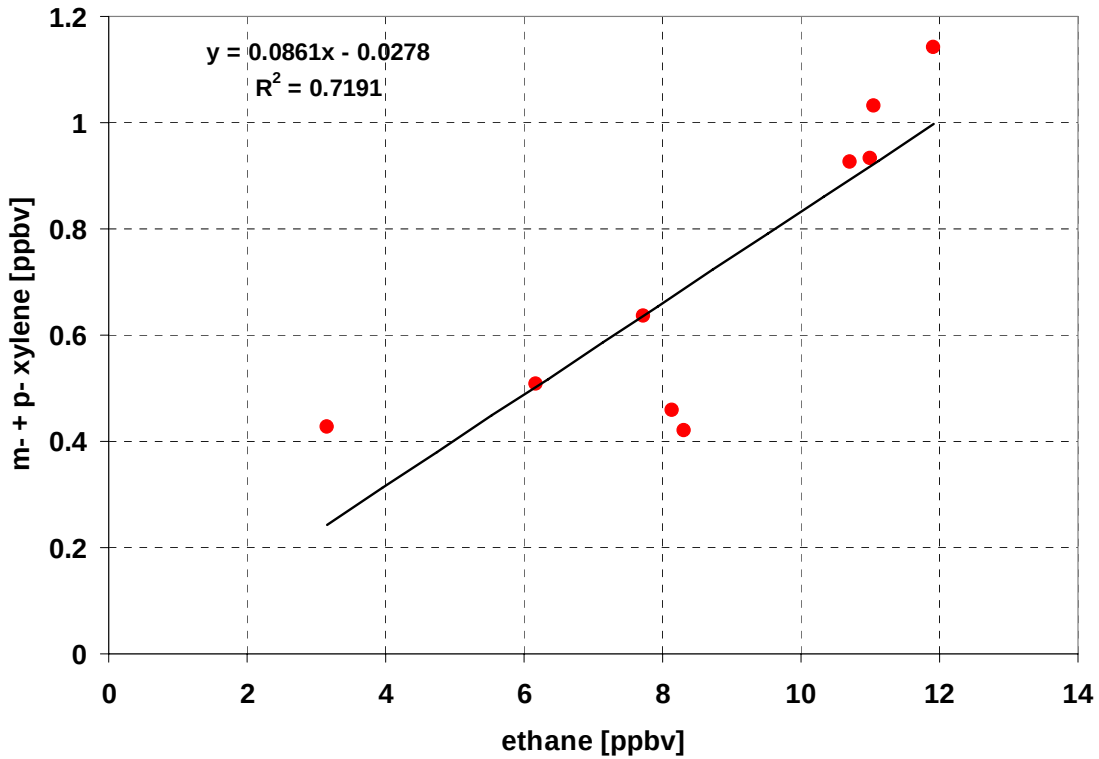
Data Analysis

- VOC correlations - ethane vs ethylene



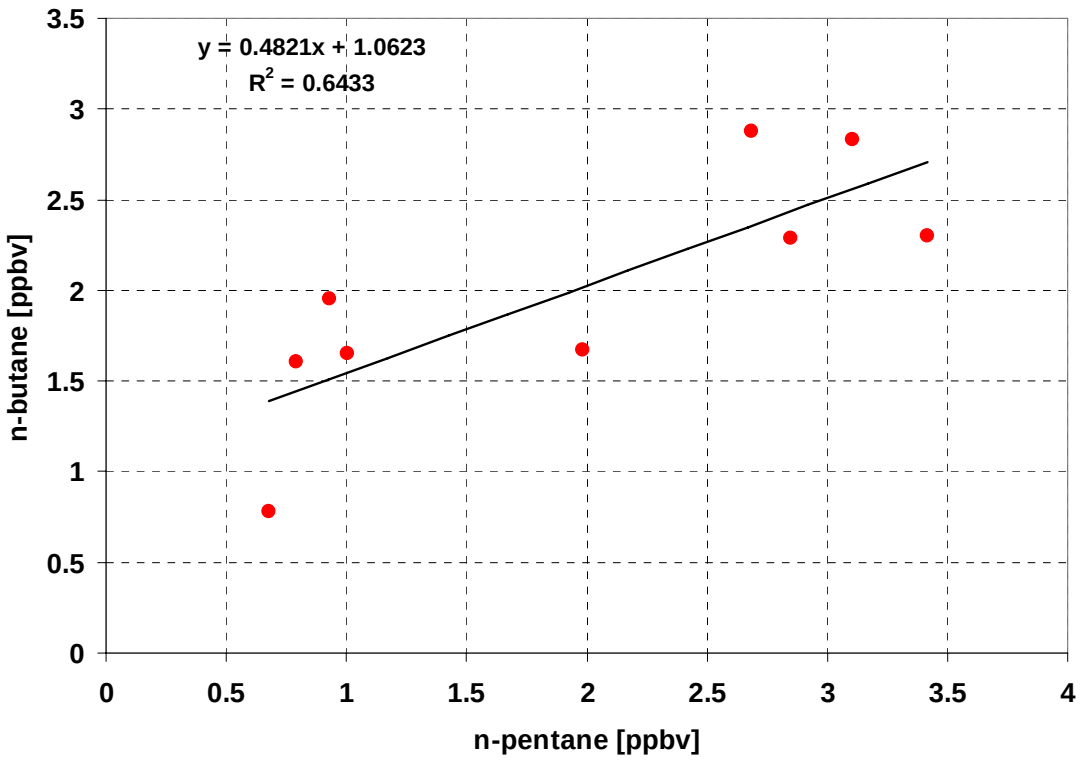
Data Analysis

- VOC correlations - m+p-xylene vs ethane



Data Analysis

- VOC correlations - alkanes vs alkanes



Data Analysis

- 1. Result

  Aromatics, acetylene, ethylene, and propylene highly correlated, most likely related to traffic emissions

- 2. Result

  1,3 butadiene, isoprene, and alkanes show less pronounced correlations. Presumably, other sources contribute.
  Indications of isoprene emissions from car exhaust.

Data Analysis

- VOC ratios
  - toluene/benzene 3.79
  - m + p-xylene/ethylbenzene 1.64 (1.3-4.48 urban*)
  - ethylbenzene/ethylene 0.16 (0.04-0.26 traffic*)
  - ethylbenzene/n-pentane 0.26 (0.18-1.1 traffic*)

  - typical urban ratios,
  - however toluene/benzene somehow slightly high

*Monod et al (2001)

Comparison with CMAQ model results

- **Emission inventory** – developed by combing three databases: National Emission Inventory (NEI99), imputed Texas Inventory (TEI2000) and link-based emissions from MOBILE6 output;

- **Models** - SMOKE2.1 and CMAQ4.4
- Modeling episode: August 01 – August 31, 2000
- Modeling domain: 4km (83x65 cells) – Houston Galveston Area (HGA)

- **Chemical mechanism** - extended SAPRC99 with 18 aromatic species explicitly represented: SAPRC99-ARO
- **Chemical solver** - Euler Backward Iterative (EBI)

Aromatic species included in the SAPRC99 mechanism
new chemical mechanism – SAPRC99-ARO

- **extracted from ARO1 lumped species:**

1. benzene
2. toluene
3. ethylbenzene
4. chlorobenzene
5. iso-propylbenzene
6. N-propylbenzene
7. p-dichloro-benzene
8. nitrobenzene
9. sec-butyl-benzene

- **extracted from ARO2 lumped species:**

1. O-xylene
2. M-xylene
3. P-xylene
4. 1,2,3-trimethylbenzene
5. 1,2,4-trimethylbenzene
6. 1,3,5-trimethylbenzene
7. naphthalene
8. methylnaphthalene
9. dimethylnaphthalene

Comparison with CMAQ model results

- Comparison traffic hour aromatic ratios
  - toluene/benzene: 3.79 (o) ↔ 2.89 (m; year 2000)
  - toluene/m+p-xylene: 2.71 (o) ↔ 3.34 (m; year 2000)
  - m+p-xylene/ethylbenzene: 1.64 (o) ↔ 2.70 (m; year 2000)
  - benzene/m+p-xylene: 0.74 (o) ↔ 1.15 (m; year 2000)

o: observed
m: modelled

Tentative Conclusions

- Houston traffic rush hour contains aromatic compounds, acetylene, ethylene and propylene as traffic emission related VOCs.
- Alkanes and isoprene present at traffic rush hour, but exhibit less close relationship with traffic emissions
- Selected VOC ratios are in good agreement with typical urban environments impacted by traffic emissions
- Model results indicate a decrease in ambient benzene