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.
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 ($F_{\text{Peak}} = 0.2$)
- Residuals within +/- 3 standard deviations
- No feasible multiple solutions
Average VOC Composition

- Industrial flare: 5%
- Industrial aromatics: 4%
- Motor vehicle: 4%
- Light olefins: 5%
- Butadiene: 2%
- Butenes: 2%
- Diesel: 2%
- Isoprene: 2%
- Mixed aromatics: 12%
- Background/Accumulation: 24%
- Evaporative/Solvents: 10%
- Evaporative/Background: 23%
- Industrial aromatics: 1%
- Pentenes: 1%
- Solvents: 3%
## Details of Sources

<table>
<thead>
<tr>
<th>Factor</th>
<th>Source ID</th>
<th>Significant Species</th>
<th>Wind Direction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Industrial flares</td>
<td>SButenes15</td>
<td>Ethane, ethene, n-butane acetylene</td>
<td>E, NW</td>
</tr>
<tr>
<td>2 Industrial aromatic hydrocarbons #1</td>
<td>W, E, SIsoprene14</td>
<td>UID, diethylbenzene</td>
<td>S, SW</td>
</tr>
<tr>
<td>3 Motor vehicle</td>
<td>W, NC10-C11 alkanes, xylenes</td>
<td>Benzene, toluene, acetylene, xylenes</td>
<td>SW, W, NW</td>
</tr>
<tr>
<td>4 Industrial light olefins</td>
<td>E, S1,3-butadiene</td>
<td>Ethene, propene</td>
<td>E, S</td>
</tr>
<tr>
<td>5 Evaporative emissions/background</td>
<td>E, SEButanes5</td>
<td>Butanes</td>
<td>E, S</td>
</tr>
<tr>
<td>6 Solvent use</td>
<td>E, W, NWC6-C9 paraffins</td>
<td>C6-C9 paraffins</td>
<td>SSE</td>
</tr>
<tr>
<td>7 Industrial pentene source</td>
<td>E, NESWUID, diethylbenzene</td>
<td>Pentenes</td>
<td>S, ESE</td>
</tr>
<tr>
<td>8 Industrial aromatic hydrocarbons #2</td>
<td>E, NUID, trimethylbenzenes</td>
<td>UID, trimethylbenzenes</td>
<td>N, E</td>
</tr>
<tr>
<td>9 Butadiene sources</td>
<td>S1,3-butadiene</td>
<td>1,3-butadiene</td>
<td>S</td>
</tr>
<tr>
<td>10 Evaporative emissions/solvents</td>
<td>W, W, NWC5-C7 paraffins</td>
<td>C5-C7 paraffins</td>
<td>E, SE, S</td>
</tr>
<tr>
<td>11 Accumulated emissions and natural gas</td>
<td>W, W, NWEthane, propane</td>
<td>Ethane, propane</td>
<td>E, N</td>
</tr>
<tr>
<td>12 Heavy aromatic sources</td>
<td>E, NEthyltoluene</td>
<td>Ethyltoluene</td>
<td>E, N</td>
</tr>
<tr>
<td>13 Diesel</td>
<td>S, SWC10-C11 alkanes, xylenes</td>
<td>C10-C11 alkanes, xylenes</td>
<td>W, N</td>
</tr>
<tr>
<td>14 Biogenic with outliers from industry</td>
<td>S, SWIsoprene</td>
<td>Isoprene</td>
<td>W, E, S</td>
</tr>
<tr>
<td>15 Industrial butene source</td>
<td>S, SWButenes</td>
<td>Butenes</td>
<td>S</td>
</tr>
</tbody>
</table>
Factor Profiles

Motor Vehicle
Ethene/Propene

Expanded on next slide
Concentrations of Chemical Species

[Graph depicting various chemical species concentrations over time]
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 25\(^{th}\) 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