

Quantifying the Contribution of Important Sources to Ambient VOC

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Overview

Why do we need to understand ozone precursor sources? When an area experiences high concentrations of ozone, particularly when the concentrations are in exceedance of the standard, research and analysis is needed to investigate the possible sources of ozone and ozone precursors leading to the high concentrations. The analysis and research required spans all aspects of the regulatory community:

- Monitoring staff should know whether or not their sampling and analysis set up is adequate to identify the precursor species that are critical for identifying potential sources in their area.
- Analysts should be able to identify potential sources and meteorological conditions to assist policy makers and modelers in developing control strategies.
- Modelers should know how well current emission inventories and dispersion models represent the ambient conditions so that they can model future control scenarios and the effect on ozone concentrations.
- Policy makers should know what sources are the principal contributors to ozone so that appropriate controls on precursor emissions can be developed and implemented.

In a previous chapter of the workbook, data analyses exploring the spatial and temporal characteristics of ozone precursor data were discussed. In this chapter, we first discuss “what is a source?”. Important emissions sources are then described as well as source attribution methods, tools, their uncertainties, and examples.

What is a “Source”?: Primary versus Secondary

- **Primary** VOC emissions are composed of material in the same chemical form as when they were emitted into the atmosphere. Concentrations of primary VOCs are a function of emission rate, transport and dispersion, and removal rate.
- **Secondary** VOCs are formed in the atmosphere by chemical interactions among primary pollutants and normal atmospheric constituents. Secondary formation is a function of many factors including: concentrations of precursors, concentrations of other gaseous reactive species (e.g., ozone, hydroxyl radical), atmospheric conditions, and cloud or fog droplet interactions.
- Some PAMS VOCs are of both primary and secondary origin. For example, formaldehyde is a primary pollutant (e.g., emitted in motor vehicle exhaust) and also an oxidation product of hydrocarbons in the atmosphere.

It is considerably more difficult to relate ambient concentrations of secondary species to sources of precursor emissions than it is to identify the sources of primary emissions.

What is a “Source”?: Local vs. Transport

- A key question analysts face is “how do I tell the difference between locally generated ozone and ozone (and precursors) transported into the area?” Policy makers need to understand how much of the ozone problem is under their jurisdiction to control.
- Techniques for assessing the difference between local and transported ozone and precursors include:
 - Spatial and temporal analyses (e.g., Are high concentrations observed on a regional basis or only at a few sites?).
 - Assessing the age of an air mass accompanied with trajectory analysis.
 - The use of “tracers-of-opportunity” and species ratios accompanied with trajectory analysis.

Source Apportionment: Overview

- Relating source emissions to their quantitative impact on ambient air pollution is referred to as source apportionment.
 - The traditional approach is dispersion modeling, in which a pollutant emission rate and meteorological information are input to a mathematical model that disperses (and may also chemically transform) the emitted pollutant, generating a prediction of the resulting pollutant concentration at a point in space and time.
 - The alternative is receptor modeling, which may be defined as "a specified mathematical procedure for identifying and quantifying the sources of ambient air contaminants at a receptor primarily on the basis of concentration measurements at that receptor."
 - In contrast to dispersion modeling, receptor modeling is diagnostic, not prognostic - it describes the past rather than the future.
- The best-known example of single-sample receptor modeling is chemical mass balance (CMB).
 - CMB has a special status in the receptor modeling toolbox as the only model up to the present that has been officially approved (i.e., supported and distributed) by EPA.
- Multivariate receptor models require the input of data from multiple samples and extract the source apportionment information from all of the sample data simultaneously. Modeling may be coupled with classification of the ambient data by wind direction, wind speed, time of day, site, season, etc.

Lewis, 1999

Source Apportionment Methods and Tools

- Source apportionment methods are used to resolve the composition of PM into components related to emission sources. Several methods are available.
- It is useful to apply more than one method and look for consensus among results.
- Methods and tools discussed in this section include the following:
 - Spatial and temporal characteristics of data
 - Cluster, factor, and other multivariate statistical techniques
 - Positive matrix factorization (PMF)
 - UNMIX
 - Chemical mass balance (CMB) model
 - Trajectory approaches
- Other multivariate receptor models include specific rotation factor analysis, target transformation factor analysis, three-mode factor analysis, source profiles by unique ratios (SPUR), and receptor model applied to patterns in space (RMAPS).

Multivariate Analyses

- Multivariate analyses are statistical procedures used to infer the mix of hydrocarbon sources impacting a receptor location (see the following table for species/source links).
- Procedures including cluster, factor/principal component, regression, and other multivariate techniques are usually available in statistical software packages.
- Literature review shows many refinements and options to these analyses.
- A drawback to these analyses is that the analyst must infer how certain statistical species groupings relate to emissions sources.
- A nice feature of these analyses is the ability to summarize a multivariate data set using a few components.

Key Species (1 of 3)

The PAMS target species list contains some species that can be used as “tracers of opportunity”:

Species	Major Sources	Comments
ethene	Mobile sources, petrochemical industry	Tracer for vehicle exhaust
acetylene	Mobile sources, combustion processes	Tracer for vehicle exhaust. More abundant in gasoline than diesel exhaust
ethane	Natural gas use	Non-reactive
propene	Refinery, chemical manufacturing, motor vehicle exhaust	More abundant in diesel than gasoline exhaust
propane	LPG and natural gas use, oil and gas production	Relatively non-reactive, often underestimated in emission inventory. Also more abundant in diesel than gasoline exhaust
i-butane	Consumer products, gasoline evaporative emissions, refining	Used as replacement of CFCs in consumer products
butene	Motor vehicle exhaust	More abundant in gasoline than diesel exhaust. A thermal decomposition product of MTBE
n-butane	Gasoline evaporative emission	Tracer of gasoline use
t-2-butene	Motor vehicle exhaust	Enriched in evaporated gasoline relative to exhaust

Key Species (2 of 3)

The PAMS target species list contains some species that can be used as “tracers of opportunity” (continued):

Species	Major Sources	Comments
i-pentane	Solvent use, refining, mobile sources	Among most abundant species in urban air. More abundant in gasoline than diesel exhaust
n-pentane	Motor vehicle exhaust, gasoline evaporative emissions	Enriched in evaporative emissions relative to exhaust
isoprene	Biogenics	Tracer of biogenic emission; reactive
internal olefins (e.g., t-2-pentene)	Gasoline evaporative emissions, plastics production	Reactive
2,2-dimethylbutane	Motor vehicle exhaust	More abundant in diesel than gasoline exhaust
benzene	Motor vehicle exhaust, combustion processes, refining	Tracer for vehicle exhaust; significantly reduced since 1995 with the introduction of reformulated gasoline
2-methylhexane	Motor vehicle exhaust	More abundant in gasoline than diesel exhaust
2,2,4-trimethylpentane	Gasoline evaporative emissions	Also in motor vehicle exhaust
n-heptane	Surface coatings, degreasing	Also in motor vehicle exhaust

Key Species (3 of 3)

The PAMS target species list contains some species that can be used as “tracers of opportunity” (concluded):

Species	Major Sources	Comments
toluene	Solvent use, refining, mobile sources	Among most abundant species in urban air
styrene	Solvent use, chemical manufacturing	Also in motor vehicle exhaust
heptane and octane isomers	Oil and gas production, asphalt, gasoline	Also in motor vehicle exhaust
n-nonane	Dry cleaning, degreasing, motor vehicles	Also in motor vehicle exhaust
xylenes	Solvent use, refining, mobile sources	Reactive
n-decane, undecane	Fuel storage, surface coatings	More abundant in diesel than gasoline exhaust
formaldehyde	Fuel combustion	Also a key photochemical reaction product (secondary source)
acetone	Surface coating	Also most abundant VOC in landfill emissions and a product of photochemistry
acetaldehyde	Fuel combustion	Also a product of photochemistry

Adapted from Stoeckenius et al., 1994a; SPECIATE; U.S. EPA, 1998

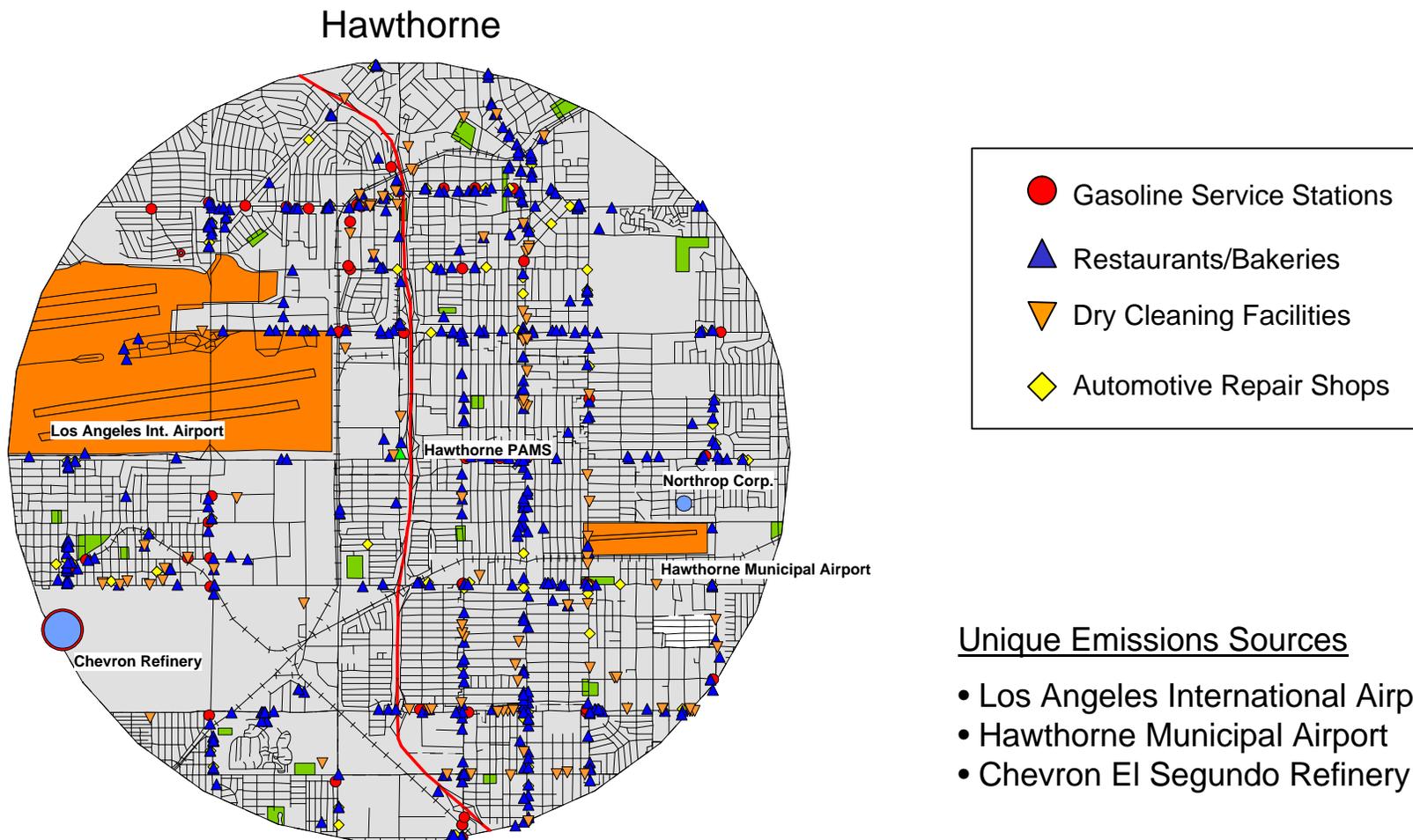
Example Approach to Source Apportionment (1 of 2)

- Understand the airshed geography and topography using maps, photographs, site visits, etc.
- Investigate the size, composition, and location of emission sources.
- Understand the typical meteorology of the site including diurnal and seasonal variations.
- Investigate the spatial and temporal characteristics of the data including meteorological dependence.
- Investigate the relationships among species using scatter plot matrices, correlation matrices, and other statistical tools.

Example Approach to Source Apportionment (2 of 2)

- Apply cluster and factor analysis techniques using standard statistical packages to get an overall understanding of VOC relationships and groupings by time of day, episode, etc.
- Apply UNMIX to investigate the possible number of factors (i.e., sources).
- Apply positive matrix factorization (PMF) using the number of factors determined by UNMIX to obtain “source” profiles with more species.
- Apply the chemical mass balance (CMB) using the “source” profiles from PMF in order to obtain source contribution estimates.
- Compare source contributions estimates and source profiles to the emission inventory.

Understanding the Monitoring Site

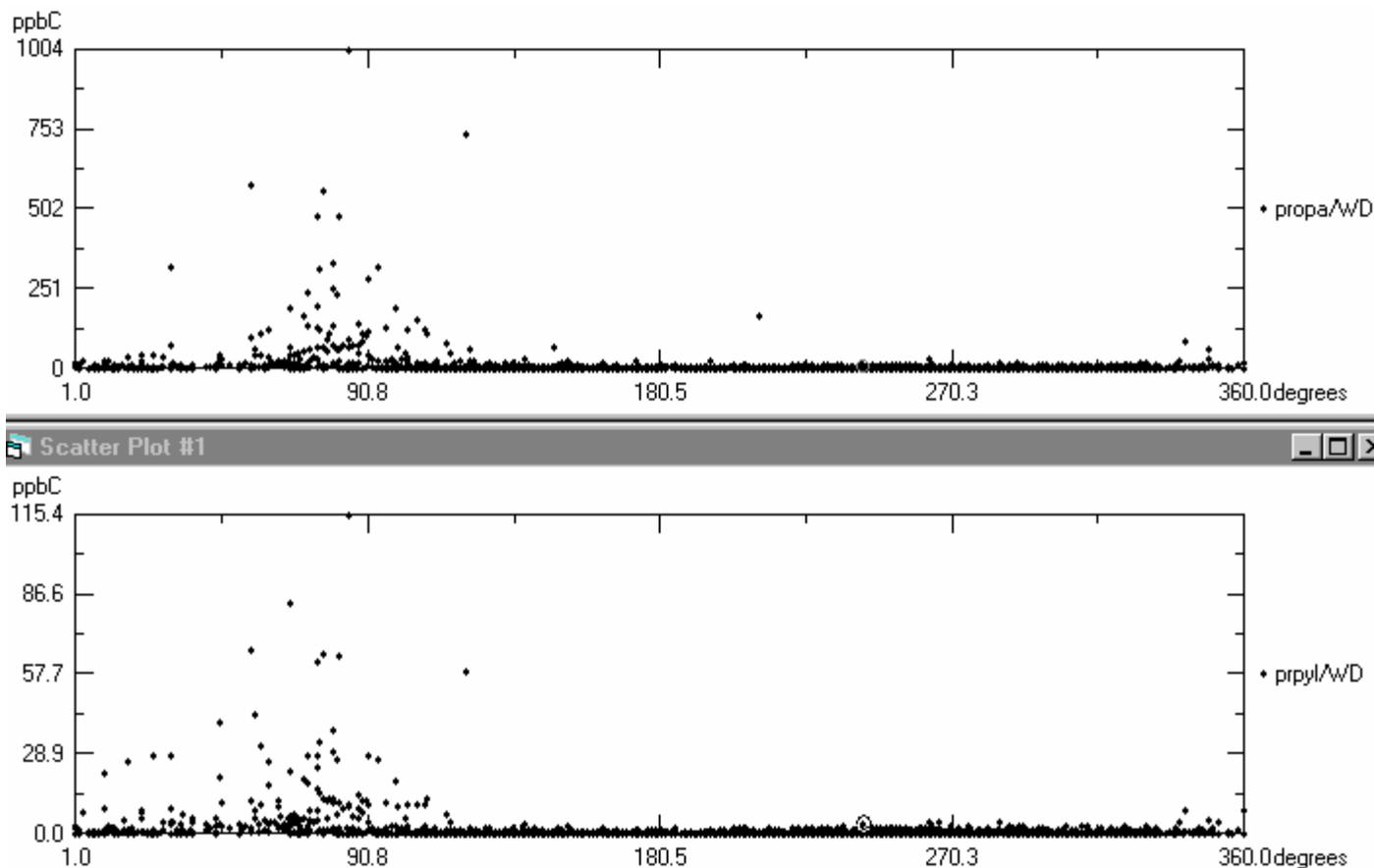


Unique Emissions Sources

- Los Angeles International Airport
- Hawthorne Municipal Airport
- Chevron El Segundo Refinery

Depiction of the Hawthorne, CA PAMS site including land features within a 5-km radius of the site. VOC emission sources such as gasoline stations are shown. Sources such as the two airports and the refinery may have unique emission profiles. (Roberts et al., 2000) Plot prepared using MAPInfo.

Meteorological Summary



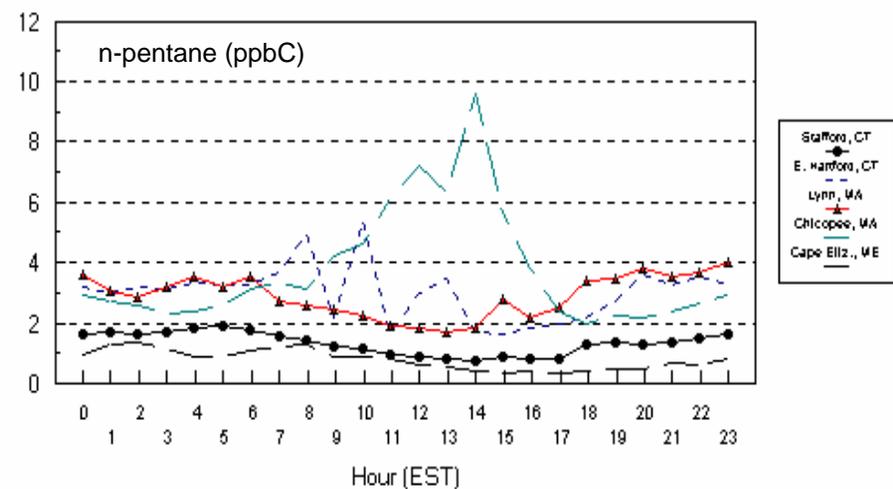
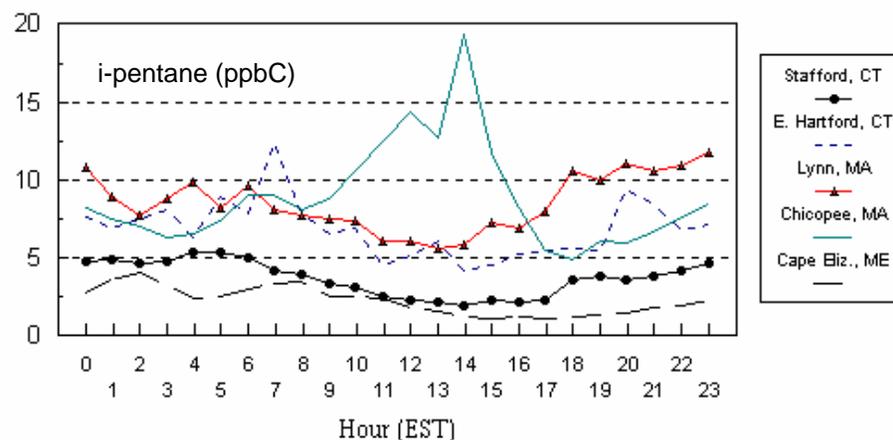
Wind direction dependence of high propane (top) and propene (bottom) concentrations (ppbC) at the Lums Pond, DE PAMS site during 1996. An industrial complex that reports significant VOC emissions is located near the site at a direction of 50 to 100 degrees (Main et al., 1999). Other useful analyses include wind roses, pollution roses (i.e., concentration as a function of wind direction), synoptic meteorological summaries, etc.

Assessing Spatial and Temporal Characteristics

- Relatively straight-forward analyses of the spatial and temporal characteristics of VOCs can be used to obtain information regarding the data.
- These investigative analyses can include the use of time series plots of total VOC and species concentrations, scatter plots, individual sample “fingerprints”, box whisker plots, and summary statistics.
- These investigations can help the analyst identify important species, species relationships, time periods of interest, and likely sources.

Example “Simple” Analysis

- This example shows the average diurnal concentrations of isopentane and n-pentane at five Northeast PAMS sites during the month of July 1994. These species show an increase during the day at Chicopee, MA compared to the other sites.
- A unique local source of these species (along with cyclopentane and 2,2-dimethylbutane) may be emitting these species.
- A next step would be to inspect source profiles to get some ideas about potential sources.



Adapted from NESCAUM, 1995

Investigation of Source Profiles Using EPA SPECIATE

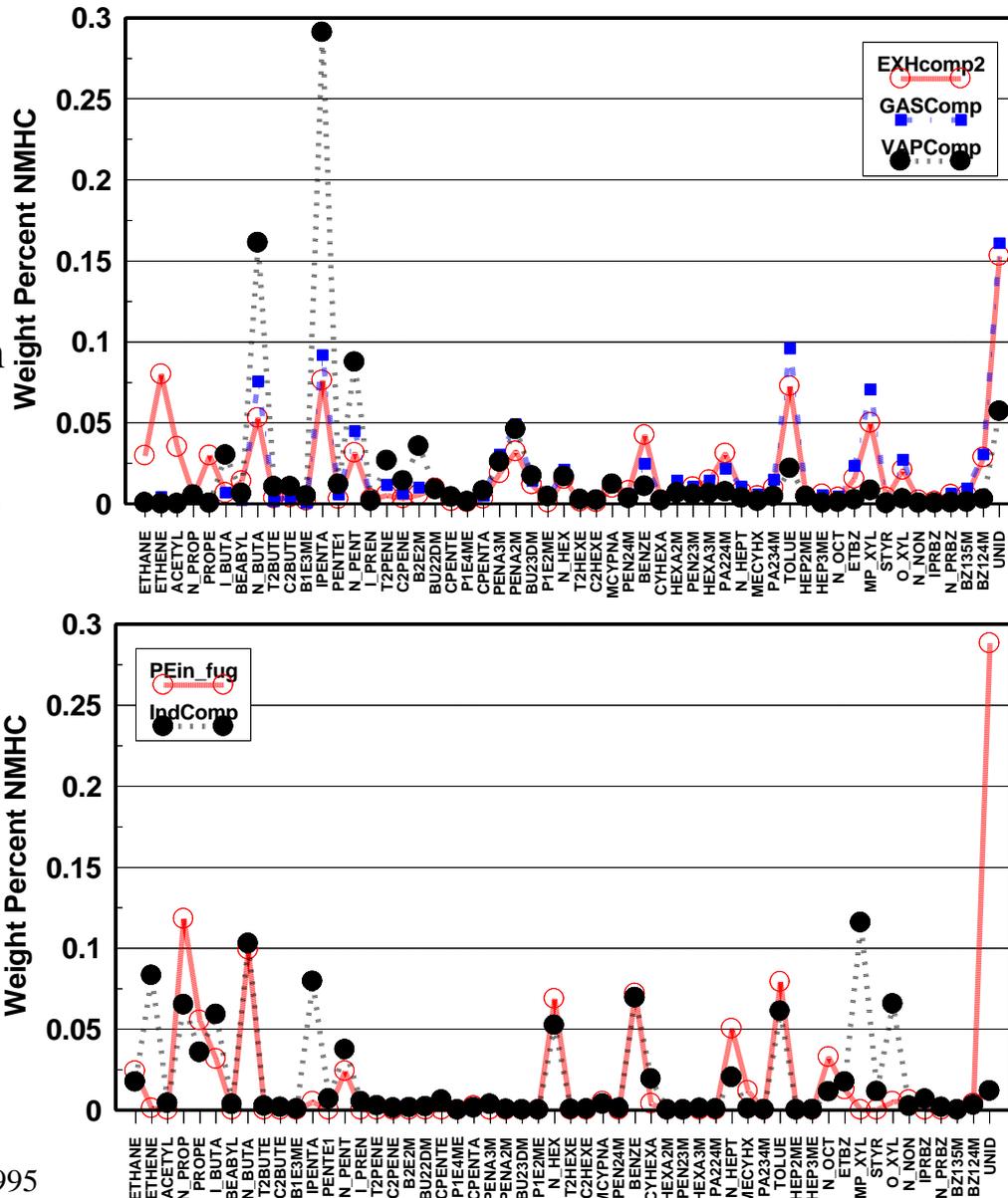
- The species i-pentane, n-pentane, cyclopentane, and 2,2-dimethylbutane stand out in the previous figure. These VOCs were found in the source profiles shown at right.
- Shading in the table indicates plausible sources based on the local emission inventory. The profile of another plausible source, jet fuel, contains only straight-chain C7 to C15 alkanes. This source cannot be fully assessed since PAMS VOCs are only reported to C11 alkanes.

SPECIATE Profile No.	Source Description
1209	Oil field pipeline tanks
1211	Refinery crude oil storage
1210	Pipeline terminal tanks
1206	Crude oil production
1207	Well heads composite
1208, 1212, 1205	Crude oil production
1306, etc.	Motor vehicle exhaust
1014, etc.	Gasoline blends

Comparing Source Profiles

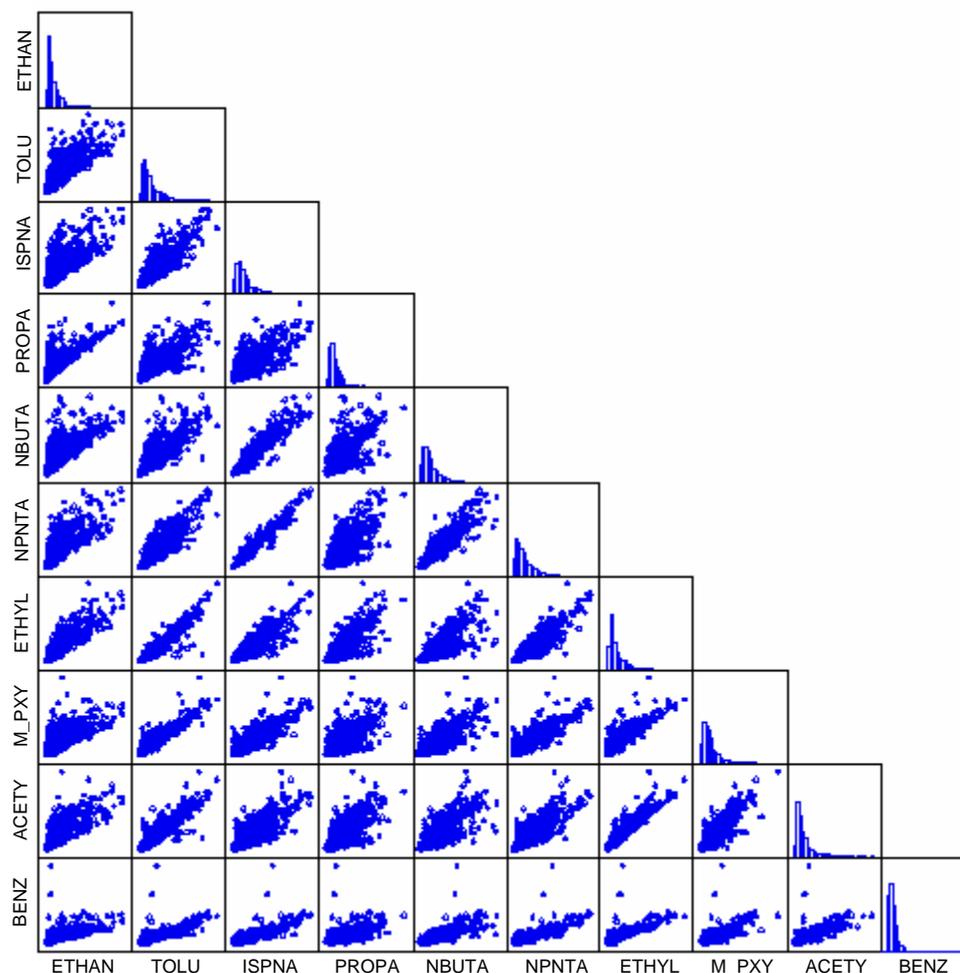
- In source apportionment, it is important to understand the similarities and differences between emission source profiles.
- This example shows source profiles from data collected in Texas during the 1993 COAST. Composite profiles for motor vehicle exhaust, liquid gasoline, gasoline vapor, petroleum industry fugitive emissions, and industry.
- Note that only a few species differ significantly between profiles. The similarities mean that it can be difficult to distinguish among the sources.

Lu and Fujita, 1995



Investigating Species Relationships

- Example scatter plot matrix (SPLOM) used to assess relationships among hydrocarbons. Hydrocarbons with well-defined edges in the scatter plots are good candidates for source apportionment (e.g., propane/ethane, acetylene/ethylene).
- To interpret a SPLOM, locate the row variable (e.g., ISPNA-isopentane) near the top left) and the column variable (TOLU-toluene) on the bottom. The intersection is the scatter plot of the row variable on the vertical axis against the column variable on the horizontal axis. Each column and row are scaled so that data points fill each frame. The diagonal plots contain histograms of the data for each row variable.



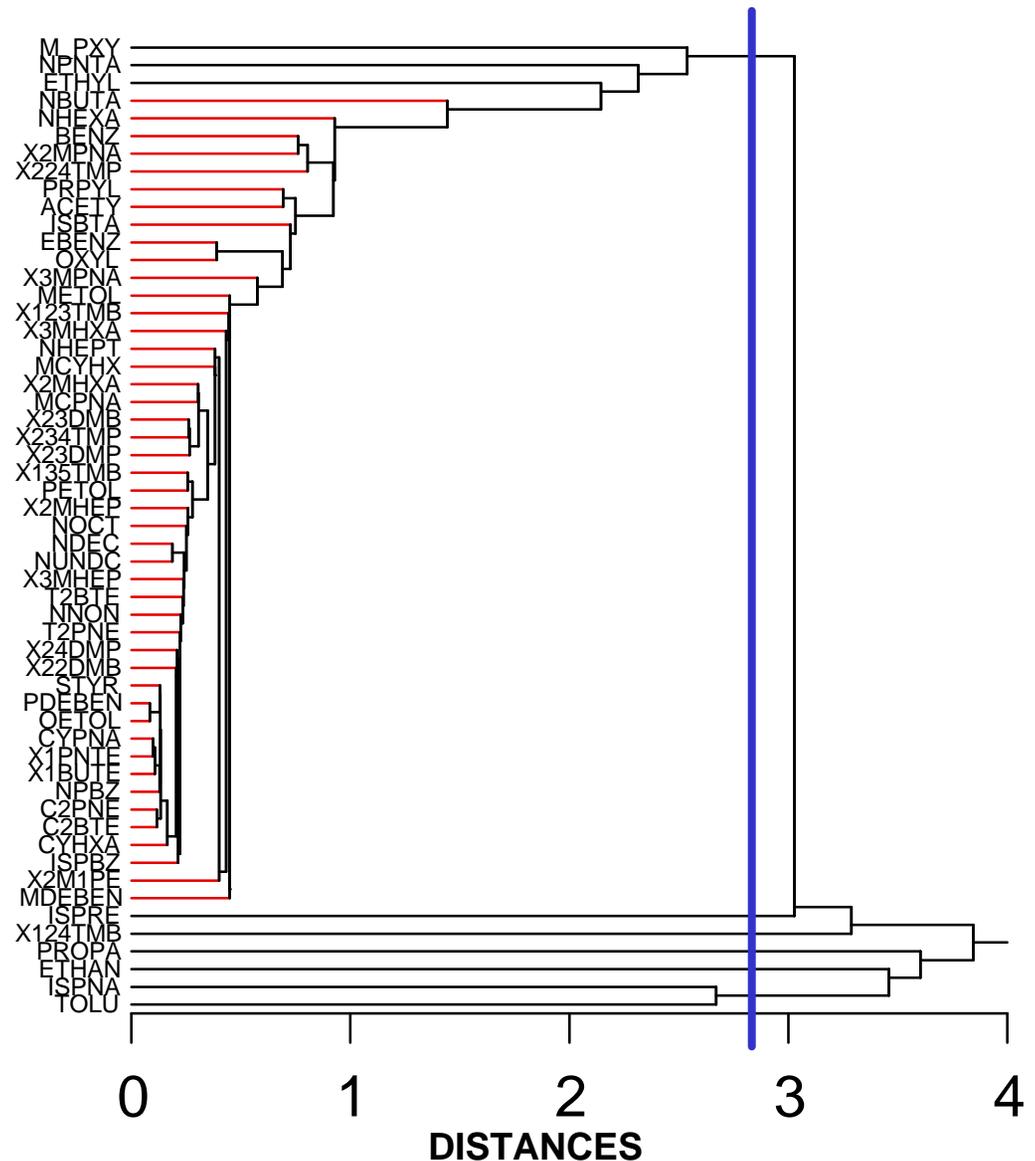
Scatter plot matrix of ten abundant hydrocarbons at Lake Clifton, MD during 1996. (Main et al., 1999)
Prepared using SYSTAT.

Cluster and Factor Analyses

- **Cluster analysis** is a multivariate procedure for grouping data by similarity between observations (i.e., observations with similar chemical compound concentrations are grouped).
 - This is typically done using a Euclidean distance between each pair of observations (squared differences between individual concentrations summed across all species).
- **Factor analysis** is a procedure for grouping data by similarity between variables (i.e., variables that are highly correlated are grouped).
 - This is typically done using the correlation between each pair of variables.
 - Correlation measures are often used because they are not influenced by differences in scale between objects. This is important because VOC species concentrations can vary over an order of magnitude or more.
 - Factors indicate the best associations among variables while regression lines indicate the best predictions.
 - The factor model expresses the variation within, and the relations among, observed variables as partly common variation among factors and partly specific variation among random errors.

Example Cluster Analyses

- This example shows a hierarchical cluster analysis of morning concentrations of PAMS VOCs at Essex, MD, prepared using SYSTAT.
- The hydrocarbons from m-&p-xylene (M_PXY) to diethylbenzene (MDEBEN) form a cluster with motor vehicle exhaust components (e.g., acetylene - ACETY and ethene - ETHYL) and evaporative emissions (e.g., n-butane - NBUTA). Other groupings include natural gas components propane (PROPA) and ethane (ETHAN), an unknown (possible industrial) source of 1,2,4-trimethylbenzene (X124TMB), and an i-pentane (ISPNA) and toluene (TOLU) cluster possibly indicative of solvent use.



Cluster analysis for Essex, MD in 1997 (morning data only).
The bold vertical line is provided for discussion purposes.
(Main et al., 1999)

Example Factor Analyses

- This example shows a Varimax-rotated factor analysis of morning concentrations of PAMS VOCs at Philadelphia, PA, prepared using SYSTAT.
- Three factors account for about 61% of the variance in the data. The first factor contains benzene (BENZ), toluene (TOLU), butanes, pentanes, and acetylene and is probably representative of motor vehicle exhaust and evaporative emissions.
- The second factor contains o-xylene, 1,2,4-trimethylbenzene, undecane, ethyl toluene, nonane, and other aromatic hydrocarbons and may be indicative of industrial emissions. Factor 3 contains isoprene, indicative of biogenic emissions.

	1	2	3
X224TMP	0.873	0.274	0.283
TOLU	0.860	0.409	0.148
T2PNE	0.859	0.358	0.076
X234TMP	0.842	0.242	0.272
X24DMP	0.840	0.335	0.227
X2MPNA	0.836	0.285	-0.062
X22DMB	0.828	0.326	0.229
M_PXY	0.828	0.494	0.126
X3MPNA	0.825	0.229	0.037
X23DMP	0.825	0.308	0.268
X3MHXA	0.818	0.242	0.155
OXYL	0.813	0.516	0.140
NPNTA	0.812	0.182	-0.034
X2MHXA	0.804	0.197	0.155
NHEXA	0.784	0.165	0.020
C2BTE	0.776	0.188	0.039
EBENZ	0.776	0.487	0.153
T2BTE	0.758	0.277	0.119
NHEPT	0.755	0.216	0.026
ISPNA	0.730	0.261	0.160
ETHAN	0.729	0.188	0.270
X3MHEP	0.721	0.303	0.067
BENZ	0.698	0.185	0.205
X2M1PE	0.667	0.185	-0.000
MCYHX	0.652	0.252	0.239
MCPNA	0.602	0.135	0.121
CYPNA	0.601	0.145	0.496
ACETY	0.593	0.234	0.338
PROPA	0.575	0.208	0.059
CYHXA	0.572	-0.052	-0.364
NBUTA	0.563	0.127	-0.107
X124TMB	0.553	0.800	0.046
X2MHEP	0.540	0.292	0.170
ISBTA	0.531	0.157	0.046
ETHYL	0.520	0.213	0.348
C2PNE	0.514	0.097	0.118
NUNDC	0.514	0.523	0.273
OETOL	0.351	0.888	0.065
X135TMB	0.486	0.823	0.021
ISPBZ	0.036	0.814	-0.215
NDEC	0.385	0.738	0.199
PETOL	0.313	0.735	-0.079
NPBZ	0.299	0.733	0.073
NNON	0.179	0.630	0.018
METOL	0.404	0.549	-0.025
MDEBEN	0.398	0.506	0.304
X1BUTE	0.213	0.004	0.836
ISPRE	0.206	-0.115	0.747
X23DMB	0.232	0.005	0.077
PRPYL	0.164	-0.006	-0.032
X123TMB	-0.074	0.138	-0.165
NOCT	0.291	0.295	-0.046
STYR	-0.016	0.461	0.080
PDEBEN	0.451	0.487	0.349

Factor analysis results for Philadelphia, PA in 1997 (morning data only). Factor loadings > 0.5 have been highlighted. Factors 1, 2, and 3 account for 39%, 16%, and 6% of the total variance respectively. (Main et al., 1999)

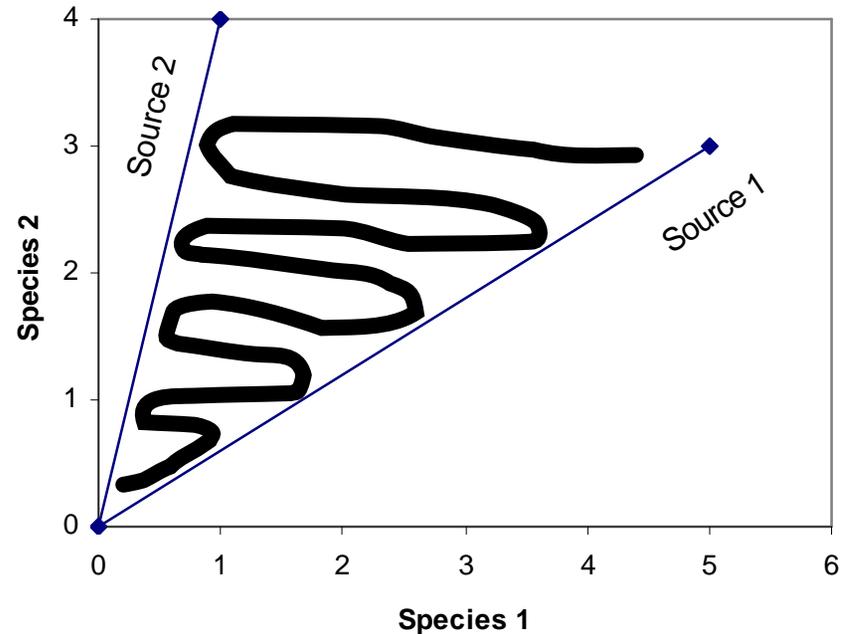
UNMIX

- **UNMIX** is a multivariate receptor modeling package that inputs observations of particulate composition and seeks to find the number, composition, and contributions of the contributing sources or source types. UNMIX also produces estimates of the uncertainties in the source compositions. UNMIX uses a generalization of the self-modeling curve resolution method developed in the chemometrics community (Henry, 1997).
- **Data Requirements:** UNMIX inputs data in tabular format as flat ASCII files. Each column represents one species and each row is one sample or observation. It is very helpful to have a measure of total mass included in the data. It is generally best to analyze data from one site at a time. Basically, the more data the better, in terms of both species and observations. The upper limit on the amount of data is determined by the size of the computer. Based on experience, the practical lower limit on the number of observations is 50 to 100.
- **System Requirements:** UNMIX is currently implemented as a MATLAB program (see the website mathworks.com for more information). UNMIX has a graphical user interface so the user need not be familiar with MATLAB itself.

Understanding UNMIX

- Consider two sources:
Source 1 =
50% species 1, 30% species 2,
and 20% other.

Source 2 =
10% species 1, 40% species 2, and
50% other.
- For sources with unique species ratios, “edges” can be observed in the relationship between species. UNMIX looks for these edges and uses them to constrain the results.



Ambient data collected at a receptor site would normally contain a mixture of both sources 1 and 2. That means that most of the data would lie between the two edges illustrated above.

Example UNMIX Analysis

- To be added.

Positive Matrix Factorization

- **Positive matrix factorization (PMF)** was developed by Dr. P. Paatero (Dept. of Physics, University of Helsinki). PMF can be used to determine source profiles and source contributions based on the ambient data. Features include the following:
 - PMF uses weighted least squares fits for data that are normally distributed and maximum likelihood estimates for data that are distributed log normally.
 - PMF weights data points by their analytical uncertainties.
 - PMF constrains factor loadings and factor scores to nonnegative values and thereby minimizes the ambiguity caused by rotating factors. This is one of the major differences between PMF and principal component analysis (PCA).
 - PMF expresses factor loadings in mass units which allows factors to be used directly as source signatures.
 - PMF provides uncertainties for factor loadings and factor scores which makes the loadings and scores easier to use in quantitative procedures such as chemical mass balance.

Example PMF Analysis

- To be added.

Chemical Mass Balance Modeling

- The purpose of CMB receptor modeling is to apportion ambient VOC (or any categorical pollutant) to emission sources. The source apportionment of ambient VOC provides independent evaluation of the relative contributions of sources to ambient levels of VOC.
- The CMB model expresses each measured chemical species concentration as a linear sum of products of source profile species and source contributions, and then solves a set of linear equations.
- Model input includes:
 - Source profile species (fractional amount of species in the VOC emissions from each source type).
 - Receptor (ambient) concentrations.
 - Realistic uncertainties for source and receptor values. Input uncertainty is used to weight the relative importance of input data to model solutions and to estimate uncertainty of the source contributions.
- Model output includes:
 - Contributions from each source type to the total ambient VOC and individual species and the uncertainty.

CMB Model Assumptions

- Composition of source emissions do not change during travel from the point of emission (where the source profile is defined) to the point of receptor site measurements (*minor contributors are frequently omitted*).
- Chemical species do not react with each other (i.e., they add linearly) (*little known about this*).
- All sources which may significantly contribute to the receptor have been identified and their emissions characterized (*minor contributors may be omitted*).
- Number of sources or source categories is less than the number of chemical species (*the larger the difference, the better*).
- Source profiles are linearly independent (*degree of independence depends on the variability of the source profile*). It may be necessary to combine chemically similar source categories or add additional fitting species to the model.
- Measurement uncertainties are random, uncorrelated, and normally distributed (*effects unknown*).

Modeling Tips (1 of 3)

Estimating Uncertainty in Ambient Data

$$\sigma (C) = ((2MDL)^2 + (CV*C)^2)^{1/2}$$

where:

- σ = root mean square error for concentration value (C)
- MDL = minimum detection limit for auto-GC (0.1 to 0.2 ppbC)
- CV = coefficient of variation of measurements (5 to 10 percent)
- C = concentration

Example for C = 10 ppbC

$$\begin{aligned}\sigma (C) &= ((2*0.2)^2 + (0.10*10)^2)^{1/2} \\ &= 1.08 \text{ ppbC}\end{aligned}$$

Modeling Tips (2 of 3)

Converting Units from ppbC to $\mu\text{g}/\text{m}^3$ (at 25°C)

$$\mu\text{g}/\text{m}^3 = \frac{\text{ppbC} * \text{MW} * 273 \text{ K}}{(22.4 * 298 \text{ K} * \#C)}$$

where

#C = number of carbons in the molecule

22.4 = liters/mole air at standard temperature and pressure (STP)

MW = molecular weight in g/mole VOC

(conversions from g to μg and liters to m^3 also are needed to obtain the proper units)

Example for 1 ppbC benzene

$$\begin{aligned}\mu\text{g}/\text{m}^3 &= \frac{10^{-9} \text{ moles VOC}}{\text{mole air}} * \frac{78.1\text{g}}{\text{mole VOC}} * \frac{273\text{K}}{298\text{K}} * \frac{\text{mole air}}{22.4\ell} * \frac{1}{6} * \frac{10^6 \mu\text{g}}{\text{g}} * \frac{10^3 \ell}{\text{m}^3} \\ &= 0.532\end{aligned}$$

Modeling Tips (3 of 3)

Handling Missing Data

- Species with > 5 percent of their values either missing or 0 may need to be excluded from multivariate analyses in order to obtain meaningful results.
- For weekday averages of continuous data, set a lower limit for the number of hours required each day, e.g., 22 of 24 hours.

Source Profile Uncertainties

- Source data should be accurate and precisely measured and uncertainty should reflect the variability expected from a number of individual emitters in the same source type. At a minimum, profiles are no more precise than the analytical techniques used to measure them.

As a first approximation, assume $\sigma =$

10-15% for values > 5 times LQL

20% for species with MDL ≥ 0.1 wt. %

$((\text{LQL})^2 + (\text{wt. \%} * \text{relative standard error})^2)^{1/2}$ for species with MDL < 0.1 wt. %

where

LQL = lower quantifiable limit

MDL = minimum detection limit

- Variability in measurements due to changes in operating conditions, type of source, etc. may far exceed measurement error.

Selecting Source Profiles

- For receptor modeling, use profiles that are representative of the study area during the period when ambient data were collected.
- Include ubiquitous sources such as motor vehicle exhaust, gasoline evaporation, liquid gasoline, and biogenics.
- Include point sources identified in the emission inventory.
- Place source data on the same basis as the ambient data (i.e., adjust source data to include only species that are measurable by GC-FID).
- Unresolved species or groups (e.g., isomers of pentane) may be allocated to individual species using average ratios from similar data sets.

Accurate source profiles are the key to successful modeling.

Selecting Fitting Species (1 of 3)

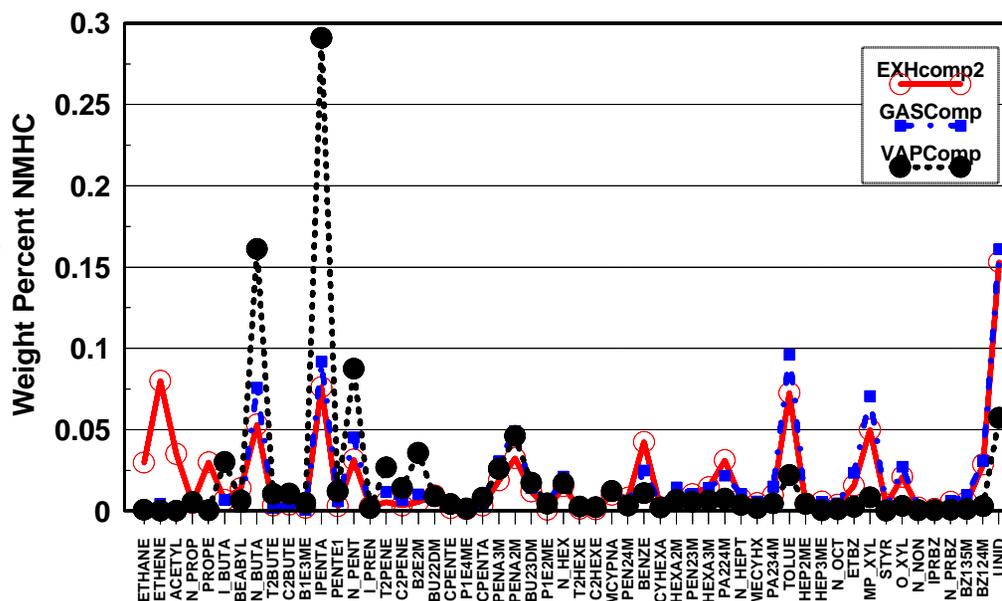
- Receptor models assume relative proportions of chemical species change little between source and receptor. Hydrocarbons are photochemically reactive and most species do not strictly meet this assumption.
- Literature recommends selection of species with "sufficiently long" atmospheric half-lives. Cut-offs have been made at 5, 11, and 33 hours (see table at the end of the section).

Isoprene is the exception. Since it is the only PAMS target species directly associated with biogenic emissions, it must be used. Therefore, source contribution estimates for isoprene should be considered a lower limit because of its reactivity.

- Investigate the available source profiles: which species are the most important, which species are unique among the sources?

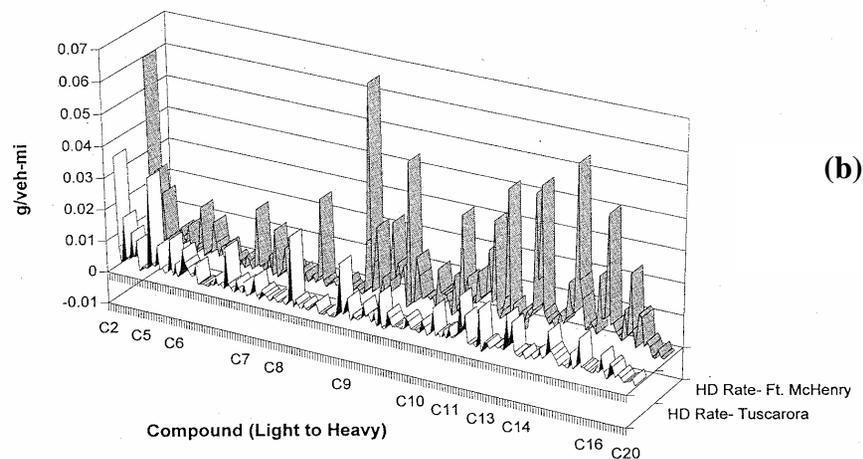
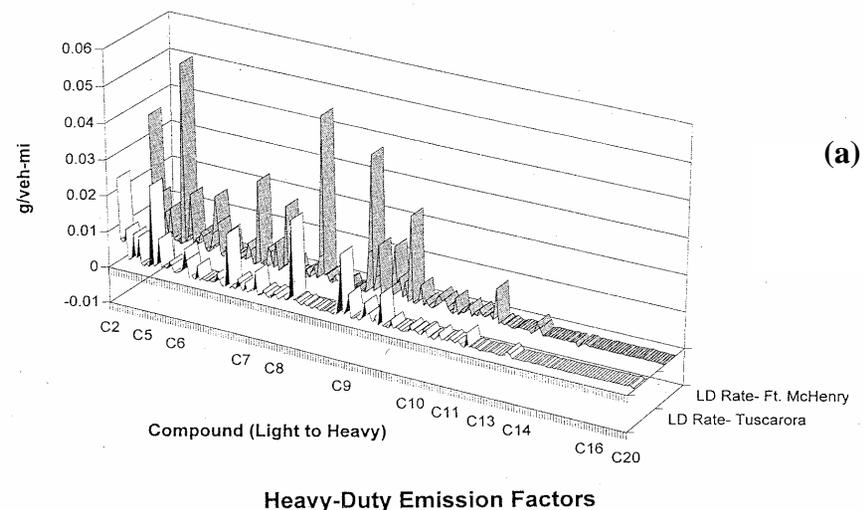
Selecting Fitting Species (2 of 3)

- This example shows three source profiles from data collected in Texas during 1993. Composite profiles for motor vehicle exhaust, liquid gasoline, and gasoline vapor are shown.
- Note that the profiles are similar making discerning between these sources difficult.
- However, differences do exist, including ethane, ethene, and acetylene (exhaust only), i-butene (vapor), low i-butene but high toluene (liquid gasoline).



Selecting Fitting Species (3 of 3)

- This comparison of light-duty and heavy-duty emissions illustrates the differences between gasoline and diesel exhaust.
- The x-axis lists the compounds by gas chromatographic retention order with the carbon number of the n-alkanes listed for reference. While there is a significant difference between the emission sources for VOCs greater than C10, the PAMS target list may not be adequate to separate the sources



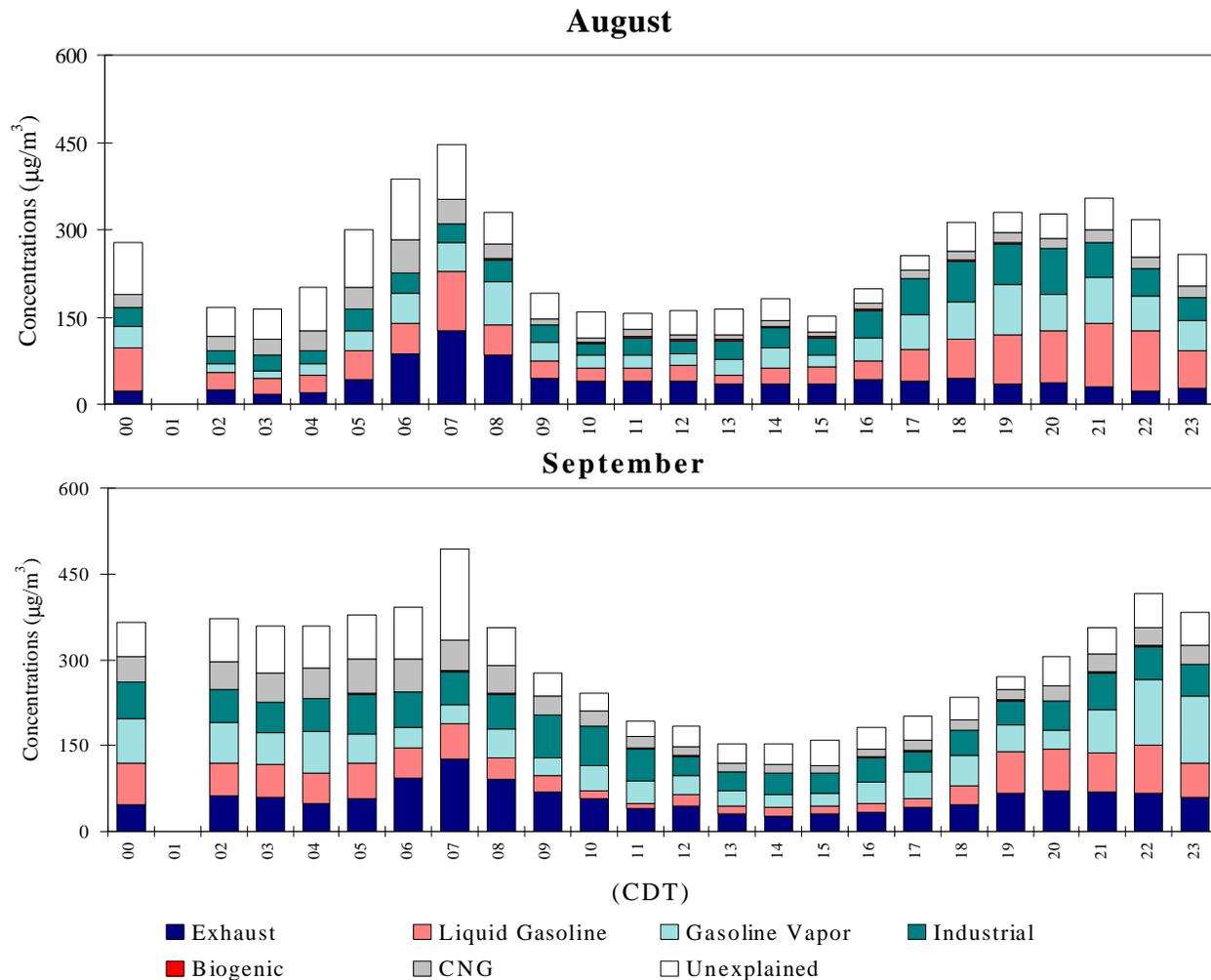
Comparison of (a) light duty (LD) and (b) heavy duty (HD) emissions at Fort McHenry Tunnel (Baltimore, MD) and Tuscarora Tunnel (PA). (Sagebiel et al., 1996)

Example Investigations Using CMB Results

CMB results can be assessed in many ways including:

- Day-of-week and diurnal analyses of source contribution estimates.
- Graphical displays of source contribution estimates by wind direction and time of day.
- Sensitivity of source contribution estimates to fitting species, particularly the reactive species.
- Scatter plots of predicted versus measured concentrations for the sum of the fitting species and sum of selected reactive species by site and time of day.

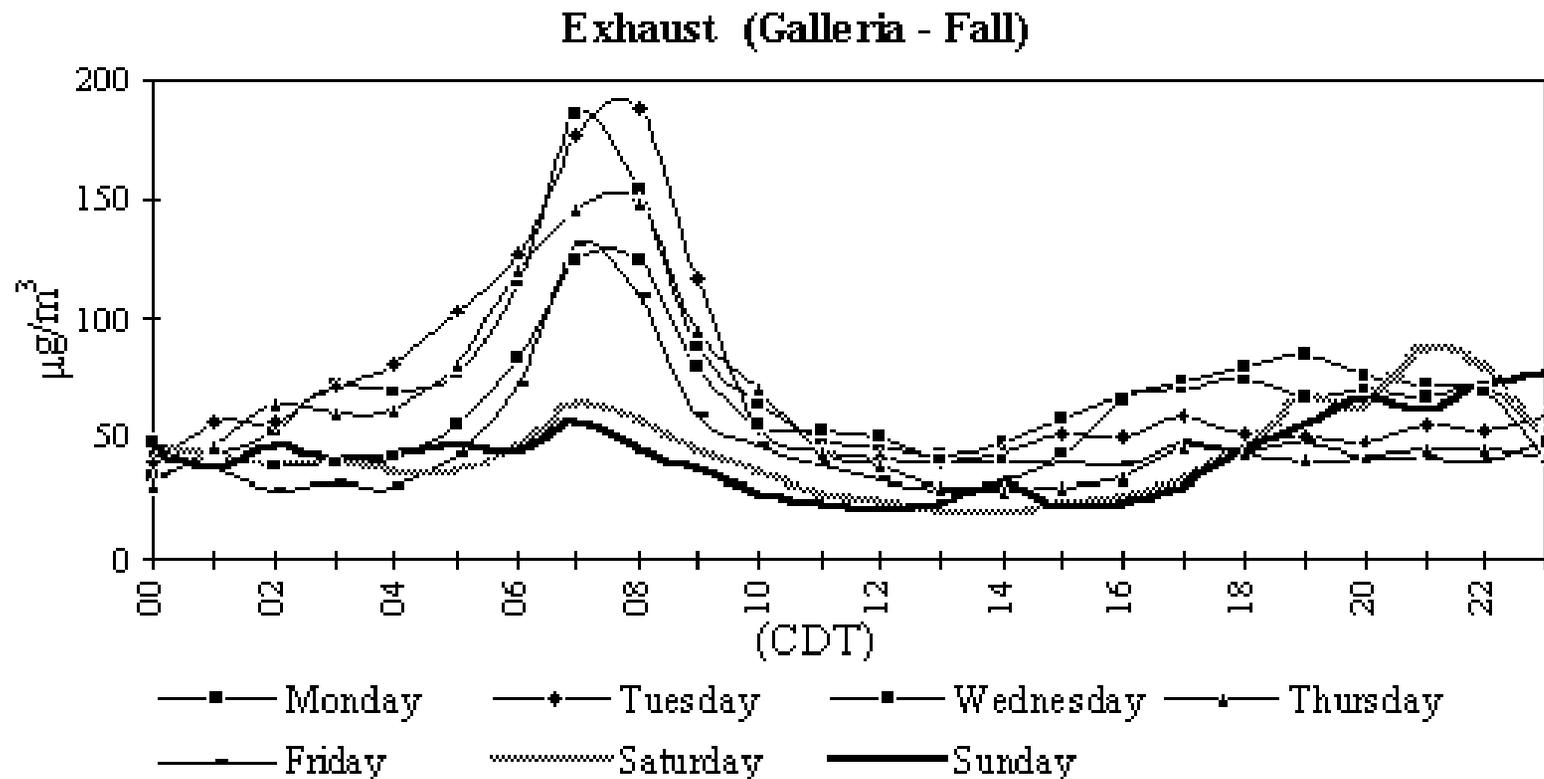
Example CMB Analyses (1 of 3)



Lu and Fujita, 1995

This example shows source contribution estimates for the 1993 auto-GC data collected at Clinton (Houston), TX by time of day and month. Note total concentrations were higher overnight in September including the gasoline vapor component. Side-by-side bar plots should be employed to best assess trends in individual source components.

Example CMB Analyses (2 of 3)

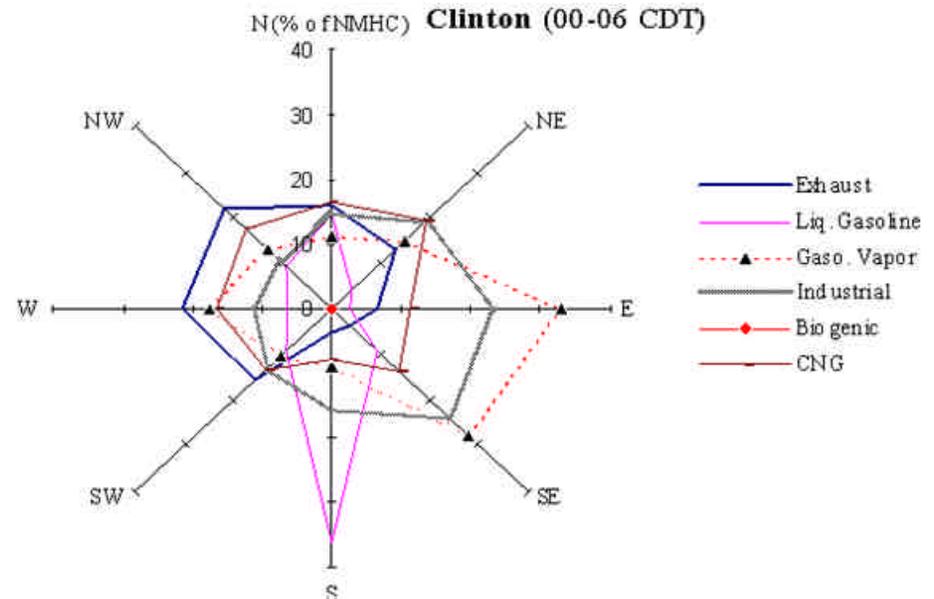


Lu and Fujita, 1995

This example shows hourly source contribution estimate averages for motor vehicle exhaust by day of week for auto-GC data collected at Galleria (Houston), TX in 1993. Note that the Saturday and Sunday diurnal profile is dramatically different than the weekdays.

Example CMB Analyses (3 of 3)

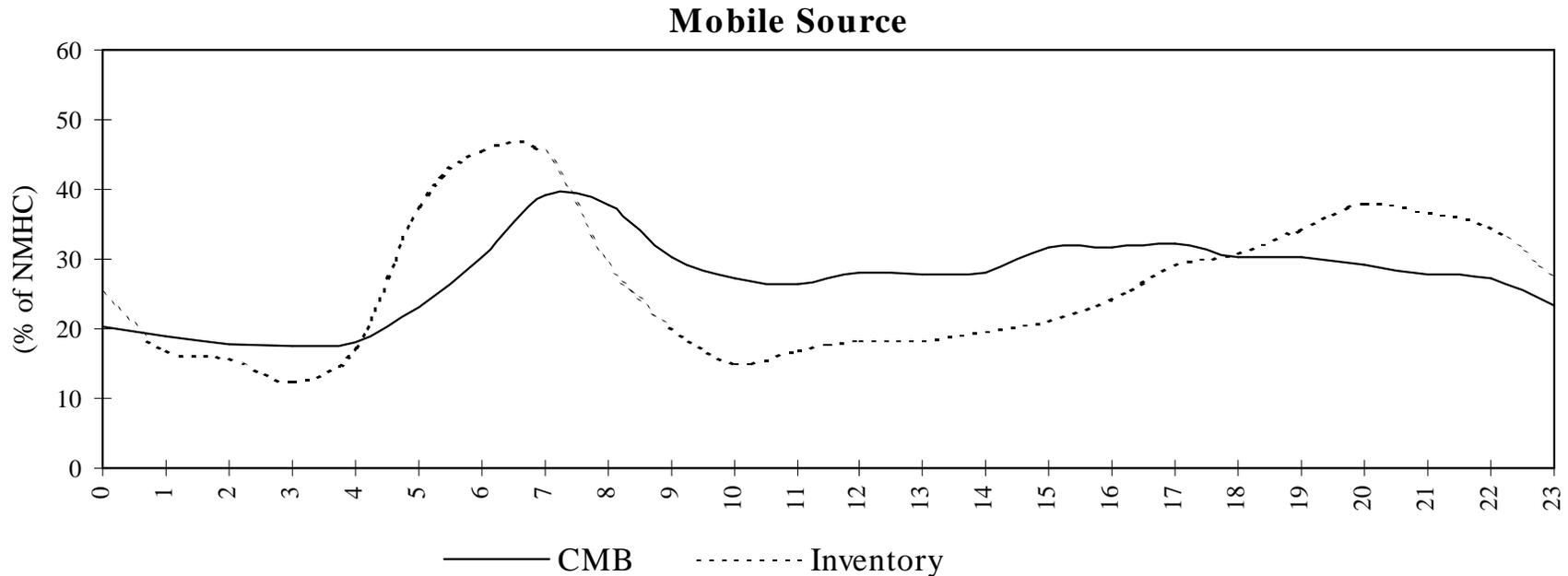
- This example shows the wind directional dependence of source contributions from 0000-0600 CDT at the Clinton (Houston), TX site in weight percent.
- The gasoline exhaust and liquid gasoline components were from different directions indicating separate sources.
- The analyst needs to compare these results to the site and source characteristics.



Lu and Fujita, 1995

Prepared in MS Excel using radar plots.

Comparing CMB Results and the Emission Inventory



Lu and Fujita, 1995

This example compares the CMB results for mobile sources by time of day with the emission inventory at Galleria (Houston), TX in 1993. The inventory appears to estimate VOC emissions occurring earlier than the ambient data indicated based on CMB results.

Uncertainties and Limitations in Source-Receptor Analyses

- **Many emitters have similar species composition profiles.** The practical implication of this limitation is that one may not be able to discern between the dust emitted by agricultural practices and dust emitted by mobile sources on unpaved roads. One approach here is to add additional species to reduce collinearity. For example, PM species could be used with VOC profiles to differentiate between diesel and gasoline emissions.
- **Species composition profiles change between source and receptor.** Most source-receptor models cannot currently account for changes due to photochemistry such as reactivity and secondary formation.
- **Receptor models cannot predict the consequences of emissions reductions.** One cannot estimate source profiles resulting from changes in emissions and predict ambient concentrations using receptor models. However, source-receptor models can check if control plans achieve their desired reductions.

Method and Tool Availability (1 of 2)

- Species relationships and the development of reasonable constraints (typical ratios) on the data can be investigated using scatter plots.
- Cluster, factor, and principal component analyses and linear regression are available in most standard statistical packages. A nice on-line description of these techniques is available at http://www.sbg.ac.at/geo/idrisi/geostat/tutorial/multivariate_statistics/gg616.html
- A version of PMF is currently being tested by EPA. The software consists of stand-alone executables (run from the DOS prompt), hence this version runs only on a PC. The order form for PMF is available at <ftp://rock.helsinki.fi/pub/misc/pmf/pmforder.pdf>. "PMF" refers to both PMF2 (a 2-way deconvolution) and PMF3 (a 3-way deconvolution). Dr. Paatero, the developer of PMF, is currently developing a more flexible version of the deconvolving concept, and that software is called ME (multi-linear engine). Information regarding the ME is also available from the website. There is a fee to purchase these tools (\$400, \$600, and \$750 for 1, 2 or 3 of the tools).

Method and Tool Availability (2 of 2)

- The current version of UNMIX is being tested by EPA and others. Contact Ron Henry for a copy (rhenry@hypatia.usc.edu). UNMIX is currently implemented as a MATLAB program (see the website www.mathworks.com for more information); therefore, the user must have a current version of MATLAB in order to run UNMIX.
- CMB is in transition. The older EPA-approved version, CMB7, is available at <http://www.epa.gov/scram001/>. A newer EPA-sponsored (but not approved) version, CMB8.0, is available from <ftp://eafs.sage.dri.edu/cmb80/model/>. The newest version, EPA-CMB8.2 is nearing completion.
- The CAPITA Monte Carlo model was developed in the 1980's to provide quantification of regional atmospheric transport, transformation, and removal processes governing the source receptor relationship. Information regarding the model is available at http://capita.wustl.edu/CAPITA/CapitaReports/MonteCarloDescr/mc_pcim0.html#monte
- Information regarding the use of air mass history models and techniques for source attribution is available at http://capita.wustl.edu/capita/capitareports/airmasshist/EPASrcAtt_jul17/index.htm
- Information regarding the NOAA trajectory cluster model is available at <http://www.arl.noaa.gov/slides/ready/index.html>

How to Obtain Source Profiles (1 of 2)

- EPA SPECIATE (<http://www.epa.gov/ttn/chief/software.html#speciate>) was recently updated (version 3.1) and now contains many measurements conducted as part of recent studies (e.g., NARSTO-Northeast) including:
 - Callahan tunnel in Boston (MA), Lincoln tunnel (NY), Fort McHenry tunnel (MD), Van Nuys and Sepulveda tunnels (CA), Tuscarora tunnel (PA), Federal building garage (MA) all from 1995.
 - Auto-Oil Program measurements for 1989 and 1983-1985 fleets.
 - Gasoline liquid and/or vapor composites from Boston, Los Angeles, Seattle, and El Paso (1995 and 1996).
 - Degreasing and solvent use, consumer products, industrial sources (i.e., refineries, chemical facilities), oil and gas production, burning, and surface coatings.

How to Obtain Source Profiles (2 of 2)

- Literature review: Additional on-road vehicle exhaust profiles have been developed from measurements in the San Francisco Bay Area, Caldecott Tunnel (Kirchstetter et al., 1999), 1993 Texas source profiles (Fujita, 1995), and elsewhere.
- Federal Test Procedure measurements for 1975-1982 model years (Sigsby et al., 1987).
- Local, state, and federal agencies; for example, California has information available at <http://arbis.arb.ca.gov/emisinv/emsmain/emsmain.htm>
- Analysis of ambient data (e.g., using UNMIX, PMF).

Summary

- When an area experiences high concentrations of ozone, particularly when the concentrations are in exceedance of the standard, research and analysis is needed to investigate the possible sources of ozone and ozone precursors leading to the high concentrations. Once the important sources are assessed, appropriate control measures can be developed.
- In this workbook section important emissions sources are described as well as source attribution methods and tools and their uncertainties.

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Converting ppbC to mg/m^3

Factors for PAMS hydrocarbon species to convert ppbC to mg/m^3 for use in CMB. To perform the conversion, multiply the concentration value by the conversion factor. Assumes room temperature of 25°C.

NAME	MW	Carbon No.	ppbC to mg/m^3	mg/m^3 to ppbC
ACETAL	44.1	2	0.901	1.109
ACETO	58.1	3	0.792	1.263
ACETYL	26.0	2	0.533	1.878
B1E3ME	70.1	5	0.574	1.743
B2E2M	70.1	5	0.574	1.743
BENZE	78.1	6	0.532	1.878
BU22DM	86.2	6	0.587	1.702
BU23DM	86.2	6	0.587	1.702
BUT1E	56.1	4	0.574	1.743
BZ124M	120.2	9	0.546	1.831
BZ135M	120.2	9	0.546	1.831
C2BUTE	56.1	4	0.574	1.743
C2HEXE	84.2	6	0.574	1.743
C2PENE	70.1	5	0.574	1.743
CPENTA	70.1	5	0.574	1.743
CPENTE	68.1	5	0.557	1.795
CYHEXA	84.2	6	0.574	1.743
ETBZ	106.2	8	0.543	1.842
ETHANE	30.1	2	0.615	1.626
ETHENE	28.1	2	0.574	1.743
FORMAL	30.0	1	1.228	0.814
HEP2ME	114.2	8	0.584	1.712
HEP3ME	114.2	8	0.584	1.712
HEXA2M	100.2	7	0.585	1.708
HEXA3M	100.2	7	0.585	1.708
IPENTA	72.2	5	0.590	1.694
IPRBZ	120.2	9	0.546	1.831
I BUTA	58.1	4	0.594	1.683
I PREN	68.1	5	0.557	1.795

NAME	MW	Carbon No.	ppbC to mg/m^3	mg/m^3 to ppbC
MCYPNA	84.2	6	0.574	1.743
MECYHX	98.2	7	0.574	1.743
MP_XYL	106.2	8	0.543	1.842
N BUTA	58.1	4	0.594	1.683
N DEC	142.3	10	0.582	1.718
N HEPT	100.2	7	0.585	1.708
N HEX	86.2	6	0.587	1.702
N NON	128.3	9	0.583	1.716
N OCT	114.2	8	0.584	1.712
N PENT	72.2	5	0.590	1.694
N PRBZ	120.2	9	0.546	1.831
N PROP	44.1	3	0.601	1.663
N UNDE	156.3	11	0.581	1.721
O_XYL	106.2	8	0.543	1.842
PA224M	114.2	8	0.584	1.712
PA234M	114.2	8	0.584	1.712
PEN23M	100.2	7	0.585	1.708
PEN24M	100.2	7	0.585	1.708
PENA2M	86.2	6	0.587	1.702
PENA3M	86.2	6	0.587	1.702
PENTE1	70.1	5	0.574	1.743
PROPE	42.1	3	0.574	1.743
STYR	104.1	8	0.532	1.878
T2BUTE	56.1	4	0.574	1.743
T2HEXE	84.2	6	0.574	1.743
T2PENE	70.1	5	0.574	1.743
TOLUE	92.1	7	0.538	1.857
UNID	13.9	1	0.566	1.765

Fujita, 1995

Converting ppbC to mg/m³

Factors for PAMS hydrocarbon species to convert ppbC to *mg/m³* for use in CMB. To perform the conversion, multiply the concentration value by the conversion factor. Assumes room temperature of 25°C.

NAME	MW	Carbon No.	ppbC to mg/m ³	mg/m ³ to ppbC
ACETAL	44.1	2	0.901	1.109
ACETO	58.1	3	0.792	1.263
ACETYL	26.0	2	0.533	1.878
B1E3ME	70.1	5	0.574	1.743
B2E2M	70.1	5	0.574	1.743
BENZE	78.1	6	0.532	1.878
BU22DM	86.2	6	0.587	1.702
BU23DM	86.2	6	0.587	1.702
BUT1E	56.1	4	0.574	1.743
BZ124M	120.2	9	0.546	1.831
BZ135M	120.2	9	0.546	1.831
C2BUTE	56.1	4	0.574	1.743
C2HEXE	84.2	6	0.574	1.743
C2PENE	70.1	5	0.574	1.743
CPENTA	70.1	5	0.574	1.743
CPENTE	68.1	5	0.557	1.795
CYHEXA	84.2	6	0.574	1.743
ETBZ	106.2	8	0.543	1.842
ETHANE	30.1	2	0.615	1.626
ETHENE	28.1	2	0.574	1.743
FORMAL	30.0	1	1.228	0.814
HEP2ME	114.2	8	0.584	1.712
HEP3ME	114.2	8	0.584	1.712
HEXA2M	100.2	7	0.585	1.708
HEXA3M	100.2	7	0.585	1.708
IPENTA	72.2	5	0.590	1.694
IPRBZ	120.2	9	0.546	1.831
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MCYPNA	84.2	6	0.574	1.743
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MP XYL	106.2	8	0.543	1.842
N BUTA	58.1	4	0.594	1.683
N DEC	142.3	10	0.582	1.718
N HEPT	100.2	7	0.585	1.708
N HEX	86.2	6	0.587	1.702
N NON	128.3	9	0.583	1.716
N OCT	114.2	8	0.584	1.712
N PENT	72.2	5	0.590	1.694
N PRBZ	120.2	9	0.546	1.831
N PROP	44.1	3	0.601	1.663
N UNDE	156.3	11	0.581	1.721
O XYL	106.2	8	0.543	1.842
PA224M	114.2	8	0.584	1.712
PA234M	114.2	8	0.584	1.712
PEN23M	100.2	7	0.585	1.708
PEN24M	100.2	7	0.585	1.708
PENA2M	86.2	6	0.587	1.702
PENA3M	86.2	6	0.587	1.702
PENTE1	70.1	5	0.574	1.743
PROPE	42.1	3	0.574	1.743
STYR	104.1	8	0.532	1.878
T2BUTE	56.1	4	0.574	1.743
T2HEXE	84.2	6	0.574	1.743
T2PENE	70.1	5	0.574	1.743
TOLUE	92.1	7	0.538	1.857
UNID	13.9	1	0.566	1.765

Fujita, 1995

Photochemical Half-lives of PAMS VOC

PAMS Species	Half Life (hour)
Acetone	875
Ethane	668
Acetylene	227
Propane	159
2,2-dimethylbutane	106
Benzene	84
i-Butane	81
n-Butane	76
i-Pentane	49
n-Pentane	49
2,2,4-trimethylpentane	41
i-Propylbenzene	36
n-hexane	36
2-methylpentane	36
2,3-dimethylbutane	35
Cyclopentane	35
Ethylbenzene	34
n-Propylbenzene	34
3-methylpentane	33
Toluene	33
Styrene	31
n-Heptane	29
2-methylhexane	28
2,4-dimethylpentane	28
2,3,4-trimethylpentane	28
o-Xylene	27
3-methylhexane	27
2,3-dimethylpentane	27
Formaldehyde	26

PAMS Species	Half Life (hour)
n-Octane	24
2-methylheptane	24
Cyclohexane	23
3-methylheptane	23
n-Nonane	20
m&p-Xylenes	20
Methylcyclohexane	19
Methylcyclopentane	19
n-Decane	19
n-Undecane	17
Acetaldehyde	12
1,2,3-Trimethylbenzene	11
1,2,4-Trimethylbenzene	11
3-methyl-1-butene	7.3
1-Butene	7.3
Propene	7.3
1-Pentene	7.3
1,3,5-Trimethylbenzene	5.0
2-methyl-1-pentene	3.7
2-methyl-2-butene	3.7
c-2-hexene	3.4
c-2-pentene	3.4
c-2-Butene	3.4
Cyclopentene	3.4
4-methyl-1-pentene	3.1
t-2-hexene	3.0
t-2-Butene	3.0
t-2-pentene	3.0
Isoprene	1.9

PES,1994