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Photochemical Assessment Monitoring Stations (PAMS)

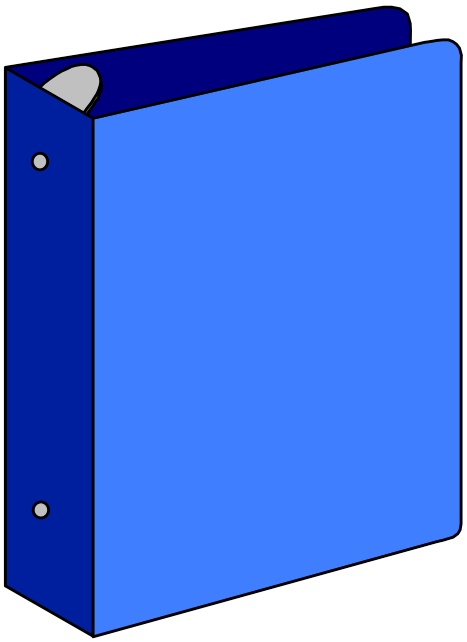
PAMS Data Analysis Workbook: Design Goals

- **Relevant.** The workbook should contain material that State PAMS data analysts need and omit material that they don't need.
- **Technically sound.** The workbook should be prepared and agreed upon by experienced PAMS analysts.
- **Educational.** The workbook content should be presented in a manner that enables PAMS data analysts to learn relevant new PAMS analysis techniques.
- **Practical.** Beyond theory, the workbook should contain practical advice and access to examples, tools and methods.
- **Gateway.** The core workbook should be a gateway to additional on-line resources.
- **Evolving.** The on-line and hard copy workbooks should improve in time through feedback from the user communities.

The on-line workbook and data analysis forum is available at http://capita.wustl.edu/EnhancedOzone/. Contributions to the workbook and site are encouraged and welcome!

Workbook Content

- Introduction (*Introduction*)
- Data Validation (*Data Validation*)
- Data Analysis Techniques Using Hydrocarbons and Carbonyl Compounds (*VOC Analyses*)
- Biogenic Emissions (*Biogenic Emissions*)
- Assessing Potentially Important Factors Contributing to Ozone (*Ozone Formation)*
- Evaluation of Emission Inventories (*E.I. Evaluation*)
- Source Apportionment (*Source Apportionment*)
- Comparison of Photochemical Model Results with Ambient Air Quality Data (*Ambient vs. Model)*
- The Relationships Between NO_x, NO_y, and Ozone (*NO_x, NO_y, and O_3*)
- Upper-Air Data Validation and Applications (*Upper-Air*)
- Trend Analyses *(Trend Analyses*)
- Pollutant Transport Analyses (*Transport Analyses*)
- Workshop Summary (*Summary*)
- Glossary and Acronyms (*Glossary*)
- Workbook References (*References*)



Workbook Objectives

- To present, explain, and discuss various methods, procedures, and tools for use in analyzing PAMS and similar aerometric data.
- To assist state and local agencies in the use of these methods, procedures, and tools in the analysis of PAMS and similar data sets.
- To provide a forum for nationwide communication and information transfer on the analysis of PAMS data (and that of supplemental air quality monitoring campaigns and/or field studies).
- To contribute to the general body of knowledge and literature on air quality analysis through demonstration of case studies and examples.

Current PAMS Data Analysis Objectives (1 of 2)

- **Emissions tracking:**
  - Corroborate ozone precursor emission inventories and trends
  - Corroborate VOC source profiles
  - Investigate air toxics compounds
- **SIP control strategy evaluation:**
  - Assess changes in emissions
  - Corroborate emissions reductions
- **Ambient trend appraisals:**
  - For NO_x, ozone, and total and speciated VOC
  - Include adjustments for meteorology

Current PAMS Data Analysis Objectives (2 of 2)

- **Attainment and control strategy development:**
  - Assess attainment/non-attainment
  - Assess relative contributions of local and upwind sources
  - Determine boundary conditions for modeling
  - Select episodes
  - Evaluate model results
- **Exposure assessment:**
  - Estimate risk levels
  - Assess the size of affected populations

U.S. EPA, 1994

Proposed PAMS Data Analysis Objectives and Goals (1 of 2)

- **Objective:** To contribute to tracking and refining emission control strategies.
- **Goal**: To help assess ozone control programs by
  - identifying key constituents and parameters
  - tracking trends
  - characterizing transport
  - assisting in forecasting episodes
  - assisting in improving emission inventories

STAPPA/ALAPCO, 2000

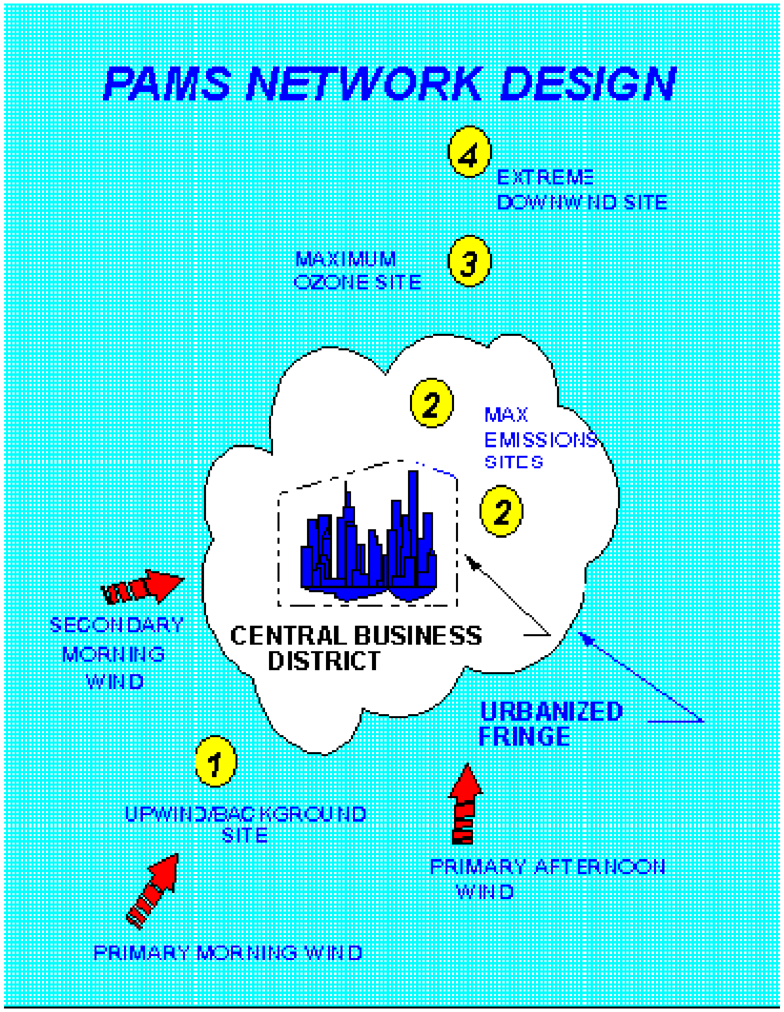
Proposed PAMS Data Analysis Objectives and Goals (2 of 2)

- States and EPA should also consider how PAMS might benefit other programs including how PAMS may:
  - help characterize ambient air toxics, support modeling, and track key trends
  - help characterize the nitrogen emissions and ambient concentrations
  - provide data for evaluation of particulate matter and regional haze
  - enhance special studies

STAPPA/ALAPCO, 2000

PAMS Site Types

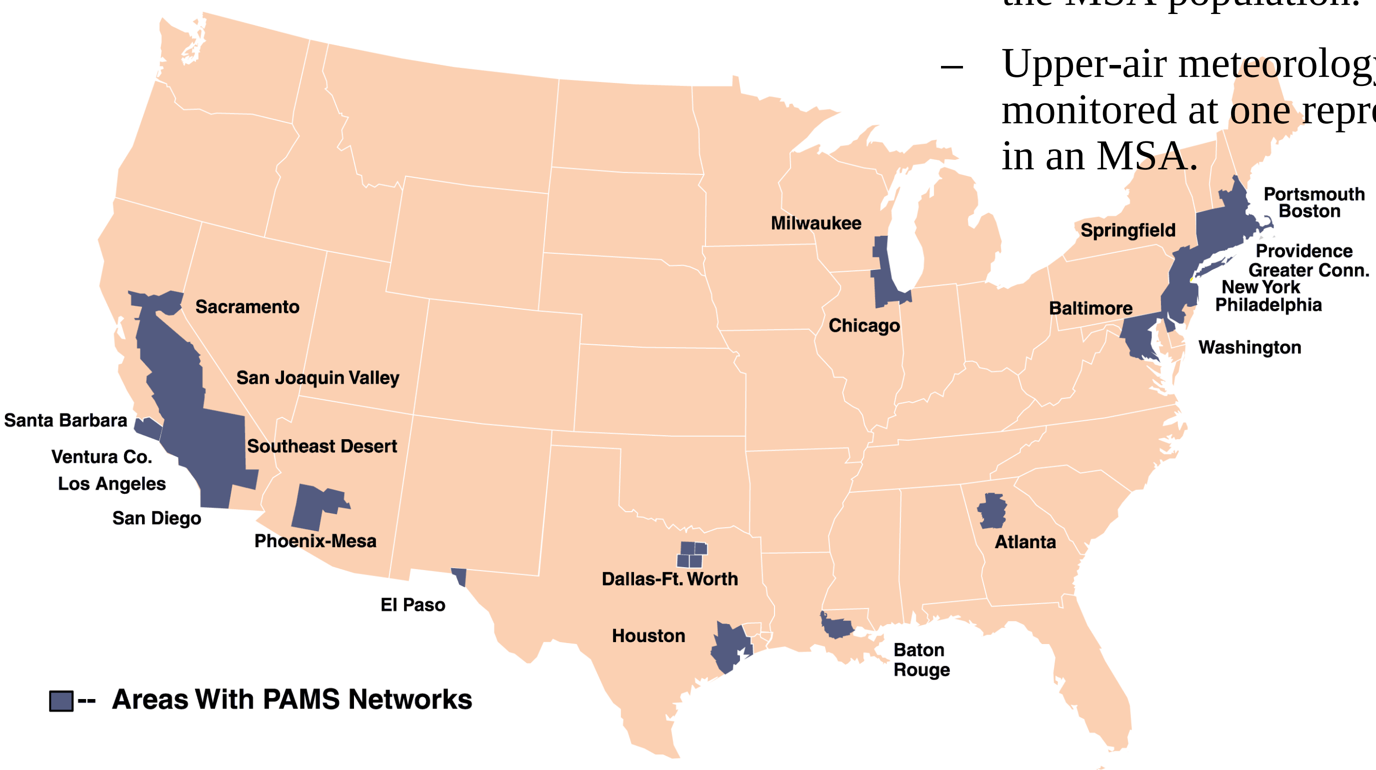
- Type I
  - Upwind and background characterization
- Type II
  - Maximum ozone precursor emissions impact
- Type III
  - Maximum ozone concentration
- Type IV
  - Extreme downwind monitoring



U.S. EPA, 1994

PAMS Sampling Considerations (1 of 2)

- Site types (Types I-IV) vary among states and regions depending on the size of the Metropolitan Statistical Area (MSA).
- The number of sites also varies among MSAs.
  - Ozone precursors (VOC and NO_x) and surface meteorology are required to be measured at two to five sites in an MSA depending on the MSA population.
  - Upper-air meteorology must be monitored at one representative site in an MSA.



PAMS Sampling Considerations (2 of 2)

- PAMS sampling frequency varies among regions, states, and sites.
  - Hydrocarbons are sampled on a 1-hr or 3-hr average basis; may or may not cover a 24-hr period; and are collected every day, every third day, or on an episodic basis.
  - Carbonyl compounds are typically collected as 3-hr averages every third day but other sampling variations exist.
  - Upper-air meteorology measurement requirements may be met in a number of ways.
- Sample speciation may vary among sites as some agencies report more hydrocarbons and/or carbonyl compounds than the PAMS target list. Differences among analytical techniques also can alter the list (e.g., co-eluters).

Technical Approach to PAMS Data Analysis

- The conceptual structure of data analysis is based on three major themes:
  - Progression from data, to data validation, to analyses.
  - Progression from simple display-and-describe analyses, to more complicated analyses, and then to analyses which interpret and integrate.
  - The use of consensus among the results from different analysis approaches.
- The workbook provides working definitions of data analyses, methods, procedures, and tools.
- The workbook is a "work in process;" please provide discussions, suggestions, and recommendations for making it better.

Prescribed Analyses (1 of 4)

- At the STAPPA/ALAPCO PAMS workshop in March, 2000, the data analysis work group recommended that a list of prescribed PAMS data analyses be compiled to provide direction on what analyses should be performed by each PAMS area. EPA has compiled this list of prescribed PAMS data analyses based on analyses that would help State, Local and Regional organizations determine what factors are contributing to ozone formation in their area and if the control strategies they have implemented have been successful at reducing ozone. This list is a proposed minimum set of analyses that each PAMS area should be examining to help solve the ozone problem in the area.
- EPA will incorporate this list into grant guidance to provide the State and local agencies direction to determine what minimum core analyses should be performed annually on the PAMS data.
- The prescribed analyses (plus any additional analyses) received from the State and local agencies, Regional organizations and EPA Headquarters will be compiled each year into an annual PAMS Data Analysis report.

Prescribed Analyses (2 of 4)

Objectives	Example Analyses	Location in Workbook
How have the data been validated? Are there any years or species measurements that have suspect data quality?	Run screening checks, review summary statistics.	Data Validation (pp. 15-31)
How would you characterize the area?		
Which are the 5 most abundant PAMS species at each site?	Determine the median concentrations and weight fractions for each pollutant.	VOC Analyses (pp. 15-16)
How do these PAMS species (benzene, propane, and 5 most abundant) vary by measurement season, month, and time of day?	Prepare box plots of monthly and hourly concentrations and weight fractions for these species.	VOC Analyses (pp. 17-19, 22) Trends (p. 12)
Do these PAMS species (benzene, propane, and 5 most abundant) show any day-of-week patterns?	Prepare time series of these species and box plots by day of week.	VOC Analyses (pp. 20-21) Trends (p. 9)
What are the source contributions in the local area?	Prepare a map showing 20 major VOC and/or NO_x sources; prepare pollution roses.	Source Apportionment (p. 13) Transport (p. 17)
Do the PAMS data corroborate the source mixture?	Examine key species noted as tracers and use scatter plots to determine species relationships.	Source Apportionment (p. 14-19) VOC Analyses (p. 23)

Prescribed Analyses (3 of 4)

Objectives	Example Analyses	Location in Workbook
Do the PAMS data corroborate the source mixture?		
Is this PAMS area, or portions of the area, NO_x- or VOC-limited?	Inspect VOC/NO_x ratios, indicator species and ratios, and apply MAPPER.	NO_x, NO_y, Ozone (pp. 6-14, 18-30, 34-35)
What are the levels of PAMS species for 1-hr ozone episode days vs. non-episode days?	Plot time series for 2 days prior to the episode and the day of the episode. Compare daily and rush hour box plots of species concentrations and median fingerprints for episode vs. non-episode days.	VOC Analyses (pp. 24-26)
What are the meteorological conditions on 1-hr ozone episode days vs. non-episode days.	Prepare scatterplot of meteorological variables vs. ozone concentrations for episode vs. non-episode days.	Transport (p. 18-19)
Can any species levels help predict ozone episodes?	Inspect time series, box plots, and fingerprint plots for ozone episodes, and 1 to 2 days prior.	VOC Analyses (p. 26)
What PAMS species are transported into the area potentially elevating ozone levels?	Prepare wind roses; examine benzene, xylenes, and toluene to TNMOC ratios on high 1-hr ozone days.	Ozone formation (pp. 7-12)

Prescribed Analyses (4 of 4)

Objectives	Example Analyses	Location in Workbook
Do the PAMS data corroborate the source mixture (continued)?		
Can the upper-air meteorology be used to corroborate transport?	Prepare trajectories, wind runs, and/or ventilation analyses at selected heights.	Upper-air (pp. 30-35) Transport (pp. 24-26, 28)
To what can we attribute changes in ozone or precursor concentrations?		
What changes have occurred in motor vehicle emission species?	For Type 2 sites, inspect box plots of key species and median fingerprints by year.	VOC Analyses (pp. 27-28) Trends (pp. 5, 27, 30)
What changes have occurred in biogenic emission species?	For Type 1, 3, and 4 sites, inspect box plots of biogenic species by year and time of day.	Biogenics (p. 11)
What changes have occurred in other major sources in the area?	Inspect box plots of key species and median fingerprints by year.	VOC Analyses (pp. 27-28) Trends (pp. 5, 27, 30)
What changes have occurred in area sources?	Inspect box plots of key species and median fingerprints by year.	VOC Analyses (pp. 27-28) Trends (pp. 5, 27, 30)
What are the trends in ozone and precursors since 1994?	Prepare annual box plots of ozone, NO_x, TNMOC, benzene, propane, and top 5 most abundant species.	Trends (pp. 3-12, 27-30)

Assumptions and Limitations of the Workbook

- Recent data analyses were included from a literature review as well as analyses custom-made for the workbook.
- This workbook provides examples from as many methods, procedures, and tools as reasonable; selection of a specific method, procedure, or tool does not imply anything beyond suitability to illustrate an issue or a specific situation.
- Space available in the workbook is limited; therefore, many details are, of necessity, provided in the literature. An extensive reference section is provided at the end of each chapter.

Motivating Examples

- The following pages are excerpts from other chapters in this workbook. These examples illustrate key PAMS data analysis and validation issues.
- Meaningful data analyses:
  - Begin with the collection and reporting of valid data.
  - Proceed through an understanding of the chemical and physical processes related to ozone formation, transport, and removal.
  - Evolve as more analysis techniques are applied to the data to obtain a consensus view of attainment and control issues.

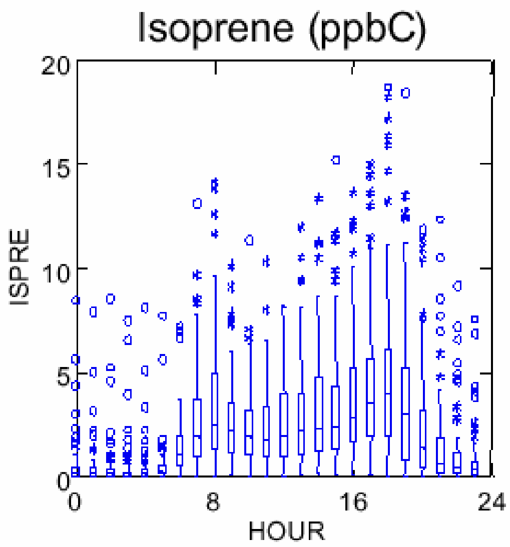
VOC Data Analysis

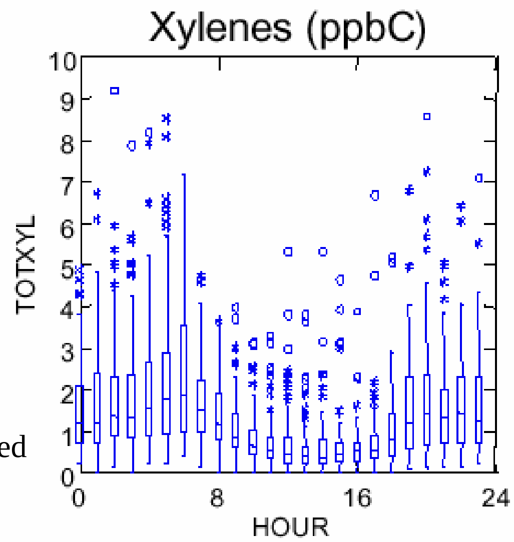
Variation of Species by Month and Time of Day

- This example illustrates the diurnal variation of isoprene and the xylenes at a Type 1/4 site (Lums Pond, DE) in 1997.

- Isoprene emissions are a function of sunlight and temperature and thus we expect higher concentrations during the daylight hours.

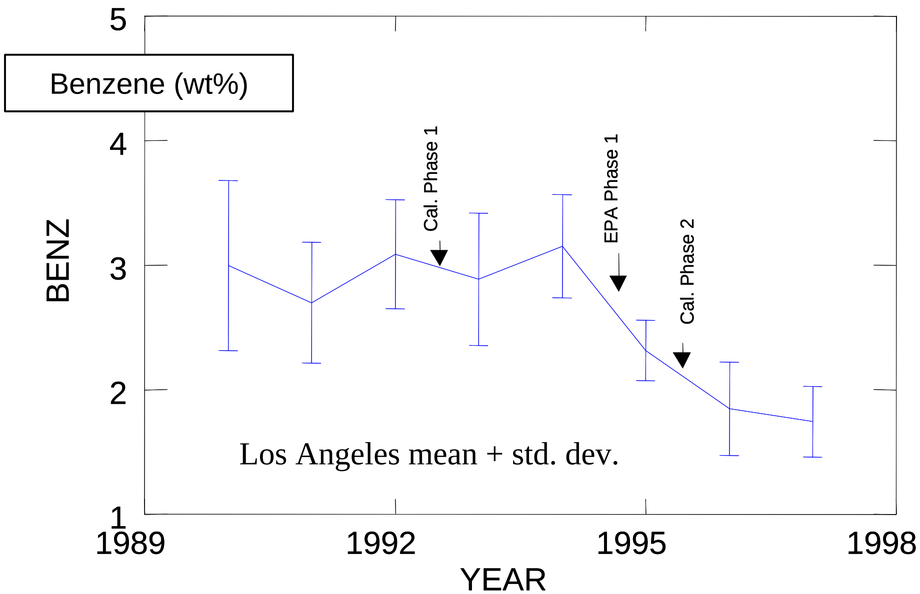
- The xylenes, key components of motor vehicle exhaust, show a marked decrease at midday, probably indicative of a more aged air mass impacting the site.



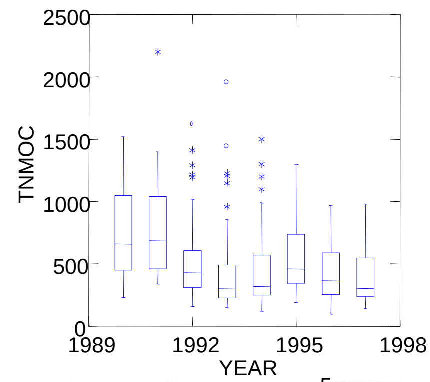


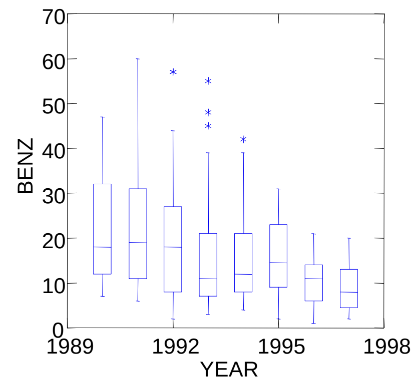
Box plots prepared using SYSTAT. Main et al., 1999

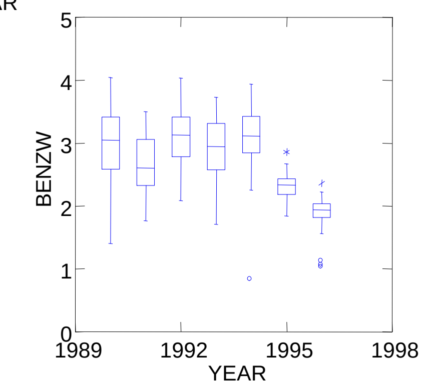
Tracking Changes in PAMS Species



Main et al., 1999



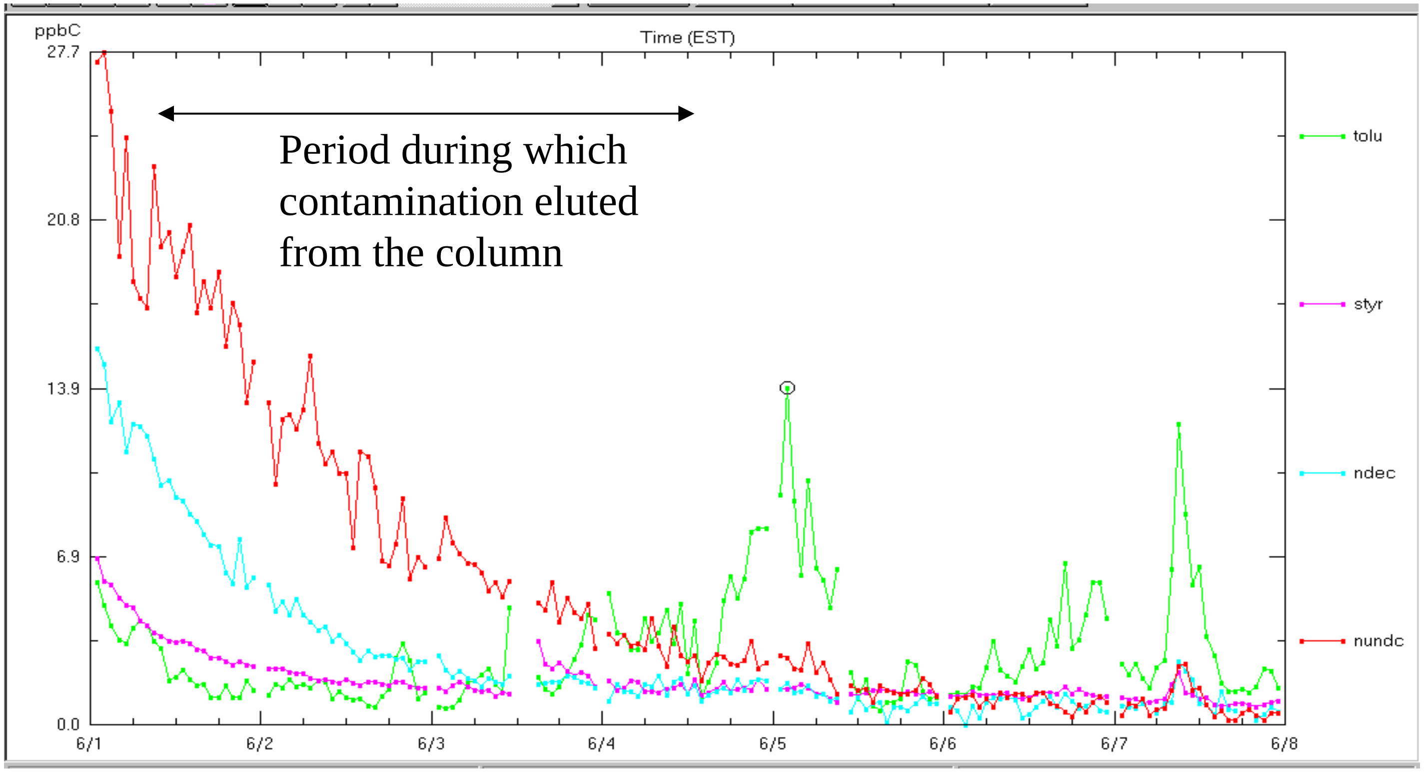




- The federal reformulated gasoline (RFG) implementation occurred in early 1995; benzene fuel levels were specifically targeted for reduction (EPA Phase 1). In addition, California had separate fuel requirements that further reduced fuel volatility (Cal. Phase 1) and benzene levels (Cal. Phase 2).
- The figures at the top right show annual box plots of ambient TNMOC (ppbC), benzene concentration (BENZ in ppbC), and benzene weight percent (BENZW) in Los Angeles. The drop in ambient benzene weight percent between 1994 and 1995 is dramatic. Additionally, fuel benzene measurements also declined between 1994 and 1995. It is important to attempt to explain the changes observed in the ambient air with the control actions.

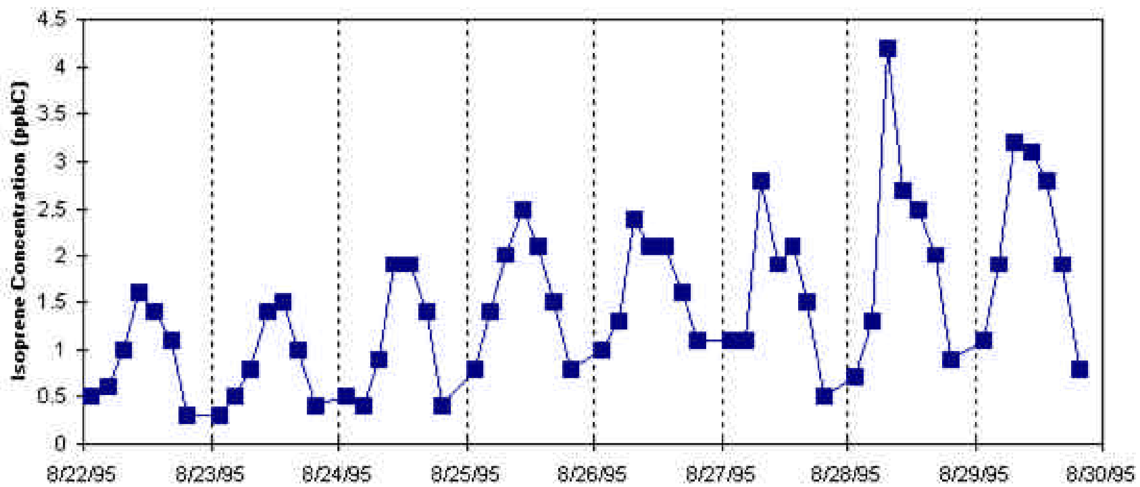
Data Validation is Important

Example of start-up problems

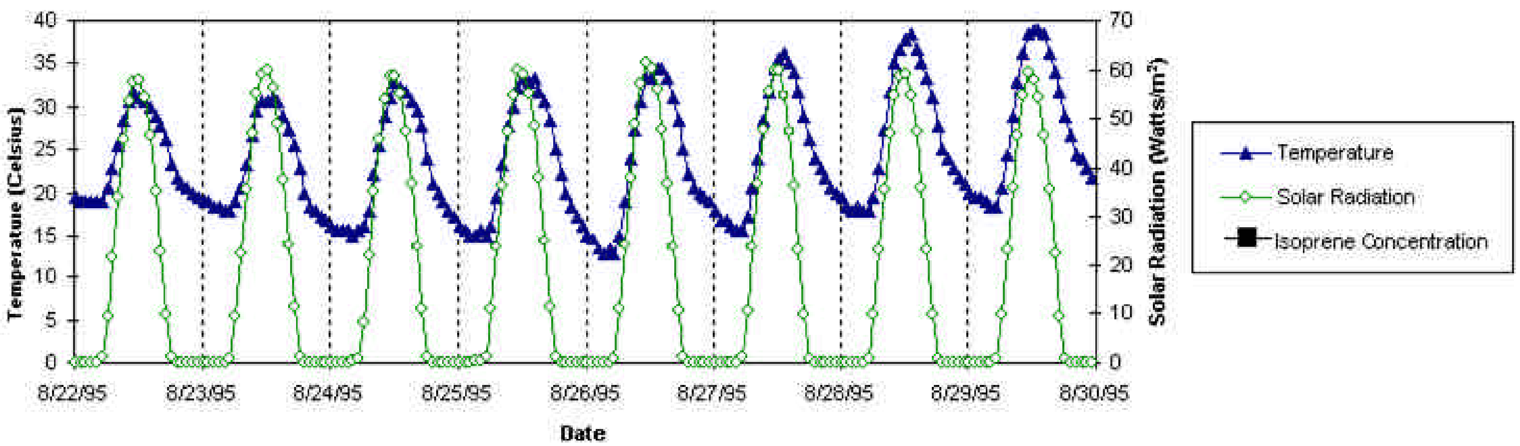


Time series plots of species groups (top) and individual species (bottom) at a PAMS site during early June 1996. Example of possible contamination of either the shelter air or the analytical equipment. (Level 1, AIRS data) Data during this time period were invalidated.

Biogenic VOC Analyses



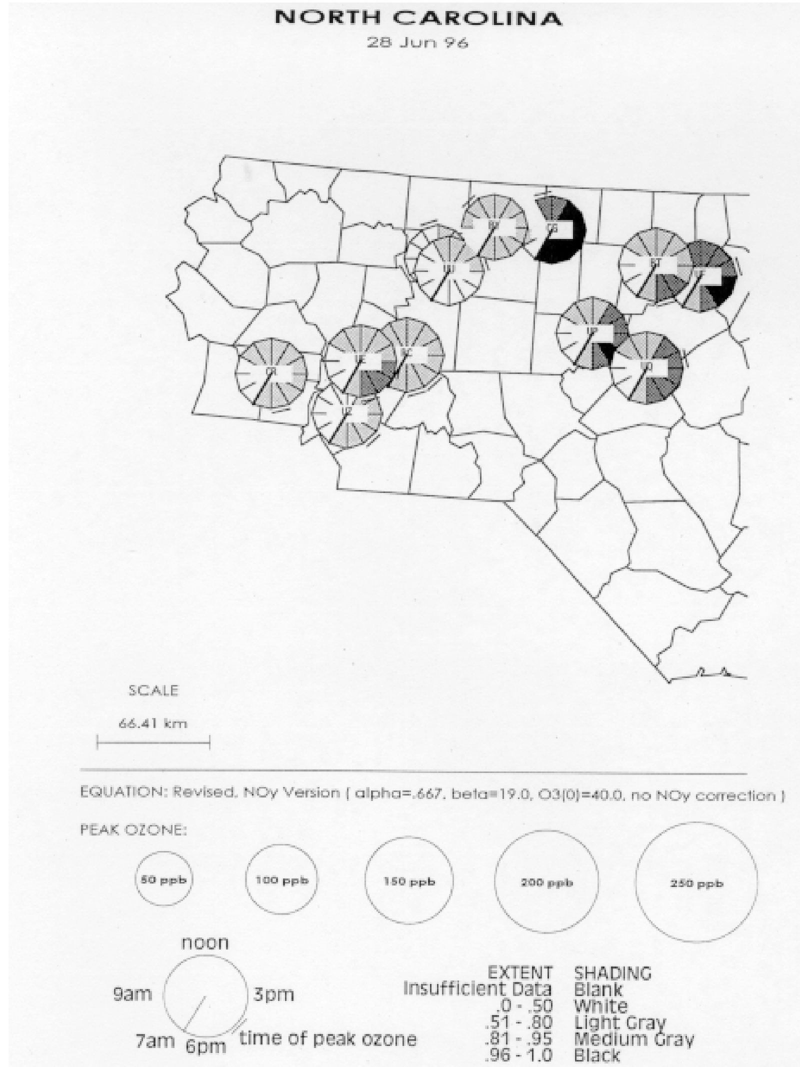
PAMS data are useful for investigating the relationship between isoprene concentrations and temperature. Understanding these relationships can help improve model performance.



Three-hour average isoprene concentrations and hourly temperature and solar radiation data collected at Pico Rivera, CA during August 22-29, 1995. The peak daily temperature and isoprene concentrations rose between August 24 and 26.

Spatial and Temporal Extent of Reaction

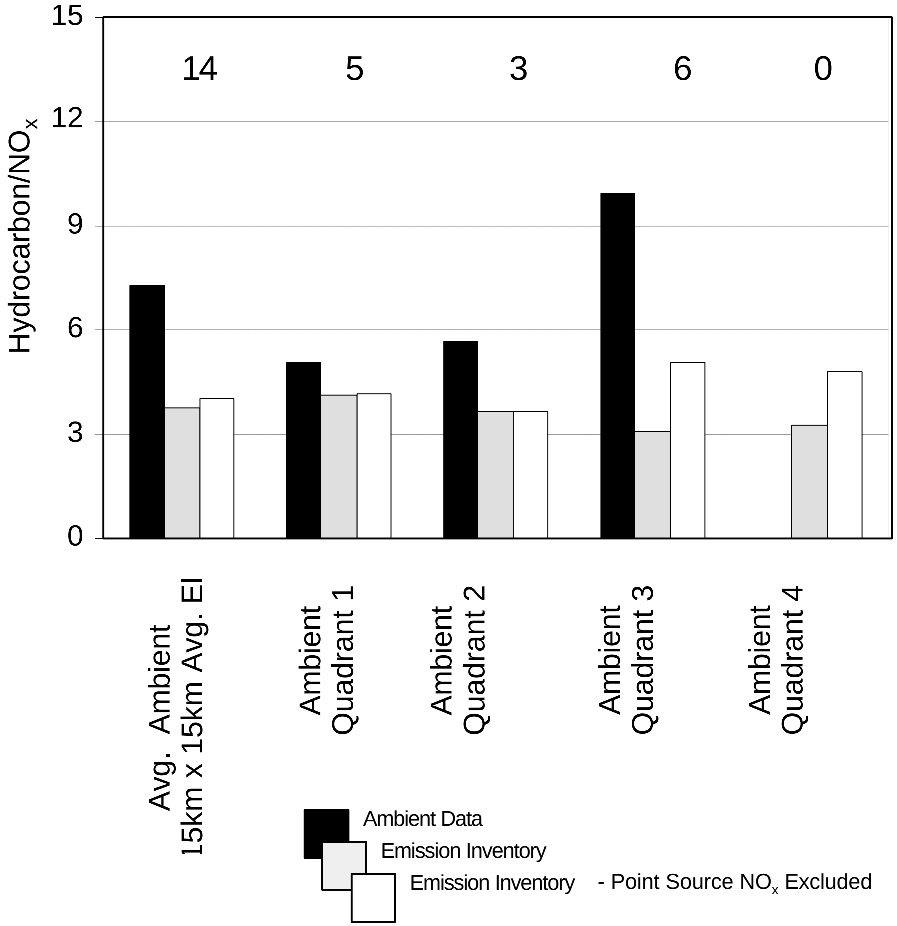
- Does extent of reaction approach one (i.e., darker in the plot) during hours when ozone concentrations are at or near peak values at a site?
- For how many hours does the extent of reaction approach one?
- Does extent approach one at the sites having the highest ozone concentrations?
- This example shows the extent of reaction was higher at a given site during the time of peak ozone, and the urban sites were more VOC-limited (denoted as white to light gray) than the downwind sites consistent with expectations.



MacDonald et al., 1998

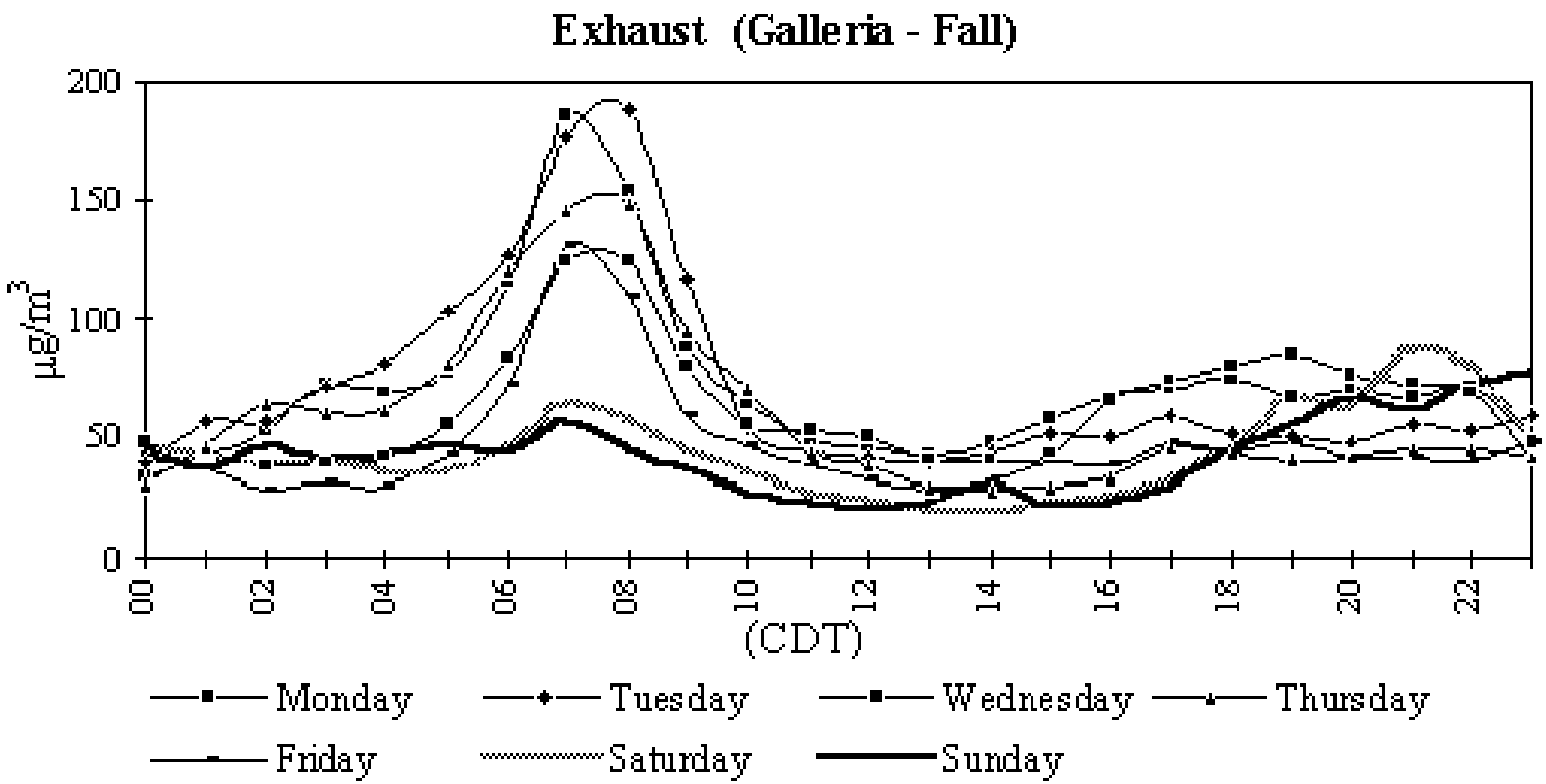
Evaluating Emission Inventories

- Prepare tables/plots of VOC/NO_x and CO/NO_x ratios for ambient and emission inventory (with and without elevated point sources).
- Notice the difference in the emission inventory and ambient ratios overall and by wind quadrant. The emission inventory underpredicts the VOC/NO_x ratios observed in ambient data; this may indicate an underestimation of VOC in the emission inventory.



Prepared using Excel. The numbers above the bars represent the number of ambient samples used in the comparison (Chinkin et al., 1999).

Source Apportionment

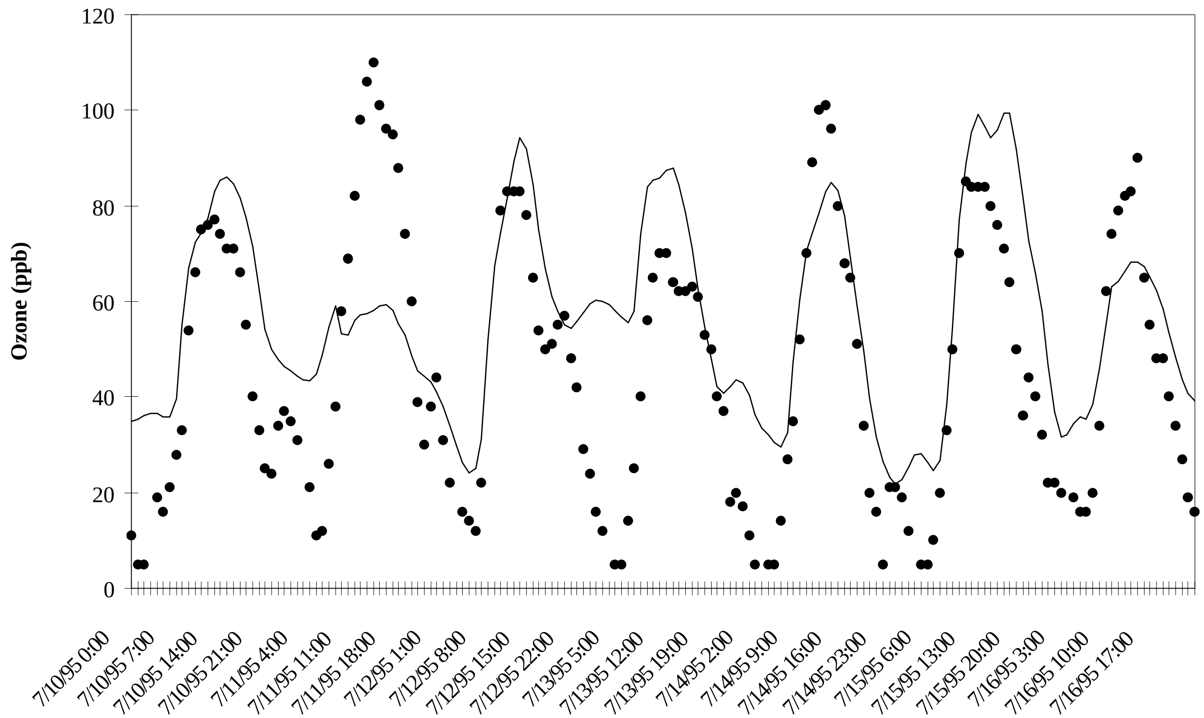


Lu and Fujita, 1995

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.

Comparing Ambient Data and Model Results

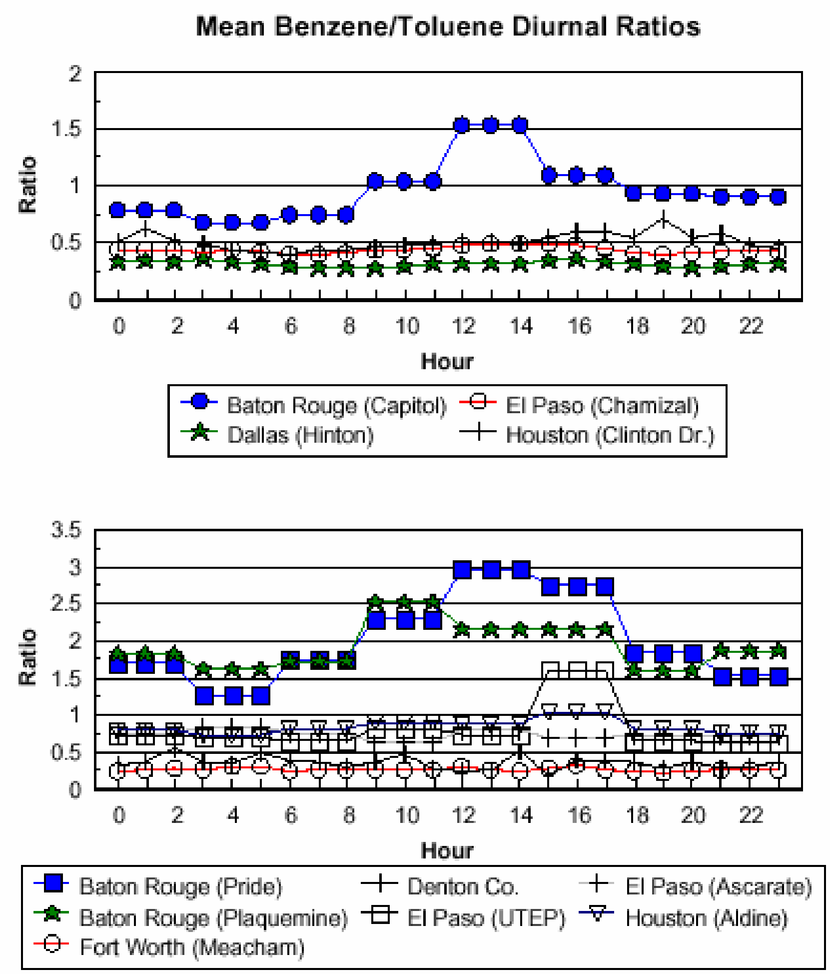
- Example time series plot comparing observed (•) and predicted (—) hourly ozone concentrations at a site.
- In this example, the model fails to estimate the low ozone concentrations at night and significantly underestimates the peak ozone on some days.
- These types of plots can help explain biases in 8-hr versus 1-hr ozone concentration predictions.



MacDonald et al., 1999

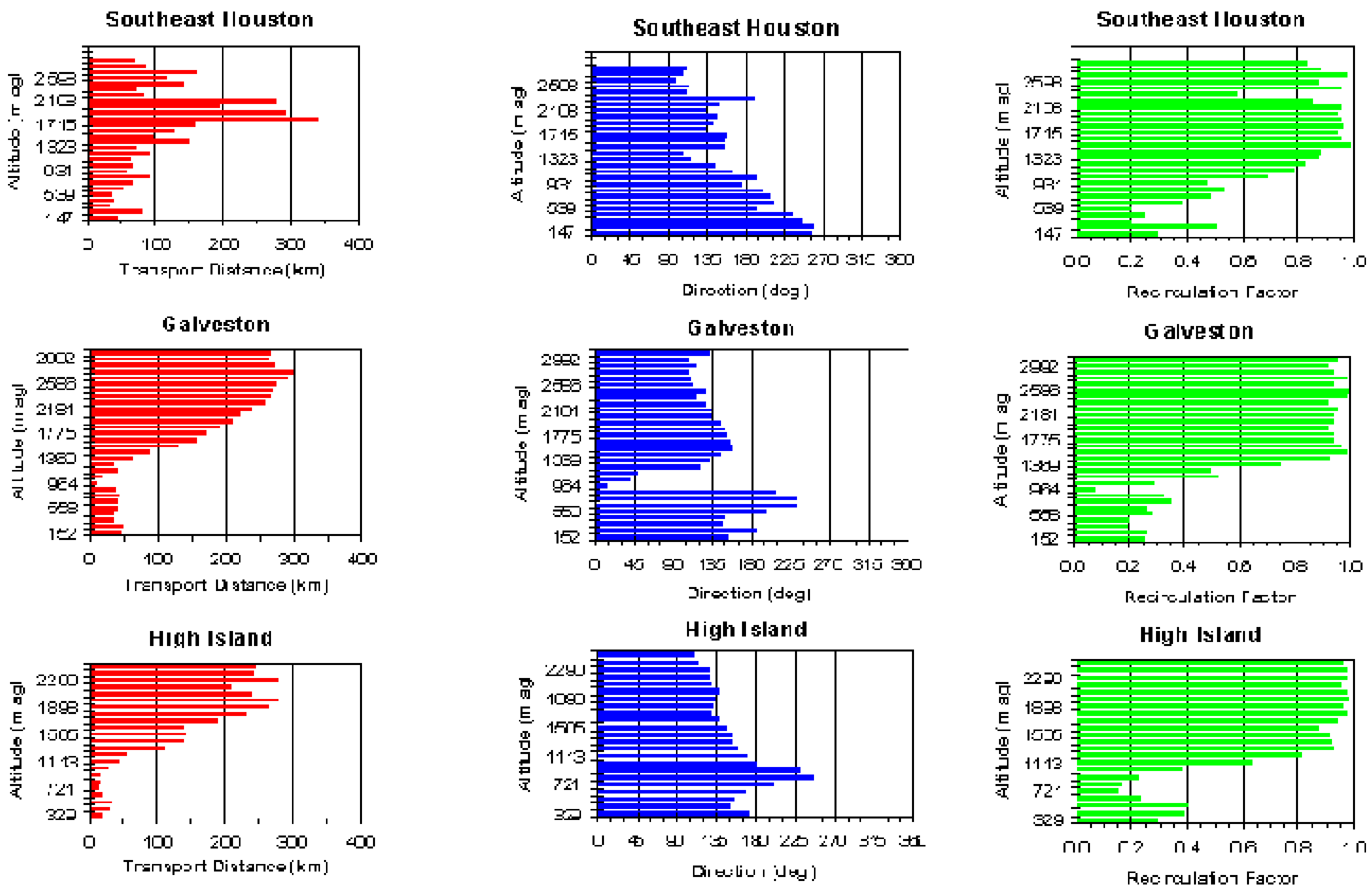
Assessing Relative Age

- In this example, the top figure shows the mean benzene to toluene ratios measured at the Baton Rouge Capitol site compared to ratios from urban sites in Texas. The bottom figure compares mean ratios at other Baton Rouge and Texas sites.
- All the Baton Rouge sites have higher benzene/toluene ratios (possibly indicating more aged air) than the sites analyzed in Houston, Dallas, and El Paso. The more downwind sites of Pride and Plaquemine near Baton Rouge are more influenced by aged air masses than the Capitol site.



Sather and Kemp, 1998

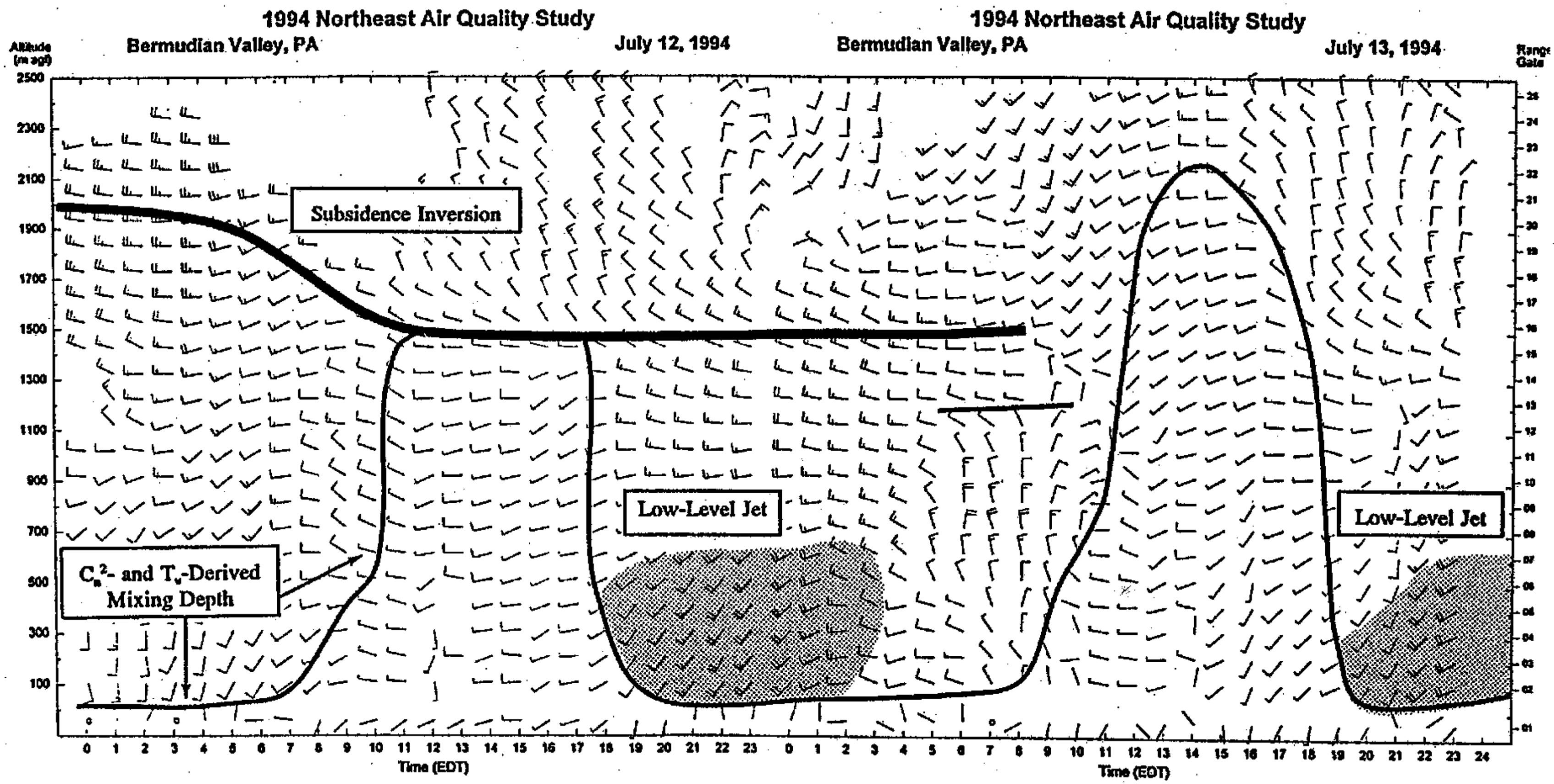
Ventilation Analysis Using Upper-Air Meteorology



SAI et al., 1995

When recirculation and carry-over of pollutants may be a consideration, ventilation analysis using upper-air meteorological data is useful. This example shows vector integrated transport distances, resultant wind directions, and recirculation factors (R) calculated from data collected at Southeast Houston, Galveston, and High Island Platform (in the Gulf) radar profilers for the period 0600 to 1700 CDT on August 19, 1993. In the surface layer, short transport distances and low recirculation factors indicate stagnation of the air mass.

Investigating Boundary Layer Structure and Evolution



- This example of upper-air data reveals a recurrent low-level, nocturnal jet. This plot shows a time series cross section of winds, mixing depth, and inversion conditions measured by the radar profiler on July 12-13, 1994 at Bermudian Valley, PA. The thin solid line denotes the height of the mixed layer estimated using C_n^2 and RASS temperature data. The thick line denotes the subsidence inversion.
- The shaded area indicates the region of the nocturnal low-level wind maxima. The maximum mixing depth was significantly different on the two days (Lindsey et al., 1995b).

Summary

PAMS DATA CAN BE USED TO MEET A WIDE RANGE OF OBJECTIVES

References (1 of 2)

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