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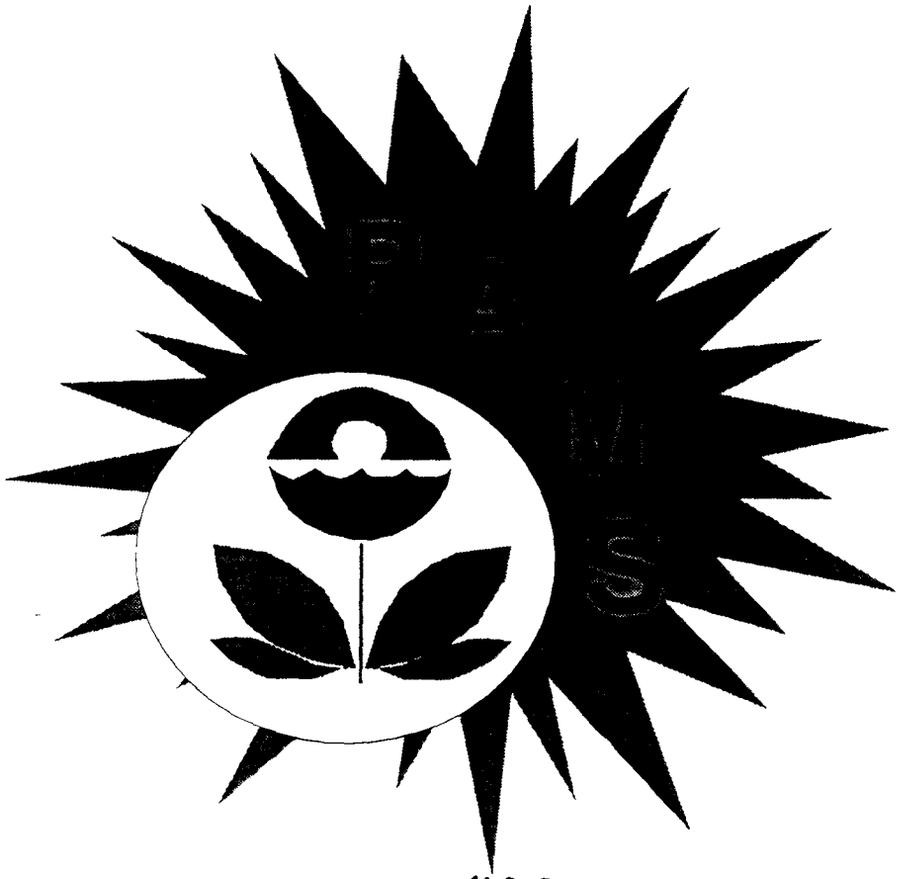
Air

EPA PHOTOCHEMICAL ASSESSMENT MONITORING STATIONS

1996 DATA ANALYSIS RESULTS REPORT



Acknowledgments

As a compilation of existing analyses and studies, this document would simply not have possible without the generosity and creative efforts of the PAMS data analysis community. Unfortunately, this collection of individual air quality analysts, modelers, and statisticians is too numerous to allow acknowledgment by name or organization. Instead, the report attempts to credit all direct and indirect contributions to the effort through footnotes within and references following each chapter. Any omissions are entirely accidental and will be corrected in future editions of this report.

The authors wish to acknowledge the invaluable contribution of Mr. William F. Hunt, Director of the Emissions, Monitoring and Analysis Division. In addition to his role as senior manager to all the report's authors and the creative energy behind the PAMS program, Mr. Hunt conceived of the idea of this document and provided the opportunity and instruction which allowed its development. We would also like to thank the following Group Leaders within EMAD, Mr. Joe Tikvart, Mr. David Mobley and Dr. Dave Guinnup for their encouragement and empowerment to craft a document true to the subject matter and to the intended audience.

A list of the report's authors (and their phone numbers[1]) is provided below. The reader is encouraged to contact the authors to convey comments and suggestions, and/or to request additional information. Each chapter's lead author is italized.

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Contents

Executive Summary

Having successfully progressed through its planning, design and implementation stages, the Photochemical Assessment Monitoring Stations (PAMS) program is currently undergoing a shift in emphasis to focus more acutely on the analysis and interpretation of the data generated. Such a change in direction is necessary to fully realize the value of this rich and voluminous data set in a regulatory and policy context.

The PAMS networks produce a wealth of information invaluable to the development and evaluation of ozone control strategies and programs. In addition to providing a long-term perspective on changes in atmospheric concentrations of ozone and its precursors, the PAMS program will specifically help to improve emissions inventories, assist in evaluating the performance of photochemical grid models, furnish information to evaluate population exposure, and provide routine measurements of selected hazardous air pollutants. Data from PAMS will also allow for the development of the critical feed-back mechanism to evaluate the efficiency and effectiveness of emission control programs. Most importantly, PAMS will assist in deriving a more complete understanding of tropospheric ozone formation and transport, so that we may move toward the best solution to this complex environmental problem.

This document presents example analyses illustrating the utility of PAMS data across the range of ozone management applications. Where appropriate, limited critical evaluation is also included to suggest future program refinements. The document is organized in a functional manner based on mix of methodology and objectives. The Chapters describe general data characterization approaches, methods for evaluating emissions inventories, the relationship of PAMS data to emissions and observation based modeling, and quality assurance of the PAMS data.

CHARACTERIZATION OF AMBIENT AIR QUALITY FOR OZONE AND ITS PRECURSORS

Accurate characterization of ozone and its precursors is extremely important for understanding tropospheric ozone formation and accumulation, and crafting effective control strategies to address this environmental issue. Analyses have demonstrated that PAMS data are invaluable in characterizing ozone episodes and identifying features that may be linked to significant pollutant transport. For example, evidence of potentially significant pollutant transport

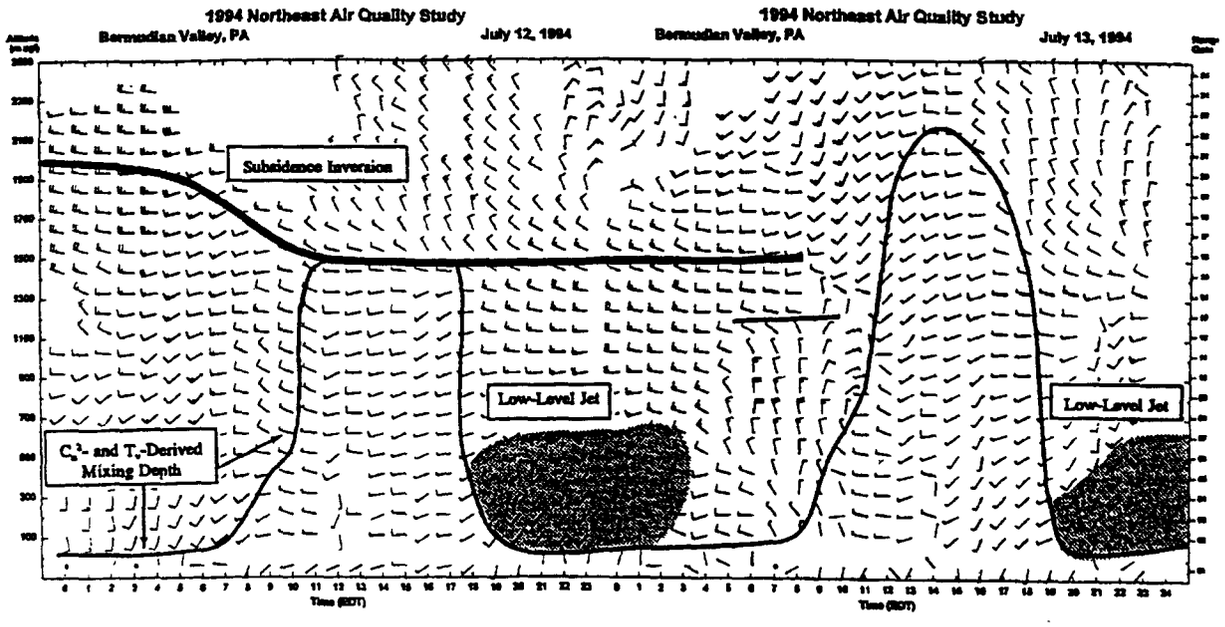

Figure E-1. Time series cross-section of winds, mixing depth, and inversion conditions measured on July 12-13, 1994 at Bermudian Valley , PA, indicating jet formation and mixing depths. The thin solid line denotes the height of the mixed layer and the thick line denotes the subsidence inversion. Each wind barb indicates direction and speed. (Lindsey et al., 1995).

(e.g, detection of a nocturnal jet as shown in Figure E-1) can be identified by combining PAMS hourly surface and upper air meteorological data. In addition, the PAMS requirement for routine measurements of organic species allows improved characterization of precursor conditions

associated with ozone episodes and provides, for the first time, a data set sufficiently detailed to power statistical investigations of the relationships between ozone and its precursors. For example, Figure E-2 compares observed ozone levels from Philadelphia, PA in 1994 with predicted ozone levels produced by two statistical models. The first uses only meteorological data to predict ozone levels while the second adds hydrocarbon data as an input. The improvement in the model's ability to "explain" downwind ozone (when hydrocarbon data are included) clearly demonstrates the value of speciated volatile organic compound (VOC) data in accurately characterizing and understanding ozone concentrations. A more detailed description of how PAMS data can be used to better characterize ambient conditions can be found in Chapter 1.

PAMS DATA IN SUPPORT OF OZONE MODELING APPLICATIONS

PAMS data support emissions-based model (EBM) applications by providing additional information for evaluating (1) model predicted concentrations for ozone and its precursors; and (2) meteorological and emissions inputs which drive model simulations. The use of PAMS data

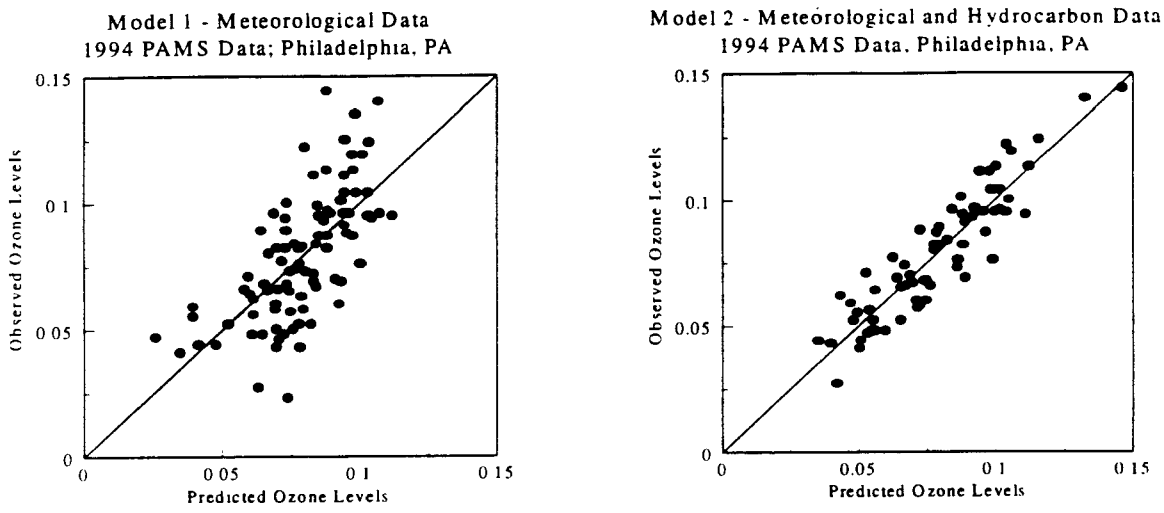

Figure E-2. Comparisons of Observed Ozone Levels with Those Predicted from Two Statistical Models Using Data from Philadelphia, PA (Model 1, R2=0.45; Model 2, R2=0.89)

to evaluate model simulated concentrations of ozone and its precursors is an important incremental contribution to the overall model performance evaluation. The addition of PAMS precursor measurements reduces the degrees of freedom in the model evaluation process and (assuming acceptable model performance) increases the probability that the model is correctly predicting surface ozone for the right reasons rather than as a result of compensating errors. In addition, the upper air meteorological monitoring requirements of PAMS yield improvements in the representativeness of simulated wind fields and mixing heights (as shown previously in Figure E-1) both of which are critically important inputs to the EBMs. Finally, key use of the PAMS speciated VOC data is the evaluation of emissions inventories (a significant component of EBMs). Such evaluations with PAMS data provide insight into the number and mix of emissions sources as well as potential gaps in emissions configurations. An example illustrating the value of PAMS-like data in model evaluation is taken from a study performed in Texas. On August 19, 1993, a highly localized ozone peak of 231 ppb was observed in Houston for which the modeling results did not replicate the timing or the magnitude. A series of across-the-board emissions sensitivity runs for VOC and oxides of nitrogen (NO_x) failed to improve model performance. An analysis of nearby VOC data indicated an anomalous peak in the total non-methane hydrocarbons (NMHC). Through further analysis of the ambient speciation, the emissions inputs were adjusted to coincide

with the ambient data. Subsequent model runs resulted in improved representation of the peak ozone as shown in Figure E-3. A more detailed explanation of this example and a thorough discussion of the use of PAMS data as a means of improving EBM simulations is provided in Chapter 2.

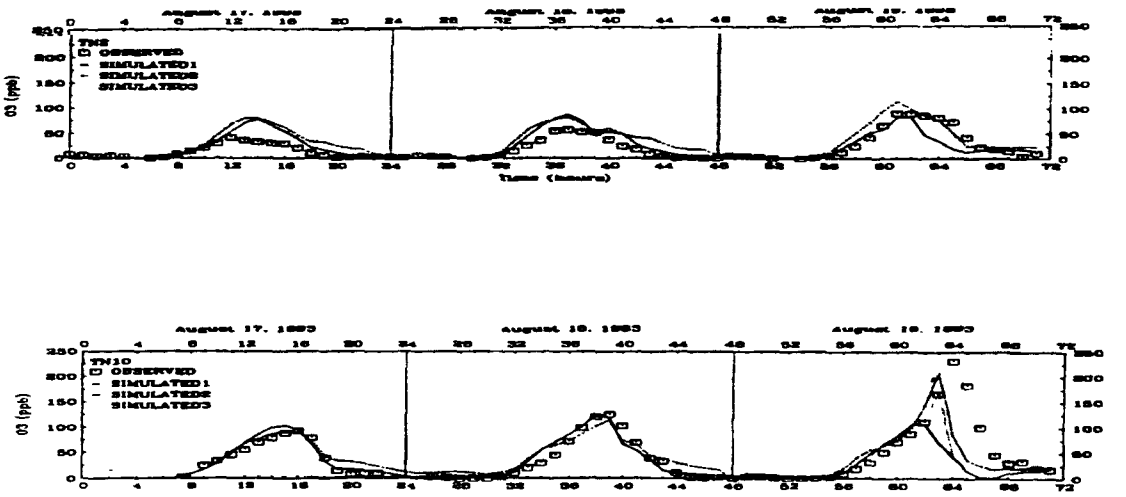

Figure E-3. Time series plots of ozone at two sites before and after correction in emissions. Notice that simulated ozone changed significantly at site TN10, responding to emissions change, and little change occurred at site TN2 (top).

EVALUATION OF EMISSIONS FACTORS, MODELS AND INVENTORIES USING PAMS DATA

As mentioned previously, data from the PAMS program provide an important tool for evaluating and refining estimates of ozone precursor emissions. The concept of using ambient measurements to improve emissions models, factors and inventories is not new, having been first used to evaluate particulate matter inventories in the 1970's. To date, several interpretive techniques have been used to evaluate emissions inventories with the PAMS data. Types of screening analyses include comparisons of ambient- and emissions-derived hydrocarbon / NO_x ratios, association of certain compounds with transport direction, time series analyses, and the detection of chemical species associated with certain events or episodes. Multi-variate models (e.g., factor analysis, Source Apportionment by Factors with Explicit Restrictions (SAFER), Chemical Mass Balance (CMB)) can also be used to interpret the data. Such analyses and studies

can reveal missing sources and/or suggest improvements to the spatial or temporal resolution of the emissions inventory. They can also determine the need for better emissions factors or activity inputs to emissions models or factors.

For example, data collected during the 1991 Lake Michigan Ozone Study (LMOS) were used to compare emissions inventory and ambient concentration ratios of non-methane organic compound (NMOC), NO_x, and carbon monoxide (CO) for Chicago, Gary, and Milwaukee. Comparisons of 7-9 a.m. ratios for two ozone episodes (June 25-28 and July 16-18) showed that the ambient computed ratios were generally higher than the inventory ratios. The relative individual NMOC species compositions of the ambient and inventory data were also examined. As a result of LMOS, the Lake Michigan Air Directors Consortium (LADCO) reevaluated the emissions inventory and made several significant changes to the point, area, and mobile source figures. Speciation profiles and background assumptions were also revised. Tables E-1 and E-2 below show the computed ambient and emission NMOC/NO_x ratios both before and after the LADCO inventory revision. Chapter 3 provides a more complete discussion of how PAMS data can be used to help improve emissions estimates.

Table E-1. Lake Michigan Area - Ambient Versus Original Set of Emissions Inventory NMOC/NO_x Ratios, 1991 (Korc, 1993)

Site	Ambient NMOC/NO_x	Emissions NMOC/NO_x	Ambient/EI
Gary[a]	5.3	4.3	1.2
Chicago	4.8	2.6	1.9
Milwaukee[a]	6.4	4.2	1.6

[a] Ambient NMOC/NO_x ratios correspond to June 26, July 16 and 18, 1991

Table E-2. Lake Michigan Area - Ambient Versus Revised Set of Emissions Inventory NMOC/NO_x Ratios, 1991 (Korc, 1993)

Site	Ambient NMOC/NO_x[b]	Emissions NMOC/NO_x	Ambient/EI
Gary[a]	4.8	5.0	1.0
Chicago	4.7	3.6	1.3
Milwaukee[a]	6.4	3.8	1.7

[a] Ambient NMOC/NO_x ratios correspond to June 26, July 16 and 18, 1991

[b] Ambient NMOC/NO_x with background correction

OBSERVATIONAL-BASED METHODS FOR DETERMINING VOC/NO_x EFFECTIVENESS

Observational-based methods, which require ambient precursor measurements as inputs, can provide directional guidance on the relative effectiveness of reducing NO_x or VOC in reducing ozone levels. As such, they serve as an important means of corroborating results obtained from EBMs. The PAMS program provides ambient air quality data of greater spatial, temporal and compositional detail than previously available and therefore improves the basis for exercising observational methods. For example, the Georgia Institute of Technology (GIT) observational-based model (OBM) requires detailed speciated VOC measurements of the type provided by PAMS. Figure E-4 illustrates an application of the GIT-OBM for Atlanta covering several monitoring locations. The model provides a relative assessment of the role of emissions groups on ozone formation. Descriptions of the uses of PAMS data in several observation-based methods are presented in Chapter 4.

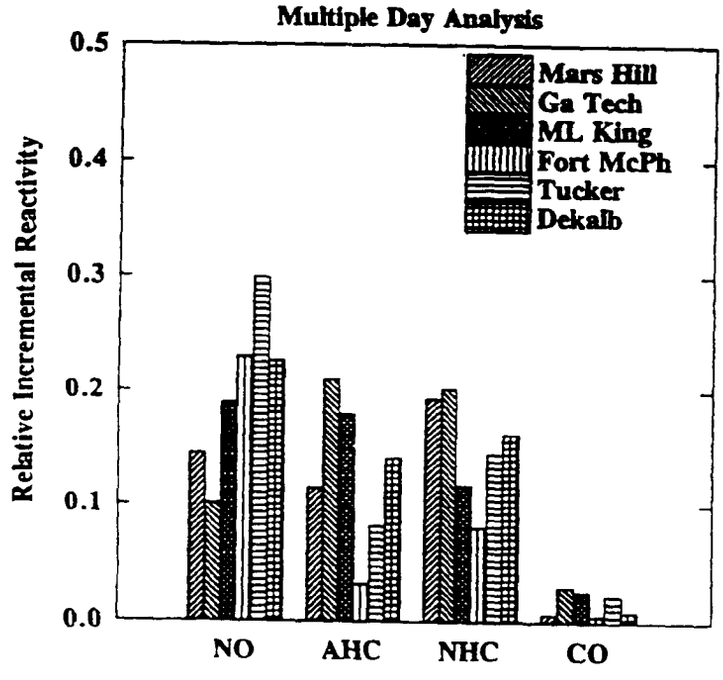

Figure E-4. Results from GIT-OBM applied to Atlanta. (Cardelino and Chamiedes, 1995).

LINKAGES AMONG TECHNIQUES

Although the examples are presented in this report as distinct entities to facilitate unambiguous descriptions, the significance of the individual analysis areas to the ozone management process is best understood when they are considered as elements of an integrated whole. For example, the value of spatial, temporal and speciated displays of ozone and precursor data is considerably greater when such displays are viewed as techniques to quality assure data and provide direction for more refined analysis. Similarly, the significance of emissions inventory evaluations is more substantial in the context of their use in improving (or corroborating) the inputs to photochemical models. The results from the application of OBMs are far more important when coupled with results from more traditional EBMs.

The step-wise air quality modeling process can be used as a framework to illustrate the linkages among these analysis categories. The modeling process can be viewed as sequential four-step process:

1. Selecting model days or episodes and specifying modeling domain;
2. Developing and evaluating meteorological and emissions inputs;
3. Testing and evaluating the model under present conditions; and
4. Applying the model in a control strategy context and evaluating/corroborating performance.

Basic data characterization efforts for air quality and meteorology form the basis for almost all model process elements. The selection of appropriate model days historically has been based on a review of meteorology and ozone data. PAMS provides these elements, and adds highly resolved upper air meteorological data and precursor data as additional factors in episode selection. Transport and aging related analyses yield other considerations in characterizing the days to be modeled. Perhaps the most important contribution of PAMS to the modeling process is an improved ability to evaluate the basic emissions and meteorological inputs to drive the simulations. The examples contained in this report describe the unique contributions of PAMS data in resolving vertical mixing phenomena (mixing heights and winds) and providing a continuous, speciated record of hydrocarbon compounds to check emissions estimates. The spatial and temporal data characterizations are also applied in evaluating "current" day EBM behavior. Finally, greater confidence in emissions-based models' predictive abilities (i.e., the ability to correctly reflect ozone response to emissions changes) is gained when observational-based models (which independently assess control strategy preference) produce agreement. Combined with a longer term trends perspective, the PAMS data can be used to continuously check the predicted response of the model leading to iterative analyses and refinements when measurements diverge from original projections. This longer term approach speaks to the greatest value of PAMS - a long-term record for ongoing evaluations of control programs.

INTRODUCTION

This document is the first edition of the PAMS Data Analysis "Results" Report, a summary and compilation of salient examples and illustrations of the uses of data from the Photochemical Assessment Monitoring Stations (PAMS) program[1]. As such, the Report utilizes examples of analyses available at the time of its development and contains no independent or "new" analyses. However, this Report will be updated annually and will include the results of future analyses performed by the Office of Air Quality Planning and Standards (OAQPS) and others. The Report summarizes the current state of PAMS data analysis as a vehicle for transferring the resultant techniques and insights, and encouraging a dialogue among analysts using the data.

I.1 PURPOSE

This report is intended to capture the best examples of the uses of PAMS data to understand the tropospheric ozone issue and to motivate regulatory and control program activity. Although the design is to show "what can be done" with PAMS data, the hope is that these examples will also serve to catalyze a commitment to making full use of this rich data set, to instruct those interested in analyzing the data and to, some degree, help guide those endeavors. In no case, have all existing examples been used. Instead, those of greatest illustrative power or unique character have been chosen for inclusion.

The primary audience for this Report is comprised of air quality data analysts charged with and/or interested in using the PAMS data. Obviously, the document also addresses issues and covers subjects which are of importance to ozone control program and regulatory staff, as well as photochemical modelers. Finally, through this Report, policy and decision-makers grappling with the complex issues of the tropospheric ozone will discover the applicability and relevancy of PAMS data to this environmental challenge.

I.2 DOCUMENT ORGANIZATION

The report is organized into the following five chapters:

- Characterization of ambient air quality data for ozone and its precursors;
- PAMS data in support of ozone modeling applications;
- Evaluating emissions factors, models and inventories with PAMS data;

[1] 40 CFR 58 Subpart E.

- Observational based methods for determining VOC/NO_x effectiveness; and
- Quality assurance.

The order of the subject matter implies neither a suggested sequence for the reader nor a required process for analyzing data from the PAMS program. Each chapter is constructed as a"stand alone" description of the associated subject and therefore can be read independently. An effort has been made through citations and footnotes to "link" all examples which transcend the individual chapters allowing the reader to reference previous discussions which dealt with the example of interest. The figures and tables for each chapter have been appended to the end of the respective text in the order presented in the material.

I.3 PAMS - A BRIEF DESCRIPTION

I.3.1 Why PAMS?

Of the six criteria pollutants, the most pervasive environmental problem continues to be ozone. The most prevalent photochemical oxidant and an important contributor to "smog", ozone is unique among the NAAQS pollutants in that it is not emitted directly into the air, but instead results from complex chemical reactions in the atmosphere between volatile organic compounds (VOCs) and nitrogen oxide (NO_x) emissions in the presence of sunlight. Further, there are literally thousands of sources of VOCs and NO_x across the country. To track and control ozone we need to understand not only the pollutant itself, but also the chemicals, reactions, and conditions that go into forming it.

In 1991, the National Academy of Sciences (NAS) released a report entitled, Rethinking the Ozone Problem in Urban and Regional Air Pollution, criticizing the EPA for failing to establish monitoring networks to adequately track trends in ozone precursor emissions, corroborate emission inventories, and support photochemical modeling. In accordance with the "enhanced monitoring" provisions of Title I of the Clean Air Act Amendments of 1990, EPA developed the PAMS program to address the concerns raised by the NAS[2,3]. The PAMS program reflects the need to complement the Agency's historically based emissions modeling approach with

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[2] In addition to the NAS report, the PAMS program is part of the Agency's response to recommendations contained in the 185b Report to Congress

[3] Another current effort reflecting the Agency's response to the recommendations of the NAS is the North American Research Strategy for Tropospheric Ozone (NARSTO), a field study and modeling research program with which the PAMS program has close interaction.

ambient techniques, consistent with the basic tenets of the NAS report.

I.3.2 Regulatory Requirements

Section 182(c)(1) of the 1990 Clean Air Act Amendments called for improved monitoring of ozone and its precursors, VOC and NO_x, to obtain more comprehensive and representative data on tropospheric ozone. Responding to this requirement, EPA promulgated regulations to initiate the PAMS program in February 1993. The PAMS program requires the establishment of enhanced monitoring networks in all ozone non attainment areas classified as serious, severe or extreme. The 22 affected ozone areas, shown in Figure I-1, cover 113 thousand square miles and have a total population of 79 million people[4].

Each PAMS network will consist of as many as five monitoring stations, depending on the area's population[5]. Table I-1 displays the ozone non-attainment areas required to implement the PAMS program and the number of sites they are expected to implement. The PAMS stations will be carefully located based on meteorology and other conditions at the site. Figure I-2 presents a schematic of a model network for a larger non-attainment area. Generally, each PAMS network will consist of as many as four different monitoring sites (Types 1, 2, 3, and 4) designed to fulfill unique data collection objectives. The Type 1 site is located upwind of the metropolitan area to measure ozone and precursors being transported into the area. The second site, Type 2, is referred to as the maximum precursor emissions impact site[6]. As the name implies, it is designed to collect data on the type and magnitude of ozone precursor emissions emanating from the metropolitan area and is typically located downwind of central business district. These sites operate according to a more intensive monitoring schedule than other PAMS stations, are capable of measuring a greater array of precursors and are suited for the evaluation of urban air toxics also. The Type 3 stations are intended to measure maximum ozone concentrations, and are sited downwind of the Type 2 sites and therefore of the urban area as well. The fourth PAMS site is

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[4] The text and map both reference the twenty-two areas originally required to participate in the PAMS program. However, Beaumont, Texas was reclassified to a moderate non attainment status effective June 1996 and therefore no longer affected by PAMS requirements. Hence, there are actually twenty-one non attainment areas subject to PAMS requirements currently.

[5] For more detailed descriptions of PAMS network requirements, see the PAMS Implementation Manual, EPA-454/B-93-051, 1994.

[6] A second type 2 site may be required in some PAMS areas and is positioned to capture the precursor emissions in the second-most predominant morning wind direction. This additional type 2 site constitutes the fifth PAMS site in the network.

located downwind of the non attainment area to assess the ozone and precursor levels exiting the area and potentially contributing to the ozone problem in other areas.

States which experience significant impact from long-range transport of ozone or its precursors, or are proximate to other nonattainment areas (even in other States) can collectively submit a network description which contains alternative sites to those that would be required for an isolated area as shown in Figure I-2[7]. Such coordinated network plans should be based on the example depicted in Figure I-3, and must include a demonstration that the alternative design satisfies the monitoring data uses and fulfills the PAMS objectives[8].

I.3.3 Status

Over its first four years, the PAMS program has exhibited steady and successful growth. Currently, there are approximately seventy PAMS surface air quality and meteorology monitoring stations established and operating across the nation. This represents at least one monitoring station in each of the twenty areas involved in the PAMS program[9]. Table I-2 lists the established and operating PAMS monitoring sites by non-attainment area and provides their AIRS site identification numbers. Table I-3 summarizes the minimum network requirements by non-attainment area and sampling frequencies by PAMS site type.

The data collected at the PAMS sites includes measurements of ozone, oxides of nitrogen, a target list of VOCs including several carbonyls (see Table I-4) as well as surface and upper air meteorology. Most PAMS sites measure 56 target hydrocarbons on an hourly basis during the ozone season. Included in the monitored VOC species are nine compounds classified as hazardous air pollutants (HAPs). The type 2 sites also collect data on carbonyl compounds every three hours during the ozone monitoring period. All stations measure ozone, nitrogen oxides and surface meteorological parameters on an hourly basis.

The PAMS networks produce a wealth of information invaluable to the development and

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[7] PAMS Implementation Manual pages 2-4 to 2-6.

[8] Both California (South Coast Air Basin and Southeast Desert Modified AQMD non attainment areas) and Lake Michigan (Chicago and Milwaukee non attainment areas) have adopted approved plans for "combined" networks.

[9] Although there are twenty-two areas classified as serious, severe or extreme for ozone, the flexibility of the PAMS program allowed areas (in close proximity to one another) in two regions consolidate their monitoring operations [see footnote 8] and one original area has been reclassified [see footnote 4]. Therefore, only nineteen PAMS networks exist

evaluation of ozone control strategies and programs. In addition to providing a long term perspective on changes in atmospheric concentrations in ozone and its precursors, the PAMS program will specifically help to improve emission inventories, serve as input to photochemical grid models, provide information to evaluate population exposure, and provide routine measurements of selected HAPs. Most importantly, PAMS will assist in delivering a more complete understanding of the complex problem of ozone, so that we may move toward the best solution[10].

I.4 FURTHER INFORMATION

I.4.1 Comments

Please forward your comments, suggestions, etc. to:

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I.4.2 Request for Additional Copies

Additional copies of this report are available through the Emissions, Monitoring and Assessment Division. Please contact Linda Ferrell at 919-541-5558 to request a copy.

[10] For a more complete discussion of the intended uses of PAMS data, see Section I of the PAMS Implementation Manual and its treatment of PAMS' data quality objectives.

Figure I-1.

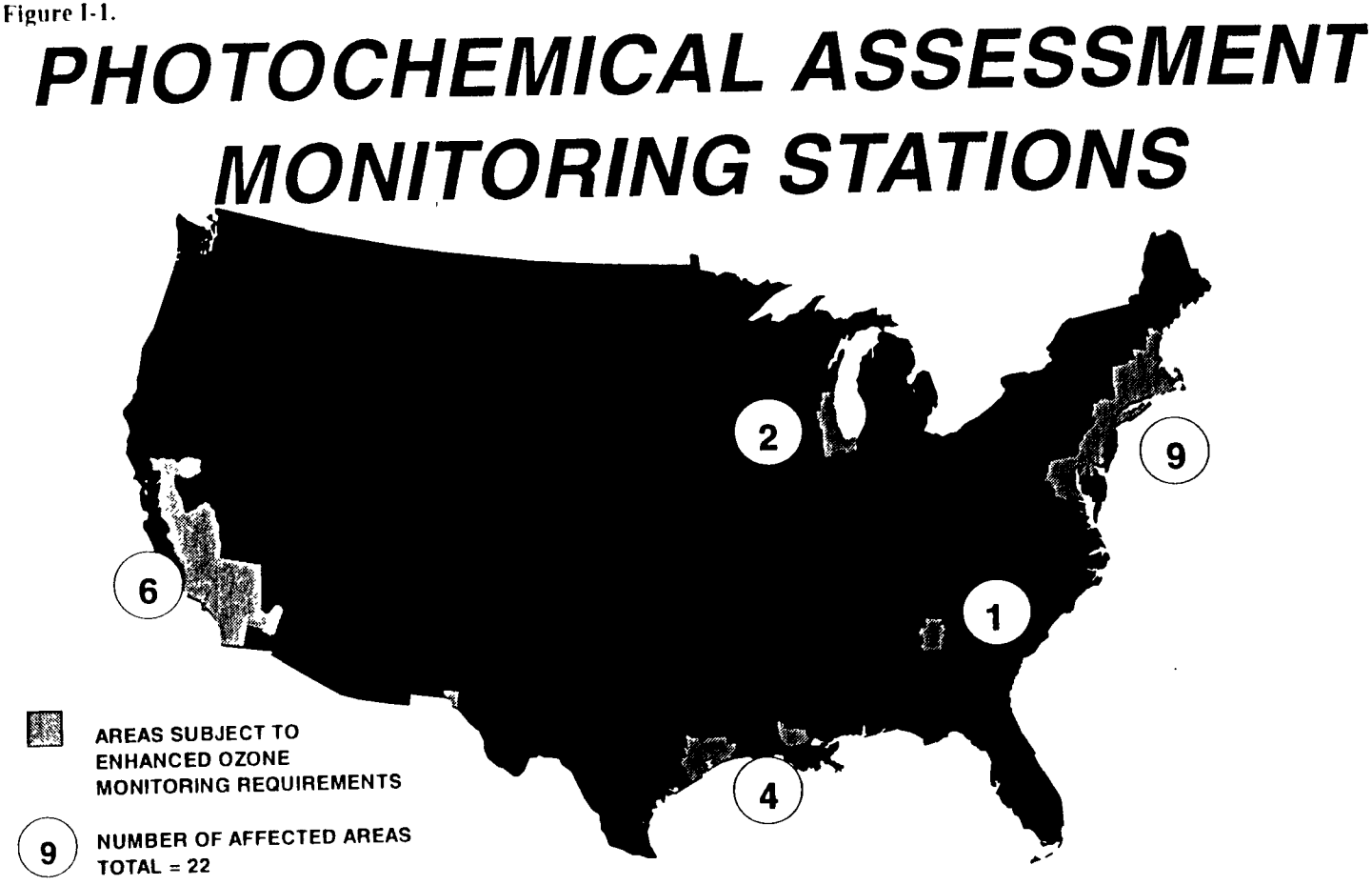

PHOTOCHEMICAL ASSESSMENT
MONITORING STATIONS
2
9
6
1
4
AREAS SUBJECT TO
ENHANCED OZONE
MONITORING REQUIREMENTS
9
NUMBER OF AFFECTED AREAS
TOTAL = 22

Figure I-2. Basic PAMS Scheme

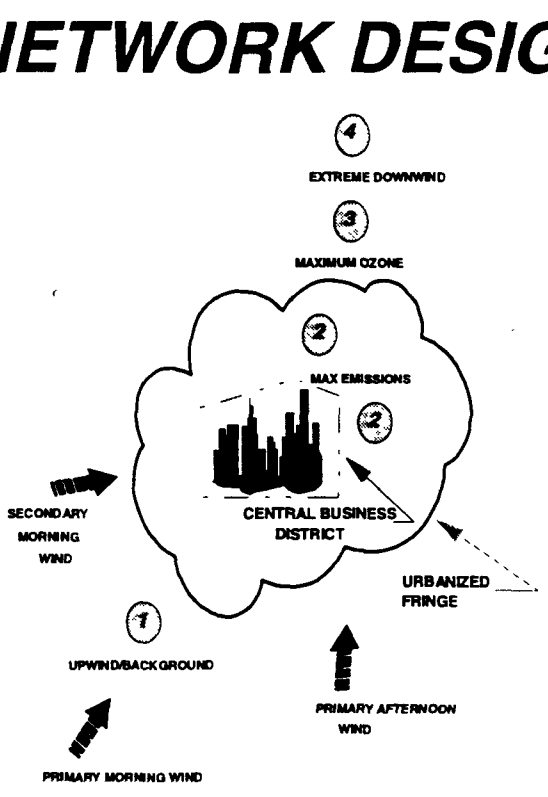
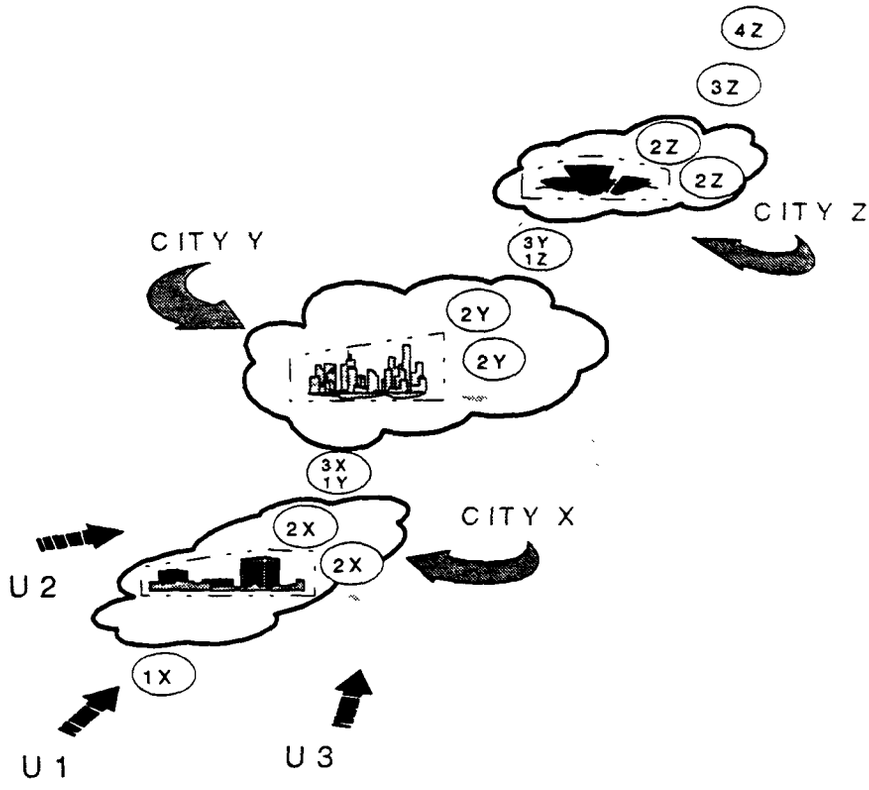


Figure I-3. Multi-Area and Transport Area Network Design



ble I-1. PAMS Requirements for Currently Affected Areas

CURRENTLY-AFFECTED AREA NAME	POPULATION RANGE	CLASSIFICATION OF NONATTAINMENT AREA	MINIMUM NUMBER OF REQUIRED SITES
Beaumont-Port Arthur, TX[1]	Less Than	Serious	2
Portsmouth-Dover-Rochester, NH-ME	500,000	Serious	2
Southeast Desert Modified AQMA, CA		Severe	2
Baton Rouge, LA		Serious	3
El Paso, TX	500,000 to	Serious	3
Springfield, MA	1,000,000	Serious	3
Ventura County, CA		Severe	3
Milwaukee-Racine, WI	1,000,000 to	Severe	4
Providence-Pawtucket-Fall River, RI-MA	2,000,000	Serious	4
Sacramento, CA		Serious	4
Atlanta, GA		Serious	5
Baltimore, MD		Severe	5
Boston-Lawrence-Worcester, MA-NH		Serious	5
Chicago-Gary-Lake County (IL), IL-IN-WI		Severe	5
Greater Connecticut, CT		Serious	5
Houston-Galveston-Brazoria, TX	More Than	Severe	5
Los Angeles-South Coast Air Basin, CA	2,000,000	Extreme	5
New York-New Jersey-Long Island, NY-NJ-CT		Severe	5
Philadelphia-Wilmington-Trenton, PA-NJ-DE-MD		Severe	5
San Diego, CA		Severe	5
San Joaquin Valley, CA		Serious	5
Washington, DC-MD-VA		Serious	5
Totals	-----	22 Areas	90

[1]Reclassified on 6/1/96 to moderate nonattainment status therefore not required to implement PAMS program.

TABLE I-2. PAMS MONITORING SITES

AREA	SITE	AIRS NUMBER
Boston	Borderland #1	25-005-1005
	Lynn - #2	25-009-2006
	Newbury - #3	25-009-4004
	Cape Eliza., ME- #4	23-005-2003
Connecticut	Sherwood Island #1/#3	09-001-9003
	E. Hartford #2	09-003-1003
	Stafford #3	09-013-1001
Portsmouth	Stratham #1	33-xxx-xxxx
	Kittery, ME #2	23-031-3002
Providence	W. Greenwich #1	09-001-0017
	E. Prov #2	44-007-1010
	(Borderland, MA #3)	25-005-1005
Springfield	Agawam #1	25-013-0003
	Chicopee #2	25-013-0008
	Ware #3	25-015-4002
New York	Purchase #2	36-119-5003
	Botanical Gardens #2	36-005-0083
	(Sherwood Island, CT #3)	09-001-9003
Baltimore	Fort Meade, MD #1	24-003-0019
	Essex #2	24-005-3001
	Morgan State #2	24-510-0050
	Aldino #3	24-025-9001
	(Lums Pond, DE #4)	10-003-1007
	Clifton Pk. or Living Rm #2A	xx-xxx-xxxx
Philadelphia	Lums Pond (DE) #1	10-003-1007
	East Lycoming Lab #2	42-101-0004
	Rider College (NJ) #3	34-021-0005
Washington	Corbin, VA #1	51-033-0001
	(Caroline Co. Met Only #1)	51-033-0002
	McMillan Reservoir #2	11-001-0043
	(Fort Meade, MD #3)	24-003-0019
	(Lums Pond, DE #4)	10-003-1007
Atlanta	Yorkville #1	13-223-0003
	So DeKalb #2	13-089-0002
	Tucker #2	13-223-0003
	Conyers #3	13-247-0001
Lake Michigan	Braidwood #1	17-197-1007
	Milwaukee UWM #2	55-079-0041
	Chicago NWU #2	17-031-0039
	Chicago-Jardine #2	17-031-0072
	Gary, IN #2	18-089-1016
	Harrington Bch #3	55-089-0009
	Zion #4	17-097-1007
	Manitowoc, WI #4	55-071-0007

AREA	SITE	AIRS NUMBER
Houston	Galveston #1	48-167-0014
	Galleria #2	48-201-0067
	Clinton Dr #2	48-201-1035
	HRM No. Three #2	48-201-0803
	Deer Park #2	48-201-1003
	Aldine #3	48-201-0024
Baton Rouge	Pride #1/#3	22-033-0008
	Capitol #2	22-033-0009
	Bayou Plaquemine #3/#1	22-047-0009
El Paso	N. Campbell #2	48-141-0027
	Chamizal #2	48-141-0044
	UTEP #3	48-141-0037
South Coast/ SEDAB	Pico Rivera #2	06-037-1601
	Azusa #3	06-037-0002
	Banning #2	06-065-0002
	Upland #4/1	06-071-1004
San Diego	El Cajon #2	06-073-0003
	Overland #2A	06-073-0006
	Alpine #3	06-073-1006
Ventura Co	El Rio #2	06-111-3001
	Simi Valley #3	06-111-2002
Sacramento	Del Paso #2	06-067-0006
	Folsom #3	06-067-1001
	Elk Grove-Bruceville	xx-xxx-xxxx
San Joaquin	Golden St Ave #2 (Bkrsfld)	06-029-0010
	Clovis-Villa #2	06-019-5001
	Arvin #3	06-029-5001
	Parlier #3	06-019-4001

Table I-3.

PAMS MINIMUM NETWORK REQUIREMENTS

MINIMUM NETWORK REQUIREMENTS

POPULATION OF MSA/CMSA	FREQ TYPE	SITE LOCATION
LESS THAN 500,000	A or C	(1)
	A/D or C/F	(2)
500,000 TO 1,000,000	A or C	(1)
	B/E	(2)
	A or C	(3)
1,000,000 TO 2,000,000	A or C	(1)
	B/E	(2)
	B/E	(2)
	A or C	(3)
GREATER THAN 2,000,000	A or C	(1)
	B/E	(2)
	B/E	(2)
	A or C	(3)
	A or C	(4)

VOC SAMPLING FREQUENCY REQUIREMENTS

Freq	Requirement
A	8 3-Hour Samples Every Third Day 1 24-Hour Sample Every Sixth Day
B	8 3-Hour Samples Everyday 1 24-Hour Sample Every Sixth Day (year-round)
C	8 3-Hr Samp 5 Hi-Event/Prev Days/Every 6th Day 1 24-Hour Sample Every Sixth Day

CARBONYL SAMPLING FREQUENCY REQUIREMENTS

Freq	Requirement
D	8 3-Hour Samples Every Third Day
E	8 3-Hour Samples Everyday
F	8 3-Hr Samp 5 Hi-Event/Prev Days/Every 6th Day

MINIMUM PHASE-IN

YEARS AFTER PROMULGATION	NUMBER OF SITES OPERATING	OPERATING SITE LOCATION RECOMMENDATION
1	1	2
2	2	2,3
3	3	1,2,3
4	4	1,2,3,4
5	5	1,2,2,3,4

Table I-4. PAMS Target Species

VOC COMPOUNDS

Ethylene
Acetylene
Ethane
Propylene
Propane
Isobutane
1-Butene
n-Butane
trans-2-Butene
cis-2-Butene
Isopentane
1-Pentene
n-Pentane
Isoprene
trans-2-Pentene
cis-2-Pentene
2,2-Dimethylbutane
Cyclopentane
Total NMOC

2,3-Dimethylbutane
2-Methylpentane
3-Methylpentane
2-Methyl-1-Pentene
n-Hexane
Methylcyclopentane
2,4-Dimethylpentane
Benzene
Cyclohexane
2-Methylhexane
2,3-Dimethylpentane
3-Methylhexane
2,2,4-Trimethylpentane
n-Heptane
Methylcyclohexane
2,3,4-Trimethylpentane
Toluene
2-Methylheptane

3-Methylheptane
n-Octane
Ethylbenzene
m/p-Xylene
Styrene
o-Xylene
n-Nonane
Isopropylbenzene
n-Propylbenzene
m-Ethyltoluene
p-Ethyltoluene
1,3,5-Trimethylbenzene
o-Ethyltoluene
1,2,4-Trimethylbenzene
n-Decane
1,2,3-Trimethylbenzene
m-Diethylbenzene
p-Diethylbenzene
n-Undecane

CARBONYL COMPOUNDS

Acetaldehyde
Acetone
Formaldehyde

Hazardous Air Pollutants (HAPs)

CHAPTER 1
CHARACTERIZATION OF AMBIENT AIR QUALITY DATA FOR OZONE AND ITS PRECURSORS

1.1 INTRODUCTION

Characterization of ozone episodes is extremely important. A key consideration in devising an effective control strategy is to ensure that the strategy works under a variety of conditions which have been observed to correspond with high measured ozone. The relative importance of ozone/precursors transported into an area is likely to be one important distinguishing characteristic of episodes. Thus, the needs to accurately characterize episodes and identify the potential role of transport are closely related. In a modeling analysis, performed to assess adequacy of proposed control strategies, it is important to have chosen a limited number of episodes which are representative of differing conditions leading to high observed ozone. More generally, a knowledge of meteorological, precursor characteristics and other ambient conditions which correspond with high ozone is useful in helping to formulate policies which are likely to lead to improvements in measured ozone levels. In this chapter, we present examples illustrating the added value of PAMS data in characterizing ozone episodes and identifying features that may be linked to significant pollutant transport.

Both Sections 1.2 and 1.3 focus on how PAMS data can be used to enhance the characterization of local ozone episodic events. The examples presented illustrate the potential uses for and the value-added of both the meteorological and ambient air quality data collected at PAMS sites. The discussions include the extent to which the PAMS data may be useful in assessing the potential role of transport in different episodes.

1.2 EPISODE CHARACTERIZATION USING METEOROLOGICAL MEASUREMENTS

Ozone conducive meteorological conditions such as high insolation, high temperature, high stability (as often reflected by low mixing heights), low winds, and low midday relative humidity have been identified by various researchers in the past (Bruntz et al., 1974; Lamb et al., 1987; Chu, 1987; Chu and Doll, 1991; Cox and Chu, 1993; Robinson, 1952; Hosler, 1961; Ludwig et al., 1977; Pagnotti, 1990). These ozone conducive meteorological conditions can thus be used to characterize the local ozone episodes.

1.2.1 Characterizing Episode "Severity"

EPA has developed relatively simple regression based models to estimate the severity of daily ozone episodes using meteorological data from the National Weather Service. Presently, this methodology considers only surface meteorological variables to characterize episode severity. Since PAMS provides on-site surface as well as upper air meteorological data, the potential for more accurate classification and characterization of distinct episode types (and eventually severity) exists. The routine upper air (rawinsonde) data collected by the National Weather Service (NWS) network are intended to resolve synoptic scale weather systems which have a length scale of about 2000 - 4000 km. Air quality episodes, however, are usually observed in a smaller domain of 1000 km or less in which meso-scale dynamics play a significant role. Thus, the region wide PAMS upper air measurements (in particular, the data collected by RASS and radar profilers) provide valuable information on local mixing height changes, as well as detecting nocturnal jets and topographically induced meso-scale circulations. These, in turn, will help better describe the local characteristics of the episodes and provide inference of possible intra- and/or inter-regional pollutant transport.

Cox and Chu (1993; 1996) have developed a statistical model to predict ozone producing potential using local surface and upper air meteorological data. The model has been applied to minimize meteorological influences on ozone trend analysis, to rank the local severity of ozone episodes, and to select episodic days for modeling and control strategy designs. The PAMS hourly surface and upper meteorological air data (e.g., winds, temperature, humidity, and mixing height data) will certainly increase the power of these models to better define the characteristics of local episodic ozone events as should PAMS air quality data described in Section 1.3. PAMS data, particularly from the RASS and radar profiler sites, will provide better estimates of mixing heights as well as other meteorological measurements aloft. These variables could improve the skill of the statistical model in ranking meteorological ozone forming potential.

1.2.2 Determining Source/receptor Orientations Corresponding to Ozone Conducive Conditions

Chu (1995) has shown that the frequency distribution of local predominant wind directions (PWD) on high ozone days is useful in describing source/receptor orientations which can be predicted by a set of ozone conducive meteorological variables: daily maximum temperature, morning (7-10 a.m.) average wind speed, afternoon (1-4 p.m.) average wind speed, and midday (10 a.m. - 4 p.m.) average relative humidity. By better characterizing local mixing heights, PAMS data help better define PWDs with accompanying high ozone forming potential. The frequency distribution of the PWDs (including near calm conditions) on high ozone days may help to identify which type of ozone episodes (i.e., stagnation or transport or a mixture) is most often observed (i.e., representative) locally. Further insight into potentially significant pollutant transport may be

possible from flux analysis using PAMS upper air wind measurements (e.g, leading to detection of a nocturnal jet, such as that shown in Figure 1-1) (Lindsey, 1995). Trajectory analyses, like that shown in Figure 1-2, are useful in classifying episodes according to source/receptor orientation (Lindsey, 1995).

1.2.3 Identifying Critical Circulations Associated with High Ozone Events

Very high local ozone concentrations observed in episodes are often heavily influenced by certain meso-scale circulations embedded in large, stagnant synoptic systems. Most of these meso-scale systems are topographically induced, as in sea/lake breeze circulations and mountain-valley flows. Under a stagnant, synoptic-scale high pressure system, these localized meso-scale systems become a major mechanism for mixing, dispersing, and transporting pollutants. For example, in coastal areas, observations often suggest that local high ozone concentrations generally coincide with the sea breeze convergent zone. Although a single PAMS upper air monitor (either a RASS or a radar profiler) may not be sufficient to resolve these meso-scale circulations, it could still provide some valuable information in the integrated analysis of the episode with surface meteorological and air quality data. An example of using the PAMS-like data in an integrated analysis of the influence of sea breeze recirculation on Houston high ozone events is illustrated in Figures 1-3 to 1-6 (Systems Applications International).

1.2.4 Identifying Boundary Layer Structures Associated with High Ozone Events

Since meteorological conditions are quite distinctive on high ozone days, it is not surprising that the structure of the atmospheric boundary layer in which the pollutants are mixing, reacting, and dispersing would be quite different from those on non-episodic days. The boundary layer profile of temperatures, winds, humidity, and mixing heights would have a direct impact on surface ozone concentrations. Due to the advanced technical capability of the instrumentation employed, the hourly winds, temperature, humidity, and reflectivity (C_n^2) data collected by the PAMS RASS and/or radar profilers add more detailed local information to the routine (and often remote) NWS rawinsonde observations and thus increase our understanding of the boundary layer structure on high ozone days. Figure 1-7 is an example showing the diurnal mixing height change derived from C_n^2 (Dye et al., 1995).

1.3 EPISODE CHARACTERIZATION USING AIR QUALITY MEASUREMENTS

PAMS data play a critical role in characterizing air quality episodes used in photochemical modeling and in the design of cost effective control measures. Since NAMS and SLAMS were originally deployed, monitor siting technology has improved considerably such that newly located PAMS stations are meeting various objectives (e.g. maximum ozone concentration levels) with greater assurance and accuracy than previously possible. More importantly, precursor data allows

characterization of episodic events by species mix which may be used to assess the likely impact of particular strategies on ozone levels. Moreover, measured species data coupled with on-site meteorological data will lead to improved statistical models used to characterize ozone formation potential and relative frequency of occurrence for various episode types. The utility of precursor measurements to help characterize episode severity is expected to increase as the period of record for the PAMS measurements increases. This follows since the number of episodes which have precursor data and which are candidates for modeling or policy analysis will increase with passing time.

1.3.1 Indicators of Ozone Episodes

Ozone levels during the summer of 1995 in much of the US are reported to be somewhat higher than found in previous years. EPA conducted a short intensive study of the relative severity of ozone levels in 1995 compared with those in previous years using statistical methods that factored in measured meteorological conditions and urban specific ozone trends over the past decade. Based on the preliminary analysis, EPA concluded that while the summer of 1995 was unusually warm, overall conditions for elevated ozone were not atypical compared with previous years having high ozone levels. While most of the ozone measurements used in this study were from NAMS/SLAMS sites, a significant number of sites (~ 50) were operating PAMS ozone sites. One of the findings from the study was the preponderance of PAMS ozone sites (47 of 50) that reported at least one exceedance of 120 ppb during 1993-1995 suggests that PAMS sites are well placed for detecting peak ozone levels.

1.3.2 Distinguishing among Episode Types

Relative importance of transport is an important means for distinguishing among ozone episodes. Some types of ozone episodes produce a distinctive trend in diurnal patterns that may be suggestive of transport conditions. An example of such an episode for July 20-22 of 1994 in which a smooth northeasterly time progression of the ozone peak was observed over sites in New England from Lynn, MA through Jonesport ME is displayed in Figure 1-8 (NESCAUM, 1995). In a companion plot (Figure 1-9), 8-hour moving average ozone showed a clear broadening of the plume over time (NESCAUM, 1995).

Although the maximum 8-hour concentrations declined with distance, the broadening of the plume caused exposures above 70 ppb over a larger portion of the day. Since PAMS sites are located at upwind and downwind locations, this phenomenon can be more fully investigated in PAMS urban areas. For example, plots of the observed diurnal pattern for ozone, NO, NO2 and VOC species should reveal general decay in primary species coupled with an increase in secondary species if significant transport is occurring.

1.3.3 Characterizing Precursor Species During Episodes

A major strength of the PAMS program is the requirement for speciated hydrocarbon measurements to be made on a continuous (hourly or 3-hour) basis for up to 55 targeted hydrocarbon (and 3 carbonyl) compounds. Utilizing this attribute, episodes can be better characterized through analysis of the abundance of precursors experienced during periods of elevated ozone levels. An analysis of the 1994 data from the Northeast by the NESCAUM Ambient Monitoring and Assessment Committee is used to illustrate such assessments below (NESCAUM, 1995).

For the ozone episodes 07/06/94-07/08/94 and 07/20/94-07/22/94, the abundance of targeted VOCs from the five PAMS sites in the Northeast is shown in Figure 1-10 (NESCAUM, 1995). The study revealed that the most prevalent species are remarkably consistent across the region for the time period of interest. Seven compounds (i.e., isopentane, toluene, propane, ethane, n-butane, m&p-xylene and n-pentane) were found to be among the ten most abundant species at all sites except the Cape Elizabeth site. Even for this site, five of the seven species were among the ten most abundant. Interestingly, the biogenic isoprene was found at significant concentrations at four of the sites[1]. The report concluded that the pattern of similar abundances throughout the urbanized portion of the region (and to some extent, the remote portions such as Cape Elizabeth) was perhaps to be expected given the ubiquity of mobile sources.

The results above were further compared to data for five Northeastern cities from the 6:00 to 9:00 AM time period from a previous study (Wixtrom, R.N., et al.). As shown in Table1-1, six of the seven compounds of greatest abundance for the 1994 PAMS data were also the most prevalent for these five cities (NESCAUM, 1995). An extensive study of speciated VOCs in the Los Angeles area (Lurmann, F.W. , et al.) found "the same seven anthropogenic compounds to be most abundant and, with the exception of propane, in virtually the same rank of occurrence."

Volatile organic compounds react at different rates and with different reaction mechanisms due to their variations in their chemical composition and structure. As a result, VOCs differ significantly in their potential to form ozone. The use of incremental reactivities of VOCs provides a way to avoid an oversimplification of treating abundance estimates of all VOCs as equivalent. Incremental reactivity allows analysis of the effect of changing the concentration/abundance of a VOC on ozone formation. In the NESCAUM analysis, the maximum incremental reactivity (MIR) scale developed by Carter was used to show the relative ozone forming potential of the various VOC and carbonyl species (Carter, 1994). The hourly average abundances (calculated from the PAMS data) were scaled by the MIRs and displayed as

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[1] At the East Hartford, CT site the isoprene concentrations were thought to be underestimated and compound misidentification is suspected of being reason for the lower abundance.

(potential) ppbv of ozone. The results are displayed graphically in Figure 1-11 (NESCAUM, 1995). The report noted that, although acetone and isopentane were found to be quite abundant, "their low reactivities result in rather low ozone forming potential". In addition, the increase in the relative significance of formaldehyde following the application of the MIR is highlighted. Although these data are preliminary and cover a short time span, the study concluded that the results were expected to be "a valid snapshot of upper limit conditions that typically exist in the Northeast" during periods of high ozone.

1.3.4 Assessing Airmass Aging Using PAMS Precursor Data

The same analysis of 1994 PAMS data from the Northeast by the NESCAUM Committee effectively used a comparison of ratios of VOC species to illustrate the effects of airmass aging. The series of graphics, Figures 1-12 through 1-17, from this study are used to describe the results (NESCAUM, 1995). Figure 1-12 displays the estimated benzene/toluene (B/T) and xylene/toluene (X/T) ratios based on 1990 Atlanta source profiles and source mix. Figure 1-13 shows the measured hourly ratios of benzene and m/p-xylene to toluene from the urban (type 2) PAMS site in E. Hartford, CT during the July, 1994 episode periods.

The scatter plot in figure shows that toluene levels at E. Hartford were highly correlated with both benzene and m/p-xylenes. This is consistent with a hypothesis that all three are primarily emitted by mobile sources. The B/T and X/T ratios at E. Hartford are also consistent with the predicted ratios displayed in Figure 1-13 derived from the Atlanta source profile data - suggesting that the E. Hartford source profiles and source mix are consistent with those in Atlanta (NESCAUM, 1995). Figure 1-14 shows the hypothetical effect of aging on Atlanta B/T and X/T ratios, while Figure 1-15 shows the measured B/T and X/T ratios for the rural type 3 PAMS site in Stafford, CT site (downwind of E. Hartford) during the July, 1994 episodes (NESCAUM).

The scatter plot in Figure 1-15 shows that the B/T ratio at the downwind, rural Stafford site has increased and the X/T ratio has decreased in comparison to the urban E. Hartford site shown previously in Figure 1-13 (NESCAUM). This is consistent with the predicted effect of airmass aging, as the more reactive species are differentially removed during transport. The points plotted in Figure 1-15 also exhibit greater scatter (B/T and X/T correlations are poorer) than Figure 1-13. While common (motor vehicle-related) sources are still anticipated to be a predominant cause of benzene, toluene and m/p-xylenes at the Stafford site, the species inter-correlations are diminished during transport, as the degree of aging depends on variable factors such as wind speed, wind direction, solar radiation, NO_x, etc.

Figures 1-16 and 1-17 show the relationships between toluene and m/p-xylenes at E. Hartford and Stafford, with different symbols to distinguish between daytime and nighttime samples (NESCAUM). At the urban E. Hartford site, there is relatively little difference in the X/T

ratios between nighttime samples (when reactivity is minimal) and daytime samples (when reactivity is maximal). This is consistent with a predominant, continuous influence of fresh, local, motor vehicle-related emissions at this site.

At the rural Stafford site (Figure 1-17), there's a more distinct difference between the daytime and nighttime X/T ratios. Nighttime ratios show a stronger correlation, and a slope similar to the predicted value of 0.6 for fresh emissions (and East Hartford's). For daytime samples at Stafford, there's a clear downward shift in the X/T slope (and a much poorer X/T correlation). This is consistent with a predominant influence of transported, motor vehicle-related emissions, which are photochemically aged (in a highly variable way) during the day, but which remain relatively unaged in the absence of sunlight.

1.3.5 Temporal Variation in PAMS Precursor Data

The typical daily patterns of hourly VOC concentration data and the comparison of these patterns with those of other PAMS areas, with national averages, and with historical data from this area are useful analyses to undertake to determine the unique source contributions from a particular area and changes in the composition of the urban area's ambient air quality. Average diurnal patterns or profiles are calculated by computing the average of all samples collected during each hour of the day. Most PAMS VOC species exhibit well defined diurnal cycles (or average values over time) which reflect source activity (e.g., traffic patterns), familiar daily meteorological patterns, and photochemical activity.

The first example result plotted in Figure 1-18 displays the average diurnal profiles of m,p-xylene and isoprene for six Northeastern PAMS sites for two ozone episodes in July 1994 (NESCAUM, 1995). The diurnal pattern for m/p xylene is similar to a number of other reactive, anthropogenic VOCs (toluene, o-xylene, isopentane, etc.), with emissions generally dominated by automotive-related sources. Isoprene is emitted predominantly by deciduous vegetation, as a function of solar radiation and temperature. As a biogenic compound, isoprene has a unique diurnal pattern which is distinct from that of the anthropogenic VOC species. While the morning (6:00 to 9:00 AM) levels and reactivities of m/p xylene and isoprene are quite similar, the reactive anthropogenic pollutants are generally depleted rapidly during the day. Although isoprene also reacts rapidly, its rate of production exceeds its rate of destruction during mid-day.

The next example result, Figure 1-19, introduces a variation on the basic diurnal pattern technique depicted above by using box plots for each hour rather than displaying simple means. Note that each panel contains 24 box plots corresponding to each hour of the day. The figure contains diurnal patterns for 1993 PAMS data on acetylene, olefins, toluene, ethylene, xylene and isoprene from Baltimore's Site #2 (Cox, 1995). The organic species for this analysis clearly indicate the typical diurnal trends for anthropogenic VOCs described above. Median values for all

species, except isoprene, show a tendency for higher morning and evening concentrations. These patterns are interpreted as follows:

- the morning maximum is associated with high emissions and limited mixing;
- the mid-day minimum is associated with decreased mobile source emissions, increased mixing due to rapid growth of the daytime boundary layer, and increased reaction rates due to higher temperatures and maximum solar radiation;
- the early evening maximum is associated with gradual build up of emissions in the boundary layer over the course of the day, increased mobile source emissions during the afternoon culminating in an early evening commute traffic peak, and decreased mixing.

The diurnal profile for isoprene reflects the fact that biogenic emissions are a strong function of temperature and solar radiation and are short-lived in the atmosphere.

The final example results for this section on diurnal patterns are from the analysis of 1993 PAMS data from Houston, Texas (Stoeckenius, November 1994). Figures 1-20a through 1-20c present separate calculations of the diurnal profiles of species concentrations for weekdays and weekends; an effort to identify the impact of differences in emissions between these two groups of days[2]. Comparisons of profiles between species and between weekdays and weekends can reveal much about underlying meteorological, chemical, and emission factors. The vertical bars in these figures indicate the 95 percent confidence limits for the mean value in each hour. Thus, pairs of hours with non-overlapping bars have significantly different mean concentrations.

At the Galleria site, weekday concentration profiles for all species except isoprene exhibit a strong morning peak. Morning peaks of acetylene, ethylene, toluene, olefins, and xylenes are noticeably lower on weekend mornings; these differences are consistent with reduced morning mobile source emissions on weekends. The lowest concentrations occur between 9:00 AM and 1:00 PM for all species (except isoprene) and the levels rise again to a second peak by early evening. These patterns are similar to those found in other analyses by other investigators.

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[2]Monday and Friday holidays were grouped in with weekends. Holidays falling in the middle of the week were left out of this analysis since traffic patterns and business activities on these days tend to differ from regular weekdays or weekends. Mean values were not computed for hours for which data was not available for at least two-thirds of sampling days. This restriction primarily affected the hours around midnight (hours 11, 0, and 1) which were sampled less frequently than other hours. A cubic spline fit was used to generate the smooth curves in these figures; the dots along the curves represent the actual hourly averages and are plotted at a position corresponding to the mid-point of the hour they correspond to. This plotting technique accentuates the diurnal patterns making graphs that are easy to read but one must be careful not to over interpret the peaks and troughs that may be shown as occurring between the actual hourly average values.

Diurnal profiles (based on weight percents) for the same VOC species above are presented in Figures 1-21a through 1-21c (Stoeckenius, November 1994). For the most part, the profiles are similar to the concentration profiles in Figures 1-20a through 1-20c. Some differences are evident, however. Toluene, olefins, and xylene weight percents exhibit smaller diurnal variations than their concentration counterparts although the pattern is basically the same.

1.3.6 Statistical Models of Relationship Between Ozone and Precursors

In the context of the PAMS program, the use of regression analysis involves developing empirical models to statistically describe the relationship (or potential relationship) between independent parameters (ozone precursors and meteorological data) and the dependent parameter (ozone). This analytic technique takes advantage of one of the unique characteristics of the PAMS data: the concurrent measurement of VOCs, meteorological parameters, nitrogen species and ozone. The results of these analyses (explanation in the variability of daily ozone maxima based on meteorological and precursor data) can lead to invaluable insights about the design of effective control strategies for the area analyzed.

However, this analytic technique and the example results which follow should only be considered as "exploratory" given the early stages of the PAMS program and the remaining further investigations that are required to verify and understand these initial evaluations. The reader is cautioned not to make inferences as to the nature of cause-effect relationships between the VOC species included in the regression models and downwind ozone (i.e., it is premature to predict or conclude how ozone levels would behave if concentrations of the included VOCs were reduced) based on these analytic results. These analyses should be viewed as another means to begin using PAMS data to develop a more complete understanding of the ozone phenomenon in PAMS cities. Finally, it is important to remember that these models have been constructed (to date) without selecting variables for inclusion in the model based on their hypothesized physical relationship to ozone.

The examples presented below demonstrate the technique using the 1994 PAMS data from the Philadelphia, PA[3]. The daily maximum ozone concentration, the dependent variable, was calculated from the downwind ozone data (Site#3). Data for the independent variables (i.e., VOCs, nitrogen species, meteorological parameters) were taken from the upwind urban site (Site #2). Several indicators for the independent variables were calculated (averages and maxima for selected intervals: three, six, twelve and twenty-four hour periods during the day of interest or lagged for earlier days). The relationships between all of these indicators and the dependent variable were then analyzed and those with the strongest correlations were then selected for

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[3] The ozone precursor and meteorological data included in the model are from the PAMS Site #2, and the downwind ozone data are from the PAMS Site #3.

inclusion in the regression model. Figure 1-22 uses a scatter plot to display how well the initial model, Model 1, estimated the observed daily maximum ozone values. This model utilized only meteorological parameters: temperature (mean for interval 12:00 PM to midnight) and wind speed (maxima for interval 6:00 to 9:00 AM). The R-square value for this model is 0.45 reflecting that the model using only meteorological parameters explains approximately 45% of the variability of downwind ozone levels.

The results presented in Figure 1-23 reveal an improvement in the model's "goodness of fit" (R-square) with the inclusion of VOCs. The following hydrocarbon species have been included with the earlier meteorological data in Model 2[4]:

VOC	Statistic/Interval
Isopentane	Mean/8 hr lag
3-Methyl pentane	Mean/9-12
n-Hexane	Mean/8 hr lag
n-Octane	Mean/19-22
Nitric Acid	Max/13-15
2,2-Dimethyl butane	Mean/6-9
Nitrogen Dioxide	Max/1-12
2-Methyl heptane	Mean/6-9
Ethyl benzene	Max/8 hr lag
Propane	Mean/8 hr lag

The resulting R-square value (0.84) is an improvement over that of the meteorology-only model. This example result suggests that the measurement of speciated hydrocarbons is essential for accurately representing and understanding the character of maximum ozone levels.

Neural networks provide a more flexible alternative to standard regression methods for relating dependent variables to a set of independent variables. Because neural networks are more general, they can accommodate both non-linearities and interactions among independent variables without explicit parameterizations required in non-linear regression models. While neural networks offer the potential for better prediction of the response variable, results are often difficult to interpret, mainly due to model complexity and multicollinearity of the process. Weights (regression coefficients) are typically unstable, usually "inflated" and vary considerably from true optima if local optima are found in the fitting process. Another major drawback is that extrapolation is risky: producing significant errors under certain conditions.

Crowe and coworkers have applied neural networks using data collected in the southeast Texas region at the Galleria Site near Houston. The data consisted of hourly meteorological data (net radiation, temperature, wind direction and speed, wind variation), nitrogen oxides (NO_2 and NO_x) and seven hydrocarbon species based on carbon bond 4 chemistry. Hourly ozone data were taken from a downwind site located at the Clinton site near east Houston. Three neural network

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[4] An additional model (not presented in this report) for the 1994 Philadelphia PAMS data was constructed and is available upon request. The model incorporated a number of additional VOC species to those already utilized in Models 1 and 2.

models were developed using proprietary software (Process Insight) developed by Pavilion Technology Inc. The predictor variables for the first model (MET) consisted of the five meteorological parameters for the same hour as the ozone measurement and also for 6 time delays to account for possible effects of transport and chemical reactions. The second model ($METNO_X$) included the same meteorological variables but added the species NO and NO_X. The third model ($METNO_XCB4$) dropped the time lagged variables (apparently unimportant) but added seven hydrocarbon species based the carbon bond 4 chemistry.

The models showed progressively better predictive capability (using the entire data set) as evidenced by increasing R^2 values from 0.70 (MET), 0.80 ($METNO_X$) and 0.91 for $METNO_XCB4$). The authors reported that selected hydrocarbon species are more sensitive predictors of hourly ozone--increasing olefins associated with decreasing ozone and increasing paraffins associated with sharply increasing ozone levels. The authors view this work as very preliminary and have neither attempted to associate any cause and effect to such relationships nor attributed any physical and/or chemical significance to their findings to date.

Capone applied neural network technology to predict down wind hourly ozone data in the Baton Rouge area using a more complicated network in which data from two downwind sites were used as predictors. The model consisted of hourly meteorological and NO_X measurements (NO2, NO and NO_x) at each site and was successful at predicting hourly ozone patterns as evidenced by graphics comparisons of the diurnal pattern and scatter plots between measure and predicted values. Interestingly Capone's model did not involve any hydrocarbon species, apparently due to a lack of relatively complete measurements in this area.

Meteorological and PAMS data for 1994 were used in an exploratory application of neural networks to predict daily maximum 1-hour ozone levels in the Philadelphia CMSA. The PAMS data were taken from an upwind Delaware site (10-003-1007) where hourly measurements are available from June-August. PAMS data included in the analysis were average TNMOC (6-9 am), olefins (6-9 am), NO (6-9 am) and NO_2 (6-9 am) and mid-day maximum hour isoprene. Daily composite meteorological variables were computed using available data from the nearest National Weather Service station. These variables included maximum surface temperature, morning and afternoon average wind speed, and mid-day average relative humidity and cloud cover. Out of 92 candidate days, only 51 days had sufficient data to be included in this analysis.

Using commercially available software, a neural network was used to relate maximum daily ozone to the combination of five meteorological and five PAMS precursor variables. For comparison purposes, neural networks of size 1 (logistic regression--11 weights) through size 3 (a total of 37 "weights") were fit using all 10 predictor variables. Figure 1-24 is a scatter plot of the log of the observed vs predicted ozone using for the smallest sized network. The fit is relatively good (R^2=0.68) which is not surprising since the five meteorological variables alone are known to

be good predictors of ozone forming potential in many U.S. urban areas. The R^2 using just the five meteorologically variables is nearly as good (0.64) suggesting that the precursor species provides only a marginal improvement in the fit.

The coefficients (weights) of the independent variables from this single node neural network may be interpreted in a similar manner as with ordinary regression models. For example, the coefficients for temperature are positive suggesting that increases in temperature are associated with higher ozone. Conversely, the coefficients for wind speed and cloud cover are negative suggesting that increases in winds and cloud cover are associated with lower ozone levels. Of the species variables, olefins and mid-day isoprene were negatively related to ozone although the magnitude of the coefficients were small relative to their standard errors.

Figure 1-25 show a similar plot of fitted ozone from a neural network of size=3. Although the R^2 statistic has increased considerably (0.89) the number of fitting parameters is large relative to the number of observations. Also, the relative complexity of the model makes interpretation of the coefficients difficult. For example, coefficients for temperature are both positive and negative in the three linear inputs feeding the hidden layer. Although the net effect of temperature is positive, it is difficult to interpret the relative role that temperature (and other variables) have within each layer. As more PAMS data becomes available, the stability of larger sized neural networks can be better assessed.

Clearly, the process of model building is very much an art at this point and will require close coordination among dispersion modelers, atmospheric scientists, and data analysts. Neural networks may help establish a practical upper bound on the predictive ability of statistical models and provide insight into reasonable model structures that may be more interpretable. Hopefully, the process will lead to development of physically meaningful input parameters that will help simplify the structure of these models and lend credibility to their potential applications. For example, better predictive models should provide better selection of episodes for modeling and more accurate assessment of the severity of episodes used in model based attainment demonstrations. Also, properly structured empirical models may provide supportive information regarding the potential effectiveness of emission control strategies including the relative benefits of VOC/NO_x emission reductions on ozone levels.

Crowe and coworkers applied neural network methods to predict hourly ozone levels using PAMS like data taken at Texas air monitoring sites during 1990-1994. They report R^2 statistics on the order of 0.75 when meteorological data alone are used in the model. When hourly precursor concentrations of selected VOC's, NO_x are included, R^2 statistics increase to approximately 0.85 suggesting that precursor species are important predictors of ozone levels.

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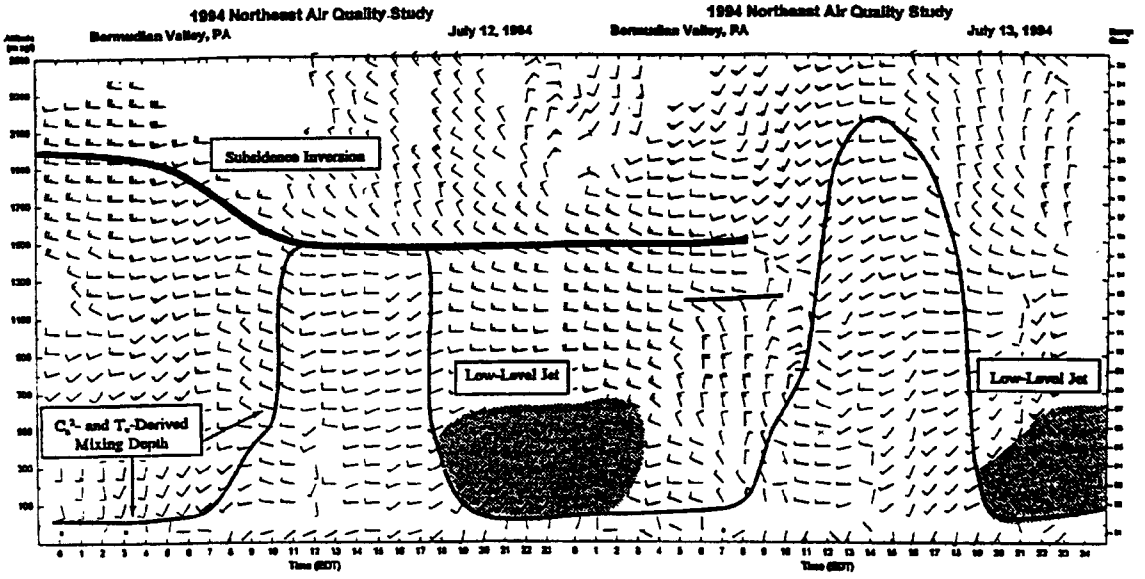
Figure 1-1.



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 (Lindsey et al., 1995b)

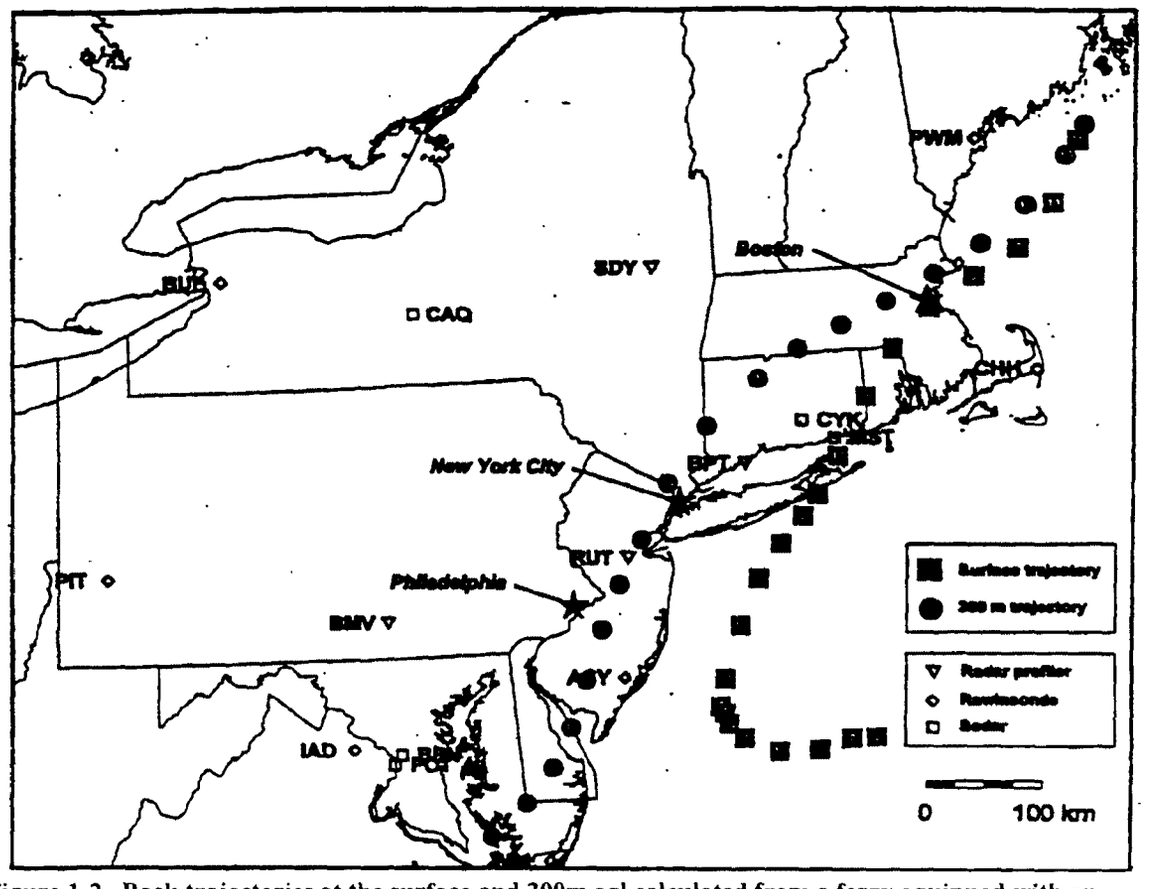
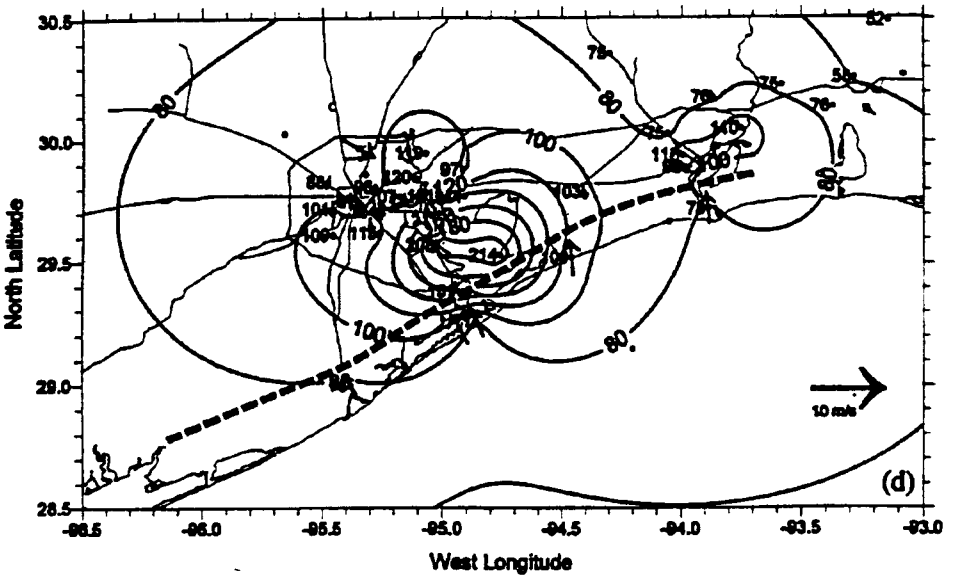


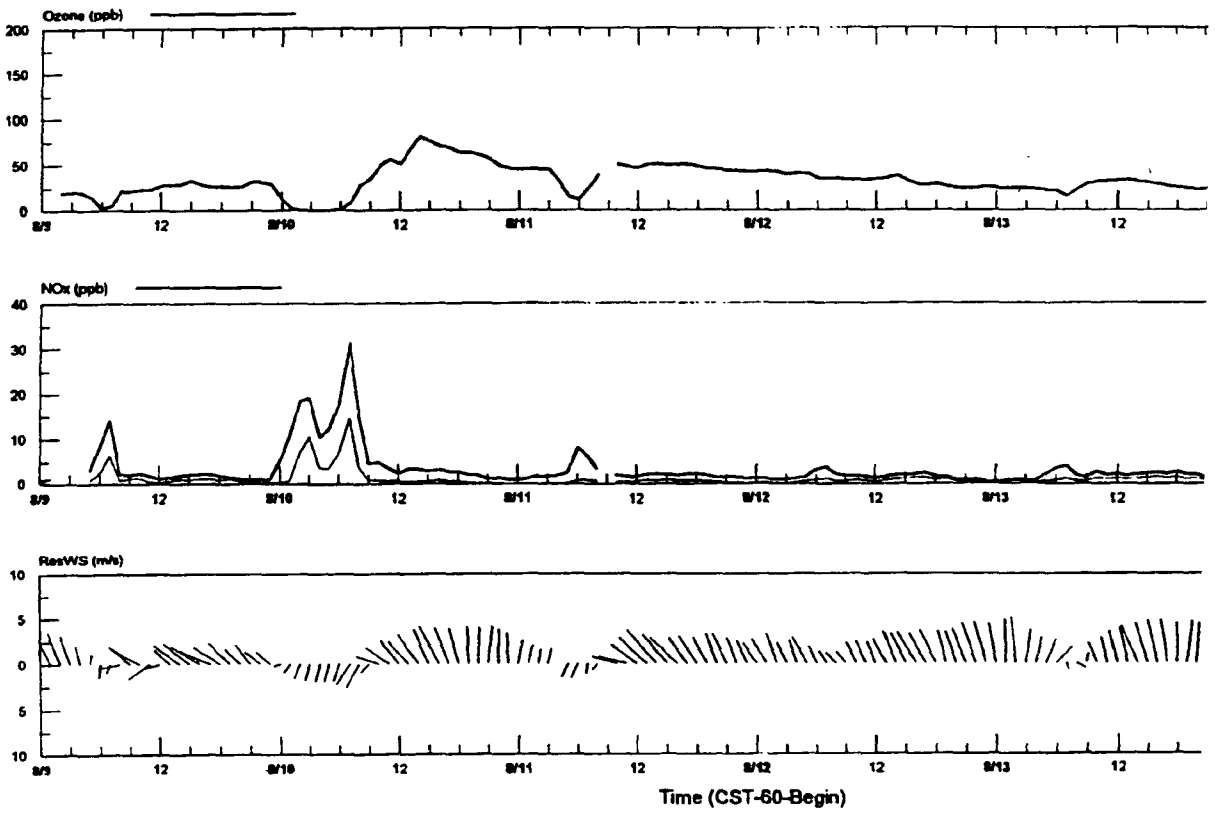
Figure 1-2. Back trajectories at the surface and 300m agl calculated from a ferry equipped with an ozone monitor (operated by the state of Maine) that recorded exceedances of the ozone standard on July 21, 1994.

Figure 1-3.



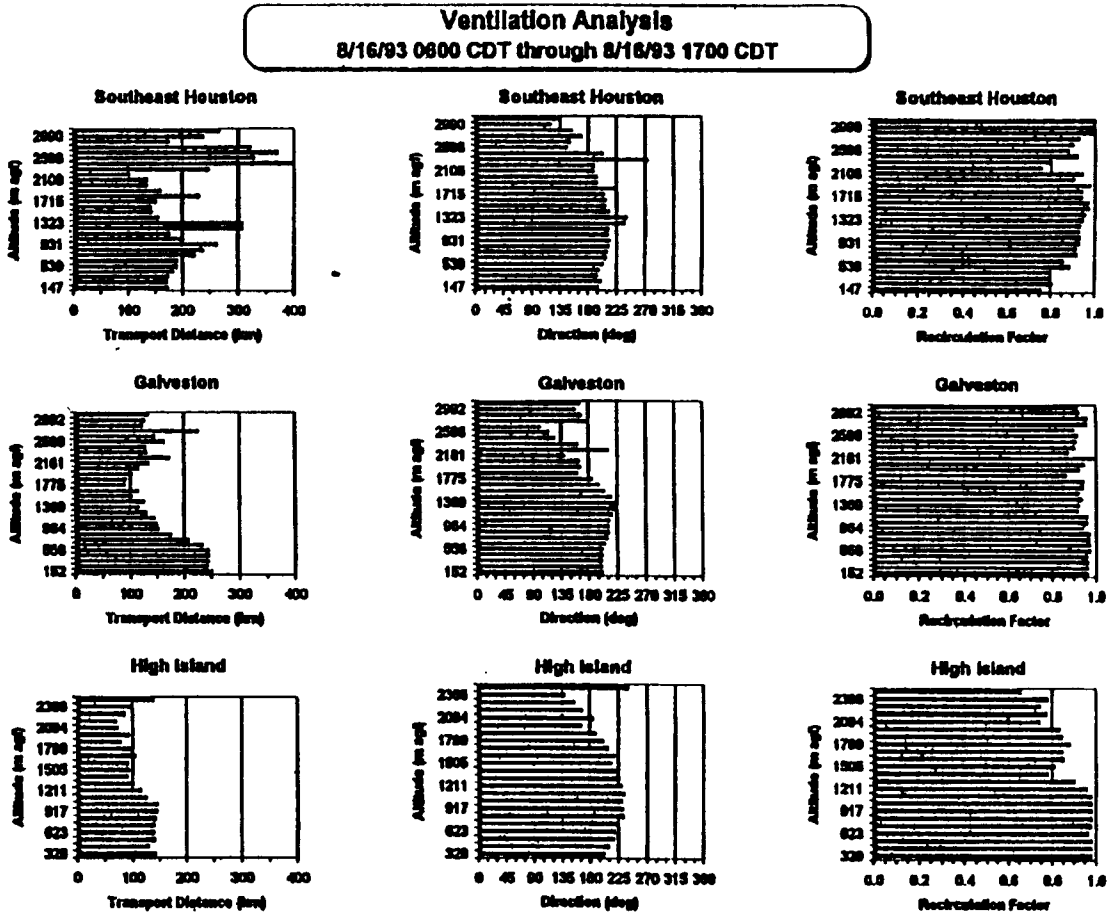
Plot of surface winds and ozone concentrations in the southeast Texas region at 1400 CST on September 8, 1993 (SAI 1995). The dashed line indicates the location of the sea breeze front.

Figure 1-4.



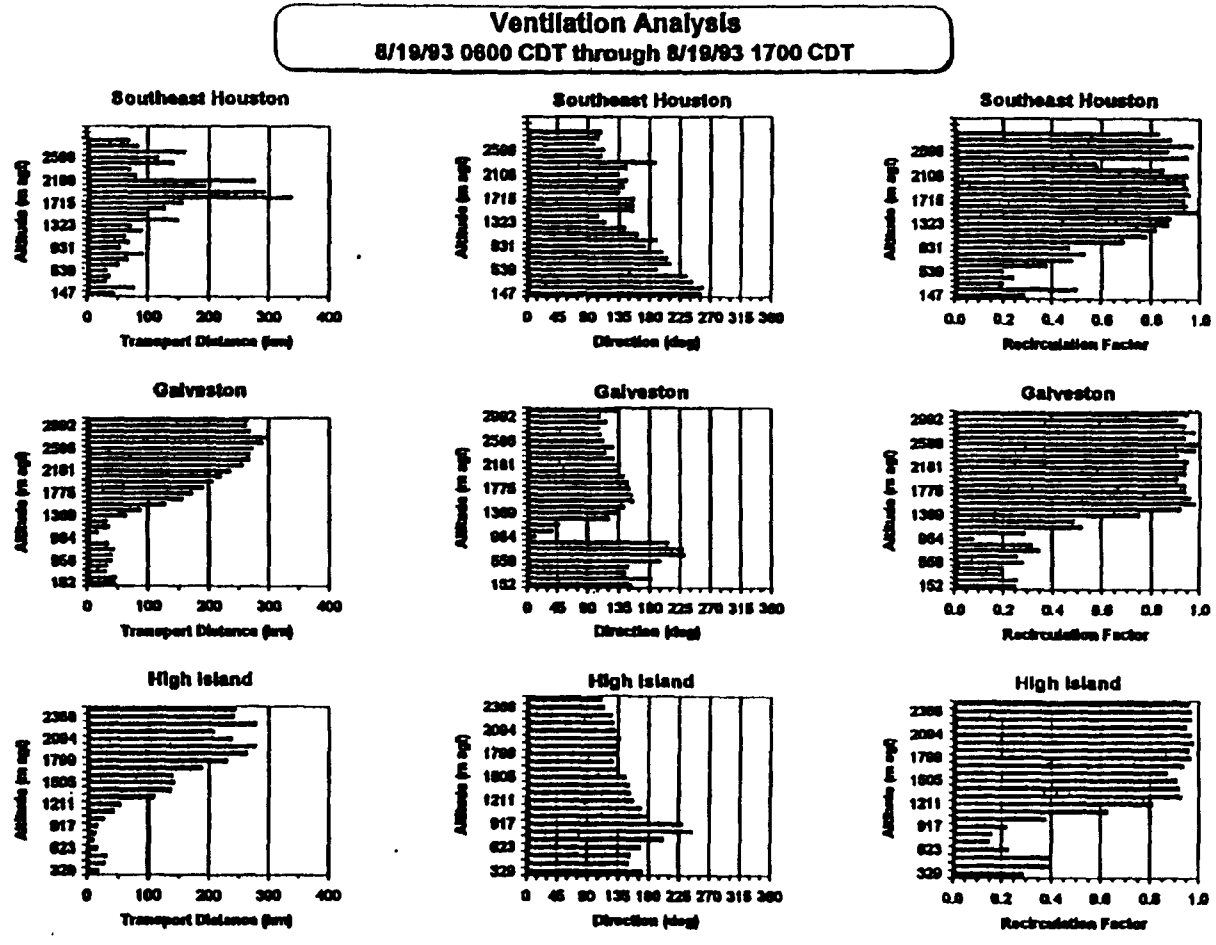
Time series of ozone, NO, NO_x, wind speed, and wind direction measured at the Gilcrest, TX surfac
period August 9-14, 1993 (SAI, 1995). When flow was offshore, high NO_x and titrated ozone was c
When the flow reversed, high ozone concentrations were observed. However, with continued onsho
concentrations decreased

Figure 1-5.



Vector-integrated transport distances, resultant wind directions, and recirculation factors (R), calculated from data collected by the southeast Houston (SEH), Galveston (GAL) and High Island Platform (HIP) radar profilers for the period 0600-1700 CDT on August 16, 1993.

Figure 1-6.



Vector-integrated transport distances, resultant wind directions, and recirculation factors (R), calculated from data collected by the southeast Houston (SEH), Galveston (GAL) and High Island Platform (HIP) radar profilers for the period 0600-1700 CDT on August 19, 1993.

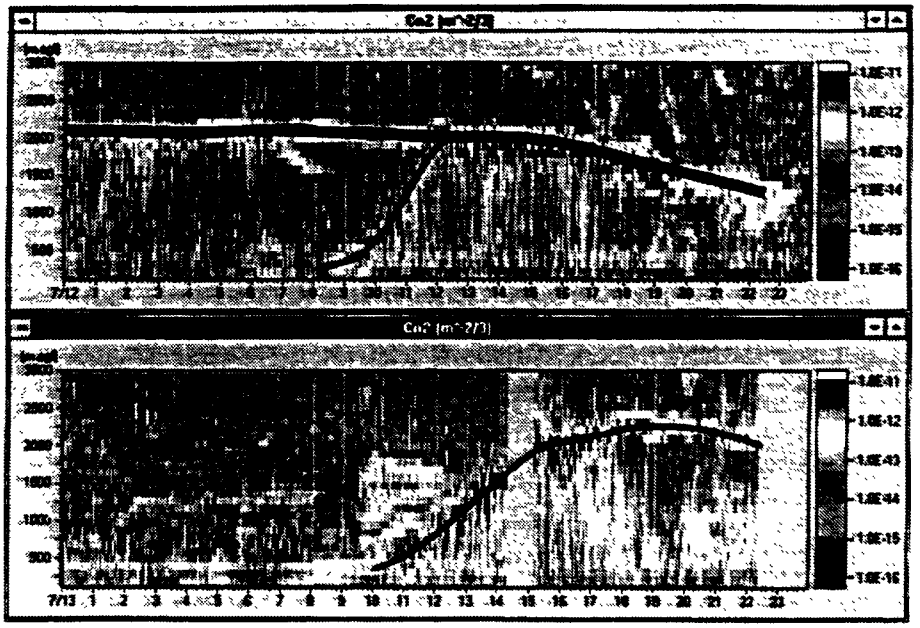


Figure 1-7. Time-height cross-section of C_N^2 for July 12-13, 1994 at New Brunswick, NY. Thick line denotes the subsidence inversion; thin line during the day denotes the top of the mixed layer. On July 12, a subsidence inversion is shown in the profiler data as a region of high reflectivity between 1750 and 2000 m agl. The inversion limited afternoon growth of the CBL to below 2000 m. A slower growth occurred on July 13 resulting in reduced vertical mixing of precursors, and an attendant elevated afternoon ozone level

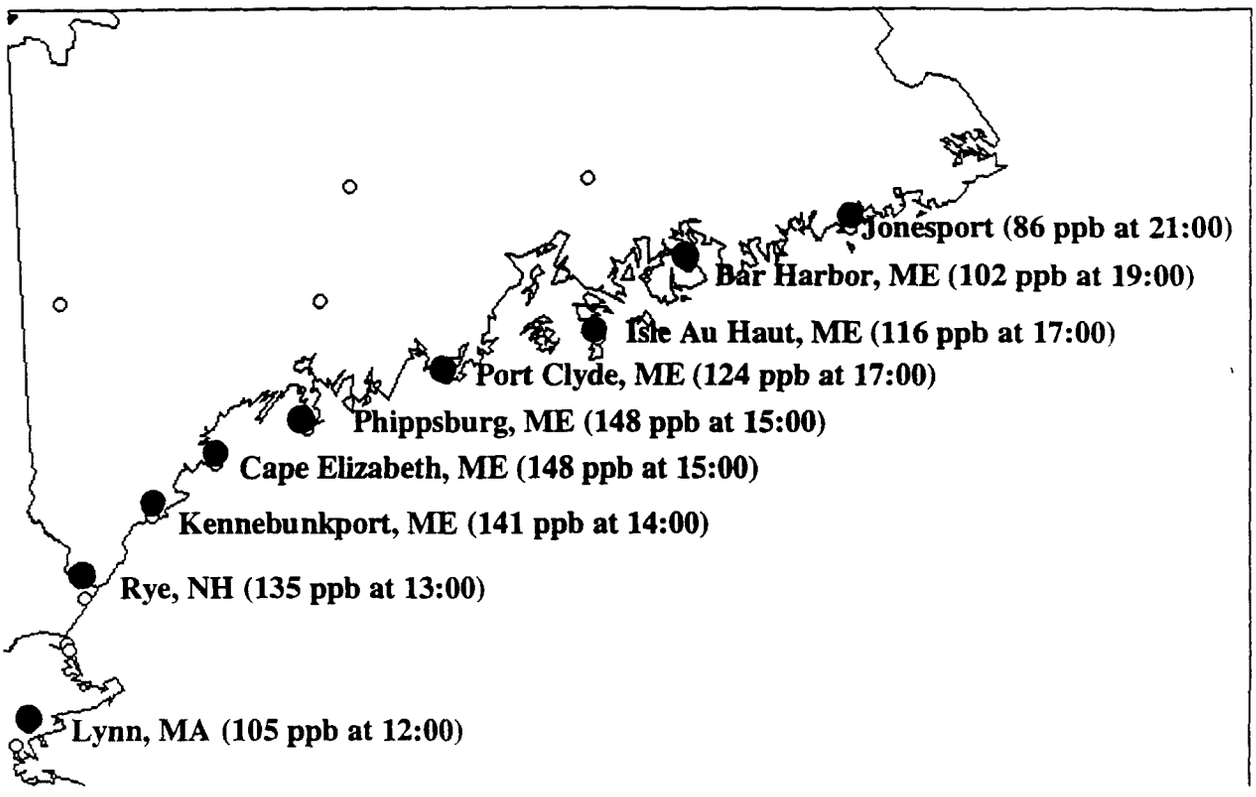


Figure 1-8. Maximum Ozone Concentrations and Hours of Occurrence, 07/21/94

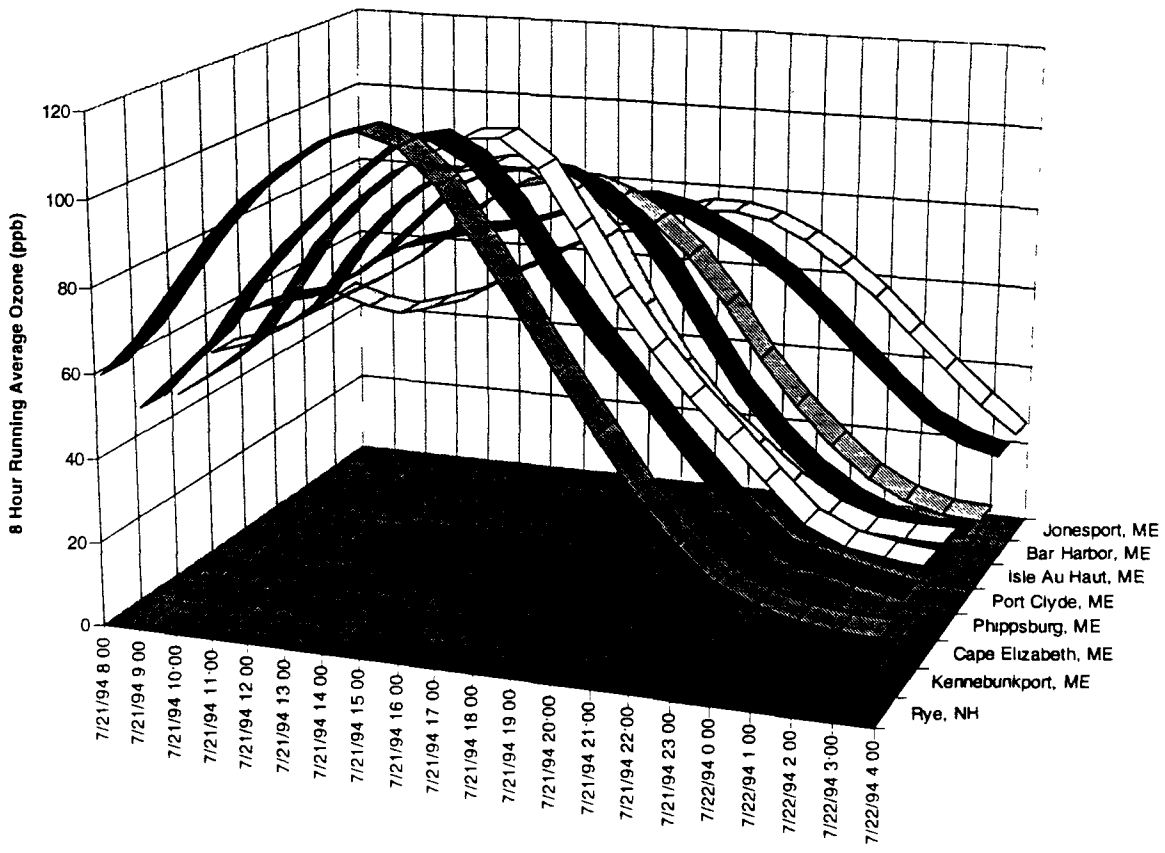


Figure 1-9. 8-Hour Moving Average Ozone Concentrations on 7/21/94

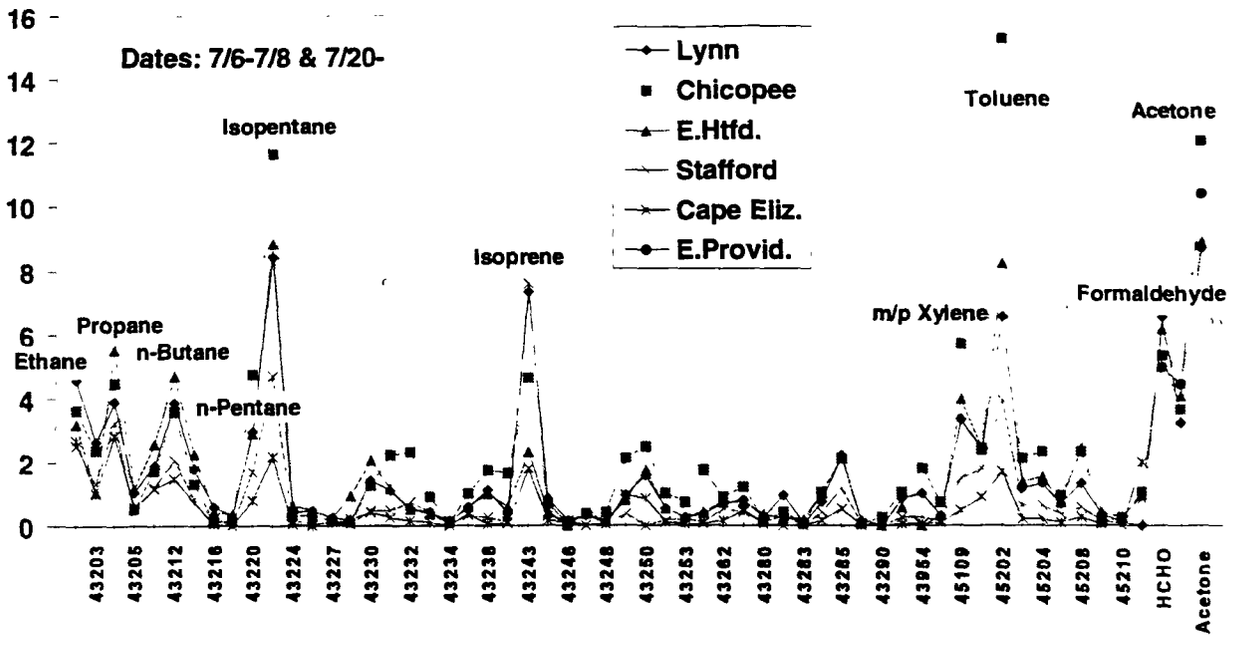


Figure 1-10. VOC Abundances for Six Northeastern PAMS Sites, July 1994.

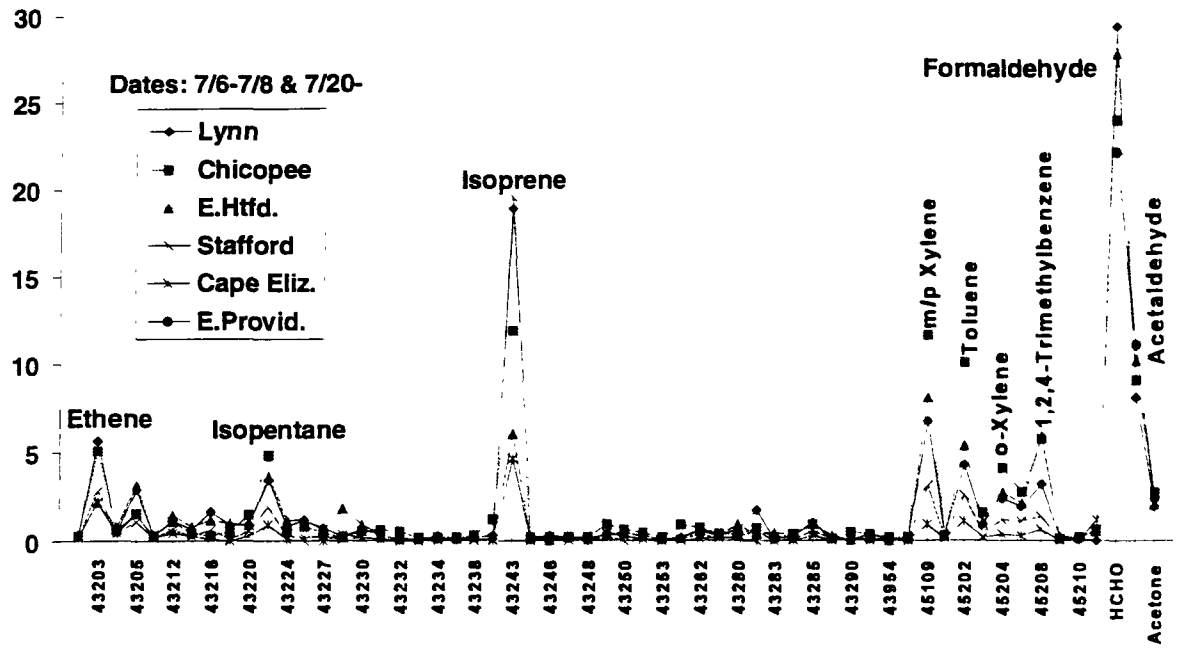


Figure 1-11. VOC Abundances Adjusted for Reactivity (Using Carter's MIRs) for Six Northeastern PAMS Sites, July 1994.

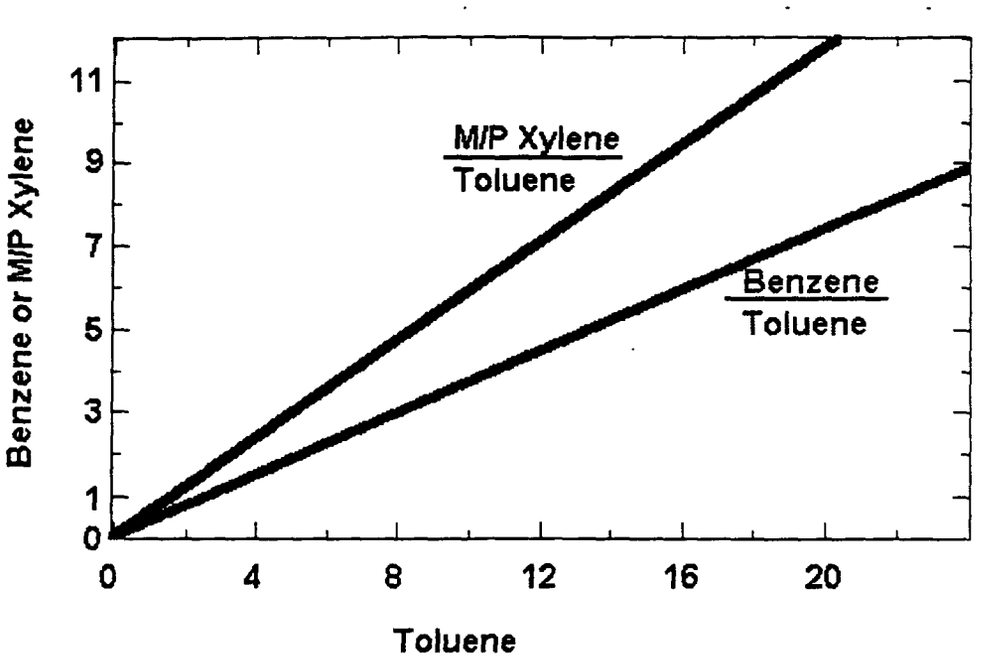


Figure 1-12. Estimated Urban B/T and X/T Ratios from Atlanta, GA Source Profiles (from Henry et al., 1994)

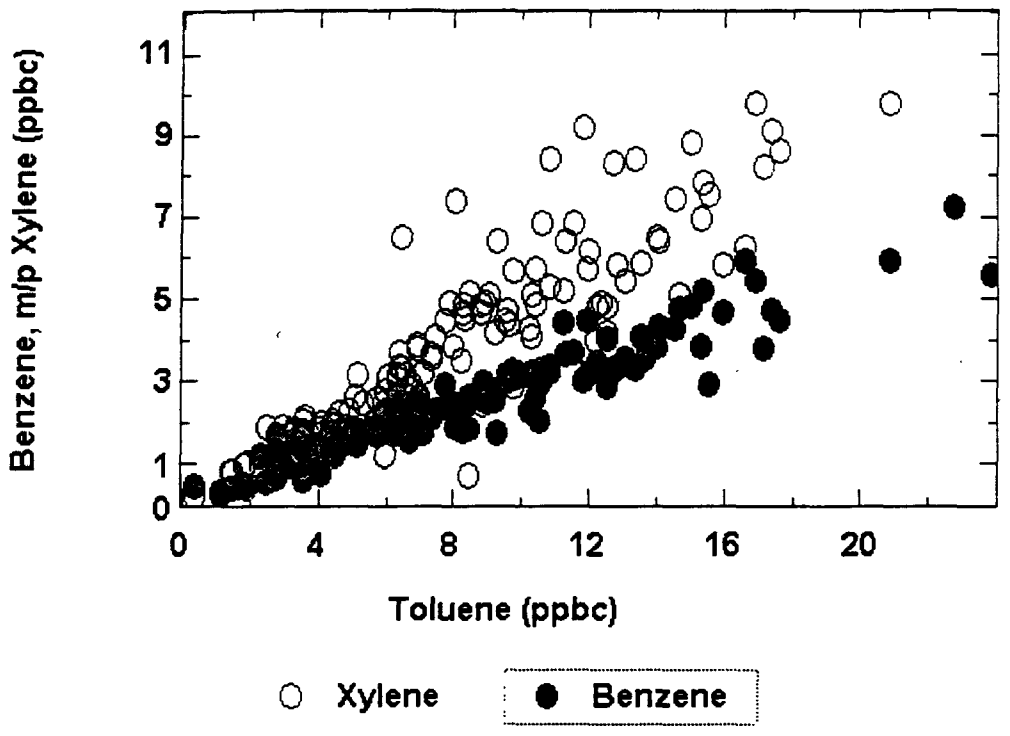


Figure 1-13. Measured Urban B/T and X/T Ratios from E. Hartford, CT PAMS Site during July 1994 Episodes

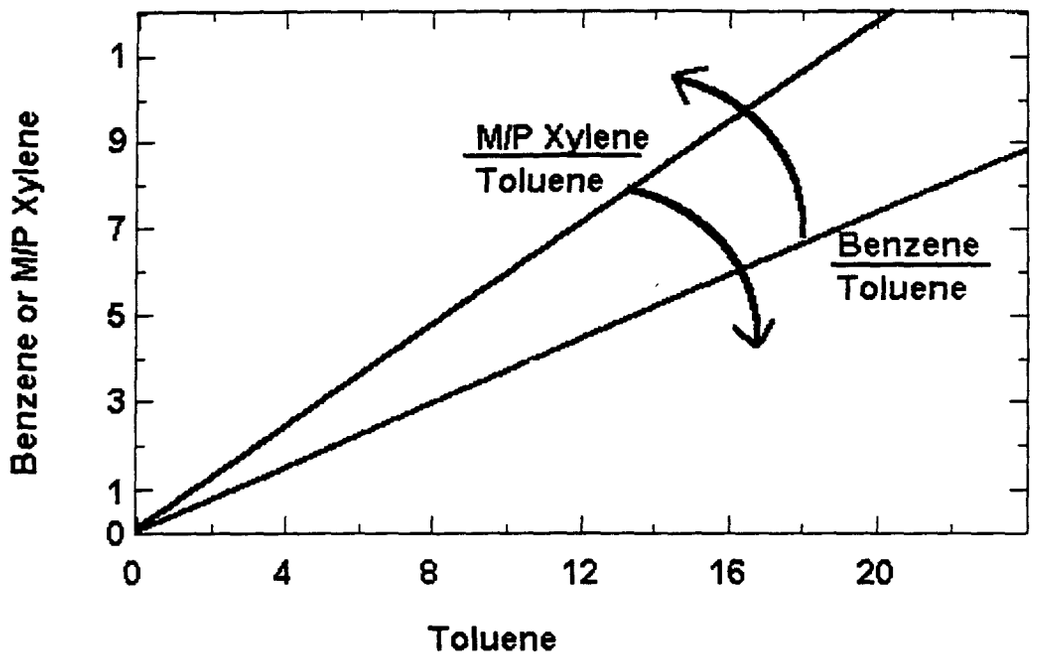


Figure 1-14. Predicted Changes in B/T and X/T Ratios at Rural Sites (Resulting from Airmass Aging)

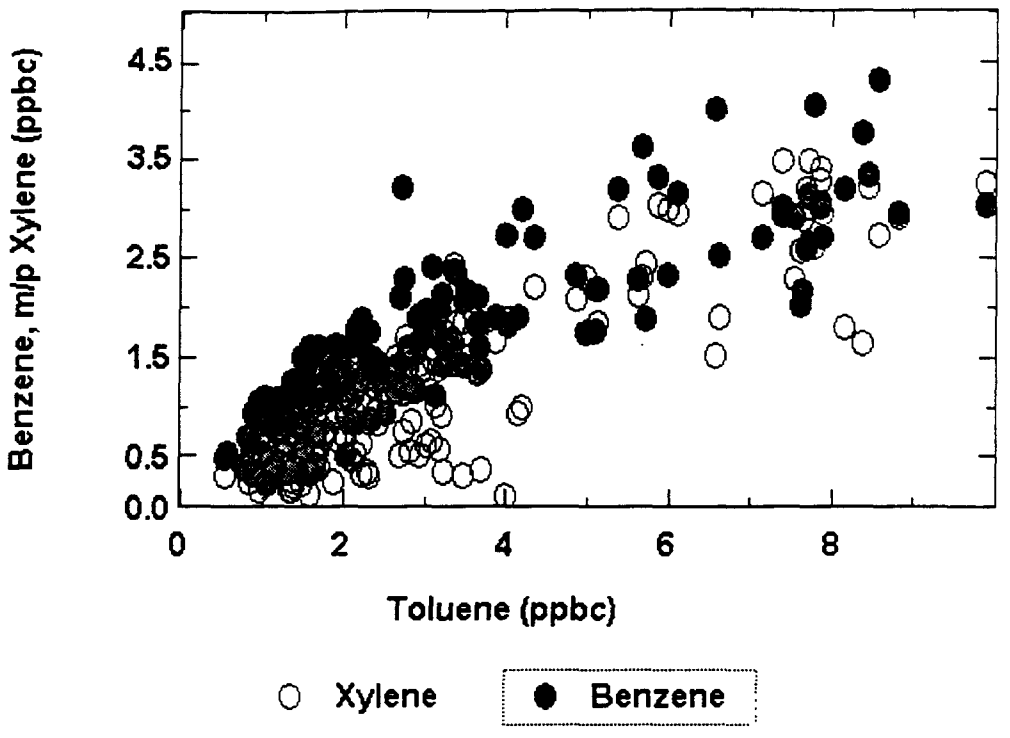


Figure 1-15. Measured Rural B/T and X/T Ratios from Stafford, CT PAMS Site during July 1994 Episodes

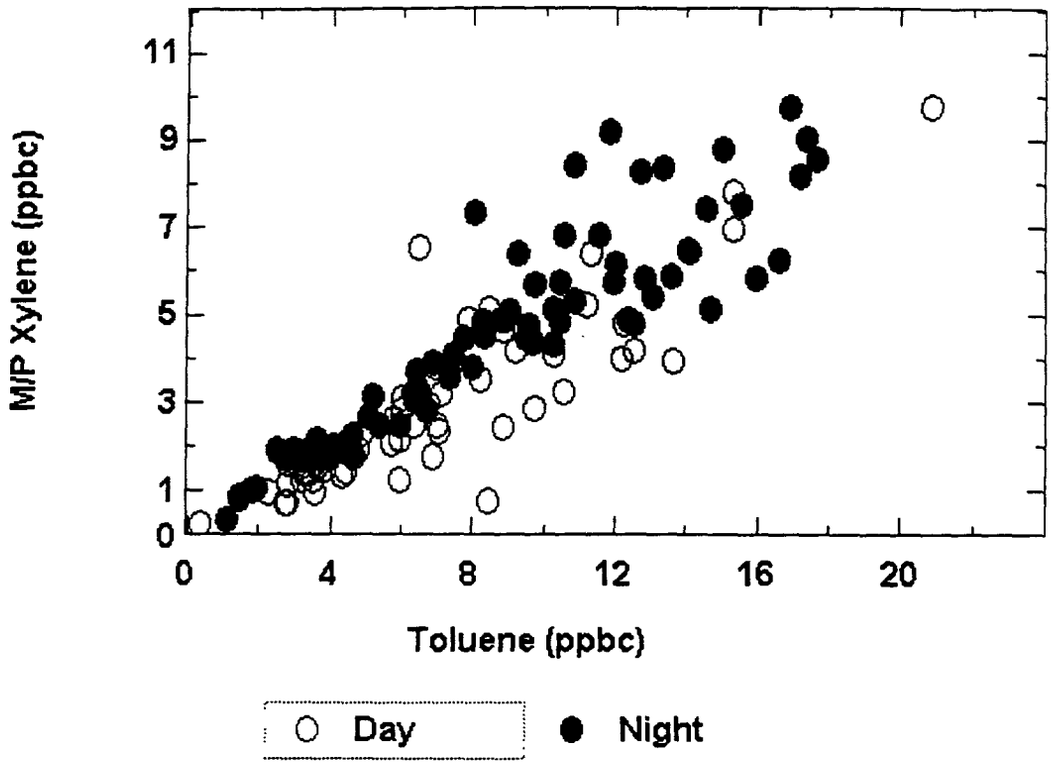


Figure 1-16. m/p-Xylene versus Toluene at E. Hartford, CT PAMS Site during July 1994 Episodes

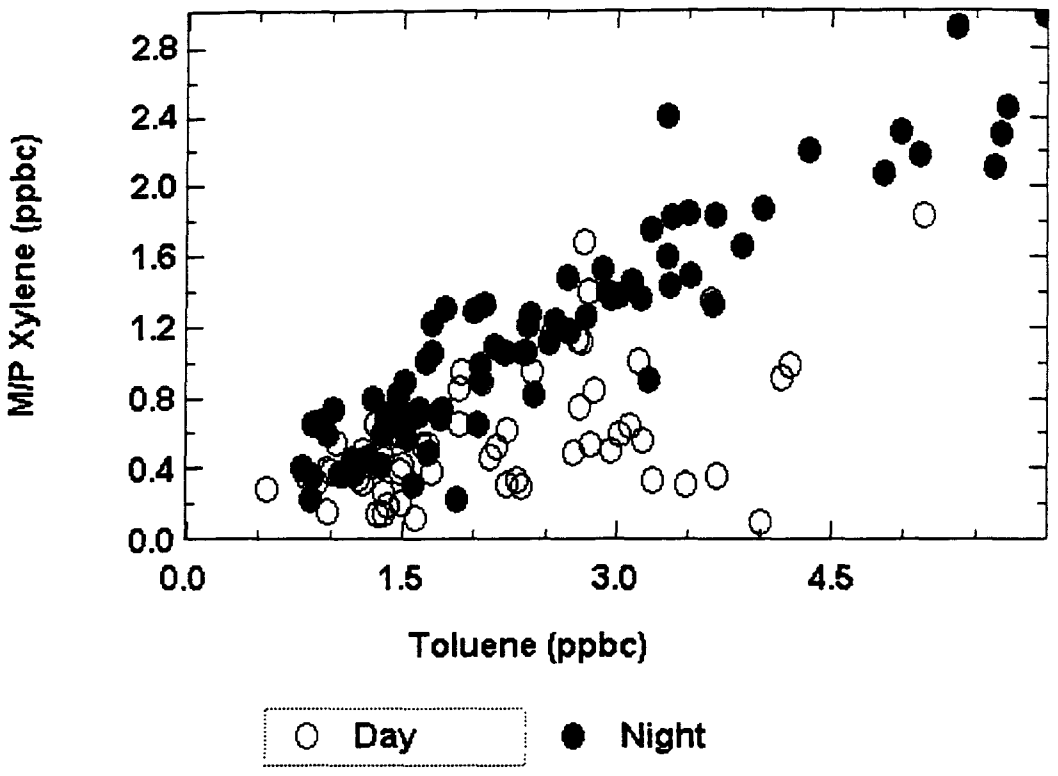


Figure 1-17. m/p-Xylene versus Toluene at Stafford, CT PAMS Site during July 1994 Episodes

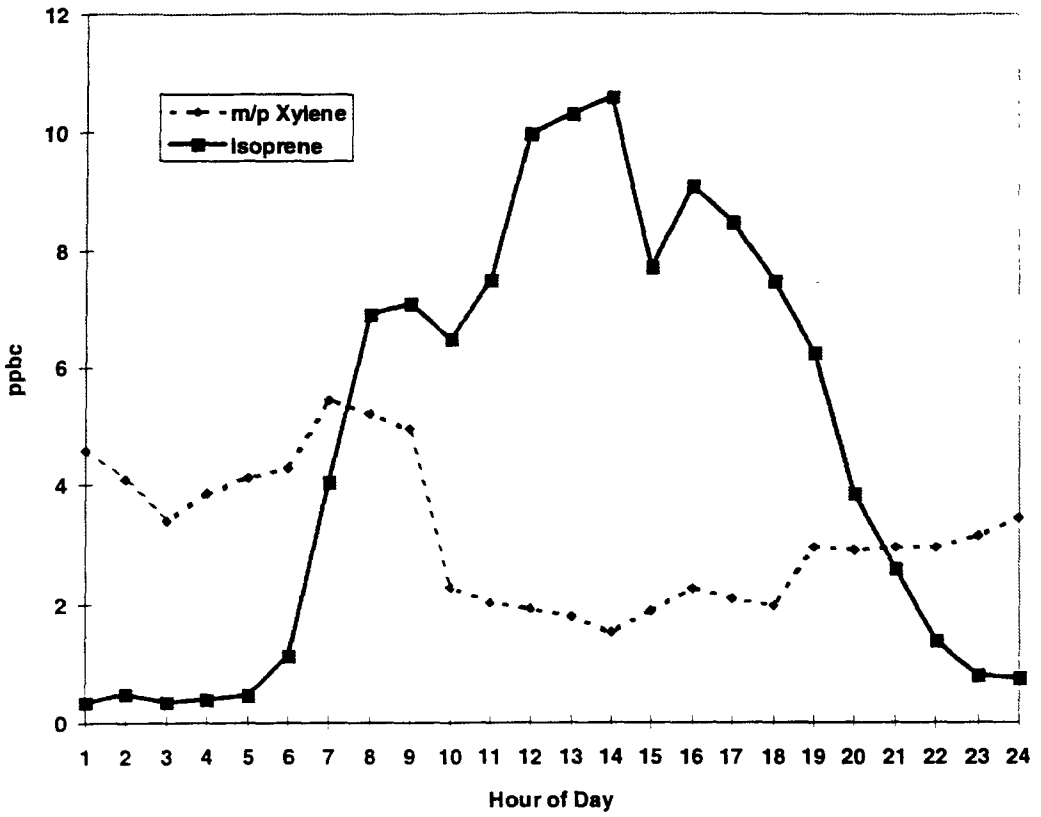


Figure 1-18 Diurnal Isoprene and m/p Xylene (averaged for 6 NESCAUM PAMS Sites for July, 1994 Episodes)

Figure 1-19.

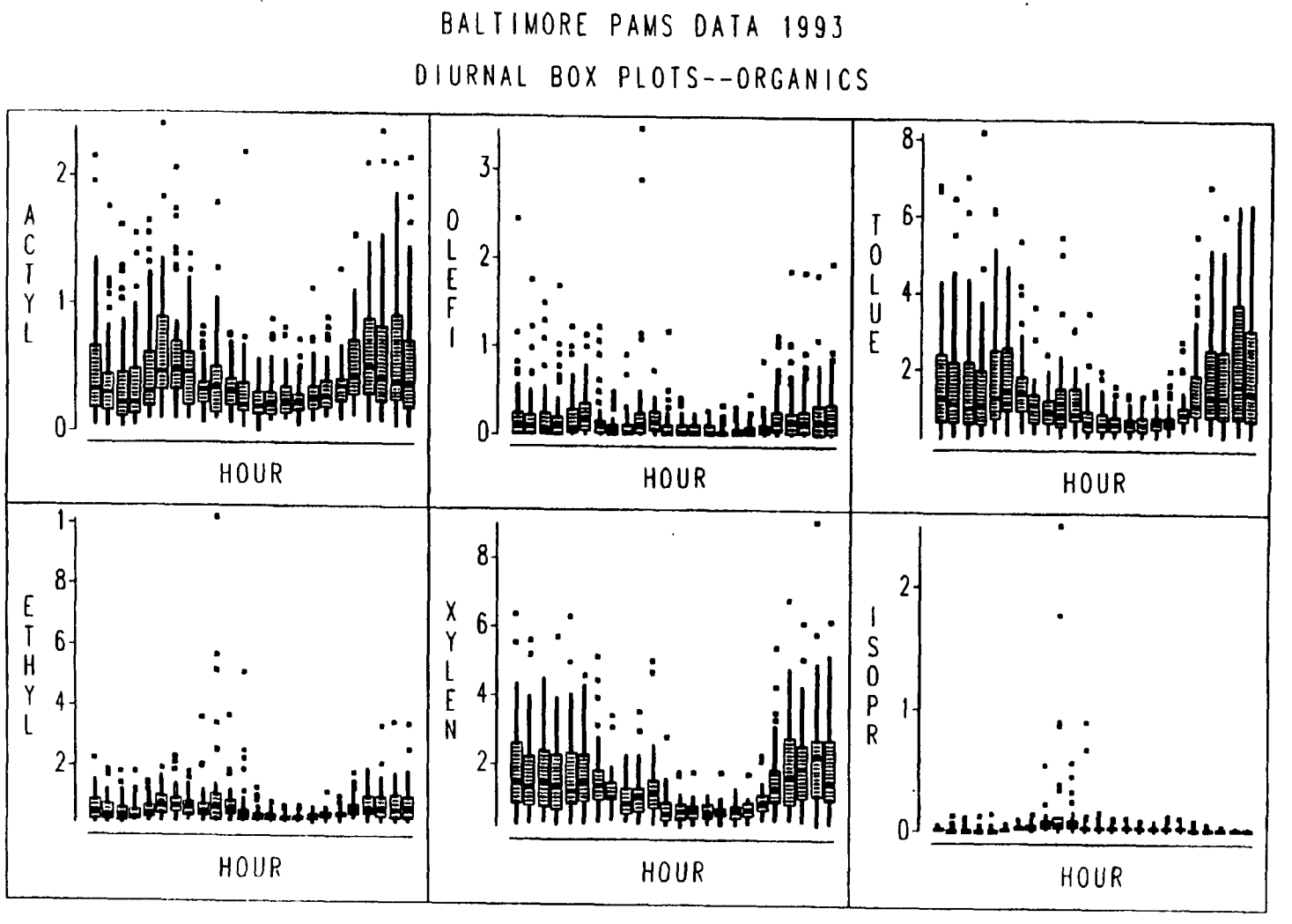

BALTIMORE PAMS DATA 1993
DIURNAL BOX PLOTS--ORGANICS
ACTYL
OLEFI
TOLUE
ETHYL
XYLEN
ISOPR
HOUR

Figure 1-20a.

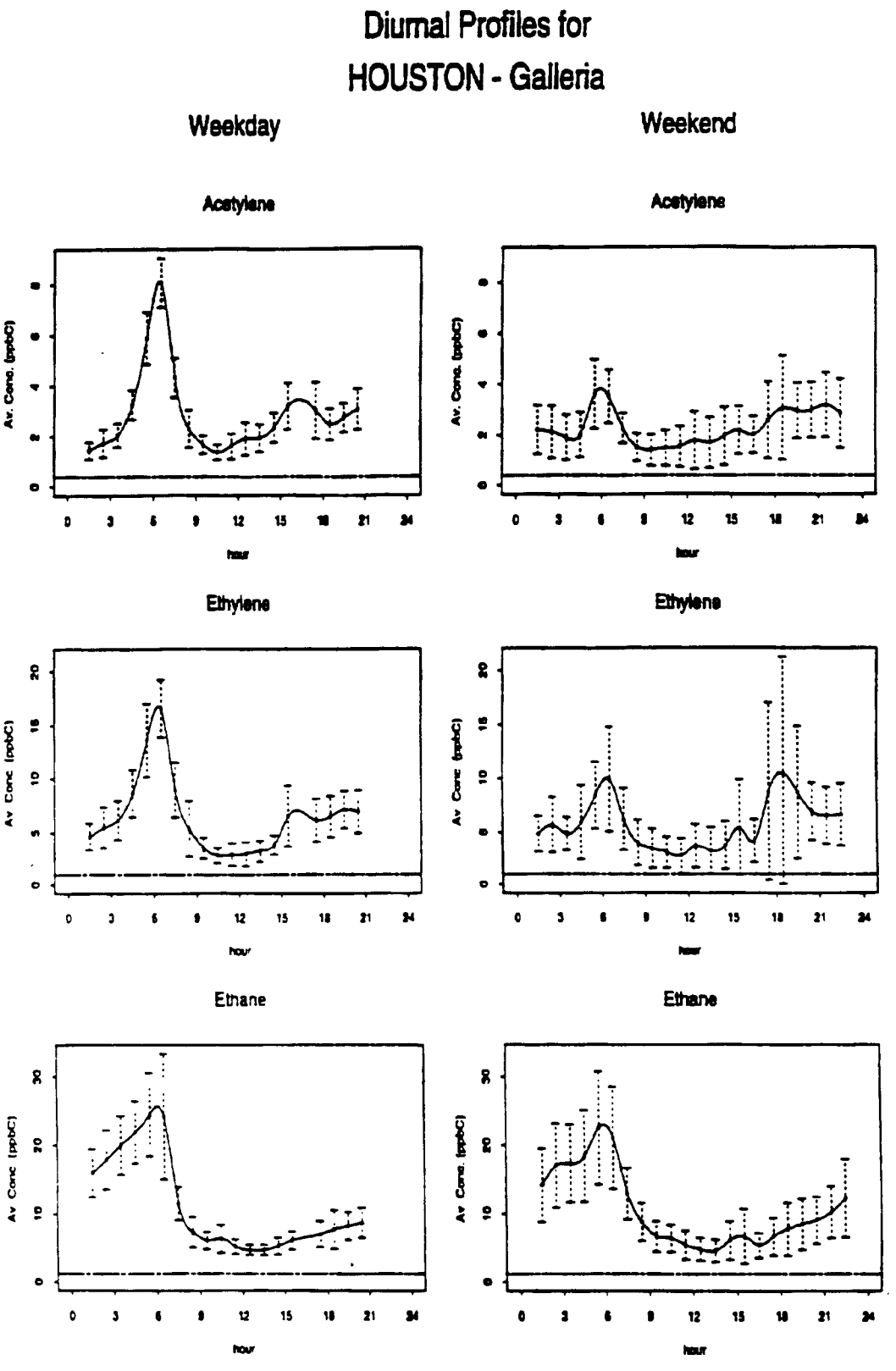

Diurnal Profiles for
HOUSTON - Galleria
Weekday
Weekend
Acetylene
Acetylene
Ethylene
Ethylene
Ethane
Ethane
Av. Conc. (ppbC)
hour

Figure 1-20b.

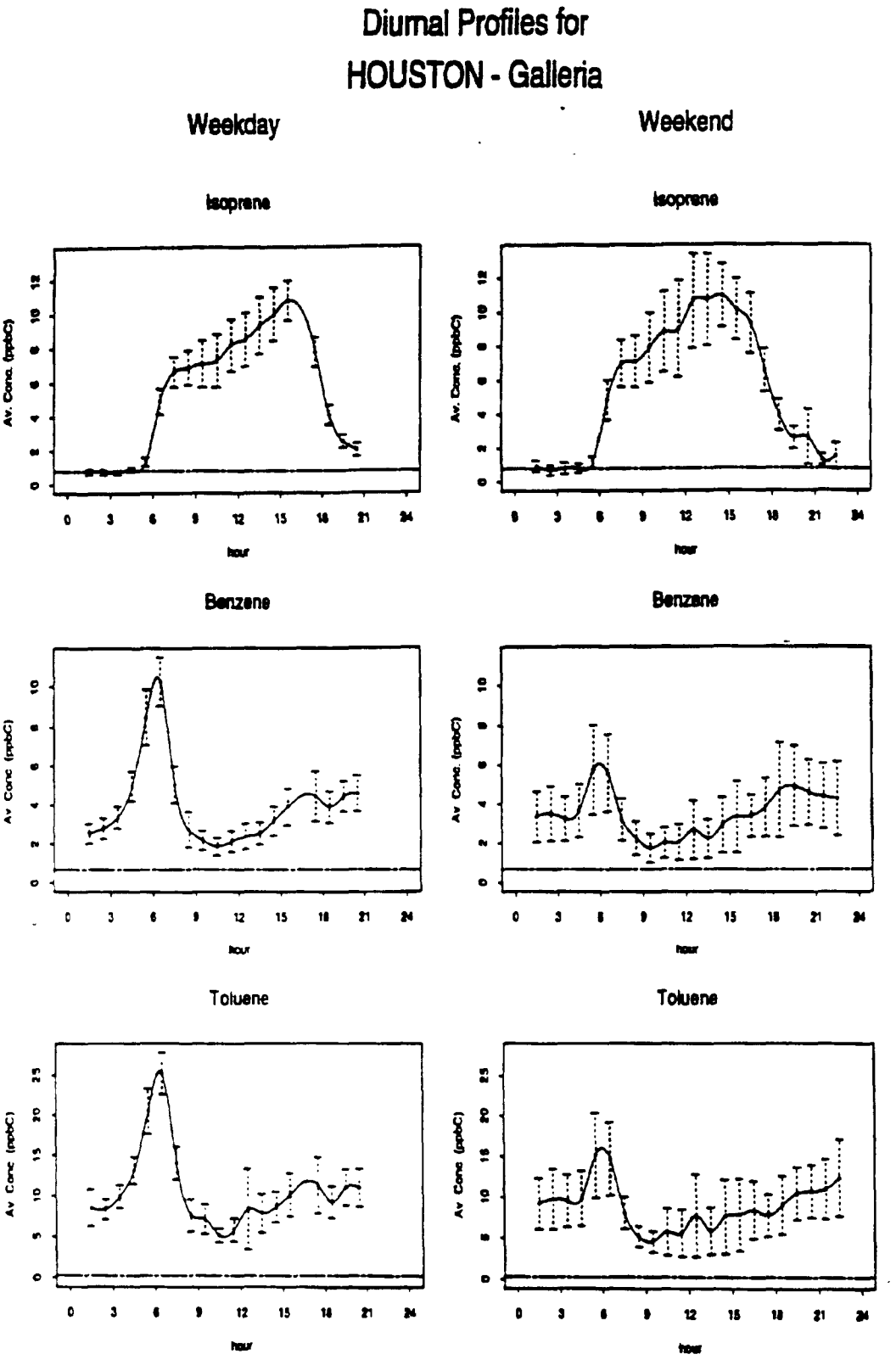

Diurnal Profiles for
HOUSTON - Galleria
Weekday
Weekend
Isoprene
Isoprene
Av. Conc. (ppbC)
hour
Benzene
Benzene
Av Conc (ppbC)
hour
Toluene
Toluene
Av Conc (ppbC)
hour

Figure 1-20c.

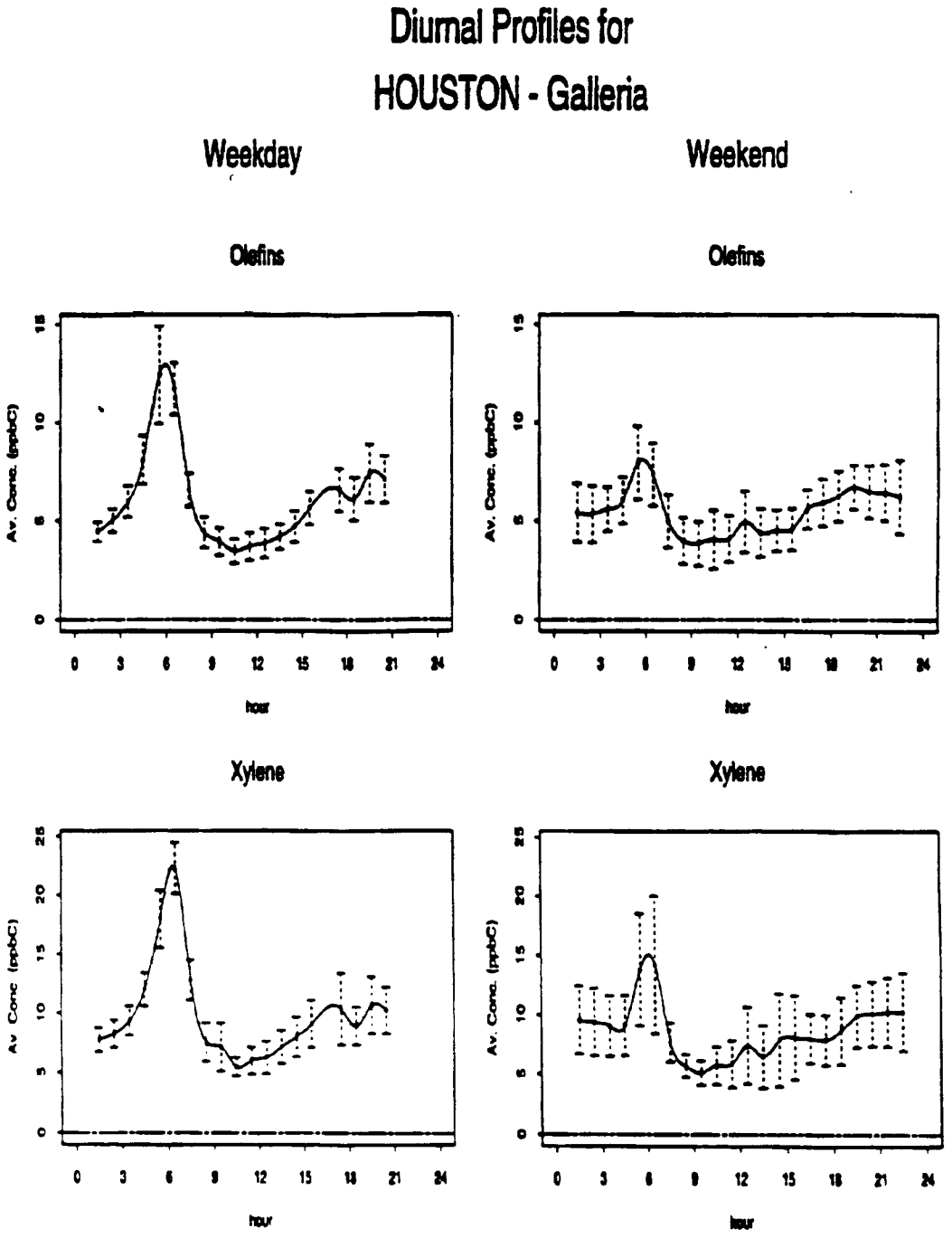

Diurnal Profiles for
HOUSTON - Galleria
Weekday
Weekend
Olefins
Olefins
Xylene
Xylene
Av. Conc. (ppbC)
hour

Figure 1-21a.

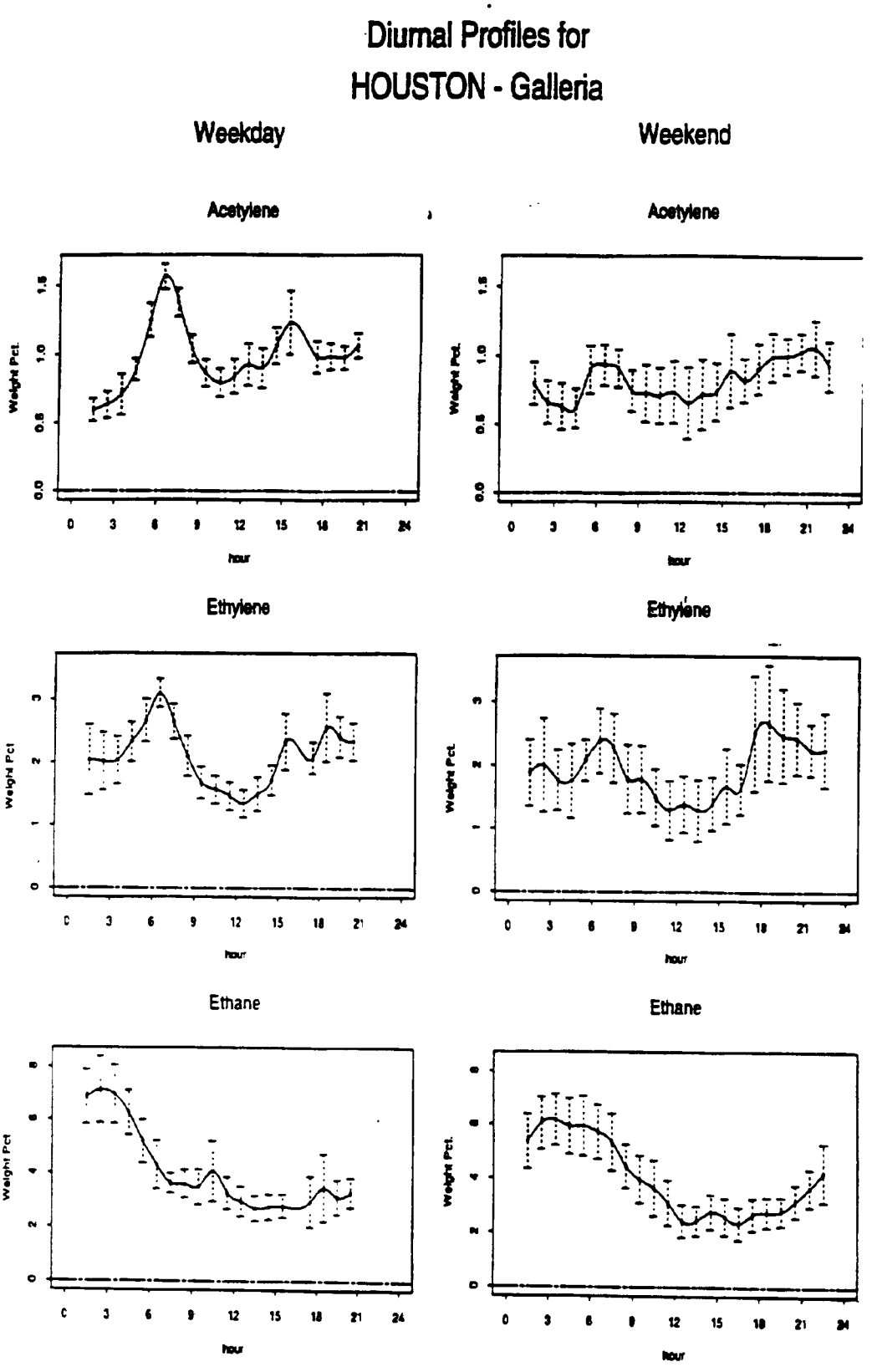

Diurnal Profiles for
HOUSTON - Galleria
Weekday
Weekend
Acetylene
Acetylene
Ethylene
Ethylene
Ethane
Ethane
Weight Pct
hour

Figure 1-21b.

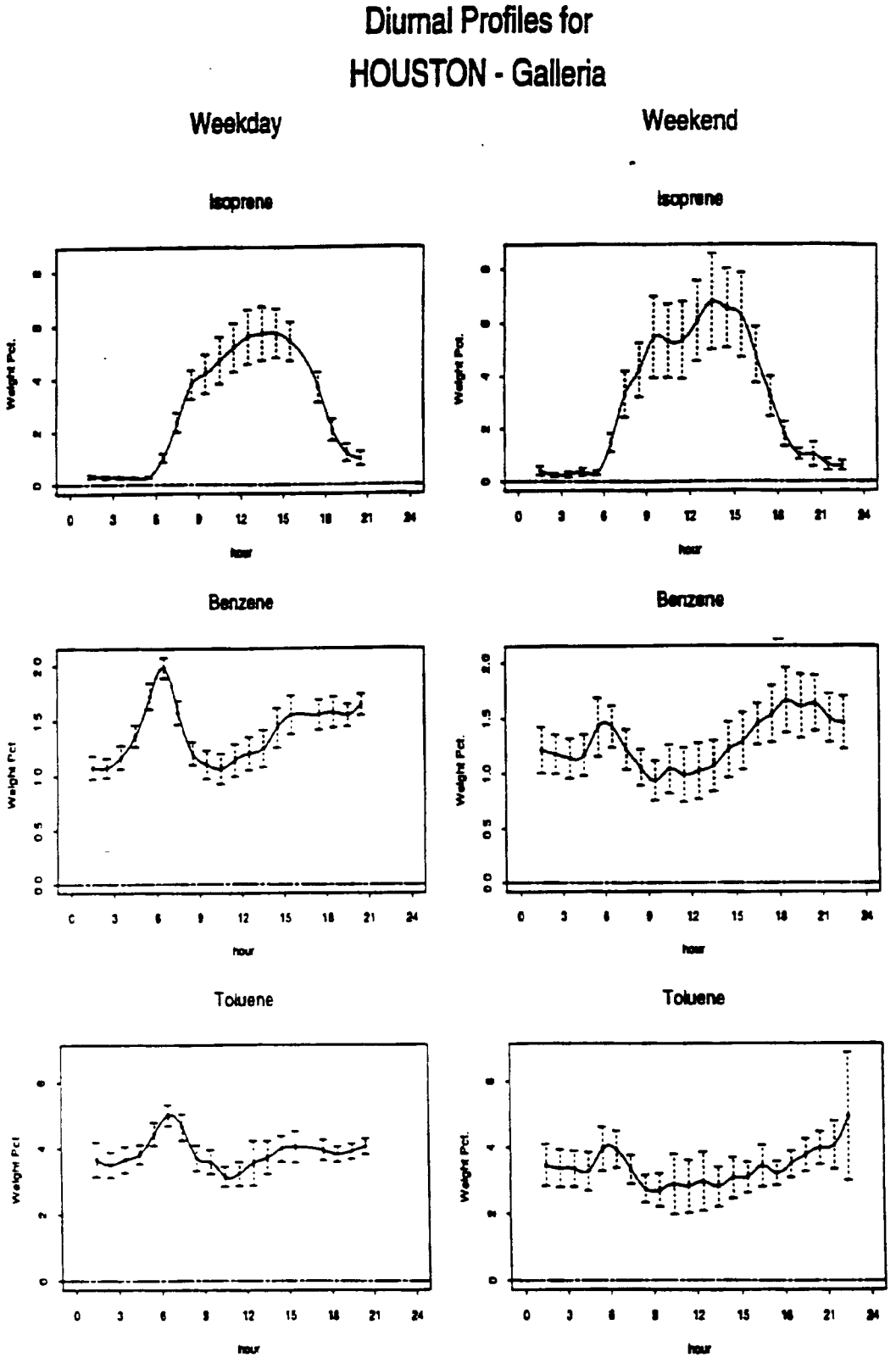
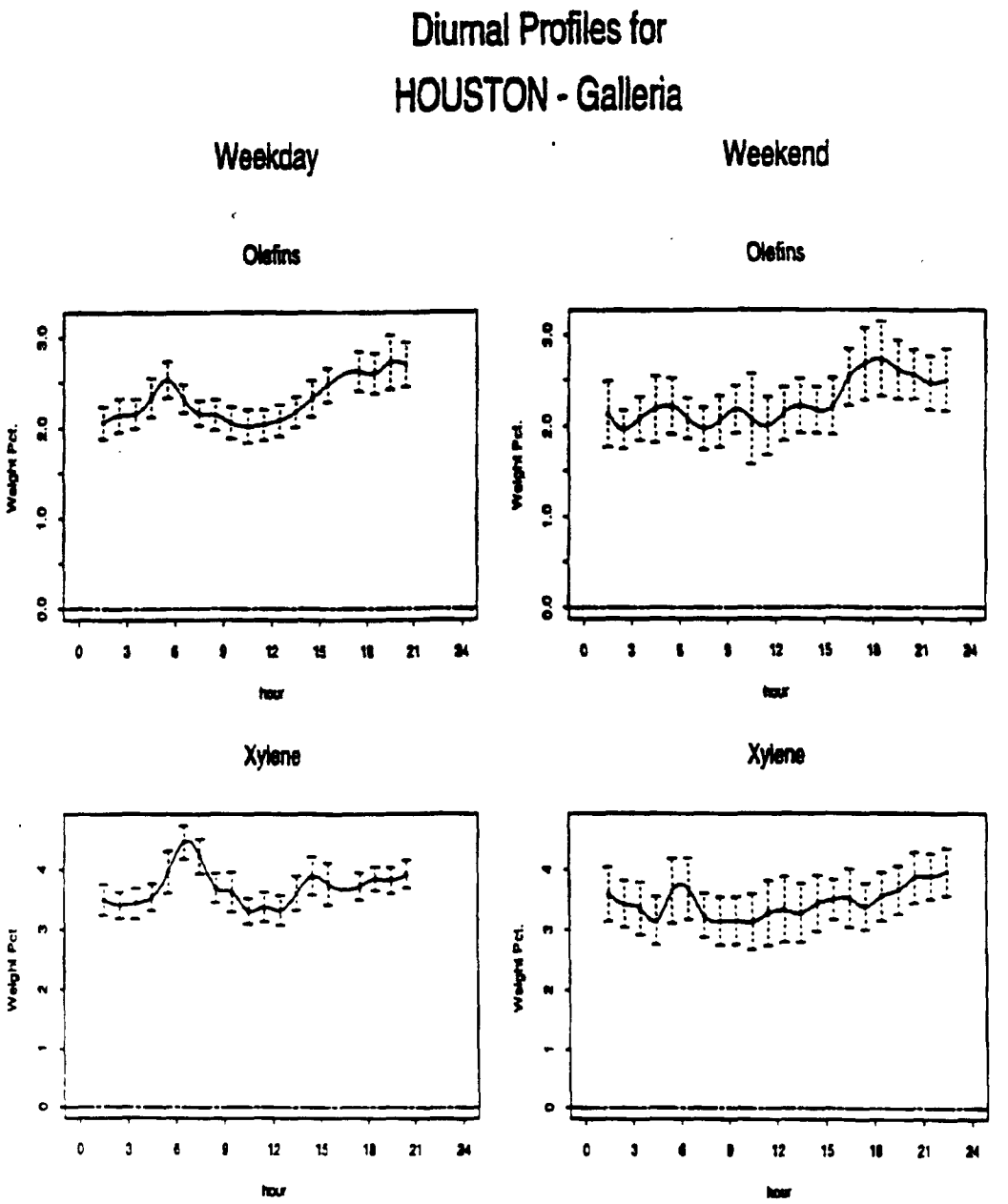

Diurnal Profiles for
HOUSTON - Galleria
Weekday
Weekend
Isoprene
Isoprene
Benzene
Benzene
Toluene
Toluene
Weight Pct.
hour

Figure 1-21c.


Diurnal Profiles for
HOUSTON - Galleria
Weekday
Weekend
Olefins
Olefins
Xylene
Xylene
Weight Pct.
hour

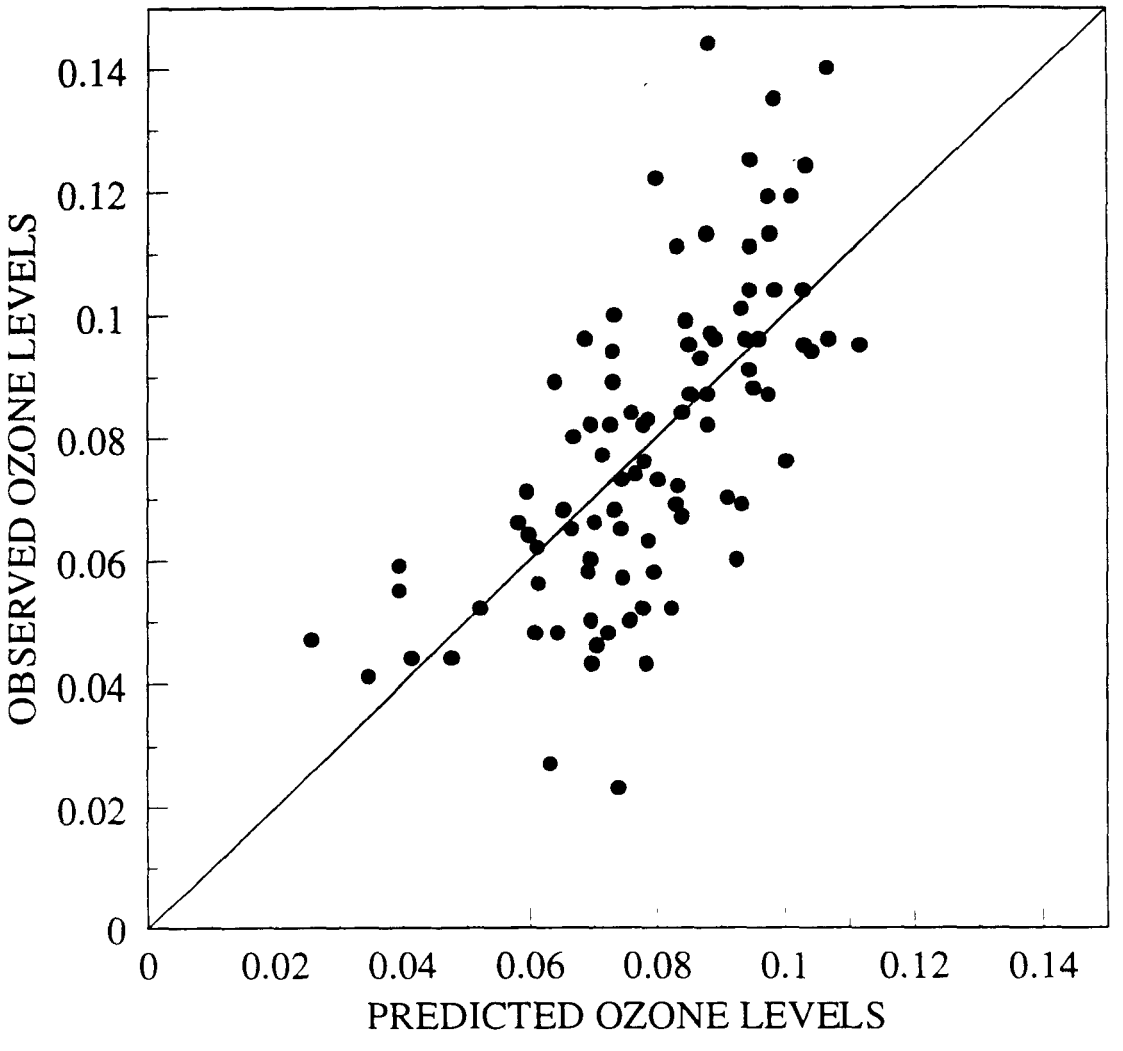


Figure 1-22. Model 1- Meteorological Data Only; 1994 PAMS Data; Phialdelphia, PA; R2=0.45, n=92.

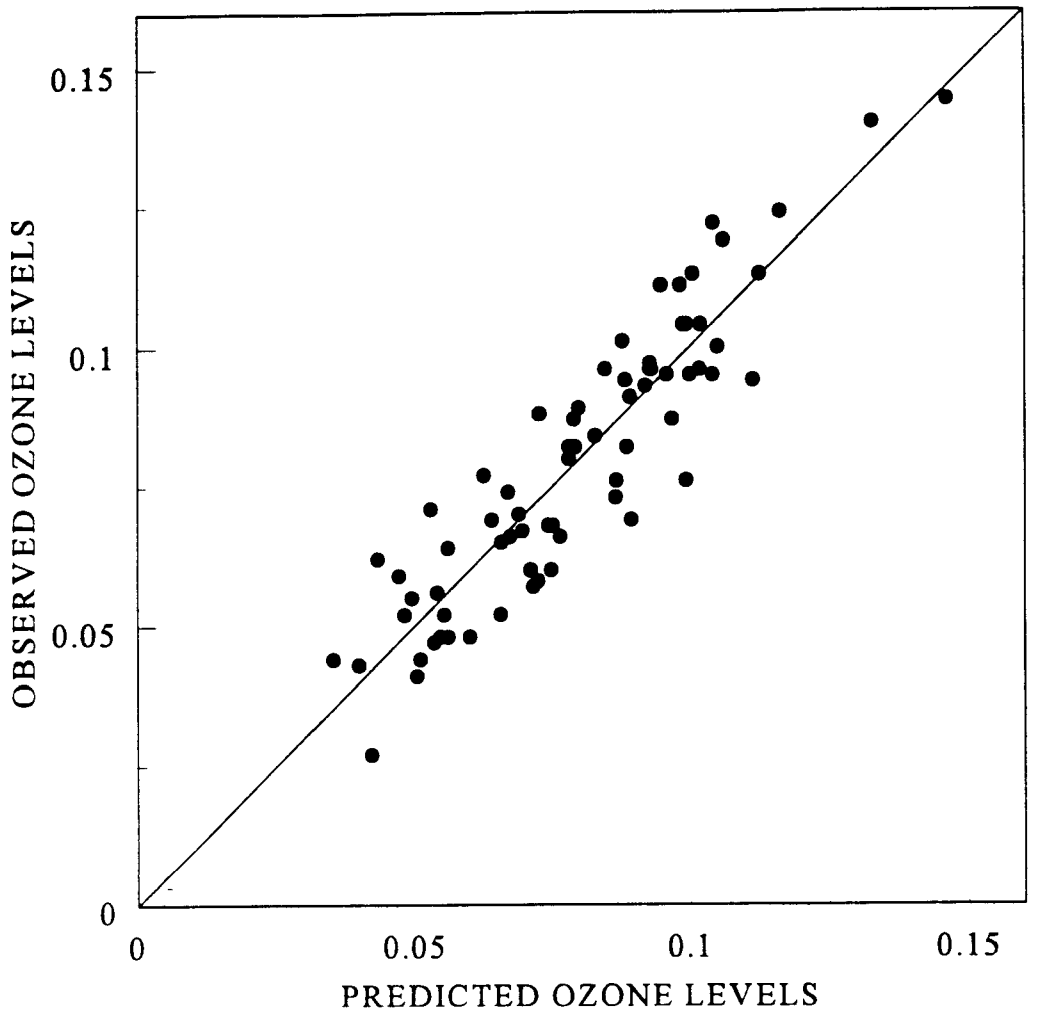


Figure 1-23. Model 2 - Meteorological and Ozone Precursor Data; 1994 PAMS Data; Philadelphia, PA; R2=0.84, n=71.

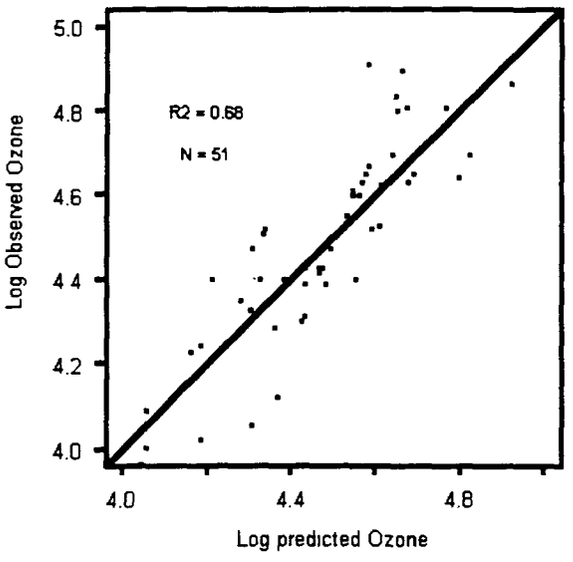


Figure 1-24. Philadelphia PAMS -Neural Network Size=1 Met, VOC and NO_x

Table 1-1. Most Abundant Anthropogenic VOCs in Selected Measurement Campaigns

	Northeast '94	5 City '84	Los Angeles '87
1.	Isopentane	Isopentane	Propane
2.	Toluene	n-Butane	Isopentane
3.	Propane	Toluene	Toluene
4.	Ethane	n-Pentane	n-Butane
5.	n-Butane	m/p-Xylene	Ethane
6.	m/p-Xylene	Propane	m/p-Xylene
7.	n-Pentane	Isobutane	n-Pentane

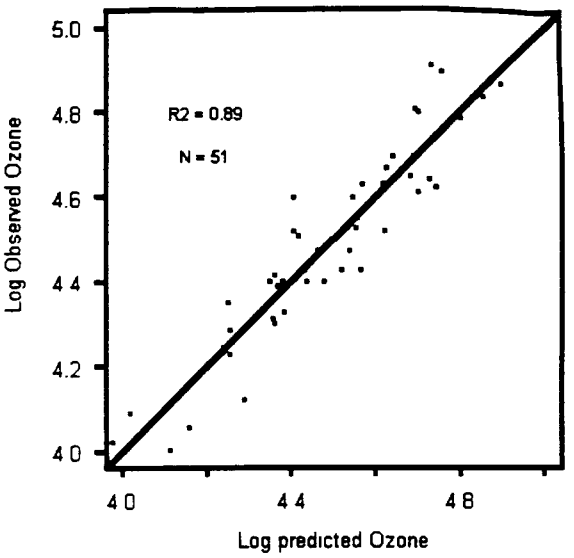


Figure 1-25. Philadelphia Neural Network Size=3--Met, VOC, NOX

CHAPTER 2
PAMS DATA IN SUPPORT OF OZONE MODELING APPLICATIONS

2.1 INTRODUCTION

Models are valuable tools that provide enormous spatial, temporal and predictive capabilities beyond the scope of monitoring networks. The use and interpretation of models are often criticized due to uncertainties in model inputs and process characterizations, as well for poor performance. The combined and complementary use of models and observations provides a more credible basis for analysis than the sum of independent analyses using models and data alone.

Support for photochemical modeling is one of several objectives targeted by the Photochemical Assessment Monitoring Station (PAMS) program. The objectives of this document are to provide example applications and recommendations for the use of PAMS data in ozone modeling applications. An emphasis is placed on the utility of PAMS type data for supporting the emissions based models (EBMs) commonly used in ozone assessment studies and State Implementation Planning (SIPs). This document does not replace existing EPA Guidance for Urban Airshed Modeling, but should be viewed as support to improve model application studies by incorporating PAMS data.

This chapter starts with an overview of ozone modeling, followed by examples illustrating the uses of PAMS data in supporting model evaluations, developing model inputs and performing weight of evidence analyses in attainment tests. The chapter ends with a discussion on the uses and caveats on a compound by compound (or compound class) basis of PAMS measurements and their relation to model support.

2.2 MODEL OVERVIEW

Photochemical air quality simulation models (PAQSMs) used in most applications are the gridded, fixed-frame (Eulerian) systems including the UAMIV, UAMV, ROM, RADM, SAQM, CALGRID, URM and others. All modeling systems invoke many approximations both in the description of physical and chemical processes as well as in the solution of the system of mathematical equations embodying the physics and chemistry. The spatial extents, or "domains", of model applications often are characterized as being of urban (100-500 km), regional (500-2000 km) or super-regional (> 2000 km) scales. Gridding refers to the horizontal resolution used to delineate simulated air quality concentrations and provide detail on the emissions distribution and meteorological variables (e.g., winds and temperatures). Typical horizontal grid resolution ranges from 2-5 km and 20- 80 km for urban and regional applications, respectively. Most

models produce hourly outputs, which can be aggregated for other averaging times of interest (e.g., 8-hr, 24-hr, seasonal, annual). Models are resolved vertically (typically 5 -15 levels or more) to account for varying meteorology and emissions and to approximate vertical mixing phenomena. Some recent systems accommodate nested or variable scale gridding schemes which allow for detailed spatial treatment in urban areas (2- 8 km) and less dense horizontal resolution in peripheral/rural portions (20-80 km) of the domain in order to optimize computational resources and apparent precision. A trend toward increasing regional-scale (or mixed regional/urban), Eulerian modeling has been apparent recently, in recognition of the interaction between regional/rural and urban areas and associated "transport" issues.

Models should be viewed as a "system" (Figure 2-1), including the meteorological and emission preprocessing models and the air quality simulation model (AQSM). Preprocessors process raw data (i.e., emissions inventories and meteorological measurements) into the spatial and temporal fields required by the AQSM. The AQSM calculates concentration fields of air quality species (i.e., compound, element, free radical, or surrogate group), which are determined by the combined interactive effects of source emissions, mixing processes (advection and dispersion), deposition and chemical transformations.

So-called "transport" into a modeling domain is quantified through boundary conditions which are user-specified concentrations surrounding the established modeled domain (planes on each side and top), which can be brought into the domain through advection and dispersion. The AQSM includes the chemical mechanism which performs the chemical transformation calculations through highly condensed approximations (e.g., 20-50 species; 100 reactions) of the thousands of actual chemical reactions occurring in the atmosphere. Several chemical mechanisms have been developed. They all use condensation schemes which utilize surrogate "species" for aggregating organic compounds. The carbon bond approach used in the urban airshed model (UAM) groups compounds (and parts of compounds) by bond characteristics. Other approaches like the Statewide Air Pollution Research Center (SAPRC) mechanism use a "lumped" approach which groups compounds by similarities in reaction mechanism attributes.

These modeling systems are driven by emission inputs and often are referred to as emissions based models (EBMs), acknowledging the difference between data driven observational based models, and semi-empirical models like EKMA/OZIPM4.

Typically, a series of steps are required for all model applications:

A. Establishment of model domain, characterization and selection of modeling episodes.

B. Raw data gathering and processing of model inputs.

C. Model performance and diagnostic testing, including component testing of emissions and meteorological preprocessers.

D. Development of emission control strategies and model application and interpretation of results.

E. Corroboration and evaluation of strategy results.

The following examples illustrate methods in which PAMS data aid the support of model evaluation and development of modeling inputs.

2.3 MODEL EVALUATION USING PAMS DATA

Two examples are presented to illustrate the use of PAMS (or PAMS-type) data in evaluating ozone modeling applications. The examples are based on field programs from the Southern California Air Quality Study (SCAQS) and the Texas-Louisiana COAST programs, both of which collected the speciated and temporally resolved data required in PAMS. The purpose of these examples are purely illustrative, to provide perspective on how PAMS can support ozone modeling.

2.3.1 Example: Los Angeles, CA

Figures 2-2 through 2-4 depict time series plots of modeled versus observed values for ozone, reactive hydrocarbon (RHC) and NO_2, respectively, based on a 1985 historical episode in Los Angeles, CA (Wallerstein et al., 1994). The figures are presented for exemplary purposes only, to show a simple plotting procedure for conducting model/measurement comparisons of ozone and precursors.

In addition to the example time-series plots, other graphical displays using tiling or isopleths could be developed to provide comprehensive, two-dimensional views relating measured and simulated data. Measured data could be superimposed on simulation maps, or side by side maps of measured and simulated results could be displayed.

2.3.2 Example: Houston Ship Channel

This example is based on a preliminary analysis trying to diagnose the cause of poor model performance using PAMS-type VOC data in Houston. The example should be viewed as a hypothetical example of the potential value-added provided by speciated hydrocarbon data.

Several subsequent analyses of this case have suggested significant problems related to both the modeling and interpretation of results. Therefore, this example should be viewed solely for illustration, no substantive conclusions are credible.

A highly localized ozone peak of 231 ppb was observed on August 19, 1993 in Houston, Texas (Figure 2-5.) UAM-V modeling was unable to replicate timing, magnitude of the peak. A series of VOC and NO_x across-the-board emission sensitivity runs failed to improve model performance. An analysis of nearby VOC data at the Clinton site indicated an anomalous peak in the total NMHC (Figure 2-6). Through further analysis of the ambient speciation, the emission inputs were adjusted to coincide with the ambient data. Subsequent model runs resulted in improved capture of the peak ozone (Figure 2-7).

2.4 DEVELOPMENT AND TESTING OF MODEL INPUTS

2.4.1 Episode Selection and Domain Specification

Procedures for evaluating and selecting meteorological episodes for UAM SIP applications have emphasized frequency and pervasiveness of high ozone concentrations (EPA, 1991). Over the last several years perspectives on episode selection have changed, largely in recognition of the need for "richer" data bases, increasing trend toward regional analyses, and the difficulty of translating results from highly stochastic events to the form of the ozone standard. Arguably, the availability of PAMS data and other more intensive field studies (e.g., NARSTO-NE, SOS) is reasonable justification (or a prerequisite) for selecting a modeling period. A model application based on supporting precursor and upper meteorological data is more informative and credible than an application with less data. Hence, any decision matrix for episode selection is likely to contain a column indicating relative strength of supporting measurements.

Domain specifications

Almost all gridded model applications utilize regional (or greater) spatial scales to account for important mixing processes due to transport, recirculation and other processes. Consequently, any reasonable extension of modeling domains to incorporate any supporting data is advised. Similar domain adjustments would hold true for urban specific domains which are modeled with nested systems (ROM/UAM) or variable grid models (UAM-V).

Episode Selection

As discussed in Chapter 1, PAMS data assist in developing various conceptual pictures of certain attributes of episodes, such as relative influence of transport, source mix, aging of air masses, and propensity toward NO_x or VOC-limiting conditions.

2.4.2 Development of Meteorological Inputs and Meteorological Model Evaluation

The spatial and temporal attributes of meteorological data used in the specification of mixing heights (or related vertical diffusivity parameterizations) and three dimensional wind fields have substantial impact on simulating atmospheric mixing processes, and subsequent air quality and control strategy predictions. Perturbations in either mixing height or wind fields have been shown to change both the level of precursor control as well as the preferred direction (i.e., VOC or NO_x) of control needed to demonstrate attainment (Sistla et al., 1994; Sistla et al, 1996). Although different meteorological modeling approaches can produce disparate results, the availability of high quality meteorological data should reduce differences in simulation results among various techniques.

The historical shortage of quality upper meteorological data, often limited to twice daily FAA soundings in one (or nearby) domain based location, has created concern in several UAM applications. The PAMS requirement for upper meteorological monitoring is potentially a major contribution toward improving model applications. PAMS minimum requirements specify 4 soundings per day of winds and temperature. While rawinsondes can be used to meet these requirements, automated remote sensing techniques such as Radar/Sodar wind profilers and Radio Acoustic Sounding Systems (RASS) offer enormous spatial (50-100 m increments, vertical Z-space) and temporal (hourly) resolution, and are used as a basis for subsequent discussions. Wind and temperature fields with greater temporal resolution should reduce much of the uncertainty associated with growth of the surface-based mixed layer, particularly during the rapid growth, late morning transition period. PAMS upper meteorological monitoring requirements reflect a commitment in the right direction toward enhancing modeling efforts. The PAMS contribution of 1 upper meteorological monitoring site per PAMS network is a foundation for developing spatially (horizontal) representative monitoring networks capable of characterizing regional gradients in mixing height and wind fields.

The following discussion focuses on the ability to improve wind and mixing depth fields brought about by the PAMS upper meteorological monitoring requirements, with an emphasis on the use of continuously operating radar profiler and RASS instrumentation. (More detailed discussions regarding the use of PAMS meteorological data are found in Dye, 1995.)

2.4.3 Mixing depth

Mixing (and associated dilution/concentration) of ozone and precursors throughout an episode impacts ozone concentrations, and subsequent control strategy calculations. Characterization of the mixed layer throughout the morning to afternoon growth period may be just as important as estimating maximum late-afternoon mixing depth. Continuously operating radar and RASS profilers provide a means to depict this growth with improved temporal and spatial (vertical) resolution. Particularly promising mixing height applications based on the use of Radar profiler reflectivity coefficients, C^2_n, should provide a strong complement to RASS

temperature profiles for characterizing mixing heights.

Advantages of Radar profiler and RASS

Information produced by profilers/sodars and RASS will improve characterization of the mixed layer depth. Both the temperature profilers produced by RASS and C^2_n coefficients have temporal resolution of at least one hour enabling improved description of diurnal mixing depth development, a vast improvement over the twice daily FAA soundings. The use of C^2_n is particularly attractive, as it is a direct indicator of mixing depth. Comparisons between aircraft measurements and C^2_n (Figure 2-8) suggest that C^2_n adequately tracks mixing depth. As profiler and RASS data from recently installed sites continues to be processed and reviewed, an improved understanding of the strengths and limitations of remote sensing techniques under different meteorological conditions will evolve. Currently, these methods suggest outstanding potential for characterizing mixing and advection processes for modeling applications in the lower troposphere.

The ability of C^2_n to depict the diurnal mixed layer growth for July 12 and 13 is shown clearly in Figure 2-9. The slower growth on the second day coincided with higher ozone concentrations, suggesting that reproducing the temporal growth of the mixed layer is a model sensitive component.

The potential value of C^2_n, relative to RASS also is illustrated in Figure 2-10. Penetration of RASS often is limited to about 1000m, falling short of many typical daytime mixing depths which often exceed 2000 m. Radar profilers penetrate well beyond the well-mixed layer. Consequently, reflectivity values provided by profilers extend to high afternoon elevations of the mixed layer that are beyond the scope of RASS. Some caution regarding the representativeness of C^2_n during night is warranted given the relatively high nighttime values.

2.4.4 Wind fields

Wind fields strongly influence the outcome and interpretation modeling results. Given that most of the air volume under consideration in any application is strongly influenced by upper air flows, the importance of characterizing vertical wind field gradients should not be understated. Upper air flow characterization dictates much of the "direct"source-receptor relationships, as well as the degree of mixing and attendant effects on atmospheric chemistry. The implementation of continuous operating sodars and radar profilers is a major improvement, providing more resolved time and space (vertical) data to better reproduce the most fundamental modeling inputs.

Additional surface stations and a local upper air station will improve the representativeness of the processed wind fields. Previously, twice-daily soundings from the nearest or most representative FAA location provided the raw data for vertical wind profiles. PAMS requirements will insure the operation of at least one upper meteorological site within an

"urban" scale domain.

Advantages of remote sensing instrumentation

Remote sensing instruments such as profilers/sodars and RASS provide a means to characterize wind flow phenomena, and often are capable of resolving various meteorological phenomena including land-sea breeze regimes, recirculation patterns and nighttime jet formation. Figure 2-11 displays an analysis of output from a radar profiler in the Northeast U.S. over a 2-day period. Various phenomena are superimposed on the diagram, based mostly on interpretation of the wind data. While the wind data (speed and direction) form the basis for direct input into meteorological models like the UAM Diagnostic Wind Model, the ability of profiler data to enable interpretation of low-level jets and mixing depths sets provide phenomena for comparison with meteorological models.

Graphical comparisons between simulated wind fields and remote sensing data should be produced for those episodes incorporating upper meteorological data. Modeled wind fields plotted in a manner compatible with that displayed in Figure 2-11 can be compared visually with observed wind fields. These comparisons should include 1-dimensional (vertical) site by site comparisons of several vertical levels and time periods, covering important temporal transition periods. Two-dimensional (horizontal) comparisons between profiler outputs and simulated wind fields for surface and elevated layers be produced to evaluate the model's ability to replicate observed horizontal gradients.

2.4.5 Additional uses for PAMS meteorological data

Upper air temperature profiles

As discussed above, the RASS vertical temperature profiles provide increased vertical and temporal resolution for estimating mixing depths. Additionally, temperature profiles are required for atmospheric chemistry calculations performed within the chemical mechanisms

Solar and UV Radiation

PAMS requires measurements of total solar (.10 to 4.0 μm) and UV (0.10 to 0.40 μm) radiation. The photolytic reactions are strongly sensitive to UV, and such measurements could be used for calculating photolysis rates of key reactions. However, calculation of photolysis rate constants often is automated within different modeling codes. UAM-IV, for example, assumes bright sky conditions and sun position (spatial/temporal coordinates) for internal calculation of photolysis rates. The UV data should be used whenever available they provide a more realistic representation of the physics driving atmospheric chemistry routines in the AQSMs. Future modeling guidance will need to address the use of radiation measurements.

Relative Humidity

Water vapor plays an important role in ozone formation, and relative humidity (in combination with temperature) can be utilized to estimate water concentrations. Relative humidity is a critically important parameter for estimating visibility impairment, and should prove valuable in future fine particle and visibility modeling applications.

Development of Boundary and Initial Conditions

The use of air quality data for developing initial and boundary conditions is largely an iterative process coupled closely with model evaluation concepts discussed above. The spatial coverage provided by PAMS is not adequate to develop comprehensive sets of air quality model inputs. Consequently, the available data are best suited to evaluating initial and boundary inputs used to drive the model simulation. Over the last ten years the spatial and temporal limits have been expanded for most model applications, partly because extended simulations are less sensitive to initial conditions. Therefore, this document places much greater emphasis on the use of data for evaluation purposes rather than input development. Nevertheless, PAMS-type data should be used for examining air quality inputs, especially boundary conditions which are a critical component of any simulation.

For most urban scale model applications, one (or possibly two) Type I "upwind" sites will be available for examination of boundary values. All of the comments regarding compensating errors, the advantages of reducing degrees of freedom for general model evaluation apply equally for evaluation of boundary conditions. Although it is important to quantify boundary ozone (supported by PAMS Type 1 sites), measurements of NMOC, NO_x and carbonyls add strong value to characterizing boundary conditions. Boundary conditions and transport are closely related, in the sense that transport phenomena are quantified as boundary values in a model application. Transport involves several factors in addition to the "additive" effect of incoming ozone. Transport includes movement of precursors or precursor "sinks" such as PAN and N_2O_5 which under certain conditions can release NO_x. The role of ozone transported from an upwind location and acting as a radical initiator downwind (ozone is the dominant source of hydroxyl radicals) is a component of transport, in addition to a strictly additive role of imported ozone.

2.5 DEVELOPMENT AND EVALUATION OF EMISSIONS INPUTS

The PAMS speciated NMOC data provide strong support for modeling by enabling evaluation of the emission inputs driving models. The reader is referred to Chapter 3 for examples of the use of PAMS data in evaluating emissions.

2.6 DISCUSSION OF PAQSM PERFORMANCE AND CORRESPONDING USES OF PAMS AIR QUALITY DATA

Traditional ozone model evaluations have relied on operational evaluations comparing surface ozone observations with modeled ozone predictions. Ozone models often produce reasonable surface level spatial and temporal reproductions of observed ozone fields. However, the use of ozone as the sole indicator of model performance/behavior can produce misleading confidence in the model's ability to correctly predict response to other meteorological episodes, or more importantly, emission reduction scenarios.

2.6.1 PAMS and Compensating Errors

Ozone is a secondarily formed pollutant with concentrations dependent on many factors many combinations of which could lead to similar ozone. Various combinations of compensating errors can produce apparently "correct" ozone fields for wrong reasons. The chance that the model is reproducing ozone for the "right" reasons may or may not be greater than the chance that some combination of compensating errors is responsible. For example, underestimates of emissions can be compensated by restricted mixing through underestimates of mixing heights or wind speeds. The complexity of the coupling of meteorological, emissions, deposition and transformation processes introduces numerous opportunities for compensating errors, and renders a very difficult identification of those processes and factors involved in compensation.

The issue underlying compensating errors is that models are applied in a prospective predictive mode with an assumed confidence, built on operational evaluation of ozone, that the physical and chemical processes are adequately characterized and therefore the model will respond correctly to emission perturbations. However, an operational evaluation only assures that surface ozone is estimated reasonably well under the existing model input scenario, a phenomenon resulting from either (1) adequate characterization of physical/chemical processes or (2) the operation of compensating errors. Because so many non-linearities exist, encountering a "flaw" in the modeling system may not happen until rather aggressive control scenarios are imposed which can not be evaluated because the testing of "projected" emission control experiments is impossible. Consequently, the model could produce misleading, and even misdirected, conclusions regarding control strategies.

The influence of compensating effects may or may not lead to incorrect conclusions regarding control strategy analysis. But the assumption that compensating errors are not present and processes are characterized appropriately because of a successful operational evaluation is not valid. A prevailing consensus does not exist on the frequency and importance of significant compensating errors in current applications.

2.6.2 Suggested Uses of PAMS Data for Model Evaluation by Compound Class

The previous discussion on compensating errors is a logical lead-in to describing the value

of PAMS data in support of the model evaluation process. Compensating errors are related to degrees of freedom within a system. Fewer data categories result in a less constrained evaluation system and consequently increase the likelihood of a strong compensating error effect. The availability of additional measurements beyond surface ozone restricts the overall freedom for " model calibration" and similarly reduces the propensity toward compensation. A simulation exhibiting good agreement with ozone and precursors would yield far greater confidence that the model is working properly, than with the use of surface ozone only. Hence, the intrinsic value of incorporating precursor data in the model evaluation process is the potential for reducing compensating errors in the modeling system.

The following sections discuss and provide examples of the use of subclasses of PAMS data in model evaluations. Somewhat more emphasis is placed on caveats associated with the data in order to forewarn the user to prevent inappropriate model-data comparisons. Any comparison of measured air quality and simulated air quality reflects the cumulative effects due to various physical/chemical processes. Insight on the relationship between physical and chemical processes and associated measurements should be used to guide the types of analyses performed on the available data. Certain types of data may be subject to greater relative influence from a specific process (e.g., less reactive NMHC and emissions), as opposed to other measurements subject to multiple processes (e.g., ozone affected by emissions, meteorology and photochemistry).

Model-measurement comparisons should make full use of the spatial and temporal ranges available in the measured data. In addition to the station by station time-series plots, 2-dimensional spatial displays during selected time periods using isopleths, tiling, or other displays should be produced to convey a sense spatial representativeness replicated by the model. Extreme care should be exerted since the sparse spatial density of PAMS sites could create misleading depictions of the true atmospheric state.

2.6.3 Total NMOC and NMHC

Comparisons of PAMS data with a corresponding estimate of modeled aggregate non-methane organic compounds (NMOC) provide a means to determine if the modeling system is capable of characterizing precursor/VOC levels. The limitations and definitions of both measured NMOC and modeled NMOC must be understood in order to develop logical comparisons. The definition of the sum of compounds reported as measured NMOC are likely to never match an analogous definition for modeled NMOC. This discrepancy is due both to the variety of "measured" NMOC definitions and the various NMOC condensation schemes incorporated in chemical mechanisms. Such differences do not preclude model/observation comparisons, but they must be understood to explain the fraction of disagreement not attributed to model error.

Measurement/reporting Issues.

Measured NMOC is not a clearly defined term, and varies with reporting procedures, instrumentation and instrument technique. The precise definition of NMOC is all organic compounds minus methane. The closest measured approximation from a typical PAMS site would include all compounds from both GC and cartridge techniques (carbonyls are NMOC). However, the NMOC reported to AIRS typically is the list of 56 or so targeted species based on Gas Chromatograph (GC) measurements. The targeted species are but a subset of all the species that elute through a GC column. Sometimes the cumulative areas under all peaks are reported as NMOC. Different instruments and techniques have substantial impacts on GC derived NMOC, adding an additional source of inconsistency concerning NMOC data reporting. For example, the loss of many oxygenated and polar acting species, including biogenic compounds (e.g., monoterpenes), associated with sample pretreatment and water management is system dependent. Generally, as sampling methods and GC instruments and techniques improve, more compounds, including carbonyl species, will be captured and passed though to the detector. This is desirable progress, but an accounting of the different techniques, changes in methods, etc. must be available to provide a basic understanding of what measured NMOC represents. Further complicating this issue is the uneven detector response to different organic compounds. These issues are especially important with respect to trends analyses.

Carbonyls can account for 30% or more of the total NMOC, yet a much smaller fraction is reported as PAMS requires the reporting of only three compounds: acetone, formaldehyde and acetaldehyde. Numerous issues are associated with carbonyl sampling and analysis as with any monitoring technique. These measurement related issues are not intended to discourage model/ambient comparisons. However, clear understanding of what is measured/reported will improve the interpretation of model/ambient comparisons.

Simulated NMOC and NMHC

Thousands of reactions and hundreds of species are required to explicitly characterize the atmospheric chemistry phenomena responsible for ozone formation. The inclusion of so many reactions and species would extract an enormous computational burden; consequently, PAQSMs utilize chemical mechanisms which condense the number reactions and species down to manageable levels. Typically, the inorganic species and reactions (e.g., principal NO_x and ozone reactions) are treated explicitly. However, the organic chemistry is highly parameterized with several "surrogate" species used to represent compound classes, bond types or other functional relationships. Aggregating all of the modeled VOC groups represents an approximation of NMOC. However, given the limitations of carbonyl measurements as well as the model's treatment (or lack of) numerous carbonyl compounds, more meaningful model/data comparisons would be conducted with estimates of non-methane hydrocarbon compounds (NMHC). In most chemical mechanisms, hydrocarbon groups are differentiated from oxygen containing organic groups allowing for an adequate aggregation to represent NMHC. As discussed earlier, an

understanding of what is actually measured and reported is a prerequisite for conducting comparisons.

2.6.4 Speciated VOC and Carbonyls (Isoprene and Formaldehyde)

Comparisons between modeled and measured species are limited by the model's ability to depict explicit species. Explicit organic species in the CB4 mechanism are formaldehyde, isoprene, ethanol and methanol. Comparisons with both formaldehyde[1] and isoprene are strongly recommended, given the potential value both species provide in characterizing important photochemical and natural emissions processes. Isoprene is the most important biogenic emission precursor specie. In the Eastern U.S., the suspected levels of biogenic emissions are so large that any observed corroboration of their predictability is worthwhile. The level of biogenic emissions influences the relative need for NO_x or VOC control strategies. Although isoprene is reactive, the emission levels are so large that resulting ambient levels (> 1 ppb) should provide a reasonable basis for comparison between modeled and observed levels.

Formaldehyde is emitted directly as a primary species, formed secondarily, and undergoes photolysis. Although formaldehyde may not act as a surrogate for other carbonyl species, the observed levels, chemical reactivity and multiple activities suggest that formaldehyde is an important indicator of model performance.

2.6.5 Nitrogen: NO_x (NO, NO2), NO_y

Comparisons of NO, NO_2 and total oxidized nitrogen (NO_y) with corresponding modeled estimates provide a basis for corroborating the NO_x emissions component and atmospheric chemistry phenomena. Comparisons of the diurnal pattern of NO concentrations are influenced mainly by proximity of NO_x emission sources, particular during the morning hours. The titration of ozone due to NO_x emissions diminishes during the day as NO is oxidized to various products.

Total NO_y comparisons, assuming measured NO_y are available, complement NO comparisons. During periods when NO_x is most likely to reduce ambient ozone, NO constitutes the major fraction of NO_y. However, as oxidation processes proceed, emitted NO eventually transforms into other more highly oxidized species (NO_2, nitric acid and PAN) which are major components of NO_y. In fact, the ratio NO/NO_y is a useful metric for comparison as it provides a relative measure of air mass aging, higher ratios reflecting air laden with "fresh" NO_x emissions. Total NO_y measurements should account for NO_x, HNO_3, PAN, and organic nitrates, many of which are semi-volatile and exist in the particle phases; species typically not accounted for in most

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[1] Certain parts of various olefin compounds are aggregated as Formaldehyde in the CB4 mechanism. Thus, the modeled formaldehyde will always be somewhat higher than "true" simulated formaldehyde.

chemical mechanisms. Thus, some unknown amount of negative (underestimate) bias due to organic nitrate species that are not modeled is present. Nevertheless, on balance modeled NO_y (sum of NO_x, HNO_3 and PAN) probably is subject to similar difficulties associated with using modeled NMHC as a basis for comparison with ambient data, and should be considered a useful, albeit rough estimate of total NO_y.

Comparisons with NO_2 provide a strong test of model's ability to capture the timing and magnitude of atmospheric chemistry phenomena, given the central role that NO_2 plays in oxidant chemistry. Unfortunately, NO_2 measurements rarely are available, limited to a few select research grade efforts in special field studies. NO_2 data reported from most monitoring sites are reported as the difference between measured NO_x and NO. The chemiluminescence technique for measuring NO_x and NO is more reliable for NO. However, the total NO_x measurement, which typically requires conversion of NO_2 to NO through a molybdenum catalyst, is subject to strong, positive interferences from other NO_y species (e.g., HNO3, PAN). Thus, the NO_x measurement is believed to be reside somewhere between actual NO_x and total NO_y.

2.7 USE OF PAMS DATA TO CORROBORATE MODELED STRATEGIES

Modeled attainment demonstrations require one to project emissions and corresponding air quality estimates several years into the future to a statutory attainment date. Model predictions are then compared to the national ambient air quality standard (NAAQS) to determine whether the simulated control strategy is likely to be sufficient to meet the NAAQS. This latter exercise is referred to as a "modeled attainment test".

There are substantial uncertainties inherent in modeled attainment demonstrations. These arise from uncertainties in the data bases driving the model, approximations of chemical/physical processes made in the model's formulation and uncertainties about a number of factors affecting emission projections. In recognition of these uncertainties, future modeled attainment tests are likely to incorporate a "weight of evidence" concept to assess adequacy of a proposed emission control strategy. In a weight of evidence analysis, air quality modeling results serve as one (perhaps the most important) element. Other elements include a series of corroborative analyses, many of which will draw on the kinds of data produced by the PAMS network. Table 2-1 illustrates elements which would be considered in a typical weight of evidence analysis. The middle column in the table identifies factors which affect the credence or "weight" given to a particular element. The right-hand column describes outcomes which would be consistent with concluding that the attainment test is passed despite air quality modeling results which do not quite show attainment.

Looking at the elements in Table 2-1, there are a number of potential uses for PAMS data. For example, we see that the more extensive the (air quality) data base used to formulate inputs to and evaluate performance of the photochemical grid model, the greater the weight that can be

assigned to its results. Looking at the trend data element, we see that presence of precursor trends which are consistent with apparent ozone trends would lend weight to results of the trend analysis. Other trend analyses may be used as means for assessing model performance, thereby affecting weight assigned to modeling in subsequent "mid-course reviews" of strategies prior to the statutory attainment date. For example, as noted in Chapter 4, observed trends in ratios of indicator species like HCHO/NO_y or trends in highly reactive to less reactive VOC species may be compared to model predictions to help assess model performance. Good performance would increase the weight given to modeled results in the attainment test. Table 2.1 also shows how results produced from observational models would be used in a weight of evidence analysis. The term "observational models" in Table 2-1 includes "receptor models" (Chapter 3, this report) as well as the observational models described in Chapter 4. The principal value of the observational models is to provide qualitative indicators of which strategies are likely to be most effective in reducing future ozone levels. Thus, they may be used to corroborate whether a proposed strategy simulated with a photochemical grid model is addressing the appropriate classes of sources. PAMS data are also of potential use for the "selected episodes" element in the weight of evidence analysis. As described in Chapter 1, the PAMS data base will provide much more extensive information about meteorological conditions aloft than is currently available. Because conditions aloft are believed to be important factors affecting observed surface ozone concentrations, this information might be used to good effect in helping us to identify distinctive meteorological regimes leading to high ozone. This will provide increased confidence that we are considering the important regimes corresponding to high ozone, thereby increasing the weight given to the estimated severity of selected episodes in the weight of evidence analysis.

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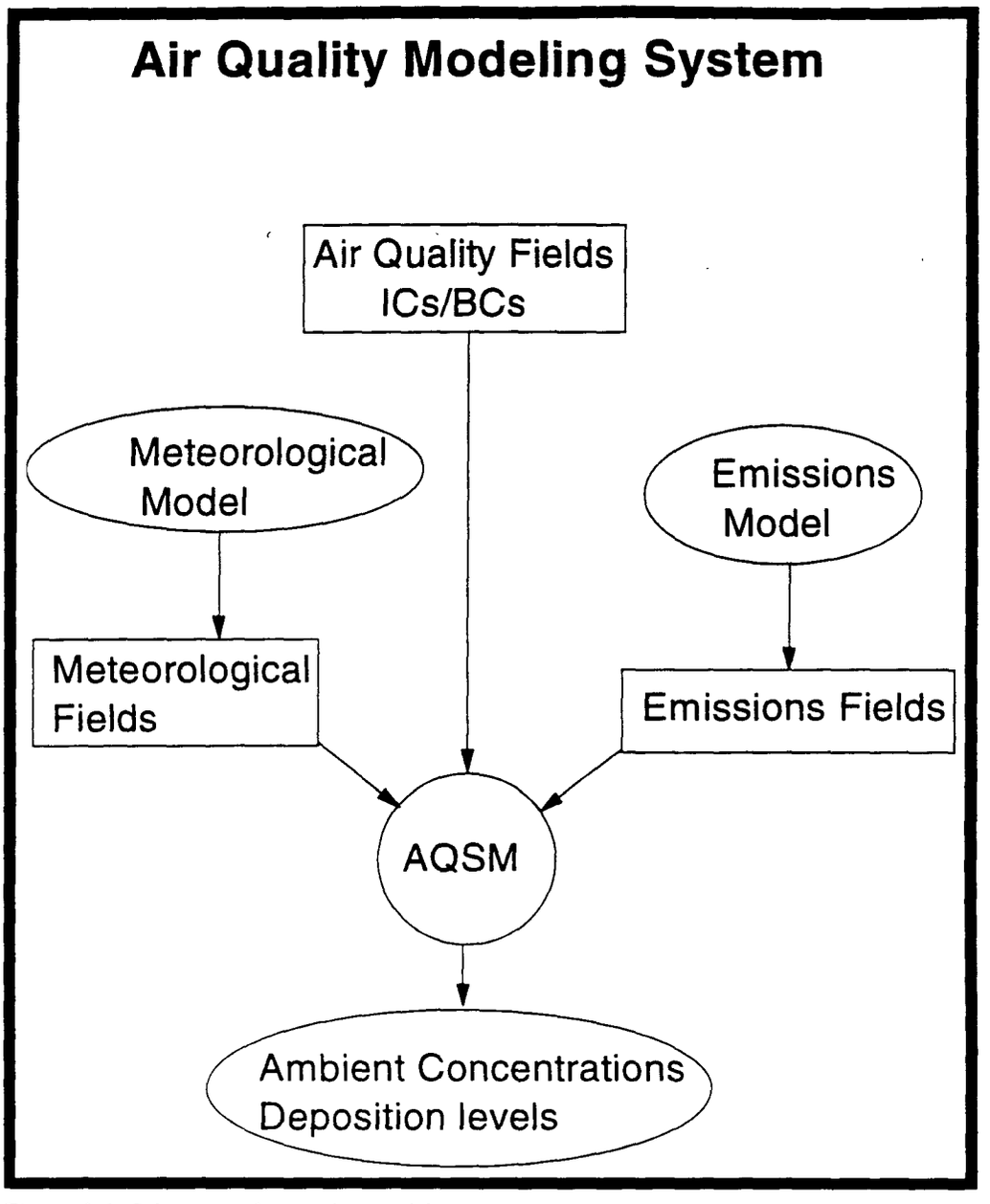


Figure 2-1. Schematic of air quality modeling system.

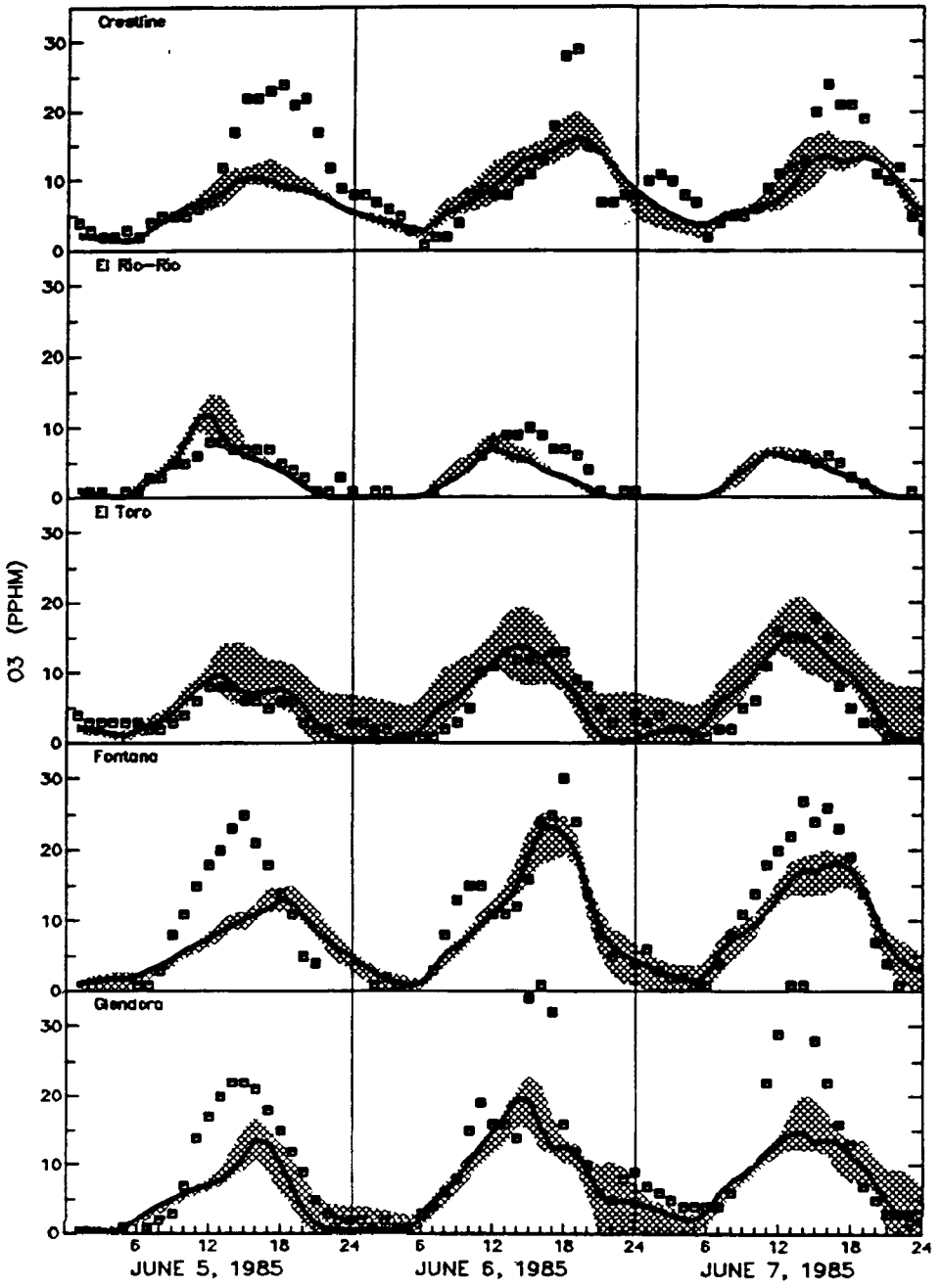


Figure 2-2. Comparison between predicted and measured ozone concentrations for June 5-7, 1985 in the South Coast Air Basin (Wallerstein et al., 1994). The solid line = distance-weighted mean value (average of 4 grid cells), shaded area=maximum and minimum value of the 9 cells around the station. Observed values are squares

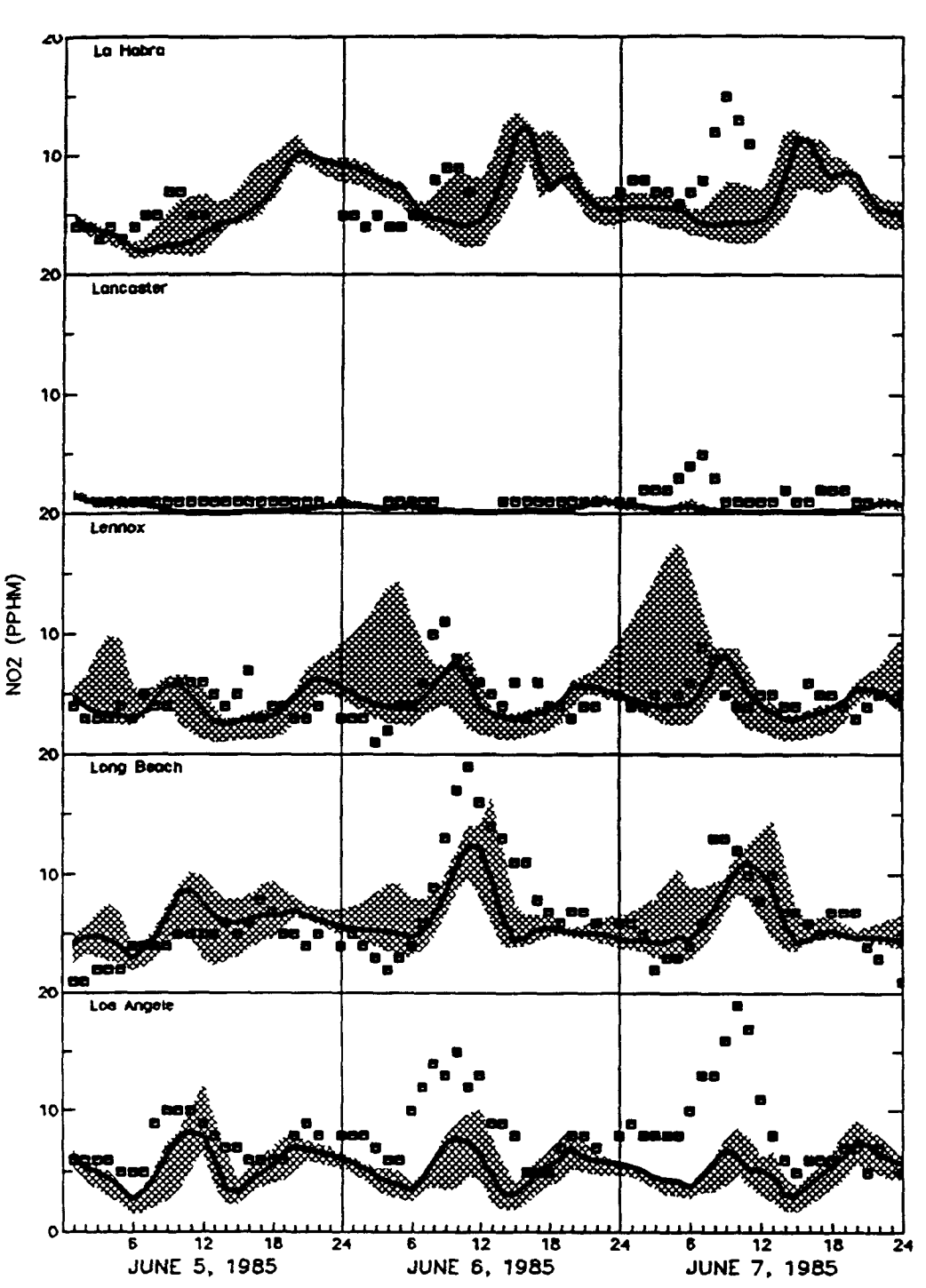


Figure 2-3. Comparison between predicted and measured NO_2 concentrations for June 5-7, 1985 in the South Coast Air Basin (Wallerstein et al., 1994) The solid line = distance-weighted mean value (average of 4 grid cells), shaded area=maximum and minimum value of the 9 cells around the station. Observed values are squares.

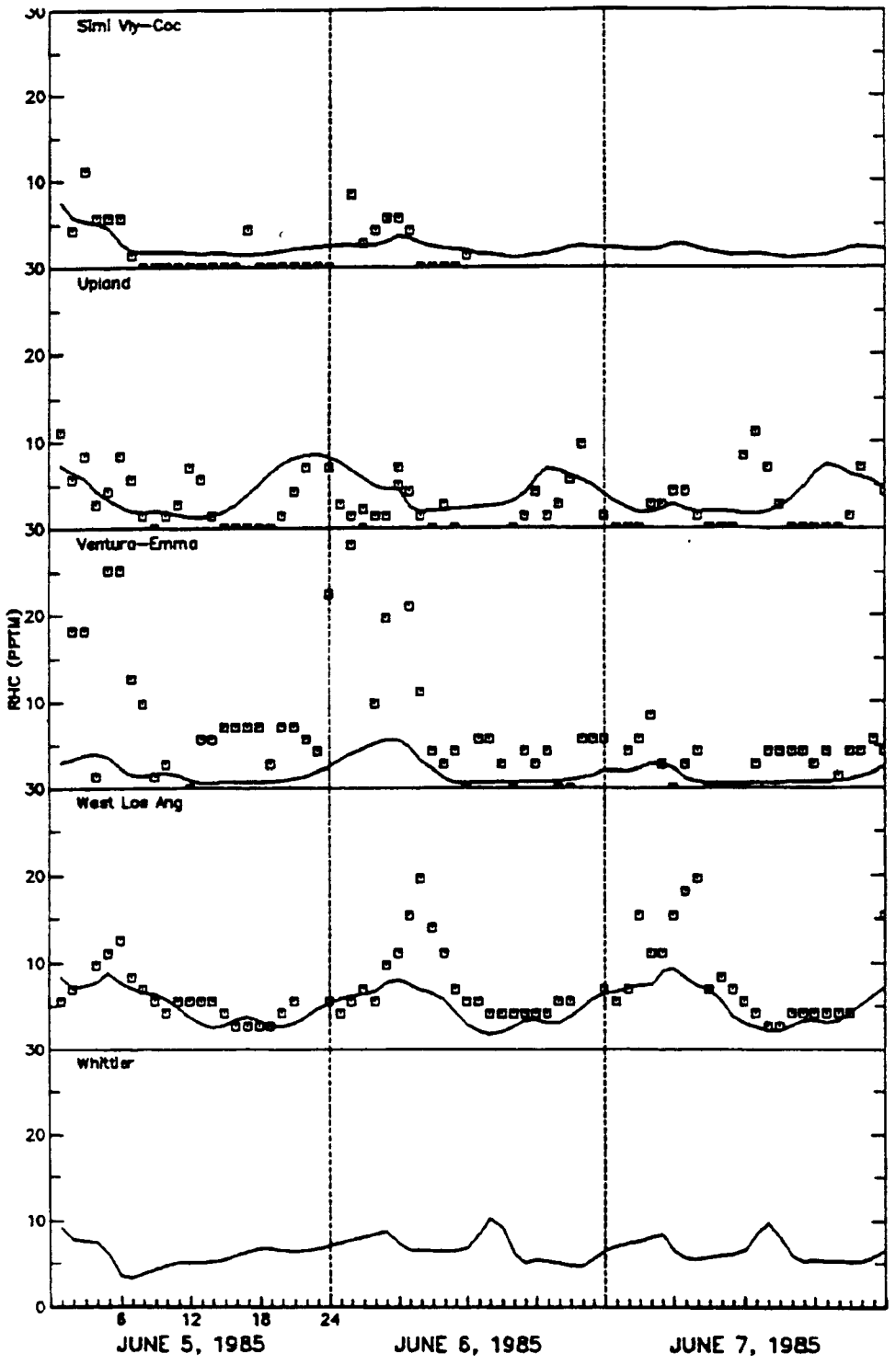


Figure 2-4. Comparison between predicted and measured reactive hydrocarbon (RHC) concentrations for June 5, 6, and 7, 1985 in the South Coast Air basin of California (Wallerstein et al., 1994) The solid line = distance weighted mean value (i.e., average of 4 grid cells).

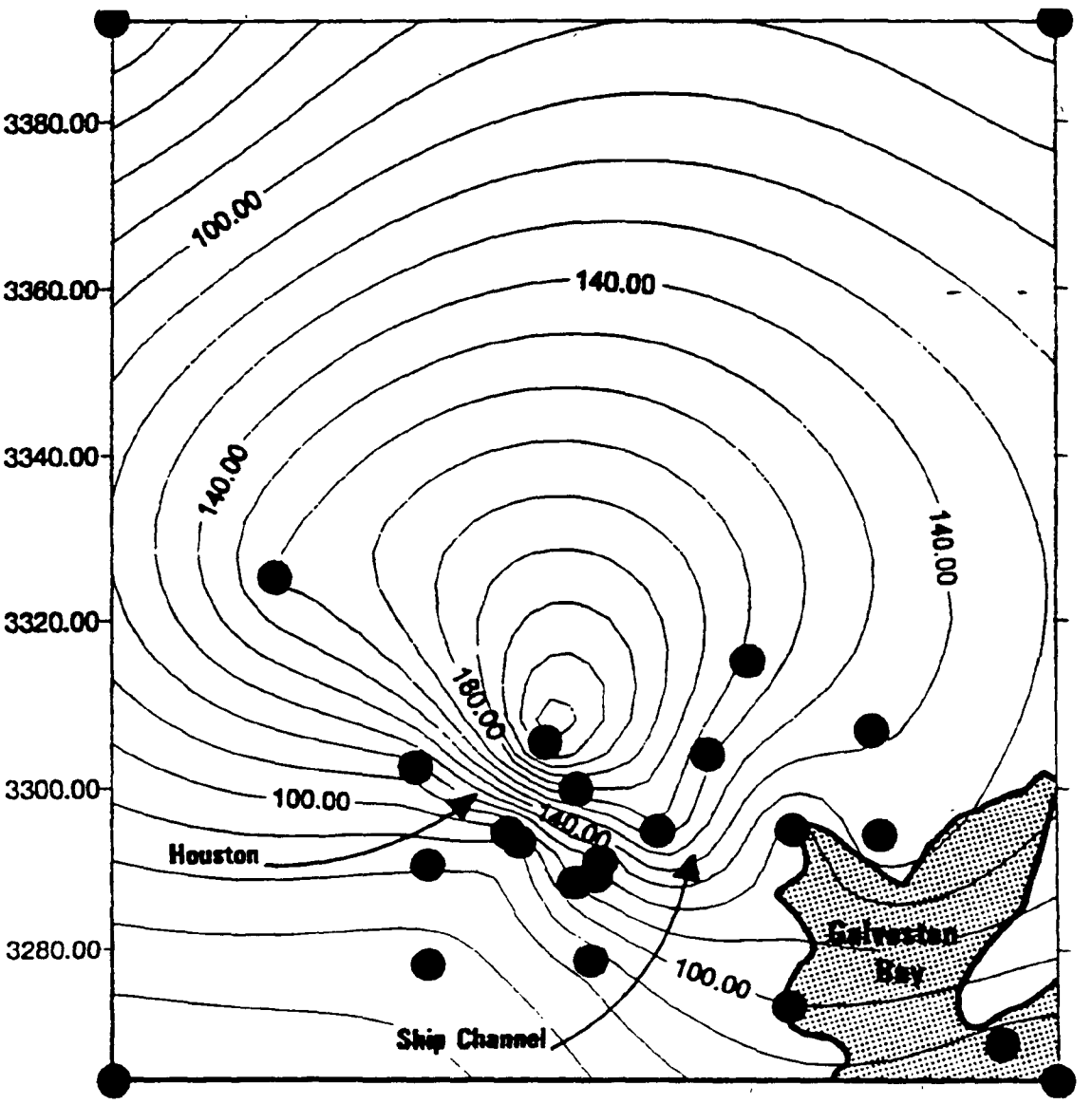
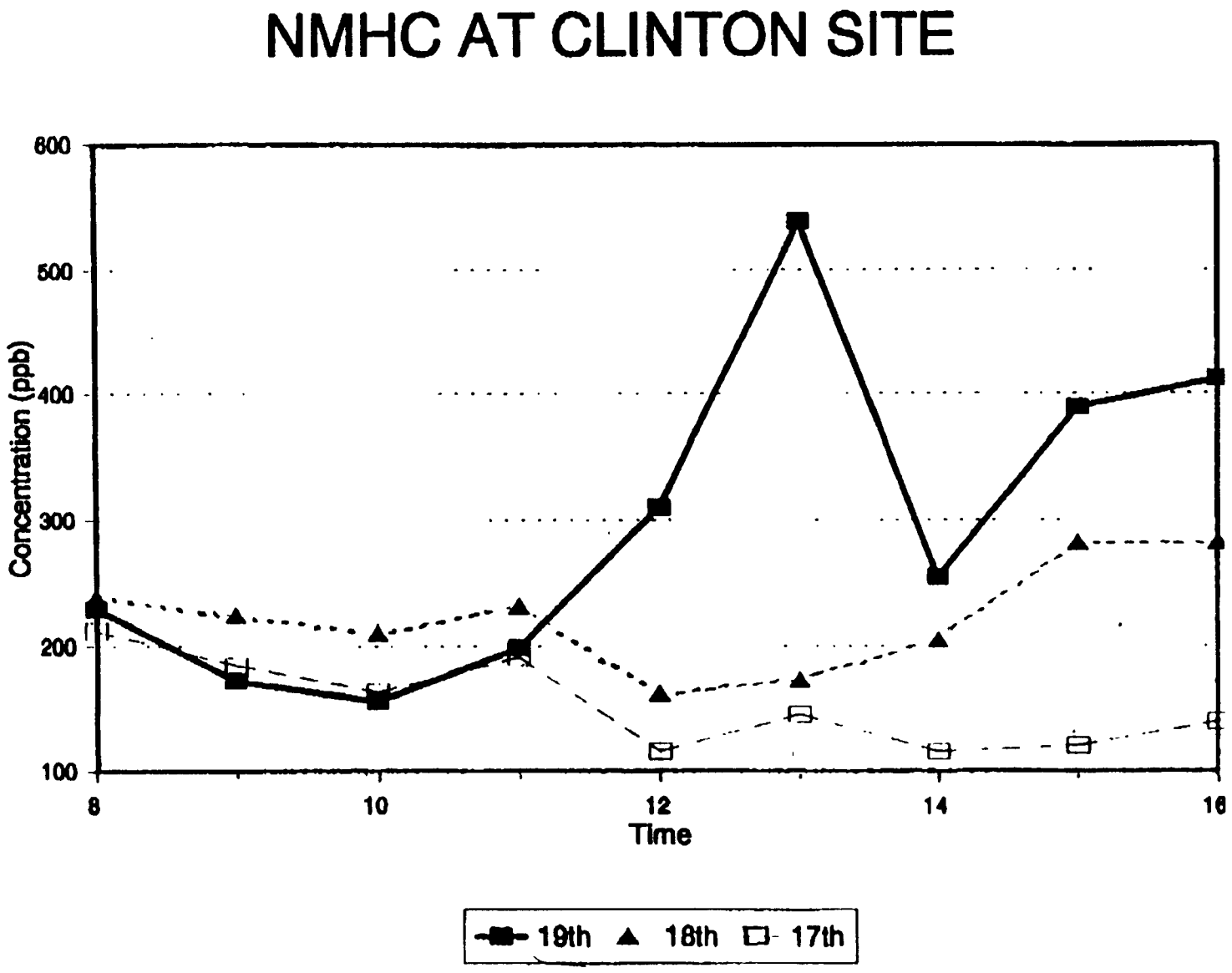


Figure 2-5. Ambient isopleths of surface level ozone for Houston, TX on August 19, 1993 (SAI, 1995?).

Figure 2-6. Ambient NMHC measured at the Clinton, TX site for August 17-19, 1993 (SAI, 1995)



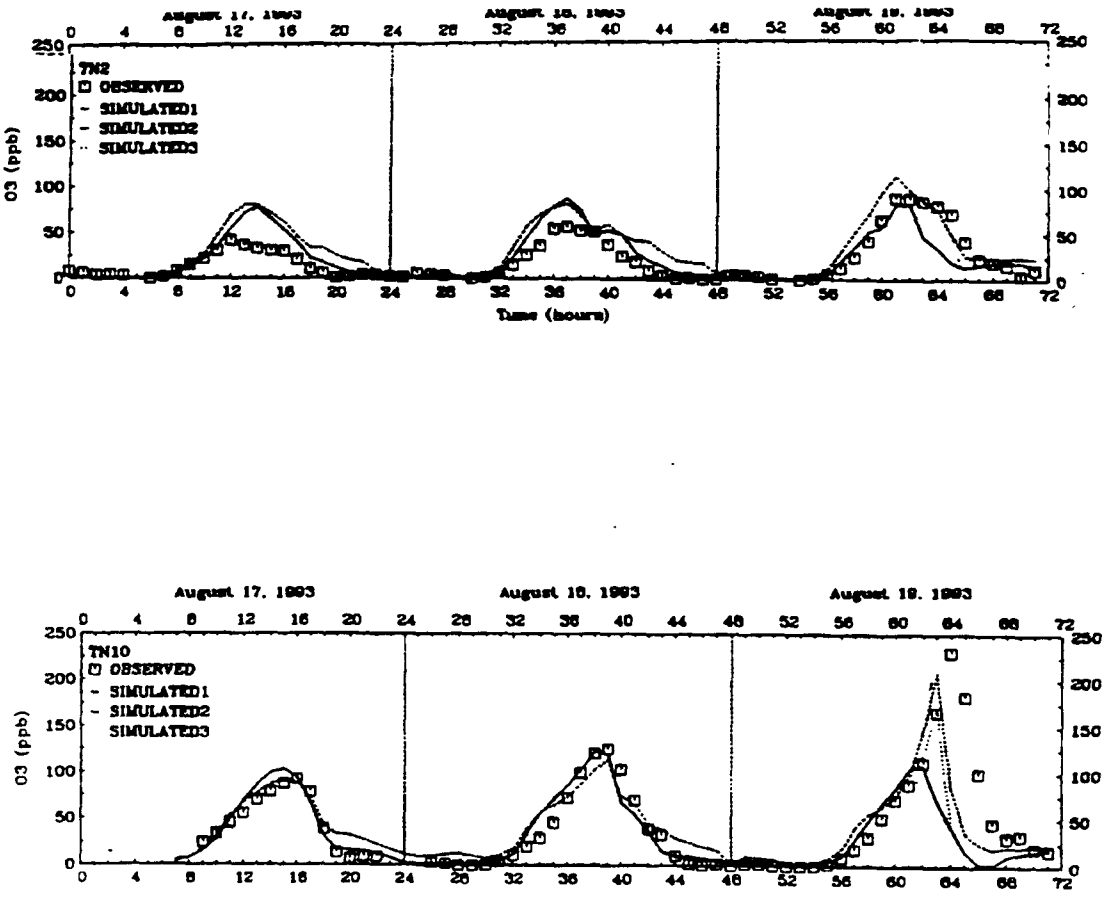


Figure 2-7. Time series plots of ozone at two sites before and after correction in emissions. Notice that simulated ozone changed significantly at site TN10, responding to emissions change, and little change occurred at site TN2 (top).

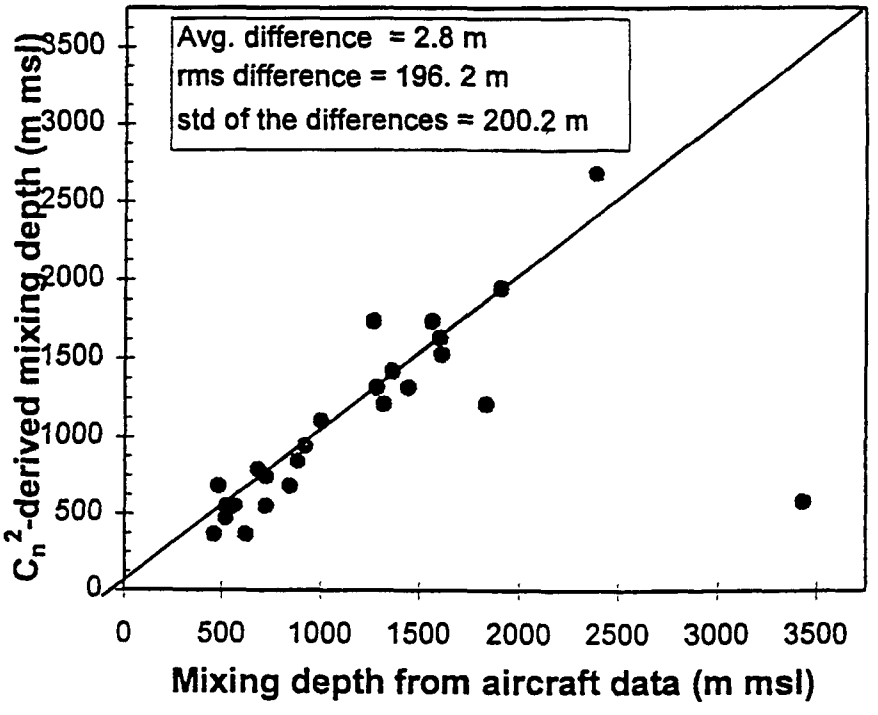


Figure 2-8. Scatter plot of C_N^2 derived mixing depths estimated from aircraft profiles of pollutant concentrations, turbulence and temperature. Twenty five comparisons were made using aircraft data collected in the afternoon near three profilers in southeast Texas (SAI, 1995).

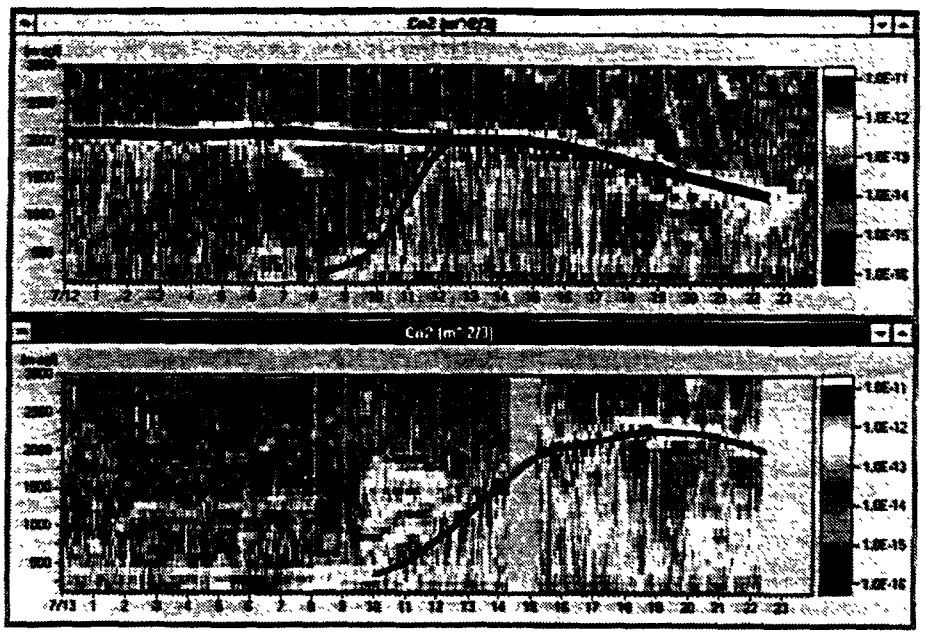


Figure 2.9 Time-height cross-section of C_N^2 for July 12-13, 1994 at New Brunswick, NY. Thick line denotes the subsidence inversion; thin line during the day denotes the top of the mixed layer. On July 12, a subsidence inversion is shown in the profiler data as a region of high reflectivity between 1750 and 2000 m agl. The inversion limited afternoon growth of the CBL to below 2000 m. A slower growth occurred on July 13 resulting in reduced vertical mixing of precursors, and an attendant elevated afternoon ozone level.

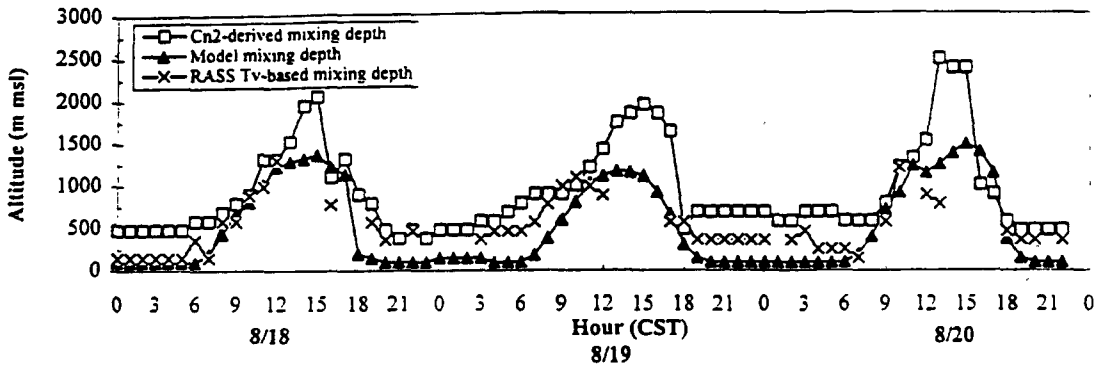


Figure 2.10 Time series plot of mixing depths estimated from C_N^2 and T_V data from a meteorological model for a radar profiler site in Houston, TX for August 18-20, 1993 (Dye, et al. 1995).

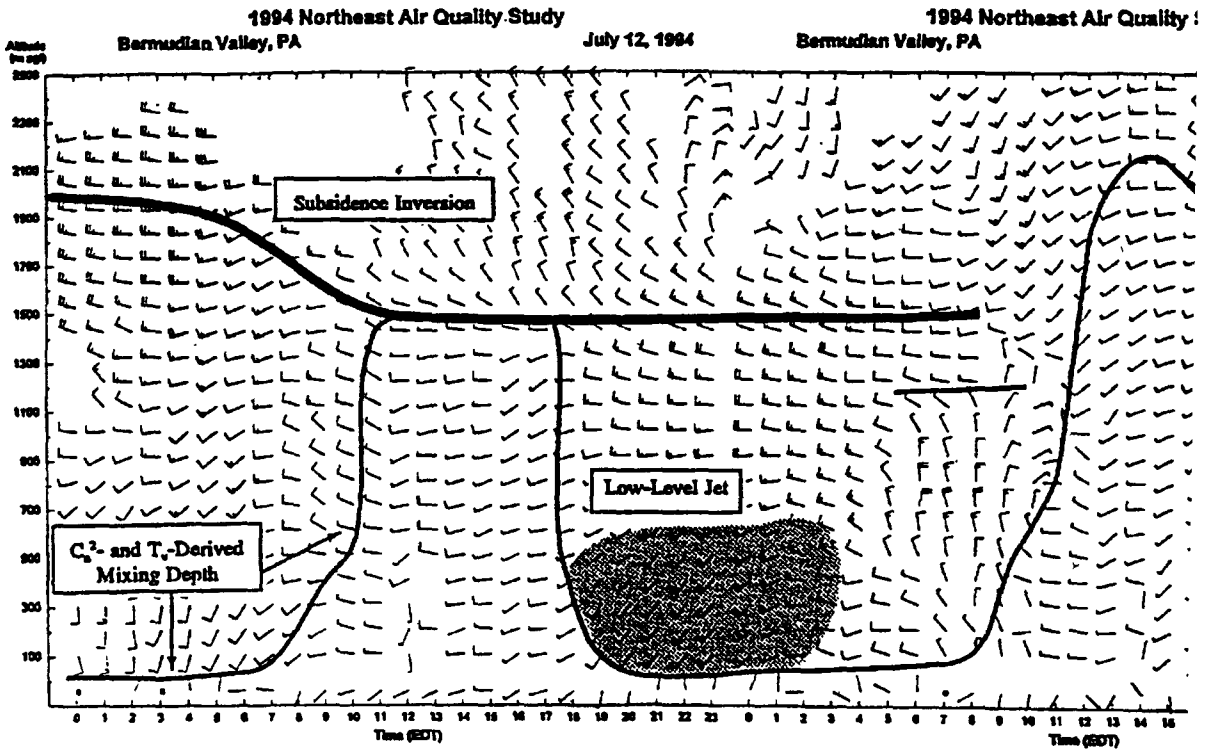


Figure 2-11. Time-height cross-section of winds on July 12-13, 1994 at Bermudian Valley, PA, indic mixing depths. Each wind barb indicates direction and speed.

Table 2-1. Factors Affecting Weight of Evidence and Acceptance of Model Results Nearly Passing the Attainment Test

Type of Analysis	Factors Increasing Weight of Evidence	Factors Supporting Deviation from Test Benchmark(s)
Photochemical Grid Model	-good performance -extensive data base -short projection period -confidence in inventories & projections	-overpredictions -major improvement in predicted AQ using a variety of indicators -results come very close to meeting the benchmark(s) -other peer-reviewed grid models predict comparable or better improvement in ozone
Trend Data	-extensive monitoring network -precursor & ozone trends avail. -statistical model normalizing trend explains much variance -little bias in statistically predicted highest ozone -short projection period -pronounced, stat. significant normalized trend -continued, comparable relative reductions in emissions provided for	-pronounced downward normalized trend exceeding that anticipated with grid model
Observational Models	-extensive monitoring network -QA'd, self-consistent results -plausible, physical explanations for findings	-indicates sources other than those in modeled strategies play significant roles

Selected Episodes	-all met.regimes corresponding w. high obs. O3 considered -met.ozone potential of episodes exceeded ~ 1/year	-observed O3 >> design value -Severity of met. conditions expected to be exceeded << 1/yr
Incremental Costs/Benefits	-good documentation for cost estimates -lack of alternatives for reducing emissions -lack of model responsiveness for variety of strategies as benchmark is approached	-lack of model responsiveness accompanied by high incremental costs
Other (optional) Analyses	-rationale documented	

CHAPTER 3
EVALUATING EMISSIONS FACTORS, MODELS & INVENTORIES WITH PAMS DATA

3.1 INTRODUCTION

One of the principal benefits of the PAMS monitoring network is the feedback it provides to the various elements of the ozone regulatory program. Emissions inventories are an important element of the ozone program. PAMS provides valuable feedback which can be used to evaluate and improve the inventory. This chapter begins with a brief background description of emissions inventories and potential inventory problems that PAMS data can elucidate. This introduction is followed by examples illustrating the use of PAMS data to evaluate and refine emissions inventories. These examples are separated into two sections: direct comparisons of the inventory components with measured data and more refined analyses using multivariate and chemical mass balance analyses. The chapter concludes with a more detailed description of the analytical techniques.

3.2 BACKGROUND

Emissions inventories have long been a cornerstone of air quality management. Emissions estimates are important for determining applicability of sources in permitting and control programs, ascertaining the air quality impact of sources and appropriate mitigation strategies, and a number of other related applications by an array of users, including federal, state, and local agencies, consultants, and industry. Data from source-specific emissions tests or continuous emissions monitors are usually preferred for estimating a source's emissions because those data provide the best representation of the tested source's emissions. However, test data from individual sources are not always available and, even if they are, the tests only represent a snapshot in time and may not reflect the variability of actual emissions over time. Continuous emissions monitors could resolve this variability concern but are expensive and technologies are unproven for some pollutants. Thus, emissions factors are frequently the best or only method available for deriving emissions estimates, in spite of their limitations.

Emissions estimates are the product of emissions factors established for various source categories of VOC, NO_x and CO as well as activity levels established for each source category. Emissions factors describe the amount of emissions produced per unit of activity at a source. Examples are "lbs. NO_x produced per megawatt of power produced by a utility" or "grams of VOC produced per vehicle mile traveled by the current mix of automotive sources". Emissions factors are often based on measurements made for a limited number of sources within a broad

source category. Further, the measurements may be dated or made at geographical locations far removed from the area of interest.

The activity level estimate from a source describes the number of units produced by a source, which result in the by-product of pollutant emissions. In the two examples cited above, activity levels would be the megawatts of power produced by the utility in question and the vehicle miles traveled by the automotive fleet over a period of interest. In some cases, such as for utilities, activity levels can be determined with considerable reliability. In others however, activity levels must be estimated using surrogate indicators like population, sales figures and employment statistics.

Emissions inventories are used for a variety of purposes. Some of these, like use in a photochemical modeling exercise, require a high degree of spatial and temporal resolution, as well as information about the chemical composition of the emissions. Emissions models are used to develop this information which, in turn, is used as input to the photochemical models. Emissions models need to address issues like, "how are emissions distributed within a city?", and "what kind of temporal or diurnal patterns are reasonable to assume for the emissions from various source categories?" These estimates are obtained from emissions factors, estimated activity levels, estimated spatial/temporal patterns of activity using various surrogates, available information on sensitivity of emissions factors to meteorological conditions and limited information on the chemical composition of emissions from the various source categories.

The concept of using ambient measurements to improve emissions models, factors and inventories is not new. In 1985, Air Pollution Control Association Specialty Conference on Receptor Methods for Source Apportionment, several authors discussed the potential application of receptor models to identify unknown sources or source categories. In that conference, several authors demonstrated the use of receptor models to interpret speciated ambient measurements of particulate matter, (Pace, 1986). One very early investigation to reconcile atmospheric hydrocarbons with sources was conducted in 1974, (Mayrsohn). Recently, a critical evaluation of studies that used ambient data to infer weaknesses in ozone precursor emissions inventories was completed, (Yarwood).

Identifying possible discrepancies in the inventory compared to the ambient data is only the first step in the process. This has to be followed up with detailed emissions surveys for sources around the monitor, careful review of the speciation and temporal profiles used to convert the inventory to something compatible with the monitored results. This is costly and time-consuming, but is the only way to truly improve the quality of an emissions inventory. Therefore, while PAMS data can provide a very good tool for assisting in the overall improvement of emissions inventories, it does have certain limitations as discussed above. This Chapter is not designed a "cookbook" on how to use PAMS data; rather, its intent is to illustrate some of the

effective uses of PAMS data for inventory evaluation.

3.2.1 Potential Inventory Problems

Potential problems that can be identified (and potentially resolved) through the use of PAMS data are of two general types: emissions factor/model representativeness and proper application of the factors, including spatial/temporal resolution. These issues are summarized in Table 3-1.

3.2.2 Difficulties in Comparing Ambient Data and Emissions Estimates

The use of ambient measurements to corroborate emissions estimates are potentially useful for focusing attention on particular assumptions underlying the emissions inventory. There are many limitations associated with using ambient data to evaluate emissions inventories and care should be taken to not over-simplify the results of such comparisons. A discussion of some of the difficulties and issues follows:

Spatial Representativeness

One issue that has not been completely resolved is determining which emissions area to compare with the ambient measurement. Several gridding techniques have been proposed [Pace (1978) and Main]. These basically consist of developing finely gridded micro inventories for comparison with the ambient data, forming concentric cells or grids representing increasingly an larger area around the site. Figure 3-1 represents one such gridding system used to analyze Hartford emissions data (Main). Under transport conditions, it may be necessary to use emissions from a sector upwind of the monitor for the time just preceding the sample collection. The representativeness of the monitoring network also needs be considered. To fully evaluate an inventory, several monitoring sites may be needed depending on the complexity of the sources and the nature of the area. The mix of emissions sources, the meteorology and the location of the monitor all influence the analysis. a consistent (or inconsistent) analysis at one urban monitor may not mean that the emissions estimates in all parts of the area are good (or poor). To get a sense of the representativeness of the PAMS data for inventory evaluation, it is useful to perform correlation analyses of total VOC and VOC species to see how they compare with data from other sites.

Meteorological Issues

The most important influence to consider when comparing emissions estimates with ambient data is to account for the influence of meteorology. All non-point source emissions in an inventory are considered to occur at the surface and may be appropriate to evaluate with ambient data. However, elevated point sources may not be accurately represented at an emissions-oriented monitor near the ground due to meteorological influences. Also, the relationship

between emissions rates and ambient air concentrations is quite complex, depending on many meteorological parameters such as wind speed and direction, atmospheric stability, temperature inversion heights, and horizontal and vertical diffusion rates. Therefore, careful analysis of the meteorological data at the site needs to accompany the analysis of the ambient data in order to define the appropriate comparisons to make.

Chemical Reactivity

As stated previously, emissions inventories are based on emissions factors and activity level estimates. These emissions factors are available for the criteria pollutants (NO_x, VOC, CO, PM, SO_2). In reality, VOC emissions are a composite of multiple hydrocarbon compounds generated through some type of chemical process. These compounds react and form other compounds once they are released into the atmosphere. Some of these reactions occur very rapidly and others may take hours to occur. This is important to consider because a monitor is measuring a point in time and may not reflect the original mix of emitted species that is being transported into that area at that point in time due in part to these chemical reactions. Thus, along with the meteorological influences mentioned above, the reactivity of the emissions from sources near the monitor may lead to concentrations or ratios that are inconsistent with the original profile of the area's emitted species.

3.3 PAMS RESULTS

PAMS data have already been useful in analyses to evaluate the viability of the emissions inventory. However, the full potential of these data are just beginning to be realized. A recent report (Yarwood et al., 1994) evaluated 25 studies related to this topic and provided objective and critical overview of each. Appendix A tabulates some of the key analyses identified in that report. When researchers have access to the vast body of data being collected in PAMS, the full benefit of the PAMS network for evaluating emissions data can be realized.

PAMS data can be useful to the regulatory community in three ways. First, measured concentrations of certain indicator species can be compared with emissions estimates. NMOC/NO_x ratios, and comparisons of inventory estimates of key VOC species with ambient measurement of these species are two common types. Second, quantitative analyses, such as Chemical Mass Balance (CMB) can be used to compare emissions estimates for specific source categories. CMB is a sophisticated least squares statistical method for identifying the most likely source categories contributing to a given ambient sample, based on the relative amounts of each species present in the sample and the relative amounts of those same species present in the emissions of source categories. The CMB differs from tracer methods in that the indicator species need not be unique to a given source category. Third, PAMS data provide an opportunity to compare the PAQSM-estimated species concentrations with ambient measurements of these species at the time of day that the measurements were taken. The value of such comparison is

obvious, both for inventory evaluation and to verify the transformation algorithms in the model. Unfortunately, chemical mechanisms commonly used in photochemical models aggregate emissions species. Thus, our ability to compare predicted and observed precursor species is limited.

This section begins with a discussion of key tracer species that can be indicative of source presence and strength at the PAMS site. Then it presents examples of both qualitative and quantitative methods that can yield valuable information about the inventory. Since the PAMS network is relatively new, this section will supplement PAMS-based examples with examples from other databases that have similar data to that being collected by PAMS.

3.3.1 Examples of Indicator Species or Compounds (Tracers)

If a chemical species measured in PAMS is unique to a particular source, considerable information can be gleaned without employing sophisticated receptor modeling techniques. e.g., CMB. These chemical species, unique or nearly unique to one source or source type, are referred to as "indicator species, compounds or tracers of convenience".[1] Table 3-2 identifies some PAMS target compounds frequently used as tracers. The Chemical Mass Balance model (see Section 3.5 for examples) is a more powerful technique because it is not limited to tracers that are uniquely associated with only one source type.

Discussion of Specific Tracers

As noted in Table 3-2, various compounds are useful in evaluating the emissions of industrial manufacturing sources. Usually, the presence of these compounds may be determined by discussion with the emissions inventory specialist. Benzene, propene, toluene, and ethene have also been suggested as tracers for motor vehicle exhaust. Benzene was used extensively in various solvent intensive industrial processes until toxicity concerns and subsequent regulations greatly curtailed that type of usage. Benzene still falls short of being an ideal tracer for motor vehicle exhaust since it is also present in evaporative emissions and emissions from various combustion processes. The introduction of reformulated gasoline (RFG) in select urban areas in 1995 (as mandated by the Clean Air Act Amendments of 1990) will impact the chemical makeup of motor vehicle exhaust. RFG exhaust and evaporative emissions speciation profiles have already been developed and included in the 1993 SPECIATE database update, though future

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[1] Since very few emissions sources have their own distinct tracer, the scope of tracer of analysis is limited. a few methods for overcoming this handicap have been explored, including adjusting the tracer concentrations to account for other sources (Yarwood 1994). Another alternative utilized (to some limited degrees of success) is the intentional release of an "artificial" tracer into source emissions. Concentrations of this distinct artificial tracer found at a receptor, indicate a definite non-zero contribution of emissions from the source. This option has been limited to point sources since it would be impractical to inject tracer material at area sources. Even with point sources, though, large costly amounts of the tracer material are required to produce detectable concentrations at the receptor (Yarwood 1994).

refinement of the profiles is anticipated[2]. Carbon monoxide (CO), a criteria pollutant, is perhaps the best of all motor vehicle exhaust tracers and should be used to supplement other tracer information for mobile sources when available.

Butane has been noted as an excellent tracer for gasoline evaporative emissions. Butane accounts for approximately 35% of those type emissions. Isopentane, one of the largest NMOC components, is also regarded as a tracer for gasoline vapor. Almost all evaporative emissions are ascribed to vehicle-related sources (U.S.EPA, 1991a).

Isoprene, α-pinene and β-pinene are the only PAMS compounds predominantly associated with natural emissions and thus are the only available for use as tracers. All, however, are extremely reactive. Because all three compounds are very reactive, analysis relating ambient concentrations to source emissions often result in emissions underestimations. Unfortunately, there are no biogenic tracer alternatives.

Toluene has been mentioned as a tracer for motor vehicle exhaust. It, like other exhaust components, is generally present in characteristic ratios. Excess beyond this characteristic portion, can be used as a tracer of graphic arts and surface coating processes. Both of these types of operations commonly use solvent-based paints or inks. Propane can be used as an area-source indicator (liquefied petroleum gas use) or a point-source indicator (oil/gas production and petroleum refineries). Moderate to high concentrations of ethane can indicate natural gas use or leakage but, as noted before, measurement difficulties are commonly encountered. Isobutane has been suggested as a tracer for consumer product emissions; most aerosol products now utilize isobutane as a propellant since chlorofluorocarbons were banned (Stoeckenius et al.).

Indicator species afford data analysts an opportunity to characterize source types from ambient concentrations with minimum inputs. Although many PAMS target species are emitted from multiple sources, some are typical to only one or two, like those in Table 3-2. When using tracers to ascertain relative source emissions, one must be careful to consider the ramifications of reactivity. Reactions breaking down tracer compounds can result in incorrect estimations of the source's impact. Interpretation of tracer data is straightforward if the compounds are unique and inert. As mentioned above, complex software models such as CMB can be used if the tracer is not unique or if multiple tracers are available for several sources.

Using Tracer Data

To be an effective tracer, a compound should be relatively inert. Otherwise, photochemical reactions breaking the compound down will result in altered (usually reduced, but possibly increased) ambient concentrations of the compound thus precipitating a mis-estimation of

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[2] U.S. EPA. "SPECIATE database." URL: http://134.67.104.12/html/chief/spec-dn.htm. October 29,1996.

the source emissions impact. Unfortunately, many PAMS target compounds are extremely reactive. Thus, one option to utilize these reactive species as tracers is to use ambient concentrations from hours when emissions are generally high and photochemical reactivity is relatively low. The 6-9 a.m. time frame is frequently mentioned for mobile related analysis. A second option is to consider only tracers which are relatively unreactive (i.e., lifetime greater than eight hours).

Ambient air samples containing inert tracers can be used to estimate the concentration contribution of all emissions (or an emission category total such as TNMOC) from the tracer source. To compute the contribution of the total emissions P from source j, simply divide the observed concentration of the tracer t by R, the relative proportion of the tracer component found in the emissions at the source: $P_j = t_j / R_j$. To find the concentration associated with a specific pollutant (p), substitute r, the relative proportion of the tracer to the specific pollutant (at the source) for R thus giving: $p_j = t_j / r_j$. If the indicator species is not truly unique, the preceding formulas can be used to compute upper limits of the emissions impact. Likewise, if a tracer is somewhat reactive, the formulae can give a lower limit to the emissions impact.

For example, a local gasoline emissions profile shows that butane accounts for 35% (weight percent) of total non-methane hydrocarbon emissions (NMHC). An ambient monitor recorded average butane levels of 3 $\mu g/m^3$ (converted from ppbC). Hence, $R = .35$ and $t = 3$. We can therefore estimate the total NMHC associated with gasoline evaporative emissions (P) to be about 8.6 μg/m3 ($P = 3 / .35$). Since butane is also present in vehicle exhaust emissions, the computed figure should be considered an upper bound. If the gas profile also showed that cyclopentane (another PAMS target compound) accounted for .5 weight percent of NMHC, we know that the relative proportion of the butane tracer to it (r) is 7 (35 / .5) and we can apportion .4 $\mu g/m^3$ of cyclopentane to that particular source (p= 3 / 7). The computed $\mu g/m^3$ values can be converted to ppbC using species-specific conversion factors.

3.3.2 Examples Using NMOC/NO_x, Directional and Time Series Analyses.

Ratio information is often of great use for making qualitative judgments about whether a source category or individual source is missing from the inventory, misplaced or otherwise grossly mischaracterized. The use of ratios or single species which serve as tracer compounds for a source category is enhanced when combined with several of the other screening tools described in this Section. This Section also describes time series analyses and the use of wind direction information to evaluate the direction associated with high concentrations of speciated data.

NMOC/NO_x Ratios and Ratios of Other Species

As mentioned previously, problems associated with species reactivity must be addressed before the ratio approach can be used effectively. One way is to confine the analysis to periods of

the day in which atmospheric chemistry is minimal. This is generally at nighttime or shortly after sunrise (e.g., 6-9 am). During such periods, one must take care to account for the lack of vertical mixing in the atmosphere (e.g., by excluding all elevated sources from the inventory) when comparing emission-derived and measured ambient ratios for a diverse set of sources since the surface level monitoring site is unlikely to see any contribution from these sources at this time of day. In general, excluding elevated point sources in calculating the emissions-derived NMOC/NO_x ratio increases the calculated ratio because elevated point sources are far more prevalent for NO_x emissions than for VOC. The second approach for discounting effects of reactivity is to consider only ratios of pollutants which are relatively unreactive [see Altshuller, Lewis or Carter for further information on reactivity].

Use of ratio data as a possible means for corroborating inventory estimates is illustrated in Figures 3-2 and 3-3. Figure 3-2 plots 6-9 am NMOC/NO_x ratios measured at two suburban New Jersey sites during summer 1993 (NESCAUM). After excluding certain sources from consideration (as described above) the emission-derived ratio can be compared to the range of observed ratios to check for possible gross errors in the estimates. If a plot like Figure 3-2 is comprised of data from more than one site, the data can be scrutinized to see whether there are any apparent systematic differences in the ratios observed at different sites. For example, in Figure 3-2, ratios at the Plainfield site appear to be somewhat higher than those measured at Newark. This interpretation can be compared with the emission-derived estimates. If not similar, other analyses such as looking at the ratio of a reactive to less reactive species could be explored to see whether the difference in the measured NMOC/NO_x ratios is attributable to greater transport at one of the sites or some alternative explanation. If the findings are not consistent with alternate explanations, this may imply a potential problem with the inventory near one or both of the sites.

Figure 3-3 illustrates how observed ratios among species might be used as a means of identifying presence of emissions from certain source categories (Chameides et al.). For example, in the figure there is a high correlation observed between trans-2-pentene and cis-2-butene. This implies a common source for the two species is impacting the monitoring site. One can check the inventory of nearby sources to see whether the emissions estimates are consistent with these observations.

Directional Associations

As the name implies, this screening analysis entails subdividing air quality observations into bins which correspond with different measured wind directions. Often eight principal wind directions are considered. Distributions of various air quality indicators can then be constructed for each of the wind directions. Comparing differences in the air quality distributions among wind directions can be readily done by graphically displaying the data in a "pollution rose". Figure 3-4 illustrates the procedure using ozone as the air quality indicator (Incecik et al., 1995). The

procedure is amenable to using a variety of air quality indicators, including individual VOC species or ratios of species.

Use of directional associations between pollutant species or ratios enables those reviewing the inventory to better focus on portions of the inventory which may need further verification and refinement. For example, for a given wind direction one can compare observed distributions of species or ratios of species with emissions estimates which are upwind from the monitoring site. Presence or dominance of species which appear to be unaccounted for by the upwind emissions estimates will help direct the analyst's attention to geographical locations where the inventory may need improvements. In a similar vein, presence of pollutant ratios which seem inconsistent with proportions of species in upwind emissions estimates would also help direct a review of the assumptions, methodology and data base underlying the emissions estimates.

Time Series Analyses

Time series analyses of VOC, its species, NO, NO_2, NO_x and ratios of VOC to NO_x are potentially useful for corroborating whether assumptions in emissions models about diurnal emissions patterns are supportable. In addition, time series plots can serve as useful guides in helping the analyst decide which portion of the inventory to compare with ambient concentrations at different times of day. For example, if a time series plot indicated that a source category impacted a monitor at midday, but not at 6-9 am, this would serve as additional rationale for excluding that source from the inventory in the 6-9 am comparison. Third, time series analyses can, when used with other information (described later), help the analyst corroborate whether assumptions in the emissions model about sensitivity of emissions to meteorological conditions are consistent with observations.

Figure 3-5 shows PAMS-based time series plots on weekdays and weekends for three VOC species (Stoekenius et al.). Recall that acetylene is a tracer for automotive exhaust. One can see from comparing weekday vs. weekend time series for acetylene that the two time series differ. This is consistent with a possible need to use differing diurnal activity levels for automotive sources on weekends vs. weekdays. Figure 3-6 is a time series plot of isoprene data measured at a suburban site in Houston (Stoekenius et al.). Note the distinctly different diurnal pattern for isoprene vs. the ones for other species shown in Figures 3-5 and 3-6. The observed pattern is consistent with our understanding of how the emissions factor for isoprene varies as a function of temperature. The pattern in Figure 3-6 also shows us that it would be unwise to include biogenic emissions (for which isoprene is a tracer) in the previously described comparisons of 6-9 am emission derived NMOC/NOx ratios with monitored ratios.

There are many reasons why it may be useful to perform previously described analyses on days with high ozone and contrast the results with other days. With respect to evaluating emissions, this may provide us with insight about whether there is something different about

emissions on days with high ozone vs. other days. Since our concern with emissions often focuses on high ozone days (e.g., for reasonable further progress calculations and for modeled attainment demonstrations), priorities may be greater to resolve discrepancies between emissions-derived estimates and monitored data on these days.

The graph shown in Figure 3-7 contrasts ozone observed on an episode day vs. mean observations for that month (Bigler-Engler et al.). Similar graphs in which other PAMS species are plotted could be used to identify possible discrepancies in average emissions estimates (often used in emissions models) vs. what appears to be consistent with observations on a limited number of episode days. Figure 3-8 plots an observed relationship between midday isoprene levels and temperatures, suggesting that inclusion of a strong temperature dependency in the emissions factor for biogenic emissions of that species is likely to be valid (Fehsenfeld et al.). Similar comparisons could be undertaken for tracers of other, anthropogenic sources.

3.4 EXAMPLE OF INVENTORY EVALUATION FOR LAKE MICHIGAN INVENTORY

Data collected during the 1991 Lake Michigan Ozone Study was the basis for comparison of the emissions inventory and ambient concentration ratios of NMOC/NO_x and NMOC/CO for Chicago, Gary, and Milwaukee (Korc et al., 1993). Comparisons of 7-9 a.m. ratios for two ozone episodes (June 25-28 and July 16-18) showed that the ambient ratios were generally higher than the inventory ratios. The relative individual NMOC species compositions of the ambient and emissions inventory data were also examined. Table 3-3 shows the overall average ambient and emissions inventory relative compositions for individual species and species groups for the three cities during the two ozone episodes. The ambient relative compositions of the major groups of organic compounds are very similar at all three sites. The paraffin content in the ambient data is about 48 percent; the olefin content is about 10 percent; the aromatic content is about 22 percent; and the carbonyl content is about 4 percent.. The relative composition of the inventory is very similar at all three sites. However, the paraffin composition of the emissions inventory is about 5 to 10 percent lower than the corresponding ambient data at all three sites. Olefins are slightly higher than the ambient data at Gary and Milwaukee and are consistent with the ambient data at Chicago. The aromatic composition is significantly higher than ambient composition at all three sites and ranges from 27 percent at Milwaukee to 33 percent at Chicago. The carbonyl compound composition is significantly lower than the ambient data at all three locations; and the other species group composition is slightly higher than the ambient data at Chicago and Gary, and is consistent with the data at Milwaukee.

In response to this study, the Lake Michigan Air Directors Consortium (LADCO) reevaluated the emissions inventory and made several significant changes to the point, area, and mobile source figures. Speciation profiles and background assumptions were also revised.

LADCO then compared the revised emissions estimates to the ambient data and found improved agreement. Tables 3-4 and 3-5 show the computed ambient and emissions NMOC/NO_x ratios both before and after the LADCO emissions inventory revision (Korc et al., 1993).

3.5 EXAMPLES USING MULTIVARIATE ANALYSES AND CHEMICAL MASS BALANCE (CMB)

Thus far, the focus of the discussion has been on various types of screening analyses for PAMS data which could serve as qualitative indicators for investigating certain assumptions underlying emissions estimates. This Section focuses on a series of analyses which has as its end product more quantitative estimates of the contributions that various source categories make to observed ambient measurements of ozone precursors. Although the end product of these analyses is quantitative, it is obtained through use of much subjective judgment. Therefore, we do not recommend using the outcome of these analyses to change emissions estimates unless the methodology for making the emissions estimates is also reexamined and the uncertainties in these procedures are consistent with the changes implied by the analyses of the ambient data. In short, although the results obtained with the techniques summarized in this section are quantitative, they should be used qualitatively to improve emissions estimates.

The Chemical Mass Balance (CMB) model (U.S. EPA, 1990a) can be used to provide quantitative source category contribution estimates to monitored data. This procedure uses distinct chemical species profiles for different source categories and then identifies the relative combination of contributions from each of the selected source categories which best explains the combination of species observed at the monitoring site. One key prerequisite for a CMB analysis is choice of the source species profiles. There are two approaches used for choosing source chemical profiles. The first is to select source categories and their corresponding species profiles from available local measurements of a source's emissions or to select profiles from a "library" of source chemical profiles. The latter approach is the simpler of the two. It may be preferred if one already has a good idea of the source categories which are likely to make important contributions and has confidence in the profiles which are used. The EPA's Air Emissions Species Manual (U.S. EPA, 1990b) documents default species profiles for many sources of VOC. When available, species profiles measured in recent local field studies should be used instead.

Although species profiles for many types of sources are included in the Air Emissions Species Manual, some of the data may be outdated or not applicable to the area in which we are seeking to corroborate emissions estimates. Further, one could argue that using default species profiles for the CMB which are the same as those underlying the inventory is not a completely rigorous corroboration of the inventory. Thus, the second approach for choosing chemical source profiles for use in the CMB is to try to use the ambient observations themselves to derive

source category profiles. Methods to implement this second approach can be broadly characterized as "multivariate analyses".

In Sections 3.5.1 and 3.5.2, we illustrate how PAMS data are useful in applying the chemical mass balance model and corroborating emissions estimates using examples in Atlanta and Southern California. [Additional information on the CMB technique may be found in U.S. EPA, 1987 and U.S. EPA, 1990a].

3.5.1 Example of Inventory Evaluation in Atlanta

Atlanta has been the focus of many receptor modeling studies in the past decade. CMB has made possible a new approach to comparing emissions inventories with ambient data using CMB calculations (Conner). This new approach make use of ranges of source estimates obtained from the ambient data, which can be used to deal with some of the inherent difficulties of comparing inventories with ambient data. Table 3-6 compares the CMB output with emissions inventory data obtained from the Georgia Department of Natural Resources. The comparison is qualified "by the fact that the CMB results reflect mostly daytime (hours 8-18) conditions, while the inventory represents 24-hour average emissions."

As seen in Table 3-6, the biogenic mass was accounted for using several different methods. The biogenic portion of the CMB estimate was set equal to the biogenic portion of the emissions inventory; then it was set equal to the isoprene percent; then set equal to the 'unexplained' percent; and then also set equal to zero. The inventory highway mobile source estimate tends to be smaller than the minimum ambient data-derived highway mobile source estimate, and the inventory area plus point source estimate tends to be larger than the maximum ambient data-derived estimate for the data set examined." Such a comparison is useful in evaluating the inventory, but in this case, only limited confirmation of the inventory can be gleaned from the CMB-based analysis; other analyses would be needed to support further evaluation of the inventory.

3.5.2 Example of Inventory Evaluation in Southern California

The Southern California Air Quality Study (SCAQS) was conducted in summer and fall 1987 to gain a better understanding of the causes of excess pollution concentrations in California's South Coast Air Basin (SoCAB). The SCAQS data was used to validate the use of CMB for NHMC source apportionment (Fujita et al.). One of the goals of their study was to reconcile source contribution estimates from the CMB with existing emissions inventory estimates. Table 3-7 shows the mean source contribution estimates for all sites combined by season and sampling period for the three motor vehicle source categories versus all other source categories in comparison to the corresponding SCAQS basin wide day-specific emissions

inventory data for August 27, 1987 and December 10, 1987 (Fujita et al.).

Fujita et al. noted that "the larger calculated contributions of vehicle exhaust and evaporative emissions were consistent with recent studies that suggest that the motor vehicle hydrocarbon emissions inventories for motor vehicles have been substantially underestimated".

Fujita et al. concluded from their evaluation that "the CMB application and validation protocol developed for PM-10 source apportionment is applicable to the validation of CMB for NMHC source apportionment". They suggested, however, that additional source profiles be designed specifically for receptor modeling. They noted that "the attribution of source contributions among the motor vehicle source categories was found to be highly sensitive to the choice of fitting species and to the relative abundance of combustion byproducts in the exhaust profile, which vary with emissions control technology, level of vehicle maintenance, and operating mode." They recommended the creation of site-specific vehicle exhaust profiles.

3.6 CASE STUDY - EXAMPLE OF INVENTORY EVALUATION IN HOUSTON, TEXAS

This case study highlights a comprehensive review of the emissions inventory in Houston TX. This example illustrates how several different techniques can be combined to build a thorough evaluation of an inventory for ozone precursors. The techniques include: ambient and emissions-derived NMOC/NOx; relative compositions of hydrocarbon groups using both ambient and emissions derived data; and CMB analysis.

NMHC/NO_x ratios were compared for two Houston sites in summer 1993 (Korc et al., 1995). Emissions inventory data were delineated to 5 different grid areas surrounding the site using two different allocation approaches. (One approach allocated emissions inventory data from upwind grid cells with a weighting function of 1; the other allocated emissions inventory data from upwind grid cells with a weighting function defined as the inverse of the distance between the ambient monitoring site and the centroid of each grid cell.) As seen in Tables 3-8 and 3-9, the ambient ratios were always significantly higher than the corresponding emissions ratios (Korc et al., 1995). At Galleria, the ambient ratios were about 2 to 6 times the emissions ratios; at Clinton, the ambient ratios were approximately 2.5 to 4 times the emissions ratios. Galleria represents a major urban source dominated by mobile emissions and Clinton represents a major industrial location.

In the report, Korc also made comparisons between the relative ambient and emissions compositions. Figure 3-9 shows comparisons of the August 19 day-specific, August 17-20 episode specific average, and August and September weekdays median 0600 CST ambient- and August 19 emission-derived relative composition of paraffins, olefins, aromatic compounds and

"other" species groups at Clinton (Korc et al.,, 1995). Note that the ambient-derived and emissions inventory relative proportions of paraffins and olefins are rather comparable, the emissions inventory estimates for aromatics is significantly higher than the ambient-derived estimates, and the emissions inventory "other" species estimate is much lower than ambient-derived figures. a similar chart comparing the relative individual species compositions (top 35 species) for the same four types of estimates is shown for Galleria in Figure 3-10 (Korc et al.,, 1995).

The data in Figure 3-10 show that the emissions inventory toluene and n-butane moleC percents of NMHC were significantly higher in the emissions inventory estimate than the ambient derived percents and the relative isopentane, ethane, and propane moleC percents were significantly lower in the emissions inventory (Korc et al.,, 1995). Evaluating the same set of ambient data, Lu and Fujita (1995) compared hourly CMB and emissions inventory source contribution estimates (as percents of NMHC) for the three source categories: mobile, biogenic, and miscellaneous. As seen in Figures 3-11 and 3-12, the mobile source emissions inventory diurnal estimates were always lower than the CMB derived estimates at Clinton; at the Galleria site the two sets of estimates were closer and the emissions inventory estimates exceeded the CMB figures for 10 of the 24 hours. The biogenic emissions inventory estimates were always higher than the CMB figures at both locations. The miscellaneous source emissions inventory diurnal estimates for Clinton exceeded the CMB estimates except for hours 2-8 p.m. when the two estimates were either very close or the CMB was slightly higher. At Galleria the situation was almost reversed, with the CMB estimates exceeding the emissions inventory data all hours but 8-11 a.m.

Based on their review, Sonoma Technologies, Inc. concluded that significant discrepancies between the ambient data and the emissions inventory still exist. Thus, they made the following recommendations to improve the inventory:

- NMHC and NO_x emissions estimates should be reviewed. Preliminary results indicate that the ambient-derived NMHC/NO_x ratios are significantly higher than the emissions-derived NMHC/NO_x ratios. These discrepancies suggest that the absolute amounts of NMHC and/or NO_x emissions were not estimated accurately. Thus, they recommended that an investigation of the possible biases in the NMHC and NO_x emissions inventories be performed. a series of bottom-up evaluations of the major components of the inventory are needed. These should be followed by further top-down evaluations.

- Speciation profiles should be reviewed. The discrepancies between ambient and emissions NMHC compositions and the significant overestimation of toluene in the inventory suggest that some of the assigned organic compound source composition libraries were not representative of some source category in the region, improper speciation profiles

were assigned, and/or the absolute amounts of NMHC emissions were not estimated accurately. Further, the significant overestimation of n-butane and toluene and the significant underestimation of isopentane in the emissions inventory suggest that the speciation profiles used for mobile sources may not reflect current gasoline reformulations and should be reviewed.

- Diurnal profiles should be reviewed. In particular, the significant overestimation of n-butane in the emissions inventory early in the morning suggests that the diurnal profiles used for motor vehicle evaporative emissions may not be representative and should be reviewed.

- Biogenic emissions estimates should be reviewed. In particular, the significant overestimation of isoprene in the emissions inventory early in the morning suggest that the biomass data, land use data, and/or the algorithm used to estimate isoprene emissions may not be accurate and should be reviewed.

3.7 CONCLUSIONS

PAMS data can provide useful information to evaluate emissions inventories. It can provide a general idea of the relative importance of certain compounds in the inventory that can suggest the need for improved speciation of the data. Also, it can provide information related to the spatial or temporal resolution of the inventory. It has been used to identify missing components of the inventory and gross over/under calculations of the inventory based on emissions factors.

Several techniques and analytical tools are available to evaluate the inventory. Simple techniques such as time series analysis, diurnal patterns and pollution roses can be augmented by Chemical mass balance and other multivariate techniques. Use of multiple techniques can provide more useful information than relying on one or two methods. Also, PAMS data provides a unique opportunity to compare the model-estimated species concentrations with ambient measurements of these species at the time of day that the measurements were taken. However, photochemical models have not yet progressed to the point where the results for individual species are tracked along with the transformation chemistry.

Several areas of the US have used PAMS data to evaluate the emissions inventory. Examples from the Texas Gulf Coast, Atlanta, Houston, Atlanta, Los Angeles and the Great Lakes have been shown. Additional analyses have been undertaken in Hartford and other cities. The real value of such analyses is just now being realized as more PAMS networks develop validated data sets.

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Emission Inventory Areas Surrounding a Site

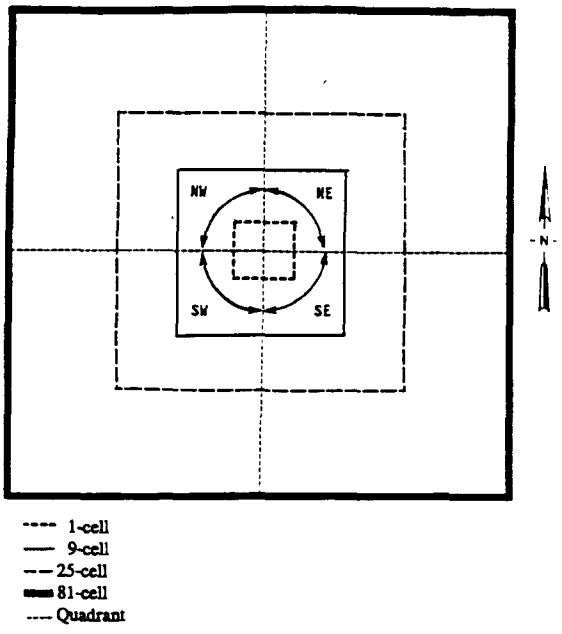


Figure 3-1. Schematic illustration of 1-cell, 9-cell, 25-cell, and 81-cell areas surrounding a site, and the upwind quadrants of the 81-cell area.

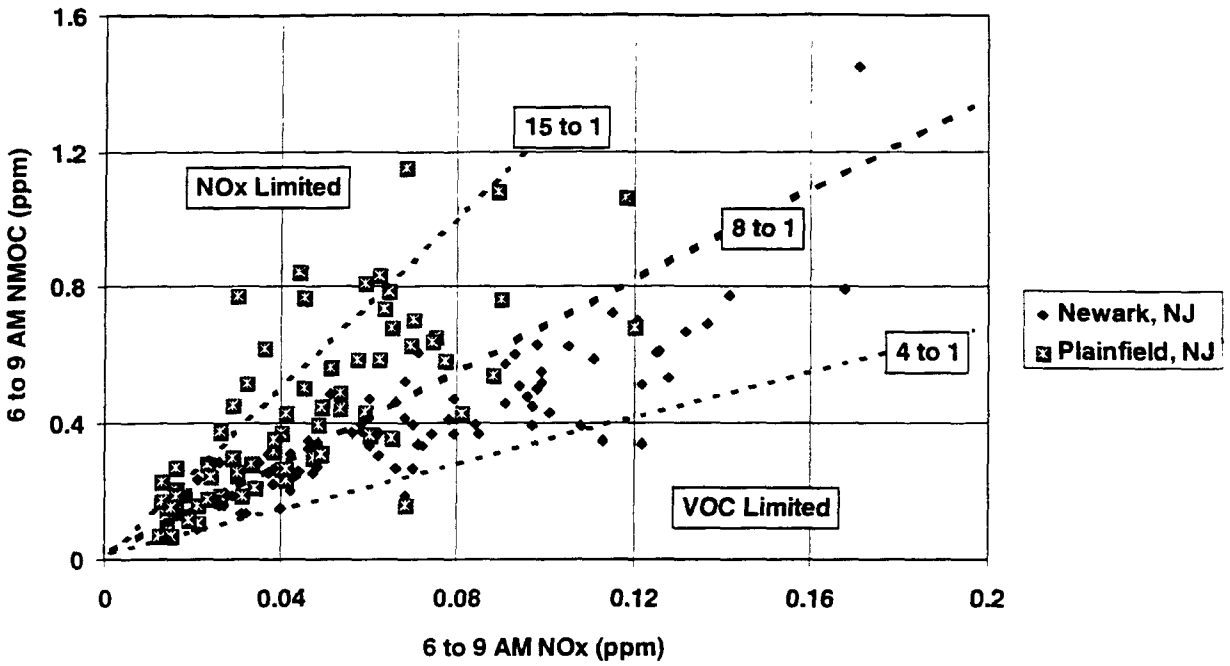


Figure 3-2. Morning NMOC:NOx Ratios at Urban and Suburban New Jersey Sites, Summer, '93

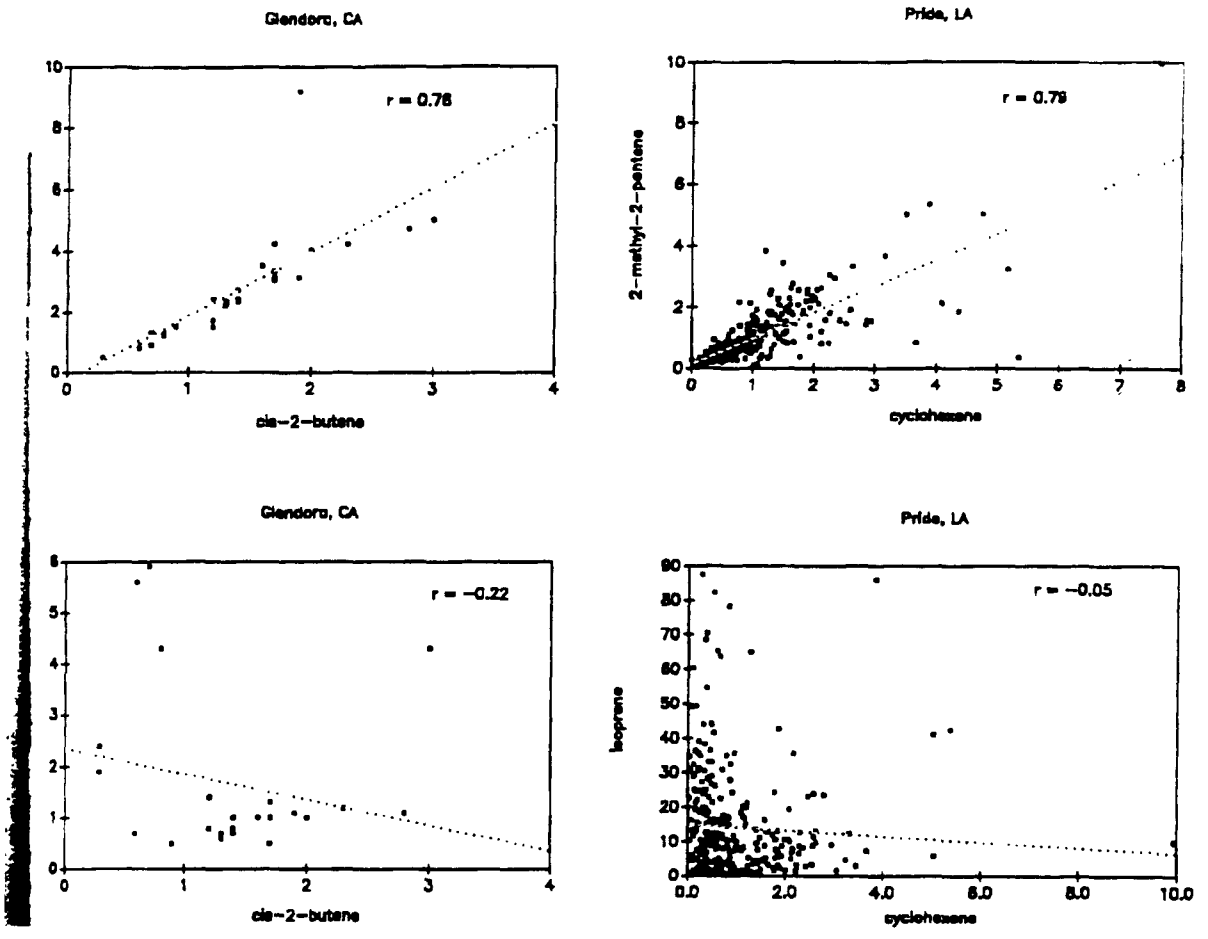


Figure 3-3. Scatterplots of the concentrations (ppbC) of trans-2-pentene, cis-2-butene, cyclohexene, 2-methyl-2-pentene and isoprene as observed in Pride, Louisiana and Glendora, California

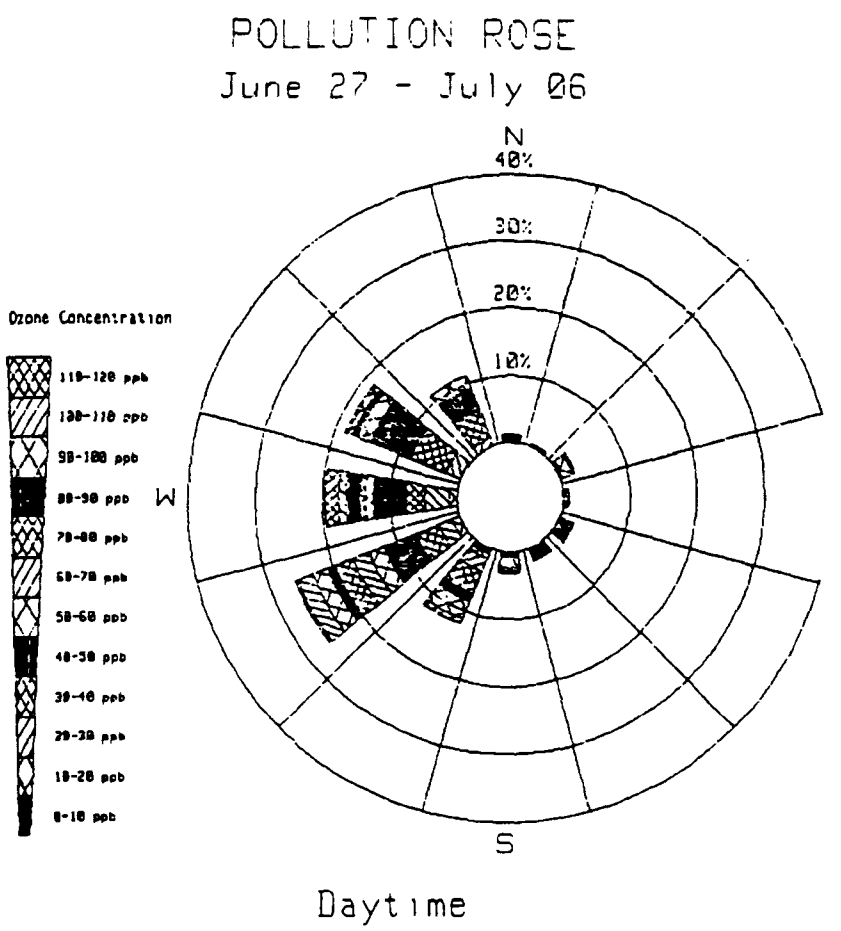


Figure 3-4. Daytime pollution (ozone) roses in a summer period.

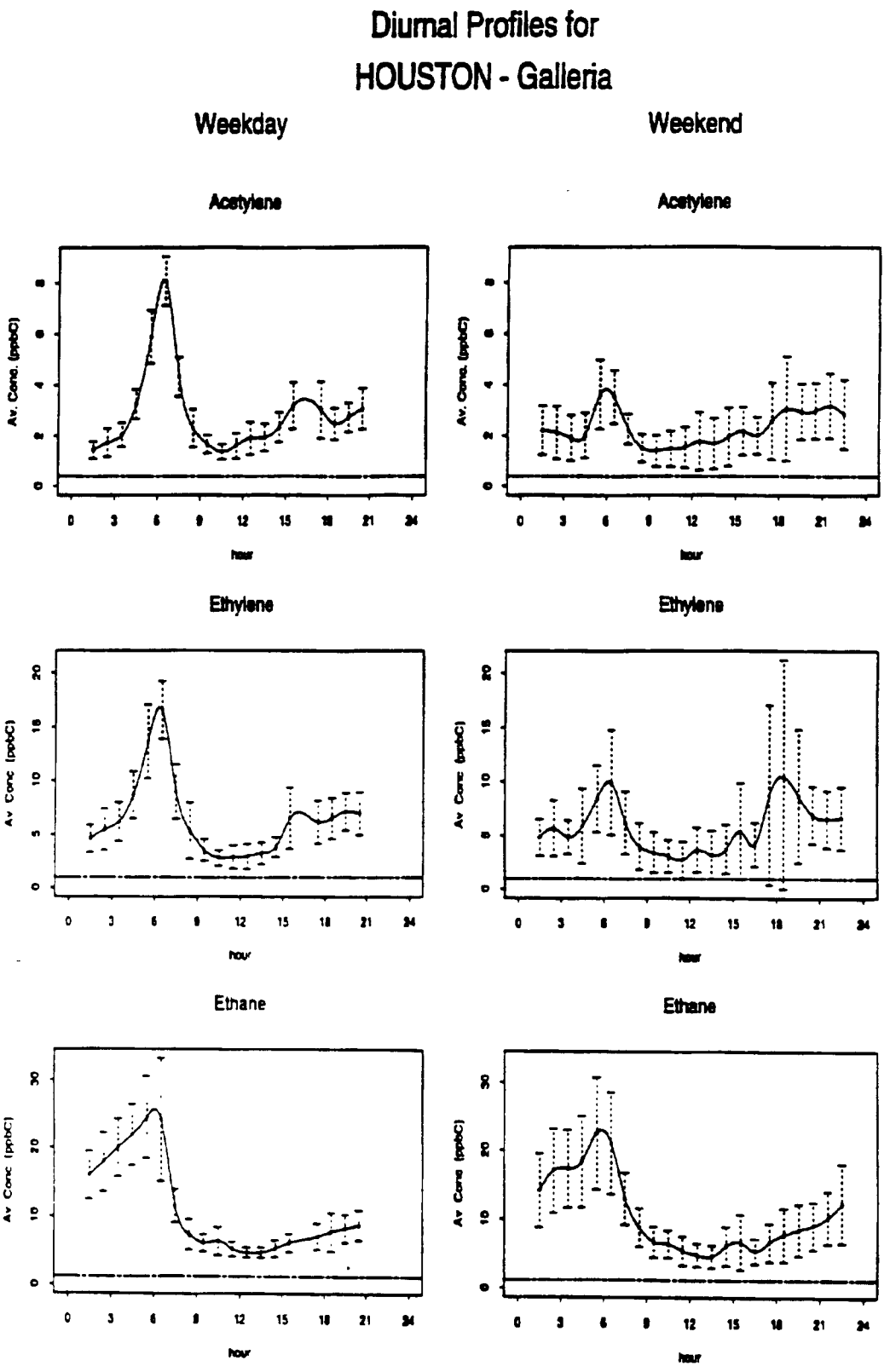

Diurnal Profiles for
HOUSTON - Galleria
Weekday
Weekend
Acetylene
Acetylene
Ethylene
Ethylene
Ethane
Ethane
Av. Conc. (ppbC)
hour

Figure 3-5.

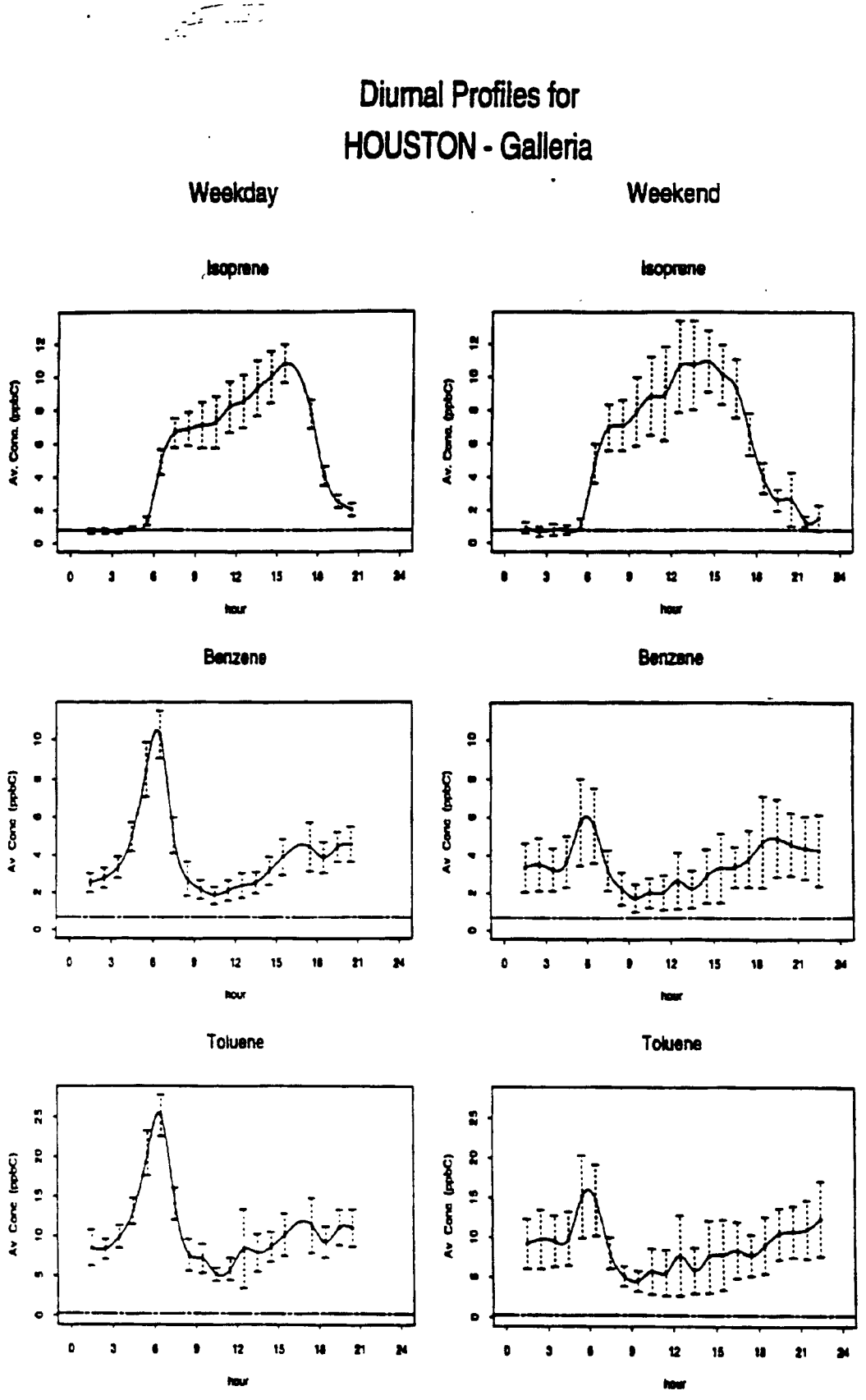

Diurnal Profiles for
HOUSTON - Galleria
Weekday
Weekend
Isoprene
Isoprene
Benzene
Benzene
Toluene
Toluene
Av. Conc. (ppbC)
hour

Figure 3-6.

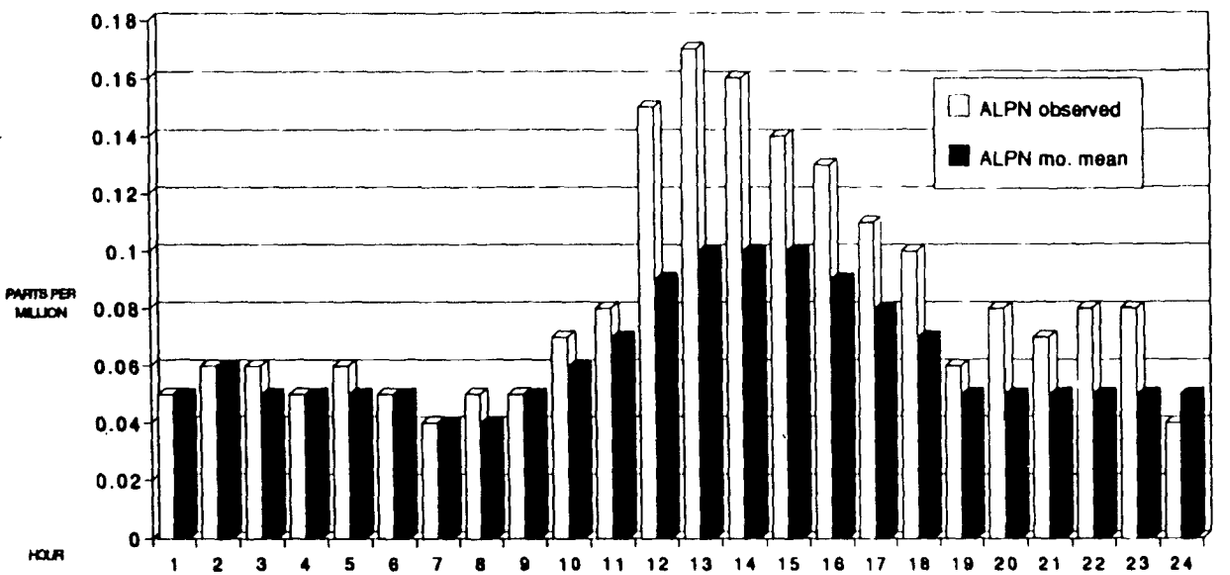


Figure 3-7. Hourly Ozone versus Mean, Alpine 9/26/89.

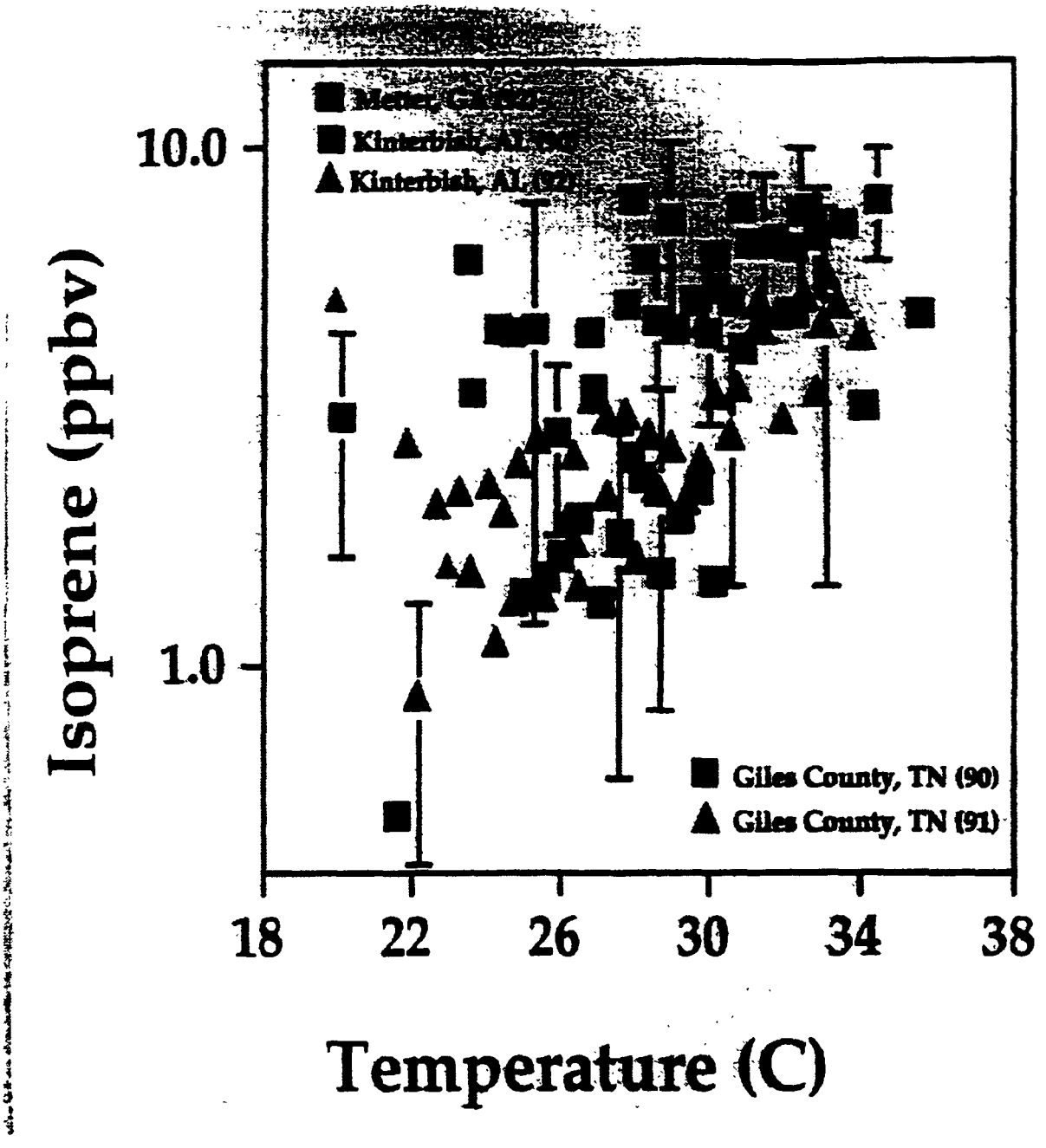


Figure 3-8. Plot of isoprene mixing ratio versus temperature taken from air concentration measurements during summer (June-August) during the daytime hours. In these plots the data for each measurement set was divided into twenty subsets, each containing 5% of the data points. The vertical bars indicate the standard deviation in the measurements for a few selected data subsets from these measurements. The measurements were made at Kinterbish, Alabama during the summers of 1990 (squares) and 1992 (triangles); at Giles County, Tennessee during the summers of 1990 (squares) and 1991 (triangles), and at Metter, Georgia in 1992 (squares).

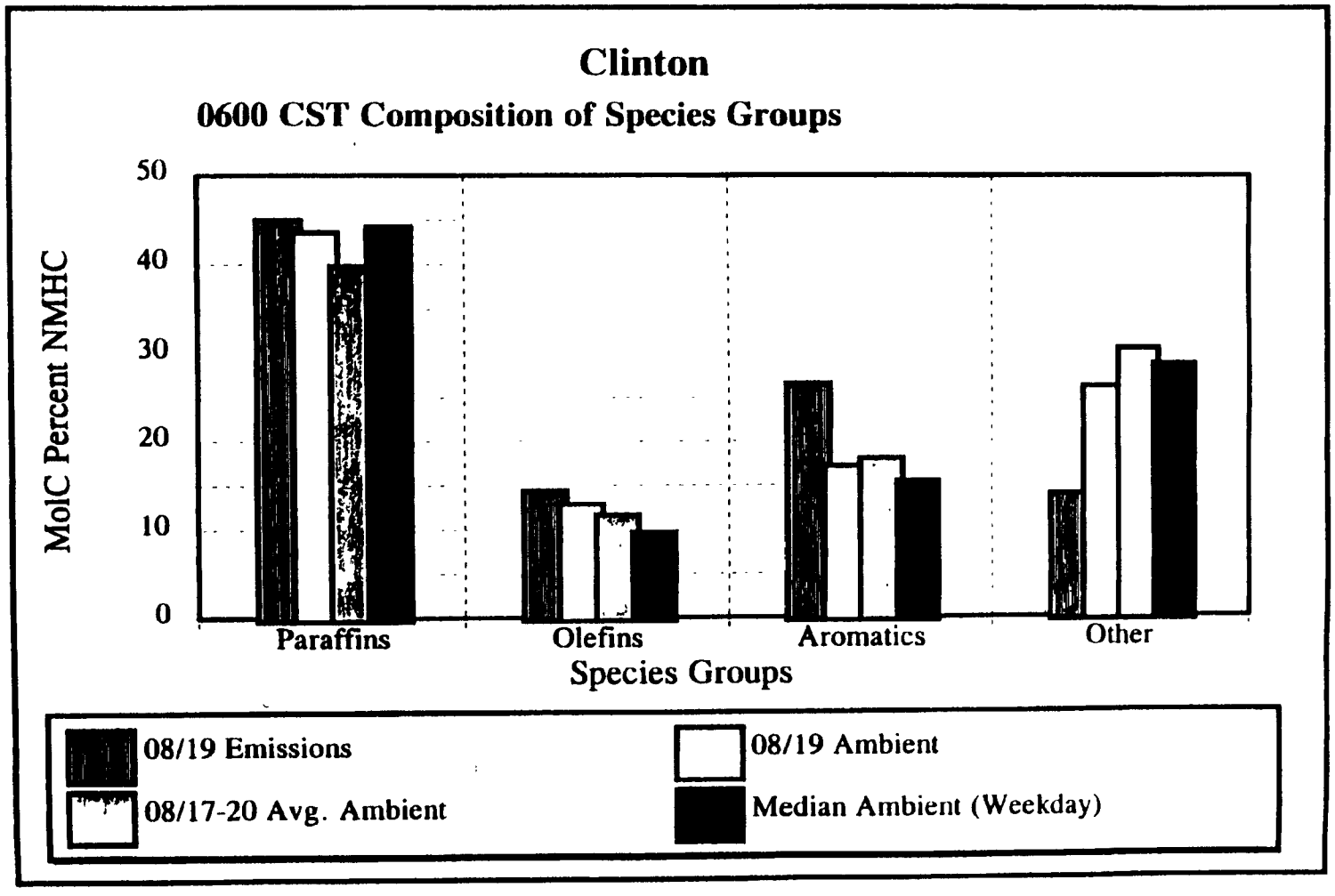


Figure 3-9. Houston (Clinton Site) - Comparisons of 0600 CST Ambient and Total Emissions-Derived Species Group Composition Estimates for the 81-Cell Area Surronding the Clinton Site, 1993

Figure 3-10.

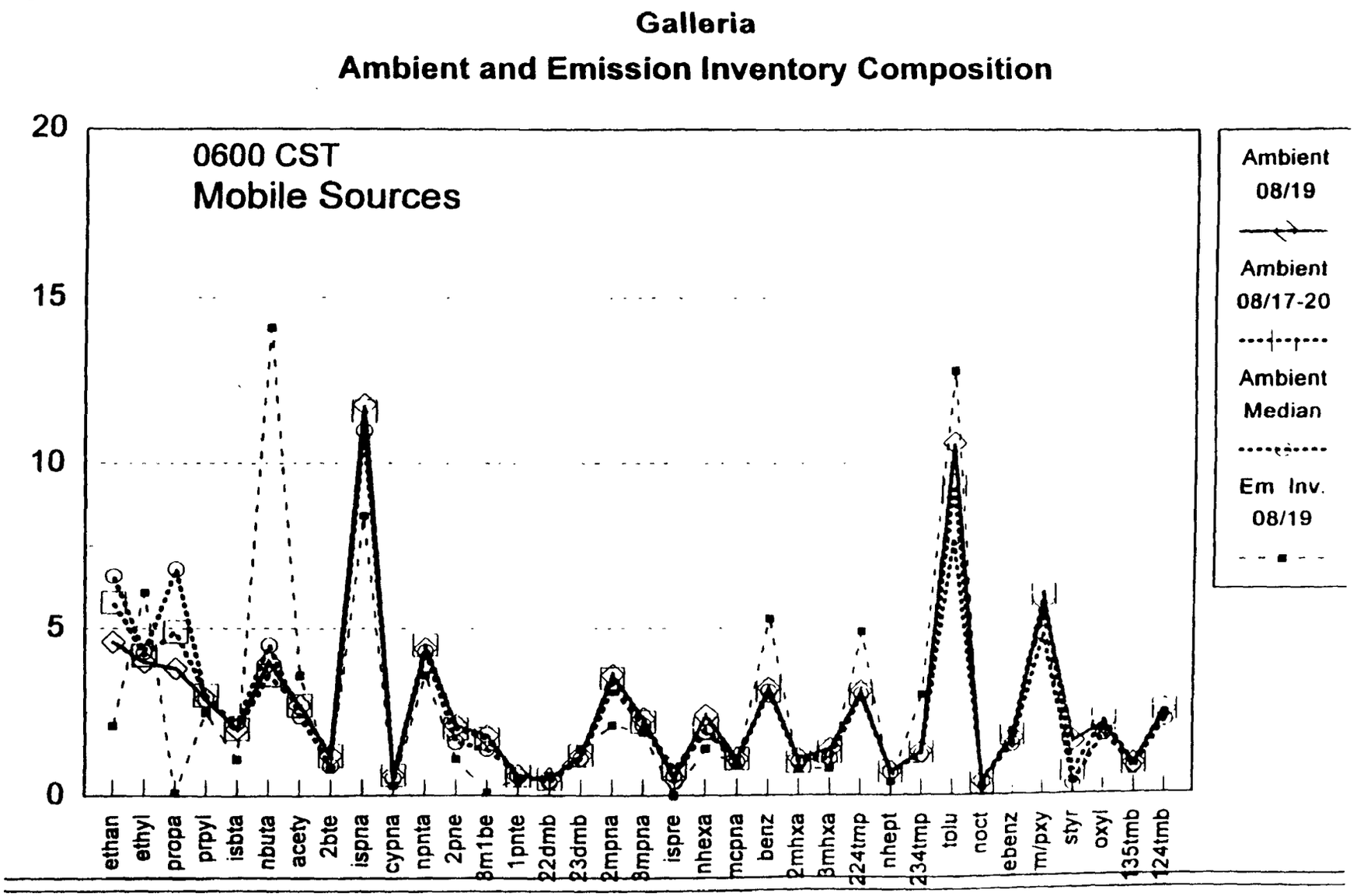
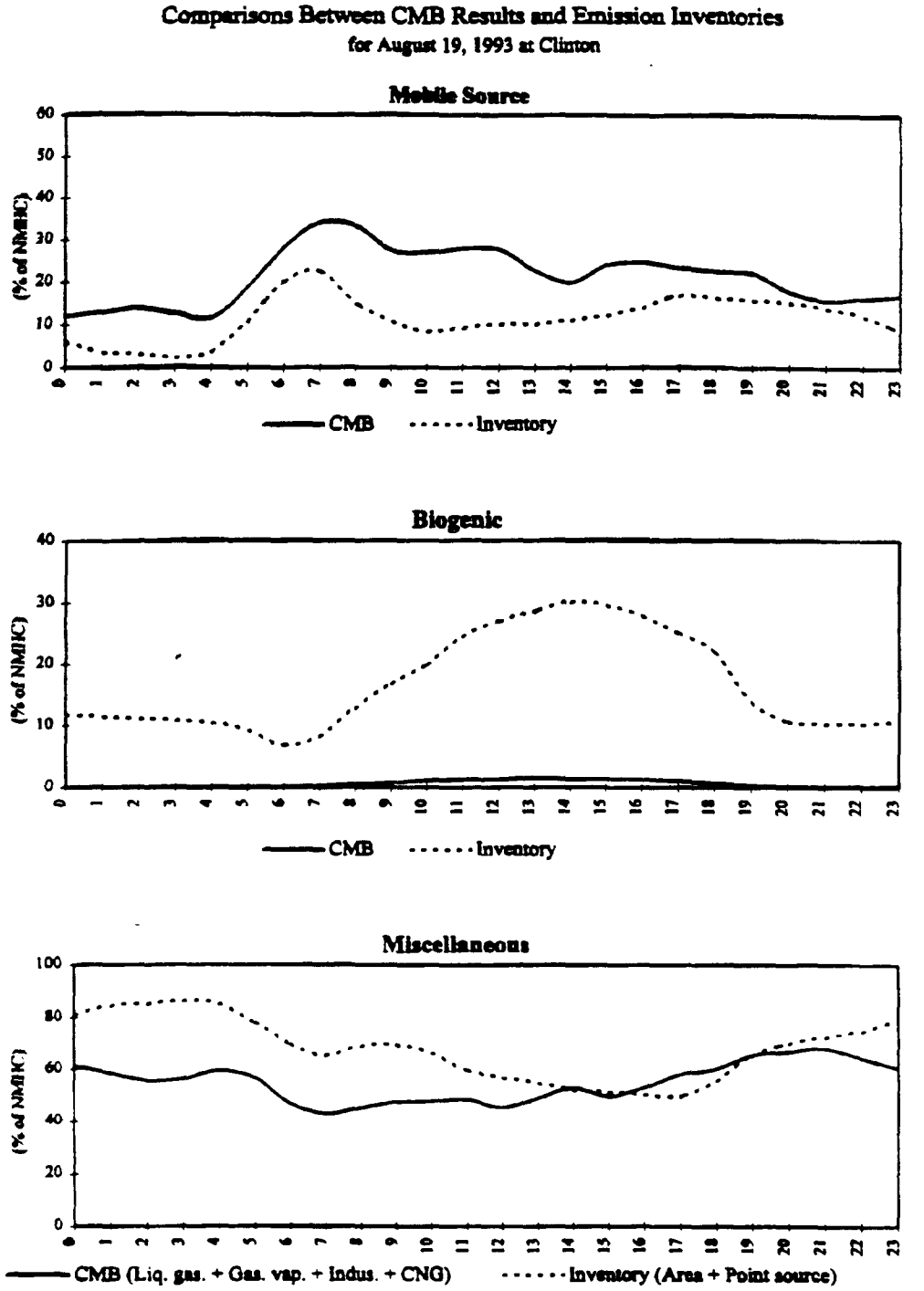
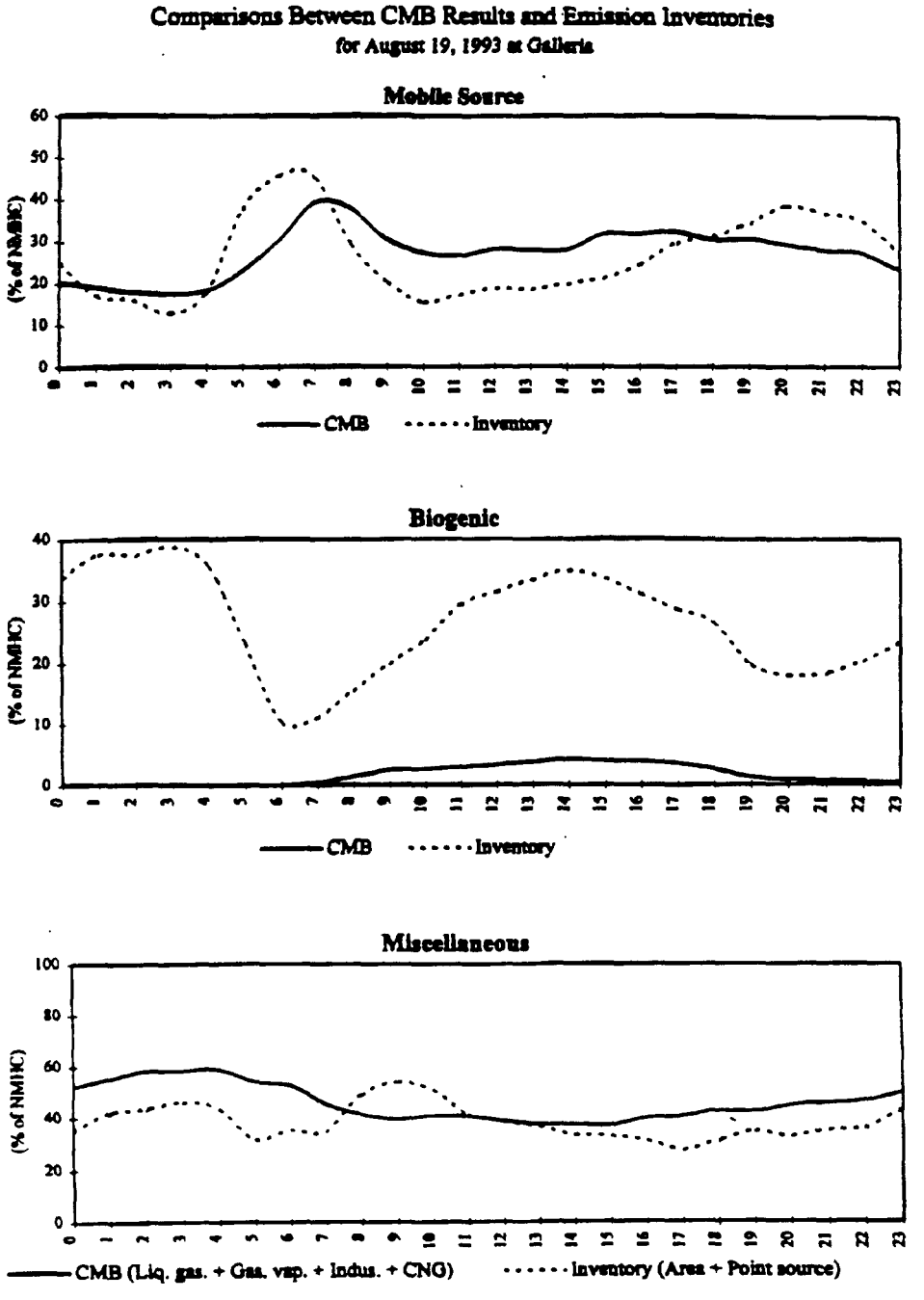

Galleria
Ambient and Emission Inventory Composition
0600 CST
Mobile Sources
20
15
10
5
0
Ambient 08/19
Ambient 08/17-20
Ambient Median
Em Inv. 08/19
ethan
ethyl
propa
prpyl
isbta
nbuta
acety
2bte
ispna
cypna
npnta
2pne
3m1be
1pnte
22dmb
23dmb
2mpna
3mpna
ispre
nhexa
mcpna
benz
2mhxa
3mhxa
224tmp
nhept
234tmp
tolu
noct
ebenz
m/pxy
styr
oxyl
135tmb
124tmb

Figure 3-11. Houston (Clinton Site) - Comparisons Between CMB Results and Emission Inventories, August 19, 1993



Source: Lu and Fujita, 1995

Figure 3-12. Houston (Galleria Site) - Comparisons Between CMB Results and Emission Inventories. August 19, 1993



Source: Lu and Fujita, 1995

Table 3-1. Emission Factor Representativeness and Application Issues

Problem	Discussion
Unrepresentative Factors and Models	There are over 9,000 processes defined in FIRE, the Factor Information and Retrieval System, but many processes are not represented for each and every pollutant. Thus, one might choose a factor for a "similar" process without knowing whether it will be entirely appropriate for the task at hand. Similarly, the factor may not be parametized all key process variables that could affect emissions, e.g., temperature, pressure, maintenance, emission control measures.
Control Efficiency	The design criteria of air pollution control equipment affect the resulting emissions. Design criteria include such items as the type of wet scrubber used, the pressure drop across a scrubber, the plate area of an electrostatic precipitator, and the alkali feed rate to an acid gas scrubber. Operation and maintenance of control devices can substantially effect emissions.
Within-source Variability	Short-term emissions from a single specific source often vary significantly with time (i.e., within-source variability) because of fluctuations in process operating conditions, control device operating conditions, raw materials, ambient conditions, and other such factors. Emission factors generally are developed to represent long-term average emissions, so testing is usually conducted at normal operating conditions.
Variability Between Sources	Average emissions differ significantly from source to source and, therefore, emission factors frequently may not provide adequate estimates of the average emissions for a specific source. The extent of between-source variability that exists, even among similar individual sources, can be large, depending on the specific process, control system, and pollutant.
Spatial Resolution	Often, the activity parameter data that must be input to use on emission factor or model is not readily available on a finely gridded scale. Most emissions models grid the county-level data based on an appropriate surrogate indicator such as population, land use, or digitized highway data. Obviously, the better the surrogate, the more accurate the gridded emissions will be that can be used for comparison to the ambient data. The acquisition of high-resolution surrogate data can be very difficult and extremely costly. Ambient measurements can help determine whether appropriate resolution has been attained.
Temporal Resolution	Photochemical models are often run for specific dates. However, emission factors are not intended to be representative of specific timeframes and are inherently less reliable under such demands. Thus, it is very important to evaluate date-specific emissions data with all available tools, including ambient data. Resolution of temporal issues is difficult because ambient measurements are generally collected on an hourly basis and most emission inventory estimates are defined on a daily or annual basis. Also, it is difficult to resolve emissions from batch processes with ambient data
Speciation Problems	A problem particular to VOC emission estimates is that the VOC emission must be speciated by a preprocessor before it is used in a photochemical model and errors can be made that offset the photochemistry calculations. Unfortunately, inventories only contain unreacted species, or Ozone precursors, and current photochemical models track groups of species that may be associated with more than one source. Thus, these comparisons can currently be made only for unreacted (or possibly for slowly reacting) species
Missing Sources	The importance of using ambient measurements to reveal missing sources or source categories became apparent as early as 1976 when the microscopic analysis of ambient particulate matter samples revealed much more soil-related particles than were accounted for by the emissions inventory. (Bradway and Pace, 1976)

Table 3-2. Commonly Used Tracers for Ozone Precursors (Stoeckenius et al., 1994 a)

Compound	Major Source	Comments
Numerous VOC's	Specific industrial processes	May be identified from emissions of various industrial facilities
α- and β-pinene	Biogenic emissions	Highly reactive, measurement difficulties, also present in consumer products such as air fresheners
Benzene	Motor vehicle exhausts	Also present in evaporative emissions and numerous combustion processes. Useful in developing upper bound estimate of motor vehicle exhaust
Butane	Gasoline evaporative emissions	Accounts for roughly 35% of motor vehicle evaporative emissions
Ethane	Natural gas use/leakage	Measurement difficulties as noted for acetylene
Isobutane	Consumer product emissions	Has replaced chlorofluorocarbons in most consumer aerosol products
Isoprene	Biogenic emissions	Highly reactive but most frequently used for tracing biogenic emissions
Propane	Liquefied petroleum gas (LPG) use, refinery emissions, oil & gas production	Difficult to use as simple tracer if more than 1 type of source in area
Toluene	Motor vehicle exhaust, surface coating processes such as those involving solvent-based paints	Present in characteristic ratios in motor vehicle exhaust; excess beyond that attributed to surface coating processes and printing

Table 3-3. Average NMOC weight percent of the individual organic species in the first LMOS emission inventory and in ambient air at Gary, Chicago and Milwaukee, 1991.

Species	Gary		Chicago		Milwaukee	
	Ambient* %NMOC	Emissions %NMOC	Ambient %NMOC	Emissions %NMOC	Ambient* %NMOC	Emissions %NMOC
Paraffins	47	39	49	40	50	45
Acetylene	**2.5**	**0.8**	2.3	1.0	2 7	1.2
Ethane	**5.7**	**0.7**	2.9	1.1	3.5	0 9
Propane	**3.9**	**0.2**	3.1	0.5	3.7	0.2
n-Butane	**4.0**	**8.4**	5.0	9.0	6.3	13.2
i-Butane	**1.9**	**2.7**	2.1	1.4	2.4	1.0
n-Pentane	2.8	2.3	3.6	2.4	3 4	3.5
Branched C5	9.5	5.7	9.9	6.0	10 4	7.0
Branched C6	6.2	3.4	6.1	3.1	6.4	4 0
Metylcyclopentane	0.9	0.5	1.1	0.4	1.1	0.6
n-Hexane	1.4	1.6	2.3	1.0	1.7	1.5
Branched C7	3.1	2.1	3.4	2.2	3.7	2.5
Cyclic C7	0.3	2.3	0.5	2.6	0.5	1.8
n-Heptane	0.6	2.4	1.0	2.8	0.9	1.7
Branched C8	3.0	4.7	3.8	4.9	4.1	5 3
n-Octane	0.6	0.3	0.5	0.3	0 4	0.2
n-Nonane	0.3	0.3	0 4	0.3	0 4	0.2
Olefins	9	11	10	10	9	12
Ethene	3.1	2.7	4.7	2.5	3.8	2 9
Propene	0.8	0.8	0.9	1.0	1.0	1.1
Terminal C4 olefins	0.8	0.7	0.7	0.3	0.7	0 4
Internal C4 olefins	0.9	0.8	1.0	0 7	1.3	0.8
Terminal C5 olefins	0.3	0.9	0.5	0 7	0.4	0.9
Internal C5 olefins	1.1	1.6	2.0	1.6	1.3	2.2
Cyclopentene	0.4	0 5	0.3	0.2	0.3	0.3
Isoprene	1.4	1.0	0.2	0.1	0 4	0.3
Terminal C6 olefins	0.1	0.9	0.1	1.1	0.3	1.5
Internal C6 olefins	0.1	1.1	0.1	1.5	0.1	2.0
Aromatics	22	31	23	33	20	27
Benzene	2.4	2.6	2.6	2.9	2.7	3.0
Toluene	7.1	14 6	8.4	19.9	7.7	12 9
Ethylbenzene	1 2	1.5	1.3	1 1	1.1	1.3
Styrene	0 6	0 1	0 4	0.5	0.5	0.2
Trimethylbenzenes	2 9	2 6	3.2	1.6	2 7	2.3
Propylbenzenes	0.5	0 6	0 9	0.3	0 4	0 4
Xylenes	7 3	9 3	6.3	6.3	5 0	7 0
Carbonyls	4	1	3	1	3	1
Formaldehyde	2 4	0 4	2 0	0 6	2 0	0 4
Acetaldehyde	1 6	0 2	0 9	0 3	1 0	0 2

* NMOC percents correspond to June 26, July 16, and July 18, 1991

Table 3-4. Lake Michigan Area - Ambient Versus Original Set of EI NMOC/NO_x Ratios, 1991

Site	Ambient NMOC/NO_x	Emission NMOC/NO_x	Ambient/EI
Gary[a]	5.3	4.3	1.2
Chicago	4.8	2.6	1.9
Milwaukee[a]	6.4	4.2	1.6

[a] Ambient NMOC/NO_x ratios correspond to June 26, July 16 and 18, 1991

Table 3-5. Lake Michigan Area - Ambient Versus Revised Set of EI NMOC/NO_x Ratios, 1991

Site	Ambient NMOC/NO_x[b]	Emission NMOC/NO_x	Ambient/EI
Gary[a]	4.8	5.0	1.0
Chicago	4.7	3.6	1.3
Milwaukee[a]	6.4	3.8	1.7

[a] Ambient NMOC/NO_x ratios correspond to June 26, July 16 and 18, 1991

[b] Ambient NMOC/NO_x with background correction

Table 3-6. CMB Vs Emission Inventory Source Contribution Estimates, 1990

Summary of CMB Results*	Summary of Emission Inventory
Assume biogenic % = % reported in inventory (16.8%): MIN. MAX. **HIGHWAY MOBILE SOURCES:** 61% 75% **POINT + AREA SOURCES:** 8% 23%	Including Biogenics: **HIGHWAY MOBILE SOURCES:** 56.0% **POINT + AREA SOURCES:** 27.2%
Assume biogenic min. % = isoprene % (1.9%): MIN. MAX. **HIGHWAY MOBILE SOURCES:** 71% 89% **POINT + AREA SOURCES:** 9% 27%	
Assume biogenic max. % = % unexplained (47.4%): MIN. MAX. **HIGHWAY MOBILE SOURCES:** 41% 51% **POINT + AREA SOURCES:** 5% 15%	
Assume no biogenics: MIN. MAX. **HIGHWAY MOBILE SOURCES:** 73% 91% **POINT + AREA SOURCES:** 9% 27%	Excluding Biogenics: **HIGHWAY MOBILE SOURCES:** 67.3% **POINT + AREA SOURCES:** 32.7%

* Results presented as percent of total apportioned NMOC (sum of source estimates).

Table 3-7. South Coast Air Basin - CMB Vs Emission Inventory Source Contribution Estimates, 1987

period	vehicle exhaust	liquid gasoline	gasoline vapor	nonMV
		Summer Study		
CMB				
0700-0800	50.5	16.6	10.9	22.1
1200-1300	53.7	14.0	11.2	21.0
1600-1700	48.8	11.4	10.3	29.5
emission inventory				
0600-0800	49.5	9.1	5.6	35.9
1100-1300	21.9	5.5	3.4	69.2
1500-1700	30.4	7.3	8.0	54.3
daily total	28.3	6.3	4.5	59.0
		Fall Study		
CMB				
0700-0800	67.9	14.5	6.8	10.8
1200-1300	53.7	14.0	11.2	21.0
1600-1700	56.2	14.7	9.5	19.6
emission inventory				
0600-0800	62.1	8.8	2.9	26.2
1100-1300	26.4	6.0	3.1	64.5
1500-1700	38.1	7.2	6.4	48.3
daily total	37.4	6.8	3.5	52.3

Table 3-8. August 19, 1993 0500-0800 CST ambient-and emissions derived NMHC/NO_x ratios for total inventory emissions at Galleria.

Time (CST)	Emission NMHC/NO_x						Ambient NMHC/ NO_x
	1-Cell	9-Cell	25-Cell	81-Cell	Quadn[a]	Quadw[b]	
5	1.2	1.4	1.5	1.7	2.2	2.0	12.1
6	1.2	1.4	1.5	1.5	1.7	1.7	9.2
7	2.0	2.4	2.7	2.6	2.8	2.7	5.7

[a] Linear combination of emission inventory data from upwind grid cells with a weighing function of 1.
[b] Linear combination of emission inventory data from upwind grid cells with a weighing function defined as the inverse of the distance between the ambient monitoring site and the centroid of each grid cell

Table 3-9. August 20, 1993 0100-0800 CST ambient-and August 19, 1993 0100-0800 CST emissions-derived NMHC/NO_x ratios for total inventory emissions at Clinton.

Time (CST)	Emission NMHC/NO_x						Ambient NMHC/ NO_X
	1-Cell	9-Cell	25-Cell	81-Cell	Quadn[a]	Quadw[b]	
1	1.6	2.6	2.0	2.7	1.9	2.0	10.5
2	1.6	2.6	2.0	2.7	1.5	1.4	11.4
3	1.6	2.5	2.0	2.7	1.5	1.4	8.6
4	1.6	2.4	1.9	2.4	1.3	1.3	7.1
5	1.7	2.3	1.9	2.2	1.5	1.5	5.3
6	1.5	2.1	1.7	1.9	1.3	1.3	4.9
7	1.7	2.5	2.2	2.6	2.1	2.0	4.8

[a] Linear combination of emission inventory data from upwind grid cells with a weighing function of 1
[b] Linear combination of emission inventory data from upwind grid cells with a weighing function defined as the inverse of the distance between the ambient monitoring site and the centroid of each grid cell

APPENDIX A. VOC SOURCE APPORTIONMENT/RECEPTOR MODELING STUDIES

No. / Study Name								
Researchers, Affiliation, Date	**Location**	**Time**	**Sponsor**	**Approach**	**No. of profiles**	**No. of fitting species**	**Conclusions**	**Comments**
A Chemical Mass Balance for Volatile Organics in Chicago								
O'Shea and Scheff, Ill Inst of Tech , 1988	Chicago (1 site)	1985 weekdays 12-1 p m		CMB/trajectory	3	9	MV 61% of 9 VOC species sum	no comparison to EI
Wintertime Source-Reconciliation of Ambient Organics								
Aronian et al , Univ Ill , 1989	Chicago (3 sites)	winter 8 am - noon	EPA	CMB	8	23	MV exh 35% of NMOC; gas vapor 5%; refineries 11%	good agreement with EI except refineries higher than EI
Source Reconciliation of Ambient Volatile Organic Compounds Measured in the 1990 Atlanta Summer Study: The Mobile Source Component								
Lewis and Conner, EPA AREAL, 1992	Atlanta (1 site)	1990 30-min diurnal	EPA	CMB	1	10	MV exh 40-100% of NMOC	source profile from local tunnel study
Toxic Volatile Organic Compounds in Urban Air in Illinois								
Sweet and Vermette, Ill. St. Water Surv., 1992	Chicago, E. St. Louis	1986-1990 various seasons	Ill. DENR	factor analysis/ CMB	6	12	MV accounts for most toxics on average day, less on polluted day	no NMOC analysis
Receptor Modeling of VOCs in Atlanta Georgia								
Kenski, Wadden, and Scheff, Univ. Ill., Lonneman, EPA, 1992	Atlanta (2 sites)	1984-86 summer 6-9 a m.	EPA	CMB	4	29	MV exh 53% of NMOC; gas vapor 16%	MV exh lower than EI

APPENDIX A. VOC source apportionment/receptor modeling studies - continued

No. / Study Name								
Researchers, Affiliation, Date	**Location**	**Time**	**Sponsor**	**Approach**	**No. of profiles**	**No. of fitting species**	**Conclusions**	**Comments**
Respeciation of Organic Gas Emissions and the Detection of Excess Unburned Gasoline in the Atmosphere								
Harley et al , Caltech, 1992	Los Angeles (9 sites)	1986, 1987 summer 4-hr avg and diurnal	EPRI	CMB	6	15	MV exhaust 35% of NMOC; unburnt gas major factor missing from EI	restricted fitting species to non-reactive VOC
Receptor Modeling of SCAQS Volatile Organic Compounds								
Gertler et al., DRI, 1993	Los Angeles (2 sites)	1987 SCAQS hourly	SCAQS	CMB	4	15-17	MV exh 60-70%	evap and refinery source could not be resolved
A Receptor Modeling Approach to VOC Emission Inventory Evaluation								
Kenski et al., Univ. Ill , 1993	Detroit Chicago Beaumont Atlanta Washington	1984-88 summer 6-9 a m. and diurnal	EPA	CMB	7	29	MV exh: 14% BMT; 28% Det; 41% Chi; 53% Atl; 56% Wash	agreement with EI generally good
Receptor Modeling of Volatile Hydrocarbons Measured in the 1990 Atlanta Ozone Precursor Study								
Lewis et al., EPA, 1993	Atlanta (1 site)	1990 30-min diurnal	EPA	CMB, source profiles from GRACE/SAFER	8	36	Total MV 63-80%, depending on def. of NMOC	
Receptor Modeling of Volatile Organic Compound I Emission Inventory and Validation								
Scheff and Wadden, Univ. Ill., 1993	Chicago (3 sites)	1987 summer 8-12	EPA, NSF	CMB, trajectory	8	23	MV 21% of 23-species sum; refinery 7%; gas vapor 7%	59% unidentified; MV good agreement with EI

APPENDIX A. VOC source apportionment/receptor modeling studies - continued.

No. / Study Name								
Researchers, Affiliation, Date	**Location**	**Time**	**Sponsor**	**Approach**	**No. of profiles**	**No. of fitting species**	**Conclusions**	**Comments**
Source Attribution of Toxic and Other VOC's in Columbus, Ohio								
Mukund et al , Battelle, 1994	Columbus (6 sites)	1989 summer 6-9 a m	EPA	CMB	5	16	MV exh 34% of 16-species sum; gas vapor 19%	primary focus on toxics
Validation of the Chemical Mass Balance Receptor Model Applied to Hydrocarbon Source Apportionment in the Souther California Air Quality Study								
Fujita, Watson, Chow, Lu. 1994.	CA South Coast Air Basin (9 sites)	1987 fall		CMB	23			
Comparison of Atlanta Emission Inventory with Ambient Data Using Chemical Mass Balance Receptor Modeling								
Conner, Collins, Lonneman, Seila EPA, 1994	Atlanta (6 sites)	1990 summer	EPA	CMB	3	18	EI undrestimates mobile sources; EI overestimates combined area & point	Ambient-derived source estimates expressed as ranges.
Volatile Organic Compound Source Apportionment for the Coastal Oxidant Assessment for southeast Texas Study (Draft)								
Lee, Fjuita	Houston (2 sites)	August 1993	TNRCC	CMB				

APPENDIX B. VOC source profile studies

No. / Study Name							
Researchers, Affiliation, Date	**Objectives**	**Location**	**Data**	**Sponsor**	**Approach**	**Conclusions**	**Comments**
Source Fingerprints for Receptor Modeling of Volatile Organics							
Scheff et al., Ill Inst of Tech, 1989	develop VOC source fingerprints for CMB		source profiles from literature	EPA, NSF	lit. review	10 source profiles developed	MV exhaust profile from Sigsby; gas vapor profile from winter blend
Volatile Organic Compound (VOC)/particulate Matter (PM) Speciation Data System, Version 1.4							
VOC/PM Speciation Data System, EPA, 1991	library of source profiles		VOC and PM source profiles	EPA	lit. review and eval.; some new data generated	over 700 profiles	MV profiles have been updated since 1991
Source Fingerprints for Volatile Non-Methane Hydrocarbons							
Doskey et al., Argonne, 1992	VOC source fingerprints	Chicago	source profiles generated	Ill. DENR	ambient VOC measurements in impacted areas	evap profiles are sensitive to season and grade of gasoline	used parking garage to obtain cold start and hot soak profiles
The Observation of a C5 Alcohol Emission in a North American Pine Forest							
Goldan et al., NOAA, 1993	characterize biogenic emissions	Niwot Ridge, Colorado	ambient VOC in remote forested area	NOAA	ambient meas.	new biogenic species, emissions = isoprene	large meas. uncertainty
Improvement of the Speciation Profiles Used in the Development of the 1991 LMOS Emission Inventory							
Korc and Chinkin, STI, 1993	review of VOC source profiles used in EI		VOC source profiles from EPA, CARB, and CIT	LADCO	lit review	replace EPA profiles for gas. evap. and surf. coating	used ambient data to identify possible problems with the profiles

APPENDIX B. VOC source profile studies - continued

No. / Study Name							
Researchers, Affiliation, Date	**Objectives**	**Location**	**Data**	**Sponsor**	**Approach**	**Conclusions**	**Comments**
Vehicle-Related Hydrocarbon Source Compositions from Ambient Data: The GRACE/SAFER Method							
Henry, USC, Lewis, EPA, and Conner, USC, 1994	development of VOC source profiles for CMB	Atlanta (1 site)	ambient NMOC	EPA	develop GRACE/SAFER method to extract source profiles from ambient data	develop city-specific profiles for "roadway", whole gasoline, and gasoline vapor	assumes acetylene is a tracer for MV exhaust

APPENDIX C. AMBIENT RATIO STUDIES

Study Name								
Researchers, Affiliation, Date	**Objectives**	**Location**	**Time**	**Data**	**Sponsor**	**Approach**	**Conclusions**	**Comments**
A Review of NMOC, NOx, and NMOC/NOx Ratios Measured in 1984 and 1985								
Baugues, EPA, 1986	develop EKMA inputs, assess MV component	30 cities	1984-85 summer avg 6-9 a m	ambient NMOC and NO_x	EPA	acetylene as MV tracer; used NMOC:acetylene = 27 for MV	MV 18-88% of NMOC; lowest in Houston; higher than EI	EI not adjusted for time of day or species meas.
Speciated Hydrocarbon and NOx Comparisons at SCAQS and Receptor Sites								
Lonneman et al., EPA, 1989	develop EKMA inputs	Los Angeles, Long Beach, Claremont	1987 summer (5 days) 6-9, 12-3, and 3-6	ambient NMOC and NO_y (SCAQS)	EPA	ambient NMOC:NO_y at source and receptor sites	NMOC:NO_y lower at receptor site	no comparison to EI NMOC:NO_x
Reconciling Differences Between Ambient and Emission Inventory Derived NMOC/NOx Ratios: Implications for Emission Inventories								
Baugues, EPA, 1991	EI validation	16 cities	1985	ambient NMOC and NO_x	EPA	adjust EI to provide best comparison with ambient NMOC:NO_x	EI ratios average 23% lower than ambient	rule effectiveness assumptions have large effect
Comparison of Emission Inventory and Ambient Concentration Ratios of CO, NMOG, and NOx in California's South Coast Air Basin								
Fujita et al., CARB, 1992	EI validation	Los Angeles (8 sites)	1987 summer, fall avg. 7-8 a m.	SCAQS ambient NMOC, CO, NO_x	CARB	comparison of ambient and EI NMOC:NO_x and CO:NO_x ratios	ambient ratios higher than EI; MV emis. underest.	speciated VOC data used qualitatively
Comparison of Emission Inventory and Ambient Concentration Ratios of NMOC, NOx, and CO in the Lake Michigan Air Quality Region								
Korc et al., STI, 1993	EI validation	Chicago, Gary, Milwaukee	1991 summer 7-9 a.m.	LMOS ambient NMOC, CO, NO_x	LADCO	ambient NMOC:NO_x and CO:NO_x ratios and VOC mass fractions	ambient ratios higher than EI; MV emis underest.	speciated VOC compared to speciated EI

APPENDIX C. Ambient ratio studies - continued

Study Name								
Researchers, Affiliation, Date	**Objectives**	**Location**	**Time**	**Data**	**Sponsor**	**Approach**	**Conclusions**	**Comments**
Use of PAMS Data to Evaluate the Texas Coast Emission Inventory								
Korc et al, STI, 1995	*EI validation*	*Southeast Texas*	*1993 summer 1-8 a m*	*COAST ambient NMOC, NO_x*	*EPA*	*comparison of ambient and EI NMHC:NO_x ratios*		

CHAPTER 4
OBSERVATIONAL BASED METHODS FOR DETERMINING VOC/NO_x EFFECTIVENESS

4.1 INTRODUCTION

Observational based models (OBMs) represent a broad group of data analysis techniques, subject to many descriptions regarding their formulations and applications. Perhaps the distinguishing feature of OBMs is that they are driven principally by observed (or ambient) data as opposed to grid models which are driven by emissions estimates. Observational analysis methods include receptor models, regression techniques, ambient ratios (e.g., VOC/NO_x), indicator species and the more semi-empirical based OBMs. This chapter is restricted to those methods which are capable of inferring control strategy effectiveness (e.g., NO_x or VOC control preference). Source attribution and related methods for assessing emissions inventories are covered in Chapter 3.

This chapter follows a method (or method class) by method approach, starting with highly empirical[1] ratio techniques and proceeding to the more semi-empirical OBMs which incorporate some degree of mechanistic-based chemistry formulations. All of the techniques discussed require "routine" data sources comparable to that available from a PAMS network, with certain exceptions in NO_x measurements. Each methodology section provides case examples taken from the literature or developed from available data sources.

4.2 EMPIRICAL TECHNIQUES

4.2.1 VOC/NO_x Ratios

Ratios based on the concentrations of VOC to NO_x have been used for relating emission inventories to ambient data, as well as delineating NO_x and VOC control requirements. Generally, the propensity of an area to be VOC- or NO_x-limited is based on the measured (or predicted) ratio. Higher and lower ratios imply NO_x- and VOC-limiting conditions, respectively. No specific cutoff ratios exist, since whether ozone formation is limited by VOC or NO_x depends on other factors in addition to the VOC/NO_x ratio. However, for the conditions often assumed in EKMA/OZIPM4 ozone isopleth diagrams ratios greater than 16 often were considered NO_x-limited and ratios less than 6 were considered VOC-limited (U.S. EPA, 1989). The VOC/NO_x ratio technique is based on well understood atmospheric chemistry processes, and represented in

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[1] All approaches have logical foundations in, or their behavior can be explained by, atmospheric chemistry principles.

ozone isopleth diagrams (Figure 4-1) derived from photochemical "box-type" models such as EPA's EKMA/OZIPM4 (U.S. EPA, 1989).

As part of the evaluations of 1993 PAMS data from three sites in Houston, Texas and Baton Rouge, Louisiana, ratios were calculated from three hour averages of TNMHC and NO_x, and TNMHC and CO for the three PAMS sites[2]. The summary statistics for the ratios are presented in Table 4-1 (Stoeckenius et al., 1994). For Houston, the TNMHC/NO_x ratios were found to be higher at the Clinton Drive than at the Galleria site, as might be expected given the dominance of petrochemical industry sources at Clinton Drive. The ratios at the Baton Rouge site are lower than at either Houston site. In contrast, morning (6–9 a.m.) ratios are very similar at all three sites. The Clinton site appears subject to higher evaporative emissions and fewer NO_x sources during the day as compared to Galleria or Capitol.

Relationships between morning TNMHC/NO_x ratios and daily maximum ozone concentrations may provide insight into the potential tradeoffs between VOC and NO_x control strategies. Scatter plots of 6–9 a.m. TNMHC/NO_x ratios with daily maximum ozone concentrations observed within the Houston non-attainment region and daily maximum temperature (as measured at the PAMS site) are presented in Figures 4-2 and 4-3 (Stoeckenius et al., 1994). At these sites, ozone concentrations above 0.10 ppm are associated exclusively with TNMHC/NO_x ratios less than about 10. There is some hint in these data that the TNMHC/NO_x ratio decreases with increasing ozone concentrations above 0.10 ppm. If this is confirmed by further analysis, it would suggest that Houston is in a NO_x limited regime.

Nearly all of the TNMHC/NO_x ratios above 10 at the Houston sites are associated with maximum ozone values substantially below 0.10 ppm. TNMHC/NO_x ratios substantially above 10 may be associated with older air masses with very low NO_x concentrations and a lower proportion of reactive NMHCs[3]. This could be confirmed by further analyses comparing the reactivity weighted TNMHC on days with different TNMHC/NO_x ratios and a more detailed examination of meteorological conditions. Figures 4-2 and 4-3 suggest that the meteorological conditions that place these aged air masses over the Houston site on certain mornings are not conducive to the formation of high ozone concentrations in the Houston area (Stoeckenius et al., 1994). As is typical of most urban areas, the daily maximum ozone concentrations in Houston are related to the daily maximum temperature with the highest ozone found on the warmest days. There are no obvious relationships between maximum temperature and 6 to 9 a.m. TNMHC/NO_x ratios.

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[2]Ratios were set to missing for 3-hour blocks with two or more missing TNMHC or NO_x concentrations.

[3]High TNMHC/NO_x ratios may also be associated with very low NO_x concentrations that are not accurately measured. Investigation of this possibility was beyond the scope of the present study but must be conducted before any final conclusions can be drawn regarding the conditions leading to high TNMHC/NO_x ratios.

While the VOC/NO_x method is theoretically sound, application of the technique has several limitations:

1. Historically, applications have relied upon morning, center-city VOC and NO_x measurements, yet the ratio varies widely in time and space. PAMS improves the spatial and temporal coverage of data, and therefore tempering this particular concern.

2. Assuming only limited measurement-related difficulties, the ratios delineating NO_x and VOC-limited regimes vary with time and location, and are affected by vertical mixing processes that often are not accounted for in surface measurements. Additionally, the prevailing atmospheric chemistry (e.g., composition and age of air mass) can impart different control responses at the same VOC/NO_x ratios.

3. Inconsistent and uncertain measurement techniques affect the ratio. These include various interpretations of total NMOC, measurement uncertainties and artifacts in NO_x and NMOC, and the representativeness of observations (this latter issue is more problematic for emission inventory evaluation).

By themselves, VOC/NO_x ratios probably cannot be used unambiguously to infer NO_x or VOC control strategy effectiveness. However, in combination with other observational (and gridded models) techniques, the VOC/NO_x method adds corroborative value.

4.2.2 Reactive (oxidized) Nitrogen (NO_y, NO_z) and Ozone Correlation Techniques

Several correlations relating ozone production to total oxidized nitrogen (NO_y) or NO_z (NO_y - NO_x) have been suggested as tools capable of implying VOC/NO_x control effectiveness, as well as relative air mass aging. These correlations (e.g., Figure 4-4, Olszyna et al., 1994) are generally based on large quantities of averaged data covering multiple days, and limited to the midafternoon time period (1 - 5 pm).

NO_z typically correlates better with ozone than NO_y. This may reflect ozone scavenging by one of the NO_y species (NO). Progressively higher slopes, $\Delta O_3/\Delta NO_z$, reflect NO_x limited regimes and negative or near zero slopes reflect VOC limiting conditions. The existing studies do not provide sufficient guidance to delineate clearly the range of slopes depicting NO_x or VOC limiting regimes, although slopes greater than 8 appear to suggest NO_x-limiting conditions. By themselves, the NO_z-O_3 correlation does not provide a reliable NO_x-VOC-limiting indicator. However, in combination with other observational approaches and photochemical modeling, the correlation can provide corroborative support for evaluating control effectiveness. Future applications with emerging data bases and cross analysis-method comparisons should provide

greater understanding of the utility of these correlation methods. Additional discussion on these techniques is found in Appendix A.

4.3 OBSERVATIONAL MODELS

The two semi-empirical OBMs discussed here, the Mapper-Smog Production Algorithm (SPA) and the Georgia Institute of Technology (GIT) model, rely on some level of mechanistic description of atmospheric chemistry (relative to correlation techniques) or produce explicit VOC and NO_x control effectiveness results and therefore are distinguished from other indicator and correlation techniques.

4.3.1 Smog Production Algorithm - MAPPER program

Figure 4-5 provides an example of MAPPER-SPA results. The map provides a visually-oriented time and space perspective of NO_x- (or VOC-) limitation. The circular elements are clocks reflecting hourly data at the monitoring site, the size of the diameter is in proportion to the maximum daily ozone observed at the site. Shading gradations are used to reflect extent, E, which is a indicator for degree of NO_x-limitation. Filled black reflects full extent of 1, situations clearly NO_x-limited; white reflects VOC limiting conditions with $E < 0.5$; and cross-hatched areas could be considered borderline NO_x-sensitive. The example is only illustrative, the shading forced to illustrate a full range of NO_x- and VOC-limiting conditions. Displays such as these can be used to corroborate control strategy results from gridded ozone models. Due to the potential for compensating errors, typical model evaluations limited to comparisons between observed and simulated concentrations do not necessarily provide confidence in the model's response to emissions perturbations. The use of OBMs which rely on observations provide a unique corroborative check on the directional ability of EBMs to respond to emissions changes.

Description

The Smog Production Algorithms (SPA) and associated MAPPER software were derived from the Integrated Empirical Rate (IER) model of Johnson (1984) and later developed by Blanchard et al. (1994). The original IER was based on smog chamber experiments in Australia. Johnson (1984) defined smog produced (SP) as:

$$SP(t) = O_3(t) - O_3(0) + NO(0) - NO(t)$$

In simple terms, SP represents the cumulative oxidation of initial NO into ozone and other oxidized "smog" products (i.e., NO_y species), presumably accounted for in the change in NO over time. With sufficient NO, SP exhibits a linear relationship with cumulative light flux until a maximum, SP_{max}, is reached. Over much of this linear period, SP can be thought of as being

VOC-limited. This maximum is related to initial NO_x in the system by,

$$SP_{max} = \beta[NO_x(0)],$$

where the parameter, β, was assumed to be a constant of 4.1 based on the chamber experiments and reflects the potential maximum amount of smog produced per unit of NO_x input. An extent of Reaction, E, is defined as:

$$E(t) = SP(t) / SP_{max}$$

where the extent, E, represents the fractional movement toward maximum smog production. When the extent =1, virtually all the NO_x in the system has been transformed to ozone and oxidized NO_x products (NO_z) and the system is NO_X limited. Recalling that the linearized region of SP(t) is associated with VOC-limiting conditions, the value of E can be interpreted as rough indicator of VOC or NO_X-limiting conditions. That is, E with values very near or equal to 1 clearly reflect NO_X-limiting conditions, and values of E far less than 1 (say less than .5) suggest VOC limiting conditions. Thus, the derivation of equations and associated algorithms which utilize measurements as independent variables directed toward the calculation of E forms the basis for MAPPER in delineating NO_X and VOC limiting conditions. Details on the derivations and algorithms for E are found in Blanchard et al. (1994). More recent forms for SP include:

$$SP(t) = O_3(t) + DO_3(t) - O_3(0) + NO(0) - NO(t),$$

and

$$SP_{max} = \beta[_{NOx}(0)]^{\alpha}$$

where the term $D_{O3}(t)$ accounts for the cumulative ozone lost to deposition from time zero to t (i.e., ozone that has been produced but deposited), and is parameterized as a function of observed ozone. Default values for β (19) and α (.67) are empirical coefficients derived from numerous smog chamber studies.

Measurement Requirements/Relation to PAMS

MAPPER algorithms require hourly measurements of ozone, NO and either NO_x or NO_y, depending on the form of the MAPPER algorithm selected. Where available, true NO_x or true NO_y data should be used in MAPPER applications. The scarcity of such data will drive many applications toward routine NO_x data. Since MAPPER operates in true NO_x and true NO_y modes and many of the available routine NO_x overestimate afternoon NO_x, the technique can provide a "bounding" associated with the positive NO_x measurement biases. In addition, PAMS locations generally are weighted toward urban core areas and the results from PAMS alone are likely to be skewed toward the urban perspective, which in many cases will infer a VOC limiting

case.

4.3.2 GIT Model

The Georgia Institute of Technology (GIT) OBM (Cardelino and Chameides, 1995) utilizes most of the data (speciated NMOC and NO_X) generated from a PAMS. The GIT-OBM quantifies the relative roles of various emission groups (e.g., natural and anthropogenic VOC, NO_x) on ozone production. Figure 4-6 illustrates a GIT-OBM application for Atlanta covering several monitoring locations.

Description[4]

Cardelino and Chameides (1995) describe the use of a box model for calculating the sensitivity of ozone to VOC or NO_x reductions, which they name the "Observation-Based Model" and is referred to here as the "GIT-OBM". The model is an OBM because it uses ambient concentrations rather than emissions estimates to drive the calculations. The calculation is carried out separately for each monitoring location. Unlike a trajectory model, each box is fixed at the location of its monitor. The OBM utilizes some features of the OZIPM4 model to account for dilution and employs a modification of the CBM-4 (Cardelino and Chameides, 1995).

Cardelino and Chameides (1995) define a quantity, $P^S_{O3\text{-}NO}$, which is the net ozone formed plus the net NO consumed over a 12-hour period (this quantity is similar to SP of the IER model but is computed as an integral over time rather than an instantaneous concentration). The fractional change in $P^S_{O3\text{-}NO}$, divided by the fractional change in the "source strengths" of precursors, are used to define relative incremental reactivities (RIRs). For each measured species, instantaneous source strengths are calculated from the measurements and from production and loss terms. The RIRs for each site are (or can be) averaged to generate area-averaged RIRs. Cardelino and Chameides (1995) sum RIR terms so as to yield RIRs for NO, anthropogenic hydrocarbons (AHC), and natural hydrocarbons (NHC). The split between RIR-AHC and RIR-NHC is accomplished by summing RIRs for species arising from anthropogenic and biogenic emissions, respectively.

Limitation/Caveats

Numerous assumptions are made in the procedure. Some of the assumptions that appear to have a potentially substantial effect on the calculations are provided in Dmerjian et al. (1995) who suggest a potential bias toward overestimating the benefits of anthropogenic NO_X reductions.

1. Nature and levels of uncertainty associated with the method. Analyses of uncertainty have not

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[4]This description as well as the section discussing limitations and caveats of the GIT-OBM are taken from a review of OBMs conducted by Demerjian et al. (1995).

been carried out for the OBM. Taking into account the uncertainties deriving from factors such as those listed in the preceding section, as well as the inaccuracies and unavailability of data for typical nonattainment cities, there is a clear need to quantitatively characterize the resulting overall uncertainties in the model output. At present, some of the assumptions appear to generate biases that would enhance the apparent benefits of controlling anthropogenic NO_X.

2. The type of output of the method and the degree of consistency between this output and the types of information needed for regulatory applications. The output consists of RIRs for NO, AHC, and NHC. RIRs can also be output for anthropogenic area and point sources, as well as for other disaggregations that would be of use. The form of the output, as RIRs, can be directly translated into qualitative control preferences. However, RIRs derived from 12-hour $P^S_{O3\text{-}NO}$ terms may not be appropriate given the present form of the ozone standard, which requires compliance with a one-hour ozone average.

3. Availability of data needed as input to the method. The method requires measurements of NO that are accurate at sub-ppbv concentrations (Cardelino and Chameides, 1995), which appears to exceed the capabilities of most instrumentation that has been, or will be, deployed in routine monitoring networks. The OBM also appears to require continuous gas chromatograph (GC) measurements of hydrocarbon species.

4.4 REFERENCES

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Appendix 4A: DISCUSSION OF NITROGEN-BASED CORRELATION TECHNIQUES

Definitions:

$NO_x = NO + NO2$
$NO_y = NO_X + PAN + HNO_3 + ORGANIC\text{-}N \text{ plus } AEROSOL\text{-}N$
$NO_z = NO_y - NO_x$

Many of the observational based analysis methods applied over the last decade have relied on high quality NO_x and NO_y measurements. Several recent studies, designed to characterize airmass aging and the relationship of in-situ ozone production to NO_x or NO_y in rural environments, have produced strong correlations between ozone and various nitrogen groupings (Trainer et al., 1993; Olszyna et al., 1994). These correlations (e.g., Figure 1) generally are based on large quantities of averaged data covering multiple days, and limited to the mid afternoon time period (1 - 5 pm), to filter out the overwhelming negative impact of fresh NO_x titration of ozone. For the same reasons, NO_z-O_3 regressions typically correlate better than NO_y. Ozone should correlate positively with NO_z under NO_x and VOC-limiting conditions, since the radical processes associated with VOC reactions during VOC-limiting conditions coincidentally produce ozone and oxidized nitrogen (NO_z) products such as nitric acid. Collectively, the various studies as well as independent analysis of photochemical model results (Sillman, 1996) suggest that the slope of the regression line can be used as a qualitative indicator for delimiting NO_x and VOC limiting regimes. Progressively higher slopes, $\Delta O_3/\Delta NO_z$, reflect NO_x limited regimes and lower slopes reflect a move towards VOC limiting conditions. The existing studies do not provide sufficient guidance to delineate clearly the range of slopes depicting NO_x or VOC limiting regimes, although slopes greater than 8 appear to suggest NO_x-limiting conditions. By themselves, the NO_z-O_3 correlation does not provide a reliable NO_x-VOC-limiting indicator. However, in combination with other observational approaches and photochemical models, the correlation can provide corroborative support for evaluating control effectiveness. Future applications with emerging data bases and cross analysis-method comparisons should provide greater understanding of the utility of these correlation methods.

In addition to providing insight on control strategy effectiveness, the interpretation of NO_x, NO_y and NO_z data can be interpreted to provide insights into air mass aging, ozone production efficiency, and other analyses. Air mass aging can be defined in many ways, but empirical indicators using NO_y and NO_z data are founded on basic, well-understood atmospheric chemistry principles. In simple terms, aging is reflected in observations by the relative amount of NO_x that is oxidized (aged) to various NO_x oxidation products (i.e., NO_z). The ratio, NO/NO_y, is one indicator of air mass aging, and typically is normalized on a range from 0 to 1, with .6 used as a suggested indicator of "photochemically aged" air (Trainer et al., 1993):

$$AGE = 1 - (NO_x/NO_y)$$

Ozone production decreases with aged air masses, and the NO_x-limited conditions almost always associate with aged air masses. Aging analyses can provide guidance as to when to expect good $NO_z/NO_y/O_3$ correlations; poor correlations should be expected with "fresh" air masses. In turn, one might expect "good" correlations between VOC (or selected groups, species) and ozone during periods which are not NO_x-limited, and poor (or coincidentally good) correlations during NO_x-limited conditions. Again, the sum value of the collective use of several analysis techniques across multiple species is greater than the sum of individual analyses.

Data limitations/Relation to PAMS. PAMS will result in an enormous expansion of the VOC data base, and significant, but inadequate, improvements in nitrogen measurements. PAMS introduces additional spatial and temporal coverage of traditional NO_x measurements. However, many of the NO_x instruments are not capable measuring sub-ppb levels. More troubling is the lack of true NO_2 or NO_y measurements. Many of the PAMS NO_x instruments overestimate NO_2 (and therefore NO_x as well), due to PAN and nitric acid interferences. This interference is stronger during daytime conditions, further compromising the utility of nitrogen-based data analysis techniques. NO_y measurements are not required in the PAMS program. Finally, the majority of currently operating PAMS sites (mostly Type II) reflect urbanized conditions with relatively fresh air masses. One would expect these locations to produce poor correlations and infer VOC limiting conditions.

Model simulation derived methods

Various indicator techniques, which utilize absolute values of selected species or species ratio values, have been developed by analyzing photochemical model simulations. These include NO_y (Milford et al., 1994; Sillman, 1995) along with nitric acid, HNO_3, hydrogen peroxide, H_2O_2 and formaldehyde, HCHO. Results from two different photochemical models suggested that ozone would be limited by VOC at ambient NO_y levels exceeding a threshold level ranging from 10 to 25 ppb, and NO_x controls would not result in increased ozone unless ambient NO_y levels exceeded 20-30 ppb (Milford et al., 1994). Sillman (1995) reported similar results for NO_y, but concluded that the ratios, $HCHO/NO_y < 0.28$ and $H2O2/NO_y < 0.4$ were effective indicators for VOC limited regimes.

Relation to PAMS. Although these studies are based on model simulations, they provide direction toward the types of measurements useful for inferring control strategy directions. The potential value of NO_y measurements is reinforced by these studies. As discussed above, NO_y measurements are not required by PAMS but are considered an incremental improvement that gradually could be incorporated in the program. In combination with HCHO, which is measured in PAMS, another possible corroborative indicator, $HCHO/NO_y$, could be available. Hydrogen peroxide is still considered a "research" level measurement. However, peroxide concentrations gradually are becoming standard components of field campaigns such as the SOS. In addition to an indicator application described here, peroxide measurement are extremely useful for model diagnosis and evaluation and should be given strong consideration as a PAMS species when and if monitoring technology allows for more routine H_2O_2 measurements.

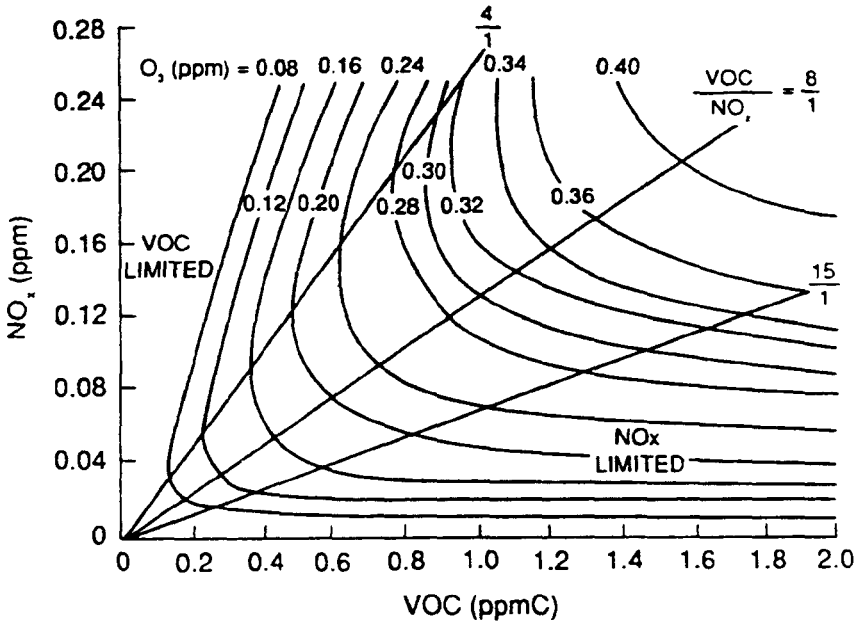


Figure 4-1. Isopleths developed from EPA's EKMA to illustrate VOC/NOx ratios. (NRC, 1991).

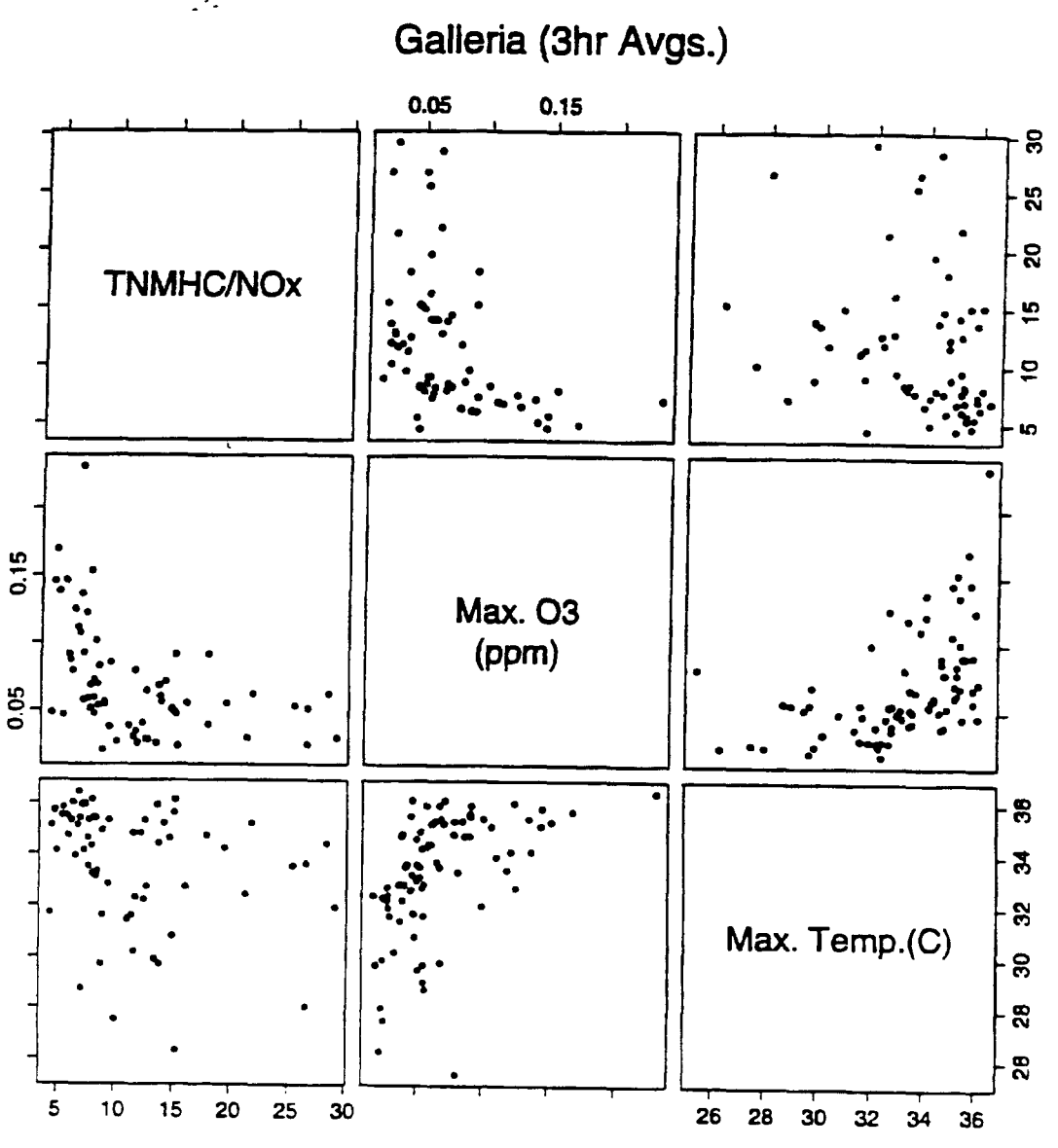


Figure 4-2. Scatter plot matrix for 6-9 a.m TNMHC/NO_x ratio, daily maximum temperature at Galleria, TX site and regional daily maximum ozone

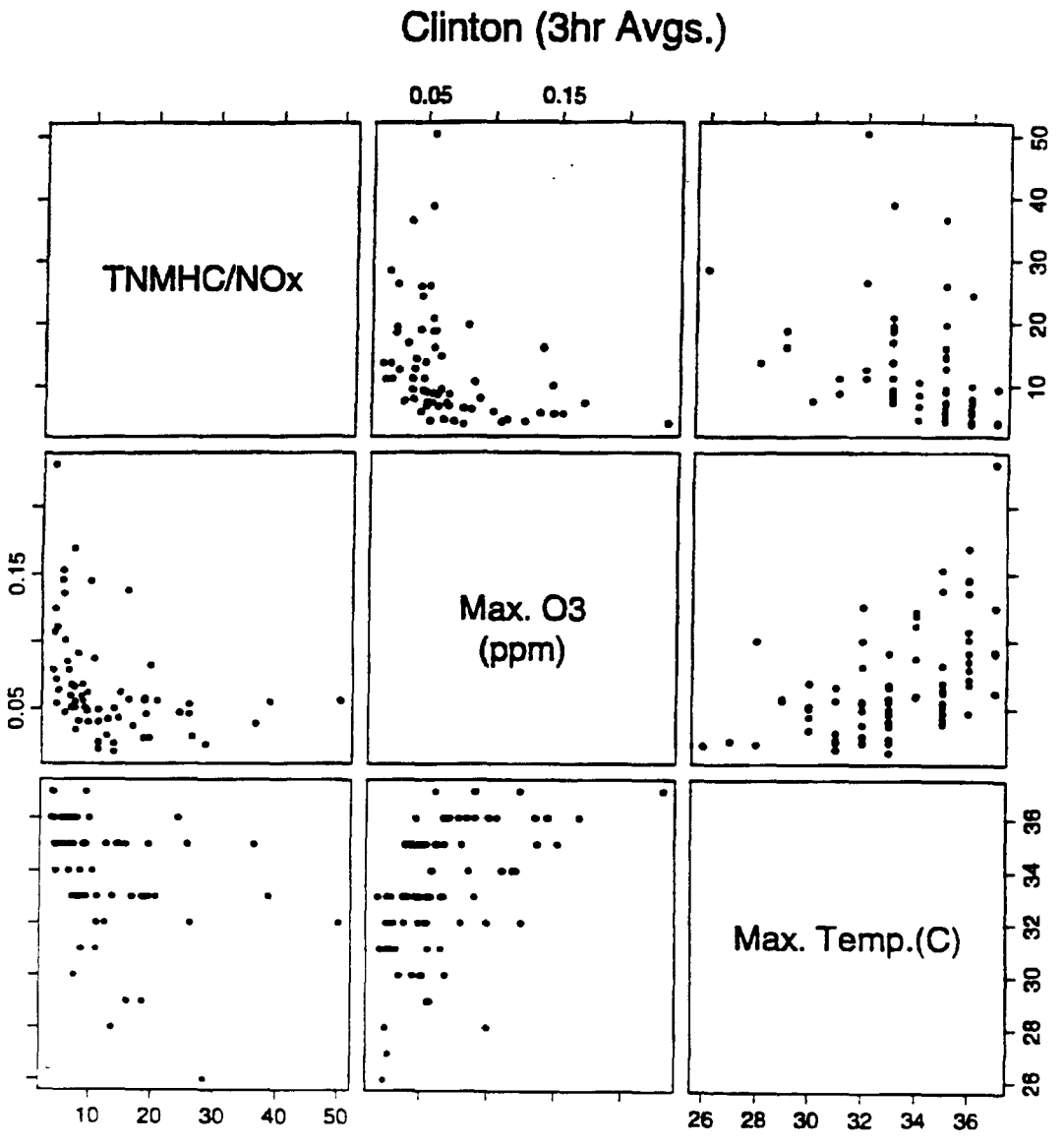


Figure 4-3. Scatter plot matrix for 6-9 a.m TNMHC/NO_x ratio, daily maximum temperature at Clinton Drive, TX site and regional daily maximum ozone

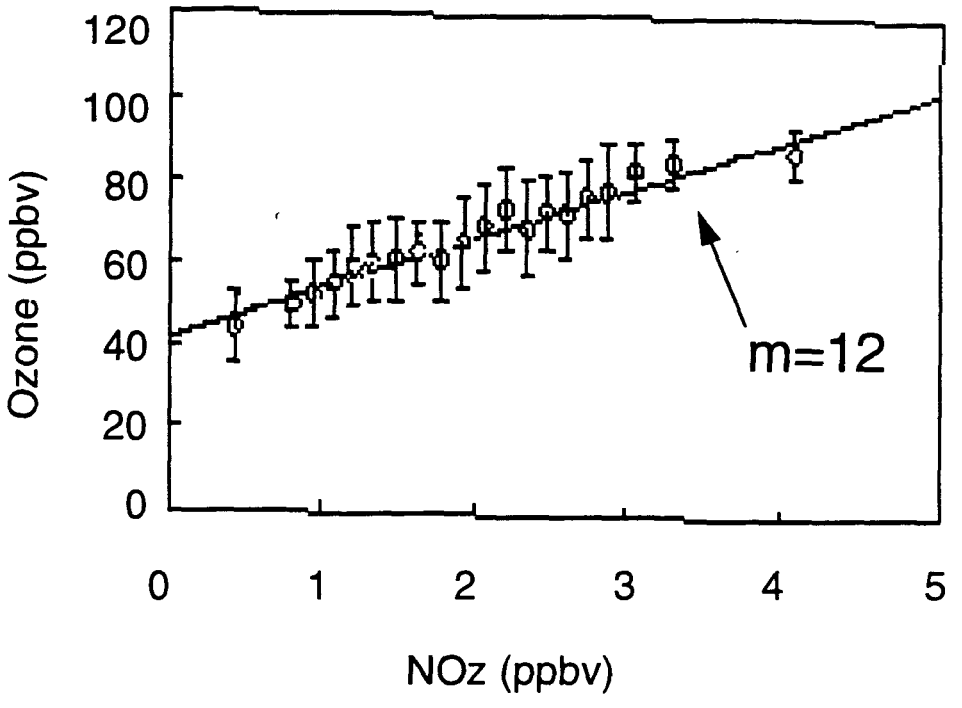


Figure 4-4. Plot of ozone versus NOz for Giles County, TN (Olszyna et al., 1994).

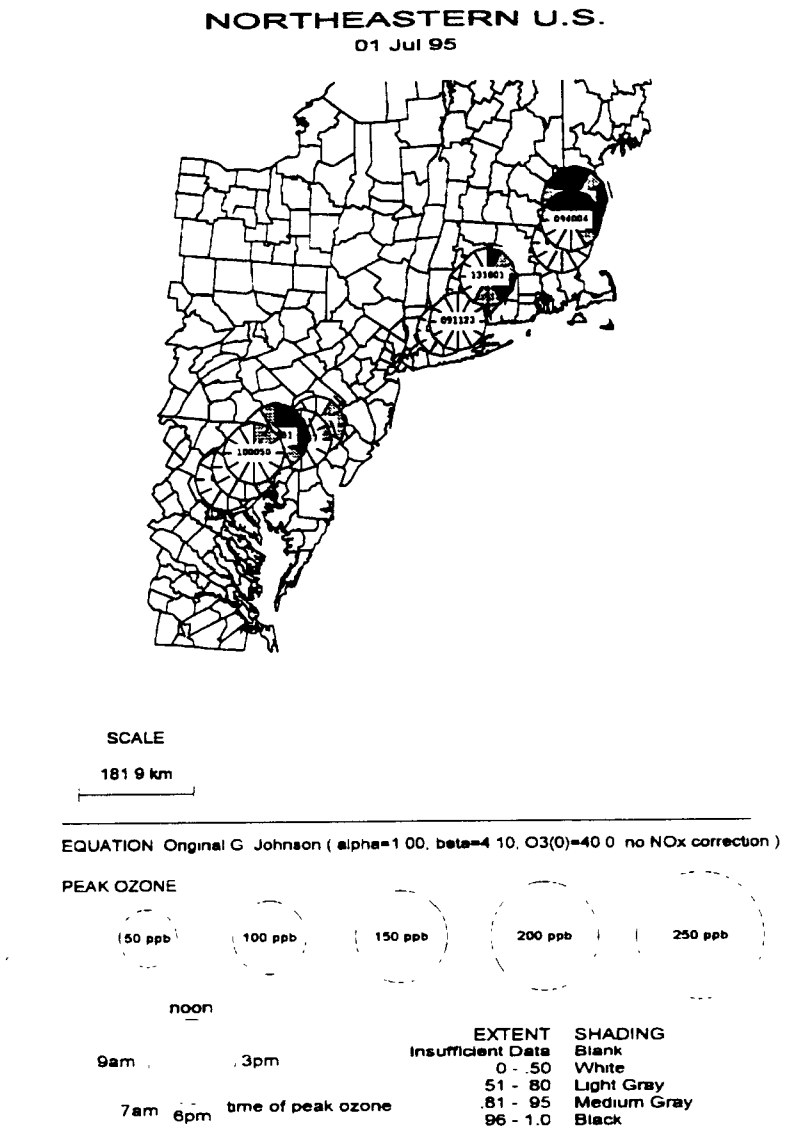


Figure 4-5. Example MAPPER output for the Northeast U.S.

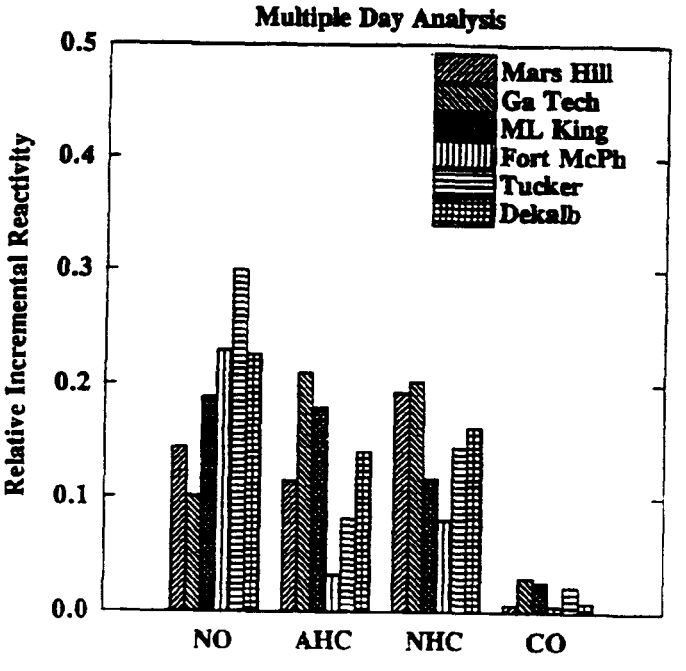


Figure 4-6. Results from GIT-OBM applied to Atlanta. The model provides a relative assessment of the role of emissions groups on ozone formation. (Cardelino and Chameides, 1995).

TABLE 4-1. Summary statistics for TNMHC/NO_x ratios calculated from 3-hour average TNMHC and NO_x concentrations.

	Min.	1st Qu.	Median	Mean	3rd Qu.	Max.	S.D.	NA's	N
All 3-Hour Values									
Galleria	4.457	9.531	13.72	16.94	19.99	94.25	11.165	218	736
Clinton	3.857	11.2	19.22	22.76	29.86	141.2	15.648	297	736
Capitol	2.475	6.927	9.562	12.19	14.48	82.6	9.536	181	739
6–9 a.m. Averages									
Galleria	4.457	7.367	9.524	11.78	14.4	29.22	6.166	28	92
Clinton	3.857	6.751	9.522	12.91	16.47	50.26	9.187	29	92
Capitol	3.738	7.558	10.2	12.51	14.66	45.28	7.798	22	92

CHAPTER 5
QUALITY ASSURANCE

5.1 INTRODUCTION

The quality and applicability of PAMS data analysis results are directly dependent on the inherent quality of the raw data itself. Data assessment information, such as that obtained from precision and accuracy (P&A) checks and performance audits, provides valuable measures of the general quality of PAMS data submitted to AIRS. Although reporting organizations and EPA are employing increasingly rigorous validation measures to insure optimum data quality, errors still get through the system. Because of the serious implications PAMS analytical results convey, PAMS data users are advised to critically examine all data before undertaking analysis in earnest. In this chapter we will highlight some recent PAMS data quality assessment information and also illustrate some useful screening procedures being used to identify potential errors that could bias results.

5.2 DATA ASSESSMENT

The assessment function of PAMS quality assurance involves two key required components: the National Performance Audit Program (NPAP) and precision and accuracy (P & A) data. EPA's Quality Assurance guidance mandates that all data collected for regulatory or research purposes be of known and documented quality. The EPA uses the National Performance Audit Program to independently quality assure the PAMS monitoring data it is receiving and permanently storing on AIRS. Audits for the PAMS compounds were added to the NPAP in 1995. Proficiency studies undertaken prior to the NPAP audits provided input to the program. Precision and accuracy checks are required for all types of PAMS monitors (meteorological, ozone, nitrogen oxides, VOC, and carbonyl).

5.2.1 NPAP and Proficiency Studies

In 1993 and 1994, the U.S. EPA National Exposure Research Laboratory (NERL), formerly, the Atmospheric Research and Exposure Assessment Laboratory, conducted cooperative efforts with the 22 State and local agencies monitoring for the PAMS compounds. This cooperative effort involved intercomparison studies (proficiency tests) in which these agencies analyzed samples for the PAMS volatile organic (VOC) and carbonyl compounds and reported their results to NERL for comparison to the NERL certified concentrations. Over the two year period, a total of twelve proficiency studies were conducted, 6 for VOCs and 6 for carbonyls. NERL compiled the results from each agency, compared the results to those from the referee laboratory and reported the results of the comparison to all agencies. The mean, median,

variance, and the difference from the referee laboratory's results were reported for each analyte. One of the goals of this cooperative effort was to develop performance limits for a nationwide audit program for PAMS measurement systems being initiated in 1995 (NPAP) which would be modeled after these proficiency studies. The intent was to set performance limits which were reasonable, i.e., limits encompassing at least 90 percent of the audit results. Due to reported instability problems, proficiency tests were not required for 2-methyl-1-pentene, alpha and beta pinenes, and isoprene. Table 5-1 shows the 90% probability limits computed from the composite data of these audits. A column displaying the computed average bias for each parameter is also included. Bias values outside the range -90% to +900% were excluded from the analysis.

As shown in the table, eleven of the fifty-one compounds had average biases exceeding ten percent. Note also that the upper and lower limits vary considerably from the allowable ±15% employed under NPAP guidance for the criteria pollutants (NO_2, O_3, etc). In fact, the "allowable" range (upper limit minus lower limit) exceeds 30% (the criteria pollutant "allowable" range) for every one of the parameters. Only one compound, Toluene, had 90% of its bias values within ± 20%. Therefore, based on these factors, EPA decided to use compound-specific limits in the 1995 NPAP PAMS VOC and carbonyl audits at the 90% probability limits shown in Table 5-1.

The NPAP's goal is to provide audit materials and devices that will enable EPA to assessed the proficiency of agencies that are operating ambient monitors. All agencies operating designated PAMS VOC and carbonyl sites were required to participate in the 1995 NPAP. The first two VOC audits proceeded as planned; however, in the third audit, over half of the compounds were found to be unstable. Sporadic stability problems were noted in all three of the carbonyl audits performed in 1995. Since the data from the affected audits are questionable, no summary report for 1995 was issued. Any future reports summarizing the PAMS audit data will not include individual audits because the NPAP policy requires that individual data results remain confidential. The 1996 NPAP PAMS audits were temporarily suspended pending outcome of research into the 1995 problems. As a precautionary measure, EPA arranged for another performance audit for the 1996 ozone season providing VOCs in canisters. The NPAP was able to provide two carbonyl audits in 1996 (June and September). A more reliable method of spiking the cartridges was designed and audit results so far have been excellent. Lengthy study of the VOC stability problem has not revealed a definitive answer, although it is believed that the passification procedure used by the manufacturer may have caused the problem. The NPAP offered one audit for VOCs in 1996 (September) by using only the cylinders that remained stable over a 4-month period.,

5.2.2 Precision and Accuracy Data

Although precision and accuracy checks are required for all types of PAMS monitors, EPA has not yet issued guidance for conducting and reporting VOC P&A checks due to the

significant number of target compounds and the non-trivial expense associated with either dual analysis of cylinder gas or operation of a collocated continuous GC/FID. EPA realizes the importance of data assessment information and is expending substantial resources researching the issue. Since guidance is pending, no VOC P&A data have yet been reported to AIRS. Many reporting organizations, however, utilize some form of P&A audits in their data validation protocol.

Because ozone and nitrogen dioxide (two parameters of interest in PAMS) are also criteria pollutants, a P&A policy has already been promulgated for them. EPA has established 95% probability limits (precision) of ± 15% for these two pollutants. Tables 5-2 and 5-3 show 1995 monitor summary P & A data for PAMS that monitor ozone and nitrogen dioxide. Table 5-2 shows the 95% probability limits of precision bias for PAMS ozone monitors and Table 5-3 shows the same for PAMS nitrogen dioxide monitors.

5.3 DATA VALIDATION

Within 6 months of the end of each quarterly reporting period, data from VOC measurement systems must be submitted to AIRS. Although data may be collected automatically, it is interpreted and entered into AIRS manually. Some common human errors observed in this data processing effort include incorrect units, misread formats, etc. Even after substantial pre-AIRS QA\QC procedures have been performed, a double check of the data is always good practice. QA is necessary to identify data errors before they are analyzed and possibly used for such policy decisions as determination of nonattainment of the standards, control technology, modeling, or trends.

5.3.1 Summary Statistics and Historic Precedence (Scatter Plots)

Time series plots are useful for locating unusually high changes in the data from one value to the next or long periods of constant or no change. Figure 5-1 is a 1994 time series plot of four species groups at Stafford, CT (Main et al., 1995). There is an easily identifiable drastic change along the paraffin plot around 5AM. An unidentified peak was misidentified as a paraffin.

Univariate statistics such as the mean, median, maximum and minimum values, are good starting points for detection of potential data problems. Figure 5-2 plots summary statistics for June, 1995 at the E. Hartford, CT and Stafford, CT PAMS sites including the 90th, 75th and 25th percentiles (Main et al., 1995).

Summary statistics can be turned into box plots to hint at the distribution and variability of the data. The dark line at the center of each box is the median, the 25th and 75th percentiles are at the ends of the box. The box plots in Figure 5-3 show that the NMOC concentrations varied

widely at E. Hartford, CT and Stafford, CT sites during June, 1995 (Main et al., 1995).

5.3.2 Frequency Distributions

The cost of monitoring and calibration measurements are just two of the causes of missing data. Missing data will occur and must be considered. Each analysis should have minimum data completeness requirements. For mean values, a 75% completeness requirement is common. Missing data are simply ignored in most statistical analysis software. For examining trends or time series analysis, missing values should be estimated. See Appendix H of part 50 40 CFR for time series modeling techniques to fill in the missing values.

Side by side box plots display the number of hours each day reported for every species in Figure 5-4 (Cox, 1995). The dark line at the center of each box is the median number of hours reported each day. The 25th and 75th percentiles are at the ends of the shaded box. Values outside of the whiskers (the narrow areas extending from the box) are isolated dots. Except for the few measurements of relative humidity, the meteorological data is relatively complete. O_3, NO, NO_2, NO_X and CO are relatively complete compared to the other continuous pollutant measurements.

Figure 5-5 displays a matrix for the reported ethylene data by hour for each day during July, 1993 at the Maryland PAMS site (Cox, 1995). After the 4th, the data is relatively complete except for morning hours.

Figure 5-6 shows frequency distributions for total NMHC concentrations measured at the E. Hartford, CT PAMS site during June, 1995 (Main et al., 1995). Data collected from 1600-2000 were almost exclusively above 50 ppbC. Afternoons make up the majority of the 50-200 ppbC groups while morning hours are a large part of the > 250 ppbC groups. Different hour and ppbC groupings would yield different distributions. Note the left to right skewness of the "all data" frequency, yet the morning or early afternoon histograms would appear to be more bimodal.

5.3.3 Spatial & Temporal Plots

Spatial and temporal plots are graphical data views which readily show easily identifiable outliers such as in the next example. The ozone exceedance at 4:00 AM on May 26, 1992 at Cape Elizabeth, ME of 139 ppb appears erroneous when viewed in spatial and temporal context. As the top map in Figure 5-7 shows, no other site in the vicinity reported concentrations as high as 50 ppb much less near 139 (NESCAUM, 1992). Because the plot is by day (x-axis), the strong diurnal (cyclic) pattern of the temporal plot is apparent. There is an obvious detectable jump on the 26th even through the flowing pattern.

The top graph in Figure 5-8 show suspect values which practically jump out from the page as well as away from the rest of the data when displayed temporally (NESCAUM, 1992). Probably because these values (for the bottom picture) are well below the standard they went undetected. It appears they were from a misplaced decimal point as shown in the table as "# Before", "# In", and "# After".

Something as simple as the way points are labeled or marked can facilitate visual identification of an outlier. In Figure 5-9, the suspect calm wind is clearly marked differently than the stronger wind vectors (Main et al., 1995). This plot of surface winds on June 27, 1991 at 1900 shows that the calm wind in Bloomington is suspect when compared to the areas around it. Had there been other calm winds nearby, the wind velocity would be neither easily identifiable nor suspect.

5.3.4 Inter-Site Comparisons & Inter-Species Comparisons

Intersite and inter-species comparisons are important to identify similarities and differences. When site similarities are apparent (e.g., similar precursors are detected) similar control measures and predictors can be used. The example depicted in Figure 5-10 compares the Stafford, CT and E. Hartford, CT PAMS sites (Main et al., 1995). It contrasts the VOC composition at the two sites at 8:00 AM on June 3, 1994. While most other species behave similarly at the two sites, species #11 differs greatly. One possible explanation could be the influence of local sources. Alternatively, if the two sites were known to have previously had similar species #11 concentrations, then this reading might be suspect.

When two species are highly correlated, they might be dependent on one another. If so, neither species would be suitable for a prediction model that required linearly independent variables as predictors. The scatter plot matrix in Figure 5-11 illustrates the strong correlations between some VOC species for Stafford, CT during in June, 1995 (Main et al., 1995).

Figure 5-12 simultaneously compares two sites and two species: isoprene and m&p-xylenes for the PAMS sites at Stafford, CT and E. Hartford, CT (Main et al., 1995). Xylene concentrations act differently while isoprene behaved similarly at the two sites. Again, one explanation could be local emissions released at those times when the patterns are different.

5.4 REFERENCES

Cox, W.M. "A Workbook for Exploratory Analysis of PAMS Data." June 1995.

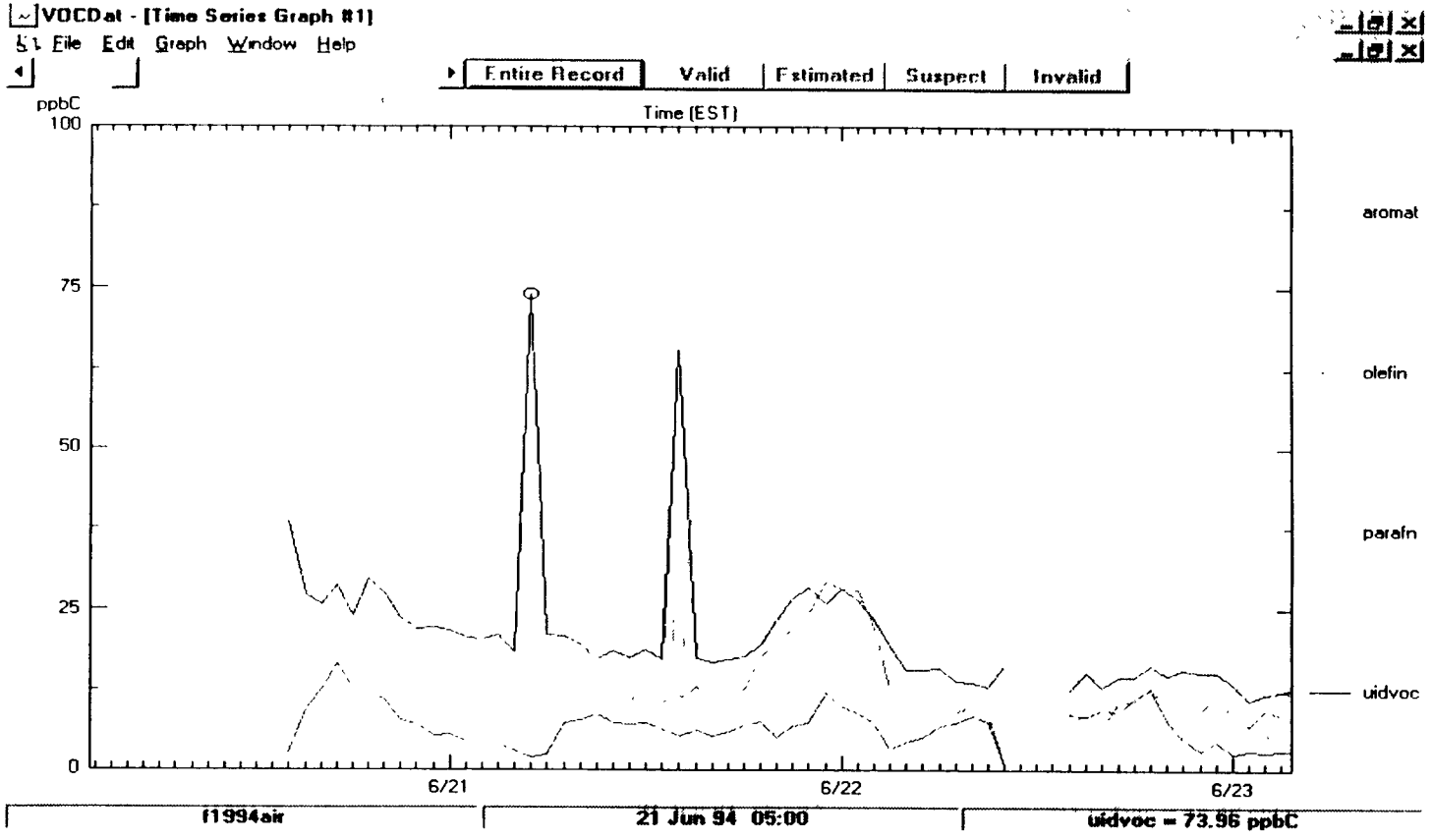
Main, H.; Roberts, P.; and Korc, M. Analysis of PAMS and NARSTO Northeast Data Supporting Evaluation and Design of Ozone Control Strategies: A Workshop. U.S. EPA Contract 68D30030, Sonoma Technologies, Inc., July 1996.

Northeast States for Coordinated Air Use Management (NESCAUM), The Ambient Monitoring and Assessment Committee. Preview of 1994 Ozone Precursor Concentrations in the Northeastern U.S. August 1995.

Northeast States for Coordinated Air Use Management (NESCAUM), The Ambient Monitoring and Assessment Committee. 1992 Regional Ozone Concentrations in the Northeastern United States. November 1993.

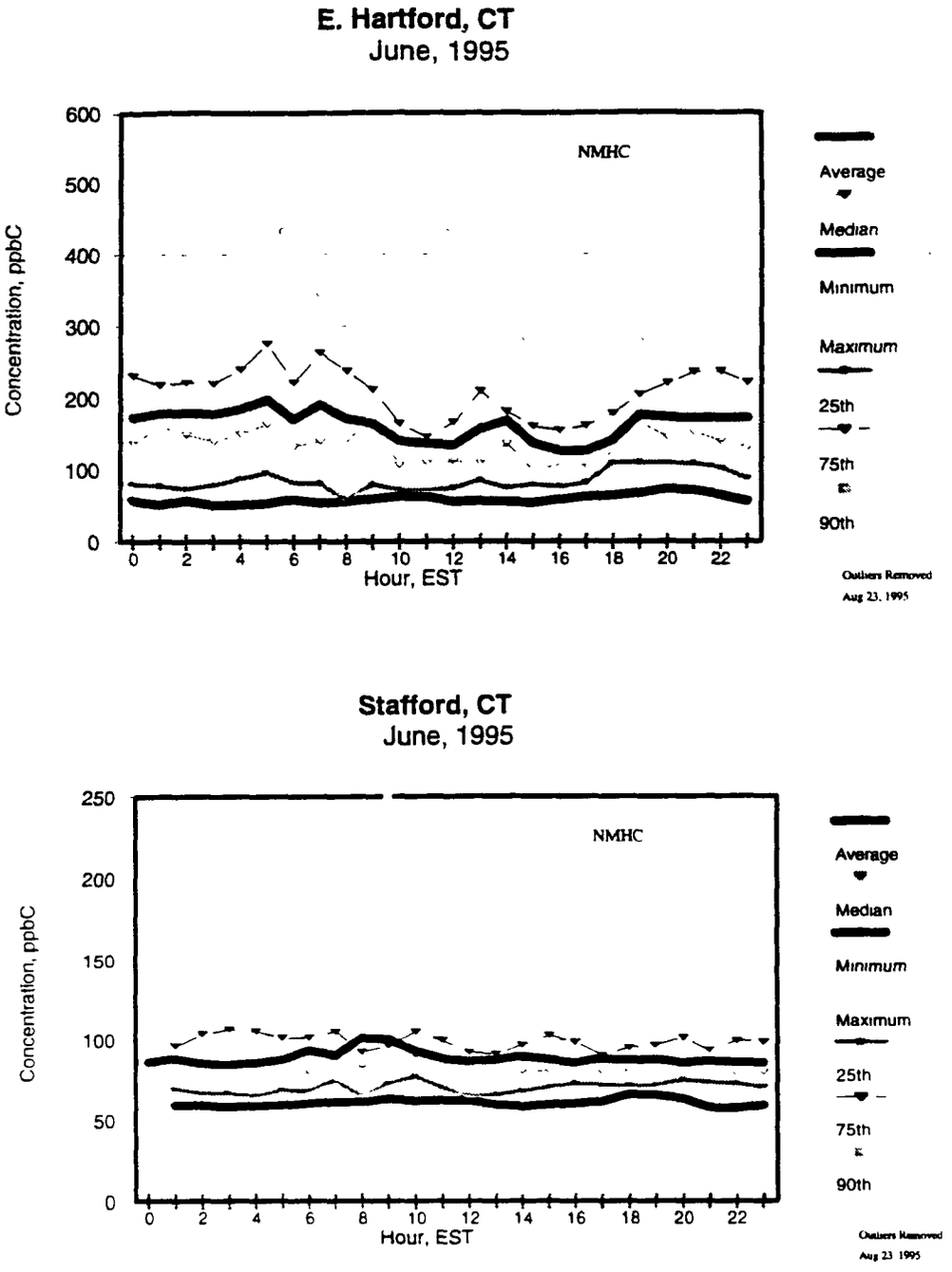
U.S. Environmental Protection Agency. Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II: Ambient Air Specific Methods (Interim Edition). EPA/600/R-94/038b, 1994.

Figure 5-1



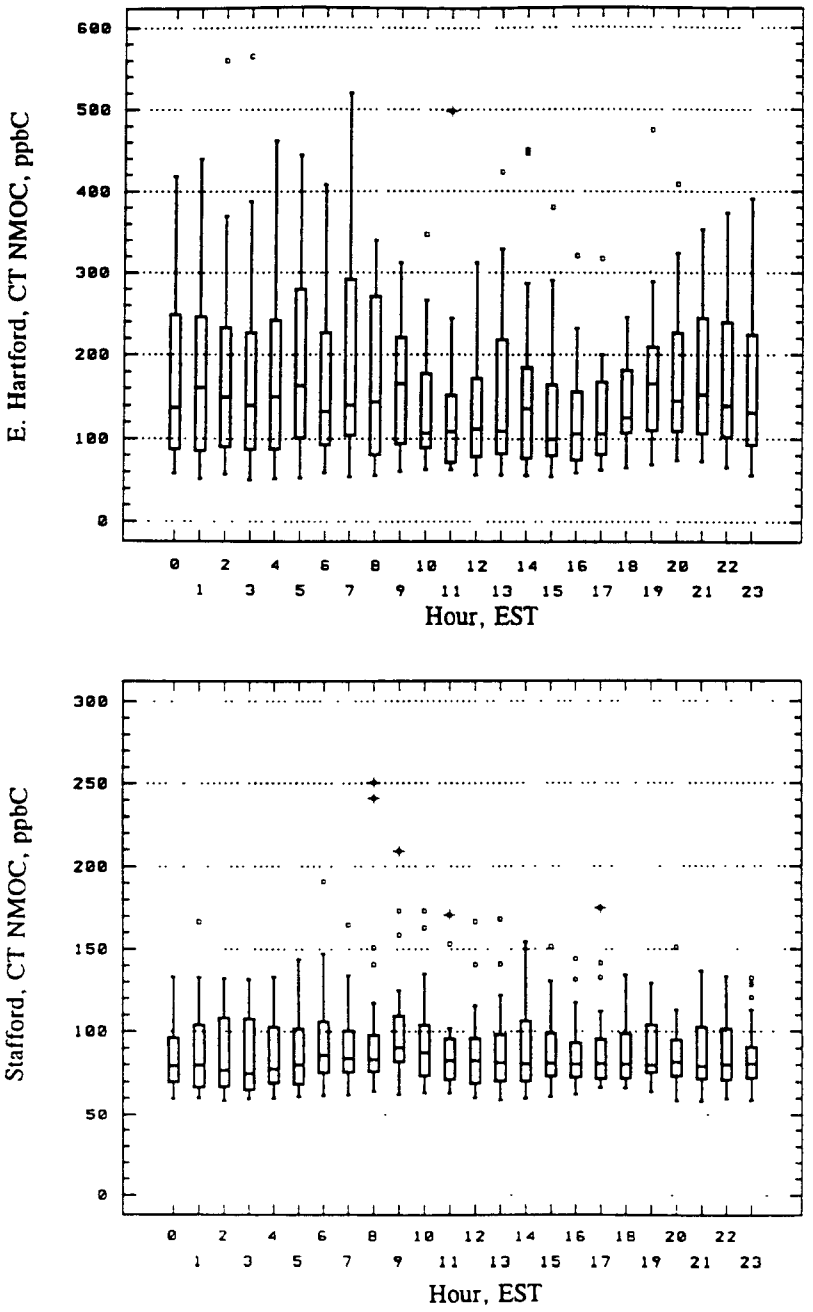
Time series plot of several species groups at Stafford, CT in 1994. Example of misidentification of a paraffin for an unidentified peak. (Level 0, preliminary data, CT DEP)

Figure 5-2.



Summary statistics plotted for East Hartford and Stafford, CT for June 1995. (Level 0, preliminary data, CT DEP)

Figure 5-3.



Box plots of NMOC by time of day during June 1995 at East Hartford, CT (top) and Stafford, CT (bottom). Concentrations varied widely at East Hartford.

Figure 5-4.

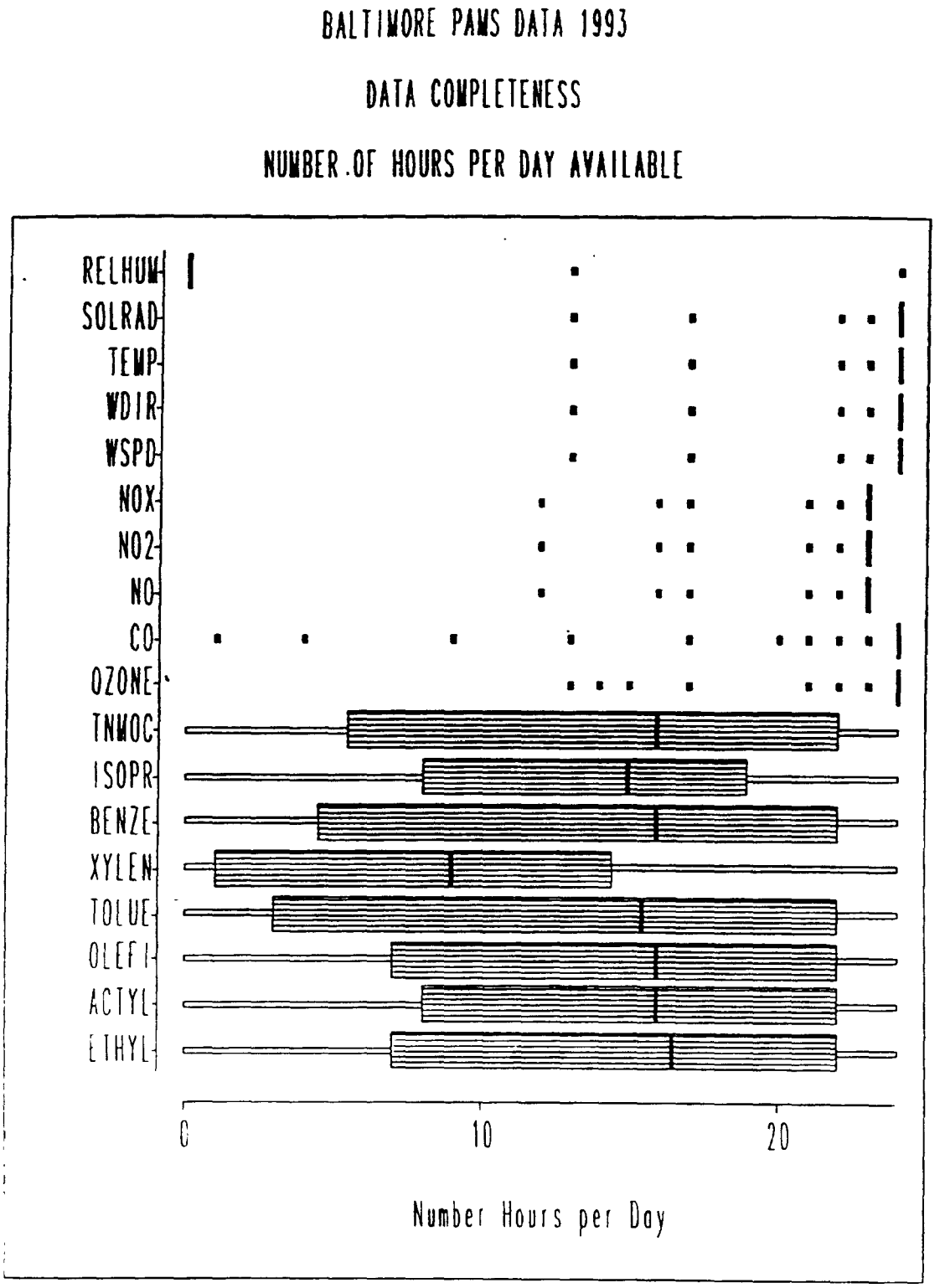

BALTIMORE PAMS DATA 1993
DATA COMPLETENESS
NUMBER OF HOURS PER DAY AVAILABLE
RELHUM
SOLRAD
TEMP
WDIR
WSPD
NOX
NO2
NO
CO
OZONE
TNMOC
ISOPR
BENZE
XYLEN
TOLUE
OLEFI
ACTYL
ETHYL
0
10
20
Number Hours per Day

Figure 5-5.

DISTRIBUTION OF MISSING VALUES
FOR ETHYLENE AT BALTIMORE PAMS SITE
DAY AND HOUR OF DAY FOR JULY 1993

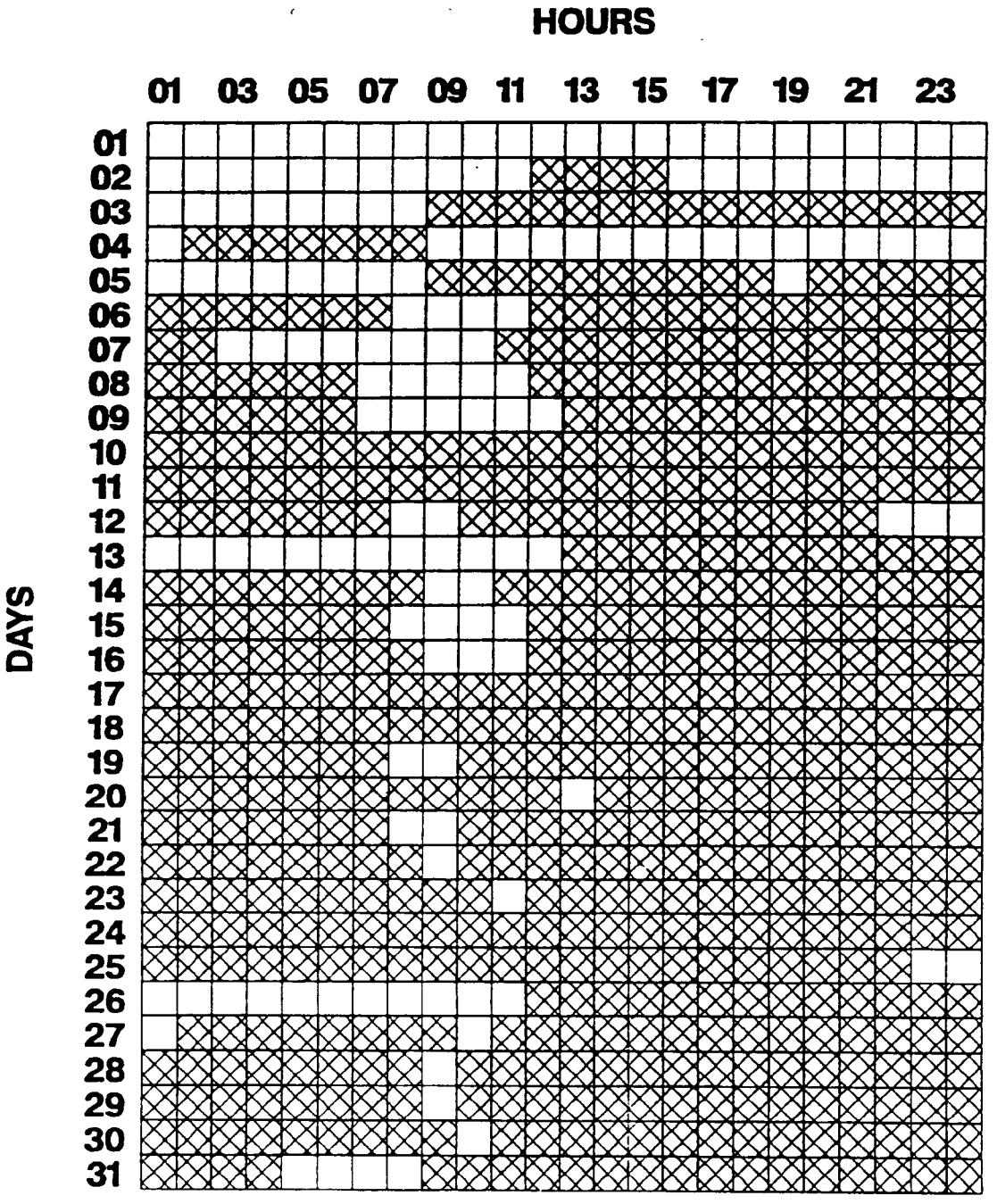
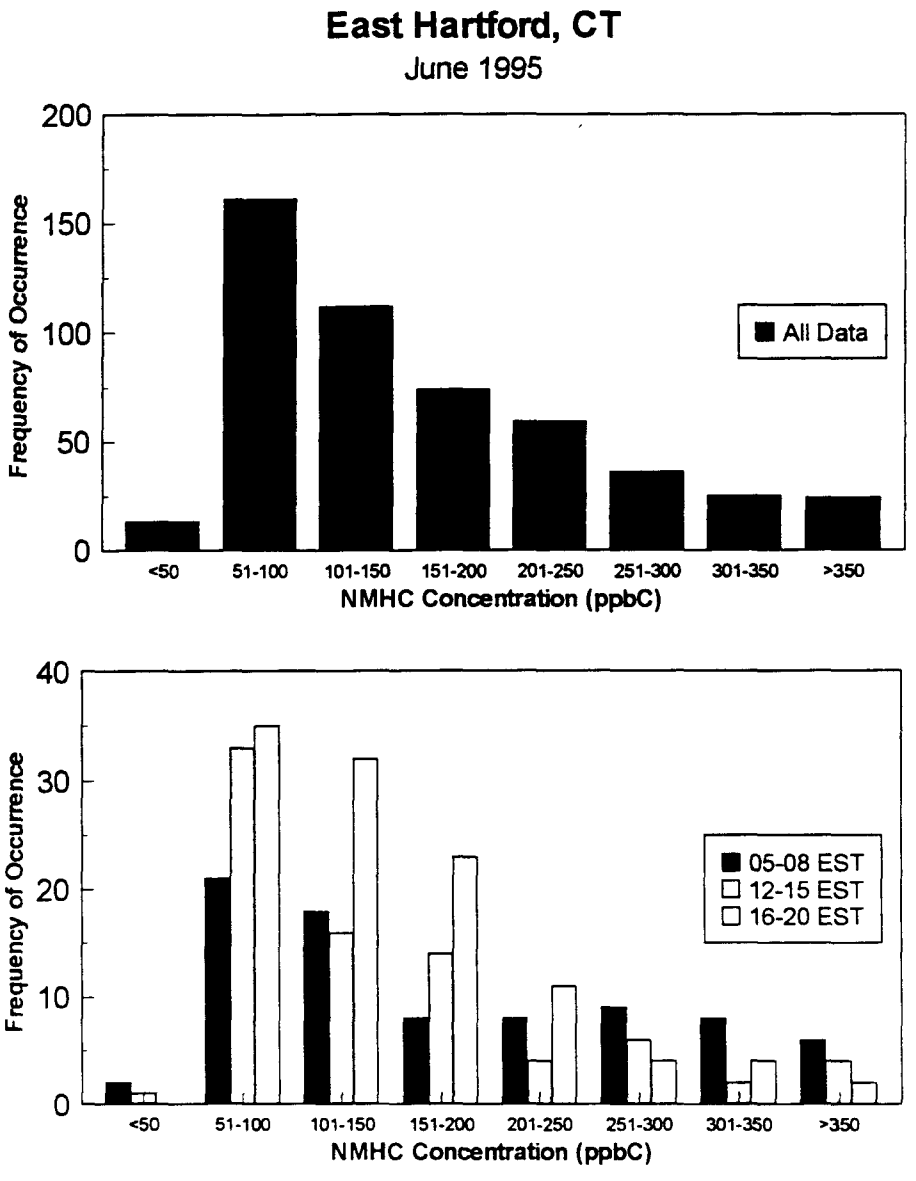


Figure 5-6.



Frequency distributions of total NMHC concentrations at East Hartford, CT for June 1995. Few data were below 50 ppbC; most data collected between 1600-2000 EST were 51 to 200 ppbC. (Level 0, preliminary data, CT DEP)

Figure 5-7.
Example of identification of suspect data values from the Northeast (NESCAUM 1993). The ozone concentration of 139 ppb reported at Cape Elizabeth, ME on May 26, 1992 at 4:00 AM appears erroneous when viewed in a spatial and temporal context.

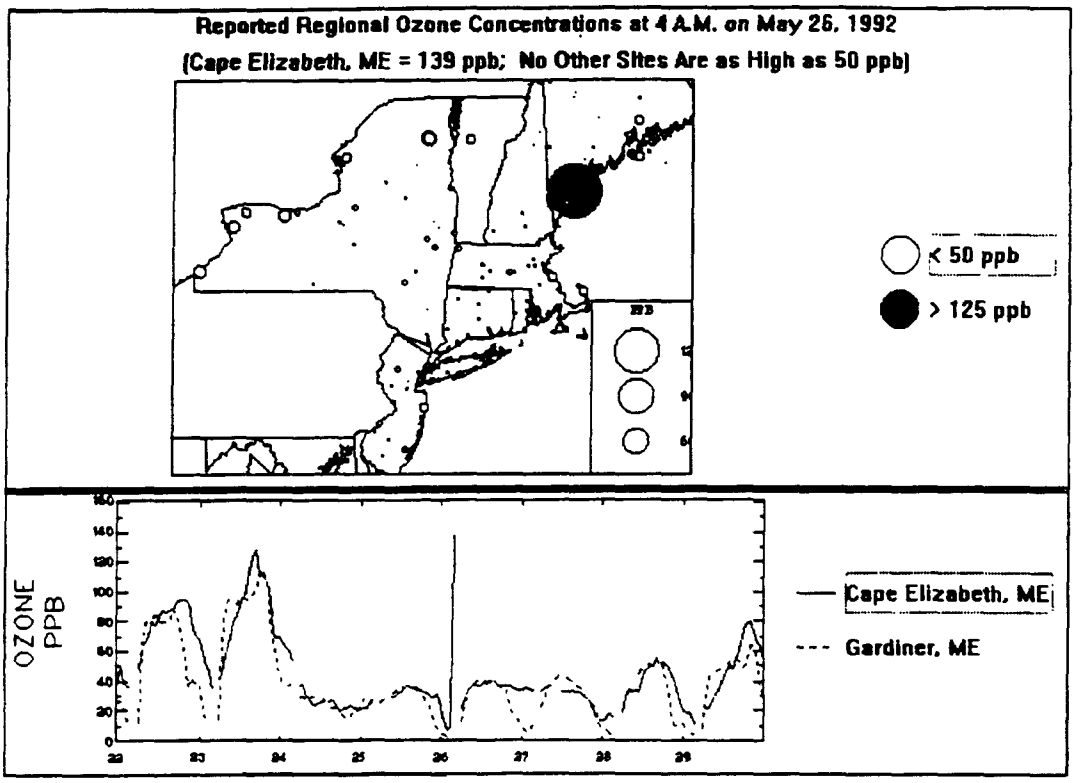
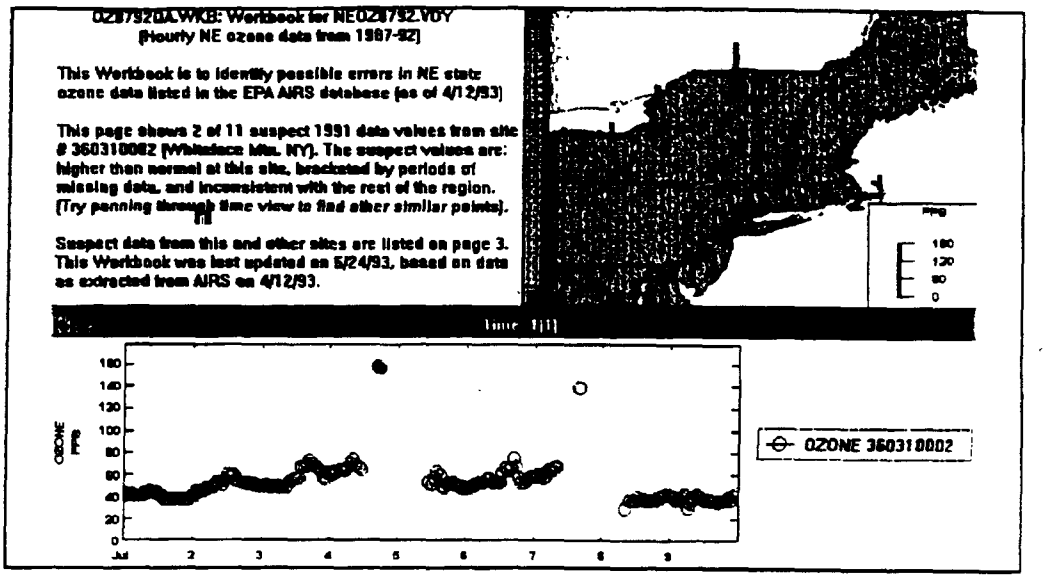


Figure 5-8.



The OZ8792QA.WKB workbook is dynamic - subject to continual revision as additional suspect data points are identified. Ultimately, these points are reported back to the original data generating state agencies - which can flag alter or eliminate the suspect data points from AIRS.

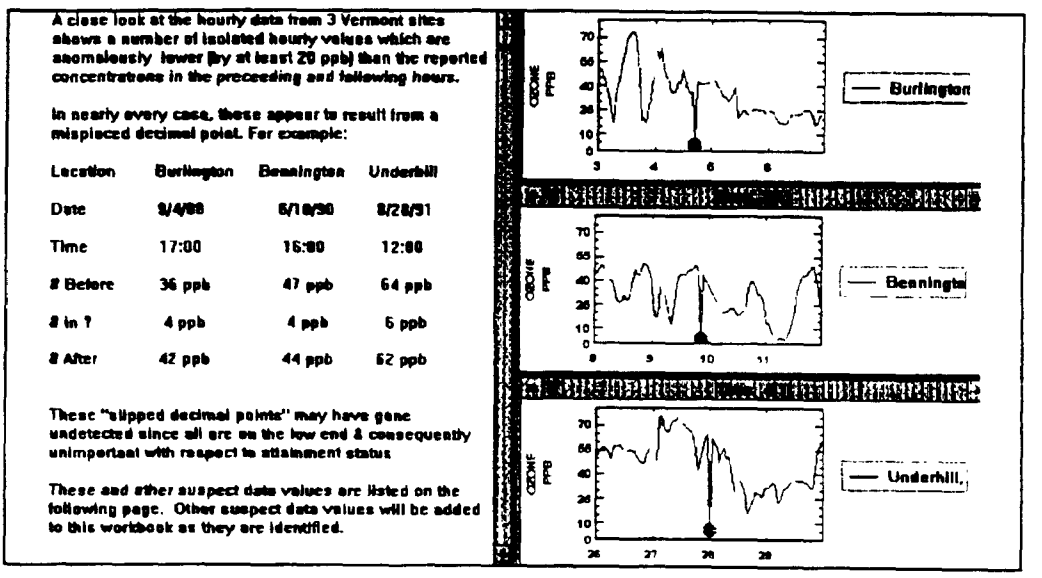
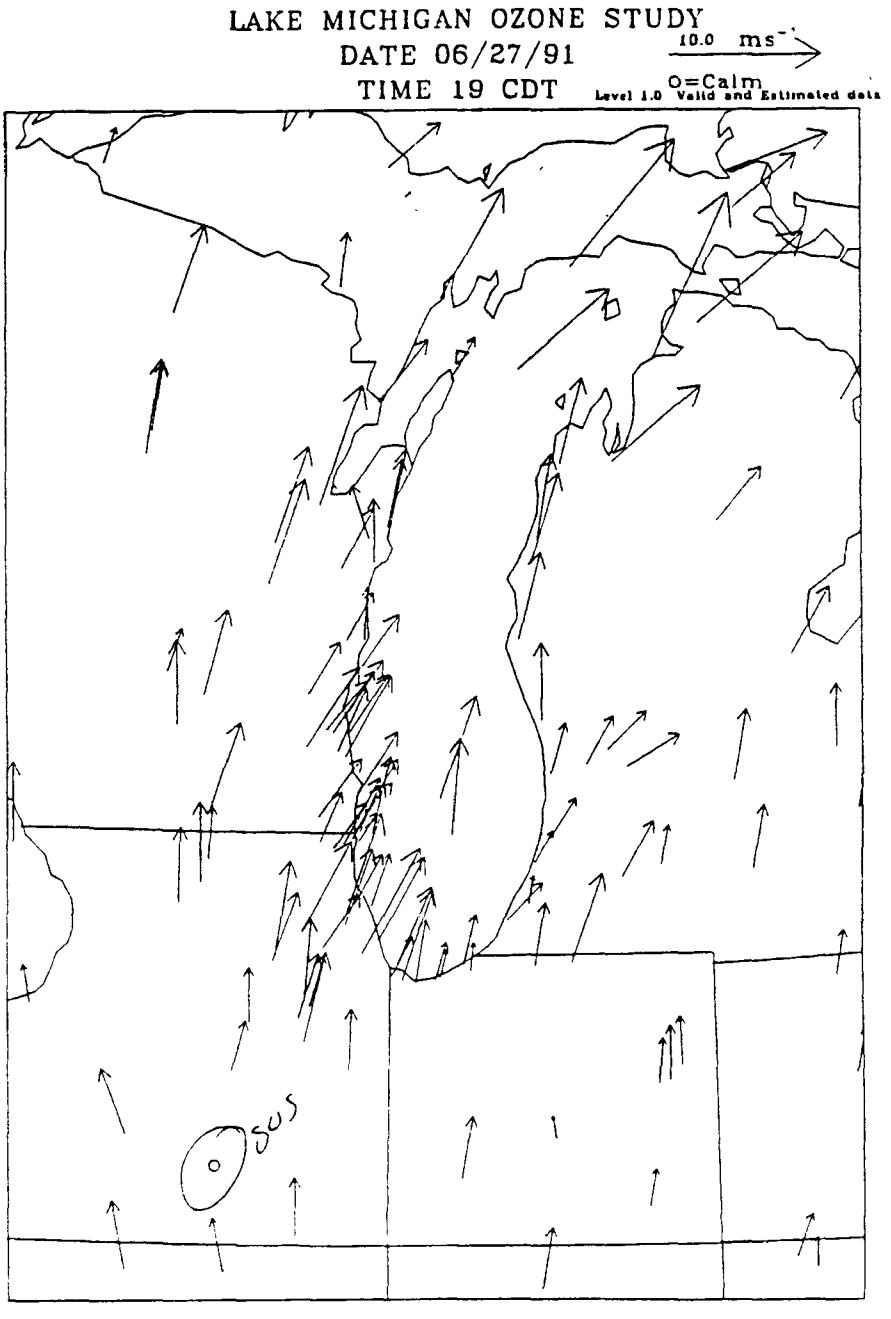
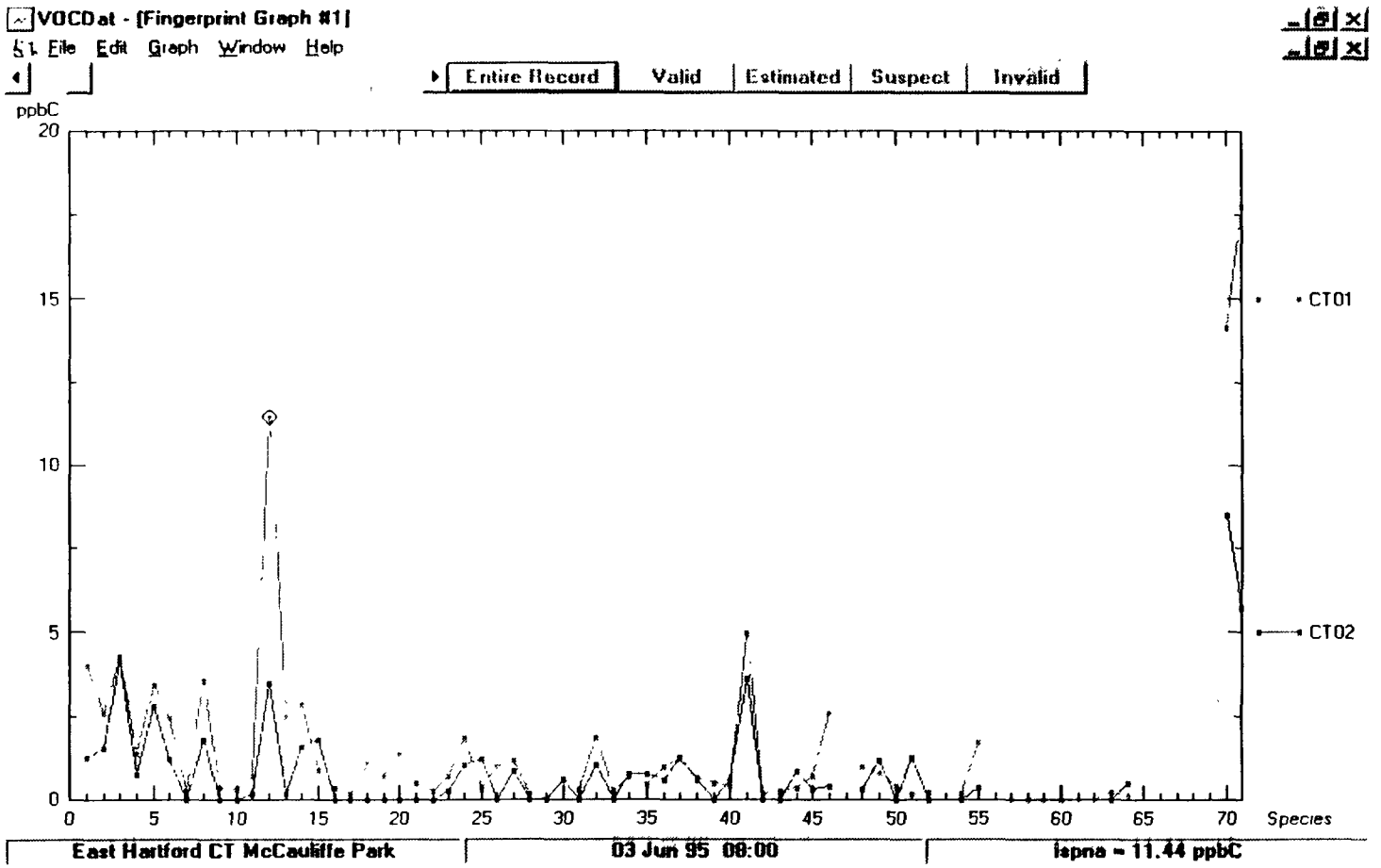


Figure 5-9.



Plot of surface winds on June 27, 1991 at 1900 CDT. The calm wind at Bloomington, Illinois was identified as suspect (SUS) during the data validation process. (Roberts et al., 1993)

Figure 5-10.



Fingerprint plot of June 3, 1994 at 0800 EST for Stafford and East Hartford, CT. This plot illustrates some of the differences between composition at the two sites. (Level 0, preliminary data, CT DEP)

Table 5-1. 90% Probability Limits for PAMS Target VOCs and Carbonyls Established by the 1993/1994 Proficiency Studies.

COMPOUND	AVERAGE BIAS	LOWER LIMIT	UPPER LIMIT
Ethylene	-13	-50	24
Acetylene	-9	-40	22
Ethane	-12	-35	11
Propylene	4	-27	35
Propane	-9	-40	22
Isobutane	-9	-34	16
1-Butene	-7	-44	30
n-Butane	-10	-34	14
trans-2-Butene	-6	-31	19
cis-2-Butene	-7	-29	15
3-Methyl-1-Butene	-6	-43	31
Isopentane	1	-29	31
1-Pentene	-6	-36	24
n-Pentane	-7	-29	15
trans-2-Pentene	4	-23	31
cis-2-Pentene	-9	-35	17
2-Methyl-2-Butene	9	-25	43
2,2-Dimethylbutane	-10	-33	13
Cyclopentene	-3	-24	18
4-Methyl-1-Pentene	-9	-42	24
Cyclopentane	-11	-35	13
2,3-Dimethylbutane	-5	-34	24
2-Methylpentane	-1	-28	26
3-Methylpentane	-6	-31	19
n-Hexane	-9	-30	12
trans-2-Hexene	-11	-42	20
cis-2-Hexene	-4	-30	22
Methylcyclopentane	-5	-32	22
2,4-Dimethylpentane	-8	-33	17
Benzene	-13	-37	11
Cyclohexane	-5	-29	19
2-Methylhexane	-3	-38	32
2,3-Dimethylpentane	-7	-31	17
3-Methylhexane	-7	-34	20
2,2,4-Trimethylpentane	-5	-31	21
n-Heptane	-8	-40	24
Methylcyclohexane	-3	-25	19
2,3,4-Trimethylpentane	-6	-33	21
Toluene	-1	-19	17
2-Methylheptane	-3	-32	26
3-Methylheptane	2	-21	25
n-Octane	-10	-47	27
Ethylbenzene	4	-35	43
m,p-Xylene	12	-42	66
Styrene	-4	-67	59
o-Xylene	-1	-51	49
n-Nonane	-6	-26	14
Isopropylbenzene	4	-46	54
n-Propylbenzene	-11	-67	45
1,3,5-Trimethylbenzene	6	-53	65
1,2,4-Trimethylbenzene	-11	-59	37
Formaldehyde - low	0	-22	23
Formaldehyde - high	-2	-24	20
Acetaldehyde - low	1	-21	24
Acetaldehyde - high	-2	-25	20
Acetone - low	1	-22	23
Acetone - high	-6	-29	16

Table 5-2. 95% Probability Limits of Bias (Precision) for PAMS Ozone Monitors, 1995.

Area	Site Type	AIRS ID	Year		Q1		Q2		Q3		Q4	
			lwr prb	upr prb	lwr prb	upr prb	lwr prb	upr prb	lwr prb	upr prb	lwr prb	upr prb
Boston	1	250051005	-3	4					-3	3	-2	4
	2	250092006	-10	8	-14	7	-9	2	-5	3	-3	13
	3	250094004	-6	4	-9	4	-4	1	-6	4	-4	6
	4	230052003	-5	2	-8	3	-5	1	-3	1	-4	1
Connecticut	2	090031003	-9	6			-11	4	-9	9	-2	2
	3	090131001	-7	3			-8	2	-3	3		
Portsmouth	2	230313002	-11	8			-9	11	-11	7	-12	5
Providence	1	090010017	-4	6			-5	4	-1	6	0	8
	2	440071010	-5	5			-2	2	-5	3	-7	11
	3	250051005	-3	4					-3	3	-2	4
Springfield	1	250130003	-10	7			-10	8	-11	4	-3	8
	2	250130008	-4	4	-7	7	-5	4	-3	3	-2	3
	3	250154002	-4	3			-4	5	-3	3	-3	0
New York	2	360050083	-6	6	-5	8	-9	7	-2	5	-3	2
Baltimore	1	240030019	-3	2	-2	1			-5	3	-3	3
	2	240053001	-4	2	-3	2	-3	1	-3	1	-5	3
	2	245100050	-4	4			-2	3	-6	5	-2	3
	3	240259001	-3	3			-3	5	-2	1	-3	2
	4	100031007	-10	11			-2	5	-14	13	-4	11
Philadelphia	1	100031007	-10	11			-2	5	-14	13	-4	11
	3	340210005	-4	4	-2	0	-5	4	-5	7	-4	4
Washington	1	510330001	-8	1			-9	-1	-6	1	-9	1
	3	240030019	-3	2	-2	1			-5	3	-3	3
	4	100031007	-10	11			-2	5	-14	13	-4	11
Atlanta	2	130890002	-6	4			-7	6	-6	1	0	2
	3	132470001	-1	11			-2	8	1	10	8	10
Lake Michigan	2	550790041	-6	3			-3	0	-6	6		
	2	170310072	-8	13			-13	15	-6	12	0	8
	2	180891016	-3	2			-4	2	-2	2		
	3	550890009	-8	8			-8	8	-9	9		
	4	170971007	-7	9	-21	0	-3	8	-4	8	-1	3
	4	550710007	-10	4			-3	4	-8	-3	-9	-2
Houston	2	482011035	-8	4	-11	0	-5	4	-4	5	-4	0
	2	482011003	-7	11	-2	17	-1	6	-8	6	-5	5
	3	482010024	-7	4	-5	2	-5	2	-11	8	-4	3
Baton Rouge	1	220330008	-3	10	-3	11	-3	7				
	2	220330009	-9	1	-6	0	-8	-3	-9	4	-8	0
	3	220470009	-5	7	-4	0	-1	8	1	7	-6	5
Beaumont	2	482450011	-6	10	-9	9	-2	12	-3	4	-4	7
El Paso	2	481410027	-8	2	-7	1	-6	1	-7	1	-11	5
	2	481410044	-12	13			-9	6	-9	16	-4	12
	3	481410037	-6	3	-4	1	-4	3	-3	0	10	4
South Coast/ SEDAB	2	060371601	-11	2	-11	-1	-11	0	-7	-5	-3	5
	3	060370002	-7	4	-4	3	-5	6	-8	2	-7	6
	2	060650002	-16	25	5	19	-6	23	-2	13	-30	11
	4	060711004	0	7	-2	4	2	8	2	5	1	5
San Diego	2	060730003	-6	6	-8	6	-5	7	-5	7		
	2	060730006	-8	4	-6	2	-7	4	-10	6		
	3	060731006	-6	5	-7	6	-3	4	-8	7		
Ventura Co.	2	061113001	-4	9	-1	2	-5	7	-2	11	-1	8
	3	061112002	-11	8	-16	14	-8	2	-13	7	-3	2
Sacramento	2	060670006	-5	8	-3	10					-2	1
	3	060671001	-12	0							-12	0
San Joaquin	2	060290010	-8	4	-5	1	-11	0	-8	7	-6	4
	2	060195001	-4	3	-4	3	-1	4	-4	3	-4	0
	3	060295001	-10	4	-9	0					-10	7
	3	060194001	-3	5	-1	4	1	4	-5	4	-1	4

Table 5-3. 95% Probability Limits of Bias (Precision) for PAMS NO_2 Monitors, 1995.

Area	Site Type	AIRS ID	Year		Q1		Q2		Q3		Q4	
			lwr prb	upr prb	lwr prb	upr prb	lwr prb	upr prb	lwr prb	upr prb	lwr prb	upr prb
Boston	2	250092006	-11	14	-2	12	-14	13	-2	14	-13	4
	3	250094004	-6	11	-2	14	-2	7	-11	8	-2	9
Connecticut	2	090031003	-9	9	-3	11	-13	13	-4	3	-8	3
	3	090131001	-10	2	-9	3	-11	2				
Portsmouth	2	230313002	-3	10					-3	10		
Providence	2	440071010	-9	3			-9	2	-8	3	-11	4
Springfield	1	250130003	-13	5							-13	5
	2	250130008	-16	13	-7	7	-10	13	-28	18	-14	7
	3	250154002	-17	6	-15	2	-14	4	-18	15	-14	-5
New York	2	360050083	-10	9			-13	5	-2	9	-8	4
Baltimore	1	240030019	-3	3			-4	3	-2	2		
	2	240053001	-4	7	-4	7	-5	7				
	2	245100050	-3	2			-5	3	-3	2	-3	3
	3	240259001	-4	5			-4	6	-4	4		
	4	100031007	-9	17	-6	10	-12	26	-8	13	0	10
Philadelphia	2	421010004	-6	5	-3	4	-7	6	-5	6	-6	6
	3	340210005	-6	7	-4	5	-4	3	-9	14	-5	3
Washington	1	510330001	-10	5	-7	6	-14	7	-7	2	-11	4
	3	240030019	-3	3			-4	3	-2	2		
	4	100031007	-9	17	-6	10	-12	26	-8	13	0	10
Atlanta	2	130890002	-15	9	-17	2	-10	0	-12	6	1	11
	3	132470001	-7	6	-8	2	-6	6	-7	9	-1	1
Lake Michigan	2	550790041	-8	7	-7	2	-6	8	-9	7	-8	11
	2	170310072	-17	9			-7	8	-19	7		
	2	180891016	-6	11	-2	6	-6	7	-7	7	-1	15
	3	550890009	-10	12			-13	13	-10	12		
	4	170971007	-7	15			-2	4	-6	20		
	4	550710007	-7	9			-9	9	-5	9		
Houston	2	482011035	-2	3	-3	4	-1	3	-3	4	-2	3
	3	482010024	-8	1	-4	0	-4	0	-11	1	-8	-2
Baton Rouge	1	220330008	-8	11	-11	10	1	8				
	2	220330009	-2	5	-2	3	-2	3	0	4	-2	8
	3	220470009	-2	8	0	6	-3	11	2	8	-2	5
El Paso	2	481410027	-13	7	-12	3	-9	0	-13	8	-13	5
	3	481410037	-12	8	-11	1	-8	3	-1	2	-18	19
South Coast/ SEDAB	2	060371601	-11	21	-21	18	-1	16	-6	10	3	24
	3	060370002	-12	8	-8	-3	-11	5	-12	11	-9	15
	4	060711004	-5	18	-5	10	-3	14	-2	24	1	8
San Diego	2	060730003	-14	20	0	15	-14	26	-11	-2		
	2	060730006	-4	17	-6	18	4	18	-3	7		
	3	060731006	-4	13	-4	7	-3	18	-1	11		
Ventura Co	2	061113001	-9	4	-5	3	-11	1	-7	2	-9	6
	3	061112002	-9	10	-11	9	-8	3	-9	13	-4	10
Sacramento	2	060670006	-4	14	-6	16					-3	14
	3	060671001	-9	10							-9	10
San Joaquin	2	060290010	-6	19	1	7	-7	5	9	15	13	15
	2	060195001	2	14	10	15	6	12	4	6	2	10
	3	060295001	-19	8	-16	-5					-13	12
	3	060194001	4	15	4	11	7	17	5	13	5	16