NORTH AMERICAN RESEARCH STRATEGY
for TROPOSPHERIC OZONE

North American Research Strategy for Tropospheric Ozone
NARSTO Northeast

ANALYSIS OF DATA FROM THE 1995 NARSTO-NORTHEAST STUDY VOLUME-III: CHEMICAL MASS BALANCE RECEPTOR MODELING

FINAL REPORT
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PREFACE

High ozone concentrations in the Northeast are the result of a complex interplay between precursor emissions and meteorological conditions. To better understand these factors, a major field data collection program was undertaken in the northeastern United States under the auspices of NARSTO-Northeast. NARSTO (the North American Research Strategy for Tropospheric Ozone) is a public/private partnership formed to conduct research on ground-level ozone concentrations in North America. While most data collection efforts during NARSTO-Northeast were focussed within and just to the west of the urban corridor running from Washington, DC to Boston, the study area included all of New England and stretched as far west as Ohio and as far south as southern Virginia. An extensive database of routine and supplemental surface and upper-air meteorological and air quality observations was compiled as a result of this effort. Among the many key features of this database are the extensive speciated VOC measurements taken both at the surface and aloft.

The NARSTO-Northeast database offers a unique opportunity to study the factors influencing ozone formation in this part of the country. In recognition of this opportunity, in 1996 the Coordinated Research Council (CRC) launched a multi-component data analysis project which represents the first comprehensive look at the NARSTO-Northeast data. Major objectives of these data analyses were to summarize the validated NARSTO Northeast data and to draw conclusions regarding mechanisms of ozone formation and transport in the Northeast, especially with respect to the relative importance of VOC and NO_X emissions, the role of transported ozone and precursors, and the importance of biogenic VOC and regional NO_X.

Results of the CRC NARSTO Northeast data analysis project are presented in five volumes:

Analysis of Data from the 1995 NARSTO-Northeast Study. Volume-I: Data Validation and Statistical Summaries of Routine Data. T.E. Stoeckenius et al., ENVIRON International Corporation, Novato, CA. and Main et al., Sonoma Technology Inc., Santa Rosa, CA., 1998.

Analysis of Data from the 1995 NARSTO-Northeast Study. Volume-II: Use of PAMS Data to Evaluate a Regional Emission Inventory. T.L.Haste et al., Sonoma Technology Inc. Santa Rosa, CA., March 1998.

Analysis of Data from the 1995 NARSTO-Northeast Study. Volume-III: Chemical Mass Balance Receptor Modeling. E.Fujita et al., Desert Research Institute, Reno, NV., 1998.

Analysis of Data from the 1995 NARSTO-Northeast Study. Volume-IV: Observation-Driven Methods for Delineating VOC and NO_X Limitation. C.Blanchard, Envair, Albany, CA., February 1998.

Analysis of Data from the 1995 NARSTO-Northeast Study. Volume-V: Three-Dimensional Analysis of Aircraft and Upper-Air Meteorological Data. P.T.Roberts et al., Sonoma Technology Inc. Santa Rosa, CA., 1998.

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1 INTRODUCTION

In the summer of 1995, a field measurement program was carried out in the northeastern United States as part of NARSTO-Northeast Study. The purpose of NARSTO-Northeast is to develop a comprehensive air quality and meteorological database for the northeastern United States that can be used to enhance the understanding of the relationship between emissions and spatial and temporal distributions of pollutants so that air quality simulation models, and ultimately, air quality management strategies can be more definitively applied or improved. NARSTO-NE represents one regional aspect of the North American Research Strategy for Tropospheric Ozone (NARSTO), which is a joint effort among governmental and non-governmental organizations in Canada, the United States, and Mexico. The prospectus for NARSTO-Northeast (Mueller et al., 1995) specifies the technical objectives and field measurement plan. Roberts et al. (1995) documented the observations made during the summer of 1995. An important component of NARSTO-NE was the acquisition of speciated hydrocarbon and carbonyl compound data, which are used to evaluate emission inventory input data and photochemical model performance, to specify photochemical model boundary and initial conditions, and to attribute source contributions through receptor modeling. This report describes the application of the Chemical Mass Balance (CMB) receptor model to the speciated hydrocarbon data obtained during the NARSTO-Northeast Air Quality Study.

During the summer 1995 field study, hydrocarbon and carbonyl samples were collected on 23 days of intensive operations. Four three-hour (beginning at 0600, 0900, 1200, and 1500 EDT) and two six-hour (beginning at 0000 and 1800 EDT) ground-level canister samples were collected on intensive operational periods (IOPs) at five sites (Holbrook, PA, Arendtsville, PA, Kunkletown, PA; Truro, MA, and Brookhaven National Laboratory, NY) by Environmental Science and Engineering (ESE) and at one site (Shenandoah National Park, VA) by the University of Maryland (UofMD). These samples were shipped to Biospheric Research Corporation (BRC) for analysis of C_2 to C_{10} hydrocarbons. Total hydrocarbon values are sums of all FID chromatographic peaks (including unidentified peaks) increasing in molecular weight up to n-decane, except peaks verified to be oxygenated or halogenated compounds. Approximately half of the samples that were collected were selected for analysis including samples collected on June 17-20, July 11-16, July 25-26, July 31-August 3, August 10-11, August 21, and August 31. Hydrocarbon grab samples were also collected three times per day at 0900, 1200, and 1500 EDT at Pinnacles State Park, Whiteface Mountain, and Loudonville, NY by the State University of New York at Albany (SUNYA) on non-IOP days until October 1. In addition, integrated three-hour samples were collected five or six times per day at the Pinnacles State Park and Loudonville sites on IOP days. All of these samples were analyzed by SUNYA. Continuous automated gas chromatographs were collocated with canister samples at Arendtsville (operated by Pennsylvania Department of Environmental Protection) and at Loudonville (operated by the New York Department of Environmental Conservation).

Carbonyl samples were collected during the field study using dinitrophenylhydrazine (DNPH)- impregnated C18 Sep-Pak cartridges, coated by Kochy Fung of Atmospheric

Assessment Associates (AtmAA). Three-hour samples were collected four times per day at 0600-0900, 0900-1200, 1200-1500, 1500-1800 EDT and six-hour samples were collected twice per day at 0000-0600 and 1800-2400 EDT on 19 days (matching the hydrocarbon sampling schedule) at four surface air quality and meteorological research sites (Holbrook, PA, Arendtsville, PA, Truro, MA, and Brookhaven National Laboratory, NY) by ESE and sent to AtmAA for analysis of C_1-C_7 carbonyl compounds. In parallel with the hydrocarbon measurements, approximately half of the carbonyl samples were analyzed.

In addition to the measurements made specifically for NARSTO-Northeast, hydrocarbon and carbonyl measurements were made during the summer of 1995 by state and local air pollution control agencies at twenty and nine PAMS (Photochemical Assessment Monitoring Stations) sites, respectively. Table 1-1 lists the PAMS sites along with the site type, measurement methods and frequency of measurements associated with each site. The 56 PAMS target hydrocarbons are listed on Table 1-2. The PAMS total hydrocarbon values are sums of all FID chromatographic peaks (including unidentified peaks) increasing in molecular weight up to n-undecane. This total is referred to here as nonmethane organic compounds (NMOC) because these values do not exclude all oxygenated or halogenated compounds that produce an FID signal. The definition of NMOC is operational, and reflects the selectivity and sensitivity of the analytical and data processing methods that are applied by different groups.

In this study, a beta test version CMB Version 8 was applied to over 15,000 hydrocarbon samples from ten PAMS sites in the NARSTO-Northeast study area. These sites include eight PAMS sites in source areas (E. Hartford, CT; McMillan Reservoir, DC; Chicopee, MA; Lynn, MA; Lake Clifton, MD; Bronx, NY; Philadelphia, PA; and E. Providence, RI) and two downwind PAMS sites (Lums Pond, DE and Rider College, NJ). Additionally, the CMB modeling was applied to a total of 512 surface and 106 aircraft canister samples collected during the NARSTO-Northeast Intensive Operational Periods. A diesel and running evaporative loss-corrected vehicle exhaust composition profile was derived for this study from measurements taken by the Desert Research Institute during the summer of 1995 in the Lincoln Tunnel in New York and the Callahan Tunnel in Boston. Other fuel, stationary, and area source composition profiles were compiled from published sources. Alternative source composition profiles were applied to test the sensitivity of the source contribution estimates and model performance to alternative profiles and to address uncertainties in model output. The residual mass that is not accounted for by the default set of source profiles used in the apportionment provides an estimate of the nonmotor vehicle emission source contribution.

1.1 Objectives and Scope of Work

Perform receptor modeling analysis with the Chemical Mass Balance model on speciated hydrocarbon data from canister samples collected during the NARSTO-Northeast intensive operating period days and from all valid samples collected during June – August, 1995 at up to ten of the Photochemical Assessment Monitoring Stations located in the NARSTO-Northeast study region. Specific tasks include:

Table 1-1
PAMS Sites in NARSTO-Northeast Study Area

State Site	Type of Site	Measurement Method		Frequency of VOC Measurements	
		Hydrocarbons	Carbonyl Compounds	Hydrocarbons	Carbonyl Compounds
Conneticut					
E. Hartford	2	Auto-GC	DNPH/HPLC		a
Stafford	3	Auto-GC			
Maine					
Cape Elizabeth	3	Auto-GC			
Kittery	2	Auto-GC	DNPH/HPLC		e
Massechusettes					
Lynn	2	Auto-GC	DNPH/HPLC		c
Newbury	3	Auto-GC			
Chicopee	2	Auto-GC	DNPH/HPLC		c
Ware (Quabbin Summit)	3	Auto-GC			
Agawam	1	Canister/GC-FID		d	
Borderland	1,3	Canister/GC-FID		d	
Rhode Island					
E. Providence	2	Canister/GC-FID	DNPH/HPLC	e,f	c
New Jersey					
Rider College	3	Auto-GC			
New York					
Bronx	2	Auto-GC	DNPH/HPLC		c
Pennsylvania					
Philadelphia	2	Canister/GC-FID	DNPH/HPLC	e	c
Delaware					
Lums Pond State Park	1,4	Auto-GC			
Maryland					
Lake Chifton	2	Both	DNPH/HPLC	g	c
Fort Meade	1,3	Canister/GC-FID		d	
Aldino	3	Canister/GC-FID		d	
District of Columbia					
Washington	2	Auto-GC	DNPH/HPLC		c
Virginia					
Corbin	1	Canister/GC-FID		d,g	

Type 1 - Upwind background.
Type 2 - Maximum precursor emissions (typically located immediately downwind of the central business district).
Type 3 - Maximum ozone concentration.
Type 4 - Extreme downwind transported ozone area that may contribute to overwhelming transport in other areas.
a - Cartridges collected every third day (four 3-hr samples from 0600 to 1800 EDT and two 6-hr samples from 1800 to 0600 EDT).
b - Cartridges collected every third day (eight 3-hr samples).
c - Cartridges collected every day (eight 3-hr samples).
d - Canisters collected every third day (eight 3-hr samples).
e - Canisters collected every day (eight 3-hr samples).
f - All the samples are analyzed with GC/FID and GC/MS.
g - Canister collected every sixth day (24-hr samples).

Table 1-2
Target Ozone Precursors for PAMS

1	Ethylene	29	2,3-Dimethylpentane
2	Acetylene	30	3-Methylhexane
3	Ethane	31	2,2,4-Trimethylpentane
4	Propene	32	n-Heptane
5	Propane	33	Methylcyclohexane
6	Isobutane	34	2,3,4-Trimethylpentane
7	1-Butene	35	Toluene
8	n-Butane	36	2-Methylheptane
9	trans-2-Butene	37	3-Methylheptane
10	cis-2-Butene	38	n-Octane
11	Isopentane	39	Ethylbenzene
12	1-Pentene	40	m&p-Xylene
13	n-Pentane	41	Styrene
14	Isoprene	42	o-Xylene
15	trans-2-Pentene	43	n-Nonane
16	cis-2-Pentene	44	Isopropylbenzene
17	2,2-Dimethylbutane	45	n-Propylbenzene
18	Cyclopentane	46	1-ethyl 3-methylbenzene
19	2,3-Dimethylbutane	47	1-ethyl 4-methylbenzene
20	2-Methylpentane	48	1,3,5-Trimethylbenzene
21	3-Methylpentane	49	1-ethyl 2-methylbenzene
22	2-Methyl-1-Pentene	50	1,2,4-Trimethylbenzene
23	n-Hexane	51	n-decane
24	Methylcyclopentane	52	1,2,3-Trimethylbenzene
25	2,4-Dimethylpentane	53	m-diethylbenzene
26	Benzene	54	p-diethylbenzene
27	Cyclohexane	55	n-undecane
28	2-Methylhexane		Total NMOC

1. Develop representative source profiles: examine the availability, quality, and applicability of speciated hydrocarbon source profiles for use in the analysis; consider profiles previously developed as part of the COAST study conducted along the Texas Gulf coast, motor vehicle profiles derived from tunnel/roadway studies (including but not necessarily limited to studies conducted in the Callahan Tunnel in Boston, the Lincoln Tunnel in New York, the Tuscarora Tunnel in Pennsylvania, the Fort McHenry Tunnel in Baltimore, and the Thomas P. O'Neill Federal Building parking garage in Boston) and published dynamometer tests results as well as profiles contained in or derived from EPA's SPECIATE database.

2. Test source profiles using a subset of the ambient speciated hydrocarbon data, evaluate sensitivities to assumptions, and select the optimum set of source profiles and fitting species.

3. Apply the Chemical Mass Balance model to the canister data collected during the NARSTO-Northeast Intensive Operational Periods and hourly (or, where appropriate, 3-hourly) data for June-August from up to 10 PAMS sites located in the NARSTO-Northeast study region.

4. Interpret results of the analysis: examine model output statistics (source contribution estimates, collinearity indicators, chi-square, R2, MPIN); determine diurnal and spatial variations in source contributions; compare source apportionment results with source contributions in the emission inventory.

5. Prepare a draft report describing the data and procedures used, results obtained, and conclusions drawn from the work described above. Prepare a final report reflecting comments received on the draft.

2 CHEMICAL MASS BALANCE RECEPTOR MODELING

The Chemical Mass Balance (CMB) receptor model (Friedlander, 1973) uses the chemical and physical characteristics of gases and particles measured at source and receptor to both identify the presence of and to quantify source contributions of pollutants measured at the receptor. The CMB model consists of a least-squares solution to a set of linear equations that expresses each receptor concentration of a chemical species as a linear sum of products of source profile species and source contributions. The source profile species (the fractional amount of each species in the VOC emissions from a given source type) and the receptor concentrations, each with uncertainty estimates, serve as input data to the CMB model. The output consists of the contributions of each source type to both total and individual ambient VOC concentrations. The model calculates values for contributions from each source and the uncertainties of those values. Input data uncertainties are used both to weight the relative importance of the input data to the model solution and to estimate uncertainties of the source contributions.

2.1 Fundamentals

The CMB procedure requires: 1) identification of the contributing source types; 2) selection of chemical species to be included; 3) estimation of the fractions of each chemical species contained in each source type; 4) estimation of the uncertainties to both ambient concentrations and source compositions; and 5) solution of the chemical mass balance equations. The CMB model assumes that: 1) compositions of source emissions are constant over the period of ambient and source sampling; 2) chemical species do not react with each other, i.e., they add linearly; 3) all sources with a potential for significant contribution to the receptor have been identified and have had their emissions characterized; 4) the source compositions are linearly independent of each other; 5) the number of source categories is less than or equal to the number of chemical species; and 6) measurement uncertainties are random, uncorrelated, and normally distributed. These assumptions are fairly restrictive and will never be totally complied with in actual practice. Fortunately, the CMB model can tolerate deviations from these assumptions, though these variations increase the stated uncertainties of the source contribution estimates.

Source contribution estimates (SCE) are the main output of the CMB model. The sum of these concentrations approximates the total mass concentrations. Negative SCE are not physically meaningful, but can occur when a source profile is collinear with another profile or when the source contribution is close to zero. Collinearity is usually identified in the similarity/uncertainty cluster display. When the SCE is less than its standard error, the source contribution is undetectable. Two or three times the standard error may be taken as the upper limit of the SCE in this case. There is about a 66% probability that the true source contribution is within one standard error and about a 95% probability that the true concentration is within two standard errors of the SCE. The reduced chi square (χ^2), R^2, and percent mass are goodness of fit measures for the least-squares calculation. The χ^2 is the weighted sum of squares of the differences between calculated and measured fitting species concentrations. The weighting is inversely proportional to the squares of the precision in the

source profiles and ambient data for each species. Ideally, there would be no difference between calculated and measured species concentrations and χ^2 would be zero. A value of less than one indicates a very good fit to the data, while values between 1 and 2 are acceptable. χ^2 values greater than 4 indicate that one or more of the fitting species concentrations are not well-explained by the source contribution estimates. R^2 is determined by the linear regression of the measured versus model-calculated values for the fitting species. R^2 ranges from 0 to 1. The closer the value is to 1.0, the better the SCEs explain the measured concentrations. When R^2 is less than 0.8, the SCEs do not explain the observations very well with the given source profiles. Percent mass is the percent ratio of the sum of model-calculated SCEs to the measured mass concentration. This ratio should equal 100%, though values ranging from 80 to 120% are acceptable.

CMB software applies the effective variance solution developed and tested by Watson et al. (1984). This method gives greater influence in the solution to chemical species that are measured more precisely in both source and receptor samples, and calculates uncertainties for source contributions from both the source and receptor uncertainties. The software also incorporates collinearity measures (Henry, 1982, 1992) to assess the effects of source profile similarity on source contribution estimates and their standard errors. The software is interactive, allowing many sensitivity and assumptions-testing calculations to be performed rapidly.

2.2 CMB Version 8

CMB Version 8 was applied to NARSTO-Northeast source apportionments. CMB8 (Watson et al., 1997) replaces CMB7 (U.S. EPA, 1989; Watson et al., 1990) as a more convenient method of estimating contributions from different sources to ambient chemical concentrations. CMB8 returns the same results of CMB7, but it operates in a Windows-base environment and accepts inputs and creates outputs in a wider variety of formats than CMB7. The major CMB8 enhancements are:

- Windows-based, menu-driven operations: CMB commands may be executed with hot-keys, drop down menus, or toolbar buttons.
- Multiple defaults for fitting source, fitting species, and sample selection: Up to ten combinations of fitting source profiles and fitting species may be specified in input data selection files. Different defaults can be selected with radio buttons during CMB8 operation. Subsets of source profiles, species, and samples may be specified in selection files to be selected from profile and ambient concentration data files.
- Improved memory management: CMB8 memory is limited only by the available RAM on the computer, not by pre-set memory limitations.
- Flexible input and output formats: Comma-separated value (CSV), xBASE (DBF), and worksheet (WKS) formats are support as input and output files, in addition to the blank-delimited ASCII text files (TXT) supported by CMB7.

- Improved graphics: Sample pie plots, spatial pie plots, time series stacked bar charts, source profile bar charts, and ambient concentration bar charts can be created within CMB8. These can be cut from their CMB8 windows and pasted into other Windows documents.
- Improved collinearity diagnostics: The uncertainty/similarity clusters have been replaced with a singular value composition eligible space treatment that allows the user to define an acceptable error and an acceptable collinearity among weighted source profiles.
- Automatic decision-making: CMB8 calculations can be automated to eliminate negative contributions and to select a default set of profiles based on a weighted optimization of performance measures.
- User-set preferences: Output directories, output file names, positions of decimal points in output, output formats, automatic calculation alternatives, performance measure weights, eligible space tolerances, receptor concentration units, and maximum iterations for convergence can be set by the user.
- Retention from previous sessions: Options and window position preferences established in one session are carried over into subsequent sessions.

The source apportionments for this project were performed using a beta version of CMB Version 8. In a previous study, we applied CMB Version 7 to a subset of the ambient samples to verify that both versions of the model yield the same results (Fujita et al., 1997).

2.3 Evaluation of Ambient Data and Candidate Fitting Species

The NARSTO-Northeast hydrocarbon data have been extensively reviewed as part of the quality assurance program for NARSTO-Northeast and through level 2 validation checks performed during this present study by investigators at ENVIRON and Sonoma Technology, Inc. Fujita et al. (1997) described the external quality assessment of the NARSTO-Northeast speciated hydrocarbon and carbonyl compound measurements. As part of the quality assurance program, a laboratory comparison study was conducted for measurement of speciated hydrocarbons. It consisted of two synthetic samples used by the Environmental Protection Agency, (EPA) in the Photochemical Assessment Monitoring Station (PAMS) program, and two ambient samples collected by EPA in the Research Triangle Park area. Participants include the two laboratories involved in the NARSTO-NE Intensive Operational Periods, Biospheric Research Corporation (BRC) and State University of New York at Albany (SUNYA), EPA Region I, and eight of the Photochemical Assessment Monitoring Station (PAMS) networks in the northeastern U.S. (Maine, Connecticut, Massachusetts, Maryland, City of Philadelphia, New Jersey, New York, and Virginia). The Desert Research Institute (DRI), which conducted measurements in roadway tunnels in New York and Boston during the summer of 1995 participated in the performance audits. The National Exposure Research Laboratory, (Atmospheric Processes Research Division) of EPA served as the reference laboratory and DRI provided coordination and data analysis. The audits were conducted to document significant systematic biases that may exist among participating

laboratories so that these differences may be taken into account during subsequent data validation and analysis for the NARSTO-NE Study.

In general, the values reported by the audited laboratories were well correlated with the values obtained by EPA. BRC, SUNYA, DRI, CT, NJ, NY, and Philadelphia reported values within 10 percent of EPA for all four audit samples. MA and MD values agree well with EPA for ambient samples, but are slightly greater than 10 percent for synthetic mixtures. Mean values greater than 1.0 ppbC with Laboratory/EPA ratio greater than 0.7 and less than 1.3 were used for determining calibration bias in order to minimize the effect of inconsistent chromatographic peak identifications on the correlations. The average number of inconsistently identified peaks (i.e., percentage of data pairs with mean concentrations greater than 1.0 ppbC with Laboratory/EPA ratio less than 0.7 and greater than 1.3) for the four audit samples were less than 10 percent for DRI, MD, and NJ, 10 to 20 percent for BRC, CT, MA, and Philadelphia, and 20 to 30 percent for SUNYA and NY. Coeluting peaks were the cause for the higher percentage of inconsistencies in peak identifications. The sum of the PAMS target compounds and total NMHC in the PAMS region of the chromatogram reported by the audited laboratories were generally within 10 percent of the corresponding EPA values.

A prerequisite for using receptor models is that the relative proportions of chemical species change little between source and receptor. Most ambient NMHCs are oxidized in the lowest 2 km of the troposphere with tropospheric lifetimes ranging from hours to several months. For the CMB calculations performed in this study, only species with lifetimes in the atmosphere greater than that of toluene (~9 hours during the summer) were used as fitting species. An exception to this is isoprene. It was included as a fitting species despite its high reactivity because it serves as a marker for biogenic emissions. Among the PAMS target species, 31 hydrocarbons satisfy the reactivity criteria defined above and are candidates for use as fitting species (shown in Table 2-1).

Beyond reactivity considerations, fitting species must be consistently identified and measured above its detection limit. Table 2-2 shows the percentage of valid measurements by species at the ten PAMS sites based upon the level 2 validation checks performed by ENVIRON and STI. Invalid samples (based on validation flags applied by STI) were not used in the CMB modeling. For valid samples, the numbers of valid species are fairly consistent from sample to sample at each site. Table 2-3 shows the default set of fitting species used in the CMB calculations. The sum of unidentified species was added to the list of fitting species for NARSTO Northeast surface and airborne samples in order to account for the higher fractions of unidentified species relative to PAMS samples. The NARSTO Northeast samples were collected in rural downwind sites. These samples tend to be more photochemically aged and generally have greater amounts of unidentified species relative to samples from Type 2 PAMS sites that are located in urban/suburban areas. The use of dryers by PAMS analytical laboratories to remove moisture from the sample prior to chromatographic analysis, also removes most of the oxygenated organic compounds that would otherwise be quantified with the unidentified fraction. Dryers were not used by BRC in the analysis of the NARSTO Northeast samples. Table 2-4 indicates the numbers of valid samples from each monitoring site that were used in the CMB modeling.

Table 2-1. Target List of Hydrocarbons for Photochemical Assessment Monitoring Stations

	Mnemonics[1]	Names		Mnemonics[1]	Names
	NMHC	total non-methane hydrocarbon	*	TOLUE	toluene
*	ETHANE	ethane	*	HEP2ME	2-methylheptane
	ETHENE	ethene	*	HEP3ME	3-methylheptane
*	ACETYL	acetylene	*	N_OCT	n-octane
	LBUT1E	1-butene		ETBZ	ethylbenzene
	LIBUTE	isobutylene		MP_XYL	mp-xylene
	PROPE	Propene		STYR	styrene
*	N_PROP	n-propane		O_XYL	o-xylene
*	I_BUTA	isobutane	*	N_NON	n-nonane
*	N_BUTA	n-butane		IPRBZ	isopropylbenzene
	T2BUTE	t-2-Butene		N_PRBZ	n-propylbenzene
	C2BUTE	c-2-butene		M_ETOL	m-ethyltoluene
*	IPENTA	isopentane		P_ETOL	p-ethyltoluene
	PENTE1	1-pentene		BZ135M	1,3,5-trimethylbenzene
*	N_PENT	n-pentane		O_ETOL	o-ethyltoluene
*	I_PREN	isoprene		BZ124M	1,2,4-trimethylbenzene
	T2PENE	t-2-Pentene	*	N_DEC	n-decane
	C2PENE	c-2-pentene		BZ123M	1,2,3-trimethylbenzene
	B2E2M	2-methyl-2-butene		DETBZ1	m-diethylbenzene
*	BU22DM	2,2-dimethylbutane		DETBZ2	p-diethylbenzene
	CPENTE	cyclopentene	*	N_UNDE	n-undecane
	P1E4ME	4-methyl-1-pentene		UNID	Unidentified
*	CPENTA	cyclopentane			
*	BU23DM	2,3-dimethylbutane			
*	PENA2M	2-methylpentane			
*	PENA3M	3-methylpentane			
	P1E2ME	2-methyl-1-pentene			
*	N_HEX	n-hexane			
	T2HEXE	t-2-Hexene			
	C2HEXE	c-2-hexene			
*	MCYPNA	Methylcyclopentane			
*	PEN24M	2,4-dimethylpentane			
*	BENZE	benzene			
*	CYHEXA	cyclohexane			
*	HEXA2M	2-methylhexane			
*	PEN23M	2,3-dimethylpentane			
*	HEXA3M	3-methylhexane			
*	PA224M	2,2,4-trimethylpentane			
*	N_HEPT	n-heptane			
*	MECYHX	methylcyclohexane			
*	PA234M	2,3,4-trimethylpentane			

[1]: Species with '*' before them are used as fitting species in CMB calculations.

Table 2-2
Percentage of Valid Measurements for theTen PAMS Sites

	RI	DC	MD	PA	DE	MA_Chi.	MA_Lynn	CT	NJ	NY
TNMOC	90	96	65	78	85	65	94	87	94	75
ACETYL	92	96	65	78	85	47	94	88	94	83
ETHENE	92	96	65	78	85	48	94	88	94	83
ETHANE	92	96	65	78	85	65	94	88	94	83
PROPE	92	96	65	78	85	51	94	88	94	83
N_PROP	92	96	65	78	85	65	94	88	94	83
I_BUTA	92	96	65	78	85	55	93	88	94	83
LBUT1E	92	96	65	78	85	18	75	88	94	83
N_BUTA	92	96	65	78	85	59	94	88	94	83
T2BUTE	92	96	65	78	85	11	94	88	94	83
C2BUTE	92	96	65	78	85	11	78	88	94	83
B1E3ME		96		78		1		88	94	83
IPENTA	92	95	65	78	85	65	94	88	94	83
PENTE1	92	96	65	78	85	38	69	88	94	83
N_PENT	92	96	65	78	85	65	94	88	94	83
I_PREN	92	96	65	78	85	59	92	88	94	83
T2PENE	92	96	65	78	85	20	73	88	94	83
C2PENE	92	96	65	78	85	10	44	88	94	83
B2E2M				78				88	94	83
BU22DM	92	96	65	78	85	56	94	88	94	83
CPENTE				78				88	94	83
P1E4ME		96		78				88	94	83
CPENTA	92	96	65	78	85	62	81	88	94	83
BU23DM	92	96	65	78	85	58	94	88	94	83
PENA2M	92	95	65	78	85	62	94	88	94	83
PENA3M	92	95	65	78	85	50	94	88	94	83
P1E2ME	92	96		78	85	14	45	88	94	72
N_HEX	92	96	65	78	85	52	90	88	94	75
T2HEXE		96		78				88	94	75
C2HEXE		96		78				88	94	75
MCYPNA	92	96	65	78	85	29	72	88	94	75
PEN24M	92	96	65	78	85	11	45	88	94	75
BENZE	92	96	65	78	85	54	93	88	94	75
CYHEXA	92	96	65	78	85	12	37	88	94	75
HEXA2M	92	96	65	78	85	34	78	88	94	75
PEN23M	92	96	65	78	85	27	83	88	94	75
HEXA3M	92	96	65	78	85	37	84	88	94	75
PA224M	92	96	65	78	85	60	92	88	94	75
N_HEPT	92	96	65	78	85	32	83	88	94	75
MECYHX	92	96	65	78	85	20	71	88	94	75
PA234M	92	96	65	78	85	30	85	88	94	75
TOLUE	92	96	65	78	85	64	94	88	94	75
HEP2ME	92	96	65	78	85	19	74	88	94	75
HEP3ME	92	96	65	78	85	19	89	88	94	75

Table 2-2 (continued)
Percentage of Valid Measurements for theTen PAMS Sites

	RI	DC	MD	PA	DE	MA_Chi.	MA_Lynn	CT	NJ	NY
N_OCT	92	96	65	78	85	27	80	88	94	75
ETBZ	92	96	65	78	85	53	93	88	94	75
MP_XYL	92	96	65	78	85	60	94	88	94	75
STYR	92	96	65	78	85	39	81	87	94	75
O_XYL	92	96	65	30	85	53	94	88	94	75
N_NON	92	96	65	78	85	39	92	88	94	75
IPRBZ	92	96	65	78	85	1		88	94	75
N_PRBZ	92	96	65	78	85	30	83	88	94	75
APINEN				78					94	
BZ135M	92	96	65	78	85	33	89	88	94	75
BZ124M	92	96	65	78	85	57	94	87	94	75
O_ETOL	92		65		85	23	86	84		66
M_ETOL	92		65		85	40	93	88		66
P_ETOL	92		65		85	24	56	87		66
DETBZ1	92	96	65			11	74	88		66
DETBZ2	92	96	65		85	14	81	88		66
BZ123M	92	96	65		85	56	93	87		66
N_DEC	92	96	65	78	85	55	94	87	94	75
N_UNDE	92	96	65		85	56	94	87	94	66
UNID	90	95	65	28	85	64	94	87	93	75
TEMP			57		88	98	0		60	84
WS			57		88	99	52		60	85
WD			57		88	99	52		60	85

Table 2-3
Default Fitting Species Used in CMB Modeling

	Auto-GC	Surface	Air		Auto-GC	Surface	Air
ETHANE	*	*	*	N_HEPT	*	*	*
ETHENE				MECYHX	*	*	*
ACETYL	*	*	*	PA234M	*	*	*
LBUT1E				TOLUE	*	*	*
PROPE				HEP2ME	*	*	*
N_PROP	*	*	*	HEP3ME	*	*	*
I_BUTA	*	*	*	N_OCT	*	*	*
N_BUTA	*	*	*	ETBZ			
T2BUTE				MP_XYL			
C2BUTE				STYR			
IPENTA	*	*	*	O_XYL			
PENTE1				N_NON	*	*	*
N_PENT	*	*	*	IPRBZ			
I_PREN	*	*	*	N_PRBZ			
T2PENE				M_ETOL			
C2PENE				P_ETOL			
B2E2M				BZ135M			
BU22DM	*	*	*	O_ETOL			
CPENTE				BZ124M			
P1E4ME				N_DEC	*	*	*
CPENTA	*	*	*	BZ123M			
BU23DM	*	*	*	DETBZ1			
PENA2M	*	*	*	DETBZ2			
PENA3M	*	*	*	N_UNDE	*	*	*
P1E2ME				UNID		*	*
N_HEX	*	*	*				
T2HEXE							
C2HEXE							
MCYPNA	*	*	*				
PEN24M	*	*	*				
BENZE	*	*	*				
CYHEXA	*	*	*				
HEXA2M	*	*	*				
PEN23M	*	*	*				
HEXA3M	*	*	*				
PA224M	*	*	*				

Table 2-4
Numbers of Valid Hydrocarbon Samples

Site	Analysis Laboratory	Method	Duration	Valid Samples
PAMS				
E. Hartford	Connecticut DEP	auto-GC	hourly	1,313
McMillan Reservoir	Washington, DC	auto-GC	hourly	2,006
Lums Pond	Delaware	auto-GC	hourly	1,892
Chicopee	Massachusettes DEP	auto-GC	hourly	1,459
Lynn	Massachusettes DEP	auto-GC	hourly	2,102
Lake Clifton	Maryland Air and Radiation	auto-GC	hourly	1,527
Rider College	New Jersey State DEP	auto-GC	hourly	2,094
Bronx	New York DEC	auto-GC	hourly	1,730
Philadelphia	Philadelphia DPH	canister	3-hours	577
E. Providence	Rhode Island	canister	3-hours	654
				15,354
NARSTO Northeast Surface				
Arendstville	Biospheric Research Corp.	canister	3-hours	93
Brookhaven	Biospheric Research Corp.	canister	3-hours	78
Capecod	Biospheric Research Corp.	canister	3-hours	78
Holbrook	Biospheric Research Corp.	canister	3-hours	110
Kunkletown	Biospheric Research Corp.	canister	3-hours	88
Shenandoah	Biospheric Research Corp.	canister	3-hours	65
				512
NARSTO Northeast Air				
Manassas	Biospheric Research Corp.	canister		14
Madison	Biospheric Research Corp.	canister		16
Brookhaven	Biospheric Research Corp.	canister		9
Kunkletown	Biospheric Research Corp.	canister		31
Lums Pond	Biospheric Research Corp.	canister		10
Arendstville	Biospheric Research Corp.	canister		12
Shenandoah	Biospheric Research Corp.	canister		14
				106

3 SOURCE COMPOSITION PROFILE DEVELOPMENT AND EVALUATION

This section describes the compilation, derivation, and evaluation of the source composition profiles that were considered and applied in the CMB analysis. Table 3-1 lists the mnemonic of the profiles that were considered in this study with short descriptions. The actual profiles are listed in Table 3-2. The profiles are expressed as weight percentages of total NMHC. Compounds other than the 55 Photochemical Assessment Monitoring Station (PAMS) target NMHCs that are identified by the DRI laboratory were grouped into a category named "others". The compounds that are included in the profiles are listed in Table 2-1. The 28 species that were used as fitting species in the CMB analysis are identified in the table with asterisks. Compounds reported as "unknown" were grouped into a category named "UNID". The profiles were constructed in this manner so that the profiles developed in this study can be applied in the future to the PAMS data archive. The PAMS target compounds typically account for about 80 percent of the ambient hydrocarbons in urban areas. Although methyl tert-butyl ether (MTBE) is a major component in reformulated gasoline and in the exhaust of vehicles using RFG, it was not included in the profiles because MTBE is not measured in the PAMS program. The source profile data reported in units of ppbC were converted to $\mu g/m^3$ prior to calculating the weight percentages using species-specific conversion factors. One-sigma uncertainties were derived from variations among multiple measurements for a particular source type or a nominal analytical uncertainty of 15 percent. The assigned uncertainties are the larger of the two values.

In urban locations, motor vehicle exhaust and evaporative emissions of gasoline are the major sources of hydrocarbon emissions. Composites of dynamometer measurements of vehicles of varying age and mileage are commonly used to represent fleet-averaged exhaust profiles. For these profiles to represent the actual fleet-average exhaust near ambient monitoring sites, the fuels in the dynamometer tests should resemble the fuels used in the study region and the mix of test vehicles should reflect the relative influence of non-catalyst vehicles or high emitters and catalyst-equipped normal emitters. Previous studies showed that source attributions between tailpipe and evaporative emissions from receptor modeling can vary greatly depending on the particular profile chosen for tailpipe emissions (Harley et al., 1992, Fujita et al., 1994, Pierson et al., 1996). This is because tailpipe emissions are a mixture of hydrocarbons produced during combustion along with unburned gasoline resulting from incomplete combustion. In the CMB calculation, liquid gasoline represents the additional unburned gasoline (due to misfiring and other engine malfunctions) that is not included in the exhaust profile, plus evaporative emissions from gasoline spillage, hot soaks, and some portion of resting losses (leaks, permeation). The profile for gasoline headspace vapor is taken to represent fuel tank vapor losses (e.g., migration of fuel vapor from the canister). Measuring exhaust in on-road tunnels is one way to obtain a composite profile for a larger mix of vehicles. While tunnel measurements are reasonable approximations for exhaust profiles of the light-duty fleet, they also include varying amounts of diesel exhaust and running evaporative losses. The composite light-duty exhaust profiles that were derived by Fujita et al. (1997a) from measurements by Gertler et al. (1997) in the Lincoln and Callahan Tunnels were used in this study.

Table 3-1

Table 3-1 Source profiles compiled for NARSTO-Northeast Source Apportionment

	Mnemonics	Explanations
1	Tu_TusHD	Tuscarora Tunnel, Heavy duty emissions
2	Tu_MchHD	Ft McHenry Tunnel, Heavy duty emissions
3	Exh_Cal0	Callahan Tunnel emissions with diesel contributions removed.
4	Exh_Lin0	Lincoln Tunnel emissions with diesel contributions removed.
5	Exh_Cal1	Callahan Tunnel emissions with diesel and 5~10% of running loss contributions removed.
6	Exh_Lin1	Lincoln Tunnel emissions with diesel and 5~10% of running loss contributions removed.
7	Exh_Cal2	Callahan Tunnel emissions with diesel and 15~25% of running loss contributions removed.
8	Exh_Lin2	Lincoln Tunnel emissions with diesel and 15~25% of running loss contributions removed.
9	WA_Tu1	Mt. Baker Tunnel emissions with diesel and 5~10% of running loss contributions removed.
10	Tu_Calla	Callahan Tunnel emissions
11	Tu_Lin	Lincoln Tunnel emissions
12	Tu_TusLD	Tuscarora Tunnel, Light duty emissions
13	Tu_MchLD	Ft McHenry Tunnel, Light duty emissions
14	BoCS_Tip	Tip O'Neill Garage emissions, Boston, cold start
15	Exh801a	Derived from the FTP tests of Sigsby et al.
16	Bogl01	Boston liquid gasoline composite.
17	LA_liqGs	LA liquid gasoline composite.
18	WA_Liq	Washington liquid gasoline composite of 15 samples, weighted by brands and grades.
19	Bogv01	Boston headspace vapor composite
20	LA_Hsvap	LA headspace vapor composite
21	WA_Vap	Washington headspace composite of 15 samples, weighted by brands and grades.
22	COATcomp	Composite of various coating emissions, weighted by total emissions.
23	CNG	Commercial natural gas
24	GNG	Geogenic natural gas
25	LPG	Liquified petroleum gas
26	Biogenic	Constructed biogenic profile
27	Unid	Sum of unidentified species.

Table 3-2 Source profiles developed for Northeast project

	TU_TUSHD	TU_MCHHD	EXH_CAL0	EXH_LIN0	EXH_CAL1	EXH_LIN1	EXH_CAL2
ETHANE	0.406 ± 0.409	1.067 ± 0.612	1.689 ± 0.185	1.356 ± 0.272	1.854 ± 0.214	1.459 ± 0.280	2.148 ± 0.265
ETHENE	9.099 ± 1.544	8.936 ± 2.548	5.940 ± 0.514	5.451 ± 0.809	6.521 ± 0.606	5.868 ± 0.819	7.554 ± 0.775
ACETYL	1.639 ± 0.636	2.311 ± 1.550	3.500 ± 0.250	3.430 ± 0.239	3.842 ± 0.301	3.700 ± 0.281	4.450 ± 0.399
LBUT1E	3.022 ± 1.009	2.675 ± 0.700	0.337 ± 0.046	0.257 ± 0.189	0.370 ± 0.050	0.274 ± 0.202	0.429 ± 0.061
PROPE	4.179 ± 0.892	3.616 ± 0.844	3.485 ± 0.210	2.516 ± 0.416	3.825 ± 0.260	2.707 ± 0.423	4.431 ± 0.358
N_PROP	0.815 ± 0.500	2.007 ± 0.947	0.076 ± 0.002	0.029 ± 0.041	0.083 ± 0.003	0.031 ± 0.044	0.097 ± 0.006
I_BUTA	0.784 ± 0.323	0.248 ± 0.265	0.496 ± 0.071	0.771 ± 0.322	0.340 ± 0.096	0.631 ± 0.365	0.065 ± 0.082
N_BUTA	2.453 ± 1.462	0.576 ± 1.433	2.085 ± 0.215	3.269 ± 1.289	0.581 ± 0.534	1.774 ± 1.545	0.000 ± 0.000
T2BUTE	0.000 ± 0.180	0.219 ± 0.396	0.505 ± 0.044	0.551 ± 0.154	0.525 ± 0.048	0.567 ± 0.175	0.551 ± 0.057
C2BUTE	0.379 ± 0.208	0.266 ± 0.097	0.300 ± 0.022	0.447 ± 0.053	0.292 ± 0.024	0.446 ± 0.063	0.267 ± 0.029
IPENTA	7.930 ± 4.899	1.184 ± 3.108	8.515 ± 0.270	9.440 ± 2.083	7.222 ± 0.583	8.086 ± 2.438	4.258 ± 1.159
PENTE1	0.814 ± 0.281	0.803 ± 0.193	0.202 ± 0.030	0.379 ± 0.068	0.170 ± 0.034	0.358 ± 0.079	0.097 ± 0.046
N_PENT	2.388 ± 1.977	1.378 ± 1.152	3.310 ± 0.093	3.049 ± 0.362	2.722 ± 0.248	2.383 ± 0.494	1.392 ± 0.510
I_PREN	0.453 ± 0.207	0.000 ± 0.274	0.004 ± 0.006	0.000 ± 0.100	0.003 ± 0.004	0.000 ± 0.000	0.002 ± 0.003
T2PENE	0.710 ± 0.473	0.324 ± 0.344	0.558 ± 0.032	0.874 ± 0.175	0.539 ± 0.036	0.872 ± 0.203	0.484 ± 0.045
C2PENE	0.276 ± 0.275	0.264 ± 0.174	0.273 ± 0.020	0.432 ± 0.076	0.261 ± 0.022	0.428 ± 0.089	0.226 ± 0.028
B2E2M	0.473 ± 0.691	0.567 ± 0.429	1.526 ± 0.182	1.404 ± 0.152	1.578 ± 0.198	1.417 ± 0.148	1.643 ± 0.231
BU22DM	3.151 ± 0.886	2.377 ± 0.891	0.554 ± 0.042	0.445 ± 0.317	0.575 ± 0.047	0.454 ± 0.324	0.604 ± 0.054
CPENTE	0.261 ± 0.166	0.039 ± 0.178	0.148 ± 0.003	0.193 ± 0.030	0.149 ± 0.003	0.196 ± 0.036	0.149 ± 0.003
P1E4ME	1.232 ± 0.160	0.228 ± 0.170	0.013 ± 0.019	0.025 ± 0.022	0.013 ± 0.018	0.023 ± 0.022	0.012 ± 0.017
CPENTA	0.223 ± 0.303	0.287 ± 0.211	0.355 ± 0.009	0.296 ± 0.015	0.331 ± 0.014	0.261 ± 0.018	0.272 ± 0.025
BU23DM	0.822 ± 0.526	0.289 ± 0.559	1.045 ± 0.023	0.901 ± 0.070	1.055 ± 0.024	0.881 ± 0.089	1.046 ± 0.029
PENA2M	2.581 ± 1.948	1.784 ± 0.979	3.092 ± 0.126	2.938 ± 0.042	3.126 ± 0.138	2.902 ± 0.081	3.104 ± 0.160
PENA3M	1.581 ± 1.213	0.828 ± 0.615	1.886 ± 0.041	1.847 ± 0.043	1.920 ± 0.047	1.843 ± 0.022	1.935 ± 0.054
P1E2ME	1.128 ± 0.334	0.203 ± 0.169	0.162 ± 0.074	0.171 ± 0.029	0.169 ± 0.081	0.176 ± 0.030	0.179 ± 0.094
N_HEX	1.586 ± 0.972	0.871 ± 0.541	1.799 ± 0.025	1.577 ± 0.160	1.814 ± 0.031	1.538 ± 0.154	1.788 ± 0.037
T2HEXE	0.112 ± 0.231	0.341 ± 0.132	0.229 ± 0.033	0.196 ± 0.037	0.243 ± 0.036	0.202 ± 0.038	0.264 ± 0.042
C2HEXE	0.026 ± 0.163	0.000 ± 0.087	0.104 ± 0.008	0.128 ± 0.009	0.110 ± 0.009	0.133 ± 0.008	0.118 ± 0.010
MCYPNA	0.978 ± 0.844	0.563 ± 0.436	0.978 ± 0.028	1.120 ± 0.065	1.069 ± 0.040	1.204 ± 0.064	1.233 ± 0.069
PEN24M	0.298 ± 0.288	0.323 ± 0.244	1.167 ± 0.021	0.704 ± 0.035	1.243 ± 0.034	0.722 ± 0.037	1.370 ± 0.056
BENZE	3.584 ± 1.283	2.893 ± 1.373	2.817 ± 0.120	2.843 ± 0.287	2.986 ± 0.145	2.957 ± 0.276	3.254 ± 0.189
CYHEXA	0.342 ± 0.340	0.211 ± 0.085	0.355 ± 0.003	0.242 ± 0.030	0.371 ± 0.005	0.243 ± 0.032	0.394 ± 0.009
HEXA2M	0.000 ± 0.100	0.000 ± 0.100	1.164 ± 0.025	1.258 ± 0.044	1.238 ± 0.037	1.317 ± 0.037	1.358 ± 0.058
PEN23M	0.490 ± 0.293	0.822 ± 0.332	2.012 ± 0.025	0.967 ± 0.057	2.151 ± 0.052	0.986 ± 0.052	2.383 ± 0.094
HEXA3M	1.059 ± 0.514	2.093 ± 1.170	1.131 ± 0.029	0.959 ± 0.295	1.194 ± 0.034	0.982 ± 0.307	1.292 ± 0.050

Table 3-2 (continued). Source profiles developed for Northeast project

	TU_TUSHD	TU_MCHHD	EXH_CAL0	EXH_LIN0	EXH_CAL1	EXH_LIN1	EXH_CAL2
PA224M	1.704 ± 0.903	1.337 ± 1.144	4.697 ± 0.136	3.589 ± 0.070	5.086 ± 0.179	3.803 ± 0.140	5.762 ± 0.298
N_HEPT	0.793 ± 0.428	0.519 ± 0.276	0.841 ± 0.007	0.708 ± 0.095	0.888 ± 0.015	0.727 ± 0.094	0.962 ± 0.029
MECYHX	0.411 ± 0.340	0.396 ± 0.244	0.564 ± 0.012	0.495 ± 0.094	0.612 ± 0.020	0.526 ± 0.098	0.695 ± 0.036
PA234M	0.473 ± 0.395	0.287 ± 0.401	1.604 ± 0.066	1.208 ± 0.043	1.737 ± 0.079	1.281 ± 0.054	1.969 ± 0.117
TOLUE	5.753 ± 3.216	4.075 ± 3.296	6.184 ± 0.236	6.967 ± 0.637	6.456 ± 0.250	7.177 ± 0.604	6.842 ± 0.314
HEP2ME	0.656 ± 0.820	0.000 ± 0.191	0.501 ± 0.019	0.494 ± 0.012	0.539 ± 0.025	0.522 ± 0.013	0.603 ± 0.036
HEP3ME	0.468 ± 0.314	0.400 ± 0.203	0.485 ± 0.075	0.479 ± 0.067	0.519 ± 0.082	0.503 ± 0.067	0.577 ± 0.096
N_OCT	0.622 ± 0.188	0.279 ± 0.152	0.433 ± 0.035	0.376 ± 0.015	0.465 ± 0.039	0.396 ± 0.014	0.521 ± 0.049
ETBZ	1.036 ± 0.728	2.579 ± 1.792	0.939 ± 0.078	0.875 ± 0.304	0.980 ± 0.083	0.889 ± 0.318	1.038 ± 0.098
MP_XYL	4.488 ± 3.018	9.953 ± 6.198	3.705 ± 0.230	3.144 ± 1.182	3.884 ± 0.246	3.194 ± 1.244	4.150 ± 0.297
STYR	1.194 ± 0.296	1.677 ± 0.659	0.139 ± 0.036	0.051 ± 0.040	0.153 ± 0.039	0.055 ± 0.043	0.177 ± 0.046
O_XYL	1.787 ± 1.208	3.382 ± 2.058	1.362 ± 0.132	1.231 ± 0.357	1.426 ± 0.143	1.254 ± 0.372	1.520 ± 0.169
N_NON	0.550 ± 0.089	1.015 ± 0.318	0.171 ± 0.014	0.136 ± 0.019	0.184 ± 0.016	0.143 ± 0.022	0.206 ± 0.020
IPRBZ	0.303 ± 0.345	0.299 ± 0.151	0.078 ± 0.013	0.037 ± 0.007	0.082 ± 0.014	0.037 ± 0.008	0.089 ± 0.016
N_PRBZ	0.428 ± 0.308	0.957 ± 0.617	0.256 ± 0.026	0.228 ± 0.102	0.270 ± 0.028	0.233 ± 0.108	0.292 ± 0.033
M_ETOL	1.692 ± 0.959	3.757 ± 2.607	1.066 ± 0.061	0.915 ± 0.423	1.137 ± 0.068	0.948 ± 0.448	1.255 ± 0.086
P_ETOL	0.644 ± 0.390	1.269 ± 0.660	0.464 ± 0.017	0.449 ± 0.117	0.494 ± 0.020	0.468 ± 0.121	0.545 ± 0.028
BZ135M	0.934 ± 0.548	1.891 ± 0.988	0.617 ± 0.026	0.573 ± 0.102	0.662 ± 0.032	0.601 ± 0.104	0.736 ± 0.044
O_ETOL	1.284 ± 0.487	1.809 ± 1.012	0.307 ± 0.042	0.245 ± 0.174	0.324 ± 0.046	0.254 ± 0.180	0.354 ± 0.054
BZ124M	2.770 ± 1.720	6.753 ± 4.203	1.519 ± 0.141	1.322 ± 0.830	1.619 ± 0.153	1.367 ± 0.886	1.784 ± 0.185
N_DEC	1.409 ± 0.110	2.369 ± 0.583	0.063 ± 0.018	0.072 ± 0.027	0.070 ± 0.020	0.078 ± 0.031	0.080 ± 0.023
BZ123M	0.963 ± 0.448	1.515 ± 0.940	0.396 ± 0.008	0.367 ± 0.108	0.425 ± 0.013	0.385 ± 0.113	0.474 ± 0.021
DETBZ1	0.000 ± 0.100	0.000 ± 0.100	0.073 ± 0.038	0.139 ± 0.128	0.078 ± 0.042	0.149 ± 0.141	0.086 ± 0.049
DETBZ2	0.000 ± 0.100	0.000 ± 0.100	0.317 ± 0.024	0.406 ± 0.047	0.348 ± 0.029	0.438 ± 0.058	0.401 ± 0.037
N_UNDE	2.654 ± 0.157	4.822 ± 0.946	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000
UNID	0.596 ± 0.060	0.365 ± 0.037	5.045 ± 0.421	6.840 ± 1.318	5.482 ± 0.490	7.340 ± 1.532	6.243 ± 0.618

Table 3-2 (continued). Source profiles developed for Northeast project

	EXH_LIN2	WA_TU1	TU_CALLA	TU_LIN	TU_TUSLD	TU_MCHLD	BOCS_TIP
ETHANE	1.690 ± 0.333	2.637 ± 0.220	1.660 ± 0.190	1.414 ± 0.255	2.099 ± 0.179	1.617 ± 0.146	0.700 ± 0.090
ETHENE	6.797 ± 0.995	9.458 ± 0.467	6.200 ± 0.690	6.342 ± 0.343	8.720 ± 0.676	6.560 ± 0.606	5.220 ± 0.670
ACETYL	4.286 ± 0.375	5.659 ± 0.442	3.470 ± 0.350	3.462 ± 0.258	2.360 ± 0.279	2.243 ± 0.369	5.310 ± 0.530
LBUT1E	0.318 ± 0.235	0.469 ± 0.039	0.500 ± 0.060	0.620 ± 0.051	3.170 ± 0.442	1.667 ± 0.167	0.570 ± 0.060
PROPE	3.136 ± 0.509	4.075 ± 0.204	3.540 ± 0.360	2.855 ± 0.240	3.490 ± 0.391	2.495 ± 0.201	3.090 ± 0.310
N_PROP	0.036 ± 0.051	1.294 ± 0.172	0.200 ± 0.060	0.205 ± 0.030	0.353 ± 0.219	0.106 ± 0.225	0.090 ± 0.010
I_BUTA	0.365 ± 0.403	0.290 ± 0.109	0.490 ± 0.080	0.713 ± 0.233	0.576 ± 0.141	0.223 ± 0.063	0.120 ± 0.020
N_BUTA	0.368 ± 0.745	2.329 ± 0.906	2.010 ± 0.290	2.953 ± 0.871	3.031 ± 0.640	1.935 ± 0.341	1.000 ± 0.100
T2BUTE	0.601 ± 0.204	0.255 ± 0.022	0.500 ± 0.060	0.519 ± 0.104	0.318 ± 0.079	0.383 ± 0.094	0.390 ± 0.040
C2BUTE	0.444 ± 0.073	0.172 ± 0.015	0.300 ± 0.050	0.443 ± 0.033	0.471 ± 0.091	0.278 ± 0.023	0.300 ± 0.190
IPENTA	5.259 ± 2.965	4.769 ± 0.987	8.140 ± 0.820	8.599 ± 1.167	8.721 ± 2.146	9.548 ± 0.740	4.990 ± 0.500
PENTE1	0.315 ± 0.093	0.171 ± 0.027	0.250 ± 0.040	0.454 ± 0.098	0.311 ± 0.123	0.325 ± 0.046	0.300 ± 0.030
N_PENT	1.017 ± 0.693	3.708 ± 0.355	3.230 ± 0.320	2.949 ± 0.191	3.286 ± 0.866	2.890 ± 0.274	2.880 ± 0.290
I_PREN	0.000 ± 0.000	0.191 ± 0.076	0.000 ± 0.040	0.000 ± 0.100	0.379 ± 0.091	0.324 ± 0.065	0.480 ± 0.050
T2PENE	0.870 ± 0.235	0.262 ± 0.037	0.540 ± 0.060	0.828 ± 0.102	0.644 ± 0.207	0.637 ± 0.082	0.790 ± 0.080
C2PENE	0.420 ± 0.103	0.138 ± 0.021	0.280 ± 0.050	0.428 ± 0.049	0.405 ± 0.121	0.382 ± 0.041	0.390 ± 0.040
B2E2M	1.457 ± 0.171	0.337 ± 0.062	1.490 ± 0.220	1.373 ± 0.196	1.131 ± 0.303	1.014 ± 0.102	1.770 ± 0.460
BU22DM	0.483 ± 0.346	0.520 ± 0.114	0.680 ± 0.080	0.776 ± 0.103	0.877 ± 0.388	0.831 ± 0.212	0.510 ± 0.050
CPENTE	0.203 ± 0.042	0.106 ± 0.006	0.140 ± 0.040	0.178 ± 0.012	0.198 ± 0.073	0.223 ± 0.042	0.190 ± 0.020
P1E4ME	0.021 ± 0.024	0.000 ± 0.150	0.020 ± 0.040	0.058 ± 0.026	0.220 ± 0.070	0.097 ± 0.041	0.070 ± 0.010
CPENTA	0.190 ± 0.031	0.411 ± 0.017	0.350 ± 0.050	0.310 ± 0.012	0.356 ± 0.133	0.333 ± 0.050	0.370 ± 0.040
BU23DM	0.844 ± 0.105	0.627 ± 0.040	1.010 ± 0.110	0.860 ± 0.010	0.843 ± 0.231	1.144 ± 0.133	0.750 ± 0.080
PENA2M	2.845 ± 0.095	2.507 ± 0.078	3.050 ± 0.310	2.935 ± 0.067	2.873 ± 0.853	3.091 ± 0.233	2.800 ± 0.280
PENA3M	1.844 ± 0.025	1.554 ± 0.027	1.840 ± 0.190	1.806 ± 0.117	1.788 ± 0.531	1.737 ± 0.146	1.690 ± 0.170
P1E2ME	0.187 ± 0.035	0.056 ± 0.006	0.170 ± 0.080	0.188 ± 0.026	0.000 ± 0.146	0.166 ± 0.040	0.160 ± 0.020
N_HEX	1.469 ± 0.180	2.204 ± 0.035	1.760 ± 0.180	1.574 ± 0.190	1.429 ± 0.426	1.405 ± 0.129	1.810 ± 0.180
T2HEXE	0.217 ± 0.044	0.088 ± 0.011	0.240 ± 0.040	0.231 ± 0.017	0.195 ± 0.101	0.201 ± 0.031	0.280 ± 0.040
C2HEXE	0.144 ± 0.010	0.054 ± 0.004	0.100 ± 0.040	0.116 ± 0.018	0.245 ± 0.072	0.135 ± 0.021	0.140 ± 0.020
MCYPNA	1.387 ± 0.094	1.304 ± 0.059	0.960 ± 0.100	1.103 ± 0.097	1.147 ± 0.370	1.062 ± 0.104	1.030 ± 0.100
PEN24M	0.766 ± 0.045	0.497 ± 0.053	1.130 ± 0.120	0.686 ± 0.049	0.581 ± 0.126	0.739 ± 0.058	1.010 ± 0.100
BENZE	3.221 ± 0.331	6.254 ± 0.271	2.860 ± 0.290	3.038 ± 0.223	5.555 ± 0.562	4.426 ± 0.327	2.850 ± 0.290
CYHEXA	0.245 ± 0.037	0.362 ± 0.016	0.350 ± 0.050	0.255 ± 0.029	0.328 ± 0.149	0.184 ± 0.020	0.330 ± 0.030
HEXA2M	1.449 ± 0.060	0.882 ± 0.022	1.100 ± 0.120	1.151 ± 0.147	0.000 ± 0.100	0.000 ± 0.100	1.170 ± 0.120
PEN23M	1.033 ± 0.062	0.881 ± 0.076	1.960 ± 0.200	1.007 ± 0.059	0.726 ± 0.128	0.896 ± 0.079	1.470 ± 0.150
HEXA3M	1.047 ± 0.357	0.968 ± 0.073	1.210 ± 0.130	1.206 ± 0.145	0.907 ± 0.225	1.465 ± 0.278	1.290 ± 0.130

Table 3-2 (continued). Source profiles developed for Northeast project

	EXH_LIN2	WA_TU1	TU_CALLA	TU_LIN	TU_TUSLD	TU_MCHLD	BOCS_TIP
PA224M	4.275 ± 0.221	1.500 ± 0.167	4.540 ± 0.460	3.460 ± 0.158	2.334 ± 0.396	3.456 ± 0.272	3.690 ± 0.370
N_HEPT	0.775 ± 0.110	0.775 ± 0.027	0.840 ± 0.090	0.732 ± 0.095	0.576 ± 0.187	0.730 ± 0.066	0.920 ± 0.090
MECYHX	0.596 ± 0.116	0.337 ± 0.028	0.550 ± 0.070	0.513 ± 0.089	0.456 ± 0.149	0.437 ± 0.058	0.280 ± 0.060
PA234M	1.440 ± 0.081	0.534 ± 0.078	1.540 ± 0.160	1.142 ± 0.089	0.782 ± 0.173	1.238 ± 0.096	1.380 ± 0.140
TOLUE	7.676 ± 0.718	11.317 ± 0.524	6.130 ± 0.610	6.991 ± 0.762	8.607 ± 1.408	8.532 ± 0.784	8.270 ± 0.830
HEP2ME	0.583 ± 0.024	0.338 ± 0.012	0.480 ± 0.060	0.451 ± 0.051	0.479 ± 0.359	0.456 ± 0.046	0.440 ± 0.040
HEP3ME	0.558 ± 0.079	0.359 ± 0.032	0.490 ± 0.080	0.503 ± 0.062	0.432 ± 0.138	0.477 ± 0.048	0.560 ± 0.060
N_OCT	0.439 ± 0.021	0.292 ± 0.014	0.430 ± 0.060	0.382 ± 0.015	0.249 ± 0.082	0.316 ± 0.036	0.350 ± 0.050
ETBZ	0.932 ± 0.369	1.607 ± 0.057	1.070 ± 0.110	1.198 ± 0.100	1.704 ± 0.319	2.102 ± 0.426	1.470 ± 0.150
MP_XYL	3.350 ± 1.443	5.930 ± 0.197	4.170 ± 0.420	4.429 ± 0.382	6.371 ± 1.322	7.149 ± 1.475	5.480 ± 0.550
STYR	0.064 ± 0.050	0.502 ± 0.062	0.240 ± 0.040	0.168 ± 0.070	0.960 ± 0.130	0.942 ± 0.157	0.430 ± 0.050
O_XYL	1.321 ± 0.432	2.140 ± 0.072	1.520 ± 0.160	1.650 ± 0.110	2.434 ± 0.529	2.620 ± 0.490	1.870 ± 0.190
N_NON	0.159 ± 0.026	0.117 ± 0.016	0.220 ± 0.040	0.274 ± 0.093	0.057 ± 0.039	0.223 ± 0.076	0.010 ± 0.020
IPRBZ	0.036 ± 0.009	0.103 ± 0.004	0.090 ± 0.040	0.076 ± 0.023	0.301 ± 0.151	0.181 ± 0.036	0.000 ± 0.010
N_PRBZ	0.249 ± 0.125	0.327 ± 0.010	0.310 ± 0.050	0.359 ± 0.028	0.501 ± 0.135	0.661 ± 0.147	0.300 ± 0.030
M_ETOL	1.036 ± 0.520	1.302 ± 0.060	1.250 ± 0.130	1.422 ± 0.113	1.909 ± 0.420	2.748 ± 0.620	1.300 ± 0.130
P_ETOL	0.515 ± 0.141	0.633 ± 0.038	0.520 ± 0.060	0.602 ± 0.035	0.761 ± 0.171	0.899 ± 0.157	0.560 ± 0.060
BZ135M	0.666 ± 0.122	0.738 ± 0.029	0.710 ± 0.080	0.810 ± 0.051	1.005 ± 0.240	1.211 ± 0.235	0.560 ± 0.060
O_ETOL	0.279 ± 0.199	0.413 ± 0.021	0.410 ± 0.050	0.484 ± 0.037	0.823 ± 0.213	1.046 ± 0.241	0.430 ± 0.050
BZ124M	1.492 ± 1.027	2.032 ± 0.095	1.880 ± 0.190	2.266 ± 0.248	3.206 ± 0.753	4.517 ± 1.000	1.820 ± 0.180
N_DEC	0.090 ± 0.035	0.101 ± 0.030	0.210 ± 0.090	0.412 ± 0.230	0.026 ± 0.048	0.233 ± 0.153	0.000 ± 0.010
BZ123M	0.427 ± 0.131	0.511 ± 0.043	0.480 ± 0.060	0.564 ± 0.041	0.843 ± 0.196	1.084 ± 0.247	0.370 ± 0.040
DETBZ1	0.168 ± 0.164	0.105 ± 0.006	0.070 ± 0.040	0.117 ± 0.097	0.000 ± 0.100	0.000 ± 0.100	0.090 ± 0.020
DETBZ2	0.506 ± 0.071	0.633 ± 0.057	0.300 ± 0.050	0.364 ± 0.018	0.000 ± 0.100	0.000 ± 0.100	0.390 ± 0.040
N_UNDE	0.000 ± 0.000	0.000 ± 0.150	0.250 ± 0.130	0.633 ± 0.408	0.000 ± 0.069	0.161 ± 0.249	0.000 ± 0.010
UNID	8.395 ± 1.808	3.598 ± 0.232	4.800 ± 0.480	6.173 ± 0.702	0.998 ± 0.100	0.510 ± 0.051	5.950 ± 0.960

Table 3-2 (continued). Source profiles developed for Northeast project

	EXH801A	BOGL01	LA_LIQGS	WA_LIQ	BOGV01	LA_HSVAP	WA_VAP
ETHANE	2.819 ± 0.570	0.000 ± 0.020	0.001 ± 0.002	0.000 ± 0.150	0.000 ± 0.050	0.000 ± 0.100	0.000 ± 0.150
ETHENE	9.744 ± 1.945	0.000 ± 0.020	0.000 ± 0.000	0.000 ± 0.150	0.000 ± 0.050	0.000 ± 0.100	0.000 ± 0.150
ACETYL	2.731 ± 0.560	0.000 ± 0.020	0.000 ± 0.100	0.000 ± 0.150	0.000 ± 0.050	0.000 ± 0.100	0.000 ± 0.150
LBUT1E	0.845 ± 0.085	0.010 ± 0.020	0.063 ± 0.053	0.000 ± 0.150	0.790 ± 0.470	0.503 ± 0.146	0.000 ± 0.150
PROPE	3.084 ± 0.619	0.000 ± 0.020	0.004 ± 0.008	0.000 ± 0.150	0.000 ± 0.050	0.031 ± 0.011	0.000 ± 0.150
N_PROP	0.422 ± 0.128	0.000 ± 0.020	0.066 ± 0.051	0.000 ± 0.150	0.030 ± 0.050	0.637 ± 0.206	0.000 ± 0.150
I_BUTA	0.904 ± 0.206	0.090 ± 0.020	0.518 ± 0.416	0.205 ± 0.106	1.130 ± 0.420	2.161 ± 0.699	2.495 ± 1.138
N_BUTA	6.335 ± 1.267	0.540 ± 0.060	2.849 ± 2.060	2.300 ± 0.950	4.800 ± 1.700	6.352 ± 1.956	21.624 ± 10.865
T2BUTE	0.216 ± 0.108	0.030 ± 0.020	0.114 ± 0.067	0.045 ± 0.024	0.210 ± 0.110	0.554 ± 0.169	0.357 ± 0.347
C2BUTE	0.580 ± 0.147	0.050 ± 0.020	0.116 ± 0.062	0.055 ± 0.031	0.310 ± 0.110	0.491 ± 0.150	0.454 ± 0.406
IPENTA	4.852 ± 0.972	5.770 ± 0.580	6.712 ± 1.339	7.604 ± 1.584	21.020 ± 5.950	17.351 ± 4.341	25.928 ± 4.169
PENTE1	0.305 ± 0.118	0.150 ± 0.020	0.214 ± 0.104	0.226 ± 0.074	0.460 ± 0.120	0.500 ± 0.119	0.633 ± 0.217
N_PENT	2.171 ± 0.442	2.060 ± 0.210	2.215 ± 0.771	5.061 ± 2.013	5.570 ± 1.350	4.334 ± 0.934	11.119 ± 3.767
I_PREN	0.000 ± 0.098	0.020 ± 0.020	0.015 ± 0.010	0.009 ± 0.009	0.070 ± 0.050	0.031 ± 0.009	0.045 ± 0.027
T2PENE	0.422 ± 0.128	0.420 ± 0.050	0.498 ± 0.205	0.394 ± 0.242	1.040 ± 0.240	0.986 ± 0.207	0.885 ± 0.562
C2PENE	0.265 ± 0.108	0.240 ± 0.030	0.288 ± 0.116	0.220 ± 0.137	0.570 ± 0.130	0.526 ± 0.108	0.478 ± 0.311
B2E2M	0.000 ± 0.098	0.580 ± 0.060	0.658 ± 0.281	0.580 ± 0.361	1.400 ± 0.240	1.148 ± 0.230	1.167 ± 0.756
BU22DM	0.432 ± 0.128	0.360 ± 0.040	0.204 ± 0.255	0.260 ± 0.074	0.690 ± 0.110	0.329 ± 0.103	0.398 ± 0.089
CPENTE	0.000 ± 0.098	0.110 ± 0.020	0.133 ± 0.051	0.099 ± 0.051	0.210 ± 0.050	0.202 ± 0.035	0.153 ± 0.084
P1E4ME	0.000 ± 0.098	0.050 ± 0.020	0.039 ± 0.021	0.047 ± 0.017	0.060 ± 0.050	0.048 ± 0.010	0.053 ± 0.018
CPENTA	0.206 ± 0.108	0.320 ± 0.040	0.169 ± 0.185	0.029 ± 0.191	0.540 ± 0.070	0.426 ± 0.067	0.708 ± 0.276
BU23DM	0.796 ± 0.187	1.140 ± 0.120	1.174 ± 0.354	1.596 ± 0.339	0.000 ± 0.050	0.000 ± 0.100	1.119 ± 0.661
PENA2M	1.876 ± 0.393	2.860 ± 0.290	3.108 ± 0.882	3.498 ± 1.153	3.890 ± 0.390	3.315 ± 0.498	3.266 ± 1.079
PENA3M	1.346 ± 0.285	1.890 ± 0.190	1.863 ± 0.519	2.129 ± 0.678	2.290 ± 0.230	1.885 ± 0.305	1.827 ± 0.657
P1E2ME	0.000 ± 0.098	0.180 ± 0.030	0.136 ± 0.061	0.148 ± 0.113	0.230 ± 0.050	0.148 ± 0.033	0.104 ± 0.071
N_HEX	0.904 ± 0.206	1.690 ± 0.170	1.520 ± 0.538	2.914 ± 1.127	1.700 ± 0.190	1.281 ± 0.260	1.972 ± 0.957
T2HEXE	0.000 ± 0.098	0.270 ± 0.030	0.203 ± 0.102	0.172 ± 0.101	0.370 ± 0.060	0.250 ± 0.077	0.105 ± 0.082
C2HEXE	0.000 ± 0.098	0.150 ± 0.020	0.111 ± 0.050	0.103 ± 0.067	0.140 ± 0.050	0.105 ± 0.027	0.058 ± 0.048
MCYPNA	0.904 ± 0.206	1.020 ± 0.100	2.154 ± 0.819	0.000 ± 0.150	1.000 ± 0.160	2.111 ± 0.491	0.044 ± 0.025
PEN24M	0.805 ± 0.187	1.410 ± 0.140	1.264 ± 0.714	0.951 ± 0.818	1.180 ± 0.260	0.936 ± 0.460	0.447 ± 0.564
BENZE	3.850 ± 0.776	0.560 ± 0.060	0.840 ± 0.249	2.436 ± 0.423	0.560 ± 0.120	0.848 ± 0.202	1.290 ± 0.544
CYHEXA	0.216 ± 0.108	0.330 ± 0.040	0.311 ± 0.403	0.409 ± 0.235	0.300 ± 0.080	0.538 ± 0.210	0.228 ± 0.151
HEXA2M	0.747 ± 0.177	1.360 ± 0.140	1.499 ± 0.314	1.260 ± 0.171	0.840 ± 0.430	1.158 ± 0.363	0.484 ± 0.325
PEN23M	0.747 ± 0.177	2.630 ± 0.260	2.245 ± 1.709	1.885 ± 1.884	1.820 ± 0.620	1.582 ± 1.080	0.690 ± 0.923
HEXA3M	1.356 ± 0.285	1.500 ± 0.150	1.590 ± 0.257	1.489 ± 0.101	1.020 ± 0.380	1.232 ± 0.369	0.578 ± 0.370

Table 3-2 (continued). Source profiles developed for Northeast project

	EXH801A	BOGL01	LA_LIQGS	WA_LIQ	BOGV01	LA_HSVAP	WA_VAP
PA224M	2.858 ± 0.580	6.520 ± 0.650	3.176 ± 2.254	2.940 ± 2.748	4.310 ± 1.720	2.430 ± 1.410	0.828 ± 0.991
N_HEPT	0.766 ± 0.177	1.110 ± 0.110	0.997 ± 0.209	1.232 ± 0.154	0.680 ± 0.290	0.786 ± 0.248	0.425 ± 0.278
MECYHX	0.629 ± 0.157	0.570 ± 0.060	0.643 ± 0.321	0.261 ± 0.128	0.390 ± 0.170	0.648 ± 0.268	0.085 ± 0.073
PA234M	0.167 ± 0.108	2.590 ± 0.260	1.459 ± 1.018	1.273 ± 1.087	1.260 ± 0.740	1.023 ± 0.812	0.276 ± 0.386
TOLUE	6.984 ± 1.395	4.430 ± 0.440	6.806 ± 1.838	12.096 ± 2.359	3.680 ± 1.700	5.584 ± 1.964	4.025 ± 2.933
HEP2ME	0.324 ± 0.118	0.710 ± 0.070	0.620 ± 0.117	0.501 ± 0.074	0.360 ± 0.160	0.467 ± 0.158	0.136 ± 0.094
HEP3ME	0.540 ± 0.147	0.680 ± 0.070	0.635 ± 0.126	0.563 ± 0.084	0.370 ± 0.170	0.489 ± 0.173	0.155 ± 0.116
N_OCT	0.432 ± 0.128	0.670 ± 0.130	0.510 ± 0.141	0.450 ± 0.087	0.280 ± 0.120	0.353 ± 0.151	0.119 ± 0.092
ETBZ	0.776 ± 0.187	1.220 ± 0.120	1.394 ± 0.291	2.144 ± 0.487	0.570 ± 0.260	0.955 ± 0.314	0.616 ± 0.650
MP_XYL	3.271 ± 0.658	4.890 ± 0.490	5.924 ± 1.165	7.932 ± 1.685	2.370 ± 0.980	4.166 ± 1.288	2.209 ± 2.343
STYR	0.000 ± 0.098	0.000 ± 0.020	0.000 ± 0.100	0.000 ± 0.150	0.040 ± 0.050	0.058 ± 0.048	0.000 ± 0.150
O_XYL	2.181 ± 0.452	2.000 ± 0.220	2.215 ± 0.479	2.988 ± 0.656	0.860 ± 0.360	1.472 ± 0.484	0.835 ± 0.866
N_NON	0.305 ± 0.118	0.210 ± 0.080	0.207 ± 0.096	0.234 ± 0.095	0.090 ± 0.030	0.131 ± 0.068	0.043 ± 0.036
IPRBZ	0.000 ± 0.098	0.110 ± 0.040	0.099 ± 0.038	0.147 ± 0.029	0.020 ± 0.010	0.035 ± 0.025	0.036 ± 0.034
N_PRBZ	0.678 ± 0.167	0.440 ± 0.200	0.421 ± 0.080	0.630 ± 0.107	0.150 ± 0.070	0.226 ± 0.087	0.135 ± 0.132
M_ETOL	1.601 ± 0.160	1.700 ± 0.170	1.562 ± 0.269	1.940 ± 0.243	0.510 ± 0.210	0.835 ± 0.295	0.397 ± 0.387
P_ETOL	0.000 ± 0.100	0.720 ± 0.090	0.682 ± 0.130	0.840 ± 0.121	0.220 ± 0.100	0.372 ± 0.134	0.178 ± 0.174
BZ135M	0.000 ± 0.098	0.000 ± 0.020	0.863 ± 0.152	0.993 ± 0.276	0.270 ± 0.110	0.458 ± 0.173	0.190 ± 0.183
O_ETOL	0.275 ± 0.028	0.480 ± 0.180	0.603 ± 0.100	0.682 ± 0.110	0.160 ± 0.070	0.272 ± 0.104	0.144 ± 0.144
BZ124M	3.281 ± 0.658	2.840 ± 0.390	2.726 ± 0.546	3.122 ± 0.885	0.790 ± 0.280	1.404 ± 0.546	0.582 ± 0.574
N_DEC	0.167 ± 0.017	0.070 ± 0.020	0.127 ± 0.065	0.017 ± 0.019	0.040 ± 0.050	0.062 ± 0.032	0.003 ± 0.006
BZ123M	0.000 ± 0.100	0.360 ± 0.300	0.584 ± 0.142	0.697 ± 0.088	0.150 ± 0.080	0.299 ± 0.132	0.120 ± 0.117
DETBZ1	0.000 ± 0.100	0.100 ± 0.080	0.159 ± 0.040	0.262 ± 0.051	0.010 ± 0.050	0.007 ± 0.007	0.032 ± 0.031
DETBZ2	0.000 ± 0.100	0.160 ± 0.110	0.000 ± 0.100	0.031 ± 0.013	0.070 ± 0.050	0.083 ± 0.059	0.008 ± 0.011
N_UNDE	0.000 ± 0.100	0.100 ± 0.050	0.083 ± 0.046	0.099 ± 0.027	0.010 ± 0.050	0.029 ± 0.023	0.013 ± 0.015
UNID	24.890 ± 6.591	20.140 ± 2.010	15.296 ± 3.789	2.721 ± 0.998	3.670 ± 1.120	4.375 ± 1.522	0.676 ± 0.360

Table 3-2 (continued). Source profiles developed for Northeast project

	COATCOMP	CNG	GNG	LPG	BIOGENIC	UNID
ETHANE	0.000 ± 0.150	68.850 ± 10.330	15.770 ± 2.370	4.110 ± 0.620	0.000 ± 0.100	0.000 ± 0.100
ETHENE	0.000 ± 0.150	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100
ACETYL	0.000 ± 0.150	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100
LBUT1E	0.000 ± 0.150	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100
PROPE	0.000 ± 0.150	0.000 ± 0.100	0.000 ± 0.100	5.110 ± 0.770	0.000 ± 0.100	0.000 ± 0.100
N_PROP	0.000 ± 0.150	21.130 ± 3.170	25.150 ± 3.770	90.580 ± 13.590	0.000 ± 0.100	0.000 ± 0.100
I_BUTA	0.000 ± 0.150	2.080 ± 0.330	5.890 ± 0.890	0.200 ± 0.100	0.000 ± 0.100	0.000 ± 0.100
N_BUTA	0.000 ± 0.150	3.080 ± 0.480	14.570 ± 2.190	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100
T2BUTE	0.000 ± 0.150	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100
C2BUTE	0.000 ± 0.150	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100
IPENTA	0.000 ± 0.001	0.690 ± 0.150	6.190 ± 0.940	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100
PENTE1	0.000 ± 0.150	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100
N_PENT	0.000 ± 0.150	0.690 ± 0.150	6.190 ± 0.940	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100
I_PREN	0.000 ± 0.150	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	100.000 ± 10.00	0.000 ± 0.100
T2PENE	0.000 ± 0.150	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100
C2PENE	0.000 ± 0.150	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100
B2E2M	0.000 ± 0.150	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100
BU22DM	0.000 ± 0.150	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100
CPENTE	0.000 ± 0.150	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100
P1E4ME	0.000 ± 0.150	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100
CPENTA	0.000 ± 0.150	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100
BU23DM	0.000 ± 0.150	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100
PENA2M	0.003 ± 0.004	0.300 ± 0.110	2.890 ± 0.450	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100
PENA3M	0.003 ± 0.024	0.100 ± 0.100	1.500 ± 0.250	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100
P1E2ME	0.000 ± 0.150	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100
N_HEX	0.000 ± 0.150	0.400 ± 0.120	1.800 ± 0.290	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100
T2HEXE	0.000 ± 0.150	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100
C2HEXE	0.000 ± 0.150	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100
MCYPNA	0.015 ± 0.020	0.990 ± 0.180	2.590 ± 0.400	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100
PEN24M	0.005 ± 0.025	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100
BENZE	0.000 ± 0.150	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100
CYHEXA	0.050 ± 0.080	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100
HEXA2M	0.097 ± 0.421	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100
PEN23M	0.040 ± 0.071	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100
HEXA3M	0.116 ± 0.155	0.200 ± 0.100	4.490 ± 0.680	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100

Table 3-2 (continued). Source profiles developed for Northeast project

	COATCOMP	CNG	GNG	LPG	BIOGENIC	UNID
PA224M	0.000 ± 0.150	0.300 ± 0.110	0.900 ± 0.170	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100
N_HEPT	0.541 ± 1.662	0.200 ± 0.100	1.200 ± 0.210	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100
MECYHX	0.901 ± 3.144	0.100 ± 0.100	2.200 ± 0.340	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100
PA234M	0.016 ± 0.036	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100
TOLUE	2.381 ± 2.364	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100
HEP2ME	0.470 ± 0.807	0.400 ± 0.120	3.290 ± 0.510	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100
HEP3ME	0.331 ± 0.557	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100
N_OCT	1.186 ± 1.828	0.000 ± 0.100	1.000 ± 0.180	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100
ETBZ	1.317 ± 0.983	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100
MP_XYL	5.310 ± 3.648	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100
STYR	0.004 ± 0.010	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100
O_XYL	2.474 ± 1.504	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100
N_NON	1.565 ± 0.793	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100
IPRBZ	0.217 ± 0.198	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100
N_PRBZ	0.505 ± 0.503	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100
M_ETOL	0.000 ± 0.150	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100
P_ETOL	1.555 ± 0.572	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100
BZ135M	1.426 ± 0.910	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100
O_ETOL	0.000 ± 0.150	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100
BZ124M	3.836 ± 1.487	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100
N_DEC	6.247 ± 2.070	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100
BZ123M	1.195 ± 0.366	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100
DETBZ1	0.135 ± 0.145	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100
DETBZ2	0.051 ± 0.081	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100
N_UNDE	3.725 ± 2.806	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100	0.000 ± 0.100
UNID	0.000 ± 0.150	0.490 ± 15.340	4.380 ± 7.660	0.000 ± 19.300	0.000 ± 14.150	100.000 ± 20.00

3.1 Derivation of Spark-Ignition Vehicle Exhaust Profiles from Tunnel Measurements

Investigators from the Desert Research Institute conducted a series of experiments in 1995 to quantify emission rates of carbon monoxide (CO), nitrogen oxides (NOx), and speciated nonmethane hydrocarbons (NMHC) from in-use vehicles at the Lincoln Tunnel in New York (August 16-18) and at the Callahan Tunnel in Boston, MA (September 18-19) (Gertler et al., 1997). Similar experiments were conducted during the same year at the Deck Park Tunnel in Phoenix, AZ (January 24-26 and again in July 25-27), and at the Van Nuys Tunnel (June 8-12) and Sepulveda Tunnel (October 3-4) in the Los Angeles area. The sampling protocol and characteristics of the vehicle traffic for each of the tunnel measurements are described by Gertler et al. (1997). In a parallel effort, ambient samples were collected by DRI at several sites in the Boston and Los Angeles areas to determine the mobile source emission contributions to total ambient NMHC using receptor modeling (Fujita et al., 1997a). Composite spark-ignition vehicle exhaust profiles were derived by Fujita et al. (1997a) from the tunnel measurements by subtracting the contributions of diesel exhaust and running evaporative losses from each tunnel sample. Because MTBE is not measured in PAMS, composite spark-ignition vehicle exhaust profiles were derived for this project without MTBE.

In the first step, we subtract the contributions of diesel exhaust by fitting a diesel exhaust profile to the tunnel samples using only decane and undecane as fitting species. These two species were used because they are enriched in diesel exhaust relative to gasoline exhaust and minimize the overestimation of the diesel contribution that would result if species common to both sources are used to determine the solution. The diesel exhaust profile developed by DRI (Sagebiel et al., 1996) from the Ft. McHenry Tunnel (shown in Table 3-2) was applied to each tunnel sample. Table 3-3 show that the resulting diesel contributions to total nonmethane hydrocarbons (C_2 to C_{11}) range from 3 to 9 percent, which are consistent with the fractions of diesel traffic that were observed for these runs. One sample from the Lincoln Tunnel had about 25 percent diesel exhaust. Even in this case, the fraction of diesel traffic (mostly buses) was consistent with the calculated contribution.

The second step in deriving spark-ignition light-duty vehicle exhaust profiles from tunnel samples is to remove the contributions of evaporative emissions. The method described above for subtracting diesel emissions cannot be used in this case because there are no species that exist in gasoline that does not also exist in tailpipe emissions. To do so would overestimate the contributions of evaporative emissions. Instead, we subtracted varying contributions of evaporative emissions from each tunnel sample in five- percent increments from 0 to 50 percent. The amounts subtracted for each species are derived by multiplying the hydrocarbon mass emission rate (grams/mile) for each tunnel run by the assumed fractional contributions of evaporative emissions, then distributing the resulting emission rates to individual species according to the evaporative emissions profiles shown in Table 3-2.

Running and resting losses are the two sources of evaporative loss from vehicles travelling through the tunnel. Running losses are releases of gasoline vapor from the fuel

Table 3-3. Apportionment of Motor Vehicle Exhaust and Running Evaporative Loss in the Callahan and Lincoln Tunnels

Sample #	Date	Hour	NMHC mg/mi	r^2	χ^2	% of NMHC	LD Exhaust Profiles[1]	HD %	LD %	Vapor %	Ratios of Calculated vs. Measured I_BUTA	N_BUTA	IPENTA
Cal_1	09/19/95	08	437.0	1.00	0.02	100.0	B1908_05	8.9	86.6	4.5	0.98	1.01	1.01
Cal_1	09/19/95	08	437.0	1.00	0.03	99.8	B1908_10	8.9	82.4	8.5	0.94	1.12	0.99
Cal_1	09/19/95	08	437.0	1.00	0.13	98.9	B1908_15	8.8	78.3	11.8	0.86	1.54	0.95
Cal_1	09/19/95	08	437.0	0.99	0.23	97.5	B1908_20	8.8	74.1	14.6	0.97	1.91	0.90
Cal_1	09/19/95	08	437.0	0.99	0.37	95.9	B1908_25	8.8	69.4	17.7	1.17	2.31	0.84
Cal_1	09/19/95	08	437.0	0.99	0.53	94.6	B1908_30	8.8	64.5	21.3	1.39	2.76	0.81
Cal_1	09/19/95	08	437.0	0.98	0.59	91.7	B1908_35	8.8	59.9	23.0	1.50	2.99	0.79
Cal_1	09/19/95	08	437.0	0.98	0.60	87.4	B1908_40	8.9	55.5	23.1	1.50	2.99	0.80
Cal_1	09/19/95	08	437.0	0.98	0.61	83.1	B1908_45	8.9	51.0	23.1	1.50	3.00	0.80
Cal_1	09/19/95	08	437.0	0.98	0.63	78.7	B1908_50	8.9	46.6	23.2	1.51	3.01	0.80
Cal_2	09/19/95	14	544.5	1.00	0.05	100.2	B1914_05	4.7	90.9	4.7	0.99	1.00	1.01
Cal_2	09/19/95	14	544.5	1.00	0.05	100.2	B1914_10	4.7	86.1	9.4	0.99	1.00	1.01
Cal_2	09/19/95	14	544.5	1.00	0.09	99.5	B1914_15	4.6	81.9	13.0	0.94	1.27	0.97
Cal_2	09/19/95	14	544.5	1.00	0.18	98.7	B1914_20	4.6	77.2	16.9	0.90	1.65	0.95
Cal_2	09/19/95	14	544.5	0.99	0.26	97.7	B1914_25	4.6	72.4	20.6	0.94	2.02	0.91
Cal_2	09/19/95	14	544.5	0.99	0.35	96.3	B1914_30	4.6	67.6	24.1	1.10	2.36	0.87
Cal_2	09/19/95	14	544.5	0.99	0.46	94.9	B1914_35	4.7	62.6	27.7	1.26	2.71	0.84
Cal_2	09/19/95	14	544.5	0.99	0.46	90.5	B1914_40	4.7	58.0	27.8	1.26	2.72	0.85
Cal_2	09/19/95	14	544.5	0.99	0.47	86.0	B1914_45	4.7	53.4	27.9	1.27	2.73	0.85
Cal_2	09/19/95	14	544.5	0.99	0.49	81.4	B1914_50	4.7	48.8	28.0	1.27	2.74	0.85
Cal_3	09/19/95	16	840.8	1.00	0.05	100.1	B1916_05	3.4	92.0	4.7	1.00	0.99	1.00
Cal_3	09/19/95	16	840.8	1.00	0.05	100.1	B1916_10	3.4	87.2	9.5	1.00	0.99	1.00
Cal_3	09/19/95	16	840.8	1.00	0.11	99.4	B1916_15	3.4	83.0	13.0	0.94	1.32	0.97
Cal_3	09/19/95	16	840.8	1.00	0.21	98.7	B1916_20	3.4	78.1	17.1	0.90	1.73	0.94
Cal_3	09/19/95	16	840.8	0.99	0.30	97.4	B1916_25	3.4	73.3	20.7	1.00	2.10	0.90
Cal_3	09/19/95	16	840.8	0.99	0.40	96.1	B1916_30	3.4	68.3	24.3	1.18	2.46	0.86
Cal_3	09/19/95	16	840.8	0.99	0.47	93.5	B1916_35	3.4	63.5	26.6	1.29	2.69	0.84
Cal_3	09/19/95	16	840.8	0.99	0.48	88.9	B1916_40	3.4	58.8	26.7	1.29	2.70	0.85
Cal_3	09/19/95	16	840.8	0.99	0.49	84.4	B1916_45	3.4	54.2	26.8	1.30	2.71	0.85
Cal_3	09/19/95	16	840.8	0.99	0.51	79.7	B1916_50	3.4	49.4	26.9	1.30	2.73	0.85

Table 3-3 (continued).

Sample #	Date	Hour	NMHC mg/mi	r^2	χ^2	% of NMHC	LD Exhaust Profiles	HD %	LD %	Vapor %	Ratios of Calculated vs. Measured I_BUTA	N_BUTA	IPENTA
Lin_1	08/16/95	17	1501.0	1.00	0.01	99.9	L1617_05	24.8	73.5	3.3	1.00	0.99	1.01
Lin_1	08/16/95	17	1501.0	1.00	0.01	99.8	L1617_10	24.8	73.3	7.0	1.00	0.99	1.01
Lin_1	08/16/95	17	1501.0	1.00	0.01	99.9	L1617_15	24.7	64.3	10.8	1.00	0.99	1.01
Lin_1	08/16/95	17	1501.0	1.00	0.01	99.8	L1617_20	24.7	60.6	14.5	1.00	0.99	1.00
Lin_1	08/16/95	17	1501.0	1.00	0.01	99.7	L1617_25	24.6	57.1	18.0	0.99	1.02	1.00
Lin_1	08/16/95	17	1501.0	1.00	0.02	99.2	L1617_30	24.4	54.0	20.7	0.97	1.16	0.97
Lin_1	08/16/95	17	1501.0	1.00	0.06	98.5	L1617_35	24.4	50.3	23.8	0.95	1.33	0.95
Lin_1	08/16/95	17	1501.0	1.00	0.10	97.9	L1617_40	24.5	46.3	27.1	0.94	1.51	0.94
Lin_1	08/16/95	17	1501.0	0.99	0.14	97.3	L1617_45	24.6	42.1	30.5	0.93	1.70	0.92
Lin_1	08/16/95	17	1501.0	0.99	0.17	95.7	L1617_50	24.7	38.1	32.8	0.90	1.83	0.92
Lin_2	08/17/95	10	734.8	1.00	0.01	100.1	L1710_05	7.9	87.6	4.6	0.99	1.00	1.01
Lin_2	08/17/95	10	734.8	1.00	0.01	100.1	L1710_10	7.9	83.0	9.2	0.99	1.00	1.01
Lin_2	08/17/95	10	734.8	1.00	0.06	99.5	L1710_15	7.8	78.9	12.7	0.93	1.33	0.97
Lin_2	08/17/95	10	734.8	1.00	0.15	98.6	L1710_20	7.8	74.4	16.4	0.94	1.71	0.93
Lin_2	08/17/95	10	734.8	0.99	0.26	97.2	L1710_25	7.9	69.7	19.6	1.12	2.05	0.88
Lin_2	08/17/95	10	734.8	0.99	0.34	94.6	L1710_30	7.9	65.0	21.7	1.24	2.26	0.85
Lin_2	08/17/95	10	734.8	0.99	0.34	90.3	L1710_35	7.9	60.6	21.8	1.24	2.27	0.85
Lin_2	08/17/95	10	734.8	0.99	0.35	85.9	L1710_40	7.9	56.2	21.8	1.24	2.27	0.86
Lin_2	08/17/95	10	734.8	0.99	0.37	81.5	L1710_45	7.9	51.7	21.9	1.24	2.28	0.86
Lin_2	08/17/95	10	734.8	0.99	0.39	77.0	L1710_50	7.9	47.2	22.0	1.25	2.29	0.86
Lin_3	08/18/95	07	580.5	1.00	0.02	99.8	L1807_05	6.4	88.9	4.6	1.00	0.99	1.00
Lin_3	08/18/95	07	580.5	1.00	0.02	99.8	L1807_10	6.3	84.3	9.2	1.00	0.99	1.00
Lin_3	08/18/95	07	580.5	1.00	0.05	99.3	L1807_15	6.3	80.2	12.8	0.96	1.22	0.97
Lin_3	08/18/95	07	580.5	1.00	0.14	98.6	L1807_20	6.3	75.6	16.7	0.92	1.59	0.95
Lin_3	08/18/95	07	580.5	0.99	0.22	97.8	L1807_25	6.3	70.8	20.8	0.91	1.97	0.92
Lin_3	08/18/95	07	580.5	0.99	0.30	96.5	L1807_30	6.3	66.0	24.2	1.06	2.29	0.88
Lin_3	08/18/95	07	580.5	0.99	0.36	94.1	L1807_35	6.3	61.3	26.5	1.16	2.52	0.86
Lin_3	08/18/95	07	580.5	0.99	0.37	89.8	L1807_40	6.3	56.8	26.6	1.16	2.52	0.86
Lin_3	08/18/95	07	580.5	0.99	0.38	85.3	L1807_45	6.3	52.3	26.7	1.17	2.53	0.87
Lin_3	08/18/95	07	580.5	0.99	0.39	80.8	L1807_50	6.3	47.7	26.8	1.17	2.54	0.87

1. The last two numbers represent the percentages of running loss removed from the tunnel measurements.

system during vehicle operation as a result of the heating of the fuel tank. Vapors are released when the rate of fuel vapor formation exceeds the capacity of the vapor storage and purge systems. The composition of running losses will tend to resemble headspace vapors if the canister is saturated, and butane-enriched vapors if the canister is not saturated. Resting loss evaporative emissions are due to migration of fuel vapors from the evaporative canister, from leaks, and from fuel permeation through joints, seals, and polymeric components of the fuel system. Most of these losses will tend to appear more like whole liquid gasoline. Of the alternative profiles for evaporative emissions, the headspace vapor profiles consistently gave the best fit (Fujita et al., 1997a).

Composite liquid and headspace vapor profiles consisting of an average of different brands and grades of gasoline were derived in conjunction with the 1995 on-road emissions and receptor modeling studies in the northeastern U. S. and the Los Angeles area (Fujita et al., 1997a). Ten gasoline samples were collected by DRI in the Boston area and were analyzed at the University of California, Riverside College of Engineering Center for Environmental Research and Technology (CE-CERT) under a subcontract to DRI. DRI analyzed the headspace vapor composition for these samples. In addition, sixty liquid gasoline samples (collected from the Los Angeles area during summer of 1995) were analyzed by CE-CERT for a separate study sponsored by the South Coast Air Quality Management District. The headspace vapors for a subset of these gasoline samples were analyzed by DRI as part of a study sponsored by the California Air Resources Board of the effect of California Phase 2 reformulated gasoline (Zielinska et al., 1997). Leakage of some of the gasoline samples from Boston raised concerns about the integrity of the remaining gasoline samples, particularly in regard to the relative amounts of light hydrocarbons that tend to be more abundant in samples of gasoline headspace. The Los Angeles gasoline profiles were used for all of the tunnel profile corrections and in the previous source apportionment study by Fujita et al. (1997a).

The survey of motor gasolines conducted by the National Institute of Petroleum and Energy Research (NIPER) for summer 1995 (Dickson and Sturm, 1996) show how RFGs sold in southern California differ from those sold in the Northeast. The average volume percents of saturates, olefins, total aromatics, and benzene in unleaded RFG in the Northeast are 55.1, 11.0, 23.1, and 0.67 respectively, versus 53.1, 8.6, 27.1, and 0.79, respectively, in southern California. The average RVP is 7.9 in the northeast and 7.2 in southern California. The average volume percent of MTBE is 9.8 and 10.7 percent in the northeast and southern California, respectively. The average RVP is the most significant difference between RFGs that were sold in 1995 in the northeastern U.S. versus southern California. These differences affect the amounts and composition of evaporative emissions.

Investigators from DRI recently analyzed fifteen samples consisting of five brands (ARCO, BP, Chevron, Texaco, and Unocal) and three grades (regular, midgrade, and premium) of gasolines sold the Seattle area as part of a hydrocarbon source apportionment study for western Washington (Fujita et al., 1997b). The average volume percent of saturates, olefins, total aromatics, and benzene in unleaded gasoline sold in the Pacific Northwest in 1996 were 56.3, 10.6, 33.0, and 2.37 percent, respectively (Dickson and Sturm,

1997). The average vapor pressure at 100 °F was 7.9 psi, which is similar to the RFG sold in 1995 in the northeastern U.S. However, the composition of headspace vapors for the gasoline samples from Boston in Table 3-2 shows substantially lower amounts of light-end hydrocarbons relative to corresponding samples from the Pacific Northwest. The fractions of n-butane, isopentane, and n-pentane in the headspace samples from Boston are 4.8, 21.0, and 5.6 percent, respectively. The corresponding fractions in the Seattle samples are 21.6, 25.9, and 11.1 percent, respectively, and 6.3, 17.4, and 4.3, respectively, in the Los Angeles samples. The profiles derived from the gasoline samples from the Seattle area were used for all of the tunnel profile corrections and ambient source apportionment in this study because of the suspected leakage problems with the Boston gasoline samples and similarity in RVP for gasolines sold in the northeastern U. S. and in the Pacific Northwest. Section 3.3 describe the sensitivity tests that were performed to determine the range of uncertainty associated with this decision.

The Chemical Mass Balance receptor model was applied to the ten alternative diesel and evaporative emissions-corrected samples for each tunnel run with diesel exhaust and evaporative emissions as source profile. The model performance parameters and comparisons of calculated and measured amounts of total NMHC, isobutane, n-butane, and isopentane were examined to determine the level of evaporative corrections that yield the best fit. Results are summarized in Table 3-3. We found that the fit deteriorates rapidly beyond a certain level of assumed headspace vapor contribution. This level is typically 15 to 25. The predicted vapor contributions do not increase above these levels of assumed vapor contribution. This is consistent with the expectation since there is a limit to the fractional contribution of running losses to hydrocarbons mixing ratios in roadway tunnels. Because the performance parameters for various levels of assumed headspace vapor contributions are similar up to the level at which the fit deteriorates, we derived three sets of corrected profiles for each tunnel run. One profile corresponding to no evaporative correction (i.e., only diesel correction), and a second set of profiles that corresponds to the maximum level of evaporative correction before the fit begins to deteriorate (15-20%). The third profile corresponds to an average between no correction and maximum correction (5-10%). Table 3-2 lists composites for the uncorrected tunnel measurements and composite of the best fitting diesel corrected profiles.

3.2 Compilation of Profiles from Previous Studies

In addition to the motor vehicle exhaust profiles that were derived from measurements in the Lincoln and Callahan Tunnels, the composite exhaust profile from the data of Sigsby et al., (1987) and cold-start exhaust profile (Fujita et al., 1997a) were also used in the source apportionment for comparison. The profile from Sigsby et al. was derived from the Federal Test Procedure (FTP) tests of 46 in-use passenger vehicles for 1975 to 1982 model years and was re-calculated by from the original measurements to provide a more complete chemical break-down of coeluting peaks (Fujita et al., 1994). A composition profile for cold-start emissions was obtained by DRI (Fujita et al., 1997a) from samples collected in the parking garage of the T. P. O'Neill Federal Building in downtown Boston on

September 12-13, 1995. One-hour canister samples were collected during a ventilation period ("background") and near the end of the workday at three locations within the garage.

The additional profiles that were found necessary to include in past source apportionment studies are listed in Table 3-2 (Fujita et al., 1994; Fujita et al., 1995). These profiles include solvent, biogenic, natural and liquefied petroleum gases. A large variety of formulations are used in surface coatings, and it is unlikely that one or two profiles adequately represent the emissions from all surface coatings. The most recent data are those of Censullo et al., (1996). Eleven categories of coating were analyzed in this study. In all detailed species profiles were obtained for 106 samples of water-based and solvent-based coating samples. Isoprene is taken to constitute 100 percent of NMHC in the biogenic emissions profile (BIOGENIC). Biogenic NMHC emissions are highly reactive in the atmosphere, and biogenic source contributions derived from CMB modeling will supply only a lower limit to the actual contributions from biogenic emissions. The commercial natural gas (CNG) profile is based on samples taken in the summer of 1972 at Los Angeles, CA and in the summer of 1973 at El Monte, CA. The geogenic natural gas (GNG) profile is based upon samples taken in the spring of 1972 in Newhall, CA and at a well head in Redondo Beach, CA in the fall of 1973. The composition of the samples of both types of natural gas did not vary despite the differences in time and location of sample collection (Fujita et al., 1994).

3.3 Evaluation of Source Profiles

The tunnel-derived exhaust profiles, uncorrected tunnel profiles, and dynamometer-derived exhaust profiles were applied to the same ambient samples to determine the sensitivity of the CMB model to alternative exhaust profiles. Table 3-4 shows the effect of alternative vehicle exhaust profiles on the average source contributions for a set of 65 ambient samples from the PAMS site at Bronx, NY. Samples for this test were collected during the 0700-0800, EDT in the summer of 1995. Each of the ambient samples were apportioned with the diesel profile, TU_MCHHD, plus twelve alternative gasoline vehicle exhaust profiles (Exh801a, Exh_Cal0, Exh_Cal1, Exh_Cal2, Exh_Lin0, Exh_Lin1, Exh_Lin2, Tu_Calla, Tu_Lin, Tu_Mchld, Tu_Tusld, and Wa_Tu1 using only fitting species that are enriched in diesel and spark-ignition vehicle exhaust (ethene, acetylene, propene, benzene, nonane, decane, and undecane).

Source contribution estimates using alternatives gasoline vehicle exhaust profiles range from 30 to 60 percent of total NMHC. Exhaust profiles for relatively cleaner fleets (e.g., Tuscarora and Mount Baker Tunnels) yield lower contributions. Exhaust contributions varied by no more than 10 percent for the three levels of assumed headspace vapor contributions for both Lincoln and Callahan Tunnels profiles. The profiles corresponding to the maximum level of evaporative correction gave exhaust contributions about 5-6 percent greater than profiles corresponding to averages between no correction and maximum correction. Profiles derived from the tunnel measurements at the Lincoln Tunnel consistently yielded the best model performance.

Table 3-4

CMB sensitivity test for various exhaust profiles[1]

# of samples	TNMOC $\mu g/m^3$	r^2	χ^2	% of NMHC	HD Profiles	LD Profiles	HD %	LD %
65	144.2	0.88	3.27	65.2	Tu_Mchhd	EXH801A	22.2	43.0
65	144.2	0.92	2.86	70.5	Tu_Mchhd	EXH_CAL0	22.0	48.6
65	144.2	0.92	2.81	66.6	Tu_Mchhd	EXH_CAL1	21.8	44.8
65	144.2	0.92	2.75	61.2	Tu_Mchhd	EXH_CAL2	21.9	39.3
65	144.2	0.93	2.40	78.8	Tu_Mchhd	EXH_LIN0	21.8	57.0
65	144.2	0.93	2.40	75.1	Tu_Mchhd	EXH_LIN1	21.6	53.5
65	144.2	0.93	2.28	68.7	Tu_Mchhd	EXH_LIN2	21.6	47.1
65	144.2	0.92	2.87	70.5	Tu_Mchhd	TU_CALLA	19.3	51.2
65	144.2	0.93	2.77	73.0	Tu_Mchhd	TU_LIN	14.5	58.5
65	144.2	0.88	4.83	66.6	Tu_Mchhd	TU_MCHLD	22.7	43.9
65	144.2	0.86	5.04	57.5	Tu_Mchhd	TU_TUSLD	24.3	33.2
65	144.2	0.91	3.46	52.2	Tu_Mchhd	WA_TU1	22.8	29.3

[1] Samples collected on 0700 EDT at Bronx, NY were used in the test

Table 3-5

CMB sensitivity test for other source profiles[1]

# of samples	TNMOC $\mu g/m^3$	r^2	χ^2	% of NMHC	Profiles[2] Liq. Gaso.	Profiles[2] Gaso. Vapor	HD %	LD %	Liquid Gaso.	Gaso. Vapor	Coating	CNG	GNG	LPG	Biogenic
65	144.2	0.82	6.52	139.4	LA_liqGS	BOgv01	19.7	44.7	53.7	18.5					
65	144.2	0.86	4.54	114.6	LA_liqGS	LA_HsVap	22.1	42.7	0.0	51.1					
65	144.2	0.82	6.30	94.8	LA_liqGS	WA_Vap	21.7	44.8	6.5	21.8					
65	144.2	0.80	6.63	124.0	WA_liq	BOgv01	21.6	44.9	0.0	57.4					
65	144.2	0.86	4.61	115.7	WA_liq	LA_HsVap	21.6	43.3	0.0	50.8					
65	144.2	0.82	6.03	90.1	WA_liq	WA_Vap	22.0	44.6	0.0	23.5					
65	144.2	0.89	2.81	109.2	WA_liq	WA_Vap	7.7	50.9	5.0	18.0	13.5	8.8	2.9	1.4	0.9

[1] Samples collected on 0700 EDT at Bronx, NY were used in the test

[2] Tu_Mchhd and Exh_Lin2 were used to represent HD and LD, respectively.

Table 3-5 shows the effect of alternative gasoline profiles on the average source contributions for the same set of 65 ambient samples from the PAMS sites in Bronx, NY during the 0700 EDT sampling period. Use of the vapor profiles for gasoline samples from either Boston or Los Angeles results in large overestimation of total NMHC. In contrast, the vapor profile for the Washington samples yield total predicted NMHC contributions that are, on average, about 90 of the observed ambient NMHC. Less than 100 percent is expected as only vehicle-related source profiles were included in these sensitivity tests. Adding the other default source profiles does not significantly alter the contributions among the tailpipe and evaporative emissions for gasoline vehicles, but reduces the contribution of diesel exhaust from 22.0 to 7.7 percent. The difference is assigned to surface coating because decane and undecane are major components of both diesel exhaust and surface coatings. Because the sensitivity tests shown in Table 3-4 indicate that diesel exhaust is the correct source of the higher molecular weight species at the Bronx site, the surface coating profiles were not used in the default set of profiles in order to avoid potential for collinearity between these two profiles.

4 SOURCE APPORTIONMENT OF PAMS HYDROCARBON DATA

This section presents the source apportionment results for ten PAMS sites in the NARSTO-Northeast study area. They include eight Type 2 PAMS sites in source areas (E. Hartford, CT; McMillan Reservoir, DC; Chicopee, MA; Lynn, MA; Lake Clifton, MD; Bronx, NY; Philadelphia, PA; and E. Providence, RI) and two downwind (Type 1,3, or 4) PAMS sites (Lums Pond, DE and Rider College, NJ). The speciated hydrocarbon data are hourly measurements by automated gas chromatographs at all sites except at the Philadelphia and E. Providence sites, which are eight, daily canister-based 3-hour integrated samples. CMB8.0 was applied with AUTOFIT to over 15,000 hydrocarbon samples covering the period from June 1, 1995 to August 31, 1995. Each sample was apportioned with the following default set of source profiles: heavy-duty diesel exhaust from the Ft. McHenry Tunnel (Tu_MchHD); "corrected" profile from the Lincoln Tunnel (Exh_Lin1), composite liquid gasoline from the Northwest (WA_Liq); composite gasoline headspace vapor from the Northwest (WA_Vap); commercial natural gas (CNG); liquefied petroleum gas (LPG); and isoprene emissions (Biogenic). Unidentified (UNID) was not used because of incompatibility between ambient and source data in the quantification total unidentified species.

The source contribution estimates for each of the ten PAM sites are presented in this section with respect to variations by time of day, day-of-the-week, and wind direction. Because the CMB analyses were performed by DRI personnel with limited knowledge of site characteristics and possible influence of local VOC sources near the sampling sites, this report does not include a reconciliation of the temporal and spatial variations in source contributions with source emissions near the sampling sites. An electronic file of the CMB results for individual samples can be obtained from the Coordinating Research Council for those interested in relating the hydrocarbon apportionments to specific ozone episodes during the 1995 field study.

4.1 Average Source Contribution Estimates

Table 4-1 and Figure 4-1 show the average 24-hour source contributions for each site for all valid samples collected between June 1, 1995 to August 31, 1995. Uncertainties in absolute source contributions (in ug/m3) are root mean squares of the individual one-sigma error propagations from CMB. The relative contributions (in percent) are normalized to sum of contributions including non-negative, unexplained contributions and their uncertainties are one standard deviations of the individual contributions.

For Type 2 sites, the significant contributors to the average 24-hour ambient NMHC are gasoline vehicle exhaust (40 percent), gasoline vapor (17 percent), and diesel exhaust (17 percent). Natural gas leak (9 percent), liquid gasoline (7 percent), liquefied petroleum gas (4 percent), and biogenic emissions (4 percent) are minor contributors to NMHC. On average, only 4 percent of the identified NMHC are unexplained. Three of the Type 2 sites (Chicopee and Lynn, MA and Bronx, NY) account for the relatively high average contribution of diesel exhaust. Higher diesel contributions are possible at the Bronx site due to diesel buses.

Table 4-1
24-Hour Average Source Contributions to Total NMHC for PAMS Measurements (6/1/95 to 8/31/95)

Site	CT	DC	DE	MA_C	MA_L	MD	NJ	NY	PA	RI
PAMS Site Type	2	2	1,4	2	2	2	3	2	2	2
Number of Samples	1306	1963	1861	1228	2096	1175	2094	1438	559	651
Concentration (ug/m3)	20.6 ± 2.3	89.5 ± 10.7	27.5 ± 5.2	41.7 ± 5.0	48.0 ± 5.5	70.7 ± 8.0	40.7 ± 4.9	118.3 ± 14.0	68.0 ± 8.1	65.2 ± 8.0
R-square	0.89 ± 0.06	0.82 ± 0.07	0.83 ± 0.07	0.81 ± 0.09	0.91 ± 0.06	0.78 ± 0.07	0.93 ± 0.04	0.81 ± 0.08	0.75 ± 0.04	0.88 ± 0.05
Chi-square	1.08 ± 0.75	2.93 ± 1.49	1.76 ± 1.40	2.37 ± 1.59	1.05 ± 0.78	5.72 ± 1.59	1.05 ± 0.86	4.57 ± 1.80	5.24 ± 1.71	1.93 ± 1.22
Percent Mass Attributed	100.3 ± 16.0	71.6 ± 12.8	109.9 ± 15.5	105.0 ± 26.6	110.0 ± 12.2	91.4 ± 13.4	90.1 ± 11.9	101.1 ± 16.6	104.5 ± 11.9	77.7 ± 14.8
Absolute Contributions (ug/m3) [a]										
Diesel Exhaust	1.7 ± 1.7	12.6 ± 3.3	1.5 ± 1.8	8.5 ± 2.3	21.0 ± 3.7	7.7 ± 2.3	4.9 ± 2.0	28.2 ± 5.5	2.2 ± 1.9	6.3 ± 2.4
Gasoline Vehicle Exhaust	8.9 ± 2.3	24.9 ± 5.8	6.6 ± 2.3	7.2 ± 4.6	14.8 ± 5.6	43.5 ± 3.7	14.6 ± 3.3	57.4 ± 8.3	37.7 ± 4.2	24.1 ± 4.2
Liquid Gasoline	2.2 ± 2.5	4.1 ± 8.5	1.5 ± 3.1	8.0 ± 4.5	3.8 ± 5.8	2.3 ± 5.0	2.9 ± 4.0	7.1 ± 10.1	1.3 ± 7.0	3.2 ± 5.6
Gasoline Vapors	2.5 ± 1.2	16.5 ± 4.1	6.8 ± 2.0	12.6 ± 3.1	7.1 ± 2.9	2.9 ± 2.7	7.4 ± 2.3	11.7 ± 5.3	21.1 ± 4.7	11.1 ± 3.4
Commerical Natural Gas	2.4 ± 0.5	7.5 ± 1.7	3.2 ± 0.8	3.6 ± 0.8	3.3 ± 0.8	7.0 ± 1.5	4.1 ± 0.9	9.4 ± 2.0	5.7 ± 1.3	5.1 ± 1.2
Liquefied Petroleum Gas	1.1 ± 0.4	1.3 ± 0.8	8.4 ± 4.6	1.8 ± 0.6	1.1 ± 0.7	1.6 ± 0.7	2.1 ± 0.8	1.7 ± 1.1	4.4 ± 1.4	2.9 ± 1.2
Biogenic	2.4 ± 0.6	1.5 ± 0.3	1.0 ± 0.3	2.0 ± 0.5	2.4 ± 0.5	0.9 ± 0.2	2.2 ± 0.5	1.9 ± 0.5	0.7 ± 0.2	1.5 ± 0.4
Unexplained	-0.6 ± 3.4	21.1 ± 9.0	-1.6 ± 5.7	-2.0 ± 6.2	-5.5 ± 8.1	4.8 ± 5.6	2.4 ± 5.4	1.0 ± 12.9	-5.2 ± 7.2	11.2 ± 7.0
Percent Contributions [b]										
Diesel Exhaust	8.1 ± 8.1	14.1 ± 3.7	5.5 ± 6.5	20.4 ± 5.5	43.8 ± 7.7	10.9 ± 3.2	12.1 ± 4.8	23.8 ± 4.6	3.2 ± 2.9	9.6 ± 3.7
Gasoline Vehicle Exhaust	43.4 ± 11.2	27.8 ± 6.5	24.0 ± 8.5	17.3 ± 11.0	30.8 ± 11.6	61.5 ± 5.3	35.8 ± 8.0	48.5 ± 7.0	55.5 ± 6.1	36.9 ± 6.4
Liquid Gasoline	10.7 ± 12.0	4.6 ± 9.5	5.6 ± 11.4	19.2 ± 10.7	8.0 ± 12.1	3.2 ± 7.1	7.1 ± 9.9	6.0 ± 8.6	2.0 ± 10.2	4.9 ± 8.6
Gasoline Vapors	12.1 ± 5.7	18.5 ± 4.6	24.8 ± 7.1	30.3 ± 7.4	14.8 ± 6.1	4.1 ± 3.8	18.3 ± 5.7	9.9 ± 4.5	31.1 ± 6.9	17.0 ± 5.2
Commerical Natural Gas	11.9 ± 2.5	8.4 ± 1.9	11.8 ± 2.8	8.5 ± 1.9	6.9 ± 1.6	9.9 ± 2.2	10.2 ± 2.2	8.0 ± 1.7	8.4 ± 1.9	7.8 ± 1.8
Liquefied Petroleum Gas	5.1 ± 1.8	1.5 ± 0.8	30.4 ± 16.8	4.2 ± 1.5	2.4 ± 1.4	2.3 ± 1.0	5.2 ± 1.9	1.4 ± 1.0	6.5 ± 2.0	4.4 ± 1.9
Biogenic	11.9 ± 3.0	1.6 ± 0.3	3.7 ± 1.0	4.9 ± 1.2	4.9 ± 1.1	1.3 ± 0.3	5.3 ± 1.2	1.6 ± 0.4	1.0 ± 0.2	2.2 ± 0.5
Unexplained	-3.1	23.6	-5.8	-4.8	-11.6	6.8	6.0	0.9	-7.7	17.1

[a] Uncertainties are root mean squares of the individual 1-sigma error propagations from CMB.

[b] Uncertainties are one standard deviations of individual percent contributions.

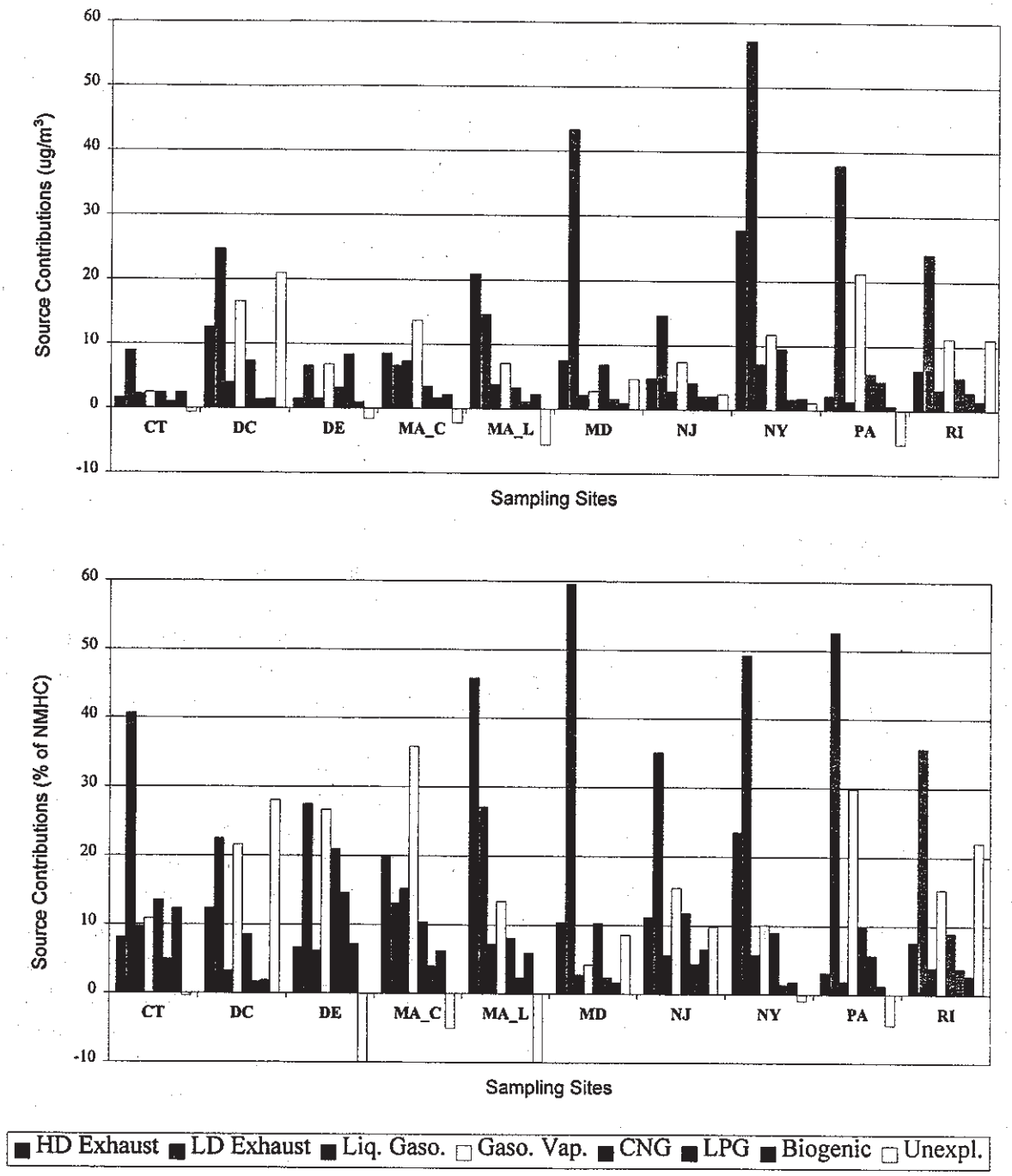

Figure 4-1. 24-hour average source contribution estimates (ug/m3 and % NMHC) during summer 1995.

However, there are no obvious sources of the high levels of heavy hydrocarbon at Chicopee and Lynn that result in high diesel contributions at those sites. Contributions of liquid gasoline and gasoline vapors are also much higher at Chicopee than for a typical Type 2 site. Removing Chicopee and Lynn from the average, decreases the average contribution of diesel exhaust for the remaining sites to 12 percent and increases gasoline vehicle exhaust to 46 percent.

The significant contributors to the average 24-hour ambient NMHC at downwind PAMS sites (Lums Pond, DE and Rider College, NJ) are gasoline vehicle exhaust (30 percent), gasoline vapor (18 percent), liquefied petroleum gas (18 percent), and natural gas (11 percent). Diesel exhaust (9 percent), liquid gasoline (6 percent), biogenic emissions (5 percent) are minor contributors to NMHC.

Biogenic emissions are a significantly larger fraction of total NMHC in suburban and rural areas than in urban area. The contributions of isoprene over a 24-hour average range from 4 to 12 percent in suburban and rural areas and are less than 2 percent in urban areas. Because isoprene is emitted only during daylight hours with peak emission rates occurring at midday, it is one of the larger sources of NMHC during the day in suburban and rural areas. For the CMB calculations performed in this study, only species with summertime lifetimes greater than that of toluene (~9 hours) were used as fitting species. An exception to this is isoprene. It was included as a fitting species despite its high reactivity because it serves as a marker for biogenic emissions. The source contribution estimates underestimated the actual source contributions of biogenic emissions, i.e., they provide a lower limit to biogenic contributions.

The actual contributions of isoprene may be estimated by examining changes between morning and afternoon samples in the ratios of reactive hydrocarbons (e.g., isomers of xylene) to a relatively unreactive hydrocarbon (e.g., benzene) from a common source (i.e., vehicle exhaust) as an indicator of the net fractional loss of reactive hydrocarbon between the two sampling periods. These ratios are invariant to atmospheric dispersion and include continuous injections of fresh emissions into the air parcel during its transport to the sampling site. The ratio of afternoon to morning xylenes/benzene ratios reflects the net fractional loss of xylenes due to atmospheric reactions. This fractional loss is adjusted to isoprene by applying the ratio of the OH radical reaction rate constants for xylenes (18.8) and isoprene (101.0). Based on this approach, Fujita (1997c) estimated that the actual daytime contributions of isoprene to total NMHC emissions may be 5 to 10 times greater than CMB estimates.

As noted earlier, unidentified compounds are not considered in the apportionment because a large fraction of these compounds are not quantified in the PAMS program due to use of dryers that remove or chemically alter the more polar compounds. These compounds include terpenes and higher molecular weight aldehydes, which are relatively more abundant in rural areas and at locations downwind of urban areas.

4.2 Diurnal and Day-of-the-Week Variations in Source Contribution Estimates

A major advantage of automated gas chromatographs is that it can be operated continuously, thereby providing time resolution that would be impractical to obtain with canister-based sampling. The CMB calculations made for hourly auto-GC data greatly enhances the understanding of the temporal variability in source contributions.

The average hourly source contribution estimates are presented for the ten PAMS sites in Table 4-2. The averages are shown as percent contributions to NMHC, and cover the period from June 1, 1995 to August 31, 1995. The time-series plots in Figure 4-2 show the same data graphically. The bar labeled unexplained is the difference between measured and calculated NMHC. Peaks in motor vehicle exhaust contributions generally correspond to morning and afternoon commute periods. The diurnal patterns in liquid gasoline contributions are essentially identical to the corresponding patterns for motor vehicle exhaust. In contrast to tailpipe contributions, the average diurnal patterns of gasoline vapor contributions show no peaks during the commute periods. Contributions of isoprene are significantly higher during the middle of the day at E. Hartford, Rider College, Chicopee, and Lynn.

Figure 4-3 shows the diurnal variations of the absolute source contributions for each source category by day of the week. While motor vehicle exhaust contributions generally peak during morning and afternoon commute periods on weekday, the average contributions are significantly lower during weekend mornings. These patterns provide confidence in the proper apportionment of vehicle emissions. The diurnal and day-of-the-week patterns in the liquid gasoline contributions are essentially identical to motor vehicle exhaust, which suggests that a large fraction of the liquid gasoline contribution may be associated with tailpipe emissions rather than evaporative emissions from either vehicle or industrial sources.

The diurnal variations in the contribution of natural gas correlate with diurnal variations in vertical mixing. This diurnal pattern and lack of day-of-the-week variations are consistent with constant leakage of natural gas. LPG generally shows the same diurnal variations. However, lower contributions for LPG during weekend mornings suggests some correlation with the vehicle exhaust profile since the latter profile is derived from roadside ambient measurements.

4.3 Wind Directional Dependence of Source Contributions

Figure 4-4 shows the average source contributions in ug/m3 of NMHC by wind sector (centered on N, NE, E, SE, S, SW, W, NW) and time of the day (00-06, 06-12, 12-18, and 18-24, EDT) for Lums Pond, Chicopee, Lynn, Lake Chifton, Rider College, and Bronx.

At Lums Pond, motor vehicle exhaust contributions are predominantly from the northwest, north, and northeast. Gasoline vapor and liquid gasoline show strong wind dependence out of the northeast. Propane, which is not shown in the plots, are the most

Table 4-2
Average Hourly Source Contributions for PAMS Measurements (6/1/95 to 8/31/95)

E. Hartford, CT

Hour EDT	# in Avg.	R^2	χ^2	% of NMHC Explained %	NMHC ($\mu g/m^3$)	HD Exhaust %	LD Exhaust %	Liquid Gasoline %	Gasoline Vapor %	CNG %	LPG %	Biogenic %	Unexpl. %
00	57	0.90	1.06	106.4	21.2	8.8	49.3	14.3	11.6	12.9	6.0	3.7	-6.5
01	60	0.89	1.11	101.8	20.9	9.7	47.5	10.4	11.4	13.4	6.3	3.1	-1.8
02	52	0.89	1.15	103.9	20.5	8.2	47.9	12.3	12.2	14.0	6.5	2.8	-3.9
03	55	0.89	1.08	104.2	19.5	8.9	46.7	12.1	12.4	14.3	7.9	2.1	-4.3
04	59	0.87	1.17	99.7	19.2	8.6	41.1	15.5	10.8	15.3	6.7	1.9	0.3
05	55	0.88	1.15	101.7	19.5	9.1	41.7	14.0	12.3	15.0	7.8	1.9	-1.7
06	54	0.89	1.06	102.5	20.6	7.4	45.2	13.0	13.4	14.2	7.4	1.9	-2.6
07	57	0.90	1.17	103.5	24.7	9.7	47.3	13.9	10.9	13.0	5.9	3.0	-3.5
08	45	0.90	1.22	105.0	25.1	7.3	47.9	14.7	11.2	12.4	5.2	6.3	-5.0
09	49	0.90	1.16	100.4	23.1	6.4	39.7	13.6	11.4	13.2	4.6	11.5	-0.4
10	49	0.88	1.18	97.6	22.1	9.9	36.8	8.2	10.8	14.3	4.4	13.3	2.4
11	45	0.89	1.10	99.3	21.1	6.3	36.8	9.2	10.4	13.7	3.7	19.2	0.6
12	55	0.88	1.17	96.9	20.2	7.5	33.6	10.5	10.4	13.8	3.9	17.2	3.1
13	57	0.88	1.10	94.6	19.2	7.9	33.2	6.6	10.1	14.8	4.0	18.1	5.4
14	50	0.89	1.00	97.2	18.5	6.2	31.9	7.0	10.4	14.5	3.5	23.7	2.8
15	53	0.89	1.05	98.7	18.4	8.7	35.0	4.4	10.6	14.0	3.3	22.7	1.3
16	57	0.88	0.98	94.7	18.5	9.0	32.7	3.6	9.2	14.3	2.7	23.2	5.3
17	55	0.89	0.96	96.0	18.4	8.3	32.0	4.1	9.8	13.5	2.7	25.6	4.0
18	57	0.89	1.00	96.5	18.6	7.8	33.5	3.5	10.5	12.8	3.6	24.9	3.5
19	59	0.89	0.93	96.2	19.7	8.5	34.4	3.5	8.8	13.3	3.4	24.3	3.8
20	54	0.90	1.01	99.3	21.9	5.8	40.5	6.0	9.5	11.3	4.5	21.6	0.7
21	56	0.89	1.13	102.6	22.2	7.7	46.0	9.5	9.9	12.1	5.0	12.3	-2.6
22	60	0.89	1.04	102.3	21.5	9.5	45.1	11.9	10.9	12.6	5.0	7.3	-2.4
23	56	0.90	1.04	106.6	20.9	8.1	49.7	12.4	13.4	12.7	5.5	4.9	-6.6
All	1306	0.89	1.08	100.3	20.6	8.1	40.6	9.8	10.9	13.6	5.0	12.3	-0.3
McMillan Reservoir, DC													
00	81	0.83	3.37	77.3	117.6	12.7	28.7	5.2	18.9	9.20	1.44	1.2	22.7
01	86	0.82	3.02	74.0	104.2	13.4	24.5	4.0	19.4	10.10	1.55	1.2	26.0
02	87	0.82	2.87	72.4	100.8	13.8	22.4	3.3	19.4	11.02	1.68	0.8	27.6
03	87	0.82	2.64	71.6	92.9	14.3	20.5	2.9	20.8	11.60	1.68	0.6	27.6
04	87	0.83	2.34	70.0	87.2	14.2	17.4	2.4	21.4	12.16	1.97	0.6	29.9
05	82	0.81	2.72	71.6	88.6	13.5	20.5	2.7	20.4	11.89	2.09	0.6	28.4
06	82	0.82	3.10	73.6	102.6	12.5	26.7	3.1	18.0	10.69	1.89	0.6	26.5
07	79	0.83	3.33	76.6	107.9	12.1	30.3	3.1	18.9	8.79	2.09	1.1	23.6
08	80	0.83	3.38	77.2	103.7	12.1	30.5	3.2	19.8	7.42	2.14	1.9	22.9
09	79	0.83	3.25	75.7	92.6	13.1	27.9	3.4	21.9	7.34	2.41	2.5	21.6
10	66	0.83	2.75	72.8	78.7	13.7	21.8	2.8	25.5	7.48	2.65	2.7	23.3
11	64	0.81	2.69	69.2	71.0	12.2	16.9	1.7	26.7	7.39	2.23	2.6	30.3
12	68	0.82	2.39	67.3	66.1	12.5	13.4	1.6	28.0	7.55	1.92	2.4	32.7
13	80	0.80	2.30	64.8	64.8	14.1	9.9	1.9	27.5	7.46	1.64	2.3	35.2
14	81	0.81	2.11	63.2	62.4	13.8	8.7	1.5	27.9	7.44	1.33	2.5	36.8
15	86	0.81	2.32	63.0	67.2	12.2	11.7	1.6	26.3	7.30	1.23	2.6	37.1
16	86	0.81	2.43	63.1	67.4	10.8	14.3	1.9	24.8	7.19	1.23	2.8	36.9
17	87	0.82	2.64	65.2	68.6	9.7	17.5	3.9	22.6	7.30	1.26	3.0	34.8
18	87	0.82	2.81	67.1	71.7	9.5	21.0	2.6	21.9	7.56	1.32	3.4	32.9
19	87	0.82	3.09	71.0	79.6	10.7	24.4	4.4	19.3	7.55	1.27	3.3	29.0
20	88	0.82	3.63	75.7	93.8	11.1	31.1	4.9	17.1	7.35	1.31	2.5	24.6
21	86	0.83	3.80	79.1	110.5	11.7	34.7	5.5	16.8	7.41	1.27	1.7	20.9
22	85	0.83	3.78	79.7	121.3	12.7	34.0	5.1	17.4	7.57	1.34	1.6	20.3
23	82	0.83	3.49	77.6	117.6	12.1	31.5	5.4	17.7	8.29	1.25	1.4	22.2
All	1963	0.82	2.93	71.6	89.1	12.4	22.5	3.3	21.6	8.5	1.7	1.9	28.1

Table 4-2 (continued)
Average Hourly Source Contributions for PAMS Measurements (6/1/95 to 8/31/95)

Lums Pond, DE

Hour EDT	# in Avg.	R^2	χ^2	% of NMHC Explained %	NMHC ($\mu g/m^3$)	HD Exhaust %	LD Exhaust %	Liquid Gasoline %	Gasoline Vapor %	CNG %	LPG %	Biogenic %	Unexpl. %
00	80	0.82	1.72	110.4	39.6	6.7	32.9	7.1	26.1	19.1	16.8	1.8	-10.5
01	77	0.82	1.86	111.3	28.3	6.4	28.9	10.7	27.8	19.7	16.2	1.6	-11.3
02	77	0.82	1.71	109.7	33.1	6.8	27.2	8.9	28.1	19.6	17.6	1.7	-9.7
03	78	0.81	1.91	109.8	38.0	6.6	26.1	10.0	27.6	18.4	20.2	0.9	-9.8
04	78	0.82	1.88	110.5	30.5	7.4	26.7	8.7	29.0	18.2	19.6	1.0	-10.5
05	77	0.81	1.97	109.6	31.5	6.8	23.6	11.0	29.0	16.9	21.3	1.0	-9.7
06	78	0.80	2.42	108.9	38.8	7.6	29.6	7.0	28.6	14.6	20.3	1.1	-8.9
07	78	0.80	2.72	110.0	38.4	6.4	32.7	7.0	28.1	14.7	18.0	3.0	-10.0
08	77	0.81	2.57	109.6	43.1	5.8	29.1	7.4	27.4	15.4	18.9	5.5	-9.6
09	63	0.81	2.26	113.0	37.9	7.1	28.8	5.3	29.5	18.6	17.2	6.6	-13.0
10	62	0.82	1.87	112.2	26.1	7.0	24.1	6.4	31.1	20.7	15.7	7.2	-12.3
11	67	0.83	1.76	109.1	29.7	4.5	25.8	5.6	30.3	21.7	13.7	7.6	-9.1
12	77	0.84	1.66	110.6	22.3	8.7	24.0	4.7	28.1	23.7	13.2	8.1	-10.7
13	80	0.84	1.46	110.7	18.5	11.5	21.1	4.6	25.3	25.1	14.3	9.0	-10.8
14	81	0.84	1.34	109.7	18.8	10.3	21.4	3.7	24.4	26.9	12.2	10.9	-9.7
15	80	0.84	1.19	108.0	12.7	8.3	20.3	3.8	24.9	28.8	9.0	13.0	-8.0
16	81	0.84	1.26	108.7	13.3	5.5	26.8	3.1	22.6	27.3	9.1	14.6	-8.8
17	80	0.85	1.10	107.9	12.8	5.3	24.8	3.9	22.2	27.1	9.1	15.7	-8.0
18	82	0.85	1.20	108.9	13.9	5.7	27.0	2.5	20.9	25.9	8.9	18.1	-8.9
19	82	0.84	1.49	107.1	19.7	4.0	25.3	4.7	23.3	22.2	9.7	18.0	-7.2
20	82	0.83	1.79	110.0	23.5	4.3	34.7	4.2	25.0	19.8	10.2	11.9	-10.0
21	81	0.83	1.86	110.5	30.5	4.3	34.1	7.6	26.0	19.9	11.8	6.9	-10.5
22	81	0.83	1.72	111.5	31.1	6.3	32.3	6.3	27.3	20.8	14.4	4.1	-11.5
23	82	0.83	1.64	111.1	33.2	7.3	32.6	5.7	27.9	19.8	15.2	2.6	-11.1
All	1861	0.83	1.77	110.0	27.7	6.7	27.5	6.2	26.7	21.0	14.7	7.2	-10.0

Chicopee, MA

00	60	0.84	2.07	104.0	47.2	21.0	17.5	22.5	25.4	10.99	4.53	2.1	-4.0
01	60	0.85	2.01	105.9	46.4	24.0	17.3	21.0	24.9	12.01	5.06	1.6	-5.9
02	55	0.84	2.01	105.3	41.6	22.6	13.0	22.6	26.8	13.29	5.03	1.9	-5.3
03	60	0.82	2.27	103.5	42.2	23.7	12.4	20.0	26.4	13.85	5.36	1.8	-3.5
04	58	0.84	2.05	104.3	40.1	20.8	12.3	22.8	26.6	14.32	5.98	1.5	-4.3
05	59	0.84	1.85	102.3	40.5	19.8	10.9	22.0	26.7	15.52	5.93	1.5	-2.3
06	59	0.85	1.99	105.0	41.7	19.4	18.1	18.4	28.1	12.74	6.50	1.9	-5.0
07	59	0.85	2.16	106.9	48.8	20.5	19.1	18.5	31.0	8.87	5.89	3.1	-6.9
08	54	0.80	3.07	101.3	56.3	19.5	18.7	15.6	31.2	7.36	5.29	3.6	-1.3
09	52	0.79	2.73	106.3	45.4	21.4	13.0	13.2	40.8	8.19	4.34	5.5	-6.3
10	44	0.77	2.94	110.0	45.6	20.3	11.3	12.0	47.4	8.49	3.88	6.7	-10.0
11	36	0.75	3.36	109.9	46.9	20.4	10.6	9.9	50.1	8.32	3.19	7.5	-9.9
12	31	0.73	3.80	107.8	48.0	21.2	8.8	7.9	51.4	7.65	2.83	8.0	-7.8
13	27	0.75	3.30	106.8	43.9	17.7	9.1	11.4	48.5	9.35	2.86	7.9	-6.9
14	30	0.73	3.16	107.3	36.9	20.8	6.7	5.9	50.8	9.51	2.29	11.3	-7.3
15	34	0.74	2.79	99.3	34.5	19.4	4.4	9.4	44.1	8.72	2.37	11.0	0.7
16	38	0.74	2.82	102.1	34.2	19.5	3.8	8.7	46.7	9.26	2.14	12.0	-2.1
17	51	0.75	2.75	102.5	32.4	17.2	6.9	6.1	47.0	9.78	2.26	13.2	-2.5
18	59	0.76	2.60	103.9	30.6	17.3	8.6	8.0	43.2	9.58	2.34	14.9	-3.9
19	60	0.81	2.04	104.4	32.3	18.1	12.6	12.8	34.8	9.71	3.10	13.3	-4.4
20	60	0.84	1.84	105.6	35.0	19.4	17.3	18.4	29.6	9.86	2.98	8.0	-5.6
21	60	0.85	1.99	105.9	38.7	19.7	20.1	18.9	27.7	10.82	3.66	5.0	-5.9
22	60	0.85	1.95	105.2	42.5	18.9	22.8	19.2	26.3	10.82	3.82	3.4	-5.2
23	62	0.86	1.99	106.7	47.9	19.6	21.0	22.3	26.0	10.84	4.46	2.5	-6.7
All	1228	0.80	2.48	105.1	41.6	20.1	13.2	15.3	35.9	10.4	4.0	6.2	-5.1

Table 4-2 (continued)
Average Hourly Source Contributions for PAMS Measurements (6/1/95 to 8/31/95)

Lynn, MA

Hour EDT	# in Avg.	R^2	χ^2	% of NMHC Explained %	NMHC (µg/m³)	HD Exhaust %	LD Exhaust %	Liquid Gasoline %	Gasoline Vapor %	CNG %	LPG %	Biogenic %	Unexpl. %
00	90	0.92	0.97	112.7	53.3	44.4	31.5	8.8	15.7	8.8	2.8	0.8	-12.7
01	89	0.91	1.05	113.4	50.6	45.1	29.1	8.6	17.1	9.4	3.3	0.8	-13.4
02	89	0.91	1.01	112.3	47.0	46.8	25.0	9.8	16.4	9.7	3.9	0.7	-12.3
03	78	0.91	0.94	111.3	43.6	47.7	23.3	9.2	16.0	10.5	4.1	0.6	-11.3
04	86	0.90	1.05	109.5	42.8	47.4	20.2	11.2	15.4	10.3	4.3	0.7	-9.5
05	85	0.89	1.18	110.3	43.2	46.8	21.1	11.3	15.4	10.4	4.6	0.7	-10.3
06	89	0.91	1.14	109.3	49.3	42.6	27.9	9.6	13.6	9.6	4.2	1.9	-9.3
07	88	0.92	1.21	110.3	56.6	38.5	34.0	8.2	14.2	7.8	3.6	4.0	-10.3
08	86	0.90	1.53	108.7	56.2	38.3	33.3	8.2	12.9	6.9	3.0	6.2	-8.7
09	83	0.90	1.51	110.8	51.3	41.5	29.5	9.1	12.7	7.2	2.5	8.2	-10.8
10	84	0.89	1.37	109.4	47.1	45.0	25.3	6.7	13.1	7.8	1.6	9.8	-9.4
11	84	0.88	1.30	107.3	44.0	47.7	21.0	5.9	12.5	7.2	1.4	11.6	-7.3
12	85	0.89	1.12	107.1	41.5	47.3	21.2	4.7	11.9	7.6	1.0	13.4	-7.1
13	88	0.89	0.95	105.9	37.4	50.8	16.8	3.5	11.7	8.0	1.0	14.2	-5.9
14	88	0.89	1.08	105.0	43.5	50.6	17.2	3.4	11.3	7.2	2.3	13.0	-5.0
15	90	0.90	0.89	106.7	41.6	51.8	19.7	3.4	10.8	7.3	0.6	13.1	-6.8
16	90	0.91	0.85	107.0	41.0	50.7	21.6	3.3	11.0	7.3	0.9	12.3	-7.0
17	90	0.92	0.81	108.8	41.1	49.4	25.4	5.3	10.0	7.4	0.9	10.3	-8.8
18	90	0.92	0.80	109.0	41.9	49.2	26.3	4.5	11.6	7.5	1.6	8.3	-9.0
19	89	0.92	0.87	110.9	47.0	46.9	33.1	4.7	12.3	7.1	1.5	5.4	-10.9
20	86	0.93	0.90	112.1	52.5	43.3	37.3	7.1	13.4	7.1	1.5	2.5	-12.1
21	90	0.93	0.98	113.9	59.1	42.6	38.2	8.6	14.1	7.0	1.6	1.7	-13.9
22	90	0.93	0.98	114.7	61.8	42.2	38.0	9.0	15.0	7.3	1.9	1.3	-14.7
23	89	0.93	0.89	112.5	56.8	43.5	34.6	8.5	14.8	7.9	2.1	1.0	-12.6
All	2096	0.91	1.06	110.0	47.9	45.8	27.1	7.2	13.5	8.1	2.3	5.9	-10.0

Lake Clifton, MD

00	54	0.80	5.46	93.5	89.8	11.5	59.1	4.3	5.8	10.21	2.17	0.6	6.5
01	49	0.80	5.56	93.7	81.3	11.5	58.5	5.2	3.1	12.32	2.41	0.6	6.3
02	52	0.78	5.68	92.7	77.6	12.5	54.9	4.1	4.1	14.22	2.50	0.5	7.3
03	49	0.76	5.51	91.3	66.9	11.5	52.0	4.8	3.9	16.19	2.67	0.4	8.7
04	49	0.76	5.71	92.0	63.6	11.5	51.9	3.1	5.1	17.31	2.85	0.3	8.0
05	49	0.78	5.39	94.4	67.0	11.7	56.0	1.7	4.5	17.44	2.93	0.2	5.6
06	51	0.81	5.38	93.4	84.7	10.9	62.4	1.8	2.3	12.84	2.77	0.4	6.6
07	47	0.82	5.77	94.1	94.6	9.9	66.4	2.3	2.2	9.76	2.66	0.9	5.9
08	39	0.82	5.83	95.6	93.9	11.0	66.6	2.5	3.3	7.75	2.68	1.9	4.3
09	43	0.80	5.93	94.0	80.4	11.1	63.7	2.3	3.9	7.92	2.83	2.3	6.0
10	47	0.78	5.89	92.4	64.6	10.3	61.9	2.1	4.4	8.64	2.89	2.3	7.6
11	38	0.77	5.52	92.1	55.0	10.9	59.5	3.3	4.4	8.91	2.84	2.3	7.9
12	50	0.74	5.95	89.7	50.4	10.7	57.8	2.8	4.7	8.30	2.85	2.5	10.3
13	40	0.74	5.87	86.8	48.5	9.8	55.7	2.2	5.3	9.04	2.73	2.1	13.2
14	42	0.74	5.86	89.0	48.0	10.1	57.4	2.5	5.1	8.96	2.23	2.8	11.0
15	50	0.72	6.04	84.9	49.9	9.4	53.4	2.6	5.5	8.85	1.94	3.2	15.1
16	53	0.73	5.80	84.1	47.2	9.8	53.5	2.4	4.4	8.68	2.01	3.3	15.9
17	53	0.75	5.94	85.1	50.9	9.5	56.7	2.0	3.4	8.42	1.83	3.2	14.9
18	54	0.76	5.95	86.8	55.3	9.0	57.6	1.8	4.6	8.38	2.09	3.3	13.3
19	53	0.80	5.55	88.6	68.4	8.8	61.7	1.4	4.4	7.47	1.84	3.0	11.4
20	51	0.82	5.62	92.4	77.4	9.2	66.0	1.7	4.0	7.71	2.02	1.9	7.6
21	54	0.82	5.55	96.9	83.8	9.4	67.3	3.2	4.8	8.56	1.88	1.0	4.0
22	55	0.82	5.92	96.0	94.4	9.6	67.5	3.1	4.7	8.48	1.94	0.7	4.0
23	53	0.81	5.59	94.7	96.3	10.0	64.0	3.7	4.4	9.99	2.04	0.6	5.3
All	1175	0.78	5.72	91.4	70.4	10.4	59.6	2.8	4.3	10.3	2.4	1.7	8.6

Table 4-2 (continued)
Average Hourly Source Contributions for PAMS Measurements (6/1/95 to 8/31/95)

Rider College, NJ

Hour EDT	# in Avg.	R^2	χ^2	% of NMHC Explained %	NMHC (µg/m³)	HD Exhaust %	LD Exhaust %	Liquid Gasoline %	Gasoline Vapor %	CNG %	LPG %	Biogenic %	Unexpl. %
00	85	0.93	0.98	89.2	41.5	13.0	36.2	8.0	15.4	10.8	4.6	1.1	10.8
01	89	0.92	1.12	89.1	44.4	12.3	34.0	11.1	15.4	10.8	4.6	0.9	10.9
02	89	0.92	1.17	89.4	45.6	12.9	33.0	10.2	16.2	11.1	5.2	0.7	10.6
03	89	0.91	1.23	90.2	47.3	12.8	32.8	9.7	17.4	11.5	5.6	0.6	9.8
04	89	0.91	1.32	90.5	49.2	12.4	33.1	9.0	18.1	11.6	5.7	0.7	9.5
05	88	0.92	1.36	90.6	52.2	11.6	33.7	7.8	18.9	12.2	5.9	0.5	9.4
06	87	0.91	1.33	90.9	54.1	11.7	33.9	7.7	19.3	11.8	5.9	0.7	9.1
07	86	0.92	1.40	91.3	58.9	11.5	36.6	6.6	17.9	10.7	5.5	2.4	8.7
08	85	0.92	1.46	92.0	58.3	10.9	37.8	6.9	17.0	10.4	5.1	4.0	8.0
09	88	0.92	1.36	92.8	49.5	11.1	37.7	6.5	16.3	10.8	5.0	5.5	7.2
10	84	0.92	1.37	92.7	45.8	12.3	35.7	5.7	16.2	11.4	4.6	6.8	7.3
11	82	0.92	1.23	93.0	39.2	11.8	35.4	5.2	15.6	12.7	4.5	7.8	7.0
12	88	0.92	1.13	91.6	33.2	11.1	34.5	4.1	15.2	13.1	4.3	9.3	8.4
13	87	0.92	1.00	89.1	29.9	9.7	34.0	3.2	14.0	13.6	3.8	10.8	10.9
14	88	0.93	0.84	89.5	28.5	9.7	33.3	2.8	13.5	14.3	3.7	12.1	10.5
15	88	0.93	0.75	88.5	27.4	9.1	32.6	1.8	13.3	14.6	3.5	13.6	11.5
16	90	0.93	0.77	87.2	27.9	8.7	31.3	1.8	13.2	13.7	3.4	15.2	12.8
17	89	0.93	0.77	88.0	29.3	8.6	32.6	1.7	13.0	12.9	3.4	15.7	12.0
18	90	0.94	0.73	88.8	30.7	9.1	32.7	2.7	13.0	12.0	3.2	16.3	11.2
19	90	0.94	0.81	90.1	34.2	10.3	35.1	3.7	13.1	10.3	3.4	14.3	9.9
20	90	0.94	0.77	89.7	36.7	10.8	38.4	4.4	13.2	10.3	3.5	9.0	10.3
21	88	0.94	0.75	90.0	36.5	12.3	39.3	4.7	14.6	10.5	3.7	4.9	10.0
22	84	0.94	0.82	90.3	37.4	12.4	40.7	4.9	15.4	10.3	4.0	2.6	9.7
23	81	0.93	0.87	88.7	39.8	12.6	37.5	6.8	15.3	10.5	4.5	1.6	11.3
All	2094	0.93	1.06	90.1	40.7	11.2	35.1	5.7	15.4	11.7	4.4	6.6	9.9

Bronx, NY

00	62	0.83	4.19	102.3	138.3	23.7	56.5	3.8	8.8	7.80	1.33	0.3	-2.3
01	47	0.84	4.16	104.1	133.4	23.4	53.3	6.2	11.2	8.71	1.11	0.2	-4.1
02	48	0.81	5.10	100.1	135.9	19.2	53.1	7.7	8.3	10.16	1.40	0.2	-0.1
03	50	0.80	5.57	96.7	130.2	13.4	51.7	7.7	10.8	11.32	1.49	0.2	3.3
04	50	0.79	5.33	98.0	103.3	12.0	49.5	9.4	11.5	13.36	2.02	0.2	2.0
05	57	0.79	4.76	102.0	100.3	17.8	45.4	10.2	11.8	14.73	1.94	0.2	-2.0
06	66	0.79	4.68	102.5	103.5	23.0	45.0	6.8	11.4	14.33	1.86	0.2	-2.5
07	65	0.84	3.88	105.4	120.6	21.8	52.0	5.7	11.4	12.36	1.87	0.4	-5.4
08	67	0.86	3.72	105.9	141.9	21.2	57.1	4.9	10.3	9.93	1.66	0.9	-5.9
09	66	0.86	3.81	104.4	144.4	20.2	58.1	4.1	10.6	8.28	1.75	1.4	-4.4
10	63	0.84	4.09	101.3	132.2	23.8	51.4	5.0	9.5	8.12	1.62	1.9	-1.3
11	63	0.82	4.34	101.3	129.2	26.8	48.2	4.9	9.9	7.47	1.65	2.5	-1.3
12	63	0.79	5.06	97.2	118.6	25.5	45.0	4.3	10.1	7.54	1.67	3.0	2.8
13	59	0.78	4.90	101.1	103.4	29.9	41.5	4.9	11.9	7.53	1.74	3.6	-1.1
14	58	0.78	4.77	102.8	96.9	30.7	39.6	6.3	12.7	7.88	1.53	4.1	-2.8
15	55	0.78	4.88	98.8	114.5	28.8	39.2	6.2	11.6	7.13	1.55	4.4	1.2
16	54	0.77	5.11	97.4	106.8	26.9	40.2	5.6	11.6	7.24	1.46	4.4	2.6
17	56	0.77	5.09	98.3	95.3	28.0	40.5	6.5	10.4	7.21	1.06	4.6	1.7
18	58	0.79	4.74	101.2	97.0	27.5	46.0	6.6	8.8	7.41	0.81	4.1	-1.2
19	68	0.79	4.88	98.1	103.6	26.2	47.0	4.9	8.3	7.36	0.81	3.5	1.9
20	66	0.82	4.54	99.8	114.3	23.1	53.8	4.7	7.7	7.41	0.84	2.3	0.2
21	68	0.83	4.21	101.5	121.1	25.7	54.1	4.0	8.4	7.15	1.09	1.0	-1.5
22	68	0.83	4.36	101.5	123.6	24.1	55.8	5.0	7.8	7.40	0.91	0.6	-1.5
23	61	0.84	4.23	101.5	127.2	22.7	58.2	3.3	8.0	7.80	1.08	0.4	-1.5
All	1438	0.81	4.60	101.0	118.1	23.6	49.3	5.8	10.1	9.0	1.4	1.9	-1.0

Table 4-2 (continued)
Average 3-Hour Source Contributions for PAMS Measurements (6/1/95 to 8/31/95)

Philadelphia, PA

Hour EDT	# in Avg.	R^2	χ^2	% of NMHC Explained %	NMHC ($\mu g/m^3$)	HD Exhaust %	LD Exhaust %	Liquid Gasoline %	Gasoline Vapor %	CNG %	LPG %	Biogenic %	Unexpl. %
00	69	0.75	5.09	103.6	78.2	2.5	46.5	2.6	33.0	11.6	7.0	0.5	-3.6
03	63	0.73	5.28	103.0	72.1	3.6	42.1	4.2	30.3	14.0	8.4	0.5	-3.0
06	68	0.76	5.84	108.3	90.6	3.6	58.0	1.6	28.2	9.7	6.5	0.7	-8.3
09	71	0.74	5.91	104.1	70.3	4.4	52.0	2.1	29.0	8.8	6.0	1.8	-4.1
12	69	0.75	4.77	102.6	51.1	3.5	50.4	0.5	31.8	9.3	5.0	2.2	-2.6
15	75	0.75	4.70	103.4	50.2	2.7	53.7	1.3	30.3	9.1	4.4	1.9	-3.5
18	75	0.77	4.92	105.2	56.7	1.7	58.6	1.5	28.8	8.7	4.2	1.7	-5.2
21	69	0.77	5.46	105.5	77.7	3.1	59.8	1.7	27.7	8.0	4.2	1.0	-5.5
All	559	0.75	5.25	104.5	68.4	3.1	52.6	1.9	29.9	9.9	5.7	1.3	-4.5
E. Providence, RI													
00	79	0.89	1.83	83.0	78.3	8.4	33.9	5.8	20.0	10.36	4.12	0.4	17.0
03	80	0.88	2.11	80.8	81.2	9.0	30.4	5.9	18.5	11.97	4.77	0.3	19.2
06	79	0.89	2.39	85.2	90.5	8.6	42.8	2.9	16.5	8.35	4.46	1.6	14.8
09	78	0.86	2.30	78.9	54.9	8.0	38.1	3.6	13.8	8.32	3.30	3.8	21.1
12	84	0.86	1.86	68.2	42.7	5.5	30.8	3.4	11.1	8.77	3.33	5.2	31.8
15	86	0.87	1.81	68.7	46.9	6.6	31.5	2.6	11.5	7.86	3.26	5.4	31.3
18	84	0.90	1.58	75.4	58.3	6.9	37.7	2.5	13.6	7.15	3.61	3.9	24.6
21	81	0.92	1.57	82.9	71.6	7.9	40.7	4.3	17.5	8.27	3.21	1.1	17.1
All	651	0.88	1.93	77.9	65.5	7.6	35.7	3.9	15.3	8.88	3.76	2.7	22.1

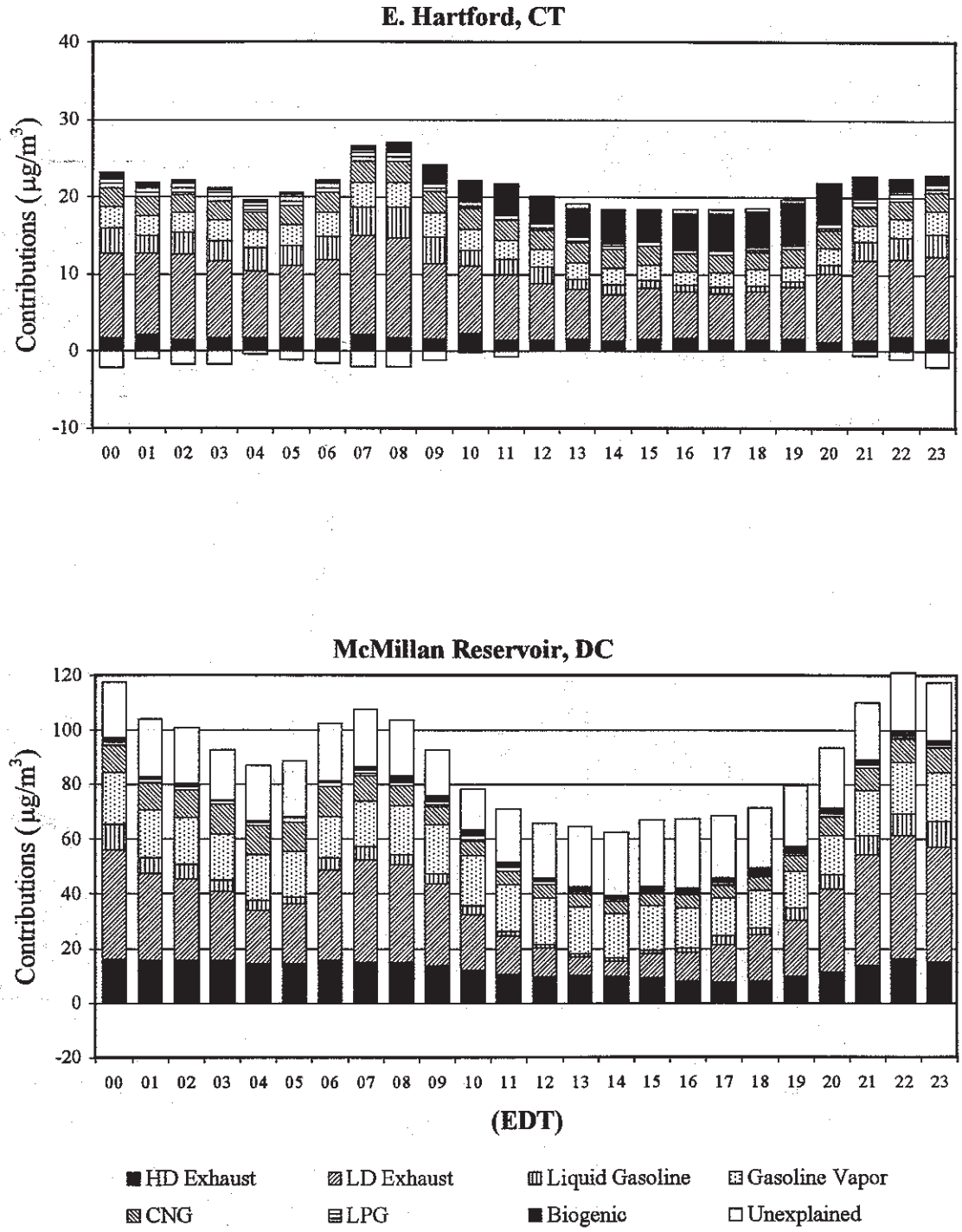

Figure 4-2. Average source contribution estimates by time of day at PAMS sites

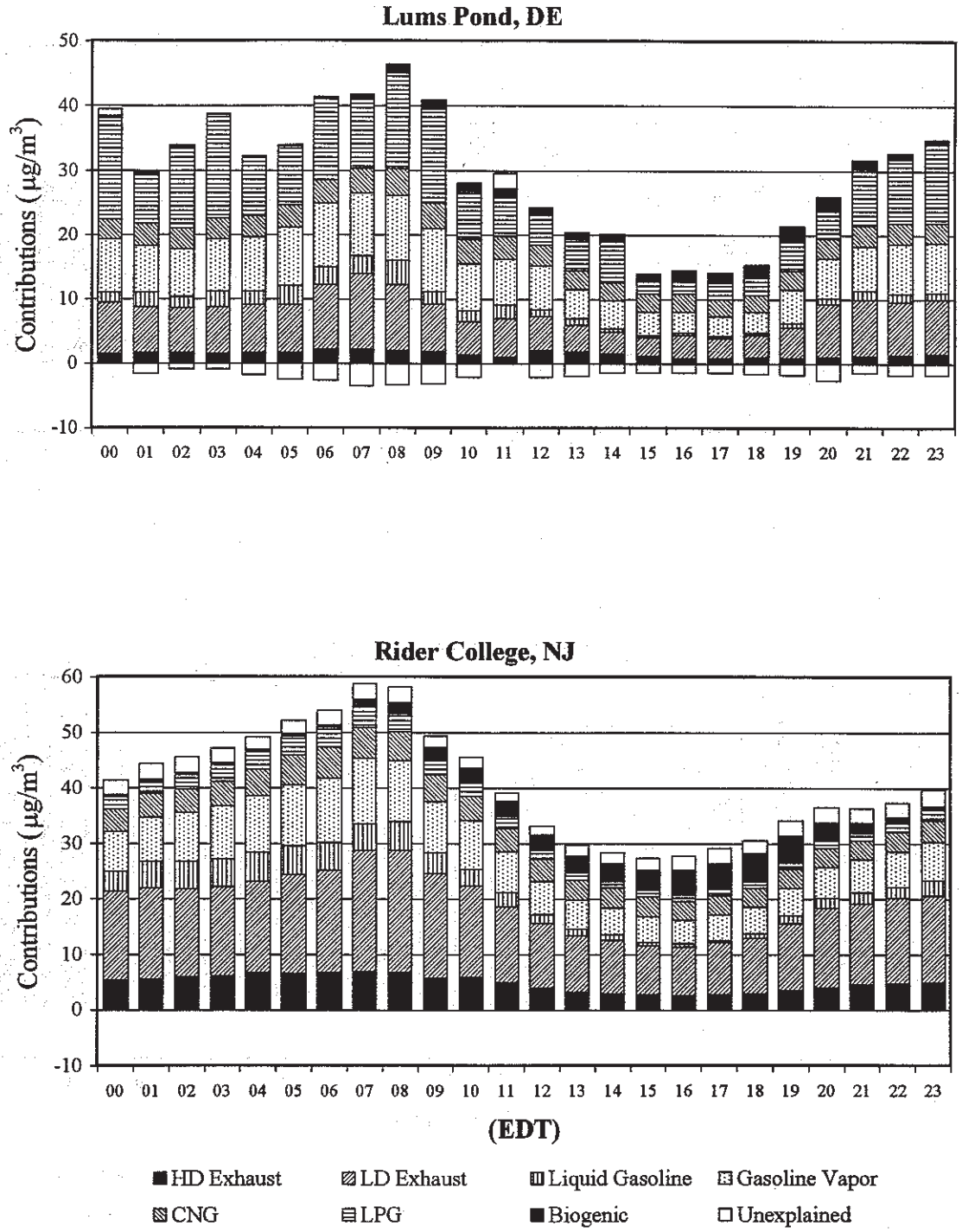

Figure 4-2 (cont). Average source contribution estimates by time of day at PAMS sites

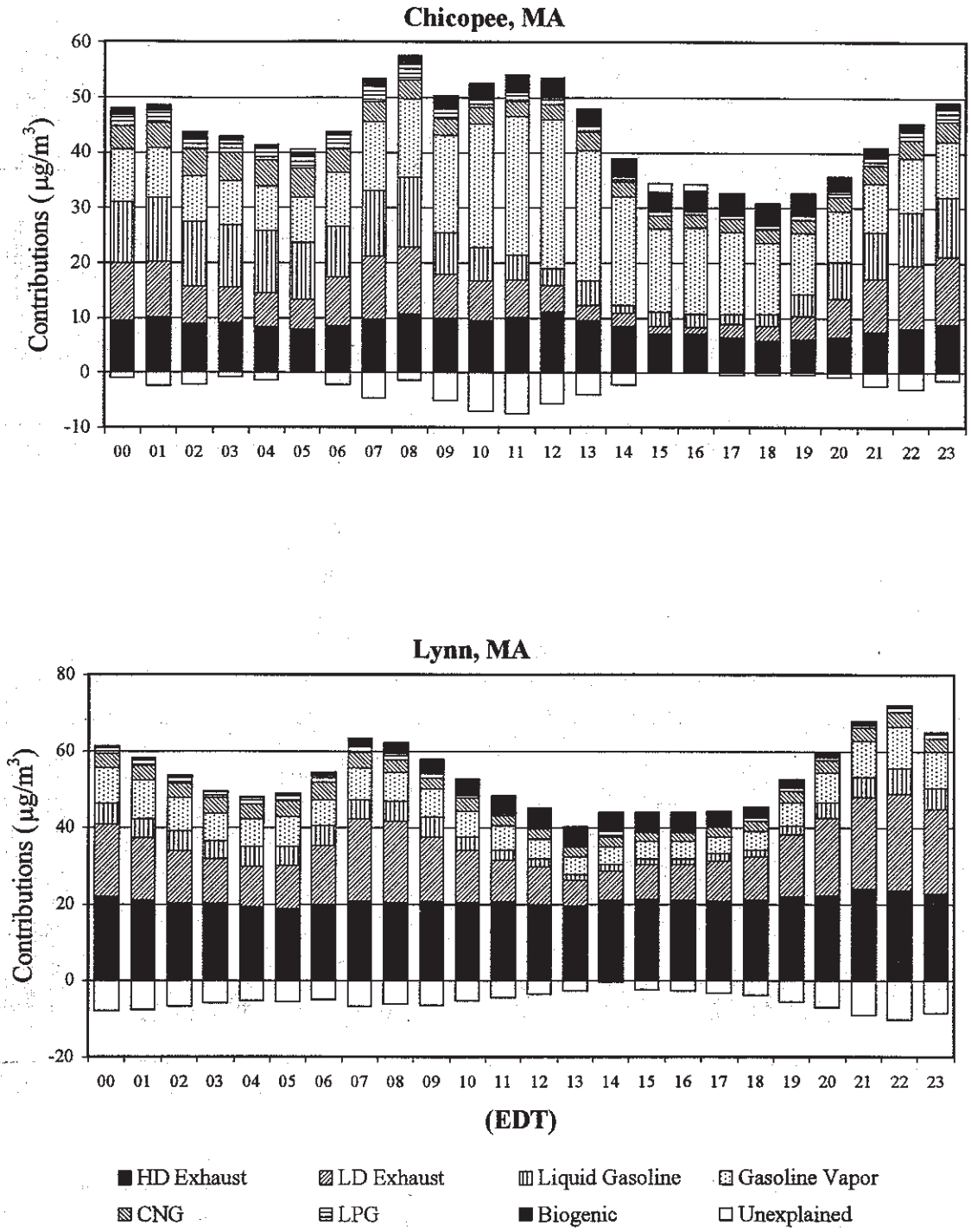

Figure 4-2 (cont). Average source contribution estimates by time of day at PAMS sites

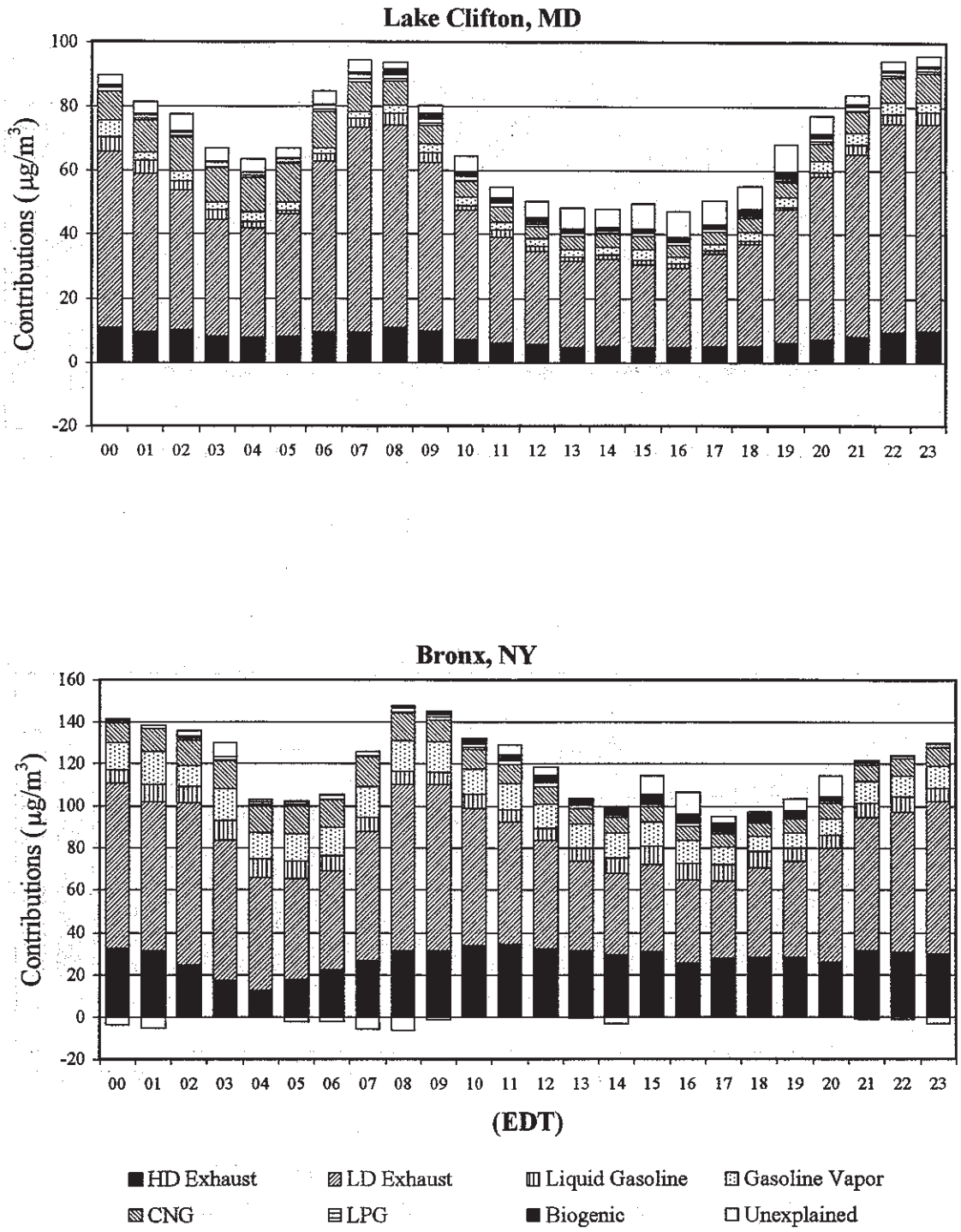

Figure 4-2 (cont). Average source contribution estimates by time of day at PAMS sites

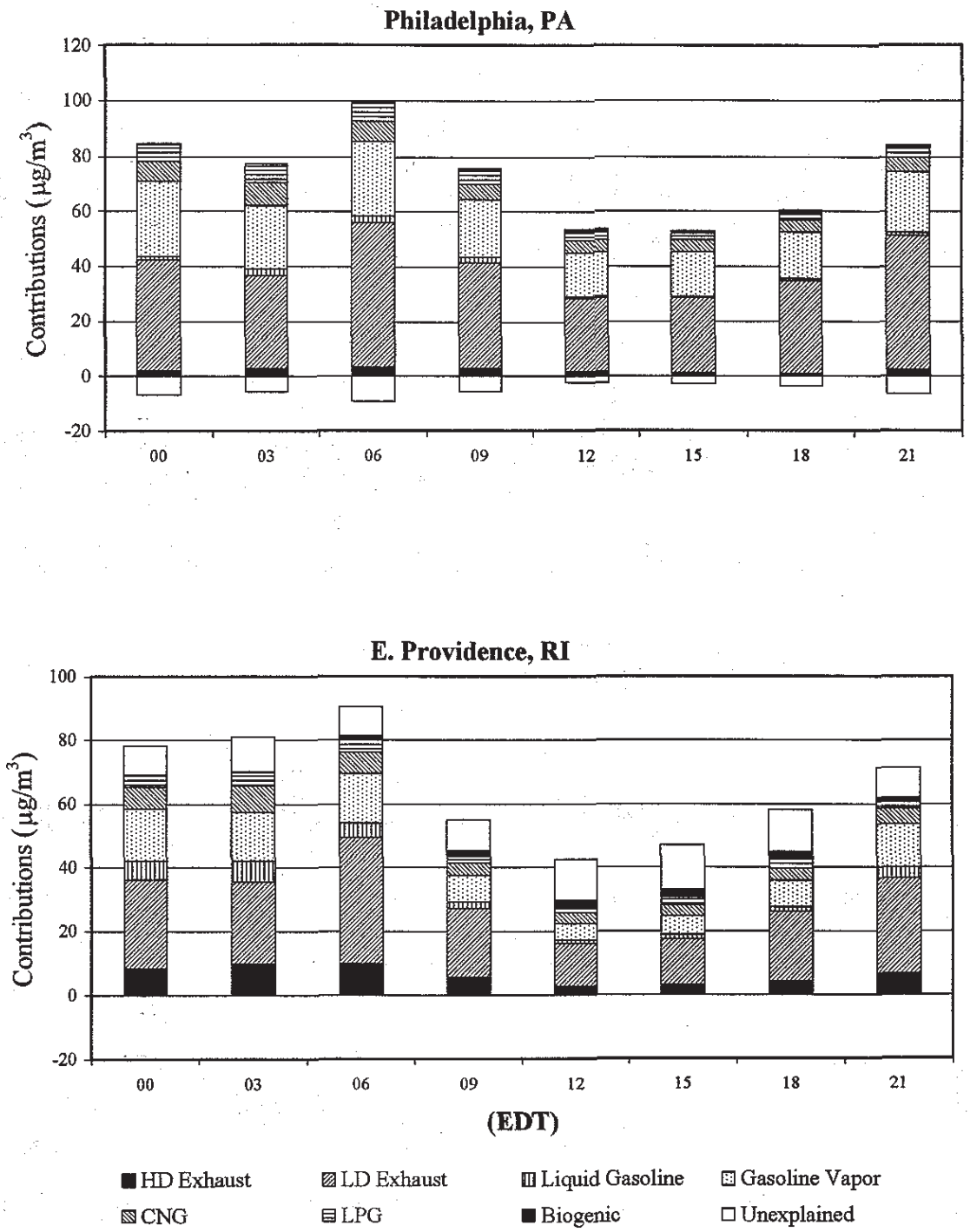

Figure 4-2 (cont). Average source contribution estimates by time of day at PAMS sites

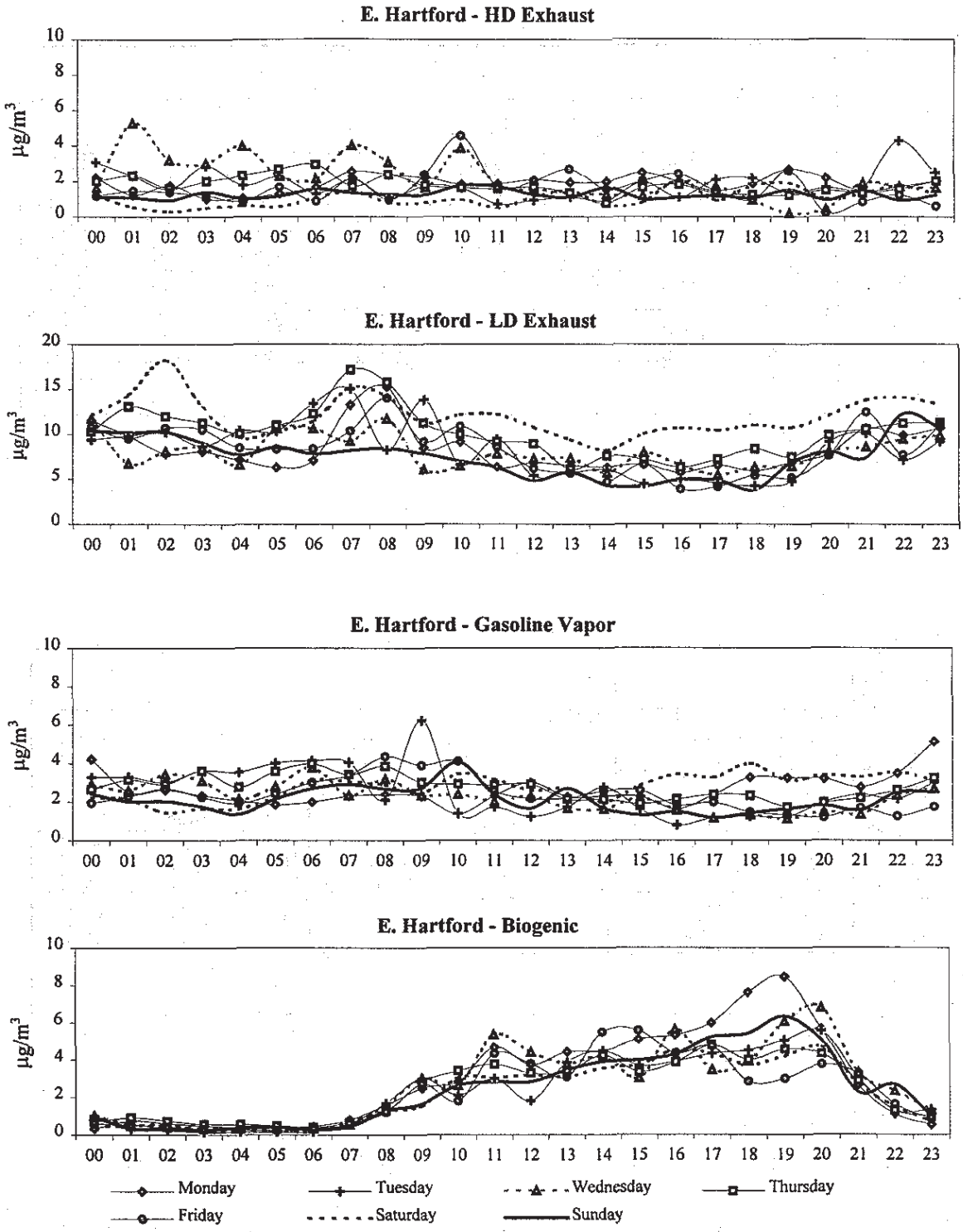

Figure 4-3a. Average SCE at E. Hartford by day of the week, summer 1995 (EDT).

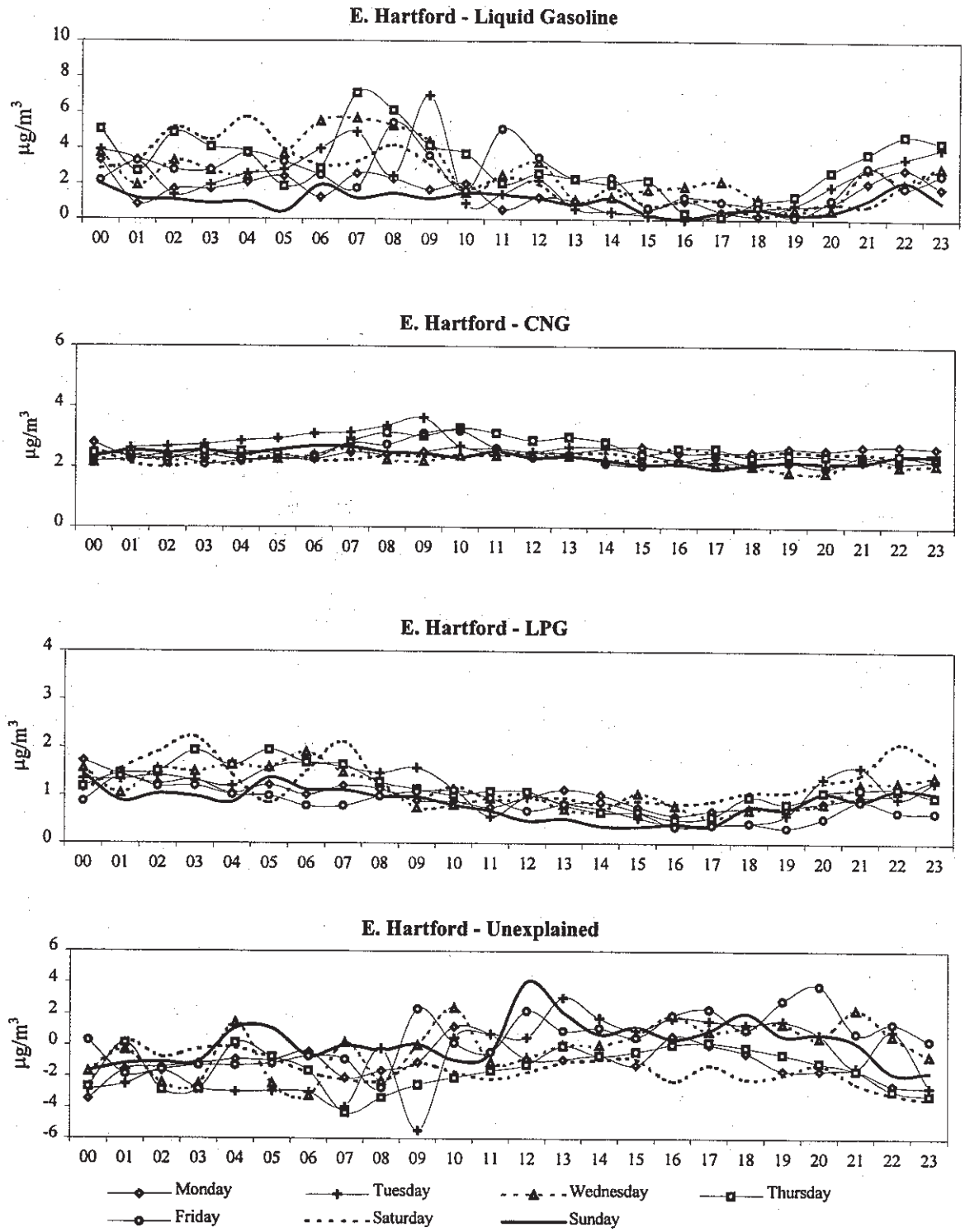

Figure 4-3a (cont). Average SCE at E. Hartford by day of the week, summer 1995 (EDT).

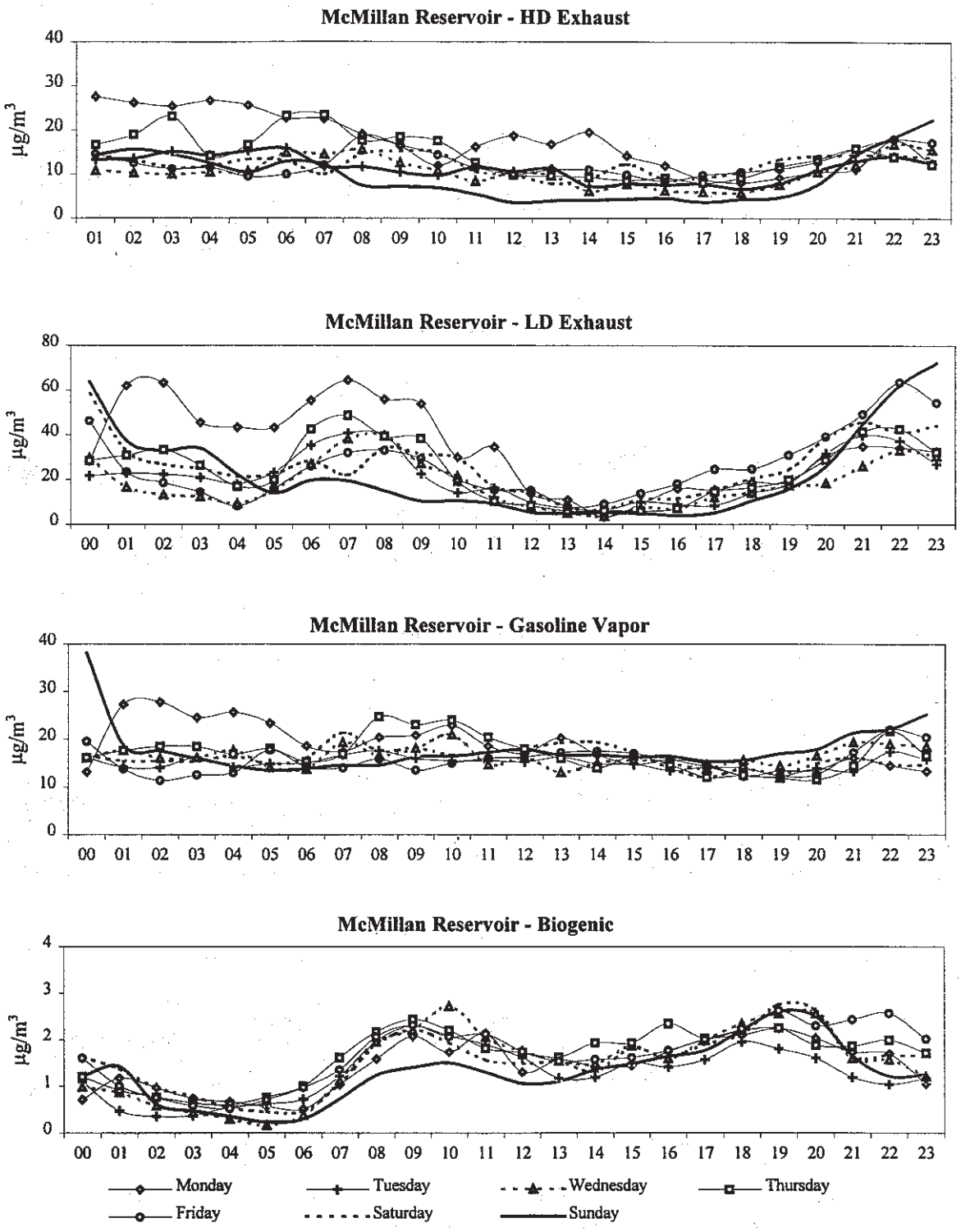

Figure 4-3b. Average SCE at McMillan Reservoir by day of the week, summer 1995 (EDT).

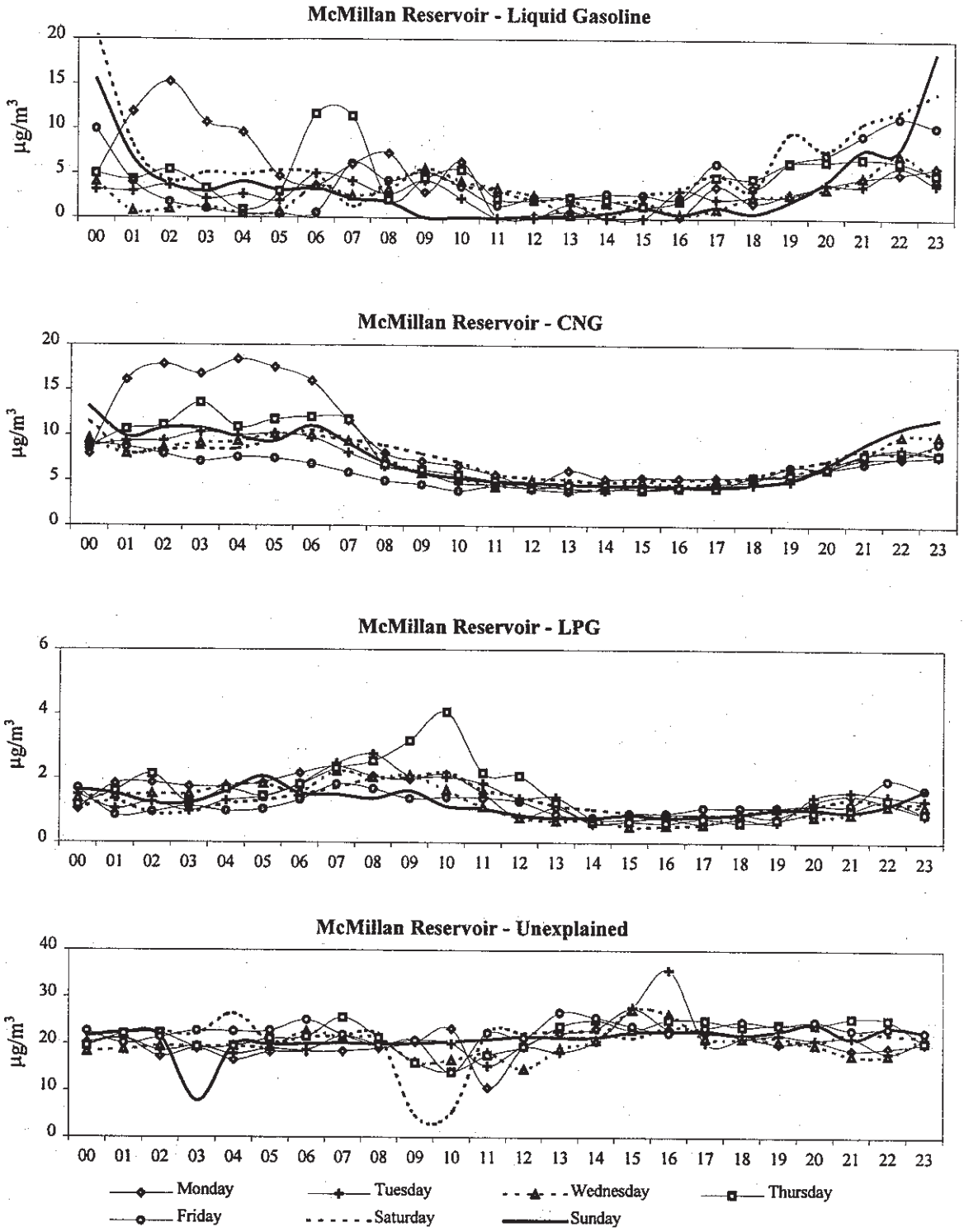

Figure 4-3b (cont). Average SCE at McMillan by day of the week, summer 1995 (EDT).

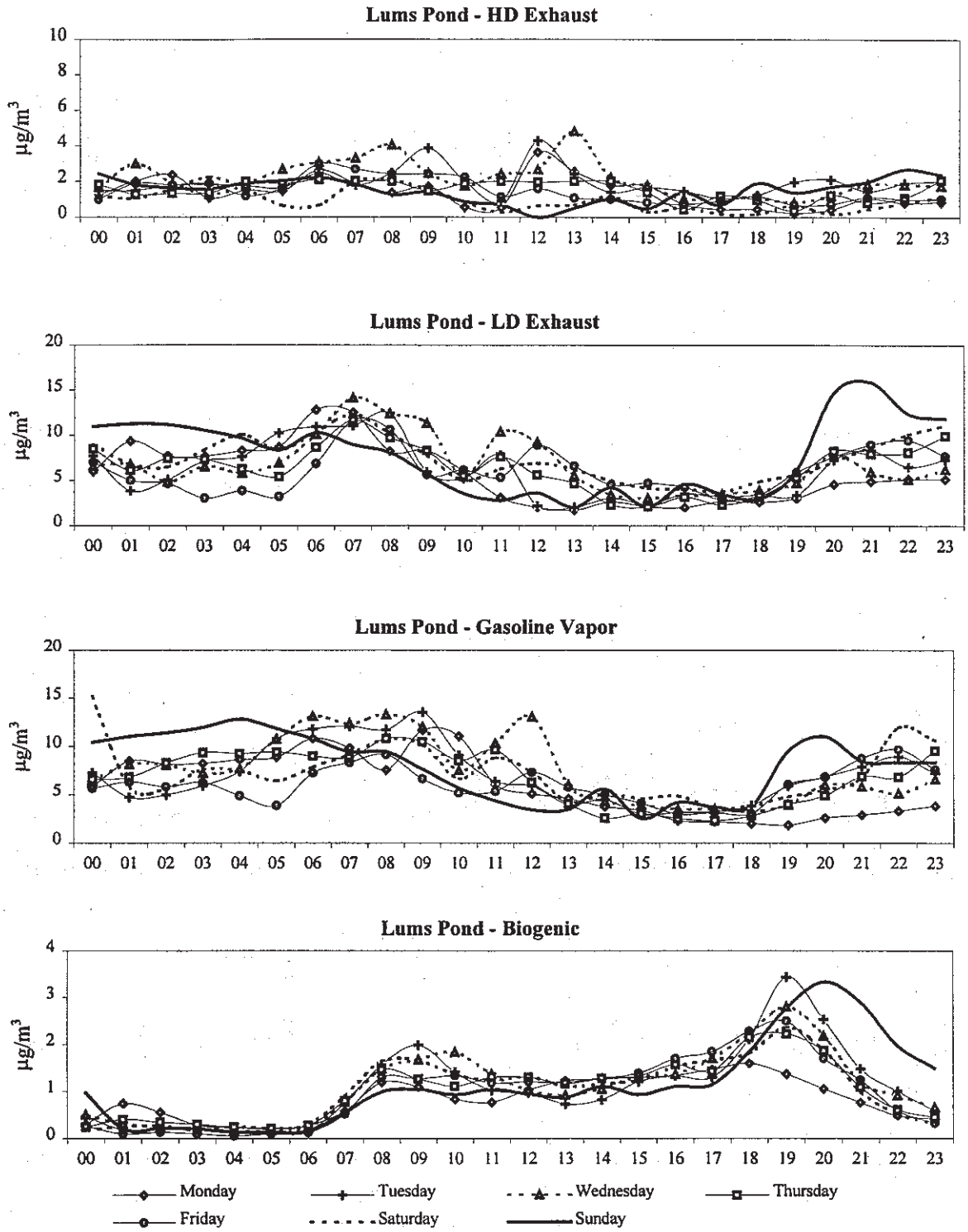

Figure 4-3c. Average SCE at Lums Pond by day of the week, summer 1995 (EDT).

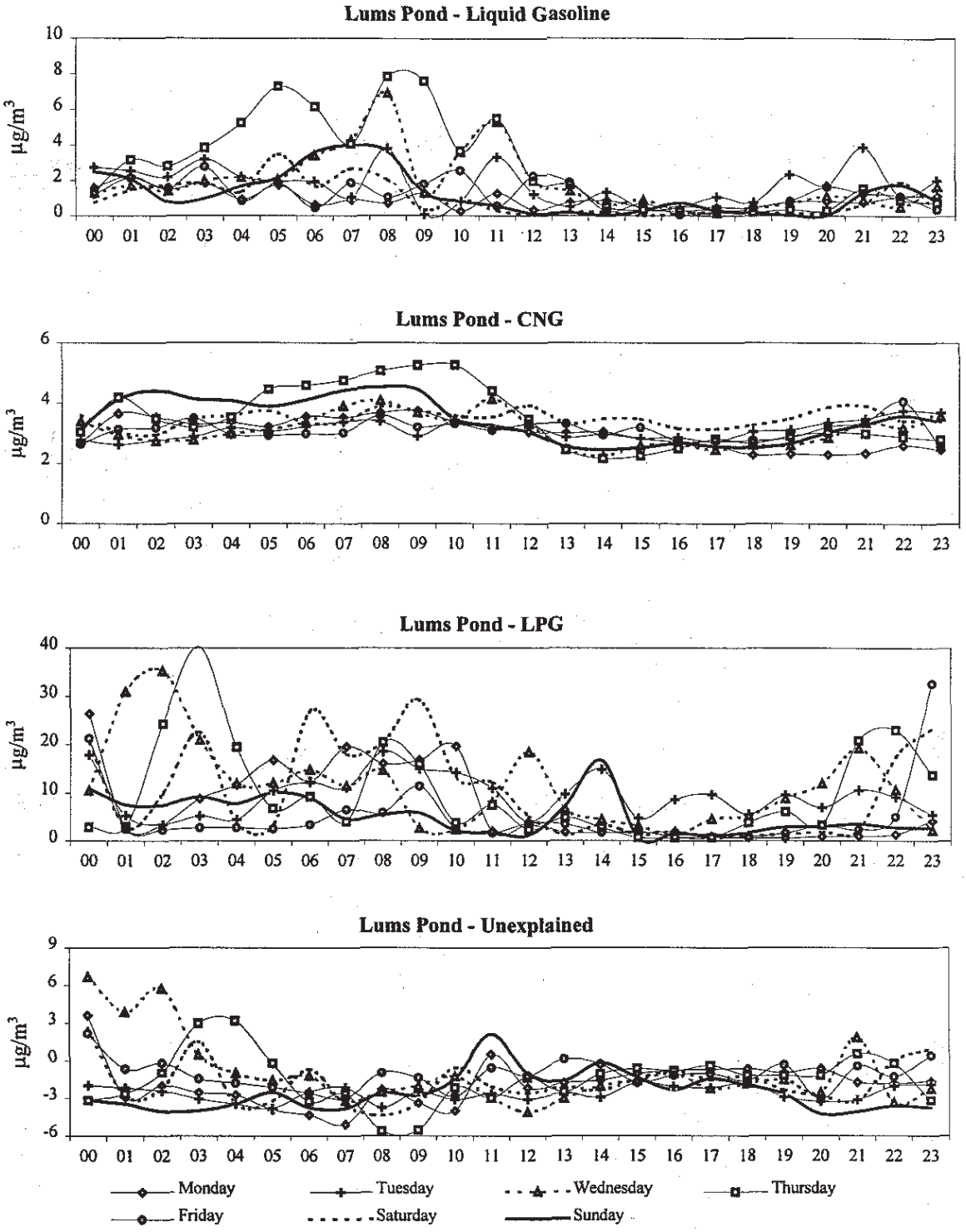

Figure 4-3c (cont). Average SCE at Lums Pond by day of the week, summer 1995 (EDT).

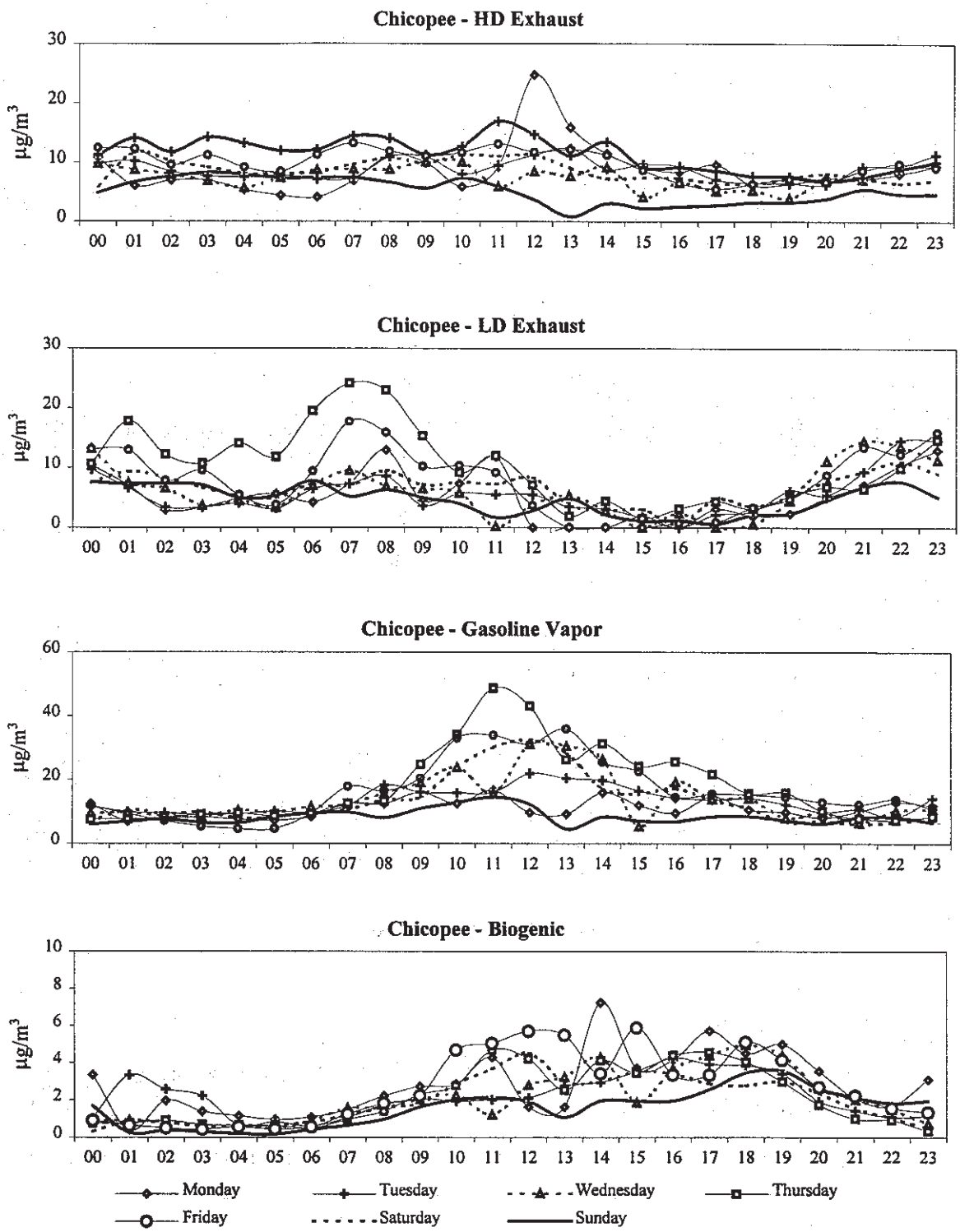

Figure 4-3d. Average SCE at Chicopee, MA by day of the week, summer 1995 (EDT).

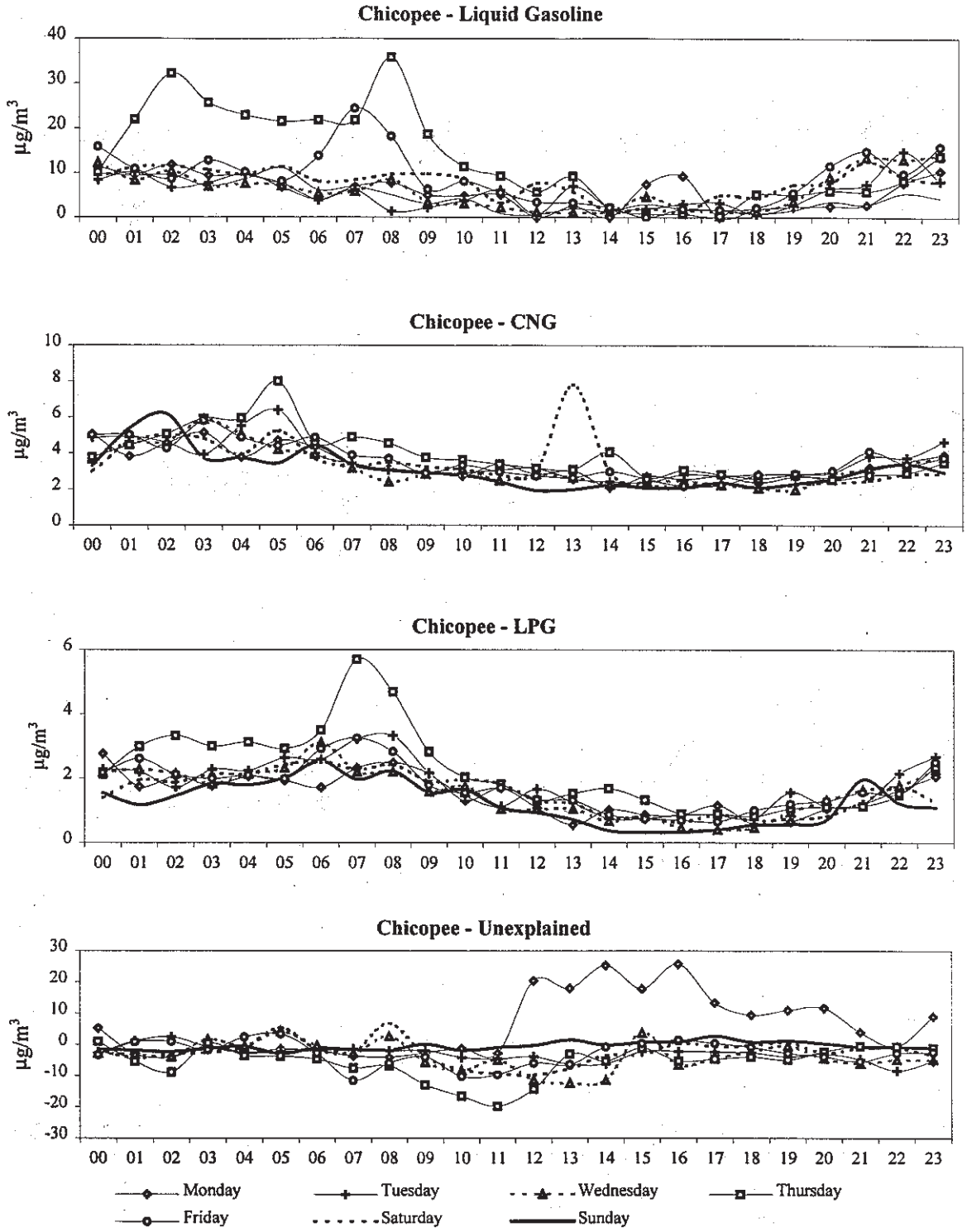

Figure 4-3d (cont). Average SCE at Chicopee, MA by day of the week, summer 1995 (EDT).

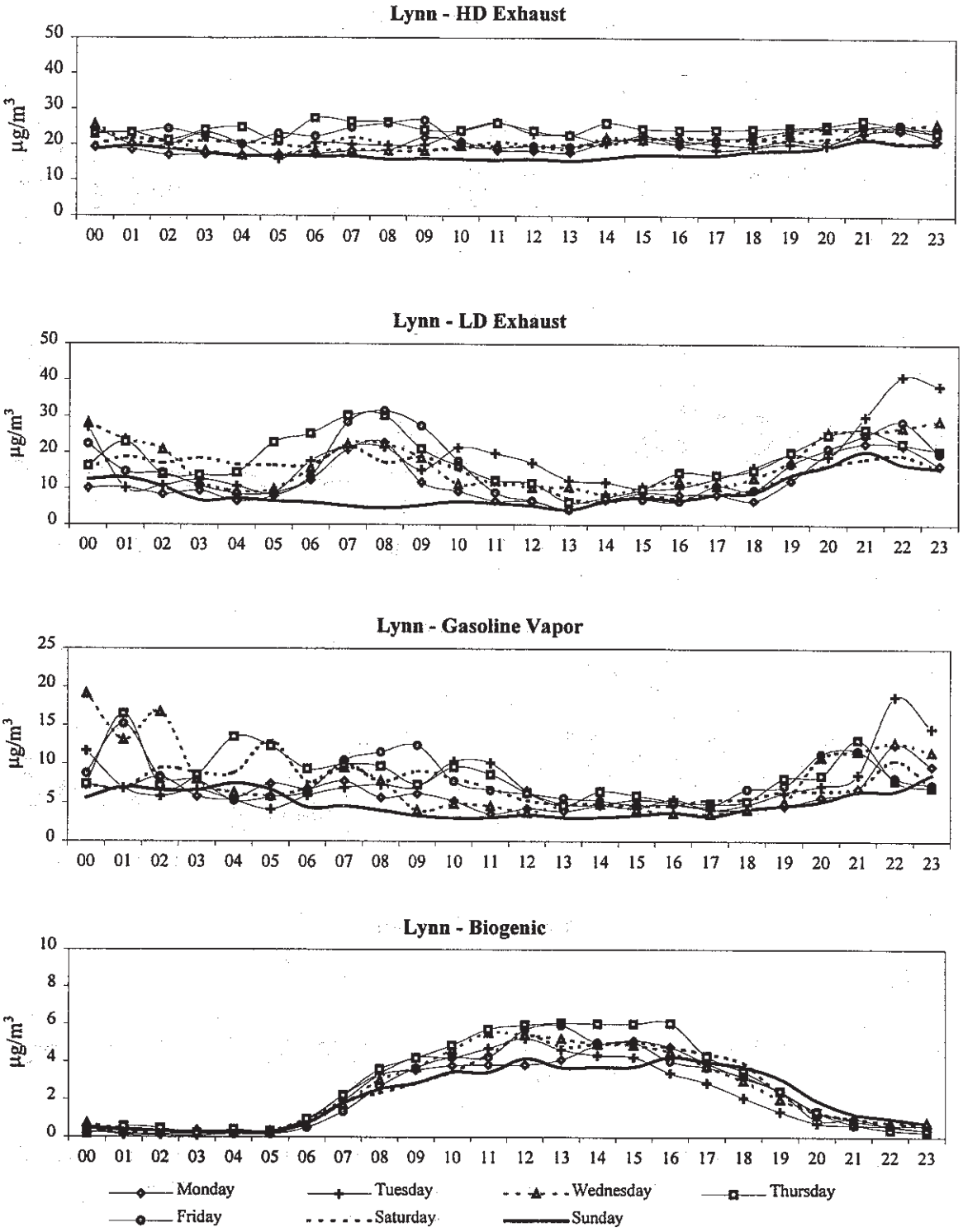

Figure 4-3e. Average SCE at Lynn, MA by day of the week, summer 1995 (EDT).

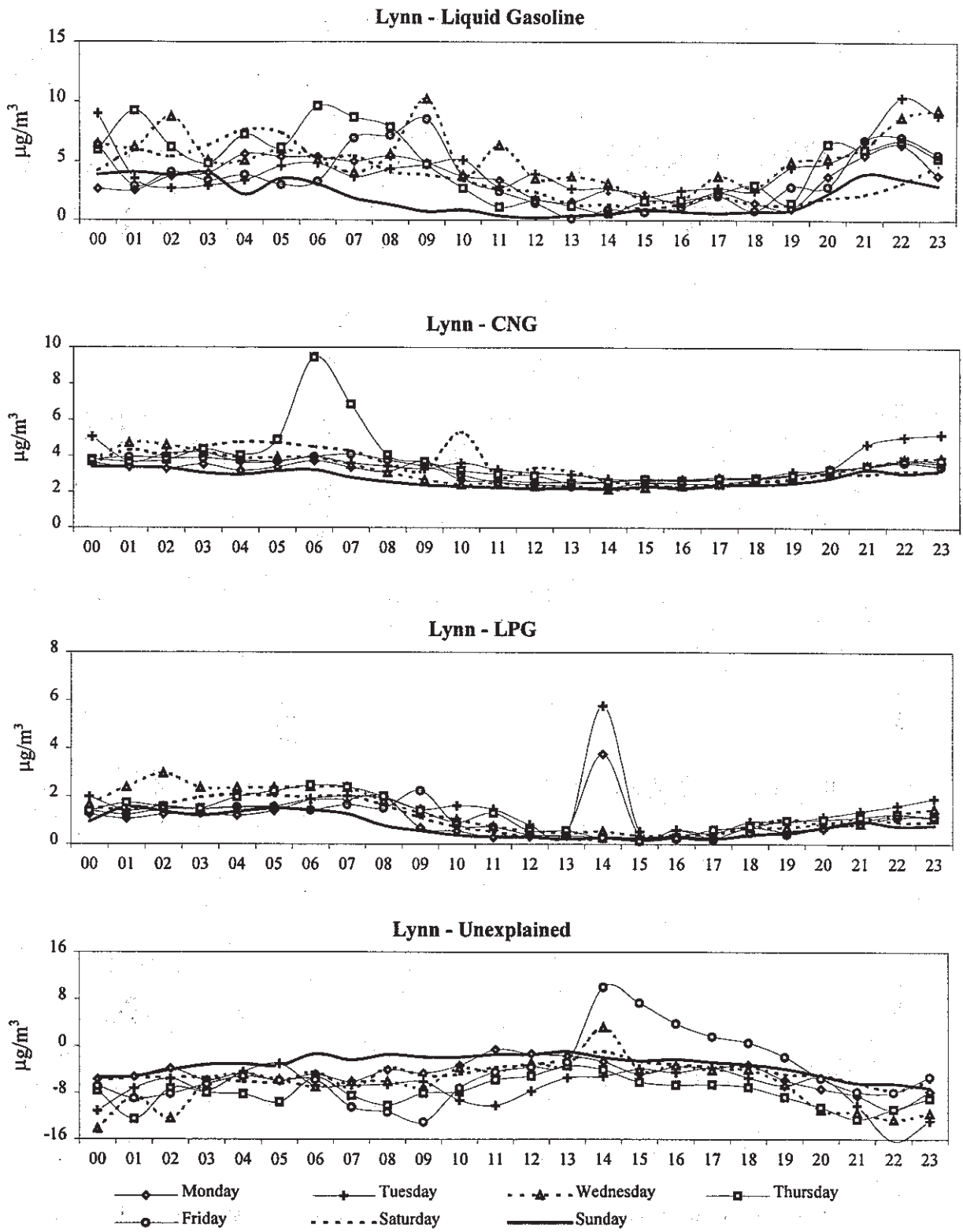

Figure 4-3e (cont). Average SCE at Lynn, MA by day of the week, summer 1995 (EDT).

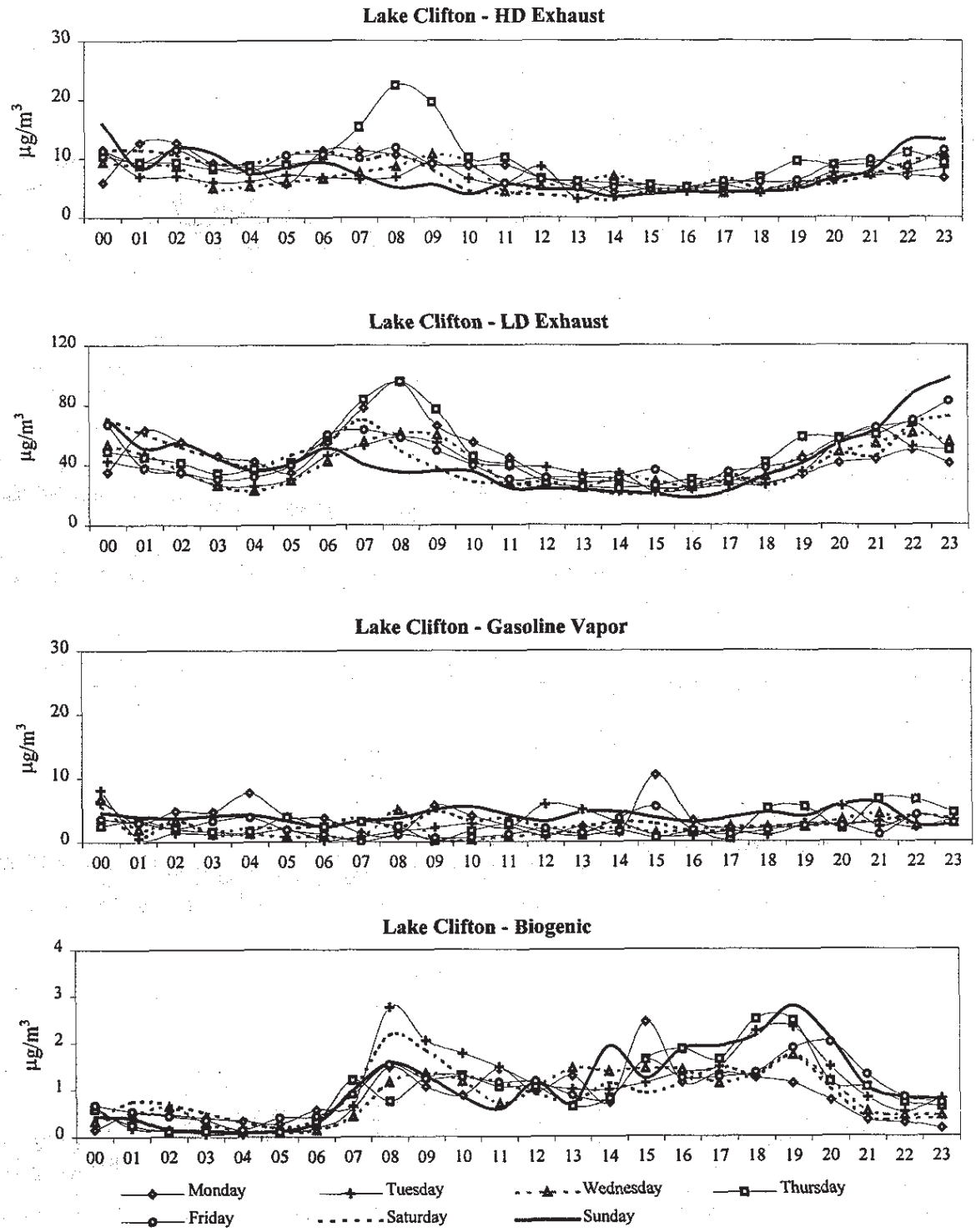

Figure 4-3f. Average SCE at Lake Clifton, MD by day of the week, summer 1995 (EDT).

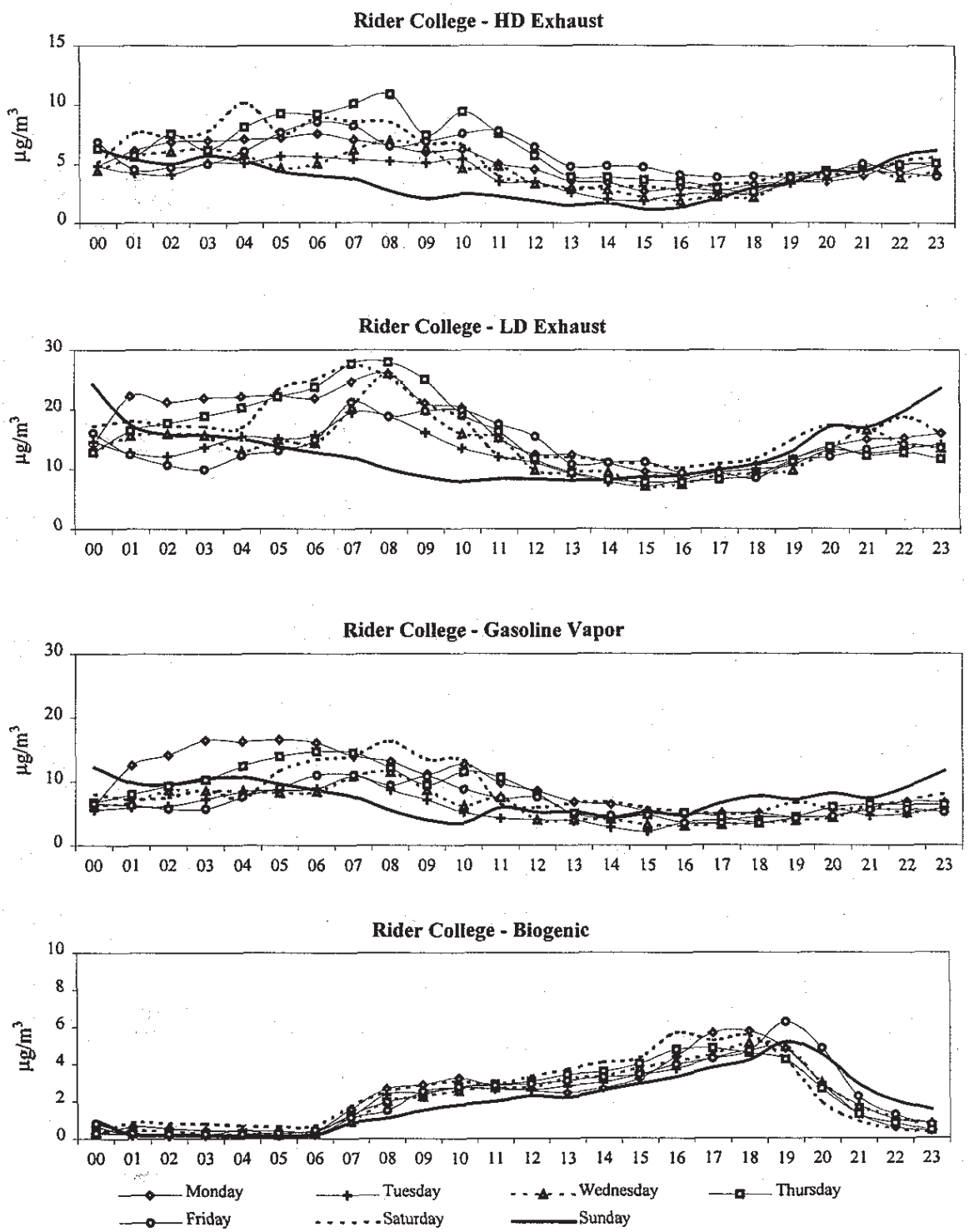

Figure 4-3g. Average SCE at Rider College, NJ by day of the week, summer 1995 (EDT).

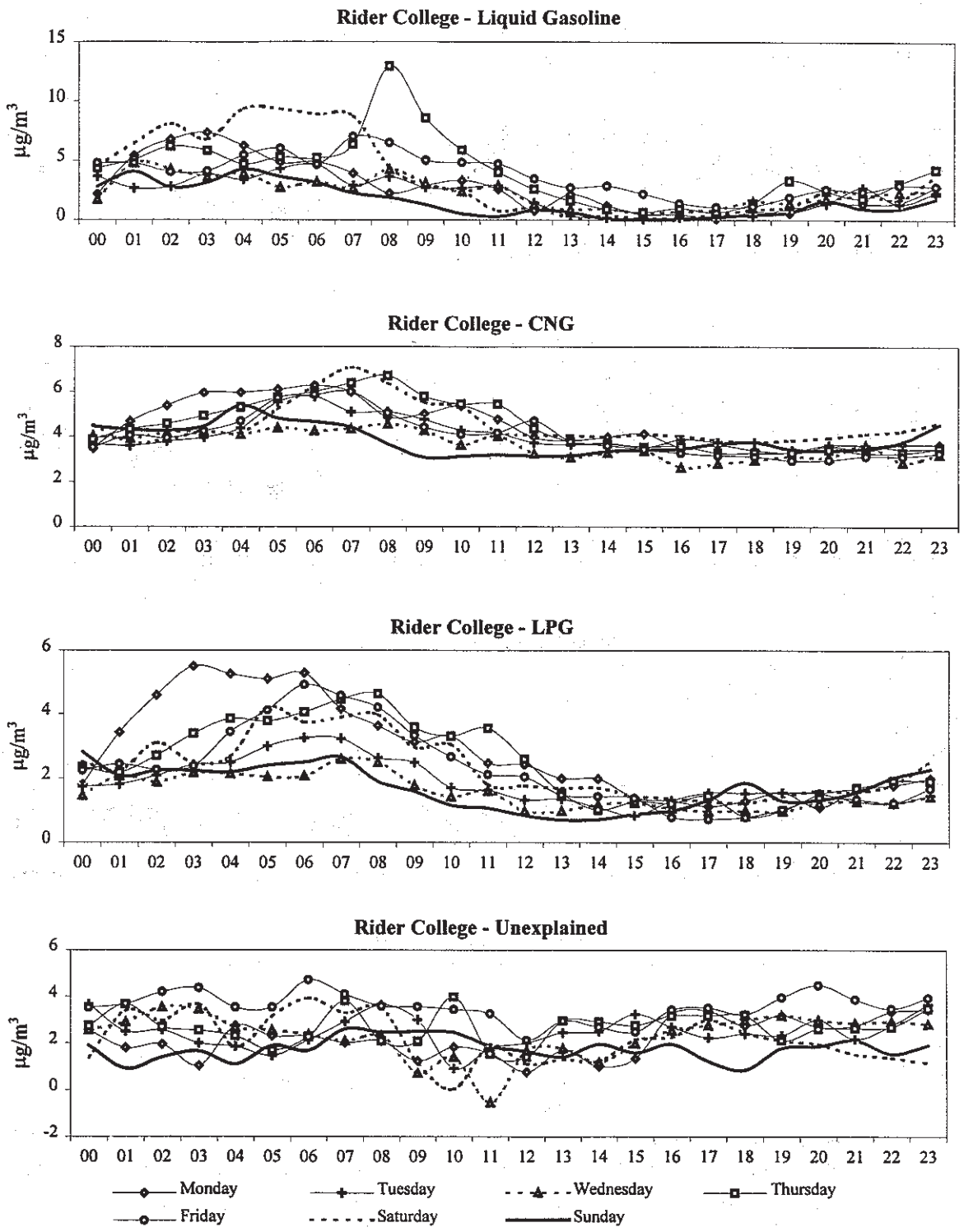

Figure 4-3g (cont). Ave. SCE at Rider College, NJ by day of the week, summer 1995 (EDT).

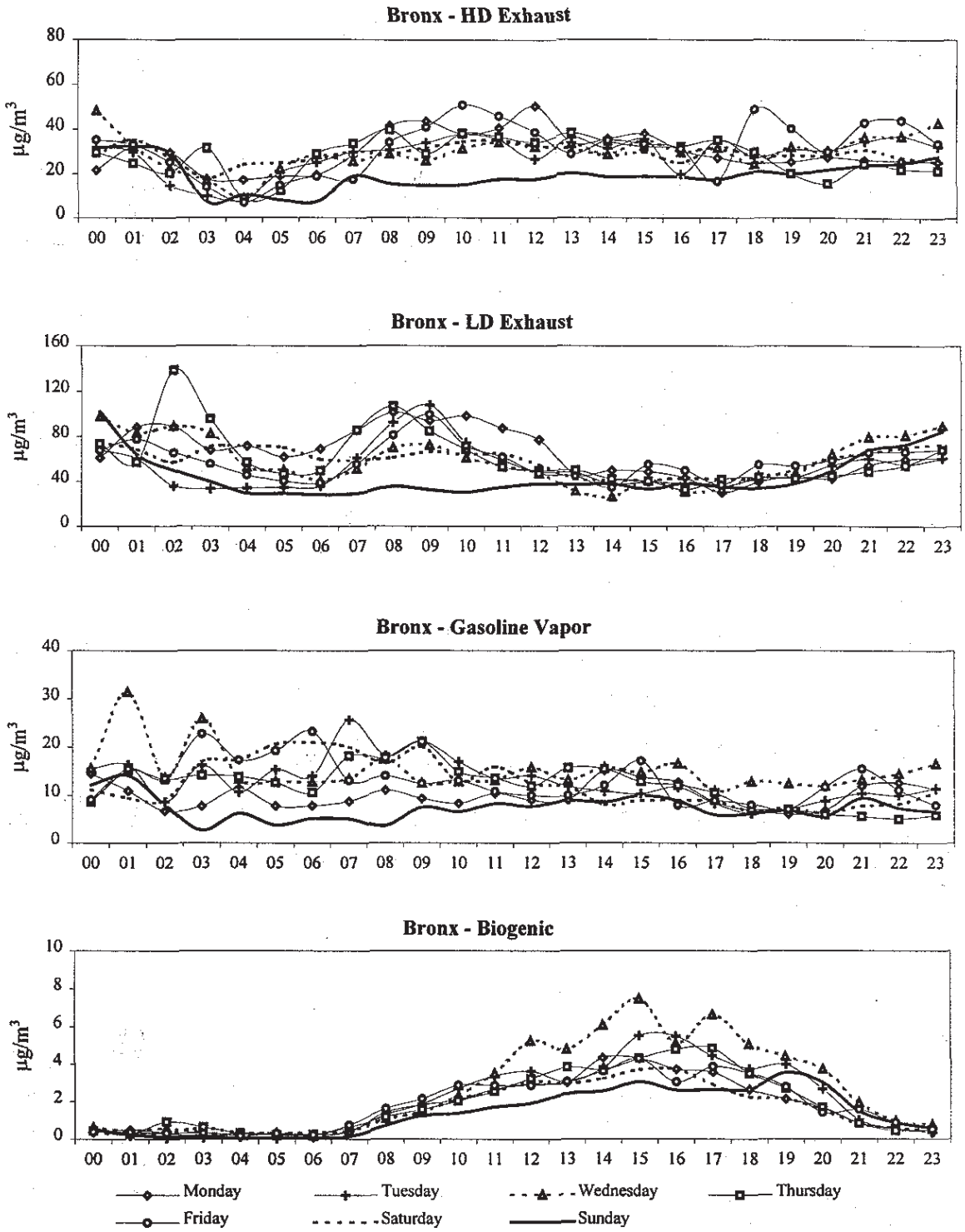

Figure 4-3h. Average SCE at Bronx, NY by day of the week, summer 1995 (EDT).

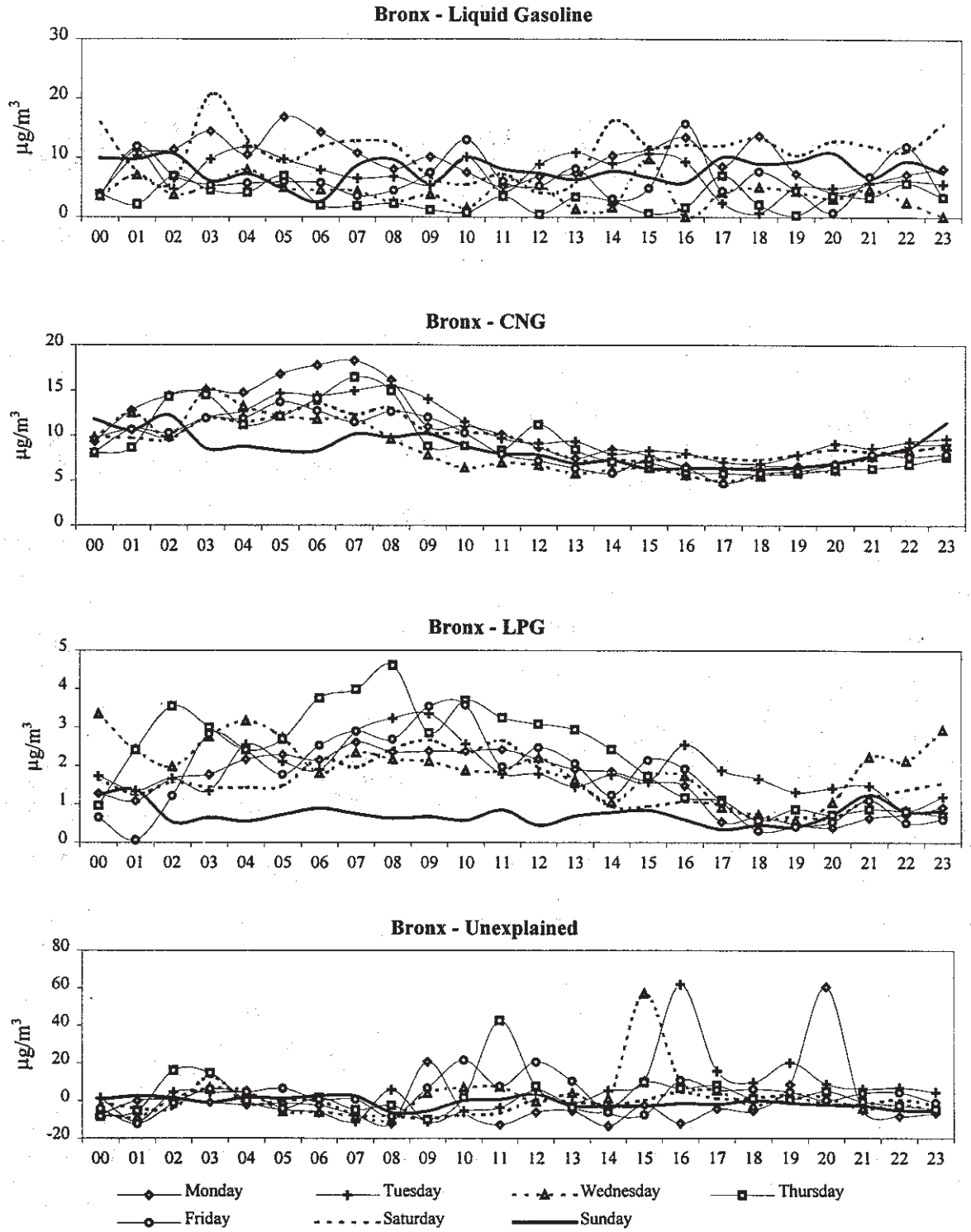

Figure 4-3h (cont). Average SCE at Bronx, NY by day of the week, summer 1995 (EDT).

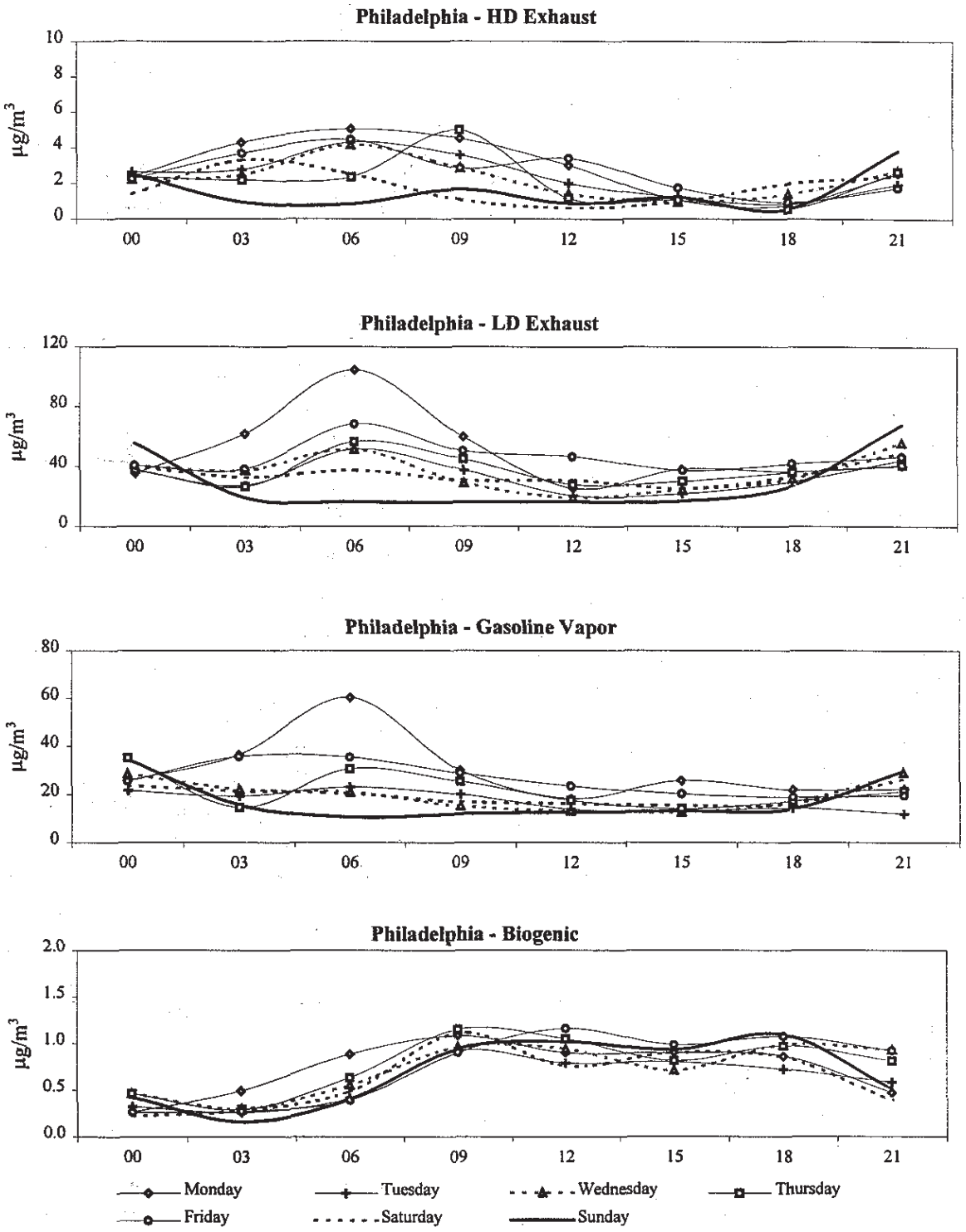

Figure 4-3i. Average SCE at Philadelphia, PA by day of the week, summer 1995 (EDT).

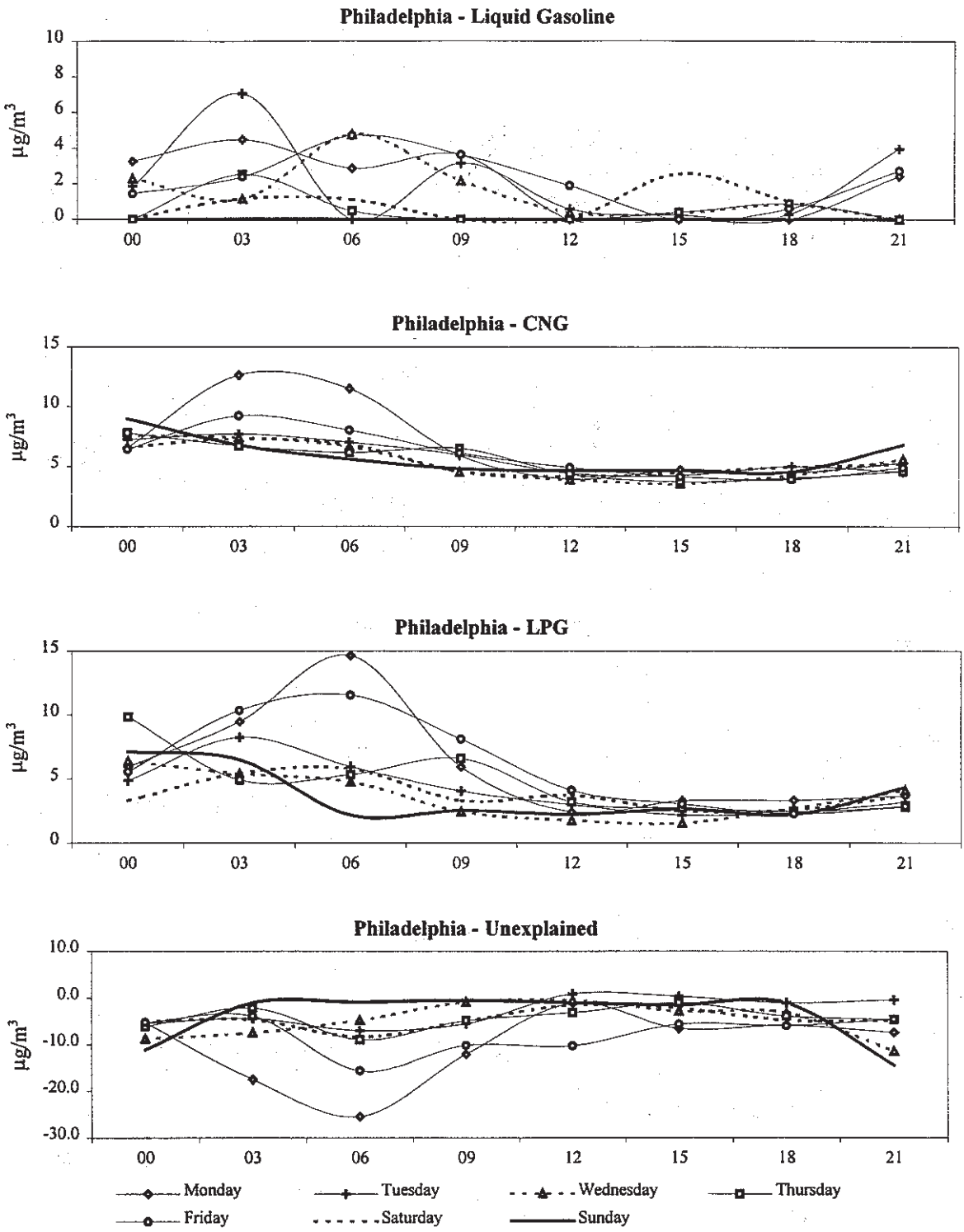

Figure 4-3i (cont). Average SCE at Philadelphia, PA by day of the week, summer 1995 (EDT).

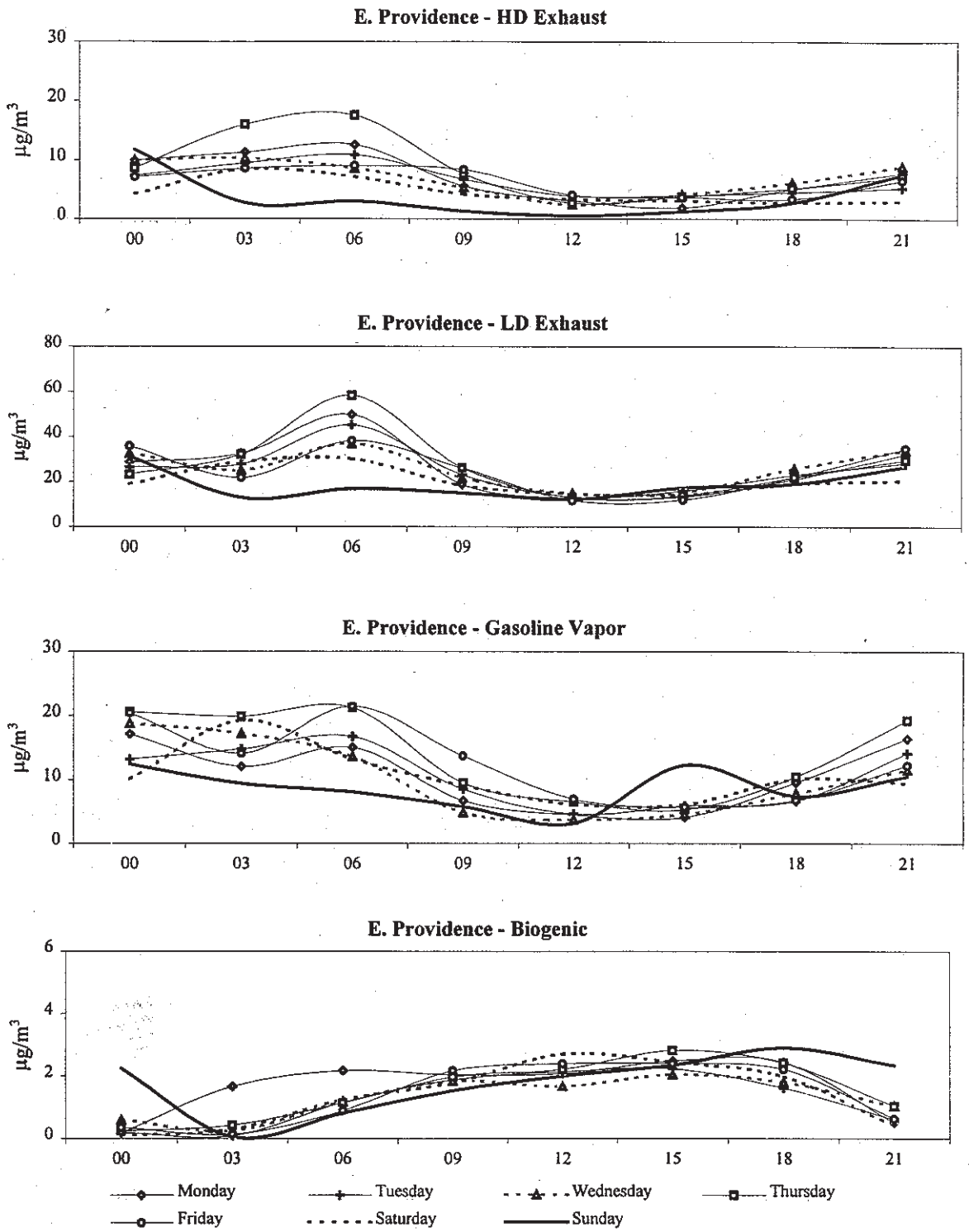

Figure 4-3j. Average SCE at E. Providence, RI by day of the week, summer 1995 (EDT).

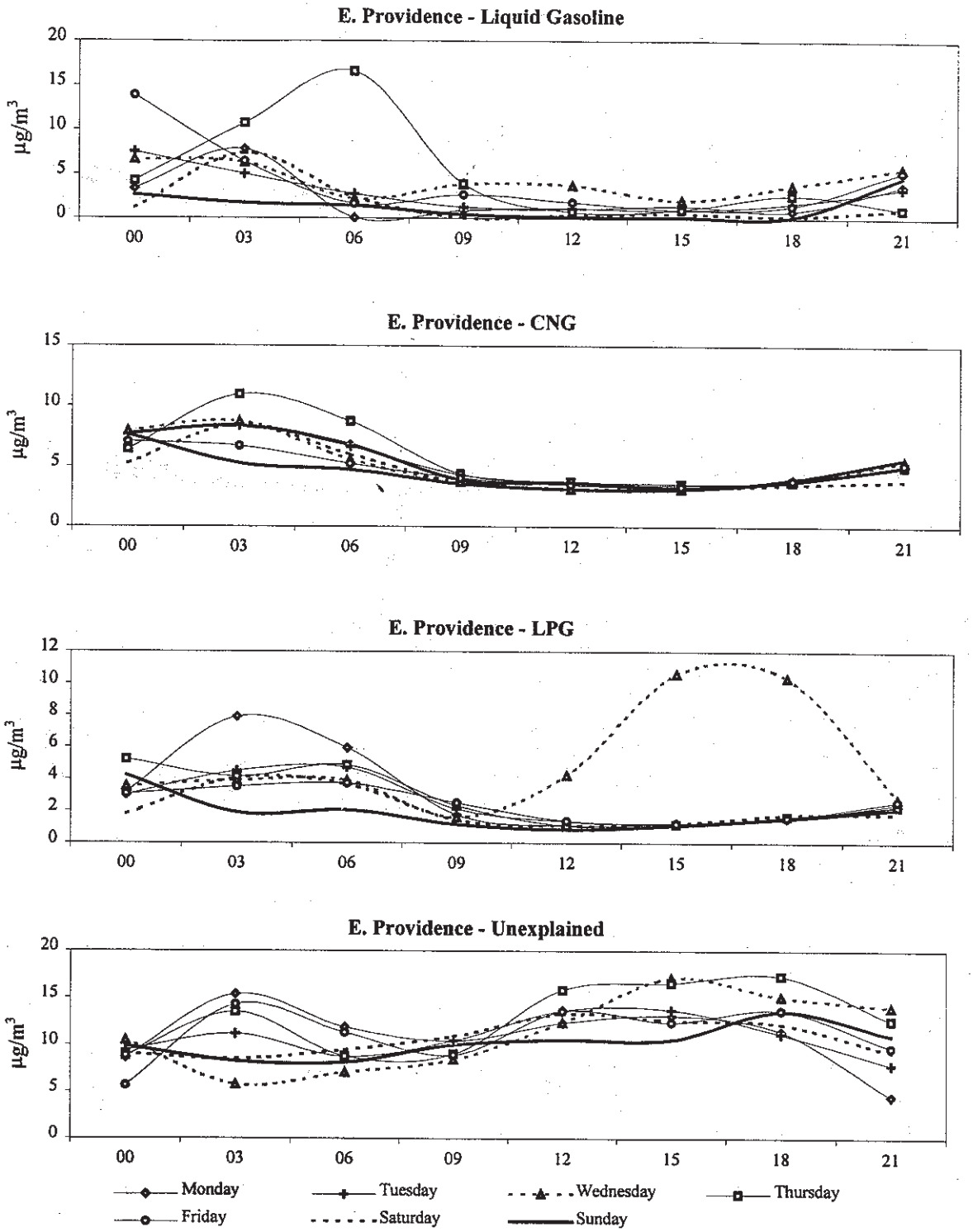

Figure 4-3j (cont). Average SCE at E. Providence by day of the week, summer 1995 (EDT).

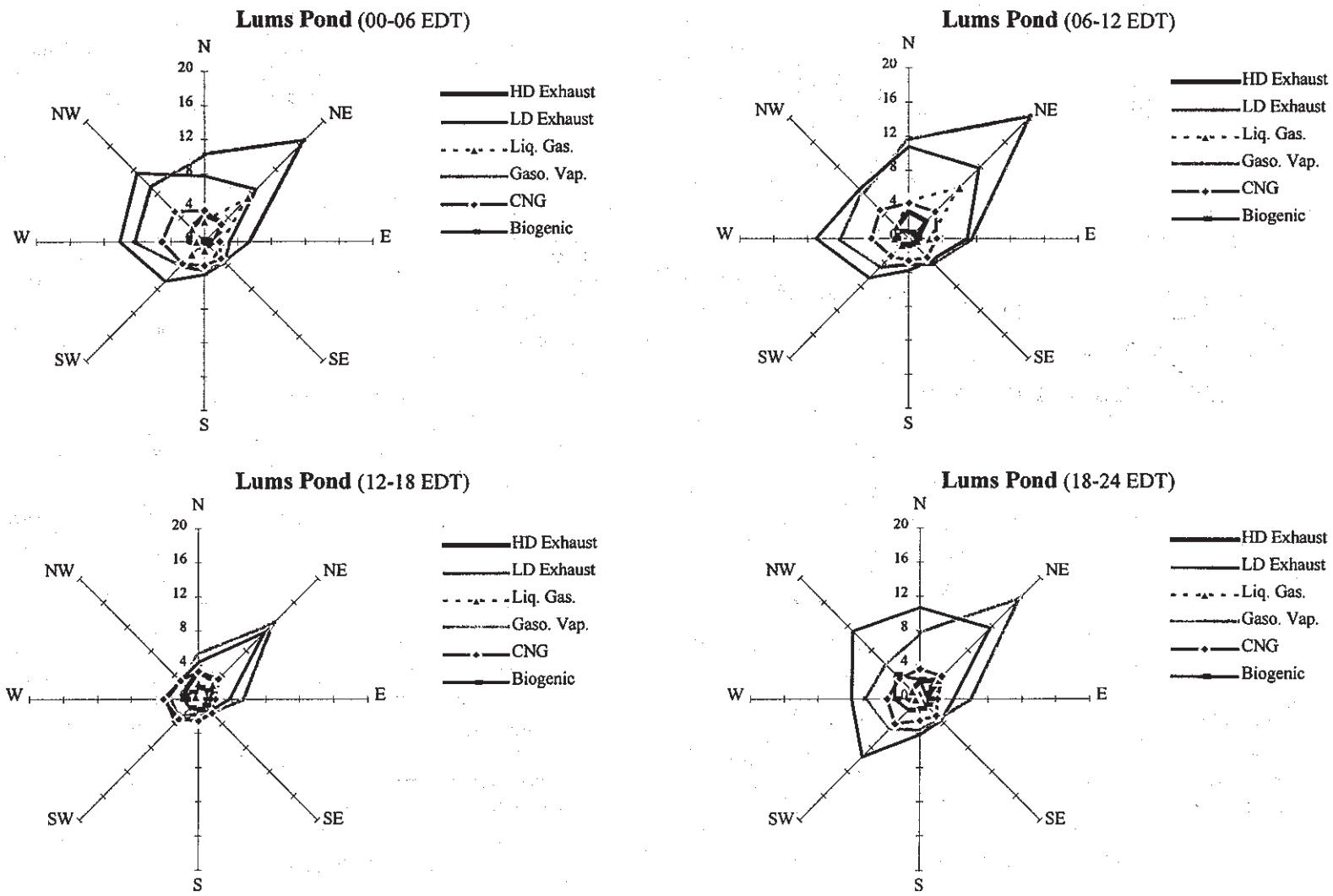

Figure 4-4a. Wind directional dependence of source contributions by time of the day at Lums Pond, DE.

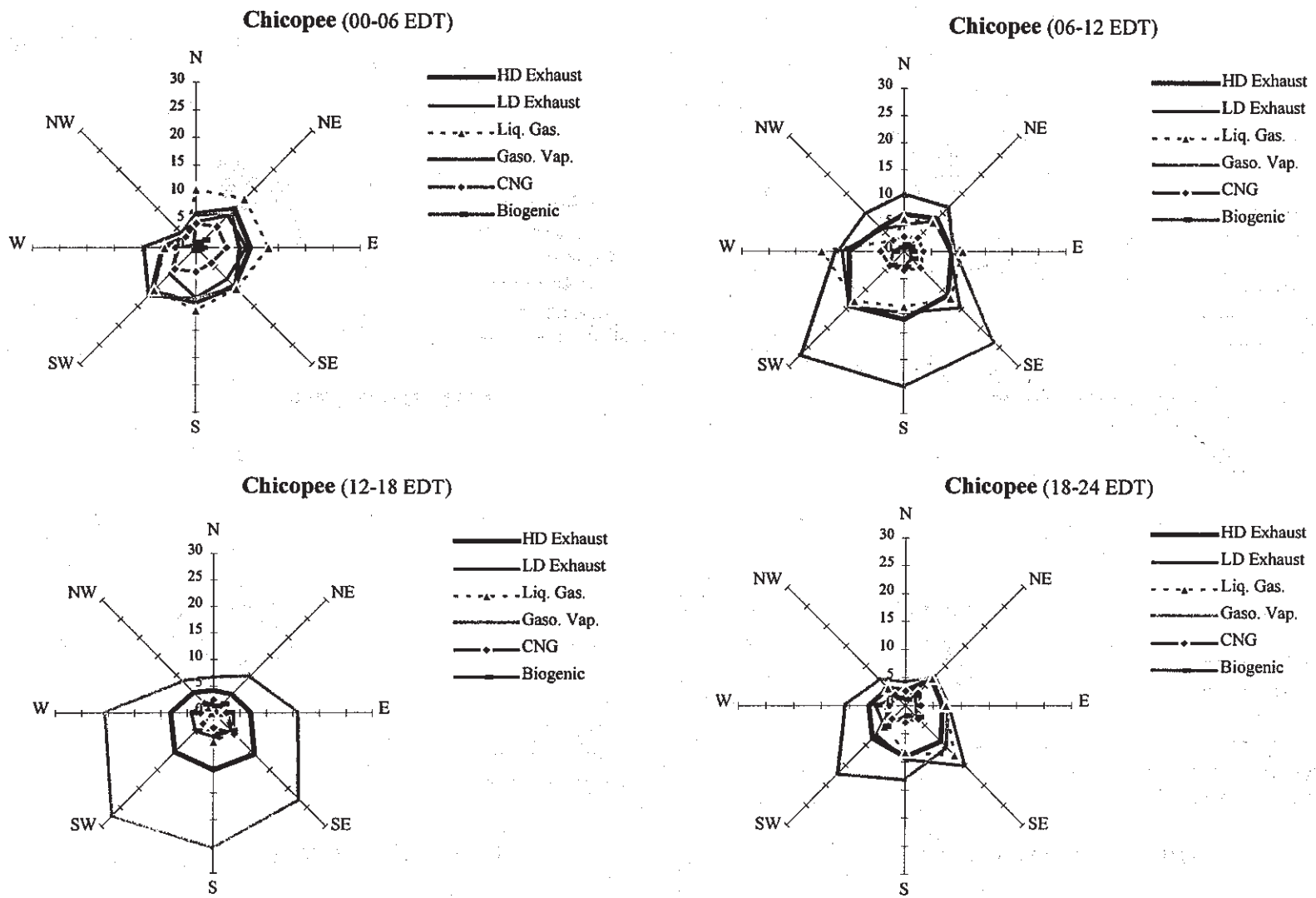

Figure 4-4b. Wind directional dependence of source contributions by time of the day at Chicopee, MA.

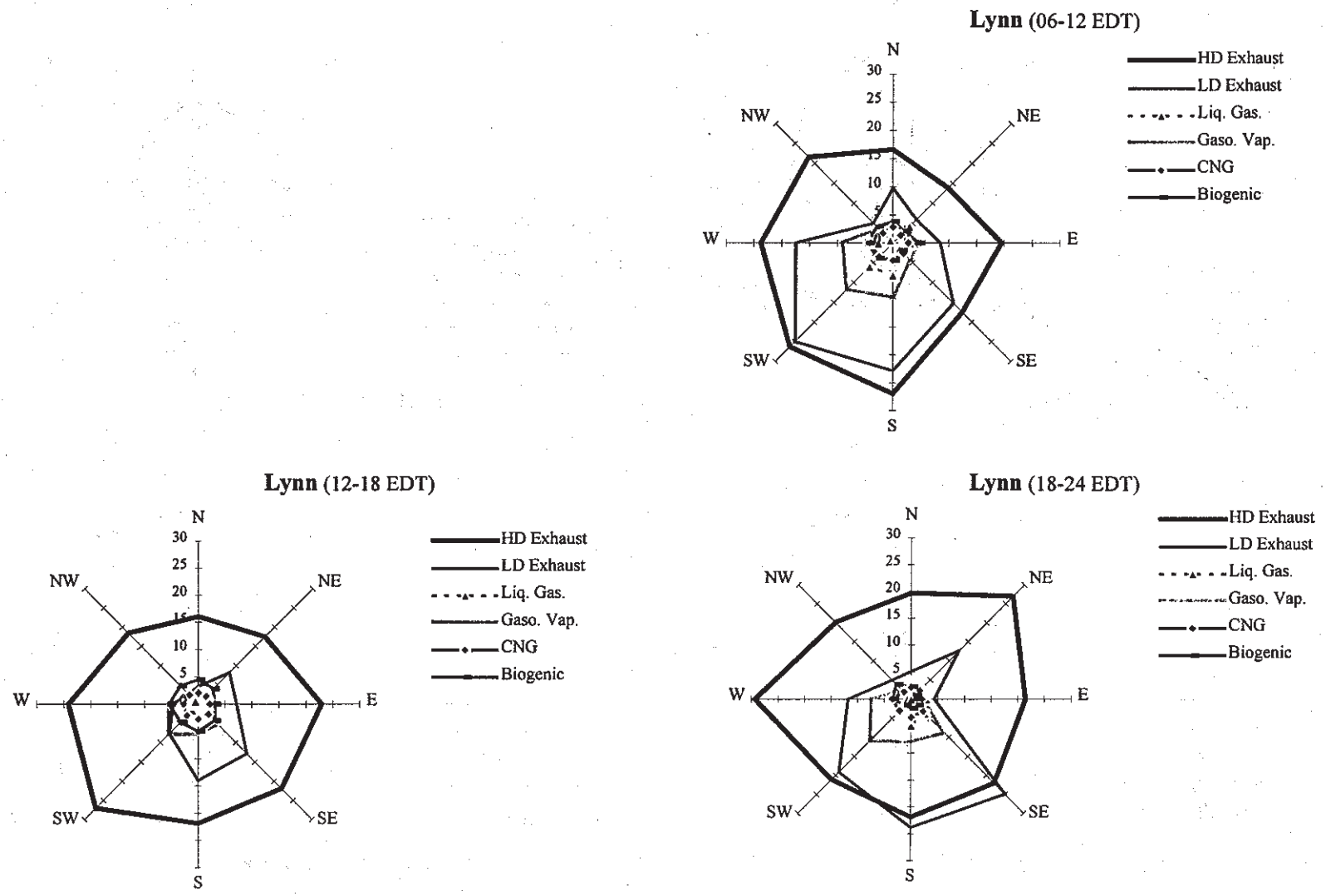

Figure 4-4c. Wind directional dependence of source contributions by time of the day at Lynn, MA.

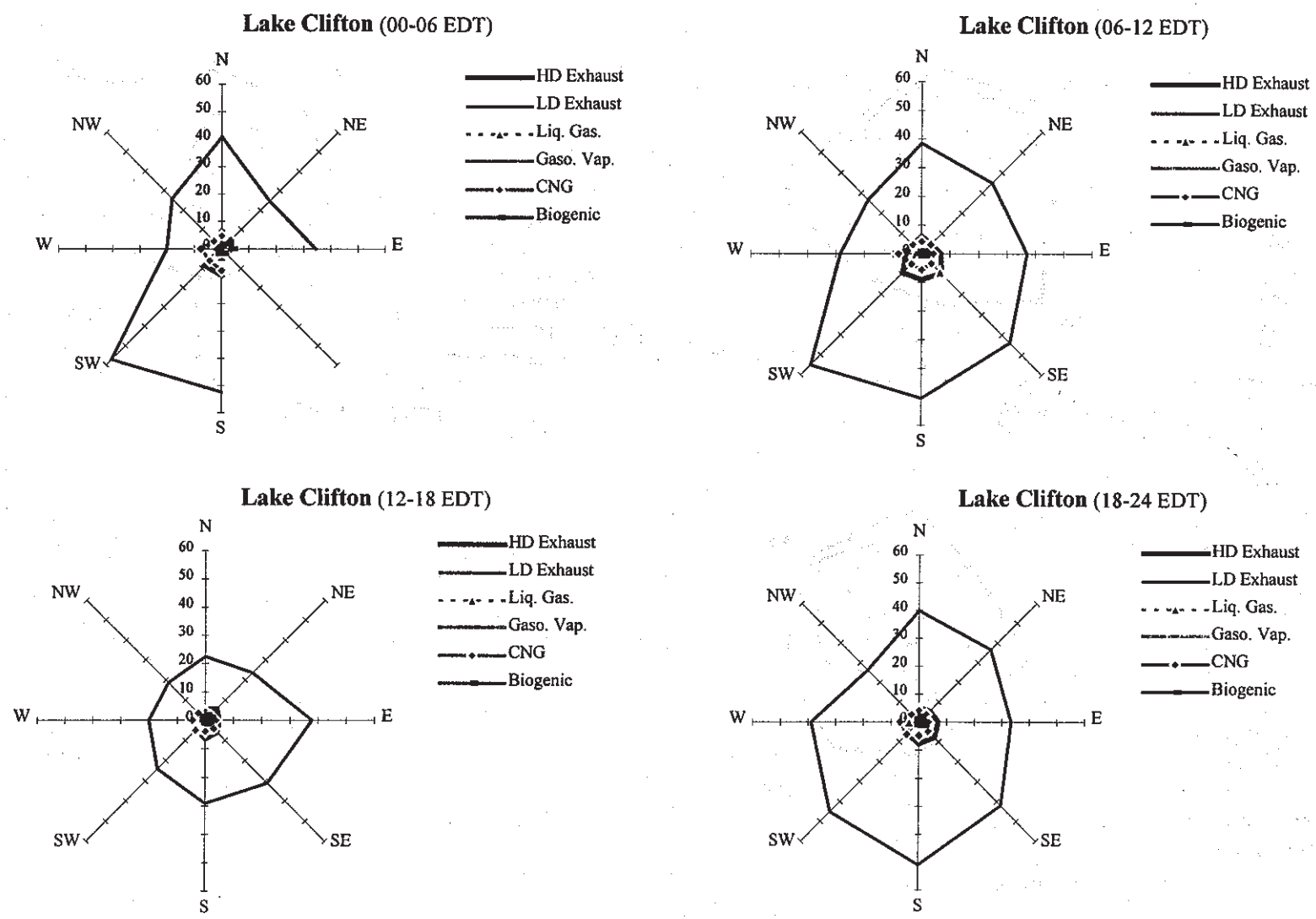

Figure 4-4d. Wind directional dependence of source contributions by time of the day at Lake Clifton, MD.

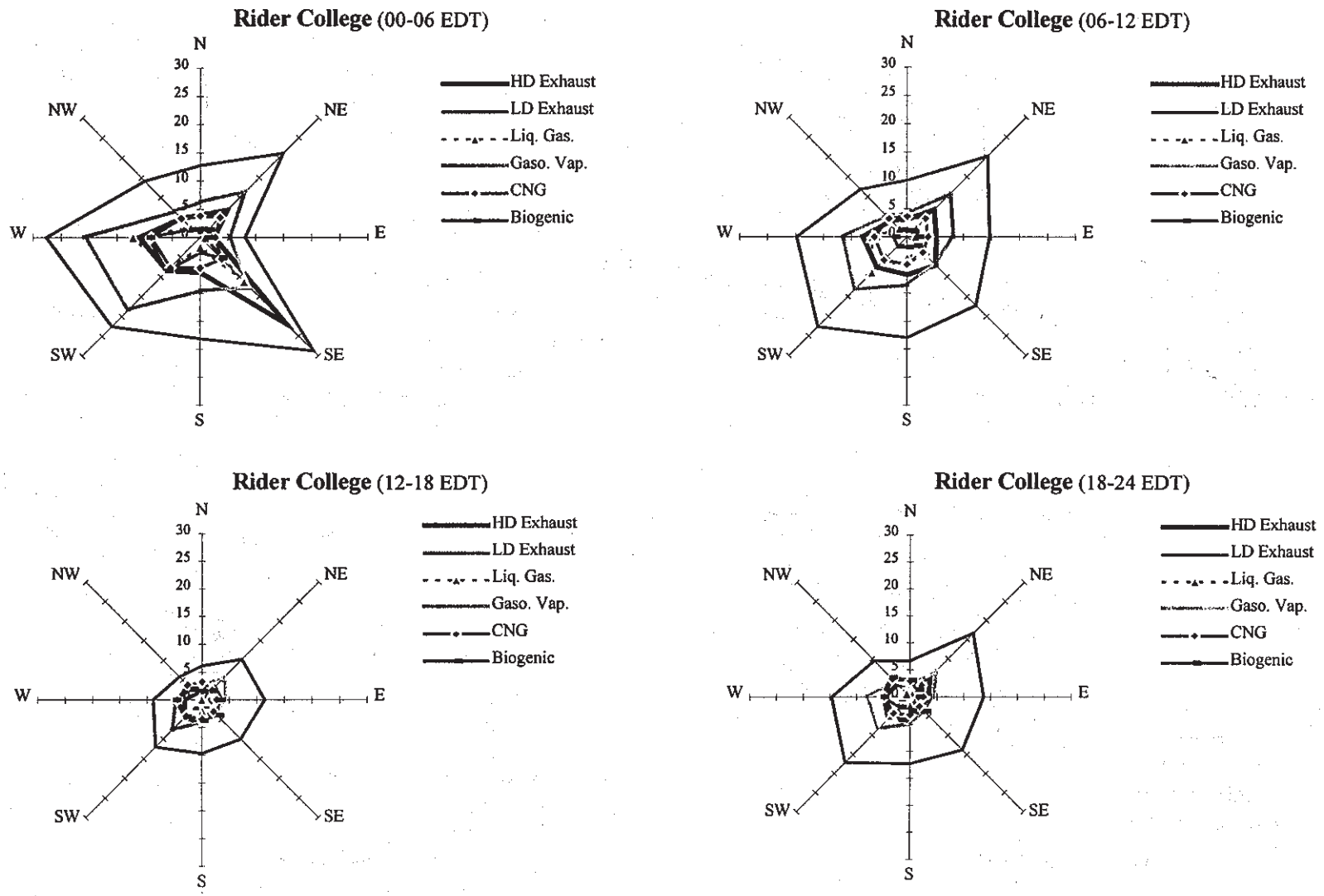

Figure 4-4e. Wind directional dependence of source contributions by time of the day at Rider College, NJ.

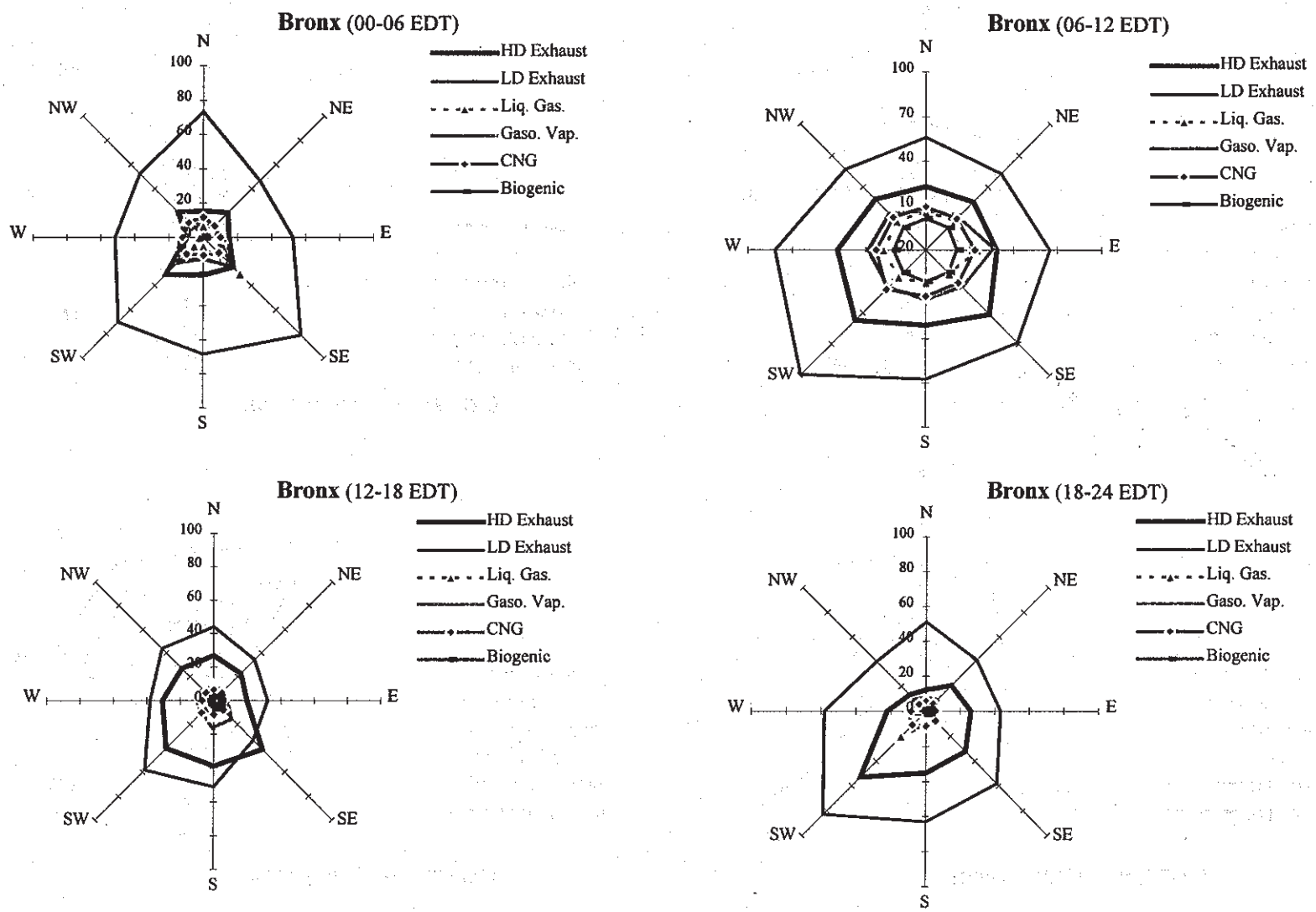

Figure 4-4f. Wind directional dependence of source contributions by time of the day at Bronx, NY.

dominant source with contributions out of the northeast and east about three times as high as for vehicle exhaust.

Most of the source contributions at Chicopee are from the southern two wind quadrants. Gasoline vapor is the largest source at Chicopee during the day. It has a wind dependence similar to diesel exhaust, which suggest that these two sources are likely from a common origin

Contributions of gasoline vehicle exhaust at Lynn, MA are predominantly from the southeast, south, and southwest. In contrast, the contribution of diesel exhaust is more or less uniform from all directions. This pattern suggests a very strong local source that dominates the ambient VOC composition near the sampling site. It also indicates that the source of the heavy hydrocarbons that are ascribed to diesel exhaust is some source other than diesel vehicles. The lack of diurnal variation in this source contribution shown in Figure 4-3e suggests that the heavy hydrocarbons measured at Lynn may be a sampling artifact.

The dominant source of hydrocarbon at Lake Clifton is gasoline-powered vehicles. This source contribution is fairly uniform from all directions. All other source contributions are small in comparison and also show no particular wind dependence.

Both Rider College and Bronx sites show uniform contributions from all directions, which indicate that these sites are centrally located within respect to major emission sources. It also indicates there are no significant local sources and that emissions are well mixed.

5 SOURCE APPORTIONMENT OF NARSTO-NORTHEAST CANISTER DATA

This section presents the source apportionment results for ambient hydrocarbon data from the 1995 NARSTO-Northeast Study surface and aloft canister samples. Four three-hour (beginning at 0600, 0900, 1200, and 1500 EDT) and two six-hour (beginning at 0000 and 1800 EDT) ground-level canister samples were collected on 23 days of intensive operations. The CMB 8.0 program was applied to 93 samples from Arendtsville, 78 samples from Brookhaven National Laboratory, NY, 78 samples from Truro (Cape Cod), MA, 110 samples from Holbrook, PA, 78 samples from Kunkletown, PA, and 68 samples from Shenandoah National Park, VA. Each sample was apportioned with the following default set of source profiles: heavy-duty diesel exhaust from the Ft. McHenry Tunnel (Tu_MchHD), gasoline vehicle exhaust (Exh_Lin1), liquid gasoline (WA-Liq), gasoline headspace vapor (WA_Vap), commercial natural gas (CNG), liquefied petroleum (LPG), isoprene emissions (Biogenic), and unidentified (UNID). This default set of source profiles was also applied to 106 aloft canister samples (14 over Manassas, 16 over Madison, 9 over Brookhaven, 31 over Kunkletown, 10 over Lums Pond, 12 over Arendstville, and 14 over Shenandoah). Appendixes A and B list the individual CMB results with propagated input uncertainties for the surface and aloft samples, respectively.

5.1 Source Contribution Estimates for Surface Samples

Table 5-1 shows the average source contributions in percent of NMHC by sampling period for each surface sampling site. Source contributions for each sample are shown in time-series plots in Figure 5-1. In contrast to many of the PAMS sites, the supplemental hydrocarbon data for the NARSTO-Northeast intensive measurement periods were collected in locations that reflect air quality on a more regional rather than urban/suburban scale. The analytical methods that were employed by Biospheric Research Corporation provide a more quantitative measure of total hydrocarbons in comparison to those used in the PAMS program. Accordingly, unidentified compounds are the largest fraction of total NMHC by a large margin at all sites, ranging from 40 to 70 percent. Mass spectrometer analysis of these samples by BRC shows that a large fraction of the unidentified compounds are associated with a homologous series of higher molecular weight aldehydes (Rasmussen, 1997). The gas chromatogram in Figure 5-2 shows similar data obtained by Desert Research Institute at Lynn, MA on 9/14/95, 1300-1600, EDT (DRI, 1997).

The apportionments of the identified hydrocarbon fraction at Arendtville, Brookhaven, and Kunkletown are similar to the source contributions at suburban PAMS sites. Cape Cod has nearly equal contributions of diesel and gasoline vehicle exhaust. Ambient mixing ratios of ethane are very high at Holbrook, which result in attribution of 25 to 45 percent of the NMHC to natural gas. Isoprene is the largest fraction of identified hydrocarbons (nearly half) at Shenandoah in the daytime samples.

Table 5-1
Average source contributions to TNMHC at six surface canister sites

Hour (EDT)	r^2	χ^2	%	NMHC (ppbc)	# in avg	Exhaust HD %	Exhaust LD %	Liquid Gasoline %	Gasoline Vapor %	CNG %	LPG %	Biogenic %	Unid %	Unexpl. %
Arendstville														
00	0.81	2.04	107.8	96.8	18	8.8	19.4	0.8	2.5	5.7	1.7	1.2	67.5	-7.8
06	0.81	2.36	106.5	124.8	18	7.4	18.8	2.6	3.7	6.2	1.6	2.3	63.8	-6.5
09	0.81	2.29	108.3	115.2	15	7.8	18.2	2.1	2.7	5.6	1.8	2.6	67.6	-8.3
12	0.77	2.38	107.0	109.6	16	7.7	12.5	3.8	1.7	5.8	1.0	3.7	70.8	-7.0
15	0.78	2.38	106.1	143.4	12	8.3	10.6	2.9	2.0	5.5	0.7	7.1	69.1	-6.1
18	0.82	1.79	105.9	106.6	14	9.0	14.1	0.8	1.6	6.2	1.0	8.7	64.5	-5.9
All	0.80	2.21	107.0	114.9	93	8.1	16.0	2.1	2.4	5.9	1.3	4.0	67.1	-7.0
Brookhaven														
00	0.89	1.69	107.1	146.5	13	6.3	33.1	1.8	3.4	2.6	6.0	1.0	52.8	-7.1
06	0.86	2.79	106.2	227.7	14	4.5	25.6	3.1	3.9	2.3	2.6	2.9	61.3	-6.2
09	0.86	2.45	107.5	191.1	12	5.6	25.6	2.2	5.0	3.1	2.6	6.4	57.1	-7.6
12	0.76	3.66	105.8	195.8	15	5.2	17.1	1.7	2.1	2.5	1.3	7.2	68.6	-5.8
15	0.72	3.75	102.5	230.5	11	5.6	12.5	2.0	2.0	1.9	0.7	6.0	71.6	-2.5
18	0.84	1.80	106.2	108.4	13	7.5	24.1	0.9	3.8	3.1	3.1	2.2	61.6	-6.2
All	0.82	2.69	106.0	182.9	78	5.8	23.1	2.0	3.4	2.6	2.7	4.3	62.1	-6.0
Cape Cod														
00	0.67	4.26	102.8	290.6	14	10.6	7.4	6.5	1.8	2.0	0.5	2.2	72.0	-2.8
06	0.67	5.11	99.6	255.0	15	8.2	14.8	1.7	2.4	3.0	0.8	1.9	66.7	0.4
09	0.74	3.07	106.7	208.9	12	8.9	11.1	4.7	2.2	2.4	0.8	5.5	71.1	-6.7
12	0.70	3.45	105.0	221.1	10	8.3	9.4	1.4	2.5	2.5	0.4	6.8	73.7	-5.0
15	0.75	2.96	106.2	189.5	15	8.1	11.7	2.8	1.3	2.5	0.4	6.7	72.6	-6.2
18	0.74	2.40	106.2	158.0	12	9.0	10.1	4.7	0.9	2.6	0.4	1.4	77.1	-6.2
All	0.71	3.60	104.2	222.4	78	8.9	10.9	3.7	1.8	2.5	0.6	4.0	72.0	-4.2
Holbrook														
00	0.73	3.66	104.2	178.0	18	6.8	8.1	0.8	6.9	34.9	5.7	0.6	40.4	-4.2
06	0.75	4.18	107.8	194.5	18	5.5	9.2	1.0	7.7	45.2	3.3	0.7	35.2	-7.8
09	0.76	3.56	107.7	183.4	19	6.1	7.3	0.5	7.1	45.0	2.4	1.6	37.8	-7.7
12	0.78	2.64	108.1	118.6	19	7.0	8.3	0.6	5.2	28.4	2.0	2.4	54.2	-8.1
15	0.81	2.01	105.6	114.7	19	6.1	5.5	0.9	5.0	24.9	2.7	3.7	56.7	-5.6
18	0.76	3.02	106.7	135.6	17	7.0	6.3	0.7	5.9	26.2	3.4	3.5	53.5	-6.7
All	0.77	3.17	106.7	153.9	110	6.4	7.4	0.7	6.3	34.1	3.2	2.1	46.3	-6.7
Kunkletown														
00	0.82	2.96	105.6	141.9	18	6.5	21.9	5.2	4.9	5.5	2.4	1.9	57.2	-5.5
06	0.84	2.33	108.5	122.7	17	7.1	24.3	3.3	4.6	5.3	2.8	2.6	58.4	-8.4
09	0.84	2.27	108.7	116.8	16	8.8	23.9	1.6	4.9	5.8	2.7	2.2	58.9	-8.7
12	0.81	2.87	105.8	153.9	12	7.4	17.3	2.2	5.4	6.0	1.7	3.1	62.6	-5.8
15	0.81	2.58	108.2	145.2	12	8.2	17.4	1.8	7.4	5.3	1.8	4.3	62.0	-8.2
18	0.83	2.13	109.9	100.5	13	7.4	19.6	4.8	2.8	5.7	1.5	5.1	62.9	-9.9
All	0.83	2.53	107.7	129.6	88	7.5	21.2	3.3	4.9	5.6	2.2	3.0	60.0	-7.7
Shenandoah														
00	0.79	2.31	107.8	112.7	13	5.6	10.7	8.3	2.2	4.6	1.3	2.4	72.7	-7.8
06	0.72	4.83	102.6	220.7	8	4.1	8.3	7.6	6.2	4.0	1.1	3.8	67.4	-2.6
09	0.79	2.37	107.3	121.6	11	5.9	9.9	5.9	0.8	5.2	1.1	12.0	66.5	-7.3
12	0.77	2.86	106.2	125.2	12	6.3	7.3	8.4	1.9	4.3	1.6	14.8	61.5	-6.2
15	0.83	1.67	108.7	97.4	10	7.3	11.4	5.1	1.2	5.2	0.9	18.4	59.3	-8.7
18	0.82	2.12	108.7	119.5	11	6.1	11.2	8.1	1.6	4.4	1.0	6.2	70.0	-8.7
All	0.79	2.60	107.1	128.6	65	5.9	9.9	7.3	2.2	4.6	1.2	9.6	66.4	-7.1

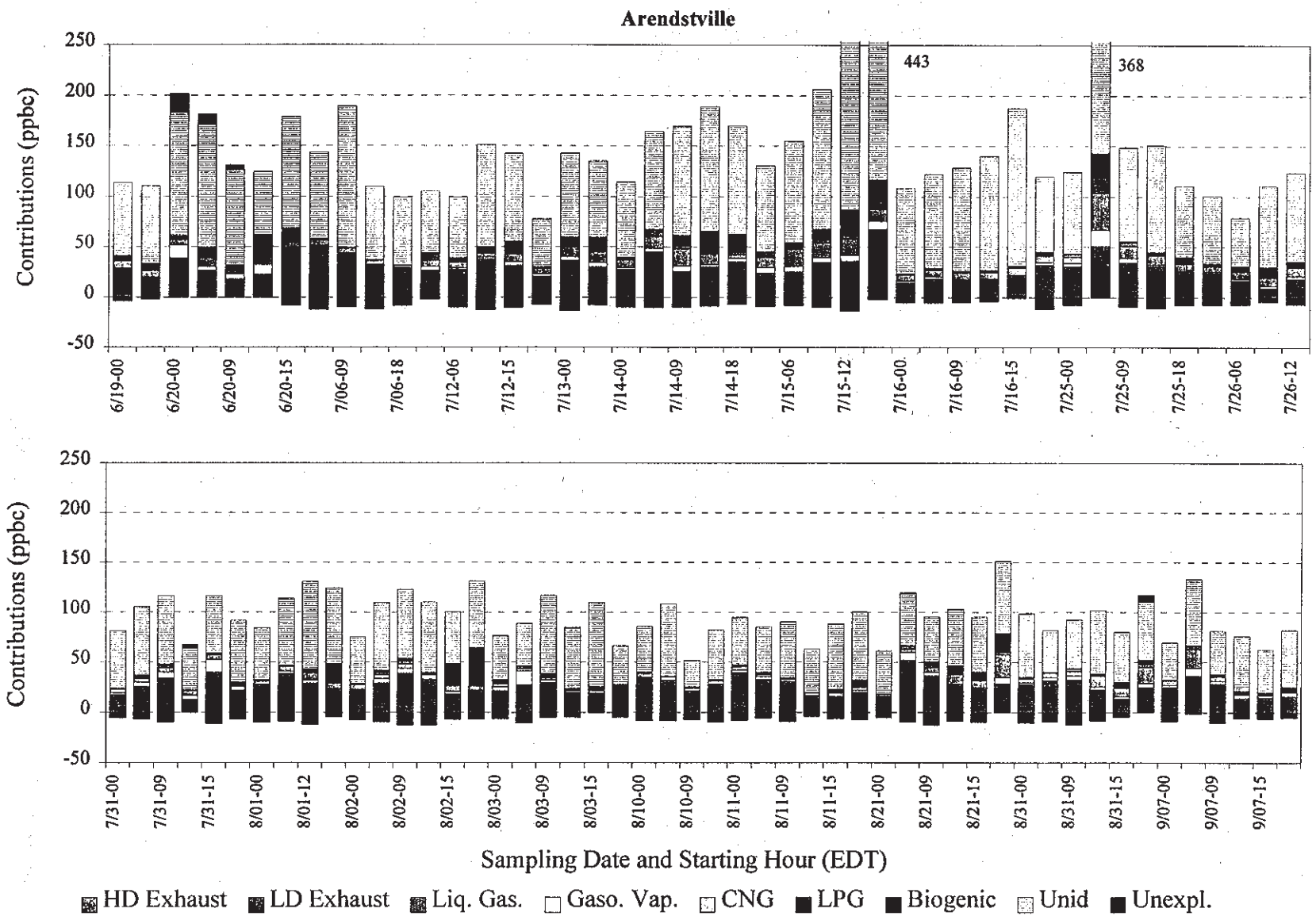

Figure 5-1a. Source contributions to NMHC at the NARSTO-Northeast site at Arendstville in 1995.

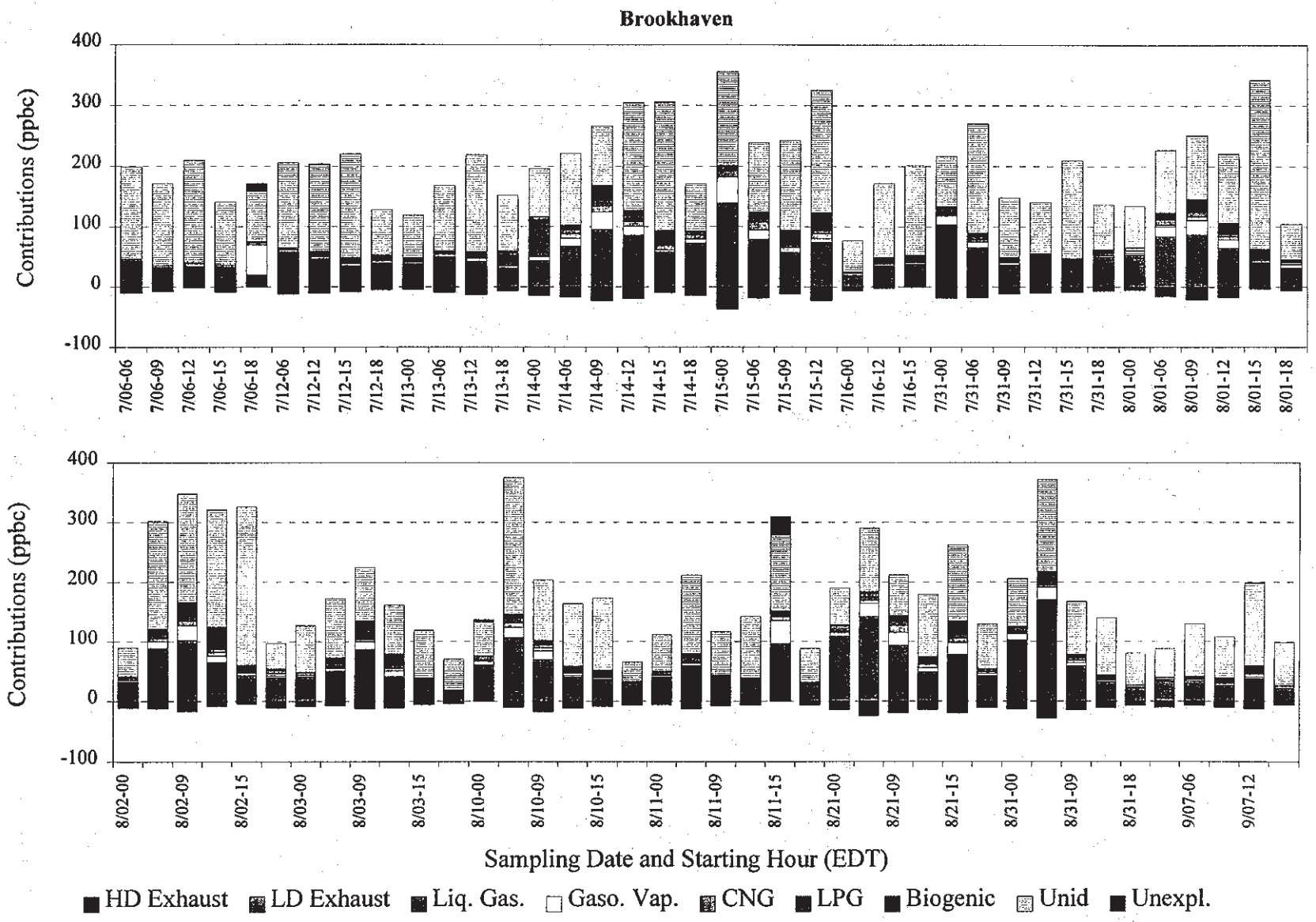

Figure 5-1b. Source contributions to NMHC at the NARSTO-Northeast site at Brookhaven in 1995.

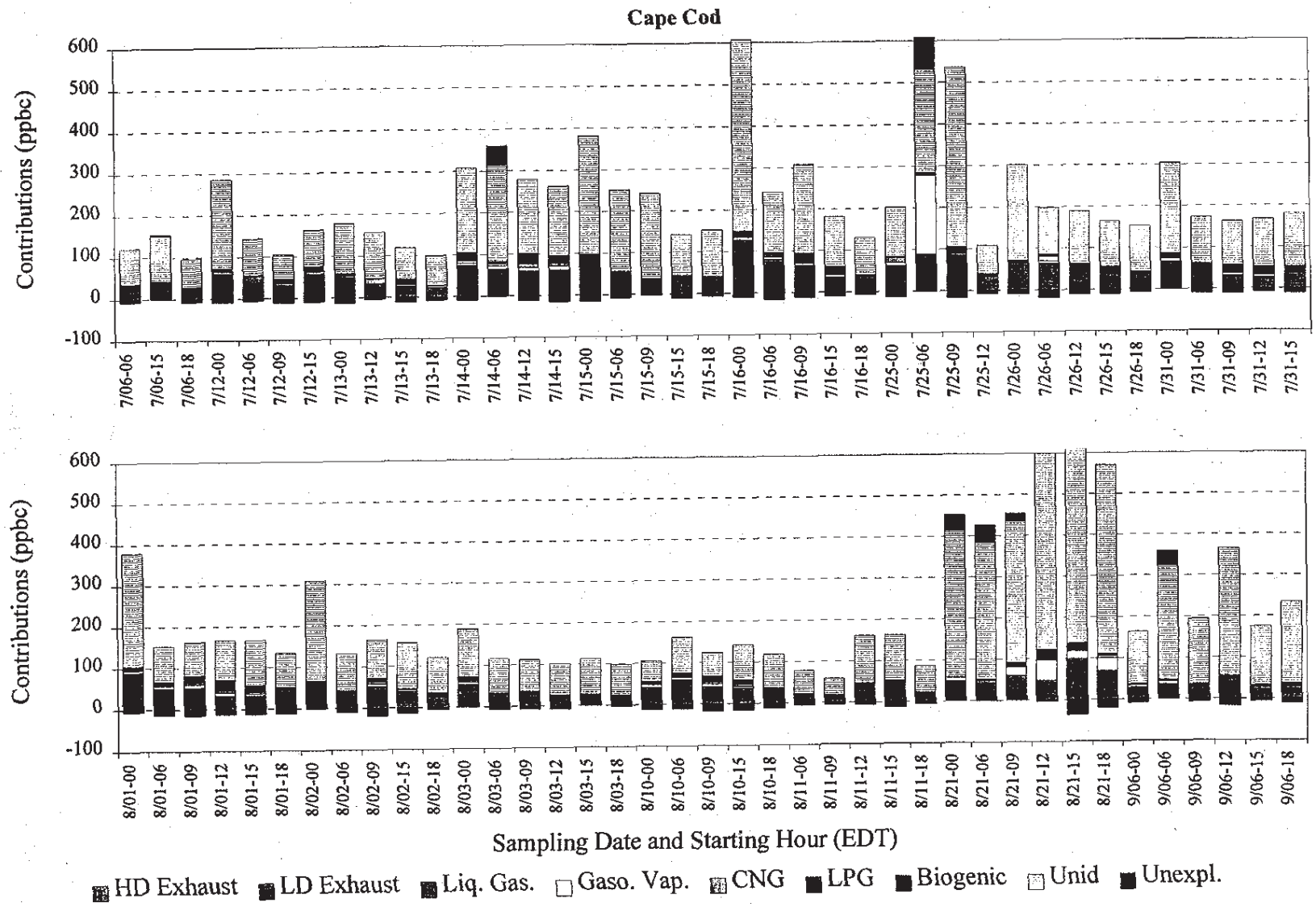

Figure 5-1c. Source contributions to NMHC at the NARSTO-Northeast site at Cape Cod in 1995.

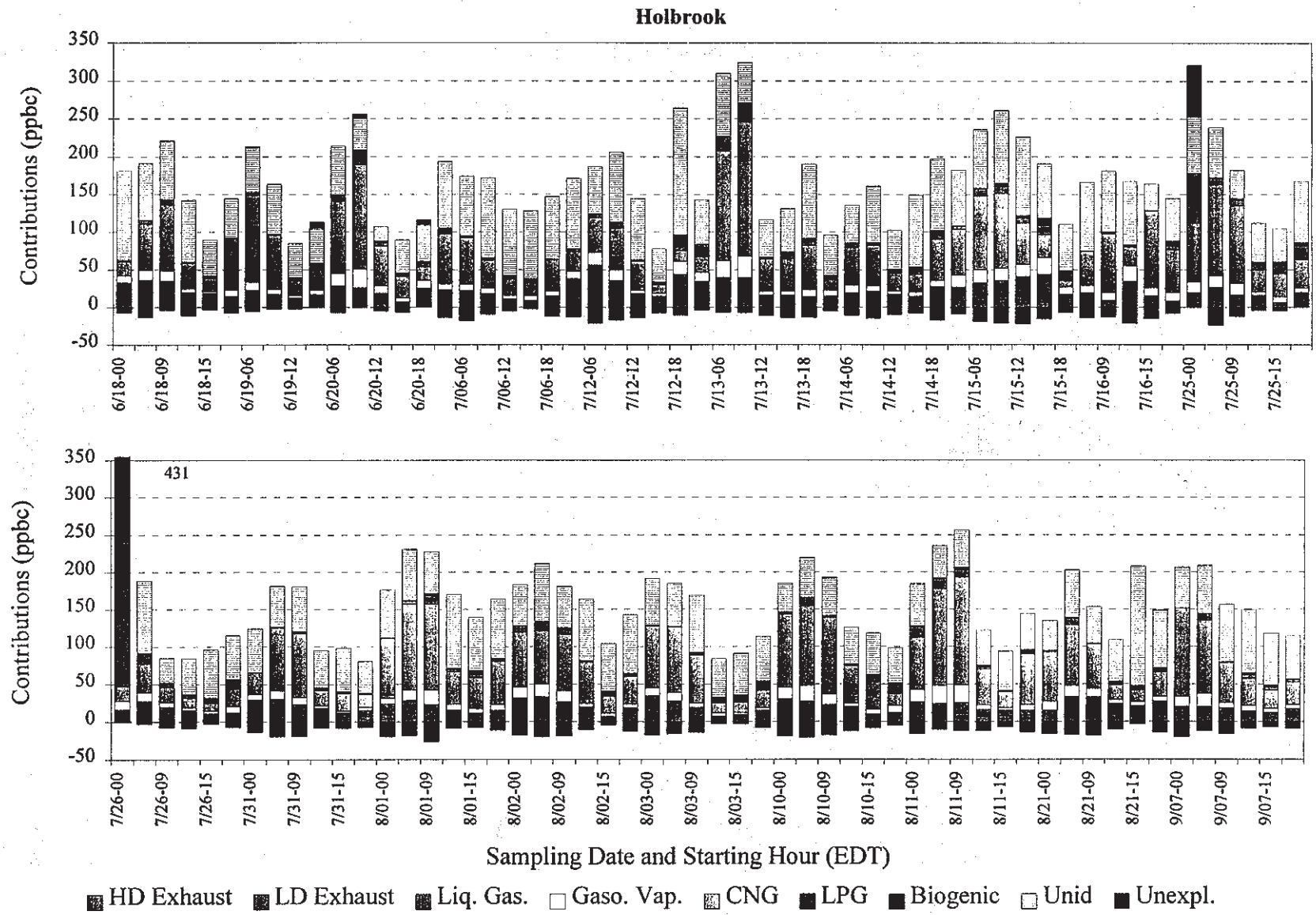

Figure 5-1d. Source contributions to NMHC at the NARSTO-Northeast site at Holbrook in 1995.

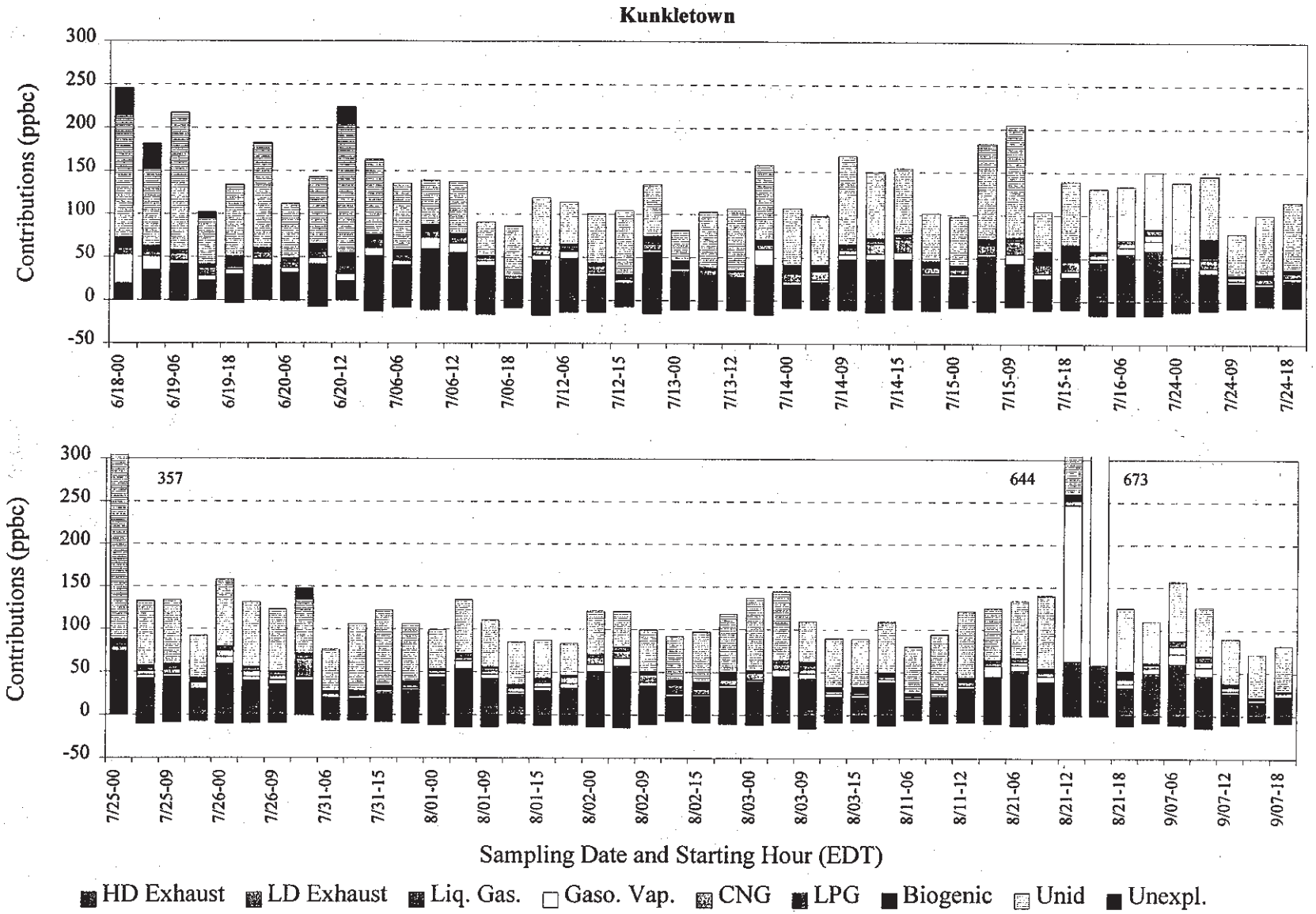

Figure 5-1e. Source contributions to NMHC at the NARSTO-Northeast site at Kunkletown in 1995.

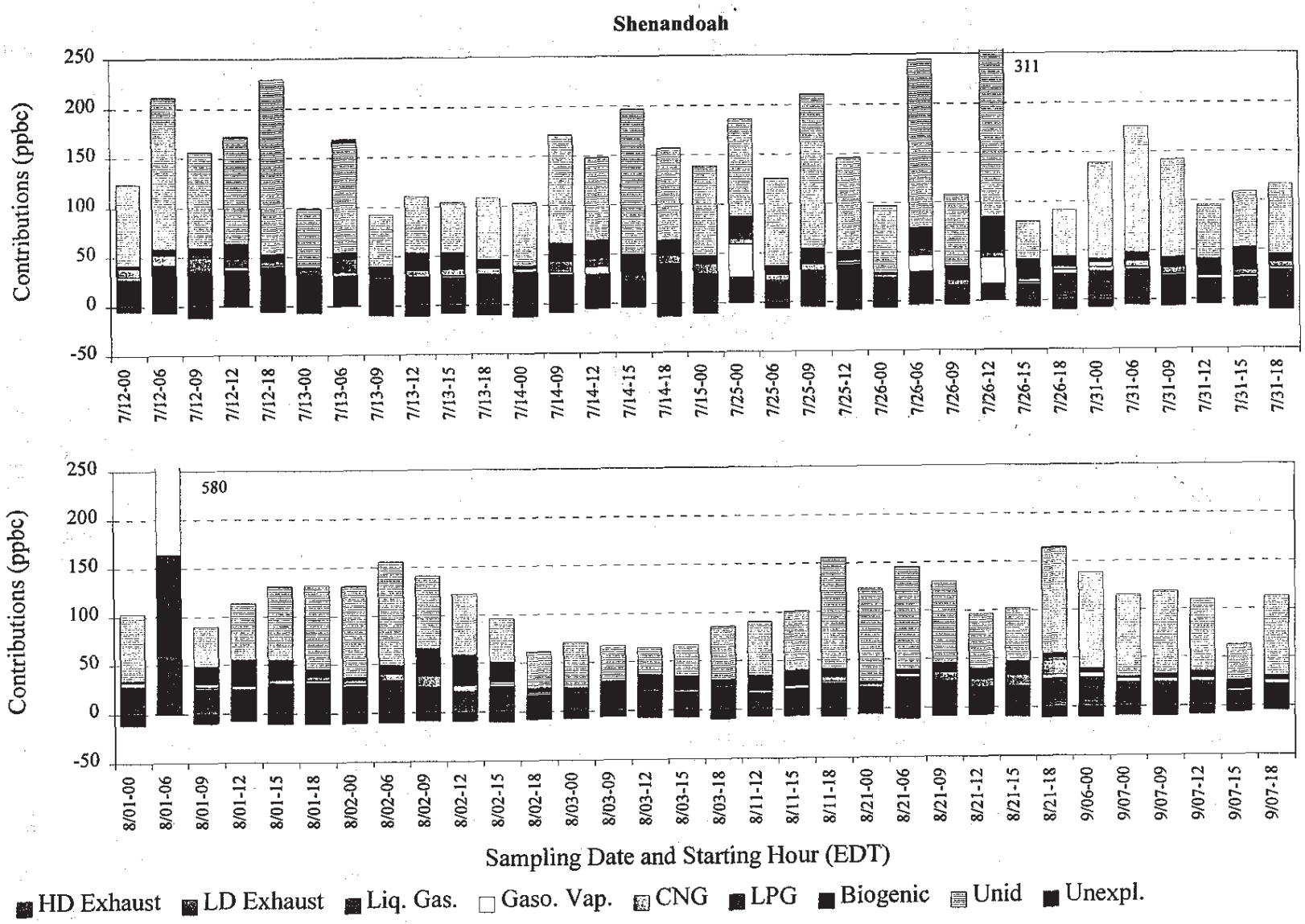

Figure 5-1f. Source contributions to NMHC at the NARSTO-Northeast site at Shenandoah in 1995.

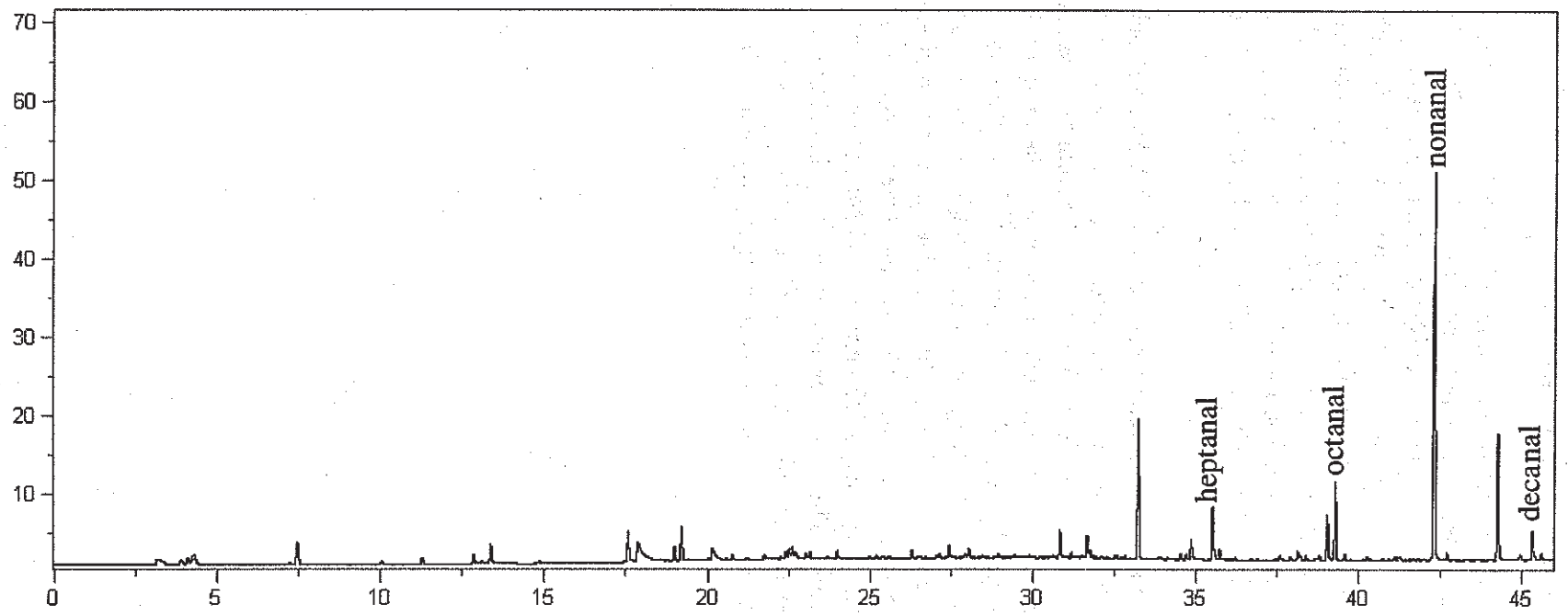

Figure 5-2. Gas chromatogram of a sample from Lynn, MA on 9/14/95 at 1300-1600, EDT (Source: Desert Research Institute).

5.2 Source Contribution Estimates for Aloft Samples

Aircraft samples were collected at a number of locations within the study area in order to address issues of transport and pollutant distribution. The flights consisted of traverse low in the boundary layer with occasional dips to the surface hear airport and spirals from the surface to the top of the boundary layer. In general, two hydrocarbon samples were collected in each of three spirals during each flight, with one sample collected between about 300 m agl and the surface, and other between about 300 m and 1000 m agl. Once per flight, a sample was collected between about 2000 and 2300 m agl. A total of 106 grab samples were collected and analyzed for C2-C10 hydrocarbon by the Oregon Graduate Institute of Science and Technology (OGI).

Table 5-2 shows the average source contributions to NMHC for each of the sampling periods and sites averaged over all the sampling days. The source contributions for individual samples are also plotted in Figure 5-3 so that temporal and spatial patterns can be more easily observed. Similar to the surface canister samples, the unidentified fraction is the largest component in all of the aloft samples. This fraction is fairly constant over a wide area during the day with morning averages ranging from 59 to 75 percent and afternoon averages ranging from 63 to 73 percent. Although highly variable from site to site, gasoline vehicle exhaust is the largest contributor to the residual, identified fraction of NMHC. This contribution is greatest over Brookhaven (22 percent) and Manassas (23 percent) and lowest over Kunkletown (9 percent). The contributions of diesel exhaust are more uniform than auto exhaust, with averages ranging from 6 to 9 percent. In comparison to surface samples, the contributions of isoprene are lower in aloft samples, which indicate losses due to photochemical reactions.

Table 5-2
Average source contributions to TNMHC at aircraft sites

Hour (EDT)	r^2	χ^2	% %	NMHC (ppbc)	# in avg	Exhaust HD %	Exhaust LD %	Liquid Gasoline %	Gasoline Vapor %	CNG %	LPG %	Biogenic %	Unid %	Unexpl. %
						Arendstville								
AM	0.76	2.47	105.7	89.1	11	8.3	16.1	3.6	2.5	7.2	1.7	0.1	66.1	-5.7
						Brookhaven								
AM	0.83	2.29	110.0	107.9	5	8.5	24.1	5.7	4.8	5.3	2.4	0.0	59.1	-10.0
PM	0.81	1.38	110.5	61.2	4	6.2	19.4	1.5	1.2	11.8	0.9	1.4	68.0	-10.5
All	0.82	1.89	110.2	87.2	9	7.5	22.0	3.8	3.2	8.2	1.8	0.6	63.1	-10.2
						Kunkletown								
AM	0.67	2.71	103.9	82.3	15	7.5	9.9	3.3	1.6	7.1	0.8	0.0	73.8	-3.9
PM	0.75	2.09	104.4	95.4	16	8.5	8.9	1.5	1.3	7.4	1.1	2.5	73.2	-4.4
All	0.71	2.39	104.2	89.0	31	8.0	9.4	2.4	1.4	7.2	1.0	1.3	73.5	-4.2
						Lums Pond								
PM	0.73	3.04	106.8	108.8	10	7.9	14.8	2.4	1.6	6.9	1.7	1.6	69.9	-6.8
						Madison								
AM	0.76	1.60	107.2	97.6	9	7.4	11.4	2.2	5.9	4.4	0.8	0.0	75.2	-7.2
PM	0.84	1.18	107.5	55.4	7	6.3	16.0	1.6	2.6	11.4	0.7	0.1	68.7	-7.5
All	0.79	1.42	107.3	79.1	16	6.9	13.4	1.9	4.4	7.5	0.7	0.1	72.4	-7.3
						Manassas								
AM	0.79	2.29	108.3	87.2	7	9.3	25.0	2.1	1.6	8.5	1.4	1.2	59.1	-8.3
PM	0.73	3.55	106.4	107.2	7	6.9	20.2	1.4	0.8	6.9	1.3	5.8	63.1	-6.4
All	0.76	2.92	107.4	97.2	14	8.1	22.6	1.8	1.2	7.7	1.4	3.5	61.1	-7.4
						Shenandoah								
AM	0.75	2.18	106.2	90.0	14	8.6	13.2	2.0	1.7	6.9	1.8	0.7	71.3	-6.2

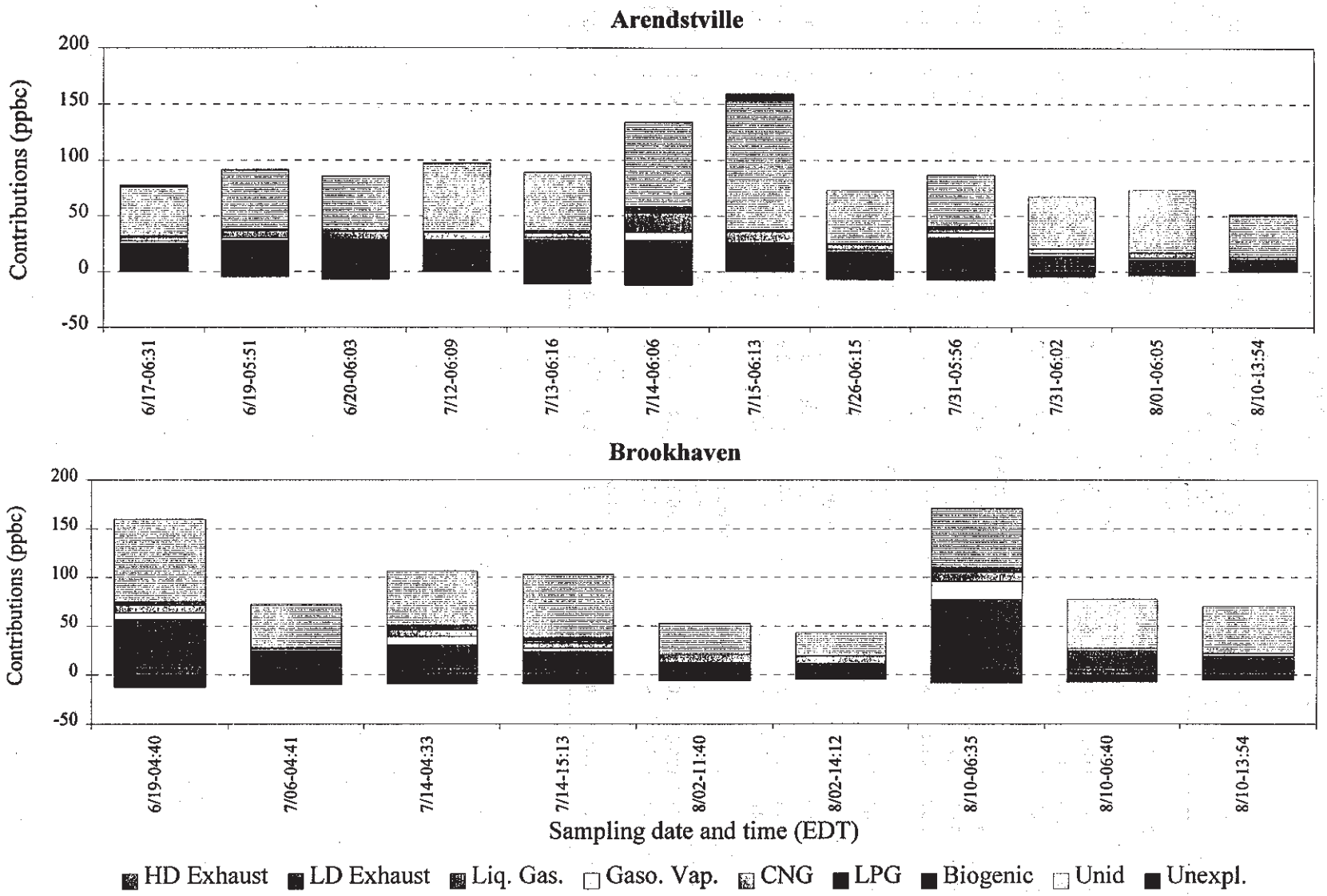

Figure 5-3. Source contributions to NMHC for aircraft canister samples

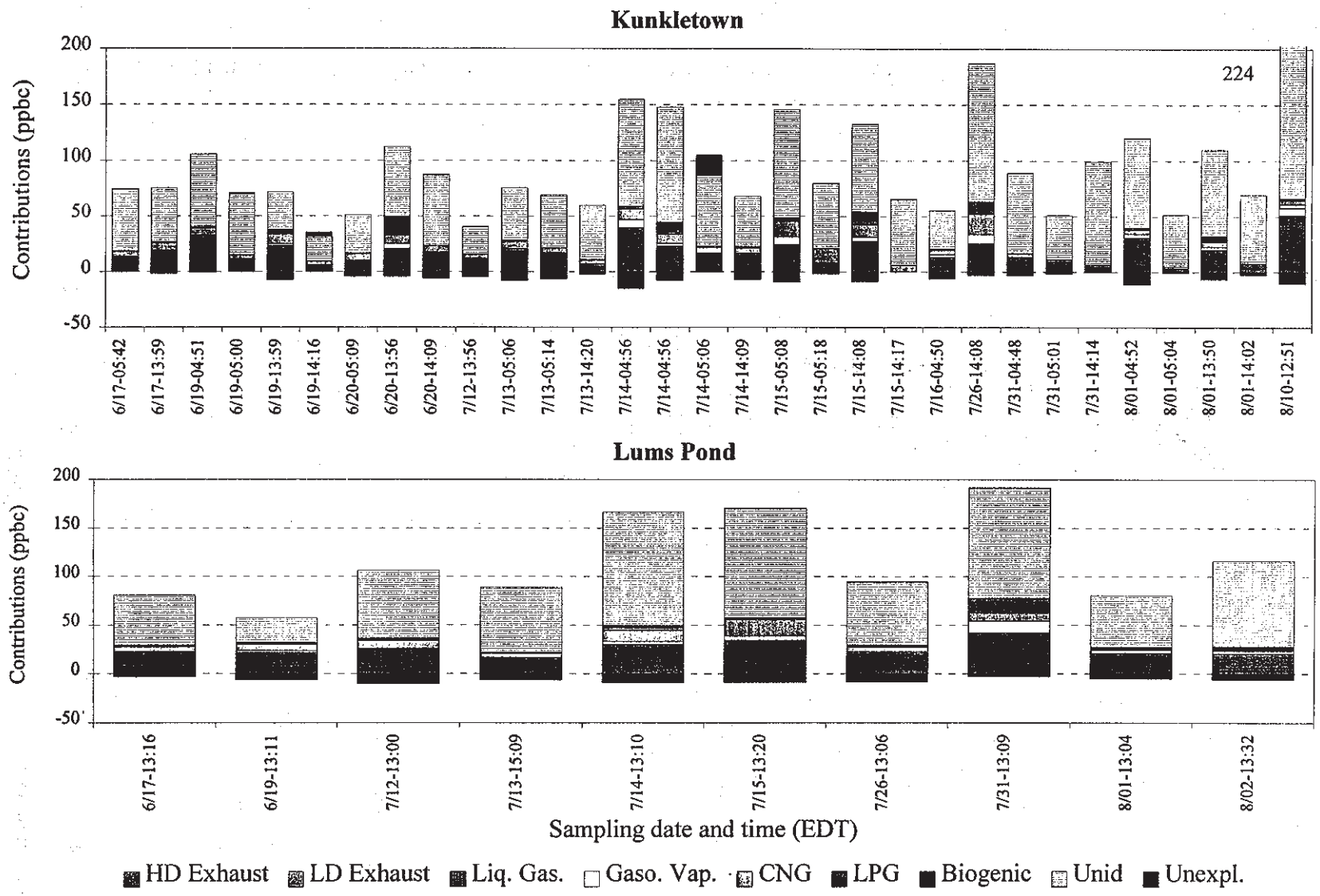

Figure 5-3 (continued). Source contributions to NMHC for aircraft canister samples

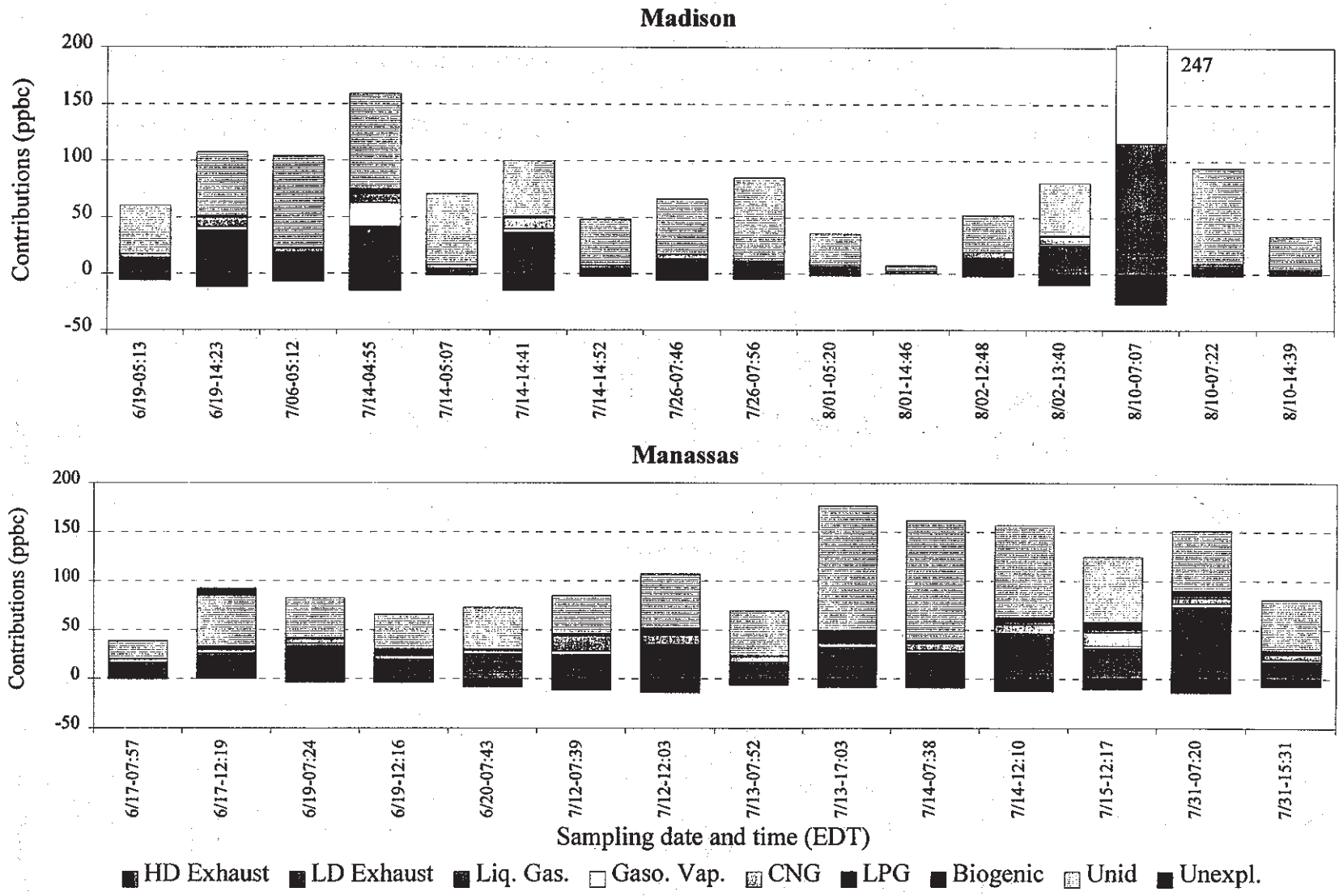

Figure 5-3 (continued). Source contributions to NMHC for aircraft canister samples

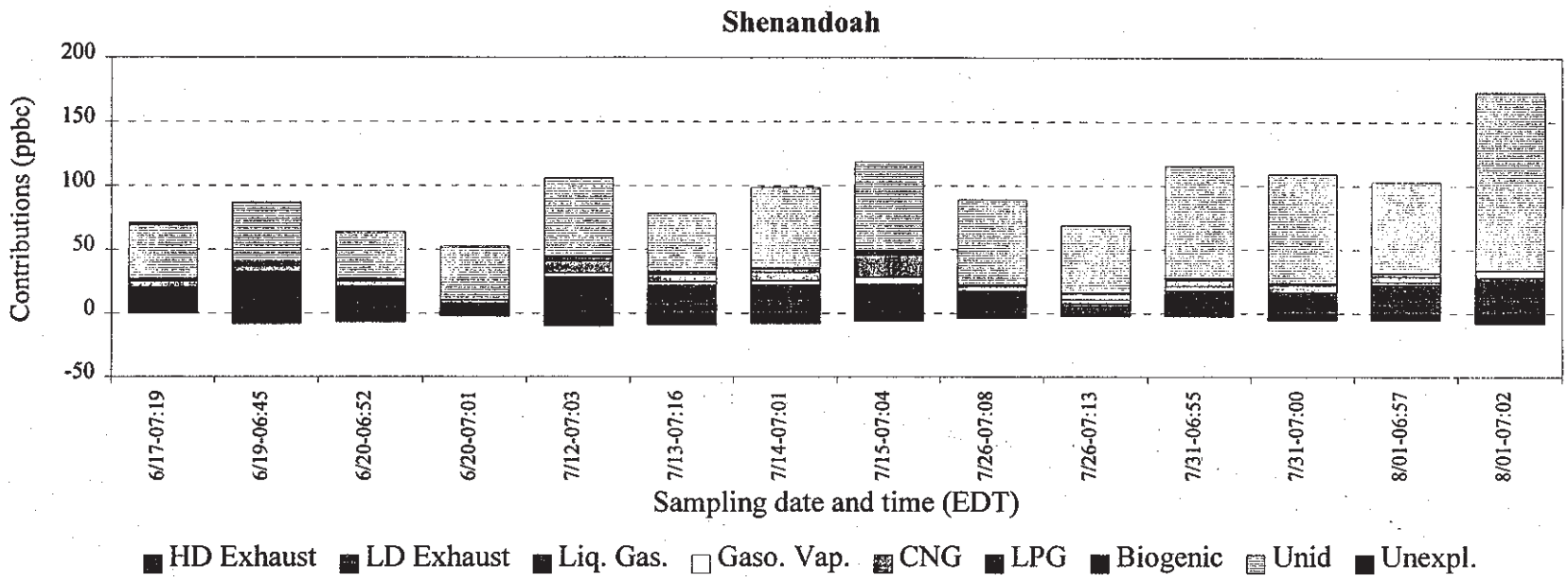

Figure 5-3 (continued). Source contributions to NMHC for aircraft canister samples

Pacific Northwest. Available source profiles for solvents, biogenic, natural and liquefied petroleum gases were also evaluated.

Source Apportionment of Auto-GC Samples

The source contribution estimates for each of the ten PAM sites are presented in this report with respect to variations by time of day, day-of-the-week, and wind direction. CMB8.0 was applied with AUTOFIT to over 15,000 hydrocarbon samples covering the period from June 1, 1995 to August 31, 1995. For Type 2 sites, the significant contributors to the average 24-hour ambient NMHC are gasoline vehicle exhaust (40 percent), gasoline vapor (17 percent), and diesel exhaust (17 percent). Natural gas leak (9 percent), liquid gasoline (7 percent), liquefied petroleum gas (4 percent), and biogenic emissions (4 percent) are minor contributors to NMHC. On average, only 4 percent of the identified NMHC are unexplained. Removing Chicopee and Lynn from the average, decreases the average contribution of diesel exhaust for the remaining sites to 12 percent and increases gasoline vehicle exhaust to 46 percent. The significant contributors to the average 24-hour ambient NMHC at downwind PAMS sites are gasoline vehicle exhaust (30 percent), gasoline vapor (18 percent), liquefied petroleum gas (18 percent), and natural gas (11 percent). Diesel exhaust (9 percent), liquid gasoline (6 percent), biogenic emissions (5 percent) are minor contributors to NMHC.

Contributions of automotive exhaust generally peak during morning and afternoon commute periods on weekdays, but are significantly lower during weekend mornings. The diurnal and day-of-the-week patterns in the liquid gasoline contributions are essentially identical to motor vehicle exhaust, which suggest that a significant fraction of the liquid gasoline contribution may be associated with tailpipe emissions rather than evaporative emissions from either vehicle or industrial sources. In contrast, average diurnal patterns of gasoline vapor contributions show no peaks during the commute periods.

The diurnal variations in the contribution of natural gas correlate with diurnal variations in vertical mixing. This diurnal pattern and lack of day-of-the-week variations are consistent with constant leakage of natural gas. LPG generally shows the same diurnal variations. Propane is the most abundant species at Lums Pond. Its contribution is predominantly from the northeast and east as are gasoline vapor and liquid gasoline.

Most of the source contributions at Chicopee are from the southern two wind quadrants. Gasoline vapor is the largest source at Chicopee during the day. It has wind dependence similar to diesel exhaust, which suggests that these two sources are likely from a common origin.

Contributions of gasoline vehicle exhaust at Lynn, MA are predominantly from the southeast, south, and southwest. In contrast, the contributions of diesel exhaust are uniformly large from all directions. This pattern suggests a local source that dominates the ambient VOC composition near the sampling site. It also indicates that the source of the heavy hydrocarbons that are ascribed to diesel exhaust is probably some source other than diesel vehicles. The lack of diurnal variation in this source contribution suggests that the heavy hydrocarbons measured at Lynn may be a sampling artifact.

Lake Clifton, Rider College, and Bronx sites show uniform contributions from all directions, which indicate that these sites are centrally located with respect to major emission sources. It also indicates that emissions are well mixed and there are no significant local sources near the sites.

Biogenic emissions are a significantly larger fraction of total NMHC in suburban and rural areas than in urban areas. The contributions of isoprene over a 24-hour average range from 4 to 12 percent in suburban and rural areas, and are less than 2 percent in urban areas. As expected, contributions of isoprene are significantly higher during the middle of the day, particularly at E. Hartford, Rider College, Chicopee, and Lynn. Because isoprene is emitted only during daylight hours with peak emission rates occurring at midday, it is one of the larger sources of NMHC during the day in suburban and rural areas. Source contribution estimates of biogenic emissions from CMB provide a lower limit because of the high reactivity of isoprene. Actual contributions may be 5 to 10 times higher than CMB estimates.

Source Apportionment of Surface and Aloft Canister Samples

Unidentified compounds are the largest fraction of total NMHC by a large margin at all sites, ranging from 40 to 70 percent. In contrast to many of the PAMS sites, the supplemental hydrocarbon data for the NARSTO-Northeast intensive measurement periods were collected in locations that reflect air quality on a more regional rather than urban/suburban scale. The analytical methods that were employed by Biospheric Research Corporation provide a more quantitative measure of total hydrocarbons in comparison to those used in the PAMS program.

The apportionments of the identified hydrocarbon fraction at Arendtville, Brookhaven, and Kunkletown are similar to the source contributions at suburban PAMS sites (i.e., dilute urban sample). Ambient mixing ratios of ethane are very high at Holbrook, which result in attribution of 25 to 45 percent of the NMHC to natural gas. Isoprene is the largest fraction of identified hydrocarbons (nearly half) at Shenandoah in daytime samples.

Unidentified compounds are also the largest component in all of the aloft samples. This fraction is fairly constant over a wide area during the day with morning averages ranging from 59 to 75 percent of NMHC and afternoon averages ranging from 63 to 73 percent. Although highly variable from site to site, automotive exhaust is the largest contributor to the identified fraction of NMHC. This contribution is greatest over Brookhaven (22 percent) and Manassas (23 percent) and lowest over Kunkletown (9 percent). The contributions of diesel exhaust are more uniform than auto exhaust, with averages ranging from 6 to 9 percent. In comparison to surface samples, the contributions of isoprene are lower in aloft samples, which indicate losses due to photochemical reactions.

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