ANALYSIS OF THE AMBIENT VOC DATA COLLECTED IN THE SOUTHERN CALIFORNIA AIR QUALITY STUDY

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ABSTRACT

A detailed analysis of ambient hydrocarbon and carbonyl data collected in the Southern California Air Quality Study (SCAQS) was undertaken to develop an improved understanding of nonmethane organic compounds (NMOC) in California's South Coast Air Basin (SoCAB). The SCAQS data set, which was the most extensive ever collected in the SoCAB, was used to:

(1) Characterize the spatial and temporal patterns of total NMOC concentrations and NMOC/NO_x ratios;

(2) Characterize the spatial and temporal patterns of individual organic compounds;

(3) Assess the consistency between ambient and emissions inventory NMOC; and

(4) Assess the extent of NMOC oxidation and carbonyl compound formation occurring in the atmosphere.

The first major finding of the study was that NMOC composition and NMOC/NO_x ratios were fairly similar throughout the basin. The spatial, temporal, and day-to-day variations in the contributions of the major organic compound groups and the abundant organic species to NMOC were smaller than expected. However, the total NMOC concentrations have significant day-to-day and seasonal variations, which are undoubtably controlled by meteorology, and they have significant spatial variation within the basin due to the nonuniformity of emission rates and the effects of transport.

The second major finding was that the NMOC/NO_x and CO/NO_x ratios in the ambient data and emissions inventories were inconsistent and there were also discrepancies between the organic speciation of the inventories and ambient data. The inconsistencies in the NMOC/NO_x and CO/NO_x ratios strongly suggest current inventories underestimate NMOC and CO emissions from motor vehicles. Problems with the emissions from other types of sources may also contribute to the discrepancies, however, there were too few tracer species for organic emissions from specific source types to identify those sources with these data.

The third finding was that there appears to be a large amount of carbonyl species formation in the urban atmosphere from photo-oxidation of hydrocarbons. The photochemical source of C1-C4 carbonyl compounds is probably larger than the emissions source. C4+ carbonyl compounds were more abundant than expected and the sources of these higher carbonyl compounds were not identified.

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EXECUTIVE SUMMARY

The ambient volatile organic compound (VOC) data collected in the Southern California Air Quality Study (SCAQS) represent one of the most extensive sets of VOC data available for any urban area in the United States. They include measurements of individual C1-C12 hydrocarbon and C1-C7 carbonyl compound concentrations collected at three or six times per day at nine locations in the summer and six locations in the fall. In addition, the data set includes aircraft measurements of VOCs between 500 and 800 meters above ground.

A detailed analysis of the SCAQS ambient hydrocarbon and carbonyl data was undertaken to develop an improved understanding of nonmethane organic compounds (NMOC) in the South Coast Air Basin (SoCAB). The specific objectives of the data analysis were: (1) to characterize the spatial and temporal patterns of total NMOC concentrations and NMOC/NO_x ratios; (2) to characterize the spatial and temporal patterns of individual organic compounds; (3) to assess the consistency between ambient and emissions inventory NMOC; and (4) to assess the extent of NMOC oxidation and carbonyl formation occurring in the atmosphere. The major features of the data and results of the data analysis are summarized below.

Characterization of Total NMOC and NMOC/NO_x Ratios

- The total NMOC levels in the SoCAB ranged from 171 to 2640 ppbC in the summer and from 182 to 4234 ppbC in the fall. The mean NMOC concentrations were 767 and 1595 ppbC in summer and fall, respectively. The mean NMOC concentration on summer mornings was 971 ppbC, which is slightly higher than occurs in most urban areas of the United States.

- The spatial pattern of NMOC had moderate concentrations in the western and southern parts of the basin (at Hawthorne, Long Beach, and Anaheim), high concentrations in the central basin (at Los Angeles and Burbank), and moderate concentrations in the eastern basin during the summer. On average, NMOC concentrations decreased with distance from a high concentration ridge between Los Angeles and Burbank in summer. In fall, there were similar NMOC concentrations (on average) in the western and central areas, and significantly lower concentrations in the eastern basin. The highest NMOC concentrations occurred at Burbank in the fall.

- The diurnal patterns of NMOC were highly variable, probably due to the complexity of meteorology in the basin. On average, NMOC concentrations were highest at 0700-0800 (local time) in summer and fall. In summer, the concentrations generally declined over the course of the day, while in the fall, concentrations declined between 0700 and 1200 and then increased between 1200 and 1600.

- The day-to-day variability of NMOC concentrations during SCAQS episodes was modest. The basinwide mean NMOC concentrations were between 576 and 795 ppbC on eight of the eleven summer days. If data from the one relatively clean summer day (June 19) are ignored, the basinwide daily mean NMOC explained 50 percent of the variance in basinwide daily ozone maxima.

- The average NMOC levels within the SoCAB were more than eight times higher than the concentrations on San Nicolas Island, which is located 120 km offshore. And only about half of the San Nicolas Island samples had concentrations low enough to be classified as "clean air" samples.

- Total NMOC was highly correlated with CO, acetylene, and NO_x which are emitted primarily by motor vehicles in the SoCAB. Afternoon total NMOC correlated well with NO_2+ozone, but not with PAN, concurrent ozone, or basinwide daily ozone maxima. NMOC levels were not highly correlated with temperature.

- The majority of NMOC/NO_x ratios at 0700-0800 were between 7 and 11 in the summer and 5 to 9 in the fall at the SCAQS monitoring sites. The mean 0700-0800 NMOC/NO_x ratios were 8.9 and 6.9 in summer and fall, respectively.

- The spatial variation in morning NMOC/NO_x ratios was small in the summer. For example, the mean morning NMOC/NO_x ratios were between 8 and 9.6 at all of the SCAQS stations in summer. Greater variance in morning NMOC/NO_x ratios were observed in the fall.

- Mid-day and afternoon NMOC/NO_x ratios were generally higher (11 to 15) than morning ratios and showed more spatial variation. However, Long Beach and Hawthorne had lower NMOC/NO_x ratios at 1600 than at any other time of the day in summer.

Characterization of NMOC Composition

- The composition of NMOC in the SoCAB was similar to many other urban areas and similar to light duty motor vehicle exhaust. On average, about 45 percent of the NMOC were paraffins, while 9, 18, and 13 percent were olefins, aromatic hydrocarbons, and carbonyl compounds, respectively. The other 15% of NMOC carbon were unidentified species. The principal seasonal differences in NMOC composition were a higher proportion of carbonyl compounds in summer and slightly higher proportions of aromatic hydrocarbons and olefins in the fall.

- The spatial, temporal, and day-to-day variations in the relative composition of NMOC were generally small. In fact, with the exception of a large diurnal variation in the carbonyl content, the NMOC composition was amazingly consistent.

- Over 110 individual organic compounds were identified in the SCAQS VOC samples. The 25 most abundant species accounted for more than 62 percent of the NMOC carbon. The 25 most abundant compounds on a carbon basis in summer were (in order of abundance): propane, isopentane, toluene, n-butane, ethane, acetone, m&p-xylene, n-pentane, ethene, isobutane, acetylene, acetaldehyde, benzene, 2-methylpentane, 3-methylpentane, formaldehyde, hexane, methylcyclopentane, o-xylene, propene, 124-trimethylbenzene, 3-methylhexane, ethylbenzene, methylcyclohexane, and heptane.

- In comparison to previous hydrocarbon measurements in the SoCAB, the two most notable differences were higher fractions of propane and lower fractions of n-butane in the SCAQS data. In comparison to the 1984-86 data from EPA's 41 non-California cities study, the SCAQS NMOC had higher fraction of acetylene, propane, toluene, and xylene. The overall reactivity of NMOC in the SoCAB was slightly lower than the 41-city average.

- SCAQS was one of the first air quality field study where higher carbonyl compounds were measured in addition to formaldehyde and acetaldehyde. The formaldehyde and acetaldehyde data were generally consistent with previous measurements, except the ratio of acetaldehyde to formaldehyde was slightly higher. The measurements showed surprisingly high amounts of C3+ carbonyl compounds. Acetone was the most abundant carbonyl compound on a carbon basis and C4+ carbonyl species accounted for more than 45% of total carbonyl compounds on average.

- The xylene to benzene ratio, which is a good indicator of the age of a NMOC mixture and, to a certain extent, the contribution of motor vehicles, showed remarkable temporal and spatial consistency in the SCAQS data set. The relative amounts of xylenes and benzene were comparable throughout the measurement network and highly correlated with NMOC and NO_x. The mean ratios in the morning were between 2.2 and 2.5 in summer (except at Azusa) and between 2.0 and 2.3 in the fall. The consistency of the xylene to benzene ratios suggests a fairly continuous and wide-spread contribution from motor vehicle emissions.

- NMOC composition at Hawthorne was distinct from other sites because of high propane levels. The NMOC composition at Long Beach and Los Angeles in the mid-day and afternoon was also somewhat different from the rest of the stations. The NMOC compositions on San Nicolas Island and aloft were more aged and contained a greater fraction of carbonyl species than the onshore samples.

- The relative reactivity of NMOC, based on Carter's Maximum Incremental Reactivity (MIR) factors, was higher at Los Angeles and Burbank, and lower at Hawthorne and Long Beach in the summer. A ranking of species' contributions to reactivity identified mostly the same species as identified by ranking their contributions to NMOC carbon.

- Isoprene was the only biogenic hydrocarbon found in the SCAQS samples. On average, isoprene contributed 0.2 percent of NMOC carbon and 0.7 percent of the NMOC reactivity. Larger isoprene contributions were found at Claremont and Anaheim. Nevertheless, the ambient isoprene concentrations were probably too low to significantly affect ozone in the SoCAB. Because isoprene reacts rapidly, the ambient observations probably underestimate its relative contribution. In addition, the measurement system was not set up to detect the known intermediate products of reaction.

Comparison of Emissions Inventory and Ambient Data

- A comparison of emissions inventory and ambient data was carried out using the average emissions within 15 x 15 km grids encompassing each SCAQS

monitor for the 0600-0800 period and the 0700-0800 ambient observations. The day-specific emissions inventories for August 28 and December 10, 1987 were used to characterize summer and fall emissions. A key finding was that the average NMOC/NO_x ratios in the emissions inventory were 54 and 39 percent lower than ambient NMOC/NO_x ratios in summer and fall, respectively. The largest discrepancies (more than 60 percent) occurred at Claremont, Azusa, Burbank, and Riverside in the summer. The smallest discrepancies occurred at Hawthorne.

- Average CO/NO_x ratios in the emissions inventory were 43 and 38 percent lower than ambient CO/NO_x ratios in summer and fall, respectively. The largest discrepancies occurred at Riverside in the summer and Long Beach in the fall. The smallest discrepancies occurred at Azusa in the summer and Los Angeles in the fall.

- The ratio analysis indicates there is a significant problem in the inventories: either NO_x emissions are substantially overestimated or NMOC and CO emissions are seriously underestimated (or some combination of the two). Because CO and NO_x are emitted primarily by motor vehicles, the CO/NO_x ratio discrepancies indicate the problem is with the motor vehicle exhaust emissions. Since the discrepancies in NMOC/NO_x and CO/NO_x ratios are comparable in magnitude, the NMOC/NO_x ratio discrepancies are probably due to inaccuracies in the motor vehicle exhaust emissions estimates. However, biases in emission estimates for other types of sources may contribute to the discrepancies.

- The discrepancies between the ambient and emissions inventory ratios are similar to those found in the SCAQS tunnel study. The CO and VOC emission rates from EMFAC7E are 56 and 52 percent lower than the measured emission rates in the Van Nuys Tunnel, whereas the NO_x emissions estimates and measurements are in close agreement.

- The relative composition of the NMOC inventory is biased towards overestimation of olefins and underestimation of aromatic hydrocarbons and higher carbonyl compounds. The average reactivities of the emissions inventory composition profiles are about 10 and 30 percent higher than the ambient composition profiles in summer and fall, respectively. The biases in the inventory composition are too small to compensate for the probable deficiencies in mass emissions of NMOC.

Data Interpretations

- The similarity of NMOC composition and NMOC/NO_x ratios throughout the day, and especially in the fall, suggests fresh NMOC emissions are continuously injected into the atmosphere in the SoCAB. While there is evidence of preferential photo-oxidation of the more reactive hydrocarbon species and formation of large amounts of carbonyl compounds, especially on summer mornings, these effects are tempered by the continuous injection of fresh emissions. This finding is not meant to imply that emission rates are constant over the course of the day, because that obviously is not the case; rather, only that the relative composition of many atmospheric constituents between 0700 and 1700 are similar to fresh emissions.

- The NMOC levels have significant day-to-day and seasonal variations, which are undoubtably controlled by meteorology. In addition, the NMOC levels have significant spatial variation within the basin due to the non-uniformity of emission rates and the effects of transport. However, the day-to-day and spatial variations in NMOC composition are relatively small in comparison. This suggests that emissions from one or more common types of sources occur throughout the basin. Since the composition profile strongly resembles that from motor vehicles and since the data show consistent xylene to benzene ratios and high correlation between CO, acetylene, NMOC, and NO_x, the dominant source is probably motor vehicles.

- The combination of the findings from the SCAQS Tunnel Study and the discrepancies between ambient NMOC/NO_x and CO/NO_x ratios and ratios in emissions inventories strongly suggest current inventories underestimate NMOC and CO emissions from motor vehicles. Problems with the emissions from other types of sources may also contribute to the discrepancies, however, there were too few tracer species for organic emissions from specific source types to identify those sources with these data.

- The ambient NMOC/NO_x ratios on summer mornings were mostly between 7 and 11, which is a range where both NMOC and NO_x emission controls are likely to be effective in reducing ozone concentrations.

- Although measurements were not obtained in outlying areas where biogenic emissions may be high, the contribution of isoprene to NMOC in the urbanized portion of the basin is small compared to anthropogenic source contributions, and it is highly unlikely that biogenic hydrocarbons substantially affect ozone formation in the urban portion of the SoCAB.

Recommendations (in order of priority)

- An investigation and correction of the biases in the NMOC, CO, and perhaps NO_x emissions inventories is needed. A series of bottom-up evaluations of the major components of the inventory, with motor vehicles coming first, are needed. These should be followed by top-down evaluations and in-use emissions surveys.

- The NMOC source composition libraries should be updated. Corrections are needed to address the significant overestimation of olefins and underestimation of higher carbonyl compounds, as well as the problem with the C9+ aromatic hydrocarbons.

- The "Level 2 validated" NMOC data base should be distributed to photochemical modeling groups for their use in performance evaluation studies. Comparison of model predictions with the data may help diagnose problems in the emissions inventory.

- Given the importance of NMOC in ozone formation and the resources devoted to the control of NMOC emissions, there is a need for long-term NMOC ambient data to assess trends and assess the effectiveness of NMOC controls. This need could be satisfied with frequent high quality measurements of total NMOC and infrequent analyses of NMOC composition.

1. INTRODUCTION

1.1 BACKGROUND

Volatile organic compounds (VOCs) are primarily of concern in the atmosphere because of their role in ozone formation and their potential effects on human health. Regulatory agencies have on-going VOC emission control programs to address these concerns. There is significant interest in ambient VOCs in the South Coast Air Basin (SoCAB) of California because of the high ozone levels and high VOC emission densities. While ambient levels of total hydrocarbons (THC) and total nonmethane hydrocarbons (NMHC) are routinely measured in the greater Los Angeles area, there is only limited information regarding the individual concentrations of hydrocarbons, aldehydes, and other organic compounds in the air. An understanding of the individual concentrations and the composition of the VOC is needed to evaluate the organic speciation of emission inventories, to advance atmospheric modeling of ozone and secondary aerosols, and to accurately characterize the health risks associated with ambient VOCs.

The ambient concentrations of individual hydrocarbons in the Los Angeles area were measured by a number of investigators in the 1960's and 1970's (Neligan, 1962; Gordon et al., 1968; Stephens and Burleson, 1967, 1969; Altschuller et al., 1971; Kopczynski et al., 1972; Calvert, 1976; ARB, 1976). Grosjean and Fung (1984) measured both the carbonyl compounds and hydrocarbon concentrations in Los Angeles in 1981. These data represent a fairly small and out-of-date data base. Speciated hydrocarbon and carbonyl data were also collected during the 1986 Carbonaceous Species Methods Comparison Study (Rasmussen, 1986; Lawson and Hering, 1990; Fung and Wright, 1990; Lawson et al. 1990), a field study conducted to evaluate sampling methods to be used in the 1987 Southern California Air Quality Study (SCAQS). The scope of most of these measurement programs was limited to sampling at one location and/or one time of day, and some of the measurements were made with now out-dated analytical methods. Furthermore, because there has been rapid population growth and a major VOC emission control program, the historical measurements probably do not characterize current conditions in the SoCAB. Both the VOC levels and composition are likely to change with time in the SoCAB.

The SCAQS provided an opportunity to obtain an up-to-date data base for ambient VOCs in the context of a large air quality study (Blumenthal et al., 1987; Hering and Blumenthal, 1989; Lawson, 1990). The scope of the SCAQS VOC monitoring program was more comprehensive than any previous program in the SoCAB or any other single urban area. Concurrent measurements of individual C1-C12 hydrocarbon and C1-C7 carbonyl concentrations were made at nine stations, at three or six times per day, and in two different seasons. These data provide a basis for developing an improved understanding of the nature of VOCs and atmospheric processes effecting VOCs in the area. This report describes the total nonmethane organic compound (NMOC) and individual hydrocarbon and carbonyl compound concentrations observed in the 1987 SCAQS.

1.2 OBJECTIVES

A detailed analysis of the SCAQS hydrocarbon and carbonyl compound data was undertaken to develop an improved understanding of VOCs in the SoCAB. The specific objectives of the study were:

- To characterize the spatial and temporal patterns of NMOC concentrations in the SoCAB;
- To characterize the spatial and temporal patterns of NMOC composition in the SoCAB;
- To assess the consistency between ambient and emissions inventory NMOC; and
- To assess the extent of VOC oxidation and carbonyl compound formation occurring in the atmosphere.

These objectives were designed to improve the conceptual model of VOC emissions and atmospheric processes in the SoCAB. Important products of the study are a "Level 2 validated" VOC data base for use in evaluating the performance of photochemical models and suggestions for improving VOC emissions inventories. These specific objectives and products were designed to support the overall goal of the SCAQS which was to develop a comprehensive air quality and meteorological data base that could be used to test, evaluate, and improve elements of the air quality simulation models for ozone, PM_{10}, fine particles, toxic air contaminants, and acidic species.

1.3 ORGANIZATION OF THE REPORT

This report is organized in six sections. Section 2 describes the database and discusses the quality control procedures used to prepare the "Level 2 validated" database. Section 3 provides a detailed discussion of the surface VOC concentrations and composition, the spatial and diurnal patterns and day-to-day variations of total NMOC, NMOC groups, and individual abundant species. NMOC to NO_x ratios, toxic organic species, carbonyl compounds and biogenic species concentrations, and relationships between species are also addressed. The VOC data collected aloft are discussed in Section 4. Concentrations of total NMOC and abundant species, temporal and spatial variability, and carbonyl compound composition aloft are described, along with a comparison of surface and aircraft data. Section 5 compares ambient and emissions inventory NMOC/NO_x and CO/NO_x ratios, and composition of major VOC groups and individual species. Finally, Section 6 summarizes the results and provides the conclusions and recommendations of the study.

A glossary of the terminology used in this report is presented in Table 1-1. It is important to note that the terms VOC and NMOC are used interchangeably in this report to describe the sum of nonmethane hydrocarbon and carbonyl species. However, the term NMHC is used to refer to the nonmethane hydrocarbons only (i.e., excluding carbonyl compounds).

Table 1-1. Abbreviations and Terminology

Abbreviation/Term	Definition
VOC	Volatile organic compounds
NMHC	Nonmethane hydrocarbons
NMOC	Nonmethane organic compounds (NMHC + Carbonyl Compounds)
Olefins	C2-C9 Alkenes and alkynes
Paraffins	C2-C10 Alkanes
Aromatic hydrocarbons	C6-C10 Aromatic hydrocarbons
Carbonyl compounds	C1-C7 aldehydes and ketones
MPAR23	C2-C3 paraffins
MPAR45	C4-C5 paraffins
MPAR6	C6-C10 paraffins
MTOLEF	Terminal C2-C9 olefins
MIOLEF	Internal C2-C8 olefins
MONAROM	Mono-substituted aromatic hydrocarbons
DIAROM	Di- and tri-substituted aromatic hydrocarbons
DNPH	2,4-dinitrophenylhydrazine
GC-FID	Gas chromatography - flame ionization detection
GC-MS	Gas chromatography - mass spectrometry
ANAH	Anaheim
BURK,BUR	Burbank
AZUS	Azusa
CLAR	Claremont
CELA	Downtown Los Angeles
HAWT,HHR	Hawthorne
LBCC	Long Beach City College
RIVR	Riverside - Rubidoux
SNI	San Nicolas Island
AMTRA	Airway Intersection 8 km W of El Monte Airport
CAB	Cable Airport
DOYLE, TANDY	Airway Intersections about 20 km W of Palos Verdes
EMT	El Monte
FUL	Fullerton
GYB	Goodyear Blimp Site in Carson
LGB	Long Beach
ONT	Ontario
PADDR	Airway Intersection 15 km S of Long Beach
POMA	Pomona
RAL	Riverside Airport
PAN	Peroxyacetylnitrate
NO	Nitric oxide
NO_x	Oxides of nitrogen
CO	Carbon monoxide

2. DATA AVAILABILITY AND QUALITY CONTROL

2.1 DATA COLLECTION AND ANALYSES

2.1.1 Surface Samples

On intensive sampling days in SCAQS, surface VOC samples were collected at Anaheim, Azusa, Burbank, downtown Los Angeles, Claremont, Hawthorne, Long Beach, Riverside, and San Nicolas Island in the summer. The monitoring site locations are shown in Figure 2-1. One-hour samples were collected beginning at 0700, 1200, and 1600 Pacific Daylight Time (PDT) at all sites. Additional samples were collected at 0500, 0900, and 1400 PDT at Claremont and Long Beach. In the fall, samples were collected at Anaheim, Burbank, downtown Los Angeles, Hawthorne, Long Beach and Riverside. One-hour samples were collected at 0700, 1200, and 1600 Pacific Standard Time (PST). Additional samples were collected at 0500, 0900, and 1400 PST at Los Angeles and Long Beach. Samples were collected on eleven days during the summer (June 19, 24-25, July 13-15, August 27-29 and September 2-3, 1987) and six days during the fall (November 11-13 and December 3, 10-11, 1987).

The hydrocarbon samples were collected in initially evacuated six-liter stainless steel canisters. The C2-C12 hydrocarbon analyses were performed by Len Stockburger at the U.S. EPA's Atmospheric Sciences Research Laboratory using gas chromatography - flame ionization detection (GC-FID) (Stockburger et al., 1989). Most of sample canisters were also analyzed for carbon monoxide (CO), methane and the C2-C4 hydrocarbons by Rei Rasmussen of the Oregon Graduate Institute (OGI). A subset of the samples were reanalyzed by William Lonneman of the EPA by GC-FID and by Stockburger and Rasmussen using gas chromatography - mass spectrometry (GC-MS).

Carbonyl compounds were collected using cartridges impregnated with 2,4-dinitrophenylhydrazine (DNPH) and phosphoric acid. Aldehydes and ketones react with the DNPH to form hydrazones, which are measured by high performance liquid chromatography. Air was sampled through the cartridges at one liter per minute for one hour intervals. Analyses were performed by ENSR (Fung, 1989). Additional details of sampling and analysis are given by Hering and Blumenthal (1989) and Lawson (1990) and references therein.

Over one hundred hydrocarbon and ten carbonyl species were identified in the analyses. On average, 85% of the detected carbon was identified either as an individual species or by carbon number and compound class (e.g., C10 alkane). The remainder consisted of four percent unidentified C2-C9 species and eleven percent unidentified ≥C10 species on average. It is important to recognize that the analyses to which the SCAQS samples were subjected are not capable of detecting all NMOCs. The methods are not quantitative for alcohols, acetates, acrolein, amines, ethers, esters, glycols, phenols, halocarbons, di-carbonyl species, and >C7 carbonyl compounds. In addition, the accuracy of concentrations of selected species such as the ≥C4 carbonyl compounds, styrene, and 1,3-butadiene are questionable. Nevertheless, the analyses captured the bulk of the individual hydrocarbons and carbonyl species that contribute to ozone formation in the basin.

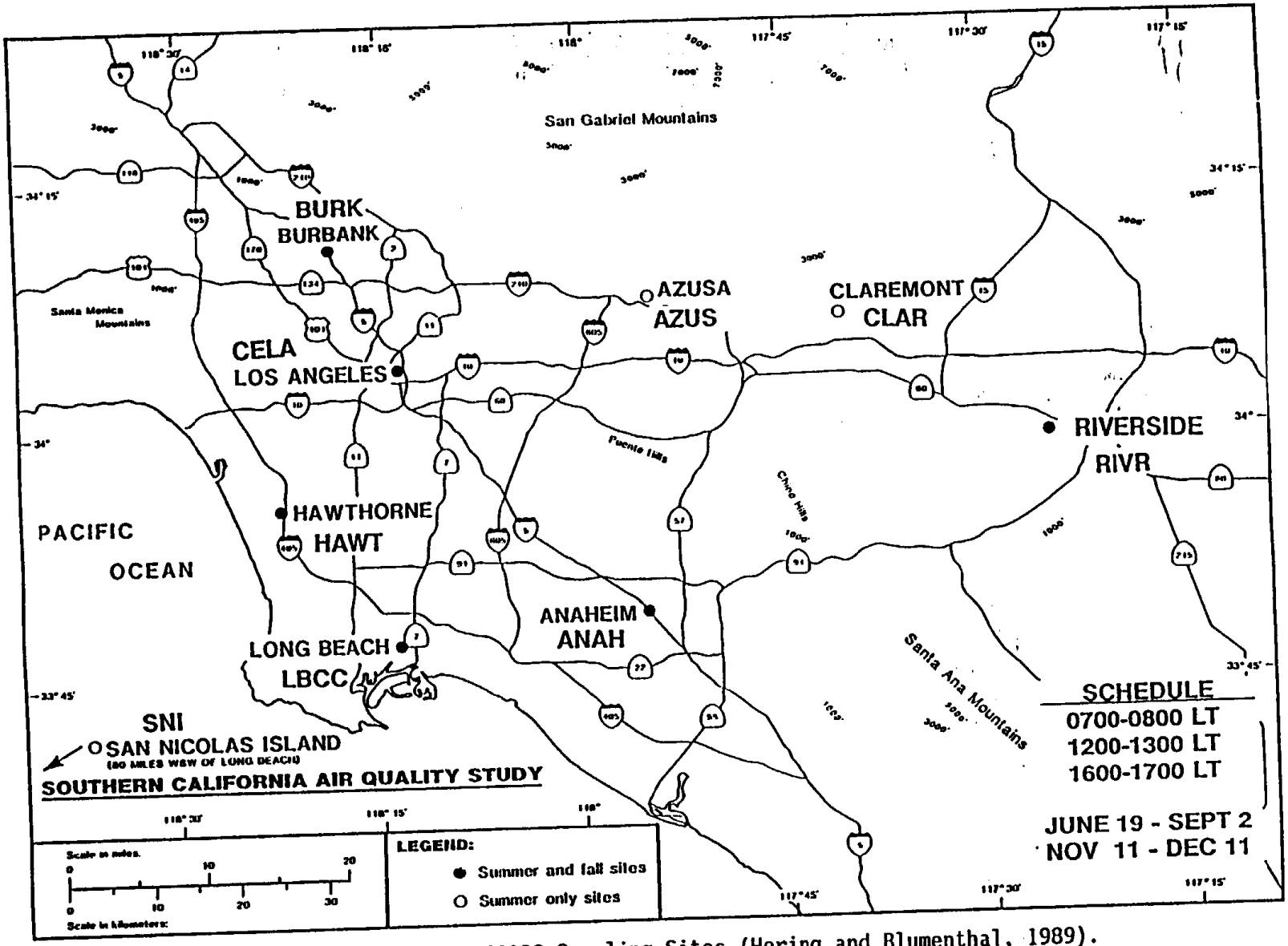

Figure 2-1. Primary SCAQS Sampling Sites (Hering and Blumenthal, 1989).

2.1.2 Aircraft Samples

The aircraft VOC samples were collected during vertical spirals and horizontal orbits flown during the mornings and afternoons of the SCAQS monitoring periods. Samples were collected both onshore and offshore at the sites shown in Figure 2-2. Two aircraft were used to collect grab samples of VOCs: one aircraft was operated by Sonoma Technology Inc. (STI) (Anderson, et al., 1989) and the other by the University of Washington (UW) (Hegg and Hobbs, 1988). The UW aircraft was operated only during the June and July summer sampling period and was used primarily to collect integrated samples at fixed locations (orbits). The STI aircraft was used during all summer and fall sampling periods. The STI aircraft collected VOC samples during both spirals and orbits.

The hydrocarbon samples were collected in 3.2-liter stainless steel canisters, similar to the canisters used at the surface. However, unlike the surface samples which filled slowly over an hour, the aircraft samples were grab samples that were filled within one to two minutes. The two-minute fill time corresponds to approximate 20% of a spiral or 7% of an orbit. The aircraft canisters were analyzed by Stockburger and Rasmussen using the same procedures as used for the surface canisters.

Carbonyl compounds were collected during orbits using DNPH cartridges. Air was sampled through the cartridges at one liter per minute for 20 to 35 minutes. The cartridges were analyzed by ENSR. Additional details of sampling and analysis are given by Anderson et al. (1989), and Hering and Blumenthal (1989).

As with the surface samples, about one hundred hydrocarbon and ten carbonyl species were identified. On average, about 85% of the carbon was identified. The remainder consisted of about 5% unidentified C2-C9 species and about 10% unidentified C10+ species.

2.2 DATA BASE PREPARATION

2.2.1 Surface Data

The ARB provided the initially archived SCAQS surface hydrocarbon data. These data included 584 samples of speciated C2-C12 hydrocarbon concentrations from Stockburger's analyses, the corresponding carbonyl concentrations from Fung, and the corresponding CO, methane, C2-C4 hydrocarbon concentrations from Rasmussen's analyses for most of the samples. These data were merged into a common data base and converted to parts-per-billion-carbon (ppbC) units. The species for which multiple laboratories supplied data were handled as follows: Rasmussen's C2-C3 hydrocarbon data were used instead of Stockburger's C2-C3 data, Stockburger's C4 hydrocarbons were used instead of Rasmussen's C4s, and Fung's acetone was used instead of Stockburger's acetone data. Rasmussen's C2-C3 data were selected because his analytical system provided better separation of the C2-C3 peaks. Stockburger's C2-C3 data were used only for the cases where the OGI C2-C3 data were missing and then, because of the uncertainty in Stockburger's individual C2 peaks, only the total C2s were included in the database. The samples with missing individual

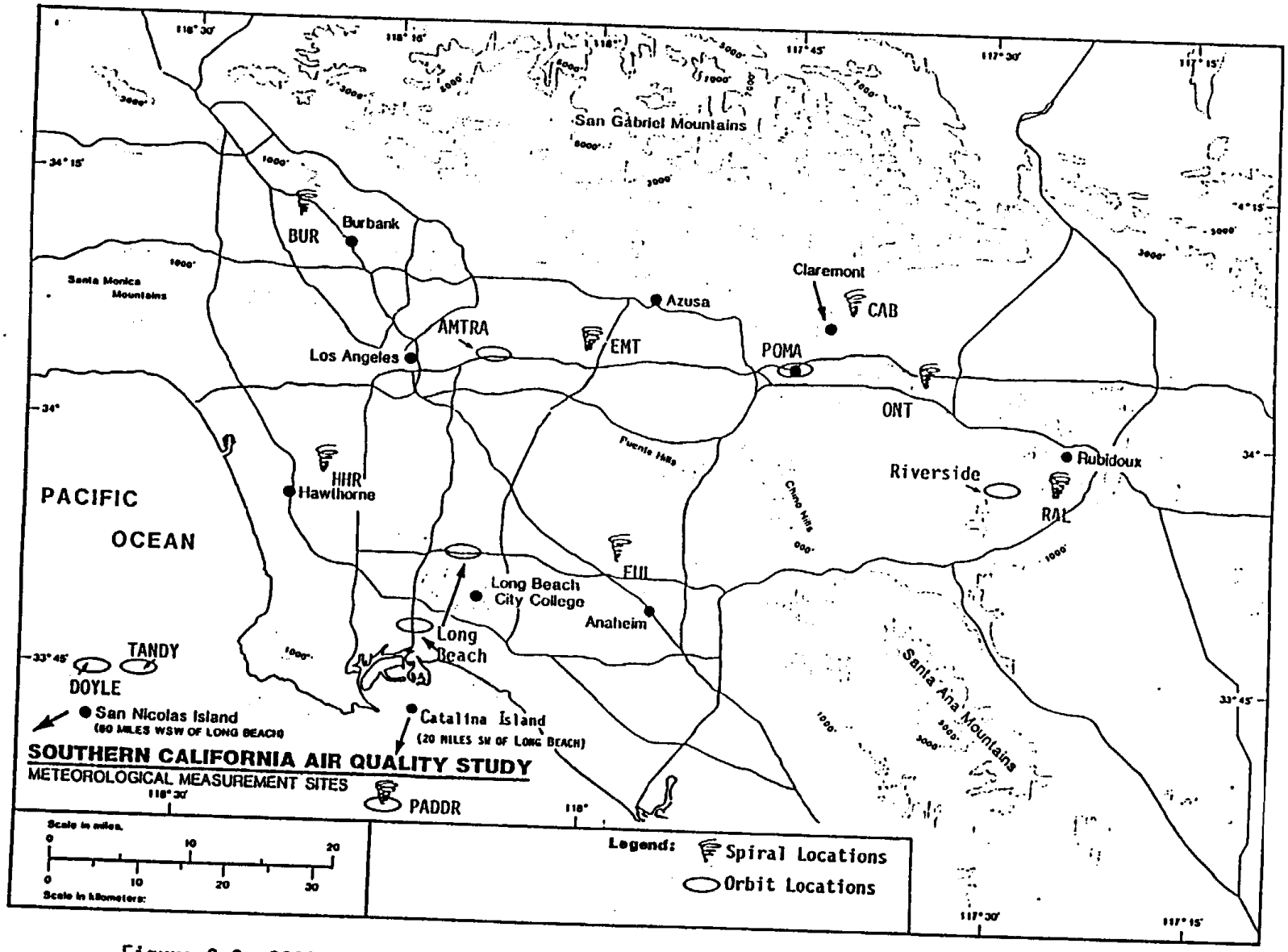

Figure 2-2. SCAQS Aircraft Spiral and Orbit Locations (Hering and Blumenthal, 1989).

C2s were identified with the special validation code (VC2C3EPA=1) in the data base. The C4 hydrocarbon concentrations measured by Stockburger and Rasmussen agreed well and Stockburger's data were selected. The two sets of acetone data were very different and Fung's data were selected because the DNPH method was considered more reliable than GC-FID for acetone at ambient levels.

As part of the SCAQS quality assurance program, the ARB staff performed an inter-laboratory comparison of speciated hydrocarbon data collected during the SCAQS (Collins and Fujita, 1990). Lonneman and Rasmussen analyzed 19 canisters that had been analyzed by Stockburger. ARB's intercomparison of the Lonneman and Stockburger data showed significant differences in the extent of species identification. Lonneman's analytical procedures were able to identify significantly more species than Rasmussen's procedures and slightly more than Stockburgers's procedures.

Based on the intercomparison, ARB developed a method to extend Stockburger's identification. Frequently occurring unnamed peaks in Stockburger's chromatographs were assigned to specific compounds based on their relative retention times (RRT). First, the relative retention times of 16 "marker" compounds that were almost always present in Lonneman's and Stockburger's analyses were calculated. Second, the mean and standard deviation of the relative retention times (between the marker compounds) of Lonneman's 85 named species were calculated. Third, the relative retention times of the named and unnamed peaks in Stockburger's analyses were determined and compared to Lonneman's. Table 2-1 lists the peak names and Lonneman's relative retention times. STI used the relative retention times calculated by ARB to extend the species identification in the initially archived SCAQS data. Unidentified peaks were assigned to a compound name if the RRT was within two standard deviations of the mean RRT. This procedure reduced the unidentified C2-C9 NMOC from 7% to 4% on the average. In addition, peaks that were not identified by this procedure were assigned to one of two classes of unidentified species based on their retention time relative to decane. Species eluting before decane were classified as unidentified C2-C9 species and species eluting after decane were classified as unidentified C10+ species.

Additional quality assurance was performed on the data. Aero-Vironment's (AV) field notes and the laboratories' analytical notes were reviewed to identify problematic samples and analyses. Samples that were improperly collected, contaminated, analytically incomplete, or contained highly unusual amounts of certain compounds were flagged. Validation codes were added to the data base based on this review. The list of the invalid samples and the accompanying validation codes is shown in Appendix A. Note that because of a sampler timer error, all of the carbonyl compound samples collected at Long Beach during the fall were invalidated.

The initially archived SCAQS data base included nearly 200 replicate hydrocarbon samples (from Stockburger). A protocol was developed to select the best estimate of concentrations for cases with duplicate samples.

- In cases where a sample was analyzed using two FID detectors (A and B), the concentrations obtained using detector B were selected, based on Stockburger's recommendation.

Table 2-1. VOC Species Identified By Lonneman and Stockburger and Their Retention Times Relative to 16 Marker Compounds

Lonneman Species	Stockburger Species	Lonneman's Relative Retention Time	
		Mean	Standard Deviation
ISOBUTANE	2M-PROPANE	1.00	Marker[a]
2-METHYLPROPYLENE,BUTENE	C4-ALKENE	1.76	0.013
1,3-BUTADIENE	1,3-BUTADIENE	1.86	0.007
n-BUTANE	n-BUTANE	2.00	Marker
t-2-BUTENE	t-BUTENE-2	2.16	0.001
c-2-BUTENE	c-BUTENE-2	2.35	0.001
3-METHYL-1-BUTENE	3METHYLBUTENE-1	2.77	0.004
ISOPENTANE	2M-BUTANE	3.00	Marker
1-PENTENE	PENTENE-1	3.59	0.002
2-METHYL-1-BUTENE	2METHYLBUTENE-1	3.86	0.005
n-PENTANE	n-PENTANE	4.00	Marker
ISOPRENE	ISOPRENE	4.07	0.004
t-2-PENTENE	t-PENTENE-2	4.13	0.003
C5 OLEFIN (c-2-pentene)	c-PENTENE-2	4.24	0.002
C5 OLEFIN (CH2Cl2)	CH2CL2	4.28	0.009
C6 PARAFFIN (Freon 113)	FREON 113	4.45	0.003
2,2-DIMETHYLBUTANE	UNKNOWN (P18D1)[b]	4.51	0.002
C6 OLEFIN	UNKNOWN	4.66	0.017
C6 OLEFIN	UNKNOWN	4.74	0.004
4-METHYL-1-PENTENE	UNKNOWN	4.83	0.008
CYCLOPENTANE	c-PENTANE	4.89	0.003
2,3-DIMETHYLBUTANE	2,3-DMBUTANE	4.93	0.001
c-4-METHYL-2-PENTENE	UNKNOWN	4.96	0.003
2-METHYLPENTANE	2M-PENTANE	5.00	Marker
t-4-METHYL-2-PENTENE	UNKNOWN	5.07	0.001
3-METHYLPENTANE	3M-PENTANE	5.45	0.004
n-HEXANE,2-ETHYL-1-BUTEN	n-HEXANE	6.00	Marker
C7 OLEFIN	UNKNOWN	6.10	0.001
2-METHYL-2-PENTENE	UNKNOWN	6.15	0.005
C7 OLEFIN	UNKNOWN	6.20	0.002
c&t-3-METHYL-2-PENTENE	UNKNOWN	6.40	0.003
METHYLCYCLOPENTANE	M-c-PENTANE	6.52	0.004
2,4-DIMETHYLPENTANE	2,4DM-PENTANE	6.60	0.006
2,2,3-TM-1-BUTENE 111tcl	111TCL-ETHANE	6.70	0.002
C7 OLEFIN	UNKNOWN	6.77	0.008
BENZENE	BENZENE	7.00	Marker
3,3-DIMETHYLPENTANE	3,3DM-PENTANE	7.19	0.013
CYCLOHEXANE	c-HEXANE	7.35	0.004
2-METHYLHEXANE	2M-HEXANE	7.67	0.006
2,3-DIMETHYLPENTANE	2,3DM-PENTANE	7.74	0.003
CYCLOHEXENE	UNKNOWN	7.86	0.004
3-METHYLHEXANE	3M-HEXANE	8.00	Marker
C7 PARAFFIN	P35D1	8.30	0.007
C7 PARAFFIN	P36D1	8.42	0.008
2,2,4-TRIMETHYLPENTANE	2,2,4TM-PENTANE	8.57	0.003
n-HEPTANE	n-HEPTANE	9.00	Marker
C8 OLEFIN	C8 OLEFIN	9.51	0.011
METHYLCYCLOHEXANE	M-c-HEXANE	10.00	Marker
C8 PARAFFIN	UNKNOWN	10.07	0.005
2,5-DIMETHYLHEXANE	UNKNOWN	10.27	0.002
25DIMEHEXANE,3Mcyclohexe	UNKNOWN	10.33	0.014
2,4-DIMETHYLHEXANE	UNKNOWN	10.38	0.020
C8 PARAFFIN	UNKNOWN	10.77	0.012
2,3,4-TRIMETHYLPENTANE	2,3,4TM-PENTANE	10.84	0.014
TOLUENE	TOLUENE	11.00	Marker

Table 2-1. VOC Species Identified By Lonneman and Stockburger and Their Retention Times Relative to 16 Marker Compounds

Lonneman Species	Stockburger Species	Lonneman's Relative Retention Time	
		Mean	Standard Deviation
C8 PARAFFIN	P46D1	11.11	0.006
2-METHYLHEPTANE	P47D1	11.22	0.008
C8 PARAFFIN	UNKNOWN	11.26	0.006
C8 PARAFFIN	UNKNOWN	11.33	0.007
3-METHYLHEPTANE	P48D1	11.41	0.005
2,2,5-TRIMETHYLHEXANE	P50D1	11.67	0.006
1-OCTENE	UNKNOWN	11.76	0.000
CYCLOHEPTANE	P51D1	11.83	0.012
C8 PARAFFIN	UNKNOWN	11.92	0.006
n-OCTANE	n-OCTANE	12.00	Marker
C9 PARAFFIN	C8 OLEFIN	12.07	0.009
C9 PARAFFIN	C2CL4	12.12	0.002
c-2-OCTENE	UNKNOWN	12.23	0.003
C9 PARAFFIN	UNKNOWN	12.30	0.006
C9 OLEFIN	UNKNOWN	12.34	0.005
2,4-DIMETHYLHEPTANE	UNKNOWN	12.40	0.005
C9 PARAFFIN	UNKNOWN	12.50	0.008
ETHYLCYCLOHEXANE	UNKNOWN	12.59	0.000
2,5-DIMETHYLHEPTANE	UNKNOWN	12.62	0.003
C9 PARAFFIN	UNKNOWN	12.67	0.002
C9 PARAFFIN	P55D1	12.77	0.005
ETHYLBENZENE	ETHYL BENZENE	12.87	0.005
2,3-DIMETHYLHEPTANE	UNKNOWN	12.92	0.002
m&p-XYLENE	m+p XYLENE	13.00	Marker
4-METHYLOCTANE	4METHYLOCTANE	13.10	0.016
3-METHYLOCTANE	3METHYL OCTANE	13.30	0.009
C9 OLEFIN	STYRENE	13.49	0.014
o-XYLENE	o-XYLENE	13.63	0.020
1-NONENE	UNKNOWN	13.71	0.002
C9 PARAFFIN	UNKNOWN	13.79	0.006
n-NONANE	n-NONANE	14.00	Marker
C10 PARAFFIN	P65D1	14.53	0.009
C10 PARAFFIN	UNKNOWN	14.63	0.002
a-PINENE	UNKNOWN	14.84	0.003
C10 PARAFFIN	P67D1	14.93	0.002
n-PROPYLBENZENE	n-PROPYLBENZENE	15.00	Marker
m-ETHYLTOLUENE	m-ETHYL TOLUENE	15.13	0.001
p-ETHYLTOLUENE	p-ETHYL TOLUENE	15.18	0.003
C9 AROMATIC	C9 AROMATIC	15.28	0.005
C9 AROMATIC	C9AROMATIC	15.28	0.005
C10 PARAFFIN	P73D1	15.36	0.010
o-ETHYLTOLUENE	o-ETHYL TOLUENE	15.51	0.007
C10 PARAFFIN	UNKNOWN	15.62	0.002
1,2,4-TRIMETHYLBENZENE	1,2,4TM BENZENE	15.80	0.011
C10 PARAFFIN	UNKNOWN	15.88	0.000
n-DECANE	n-DECANE	16.00	Marker

[a] Marker compounds were chosen based on abundance and frequency of occurrence in the samples.

[b] Some peaks were found in most samples, but were not given a species name. Instead, these peaks were identified by peak number, P##D1.

- There were numerous cases where multiple analyses were performed using a single FID detector. When the unidentified portions of the samples were within 20% of each other and other VOC species and groups of species were consistent, the best estimate concentrations were the average concentrations determined from all of the samples. When the unidentified portions varied by more than 20%, the sample with the lowest concentration of unidentified VOC was selected.

- A sample storage study was performed where multiple analyses of the same canister were performed over several months. Stockburger found that the styrene decayed much faster than other compounds in the canisters and that the unidentified portion of NMHC increased with storage time. The best estimate concentrations were determined from the sample with the lowest unidentified and highest styrene concentrations.

Lastly, a series of lumped VOC groups were defined in the data base. The groups included: NMHC, NMOC, paraffins, olefins, aromatic hydrocarbons, carbonyl compounds and related subgroups such as C2-C3, C4-C5, and C6+ paraffins, terminal and internal olefins, and mono- and di/tri-substituted aromatic hydrocarbons. Finally, a separate file was prepared which contained the carbon fractions relative to NMOC of each species and VOC group.

2.2.2 Aircraft Data

The initially archived aircraft VOC data base included 89 samples. These samples were processed in the same manner as the surface data. The principal problem encountered in merging data sets was that in the fall, carbonyl samples were not collected during the same portion of the flights as the hydrocarbon samples, and the differences in collection times were significant enough that the data could not be merged. The aircraft samples were subjected to the same quality assurance analysis as the surface samples. Appendix A lists the invalid aircraft samples and the nature of the problem with the invalid data. Because of the problems with aircraft carbonyl sample collection in the fall, only samples collected during the summer are discussed in this report.

2.2.3 Supplemental Data

Other observed parameters were compiled in a supplementary data base for use in the exploratory data analysis (see Table 2-2). Hourly average ozone, NO, NO_x, PAN, and temperature for each VOC sampling interval were available at all sites and were included in the data base. Twenty-four hour average concentrations of selected toxic organic compounds were collected by ARB and OGI at Long Beach, downtown Los Angeles, Claremont, and Riverside (Hering and Blumenthal, 1989). These samples were analyzed by ARB and OGI, and were added to the data base. NMOC data collected by Lonneman for the 6-9 AM period were available for Long Beach, downtown Los Angeles, and Claremont in the summer (Lonneman et al., 1989). The latter two data sets were used to compare VOC concentrations collected with different averaging times. In addition, hourly emissions data in the nine 5x5 km grid cells surrounding each monitor were provided by ARB and added to the data base. The emissions rates were provided for each SAROAD species. The summer and fall emissions inventory data were based on conditions for August 28, 1987 and December 10, 1987, respectively.

Table 2-2. Summary of SCAQS Data

Data	Averaging/ Sampling Interval (hours)	Source/ Laboratory	Location[a]								
Surface:			ANAH	AZUS	BURK	CELA	CLAR	HAWT	LBCC	RIVR	SNI
CO, Methane	1	Rasmussen	S,F	S	S	S,F	S	S,F	S,F	S,F	S
C2-C4 VOC	1	Rasmussen	S,F	S	S	S,F	S	S,F	S,F	S,F	S
C2+ VOC	1	Stockburger	S,F	S	S	S,F	S	S,F	S,F	S,F	S
C1-C7 Carbonyls	1	ENSR	S,F	S	S	S,F	S	S,F	S[b]	S,F	S
C2+ VOC	3	Lonneman				S	S		S		
C2+ VOC[c]	24	Rasmussen				S,F	S		S,F	S	
Toxic Organics	24	Rasmussen				S,F	S		S,F	S	
Toxic Organics	24	ARB				S	S		S	S	
PAN	1	DGA	S,F		S,F	S,F	S	S,F	S,F	S	S
Temperature	1	ARB	S,F	S	S,F	S,F	S	S,F	S,F	S,F	S
Ozone, NO/NO_x	1	ARB	S,F	S	S,F	S,F	S	S,F	S,F	S,F	S
Emissions Inventory	1	ARB	S,F	S	S,F	S,F	S	S,F	S,F	S,F	S
Aircraft:			AMTRA	DOYLE	GYB	LGB	PADDR	POMA	RIVR		
CO, Methane		Rasmussen	S	S	S	S	S	S	S		
C2-C4 VOC		Rasmussen	S	S	S	S	S	S	S		
C2+ VOC		Stockburger	S	S	S	S	S	S	S		
C1-C7 Carbonyls[d]		ENSR	S	S	S	S	S	S	S		

[a] S = Summer, F = Fall
[b] Fall data were invalid.
[c] Only selected species.
[d] Fall data not collected concurrently with VOC Samples.

2.3 QUALITY CONTROL ASSESSMENT

Summary statistics were computed for all of the species and species groups in the data base. The mean, median, maximum, minimum, standard deviation, coefficient of variation, and quartiles were calculated separately for the summer and fall data sets. In addition, the data were stratified by date, time of day, and site and appropriate summary statistics were computed. The statistics were carefully examined for outliers and unusual characteristics. Several procedures were used to identify potential outliers including: examining the data for each species sorted by concentration, examining box-whisker plots of the concentrations, and examining scatter plots of important species versus NMOC, CO, benzene, and toluene. Samples containing gross outliers were identified and appropriate validation codes were assigned.

Internal consistency checks were made using ratios of individual species or species group concentrations to NMOC and CO. Samples were flagged as having unusually high fractions of selective species:

- if the carbon fraction of a particular species exceeded the median carbon fraction by more than a factor of ten;
- if the carbon fraction of a species exceeded 10% of the NMOC;
- if the total unidentified NMOC exceeded 30% on a carbon basis; or
- if the total carbonyl compounds exceeded 33% of NMOC on a carbon basis.

Unusually low-weighted fractions were generally not flagged. However, in the case of toluene, which is one of the most abundant compounds in urban air, examination of the surface carbon fraction data revealed ten cases where toluene was assigned to the wrong peak in the chromatograph. In every case with low or zero toluene carbon fraction, there was a large peak with an elution time very close to toluene (which was previously identified as an outlier). These ten large peaks were reassigned to toluene.

2.4 DATA AVAILABILITY AND CAVEATS

The processed SCAQS VOC data base was delivered to the ARB on magnetic media. The data will be included in the SCAQS data archive. The data base includes the best estimate concentrations for each site and time for which there is some valid data. It is important to recognize that data are missing, incomplete, or invalid for about 25% of the site-times (see Tables 2-3 and 2-4). In fact, there are no days with valid and complete data for all sites and sampling times. The amount of missing data is significant enough to potentially bias comparisons made between sampling times, dates, and sites. In order to minimize the problems caused by missing data, only the data collected three times per day (at 0700, 1200, and 1600) were used when all summer or all fall data were compared. Additional samples collected at 0500, 0900, 1400 at Claremont and Long Beach during the summer and at Long Beach and Los Angeles during the fall were only used in investigations of temporal patterns and variability.

Table 2-3. The Sites and Sampling Times With Missing, Incomplete, or Invalid Data in the Summer SCAQS 1987 Data Base

	0700 PDT	1200 PDT	1600 PDT
JUN 19	ANAH BURK LBCC	ANAH BURK LBCC	ANAH HAWT AZUS RIVR BURK
JUN 24	ANAH HAWT AZUS RIVR BURK	AZUS CLAR RIVR	ANAH LBCC HAWT
JUN 25	BURK HAWT CELA LBCC CLAR RIVR	ANAH HAWT AZUS RIVR CLAR	AZUS LBCC CELA RIVR HAWT
JUL 13	BURK HAWT		ANAH HAWT
JUL 14	AZUS LBCC		RIVR
JUL 15	CELA LBCC	CELA LBCC	
AUG 27	BURK HAWT RIVR	CELA LBCC RIVR	ANAH CELA
AUG 28	AZUS CELA	HAWT	
AUG 29		AZUS CELA RIVR	CELA CLAR HAWT
SEP 2		ANAH AZUS RIVR	BURK CELA RIVR
SEP 3	CLAR LBCC	BURK CELA CLAR	AZUS CELA HAWT

Table 2-4. The Sites and Sampling Times With Missing, Incomplete, or Invalid Data in the Fall SCAQS 1987 Data Base

	0700 PST	1200 PST	1600 PST
NOV 11	LBCC	LBCC	HAWT LBCC
NOV 12	LBCC	HAWT LBCC	LBCC
NOV 13	LBCC	LBCC RIVR	LBCC
DEC 3	LBCC	LBCC	LBCC
DEC 10	LBCC RIVR	BURK LBCC	HAWT LBCC
DEC 11	LBCC	LBCC	LBCC

3. CHARACTERIZATION OF SURFACE VOC

3.1 TOTAL NMOC CONCENTRATIONS

The distributions of total NMOC concentrations observed in the summer and fall studies are shown in Figure 3-1. The distributions include all of the NMOC data, except those collected on San Nicolas Island which are discussed separately in Section 3.10. There are no NMOC data for Long Beach in the fall because there were no valid carbonyl compound data for this period at the site. The concentration distributions show that the majority of the observations were between 250 and 1000 ppbC in the summer and between 500 and 2000 ppbC in the fall. The "all-site" average NMOC concentrations were 767 and 1595 ppbC in the summer and fall, respectively. The minimum and maximum NMOC concentrations were 171 and 2640 ppbC in the summer study and 182 to 4234 ppbC in the fall study. Thus, in an overall sense, the fall NMOC levels were about a factor of two higher than the summer levels.

3.1.1 Spatial Patterns of Total NMOC

The SCAQS VOC data provide an improved understanding of the spatial and temporal variability in total NMOC concentrations in the SoCAB. The spatial pattern and variability in NMOC levels are shown in Table 3-1 (summary statistics) and Figure 3-2 (box-whisker plot)[1]. The summer data indicate the spatial pattern of NMOC concentrations is approximately dome-shaped, with its center located somewhere between downtown Los Angeles and Burbank. The average NMOC concentrations increase from a low of about 450 ppbC at Hawthorne (near the coast) and 620-660 ppbC at Long Beach and Anaheim to about 1100 ppbC at central Los Angeles and Burbank in summer. Farther inland, the mean NMOC concentrations were lower; the mean NMOC concentrations were 860, 800, and 660 ppbC at Azusa, Claremont, and Riverside, respectively. These data exhibit a trend of decreasing concentrations with increasing distance from central Los Angeles and Burbank. Note that Figure 3-2 shows several outliers in the NMOC concentration data. These samples were retained in the database because they met all the quality control criteria outlined in Section 2.3 and, importantly, had compositions similar to the other samples.

The SCAQS summer network provides reasonably good resolution of the east-west gradients in NMOC concentrations, and it is in this direction that a dome-shaped concentration pattern is most evident. There are also significant concentration gradients in the north-south direction, as evidenced by the increases between Long Beach and Los Angeles, and between Anaheim and Azusa. Unfortunately, the network could not resolve the spatial pattern north or west of Burbank. Presumably, given the current population distribution and traffic

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[1] In box-whisker plots, the lower and upper ends of the box show the 25th and 75th percentiles of the data, and the line across the middle of the box indicates the median value. The whiskers extend out to the minimum and maximum values which are within 1.5 times the inter-quartile range. Outliers and far outliers are shown as squares and squares with plus symbols, respectively.

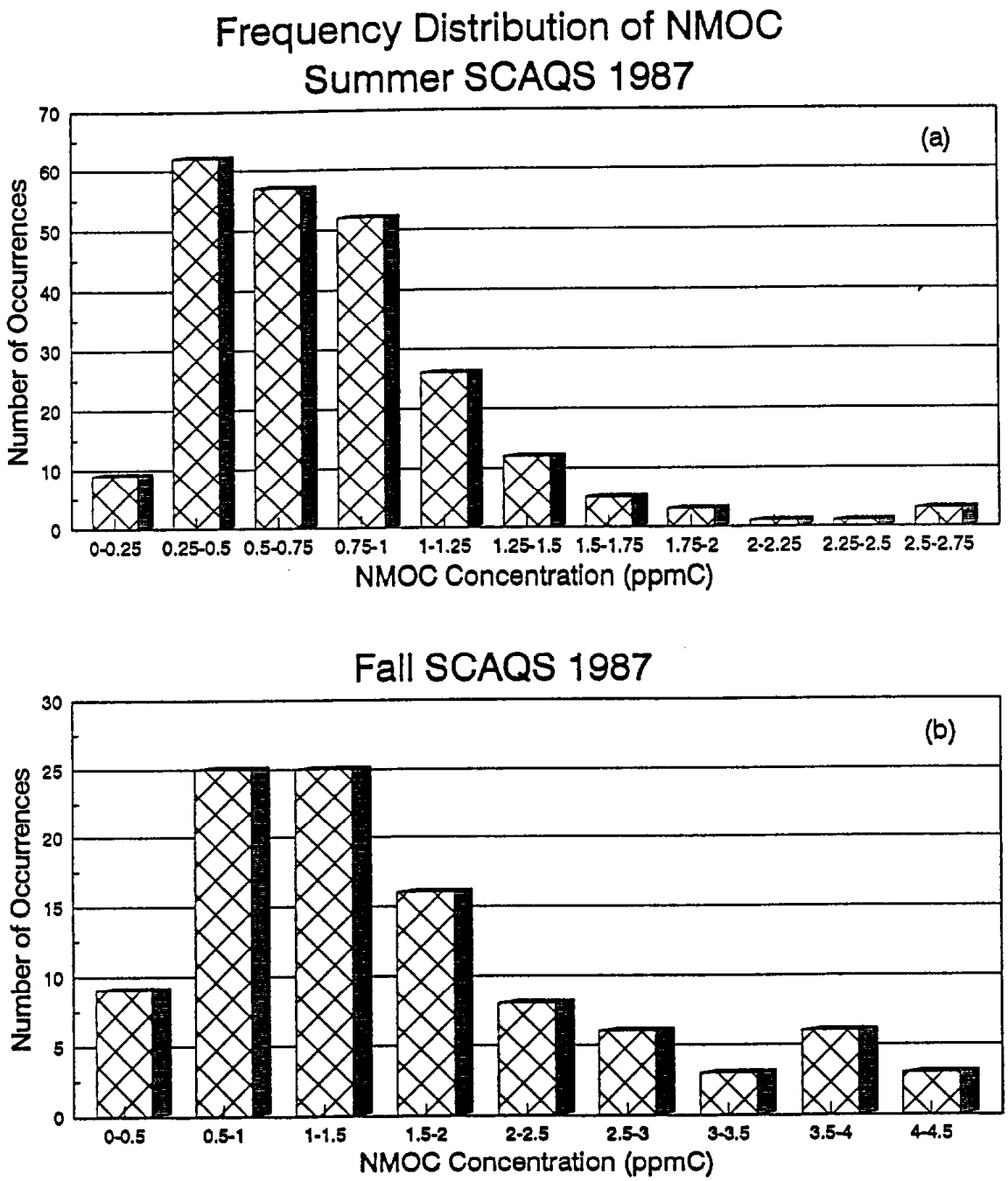


Figure 3-1. Frequency Distribution of NMOC in the a) Summer and b) Fall SCAQS 1987.

Table 3-1. Summary Statistics for NMOC Concentrations by Location and Season

Season/Location	Minimum	25%	Median	Mean	75%	Maximum	No. Of Samples
Summer:							
Long Beach	171	328	432	619	725	2563	47
Hawthorne	187	286	404	447	540	907	21
Anaheim	300	360	514	660	774	2594	24
Los Angeles	499	790	1074	1086	1228	2257	21
Burbank	696	784	990	1108	1289	2640	24
Azusa	451	663	779	858	969	1619	23
Claremont	389	536	794	798	937	1609	50
Riverside	264	402	505	657	945	1438	21
8-Sites Combined	171	439	696	767	948	2640	231
Fall:							
Hawthorne	300	727	1189	1772	2866	4234	15
Anaheim	290	829	1343	1591	2342	3539	18
Los Angeles	445	1140	1413	1575	1903	3548	35
Burbank	623	1116	1879	2125	3598	4197	17
Riverside	182	348	666	912	1310	2340	16
5-Sites Combined	182	844	1383	1595	2104	4234	101

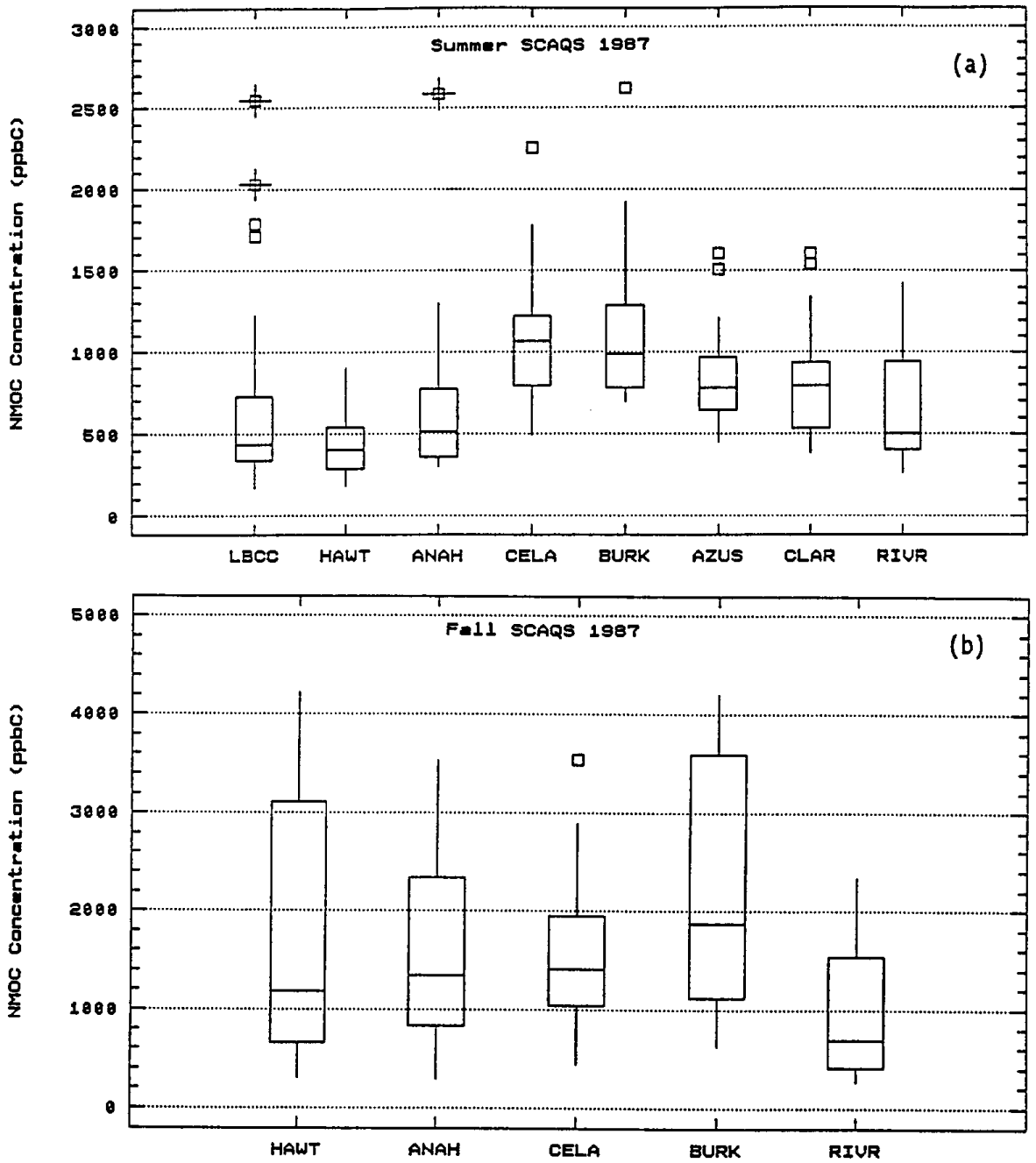


Figure 3-2. Box Plots of NMOC Concentration at Each SCAQS Site During the a) Summer and b) Fall SCAQS. Sites are ordered from coastal to central to eastern basin. The lower and upper ends of the box show the 25th and 75th percentiles of the data, and the line across the middle of the box indicates the median value. The whiskers extend out to the minimum and maximum values which are within 1.5 times the inter-quartile range. Outliers and far outliers are shown as squares and squares with plus symbols, respectively.

patterns, lower concentrations are expected west of the San Fernando Valley and northeast of Burbank in the high desert region.

In the fall, mean NMOC concentrations of 1770, 1590, 1570, 2120, and 910 ppbC were observed at Hawthorne, Anaheim, Los Angeles, Burbank, and Riverside, respectively. Unlike the summer data that showed comparable NMOC levels at Los Angeles and Burbank, the fall data show significantly higher levels at Burbank than anywhere else. Hawthorne had the second highest average concentration, which is in contrast to the summer where it had the lowest average concentrations. The lowest NMOC concentrations in the fall were observed far inland at Riverside. Thus, the fall spatial pattern shows relatively constant NMOC over a broad area extending from Hawthorne to Anaheim and up to Los Angeles, then higher NMOC to the north at Burbank and lower NMOC to the east at Riverside.

The seasonal differences in NMOC levels and spatial patterns are consistent with the prevailing meteorological conditions (Zeldin et al., 1989). The fall measurement days had low wind speeds and low mixing heights, which lead to higher NMOC levels than in the summer. Because of the low wind speeds in the fall, the spatial pattern probably reflects local NMOC emission strengths more closely than the summer pattern. The summer daytime meteorology in the basin is dominated by the westerly sea breeze, which transports the NMOC across the basin. The dilution and transport effects of the sea breeze are clearly evident at the coastal sites (Hawthorne and Long Beach), which had significantly lower NMOC levels than the central basin sites (especially in the midday and late afternoon).

3.1.2 Diurnal Patterns of Total NMOC

The diurnal pattern and variability in total NMOC concentrations are shown in Table 3-2 and Figure 3-3. The eight-site average diurnal pattern of NMOC in summer is one of decreasing concentration from morning to afternoon. The decrease is from an average of 971 ppbC at 0700-0800 to 771 ppbC at 1200-1300 and to 607 ppbC at 1600-1700 PDT. The five-site average concentrations for the fall days were 2560, 937, and 1179 ppbC at 0700-0800, 1200-1300, and 1600-1700 PST, respectively.

The average NMOC concentrations for each time of day at each site are shown in Figure 3-4. The summer data for Hawthorne, Anaheim, Long Beach, Burbank, Azusa, and Riverside show decreasing concentrations between 0700 and 1700, on average. Downtown Los Angeles was the only site where the mean mid-day concentration exceeded the morning and late afternoon levels in summer. Claremont experienced its highest and lowest concentrations at 0900-1000 and 1200-1300, respectively, in the summer. However, Claremont also had the least diurnal variation in NMOC concentrations of any site in the summer.

The diurnal profiles of NMOC in the fall show maxima at 0700-0800 and minima at 1200-1300 at all of the sites, except Hawthorne. The average NMOC levels at 1600-1700 were slightly greater than the 1200-1300 levels at most sites in the fall. Hawthorne had the greatest variance in NMOC concentrations over the day, dropping from a mean of 3130 ppbC at 0700-0800 to 1080 ppbC at 1200-1300 and to 580 ppbC at 1600-1700 in the fall. The 0500-0600 data for Los Angeles and Long Beach are only slightly lower on average than the

Table 3-2. Summary Statistics for NMOC Concentrations by Time of Day

Time/Location	Minimum	25%	Median	Mean	75%	Maximum	No. Of Samples
Summer (PDT):							
0500 - 2 Sites	171	432	536	671	895	1551	17
0700 - 8 Sites	321	579	882	971	1212	2640	61
0900 - 2 Sites	266	356	732	786	885	2563	17
1200 - 8 Sites	187	431	670	771	1046	2257	62
1400 - 2 Sites	201	486	608	637	796	1102	13
1600 - 8 Sites	199	409	578	607	785	1205	61
Fall (PST):							
0500 - Los Angeles	988	1373	1601	1651	1853	2491	6
0700 - 5 Sites	829	1562	2623	2560	3539	4234	29
0900 - Los Angeles	1437	1544	1746	1729	1953	1968	5
1200 - 5 Sites	265	568	862	937	1356	1935	27
1400 - Los Angeles	510	854	1442	1664	2832	2906	6
1600 - 5 Sites	182	675	1053	1179	1455	3621	28

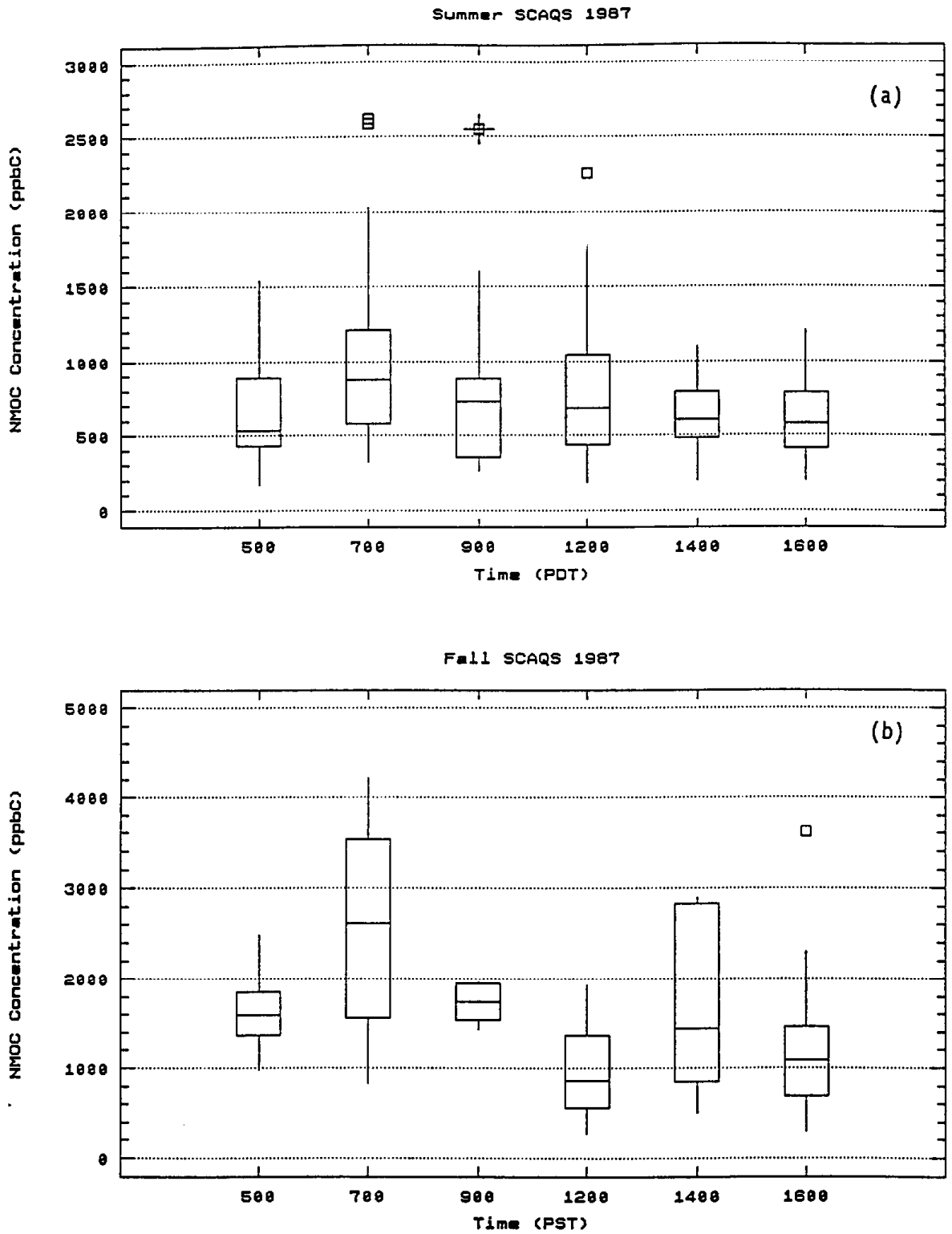
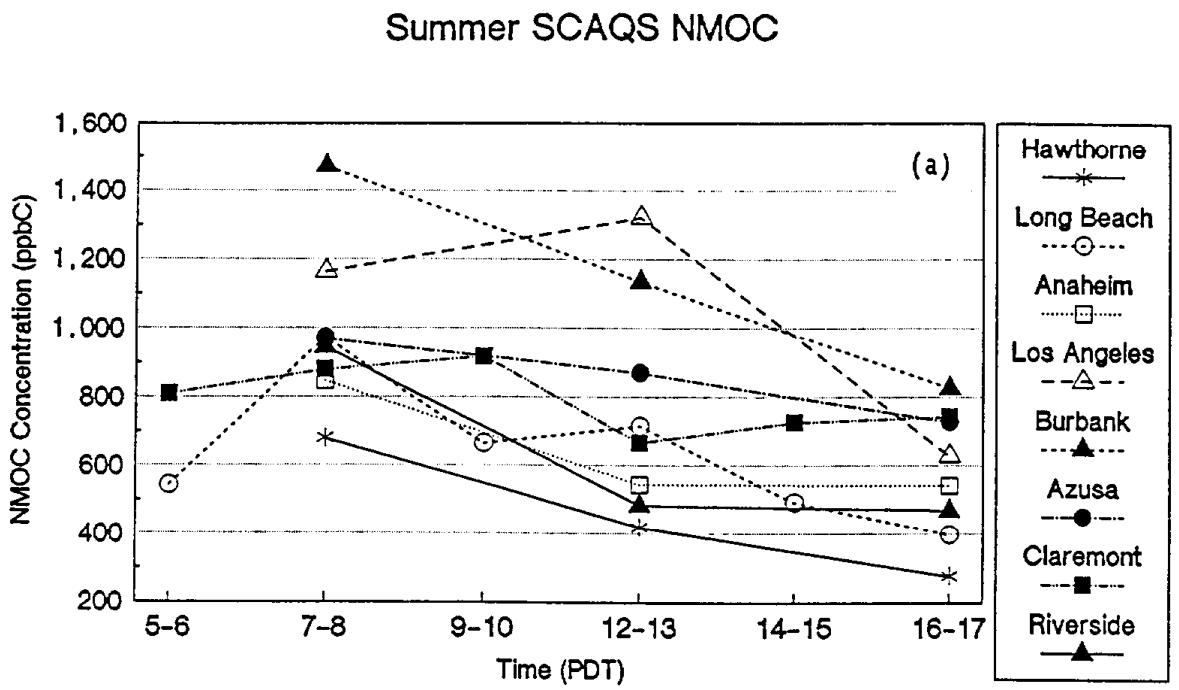
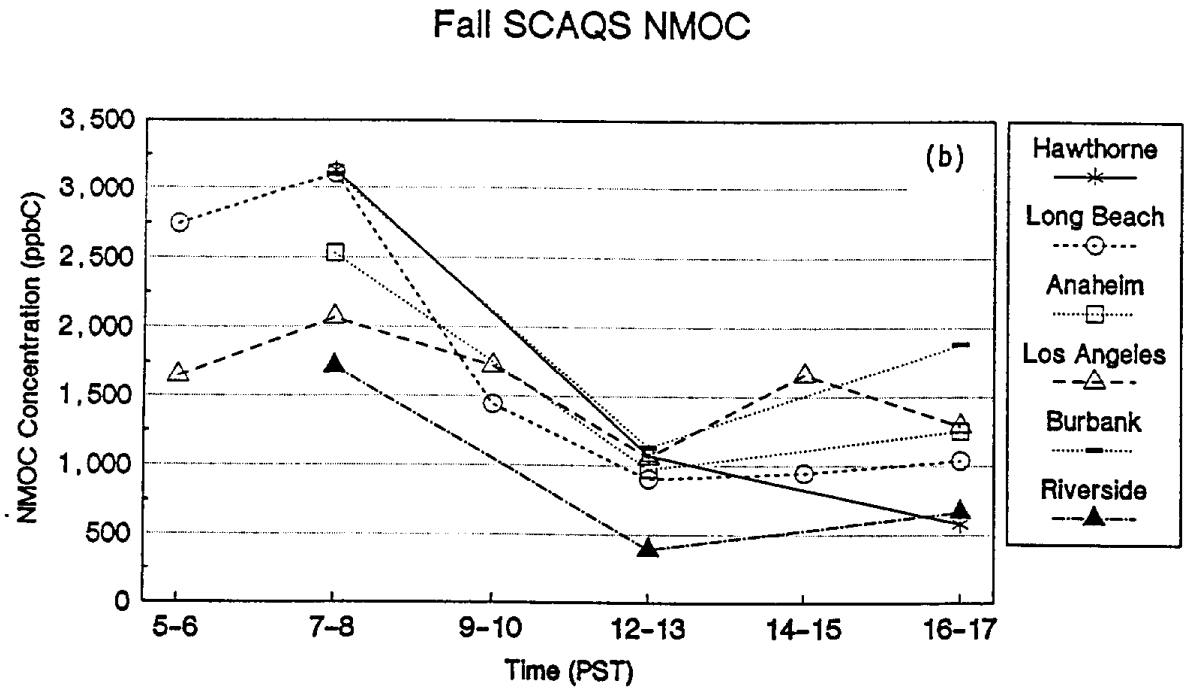


Figure 3-3. Box Plots of NMOC Concentration With Time of Day (PDT Summer, PST Fall) for the a) Summer and b) Fall SCAQS 1987. Fewer samples were collected at 0500, 0900 and 1400.





Long Beach data are NHMC, rather than NMOC

Figure 3-4. Diurnal Variation of Mean NMOC Concentration at Each Site for a) Summer and b) Fall SCAQS.

0700-0800 levels, which suggests there may be substantial carry-over of NMOC in the fall.

The fall data show greater diurnal variability than the summer data. For example, on average, the concentrations decreased by 64% and 21% between 0700-0800 and 1200-1300 in the fall and summer, respectively. The mean concentrations at 1600-1700 were 26% greater and 17% smaller than the 1200-1300 mean concentrations in the fall and summer, respectively.

It is important to recognize that there is considerable day-to-day variability in the diurnal pattern of NMOC in the SoCAB. Figure 3-5 compares the data from several sites for July 13-15 with the basinwide average diurnal profile of NMOC in summer. Few of the observations from this period follow the average pattern closely. Instead the data show a mixture of cases where the mid-day NMOC exceeds the morning NMOC, where the afternoon NMOC exceeds the mid-day levels, and where there is little diurnal variation in NMOC. Hence, considerable averaging is required for consistent diurnal patterns to appear.

The average diurnal patterns in summer and fall are generally consistent with the prevailing meteorology and the diurnal pattern of emissions. Concentrations are highest at 0700-0800 because of the combination of high emission rates from the morning traffic and low mixing heights that occur at this time of day. Concentrations decrease over the course of the day in the summer because wind speeds and mixing heights increase during the daylight hours, while emissions are relatively constant (at least until the evening traffic increase occurs). All of the average summer data follow this pattern except those at Los Angeles, which had 14% higher concentrations at 1200 than 0700 PDT on average. The differences between the summer and fall diurnal patterns mostly reflect the mixing height differences. Lower mixing heights in the fall limit the dilution of fresh emissions. Daytime mixing heights are driven by the surface heat flux. The mixing heights are much lower at 0700 and 1600 in the fall than summer because the sampling times are closer to sunrise and sunset, respectively, when the heat flux is smaller than midday. Concentrations generally increased from 1200 to 1600 in the fall because the wind speeds and mixing heights were lower at 1600-1700 than 1200-1300 (which was often not the case in the summer).

3.1.3 Day-to-Day Variations in Total NMOC

The day-to-day variations in total NMOC concentrations are shown in Table 3-3 and Figure 3-6. When examining these data, it is important to recognize that all of the sampling days had moderate or high air pollution and, therefore, the variance between days is much less than would occur for the full range of conditions within a season. The daily "all-site" means varied from 488 ppbC on July 15th to 1369 ppbC September 2nd, and from 1052 ppbC on November 13th to 2182 ppbC on December 11th. The day-to-day variance in the summer was less than expected; eight of the eleven days had daily mean NMOC levels between 576 and 795 ppbC.

The daily "all-site" NMOC means are plotted against the summer basinwide 1-hr ozone maxima and fall basinwide 24-hr PM_{10} maxima in Figure 3-7. These data show the daily mean NMOC varied by a factor 2.8 and 2.1 in summer and

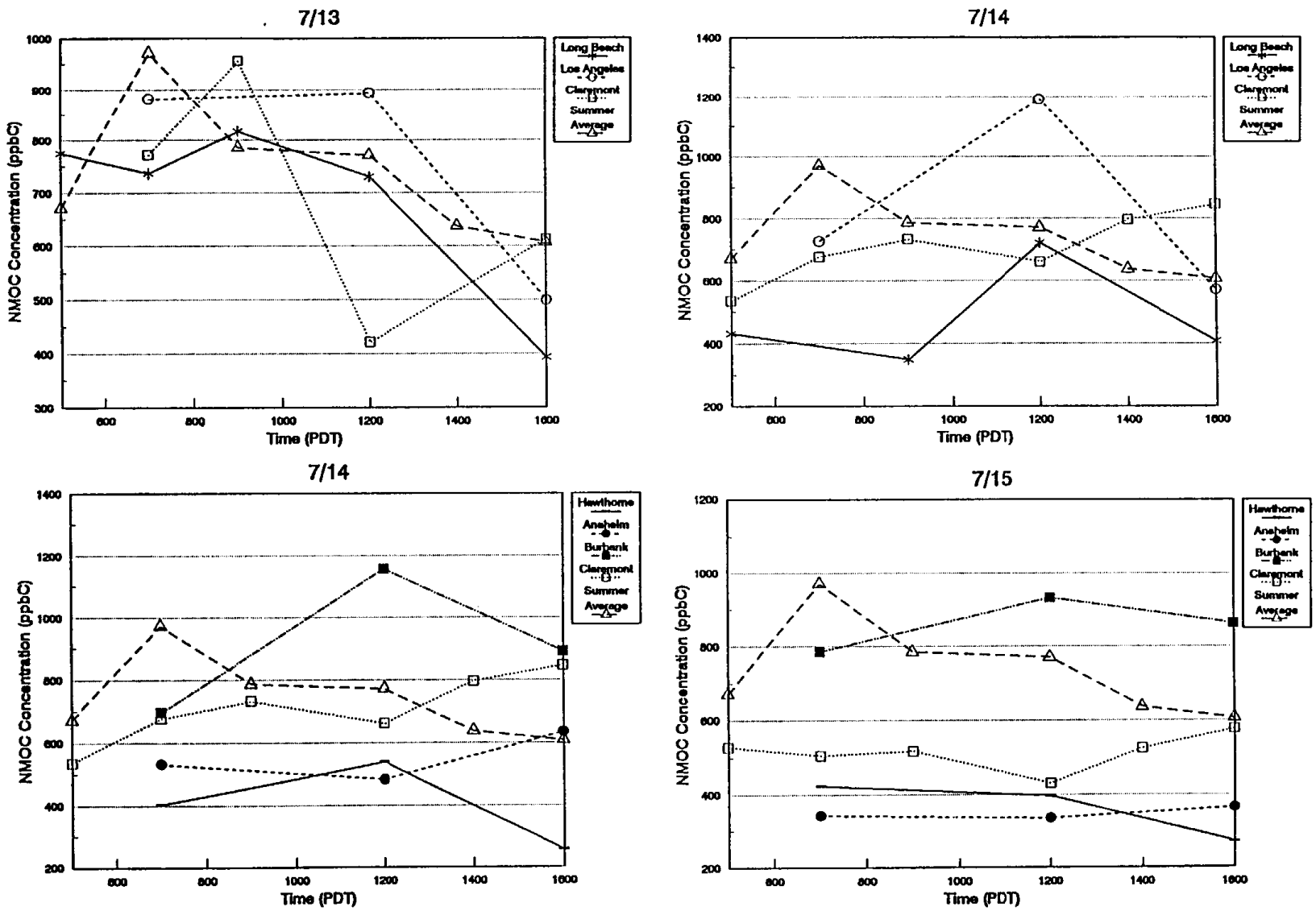


Figure 3-5. Diurnal Variation of NMOC Concentration at Each Site for the July 13-15 SCAQS Sampling Episode.

Table 3-3. Summary Statistics for NMOC Concentrations by Date

Date	Minimum	25%	Median	Mean	75%	Maximum	No. Of Samples
June 19	267	487	620	672	847	1287	18
June 24	210	398	673	671	894	1228	16
June 25	249	319	447	576	767	1168	12
July 13	331	475	772	695	862	1012	23
July 14	256	484	647	642	732	1191	26
July 15	171	343	497	488	578	933	25
August 27	187	659	783	795	959	1328	21
August 28	234	681	934	991	1337	1924	26
August 29	266	425	712	780	1116	1551	22
September 02	422	779	1228	1369	1787	2640	21
September 03	173	356	514	672	807	1609	21
November 11	265	566	959	1106	1272	2629	16
November 12	286	745	1231	1531	1968	3598	17
November 13	300	666	1267	1052	1389	1570	17
December 03	573	1083	1529	1735	2104	4164	18
December 10	563	1136	1544	1931	2573	4234	15
December 11	182	1470	2042	2182	3108	4197	18

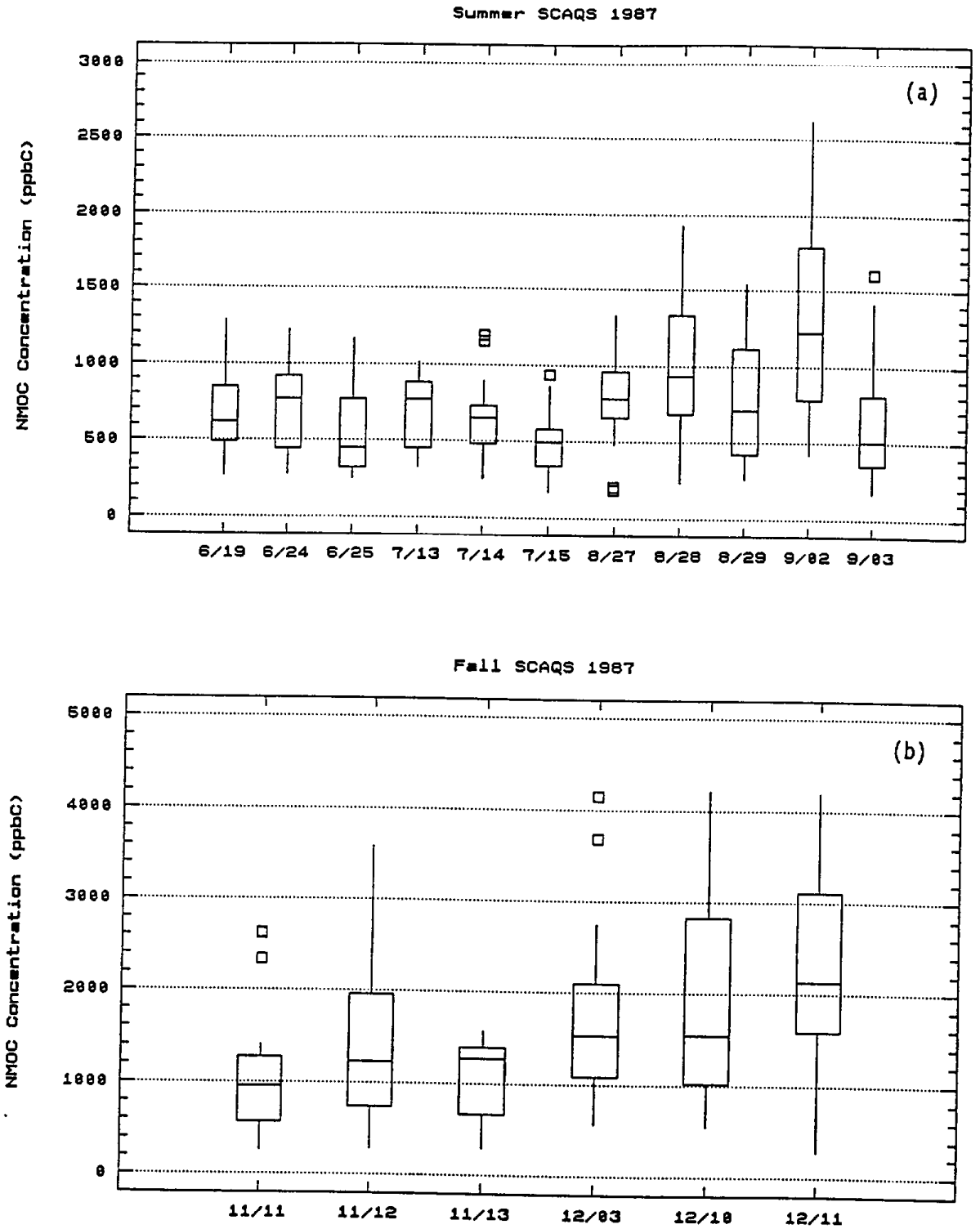


Figure 3-6. Box Plots of NMOC Concentrations for Each SCAQS Sampling Day During the a) Summer and b) Fall.

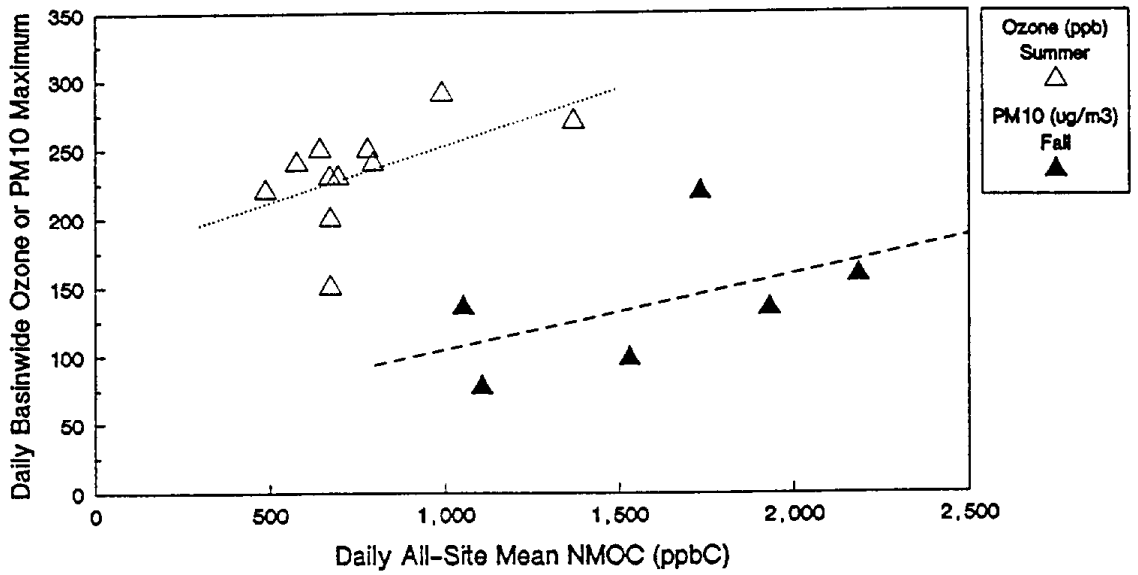


Figure 3-7. Relationship Between the Daily All-Site Mean NMOC Concentration and the Daily Basinwide Ozone or PM_{10} Maximum.

fall, respectively, while the ozone and PM_{10} maxima varied by about a factor of two during the study. Analysis of the correlation between these variables indicates the daily mean NMOC values explain little of the variance in daily ozone maxima in summer (r^2=0.28) and daily PM_{10} maxima in the fall (r^2=0.25). This ozone result is somewhat surprising because NMOC is an important ozone precursor. Nevertheless, the data show that on days with virtually identical mean NMOC levels of about 650 ppbC the maximum ozone levels varied from 15 to 25 pphm. Moderate to strong onshore flow occurred on June 19 and the maximum basin ozone concentration of 15 pphm on June 19 was considerably lower than the maximum ozone on other SCAQS days. When this data point is removed from the correlation between mean NMOC and ozone concentration, the correlation improves to r^2=0.5. The results suggest the details of the meteorology (or perhaps emissions) may be more important than the mean NMOC levels on any particular day.

3.2 NMOC TO NO_x RATIOS

The ratio of NMOC to NO_x in the morning hours is an important parameter for photochemical systems. The ratio characterizes the efficiency of ozone formation in NMOC-NO_x-air mixtures. Both environmental chamber experiments and photochemical model calculations show that at low NMOC/NO_x ratios (below 5 ppbC/ppb), ozone formation is slow and inefficient. Likewise, at high NMOC/NO_x ratios (above about 15) ozone formation is limited by the availability of NO_x, rather than NMOC, which means that variations in NMOC levels when the NMOC/NO_x ratios are high do not significantly influence ozone formation. For typical urban NMOC mixtures, the maximum ozone formation potential of a given amount of NO_x occurs when the morning NMOC/NO_x ratio is between 10 and 12. In addition, Carter (1991) has shown that the ozone formation potential of mixtures with morning NMOC/NO_x ratios of 6 to 8 have the largest sensitivity to changes in NMOC composition. Thus, knowledge of the NMOC/NO_x ratios in an air basin is important for selection of appropriate emission control strategies.

The distribution of morning NMOC/NO_x ratios observed during the summer SCAQS are shown in Figure 3-8. Only ratios with NO_x concentrations equal to or greater than 35 ppb are included in the distribution because the roundoff errors are far larger below 35 ppb. The data show the majority of ratios were between 7 and 11, and the extreme values were 5 and 15. The average ratio was 8.9. Figure 3-8 also shows a scatter plot of morning NMOC versus NO_x concentrations from all stations, while Figure 3-9 shows a scatter plot of the mean NMOC and mean NO_x from each station. These data show the morning NMOC and NO_x levels are well correlated (r^2=0.78, for all data and 0.94, for the mean data). Figure 3-9 shows the mean ratios at each station at 0700, 1200, and 1600. These data show that morning NMOC/NO_x ratios were similar at all of the stations. The mid-day ratios were higher than the morning ratios at all of the stations, as is expected since NO_x is oxidized more rapidly than NMOC in the daylight. The majority of mid-day ratios were between 11 and 15. The largest spatial variations in ratios occurred in the afternoon samples where the mean ratios varied from a low of 5 at Hawthorne to a high of 15 at Los Angeles.

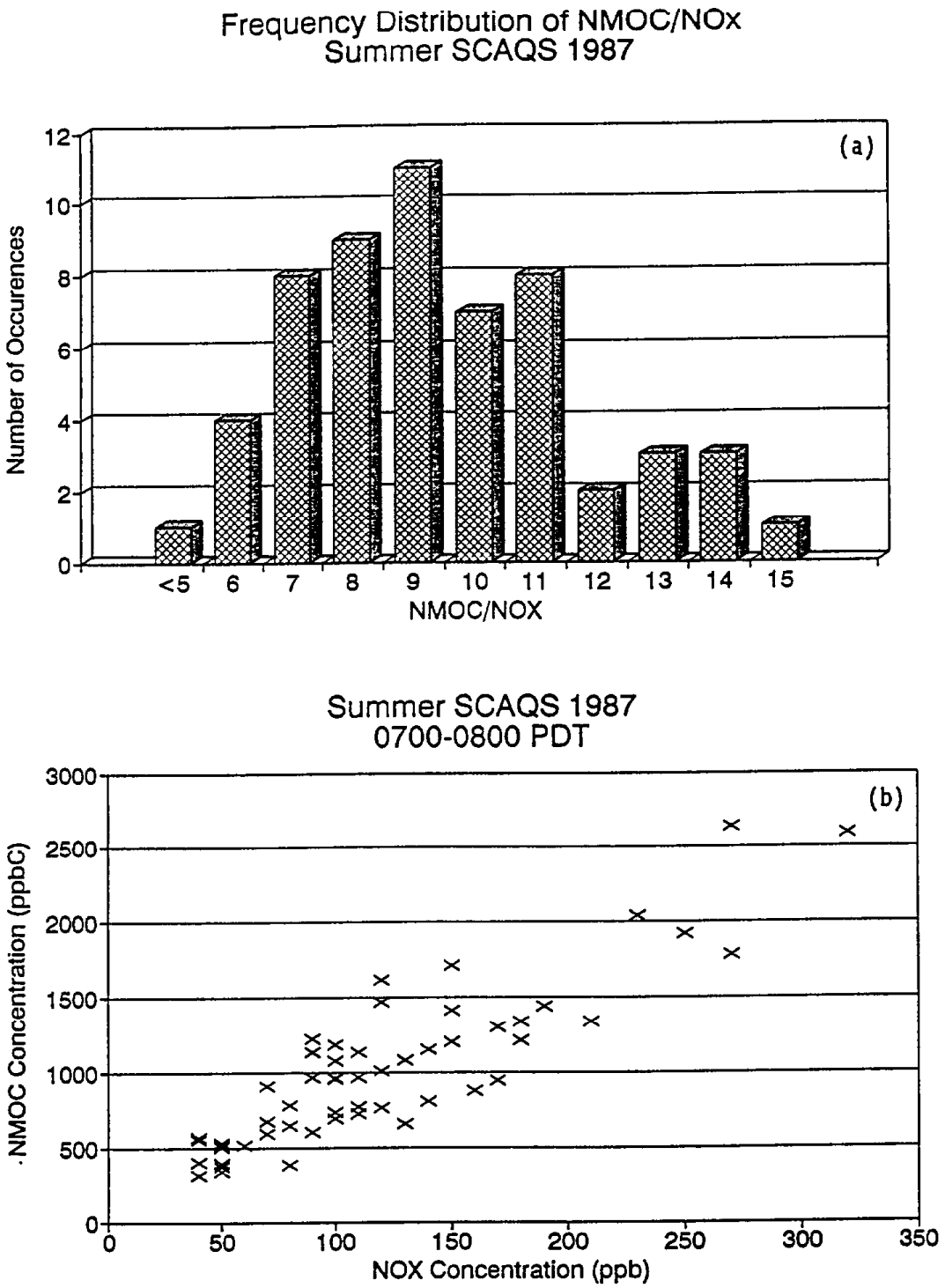
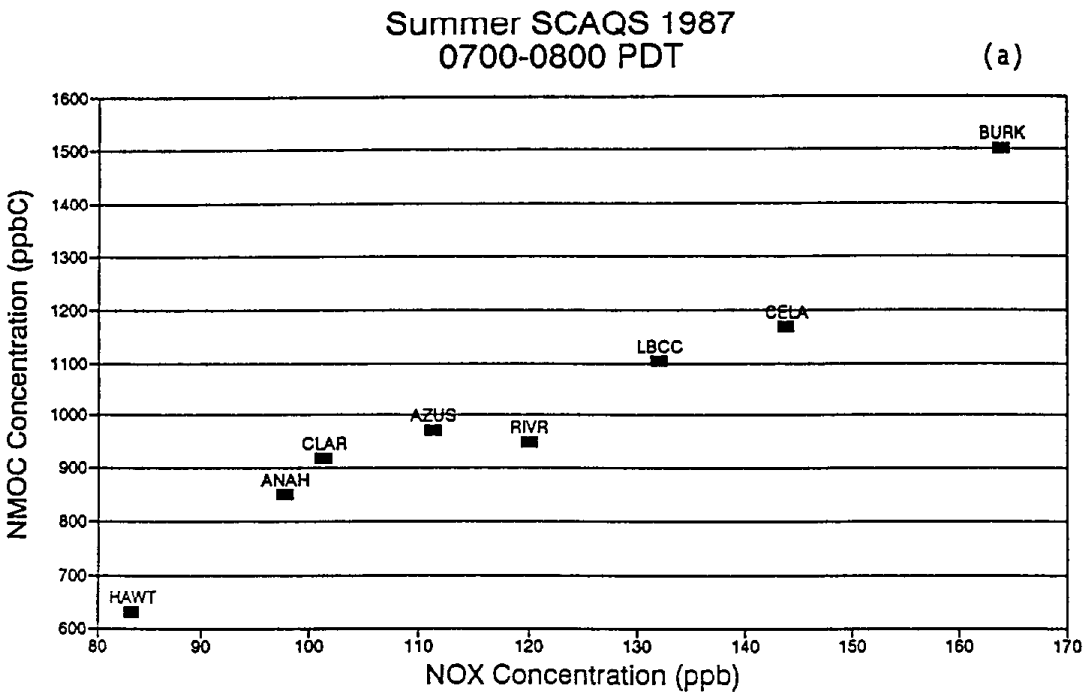


Figure 3-8. SCAQS Summer Morning NMOC and NO_X Concentrations: a) Frequency Distribution of NMOC to NO_X Ratios and b) Scatterplot (r^2 = 0.78). NO_X concentrations below 35 ppb were excluded from the data base.



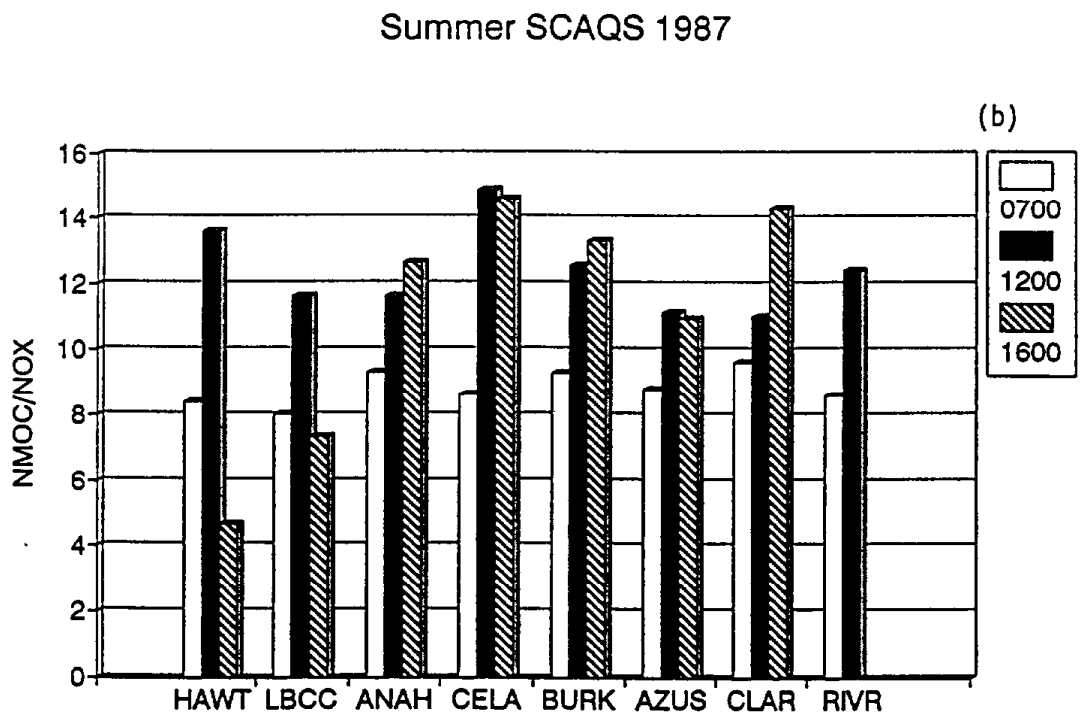


Figure 3-9. Mean NMOC to NO_x Ratios by Site: a) Mean Summer Morning Concentrations (r^2 = 0.94) and b) Diurnal Variation. NO_x concentrations below 35 ppb were excluded from the data base. Sites are ordered from coastal to central to eastern basin.

The distribution of morning NMOC/NO_x ratios from the fall study are shown in Figure 3-10. The majority of ratios were between 5 and 9, with extreme values of 2.4 and 11. The mean NMOC/NO_x ratio was 6.8 in the fall. The morning NMOC and NO_x concentrations are reasonably well correlated, as shown in Figure 3-10, however, the correlation coefficient (r^2=0.5) is not as high as in the summer observations. Figure 3-11 shows the mean ratios at 0700, 1200, and 1600 at each station in the fall. The data show mean morning ratios of 5.9, 7.6, 5.1, 9.5, and 5.6 at Hawthorne, Anaheim, Los Angeles, Burbank, and Riverside, respectively. The diurnal behavior of the ratios varies considerably. Anaheim and Burbank had only small variations in the ratios over the course of the day, whereas Hawthorne, Los Angeles, and Riverside, which have low ratios in the morning, show significantly higher ratios at 1200 and 1600.

The SCAQS NMOC/NO_x ratios support several hypotheses concerning current emissions and ozone control strategies in the SoCAB. Our interpretation is predicated on the assumption that the ambient ratios in the morning closely reflect those in the morning emissions inventory because this is the time-of-day when emission rates are high, mixing heights are low, and photochemical reactions are slow. Because of pollutant carry-over in the fall, the morning ambient ratios may correspond more closely to nighttime plus early morning emissions, rather than morning emissions alone. These hypotheses include:

- First, the spatial consistency of the morning ratios, especially in summer, suggest there is a common type of emissions source throughout the basin. Motor vehicles are the most likely source.

- Second, the absence of large variations in ratios over the course of the day suggests the emission sources continuously emit NMOC and NO_x. We believe the mid-day and afternoon ratios would be much higher if morning NMOC and NO_x reacted without the addition of fresh emissions during the day. The data are not sufficient to determine how the emission rates vary with time-of-day; they only provide evidence that fresh emissions affect all of the stations.

- Third, the data indicate there are seasonal variations in the emissions that produce somewhat lower NMOC/NO_x ratios in the fall than summer. The data are not sufficient to determine whether seasonality of the ratio is caused by NO_x increases in the fall or NMOC increases in the summer (or a combination of the two).

- Fourth, the ambient NMOC/NO_x ratios on summer mornings are mostly between 7 and 11, which suggests that NMOC and NO_x emissions control strategies will be effective in reducing ozone formation rates in the SoCAB.

3.3 NMOC GROUPS

It is informative to examine the NMOC composition in terms of the four major classes of organic compounds: paraffins, olefins, aromatic hydrocarbons, and carbonyl compounds. Each class of compounds has different oxidation pathways, rates, and products, and therefore contributes in different manners to ozone and aerosol formation. The basinwide mean NMOC

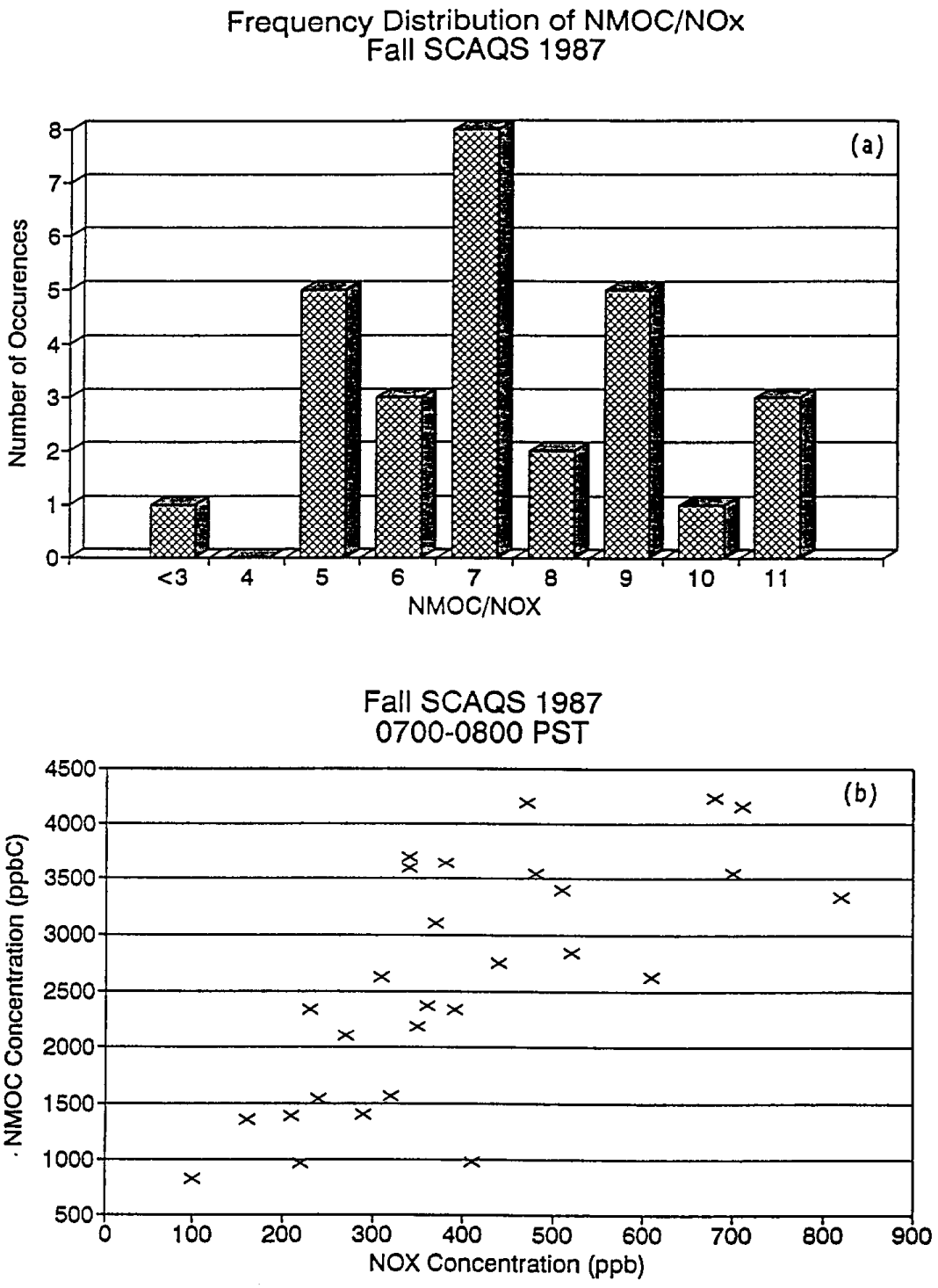


Figure 3-10. SCAQS Fall Morning NMOC and NO_x Concentrations: a) Frequency Distribution of NMOC to NO_x Ratios and b) Scatterplot (r^2 = 0.49). NO_x concentrations below 35 ppb were excluded from the data base.

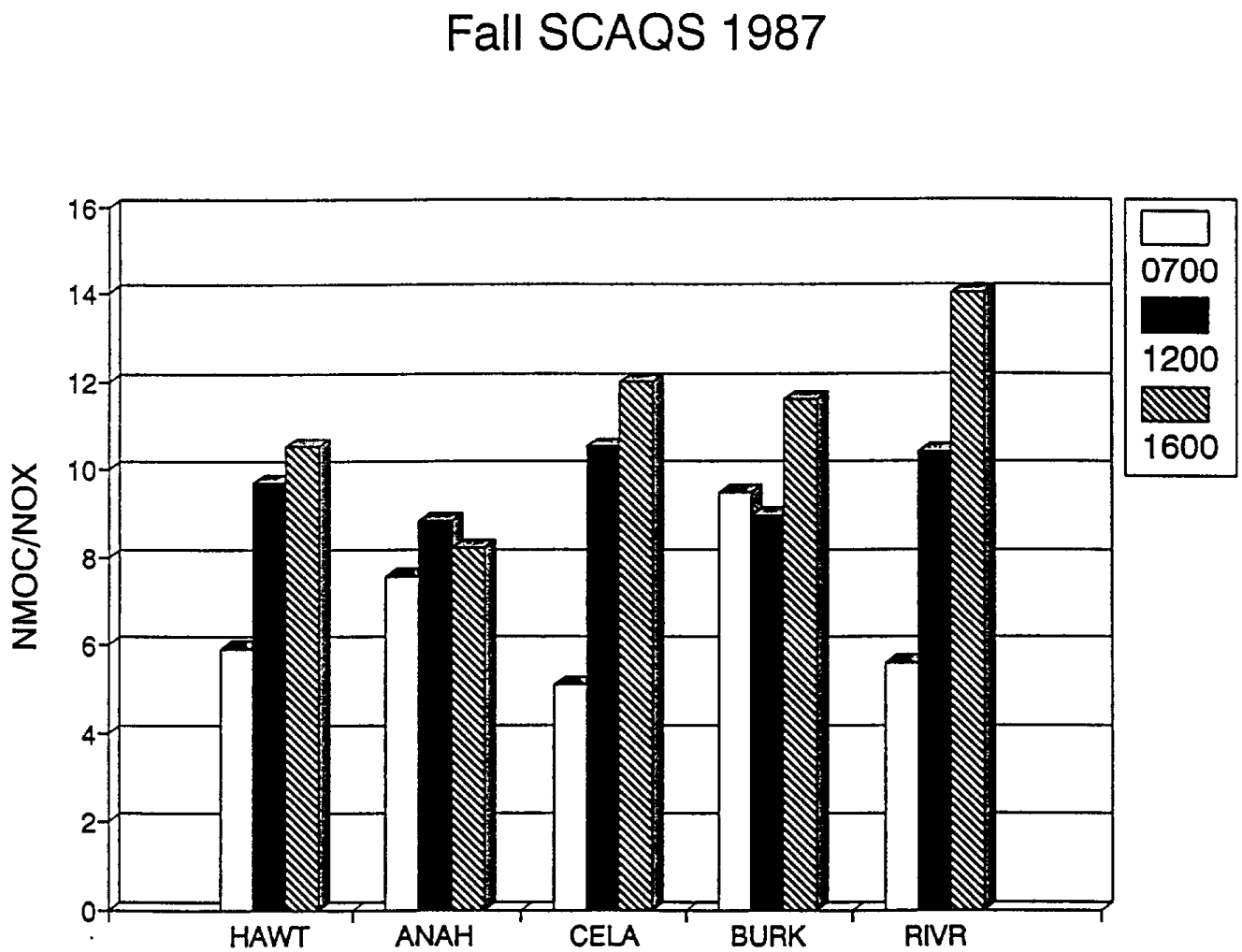


Figure 3-11. Diurnal Variation of Mean Fall NMOC to NO_x Ratios for Each SCAQS Site. Sites are ordered from coastal to central to eastern basin.

carbon fractions of each major class of organics and the unidentified carbon are shown below.

Compound Class	Summer	Fall	Average
paraffins	.444	.454	.449
aromatics	.163	.201	.182
olefins	.083	.100	.091
carbonyls	.161	.099	.130
unidentified	.148	.152	.150

These fractions are based on data collected at all sampling times. The data indicate paraffins were the most abundant class of compounds, followed by aromatic hydrocarbons, carbonyl compounds, and olefins. The seasonal variations in the paraffin and unidentified fractions were small; however, the aromatic and olefin fractions were somewhat lower in the summer than in the fall. Most aromatic hydrocarbons and olefins react rapidly in the atmosphere. While there may be seasonal differences in the composition of NMOC emissions, the observed differences may also be explained by the seasonal differences in the atmospheric oxidation rates. The enhanced level of photochemical activity in the summer causes the aromatic hydrocarbons and olefins to disappear more rapidly than in the fall. Likewise, the mean carbonyl fraction was significantly higher in summer than fall, which corresponds with carbonyl compounds being a major product of photochemical reactions.

It is well known that because the allowable Reed Vapor Pressure (RVP) limits differ in summer and fall, the composition of gasoline differs somewhat by season. Fall gasolines have more n-butane, which has a high vapor pressure, than summer gasolines. However, ambient temperatures are lower in the fall and the amount of evaporative emissions may be significantly lower. The basinwide mean data show slightly higher paraffin levels in fall than summer, which is consistent with the fuel differences, however, the difference is so small that it is not significant.

The variance in the paraffin, aromatic, olefin, and carbonyl fractions of NMOC is illustrated by box-whisker plots in Figures 3-12 and 3-13. The inter-quartile range of the paraffin, aromatic, and olefin fractions at each site is small compared to the median levels. The variance in the carbonyl fractions is considerably greater, as is expected for photochemical products.

The spatial variance in composition is relatively small: the median paraffin, aromatic, and olefin fractions varied from 0.42 to 0.51, 0.12 to 0.20, and 0.07 to 0.09 in the summer, and 0.42 to 0.48, 0.18 to 0.21, and 0.08 to 0.10 in the fall, respectively. These data suggest that emission sources with similar NMOC profiles affected most of the stations.

Nevertheless, a spatial pattern of composition is evident in the data. The paraffin fractions are higher and the aromatic and carbonyl fractions are lower in the western portion of the basin (Hawthorne and Long Beach) than elsewhere. The carbonyl fractions are highest at Riverside, which is the farthest inland station and generally the farthest downwind station. The contributions of stationary sources in the western basin, such as refineries,

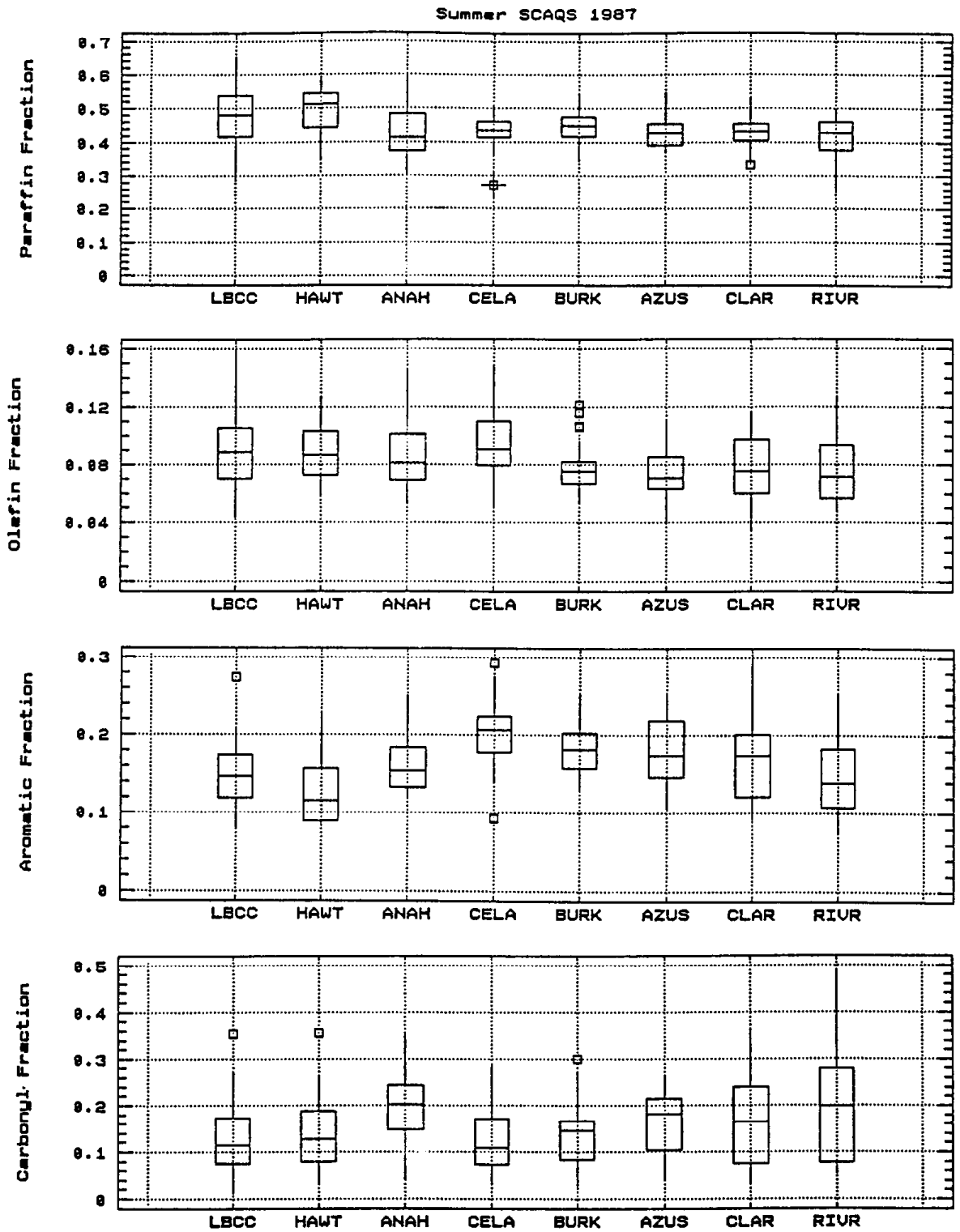


Figure 3-12. Box Plots of Paraffin, Olefin, Aromatic, and Carbonyl Fractions at Each Site During the Summer SCAQS. Sites are ordered from coastal to central to eastern basin.

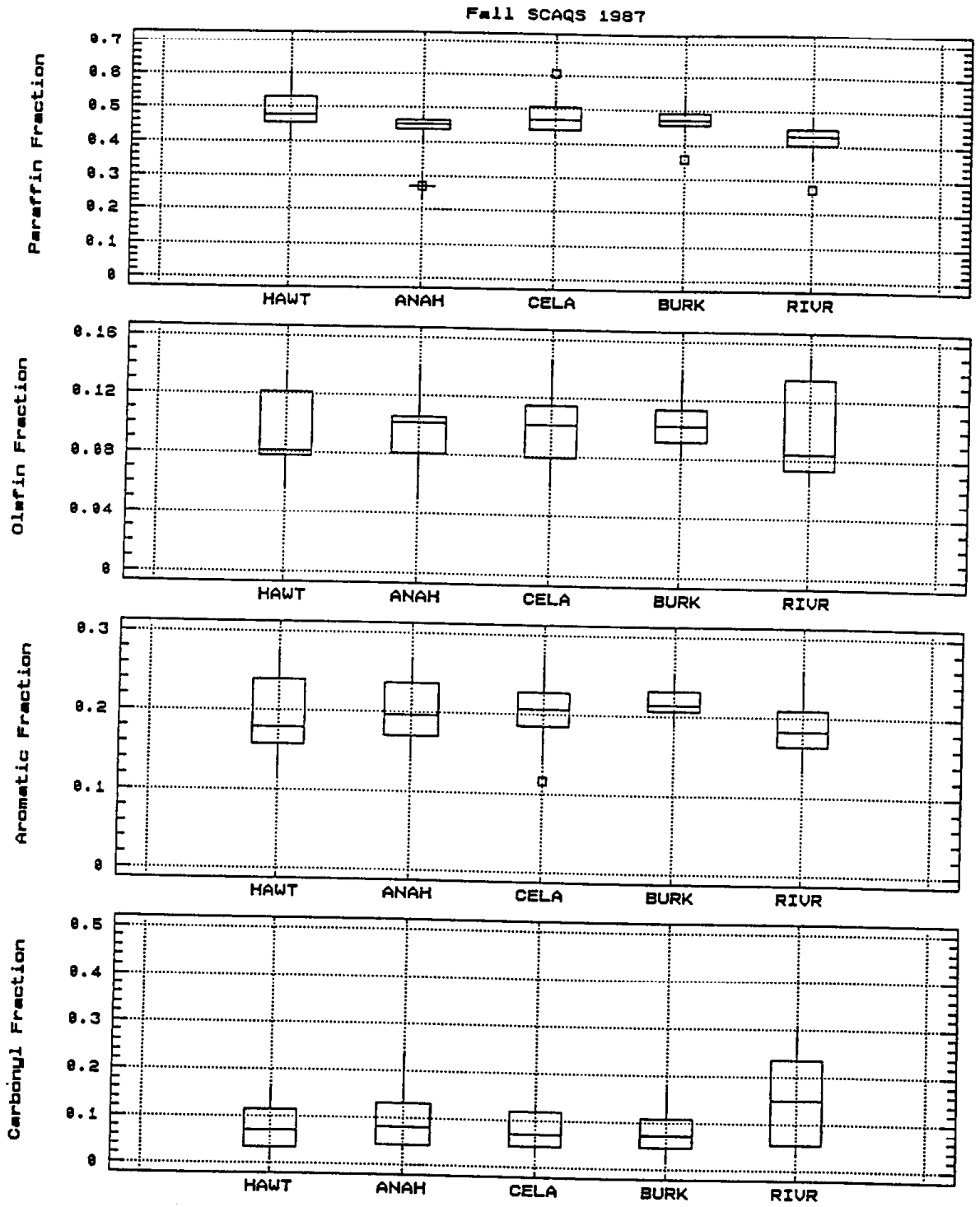


Figure 3-13. Box Plots of Paraffin, Olefin, Aromatic, and Carbonyl Fractions at Each Site During the Fall SCAQS. Sites are ordered from coastal to central to eastern basin.

that have mostly paraffinic emissions, probably explain the higher paraffin and lower aromatic fractions in those locations. The spatial pattern of carbonyl compounds is consistent with the transport of pollutants to the east and their photochemical oxidation during the daylight.

The temporal differences in NMOC composition are shown in Figure 3-14 by season. The data show that the diurnal variations in the fractions are small on the average for all groups except carbonyl compounds which more than double between 0700 and 1200. The average paraffin, olefin, and aromatic fractions decreased between 0700 and 1200 in summer and fall. This diurnal pattern is consistent with oxidation of the hydrocarbons and formation of carbonyl compounds. However, the extent of oxidation of olefins is less than would be expected in the absence of fresh emissions.

Most of the late afternoon fractions are similar to the noontime fractions on the average. In the fall, the aromatic and carbonyl fractions at 1600 are between those observed at 0700 and 1200. The similarities in mid-day and afternoon fractions lends support to the notion that significant amounts of fresh NMOC emissions are injected in the afternoon and these emissions strongly influence the NMOC composition. Given that oxidation is expected to proceed as rapidly in the afternoon as in the morning, the lack of composition differences in the afternoon may suggest the olefin and aromatic fractions of NMOC emissions are higher in the afternoon than the morning.

The unidentified compounds show very little spatial and temporal variability. This is fortunate because it allows one to interpret the trends in the other groups without worrying that the differences in the other fractions may be caused by differences in the extent of species identification. Nevertheless, there is no assurance that the composition of the unidentified hydrocarbons is invariant, and this does represent a source of uncertainty in the data. Given that the unidentified compounds are about 30% C2-C9 compounds and 70% C10+ compounds in average, our speculation is that they are mostly aromatic hydrocarbons and paraffins, rather than olefins. Thus, the actual paraffin and aromatic fractions may be significantly higher than reported here.

3.4 ABUNDANT SPECIES CONCENTRATIONS AND NMOC COMPOSITION

3.4.1 The Twenty-Five Most Abundant Species

There are a large number of organic species in urban air. The gas chromatographs of hydrocarbon samples from the SoCAB show several hundred peaks, of which 68 were identified as individual organic species and 31 were identified by their compound class and the number of carbons. Many of the small peaks were not identifiable, and their carbon was lumped into the unidentified category. For purpose of this study, we decided to focus our analysis on the 25 most abundant organic species in the SCAQS data set. These species were detected in almost all of the SCAQS samples.

The abundant species were identified by ranking the carbon fractions of the compounds in each sample and determining the frequency at which compounds were among the 30 most abundant in samples. These frequencies were then

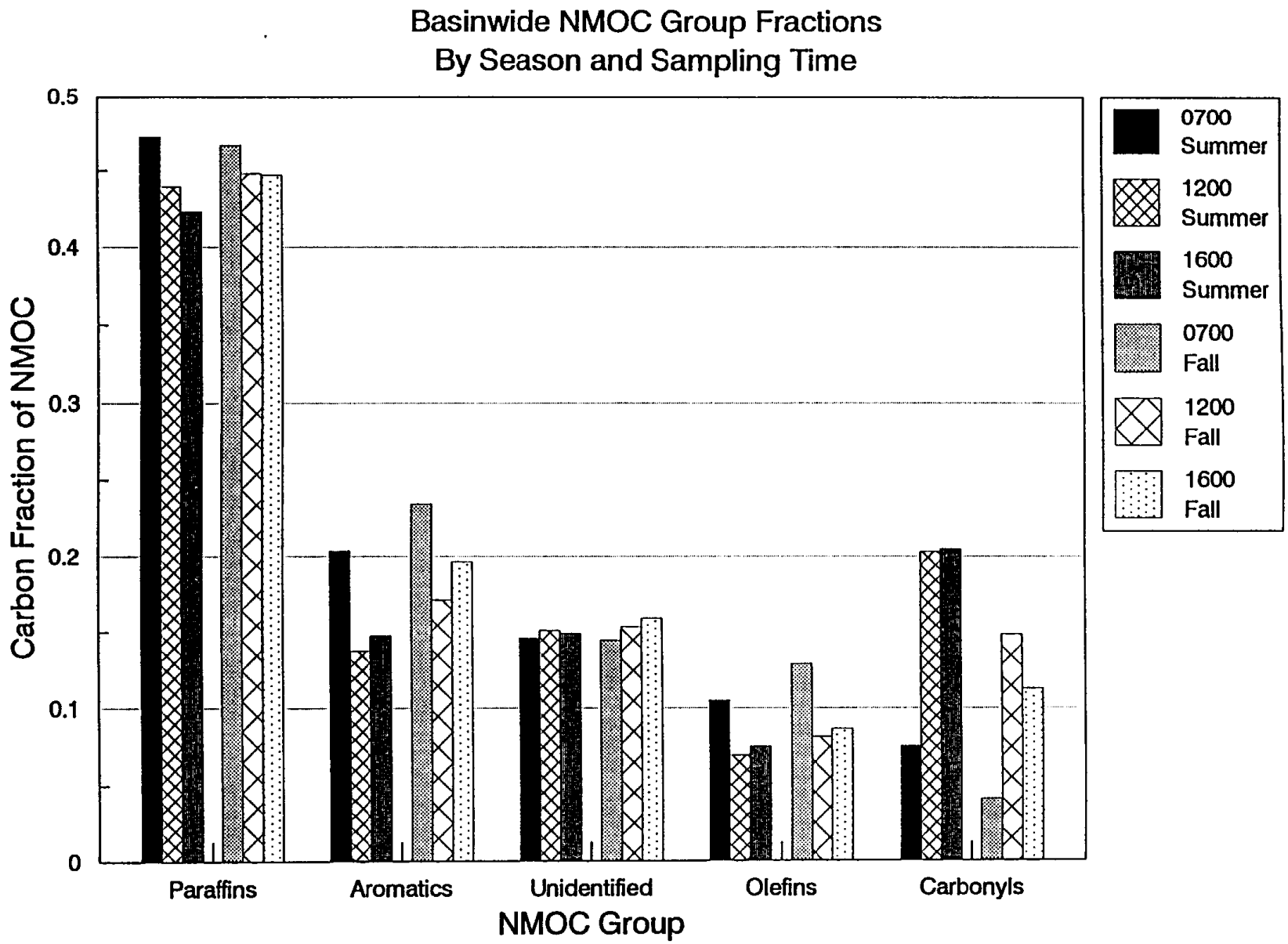


Figure 3-14. Variation of Basinwide NMOC Group Fractions by Season and Time of Day.

ranked to identify the 25 most abundant species in the summer and fall, which are shown in Table 3-4. These 25 species accounted for 62% and 65% of the NMOC carbon in the summer and fall on average. Twenty-two of the 28 species made both the summer and fall lists. The ranking based on abundance was also similar: ethene, ethane, acetylene, isobutane, n-pentane, toluene, and m- & p-xylenes were among the ten most abundant in both seasons. In addition, propane, isopentane, 2-methylpentane, 3-methylpentane, hexane, and benzene were among the 15 most abundant in both seasons.

The primary differences in abundance between the fall and summer were in carbonyl compounds and C3-C5 paraffins. Formaldehyde, acetaldehyde, and acetone were not among the 25 most abundant compounds in the fall samples. Since the carbonyl compounds are both directly emitted and a product of photochemical oxidation, one or both of these sources is reduced in the fall (more than likely, it is the photochemical source). The fall data show much higher rankings for n-butane, isopentane, and propane than in the summer. This may be indicative of the seasonal differences in fuel composition. During the summer, fuels usually have lower n-butane levels in order to meet the stricter RVP requirements.

3.4.2 Mean Concentrations and Relative Abundance

The basinwide means and standard deviations of the concentration and percent of NMOC for the 25 most abundant species are shown in Table 3-5. The table also provides data for the four major classes of organic species and the following sub-classes in order to complete the description of NMOC.

C2-C3 paraffins	(MPAR23)
C4-C5 paraffins	(MPAR45)
C6+ paraffins	(MPAR6)
terminal olefins	(MTOLEF)
internal olefins	(MIOLEF)
mono-substituted aromatic hydrocarbons	(MONAROM)
di/tri-substituted aromatic hydrocarbons	(DIAROM)

The inclusion of data for these classes complements the data for individual species and shows that the sub-classes usually have the same characteristics as the abundant species.

The basinwide mean data for the abundant species show the concentrations of most species were about twice as high in the fall as the summer. The principal exceptions were the carbonyl compounds, which had similar concentrations during both seasons. In the summer, the mean concentrations of propane, isopentane, toluene, n-butane, ethane, m- & p-xylenes, n-pentane, ethene, and acetone were 56, 52, 49, 42, 27, 25, 24, 22, and 22 ppbC, respectively. In fall, the concentrations of these same species were 80, 110, 115, 109, 51, 65, 49, 59, and 29 ppbC, respectively. The mean concentrations of isobutane, benzene, acetylene, 2-methylpentane, acetaldehyde, 3-methylpentane, hexane, methylcyclopentane, o-xylene, and formaldehyde were 19, 17, 17, 16, 15, 12, 11, 10, 10, and 9 ppbC in summer, respectively. The mean concentrations of these same species in the fall were 39, 43, 50, 37, 14, 28, 24, 22, 24, and 11 ppbC, respectively.

Table 3-4. The Twenty-Five Most Abundant Species Based on Fraction of Nonmethane Organic Carbon During the SCAQS 1987

Species	Rank Summer	Rank Fall
Toluene	1	3
i-Butane	2	10
Benzene	3	11
Pentane	4	8
2-Methylpentane	5	12
Acetylene	6	9
Ethene	7	5
Ethane	8	7
m- & p-Xylene	9	6
Acetone	10	
3-Methylpentane	11	13
3-Methylhexane	12	21
Hexane	13	14
i-Pentane	14	2
Propane	15	4
Butane	16	1
Methylcyclopentane	17	15
Ethylbenzene	18	20
o-Xylene	19	17
Methylcyclohexane	20	23
Acetaldehyde	21	
Heptane	22	25
1,2,4-Trimethylbenzene	23	19
Formaldehyde	24	
Propene	25	16
2-Methylhexane		22
2,2,4-Trimethylpentane		18
m-Ethyltoluene		24

Table 3-5. Mean Concentrations and Percents of Abundant Species and Species Groups for Overall Summer and Fall Surface Data From SCAQS 1987

	Concentration, ppbC				Percent of NMOC			
	Summer[a]		Fall[b]		Summer[a]		Fall[b]	
	Mean	Standard Deviation	Mean	Standard Deviation	Mean	Standard Deviation	Mean	Standard Deviation
Ethane	27.1	19.7	50.9	42.7	3.48	1.13	3.08	1.05
Ethene	22.3	15.0	59.4	47.3	2.85	0.98	3.46	0.90
Acetylene	17.3	11.6	49.9	48.1	2.25	0.74	2.73	0.85
Propane	56.0	40.0	79.7	59.0	7.41	3.33	5.16	2.40
Propene	7.8	7.5	21.7	20.9	1.00	0.67	1.18	0.52
i-Butane	19.4	14.4	39.0	30.2	2.49	1.05	2.38	0.82
Butane	42.0	31.1	108.8	84.5	5.25	1.71	6.61	1.92
i-Pentane	52.4	38.4	109.9	79.5	6.37	1.34	6.73	0.91
Pentane	24.0	19.3	49.2	36.2	2.89	0.65	3.01	0.42
2-Methylpentane	16.0	11.4	36.6	27.3	1.93	0.37	2.21	0.30
3-Methylpentane	11.8	7.4	27.6	20.8	1.51	0.48	1.68	0.38
Hexane	10.8	7.6	23.8	17.0	1.31	0.29	1.46	0.22
Methylcyclopentane	10.1	7.5	22.3	16.8	1.24	0.29	1.33	0.20
Benzene	17.0	12.0	42.8	33.7	2.07	0.48	2.54	0.44
3-Methylhexane	7.4	5.0	15.4	11.6	0.91	0.24	0.94	0.15
Heptane	6.0	5.2	13.8	10.8	0.70	0.24	0.82	0.20
Methylcyclohexane	7.0	6.5	14.2	10.8	0.84	0.41	0.86	0.28
Toluene	49.1	35.8	115.4	90.5	5.90	1.60	6.84	1.31
Ethylbenzene	7.6	5.8	17.5	13.2	0.90	0.27	1.06	0.16
m- & p-Xylenes	25.2	21.6	64.9	54.1	2.97	1.22	3.74	0.88
o-Xylene	10.0	7.6	23.7	18.6	1.20	0.40	1.40	0.28
1,2,4-Trimethylbenzene	8.2	7.6	24.6	20.8	0.97	0.52	1.43	0.39
Formaldehyde	9.1	5.8	11.1	5.1	1.37	1.12	0.94	0.52
Acetaldehyde	14.8	8.8	13.6	7.0	2.19	1.26	1.27	0.90
Acetone	22.4	11.8	29.2	28.1	3.21	1.63	2.20	2.01
Olefins	65.3	46.0	181	160	8.28	2.40	9.99	2.60
Paraffins	353	229	756	568	44.4	6.91	45.4	6.08
Aromatics	139	104	342	272	16.3	4.81	20.1	3.70
Total Carbonyls	109	63.4	107	50	16.1	9.21	9.93	6.83
Total Unidentified	115	68.3	225	140	14.9	4.63	15.2	3.64
MPAR23	83.7	57.7	136	101	11.0	4.12	8.63	3.31
MPAR45	138	97.8	307	225	17.0	3.62	18.7	3.38
MPAR6	135	90.7	305	220	16.6	2.88	18.6	2.20
MTOLEF	17.1	16.3	44.7	40.7	2.11	1.15	2.50	0.86
MIOLEF	7.3	6.7	22.1	22.0	0.90	0.48	1.21	0.50
MONAROM	58.4	42.6	137	107	7.01	1.88	8.12	1.47
DIAROM	59.3	49.6	153	125	7.05	2.80	8.96	1.93
NMOC	783	433	1580	1069				
NMHC	674	418	1470	1060				

[a] San Nicolas Island data excluded. Data from other sites only includes 0700, 1200, and 1600 PDT samples.
[b] Long Beach data excluded. Data from other sites only includes 0700, 1200, and 1600 PST samples.

Figure 3-15 compares basinwide mean fractions of NMOC in summer and fall for the abundant species. These data show the summer and fall carbon fractions of most of the abundant species were similar. The propane, ethane, formaldehyde, acetaldehyde, and acetone carbon fractions were higher in summer than in fall, while the n-butane, ethene, benzene, toluene, m- & p-xylene, and 1,2,4-trimethylbenzene fractions were higher in fall than in summer. The individual species data are consistent with the trend toward higher aromatic hydrocarbons and lower carbonyl compounds in fall. The largest seasonal differences were in propane which was 5.2% and 7.4% of NMOC in fall and summer, and in n-butane which was 6.6% and 5.2% in fall and summer, respectively. The seasonal difference in n-butane is consistent with fuel composition changes, however, neither the seasonal difference in propane nor n-butane's high abundance are adequately understood.

Examination of the variance in the concentrations and carbon fractions reveals a fairly consistent picture. For most of the species, the coefficient of variation (COV = standard deviation divided by the mean) is between 0.6 and 0.8 for ambient concentrations. For the carbon fractions of NMOC, the coefficients of variation are much smaller: between 0.2 and 0.5 for most species. Hence, while concentrations vary significantly from day to day and site to site, the relative contributions of the abundant species to NMOC varies little. NMOC composition was fairly consistent throughout the SCAQS.

3.4.3 Temporal Variability

The basinwide average concentrations and standard deviations for abundant species and compound groups by time of day are shown in Tables 3-6 and 3-7. The summer data show concentrations of the abundant paraffins, olefins, and aromatic hydrocarbons decreased substantially between 0700 and 1200, and decreased by a small amount between 1200 and 1600. The diurnal profile of toluene is typical of the summer pattern; the mean toluene concentrations were 68, 45, and 34 ppbC at 0700, 1200, and 1600, respectively. The fall data show concentrations of the abundant paraffins, olefins, and aromatic hydrocarbons decreased substantially between 0700 and 1200, and increased by a small amount between 1200 and 1600. Isopentane's diurnal profile is typical of other paraffins in the fall; the mean isopentane concentrations were 179, 68, and 79 ppbC at 0700, 1200,and 1600, respectively.

The carbonyl species exhibited a different diurnal pattern. The mean formaldehyde concentrations in summer were 6.8, 11.5, and 9.1 ppb at 0700, 1200, and 1600 and the mean acetaldehyde concentrations were 8.4, 20.1, and 15.8 ppbC at 0700, 1200, and 1600, respectively. The summer acetone data followed this same pattern. In the fall, the mean formaldehyde concentrations were 11 ppb at all three sampling times while the mean acetaldehyde concentrations were 9.9, 16.1, and 15.0 ppbC at 0700, 1200, and 1600, respectively. The fall acetone concentrations were about 29 ppbC at all three sampling times. If one assumes the carbonyl emissions follow approximately the same diurnal pattern as hydrocarbons, the diurnal pattern of ambient carbonyl compounds strongly suggests their primary origin is hydrocarbon oxidation rather than direct emissions.

The basinwide mean NMOC composition by time of day is shown in Figure 3-16 and Tables 3-8 and 3-9. To facilitate a direct comparison between

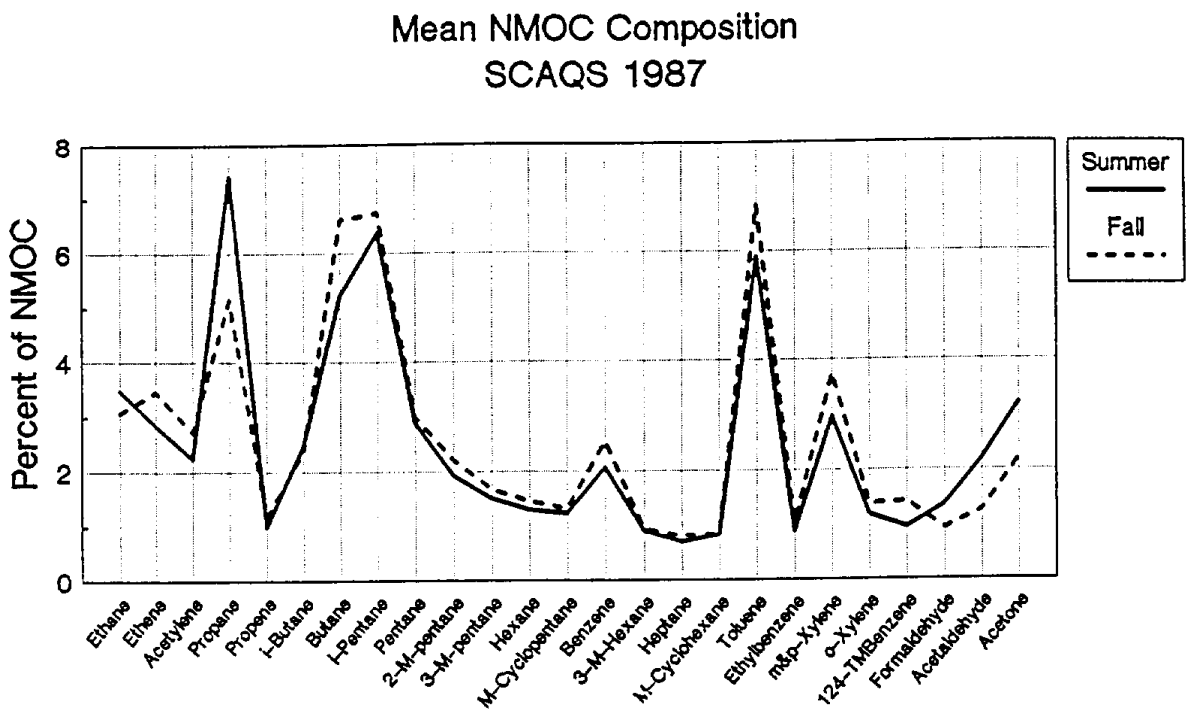


Figure 3-15. Mean Percent NMOC Composition of Morning Summer and Fall SCAQS Data.

Table 3-6. Mean Concentration of Abundant Species and Species Groups for Summer Surface Data From the SCAQS 1987

Time (PST):	600	600	1100	1100	1500	1500
	Concentration, ppbC					
	Mean	Standard Deviation	Mean	Standard Deviation	Mean	Standard Deviation
Ethane	37.1	24.3	25.8	18.1	19.1	10.4
Ethene	33.6	18.1	18.6	11.4	15.5	6.9
Acetylene	24.4	15.0	15.4	9.4	12.7	5.1
Propane	61.6	42.7	61.0	46.0	45.4	27.0
Propene	14.0	9.6	5.1	3.7	4.4	2.6
i-Butane	23.3	18.3	20.2	13.8	14.5	8.2
Butane	53.0	39.1	41.9	27.1	31.2	20.8
i-Pentane	68.5	48.8	52.0	35.8	36.8	17.2
Pentane	33.1	26.0	22.8	16.0	16.0	7.4
2-Methylpentane	22.1	14.3	14.9	10.2	10.9	5.0
3-Methylpentane	15.1	9.2	10.9	6.6	9.3	4.7
Hexane	15.1	9.4	10.0	6.8	7.2	3.1
Methylcyclopentane	14.8	9.3	9.1	6.2	6.6	2.7
Benzene	23.9	14.8	15.3	10.5	11.9	5.4
3-Methylhexane	10.0	5.7	6.9	4.9	5.3	2.9
Heptane	8.5	5.8	5.7	5.6	3.8	2.1
Methylcyclohexane	9.5	7.0	6.8	7.8	4.6	2.7
Toluene	68.2	43.0	44.8	33.6	34.4	17.2
Ethylbenzene	11.3	7.2	6.5	4.8	5.0	2.3
m- & p-Xylenes	42.4	26.6	18.6	14.3	14.7	7.6
o-Xylene	15.4	9.3	8.1	5.7	6.4	3.2
1,2,4-Trimethylbenzene	14.3	9.2	5.3	4.3	4.9	3.6
Formaldehyde	6.8	4.2	11.5	6.3	9.1	5.7
Acetaldehyde	8.4	4.6	20.1	8.6	15.8	8.2
Acetone	17.9	10.1	25.7	12.5	23.4	11.5
Olefins	102	59.0	52.4	28.1	43.6	16.9
Paraffins	465	283	345	214	257	119
Aromatics	209	129	115	81.8	90.8	43.2
Total Carbonyls	63.2	31.2	139	62.4	124	63.4
Total Unidentified	139	71.6	116	71.2	90.7	52.1
NMOC	972	517	771	414	607	251
NMHC	908	503	631	371	483	209
MPAR23	101	63.4	87.3	64.1	64.4	36.7
MPAR45	178	127	137	86.2	98.5	49.0
MPAR6	184	108	126	85.0	95.6	43.7
MTOLEF	30.5	21.2	11.8	8.0	9.2	4.7
MIOLEF	11.7	8.9	5.3	3.9	4.9	3.5
MONAROM	81.9	51.4	52.8	39.4	40.5	19.9
DIAROM	98.2	61.4	43.8	31.9	36.0	18.8

Table 3-7. Mean Concentration of Abundant Species and Species Groups for Fall Surface Data From the SCAQS 1987

Time (PST):	700	700	1200	1200	1600	1600
	Concentration, ppbC					
	Mean	Standard Deviation	Mean	Standard Deviation	Mean	Standard Deviation
Ethane	86.5	46.9	29.4	21.5	33.1	25.7
Ethene	103	42.6	31.8	24.7	38.9	33.7
Acetylene	94.6	52.3	21.8	13.9	28.6	23.8
Propane	120	62.6	50.1	39.3	66.4	48.2
Propene	43.1	20.9	8.5	8.2	12.2	8.5
i-Butane	58.1	30.2	27.4	25.7	30.3	25.0
Butane	165	93.4	74.5	51.8	83.2	70.8
i-Pentane	179	81.9	67.6	41.4	79.2	54.3
Pentane	82.4	36.6	28.7	17.4	34.6	23.0
2-Methylpentane	61.3	27.6	20.0	11.5	26.8	18.5
3-Methylpentane	46.5	20.8	15.0	9.1	20.2	14.3
Hexane	39.6	15.6	13.1	7.8	17.9	12.6
Methylcyclopentane	38.2	16.4	11.7	7.1	15.9	10.7
Benzene	74.6	34.7	21.3	12.3	30.6	20.0
3-Methylhexane	25.9	11.7	8.4	4.8	11.3	8.0
Heptane	23.7	10.1	7.3	4.8	9.8	8.1
Methylcyclohexane	23.1	10.1	8.6	6.1	10.4	9.5
Toluene	199	91.0	59.7	35.8	82.9	60.6
Ethylbenzene	30.0	13.0	9.1	5.2	12.8	8.6
m- & p-Xylenes	119	52.5	28.2	16.0	44.0	30.2
o-Xylene	41.8	18.1	11.3	6.3	17.0	11.4
1,2,4-Trimethylbenzene	45.5	20.6	9.7	5.2	17.5	11.2
Formaldehyde	11.1	4.2	11.0	5.2	11.3	6.0
Acetaldehyde	9.9	4.0	16.1	6.8	15.0	8.0
Acetone	30.4	23.7	28.7	35.1	28.3	25.6
Olefins	342	147	79.8	54.0	104	88.1
Paraffins	1229	536	444	294	543	476
Aromatics	609	267	162	90.9	239	160
Total Carbonyls	90.8	32.3	120	58.4	111	53.0
Total Unidentified	358	140	134	58.5	175	83.4
NMOC	2560	1051	937	489	1179	724
NMHC	2469	1037	817	453	1067	689
MPAR23	214	99.8	85.1	64.9	102	81.0
MPAR45	485	235	198	133	227	172
MPAR6	507	213	170	95.0	226	157
MTOLEF	87.8	38.0	17.6	13.1	26.2	18.4
MIOLEF	44.9	22.6	7.3	4.7	12.8	8.1
MONAROM	236	107	71.0	42.2	99.0	71.4
DIAROM	277	122	67.0	36.2	106	68.5

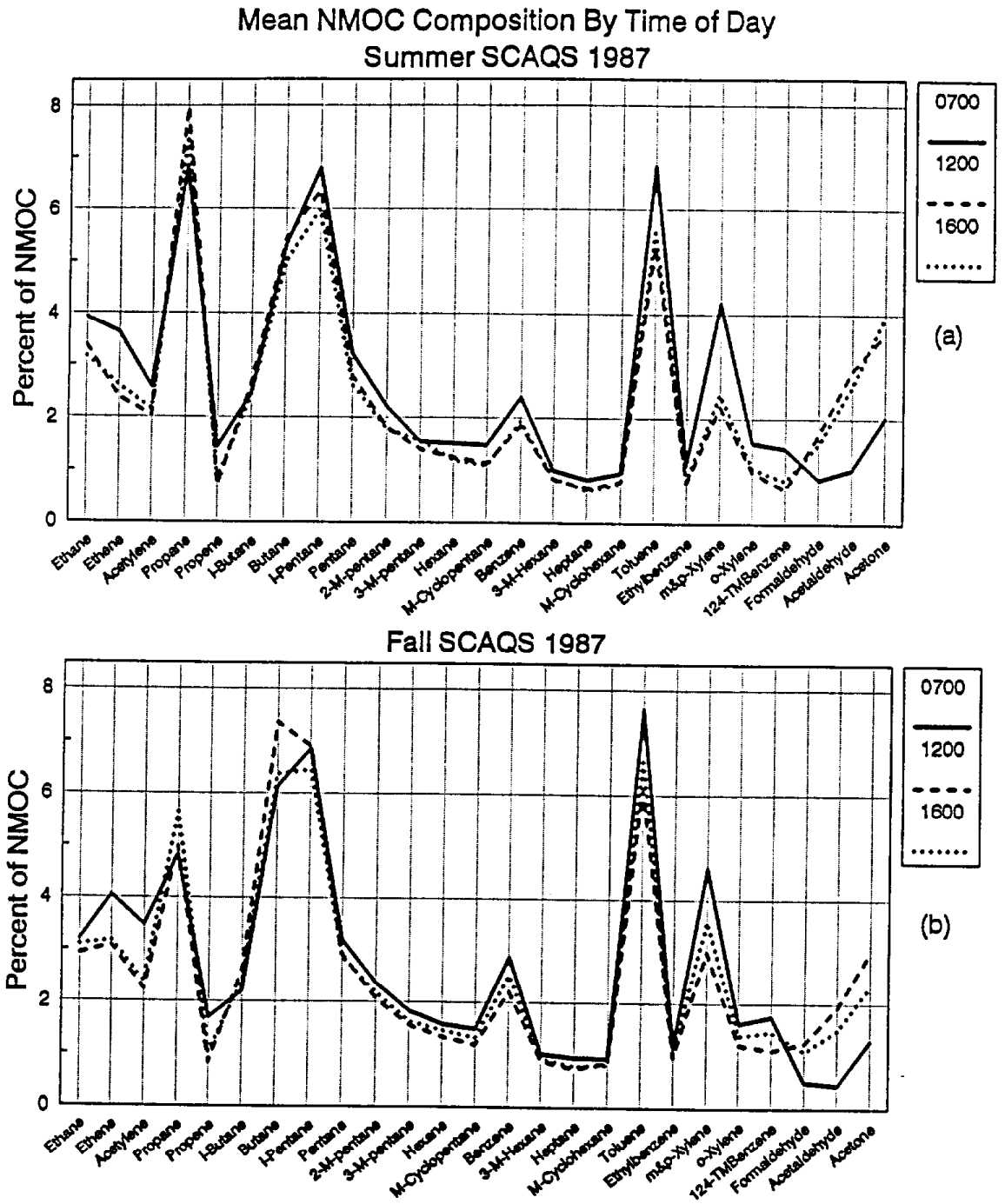


Figure 3-16. Variation of the Mean NMOC Composition During the a) Summer and b) Fall SCAQS by Time of Day.

Table 3-8. Mean Percent of NMOC of Abundant Species and Species Groups for Summer Surface Data From the SCAQS 1987

Time (PST):	600	600	1100	1100	1500	1500
	Percent NMOC					
	Mean	Standard Deviation	Mean	Standard Deviation	Mean	Standard Deviation
Ethane	3.92	1.16	3.38	1.16	3.16	0.95
Ethene	3.63	0.97	2.38	0.59	2.60	0.87
Acetylene	2.58	0.89	2.03	0.66	2.15	0.54
Propane	6.83	3.18	7.98	3.80	7.41	2.88
Propene	1.44	0.56	0.71	0.53	0.84	0.69
i-Butane	2.44	1.16	2.63	0.99	2.41	1.00
Butane	5.32	1.55	5.44	1.69	5.00	1.88
i-Pentane	6.78	1.22	6.35	1.64	5.99	0.97
Pentane	3.22	0.72	2.80	0.63	2.63	0.41
2-Methylpentane	2.21	0.31	1.82	0.37	1.78	0.27
3-Methylpentane	1.55	0.34	1.41	0.42	1.57	0.62
Hexane	1.52	0.23	1.25	0.29	1.20	0.19
Methylcyclopentane	1.49	0.22	1.14	0.26	1.10	0.23
Benzene	2.40	0.41	1.86	0.47	1.94	0.36
3-Methylhexane	1.01	0.16	0.84	0.23	0.86	0.21
Heptane	0.83	0.20	0.66	0.30	0.62	0.17
Methylcyclohexane	0.96	0.46	0.79	0.46	0.75	0.26
Toluene	6.82	1.38	5.30	1.52	5.63	1.50
Ethylbenzene	1.12	0.27	0.78	0.24	0.82	0.20
m- & p-Xylenes	4.22	0.90	2.23	0.72	2.46	0.89
o-Xylene	1.55	0.29	1.00	0.27	1.07	0.37
1,2,4-Trimethylbenzene	1.44	0.45	0.65	0.28	0.82	0.45
Formaldehyde	0.85	0.83	1.72	1.22	1.54	1.08
Acetaldehyde	1.04	0.74	2.92	1.12	2.61	0.95
Acetone	2.01	1.13	3.64	1.51	3.97	1.49
Olefins	10.5	2.08	6.95	1.38	7.51	2.02
Paraffins	47.2	5.91	43.9	7.73	42.3	6.11
Aromatics	20.4	4.11	13.7	3.56	14.7	3.84
Total Carbonyls	7.52	4.09	20.3	8.36	20.5	7.62
Total Unidentified	14.6	3.50	15.0	5.60	14.9	4.59
MPAR23	10.9	3.99	11.4	4.75	10.6	3.59
MPAR45	17.7	3.74	17.2	3.91	16.0	2.93
MPAR6	18.6	2.17	15.6	2.92	15.8	2.45
MTOLEF	3.04	0.85	1.60	0.97	1.71	1.00
MIOLEF	1.12	0.40	0.75	0.51	0.85	0.45
MONAROM	8.15	1.66	6.26	1.76	6.63	1.68
DIAROM	9.75	2.19	5.39	1.64	6.07	2.27

Table 3-9. Mean Percent of NMOC of Abundant Species and Species Groups for Fall Surface Data From the SCAQS 1987

Time (PST):	700	700	1200	1200	1600	1600
	Percent of NMOC					
	Mean	Standard Deviation	Mean	Standard Deviation	Mean	Standard Deviation
Ethane	3.20	0.82	2.93	1.18	3.10	1.15
Ethene	4.05	0.89	3.09	0.88	3.18	0.61
Acetylene	3.47	0.83	2.24	0.59	2.38	0.40
Propane	4.83	2.08	4.98	2.41	5.64	2.69
Propene	1.69	0.53	0.83	0.36	1.02	0.25
i-Butane	2.20	0.60	2.58	1.15	2.38	0.67
Butane	6.13	1.40	7.36	2.16	6.37	1.99
i-Pentane	6.86	0.65	6.90	1.25	6.46	0.72
Pentane	3.20	0.35	2.93	0.53	2.87	0.30
2-Methylpentane	2.37	0.24	2.07	0.32	2.19	0.28
3-Methylpentane	1.83	0.34	1.56	0.43	1.63	0.38
Hexane	1.58	0.20	1.34	0.20	1.46	0.22
Methylcyclopentane	1.49	0.14	1.19	0.20	1.31	0.16
Benzene	2.87	0.34	2.21	0.41	2.52	0.35
3-Methylhexane	1.01	0.15	0.88	0.15	0.92	0.12
Heptane	0.94	0.16	0.73	0.21	0.78	0.14
Methylcyclohexane	0.93	0.27	0.85	0.32	0.80	0.22
Toluene	7.65	1.02	6.12	1.34	6.64	1.09
Ethylbenzene	1.16	0.13	0.96	0.14	1.04	0.15
m- & p-Xylenes	4.61	0.55	3.00	0.50	3.59	0.67
o-Xylene	1.62	0.20	1.20	0.20	1.39	0.25
1,2,4-Trimethylbenzene	1.75	0.31	1.10	0.28	1.46	0.30
Formaldehyde	0.50	0.24	1.25	0.40	1.09	0.55
Acetaldehyde	0.44	0.18	1.94	0.74	1.50	0.81
Acetone	1.29	0.96	3.01	2.76	2.35	1.59
Olefins	12.9	1.30	8.13	1.37	8.66	1.66
Paraffins	46.7	2.87	44.8	8.49	44.7	5.81
Aromatics	23.5	2.65	17.1	2.54	19.6	2.71
Total Carbonyls	4.05	1.73	14.8	6.74	11.3	5.80
Total Unidentified	14.4	2.40	15.4	4.43	15.9	3.82
MPAR23	8.39	2.75	8.44	3.67	9.13	3.67
MPAR45	18.4	2.22	19.7	4.49	18.1	2.99
MPAR6	19.9	1.85	17.6	2.26	18.4	2.00
MTOLEF	3.42	0.53	1.86	0.52	2.17	0.54
MIOLEF	1.70	0.31	0.79	0.26	1.12	0.39
MONAROM	9.07	1.13	7.31	1.47	7.93	1.27
DIAROM	10.7	1.30	7.28	1.23	8.83	1.54

the fall and summer data, the "summer" abundant species are shown on both plots. For many of the abundant species, the diurnal variations in their contributions to NMOC are small. The summer and fall data show that the fractions of ethene, propene, m- & p-xylene, o-xylene, and 1,2,4 trimethylbenzene, which are the most reactive species on the list, decrease significantly between 0700 and 1200 and increase slightly between 1200 and 1600. The data for propene are a good example of this pattern; propene's contributions to NMOC are 1.44%, 0.71%, and 0.84% in summer and 1.69%, 0.83%, and 1.02% in the fall at 0700, 1200, and 1600, respectively. In summer, fractions of all other abundant hydrocarbons except propane are lower at 1200 and 1600 than 0700, and correspondingly, the fractions of formaldehyde, acetaldehyde, and acetone are higher in the and afternoon than the morning. The diurnal variations in the NMOC fractions of the less reactive species, such as ethane, acetylene, n-butane, isopentane, toluene, and benzene are smaller than the more reactive species. For example, the toluene contributions were 6.82%, 5.30%, and 5.63% and the isopentane contributions were 6.78%, 6.35%, and 5.99% at 0700, 1200, and 1600, respectively, in summer. The contributions of ethane, which is the least reactive species on the list, were 3.92%, 3.38%, and 3.16% at 0700, 1200, and 1600, respectively, in summer.

The diurnal patterns of abundant species concentrations and NMOC composition follow those for NMOC and the major NMOC groups. The detailed data suggest there are significant quantities of fresh emissions occurring between 1200 and 1600, because the 1600 composition is between that observed at 0700 and 1200, and ambient concentrations of most species are higher at 1600 than 1200 in the fall. This is consistent with the expected diurnal pattern in emissions that shows an increase in emissions starting around 1600 from the evening traffic activity.

The diurnal variation in the NMOC composition presumably reflect both diurnal variations in NMOC emissions composition and the effects of atmospheric oxidation of the hydrocarbons and formation of carbonyl compounds. If the data for abundant species are examined as a percentage of NMHC (see Table 3-10), rather than NMOC (which eliminates the large diurnal change in carbonyl compounds), the fractions are more revealing in terms of processes. The NMHC fractions for the more reactive species show significant decreases during the morning hours (similar to the NMOC fractions), however, the less reactive species show a mixture of increases and decreases. The NMHC fractions for n-butane and isopentane, which are major constituents of gasoline evaporation, increase in the middle of the day, while the NMHC fractions of other less reactive compounds show small decreases. Mobile source evaporative emissions are expected to vary with temperature and reach a maximum in the afternoon. Hence, the NMHC composition data show evidence of enhanced evaporative emissions and differential rates of oxidation of the more and less reactive species.

3.4.4 Day-by-Day Diurnal Variability

As discussed in Section 3.1.2, the NMOC levels and the diurnal pattern of NMOC on any day may deviate by large amounts from the mean diurnal pattern because of the controlling influence of meteorology. Nevertheless, because the abundant species' contributions to NMOC are so consistent, the day to day variations of most abundant species track the day to day variations in NMOC

Table 3-10. Mean Percent of NMHC by Time of Day for Selected Species

Species	Summer (PDT)			Fall (PST)		
	0700	1200	1600	0700	1200	1600
More Reactive:						
Ethene	3.93	3.00	3.24	4.21	3.61	3.67
Propene	1.55	0.89	1.02	1.75	0.97	1.14
m&p-Xylene	4.54	2.78	3.05	4.79	3.52	4.02
o-Xylene	1.67	1.25	1.33	1.68	1.41	1.52
1,2,4-Trimethylbenzene	1.54	0.81	1.01	1.82	1.30	1.63
Less Reactive:						
Ethane	4.22	4.27	4.00	3.22	3.41	3.58
Acetylene	2.72	2.60	2.71	3.60	2.64	2.75
Benzene	2.59	2.35	2.45	2.98	2.58	2.83
n-Butane	5.72	6.84	6.35	6.37	8.57	7.14
Isopentane	7.29	7.94	7.54	7.14	8.07	7.26
Toluene	7.35	6.65	7.06	7.95	7.14	7.46

concentrations well. However, there are a few exceptions. The summer formaldehyde fractions and the fall acetone fractions have high coefficients of variation (>0.8). It is not clear whether the variance is real (and due to differences in levels of photochemical activity) or the variance is indicative of an analytical problem.

The day-by-day diurnal variability of all of the identified species' contributions to NMOC were examined and, as expected, the coefficients of variation in carbon fractions were small (<0.50) for most abundant species. However, the variance was often large for the less abundant species. Table 3-11 lists the within-day coefficient of variance for all of the species that had more than one day with coefficients of variation greater than one. There is a fairly strong relationship between the number of days with high variance and the mean concentration of the species in summer. As Figure 3-17 shows, the within-day variance of hydrocarbons increases dramatically as the mean concentrations decrease below about 1 ppbC. The detection limit for most of the hydrocarbons was about 0.2 ppbC, so much of this variance may be due to the analytical limitations. The accuracy is low near the detection limit and the carbon in these small peaks may be assigned to the correct species in some samples and lumped with the unidentified in other samples, creating the appearance of high variance.

Table 3-11 also shows that many of the highly variable species were highly reactive olefins and carbonyl compounds. Carbonyl compounds are formed primarily from photochemical reactions of olefins. Carbonyl compounds are also directly emitted and are destroyed by photolysis and oxidation. The high within-day variance in olefins is probably due to their fast reaction rates. Many of the olefins were detected only in the morning samples; later in the day their reactions may be fast enough that they are oxidized to levels below the detection limits. Carbonyl levels were low relative to NMOC in the morning, while later in the day they represented a substantial portion of the NMOC. Hence, the high within-day variance of these species is consistent with known processes and is probably not an artifact of analytical limitations. In contrast, the high variability in heavier paraffins and aromatic hydrocarbons is probably analytical.

3.4.5 Spatial and Temporal Variability

The mean concentrations of abundant species and their mean contributions to NMOC at each site and sampling time are shown in Figures 3-18 through 3-21. Detailed tabulations of these data, including their standard deviations, are presented in Appendix D, Tables D-1 through D-29. The mean coefficients of variation of the carbon fractions at each sampling time are shown in Table 3-12.

The spatial variation in NMOC composition was small or modest, and consistent for the three sampling periods of the day. The spatial variance in abundant species' contributions to NMOC varied by species, sampling time, and season. The contributions of ethane, ethene, propene, propane, isobutane, n-butane, isopentane, methylcyclohexane, toluene, xylenes, 1,2,4-trimethylbenzene, formaldehyde, acetaldehyde, and acetone to NMOC were more spatially-varying than those for other abundant species. In addition, there

Table 3-11. Species With a Standard Deviation Greater Than the Mean for the Fraction of NMOC During the SCAQS 1987

Species	Mean[a] Conc. ppbC	June 19	June 24	June 25	July 13	July 14	July 15	August 27	August 28	August 29	September 2	September 3	November 11	November 12	November 13	December 3	December 10	December 11
1,3-Butadiene	1.0	x	x		x			x		x		x	x					
t-2-Butene	1.0	x	x	x	x					x								
c-2-Butene	0.9	x			x	x	x											
3-Methylbutene-1	0.5			x	x					x		x						
Pentene-1	1.8	x				x					x	x			x			
2-Methylbutene-1	1.7		x					x		x	x	x						
Isoprene	1.4	x					x		x	x	x	x		x				
c-2-Pentene	0.9	x					x					x						
2,2-Dimethylbutane	0.3	x	x		x	x	x	x	x	x	x	x	x			x	x	
C6 Olefin	0.3	x		x	x		x		x	x	x	x						
C6 Olefin	0.3	x			x	x	x	x	x	x		x	x					
C7 Olefin	0.2	x	x	x	x	x		x	x	x	x	x	x	x		x		x
2-Methyl-2-pentene	0.4	x	x	x			x	x	x	x		x					x	
C7 Olefin	<0.1	x	x	x	x	x	x	x	x	x	x		x	x		x	x	x
3-Methyl-2-pentene	0.1	x	x	x	x	x	x	x		x	x		x	x	x	x		
3,3-Dimethylpentane	0.5	x		x	x			x	x				x					
C7 Paraffin	2.5								x	x								
C8 Olefin	1.2	x	x	x					x	x					x			x
2,2,5-Methylhexane	1.1		x	x	x		x		x	x	x							
2,5-Dimethylheptane	0.4	x		x	x	x	x			x	x	x		x	x	x	x	x
C9 Paraffin	0.1	x	x	x	x		x			x		x		x	x	x	x	x
C9 Paraffin	0.3	x	x	x	x		x	x		x		x	x		x		x	x
Styrene	3.3									x			x	x				
Nonene-1	0.2	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x
C9 Paraffin	0.2	x	x			x	x	x		x	x	x	x					
C10 Paraffin	0.6							x	x			x			x	x	x	x
C10 Paraffin	<0.1		x	x					x		x		x	x	x	x	x	x
C9 Aromatic	2.2	x	x	x														
C9 Aromatic	0.9	x	x	x	x	x	x	x	x	x	x	x						
C10 Paraffin	1.6	x	x	x					x			x	x				x	
o-Ethyltoluene	2.5		x	x														
Decane	2.5		x	x	x			x										
C10 Aromatic	1.9	x	x	x	x													
C6 Alkane	1.7		x				x								x	x	x	x
Formaldehyde*	9.0						x	x		x								
Propanal	5.1	x				x			x		x			x			x	x
Methyl ethyl ketone	10.4	x			x	x	x						x	x				
Butanal	4.4	x	x		x		x	x	x	x	x	x	x	x	x	x	x	x
Pentanal	14.9			x				x					x	x		x	x	x
C5 carbonyl	10.8	x	x		x	x	x	x	x		x	x	x	x	x	x	x	x
C6 carbonyl	9.6				x	x			x	x								
C7 carbonyl	4.5	x	x	x	x	x	x	x	x	x	x	x	x	x	x			x

* Species is one of the 25 most abundant.

[a] Summer Data.

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13. ABSTRACT (Maximum 200 words)

This Study undertook a detailed analysis of ambient hydrocarbon and carbonyl compound data collected i the 1987 So. CA air Quality Study (CSAQS). The objectives were to characterize spatial and temporal patterns of total and individual nonmethane organic compound (NMOC) concentrations and NMOC to NOx rat in California's So. Coast Air Basin, to assess the consistency between ambient data and emission inventory estimates of NMOC, and to examine the extent of NMOC oxidation and carbonyl compound formati occurring in the atmosphere. The study found that NMOC composition and NMOC to NOx ratios were fairly similar throughout the Basin However, the total NMOC concentrations had significant spatial, day-to-d and seasonal variations due to meterorological factors and the non-uniformity of emission rates. Discrepancies between ambient concentration and emission inventory ratios of NMOC to NOx and CO to NO indicate the motor vehicle inventories underestimated NMOC and CO emissions. Problems with emission estimates of other sources may also contribute to the discrepancy, but there were too few tracer spec for non-motor vehicle emissions to identify unique source signatures. There were also discrepancies between the organic composition of ambient data and emission estimates. There appeared to be a large amount of carbonyl species formation in the urban atmosphere from photo-oxidation of hydrocarbons. The photochemical sources of C1 to C4 carbonyl compounds are probably larger than the emission source while the sources of C4+ carbonyl compounds could not be identified.

14. SUBJECT TERMS
Ambient nonmethane hydrocarbon concentration data, ambient carbonyl compound concentration data, NMOC speciation, CO, NOx, emission inventory uncertainty and underestimation, South Coast Air Basin, Los Angeles.

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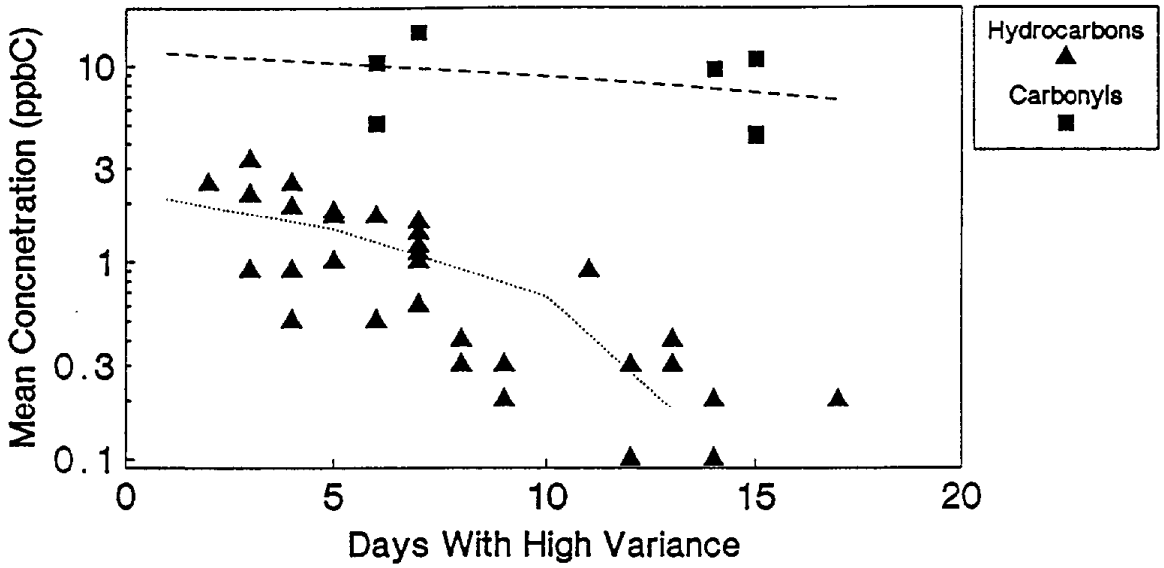


Figure 3-17. Mean Concentrations of Hydrocarbons and Carbonyl Compounds on Days with High Variance in Concentration (Standard Deviation/Mean > 1).

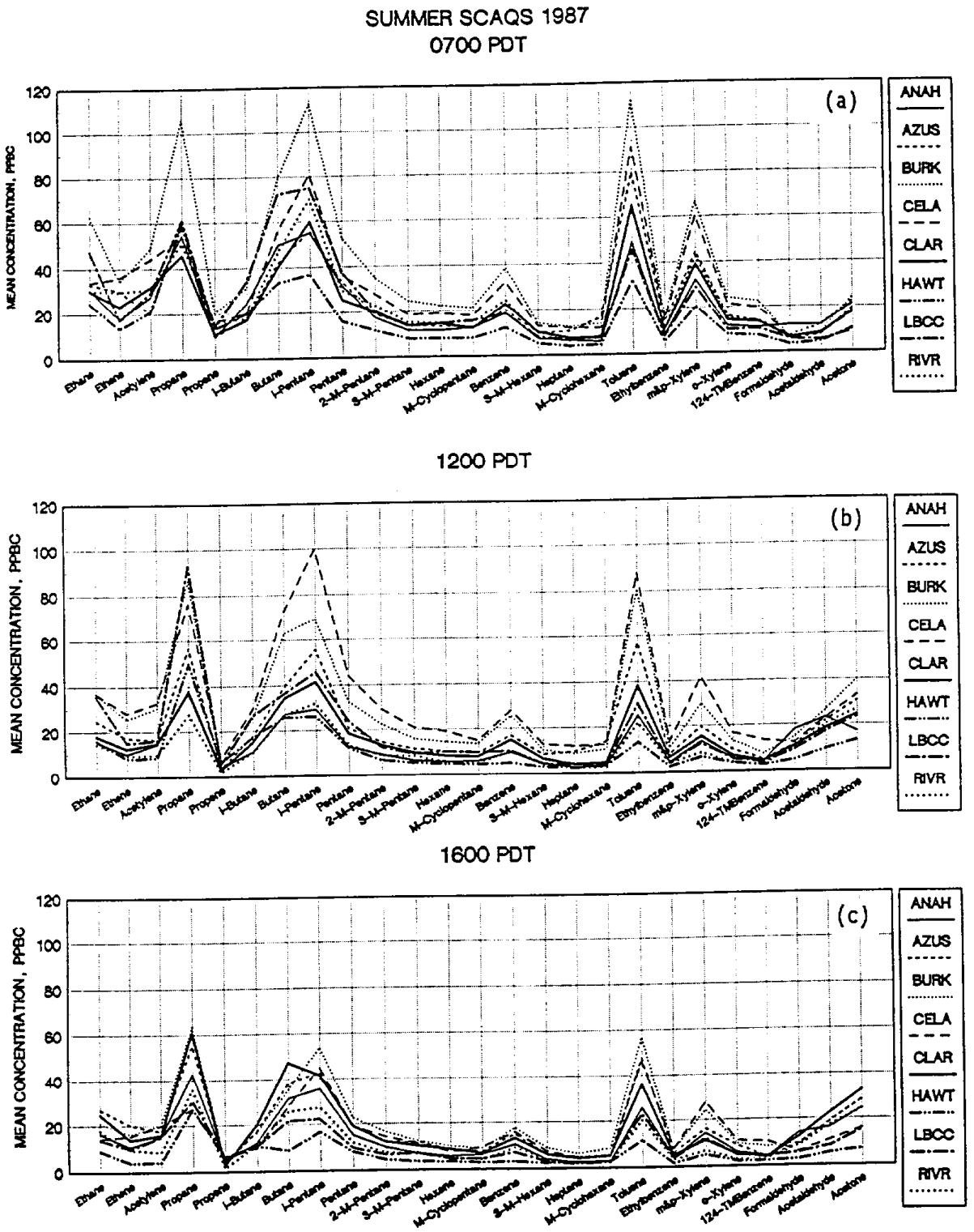


Figure 3-18. Variation of the Mean NMOC Concentrations by Site During the Summer SCAQS at a) 0700, b) 1200, and c) 1600 PDT.

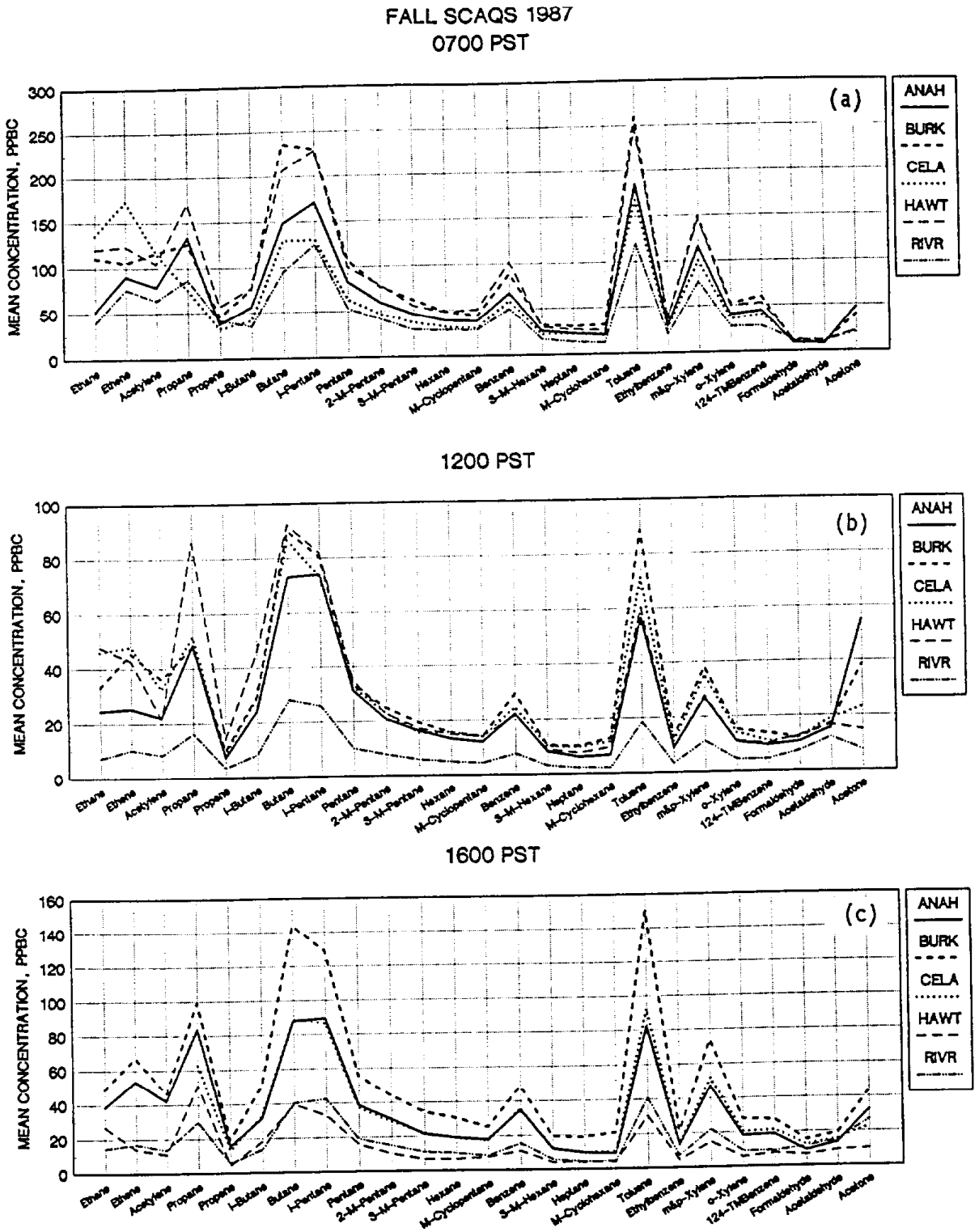


Figure 3-19. Variation of the Mean NMOC Concentrations by Site During the Fall SCAQS at a) 0700, b) 1200, and c) 1600 PST.

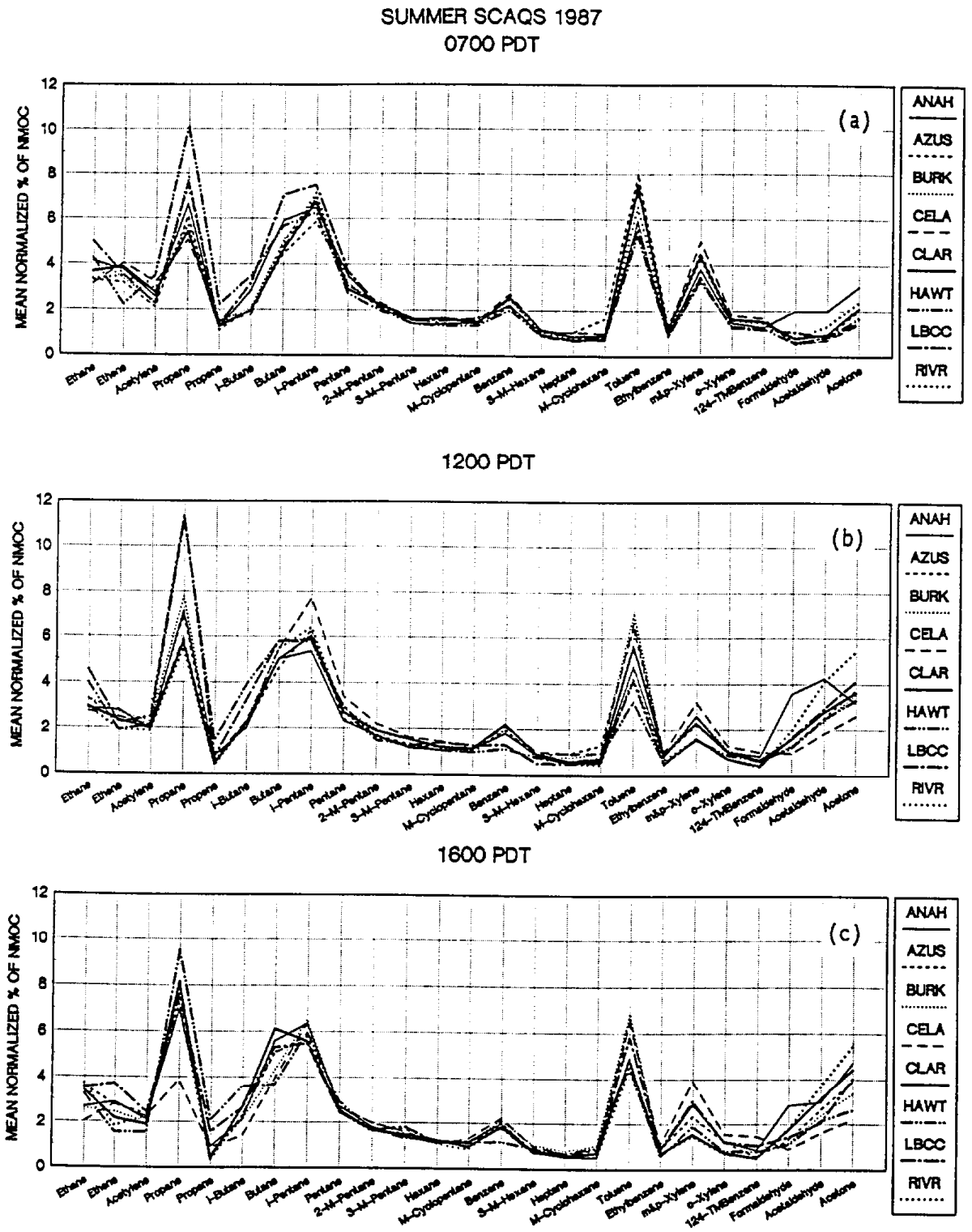


Figure 3-20. Variation of the Mean NMOC Composition by Site During the Summer SCAQS at a) 0700, b) 1200, and c) 1600 PDT.

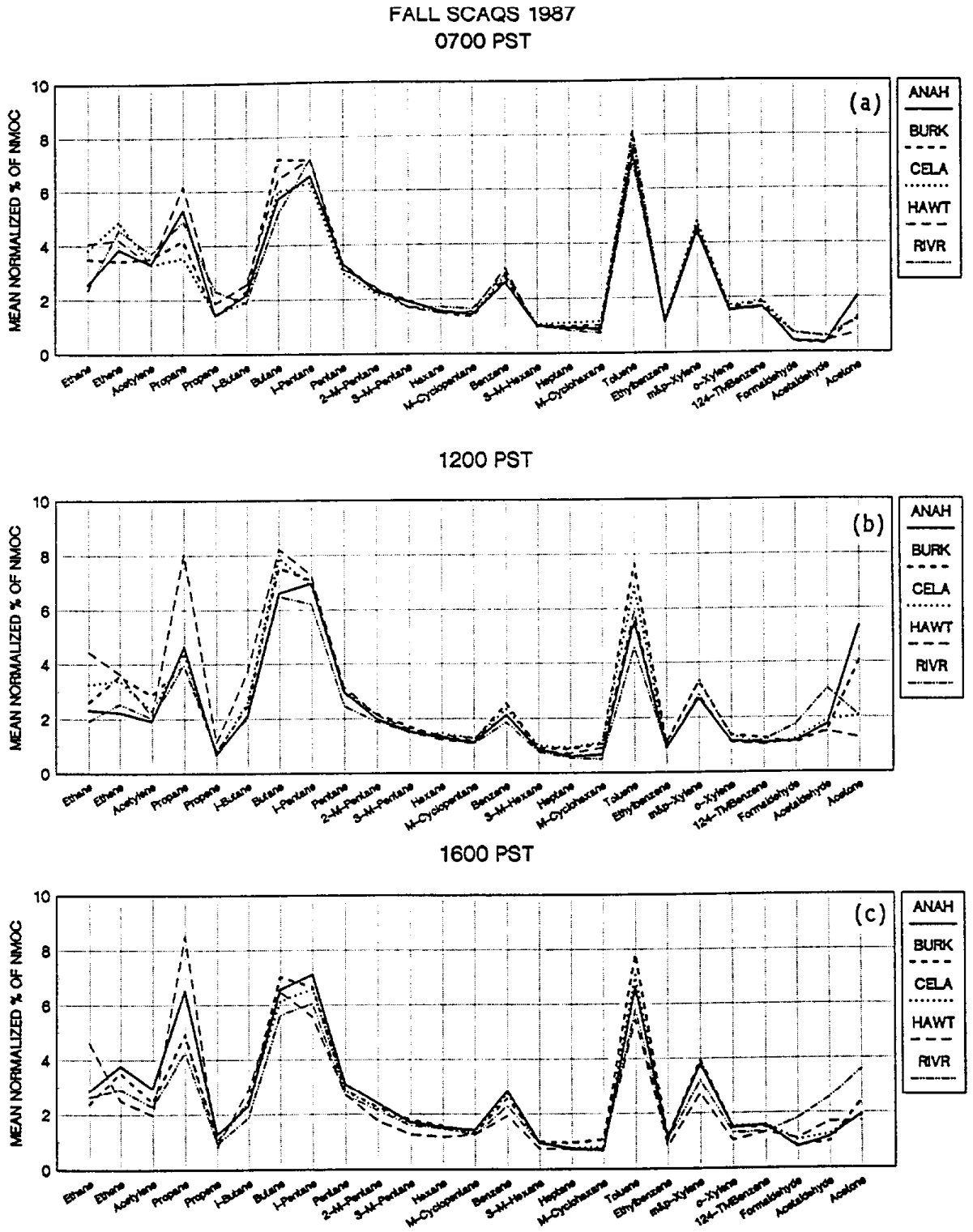


Figure 3-21. Variation of the Mean NMOC Composition by Site During the Fall SCAQS at a) 0700, b) 1200, and c) 1600 PDT.

Table 3-12. Coefficients of Variation in Abundant Species' Contributions to NMOC

Species	Summer			Fall		
	700	1200	1600	700	1200	1600
Ethane	0.654	0.701	0.545	0.543	0.732	0.777
Ethene	0.537	0.616	0.445	0.414	0.777	0.868
Acetylene	0.612	0.614	0.405	0.553	0.639	0.830
Propane	0.694	0.754	0.594	0.521	0.784	0.726
Propene	0.690	0.729	0.601	0.486	0.965	0.694
i-Butane	0.785	0.680	0.565	0.520	0.938	0.824
Butane	0.739	0.646	0.666	0.565	0.695	0.851
i-Pentane	0.712	0.689	0.468	0.458	0.613	0.685
Pentane	0.787	0.700	0.462	0.444	0.607	0.663
2-Methylpentane	0.645	0.685	0.457	0.450	0.575	0.688
3-Methylpentane	0.604	0.610	0.503	0.447	0.611	0.707
Hexane	0.621	0.676	0.423	0.394	0.592	0.706
Methylcyclopentane	0.631	0.686	0.412	0.428	0.603	0.670
Benzene	0.622	0.687	0.453	0.465	0.576	0.655
3-methylhexane	0.575	0.715	0.541	0.450	0.574	0.710
Heptane	0.678	0.980	0.540	0.427	0.651	0.820
Methylcyclohexane	0.735	1.143	0.578	0.437	0.709	0.908
Toluene	0.630	0.751	0.498	0.458	0.601	0.731
Ethylbenzene	0.637	0.728	0.469	0.432	0.574	0.676
m&p-Xylene	0.627	0.771	0.519	0.440	0.566	0.685
o-Xylene	0.602	0.701	0.499	0.434	0.556	0.673
1,2,4-Trimethylbenzene	0.646	0.809	0.723	0.454	0.538	0.643
Formaldehyde	0.622	0.546	0.626	0.374	0.475	0.530
Acetaldehyde	0.550	0.425	0.518	0.404	0.425	0.535
Acetone	0.566	0.486	0.489	0.778	1.223	0.904

was generally greater spatial variability in the summer than fall, and in the middle of the day than in the morning or late afternoon.

Notable features of the NMOC composition data are as follows:

- Propane was the most abundant species in summer and one of the most spatially-varying species in summer and fall. Hawthorne had consistently higher propane fractions of NMOC than elsewhere. Los Angeles had the lowest propane fractions of NMOC. Long Beach, which was thought to be influenced by the same types of stationary sources that influence Hawthorne, did not have disproportionately high propane levels.

- Propene had fairly high spatial variance in summer and fall. The propene contributions to NMOC were higher at Hawthorne than other stations in the summer. There was no consistent pattern in the fall; the highest propene fractions of NMOC at 0700, 1200, and 1600 were observed at Riverside, Hawthorne, and Anaheim, respectively. It is possible that the high propene and propane components at Hawthorne are from emissions of liquid petroleum gas (LPG) since these species are both present in significant quantities in LPG.

- Ethane, isobutane, n-butane, and isopentane had significant spatial variations in their contributions to NMOC, yet these species did not exhibit a consistent spatial pattern. The highest isopentane fractions were seen at Los Angeles and Long Beach.

- Methylcyclohexane exhibited high spatial variance. The relative abundance of methylcyclohexane was consistently higher at Los Angeles and Burbank than elsewhere.

- Toluene, m- & p-xylene, and 1,2,4-trimethylbenzene showed significant spatial variation, especially at 1200 in summer. The highest toluene fractions occurred at Burbank and Los Angeles. The highest m- & p-xylene and 1,2,4-trimethylbenzene fractions occurred at Los Angeles. The high relative abundance of these species and methylcyclohexane at Los Angeles and Burbank suggest the mobile source NMOC contribution may be greater at these sites than elsewhere. Hawthorne often had the lowest toluene and m- & p-xylene fractions. The spatial variations in other aromatic hydrocarbons, such as benzene, o-xylene, ethylbenzene, were slightly smaller than those of toluene and m- & p-xylene.

- Formaldehyde fractions of NMOC were highest at Anaheim and lowest at downtown Los Angeles in the summer. In the fall, Riverside had the highest, and Anaheim had the lowest, formaldehyde fractions of NMOC.

- Acetaldehyde fractions of NMOC were high at Anaheim and Riverside, and low in Los Angeles in the summer. In the fall, Riverside had significantly higher acetaldehyde fractions of NMOC than other sites.

- Acetone fractions of NMOC were high at Anaheim (except 1600) and Riverside, and low in Los Angeles in the summer. In the fall, Anaheim and Riverside had significantly higher acetone fractions of NMOC than

other sites. The spatial variance of acetone was usually high in the fall, but not in the summer.

Notable features of the NMOC concentration data are as follows:

- Like total NMOC, the highest summer concentrations of most abundant species occurred at 0700 while the lowest concentrations occurred at 1600. Typically, the summer concentrations of abundant species were higher at Burbank and downtown Los Angeles than at other sites. The concentrations of most species were lower at Hawthorne, Long Beach, and Riverside than other urban sites. Carbonyl concentrations were lower at coastal sites (Long Beach and Hawthorne) than at eastern basin sites (such as Claremont and Riverside).

- In the fall, concentrations were highest in the early morning at Burbank. The concentrations at Riverside were typically much lower than at other sites at all three time periods shown. Hawthorne concentrations were also low at 1600 PST. The highest concentrations of most species were measured at Burbank, however, the highest ethane and ethene concentrations were observed at Hawthorne and Los Angeles. Higher concentrations of propane were measured at Hawthorne earlier in the day than at other sites.

Overall, the SCAQS NMOC data showed less spatial and temporal variability in composition than expected when the experiment was designed. For many species, the coefficient of variation in carbon fraction of NMOC due to site to site and day to day changes was less than 0.3, which is amazingly low. The spatial consistency in the data support the notions that there is good mixing, or one or more major source types dominate NMOC concentration. The temporal consistency in the data provide support for the hypothesis that there are significant fresh emissions emitted throughout the day in the SoCAB.

3.4.6 Comparison to NMOC Data Collected in Other Areas

It is instructive to compare the NMOC composition in the SoCAB to that in other urban areas. We chose to compare the SCAQS data to NMOC data collected in 41 non-California cities by EPA in the summer of 1984-1986 (Jeffries et al., 1988). The EPA data set is reasonably robust (773 samples) and has been carefully screened for outliers. Figure 3-22 compares the abundant species fractions of NMOC in SCAQS to the 41-city average, where the SCAQS data are from the 0700-0800 sampling period and the EPA data are from the 0600-0900 sampling period. Appendix B shows a comparison of the fractions of all measured species from the summer SCAQS data and the EPA 41-city data. Both the summer and fall hydrocarbon composition profiles from SCAQS compare reasonably well with the EPA composite data. These data suggest there is a common urban NMOC composition in many cities.

The fractions of the most abundant species (shown below) are quite similar, except for propane and n-butane in the summer, and toluene and

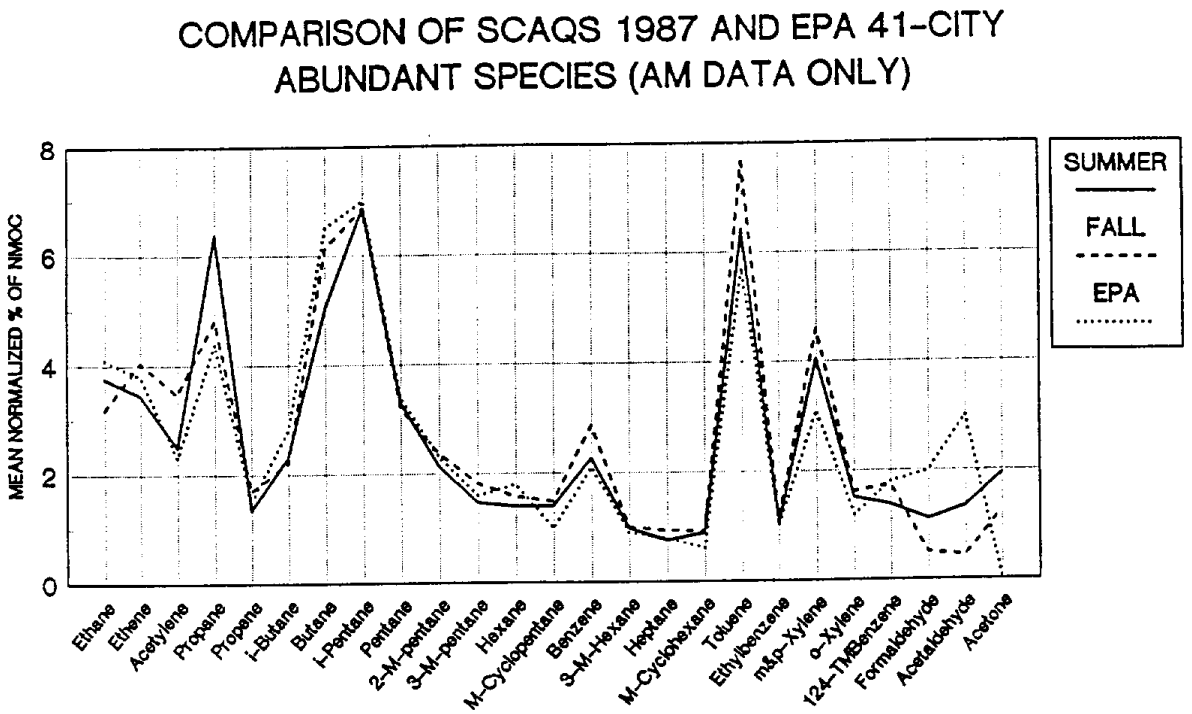


Figure 3-22. Mean Morning Percent NMOC Composition of EPA 41-City Average and SCAQS 0700-0800 Summer (PDT) and Fall (PST) Data.

Species	Percent NMOC Summer SCAQS	EPA 41-Cities	Fall SCAQS
Ethane	3.8	4.1	3.2
Ethene	3.5	3.8	4.1
Propane	6.4	4.4	4.8
n-Butane	5.1	6.5	6.1
Isopentane	6.9	7.0	6.9
Toluene	6.4	5.7	7.6
m- & p-xylene	4.0	3.1	4.6

m- & p-xylene in the fall. The lower n-butane fractions in the SCAQS data are consistent with California's stricter summer gasoline RVP limits. Reasons for the differences in propane and aromatic hydrocarbons are unclear.

The EPA data set did not include carbonyl data and we have shown EPA's recommended fractions of formaldehyde and acetaldehyde for EKMA modeling (Hogo and Gery, 1988) in Figure 3-22. The measured formaldehyde and acetaldehyde fractions in the SoCAB are about half of the EPA's recommended values. In addition, significant amounts of acetone, methyl ethyl ketone (MEK), and C3+ aldehydes were observed in the SoCAB.

Table 3-13 shows a comparison of the composition using the lumped VOC classes of the Carbon Bond 4 (CB4) mechanism and the Carter/Atkinson/Lurmann (CAL) mechanism. These lumped profiles indicate there are smaller fractions of terminal olefins, internal olefins, isoprene, and trialkyl-benzenes in the SoCAB than in the 41-City average. In addition, the measured formaldehyde and acetaldehyde fractions in the SoCAB are about half of the EPA's recommended fractions for EKMA modeling, and there are significant fractions of C3+ aldehydes, acetone, and methyl ethyl ketone.

In order to quantify the implications of these differences, a series of photochemical box model calculations were performed using a trajectory to Glendora on August 24, 1984. The EKMA model was run using the CAL and CB4 chemical mechanisms for four sets of NMOC composition: the 41-city NMOC with EPA-recommended aldehyde levels; the summer SCAQS 0700-0800 NMOC composition; the 41-city NMOC re-normalized for zero carbonyl compounds; and the summer SCAQS 0700-0800 NMOC re-normalized for zero carbonyl compounds. The predicted ozone concentration from the simple 10-hr EKMA simulations with the CAL mechanism are shown in Figure 3-23. The 41-city NMOC composition results in higher predicted ozone than the SCAQS data (0.35 versus 0.32 with carbonyl inputs, and 0.31 versus 0.24 without carbonyl inputs). Comparable results were obtained with the CB4 mechanism. These results suggest the carbonyl differences are probably more significant than the hydrocarbon differences, and the SCAQS composition is somewhat less reactive than the average 41-city mixture.

Table 3-13. Comparison of the Morning NMOC Composition[a] at SCAQS Stations With EPA's 41-City Average Using the CB4 and CAL Lumped VOC Classes

VOC Class	No. Carbons	EPA 41-City Average[b] % NMOC	SCAQS Average[c] % NMOC
CB4:			
ETH	2	3.86	4.20
OLE	2	3.25	2.34
ISOP	5	0.34	0.28
PAR	1	55.36	54.95
TOL	7	9.24	9.60
XYL	8	12.27	10.35
HCHO	1	2.14[d]	1.04
ALD	2	5.06[d]	3.51
NR	1	8.47	13.75
CAL:			
ETH	2	3.86	4.20
PRPE	3	4.59	3.33
TBUT	4	2.51	1.19
ISOP	5	0.34	0.28
ALK4	4.5	20.78	23.47
ALK7	7	28.15	27.22
TOLU	7	8.15	9.60
XYLE	8	8.24	8.75
TMB	9	4.53	1.80
HCHO	1	2.00[d]	1.04
ALD2	2	3.00[d]	1.23
RCHO	3	0.00[d]	2.12
ACET	3	0.00[d]	2.36
MEK	4	0.00[d]	1.03
MISS	1	9.60	6.99
NR	1	4.24	5.41

[a] The composition profiles are based only on the identified species. The unidentified hydrocarbons were 1.2% and 15% of NMOC in the 41 City and SCAQS data, respectively.

[b] Based on the average of 773 6-9 AM samples (Jeffries, et al., 1988).

[c] Based on the average of 84 7-8 AM PDT samples collected at SCAQS stations in the summer. San Nicolas Island data are not included in the average.

[d] The carbonyl fractions for the 41-City average are based on EPA's default recommendations for EKMA modeling (the EPA samples were not analyzed for carbonyls).

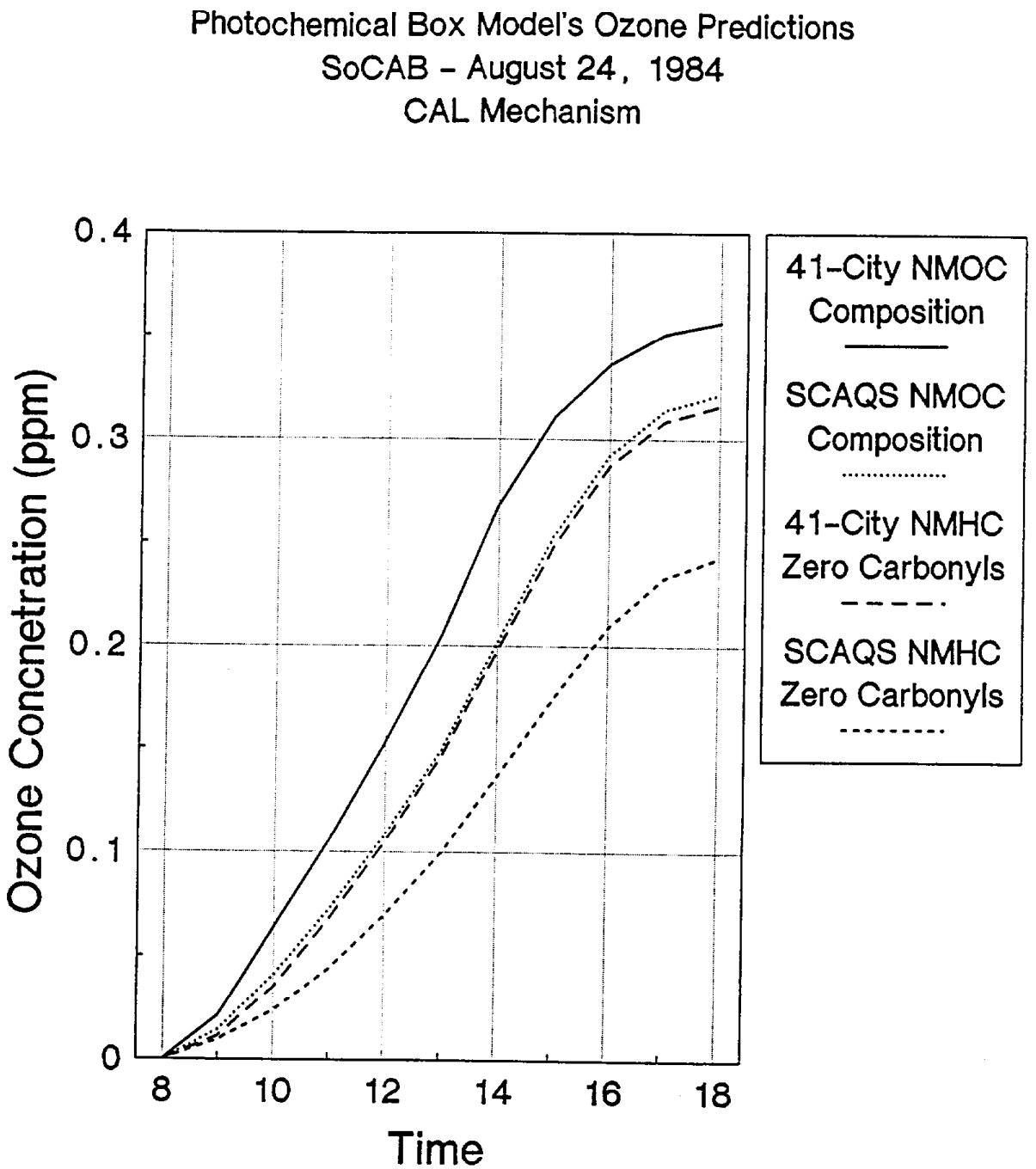


Figure 3-23. Photochemical Box Model's Ozone Predictions for the SoCAB on August 24, 1984 Using the CAL Mechanism. Ozone predictions were made using the EPA 41-city NMOC and summer SCAQS NMOC compositions as well as the 41-city and summer SCAQS data re-normalized with zero carbonyl compounds. Comparable results were obtained with the CB4 mechanism.

3.5 CARBONYL COMPOUND CONCENTRATIONS

The SCAQS program was the first large scale atmospheric study to obtain higher carbonyl data from a network of stations. While the higher carbonyl data may be less certain than the formaldehyde and acetaldehyde data, they provide insight to a part of the NMOC mixture that has previously been ignored. The all-site average composition of the carbonyl species by time of day is shown in Figure 3-24. The carbonyl composition is reported on a carbon basis. The data include three carbonyl peaks (C5, C6, and C7) that could not be reliably identified as individual species, however, it is likely that the C7 is benzaldehyde. The SCAQS data show several important features:

- Acetone was the most abundant carbonyl species in the summer and fall;
- Acetaldehyde and pentanal were the next most abundant species in summer;
- MEK, acetaldehyde, and formaldehyde were the next most abundant species in the fall;
- C4+ carbonyl compounds accounted for a larger fraction of the carbonyls (and NMOC) than expected (48.8% in summer and 45.7% in fall);
- During the summer, the formaldehyde and C6 carbonyl fractions decreased with time of day, while butanal and pentanal fractions increased; and
- Acetone and MEK were proportionately more abundant during the fall than during the summer.

The carbonyl composition was examined as a function of the time of day by site. The composition was consistent between sites with a few exceptions. The MEK fraction was proportionately higher at Azusa, Long Beach, and Riverside than at other sites, and Anaheim's formaldehyde and acetaldehyde fractions were higher than at other sites. In the fall, the C5 carbonyl compounds were more abundant at Riverside than at other sites.

Figures 3-25 and 3-26 show plots of the total NMHC and total carbonyl concentrations for the summer and fall periods, respectively. The data are identified by site and time of day. The summer data show relatively good correlation between NMHC and total carbonyl compounds when the data are stratified by sampling times. The early morning samples have significantly lower carbonyl compound levels relative to NMHC than the midday and afternoon samples. As discussed in Section 3.2, this diurnal pattern of carbonyls suggests there is either a large midday photochemical source or a large midday emission source of carbonyl compounds. We believe photochemical production of carbonyls, especially C1-C4 species, is a more plausible explanation than enhanced midday emissions.

The spatial variation in concentration of carbonyl compounds is illustrated in Figure 3-27, which shows box-whisker plots of the carbonyl concentration at each site during the summer and the fall. In the summer, the median carbonyl concentrations were lowest at the coastal sites (Long Beach and Hawthorne) and highest in the central basin, near Burbank and Azusa. However, the interquartile range (25th to 75th percentile) of concentrations

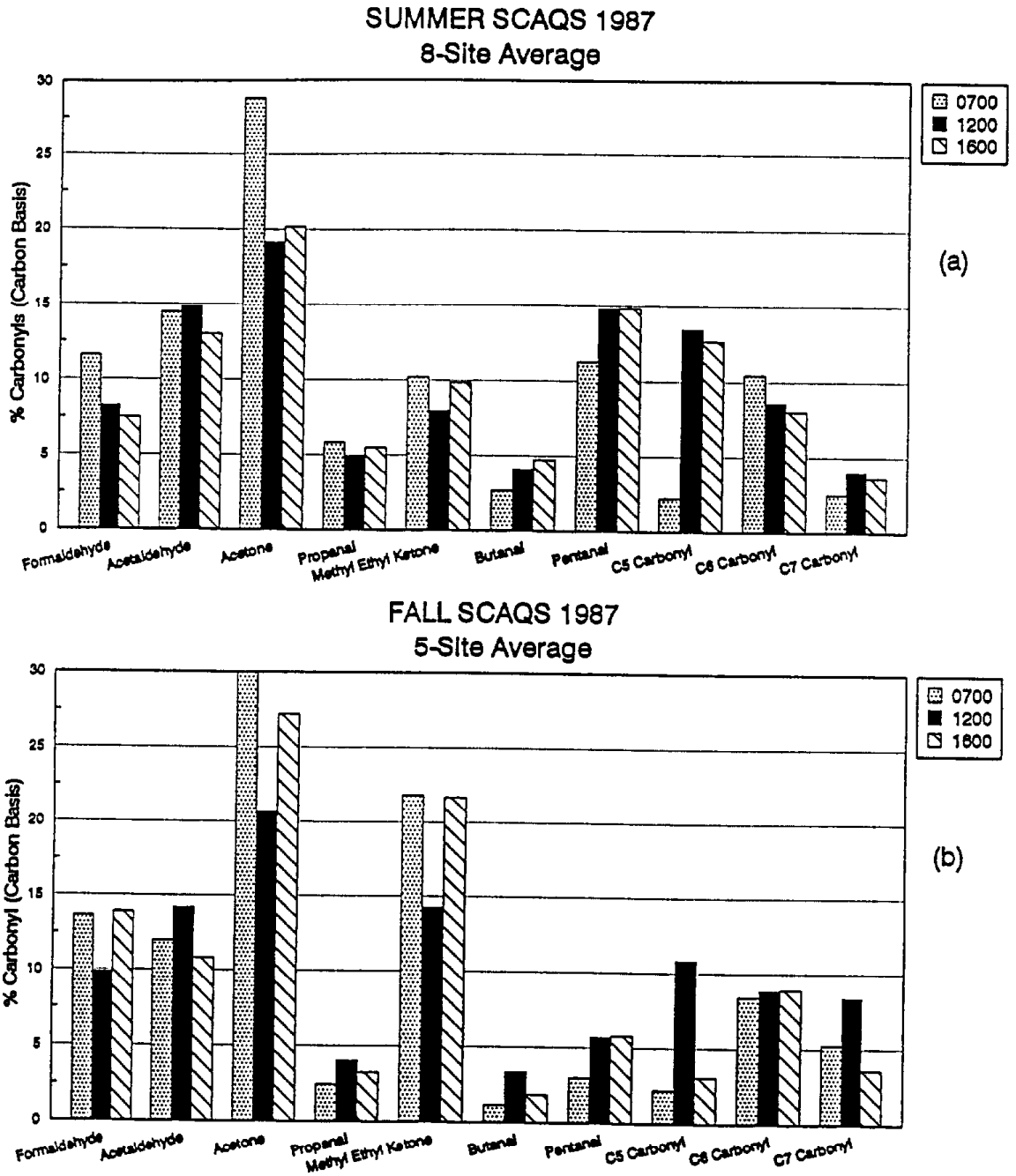


Figure 3-24. Variation of Carbonyl Compound Composition with Time of Day (PDT Summer, PST Fall) for the a) 8-Site Average in the Summer and b) 5-Site Average in the Fall SCAQS 1987. San Nicolas Island data are not included in the summer average and Long Beach data are not included in the fall average.

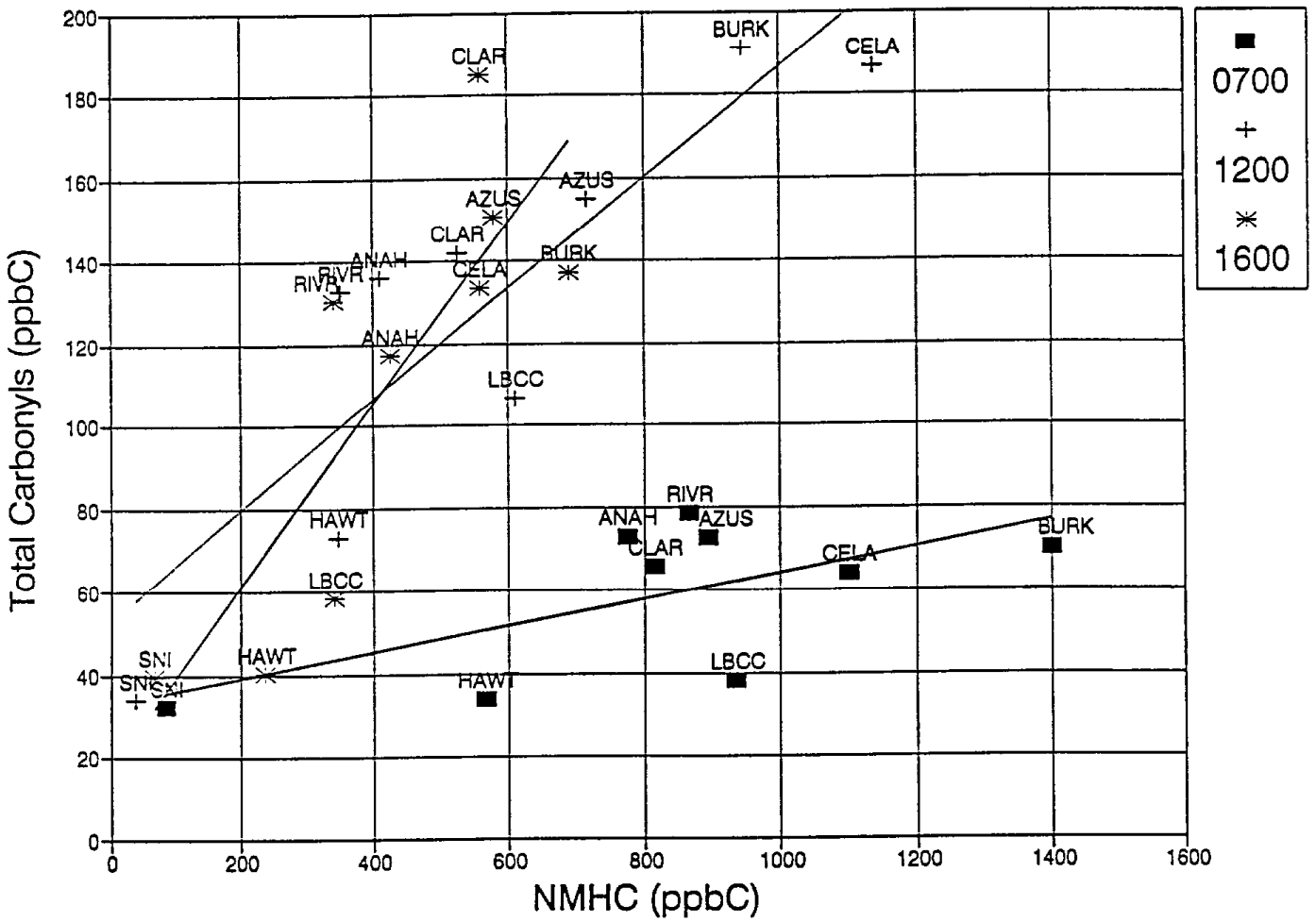


Figure 3-25. Scatter Plot of Summer SCAQS NMHC and Carbonyl Compound Concentrations Identified by Site and Time of Day. The linear regression lines are shown for 0700 (r^2 = 0.38), 1200 (r^2 = 0.77), and 1600 (r^2 = 0.69).

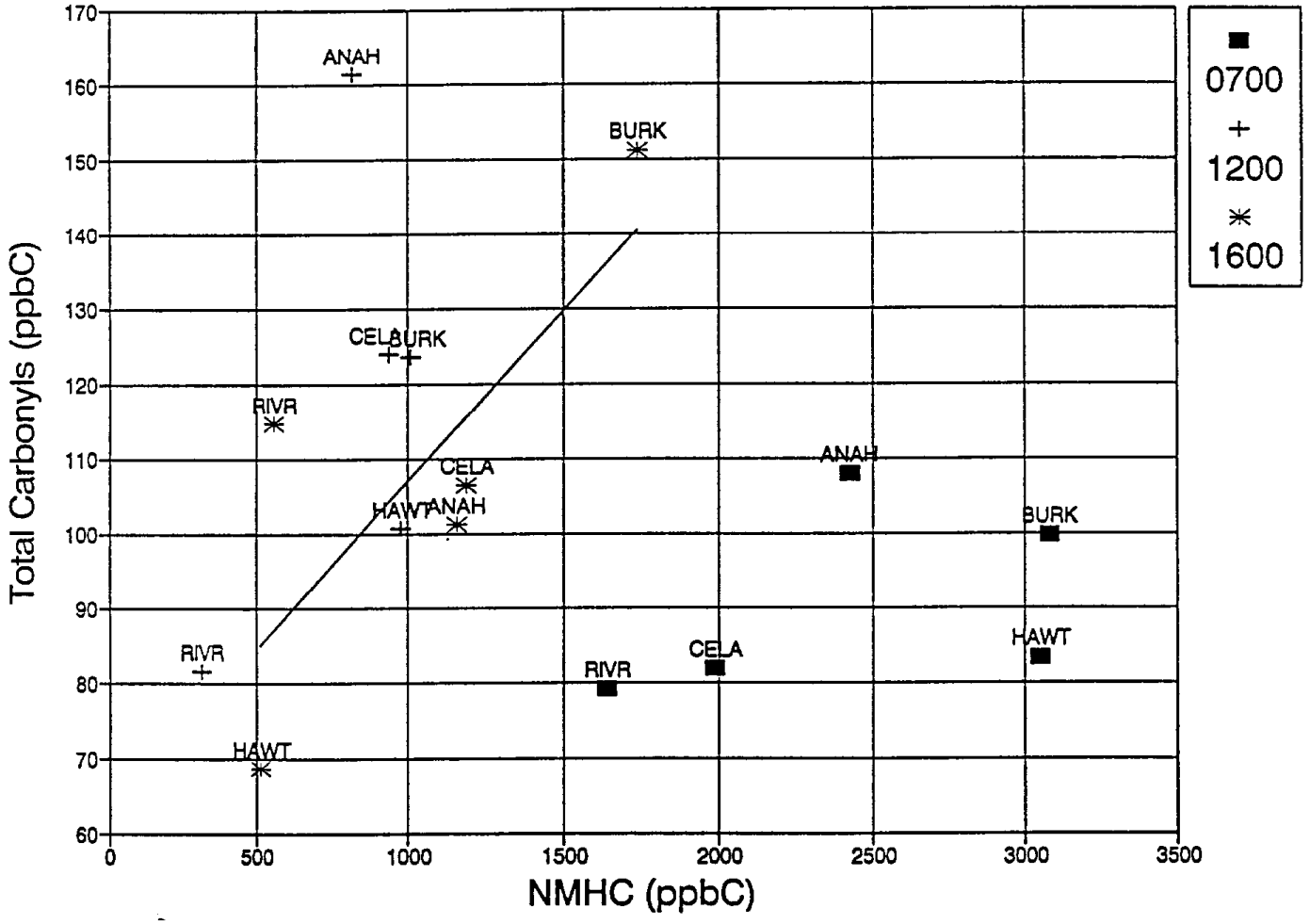


Figure 3-26. Scatter Plot of Fall SCAQS NMHC and Carbonyl Compound Concentrations Identified by Site and Time of Day. The linear regression line is shown for 1600 (r^2 = 0.60); the 0700 and 1200 data correlated poorly (r^2 = 0.19 and 0.25, respectively).

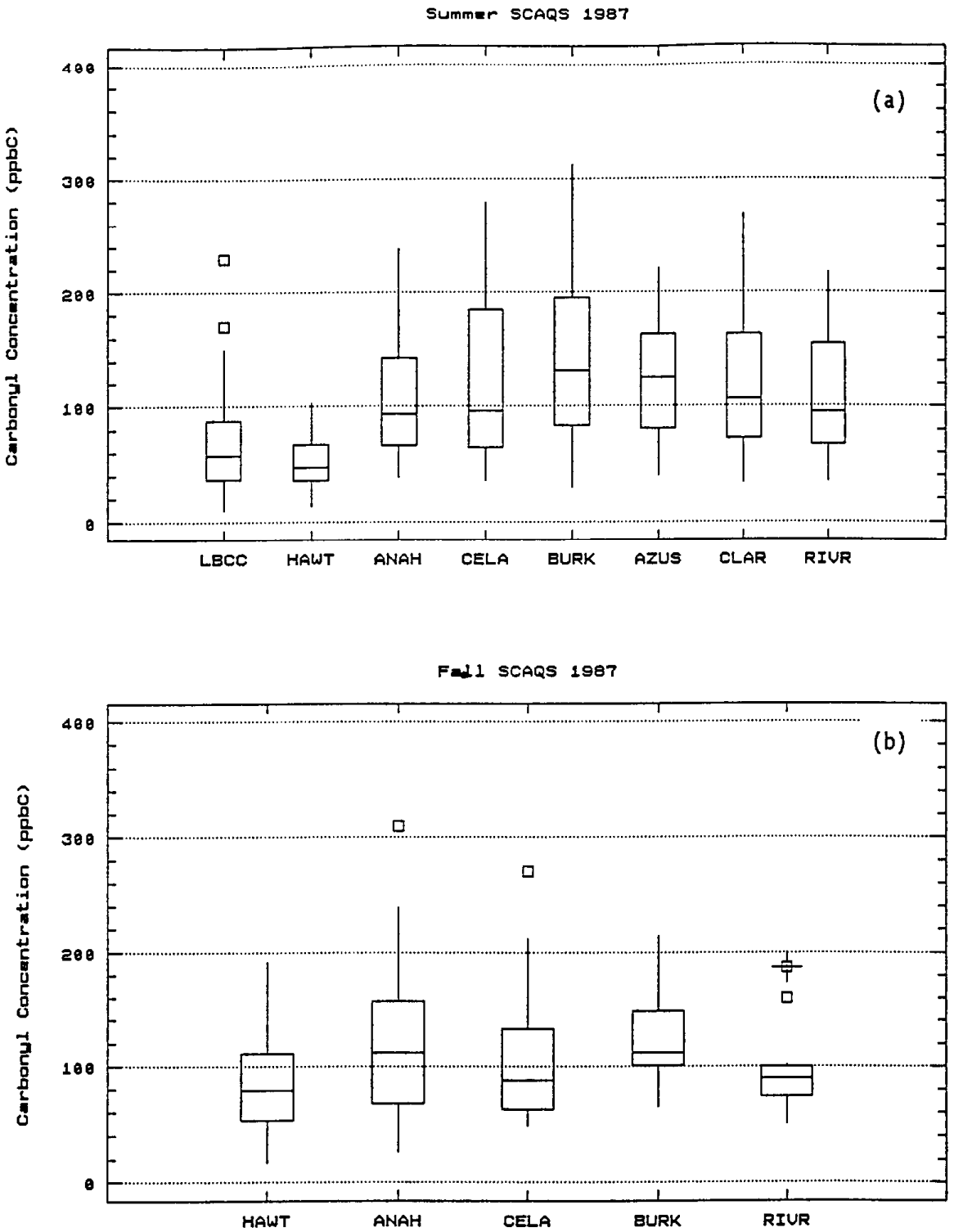


Figure 3-27. Box Plots of the Carbonyl Concentrations Measured at Each SCAQS Site During the a) Summer and b) Fall. Sites are ordered from coastal to central to eastern basin.

was quite similar everywhere between Anaheim and Riverside in the summer. Likewise, in the fall, the median carbonyl concentrations varied little between sites.

Summary statistics for the individual carbonyl concentrations are shown in Tables 3-14 and 3-15 for the summer and fall, respectively. The minimum, median, mean, and maximum concentrations of the carbonyl compounds are given for each site. In the summer, the highest formaldehyde and acetaldehyde concentrations were measured at Anaheim, where formaldehyde reached 34 ppb and acetaldehyde reached 39 ppbC. The highest concentrations of most other carbonyl species occurred at Azusa, Claremont, and Los Angeles. In the fall, the highest formaldehyde (29 ppbC) and acetaldehyde (39 ppbC) concentrations were measured at Burbank. The highest levels of other species were found primarily at Burbank and Los Angeles, except the C5 carbonyl was highest at Hawthorne, while the MEK and acetone maximums were at Anaheim.

The spatial and temporal differences in formaldehyde and acetaldehyde concentrations are illustrated in Figures 3-28 and 3-29. Formaldehyde concentrations in summer peak in the middle of the day everywhere except at Claremont, where they are slightly higher at 1600 than 1200. In the western and central basin, the late afternoon levels are comparable to the 0700 levels, whereas in the eastern basin the late afternoon levels are closer to the noontime levels. Anaheim stands out as having unusually high formaldehyde concentrations relative to the other sampling locations at all times of the day. Since there is no reason to expect higher photochemical production near Anaheim than other sites, this difference is probably due to local formaldehyde emission sources. The summer acetaldehyde data show the same diurnal pattern, with somewhat larger differences between the 0700 and 1200 levels of acetaldehyde than formaldehyde. The spatial pattern of acetaldehyde is also similar to formaldehyde's, except Anaheim does not stand out. Stations in the western basin have lower concentrations than those in the central and eastern basin at all times of day. In addition, it is worth noting that on a carbon basis, there is more acetaldehyde than formaldehyde at all stations and sampling times.

The fall formaldehyde and acetaldehyde data exhibit different temporal and spatial patterns. The formaldehyde data do not show the spike that consistently appeared in the summer data; instead there is a mixture of diurnal patterns, ranging from Hawthorne where concentrations declined over the course of the day, to Los Angeles where concentrations were time invariant on the average, and to Burbank were concentrations increased significantly over the course of the day. Riverside showed higher formaldehyde at 0700 and 1600 than 1200. The fall acetaldehyde data were more similar to the summer data. Concentrations increased from 0700 to 1200 at all stations, and in the afternoon declined at Hawthorne and Anaheim, and increased at Los Angles, Burbank, and Riverside. The spatial variations in formaldehyde and acetaldehyde were smaller in fall than summer. Overall, these data support the notion that there are both direct emissions and photochemical production of formaldehyde and acetaldehyde, and that the photochemical production is greater in the summer than the fall.

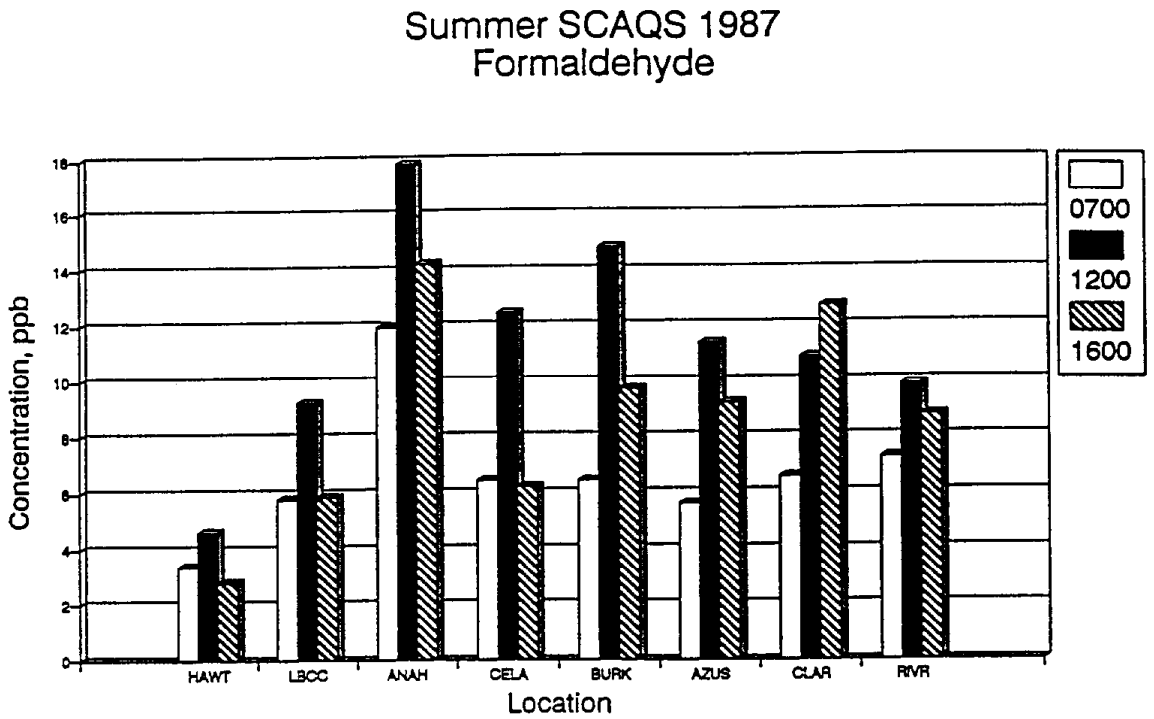
The levels of formaldehyde and acetaldehyde found in the SCAQS are fairly consistent with previous measurements (Grosjean 1991, 1988). The SCAQS

Table 3-14. Range of Carbonyl Compound Concentrations in the Summer SCAQS 1987

	Concentrations (ppbC)							
	Anaheim				Azusa			
	Minimum	Median	Mean	Maximum	Minimum	Median	Mean	Maximum
Formaldehyde	3.4	13.8	14.6	33.8	3.6	8.4	8.7	19.3
Acetaldehyde	5.0	14.0	17.0	38.8	3.0	15.0	15.9	34.8
Acetone	4.5	17.6	20.9	45.6	7.5	26.7	26.0	43.5
Propanal	1.8	4.5	5.4	11.7	0.3	4.8	5.8	12.9
Methyl Ethyl Ketone	0.0	5.8	7.7	20.0	0.0	13.6	15.4	57.6
Butanal	0.0	4.4	4.7	12.0	0.0	4.0	4.7	19.2
Pentanal	0.0	7.3	11.7	41.0	2.0	18.5	18.9	44.5
C5 Carbonyl	0.0	6.0	11.9	44.0	0.0	6.0	13.5	56.0
C6 Carbonyl	0.2	7.3	9.9	27.0	0.0	13.2	14.1	30.0
C7 Carbonyl	0.0	2.5	3.1	13.6	0.0	1.4	1.8	8.4
Total Carbonyl	38.2	93.7	107	238	40.3	125	125	221
	Burbank				Claremont			
	Minimum	Median	Mean	Maximum	Minimum	Median	Mean	Maximum
Formaldehyde	3.3	10.7	11.1	27.3	3.0	9.9	10.1	18.5
Acetaldehyde	6.2	19.8	19.8	34.2	3.0	13.8	15.8	34.6
Acetone	9.0	32.6	31.5	51.3	8.4	23.6	25.1	46.8
Propanal	1.8	6.6	6.9	14.7	1.2	5.3	5.6	15.9
Methyl Ethyl Ketone	0.0	11.0	11.5	35.6	0.0	9.4	10.6	43.6
Butanal	0.0	6.2	7.7	22.4	0.0	4.0	5.5	29.2
Pentanal	0.0	18.5	17.8	47.0	3.5	17.3	18.8	42.0
C5 Carbonyl	0.0	17.8	17.0	51.5	0.0	3.8	11.3	52.0
C6 Carbonyl	0.0	8.7	12.3	30.0	0.0	9.6	11.3	42.6
C7 Carbonyl	0.0	3.2	5.0	19.6	0.0	3.5	10.8	83.3
Total Carbonyl	29.4	131	141	313	33.8	109	125	333
	Hawthorne				Long Beach			
	Minimum	Median	Mean	Maximum	Minimum	Median	Mean	Maximum
Formaldehyde	0.9	3.3	3.6	6.9	1.0	6.1	6.6	15.6
Acetaldehyde	2.6	5.2	6.5	13.2	0.0	8.8	9.8	32.2
Acetone	2.4	9.3	11.0	32.1	0.0	13.5	15.5	52.2
Propanal	0.9	2.4	2.6	6.6	0.0	2.4	3.0	8.7
Methyl Ethyl Ketone	0.0	2.4	3.2	11.2	0.0	9.6	11.0	29.2
Butanal	0.0	1.6	2.0	6.8	0.0	0.8	1.8	8.8
Pentanal	3.0	9.0	9.1	22.0	0.0	7.5	9.5	33.0
C5 Carbonyl	0.0	4.5	6.8	21.5	0.0	2.0	3.4	17.0
C6 Carbonyl	0.0	4.8	5.9	24.0	0.0	0.6	3.0	40.8
C7 Carbonyl	0.0	0.7	1.3	7.7	0.0	0.7	1.2	8.4
Total Carbonyl	13.2	47.2	52.0	103	9.8	57.7	64.9	229
	Los Angeles				Riverside			
	Minimum	Median	Mean	Maximum	Minimum	Median	Mean	Maximum
Formaldehyde	4.4	7.4	8.7	18.9	1.7	8.5	8.4	16.1
Acetaldehyde	4.4	12.2	14.4	30.4	2.4	14.2	16.1	31.4
Acetone	7.2	20.1	21.9	57.0	3.9	25.2	24.5	41.4
Propanal	1.2	7.2	8.2	23.7	1.8	4.5	5.2	12.0
Methyl Ethyl Ketone	0.0	7.2	9.7	27.6	1.2	10.4	12.8	30.4
Butanal	0.0	4.8	6.1	16.4	0.0	2.8	4.1	19.2
Pentanal	3.5	15.5	19.1	51.5	0.0	14.0	14.7	36.0
C5 Carbonyl	0.0	9.0	15.1	52.0	0.0	11.0	14.2	51.5
C6 Carbonyl	3.0	9.6	15.6	57.6	0.0	5.4	8.9	25.8
C7 Carbonyl	0.0	2.1	5.9	49.0	0.0	1.4	2.3	14.0
Total Carbonyl	36.1	95.8	125	279	34.8	95.3	111	218

Table 3-15. Range of Carbonyl Compound Concentrations in the Fall SCAQS 1987

	Concentrations (ppbC)											
	Anaheim				Burbank				Hawthorne			
	Minimum	Median	Mean	Maximum	Minimum	Median	Mean	Maximum	Minimum	Median	Mean	Maximum
Formaldehyde	2.4	10.5	9.5	16.7	4.3	10.8	12.5	29.2	1.4	10.9	11.1	22.9
Acetaldehyde	4.6	10.6	12.3	24.0	6.2	11.0	14.8	39.4	3.8	11.6	12.7	27.2
Acetone	3.9	27.6	45.1	186.0	19.8	36.0	40.7	71.7	0.6	13.8	16.4	45.0
Propanal	0.0	3.0	3.1	6.0	0.6	3.0	5.0	22.2	0.6	3.0	2.6	4.5
Methyl Ethyl Ketone	0.0	23.0	22.4	55.2	9.2	20.8	25.1	47.6	0.0	18.4	16.1	38.8
Butanal	0.0	0.0	0.6	3.6	0.0	0.4	3.0	27.2	0.0	1.6	2.1	7.2
Pentanal	0.0	2.8	4.2	13.0	0.0	6.5	8.0	23.5	0.0	1.0	2.6	10.0
C5 Carbonyl	0.0	4.0	5.9	21.0	0.0	1.0	2.2	15.5	0.0	4.5	8.9	39.5
C6 Carbonyl	1.2	9.6	9.1	18.0	0.0	6.0	7.6	19.8	1.2	7.2	7.1	12.6
C7 Carbonyl	0.0	7.4	11.3	36.4	0.0	2.8	5.9	18.9	0.0	4.2	5.6	16.1
Total Carbonyl	26.7	112	124	310	65.7	112	125	214	17.2	79.2	85.2	191
	Los Angeles				Riverside							
	Minimum	Median	Mean	Maximum	Minimum	Median	Mean	Maximum				
Formaldehyde	5.6	11.1	11.6	20.6	3.2	10.0	10.4	19.9				
Acetaldehyde	5.2	15.0	15.7	38.6	6.2	10.0	12.4	25.0				
Acetone	0.0	20.1	22.6	73.2	0.0	16.1	19.1	49.5				
Propanal	0.6	3.3	3.8	12.0	0.9	2.3	3.0	6.9				
Methyl Ethyl Ketone	3.2	18.0	19.2	49.6	2.4	20.4	17.9	31.6				
Butanal	0.0	2.4	3.8	16.4	0.0	0.0	3.1	15.6				
Pentanal	0.0	5.0	6.6	23.5	0.0	0.0	0.0	0.0				
C5 Carbonyl	0.0	2.0	3.5	22.0	0.0	15.8	13.2	24.5				
C6 Carbonyl	2.4	9.6	11.1	30.6	1.8	5.4	6.2	10.8				
C7 Carbonyl	0.0	4.2	8.0	44.8	0.0	7.4	7.8	16.8				
Total Carbonyl	48.8	87.9	106	270	48.4	88.7	93.2	187				



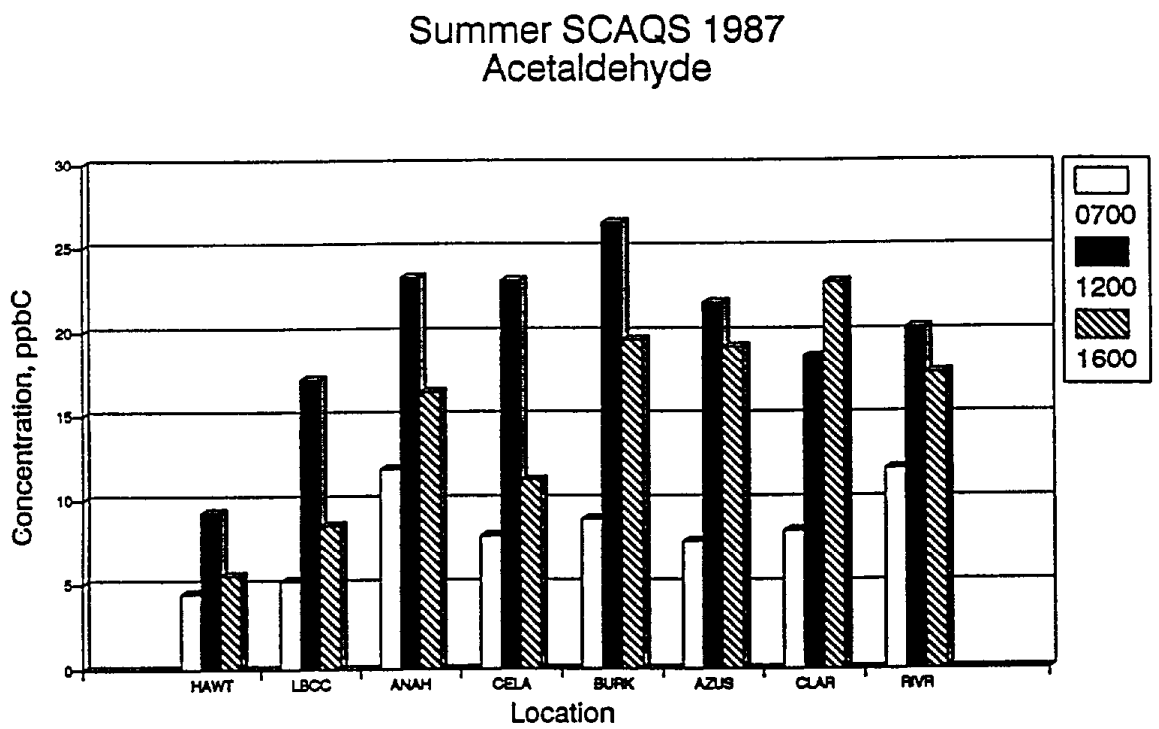
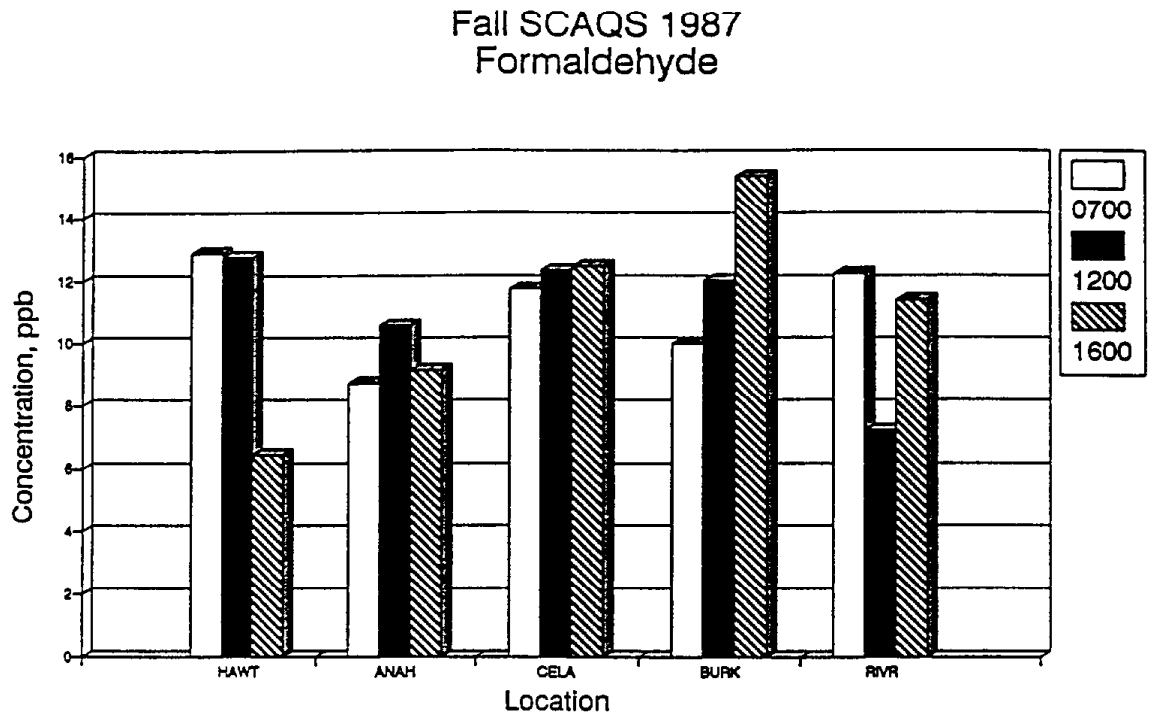


Figure 3-28. Diurnal Variation of Formaldehyde and Acetaldehyde Concentrations at Summer SCAQS Sites. Sites are ordered from coastal to central to eastern basin.



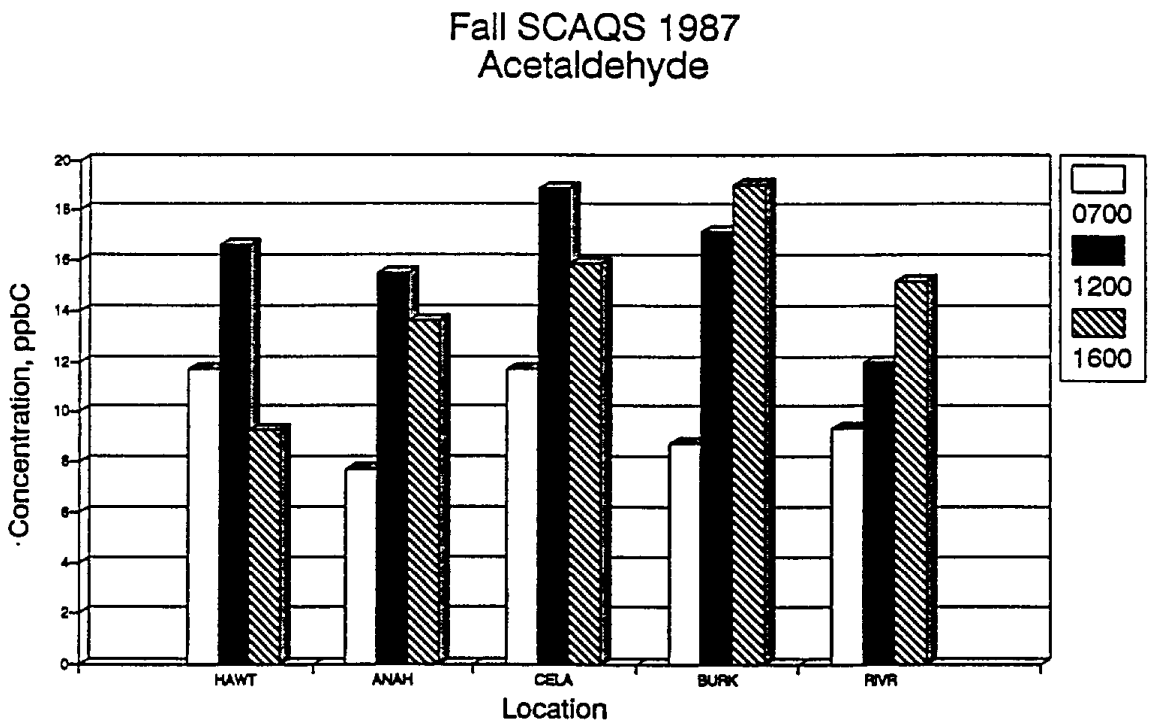


Figure 3-29. Diurnal Variation of Formaldehyde and Acetaldehyde Concentrations at Fall SCAQS Sites. Sites are ordered from coastal to central to eastern basin.

data show higher acetaldehyde to formaldehyde ratios than Grosjean's data, but the ratios are still consistent. However, the high levels of C4+ carbonyl compounds observed in the SCAQS data were not expected, mostly because the current understanding of hydrocarbon oxidation does not suggest large amounts of these species should be photochemically produced. A possible explanation for their abundance is that they are emitted by landfills. Landfills are known to emit large amounts of methane and other hydrocarbons. Kochy Fung of AtmAA has analyzed landfill gases for carbonyl compounds. Figure 3-30 shows a chromatograph from one of his analyses. Copious amounts of C3+ carbonyl compounds are present. The ratios of these carbonyl compounds to formaldehyde were similar to the ambient ratios found in the SCAQS data. Hence, it is possible that the higher than expected C3+ carbonyl levels may be at least partially due to these uncharacterized sources. Landfills may also be a more important source of formaldehyde and acetaldehyde than previously thought. The current SoCAB emissions inventory has zero carbonyl emissions from landfills.

3.6 RELATIONSHIPS BETWEEN SPECIES

Another objective of this study was to identify relationships between important species, species groups, and other pollutants. A large number of scatter plots were created and evaluated in order to identify the species for which relationships exist. Linear regression was then used to determine the linear correlation between the selected constituents.

Figures 3-31 through 3-38 show scatter plot matrices for important species using the concentration data collected during the summer and the fall. Scatter plot matrices are similar to correlation matrices; to read the scatter plot matrices, locate the row variable (e.g., NMOC on the first row) and the column variable (e.g., Toluene in the second column). The intersection is the scatter plot of the row variable on the vertical axis against the column variable on the horizontal. Each column and row is scaled so that the points fill each frame. Scale information is omitted for clarity. These plots are useful to distinguish inter-species relationships and outliers in the data.

First, relationships between major VOC groups were examined. The summer data (Figure 3-31) show that the aromatic species correlate well with each other and with NMOC. The 1,2,4-trimethylbenzene data show more scatter and have less correlation with NMOC than the other species. The paraffins, shown in Figure 3-32, show significantly more scatter than the aromatic hydrocarbons. The C5+ paraffinic species correlate better with the NMOC and with each other than do the C2 to C4 species. The C2-C4 paraffins correlate reasonably well with each other. The olefins, shown in Figure 3-33, show poor correlations with each other and with NMOC. With the exception of propene and a C4 olefin, this is probably due to their high reactivity and high variability compared to the aromatic hydrocarbons and paraffins. As noted above, most of the olefins are not very abundant. While formaldehyde and acetaldehyde show some degree of correlation, the other carbonyl species shown in Figure 3-34 do not correlate well with NMOC.

The fall hydrocarbon data, shown in Figures 3-35 to 3-37, exhibit good correlations among the aromatic, paraffinic and olefinic species. The

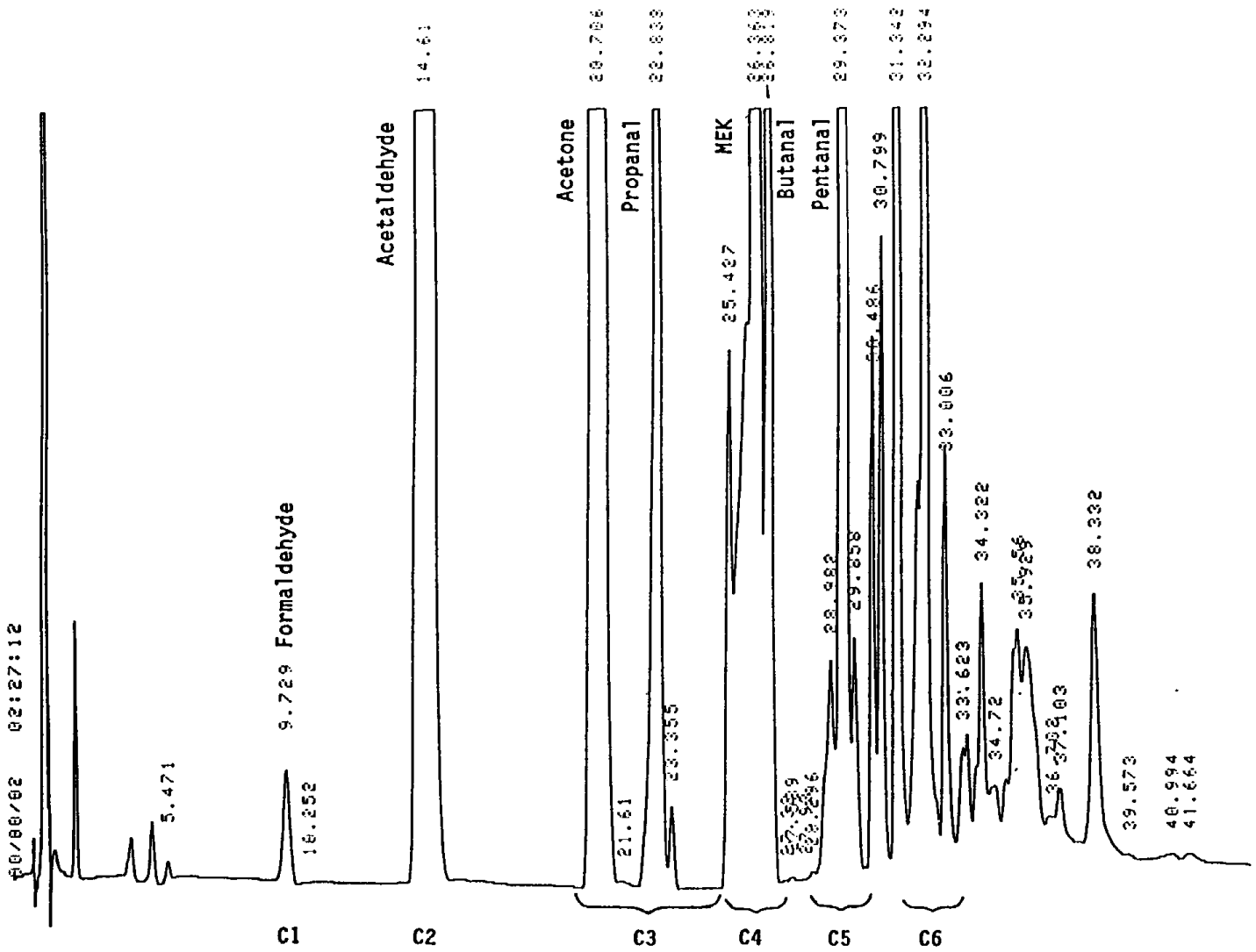


Figure 3-30. Chromatograph of Landfill Gas Showing Presence of C4+ Carbonyls (Fung, 1991).

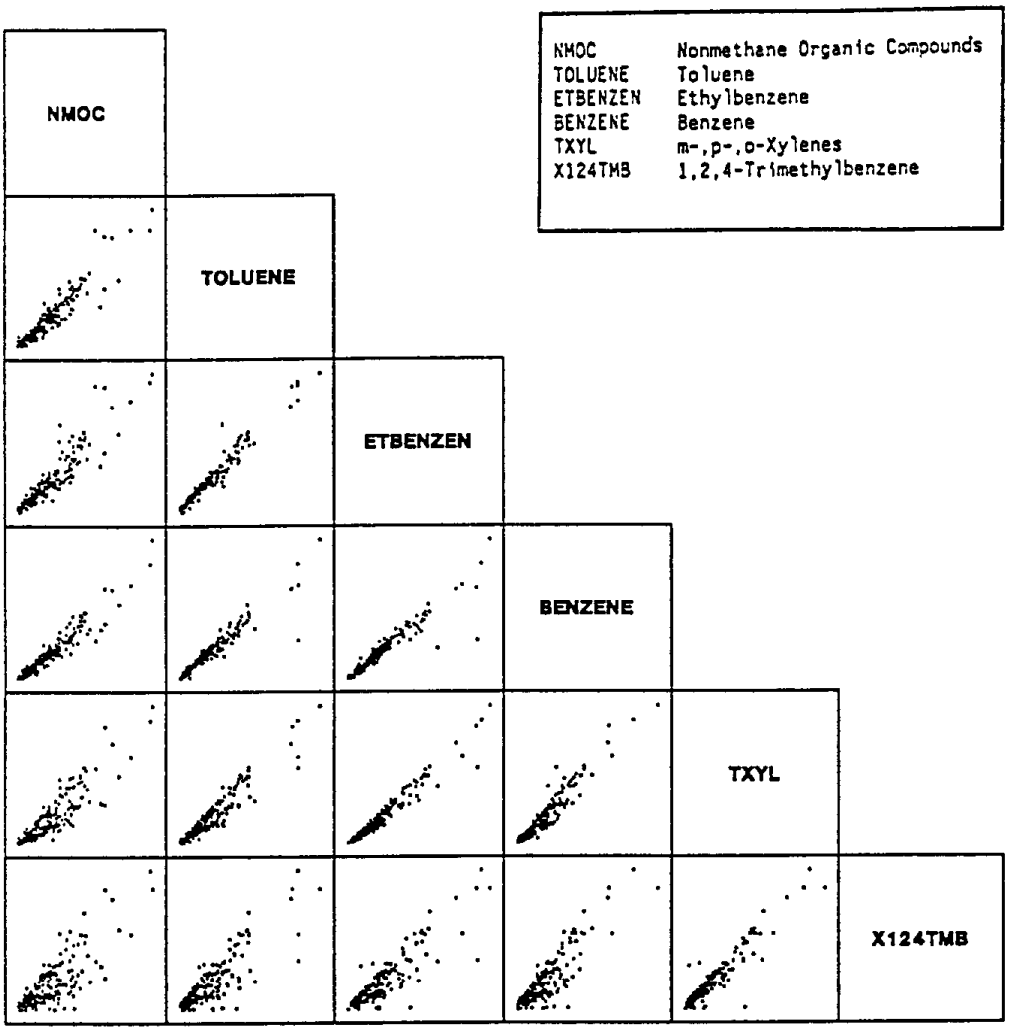


Figure 3-31. Scatter Plot Matrices of Summer NMOC and Aromatic Species.

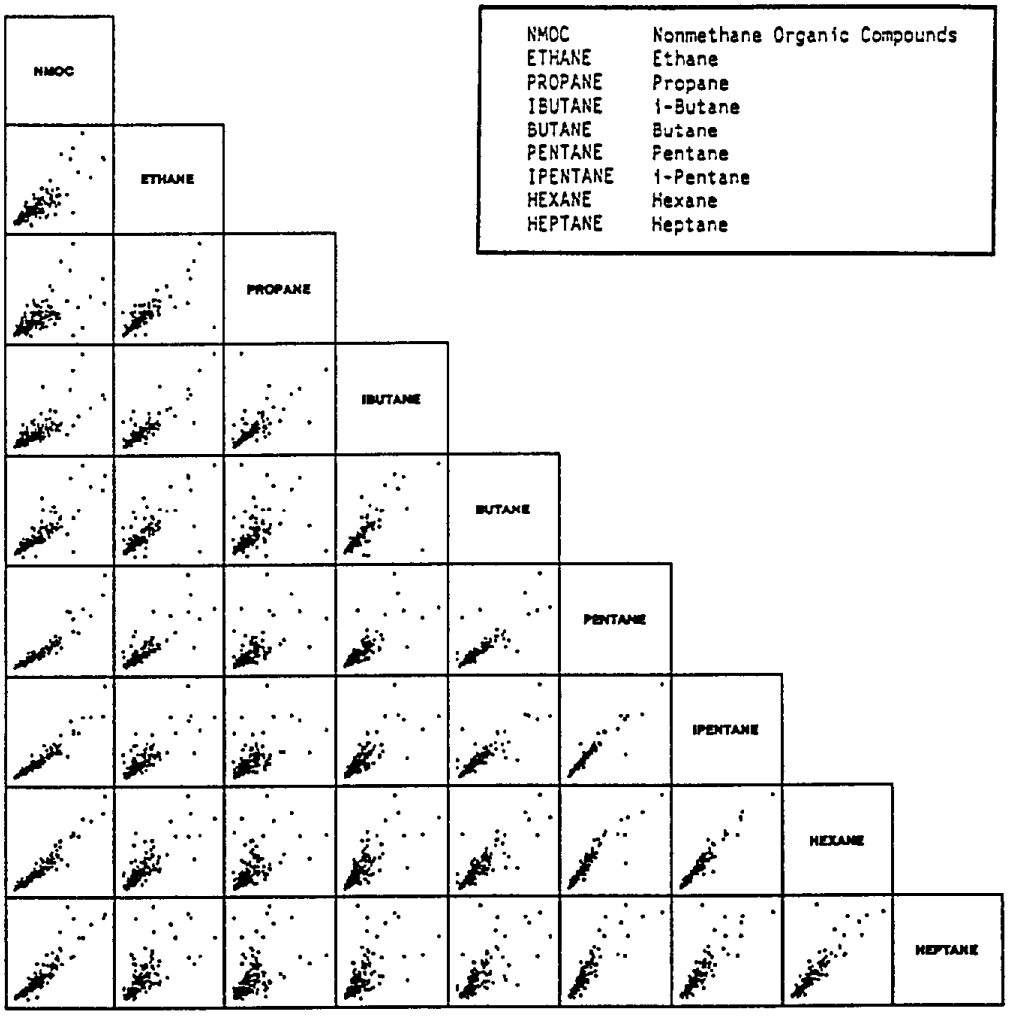


Figure 3-32. Scatter Plot Matrices of Summer NMOC and Paraffin Species.

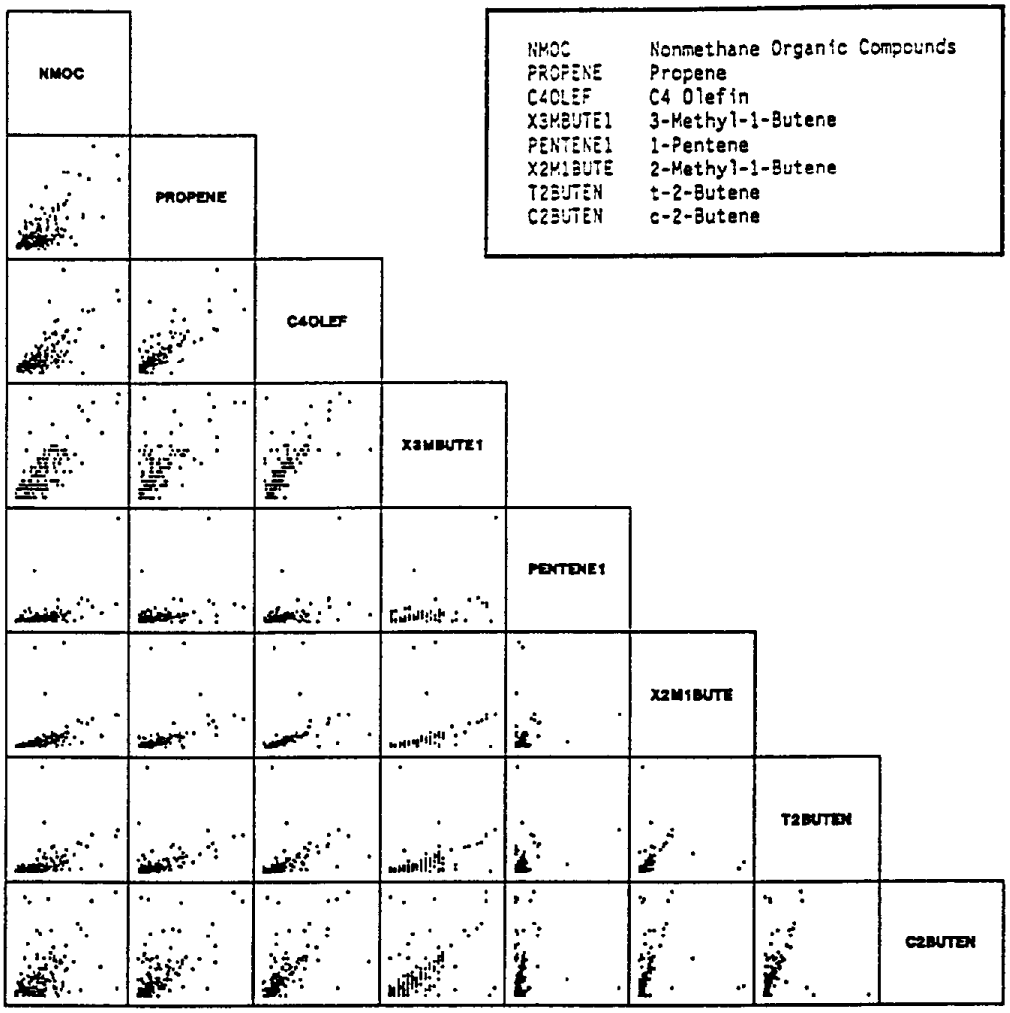


Figure 3-33. Scatter Plot Matrices of Summer NMOC and Olefin Species.

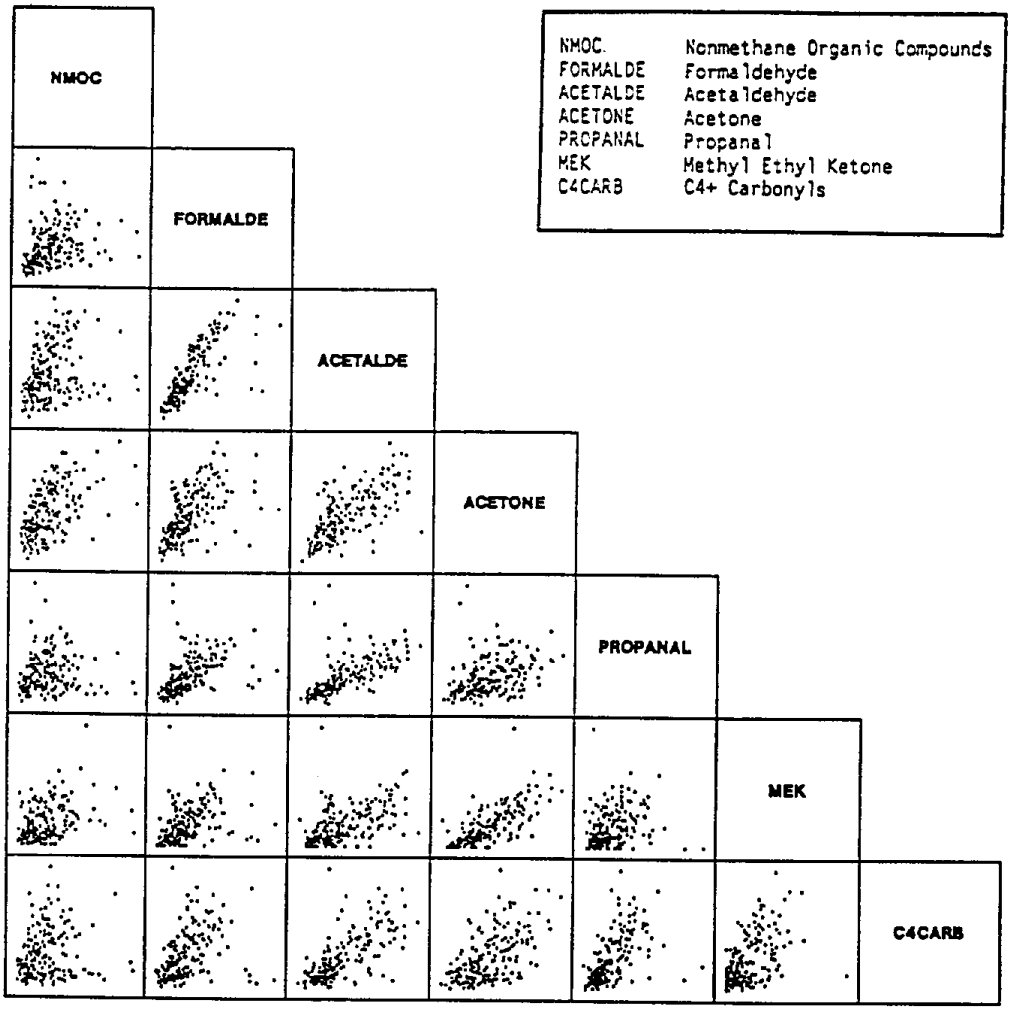


Figure 3-34. Scatter Plot Matrices of Summer NMOC and Carbonyl Species.

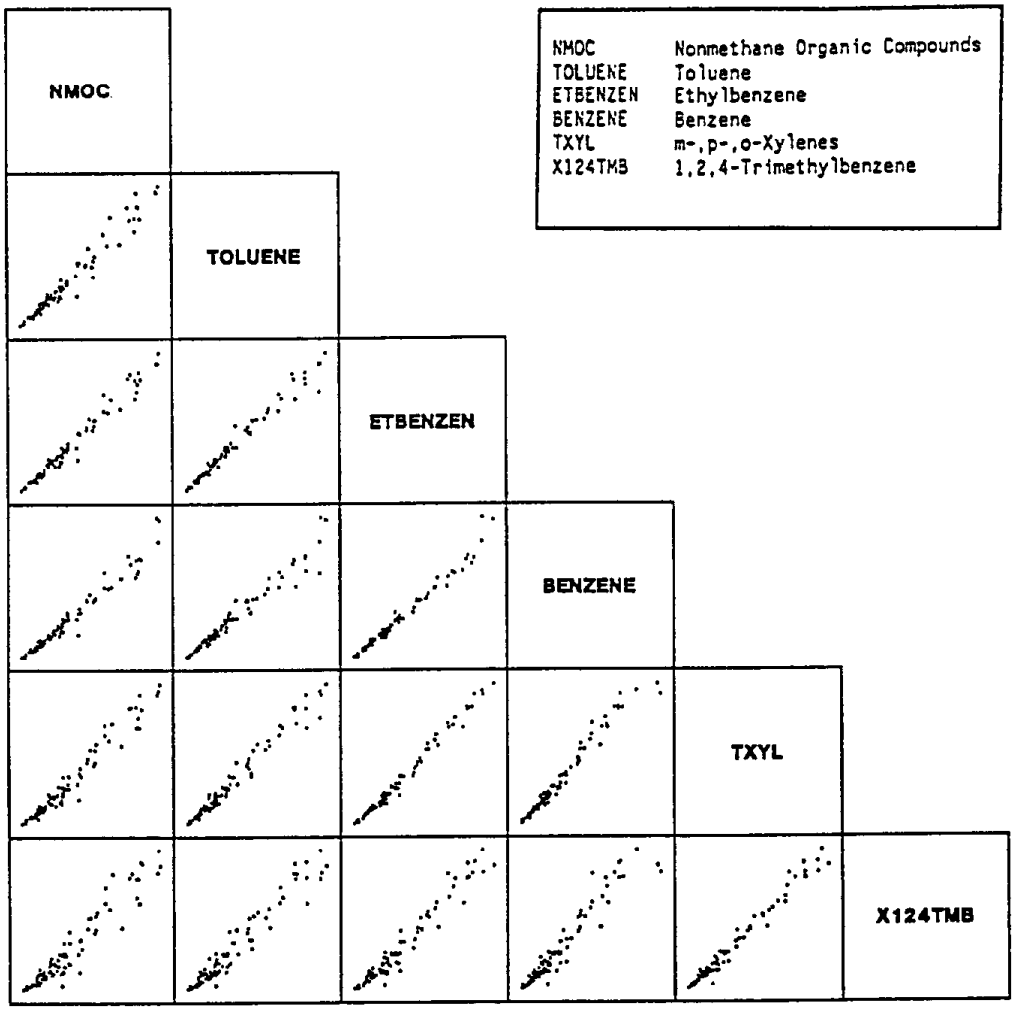


Figure 3-35. Scatter Plot Matrices of Fall NMOC and Aromatic Species.

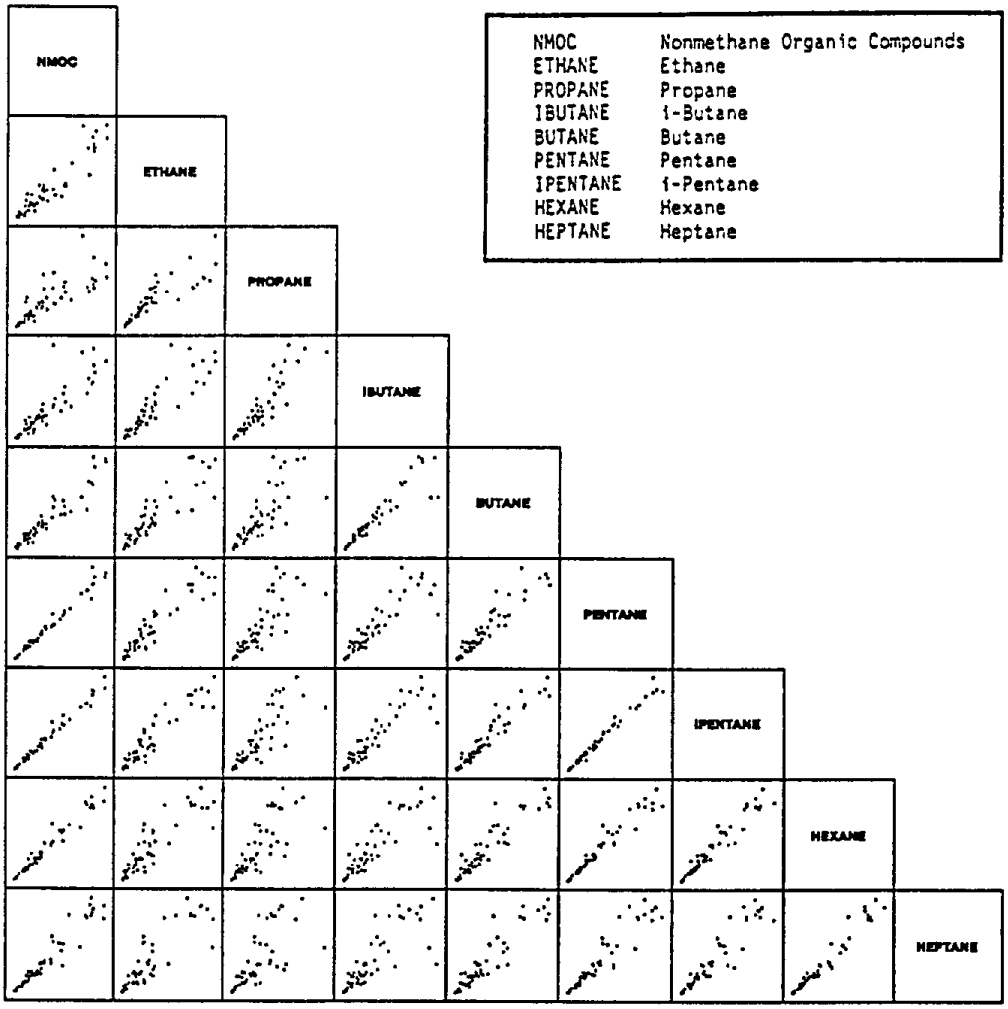


Figure 3-36. Scatter Plot Matrices of Fall NMOC and Paraffin Species.

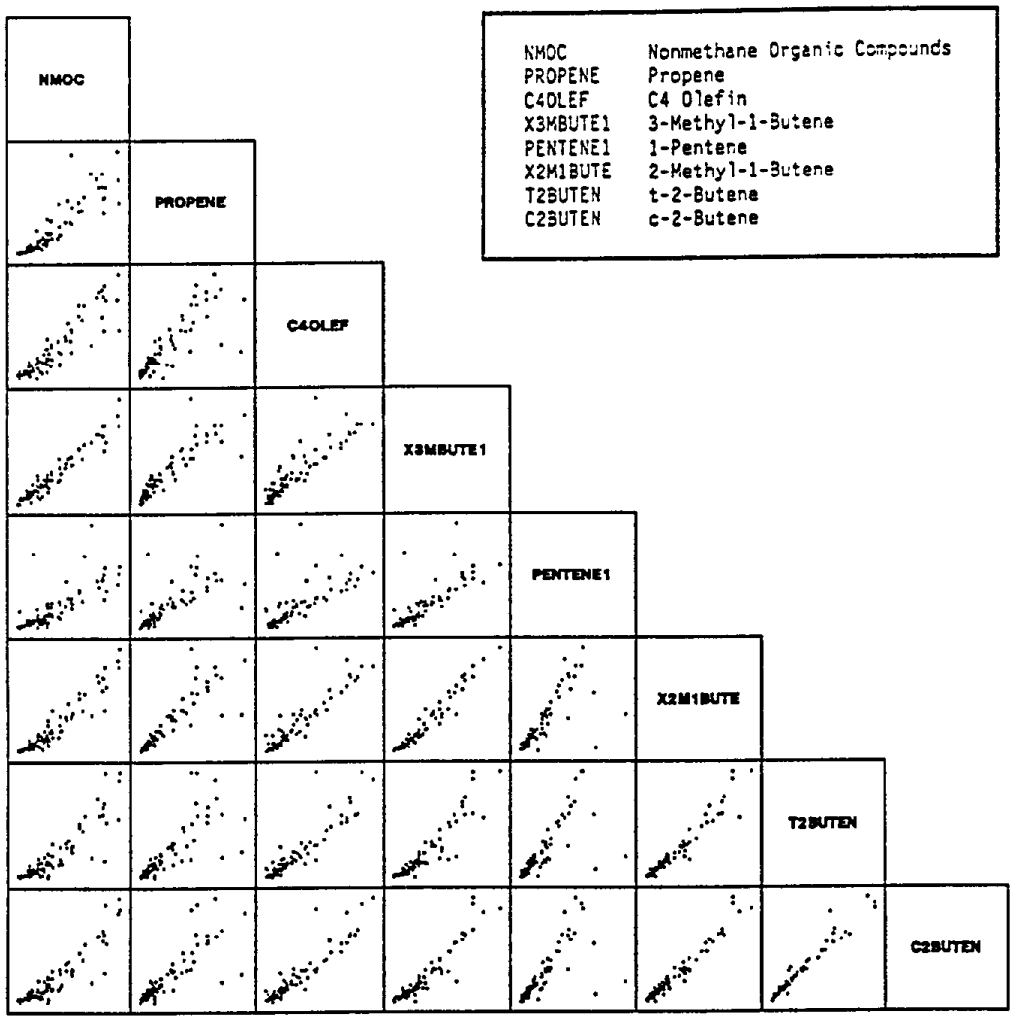


Figure 3-37. Scatter Plot Matrices of Fall NMOC and Olefin Species.

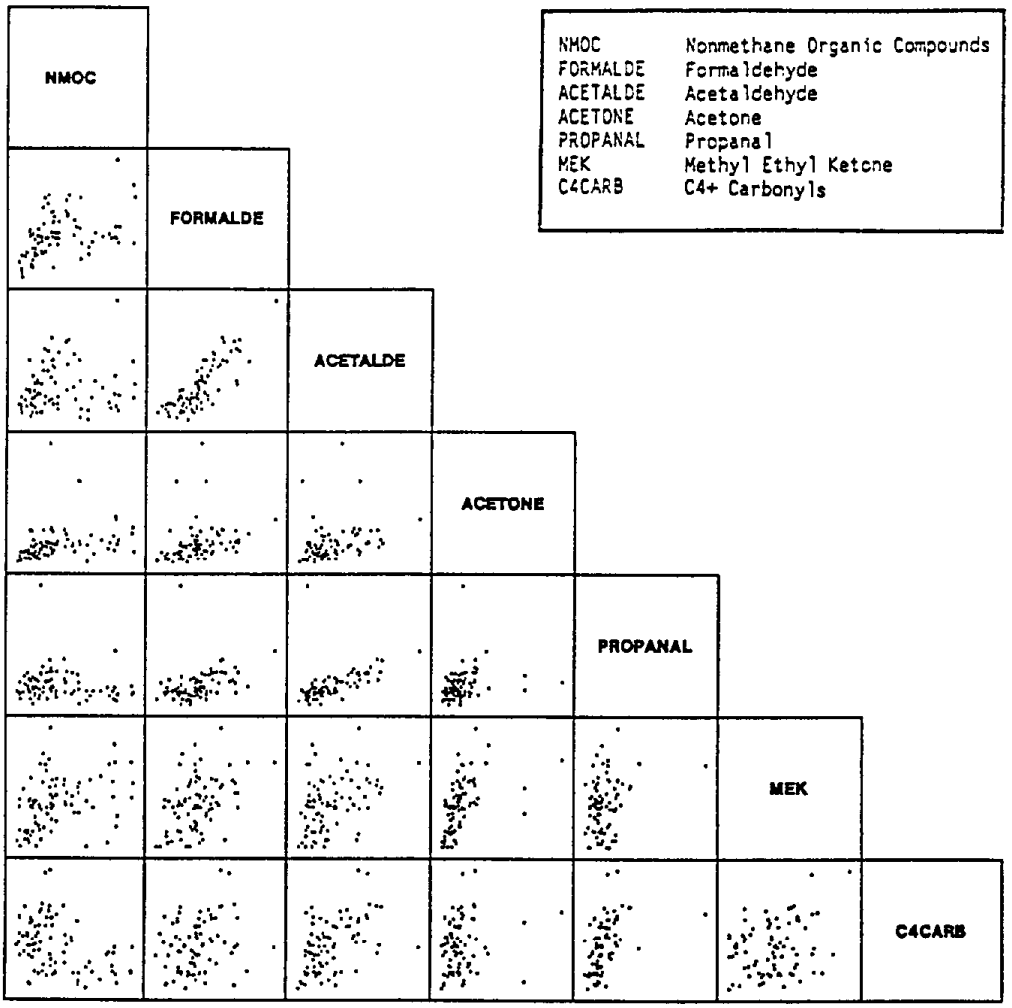


Figure 3-38. Scatter Plot Matrices of Fall NMOC and Carbonyl Species.

correlations are comparable to summer for aromatic species and much better than summer for paraffins and olefins. These figures strongly support the hypothesis that there are common sources of urban NMOC that influence all of the SCAQS stations during all of the sampling periods. That is, while the NMOC levels vary with changes in meteorology and emissions strengths, the relative composition of the hydrocarbons varies only by small amounts. The fall carbonyl data do not show the high inter-species correlation exhibited by the hydrocarbons. Like the summer data, Figure 3-38 shows that the only significant carbonyl correlation is between formaldehyde and acetaldehyde.

Second, it is insightful to examine the relationships between NMOC, CO, methane, and acetylene, which are all emitted by motor vehicles. Scatter plots of these species indicate they are well correlated. As shown in Table 3-16, the correlation between NMOC and CO was excellent for both the summer and fall data. For the summer, the correlation coefficient ranged from 0.0 at San Nicolas Island to 0.93 at Riverside and Anaheim, and 0.78 on average (excluding San Nicolas Island). For the fall, r^2 ranged from 0.58 at Los Angeles to 0.98 at Burbank and Riverside with 0.82 on average. The high correlations between CO and NMOC suggest motor vehicles are probably a major source of the NMOC in the SoCAB.

NMOC and methane correlated well with r^2 of 0.54 (excluding San Nicolas Island) for the summer and 0.78 for the fall. The higher correlations in fall are probably a result of having methane levels that exceed the background methane concentration (1.8 ppm) by greater amounts in the fall. CO and acetylene also correlated well in the summer (r^2=0.70) and fall (r^2=0.87). At San Nicolas Island, CO and acetylene data correlated poorly.

Third, the relationships between NMOC and other pollutants, including NO, NO_2, NO_x, ozone, NO_2+ozone, PAN, and basinwide daily ozone maximum, and temperature were investigated. Scatter plots of some of these relationships are shown in Figures 3-39 and 3-40 for the summer and fall data, respectively. Few good correlations were found when the entire database was used. However, when the data were separated by time of day, numerous relationships were identified. Table 3-17 lists selected correlations using the summer data as a function of the time of day. Propane, C4 olefin, and total xylenes results are reported because their relationships are representative of other species in their classes. The results show reasonably good correlation between morning NMOC and the species emitted by vehicles, such as NO, NO_x, CO, and most hydrocarbons. In the afternoon, NMOC correlates well with NO_2, NO_2+ozone, and CO, but not concurrent ozone, basinwide daily ozone maximum, or PAN. These relationships are generally consistent with the current understanding of the relationships of NMOC, NO_x, and ozone with time of day.

The summer data show there is some relationship between NMOC and temperature (r^2=0.39, 0.42, and 0.45 at 0700, 1200, and 1600), however, this must be interpreted cautiously because temperature and mixing heights are generally correlated which means concentrations of all precursor species should correlate with temperature. If there was an evaporative emission source whose strength increased drastically with temperature, we probably would see much better correlation in the midday or afternoon than in the morning. However, the data show the correlation is about the same at all sampling times. Thus, there is not much support for this hypothesis.

Table 3-16. Regression and Correlation Coefficients for NMOC, CO, Methane, and Acetylene From SCAQS 1987 Data

	[NMOC]=C+M*[CO]			[NMOC]=C+M*[CH_4]			[CO]=C+M*[Acetylene]		
Summer:									
	C	M	r^2	C	M	r^2	C	M	r^2
OVERALL[a]	135	.404	.776	-1254	.947	.535	341	69.9	.704
0600[a]	100	.406	.740	- 865	.782	.458	655	60.5	.674
1100[a]	110	.446	.868	-1798	1.20	.525	118	85.4	.867
1500[a]	135	.404	.776	-1254	.95	.535	341	69.8	.704
ANAH	- 43	.521	.931	-1857	1.25	.885	225	83.5	.851
AZUS	- 9	.511	.659	- 925	.819	.345	578	59.0	.533
BURK	100	.442	.846	- 800	.856	.473	259	81.6	.884
CELA	297	.322	.748	-1761	1.36	.686	1065	48.6	.436
CLAR	301	.275	.534	-1144	.883	.352	486	72.4	.494
HAWT	201	.379	.787	-2155	1.35	.485	- 31	78.2	.780
LBCC	10	.583	.790	-2187	1.38	.900	218	61.4	.674
RIVR	64	.405	.926	- 719	.571	.775	589	50.6	.833
SNI	-	-	.004	-	-	.008	-	-	.083
Fall:									
	C	M	r^2	C	M	r^2	C	M	r^2
OVERALL[b]	390	.305	.817	-1487	1.12	.780	812	60.5	.868
0700[b]	797	.253	.695	-1320	1.10	.601	1947	50.4	.757
1200[b]	236	.333	.745	-1492	1.05	.722	46	86.2	.994
1600[b]	147	.351	.866	-3025	1.83	.732	60	85.7	.998
ANAH	381	.282	.848	-1527	1.18	.827	432	73.5	.784
BURK	7	.432	.975	-1780	1.37	.823	2015	43.0	.795
CELA	546	.264	.576	- 538	.754	.577	755	63.7	.746
HAWT	640	.255	.876	-2904	1.59	.968[d]	182	78.2	.998
LBCC[c]	-	-	-	-	-	-	-2.3	88.0	.992
RIVR	121	.345	.978	-1093	.798	.973	265	69.2	.993

[a] San Nicolas Island data excluded.
[b] LBCC NMOC data excluded (invalid carbonyls).
[c] Carbonyl data invalid.
[d] One methane value less than 1000 ppb excluded.

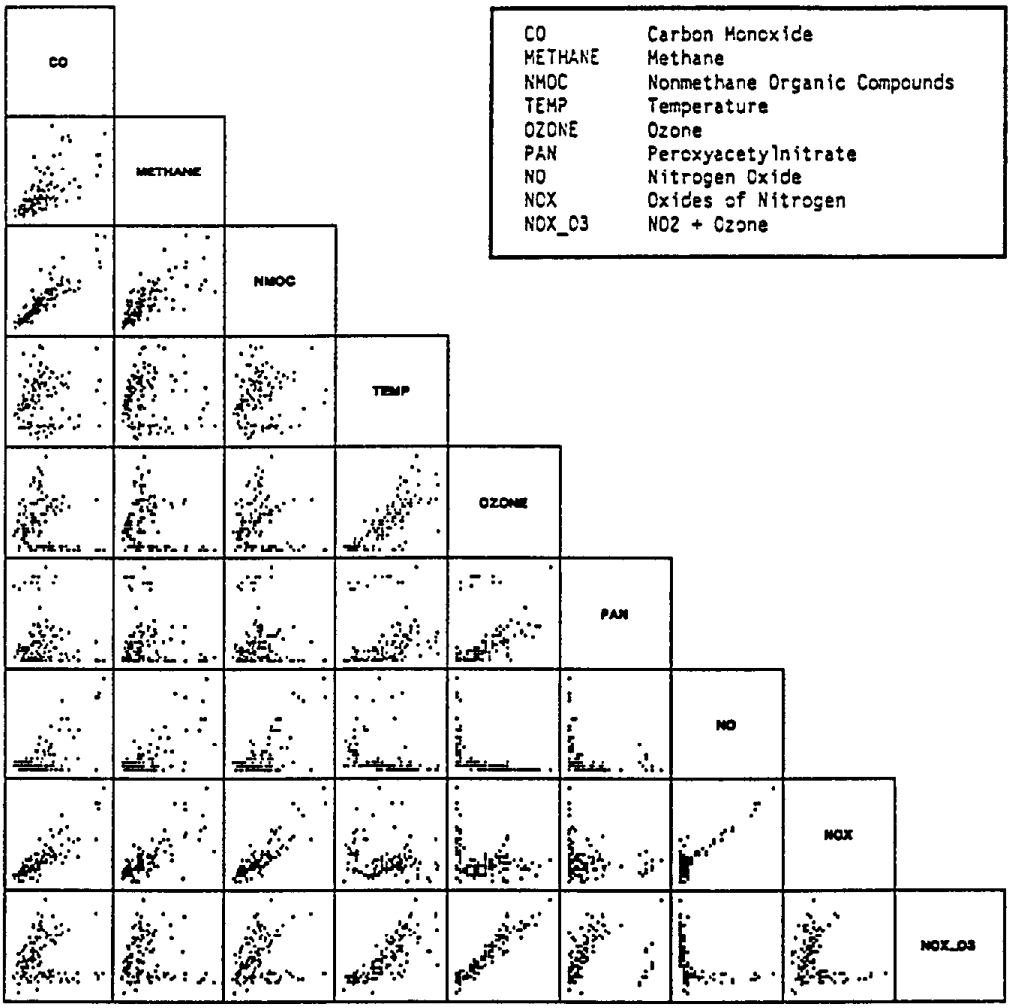


Figure 3-39. Scatter Plot Matrices of Various NMOC and Air Quality Parameters for Summer SCAQS 1987.

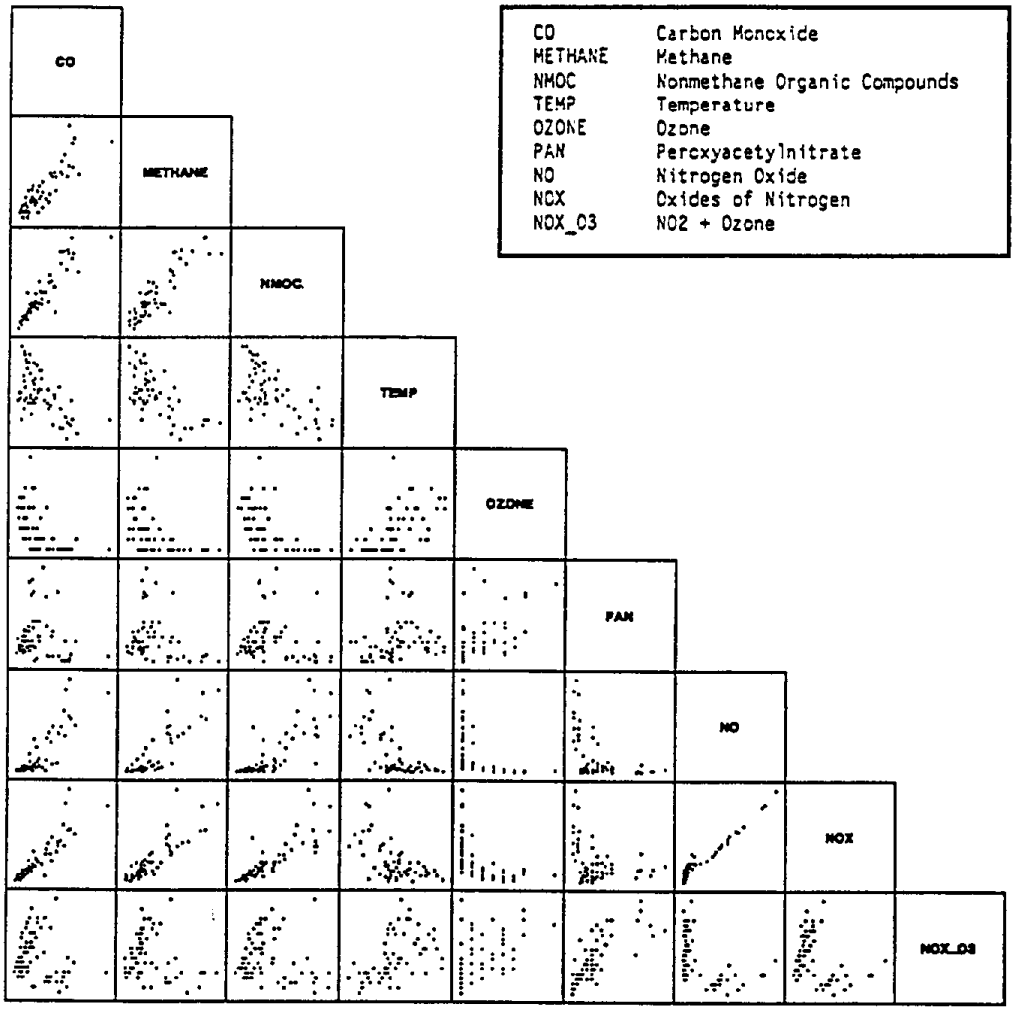


Figure 3-40. Scatter Plot Matrices of Various NMOC and Air Quality Parameters for Fall SCAQS 1987.

Table 3-17. Selected Correlations Between Concentrations of Organic Species and Other Air Quality Parameters From the Summer SCAQS 1987

		700	1200	1600 PDT
Species, y	Species, x	r^2	r^2	r^2
NMOC	NO	0.769	-	-
	NO_2	0.460	0.837	0.604
	NO_x	0.830	0.846	0.435
	Ozone	0.278	0.345	0.390
	NO_2+Ozone	0.264	0.660	0.537
	PAN	-	-	0.142
	Basin Ozone Max.	0.104	-	-
	Temperature	0.389	0.417	0.454
	CO	0.791	0.864	0.800
	Methane	0.536	0.511	0.441
Propane	NMOC	0.400	0.547	0.586
	NO	0.123	-	-
	NO_2	0.111	0.467	0.286
	NO_x	0.232	0.546	0.312
	NO_2+Ozone	0.127	0.344	0.524
	Temperature	-	0.116	0.402
	CO	0.168	0.292	0.478
	Methane	0.145	0.312	0.546
C4 Olefin	NMOC	0.735	0.269	0.207
	NO	0.688	-	-
	NO_2	0.137	-	-
	NO_x	0.709	0.171	0.242
	NO_2+Ozone	-	0.129	-
	Temperature	0.296	-	-
	CO	0.685	0.202	0.184
	Methane	0.468	-	-
o,m,p-Xylenes	NMOC	0.890	0.876	0.551
	NO	0.747	-	-
	NO_2	0.296	0.755	0.285
	NO_x	0.820	0.714	0.365
	NO_2+Ozone	0.218	0.458	-
	Temperature	0.419	0.364	-
	CO	0.892	0.835	0.504
	Methane	0.464	0.332	-
Formaldehyde	NMOC	-	0.299	0.229
	NO	-	-	0.113
	NO_2	-	0.323	-
	NO_x	-	0.332	-
	NO_2+Ozone	-	0.292	0.245
	Temperature	-	0.176	0.196
	CO	-	0.315	0.292
	Methane	-	0.150	0.182
Acetaldehyde	PAN	-	0.115	-

A dash represents a correlation coefficient, r^2, less than 0.100.

The inter-correlation among species in the fall is described in Table 3-18. Strong relationships between co-emitted precursors are apparent in the morning and reasonably good relationships exist between NMOC and photochemical products, such as NO_2 and NO_2+ozone, in the afternoon. However, there was little correlation between NMOC and ozone, basin maximum ozone, PAN, or temperature at all times.

The correlation of propane with NMOC was reasonably good in summer and fall, especially at 1200 and 1600 (r^2= 0.55 to 0.73). Propane's correlation with CO and methane was poor in the morning and midday, yet acceptable at 1600. In the fall afternoons, propane correlated well with every other species shown in Table 3-18 except NO. The poor correlation of propane with CO and other species in the morning suggests it is not a major component of the morning motor vehicle emissions.

The C4 olefin data show good correlation with NMOC, CO, and NO_x in the summer mornings and fall afternoons. The C4 olefins exhibit high correlation (r^2=0.86) with temperature at 1200 in the fall, but at no other times. The reasons for these correlations are unclear.

The xylenes are highly correlated with NMOC and NO_x at 0700 and 1200 in summer, and 1200 and 1600 in the fall. They are also extremely well correlated with NMOC at 0700 in the fall (r^2= 0.95) and somewhat correlated with NO_x in fall mornings (r^2=0.57). These relationships suggest the xylenes are co-emitted with NO_x throughout the basin and are an important ingredient of the morning NMOC, which is primarily from motor vehicle emissions. The xylenes also exhibited a high correlation with temperature at 1200 in the fall, but at no other times.

Formaldehyde concentrations correlated well with NMOC, NO_x, and CO in the midday and afternoon fall samples, but not with most other species in the fall and any other species in the summer. Formaldehyde correlates well with methane (which is co-emitted by vehicles and is a formaldehyde precursor) in the later afternoon of the fall. Acetaldehyde correlates better with PAN in the fall than in the summer, perhaps due to lower temperatures in the fall which enhanced PAN stability.

Overall, the correlation analysis identified qualitative relationships between NMOC, NO_x, CO, and photochemical products such as NO_2+ozone. It also found that many of the relationships of other species with NMOC also hold for xylenes, and to a lesser extent for C4 olefins and propane, but not for formaldehyde. The existence of these relationships in the data lend support for emission control programs that address both NMOC and NO_x emissions in the SoCAB (i.e., NO_2 and ozone will probably be reduced by reductions in NMOC and NO_x).

3.7 NMOC REACTIVITY

The atmospheric reactivity of NMOC with respect to ozone formation is a complex phenomenon. The reactivity of an organic species depends not only on the rate at which it reacts and the reactivity of its photooxidation products, but also on other chemical and physical aspects of the environment in which it

Table 3-18. Selected Correlations Between Concentrations of Organic Species and Other Air Quality Parameters From the Fall SCAQS 1987

		700	1200	1600 PST
Species, y	Species, x	r^2	r^2	r^2
NMOC	NO	0.499	0.627	0.414
	NO_2	-	0.710	0.831
	NO_x	0.494	0.807	0.841
	Ozone	-	0.139	0.252
	NO_2+Ozone	-	0.491	0.682
	PAN	-	0.200	0.332
	Basin Ozone Max.	-	-	-
	Temperature	0.165	0.226	-
	CO	0.695	0.745	0.866
	Methane	0.601	0.722	0.732
Propane	NMOC	0.444	0.657	0.726
	NO	0.103	0.356	0.303
	NO_2	0.144	0.362	0.706
	NO_x	0.119	0.423	0.690
	NO_2+Ozone	0.119	0.199	0.685
	Temperature	0.191	0.500	-
	CO	0.306	0.275	0.596
	Methane	0.342	0.602	0.604
C4 Olefin	NMOC	0.712	0.564	0.732
	NO	0.401	0.584	0.228
	NO_2	-	0.447	0.589
	NO_x	0.393	0.484	0.563
	NO_2+Ozone	-		0.466
	Temperature	-	0.857	-
	CO	0.315	0.359	0.639
	Methane	0.385	0.227	0.488
o,m,p-Xylenes	NMOC	0.945	0.766	0.963
	NO	0.584	0.622	0.439
	NO_2	-	0.664	0.790
	NO_x	0.570	0.780	0.822
	NO_2+Ozone	-	0.115	0.586
	Temperature	-	0.797	-
	CO	0.644	0.531	0.893
	Methane	0.559	0.418	0.646
Formaldehyde	NMOC	0.192	0.634	0.591
	NO	0.299	0.537	0.106
	NO_2	-	0.541	0.469
	NO_x	0.278	0.593	0.402
	NO_2+Ozone	-	0.238	0.492
	Temperature	0.192	0.238	-
	CO	0.374	0.675	0.460
	Methane	0.373	0.426	0.649
Acetaldehyde	PAN	-	0.299	0.530

A dash represents a correlation coefficient, r^2, less than 0.100.

is emitted, such as the NMOC/NO_x ratio, the temperature and solar radiation intensity. The maximum incremental reactivity (MIR) scale developed by Carter (1991) was used to characterize the NMOC reactivity of the SCAQS samples. The MIR scale provides an estimate of moles ozone formed per mole carbon of each organic species measured in the SCAQS, where the ozone formation estimates are intended to be used in a relative rather than absolute manner. The reactivity of each compound is estimated by multiplication of its concentration in ppbC by its MIR factor, and the reactivity of a sample is estimated by summing the reactivity of its constituents.

The MIR scale was developed for summer conditions of temperature and solar radiation, and may not be accurate for conditions in the fall. In the absence of a scale that is appropriate for the fall, we applied the MIR factors to the fall data with the understanding that it would overestimate the absolute NMOC reactivity, but give the correct relative reactivities.

It is instructive to rank the relative abundance of species based on contributions to reactivity, rather than concentration. Table 3-19 shows the 25 most abundant species based on reactivity for summer and fall data. The most notable differences between the summer "top 25" lists are the presence of C4 olefin, o-, m- and p-ethyltoluenes, propanal, pentanal and C6 carbonyl species and the absence of acetylene, ethane, and acetone from the list based on reactivity. Thus, abundant, low reactivity species like ethane are replaced by scarce, but more reactive compounds, like the ethyltoluenes.

The spatial and temporal patterns of NMOC concentrations and reactivity are illustrated in Figures 3-41 and 3-42. The reactivities of all of the samples are provided in Appendix C. In the summer, the morning and mid-day NMOC at downtown Los Angeles and Burbank had the highest reactivity, while Long Beach and Hawthorne had the lowest. In the fall, the morning NMOC at Burbank, Los Angeles, and Hawthorne had highest reactivity compared to the NMOC at Anaheim and Riverside. The reactivity of the fall NMOC is about a factor of two higher than summer values, which is consistent with the difference in concentrations. The highest reactivities were measured on August 27 - 28 and September 2 - 3. Comparison of the concentration and reactivity plots show they describe essentially the same spatial and temporal patterns in the data.

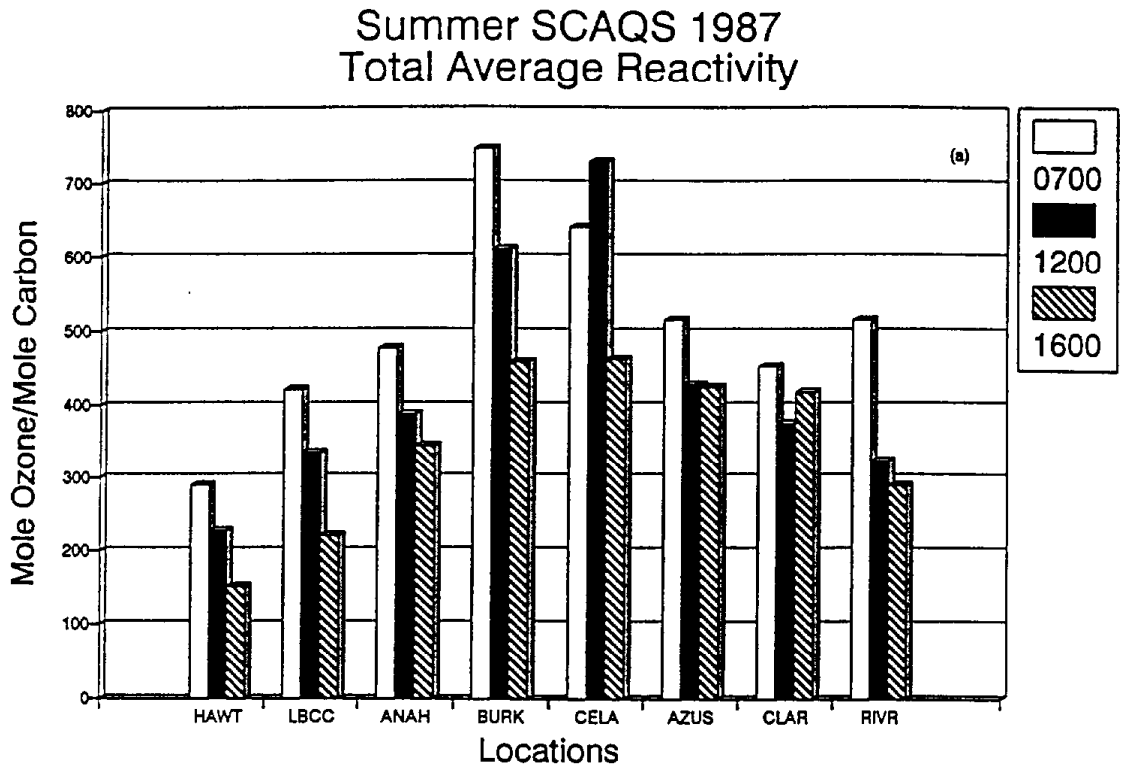
3.8 BIOGENIC HYDROCARBONS

One of the objectives of the SCAQS measurement program was to assess whether biogenic hydrocarbons played a role in ozone formation in the SoCAB. Isoprene is the principal hydrocarbon emitted by vegetation in the SoCAB (Winer et al., 1982), however, the current SoCAB emissions inventory also contains emissions of α-pinene and β-pinene, d-limonene, and 3-carene. Isoprene was the only biogenic hydrocarbon observed during SCAQS. The measurement system was set up to detect monoterpenes, such as α-pinene and β-pinene, however none were found. Isoprene and the monoterpines react rapidly in the atmosphere. The measurement system was not set up to detect the known intermediate products of the reactions, such as methylvinylketone and methacrolein from isoprene or pinene-aldehyde from α-pinene. Isoprene was not one of the abundant species, however, it was found in about 97% of the summer

Table 3-19. The Twenty-Five Most Abundant Species Based on Reactivity (Weight Fraction of NMOC Multiplied by the Carter Reactivity in Maximum Moles Ozone/Mole Carbon) During the SCAQS 1987

Species	Rank Summer	Rank Fall
m- & p-Xylene	1*	1*
Ethene	2*	2*
Acetaldehyde	3*	23
Toluene	4*	3*
Formaldehyde	5*	19
i-Pentane	6*	7*
Propene	7*	5*
o-Xylene	8*	6*
Butane	9*	8*
Methylcyclopentane	10*	10*
2-Methylpentane	11*	12*
Pentane	12*	13*
1,2,4-Trimethylbenzene	13*	4*
Benzene	14*	
m-Ethyltoluene	15	18*
Pentanal	16	
Propane	17*	16*
Propanal	18	
i-Butane	19*	11*
C6 Carbonyl	20	
Ethylbenzene	21*	15*
p-Ethyltoluene	22	9
C4 Olefin	23	22
3-Methylpentane	24*	17*
o-Ethyltoluene	25	14
2,2,4-Trimethylpentane		20*
Hexane		21*
Acetylene		24*
Methylcyclohexane		25*

* Species is also on the 25 most abundant list based on fraction of NMOC.



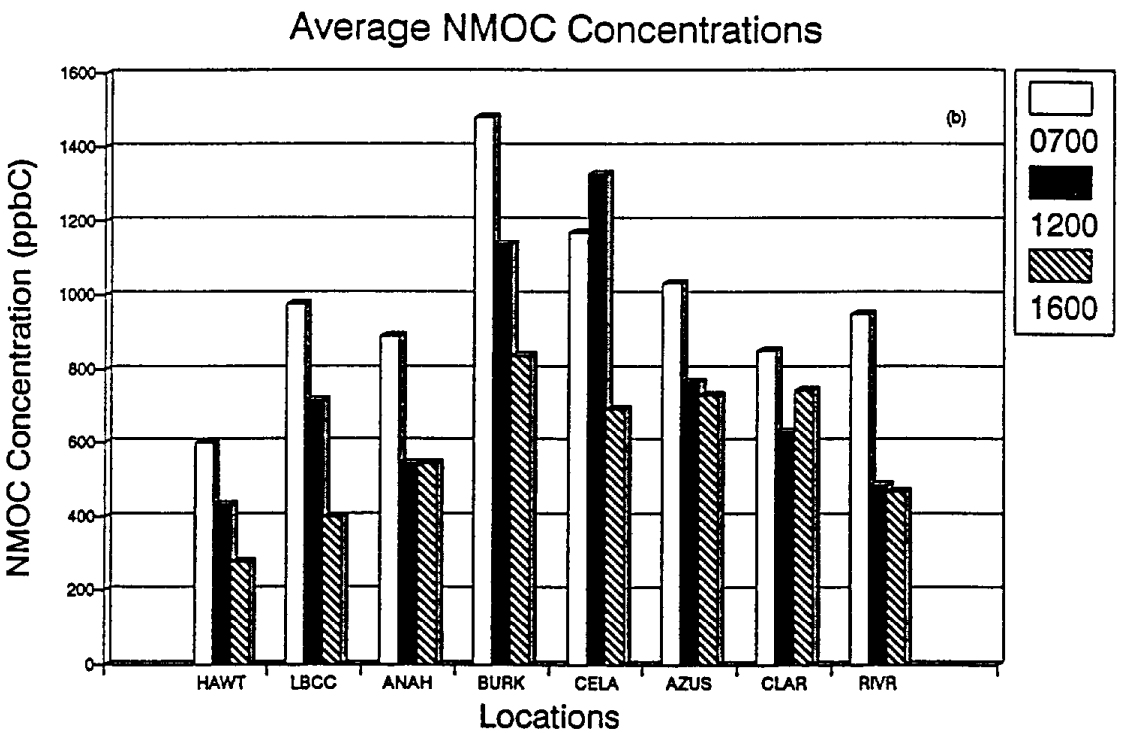
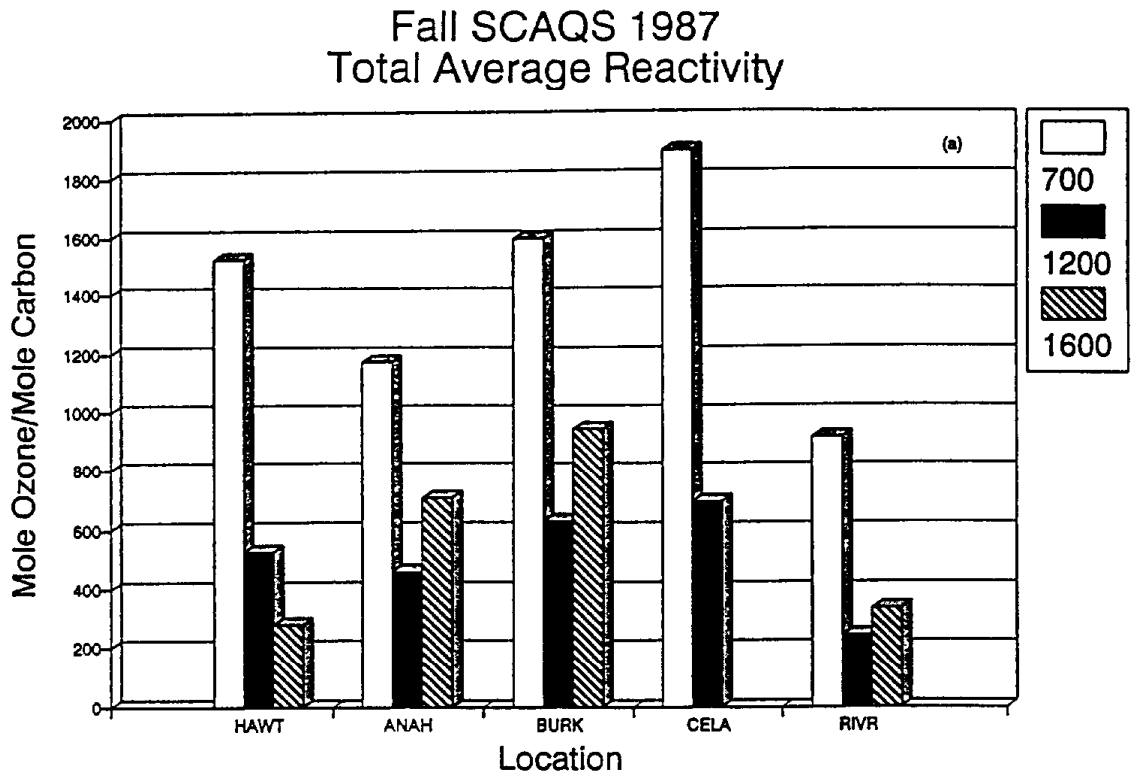


Figure 3-41. Average a) Total Sample Reactivity and b) NMOC Concentrations for Each Site by Time of Day for Summer SCAQS Data. Reactivity was calculated by multiplying each species concentration by the Carter reactivity value in moles ozone per mole carbon and summing over all species.



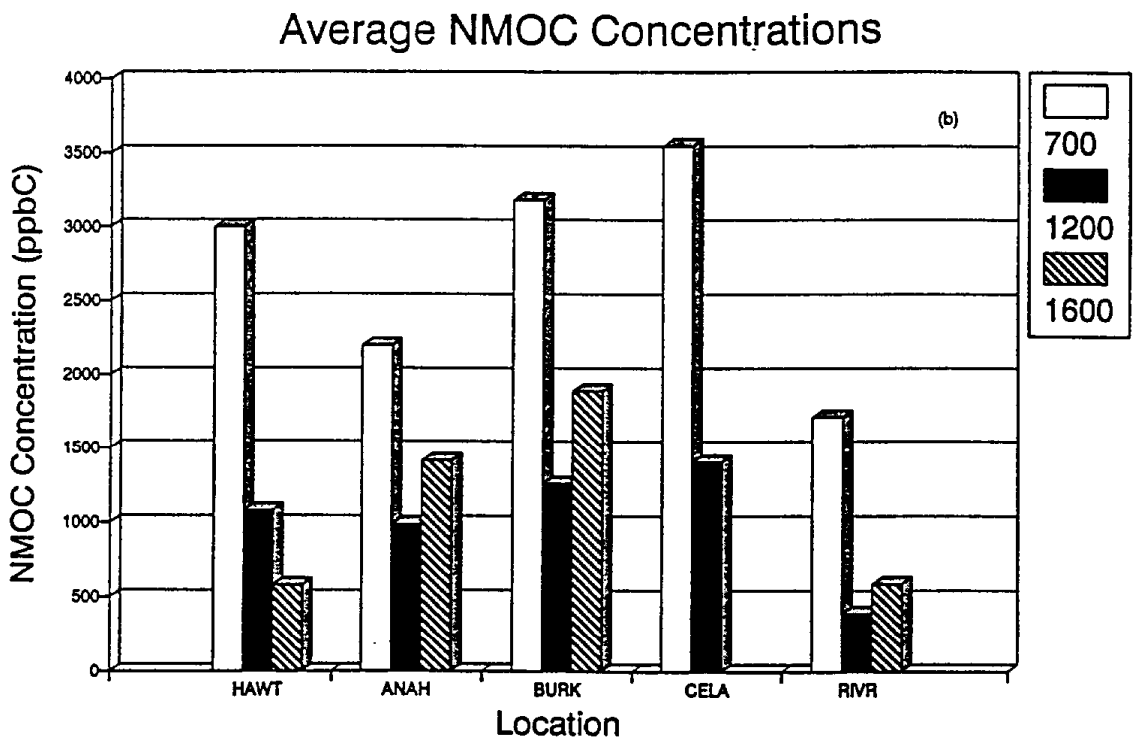


Figure 3-42. Average a) Total Sample Reactivity and b) NMOC Concentrations for Each Site by Time of Day for Fall SCAQS Data. Reactivity was calculated by multiplying each species concentration by the Carter reactivity value in moles ozone per mole carbon and summing over all species.

samples. It is important to note that all of the samples were collected at urban sites which probably have lower biogenic hydrocarbon emissions than might occur at outlying forested sites.

The basinwide average isoprene concentrations were 1.4, 1.4, and 1.3 ppbC at 0700, 1200, and 1600, respectively in summer. On a site-by-site basis, the mean isoprene concentrations were highest in the morning at all sites except Claremont and Long Beach, where the midday and afternoon isoprene concentrations were the highest. The diurnal pattern at Claremont and Long Beach is qualitatively consistent with the expected increases of isoprene emission rates with increases in temperature and solar radiation intensity. The mean and maximum isoprene concentrations measured at each SCAQS station are given below:

	Concentration, ppbC	
Site	Mean	Maximum
Anaheim	1.8	13.4
Azusa	1.0	4.1
Burbank	1.2	3.4
Claremont	3.5	22.7
Hawthorne	0.4	1.3
Long Beach	0.6	2.0
Los Angeles	1.1	2.8
Riverside	0.9	2.6

The highest concentrations were observed at Claremont.

On average, isoprene contributed 0.2% of the NMOC carbon and 0.7% of the NMOC reactivity in the summer. The observed frequency distributions of the isoprene contributions to NMOC and NMOC reactivity are shown in Figure 3-43. The distributions are similar and show that isoprene was almost always a small fraction of the NMOC and reactivity. However, in 10 of the 290 samples, isoprene contributed more than 10% of the NMOC reactivity. Overall, biogenic hydrocarbons appear to play a small role in ozone formation in the urban portion of the SoCAB. However, because isoprene reacts rapidly (with OH, ozone, and NO_3) the ambient observations probably underestimate its relative contribution.

3.9 RELATIVE AGE OF NMOC MIXTURES

The present understanding of the atmospheric oxidation of organic species suggests that, assuming the composition of emissions are relatively constant, the relative abundance of the more reactive species (olefins and more reactive aromatic hydrocarbons such as xylenes) should decrease with time during the daylight hours and the relative abundance of carbonyl compounds, alkanes, and less reactive aromatic species should increase with time during the daylight hours. Figure 3-16 shows that the fractions of

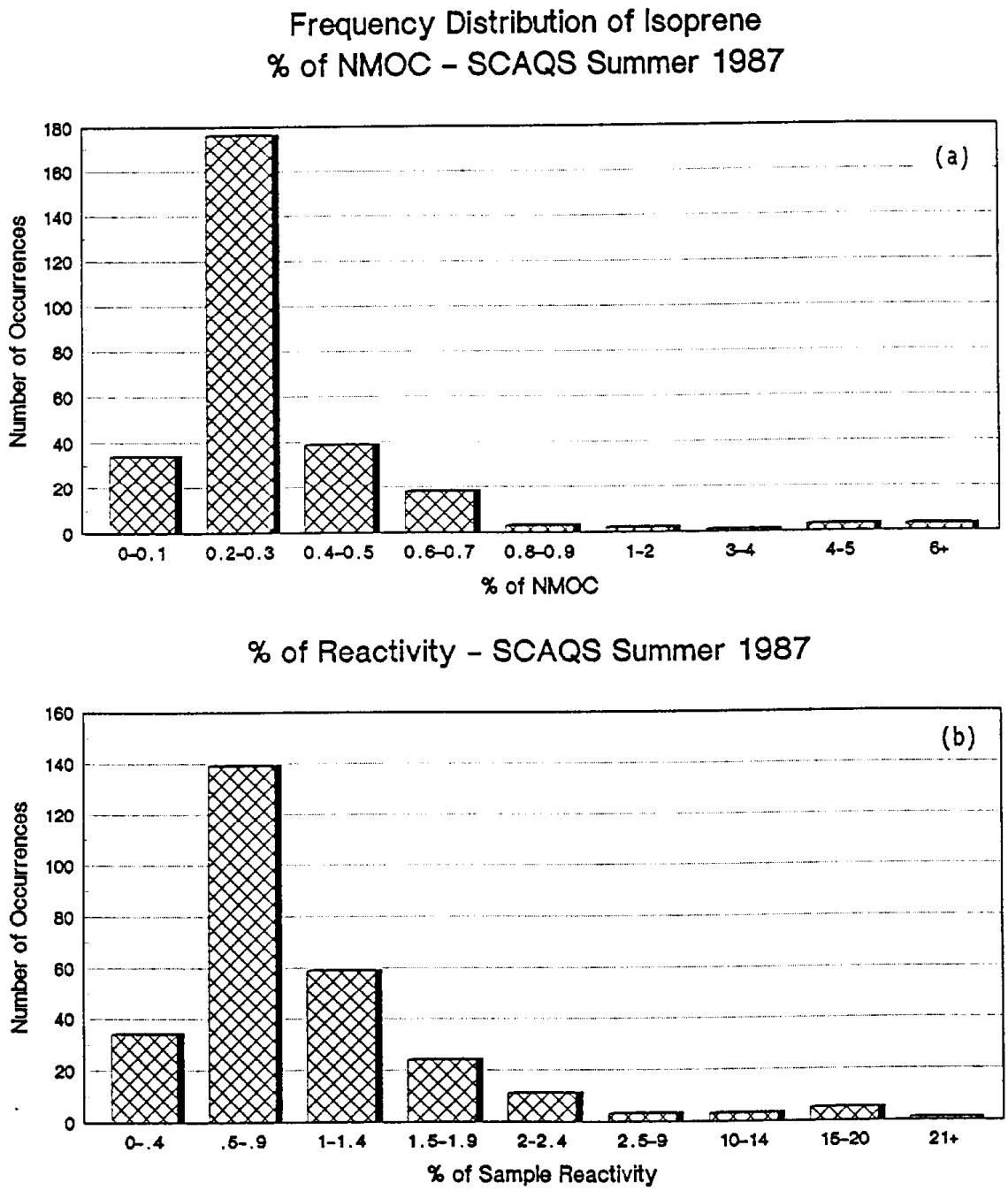


Figure 3-43. Frequency Distributions of Isoprene by a) Percent of NMOC and b) Percent of NMOC Reactivity.

the xylenes, propene and ethene decreased during the day while the fractions of propane and carbonyls increased. Contrary to expectation, the contribution of benzene, which is the least reactive aromatic species, decreased by a small amount over the course of the day. Large diurnal variations are expected for carbonyl compounds since they are a major product of the oxidation cycle. The data clearly show carbonyl species become an increasingly large fraction of NMOC over the course of the day.

The ratios of more reactive species concentrations to less reactive species concentrations are also indicative of the relative changes in species composition and age. Lower ratios correspond to more aged NMOC mixtures (for example, Nelson & Quigley, 1983). The ratios of several olefins to ethene, paraffins to propane, and aromatic hydrocarbons to benzene were examined in this study. The ratios of the sum of o-, p-, and m-xylenes to benzene, which are shown in Figure 3-44, are representative of the results from our ratio analysis. Xylenes and benzene are emitted primarily by motor vehicles and, based on OH rate constants for the mix of xylenes in the SoCAB, the xylenes are expected to react 14 times faster than benzene (Atkinson, 1990).

The average summer xylene to benzene ratios were between 2.2 and 2.5 in the morning at all sites except Azusa where the ratio was 2.9. In the fall, the morning ratios were between 2 and 2.3. The remarkable spatial consistency of the morning xylene to benzene ratios suggests all of the sites were strongly influenced by fresh emissions from a common type of source, which was most likely motor vehicles.

The xylene to benzene ratios exhibited modest diurnal variation at most sites in the summer and little diurnal variation in the fall. The midday ratios were lower than the morning ratios at all sites except Riverside in the fall. The decrease in the ratio during the morning is presumably from oxidation and aging of the mixtures. In theory, if there were no fresh emissions added between 0700 and 1200, atmospheric oxidation would reduce the morning ratio by 50% to 75% in 5 hours in the summer, based on the known OH rate constants and OH concentrations of 1 to 2×10^{-7} ppm. In the summer, the average noontime ratios were between 5% and 20% lower than the 0700 ratios at all sites except Azusa and Riverside where they were about 50% lower. In the fall, they were mostly 5% to 10% lower. This pattern could occur if the oxidation was much slower than expected, if there were large area sources of xylenes with little or no co-emitted benzene, or if there was significant amounts of fresh emissions with comparable xylene to benzene ratios throughout the morning which offset the effects of oxidation on the ratio.

The xylene to benzene ratios observed in the afternoon were generally higher than the midday ratios and comparable to the morning ratios in the summer at Hawthorne, Long Beach, Anaheim, and Los Angeles. At Burbank and at other sites in the eastern part of the air basin, the afternoon ratios were comparable to the midday ratios in summer. In the fall, the afternoon ratios were similar to the midday ratio. Thus, there was little evidence of oxidation between 1200 and 1600 in either season. Our interpretation of the summer data is that the western and central portion of the air basin have continuous emissions of xylene and benzene which maintain the ambient

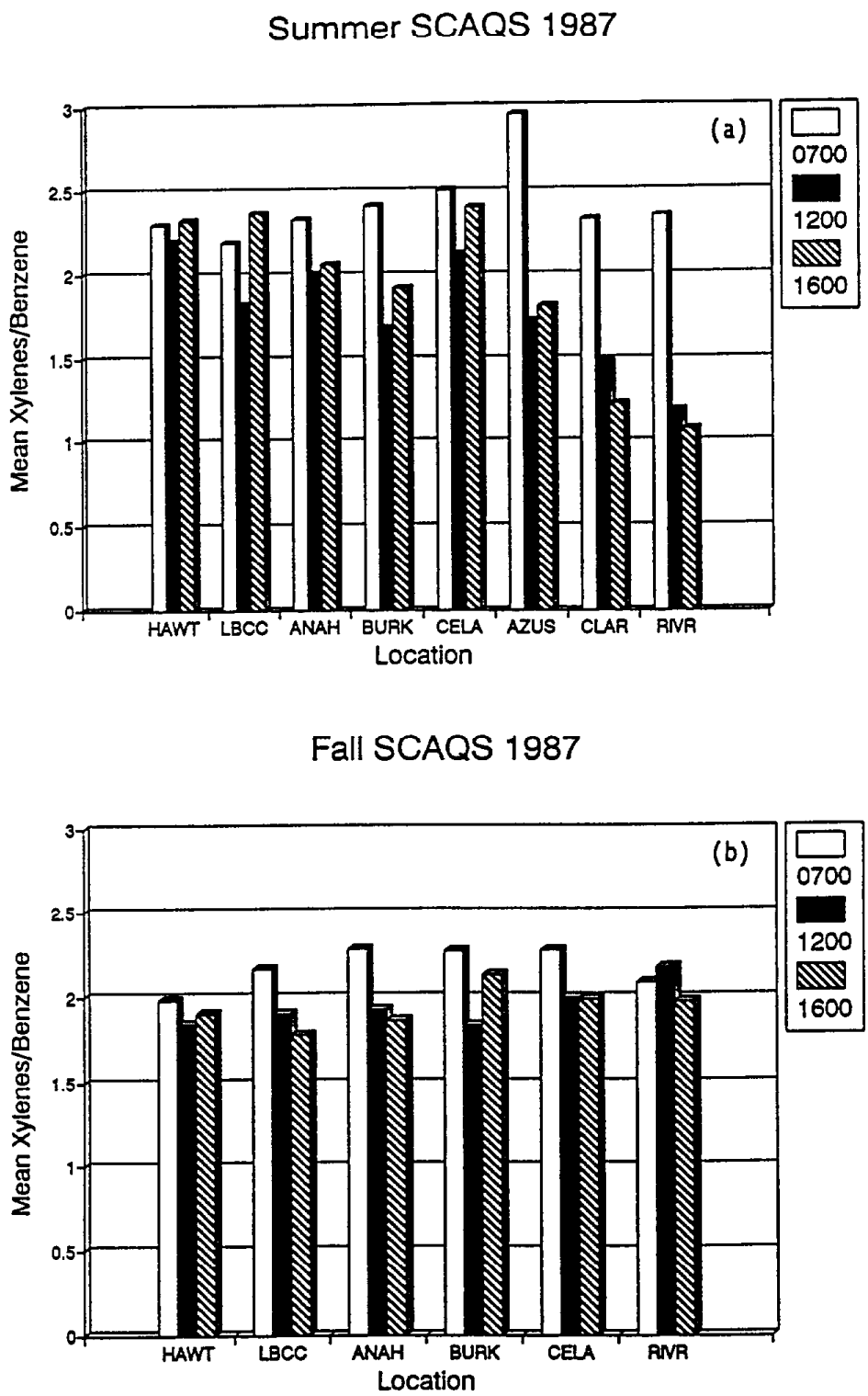


Figure 3-44. Mean Xylenes to Benzene Ratios for Each Site by Time of Day for the a) Summer (PDT) and b) Fall (PST) SCAQS 1987. Sites are ordered from coastal to central to eastern basin.

ratio close to the fresh emissions ratio, and the eastern portion of the air basin is influenced by a combination of aging transported NMOC and fresh emissions. In the fall, there is less oxidation and the ambient ratio is maintained close to the "fresh emissions" ratio by continuous emissions throughout the basin. The absence of strong diurnal trends in the ratios of other more reactive to less reactive species that we examined provides additional support for this interpretation.

3.10 SAN NICOLAS ISLAND NMOC DATA

During the summer SCAQS, hydrocarbon and carbonyl samples were collected three times per day on San Nicolas Island which is located 120 km offshore. These data were collected to characterize the background levels of pollutants flowing into the SoCAB. Detailed summaries of the average concentrations of abundant species and compound groups are presented in Tables D-9 and D-18 by sampling time. Main et al. (1990) analyzed these data along with other southern California background NMOC data and found it necessary to partition the observations into "clean" and "dirty" samples, because not all of the data resembled background air. Their criteria for a clean sample were as follows:

Methane	$\leq$ 2000 ppb,
Carbon Monoxide	$\leq$ 200 ppb,
Ethane	$\leq$ 10 ppbC,
Ethane	$\leq$ 2 ppbC,
Ethene	$\leq$ 2 ppbC,
Acetylene	$\leq$ 2 ppbC,
Total Xylenes	$\leq$ 2 ppbC, and
Ozone	$\leq$ 70 ppb.

The restriction on xylene concentration proved to be most stringent for these samples. About half of the 25 San Nicolas Island samples had total xylenes in excess of 2 ppbC which was interpreted as evidence of relatively fresh emissions. There were military operations on the island which could have caused the elevated levels.

Table 3-20 lists the summary statistics for the NMHC and NMOC concentrations of the clean, dirty, and unscreened samples from San Nicolas Island. The median NMHC and NMOC concentrations in clean samples were 51 and 71 ppbC, respectively. In the dirty samples, the median NMHC and NMOC concentrations were 81 and 114 ppbC, respectively. The unscreened data set had median NMHC and NMOC concentrations of 61 and 99 ppbC, respectively. These NMHC levels are substantially higher than expected in clean tropospheric air. Even the clean NMHC concentrations were more than double the median levels observed by aircraft in the Santa Barbara Channel during the South Central Coast Cooperative Aerometric Monitoring Program (SCCCAMP) and at the remote Santa Barbara County coastal sites of Point Arguello and Jalama Beach (Main et al., 1990).

Table 3-20 also lists the summary statistics for the total carbonyl concentrations and the ratio of carbonyl compounds to NMOC (carbon basis). The median carbonyl concentrations were 13 and 34 ppbC in the clean and

Table 3-20. Carbonyl and NMOC Concentrations for San Nicolas Island Samples

	Concentrations (ppbC)				
	Minimum	25%	Median	75%	Maximum
Unscreened					
NMOC	42.2	64.2	99.2	143	241
NMHC	20.1	46.4	60.7	108	206
Carbonyl	0.6	8.4	33.7	41.4	72.1
Carbonyl/NMOC	0.03	0.15	0.30	0.41	0.70
Clean					
NMOC	42.2	57.9	70.9	143	189
NMHC	20.1	45.9	50.7	101	181
Carbonyl	0.6	7.2	12.6	46.7	72.1
Carbonyl/NMOC	0.03	0.12	0.30	0.33	0.70
Dirty					
NMOC	64.2	94.6	114	140	241
NMHC	36.9	55.1	80.7	118	206
Carbonyl	3.5	30.5	33.8	38.4	48.2
Carbonyl/NMOC	0.06	0.18	0.30	0.45	0.54

dirty samples, respectively. The relative abundance of carbonyl species was high on San Nicolas Island, much higher than onshore in the SoCAB. The median and maximum carbonyl to NMOC ratios were 0.30 and 0.70, respectively. Aged NMOC mixtures are expected to have higher carbonyl content than fresh urban NMOC because of hydrocarbon oxidation. The C1-C3 carbonyl concentrations are consistent with chemical expectations. However, these data also have surprisingly large amounts of C4+ carbonyl compounds, the source of which is unknown.

Figures 3-45 and 3-46 show the concentrations of individual species and compound groups in the clean and dirty samples. These figures show that many of the species that were abundant onshore were also abundant far offshore. For example, propane, isopentane, n-pentane, toluene, m- & p-xylene, and 1,2,4-trimethylbenzene were relatively abundant compared to most other species. However, Figure 3-47 shows that the normalized composition of the offshore NMOC is significantly different than the onshore NMOC. The contributions of most of the abundant hydrocarbons to NMOC are significantly lower and the contributions of the carbonyl compounds are significantly higher than onshore.

3.11 CLUSTER AND PRINCIPAL COMPONENT ANALYSES

Cluster, factor and principal component analyses were used to investigate spatial and temporal relationships in the NMOC data. Cluster analysis is a multi-variate procedure for detecting groupings in data. For this analysis, we used hierarchical clusters which consists of clusters that completely contain other clusters. Hierarchical clusters have tree-like structure. The Pearson correlation method was used to measure similarity in patterns across profiles regardless of overall magnitude.

Principle component (PC) analysis is a form of regression analysis used to identify the linear combination of variables that explain the most variability in the data. This analysis method is used to reduce the number of variables needed to explain variance in the data. The coefficients of each PC are determined by computing the eigenvalues and then determining the proportion of total variance accounted for by each component. The component weights are a linear combination of the variables. Each coefficient is analogous to a correlation coefficient.

Factor analysis extracts PC's for variables. The method is similar to PC analysis except that factor weights are scaled so that the sum of the squares equals the associated eigenvalue and is related to the total variance explained by that factor. Communalities are estimated using the squared multiple correlation between that variable and all other variables. The communality indicates the proportion of the variability of each variable that is shared with other variables in the data set.

These three analyses were performed using data for the 35 most abundant species, which include the 25 most abundant species, shown in Table 3-4, and ten others: 2,4-dimethylpentane, 2,3-dimethylbutane, pentanal, 3-methylhexane, 2,3-dimethylpentane, m-ethyltoluene, propanal, C6 carbonyl and MEK. These 35 species account for 71% of the total carbon of

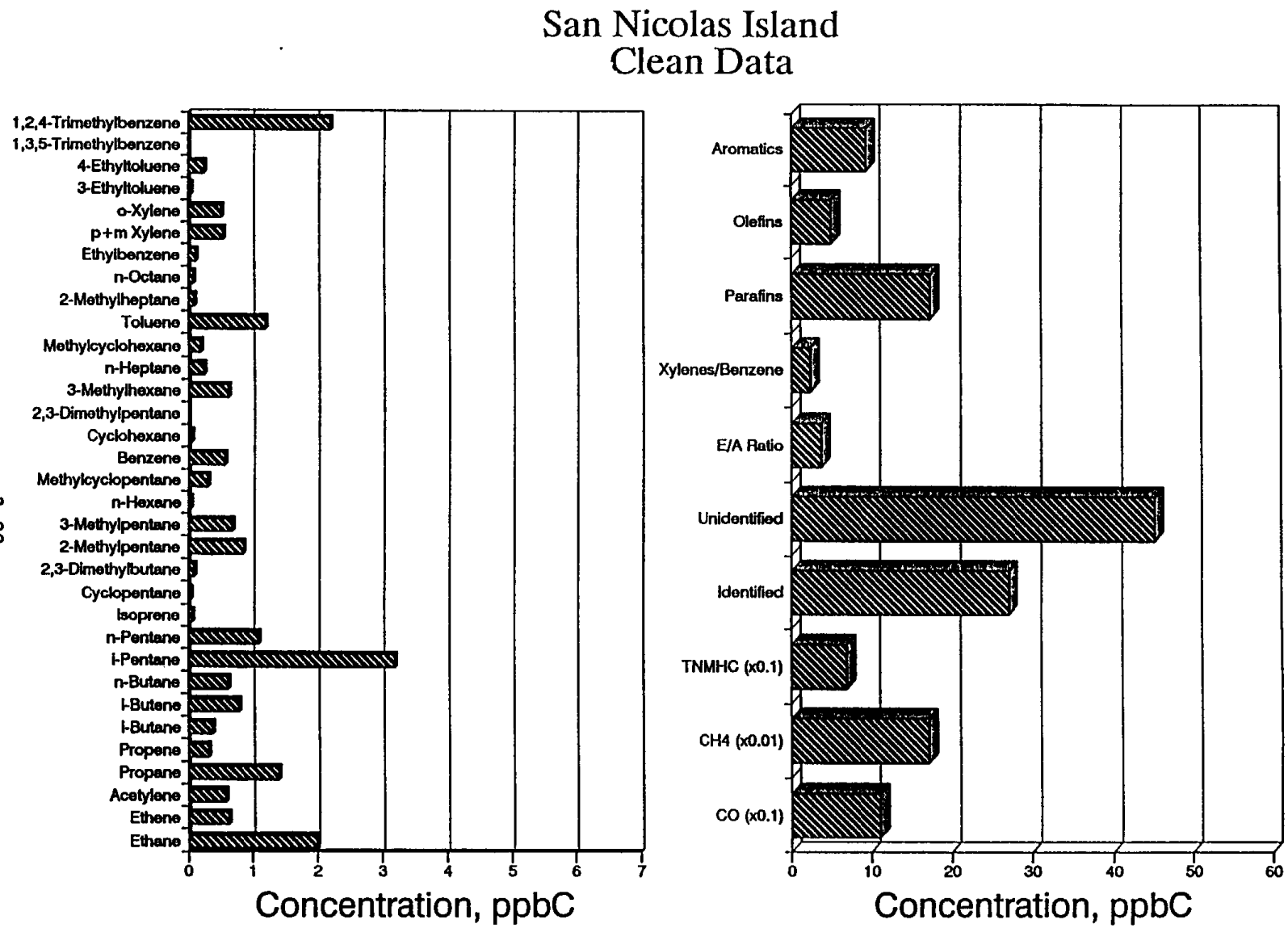


Figure 3-45. Clean San Nicolas Island Surface Data (13 Samples). The average concentration profile of 33 common VOC species and of CO, methane, total nonmethane hydrocarbons and major hydrocarbon groups.

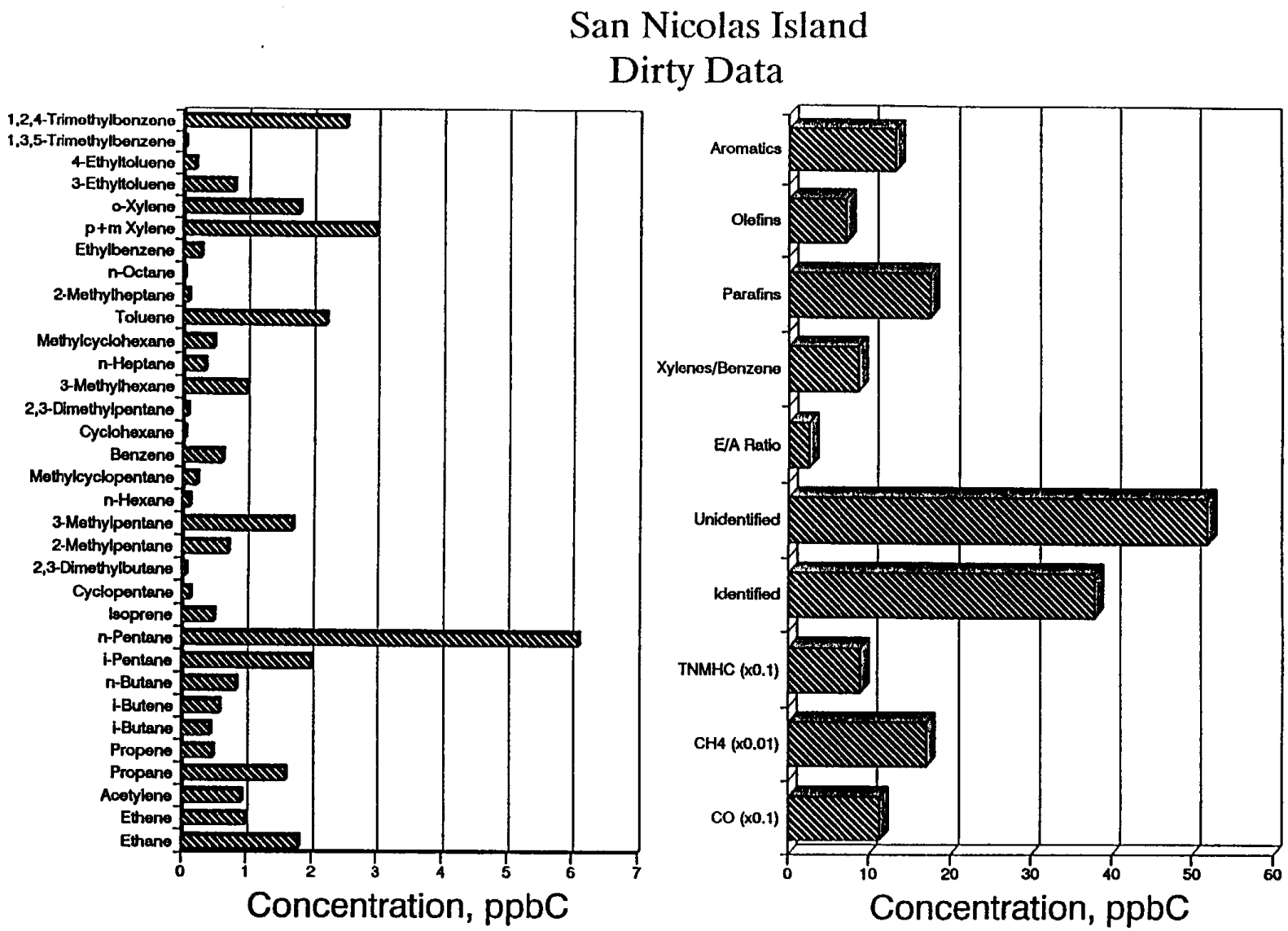


Figure 3-46. Dirty San Nicolas Island Surface Data (23 Samples). The average concentration profile of 33 common VOC species and of CO, methane, total nonmethane hydrocarbons and major hydrocarbon groups.

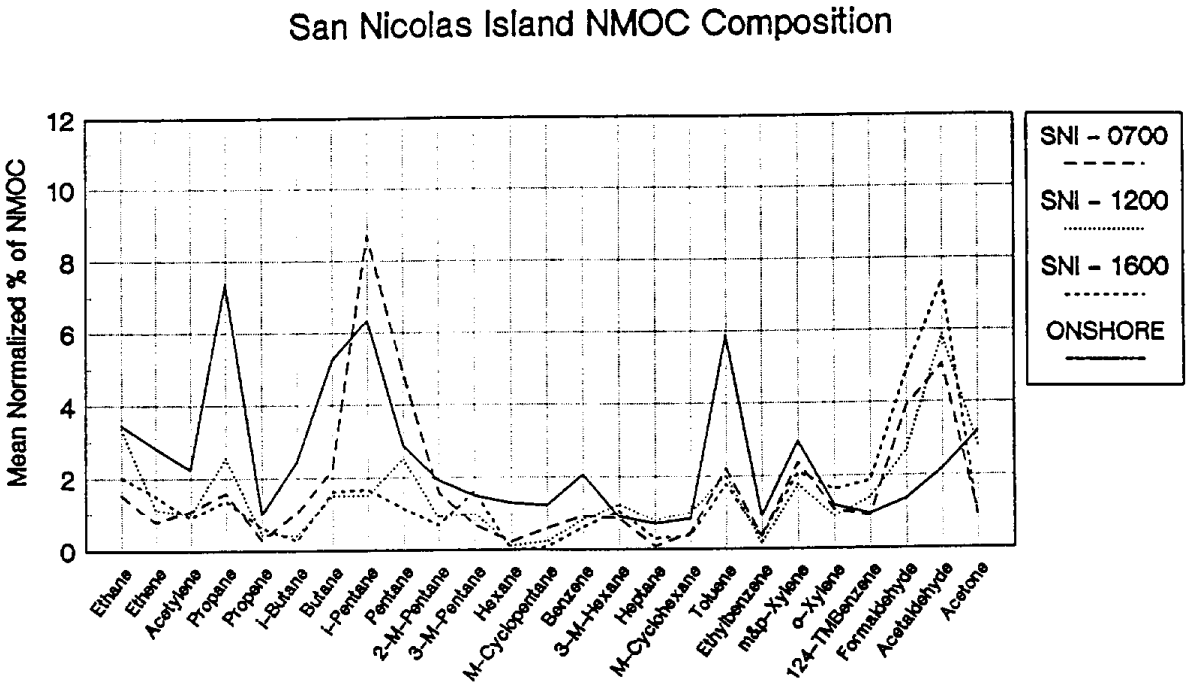


Figure 3-47. Normalized Composition of NMOC at San Nicolas Island by Time of Day Compared to the Onshore Average Composition.

both the summer and fall samples on average. The analyses were performed first using all valid samples and then with the samples averaged by site and time of day. The results were compared and found to be very similar. The analyses were also performed with the species lumped into the modeling groups and those results were consistent with the results obtained using the 35 species. Analyses were performed on concentrations, carbon fractions, and reactivity-weighted concentrations. San Nicolas Island data were not included in these analyses after an initial investigation showed that these data were always very different from the inland data.

3.11.1 Cluster Analysis

Figure 3-48 shows the clustering of the average carbon fraction data by site and time in the summer. At the highest level, the cluster analysis shows the morning samples are distinct from the mid-day and afternoon samples. The clustering of morning samples is consistent with the hypothesis that fresh vehicle emissions contribute the majority of the ambient NMOC at all sites in the morning and that the fresh motor vehicle emissions profile is somewhat distinct from that observed later in the day, which probably includes partially reacted NMOC and significant amounts of NMOC from both stationary and mobile sources. The close clustering of all the mid-day and afternoon samples suggests that neither the spatial variations nor temporal variations between 1200 and 1600 are particularly large. The analysis of the summer concentration data and reactivity-weighted data showed similar clustering. At a finer level, six distinct groupings are apparent:

(1) samples collected at Hawthorne at 0700,
(2) other samples collected at 0700,
(3) samples collected at Los Angeles at 1600,
(4) samples collected at Long Beach at 1600,
(5) samples collected at Long Beach and Hawthorne at 1200 and at Hawthorne at 1600, and
(6) the rest of the samples collected at 1200 and 1600.

The analysis shows that the NMOC composition and concentrations at Hawthorne were quite different than other stations at all times of the day. Long Beach and Los Angeles also stand out late in the day. These findings are consistent with the analyses of spatial and temporal patterns discussed in Sections 3.1 through 3.4.

Figure 3-49 shows the clustering of the species averaged by site and time for the summer. The two major clusters are hydrocarbons and carbonyl compounds. At a finer level, the species were grouped into seven distinct clusters:

(1) ethane,
(2) n-butane,
(3) propane and isobutane,
(4) 3-methylpentane,
(5) propene,
(6) other hydrocarbons, and
(7) carbonyl compounds.

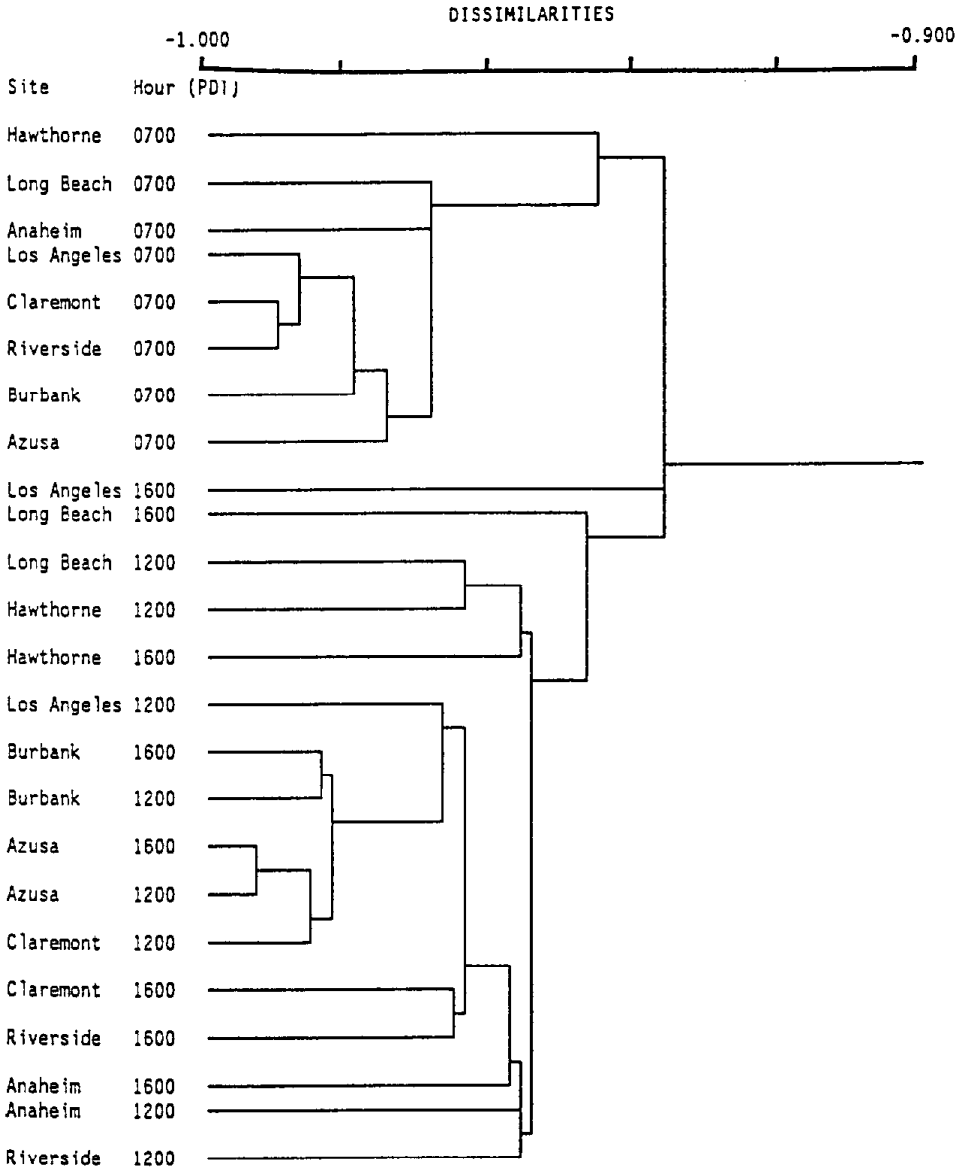


Figure 3-48. Hierarchical Tree Diagram of Site/Time Averaged Fraction of NMOC for the Summer SCAQS 1987. The 35 most abundant species were used in this analysis. Note that the dissimilarities are small; the sites had similar compositions.

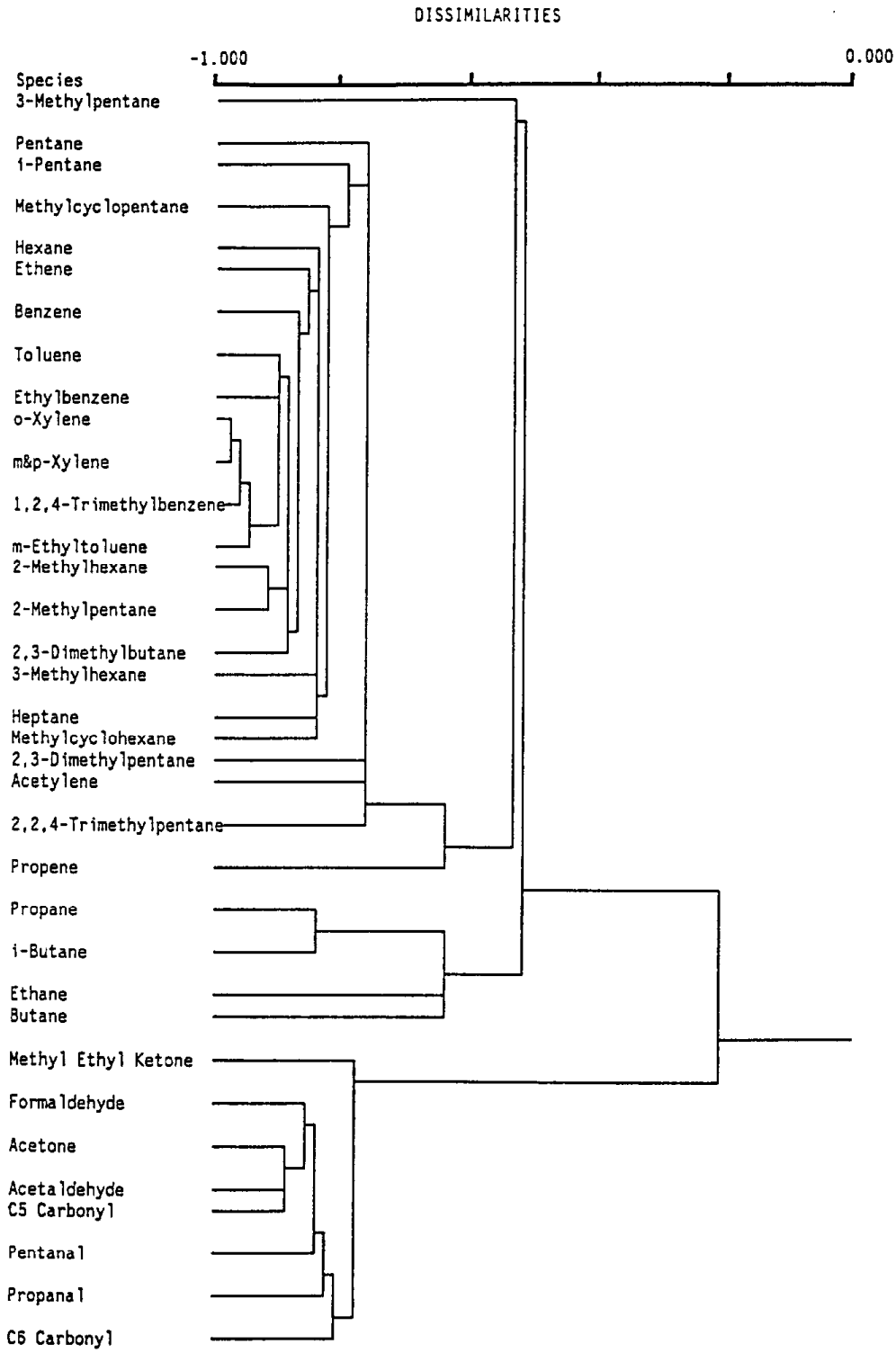


Figure 3-49. Hierarchical Tree Diagram of Species for the Summer SCAQS 1987. The site/time-averaged fractions of the most abundant 35 species were used in this analysis. Note that the dissimilarities are larger than those in Figure 3-48.

This analysis suggests there may be distinct sources of C2-C4 paraffins in the basin. Ethane may have less spatial and temporal variability because there is a significant global background concentration over which the urban contributions are superimposed. Likewise, there may be distinct stationary sources of propane, such as in refinery operations. N-butane and isobutane may appear distinct because the pattern of evaporative emissions differs significantly from the other sources of these species; however, it is odd that isobutane was grouped with propane rather than with n-butane. The analysis also shows 3-methylpentane is distinct, however, we are not aware of any unique sources of this compound. Propene is the only highly reactive compound identified by the analysis. Propene may appear distinct either because it is one of the most abundant species that reacts quickly or because there are unique sources of propene.

The application of cluster analysis to the fall data, shown in Figure 3-50, indicated there were smaller temporal differences and larger spatial differences than in the summer data. Mid-day and afternoon samples collected at Riverside and Anaheim were most distinct from other samples. Figure 3-51 shows the species clustering in the fall. It shows that the two major groups are the hydrocarbons and carbonyl compounds, as were found in the summer data. At a finer level, the distinct species groups are:

(1) ethane and isobutane,
(2) propane,
(3) n-butane,
(4) 3-methylpentane,
(5) n-pentane, and
(6) other hydrocarbons, and
(7) carbonyl compounds.

These results are similar to those for the summer except isobutane is grouped with ethane, rather than propane, and n-pentane replaced propene. Like the summer, these results suggest there may be some unique sources of light (C2-C5) paraffins in the basin during the fall, such as refinery operations and mobile source evaporative emissions.

3.11.2 Principal Component and Factor Analyses

Principal component analysis and factor analysis were carried out to determine if their were factors in the data that provided evidence for contributions of different types of sources at different stations or at different times of day. Based on current emissions inventories, we hoped to find a motor vehicle exhaust component, a motor vehicle evaporative component, and one or more stationary source components.

Table 3-21 shows the factor loadings from factor analysis of the summer carbon fraction data. The principal component analysis indicated 86 percent of the variance was explained by one component, and the second component explained less than 8 percent of the variance. All of the site/time averages were highly correlated with the first component. However, the 0700 data were also modestly well correlated (r^2 = 0.16 to 0.5) with the second component. The rotated factors, also shown in Table 3-21,

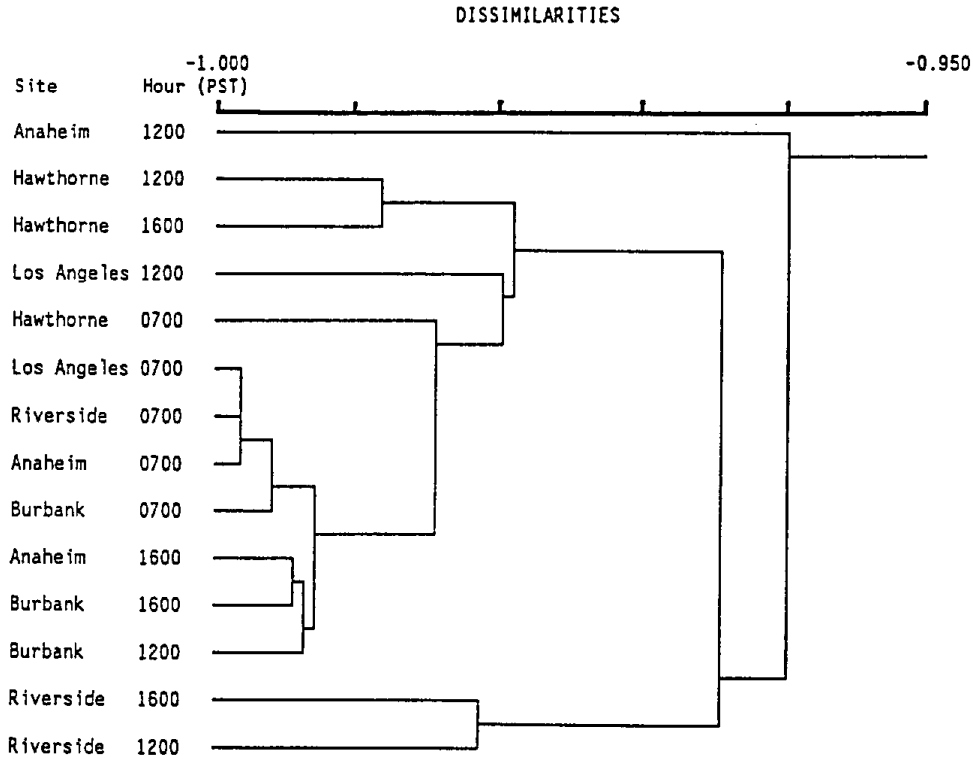


Figure 3-50. Hierarchical Tree Diagram of Site/Time Averaged Fraction of NMOC for the Fall SCAQS 1987. The 35 most abundant species were used in this analysis. Note that the dissimilarities are very small; the sites had very similar compositions.

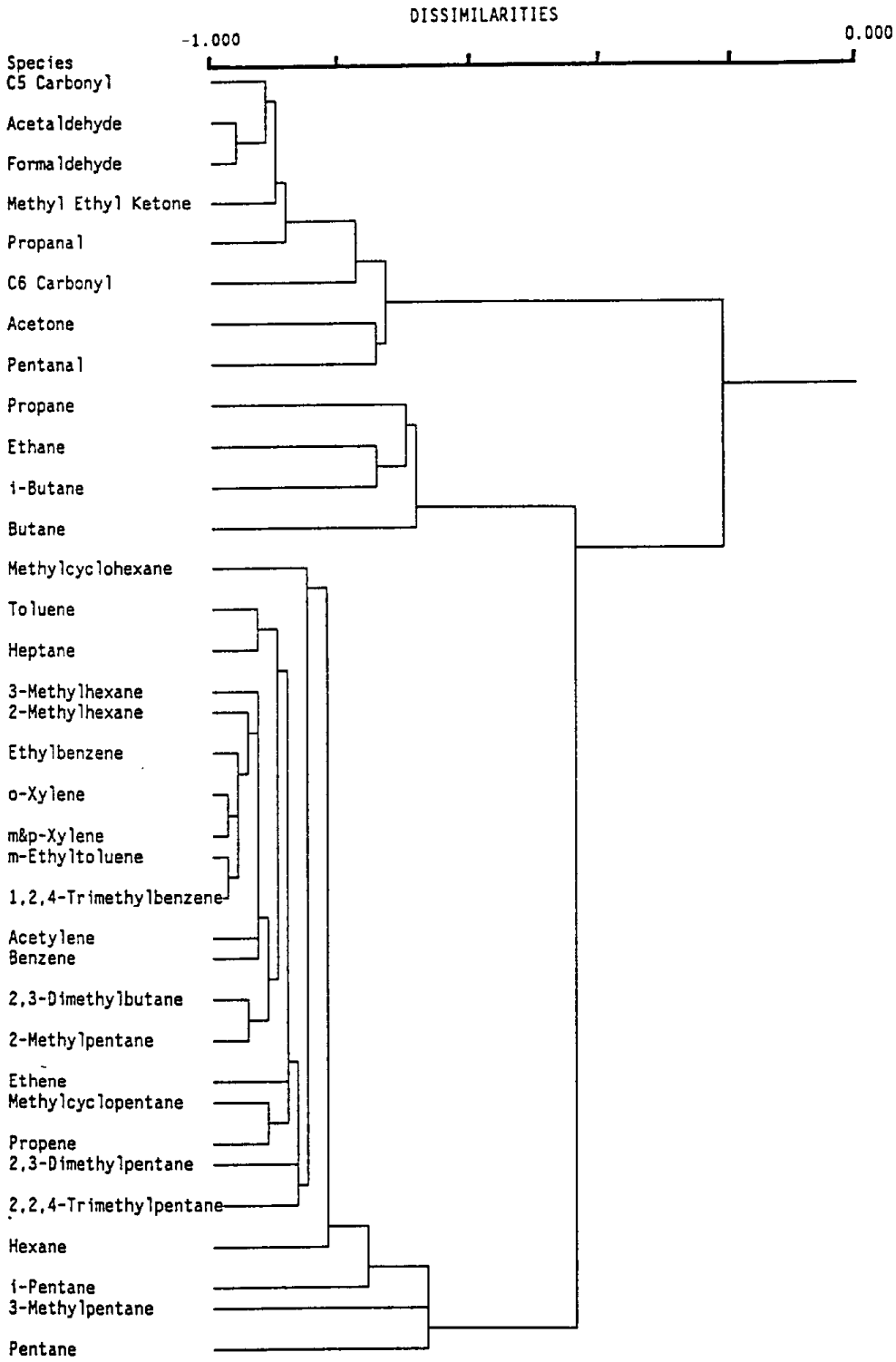


Figure 3-51. Hierarchical Tree Diagram of Species for the Fall SCAQS 1987. The site/time averaged fractions of the most abundant 35 species were used in this analysis. Note that the dissimilarities are larger than those in Figure 3-50.

Table 3-21. Results of Factor Analysis on the Mean Site/Time Fraction of NMOC Data From Summer SCAQS 1987

		Factor Matrix			
		Factor Loadings		Varimax Rotated Factor Loadings	
Site	Hour	1	2	1	2
Anaheim	0700	0.954	0.229	0.519	0.833
Anaheim	1200	0.911	-0.297	0.858	0.427
Anaheim	1600	0.955	-0.191	0.815	0.534
Azusa	0700	0.900	0.376	0.378	0.900
Azusa	1200	0.978	-0.152	0.804	0.577
Azusa	1600	0.974	-0.143	0.795	0.581
Burbank	0700	0.924	0.362	0.404	0.906
Burbank	1200	0.993	-0.020	0.722	0.681
Burbank	1600	0.978	0.019	0.684	0.700
Los Angeles	0700	0.862	0.490	0.270	0.954
Los Angeles	1200	0.966	0.091	0.624	0.743
Los Angeles	1600	0.901	0.107	0.567	0.708
Claremont	0700	0.912	0.392	0.375	0.919
Claremont	1200	0.962	-0.177	0.810	0.548
Claremont	1600	0.936	-0.319	0.892	0.428
Hawthorne	0700	0.917	0.158	0.542	0.756
Hawthorne	1200	0.889	-0.281	0.831	0.423
Hawthorne	1600	0.918	-0.143	0.755	0.542
Long Beach	0700	0.916	0.280	0.456	0.842
Long Beach	1200	0.910	-0.254	0.827	0.456
Long Beach	1600	0.960	0.032	0.661	0.696
Riverside	0700	0.926	0.349	0.415	0.898
Riverside	1200	0.827	-0.458	0.911	0.253
Riverside	1600	0.865	-0.474	0.949	0.268

again indicated that the 0700 early morning samples were more correlated with the second factor than with the first. Principal component analysis on the species (concentrations) indicated 65 percent of the variance was explained by one component, and the second component explained 19 percent of the variance. Figure 3-52 shows the plot of the component weights for each species. It shows that the first component included relatively high weights for hydrocarbons and low weights for carbonyl compounds, whereas the second component had the high carbonyl compound weights and a mixture of negative and positive hydrocarbon weights. The second factor is probably physically meaningless because of the negative concentration weights. Similar results were obtained using reactivity-weighted concentration and composition data.

Application of principal component analysis to the fall composition data identified two factors which explained 94 percent of the variance; 87 percent by the first component and 7 percent by the second component. The correlation of sites and sampling times with the two factors are shown in Table 3-22. The site/time data were all well correlated with the first factor. The rotated factors, also shown in Table 3-22, indicated the samples from Riverside at 1200 and 1600 and from Anaheim at 1200 were more correlated with the second factor than with the first. Application of factor analysis to the fall concentration data and reactivity-weighted concentration and composition data also only identified one major factor.

Overall, the principal component and factor analysis did not identify multiple factors which could be physically interpreted as contribution from different source types. Rather, the analysis indicated there was one major factor, "the urban NMOC composition factor", that explained the majority of the variance at all sites and times.

3.12 TOXIC ORGANIC SPECIES

Twenty-four hour average NMOC samples were collected and analyzed to determine the concentrations of selected toxic organic compounds during the SCAQS. The analysis focused on the following chlorinated and brominated compounds:

1) carbon tetrachloride,
2) dichloromethane
3) trichloromethane,
4) trichloroethene,
5) trichloroethane,
6) tetrachloroethene,
7) bromomethane, and
8) dibromoethene.

Samples were collected on SCAQS intensive days at Long Beach, Los Angeles, Claremont, and Riverside in the summer. The ARB and OGI collected samples in 50-liter Tedlar bags and 15-liter canisters, respectively, at all sites. The data were analyzed by gas chromatography using photo-ionization detection and electron capture detection (Rasmussen, 1989; Hering and Blumenthal, 1989).

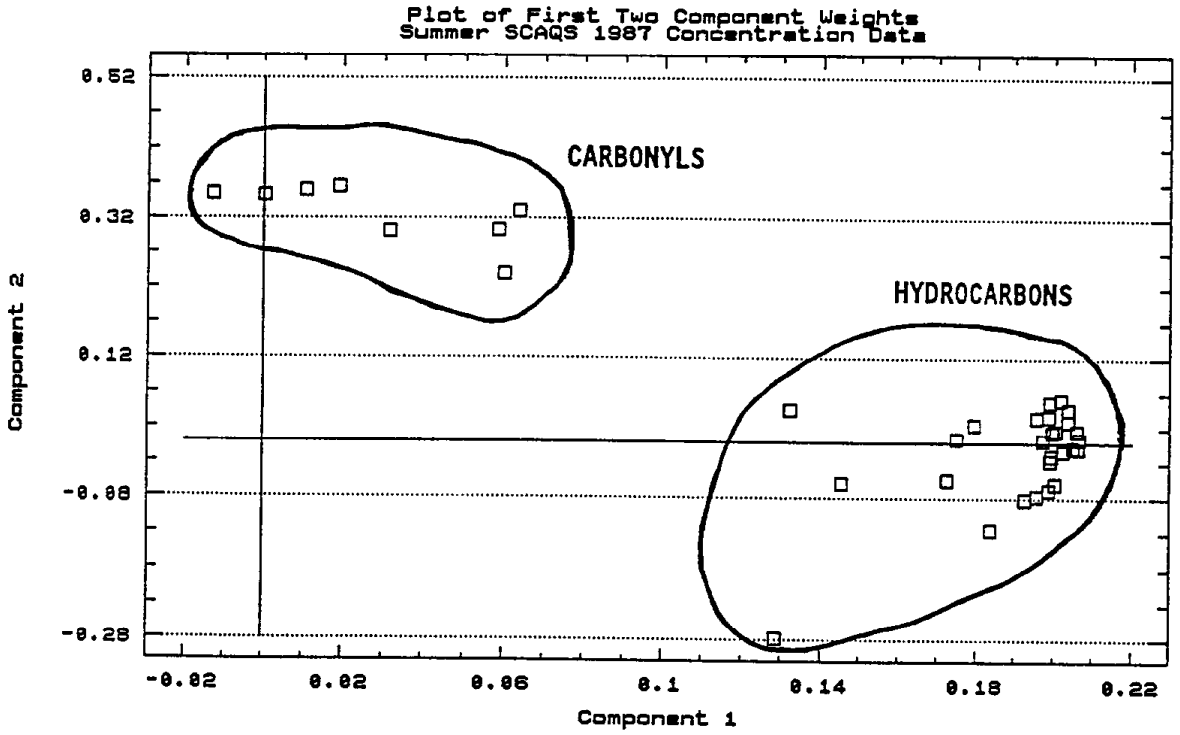


Figure 3-52. Scatter Plot of the First Two Principal Component Weights for Summer Speciated Data. Carbonyl compounds and hydrocarbons are in separate groupings.

Table 3-22. Results of Factor Analysis on the Mean Site/Time Fraction of NMOC Data From the Fall SCAQS 1987

		Factor Matrix			
		Factor Loadings		Varimax Rotated Factor Loadings	
Site	Hour	1	2	1	2
Anaheim	0700	0.963	-0.230	0.901	0.411
Anaheim	1200	0.799	0.362	0.406	0.777
Anaheim	1600	0.992	-0.036	0.804	0.582
Burbank	0700	0.955	-0.234	0.897	0.404
Burbank	1200	0.974	-0.011	0.774	0.590
Burbank	1600	0.980	-0.083	0.823	0.538
Los Angeles	0700	0.938	-0.289	0.917	0.350
Los Angeles	1200	0.940	0.041	0.715	0.612
Hawthorne	0700	0.962	-0.203	0.883	0.432
Hawthorne	1200	0.954	0.039	0.728	0.618
Hawthorne	1600	0.919	0.142	0.636	0.678
Riverside	0700	0.945	-0.250	0.898	0.385
Riverside	1200	0.798	0.485	0.330	0.874
Riverside	1600	0.859	0.458	0.394	0.890

The mean concentrations of the toxic compounds are shown in Table 3-23 and Figure 3-53. Also shown are the average formaldehyde, acetaldehyde, and 1,3-butadiene concentrations based on ENSR's and EPA's analysis of the 1-hr samples collected at all stations. The ARB and OGI mean concentration data agree within a factor of two at all stations for several important species, such as benzene, carbon tetrachloride, and tetrachloroethene, however, the data for other species compare poorly. For example, the mean dichloromethane concentrations reported by ARB and OGI are 3.2 and 9.1 ppb, respectively. The reasons for the poor comparison are unknown.

The data indicate ambient concentrations of most chlorinated and brominated organic species were higher at Los Angeles than at other sites. Progressively lower concentrations were observed at Claremont, Long Beach, and Riverside. The concentrations of benzene and 1,3-butadiene were significantly higher at Los Angeles than elsewhere. The concentrations of formaldehyde and acetaldehyde were highest at Claremont and lowest at Long Beach. Trichloroethene and dibromoethane showed the most day-to-day variability while carbon tetrachloride varied the least. In addition, the highest concentrations of toxics occurred on September 2nd, which was the day when the concentrations of other VOCs were highest.

3.13 AVERAGING TIME EFFECTS

The SCAQS VOC data provided an opportunity to compare VOC data collected for different averaging times. A comparison of 22 abundant VOC species as a function of the duration of the sampling period was made using Stockburger's one-hour samples, Lonneman's 3-hr samples, and Rasmussen's 24-hr samples. The comparison included samples taken during the summer at Claremont, Los Angeles, and Long Beach. Lonneman's 3-hr samples were collected from 0600 to 0900 PDT. The 1-hr data used in the comparison were taken from 0700 to 0800 PDT (the 0900 to 1000 PDT data were only slightly lower than the 0700 data). As shown in Figure 3-54, the 0700 1-hr concentrations and the 3-hr concentrations were quite similar on average with the exception of the C2 species and isopentane. The concentrations of species collected in 24-hr samples were typically 10 to 30 percent lower than the 1-hr and 3-hr average data. The differences between the 24-hr concentrations and those for shorter averaging times were smaller than expected and provide additional support for the "continuous emissions" hypothesis.

Table 3-23. Average Concentrations of Toxic Organic Species for Summer SCAQS 1987

	24-Hour Average Concentration, ppb									
	Los Angeles		Claremont		Long Beach		Riverside		Overall	
	Mean	Standard Deviation	Mean	Standard Deviation	Mean	Standard Deviation	Mean	Standard Deviation	Mean	Standard Deviation
Oregon Graduate Institute										
Dichloromethane[a]	8.15	2.68	12.1	6.43	10.2	4.13	5.87	1.86	9.14	4.77
Trichloromethane[b]	0.08	0.03	0.13	0.06	0.06	0.02	0.06	0.01	0.08	0.05
Trichloroethane	3.25	1.09	2.22	0.47	3.22	1.17	1.57	0.38	2.59	1.11
Carbon Tetrachloride[c]	0.12	0.01	0.11	0.01	0.11	0.01	0.11	0.00	0.11	0.01
Trichloroethene	0.30	0.20	0.07	0.04	0.14	0.12	0.51	0.61	0.25	0.36
Tetrachloroethene	1.13	0.42	0.80	0.16	0.56	0.47	0.42	0.06	0.73	0.42
Benzene	5.44	2.51	3.07	0.73	1.59	0.84	2.45	0.59	3.15	2.02
Dibromoethane[d]	0.06	0.04	0.02	0.01	0.02	0.00	BD		0.03	0.03
Bromomethane	0.29	0.20	0.25	0.07	0.20	0.07	0.23	0.07	0.24	0.09
Air Resources Board										
Dichloromethane[a]	1.60	1.66	1.43	1.43	8.45	2.94	0.98	0.24	3.22	3.60
Trichloromethane[b]	0.08	0.04	0.21	0.21	0.85	0.92	0.07	0.03	0.32	0.58
1,1,1-Trichloroethane	5.35	4.36	2.94	2.94	8.59	6.05	2.20	0.49	4.89	4.62
Carbon Tetrachloride[c]	0.12	0.05	0.11	0.11	0.10	0.05	0.10	0.03	0.11	0.04
Trichloroethene	0.20	0.08	0.14	0.14	0.21	0.18	0.10	0.08	0.16	0.13
Tetrachloroethene	1.42	0.37	0.86	0.86	0.87	0.77	0.56	0.11	0.94	0.56
Benzene	2.96	0.84	2.69	0.49	2.25	0.74	2.32	0.62	2.57	0.75
1,2-Dibromoethane	0.01	0.00	0.01	0.00	0.01	0.01	0.01	0.00	0.01	0.01
1-Hr Samples EPA/ENSR										
Formaldehyde	8.70	4.08	10.1	4.49	6.90	3.81	8.40	4.04	9.10	5.77
Acetaldehyde	7.22	4.07	8.36	4.17	5.45	3.77	8.05	4.05	7.41	4.38
1,3-Butadiene	0.51	0.41	0.18	0.26	0.20	0.24	0.28	0.35	0.27	0.35

BD = Below detection
[a] or Methylene Chloride
[b] or Chloroform
[c] or Tetrachloromethane
[d] or Ethylene dibromide

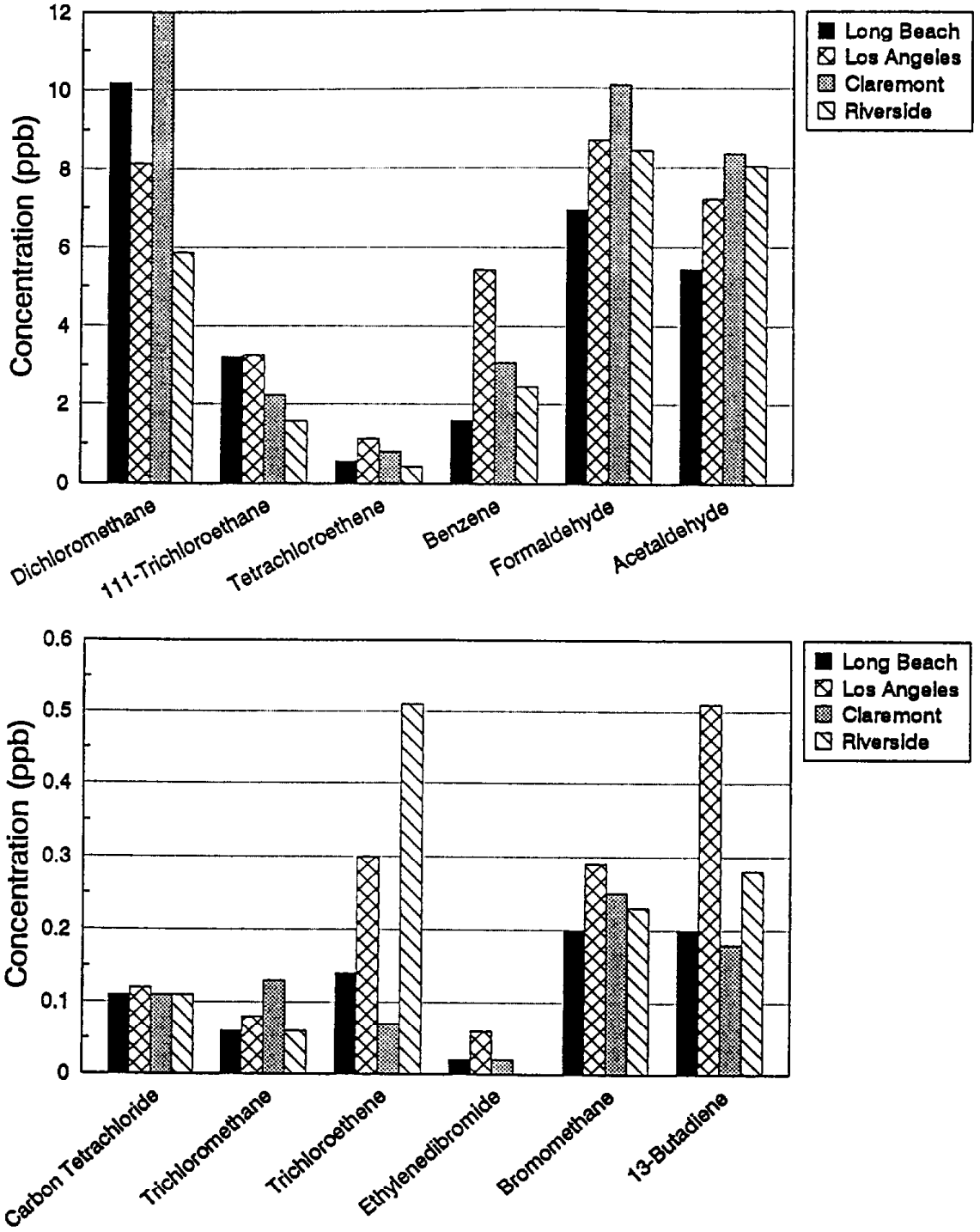


Figure 3-53. Twenty-Four Hour Average Concentrations of 12 Toxic Organic Species at Four SCAQS Sites During the Summer. Analyses of the chlorinated species and benzene were performed by OGI. Formaldehyde, acetaldehyde, and 1,3-butadiene concentrations are the overall average of the 1-hour samples analyzed by ENSR and the EPA.

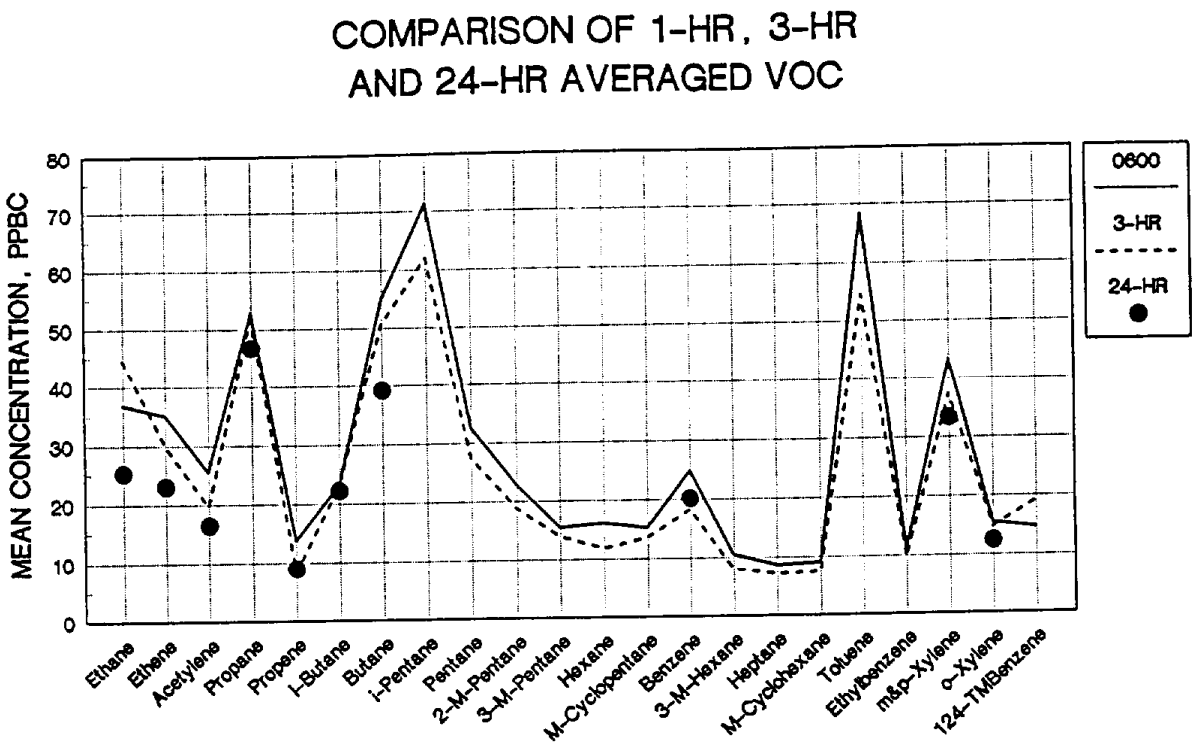


Figure 3-54. Comparison of Mean Concentrations of 22 Species Collected over 1-, 3- and 24-Hour Sampling Periods.