WEEKEND/WEEKDAY OZONE OBSERVATIONS IN THE SOUTH COAST AIR BASIN: VOLUME II - ANALYSIS OF AIR QUALITY DATA

FINAL REPORT

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PREFACE

The Desert Research Institute (DRI) and Sonoma Technology, Inc. (STI) conducted a study of the causes of elevated ozone levels on weekends in the South Coast (Los Angeles) Air Basin (SoCAB). This work was conducted over a period of 30 months beginning in December 1999. In the initial phase of the study, DRI examined the spatial, temporal, and statistical distributions of ozone, carbon monoxide, total non-methane hydrocarbons, and nitrogen oxides for routine monitoring sites in the SoCAB with continuous data from 1981 to 1998. STI reviewed available activity data for VOC and NOx emissions and investigated important meteorological phenomena in the SoCAB in the context of day-of-week variations. The results and findings from these retrospective analyses are summarized in the following three volumes:

- Fujita, E.M., W. Stockwell, R.E. Keislar, D.E. Campbell, P.T. Roberts, T.H. Funk, C.P. MacDonald, H.H. Main, and LR. Chinkin (2000a). Weekend/Weekday Ozone Observations in the South Coast Air Basin: Retrospective Analysis of Ambient and Emissions Data and Refinement of Hypotheses, Volume I – Executive Summary. Final report prepared by the Desert Research Institute, Reno, NV and Sonoma Technology, Petaluma, CA for the National Renewable Energy Laboratory, Golden, CO, December 2000.

- Fujita, E.M., W. Stockwell, R.E. Keislar, and D.E. Campbell (2000b). Weekend/Weekday Ozone Observations in the South Coast Air Basin: Retrospective Analysis of Ambient and Emissions Data and Refinement of Hypotheses, Volume II – Desert Research Institute Tasks 1 and 2. Prepared by the Desert Research Institute, Reno, NV for the National Renewable Energy Laboratory, Golden, CO, December 2000.

- Roberts, P.T., T. H. Funk, C.P. MacDonald, H.H. Main, and L.R. Chinkin (2001). Weekend/Weekday Ozone Observations in the South Coast Air Basin: Retrospective Analysis of Ambient and Emissions Data and Refinement of Hypotheses, Volume III – Final Report Prepared by Sonoma Technology, Inc., Petaluma, CA for the National Renewable Energy Laboratory, Golden, CO, January 2001.

In the second phase of the study, a field measurement program was conducted in September-October 2000 to collect and assemble air quality and emission activity databases to examine relationships between emission patterns and key air quality parameters relevant to the weekend ozone effect. The following interim report presents preliminary results from the field study and describes the applicable measurement methods and approaches for data analysis:

- Fujita, E.M., D.E. Campbell, W. Stockwell, B. Zielinska, J.C. Sagebiel, W. Goliff, M.Keith, and J.L. Bowen (2001). Weekend/Weekday Ozone Observations in the South Coast Air Basin: Phase II Field Study. Interim report prepared by the Desert Research Institute, Reno, NV for the National Renewable Energy Laboratory, Golden, CO, November 2001.

The final report of this study consists of the three volumes referenced below. The Executive Summary (Volume I) provides a synthesis of the results obtained by DRI and STI with respect to a variety of hypotheses for the weekend ozone effect. Volume II documents the results

obtained by DRI from the Phase II field study. It also summarizes the retrospective analyses performed during Phase I and additional analyses that were conducted by DRI to update the findings from Phase I. Volume III is a summary of STI's analysis of the prevailing meteorology during the Phase II field study and their collection of emission activity data in support of this study. Volume III also includes a discussion of weekday/weekend differences in hydrocarbons.

- Fujita, E.M., D.E. Campbell, W. Stockwell, P.T. Roberts, T.H. Funk, C.P. MacDonald, H.H. Main, and LR. Chinkin (2002). Weekend/Weekday Ozone Observations in the South Coast Air Basin Volume I – Executive Summary. Report prepared by the Desert Research Institute, Reno, NV and Sonoma Technology, Petaluma, CA for the National Renewable Energy Laboratory, Golden, CO, and the Coordinating Research Council, May 2002.

- Fujita, E.M., D.E. Campbell, W. Stockwell, R. Keislar, B. Zielinska, J.C. Sagebiel, W. Goliff, M. Keith, and J.L. Bowen (2002). Weekend/Weekday Ozone Observations in the South Coast Air Basin Volume II: Analysis of Air Quality Data. Final report prepared by the Desert Research Institute, Reno, NV for the National Renewable Energy Laboratory, Golden, CO, and the Coordinating Research Council, April 2002.

- Chinkin L.R., H.H. Main, and P.T Roberts. (2002). Weekend/Weekday Ozone Observations in the South Coast Air Basin Volume III: Analysis of Summer 2000 Field Measurements and Supporting Data. Final report prepared by Sonoma Technology, Inc., Petaluma, CA for the National Renewable Energy Laboratory, Golden, CO, April 2002.

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TABLE OF CONTENTS

Preface ii
Acknowledgment iv
Table of Contents v
List of Tables vii
List of Figures x
Abbreviations and Acronyms xvi

1.0 STUDY PERSPECTIVE AND SUMMARY 1-1
1.1 Introduction 1-1
1.2 Study Objectives and Hypotheses 1-3
1.3 Methods and Approach 1-4
1.4 Results and Discussion 1-7
1.4.1 Fundamentals of Ozone Formation 1-8
1.4.2 Evolution of the Weekend Effect in the South Coast Air Basin 1-11
1.4.3 Identification and Evaluation of Relevant Factors 1-12
1.4.4 Source Apportionment of Ozone Precursors 1-15
1.4.5 Reconciliation of Study Results with Proposed Hypotheses 1-17
1.5 Recommendations 1-20

2.0 EVOLUTION OF THE WEEKEND OZONE EFFECT IN THE SOUTH COAST AIR BASIN FROM 1981 to 1998 2-1
2.1 Trends in Ambient Ozone Concentrations 2-2
2.2 Trends in Spatial Extent and Magnitude of the Weekend Ozone Effect 2-3
2.3 Carryover of Ozone Precursors 2-3
2.4 Extent of Ozone Inhibition 2-4
2.5 Duration and Rate of Ozone Accumulation 2-4
2.6 Spatial, Temporal, and Statistical Distributions of Volatile Organic Compounds and NMHC/NOx Ratios 2-6
2.7 Summary of Findings 2-6

3.0 CHARACTERIZATION OF THE CURRENT WEEKEND OZONE EFFECT IN THE SOUTH COAST AIR BASIN 3-1
3.1 Weekday Differences in Peak Levels and Diurnal Variations of Ozone 3-2
3.2 Weekday Differences in Diurnal Variations of VOC, NOx, and VOC/NOx Ratios 3-3
3.3 Weekday Variations in VOC Reactivity 3-4
3.4 Weekday Variations in Diurnal Patterns of Ozone 3-4
3.5 Theoretical Relationships Between Precursor Emissions and Ozone 3-5
3.6 Weekday Variations in Empirically-Estimated Photolysis Parameter 3-7
3.7 Summary of Findings 3-8

4.0 WEEKDAY VARIATIONS IN THE SOURCE APPORTIONMENT OF OZONE PRECURSORS 4-1
4.1 Field Measurement Program 4-2
4.2 Measurement Methods 4-3

4.3 Spatial and Temporal Variations in Pollutant Concentrations and VOC/NOx Ratios 4-5
4.3.1 Pollutant Variations in On-Road, Regional, and Background Samples 4-6
4.3.2 Pollutant Variations at Ambient Monitoring Sites 4-7
4.4 Source Apportionment of VOC 4-8
4.4.1 Source Composition Profiles 4-8
4.4.2 CMB Analysis of PAMS VOC Data for 1999-2000 4-10
4.4.3 CMB Analysis of VOC Data from the Fall 2000 Field Study 4-11
4.5 Source Apportionment of NOx 4-11
4.5.1 NOx Apportionment by Multiple Linear Regression 4-11
4.5.2 Apportionment of NOx by Chemical Mass Balance 4-13
4.6 Summary of Findings 4-14

5.0 REFERENCES 5-1

LIST OF TABLES

Table No.		Page No.
Table 1.4-1	Trends in Duration and Rate of Ozone Accumulation in the SoCAB on Sunday, Wednesday, and Sunday Minus Wednesday, 1981-1999	1-21
Table 1.4-2	Weekend/Weekday Differences in Ambient NOx Associated with CO and Black Carbon in the SoCAB	1-22
Table 1.4-3	Regression Statistics for the Correlations of Mean Hourly Ozone and Nitric Oxide Mixing Ratios During Friday, Saturday and Sunday Versus Midweek.	1-23
Table 2-1	Air Quality Parameters for the Conceptual Explanation of the Weekend Effect	2-9
Table 3.1-1a	Mean Daily Maximum Ozone by Day-of-the-Week (ppb)	3-12
Table 3.1-1b	Ratio of Mean Daily Maximum Ozone to Mean Midweek (Tuesday to Thursday) Maximum (Percent)	3-12
Table 3.2-1	Day-of-the-Week Variations in Mean Nitric Oxide (ppb) by Time of Day for Azusa, Los Angeles N. Main, Pico Rivera, and Upland for Summer 1999-2000.	3-13
Table 3.2-2	Day-of-the-Week Variations in Mean Nitrogen Dioxide (ppb) by Time of Day for Azusa, Los Angeles N. Main, Pico Rivera, and Upland for Summer 1999-2000.	3-14
Table 3.2-3	Day-of-the-Week Variations in Mean Nitrogen Oxides (ppb) by Time of Day for Azusa, Los Angeles N. Main, Pico Rivera, and Upland for Summer 1999-2000.	3-15
Table 3.2-4	Day-of-the-Week Variations in Mean Nonmethane Hydrocarbons (ppb) by Time of Day for Azusa, Los Angeles N. Main, Pico Rivera, and Upland for Summer 1999-2000.	3-16
Table 3.2-5	Day-of-the-Week Variations in Mean NMHC/NOx Ratios by Time of Day for Azusa, Los Angeles N. Main, Pico Rivera, and Upland for Summer 1999-2000.	3-17
Table 3.3-1a.	Day-of-the-Week Differences in Diurnal Variations of Sum of PAMS Species, NMHC, CO, NOx, and Ratios of Acetylene to PAMS and NMHC at Pico Rivera, Summer 1999-2000.	3-18
Table 3.3-1b	Day-of-the-Week Differences in Diurnal Variations of Photochemical Reactivity of Volatile Organic Compounds at Pico Rivera, Summer 1999-2000.	3-19
Table 3.4-1.	Initial Chemical Conditions for Model Simulations with Varying NOx and NMHC	3-20

Table 4.1-1 Average ambient concentrations of NO, NOy, CO, MTBE, black carbon, heavy hydrocarbons, and VOC during the carryover, inhibition, and accumulation periods by day: October 2 - October 18, 2000 4-18

Table 4.4-1 Default Source Composition Profiles Used in CMB Source Apportionment.... 4-19

Table 4.4-1a Number of observations, mean measured NMHC (ug/m^3), mean CMB performance parameters and mean estimated source contributions (ug/m3) +/- standard deviation; during the carryover (3:00-6:00), inhibition (6:00-9:00), accumulation (9:00-12:00), and peak ozone (12:00-15:00) periods by day-of-week at Azusa for summers 1999 and 2000..... 4-21

Table 4.4-1b Number of observations, mean measured NMHC (ug/m^3), mean CMB performance parameters and mean estimated source contributions (ug/m3) +/- standard deviation; during the carryover (3:00-6:00), inhibition (6:00-9:00), accumulation (9:00-12:00), and peak ozone (12:00-15:00) periods by day-of-week at Pico Rivera for summer 1999 4-22

Table 4.4-1c Number of observations, mean measured NMHC (ug/m^3), mean CMB performance parameters and mean estimated source contributions (ug/m3) +/- standard deviation; during the carryover (3:00-6:00), inhibition (6:00-9:00), accumulation (9:00-12:00), and peak ozone (12:00-15:00) periods by day-of-week at Upland for summers 1999 and 2000..... 4-23

Table 4.4-1d Number of observations, mean measured NMHC (ug/m^3), mean CMB performance parameters and mean estimated source contributions (ug/m3) +/- standard deviation; during the carryover (3:00-6:00), inhibition (6:00-9:00), accumulation (9:00-12:00), and peak ozone (12:00-15:00) periods by day-of-week at Los Angeles N. Main for summers 1999 and 2000..... 4-24

Table 4.4-2a Number of observations, mean measured NMHC (ug/m^3), mean CMB performance parameters and mean estimated source contributions (% of NMHC) +/- standard deviation; during the carryover (3:00-6:00), inhibition (6:00-9:00), accumulation (9:00-12:00), and peak ozone (12:00-15:00) periods by day-of-week at Azusa for summers 1999 and 2000..... 4-25

Table 4.4-2b Number of observations, mean measured NMHC (ug/m^3), mean CMB performance parameters and mean estimated source contributions (% of NMHC) +/- standard deviation; during the carryover (3:00-6:00), inhibition (6:00-9:00), accumulation (9:00-12:00), and peak ozone (12:00-15:00) periods by day-of-week at Pico Rivera for summer 1999 4-26

Table 4.4-2c Number of observations, mean measured NMHC (ug/m^3), mean CMB performance parameters and mean estimated source contributions (% of NMHC) +/- standard deviation; during the carryover (3:00-6:00), inhibition (6:00-9:00), accumulation (9:00-12:00), and peak ozone (12:00-15:00) periods by day-of-week at Upland for summers 1999 and 2000..... 4-27

Table 4.4-2d Number of observations, mean measured NMHC (ug/m^3), mean CMB performance parameters and mean estimated source contributions (% of NMHC) +/- standard deviation; during the carryover (3:00-6:00), inhibition (6:00-9:00), accumulation (9:00-12:00), and peak ozone (12:00-15:00)

periods by day-of-week at Los Angeles N. Main for summers 1999 and 2000 4-28
Table 4.4-3a CMB Performance Parameters for Mobile Van Samples 4-29
Table 4.4-3b Source Contribution Estimates (μg/m^3) for Mobile Van Samples 4-30
Table 4.4-3c Source Contribution Estimates (Percent) for Mobile Van Samples 4-31
Table 4.5-1 Ambient NOx (ppb) Associated with CO and Black Carbon at On-Road and Regional Locations in the SoCAB 4-32
Table 4.5-2 Weekend/Weekday Differences in Ambient NOx Associated with CO and Black Carbon in the SoCAB 4-33

LIST OF FIGURES

Figure No. — Page No.

Figure 1.3-1. Map of the South Coast Air Basin showing the location of the Pico Rivera, Azusa, and Upland PAMS sites, the Los Angeles North Main monitoring station, and the three freeway loops and two regional/background sites used during the September 30 to October 8, 2000 field study. 1-24

Figure 1.4-1. Schematic of the photochemical pathways leading to the production of ozone in the troposphere and the main termination reactions at high and low VOC/NOx ratios. 1-25

Figure 1.4-2. Typical ozone isopleth plot showing 1-hour maximum ozone concentrations (in ppb) calculated as a function of initial VOC and NOx concentrations and the regions of the diagram that are characterized as VOC- or NOx-limited. 1-26

Figure 1.4-3. Mean maximum 1-hour mixing ratios of ozone during summers (June 1 to September 30) of 1981-1984 and 1995 to 1998 in the South Coast Air Basin. Sites in the western, northern and central, and central to eastern basin are denoted by solid, dash, and dotted lines, respectively. 1-27

Figure 1.4-4. Average summer 1995 diurnal variations of ozone, nitric oxide, nitrogen dioxide, carbon monoxide at Azusa during the weekday and weekend.. 1-28

Figure 1.4-5. Twelve-site average NO and NMHC (estimated from CO) at 4-5 a.m. and 7-8 a.m. (PDT) by day of the week in the SoCAB during 1981 to 1998..... 1-29

Figure 1.4-6. Twelve-site average NO_2/NOx ratios at 7-8 a.m. (PDT) by day of the week.... 1-30

Figure 1.4-7. Sunday versus Wednesday differences in duration and rate of ozone accumulation for twelve sites in the SoCAB during 1981-84, 1985-89, 1990-94, and 1995-98. 1-31

Figure 1.4-8. Sunday minus Wednesday differences in the duration and rates of ozone accumulation for the years 1981-84, 1985-1989, 1990-1994, and 1995-1998.. 1-32

Figure 1.4-9. Day-of-the-week variations in the mean NMHC/NOx ratios during carryover (0300-0600, PDT), ozone inhibition (0600-0900), ozone accumulation ((0900-1200), and ozone peak (1200-1500) at Los Angeles – North Main*, Azusa, Pico Rivera, and Upland during the summers (July-September) of 1999 and 2000..... 1-33

Figure 1.4-10. Diurnal variations in the ratios of ozone to potential ozone (O_3 + NOx) on Sundays, Saturdays, and Weekdays at Azusa for the years 1980-85, 1986-1990, 1991-1994, 1995-1998, and 1999-2000. 1-34

Figure 1.4-11. Mean ratio of peak ozone to potential ozone (O_3 + NOx) on weekdays at three sites for the years 1980-85, 1986-1990, 1991-1994, 1995-1998, and 1999-2000. 1-35

Figure 1.4-12. Estimated mean photolysis rate parameter for NO_2 (J_{NO2}) at Azusa on Sunday, and Midweek (Tuesday to Thursday) for the periods 1980-85, 1986-90, 1991-94, 1995-98, and 1999-2000.. 1-36

Figure 1.4-13. Hourly average nitrogen oxides, CO, and black carbon at Azusa September 30-October 8, 2000. 1-37

Figure 1.4-14a. Estimated ambient NOx associated with CO and black carbon for mobile lab samples on Wednesday, October 4. 1-38

Figure 1.4-14b. Estimated ambient NOx associated with CO and black carbon for mobile lab samples on Sunday, October 8. 1-39

Figure 1.4-15. Source apportionment of non-methane hydrocarbons for mobile sampling loops and regional background sites – absolute contributions. 1-40

Figure 1.4-16. Mean estimated source contributions of total nonmethane hydrocarbons during 6-9 a.m. (PDT) by day of the week at Azusa for summer 1999 and 2000. 1-41

Figure 1.4-17. Correlation plots of mean hourly ozone and NO mixing ratios during midweek (Tues-Thur) versus Sunday. Separate linear regressions are shown for nighttime (9:00 p.m. – 5:00 a.m.) and daytime (6:00 a.m. – 9:00 p.m.) hours. 1-42

Figure 1.4-18. Ozone EKMA plot. 1-43

Figure 1.4-19. Plots of VOC/NOx ratio, ozone production efficiency, hydroxyl radical, and nitric acid superimposed on a color O_3 EKMA plot. 1-44

Figure 2-1. Average summer 1995 diurnal variations of O_3, NO, NO_2, and CO at Azusa during weekday and weekend. 2-10

Figure 2-2. Average summer 1995 diurnal variations of O_3 and VOC/NOx at Azusa during weekday and weekend. 2-11

Figure 2-3 CO versus NMHC from DRI canister samples during summers 1995 and 1996. 2-12

Figure 2.1-1. Trend in number of annual exceedances of the federal 1-hour ozone standard in the South Coast Air Basin from 1976 to 1999 2-13

Figure 2.1-2. Trends in average maximum 1-hour ozone from 1980 to 1997 in the western, central and eastern portions of the South Coast Air Basin. 2-13

Figure 2.2-1. Average summer daily maximum 1-hour ozone (ppb) in the SoCAB by day of the week. 2-14

Figure 2.3-1. Average daily 4-5 a.m (PDT) NO (ppb) in the SoCAB by day of the week. 2-15

Figure 2.3-2. Average daily 4-5 a.m (PDT) NO_2 (ppb) in the SoCAB by day of the week. 2-16

Figure 2.3-3. Average daily 4-5 a.m (PDT) NO_2/NOx (ppb) in the SoCAB by day of the week. 2-17

Figure 2.3-4. Average daily 4-5 a.m. (PDT) NMHC (ppbC) in the SoCAB by day of the week. 2-18

Figure 2.4-1. Average daily 7-8 a.m. (PDT) NO (ppb) in the SoCAB by day of the week. 2-19

Figure 2.4-2. Average daily 7-8 a.m. (PDT) NO_2 (ppb) in the SoCAB by day of the week. 2-20

Figure 2.4-3. Average daily 7-8 a.m. (PDT) CO (ppm) in the SoCAB by day of the week. . 2-21
Figure 2.4-4. Average daily 7-8 a.m. (PDT) NMHC (ppbC) in the SoCAB by day of the week. 2-22
Figure 2.4-5. Average time (PDT) in the morning when NO equals O_3 by day of the week. 2-23
Figure 2.4-6. Twelve-site average NO_2/NOx ratios at 7-8 a.m. (PDT) by day of the week. 2-24
Figure 2.4-7. Twelve-site average NMHC and NO concentrations at 4-5 a.m. (PDT) and 7-8 a.m. (PDT) by day of the week. 2-25
Figure 2.5-1. Average time (PDT) at maximum O_3 by day of the week 2-26
Figure 2.5-2. Duration (hours) of ozone accumulation by day of the week. 2-27
Figure 2.5-3. Ozone accumulation rate (ppb O_3 per hour) by day of the week. 2-28
Figure 2.5-4. Average duration between $t_{NO=O3}$ and t_{maxO3} and average rates of accumulation of ozone on Sunday and Wednesday during 1981-84 and the differences. 2-29
Figure 2.5-5. Average duration between $t_{NO=O3}$ and t_{maxO3} and average rates of accumulation of ozone on Sunday and Wednesday during 1985-89 and the differences. 2-30
Figure 2.5-6. Average duration between $t_{NO=O3}$ and t_{maxO3} and average rates of accumulation of ozone on Sunday and Wednesday during 1990-94 and the differences. 2-31
Figure 2.5-7. Average duration between $t_{NO=O3}$ and t_{maxO3} and average rates of accumulation of ozone on Sunday and Wednesday during 1995-98 and the differences. 2-32
Figure 2.5-8. Trends in ozone accumulation rate by site for Sunday, Wednesday, and the difference between Sunday and Wednesday. 2-33
Figure 2.5-9. Trends in ozone accumulation rate for western, central, and eastern SoCAB for Sunday, Wednesday, and the difference between Sunday and Wednesday. 2-34
Figure 2.6-1. Average daily 6-9 a.m. (PDT) NMHC/NOx in the SoCAB by day of the week. 2-35
Figure 2.6-2. Average daily NMHC/NOx at maximum ozone in the SoCAB by day of the week. 2-36
Figure 3.1-1a Mean diurnal variations in ozone mixing ratios on Saturdays, Sundays, and Weekdays at Los Angeles North Main in 1999-2000 and 1980-1998..... 3-21
Figure 3.1-1b Mean diurnal variations in ozone mixing ratios on Saturdays, Sundays, and Weekdays at Azusa in 1999-2000 and 1980-1998. 3-22
Figure 3.1-1c Mean diurnal variations in ozone mixing ratios on Saturdays, Sundays, and Weekdays at Upland in 1999-2000 and 1980-1998. 3-23
Figure 3.1-1d Mean diurnal variations in ozone mixing ratios on Saturdays, Sundays, and Weekdays at Rubidoux in 1980-1998. 3-24

Figure 3.1-2 Mean day-of-the-week variations in daily maximum ozone mixing ratios at Los Angeles North Main, Azusa, Pico Rivera, and Upland during the summers (July-September) of 1999 and 2000. 3-25

Figure 3.2-1a Day-of-the-week variations in NO and NO_2 mixing ratios during carryover (0000-0300, PDT), ozone inhibition (0600-0900), ozone accumulation ((0900-1200), and ozone peak (1200-1500). Mean and standard deviations of the mean mixing ratios at Los Angeles North Main, Azusa, Pico Rivera, and Upland during the summers (July-September) of 1999 and 2000. 3-26

Figure 3.2-1b Day-of-the-week variations in NMHC/NOx ratio and total NMHC mixing ratios during carryover (0000-0300, PDT), ozone inhibition (0600-0900), ozone accumulation ((0900-1200), and ozone peak (1200-1500). Mean and standard deviations of the mean mixing ratios at Los Angeles North Main, Azusa, Pico Rivera, and Upland during the summers (July-September) of 1999 and 2000. 3-27

Figure 3.4-1 Mean diurnal variations in ozone and nitric oxide mixing ratios on Sunday and Midweek at Los Angeles North Main, Azusa, Pico Rivera, and Upland during the summers (July-September) of 1999 and 2000. 3-28

Figure 3.4-2a Correlation plots of mean hourly ozone and NO mixing ratios during midweek (Tues-Thur) versus Friday. Separate linear regressions are shown for nighttime (9:00 p.m. – 5:00 a.m.) and daytime (6:00 a.m. – 9:00 p.m.) hours.. 3-29

Figure 3.4-2b Correlation plots of mean hourly ozone and NO mixing ratios during midweek (Tues-Thur) versus Saturday. Separate linear regressions are shown for nighttime (9:00 p.m. – 5:00 a.m.) and daytime (6:00 a.m. – 9:00 p.m.) hours.. 3-30

Figure 3.4-2c Correlation plots of mean hourly ozone and NO mixing ratios during midweek (Tues-Thur) versus Sunday. Separate linear regressions are shown for nighttime (9:00 p.m. – 5:00 a.m.) and daytime (6:00 a.m. – 9:00 p.m.) hours.. 3-31

Figure 3.5-1 Plots of ozone, VOC/NOx ratio, ozone production efficiency ($\Delta[O_3]/(\Delta[HNO_3] + \Delta[\text{Organic Nitrates}])$ and hydroxyl radical superimposed on a color O_3 EKMA plot. 3-32

Figure 3.5-2 Plots of PAN, HCHO, aldehyde and nitric acid superimposed on a color O_3 EKMA plot..... 3-33

Figure 3.5-3 Plots of organic nitrates, H_2O_2, HNO_3/H_2O_2 ratio and H_2O_2/HCHO ratio superimposed on a color O_3 EKMA plot. 3-34

Figure 3.6-1. Estimated mean photolysis rate parameter for NO_2 (J_{NO2}) at Azusa on Sunday, and midweek (Tuesday to Thursday) for the periods 1980-85, 1986-90, 1991-94, 1995-98, and 1999-2000. J_{NO2} was calculated from an extended version of the O_3-NO-NO_2 photostationary state expression. 3-35

Figure 3.6-2. Diurnal variations in the ratios of ozone to potential ozone (O_3 + NOx) on Sundays, Saturdays, and weekdays at Azusa for the years 1980-85, 1986-1990, 1991-1994, 1995-1998, and 1999-2000. 3-36

Figure 4.1-1. Map of study area showing the locations of freeway loops and for regional/background and source-dominated samples. Relevant district air monitoring stations are also shown 4-34

Figure 4.3-1. Continuous measurements of NO and NOy in the mobile sampling van on Wednesday, 10/4/00 (top) and Sunday, 10/8/00 (bottom) 4-35

Figure 4.3-2. Average NO, black carbon, and CO concentrations for each of the freeway loops and regional/background sites for two weekend days (Saturday, 10/7/00 and Sunday, 10/8/00) and two weekdays (Monday, 10/2/00 and Wednesday, 10/4/00). 4-36

Figure 4.3-3a. Average NOy and black carbon on freeway loops during carryover, ozone inhibition, and ozone accumulation periods compared to regional sites and source-dominated samples. 4-37

Figure 4.3-3b. Average carbon monoxide and volatile organic compounds on freeway loops during carryover, ozone inhibition, and ozone accumulation periods compared to regional sites and source-dominated samples. 4-38

Figure 4.3-4. Average VOC/NOy ratios on freeway loops during carryover, ozone inhibition, and ozone accumulation periods compared to regional sites and source-dominated samples. 4-39

Figure 4.3-5a. Hourly average Nitrogen Oxides, CO, and black carbon at Azusa 9/30/00 – 10/8/00. 4-40

Figure 4.3-5b. Average nitrogen oxides and black carbon at Azusa during carryover, accumulation, and inhibition periods 9/30/00 – 10/8/00. 4-41

Figure 4.3-6a. Hourly average Nitrogen Oxides, CO, and black carbon at Pico Rivera 9/30/00 – 10/8/00. 4-42

Figure 4.3-6b. Average nitrogen oxides and black carbon at Pico Rivera during carryover, accumulation, and inhibition periods 9/30/00 – 10/8/00. 4-43

Figure 4.3-7a. Diurnal variations in CO, nonmethane hydrocarbons, and nonmethane organic gases at Azusa 9/30/00 – 10/8/00 4-44

Figure 4.3-7b. Day-to-day variations in CO and nonmethane organic gases at Azusa during carryover, accumulation, and inhibition periods 9/30/00 – 10/8/00 4-45

Figure 4.3-8a. Diurnal variations in CO, and nonmethane organic gases at Pico Rivera 9/30/00 – 10/8/00. 4-46

Figure 4.3-8b. Day-to-day variations in CO and nonmethane organic gases at Pico Rivera during carryover, accumulation, and inhibition periods 9/30/00 – 10/8/00 4-47

Figure 4.3-9a. VOC/NOx ratios at Azusa and Pico Rivera 9/30/00 – 10/8/00. 4-48

Figure 4.3-9b. Average VOC/NOx ratios at Azusa and Pico Rivera during carryover, accumulation, and inhibition periods 9/30/00 – 10/8/00. 4-49

Figure 4.4-1a. Mean estimated source contributions by day-of-week at Azusa for summers 1999 and 2000. 4-50

Figure 4.4-1b. Mean estimated source contributions by day-of-week at Pico Rivera for summer 1999. 4-51
Figure 4.4-1c. Mean estimated source contributions by day-of-week at Upland for summers 1999 and 2000. 4-52
Figure 4.4-2. Source apportionment of non-methane hydrocarbons for mobile sampling loops and regional background sites – absolute contributions. 4-53
Figure 4.4-3. Source apportionment of non-methane hydrocarbons for mobile sampling loops and regional background sites – percent contributions. 4-54
Figure 4.5-1a. Correlations of NO and NOx to black carbon at Azusa for different sets of weekdays and hours of the day. 4-55
Figure 4.5-1b. Correlations of NO and NOx to black carbon at Pico Rivera for different sets of weekdays and hours of the day. 4-56
Figure 4.5-2a. Correlations of NO and NOx to CO at Azusa for different sets of weekdays and hours of the day. 4-57
Figure 4.5-2b. Correlations of NO and NOx to CO at Pico Rivera for different sets of weekdays and hours of the day. 4-58
Figure 4.5-3a. Estimated ambient NOx associated with CO and black carbon for mobile lab samples 10/2/00 (Monday). 4-59
Figure 4.5-3b. Estimated ambient NOx associated with CO and black carbon for mobile lab samples 10/4/00 (Wednesday). 4-60
Figure 4.5-3c. Estimated ambient NOx associated with CO and black carbon for mobile lab samples 10/7/00 (Saturday). 4-61
Figure 4.5-3d. Estimated ambient NOx associated with CO and black carbon for mobile lab samples 10/8/00 (Sunday). 4-62
Figure 4.5-4 Estimated ambient NOx associated with CO and black carbon for mobile lab samples - surface streets 10/6/00 (Friday). 4-63
Figure 4.5-5 Estimated ambient NOx associated with CO and black carbon at Azusa 9/30/00 – 10/8/00 4-64
Figure 4.5-6 Estimated ambient NOx associated with CO and black carbon at Pico Rivera 9/30/00 10/8/00. 4-65
Figure 4.5-7 Correlation of predicted to measured NOx concentrations at Azusa and Pico Rivera 4-66
Figure 4.5-8. Source apportionment of NOx for mobile sampling loops and regional background sites – absolute contributions. 4-67
Figure 4.5-9. Source apportionment of NOx for mobile sampling loops and regional background sites – percent contributions. 4-68

GLOSSARY OF ABBREVIATIONS AND ACRONYMS

ARB	California Air Resources Board
CMB	Chemical Mass Balance receptor model
CO	carbon monoxide
DRI	Desert Research Institute
EKMA	Empirical Kinetic Modeling Approach
EPA	United States Environmental Protection Agency
GC	gas chromatograph
GC-FID	gas chromatograph with flame ionization detection
GC/MS	gas chromatograph with mass spectrometry
H_2O_2	hydrogen peroxide
HNO_3	nitric acid
HCHO	formaldehyde
HO	hydroxyl radical
HO_2	hydroperoxy radical
HONO	nitrous acid
J_{NO2}	NO_2 photolysis rate parameter
MIR	maximum incremental reactivity
MTBE	methyl tert butyl ether
NAAQS	National Ambient Air Quality Standard
NMHC	nonmethane hydrocarbons
NMOC	nonmethane organic compounds
NO	nitric oxide
NO_2	nitrogen dioxide
NOx	nitrogen oxides
NOy	oxidize nitrogen species
O_3	ozone
PAMS	Photochemical Assessment Monitoring Stations
PAN	peroxyacetyl nitrate
ppb	parts per billion
ppbC	parts per billion carbon
RACM	Regional Atmospheric Chemical Medium
RADM2	Regional Atmospheric Deposition Model version 2
ROG	reactive organic compounds
SoCAB	South Coast Air Basin
SCAQMD	South Coast Air Quality Management District
STI	Sonoma Technology, Inc.
VOC	volatile organic compounds

1. STUDY PERSPECTIVE AND SUMMARY

This study investigated the causes of elevated ozone levels on weekends in the South Coast (Los Angeles) Air Basin (SoCAB). The study was conducted by the Desert Research Institute (DRI) and Sonoma Technology, Inc. (STI) over a period of 30 months beginning in December 1999. In the initial phase of the study, DRI examined the spatial, temporal, and statistical distributions of ozone, carbon monoxide, total non-methane hydrocarbons, and nitrogen oxides for routine monitoring sites in the SoCAB with continuous data from 1981 to 1998. STI reviewed available activity data for volatile organic compounds (VOC)[1] and NOx emissions and investigated important meteorological phenomena in the SoCAB in the context of day-of-week variations. In the second phase of the study, DRI and STI conducted a field measurement program in September-October 2000 to collect and assemble air quality and emission activity databases to examine relationships between emission patterns and key air quality parameters relevant to the weekend ozone effect. This report (Volume II) documents the results obtained by DRI from the Phase II field study. It also summarizes the retrospective analyses performed during Phase I and additional analyses that were conducted to update the findings from Phase I. Volume III (Chinkin et al., 2002) summarizes STI's analysis of the prevailing meteorology during the Phase II field study and their collection of emission activity data in support of the field study. It also includes a discussion of weekday/weekend differences in hydrocarbons. The Executive Summary (Volume I) (Fujita et al., 2002) provides a synthesis of the results obtained by DRI and STI with respect to a variety of hypotheses for the weekend ozone effect.

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[1] Volatile organic compounds are normally defined as all organic compounds that may be present in the ambient air irrespective of their photochemical reactivity or ability of measurement methods to quantify their concentrations. The following subsets of VOC are used throughout this report. These terms are operational definitions that reflect the sensitivity and selectivity of the analytical methods or photochemical reactivity.

- Non-methane hydrocarbons (NMHC): C_2 through C_{11} hydrocarbons collected in stainless steel canisters and measured by gas chromatography with flame ionization detection (GC-FID) by EPA method TO-14A (U.S. EPA, 1997). Known halocarbons and oxygenated compounds (e.g., aldehydes, ketones, ethers and alcohols) are excluded from NMHC.

- Carbonyls: Aldehydes and ketones, the most common being formaldehyde, acetaldehyde, and acetone. Carbonyls are operationally defined as C_1 through C_7 oxygenated compounds measured by collection on acidified 2,4-dinitrophenylhydrazine (DNPH)-impregnated C18 or silica gel cartridges and analyzed by high performance liquid chromatography with UV detection (HPLC/UV). PAMS carbonyl data normally include only formaldehyde, acetaldehyde, and acetone.

- Non-methane organic compounds (NMOC): Sum of quantifiable peak by EPA Method TO-14A, including unidentified but excluding halocarbons, or by continuous instruments with flame ionization detection. Measured NMOC will be lower for laboratories employing water management. NMOC also refers to the sum of NMHC plus carbonyl compounds by EPA Method TO-11.

- Heavy hydrocarbons: C_{12} through C_{20} hydrocarbons collected on Tenax absorbing substrates and analyzed by thermal desorption and gas chromatography with detection by flame ionization or by mass spectrometry.

- Reactive organic gases (ROG): Organic gases with potential to react with the hydroxyl radical and other chemicals with half-life of <30 days that produce in ozone and secondary organic aerosol. ROG is typically used in reference to inventories of VOC emissions.

1.1 Introduction

Since the mid 1970's it has been documented that ozone levels in California's South Coast Air Basin (SoCAB) are higher on weekends than on weekdays, in spite of the fact that emissions of ozone precursors, oxides of nitrogen (NOx) and to a lesser extent volatile organic compounds (VOC), are lower on weekends than on weekdays (Elkus and Wilson, 1977; Horie et al., 1979; Levitt and Chock, 1976; Zeldin et al., 1989; Blier et al., 1996; Blier et al., 1999; and Austin and Tran, 1999). Similar weekend ozone effects have been observed in San Francisco (Altshuler et al. 1995), the northeastern cities of Washington D.C., Philadelphia, New York (SAIC, 1997) and Chicago, with a lesser effect in Atlanta (Pun et al. 2001). The weekend effect is an observable demonstration that the rate of ozone production is a non-linear function of the mixture of VOC and NOx in the atmosphere. Depending upon the relative concentrations[2] of VOC and NOx and the specific mix of VOC present, the rate of O_3 formation can be most sensitive to changes in VOC alone or to changes in NOx alone or to simultaneous changes in both VOC and NOx. Understanding the response of ozone concentrations to specific changes in VOC or NOx emissions is fundamental to understanding the weekend ozone effect.

Previous studies have shown that while peak ozone levels in the SoCAB have dropped from ~ 0.45 ppm in the early 1980s to ~ 0.18 in the late 1990's, the occurrences of higher ozone levels on weekends have become more frequent and widespread over the past two decades. From the mid-1980s to mid-1990s, decreases in peak ozone levels were greatest in the western and middle portions of the SoCAB and on weekdays than on weekends; hence the magnitude of the weekend ozone effect increased in the 1990s over the 1980s (Blier and Winer, 1996). Along with a strengthening of the weekend ozone effect, the occurrences of highest ozone levels shifted toward the eastern basin. During 1992-94, daily maximum ozone in the western and central basin typically increased by about 30 percent from Friday to Saturday, decreased slightly from Saturday to Sunday, and decreased back to Friday levels on Monday (Austin and Tran, 1999). By 1996-98, ozone levels were consistently higher on Sundays (Austin and Tran, 1999). During the period from 1965 to 1972, peak ozone levels occurred on Sunday in the western portion (Long Beach, Lennox, and West Los Angeles) of the SoCAB and on Saturday at downtown Los Angeles. Ozone levels were generally higher on weekdays in the central and northern portions of the basin (Azusa, Burbank, Reseda) (Elkus and Wilson, 1977). These trends in weekday ozone patterns parallel a trend to lower VOC/NOx ratios.

Mobile sources are the single largest source category for ozone precursor pollutants, accounting in 2000 for about 62%, 88%, and 95% of the average daily (summer) reactive organic gases (ROG), NOx, and CO emissions, respectively, in the SoCAB according to official government inventories (based on EMFAC2000 estimates) (CARB, 2001)[3]. According to emissions backcasts from the 2000 base year, the ratios of current emissions to emissions in 1980 are 0.34 and 0.75 for ROG and NOx, respectively. During the past 20 years, NOx emissions from gasoline vehicles decreased by 37 percent, while NOx emissions from diesel increased by

[2] Gas-phase species are usually measured as molar ratios (e.g., ppbv or ppmv), which are technically mixing ratios. The term concentration denotes units of mass per unit volume (e.g, $\mu g/m^3$). In common usage, these terms are used interchangeably.

[3] Vehicle emission models have historically underestimated emissions (Ingalls et al., 1989; Pierson et al. 1990; and Fujita et al., 1992). Although many improvements have been incorporated into vehicle emissions models, the uncertainties of the emission estimates are not known.

40 percent. Consequently, the contribution of diesel trucks to NOx from on-road vehicles increased from 16 to 29 percent. Diesel vehicles are not significant emitters of ROG according to the inventory. Mobile sources follow pronounced weekday-weekend patterns of activity. Urban freeway traffic drops off on Saturday, and drops even further on Sunday. Fuel-based estimates of emissions from diesel trucks show 70-80% reductions of NOx and black carbon emissions on weekends (Dreher and Harley, 1998). Ozone formation in the SoCAB is VOC-limited in most part of the basin, which coincides with the spatial pattern of higher weekend peak ozone (Blanchard and Tanenbaum, 2000).

The weekend ozone effect has generated strong interest because of its implications for ozone control strategies. In November 1998, the California Air Resources Board (ARB) adopted the Low Emission Vehicle (LEV-II) regulations, which include significant future NOx emission reductions. The weekend ozone effect was cited at the LEV-II hearing as evidence that further reduction of NOx emissions at this time may be counterproductive for ozone attainment in the SoCAB and other coastal metropolitan areas of the state. At the direction of the Board, ARB Staff conducted a three-year (1999-2002) examination of the weekend effect and the implications of NOx reduction as an ozone control strategy. At the same time, the U.S. Department of Energy's Office of Heavy Vehicle Technologies and industry sponsors also initiated studies of the weekend ozone effect. During this investigation, the ARB hosted several workshops to provide a forum for exchange of information and preliminary results among the investigators conducting research on the weekend ozone effect (information presented at these workshops can be found at the ARB web site www.arb.ca.gov/aqd/weekendeffect/weekendeffect.htm). In addition to the ARB (ARB, 2001) and DRI/STI (Fujita et al., 2000a; Fujita et al., 2000b; Roberts et al., 2000; and Fujita et al., 2001), Atmospheric Environmental Research, Inc. (Pun et al., 2001), ENVIRON, and Envair (Blanchard and Tanenbaum, 2000) conducted studies of the weekend ozone effect and participated in the workshops.

1.2 Study Objectives

The purpose of this study is to derive a conceptual explanation of the weekend ozone effect that is consistent with the fundamentals of ozone photochemistry, historic trends in the magnitude and spatial extent of the weekend effect, the diurnal and day-of-the week variations in ambient VOC and NOx concentrations and VOC/NOx ratios, and the diurnal and day-of-the week variations and source contributions of VOC and NOx. Several hypotheses have been proposed to explain the weekly behavior of ozone in the SoCAB. These hypotheses are similar to those proposed by the ARB (ARB, 2001).

NOx reduction. Reduced diesel truck traffic on Sunday and to a lesser extent on Saturday leads to greater reduction in NOx relative to VOC and higher VOC/NOx ratios. Because the SoCAB is VOC-limited with respect to ozone formation, the higher VOC/NOx ratios resulting from lower weekend NOx emissions increase the efficiency and rate of ozone formation on weekends. In addition, the reduced weekend NOx emissions from automobiles during the morning period corresponding to the weekday commute period, coupled with the reduced NOx emissions from diesel trucks, reduce the extent of ozone inhibition by titration of ozone with NO and allow ozone to accumulate earlier in the day on weekends.

NOx timing. While NOx emissions are substantially lower on weekends than on weekdays for several hours following sunrise, the traffic near mid-day is similar on weekdays and weekends. NOx emitted on weekends into an aged photochemical system causes these emissions to produce ozone more efficiently compared to the NOx emitted on weekdays. This hypothesis requires that the mix of ozone precursors on weekend mornings has aged sufficiently such that the VOC/NOx ratio has switched from VOC-limited to NOx-limited.

Pollutant carryover near the ground. Light-duty gasoline vehicle traffic is increased while heavy-duty diesel traffic is decreased on Friday and Saturday evenings compared to other evenings resulting in overnight carry over of pollutants with higher VOC/NOx ratios on Saturday and Sunday mornings.

Pollutant carryover aloft. Contribution of ozone and ozone precursors from aloft, which is NOx-limited, combined with lower NOx emissions on weekend mornings results in more efficient ozone production during the ozone accumulation period on weekends. Because ozone inhibition is lower on weekends, nitrous acid (HONO), formaldehyde (HCHO), peroxyacetyl nitrate (PAN), or other early-morning radical sources increase in relative importance.

Increased weekend VOC emissions. The increased use of lawn and garden equipment, recreational vehicles, backyard barbecues, and household solvents on weekends compared to weekdays results in higher weekend VOC/NOx ratios.

Increased photolysis due to decreased emissions of fine particles. Reduced diesel truck traffic on weekends results in lower emissions of soot particles that absorb light. Lower PM concentrations during weekends increases the direct and scattered UV radiation available for photolysis, thus increasing the rate of ozone formation compared to weekdays.

This report provides a conceptual explanation of the weekend effect based upon the analysis of ambient data and reconciles our findings with the alternative hypotheses for the effect. The Executive Summary (Volume I) provides a synthesis of the results obtained by DRI and STI with respect to these hypotheses.

1.3 Methods and Approach

In the initial phase of the study, we examined historic trends in the average daily maximum hour ozone in the SoCAB from 1981 to 1998 and the evolution of the magnitude and spatial extent of the weekend ozone effect over this period. Air quality data for summers (June 1 to September 30) of 1981 to 1998 were obtained from the latest (February 2000) ARB ambient data CD. The database was validated and screened for invalid and suspicious data according to the procedures and criteria described by Fujita et al. (2000). Monitoring sites include N. Long Beach, Anaheim, Lynwood, Los Angeles–N. Main, Reseda, Burbank, Pico Rivera, La Habra; Azusa, Pomona, Upland, and Rubidoux. Mean statistics were averaged into four time periods covering the years 1981-84, 1985-89, 1990-94, and 1995-98. The ozone trends were associated with day-of-the-week variations in the diurnal behavior of ozone, nitric oxide (NO), nitrogen

dioxide (NO_2)[4], and carbon monoxide (CO), which serves as an estimate of nonmethane hydrocarbons (NMHC). Non-methane hydrocarbons (NMHC) were estimated from CO using an empirical relationship between NMHC and CO from canister samples collected by Desert Research Institute at three sites in the SoCAB during the summers of 1995 and 1996 (Zielinska et al. 1999)[5]. The retrospective analysis of ambient data focused on day-of-the-week differences in the overnight carryover of ozone precursors, the extent of inhibition of ozone formation during the morning due to titration with NO, and the rate of ozone accumulation from the end of the inhibition period to time of peak ozone. For the purposes of this analysis, the time at which [NO] = [O_3] was used to mark the end of the ozone inhibition period. Changes in the rate of ozone accumulation were correlated to historic trends in CO/NOx ratios, which served as partial surrogates for trends in VOC/NOx ratios.

Current observations of the weekend effect were characterized by examining the summer 1999 and 2000 ambient data from the South Coast Air Quality Management District (SCAQMD) Photochemical Assessment Monitoring Stations (PAMS) in Azusa, Pico Rivera, and Upland and from the California Air Resources Board ozone precursor trends site in downtown Los Angeles (North Main). The analyses focused on relating weekday differences in the diurnal variations of CO, NMHC, NO, and NO_2, and NOx with variations in ozone, VOC/NOx ratios, and the ratios of O_3 to potential ozone (i.e., O_3 plus NOx). Weekday variations of ozone were also related to VOC reactivity, photochemical aging, and estimated photolysis rate parameter for NO_2. Current weekday and weekend observations of the VOC and NOx mixing ratios are superimposed on an ozone isopleth plot along with similar observations from 1987.

The experimental phase of this study focused on time-resolved measurements of VOC, NOx, CO, and particulate black carbon to examine relationships between emissions sources and the diurnal and day-of-the-week variations of ozone precursors and VOC/NOx ratios. The field study was conducted in the Los Angeles area over a period of 9 days from September 30, 2000 to October 8, 2000. The field measurements involved two approaches: supplemental measurements at existing SCAQMD monitoring sites and mobile sampling along freeway and surface street loops and at regional/background sites. Supplemental measurements made by DRI at the monitoring stations included hourly C_2 to C_{11} volatile organic compounds by automated gas chromatography with mass spectrometry (Varian 3800 GC interfaced to an Entech model 7100 automated preconcentrator and a Varian Saturn 2000 ion trap mass spectrometer) at Azusa, continuous black carbon by light absorption with an Anderson RTAA-1000 aethalometer (approximately 5-minute averages) at Azusa and Pico Rivera, and 3-hour composite Tenax samples for C_8 to C_{18} hydrocarbons beginning at 2, 6, and 9 a.m. PDT on September 30, October

[4] NO_2 is determined by the difference of NOx and NO measured by chemiluminescence analyzers. In addition to NO_2, analyzers that are commonly used at air quality monitoring stations also convert other reactive nitrogen oxide species such as PAN to NO, thereby causing interference. NO_2 reported by these instruments must be considered upper limits. The magnitude of the interference is relatively small in the urban center where NO sources are large, but can be substantial in downwind and rural areas.

[5] Because data were not available prior to the early 1990s, NMHC is estimated from CO using an empirical relationship between NMHC and CO for data collected in 1995 and 1996. While these estimates are reasonably valid for determining day-of-the-week variations in NMHC concentrations and NMHC/NOx ratios for any year within the 18-year period of interest, they are less reliable for estimating long-term trends in NMHC and NMHC/NOx ratios because the slope of the regression between CO and NMHC may have changed over time with changing emission control technology.

1,2,4,6,7, and 8. ARB also collected canister samples at Los Angeles – N. Main for speciated hydrocarbons on the same schedule, and SCAQMD measured 3-hour average speciated VOC with an automated gas chromatograph at Pico Rivera.

Primary pollutants (CO, NO, black carbon [BC] and speciated hydrocarbons) were measured simultaneously in a mobile van along several freeway loops in different areas of the Basin. Carbon monoxide, NO/NOy and black carbon estimated from light absorption were measured continuously with averaging times of 1, 1, and 5 minutes, respectively. Canister and Tenax cartridge samples were integrated over a period of approximately 50 minutes for each freeway loop and fixed locations. Mobile sampling was conducted during the carryover period between 2-5 a.m. (PDT), the ozone inhibition period between 6 to 9 a.m., and during the ozone accumulation period between 9 a.m. and noon. Sampling was conducted on Saturday, September 30, 2000, Sunday, October 1, Monday, October 2, Wednesday, October 4, Friday, October 6, Saturday, October 7, and Sunday, October 8 along the following loops and fixed locations (see Figure 1.3-1).

- 0200 to 0245 – (IH1) Industry Hills Conference Center (overflow parking lot on the south end of the conference center) on all days.

- 0300 to 0345 – (CV1) Covina Loop (east on S-60 from Azusa Blvd on-ramp, north on S-57, west on I-10 to I-5) on all days.

- 0415 to 0500 – (DS1) Dodger Stadium (four loops around the perimeter of the Stadium) on all days.

- 0515 to 0600 – (CO1) Compton Loop (south on S-110 from Stadium Way onramp, east on I-405, north on I-710 to I-10) on all days.

- 0630 to 0715 – (HF1) Source-dominated samples for the SI vehicle exhaust profile (fixed location sampling on southbound S-110 just south of Stadium Way onramp) on October 2, 4, 6, 7, and 8. This section of the 110 (Harbor Freeway) is restricted to automotive traffic only.

- 0730 to 0815 – (DS2) Dodger Stadium on all days.

- 0830 to 0915 – (CO2) Compton Loop on all days.

- 0930 to 1015 – (CV2) Covina Loop (east on I-10 at I-710, south on S-57, west on S-60 to Azusa Blvd off-ramp) on all days.

- 1030 to 1115 – (IH2) Industry Hills Conference Center on all days.

- 1130 to 1215 – (PO1) Pomona Loop (east on S-60 at Azusa Blvd onramp, north I-15, west of I-10 north on 210 to Azusa Blvd off-ramp on October 2, 4, 6, 7, and 8.

Five sets of canister and Tenax samples and continuous CO, NO, NOy and black carbon measurements were taken at a truck stop near I-10 and I-15. Measurements were made during the early morning hours from 0100 to 0500, and consisted of three sets of samples at the truck stop

and upwind samples before and after the truck stop samples. Additionally, ten gasoline and two diesel fuel samples were collected for analysis of speciated VOCs. Sonoma Technology, Inc. conducted concurrent traffic and emission source surveys during the field study.

For each sampling loop, the time series of NO and CO were related to indicators of compression-ignition exhaust (black carbon and heavy hydrocarbons) and spark-ignition exhaust (CO and MTBE) by time of day and day of the week. Multiple regression analysis was used to estimate the amounts of NOx associated with CO and MTBE relative to the NOx associated with black carbon and nC_{10}-nC_{15}. Diurnal and day-of-the-week variations in the associations of NOx to pollutants are correlated to the relative contributions of diesel and gasoline exhaust to ambient NOx. The premise of this approach is that gasoline exhaust is enriched in CO and MTBE relative to diesel exhaust while diesel exhaust is enriched in black carbon and heavy hydrocarbons relative to gasoline exhaust. The source contributions of gasoline engine and diesel engine exhaust to NMHC and NOx were estimated by Chemical Mass Balance (CMB) receptor modeling. Source composition profiles were derived for diesel and gasoline exhaust from samples collected at a truck stop and on a stretch of the 110 Freeway where heavy trucks are prohibited. Source profiles were also developed from analysis of gasoline and diesel fuel samples. In addition to the relative contributions of gasoline and diesel exhaust, the detailed speciation of VOC from the mobile sampling and the time-resolved VOC speciation at Los Angeles, Azusa, and Pico Rivera monitoring stations provided source attribution of other sources of VOC by time of day and day of the week. These analyses address questions regarding the source contributions of VOC carried over from the previous evening and the relative importance of on-road versus other area sources in the diurnal variations in VOC/NOx ratios. Diurnal variations in VOC composition were also used to examine day-of-the-week differences in ozone formation potential and reactivity of the VOC mix. Sonoma Technology, Inc. conducted concurrent traffic and emission source surveys during the field study

The Regional Atmospheric Chemical Model (RACM; Stockwell et al., 1997) was used in a chemical box model to calculate ozone isopleths from initial concentrations of VOC determined from measured VOC concentrations obtained between 6-9 a.m. The simulations were made for periods lasting up to four days using a range of initial VOC and NOx. EKMA simulations were performed over a range of observed NO_x and VOC mixing ratios. The RADM2 mechanism was developed for the modeling of atmospheric chemistry on urban and regional scales. The RADM2 gas phase mechanism has been independently evaluated and tested against environmental chamber data from the Statewide Air Pollution Research Center (SAPRC) of the University of California at Riverside, and from the outdoor chamber at the University of North Carolina (Carter and Lurmann, 1989). The simulations are representative of typical atmospheric chemical conditions. A detailed discussion of the conditions used in these simulations is given in Stockwell et al. (1988). The photolysis rates of twenty-one species were varied over a diurnal cycle representative of conditions near sea level for 40°N latitude (temperature: 298.15 ˚K; pressure: 1 atm) throughout a typical midsummer day, June 21. The initial conditions for the simulations are given in Table 3.5-1. The total initial NMHC used in the simulations was the sum of a fixed background of NMHC and a varying concentration of anthropogenic NMHC with a speciation typical of atmospheric conditions given in Table 3.4-1. The simulations were started at sunrise (210 minutes after midnight) and run until noon. They were made without emissions of NO_x or NMHC because these have little effect on the comparison of mechanisms (Stockwell and Lurmann, 1989). The results were plotted as EKMA diagrams. For ozone, ozone efficiency,

HO and HO_2 the contour plots were made for solar noon while all other plots were made for sunset of the first simulated day.

1.4 Results and Discussion

The weekend ozone effect is rooted in ozone's complex photochemistry, and arises from the day-of-the-week differences in the temporal and spatial patterns of VOC and NOx emissions. These emission-activity differences alter the diurnal and spatial variations in VOC and NOx concentrations and VOC/NOx ratios, which affect the diurnal evolution of ozone chemistry. Day-of-the-week differences in the concentrations of ozone were examined with respect to its diurnal patterns, the diurnal patterns of NO, ratios of peak ozone to potential ozone, VOC reactivity, photochemical aging, and NO_2 photolysis rates. The results of these analyses were synthesized with the fundamental knowledge of ozone formation, theoretical analysis of ozone and its precursors, and time-variations in the source contributions of VOC and NOx to develop a self-consistent explanation for the weekend ozone effect.

1.4.1 Fundamentals of Ozone Formations

The chemistry of ozone formation is well established. Ozone is produced in the atmosphere by the reaction of a ground state oxygen atom, O (^3P), and molecular oxygen (O_2). While O_2 is abundant in the atmosphere, free oxygen atoms are not. At lower altitudes, where only UV radiation with wavelengths greater than 280 nm is present, the only significant net oxygen atom production is from photodissociation of NO_2 into NO and ground state oxygen atoms, Reaction (1). The ground state oxygen atoms react with molecular oxygen to produce O_3, Reaction (2), (where M is a third body such as N_2 or O_2).

$$NO_2 + h\nu \rightarrow NO + O(^3P) \quad (1)$$

$$O(^3P) + O_2 + M \rightarrow O_3 + M \quad (2)$$

When nitric oxide molecules are present, O_3 reacts rapidly with NO to regenerate NO_2, Reaction (3).

$$O_3 + NO \rightarrow NO_2 + O_2 \quad (3)$$

The first and third reactions occur rapidly, establishing a steady-state equilibrium ozone concentration $[O_3]$ that is determined by the "NO-photostationary state equation," Equation (4)

$$[O_3] = \frac{J_1[NO_2]}{k_3[NO]} \quad (4)$$

where J_1 is the photolysis frequency of Reaction (1), k_3 is the rate constant for Reaction (3), $[NO_2]$ is the concentration of nitrogen dioxide and [NO] is the concentration of nitric oxide. Because these reactions only recycle O_3 and NO_x, they are insufficient, by themselves, to create excessive ozone levels. When carbon monoxide or volatile organic compounds are present, however, their oxidation produces the hydroperoxy radical (HO_2) and organic peroxy radicals (RO_2), which react with NO to form NO_2 without destruction of ozone, thereby allowing ozone to accumulate.

The hydroxyl radical (HO) initiates the oxidation of VOCs that form the peroxy radicals. A fraction of O_3 photolyzes to produce an excited oxygen atom, $O(^1D)$, Reaction (5), which reacts with water to produce hydroxyl (HO) radicals, Reaction (6).

$$O_3 + h\nu \rightarrow O(^1D) + O_2 \qquad (5)$$

$$O(^1D) + H_2O \rightarrow 2\ HO \qquad (6)$$

Other sources of HOx radicals include the photolysis of carbonyl compounds and smaller contributions due to nitrous acid (HONO) and other radical precursors. The HO radicals react with CO or organic compounds (RH) to produce peroxy radicals (HO_2 or RO_2). The peroxy radicals react with NO to produce NO_2 which photolyzes to produce additional O_3:

$$CO + HO\ (+O_2) \rightarrow CO_2 + HO_2 \qquad (7)$$

$$RH + HO \rightarrow R + H_2O \qquad (8)$$

$$R + O_2 + M \rightarrow RO_2 + M \qquad (9)$$

$$RO_2 + NO \rightarrow RO + NO_2 \qquad (10)$$

$$RO + O_2 \rightarrow HO_2 + CARB \qquad (11)$$

$$HO_2 + NO \rightarrow HO + NO_2 \qquad (12)$$

The net reaction is the sum of Reactions (8) through (12) plus twice Reactions (1) and (2):

$$RH + 4\ O_2 + 2\ h\nu \rightarrow CARB + H_2O + 2\ O_3 \qquad (13)$$

where CARB is a carbonyl species, either an aldehyde (R'CHO) or a ketone (R'CR"O). The carbonyl compounds may further react with HO or they may photolyze to produce additional peroxy radicals that react with NO to produce NO_2 (Seinfeld, 1986; Finlayson-Pitts and Pitts, 1986). Peroxy radical reactions with NO reduce the concentration of NO and increase the concentration of NO_2. This reduces the rate of Reaction (3), which destroys O_3 and increases the rate of reaction (1), which eventually produces ozone. The increase in $[NO_2]/[NO]$ ratio leads to higher O_3 concentration according to Equation (4).

For the majority of VOCs emitted from anthropogenic and natural sources, reaction with the hydroxyl radical is the major cause of chemical change. Acetylene, most of the smaller alkanes, and benzene have lifetimes which exceed the typical summer residence time of air masses in the South Coast Air Basin (~12 hours, Douglas et al., 1991). Most of the other hydrocarbons will have substantially changed in proportion to the other species after the air mass containing them has aged for a few hours. The degradation reactions for all classes of VOCs, in addition to the conversion of NO to NO_2 and the formation of ozone, lead to the formation of carbonyl compounds (aldehydes, ketones, hydroxycarbonyls, and dicarbonyls), organic acids, organic nitrates (including peroxyacyl nitrates, the simplest member of which is peroxyacetyl nitrate [PAN]). PAN thermally decomposes back to its reactants, NO_2 and acetylperoxy radical. Thus, PAN can serve as a nighttime reservoir for NOx and a means of transport of NOx to downwind areas. Carbonyl compounds that are produced from hydrocarbon oxidation can be important reactive VOCs themselves, and thus important sources of peroxy radicals responsible for ozone production.

In the lower troposphere, the formation of nitric acid (HNO_3) by reaction of NO_2 with HO is a major sink of NO_x because HNO_3 reacts slowly in the lower troposphere, and it is rapidly removed due to dry and wet deposition. Reaction of HNO_3 with ammonia (NH_3) yields particulate ammonium nitrate (NH_4NO_3), which is in equilibrium with NH_3 and HNO_3 at typical summertime temperatures in southern California. NO_x can also be removed during the night through heterogeneous reactions of nitrogen pentoxide (N_2O_5) on water coated aerosol particles. N_2O_5 is produced by the reaction of NO_2 with nitrate radicals (NO_3), which are produced by the reaction of NO_2 with O_3. Because NO_3 radicals rapidly photolyze and react rapidly with NO, concentrations of the NO_3 radical and N_2O_5 remain low during daytime but can increase during evening and nighttime hours in the absence of NO.

Ozone formation is nonlinear with respect to concentrations of VOCs and NOx because they compete with one another for the HO radicals. Figure 1.4-1 shows the linkages among the reactions that propagate radicals and those that remove them. VOCs are consumed in the sequence of ozone formation, while HO, HO_2, and NOx act as catalysts. Termination occurs by reaction of HO with NO_2 to form nitric acid (HNO_3) or when HO_2 combines to form hydrogen peroxide (H_2O_2). The production efficiency of O_3 per molecule of NOx varies with total concentration of NOx and the ratio of VOC to NOx. At low VOC-to-NO_2 ratios, HO reacts predominantly with NO_2, removing radicals and retarding O_3 formation. Under these conditions, a decrease in NOx concentration favors ozone formation. High ratios of VOC to NOx concentration favor HO reaction with VOCs that generate new radicals that accelerate O_3 production. At a sufficiently low concentration of NOx, or a sufficiently high VOC-to NO_2 ratio, a further decrease in NOx favors peroxy-peroxy reactions, which retard O_3 formation by removing free radicals from the system. At a given level of VOC, there exists a NOx mixing ratio at which a maximum amount of ozone is produced. This optimum VOC/NOx ratio depends upon the reactivity to HO of the particular mix of VOCs that are present. For ratios less than this optimum ratio, increasing NOx decreases ozone.

The ozone isopleth diagram shown in Figure 1.4-2 illustrates the dependence of O_3 production on the initial amounts of VOC and NOx. To generate this plot, ozone formation is simulated in a hypothetical well-mixed box of air from ground to the mixing height that is

transported from an urban center to a downwind location of maximum ozone concentrations. Multiple simulations are performed with varying initial concentrations of NOx and anthropogenic VOC. The ozone ridge in the isopleth diagrams corresponds to the maximum O_3 concentration that can be achieved at a given VOC level. The VOC/NOx ratio at the ridgeline is about 10 to 12. The HO radical chain length, which is the number of times a newly formed HO radical is regenerated through radical chain propagation before it is destroyed, reaches a maximum at this VOC/NOx ratio. Thus, the ridgeline corresponds to the VOC/NOx ratio at which O_3 is most efficiently formed. Above the ridgeline, a reduction of NOx lowers the rate at which HO and NO_2 are removed by formation of HNO_3 and leads to an increase in maximum O_3. This region is commonly described as "VOC-limited" and "VOC-sensitive" (i.e., lowering VOC most effectively reduces O_3). "NOx-disbenefit" refers to a situation when NOx reduction leads to an increase in ozone. This disbenefit occurs only in the VOC-limited region. Below the ridgeline at low NOx concentrations, there is a large region where lowering NOx most effectively reduces O_3 and large reductions in VOC have practically no effect on maximum O_3. This region is described as "NOx-limited". Note that unlike VOC-limitation, "NOx-limited" is not synonymous with "NOx-sensitive" because peak ozone concentrations are sensitive to NOx concentrations both above and below the ridgeline. A decrease in NOx above the ridgeline increases ozone while a decrease in NOx below the ridgeline decreases ozone.

In addition to the rate of ozone formation, the intensity and spatial extent of the weekend (WE) effect also depend upon the degree of inhibition of ozone accumulation due to titration of O_3 with NO. NO exists in excess of O_3 in the urban center overnight, and suppresses the concentration of O_3 to zero or near zero in the surface layer. Fresh NO emissions during the morning commute prolong the inhibition of ozone accumulation after sunrise. During this inhibition period, the photolysis of carbonyl compounds and smaller contributions of nitrous acid (HONO) and other radical precursors are the primary source of HO radicals until a sufficient amount of NO has been converted to NO_2. O_3 carried over aloft from the previous day can mix down in the morning and contribute O_3 and radicals to the developing surface ozone chemistry. Lower NOx emissions on weekends decrease NO titration of the O_3 newly formed at the surface and the ozone transported from aloft. Accordingly, ozone formation begins earlier on weekends.

VOC/NOx ratios vary within air basins, resulting in either NOx-limited or VOC-limited areas depending upon the time of day, the mix and type of emission sources, timing of additional fresh emissions, and pattern of pollutant transport. The instantaneous VOC/NOx ratios tend to increase during transport (absent injection of fresh emissions) because HO reacts more rapidly with NO_2 than with VOCs. Thus, NOx is removed more rapidly from the system than VOCs. It is possible that a pollutant mix that is initially VOC-limited will become NOx-limited in downwind areas. Addition of dispersed NOx sources in downwind suburban areas may extend the area of VOC limitation further downwind. An increase in the rate of ozone formation due to the increase in VOC/NOx ratio during transport may be offset by dilution in the absence of fresh emissions.

1.4.2 Evolution of the Weekend Effect in the South Coast Air Basin

Southern California has historically experienced the most severe smog in the United States. High ambient levels of ozone result from the combination of emissions from the second largest urban area in the U.S., high mountains that restrain transport of air pollutants, and adverse meteorology that limit atmospheric dispersion. Prior to the implementation of emission reduction

measures, hourly averaged ozone concentrations approaching 0.70 ppm were reported in the South Coast Air Basin (SoCAB), and Stage III episodes (ozone exceeding 0.50 ppm) were relatively frequent events in the 1960s. Because of three decades of progressively more stringent controls on emissions of reactive organic gases and oxides of nitrogen, the frequency and intensity of excessive ozone concentrations in the SoCAB have been significantly reduced. By the mid-1990's, the exhaust emission rates of new passenger cars (based on the Federal Test Procedures) were about 97% lower than pre-control (before 1966) levels for VOC, and about 85% lower for NOx. More stringent evaporative emissions standards for motor vehicles have been mandated. Reformulated gasoline was introduced in the mid-1990s. Regulations were also adopted to reduce VOC from non-motor vehicles ranging from large petroleum processing and marketing operations to industrial and domestic solvent usage. Because of these control measures, the frequency and intensity of excessive ozone concentrations in the SoCAB have decreased significantly. The Basin recorded 167 days exceeding the National Ambient Air Quality Standard (NAAQS) of 0.12 ppm maximum hourly average in 1980, 158 days in 1985, 130 days in 1990, 98 days in 1995 and 33 days in 2000 (SCAQMD, 2001). The maximum hourly average concentrations of ozone in the basin declined during this twenty-year period from 0.45 ppm to 0.18 ppm.

While peak levels of ozone have dropped sharply in the SoCAB, the highest levels of ozone now occur more frequently on Sundays throughout the basin. Figure 1.4-3 shows that in the period 1981-84, peak ozone levels were higher on weekdays in most of the central and eastern portions of the basin. Most monitoring sites in the western basin showed slightly higher weekend ozone concentrations. By 1990-94, ozone concentrations were higher on weekends throughout the basin and the weekend effect continued to strengthen after 1995. The twelve-sites average Sunday/Wednesday ratios in peak ozone for the periods 1981-84, 1985-89, 1990-94, and 1995-98 were 1.00, 1.02, 1.18 and 1.26, respectively. The corresponding Saturday/Wednesday ozone ratios were 1.03, 1.04, 1.17, and 1.24, respectively. Ozone concentrations in 1995-98 expressed as ratios of the 1981-84 values range from 0.54 to 0.59 on Monday through Friday, 0.67 on Saturday, and 0.70 on Sunday. Larger reductions in peak ozone concentrations have occurred on weekdays, and the location of the peak ozone levels shifted from the central portion of the basin to the eastern end of the basin. In the western basin, represented by Los Angeles – North Main, the current (1999-2000) mean peak ozone levels are about 60 ppb lower than in 1980-85 for all days of the week. In contrast, decreases in peak ozone in the central basin (Azusa and Upland) have been greater on weekdays (~ 100 to 110 ppb) than on Saturdays (~ 70 to 90 ppb) or Sundays (60 to 70 ppb). The peak ozone levels on Sundays and Saturdays are currently about 40 and 25 percent higher than midweek values, respectively.

1.4.3 Identification and Evaluation of Relevant Factors

The diurnal ozone cycle consists of four phases: overnight carryover of ozone precursors; inhibition of ozone formation during the morning due to titration with NO; accumulation of ozone from the end of the inhibition period to the time ozone reaches its maximum; and post ozone maximum, which is characterized by increased vertical mixing and horizontal advection, declining actinic flux, and titration of ozone by fresh NO emissions during the afternoon. Figure 1.4-4 shows the average diurnal variations of O_3, NO, NO_2, and CO at Azusa for summer 1995. The overnight carryover of NO is lower on Sunday and Monday mornings and higher at the end

of the week on Friday and Saturday. NO carryover is 10-20 percent lower on Sunday and Monday relative to midweek and about 10-15 percent higher on Friday and Saturday mornings. Overnight carryover of NMHC is greatest on Saturday and Sunday mornings with ratios to Wednesday of 1.20 and 1.12, respectively, and least on Monday mornings. Higher carryover of NMHC on Sunday relative to Wednesday coupled with lower relative carry-over of NO suggests that the carryover of NO and NMHC emissions is driven by different sources. NO_2 shows no significant day-of-the-week differences. The magnitude of the carryover of NO and NO_2 has decreased about 20 percent over the past 18 years. The fraction of NOx that is NO_2 ranges from 60 to 90 percent with lowest fractions at Los Angeles–N. Main, Pico Rivera, Burbank and Pomona and highest fractions at N. Long Beach, Anaheim, and Upland. There are no significant day-of-the-week variations in the NO_2/NOx ratios during the overnight carryover period.

Extent of Ozone Inhibition and Rate of Ozone Accumulation

Initially, ozone formation is inhibited by high concentrations of NO, which inhibit radical formation by titrating ozone. During this period HCHO and, to a lesser extent, HONO are the main source of HO radicals. The length of the morning ozone inhibition period is largely determined by the concentration of NO and NO_2/NOx ratios. The ozone inhibition period ends earlier on weekends than on weekdays because NO concentrations during the morning, especially during (6-9 a.m.) are substantially lower on weekends. Average 7-8 a.m. NO concentrations on Saturday and Sunday are 55-70 percent and 33-39 percent of the average weekday concentrations, respectively (see Figure 1.4-5). The average NO_2/NOx ratios at 7-8 a.m. (PDT) are about 0.4 on weekdays, about 0.5 on Saturday and close to 0.6 on Sunday (see Figure 1.4-6). We use the morning crossover of NO and O_3 ($t_{NO=O3}$) as an indicator of the end of the inhibition period and beginning of O_3 production via conversion of NO to NO_2 by peroxy radical. Note in Figure 1.4-4 that the crossover occurs an hour earlier on weekends. Thus ozone formation begins earlier on weekends. The ozone inhibition period ends 0.5 to 0.7 hours earlier on Saturdays and about 1.1 to 1.3 hours earlier on Sundays. In general, ozone inhibition ends earlier in downwind areas and later in areas of highest amounts of fresh NO emissions. Under typical summer transport pattern in the Basin, less time is available near the coast for ozone to accumulate before ventilation occurs. However, the delay in the start of ozone accumulation due to inhibition on weekdays relative to weekends has changed very little in 18 years (see Table 1.4-1). Thus, the observed long-term changes in the magnitude and spatial extent of the weekend effect are not due to the changes in the duration of ozone accumulation.

In contrast to the duration of ozone accumulation, which has remained relatively constant during 1981 to 1998, ozone accumulation rates were cut in half during the 18-year period with the largest reductions in the central basin. Table 1.4-1 and Figure 1.4-7 shows that ozone accumulation rates were consistently lower on weekends than weekdays through most of the 1980's but became consistently higher on weekends during the 1990s. The switch from lower to higher ozone accumulation rates on weekends relative to weekdays coincides with increases in the magnitude and spatial extent of the weekend effect in the SoCAB and with a steeper decline in ozone during the 1990s, especially in the western and central parts of the Basin. Figure 1.4-8 shows the trends in the differences between Sunday and Wednesday ozone accumulation rates as three-year running averages for western, central, and eastern SoCAB sites. Changes in emissions from weekday to weekend in the early 1980s resulted in little change in the ozone accumulation rate at western sites and generally lower weekend rates at central and eastern sites. The lower

weekend ozone accumulation rate offsets the shorter ozone inhibition period on weekends at central and eastern locations resulting in either no change or slightly lower ozone concentrations on weekends (i.e., no weekend effect). The weekend ozone effect in the western basin during the early 1980s was largely due to deceased ozone inhibition. The switch to higher weekend ozone accumulation rates occurred in the mid-1980s in the western basin and in late-1980s in the central basin. Ozone accumulation rates have been about equal on weekdays and weekends since the early 1990's in the eastern basin. Coupled with the shorter inhibition period, ozone concentrations were consistently higher on weekends during the 1990s with the strongest weekend effect occurring in the western and central basin.

VOC/NOx Ratios

Trends in concentrations of ozone precursor over the past 20 years show a gradual transition in the SoCAB to lower VOC/NOx ratios in much of the basin. The data show that differences between weekday and weekend VOC/NOx ratios have steadily increased over time. The ratios of the average 6-9 a.m. (PDT) NMHC/NOx ratio on Saturday to that on Wednesday were 1.05, 1.06, 1.17, and 1.18 for the years 1981-84, 1985-89, 1990-94, and 1995-98, respectively. The corresponding Sunday/Wednesday ratios are 1.10, 1.17, 1.27 and 1.42. Consequently, ozone formation has become more VOC-limited on weekends relative to weekdays. This transition parallels the downward trend in peak ozone levels, a shift in the location of peak ozone levels from the central to eastern portion of the basin, and an increase in the magnitude and spatial extent of the weekend ozone effect in the SoCAB.

Current (1999-2000) NMHC/NOx ratios in the SoCAB are about half relative to the ratios observed during the 1987 Southern California Air Quality Study. The mean NMHC/NOx ratios (mean of Los Angeles North Main, Pico Rivera, Azusa, and Upland) during 0600-0900 ranged from 31 to 59 percent higher on Sunday (mean of 46 percent) and 20 to 39 percent higher on Saturday (mean of 29 percent) (see Figure 1.4-9). The mean 6-9 a.m. NMHC/NOx ratio (ppbC/ppbv) is 4.9 and 5.5 on Saturday and Sunday, respectively and increases to a high of 6.7 and 7.5 during the period of peak ozone (1200-1500). The mean NMHC/NOx ratio is 4.6 on Monday and ranges from 3.7 to 3.9 for other weekdays. The mean midday NMHC/NOx ratios do not exceed seven. This decrease is due primarily to reductions in hydrocarbon emissions.

Ratios of peak ozone to potential ozone

Along with a decrease in the rate of ozone accumulation, Figure 1.4-10 and 1.4-11 show that weekday peak ozone concentrations have steadily decreased relative to its maximum potential (sum of O_3 and NOx). In contrast, peak ozone on Sundays has remained constant relative to its maximum potential. The ratios of peak to maximum potential ozone on Saturdays were similar to Sundays during the 1980s through mid-1990s, but have since decreased. The decrease in the ozone accumulation rates and higher ratio of peak ozone to maximum potential ozone on weekends relative to weekdays in the western and central basin coupled with lower weekend concentrations of NOx and higher weekend VOC/NOx ratios indicate that ozone formation in the SoCAB has become increasing VOC-limited.

VOC reactivity, photochemical aging

In addition to VOC to NOx ratios, the reactivity of individual organic species with HO radical also affects the rate of ozone formation. The maximum incremental reactivity of the 55 PAMS target species is slightly lower on weekends. Formaldehyde is slightly higher during weekends in the afternoon. With the addition of carbonyl compounds in the MIR calculations, weekend MIRs are equal to weekdays during the morning and slightly higher during the afternoons. These results are consistent with Franzwa M. and R. Pasek (1999). While the reactivity of the VOCs are comparable or slightly lower on weekends, higher ratios of formaldehyde to sum of PAMS, lower ratios of more reactive species to less reactive species (i.e., xylenes/benzene) indicate greater photochemical activity on weekends.

NO_2 photolysis rate parameter

The photolysis rate parameter for NO_2 (J_{NO2}) was calculated from an extended version of the O_3-NO-NO_2 photostationary state expression. Although there is a large uncertainty in J_{NO2} calculated by this method the analysis showed that J_{NO2} increased over the period from 1980 to 2000 (see Figure 1.4-12). The long-term trend in J_{NO2} is consistent with the trend to lower soot emissions. The weekend/weekday variation in J_{NO2} is not consistent with the hypothesis that increased soot concentrations reduce J_{NO2} on weekdays. The differences in J_{NO2} were small but the maximum J_{NO2} on weekdays was higher than on Sunday for the entire period from 1980 to 2000.

1.4.4 Source Apportionment of Ozone Precursors

The concentrations of NO and black carbon are well correlated and exhibit similar diurnal and spatial variations, and weekday/weekend differences (see Figure 1.4-13). The day-to-day variations in pollutant concentrations showed a midweek dip during the September 30 to October 8, 2000 field study, which was coincident with the passage of a low-pressure system. Despite meteorological conditions that were unfavorable for pollutant buildup during the middle of the week, both NOx and black carbon were much higher on weekdays than during the weekends, especially during the ozone inhibition and accumulation periods. CO and VOC have temporal and spatial variations that are similar to each other, but they differed significantly from those exhibited by NOx and black carbon. CO and VOC showed no significant weekend/weekday differences during the ozone inhibition and accumulation periods. Rather, it reasonably tracks the day-to-day variations in meteorological conditions. Overnight carryover appears to be more significant for CO and VOC than for NO and black carbon on weekends, especially on Sunday morning.

NO concentrations were 1-2 orders of magnitude higher on freeways than on surface streets or at the SCAQMD Azusa monitoring station and other regional/background sites. NO concentrations are substantially lower for the HF1 sample (freeway with no trucks) than other freeway samples with a mixed fleet of gasoline- and diesel-powered vehicles. In contrast, CO and hydrocarbon concentrations were about a factor of 2-3 higher on freeways than at the SCAQMD Azusa monitoring station and other regional/background sites. CO and hydrocarbon concentrations for the HF1 sample (freeway with no trucks) are comparable to other freeway samples with a mixed fleet of gasoline- and diesel-powered vehicles.

VOC/NOx (ppbC of VOC to ppb of NOx) ratios on freeways ranged from 0.5 to 2. These ratios are slightly higher than the average ratio of 0.9 measured at a truck stop. One notable exception was early Sunday morning at 2:00 to 5:00 a.m. when VOC/NOy reached about four. Greater carryover of VOC accounted for the larger VOC/NOy ratio during this time. Larger concentrations of MTBE during this period indicate greater contributions from gasoline-powered vehicles. The light-duty gasoline-powered vehicle fleet, as represented by the freeway HF1 samples, has an average VOC/NOy ratio of about 3.5. This value is similar to the VOC/NOy ratios measured at Industry Hills and Dodger Stadium. VOC/NOx ratios at Azusa are consistently about five during the weekdays with little diurnal variation. Ratios were greater during the weekends, ranging between 5 and 10.

Source Apportionment of Nitrogen Oxides

The weekend/weekday differences in the relative contribution of NOx associated with CO and black carbon at Industry Hills are consistent with those found at the Azusa and Pico Rivera monitoring stations. These results show that the contribution of gasoline-powered vehicles to ambient NOx on a typical Saturday during the ozone accumulation period (9 a.m. to noon) is comparable to their contribution on weekdays. This conclusion is consistent with traffic counts, which show comparable light-duty gasoline vehicle traffic volumes on weekdays and Saturday during this time of the day. The contribution of gasoline-powered vehicles to ambient NOx is about 25 percent lower on Sunday compared to weekdays. In contrast, the contributions of diesel vehicles during the ozone accumulation period to ambient NOx on Saturday and Sunday are about one-half and one-third of its weekday contribution, respectively. The time series for NOx is closely correlated to the time series for black carbon.

During the overnight carryover period, the amount of NOx associated with CO and black carbon on freeway loops is similar to that at regional sites, with CO-associated NOx ranging mostly between 50 and 60 percent on weekdays, 60 to 65 percent on Saturday, and 65 to 70 percent on Sunday. There are large spikes of BC-associated NOx on freeway loops during the ozone inhibition and accumulation periods weekdays (see Figure 1.4-14a). These spikes exist to a lesser extent on Saturday and are almost entirely absent on Sunday (see Figure 1.4-14b). The percentage of CO-associated NOx for the three freeway loops during this time of day, CO2, CV2, and PO1, are 47, 35, and 41 percent, respectively, on Monday, 38, 40, and 30 percent on Wednesday, 43, 59, and 57 percent on Saturday, and 63, 68, and 59 percent on Sunday. At the Azusa and Pico Rivera monitoring stations, the percentage of NOx associated with CO is consistently larger on weekends and the largest fractions of NOx associated with black carbon occur midday during weekdays. These patterns are consistent with the diurnal and day-of-the-week variations in relative traffic volume of gasoline and diesel powered vehicles.

At Industry Hills, the most regionally representative site where the mobile sampling was conducted, the percentages of CO-associated NOx in the 10:00 to 10:45 a.m. samples are 44, 48, 62, and 72 percent for Monday, October 2, Wednesday, October 4, Saturday, October 7, and Sunday, October 8, respectively (see Table 1.4-2 for attributions in ppb of NOx). Based upon STI's analysis of the study period meteorology, Monday, October 2 is meteorologically similar to Sunday, October 8, and Wednesday, October 4 is similar to Saturday, October 7. The Saturday/Wednesday ratios of the CO and BC associated NOx are 1.01 and 0.58, respectively. The Sunday/Monday ratios of the CO and BC associated NOx are 0.84 and 0.25. The

corresponding source attributions are shown in Table 1.4-2 for Azusa and Pico Rivera during the 9 a.m. to noon sampling period. According to the SoCAB emission inventory (using EMFC2000), gasoline-powered vehicles account for 71 percent of the total NOx emissions from on-road vehicles for a typical summer day. From the multiple regression analysis, the corresponding attributions of gasoline-powered vehicles to on-road emissions of NOx during the 9 a.m. to noon period are 45, 57 and 66 percent for weekday, Saturday, and Sunday, respectively. These results suggest that NOx emissions from diesel-powered vehicles may be underestimated in the inventory.

Source Apportionment of VOC

Gasoline exhaust is the predominant source in all samples ranging from 60-80% for on-road samples and samples taken at more regionally representative locations (see Figure 1.4-15). The diurnal and weekday/weekend variations in the relative contributions of NMHC are more variable for diesel exhaust than gasoline exhaust. The relative contributions of diesel exhaust are greatest during the weekday on freeway loops with the greatest fraction of diesel traffic. Diesel exhaust contributed 20 percent of NMHC on the Pomona Loop on Monday, October 2, compared to only 3 percent on Sunday, October 8. The same percentages are 18 and 6 percent on Wednesday, October 4 and Saturday, October 7. Day-of-the-week changes in the contributions of diesel exhaust have much less impact on NMHC/NOx ratios than day-of-the-week changes in the contribution of diesel exhaust to ambient NOx concentrations. Based on the apportionment of ambient NMHC from the PAMS sites (e.g., see Figure 1.4-16), NMHC emissions from non-mobile sources do not show significant day-of-the week variations and have little effect on weekday variations in VOC/NOx ratios.

1.4.5 Conceptual Explanation of the Weekend Ozone Effect

The retrospective analysis of the ambient data showed that the intensity and spatial extent of the weekend ozone effect are associated with weekday-weekend differences in the degree of ozone inhibition and rate of ozone accumulation. Lower NO concentrations and higher NO_2/NOx ratios during weekend mornings decrease the removal of ozone by titration with NO, thereby allowing ozone to accumulate about an hour earlier on weekends compared to weekdays. This advance in timing of ozone accumulation on weekends is similar throughout the Basin, and it has remained relatively constant from 1981 to 1999. In contrast, the rate of ozone accumulation from the end of ozone inhibition to the time of ozone maximum decreased by one-half over the same time period with largest reductions occurring in the central basin. Rates of ozone accumulation were consistently lower on weekends than weekdays through most of the 1980s but became consistently higher on weekends during the 1990s. Central and eastern parts of the Basin showed either no change or slightly lower ozone concentrations on weekends (i.e., no weekend effect) in the 1980s because the shorter ozone inhibition periods were offset by the lower rates of ozone accumulation. A switch to higher weekend ozone accumulation rates in the 1990s, coupled with a shorter inhibition period, resulted in higher weekend ozone concentrations during the 1990s and a strengthening of the weekend ozone effect within the Basin.

The evolution of the weekend ozone effect in the SoCAB over the past twenty years is rooted in ozone's complex photochemistry in that differences in the efficiency and rate of ozone production cause the variations between weekdays and weekends. These differences arise from

day-of-the-week differences in the temporal and spatial patterns of VOC and NOx emissions. The fundamentals of ozone photochemistry impose two necessary conditions in order for a reduction in NOx on the weekend to result in higher production of ozone. The first condition is that ozone formation be VOC-limited. Removing NOx from a VOC-limited system reduces the removal of HO radical by reaction with NO_2 to form nitric acid, thereby increasing the efficiency and rate of ozone formation. The weekend effect is greatest where the ozone formation is more VOC-limited during the weekday and less VOC-limited during the weekends. The second condition is that the peak ozone level on weekdays does not reach its maximum potential and time is a limiting factor in ozone production. If the second condition is true, the peak ozone is determined by the duration and rate of ozone accumulation. Although the amount of ozone that can potentially form on weekdays may be greater, peak ozone levels are higher on weekends because the duration of ozone accumulation is longer and the rate of ozone formation is greater on weekends.

VOC/NOx ratios affect both the rate and efficiency of ozone production. Photochemical reactivity of the VOC mixture also affects the rate of ozone formation, but reactivity of the VOC is lower on weekends and does not account for the higher ozone formation rates on weekends. The weekend effect is greatest where the ozone formation is more VOC-limited during the weekday and less VOC-limited during the weekends. VOC/NOx ratios have decreased in half over the past 15 years. The increase in VOC/NOx ratio on weekends due to decreased NO emission is consistent with the observed evolution of the weekend effect in the SoCAB over the past two decades and current diurnal and day-of-the-week variations in ozone relative to VOC, NO and NO_2 concentrations and NO_2/NOx, VOC/NOx ratios. This transition parallels the downward trend in peak ozone levels, a shift in the location of peak ozone levels from the central portion of the basin (e.g., Pasadena to Azusa) to the eastern portion of the basin (e.g., Lake Gregory), and an increase in the magnitude and spatial extent of the weekend ozone effect in the SoCAB.

The current weekend ozone effect in the SoCAB is summarized by the correlations in Figure 1.4-17 of the hourly ozone and NO mixing ratios during midweek (Tuesday to Thursday) versus Sunday. The data are correlated separately by daylight hours (open symbols) and nighttime hours (solid symbols). During the daylight hours, the relative differences between weekdays and weekends in the mixing ratios of NO and O_3 are constant throughout the daylight hours. NO is lower on Sunday relative to midweek by about the same ratio for all hours from 0600 to 2000 PDT. Conversely, ozone is higher on Sunday relative to midweek by the same ratio for all daylight hours despite the greater influence of local traffic on NO mixing ratios at Los Angeles – North Main and Pico Rivera relative to Azusa and Upland. The regression statistics are presented in Table 1.4-3. As would be expected, correlations of the midweek hourly NO and O_3 mixing ratios with the corresponding hourly values on Friday show little variance with one another. The Saturday/midweek ratios for ozone during the daylight hours ranged from 1.26 to 1.31 at the four sites with a mean of 1.28. The corresponding ratios for NO ranged from 0.51 to 0.69 with a mean of 0.61. The Sunday/midweek ratios for ozone during daylight hours ranged from 1.44 to 1.55 with a mean of 1.50. The ratios for NO ranged from 0.29 to 0.43 with a mean of 0.35. The correlations are extremely good with R^2s of 0.98 or better.

These results indicate that each of sites we examined has its own relative ozone pattern that is fixed for all days of the week and that what differentiates weekday from weekend is a

multiplicative constant. This constant factor results suggest that the weekday-weekend differences in the diurnal pattern of NO and ozone are established early in the morning and the influence of the chemical factors (either emissions and/or rate and efficiency of ozone formation) related to this "constant" is maintained throughout the day. The constant offset in the diurnal pattern of ozone and NO is related to the initial (i.e., 6-9 a.m.) VOC/NOx ratios. These results are counter to the expectations of the NOx timing hypothesis, which requires a proportional increase in NO and O_3 mixing ratios on weekends later in the morning compared to weekdays. Furthermore, increases in NO emissions under VOC-limited conditions will initially decrease ozone production and lead to increased ozone in downwind areas after the chemical system has transition to NOx-limited conditions. During the summers of 1999 and 2000, the NMHC/NOx ratios at the four SoCAB PAMS sites were in the range of four to eight from sunrise to the time of peak ozone so that ozone formation is VOC-limited throughout this period. Blanchard and Tanenbaum (2000) concluded based on estimates of the extent of reaction that most monitoring sites in the SoCAB are VOC-limited.

The soot hypothesis is inconsistent with the trend in ratio of ozone to potential ozone ($[O_3]/([O_3] + [NOx])$ from 1980 to 2000, Figure 1.4-12. If all other conditions were constant, higher J_{NO2} should yield more complete conversion of NO_2 to ozone. This has not happened, and the ratio of ozone to potential ozone has dropped markedly on weekdays over this time interval. Therefore it appears the fraction of NO_2 converted to ozone is not simply related to J_{NO2}. There was no evidence that the weekday/weekend ozone effect is caused by variations in soot concentrations affecting J_{NO2}. Neither the NOx timing or aerosol/photolysis hypotheses explain the greater decrease in ozone accumulation rates on weekdays during the past two decades, or the decrease in peak ozone relative to its maximum potential ozone on weekdays.

Theoretical analysis in Figures 1.4-18 and 1.4-19 shows why VOC control measures undertaken between 1987 and 2000 have been effective in reducing ozone. Ozone mixing ratios estimated from the EKMA diagram are predicted to have been reduced from 200 ppb to an average near 100 ppb, which is in reasonable agreement with observations. The current mixing ratios of VOC and NOx are on the VOC-limited portion of the EKMA diagram for both weekends and weekdays. There is little change in VOC mixing ratios between weekend and weekday, but on weekends there is now a significant reduction in the NO_x mixing ratios. Additional control of NOx in the future in the absence of additional VOC control is likely to increase peak ozone levels in the central basin although it is possible that they will decrease 8-hour O_3 levels in downwind areas such as the San Bernardino Mountains, Palm Springs, and Mohave Desert. The EKMA diagram shows that the decrease in NO_x leads to an increase in ozone mixing ratios of about 40 ppb between weekdays and weekends, and this is consistent with the observations. The EKMA diagram shows that that an ozone disbenefit will result if NO_x emissions are decreased at current levels of VOC until the NO_x mixing ratios decrease to about 10 or 12 ppb where ozone production becomes NO_x limited. The indicator ratios for photochemical activity on the EKMA diagrams, including $[HNO_3]/[H_2O_2]$ and $[H_2O_2]/[HCHO]$, show that ozone production is VOC limited for current NO_x and VOC mixing ratios.

The simulations showed that the VOC/NO_x ratio decreased from near an average of 7.5 during 1987 down to between 3 and 5 during 1999-2000. On weekends, the VOC/NOx ratio increases to between 4 and 7 and it may reach 10 or 12. The shift in VOC/NO_x ratio increases the average ozone production efficiency from less than 4 to between 4 and 6. The simulations also

show that hydroxyl radical mixing ratios increase with decreasing NO_x mixing ratios. Daytime nitric acid production has decreased between 1987 and 2000 due to the decrease in VOC mixing ratios. Now the production of HNO_3 would be expected to be lower by about 9 ppb between weekend and weekday. PAN, HCHO, aldehyde and organic nitrates have been reduced due to reductions in VOC mixing ratios but their mixing ratios are not strongly affected by the NO_x mixing ratios at current concentrations so a weekend effect is not expected for these species.

Our simulations for EKMA are consistent with a study by Milford et al. (1994) as quoted by Finlayson-Pitts and Pitts (1999). Milford et al. found that for conditions that are similar to present-day conditions in the SoCAB on Sundays (i.e., VOC near 300 ppbC and NO_x at 20 to 30 ppb) the rate of ozone production increases with decreasing NO_x concentrations. The study showed that an ozone disbenefit results if present-day Sunday NO_x concentrations are reduced. The Milford et al. (1994) study also shows that ozone production rates increase during the day because NO_x is consumed faster than VOC, which increases the VOC to NO_x ratio. Given the present-day concentrations of NO_x, increases in its emissions during the day will decrease, not increase, ozone production rates. However, based on the Milford, et al. study the NO_x timing hypotheses will become an important mechanism at the same point when reductions in NO_x emissions lead to lower ozone production rates. Modeling studies should be made with updated emissions inventories and models to verify the our modeling results and those of Milford, et al. (1994).

1.5 Recommendations

The varying emissions that occur between weekday and weekend periods provide a natural test of the ability of air quality simulation models to simulate accurately weekday-weekend differences in precursors and ozone. One of the most important applications of this test is that it helps to probe the relative sensitivity of ozone concentrations to VOC and NOx. The Coordinating Research Council has sponsored a study by ENVIRON to conduct proximate modeling of weekday/weekend ozone episodes in the SoCAB using input data collected during the SCOS97-NARSTO field study in order to determine whether proposed hypotheses explain the weekend ozone effect. Similar modeling is planned by the ARB after developing a weekend emissions inventory for SoCAB. These modeling results should be compared against the measured temporal and spatial variations of ozone and ozone precursors. These operational evaluations of modeling results should be accompanied by an evaluation of the accuracy of the temporal and spatial patterns of precursor emissions on weekdays and weekends. In addition to probing the underlying physical and chemical processes that drive the weekend effect, a series of modeling runs should be made using plausible alternative future emissions inventories for 5, 10 and 15 years into the future. These runs should be used to assess the direction and sensitivity of projected concentrations of ozone, PAN, nitric acid, particulate nitrate, and formaldehyde to future VOC and NOx controls. These assessments will be particularly important for downwind areas where emissions transported from the SoCAB could transition from VOC limited to NOx-limited and for assessing strategies that might achieve the 8-hour ozone standard in downwind areas but increase peak ozone concentrations in the central basin. Species such NOy, PAN, HCHO, and speciated hydrocarbons should be measured in these downwind area to provide corroboration of modeling results.

Table 1.4-1
Trends in Duration and Rate of Ozone Accumulation in the SoCAB on Sunday, Wednesday, and Sunday Minus Wednesday, 1981-1999

	Duration of Ozone Accumulation (hours) [1]			Ozone Accumulation Rate (ppb/hour) [1]		
Years	Sun	Wed	Sun-Wed	Sun	Wed	Sun-Wed
1981-84	5.5 ± 0.2	4.2 ± 0.3	1.3 ± 0.2	21.3 ± 1.0	24.3 ± 1.2	-3.1 ± 0.8
1984-89	5.3 ± 0.3	4.2 ± 0.3	1.1 ± 0.1	19.5 ± 1.2	20.6 ± 1.6	-1.1 ± 0.8
1990-94	5.2 ± 0.3	4.4 ± 0.3	0.8 ± 0.1	18.2 ± 0.9	16.3 ± 1.0	1.9 ± 0.6
1995-98	5.8 ± 0.3	4.5 ± 0.2	1.3 ± 0.2	13.8 ± 0.9	12.2 ± 0.9	1.6 ± 0.5

1 Twelve-site means and standard errors of the means.

Table 1.4-2
Weekend/Weekday Differences in
Ambient NOx Associated with CO and Black Carbon in the SoCAB

Location	Industry Hills		Azusa		Pico Rivera			
Time Interval	10:00 to 10:45		9:00 to noon		9:00 to noon		**Mean**	
Date	NOx (CO)	NOx (BC)	NOx (CO)	NOx (BC)	NOx (CO)	NOx (BC)	**NOx (CO)**	**NOx (BC)**
Mon, 10/2	37	47	54	56	34	47	**42**	**50**
Wed, 10/4	28	30	26	44	30	33	**28**	**36**
Sat, 10/7	29	18	26	22	25	21	**27**	**20**
Sun, 10/8	31	12	33	19	30	18	**31**	**16**
Ratios								
Sat/Wed	1.01	0.58	1.00	0.50	0.83	0.63	**0.94**	**0.56**
Sun/Mon	0.84	0.25	0.61	0.35	0.88	0.39	**0.75**	**0.33**

Table 1.4-3
Regression Statistics for the Correlations of Mean Hourly Ozone and Nitric Oxide Mixing Ratios During Friday, Saturday and Sunday Versus Midweek.

	Daylight (0600-2100)				Nighttime (2100-0600)			
	Ozone		Nitric Oxide		Ozone		Nitric Oxide	
Location	Slope	R^2	Slope	R^2	Slope	R^2	Slope	R^2
Friday/Midweek [1]								
Los Angeles N. Main	0.98	1.00	0.89	0.99	1.03	0.52	0.91	0.89
Pico Rivera	0.96	1.00	0.86	0.98	0.94	0.90	0.92	0.92
Azusa	0.98	0.99	0.94	0.96	0.94	0.97	0.83	0.93
Upland	1.02	1.00	1.03	0.99	1.08	0.96	1.19	0.35
Saturday/Midweek								
Los Angeles N. Main	1.29	0.98	0.61	0.99	1.30	0.76	0.91	0.72
Pico Rivera	1.27	1.00	0.69	0.99	1.31	0.97	0.80	0.90
Azusa	1.31	0.99	0.51	0.98	1.39	0.90	0.68	0.87
Upland	1.26	0.99	0.62	0.99	1.58	0.93	0.83	-0.28
Sunday/Midweek								
Los Angeles N. Main	1.49	0.96	0.43	0.97	1.14	0.61	0.87	0.66
Pico Rivera	1.50	0.98	0.39	0.99	1.35	0.95	0.69	0.85
Azusa	1.55	0.99	0.29	0.98	1.39	0.91	0.47	0.83
Upland	1.44	0.97	0.29	0.91	1.74	0.97	0.72	-0.10
Means								
Friday/Midweek	0.99	1.00	0.93	0.98	1.00	0.84	0.96	0.77
Saturday/Midweek	1.28	0.99	0.61	0.99	1.40	0.89	0.81	0.55
Sunday/Midweek	1.50	0.98	0.35	0.96	1.41	0.86	0.69	0.56

[1] mean to Tuesday, Wednesday, and Thursday

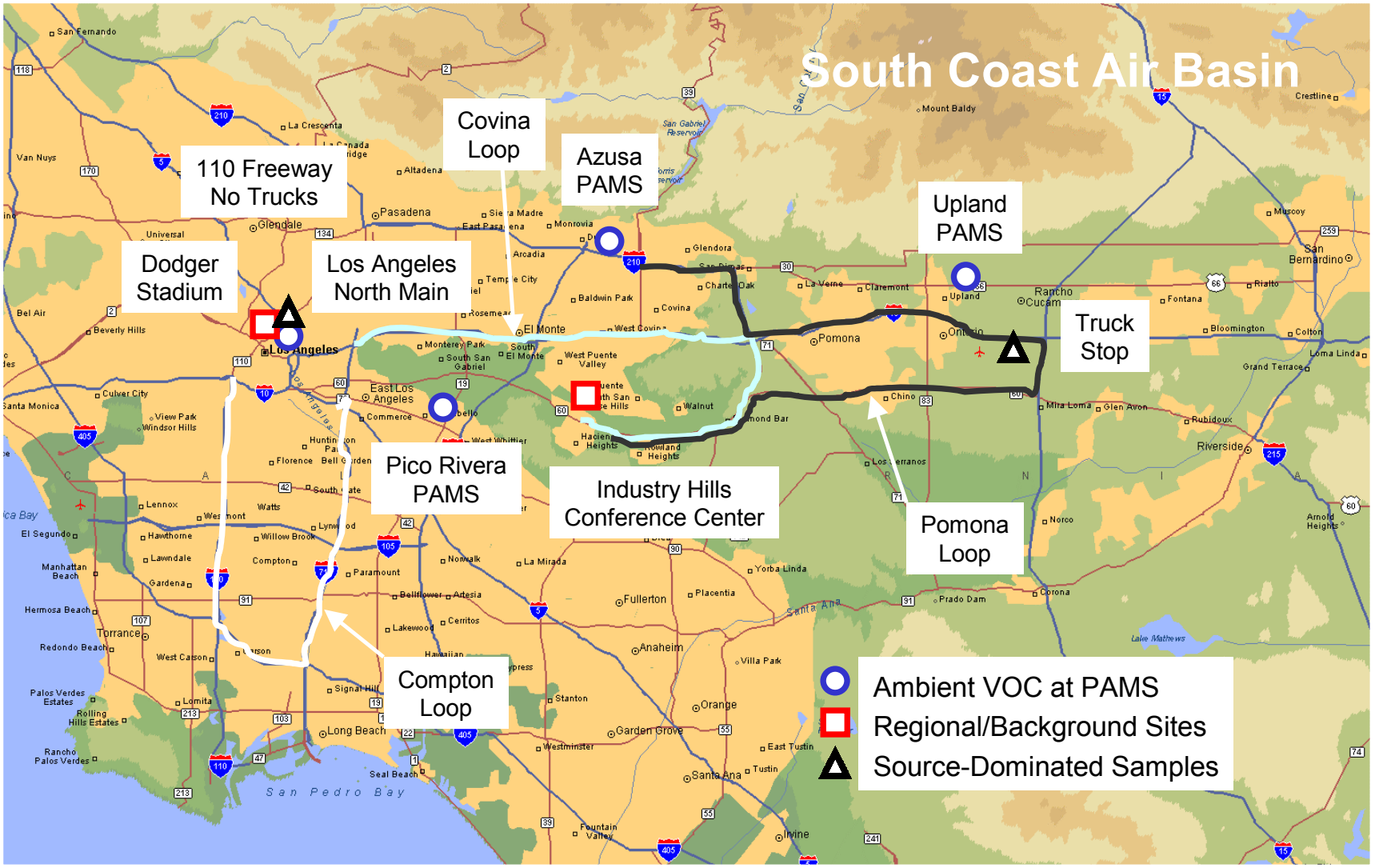


Figure 1.3-1. Map of the South Coast Air Basin showing the location of the Pico Rivera, Azusa, and Upland PAMS sites, the Los Angeles North Main monitoring station, and the three freeway loops and two regional/background sites used during the September 30 to October 8, 2000 field study.

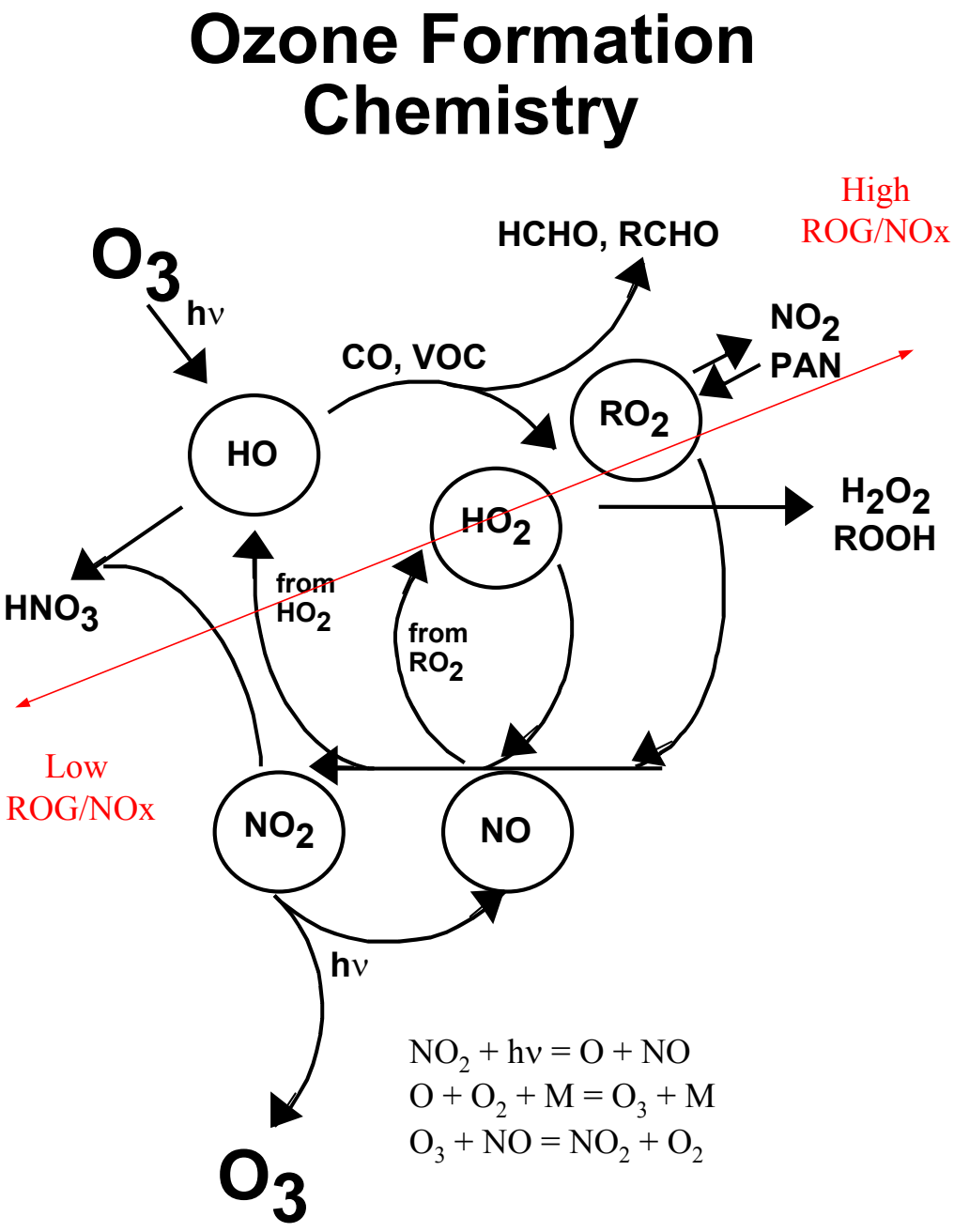


Figure 1.4-1. Schematic of the photochemical pathways leading to the production of ozone in the troposphere and the main termination reactions at high and low VOC/NOx ratios.

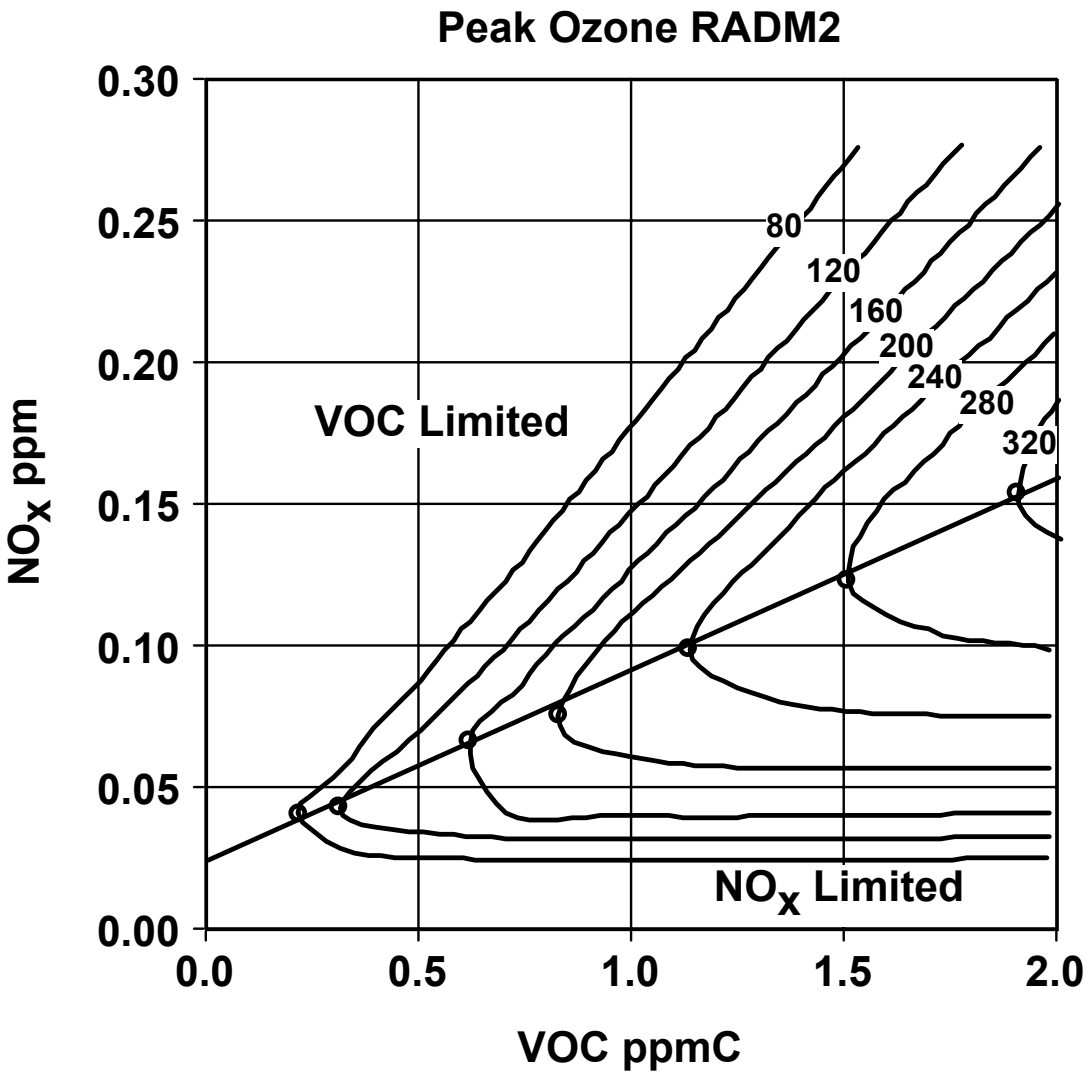


Figure 1.4-2. Typical ozone isopleth plot showing 1-hour maximum ozone concentrations (in ppb) calculated as a function of initial VOC and NOx concentrations and the regions of the diagram that are characterized as VOC- or NOx-limited. The ozone isopleth plot was generated using the Ozone Isopleth Plotting Program, Research Version (OZIPR) with the RADM2 chemical mechanism (Stockwell et al. 1990)

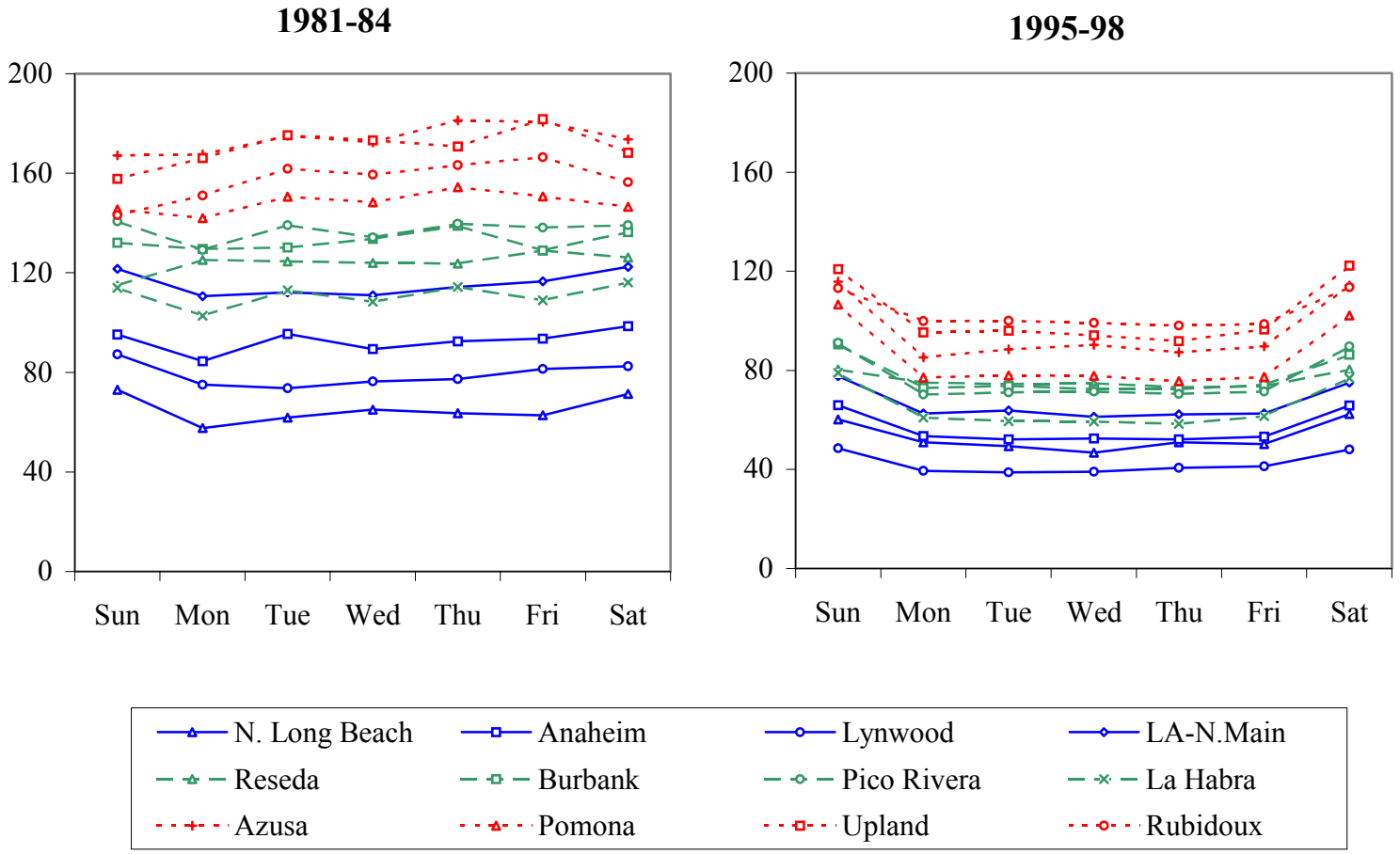


Figure 1.4-3. Mean maximum 1-hour mixing ratios of ozone during summers (June 1 to September 30) of 1981-1984 and 1995 to 1998 in the South Coast Air Basin. Sites in the western, northern and central, and central to eastern basin are denoted by solid, dash, and dotted lines, respectively.

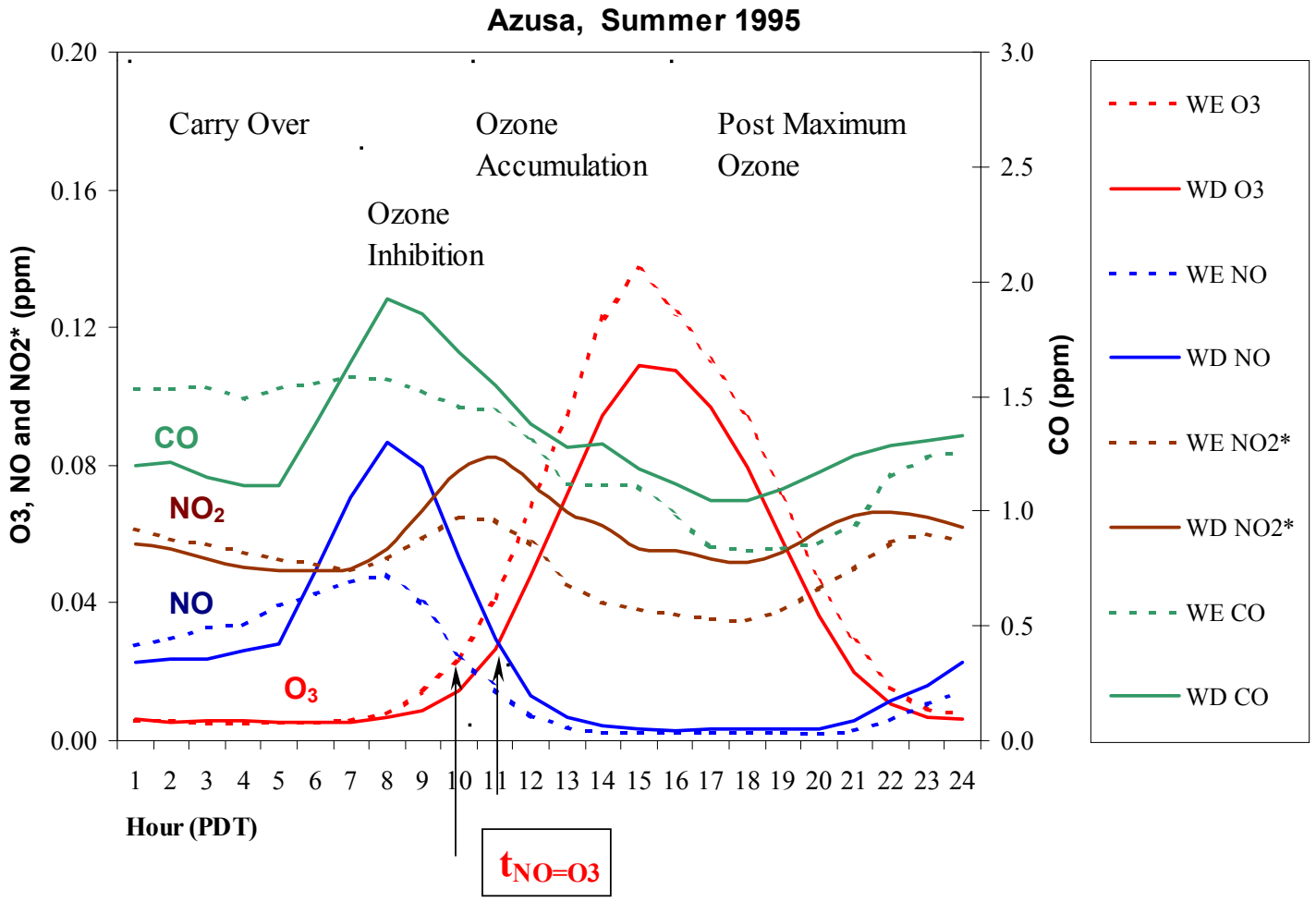


Figure 1.4-4. Average summer 1995 diurnal variations of ozone, nitric oxide, nitrogen dioxide, carbon monoxide at Azusa during the weekday and weekend. The shorter ozone inhibition period and higher rate of ozone formation are the main factors that result in higher ozone on weekends.

* In addition to NO_2, analyzers that are commonly used at air monitoring stations also convert other reactive nitrogen oxide species such as PAN to NO, thereby causing interference. NO_2 reported by these instruments must be considered upper limits.

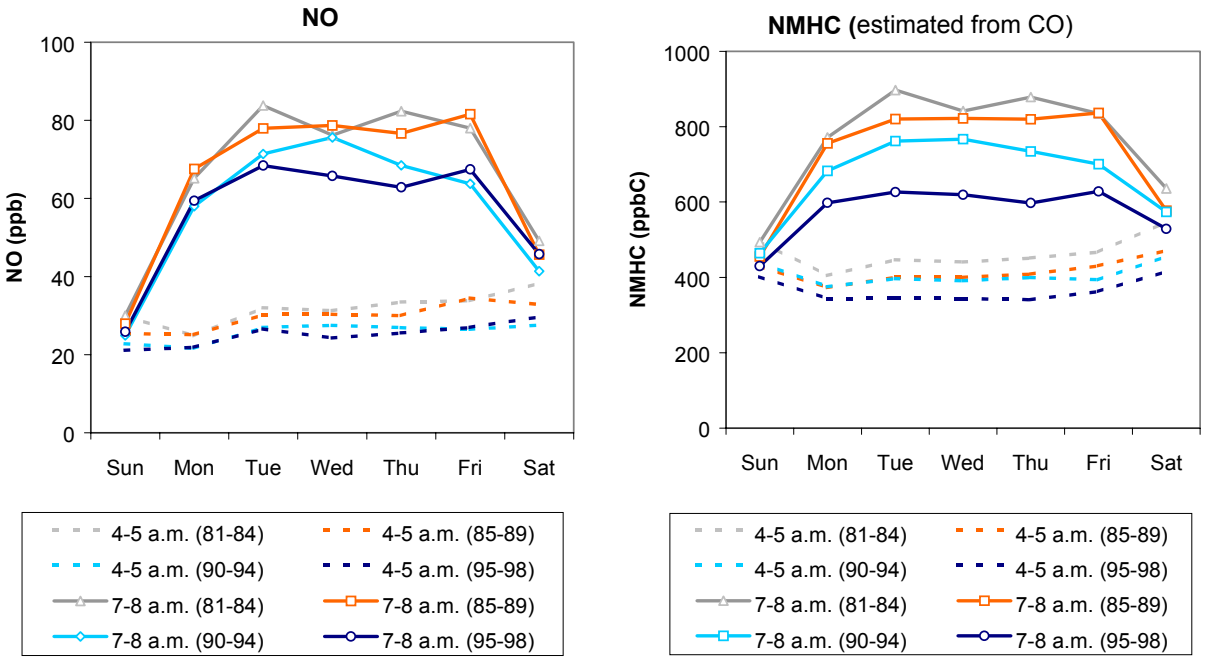


Figure 1.4-5. Twelve-site average NO and NMHC (estimated from CO) at 4-5 a.m. and 7-8 a.m. (PDT) by day of the week in the SoCAB during 1981 to 1998.

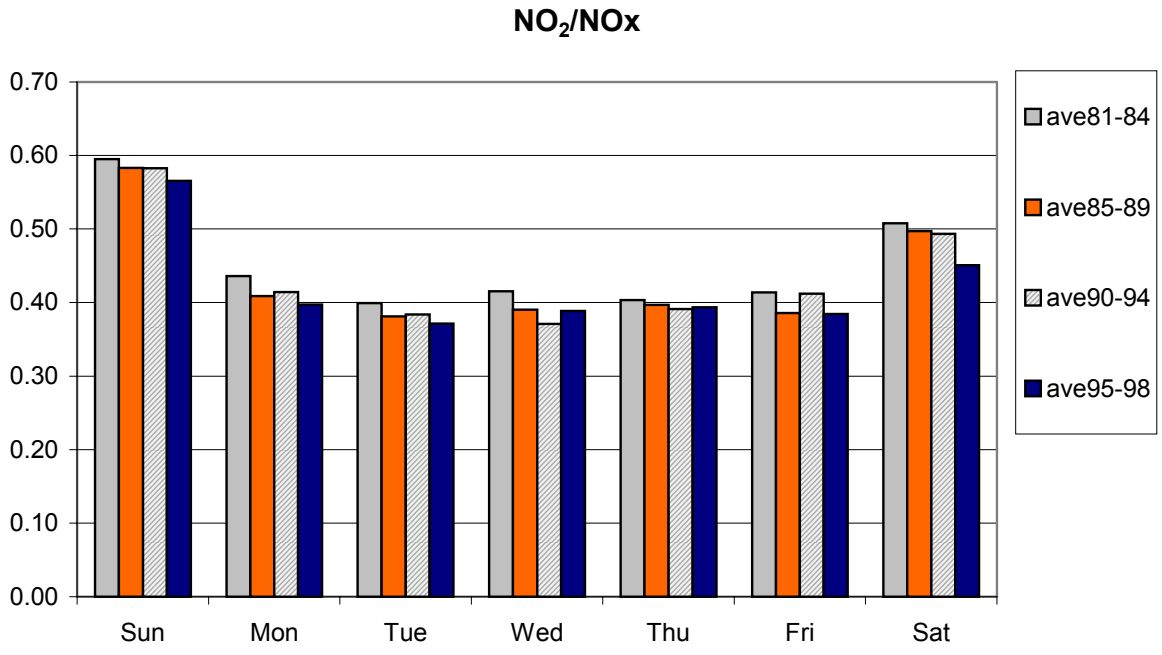


Figure 1.4-6. Twelve-site average NO_2/NOx ratios at 7-8 a.m. (PDT) by day of the week.

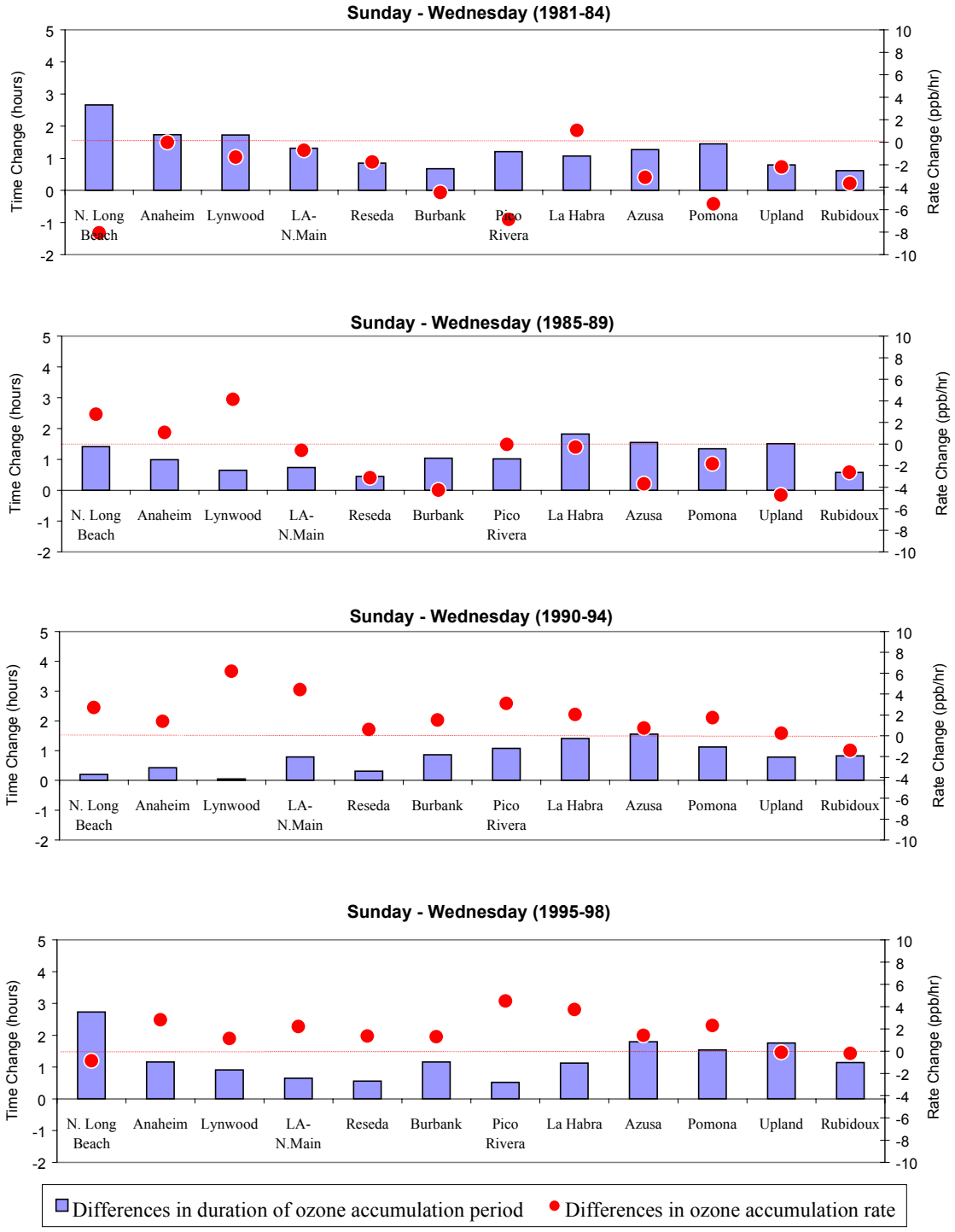


Figure 1.4-7. Sunday versus Wednesday differences in duration and rate of ozone accumulation for twelve sites in the SoCAB during 1981-84, 1985-89, 1990-94, and 1995-98. Sites are arranged in order of location from west to east with the western sites toward the left side of the plot.

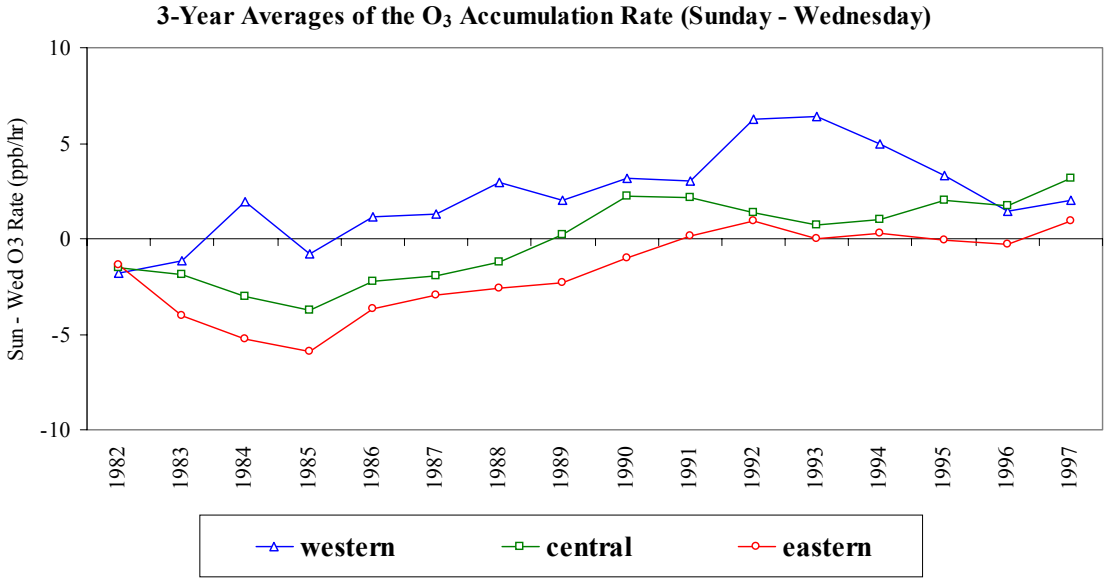


Figure 1.4-8. Sunday minus Wednesday differences in the duration and rates of ozone accumulation for the years 1981-84, 1985-1989, 1990-1994, and 1995-1998.

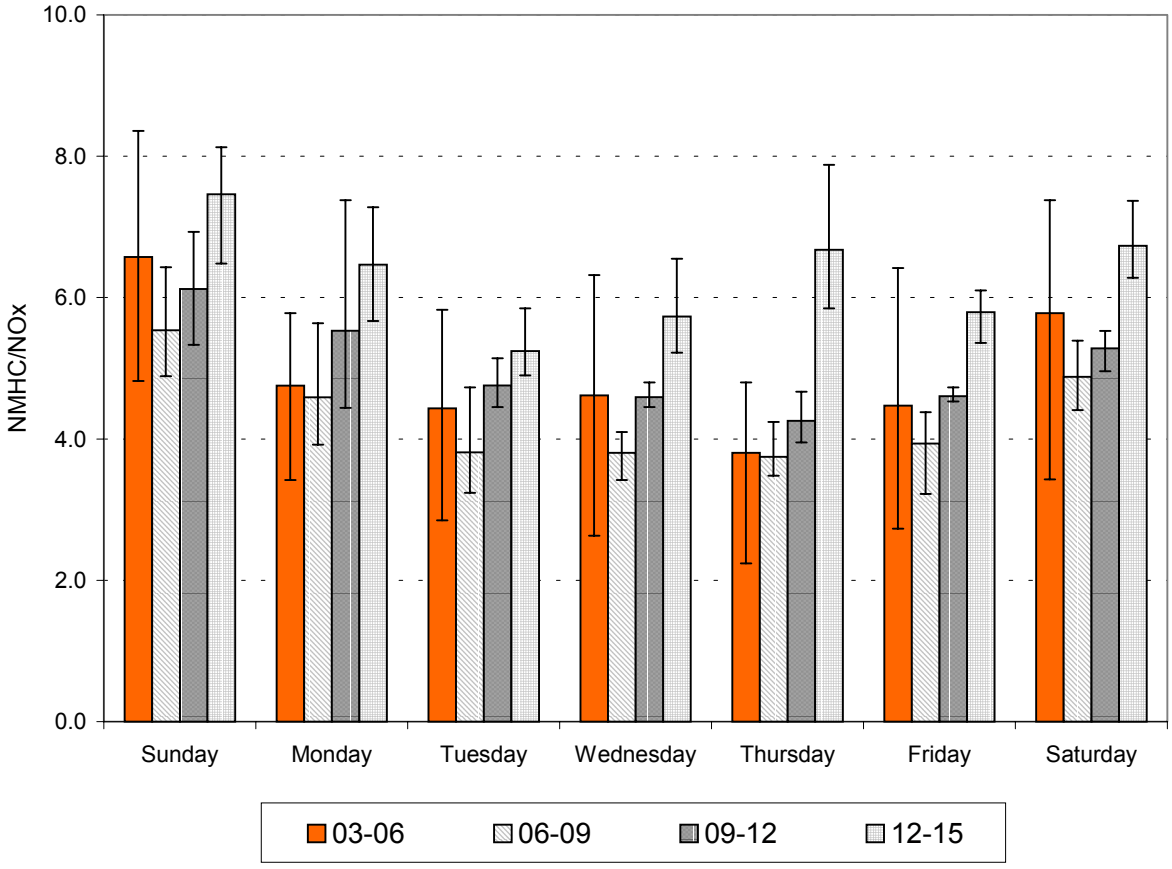


Figure 1.4-9. Day-of-the-week variations in the mean NMHC/NOx ratios during carryover (0300-0600, PDT), ozone inhibition (0600-0900), ozone accumulation ((0900-1200), and ozone peak (1200-1500) at Los Angeles – North Main*, Azusa, Pico Rivera, and Upland during the summers (July-September) of 1999 and 2000. Error bars denote maximum and minimum ratios among the four sites. *Data for Los Angeles were available only for the inhibition period.

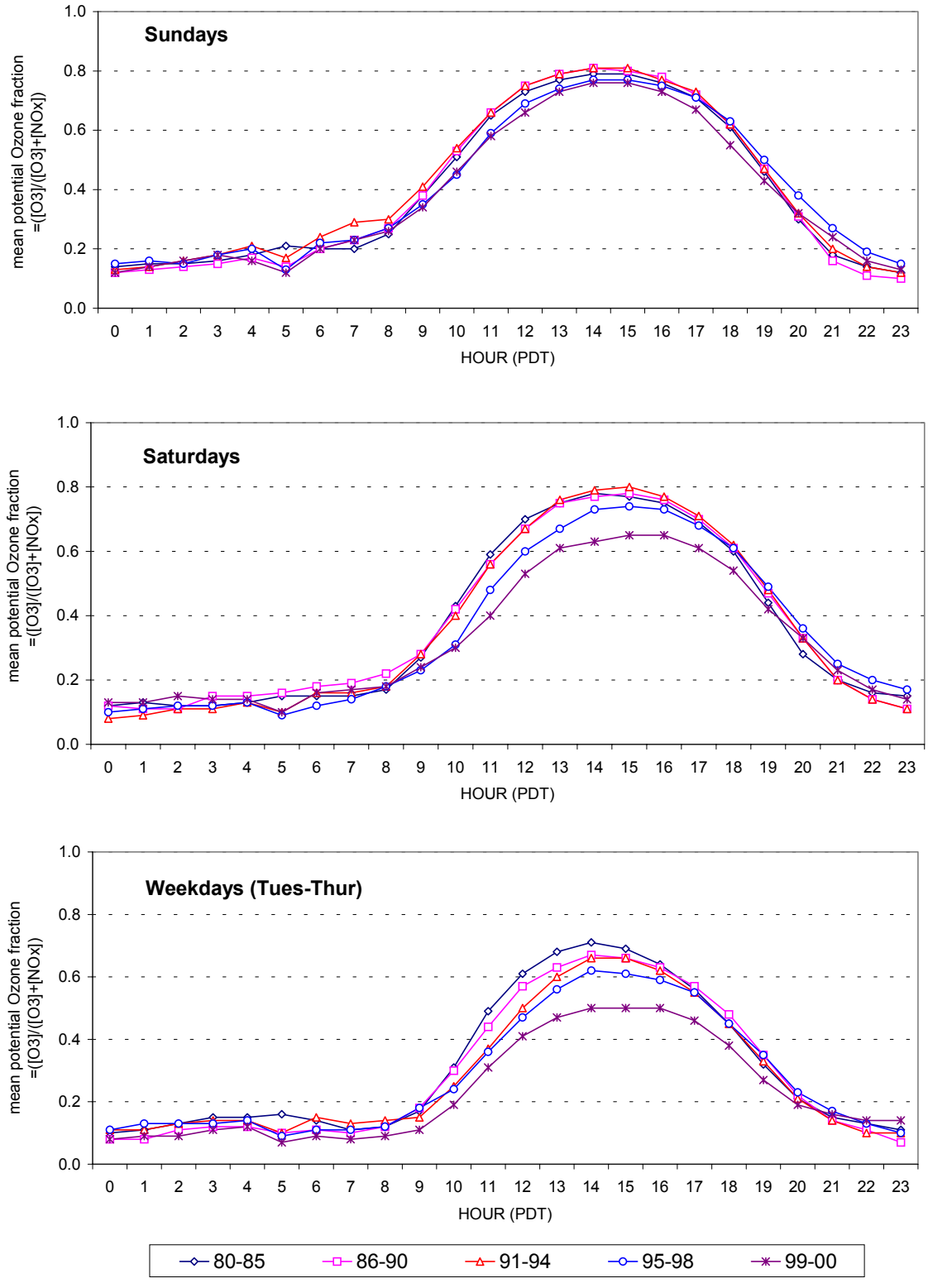


Figure 1.4-10. Diurnal variations in the ratios of ozone to potential ozone (O_3 + NOx) on Sundays, Saturdays, and Weekdays at Azusa for the years 1980-85, 1986-1990, 1991-1994, 1995-1998, and 1999-2000.

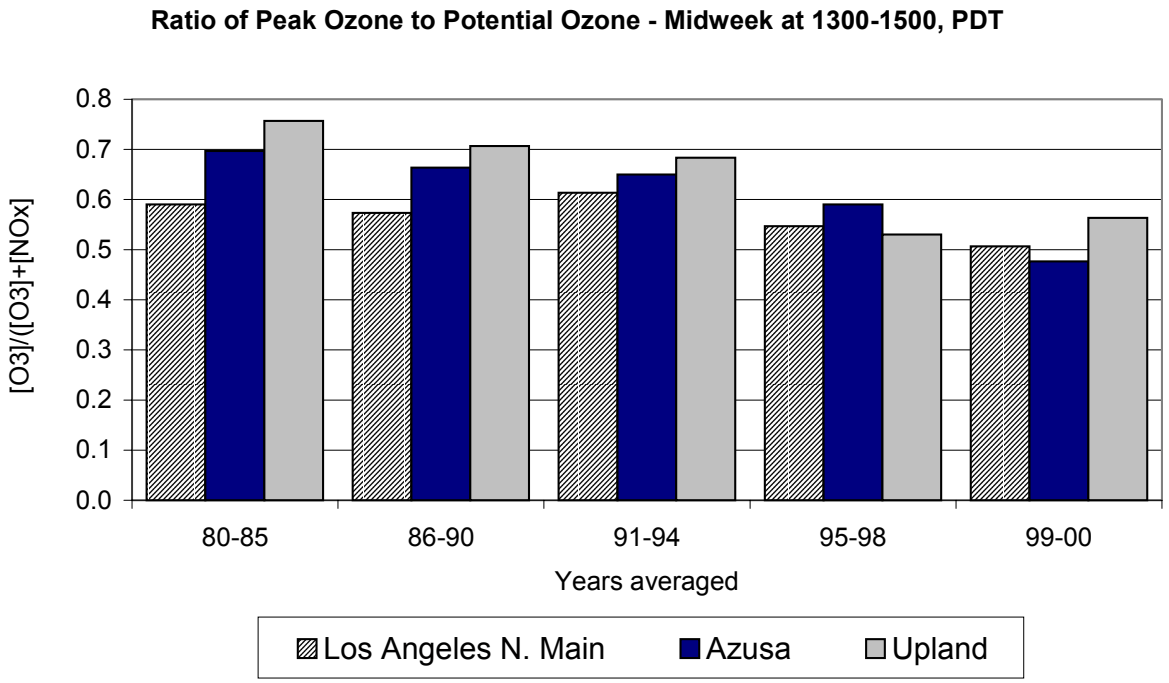


Figure 1.4-11. Mean ratio of peak ozone to potential ozone (O_3 + NOx) on weekdays at three sites for the years 1980-85, 1986-1990, 1991-1994, 1995-1998, and 1999-2000.

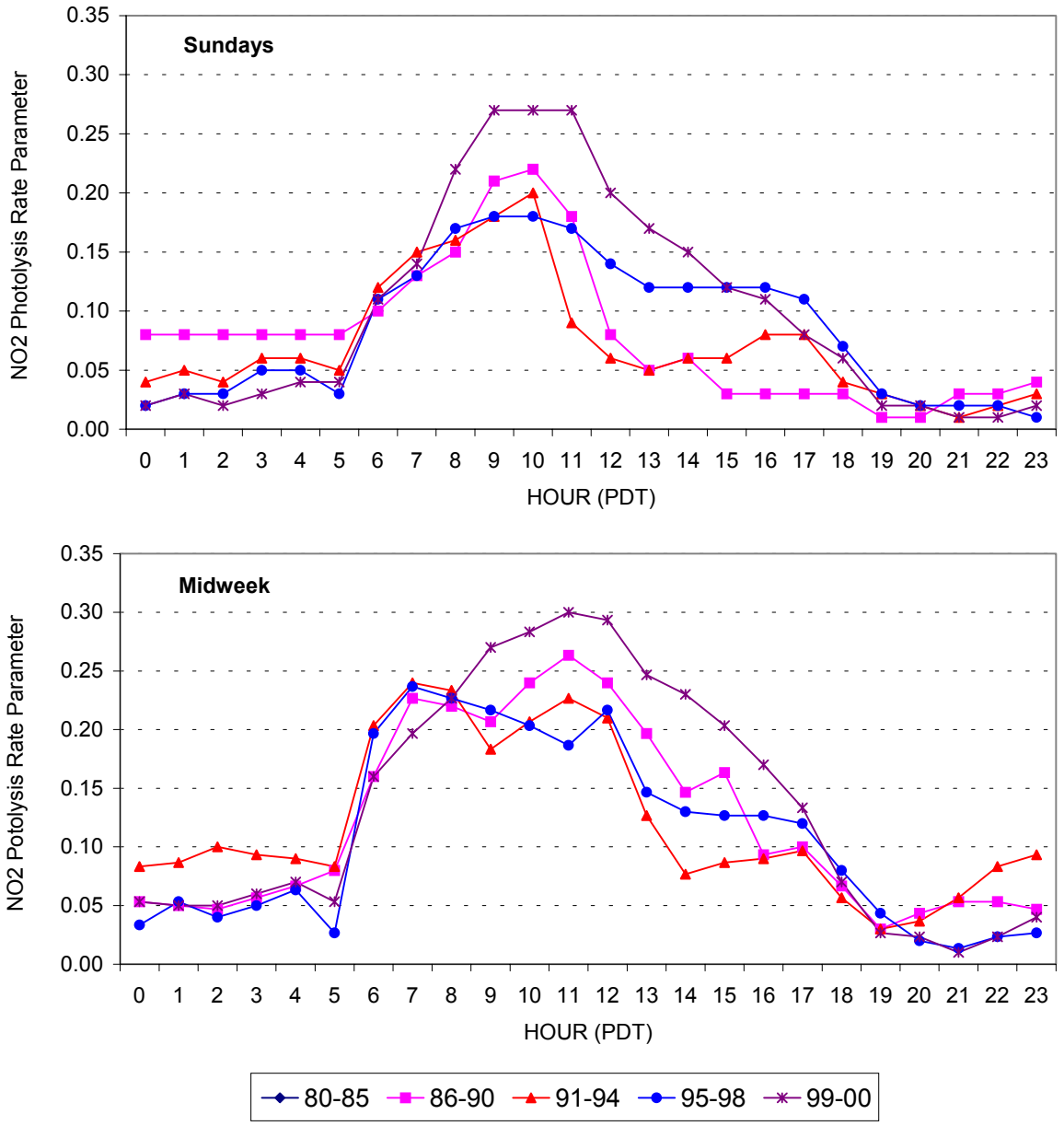


Figure 1.4-12. Estimated mean photolysis rate parameter for NO_2 (J_{NO2}) at Azusa on Sunday, and Midweek (Tuesday to Thursday) for the periods 1980-85, 1986-90, 1991-94, 1995-98, and 1999-2000. J_{NO2} was calculated from an extended version of the O_3-NO-NO_2 photostationary state expression.

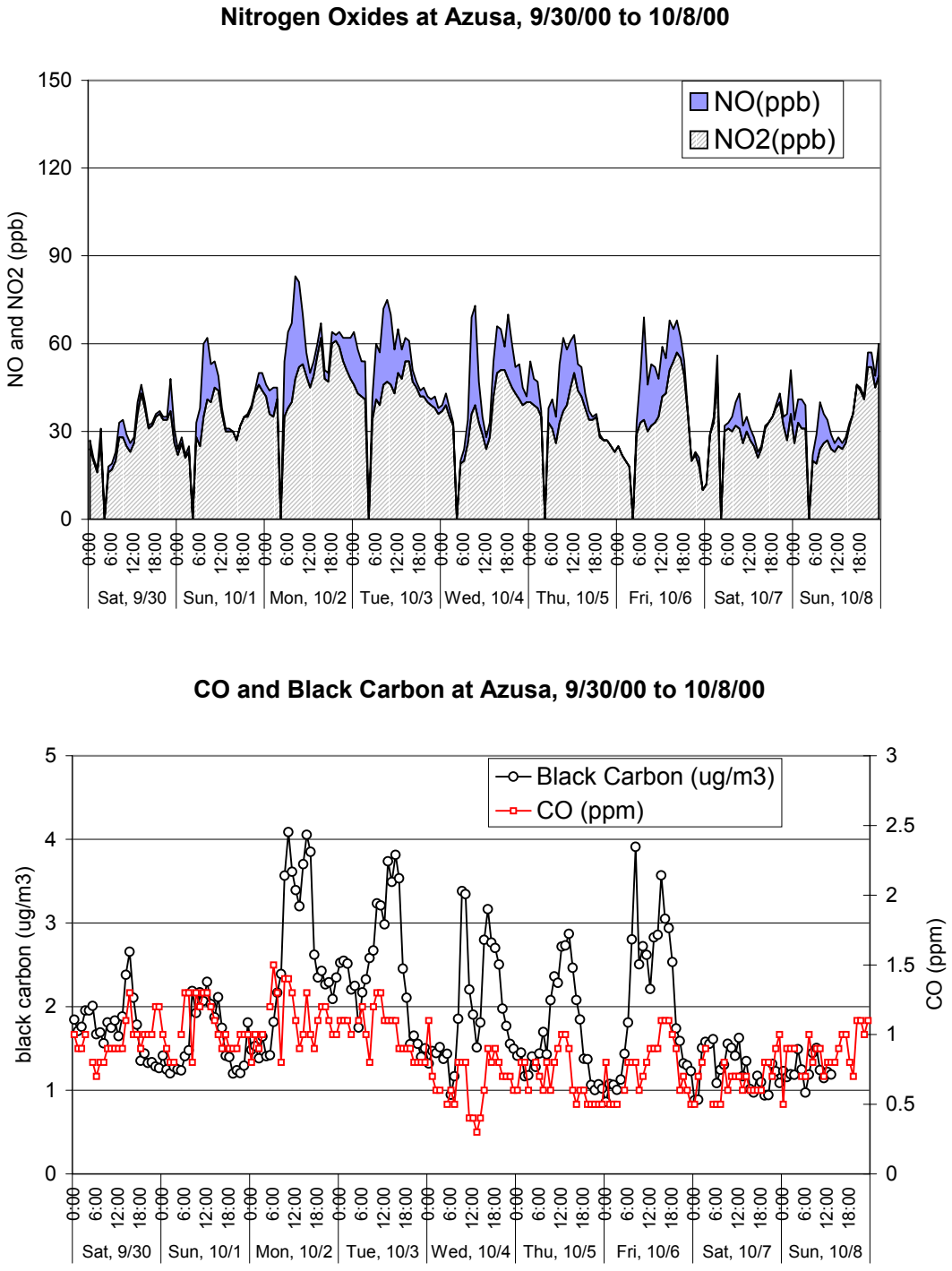
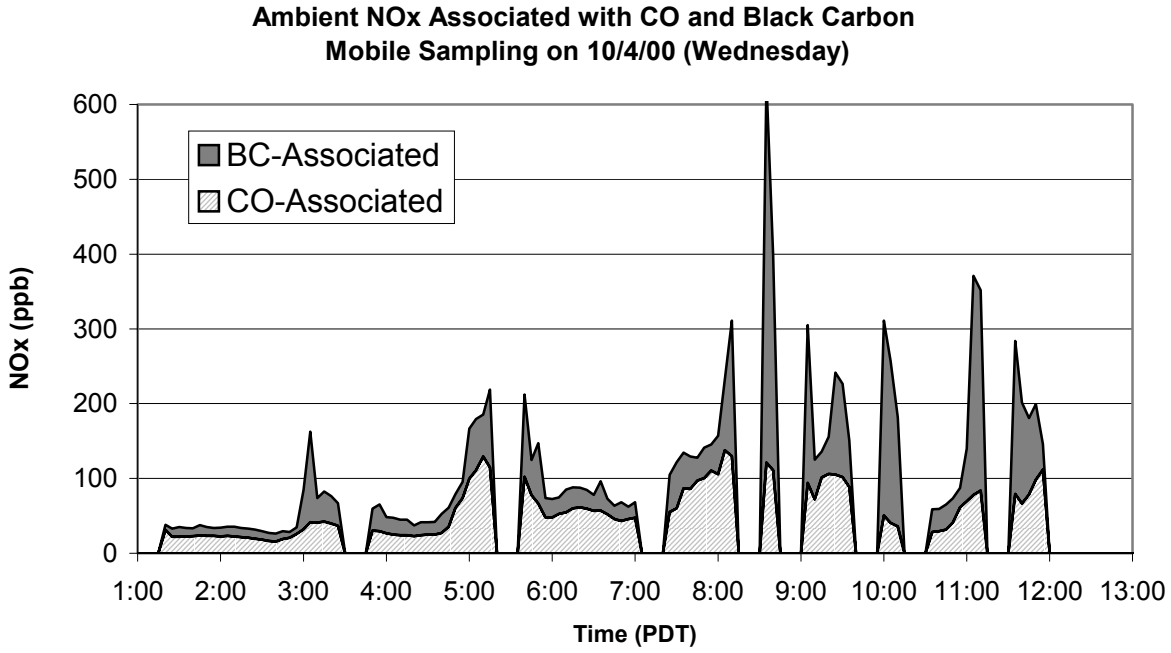


Figure 1.4-13. Hourly average nitrogen oxides, CO, and black carbon at Azusa, September 30-October 8, 2000.



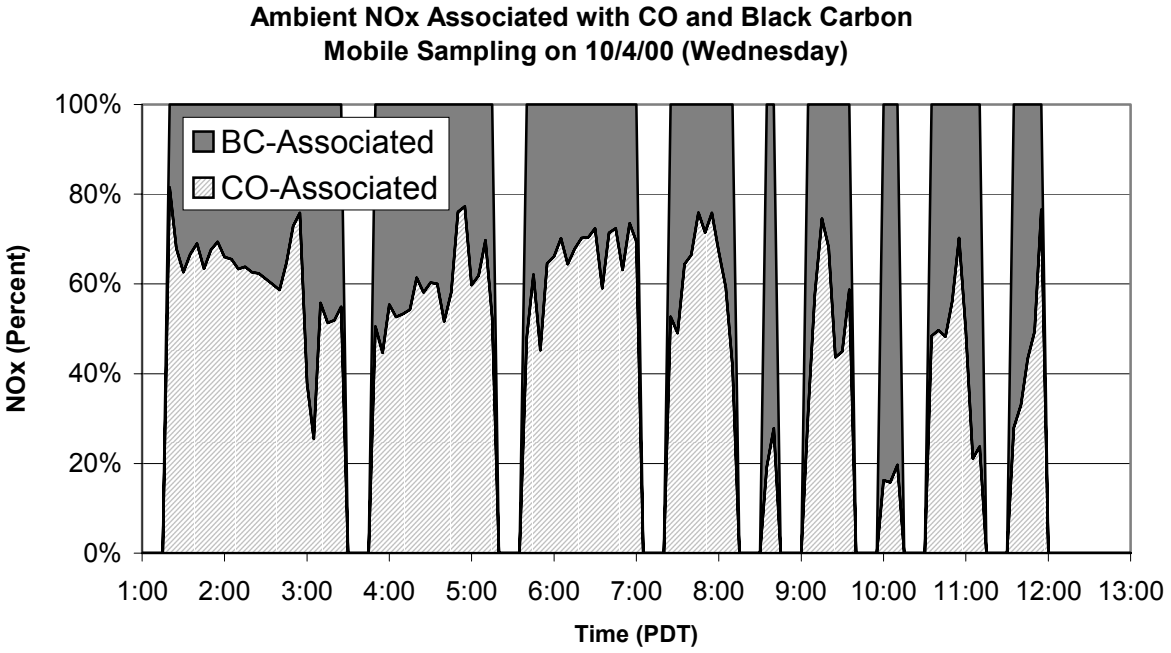
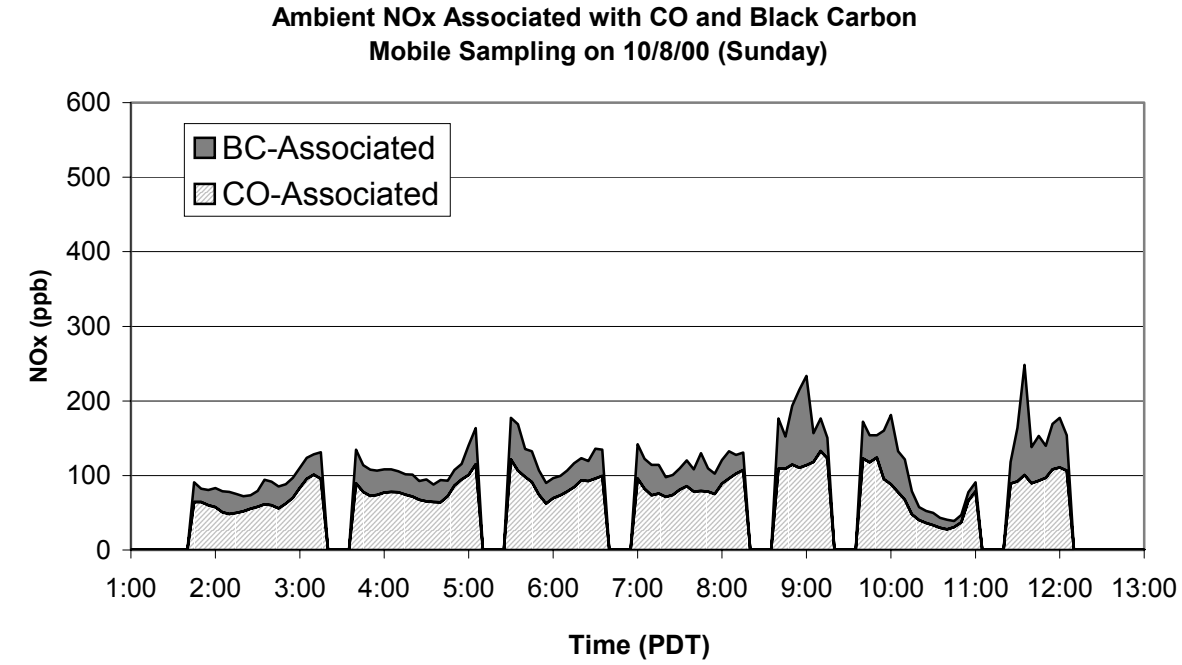


Figure 1.4-14a. Estimated ambient NOx associated with CO and black carbon for mobile lab samples on Wednesday, October 4.



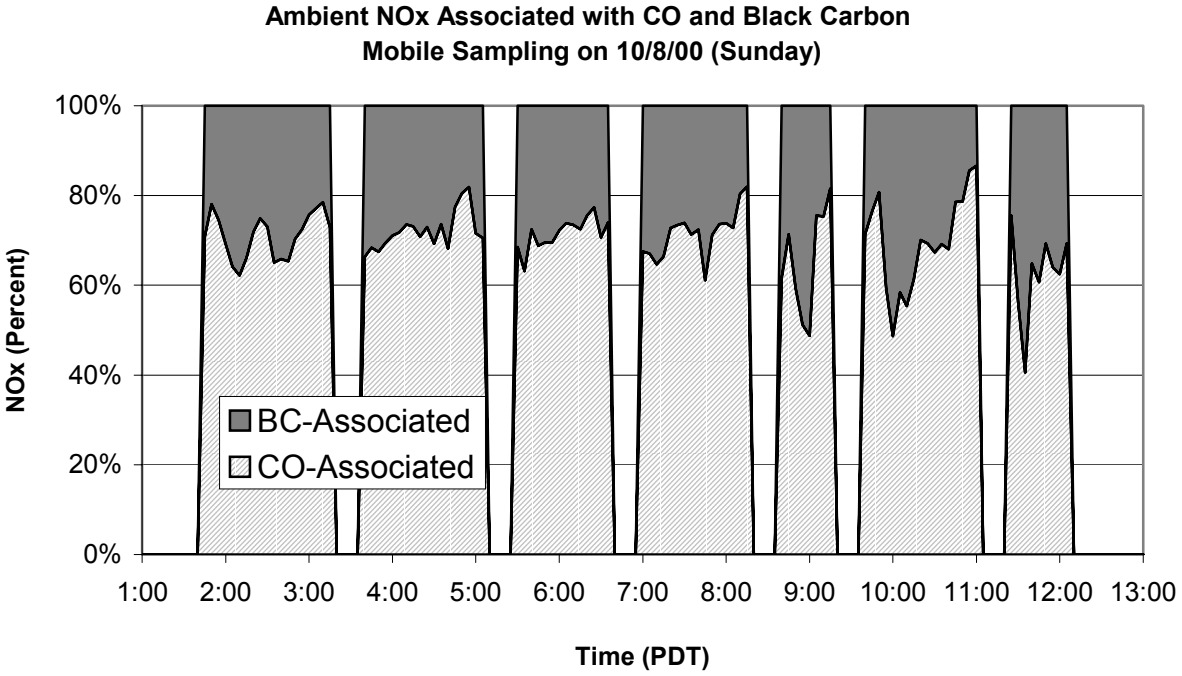


Figure 1.4-14b. Estimated ambient NOx associated with CO and black carbon for mobile lab samples on Sunday, October 8.

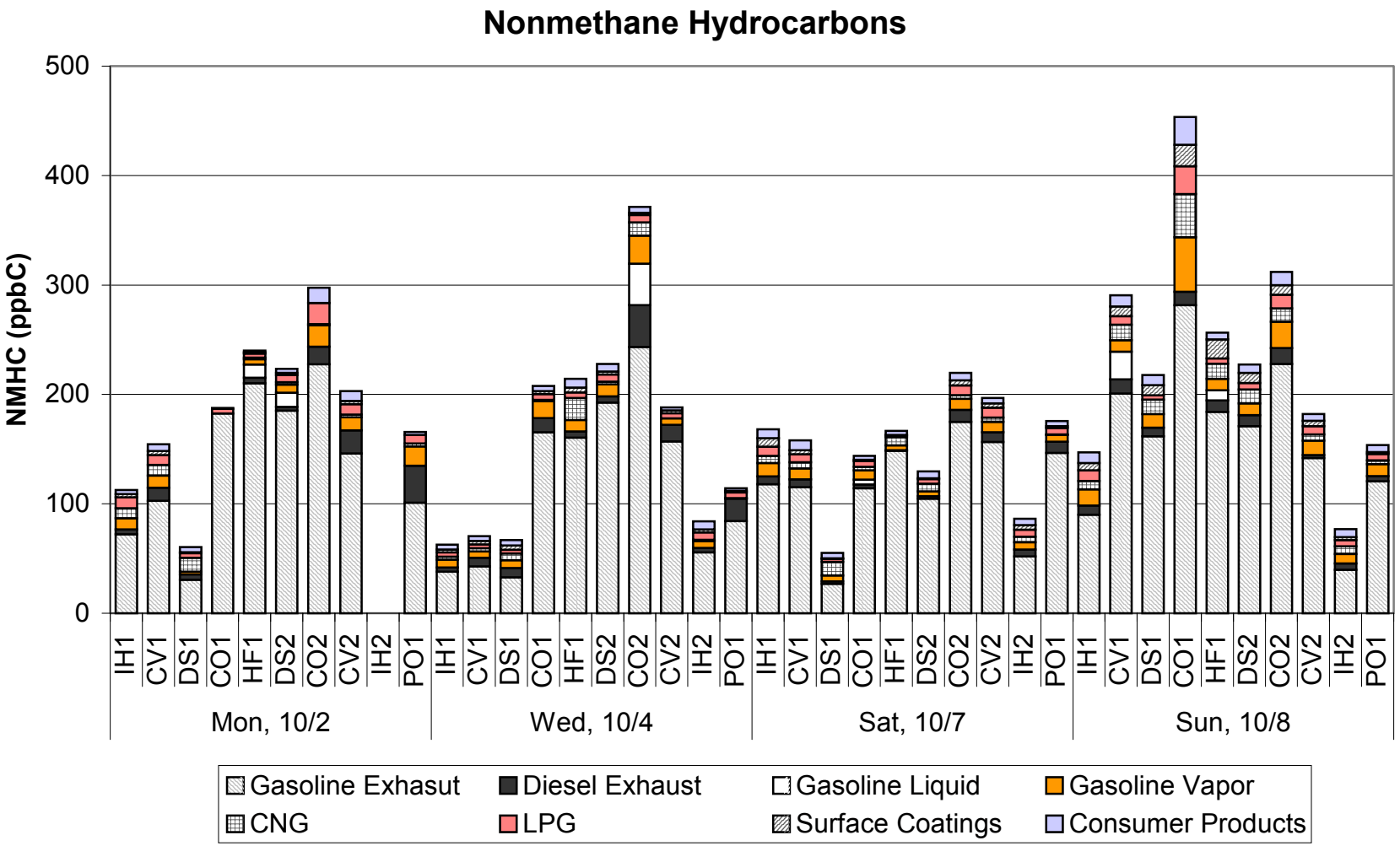


Figure 1.4-15. Source apportionment of non-methane hydrocarbons for mobile sampling loops and regional background sites – absolute contributions.

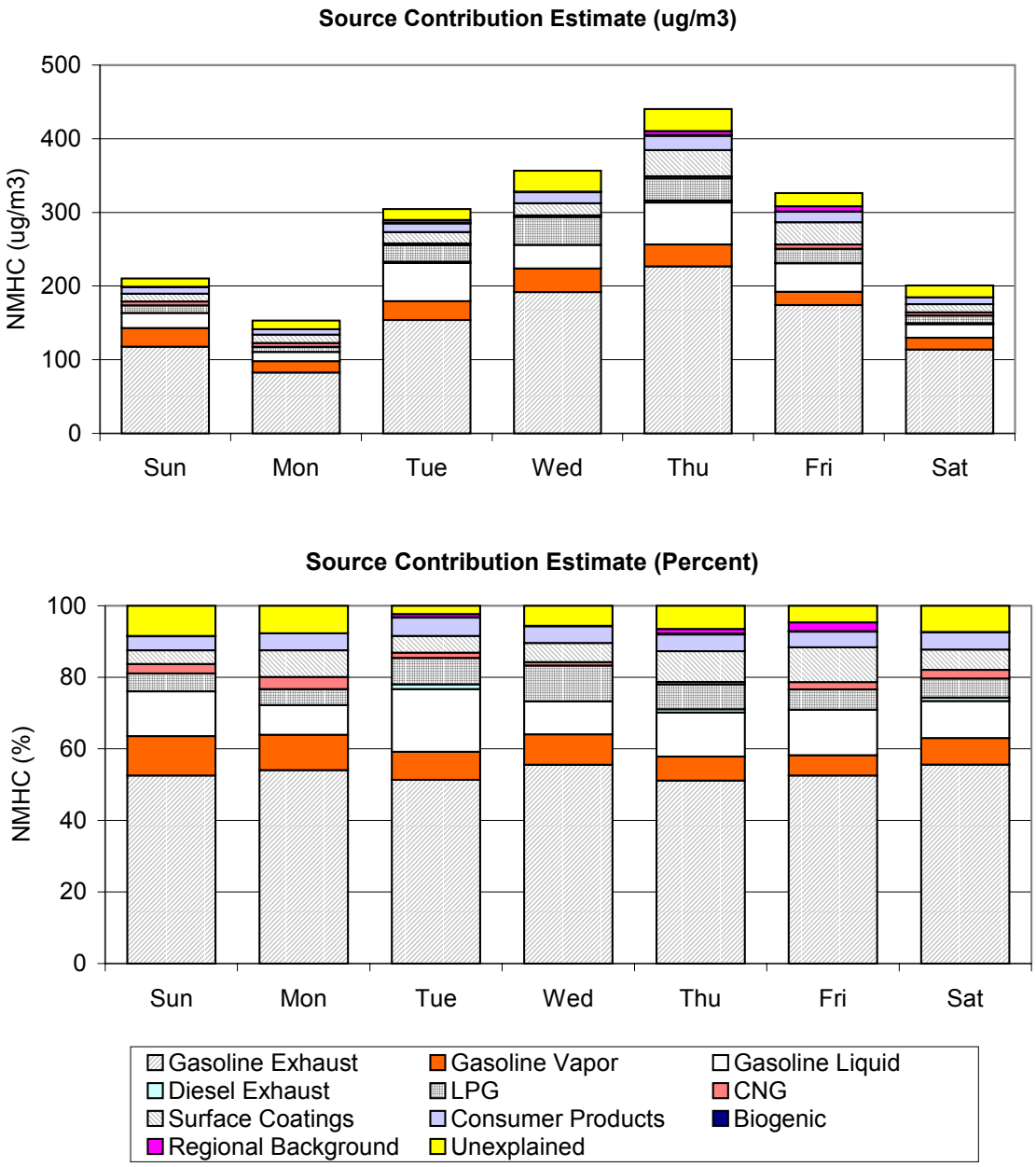


Figure 1.4-16. Mean estimated source contributions of total nonmethane hydrocarbons during 6-9 a.m. (PDT) by day of the week at Azusa for summer 1999 and 2000.

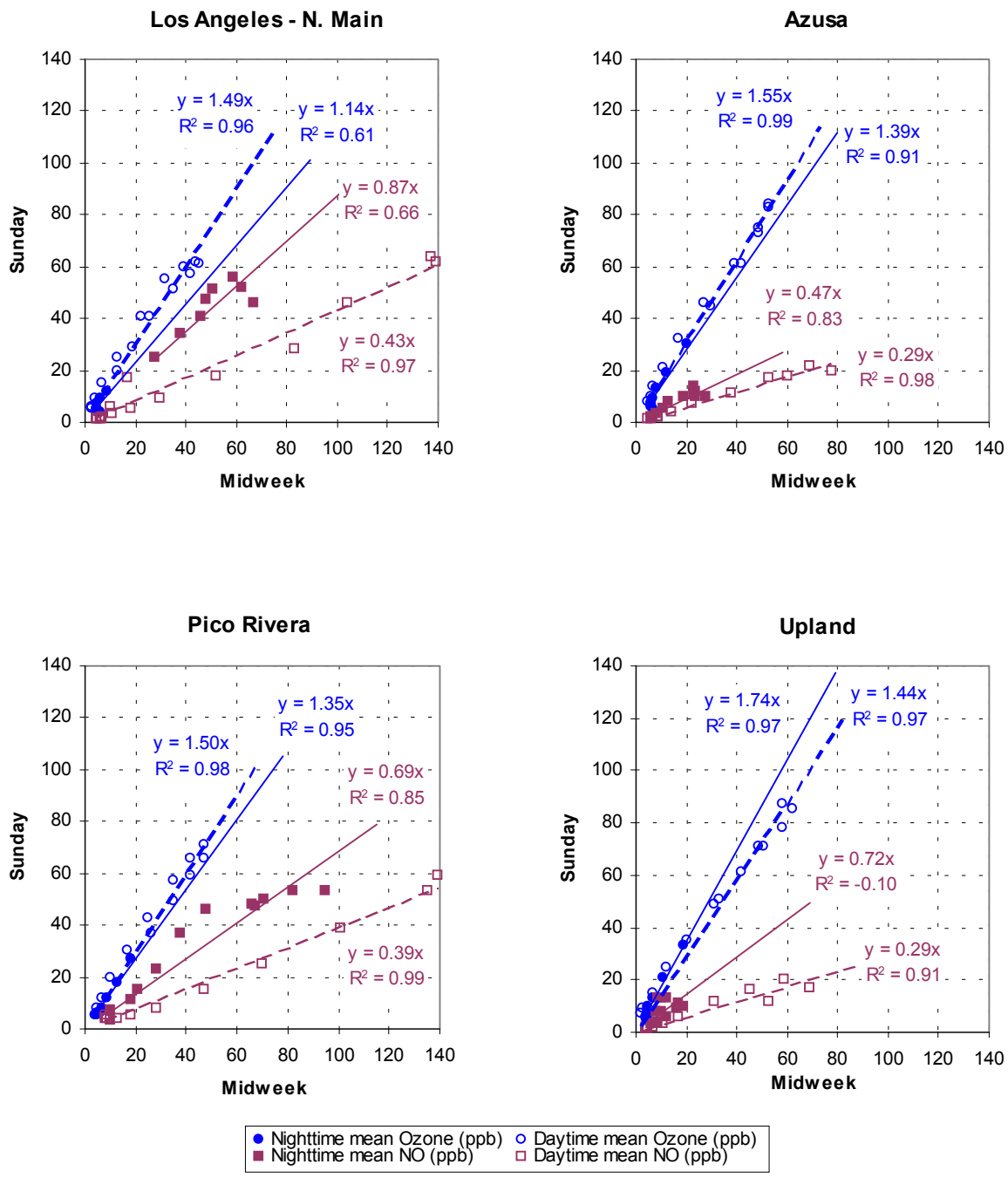


Figure 1.4-17. Correlation plots of mean hourly ozone and NO mixing ratios during midweek (Tues-Thur) versus Sunday. Separate linear regressions are shown for nighttime (9:00 p.m. – 5:00 a.m.) and daytime (6:00 a.m. – 9:00 p.m.) hours.

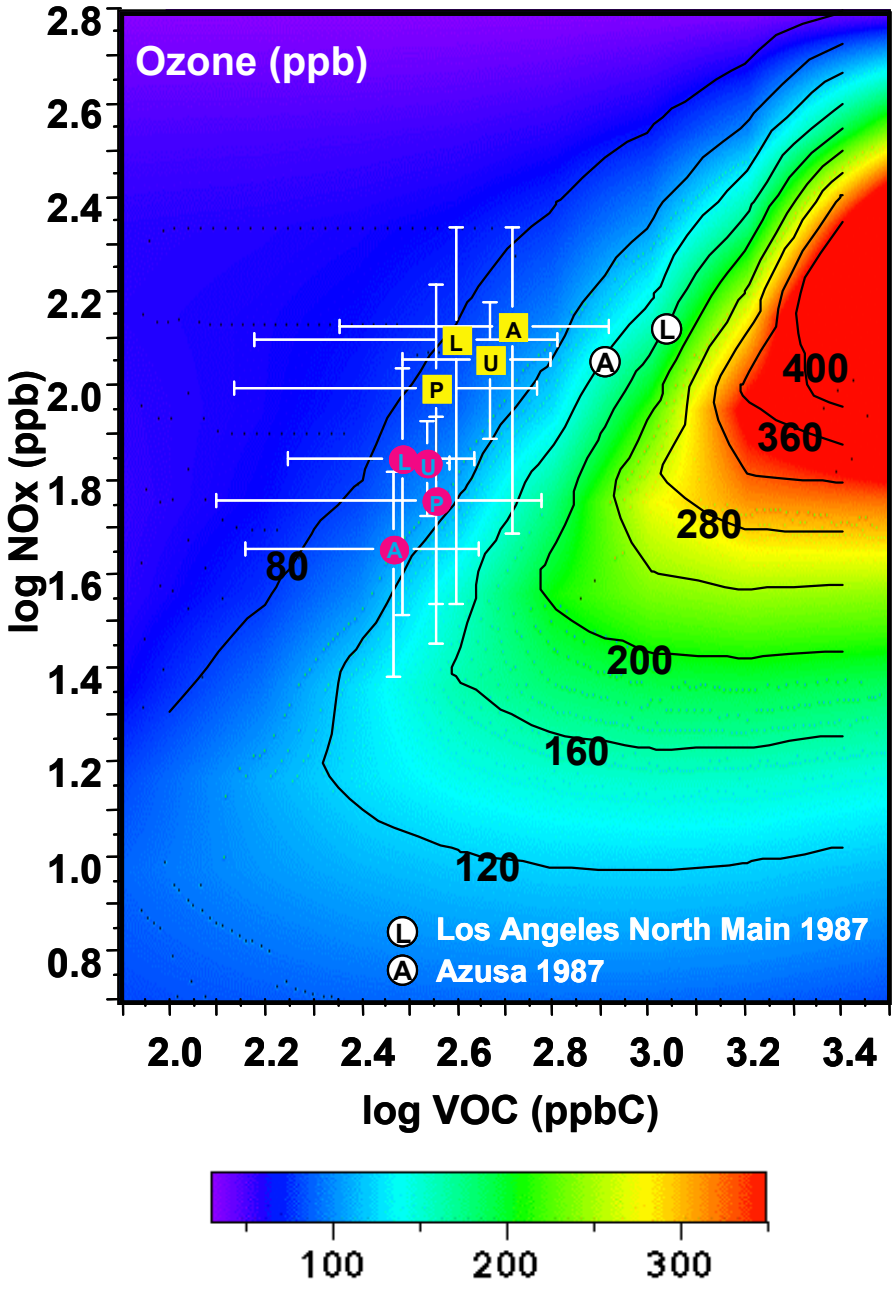


Figure 1.4-18. Ozone EKMA plot. Mixing ratios for NOx and NMHC during the summer of 1999 and 2000 with error bars representing one standard deviation from the average with the labels (A) representing Azusa, (L) representing Los Angeles-North Main, (P) representing Pico and (U) representing Upland. The yellow squares represent Wednesday and the dark red dots represent Sunday. The error bars are not symmetrical because of the logarithmic scale. The two white dots labeled (L) and (A) represent the average conditions for Los Angeles-North Main and Azusa during 1987, respectively. The simulation conditions are given in Chapter 3 of this report.

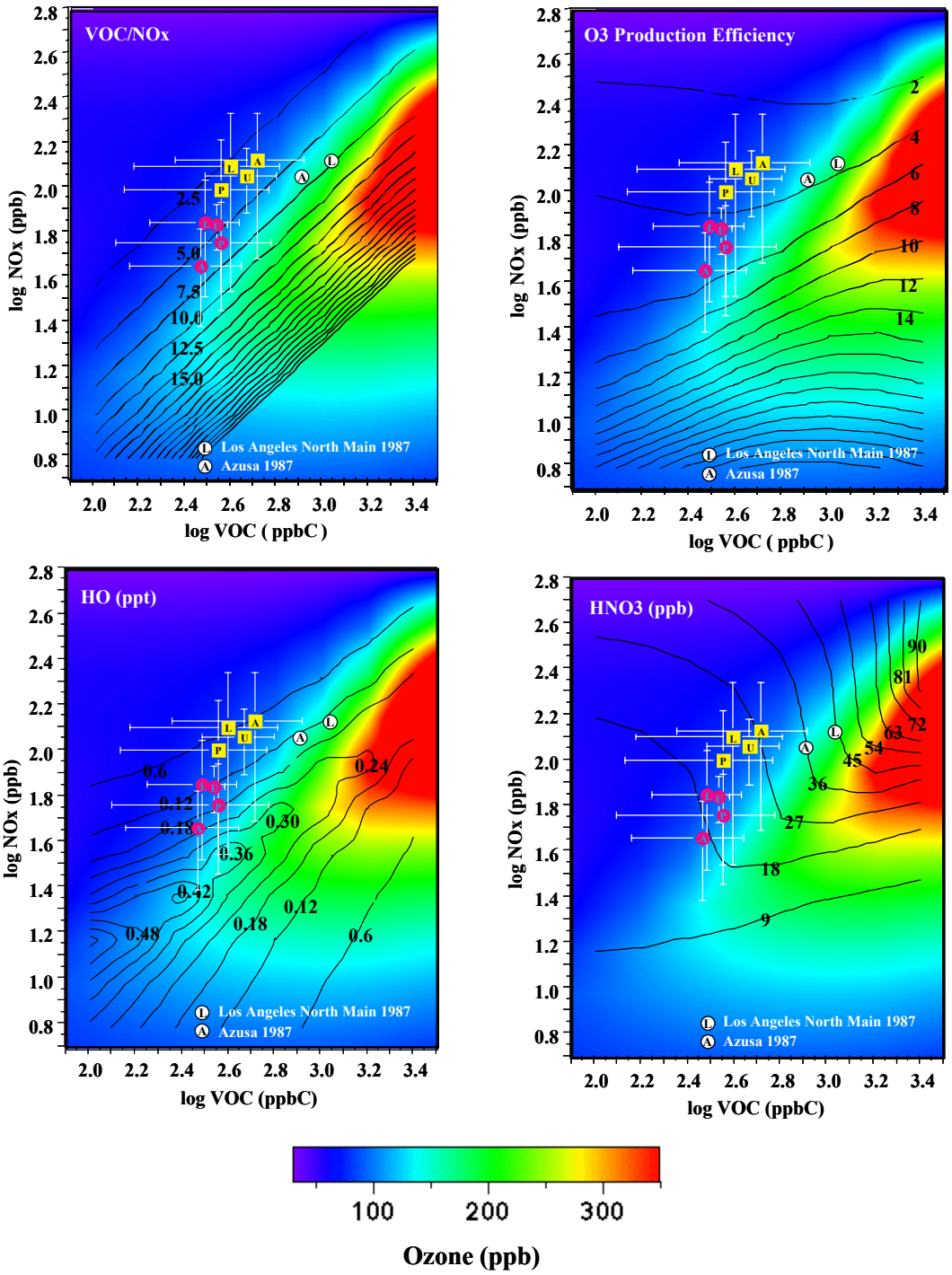


Figure 1.4-19 Plots of VOC/NO_x ratio, ozone production efficiency ($\Delta[O_3]/(\Delta[HNO_3] + \Delta[\text{Organic Nitrates}])$, hydroxyl radical, and nitric acid superimposed on a color O_3 EKMA plot.. Also plotted are mixing ratios for NO_x and NMHC during the summer of 1999 and 2000 with error bars representing one standard deviation from the average with the labels (A) representing Azusa, (L) representing Los Angeles–North Main, (P) representing Pico Rivera and (U) representing Upland. The yellow squares represent Wednesday and the dark red dots represent Sunday. The error bars are not symmetrical because of the logarithmic scale. The two white dots labeled (L) and (A) represent the average conditions for Los Angeles–North Main and Azusa during 1987, respectively.

2. EVOLUTION OF THE OZONE EFFECT IN THE SOUTH COAST AIR BASIN FROM 1981 TO 1998

This section examines historic trends in the average daily maximum hour ozone in the SoCAB from 1981 to 1998 and the evolution of the magnitude and spatial extent of the weekend ozone effect over this period. These trends are associated with day-of-the-week variations in the diurnal behavior of ozone, nitric oxide (NO), nitrogen dioxide (NO_2), carbon monoxide (CO), and nonmethane hydrocarbons (NMHC). The retrospective data analysis compares the day-of-the-week variations in the diurnal behavior of ozone and precursor concentrations in the four phases of the diurnal cycle: overnight carryover, ozone inhibition, ozone accumulation, and post-ozone maximum. The analysis focuses on day-of-the-week differences in the extent of inhibition of ozone formation during the morning due to titration with NO and the rate of ozone accumulation from the end of the inhibition period to time of peak ozone. Changes in the rate of ozone accumulation are correlated to historic trends in CO/NOx ratios, which serve as partial surrogates for trends in VOC/NOx ratios.

First, we examined the average diurnal variations in ozone and ozone precursors at Azusa for the summers of 1995 to 1997 to determine the parameters that would best serve as surrogates for the extent of ozone inhibition and rate of ozone accumulation. Figure 2-1 shows the average diurnal variations of O_3, NO, NO_2, and CO at Azusa for summer 1995. During the carry–over phase, there is little difference in concentration of NO_2 and O_3 between weekend and weekday. NO is slightly higher on weekends and CO is about 25% higher on weekends. Although carryover of ozone precursors is higher on weekends, the differences are relatively small compared to the higher weekday concentrations of ozone precursors during the morning commute periods. Fresh NO emissions during this period inhibit radical formation by titrating ozone with NO. During this inhibition period, formaldehyde (HCHO) and, to a lesser extent, nitrous acid (HONO) are the main source of HO radicals. We selected the time in the morning when NO and O_3 crosses over (i.e., $t_{NO=O3}$) as a marker for the end of the inhibition period and beginning of O_3 production via conversion of NO to NO_2 by peroxy radical. Note in Figure 2-1 that the crossover occurs an hour earlier on weekends. Thus, ozone formation begins earlier on weekends and provides one reason why ozone might be higher on weekends.

Another reason for higher ozone on weekends is the higher rate of ozone accumulation on weekends during the ozone accumulation period. Duration of ozone accumulation was estimated by the difference between time of maximum ozone (t_{maxO3}) and $t_{NO=O3}$. The rate of ozone accumulation (ppb/hour) is the increase in ozone from $t_{NO=O3}$ to t_{maxO3} divided by the duration of ozone accumulation. Figure 2-2 shows higher VOC/NOx ratios during weekends, which result in a higher rate of ozone formation. Ozone is higher on weekends at Azusa because the duration of ozone accumulation is longer and the rate of ozone accumulation is higher. We examined these statistics for twelve monitoring sites throughout the basin for the period 1981 to 1999 to develop a conceptual explanation that accounts for the spatial and temporal variations in the strength of the weekend effect.

Air quality data for summers (June 1 to September 30) of 1981 to 1998 were obtained from the latest (February 2000) ARB ambient data CD. The database was validated and screened for invalid and suspicious data according to the procedures and criteria described by Fujita et al. (2000a). When forming composite averages by day-of-the-week, holidays were removed if

driving patterns may have been influenced by the holiday. Table 2-1 shows a list of the key daily parameters of interest. Values of pollutants from 0400-0500 PDT are surrogates for carry-over from the previous day. Values of pollutants from 0600-0900 PDT represent the morning commute. The end of the ozone inhibition period, defined to be the time at which [NO] = [O3], is found by computing the difference [NO] - [O3] from 0700-1400 PDT and finding the hour t at which this difference transitions from greater than to less than zero. The interpolation involves the intersection of the two line segments represented by the decreasing NO and the increasing O_3. Each variable was computed as defined in Table 2-1. Annual means are compiled by Fujita et al. (2000). The parameters are listed by site and day-of-the-week with standard errors and numbers of observations. Monitoring sites include: N. Long Beach, Anaheim, Lynwood, and Los Angeles–N. Main on the western SoCAB; Reseda, Burbank, Pico Rivera, and La Habra in the central SoCAB; and Azusa, Pomona, Upland, and Rubidoux in the eastern SoCAB. In the following discussion, the annual averages are averaged into four time periods covering years 1981-84, 1985-89, 1990-94, and 1995-98.

Non-methane hydrocarbons (NMHC) were estimated from CO using an empirical relationship between NMHC and CO in canister samples collected by Desert Research Institute at three sites in the SoCAB during the summers of 1995 and 1996 (Zielinska et al. 1999). DRI collected canister and DNPH cartridge samples twice daily (6-9 a.m. and 1-4 p.m. PDT) at downtown Los Angeles, Burbank and Azusa during six, seven-day periods during each summer (504 samples). The canister samples were analyzed for methane, CO, CO_2, and speciated C_2 to C_{12} hydrocarbons. Figure 2-3 shows scatterplots of CO versus NMHC for each of the three sampling sites and data combined from all three sites. The R-squares of the regression range from 0.84 to 0.93. These correlations suggest a common source for CO and NMHC. The zero intercepts for CO at 40 to 90 ppbC NMHC indicate that contributions other than mobile sources are relatively small near each of the three monitoring sites. We assume that estimates of NMHC from regression with CO for 1995 and 1996 are reasonably valid for determining day-of-the-week variations in NMHC concentrations and NMHC/NOx ratios for any year within the 18-year period of interest. However, they are probably not valid for establishing long-term trends in NMHC and NMHC/NOx ratios because the slope of the regression between CO and NMHC may have changed over time with changing emission control technology.

2.1 Trends in Ambient Ozone Concentrations

Ambient ozone trends are governed by changes in the temporal and spatial patterns of precursor emissions. These changes are driven by emission control measures in the state implementation plans. The nation's ozone strategy in the decades of the 70s and 80s favored VOC control over NOx control, based on the premise that VOC/NOx ratios in most ozone nonattainment areas were below 10 (i.e., VOC-limited). Despite two decades of increasingly stringent emission controls, progress toward attainment of the ozone standard during this period was slow, and the National Research Council (NRC) Committee on Tropospheric Ozone Formation and Measurement concluded that the 20-year effort to attain the ozone National Ambient Air Quality Standard (NAAQS) had largely failed (NRC, 1991). The NRC Committee suggested that past ozone control strategies might have been misdirected due to a significant underestimation of anthropogenic VOC emissions. Since the beginning of the decade of the 1990s, however, the number of annual exceedances of the federal 1-hour NAAQS for ozone in

the SoCAB has dropped sharply as shown in Figure 2.1-1. The trend plots of the average maximum 1-hour ozone in Figure 2.1-2 show that peak ozone levels decreased in the 1980s, although clearly at a slower pace than during the decade of the 1990s. The location of the peak ozone levels shifted from the central portion of the basin (e.g., Glendora) to the eastern end of the basin (e.g., Lake Gregory).

Studies have shown that the weekend effect has become more pronounced during the 1990s. At the same time, ozone has dropped sharply and the maximum ozone concentrations have shifted eastward in the SoCAB. These observations suggest that ozone formation may have been NOx-limited prior to the 1990s and that VOC reductions were largely ineffective until VOC/NOx ratios approached VOC-limited conditions in the second half of the 1980s. Since that time, a transition to VOC-limited ozone formation in all but the eastern edge of the basin is most likely responsible for the sharp reduction in ozone during the 1990s. Studies have also shown that anthropogenic NOx emissions in the SoCAB are generally lower on weekends, especially during the ozone inhibition period.

2.2 Trends in Spatial Extent and Magnitude of the Weekend Ozone Effect

The average maximum 1-hour ozone concentrations by day-of-the-week are shown for twelve sites in Figure 2.2-1. It is readily evident from the line plots that the weekend effect has changed significantly over the past 18 years. In the period 1981-84, ozone levels were higher on weekdays in most of the central and eastern portions of the basin. Most monitoring sites in the western basin showed slightly higher weekend ozone concentrations. The weekend effect remained relatively weak during 1985-89 with a pronounced dip in ozone concentrations on Mondays. Weekend ozone values were not statistically different from Tuesday-Friday values at most sites in the central and eastern basin. By 1990-94, ozone concentrations were higher on weekends throughout the basin, and the weekend effect continued to strengthen during 1995-98. The average Sunday/Wednesday ozone ratios for all twelve sites for the periods 1981-84, 1985-89, 1990-94, and 1995-98 are 1.00, 1.02, 1.18 and 1.26, respectively. The corresponding Saturday/Wednesday ozone ratios are 1.03, 1.04, 1.17, and 1.24, respectively.

Larger reductions in peak ozone concentrations have occurred on weekdays. The mean peak ozone concentrations in 1995-98 expressed as ratios of 1981-84 values range from 0.54 to 0.59 on Monday through Friday, 0.67 on Saturday, and 0.70 on Sunday. The differences among the twelve sites in average peak 1-hour ozone are significantly smaller now than in years past due to larger reductions in the central portion of the basin.

2.3 Carryover of Ozone Precursors

The average 4-5 a.m. (PDT) NO, NO_2, NO_2/NOx, and NMHC by day-of-the-week are displayed as line plots in Figures 2.3-1 to 2.3-4. The overnight carryover of NO is lower on Sunday and Monday mornings and higher at the end of the week on Friday and Saturday. NO carryover is 10-20 percent lower on Sunday and Monday relative to midweek and about 10-15 percent higher on Friday and Saturday mornings. Overnight carryover of NMHC is greatest on Saturday and Sunday mornings with ratios to Wednesday of 1.20 and 1.12, respectively, and least on Monday mornings. Higher carryover of NMHC on Sunday relative to Wednesday

coupled with lower relative carry-over of NO suggests that the carryover of NO and NMHC emissions is driven by different sources. With the exception of a Monday dip during 1981-84, NO_2 shows no significant day-of-the-week differences.

The magnitude of the carryover of NO and NO_2 has decreased about 20 percent over the past 18 years. The fraction of NOx that is NO_2 ranges from 60 to 90 percent with lowest fractions at Los Angeles–N. Main, Pico Rivera, Burbank and Pomona and highest fractions at N. Long Beach, Anaheim, and Upland. There are no significant day-of-the-week variations in the NO_2/NOx ratios.

2.4 Extent of Ozone Inhibition

The 7-8 a.m. NO, CO, and NMHC concentrations are all substantially lower on weekends. Figures 2.4-1 to 2.4-4 are line plots of the average 7-8 a.m. (PDT) NO, NO_2, CO, and NMHC by day-of-the-week, respectively. Average 7-8 a.m. NO concentrations on Saturday and Sunday are 55-70 percent and 33-39 percent of the average weekday concentrations, respectively. Average 7-8 a.m. CO and NMHC (estimated from CO) on Saturday and Sunday are 67-83 percent and 50-65 percent of the average weekday concentrations, respectively.

NO emissions during this period inhibit radical formation by titrating ozone. During this period formaldehyde (HCHO) and, to a lesser extent, nitrous acid (HONO) are the main source of HO radicals. We use the morning crossover of NO and O_3 ($t_{NO=O3}$) as an indicator of the end of the inhibition period and beginning of O_3 production via conversion of NO to NO_2 by peroxy radical. Note in Figure 2-1 that the crossover occurs an hour earlier on weekends. Thus, ozone formation begins earlier on weekends. Figure 2.4-5 shows the average times (PDT) in the morning when NO equals O_3 by day of the week and the corresponding line plots. On average, the ozone inhibition period ends about 0.5 to 0.7 hours earlier on Saturdays and about 1.1 to 1.3 hours earlier on Sundays. The early end of the inhibition period on the weekends is consistent with the higher weekend 7-8 a.m. NO_2/NOx ratios shown in Figure 2.4-6. In general, ozone inhibition ends earlier in downwind areas and later in areas of high NO emissions.

Figure 2.4-7 shows the average changes in NO and NMHC concentrations due to addition of fresh emissions during the morning commute period. The concentrations of NO at 7-8 a.m. (PDT) are about 3 to 4 times higher than before the morning commute period on weekdays. In contrast, NO is only slightly higher during 7-8 a.m. on Saturdays and is essentially constant between 4 to 8 a.m. on Sundays. While NO concentrations vary from site to site, the relative changes are similar at all sites. This general pattern has changed very little in 18 years, indicating that the degree of ozone inhibition by NO titration of ozone has remained fairly constant over this time period. Thus, the magnitude and spatial extent of the weekend effect would not have changed if ozone inhibition by NO emissions were the only cause of the weekend effect. Note that relative changes from weekday to weekend are larger for NO than NMHC resulting in higher NMHC/NOx ratios during the weekends, which increases the ozone formation rate.

2.5 Duration and Rate of Ozone Accumulation

The duration of ozone accumulation was determined by the difference between the time of maximum ozone concentration (t_{maxO3}) and $t_{NO=O3}$. The average times of maximum ozone and

the duration of ozone accumulation, respectively, by day of the week are shown in Figures 2.5-1 and 2.5-2. Timing of maximum ozone generally coincides with distance of pollutant transport. Interestingly the timing of maximum ozone has not changed in over two decades in downwind areas, but has shifted about 1 to 1.5 hours later in the western and central part of the basin. Timing of maximum ozone does not vary significantly by day of the week. Compared to Wednesdays, the duration of ozone accumulation is about 1.2 hours and 1.3 hours longer on Saturdays and Sundays, respectively, with no significant long-term changes. Duration of ozone accumulation is shortest in the western part of the basin and longest in the eastern basin.

Of all the parameters examined, the rate of ozone accumulation stands out as the most significant parameter with respect to the weekend effect and the long-term trend in ozone concentrations. Figure 2.5-3 shows the rate of ozone accumulation by day of the week for four periods between 1981 and 1998. The rate (ppb O_3/hour) was determined by difference between O_3 concentrations at maximum ozone and $t_{NO=O3}$ divided by the duration of ozone accumulation (i.e., $t_{maxO3} - t_{NO=O3}$). During 1981-84, the ozone accumulation rate was highest in the central basin and higher on weekdays than weekends at all sites. By 1995-98, the rate was highest in the eastern basin and higher on weekends than weekdays in most of the basin except the extreme western and eastern portions of the basin. On average, ozone accumulation rates were cut in half during the 18-year period with the largest reductions in the central basin.

To summarize, the key parameters (end of ozone inhibition, duration of ozone accumulation, and rate of ozone formation) are plotted by site for Sunday, Wednesday, and Sunday minus Wednesday in Figures 2.5-4, 2.5-5, 2.5-6, and 2.5-7 for the periods 1981-84, 1985-89, 1990-94, and 1995-98, respectively. Sites are arranged in order of location from west to east with the western sites on the left side of the plot. For all sites and years, the duration of ozone formation is consistently greater on Sunday than Wednesday by one to two hours. In contrast, the Sunday minus Wednesday differences in the ozone accumulation rates are mostly negative during the 1980s and consistently positive during the 1990s. The switch from lower to higher ozone accumulation rates on weekends relative to weekdays coincides with the sharp decline in the ozone trend and an increase in the magnitude and spatial extent of the weekend effect.

Figure 2.5-8 compares the trends in the ozone accumulation rates on Sunday and Wednesday for each of the twelve sites and Figure 2.5-9 shows the corresponding trends averaged by western, central, and eastern sites. The trends in the ozone accumulation rate for Wednesday mirror the trends in maximum 1-hour ozone trends shown in Figure 1.3-4. In the 1980s, differences in emission patterns from weekday to weekend resulted in little difference in the ozone accumulation rate at western sites and generally lower weekend rates at central and eastern sites. The lower weekend ozone accumulation rate counteracts the shorter ozone inhibition period on weekends at central and eastern locations resulting in either no change or slightly lower ozone concentrations on weekends (i.e., no weekend effect). In the 1990s, the ozone accumulation rates were generally higher on Sunday than Wednesday. Coupled with the shorter inhibition period, this resulted in consistently higher ozone concentrations on weekends during the 1990s.

2.6 Spatial, Temporal, and Statistical Distributions of Volatile Organic Compounds and NMHC/NOx Ratios

The previous section showed that the difference between weekend and weekday rates of ozone accumulation is a major factor contributing to the magnitude of the weekend effect. As discussed in previous sections, VOC/NOx ratios[1] affect both the rate and efficiency of ozone production. The average NMHC/NOx ratios at 6-9 a.m. (PDT) and time of maximum ozone by day-of-the-week are shown in Figures 2.6-1 and 2.6-2, respectively. The data show that relative differences between weekend and weekday VOC/NOx ratios have steadily increased over time. The ratios of the average 6-9 a.m. (PDT) VOC/NOx ratio on Saturday to that on Wednesday are 1.05, 1.06, 1.17, and 1.18 for the years 1981-84, 1985-89, 1990-94, and 1995-98, respectively. The corresponding Sunday/Wednesday ratios are 1.10, 1.17, 1.27 and 1.42. Similar differences are observed for the VOC/NOx ratios during the time of maximum ozone. The average weekday 6-9 a.m. (PDT) VOC/NOx ratios during the 1990s are about 7 compared to 8-9 on Saturdays and 9-10 on Sundays, and the ratios at maximum ozone are 10-11 on weekdays, 12-13 on Saturdays and 13-14 on Sundays. The morning VOC/NOx ratios are above the ridgeline in the ozone isopleth plot (Figure 1.3-2) during weekdays, and therefore VOC limited, but move toward the ridgeline on weekends. While greater carryover of VOC on weekends contributes to greater weekend morning VOC/NOx ratios, most of the increase is due to lower NO emissions during weekend mornings.

2.7 Summary of Findings

The observed weekend effect in the South Coast Air Basin arises from differences in the diurnal patterns of VOC and NOx emissions. These emission differences result in day-of-the-week variation in the overnight carryover of ozone precursors, the degree of inhibition of ozone formation during the morning due to titration with NO, and varying rates of ozone accumulation due to changing VOC/NOx ratios. The following are findings relevant to the effect of these factors on the magnitude and spatial extent of the weekend effect in the South Coast Air Basin.

Carry-over of Ozone Precursors

- NO carryover is 10-20 percent lower on Sunday and Monday relative to Wednesday and about 10-15 percent higher on Friday and Saturday mornings.

- NMHC carryover is greatest on Saturday and Sunday mornings with ratios to Wednesday of 1.20 and 1.12, respectively, and least on Monday mornings.

- Higher carryover of NMHC on Sunday relative to Wednesday coupled with lower relative carry-over of NO suggests that the carry-over of NO and NMHC emissions is driven by different sources.

[1] As explained in Section 2.2, NMHC is estimated from CO using an empirical relationship between NMHC and CO for data collected in 1995 and 1996. While these estimates are reasonably valid for determining day-of-the-week variations in NMHC concentrations and NMHC/NOx ratios for any year within the 18-year period of interest, they are probably not valid for estimating long-term trends in NMHC and NMHC/NOx ratios because the slope of the regression between CO and NMHC may have changed over time with changing emission control technology.

- NO_2 concentrations and NO_2/NOx ratios at 4-5 a.m. (PDT) show no significant day-of-the-week differences.

- The magnitude of the carryover of NO and NO_2 has decreased about 20 percent over the past 18 years.

Ozone Inhibition Period

- Average 7-8 a.m. (PDT) NO concentrations on Saturday and Sunday are 55-70 percent and 33-39 percent of the average weekday concentrations, respectively. This general pattern has changed very little in 18 years indicating that the degree of ozone inhibition by NO titration of ozone has remained fairly constant over this time period.

- Average 7-8 a.m. (PDT) CO and NMHC (estimated from CO) on Saturday and Sunday are 67-83 percent and 50-65 percent of the average weekday concentrations, respectively. The relative changes from weekday to weekend are larger for NO than NMHC resulting in higher NMHC/NOx ratios during the weekends.

- On average, the ozone inhibition period ends about 0.5 to 0.7 hours earlier on Saturdays and about 1.1 to 1.3 hours earlier on Sundays. In general, ozone inhibition ends earlier in downwind areas and later in areas of highest density of fresh NO emissions.

Ozone Accumulation Period

- The timing of maximum ozone has not changed in over two decades in downwind areas, but has shifted about 1 to 1.5 hours later in the western and central parts of the basin. Timing of maximum ozone does not vary significantly by day of the week.

- Compared to Wednesdays, the duration of ozone accumulation is about 1.2 hours and 1.3 hours longer on Saturdays and Sundays, respectively, with no significant long-term changes. Duration of ozone accumulation is shortest in the western part of the basin and longest in the eastern basin.

- During 1981-84, the ozone accumulation rate was highest in the central basin and higher on weekdays than weekends at all sites. By 1995-98, the rate was highest in the eastern basin and higher on weekends than weekdays in most of the basin except the extreme western and eastern portions of the basin. On average, ozone accumulation rates were cut in half during the 18-year period with the largest reductions in the central basin.

- A switch from lower to higher ozone accumulation rates on weekends relative to weekdays coincides with the sharp declining ozone trend in the 1990s and an increase in the magnitude and spatial extent of the weekend effect.

Spatial, Temporal, and Statistical Distributions of Volatile Organic Compounds and NMHC/NOx Ratios

- The ratios of the average 6-9 a.m. (PDT) VOC/NOx ratio on Saturday to that on Wednesday are 1.05, 1.06, 1.17, and 1.18 for the years 1981-84, 1985-89, 1990-94, and 1995-98, respectively. The corresponding Sunday/Wednesday ratios are 1.10, 1.17, 1.27 and 1.42. Similar differences are observed for the VOC/NOx ratios during the time of maximum ozone.

- The average weekday 6-9 a.m. (PDT) VOC/NOx ratios during the 1990s are about 7 compared to 8-9 on Saturdays and 9-10 on Sundays, and the ratios at maximum ozone are 10-11 on weekdays, 12-13 on Saturdays and 13-14 on Sundays.

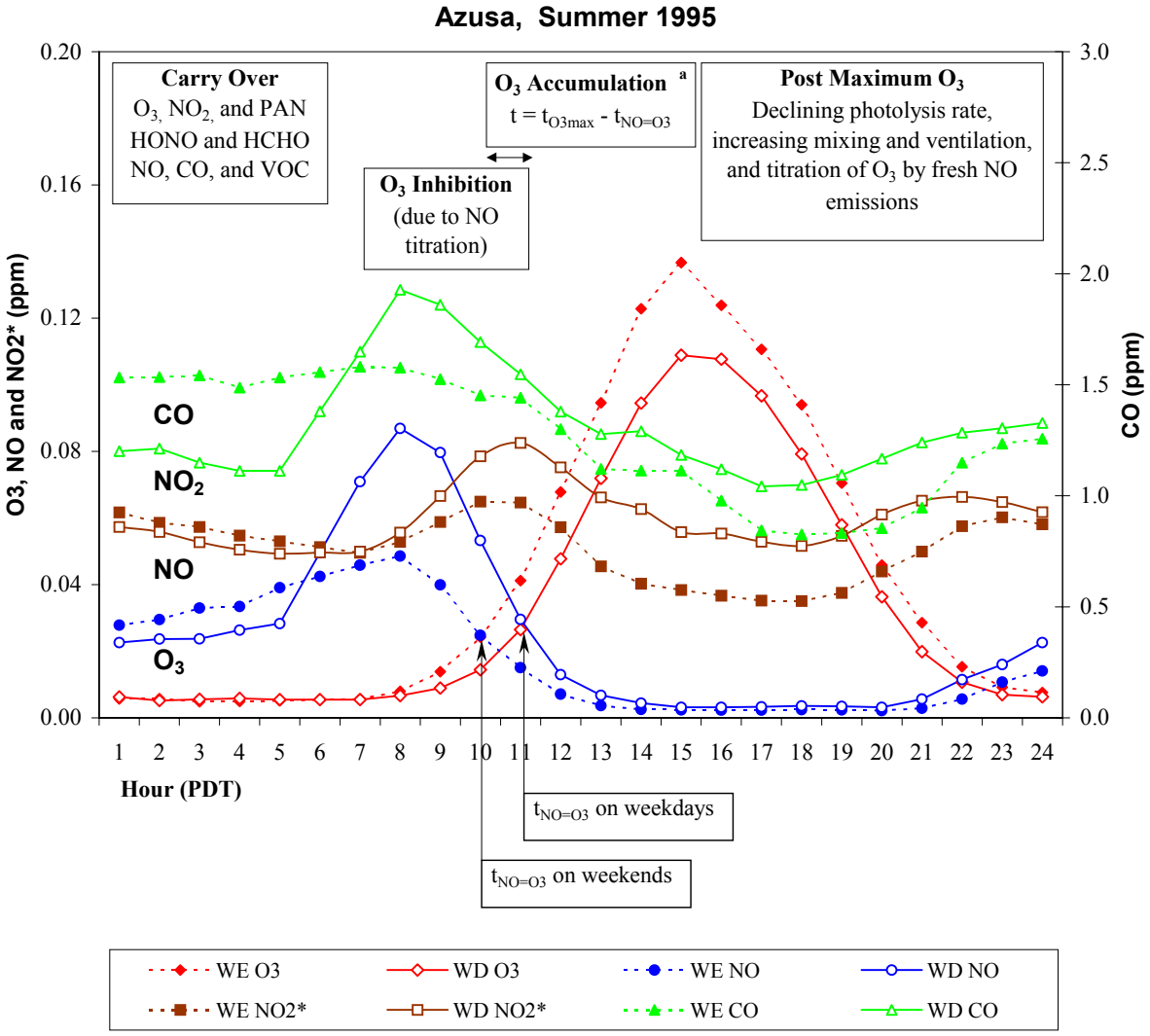
- The morning VOC/NOx ratios are above the ridgeline in the ozone isopleth plot or VOC-limited during weekdays and move toward the ridgeline on weekends. While greater carryover of VOC on weekends contributes to greater weekend morning VOC/NOx ratios, most of the increase is due to lower NO emissions during weekend mornings.

Table 2-1
Air Quality Parameters for the Conceptual Explanation of the Weekend Effect[2]

No.	Parameter	Purpose
1	$[O_3]$max (ppb)	WE/WD effect indicator
2	4-5 PDT [NO] (ppb)	Carryover
3	4-5 PDT [NO2] (ppb)	Carryover
4	4-5 PDT [NO2]/[NOx] (ppb)	Carryover
5	4-5 PDT [NMHC] (ppbC)	Carryover (via Bendix or regression with CO)
6	7-8 PDT [NO] (ppb)	Ozone titration potential (morning rush hour)
7	7-8 PDT [NO2] (ppb)	For NO_2-NO comparison
8	7-8 PDT [CO] (ppm)	Surrogate for gas-powered morning emissions
9	7-8 PDT [NMHC] (ppbC)	Fresh emissions (morning rush hour)
10	6-9 PDT NMHC/NOx	Reaction efficiency/rate for morning commute
11	tNO=O3 (PST)	Interpolated time of morning crossover of O_3 and NO. Marks ends of O_3 inhibition period and the beginning of the ozone accumulation period.
12	tO3max (PST)	Interpolated time of daily maximum O_3
13	tO3max-tNO=O3	Duration of O_3 accumulation
14	O_3rate (ppb/hour)	Rate of O_3 accumulation (see definition below)
15	NMHC/NOx(t_{O3max})	Reaction efficiency/rate at t_{O3max}

Rate of O3 accumulation: ([O3]max-[O3(tNO=O3)])/(tO3max-tNO=O3)

[2] Data are tabulated in Appendix A of Fujita et al. (2000b).



a. O3 accumulation rate = [O3(max) - O3 ($t_{NO=O3}$)]/(t_{O3max} - $t_{NO=O3}$)

Figure 2-1. Average summer 1995 diurnal variations of O3, NO, NO2, and CO at Azusa during weekday and weekend. The shorter ozone inhibition period and higher rate of ozone formation are the main factors causing higher ozone on weekends.

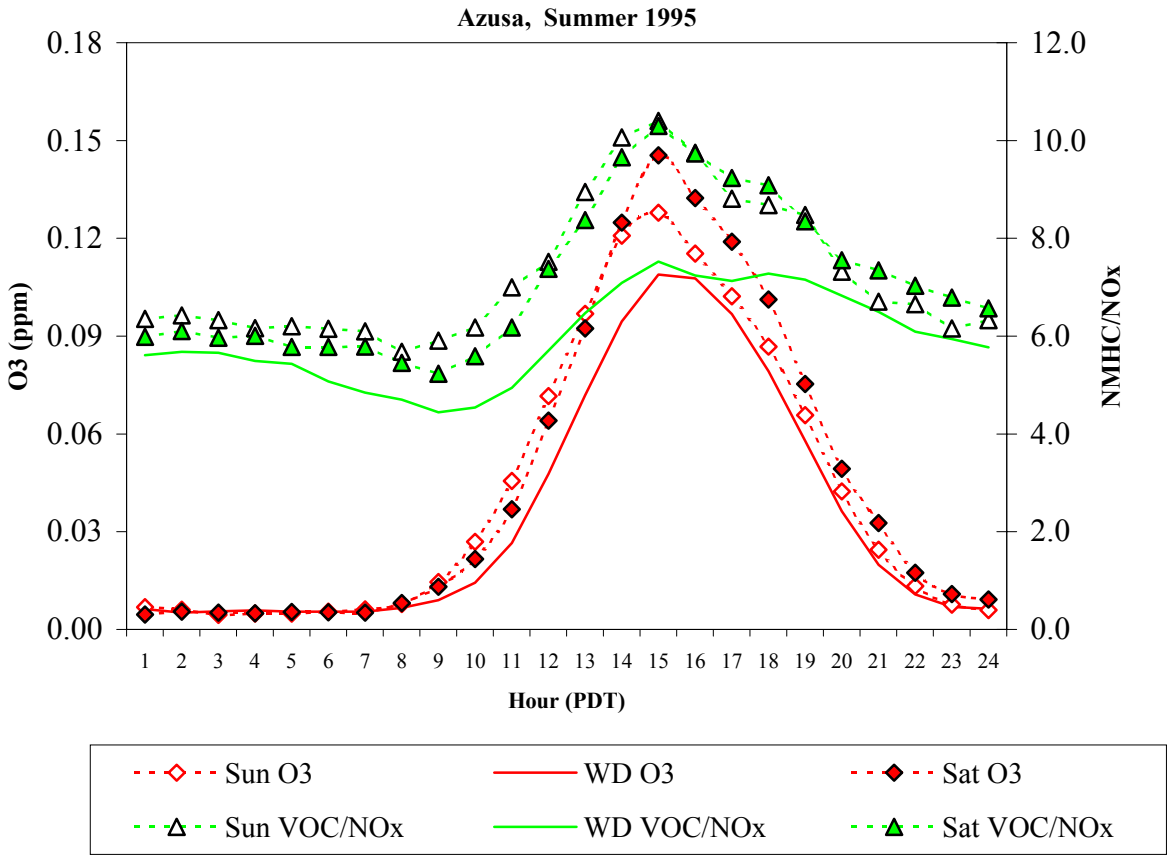


Figure 2-2. Average summer 1995 diurnal variations of O3 and VOC/NOx at Azusa during weekday and weekend. Higher VOC/NOx on weekends result in higher rate of ozone formation.

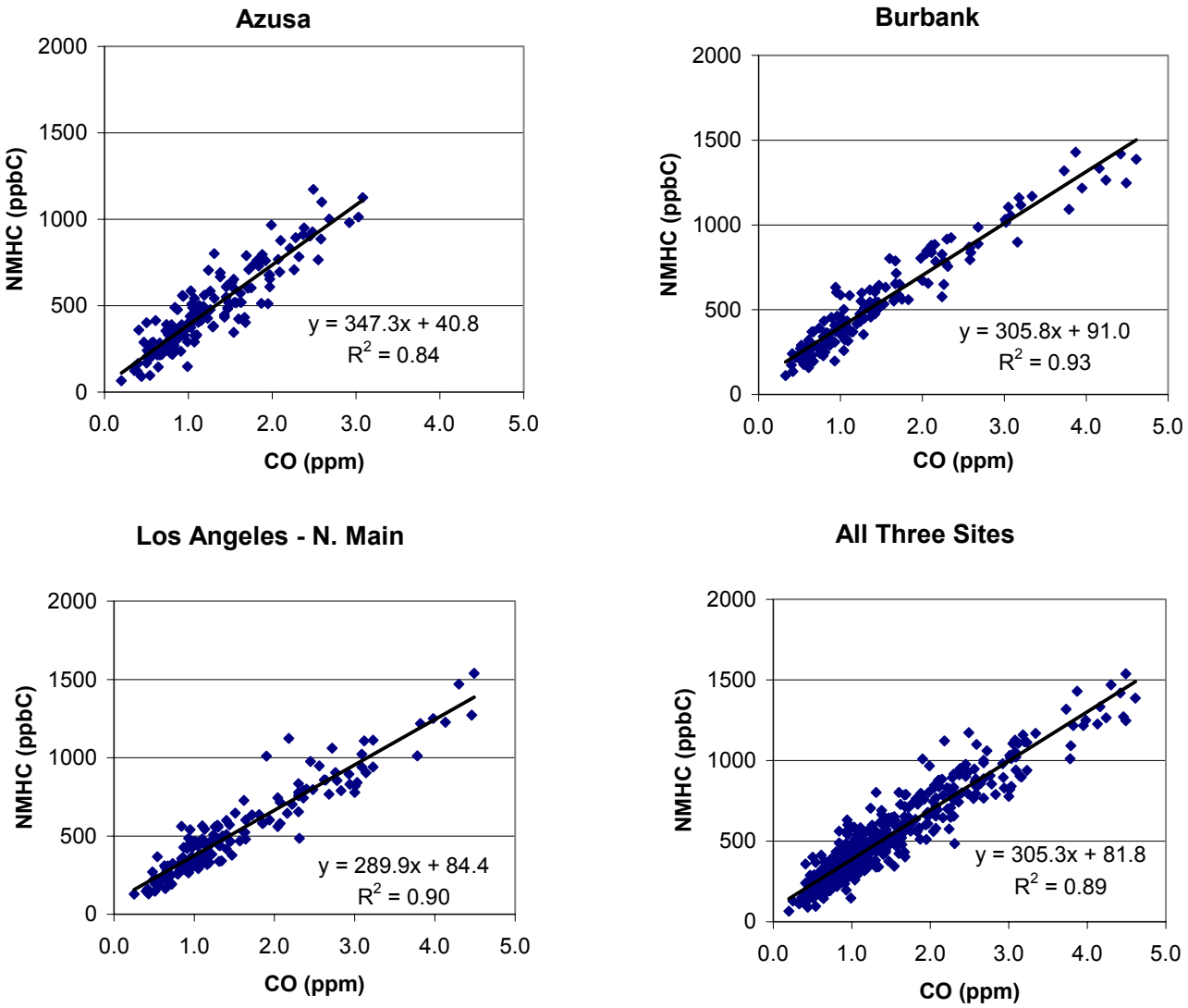


Figure 2.3. CO versus NMHC from DRI canister samples during summers 1995 and 1996.

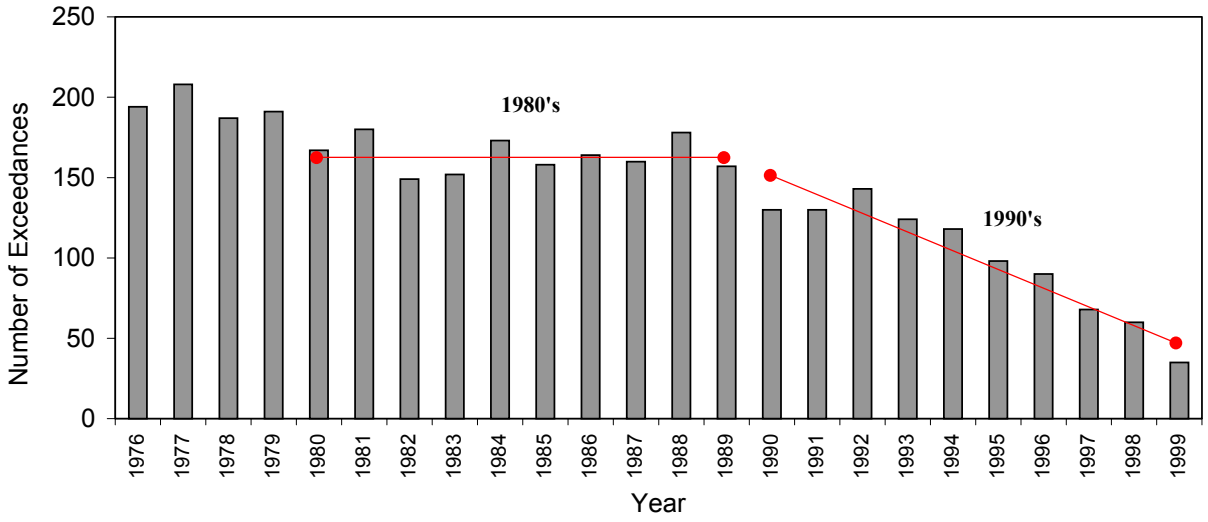


Figure 2.1-1. Trend in number of annual exceedances of the federal 1-hour ozone standard in the South Coast Air Basin from 1976 to 1999.

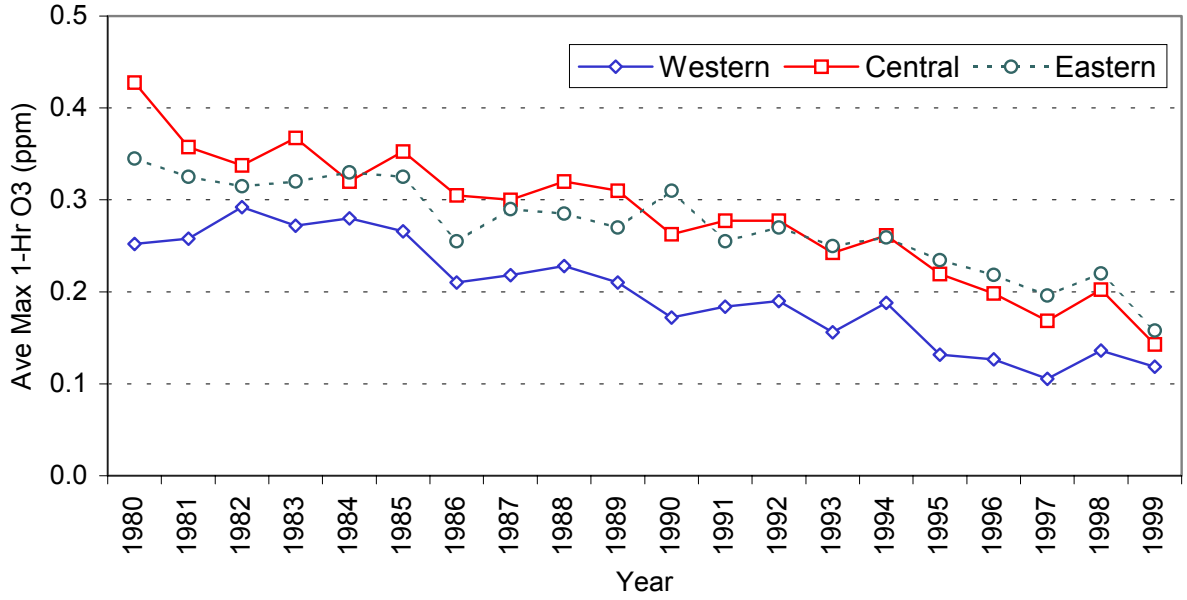


Figure 2.1-2. Trends in average maximum 1-hour ozone from 1980 to 1997 in the western, central and eastern portions of the South Coast Air Basin. Monitoring sites included in the averages are Los Angeles–N. Main, Lynwood, N. Long Beach, Anaheim, and La Habra, for Western, Azusa, Glendora, Pomona, and Upland for Central, and Riverside and Lake Gregory for Eastern.

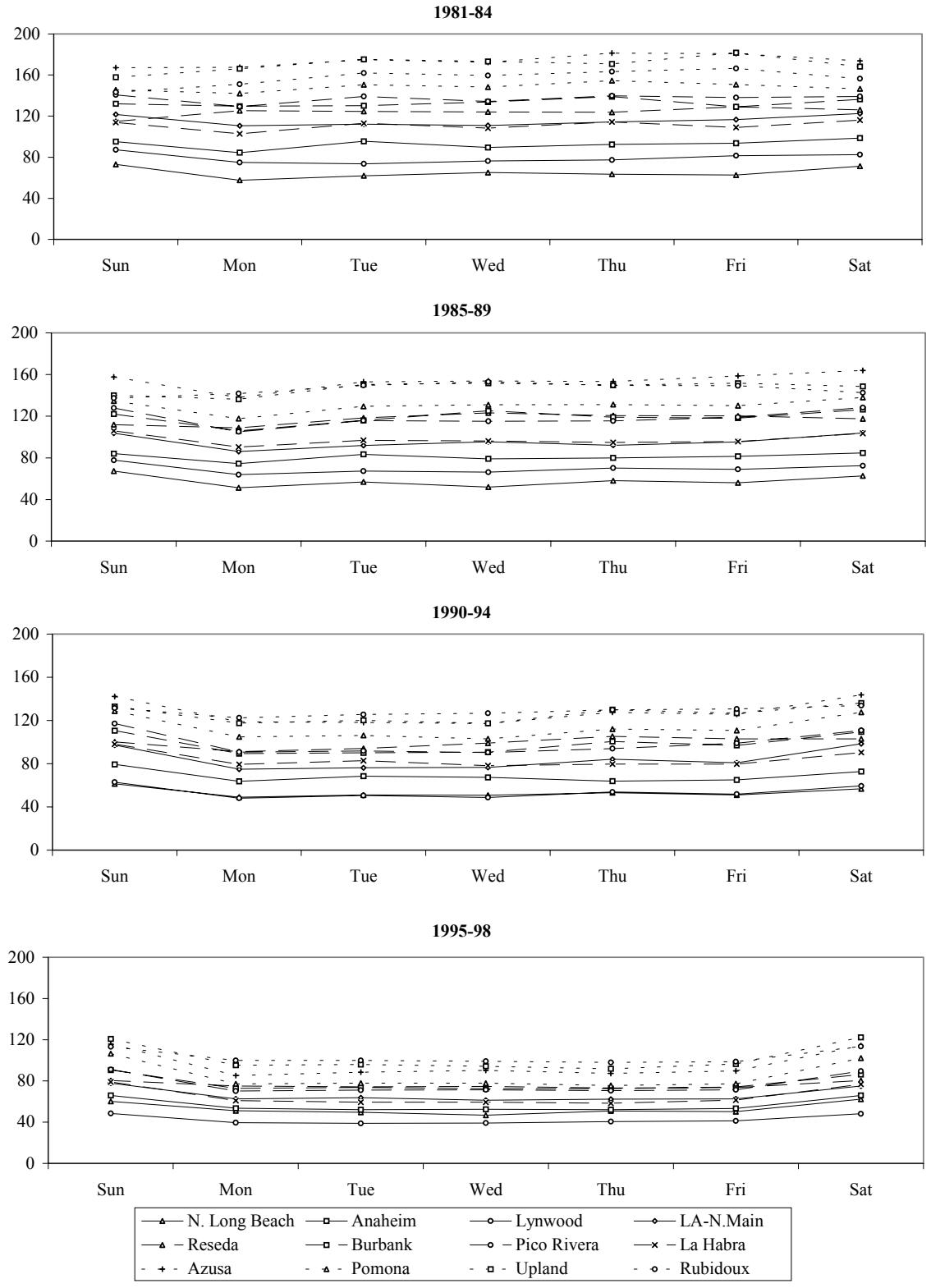


Figure 2.2-1. Average summer daily maximum 1-hour ozone (ppb) in the SoCAB by day of the week.

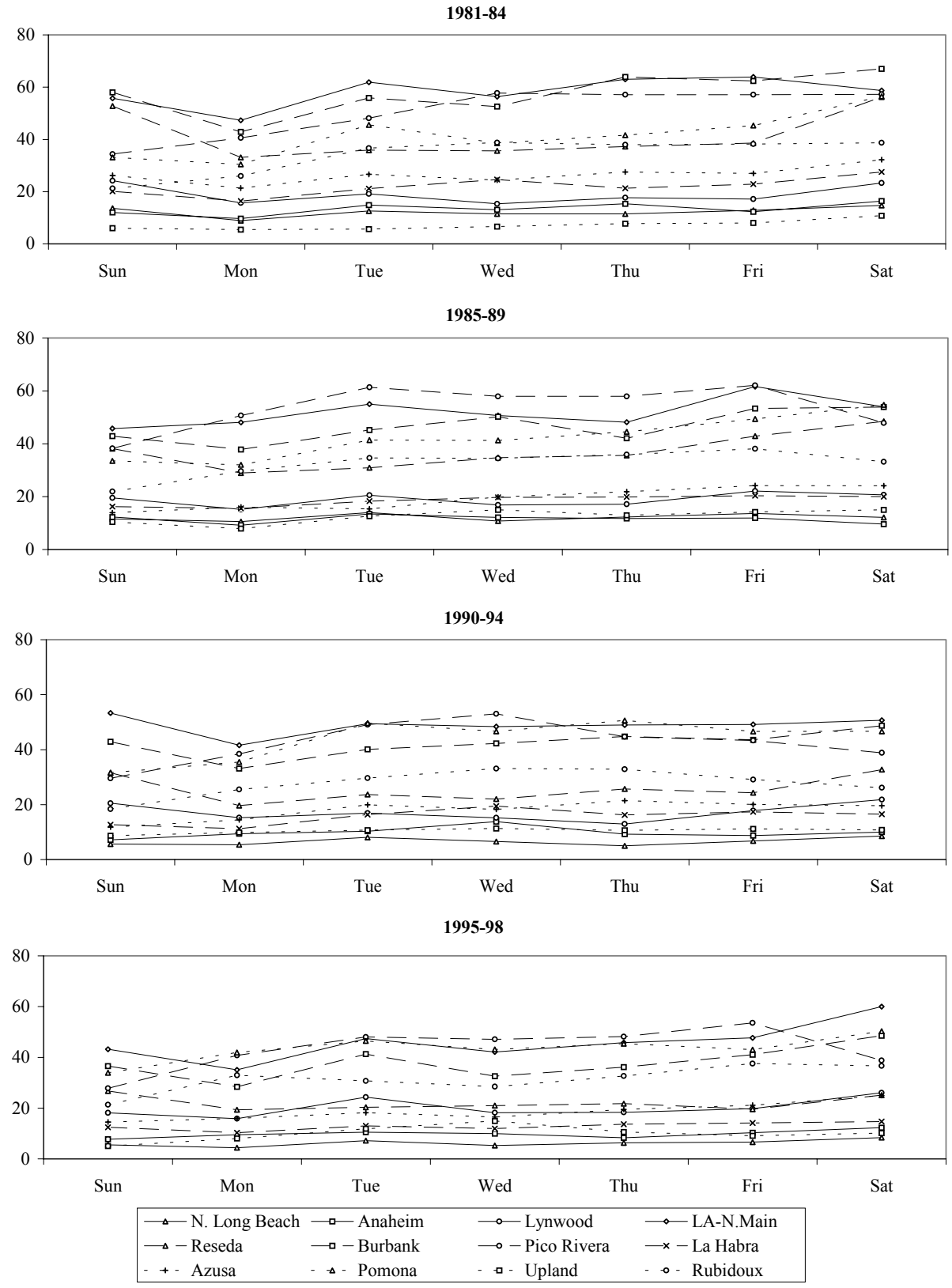


Figure 2.3-1. Average daily 4-5 a.m (PDT) NO (ppb) in the SoCAB by day of the week.

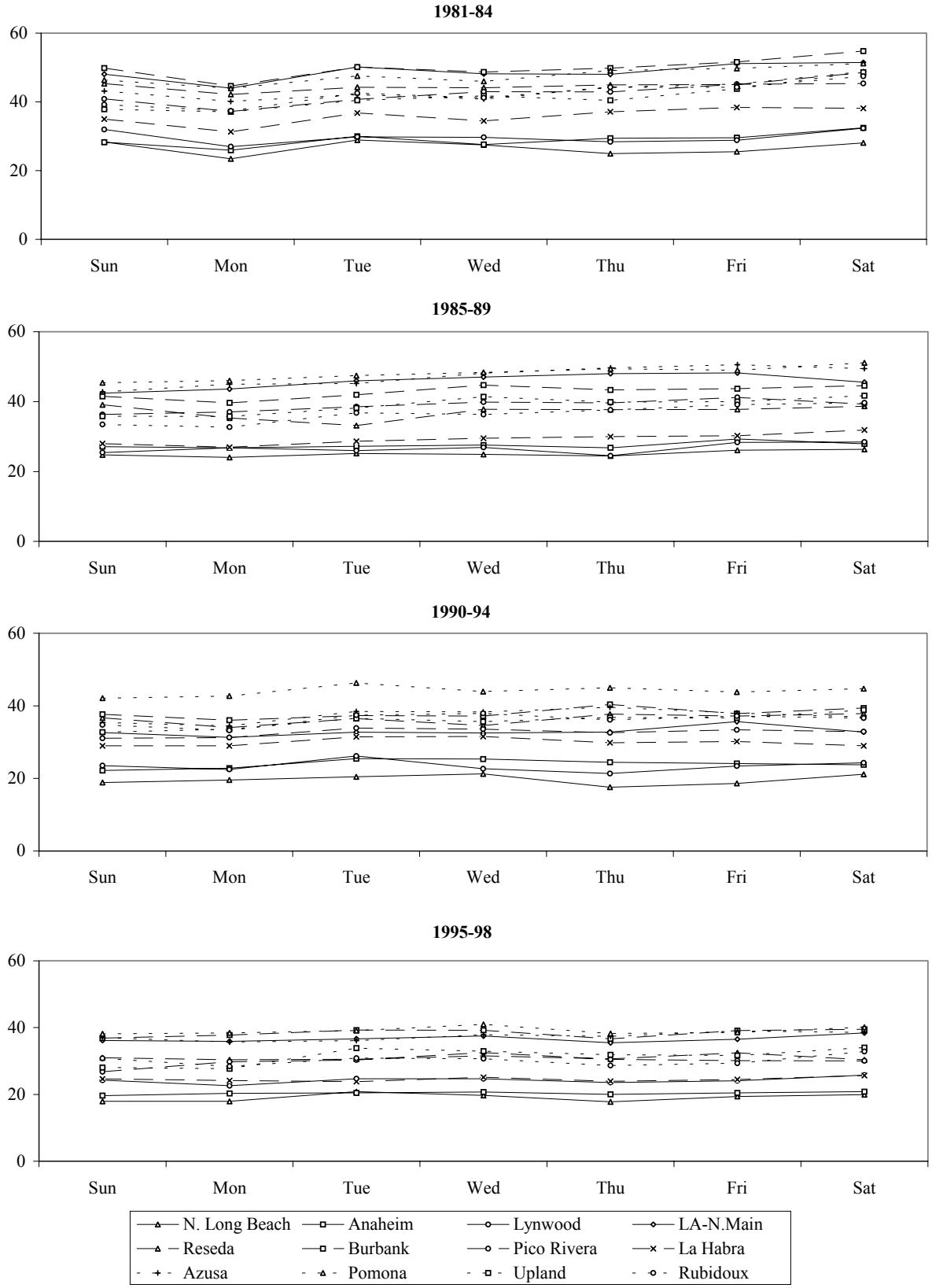


Figure 2.3-2. Average daily 4-5 a.m (PDT) NO_2 (ppb) in the SoCAB by day of the week.

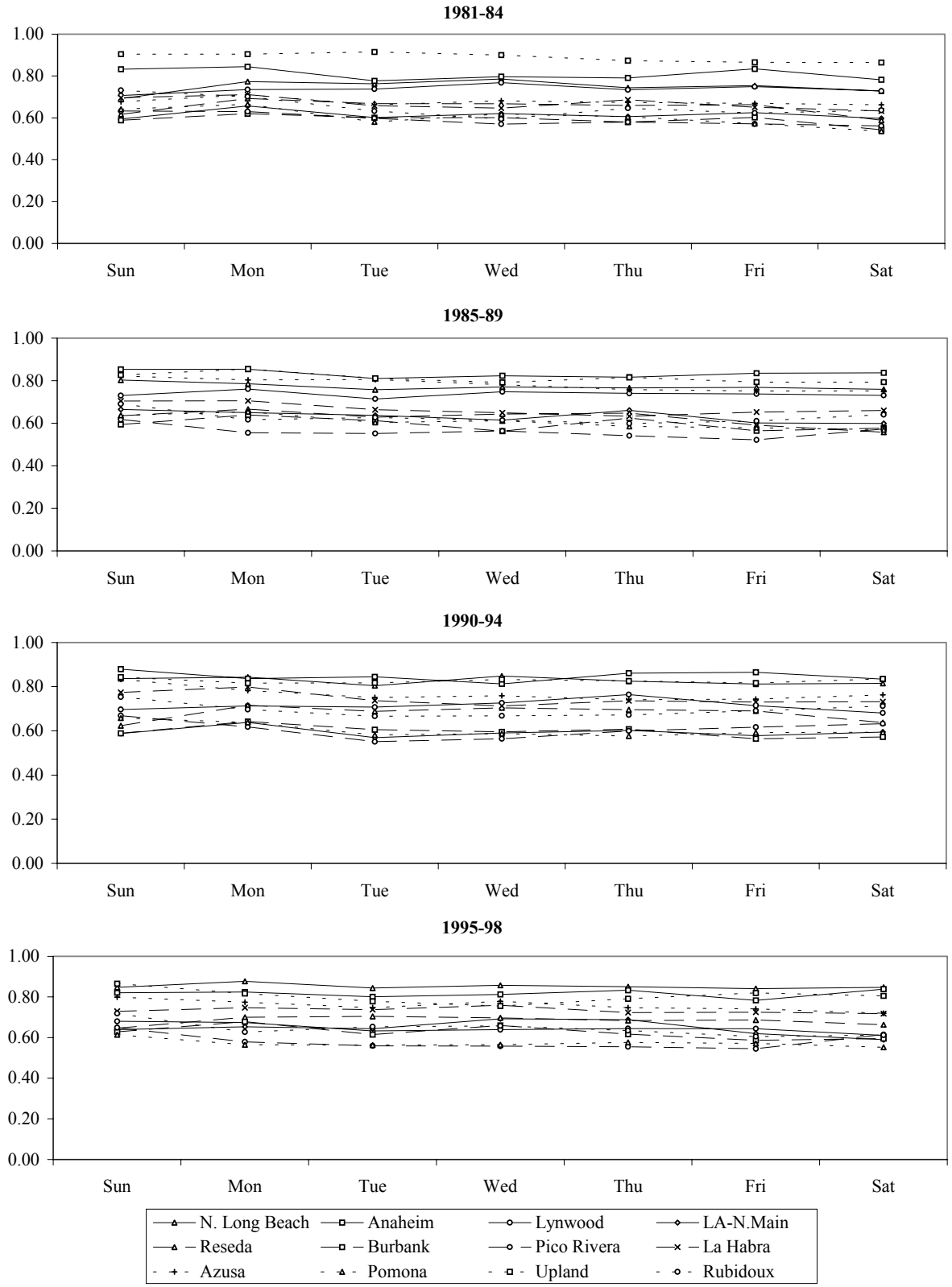


Figure 2.3-3. Average daily 4-5 a.m (PDT) NO_2/NOx (ppb) in the SoCAB by day of the week.

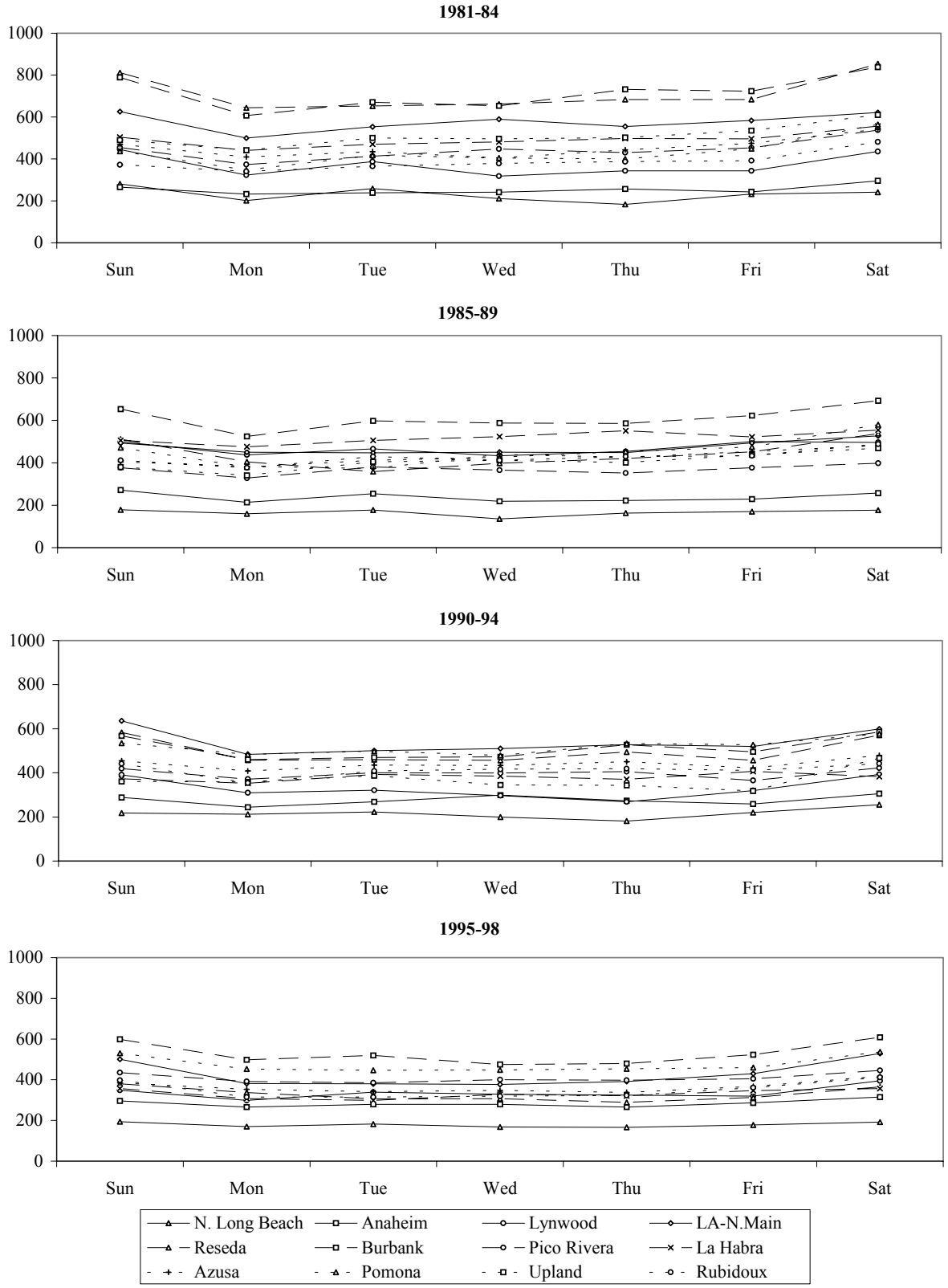


Figure 2.3-4. Average daily 4-5 a.m. (PDT) NMHC (ppbC) in the SoCAB by day of the week. NMHC is estimated from carbon monoxide.

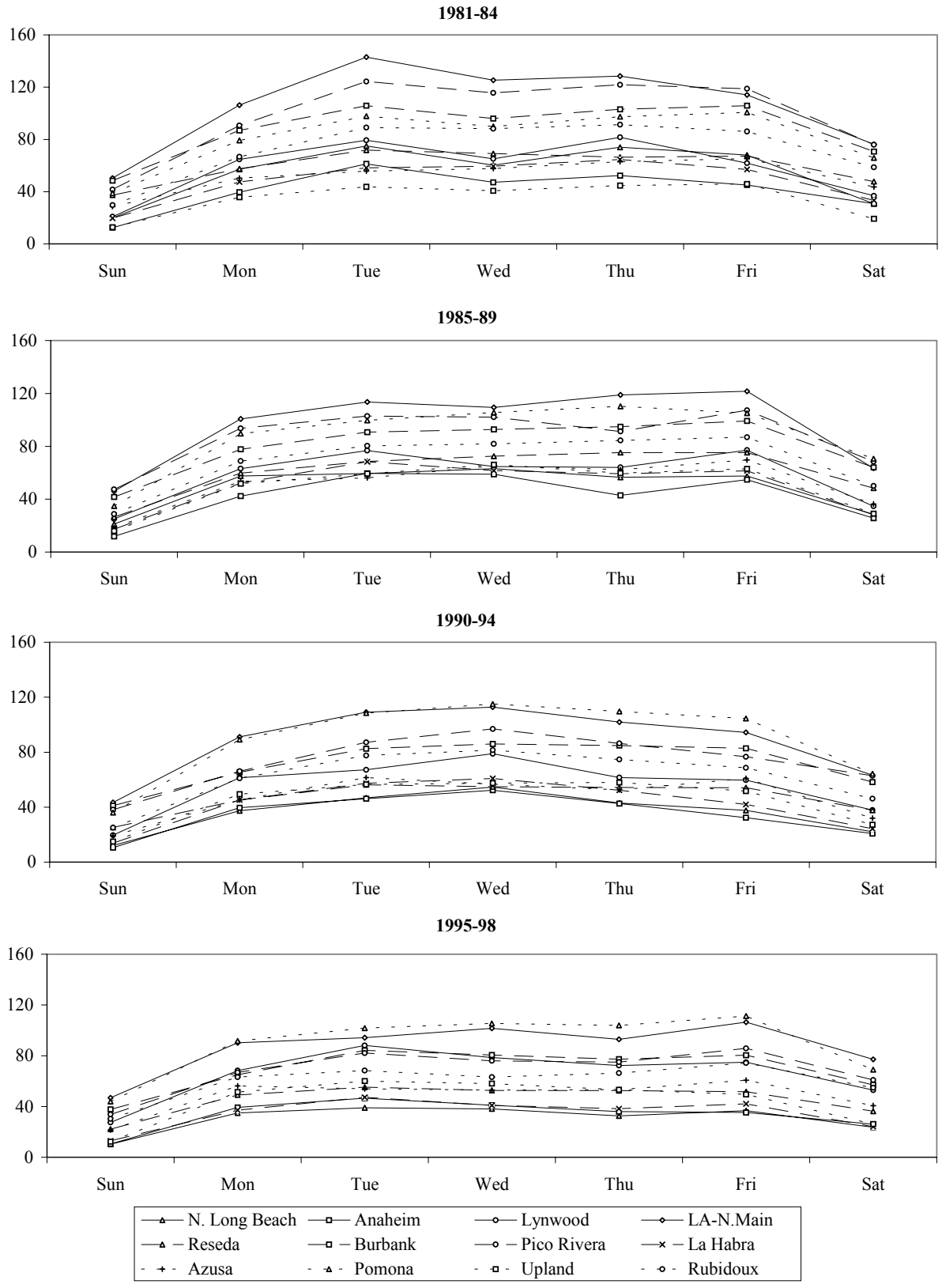


Figure 2.4-1. Average daily 7-8 a.m. (PDT) NO (ppb) in the SoCAB by day of the week.

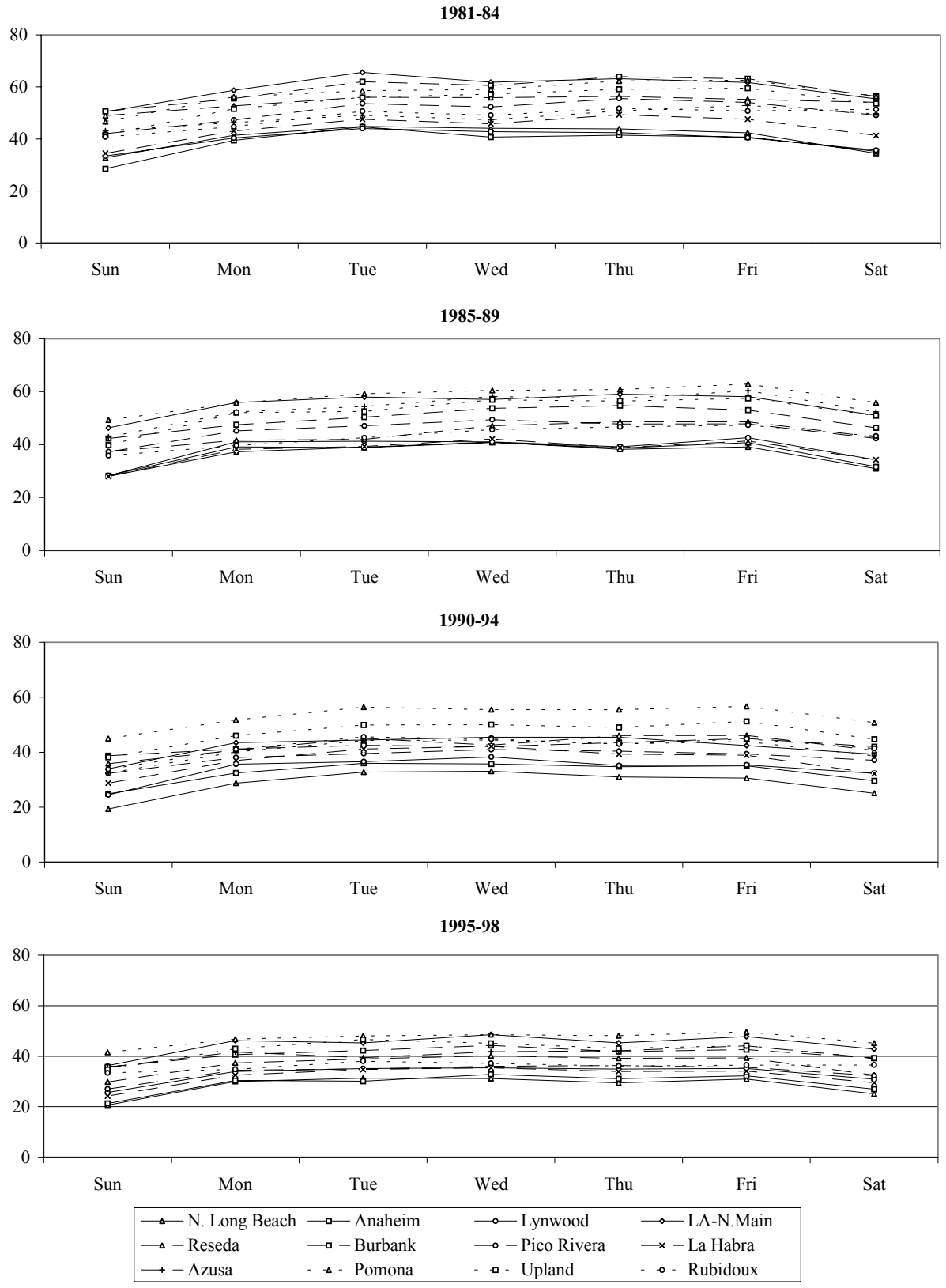


Figure 2.4-2. Average daily 7-8 a.m. (PDT) NO_2 (ppb) in the SoCAB by day of the week.

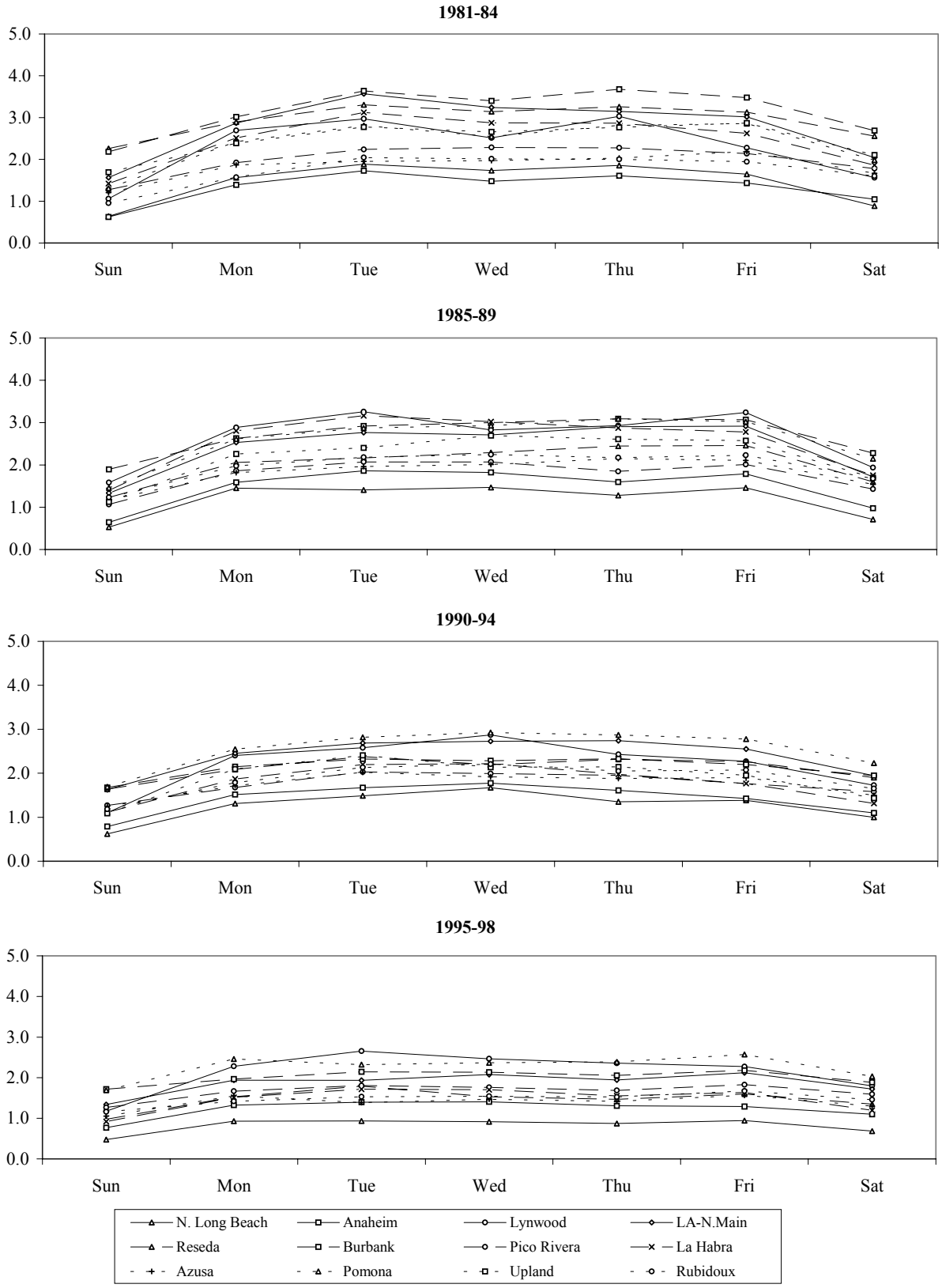


Figure 2.4-3. Average daily 7-8 a.m. (PDT) CO (ppm) in the SoCAB by day of the week.

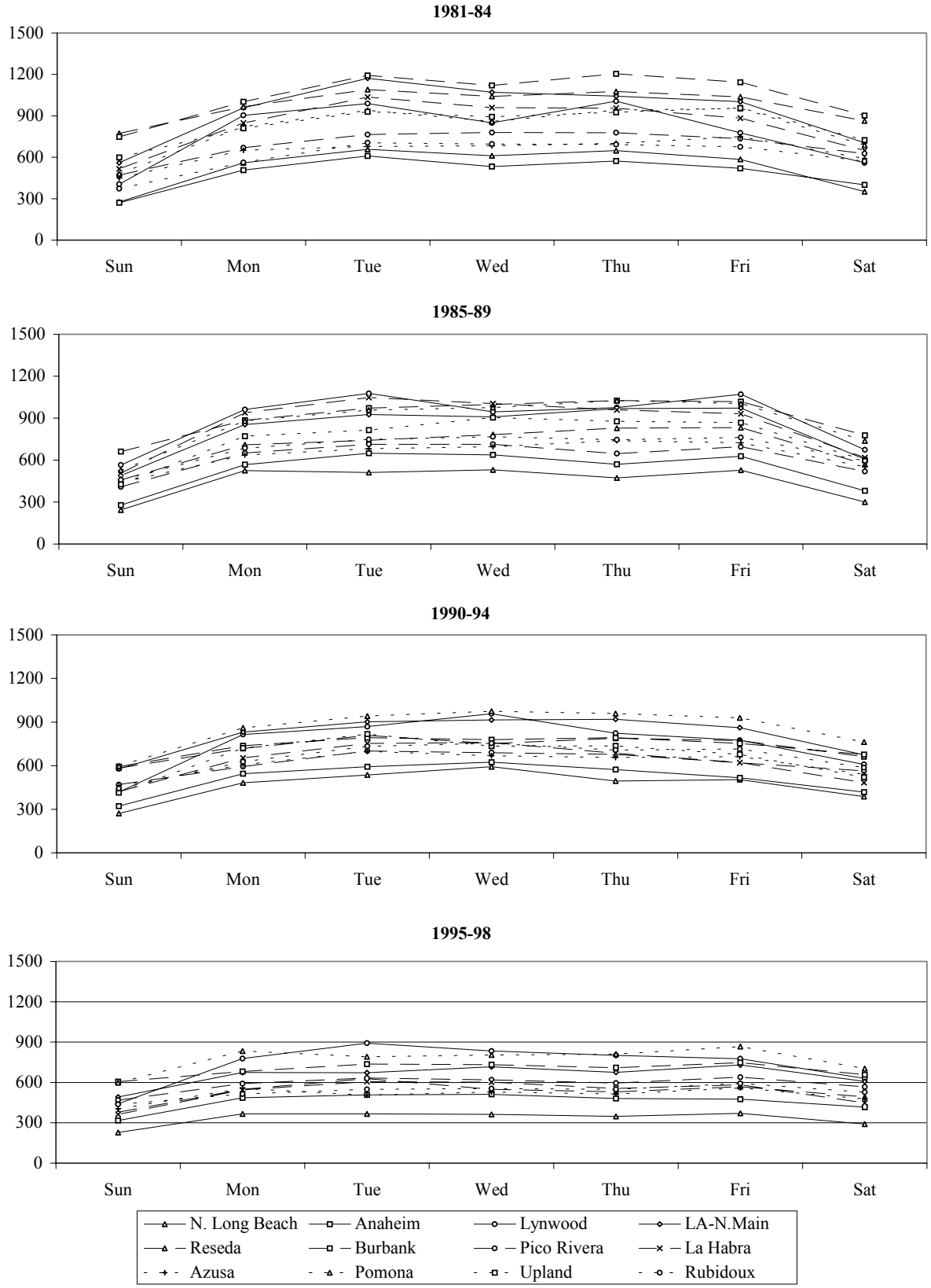


Figure 2.4-4. Average daily 7-8 a.m. (PDT) NMHC (ppbC) in the SoCAB by day of the week.

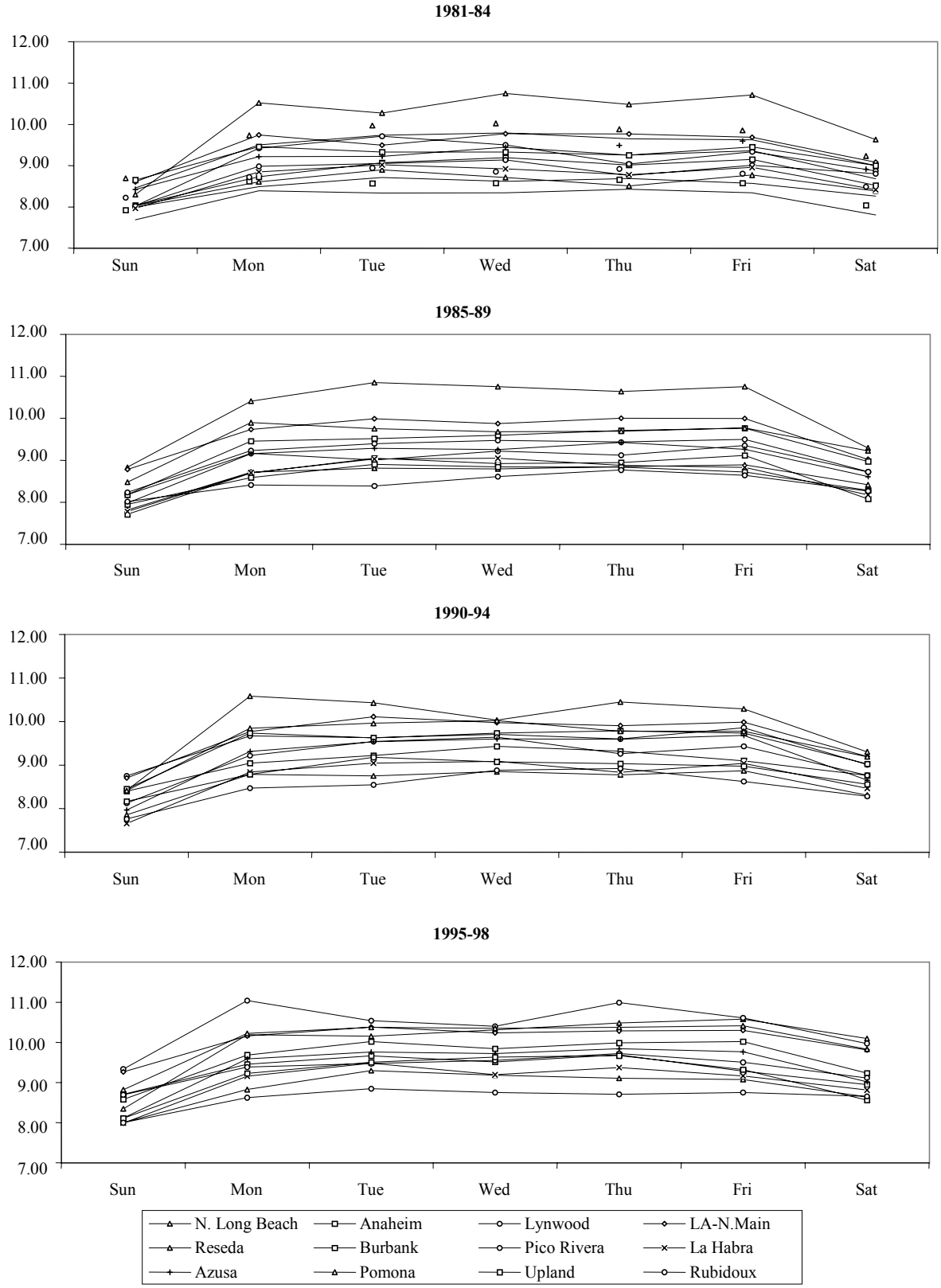


Figure 2.4-5. Average time (PDT) in the morning when NO equals O_3 by day of the week.

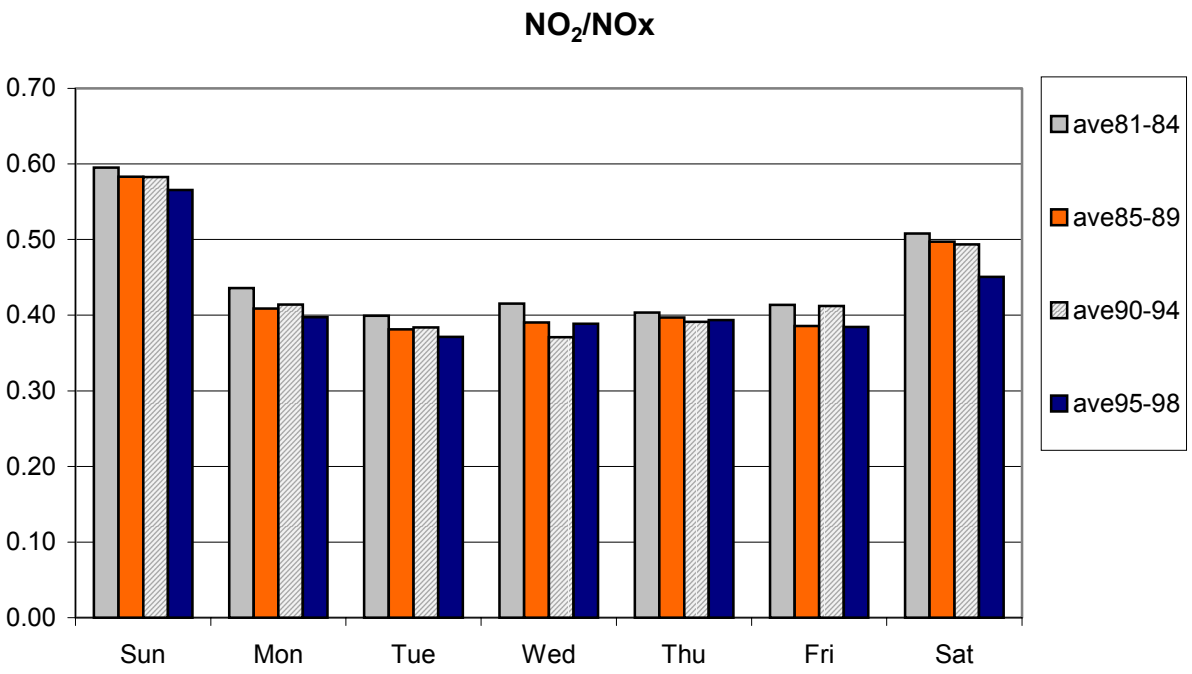


Figure 2.4-6. Twelve-site average NO_2/NOx ratios at 7-8 a.m. (PDT) by day of the week.

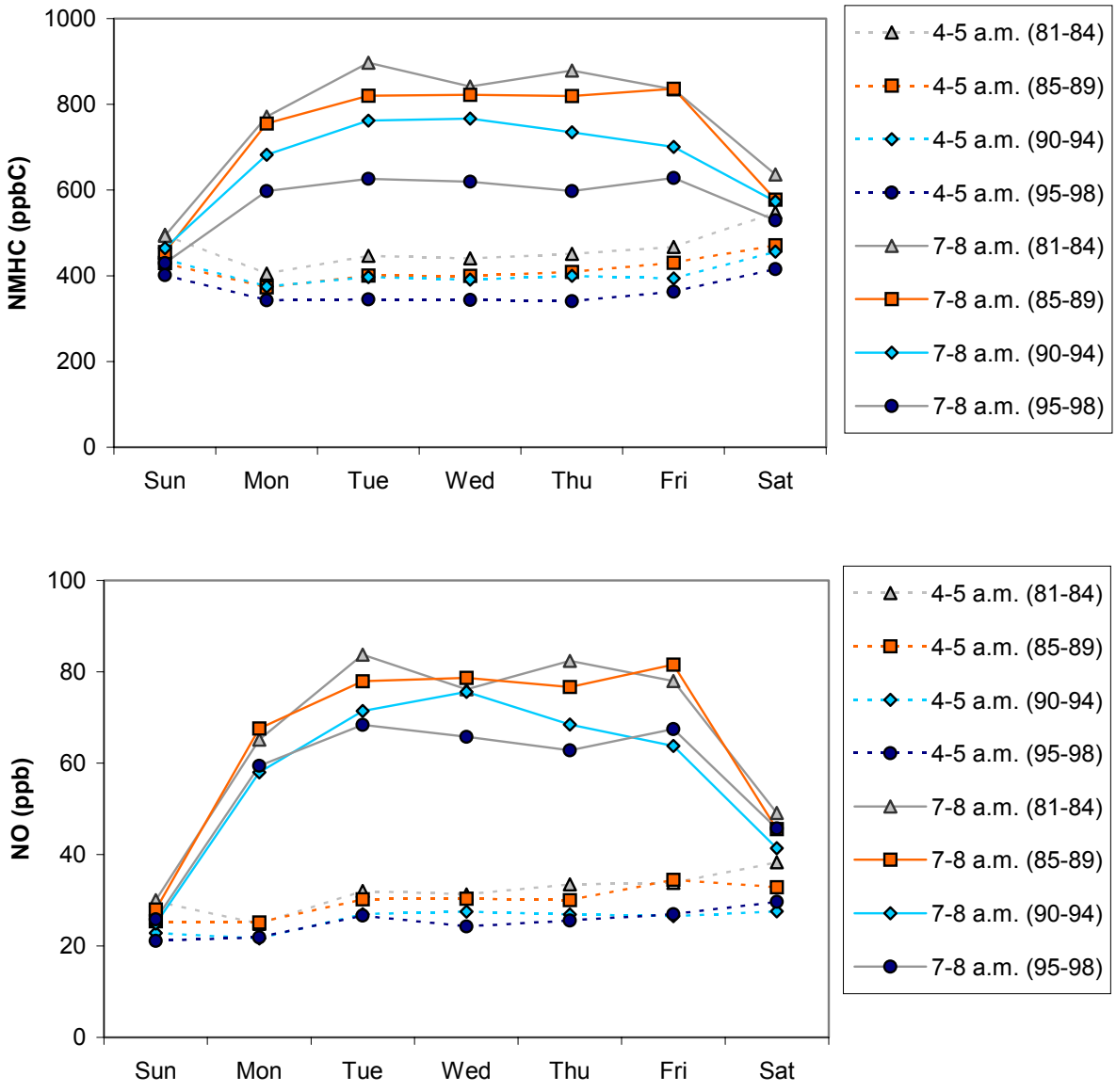


Figure 2.4-7. Twelve-site average NMHC and NO concentrations at 4-5 a.m. (PDT) and 7-8 a.m. (PDT) by day of the week.

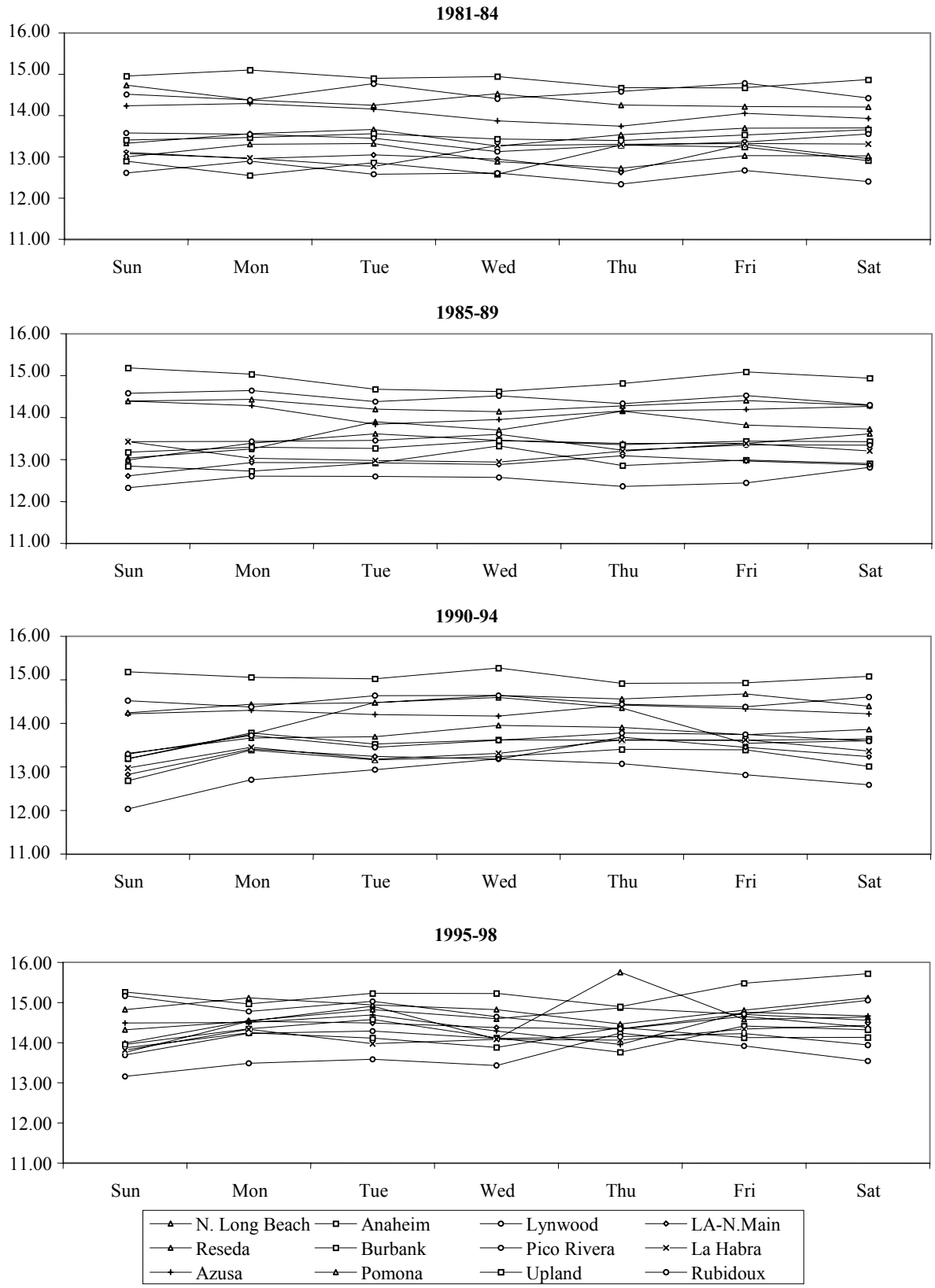


Figure 2.5-1. Average time (PDT) at maximum O_3 by day of the week.

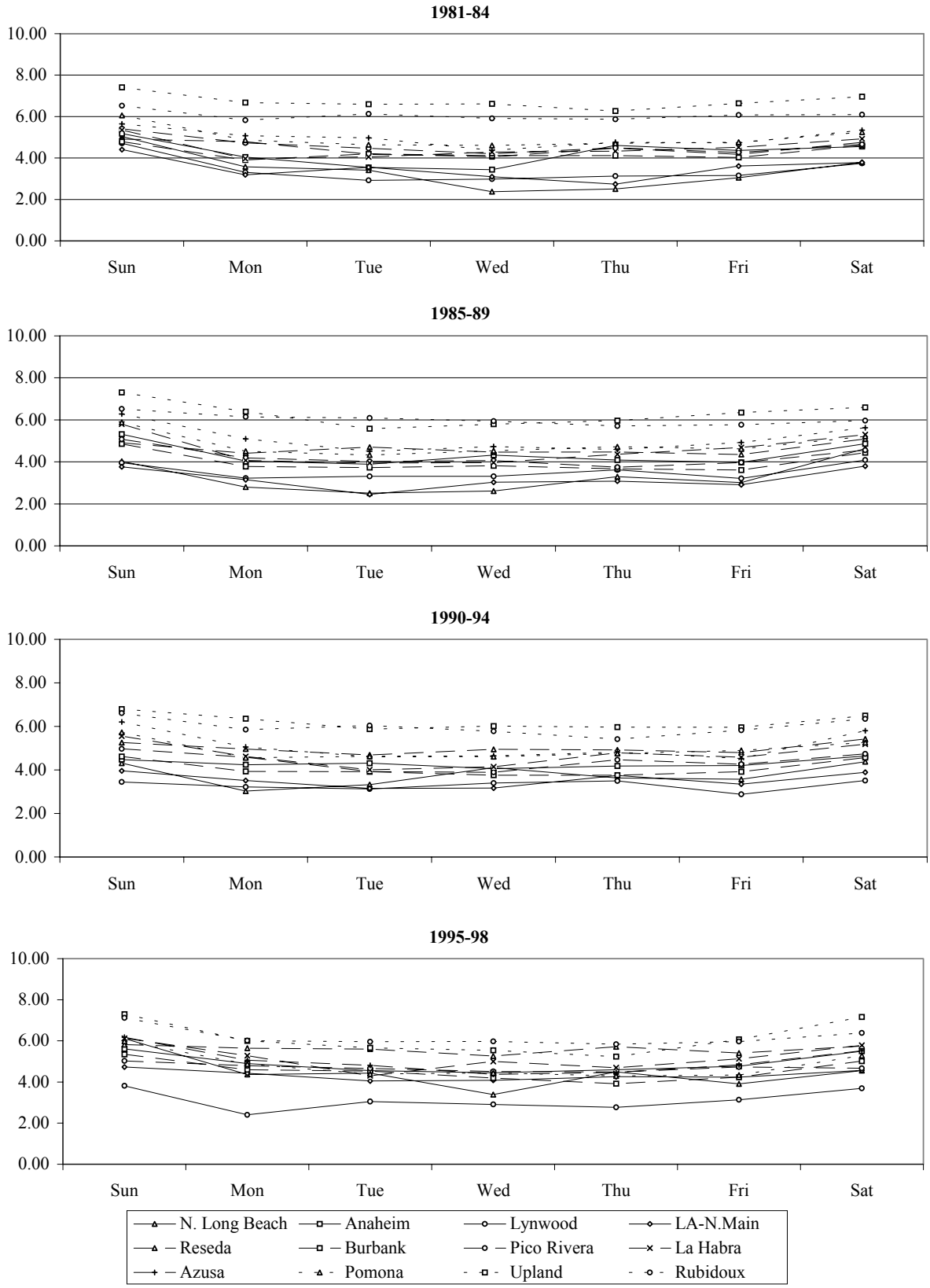


Figure 2.5-2. Duration (hours) of ozone accumulation by day of the week.

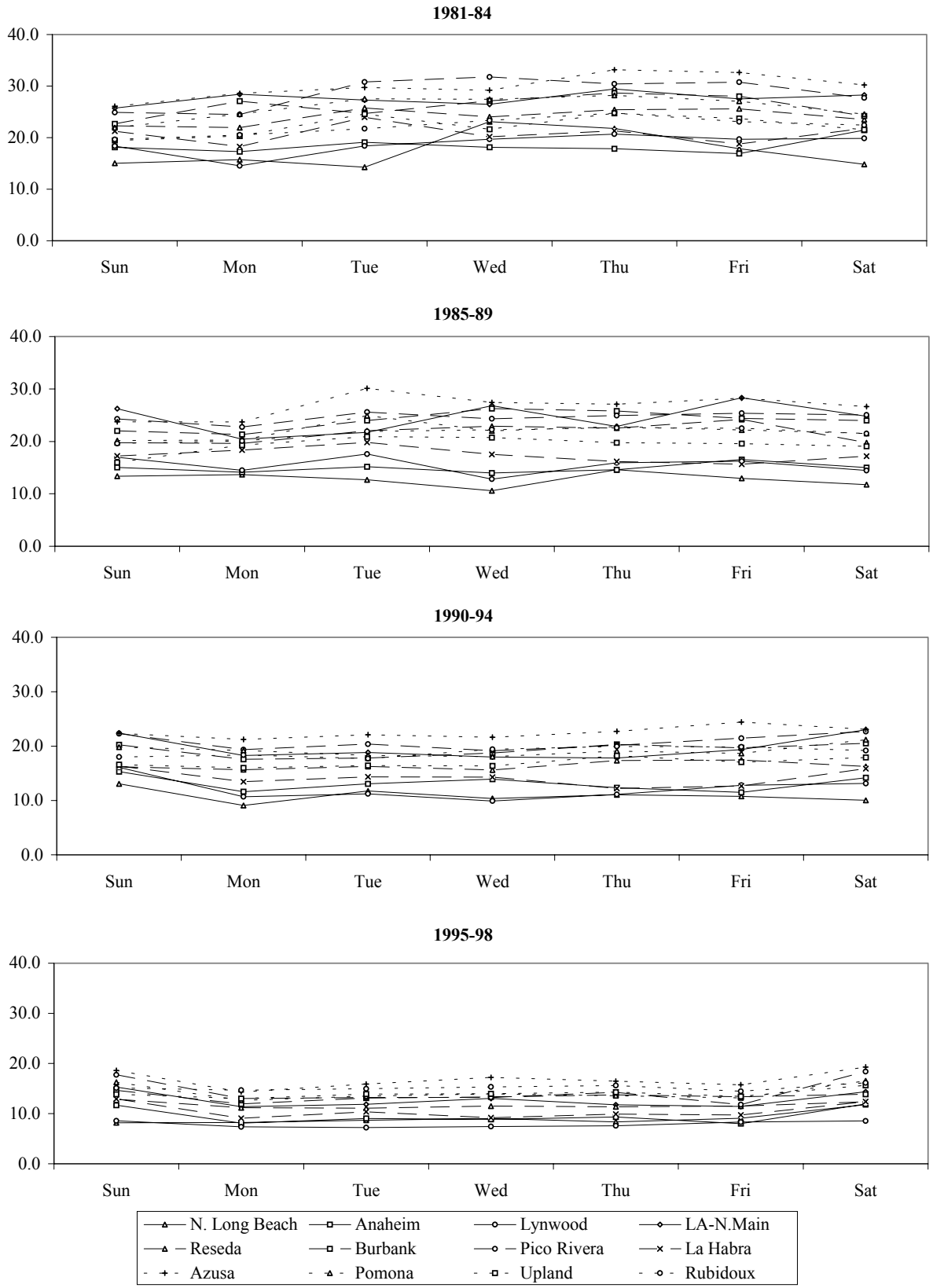


Figure 2.5-3. Ozone accumulation rate (ppb O_3 per hour) by day of the week.

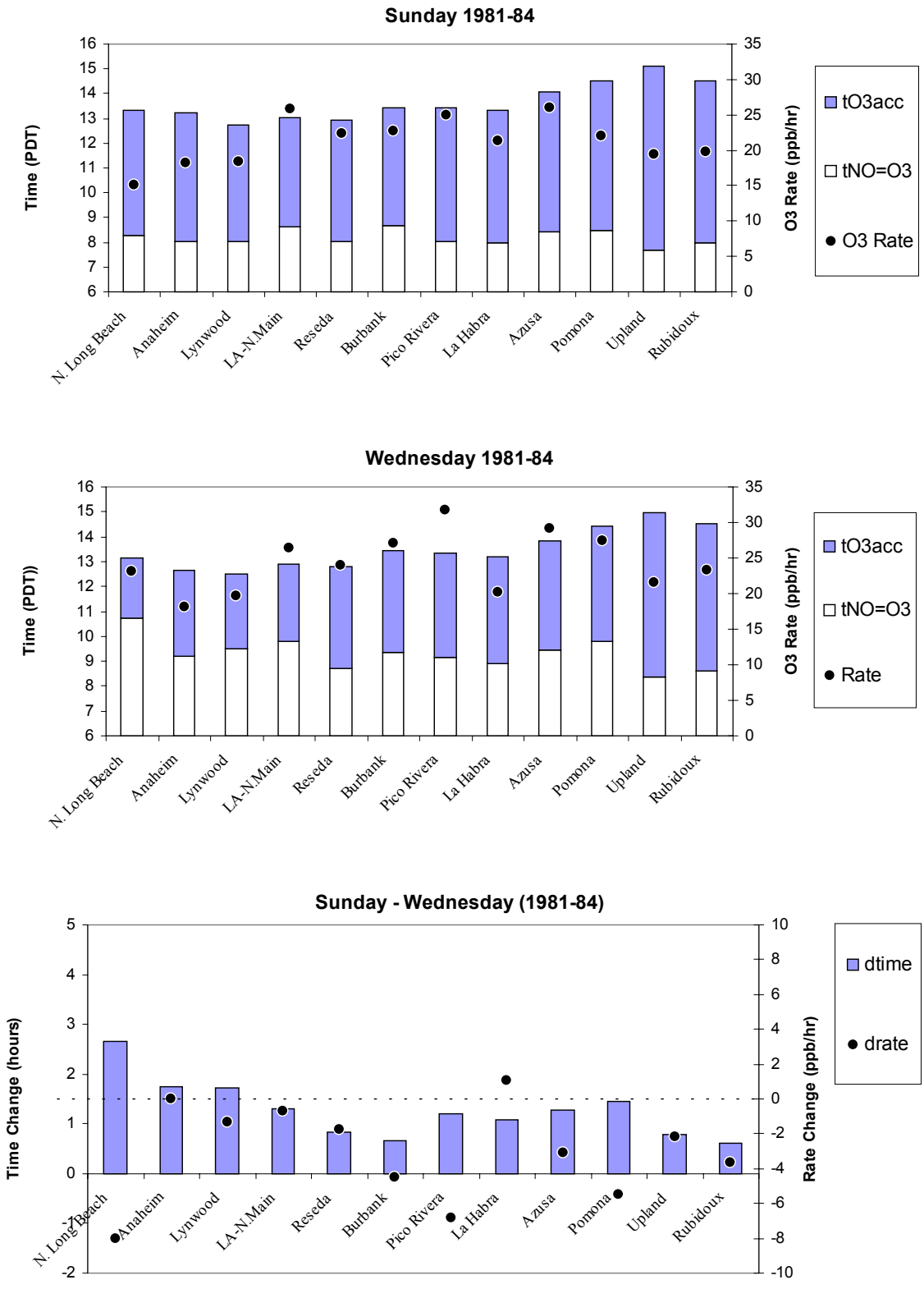


Figure 2.5-4. Average duration between $t_{NO=O3}$ and t_{maxO3} and average rates of accumulation of ozone on Sunday and Wednesday during 1981-84 and the differences.

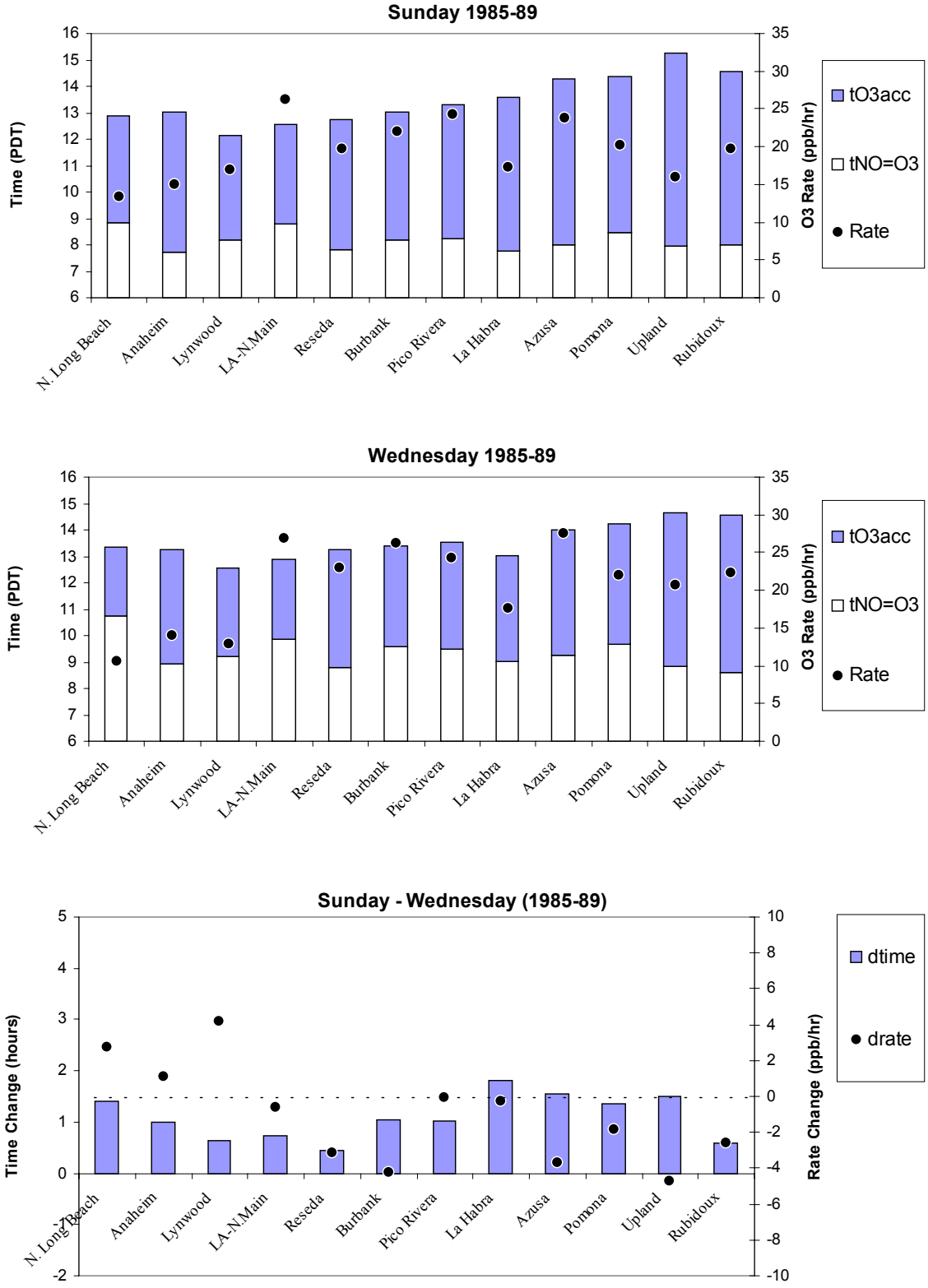


Figure 2.5-5. Average duration between $t_{NO=O3}$ and t_{maxO3} and average rates of accumulation of ozone on Sunday and Wednesday during 1985-89 and the differences.

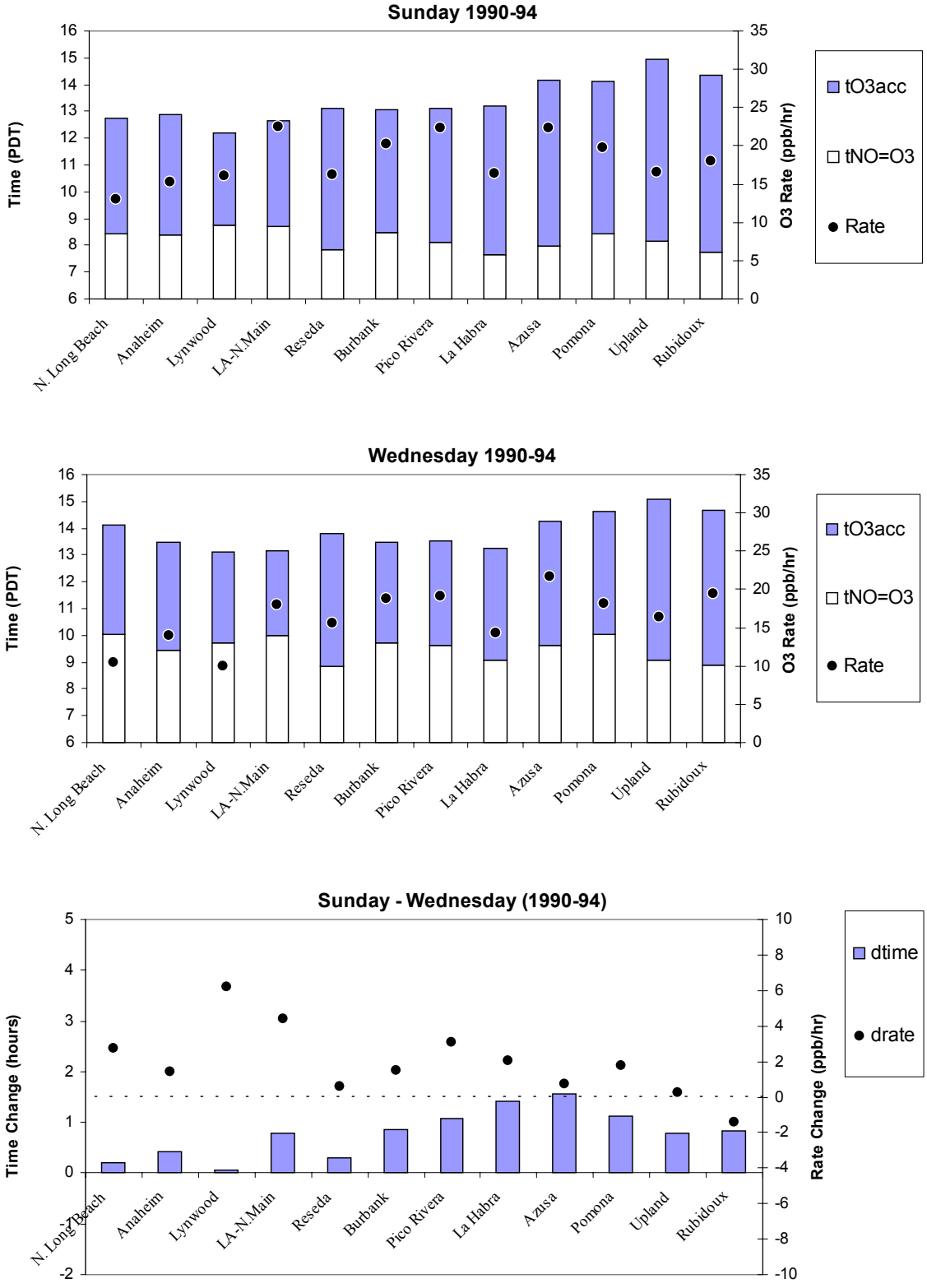


Figure 2.5-6. Average duration between $t_{NO=O3}$ and t_{maxO3} and average rates of accumulation of ozone on Sunday and Wednesday during 1990-94 and the differences.

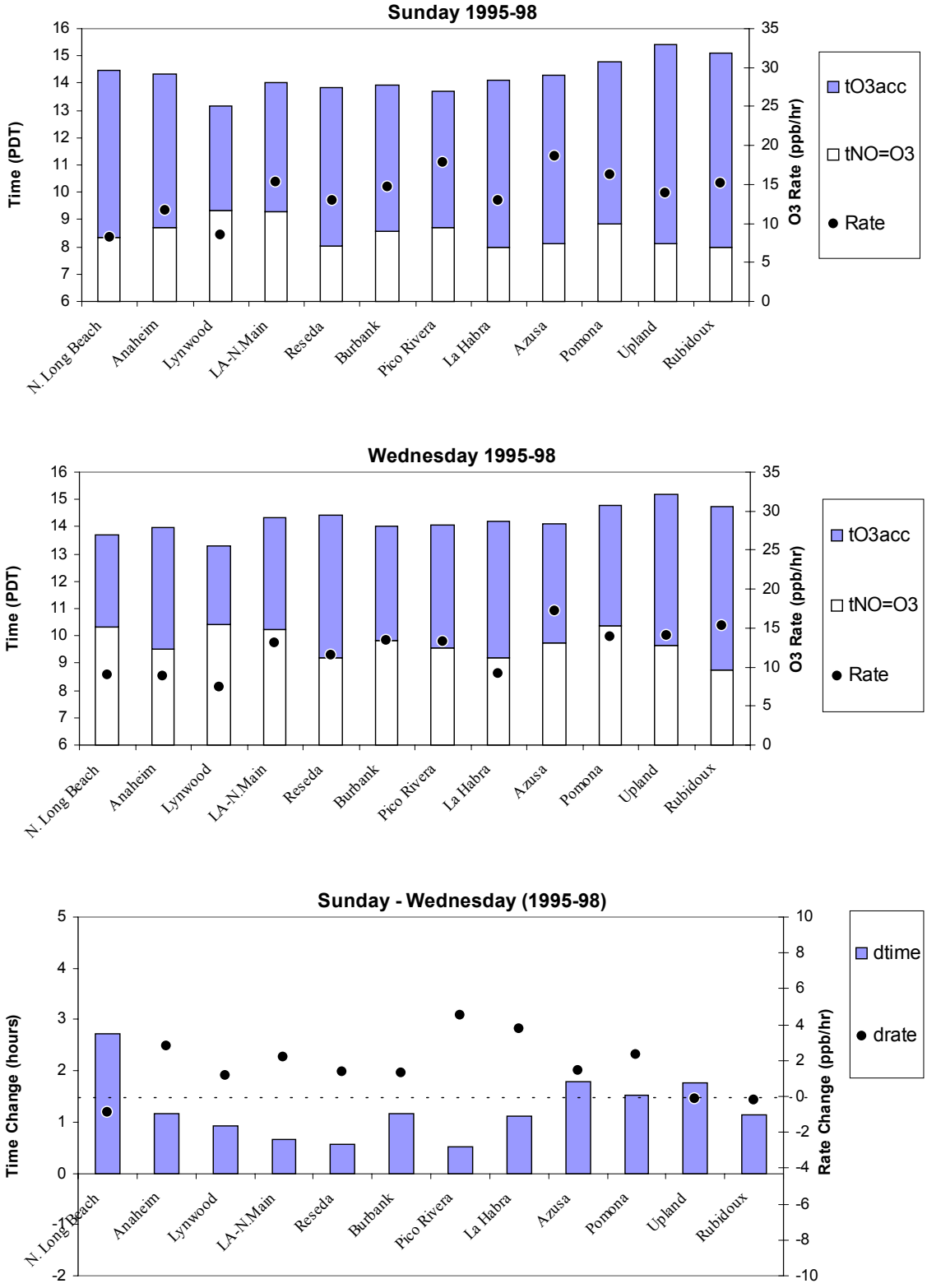


Figure 2.5-7. Average duration between $t_{NO=O3}$ and t_{maxO3} and average rates of accumulation of ozone on Sunday and Wednesday during 1995-98 and the differences.

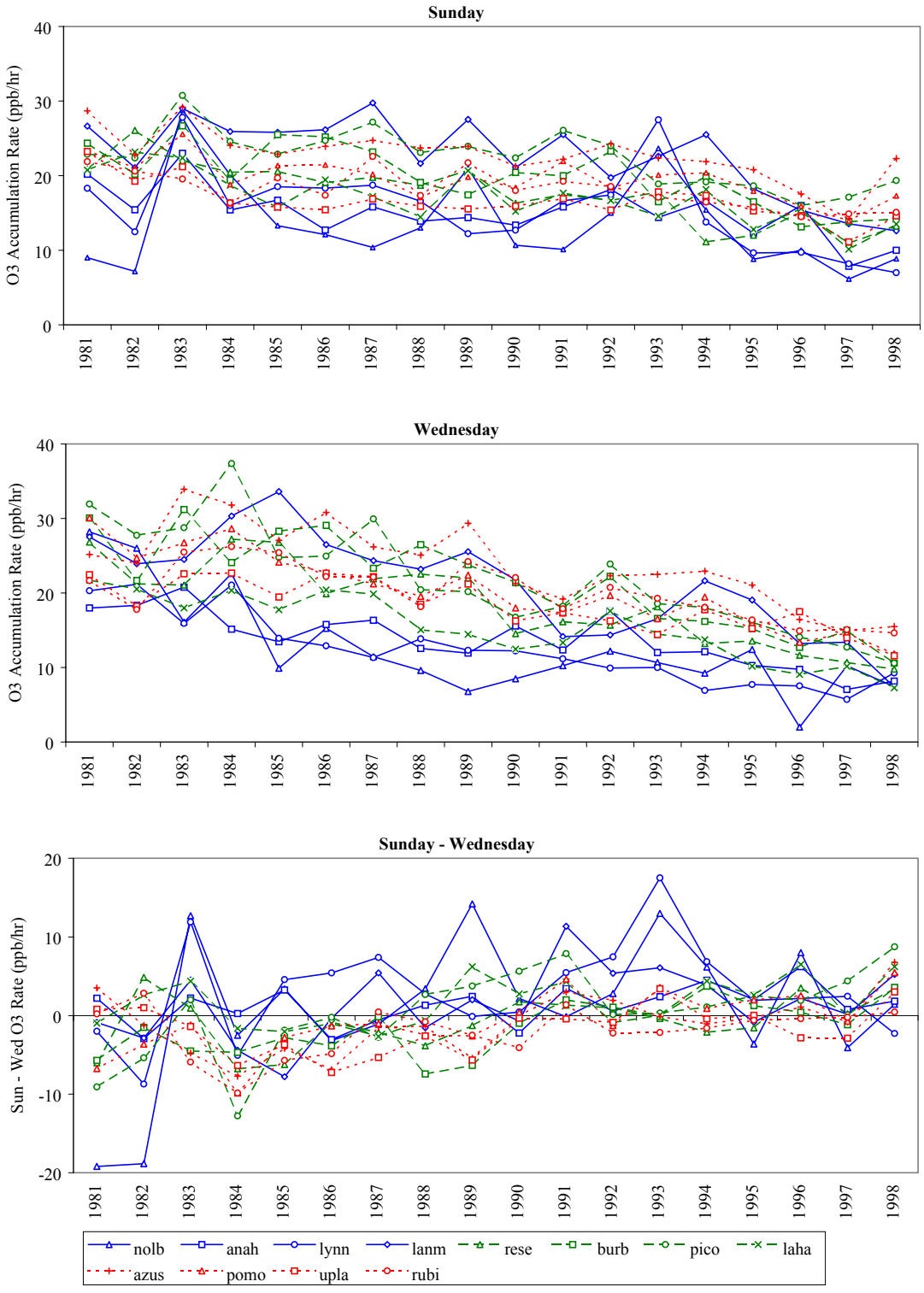


Figure 2.5-8. Trends in ozone accumulation rate by site for Sunday, Wednesday, and the difference between Sunday and Wednesday.

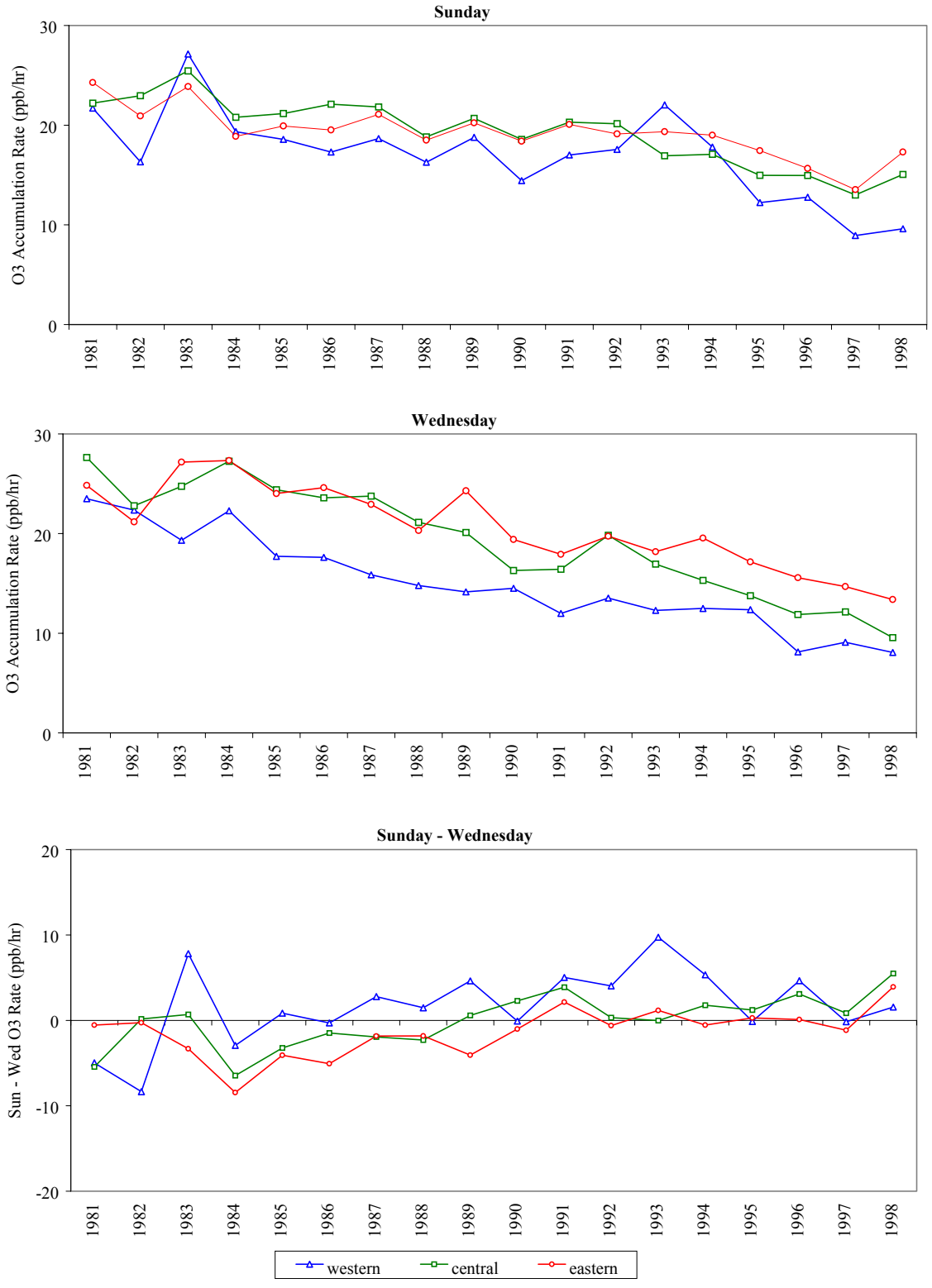


Figure 2.5-9. Trends in ozone accumulation rate for western, central, and eastern SoCAB for Sunday, Wednesday, and the difference between Sunday and Wednesday.

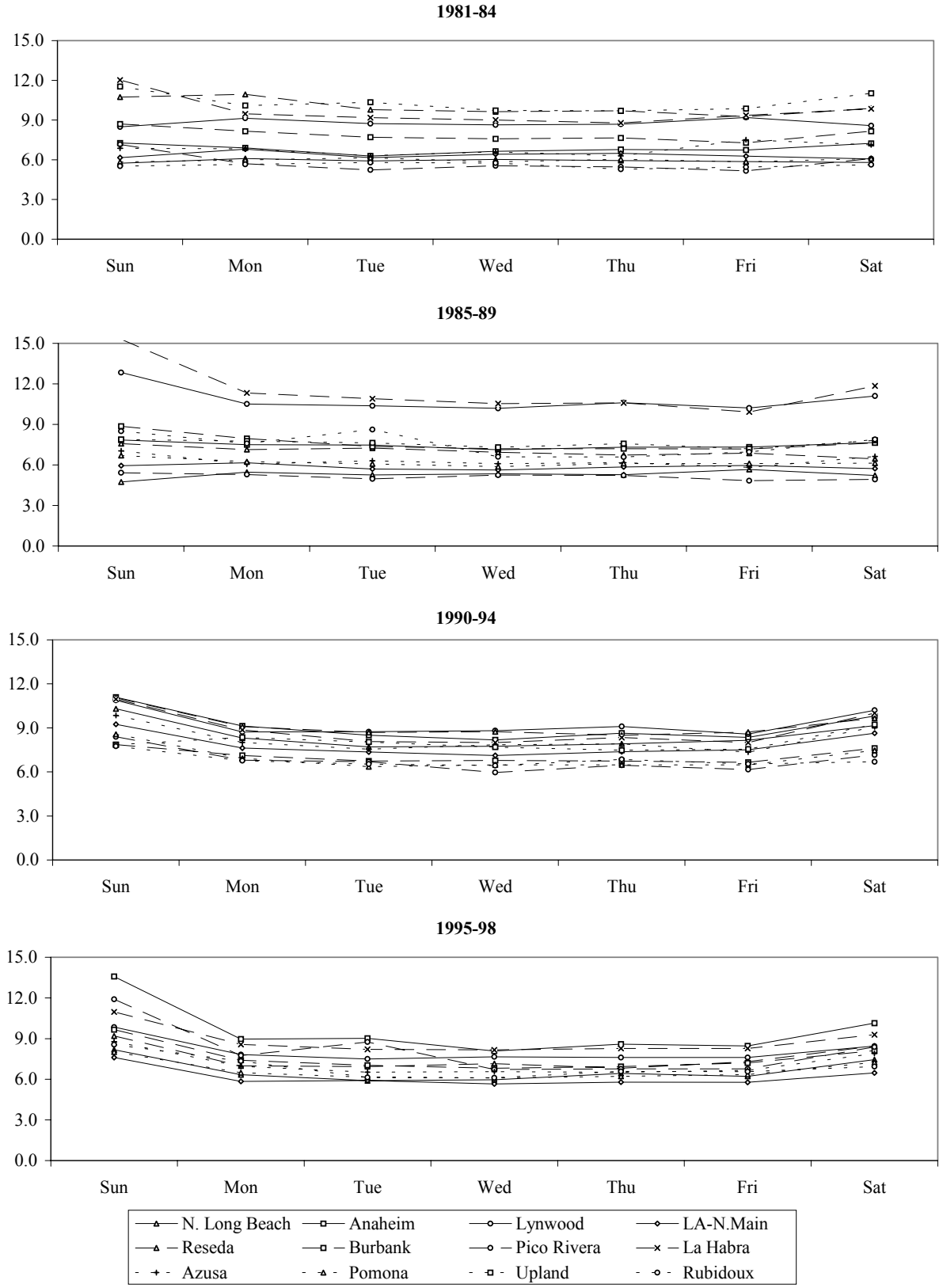


Figure 2.6-1. Average daily 6-9 a.m. (PDT) NMHC/NOx in the SoCAB by day of the week.

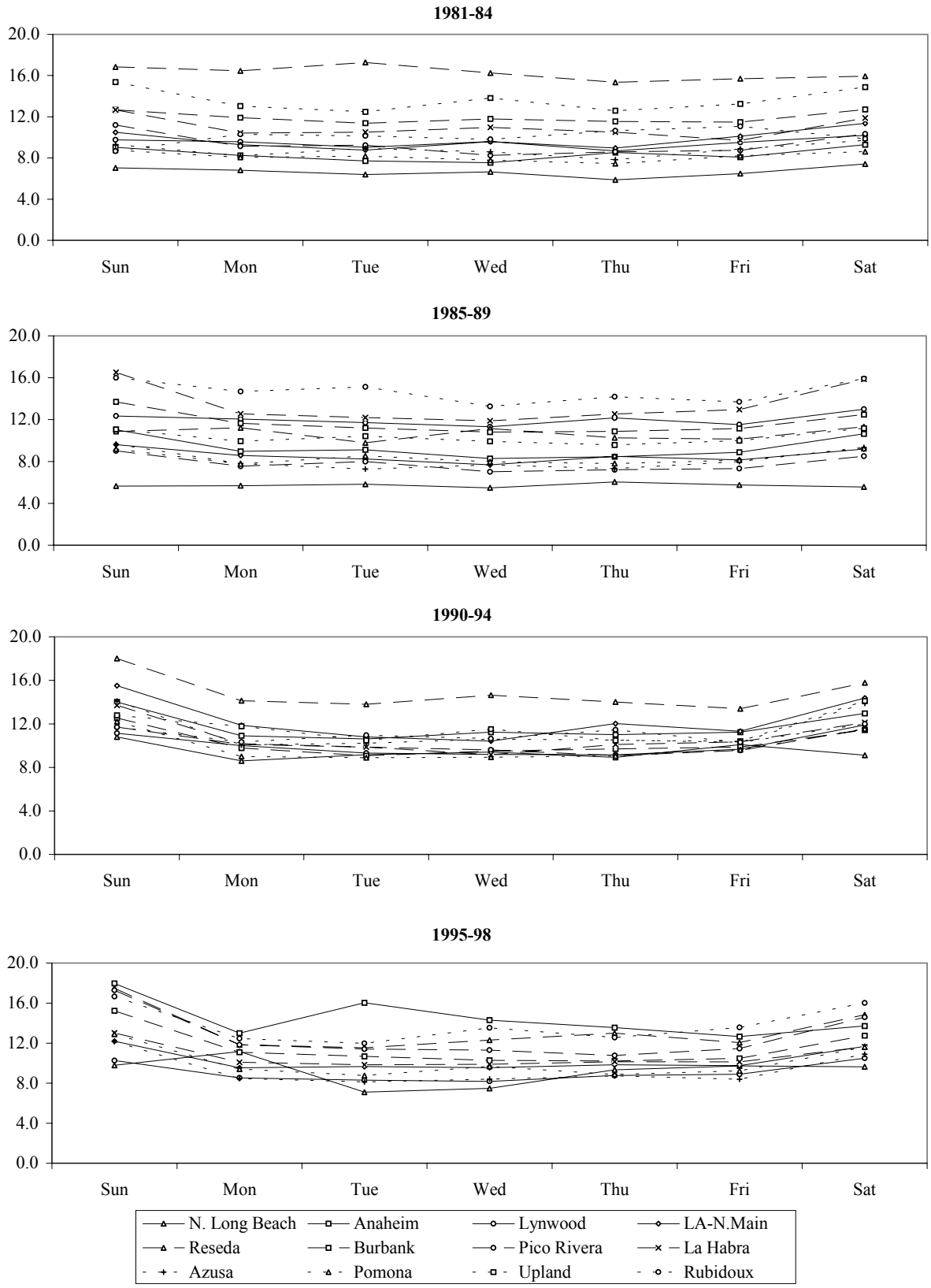


Figure 2.6-2. Average daily NMHC/NOx at maximum ozone in the SoCAB by day of the week.

3. CHARACTERIZATION OF THE CURRENT WEEKEND OZONE EFFECT IN THE SOUTH COAST AIR BASIN

This section summarizes current observations of the weekend effect for the summers of 1999 and 2000 based upon ambient data from the South Coast Air Quality Management District (SCAQMD) Photochemical Assessment Monitoring Stations (PAMS) in Azusa, Pico Rivera, and Upland and the California Air Resources Board ozone precursor trends monitoring at the SCAQMD monitoring station in downtown Los Angeles – North Main. The analyses focused on relating weekday differences in the diurnal variations of CO, NMHC, NO, and NO2, and NOx with variations in ozone, VOC/NOx ratios, and the ratios of O3 to potential ozone (i.e., O3 plus NOx). Weekday variations of ozone are also related to VOC reactivity, photochemical aging, and estimated photolysis rate parameter for NO2. Current weekdays and weekends observations of the VOC and NOx mixing ratios are superimposed on an ozone isopleth plot along with similar observations from 1987

PAMS ozone precursor monitoring is conducted annually in California during the peak ozone season (July 1 to September 30). The enhanced ambient air monitoring at PAMS was established under Title I, Section 182, of the 1990 CAAA. There are five PAMS sites in operation in the SoCAB. The PAMS network includes sites to characterize precursor emission sources within the area (Type 2), and transport of ozone and its precursors into (Type 1) and out of the area (Type 3 and 4). Each station measures speciated hydrocarbons, ozone, oxides of nitrogen, and surface meteorological data. Sampling for carbonyl compounds is required at Type 2 sites only. PAMS network operations in the South Coast Air Basin (SoCAB) began in 1994 at the Pico Rivera (Type 2) and Upland (Type 4) monitoring stations. The network was completed with the addition of PAMS operations at Azusa (Type 3) in 1995, and at Hawthorne (Type 1) and Burbank (Type 2) in 1997. In addition, the ARB continues to measure speciated nonmethane organic compounds (NMOC) at Los Angeles – North Main as part of the long-term trends network that was originally established by the NMOC program. PAMS use EPA methods TO-14 and TO-11 for sampling and analysis of speciated hydrocarbons (EPA, 1991) and carbonyl compounds, respectively. The database consists of 55 individual hydrocarbons, total NMOC, and three carbonyl compounds (formaldehyde, acetaldehyde, and acetone). ARB collects one 3-hour sample every third day at Los Angeles – North Main beginning at 0600, PDT. Eight 3-hour hydrocarbon samples (0000-0300, 0300-0600, 0600-0900, 0900-1200, 1200-1500, 1500-1800, 1800-2100, and 2100-2400, PDT) are collected every day at Type 2 PAMS sites and every third day at all other PAMS sites. In addition, one 24-hour sample is required every sixth day year-round at Type 2 sites and during the summer monitoring period at all other sites.

Several terms are used in this section that represent subsets of VOC. These terms are operational definitions and reflect the sensitivity and selectivity of the analytical methods. Non-methane hydrocarbons (NMHC) are defined as C_2 through C_{11} hydrocarbons collected in stainless steel canisters and measured by gas chromatography with flame ionization detection (GC-FID) by EPA method TO-14A (U.S. EPA, 1997). Known halocarbons and oxygenated compounds (e.g., aldehydes, ketones, ethers and alcohols) are excluded from NMHC. Carbonyl compounds are aldehydes and ketones, the most common being formaldehyde, acetaldehyde, and acetone. Carbonyl compounds are operationally defined as C_1 to C_7 oxygenated compounds measured by collection on acidified 2,4-dinitrophenylhydrazine (DNPH)-impregnated C_{18} or silica gel cartridges and analyzed by high performance liquid chromatography with UV detection

(HPLC/UV). PAMS carbonyl data normally include only formaldehyde, acetaldehyde, and acetone. Total non-methane organic compounds (NMOC) are the sum of quantifiable peaks by EPA method TO-14A, including unidentified but excluding halocarbons, or by continuous instruments with flame ionization detection. Measured NMOC will be lower for laboratories employing water management. NMOC also refers to the sum of NMHC plus carbonyl compounds by TO-11.

3.1 Weekday Differences in Peak Levels and Diurnal Variations of Ozone

Historic trends in the average daily maximum hour ozone in the SoCAB show that both the magnitude and spatial extent of the weekend ozone effect have increased over the period from 1981 to 1998, especially during the 1990's. Reductions in peak ozone levels in the central portion of the basin were also greater during the 1990s. Data for the summers of 1999 and 2000 show a continuation of these trends through the end of the decade. Figures 3.1-1a through 3.1-1d show the mean diurnal variations in ozone mixing ratios on Saturdays, Sundays, and weekdays for the years 1980-85, 1986-1990, 1991-94, 1995-98, and 1999-2000 for Los Angeles – North Main, Azusa, Upland, and Rubidoux (listed in order of location from the western to eastern portion of the basin), respectively.

In the early 1980s, the highest ozone levels occurred on weekdays at Upland and Rubidoux, and on Saturdays and weekdays at Azusa. Occurrences of highest peak ozone levels on Sundays were observed at Los Angeles – North Main. By the late 1990s, the highest ozone levels occur on Sundays at all sites with the exception of Rubidoux where the highest ozone occurred on Saturday. The largest reductions in peak ozone levels over the past two decades are in the central basin. In the western basin, represented by Los Angeles – North Main, the mean peak current (1999-2000) ozone levels are about 60 ppb lower than in 1980-85 for all days of the week. In contrast, decreases in peak ozone in the central basin (Azusa and Upland) have been greater on weekdays (~ 100 to 110 ppb) than on Saturdays (~ 70 to 90 ppb) or Sundays (60 to 70 ppb). While the reductions in peak ozone for weekdays were roughly linear over the past two decades, most of the reductions on weekends occurred during mid to late 1990's. The diurnal variations of ozone at Los Angeles – North Main show a shift of about 2 hours in the timing of peak ozone during the past two decades. While ozone reached its peak earlier in the western basin in the 1980s and early 90s, there is now little difference in the timing of maximum ozone between the western and central basin. With decreasing rates of ozone accumulation and therefore lower ozone concentrations, we speculate that the onset of ventilation has become a more significant factor in the diurnal variation of ozone in the western basin. Diurnal variations in patterns of transport and solar radiation, factors that have not changed with time, are probably more important in the timing of maximum ozone in downwind areas.

The plot of the mean day-of-the-week variations in daily maximum ozone mixing ratios in Figure 3.1-2 shows that the weekday differences are similar throughout the western and central basin. Table 3.1-1a lists the mean daily maximum ozone at Los Angeles – North Main, Azusa, Pico Rivera, and Upland by day of the week for summer 1999 and 2000. Ratios of the mean daily maximum ozone to the midweek values (mean of Tuesday to Thursday) are shown in Table 3.1-1b. The peak ozone levels on Sundays and Saturdays are about 40 and 25 percent higher than midweek values, respectively. The majority of ozone exceedances in the SoCAB now occur on Sundays.

3.2 Weekday Differences in Diurnal Variations of VOC, NOx, and VOC/NOx Ratios

The diurnal variations in the mixing ratios of VOC and NOx depend on the spatial and temporal variations of their emissions, and the diurnal variations in the chemical and physical processes that affect their transformations and dispersion. Tables 3.2-1 through 3.2-5 show the mean concentrations of NO, NO_2, NOx, and NMHC and NMHC/NOx ratios by 3-hour periods for each day of the week for Azusa, Los Angeles – N. Main, Pico Rivera, and Upland for the summers of 1999 and 2000. The averages for NO, NO_2 and NOx include only periods that correspond to the PAMS NMHC data (i.e., every third day for type 1, 3, and 4 sites). The mean NMHC/NOx ratios are means of the individual 3-hour periods. The ratios of the concentrations of NO on Saturday and Sunday to midweek (Tuesday to Thursday) are about one-half and one-third, respectively, during the 12-hour period from 0300 to 1500 (PDT). These ratios are constant throughout this period with mean Sunday/midweek ratios of 0.86, 0.35, 0.34, and 0.33 during the carryover (0000-0300), ozone inhibition (0600-0900), ozone accumulation (0900-1200), and peak ozone (1200-1500) periods, respectively. The corresponding Saturday/midweek ratios are 1.15, 0.60, 0.59, and 0.54, respectively. The four-site mean weekend to midweek ratios for NO_2, NOx and NMHC during 0600-0900 are 0.73, 0.48, and 0.61, respectively, on Sunday and 0.89, 0.69, and 0.77, respectively, on Saturday. The day-of-the-week variations for NO and NO_2 are shown as column plots in Figure 3.2-1a for times corresponding to the carryover, ozone inhibition, ozone accumulation, and peak ozone periods. The corresponding day-of-the-week variations are shown for NMHC and NMHC/NOx in Figure 3.2-1b. The ranges in the columns are the standard deviations of the mean mixing ratios at the four sites. The decrease in mixing ratios on weekends relative to weekdays is proportionately greater for NO than NMHC for all times of the day resulting in lower weekend NMHC/NOx ratios.

The four-site mean NMHC/NOx ratios during 0600-0900 ranged from 31 to 59 percent higher on Sunday (mean of 46 percent) and 20 to 39 percent higher on Saturday (mean of 29 percent). The mean 6-9 a.m. NMHC/NOx ratio (ppbC/ppbv) is 4.9 and 5.5 on Saturday and Sunday, respectively and increases to a high of 6.7 and 7.5 during the period of peak ozone (1200-1500). The mean NMHC/NOx ratio is 4.6 on Monday and ranges from 3.7 to 3.9 for other weekdays. The mean midday NMHC/NOx ratios do not exceed seven. NMHC/NOx ratios have steadily decreased over time because of the greater proportional reduction of VOC emissions. Current NMHC/NOx ratios in the SoCAB are about half relative to the ratios observed during the 1987 Southern California Air Quality Study (SCAQS). SCAQS (Lawson, 1990) included eleven days of intensive measurements during the summer of 1987. One of the eleven days occurred on a Saturday. All other sampling days were on weekdays. Mean 7-8 a.m. NMHC/NOx ratios of 8.8 (standard error of 1.0) and 7.5 (standard error of 0.4) were observed during SCAQS at Los Angeles – North Main and Azusa, respectively (Fujita et al., 1992). Current mean 6-9 a.m. weekday NMHC/NOx ratios range from 3.2 to 4.6 at Los Angeles – North Main and from 3.5 to 5.6 at Azusa. The mean 7-8 a.m. NMHC and NOx mixing ratios during SCAQS were 1087 ppbC and 139 ppb, respectively, at Los Angeles – North Main and 812 ppbC and 117 ppb, respectively at Azusa. Current mean 6-9 a.m. weekday NMHC and NOx mixing ratios range from 322 to 544 ppbC and 119 to 172 ppb, respectively, for Los Angeles – North Main and 348 to 598 ppbC and 96 to 122 ppb, respectively, for Azusa. These data indicate that the ~50 percent decrease in NMHC/NOx ratios in the SoCAB from 1987 to 1999-2000 can be attributed primarily to reductions in hydrocarbon emissions.

3.3 Weekday Variations in VOC Reactivity

In addition to VOC to NOx ratios, the reactivity of individual organic species with HO radical also affects the rate of ozone formation. Table 3.3-1a shows the day-of-the-week differences in the diurnal variations of sum of PAMS species, NMHC, CO, NOx, and ratios of acetylene to PAMS and NMHC at Pico Rivera, summer 1999-2000. Formaldehyde (ppbv), xylene/benzene and formaldehyde/NMHC ratios, maximum incremental reactivity (MIR) (grams of ozone per gram) for NMHC and NMHC plus carbonyl compounds are shown in Table 3.3-1b. The MIR scale (Carter, 1994) measures the effect of a VOC on O_3 formation in a set of standard airshed scenarios that represent NOx conditions where ozone formation is most sensitive to VOCs (Carter, 1994; CARB, 1993). The MIR of the 55 PAMS target species is slightly lower on weekends. Formaldehyde is slightly higher during weekends in the afternoon. With the addition of carbonyl compounds in the MIR calculations, weekend MIRs are equal to weekdays during the morning and slightly higher during the afternoons. While the reactivity of the VOCs are comparable or slightly lower on weekends, higher ratios of formaldehyde to sum of PAMS, lower ratios of more reactive species to less reactive species (i.e., xylenes/benzene) indicate greater photochemical activity on weekends.

3.4 Weekday Variations in Diurnal Patterns of Ozone

During the daylight hours, the relative differences between weekdays and weekends in the mixing ratios of NO and O_3 are constant throughout the daylight hours (see Figure 3.4-1). NO is lower on Sunday relative to midweek by about the same ratio for all hours from 0600 to 2000 PDT. Conversely, ozone is higher on Sunday relative to midweek by the same ratio for all daylight hours despite the greater influence of local traffic on NO mixing ratios at Los Angeles – North Main and Pico Rivera relative to Azusa and Upland. These correlations are shown in a series of scatterplots in Figures 3.4-2. The mean hourly ozone and NO mixing ratios during midweek (Tuesday to Thursday) are plotted against the corresponding values for Friday, Saturday and Sunday for Los Angeles, North Main, Pico Rivera, Azusa, and Upland. The data are correlated separately by daylight hours (open symbols) and nighttime hours (solid symbols). As would be expected, correlations of the midweek hourly NO and O_3 mixing ratios with the corresponding hourly values on Friday show little variance with one another. The Saturday/midweek ratios for ozone during the daylight hours ranged from 1.26 to 1.31 at the four sites with a mean of 1.28. The corresponding ratios for NO ranged from 0.51 to 0.69 with a mean of 0.61. The Sunday/midweek ratios for ozone during daylight hours ranged from 1.44 to 1.55 with a mean of 1.50. The ratios for NO ranged from 0.29 to 0.43 with a mean of 0.35. The correlations are extremely good with R^2s of 0.98 or better.

These results suggest that each site has its own relative ozone pattern is fixed for all days of the week for the sites examined. What differentiates weekday from weekend is a multiplicative constant. These results suggest that the weekday-weekend differences in the diurnal pattern of NO and ozone are established early in the morning and the influence of the chemical factors (either emission and/or rate and efficiency of ozone formation) related to this "constant" is maintained throughout the day. The constant offset in the diurnal pattern of ozone and NO is likely related to the initial (i.e., 6-9 a.m.) VOC/NOx ratios. The NMHC/NOx ratio is within the range of four to eight from sunrise to the time of peak ozone so that ozone formation is VOC-sensitive throughout this period. These results are counter to the expectations of NOx

timing hypothesis, which requires a proportional increases in NO and O_3 mixing ratios on weekends later in the morning compared to weekdays The constant proportional offset in the diurnal pattern of ozone and NO is likely related to the initial (i.e., 6-9 a.m.) VOC/NOx ratios. This ratio varies during the weekends from about 4-6 at sunrise to about 6-8 near the time of peak ozone. At this range of NMHC/NOx, ozone formation is VOC-sensitive, which is also counter to the NOx timing hypothesis.

3.5 Theoretical Relationship Between Precursor Emissions and Ozone

Observed ozone concentrations in urban areas are a complicated function of chemistry, transport and time that occur between sources and receptors. Although 3-d grid models, such as UAM-V, allow the direct analysis of the coupling between chemical and physical processes, the treatment of each process must be relatively simple due to computational constraints. In contrast, box models allow more complete representation and analysis of the chemistry. In this section, we use a chemical box model to analyze the chemical transformations that occur as NOx and VOC emissions are transported between sources and receptors. The Regional Atmospheric Chemical Medium (RACM; Stockwell et al., 1997) was used in a chemical box model to calculate ozone isopleths from initial concentrations of VOC determined from measured VOC Concentrations obtained between 6-9 a.m. The simulations were made for periods lasting up to four days using a range of initial VOC and NOx.

EKMA simulations were performed over a range of observed NO_x and VOC mixing ratios. The gas-phase chemical mechanism for the Regional Acid Deposition Model version 2 (RADM2) (Stockwell et al., 1990) was used for this study. The RADM2 mechanism was developed for the modeling of atmospheric chemistry on a regional scale. The inorganic scheme consists of seventeen stable inorganic species and four reactive intermediates. The mechanism includes: (1) alkane chemistry represented by methane, ethane, and three classes of higher alkanes; (2) alkene chemistry represented by ethene, two higher alkene classes representing internal and terminal alkenes and isoprene; (3) a reasonably detailed treatment of aromatic chemistry; (4) carbonyl chemistry represented by formaldehyde, aldehydes, ketones and dicarbonyl species; and (5) most important for this study, explicit, detailed treatment of peroxy radical - peroxy radical reactions. The RADM2 gas phase mechanism has been independently evaluated and tested against environmental chamber data from the Statewide Air Pollution Research Center (SAPRC) of the University of California at Riverside, and from the outdoor chamber at the University of North Carolina (Carter and Lurmann, 1989).

The simulations were not optimized to the conditions of the South Coast Air Basin but they are representative of typical atmospheric chemical conditions. A detailed discussion of the conditions used in these simulations is given in Stockwell et al. (1988). Since summer is the most important season for ozone production the simulations were made for summer conditions. The photolysis rates of twenty-one species were varied over a diurnal cycle representative of conditions near sea level for 40 °N latitude (temperature: 298.15 ˚K; pressure: 1 atm) throughout a typical midsummer day, June 21. The box model simulations employed rate constants diurnally varying solar radiation for 40° latitude and 90° longitude. The fluxes are calculated from a radiative transfer model based on the delta-Eddington technique (Joseph et al., 1976; Madronich, 1987). The transfer model assumes seasonally averaged ozone and aerosol distributions for the continental United States. The model divides the region from the surface of the earth to the top of

the atmosphere into 50 layers. The actinic flux is calculated for 130 spectral intervals. The spectral intervals vary from 1 to 10 nm and are smaller where changes in light absorption by O_3 and large variations in the Raleigh scattering can become a problem. The actinic fluxes are calculated and then integrated with the absorption cross sections and the photodissociation quantum yields to produce the clear sky photolysis rates.

The initial conditions for the simulations are given in Table 3.5-1. The relative humidity was 50%. To calculate the ozone and peroxyacetyl nitrate isopleths, over 650 simulations were performed with varying initial concentrations of NO_x and anthropogenic NMHC. The initial NO_x was varied from 10^{-1} to 10^3 ppb while the initial anthropogenic NMHC was varied from 10^0 to 10^4 ppbC. These ranges are based upon a survey of ambient measurements and span the range observed in both urban and rural areas of the contiguous United States (Kasting and Augustsson, 1980; Roberts, 1983; Sexton and Westburg, 1984; Duce et al., 1983; Arnts and Meeks, 1981; Lonnemann et al., 1978). The total initial NMHC used in the simulations was the sum of a fixed background of NMHC and a varying concentration of anthropogenic NMHC with a speciation typical of atmospheric conditions. The background NMHC composition and concentrations are given in Table 3.5-1 along with the composition of the anthropogenic component. Initial concentrations for ozone, methane and water vapor were fixed for all simulations as listed in Table 3.4-1. The initial SO_2 concentration was taken to be 1 ppb. The simulations were started at sunrise (210 minutes after midnight) and run until noon. They were made without emissions of NO_x or NMHC because these have little effect on the comparison of mechanisms (Stockwell and Lurmann, 1989). The results were plotted as EKMA diagrams. For ozone, ozone efficiency, HO and HO_2 the contour plots were made for solar noon while all other plots were made for sunset of the first simulated day.

Figure 3.5-1 shows that VOC control measures undertaken between 1987 and 2000 have been effective in reducing VOC mixing ratios. Ozone mixing ratios estimated from the EKMA diagram should have been reduced from 200 ppb to an average near 100 ppb in reasonable agreement with observations. The current mixing ratios of VOC and NOx are on the VOC-limited portion of the EKMA diagram for both weekends and weekdays. There is little change in VOC mixing ratios between weekend and weekday, but on weekends there is now a significant reduction in the NO_x mixing ratios. Additional control of NOx in the future in the absence of additional VOC control is likely to increase ozone peak levels in the central basin although it is possible that they will decrease 8-hour O_3 levels in downwind areas such as the San Bernardino Mountains, Palm Springs, and Mohave Desert. The EKMA diagram shows that the decrease in NO_x leads to an increase in ozone mixing ratios of about 40 ppb between weekdays and weekends, and this is consistent with the observations. The EKMA diagram shows that that an ozone disbenefit will result if NO_x emissions are decreased at current levels of VOC until the NO_x mixing ratios decrease to about 10 or 12 ppb where ozone production becomes NO_x-limited.

The VOC/NO_x ratio decreased from near an average of 7.5 during 1987 down to between 3 and 5 during 1999-2000, Figure 3.5-1. On weekends the VOC ratio increases to between 4 and 7 and it may reach 10 or 12. The ozone production efficiency was defined to be the ozone production divided by the sum of NO_x converted to nitric acid and organic nitrates. The efficiency is roughly proportional to the peroxy radical chain length because ozone is generated

through the conversion of NO to NO_2 by peroxy radicals (radical propagation step) and the production of nitric acid and organic nitrates is produced by radical termination steps. The shift in VOC/NO_x ratio increases the average ozone production efficiency from less than 4 to between 4 and 6. Reduced NOx mixing ratios lead to increased HO mixing ratios because there is less radical termination through the HO + NO2 reaction. The simulations show that hydroxyl radical mixing ratios increase with decreasing NO_x mixing ratios. The higher HO mixing ratios lead to the more efficient formation of ozone.

Daytime nitric acid production has decreased between 1987 and 2000 due to the decrease in VOC mixing ratios, Figure 3.5-2. At present mixing ratios of NO_x and VOC, the production of HNO_3 may be reduced by reductions in NO_x. The difference between nitric acid production on Sunday and weekdays would be expected to be lower by about 9 ppb on weekdays. PAN, HCHO, aldehyde and organic nitrates have been reduced due to reductions in VOC mixing ratios but their mixing ratios are not strongly affected by the NO_x mixing ratios at current concentrations so a weekend effect is not expected for these species.

Hydrogen peroxide, organic nitrates and the indicators for photochemical activity $[HNO_3]/[H_2O_2]$ and $[H_2O_2]/[HCHO]$ (Stockwell, 1986) are plotted in Figure 3.5-3. The ozone ridge line is well marked by a value of 10 for the indicator $[HNO_3]/[H_2O_2]$ and by a value of 0.2 for the indicator $[H_2O_2]/[HCHO]$. Comparison of the current NO_x and VOC mixing ratios with the EKMA diagrams shows that the indicator ratios for photochemical activity including $[HNO_3]/[H_2O_2]$ and $[H_2O_2]/[HCHO]$ that ozone production is VOC limited.

Our simulations for EKMA are consistent with a study by Milford et al. (1994) as quoted by Finlayson-Pitts and Pitts (2000). Milford et al. found that for conditions that are similar to present-day conditions in the SoCAB on Sundays, VOC near 300 ppbC and NO_x at 20 to 30 ppb, that the rate of ozone production increases with decreases in NO_x concentrations. The study showed that an ozone disbenefit results if present-day Sunday NO_x concentrations are reduced. The Milford et al. (1994) study also shows that ozone production rates increase during the day because NO_x is consumed faster than VOC, which increases the VOC to NO_x ratio. Given the present-day concentrations of NO_x, increases in its emissions during the day will decrease, not increase, ozone production rates. However, on the basis of the Milford et al. study, the NO_x timing hypotheses will become an important mechanism at the same point when reductions in NO_x emissions lead to lower ozone production rates. Modeling studies should be made with updated emissions inventories and models to verify the results of our modeling results and Milford et al. (1994).

3.6 Weekday Variations in Empirically-Estimated Photolysis Parameter

There was no evidence that the weekday/weekend ozone effect is caused by variations in soot concentrations affecting J_{NO2}. The photolysis rate parameter for NO_2 (J_{NO2}) was calculated from an extended version of the O_3-NO-NO photostationary state expression.

$$j_{NO_2} = \frac{k_{NO+O_3}[O_3][NO]}{[NO_2]} + \frac{1}{[NO_2]}\frac{\Delta[O_3]}{\Delta t}$$

Although there is a large uncertainty in J_{NO2}, calculated by this method the analysis showed that J_{NO2} increased over the period from 1980 to 2000, Figure 3.6-1. This long-term trend in J_{NO2} is consistent with the trend to lower soot emissions. However, the maximum J_{NO2} values were slightly higher on weekdays than on Sunday for the entire period from 1980 to 2000. These weekend/weekday variations in J_{NO2} are not consistent with the hypothesis that increased soot concentrations reduce J_{NO2} on weekdays.

The ratio of ozone to potential ozone, $[O_3]/([O_3] + [NO_x]$, is a measure of the fraction of the possible ozone mixing ratio for a given amount of NO_x. A value of zero indicates that there is no ozone while a value of unity indicates that all of the NO_x has been converted to ozone. The long-term trend of the ratio from 1980 to 2000 is not constant (or consistent??)with the soot hypothesis, Figure 3.6-2. If all other conditions were constant, a higher J_{NO2} should yield a more complete conversion of NO_x to ozone. The figure shows that this has not happened. The ratio of ozone to potential ozone has dropped markedly on weekdays over this time interval. The figure shows that there is a more complete conversion of NO_x to ozone on weekends, but as the previous EKMA analysis has shown this is caused by the more efficient production of ozone due to lower NO_x mixing ratios rather than an increase in J_{NO2}.

3.7 Summary of Findings

Weekday Differences in Peak Levels and Diurnal Variations of Ozone

- The peak ozone levels on Sundays and Saturdays are currently about 40 and 25 percent higher than midweek values, respectively. The majority of ozone exceedances in the SoCAB now occur on Sundays.

- While the reductions in peak ozone for weekdays were roughly linear over the past two decades, most of the reductions on weekends occurred during mid to late 1990s. Weekday differences are similar throughout the western and central basin.

- In the early 1980s, the highest ozone levels occurred on weekdays at Upland and Rubidoux, and on Saturdays and weekdays at Azusa. Occurrences of highest peak ozone levels on Sundays were observed at Los Angeles – North Main. By the late 1990s, the highest ozone levels occur on Sundays at all sites with the exception of Rubidoux where the highest ozone occurred on Saturday.

- The largest reductions in peak ozone levels over the past two decades are in the central basin. In the western basin, represented by Los Angeles – North Main, the mean peak current (1999-2000) ozone levels are about 60 ppb lower than in 1980-85 for all days of the week. In contrast, decreases in peak ozone in the central basin (Azusa and Upland) have been greater on weekdays (~ 100 to 110 ppb) than on Saturdays (~ 70 to 90 ppb) or Sundays (60 to 70 ppb).

Weekday Differences in Diurnal Variations of VOC, NOx, and VOC/NOx Ratios

- The ratios of the concentrations of NO on Saturday and Sunday to midweek (Tuesday to Thursday) are about one-half and one-third, respectively, during the 12-hour period from 0300 to 1500 (PDT).

- The decrease in mixing ratios on weekends relative to weekdays is proportionately greater for NO than NMHC for all times of the day resulting in lower weekend NMHC/NOx ratios.

- The four-site mean NMHC/NOx ratios during 0600-0900 ranged from 31 to 59 percent higher on Sunday (mean of 46 percent) and 20 to 39 percent higher on Saturday (mean of 29 percent). The mean 6-9 a.m. NMHC/NOx ratio (ppbC/ppbv) is 4.9 and 5.5 on Saturday and Sunday, respectively and increases to a high of 6.7 and 7.5 during the period of peak ozone (1200-1500). The mean NMHC/NOx ratio is 4.6 on Monday and ranges from 3.7 to 3.9 for other weekdays. The mean midday NMHC/NOx ratios do not exceed seven.

- Current (1999-2000) NMHC/NOx ratios in the SoCAB are about half relative to the ratios observed during the 1987 Southern California Air Quality Study. This decrease is due primarily to reductions in hydrocarbon emissions.

- The NMHC/NOx ratio varies during the weekends in the western and central basin from about 4-6 at sunrise to about 6-8 near the time of peak ozone.

- During the daylight hours, the relative differences between weekdays and weekends in the mixing ratios of NO and O_3 are constant throughout the daylight hours. Weekday-weekend differences in ozone mixing ratios are determined by a single constant for all daylight hours. The same is true of NO mixing ratios.

Weekday Variations in VOC Reactivity

- The maximum incremental reactivity of the 55 PAMS target species is slightly lower on weekends. Formaldehyde is slightly higher during weekends in the afternoon. With the addition of carbonyl compounds in the MIR calculations, weekend MIRs are equal to weekdays during the morning and slightly higher during the afternoons.

- While the reactivity of the VOCs are comparable or slightly lower on weekends, higher ratios of formaldehyde to sum of PAMS, lower ratios of more reactive species to less reactive species (i.e., xylenes/benzene) indicate greater photochemical activity on weekends.

Comparison of Weekday Variations in Diurnal Patterns of Nitric Oxides and Ozone

- During the daylight hours, NO is lower on weekends relative to midweek by about the same ratio for all daylight hours. Conversely, ozone is higher on Sunday relative to midweek by the same ratio for all daylight hours.

- Results suggest that the weekday-weekend differences in the diurnal pattern of NO and ozone are established early in the morning and the influence of the factors related to this "constant" is maintained throughout the day.

- The constant offset in the diurnal pattern of ozone and NO is likely related to the initial (i.e., 6-9 a.m.) VOC/NOx ratios. The NMHC/NOx ratio is within the range of four to eight from sunrise to the time of peak ozone so that ozone formation is VOC-limited throughout this period.

Theoretical Relationship Between Precursor Emissions and Ozone

- The current mixing ratios of VOC and NOx are on the VOC- limited portion of the EKMA diagram for both weekends and weekdays. The EKMA diagram shows that the decrease in NO_x leads to an increase in ozone mixing ratios of about 40 ppb between weekdays and weekends, and this is consistent with the observations.

- The EKMA diagram shows that that an ozone disbenefit will result if NO_x emissions are decreased at current levels of VOC until the NO_x mixing ratios decrease to about 10 or 12 ppb where ozone production becomes NO_x- limited.

- VOC control measures undertaken between 1987 and 2000 have been effective in reducing VOC mixing ratios. Ozone mixing ratios estimated from the EKMA diagram should have been reduced from 200 ppb to an average near 100 ppb in reasonable agreement with observations. The 6-9 a.m. VOC/NO_x ratio decreased from near an average of 7.5 during 1987 down to between three and five during 1999-2000.

- Reduced NOx mixing ratios lead to increased HO mixing ratios because there is less radical termination through the HO + NO2 reaction. The simulations show that hydroxyl radical mixing ratios increase with decreasing NO_x mixing ratios. The higher HO mixing ratios lead to the more efficient formation of ozone.

- The shift in VOC/NO_x ratio increases the average ozone production efficiency from less than 4 to between 4 and 6. The ozone production efficiency is defined to be the ozone production divided by the sum of NO_x converted to nitric acid and organic nitrates.

- Daytime nitric acid production has decreased between 1987 and 2000 due to the decrease in VOC mixing ratios. At present mixing ratios of NO_x and VOC, the production of HNO_3 may be reduced by lowering NO_x. The difference between nitric acid production on Sunday and weekdays would be expected to be lower by about 9 ppb on weekdays. PAN, HCHO, aldehyde and organic nitrates have been reduced due to reductions in VOC mixing ratios but their mixing ratios are not strongly affected by the NO_x mixing ratios at current concentrations so a weekend effect is not expected for these species.

- The ozone ridgeline is well marked by a value of 10 for the indicator $[HNO_3]/[H_2O_2]$ and by a value of 0.2 for the indicator $[H_2O_2]/[HCHO]$. Comparison of the current NO_x and VOC mixing ratios with the EKMA diagrams shows that the indicator ratios for photochemical

activity including $[HNO_3]/[H_2O_2]$ and $[H_2O_2]/[HCHO]$ that ozone production is VOC limited.

Weekday Variations in Empirically-Estimated Photolysis Parameter

- The long-term trend in J_{NO2} is consistent with the trend to lower soot emissions. However, the weekday-weekend differences in J_{NO2} were small, and the maximum J_{NO2} on weekdays was slightly higher than on Sunday for the entire period from 1980 to 2000. The weekend/weekday variation in J_{NO2} is not consistent with the hypothesis that increased soot concentrations reduce J_{NO2} on weekdays.

- The ratio of ozone to potential ozone has dropped markedly on weekdays from 1980 to 2000 relative to weekends, indicating that there is a more complete conversion of NO_x to ozone on weekends. The long-term trend of the ratio from 1980 to 2000 is not consistent with the soot hypothesis. If all other conditions were constant, a higher J_{NO2} should yield a more complete conversion of NO_x to ozone. The data show that this has not happened. However, as the EKMA analysis has shown this is caused by the more efficient production of ozone due to lower NO_x mixing ratios rather than an increase in J_{NO2}.

Table 3.1-1a
Mean daily maximum ozone by day-of-week (ppb)

	Sunday	Monday	Tuesday	Wednesday	Thursday	Friday	Saturday
Los Angeles							
1999	71	65	55	50	40	50	61
2000	66	50	51	51	52	49	58
Azusa							
1999	85	63	53	54	55	54	71
2000	91	64	59	64	62	61	79
Pico Rivera							
1999	78	64	55	53	50	54	67
2000	70	53	52	52	52	50	63
Upland							
1999	93	74	64	67	61	67	83
2000	90	63	64	73	67	66	81

Table 3.1-1b
Ratio of mean daily maximum ozone to mean midweek (Tues-Thur) maximum (percent)

	Sunday	Monday	Tuesday	Wednesday	Thursday	Friday	Saturday
Los Angeles							
1999	147%	134%	114%	104%	82%	103%	127%
2000	129%	98%	100%	99%	101%	96%	113%
Azusa							
1999	157%	117%	98%	100%	101%	99%	132%
2000	148%	104%	96%	104%	100%	99%	128%
Pico Rivera							
1999	149%	122%	104%	101%	95%	103%	127%
2000	135%	103%	100%	100%	100%	96%	123%
Upland							
1999	146%	115%	100%	105%	95%	105%	129%
2000	133%	93%	95%	107%	98%	98%	119%

Table 3.2-1
Day-of-the-Week Variations in Mean Nitric Oxide (ppb) by Time of Day for Azusa, Los Angeles N. Main, Pico Rivera, and Upland for Summer 1999-2000

HOUR (PDT):	00-03	03-06	06-09	09-12	12-15	15-18	18-21	21-24
Azusa								
Sunday	13	12	22	12	3	2	1	5
Monday	11	19	60	30	8	4	4	12
Tuesday	20	26	81	38	11	6	4	12
Wednesday	21	27	70	36	9	5	4	10
Thursday	20	21	65	36	10	5	5	12
Friday	20	26	65	34	9	5	3	12
Saturday	19	20	38	21	5	2	2	6
Los Angeles								
Sunday	32	38	47	15	4	1	1	12
Monday	32	43	81	38	9	5	4	23
Tuesday	46	67	126	53	11	5	5	21
Wednesday	38	53	104	44	9	4	6	23
Thursday	34	44	102	49	9	5	7	21
Friday	29	43	92	43	9	5	5	16
Saturday	34	37	61	27	6	3	3	13
Pico Rivera								
Sunday	30	35	36	12	4	5	6	19
Monday	38	49	79	36	11	7	5	19
Tuesday	54	81	109	42	14	8	12	19
Wednesday	47	74	102	40	10	6	10	25
Thursday	55	68	113	42	13	9	11	26
Friday	44	61	85	33	11	7	5	24
Saturday	47	49	67	22	6	4	4	17
Upland								
Sunday	14	10	18	13	2	1	2	7
Monday	8	7	45	28	7	3	5	11
Tuesday	10	8	61	32	8	4	5	11
Wednesday	9	10	46	26	6	3	6	16
Thursday	11	9	63	30	8	4	7	17
Friday	18	18	62	34	7	4	5	14
Saturday	19	15	39	21	4	1	2	7
Mean								
Sunday	22	24	31	13	3	2	3	11
Monday	22	30	66	33	9	5	5	16
Tuesday	33	46	94	41	11	6	7	16
Wednesday	29	41	81	37	9	5	7	19
Thursday	30	36	86	39	10	6	8	19
Friday	28	37	76	36	9	5	5	17
Saturday	30	30	51	23	5	3	3	11

Table 3.2-2
Day-of-the-Week Variations in Mean Nitrogen Dioxide (ppb) by Time of Day for Azusa, Los Angeles N. Main, Pico Rivera, and Upland for Summer 1999-2000

HOUR (PDT):	00-03	03-06	06-09	09-12	12-15	15-18	18-21	21-24
Azusa								
Sunday	39	33	29	31	27	25	32	40
Monday	35	32	36	48	45	40	47	51
Tuesday	43	38	41	54	55	45	47	51
Wednesday	44	38	40	52	50	40	42	46
Thursday	39	35	39	52	51	44	43	48
Friday	40	35	37	50	50	39	42	47
Saturday	40	36	34	42	37	30	34	43
Los Angeles								
Sunday	34	31	31	33	26	18	25	33
Monday	32	30	38	50	37	28	36	40
Tuesday	39	36	46	60	42	29	35	41
Wednesday	36	32	41	54	37	27	36	37
Thursday	34	31	42	53	36	26	33	38
Friday	33	31	39	51	36	24	32	37
Saturday	35	31	35	44	33	21	28	35
Pico Rivera								
Sunday	32	28	25	25	25	23	29	34
Monday	28	28	30	45	41	34	40	41
Tuesday	37	33	38	53	49	37	42	42
Wednesday	36	33	36	50	41	31	37	40
Thursday	35	31	35	49	44	32	38	38
Friday	32	29	34	45	41	31	37	38
Saturday	33	29	31	38	34	25	31	36
Upland								
Sunday	38	30	35	40	24	24	38	43
Monday	35	29	41	50	37	38	52	52
Tuesday	43	35	44	56	43	44	52	51
Wednesday	43	35	42	52	39	39	50	50
Thursday	39	34	46	57	42	43	51	51
Friday	41	35	45	60	41	38	48	50
Saturday	41	36	41	48	33	29	41	45
Mean								
Sunday	36	31	30	32	26	23	31	38
Monday	33	30	36	48	40	35	44	46
Tuesday	41	36	42	56	47	39	44	46
Wednesday	40	35	40	52	42	34	41	43
Thursday	37	33	41	53	43	36	41	44
Friday	37	33	39	52	42	33	40	43
Saturday	37	33	35	43	34	26	34	40

Table 3.2-3
Day-of-the-Week Variations in Mean Nitrogen Oxides (ppb) by Time of Day for Azusa, Los Angeles N. Main, Pico Rivera, and Upland for Summer 1999-2000

HOUR (PDT):	00-03	03-06	06-09	09-12	12-15	15-18	18-21	21-24
Azusa								
Sunday	52	45	52	44	30	27	34	45
Monday	47	51	96	78	53	44	51	64
Tuesday	63	64	122	93	66	51	51	63
Wednesday	65	65	110	88	59	45	46	57
Thursday	60	57	105	88	62	50	48	60
Friday	60	61	103	84	60	45	46	60
Saturday	60	56	73	64	43	32	36	49
Los Angeles								
Sunday	67	69	78	48	30	20	26	45
Monday	65	73	119	89	46	33	40	63
Tuesday	85	103	172	113	53	34	41	63
Wednesday	75	85	146	99	47	32	42	61
Thursday	69	76	144	102	46	32	40	60
Friday	63	74	132	94	45	30	37	54
Saturday	70	68	96	71	39	25	32	48
Pico Rivera								
Sunday	63	63	62	38	30	29	35	53
Monday	67	77	110	82	52	42	46	60
Tuesday	91	115	147	96	63	45	54	61
Wednesday	84	107	139	91	52	38	48	66
Thursday	90	99	148	91	58	42	49	65
Friday	77	90	119	78	52	38	42	62
Saturday	80	79	99	61	41	30	35	53
Upland								
Sunday	52	41	53	53	27	25	41	50
Monday	44	37	87	78	44	42	57	64
Tuesday	54	43	106	89	51	48	58	62
Wednesday	52	45	88	79	45	43	57	66
Thursday	50	44	109	88	50	48	58	68
Friday	60	54	107	95	48	42	53	65
Saturday	61	51	81	69	37	31	43	53
Mean								
Sunday	59	55	61	46	29	25	34	48
Monday	56	60	103	82	49	40	49	63
Tuesday	73	81	137	98	58	45	51	62
Wednesday	69	76	121	89	51	40	48	63
Thursday	67	69	127	92	54	43	49	63
Friday	65	70	115	88	51	39	45	60
Saturday	68	64	87	66	40	30	37	51

Table 3.2-4
Day-of-the-Week Variations in Mean Nonmethane Hydrocarbons (ppb) by Time of Day for Azusa, Los Angeles N. Main, Pico Rivera, and Upland for Summer 1999-2000

HOUR (PDT):	00-03	03-06	06-09	09-12	12-15	15-18	18-21	21-24
Azusa								
Sunday	170	284	296	241	184	192	201	232
Monday	273	252	348	349	296	231	260	243
Tuesday	269	402	529	360	294	284	255	310
Wednesday	337	449	530	392	342	314	303	320
Thursday	233	431	598	354	373	293	282	537
Friday	189	389	491	373	356	324	260	286
Saturday	211	378	378	295	311	208	199	246
Los Angeles								
Sunday			311					
Monday			322					
Tuesday			421					
Wednesday			544					
Thursday			529					
Friday			463					
Saturday			365					
Pico Rivera								
Sunday	201	202	206	187	193	165	162	208
Monday	202	230	370	341	293	221	212	206
Tuesday	212	293	470	465	326	254	237	251
Wednesday	278	325	426	341	243	218	211	262
Thursday	261	278	408	342	349	281	246	261
Friday	234	231	358	327	267	200	179	220
Saturday	220	229	288	261	236	174	158	208
Upland								
Sunday	228	347	350	236	184	148	195	331
Monday	290	315	317	286	253	297	250	279
Tuesday	174	250	318	199	225	240	187	362
Wednesday	284	480	466	352	251	318	370	280
Thursday	316	445	550	369	287	315	272	349
Friday	315	489	515	375	275	262	247	330
Saturday	284	486	441	325	265	266	247	354
Mean								
Sunday	200	278	291	221	187	168	186	257
Monday	255	266	339	325	281	250	241	243
Tuesday	218	315	435	341	282	259	226	308
Wednesday	300	418	492	362	279	283	295	287
Thursday	270	385	521	355	336	296	267	382
Friday	246	370	457	358	299	262	229	279
Saturday	238	364	368	294	271	216	201	269

Table 3.2-5
Day-of-the-Week Variations in Mean NMHC/NOx Ratios by Time of Day for Azusa, Los Angeles N. Main, Pico Rivera, and Upland for Summer 1999-2000

HOUR (PDT):	00-03	03-06	06-09	09-12	12-15	15-18	18-21	21-24
Azusa								
Sunday	3.7	8.4	6.4	6.9	7.8	6.9	5.2	4.4
Monday	5.0	5.1	5.6	7.4	7.3	5.9	5.3	4.6
Tuesday	3.2	5.8	4.7	5.1	5.0	5.7	4.7	4.6
Wednesday	4.7	4.9	4.1	4.8	6.6	6.7	5.0	4.8
Thursday	3.0	4.4	3.5	4.0	5.9	5.3	4.3	6.8
Friday	2.5	4.3	4.3	4.7	6.1	7.6	4.6	4.2
Saturday	2.7	6.5	5.4	5.0	7.4	6.3	5.2	4.5
Los Angeles								
Sunday			4.9					
Monday			4.6					
Tuesday			3.2					
Wednesday			3.7					
Thursday			4.2					
Friday			3.2					
Saturday			4.5					
Pico Rivera								
Sunday	5.3	4.8	5.7	6.1	6.5	5.1	3.9	3.6
Monday	4.6	3.4	3.9	4.4	5.7	5.1	4.3	3.1
Tuesday	2.7	2.9	3.8	4.7	5.9	5.1	3.9	3.3
Wednesday	3.3	2.6	3.4	4.5	5.4	5.2	3.7	3.2
Thursday	3.7	2.2	3.5	4.2	7.9	7.7	4.2	3.3
Friday	3.4	2.7	3.8	4.5	5.4	4.9	3.9	3.6
Saturday	4.4	3.4	4.4	5.4	6.3	5.3	4.4	3.9
Upland								
Sunday	3.2	6.5	5.2	5.3	8.1	5.0	3.7	5.5
Monday	7.7	5.8	4.2	4.8	6.5	6.3	4.6	5.0
Tuesday	2.3	4.6	3.5	4.5	4.9	4.9	3.2	5.1
Wednesday	4.8	6.3	4.0	4.5	5.2	6.1	4.8	4.8
Thursday	5.4	4.8	3.8	4.7	6.3	5.0	3.5	4.3
Friday	5.2	6.4	4.4	4.6	5.9	4.8	4.3	4.8
Saturday	4.3	7.4	5.2	5.5	6.6	6.5	4.9	5.2
Mean								
Sunday	4.1	6.6	5.5	6.1	7.5	5.7	4.3	4.5
Monday	5.8	4.8	4.6	5.5	6.5	5.8	4.7	4.2
Tuesday	2.8	4.4	3.8	4.8	5.2	5.2	3.9	4.3
Wednesday	4.3	4.6	3.8	4.6	5.7	6.0	4.5	4.3
Thursday	4.1	3.8	3.7	4.3	6.7	6.0	4.0	4.8
Friday	3.7	4.5	3.9	4.6	5.8	5.8	4.2	4.2
Saturday	3.8	5.8	4.9	5.3	6.7	6.0	4.8	4.6

Table 3.3-1a
Day-of-the-Week Differences in Diurnal Variations of Sum of PAMS Species, NMHC, CO, NOx, and Ratios of Acetylene to PAMS and NMHC at Pico Rivera, Summer 1999-2000

	Hour (PDT)	Sunday	Monday	Tuesday	Wednesday	Thursday	Friday	Saturday
Count of Obs	00	12	13	13	13	12	11	12
	03	12	13	13	12	11	12	12
	06	12	13	13	12	12	13	12
	09	13	13	13	13	13	13	12
	12	12	12	10	11	9	12	11
	15	13	13	13	13	12	13	12
	18	13	13	13	12	13	13	12
	21	13	13	13	11	13	13	11
PAMS	00	161	163	171	223	209	189	181
	03	161	185	231	256	220	185	184
	06	165	300	379	346	329	286	231
	09	148	274	371	270	275	262	209
	12	155	235	260	194	291	213	191
	15	134	174	201	169	231	155	143
	18	129	170	188	165	199	145	129
	21	166	167	202	208	211	180	165
TNMHC	00	202	202	213	279	262	235	221
	03	202	231	293	325	278	232	230
	06	206	371	471	426	409	358	289
	09	187	341	465	342	343	327	262
	12	193	293	327	243	349	267	237
	15	165	221	255	219	282	200	175
	18	162	212	237	212	246	179	158
	21	208	207	251	262	262	221	209
CO	00	1008	1077	1023	1100	1217	945	1125
	03	867	892	1023	1058	973	892	917
	06	1017	1423	1738	1742	1592	1546	1333
	09	915	1415	1623	1254	1546	1261	1050
	12	900	1283	1220	1173	1089	1133	1118
	15	862	992	1031	908	975	1008	958
	18	769	969	1123	925	1008	877	817
	21	969	985	1131	1082	1085	954	845
NOX	00	49	78	88	91	105	79	68
	03	43	76	111	109	96	88	61
	06	51	111	157	156	144	142	97
	09	41	92	113	100	110	79	52
	12	30	63	69	59	61	60	44
	15	31	45	52	38	48	48	33
	18	36	42	56	44	47	40	33
	21	47	49	58	65	67	47	37
acetylene/PAMS (%)	00	3.1	3.3	3.4	3.3	3.2	3.3	3.1
	03	2.6	2.9	3.0	3.3	3.0	3.3	2.7
	06	2.7	3.3	3.2	3.7	3.3	3.8	3.2
	09	3.2	3.7	3.4	3.4	3.6	3.6	3.2
	12	3.0	3.1	2.7	3.1	2.6	3.0	3.3
	15	2.9	3.1	3.0	3.0	3.1	3.4	3.2
	18	3.3	3.4	3.5	3.4	3.5	3.5	3.4
	21	3.4	3.4	3.4	3.2	3.3	3.3	3.1
acetylene/NMHC (%)	00	2.5	2.7	2.7	2.7	2.5	2.7	2.6
	03	2.0	2.3	2.4	2.6	2.3	2.6	2.2
	06	2.2	2.7	2.6	3.0	2.7	3.0	2.5
	09	2.6	3.0	2.7	2.7	2.8	2.9	2.6
	12	2.4	2.5	2.1	2.5	2.1	2.4	2.7
	15	2.3	2.5	2.4	2.4	2.4	2.7	2.6
	18	2.7	2.8	2.8	2.7	2.8	2.9	2.8
	21	2.7	2.7	2.7	2.5	2.7	2.7	2.5

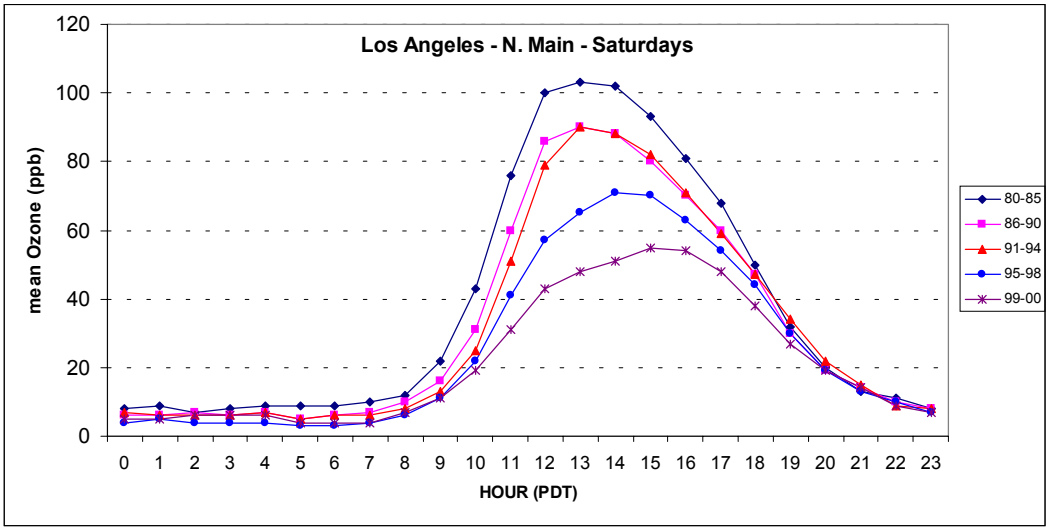
Table 3.3-1b
Day-of-the-Week Differences in Diurnal Variations of Photochemical Reactivity of Volatile Organic Compounds at Pico Rivera, Summer 1999-2000

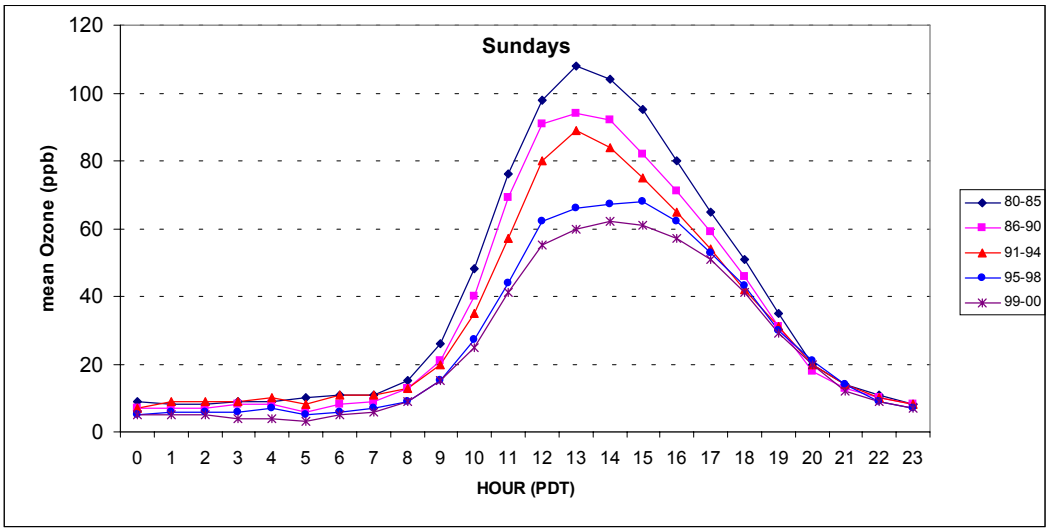
	Hour (PDT)	Sunday	Monday	Tuesday	Wednesday	Thursday	Friday	Saturday
xylenes/benzene	0	2.85	3.15	3.24	3.34	3.26	2.97	2.83
	3	2.81	2.60	2.94	3.14	3.52	3.02	2.95
	6	2.66	2.76	2.99	2.84	3.02	3.06	3.05
	9	2.02	2.70	3.26	3.00	2.93	2.83	2.52
	12	1.44	2.74	2.83	2.99	2.74	2.60	1.89
	15	1.77	2.82	3.00	3.30	3.24	2.87	2.25
	18	2.47	3.04	3.11	3.53	3.22	3.07	2.81
	21	2.76	2.71	3.01	3.12	3.31	3.08	2.96
formaldehyde (ppb)	0	4.9	5.9	6.4	4.5	4.1	4.3	4.6
	3	4.5	4.4	5.8	5.7	5.1	4.5	4.1
	6	5.7	5.8	7.8	6.2	4.8	5.9	5.3
	9	6.8	9.4	10.6	10.1	7.1	8.3	7.6
	12	10.5	8.0	10.3	10.0	9.3	9.1	9.3
	15	8.7	7.5	8.3	6.3	6.4	7.4	7.6
	18	6.3	5.6	7.4	5.8	5.3	5.8	5.6
	21	5.5	5.2	6.3	5.6	4.1	5.1	5.0
formaldehyde/pams	0	3%	3%	3%	3%	4%	4%	3%
	3	3%	2%	3%	3%	4%	4%	4%
	6	4%	2%	3%	2%	3%	4%	4%
	9	7%	5%	5%	6%	5%	7%	7%
	12	11%	7%	8%	8%	6%	8%	10%
	15	12%	7%	8%	7%	6%	8%	10%
	18	8%	5%	6%	5%	5%	6%	7%
	21	5%	4%	5%	4%	3%	5%	4%
MIR sum of PAMS	0	3.2	3.2	3.3	3.3	3.3	3.3	3.3
	3	3.1	2.8	3.0	3.0	3.2	3.1	3.0
	6	3.0	3.1	3.1	2.9	3.1	3.3	3.0
	9	2.9	3.0	3.0	3.1	3.1	3.2	3.0
	12	2.7	3.0	2.9	3.1	2.8	3.0	2.8
	15	3.0	3.2	3.2	3.4	3.1	3.3	3.1
	18	3.4	3.5	3.4	3.5	3.3	3.4	3.5
	21	3.4	3.4	3.3	3.3	3.2	3.1	3.3
MIR sum of PAMS + carbonyl compounds	0	3.4	3.4	3.5	3.4	3.4	3.6	3.6
	3	3.3	3.0	3.2	3.1	3.3	3.3	3.3
	6	3.3	3.2	3.2	2.9	3.2	3.4	3.2
	9	3.4	3.3	3.3	3.3	3.3	3.5	3.4
	12	3.5	3.3	3.4	3.4	3.1	3.5	3.4
	15	3.7	3.6	3.6	3.6	3.4	3.6	3.7
	18	3.9	3.7	3.7	3.7	3.5	3.8	3.9
	21	3.7	3.6	3.6	3.5	3.3	3.4	3.5

Table 3.4-1. Initial Chemical Conditions for Model Simulations with Varying NOx and NMHC

Inorganic Species	Species	Concentration ppbv
	Ozone	30
	Methane	1700
	Water	1.56×10^7
	Carbon Monoxide	100 (Rural); 1000 (Urban)
	Sulfur Dioxide	1

Organic Species	Background NMHC and Other Organics ppbC	Anthropogenic NMHC and Other Organics Percent by Carbon
Ethane	2	11.5
Least Reactive Alkanes	4	27.5
Moderately Reactive Alkanes	14	17
Very Reactive Alkanes	10	12
Ethene	1	8
Terminal Alkenes	0.6	5
Internal Alkenes	1.6	2
Toluene	0.7	8
Xylene	0.4	4.5
Formaldehyde	2	1
Aldehyde	2	1
Ketone	3.5	2
Isoprene	2.5	----
Peroxyacetyl Nitrate	2	----





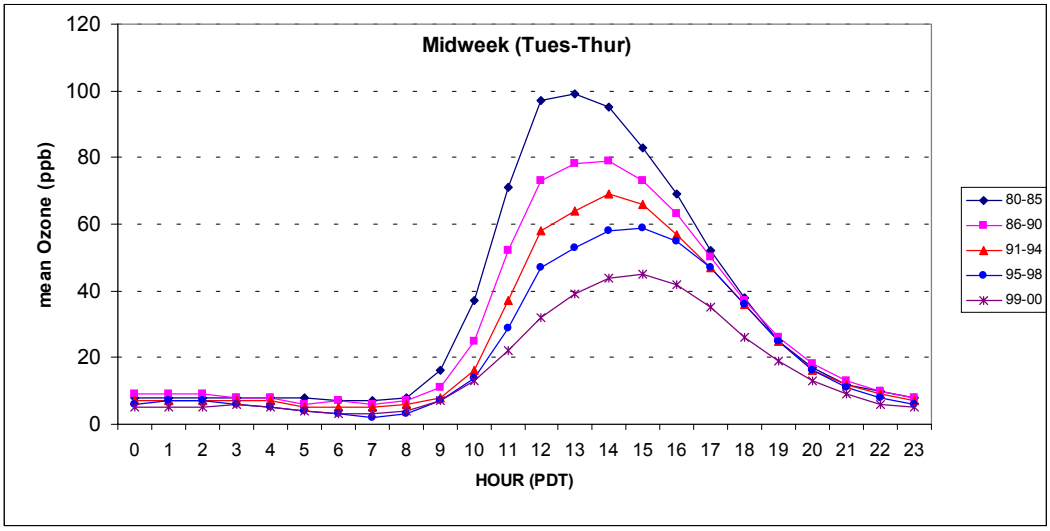
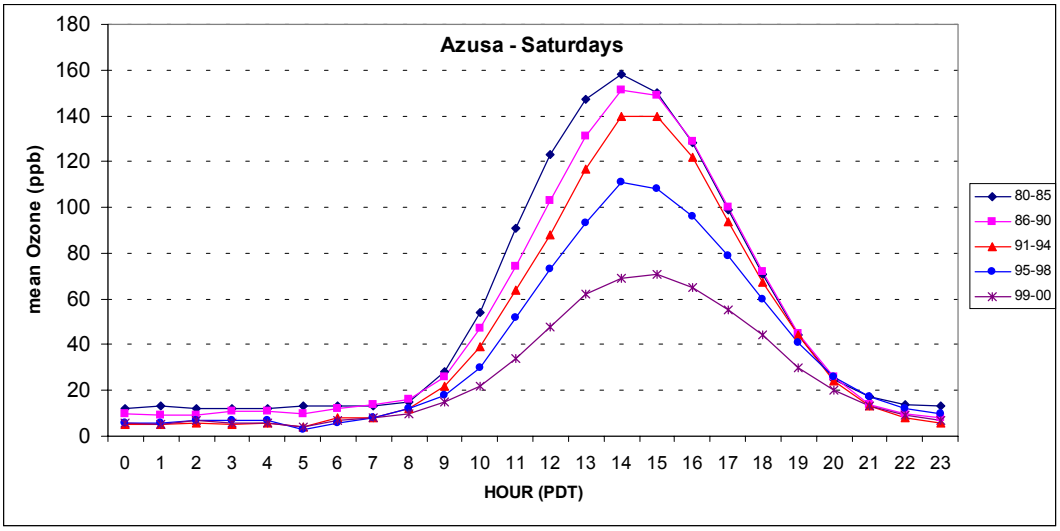
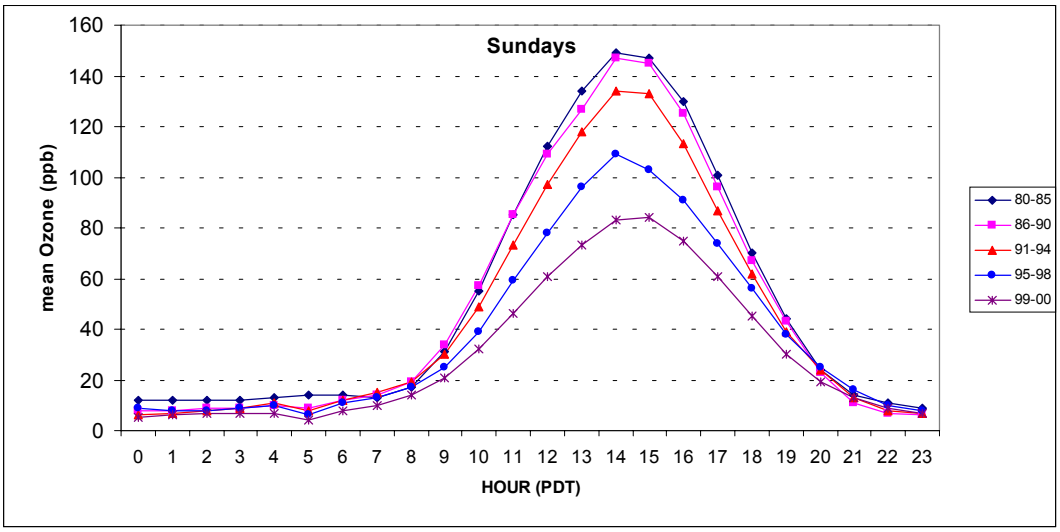


Figure 3.1-1a. Mean diurnal variations in ozone mixing ratios on Saturdays, Sundays, and weekdays at Los Angeles – North Main in 1999-2000 and 1980-1998.





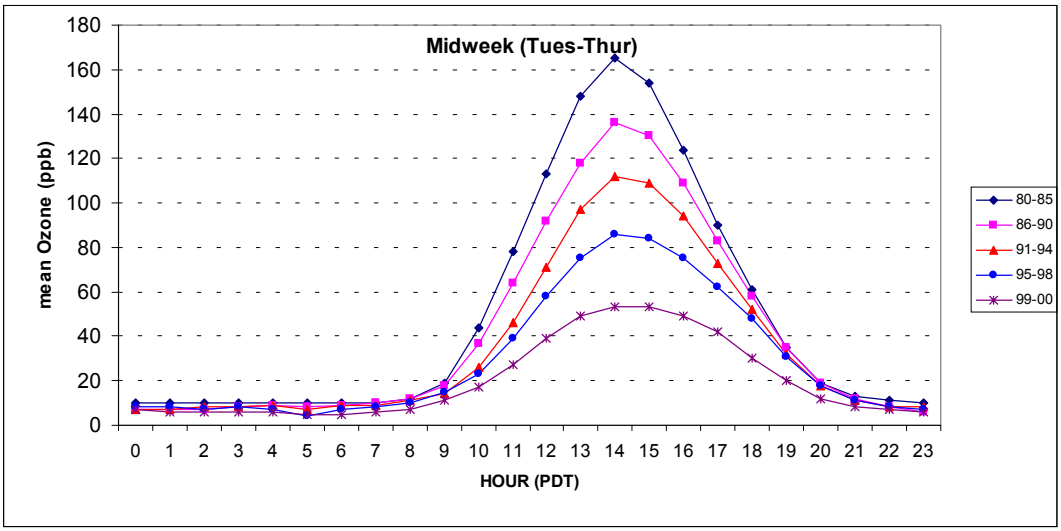


Figure 3.1-1b. Mean diurnal variations in ozone mixing ratios on Saturdays, Sundays, and weekdays at Azusa in 1999-2000 and 1980-1998.

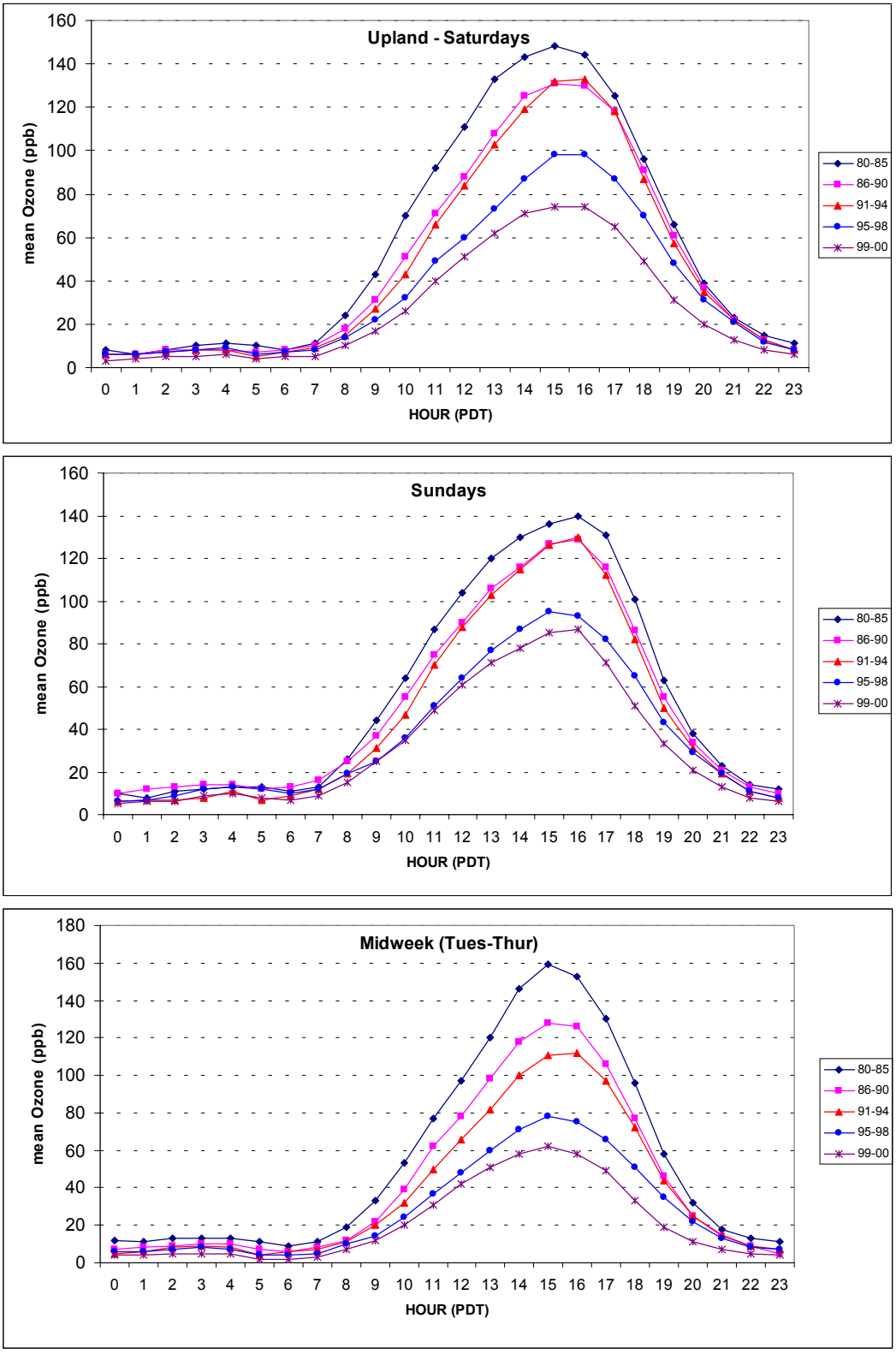


Figure 3.1-1c. Mean diurnal variations in ozone mixing ratios on Saturdays, Sundays, and weekdays at Upland in 1999-2000 and 1980-1998.

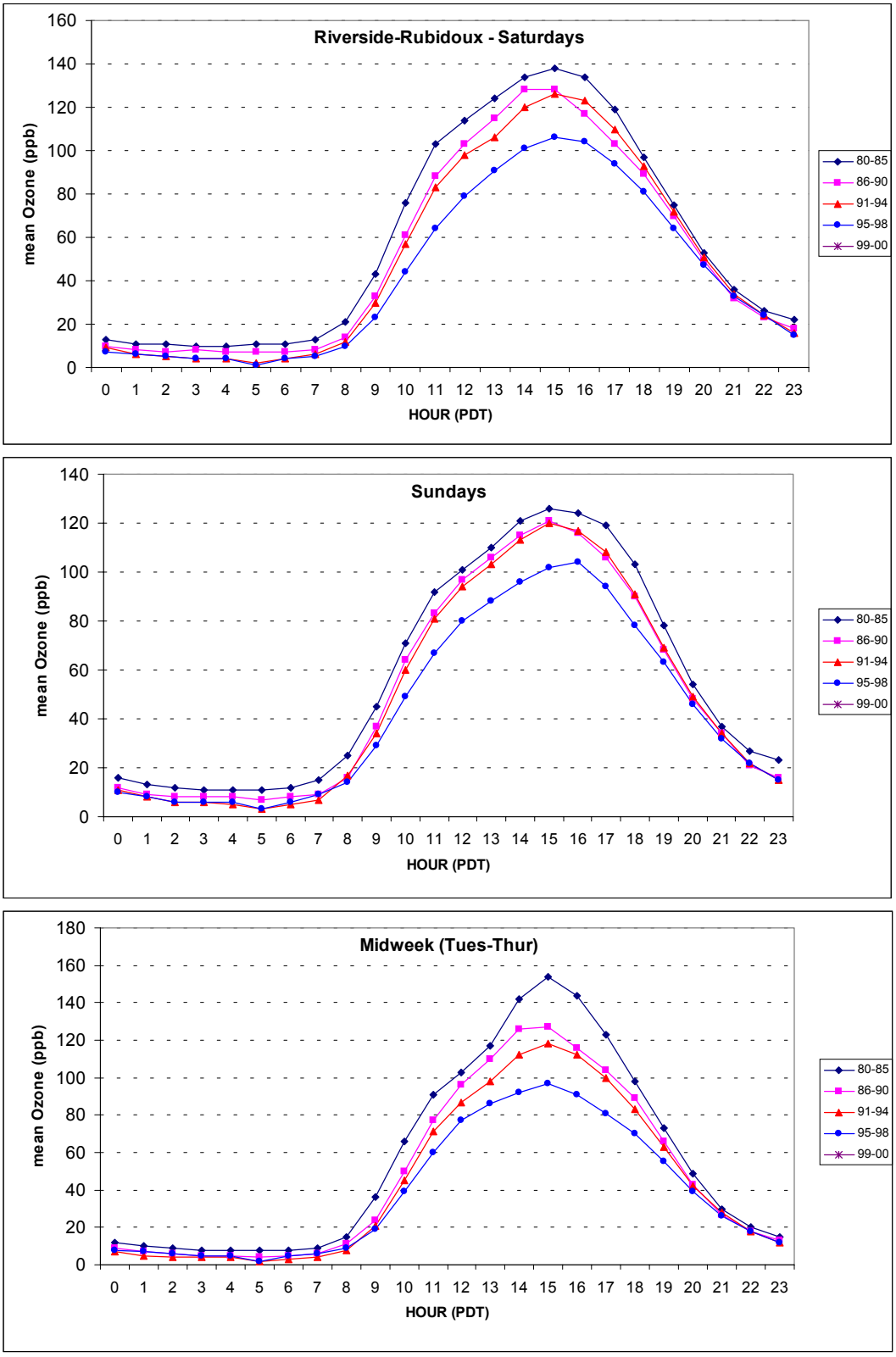


Figure 3.1-1d. Mean diurnal variations in ozone mixing ratios on Saturdays, Sundays, and weekdays at Rubidoux, 1980-1998.

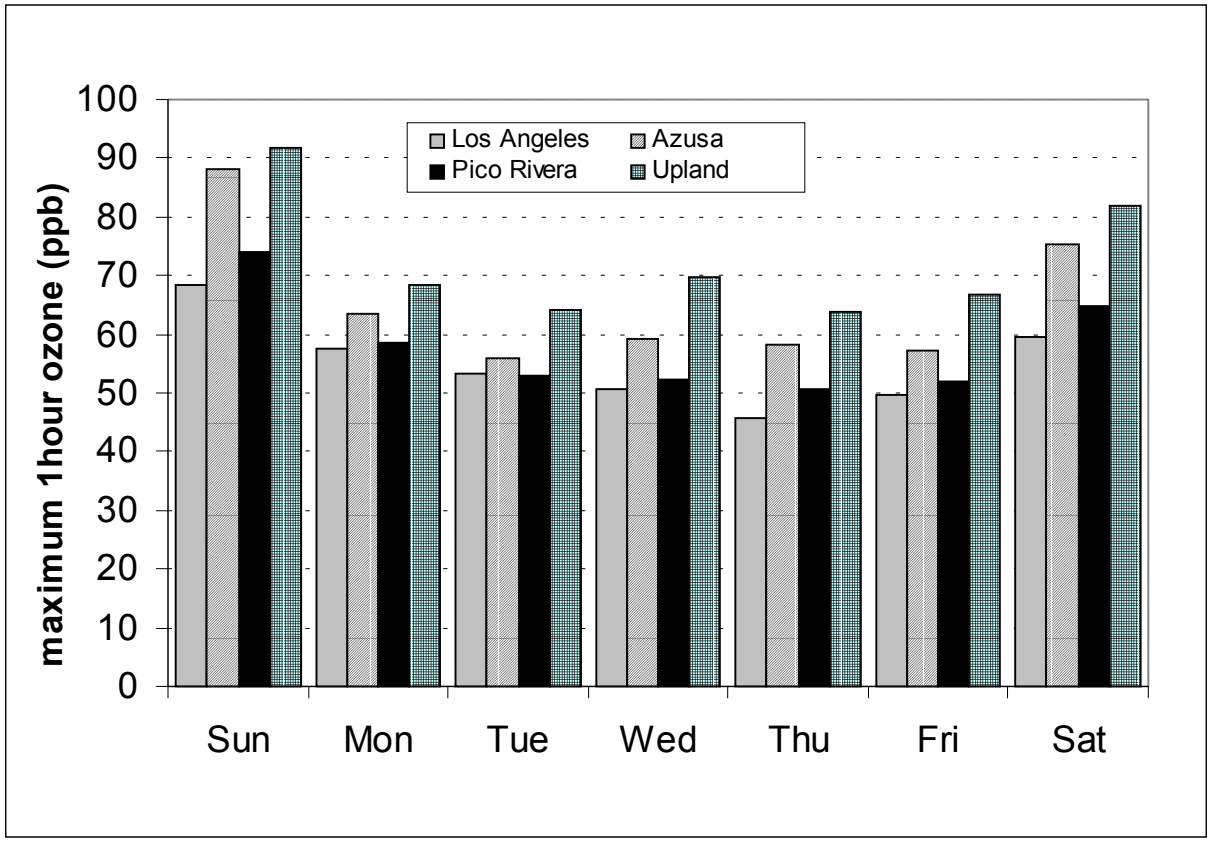


Figure 3.1-2. Mean day-of-the-week variations in daily maximum ozone mixing ratios at Los Angeles – North Main, Azusa, Pico Rivera, and Upland during the summers (July-September) of 1999 and 2000.

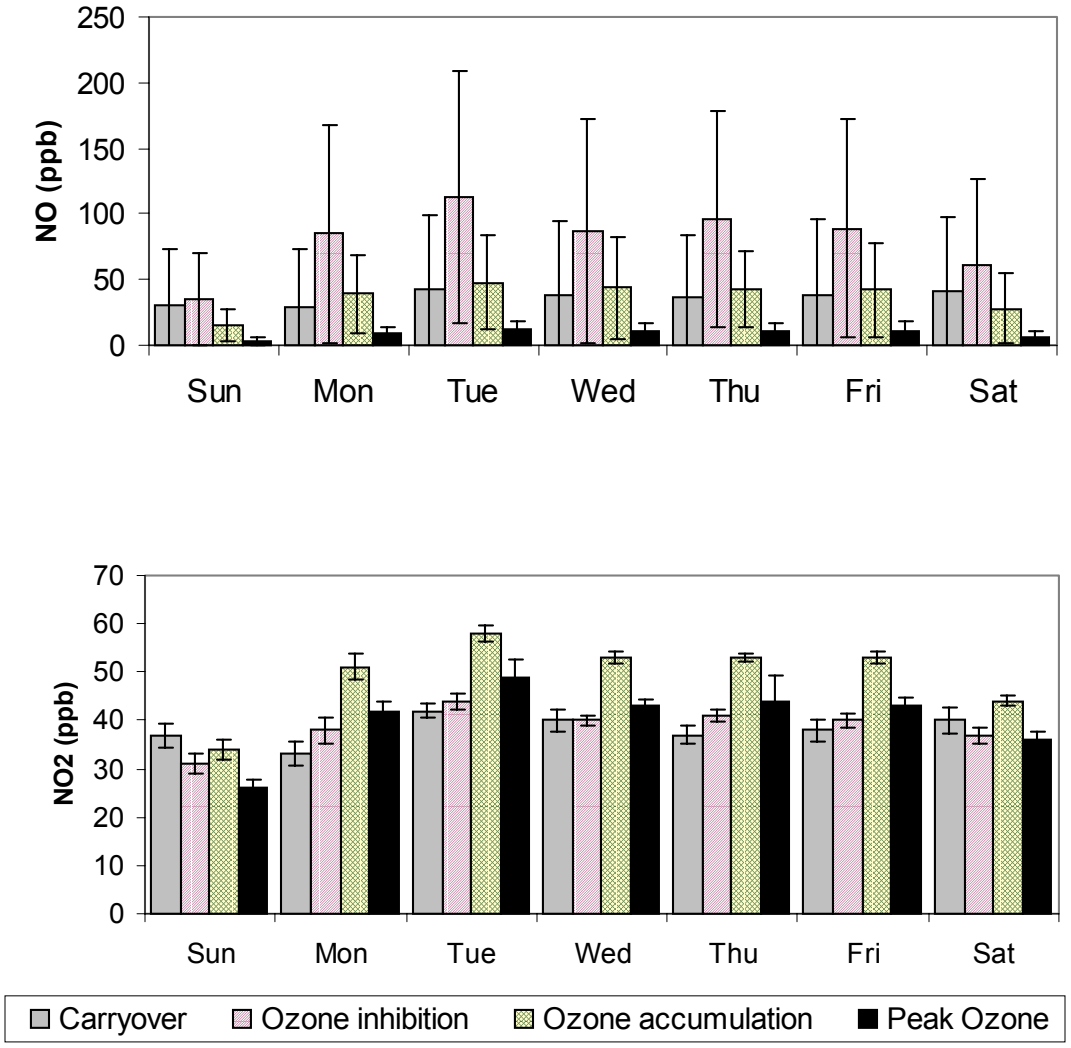


Figure 3.2-1a. Day-of-the-week variations in NO and NO2 mixing ratios during carryover (0000-0300, PDT), ozone inhibition (0600-0900), ozone accumulation ((0900-1200), and ozone peak (1200-1500) periods. Mean and standard deviations of the mean mixing ratios at Los Angeles – North Main, Azusa, Pico Rivera, and Upland during the summers (July-September) of 1999 and 2000.

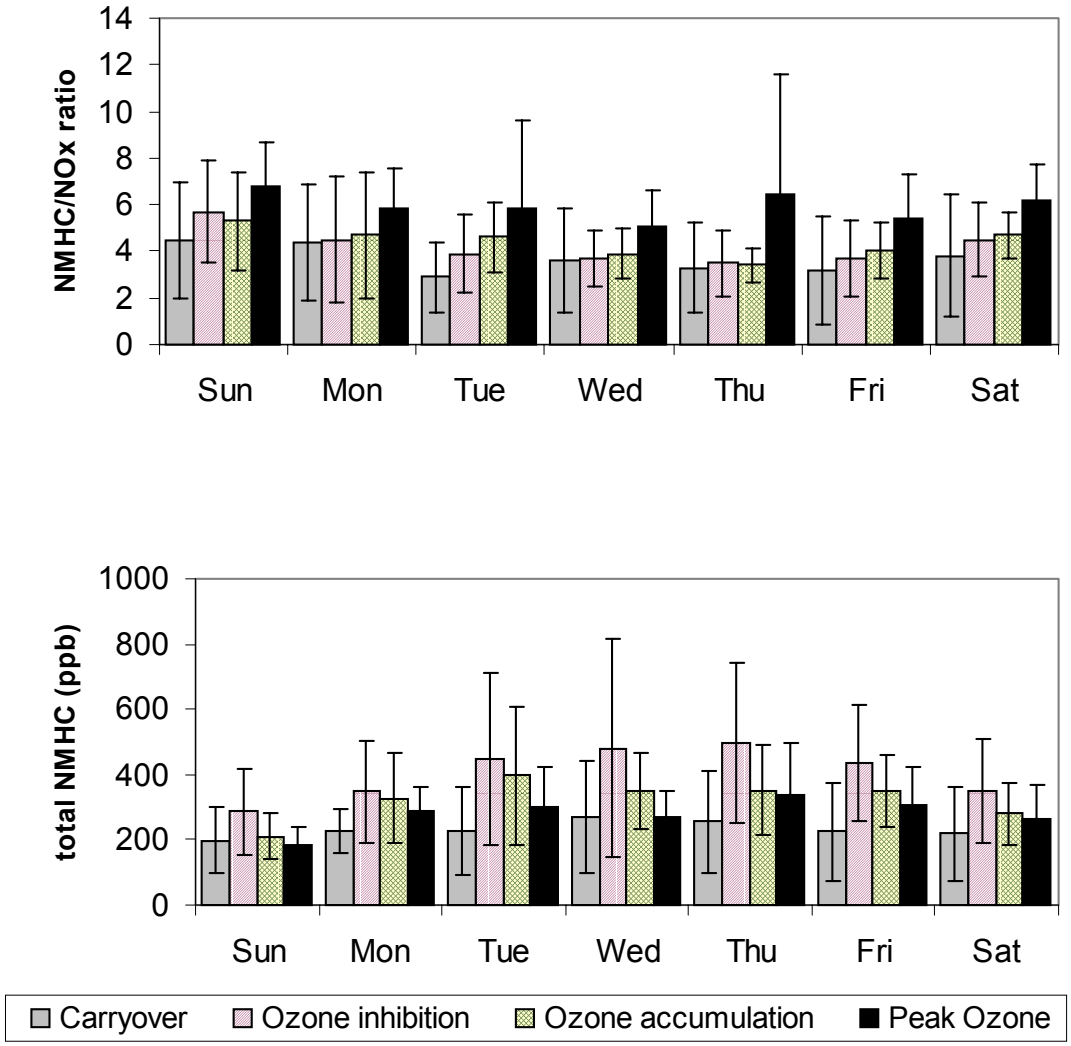


Figure 3.2-1b. Day-of-the-week variations in NMHC/NOx ratio and total NMHC mixing ratios during carryover (0000-0300, PDT), ozone inhibition (0600-0900), ozone accumulation ((0900-1200), and ozone peak (1200-1500). Mean and standard deviations of the mean mixing ratios at Los Angeles – North Main*, Azusa, Pico Rivera, and Upland during the summers (July-September) of 1999 and 2000.
*Data for Los Angeles were available only for the inhibition period.
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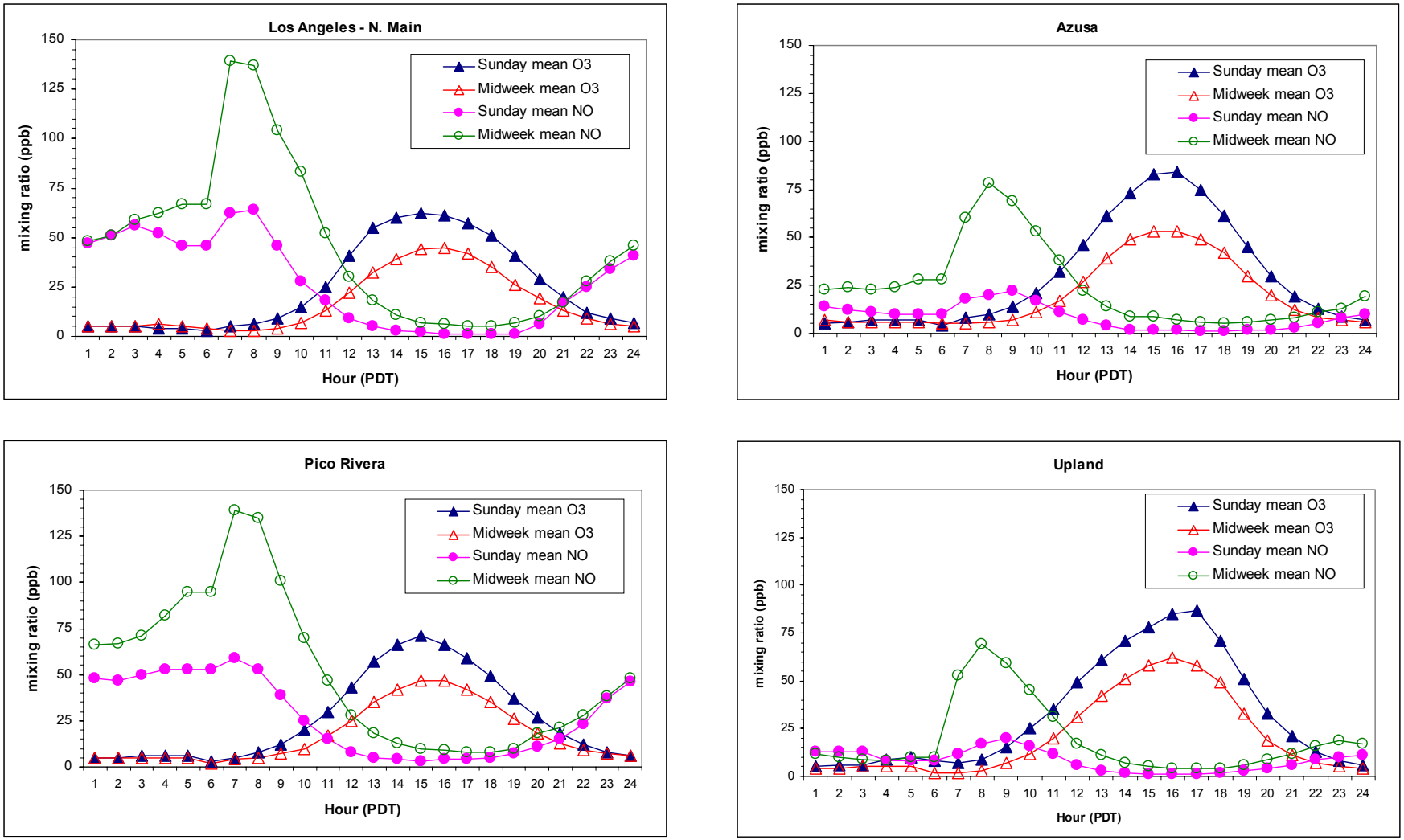


Figure 3.4-1 Mean diurnal variations in ozone and nitric oxide mixing ratios on Sunday and midweek (Tues-Thurs) at Los Angeles – North Main, Azusa, Pico Rivera, and Upland during the summers (July-September) of 1999 and 2000.

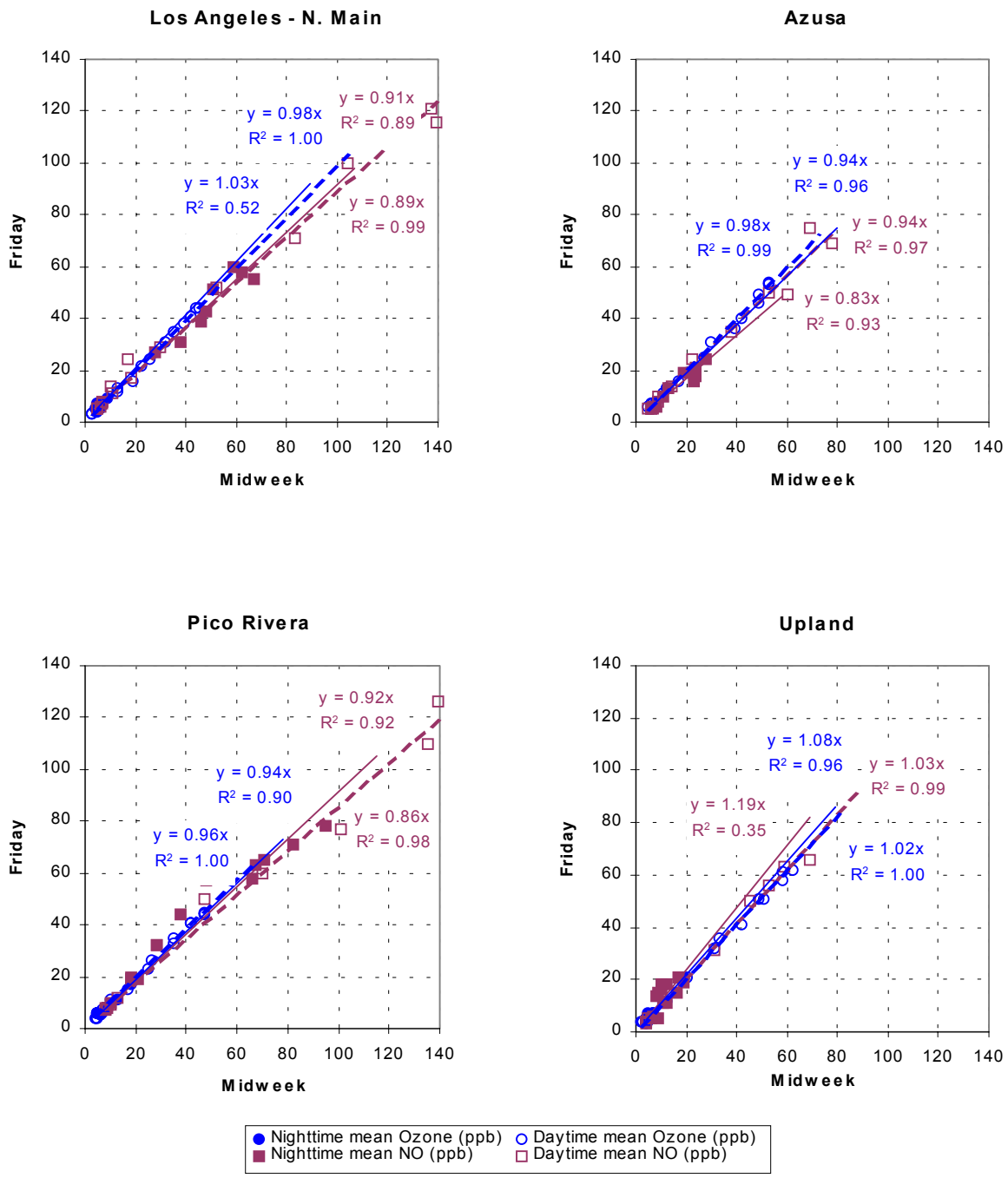


Figure 3.4-2a. Correlation plots of mean hourly ozone and NO mixing ratios during midweek (Tues-Thur) versus Friday. Separate linear regressions are shown for nighttime (9:00 p.m. – 5:00 a.m.) and daytime (6:00 a.m. – 9:00 p.m.) hours.

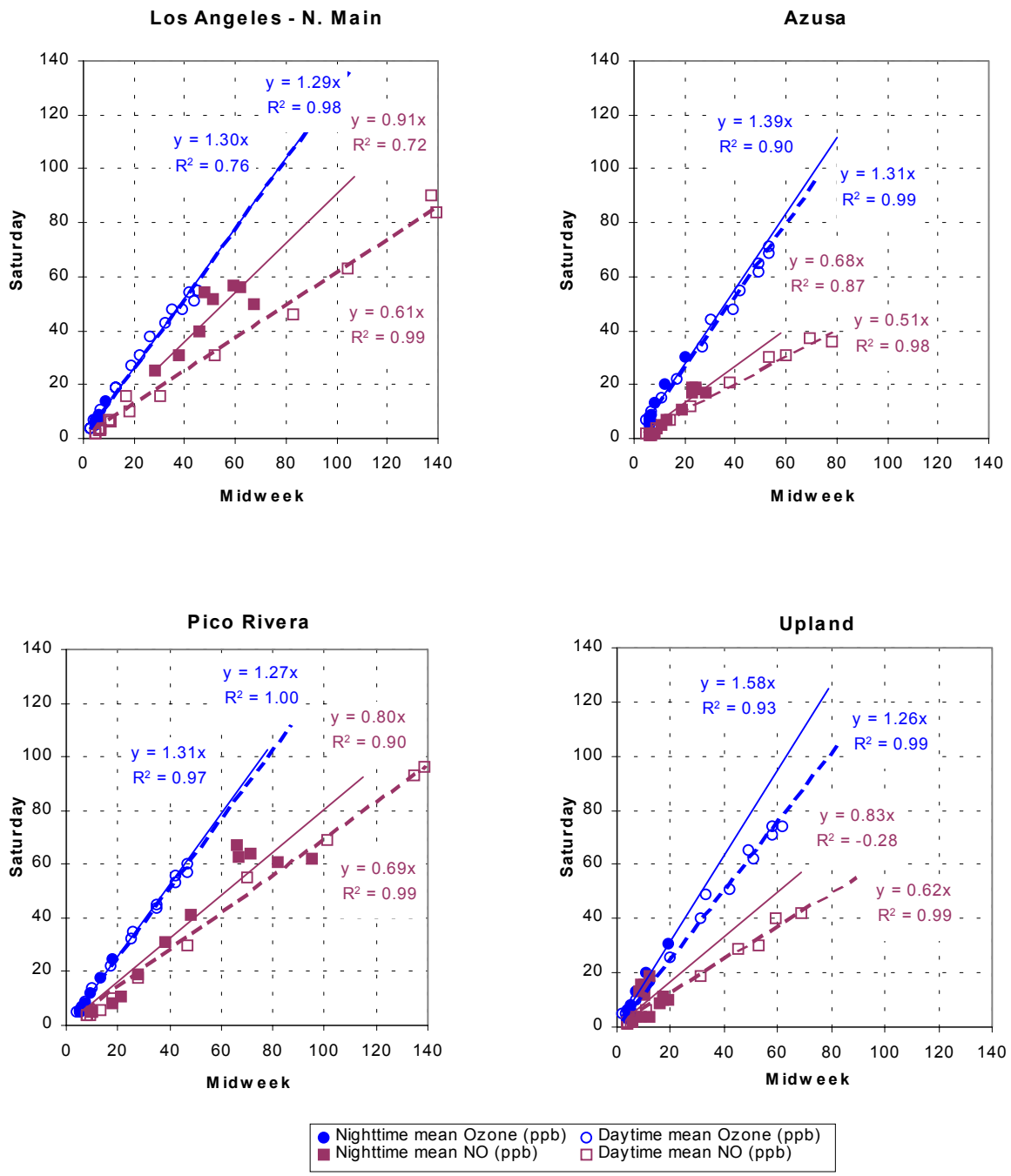


Figure 3.4-2b. Correlation plots of mean hourly ozone and NO mixing ratios during midweek (Tues-Thur) versus Saturday. Separate linear regressions are shown for nighttime (9:00 p.m. – 5:00 a.m.) and daytime (6:00 a.m. – 9:00 p.m.) hours.

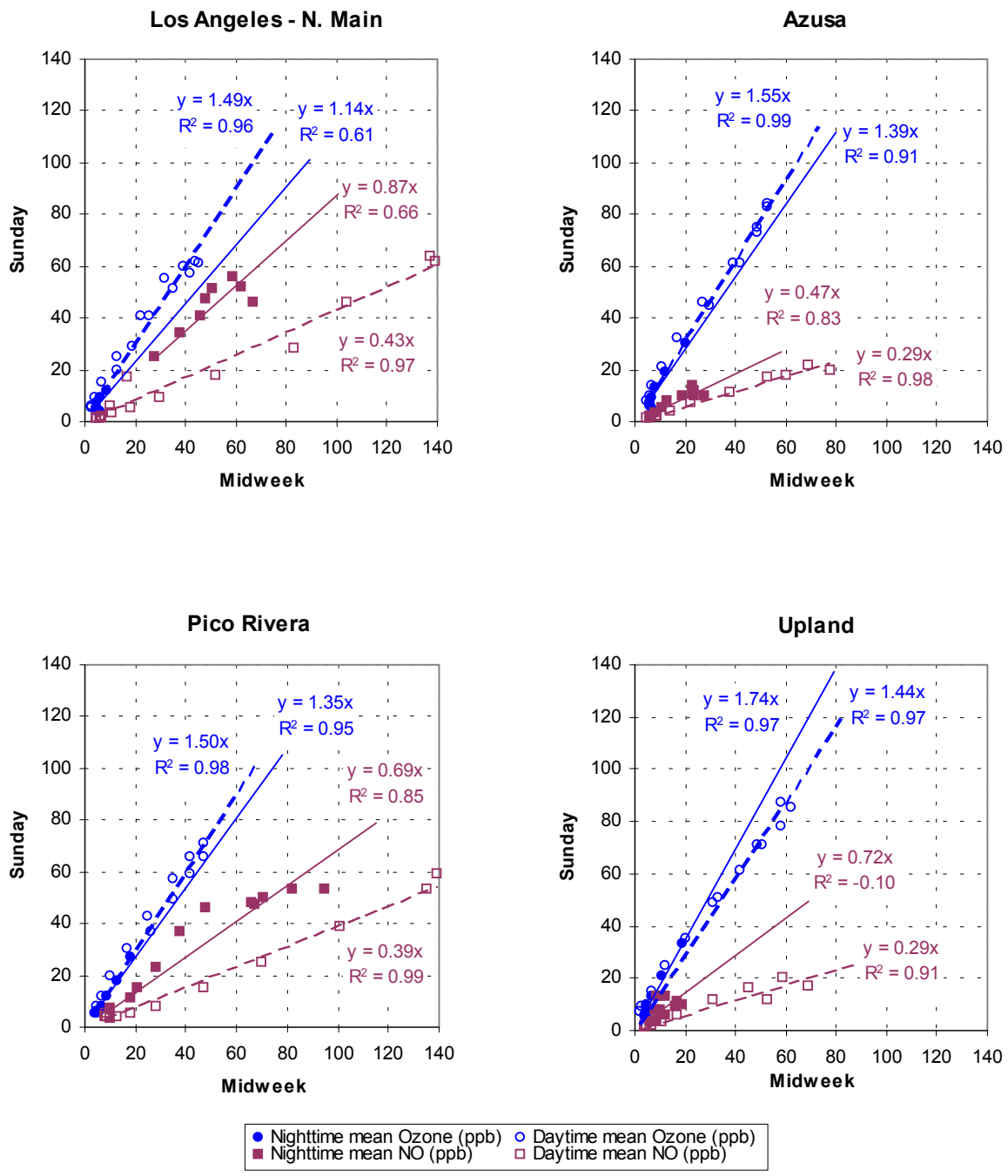


Figure 3.4-2c. Correlation plots of mean hourly ozone and NO mixing ratios during midweek (Tues-Thur) versus Sunday. Separate linear regressions are shown for nighttime (9:00 p.m. – 5:00 a.m.) and daytime (6:00 a.m. – 9:00 p.m.) hours.

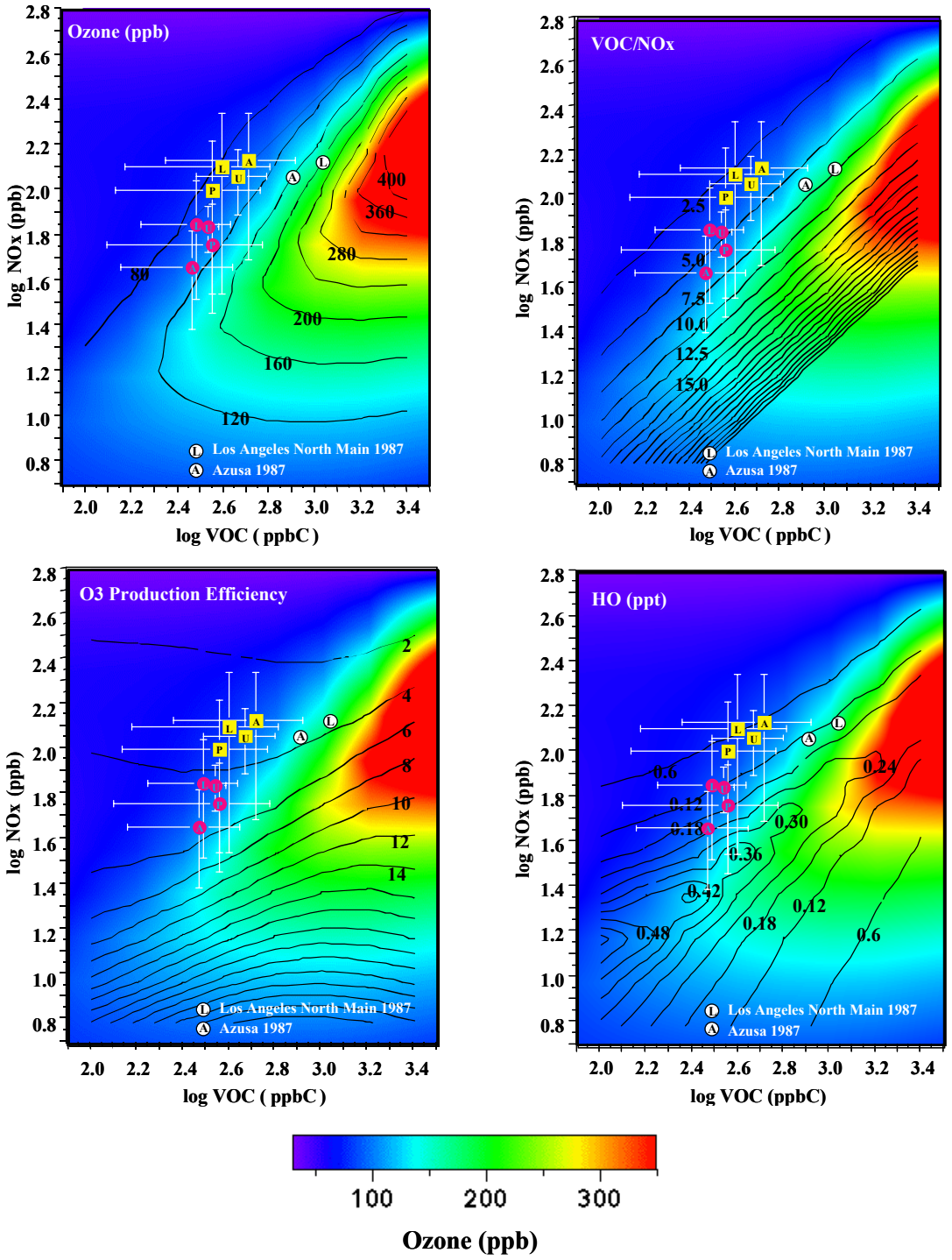


Figure 3.5-1 Plots of ozone, VOC/NO_x ratio, ozone production efficiency ($\Delta[O_3]/(\Delta[HNO_3] + \Delta[\text{Organic Nitrates}]$) and hydroxyl radical superimposed on a color O_3 EKMA plot. Also plotted are mixing ratios for NO_x and NMHC during the summer of 1999 and 2000 with error bars representing one standard deviation from the average with the labels (A) representing Azusa, (L) representing Los Angeles – North Main, (P) representing Pico Rivera and (U) representing Upland and the yellow squares representing Wednesday and the dark red dots representing Sunday. The error bars are not symmetrical because of the logarithmic scale. The two white dots labeled (L) and (A) represent the average conditions for Los Angeles – North Main and Azusa during 1987, respectively.

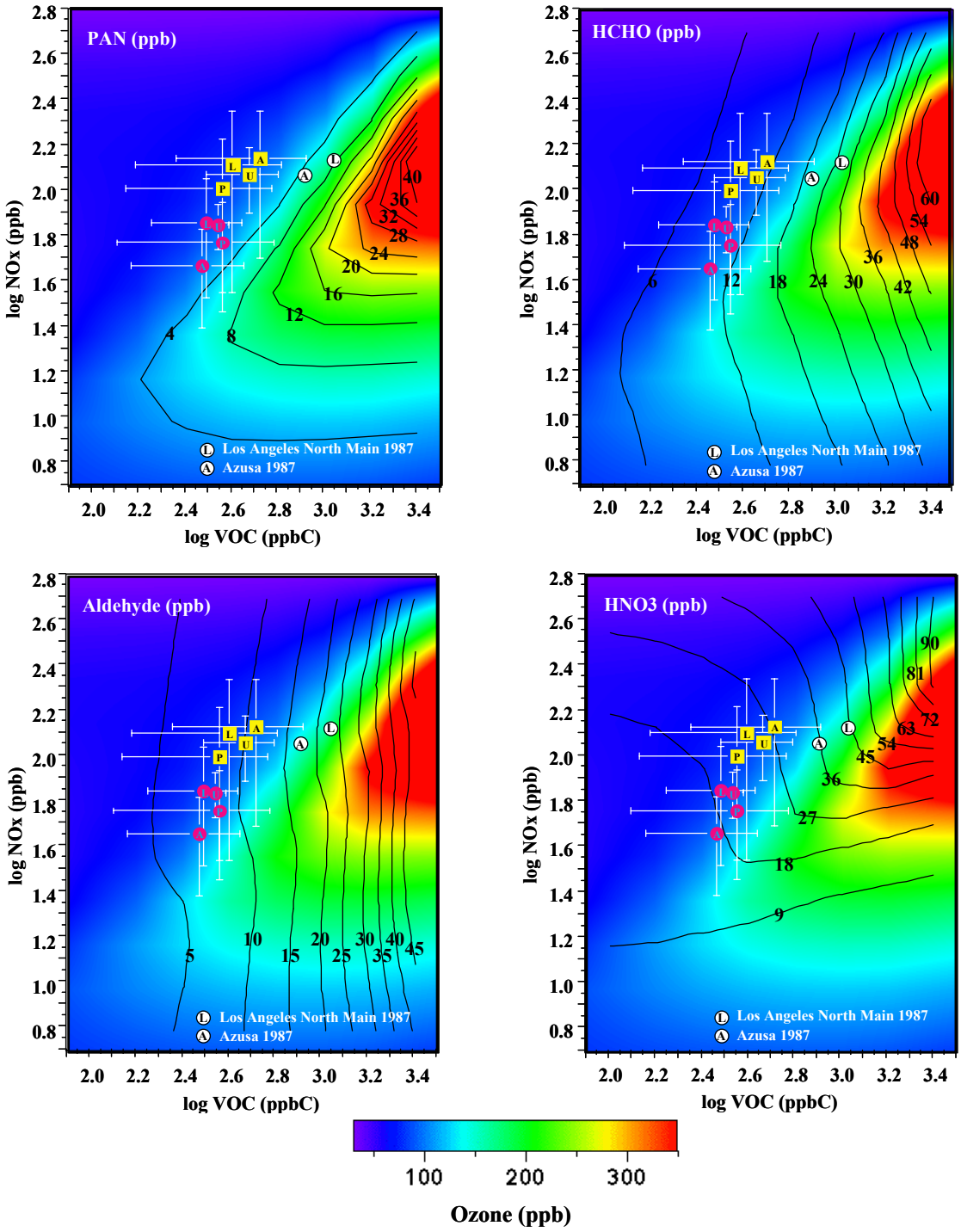


Figure 3.5-2 Plots of PAN, HCHO, aldehyde and nitric acid superimposed on a color O_3 EKMA plot. Also plotted are mixing ratios for NO_x and NMHC during the summer of 1999 and 2000 with error bars representing one standard deviation from the average with the labels (A) representing Azusa, (L) representing Los Angeles – North Main, (P) representing Pico Rivera and (U) representing Upland and the yellow squares representing Wednesday and the dark red dots representing Sunday. The error bars are not symmetrical because of the logarithmic scale. The two white dots labeled (L) and (A) represent the average conditions for Los Angeles – North Main and Azusa during 1987, respectively.

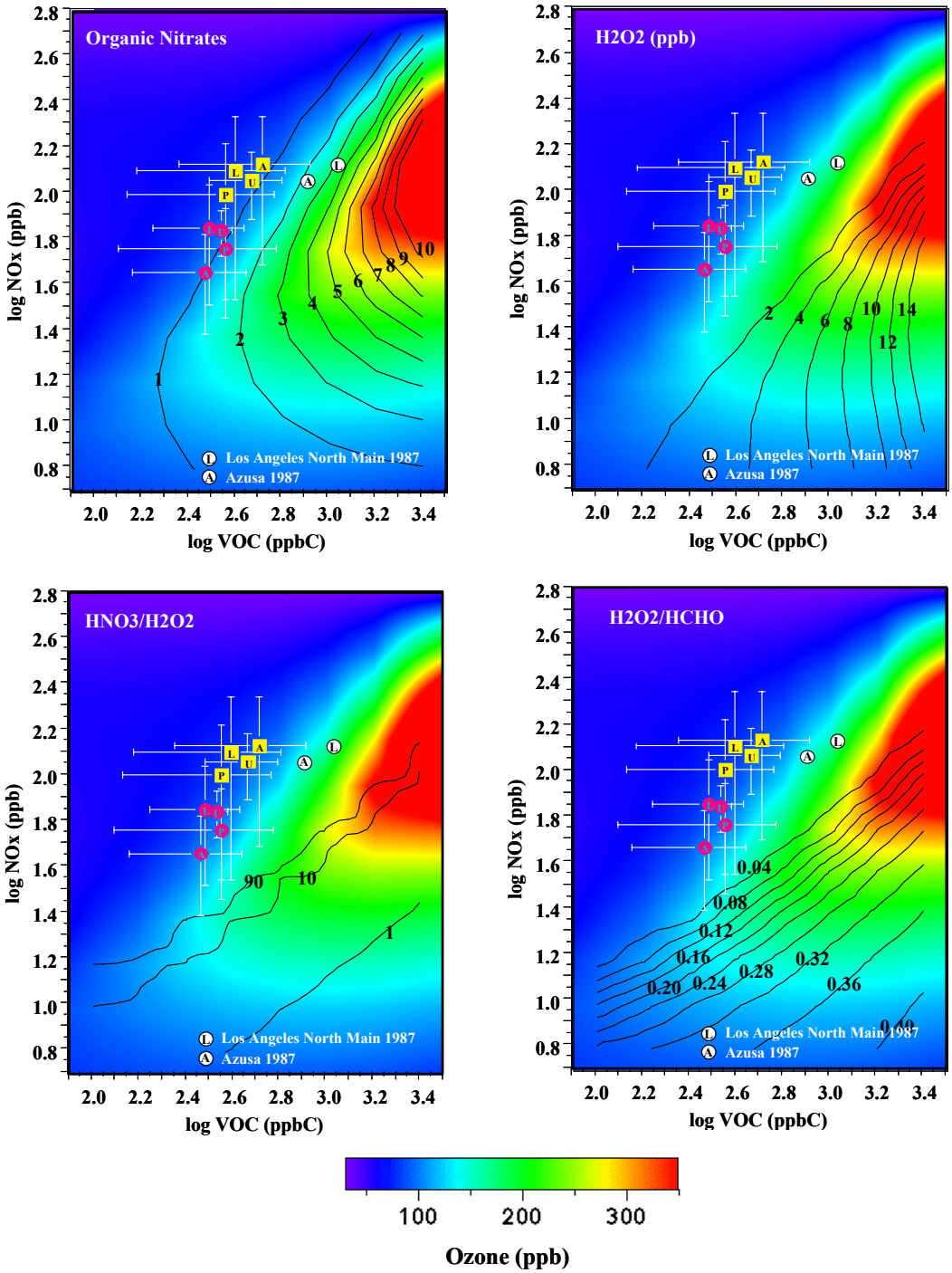


Figure 3.5-3 Plots of organic nitrates, H_2O_2, HNO_3/H_2O_2 ratio and $H_2O_2/HCHO$ ratio superimposed on a color O_3 EKMA plot. Also plotted are mixing ratios for NO_x and NMHC during the summer of 1999 and 2000 with error bars representing one standard deviation from the average with the labels (A) representing Azusa, (L) representing Los Angeles – North Main, (P) representing Pico Rivera and (U) representing Upland and the yellow squares representing Wednesday and the dark red dots representing Sunday. The error bars are not symmetrical because of the logarithmic scale. The two white dots labeled (L) and (A) represent the average conditions for Los Angeles – North Main and Azusa during 1987, respectively.

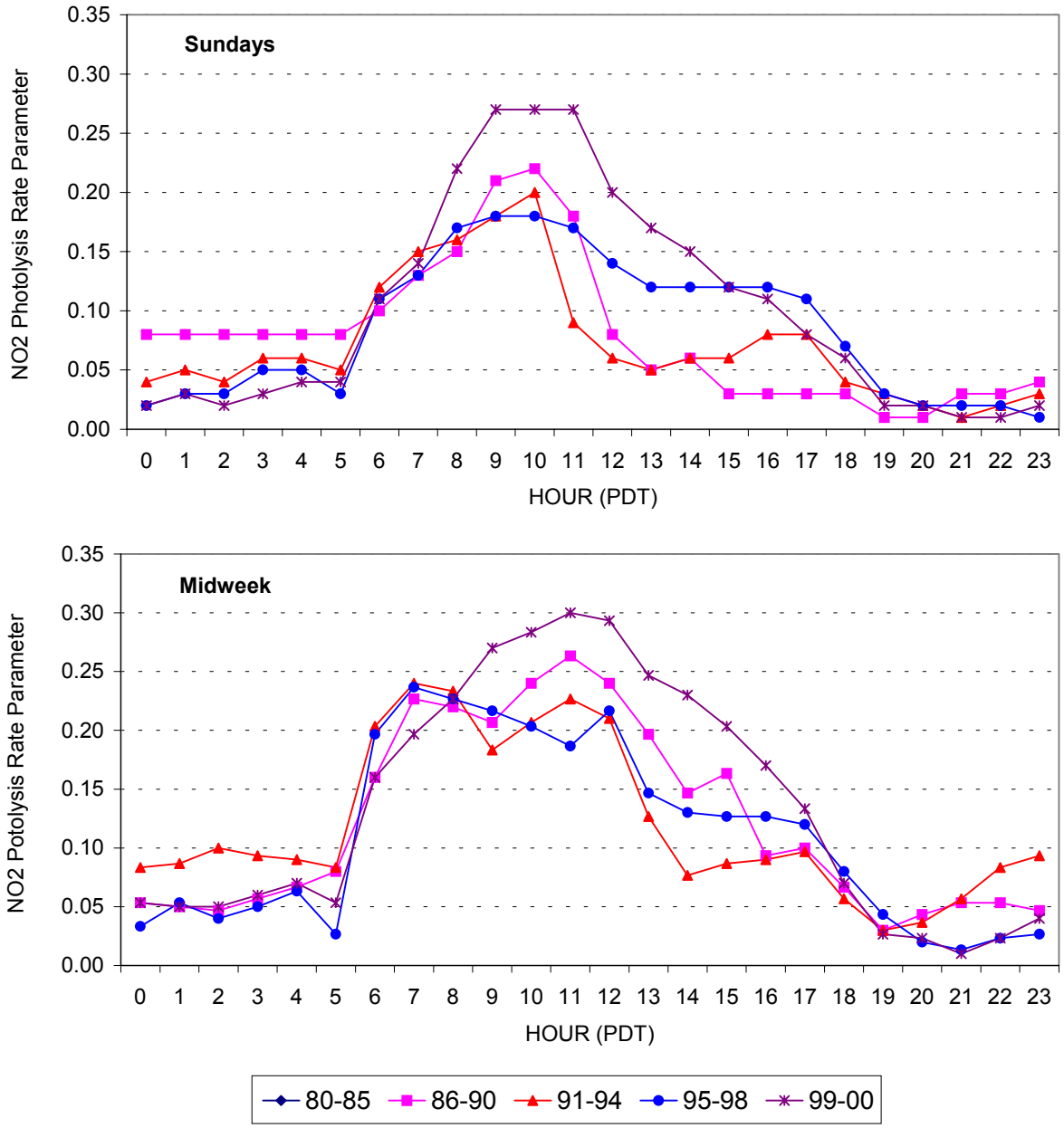


Figure 3.6-1. Estimated mean photolysis rate parameter for NO_2 (J_{NO2}) at Azusa on Sunday, and midweek (Tuesday to Thursday) for the periods 1980-85, 1986-90, 1991-94, 1995-98, and 1999-2000. J_{NO2} was calculated from an extended version of the O_3-NO-NO_2 photostationary state expression.

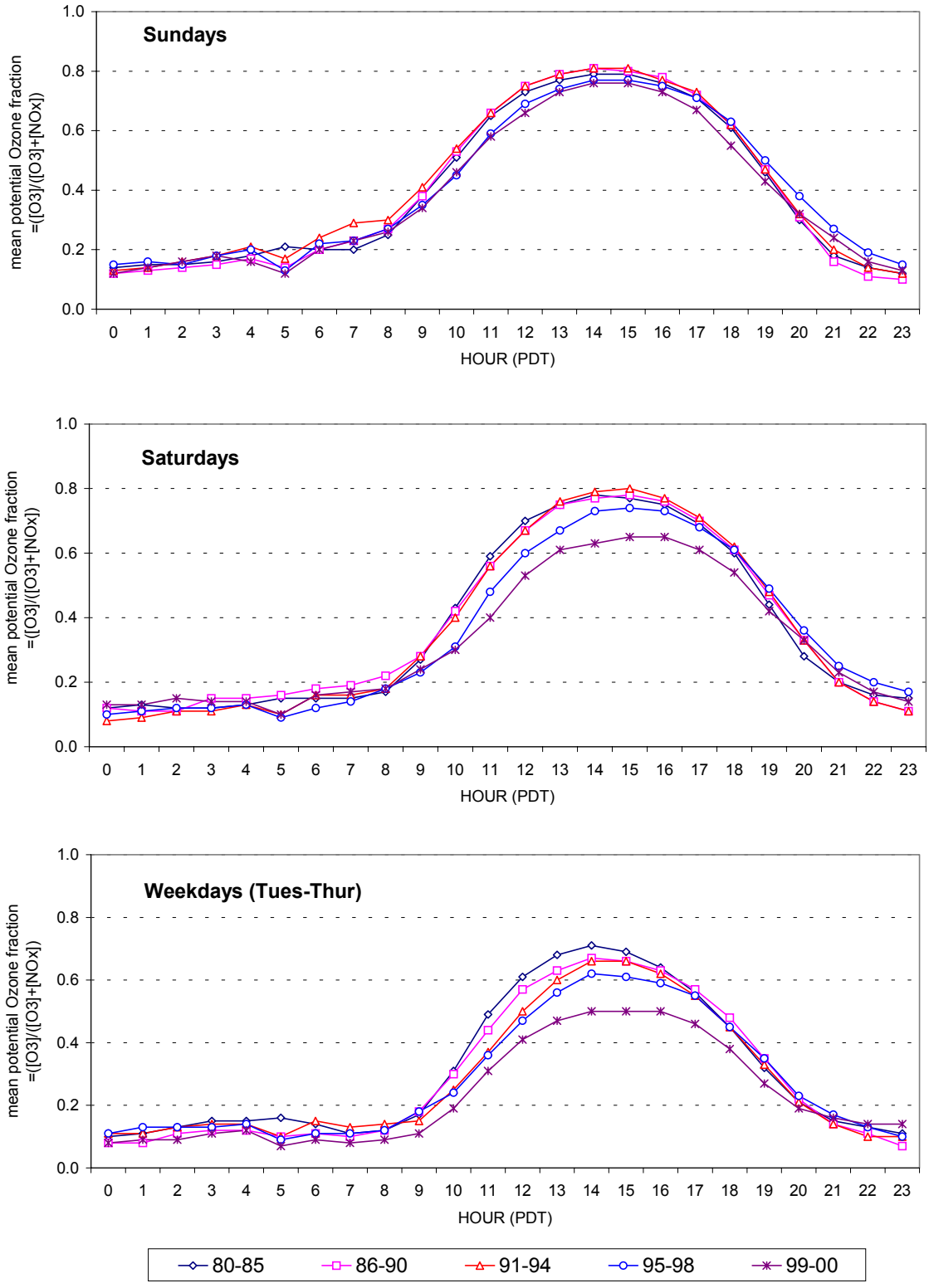


Figure 3.6-2. Diurnal variations in the ratios of ozone to potential ozone (O_3 + NOx) on Sundays, Saturdays, and weekdays at Azusa for the years 1980-85, 1986-1990, 1991-1994, 1995-1998, and 1999-2000.

4. WEEKDAY VARIATIONS IN THE SOURCE APPORTIONMENT OF OZONE PRECURSORS

This section examines the attribution of ambient NOx and VOC to emission sources with particular focus on the relative contributions of on-road diesel-powered and gasoline-powered vehicles. Multiple linear regression and Chemical Mass Balance (CMB) were used to derive approximate attributions of NOx to gasoline and diesel exhaust. CMB was used to determine the diurnal variations in source attributions of ambient VOC by day-of-the-week. A field measurement program was conducted from September 30, 2000 through October 8, 2000 to collect and assemble air quality and emission activity databases to examine relationships between emissions sources and the diurnal and day-of-the-week variations in CO, NO, NOx, VOC, VOC/NOx and NO_2/NOx. The field study measurements focused on attribution of ambient precursor concentrations to major sources of VOC and NOx. The field measurements involved mobile sampling during periods that coincide with overnight carryover of ozone precursors, ozone inhibition, and ozone accumulation plus supplemental measurements at existing SCAQMD monitoring sites.

A mobile sampling van was used to collect data to characterize the diurnal variations in relative contributions of gasoline and diesel vehicles to the ambient level of ozone precursors by day of the week. Primary pollutants (CO, NO, black carbon [BC], and speciated hydrocarbons) were measured simultaneously in the mobile van along several freeway and surface-street loops and at several regional/background locations during the carry over, ozone inhibition, and ozone accumulation periods. For each loop, the time series of NO and CO were related to indicators of compression-ignition exhaust (black carbon and heavy hydrocarbons) and spark-ignition exhaust (CO and MTBE) for the carry over, ozone inhibition, and ozone accumulation period by day of the week. The premise of this approach is that gasoline exhaust is enriched in CO and MTBE relative to diesel exhaust while diesel exhaust is enriched in black carbon and heavy hydrocarbons (nC_{10}-nC_{15}) relative to gasoline exhaust. Multiple regression was used to estimate the amounts of NOx associated with CO and MTBE relative to the NOx associated with black carbon and nC_{10}-nC_{15}. Diurnal and day-of-the-week variations in the associations of NOx to primary pollutants are correlated to the relative contributions of diesel and gasoline exhaust to ambient NOx. These variations are examined for a variety of sampling locations, which included freeways and surface streets with varying ratios of gasoline- and diesel-powered vehicles, district monitoring stations, and other regional and background sites.

The source contributions of gasoline engine exhaust and diesel engine exhaust to NMHC and NOx were estimated by Chemical Mass Balance (CMB) receptor modeling. Source composition profiles were derived for diesel and gasoline exhaust from samples collected at a truck stop and on a stretch of the 110 Freeway where heavy trucks are prohibited. Source profiles were also developed from analysis of gasoline and diesel fuel samples. In addition to the relative contributions of gasoline and diesel exhaust, the detailed speciation of VOC from the mobile sampling and the time-resolved VOC speciation at Los Angeles, Azusa, and Pico Rivera monitoring stations provided source attribution of other sources of VOC by time of day and day-of-the-week. These analyses address questions regarding the source contributions to VOC carried over from the previous evening and the relative importance of on-road versus other area sources on the diurnal variations of VOC/NOx ratios. Diurnal variations in VOC composition were also used to examine day-of-the-week differences in ozone formation potential and reactivity of the

VOC mix. Sonoma Technology, Inc. conducted concurrent traffic and emission source surveys during the field study

Supplemental measurements by DRI at the monitoring stations included hourly C_2 to C_{11} VOC by automated gas chromatography with ion-trap mass spectrometry at Azusa, continuous black carbon by light absorption with an aethalometer at Azusa and Pico Rivera, and 3-hour composite Tenax samples for C8 to C18 hydrocarbons. The California Air Resources Board collected canister samples at Los Angeles – N. Main for speciated hydrocarbons on the same schedule, and SCAQMD measured 3-hour average speciated VOC with an automated gas chromatograph at Pico Rivera.

4.1 Field Measurement Program

Desert Research Institute (DRI) conducted a 9-day field study in the Los Angeles area from September 30, 2000 to October 8, 2000 as part of Phase II of this Weekend Ozone Study. The study was conducted in accordance with the study plan in Chapter 4 of the August 23, 2000 draft report for Phase I (Fujita et al., 2000a). The plan presented in the draft report was modified in response to comments from the National Renewable Energy Laboratory (NREL), Coordinating Research Council (CRC), and the California Air Resources Board (ARB). This section describes the experimental approach and methods used in field study.

The field study focused on detailed time-resolved measurements to test the hypothesized relationship between emissions sources and the diurnal and day-of-the-week variations in VOC and NOx, and VOC/NOx ratios. The field measurements involved two approaches: supplemental measurements at existing SCAQMD monitoring sites and mobile sampling during periods that coincide with overnight carryover, ozone inhibition, and ozone accumulation. Supplemental measurements made by DRI at the monitoring stations included hourly C_2 to C_{11} volatile organic compounds by automated gas chromatography with ion-trap mass spectrometry at Azusa, continuous black carbon by light absorption with an aethalometer (approximately 5-minute averages) at Azusa and Pico Rivera, and 3-hour composite Tenax samples for $C_8$to C_{18}hydrocarbons beginning at 2, 6, and 9 a.m. PDT on September 30, October 1,2,4,6,7, and 8. ARB also collected canister samples at Los Angeles – N. Main for speciated hydrocarbons on the same schedule, and SCAQMD measured 3-hour average speciated VOC with an automated gas chromatograph at Pico Rivera. Figure 4.1-1 shows the locations of District monitoring stations along with the locations of freeway loops and regional/background sites used during the mobile sampling.

Primary pollutants (CO, NO, black carbon [BC] and speciated hydrocarbons) were measured simultaneously in a mobile van along several freeway loops in different areas of the Basin. Carbon monoxide, NO/NOy and black carbon estimated from light absorption were measured continuously with averaging times of 1, 1, and 5 minutes, respectively. Canister and Tenax cartridge samples were integrated over a period of approximately 50 minutes for each freeway loop and fixed locations. Sonoma Technology, Inc. conducted concurrent traffic and emission source surveys during the field study.

Mobile sampling was conducted during the carryover period between 2-5 a.m. (PDT), the ozone inhibition period between 6 to 9 a.m., and during the ozone accumulation period between

9 a.m. andnoon. Sampling was conducted on Saturday, September 30, 2000, Sunday, October 1, Monday, October 2, Wednesday, October 4, Friday, October 6, Saturday, October 7, and Sunday, October 8 along the following loops and fixed locations.

- 0200 to 0245 – (IH1) Industry Hills Conference Center (overflow parking lot on the south end of the conference center) on all days.

- 0300 to 0345 – (CV1) Covina Loop (east on S-60 from Azusa Blvd on-ramp, north on S-57, west on I-10 to I-5) on all days.

- 0415 to 0500 – (DS1) Dodger Stadium (four loops around the perimeter of the Stadium) on all days.

- 0515 to 0600 – (CO1) Compton Loop (south on S-110 from Stadium Way onramp, east on I-405, north on I-710 to I-10) on all days.

- 0630 to 0715 – (HF1) Source-dominated samples for the spark ignition vehicle exhaust profile (fixed location sampling on southbound S-110 just south of Stadium Way onramp) on October 2, 4, 6, 7, and 8. This section of the 110 (Harbor Freeway) is restricted to automotive traffic only.

- 0730 to 0815 – (DS2) Dodger Stadium onall days.

- 0830 to 0915 – (CO2) Compton Loop on all days.

- 0930 to 1015 – (CV2) Covina Loop (east on I-10 at I-710, south on S-57, west on S-60 to Azusa Blvd off-ramp) on all days.

- 1030 to 1115 – (IH2) Industry Hills Conference Center on all days.

- 1130 to 1215 – (PO1) Pomona Loop (east on S-60 at Azusa Blvd onramp, north I-15, west of I-10 north on 210 to Azusa Blvd off-ramp on October 2, 4, 6, 7, and 8.

Five sets of canister and Tenax samples and continuous CO, NO, NOy and black carbon measurements were taken at a truck stop near I-10 and I-15. Measurements were made during the early morning hours from 0100 to 0500, and consisted of three sets of samples at the truck stop and upwind samples before and after the truck stop samples. Additionally, ten gasoline and two diesel fuel samples were collected for analysis of speciated VOCs.

4.2 Measurement Methods

The concentrations of black carbon were determined using an Anderson RTAA-1000 Aethalometer. The instrument continuously collects aerosol on a quartz-fiber filter tape. During the deposition process, the light attenuation through the aerosol collection spot and an unloaded reference spot are monitored. Their difference yields the absorption due to the integral of all light-absorbing materials collected on a particular spot. The time derivative of this quantity is a measure of the current aerosol light absorption. The Aethalometer converts the result of its filter

attenuation measurement into BC mass concentration by a conversion factor of 19.2 m2/g. Aethalometer BC agrees with collocated filter samples analyzed for elemental carbon (Hansen and McMurry, 1990). When the optical density of the aerosol spot reaches a certain value, the filter tape advances automatically. The Aethalometer was operated with a time resolution of five minutes. Because of the high black carbon concentrations encountered during on-road sampling, the time intervals between tape advances were as short as 30 minutes, which is substantially shorter than under typical ambient sampling. During each tape advance and associated instrument calibration, data collection was suspended for 20 minutes.

Nitric oxide (NO) was continuously measured by a high sensitivity chemiluminescence analyzer (TEI 42S). The instrument was the property of the Bay Area Air Quality Management District and was on loan to DRI. The instrument contained, as part of its sampling flow path, an internal zeroing component to provide essentially continuous zero correction. The NO/NOy version as used in the van had the molybdenum NOy to NO converter removed from the instrument and placed outside on the roof of the van. The placement of the converter reduced the losses of the more reactive species that are included in the general category of oxides of nitrogen, such as $HNO_3$and PAN.

The analyzer was calibrated by DRI personnel. The calibration system consisted of an Environics calibrator with an internal ozone generator to produce NO_2 by gas phase titration (GPT), a cylinder of compressed NO gas in nitrogen with concentration near 50 ppm that was traceable to NIST standards, and an Aadco zero air generator. The response of the instrument to zero air averaged –0.1 ppb for the NO channel and 0.3 ppb for the NOy channel. A gradual decrease in the recorded NO and NOy concentrations relative to actual concentrations over the weeklong period of the study was observed in the calibration data. This discrepancy reached a maximum of 30%, but no correction was applied to the data since the mobile NO measurements showed generally good agreement with values from the AQMD instrument at Azusa when the two were collocated each evening. The NOy measurements collected during mobile sampling showed a tendency to read high after encountering large spikes in NO concentration. In some cases, when spikes of 200-300 ppb NO were observed, NOy readings did not return to expected baseline values for almost an hour even though NO was below the minimum detection limit (MDL) in the area. This behavior was also observed during calibration, so the mobile NOy measurements were deemed unreliable for on-road sampling periods. Estimated NOy values were substituted where necessary. By assuming that all of the NO measured on-road was due to fresh vehicle emissions, NOy was estimated as 105% of observed NO plus 30 ppb (the average regional background level of NOy observed in this study).

The TEI Model 48C carbon analyzer was used in the mobile sampling. The instrument has a lower detection limit of 0.4 ppm. The analyzer is based on EPA Method EQSA-0486-060. Periodic calibrations of the CO analyzer showed no consistent bias at levels from 0 to 6 ppm, and zero stability to within 0.3 ppm.

Measurements of speciated volatile organic compounds were made by DRI at the SCAQMD Azusa monitoring station using an automated gas chromatograph with mass spectrometer. The measurements were made continuously on an hourly basis during the nine-day field study. The system use for this project was the unit used by DRI in the Central California Ozone Study. The system consists of a Varian 3800 gas chromatograph that is

interfaced to an Entech model 7100 automated preconcentrator, a Varian Saturn 2000 ion trap mass spectrometer, and a windows-based PC to manage the analytical and data acquisition operations. The target species included C_2 to C_{12} hydrocarbons, methanol, ethanol, and other alcohols. Also included are C_2 and larger carbonyls including acetone, methyl ethyl ketone (butanone), benzaldehyde and others. MTBE and other oxygenates used in fuels are included as is isobutene, an important breakdown product of MTBE. Oxygenated compounds in surface coatings such as benzaldehyde, benzoic acid, and butylacetate are also included, as are the biogenic species isoprene, alpha and beta pinene, and limonene. Commonly detected halocarbons are also included. The detection limits for these species are about 0.2 ppbv for all targeted species.

Stainless steel SUMMA™-polished canisters of 3-L capacity were used for volatile hydrocarbon (C_2-C_{12}) collection. These canister samples are suitable for analysis of speciated hydrocarbons by EPA Method TO-14, as well as for analyses of CO, CO_2, methane, and oxygenated species. Prior to sampling, the canisters were cleaned by repeated evacuation and pressurization with humidified zero air, and certified as described below. The sampling procedure essentially follows the pressurized sampling method described by EPA Methods TO-12 and TO-14 and the EPA document "Technical Assistance Document for Sampling and Analysis of Ozone Precursors" (October 1991, EPA 600/8-91-215). Gas chromatography with flame ionization detector is the established technique for monitoring volatile hydrocarbons in ambient air. The DRI analytical procedure for analysis of C_2-C_{12} hydrocarbons is consistent with the EPA document "Technical Assistance Document for Sampling and Analysis of Ozone Precursors" (October 1991, EPA 600/8-91-215). The GC/FID response is calibrated in ppbC, using primary calibration standards traceable to the National Institute of Standards and Technology (NIST) Standard Reference Materials (SRM) C_8 to C_{20} Hydrocarbons by GC-FID Analysis of Tenax Cartridges.

Heavy hydrocarbons, defined as hydrocarbons in the range of $C_8$to C_{20}, were collected using Tenax-TA (Alltech) solid adsorbent. The Tenax samples were analyzed by thermal desorption-cryogenic pre-concentration, using the Chrompack Thermal Desorption – Cold Trap Injection unit (Chrompack International BV), followed by high resolution gas chromatography and Fourier transform infrared detection (IRD) – mass spectrometry detection (MSD) (Hewlett Packard 5890II GC, 5965 IRD and 5970 MSD)

4.3 Spatial and Temporal Variations in Pollutant Concentrations and VOC/NOx Ratios

This section examines the spatial and temporal variations in NO, NOy, black carbon, CO, MTBE, VOC and semi-volatile hydrocarbons. We recognized that meteorological conditions could be a major factor in the day-to-day variations in pollutant concentrations. Our collaborators in this study at Sonoma Technology, Inc. (STI) examined the meteorological conditions on each day from September 29, 2000 to October 9, 2000. STI's analysis showed the presence of a trough over Southern California on a majority of the days during the study. STI examined eleven meteorological parameters and applied a subjective rating of favorable, not favorable, or neutral with respect to the probable influence of each parameter on ambient concentrations of primary pollutants. The period from Wednesday, October 4 to Saturday, October 7 was not conducive to high pollutant concentrations. The two Sundays (October 1 and 8) and both Mondays (October 2 and 9) were overall neutral for pollutant buildup. Each weekend day during the study was found

to have a companion weekday with similar meteorology. Pollutants that have minimal day-of-the-week variations in emissions should exhibit daily variations in concentrations that are consistent with meteorological variations. Thus, such pollutants are expected to show higher concentrations at the beginning and end of our study period and lower levels midway through the study. These expectations provide valuable perspective for interpreting the temporal variations in pollutant concentration. It is important to note, however, that our conclusions are based primarily upon relationships among pollutants, which are affected less by daily meteorological variations.

4.3.1 Pollutant Variations in On-Road, Regional, and Background Samples

A complete set of data was obtained from the mobile sampling van for the following four days – October 2, 2000 (Monday), October 4 (Wednesday), October 7 (Saturday), and October 8 (Sunday). Data for CO, NO/NOy, and black carbon were acquired continuously starting at 0100, PDT and ending each day at about noon. Ten sets of canister and Tenax samples were collected each day with sampling times of 45 to 50 minutes per sample. During the overnight carryover period, VOC samples were collected along the Covina (CV1) and Compton (CO1) Loops and at regional/background sites at Industry Hills (IH1) and Dodger Stadium (DS1) (Figure B.1-1). Sampling was repeated along the two freeway loops (CV2 and CO2) and at Dodger Stadium (DS2) during the ozone inhibition period. In addition, a sample was collected on southbound 110 (Harbor) Freeway near Dodger Stadium (HF1). This sample should be dominated by gasoline vehicle exhaust as heavy trucks are prohibited on this section of the 110. The final two samples were collected during the ozone accumulation period at Industry Hills (IH2) and on the Pomona (PO1) Loop.

The time series plots of NO and NOy in Figure 4.3-1 for Wednesday, October 4 show that NO concentrations were 1-2 orders of magnitude higher on freeways than on surface streets or at the SCAQMD Azusa monitoring station and other regional/background sites. The plot also shows that NO concentrations are substantially lower for the HF1 sample (freeway with no trucks) than other freeway samples with a mixed fleet of gasoline- and diesel-powered vehicles. NO concentrations are about a factor of two higher on Wednesday compared to Sunday, October 8 during the ozone inhibition period and a factor of three higher during ozone accumulation period in the eastern basin despite the fact the meteorological conditions were more stable on Sunday.

Figure 4.3-2 shows the average NO, black carbon, and CO concentrations for each of the freeway loops and regional/backgrounds sites for two weekend days (Saturday, October 7 and Sunday, Ocotber 8) and two weekdays (Monday, October 2 and Wednesday, October 4). Weekend/weekday differences for black carbon mirror those of NO with much higher weekday NO concentrations for all freeway loops. In contrast, CO exhibits minimal weekday/weekend differences. CO concentrations are higher on weekends during the carryover period while both NO and black carbon exhibit little weekend/weekday differences during this period.

The NOy, black carbon, CO, MTBE, semi-volatile hydrocarbons, and VOC concentrations, and VOC/NOy ratios are averaged in Table 4.3-1 for freeway loops (separate averages for carryover, ozone inhibition, and ozone accumulation periods), regional/background, and sites dominated by light-duty gasoline vehicles (sample HF1), and heavy-duty diesel trucks (truck stop). The four plots in Figure 4.3-3 show these averages in relation to corresponding

values measured at the regional sites and source-dominated areas. Figure 4.3-3a shows that NOy and black carbon exhibit very similar diurnal and spatial variations, and weekday/weekend differences. Both NOy and black carbon are much higher on weekdays, especially during the ozone inhibition and accumulation periods. During weekdays, their concentrations along the freeway loops were about an order of magnitude higher than at Dodger Stadium or Industry Hills. Figure 4.3-3b shows that CO and VOC have similar temporal and spatial variations, which differ significantly from those exhibited by NOy and black carbon. CO and VOC showed no significant weekend/weekday differences during the ozone inhibition and accumulation periods. Overnight carryover appears to be more significant for CO and VOC than for NOy and black carbon on weekends, especially Sunday morning.

The variations in VOC/NOy ratios(ppbC of VOC to ppb of NOy), shown in Figure 4.3-4, are straightforward given the variations that are observed for NOy, CO, black carbon, and VOC. VOC/NOy ratios are lower on freeways because NO concentrations are substantially higher on freeways than other areas. The high NO concentrations are always accompanied by higher black carbon and semi-volatile hydrocarbons. Although diesel exhaust is not the sole source of black carbon and semi-volatile hydrocarbons, it is the predominant source during hot, stabilized driving conditions on freeways, and diesel trucks are a major source of the large spikes in NO concentrations on freeways. VOC/NOy ratios on freeways ranged from 0.5 to 2. These ratios are comparable to the average ratio of 0.9 measured at the truck stop. One notable exception was early Sunday morning at 2:00 to 5:00 a.m. when VOC/NOy reached about four. Greater carryover of VOC accounted for the larger VOC/NOy ratio during this time. Larger concentrations of MTBE during this period indicate greater contributions from gasoline-powered vehicles. The light-duty gasoline-powered vehicle fleet, as represented by the HF1 samples, has an average VOC/NOy ratio of about 3.5. This value is similar to the VOC/NOy ratios measured at Industry Hills and Dodger Stadium.

4.3.2 Pollutant Variations at Ambient Monitoring Sites

Datasets that are comparable to that compiled from the mobile van were acquired at the SCAQMD Azusa and Pico Rivera monitoring stations. In general, the weekend/weekday patterns in pollutant concentrations at the monitoring stations and for the on-road measurements are consistent, as are the associations among pollutants.

Figure 4.3-5a shows time series of hourly average concentrations of NO, NO_2, black carbon and CO at the Azusa monitoring station during the study period. Figure 4.3-5b shows the same data averaged over the carryover, ozone inhibition, and ozone accumulation periods. The time series for NOx is closely correlated to the time series for black carbon. The day-to-day variations show a midweek dip, which is coincident with the passage of a trough. Despite meteorological conditions that were unfavorable for pollutant buildup during the middle of the week, however, both NOx and black carbon are much higher on weekdays than during the weekends. CO shows no discernible differences between weekdays and weekends that might be ascribed to changes in emission patterns. Rather, it reasonably tracks the day-to-day variations in meteorological conditions. Similar time series are shown for Pico Rivera in Figures 4.3-6a and 4.3-6b. The trends at the Pico Rivera monitoring station are more complex than for Azusa due, most likely, to its close proximity to a major freeway (I-605) and diurnal variations in wind speed and direction. During the prevailing sea breeze in the afternoon, the station is upwind of

the freeway, and the daily minimum NOx concentrations are measured during this period. During summer nights, the winds are calm and typically offshore causing the highest NOx concentrations to occur overnight.

Like CO, VOC shows no discernible differences between weekdays and weekends that might be ascribed to changes in emission patterns, and day-to-day variations track the trend in meteorological conditions. Figures 4.3-7 and 4.3-8 show the diurnal and day-to-day variations in CO, nonmethane hydrocarbons, and nonmethane organic gases at Azusa and Pico Rivera, respectively. The effect of Pico Rivera's microenvironment is also evident on the diurnal variations of CO and VOC. Accordingly, the VOC/NOx ratios are more variable at Pico Rivera than at the Azusa monitoring station. Figure 4.3-9 shows that the VOC/NOx ratios at Azusa are consistently about five during the weekdays with little diurnal variation. Ratios were greater during the weekends, ranging between 5 and 10. In contrast, the ratios at Pico Rivera are considerably more variable with ratios around five during the night and ratios in the range of 15 to 20 during the afternoon. The large afternoon ratios are due to low NOx concentrations resulting from the impact of a well-mixed, aged air mass during this time of day.

4.4 Source Apportionment of VOC

The Chemical Mass Balance (CMB) receptor model consists of a least-squares solution to a set of linear equations, which expresses each receptor concentration of a chemical species as a linear sum of products of source profile species and source contributions. The source profile species (the fractional amount of the species in the VOC emissions from each source type) and the receptor concentrations, each with uncertainty estimates, serve as input data to the CMB model. The output consists of the contributions for each source type to the total ambient VOC as well as to individual VOC species concentrations. Gasoline and diesel exhaust profiles were derived from samples collected during the field study along the Harbor Freeway (HF1) and at the truck stop near I-10 and I-15. Profiles for fuels were developed from analysis of gasoline samples collected during the field study. In addition to the relative contributions of gasoline and diesel exhaust, the detailed speciation of VOC from the mobile sampling and the time-resolved VOC speciation at Los Angeles, Azusa, and Pico Rivera monitoring stations provide source attribution of other sources of VOC by time of day and day of the week. These analyses address questions regarding the source contributions of VOC carried over from the previous evening and the relative importance of sources other than gasoline and diesel combustion sources in the diurnal variations in VOC/NOx ratios.

4.4.1 Source Composition Profiles

The profiles are expressed as weight percentages and are normalized to the sum of the 55 Photochemical Assessment Monitoring Station (PAMS) target NMHCs. The PAMS species typically account for 70 to 80 percent of the total ambient hydrocarbons at most urban locations. The PAMS hydrocarbon data are ideally suited for CMB analysis because of the level of hydrocarbon speciation, consistency among networks in measurement methods and quality assurance, and the available spatial and temporal resolution of the data. Compounds other than the 55 PAMS species that are identified by the DRI laboratory are retained in the database individually and as a subtotal named "OTHER." Compounds reported as "unknown" are grouped

into a category named "UNID." The source profile data reported in units of ppbC or ppbv are converted to $\mu g/m^3$ prior to calculating the weight percentages using species-specific conversion factors. One-sigma uncertainties were derived from variations among multiple measurements for a particular source type or a nominal analytical uncertainty of 15 percent. The assigned uncertainties are the larger of the two values.

The source composition profiles used in the CMB analysis are shown in Table 4.4-1. They include gasoline and diesel exhaust, gasoline liquid and vapor, commercial natural gas and liquefied petroleum gas, surface coatings, consumer products ,and isoprene.

Gasoline Exhaust. A profile for gasoline exhaust was derived for this study from the four samples collected along the Harbor Freeway (HF1). Each HF1 sample was corrected for surrounding background VOC concentrations by subtracting the Dodger Stadium sample (DS1), which preceded each HF1 sample. The composition profile included CO and NOx in proportion to the sum of PAMS species. The two weekday samples generally reflect vehicle operation in stop-and-go traffic and the two weekend samples reflect free-flow conditions.

Diesel Exhaust. A profile for diesel exhaust was derived for this study from the three samples collected at a truck stop near the intersection of I-10 and I-15. These samples were collected between 2:00 and 5:00 a.m. on Tuesday, October 3. Each truck stop sample was corrected for background VOC concentrations by subtracting the average of the 2:00-2:45 a.m. samples that were collected at Industry Hills (IH1) on Monday, 10/2/00 and Wednesday, October 4. The background correction was adjusted in order to yield zero abundance of MTBE in the background-corrected diesel profile.

Gasoline Liquid and Vapor. Gasoline samples that were collected and analyzed for this study consist of the two grades (regular and premium) for five brands (ARCO, Union 76, Shell, Chevron, and Mobil). In addition to profiles for individual samples, composites were derived for each grade of gasoline from a combination of the five brands. An overall composite liquid gasoline profile was constructed based on this relative weighting of 68% regular and 32% premium (Kirchstetter et al., 1999).

The compositions of gasoline headspace vapors were predicted from the measured composition of liquid gasoline using the method described by Kirchstetter et al. (1999). This method is based on the proportionality between the equilibrium headspace partial pressure for each compound identified in gasoline with its mole fraction in liquid gasoline times the vapor pressure of the pure species. The individual vapor pressures are determined using the Wagner equation.

Commercial Natural Gas and Liquefied Petroleum Gas. The commercial natural gas (CNG) and liquefied petroleum gas profiles are based on samples taken in the summer of 1972 at Los Angeles, CA and in the summer of 1973 at El Monte, CA (Mayrsohn et al., 1976, 1977). Contribution of aged emissions is a plausible alternative interpretation of these two sources. The combination of the two profiles accounts for the excess ethane and propane that typically exist in most urban areas.

Surface Coatings. A large variety of formulations are used in surface coatings, and it is

unlikely that one or two profiles adequately represent the emissions from all surface coatings. The most recent data are those of Censullo et al., (1996). Eleven categories of coatings were analyzed in this study. Detailed species profiles were obtained for 106 samples of water-based and solvent-based coating samples. Surface coating profiles for solvent-based industrial maintenance coatings, solvent-based medium gloss/high gloss, solvent-based primers and sealers, quick dry primers and enamels, and thinning solvent were applied in the apportionments. These are largely depleted in the species common to fuel use and production, with larger abundances of styrene, n-decane, and especially "other" compounds. The "other" VOCs are quantified and differ substantially among the different coatings tested. Most of these other compounds are oxygenated compounds that are not measured in PAMS.

Consumer Products. This profile is a composite of various consumer products compiled by the U.S. Environmental Protection Agency. This profile is also contained in the California Air Resources Board's list of profiles in the modeling emission data system.

Isoprene was used as a single-component biogenic profile. Biogenic NMHC emissions are highly reactive in the atmosphere, and biogenic source contributions derived from CMB modeling will supply only a lower limit to the actual contributions from biogenic emissions.

Regional Background is a composite of several ambient samples collected at sites located off the coast of southern California from midnight to noon. It represents air masses transported into the basin that are low in fresh emissions.

4.4.2 CMB Analysis of PAMS VOC Data for 1999-2000

CMB Version 8 was applied to the ambient site VOC data using the default set of source composition profiles described in the previous section. These sources account for greater than 90 percent of the measured ambient NMHC in most cases. Source contribution estimates (SCEs) were calculated for all valid samples collected at Azusa, Pico Rivera, and Upland by the SCAQMD and at Los Angeles N. Main by CARB. The results were grouped by site, day-of-the-week, and sample period and the average and standard deviation of the resulting apportionments calculated. The statistics and diagnostic information and SCEs for the carryover, ozone inhibition, ozone accumulation, and peak ozone periods are given in Tables 4.4-2 and 4.4-3 in $\mu g/m^3$ of NMHC and percentage of NMHC, respectively. The source contributions are presented graphically in Figure 4.4-1. Results for Los Angeles are only included in the tables due to the different sampling schedule at that site (6:00 a.m. and 1:00 p.m.). Results from both years were combined in the averages except for the Pico Rivera auto-GC/MS data, where only 1999 data were used due to unusually high unidentified hydrocarbon concentrations in 2000 at that site. In the CMB calculation, liquid gasoline represents the additional unburned gasoline (due to misfiring and other engine malfunctions) that is not included in the exhaust profile, plus evaporative emissions from gasoline spillage, hot soaks, and some portion of resting losses (leaks, permeation). Previous studies showed that the source attribution between tailpipe and liquid gasoline from receptor modeling can vary greatly depending on the particular profile chosen for tailpipe emissions (Harley et al., 1992, Fujita et al., 1994, Pierson et al., 1999).

Gasoline exhaust is the predominant source, ranging from 40-60% for all sites during the four periods studied. Diesel exhaust was not consistently identified, and was rarely apportioned

more than a few percent of the total NMHC. The lack of heavier hydrocarbon species (>C11) in the data may be preventing diesel sources to be recognized. Contributions of CNG and LPG are in the range of 5-10 percent combined. The sum of surface and consumer products is only slightly larger. There is little variation in the relative source contributions between days of the week, but a slightly higher predominance of gasoline engine sources on weekends is suggested in some cases.

4.4.3 CMB Analysis of VOC Data from the Fall 2000 Field Study

CMB Version 8 was applied to the mobile van VOC data using the same default set of source composition profiles as for the ambient data analysis. These sources account for close to 100 percent of the ambient NMHC. Source contribution estimates (SCEs) and the statistics and diagnostic information are given in Table 4.4-3a. The SCEs are given in $\mu g/m^3$ of NMHC and percentage of NMHC in Tables 4.4-3b and 4.4-3c, respectively. The source contributions are presented graphically in Figures 4.4-2 and 4.4-3 for $\mu g/m^3$ of NMHC and percentage of NMHC, respectively. Apportionments of liquid gasoline are significant in only a few samples and combined with gasoline exhaust in Table 4.4-3.

Gasoline exhaust is the predominant source in all samples, ranging from 60-80% for on-road samples and samples taken at more regionally representative locations. The diurnal and weekday/weekend variations in the relative contributions of NMHC are more variable for diesel exhaust than gasoline exhaust. The relative contributions of diesel exhaust are greatest during the weekdays on freeway loops with the greatest fraction of diesel traffic. Diesel exhaust contributed 20 percent of NMHC on the Pomona Loop on Monday, October 2, compared to only 3 percent on Sunday, October 8. These percentages are 18 and 6 percent on Wednesday, October 4 and Saturday, October 7, respectively. Day-of-the-week changes in the contributions of diesel exhaust have considerably less impact on NMHC/NOx ratios than day-of-the-week changes in the contributions of diesel exhaust to ambient NOx concentrations. The sum of surface and consumer products typically account for less than 10 percent of the observed species. Contributions of CNG and LPG are mostly in the range of 5-10 percent combined. The contributions of non-mobile sources to ambient NMHC emissions do not show significant day-of-the week variations and have little effect on weekday variations in ambient VOC/NOx ratios.

4.5 Source Apportionment of NOx

4.5.1 NOx Apportionment by Multiple Linear Regression

Mobile sources (on-road and off-road) were estimated to account for 86% of all NOx emissions in the South Coast Air Basin in 1996 (EMFAC2000). The ratio of the contribution of gasoline-powered vehicles and diesel-powered vehicles is 70:30 for on-road NOx and 54:46 for the sum of on-road and off-road. Given that mobile sources are the dominant source of NOx emissions in the Basin, it is likely that variations in ambient NOx concentrations are related to copollutants in gasoline and diesel exhaust that also have little contribution from sources other than mobile. Carbon monoxide is the obvious copollutant of choice for gasoline exhaust. Mobile sources account for 94% of the basinwide total CO emissions with gasoline vehicle exhaust accounting for 92% of this total. Source apportionment studies of ambient carbonaceous particles

have shown that diesel exhaust is the largest source of black carbon (Schauer et al., 1996; Watson et al., 1998; and Fujita et al., 1998). The experimental design for apportioning ambient NOx is based upon the premise that variations in the relative contributions to ambient NOx of gasoline and diesel exhaust can be estimated from variations in concentrations of CO and black carbon.

Multiple regression is used in this analysis to account for the variance in ambient NOx concentrations, based on linear combinations of CO and black carbon. The multiple regression takes the form $[NOx] = b_0 + b_1[CO] + b_2[BC]$. The b's are the regression coefficients, representing the amount that [NOx] changes when either [CO] and [BC] changes by 1 unit with the other independent variable held constant. The b_0 is the constant, where the regression line intercepts the [NOx] axis, representing the concentration of NOx when both CO and BC are zero. The scatterplots in Figures 4.5-1 and 4.5-2 show the correlations of NO and NOx to black carbon and CO, respectively, at Azusa and Pico Rivera for different sets of weekdays and hours of the day. The correlations with CO and black carbon are higher for NOx than NO. The degree of correlation is not significantly different for a dataset consisting of only weekdays versus all days and all hours or versus 6 to 9 a.m. only.

The regression coefficients were first derived using on-road measurements from the mobile van consisting of simultaneous 5-minute average concentrations of NO/NOy, CO, and black carbon in varying mix of traffic during weekdays and weekends. The dataset excludes NOy data when NO is less than 10 ppb and sampling times during the ozone accumulation period to minimize the effect of photochemical depletion of NOx on the regression. We also excluded the data from the truck stop because the ratios of NOx to black carbon for idling trucks differ considerably from trucks on the open road. The NOx to black carbon ratios that were measured on freeway loops averaged 27 ppb of NOx per $\mu g/m^3$ of black carbon compared to a ratio of 67 at the truck stop. The final dataset includes about 350 sets of observations. For the most part, the dataset consists of on-road sampling of fresh mobile source emissions so that the b_1 and b_2 in the regression equation is the average contribution to NOx per unit of CO and black carbon, respectively. Thus $b_1[CO]$ is the NOx associated with CO and $b_2[BC]$ is the NOx associated with black carbon. The dataset yielded the following regression equation:

$$[NOx, ppb] = -1.34 + 39.42 * [CO, ppm] + 14.84 * [BC, \mu g/m^3]$$

with standard errors for b_0, b_1, and b_2 of 7.32, 3.94, and 0.94, respectively, and R^2 of 0.6. These coefficients were applied to the full set of data from the mobile van and at the Azusa and Pico Rivera monitoring sites. We also examined the use of MTBE and the sum of nC_{10}-nC_{15} as alternative independent variables. Both of these variables are from time-integrated rather than continuous measurements, so the regression was less robust. Furthermore, there are evaporative sources of MTBE that can complicate the association with NOx.

Figures 4.5-3a through 4.5-3d show the amounts of ambient NOx associated with CO and black carbon for the mobile sampling conducted on Monday, October 2, Wednesday, October 4, Saturday, October 7, and Sunday, October 8, respectively. The contributions are shown in ppb and percentage of NOx. Breaks in the data are due to advances of the tape in the aethalometer. Each advance causes a 20-minute gap in the data. The averages corresponding to each of the freeway loops and regional/background sites are in Table 4.5-1. During the overnight carryover

period, the amount of NOx associated with CO and black carbon on freeway loops is similar to that at regional sites, with CO-associated NOx ranging mostly between 50 and 60 percent on weekdays, 60 to 65 percent on Saturday, and 65 to 70 percent on Sunday. There are large spikes of BC-associated NOx for the two weekdays on freeway loops during the ozone inhibition and accumulation periods. These spikes exist to a lesser extent on Saturday and are almost entirely absent on Sunday. The percentage of CO-associated NOx for the three freeway loops during this time of day, CO2, CV2, and PO1, are 47, 35, and 41 percent, respectively, on Monday, 38, 40, and 30 percent on Wednesday, 43, 59, and 57 percent on Saturday, and 63, 68, and 59 percent on Sunday. Figure 4.5-4 shows the amounts of ambient NOx associated with CO and black carbon for six surface street loops. The loops were distributed within the Compton and Covina Loops and designed to provide comparisons of the surface street traffic with freeway traffic in the area. The percentage of CO-associated NOx ranged from 44 to 73 percent with a mean and standard error of 56 ± 4 percent.

Figures 4.5-5 and 4.5-6 show the ambient NOx associated with CO and black carbon for the ambient data at the Azusa and Pico Rivera monitoring stations, respectively. The percentage of NOx associated with CO is consistently larger on weekends and the largest fractions of NOx associated with black carbon occur midday during weekdays. These patterns are consistent with the diurnal and day-of-the-week variations in relative traffic volume of gasoline and diesel powered vehicles. The scatterplots in Figure 3.5-7 show similar correlations of predicted versus measured NOx at Azusa and Pico Rivera. The predicted values are reasonably correlated with measured value with a slope of 0.70 and 0.83 at Pico Rivera and Azusa, respectively.

We particularly focused on locations that are regionally representative and times that coincide with ozone accumulation. At Industry Hills, the most regionally representative of the mobile sampling sites, the percentages of CO-associated NOx in the 10:30 to 11:15 a.m. samples are 44, 48, 62, and 72 percent for Monday, Wednesday, Saturday, and Sunday, respectively. Based upon STI's analysis of the study period meteorology, Monday, October 2 is meteorologically similar to Sunday, October 8, and Wednesday, October 4 is similar to Saturday, October 7. The Saturday/Wednesday ratios of the CO and BC associated NOx are 1.01 and 0.58, respectively. The Sunday/Monday ratios of the CO and BC associated NOx are 0.84 and 0.25. These ratios are summarized in Table 4.5-2 along with the ratios for Azusa and Pico Rivera. The three locations are very consistent with each other in the weekend/weekday differences in the relative contribution of NOx associated with CO and black carbon. These results show that the contribution of gasoline-powered vehicles to ambient NOx on a typical Saturday during the ozone accumulation period is comparable to their contribution on weekdays. This conclusion is consistent with traffic counts, which show comparable light-duty gasoline vehicle traffic volumes on weekday and Saturday during this time of day. The contribution of gasoline-powered vehicles to ambient NOx is about 25 percent lower on Sunday compared to weekdays. In contrast, the contributions of diesel vehicles during the ozone accumulation period to ambient NOx on Saturday and Sunday are about one-half and one-third of its weekday contribution, respectively.

4.5.2 Source Apportionment of NOx by Chemical Mass Balance

In addition to apportionment of VOC, we also apportioned NOx to gasoline and diesel exhaust by including NOx in the source profiles. Apart from reactions of NOx that occur in the

atmosphere, a key issue with this approach is whether the proportion of NOx in the VOC profile is representative of the vehicles that are actually on the road. The gasoline exhaust profile is based upon on-road measurements of predominantly gasoline-powered vehicles (i.e., sample HF1) with background correction. This profile should be reasonably representative. Samples collected at the truck stop reflect mostly idle emissions, which have lower ratios of NOx to VOC than on-road emissions. The truck stop profile will likely overestimate the NOx contributions of diesel exhaust when applied in CMB to ambient samples containing on-road diesel NOx emissions. Because of these uncertainties, CMB is used to examine the weekday/weekend differences in NOx source contributions, and the multiple regression approach is used for the quantitative NOx apportionment.

Figures 4.5-8 and 4.5-9 show the apportionment of NOx for mobile sampling loops and regional background sites in concentration and percentage contributions, respectively. As explained above, the diesel exhaust contributions are greater than estimates derived by multiple regression but consistent with the regression approach with respect to sample-to-sample variations and weekday/weekend variations.

4.6 Summary of Findings

Pollutant Variations on Freeway Loops, and Regional and Source-Dominated Locations

- NO concentrations were 1-2 orders of magnitude higher on freeways than on surface streets or at the SCAQMD Azusa monitoring station and other regional/background sites. NO concentrations are substantially lower for the HF1 sample (freeway with no trucks) than other freeway samples with a mixed fleet of gasoline- and diesel-powered vehicles.

- CO and hydrocarbon concentrations were about a factor of 2-3 higher on freeways than at the SCAQMD Azusa monitoring station and other regional/background sites. CO and hydrocarbon concentrations for the HF1 sample (freeway with no trucks) are comparable to other freeway samples with a mixed fleet of gasoline- and diesel-powered vehicles.

- NO concentrations are about a factor of two higher on Wednesday, October 4 compared to Sunday, October 8 during the ozone inhibition period and a factor of three higher during ozone accumulation period in the eastern basin despite the fact the meteorological conditions were more stable on Sunday.

- Weekend/weekday differences for black carbon mirror those of NO with much higher weekday NO concentrations for all freeway loops. In contrast, CO exhibits minimal weekday/weekend differences. CO concentrations are higher on weekends during the carryover period while both NO and black carbon exhibits little weekend/weekday differences during this period.

- NOx and black carbon exhibit very similar diurnal and spatial variations, and weekday/weekend differences. Both NOy and black carbon are much higher on weekdays, especially during the ozone inhibition and accumulation periods. CO and VOC have temporal and spatial variations that are similar to each other, but they differ significantly from those exhibited by NOx and black carbon. CO and VOC showed no significant

weekend/weekday differences during the ozone inhibition and accumulation periods. Overnight carryover appears to be more significant for CO and VOC than for NOy and black carbon on weekends, especially on Sunday morning, October 8.

- VOC/NOx (ppbC of VOC to ppb of NOx) ratios on freeways ranged from 0.5 to 2. These ratios are slightly higher than the average ratio of 0.9 measured at the truck stop. One notable exception was early Sunday morning at 2:00 to 5:00 a.m. when VOC/NOy reached about four. Greater carryover of VOC accounted for the larger VOC/NOy ratio during this time. Larger concentrations of MTBE during this period indicate greater contributions from gasoline-powered vehicles.

- The light-duty gasoline-powered vehicle fleet, as represented by the freeway HF1 samples, has an average VOC/NOy ratio of about 3.5. This value is similar to the VOC/NOy ratios measured at Industry Hills and Dodger Stadium.

Pollutant Variations at Ambient Monitoring Sites

- The time series for NOx is closely correlated to the time series for black carbon. The day-to-day variations show a midweek dip, which is coincident with the passage of a trough through the Los Angeles area. Despite meteorological conditions that were unfavorable for pollutant buildup during the middle of the week, however, both NOx and black carbon are much higher on weekdays than during the weekends.

- CO shows no discernible differences between weekdays and weekends that might be ascribed to changes in emission patterns. Rather, it reasonably tracks the day-to-day variations in meteorological conditions.

- Like CO, VOC shows no discernible differences between weekdays and weekends that might be ascribed to changes in emission patterns, and day-to-day variations track the trend in meteorological conditions.

- VOC/NOx ratios at Azusa are consistently about five during the weekdays with little diurnal variation. Ratios were greater during the weekends, ranging between 5 and 10. In contrast, the ratios at Pico Rivera are considerably more variable with ratios around five during the night and ratios in the range of 15 to 20 during the afternoon. The large afternoon ratios are due to low NOx concentrations resulting from the impact of a well-mixed, aged air mass during this time of day.

NOx Apportionment by Multiple Linear Regression

- During the overnight carryover period, the amount of NOx associated with CO and black carbon on freeway loops is similar to that at regional sites, with CO-associated NOx ranging mostly between 50 and 60 percent on weekdays, 60 to 65 percent on Saturday, and 65 to 70 percent on Sunday.

- There are large spikes of BC-associated NOx on freeway loops during the ozone inhibition and accumulation periods on the two weekdays. These spikes exist to a lesser extent on

Saturday and are almost entirely absent on Sunday. The percentage of CO-associated NOx for the three freeway loops during this time of day, CO2, CV2, and PO1, are 47, 35, and 41 percent, respectively, on Monday, 38, 40, and 30 percent on Wednesday, 43, 59, and 57 percent on Saturday, and 63, 68, and 59 percent on Sunday.

- At the Azusa and Pico Rivera monitoring stations, the percentage of NOx associated with CO is consistently larger on weekends and the largest fractions of NOx associated with black carbon occur midday during weekdays. These patterns are consistent with the diurnal and day-of-the-week variations in relative traffic volume of gasoline and diesel powered vehicles.

- At Industry Hills, the most regionally representative site where the mobile sampling was conducted, the percentages of CO-associated NOx in the 10:30 to 11:15 a.m. samples are 44, 48, 62, and 72 percent for Monday, October 2, Wednesday, October 4, Saturday, October 7, and Sunday, October 8, respectively. Based upon STI's analysis of the study period meteorology, Monday, October 2 is meteorologically similar to Sunday, October 8, and Wednesday, October 4 is similar to Saturday, October 7. The Saturday/Wednesday ratios of the CO and BC associated NOx are 1.01 and 0.58, respectively. The Sunday/Monday ratios of the CO and BC associated NOx are 0.84 and 0.25.

- The weekend/weekday differences in the relative contribution of NOx associated with CO and black carbon at Industry Hills are consistent with those found at the Azusa and Pico Rivera monitoring stations. These results show that the contribution of gasoline-powered vehicles to ambient NOx on a typical Saturday during the ozone accumulation period is comparable to their contribution on weekdays. This conclusion is consistent with traffic counts, which show comparable light-duty gasoline vehicle traffic volumes on weekday and Saturday during this time of day. The contribution of gasoline-powered vehicles to ambient NOx is about 25 percent lower on Sunday compared to weekdays. In contrast, the contributions of diesel vehicles during the ozone accumulation period to ambient NOx on Saturday and Sunday are about one-half and one-third of its weekday contribution, respectively.

<u>VOC and NOx Source Apportionment by Chemical Mass Balance</u>

- Gasoline exhaust is the predominant source in all samples ranging from 60-80% for on-road samples and samples taken at more regionally representative locations.

- The diurnal and weekday/weekend variations in the relative contributions of NMHC are more variable for diesel exhaust than gasoline exhaust.

- The relative contributions of diesel exhaust are greatest during the weekday on freeway loops with the greatest fraction of diesel traffic. Diesel exhaust contributed 20 percent of NMHC on the Pomona Loop on Monday, October 2, compared to only 3 percent on Sunday, October 8. The same percentages are 18 and 6 percent on Wednesday, October 4 and Saturday, October 7.

- Day-of-the-week changes in the contributions of diesel exhaust have much less impact on NMHC/NOx ratios than day-of-the-week changes in the contribution of diesel exhaust to ambient NOx concentrations.

- The diesel exhaust contributions to ambient NOx are greater than estimates derived by multiple regression but consistent with the regression approach with respect to sample-to-sample variations and weekday/weekend variations.

- From the multiple regression analysis, the corresponding attributions of gasoline-powered vehicles to on-road emissions of NOx during the 9 a.m. to noon period are 45, 57 and 66 percent for weekday, Saturday, and Sunday, respectively. According to the SoCAB emission inventory (using EMFC2000), gasoline-powered vehicles account for 71 percent of the total NOx emission from on-road vehicles for a typical summer day. These results suggest that NOx emission from diesel-powered vehicles may be underestimated in the inventory.

- Contributions of non-mobile sources to ambient NMHC emissions do not show significant day-of-the week variations and have little effect on weekday variations in VOC/NOx ratios.

Table 4.3-1

Average ambient concentrations of NO, NOy, CO, MTBE, black carbon, heavy hydrocarbons, and VOC during the carryover, inhibition, and accumulation periods by day: October 2-October 8, 2000

Parameter	Date	Freeway Loops			Regional	No Trucks	Stop**
		Carryover	Inhibition	Accumulation	Carryover*	Freeway	Truck
NO (ppb)	Mon, 10/2	168	321	288	2	70	313
	Wed, 10/4	163	287	357	3	59	
	Sat, 10/7	97	162	166	6	29	
	Sun, 10/8	113	168	110	43	88	
est. NOy'	Mon, 10/2	207	368	333	32	105	359
	Wed, 10/4	202	332	406	33	90	
	Sat, 10/7	132	201	205	36	77	
	Sun, 10/8	149	207	146	75	151	
CO (ppm)	Mon, 10/2	2.5	3.1	2.4	0.8	2.3	1.3
	Wed, 10/4	2.0	3.2	2.1	0.6	1.6	
	Sat, 10/7	2.0	2.9	3.0	0.9	1.8	
	Sun, 10/8	2.6	3.1	2.6	1.6	2.6	
MTBE (ppbC)	Mon, 10/2	14.6	15.9	15.0	5.7	17.4	12.3
	Wed, 10/4	11.1	23.1	2.3	5.4	12.7	
	Sat, 10/7	12.5	16.7	12.3	8.4	11.3	
	Sun, 10/8	46.0	18.6	11.9	13.4	21.3	
BC (ug/m3)	Mon, 10/2	5.1	13.3	11.3	1.7	2.5	4.7
	Wed, 10/4	4.5	13.0	13.5	1.1	1.6	
	Sat, 10/7	2.7	7.8	4.8	1.3	1.5	
	Sun, 10/8	2.5	4.2	4.6	1.8	2.8	
Sum of HC >C11 (ug/m3)	Mon, 10/2	1.0	2.0	5.2	0.9	0.8	6.6
	Wed, 10/4	1.1	2.9	2.0	0.7	0.8	
	Sat, 10/7	0.4	1.6	1.0	0.5	0.1	
	Sun, 10/8	1.3	1.3	0.7	1.0	1.3	
VOC (ppbC)	Mon, 10/2	308	412	259	135	369	305
	Wed, 10/4	236	447	215	106	333	
	Sat, 10/7	239	335	279	169	263	
	Sun, 10/8	575	391	238	266	382	
VOC/NOy	Mon, 10/2	1.5	1.1	0.8	4.2	3.5	0.9
	Wed, 10/4	1.1	1.4	0.5	3.2	3.7	
	Sat, 10/7	1.8	1.7	1.4	4.5	3.4	
	Sun, 10/8	3.9	1.9	1.6	3.5	2.5	

*average of two locations: Dodger Stadium (downtown LA) and Industry Hills (interior basin).
' NOy estimated as 1.05*(measured NO) + (average baseline NO2 + NOz).
**HDDV profiles collected early AM Tues at 1 location (truck stop).

Table 4.4-1
Default Source Composition Profiles Used in CMB Source Apportionment

Parameter	WEOzLDV1	Gas00LRPC	Gas00VRPC	WEOzHDD1	CNG	LPG	COATcomp	CPcomp_1	Biogenic
OTHER	0.000 ± 0.000	0.238 ± 0.048	0.089 ± 0.014	0.000 ± 0.000	0.000 ± 0.001	0.000 ± 0.001	0.000 ± 0.001	0.000 ± 0.002	0.000 ± 0.001
UNID	0.000 ± 0.000	0.249 ± 0.059	0.000 ± 0.000	0.000 ± 0.000	0.005 ± 0.154	0.000 ± 0.193	1.865 ± 0.227	0.714 ± 0.071	0.000 ± 0.001
NMHC	1.211 ± 0.121	1.488 ± 0.149	1.089 ± 0.109	1.375 ± 0.137	1.005 ± 0.100	1.000 ± 0.100	2.865 ± 0.286	2.225 ± 0.222	1.000 ± 0.100
NMOC	1.310 ± 0.131	1.689 ± 0.169	1.336 ± 0.134	1.388 ± 0.139	1.005 ± 0.101	1.000 ± 0.100	2.865 ± 0.286	2.428 ± 0.243	1.000 ± 0.100
IDOXY	0.141 ± 0.014	0.201 ± 0.021	0.247 ± 0.025	0.000 ± 0.000	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002
CARB	0.023 ± 0.002	0.000 ± 0.000	0.000 ± 0.000	0.013 ± 0.001	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002
HALO	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002
TENAX	0.001 ± 0.000	0.025 ± 0.006	0.000 ± 0.000	0.137 ± 0.014	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002
CO_PPM	12.228 ± 1.223	0.000 ± 0.000	0.000 ± 0.000	8.670 ± 0.867	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002
ETHENE	0.070 ± 0.007	0.000 ± 0.000	0.000 ± 0.000	0.137 ± 0.014	0.000 ± 0.001	0.000 ± 0.001	0.000 ± 0.004	0.002 ± 0.002	0.000 ± 0.001
ACETYL	0.055 ± 0.005	0.000 ± 0.000	0.000 ± 0.000	0.049 ± 0.005	0.000 ± 0.001	0.000 ± 0.001	0.000 ± 0.004	0.000 ± 0.002	0.000 ± 0.001
ETHANE	0.059 ± 0.006	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.692 ± 0.104	0.041 ± 0.006	0.000 ± 0.004	0.000 ± 0.002	0.000 ± 0.001
PROPE	0.036 ± 0.004	0.000 ± 0.000	0.000 ± 0.000	0.029 ± 0.003	0.000 ± 0.001	0.051 ± 0.008	0.000 ± 0.004	0.000 ± 0.002	0.000 ± 0.001
N_PROP	0.018 ± 0.002	0.000 ± 0.000	0.000 ± 0.000	0.047 ± 0.005	0.212 ± 0.032	0.906 ± 0.136	0.000 ± 0.004	0.132 ± 0.013	0.000 ± 0.001
I_BUTA	0.007 ± 0.001	0.002 ± 0.000	0.029 ± 0.005	0.019 ± 0.002	0.021 ± 0.003	0.002 ± 0.001	0.000 ± 0.004	0.420 ± 0.042	0.000 ± 0.001
LBUT1E	0.006 ± 0.001	0.001 ± 0.000	0.008 ± 0.003	0.001 ± 0.000	0.000 ± 0.001	0.000 ± 0.001	0.000 ± 0.004	0.000 ± 0.002	0.000 ± 0.001
N_BUTA	0.018 ± 0.002	0.015 ± 0.002	0.130 ± 0.013	0.018 ± 0.002	0.031 ± 0.005	0.000 ± 0.001	0.000 ± 0.004	0.078 ± 0.008	0.000 ± 0.001
T2BUTE	0.002 ± 0.000	0.001 ± 0.001	0.010 ± 0.004	0.000 ± 0.000	0.000 ± 0.001	0.000 ± 0.001	0.000 ± 0.004	0.000 ± 0.002	0.000 ± 0.001
C2BUTE	0.003 ± 0.000	0.001 ± 0.001	0.011 ± 0.005	0.002 ± 0.000	0.000 ± 0.001	0.000 ± 0.001	0.000 ± 0.004	0.000 ± 0.002	0.000 ± 0.001
IPENTA	0.095 ± 0.009	0.125 ± 0.013	0.414 ± 0.041	0.048 ± 0.005	0.007 ± 0.002	0.000 ± 0.001	0.000 ± 0.001	0.000 ± 0.002	0.000 ± 0.001
PENTE1	0.001 ± 0.000	0.002 ± 0.001	0.007 ± 0.002	0.002 ± 0.000	0.000 ± 0.001	0.000 ± 0.001	0.000 ± 0.004	0.000 ± 0.002	0.000 ± 0.001
N_PENT	0.030 ± 0.003	0.047 ± 0.008	0.116 ± 0.016	0.029 ± 0.003	0.007 ± 0.002	0.000 ± 0.001	0.000 ± 0.004	0.001 ± 0.002	0.000 ± 0.001
I_PREN	0.003 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.004 ± 0.000	0.000 ± 0.001	0.000 ± 0.001	0.000 ± 0.004	0.000 ± 0.002	1.000 ± 0.100
T2PENE	0.003 ± 0.000	0.006 ± 0.001	0.014 ± 0.003	0.002 ± 0.000	0.000 ± 0.001	0.000 ± 0.001	0.000 ± 0.001	0.000 ± 0.002	0.000 ± 0.001
C2PENE	0.002 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.001	0.000 ± 0.001	0.000 ± 0.004	0.000 ± 0.002	0.000 ± 0.001
BU22DM	0.010 ± 0.001	0.013 ± 0.008	0.020 ± 0.012	0.007 ± 0.001	0.000 ± 0.001	0.000 ± 0.001	0.000 ± 0.004	0.000 ± 0.002	0.000 ± 0.001
CPENTA	0.004 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.001 ± 0.000	0.000 ± 0.001	0.000 ± 0.001	0.000 ± 0.004	0.000 ± 0.002	0.000 ± 0.001
BU23DM	0.014 ± 0.001	0.016 ± 0.007	0.018 ± 0.008	0.004 ± 0.000	0.000 ± 0.001	0.000 ± 0.001	0.000 ± 0.004	0.000 ± 0.002	0.000 ± 0.001
PENA2M	0.035 ± 0.003	0.061 ± 0.006	0.064 ± 0.008	0.016 ± 0.002	0.003 ± 0.001	0.000 ± 0.001	0.000 ± 0.001	0.001 ± 0.002	0.000 ± 0.001
PENA3M	0.021 ± 0.002	0.038 ± 0.004	0.035 ± 0.005	0.008 ± 0.001	0.001 ± 0.001	0.000 ± 0.001	0.000 ± 0.001	0.000 ± 0.002	0.000 ± 0.001
P1E2ME	0.001 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.001	0.000 ± 0.001	0.000 ± 0.001	0.000 ± 0.002	0.000 ± 0.001
N_HEX	0.015 ± 0.002	0.028 ± 0.003	0.021 ± 0.002	0.000 ± 0.000	0.004 ± 0.001	0.000 ± 0.001	0.000 ± 0.004	0.047 ± 0.005	0.000 ± 0.001
MCYPNA	0.021 ± 0.002	0.000 ± 0.000	0.000 ± 0.000	0.006 ± 0.001	0.010 ± 0.002	0.000 ± 0.001	0.000 ± 0.001	0.000 ± 0.002	0.000 ± 0.001
PEN24M	0.012 ± 0.001	0.022 ± 0.005	0.011 ± 0.003	0.005 ± 0.001	0.000 ± 0.001	0.000 ± 0.001	0.000 ± 0.001	0.000 ± 0.002	0.000 ± 0.001
BENZE	0.033 ± 0.003	0.012 ± 0.002	0.005 ± 0.001	0.015 ± 0.002	0.000 ± 0.001	0.000 ± 0.001	0.000 ± 0.004	0.000 ± 0.002	0.000 ± 0.001
CYHEXA	0.009 ± 0.001	0.015 ± 0.006	0.007 ± 0.003	0.007 ± 0.001	0.000 ± 0.001	0.000 ± 0.001	0.001 ± 0.002	0.001 ± 0.002	0.000 ± 0.001
HEXA2M	0.016 ± 0.002	0.029 ± 0.003	0.010 ± 0.001	0.008 ± 0.001	0.000 ± 0.001	0.000 ± 0.001	0.003 ± 0.012	0.001 ± 0.002	0.000 ± 0.001
PEN23M	0.019 ± 0.002	0.035 ± 0.012	0.012 ± 0.004	0.006 ± 0.001	0.000 ± 0.001	0.000 ± 0.001	0.001 ± 0.002	0.000 ± 0.002	0.000 ± 0.001
HEXA3M	0.018 ± 0.002	0.030 ± 0.003	0.010 ± 0.001	0.011 ± 0.001	0.002 ± 0.001	0.000 ± 0.001	0.003 ± 0.004	0.000 ± 0.002	0.000 ± 0.001
PA224M	0.031 ± 0.003	0.029 ± 0.018	0.007 ± 0.005	0.018 ± 0.002	0.003 ± 0.001	0.000 ± 0.001	0.000 ± 0.004	0.000 ± 0.002	0.000 ± 0.001
N_HEPT	0.013 ± 0.001	0.020 ± 0.002	0.005 ± 0.001	0.010 ± 0.001	0.002 ± 0.001	0.000 ± 0.001	0.016 ± 0.048	0.032 ± 0.004	0.000 ± 0.001
MECYHX	0.011 ± 0.001	0.017 ± 0.003	0.004 ± 0.001	0.013 ± 0.001	0.001 ± 0.001	0.000 ± 0.001	0.026 ± 0.091	0.002 ± 0.002	0.000 ± 0.001
PA234M	0.012 ± 0.001	0.017 ± 0.009	0.002 ± 0.001	0.004 ± 0.000	0.000 ± 0.001	0.000 ± 0.001	0.000 ± 0.001	0.000 ± 0.002	0.000 ± 0.001
TOLUE	0.084 ± 0.008	0.116 ± 0.013	0.017 ± 0.002	0.091 ± 0.009	0.000 ± 0.001	0.000 ± 0.001	0.069 ± 0.069	0.192 ± 0.019	0.000 ± 0.001
HEP2ME	0.007 ± 0.001	0.013 ± 0.001	0.001 ± 0.000	0.012 ± 0.001	0.004 ± 0.001	0.000 ± 0.001	0.014 ± 0.023	0.000 ± 0.002	0.000 ± 0.001
HEP3ME	0.006 ± 0.001	0.013 ± 0.001	0.001 ± 0.000	0.010 ± 0.001	0.000 ± 0.001	0.000 ± 0.001	0.010 ± 0.016	0.000 ± 0.002	0.000 ± 0.001
N_OCT	0.004 ± 0.000	0.009 ± 0.002	0.001 ± 0.000	0.015 ± 0.002	0.000 ± 0.001	0.000 ± 0.001	0.034 ± 0.053	0.001 ± 0.002	0.000 ± 0.001
ETBZ	0.016 ± 0.002	0.023 ± 0.002	0.001 ± 0.000	0.018 ± 0.002	0.000 ± 0.001	0.000 ± 0.001	0.038 ± 0.029	0.003 ± 0.002	0.000 ± 0.001
MP_XYL	0.066 ± 0.007	0.091 ± 0.007	0.004 ± 0.000	0.067 ± 0.007	0.000 ± 0.001	0.000 ± 0.001	0.154 ± 0.106	0.019 ± 0.003	0.000 ± 0.001
STYR	0.005 ± 0.001	0.000 ± 0.000	0.000 ± 0.000	0.061 ± 0.006	0.000 ± 0.001	0.000 ± 0.001	0.000 ± 0.001	0.001 ± 0.002	0.000 ± 0.001
O_XYL	0.023 ± 0.002	0.034 ± 0.003	0.001 ± 0.000	0.022 ± 0.002	0.000 ± 0.001	0.000 ± 0.001	0.072 ± 0.044	0.014 ± 0.002	0.000 ± 0.001
N_NON	0.004 ± 0.000	0.007 ± 0.001	0.000 ± 0.000	0.021 ± 0.002	0.000 ± 0.001	0.000 ± 0.001	0.045 ± 0.023	0.059 ± 0.006	0.000 ± 0.001
IPRBZ	0.002 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.002 ± 0.000	0.000 ± 0.001	0.000 ± 0.001	0.006 ± 0.006	0.000 ± 0.002	0.000 ± 0.001
N_PRBZ	0.004 ± 0.000	0.001 ± 0.000	0.000 ± 0.000	0.004 ± 0.000	0.000 ± 0.001	0.000 ± 0.001	0.015 ± 0.015	0.009 ± 0.002	0.000 ± 0.001
M_ETOL	0.017 ± 0.002	0.025 ± 0.003	0.000 ± 0.000	0.019 ± 0.002	0.000 ± 0.001	0.000 ± 0.001	0.000 ± 0.004	0.000 ± 0.002	0.000 ± 0.001
P_ETOL	0.008 ± 0.001	0.011 ± 0.001	0.000 ± 0.000	0.008 ± 0.001	0.000 ± 0.001	0.000 ± 0.001	0.045 ± 0.017	0.000 ± 0.002	0.000 ± 0.001
BZ135M	0.009 ± 0.001	0.013 ± 0.001	0.000 ± 0.000	0.015 ± 0.002	0.000 ± 0.001	0.000 ± 0.001	0.041 ± 0.026	0.000 ± 0.002	0.000 ± 0.001
O_ETOL	0.005 ± 0.001	0.006 ± 0.002	0.000 ± 0.000	0.010 ± 0.001	0.000 ± 0.001	0.000 ± 0.001	0.000 ± 0.004	0.003 ± 0.002	0.000 ± 0.001
BZ124M	0.024 ± 0.002	0.041 ± 0.004	0.000 ± 0.000	0.041 ± 0.004	0.000 ± 0.001	0.000 ± 0.001	0.111 ± 0.043	0.000 ± 0.002	0.000 ± 0.001

Table 4.4-1 (Continued)
Default Source Composition Profiles Used in CMB Source Apportionment

Parameter	WEOzLDV1	Gas00LRPC	Gas00VRPC	WEOzHDD1	CNG	LPG	COATcomp	CPcomp_1	Biogenic
N_DEC	0.002 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.016 ± 0.002	0.000 ± 0.001	0.000 ± 0.001	0.181 ± 0.060	0.001 ± 0.002	0.000 ± 0.001
BZ123M	0.006 ± 0.001	0.010 ± 0.001	0.000 ± 0.000	0.019 ± 0.002	0.000 ± 0.001	0.000 ± 0.001	0.000 ± 0.001	0.000 ± 0.002	0.000 ± 0.001
DETBZ1	0.001 ± 0.000	0.001 ± 0.001	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.001	0.000 ± 0.001	0.004 ± 0.004	0.000 ± 0.002	0.000 ± 0.001
DETBZ2	0.005 ± 0.001	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.001	0.000 ± 0.001	0.000 ± 0.001	0.000 ± 0.002	0.000 ± 0.001
N_UNDE	0.001 ± 0.000	0.002 ± 0.000	0.000 ± 0.000	0.021 ± 0.002	0.000 ± 0.001	0.000 ± 0.001	0.108 ± 0.081	0.001 ± 0.002	0.000 ± 0.001
LIBUTE	0.035 ± 0.003	0.004 ± 0.001	0.000 ± 0.000	0.002 ± 0.000	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002
BUDI13	0.008 ± 0.001	0.000 ± 0.000	0.000 ± 0.000	0.015 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002
MTBE	0.076 ± 0.008	0.201 ± 0.021	0.247 ± 0.025	0.000 ± 0.000	0.000 ± 0.001	0.000 ± 0.001	0.000 ± 0.001	0.000 ± 0.002	0.000 ± 0.001
A_PINE	0.001 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.007 ± 0.001	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.049 ± 0.005	0.000 ± 0.002
B_PINE	0.001 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.004 ± 0.000	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002
LIMON	0.001 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.051 ± 0.005	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002
OCTAL	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002
NONAL	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002
NAPHTH	0.001 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.015 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.061 ± 0.006	0.000 ± 0.002
DECAL	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002
N_DODE	0.001 ± 0.000	0.001 ± 0.000	0.000 ± 0.000	0.030 ± 0.003	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002
NAP_2M	0.001 ± 0.000	0.003 ± 0.001	0.000 ± 0.000	0.007 ± 0.001	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002
NAP_1M	0.001 ± 0.000	0.001 ± 0.000	0.000 ± 0.000	0.007 ± 0.001	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002
N_TRID	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.019 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002
DMN267	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002
N_TETD	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.015 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002
DM1367	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002
D14523	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002
N_PEND	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.018 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002
N_HEXD	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.020 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002
N_HEPD	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.012 ± 0.001	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002
N_OCTD	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.008 ± 0.001	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002
N_NOND	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.003 ± 0.000	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002
N_EICO	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002
FORMAL	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.002 ± 0.002	0.000 ± 0.002
ACETAL	0.009 ± 0.001	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002
ACETO	0.007 ± 0.001	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.129 ± 0.013	0.000 ± 0.002
PROAL	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002
MEK	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.073 ± 0.008	0.000 ± 0.002
BUAL	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002
BENZAL	0.001 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.005 ± 0.001	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002
VALAL	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002
HEXAL	0.005 ± 0.001	0.000 ± 0.000	0.000 ± 0.000	0.008 ± 0.001	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002
F12	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002
F11	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002
MECL2	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.017 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.011 ± 0.002	0.000 ± 0.002
F113	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002
CCL3	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002
MECCL3	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.285 ± 0.029	0.000 ± 0.002
CCL4	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002
PERC	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.029 ± 0.004	0.000 ± 0.002
NOX	0.956 ± 0.096	0.000 ± 0.000	0.000 ± 0.000	17.226 ± 1.723	0.000 ± 0.002	0.000 ± 0.002	0.000 ± 0.002	0.019 ± 0.003	0.000 ± 0.002

Table 4.4-1a

Number of observations, mean measured NMHC (ug/m^3), mean CMB performance parameters and mean estimated source contributions (ug/m^3) +/- standard deviation; during the carryover (3:00-6:00), inhibition (6:00-9:00), accumulation (9:00-12:00), and peak ozone (12:00-15:00) periods by day-of-week at Azusa for summers 1999 and 2000

TIME	DAY	OBS	totNMHC	rSquared	ChiSquar	%explained	GasExhaust	GasVapor	LiquidGas	Diesel	CNG	LPG	Coatings	ConsProd	Biogen	Backgrd	Unexpl
3:00-6:00	Sun	6	197+/-70	.93+/-.06	4.4+/-3.2	90.1+/-9.8	100.5+/-52.4	18.6+/-9.9	22.9+/-6.8	0.0+/-0.0	4.6+/-3.3	9.6+/-3.9	12.6+/-4.0	9.1+/-5.3	0.2+/-0.2	4.4+/-4.2	14.9+/-8.7
3:00-6:00	Mon	4	184+/-96	.93+/-.02	4.2+/-1.4	94.0+/-5.0	97.1+/-46.0	17.9+/-8.2	16.4+/-14.7	0.0+/-0.0	4.1+/-1.2	10.8+/-9.3	10.7+/-6.0	10.0+/-4.7	0.1+/-0.3	4.2+/-3.5	12.6+/-15.2
3:00-6:00	Tue	6	268+/-152	.94+/-.00	3.7+/-1.2	93.0+/-5.0	132.4+/-75.8	18.0+/-9.1	34.7+/-16.7	0.0+/-0.0	4.1+/-3.5	17.2+/-11.2	18.4+/-11.1	10.7+/-5.3	2.6+/-5.3	6.9+/-7.6	23.4+/-31.2
3:00-6:00	Wed	7	301+/-199	.92+/-.05	4.9+/-2.3	89.9+/-9.2	126.3+/-63.5	25.6+/-23.3	40.5+/-26.8	0.0+/-0.0	4.3+/-2.8	18.3+/-16.3	20.4+/-13.5	11.4+/-5.0	0.7+/-0.7	8.9+/-8.4	44.9+/-62.5
3:00-6:00	Thu	7	322+/-150	.94+/-.02	4.0+/-1.4	90.7+/-4.1	152.6+/-82.4	27.6+/-13.8	44.2+/-22.6	0.0+/-0.0	3.5+/-3.1	25.2+/-23.3	19.7+/-4.3	14.5+/-8.7	0.7+/-0.4	5.7+/-7.8	28.8+/-19.2
3:00-6:00	Fri	8	256+/-88	.95+/-.03	3.5+/-1.4	92.2+/-6.5	128.2+/-37.6	17.9+/-9.3	30.3+/-11.0	0.0+/-0.0	4.5+/-4.2	13.8+/-5.6	18.9+/-5.6	10.2+/-3.7	0.4+/-0.4	7.5+/-7.7	24.7+/-24.5
3:00-6:00	Sat	7	250+/-115	.95+/-.04	3.6+/-2.2	95.2+/-3.2	141.6+/-65.9	19.9+/-11.3	21.6+/-16.4	0.0+/-0.0	6.5+/-3.9	12.5+/-5.9	16.8+/-10.3	10.5+/-4.5	0.3+/-0.4	5.9+/-7.5	13.8+/-10.9
6:00-9:00	Sun	6	214+/-92	.93+/-.05	4.4+/-2.8	92.1+/-5.7	119.3+/-64.5	20.6+/-14.4	23.2+/-9.5	0.0+/-0.0	3.4+/-3.1	10.5+/-5.8	11.7+/-6.2	7.9+/-4.3	0.2+/-0.2	4.3+/-6.2	13.0+/-3.8
6:00-9:00	Mon	4	248+/-191	.94+/-.03	3.9+/-1.8	94.4+/-6.5	133.9+/-93.8	12.2+/-9.3	31.8+/-45.0	0.0+/-0.0	2.2+/-2.6	13.4+/-11.4	12.3+/-8.6	12.2+/-7.4	0.2+/-0.5	9.8+/-8.5	20.4+/-33.6
6:00-9:00	Tue	7	348+/-212	.95+/-.01	3.5+/-1.1	95.1+/-4.9	187.4+/-110.9	25.2+/-20.3	42.8+/-36.6	1.5+/-2.5	1.8+/-1.8	26.2+/-18.2	20.0+/-12.6	12.4+/-5.5	1.2+/-2.0	5.7+/-9.0	23.7+/-23.8
6:00-9:00	Wed	7	356+/-205	.95+/-.02	3.1+/-0.8	93.1+/-5.7	190.3+/-112.1	24.3+/-15.3	30.8+/-16.8	3.2+/-8.0	0.9+/-1.6	26.6+/-20.2	21.5+/-15.6	14.3+/-6.8	0.7+/-0.8	11.1+/-12.0	32.7+/-36.2
6:00-9:00	Thu	7	384+/-144	.94+/-.03	3.7+/-1.1	90.5+/-5.6	196.3+/-86.5	25.6+/-10.2	48.0+/-21.1	1.2+/-3.1	1.3+/-3.0	23.7+/-10.5	28.8+/-8.2	16.3+/-5.6	1.1+/-0.4	4.7+/-5.9	36.7+/-25.8
6:00-9:00	Fri	8	325+/-123	.96+/-.03	2.7+/-0.7	91.6+/-6.0	179.1+/-83.2	18.6+/-8.4	33.5+/-12.8	0.2+/-0.4	3.3+/-4.2	21.0+/-9.6	24.3+/-12.0	12.1+/-3.9	0.4+/-0.3	6.4+/-5.4	26.3+/-17.8
6:00-9:00	Sat	7	251+/-132	.95+/-.02	3.2+/-0.6	93.3+/-5.7	138.3+/-72.6	18.6+/-10.7	20.0+/-9.5	1.2+/-2.1	6.5+/-5.2	13.5+/-6.8	15.7+/-9.6	11.1+/-4.4	0.3+/-0.3	7.6+/-14.3	18.4+/-13.3
9:00-12:00	Sun	6	165+/-45	.96+/-.01	2.7+/-0.7	95.7+/-4.4	94.5+/-28.1	17.5+/-4.8	10.8+/-5.7	0.1+/-0.3	3.0+/-2.2	7.4+/-2.7	13.1+/-15.2	6.9+/-2.7	0.6+/-0.4	5.0+/-5.7	5.6+/-5.3
9:00-12:00	Mon	4	176+/-52	.95+/-.00	3.1+/-1.2	96.0+/-4.2	93.0+/-18.3	16.2+/-5.8	12.2+/-8.1	0.3+/-0.6	1.6+/-1.9	10.2+/-4.2	7.4+/-1.5	11.2+/-5.3	0.4+/-0.6	15.2+/-16.4	7.9+/-8.5
9:00-12:00	Tue	8	240+/-122	.94+/-.02	3.3+/-1.0	94.1+/-5.2	126.2+/-74.8	17.4+/-15.6	15.2+/-13.1	7.7+/-19.2	1.0+/-1.5	16.0+/-16.0	15.8+/-10.8	10.7+/-8.0	1.4+/-1.4	12.1+/-18.1	17.2+/-15.6
9:00-12:00	Wed	7	263+/-67	.95+/-.01	3.1+/-1.0	95.2+/-2.9	139.4+/-50.8	17.5+/-7.0	22.6+/-18.9	8.3+/-12.1	0.3+/-0.5	15.8+/-6.4	18.7+/-9.9	13.1+/-3.7	0.9+/-0.6	12.2+/-6.5	13.7+/-12.8
9:00-12:00	Thu	7	249+/-59	.95+/-.02	3.3+/-1.0	94.3+/-2.6	129.6+/-41.6	24.1+/-5.7	21.5+/-10.9	7.3+/-12.6	2.2+/-3.5	15.1+/-4.0	14.8+/-4.5	12.5+/-4.0	1.4+/-0.5	6.4+/-7.7	14.1+/-6.7
9:00-12:00	Fri	7	246+/-23	.96+/-.00	2.5+/-0.5	95.6+/-2.5	138.4+/-9.6	17.7+/-2.8	13.3+/-7.8	2.6+/-4.9	2.1+/-3.9	15.5+/-1.4	17.4+/-3.8	14.7+/-4.4	0.8+/-0.2	12.4+/-7.6	11.2+/-6.7
9:00-12:00	Sat	7	196+/-85	.95+/-.02	2.9+/-0.8	96.7+/-5.0	113.4+/-42.3	13.8+/-5.8	9.4+/-7.6	1.9+/-2.6	2.6+/-2.2	9.9+/-4.0	10.4+/-7.6	8.4+/-3.1	0.5+/-0.5	18.2+/-22.6	7.6+/-14.0
12:00-15:00	Sun	8	126+/-42	.95+/-.00	3.5+/-1.1	93.3+/-5.6	66.1+/-26.9	17.1+/-6.6	6.8+/-5.0	1.7+/-4.1	3.2+/-2.1	5.1+/-2.0	5.9+/-2.4	5.6+/-2.2	0.5+/-0.2	5.7+/-6.3	8.0+/-8.1
12:00-15:00	Mon	4	198+/-47	.95+/-.00	3.0+/-1.1	87.5+/-6.5	91.9+/-22.6	14.7+/-4.5	12.1+/-16.3	0.7+/-0.8	1.5+/-1.7	12.5+/-4.1	8.5+/-2.9	12.0+/-6.5	0.6+/-0.4	20.2+/-19.3	23.5+/-8.6
12:00-15:00	Tue	8	196+/-105	.94+/-.03	4.2+/-1.3	95.5+/-3.4	99.0+/-57.6	23.1+/-14.5	11.9+/-8.5	4.5+/-7.4	2.4+/-2.7	12.2+/-7.6	11.3+/-6.7	13.3+/-11.5	1.0+/-0.7	10.5+/-14.2	6.8+/-3.9
12:00-15:00	Wed	6	230+/-26	.93+/-.03	3.1+/-1.2	93.5+/-5.4	86.6+/-38.8	11.8+/-8.5	31.9+/-16.8	9.0+/-11.2	2.0+/-2.9	11.0+/-2.0	32.0+/-24.0	11.1+/-2.7	1.1+/-0.6	19.4+/-17.1	14.4+/-11.7
12:00-15:00	Thu	7	250+/-86	.91+/-.09	5.1+/-4.6	87.7+/-8.7	102.9+/-43.9	17.9+/-10.7	20.6+/-18.8	8.8+/-14.8	2.0+/-2.3	12.8+/-5.4	22.6+/-22.1	21.1+/-23.9	1.4+/-0.4	7.2+/-6.8	33.0+/-34.2
12:00-15:00	Fri	7	234+/-54	.95+/-.03	2.9+/-1.5	94.3+/-11.6	127.6+/-35.8	20.8+/-9.1	8.5+/-8.8	4.7+/-6.6	2.3+/-2.9	14.3+/-3.3	16.9+/-6.1	12.7+/-3.3	0.9+/-0.5	9.6+/-8.8	16.1+/-31.9
12:00-15:00	Sat	7	207+/-77	.94+/-.02	3.7+/-1.8	93.1+/-11.0	100.9+/-35.1	26.0+/-19.3	11.2+/-11.5	3.3+/-5.6	2.7+/-1.6	11.5+/-5.8	8.6+/-6.2	9.7+/-4.3	0.7+/-0.6	15.2+/-18.5	17.1+/-24.3

Table 4.4-1b

Number of observations, mean measured NMHC (ug/m^3), mean CMB performance parameters and mean estimated source contributions (ug/m^3) +/- standard deviation; during the carryover (3:00-6:00), inhibition (6:00-9:00), accumulation (9:00-12:00), and peak ozone (12:00-15:00) periods by day-of-week at Pico Rivera for summer 1999

TIME	DAY	OBS	totNMHC	rSquared	ChiSquar	%explained	GasExhaust	GasVapor	LiquidGas	Diesel	CNG	LPG	Coatings	ConsProd	Biogen	Backgrd	Unexpl
3:00-6:00	Sun	12	140+/-42	.95+/-.01	2.9+/-0.9	94.8+/-14.6	72.6+/-28.0	18.1+/-6.6	6.6+/-8.3	0.0+/-0.1	4.9+/-1.9	6.5+/-2.1	9.3+/-3.7	8.0+/-2.7	0.0+/-0.1	3.7+/-4.7	10.2+/-24.9
3:00-6:00	Mon	13	160+/-64	.96+/-.02	2.4+/-1.0	91.7+/-16.6	87.3+/-48.3	20.1+/-8.7	0.1+/-0.5	0.0+/-0.1	7.1+/-4.4	8.5+/-4.4	9.1+/-3.2	9.8+/-3.6	0.0+/-0.0	5.0+/-3.4	13.0+/-25.8
3:00-6:00	Tue	12	196+/-68	.95+/-.02	2.7+/-1.1	88.6+/-18.9	96.7+/-44.3	19.5+/-10.0	5.1+/-6.4	0.0+/-0.1	6.6+/-3.6	11.2+/-6.0	10.9+/-4.2	10.7+/-5.3	0.0+/-0.0	13.8+/-11.8	21.5+/-33.9
3:00-6:00	Wed	12	223+/-151	.96+/-.10	2.3+/-0.8	92.0+/-14.0	117.4+/-76.4	21.2+/-13.1	4.1+/-6.8	2.1+/-4.8	3.6+/-4.4	14.7+/-12.8	13.5+/-9.0	10.1+/-7.3	0.0+/-0.0	15.3+/-21.6	21.1+/-34.4
3:00-6:00	Thu	11	196+/-115	.95+/-.03	2.5+/-1.1	89.9+/-21.4	96.1+/-60.6	21.4+/-11.9	5.1+/-9.3	1.3+/-2.9	5.3+/-3.8	12.5+/-10.5	13.7+/-11.3	10.0+/-6.6	0.1+/-0.1	10.0+/-8.8	20.6+/-34.0
3:00-6:00	Fri	12	160+/-68	.95+/-.02	2.8+/-1.5	94.9+/-14.3	84.0+/-42.9	16.0+/-8.2	3.2+/-5.2	1.2+/-3.2	4.7+/-4.1	9.1+/-4.5	10.2+/-3.2	9.6+/-5.8	0.0+/-0.0	9.7+/-7.6	12.1+/-27.4
3:00-6:00	Sat	12	160+/-64	.95+/-.10	2.9+/-1.0	94.2+/-16.6	83.1+/-42.9	17.7+/-8.2	4.8+/-4.6	0.2+/-0.7	5.6+/-4.1	10.7+/-8.2	11.6+/-3.6	8.7+/-4.7	0.0+/-0.1	5.2+/-3.5	12.3+/-30.1
6:00-9:00	Sun	12	145+/-50	.95+/-.02	2.7+/-1.0	93.6+/-17.0	75.5+/-30.2	19.8+/-6.7	0.7+/-1.4	0.0+/-0.1	5.9+/-2.3	7.5+/-3.3	8.3+/-2.7	9.1+/-2.8	0.1+/-0.1	4.3+/-2.8	13.8+/-31.5
6:00-9:00	Mon	13	251+/-115	.94+/-.08	3.0+/-2.7	93.1+/-11.7	143.0+/-84.9	23.0+/-12.0	6.4+/-12.7	0.0+/-0.1	4.5+/-4.7	18.1+/-14.2	9.7+/-6.5	10.7+/-3.4	0.2+/-0.3	17.8+/-15.4	17.4+/-24.8
6:00-9:00	Tue	13	318+/-183	.94+/-.03	3.3+/-1.3	95.6+/-10.8	172.5+/-110.7	28.1+/-15.0	12.7+/-25.7	0.0+/-0.1	6.7+/-6.9	25.1+/-19.0	12.9+/-9.2	16.0+/-9.3	0.2+/-0.3	30.0+/-25.1	13.7+/-24.5
6:00-9:00	Wed	12	284+/-228	.95+/-.02	2.7+/-1.1	96.9+/-6.5	160.4+/-122.8	23.4+/-14.6	11.1+/-17.3	5.2+/-9.9	1.9+/-5.0	23.1+/-21.7	8.1+/-5.9	11.4+/-6.8	0.3+/-0.3	22.9+/-22.7	15.9+/-35.9
6:00-9:00	Thu	12	276+/-204	.95+/-.02	2.8+/-1.5	94.9+/-14.1	156.7+/-129.2	21.5+/-12.3	16.5+/-25.4	1.7+/-3.8	4.7+/-5.4	17.5+/-14.7	14.6+/-14.4	11.3+/-7.9	0.4+/-0.6	15.3+/-14.3	15.4+/-28.6
6:00-9:00	Fri	13	245+/-88	.93+/-.05	3.3+/-1.9	92.5+/-14.9	131.6+/-59.4	17.9+/-10.0	11.2+/-18.3	0.8+/-2.1	1.7+/-3.7	15.8+/-6.8	9.8+/-4.3	10.9+/-5.8	0.2+/-0.3	26.9+/-23.5	17.7+/-29.5
6:00-9:00	Sat	12	201+/-82	.94+/-.05	3.2+/-2.1	93.3+/-17.4	101.2+/-38.4	18.5+/-9.3	8.8+/-14.1	0.0+/-0.1	3.4+/-4.0	13.4+/-9.3	10.4+/-4.8	9.3+/-4.7	0.2+/-0.2	18.3+/-17.2	17.4+/-39.6
9:00-12:00	Sun	13	133+/-56	.96+/-.01	2.0+/-0.6	95.8+/-16.9	70.4+/-27.5	18.7+/-6.6	0.0+/-0.1	0.1+/-0.3	4.1+/-2.7	6.7+/-2.3	6.7+/-2.1	8.6+/-4.1	0.3+/-0.2	5.6+/-4.1	11.3+/-34.5
9:00-12:00	Mon	13	230+/-92	.94+/-.04	3.2+/-2.3	95.7+/-8.7	120.0+/-50.6	23.1+/-11.8	11.5+/-16.3	4.1+/-11.5	2.1+/-3.6	16.9+/-8.4	9.3+/-4.9	10.3+/-3.6	0.6+/-0.4	22.7+/-17.4	9.8+/-19.6
9:00-12:00	Tue	13	315+/-158	.93+/-.04	4.0+/-2.1	96.3+/-5.5	160.5+/-94.5	26.4+/-12.6	19.6+/-21.9	3.4+/-7.5	2.8+/-4.0	24.1+/-12.5	13.0+/-10.2	16.3+/-7.8	0.7+/-0.5	34.8+/-23.7	13.0+/-15.4
9:00-12:00	Wed	13	246+/-99	.93+/-.05	3.7+/-3.3	91.3+/-20.9	116.1+/-62.7	20.5+/-11.9	13.1+/-22.8	3.0+/-4.3	1.0+/-2.7	16.3+/-7.3	14.6+/-8.3	12.7+/-5.8	1.1+/-1.5	20.2+/-12.6	27.2+/-74.8
9:00-12:00	Thu	13	231+/-119	.94+/-.03	3.4+/-1.6	94.6+/-12.6	120.2+/-61.5	20.4+/-9.4	10.0+/-13.0	3.0+/-4.8	1.2+/-2.9	17.8+/-9.2	12.5+/-7.1	12.3+/-8.7	0.9+/-1.3	23.4+/-28.4	9.6+/-15.2
9:00-12:00	Fri	13	221+/-80	.93+/-.04	3.6+/-1.7	95.0+/-11.2	112.5+/-46.7	20.1+/-10.5	9.9+/-13.4	1.6+/-2.8	0.6+/-1.6	17.7+/-7.2	11.6+/-5.1	11.6+/-6.2	0.5+/-0.3	28.0+/-16.7	7.1+/-12.9
9:00-12:00	Sat	11	176+/-64	.93+/-.04	3.7+/-1.8	96.8+/-15.0	89.9+/-38.5	21.1+/-8.7	6.8+/-8.8	0.0+/-0.1	2.6+/-2.9	11.4+/-4.5	7.5+/-2.9	10.0+/-3.4	0.5+/-0.4	18.5+/-14.3	8.0+/-31.0
12:00-15:00	Sun	12	132+/-50	.95+/-.02	2.7+/-1.5	96.8+/-9.4	61.8+/-20.7	27.8+/-14.1	0.0+/-0.1	0.0+/-0.1	4.5+/-2.9	7.6+/-3.5	6.2+/-1.8	10.1+/-4.4	0.7+/-0.3	7.2+/-4.1	6.1+/-16.7
12:00-15:00	Mon	12	198+/-47	.94+/-.03	3.2+/-1.5	98.2+/-5.8	95.3+/-27.3	28.0+/-10.0	5.6+/-9.7	2.4+/-5.2	1.7+/-2.4	15.1+/-4.0	12.2+/-4.0	13.5+/-4.3	1.0+/-0.5	18.5+/-8.7	4.9+/-11.5
12:00-15:00	Tue	10	222+/-62	.90+/-.03	4.9+/-1.7	94.5+/-11.4	86.0+/-28.0	30.0+/-20.1	17.3+/-20.0	1.8+/-3.9	1.6+/-2.2	18.8+/-7.9	9.2+/-6.0	15.9+/-9.0	1.1+/-0.5	30.9+/-33.0	9.8+/-19.8
12:00-15:00	Wed	11	164+/-59	.91+/-.05	4.5+/-2.2	98.1+/-5.6	66.5+/-22.1	18.3+/-11.1	15.4+/-15.9	1.8+/-4.1	0.1+/-0.1	12.9+/-5.0	9.6+/-2.9	10.3+/-6.7	0.9+/-0.4	25.9+/-18.4	2.5+/-7.1
12:00-15:00	Thu	9	231+/-125	.86+/-.14	8.4+/-10.6	92.7+/-18.3	79.2+/-31.7	23.9+/-19.6	33.7+/-58.3	0.5+/-1.5	0.8+/-1.4	13.8+/-8.1	10.0+/-4.3	13.8+/-10.4	1.0+/-0.2	19.4+/-20.4	35.0+/-96.8
12:00-15:00	Fri	12	181+/-84	.91+/-.03	4.5+/-1.3	97.1+/-7.4	73.7+/-30.4	22.2+/-11.8	11.9+/-13.3	2.2+/-4.2	0.5+/-0.7	12.9+/-6.9	9.7+/-3.7	14.5+/-9.1	0.9+/-0.4	30.0+/-25.1	2.5+/-9.0
12:00-15:00	Sat	11	159+/-80	.96+/-.02	2.2+/-1.1	100.4+/-4.7	87.2+/-40.8	27.8+/-16.0	0.1+/-0.3	0.0+/-0.1	2.2+/-2.7	9.3+/-5.0	8.5+/-2.9	11.3+/-7.1	0.7+/-0.4	11.6+/-10.4	0.3+/-6.6

Table 4.4-1c

Number of observations, mean measured NMHC (ug/m3), mean CMB performance parameters and mean estimated source contributions (ug/m^3) +/- standard deviation; during the carryover (3:00-6:00), inhibition (6:00-9:00), accumulation (9:00-12:00), and peak ozone (12:00-15:00) periods by day-of-week at Upland for summers 1999 and 2000

TIME	DAY	OBS	totNMHC	rSquared	ChiSquar	%explained	GasExhaust	GasVapor	LiquidGas	Diesel	CNG	LPG	Coatings	ConsProd	Biogen	Backgrd	Unexpl
3:00-6:00	Sun	7	214+/-68	.94+/-.01	4.1+/-1.2	94.3+/-6.0	108.5+/-48.8	23.5+/-8.7	41.2+/-24.0	0.0+/-0.0	6.2+/-3.7	7.3+/-1.9	10.3+/-3.2	6.8+/-2.4	0.5+/-0.5	0.0+/-0.0	9.9+/-9.6
3:00-6:00	Mon	6	217+/-51	.96+/-.01	2.8+/-0.8	92.5+/-8.5	129.7+/-49.0	16.9+/-4.2	24.4+/-6.6	0.0+/-0.0	1.9+/-1.9	7.7+/-1.6	9.0+/-2.1	8.7+/-1.8	0.4+/-0.3	3.9+/-4.0	14.7+/-16.7
3:00-6:00	Tue	7	179+/-81	.94+/-.03	3.5+/-1.3	91.7+/-8.6	92.8+/-39.7	11.8+/-7.3	31.2+/-33.9	1.0+/-2.7	1.6+/-2.0	8.2+/-4.0	8.7+/-4.8	5.4+/-3.1	0.5+/-0.6	3.2+/-4.8	14.2+/-13.5
3:00-6:00	Wed	8	307+/-76	.95+/-.00	3.4+/-1.1	93.4+/-4.4	165.0+/-31.2	30.6+/-16.8	43.5+/-43.5	0.0+/-0.0	2.6+/-3.1	11.1+/-4.6	13.4+/-3.6	12.1+/-6.0	1.4+/-2.7	5.9+/-9.0	21.5+/-16.3
3:00-6:00	Thu	6	302+/-67	.95+/-.03	3.3+/-1.0	93.3+/-3.6	163.0+/-18.4	22.9+/-13.5	59.9+/-31.2	0.0+/-0.0	0.4+/-0.6	10.3+/-3.5	15.5+/-4.9	8.2+/-2.2	0.6+/-0.2	0.4+/-0.8	20.8+/-11.4
3:00-6:00	Fri	5	331+/-75	.94+/-.01	3.9+/-2.2	90.9+/-9.2	157.1+/-39.0	22.1+/-10.4	81.9+/-74.6	0.0+/-0.0	0.3+/-0.8	8.7+/-1.6	16.8+/-7.8	7.8+/-2.6	0.7+/-0.5	5.8+/-7.8	30.1+/-31.6
3:00-6:00	Sat	5	323+/-111	.93+/-.06	4.9+/-4.0	89.8+/-3.2	158.1+/-51.4	31.2+/-14.9	55.8+/-42.0	0.0+/-0.0	2.1+/-1.9	10.7+/-3.2	14.6+/-4.6	12.1+/-7.5	0.9+/-0.9	3.2+/-3.3	34.4+/-19.2
6:00-9:00	Sun	8	248+/-92	.94+/-.04	4.1+/-2.1	94.1+/-5.2	131.5+/-34.6	28.0+/-20.0	45.9+/-50.0	0.0+/-0.0	2.0+/-1.6	8.9+/-2.1	9.5+/-4.2	5.9+/-3.5	1.4+/-1.2	1.5+/-2.8	13.3+/-10.4
6:00-9:00	Mon	7	219+/-42	.95+/-.01	3.3+/-0.8	94.7+/-4.9	122.8+/-34.0	21.0+/-8.2	25.9+/-16.9	0.0+/-0.0	0.3+/-0.3	10.5+/-4.3	8.9+/-2.0	7.3+/-3.1	0.9+/-0.9	10.6+/-10.1	11.1+/-11.3
6:00-9:00	Tue	6	213+/-74	.96+/-.02	2.5+/-0.7	96.2+/-4.6	127.7+/-35.1	15.4+/-6.9	23.0+/-10.6	0.8+/-1.3	0.8+/-1.3	9.7+/-6.3	14.1+/-8.9	8.5+/-3.8	1.0+/-1.0	2.3+/-4.0	9.9+/-12.2
6:00-9:00	Wed	8	303+/-91	.95+/-.03	2.8+/-0.5	92.8+/-7.6	159.2+/-66.0	26.9+/-10.1	36.1+/-18.4	0.0+/-0.0	0.2+/-0.5	12.6+/-5.3	13.8+/-8.6	11.1+/-3.9	2.1+/-2.0	17.3+/-35.8	23.9+/-25.2
6:00-9:00	Thu	5	362+/-64	.96+/-.01	2.9+/-0.7	91.0+/-8.9	202.9+/-15.7	30.6+/-9.3	55.1+/-36.1	0.0+/-0.0	0.0+/-0.0	12.7+/-5.2	14.9+/-4.9	7.6+/-1.9	1.9+/-1.9	0.0+/-0.0	36.6+/-44.1
6:00-9:00	Fri	5	338+/-96	.94+/-.03	3.5+/-2.2	85.6+/-10.2	151.7+/-18.8	21.3+/-12.1	76.4+/-99.8	0.0+/-0.0	0.0+/-0.0	10.5+/-4.1	17.2+/-6.7	8.3+/-4.7	2.1+/-1.9	5.4+/-5.4	45.1+/-29.3
6:00-9:00	Sat	5	287+/-91	.94+/-.05	4.0+/-3.1	91.2+/-5.6	154.9+/-41.2	26.7+/-12.6	35.2+/-18.8	0.0+/-0.0	0.9+/-0.9	12.9+/-3.1	14.1+/-5.1	10.2+/-6.7	1.5+/-0.8	2.7+/-6.1	28.0+/-24.4
9:00-12:00	Sun	8	152+/-57	.95+/-.02	3.0+/-0.9	93.1+/-7.2	81.1+/-35.9	16.6+/-5.5	16.3+/-11.6	0.0+/-0.0	2.4+/-3.5	5.9+/-3.0	6.7+/-3.2	5.4+/-2.6	1.9+/-1.0	3.5+/-5.7	11.8+/-12.1
9:00-12:00	Mon	7	193+/-48	.96+/-.03	2.7+/-1.4	90.7+/-3.9	104.6+/-28.4	16.5+/-3.9	17.5+/-12.3	0.0+/-0.0	0.4+/-0.5	8.7+/-3.7	10.2+/-3.9	7.3+/-1.9	1.6+/-1.4	9.0+/-9.6	17.7+/-7.1
9:00-12:00	Tue	6	191+/-117	.95+/-.03	3.3+/-0.8	92.0+/-4.6	101.9+/-72.1	14.8+/-7.3	18.8+/-13.6	3.7+/-2.9	0.5+/-0.7	9.8+/-6.4	9.6+/-6.1	8.5+/-4.5	1.6+/-1.3	6.7+/-8.1	14.8+/-10.0
9:00-12:00	Wed	8	219+/-81	.94+/-.02	3.3+/-0.8	91.6+/-3.1	109.4+/-45.1	24.0+/-10.2	18.2+/-11.7	0.2+/-0.6	0.7+/-0.8	11.3+/-4.4	13.0+/-8.3	10.0+/-3.3	2.2+/-1.2	11.5+/-26.9	19.0+/-11.8
9:00-12:00	Thu	7	248+/-76	.96+/-.00	2.9+/-0.7	91.4+/-3.6	126.8+/-50.0	21.0+/-5.0	36.4+/-27.8	1.1+/-1.8	7.9+/-20.6	8.8+/-4.6	13.0+/-3.0	7.6+/-3.8	2.6+/-1.9	2.6+/-6.9	20.4+/-8.0
9:00-12:00	Fri	6	248+/-107	.96+/-.00	3.0+/-1.0	92.9+/-1.9	130.4+/-49.5	22.5+/-10.9	39.9+/-51.1	0.5+/-1.2	0.9+/-1.4	10.6+/-2.4	14.2+/-2.7	9.8+/-3.9	2.1+/-1.5	0.8+/-1.9	15.8+/-1.9
9:00-12:00	Sat	5	204+/-70	.94+/-.03	3.5+/-0.8	91.5+/-3.4	107.9+/-42.7	21.4+/-7.3	17.5+/-9.8	0.9+/-2.0	0.7+/-0.7	8.5+/-2.6	8.7+/-4.2	7.3+/-4.4	2.2+/-1.5	11.0+/-19.0	17.4+/-10.6
12:00-15:00	Sun	8	120+/-30	.95+/-.00	3.2+/-0.8	87.4+/-7.4	55.5+/-14.6	17.6+/-4.9	8.7+/-7.6	0.0+/-0.0	2.1+/-1.9	4.1+/-1.4	3.3+/-1.1	3.7+/-1.7	2.6+/-1.2	6.8+/-8.4	15.9+/-13.0
12:00-15:00	Mon	7	182+/-66	.95+/-.03	2.9+/-0.6	90.9+/-4.5	97.9+/-43.9	19.0+/-8.8	16.4+/-17.0	0.0+/-0.0	1.2+/-1.6	8.2+/-3.6	7.3+/-3.6	7.4+/-3.8	2.5+/-1.7	6.7+/-8.4	15.2+/-4.8
12:00-15:00	Tue	7	181+/-83	.96+/-.00	2.8+/-0.6	90.3+/-3.1	93.4+/-49.7	15.9+/-5.0	19.1+/-18.4	0.1+/-0.3	1.5+/-1.8	9.5+/-4.5	12.0+/-8.2	7.9+/-3.3	2.3+/-1.9	2.6+/-4.6	16.6+/-6.9
12:00-15:00	Wed	7	171+/-49	.95+/-.02	3.1+/-1.2	85.4+/-9.4	81.4+/-30.3	16.2+/-4.0	10.6+/-7.0	0.5+/-1.4	0.8+/-1.0	10.1+/-3.6	6.8+/-3.6	9.2+/-2.6	2.9+/-1.9	7.4+/-9.8	24.8+/-16.5
12:00-15:00	Thu	5	192+/-73	.94+/-.03	3.5+/-0.6	91.5+/-5.1	95.0+/-42.5	22.4+/-19.4	24.7+/-24.7	0.0+/-0.0	1.0+/-1.5	10.2+/-6.5	11.6+/-8.4	8.0+/-3.8	2.8+/-2.6	0.8+/-1.1	15.0+/-7.1
12:00-15:00	Fri	6	216+/-84	.94+/-.03	4.0+/-2.3	84.6+/-14.6	99.0+/-23.7	18.0+/-4.3	10.4+/-7.8	0.8+/-1.9	1.4+/-1.8	14.2+/-11.5	9.0+/-4.3	12.3+/-6.3	3.2+/-1.8	5.6+/-6.3	42.1+/-59.0
12:00-15:00	Sat	5	176+/-58	.94+/-.02	3.4+/-0.6	90.8+/-4.5	86.5+/-35.2	19.3+/-7.3	13.7+/-11.9	0.0+/-0.0	2.3+/-2.1	7.3+/-2.7	5.6+/-3.4	7.0+/-4.4	2.6+/-1.8	16.1+/-29.5	15.9+/-10.7

Table 4.4-1d

Number of observations, mean measured NMHC (ug/m3), mean CMB performance parameters and mean estimated source contributions (ug/m^3) +/- standard deviation; during the carryover (3:00-6:00), inhibition (6:00-9:00), accumulation (9:00-12:00), and peak ozone (12:00-15:00) periods by day-of-week at Los Angeles N. Main for summers 1999 and 2000

TIME	DAY	OBS	totNMHC	rSquared	ChiSquar	%explained	GasExhaust	GasVapor	LiquidGas	Diesel	CNG	LPG	Coatings	ConsProd	Biogen	Backgrd	Unexpl
6:00-9:00	Sun	9	199+/-83	.96+/-.03	2.0+/-1.3	105.9+/-6.2	118.9+/-70.6	21.9+/-11.5	8.0+/-14.0	0.9+/-2.8	12.7+/-10.2	8.5+/-4.4	18.3+/-11.0	10.3+/-5.4	0.1+/-0.1	13.1+/-11.5	-13.4+/-15.6
6:00-9:00	Mon	9	208+/-104	.95+/-.05	2.6+/-1.8	101.1+/-6.8	132.8+/-85.3	20.3+/-13.0	5.9+/-11.3	1.7+/-4.0	5.4+/-3.5	9.8+/-5.7	13.7+/-6.7	9.6+/-4.2	0.2+/-0.2	11.9+/-6.2	-3.6+/-15.4
6:00-9:00	Tue	8	271+/-191	.97+/-.01	1.6+/-0.7	102.7+/-6.2	177.3+/-155.2	20.3+/-13.6	7.9+/-11.3	6.7+/-14.1	7.1+/-8.4	16.4+/-11.1	20.4+/-15.8	11.4+/-7.3	0.3+/-0.2	17.6+/-13.6	-14.5+/-21.8
6:00-9:00	Wed	8	252+/-154	.96+/-.00	2.0+/-0.7	104.5+/-2.7	156.7+/-114.2	17.9+/-7.4	14.9+/-22.4	2.7+/-5.9	4.6+/-4.6	15.9+/-10.4	17.5+/-10.2	11.7+/-8.1	0.2+/-0.2	23.5+/-25.9	-13.7+/-13.4
6:00-9:00	Thu	8	343+/-138	.95+/-.04	2.6+/-2.3	103.9+/-8.5	223.9+/-111.1	22.4+/-12.8	8.4+/-15.8	10.3+/-20.0	4.6+/-4.8	18.1+/-9.8	30.5+/-17.1	12.7+/-7.4	0.4+/-0.5	28.9+/-27.6	-17.8+/-19.2
6:00-9:00	Fri	9	298+/-146	.96+/-.02	2.2+/-2.1	105.1+/-4.7	198.5+/-108.5	21.8+/-13.8	9.9+/-15.6	2.1+/-3.8	6.5+/-6.6	17.2+/-9.2	24.5+/-10.8	16.5+/-13.9	0.2+/-0.3	16.7+/-12.1	-15.6+/-12.8
6:00-9:00	Sat	8	237+/-135	.96+/-.03	2.5+/-0.6	103.5+/-5.8	133.7+/-91.7	19.9+/-5.5	11.6+/-13.5	11.0+/-21.4	12.9+/-9.6	10.6+/-5.8	18.6+/-15.7	12.4+/-5.1	0.1+/-0.2	16.5+/-11.3	-10.2+/-16.0
13:00-16:00	Sun	4	122+/-28	.96+/-.03	2.3+/-0.7	103.4+/-1.6	64.5+/-11.8	22.2+/-8.3	0.0+/-0.0	0.0+/-0.0	7.7+/-3.0	5.5+/-3.2	10.6+/-3.3	11.8+/-5.9	0.2+/-0.2	3.7+/-4.5	-4.1+/-1.8
13:00-16:00	Mon	5	144+/-30	.95+/-.00	2.4+/-1.4	101.9+/-5.5	71.8+/-22.0	20.8+/-7.8	2.6+/-3.5	0.0+/-0.0	5.6+/-4.1	6.7+/-3.4	12.6+/-2.7	12.1+/-4.8	0.2+/-0.1	14.8+/-11.7	-3.0+/-8.5
13:00-16:00	Tue	4	136+/-24	.96+/-.03	2.1+/-0.1	103.9+/-5.6	71.8+/-19.0	13.1+/-3.6	1.4+/-1.7	3.3+/-6.6	2.1+/-1.5	7.8+/-1.7	12.3+/-2.6	6.9+/-2.7	0.3+/-0.2	21.7+/-10.7	-5.2+/-7.4
13:00-16:00	Wed	4	212+/-50	.97+/-.04	2.1+/-0.5	104.4+/-7.9	115.9+/-28.2	25.0+/-2.6	3.3+/-4.1	0.7+/-1.5	10.3+/-8.3	13.0+/-0.8	19.4+/-4.8	18.5+/-9.3	0.4+/-0.5	12.3+/-5.8	-7.0+/-15.6
13:00-16:00	Thu	5	225+/-141	.97+/-.03	1.8+/-0.3	106.3+/-3.6	140.7+/-112.0	17.2+/-7.4	17.4+/-30.1	4.6+/-7.4	2.8+/-2.8	10.2+/-4.2	23.7+/-11.2	9.3+/-4.8	0.5+/-0.2	11.2+/-9.9	-12.9+/-6.8
13:00-16:00	Fri	5	155+/-59	.96+/-.01	2.2+/-1.0	106.4+/-2.6	86.1+/-33.2	20.6+/-12.2	1.1+/-2.4	0.0+/-0.0	4.3+/-4.4	8.9+/-4.5	19.4+/-5.9	12.5+/-10.9	0.4+/-0.3	12.8+/-6.8	-10.8+/-7.5
13:00-16:00	Sat	3	193+/-71	.95+/-.04	2.8+/-1.2	98.3+/-19.3	99.3+/-32.0	25.6+/-3.4	0.0+/-0.0	0.0+/-0.0	7.6+/-1.6	9.9+/-2.8	15.0+/-12.5	15.8+/-5.6	0.5+/-0.5	8.1+/-6.2	10.9+/-45.2

Table 4.4-2a

Number of observations, mean measured NMHC (ug/m^3), mean CMB performance parameters and mean estimated source contributions (% of NMHC) +/- standard deviation; during the carryover (3:00-6:00), inhibition (6:00-9:00), accumulation (9:00-12:00), and peak ozone (12:00-15:00) periods by day-of-week at Azusa for summers 1999 and 2000

TIME	DAY	OBS	totNMHC	rSquared	ChiSquar	%explained	GasExhaust	GasVapor	LiquidGas	Diesel	CNG	LPG	Coatings	ConsProd	Biogen	Backgrd	Unexpl
3:00-6:00	Sun	6	197+/-70	.93+/-.06	4.4+/-3.2	90.1+/-9.8	47.8+/-12.5	9.1+/-2.2	12.4+/-4.2	0.0+/-0.0	2.5+/-1.8	4.9+/-1.0	6.5+/-0.6	4.4+/-1.4	0.1+/-0.2	2.4+/-2.4	9.9+/-0.9
3:00-6:00	Mon	4	184+/-96	.93+/-.02	4.2+/-1.4	94.0+/-5.0	53.6+/-5.4	10.1+/-3.4	8.6+/-5.5	0.0+/-0.0	2.7+/-1.4	5.2+/-1.8	5.8+/-0.8	5.8+/-2.5	0.0+/-0.1	2.3+/-1.8	6.0+/-0.8
3:00-6:00	Tue	6	268+/-152	.94+/-.00	3.7+/-1.2	93.0+/-5.0	50.1+/-4.2	6.9+/-1.9	13.7+/-3.8	0.0+/-0.0	2.0+/-1.6	6.1+/-2.2	6.7+/-2.1	4.2+/-1.1	0.5+/-1.0	2.9+/-3.6	7.0+/-2.2
3:00-6:00	Wed	7	301+/-199	.92+/-.05	4.9+/-2.3	89.9+/-9.2	45.4+/-10.6	7.7+/-2.8	14.1+/-5.6	0.0+/-0.0	1.7+/-1.3	5.5+/-2.5	6.9+/-1.3	4.6+/-1.5	0.2+/-0.2	3.8+/-4.3	10.1+/-2.0
3:00-6:00	Thu	7	322+/-150	.94+/-.02	4.0+/-1.4	90.7+/-4.1	44.7+/-8.9	8.2+/-2.1	14.6+/-5.5	0.0+/-0.0	1.4+/-1.1	7.1+/-3.5	8.6+/-7.3	4.3+/-1.4	0.2+/-0.1	1.6+/-2.0	9.3+/-8.0
3:00-6:00	Fri	8	256+/-88	.95+/-.03	3.5+/-1.4	92.2+/-6.5	50.9+/-4.2	7.0+/-1.8	12.0+/-2.6	0.0+/-0.0	2.1+/-2.1	5.3+/-0.9	7.6+/-1.1	4.1+/-1.3	0.1+/-0.1	3.1+/-2.7	7.8+/-1.1
3:00-6:00	Sat	7	250+/-115	.95+/-.04	3.6+/-2.2	95.2+/-3.2	57.0+/-5.0	7.9+/-2.0	9.0+/-4.6	0.0+/-0.0	3.0+/-1.8	5.0+/-1.1	6.6+/-2.3	4.3+/-0.9	0.1+/-0.1	2.3+/-3.0	4.8+/-1.7
6:00-9:00	Sun	6	214+/-92	.93+/-.05	4.4+/-2.8	92.1+/-5.7	52.9+/-9.7	9.4+/-3.6	12.4+/-6.2	0.0+/-0.0	1.8+/-1.3	4.8+/-1.0	5.1+/-2.9	3.6+/-1.2	0.1+/-0.1	2.2+/-3.2	7.9+/-4.4
6:00-9:00	Mon	4	248+/-191	.94+/-.03	3.9+/-1.8	94.4+/-6.5	55.3+/-4.6	7.8+/-5.3	9.6+/-6.7	0.0+/-0.0	1.6+/-1.9	5.1+/-1.0	5.4+/-2.2	5.2+/-1.7	0.0+/-0.1	4.4+/-4.2	5.6+/-2.3
6:00-9:00	Tue	7	348+/-212	.95+/-.01	3.5+/-1.1	95.1+/-4.9	54.2+/-5.2	6.9+/-2.0	12.8+/-7.2	1.0+/-2.0	1.1+/-1.2	7.3+/-1.5	5.4+/-1.3	4.4+/-2.3	0.2+/-0.3	1.8+/-3.2	4.9+/-1.2
6:00-9:00	Wed	7	356+/-205	.95+/-.02	3.1+/-0.8	93.1+/-5.7	53.7+/-4.3	6.7+/-2.0	9.0+/-1.6	1.7+/-4.3	0.4+/-0.8	7.2+/-3.4	6.1+/-1.8	4.3+/-1.4	0.2+/-0.1	3.9+/-4.7	6.9+/-2.0
6:00-9:00	Thu	7	384+/-144	.94+/-.03	3.7+/-1.1	90.5+/-5.6	49.9+/-9.8	6.7+/-1.5	13.0+/-4.9	0.4+/-1.0	0.3+/-0.6	6.0+/-1.2	8.3+/-3.9	4.3+/-1.1	0.3+/-0.2	1.2+/-1.6	9.5+/-4.4
6:00-9:00	Fri	8	325+/-123	.96+/-.03	2.7+/-0.7	91.6+/-6.0	53.3+/-7.2	5.6+/-1.0	10.6+/-3.4	0.0+/-0.1	1.2+/-1.5	6.6+/-2.0	7.6+/-3.9	3.8+/-0.8	0.1+/-0.1	2.7+/-3.1	8.4+/-4.3
6:00-9:00	Sat	7	251+/-132	.95+/-.02	3.2+/-0.6	93.3+/-5.7	55.3+/-4.9	7.4+/-1.6	8.7+/-3.2	0.6+/-1.4	2.6+/-1.0	5.5+/-0.5	6.1+/-1.0	4.8+/-1.3	0.1+/-0.1	2.1+/-4.1	6.7+/-1.1
9:00-12:00	Sun	6	165+/-45	.96+/-.01	2.7+/-0.7	95.7+/-4.4	57.2+/-4.2	10.8+/-2.1	6.9+/-4.1	0.1+/-0.4	1.8+/-1.2	4.4+/-0.7	7.1+/-6.9	4.2+/-0.9	0.3+/-0.2	3.0+/-3.4	4.3+/-4.2
9:00-12:00	Mon	4	176+/-52	.95+/-.00	3.1+/-1.2	96.0+/-4.2	54.2+/-5.9	9.4+/-2.6	6.9+/-4.1	0.2+/-0.4	1.1+/-1.4	5.8+/-1.8	4.3+/-0.8	6.2+/-1.6	0.2+/-0.3	7.6+/-6.8	4.0+/-0.8
9:00-12:00	Tue	8	240+/-122	.94+/-.02	3.3+/-1.0	94.1+/-5.2	52.0+/-8.1	7.0+/-5.0	8.4+/-7.4	3.0+/-7.3	0.6+/-0.9	6.0+/-2.2	6.9+/-3.5	4.5+/-1.8	0.5+/-0.4	5.4+/-7.4	5.9+/-3.0
9:00-12:00	Wed	7	263+/-67	.95+/-.01	3.1+/-1.0	95.2+/-2.9	52.1+/-9.0	6.6+/-1.9	9.5+/-8.3	2.9+/-3.7	0.1+/-0.2	6.0+/-2.3	7.6+/-4.8	5.1+/-1.2	0.3+/-0.2	5.0+/-3.0	4.8+/-3.0
9:00-12:00	Thu	7	249+/-59	.95+/-.02	3.3+/-1.0	94.3+/-2.6	51.2+/-7.9	10.0+/-2.5	9.5+/-6.4	2.3+/-4.0	0.8+/-1.3	6.0+/-0.9	5.9+/-1.1	5.1+/-1.8	0.6+/-0.3	2.7+/-3.2	5.7+/-1.0
9:00-12:00	Fri	7	246+/-23	.96+/-.00	2.5+/-0.5	95.6+/-2.5	56.5+/-3.6	7.3+/-1.7	5.3+/-2.9	1.0+/-1.9	0.9+/-1.7	6.3+/-0.7	7.1+/-1.5	5.9+/-1.5	0.3+/-0.1	4.9+/-2.6	4.4+/-0.9
9:00-12:00	Sat	7	196+/-85	.95+/-.02	2.9+/-0.8	96.7+/-5.0	58.8+/-5.2	7.6+/-2.8	5.2+/-3.9	0.8+/-1.1	1.6+/-1.3	5.2+/-0.6	4.9+/-1.8	4.6+/-1.6	0.2+/-0.2	7.8+/-10.3	3.3+/-1.2
12:00-15:00	Sun	8	126+/-42	.95+/-.00	3.5+/-1.1	93.3+/-5.6	51.8+/-5.4	13.5+/-2.8	6.2+/-4.7	1.6+/-3.7	2.7+/-1.6	4.0+/-0.7	4.7+/-1.2	4.5+/-1.2	0.5+/-0.2	3.7+/-4.3	6.7+/-1.7
12:00-15:00	Mon	4	198+/-47	.95+/-.00	3.0+/-1.1	87.5+/-6.5	47.0+/-8.4	7.7+/-2.6	5.7+/-6.9	0.4+/-0.5	0.9+/-1.1	6.3+/-1.5	4.3+/-1.4	5.9+/-2.2	0.3+/-0.2	9.1+/-7.7	12.5+/-4.1
12:00-15:00	Tue	8	196+/-105	.94+/-.03	4.2+/-1.3	95.5+/-3.4	50.2+/-8.4	11.7+/-3.3	6.7+/-5.3	3.0+/-4.9	1.1+/-1.0	6.0+/-0.9	5.9+/-2.8	6.0+/-1.8	0.5+/-0.3	4.3+/-5.1	4.5+/-2.1
12:00-15:00	Wed	6	230+/-26	.93+/-.03	3.1+/-1.2	93.5+/-5.4	36.9+/-14.3	5.0+/-3.2	14.3+/-8.2	3.7+/-4.4	0.8+/-1.1	4.8+/-0.5	14.1+/-11.4	4.8+/-1.2	0.4+/-0.2	8.7+/-8.3	6.5+/-5.3
12:00-15:00	Thu	7	250+/-86	.91+/-.09	5.1+/-4.6	87.7+/-8.7	43.1+/-14.6	7.9+/-3.9	7.7+/-5.2	3.5+/-5.9	0.7+/-0.9	5.0+/-1.1	7.9+/-5.2	7.2+/-5.5	0.7+/-0.4	4.0+/-5.0	12.3+/-8.1
12:00-15:00	Fri	7	234+/-54	.95+/-.03	2.9+/-1.5	94.3+/-11.6	54.5+/-8.4	8.8+/-2.6	4.2+/-4.4	1.9+/-2.5	1.0+/-1.3	6.1+/-0.6	7.4+/-2.4	5.4+/-0.8	0.4+/-0.2	4.7+/-4.8	5.7+/-1.8
12:00-15:00	Sat	7	207+/-77	.94+/-.02	3.7+/-1.8	93.1+/-11.0	51.2+/-16.1	11.4+/-4.3	5.9+/-8.2	2.1+/-3.8	1.5+/-1.0	5.5+/-1.4	3.8+/-1.4	4.9+/-2.0	0.3+/-0.2	6.5+/-7.2	6.9+/-2.6

Table 4.4-2b

Number of observations, mean measured NMHC (ug/m^3), mean CMB performance parameters and mean estimated source contributions (% of NMHC) +/- standard deviation; during the carryover (3:00-6:00), inhibition (6:00-9:00), accumulation (9:00-12:00), and peak ozone (12:00-15:00) periods by day-of-week at Pico Rivera for summer 1999

TIME	DAY	OBS	totNMHC	rSquared	ChiSquar	%explained	GasExhaust	GasVapor	LiquidGas	Diesel	CNG	LPG	Coatings	ConsProd	Biogen	Backgrd	Unexpl
3:00-6:00	Sun	12	140+/-42	.95+/-.01	2.9+/-0.9	94.8+/-14.6	52.0+/-10.2	13.8+/-5.4	4.9+/-6.1	0.0+/-0.1	3.9+/-2.1	4.8+/-1.3	6.8+/-2.0	6.1+/-2.4	0.0+/-0.0	2.4+/-2.6	5.2+/-1.5
3:00-6:00	Mon	13	160+/-64	.96+/-.02	2.4+/-1.0	91.7+/-16.6	53.1+/-13.0	13.0+/-3.7	0.2+/-0.7	0.0+/-0.1	4.4+/-1.7	5.3+/-1.6	6.2+/-2.2	6.4+/-2.2	0.0+/-0.0	3.1+/-1.8	8.3+/-2.9
3:00-6:00	Tue	12	196+/-68	.95+/-.02	2.7+/-1.1	88.6+/-18.9	49.3+/-12.5	9.9+/-2.9	2.6+/-3.0	0.0+/-0.1	3.3+/-1.3	5.4+/-1.9	5.9+/-2.1	5.4+/-1.4	0.0+/-0.0	6.7+/-4.1	11.4+/-4.1
3:00-6:00	Wed	12	223+/-151	.96+/-.10	2.3+/-0.8	92.0+/-14.0	52.8+/-9.6	10.2+/-4.1	2.1+/-2.8	0.9+/-2.6	2.0+/-1.8	6.0+/-1.8	7.1+/-2.8	4.8+/-3.0	0.0+/-0.0	6.1+/-5.8	8.0+/-3.1
3:00-6:00	Thu	11	196+/-115	.95+/-.03	2.5+/-1.1	89.9+/-21.4	49.9+/-13.4	11.4+/-3.8	1.8+/-2.7	0.8+/-1.8	2.7+/-1.3	5.9+/-1.8	6.9+/-2.4	5.2+/-1.9	0.0+/-0.0	5.4+/-3.3	10.1+/-3.5
3:00-6:00	Fri	12	160+/-68	.95+/-.02	2.8+/-1.5	94.9+/-14.3	52.0+/-12.6	10.0+/-4.3	4.0+/-10.2	0.7+/-1.6	3.0+/-1.7	5.4+/-1.4	7.4+/-3.2	5.7+/-3.4	0.0+/-0.0	6.6+/-4.3	5.1+/-2.2
3:00-6:00	Sat	12	160+/-64	.95+/-.10	2.9+/-1.0	94.2+/-16.6	51.1+/-12.2	11.4+/-3.6	4.0+/-4.6	0.1+/-0.4	3.9+/-2.9	6.7+/-3.6	8.0+/-2.8	5.7+/-3.3	0.0+/-0.0	3.4+/-2.0	5.8+/-2.1
6:00-9:00	Sun	12	145+/-50	.95+/-.02	2.7+/-1.0	93.6+/-17.0	53.3+/-12.8	14.5+/-4.3	0.6+/-1.1	0.0+/-0.1	4.4+/-1.9	5.3+/-1.6	6.1+/-1.8	6.5+/-1.6	0.0+/-0.1	2.8+/-1.7	6.4+/-2.0
6:00-9:00	Mon	13	251+/-115	.94+/-.08	3.0+/-2.7	93.1+/-11.7	55.4+/-13.1	9.8+/-4.2	2.7+/-5.9	0.0+/-0.0	2.0+/-1.8	6.7+/-3.1	4.1+/-2.1	4.8+/-2.0	0.1+/-0.1	7.6+/-5.4	6.9+/-3.5
6:00-9:00	Tue	13	318+/-183	.94+/-.03	3.3+/-1.3	95.6+/-10.8	54.0+/-11.7	9.3+/-3.3	3.8+/-5.4	0.0+/-0.1	2.2+/-2.2	7.3+/-2.3	4.2+/-1.3	5.8+/-2.9	0.1+/-0.1	9.0+/-4.9	4.4+/-1.4
6:00-9:00	Wed	12	284+/-228	.95+/-.02	2.7+/-1.1	96.9+/-6.5	57.8+/-4.5	9.2+/-3.7	3.6+/-4.2	1.3+/-1.8	0.5+/-0.9	7.8+/-2.1	4.1+/-2.5	4.8+/-3.4	0.1+/-0.1	7.7+/-5.6	3.1+/-1.9
6:00-9:00	Thu	12	276+/-204	.95+/-.02	2.8+/-1.5	94.9+/-14.1	55.8+/-8.6	8.5+/-2.5	6.8+/-10.5	0.6+/-1.6	1.7+/-1.5	6.1+/-1.3	5.2+/-2.1	4.0+/-1.4	0.1+/-0.1	6.0+/-4.4	5.1+/-2.0
6:00-9:00	Fri	13	245+/-88	.93+/-.05	3.3+/-1.9	92.5+/-14.9	53.1+/-12.1	7.2+/-3.6	5.5+/-8.0	0.4+/-0.9	0.6+/-1.3	6.5+/-1.4	4.3+/-1.5	4.5+/-2.5	0.1+/-0.1	10.4+/-6.4	7.5+/-2.7
6:00-9:00	Sat	12	201+/-82	.94+/-.05	3.2+/-2.1	93.3+/-17.4	53.1+/-14.9	9.6+/-3.5	3.5+/-5.0	0.0+/-0.1	1.7+/-1.5	6.4+/-2.3	5.9+/-2.9	4.7+/-2.2	0.1+/-0.1	8.2+/-6.6	6.7+/-3.4
9:00-12:00	Sun	13	133+/-56	.96+/-.01	2.0+/-0.6	95.8+/-16.9	55.3+/-12.0	15.2+/-4.6	0.0+/-0.1	0.1+/-0.4	3.2+/-1.5	5.4+/-1.3	5.5+/-1.5	6.6+/-1.8	0.3+/-0.2	4.2+/-2.6	4.2+/-1.1
9:00-12:00	Mon	13	230+/-92	.94+/-.04	3.2+/-2.3	95.7+/-8.7	52.8+/-9.3	10.4+/-3.9	4.1+/-5.6	1.5+/-3.9	1.2+/-2.1	7.1+/-1.4	4.2+/-1.3	4.7+/-1.4	0.2+/-0.1	9.4+/-4.7	4.3+/-1.4
9:00-12:00	Tue	13	315+/-158	.93+/-.04	4.0+/-2.1	96.3+/-5.5	50.4+/-6.2	9.0+/-3.9	6.5+/-6.4	0.7+/-1.5	0.8+/-1.0	7.7+/-1.5	4.5+/-2.5	5.6+/-2.9	0.2+/-0.1	10.9+/-6.2	3.7+/-2.0
9:00-12:00	Wed	13	246+/-99	.93+/-.05	3.7+/-3.3	91.3+/-20.9	47.4+/-12.2	8.5+/-3.7	5.4+/-8.6	1.4+/-1.9	0.3+/-0.8	6.9+/-2.4	6.5+/-3.9	5.4+/-2.4	0.4+/-0.5	9.1+/-6.2	8.7+/-5.2
9:00-12:00	Thu	13	231+/-119	.94+/-.03	3.4+/-1.6	94.6+/-12.6	51.3+/-8.0	9.0+/-2.6	4.4+/-4.9	1.5+/-2.6	0.4+/-0.9	7.8+/-1.6	5.5+/-1.8	5.1+/-2.9	0.4+/-0.5	9.2+/-6.3	5.4+/-1.7
9:00-12:00	Fri	13	221+/-80	.93+/-.04	3.6+/-1.7	95.0+/-11.2	49.8+/-8.1	8.6+/-2.8	5.3+/-6.3	0.8+/-1.4	0.2+/-0.5	7.8+/-1.3	5.4+/-1.9	5.0+/-1.8	0.2+/-0.1	11.8+/-4.8	5.0+/-1.8
9:00-12:00	Sat	11	176+/-64	.93+/-.04	3.7+/-1.8	96.8+/-15.0	51.6+/-11.8	12.1+/-3.5	4.4+/-5.8	0.0+/-0.1	1.4+/-1.0	6.5+/-1.5	4.5+/-1.7	5.8+/-1.8	0.3+/-0.2	10.2+/-8.8	3.2+/-1.2
12:00-15:00	Sun	12	132+/-50	.95+/-.02	2.7+/-1.5	96.8+/-9.4	48.0+/-8.9	20.9+/-6.2	0.0+/-0.1	0.0+/-0.1	3.3+/-1.3	5.8+/-1.2	4.9+/-1.2	7.6+/-2.2	0.6+/-0.2	5.8+/-3.4	3.2+/-0.8
12:00-15:00	Mon	12	198+/-47	.94+/-.03	3.2+/-1.5	98.2+/-5.8	47.7+/-5.6	14.6+/-4.9	2.9+/-4.6	1.2+/-2.8	1.0+/-1.4	7.6+/-1.3	6.2+/-1.2	7.0+/-2.1	0.5+/-0.2	9.5+/-4.4	1.8+/-0.4
12:00-15:00	Tue	10	222+/-62	.90+/-.03	4.9+/-1.7	94.5+/-11.4	39.5+/-10.1	13.0+/-7.0	7.8+/-8.7	0.7+/-1.6	0.7+/-1.2	8.2+/-2.4	4.4+/-2.6	7.1+/-3.7	0.5+/-0.1	12.4+/-9.6	5.5+/-3.3
12:00-15:00	Wed	11	164+/-59	.91+/-.05	4.5+/-2.2	98.1+/-5.6	42.0+/-9.3	10.7+/-5.0	9.1+/-7.3	1.5+/-3.4	0.0+/-0.1	7.9+/-1.0	6.6+/-3.6	5.7+/-3.0	0.6+/-0.2	13.9+/-6.8	1.9+/-1.1
12:00-15:00	Thu	9	231+/-125	.86+/-.14	8.4+/-10.6	92.7+/-18.3	39.6+/-15.0	11.4+/-7.4	12.6+/-12.6	0.2+/-0.7	0.3+/-0.5	6.6+/-2.8	5.2+/-2.1	6.5+/-4.0	0.5+/-0.2	9.7+/-8.5	7.3+/-2.9
12:00-15:00	Fri	12	181+/-84	.91+/-.03	4.5+/-1.3	97.1+/-7.4	41.7+/-6.4	12.1+/-4.4	6.2+/-5.4	1.3+/-2.7	0.3+/-0.5	7.0+/-0.9	6.0+/-2.4	7.4+/-3.1	0.5+/-0.2	14.6+/-6.1	2.9+/-1.2
12:00-15:00	Sat	11	159+/-80	.96+/-.02	2.2+/-1.1	100.4+/-4.7	56.4+/-6.2	17.0+/-3.9	0.1+/-0.4	0.0+/-0.1	1.3+/-1.3	5.7+/-1.0	5.9+/-1.9	6.8+/-2.0	0.5+/-0.3	6.7+/-3.1	-0.4+/--0.1

Table 4.4-2c

Number of observations, mean measured NMHC (ug/m^3), mean CMB performance parameters and mean estimated source contributions (% of NMHC) +/- standard deviation; during the carryover (3:00-6:00), inhibition (6:00-9:00), accumulation (9:00-12:00), and peak ozone (12:00-15:00) periods by day-of-week at Upland for summers 1999 and 2000

TIME	DAY	OBS	totNMHC	rSquared	ChiSquar	%explained	GasExhaust	GasVapor	LiquidGas	Diesel	CNG	LPG	Coatings	ConsProd	Biogen	Backgrd	Unexpl
3:00-6:00	Sun	7	214+/-68	.94+/-.01	4.1+/-1.2	94.3+/-6.0	49.0+/-11.9	11.2+/-3.4	18.7+/-8.1	0.0+/-0.0	3.3+/-2.5	3.5+/-0.6	4.9+/-0.9	3.4+/-1.4	0.2+/-0.3	0.0+/-0.0	5.7+/-1.0
3:00-6:00	Mon	6	217+/-51	.96+/-.01	2.8+/-0.8	92.5+/-8.5	58.3+/-11.5	7.8+/-1.1	11.4+/-2.0	0.0+/-0.0	1.0+/-1.1	3.6+/-0.6	4.3+/-1.2	4.0+/-0.4	0.2+/-0.2	1.9+/-2.0	7.5+/-2.1
3:00-6:00	Tue	7	179+/-81	.94+/-.03	3.5+/-1.3	91.7+/-8.6	52.4+/-5.5	6.3+/-3.3	16.4+/-9.6	0.5+/-1.4	1.0+/-1.4	4.6+/-1.2	5.0+/-1.7	3.2+/-1.9	0.3+/-0.3	2.0+/-3.2	8.3+/-2.8
3:00-6:00	Wed	8	307+/-76	.95+/-.00	3.4+/-1.1	93.4+/-4.4	55.3+/-9.4	9.5+/-3.9	13.7+/-11.9	0.0+/-0.0	0.9+/-1.0	3.6+/-0.9	4.4+/-0.7	4.0+/-1.7	0.4+/-0.7	1.7+/-2.5	6.6+/-1.0
3:00-6:00	Thu	6	302+/-67	.95+/-.03	3.3+/-1.0	93.3+/-3.6	55.4+/-8.9	7.2+/-2.5	18.9+/-5.7	0.0+/-0.0	0.1+/-0.2	3.4+/-0.9	5.2+/-1.7	2.8+/-0.9	0.2+/-0.1	0.1+/-0.3	6.7+/-2.2
3:00-6:00	Fri	5	331+/-75	.94+/-.01	3.9+/-2.2	90.9+/-9.2	49.0+/-15.0	6.5+/-1.9	22.8+/-17.9	0.0+/-0.0	0.1+/-0.3	2.8+/-1.0	5.0+/-2.0	2.6+/-1.4	0.2+/-0.2	1.9+/-2.3	9.1+/-3.7
3:00-6:00	Sat	5	323+/-111	.93+/-.06	4.9+/-4.0	89.8+/-3.2	50.4+/-8.5	9.2+/-2.0	16.0+/-8.2	0.0+/-0.0	0.9+/-1.0	3.5+/-0.8	4.7+/-1.1	3.9+/-1.9	0.3+/-0.2	0.9+/-1.0	10.2+/-2.4
6:00-9:00	Sun	8	248+/-92	.94+/-.04	4.1+/-2.1	94.1+/-5.2	54.8+/-9.5	10.6+/-3.4	15.9+/-9.0	0.0+/-0.0	1.0+/-1.0	3.7+/-0.7	4.0+/-1.4	2.8+/-1.6	0.6+/-0.5	0.7+/-1.3	5.9+/-2.1
6:00-9:00	Mon	7	219+/-42	.95+/-.01	3.3+/-0.8	94.7+/-4.9	55.6+/-8.2	9.3+/-2.4	11.6+/-6.1	0.0+/-0.0	0.1+/-0.2	4.7+/-1.4	4.1+/-0.9	3.5+/-1.5	0.4+/-0.3	5.3+/-5.1	5.3+/-1.2
6:00-9:00	Tue	6	213+/-74	.96+/-.02	2.5+/-0.7	96.2+/-4.6	61.1+/-4.7	7.1+/-1.7	11.0+/-4.3	0.5+/-0.7	0.4+/-0.6	4.3+/-1.2	6.3+/-3.0	3.9+/-1.0	0.4+/-0.3	1.2+/-2.3	3.8+/-1.8
6:00-9:00	Wed	8	303+/-91	.95+/-.03	2.8+/-0.5	92.8+/-7.6	54.0+/-17.1	8.8+/-1.8	11.7+/-4.1	0.0+/-0.0	0.2+/-0.4	4.1+/-0.8	4.3+/-1.7	3.8+/-1.0	0.7+/-0.6	5.3+/-10.8	7.2+/-2.9
6:00-9:00	Thu	5	362+/-64	.96+/-.01	2.9+/-0.7	91.0+/-8.9	57.1+/-8.4	8.5+/-2.0	14.9+/-9.2	0.0+/-0.0	0.0+/-0.0	3.7+/-2.0	4.0+/-0.8	2.2+/-0.8	0.6+/-0.6	0.0+/-0.0	9.0+/-1.8
6:00-9:00	Fri	5	338+/-96	.94+/-.03	3.5+/-2.2	85.6+/-10.2	46.9+/-11.0	6.0+/-1.9	18.7+/-17.6	0.0+/-0.0	0.0+/-0.0	3.3+/-1.7	5.3+/-2.5	2.8+/-1.7	0.7+/-0.6	1.8+/-1.8	14.4+/-6.7
6:00-9:00	Sat	5	287+/-91	.94+/-.05	4.0+/-3.1	91.2+/-5.6	55.1+/-6.1	9.1+/-2.3	12.2+/-3.8	0.0+/-0.0	0.4+/-0.5	4.7+/-0.9	4.9+/-0.9	3.7+/-1.9	0.5+/-0.3	0.7+/-1.6	8.8+/-1.7
9:00-12:00	Sun	8	152+/-57	.95+/-.02	3.0+/-0.9	93.1+/-7.2	53.2+/-10.1	11.3+/-2.6	11.3+/-7.3	0.0+/-0.0	1.6+/-2.2	4.0+/-1.2	4.6+/-1.9	3.8+/-1.5	1.2+/-0.5	2.1+/-2.7	6.9+/-2.8
9:00-12:00	Mon	7	193+/-48	.96+/-.03	2.7+/-1.4	90.7+/-3.9	53.7+/-4.2	8.8+/-2.2	8.4+/-4.0	0.0+/-0.0	0.2+/-0.3	4.7+/-2.0	5.3+/-2.0	3.9+/-1.0	0.8+/-0.7	4.8+/-5.4	9.3+/-3.4
9:00-12:00	Tue	6	191+/-117	.95+/-.03	3.3+/-0.8	92.0+/-4.6	51.9+/-6.6	8.1+/-1.4	9.9+/-4.3	2.5+/-1.9	0.3+/-0.6	5.1+/-0.7	5.1+/-0.9	4.6+/-0.9	1.0+/-1.0	3.5+/-4.7	8.0+/-1.4
9:00-12:00	Wed	8	219+/-81	.94+/-.02	3.3+/-0.8	91.6+/-3.1	51.0+/-11.3	11.0+/-2.4	8.1+/-3.3	0.1+/-0.2	0.5+/-0.9	5.3+/-1.2	5.5+/-2.2	4.8+/-1.2	1.1+/-0.6	4.1+/-9.3	8.4+/-3.3
9:00-12:00	Thu	7	248+/-76	.96+/-.00	2.9+/-0.7	91.4+/-3.6	50.5+/-7.3	8.6+/-1.4	14.5+/-9.4	0.5+/-0.8	2.8+/-7.4	3.8+/-2.1	5.5+/-1.6	3.2+/-1.7	1.1+/-0.8	0.9+/-2.5	8.6+/-2.5
9:00-12:00	Fri	6	248+/-107	.96+/-.00	3.0+/-1.0	92.9+/-1.9	53.2+/-4.1	9.0+/-1.7	13.1+/-9.6	0.2+/-0.6	0.4+/-0.7	4.7+/-1.4	6.2+/-1.7	4.6+/-2.3	1.0+/-0.8	0.5+/-1.2	7.1+/-2.0
9:00-12:00	Sat	5	204+/-70	.94+/-.03	3.5+/-0.8	91.5+/-3.4	53.7+/-10.7	10.5+/-1.7	8.8+/-3.2	0.6+/-1.4	0.5+/-0.6	4.2+/-0.4	4.1+/-0.7	3.7+/-1.7	1.1+/-0.6	4.2+/-7.3	8.5+/-1.6
12:00-15:00	Sun	8	120+/-30	.95+/-.00	3.2+/-0.8	87.4+/-7.4	46.8+/-8.4	14.7+/-3.0	7.4+/-6.8	0.0+/-0.0	1.9+/-1.7	3.4+/-0.7	2.8+/-0.7	3.3+/-1.6	2.2+/-1.0	4.8+/-5.9	12.6+/-3.3
12:00-15:00	Mon	7	182+/-66	.95+/-.03	2.9+/-0.6	90.9+/-4.5	52.7+/-5.1	10.9+/-4.0	8.4+/-5.3	0.0+/-0.0	0.8+/-1.0	4.6+/-1.3	3.9+/-0.5	4.2+/-1.8	1.6+/-0.9	3.8+/-5.2	9.1+/-1.2
12:00-15:00	Tue	7	181+/-83	.96+/-.00	2.8+/-0.6	90.3+/-3.1	50.1+/-7.7	9.4+/-2.1	9.9+/-6.3	0.1+/-0.2	0.8+/-0.9	5.3+/-1.0	6.2+/-1.6	4.6+/-1.3	1.6+/-1.3	2.4+/-4.2	9.7+/-2.5
12:00-15:00	Wed	7	171+/-49	.95+/-.02	3.1+/-1.2	85.4+/-9.4	47.3+/-7.7	9.6+/-1.3	6.2+/-3.3	0.6+/-1.5	0.6+/-0.8	6.1+/-2.1	3.8+/-1.1	5.4+/-1.1	1.8+/-1.2	3.9+/-5.6	14.6+/-4.3
12:00-15:00	Thu	5	192+/-73	.94+/-.03	3.5+/-0.6	91.5+/-5.1	48.6+/-7.3	10.6+/-7.4	14.2+/-14.5	0.0+/-0.0	0.6+/-0.9	5.1+/-1.4	6.2+/-4.2	4.3+/-2.0	1.5+/-1.5	0.5+/-0.8	8.5+/-5.8
12:00-15:00	Fri	6	216+/-84	.94+/-.03	4.0+/-2.3	84.6+/-14.6	48.4+/-9.8	9.4+/-3.6	4.8+/-3.1	0.3+/-0.7	0.8+/-1.1	6.1+/-2.3	4.3+/-1.5	5.7+/-2.2	1.6+/-1.0	3.1+/-4.0	15.4+/-5.3
12:00-15:00	Sat	5	176+/-58	.94+/-.02	3.4+/-0.6	90.8+/-4.5	50.4+/-14.6	11.0+/-3.0	7.8+/-5.2	0.0+/-0.0	1.4+/-1.0	4.1+/-0.9	3.2+/-1.3	4.3+/-2.2	1.6+/-1.0	7.0+/-12.7	9.2+/-3.7

Table 4.4-2d

Number of observations, mean measured NMHC (ug/m^3), mean CMB performance parameters and mean estimated source contributions (% of NMHC) +/- standard deviation; during the carryover (3:00-6:00), inhibition (6:00-9:00), accumulation (9:00-12:00), and peak ozone (12:00-15:00) periods by day-of-week at Los Angeles N. Main for summers 1999 and 2000

TIME	DAY	OBS	totNMHC	rSquared	ChiSquar	%explained	GasExhaust	GasVapor	LiquidGas	Diesel	CNG	LPG	Coatings	ConsProd	Biogen	Backgrd	Unexpl
6:00-9:00	Sun	9	199+/-83	.96+/-.03	2.0+/-1.3	105.9+/-6.2	56.6+/-13.6	12.3+/-6.4	3.6+/-6.3	0.4+/-1.1	6.4+/-4.8	4.4+/-1.4	9.0+/-2.7	5.3+/-2.3	0.1+/-0.1	8.0+/-7.7	-5.9+/--1.8
6:00-9:00	Mon	9	208+/-104	.95+/-.05	2.6+/-1.8	101.1+/-6.8	60.7+/-11.5	10.2+/-4.6	2.0+/-3.5	0.6+/-1.5	2.8+/-2.1	4.8+/-1.3	7.0+/-3.3	5.0+/-2.4	0.1+/-0.1	7.8+/-5.7	-1.1+/--0.5
6:00-9:00	Tue	8	271+/-191	.97+/-.01	1.6+/-0.7	102.7+/-6.2	57.3+/-14.8	8.1+/-3.3	3.2+/-5.3	2.5+/-3.9	2.1+/-1.8	6.1+/-1.8	7.4+/-3.2	4.6+/-1.9	0.1+/-0.1	11.3+/-13.2	-2.7+/--1.2
6:00-9:00	Wed	8	252+/-154	.96+/-.00	2.0+/-0.7	104.5+/-2.7	58.8+/-8.6	8.3+/-3.9	4.1+/-4.6	0.6+/-1.2	1.8+/-1.6	6.6+/-2.5	7.2+/-1.8	5.0+/-3.6	0.1+/-0.1	12.1+/-9.0	-4.5+/--1.1
6:00-9:00	Thu	8	343+/-138	.95+/-.04	2.6+/-2.3	103.9+/-8.5	61.9+/-14.6	7.1+/-4.1	1.9+/-3.3	3.4+/-5.5	1.6+/-1.4	5.1+/-1.7	8.5+/-4.4	3.7+/-2.0	0.2+/-0.2	10.6+/-9.4	-3.9+/--2.0
6:00-9:00	Fri	9	298+/-146	.96+/-.02	2.2+/-2.1	105.1+/-4.7	64.8+/-6.5	7.1+/-1.8	2.6+/-3.5	0.7+/-1.3	2.6+/-2.9	5.7+/-1.1	9.0+/-3.5	5.7+/-3.7	0.1+/-0.1	7.0+/-4.7	-5.1+/--2.0
6:00-9:00	Sat	8	237+/-135	.96+/-.03	2.5+/-0.6	103.5+/-5.8	54.4+/-6.6	9.7+/-3.1	4.1+/-3.9	3.5+/-6.4	5.9+/-4.6	4.7+/-1.5	7.5+/-2.4	6.0+/-2.8	0.1+/-0.1	7.8+/-6.1	-3.5+/--1.1
13:00-16:00	Sun	4	122+/-28	.96+/-.03	2.3+/-0.7	103.4+/-1.6	53.2+/-2.3	17.7+/-3.1	0.0+/-0.0	0.0+/-0.0	6.3+/-2.3	4.2+/-1.5	8.8+/-2.7	9.3+/-2.3	0.2+/-0.1	3.7+/-4.5	-3.4+/--1.0
13:00-16:00	Mon	5	144+/-30	.95+/-.00	2.4+/-1.4	101.9+/-5.5	49.4+/-7.0	14.3+/-4.4	1.5+/-2.1	0.0+/-0.0	4.3+/-2.9	4.5+/-1.5	8.9+/-2.1	8.3+/-2.3	0.1+/-0.1	10.5+/-8.6	-1.9+/--0.4
13:00-16:00	Tue	4	136+/-24	.96+/-.03	2.1+/-0.1	103.9+/-5.6	52.8+/-7.7	10.0+/-3.7	0.9+/-1.1	2.3+/-4.6	1.4+/-1.2	5.8+/-0.9	9.6+/-4.0	5.2+/-2.2	0.2+/-0.1	15.5+/-7.2	-3.9+/--1.6
13:00-16:00	Wed	4	212+/-50	.97+/-.04	2.1+/-0.5	104.4+/-7.9	54.8+/-4.9	12.4+/-3.5	1.7+/-2.4	0.3+/-0.5	4.5+/-2.7	6.3+/-1.1	9.2+/-1.4	9.4+/-5.6	0.2+/-0.2	5.7+/-2.0	-4.4+/--0.7
13:00-16:00	Thu	5	225+/-141	.97+/-.03	1.8+/-0.3	106.3+/-3.6	59.4+/-11.4	9.5+/-4.5	5.4+/-7.1	1.8+/-3.4	1.7+/-1.5	4.9+/-1.0	11.4+/-4.4	4.6+/-2.2	0.3+/-0.1	7.4+/-7.7	-6.3+/--2.4
13:00-16:00	Fri	5	155+/-59	.96+/-.01	2.2+/-1.0	106.4+/-2.6	55.4+/-5.0	12.8+/-3.0	1.1+/-2.4	0.0+/-0.0	2.3+/-2.2	5.6+/-1.3	13.6+/-5.8	7.3+/-3.6	0.2+/-0.1	8.0+/-2.7	-6.4+/--2.7
13:00-16:00	Sat	3	193+/-71	.95+/-.04	2.8+/-1.2	98.3+/-19.3	52.6+/-13.1	14.7+/-6.4	0.0+/-0.0	0.0+/-0.0	4.2+/-1.6	5.5+/-2.2	7.0+/-3.4	8.8+/-3.9	0.2+/-0.2	5.2+/-5.2	1.7+/-0.9

Table 4.4-3a
CMB Performance Parameters for Mobile Van Samples

Date	Sample ID	Location	Start Time	Measured NMHC	Predicted NMHC	Percent Mass	R^2	χ^2
Mon, 10/2/00	IH1	Industry Hills #1	02	114	112	98.4	0.92	3.85
	CV1	Covina Loop #1	03	163	154	95.0	0.98	0.93
	DS1	Dodger Stadium #1	04	61	61	98.9	0.95	2.29
	CO1	Compton Loop #1	05	237	188	79.2	0.88	5.72
	HF1	Harbor Freeway #1	06	240	240	100.0	1.00	0.31
	DS2	Dodger Stadium #2	07	238	223	93.6	0.99	0.86
	CO2	Compton Loop #2	08	322	298	92.3	0.98	1.06
	CV2	Covina Loop #2	09	206	203	98.5	0.98	1.12
	IH2	Industry Hills #2	10	NA	NA	NA	NA	NA
	PO1	Pomona Loop #1	11	169	166	98.2	0.93	5.12
Wed, 10/4/00	IH1	Industry Hills #1	02	67	63	92.9	0.92	3.58
	CV1	Covina Loop #1	03	76	70	92.8	0.97	1.39
	DS1	Dodger Stadium #1	04	67	67	99.5	0.97	1.44
	CO1	Compton Loop #1	05	227	208	91.6	0.98	0.98
	HF1	Harbor Freeway #1	06	214	214	100.0	0.99	0.69
	DS2	Dodger Stadium #2	07	230	228	99.0	0.99	0.55
	CO2	Compton Loop #2	08	378	371	98.1	0.96	3.32
	CV2	Covina Loop #2	09	202	188	93.2	0.98	1.06
	IH2	Industry Hills #2	10	82	84	102.7	0.97	1.27
	PO1	Pomona Loop #1	11	129	114	88.5	0.96	2.56
Sat, 10/7/00	IH1	Industry Hills #1	02	159	168	105.5	0.97	1.46
	CV1	Covina Loop #1	03	159	158	99.7	0.98	1.18
	DS1	Dodger Stadium #1	04	59	55	94.2	0.97	1.47
	CO1	Compton Loop #1	05	153	144	94.0	0.96	2.04
	HF1	Harbor Freeway #1	06	171	167	97.3	0.99	0.41
	DS2	Dodger Stadium #2	07	134	130	96.8	0.98	0.99
	CO2	Compton Loop #2	08	231	220	95.2	0.98	1.37
	CV2	Covina Loop #2	09	205	197	96.1	0.99	0.68
	IH2	Industry Hills #2	10	82	86	105.6	0.97	1.69
	PO1	Pomona Loop #1	11	180	176	97.5	0.99	0.91
Sun, 10/8/00	IH1	Industry Hills #1	02	142	147	103.5	0.97	1.74
	CV1	Covina Loop #1	03	355	291	81.8	0.92	4.92
	DS1	Dodger Stadium #1	04	207	218	105.2	0.98	0.94
	CO1	Compton Loop #1	05	431	453	105.3	0.97	1.68
	HF1	Harbor Freeway #1	06	254	256	101.0	0.99	0.52
	DS2	Dodger Stadium #2	07	221	227	102.6	0.99	0.62
	CO2	Compton Loop #2	08	319	312	97.9	0.98	1.33
	CV2	Covina Loop #2	09	190	182	95.8	0.97	1.70
	IH2	Industry Hills #2	10	70	77	109.0	0.95	2.60
	PO1	Pomona Loop #1	11	155	154	98.9	0.96	2.14
Tue, 10/3/00	TSD	Truck Stop Downwind	01	205	199	97.3	0.97	1.87
	TS1	Truck Stop #1	02	200	202	100.9	0.97	2.00
	TS2	Truck Stop #2	03	179	175	97.9	0.95	3.36
	TS3	Truck Stop #3	03	199	188	94.2	0.97	2.24
	TSU	Truck Stop Upwind	04	158	140	88.3	0.93	4.05
Fri, 10/6/00	SC	South Central	06	475	450	94.6	0.98	1.12
	CS	Compton	07	503	487	96.8	0.96	2.25
	DH	Dominguez Hills	08	198	194	97.9	0.97	1.60
	DL	Downey	09	297	300	101.3	0.98	0.85
	PS	Pico Rivera	10	206	220	106.6	0.97	1.70
	MH	Montebello Hills	11	224	233	103.7	0.95	2.71

Table 4.4-3b
Source Contribution Estimates (µg/m^3) for Mobile Van Samples

Date	Sample ID	Gasoline Exhaust	Diesel Exhaust	Gasoline Vapor	CNG	LPG	Surface Coatings	Consumer Products	Unexplained
Mon, 10/2/00	IH1	72.10	4.57	10.09	9.07	10.11	2.83	3.64	1.80
	CV1	102.70	12.12	10.81	9.90	8.96	3.69	6.22	8.13
	DS1	30.49	5.06	2.43	12.76	4.08	0.91	4.78	0.67
	CO1	182.37				4.59		0.58	49.30
	HF1	221.99	5.17	5.11	1.36	3.56	1.32	1.37	0.00
	DS2	197.84	3.62	7.34	2.23	6.67	2.05	3.49	15.15
	CO2	227.45	16.10	19.57	1.06	19.43		13.85	24.88
	CV2	146.14	20.95	11.96	2.47	9.60	2.80	9.15	3.08
	IH2	NA	NA	NA	NA	NA	NA	NA	NA
	PO1	101.03	33.74	17.53	2.88	7.75		2.58	3.11
Wed, 10/4/00	IH1	37.82	3.95	7.25	2.54	3.86	2.80	4.34	4.79
	CV1	42.85	7.76	5.80	2.97	3.43	3.13	4.40	5.50
	DS1	32.78	8.49	7.12	6.08	3.48	3.88	4.83	0.31
	CO1	165.29	13.14	15.31	1.19	5.44	2.73	4.65	19.12
	HF1	160.46	5.60	10.57	20.00	5.17	4.32	8.25	
	DS2	192.49	5.73	11.02	2.36	6.57	2.69	6.93	2.27
	CO2	281.46	38.06	25.61	11.98	6.90	2.04	5.18	7.12
	CV2	157.08	15.09	5.97		4.67	2.52	2.72	13.71
	IH2	55.46	4.33	6.08	1.24	6.77	2.76	7.32	
	PO1	84.20	20.48	0.55	0.04	5.16	1.33	2.42	14.86
Sat, 10/7/00	IH1	117.92	7.15	12.17	6.57	8.39	7.66	8.27	
	CV1	115.23	7.13	9.86	5.82	7.39	3.49	9.12	0.54
	DS1	27.02	1.98	5.51	12.35	2.87	0.32	5.06	3.39
	CO1	118.72	3.45	8.43	3.27	5.03	1.29	3.59	9.17
	HF1	148.60	0.32	4.38	7.57	1.93	0.01	3.73	4.56
	DS2	104.70	2.17	4.36	7.19	4.24	0.55	6.50	4.23
	CO2	174.93	11.02	10.00	3.40	8.83	4.67	6.75	11.01
	CV2	156.61	8.82	9.55	3.81	9.04	4.03	4.78	7.97
	IH2	51.88	6.35	6.70	5.04	6.41	4.18	5.77	
	PO1	146.48	10.29	6.06	0.56	5.97	1.53	4.69	4.57
Sun, 10/8/00	IH1	90.02	8.22	14.93	7.66	9.82	6.53	9.91	
	CV1	226.08	12.98	10.48	14.08	7.81	8.88	10.28	64.49
	DS1	161.61	7.98	12.35	13.24	3.95	9.26	9.22	
	CO1	281.55	12.27	49.80	39.38	25.61	19.38	25.41	
	HF1	193.34	10.36	10.47	13.86	4.92	17.23	6.06	
	DS2	170.97	10.08	10.71	12.73	5.81	9.43	7.47	
	CO2	227.84	14.64	23.99	12.14	12.54	8.69	12.12	6.66
	CV2	141.92	2.70	13.19	5.66	7.54	4.88	6.18	7.92
	IH2	39.61	5.79	8.71	7.12	5.61	2.74	7.26	
	PO1	120.70	4.65	10.93	3.49	5.91	1.62	6.44	1.69
Tue, 10/3/00	TSD	122.60	42.96	7.84	4.49	7.51	8.32	5.71	5.48
	TS1	95.42	71.84	9.90	6.75	9.78	3.70	4.71	
	TS2	82.26	47.25	14.57	7.97	9.89	4.44	9.05	3.77
	TS3	87.72	49.88	13.99	7.22	11.95	6.26	10.64	11.61
	TSU	71.74	14.68	17.88	8.19	11.13	5.44	10.89	18.52
Fri, 10/6/00	SC	399.01	5.93	11.01		11.31	10.22	12.15	25.84
	CS	400.54	14.20	21.20		29.54	8.60	13.02	15.99
	DH	143.97	13.86	15.42		9.66	5.46	5.95	4.15
	DL	238.29	12.08	19.86		8.98	7.67	13.51	
	PS	165.92	13.32	11.54		7.54	9.40	12.04	
	MH	141.47	9.70	14.82	22.90	16.93	6.01	20.76	

Table 4.4-3c
Source Contribution Estimates (Percent) for Mobile Van Samples

Date	Sample ID	Gasoline Exhasut	Diesel Exhaust	Gasoline Vapor	CNG	LPG	Surface Coatings	Consumer Products	Unexplained
Mon, 10/2/00	IH1	64.14	4.07	8.98	8.07	8.99	2.52	3.24	1.60
	CV1	66.52	7.85	7.00	6.41	5.80	2.39	4.03	5.26
	DS1	50.38	8.37	4.02	21.09	6.74	1.50	7.90	1.12
	CO1	97.17	0.00	0.00	0.00	2.44	0.00	0.31	26.27
	HF1	92.54	2.15	2.13	0.57	1.49	0.55	0.57	0.00
	DS2	88.62	1.62	3.29	1.00	2.99	0.92	1.56	6.79
	CO2	76.43	5.41	6.58	0.36	6.53	0.00	4.66	8.36
	CV2	71.89	10.31	5.88	1.21	4.72	1.38	4.50	1.51
	IH2	NA	NA	NA	NA	NA	NA	NA	NA
	PO1	60.87	20.33	10.56	1.73	4.67	0.00	1.56	1.87
Wed, 10/4/00	IH1	60.46	6.32	11.59	4.06	6.17	4.47	6.93	7.66
	CV1	60.91	11.03	8.25	4.22	4.87	4.45	6.26	7.82
	DS1	49.17	12.73	10.68	9.12	5.23	5.82	7.25	0.46
	CO1	79.55	6.32	7.37	0.57	2.62	1.31	2.24	9.20
	HF1	74.85	2.61	4.93	9.33	2.41	2.01	3.85	0.00
	DS2	84.50	2.52	4.84	1.04	2.89	1.18	3.04	1.00
	CO2	75.79	10.25	6.90	3.23	1.86	0.55	1.40	1.92
	CV2	83.53	8.02	3.17	0.00	2.49	1.34	1.44	7.29
	IH2	66.06	5.15	7.24	1.48	8.07	3.28	8.72	0.00
	PO1	73.70	17.93	0.48	0.04	4.52	1.16	2.12	13.00
Sat, 10/7/00	IH1	70.13	4.25	7.24	3.91	4.99	4.56	4.92	0.00
	CV1	72.92	4.51	6.24	3.68	4.67	2.21	5.77	0.34
	DS1	49.02	3.59	9.99	22.41	5.22	0.59	9.17	6.16
	CO1	82.57	2.40	5.86	2.27	3.50	0.90	2.49	6.38
	HF1	89.22	0.19	2.63	4.55	1.16	0.00	2.24	2.74
	DS2	80.73	1.67	3.36	5.54	3.27	0.42	5.01	3.26
	CO2	79.66	5.02	4.55	1.55	4.02	2.13	3.07	5.01
	CV2	79.64	4.49	4.86	1.94	4.60	2.05	2.43	4.05
	IH2	60.03	7.35	7.75	5.84	7.42	4.84	6.68	0.00
	PO1	83.39	5.86	3.45	0.32	3.40	0.87	2.67	2.60
Sun, 10/8/00	IH1	61.20	5.59	10.15	5.21	6.68	4.44	6.74	0.00
	CV1	77.80	4.47	3.61	4.84	2.69	3.06	3.54	22.19
	DS1	74.26	3.67	5.67	6.08	1.82	4.25	4.24	0.00
	CO1	62.10	2.71	10.98	8.69	5.65	4.27	5.60	0.00
	HF1	75.44	4.04	4.08	5.41	1.92	6.72	2.37	0.00
	DS2	75.25	4.44	4.71	5.60	2.56	4.15	3.29	0.00
	CO2	73.03	4.69	7.69	3.89	4.02	2.78	3.88	2.14
	CV2	77.91	1.48	7.24	3.11	4.14	2.68	3.39	4.35
	IH2	51.54	7.54	11.34	9.27	7.30	3.57	9.44	0.00
	PO1	78.49	3.03	7.11	2.27	3.84	1.05	4.18	1.10
Tue, 10/3/00	TSD	61.48	21.54	3.93	2.25	3.77	4.17	2.86	2.75
	TS1	47.21	35.55	4.90	3.34	4.84	1.83	2.33	0.00
	TS2	46.89	26.93	8.31	4.54	5.64	2.53	5.16	2.15
	TS3	46.74	26.58	7.46	3.85	6.37	3.33	5.67	6.19
	TSU	51.26	10.49	12.78	5.85	7.95	3.89	7.78	13.23
Fri, 10/6/00	SC	88.74	1.32	2.45	0.00	2.51	2.27	2.70	5.75
	CS	82.23	2.92	4.35	0.00	6.06	1.76	2.67	3.28
	DH	74.09	7.13	7.94	0.00	4.97	2.81	3.06	2.14
	DL	79.33	4.02	6.61	0.00	2.99	2.55	4.50	0.00
	PS	75.50	6.06	5.25	0.00	3.43	4.28	5.48	0.00
	MH	60.82	4.17	6.37	9.84	7.28	2.58	8.93	0.00

Table 4.5-1
Ambient NOx (ppb) Associated with CO and Black Carbon at On-Road and Regional Locations in the SoCAB [1]

		Sampling	Mon, 10/2/00			Wed, 10/4/00			Sat, 10/7/00			Sun, 10/8/00		
ID	Location	Period	Obs.	NOx [CO]	NOx [BC]	Obs.	NOx [CO]	NOx [BC]	Obs.	NOx [CO]	NOx [BC]	Obs.	NOx [CO]	NOx [BC]
Concentration (ppb) ± standard deviation														
IH1	Industry Hills	0200-0245		36 ± 4	29 ± 1		22 ± 3	12 ± 1		47 ± 2	24 ± 1		54 ± 8	26 ± 5
CV1	Covina Loop	0300-0345		70 ± 19	68 ± 29		37 ± 16	52 ± 35		64 ± 8	45 ± 12		73 ± 29	30 ± 4
DS1	Dodger Stadium	0415-0500		26 ± 1	22 ± 6		25 ± 4	20 ± 4		21 ± 2	14 ± 14		73 ± 8	28 ± 3
CO1	Compton Loop	0515-0600		122 ± 49	82 ± 48		100 ± 52	81 ± 24		60 ± 24	36 ± 22		111 ± 26	45 ± 11
HF1	Pasadena Fwy	0630-0715		93 ± 41	37 ± 5		58 ± 13	24 ± 7		72 ± 17	23 ± 8		102 ± 11	41 ± 3
DS2	Dodger Stadium	0730-0815		102 ± 64	51 ± 9		56 ± 14	46 ± 10		46 ± 9	15 ± 2		79 ± 15	33 ± 8
CO2	Compton Loop	0830-0915		149 ± 64	191 ± 105		106 ± 42	225 ± 183		102 ± 35	157 ± 88		117 ± 25	71 ± 32
CV2	Covina Loop	0930-1015		98 ± 20	203 ± 96		105 ± 64	160 ± 79		106 ± 27	75 ± 25		120 ± 46	55 ± 21
IH2	Industry Hills	1030-1115		37 ± 1	47 ± 6		28 ± 1	30 ± 3		29 ± 1	18 ± 1		31 ± 7	12 ± 3
PO1	Pomona Loop	1130-1215		104 ± 19	168 ± 86		78 ± 32	201 ± 82		90 ± 27	71 ± 36		98 ± 36	68 ± 34
Percent of sum of NOx[CO] + NOx[BC] ± standard error														
IH1	Industry Hills	0200-0245	9	55 ± 0.9	45 ± 0.9	9	65 ± 0.7	35 ± 0.7	9	66 ± 0.3	34 ± 0.3	9	67 ± 0.8	33 ± 0.8
CV1	Covina Loop	0300-0345	6	52 ± 4.2	48 ± 4.2	6	43 ± 7.6	57 ± 7.6	4	59 ± 3.4	41 ± 3.4	4	70 ± 3.8	30 ± 3.8
DS1	Dodger Stadium	0415-0500	6	54 ± 2.4	46 ± 2.4	10	56 ± 1.6	44 ± 1.6	7	66 ± 5.9	34 ± 5.9	9	72 ± 1.0	28 ± 1.0
CO1	Compton Loop	0515-0600	7	60 ± 5.5	40 ± 5.5	5	52 ± 6.2	48 ± 6.2	8	64 ± 5.6	36 ± 5.6	7	71 ± 2.6	29 ± 2.6
HF1	Pasadena Fwy	0630-0715	10	69 ± 2.2	31 ± 2.2	9	70 ± 2.1	30 ± 2.1	7	76 ± 3.1	24 ± 3.1	4	71 ± 0.6	29 ± 0.6
DS2	Dodger Stadium	0730-0815	6	63 ± 5.3	37 ± 5.3	6	55 ± 4.3	45 ± 4.3	7	74 ± 1.6	26 ± 1.6	9	71 ± 1.6	29 ± 1.6
CO2	Compton Loop	0830-0915	6	47 ± 5.9	53 ± 5.9	5	38 ± 6.3	62 ± 6.3	4	43 ± 10.6	57 ± 10.6	7	63 ± 5.5	37 ± 5.5
CV2	Covina Loop	0930-1015	6	35 ± 3.3	65 ± 3.3	5	40 ± 10.4	60 ± 10.4	8	59 ± 3.9	41 ± 3.9	7	68 ± 4.7	32 ± 4.7
IH2	Industry Hills	1030-1115	7	44 ± 1.2	56 ± 1.2	5	48 ± 1.2	52 ± 1.2	5	62 ± 1.0	38 ± 1.0	7	72 ± 1.1	28 ± 1.1
PO1	Pomona Loop	1130-1215	4	41 ± 7.2	59 ± 7.2	5	30 ± 5.8	70 ± 5.8	7	57 ± 3.4	43 ± 3.4	8	59 ± 2.6	41 ± 2.6

[1] Appportionment derived from the following multiple linear regression equation: [NOx, ppb] = -1.34 + 39.42 * [CO, ppm] + 14.84 * [BC, $\mu g/m^3$].

Table 4.5-2
Weekend/Weekday Differences in Ambient NOx Associated with CO and Black Carbon in the SoCAB

Location	Industry Hills		Azusa		Pico Rivera			
Time Interval	10:00 to 10:45		9:00 to noon		9:00 to noon		**Mean**	
Date	NOx (CO)	NOx (BC)	NOx (CO)	NOx (BC)	NOx (CO)	NOx (BC)	**NOx (CO)**	**NOx (BC)**
Mon, 10/2	37	47	54	56	34	47	**42**	**50**
Wed, 10/4	28	30	26	44	30	33	**28**	**36**
Sat, 10/7	29	18	26	22	25	21	**27**	**20**
Sun, 10/8	31	12	33	19	30	18	**31**	**16**
Ratios								
Sat/Wed	1.01	0.58	1.00	0.50	0.83	0.63	**0.94**	**0.56**
Sun/Mon	0.84	0.25	0.61	0.35	0.88	0.39	**0.75**	**0.33**

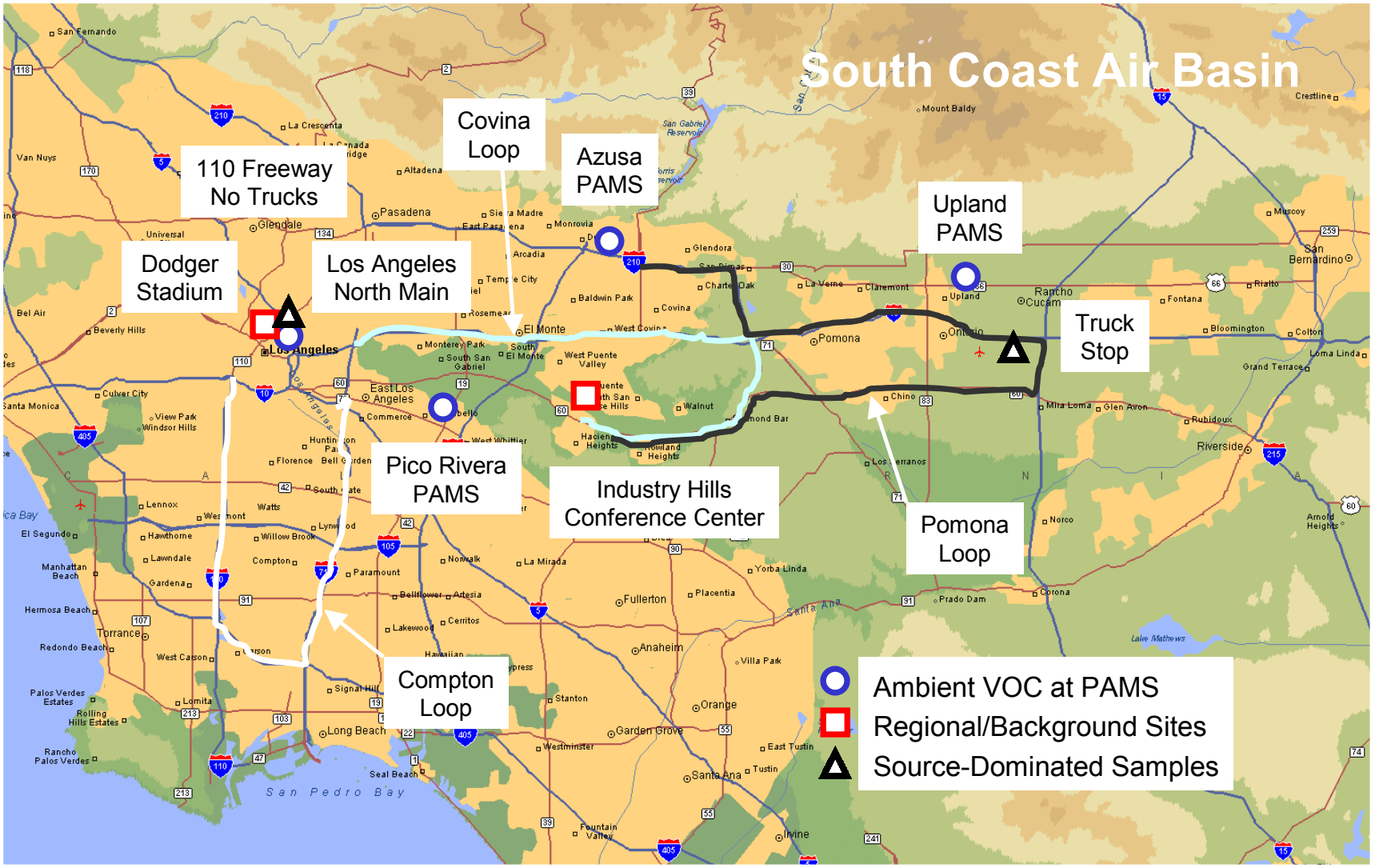


Figure 4.1-1. Map of study area showing the locations of freeway loops and for regional/background and source-dominated samples. Relevant district air monitoring stations are also shown.

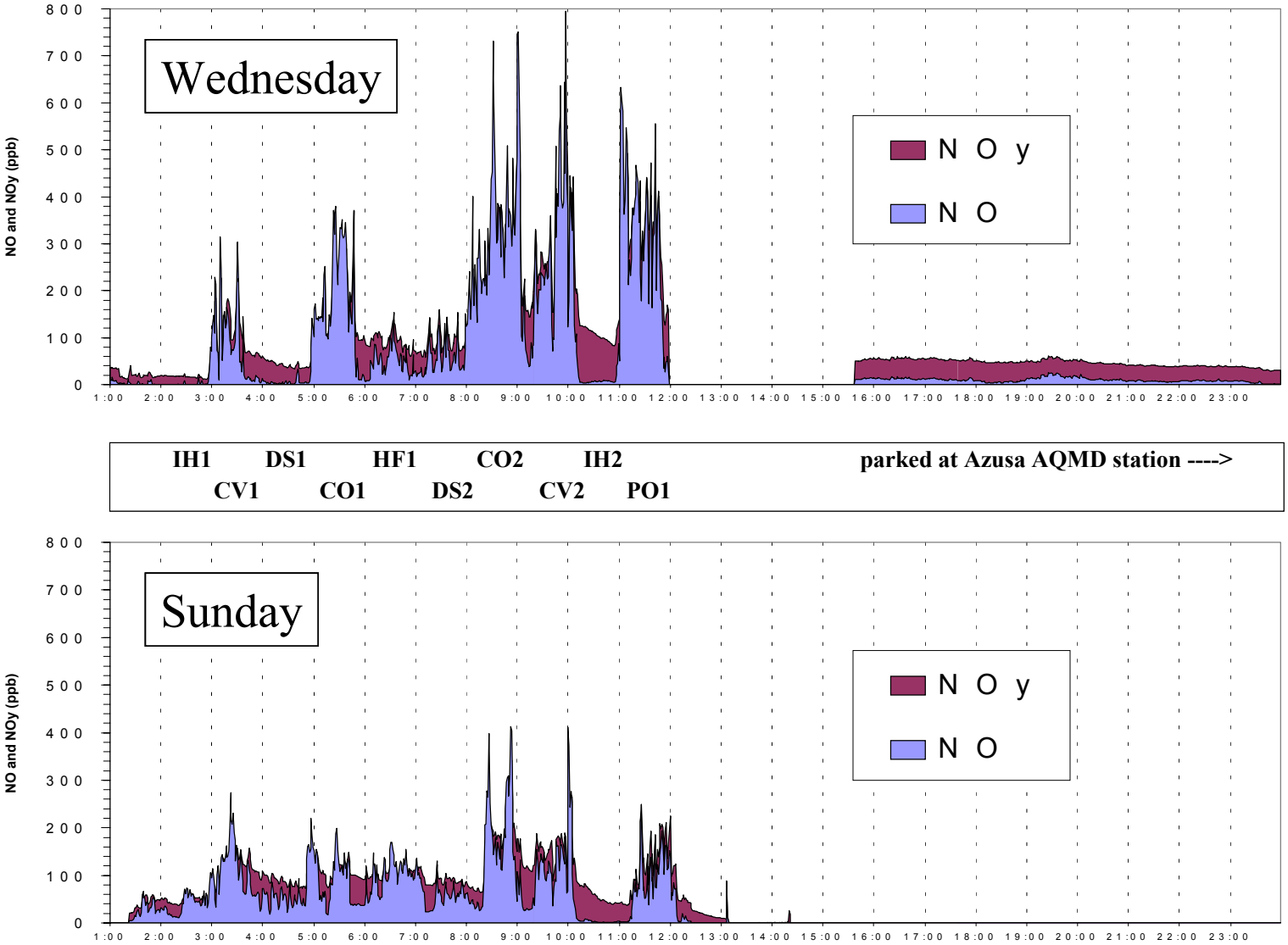
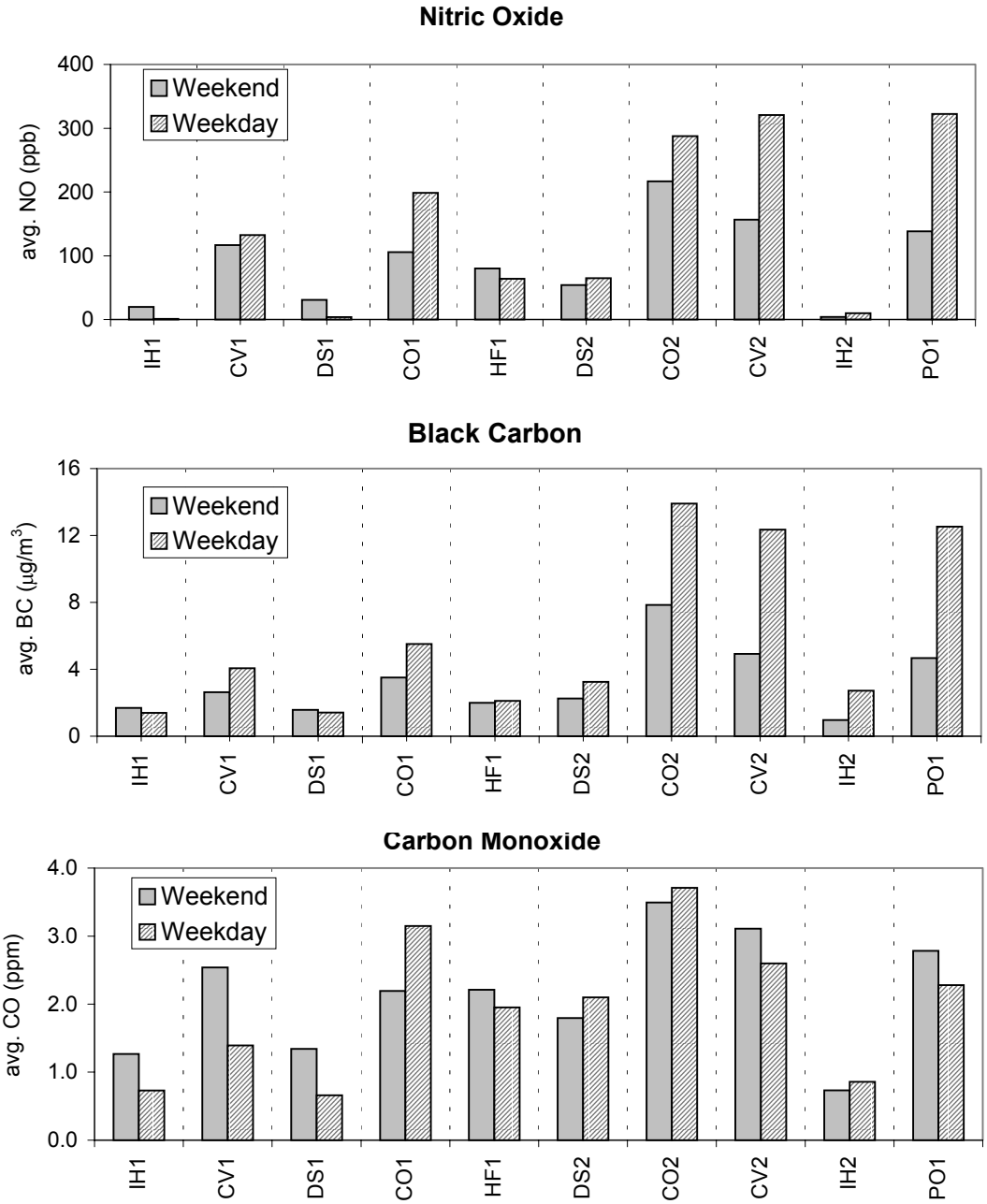


Figure 4.3-1. Continuous measurements of NO and NOy in the mobile sampling van on Wednesday, October 4, 2000 (top) and Sunday, October 8, 2000 (bottom)



Location	start time	Name	Location	start time	Name
IH1	2:00	Industry Hills 1	DS2	7:00	Dodger Stadium 2
CV1	3:00	Covina 1	CO2	8:00	Compton 2
DS1	4:00	Dodger Stadium 1	CV2	9:00	Covina 2
CO1	5:00	Compton 1	IH2	10:00	Industry Hills 2
HF1	6:00	Harbor Freeway (cars only)	PO1	11:00	Pomona

Figure 4.3-2. Average NO, black carbon, and CO concentrations for each of the freeway loops and regional/background sites for two weekend days (Saturday, October 7, 2000 and Sunday, October 8, 2000) and two weekdays (Monday, October 2, 2000 and Wednesday, October 4, 2000).

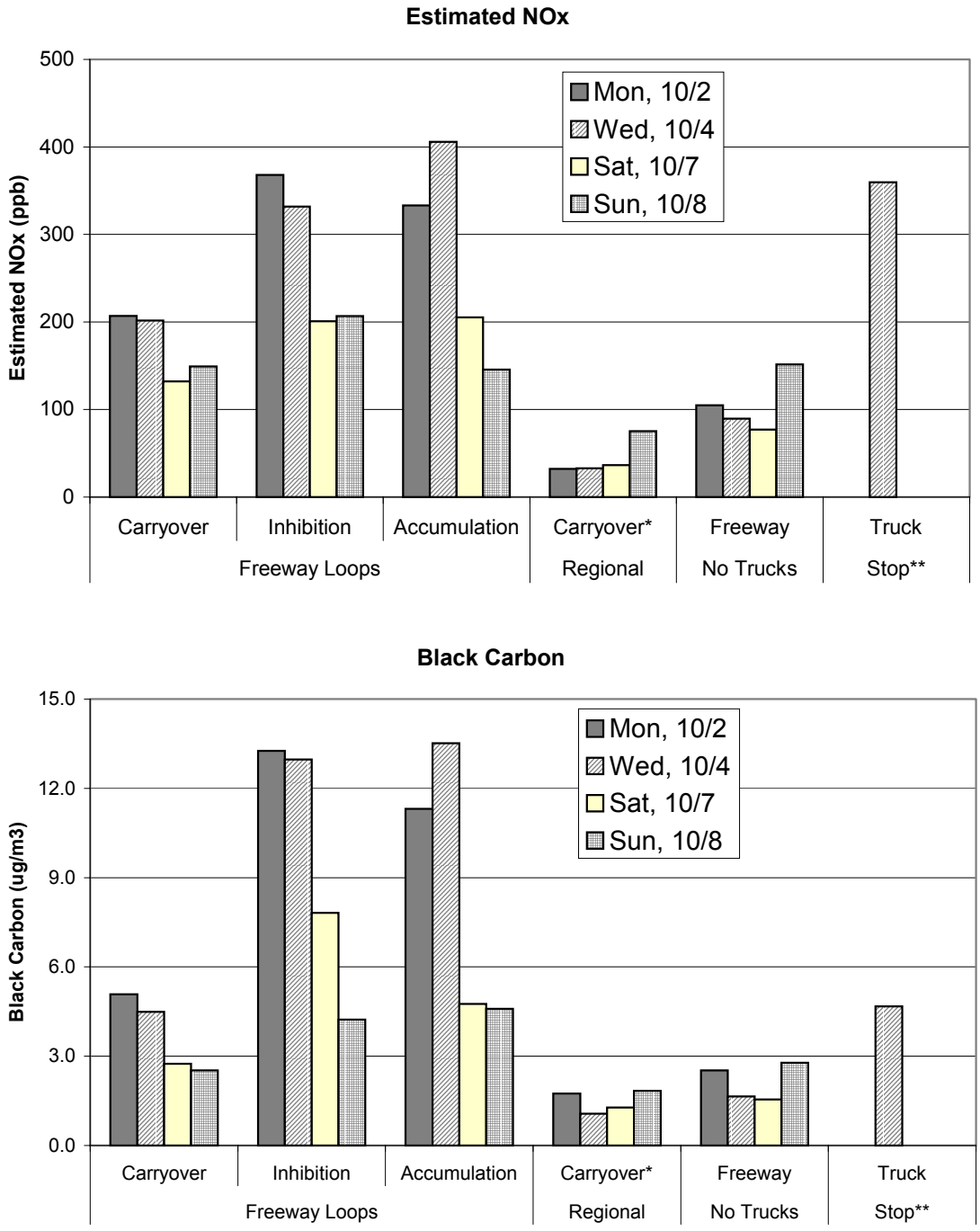


Figure 4.3-3a. Average NOy and black carbon on freeway loops during carryover, ozone inhibition, and ozone accumulation periods compared to regional sites and source-dominated samples.

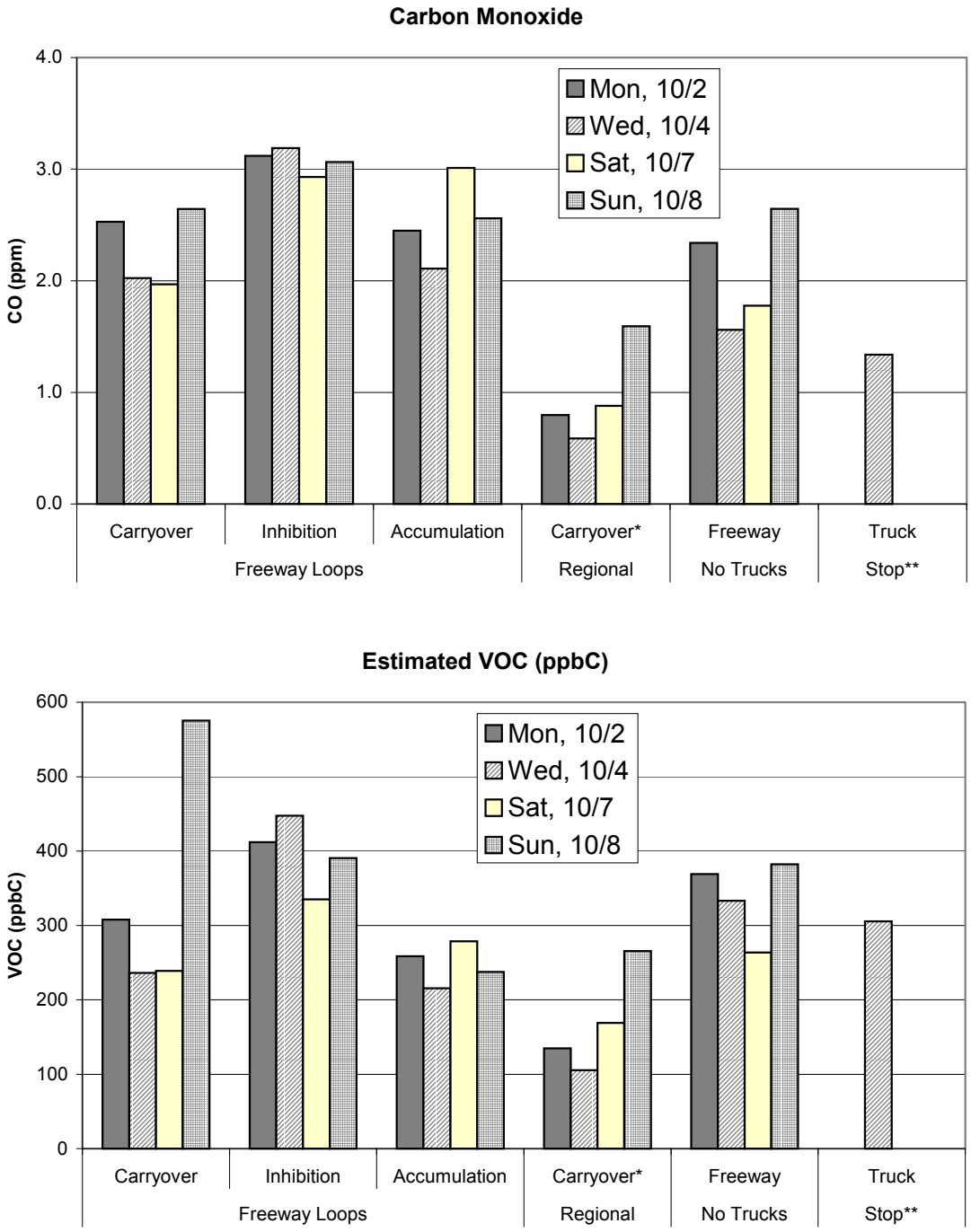


Figure 4.3-3b. Average carbon monoxide and volatile organic compounds on freeway loops during carryover, ozone inhibition, and ozone accumulation periods compared to regional sites and source-dominated samples.

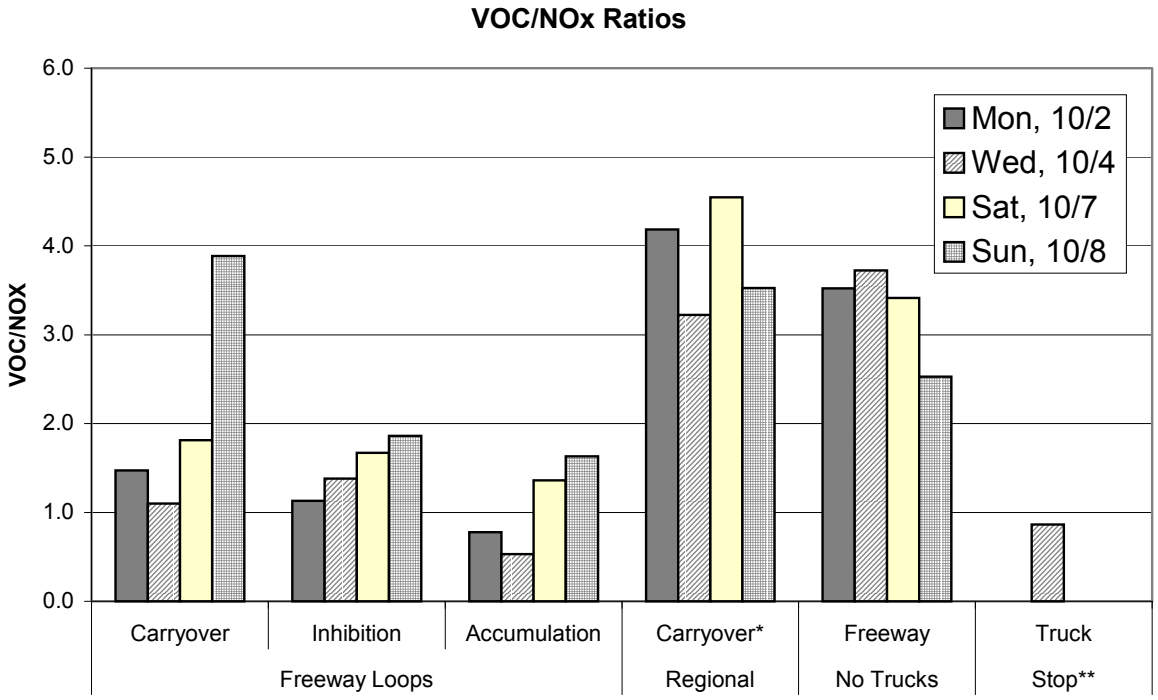


Figure 4.3-4. Average VOC/NOy ratios on freeway loops during carryover, ozone inhibition, and ozone accumulation periods compared to regional sites and source-dominated samples.

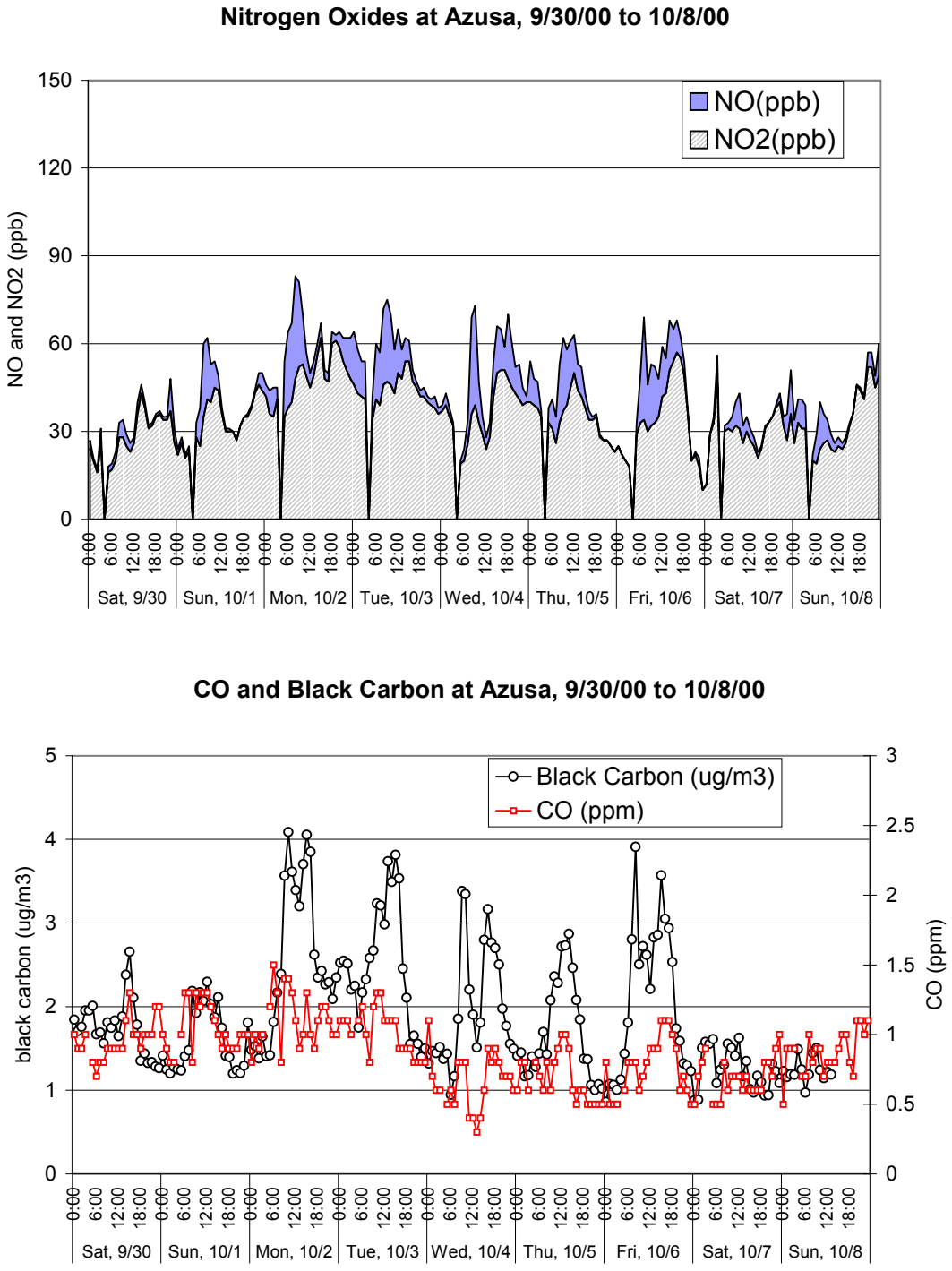


Figure 4.3-5a. Hourly average Nitrogen Oxides, CO, and black carbon at Azusa September 30-October 8, 2000.

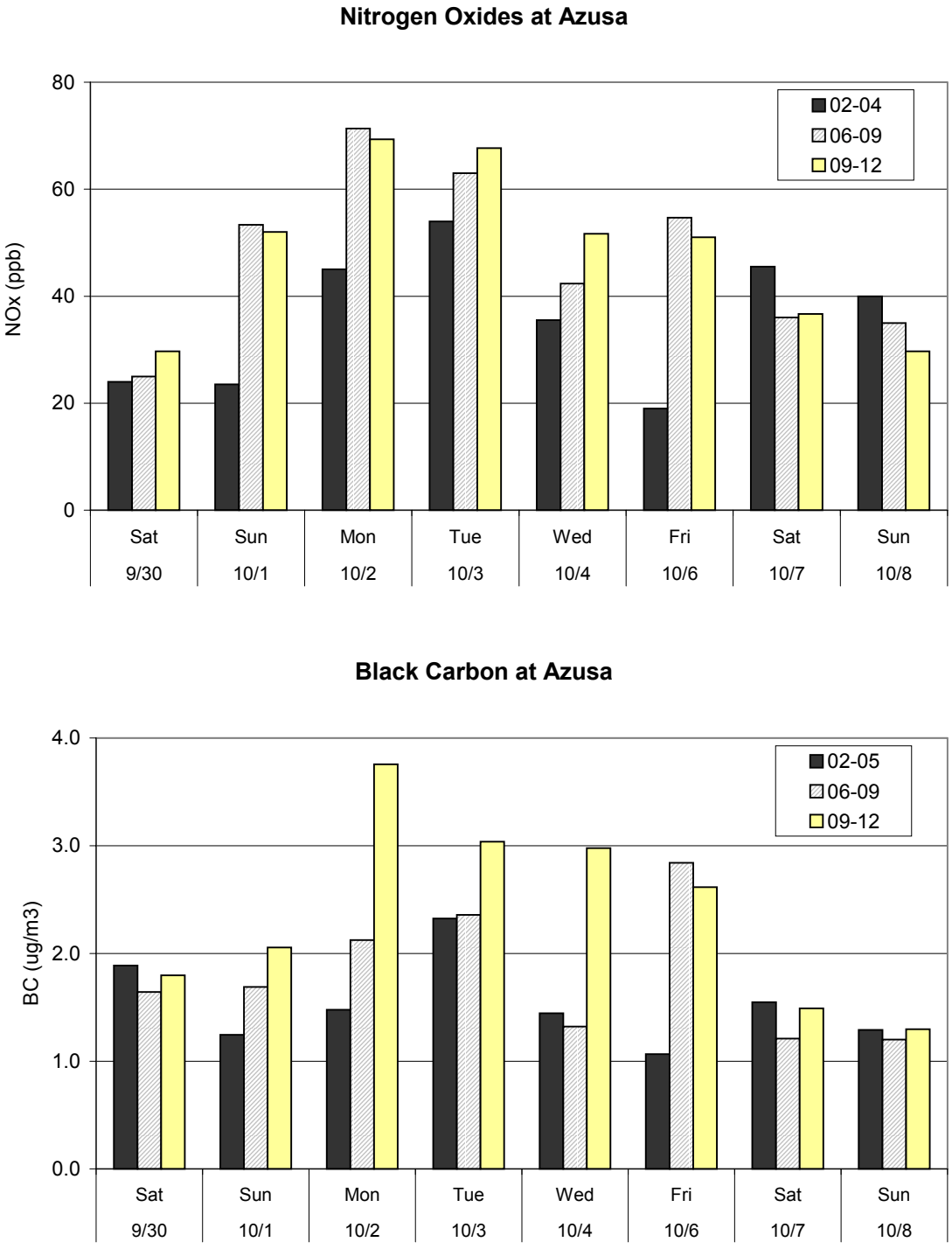


Figure 4.3-5b. Average nitrogen oxides and black carbon at Azusa during carryover, accumulation, and inhibition periods September 30-October 8, 2000.

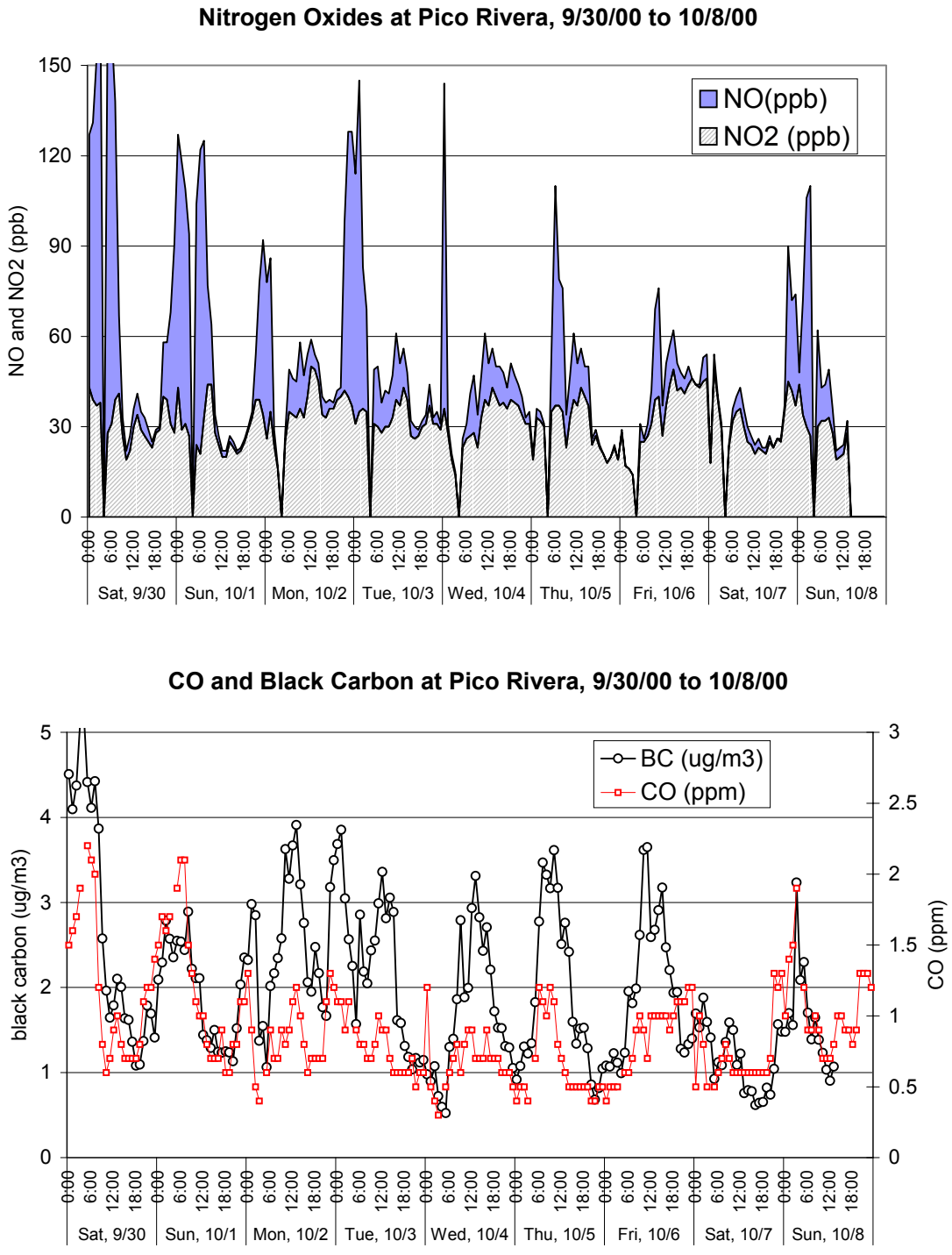


Figure 4.3-6a. Hourly average nitrogen oxides, CO, and black carbon at Pico Rivera September 30-October 8, 2000.

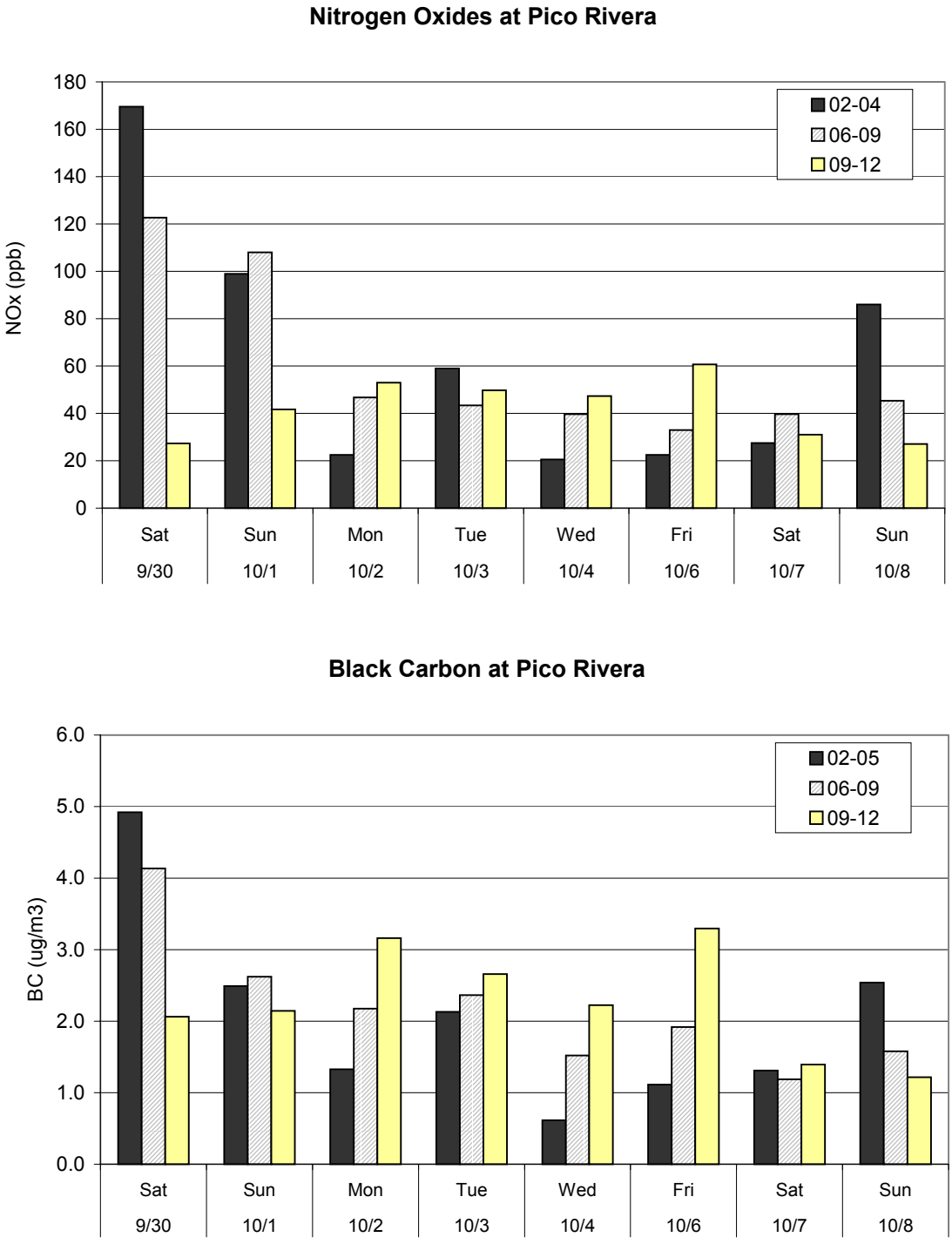


Figure 4.3-6b. Average nitrogen oxides and black carbon at Pico Rivera during carryover, accumulation, and inhibition periods September 30-October 8, 2000.

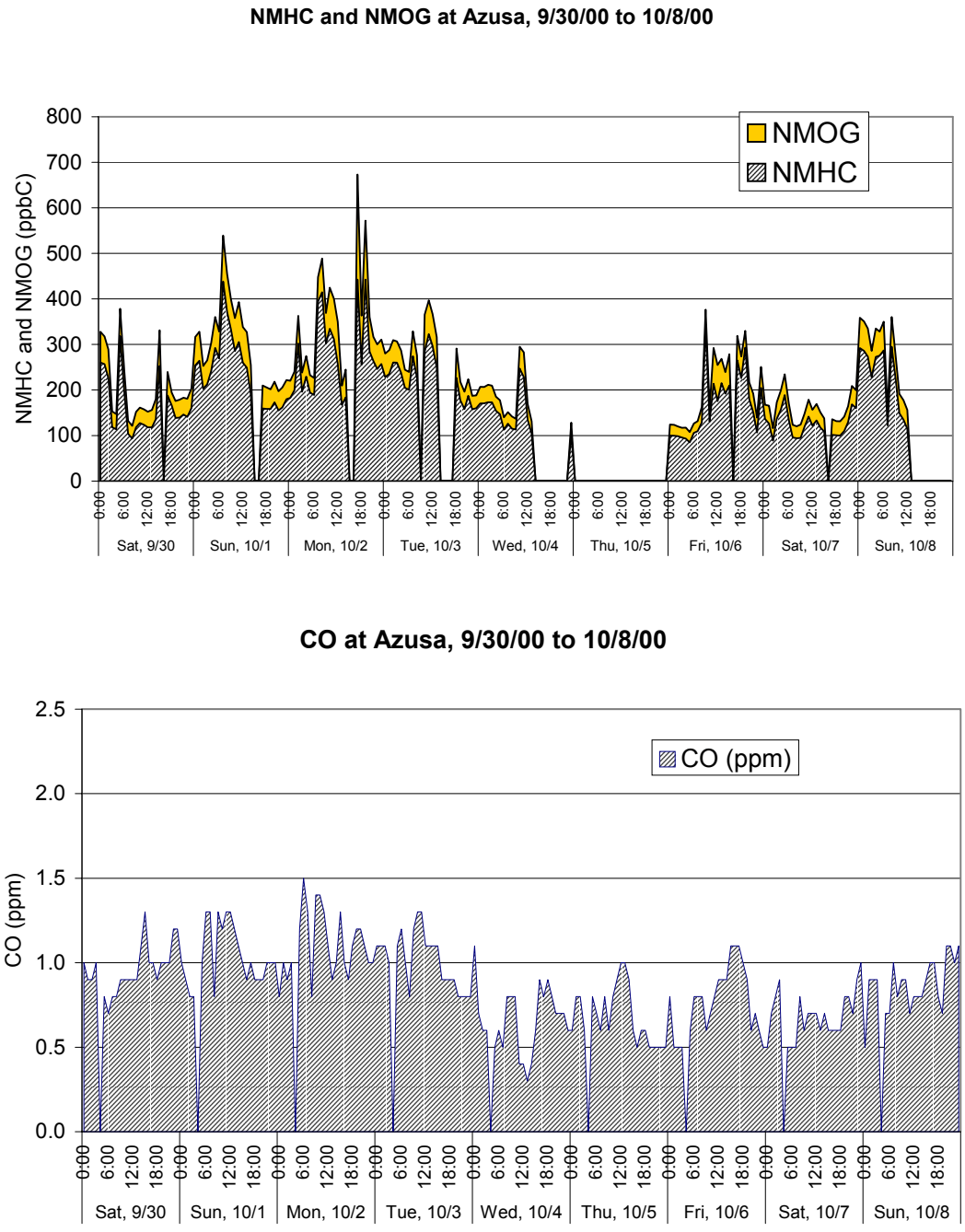


Figure 4.3-7a. Diurnal variations in CO, nonmethane hydrocarbons, and nonmethane organic gases at Azusa September 30-October 8, 2000.

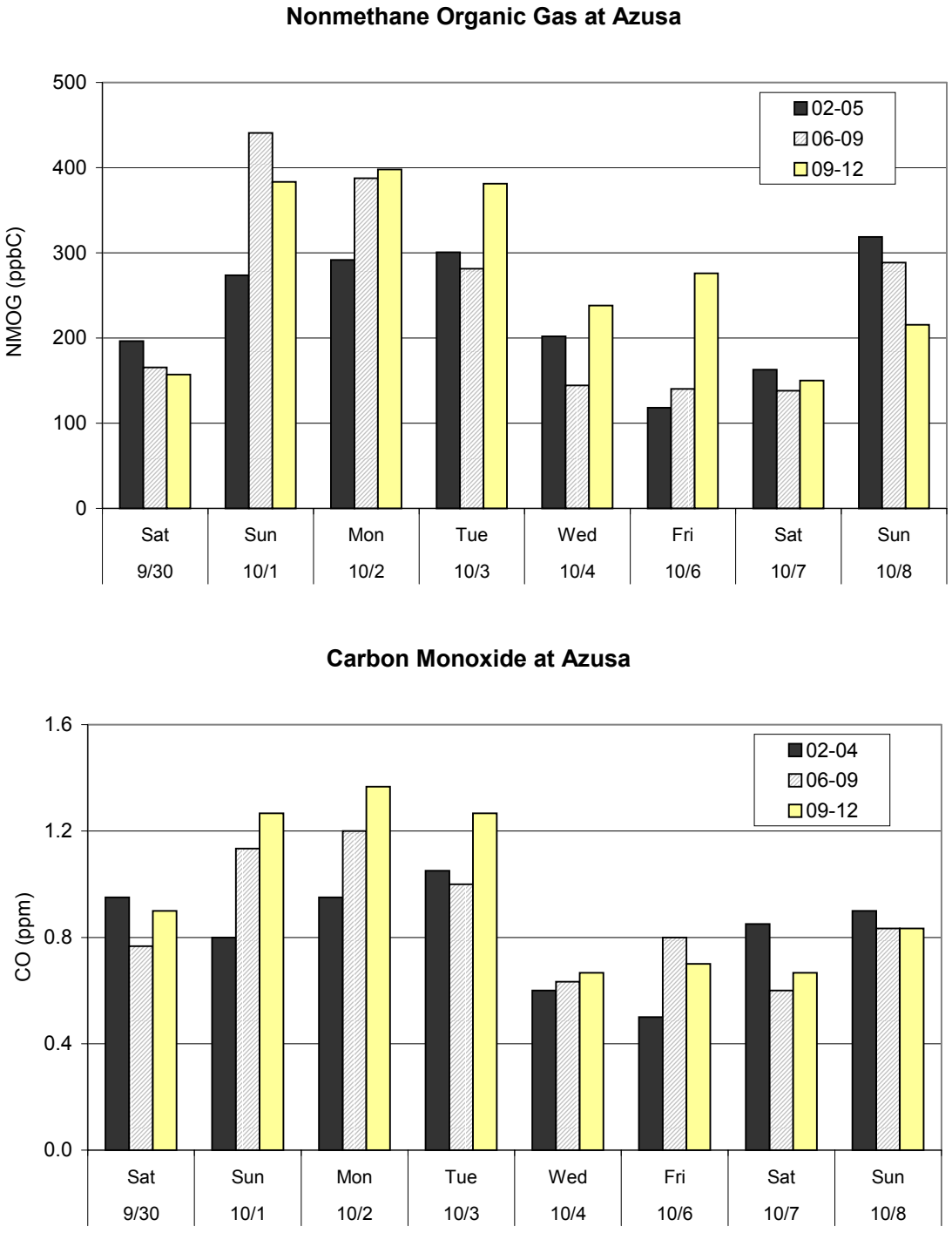


Figure 4.3-7b. Day-to-day variations in CO and nonmethane organic gases at Azusa during carryover, accumulation, and inhibition periods September 30-October 8, 2000.

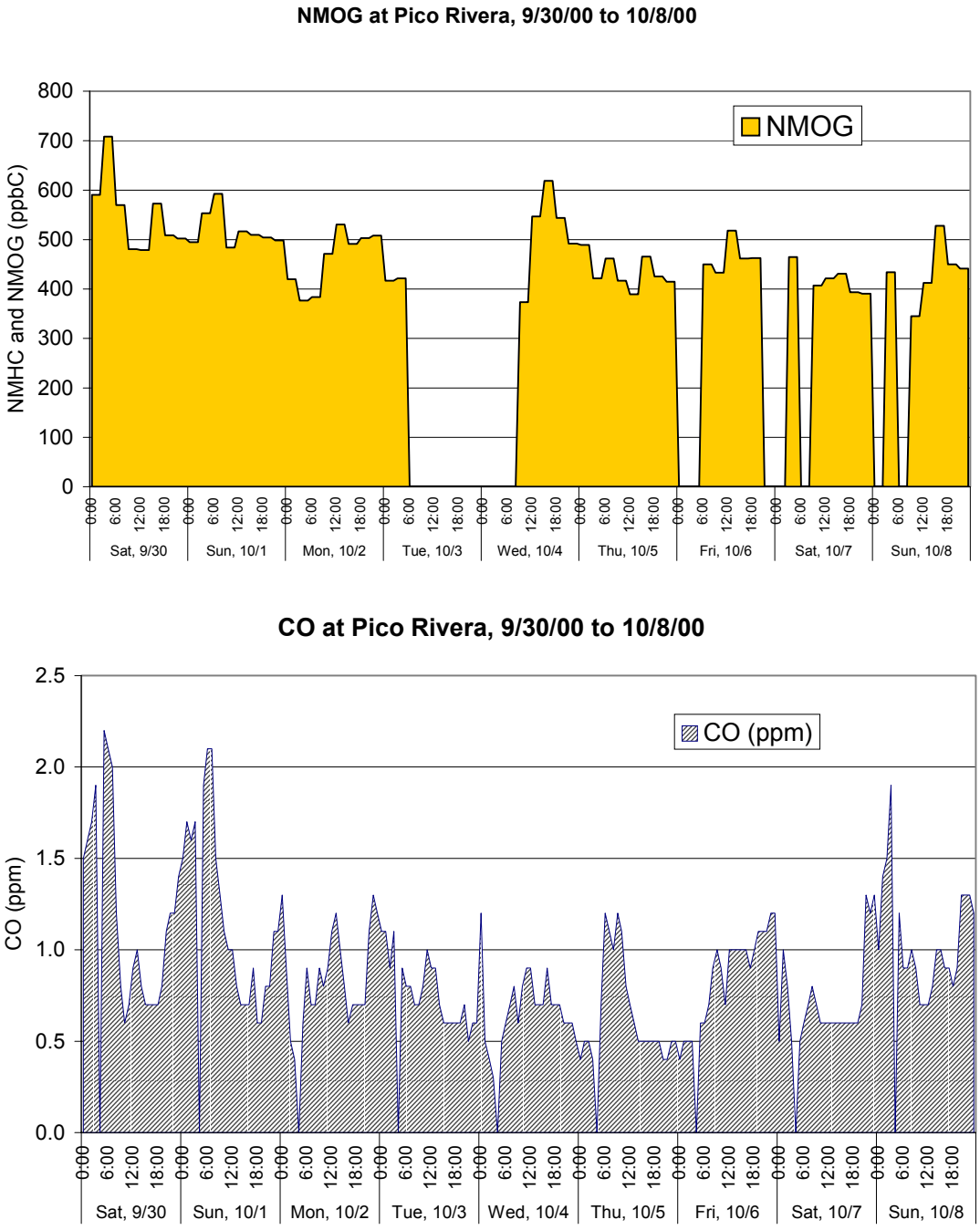


Figure 4.3-8a. Diurnal variations in CO, and nonmethane organic gases at Pico Rivera 9/30/00 – 10/8/00.

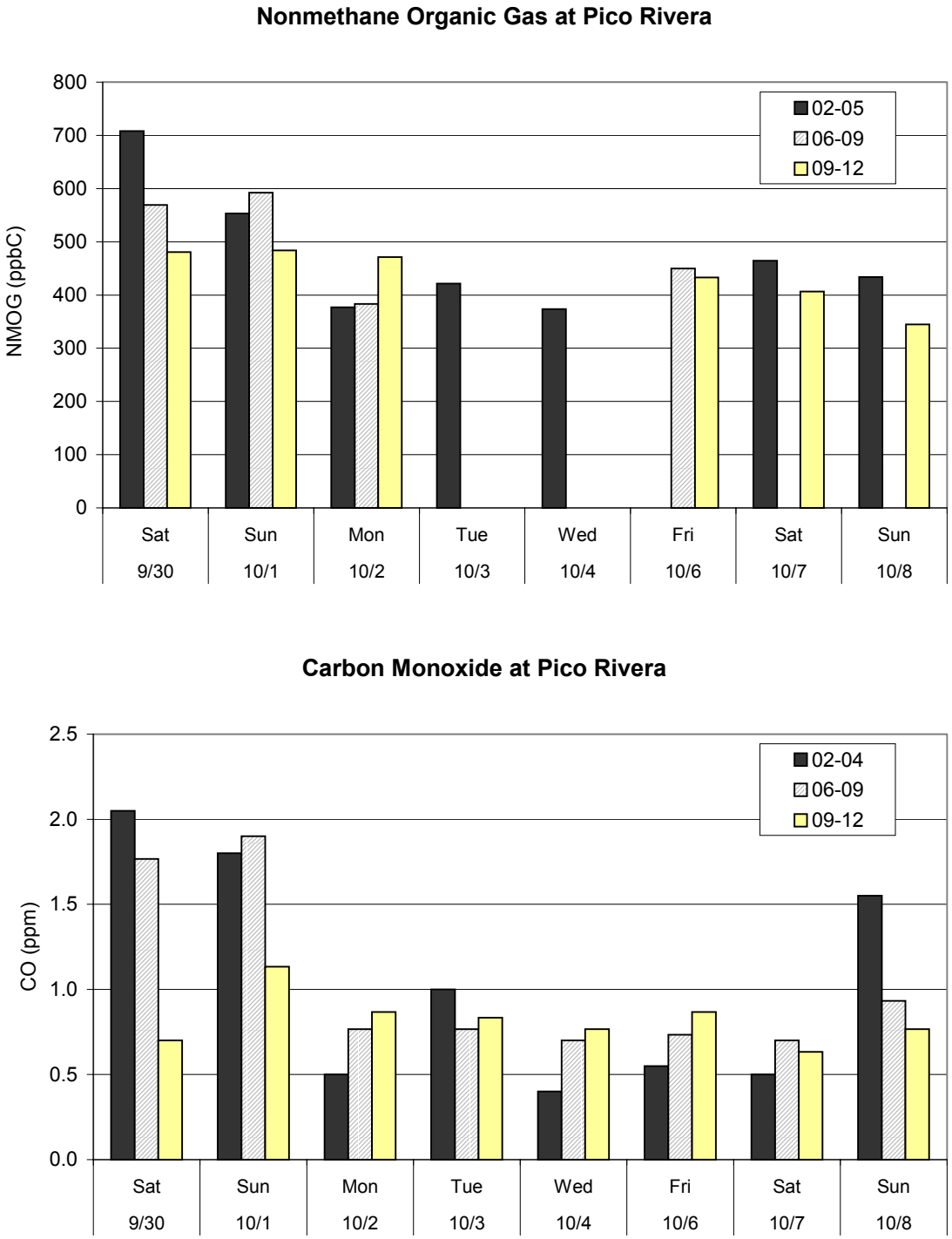


Figure 4.3-8b. Day-to-day variations in CO and nonmethane organic gases at Pico Rivera during carryover, accumulation, and inhibition periods September 30-October 8, 2000.

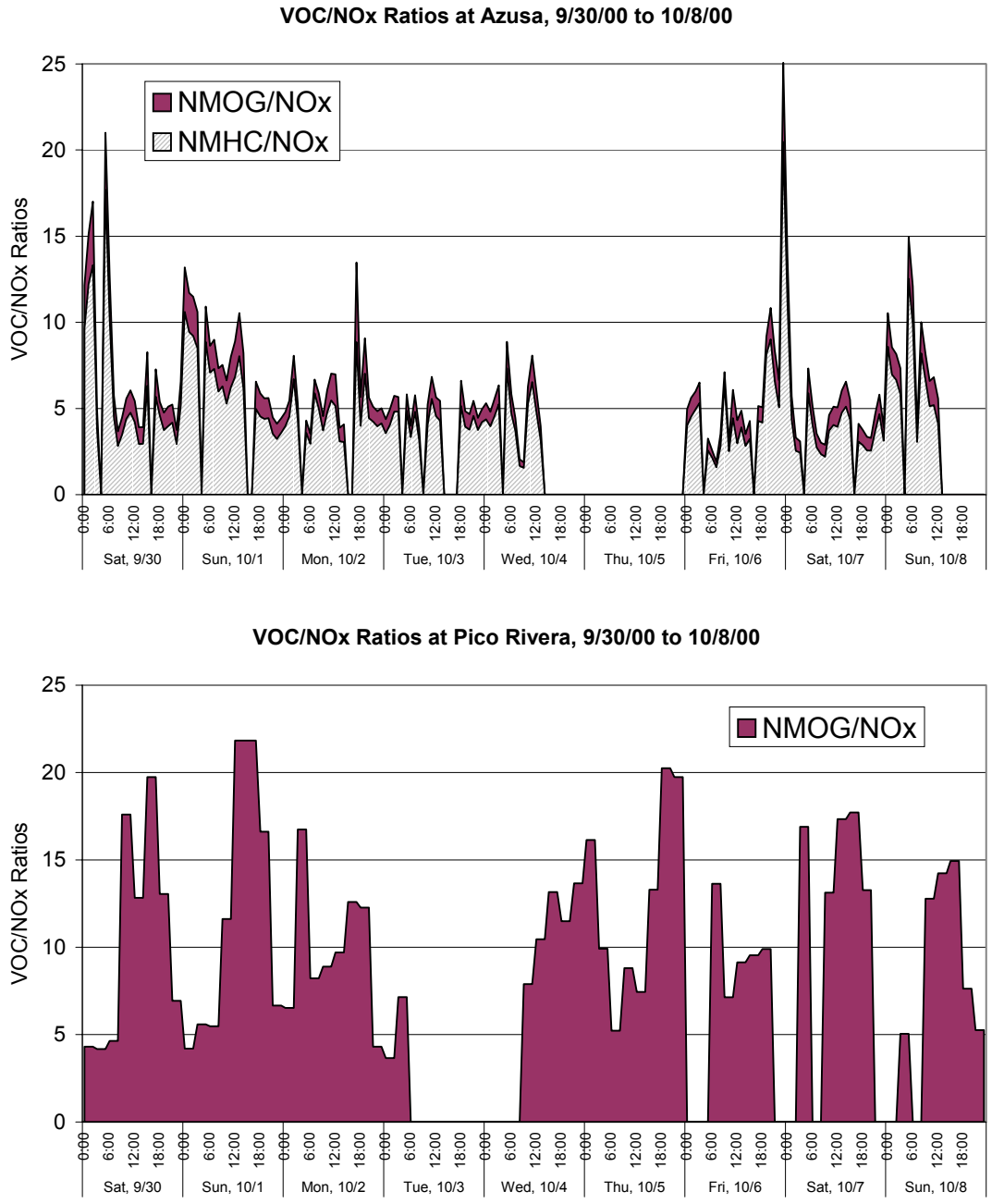


Figure 4.3-9a. . VOC/NOx ratios at Azusa and Pico Rivera September 30-October 8, 2000.

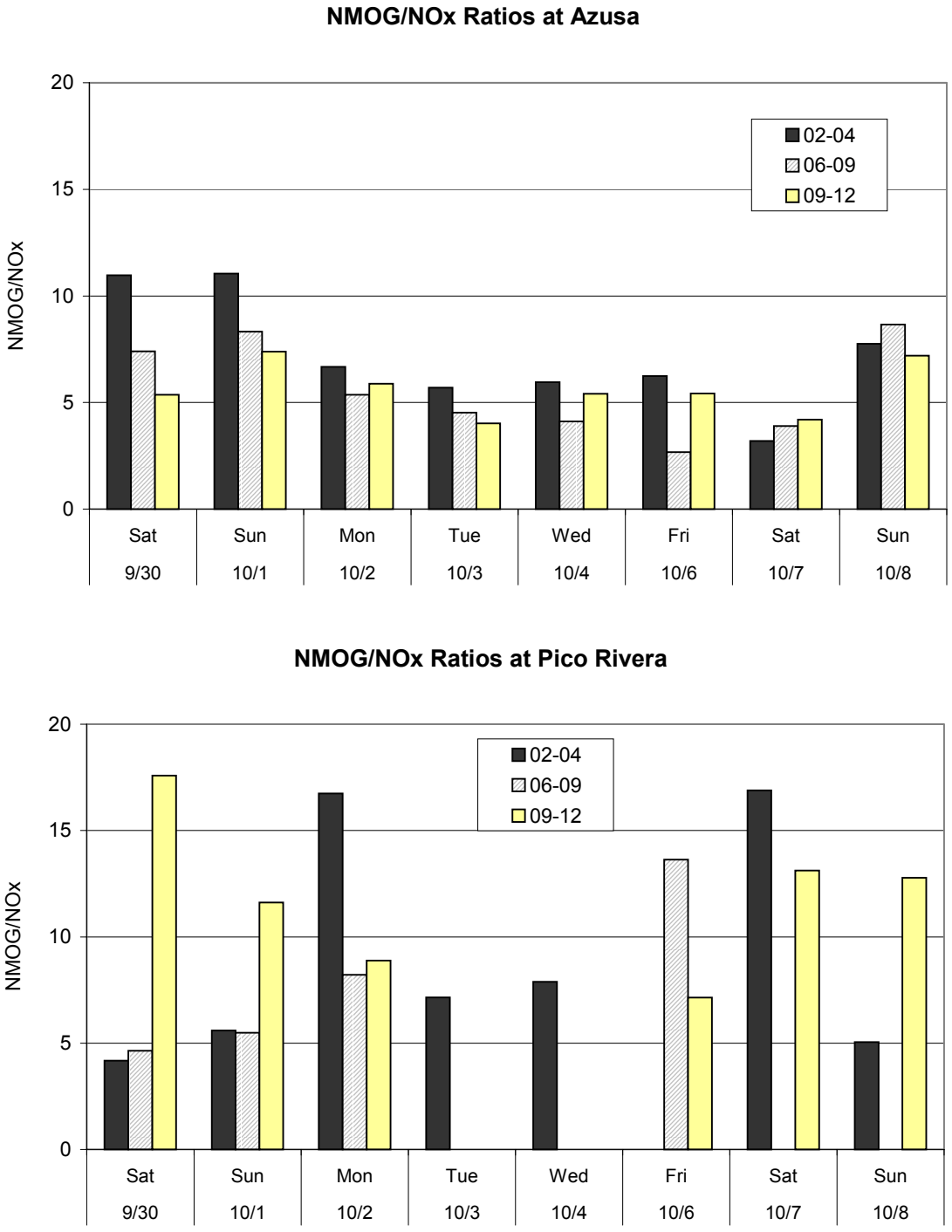


Figure 4.3-9b. Average VOC/NOx ratios at Azusa and Pico Rivera during carryover, accumulation, and inhibition periods September 30-October 8, 2000.

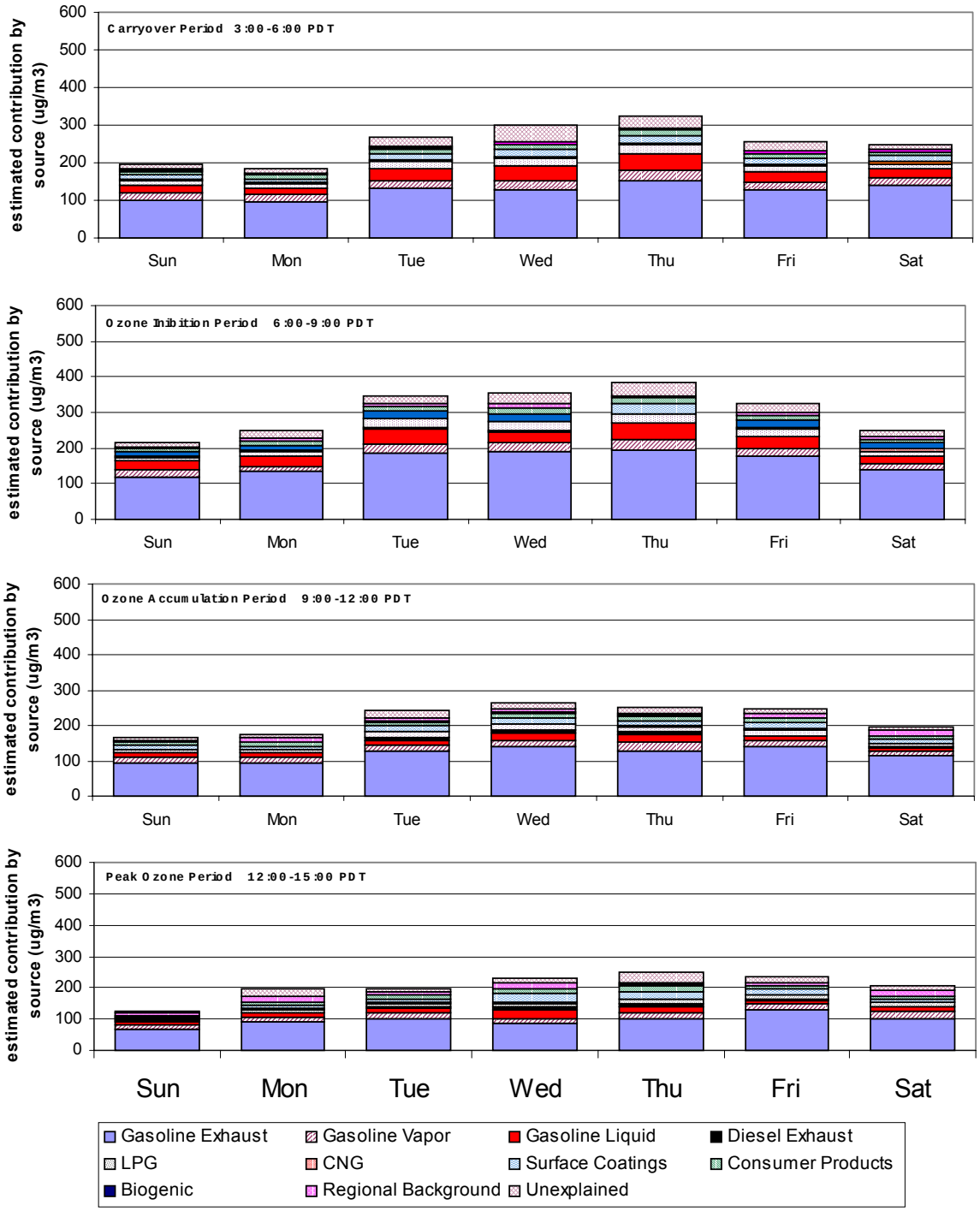


Figure 4.4-1a. Mean estimated source contributions by day-of-week at Azusa for summers 1999 and 2000.

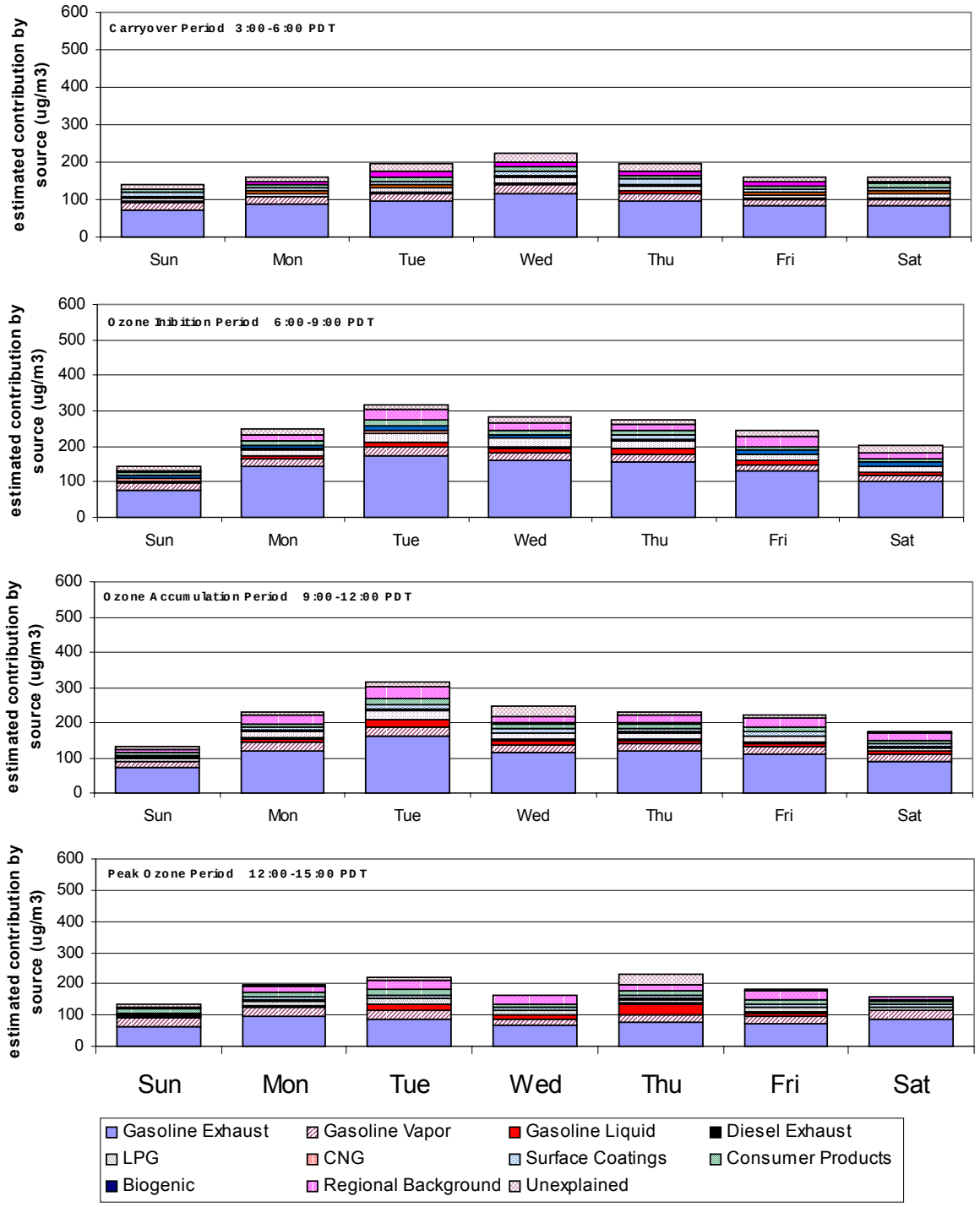


Figure 4.4-1b. Mean estimated source contributions by day-of-week at Pico Rivera for summer 1999.

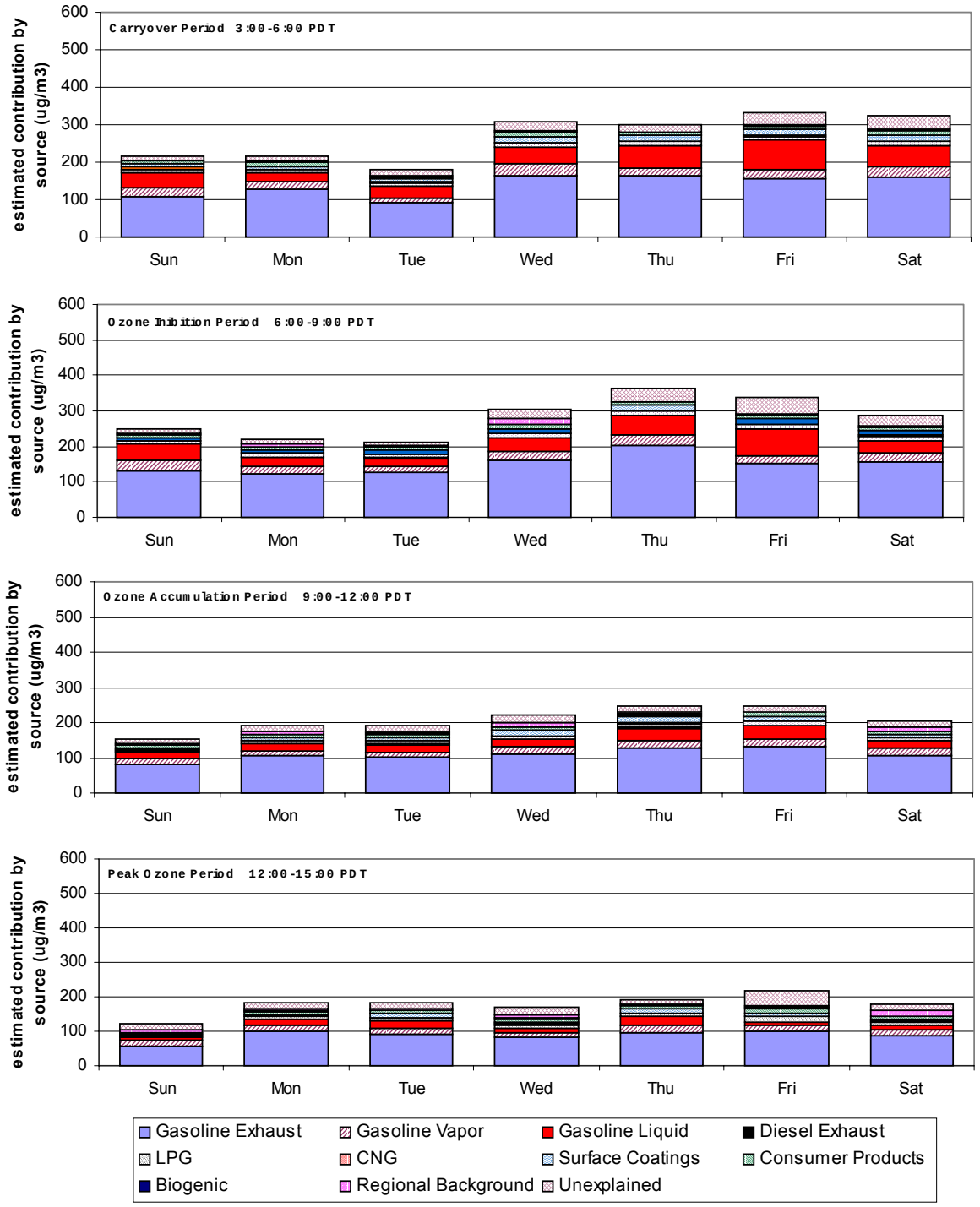


Figure 4.4-1c. Mean estimated source contributions by day-of-week at Upland for summers 1999 and 2000.

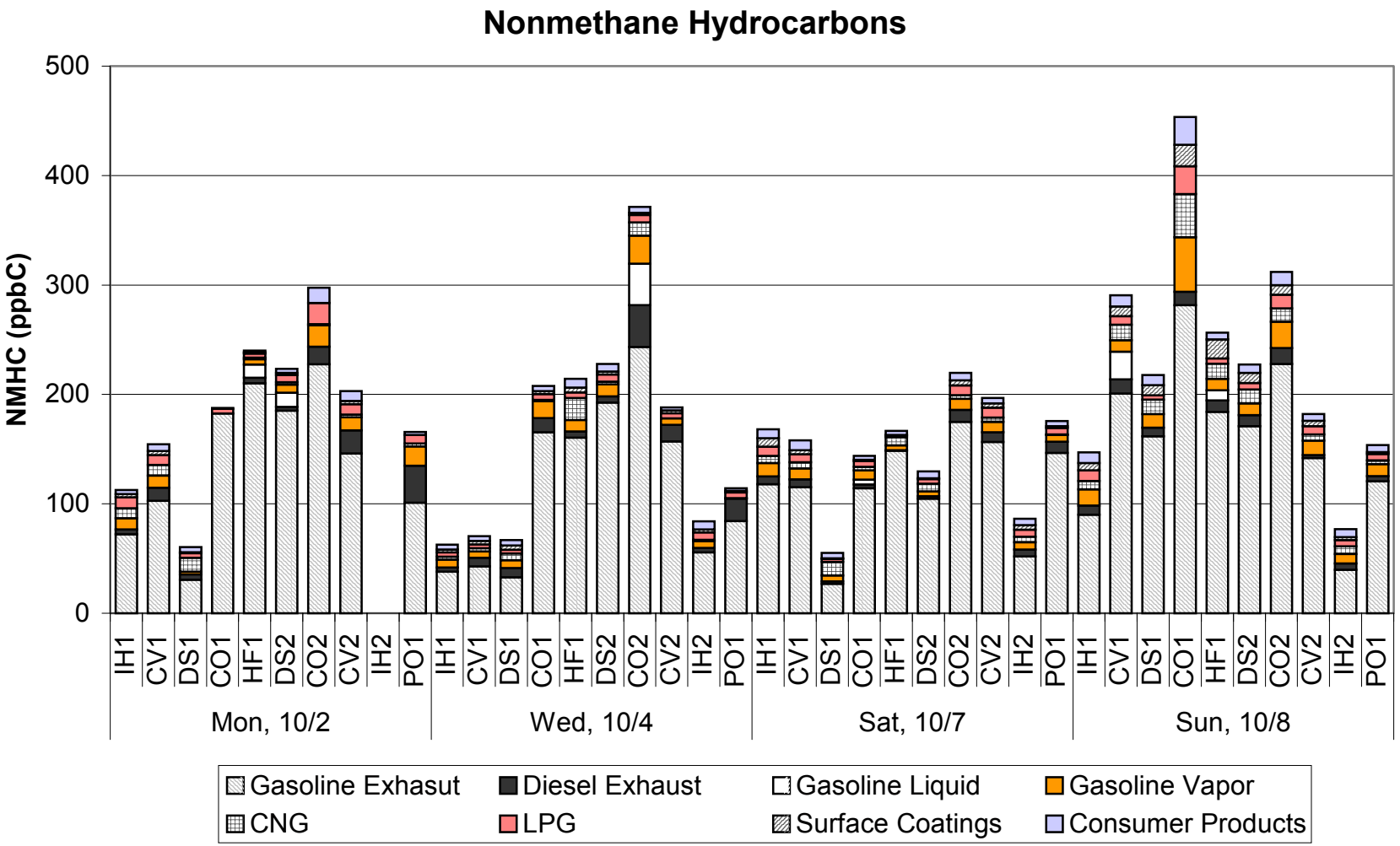


Figure 4.4-2. Source apportionment of non-methane hydrocarbons for mobile sampling loops and regional background sites – absolute contributions.

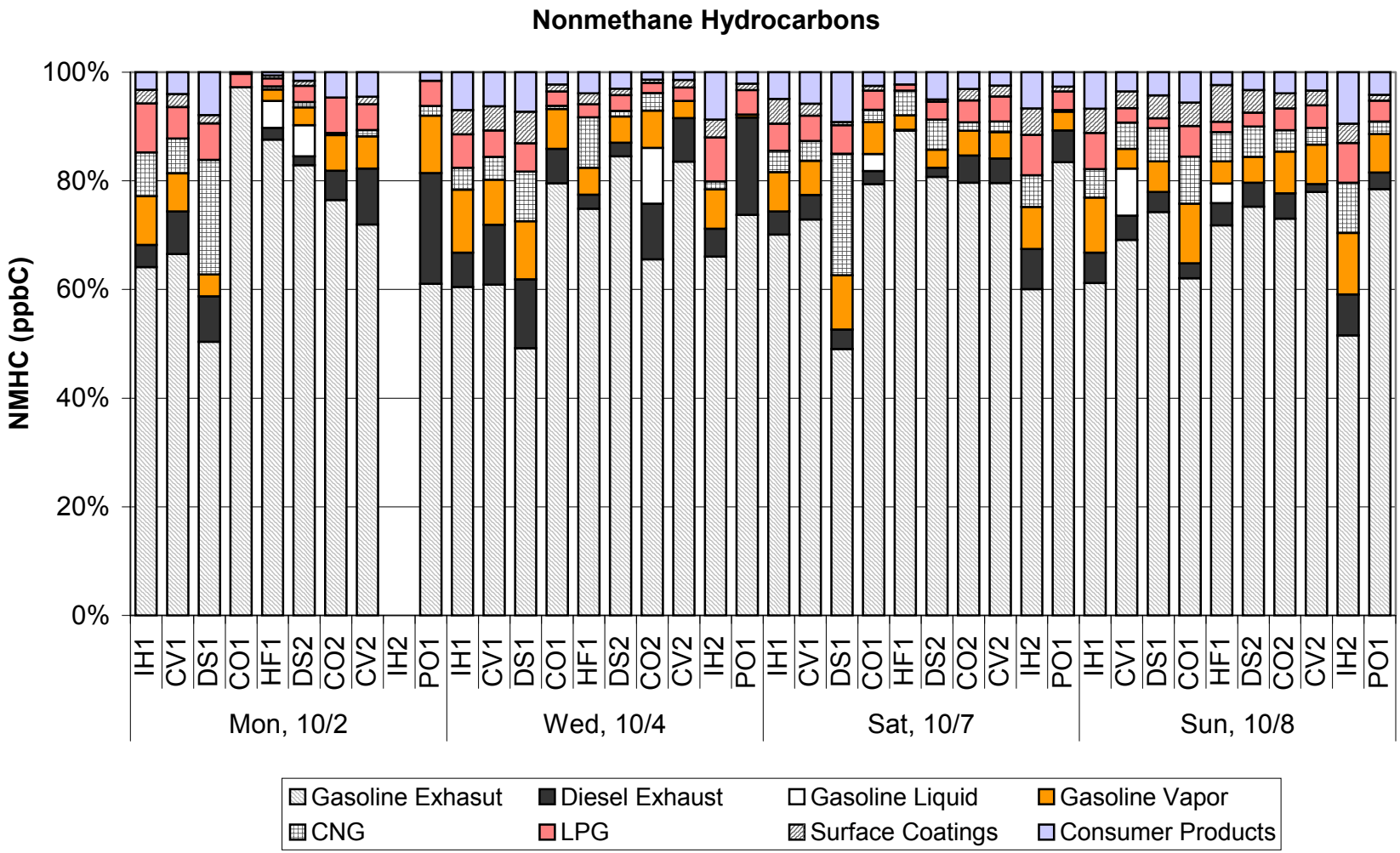


Figure 4.4-3. Source apportionment of non-methane hydrocarbons for mobile sampling loops and regional background sites – percent contributions.

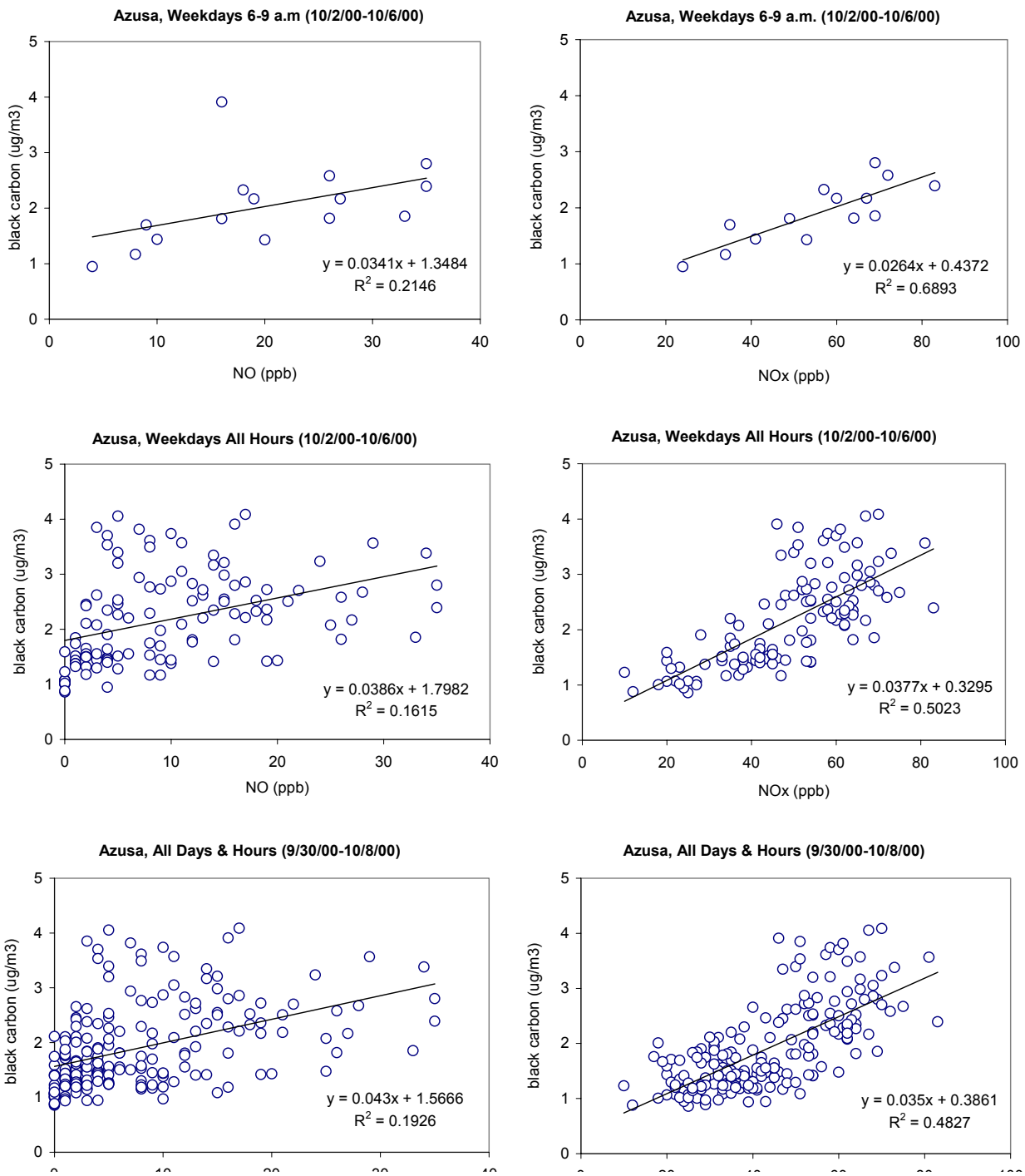


Figure 4.5-1a. Correlations of NO and NOx to black carbon at Azusa for different sets of weekdays and hours of the day.

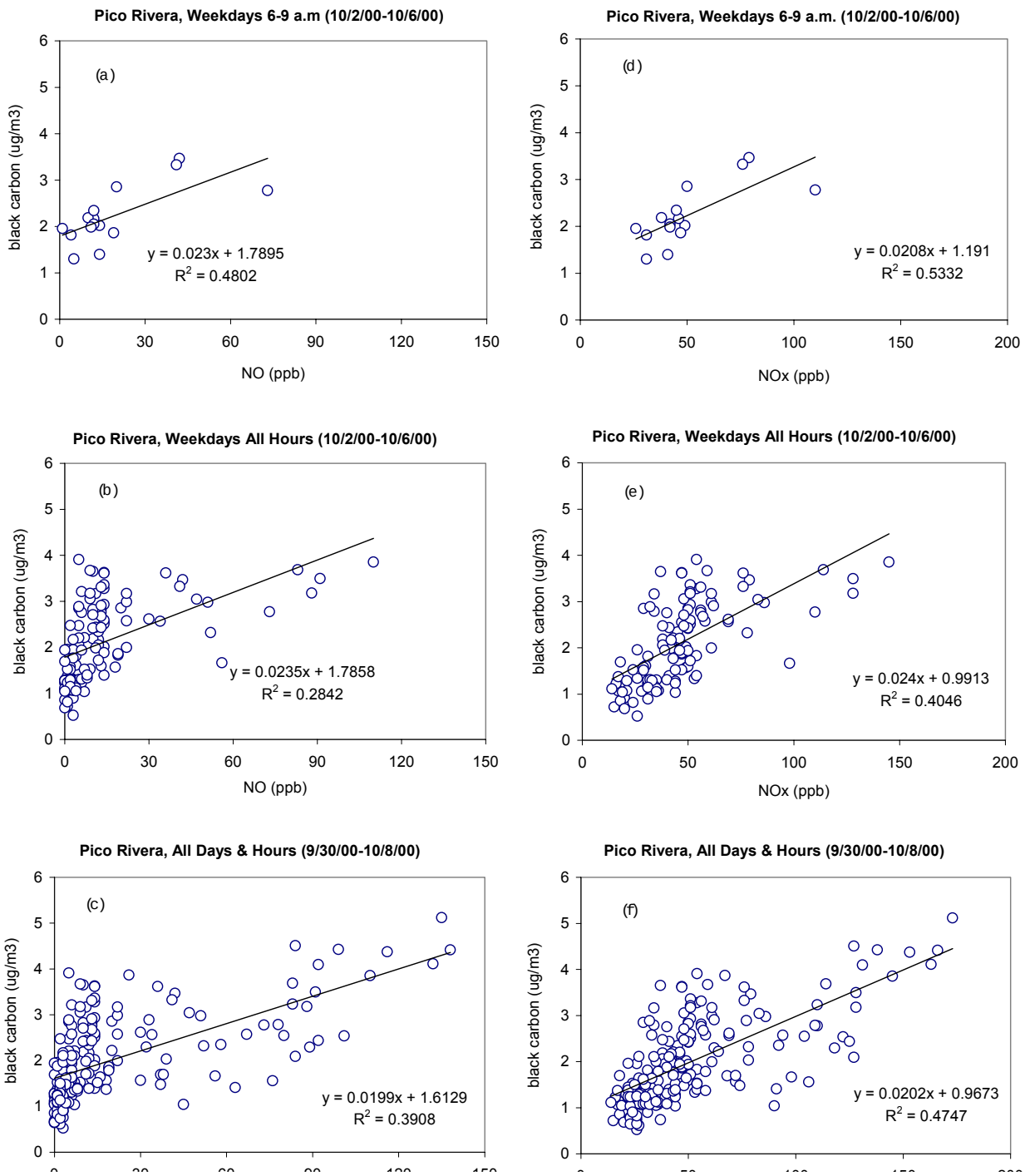


Figure 4.5-1b. Correlations of NO and NOx to black carbon at Pico Rivera for different sets of weekdays and hours of the day.

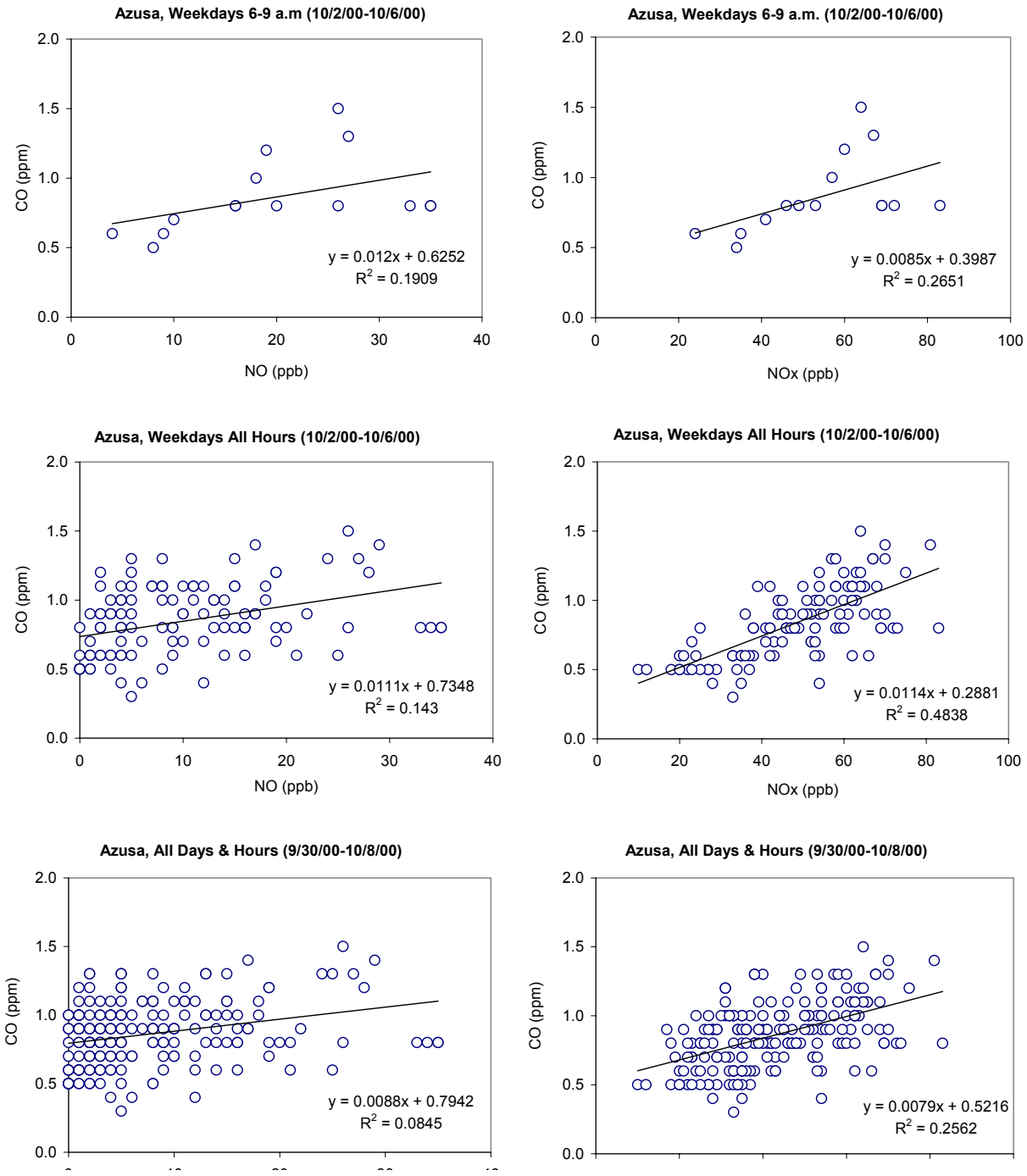


Figure 4.5-2a. Correlations of NO and NOx to CO at Azusa for different sets of weekdays and hours of the day.

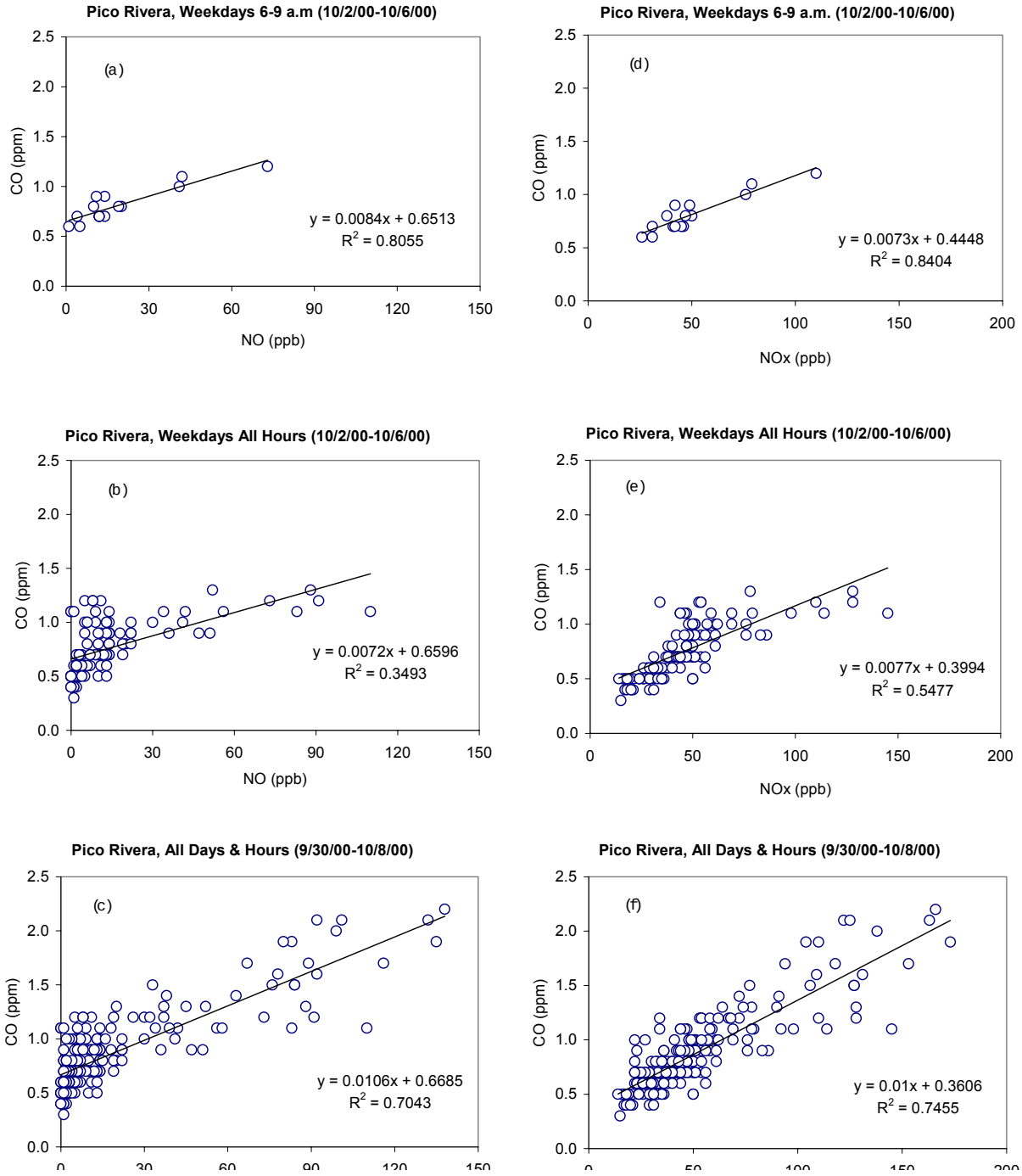
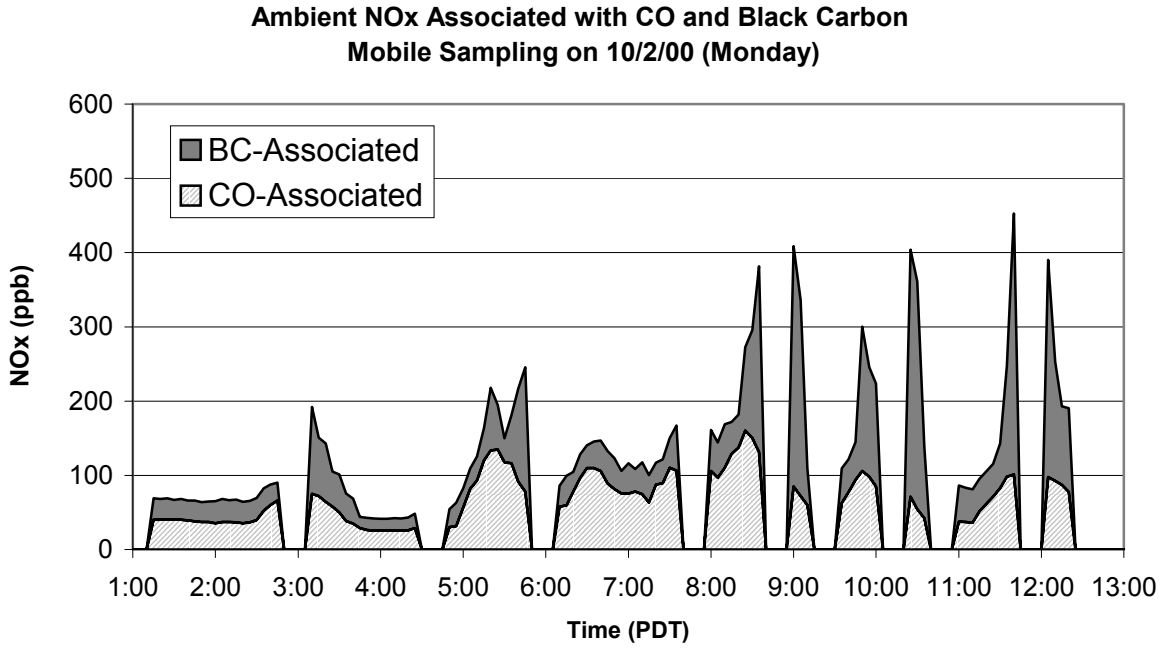


Figure 4.5-2b. . Correlations of NO and NOx to CO at Pico Rivera for different sets of weekdays and hours of the day.



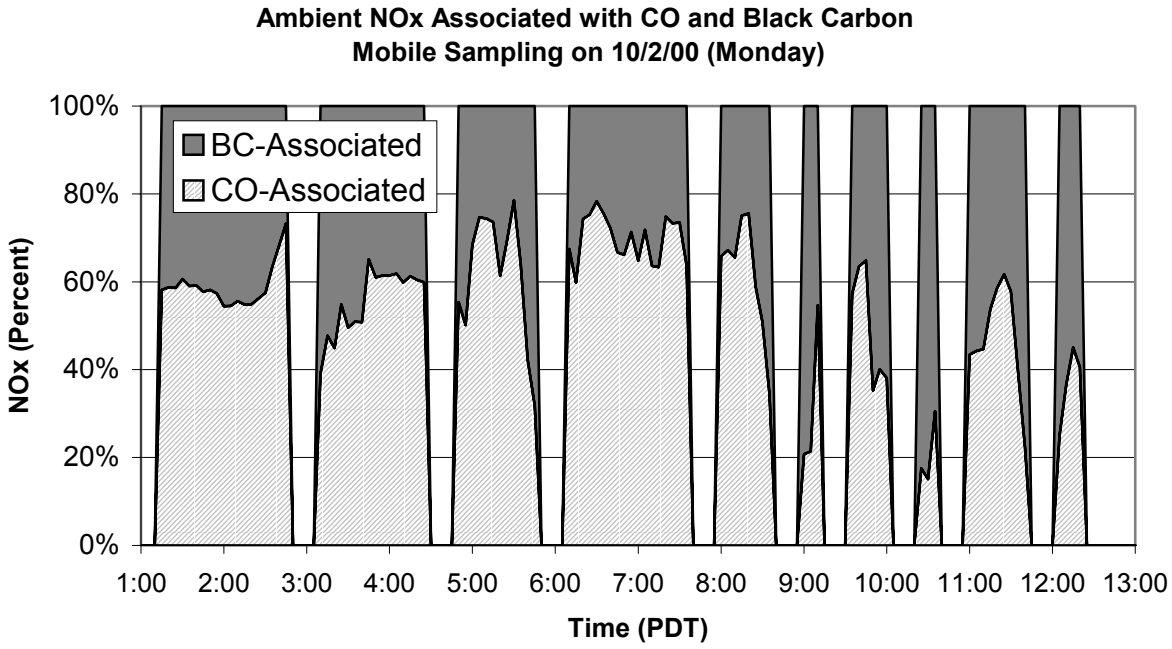
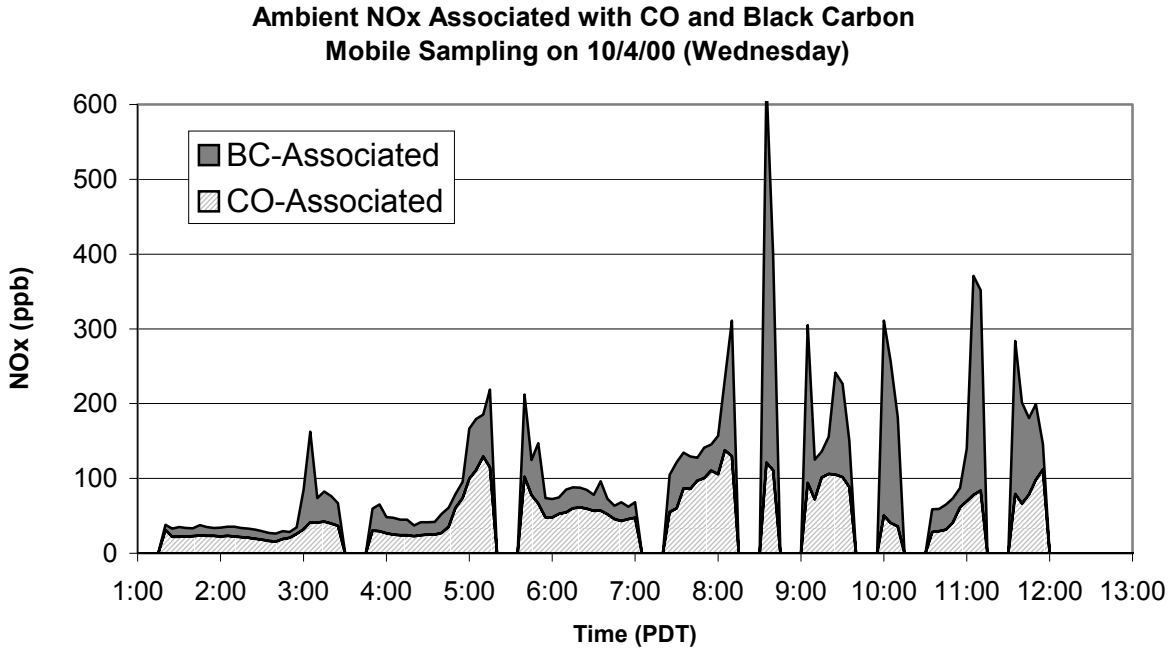


Figure 4.5-3a. Estimated ambient NOx associated with CO and black carbon for mobile lab samples Monday, October 2.



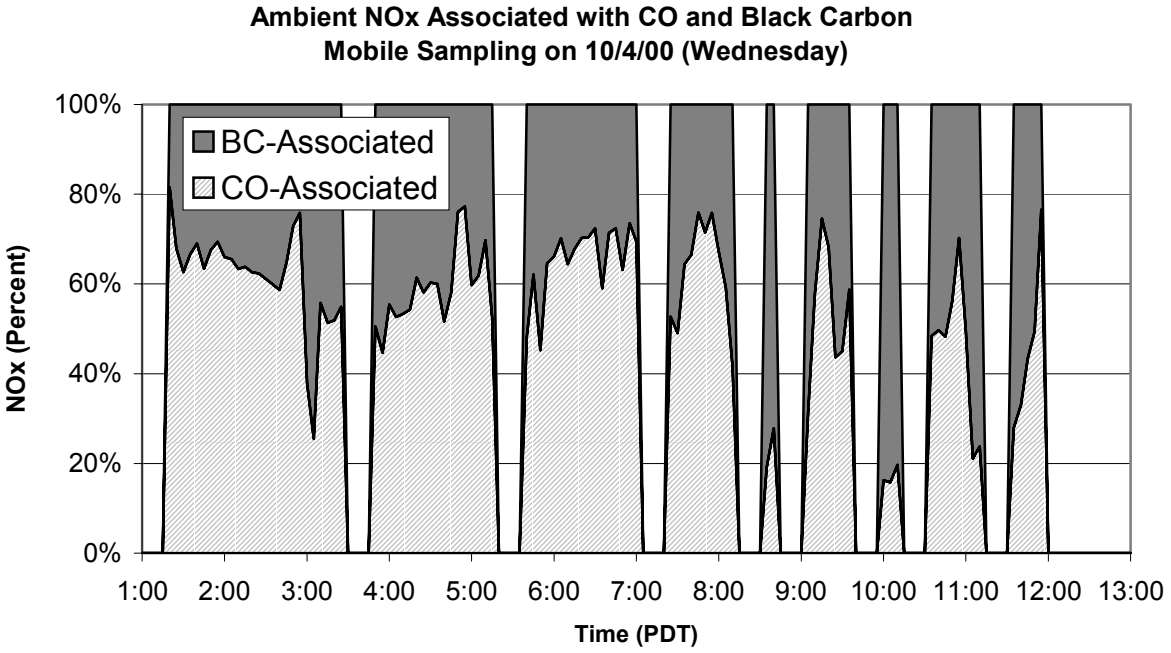
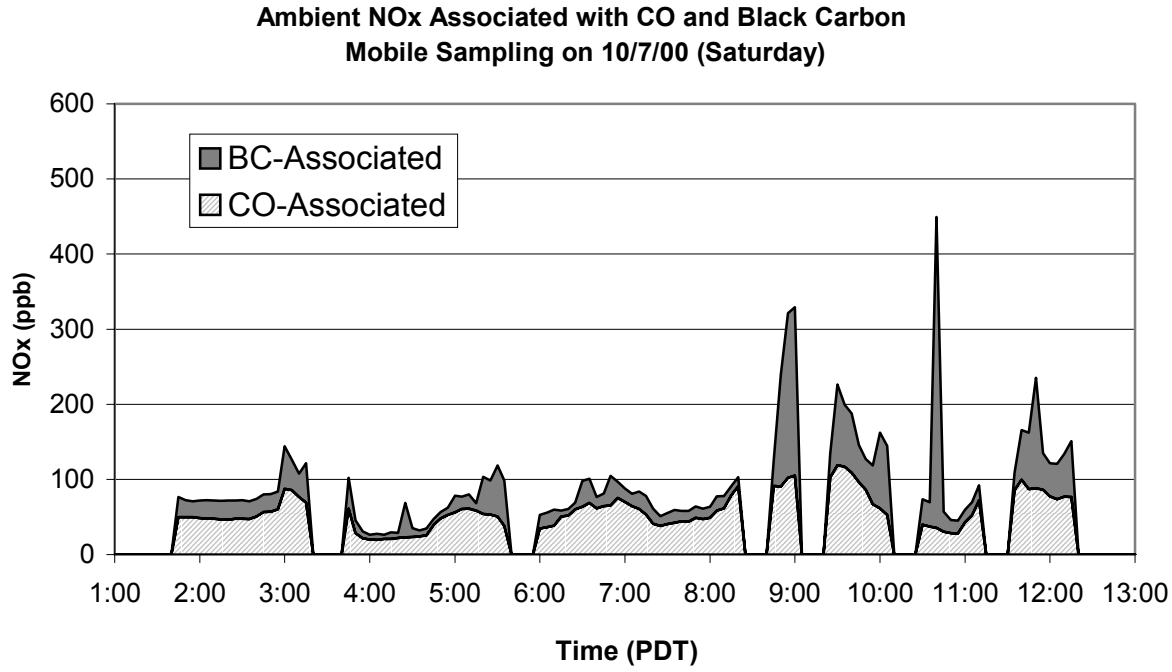


Figure 4.3-3b. Estimated ambient NOx associated with CO and black carbon for mobile lab samples Wednesday< October 4.



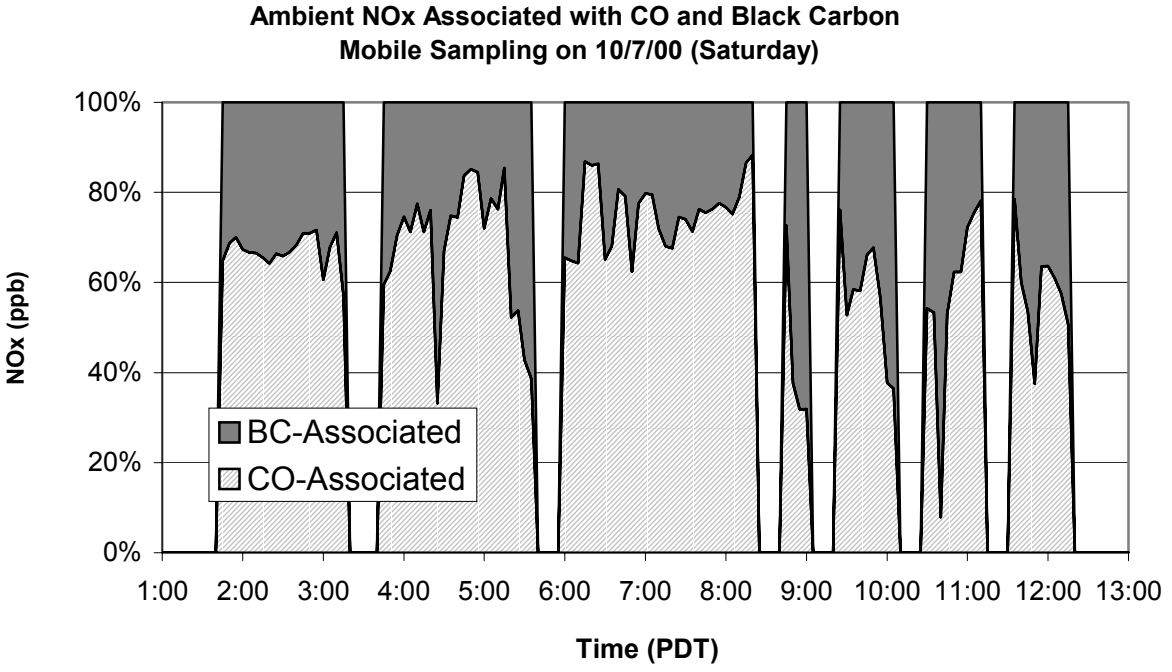
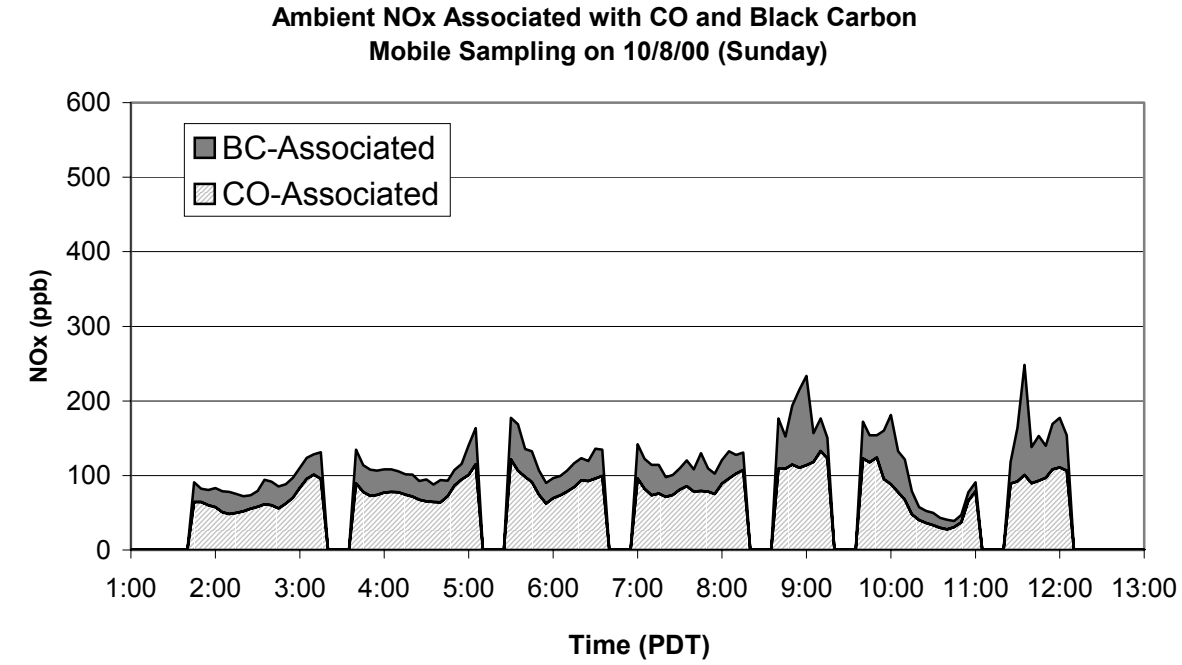


Figure 4.3-3c. Estimated ambient NOx associated with CO and black carbon for mobile lab samples 10/7/00 (Saturday).



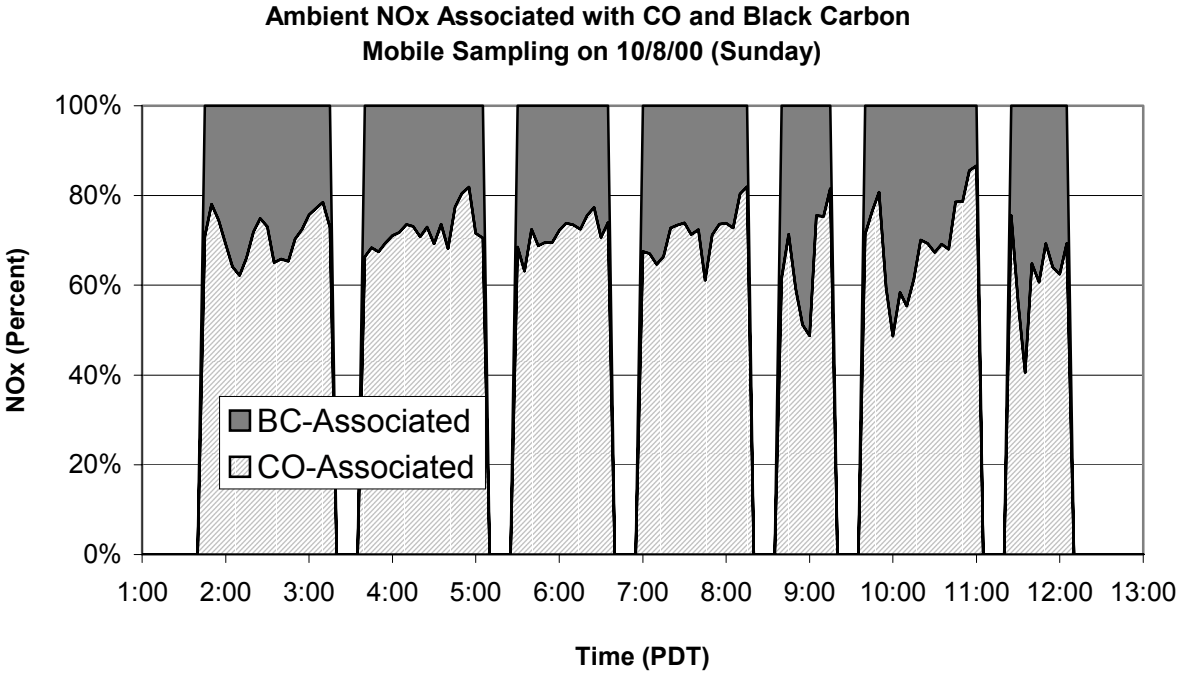
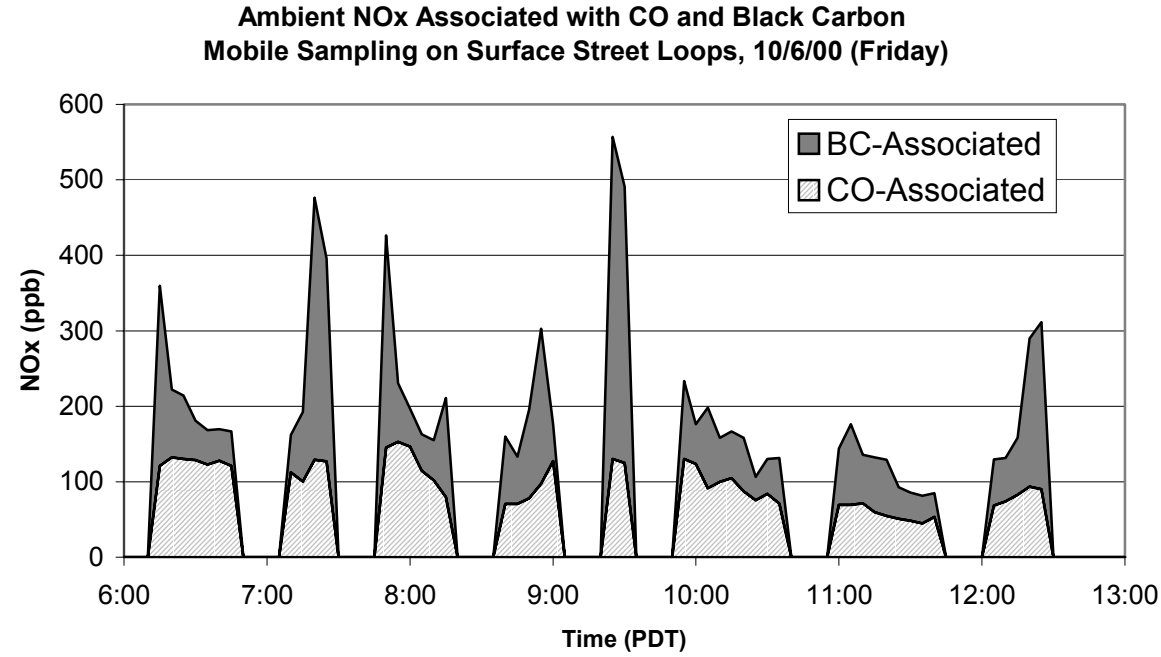


Figure 4.5-3d. Estimated ambient NOx associated with CO and black carbon for mobile lab samples Sunday, October 8.



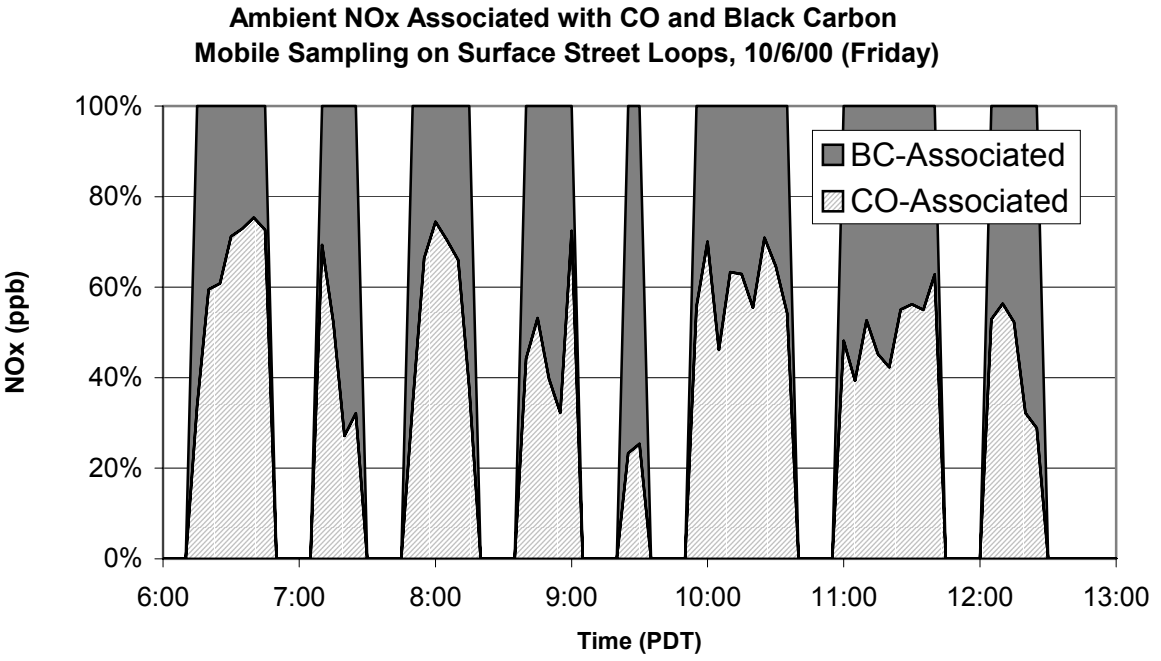


Figure 4.5-4. Estimated ambient NOx associated with CO and black carbon for mobile lab samples - surface streets Friday, October 6.

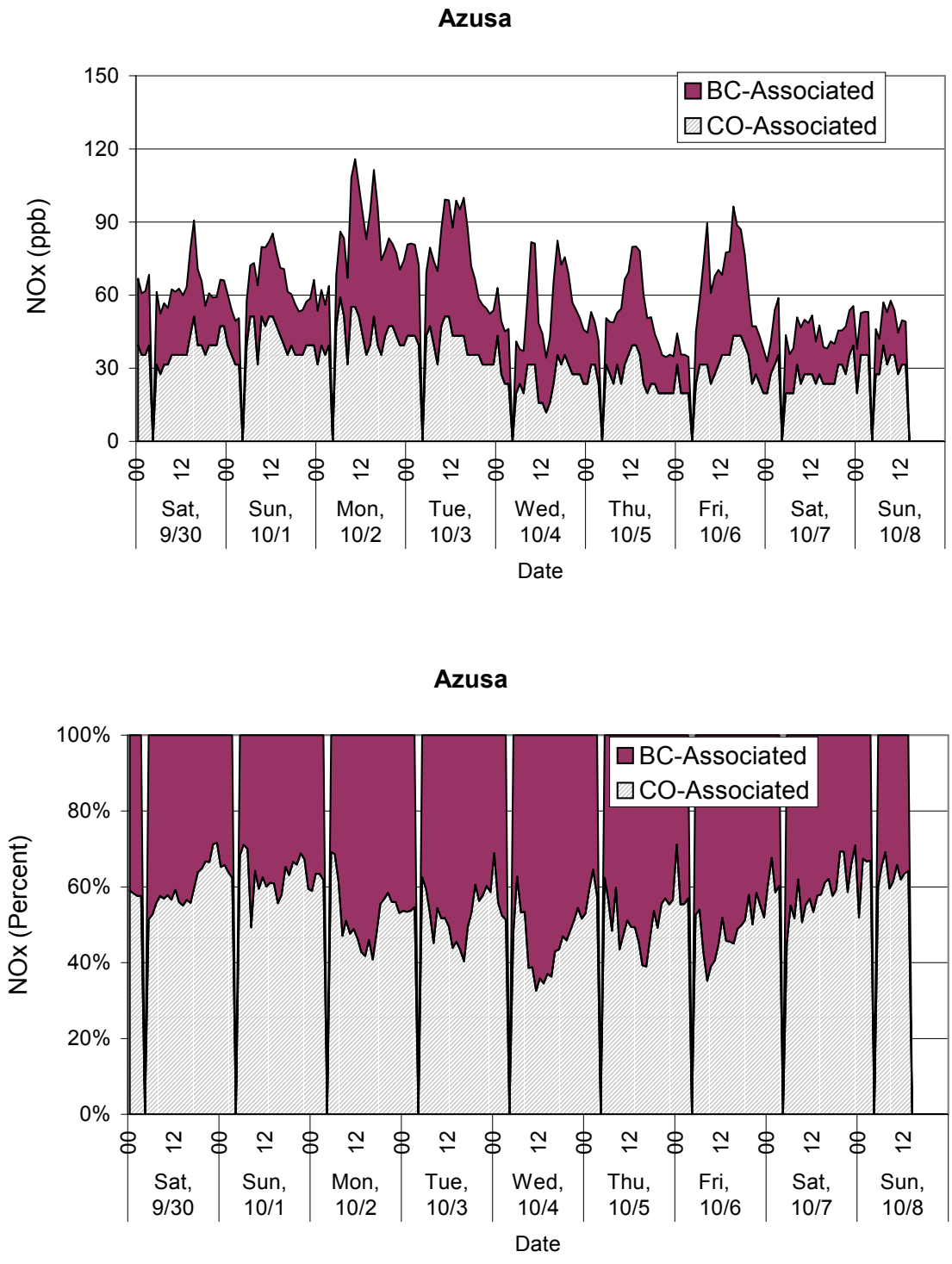


Figure 4.5-5 Estimated ambient NOx associated with CO and black carbon at Azusa September 30-October 8, 2000.

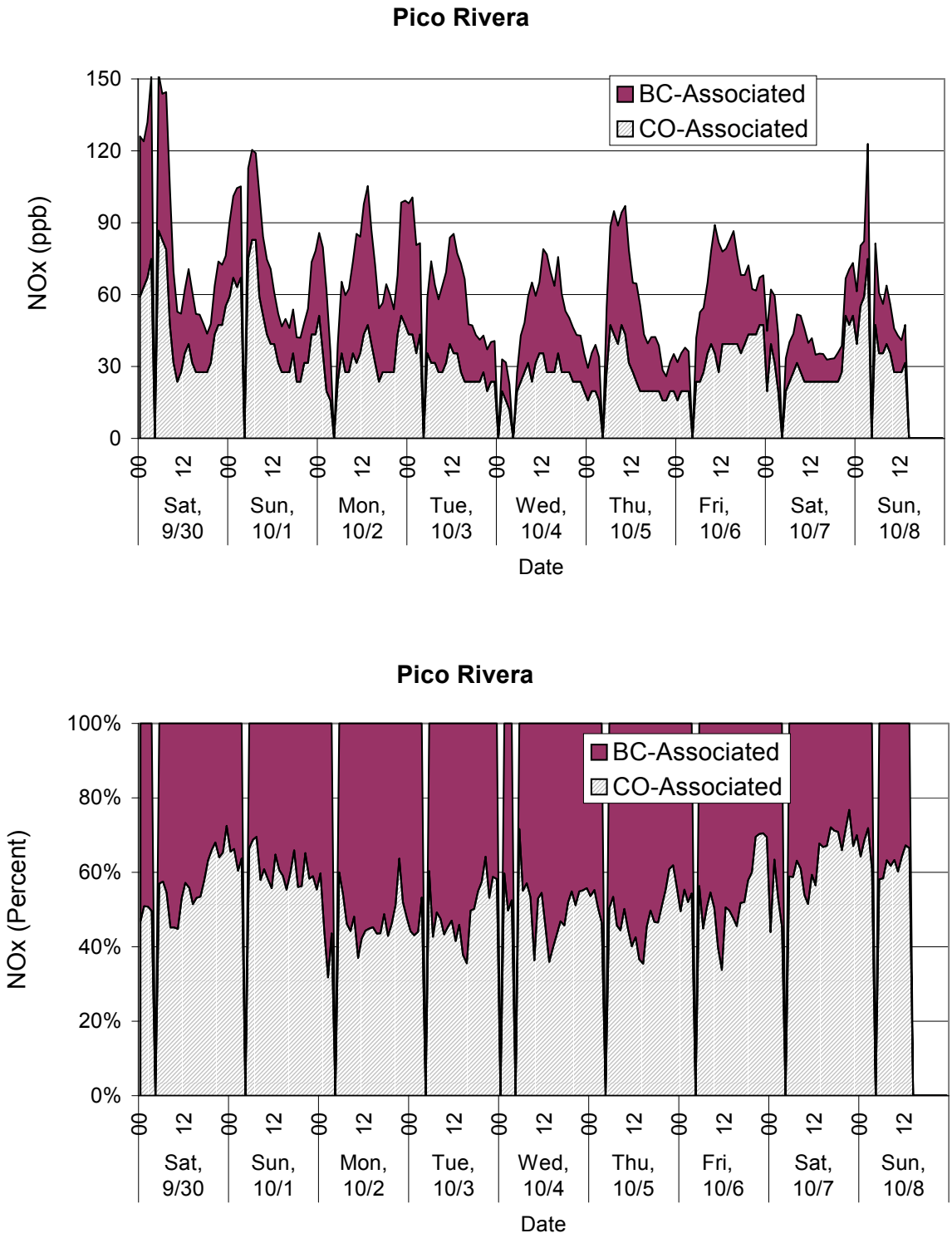


Figure 4.5-6. Estimated ambient NOx associated with CO and black carbon at Pico Rivera September 30-October 8, 2000..

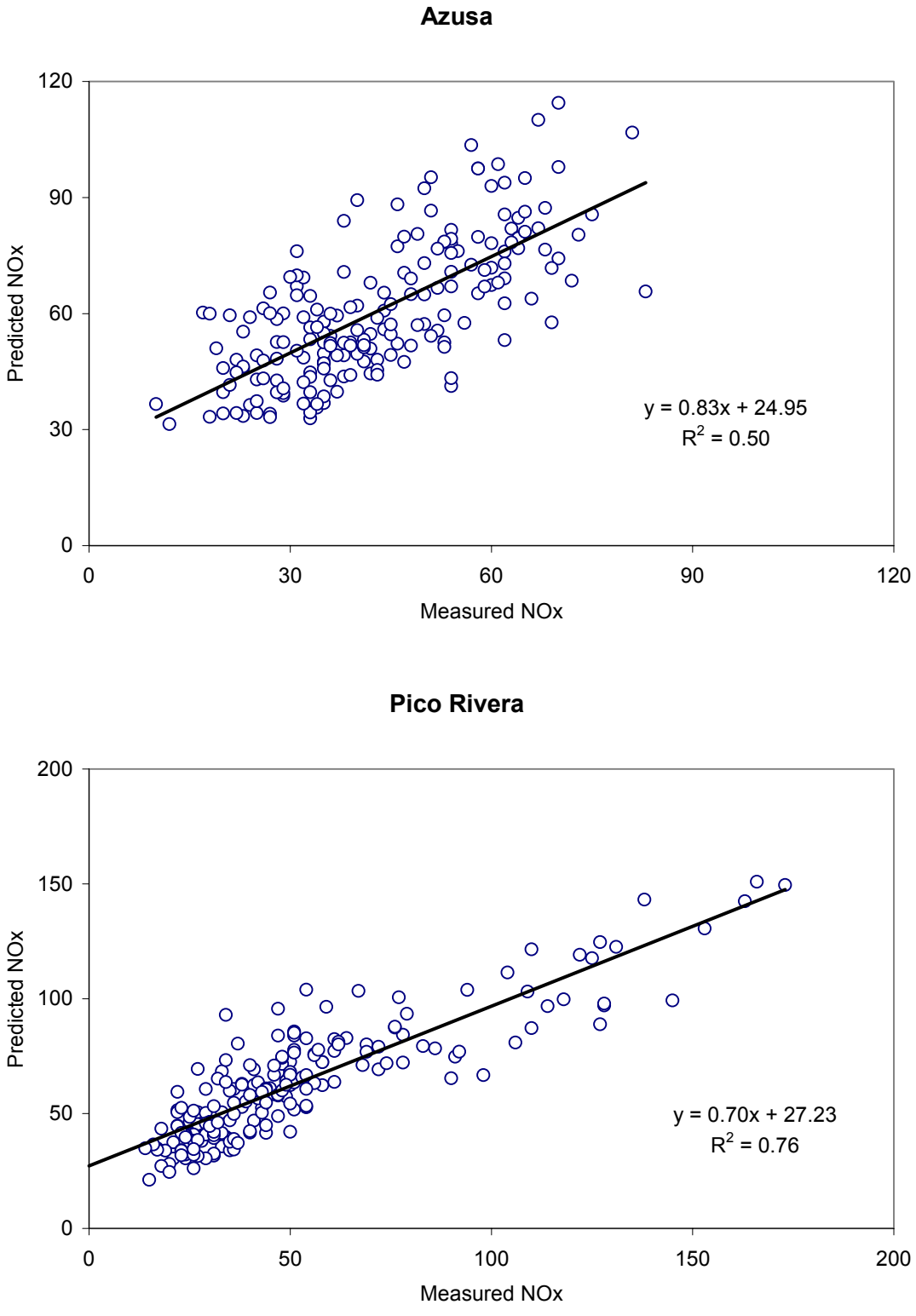


Figure 4.5-7. Correlation of predicted to measured NOx concentrations at Azusa and Pico Rivera

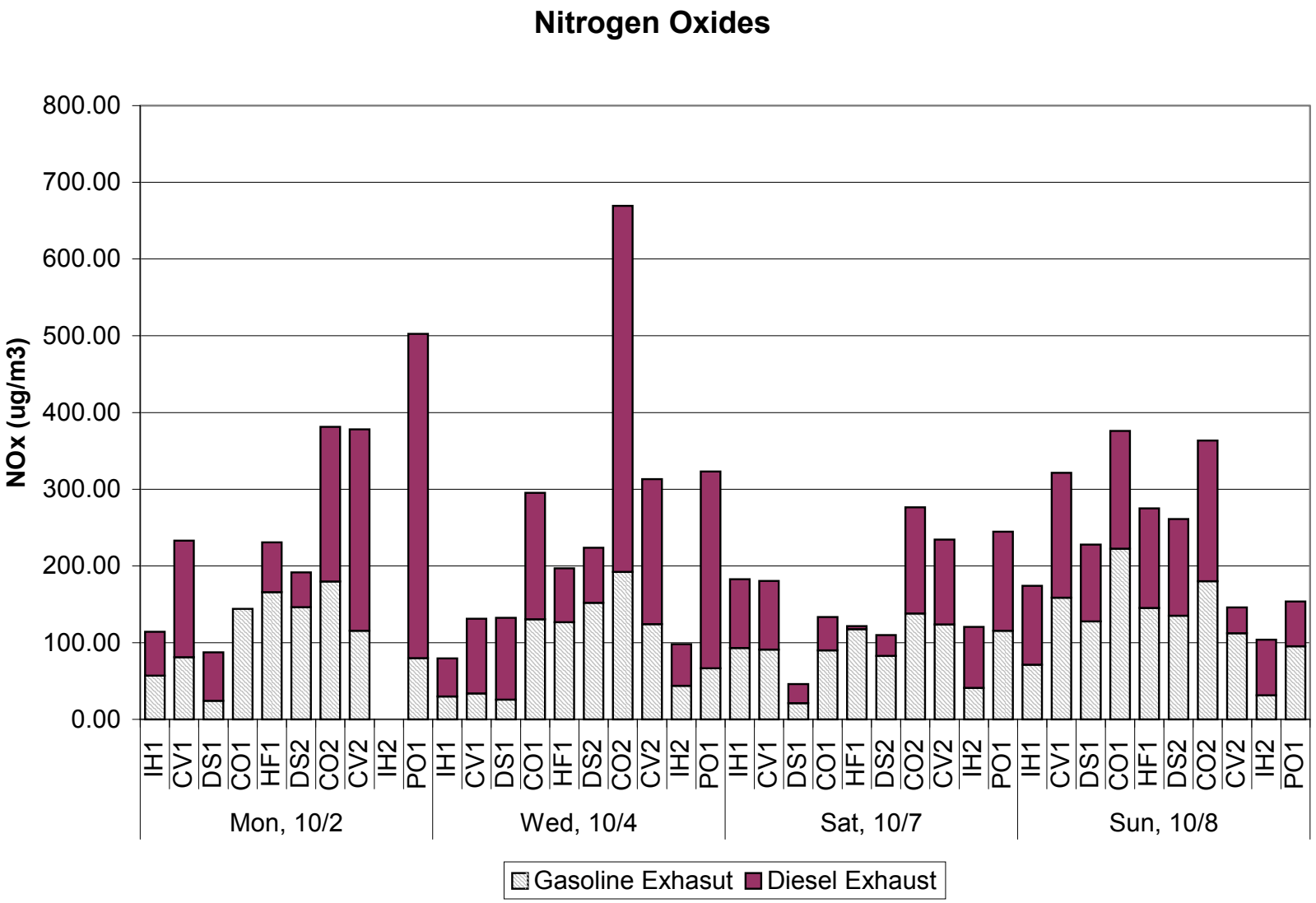


Figure 4.5-8. Source apportionment of NOx for mobile sampling loops and regional background sites – absolute contributions.

Figure 4.5-9. Source apportionment of NOx for mobile sampling loops and regional background sites – percent contributions.

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