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FINAL REPORT
FEBRUARY 1999

Air Monitoring Program for Determination of the Impacts of the Introduction of California's Phase 2 Reformulated Gasoline on Ambient Air Quality in the South Coast Air Basin

CALIFORNIA ENVIRONMENTAL PROTECTION AGENCY

AIR RESOURCES BOARD
Research Division

AIR MONITORING PROGRAM FOR DETERMINATION OF THE IMPACTS OF THE INTRODUCTION OF CALIFORNIA'S PHASE 2 REFORMULATED GASOLINE ON AMBIENT AIR QUALITY IN THE SOUTH COAST AIR BASIN

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1.0 PROJECT SUMMARY

1.1 Background and Statement of the Problem

The South Coast Air Basin experiences the most severe air pollution in the United States due to a unique combination of stagnant meteorological conditions, confining geography, and high concentrations of people and industrial activity. It is the only area in the country classified as in "extreme" nonattainment for ozone. Reformulated gasoline is the latest control measure in the three-decade effort to meet air quality standards in the SoCAB. Both the federal government and the State of California have developed specifications for reformulated gasoline (RFG). The federal program is required for all severe and extreme ozone nonattainment areas, whereas the California program applies throughout the state. Both the California and federal RFGs are being introduced in two phases. California Phases 1 and 2 were introduced in 1992 and in June 1996, respectively. Phase I of the federal program was introduced in 1995, and Phase II is scheduled for introduction in 2000.

To meet the reduction in O_3 and CO concentrations required by Title II of the Clean Air Act Amendments (CAAA) of 1990, average specifications for federal Phase I gasoline include a maximum RVP of 7.2 psi, a minimum 2.0% by weight oxygen content, and a maximum 1.0% by weight benzene content. These requirements were effective as of January 1, 1995, and apply to the South Coast Air Basin, Ventura County, and the San Diego Air Basin. The California Phase 2 RFG specifications apply to all gasoline sold in California beginning January 1, 1996, and include a maximum 40 ppmw sulfur content for any batch (average of 30 ppmw); a maximum 1.0% benzene content by volume (average of 0.8); a maximum 6.0% olefin content (average of 4.0); a minimum 1.8% and maximum 2.2% oxygen content by weight; a maximum T90 and T50 of 300 °F and 210 °F, respectively; a maximum 25% aromatic hydrocarbon content by volume (average of 22%); and a maximum RVP of 7.0 psi. California Phase 2 RFG is projected to reduce basin-wide ROG, NO_x, CO, and SO_x emissions by 80, 35, 350, and about 10 tons/day, respectively, by the year 2000 (Stoeckenius et al., 1995). In comparison, basin-wide ROG emissions during the summer of 1990 averaged 1507 tons/day distributed between stationary (42%) and mobile (58%) sources. Compared to motor vehicles using gasoline meeting California Phase 1 RFG criteria, CARB estimates that Phase 2 RFG will achieve about a 17% reduction in ROG from on-road motor vehicles and an 11% reduction in NO_x emissions (CARB, 1996). Actual reductions in southern California in 1996 were less than these estimates since gasoline marketed there in 1995 conformed to the federal Phase I RFG specifications rather than California Phase 1 specifications.

Changes in emissions due to the RFG requirements provide a unique opportunity to measure relationships between emissions and atmospheric concentrations of directly emitted pollutants and photochemical reaction products. In order to provide the data required to determine air quality impacts of the introduction of California's Phase 2 RFG, ambient measurements of speciated hydrocarbons, oxygenated organic gases, methane, carbon monoxide (CO), and carbon dioxide (CO_2) were conducted during the Summers of 1995 and 1996 in the South Coast Air Basin (SoCAB).

In addition, in the Summer of 1997, the Southern California Ozone Study (SCOS97) was conducted in order to update and improve existing aerometric and emission databases and model applications for representing urban-scale ozone episodes in Southern California, and to quantify the contributions of ozone generated from emissions in one Southern California air basin to federal and state ozone standard exceedances in neighboring air basins. These goals are to be met through a five-year process which includes analysis of existing data; execution of a large-scale field study to acquire a comprehensive database to support modeling and analysis; analysis of the data collected during the field study; and the development, evaluation, and application of an air quality simulation model for Southern California. SCOS97 was intended to provide another milestone in the understanding of relationships between emissions, transport, and ozone standard exceedances in Southern California as well as to facilitate planning for further emission reductions needed to attain the NAAQS. As part of SCOS97, DRI collected hydrocarbon and carbonyl samples in selected locations; this effort was conducted as an extension of the 1995-1996 RFG study. This study is described in Section 6.0 of this Report.

The SCOS97-NARSTO program was a $7+ million study that brought together a large number of interested governmental entities as stakeholders, and benefited from consultation and cooperation with the atmospheric sciences academic community. The study featured the most comprehensive network of instruments ever assembled to measure both ground level and upper air meteorological and air quality data. The data collected in support of the SCOS97-NARSTO study will be added to other data collected to make one of the most complete data sets ever collected in the southern California area. The information will be used for modeling and data analysis to support ozone and particulate matter attainment strategies, and to resolve intra-regional air pollution transport issues.

1.2 Project Objectives

The objectives of this study were as follows:

1. To conduct ambient measurements of speciated hydrocarbons, oxygenated organic gases, methane, carbon monoxide (CO), and carbon dioxide (CO_2) during the summers of 1995 and 1996 in the South Coast Air Basin (SoCAB) in order to provide the data required to determine air quality impacts of the introduction of California's Phase 2 RFG.

2. To conduct ambient measurements of speciated C_2-C_{12} hydrocarbons, carbonyl compounds (C_1-benzaldehyde range), methyl t-butyl ether (MTBE), methane (CH_4), carbon dioxide (CO_2), and carbon monoxide (CO) from selected ground-level monitoring stations in the South Coast Air Basin (SoCAB) during the intensive observational periods (IOP) during the summers of 1997.

1.3 Conclusions of the RFG Sampling Program

1. The introduction of California Phase 2 RFG resulted in measurable changes in the ambient concentrations of certain oxygenated and hydrocarbon species. In general, these changes were in agreement with those predicted prior to RFG introduction.

2. The most significant reduction in mean ambient concentratons (in both absolute and relative terms) is observed for C_6 olefins, C_9 and C_{10} aromatics. Since these species are very reactive in terms of their ozone formation potential, the reduction in their concentrations may help reduce ozone concentration in the SoCAB.

3. Mean ambient concentration of benzene (hazardous air pollutant) was reduced significantly in all sampling sites.

4. Mean ambient concentrations of MTBE increased significantly from 1995 to 1996. The increase in weight % of MTBE is very consistent in all three sampling sites — two source-dominated sites (North Main and Burbank) and a downwind receptor site (Azusa) — showing approximately a 40% increase during morning hours and nearly 50% during the afternoons. The background site (Santa Monica) shows approximately a 30% increase in MTBE concentrations (by weight %).

5. Excellent correlation between CO and MTBE was observed at all three sampling sites, confirming motor vehicle emissions as a source of MTBE.

6. A decrease in mean ambient CO concentrations was observed from 1995 to 1996; it ranged from 10 to 20% in the afternoons and from 20 to 30% in the mornings. No significant changes in mean ambient CO_2 concentrations were observed.

7. The mean concentrations of TNMHC were reduced from 1995 to 1996.

8. The mean ambient concentrations of isobutene, and to lesser extent, toluene increased from 1995 to 1996.

9. Mean ambient formaldehyde concentrations increased during the afternoon hours from 1995 to 1996 at all three sampling sites. However, the morning concentrations show a decrease in absolute terms (ppbv) or nearly no change in weight %.

10. The reduction in mean ambient concentrations of 1,3-butadiene and n-butane was lower than predicted.

1.4 Presentations and Publications

Part of the data included in this report were presented in CRC On-road Vehicle Emissions Workshops in April 1997 (Pasek and Zielinska, 1997) and at the Air & Waste Management Association's 90th Annual Meeting & Exhibition, June 8-13, 1997, Toronto, Ontario, Canada. The two papers submitted for the proceeding of A&WMA conference (Zielinska et al., 1997a, 1997b) are included in Appendix A. One M.Sc. thesis, "Analytical Methods for the Quantification of Oxygenated Volatile Organic Compounds, Carbon Monoxide, and Carbon Dioxide in Ambient Air" (Shire, 1996) was prepared in connection with this project. This thesis is included in Appendix B.

2.0 SAMPLING SITES AND AMBIENT AIR SAMPLING PROCEDURES

2.1 Ambient Sampling Sites and Schedule

Samples were collected at four sites (shown in Figure 2-1): two source-dominated sites (downtown Los Angeles at North Main and Burbank), a downwind receptor site (Azusa), and a background site (Santa Monica). Los Angeles (North Main), Burbank and Azusa sites are existing monitoring stations operated by the South Coast Air Quality Management District (SCAQMD). The North Main site is located at the Los Angeles Department of Water and Power building and is within an industrial area just north of the central business district. Three of the busiest freeway interchanges in the Los Angeles metropolitan area are within 2-4 kilometers of this site. The Burbank site is in an urban/industrial area on the eastern edge of the San Fernando Valley approximately 15 kilometers north of downtown Los Angeles. This is a future Type-2 (maximum emission) Photochemical Assessment Monitoring Station (PAMS) site and is scheduled to go into operation in 1997. Azusa is an existing Type-3 (downwind maximum ozone) PAMS site and is approximately 40 kilometers east-northeast of downtown Los Angeles. The Santa Monica site is located next to the beach, on the roof of the Lifeguard Headquarters building. Samples were collected at the Burbank, Azusa and North Main sites on 42 days (6 weeks) throughout the Summers of 1995 and 1996, from July to the end of September. Specifically, the sampling weeks were as follows:

<u>1995</u>	<u>1996</u>
July 8 – 14	July 7 – 13
July 17 – 23	July 28 – August 3
August 1 – 7	August 12 – 18
August 31 – September 6	August 27 – September 2
September 9 – 15	September 11 – 17
September 24 – 30	September 23 – 29

Two 3-hour samples were taken per sampling day, one in the morning during rush-hour traffic and one in the afternoon. During the first week of sampling in 1995, the sampling was performed from 0500 to 0800 and from 1200 to 1500 PST (which corresponds to 0600–0900 and from 1300–1600 local time, PDT). However, we found that the SCAQMD performed their sampling from 0600 to 0900 and from 1300 to 1600 PST, which corresponds to 0700–1000 and 1400–1700 PDT. After consultation with the CARB project manager, it has been decided to change our sampling time to that used by the district, in order for our data and that of SCAQMD to be comparable. Thus, in 1995, starting from the second week of sampling (July 17–23, 1995) all samples were collected from 0600 to 0900 and from 1300 to 1600 PST. However, in 1996, the SCAQMD changed their sampling time to 0500 to 0800 and 1200 to 1500 PST (which corresponds to 0600–0900 and 1300–1600 local time). In order to be comparable with the district data, we also collected our 1996 samples at the same schedule. At the Santa Monica site

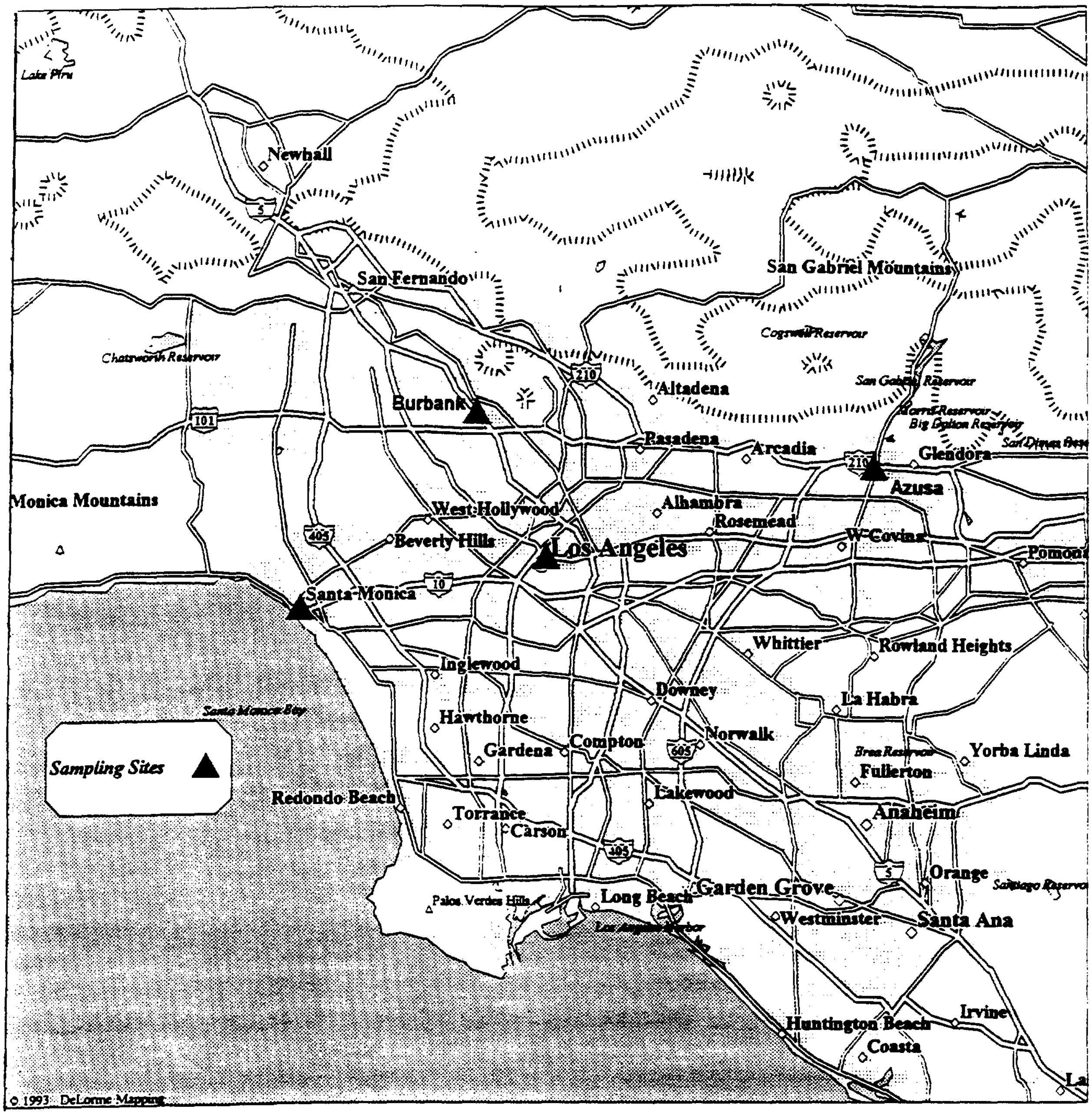


Figure 2-1. Locations of all four sampling sites in the SoCAB.

samples were collected once per sampling week, from 1200 to 1500 PDT, when an off-shore wind prevailed.

2.2 Source Sampling Sites and Schedule

The project required to include special sampling sites to obtain representative source composition profiles for cold start, hot stabilized, and evaporative emissions from motor vehicles that would be suitable for receptor modeling. The following source sampling sites were selected:

1. For cold start emissions sampling we selected parking garages. In June 1995, sampling was performed at the UCLA parking garage. This is a multilevel, open structure type of garage. The sampling was performed on Level 3, which had the highest proportion of vehicles with parking permits; we anticipated more regular working hours for these vehicles' owners. In order to check the uniformity of the samples, three parallel sampling sites, labeled A, B, and C, were established on Level 3. Sampling was performed between 1400–1500 PDT ("background") and 1615–1715 PDT (background plus cold-start emissions). Eleven valid samples were collected during the two-day sampling period (June 29–30).

The UCLA garage had several drawbacks. Its open structure allowed for mixing of inside and outside air, thus diluting the concentrations of VOC emitted during the cold-start. In addition, there was considerable traffic during the day. Therefore, for 1996, we selected an underground parking garage located in the Ronald Reagan Federal Building in downtown Los Angeles. This garage was ideal in that there was very little traffic during the day and most vehicles left the garage at about the same time at the end of the workday. We collected 1-hr samples beginning at 1400 ("background") and 1630 hr (background plus cold-start emissions) on July 24–25, 1996.

2. Tunnel measurements were utilized for obtaining VOC profiles for hot-stabilized motor vehicle exhaust emissions. In 1995, DRI performed a series of studies, funded by the Coordinating Research Council, of on-road emissions in tunnels located across the U.S. (Gertler et al., 1997b). In the South Coast Air Basin area, experiments were conducted at the Van Nuys Tunnel (June 8–12, 1995) and Sepulveda Tunnel (October 3–4, 1995) in Los Angeles. In 1996, additional measurements, funded by SCAQMD, were made in Sepulveda Tunnel (July 23-27, 1996). The sampling protocol, characteristics of the vehicle traffic, and the obtained results are described by Gertler et al. (1997a, 1997b).

3. The VOC composition of evaporative emissions is more difficult to characterize by ambient measurements than exhaust emissions due to difficulties in isolating the contributions of evaporative from exhaust emissions. The composition profile for liquid gasoline is a reasonable approximation of evaporative emissions from gasoline spillage and hot soak emissions. Whole gasoline also reflects the additional unburned gasoline (due to misfiring and other engine malfunctions) that is not included in the exhaust profile. The profile for gasoline headspace vapor reflects evaporative emissions due to refueling, diurnal evaporation, and running losses. VOC profiles for liquid gasoline and headspace profiles were obtained specifically for this project. The composition of whole gasoline was studied by the University of

California, Riverside (UCR, CE-CERT) in a SCAQMD–sponsored study. We obtained up to 20 of the same gasoline samples analyzed by UCR and characterized the composition of the headspace vapors. All major brands and grades of gasolines were included in this survey. Analysis was performed for hydrocarbons and oxygenated organic compounds.

The gasoline samples analyzed by the headspace technique are listed in Table 2-1.

2.3 Ambient Air Sampling Procedures

2.3.1 VOC Sampling Method

Volatile organic compounds (in the range of $C_2 - C_{12}$) were collected using stainless-steel polished canisters. Stainless-steel SUMMA^{TM}-polished canisters (Scientific Instrument Specialists, Moscow, ID) and Stabilizer^{TM} canisters (Meriter, San Jose, CA) of 6 L capacity were cleaned by repeated evacuation and pressurization with humidified zero air at ~140 °C prior to sampling and certified as described by U.S. EPA Method TO-14. The sampling procedure is based on the pressurized sampling method described by EPA Method TO-14. Figure 2-2 shows the main components of this sampling system. A metal bellows-type pump draws in ambient air from the sampling manifold to fill and pressurize the sample canisters. A flow control device maintains a constant flow into the canisters over the desired sample period. This flow rate is preset to fill the canisters to about 1 atm above ambient pressure at the end of the sampling period (as described by U.S. EPA Method TO-14). A timer is used to automatically start and stop the pump at the appropriate time. The timer also controls the solenoid valve, opening it when the pump starts and closing it when the pump stops. The canister sampling systems were custom-built at DRI. They are multiple-event sampling systems, allowing unattended collection of three canister samples.

After sampling, an identification tag was attached to each canister and the canister serial number, sample number, and sampling location, date, and time were recorded on this tag. In addition a field sampling form and chain-of-custody form were filled out giving all pertinent information on the collection of the sample.

2.3.1.1 Canister and Sampling System Cleaning and Certification

Prior to sampling, the canisters were cleaned by repeated evacuation and pressurization with humidified zero air, as described in the EPA document "Technical Assistance Document for Sampling and Analysis of Ozone Precursors" (October 1991, EPA/600-8-91/215). Six repeatable cycles of evacuation to ~0.5 mm Hg absolute pressure, followed by pressurization with ultra-high-purity (UHP) humid zero air to ~20 psig are used. The differences between the DRI procedure and the EPA recommended method are that, in the DRI method, canisters are heated to 140 °C during the vacuum cycle, and more cycles of pressure and vacuum are used. Based on our experience and that of others (Rasmussen, 1992), heating is essential to achieve the desired canister cleanliness. Also, the canisters are kept longer under vacuum cycles, about one hour in the DRI method, as opposed to half an hour in the EPA method.

Table 2-1. Gasoline Samples.

Sample ID	Station	Grade
1995		
95-73-1A	Mobil	87
95-73-1B	Mobil	92
95-73-2A	Chevron	87
95-73-2B	Chevron	92
95-73-3A	Unocal	87
9573-3B	Unocal	92
95-73-4A	Arco	87
95-73-4B	Arco	92
95-73-5A	Texaco	87
95-73-5B	Texaco	92
95-73-6A	Shell	87
95-73-6B	Shell	92
95-73-7A	Ultramar	87
95-73-7B	Ultramar	92
95-73-8A	Gasco	87
95-73-8B	Gasco	91
95-73-9A	Thrifty	87
95-73-9B	Thrifty	92
1996		
96-83-1A	Mobil	87
96-83-1B	Mobil	92
96-83-2A	Chevron	87
96-83-2B	Chevron	92
96-83-3A	Unocal	87
96-83-3B	Unocal	92
96-83-4A	Arco	87
96-83-4B	Arco	92
96-83-5A	Texaco	87
96-83-5B	Texaco	92
96-83-6A	Shell	87
96-83-6B	Shell	92
96-83-7A	Ultramar	87
96-83-7B	Ultramar	92
96-83-8A	USA	87
96-83-8B	USA	92
96-83-9A	Thrifty	87
96-83-9B	Thrifty	92

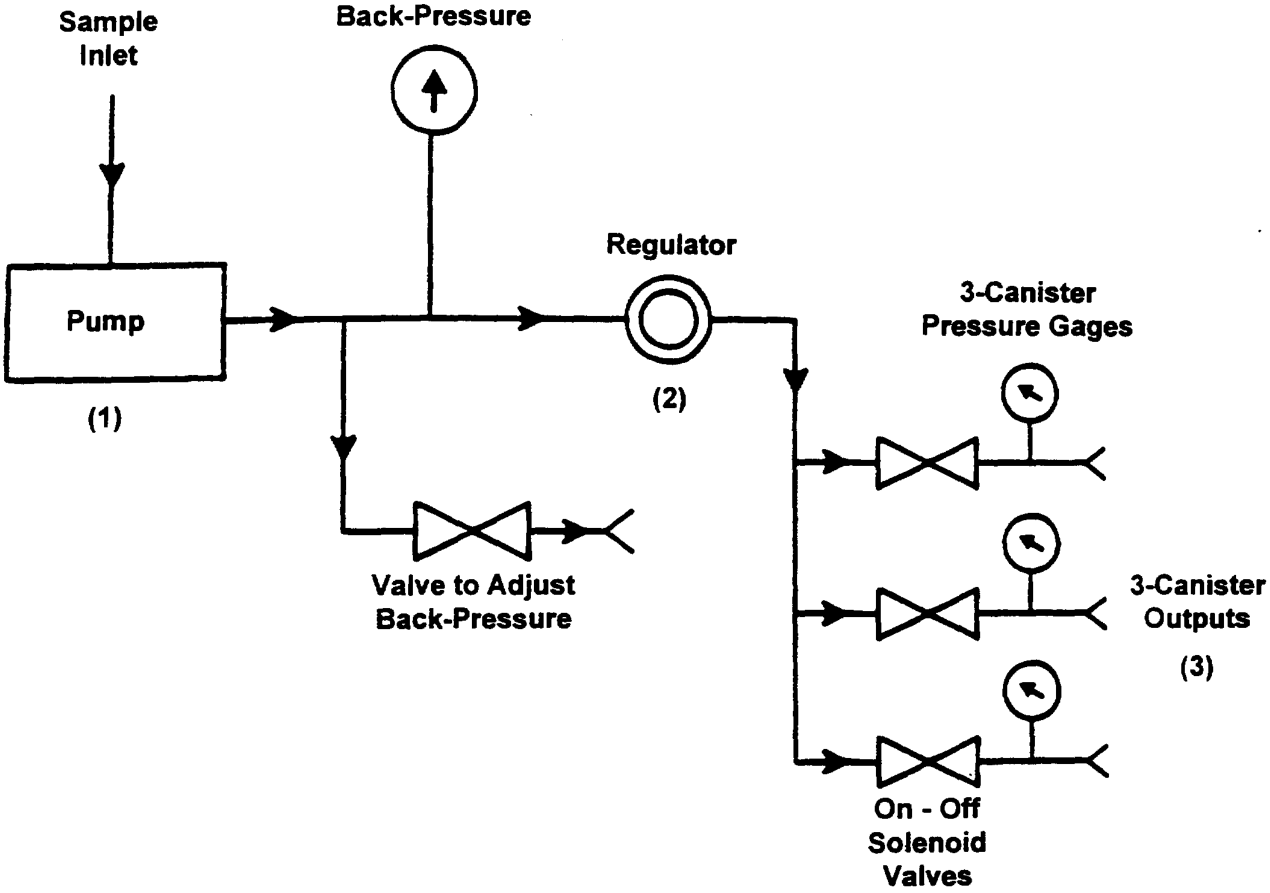


Figure 2-2. Canister Sampler Flow Schematic.

At the end of the cleaning procedure, one canister out of six in a lot is filled with humidified UHP zero air and analyzed by the gas chromatograph/flame ionization detection (GC/FID) method. The canisters are considered clean if the total non-methane organic compound (NMOC) concentration is less than 20 ppbC.

The canister sampling systems are cleaned prior to field sampling by purging them with humidified zero air for 48 hours, followed by purging with dry UHP zero air for 1 hour. Each canister sampling system is certified clean by the GC/FID analysis of humidified zero air collected through this sampling system. The system is considered clean if the concentration of any individual targeted compound is less than 0.2 ppbv and total NMOC concentration is less than 20 ppbC. In addition, a challenge sample, consisting of a blend of organic compounds of known concentration in clean humidified zero air, is collected through the sampling system and analyzed by the GC/FID method. The sampling system is considered non-biasing if recoveries of each of the challenge compounds is in the range of 80–120% (EPA document EPA/600-8-91/215).

2.3.2 Carbonyl Compounds

The measurement technique used for this study is an established procedure using C_{18} Sep-Pak cartridges (Waters Associates, Milford, MA) which have been impregnated with purified acidified 2,4-dinitrophenylhydrazine (DNPH). When ambient air is drawn through the cartridge, carbonyls in the air sample react with the DNPH to form hydrazones, which are separated and quantified using high performance liquid chromatography (HPLC) in the laboratory (Fung and Grosjean, 1981). This is the most-often used method for measuring these compounds in ambient air. Significant improvements in the preparation of the cartridges as well as sampler design have made routine monitoring of carbonyl compounds at 1 ppb or lower possible (Fung and Wright, 1986). DNPH-impregnated C_{18} SepPack cartridges were provided by Dr. Kochy Fung of AtmAA, Inc.

2.3.2.1 Carbonyl Compounds Sampling Equipment

The DRI carbonyl sampling systems are consistent with the sampling systems described in EPA Method TO-11 and the EPA document "Technical Assistance Document for Sampling and Analysis of Ozone Precursors" (October 1991, EPA/600-8-91/215). Six such systems were custom-built at the DRI and were used for this study.

Figure 2-3 shows a schematic of the carbonyl sampling system. The system consists of a diaphragm pump capable of maintaining air flow through the cartridges of 500–1500 ml/min, flowmeter, six-port solenoid manifold allowing unattended collection of up to six carbonyl samples, needle valves for flow rate regulation, and check valves to protect cartridges from outside air when air is not being sampled through a given cartridge. For automatic operation, the memory-protected programmable timer starts and stops the pump at the appropriate time. The timer also opens the six-port solenoid valve when the pump starts and closes it when the pump

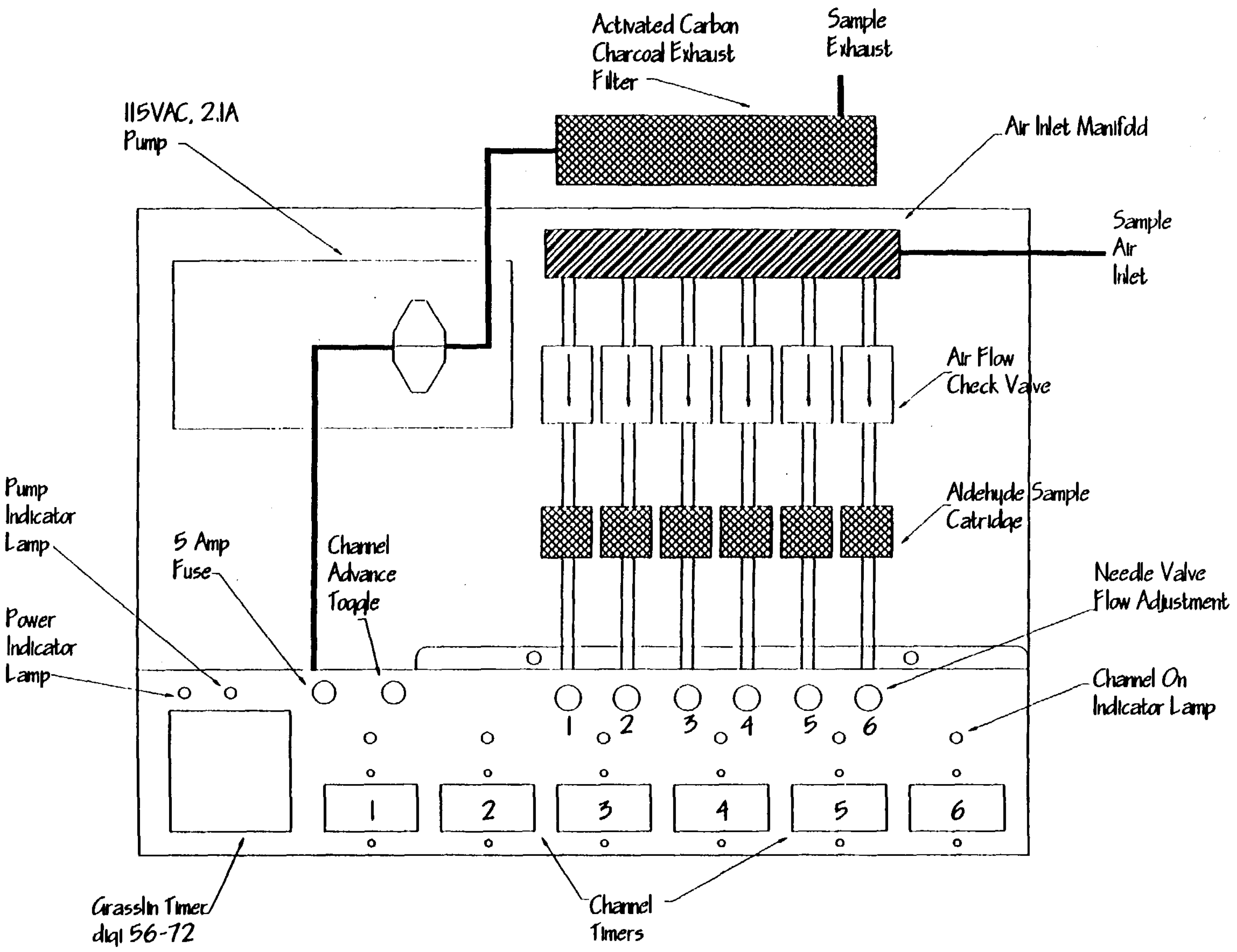


Figure 2-3. Schematic of DRI Carbonyl Sampling System.

stops (since cartridges will naturally sorb carbonyl compounds from the surrounding air if left open, the sampler has been designed such that cartridges loaded into the sampler are isolated from the environment and from each other by check valves upstream and solenoid valves downstream). Duplicate samples can be collected on collocated cartridges by activating a parallel channel simultaneously. A mode selection switch converts the parallel channel for field blank collection as well. Sampling flow rates are controlled at ~1.0 L/min using a differential flow controller with a typical precision of ±5% or less. A charcoal filter is attached to the pump outlet in order to remove traces of acetonitrile from the DNPH cartridges.

3.0 ANALYTICAL PROCEDURES

3.1 Canister Sample Analysis

An air sample is taken from the canister and passed through the sample concentration system. This system is shown schematically in Figure 3-1. It consists of a freeze-out loop, made from chromatographic-grade stainless-steel tubing packed with 60/80 mesh deactivated glass beads, and a 10-port sampling valve (V-1). When the valve is in position 1, as shown in Figure 3-1, the sample is transferred from the canister through the loop immersed in liquid oxygen to the volume transfer measurement apparatus, shown in Figure 3-2. The C_2 and heavier hydrocarbons are cryogenically trapped inside the loop when air is transferred to an evacuated flask of known volume. From the difference in pressure inside the flask, the volume of the air sample can be calculated, based on the Ideal Gas Law. When a sufficient volume of the air sample has been transferred from the canister to the concentration system, the 10-port valve is switched to position 2 (shown in Figure 3-3), the liquid oxygen is replaced with boiling water, and the contents of the trap are injected into a chromatographic column where separation of the C_2–C_{12} hydrocarbons takes place. No Perma-Pure permeable membrane or other moisture-removal device is used prior to concentration, since the use of such drying devices results in the loss of certain volatile organic compounds (VOC) of interest (all polar compounds and some olefins and aromatics). It can also introduce contaminants into the system and it lowers the total NMHC by 10–20% (Sagebiel and Zielinska, 1994). The entire inlet is heated (up to ~100 °C) to prevent any condensation of compounds during the transfer.

The chromatographic column used for C_2–C_{12} hydrocarbon analysis in the DRI system is a 60 m long J&W DB-1 fused silica capillary column with a 0.32 mm inside diameter and 1 μm phase thickness. The oven temperature program is: -65 °C for 2 min., to 220 °C at 6 °C/min. The gas chromatograph is a Hewlett-Packard 5890 Series II, equipped with an FID detector. However, the DB-1 column does not provide complete separation of the light C_2 and some important C_4 hydrocarbons. Therefore, a separate analysis of the canister sample is necessary to obtain accurate concentrations for ethane, ethylene, acetylene, 1-butene, 2-butenes and isobutylene. The chromatographic column used for this analysis is a J&W GS-Alumina PLOT fused silica capillary column with an internal diameter of 0.53 mm and a length of 30 m. A separate gas chromatograph (Varian Model 3700) is dedicated to this analysis.

3.1.1 Hydrocarbon Calibration and Compound Identification

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). The NIST SRM 1805 (254 ppb of benzene in nitrogen) is used for calibrating the analytical system for C_2–C_{12} hydrocarbon analysis, whereas 1 ppm propane in a nitrogen standard (Scott Specialty Gases), periodically traced to SRM 1805, is used for calibrating the light hydrocarbon analytical system. Based on the uniform carbon response of the FID to hydrocarbons, the response factors determined from these calibration standards are used to convert area counts into concentration units (ppbC) for every peak in the chromatogram.

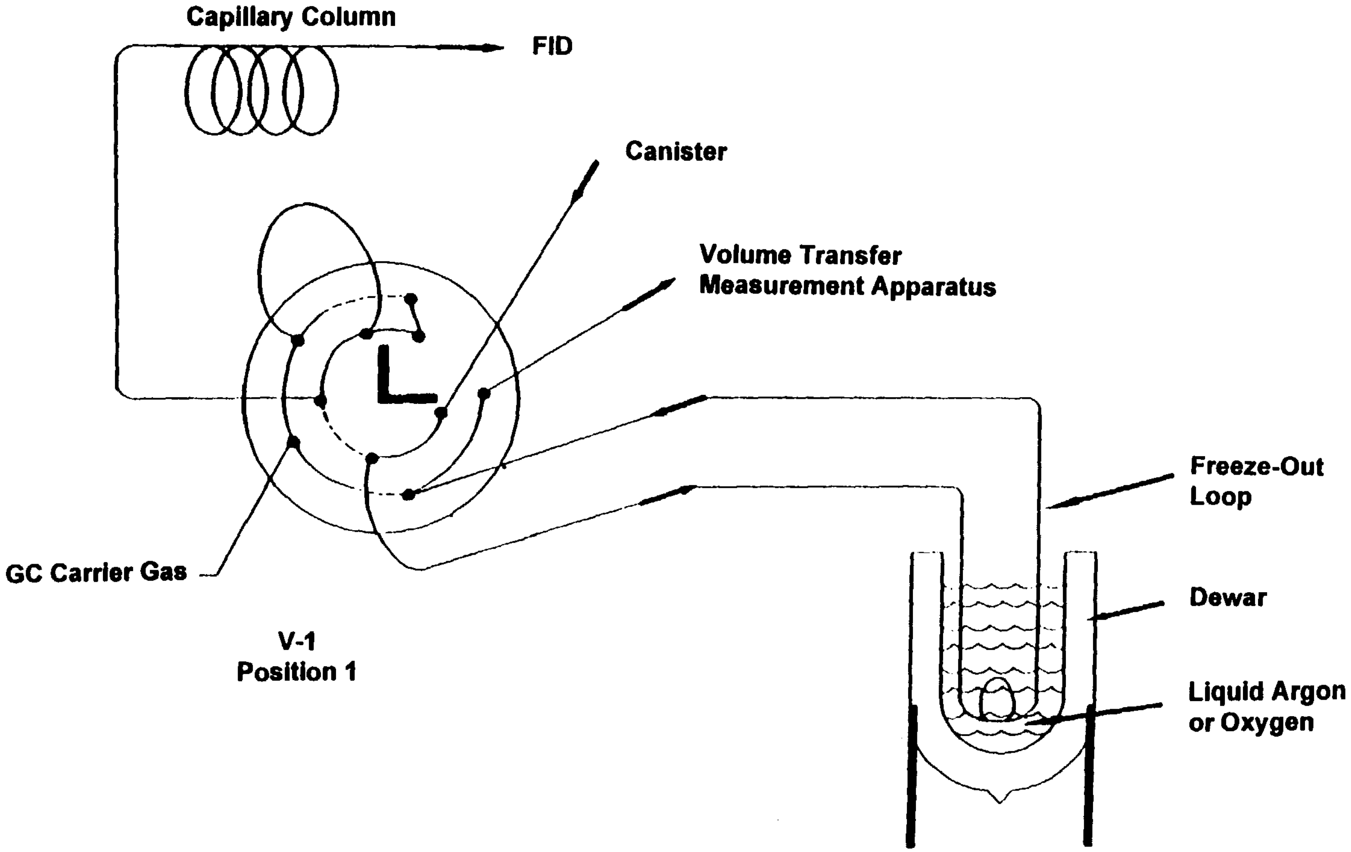


Figure 3-1. Gaseous sample concentration system, sampling position.

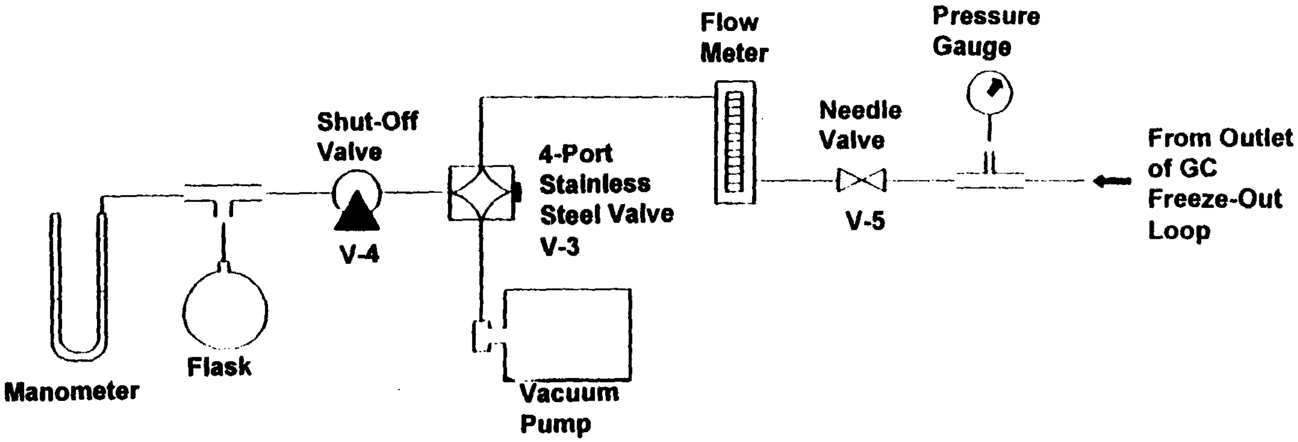


Figure 3-2. Volume transfer measurement apparatus.

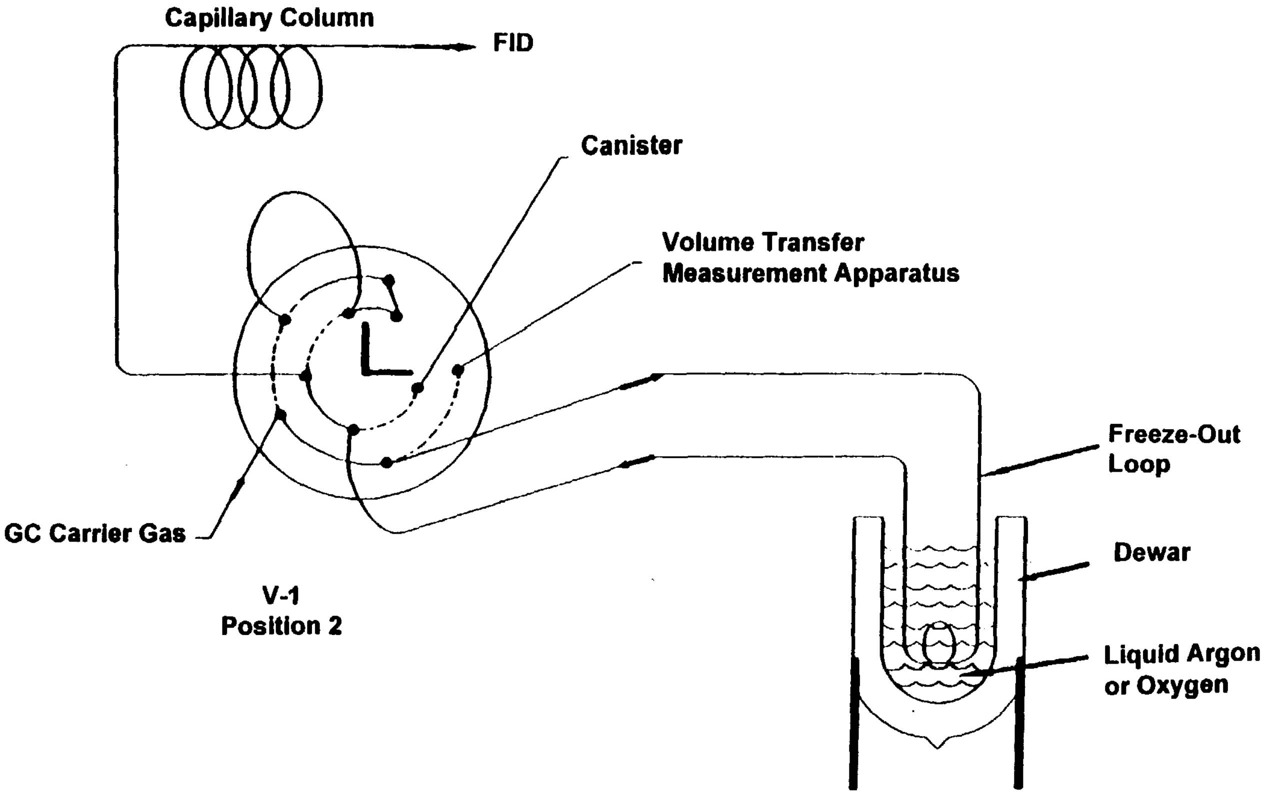


Figure 3-3. Gaseous sample concentration system, inject position.

Identification of individual compounds in an air sample is based on the comparison of linear retention indices (RI) with those RI values of authentic standard compounds, as well as with the RI values obtained by other laboratories performing the same type of analysis using the same chromatographic conditions (Auto/Oil Program, Atmospheric Research and Exposure Assessment Laboratory, U.S. EPA). The DRI laboratory calibration table contains ~160 species.

All of the gas chromatographs are connected to a data acquisition system (ChromPerfect, designed and marketed by Justice Innovation, Inc.). The software performs data acquisition, peak integration and identification, hardcopy output, post-run calculations, calibrations, peak re-integration, and user program interfacing. Acquired data are automatically stored on a hard disk. A custom-designed database management system is used to confirm all peak identifications. This step is described in Section 3.4, below.

3.1.2 Methyl t-Butyl Ether (MTBE)

Methyl t-butyl ether was quantified from canister samples, using our method of analysis for C_3–C_{12} hydrocarbons, i.e., a 60 m long J&W DB-1 fused silica capillary column with a 0.32 mm inside diameter and 1 µm phase thickness, and the injection system described above. The individual response factor was determined for MTBE and its concentration is reported in ppbv. Since reliable NIST traceable standards for MTBE and other oxygenated compounds were not commercially available in 1995, we determined effective carbon numbers (ECN) for these compounds and used these numbers to convert GC/FID concentration numbers reported in ppbC to ppbv (see Appendix B, J. Shire Thesis, Section 3). Briefly, using a suitable solvent, repeated, approximately equimolar, liquid solutions of an oxygenated compound and benzene were injected neatly into the GC and the calculations were done similar to those described by Yieru et al. (1990) and Scanlon and Willis (1985) to determine an ECN for each of the oxygenated VOCs of interest. The ECN for MTBE was determined to be 4.37.

For comparison, MTBE was also quantified by trapping an aliquot from a canister onto a multibed adsorbent tube and analyzing it by the thermal desorption method. This method is described in detail by Shire (1996) in his Master Thesis (Appendix B, Section 3) and, briefly, below in Section 3.1.3. All canister samples collected in 1996 were analyzed by this method.

3.1.3 Methanol and Ethanol

Methanol and ethanol were quantified using the multi-adsorbent tube method. In this method, described in detail by Shire (1996, M.Sc. Thesis, Appendix B), an air sample from a canister (500–1000 ml) is passed through an 1/8-inch stainless-steel tubing coated on the inside with silicon (Restek) and heated to 70 °C. At a flow of 50 ml/min the sample is trapped onto a multibed adsorbent tube (6 in. x 1/4 in. Pyrex®) of 100 mg Tenax TA®, 85 mg Carbotrap B, and 180 mg Carbosieve III (Supelco) with Pyrex wool plugs containing and separating the sorbents. The sample is then purged with UHP helium which has been passed through a hydrocarbon trap at 100 ml/min (where the purge volume = 2X trapped volume) to remove water in preparation for injection via a standard Thermal Desorption Cold Trap injector unit (Chrompack). The Hewlett-Packard 5890 Series II GC/FID is equipped with a Chrompack CP-Sil 13CB capillary column, 50 m long x 0.32 mm inner-diameter with a 1.2 μm film thickness. The oven temperature program is: -20 °C for 2 min initially, with a 3 °C/min ramp to 200 °C. Temperature settings for the Thermal Desorption Cold Trap are: -170 °C, cold trap; 280 °C, desorption; and an 80 °C heating of the cold trap for the 2 min injection. The GC/FID response is calibrated in ppbC, using a gaseous standard (2600 ppbC of n-pentane in nitrogen, from Spectra Gases, Alpha, NJ) trapped onto multibed adsorbent tubes and analyzed by the thermal desorption method. Three concentration levels of n-pentane were used. The ppbC values for methanol, ethanol, and MTBE are then converted to ppbv using the ECN of each chemical.

The ECNs were experimentally determined for methanol and ethanol as described for MTBE, Section 3.1.2, above. They were 0.58 and 1.18 for methanol and ethanol, respectively.

3.1.4 Methane, Carbon Monoxide and Carbon Dioxide

Methane (CH_4), carbon monoxide (CO) and carbon dioxide (CO_2) are measured from the canister samples using GC/FID. Since the FID does not respond to CO and CO_2 these species are converted to methane by a methanator, positioned right after a GC column, but ahead of the FID. The methanator comprises a firebrick powder impregnated with nickel catalyst, through which a stream of hydrogen gas flows continuously at ~550 °C.

For compound separation, a 20 feet x 1/8 inch inner-diameter (i.d.) column, packed with a 60/80 mesh of Carboxen 1000 (Supelco) is used. This column provides sufficient separation between CH_4 and CO without retaining CO_2. Five ml samples are injected using a constant volume loop. The response factors are determined by the calibrations with the gaseous standard mixtures (Scott Specialty Gases or AGA Specialty Gases, NIST-traceable) containing CO, CO_2 and CH_4 in zero air.

The minimum detection limit for CO is 0.06 ppmv and for CH_4 it is 0.2 ppmv, whereas for CO_2 it is ~3 ppmv. The precision of measurements is generally better than 10%. The detailed description of the method and the method validation are included in the Appendix B (Shire, M.Sc. Thesis, Section 5).

3.2 Carbonyl Compound Analysis

The samples were analyzed in batches by Dr. Kochy Fung at the AtmAA, Inc., laboratory. Analysis was performed by injecting each sample cartridge with a known amount of an internal standard and eluting with acetonitrile. The eluent was injected by an autosampler into a high performance liquid chromatograph (Shimadzu LC-6) for separation and quantitation of the hydrazones (Fung and Grosjean, 1981). Ambient air samples typically contain C_1–C_6 carbonyls and benzaldehyde, with formaldehyde, acetaldehyde, and acetone being most abundant. Higher carbonyls include methyl ethyl ketone (MEK), pentanones, and cyclohexanone. Aldehydes $>C_3$ are generally found in much lower concentrations than the corresponding ketones.

Complete speciation of C_1–C_6 carbonyls was possible, but at the expense of increased cost to the program due to significant lengthening of the analysis and data processing time.

Since photochemical modelers, the end users of the data, routinely group higher carbonyls together for their work, it was decided that the program would benefit from reduced costs without impact on quality by obtaining individual species data only for C_1–C_3 carbonyls, and group concentration data (by carbon number) for C_4–C_6 carbonyls (e.g., sum of C_4s, C_5s, etc.).

3.3 Gasoline Headspace Analysis

For gasoline headspace vapor analysis, approximately 2 ml of each gasoline sample was placed in a 4 ml amber glass vial with a Teflon septum. The vials were equilibrated at room temperature for approximately 6 hr. Seven microliters of the vapor phase from above the liquid was drawn into a gas-tight syringe and injected in the splitless mode into a 100 m long Supelco Petrocol DH capillary column (0.25 mm ID, 0.5 µm film thickness). The injector temperature was 200 °C and the GC conditions were as follows: -60 °C for 1 min, than increased to 45 °C with the rate of 8 °C/min, held for 15 min at this temperature, than increased to 60 °C at 1 °C/min, held for 15 min and finally increased to 220 °C at 2 °C/min and held at 220 °C for another 5 min. The total run was approximately 1 hr 30 min.

3.4 Data Processing

The general scheme for our data processing is presented here. The goal of our data processing is to provide accurate data combined into a single database for each analysis type. A raw data signal is collected from the detector and stored as a digitized signal by the computer system. This signal is translated into a chromatogram by the chromatography software and integrated to give peaks and areas of those peaks. Using the appropriate response factors, area counts are converted to the calibration parameter (mass or concentration, depending on the instrument). The laboratory technician reviews this information and adjusts the integration as necessary. A report is generated by the chromatography system.

For canister measurements, the report is examined immediately after the run to verify that peak integrations have been performed properly. The peak integration, retention times, and peak identifications assigned by the ChromPerfect software are stored to disk as an ASCII file. The files are then read into a Foxpro data file for additional processing and verification of peak identifications. The peak assignments for the major constituents (typically about a dozen peaks) in the chromatogram are manually verified and retention times are recalculated for all detectable peaks based upon regression between sample and reference retention times for the manually identified peaks. The adjusted retention times are used to assign peak identifications for all detectable peaks (the reference file currently contains 160 identified compounds). The retention time adjustments and peak assignments are executed automatically by a Foxpro program. The ChromPerfect and subsequent confirmatory peak identifications are then compared and discrepancies are resolved by the analyst based on peak patterns or confirmatory identification by GC/MS. In the final step, the Level I validated data are appended to the master database. Each sample appears as a record within the database and is identified by a unique sample identification, site, date, and time and as a primary, collocated, blank, spiked, or replicate sample. This database is submitted in dBase format on 3.5" diskettes with this report.

4.0 RESULTS AND DISCUSSION

4.1 Canister Samples

Table 4-1 lists VOC quantified from the canister samples by three different methods (cryogenic preconcentration and analysis using the DB-1 capillary column and using the GS-Alumina PLOT column, and $CO/CO_2/CH_4$ analysis) together with their corresponding mnemonics. The third column in Table 4-1 describes the type of compound: '**n**' means non-hydrocarbon and '**o**' means oxygenated compound. The fourth column lists the carbon number for a given compound; note that only methanol, ethanol and MTBE have had their effective carbon numbers determined experimentally (see Sections 3.1.2 and 3.1.3) and these numbers are used to convert the GC/FID concentration numbers reported in ppbC to true ppbv concentrations for these compounds. Since the GC/FID systems are calibrated in ppbC based on the uniform carbon response of the FID to hydrocarbons, and the compound-specific calibration for species flagged as '**o**' and '**n**' are not performed (with the exception of methanol, ethanol and MTBE), these species are not reported individually in the final database. The ppbC concentration numbers for species flagged with '**n**' and '**o**' are summed together and reported as 'Identified other compounds' (IDOTHER). 'Identified oxygenated (ppbv)' (IDOXY) gives the total concentration of methanol, ethanol and MTBE only (in ppbv). CO, CO_2 and CH_4 concentrations are reported in ppmv, based on the calibration with standard compounds.

The results of analysis of all ambient canister samples collected in 1995 and 1996 are submitted in dBase format on a 3.5" diskette (no. I) with this report. The files RGALC_95 and RGALC_96 contain data for all ambient samples collected in 1995 and in 1996, respectively. The files GAR_95 and GAR_96 contain data for canister samples collected in the UCLA garage in 1995, and in the Ronald Reagan garage in 1996, respectively. The structure for these files is listed in Table 4-2. Field #1 gives the sampling location; field gives #2 the canister identification number; field #3 lists the QA lot for canister certification; fields # 4 and 5 give sampling and analysis date, respectively; field #6 lists the identification of the sample's raw chromatographic file; field #7 lists the sample's identification code; field #8 defines the analysis type as primary (p) or replicate (r); and field #9 is used as needed by the program. Fields #10 through 162 give the concentrations for individual compounds (see Table 4-1 for explanation of mnemonics) and fields #163 through 166 give the total concentrations for identified NMHC, unidentified compounds, identified oxygenated compounds, identified other compounds, and total background from the column. Please note that concentrations of all compounds are listed in ppbC, with exception of CO, CO_2, CH_4 (in ppmv) and methanol, ethanol, MTBE, and identified oxy (in ppbv).

Although methanol and ethanol concentrations are listed in these files, these numbers are not very accurate. As determined by Shire (1996) (see Appendix B, M.Sc. thesis, Section 3), the three-bed adsorbent method is superior for methanol and ethanol quantification, and the results from this analysis are discussed below in Section 4.1.1.

Table 4-1. List of VOC Quantified from Canisters

Name	Mnemonic	Flag	Carbon No.
carbon monoxide	CO_PPM		1
carbon dioxide	CO2PPM		1
methane	METHAN		1
ethane	ETHANE		2
ethene	ETHENE		2
acetylene	ACETYL		2
1-butene	LBUT1E		4
iso-butene	LIBUTE		4
C2 compounds	C2CMPD		2
propene	PROPE		3
propane	N_PROP		3
Freon 12	FRE12	n	1
isobutane	I_BUTA		4
1-butene&i-butene	BEABYL		4
1,3-butadiene	BUDI13		4
n-butane	N_BUTA		4
methanol	METOH	o	0.58
t-2-butene	T2BUTE		4
1&2-butyne	BUTYN		4
c-2-butene	C2BUTE		4
3-methyl-1-butene	B1E3ME		5
ethanol	ETHOH	o	1.18
acetonitrile	ACN	n	2
isopentane	IPENTA		5
acetone	ACETO	o	3
1-pentene	PENTE1		5
2-methyl-1-butene	B1E2M		5
n-pentane	N_PENT		5
isoprene	I_PREN		5
t-2-pentene	T2PENE		5
c-2-pentene	C2PENE		5
2-methyl-2-butene	B2E2M		5
F113	F113	n	2
2,2-dimethylbutane	BU22DM		6
2-methylpropanal	PRAL2M	o	4
cyclopentene	CPENTE		5
methacrolein	MEACRO	o	2
4-methyl-1-pentene	P1E4ME		6
cyclopentane	CPENTA		5
2,3-dimethylbutane	BU23DM		6
MTBE	MTBE	o	4.37
2-methylpentane	PENA2M		6
butanal	BUAL	o	4
butanone	BUONE	o	4
3-methylpentane	PENA3M		6
2-methyl-1-pentene	P1E2ME		6
1-hexene	HEX1E		6
C6 olefin	C6OLE1		6
n-hexane	N_HEX		6
t-3-hexene + chloroform	T3HEXE		6
c-3-hexene	C3HEXE		6
t-2-hexene	T2HEXE		6
2-methyl-2-pentene	P2E2ME		6
c-2-hexene	C2HEXE		6
3-methyl-2-pentene	P2E3ME		6
2,2-dimethylpentane	PEN22M		7
methylcyclopentane	MCYPNA		6
2,4-dimethylpentane	PEN24M		7
mechloroform	MECLOR	n	2
2,2,3-trimethylbutane	BU223M		7
1-methylcyclopentene	CPENE1		6
benzene	BENZE		6
3,3-dimethylpentane	PEN33M		7
cyclohexane	CYHEXA		6
4-methylhexene	HEXE4M		7
2-methylhexane	HEXA2M		7
2,3-dimethylpentane	PEN23M		7
cyclohexene	CYHEXE		6
3-methylhexane + pentanal	HEXA3M		7
C7 olefin	C7OLE1		7
1,3-dimethylcyclopentane	CPA13M		7
3-ethylpentane	PA3ET		8

Table 4-1. List of VOC Quantified from Canisters (cont.)

Name	Mnemonic	Flag	Carbon No.	Name	Mnemonic	Flag	Carbon No.
2,2,4-trimethylpentane	PA224M		8	m- & p-xylene	MP_XYL		8
C7 olefin	C7OLE2		7	2-methyloctane	OCT2ME		9
t-3-heptene	T3HEPE		7	3-methyloctane	OCT3ME		9
n-heptane	N_HEPT		7	C9 paraffin	C9PAR1		9
C8 olefin	C8OLE1		8	styrene + heptanal	STYR		8
C8 olefin	C8OLE2		8	o-xylene	O_XYL		8
C8 olefin	C8OLE3		8	nonene-1	NONE1		9
2,4,4-trimethyl-1-pentene	P1E244		8	C9 paraffin	C9PAR2		9
methylcyclohexane	MECYHX		7	n-nonane	N_NON		9
C8 paraffin	C8PA1		8	C9 paraffin	C9PAR3		9
2,5-diemthylhexane	HEX25M		8	C9 olefin	C9OLE4		9
2,4-diemthylhexane	HEX24M		8	C9 paraffin	C9PAR4		9
C8 paraffin	C8PA2		8	isopropylbenzene	IPRBZ		9
2,3,4-trimethylpentane	PA234M		8	isopropylcyclohexane	IPCYHX		9
toluene	TOLUE		7	alpha-pinene	A_PINE		10
2,3-dimethylhexane	HX23DM		8	benzaldehyde	BZALDE	o	7
2-methylheptane	HEP2ME		9	2,6-dimethyloctane	OCT26D		10
4-methylheptane	HEP4ME		9	C10 olefin	C10OL1		10
C8 paraffin	C8PA3		8	3,6-dimethyloctane	OCT36M		10
3-methylheptane	HEP3ME		8	n-propylbenzene	N_PRBZ		9
hexanal	HEXAL	o	6	m-ethyltoluene	M_ETOL		9
2,2,5-trimethylhexane	HEX225		9	p-ethyltoluene	P_ETOL		9
octene-1	OCT1E		8	1,3,5-trimethylbenzene	BZ135M		9
1,1-dimethylcyclohexane	CHX11M		8	C10 paraffin	C10P_A		10
n-octane	N_OCT		8	o-ethyltoluene	O_ETOL		9
2,3,5-trimethylhexane	HEX235		9	beta-pinene	B_PINE		10
2,4-dimethylheptane	HEP24D		9	1,2,4-trimethylbenzene	BZ124M		9
4,4-dimethylheptane	HEP44D		9	n-decane	N_DEC		10
2,6-dimethylheptane	HEP26D		9	C10 aromatic	C10AR1		10
2,5-dimethylheptane	HEP25D		9	isobutylbenzene	I_BUBZ		10
3,3-dimethylheptane	HEP33D		9	C10 olefin	C10OL2		10
C9 olefin	C9OLE1		9	1,2,3-trimethylbenzene	BZ123M		9
C9 olefin	C9OLE2		9	C10 paraffin	C10P_C		10
ethylbenzene	ETBZ		8	indan	INDAN		9
C9 olefin	C9OLE3		9	indene	INDENE		9

Table 4-1. List of VOC Quantified from Canisters (cont.)

Name	Mnemonic	Flag	Carbon No.
diethylbenzene	DETBZ1		10
C10 aromatic	C10AR2		10
diethylbenzene	DETBZ2		10
n-butylbenzene	N_BUBZ		10
diethylbenzene	DETBZ3		10
C10 aromatic	C10AR3		10
1,3-dimethyl-4-ethylbenzene	BZDME		10
C10 aromatic	C10AR4		10
isopropyltoluene	IPRTOL		10
n-undecane	N_UNDE		11
C10 aromatic	C10AR5		10
C11 paraffin	C11P_A		11
1,2,4,5-tetramethylbenzene	BZ1245		10
1,2,3,5-tetramethylbenzene	BZ1235		10
C11 paraffin	C11P_B		11
2-methylindan	IND_2M		10
1-methylindan	IND_1M		10
C11 aromatic	C11AR1		11
C11 aromatic	C11AR3		11
naphthalene	NAPHTH		10
n-dodecane	N_DODE		12
Total Identified NMHC	IDNMHC		1
Unidentified	UNID		1
Identified oxygenated (ppbv)	IDOXY		1
Identified other compounds	IDOTHR		1
Total Background	T_BKG		1
cis-3-methyl-2-pentene	P2E3MC		6
trans-3-methyl-2-pentene	P2E3MT		6
3-methyl-1-pentene	P1E3ME		6
sec-butylbenzene	S_BUBZ		10
limonene	LIMON		10

Table 4-2. Structure for Database Files in FoxPro

Structure for table: h:\arb_rfg\rgalc_96.dbf
Number of data records: 280
Date of last update: 04/23/97

Field	Field Name	Field Type	Width	Dec
1	LOCATION	C	10	0
2	CANISTER	C	7	0
3	QA_LOT	N	3	0
4	SMPL_DATE	D	8	0
5	AN_DATE	D	8	0
6	RAW_FILE	C	14	0
7	CID	C	14	0
8	AN_TYPE	C	2	0
9	SAVE1	C	10	0
10	CO_PPM	N	9	2
11	CO2PPM	N	9	2
12	METHAN	N	9	2
13	ETHANE	N	9	2
14	ETHENE	N	9	2
15	ACETYL	N	9	2
16	LBUT1E	N	9	2
17	LIBUTE	N	9	2
18	C2CMPD	N	9	2
19	PROPE	N	9	2
20	N_PROP	N	9	2
21	I_BUTA	N	9	2
22	BEABYL	N	9	2
23	BUDI13	N	9	2
24	N_BUTA	N	9	2
25	T2BUTE	N	9	2
26	BUTYN	N	9	2
27	C2BUTE	N	9	2
28	B1E3ME	N	9	2
29	IPENTA	N	9	2
30	PENTE1	N	9	2
31	B1E2M	N	9	2
32	N_PENT	N	9	2
33	I_PREN	N	9	2
34	T2PENE	N	9	2
35	C2PENE	N	9	2
36	B2E2M	N	9	2
37	BU22DM	N	9	2
38	CPENTE	N	9	2
39	P1E4ME	N	9	2
40	CPENTA	N	9	2
41	BU23DM	N	9	2
42	PENA2M	N	9	2
43	PENA3M	N	9	2
44	P1E2ME	N	9	2
45	HEX1E	N	9	2
46	C6OLE1	N	9	2
47	N_HEX	N	9	2
48	T3HEXE	N	9	2
49	C3HEXE	N	9	2
50	T2HEXE	N	9	2
51	P2E2ME	N	9	2
52	C2HEXE	N	9	2
53	P2E3ME	N	9	2
54	PEN22M	N	9	2
55	MCYPNA	N	9	2
56	PEN24M	N	9	2
57	BU223M	N	9	2
58	CPENE1	N	9	2
59	BENZE	N	9	2
60	PEN33M	N	9	2
61	CYHEXA	N	9	2
62	HEXE4M	N	9	2
63	HEXA2M	N	9	2
64	PEN23M	N	9	2
65	CYHEXE	N	9	2
66	HEXA3M	N	9	2
67	C7OLE1	N	9	2
68	CPA13M	N	9	2
69	PA3ET	N	9	2
70	PA224M	N	9	2
71	C7OLE2	N	9	2
72	T3HEPE	N	9	2
73	N_HEPT	N	9	2
74	C8OLE1	N	9	2
75	C8OLE2	N	9	2
76	C8OLE3	N	9	2
77	P1E244	N	9	2
78	MECYHX	N	9	2
79	C8PA1	N	9	2
80	HEX25M	N	9	2
81	HEX24M	N	9	2
82	C8PA2	N	9	2

Table 4-2.   Structure for Database Files in FoxPro (cont.)

Structure for table: h:\arb_rfg\rgalc_96.dbf
Number of data records: 280
Date of last update: 04/23/97

Field	Field Name	Field Type	Width	Dec
83	PA234M	N	9	2
84	TOLUE	N	9	2
85	HX23DM	N	9	2
86	HEP2ME	N	9	2
87	HEP4ME	N	9	2
88	C8PA3	N	9	2
89	HEP3ME	N	9	2
90	HEX225	N	9	2
91	OCT1E	N	9	2
92	CHX11M	N	9	2
93	N_OCT	N	9	2
94	HEX235	N	9	2
95	HEP24D	N	9	2
96	HEP44D	N	9	2
97	HEP26D	N	9	2
98	HEP25D	N	9	2
99	HEP33D	N	9	2
100	C9OLE1	N	9	2
101	C9OLE2	N	9	2
102	ETBZ	N	9	2
103	C9OLE3	N	9	2
104	MP_XYL	N	9	2
105	OCT2ME	N	9	2
106	OCT3ME	N	9	2
107	C9PAR1	N	9	2
108	STYR	N	9	2
109	O_XYL	N	9	2
110	NONE1	N	9	2
111	C9PAR2	N	9	2
112	N_NON	N	9	2
113	C9PAR3	N	9	2
114	C9OLE4	N	9	2
115	C9PAR4	N	9	2
116	IPRBZ	N	9	2
117	IPCYHX	N	9	2
118	A_PINE	N	9	2
119	OCT26D	N	9	2
120	C10OL1	N	9	2
121	OCT36M	N	9	2
122	N_PRBZ	N	9	2
123	M_ETOL	N	9	2
124	P_ETOL	N	9	2
125	BZ135M	N	9	2
126	C10P_A	N	9	2
127	B_PINE	N	9	2
128	O_ETOL	N	9	2
129	BZ124M	N	9	2
130	N_DEC	N	9	2
131	C10AR1	N	9	2
132	I_BUBZ	N	9	2
133	C10OL2	N	9	2
134	BZ123M	N	9	2
135	C10P_C	N	9	2
136	INDAN	N	9	2
137	INDENE	N	9	2
138	DETBZ1	N	9	2
139	C10AR2	N	9	2
140	DETBZ2	N	9	2
141	N_BUBZ	N	9	2
142	DETBZ3	N	9	2
143	C10AR3	N	9	2
144	BZDME	N	9	2
145	C10AR4	N	9	2
146	IPRTOL	N	9	2
147	N_UNDE	N	9	2
148	C10AR5	N	9	2
149	C11P_A	N	9	2
150	BZ1245	N	9	2
151	BZ1235	N	9	2
152	C11P_B	N	9	2
153	IND_2M	N	9	2
154	IND_1M	N	9	2
155	C11AR1	N	9	2
156	C11AR3	N	9	2
157	NAPHTH	N	9	2
158	N_DODE	N	9	2
159	OXY_PPBV	N	9	2
160	METOH	N	9	2
161	ETHOH	N	9	2
162	MTBE	N	9	2
163	IDNMHC	N	9	2
164	UNID	N	9	2
165	IDOXY	N	9	2
166	IDOTHR	N	9	2
167	T_BKG	N	9	2
168	EMPTY	N	9	2

4.1.1 Methanol and Ethanol

The method for measuring methanol and ethanol by three-bed solid adsorbent cartridges and thermal desorption is described in detail by Shire (1996) (Appendix B, M.Sc. Thesis, Section 3). Since this method was not validated in time for the analysis of the Summer 1995 samples, only the results from the analysis of 1996 samples are given here. After the analysis for C_2–C_{12} hydrocarbons was completed, the aliquot from the canister samples was adsorbed onto a three-bed solid adsorbent cartridge and the cartridge was analyzed within two weeks by the thermal desorption method, as described in Section 3.1.3. The solid adsorbent data were compared with data obtained from the analysis of canister samples by the preconcentration method (modified TO-14 method) and were validated as follows:

1. The ratios of MTBE (as measured by the solid adsorbent and TO-14 methods) to benzene (from the TO-14 method) were compared and the outliers were removed from the solid adsorbent database; approximately 5% of the samples were invalidated during this step.

2. The concentrations of n-pentane measured by the solid adsorbent and TO-14 methods were compared; if the difference in concentrations exceeded 35%, the cartridge results were invalidated and removed from the database.

Approximately 25% of the total measurements were invalidated during this two-step validation procedure. The concentrations of methanol and ethanol measured in the remaining samples are shown in Figure 4-1 and in Table 4-3. Several 'spikes' in methanol and ethanol concentrations observed at all three sites are probably due to local sources; they do not correlate with other motor vehicle related pollutants, and they occurred at different times at each site. Gasoline currently sold in California does not contain methanol or ethanol as sources of oxygen. Methanol and ethanol might be present in very small amounts as contaminants in MTBE. Also, there is little M85 gasoline used in California. Thus, a rise in the concentrations of these alcohols due to the introduction of RFG is not expected to occur. Mean morning concentrations at Azusa, Burbank and North Main are 14, 15, and 30 ppbv for methanol and 6, 9, and 5 ppbv for ethanol, respectively. Afternoon concentrations are 10, 11, and 15 ppbv for methanol and 3, 4, and 5 ppbv for ethanol at Azusa, Burbank and North Main, respectively.

4.1.2 MTBE

Two analytical methods were compared for quantifying MTBE (Shire, 1996, M.Sc. Thesis, Appendix B, Section 4); the solid multi-adsorbent method and the preconcentration method (modified TO-14 method). It has been found that MTBE can be quantified, along with C_2–C_{12} hydrocarbons, using both the modified TO-14 method (no Nafion® permeable membrane or other moisture-removal device used prior to injection) and the solid multi-adsorbent method. The comparison of MTBE concentrations obtained by these two independent methods shows excellent agreement; the values obtained from the multibed adsorbent method were on average 6% higher than the values obtained by modified TO-14 method.

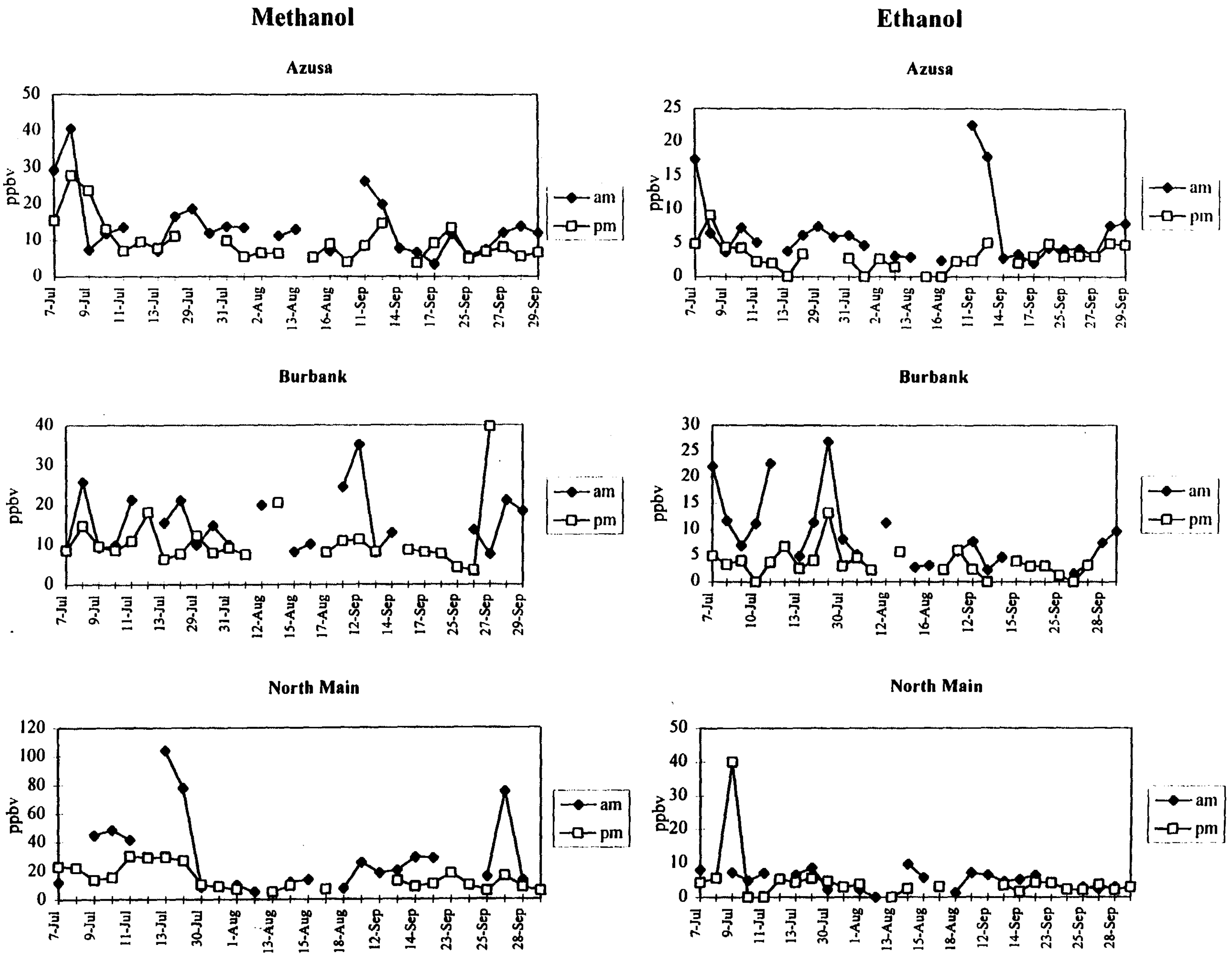


Figure 4-1. Methanol and ethanol concentrations measured at Azusa, Burbank and Los Angeles (N. Main) sampling sites during 1996 sampling campaign.

Table 4-3. Methanol and Ethanol Concentrations (ppbv) Observed In SoCAB in Summer 1996

Sampling	Azusa				Burbank				Los Angeles (N. Main)			
	Methanol		Ethanol		Methanol		Ethanol		Methanol		Ethanol	
Date	am	pm	am	pm	am	pm	am	pm	am	pm	am	pm
7-Jul	29.27	15.52	17.51	4.91	8.69	8.54	22.12	4.94	11.97	23.00	8.09	4.33
8-Jul	40.56	27.79	6.49	9.15	25.73	14.72	11.71	3.36		22.07		5.63
9-Jul	7.30	23.74	3.71	4.39	9.17	9.57	6.91	4.03	44.78	13.66	7.29	40.04
10-Jul	11.83	13.03	7.31	4.27	9.78	8.54	11.12	0.00	48.60	15.39	4.90	0.00
11-Jul	13.62	7.04	5.15	2.23	21.17	10.82	22.64	3.71	41.65	30.18	7.04	0.00
12-Jul		9.58		1.98		18.06		6.73		29.22		5.24
13-Jul	7.01	7.81	3.82		15.51	6.26	4.87	2.58	104.07	29.47	6.57	4.32
28-Jul	16.68	11.14	6.18	3.36	21.10	7.65	11.32	4.07	77.94	27.07	8.64	5.52
29-Jul	18.77		7.49		9.91	12.26	26.85	13.14				
30-Jul	12.03		5.97		14.77	7.88	8.11	3.02	8.45	10.20	2.24	4.66
31-Jul	13.88	9.85	6.19	2.74	9.93	9.07	5.19	4.56		8.83		2.94
1-Aug	13.48	5.41	4.68	0.00					10.08	6.96	2.20	3.76
2-Aug		6.51		2.66		7.44		2.30	5.21		0.00	
12-Aug	11.25	6.38	3.10	1.46	19.87		11.26					
13-Aug	12.99		2.94			20.49		5.68		5.12		0.00
14-Aug		5.30							11.91	9.49	9.75	2.53
15-Aug					8.12		2.83		13.68		5.74	
16-Aug	7.05	8.95	2.43	0.00	10.12		3.18					
17-Aug						7.96		2.33		6.97		3.13
18-Aug		4.01		2.30					7.50		1.29	
11-Sep	26.28	8.52	22.50	2.37	24.40	10.87	5.74	5.93	25.56		7.16	
12-Sep	19.93	14.71	17.91	5.08	35.17	11.21	7.66	2.42	18.22		6.58	
13-Sep					7.75	8.06	2.33	0.00	20.11	13.03	4.63	3.55
14-Sep	7.83		2.83		12.90		4.68		29.11	8.73	5.22	1.66
15-Sep						8.61		3.90				
16-Sep	6.75	3.81	3.37	2.05								
17-Sep	3.47	9.28	2.03	3.01		8.00		2.97	28.62	10.54	6.46	4.34
23-Sep						7.61		3.02		18.02		4.20
24-Sep	11.77	13.50	4.33	4.90						9.72		2.34
25-Sep	5.86	5.03	4.14	3.01		4.14		1.26	15.73	5.80	2.93	2.17
26-Sep	7.60	6.89	4.25	3.15	13.57	3.41	1.57	0.00				
27-Sep	12.13	8.15	3.14	3.07	7.49	39.65	3.35	3.16	75.35	16.22	2.42	3.70
28-Sep	13.92	5.56	7.67	4.99	21.04		7.42		13.21	8.31	3.04	2.13
29-Sep	12.02	6.63	7.98	4.80	18.35		9.60			5.59		2.98
Average	13.73	9.77	6.53	3.30	15.45	10.90	9.07	3.61	30.59	14.50	5.11	4.75

We found during the analysis of MTBE gaseous standards (520 ppb of MTBE in dry nitrogen, Spectra Gases, Aloha, NJ) that heating of the stainless-steel injection transfer lines in the modified TO-14 method produces a significant reduction in MTBE concentration. This was most probably due to the thermal decomposition of MTBE, since the concentration of isobutene (thermal decomposition product of MTBE) increased simultaneously. If the MTBE standard was made in humid UHP zero air, the decomposition was not so severe. Our standard operating procedures for the analysis of the canister samples require a heating of the stainless-steel injection transfer lines for the modified TO-14 method, in order to account for VOC with higher boiling point, $>C_{10}$. In analyzing the ambient air samples collected in the SoCAB area, we found that, when the transfer lines were heated, the measured values of MTBE were approximately 7% lower than when the lines were not heated. For consistency, all of the samples collected during 1995 and 1996 sampling campaign in SoCAB were analyzed with the transfer line heated to ~100 °C. The reported MTBE values are not corrected for this decomposition, since we judged it to be not very significant. This explains why the MTBE concentrations obtained from the multibed adsorbent method were, on average, 6% higher than the values obtained by the modified TO-14 method.

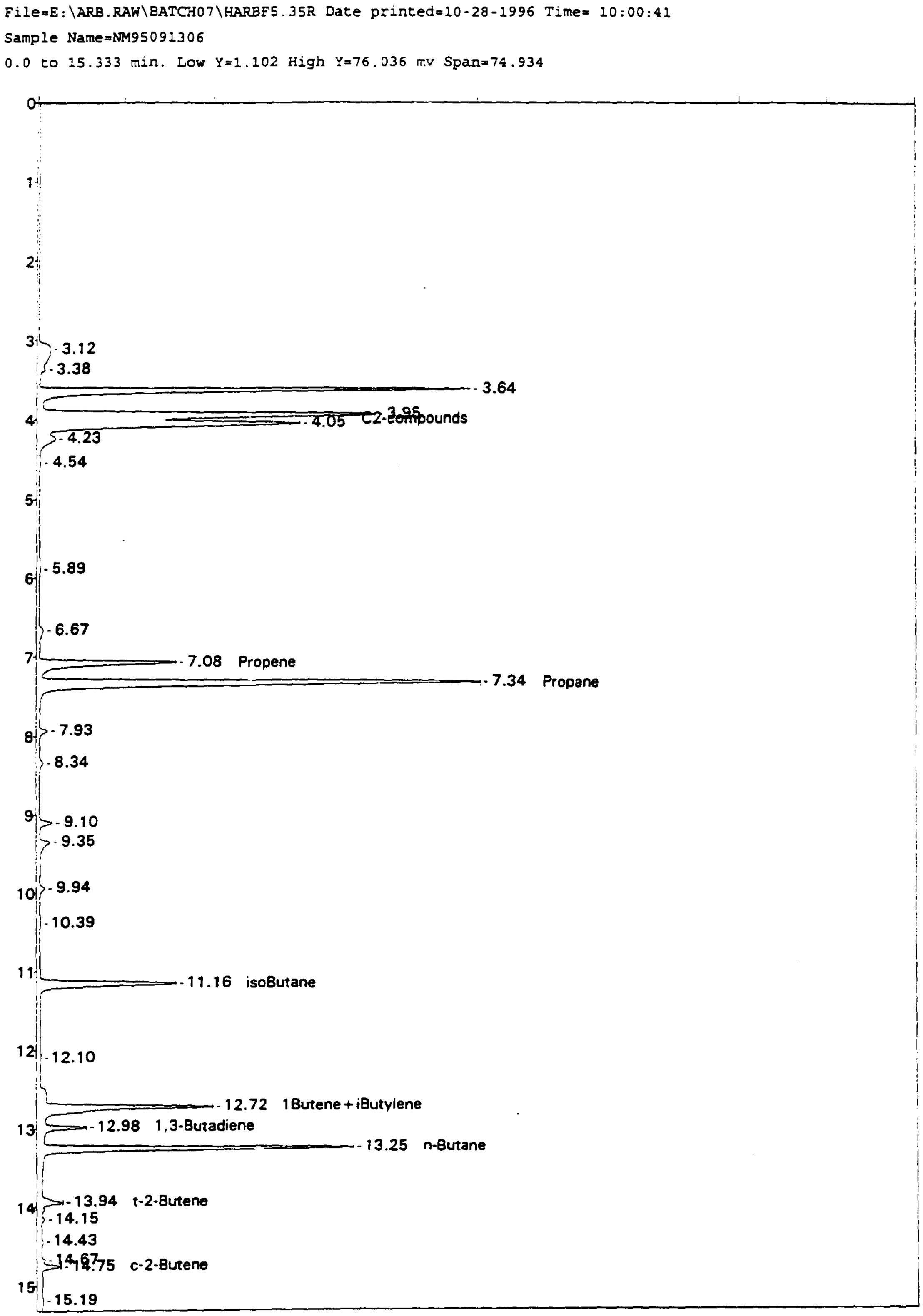
Figures 4-2 and 4-3 show the typical gas chromatogram of ambient samples collected during the 1995 and 1996 sampling campaigns, respectively. It can be seen from the comparison of these two chromatograms that the resolution between 2,3-dimethylbutane and MTBE was better in 1995 than in 1996, although an identical type of column (J&W DB-1 60 m capillary column) and chromatographic conditions were used in both years. In order to account for the differences in this chromatographic resolution between two different years, in comparing mean MTBE values in 1995 and 1996, we added 2,3-dimethylbutane concentrations (in ppbv, ppbC/6) to MTBE concentrations for both years and compared the mean MTBE values for each site for morning and afternoon sampling. Table 4-4 shows the differences in mean absolute and relative (weight %, in relation to TNMHC) MTBE concentration with and without adding 2,3-dimethylbutyl to MTBE concentrations.

As can be seen from this table, adding 2,3-dimethylbutane peak to MTBE peak did not change the percent difference between 1995 and 1996 significantly, especially for relative mean weight % abundances.

4.1.3 $CO/CO_2/CH_4$

The detailed description of the $CO/CO_2/CH_4$ analysis method and its validation is described in Appendix B (Shire M.Sc. Thesis, Section 5). In addition to the tests described by Shire (1996), we performed two additional method comparisons:

1. The influence on CO_2 collection efficiency of water condensation during sampling in the canister sampling equipment and in the canister was investigated. Since the CO_2 concentrations in some 1995 canister samples were lower than expected, we were concerned that water condensing during sampling in the sampling lines might scrub out some of the ambient CO_2. To test this possibility, we collected ambient air in Reno, NV, on June 5, 1996, using three



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Sample Name=NM95091306
0.0 to 15.333 min. Low Y=1.102 High Y=76.036 mv Span=74.934
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Figure 4-2. Chromatogram of ambient air sample collected in downtown Los Angeles (N. Main), September 13, 1995, and analyzed on DB-1 column for C_3–C_{12} hydrocarbons and MTBE.

```
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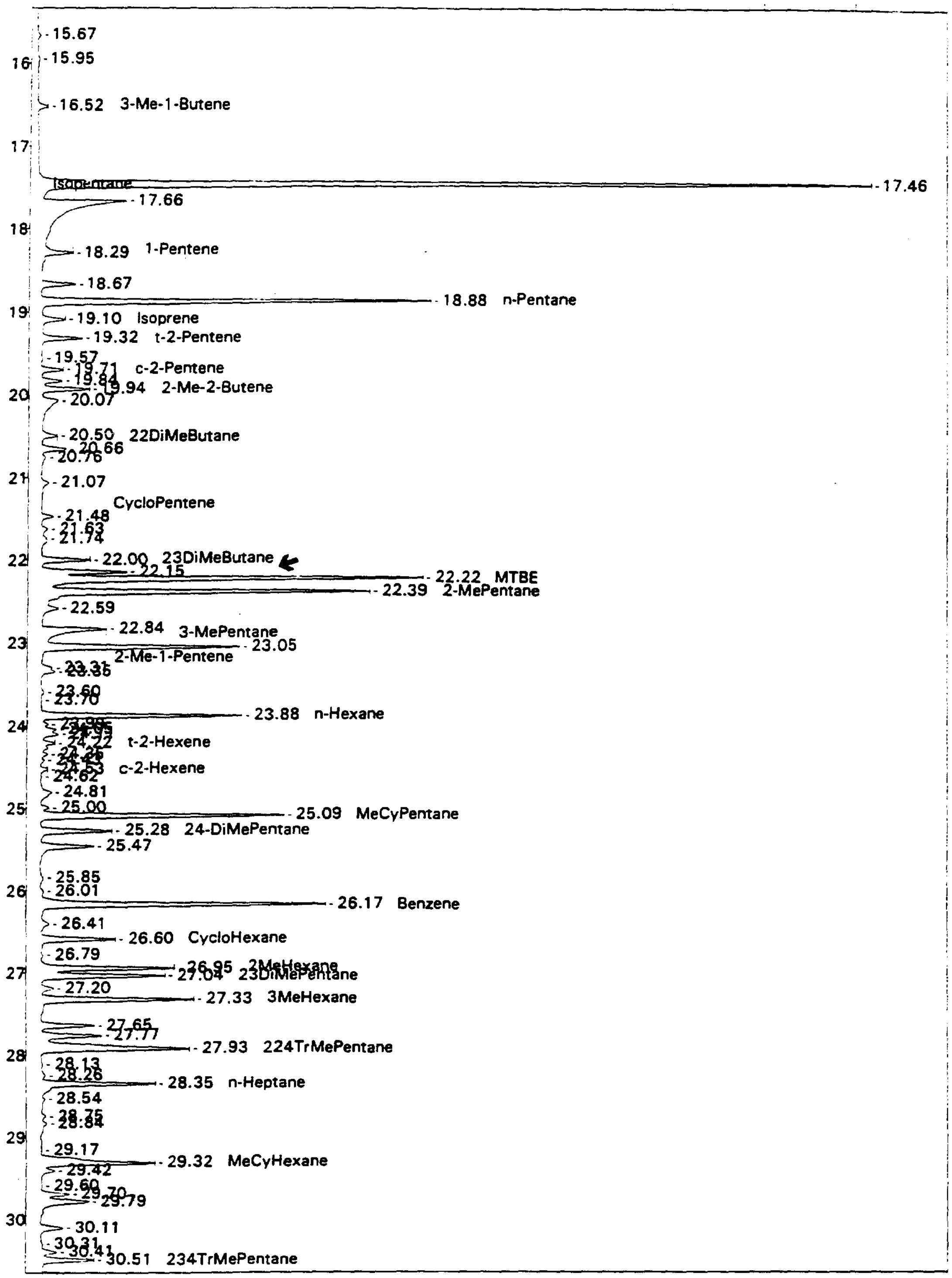

Figure 4-2. Chromatogram of ambient air sample collected in downtown Los Angeles (N. Main), September 13, 1995, and analyzed on DB-1 column for C_3–C_{12} hydrocarbons and MTBE (cont.).

```
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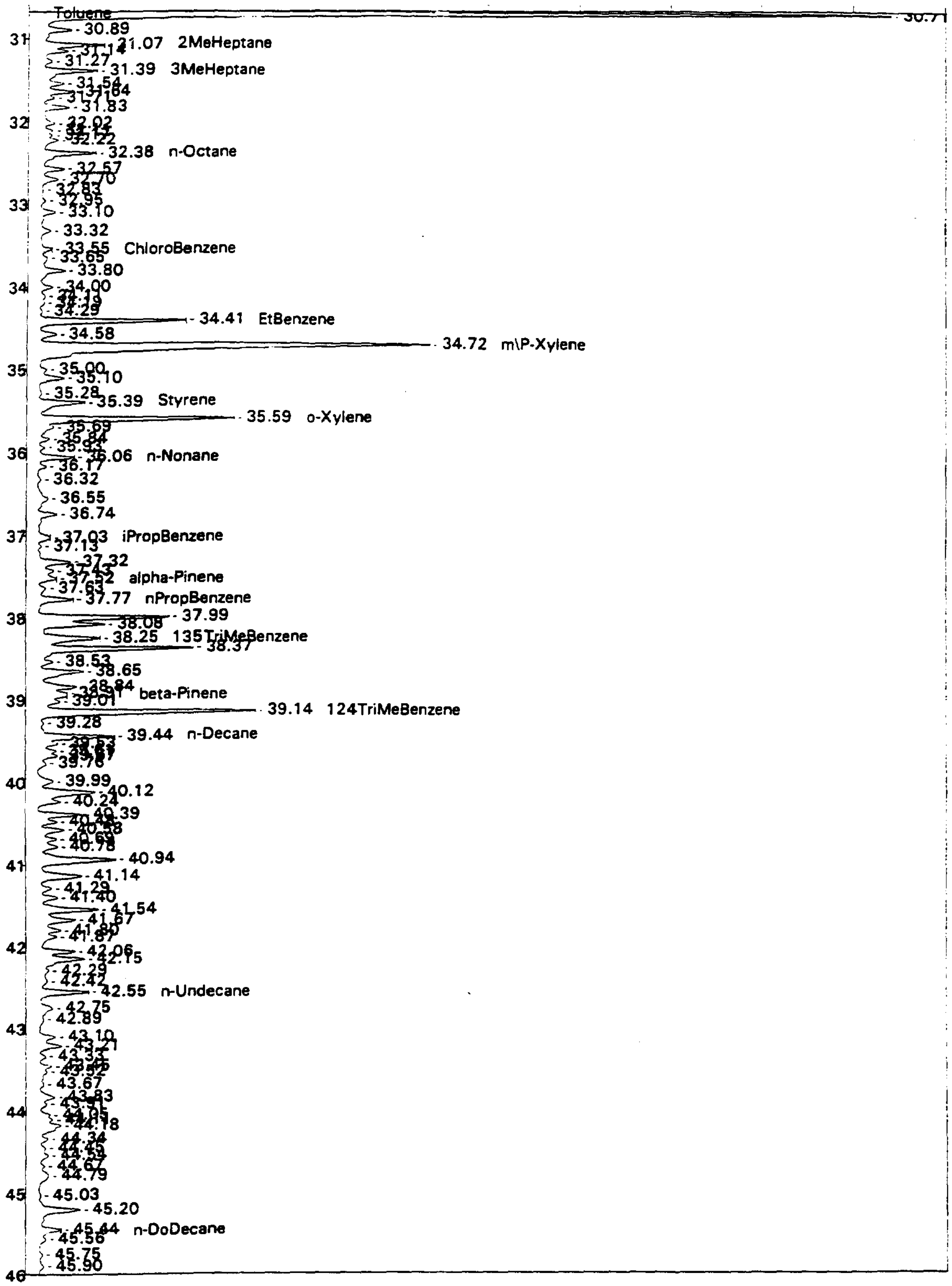

Figure 4-2. Chromatogram of ambient air sample collected in downtown Los Angeles (N. Main), September 13, 1995, and analyzed on DB-1 column for C_3–C_{12} hydrocarbons and MTBE (cont.).

NM96091313 Page1

Plot Panel 1 of 3: from 0.0 to 15.3 min.

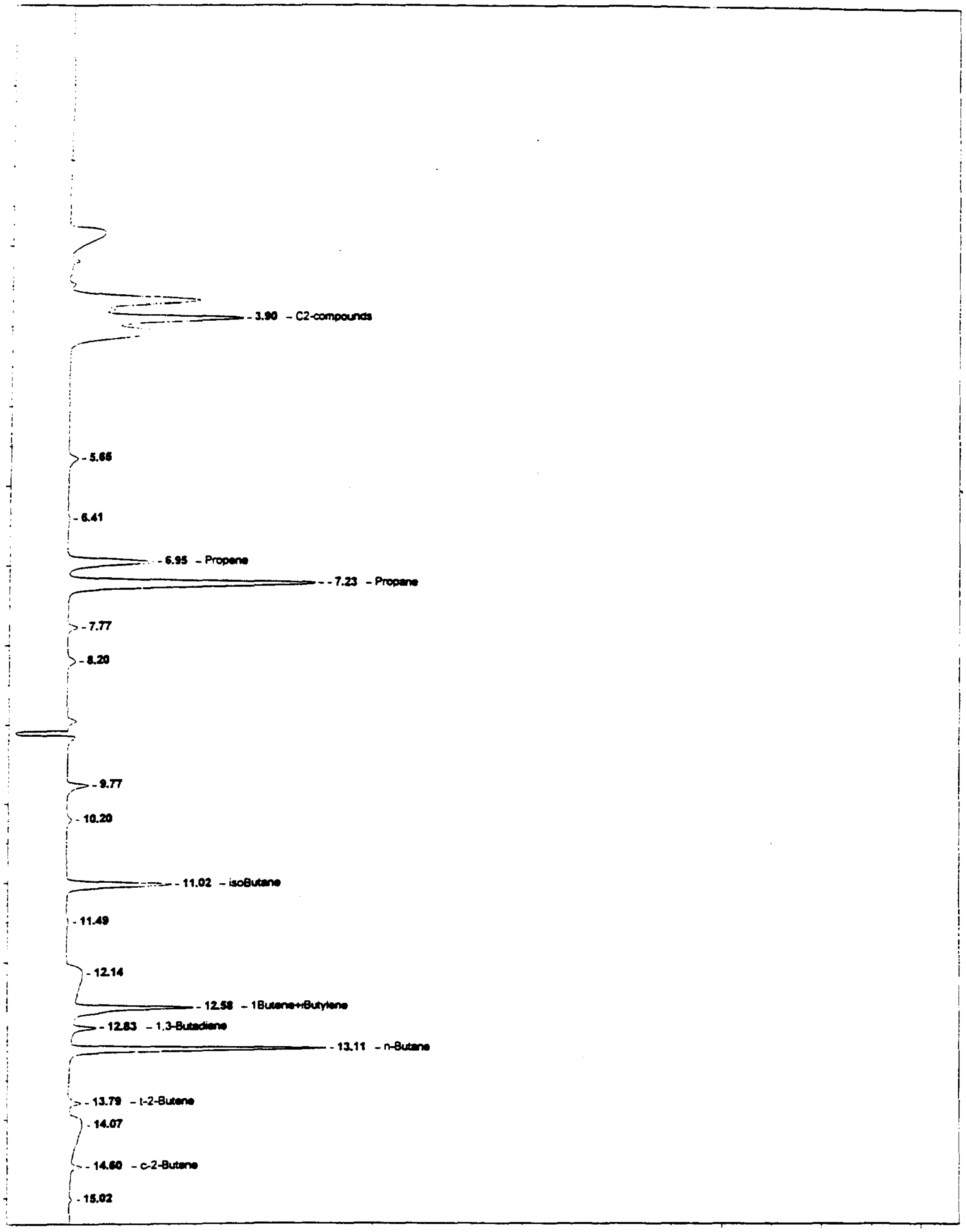

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Figure 4-3. Chromatogram of ambient air sample collected in downtown Los Angeles (N. Main), September 13, 1996 and analyzed on DB-1 column for C_3-C_{12} hydrocarbons and MTBE.

NM96091313 Page2

Plot Panel 2 of 3: from 15.3 to 30.7 min.

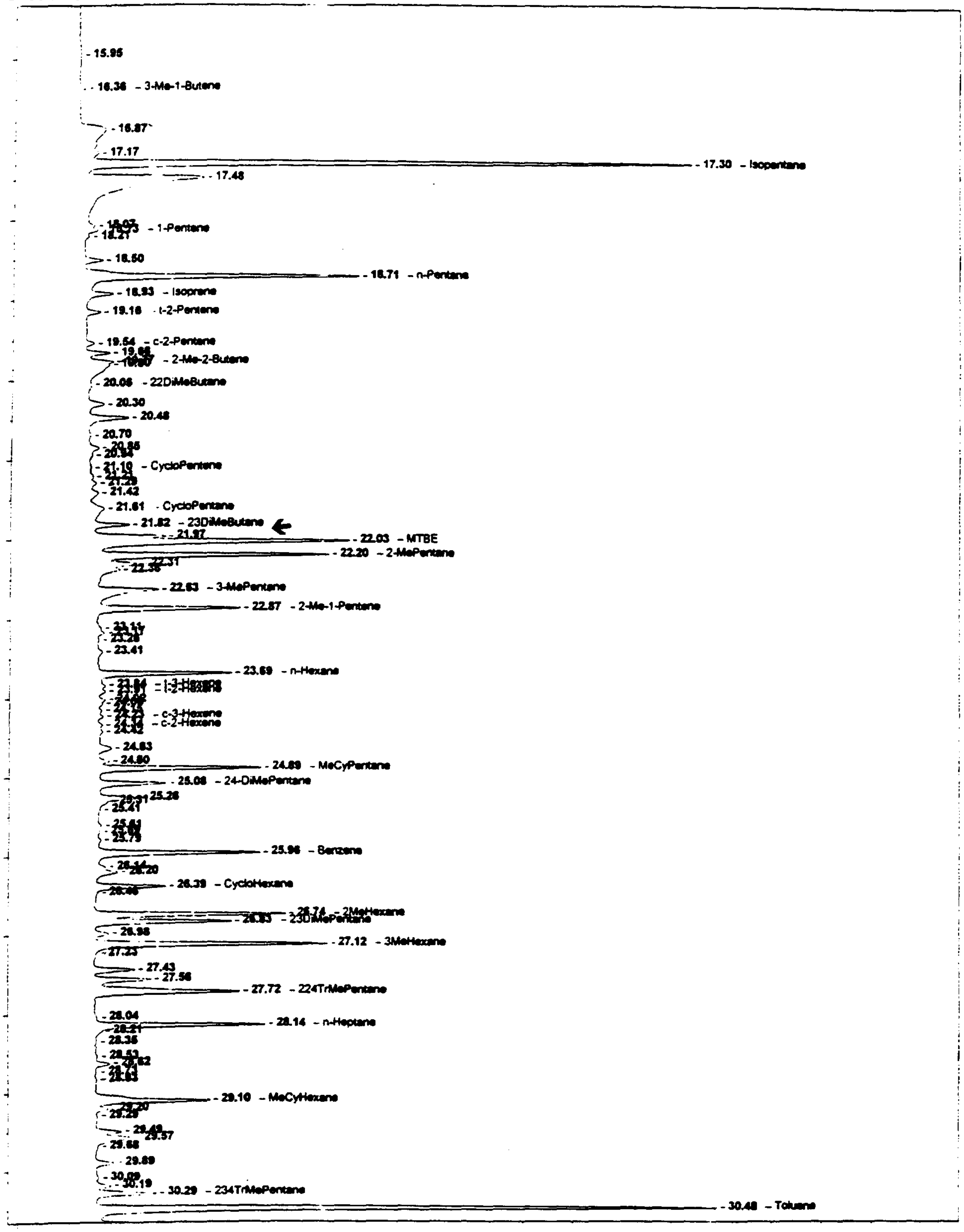

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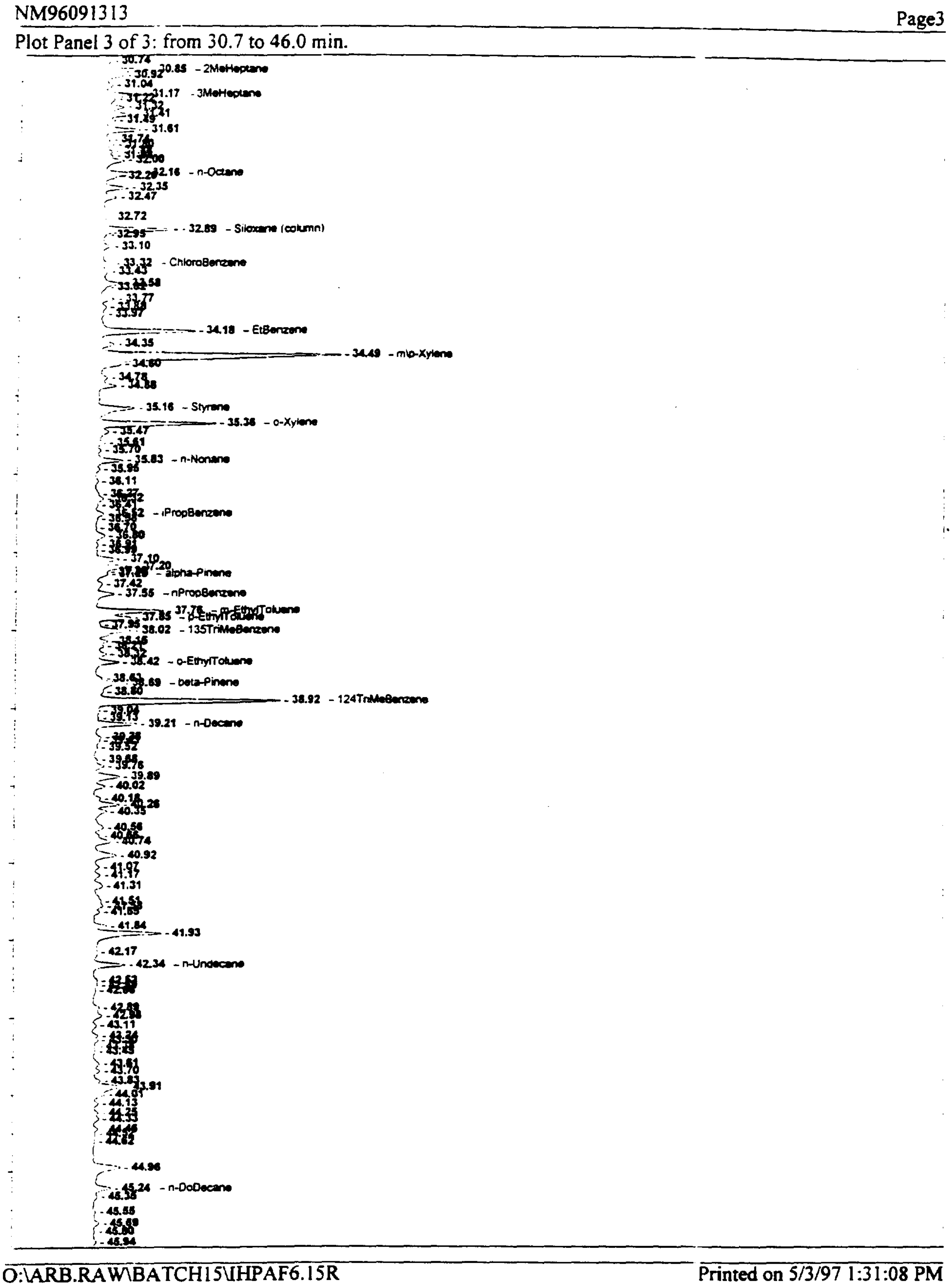
Figure 4-3. Chromatogram of ambient air sample collected in downtown Los Angeles (N. Main), September 13, 1996 and analyzed on DB-1 column for C_3-C_{12} hydrocarbons and MTBE (cont.).


NM96091313 Page3

Plot Panel 3 of 3: from 30.7 to 46.0 min.

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Figure 4-3. Chromatogram of ambient air sample collected in downtown Los Angeles (N. Main), September 13, 1996 and analyzed on DB-1 column for C_3-C_{12} hydrocarbons and MTBE (cont.).

Table 4-4. The Differences in Mean Concentrations of MTBE (±Standard Error) Observed from 1995 to 1996.

Without 2,3-dimethylbutane

	Morning			Afternoon		
Site	1995	1996	% Diff	1995	1996	% Diff
Azusa (ppbv)	4.62 ± 0.32	5.77 ± 0.47	22.12	2.70 ± 0.18	4.03 ± 0.34	39.43
Azusa (wt%)	3.51 ± 0.10	5.22 ± 0.11	39.10	3.66 ± 0.10	5.66 ± 0.15	43.03
Burbank (ppbv)	6.60 ± 0.47	7.18 ± 0.64	8.47	2.70 ± 0.17	3.94 ± 0.26	37.14
Burbank (wt%)	3.85 ± 0.10	5.64 ± 0.14	37.62	3.42 ± 0.10	5.77 ± 0.16	51.19
N. Main (ppbv)	5.32 ± 0.38	6.40 ± 0.54	18.41	2.80 ± 0.13	3.51 ± 0.22	22.51
N. Main (wt%)	3.46 ± 0.08	5.15 ± 0.13	39.38	3.40 ± 0.09	5.63 ± 0.14	49.23
S. Monica (ppbv)				0.89 ± 0.10	0.60 ± 0.15	-38.30
S. Monica (wt%)				2.16 ± 0.11	2.94 ± 0.55	30.67

With 2,3-dimethylbutane

	Morning			Afternoon		
Site	1995	1996	% Diff	1995	1996	% Diff
Azusa (ppbv)	5.03 ± 0.32	5.78 ± 0.47	13.88	2.92 ± 0.18	4.05 ± 0.34	32.42
Azusa (wt%)	3.82 ± 0.10	5.25 ± 0.11	31.53	3.95 ± 0.10	5.71 ± 0.15	36.44
Burbank (ppbv)	7.2 ± 0.47	7.12 ± 0.64	-1.12	2.96 ± 0.17	3.98 ± 0.26	29.39
Burbank (wt%)	4.21 ± 0.10	5.64 ± 0.14	29.04	3.73 ± 0.10	5.78 ± 0.16	43.11
N. Main (ppbv)	5.86 ± 0.38	6.3 ± 0.54	7.24	3.07 ± 0.13	3.54 ± 0.22	14.22
N. Main (wt%)	3.78 ± 0.08	5.64 ± 0.13	39.49	3.73 ± 0.09	5.64 ± 0.14	40.77
S. Monica (ppbv)				0.99 ± 0.10	0.65 ± 0.15	-41.46
S. Monica (wt%)				2.4 ± 0.11	3.18 ± 0.55	27.96

wt% = weight percent of given species in relation to TNMHC (both concentrations in ppbC).
Standard Error = defined as a standard deviation of all measurements divided by the square root of number of measurements .
% diff = (1996 concentration-1995 concentration)/((1995+1996 concentrations)/2))*100.

parallel samplers. Sampler #1 was equipped with a water trap, which constantly trapped and removed the condensed water before ambient air entered a canister. Sampler #2 had 2 ml of water injected into the water trap and this water was not removed during sampling. Sampler #3 was equipped with a water trap and sampled ambient air into a canister which was injected with 150 μl of water. Table 4-5 presents the results of these experiments.

Table 4-5. Influence of Water on Collection Efficiency of CO_2, CO and CH_4.

Sampler No.	Water Content	CO (ppm)	CH_4 (ppm)	CO_2 (ppm)	% difference (wet vs. dry) CO	CH_4	CO_2
1	dry	0.28	1.67	348.9			
2	2 ml	0.1	1.34	335.6	95	22	4
3	150 μl	0.28	1.61	346.19	0	3.7	0.3

It can be concluded from this experiment that the large amount of water accumulating during sampling affected, to some degree, all three compound concentrations (however, the ambient concentration of CO was close to our detection limit). Water present in a canister does not affect CO, CH_4 and CO_2 concentrations at all. For the 1996 sampling campaign all canister samplers were equipped with water traps which constantly removed any water accumulated during sampling.

2. To compare our CO_2 analysis method with the continuous CO_2 analyzer we sampled ambient air in Reno, NV, on July 17, 1996, into a canister and a Tedlar bag in parallel with a continuous Thermo Environmental Instruments Model 40 CO_2 analyzer over a three-hour period. The average reading for the CO_2 analyzer over this time period was 390.7 ppm. The Tedlar bag was analyzed and a value of 383.9 ppm was obtained, a -2% difference compared with the continuous CO_2 instrument The canister sample was analyzed using our GC method and a value 411.4 ppm was obtained for CO_2. Thus, the difference between our analysis method and the continuous analyzer is 5.2%.

4.2 Carbonyl Compounds

The analysis of all samples collected on DNPH impregnated C_{18} SepPak cartridges was performed by Dr. Kochy Fung of AtmAA, Inc. The results of these analyses are submitted in Excel 5.0 format on a 3.5" diskette (no. II) with this report. Ambient air data are included in the files CHO_95 and CHO_96 for the summer of 1995 and 1996, respectively and the garage and tunnel samples are reported in files GATU_95 and GATU_96 for 1995 and 1996, respectively. The corresponding replicate samples and blanks are reported in the same files, on separate data sheets.

4.3 Tunnel Study

At the same time this program was being conducted several tunnel studies were conducted by DRI with funding from the Coordinating Research Council (CRC) and other interested agencies. It was anticipated that these data could be shared with ARB and other interested programs. This section summarizes these tunnel studies and provides some additional information not included in the CRC reports.

In 1995, sampling was conducted in both the Van Nuys and Sepulveda Tunnels. In 1996 another experiment was conducted in the Sepulveda Tunnel only.

The results of the 1995 tunnel studies have been reported to CRC and these data are available in the CRC report. The 1996 tunnel study draft report has been submitted, but not yet accepted by CRC. Once that report has been accepted, those data will be available.

4.3.1 Tunnel Descriptions

The Van Nuys Tunnel is a two-bore, urban tunnel, 222 m in length, running east/west under the runway of the Van Nuys Airport. There are three lanes per bore along with a narrow walkway adjacent to the north and south lanes. Vent buildings are located on the southeast and northeast edges of the tunnel and were not in operation during the experiment. There are nine door-size openings between the bores. The openings were covered with plywood prior to the commencement of sampling. Traffic lights are located within a few hundred meters of both the tunnel exit and entrance. Because of the lights, vehicles accelerated upon entering the tunnel and often decelerated at the exit. Sampling was conducted in the North Bore, the same as in the 1987 experiment. The experiment was conducted June 9–12, 1995.

The Sepulveda Tunnel was chosen to represent a different fleet from that of LA with potentially lower emissions. The tunnel is a covered roadway the top portion of which is part of the airplane runway and taxiway for the Los Angeles International Airport (LAX). The covered portion of the roadway is 582 m long, straight, and approximately flat in the covered portions, although there is a downgrade approaching the tunnel and an upgrade leaving it. There are two bores, three lanes each, with a sidewalk on the right side of each bore. The two bores of the tunnel are separated by a concrete wall running most of the length of the tunnel. There are 17 openings in this wall, each approximately 10 ft wide by 12 to 14 ft tall. In order to obtain mass emission factors in the tunnel, we sealed off these openings so there would be no air transfer between the two bores. The ventilation system in the tunnel was not in operation when we were sampling. The experiment was conducted in the west bore, which carries Sepulveda Boulevard southbound from the LAX terminals. The experiment was conducted June 9–12, 1995.

4.3.2 Comparison of CO and CO_2 Data

In these tunnel studies the protocol involved filling both a Tedlar bag and a canister at each sampling location. The Tedlar bags were analyzed on-site using a Dasibi Instruments Model 3003 analyzer for CO and a Thermo Environmental Instruments Model 40 analyzer for

CO_2. The canisters were analyzed in the DRI Organic Analysis laboratory as described in Section 3.1.4 for CO, CO_2 and methane, in addition to the hydrocarbon species. This allowed an opportunity to compare these two methods. The results are presented in Figures 4-4 to 4-7. Figure 4-4, the comparison of the two analyses for CO in 1995, shows some scatter but overall presents a very good comparison. There is a slight bias shown with the on-site analyzer slightly lower than the canisters. The same comparison for CO_2 is shown in Figure 4-5, where the overall comparison is even better between the two methods. There is one outlier in this figure where the canister analysis read much lower than the on-site method. Looking at the data, it appears that the on-site analysis produced a more physically reasonable number.

Various changes in sampling techniques were made between 1995 and 1996 and a similar comparison was then done with the 1996 data. Figure 4-6 presents the CO data; there appears to be the same slight bias as in the previous year, with the on-site analysis lower than the canister analysis. Figure 4-7 presents the 1996 CO_2 data which show almost no bias and no extreme outliers as were seen in 1995.

One additional check of the analysis system was an intercomparison done with the Bay Area Air Quality Management (BAAQMD) Laboratory. Professor Rob Harley of UC, Berkeley collected two canister samples in the Caldecott Tunnel on July 31, 1996, and sent one can to DRI and one to BAAQMD. Both groups analyzed the canisters for CO_2 and methane in addition to the NMHC species. DRI's value for CO_2 was 1080 ppm, BAAQMD's was 1085 ppm and the on-site analyzer read 1093 ppm. For methane, DRI analysis produced 2.22 ppm and BAAQMD 2.11 ppm. This additional intercomparison gave us confidence in our measurement techniques.

4.3.3 Hydrocarbons in the Tunnels

The data file, 95tunl.xls, includes the concentrations of the species measured in the tunnel, and the resulting emission factors calculated for these species. The emission rates are presented in mg/mile. The data are for both the 1995 Van Nuys and Sepulveda Tunnel studies. The concentrations can be much higher than ambient levels, as is expected in this type of experiment. Emission rates can be used to develop source profiles.

4.4 Gasoline Headspace Analyses

The data from the 1995 and 1996 gasoline headspace analyses are included in the files HGAS_95.XSL and HGAS_96.XLS in Excel 5.0 format (Disk III). All data are presented in weight %, relative to the total mass of all components. The analysis for 1996 samples was carried out on 100 m Petrocol capillary column, whereas the analysis for 1995 samples was performed on 60 m DB-1 capillary column, the same we used for canister sample analysis. Because of this difference, more compounds were identified in 1996 than in 1995. The list of compounds with their corresponding mnemonics is included on Disk III (GASHS4.XLS).

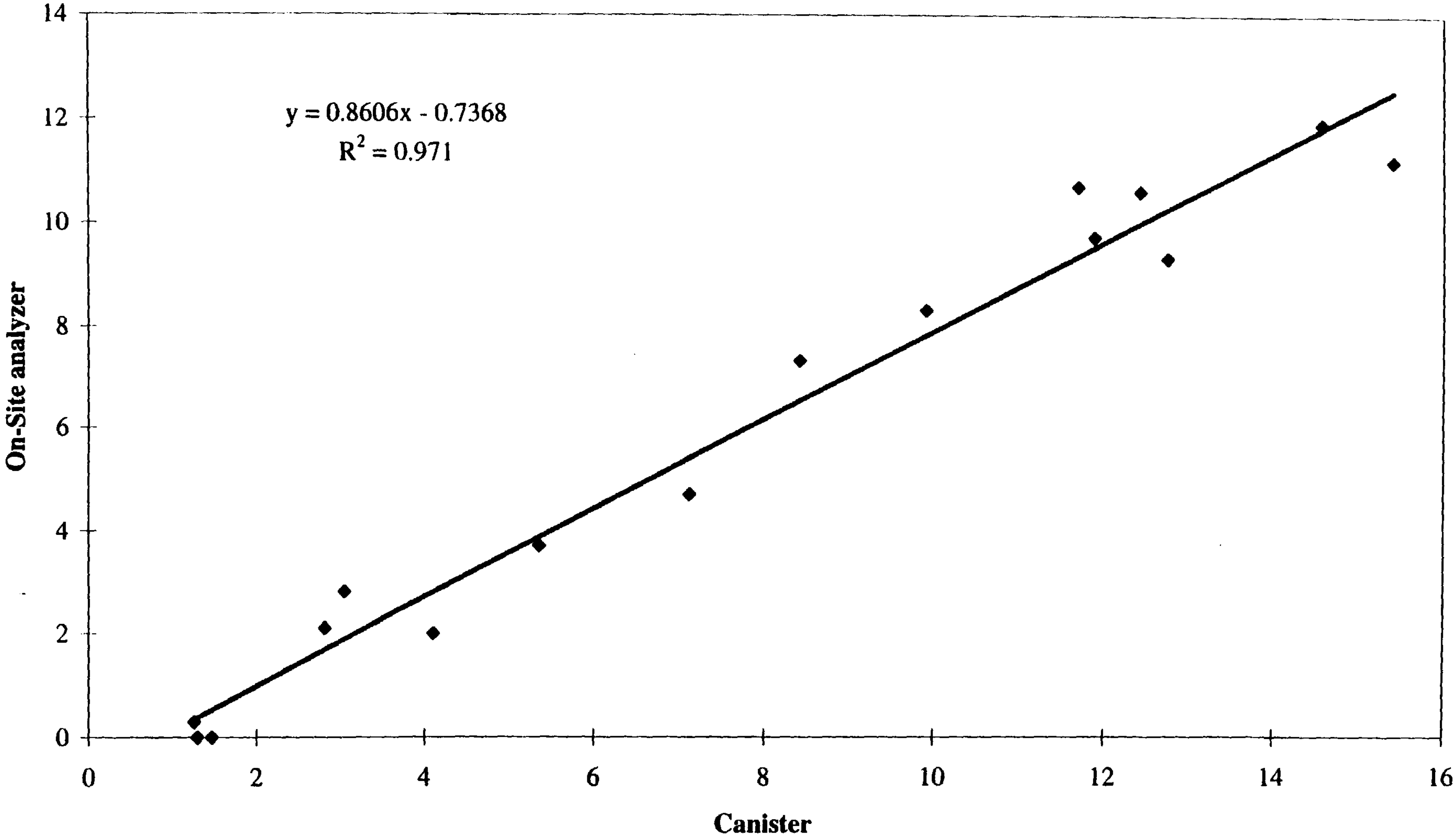


Figure 4-4. 1995 Sepulveda Tunnel Study, Carbon Monoxide Measurements — Comparison of On-site (Tedlar bag) Analysis versus Laboratory (canister) Analysis.

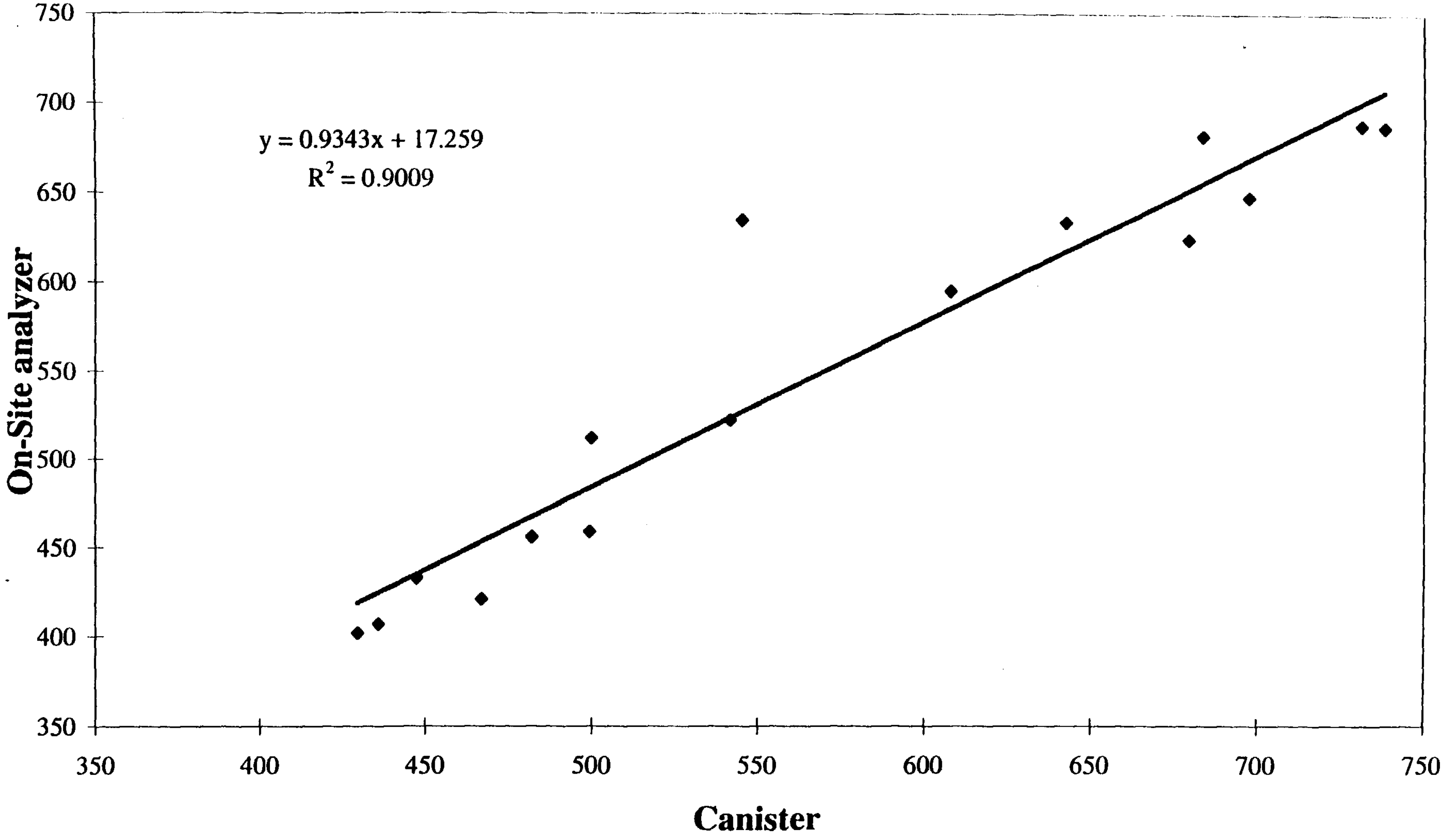


Figure 4-5. 1995 Sepulveda Tunnel Study, Carbon Dioxide Measurements — Comparison of On-site (Tedlar bag) Analysis versus Laboratory (canister) Analysis.

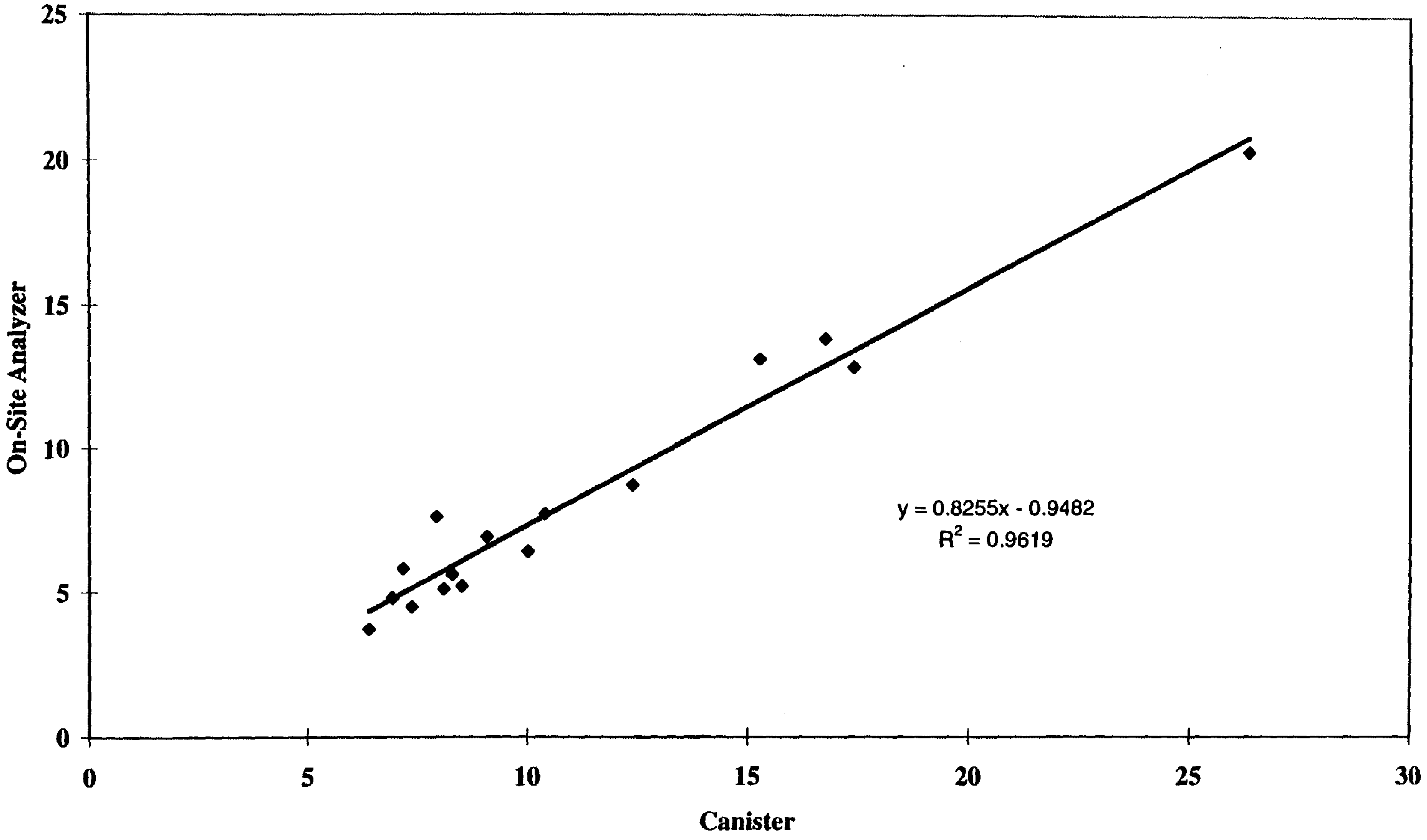


Figure 4-6. 1996 Sepulveda Tunnel Study, Carbon Monoxide Measurements — Comparison of On-site (Tedlar bag) Analysis versus Laboratory (canister) Analysis.

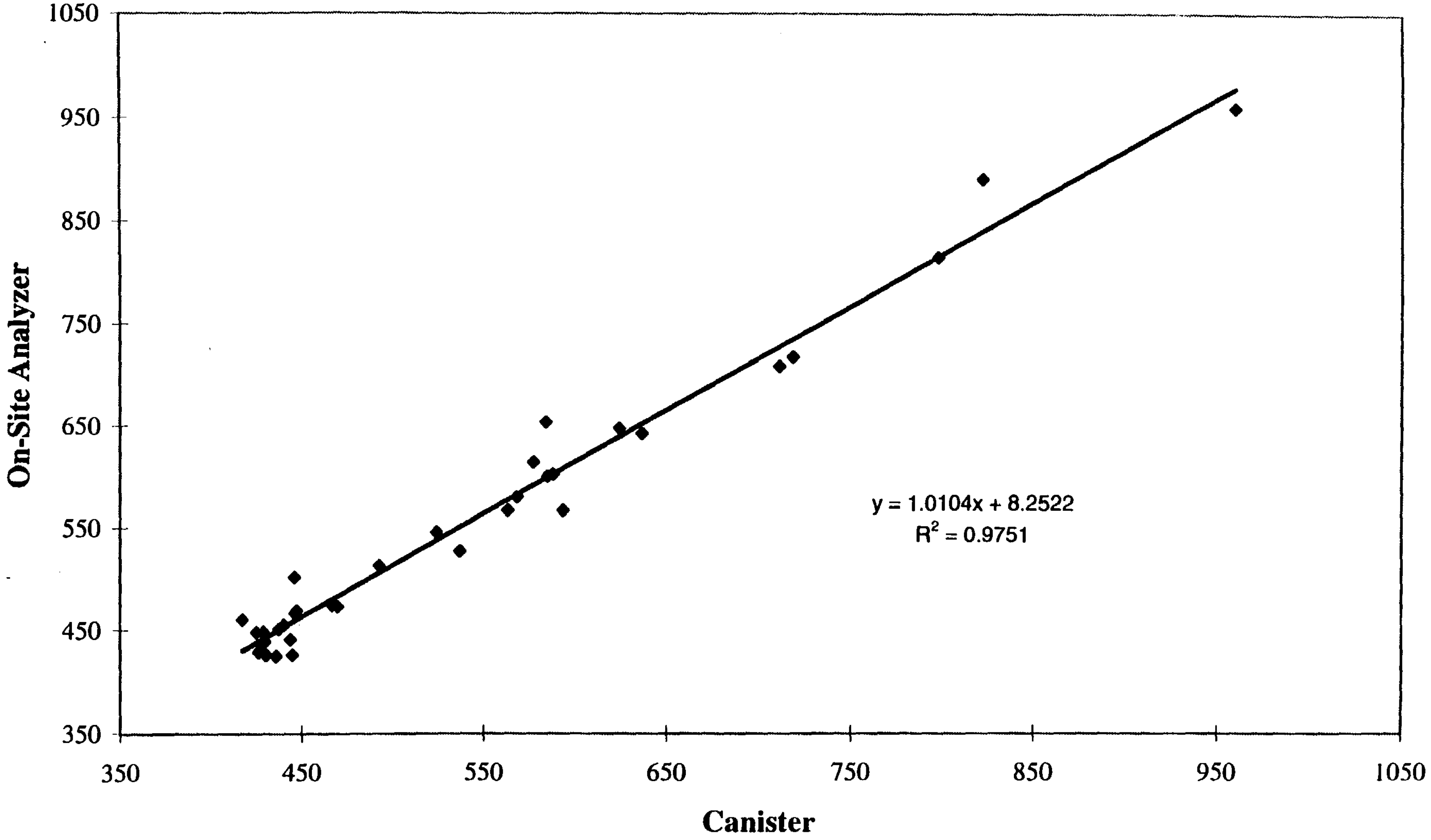


Figure 4-7. 1996 Sepulveda Tunnel Study, Carbon Monoxide Measurements — Comparison of On-site (Tedlar bag) Analysis versus Laboratory (canister) Analysis.

4.5 Quality Control and Level 1 Validation

Prior to analysis, all analytical systems (i.e., GC/ECD/FID, GC/MSD, and GC/IRD/MSD) were checked for purity with humidified zero air and certified clean (less than 0.2 ppbv of targeted VOC). Quality control in the laboratory includes daily instrument calibration, replicates of standards, and analysis of approximately 10% of the samples for estimation of analytical precision, which historically has been better than 6%. In past programs, field blanks were at the 1–2 ppb levels, based on the air volume of the samples. Coefficients of variation (CV) calculated from observed differences between duplicate sample pairs were less than 10%.

Primary reference standards are traceable to a National Institute of Standards and Technology (NIST) Standard Reference Material (SRM). NIST SRM 1805, which consists of 254 ppb of benzene in nitrogen, was used for canister hydrocarbon speciation. In addition, NIST SRM 2764 (245 ppb of propane in nitrogen), was used for calibrating the light hydrocarbon analytical system. The GC/FID system was calibrated initially by multipoint calibration (i.e., three levels plus humid zero air), and regularly checked by a one-point calibration, using SRM 1805 or the propane standard. The day-to-day reproducibility of ±10% is acceptable for either standard.

During the course of analysis, calibration standards are routinely analyzed to ensure that the instrument response has not changed. The criterion of 10% of expected response is used by the analyst to determine whether the instrument must be recalibrated. Retention time windows for each analyte are established prior to analysis and re-established continuously throughout the course of the analytical period.

Accuracy involves the closeness of a measurement to a reference value and reflects elements of both bias and precision. Relative accuracy of canister sampling is determined by measuring an NIST hydrocarbon standard into a sampler. The contents are then analyzed for the component contained in the audit cylinder. Percent relative accuracy is calculated:

$$\%\,\text{Relative Accuracy} = \frac{X - Y}{X} \times 100$$

where:

Y = concentration of the targeted compound recovered from the sampler, and

X = concentration of targeted compound in the NIST standard.

If the relative accuracy does not fall between 90 and 110%, the field sampler is not used. Accuracy is determined by repeatable analysis of an NIST standard cylinder (for canisters). Percent relative accuracy is then determined as described above.

Level I sample validation takes place in the field or in the laboratory and consists of: 1) flagging samples when significant deviations from measurement assumptions have occurred; 2) verifying computer file entries against data sheets; 3) eliminating values for measurements which are known to be invalid because of instrument malfunctions; and 4) adjustment of measurement values for quantifiable calibration or interference biases. Each gas chromatogram is examined immediately after the run to verify that peak integrations have been performed properly. The peak integration, retention times, and peak identifications assigned by the ChromPerfect software are stored to disk as an ASCII file. The files are then read into a Foxpro data file for additional processing and verification of peak identifications. The peak assignments for the major constituents (typically about a dozen peaks) in the chromatogram are manually verified, and retention times are recalculated for all detectable peaks based upon regression between sample and reference retention times for the manually identified peaks. The adjusted retention times are used to assign peak identifications for all detectable peaks (the reference file currently contains 160 identified compounds). The retention time adjustments and peak assignments are executed automatically by a Foxpro program. The ChromPerfect and subsequent confirmatory peak identifications are then compared and discrepancies are resolved by the analyst based on peak patterns or confirmatory identification by GC/MS. In the final step, the Level I validated data are appended to the master database. Each sample appears as a record within the database and is identified by a unique sample identification, site, date, and time and as a primary, collocated, blank, spiked, or replicate sample.

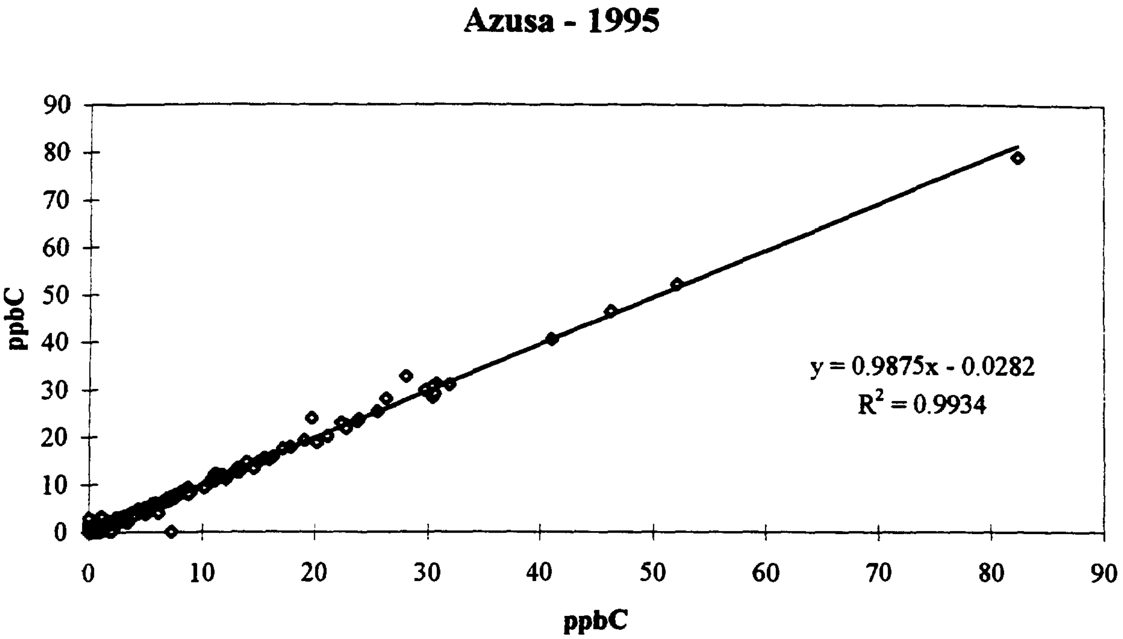
4.5.1 Replicate Analyses

For canister samples, all primary and replicate analysis data are included in the files RGALC_95 and RGALC_96, which contain data for all ambient canister samples collected in 1995 and in 1996, respectively (Disk #I). For carbonyl compounds, the corresponding replicate samples and blanks are reported in the same files as the primary samples, CHO_95 and CHO_ 96 (Disk #II) but on separate data sheets. In addition, for canister samples there is a separate file containing all primary-replicate pairs of samples, REPCAN.XLS, in Excel 5.0 format (Disk #III).

Figures 4-8, 4-9 and 4-10 show the comparisons of primary and replicate analyses for all individual hydrocarbon samples collected in Azusa, Burbank and Los Angeles (N. Main), respectively. Carbon monoxide, CO_2, methane and total hydrocarbons are not included in this comparison. It can be seen from these figures that excellent reproducibility was achieved for the canister sample analyses.

4.5.2 External Performance Audits and Comparison Studies

The DRI Organic Analytical Laboratory participated in the International Hydrocarbon Intercomparison Experiment, organized by National Center for Atmospheric Research (NCAR). The results of Tasks I and II of this intercomparison have been published recently (Apel et al., 1994). The first task involved the circulation of a two-component hydrocarbon mixture of known composition and unknown concentration, prepared by NIST. The DRI values were within 5% of the nominal values provided by NIST. Task II was more complex — the participating laboratories were asked to identify and quantify 16 components present, in the ppb range, in a mixture prepared by NIST. The agreement between the DRI values and the NCAR values, as well as with nominal values provided by NIST, was generally within 15%. The next



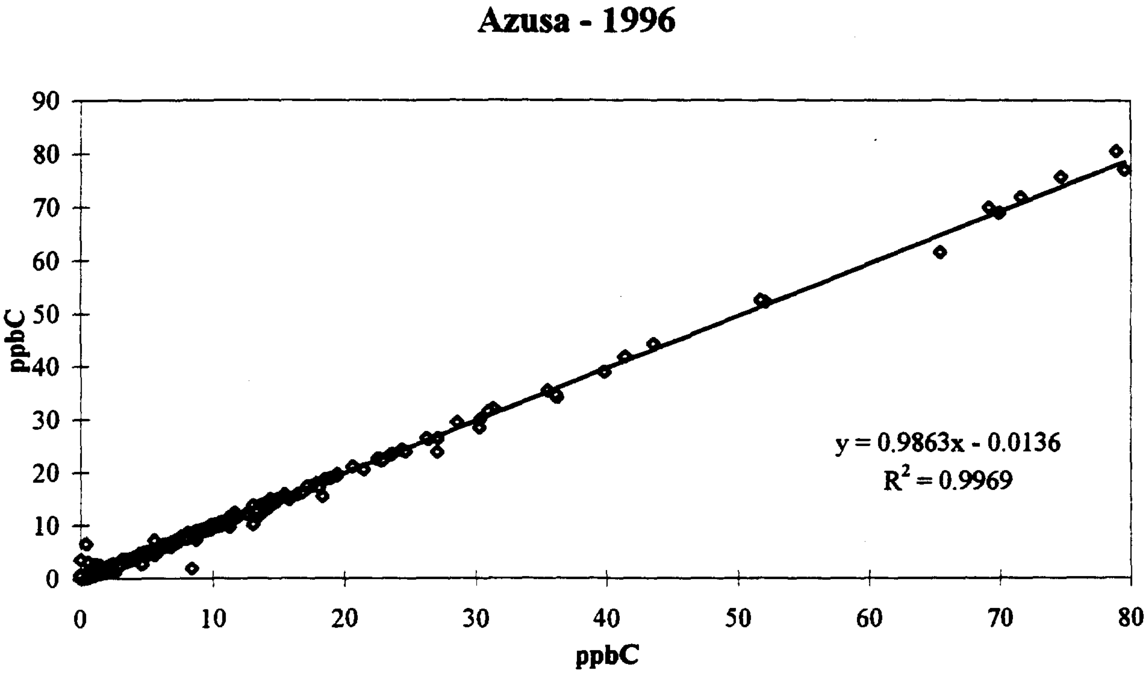
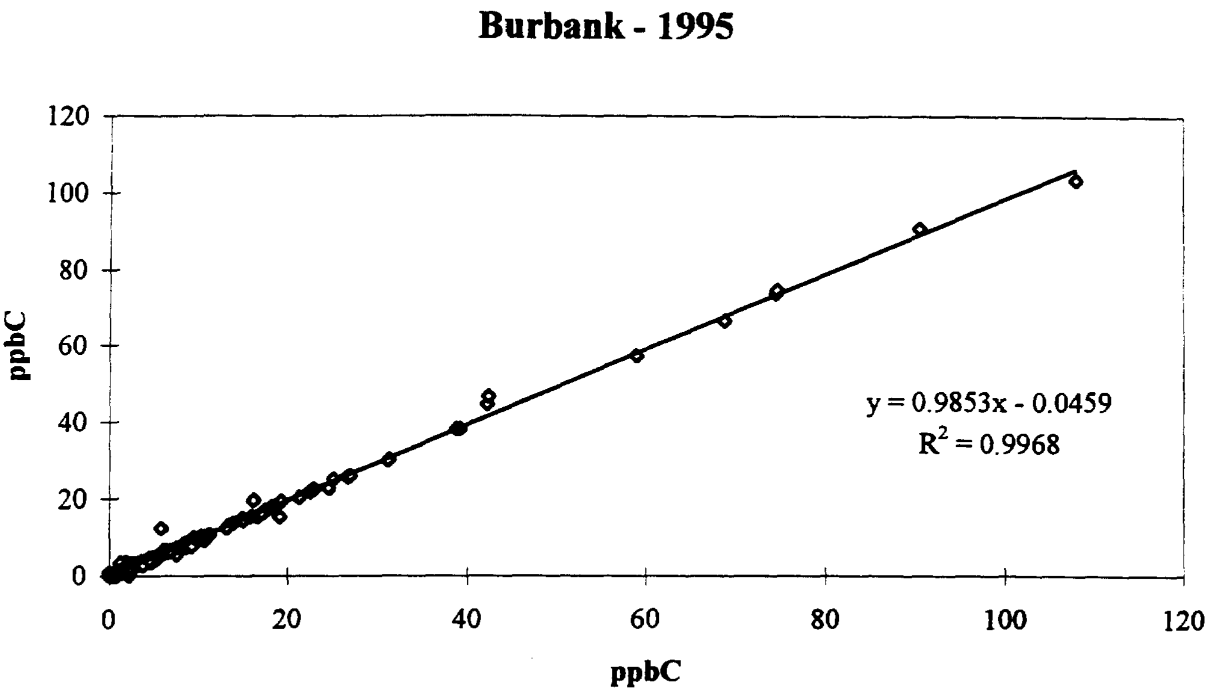


Figure 4-8. Comparison of primary and replicate analyses for all individual hydrocarbon samples collected in Azusa in 1995 and 1996.



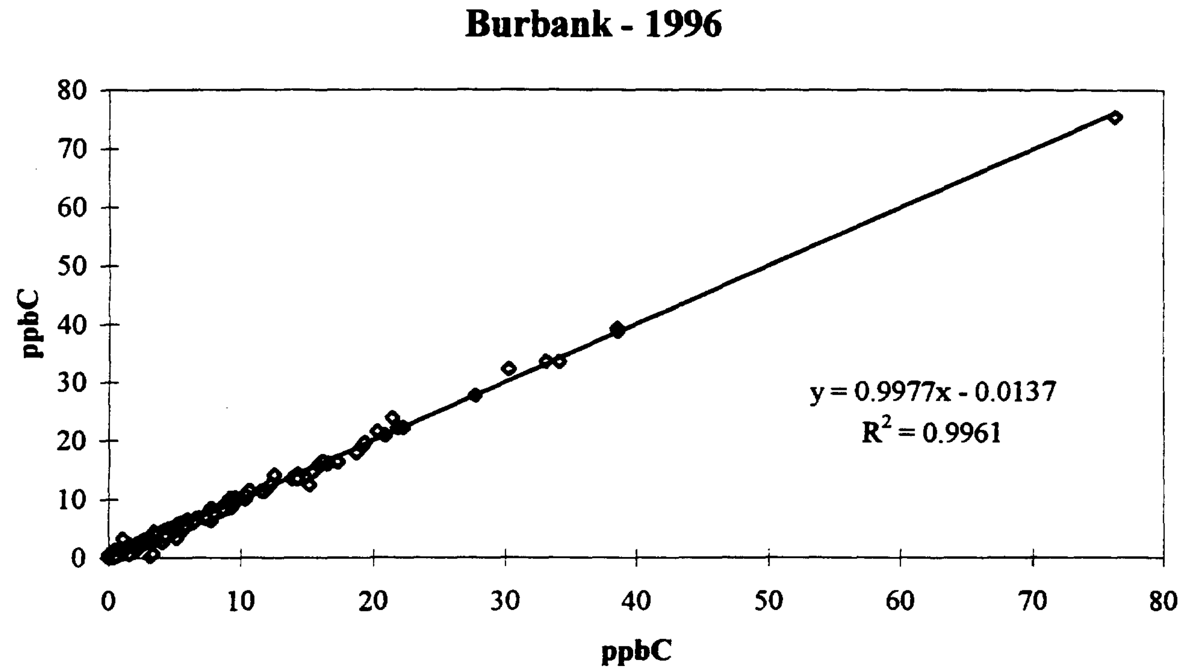


Figure 4-9. Comparison of primary and replicate analyses for all individual hydrocarbon samples collected in Burbank in 1995 and 1996.

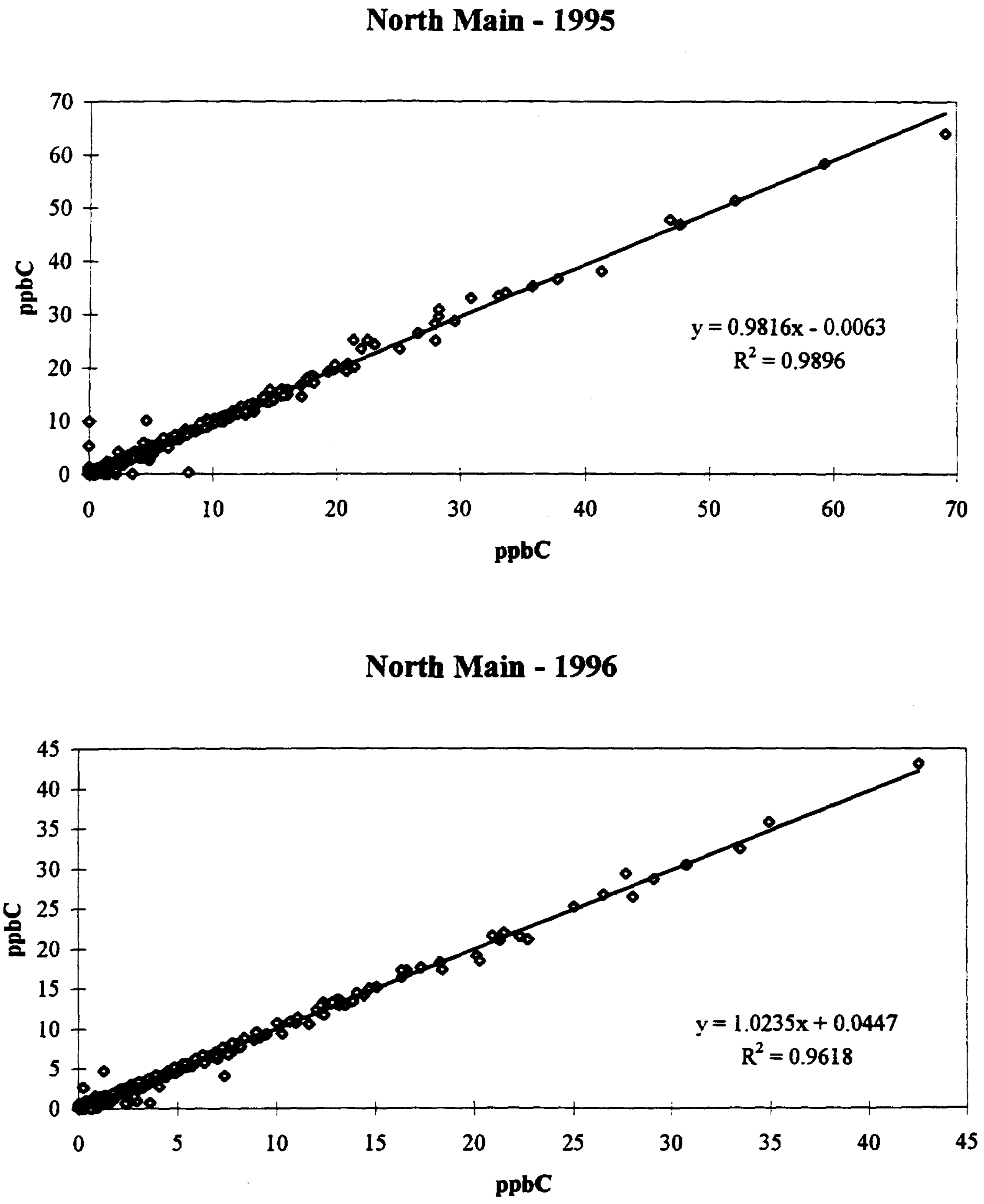


Figure 4-10. Comparison of primary and replicate analyses for all individual hydrocarbon samples collected in Los Angeles (N. Main) in 1995 and 1996.

tasks, which were carried out at the beginning of 1996, involved the analysis of ambient air samples. The DRI has successfully completed these tasks — the agreement between the DRI values and the NCAR values was generally within 10%. The results of these tasks are currently being prepared for publication. Phase V of the NCAR International Hydrocarbon Intercomparison Experiment (involving analysis of ambient samples of very low concentrations) is currently underway.

In the summer of 1995 the DRI laboratory participated in the NARSTO-Northeast hydrocarbon intercomparison study, involving the analysis of two ambient air samples by participating laboratories (Fujita et al., 1996). This audit occurred during the same time the samples were collected and analyzed for the CRC study. Participants included Biospheric Research Corporation (BRC), State University of New York at Albany (SUNYA), EPA Region I, DRI, and 8 of the PAMS networks in the northeastern U.S. EPA (Bill Lonneman) served as the reference laboratory. Figure 4-11 shows that the agreement between the DRI laboratory and the EPA Atmospheric Research and Exposure Assessment Laboratory was generally excellent.

In addition, the DRI laboratory participated in several non-methane hydrocarbon laboratory performance audits, organized by Quality Assurance Section, Monitoring and Laboratory Division, of the CARB. The last intercomparison, organized in September 1996, involved the analysis of ambient air sample by four California district laboratories (labeled A, B, C and D) and the DRI laboratory. The results are included in Appendix C.

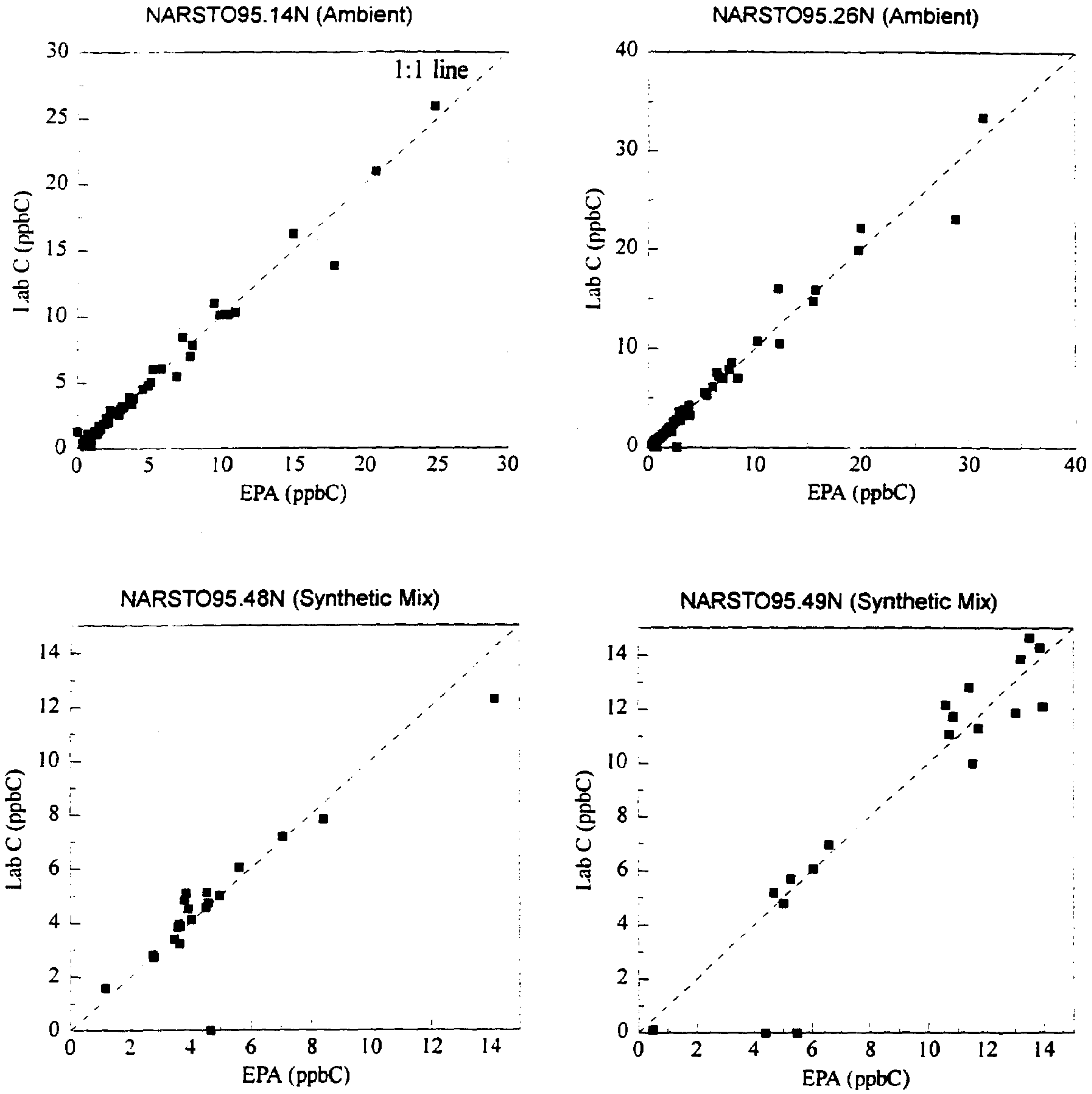


Figure 4-11. Correlations of values reported by DRI versus EPA for analysis of NARSTO-Northeast hydrocarbon performance audit samples.

5.0 EVALUATION OF AMBIENT HYDROCARBON DATA

The data validation process consists of procedures that identify deviations from measurement assumptions and procedures. Three levels of validation are applied which will result in the assignment to each measurement of one of the following ratings: 1) valid; 2) valid but suspect; or 3) invalid. Level 1 data validation normally takes place in the field or in the laboratory and consists of: 1) flagging samples when significant deviations from measurement assumptions have occurred; 2) verifying computer file entries against data sheets; 3) eliminating values for measurements which are known to be invalid because of instrument malfunctions; 4) adjustment of measurement values for quantifiable calibration or interference biases; 5) determining measurement precision by replicate analyses and by collection of field blanks and collocated samples. Section 4.4 summarizes the results of Level 1 validation. Level 2 validation, the subject of this section, takes place after the data from various measurement methods have been assembled in a master database. Level 2 applies consistency tests, based on known physical relationships among variables, to the assembled data. These tests fall into three categories: detection of extreme values; consistency among co-pollutants and between redundant measurements by alternative measurement methods; and examination of temporal and spatial variations. Level 3 validation is part of the subsequent data interpretation process. Receptor modeling, factor and other statistical analyses, and photochemical air quality simulation models are several examples. Unusual values are identified during the data interpretation process as: 1) extreme values; 2) values which would otherwise normally track the values of the other variables in a time series; and 3) values for observables which would normally follow a qualitatively predictable spatial or temporal pattern.

Examination of spatial and temporal distributions of atmospheric constituents and relative abundances of certain chemical species is a useful prelude to receptor modeling. When coupled with a conceptual understanding of the emissions sources, meteorology, and chemical transformation mechanisms, this receptor-oriented analysis provides qualitative, and even semi-quantitative, evidence of relationships between source emissions and receptor mixing ratios. This section examines the spatial and temporal distributions of ambient hydrocarbons in the South Coast Air Basin area.

Although Level 2 data validation was not required for this project, Dr. Eric Fujita performed this validation for the Coordinating Research Council (CRC)-funded project "Determination of Mobile Source Emission Source Fraction Using Ambient Field Measurements" (Fujita, 1997). The following sections are adapted from this report.

5.1 Statistical Summary

DRI made speciated hydrocarbon and carbonyl measurements at downtown Los Angeles, Burbank and Azusa during the summer of 1995 as part of a CARB-sponsored study that examined the air quality impacts of the introduction of California Phase 2 reformulated gasoline. Samples were collected twice a day (0700-1000 and 1400-1700 PDT) for six seven-day periods (July 8–14 and 17–23, August 1–7, August 31–September 6, September 9–15 and 24–30) for a total of 252 samples.

Table 5-1 presents averages, standard deviations, and maximum mixing ratios for the 25 most abundant hydrocarbon species for the samples collected by DRI for the CARB study. Averages are shown separately for morning and afternoon samples and include samples for all six seven-day periods during the summer of 1995. The ten most abundant hydrocarbons were toluene, isopentane, n-propane, m,p-xylene, ethane, acetylene, ethylene, n-butane, n-pentane and 2-methylpentane. The average morning NMHC mixing ratios were 567 ppbC at Azusa, 744 ppbC at Burbank and 676 ppbC at Los Angeles (N. Main). The corresponding average afternoon mixing ratios were 311, 337 and 348 ppbC, respectively. On average, the 25 most abundant species accounted for approximately 70% of the total NMHC at all three sites for both morning and afternoon samples. MTBE accounted for about 5% of the total NMHC on a ppbC basis and was comparable to isopentane in relative abundance. Figure 5-1 shows a plot of the average mixing ratios of the 25 most abundant species. The similarity among the three sites in the relative mixing ratios of the major hydrocarbon species is readily apparent and indicates a common source of ambient hydrocarbons at the three sampling sites.

5.2 Correlations Between Species

Comparisons of co-pollutants are important Level 2 validation checks for determining the overall accuracy and validity of the measurements. Species emitted from the same source type should correlate in the absence of other significant sources of these species, and exhibit average ratios of species that reflect the nature of the source or their relative persistence in the atmosphere. For example, hydrocarbons such as ethylene and acetylene are produced from combustion of hydrocarbon fuels in internal combustion engines. The main source of methyl-tert-butyl ether (MTBE) is gasoline, in either evaporative or tailpipe emissions. The thermal breakdown of MTBE in internal combustion engines produces isobutylene. Toluene is a major constituent of gasoline and vehicle exhaust and is a component of surface coatings and industrial solvents.

Figures 5-2 and 5-3 show scatterplots of acetylene and benzene versus carbon monoxide for all of the CARB Study samples. These three compounds should correlate with each other since they are associated primarily with vehicle exhaust and are inert to chemical transformation in the atmosphere. The morning samples from Azusa and Los Angeles (North Main), in particular, show excellent correlations. While slopes for the same correlations of the Burbank samples are similar to those of the other two sites, the correlations are not as good. Because the correlations between benzene and acetylene are generally very good, there are probably other sources of CO near the site. With the exception of some outliers, the correlation of the afternoon samples is generally good and they have slopes that are similar to those of the morning samples. The fact that afternoon mixing ratios are consistently lower than corresponding morning mixing ratios for all species satisfies a consistency check as mixing ratios decrease from morning to afternoon due to increasing mixing depths.

Table 5-1. Statistical Summaries for the 25 Most Abundant Species (ppbC) at the Three ARB Sites — Azusa

Morning				Afternoon				All day			
Species	Avg. (42 samples)	Std.	Max.	Species	Avg. (42 samples)	Std.	Max.	Species	Avg. (84 samples)	Std.	Max.
NMHC	567.2	229.3	1280.2	NMHC	310.6	102.4	573.6	NMHC	438.9	219.1	1280.2
UNID	77.5	37.6	192.3	UNID	55.7	25.4	114.2	UNID	66.6	33.9	192.3
TOLUE	42.9	17.4	80.1	TOLUE	23.5	9.6	51.8	TOLUE	33.2	17.1	80.1
N_PROP	39.5	24.7	140.3	IPENTA	23.1	9.0	47.4	IPENTA	30.0	14.2	69.6
IPENTA	37.0	15.1	69.6	N_PROP	20.3	7.8	33.8	N_PROP	29.9	20.7	140.3
MP_XYL	25.0	11.3	55.7	ETHANE	13.8	4.8	23.2	ETHANE	18.6	8.6	41.5
ETHANE	23.5	8.9	41.5	N_BUTA	12.6	4.8	21.7	MP_XYL	17.1	11.5	55.7
N_PENT	22.3	12.1	54.7	ACETYL	12.1	5.1	30.1	N_PENT	16.9	10.6	54.7
ACETYL	20.1	8.3	37.8	N_PENT	11.5	4.2	23.9	ACETYL	16.1	8.0	37.8
ETHENE	18.6	7.5	34.6	BZ124M	10.1	11.7	82.4	N_BUTA	14.8	6.7	47.6
N_BUTA	16.9	7.7	47.6	PENA2M	9.9	3.4	22.8	BZ124M	13.5	10.5	82.4
BZ124M	16.9	8.0	55.6	MP_XYL	9.3	3.9	20.0	PENA2M	13.4	6.1	30.9
PENA2M	16.9	6.1	30.9	ETHENE	8.1	2.8	14.0	ETHENE	13.3	7.7	34.6
BENZE	13.3	5.2	25.1	BENZE	8.0	2.4	14.4	BENZE	10.7	4.8	25.1
MCYPNA	10.5	4.2	20.4	I_BUTA	7.0	3.0	14.9	I_BUTA	8.5	4.2	27.4
I_BUTA	10.0	4.6	27.4	MCYPNA	5.3	2.0	13.0	MCYPNA	7.9	4.2	20.4
N_HEX	9.5	4.1	19.2	N_HEX	5.1	1.8	10.9	N_HEX	7.3	3.9	19.2
PA224M	9.1	3.7	17.8	PENA3M	5.1	1.7	11.5	PENA3M	7.1	3.3	17.1
PENA3M	9.0	3.4	17.1	HEXA3M	4.9	1.9	10.1	PA224M	7.0	3.6	17.8
O_XYL	8.9	4.0	20.6	PA224M	4.8	1.7	10.0	HEXA3M	6.6	3.0	14.8
HEXA3M	8.2	3.0	14.8	O_XYL	3.8	1.4	7.8	O_XYL	6.3	3.9	20.6
PROPE	7.5	3.1	14.3	MECYH	3.6	1.9	9.9	MECYH	5.4	3.3	19.6
MECYH	7.2	3.5	19.6	HEXA2M	3.5	1.5	7.6	ETBZ	5.0	2.9	16.2
ETBZ	6.7	3.1	16.2	N_HEPT	3.4	1.9	9.7	HEXA2M	5.0	2.6	12.7
HEXA2M	6.4	2.7	12.7	ETBZ	3.3	1.3	7.2	PROPE	4.8	3.5	14.3
STYR	5.9	4.7	22.1	PEN23M	2.8	1.2	6.1	N_HEPT	4.6	2.5	12.6

Table 5-1. Statistical Summaries for the 25 Most Abundant Species (ppbC) at the Three ARB Sites — Burbank

Morning				Afternoon				All day			
Species	Avg. (42 samples)	Std.	Max.	Species	Avg. (42 samples)	Std.	Max.	Species	Avg. (84 samples)	Std.	Max.
NMHC	743.6	264.0	1312.2	NMHC	337.2	111.9	684.8	NMHC	540.4	287.0	1312.2
UNID	85.8	39.1	224.4	UNID	60.5	31.9	193.7	UNID	73.1	37.8	224.4
TOLUE	59.6	27.2	137.1	N_PROP	28.9	21.5	93.2	TOLUE	42.7	27.3	137.1
IPENTA	50.5	21.7	96.2	TOLUE	25.7	13.2	78.8	IPENTA	37.1	21.4	96.2
N_PROP	42.0	15.1	90.8	IPENTA	23.7	9.4	54.3	N_PROP	35.5	19.7	93.2
ETHANE	41.0	15.6	74.6	ETHANE	13.8	5.2	25.3	ETHANE	27.4	17.9	74.6
MP_XYL	36.3	15.6	68.8	MP_XYL	13.6	5.9	36.0	MP_XYL	25.0	16.4	68.8
ACETYL	28.2	10.8	49.2	N_BUTA	13.6	5.3	27.5	ACETYL	19.9	11.8	49.2
ETHENE	25.2	9.4	43.4	ACETYL	11.6	4.9	25.7	N_BUTA	17.0	7.3	46.0
N_PENT	22.8	10.4	46.3	N_PENT	10.7	4.2	23.8	ETHENE	16.8	10.9	43.4
PENA2M	22.7	8.7	39.5	PENA2M	10.4	3.6	21.6	N_PENT	16.8	10.0	46.3
N_BUTA	20.4	7.3	46.0	ETHENE	8.4	3.0	17.9	PENA2M	16.6	9.1	39.5
BENZE	17.9	7.1	32.1	BENZE	7.6	2.7	16.7	BENZE	12.7	7.4	32.1
BZ124M	16.8	10.4	74.6	N_HEX	7.0	3.9	15.9	BZ124M	11.5	9.4	74.6
N_HEX	14.7	6.6	41.2	I_BUTA	6.3	2.7	13.8	N_HEX	10.9	6.7	41.2
MCYPNA	14.6	6.2	26.6	BZ124M	6.2	3.0	18.8	MCYPNA	10.0	6.6	26.6
PA224M	13.9	5.3	26.9	PA224M	6.1	2.0	11.7	PA224M	10.0	5.6	26.9
PENA3M	13.2	5.1	23.4	PENA3M	5.7	2.2	11.4	PENA3M	9.5	5.4	23.4
O_XYL	12.8	5.4	24.5	MCYPNA	5.5	2.7	12.5	O_XYL	8.8	5.7	24.5
I_BUTA	11.3	4.0	21.4	MECYH	5.4	3.8	18.8	I_BUTA	8.8	4.3	21.4
MECYH	10.3	5.4	33.3	HEXA3M	5.1	1.8	10.7	MECYH	7.9	5.3	33.3
PROPE	10.3	4.0	17.8	O_XYL	4.9	1.9	12.5	HEXA3M	7.7	4.1	18.2
HEXA3M	10.3	4.1	18.2	ETBZ	4.1	1.9	10.5	ETBZ	6.7	4.0	17.5
ETBZ	9.3	4.0	17.5	N_HEPT	4.0	2.1	12.0	PROPE	6.5	4.8	17.8
PEN23M	8.7	3.7	17.3	PEN23M	3.8	1.3	7.7	PEN23M	6.3	3.7	17.3
HEXA2M	8.6	3.7	16.2	HEXA2M	3.7	1.4	7.1	HEXA2M	6.2	3.7	16.2
N_HEPT	8.0	3.3	17.5	MTBE	2.7	1.1	6.5	N_HEPT	6.0	3.4	17.5

Table 5-1. Statistical Summaries for the 25 Most Abundant Species (ppbC) at the Three ARB Sites — Los Angeles (N. Main)

	Morning				Afternoon				All day		
Species	Avg. (42 samples)	Std.	Max.	Species	Avg. (42 samples)	Std.	Max.	Species	Avg. (84 samples)	Std.	Max.
NMHC	676.1	274.2	1313.2	NMHC	348.3	92.2	524.2	NMHC	512.2	262.1	1313.2
UNID	84.9	45.0	241.9	UNID	66.9	33.0	170.0	UNID	75.9	40.5	241.9
TOLUE	50.6	21.8	102.3	IPENTA	28.6	15.8	94.9	TOLUE	37.7	20.8	102.3
IPENTA	42.3	18.1	91.5	TOLUE	24.8	7.5	46.8	IPENTA	35.5	18.3	94.9
N_PROP	35.2	15.6	81.8	N_PROP	17.9	7.4	41.3	N_PROP	26.6	15.0	81.8
MP_XYL	34.0	14.6	65.3	ETHANE	17.3	7.2	40.0	ETHANE	24.6	13.2	69.2
ETHANE	31.9	13.8	69.2	MP_XYL	14.1	3.7	21.8	MP_XYL	24.0	14.6	65.3
ACETYL	26.8	11.3	53.8	N_PENT	13.2	6.0	36.7	ACETYL	19.7	11.1	53.8
ETHENE	25.3	9.9	47.0	N_BUTA	13.0	5.5	32.1	ETHENE	18.0	10.4	47.0
N_PENT	21.7	10.3	55.9	ACETYL	12.6	4.3	24.6	N_PENT	17.5	9.4	55.9
PENA2M	19.9	8.0	41.3	ETHENE	10.8	3.7	20.9	N_BUTA	16.1	8.2	57.3
N_BUTA	19.2	9.2	57.3	PENA2M	10.4	2.8	15.6	PENA2M	15.2	7.6	41.3
BENZE	17.1	6.9	33.1	BZ124M	8.8	3.0	17.1	BENZE	12.7	6.7	33.1
BZ124M	15.7	5.1	25.3	I_BUTA	8.6	8.2	55.7	BZ124M	12.2	5.4	25.3
MCYPNA	13.3	5.7	27.7	BENZE	8.3	1.9	13.0	MCYPNA	9.8	5.5	27.7
O_XYL	11.9	5.1	22.6	MCYPNA	6.4	1.6	10.2	I_BUTA	9.5	6.7	55.7
PA224M	11.6	5.0	23.4	PENA3M	5.6	1.4	8.6	O_XYL	8.5	5.0	22.6
PENA3M	11.1	4.6	22.5	N_HEX	5.6	1.7	10.2	PA224M	8.5	4.7	23.4
N_HEX	10.8	4.5	22.6	PA224M	5.5	1.3	8.5	PENA3M	8.3	4.4	22.5
PROPE	10.5	4.1	19.1	HEXA3M	5.3	1.7	13.2	N_HEX	8.2	4.3	22.6
I_BUTA	10.4	4.5	25.1	O_XYL	5.1	1.2	8.0	HEXA3M	7.3	3.6	20.2
HEXA3M	9.3	3.8	20.2	PROPE	4.0	1.3	8.2	PROPE	7.3	4.5	19.1
ETBZ	8.6	3.6	16.8	ETBZ	4.0	1.0	6.7	ETBZ	6.3	3.5	16.8
MECYH	8.6	3.7	16.7	MECYH	3.8	1.2	6.4	MECYH	6.2	3.7	16.7
HEXA2M	7.8	3.4	16.4	HEXA2M	3.7	1.0	6.7	HEXA2M	5.8	3.2	16.4
LIBUTE	7.2	3.2	14.0	PEN23M	3.4	0.9	5.5	PEN23M	5.2	2.9	15.1
PEN23M	6.9	3.1	15.1	STYR	3.2	1.4	7.2	LIBUTE	5.1	3.2	14.0

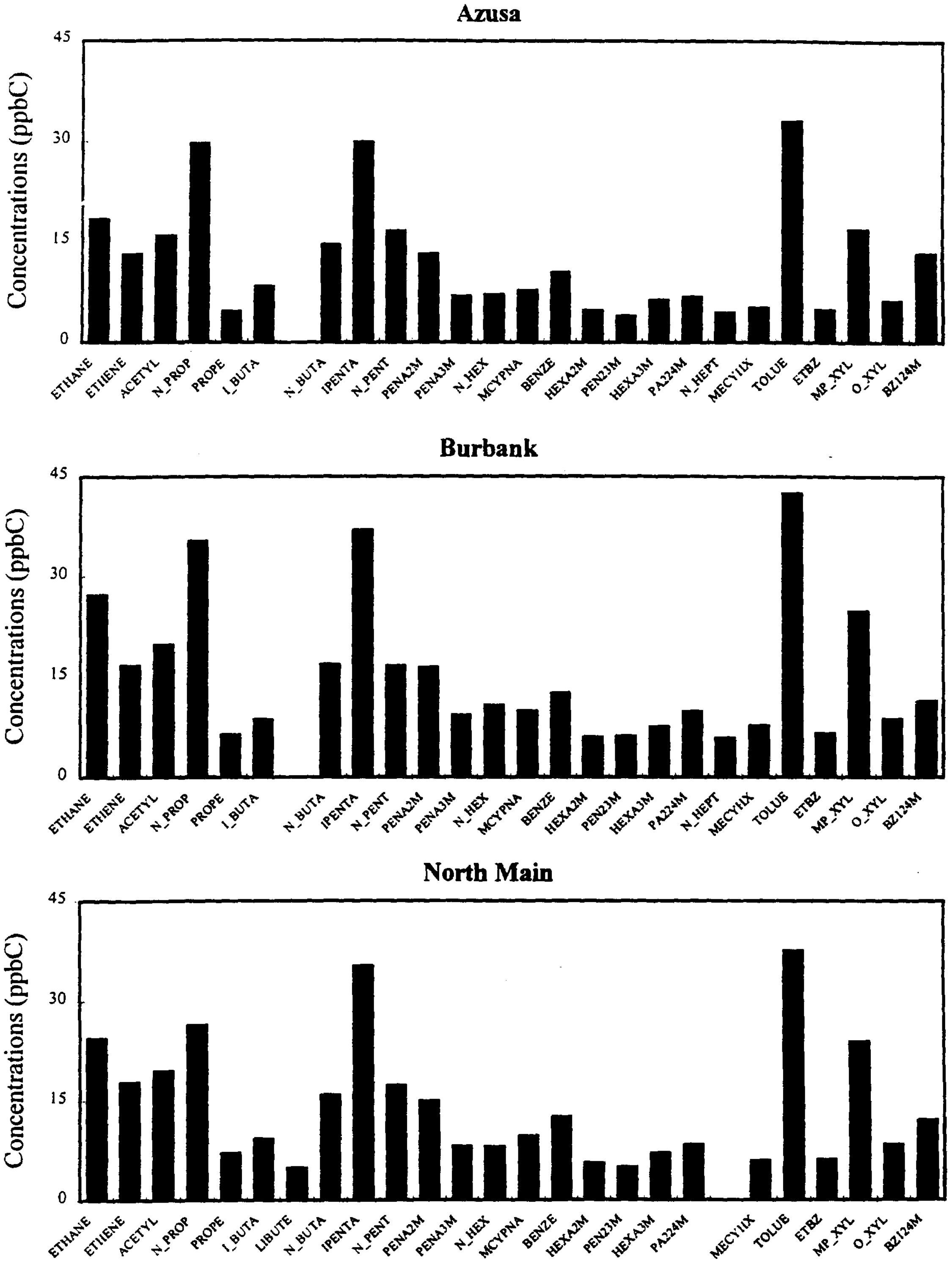


Figure 5-1. Average concentrations for 25 most abundant species at three LA sites (averaged for all morning and afternoon samples).

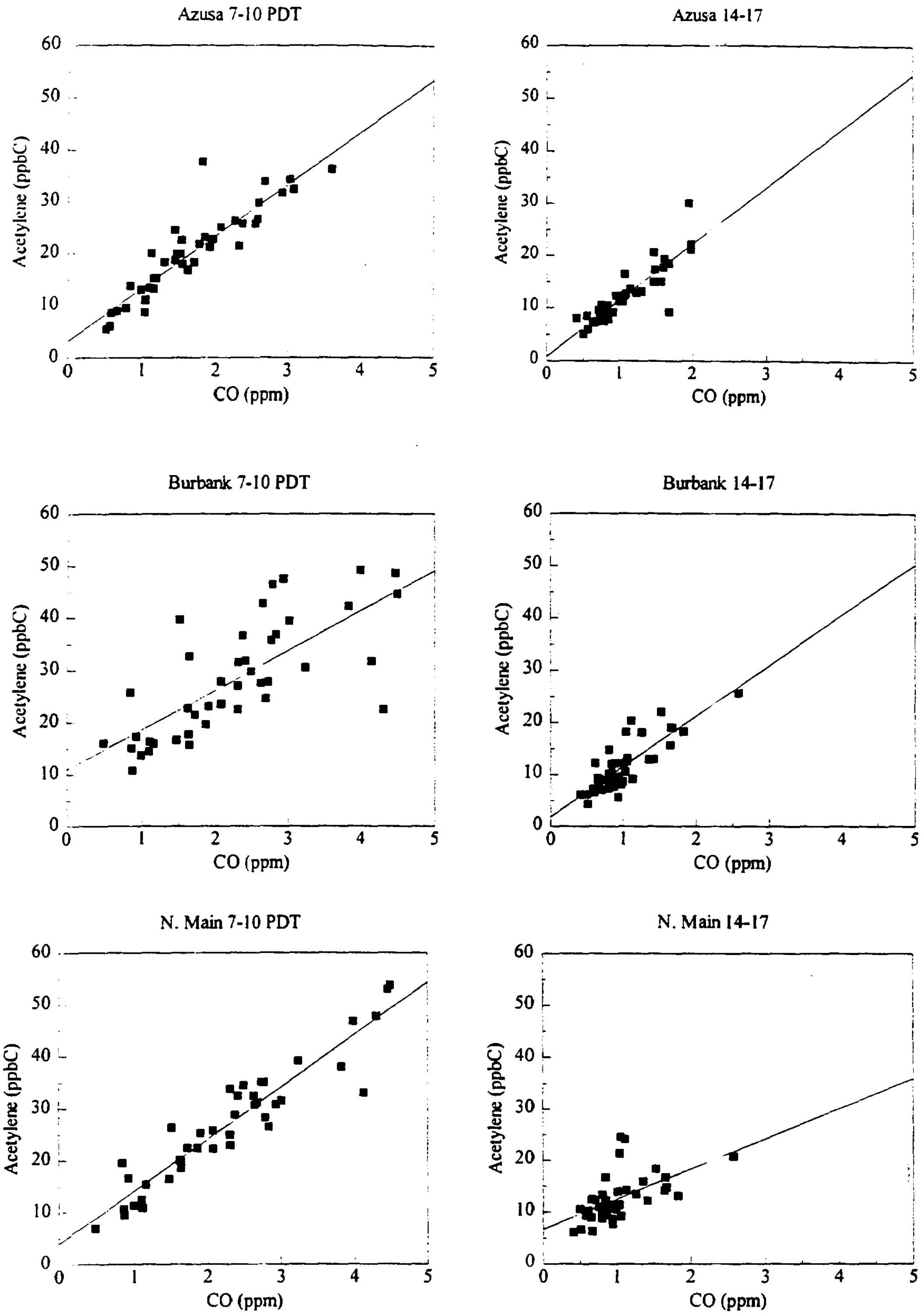


Figure 5-2. Scatterplots of acetylene versus carbon monoxide for SoCAB samples

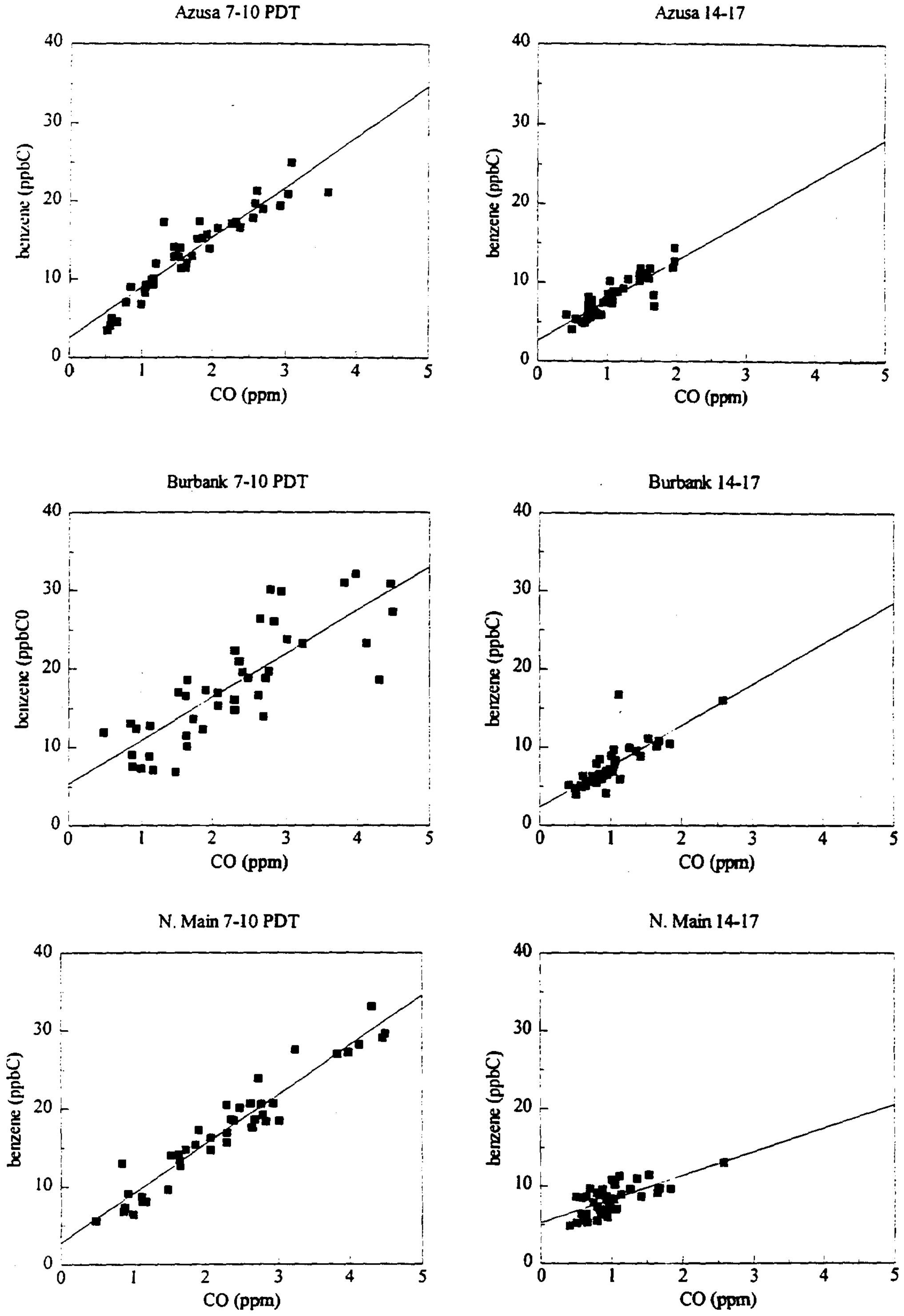


Figure 5-3. Scatterplots of benzene versus carbon monoxide for SoCAB

Figure 5-4 shows scatterplots of acetylene versus ethylene. As expected, these two species show excellent correlation at all three sites. The ratios of ethylene to acetylene for the morning samples are 0.89, 0.85 and 0.87 at Azusa, Burbank and Los Angeles, respectively. The corresponding ratios for the afternoon samples are lower at Azusa and Burbank (0.51 and 0.59, respectively), which are both downwind of downtown Los Angeles. The downtown site is located in the western part of the basin where onshore breezes tend to maintain a nearly constant ethylene to acetylene ratio (0.82).

Figures 5-5, 5-6, and 5-7 show correlations of acetylene versus n-butane, acetylene versus toluene and MTBE versus isobutylene, respectively. Acetylene is generally well correlated with both n-butane and toluene at all three sites. The n-butane/acetylene ratios are much higher in the afternoon than during the morning, which may be due to higher contributions of evaporative emissions during the afternoon period. This could also explain the lower isobutylene/MTBE ratios in the afternoon relative to morning ratios since isobutylene is found in tailpipe emissions, while MTBE is found in both tailpipe and evaporative emissions. Another explanation for the lower isobutylene/MTBE ratios is the greater reactivity of isobutylene relative to MTBE. This could account for the higher isobutylene/MTBE ratios at downtown Los Angeles compared to the same ratios at Azusa and Burbank, as in the case of the ethylene/acetylene ratios.

5.3 Temporal and Spatial Variations

The morning and afternoon NMHC mixing ratios for the six seven-day periods are plotted in Figure 5-8. These diurnal patterns are consistent with the prevailing meteorology and the diurnal pattern of emissions. Mixing ratios are highest during the morning because of the combination of high emission rates from the morning traffic and low mixing heights that occur at this time of day. Mixing ratios decrease over the course of the day because wind speeds and mixing heights increase during the daylight hours, while emissions are relatively constant. Mixing ratios typically increase after 1700 hrs because of the increased evening traffic and lowering of mixing heights. Figure 5-8 shows that the morning and afternoon NMHC mixing ratios at each site generally track each other despite large day-to-day variations caused by changes in meteorological conditions. Additionally, NMHC mixing ratios show similar time-series patterns at the three sites. Figure 5-9 shows the time-series plot of carbon monoxide and MTBE. The two time series are virtually identical, indicating that the two species are from the same source. These time series are consistent with our understanding of the physical relationship between emissions, meteorological conditions and resulting spatial and temporal variations in ambient concentration.

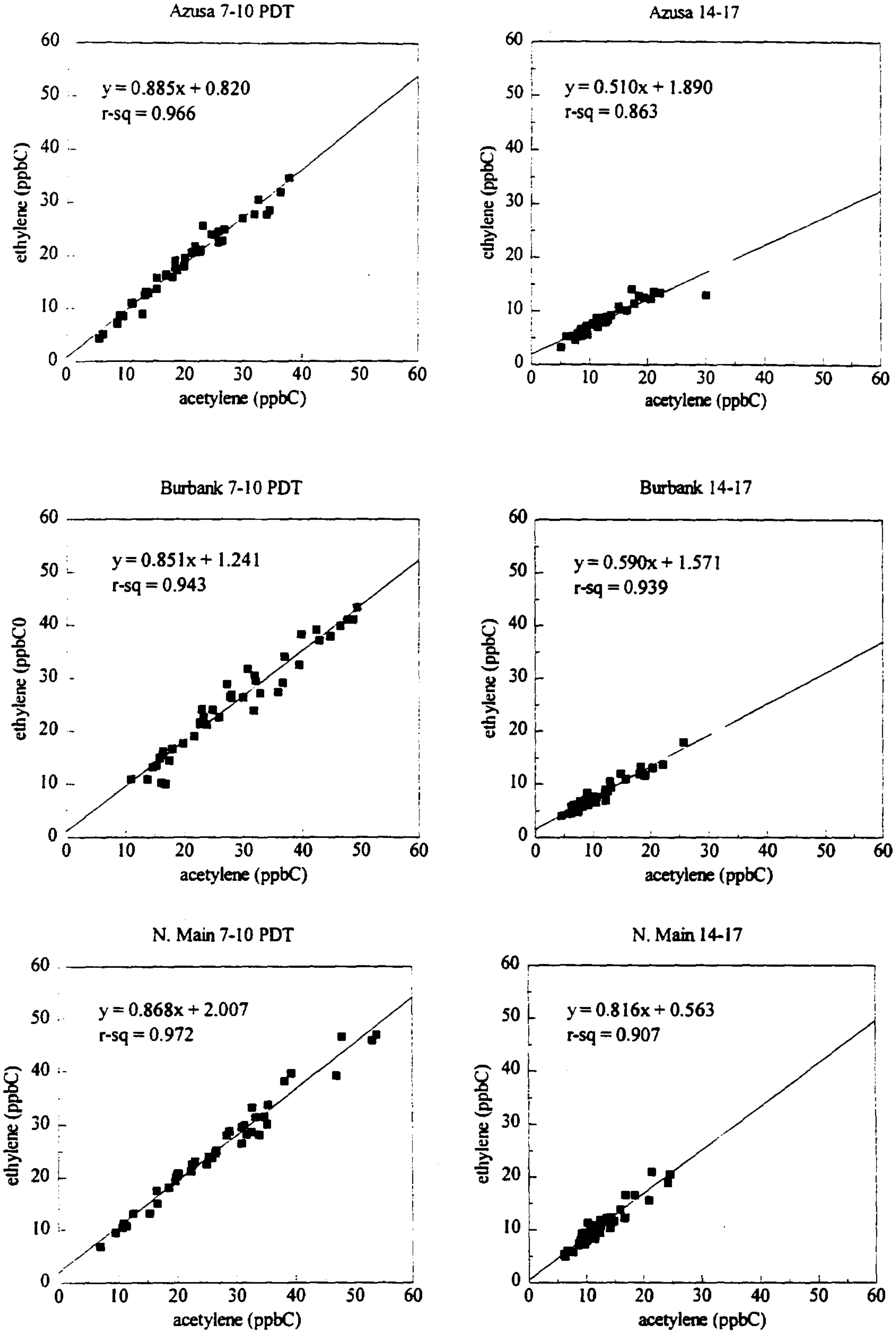


Figure 5-4. Scatterplots of ethylene versus acetylene for SoCAB samples.

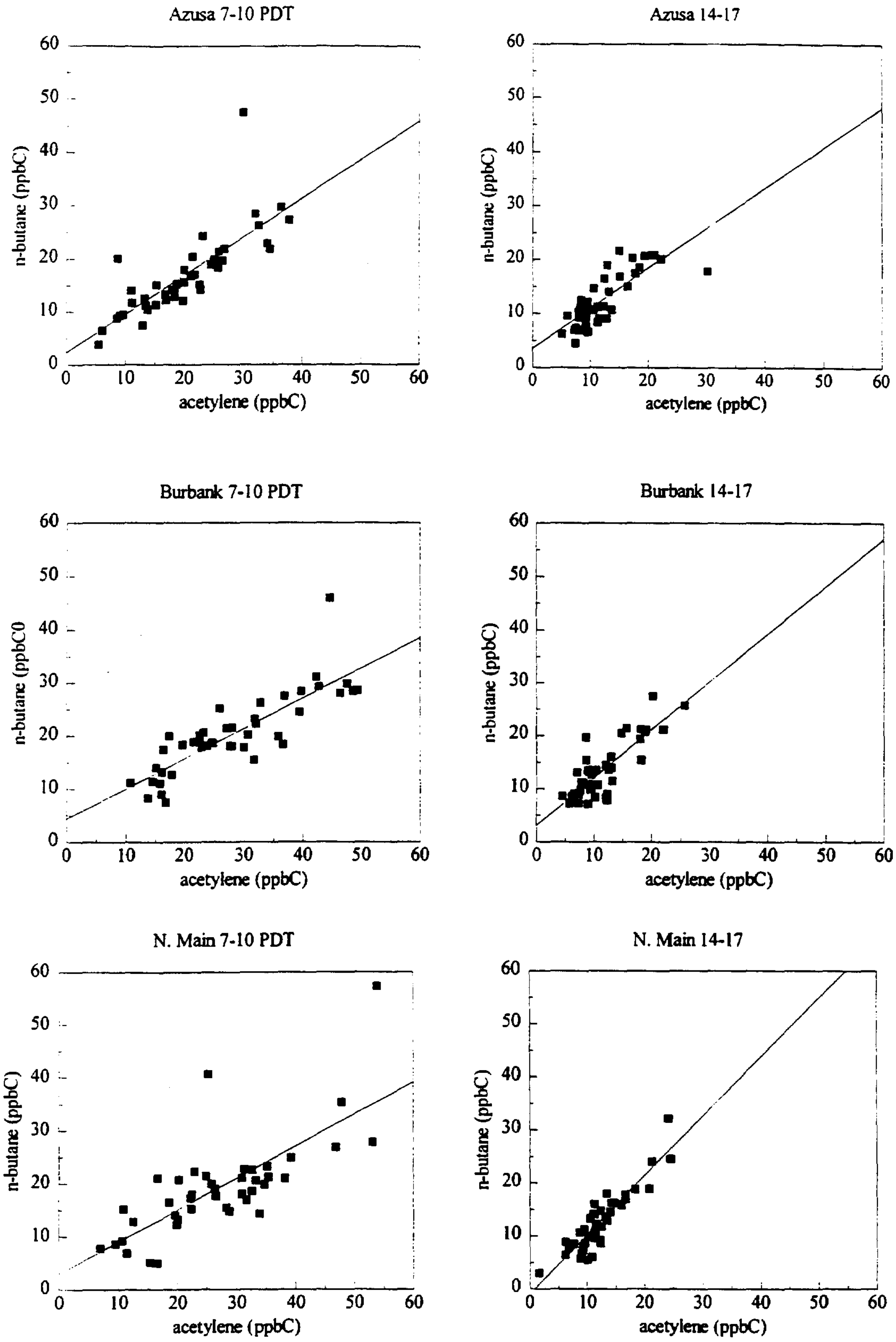


Figure 5-5. Scatterplots of n-butane versus acetylene for SoCAB samples.

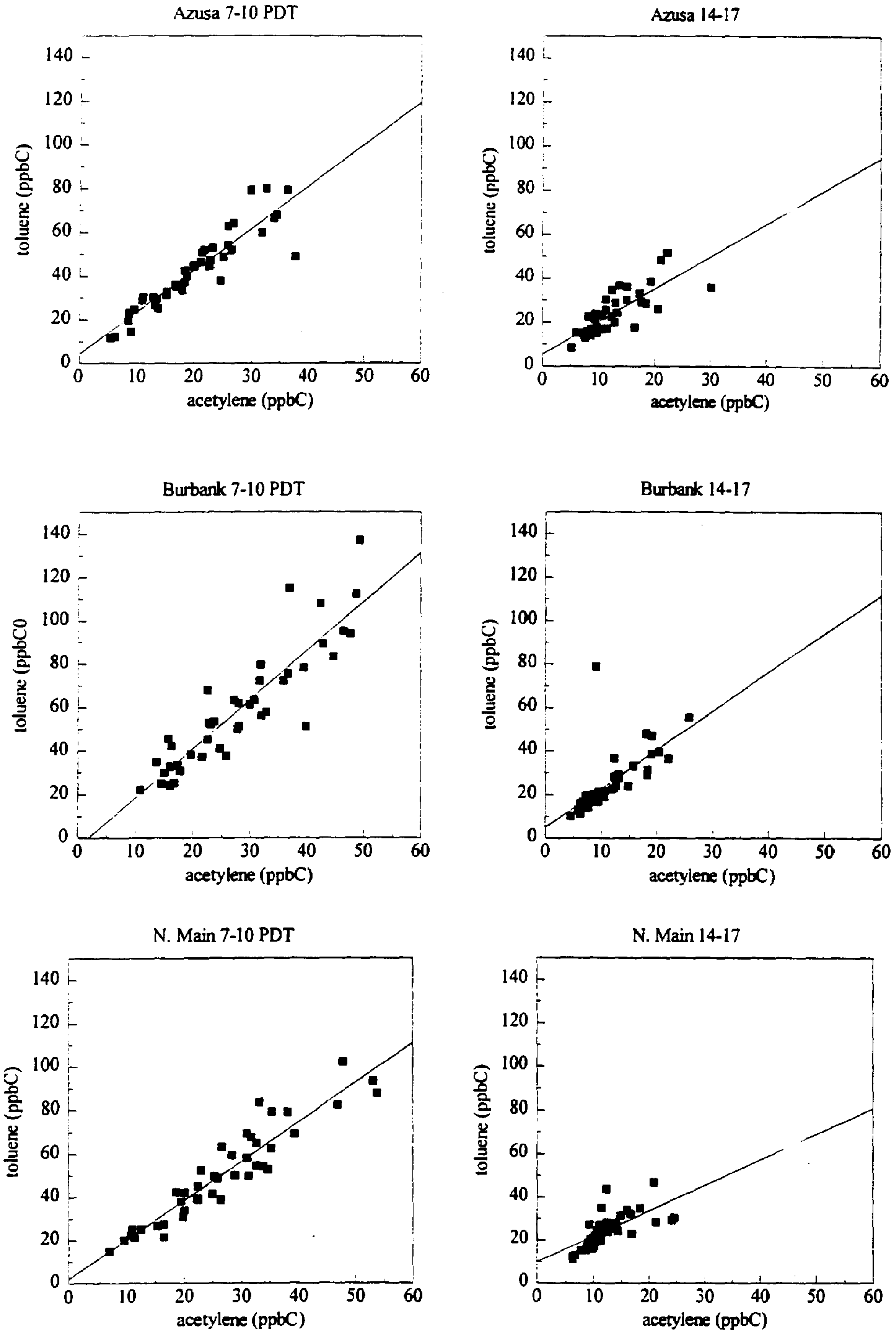


Figure 5-6. Scatterplots of toluene versus acetylene for SoCAB samples.

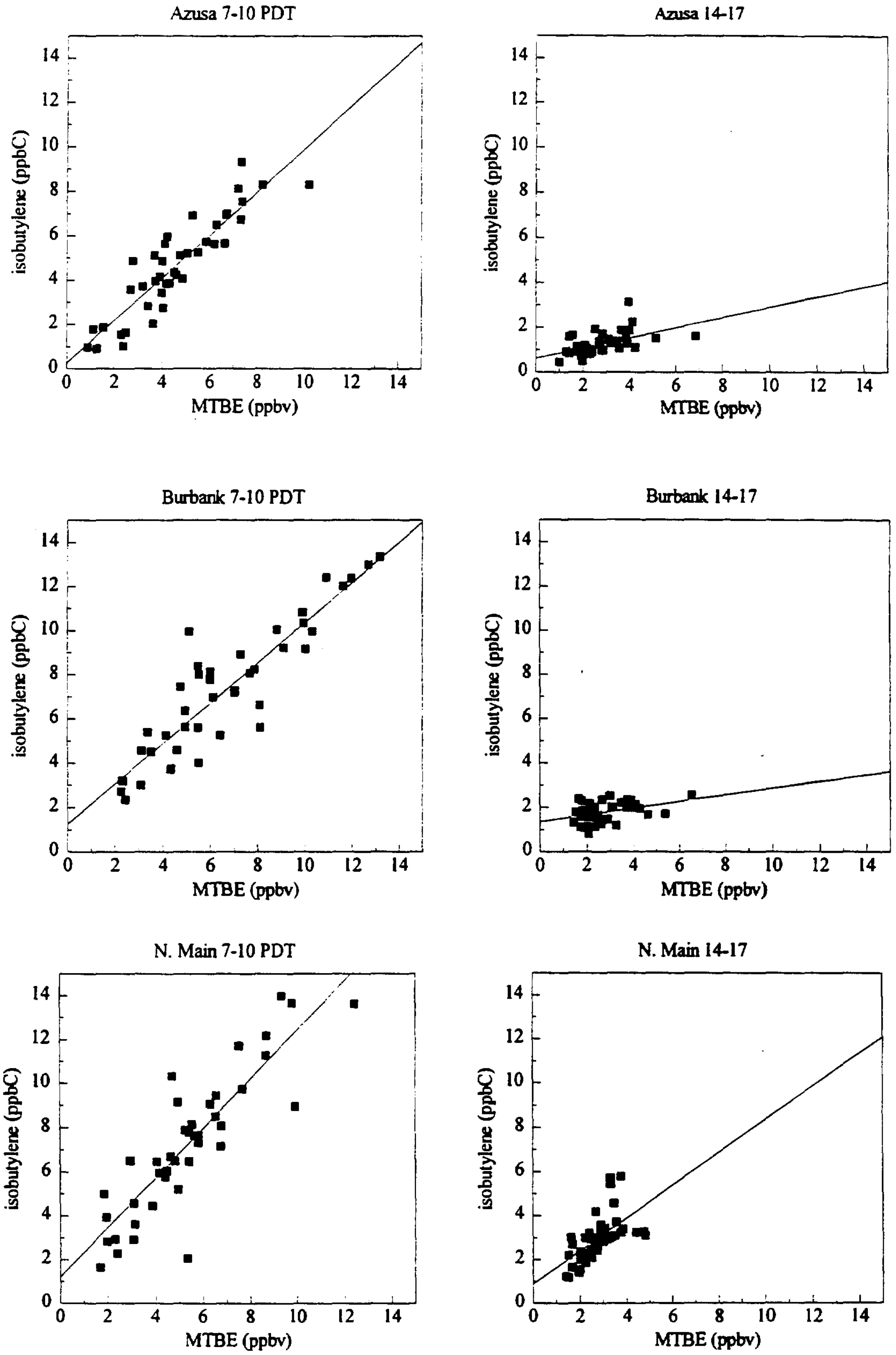
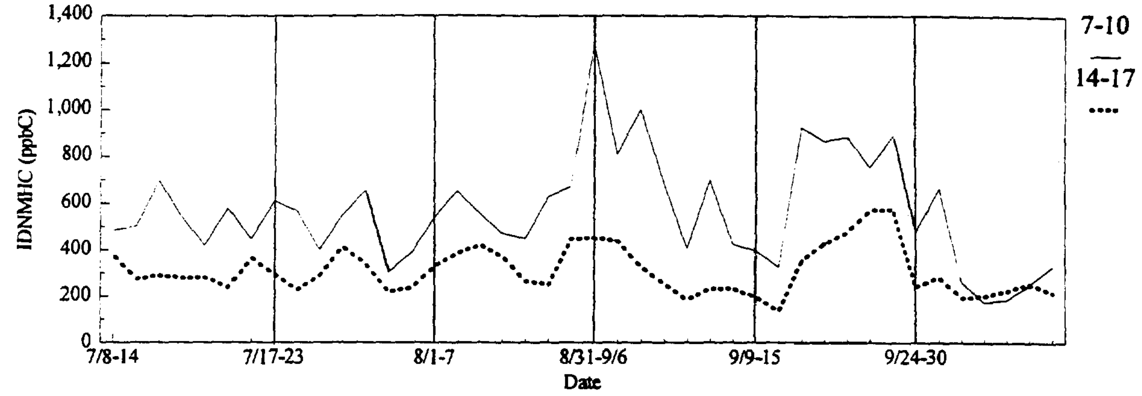
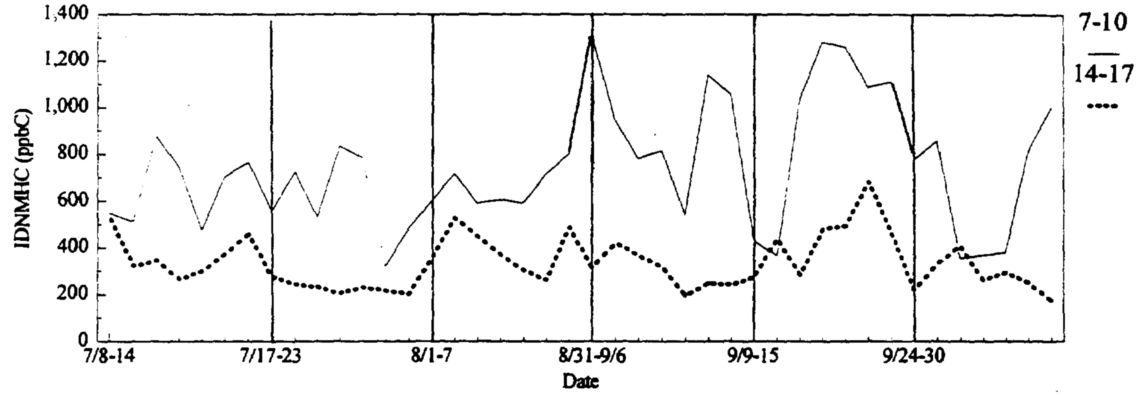


Figure 5-7. Scatterplots of isobutylene versus MTBE for SoCAB samples.

Azusa



Burbank



Los Angeles N. Main

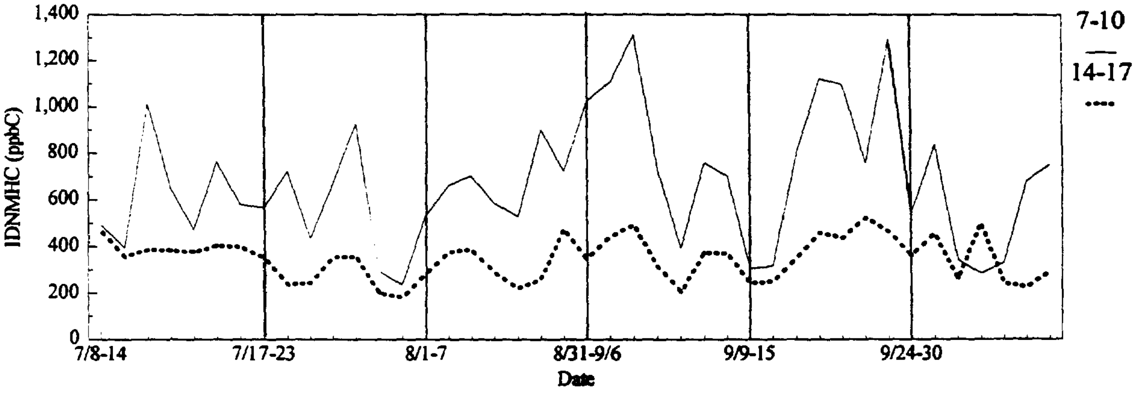
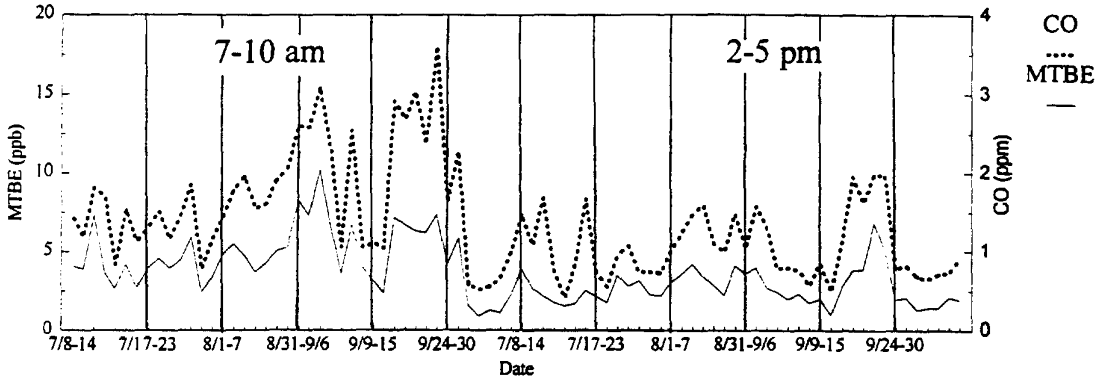
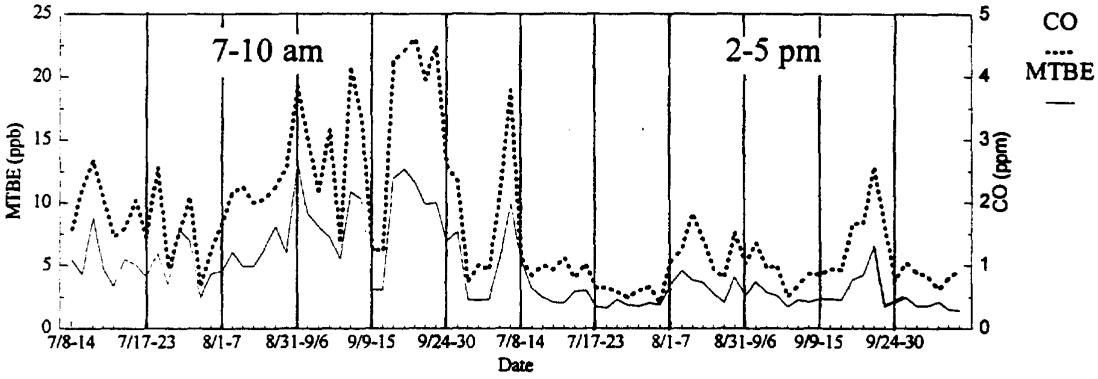


Figure 5-8. Time series plots of total NMHC for SoCAB samples.

Azusa



Burbank



Los Angeles N. Main

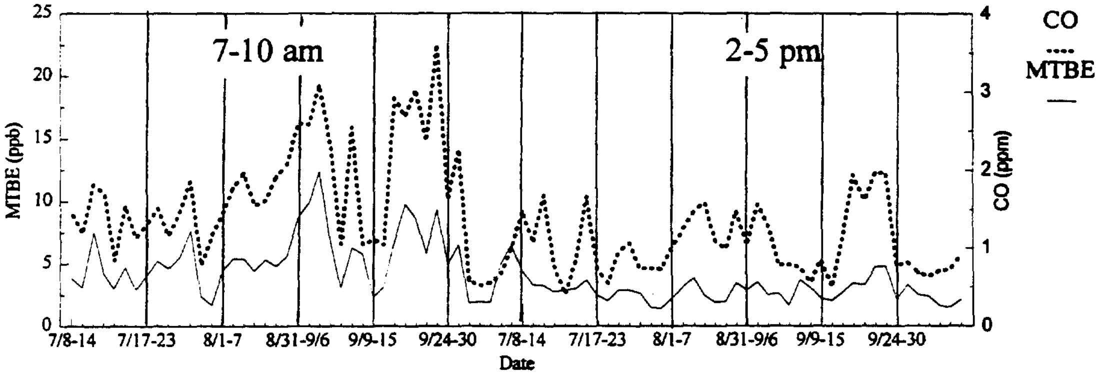


Figure 5-9. Time series plots of carbon monoxide and MTBE for SoCAB samples.

6.0 1997 SOUTHERN CALIFORNIA OZONE STUDY (SCOS97)

The $7+ million 1997 Southern California Ozone Study (SCOS97) was conducted in coordination with the North American Research Strategy for Tropospheric Ozone (NARSTO). The SCOS97 brought together a large number of interested governmental entities as stakeholders, and benefited from consultation and cooperation with the atmospheric sciences academic community. The resultant modeling and data analyses will be used to design ozone attainment strategies and to resolve intra-regional air pollution transport issues.

This study featured the most comprehensive network of instruments ever assembled to measure both ground level and upper air meteorological and air quality data. In addition to enhancing the existing surface monitoring network with more locations and additional measurements, sophisticated technologies were used to gather important data. The study, which included aerosol, solar radiation, and trace compound measurements, featured a vast array of remote sensing instruments using radio and light waves to measure weather and air quality conditions above ground level. More traditional but less commonly used methods included aircraft and balloons to gather critical information about conditions aloft.

The data collected during SCOS97 will be used in modeling and data analyses to provide the most definitive answers yet to solving the persistent air quality problems in a complex region. Analysis of these data will improve the current emission control plans to attain existing ambient air quality standards and will also help design technically defensible plans for the new national standards for 24-hour-average $PM_{2.5}$ and 8-hour-average ozone. The cooperation of the study sponsors and supporters in integrating and piggybacking projects made it possible to leverage the available public funds for maximum scientific benefit.

6.1 Ambient Sampling Sites and Schedule

Table 6-1 shows SCOS97 sampling sites and sampling schedule employed in each site.

6.2 Ambient Air Sampling Procedures

Volatile organic compounds (in the range of $C_2 - C_{12}$) were collected using stainless-steel polished canisters, as described in Section 2.3.1, above. Carbonyl compounds were collected using C_{18} Sep-Pak cartridges (Waters Associates, Milford, MA) which have been impregnated with purified acidified 2,4-dinitrophenylhydrazine (DNPH), as described in Section 2.3.2. DNPH-impregnated C_{18} SepPack cartridges were prepared and analyzed by the DRI Organic Analytical Laboratory.

During the Caldecott Tunnel experiment, in addition to canister and carbonyl samples, semi-volatile organic compounds (SVOC) were collected using the DRI-constructed Sequential Fine Particulate/Semi-Volatile Organic Compounds Sampler (PSVOC sampler). Figures 6-1 and 6-2 show the PSVOC sampler. This is a multiple-event sampler which allows unattended collection of up to four samples. The air sample is drawn through a cyclone separator with a cut-off diameter of 2.5 µm, operating at 113 lpm. Downstream of the cyclone, a ½-inch copper manifold leads to four momentum diffuser chambers. Each chamber is followed by a filter/PUF/XAD/PUF/filter cartridge holder and is connected to a vacuum pump through a solenoid valve, a ball valve, and a flow controller. When one of the solenoid valves is opened

Table 6-1. SCOS97 Sampling Sites and Schedules

Sampling Site	Sampling Dates	Sampling Time	Comments
Anaheim	8/04-8/06; 8/22-8/23; 9/04-9/06; 9/28-9/29; 10/03-10/04	0600-0900	
Barstow	7/14; 8/04-8/06; 8/22-8/23; 9/04-9/06; 10/03-10-04	0200-0500, 0800-1100, 1200-1500, 1600-1900 and 2000-2300 each sampling day	Carbonyls only
Burbank	8/04-8/06; 8/22-8/23; 9/04-9/06; 9/28-9/29; 10/03-10/04	0600-0900 and 1300-1600 each sampling day	High acetone; high >C_{10} concentrations
Caldecott Tunnel	11/16-11/18	1200-1500 each sampling day	VOC, carbonyls and PAH
	11/19-11/20	1530-1830	
Catalina Island	8/04-8/06; 8/22-8/23; 9/04-9/06; 9/28-9/29; 10/03-10/04	0600-1800 and 1800-0600 each sampling day	
Mexicali	7/14	1500-1800	
	8/04-8/06;	6000-9000 and 1500-1800 each sampling day	
	8/22-8/23; 9/04-9/06; 9/28-9/29; 10/03-10/04		
Mount Baldy	9/28	1300-1600 and 1700-2000	As below for Pine Mountain
	9/29, 10/3-10/4	0300-0600, 0600-0900, 1300-1600, 1700-2000 and 2000-2300 each sampling day	
Pine Mountain	8/04	1700-2000 and 2030-2115	Comparison with UCR Tenax biogenic hydrocarbons
	8/05	0300-0530; 0600-0900; 0900-1130; 1700-2000	
	8/06	0300-0600; 0600-0900; 1300-1600	
	9/04	1700-2000; 2000-2400	
	9/05	0000-0330; 0345-0600; 0600-0900; 1300-1600; 1700-2000; 2000-0300	

Table 6-1. SCOS97 Sampling Sites and Schedules (cont.).

Sampling Site	Sampling Dates	Sampling Time	Comments
Pine Mountain (cont.)	9/06	0300-0600; 0600-0900; 1300-1600; 1700-2000; 2000-2400	
	9/07	0000-0300; 0300-0600; 0600-0900	
Point Conception	8/11-8-12; 8/22-8/23; 9/04-9/06; 9/28-9/29; 10/03-10/04	0600-1800 and 1800-0600 each sampling day	Late start (8/11/97)
San Nicholas Island	7/14	0600-0630, 1100-1800	
	8/04	1030-1748, and 1800-0600	
	8/05-8/06, 8/22-8/23, 9/04-9/06, 9/28-9/29, 10/03-10/04	0600-1800 and 1800-0600 each sampling day	
Tijuana-Rosarito	7/14; 8/04-8/06; 8/22-8/23; 9/04-9/06; 9/28-9/29; 10/03-10/04	1000-1300 and 1300-1600 each sampling day	

and three others are closed, the air stream enters only this one chamber which is connected to the pump. The sampling time is controlled by a four-channel Grasslin timer, which automatically opens and closes solenoid valves at the appropriate time. An independent elapsed time meter records the sampling time for each channel. The flow is set using a calibrated rotameter on the inlet side of the copper sampling line and is maintained at a constant 113 lpm during sampling by a flow controller.

Prior to sampling, all sampling media were cleaned in the laboratory. The Amberlite XAD-4 resin (20-60 mesh, purchased from Aldrich Chemical Company. Inc.) was Soxhlet extracted with methanol followed by dichloromethane (CH_2Cl_2), each for 8 hours. The cleaned resin was dried in a vacuum oven heated to 40 °C and stored in sealed glass containers in a clean freezer. The PUF plugs (purchased from ER Carpenter Company, Inc., Richmond, VA, and cut into 2" diameter plugs at DRI) were Soxhlet extracted with 10% diethyl ether in hexane, followed by acetone. The TIGF filters (Pallflex, Putnam, CT, T60A20, 102 mm diameter) were cleaned by sonification in CH_2Cl_2 for 30 minutes, followed by another 30-minute sonification in methanol. Then they were dried, placed in aluminum foil, and labeled. Each batch of precleaned XAD-4 resin and ~10% of precleaned TIGF filters and PUF plugs were checked for purity by solvent extraction and GC/MS analysis of the extracts. The PUF plugs and XAD-4 resins were assembled into glass cartridges (10 g of XAD between two PUF plugs), wrapped in aluminum foil and stored in a clean freezer prior to shipment to the field.

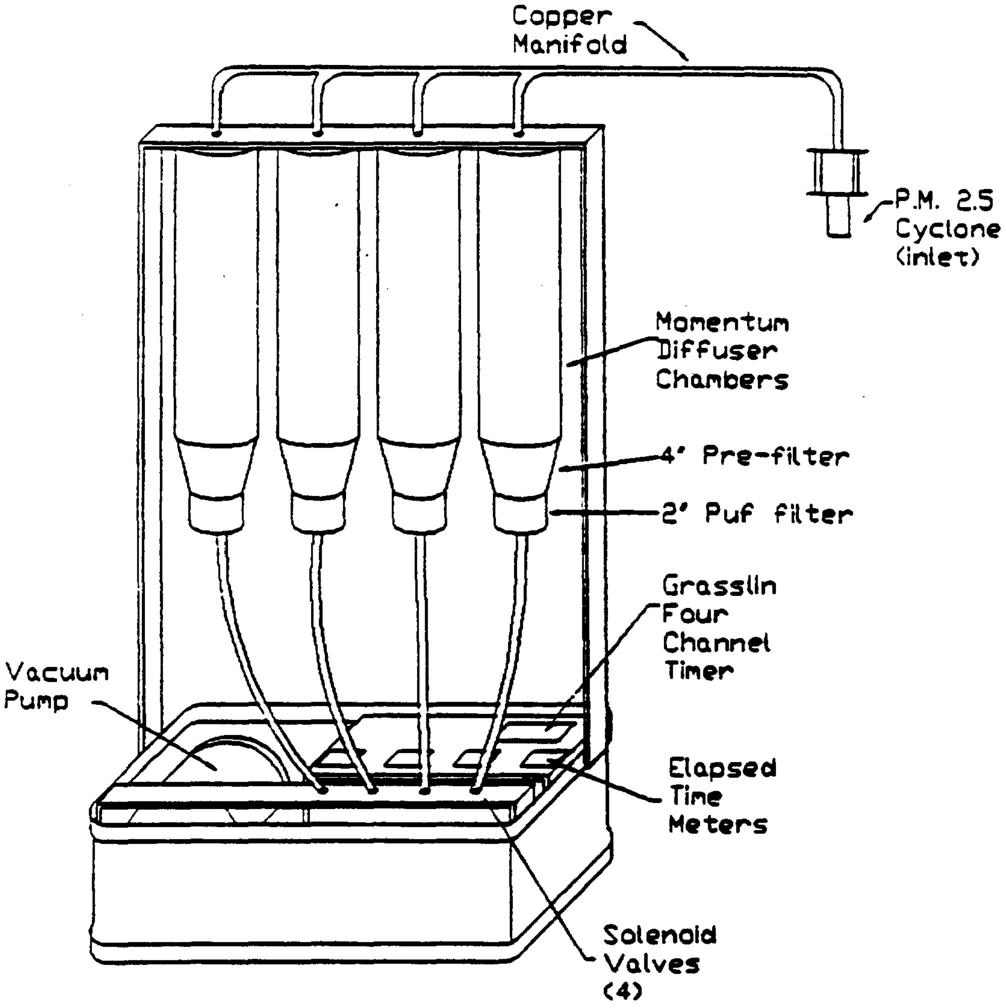


Figure 6-1. DRI Sequential Fine Particulate/Semi-Volatile Organic Compounds Sampler.

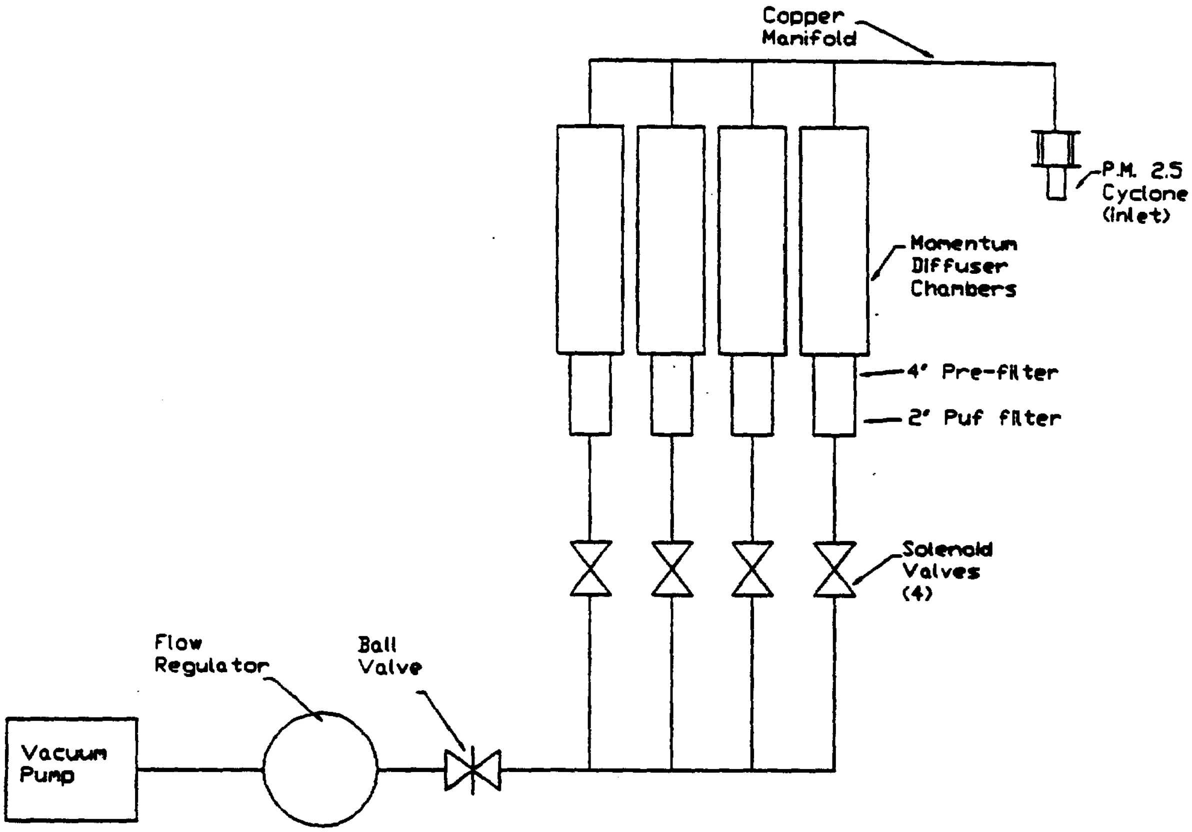


Figure 6-2. Schematic of the DRI Sequential Fine Particulate/Semi-Volatile Organic Compounds Sampler.

Table 6-2. List of Halogenated Compounds and Their Mnemonics Analyzed by GC/ECD Method

Compound	Mnemonic
Freon 12 (dichlorodifluoromethane)	F12
Methylbromide	MEBR
Freon 11 (trichlorofluoromethane)	F11
Vinylidenechloride	VINECL
Methylene chloride	MECL2
Freon 113 (1,1,2-trichloro-1,2,2-	F113
Trans-1,2-dichloroethylene	T12DCE
Cis-1,2,-dichloroethylene	C12DCE
Chloroform	CCL3
1,2-dichloroethane	ETDC12
Methyl chloroform	MECCL3
Carbon tetrachloride	CCL4
1,3-Dibromomethane	DBRME
Trichloroethylene	TCENE
1,1,2-Trichloroethane	TCE112
Chlorodibromomethane	CLDBRM
1,2-Dibromoethane	ETDB12
Perchloroethylene	PERC
m-Dichlorobenzene	MDCBZ
p-Dichlorobenzene	PDCBZ
o-Dichlorobenzene	ODCBZ

6.3 Analytical Procedures

Canister samples were analyzed for C_2-C_{12} hydrocarbons, $CO/CO_2/CH_4$ and MTBE by the methods described in Section 3.1 above. For the Mexican sites (Mexicali and Rosarito), the analysis for halogenated compounds was also performed by GC/ECD method (analogous to EPA TO-14 Method). Table 6-2 lists the compounds analyzed by this method.

Carbonyl Compounds. Each DNPH-impregnated cartridge after sampling was eluted slowly with 2 ml of HPLC-grade carbonyl-free acetonitrile. The eluted solutions were transferred into a vial with a PTFE lined septum and injected into the analytical column using an auto sampler for quantitation of hydrazones. Carbonyl identification and quantitation involve comparison with external standards, i.e., acetonitrile solutions of precisely weighed amounts of pure hydrazones synthesized in the DRI laboratory and those obtained from Radian's Standards Division. The HPLC response factors to formaldehyde or any other carbonyl hydrazone (at 360 nm wavelength) are calculated from absorbance vs. concentration plots for known standards. Multipoint calibration curves with a minimum of 3 concentration levels are established prior to sample analysis using carbonyls obtained from Radian's Standards Division. These calibrations are checked every 12 samples during the analysis of field samples. If a continuing calibration shows deviation of more than 10%, a full calibration of the instrument is performed and the cause of this calibration drift is investigated. Calibration standards for each parameter are chosen to bracket the expected concentrations of these parameters in the sample and to operate within the linear dynamic range of the instrument. Samples that fall outside the calibration range are diluted until bracketed by the calibration curve. Instrument responses to calibration standards for each parameter are analyzed using a least squares linear regression. The calibration must generate a correlation coefficient (R^2) of 0.99 to be acceptable. Typical calibration curves for carbonyl compounds (formaldehyde, acetaldehyde and acetone) are shown in the DRI SOP "Analysis of Carbonyl Compounds in Air Samples on DNPH-Impregnated Cartridges," which is available upon request.

Detection limits for air samples are determined either by the analytical detection limit or by the background carbonyl hydrazone content of the cartridges. DRI has found the latter to be the determining factor for formaldehyde, acetaldehyde and acetone. The ambient air detection limit for carbonyl compounds during one-hour sampling at 1.0 lpm would be in the range of 0.5-1 ppbv. A list of carbonyls analyzed by DRI along with their mnemonics and detection limits is given in Table 6-3.

Table 6-3. Detection Limits of Carbonyls.

Analyte	Mnemonic	Detection Limit (ppbv)	
		[a]	[b]
Formaldehyde	Formal	0.5	0.2
Acetaldehyde	Acetal	0.5	0.2
Acetone	Aceto	0.5	0.2
Methyl Ethyl Ketone (MEK)	MEK	0.5	0.2
Acrolein	Acroln	0.5	0.2
Acrolein X[c]	Acrolx	0.5	0.2
Methacrolein	Macrol	0.5	0.2
Propionaldehyde	Proal	0.5	0.2
Butyraldehyde	Butal	0.5	0.2
Crotonaldehyde	Croton	0.5	0.2
Benzaldehyde	Benzal	0.5	0.2
Tolualdehyde	Tolual	0.5	0.2
Valeraldehyde	Valal	0.5	0.2
Hexanaldehyde	Hexal	0.5	0.2
Glyoxal	Gloxl	0.5	0.2

[a] This detection limit is based on 60 liters of air sampled at 1.0 lpm through DNPH cartridge.

[b] This detection limit is based on 180 liters of air sampled at 1.0 lpm through DNPH cartridge.

[c] Acrolein X is a product of rearrangement of acrolein that occurs during sampling through acidified DNPH-impregnated cartridges.

Along with ambient samples, laboratory blanks and field blanks are analyzed. Laboratory blanks for carbonyls consists of a DNPH-coated silica gel cartridge followed by elution with 2 ml of carbonyl-free acetonitrile and analyzed in the same conditions as used for field samples. Field blanks are treated identically as actual samples, except that no air is sampled through the cartridges. Ten percent of all field samples will undergo duplicate analysis. A laboratory duplicate is an aliquot of a field sample taken through the entire analytical procedure. For aldehydes and ketones the laboratory duplicates are taken from the sample after extraction from the media.

PAH. All PUF/XAD/PUF/filter cartridges were analyzed as follows: prior to extraction, the following deuterated internal standards were added to each filter-sorbent pair: naphthalene-d_8, acenaphthylene-d_8, phenanthrene-d_{10}, anthracene-d_{10}, chrysene-d_{12}, fluoranthene-d_{10}, pyrene-d_{10}, benz[a]anthracene-d_{12}, benzo[e]pyrene-d_{12}, benzo[a]pyrene-d_{12}, benzo[k]fluoranthene-d-$_{12}$, coronene-d-$_{12}$, and benzo[g,h,i]perylene-d_{12}. Since PUF should not be extracted with dichloromethane, the PUF plugs were Soxhlet extracted separately with 10% diethyl ether in hexane, and the filter-XAD pairs were microwave extracted with dichloromethane; these extraction methods have been reported to yield a high recovery of PAH (Chuang et al., 1990) and other compounds of interest (Hawthorne et al., 1988, 1989).

The extracts were then concentrated by rotary evaporation at 20 °C under gentle vacuum to ~1 ml and filtered through 0.45 mm Acrodiscs (Gelman Scientific), with the sample flask rinsed twice with 1 ml CH_2Cl_2 each time. Approximately 100 µl of acetonitrile was added to the sample and CH_2Cl_2 was evaporated under a gentle stream of nitrogen. The final sample volume was adjusted to 1 ml with ACN. This procedure has been tested by Atkinson et al. (1988). The detailed procedure is described in the DRI SOP "Analysis of Semi-Volatile Organic Compounds by GC/MS," available on request.

The samples were analyzed by the EI (electron impact) GC/MS technique, using a Hewlett-Packard 5890 GC equipped with a 7673A Automatic Sampler and interfaced to a 5970B Mass Selective Detector (MSD) for PAH. Injections (1 µl) were made in the splitless mode onto a 60 m 5% phenylmethylsilicone fused-silica capillary column (DB-5ms, J&W Scientific). Quantification of the PAH was obtained by the multiple ion detection (MID, HP5970B MSD) technique, monitoring the molecular ion of each compound of interest and deuterated PAH, added prior to extraction as internal standards. Calibration curves for the GC/MS quantification were made for the molecular ion peaks of the PAH and all other compounds of interest using the corresponding deuterated species (or the deuterated species most closely matched in volatility and retention characteristics) as internal standards. National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 1647 (certified PAH) with the addition of deuterated internal standards and of those compounds not present in the SRM were used to make calibration solutions. A three-level calibration was performed for each compound of interest and the calibration check (using median calibration standards) was run every ten samples to check for accuracy of analyses. If the relative accuracy of measurement (defined as a percentage difference from the standard value) was less than 30%, the instrument was recalibrated. For quantification of these compounds, the deuterated PAH most closely matched in volatility and retention characteristics were used.

6.4 Results

Table 4-1 (Section 4) lists VOC quantified from the canister samples. Please note that concentrations of MTBE, ethanol, methanol and other oxygenated compounds are given in ppbC, in contrast to the 1995-1996 data, where ppbv units were used (to convert from ppbC to ppb divide by the number of carbon atoms). With the exception of methanol, ethanol and MTBE, the compound-specific calibration for species flagged as '**o**' and '**n**' are not performed, and the concentrations for these compounds are approximate only. The results of analysis of all ambient canister samples collected during SCOS97 are submitted in dBase format on two 3.5" diskettes (nos. IVand V) with this report. The files "smrpt03c" and "smrpt03u" contain hydrocarbon concentration data and their uncertainties, respectively, and "smecd03c" and "smecd03u" contain halocarbon data and their uncertainties, respectively, for the Mexican sites. Files "scrpt08c" and "scrpt08u" contain Caldecott Tunnel canister data and files "scrpt09c" and "scrpt09u" contain all remaining SCOS canister data. The following files contain carbonyl compound concentration and field data: "sccov09d" and "scfld09d" (all SCOS sites including Caldecott Tunnel), "smcov03d" and "smfld03d" (Mexicali and Rosarito), and "bacov01d" and "bafld01d" (Barstow). PAH data from Caldecott Tunnel are contained in the file "sccon08p". In summary, 194 canister samples (including 19 replicates), 232 carbonyl samples (including 26 replicates and 21 field blanks) and 9 PAH samples (including 2 replicates and 2 field blanks) were analyzed for this part of the study. The replicate and blank data for carbonyl and PAH measurements are included in the file "repblank.xls" and the replicate data for canister samples are in the file "rep_can.xls." The full list of carbonyl and canister samples is shown in the files "list_all.xls" and "list_cans.xls", respectively.

For carbonyl compounds, only the samples collected during the August 4-6, September 4-6 and September 28-29 IOP days were analyzed. The exception is Barstow — all valid carbonyl samples were analyzed. Field blank concentrations for carbonyl samples collected at the Rosarito site are high and variable; there is a possibility that actual samples and field blanks were mislabeled by the sampling crew at this site. This is the reason that the two Rosarito samples, TR97080410 and TR97080613, show zero concentrations for all carbonyl compounds after subtraction of the field blank values. Acetone concentrations at Burbank are very high; in fact they cannot be measured quantitatively, since the back-up cartridge (labeled as 2) shows nearly the same concentration of acetone as the first cartridge (labeled as 1). It was found during the site survey that the small metal shop adjacent to the Burbank station uses acetone as a degreasing agent (Dr. Fujita, personal communication). Also, in Burbank site, the concentrations of higher mw hydrocarbons measured from canisters were unusually high; it was established (Dr. Fujita, personal communication) that roofing was done at the station, just prior to the beginning of the sampling program.

7.0 REFERENCES CITED

Apel, E.C., J.G. Calvert and F.C. Fehsenfeld (1994). "The Nonmethane Hydrocarbon Intercomparison Experiment (NOMHICE): Tasks 1 and 2." *J. Geophys. Res.*, **99**, 16,651-16,664.

Atkinson, R., J. Arey, A.M. Winer and B. Zielinska (1988). "A survey of ambient concentrations of selected polycyclic aromatic hydrocarbons (PAH) at various locations in California." Final Report, prepared under Contract No. A5-185-32, for the California Air Resources Board, Sacramento, CA, by Statewide Air Pollution Research Center, University of California, Riverside, CA.

California Air Resources Board, "Clean Air Benefits." Cleaner Burning Gasoline Backgrounder I, California Air Resources Board, Sacramento, CA, 1996.

Chuang, J.C., M.R. Kuhlman and N. Wilson (1990). "Evaluation of methods for simultaneous collection and determination of nicotine and polynuclear aromatic hydrocarbons in indoor air." *Environ. Sci. Technol.*, **24**, 661-665.

Fujita, E.M., W.A. Lonneman, A. Van Arsdale and A. Oi (1996). "NARSTO-NE Hydrocarbon Laboratory Comparison." Presented at International Symposium, "Measurement of Toxic and Related Air Pollutants," Raleigh-Durham, NC, May 7-9, 1996. Air & Waste Management Association, Pittsburgh, PA.

Fujita, E.M., Z. Lu, L. Sheetz, G. Harshfield and B. Zielinska (1997). "Determination of Mobile Source Emission Source Fraction Using Ambient Field Measurements." Draft Final Report, CRC Project No. E-5a, prepared for Coordinating Research Council, Atlanta, GA, by Desert Research Institute, Reno, NV.

Fung, K., and D. Grosjean (1981). "Determination of Nanogram Amounts of Carbonyls as 2,4-Dinitrophenylhydrazones by High Performance Liquid Chromatography." *Anal. Chem.*, **53**, 168-171.

Fung, K., and B. Wright (1986). "Considerations in Aldehyde Measurements at Sub-ppb Levels with 2,4-Dinitrophenylhydrazine." Presented at 8th American Chemical Society Rocky Mountain Regional Meeting, Denver, CO, June 8-12.

Gertler, A.W., J.C. Sagebiel, and W.A. Dippel (1997a). "The Impact of California Phase 2 RFG on In-use Vehicle Emissions: Gas Phase Species." Draft Final Report, CRC Project No. E-27, prepared for Coordinating Research Council, Atlanta, GA, and South Coast Air Quality Management District, Diamond Bar, CA, by Desert Research Institute, Reno, NV.

Gertler, A.W., J.C. Sagebiel, D.N. Wittorff, W.R. Pierson, W.A. Dippel, D. Freeman and L. Sheetz (1997b). "Vehicle Emissions in Five Urban Tunnels." Final Report, CRC Project No. E-5, prepared for Coordinating Research Council, Atlanta, GA, by Desert Research Institute, Reno, NV.

Hawthorne, S.B., D.J. Miller, R.M. Barkley and M.S. Kreiger (1988). "Identification of Methoxylated Phenols as Candidate Tracers of Atmospheric Smoke Pollution." *Environ. Sci. Technol.,* **22**, 1191-1196.

Hawthorne, S.B., M.S. Krieger, D.J. Miller and M.B. Mathiason (1989). "Collection and Quantitation of Methoxylated Phenol Tracers for Atmospheric Pollution from Residential Wood Stoves." *Environ. Sci. Technol.,* **23**, 470-475.

Pasek, R., and B. Zielinska (1997). "Changes in ambient hydrocarbon concentrations in the Los Angeles area after the introduction of reformulated gasolines." Presented at Seventh CRC On-Road Vehicle Emissions Workshop, San Diego, CA, April 9-11, 1997. Coordinating Research Council, Atlanta, GA.

Rasmussen, R.A. (1992). "The ABCs of stainless steel canister clean-up and certification." Presented at the 1992 U.S. EPA/A&WMA International Symposium on Measurement of Toxic and Related Air Pollutants, Durham, NC, May 1992. Air & Waste Management Association, Pittsburgh, PA.

Sagebiel, J.C., B. Zielinska, B. (1994). "Effects of using Nafion® dryer on hydrocarbons analyzed from canisters by modified EPA Method TO-14." presented at the U.S. EPA/A&WMA International Symposium on Measurements of Toxic and Related Air Pollutants, Durham, NC. Air & Waste Management Association, Pittsburgh, PA.

Scanlon, J.T., and D.E. Willis (1985). "Calculation of flame ionization detector relative response factors using the effective carbon number concept." *J. Chromat. Sci.,* **23**, 333-340.

Shire, J.D. (1996). *Analytical Methods for the Quantification of Oxygenated Volatile Organic Compounds, Carbon Monoxide and Carbon Dioxide in Ambient Air Samples.* M.Sc. Thesis, University of Nevada, Reno.

Stoeckenius, T.E., G. Yarwood, M.P. Ligocki, J.P. Cohen, S.B. Shepard, R.E. Looker, E.M. Fujita, H.H. Main and P.T. Roberts (1995). "Feasibility Study for a 1995-1996 Southern California Air Quality Monitoring Program." Final Report SYSAPP94-94/065d, prepared for Coordinating Research Council, Atlanta, GA, by Systems Applications International, San Rafael, CA.

Yieru, R., O. Qingyu and Y. Weile (1990). "Characteristics of flame ionization detection for the quantitative analysis of complex organic matters." *Anal. Chem.,* **62**, 2063-2064.

Zielinska, B., G. Harshfield, E. Fujita, J. Sagebiel and R. Pasek (1997). "Volatile organic compound concentrations in the South Coast Air Basin (CA) during the summers of 1995 and 1996." Paper invited for presentation at 90th Annual Meeting, Toronto, Canada, June 8-13, 1997. Air & Waste Management Association, Pittsburgh, PA.

Zielinska, B., J. Shire, G. Harshfield, and R. Pasek (1997). "The concentration of oxygenated compounds in the Los Angeles, CA, area following the introduction of reformulated gasoline." Paper invited for presentation at 90th Annual Meeting, Toronto, Canada, June 8-13, 1997. Air & Waste Management Association, Pittsburgh, PA.

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FINAL REPORT
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Air Monitoring Program for Determination of the Impacts of the Introduction of California's Phase 2 Reformulated Gasoline on Ambient Air Quality in the South Coast Air Basin

CALIFORNIA ENVIRONMENTAL PROTECTION AGENCY

AIR RESOURCES BOARD
Research Division

AIR MONITORING PROGRAM FOR DETERMINATION OF THE IMPACTS OF THE INTRODUCTION OF CALIFORNIA'S PHASE 2 REFORMULATED GASOLINE ON AMBIENT AIR QUALITY IN THE SOUTH COAST AIR BASIN

FINAL REPORT
CONTRACT NO. 94-332

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1.0 PROJECT SUMMARY

1.1 Background and Statement of the Problem

The South Coast Air Basin experiences the most severe air pollution in the United States due to a unique combination of stagnant meteorological conditions, confining geography, and high concentrations of people and industrial activity. It is the only area in the country classified as in "extreme" nonattainment for ozone. Reformulated gasoline is the latest control measure in the three-decade effort to meet air quality standards in the SoCAB. Both the federal government and the State of California have developed specifications for reformulated gasoline (RFG). The federal program is required for all severe and extreme ozone nonattainment areas, whereas the California program applies throughout the state. Both the California and federal RFGs are being introduced in two phases. California Phases 1 and 2 were introduced in 1992 and in June 1996, respectively. Phase I of the federal program was introduced in 1995, and Phase II is scheduled for introduction in 2000.

To meet the reduction in O_3 and CO concentrations required by Title II of the Clean Air Act Amendments (CAAA) of 1990, average specifications for federal Phase I gasoline include a maximum RVP of 7.2 psi, a minimum 2.0% by weight oxygen content, and a maximum 1.0% by weight benzene content. These requirements were effective as of January 1, 1995, and apply to the South Coast Air Basin, Ventura County, and the San Diego Air Basin. The California Phase 2 RFG specifications apply to all gasoline sold in California beginning January 1, 1996, and include a maximum 40 ppmw sulfur content for any batch (average of 30 ppmw); a maximum 1.0% benzene content by volume (average of 0.8); a maximum 6.0% olefin content (average of 4.0); a minimum 1.8% and maximum 2.2% oxygen content by weight; a maximum T90 and T50 of 300 °F and 210 °F, respectively; a maximum 25% aromatic hydrocarbon content by volume (average of 22%); and a maximum RVP of 7.0 psi. California Phase 2 RFG is projected to reduce basin-wide ROG, NO_x, CO, and SO_x emissions by 80, 35, 350, and about 10 tons/day, respectively, by the year 2000 (Stoeckenius et al., 1995). In comparison, basin-wide ROG emissions during the summer of 1990 averaged 1507 tons/day distributed between stationary (42%) and mobile (58%) sources. Compared to motor vehicles using gasoline meeting California Phase 1 RFG criteria, CARB estimates that Phase 2 RFG will achieve about a 17% reduction in ROG from on-road motor vehicles and an 11% reduction in NO_x emissions (CARB, 1996). Actual reductions in southern California in 1996 were less than these estimates since gasoline marketed there in 1995 conformed to the federal Phase I RFG specifications rather than California Phase 1 specifications.

Changes in emissions due to the RFG requirements provide a unique opportunity to measure relationships between emissions and atmospheric concentrations of directly emitted pollutants and photochemical reaction products. In order to provide the data required to determine air quality impacts of the introduction of California's Phase 2 RFG, ambient measurements of speciated hydrocarbons, oxygenated organic gases, methane, carbon monoxide (CO), and carbon dioxide (CO_2) were conducted during the Summers of 1995 and 1996 in the South Coast Air Basin (SoCAB).

In addition, in the Summer of 1997, the Southern California Ozone Study (SCOS97) was conducted in order to update and improve existing aerometric and emission databases and model applications for representing urban-scale ozone episodes in Southern California, and to quantify the contributions of ozone generated from emissions in one Southern California air basin to federal and state ozone standard exceedances in neighboring air basins. These goals are to be met through a five-year process which includes analysis of existing data; execution of a large-scale field study to acquire a comprehensive database to support modeling and analysis; analysis of the data collected during the field study; and the development, evaluation, and application of an air quality simulation model for Southern California. SCOS97 was intended to provide another milestone in the understanding of relationships between emissions, transport, and ozone standard exceedances in Southern California as well as to facilitate planning for further emission reductions needed to attain the NAAQS. As part of SCOS97, DRI collected hydrocarbon and carbonyl samples in selected locations; this effort was conducted as an extension of the 1995-1996 RFG study. This study is described in Section 6.0 of this Report.

The SCOS97-NARSTO program was a $7+ million study that brought together a large number of interested governmental entities as stakeholders, and benefited from consultation and cooperation with the atmospheric sciences academic community. The study featured the most comprehensive network of instruments ever assembled to measure both ground level and upper air meteorological and air quality data. The data collected in support of the SCOS97-NARSTO study will be added to other data collected to make one of the most complete data sets ever collected in the southern California area. The information will be used for modeling and data analysis to support ozone and particulate matter attainment strategies, and to resolve intra-regional air pollution transport issues.

1.2 Project Objectives

The objectives of this study were as follows:

1. To conduct ambient measurements of speciated hydrocarbons, oxygenated organic gases, methane, carbon monoxide (CO), and carbon dioxide (CO_2) during the summers of 1995 and 1996 in the South Coast Air Basin (SoCAB) in order to provide the data required to determine air quality impacts of the introduction of California's Phase 2 RFG.

2. To conduct ambient measurements of speciated C_2-C_{12} hydrocarbons, carbonyl compounds (C_1-benzaldehyde range), methyl t-butyl ether (MTBE), methane (CH_4), carbon dioxide (CO_2), and carbon monoxide (CO) from selected ground-level monitoring stations in the South Coast Air Basin (SoCAB) during the intensive observational periods (IOP) during the summers of 1997.

1.3 Conclusions of the RFG Sampling Program

1. The introduction of California Phase 2 RFG resulted in measurable changes in the ambient concentrations of certain oxygenated and hydrocarbon species. In general, these changes were in agreement with those predicted prior to RFG introduction.

2. The most significant reduction in mean ambient concentratons (in both absolute and relative terms) is observed for C_6 olefins, C_9 and C_{10} aromatics. Since these species are very reactive in terms of their ozone formation potential, the reduction in their concentrations may help reduce ozone concentration in the SoCAB.

3. Mean ambient concentration of benzene (hazardous air pollutant) was reduced significantly in all sampling sites.

4. Mean ambient concentrations of MTBE increased significantly from 1995 to 1996. The increase in weight % of MTBE is very consistent in all three sampling sites — two source-dominated sites (North Main and Burbank) and a downwind receptor site (Azusa) — showing approximately a 40% increase during morning hours and nearly 50% during the afternoons. The background site (Santa Monica) shows approximately a 30% increase in MTBE concentrations (by weight %).

5. Excellent correlation between CO and MTBE was observed at all three sampling sites, confirming motor vehicle emissions as a source of MTBE.

6. A decrease in mean ambient CO concentrations was observed from 1995 to 1996; it ranged from 10 to 20% in the afternoons and from 20 to 30% in the mornings. No significant changes in mean ambient CO_2 concentrations were observed.

7. The mean concentrations of TNMHC were reduced from 1995 to 1996.

8. The mean ambient concentrations of isobutene, and to lesser extent, toluene increased from 1995 to 1996.

9. Mean ambient formaldehyde concentrations increased during the afternoon hours from 1995 to 1996 at all three sampling sites. However, the morning concentrations show a decrease in absolute terms (ppbv) or nearly no change in weight %.

10. The reduction in mean ambient concentrations of 1,3-butadiene and n-butane was lower than predicted.

1.4 Presentations and Publications

Part of the data included in this report were presented in CRC On-road Vehicle Emissions Workshops in April 1997 (Pasek and Zielinska, 1997) and at the Air & Waste Management Association's 90th Annual Meeting & Exhibition, June 8-13, 1997, Toronto, Ontario, Canada. The two papers submitted for the proceeding of A&WMA conference (Zielinska et al., 1997a, 1997b) are included in Appendix A. One M.Sc. thesis, "Analytical Methods for the Quantification of Oxygenated Volatile Organic Compounds, Carbon Monoxide, and Carbon Dioxide in Ambient Air" (Shire, 1996) was prepared in connection with this project. This thesis is included in Appendix B.

2.0 SAMPLING SITES AND AMBIENT AIR SAMPLING PROCEDURES

2.1 Ambient Sampling Sites and Schedule

Samples were collected at four sites (shown in Figure 2-1): two source-dominated sites (downtown Los Angeles at North Main and Burbank), a downwind receptor site (Azusa), and a background site (Santa Monica). Los Angeles (North Main), Burbank and Azusa sites are existing monitoring stations operated by the South Coast Air Quality Management District (SCAQMD). The North Main site is located at the Los Angeles Department of Water and Power building and is within an industrial area just north of the central business district. Three of the busiest freeway interchanges in the Los Angeles metropolitan area are within 2-4 kilometers of this site. The Burbank site is in an urban/industrial area on the eastern edge of the San Fernando Valley approximately 15 kilometers north of downtown Los Angeles. This is a future Type-2 (maximum emission) Photochemical Assessment Monitoring Station (PAMS) site and is scheduled to go into operation in 1997. Azusa is an existing Type-3 (downwind maximum ozone) PAMS site and is approximately 40 kilometers east-northeast of downtown Los Angeles. The Santa Monica site is located next to the beach, on the roof of the Lifeguard Headquarters building. Samples were collected at the Burbank, Azusa and North Main sites on 42 days (6 weeks) throughout the Summers of 1995 and 1996, from July to the end of September. Specifically, the sampling weeks were as follows:

1995	1996
July 8 – 14	July 7 – 13
July 17 – 23	July 28 – August 3
August 1 – 7	August 12 – 18
August 31 – September 6	August 27 – September 2
September 9 – 15	September 11 – 17
September 24 – 30	September 23 – 29

Two 3-hour samples were taken per sampling day, one in the morning during rush-hour traffic and one in the afternoon. During the first week of sampling in 1995, the sampling was performed from 0500 to 0800 and from 1200 to 1500 PST (which corresponds to 0600–0900 and from 1300–1600 local time, PDT). However, we found that the SCAQMD performed their sampling from 0600 to 0900 and from 1300 to 1600 PST, which corresponds to 0700–1000 and 1400–1700 PDT. After consultation with the CARB project manager, it has been decided to change our sampling time to that used by the district, in order for our data and that of SCAQMD to be comparable. Thus, in 1995, starting from the second week of sampling (July 17–23, 1995) all samples were collected from 0600 to 0900 and from 1300 to 1600 PST. However, in 1996, the SCAQMD changed their sampling time to 0500 to 0800 and 1200 to 1500 PST (which corresponds to 0600–0900 and 1300–1600 local time). In order to be comparable with the district data, we also collected our 1996 samples at the same schedule. At the Santa Monica site

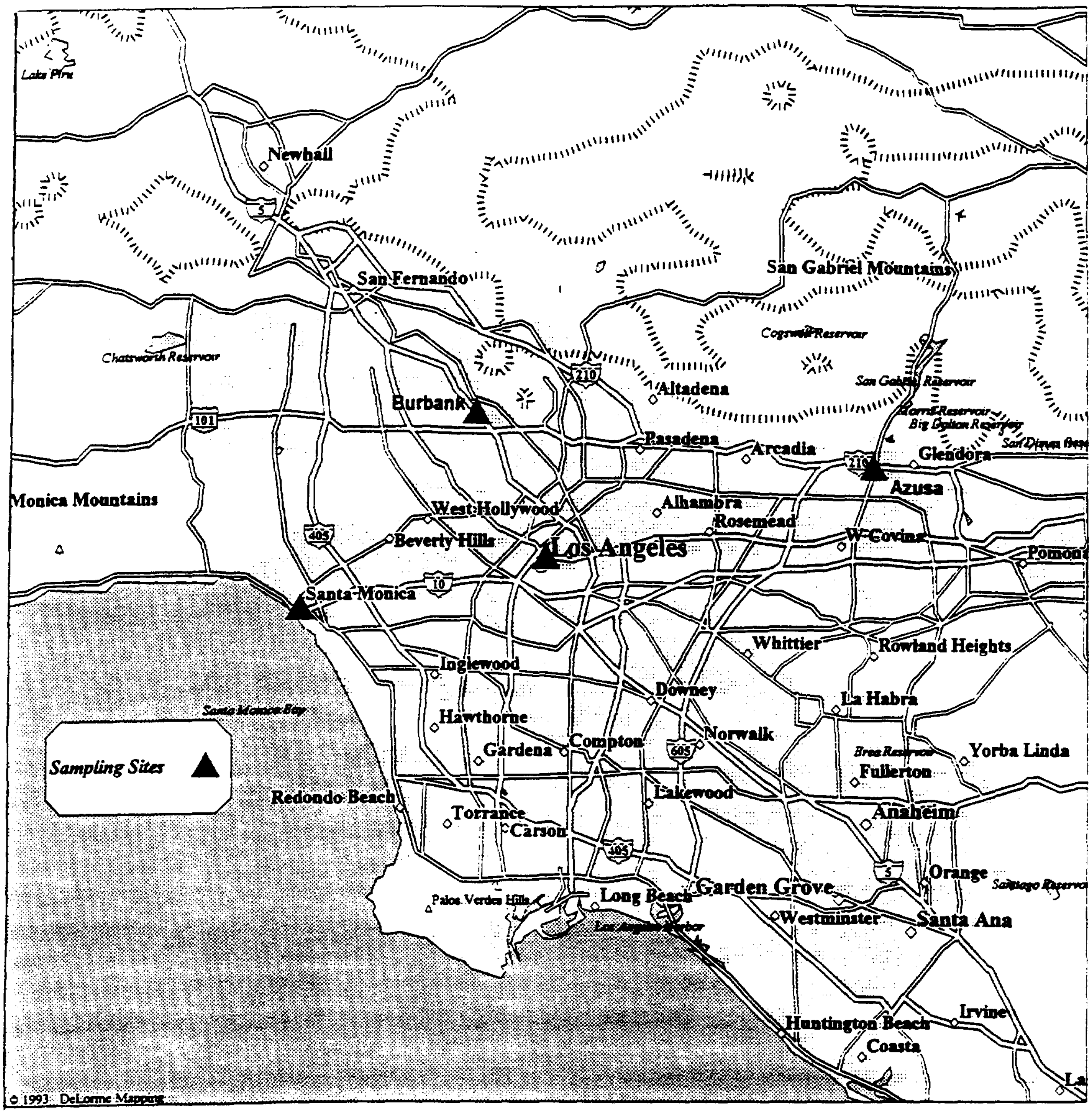

Figure 2-1. Locations of all four sampling sites in the SoCAB.

samples were collected once per sampling week, from 1200 to 1500 PDT, when an off-shore wind prevailed.

2.2 Source Sampling Sites and Schedule

The project required to include special sampling sites to obtain representative source composition profiles for cold start, hot stabilized, and evaporative emissions from motor vehicles that would be suitable for receptor modeling. The following source sampling sites were selected:

1. For cold start emissions sampling we selected parking garages. In June 1995, sampling was performed at the UCLA parking garage. This is a multilevel, open structure type of garage. The sampling was performed on Level 3, which had the highest proportion of vehicles with parking permits; we anticipated more regular working hours for these vehicles' owners. In order to check the uniformity of the samples, three parallel sampling sites, labeled A, B, and C, were established on Level 3. Sampling was performed between 1400–1500 PDT ("background") and 1615–1715 PDT (background plus cold-start emissions). Eleven valid samples were collected during the two-day sampling period (June 29–30).

The UCLA garage had several drawbacks. Its open structure allowed for mixing of inside and outside air, thus diluting the concentrations of VOC emitted during the cold-start. In addition, there was considerable traffic during the day. Therefore, for 1996, we selected an underground parking garage located in the Ronald Reagan Federal Building in downtown Los Angeles. This garage was ideal in that there was very little traffic during the day and most vehicles left the garage at about the same time at the end of the workday. We collected 1-hr samples beginning at 1400 ("background") and 1630 hr (background plus cold-start emissions) on July 24–25, 1996.

2. Tunnel measurements were utilized for obtaining VOC profiles for hot-stabilized motor vehicle exhaust emissions. In 1995, DRI performed a series of studies, funded by the Coordinating Research Council, of on-road emissions in tunnels located across the U.S. (Gertler et al., 1997b). In the South Coast Air Basin area, experiments were conducted at the Van Nuys Tunnel (June 8–12, 1995) and Sepulveda Tunnel (October 3–4, 1995) in Los Angeles. In 1996, additional measurements, funded by SCAQMD, were made in Sepulveda Tunnel (July 23-27, 1996). The sampling protocol, characteristics of the vehicle traffic, and the obtained results are described by Gertler et al. (1997a, 1997b).

3. The VOC composition of evaporative emissions is more difficult to characterize by ambient measurements than exhaust emissions due to difficulties in isolating the contributions of evaporative from exhaust emissions. The composition profile for liquid gasoline is a reasonable approximation of evaporative emissions from gasoline spillage and hot soak emissions. Whole gasoline also reflects the additional unburned gasoline (due to misfiring and other engine malfunctions) that is not included in the exhaust profile. The profile for gasoline headspace vapor reflects evaporative emissions due to refueling, diurnal evaporation, and running losses. VOC profiles for liquid gasoline and headspace profiles were obtained specifically for this project. The composition of whole gasoline was studied by the University of

California, Riverside (UCR, CE-CERT) in a SCAQMD–sponsored study. We obtained up to 20 of the same gasoline samples analyzed by UCR and characterized the composition of the headspace vapors. All major brands and grades of gasolines were included in this survey. Analysis was performed for hydrocarbons and oxygenated organic compounds.

The gasoline samples analyzed by the headspace technique are listed in Table 2-1.

2.3 Ambient Air Sampling Procedures

2.3.1 VOC Sampling Method

Volatile organic compounds (in the range of $C_2 - C_{12}$) were collected using stainless-steel polished canisters. Stainless-steel SUMMA™-polished canisters (Scientific Instrument Specialists, Moscow, ID) and Stabilizer™ canisters (Meriter, San Jose, CA) of 6 L capacity were cleaned by repeated evacuation and pressurization with humidified zero air at ~140 °C prior to sampling and certified as described by U.S. EPA Method TO-14. The sampling procedure is based on the pressurized sampling method described by EPA Method TO-14. Figure 2-2 shows the main components of this sampling system. A metal bellows-type pump draws in ambient air from the sampling manifold to fill and pressurize the sample canisters. A flow control device maintains a constant flow into the canisters over the desired sample period. This flow rate is preset to fill the canisters to about 1 atm above ambient pressure at the end of the sampling period (as described by U.S. EPA Method TO-14). A timer is used to automatically start and stop the pump at the appropriate time. The timer also controls the solenoid valve, opening it when the pump starts and closing it when the pump stops. The canister sampling systems were custom-built at DRI. They are multiple-event sampling systems, allowing unattended collection of three canister samples.

After sampling, an identification tag was attached to each canister and the canister serial number, sample number, and sampling location, date, and time were recorded on this tag. In addition a field sampling form and chain-of-custody form were filled out giving all pertinent information on the collection of the sample.

2.3.1.1 Canister and Sampling System Cleaning and Certification

Prior to sampling, the canisters were cleaned by repeated evacuation and pressurization with humidified zero air, as described in the EPA document "Technical Assistance Document for Sampling and Analysis of Ozone Precursors" (October 1991, EPA/600-8-91/215). Six repeatable cycles of evacuation to ~0.5 mm Hg absolute pressure, followed by pressurization with ultra-high-purity (UHP) humid zero air to ~20 psig are used. The differences between the DRI procedure and the EPA recommended method are that, in the DRI method, canisters are heated to 140 °C during the vacuum cycle, and more cycles of pressure and vacuum are used. Based on our experience and that of others (Rasmussen, 1992), heating is essential to achieve the desired canister cleanliness. Also, the canisters are kept longer under vacuum cycles, about one hour in the DRI method, as opposed to half an hour in the EPA method.

Table 2-1. Gasoline Samples.

Sample ID	**Station**	**Grade**
1995		
95-73-1A	Mobil	87
95-73-1B	Mobil	92
95-73-2A	Chevron	87
95-73-2B	Chevron	92
95-73-3A	Unocal	87
9573-3B	Unocal	92
95-73-4A	Arco	87
95-73-4B	Arco	92
95-73-5A	Texaco	87
95-73-5B	Texaco	92
95-73-6A	Shell	87
95-73-6B	Shell	92
95-73-7A	Ultramar	87
95-73-7B	Ultramar	92
95-73-8A	Gasco	87
95-73-8B	Gasco	91
95-73-9A	Thrifty	87
95-73-9B	Thrifty	92
1996		
96-83-1A	Mobil	87
96-83-1B	Mobil	92
96-83-2A	Chevron	87
96-83-2B	Chevron	92
96-83-3A	Unocal	87
96-83-3B	Unocal	92
96-83-4A	Arco	87
96-83-4B	Arco	92
96-83-5A	Texaco	87
96-83-5B	Texaco	92
96-83-6A	Shell	87
96-83-6B	Shell	92
96-83-7A	Ultramar	87
96-83-7B	Ultramar	92
96-83-8A	USA	87
96-83-8B	USA	92
96-83-9A	Thrifty	87
96-83-9B	Thrifty	92

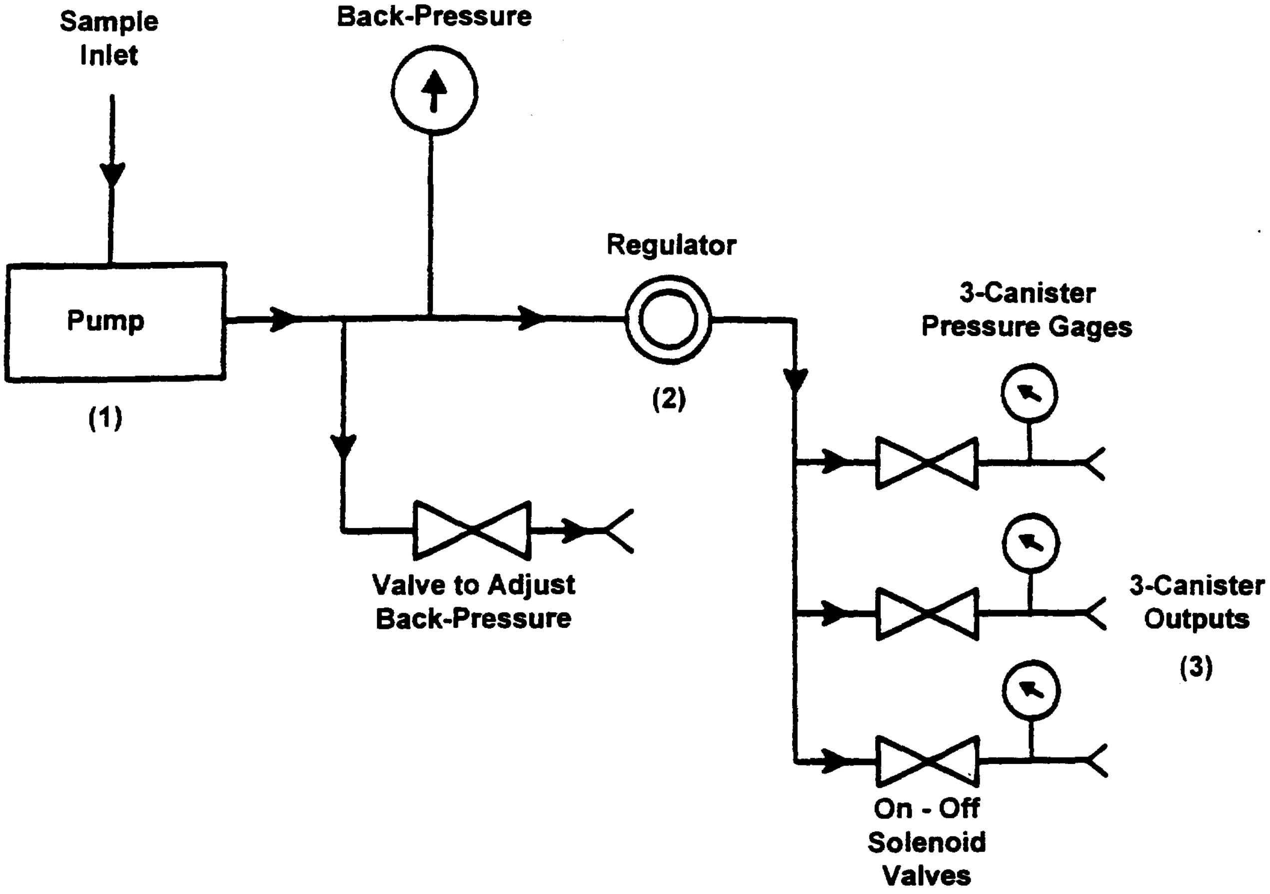

Figure 2-2. Canister Sampler Flow Schematic.

At the end of the cleaning procedure, one canister out of six in a lot is filled with humidified UHP zero air and analyzed by the gas chromatograph/flame ionization detection (GC/FID) method. The canisters are considered clean if the total non-methane organic compound (NMOC) concentration is less than 20 ppbC.

The canister sampling systems are cleaned prior to field sampling by purging them with humidified zero air for 48 hours, followed by purging with dry UHP zero air for 1 hour. Each canister sampling system is certified clean by the GC/FID analysis of humidified zero air collected through this sampling system. The system is considered clean if the concentration of any individual targeted compound is less than 0.2 ppbv and total NMOC concentration is less than 20 ppbC. In addition, a challenge sample, consisting of a blend of organic compounds of known concentration in clean humidified zero air, is collected through the sampling system and analyzed by the GC/FID method. The sampling system is considered non-biasing if recoveries of each of the challenge compounds is in the range of 80–120% (EPA document EPA/600-8-91/215).

2.3.2 Carbonyl Compounds

The measurement technique used for this study is an established procedure using C_{18} Sep-Pak cartridges (Waters Associates, Milford, MA) which have been impregnated with purified acidified 2,4-dinitrophenylhydrazine (DNPH). When ambient air is drawn through the cartridge, carbonyls in the air sample react with the DNPH to form hydrazones, which are separated and quantified using high performance liquid chromatography (HPLC) in the laboratory (Fung and Grosjean, 1981). This is the most-often used method for measuring these compounds in ambient air. Significant improvements in the preparation of the cartridges as well as sampler design have made routine monitoring of carbonyl compounds at 1 ppb or lower possible (Fung and Wright, 1986). DNPH-impregnated C_{18} SepPack cartridges were provided by Dr. Kochy Fung of AtmAA, Inc.

2.3.2.1 Carbonyl Compounds Sampling Equipment

The DRI carbonyl sampling systems are consistent with the sampling systems described in EPA Method TO-11 and the EPA document "Technical Assistance Document for Sampling and Analysis of Ozone Precursors" (October 1991, EPA/600-8-91/215). Six such systems were custom-built at the DRI and were used for this study.

Figure 2-3 shows a schematic of the carbonyl sampling system. The system consists of a diaphragm pump capable of maintaining air flow through the cartridges of 500–1500 ml/min, flowmeter, six-port solenoid manifold allowing unattended collection of up to six carbonyl samples, needle valves for flow rate regulation, and check valves to protect cartridges from outside air when air is not being sampled through a given cartridge. For automatic operation, the memory-protected programmable timer starts and stops the pump at the appropriate time. The timer also opens the six-port solenoid valve when the pump starts and closes it when the pump

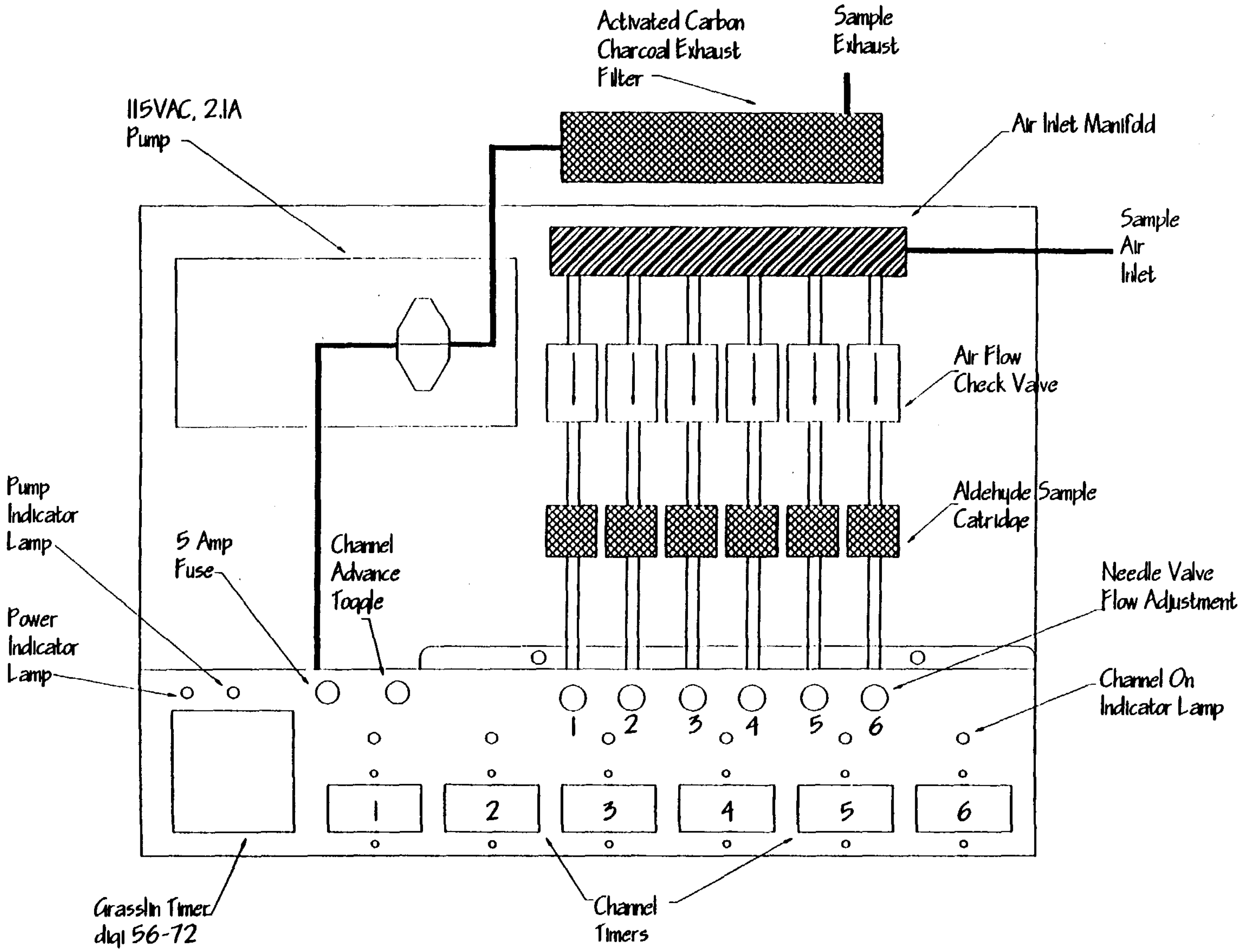

Figure 2-3. Schematic of DRI Carbonyl Sampling System.

stops (since cartridges will naturally sorb carbonyl compounds from the surrounding air if left open, the sampler has been designed such that cartridges loaded into the sampler are isolated from the environment and from each other by check valves upstream and solenoid valves downstream). Duplicate samples can be collected on collocated cartridges by activating a parallel channel simultaneously. A mode selection switch converts the parallel channel for field blank collection as well. Sampling flow rates are controlled at ~1.0 L/min using a differential flow controller with a typical precision of ±5% or less. A charcoal filter is attached to the pump outlet in order to remove traces of acetonitrile from the DNPH cartridges.

3.0 ANALYTICAL PROCEDURES

3.1 Canister Sample Analysis

An air sample is taken from the canister and passed through the sample concentration system. This system is shown schematically in Figure 3-1. It consists of a freeze-out loop, made from chromatographic-grade stainless-steel tubing packed with 60/80 mesh deactivated glass beads, and a 10-port sampling valve (V-1). When the valve is in position 1, as shown in Figure 3-1, the sample is transferred from the canister through the loop immersed in liquid oxygen to the volume transfer measurement apparatus, shown in Figure 3-2. The C_2 and heavier hydrocarbons are cryogenically trapped inside the loop when air is transferred to an evacuated flask of known volume. From the difference in pressure inside the flask, the volume of the air sample can be calculated, based on the Ideal Gas Law. When a sufficient volume of the air sample has been transferred from the canister to the concentration system, the 10-port valve is switched to position 2 (shown in Figure 3-3), the liquid oxygen is replaced with boiling water, and the contents of the trap are injected into a chromatographic column where separation of the C_2–C_{12} hydrocarbons takes place. No Perma-Pure permeable membrane or other moisture-removal device is used prior to concentration, since the use of such drying devices results in the loss of certain volatile organic compounds (VOC) of interest (all polar compounds and some olefins and aromatics). It can also introduce contaminants into the system and it lowers the total NMHC by 10–20% (Sagebiel and Zielinska, 1994). The entire inlet is heated (up to ~100 °C) to prevent any condensation of compounds during the transfer.

The chromatographic column used for C_2–C_{12} hydrocarbon analysis in the DRI system is a 60 m long J&W DB-1 fused silica capillary column with a 0.32 mm inside diameter and 1 µm phase thickness. The oven temperature program is: -65 °C for 2 min., to 220 °C at 6 °C/min. The gas chromatograph is a Hewlett-Packard 5890 Series II, equipped with an FID detector. However, the DB-1 column does not provide complete separation of the light C_2 and some important C_4 hydrocarbons. Therefore, a separate analysis of the canister sample is necessary to obtain accurate concentrations for ethane, ethylene, acetylene, 1-butene, 2-butenes and isobutylene. The chromatographic column used for this analysis is a J&W GS-Alumina PLOT fused silica capillary column with an internal diameter of 0.53 mm and a length of 30 m. A separate gas chromatograph (Varian Model 3700) is dedicated to this analysis.

3.1.1 Hydrocarbon Calibration and Compound Identification

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). The NIST SRM 1805 (254 ppb of benzene in nitrogen) is used for calibrating the analytical system for C_2–C_{12} hydrocarbon analysis, whereas 1 ppm propane in a nitrogen standard (Scott Specialty Gases), periodically traced to SRM 1805, is used for calibrating the light hydrocarbon analytical system. Based on the uniform carbon response of the FID to hydrocarbons, the response factors determined from these calibration standards are used to convert area counts into concentration units (ppbC) for every peak in the chromatogram.

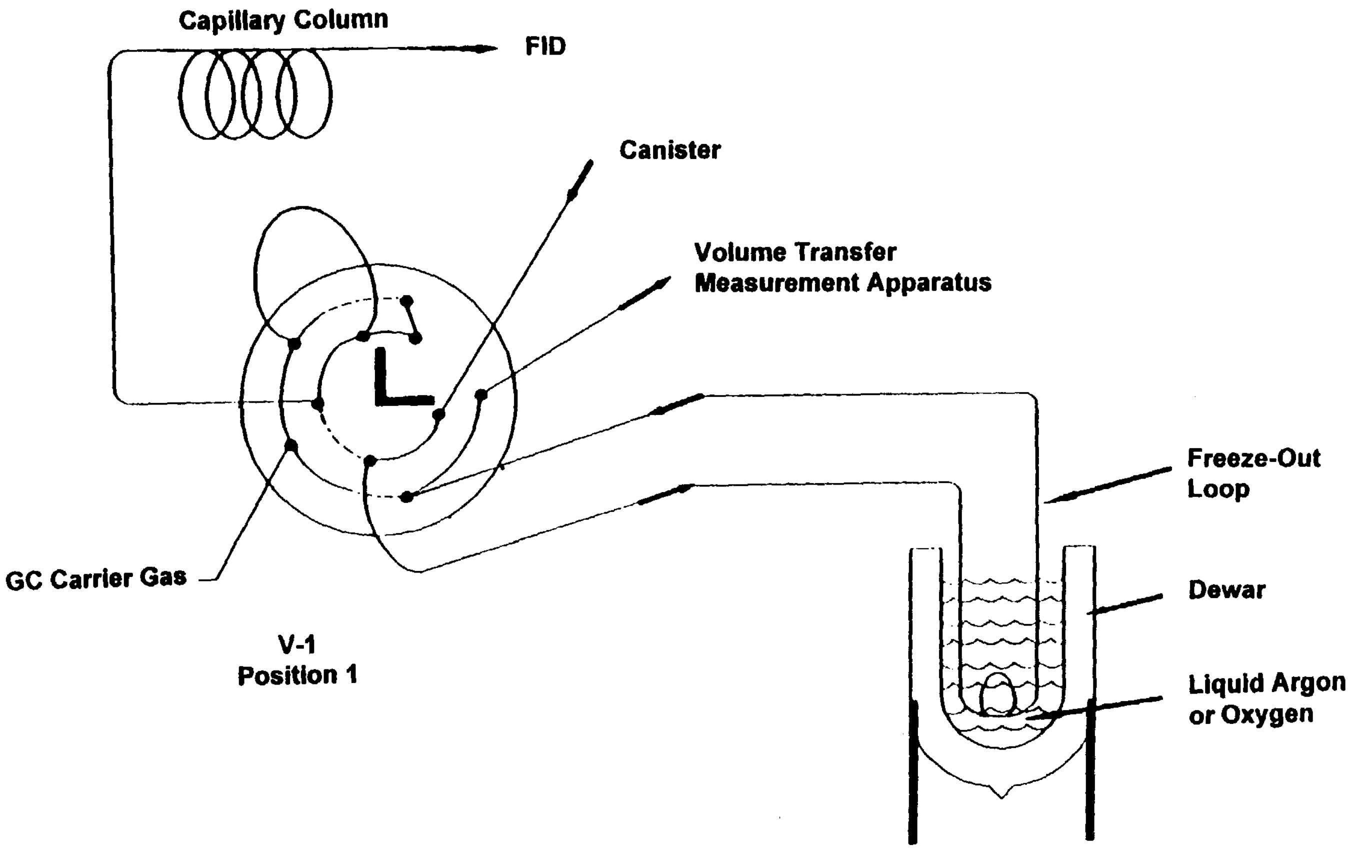

Figure 3-1. Gaseous sample concentration system, sampling position.

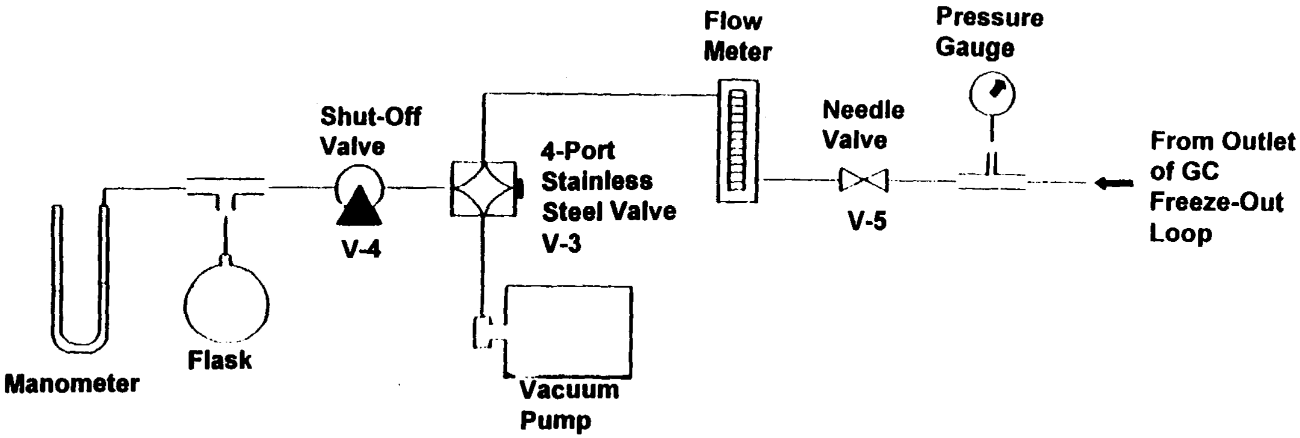

Figure 3-2. Volume transfer measurement apparatus.

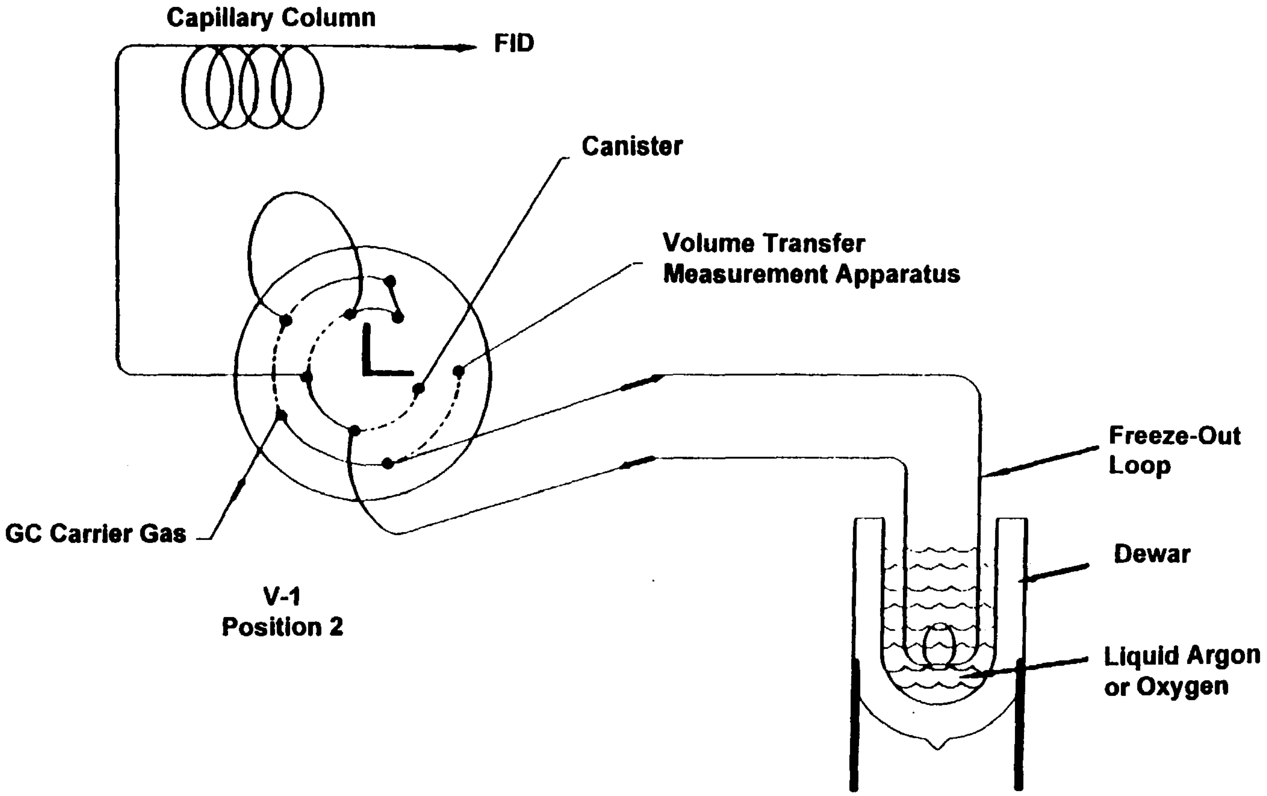

Figure 3-3. Gaseous sample concentration system, inject position.

Identification of individual compounds in an air sample is based on the comparison of linear retention indices (RI) with those RI values of authentic standard compounds, as well as with the RI values obtained by other laboratories performing the same type of analysis using the same chromatographic conditions (Auto/Oil Program, Atmospheric Research and Exposure Assessment Laboratory, U.S. EPA). The DRI laboratory calibration table contains ~160 species.

All of the gas chromatographs are connected to a data acquisition system (ChromPerfect, designed and marketed by Justice Innovation, Inc.). The software performs data acquisition, peak integration and identification, hardcopy output, post-run calculations, calibrations, peak re-integration, and user program interfacing. Acquired data are automatically stored on a hard disk. A custom-designed database management system is used to confirm all peak identifications. This step is described in Section 3.4, below.

3.1.2 Methyl t-Butyl Ether (MTBE)

Methyl t-butyl ether was quantified from canister samples, using our method of analysis for C_3–C_{12} hydrocarbons, i.e., a 60 m long J&W DB-1 fused silica capillary column with a 0.32 mm inside diameter and 1 μm phase thickness, and the injection system described above. The individual response factor was determined for MTBE and its concentration is reported in ppbv. Since reliable NIST traceable standards for MTBE and other oxygenated compounds were not commercially available in 1995, we determined effective carbon numbers (ECN) for these compounds and used these numbers to convert GC/FID concentration numbers reported in ppbC to ppbv (see Appendix B, J. Shire Thesis, Section 3). Briefly, using a suitable solvent, repeated, approximately equimolar, liquid solutions of an oxygenated compound and benzene were injected neatly into the GC and the calculations were done similar to those described by Yieru et al. (1990) and Scanlon and Willis (1985) to determine an ECN for each of the oxygenated VOCs of interest. The ECN for MTBE was determined to be 4.37.

For comparison, MTBE was also quantified by trapping an aliquot from a canister onto a multibed adsorbent tube and analyzing it by the thermal desorption method. This method is described in detail by Shire (1996) in his Master Thesis (Appendix B, Section 3) and, briefly, below in Section 3.1.3. All canister samples collected in 1996 were analyzed by this method.

3.1.3 Methanol and Ethanol

Methanol and ethanol were quantified using the multi-adsorbent tube method. In this method, described in detail by Shire (1996, M.Sc. Thesis, Appendix B), an air sample from a canister (500–1000 ml) is passed through an 1/8-inch stainless-steel tubing coated on the inside with silicon (Restek) and heated to 70 °C. At a flow of 50 ml/min the sample is trapped onto a multibed adsorbent tube (6 in. x 1/4 in. Pyrex®) of 100 mg Tenax TA®, 85 mg Carbotrap B, and 180 mg Carbosieve III (Supelco) with Pyrex wool plugs containing and separating the sorbents. The sample is then purged with UHP helium which has been passed through a hydrocarbon trap at 100 ml/min (where the purge volume = 2X trapped volume) to remove water in preparation for injection via a standard Thermal Desorption Cold Trap injector unit (Chrompack). The Hewlett-Packard 5890 Series II GC/FID is equipped with a Chrompack CP-Sil 13CB capillary column, 50 m long x 0.32 mm inner-diameter with a 1.2 µm film thickness. The oven temperature program is: -20 °C for 2 min initially, with a 3 °C/min ramp to 200 °C. Temperature settings for the Thermal Desorption Cold Trap are: -170 °C, cold trap; 280 °C, desorption; and an 80 °C heating of the cold trap for the 2 min injection. The GC/FID response is calibrated in ppbC, using a gaseous standard (2600 ppbC of n-pentane in nitrogen, from Spectra Gases, Alpha, NJ) trapped onto multibed adsorbent tubes and analyzed by the thermal desorption method. Three concentration levels of n-pentane were used. The ppbC values for methanol, ethanol, and MTBE are then converted to ppbv using the ECN of each chemical.

The ECNs were experimentally determined for methanol and ethanol as described for MTBE, Section 3.1.2, above. They were 0.58 and 1.18 for methanol and ethanol, respectively.

3.1.4 Methane, Carbon Monoxide and Carbon Dioxide

Methane (CH_4), carbon monoxide (CO) and carbon dioxide (CO_2) are measured from the canister samples using GC/FID. Since the FID does not respond to CO and CO_2 these species are converted to methane by a methanator, positioned right after a GC column, but ahead of the FID. The methanator comprises a firebrick powder impregnated with nickel catalyst, through which a stream of hydrogen gas flows continuously at ~550 °C.

For compound separation, a 20 feet x 1/8 inch inner-diameter (i.d.) column, packed with a 60/80 mesh of Carboxen 1000 (Supelco) is used. This column provides sufficient separation between CH_4 and CO without retaining CO_2. Five ml samples are injected using a constant volume loop. The response factors are determined by the calibrations with the gaseous standard mixtures (Scott Specialty Gases or AGA Specialty Gases, NIST-traceable) containing CO, CO_2 and CH_4 in zero air.

The minimum detection limit for CO is 0.06 ppmv and for CH_4 it is 0.2 ppmv, whereas for CO_2 it is ~3 ppmv. The precision of measurements is generally better than 10%. The detailed description of the method and the method validation are included in the Appendix B (Shire, M.Sc. Thesis, Section 5).

3.2 Carbonyl Compound Analysis

The samples were analyzed in batches by Dr. Kochy Fung at the AtmAA, Inc., laboratory. Analysis was performed by injecting each sample cartridge with a known amount of an internal standard and eluting with acetonitrile. The eluent was injected by an autosampler into a high performance liquid chromatograph (Shimadzu LC-6) for separation and quantitation of the hydrazones (Fung and Grosjean, 1981). Ambient air samples typically contain C_1–C_6 carbonyls and benzaldehyde, with formaldehyde, acetaldehyde, and acetone being most abundant. Higher carbonyls include methyl ethyl ketone (MEK), pentanones, and cyclohexanone. Aldehydes $>C_3$ are generally found in much lower concentrations than the corresponding ketones.

Complete speciation of C_1–C_6 carbonyls was possible, but at the expense of increased cost to the program due to significant lengthening of the analysis and data processing time.

Since photochemical modelers, the end users of the data, routinely group higher carbonyls together for their work, it was decided that the program would benefit from reduced costs without impact on quality by obtaining individual species data only for C_1–C_3 carbonyls, and group concentration data (by carbon number) for C_4–C_6 carbonyls (e.g., sum of C_4s, C_5s, etc.).

3.3 Gasoline Headspace Analysis

For gasoline headspace vapor analysis, approximately 2 ml of each gasoline sample was placed in a 4 ml amber glass vial with a Teflon septum. The vials were equilibrated at room temperature for approximately 6 hr. Seven microliters of the vapor phase from above the liquid was drawn into a gas-tight syringe and injected in the splitless mode into a 100 m long Supelco Petrocol DH capillary column (0.25 mm ID, 0.5 µm film thickness). The injector temperature was 200 °C and the GC conditions were as follows: -60 °C for 1 min, than increased to 45 °C with the rate of 8 °C/min, held for 15 min at this temperature, than increased to 60 °C at 1 °C/min, held for 15 min and finally increased to 220 °C at 2 °C/min and held at 220 °C for another 5 min. The total run was approximately 1 hr 30 min.

3.4 Data Processing

The general scheme for our data processing is presented here. The goal of our data processing is to provide accurate data combined into a single database for each analysis type. A raw data signal is collected from the detector and stored as a digitized signal by the computer system. This signal is translated into a chromatogram by the chromatography software and integrated to give peaks and areas of those peaks. Using the appropriate response factors, area counts are converted to the calibration parameter (mass or concentration, depending on the instrument). The laboratory technician reviews this information and adjusts the integration as necessary. A report is generated by the chromatography system.

For canister measurements, the report is examined immediately after the run to verify that peak integrations have been performed properly. The peak integration, retention times, and peak identifications assigned by the ChromPerfect software are stored to disk as an ASCII file. The files are then read into a Foxpro data file for additional processing and verification of peak identifications. The peak assignments for the major constituents (typically about a dozen peaks) in the chromatogram are manually verified and retention times are recalculated for all detectable peaks based upon regression between sample and reference retention times for the manually identified peaks. The adjusted retention times are used to assign peak identifications for all detectable peaks (the reference file currently contains 160 identified compounds). The retention time adjustments and peak assignments are executed automatically by a Foxpro program. The ChromPerfect and subsequent confirmatory peak identifications are then compared and discrepancies are resolved by the analyst based on peak patterns or confirmatory identification by GC/MS. In the final step, the Level I validated data are appended to the master database. Each sample appears as a record within the database and is identified by a unique sample identification, site, date, and time and as a primary, collocated, blank, spiked, or replicate sample. This database is submitted in dBase format on 3.5" diskettes with this report.

4.0 RESULTS AND DISCUSSION

4.1 Canister Samples

Table 4-1 lists VOC quantified from the canister samples by three different methods (cryogenic preconcentration and analysis using the DB-1 capillary column and using the GS-Alumina PLOT column, and $CO/CO_2/CH_4$ analysis) together with their corresponding mnemonics. The third column in Table 4-1 describes the type of compound: '**n**' means non-hydrocarbon and '**o**' means oxygenated compound. The fourth column lists the carbon number for a given compound; note that only methanol, ethanol and MTBE have had their effective carbon numbers determined experimentally (see Sections 3.1.2 and 3.1.3) and these numbers are used to convert the GC/FID concentration numbers reported in ppbC to true ppbv concentrations for these compounds. Since the GC/FID systems are calibrated in ppbC based on the uniform carbon response of the FID to hydrocarbons, and the compound-specific calibration for species flagged as '**o**' and '**n**' are not performed (with the exception of methanol, ethanol and MTBE), these species are not reported individually in the final database. The ppbC concentration numbers for species flagged with '**n**' and '**o**' are summed together and reported as 'Identified other compounds' (IDOTHER). 'Identified oxygenated (ppbv)' (IDOXY) gives the total concentration of methanol, ethanol and MTBE only (in ppbv). CO, CO_2 and CH_4 concentrations are reported in ppmv, based on the calibration with standard compounds.

The results of analysis of all ambient canister samples collected in 1995 and 1996 are submitted in dBase format on a 3.5" diskette (no. I) with this report. The files RGALC_95 and RGALC_96 contain data for all ambient samples collected in 1995 and in 1996, respectively. The files GAR_95 and GAR_96 contain data for canister samples collected in the UCLA garage in 1995, and in the Ronald Reagan garage in 1996, respectively. The structure for these files is listed in Table 4-2. Field #1 gives the sampling location; field gives #2 the canister identification number; field #3 lists the QA lot for canister certification; fields # 4 and 5 give sampling and analysis date, respectively; field #6 lists the identification of the sample's raw chromatographic file; field #7 lists the sample's identification code; field #8 defines the analysis type as primary (p) or replicate (r); and field #9 is used as needed by the program. Fields #10 through 162 give the concentrations for individual compounds (see Table 4-1 for explanation of mnemonics) and fields #163 through 166 give the total concentrations for identified NMHC, unidentified compounds, identified oxygenated compounds, identified other compounds, and total background from the column. Please note that concentrations of all compounds are listed in ppbC, with exception of CO, CO_2, CH_4 (in ppmv) and methanol, ethanol, MTBE, and identified oxy (in ppbv).

Although methanol and ethanol concentrations are listed in these files, these numbers are not very accurate. As determined by Shire (1996) (see Appendix B, M.Sc. thesis, Section 3), the three-bed adsorbent method is superior for methanol and ethanol quantification, and the results from this analysis are discussed below in Section 4.1.1.

Table 4-1. List of VOC Quantified from Canisters

Name	Mnemonic	Flag	Carbon No.	Name	Mnemonic	Flag	Carbon No.
carbon monoxide	CO_PPM		1	methacrolein	MEACRO	o	2
carbon dioxide	CO2PPM		1	4-methyl-1-pentene	P1E4ME		6
methane	METHAN		1	cyclopentane	CPENTA		5
ethane	ETHANE		2	2,3-dimethylbutane	BU23DM		6
ethene	ETHENE		2	MTBE	MTBE	o	4.37
acetylene	ACETYL		2	2-methylpentane	PENA2M		6
1-butene	LBUT1E		4	butanal	BUAL	o	4
iso-butene	LIBUTE		4	butanone	BUONE	o	4
C2 compounds	C2CMPD		2	3-methylpentane	PENA3M		6
propene	PROPE		3	2-methyl-1-pentene	P1E2ME		6
propane	N_PROP		3	1-hexene	HEX1E		6
Freon 12	FRE12	n	1	C6 olefin	C6OLE1		6
isobutane	I_BUTA		4	n-hexane	N_HEX		6
1-butene&i-butene	BEABYL		4	t-3-hexene + chloroform	T3HEXE		6
1,3-butadiene	BUDI13		4	c-3-hexene	C3HEXE		6
n-butane	N_BUTA		4	t-2-hexene	T2HEXE		6
methanol	METOH	o	0.58	2-methyl-2-pentene	P2E2ME		6
t-2-butene	T2BUTE		4	c-2-hexene	C2HEXE		6
1&2-butyne	BUTYN		4	3-methyl-2-pentene	P2E3ME		6
c-2-butene	C2BUTE		4	2,2-dimethylpentane	PEN22M		7
3-methyl-1-butene	B1E3ME		5	methylcyclopentane	MCYPNA		6
ethanol	ETHOH	o	1.18	2,4-dimethylpentane	PEN24M		7
acetonitrile	ACN	n	2	mechloroform	MECLOR	n	2
isopentane	IPENTA		5	2,2,3-trimethylbutane	BU223M		7
acetone	ACETO	o	3	1-methylcyclopentene	CPENE1		6
1-pentene	PENTE1		5	benzene	BENZE		6
2-methyl-1-butene	B1E2M		5	3,3-dimethylpentane	PEN33M		7
n-pentane	N_PENT		5	cyclohexane	CYHEXA		6
isoprene	I_PREN		5	4-methylhexene	HEXE4M		7
t-2-pentene	T2PENE		5	2-methylhexane	HEXA2M		7
c-2-pentene	C2PENE		5	2,3-dimethylpentane	PEN23M		7
2-methyl-2-butene	B2E2M		5	cyclohexene	CYHEXE		6
F113	F113	n	2	3-methylhexane + pentanal	HEXA3M		7
2,2-dimethylbutane	BU22DM		6	C7 olefin	C7OLE1		7
2-methylpropanal	PRAL2M	o	4	1,3-dimethylcyclopentane	CPA13M		7
cyclopentene	CPENTE		5	3-ethylpentane	PA3ET		8

Table 4-1. List of VOC Quantified from Canisters (cont.)

Name	Mnemonic	Flag	Carbon No.
2,2,4-trimethylpentane	PA224M		8
C7 olefin	C7OLE2		7
t-3-heptene	T3HEPE		7
n-heptane	N_HEPT		7
C8 olefin	C8OLE1		8
C8 olefin	C8OLE2		8
C8 olefin	C8OLE3		8
2,4,4-trimethyl-1-pentene	P1E244		8
methylcyclohexane	MECYHX		7
C8 paraffin	C8PA1		8
2,5-diemthylhexane	HEX25M		8
2,4-diemthylhexane	HEX24M		8
C8 paraffin	C8PA2		8
2,3,4-trimethylpentane	PA234M		8
toluene	TOLUE		7
2,3-dimethylhexane	HX23DM		8
2-methylheptane	HEP2ME		9
4-methylheptane	HEP4ME		9
C8 paraffin	C8PA3		8
3-methylheptane	HEP3ME		8
hexanal	HEXAL	o	6
2,2,5-trimethylhexane	HEX225		9
octene-1	OCT1E		8
1,1-dimethylcyclohexane	CHX11M		8
n-octane	N_OCT		8
2,3,5-trimethylhexane	HEX235		9
2,4-dimethylheptane	HEP24D		9
4,4-dimethylheptane	HEP44D		9
2,6-dimethylheptane	HEP26D		9
2,5-dimethylheptane	HEP25D		9
3,3-dimethylheptane	HEP33D		9
C9 olefin	C9OLE1		9
C9 olefin	C9OLE2		9
ethylbenzene	ETBZ		8
C9 olefin	C9OLE3		9
m- & p-xylene	MP_XYL		8
2-methyloctane	OCT2ME		9
3-methyloctane	OCT3ME		9
C9 paraffin	C9PAR1		9
styrene + heptanal	STYR		8
o-xylene	O_XYL		8
nonene-1	NONE1		9
C9 paraffin	C9PAR2		9
n-nonane	N_NON		9
C9 paraffin	C9PAR3		9
C9 olefin	C9OLE4		9
C9 paraffin	C9PAR4		9
isopropylbenzene	IPRBZ		9
isopropylcyclohexane	IPCYHX		9
alpha-pinene	A_PINE		10
benzaldehyde	BZALDE	o	7
2,6-dimethyloctane	OCT26D		10
C10 olefin	C10OL1		10
3,6-dimethyloctane	OCT36M		10
n-propylbenzene	N_PRBZ		9
m-ethyltoluene	M_ETOL		9
p-ethyltoluene	P_ETOL		9
1,3,5-trimethylbenzene	BZ135M		9
C10 paraffin	C10P_A		10
o-ethyltoluene	O_ETOL		9
beta-pinene	B_PINE		10
1,2,4-trimethylbenzene	BZ124M		9
n-decane	N_DEC		10
C10 aromatic	C10AR1		10
isobutylbenzene	I_BUBZ		10
C10 olefin	C10OL2		10
1,2,3-trimethylbenzene	BZ123M		9
C10 paraffin	C10P_C		10
indan	INDAN		9
indene	INDENE		9

Table 4-1. List of VOC Quantified from Canisters (cont.)

Name	Mnemonic	Flag	Carbon No.
diethylbenzene	DETBZ1		10
C10 aromatic	C10AR2		10
diethylbenzene	DETBZ2		10
n-butylbenzene	N_BUBZ		10
diethylbenzene	DETBZ3		10
C10 aromatic	C10AR3		10
1,3-dimethyl-4-ethylbenzene	BZDME		10
C10 aromatic	C10AR4		10
isopropyltoluene	IPRTOL		10
n-undecane	N_UNDE		11
C10 aromatic	C10AR5		10
C11 paraffin	C11P_A		11
1,2,4,5-tetramethylbenzene	BZ1245		10
1,2,3,5-tetramethylbenzene	BZ1235		10
C11 paraffin	C11P_B		11
2-methylindan	IND_2M		10
1-methylindan	IND_1M		10
C11 aromatic	C11AR1		11
C11 aromatic	C11AR3		11
naphthalene	NAPHTH		10
n-dodecane	N_DODE		12
Total Identified NMHC	IDNMHC		1
Unidentified	UNID		1
Identified oxygenated (ppbv)	IDOXY		1
Identified other compounds	IDOTHR		1
Total Background	T_BKG		1
cis-3-methyl-2-pentene	P2E3MC		6
trans-3-methyl-2-pentene	P2E3MT		6
3-methyl-1-pentene	P1E3ME		6
sec-butylbenzene	S_BUBZ		10
limonene	LIMON		10

Table 4-2. Structure for Database Files in FoxPro

Structure for table: h:\arb_rfg\rgalc_96.dbf
Number of data records: 280
Date of last update: 04/23/97

Field	Field Name	Field Type	Width	Dec
1	LOCATION	C	10	0
2	CANISTER	C	7	0
3	QA_LOT	N	3	0
4	SMPL_DATE	D	8	0
5	AN_DATE	D	8	0
6	RAW_FILE	C	14	0
7	CID	C	14	0
8	AN_TYPE	C	2	0
9	SAVE1	C	10	0
10	CO_PPM	N	9	2
11	CO2PPM	N	9	2
12	METHAN	N	9	2
13	ETHANE	N	9	2
14	ETHENE	N	9	2
15	ACETYL	N	9	2
16	LBUT1E	N	9	2
17	LIBUTE	N	9	2
18	C2CMPD	N	9	2
19	PROPE	N	9	2
20	N_PROP	N	9	2
21	I_BUTA	N	9	2
22	BEABYL	N	9	2
23	BUDI13	N	9	2
24	N_BUTA	N	9	2
25	T2BUTE	N	9	2
26	BUTYN	N	9	2
27	C2BUTE	N	9	2
28	B1E3ME	N	9	2
29	IPENTA	N	9	2
30	PENTE1	N	9	2
31	B1E2M	N	9	2
32	N_PENT	N	9	2
33	I_PREN	N	9	2
34	T2PENE	N	9	2
35	C2PENE	N	9	2
36	B2E2M	N	9	2
37	BU22DM	N	9	2
38	CPENTE	N	9	2
39	P1E4ME	N	9	2
40	CPENTA	N	9	2
41	BU23DM	N	9	2
42	PENA2M	N	9	2
43	PENA3M	N	9	2
44	P1E2ME	N	9	2
45	HEX1E	N	9	2
46	C6OLE1	N	9	2
47	N_HEX	N	9	2
48	T3HEXE	N	9	2
49	C3HEXE	N	9	2
50	T2HEXE	N	9	2
51	P2E2ME	N	9	2
52	C2HEXE	N	9	2
53	P2E3ME	N	9	2
54	PEN22M	N	9	2
55	MCYPNA	N	9	2
56	PEN24M	N	9	2
57	BU223M	N	9	2
58	CPENE1	N	9	2
59	BENZE	N	9	2
60	PEN33M	N	9	2
61	CYHEXA	N	9	2
62	HEXE4M	N	9	2
63	HEXA2M	N	9	2
64	PEN23M	N	9	2
65	CYHEXE	N	9	2
66	HEXA3M	N	9	2
67	C7OLE1	N	9	2
68	CPA13M	N	9	2
69	PA3ET	N	9	2
70	PA224M	N	9	2
71	C7OLE2	N	9	2
72	T3HEPE	N	9	2
73	N_HEPT	N	9	2
74	C8OLE1	N	9	2
75	C8OLE2	N	9	2
76	C8OLE3	N	9	2
77	P1E244	N	9	2
78	MECYHX	N	9	2
79	C8PA1	N	9	2
80	HEX25M	N	9	2
81	HEX24M	N	9	2
82	C8PA2	N	9	2

Table 4-2. Structure for Database Files in FoxPro (cont.)

Structure for table: h:\arb_rfg\rgalc_96.dbf
Number of data records: 280
Date of last update: 04/23/97

Field	Field Name	Field Type	Width	Dec
83	PA234M	N	9	2
84	TOLUE	N	9	2
85	HX23DM	N	9	2
86	HEP2ME	N	9	2
87	HEP4ME	N	9	2
88	C8PA3	N	9	2
89	HEP3ME	N	9	2
90	HEX225	N	9	2
91	OCT1E	N	9	2
92	CHX11M	N	9	2
93	N_OCT	N	9	2
94	HEX235	N	9	2
95	HEP24D	N	9	2
96	HEP44D	N	9	2
97	HEP26D	N	9	2
98	HEP25D	N	9	2
99	HEP33D	N	9	2
100	C9OLE1	N	9	2
101	C9OLE2	N	9	2
102	ETBZ	N	9	2
103	C9OLE3	N	9	2
104	MP_XYL	N	9	2
105	OCT2ME	N	9	2
106	OCT3ME	N	9	2
107	C9PAR1	N	9	2
108	STYR	N	9	2
109	O_XYL	N	9	2
110	NONE1	N	9	2
111	C9PAR2	N	9	2
112	N_NON	N	9	2
113	C9PAR3	N	9	2
114	C9OLE4	N	9	2
115	C9PAR4	N	9	2
116	IPRBZ	N	9	2
117	IPCYHX	N	9	2
118	A_PINE	N	9	2
119	OCT26D	N	9	2
120	C10OL1	N	9	2
121	OCT36M	N	9	2
122	N_PRBZ	N	9	2
123	M_ETOL	N	9	2
124	P_ETOL	N	9	2
125	BZ135M	N	9	2
126	C10P_A	N	9	2
127	B_PINE	N	9	2
128	O_ETOL	N	9	2
129	BZ124M	N	9	2
130	N_DEC	N	9	2
131	C10AR1	N	9	2
132	I_BUBZ	N	9	2
133	C10OL2	N	9	2
134	BZ123M	N	9	2
135	C10P_C	N	9	2
136	INDAN	N	9	2
137	INDENE	N	9	2
138	DETBZ1	N	9	2
139	C10AR2	N	9	2
140	DETBZ2	N	9	2
141	N_BUBZ	N	9	2
142	DETBZ3	N	9	2
143	C10AR3	N	9	2
144	BZDME	N	9	2
145	C10AR4	N	9	2
146	IPRTOL	N	9	2
147	N_UNDE	N	9	2
148	C10AR5	N	9	2
149	C11P_A	N	9	2
150	BZ1245	N	9	2
151	BZ1235	N	9	2
152	C11P_B	N	9	2
153	IND_2M	N	9	2
154	IND_1M	N	9	2
155	C11AR1	N	9	2
156	C11AR3	N	9	2
157	NAPHTH	N	9	2
158	N_DODE	N	9	2
159	OXY_PPBV	N	9	2
160	METOH	N	9	2
161	ETHOH	N	9	2
162	MTBE	N	9	2
163	IDNMHC	N	9	2
164	UNID	N	9	2
165	IDOXY	N	9	2
166	IDOTHR	N	9	2
167	T_BKG	N	9	2
168	EMPTY	N	9	2

4.1.1 Methanol and Ethanol

The method for measuring methanol and ethanol by three-bed solid adsorbent cartridges and thermal desorption is described in detail by Shire (1996) (Appendix B, M.Sc. Thesis, Section 3). Since this method was not validated in time for the analysis of the Summer 1995 samples, only the results from the analysis of 1996 samples are given here. After the analysis for C_2–C_{12} hydrocarbons was completed, the aliquot from the canister samples was adsorbed onto a three-bed solid adsorbent cartridge and the cartridge was analyzed within two weeks by the thermal desorption method, as described in Section 3.1.3. The solid adsorbent data were compared with data obtained from the analysis of canister samples by the preconcentration method (modified TO-14 method) and were validated as follows:

1. The ratios of MTBE (as measured by the solid adsorbent and TO-14 methods) to benzene (from the TO-14 method) were compared and the outliers were removed from the solid adsorbent database; approximately 5% of the samples were invalidated during this step.

2. The concentrations of n-pentane measured by the solid adsorbent and TO-14 methods were compared; if the difference in concentrations exceeded 35%, the cartridge results were invalidated and removed from the database.

Approximately 25% of the total measurements were invalidated during this two-step validation procedure. The concentrations of methanol and ethanol measured in the remaining samples are shown in Figure 4-1 and in Table 4-3. Several 'spikes' in methanol and ethanol concentrations observed at all three sites are probably due to local sources; they do not correlate with other motor vehicle related pollutants, and they occurred at different times at each site. Gasoline currently sold in California does not contain methanol or ethanol as sources of oxygen. Methanol and ethanol might be present in very small amounts as contaminants in MTBE. Also, there is little M85 gasoline used in California. Thus, a rise in the concentrations of these alcohols due to the introduction of RFG is not expected to occur. Mean morning concentrations at Azusa, Burbank and North Main are 14, 15, and 30 ppbv for methanol and 6, 9, and 5 ppbv for ethanol, respectively. Afternoon concentrations are 10, 11, and 15 ppbv for methanol and 3, 4, and 5 ppbv for ethanol at Azusa, Burbank and North Main, respectively.

4.1.2 MTBE

Two analytical methods were compared for quantifying MTBE (Shire, 1996, M.Sc. Thesis, Appendix B, Section 4); the solid multi-adsorbent method and the preconcentration method (modified TO-14 method). It has been found that MTBE can be quantified, along with C_2–C_{12} hydrocarbons, using both the modified TO-14 method (no Nafion® permeable membrane or other moisture-removal device used prior to injection) and the solid multi-adsorbent method. The comparison of MTBE concentrations obtained by these two independent methods shows excellent agreement; the values obtained from the multibed adsorbent method were on average 6% higher than the values obtained by modified TO-14 method.

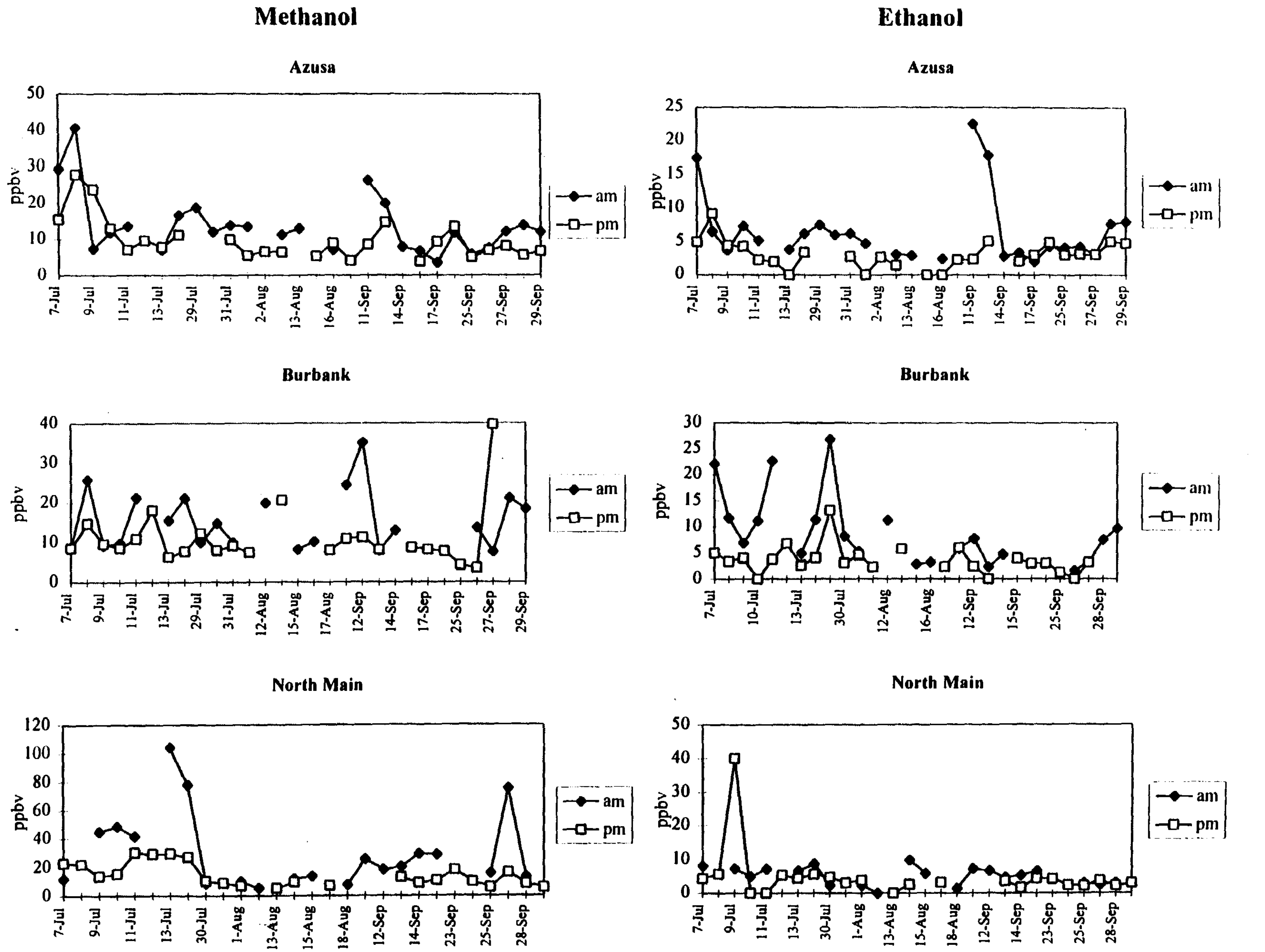

Figure 4-1. Methanol and ethanol concentrations measured at Azusa, Burbank and Los Angeles (N. Main) sampling sites during 1996 sampling campaign.

Table 4-3. Methanol and Ethanol Concentrations (ppbv) Observed In SoCAB in Summer 1996

Sampling Date	**Azusa**				**Burbank**				**Los Angeles (N. Main)**			
	Methanol		**Ethanol**		**Methanol**		**Ethanol**		**Methanol**		**Ethanol**	
	am	**pm**	**am**	**pm**	**am**	**pm**	**am**	**pm**	**am**	**pm**	**am**	**pm**
7-Jul	29.27	15.52	17.51	4.91	8.69	8.54	22.12	4.94	11.97	23.00	8.09	4.33
8-Jul	40.56	27.79	6.49	9.15	25.73	14.72	11.71	3.36		22.07		5.63
9-Jul	7.30	23.74	3.71	4.39	9.17	9.57	6.91	4.03	44.78	13.66	7.29	40.04
10-Jul	11.83	13.03	7.31	4.27	9.78	8.54	11.12	0.00	48.60	15.39	4.90	0.00
11-Jul	13.62	7.04	5.15	2.23	21.17	10.82	22.64	3.71	41.65	30.18	7.04	0.00
12-Jul		9.58		1.98		18.06		6.73		29.22		5.24
13-Jul	7.01	7.81	3.82		15.51	6.26	4.87	2.58	104.07	29.47	6.57	4.32
28-Jul	16.68	11.14	6.18	3.36	21.10	7.65	11.32	4.07	77.94	27.07	8.64	5.52
29-Jul	18.77		7.49		9.91	12.26	26.85	13.14				
30-Jul	12.03		5.97		14.77	7.88	8.11	3.02	8.45	10.20	2.24	4.66
31-Jul	13.88	9.85	6.19	2.74	9.93	9.07	5.19	4.56		8.83		2.94
1-Aug	13.48	5.41	4.68	0.00					10.08	6.96	2.20	3.76
2-Aug		6.51		2.66		7.44		2.30	5.21		0.00	
12-Aug	11.25	6.38	3.10	1.46	19.87		11.26					
13-Aug	12.99		2.94			20.49		5.68		5.12		0.00
14-Aug		5.30							11.91	9.49	9.75	2.53
15-Aug					8.12		2.83		13.68		5.74	
16-Aug	7.05	8.95	2.43	0.00	10.12		3.18					
17-Aug						7.96		2.33		6.97		3.13
18-Aug		4.01		2.30					7.50		1.29	
11-Sep	26.28	8.52	22.50	2.37	24.40	10.87	5.74	5.93	25.56		7.16	
12-Sep	19.93	14.71	17.91	5.08	35.17	11.21	7.66	2.42	18.22		6.58	
13-Sep					7.75	8.06	2.33	0.00	20.11	13.03	4.63	3.55
14-Sep	7.83		2.83		12.90		4.68		29.11	8.73	5.22	1.66
15-Sep						8.61		3.90				
16-Sep	6.75	3.81	3.37	2.05								
17-Sep	3.47	9.28	2.03	3.01		8.00		2.97	28.62	10.54	6.46	4.34
23-Sep						7.61		3.02		18.02		4.20
24-Sep	11.77	13.50	4.33	4.90						9.72		2.34
25-Sep	5.86	5.03	4.14	3.01		4.14		1.26	15.73	5.80	2.93	2.17
26-Sep	7.60	6.89	4.25	3.15	13.57	3.41	1.57	0.00				
27-Sep	12.13	8.15	3.14	3.07	7.49	39.65	3.35	3.16	75.35	16.22	2.42	3.70
28-Sep	13.92	5.56	7.67	4.99	21.04		7.42		13.21	8.31	3.04	2.13
29-Sep	12.02	6.63	7.98	4.80	18.35		9.60			5.59		2.98
Average	13.73	9.77	6.53	3.30	15.45	10.90	9.07	3.61	30.59	14.50	5.11	4.75

We found during the analysis of MTBE gaseous standards (520 ppb of MTBE in dry nitrogen, Spectra Gases, Aloha, NJ) that heating of the stainless-steel injection transfer lines in the modified TO-14 method produces a significant reduction in MTBE concentration. This was most probably due to the thermal decomposition of MTBE, since the concentration of isobutene (thermal decomposition product of MTBE) increased simultaneously. If the MTBE standard was made in humid UHP zero air, the decomposition was not so severe. Our standard operating procedures for the analysis of the canister samples require a heating of the stainless-steel injection transfer lines for the modified TO-14 method, in order to account for VOC with higher boiling point, $>C_{10}$. In analyzing the ambient air samples collected in the SoCAB area, we found that, when the transfer lines were heated, the measured values of MTBE were approximately 7% lower than when the lines were not heated. For consistency, all of the samples collected during 1995 and 1996 sampling campaign in SoCAB were analyzed with the transfer line heated to ~100 °C. The reported MTBE values are not corrected for this decomposition, since we judged it to be not very significant. This explains why the MTBE concentrations obtained from the multibed adsorbent method were, on average, 6% higher than the values obtained by the modified TO-14 method.

Figures 4-2 and 4-3 show the typical gas chromatogram of ambient samples collected during the 1995 and 1996 sampling campaigns, respectively. It can be seen from the comparison of these two chromatograms that the resolution between 2,3-dimethylbutane and MTBE was better in 1995 than in 1996, although an identical type of column (J&W DB-1 60 m capillary column) and chromatographic conditions were used in both years. In order to account for the differences in this chromatographic resolution between two different years, in comparing mean MTBE values in 1995 and 1996, we added 2,3-dimethylbutane concentrations (in ppbv, ppbC/6) to MTBE concentrations for both years and compared the mean MTBE values for each site for morning and afternoon sampling. Table 4-4 shows the differences in mean absolute and relative (weight %, in relation to TNMHC) MTBE concentration with and without adding 2,3-dimethylbutyl to MTBE concentrations.

As can be seen from this table, adding 2,3-dimethylbutane peak to MTBE peak did not change the percent difference between 1995 and 1996 significantly, especially for relative mean weight % abundances.

4.1.3 $CO/CO_2/CH_4$

The detailed description of the $CO/CO_2/CH_4$ analysis method and its validation is described in Appendix B (Shire M.Sc. Thesis, Section 5). In addition to the tests described by Shire (1996), we performed two additional method comparisons:

1. The influence on CO_2 collection efficiency of water condensation during sampling in the canister sampling equipment and in the canister was investigated. Since the CO_2 concentrations in some 1995 canister samples were lower than expected, we were concerned that water condensing during sampling in the sampling lines might scrub out some of the ambient CO_2. To test this possibility, we collected ambient air in Reno, NV, on June 5, 1996, using three

```
File=E:\ARB.RAW\BATCH07\HARBF5.35R Date printed=10-28-1996 Time= 10:00:41
Sample Name=NM95091306
0.0 to 15.333 min. Low Y=1.102 High Y=76.036 mv Span=74.934
```

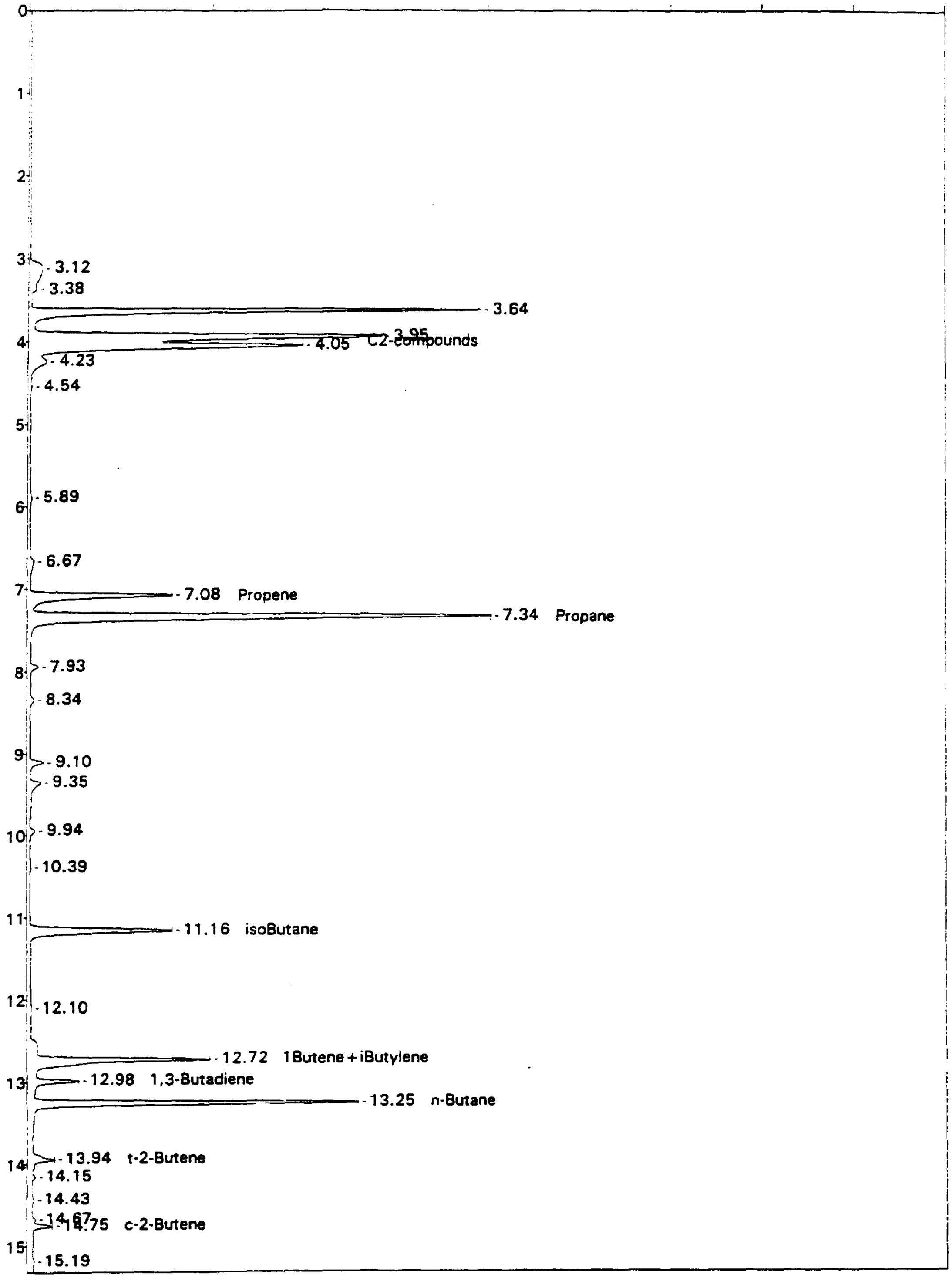

Figure 4-2. Chromatogram of ambient air sample collected in downtown Los Angeles (N. Main), September 13, 1995, and analyzed on DB-1 column for C_3–C_{12} hydrocarbons and MTBE.

```
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Sample Name=NM95091306
15.333 to 30.667 min. Low Y=1.102 High Y=76.036 mv Span=74.934
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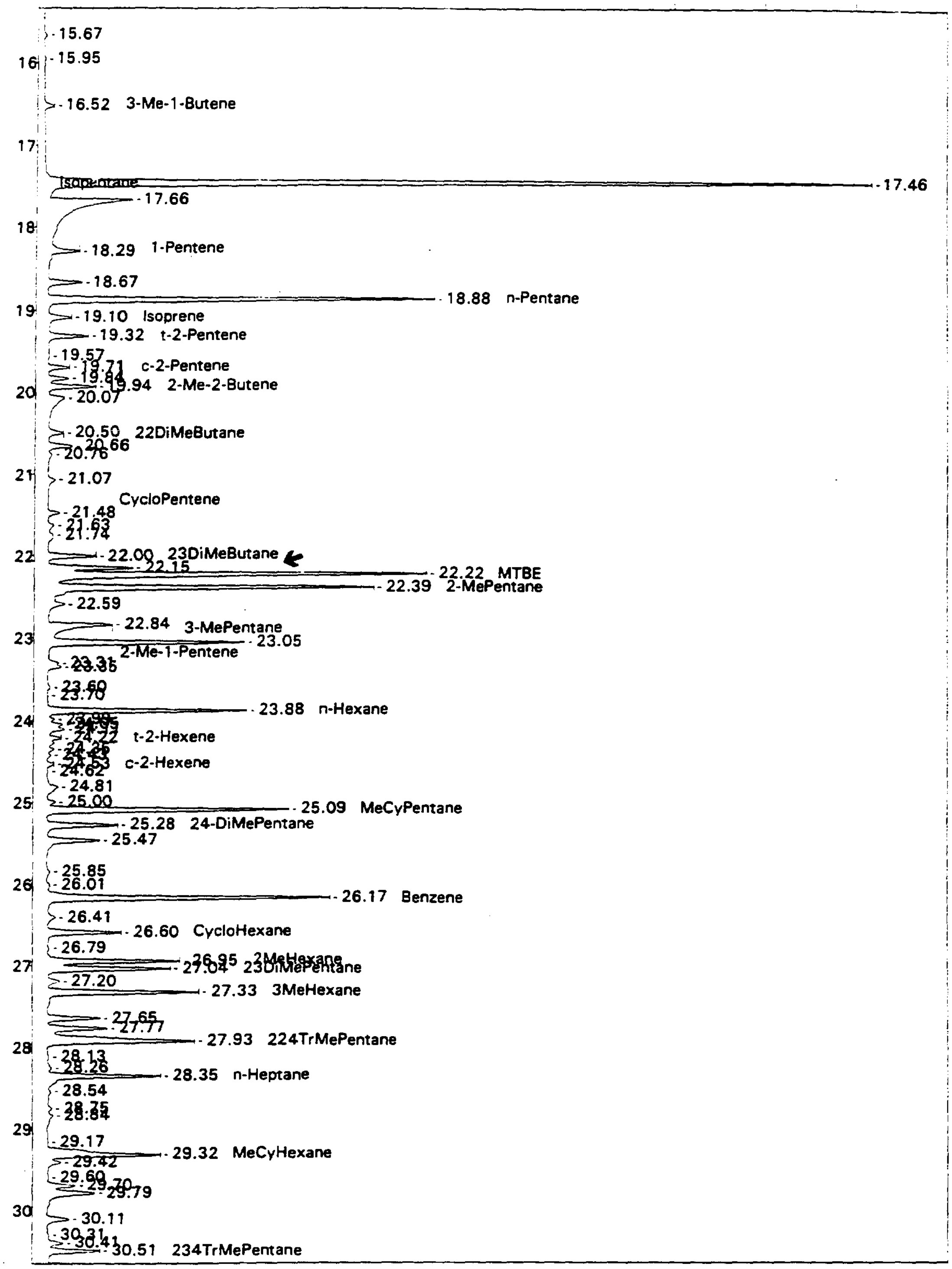

Figure 4-2. Chromatogram of ambient air sample collected in downtown Los Angeles (N. Main), September 13, 1995, and analyzed on DB-1 column for C_3–C_{12} hydrocarbons and MTBE (cont.).

```
File=E:\ARB.RAW\BATCH07\HARBF5.35R Date printed=10-28-1996 Time= 10:00:54
Sample Name=NM95091306
30.667 to 46.0 min. Low Y=1.102 High Y=76.036 mv Span=74.934
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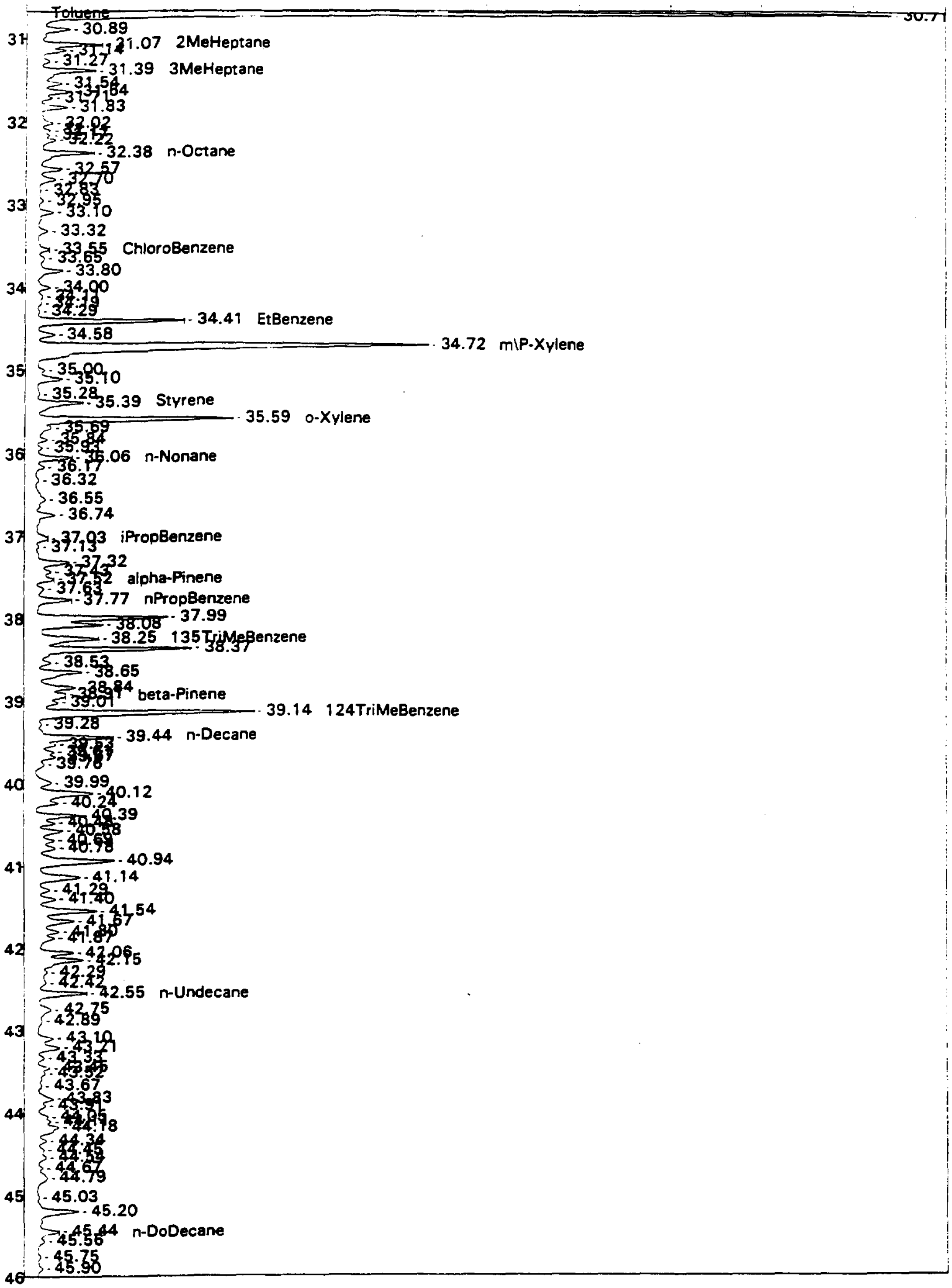
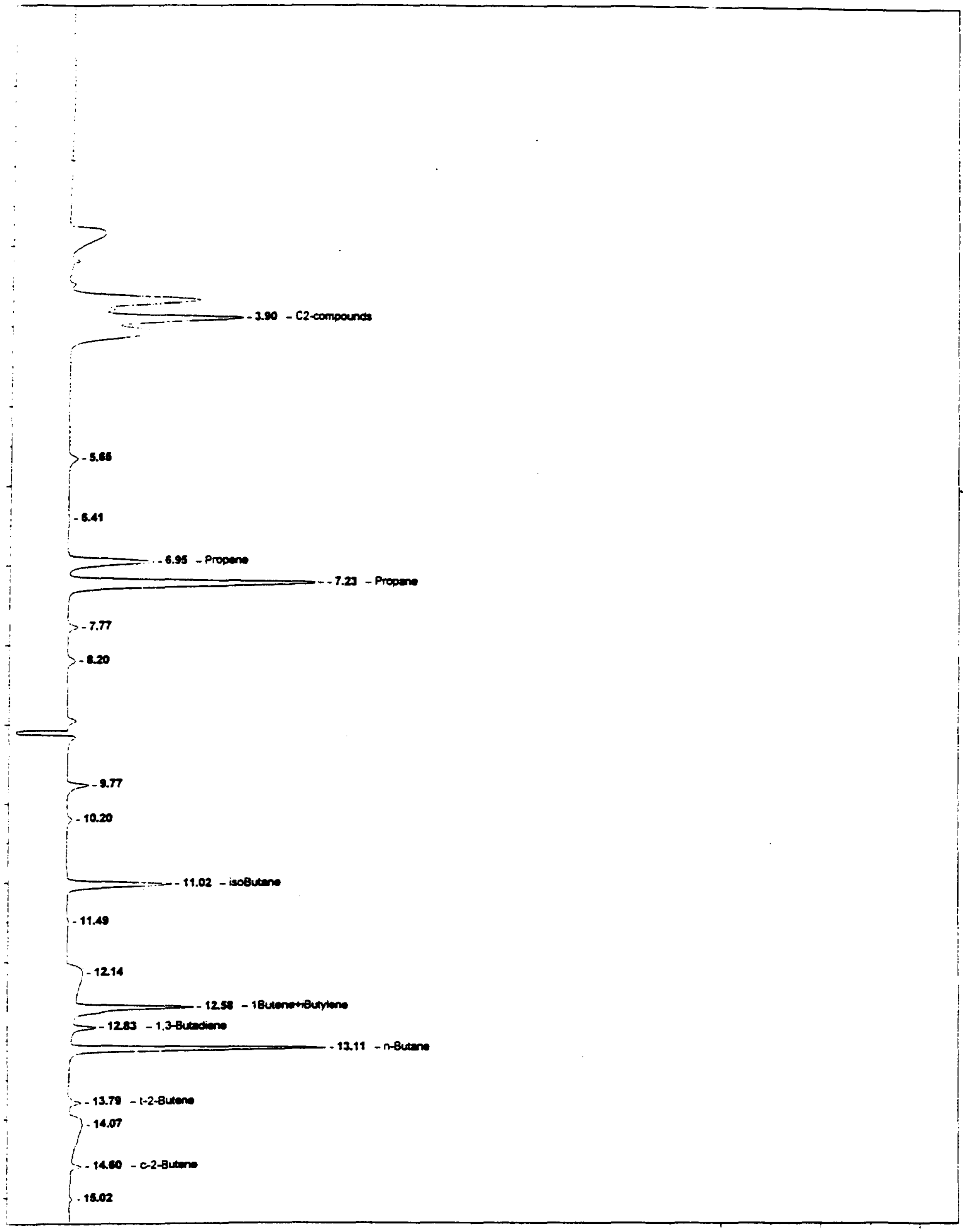


Figure 4-2. Chromatogram of ambient air sample collected in downtown Los Angeles (N. Main), September 13, 1995, and analyzed on DB-1 column for C_3–C_{12} hydrocarbons and MTBE (cont.).

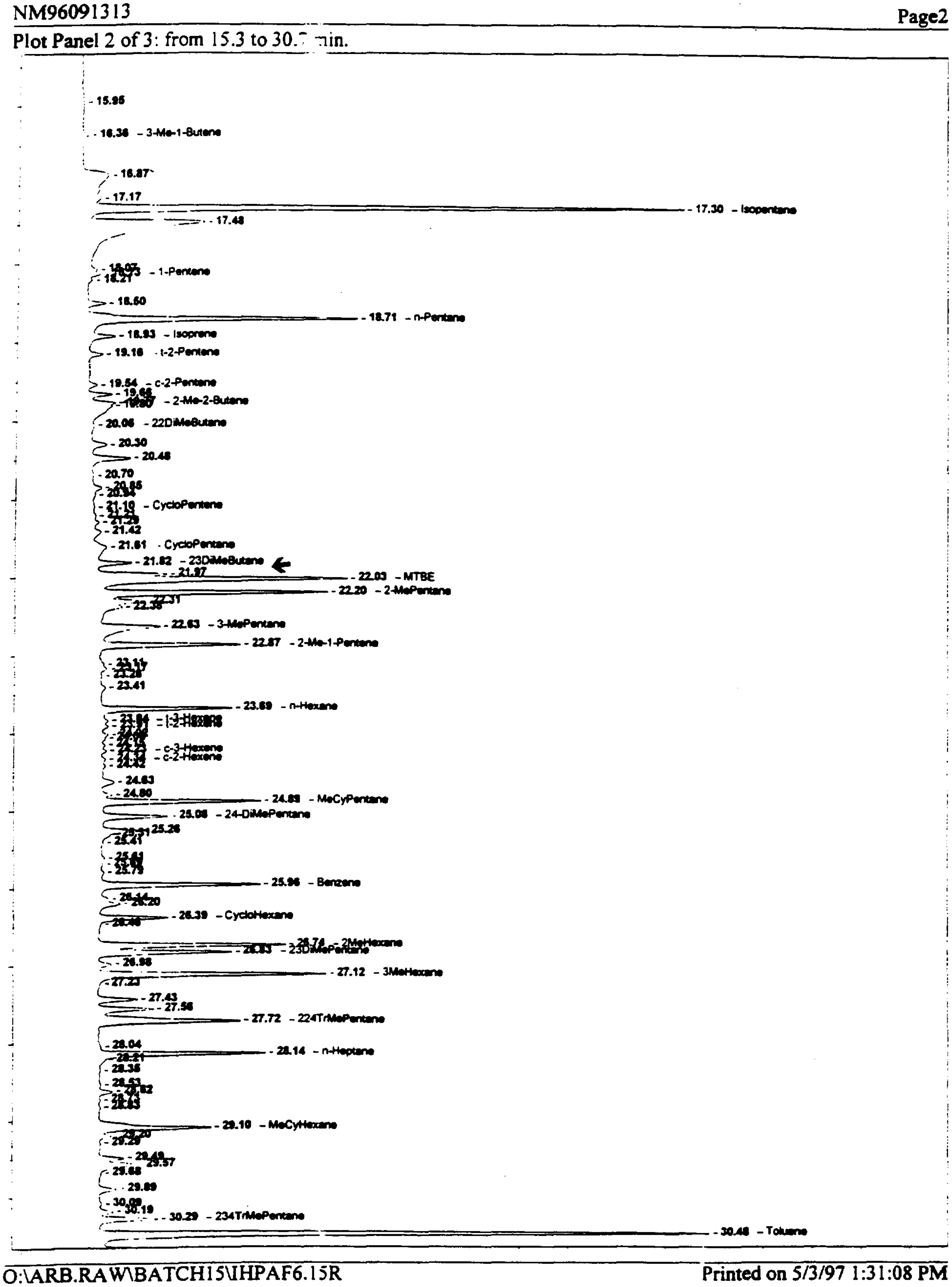
NM96091313 Page1

Plot Panel 1 of 3: from 0.0 to 15.3 min.



O:\ARB.RAW\BATCH15\IHPAF6.15R Printed on 5/3/97 1:31:08 PM

Figure 4-3. Chromatogram of ambient air sample collected in downtown Los Angeles (N. Main), September 13, 1996 and analyzed on DB-1 column for C_3-C_{12} hydrocarbons and MTBE.



NM96091313 Page2

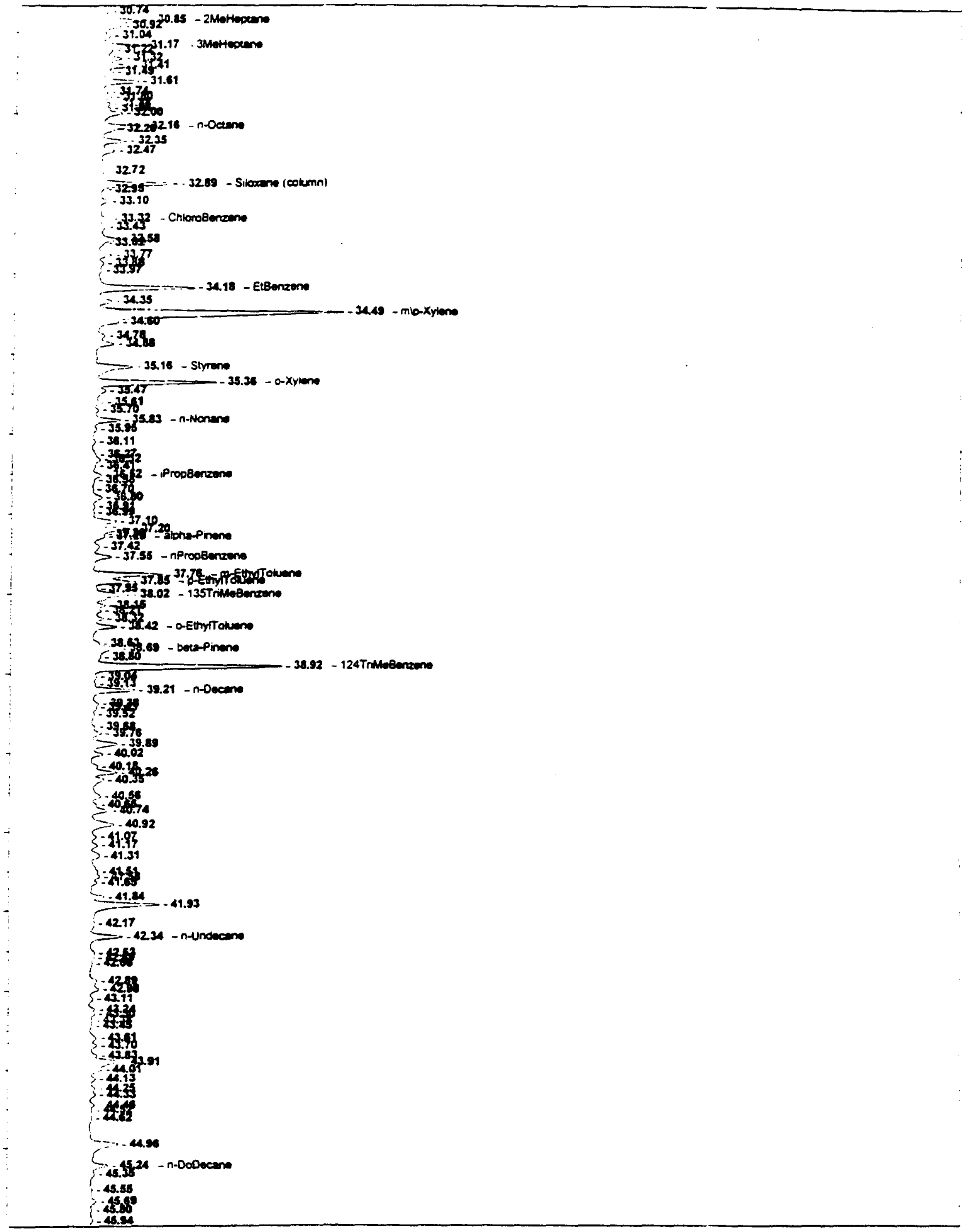
Plot Panel 2 of 3: from 15.3 to 30.7 min.

O:\ARB.RAW\BATCH15\IHPAF6.15R Printed on 5/3/97 1:31:08 PM

Figure 4-3. Chromatogram of ambient air sample collected in downtown Los Angeles (N. Main), September 13, 1996 and analyzed on DB-1 column for C_3-C_{12} hydrocarbons and MTBE (cont.).

NM96091313 Page3

Plot Panel 3 of 3: from 30.7 to 46.0 min.



O:\ARB.RAW\BATCH15\IHPAF6.15R Printed on 5/3/97 1:31:08 PM

Figure 4-3. Chromatogram of ambient air sample collected in downtown Los Angeles (N. Main), September 13, 1996 and analyzed on DB-1 column for C_3-C_{12} hydrocarbons and MTBE (cont.).

Table 4-4. The Differences in Mean Concentrations of MTBE (±Standard Error) Observed from 1995 to 1996.

Without 2,3-dimethylbutane

	Morning			Afternoon		
Site	**1995**	**1996**	**% Diff**	**1995**	**1996**	**% Diff**
Azusa (ppbv)	4.62 ± 0.32	5.77 ± 0.47	22.12	2.70 ± 0.18	4.03 ± 0.34	39.43
Azusa (wt%)	3.51 ± 0.10	5.22 ± 0.11	39.10	3.66 ± 0.10	5.66 ± 0.15	43.03
Burbank (ppbv)	6.60 ± 0.47	7.18 ± 0.64	8.47	2.70 ± 0.17	3.94 ± 0.26	37.14
Burbank (wt%)	3.85 ± 0.10	5.64 ± 0.14	37.62	3.42 ± 0.10	5.77 ± 0.16	51.19
N. Main (ppbv)	5.32 ± 0.38	6.40 ± 0.54	18.41	2.80 ± 0.13	3.51 ± 0.22	22.51
N. Main (wt%)	3.46 ± 0.08	5.15 ± 0.13	39.38	3.40 ± 0.09	5.63 ± 0.14	49.23
S. Monica (ppbv)				0.89 ± 0.10	0.60 ± 0.15	-38.30
S. Monica (wt%)				2.16 ± 0.11	2.94 ± 0.55	30.67

With 2,3-dimethylbutane

	Morning			Afternoon		
Site	**1995**	**1996**	**% Diff**	**1995**	**1996**	**% Diff**
Azusa (ppbv)	5.03 ± 0.32	5.78 ± 0.47	13.88	2.92 ± 0.18	4.05 ± 0.34	32.42
Azusa (wt%)	3.82 ± 0.10	5.25 ± 0.11	31.53	3.95 ± 0.10	5.71 ± 0.15	36.44
Burbank (ppbv)	7.2 ± 0.47	7.12 ± 0.64	-1.12	2.96 ± 0.17	3.98 ± 0.26	29.39
Burbank (wt%)	4.21 ± 0.10	5.64 ± 0.14	29.04	3.73 ± 0.10	5.78 ± 0.16	43.11
N. Main (ppbv)	5.86 ± 0.38	6.3 ± 0.54	7.24	3.07 ± 0.13	3.54 ± 0.22	14.22
N. Main (wt%)	3.78 ± 0.08	5.64 ± 0.13	39.49	3.73 ± 0.09	5.64 ± 0.14	40.77
S. Monica (ppbv)				0.99 ± 0.10	0.65 ± 0.15	-41.46
S. Monica (wt%)				2.4 ± 0.11	3.18 ± 0.55	27.96

wt% = weight percent of given species in relation to TNMHC (both concentrations in ppbC).
Standard Error = defined as a standard deviation of all measurements divided by the square root of number of measurements .
% diff = (1996 concentration-1995 concentration)/((1995+1996 concentrations)/2))*100.

parallel samplers. Sampler #1 was equipped with a water trap, which constantly trapped and removed the condensed water before ambient air entered a canister. Sampler #2 had 2 ml of water injected into the water trap and this water was not removed during sampling. Sampler #3 was equipped with a water trap and sampled ambient air into a canister which was injected with 150 µl of water. Table 4-5 presents the results of these experiments.

Table 4-5. Influence of Water on Collection Efficiency of CO_2, CO and CH_4.

					% difference (wet vs. dry)		
Sampler No.	**Water Content**	**CO (ppm)**	**CH_4 (ppm)**	**CO_2 (ppm)**	**CO**	**CH_4**	**CO_2**
1	dry	0.28	1.67	348.9			
2	2 ml	0.1	1.34	335.6	95	22	4
3	150 µl	0.28	1.61	346.19	0	3.7	0.3

It can be concluded from this experiment that the large amount of water accumulating during sampling affected, to some degree, all three compound concentrations (however, the ambient concentration of CO was close to our detection limit). Water present in a canister does not affect CO, CH_4 and CO_2 concentrations at all. For the 1996 sampling campaign all canister samplers were equipped with water traps which constantly removed any water accumulated during sampling.

2. To compare our CO_2 analysis method with the continuous CO_2 analyzer we sampled ambient air in Reno, NV, on July 17, 1996, into a canister and a Tedlar bag in parallel with a continuous Thermo Environmental Instruments Model 40 CO_2 analyzer over a three-hour period. The average reading for the CO_2 analyzer over this time period was 390.7 ppm. The Tedlar bag was analyzed and a value of 383.9 ppm was obtained, a -2% difference compared with the continuous CO_2 instrument The canister sample was analyzed using our GC method and a value 411.4 ppm was obtained for CO_2. Thus, the difference between our analysis method and the continuous analyzer is 5.2%.

4.2 Carbonyl Compounds

The analysis of all samples collected on DNPH impregnated C_{18} SepPak cartridges was performed by Dr. Kochy Fung of AtmAA, Inc. The results of these analyses are submitted in Excel 5.0 format on a 3.5" diskette (no. II) with this report. Ambient air data are included in the files CHO_95 and CHO_96 for the summer of 1995 and 1996, respectively and the garage and tunnel samples are reported in files GATU_95 and GATU_96 for 1995 and 1996, respectively. The corresponding replicate samples and blanks are reported in the same files, on separate data sheets.

4.3 Tunnel Study

At the same time this program was being conducted several tunnel studies were conducted by DRI with funding from the Coordinating Research Council (CRC) and other interested agencies. It was anticipated that these data could be shared with ARB and other interested programs. This section summarizes these tunnel studies and provides some additional information not included in the CRC reports.

In 1995, sampling was conducted in both the Van Nuys and Sepulveda Tunnels. In 1996 another experiment was conducted in the Sepulveda Tunnel only.

The results of the 1995 tunnel studies have been reported to CRC and these data are available in the CRC report. The 1996 tunnel study draft report has been submitted, but not yet accepted by CRC. Once that report has been accepted, those data will be available.

4.3.1 Tunnel Descriptions

The Van Nuys Tunnel is a two-bore, urban tunnel, 222 m in length, running east/west under the runway of the Van Nuys Airport. There are three lanes per bore along with a narrow walkway adjacent to the north and south lanes. Vent buildings are located on the southeast and northeast edges of the tunnel and were not in operation during the experiment. There are nine door-size openings between the bores. The openings were covered with plywood prior to the commencement of sampling. Traffic lights are located within a few hundred meters of both the tunnel exit and entrance. Because of the lights, vehicles accelerated upon entering the tunnel and often decelerated at the exit. Sampling was conducted in the North Bore, the same as in the 1987 experiment. The experiment was conducted June 9–12, 1995.

The Sepulveda Tunnel was chosen to represent a different fleet from that of LA with potentially lower emissions. The tunnel is a covered roadway the top portion of which is part of the airplane runway and taxiway for the Los Angeles International Airport (LAX). The covered portion of the roadway is 582 m long, straight, and approximately flat in the covered portions, although there is a downgrade approaching the tunnel and an upgrade leaving it. There are two bores, three lanes each, with a sidewalk on the right side of each bore. The two bores of the tunnel are separated by a concrete wall running most of the length of the tunnel. There are 17 openings in this wall, each approximately 10 ft wide by 12 to 14 ft tall. In order to obtain mass emission factors in the tunnel, we sealed off these openings so there would be no air transfer between the two bores. The ventilation system in the tunnel was not in operation when we were sampling. The experiment was conducted in the west bore, which carries Sepulveda Boulevard southbound from the LAX terminals. The experiment was conducted June 9–12, 1995.

4.3.2 Comparison of CO and CO_2 Data

In these tunnel studies the protocol involved filling both a Tedlar bag and a canister at each sampling location. The Tedlar bags were analyzed on-site using a Dasibi Instruments Model 3003 analyzer for CO and a Thermo Environmental Instruments Model 40 analyzer for

CO_2. The canisters were analyzed in the DRI Organic Analysis laboratory as described in Section 3.1.4 for CO, CO_2 and methane, in addition to the hydrocarbon species. This allowed an opportunity to compare these two methods. The results are presented in Figures 4-4 to 4-7. Figure 4-4, the comparison of the two analyses for CO in 1995, shows some scatter but overall presents a very good comparison. There is a slight bias shown with the on-site analyzer slightly lower than the canisters. The same comparison for CO_2 is shown in Figure 4-5, where the overall comparison is even better between the two methods. There is one outlier in this figure where the canister analysis read much lower than the on-site method. Looking at the data, it appears that the on-site analysis produced a more physically reasonable number.

Various changes in sampling techniques were made between 1995 and 1996 and a similar comparison was then done with the 1996 data. Figure 4-6 presents the CO data; there appears to be the same slight bias as in the previous year, with the on-site analysis lower than the canister analysis. Figure 4-7 presents the 1996 CO_2 data which show almost no bias and no extreme outliers as were seen in 1995.

One additional check of the analysis system was an intercomparison done with the Bay Area Air Quality Management (BAAQMD) Laboratory. Professor Rob Harley of UC, Berkeley collected two canister samples in the Caldecott Tunnel on July 31, 1996, and sent one can to DRI and one to BAAQMD. Both groups analyzed the canisters for CO_2 and methane in addition to the NMHC species. DRI's value for CO_2 was 1080 ppm, BAAQMD's was 1085 ppm and the on-site analyzer read 1093 ppm. For methane, DRI analysis produced 2.22 ppm and BAAQMD 2.11 ppm. This additional intercomparison gave us confidence in our measurement techniques.

4.3.3 Hydrocarbons in the Tunnels

The data file, 95tunl.xls, includes the concentrations of the species measured in the tunnel, and the resulting emission factors calculated for these species. The emission rates are presented in mg/mile. The data are for both the 1995 Van Nuys and Sepulveda Tunnel studies. The concentrations can be much higher than ambient levels, as is expected in this type of experiment. Emission rates can be used to develop source profiles.

4.4 Gasoline Headspace Analyses

The data from the 1995 and 1996 gasoline headspace analyses are included in the files HGAS_95.XSL and HGAS_96.XLS in Excel 5.0 format (Disk III). All data are presented in weight %, relative to the total mass of all components. The analysis for 1996 samples was carried out on 100 m Petrocol capillary column, whereas the analysis for 1995 samples was performed on 60 m DB-1 capillary column, the same we used for canister sample analysis. Because of this difference, more compounds were identified in 1996 than in 1995. The list of compounds with their corresponding mnemonics is included on Disk III (GASHS4.XLS).

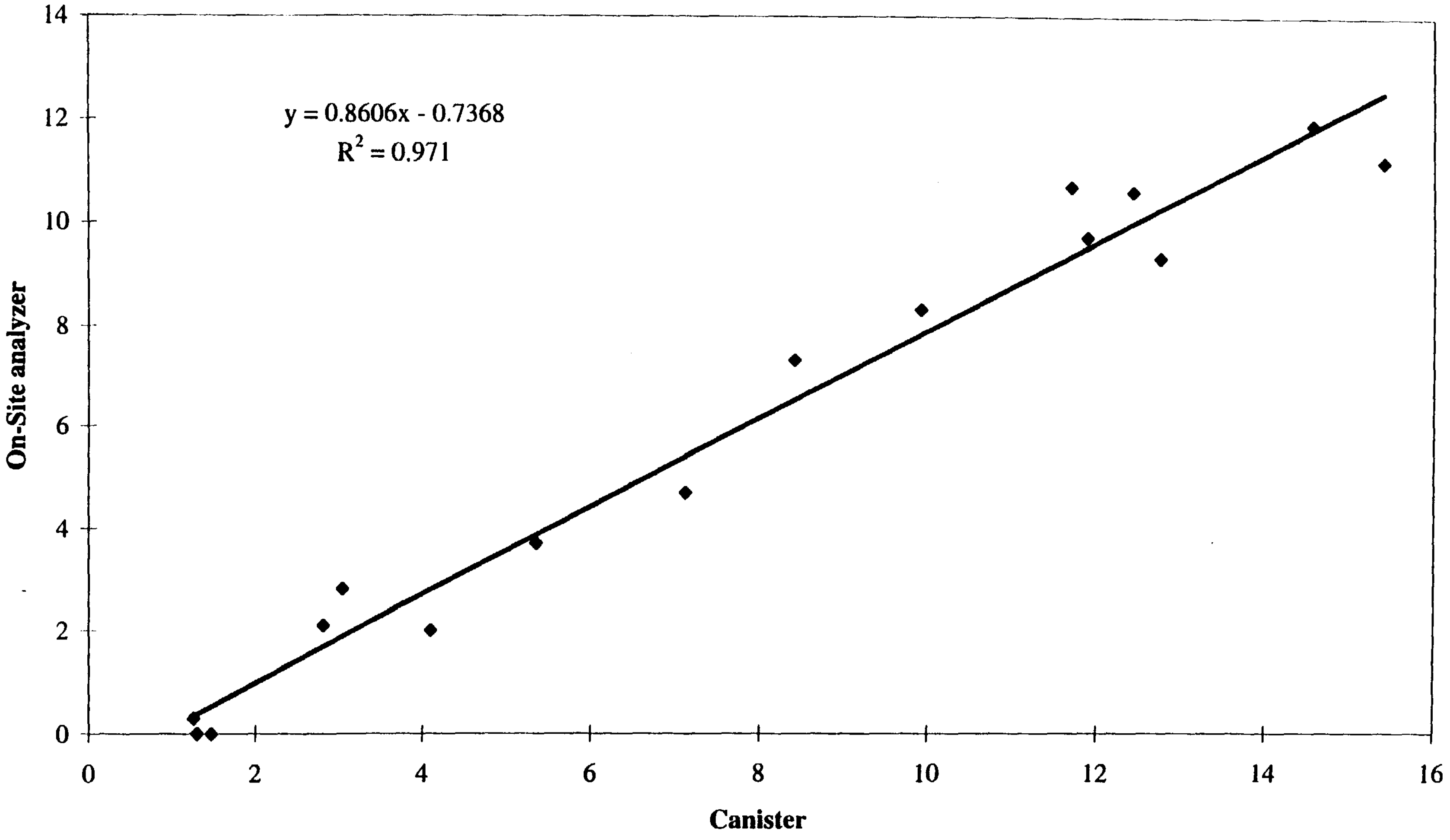


Figure 4-4. 1995 Sepulveda Tunnel Study, Carbon Monoxide Measurements — Comparison of On-site (Tedlar bag) Analysis versus Laboratory (canister) Analysis.

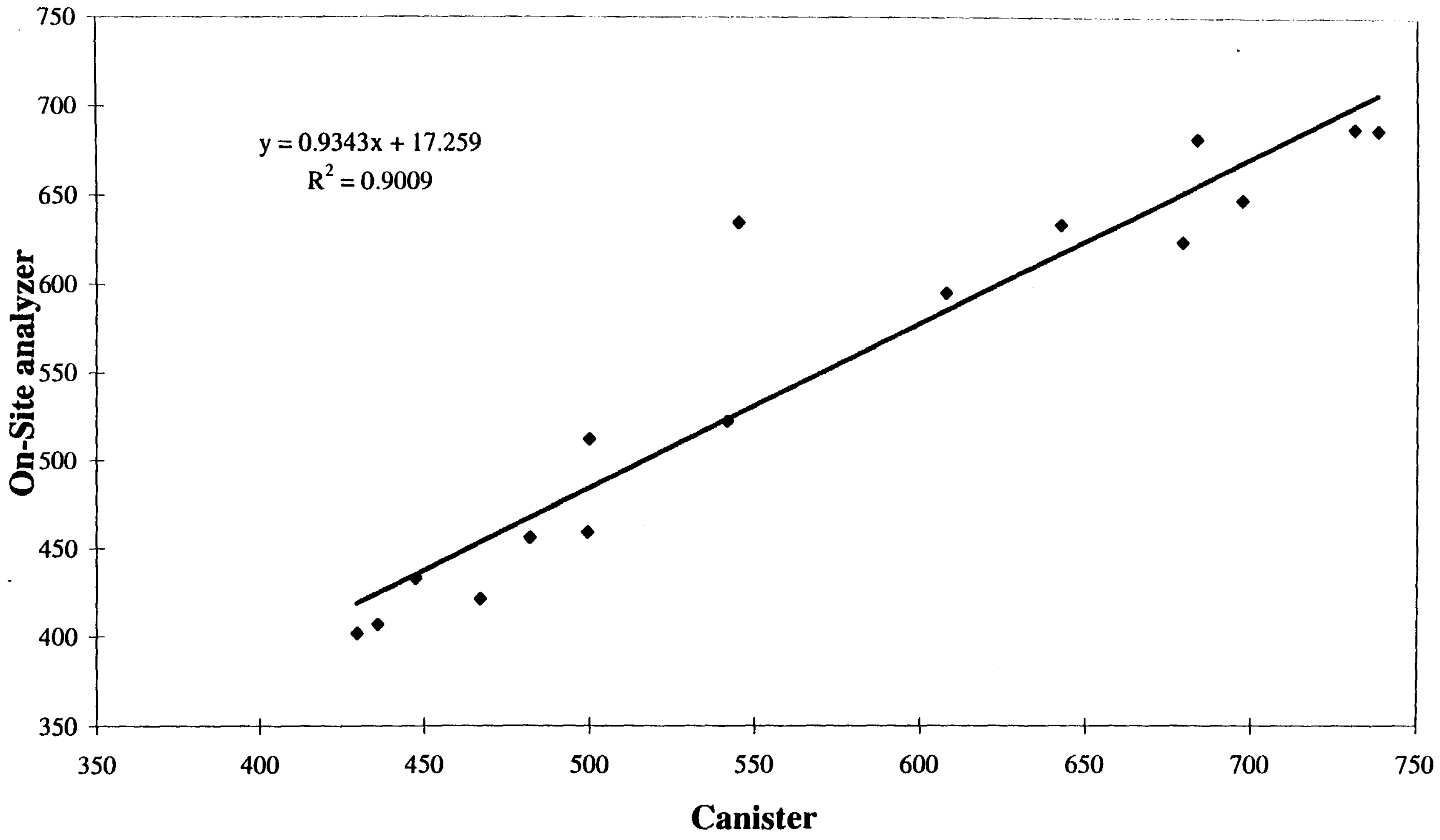


Figure 4-5. 1995 Sepulveda Tunnel Study, Carbon Dioxide Measurements — Comparison of On-site (Tedlar bag) Analysis versus Laboratory (canister) Analysis.

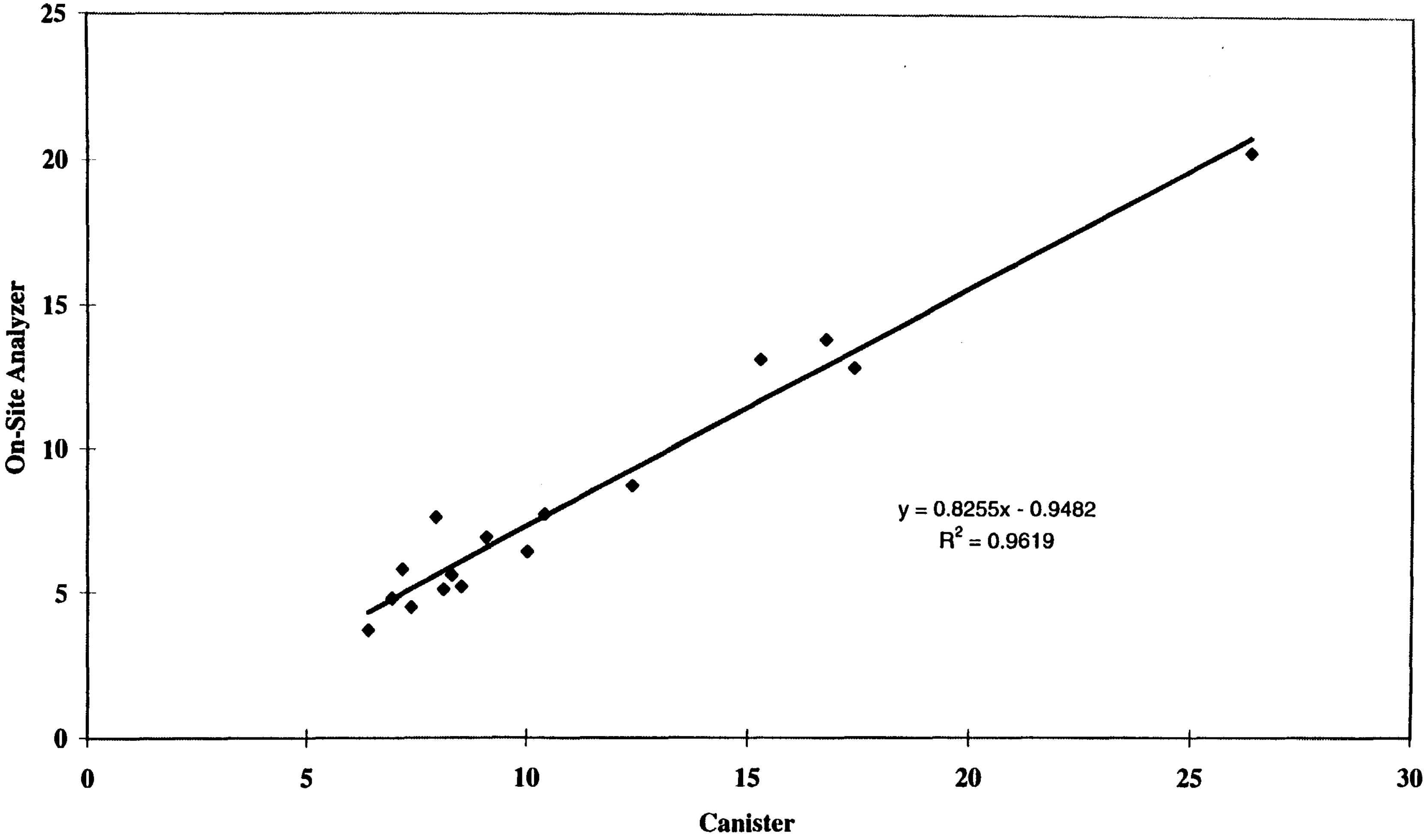


Figure 4-6. 1996 Sepulveda Tunnel Study, Carbon Monoxide Measurements — Comparison of On-site (Tedlar bag) Analysis versus Laboratory (canister) Analysis.

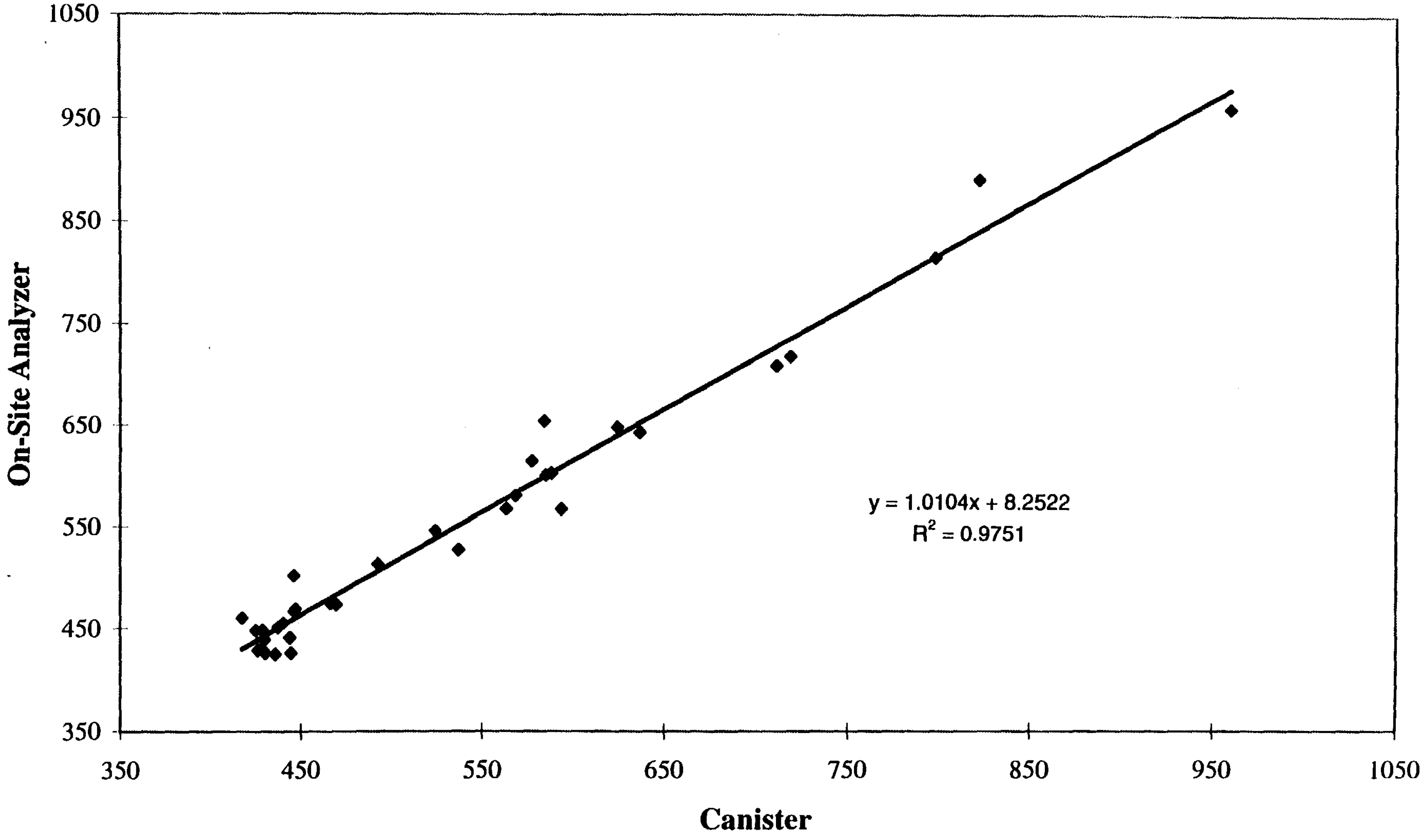


Figure 4-7. 1996 Sepulveda Tunnel Study, Carbon Monoxide Measurements — Comparison of On-site (Tedlar bag) Analysis versus Laboratory (canister) Analysis.

4.5 Quality Control and Level 1 Validation

Prior to analysis, all analytical systems (i.e., GC/ECD/FID, GC/MSD, and GC/IRD/MSD) were checked for purity with humidified zero air and certified clean (less than 0.2 ppbv of targeted VOC). Quality control in the laboratory includes daily instrument calibration, replicates of standards, and analysis of approximately 10% of the samples for estimation of analytical precision, which historically has been better than 6%. In past programs, field blanks were at the 1–2 ppb levels, based on the air volume of the samples. Coefficients of variation (CV) calculated from observed differences between duplicate sample pairs were less than 10%.

Primary reference standards are traceable to a National Institute of Standards and Technology (NIST) Standard Reference Material (SRM). NIST SRM 1805, which consists of 254 ppb of benzene in nitrogen, was used for canister hydrocarbon speciation. In addition, NIST SRM 2764 (245 ppb of propane in nitrogen), was used for calibrating the light hydrocarbon analytical system. The GC/FID system was calibrated initially by multipoint calibration (i.e., three levels plus humid zero air), and regularly checked by a one-point calibration, using SRM 1805 or the propane standard. The day-to-day reproducibility of ±10% is acceptable for either standard.

During the course of analysis, calibration standards are routinely analyzed to ensure that the instrument response has not changed. The criterion of 10% of expected response is used by the analyst to determine whether the instrument must be recalibrated. Retention time windows for each analyte are established prior to analysis and re-established continuously throughout the course of the analytical period.

Accuracy involves the closeness of a measurement to a reference value and reflects elements of both bias and precision. Relative accuracy of canister sampling is determined by measuring an NIST hydrocarbon standard into a sampler. The contents are then analyzed for the component contained in the audit cylinder. Percent relative accuracy is calculated:

$$\%\,\text{Relative Accuracy} = \frac{X - Y}{X} \text{ x } 100$$

where:

Y = concentration of the targeted compound recovered from the sampler, and

X = concentration of targeted compound in the NIST standard.

If the relative accuracy does not fall between 90 and 110%, the field sampler is not used. Accuracy is determined by repeatable analysis of an NIST standard cylinder (for canisters). Percent relative accuracy is then determined as described above.

Level I sample validation takes place in the field or in the laboratory and consists of: 1) flagging samples when significant deviations from measurement assumptions have occurred; 2) verifying computer file entries against data sheets; 3) eliminating values for measurements which are known to be invalid because of instrument malfunctions; and 4) adjustment of measurement values for quantifiable calibration or interference biases. Each gas chromatogram is examined immediately after the run to verify that peak integrations have been performed properly. The peak integration, retention times, and peak identifications assigned by the ChromPerfect software are stored to disk as an ASCII file. The files are then read into a Foxpro data file for additional processing and verification of peak identifications. The peak assignments for the major constituents (typically about a dozen peaks) in the chromatogram are manually verified, and retention times are recalculated for all detectable peaks based upon regression between sample and reference retention times for the manually identified peaks. The adjusted retention times are used to assign peak identifications for all detectable peaks (the reference file currently contains 160 identified compounds). The retention time adjustments and peak assignments are executed automatically by a Foxpro program. The ChromPerfect and subsequent confirmatory peak identifications are then compared and discrepancies are resolved by the analyst based on peak patterns or confirmatory identification by GC/MS. In the final step, the Level I validated data are appended to the master database. Each sample appears as a record within the database and is identified by a unique sample identification, site, date, and time and as a primary, collocated, blank, spiked, or replicate sample.

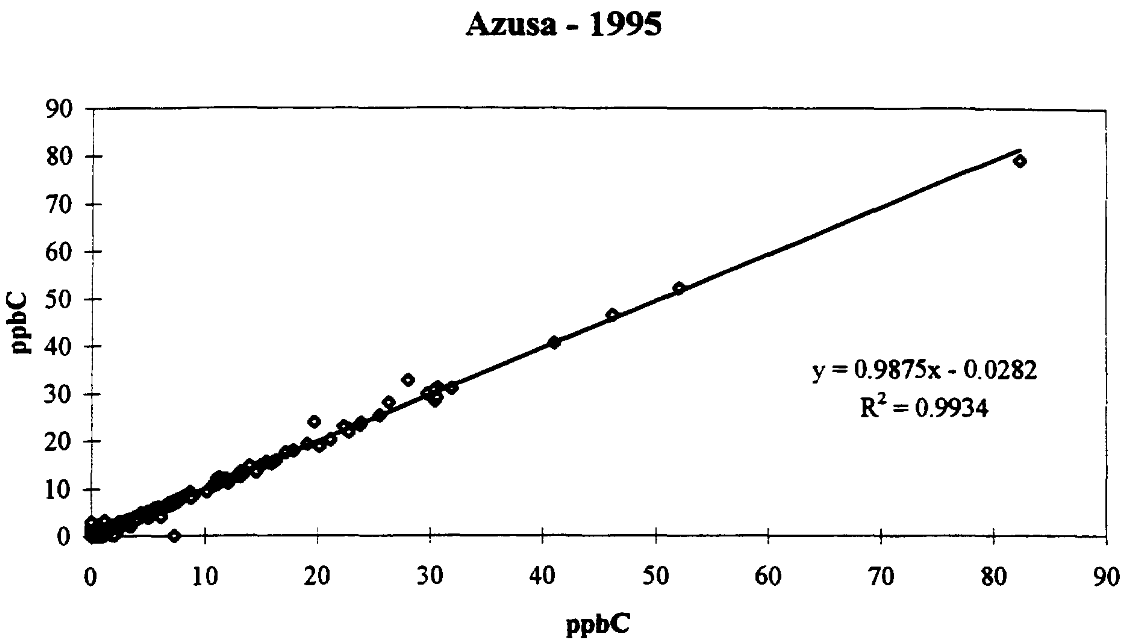
4.5.1 Replicate Analyses

For canister samples, all primary and replicate analysis data are included in the files RGALC_95 and RGALC_96, which contain data for all ambient canister samples collected in 1995 and in 1996, respectively (Disk #I). For carbonyl compounds, the corresponding replicate samples and blanks are reported in the same files as the primary samples, CHO_95 and CHO_ 96 (Disk #II) but on separate data sheets. In addition, for canister samples there is a separate file containing all primary-replicate pairs of samples, REPCAN.XLS, in Excel 5.0 format (Disk #III).

Figures 4-8, 4-9 and 4-10 show the comparisons of primary and replicate analyses for all individual hydrocarbon samples collected in Azusa, Burbank and Los Angeles (N. Main), respectively. Carbon monoxide, CO_2, methane and total hydrocarbons are not included in this comparison. It can be seen from these figures that excellent reproducibility was achieved for the canister sample analyses.

4.5.2 External Performance Audits and Comparison Studies

The DRI Organic Analytical Laboratory participated in the International Hydrocarbon Intercomparison Experiment, organized by National Center for Atmospheric Research (NCAR). The results of Tasks I and II of this intercomparison have been published recently (Apel et al., 1994). The first task involved the circulation of a two-component hydrocarbon mixture of known composition and unknown concentration, prepared by NIST. The DRI values were within 5% of the nominal values provided by NIST. Task II was more complex — the participating laboratories were asked to identify and quantify 16 components present, in the ppb range, in a mixture prepared by NIST. The agreement between the DRI values and the NCAR values, as well as with nominal values provided by NIST, was generally within 15%. The next


Azusa - 1995

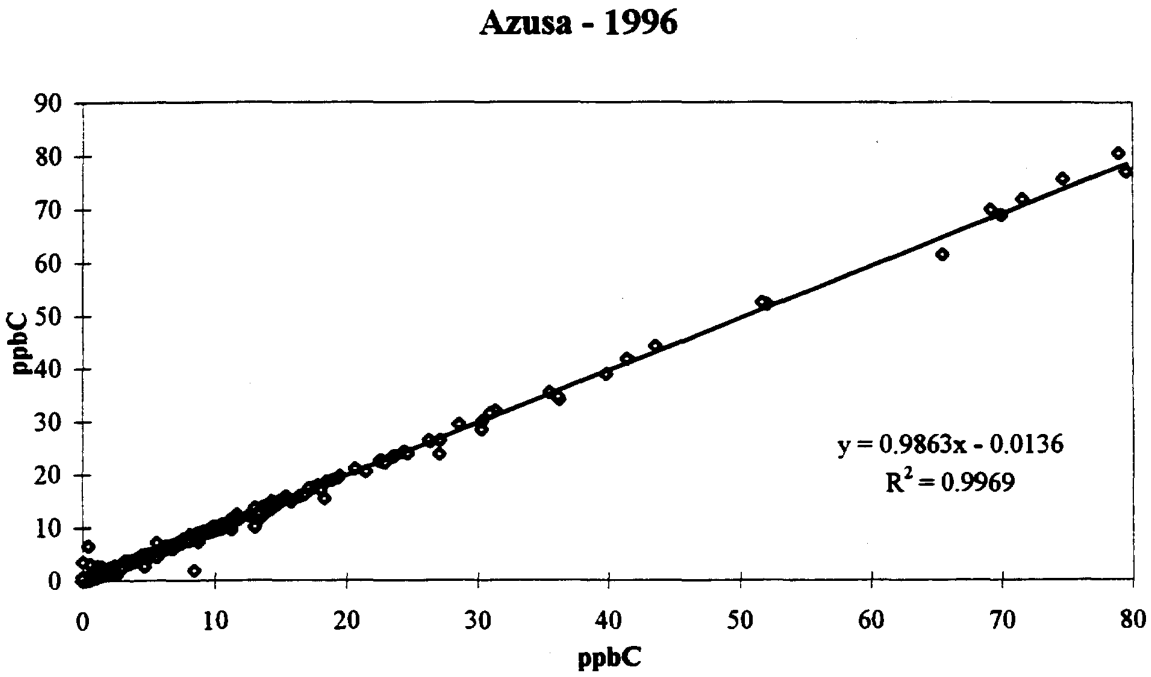
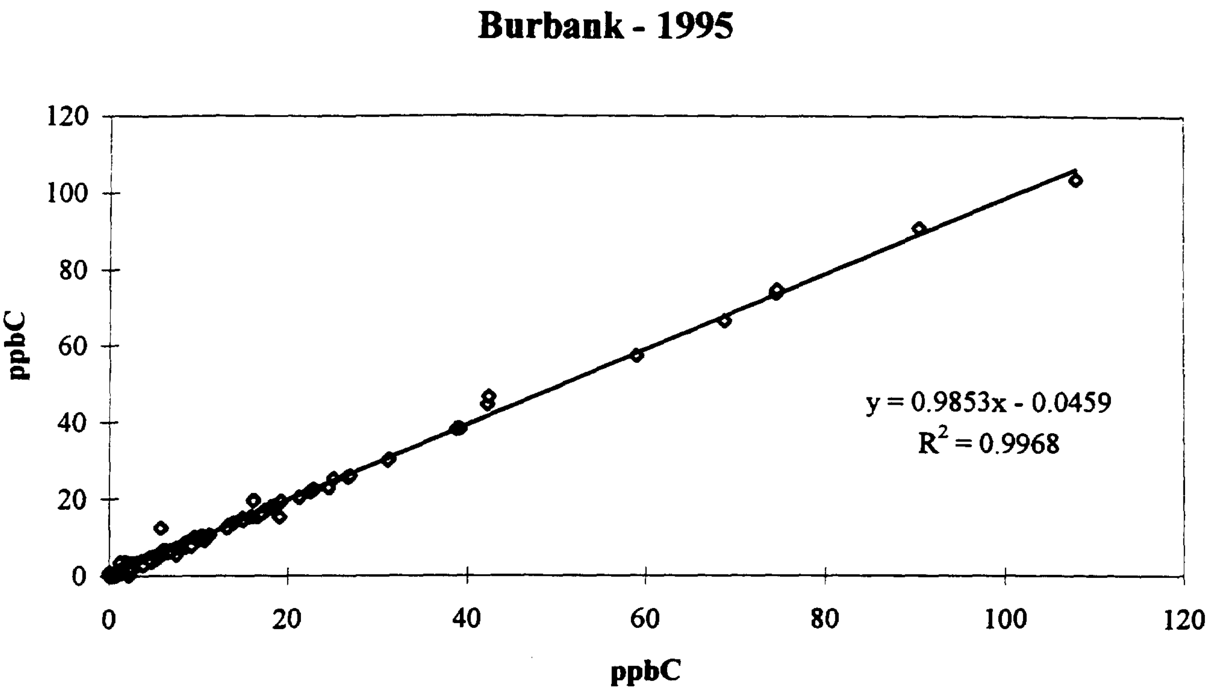

Azusa - 1996

Figure 4-8. Comparison of primary and replicate analyses for all individual hydrocarbon samples collected in Azusa in 1995 and 1996.



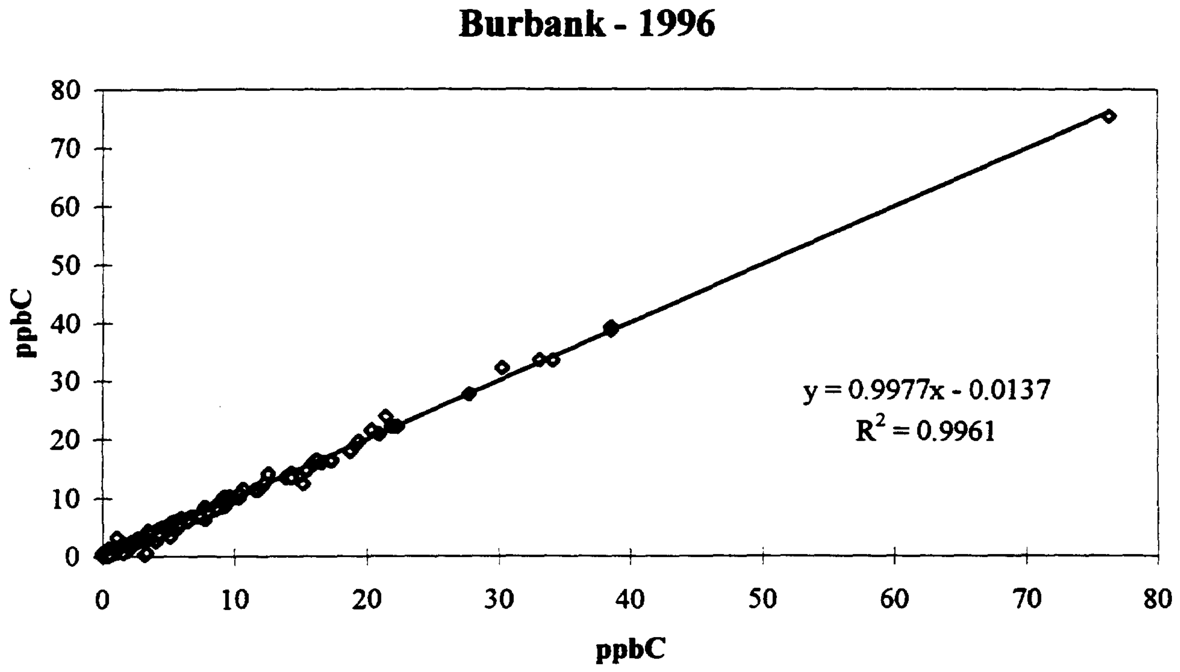
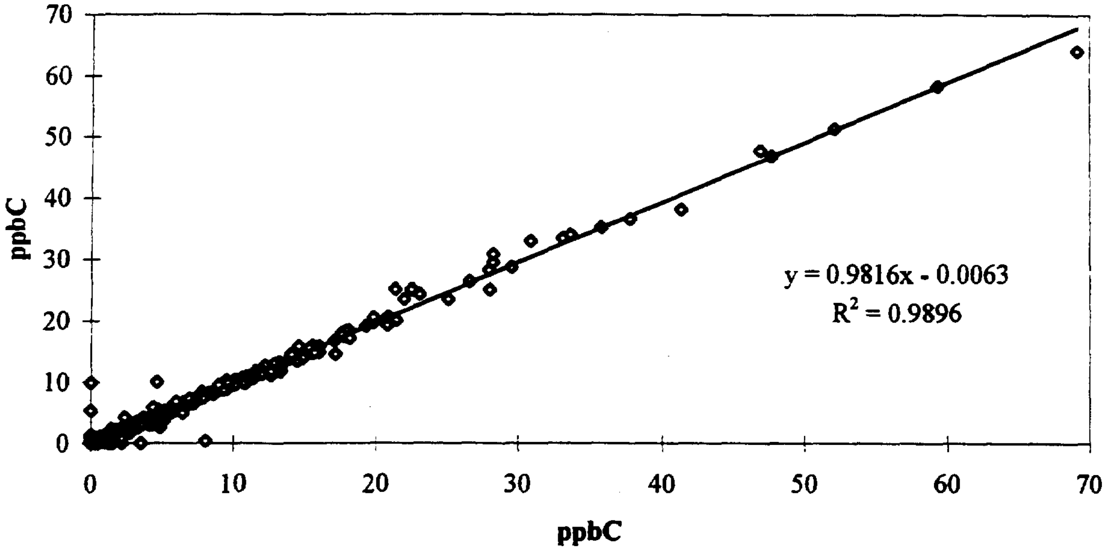


Figure 4-9. Comparison of primary and replicate analyses for all individual hydrocarbon samples collected in Burbank in 1995 and 1996.

North Main - 1995



North Main - 1996

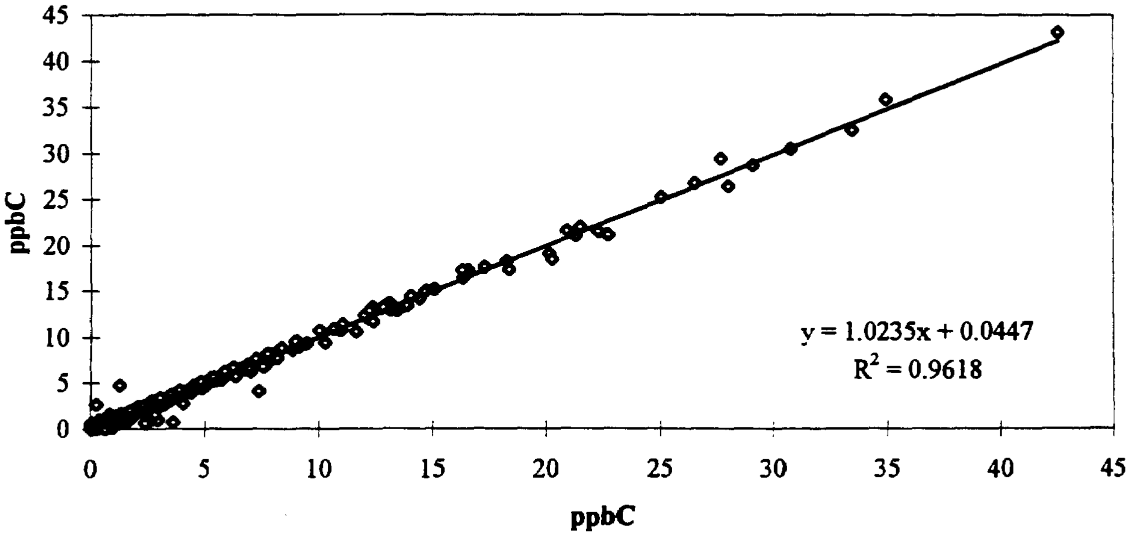
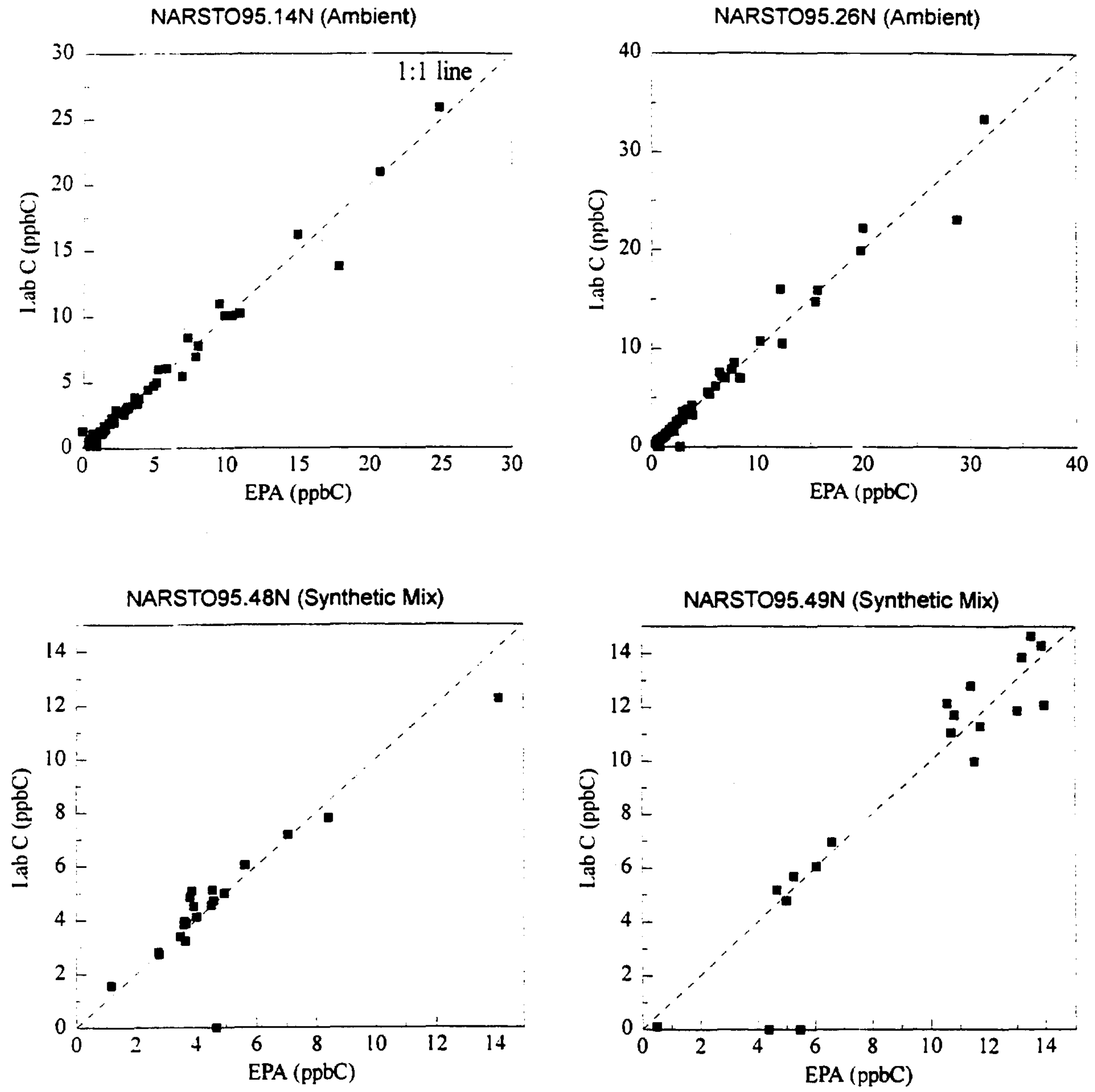


Figure 4-10. Comparison of primary and replicate analyses for all individual hydrocarbon samples collected in Los Angeles (N. Main) in 1995 and 1996.

tasks, which were carried out at the beginning of 1996, involved the analysis of ambient air samples. The DRI has successfully completed these tasks — the agreement between the DRI values and the NCAR values was generally within 10%. The results of these tasks are currently being prepared for publication. Phase V of the NCAR International Hydrocarbon Intercomparison Experiment (involving analysis of ambient samples of very low concentrations) is currently underway.

In the summer of 1995 the DRI laboratory participated in the NARSTO-Northeast hydrocarbon intercomparison study, involving the analysis of two ambient air samples by participating laboratories (Fujita et al., 1996). This audit occurred during the same time the samples were collected and analyzed for the CRC study. Participants included Biospheric Research Corporation (BRC), State University of New York at Albany (SUNYA), EPA Region I, DRI, and 8 of the PAMS networks in the northeastern U.S. EPA (Bill Lonneman) served as the reference laboratory. Figure 4-11 shows that the agreement between the DRI laboratory and the EPA Atmospheric Research and Exposure Assessment Laboratory was generally excellent.

In addition, the DRI laboratory participated in several non-methane hydrocarbon laboratory performance audits, organized by Quality Assurance Section, Monitoring and Laboratory Division, of the CARB. The last intercomparison, organized in September 1996, involved the analysis of ambient air sample by four California district laboratories (labeled A, B, C and D) and the DRI laboratory. The results are included in Appendix C.


NARSTO95.14N (Ambient)

NARSTO95.26N (Ambient)

NARSTO95.48N (Synthetic Mix)

NARSTO95.49N (Synthetic Mix)

Figure 4-11. Correlations of values reported by DRI versus EPA for analysis of NARSTO Northeast hydrocarbon performance audit samples.

5.0 EVALUATION OF AMBIENT HYDROCARBON DATA

The data validation process consists of procedures that identify deviations from measurement assumptions and procedures. Three levels of validation are applied which will result in the assignment to each measurement of one of the following ratings: 1) valid; 2) valid but suspect; or 3) invalid. Level 1 data validation normally takes place in the field or in the laboratory and consists of: 1) flagging samples when significant deviations from measurement assumptions have occurred; 2) verifying computer file entries against data sheets; 3) eliminating values for measurements which are known to be invalid because of instrument malfunctions; 4) adjustment of measurement values for quantifiable calibration or interference biases; 5) determining measurement precision by replicate analyses and by collection of field blanks and collocated samples. Section 4.4 summarizes the results of Level 1 validation. Level 2 validation, the subject of this section, takes place after the data from various measurement methods have been assembled in a master database. Level 2 applies consistency tests, based on known physical relationships among variables, to the assembled data. These tests fall into three categories: detection of extreme values; consistency among co-pollutants and between redundant measurements by alternative measurement methods; and examination of temporal and spatial variations. Level 3 validation is part of the subsequent data interpretation process. Receptor modeling, factor and other statistical analyses, and photochemical air quality simulation models are several examples. Unusual values are identified during the data interpretation process as: 1) extreme values; 2) values which would otherwise normally track the values of the other variables in a time series; and 3) values for observables which would normally follow a qualitatively predictable spatial or temporal pattern.

Examination of spatial and temporal distributions of atmospheric constituents and relative abundances of certain chemical species is a useful prelude to receptor modeling. When coupled with a conceptual understanding of the emissions sources, meteorology, and chemical transformation mechanisms, this receptor-oriented analysis provides qualitative, and even semi-quantitative, evidence of relationships between source emissions and receptor mixing ratios. This section examines the spatial and temporal distributions of ambient hydrocarbons in the South Coast Air Basin area.

Although Level 2 data validation was not required for this project, Dr. Eric Fujita performed this validation for the Coordinating Research Council (CRC)-funded project "Determination of Mobile Source Emission Source Fraction Using Ambient Field Measurements" (Fujita, 1997). The following sections are adapted from this report.

5.1 Statistical Summary

DRI made speciated hydrocarbon and carbonyl measurements at downtown Los Angeles, Burbank and Azusa during the summer of 1995 as part of a CARB-sponsored study that examined the air quality impacts of the introduction of California Phase 2 reformulated gasoline. Samples were collected twice a day (0700-1000 and 1400-1700 PDT) for six seven-day periods (July 8–14 and 17–23, August 1–7, August 31–September 6, September 9–15 and 24–30) for a total of 252 samples.

Table 5-1 presents averages, standard deviations, and maximum mixing ratios for the 25 most abundant hydrocarbon species for the samples collected by DRI for the CARB study. Averages are shown separately for morning and afternoon samples and include samples for all six seven-day periods during the summer of 1995. The ten most abundant hydrocarbons were toluene, isopentane, n-propane, m,p-xylene, ethane, acetylene, ethylene, n-butane, n-pentane and 2-methylpentane. The average morning NMHC mixing ratios were 567 ppbC at Azusa, 744 ppbC at Burbank and 676 ppbC at Los Angeles (N. Main). The corresponding average afternoon mixing ratios were 311, 337 and 348 ppbC, respectively. On average, the 25 most abundant species accounted for approximately 70% of the total NMHC at all three sites for both morning and afternoon samples. MTBE accounted for about 5% of the total NMHC on a ppbC basis and was comparable to isopentane in relative abundance. Figure 5-1 shows a plot of the average mixing ratios of the 25 most abundant species. The similarity among the three sites in the relative mixing ratios of the major hydrocarbon species is readily apparent and indicates a common source of ambient hydrocarbons at the three sampling sites.

5.2 Correlations Between Species

Comparisons of co-pollutants are important Level 2 validation checks for determining the overall accuracy and validity of the measurements. Species emitted from the same source type should correlate in the absence of other significant sources of these species, and exhibit average ratios of species that reflect the nature of the source or their relative persistence in the atmosphere. For example, hydrocarbons such as ethylene and acetylene are produced from combustion of hydrocarbon fuels in internal combustion engines. The main source of methyl-tert-butyl ether (MTBE) is gasoline, in either evaporative or tailpipe emissions. The thermal breakdown of MTBE in internal combustion engines produces isobutylene. Toluene is a major constituent of gasoline and vehicle exhaust and is a component of surface coatings and industrial solvents.

Figures 5-2 and 5-3 show scatterplots of acetylene and benzene versus carbon monoxide for all of the CARB Study samples. These three compounds should correlate with each other since they are associated primarily with vehicle exhaust and are inert to chemical transformation in the atmosphere. The morning samples from Azusa and Los Angeles (North Main), in particular, show excellent correlations. While slopes for the same correlations of the Burbank samples are similar to those of the other two sites, the correlations are not as good. Because the correlations between benzene and acetylene are generally very good, there are probably other sources of CO near the site. With the exception of some outliers, the correlation of the afternoon samples is generally good and they have slopes that are similar to those of the morning samples. The fact that afternoon mixing ratios are consistently lower than corresponding morning mixing ratios for all species satisfies a consistency check as mixing ratios decrease from morning to afternoon due to increasing mixing depths.

Table 5-1. Statistical Summaries for the 25 Most Abundant Species (ppbC) at the Three ARB Sites — Azusa

Morning				Afternoon				All day			
Species	Avg.	Std.	Max.	Species	Avg.	Std.	Max.	Species	Avg.	Std.	Max.
	(42 samples)				(42 samples)				(84 samples)		
NMHC	567.2	229.3	1280.2	NMHC	310.6	102.4	573.6	NMHC	438.9	219.1	1280.2
UNID	77.5	37.6	192.3	UNID	55.7	25.4	114.2	UNID	66.6	33.9	192.3
TOLUE	42.9	17.4	80.1	TOLUE	23.5	9.6	51.8	TOLUE	33.2	17.1	80.1
N_PROP	39.5	24.7	140.3	IPENTA	23.1	9.0	47.4	IPENTA	30.0	14.2	69.6
IPENTA	37.0	15.1	69.6	N_PROP	20.3	7.8	33.8	N_PROP	29.9	20.7	140.3
MP_XYL	25.0	11.3	55.7	ETHANE	13.8	4.8	23.2	ETHANE	18.6	8.6	41.5
ETHANE	23.5	8.9	41.5	N_BUTA	12.6	4.8	21.7	MP_XYL	17.1	11.5	55.7
N_PENT	22.3	12.1	54.7	ACETYL	12.1	5.1	30.1	N_PENT	16.9	10.6	54.7
ACETYL	20.1	8.3	37.8	N_PENT	11.5	4.2	23.9	ACETYL	16.1	8.0	37.8
ETHENE	18.6	7.5	34.6	BZ124M	10.1	11.7	82.4	N_BUTA	14.8	6.7	47.6
N_BUTA	16.9	7.7	47.6	PENA2M	9.9	3.4	22.8	BZ124M	13.5	10.5	82.4
BZ124M	16.9	8.0	55.6	MP_XYL	9.3	3.9	20.0	PENA2M	13.4	6.1	30.9
PENA2M	16.9	6.1	30.9	ETHENE	8.1	2.8	14.0	ETHENE	13.3	7.7	34.6
BENZE	13.3	5.2	25.1	BENZE	8.0	2.4	14.4	BENZE	10.7	4.8	25.1
MCYPNA	10.5	4.2	20.4	I_BUTA	7.0	3.0	14.9	I_BUTA	8.5	4.2	27.4
I_BUTA	10.0	4.6	27.4	MCYPNA	5.3	2.0	13.0	MCYPNA	7.9	4.2	20.4
N_HEX	9.5	4.1	19.2	N_HEX	5.1	1.8	10.9	N_HEX	7.3	3.9	19.2
PA224M	9.1	3.7	17.8	PENA3M	5.1	1.7	11.5	PENA3M	7.1	3.3	17.1
PENA3M	9.0	3.4	17.1	HEXA3M	4.9	1.9	10.1	PA224M	7.0	3.6	17.8
O_XYL	8.9	4.0	20.6	PA224M	4.8	1.7	10.0	HEXA3M	6.6	3.0	14.8
HEXA3M	8.2	3.0	14.8	O_XYL	3.8	1.4	7.8	O_XYL	6.3	3.9	20.6
PROPE	7.5	3.1	14.3	MECYH	3.6	1.9	9.9	MECYH	5.4	3.3	19.6
MECYH	7.2	3.5	19.6	HEXA2M	3.5	1.5	7.6	ETBZ	5.0	2.9	16.2
ETBZ	6.7	3.1	16.2	N_HEPT	3.4	1.9	9.7	HEXA2M	5.0	2.6	12.7
HEXA2M	6.4	2.7	12.7	ETBZ	3.3	1.3	7.2	PROPE	4.8	3.5	14.3
STYR	5.9	4.7	22.1	PEN23M	2.8	1.2	6.1	N_HEPT	4.6	2.5	12.6

Table 5-1. Statistical Summaries for the 25 Most Abundant Species (ppbC) at the Three ARB Sites — Burbank

Morning				Afternoon				All day			
Species	Avg. (42 samples)	Std.	Max.	Species	Avg. (42 samples)	Std.	Max.	Species	Avg. (84 samples)	Std.	Max.
NMHC	743.6	264.0	1312.2	NMHC	337.2	111.9	684.8	NMHC	540.4	287.0	1312.2
UNID	85.8	39.1	224.4	UNID	60.5	31.9	193.7	UNID	73.1	37.8	224.4
TOLUE	59.6	27.2	137.1	N_PROP	28.9	21.5	93.2	TOLUE	42.7	27.3	137.1
IPENTA	50.5	21.7	96.2	TOLUE	25.7	13.2	78.8	IPENTA	37.1	21.4	96.2
N_PROP	42.0	15.1	90.8	IPENTA	23.7	9.4	54.3	N_PROP	35.5	19.7	93.2
ETHANE	41.0	15.6	74.6	ETHANE	13.8	5.2	25.3	ETHANE	27.4	17.9	74.6
MP_XYL	36.3	15.6	68.8	MP_XYL	13.6	5.9	36.0	MP_XYL	25.0	16.4	68.8
ACETYL	28.2	10.8	49.2	N_BUTA	13.6	5.3	27.5	ACETYL	19.9	11.8	49.2
ETHENE	25.2	9.4	43.4	ACETYL	11.6	4.9	25.7	N_BUTA	17.0	7.3	46.0
N_PENT	22.8	10.4	46.3	N_PENT	10.7	4.2	23.8	ETHENE	16.8	10.9	43.4
PENA2M	22.7	8.7	39.5	PENA2M	10.4	3.6	21.6	N_PENT	16.8	10.0	46.3
N_BUTA	20.4	7.3	46.0	ETHENE	8.4	3.0	17.9	PENA2M	16.6	9.1	39.5
BENZE	17.9	7.1	32.1	BENZE	7.6	2.7	16.7	BENZE	12.7	7.4	32.1
BZ124M	16.8	10.4	74.6	N_HEX	7.0	3.9	15.9	BZ124M	11.5	9.4	74.6
N_HEX	14.7	6.6	41.2	I_BUTA	6.3	2.7	13.8	N_HEX	10.9	6.7	41.2
MCYPNA	14.6	6.2	26.6	BZ124M	6.2	3.0	18.8	MCYPNA	10.0	6.6	26.6
PA224M	13.9	5.3	26.9	PA224M	6.1	2.0	11.7	PA224M	10.0	5.6	26.9
PENA3M	13.2	5.1	23.4	PENA3M	5.7	2.2	11.4	PENA3M	9.5	5.4	23.4
O_XYL	12.8	5.4	24.5	MCYPNA	5.5	2.7	12.5	O_XYL	8.8	5.7	24.5
I_BUTA	11.3	4.0	21.4	MECYH	5.4	3.8	18.8	I_BUTA	8.8	4.3	21.4
MECYH	10.3	5.4	33.3	HEXA3M	5.1	1.8	10.7	MECYH	7.9	5.3	33.3
PROPE	10.3	4.0	17.8	O_XYL	4.9	1.9	12.5	HEXA3M	7.7	4.1	18.2
HEXA3M	10.3	4.1	18.2	ETBZ	4.1	1.9	10.5	ETBZ	6.7	4.0	17.5
ETBZ	9.3	4.0	17.5	N_HEPT	4.0	2.1	12.0	PROPE	6.5	4.8	17.8
PEN23M	8.7	3.7	17.3	PEN23M	3.8	1.3	7.7	PEN23M	6.3	3.7	17.3
HEXA2M	8.6	3.7	16.2	HEXA2M	3.7	1.4	7.1	HEXA2M	6.2	3.7	16.2
N_HEPT	8.0	3.3	17.5	MTBE	2.7	1.1	6.5	N_HEPT	6.0	3.4	17.5

Table 5-1. Statistical Summaries for the 25 Most Abundant Species (ppbC) at the Three ARB Sites — Los Angeles (N. Main)

Morning				Afternoon				All day			
Species	Avg. (42 samples)	Std.	Max.	Species	Avg. (42 samples)	Std.	Max.	Species	Avg. (84 samples)	Std.	Max.
NMHC	676.1	274.2	1313.2	NMHC	348.3	92.2	524.2	NMHC	512.2	262.1	1313.2
UNID	84.9	45.0	241.9	UNID	66.9	33.0	170.0	UNID	75.9	40.5	241.9
TOLUE	50.6	21.8	102.3	IPENTA	28.6	15.8	94.9	TOLUE	37.7	20.8	102.3
IPENTA	42.3	18.1	91.5	TOLUE	24.8	7.5	46.8	IPENTA	35.5	18.3	94.9
N_PROP	35.2	15.6	81.8	N_PROP	17.9	7.4	41.3	N_PROP	26.6	15.0	81.8
MP_XYL	34.0	14.6	65.3	ETHANE	17.3	7.2	40.0	ETHANE	24.6	13.2	69.2
ETHANE	31.9	13.8	69.2	MP_XYL	14.1	3.7	21.8	MP_XYL	24.0	14.6	65.3
ACETYL	26.8	11.3	53.8	N_PENT	13.2	6.0	36.7	ACETYL	19.7	11.1	53.8
ETHENE	25.3	9.9	47.0	N_BUTA	13.0	5.5	32.1	ETHENE	18.0	10.4	47.0
N_PENT	21.7	10.3	55.9	ACETYL	12.6	4.3	24.6	N_PENT	17.5	9.4	55.9
PENA2M	19.9	8.0	41.3	ETHENE	10.8	3.7	20.9	N_BUTA	16.1	8.2	57.3
N_BUTA	19.2	9.2	57.3	PENA2M	10.4	2.8	15.6	PENA2M	15.2	7.6	41.3
BENZE	17.1	6.9	33.1	BZ124M	8.8	3.0	17.1	BENZE	12.7	6.7	33.1
BZ124M	15.7	5.1	25.3	I_BUTA	8.6	8.2	55.7	BZ124M	12.2	5.4	25.3
MCYPNA	13.3	5.7	27.7	BENZE	8.3	1.9	13.0	MCYPNA	9.8	5.5	27.7
O_XYL	11.9	5.1	22.6	MCYPNA	6.4	1.6	10.2	I_BUTA	9.5	6.7	55.7
PA224M	11.6	5.0	23.4	PENA3M	5.6	1.4	8.6	O_XYL	8.5	5.0	22.6
PENA3M	11.1	4.6	22.5	N_HEX	5.6	1.7	10.2	PA224M	8.5	4.7	23.4
N_HEX	10.8	4.5	22.6	PA224M	5.5	1.3	8.5	PENA3M	8.3	4.4	22.5
PROPE	10.5	4.1	19.1	HEXA3M	5.3	1.7	13.2	N_HEX	8.2	4.3	22.6
I_BUTA	10.4	4.5	25.1	O_XYL	5.1	1.2	8.0	HEXA3M	7.3	3.6	20.2
HEXA3M	9.3	3.8	20.2	PROPE	4.0	1.3	8.2	PROPE	7.3	4.5	19.1
ETBZ	8.6	3.6	16.8	ETBZ	4.0	1.0	6.7	ETBZ	6.3	3.5	16.8
MECYH	8.6	3.7	16.7	MECYH	3.8	1.2	6.4	MECYH	6.2	3.7	16.7
HEXA2M	7.8	3.4	16.4	HEXA2M	3.7	1.0	6.7	HEXA2M	5.8	3.2	16.4
LIBUTE	7.2	3.2	14.0	PEN23M	3.4	0.9	5.5	PEN23M	5.2	2.9	15.1
PEN23M	6.9	3.1	15.1	STYR	3.2	1.4	7.2	LIBUTE	5.1	3.2	14.0

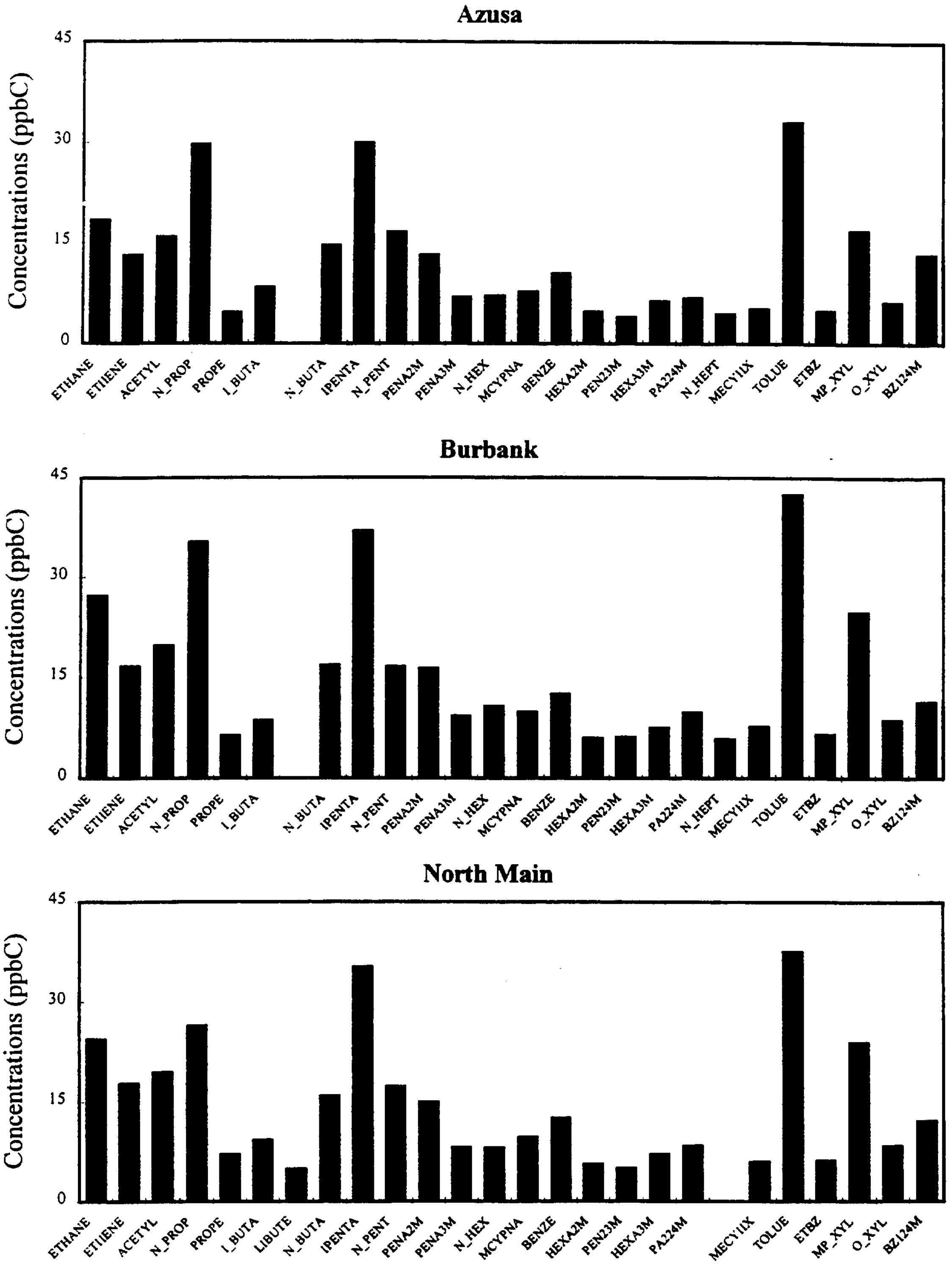


Figure 5-1. Average concentrations for 25 most abundant species at three LA sites (averaged for all morning and afternoon samples).

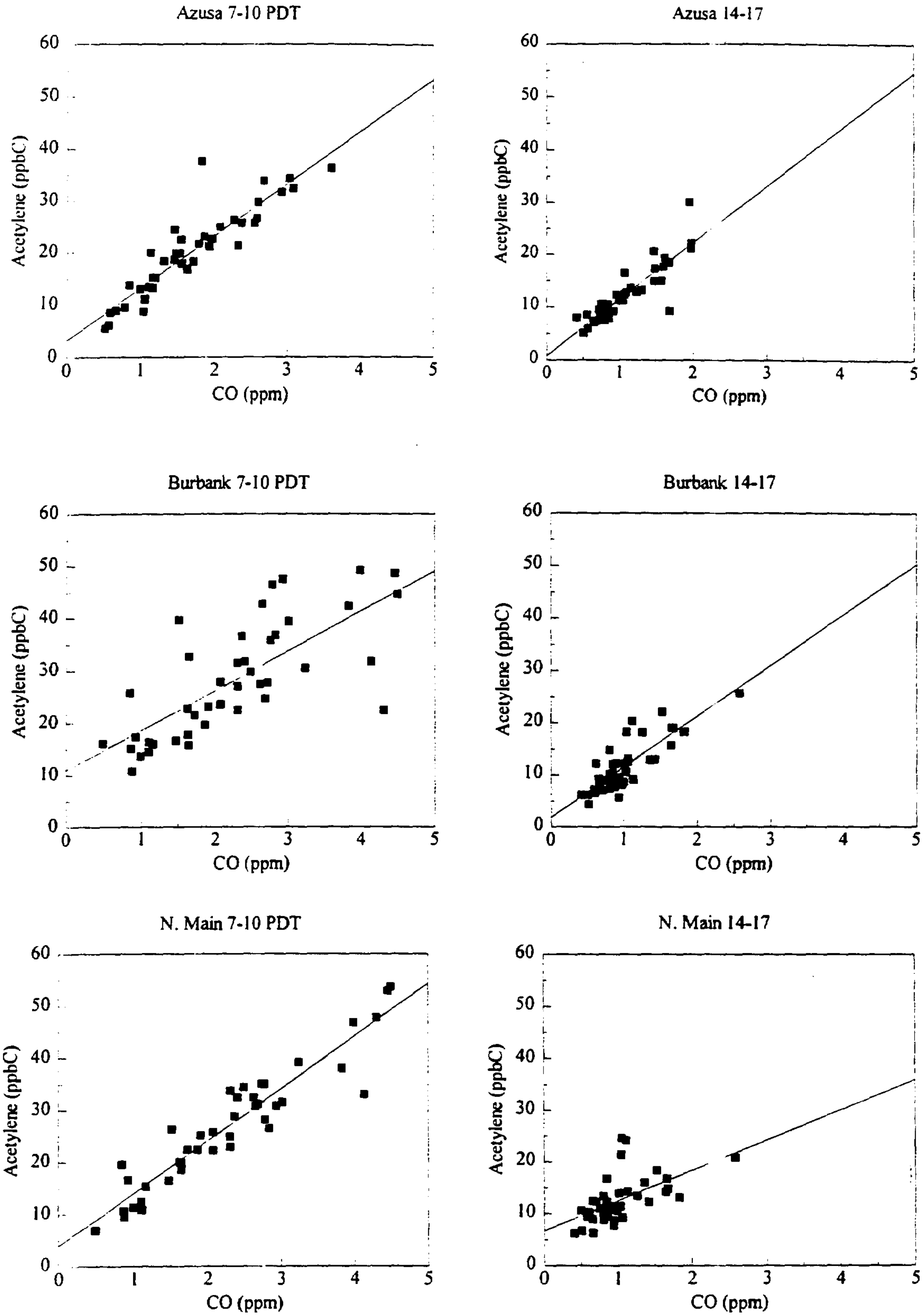


Figure 5-2. Scatterplots of acetylene versus carbon monoxide for SoCAB samples

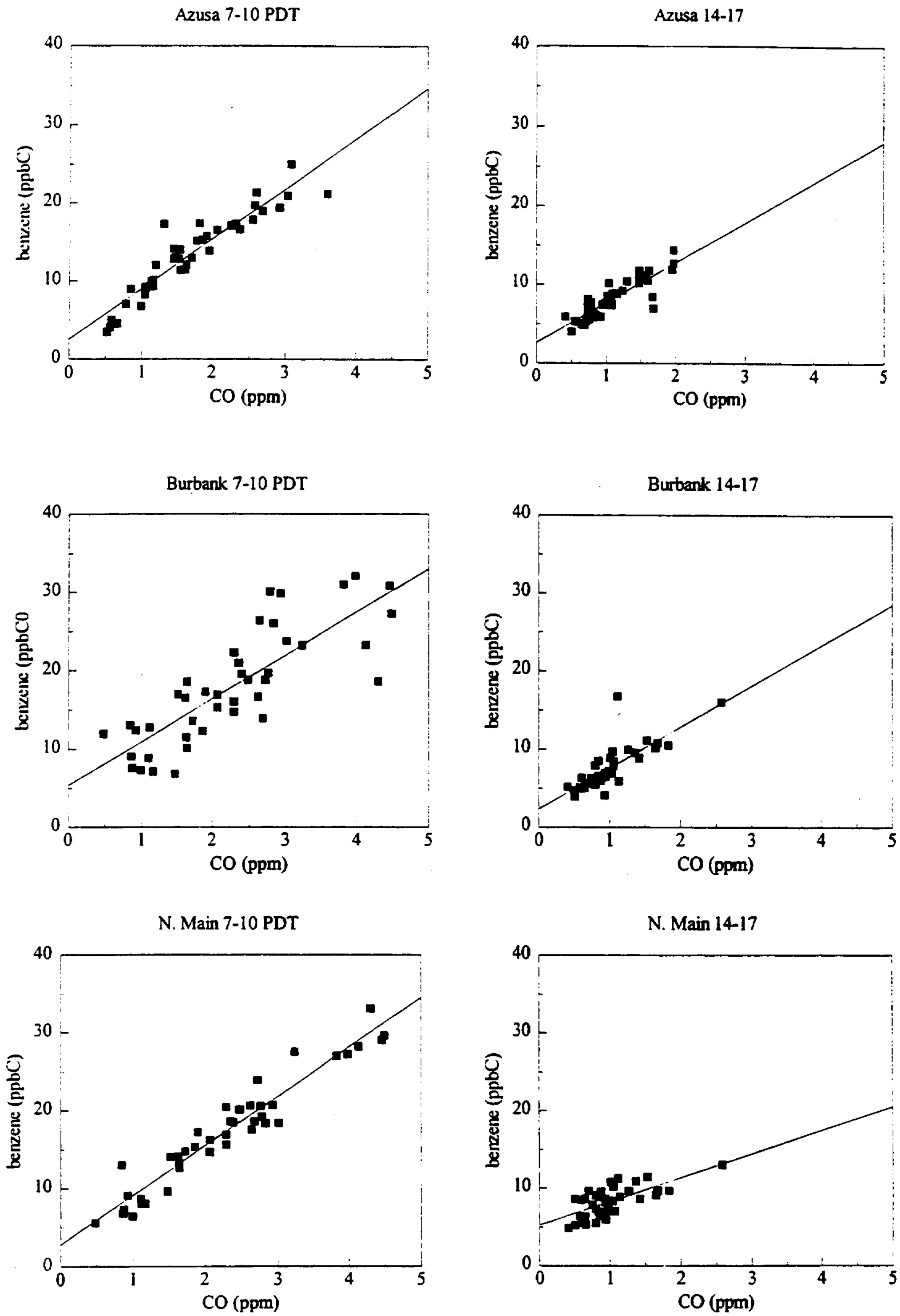


Figure 5-3. Scatterplots of benzene versus carbon monoxide for SoCAB

Figure 5-4 shows scatterplots of acetylene versus ethylene. As expected, these two species show excellent correlation at all three sites. The ratios of ethylene to acetylene for the morning samples are 0.89, 0.85 and 0.87 at Azusa, Burbank and Los Angeles, respectively. The corresponding ratios for the afternoon samples are lower at Azusa and Burbank (0.51 and 0.59, respectively), which are both downwind of downtown Los Angeles. The downtown site is located in the western part of the basin where onshore breezes tend to maintain a nearly constant ethylene to acetylene ratio (0.82).

Figures 5-5, 5-6, and 5-7 show correlations of acetylene versus n-butane, acetylene versus toluene and MTBE versus isobutylene, respectively. Acetylene is generally well correlated with both n-butane and toluene at all three sites. The n-butane/acetylene ratios are much higher in the afternoon than during the morning, which may be due to higher contributions of evaporative emissions during the afternoon period. This could also explain the lower isobutylene/MTBE ratios in the afternoon relative to morning ratios since isobutylene is found in tailpipe emissions, while MTBE is found in both tailpipe and evaporative emissions. Another explanation for the lower isobutylene/MTBE ratios is the greater reactivity of isobutylene relative to MTBE. This could account for the higher isobutylene/MTBE ratios at downtown Los Angeles compared to the same ratios at Azusa and Burbank, as in the case of the ethylene/acetylene ratios.

5.3 Temporal and Spatial Variations

The morning and afternoon NMHC mixing ratios for the six seven-day periods are plotted in Figure 5-8. These diurnal patterns are consistent with the prevailing meteorology and the diurnal pattern of emissions. Mixing ratios are highest during the morning because of the combination of high emission rates from the morning traffic and low mixing heights that occur at this time of day. Mixing ratios decrease over the course of the day because wind speeds and mixing heights increase during the daylight hours, while emissions are relatively constant. Mixing ratios typically increase after 1700 hrs because of the increased evening traffic and lowering of mixing heights. Figure 5-8 shows that the morning and afternoon NMHC mixing ratios at each site generally track each other despite large day-to-day variations caused by changes in meteorological conditions. Additionally, NMHC mixing ratios show similar time-series patterns at the three sites. Figure 5-9 shows the time-series plot of carbon monoxide and MTBE. The two time series are virtually identical, indicating that the two species are from the same source. These time series are consistent with our understanding of the physical relationship between emissions, meteorological conditions and resulting spatial and temporal variations in ambient concentration.

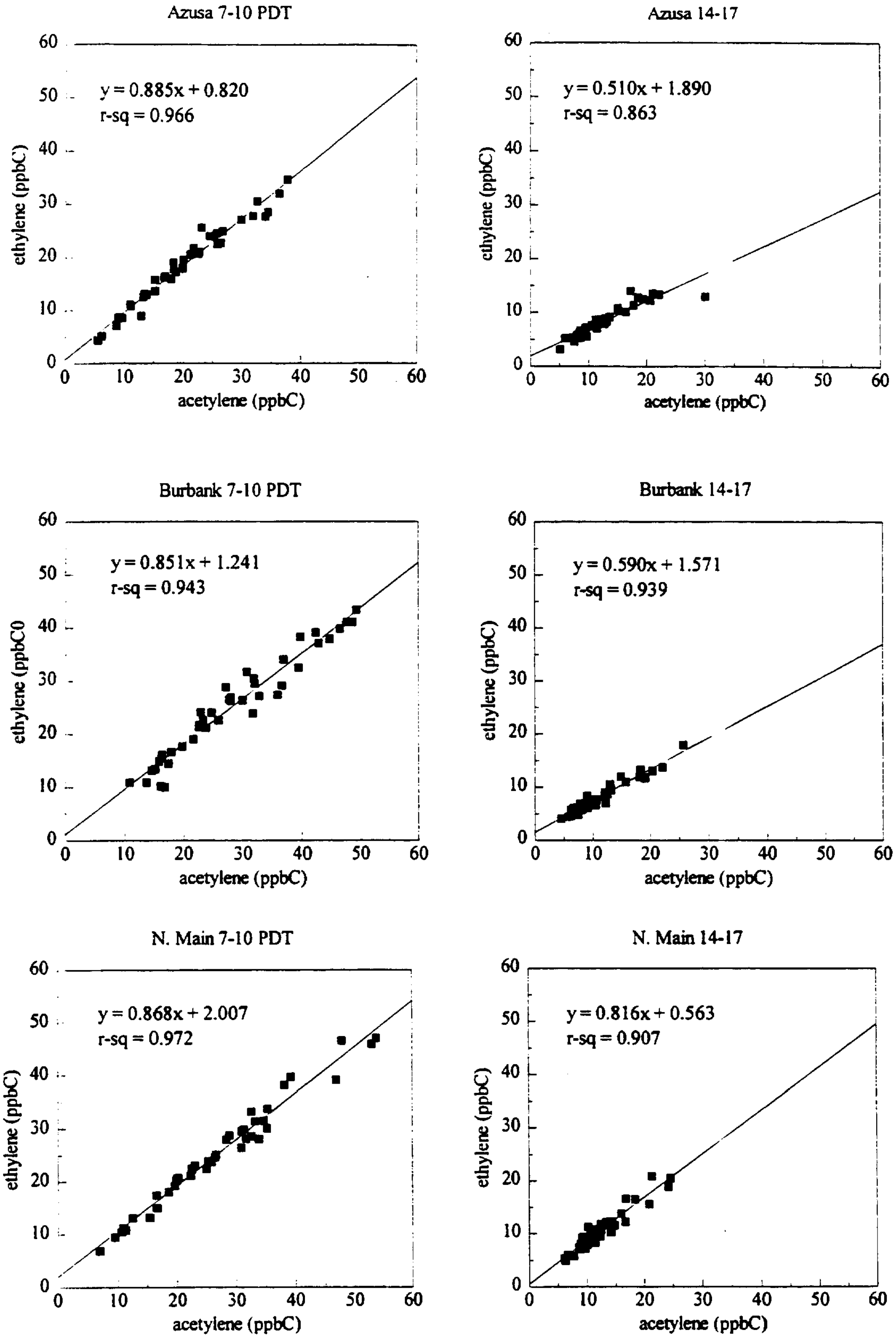


Figure 5-4. Scatterplots of ethylene versus acetylene for SoCAB samples.

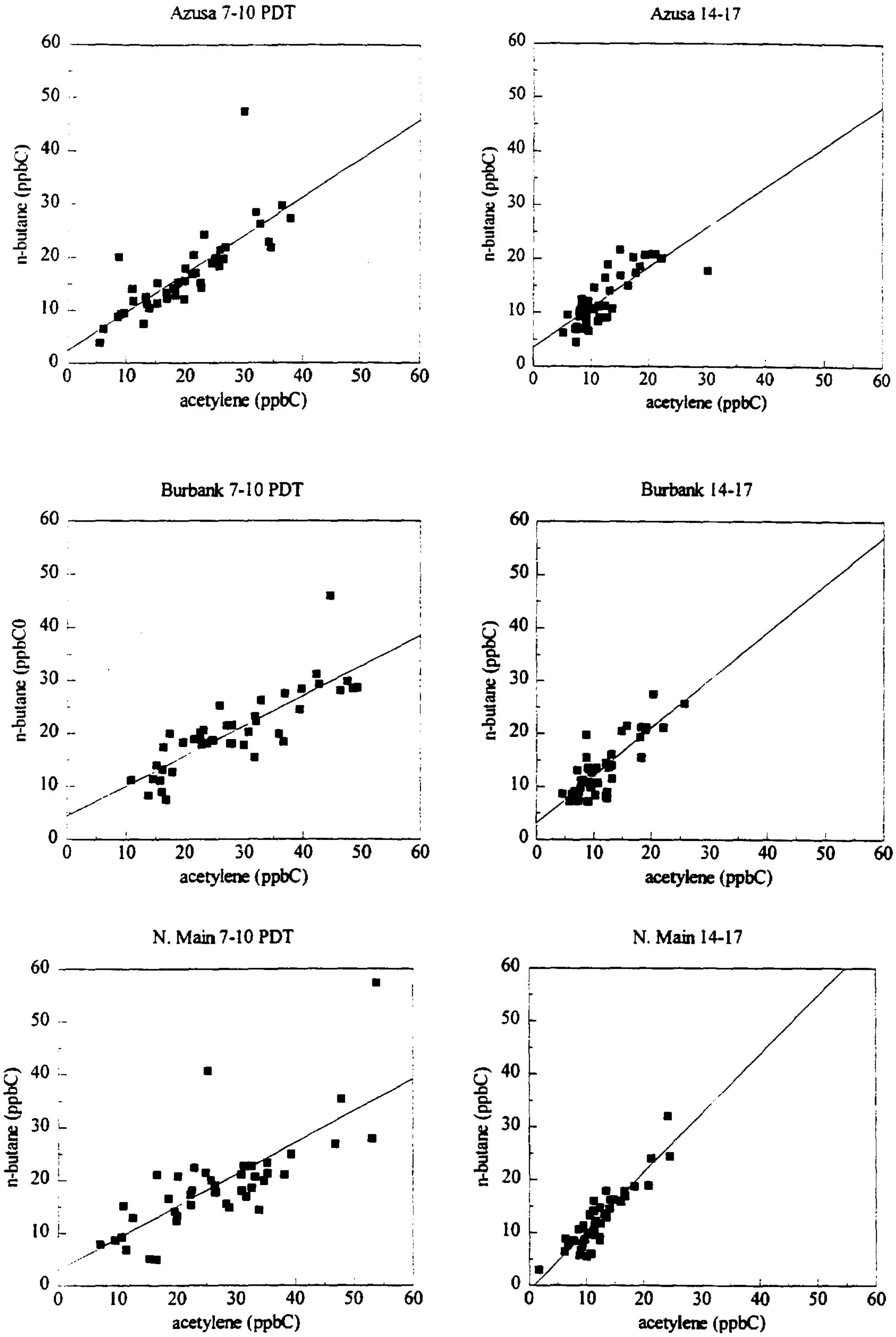


Figure 5-5. Scatterplots of n-butane versus acetylene for SoCAB samples.

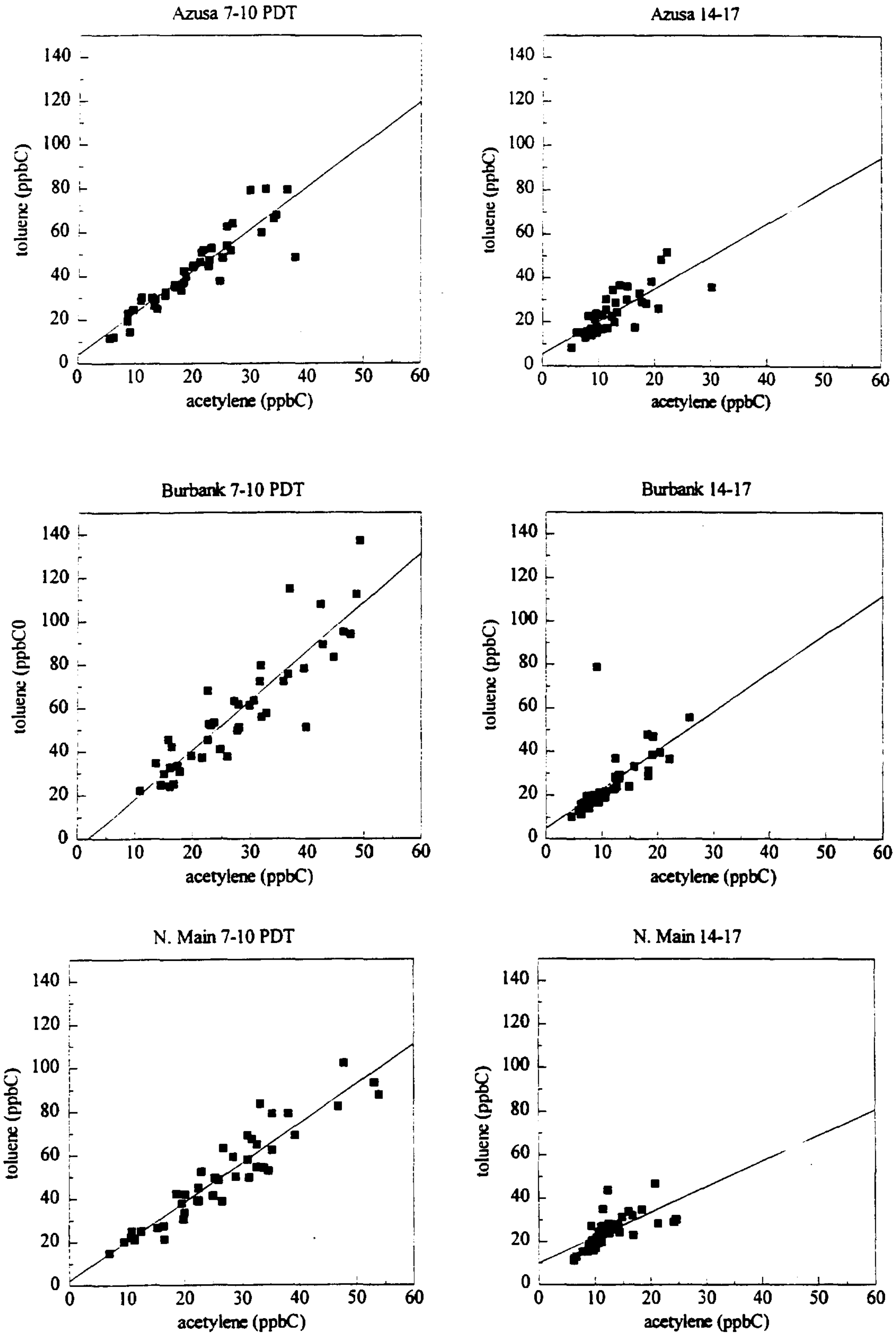


Figure 5-6. Scatterplots of toluene versus acetylene for SoCAB samples.

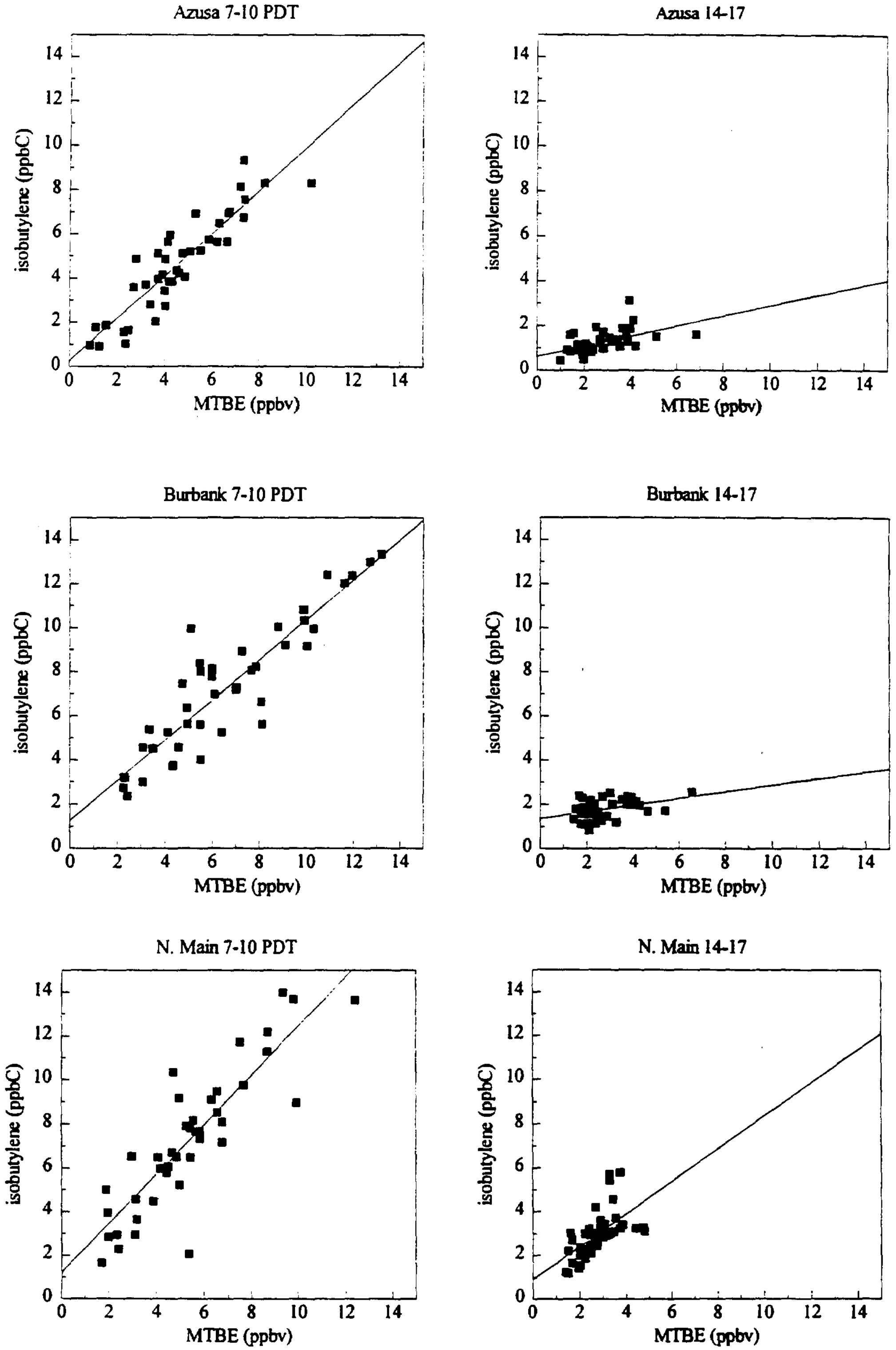
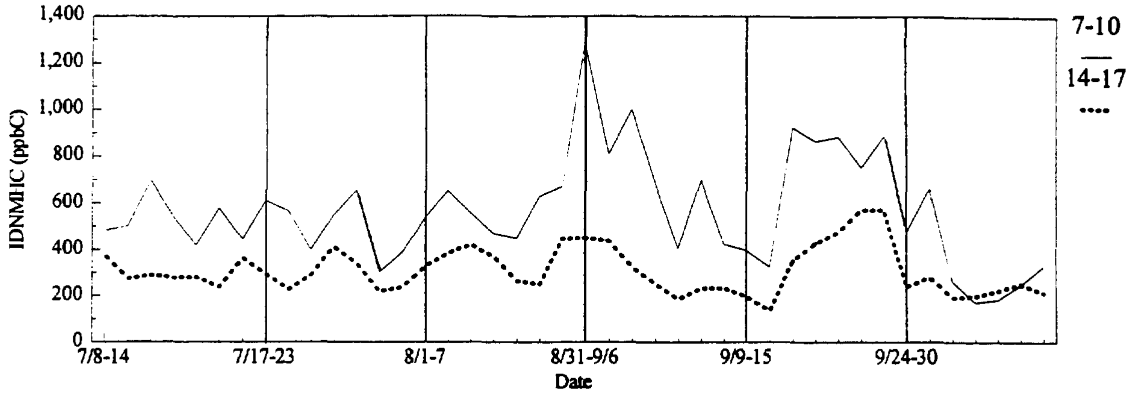
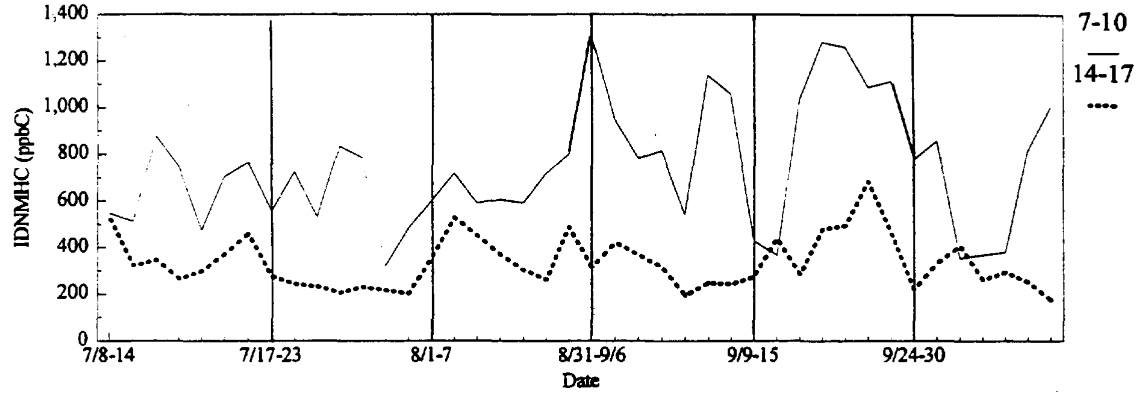


Figure 5-7. Scatterplots of isobutylene versus MTBE for SoCAB samples.

Azusa



Burbank



Los Angeles N. Main

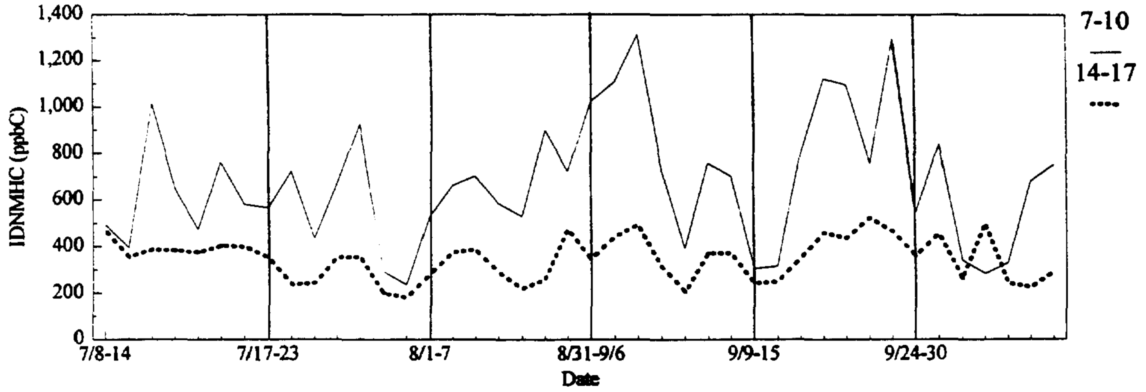
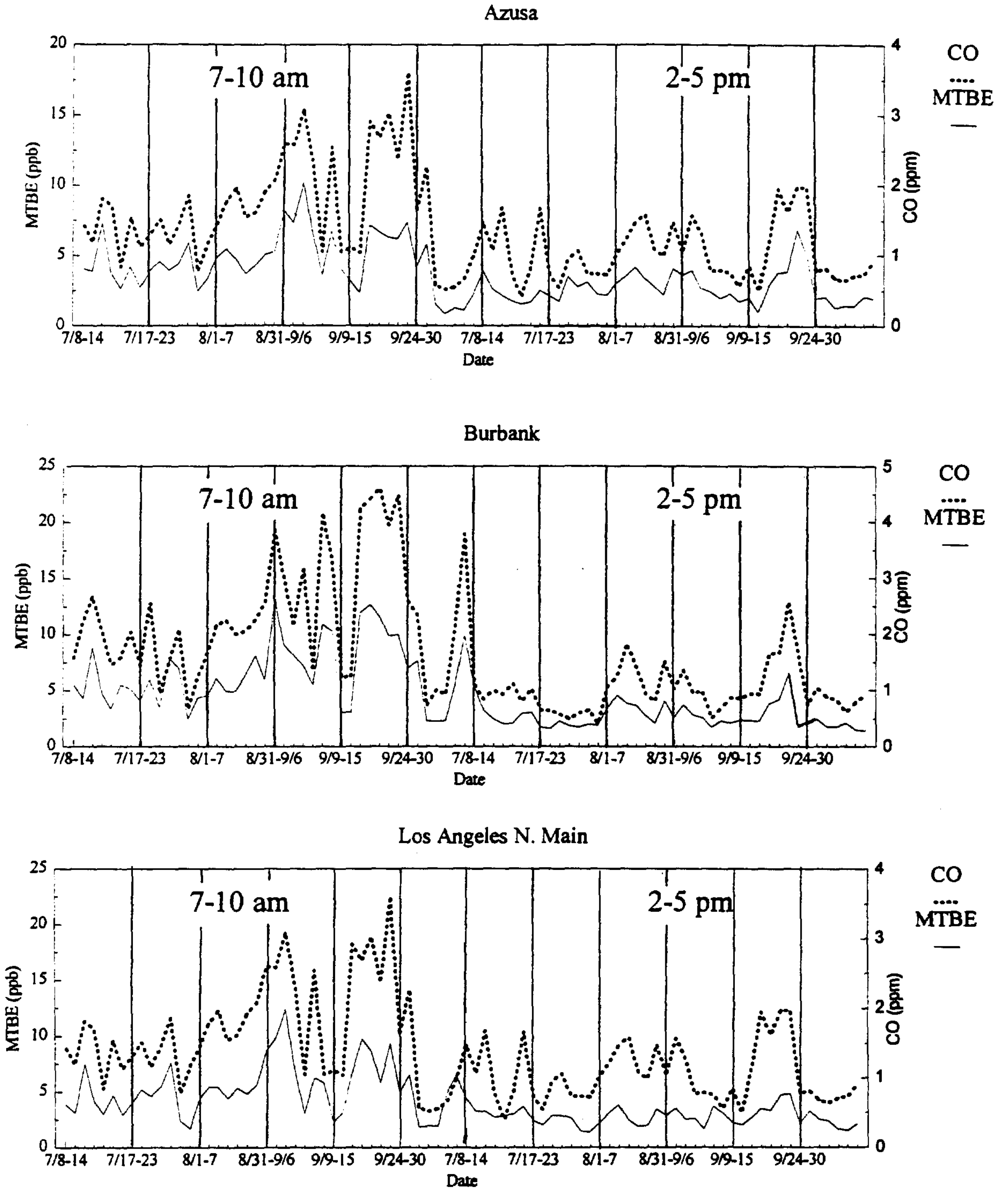


Figure 5-8. Time series plots of total NMHC for SoCAB samples.



Azusa

Burbank

Los Angeles N. Main

Figure 5-9. Time series plots of carbon monoxide and MTBE for SoCAB samples.

6.0 1997 SOUTHERN CALIFORNIA OZONE STUDY (SCOS97)

The $7+ million 1997 Southern California Ozone Study (SCOS97) was conducted in coordination with the North American Research Strategy for Tropospheric Ozone (NARSTO). The SCOS97 brought together a large number of interested governmental entities as stakeholders, and benefited from consultation and cooperation with the atmospheric sciences academic community. The resultant modeling and data analyses will be used to design ozone attainment strategies and to resolve intra-regional air pollution transport issues.

This study featured the most comprehensive network of instruments ever assembled to measure both ground level and upper air meteorological and air quality data. In addition to enhancing the existing surface monitoring network with more locations and additional measurements, sophisticated technologies were used to gather important data. The study, which included aerosol, solar radiation, and trace compound measurements, featured a vast array of remote sensing instruments using radio and light waves to measure weather and air quality conditions above ground level. More traditional but less commonly used methods included aircraft and balloons to gather critical information about conditions aloft.

The data collected during SCOS97 will be used in modeling and data analyses to provide the most definitive answers yet to solving the persistent air quality problems in a complex region. Analysis of these data will improve the current emission control plans to attain existing ambient air quality standards and will also help design technically defensible plans for the new national standards for 24-hour-average $PM_{2.5}$ and 8-hour-average ozone. The cooperation of the study sponsors and supporters in integrating and piggybacking projects made it possible to leverage the available public funds for maximum scientific benefit.

6.1 Ambient Sampling Sites and Schedule

Table 6-1 shows SCOS97 sampling sites and sampling schedule employed in each site.

6.2 Ambient Air Sampling Procedures

Volatile organic compounds (in the range of $C_2 - C_{12}$) were collected using stainless-steel polished canisters, as described in Section 2.3.1, above. Carbonyl compounds were collected using C_{18} Sep-Pak cartridges (Waters Associates, Milford, MA) which have been impregnated with purified acidified 2,4-dinitrophenylhydrazine (DNPH), as described in Section 2.3.2. DNPH-impregnated C_{18} SepPack cartridges were prepared and analyzed by the DRI Organic Analytical Laboratory.

During the Caldecott Tunnel experiment, in addition to canister and carbonyl samples, semi-volatile organic compounds (SVOC) were collected using the DRI-constructed Sequential Fine Particulate/Semi-Volatile Organic Compounds Sampler (PSVOC sampler). Figures 6-1 and 6-2 show the PSVOC sampler. This is a multiple-event sampler which allows unattended collection of up to four samples. The air sample is drawn through a cyclone separator with a cut-off diameter of 2.5 µm, operating at 113 lpm. Downstream of the cyclone, a ½-inch copper manifold leads to four momentum diffuser chambers. Each chamber is followed by a filter/PUF/XAD/PUF/filter cartridge holder and is connected to a vacuum pump through a solenoid valve, a ball valve, and a flow controller. When one of the solenoid valves is opened

Table 6-1. SCOS97 Sampling Sites and Schedules

Sampling Site	Sampling Dates	Sampling Time	Comments
Anaheim	8/04-8/06; 8/22-8/23; 9/04-9/06; 9/28-9/29; 10/03-10/04	0600-0900	
Barstow	7/14; 8/04-8/06; 8/22-8/23; 9/04-9/06; 10/03-10-04	0200-0500, 0800-1100, 1200-1500, 1600-1900 and 2000-2300 each sampling day	Carbonyls only
Burbank	8/04-8/06; 8/22-8/23; 9/04-9/06; 9/28-9/29; 10/03-10/04	0600-0900 and 1300-1600 each sampling day	High acetone; high >C_{10} concentrations
Caldecott Tunnel	11/16-11/18	1200-1500 each sampling day	VOC, carbonyls and PAH
	11/19-11/20	1530-1830	
Catalina Island	8/04-8/06; 8/22-8/23; 9/04-9/06; 9/28-9/29; 10/03-10/04	0600-1800 and 1800-0600 each sampling day	
Mexicali	7/14	1500-1800	
	8/04-8/06; 8/22-8/23; 9/04-9/06; 9/28-9/29; 10/03-10/04	6000-9000 and 1500-1800 each sampling day	
Mount Baldy	9/28	1300-1600 and 1700-2000	As below for Pine Mountain
	9/29, 10/3-10/4	0300-0600, 0600-0900, 1300-1600, 1700-2000 and 2000-2300 each sampling day	
Pine Mountain	8/04	1700-2000 and 2030-2115	Comparison with UCR Tenax biogenic hydrocarbons
	8/05	0300-0530; 0600-0900; 0900-1130; 1700-2000	
	8/06	0300-0600; 0600-0900; 1300-1600	
	9/04	1700-2000; 2000-2400	
	9/05	0000-0330; 0345-0600; 0600-0900; 1300-1600; 1700-2000; 2000-0300	

Table 6-1. SCOS97 Sampling Sites and Schedules (cont.).

Sampling Site	Sampling Dates	Sampling Time	Comments
Pine Mountain (cont.)	9/06	0300-0600; 0600-0900; 1300-1600; 1700-2000; 2000-2400	
	9/07	0000-0300; 0300-0600; 0600-0900	
Point Conception	8/11-8-12; 8/22-8/23; 9/04-9/06; 9/28-9/29; 10/03-10/04	0600-1800 and 1800-0600 each sampling day	Late start (8/11/97)
San Nicholas Island	7/14	0600-0630, 1100-1800	
	8/04	1030-1748, and 1800-0600	
	8/05-8/06, 8/22-8/23, 9/04-9/06, 9/28-9/29, 10/03-10/04	0600-1800 and 1800-0600 each sampling day	
Tijuana-Rosarito	7/14; 8/04-8/06; 8/22-8/23; 9/04-9/06; 9/28-9/29; 10/03-10/04	1000-1300 and 1300-1600 each sampling day	

and three others are closed, the air stream enters only this one chamber which is connected to the pump. The sampling time is controlled by a four-channel Grasslin timer, which automatically opens and closes solenoid valves at the appropriate time. An independent elapsed time meter records the sampling time for each channel. The flow is set using a calibrated rotameter on the inlet side of the copper sampling line and is maintained at a constant 113 lpm during sampling by a flow controller.

Prior to sampling, all sampling media were cleaned in the laboratory. The Amberlite XAD-4 resin (20-60 mesh, purchased from Aldrich Chemical Company. Inc.) was Soxhlet extracted with methanol followed by dichloromethane (CH_2Cl_2), each for 8 hours. The cleaned resin was dried in a vacuum oven heated to 40 °C and stored in sealed glass containers in a clean freezer. The PUF plugs (purchased from ER Carpenter Company, Inc., Richmond, VA, and cut into 2" diameter plugs at DRI) were Soxhlet extracted with 10% diethyl ether in hexane, followed by acetone. The TIGF filters (Pallflex, Putnam, CT, T60A20, 102 mm diameter) were cleaned by sonification in CH_2Cl_2 for 30 minutes, followed by another 30-minute sonification in methanol. Then they were dried, placed in aluminum foil, and labeled. Each batch of precleaned XAD-4 resin and ~10% of precleaned TIGF filters and PUF plugs were checked for purity by solvent extraction and GC/MS analysis of the extracts. The PUF plugs and XAD-4 resins were assembled into glass cartridges (10 g of XAD between two PUF plugs), wrapped in aluminum foil and stored in a clean freezer prior to shipment to the field.

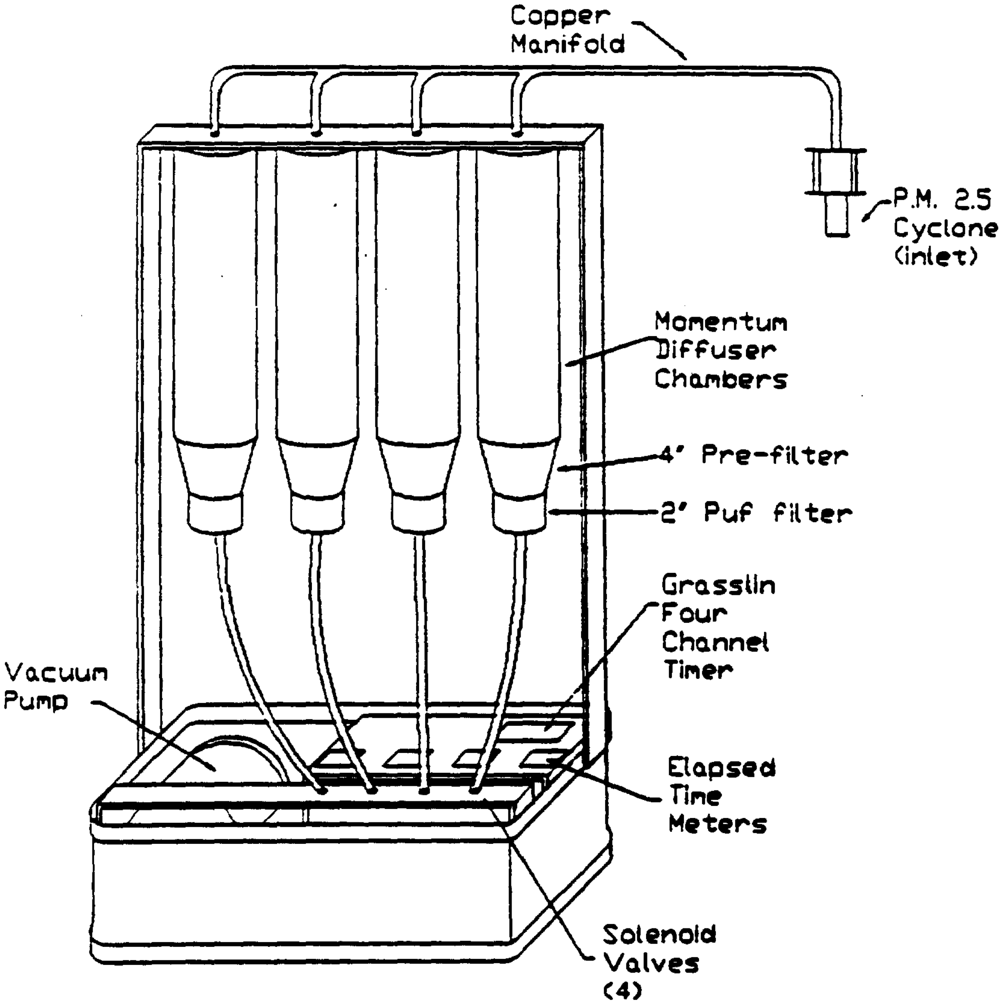


Figure 6-1. DRI Sequential Fine Particulate/Semi-Volatile Organic Compounds Sampler.

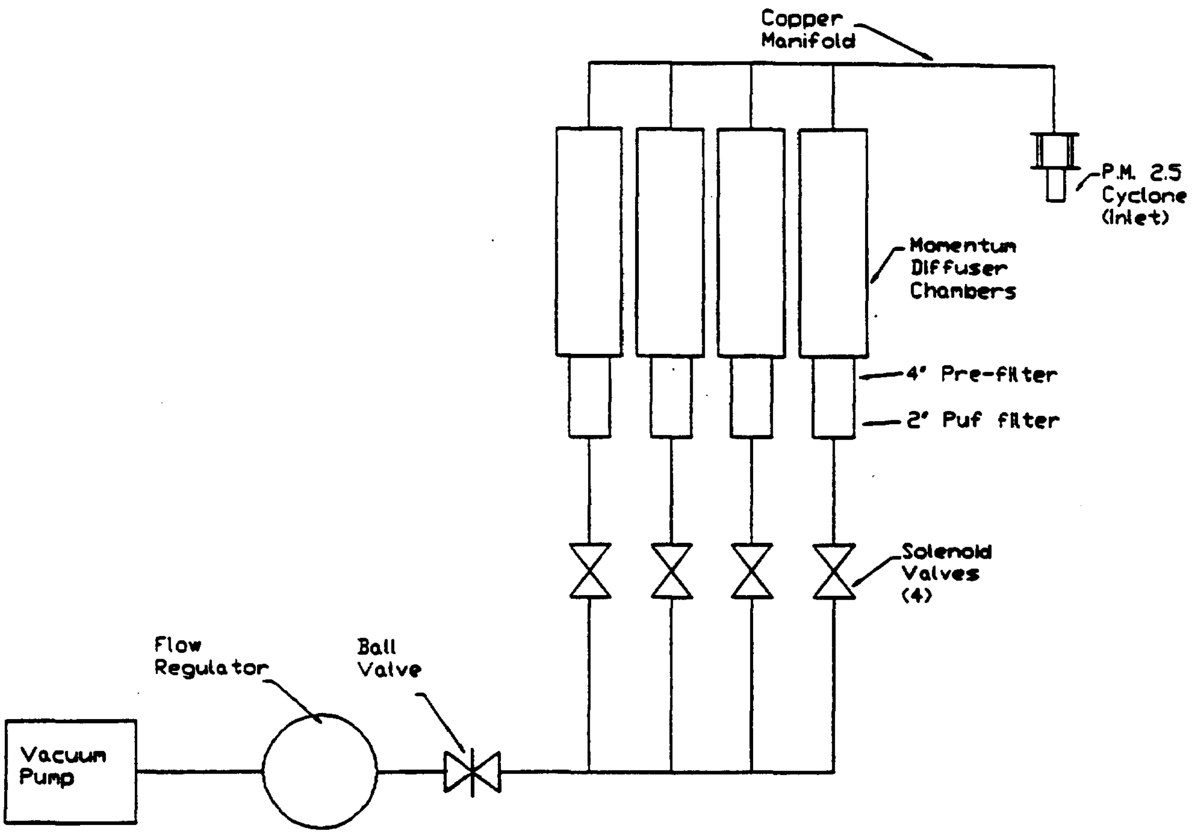


Figure 6-2. Schematic of the DRI Sequential Fine Particulate/Semi-Volatile Organic Compounds Sampler.

Table 6-2. List of Halogenated Compounds and Their Mnemonics Analyzed by GC/ECD Method

Compound	Mnemonic
Freon 12 (dichlorodifluoromethane)	F12
Methylbromide	MEBR
Freon 11 (trichlorofluoromethane)	F11
Vinylidenechloride	VINECL
Methylene chloride	MECL2
Freon 113 (1,1,2-trichloro-1,2,2-	F113
Trans-1,2-dichloroethylene	T12DCE
Cis-1,2,-dichloroethylene	C12DCE
Chloroform	CCL3
1,2-dichloroethane	ETDC12
Methyl chloroform	MECCL3
Carbon tetrachloride	CCL4
1,3-Dibromomethane	DBRME
Trichloroethylene	TCENE
1,1,2-Trichloroethane	TCE112
Chlorodibromomethane	CLDBRM
1,2-Dibromoethane	ETDB12
Perchloroethylene	PERC
m-Dichlorobenzene	MDCBZ
p-Dichlorobenzene	PDCBZ
o-Dichlorobenzene	ODCBZ

6.3 Analytical Procedures

Canister samples were analyzed for C_2-C_{12} hydrocarbons, $CO/CO_2/CH_4$ and MTBE by the methods described in Section 3.1 above. For the Mexican sites (Mexicali and Rosarito), the analysis for halogenated compounds was also performed by GC/ECD method (analogous to EPA TO-14 Method). Table 6-2 lists the compounds analyzed by this method.

Carbonyl Compounds. Each DNPH-impregnated cartridge after sampling was eluted slowly with 2 ml of HPLC-grade carbonyl-free acetonitrile. The eluted solutions were transferred into a vial with a PTFE lined septum and injected into the analytical column using an auto sampler for quantitation of hydrazones. Carbonyl identification and quantitation involve comparison with external standards, i.e., acetonitrile solutions of precisely weighed amounts of pure hydrazones synthesized in the DRI laboratory and those obtained from Radian's Standards Division. The HPLC response factors to formaldehyde or any other carbonyl hydrazone (at 360 nm wavelength) are calculated from absorbance vs. concentration plots for known standards. Multipoint calibration curves with a minimum of 3 concentration levels are established prior to sample analysis using carbonyls obtained from Radian's Standards Division. These calibrations are checked every 12 samples during the analysis of field samples. If a continuing calibration shows deviation of more than 10%, a full calibration of the instrument is performed and the cause of this calibration drift is investigated. Calibration standards for each parameter are chosen to bracket the expected concentrations of these parameters in the sample and to operate within the linear dynamic range of the instrument. Samples that fall outside the calibration range are diluted until bracketed by the calibration curve. Instrument responses to calibration standards for each parameter are analyzed using a least squares linear regression. The calibration must generate a correlation coefficient (R^2) of 0.99 to be acceptable. Typical calibration curves for carbonyl compounds (formaldehyde, acetaldehyde and acetone) are shown in the DRI SOP "Analysis of Carbonyl Compounds in Air Samples on DNPH-Impregnated Cartridges," which is available upon request.

Detection limits for air samples are determined either by the analytical detection limit or by the background carbonyl hydrazone content of the cartridges. DRI has found the latter to be the determining factor for formaldehyde, acetaldehyde and acetone. The ambient air detection limit for carbonyl compounds during one-hour sampling at 1.0 lpm would be in the range of 0.5-1 ppbv. A list of carbonyls analyzed by DRI along with their mnemonics and detection limits is given in Table 6-3.

Table 6-3. Detection Limits of Carbonyls.

Analyte	Mnemonic	Detection Limit (ppbv)	
		[a]	[b]
Formaldehyde	Formal	0.5	0.2
Acetaldehyde	Acetal	0.5	0.2
Acetone	Aceto	0.5	0.2
Methyl Ethyl Ketone (MEK)	MEK	0.5	0.2
Acrolein	Acroln	0.5	0.2
Acrolein X [c]	Acrolx	0.5	0.2
Methacrolein	Macrol	0.5	0.2
Propionaldehyde	Proal	0.5	0.2
Butyraldehyde	Butal	0.5	0.2
Crotonaldehyde	Croton	0.5	0.2
Benzaldehyde	Benzal	0.5	0.2
Tolualdehyde	Tolual	0.5	0.2
Valeraldehyde	Valal	0.5	0.2
Hexanaldehyde	Hexal	0.5	0.2
Glyoxal	Gloxl	0.5	0.2

[a] This detection limit is based on 60 liters of air sampled at 1.0 lpm through DNPH cartridge.

[b] This detection limit is based on 180 liters of air sampled at 1.0 lpm through DNPH cartridge.

[c] Acrolein X is a product of rearrangement of acrolein that occurs during sampling through acidified DNPH-impregnated cartridges.

Along with ambient samples, laboratory blanks and field blanks are analyzed. Laboratory blanks for carbonyls consists of a DNPH-coated silica gel cartridge followed by elution with 2 ml of carbonyl-free acetonitrile and analyzed in the same conditions as used for field samples. Field blanks are treated identically as actual samples, except that no air is sampled through the cartridges. Ten percent of all field samples will undergo duplicate analysis. A laboratory duplicate is an aliquot of a field sample taken through the entire analytical procedure. For aldehydes and ketones the laboratory duplicates are taken from the sample after extraction from the media.

PAH. All PUF/XAD/PUF/filter cartridges were analyzed as follows: prior to extraction, the following deuterated internal standards were added to each filter-sorbent pair: naphthalene-d_8, acenaphthylene-d_8, phenanthrene-d_{10}, anthracene-d_{10}, chrysene-d_{12}, fluoranthene-d_{10}, pyrene-d_{10}, benz[a]anthracene-d_{12}, benzo[e]pyrene-d_{12}, benzo[a]pyrene-d_{12}, benzo[k]fluoranthene-d-$_{12}$, coronene-d-$_{12}$, and benzo[g,h,i]perylene-d_{12}. Since PUF should not be extracted with dichloromethane, the PUF plugs were Soxhlet extracted separately with 10% diethyl ether in hexane, and the filter-XAD pairs were microwave extracted with dichloromethane; these extraction methods have been reported to yield a high recovery of PAH (Chuang et al., 1990) and other compounds of interest (Hawthorne et al., 1988, 1989).

The extracts were then concentrated by rotary evaporation at 20 °C under gentle vacuum to ~1 ml and filtered through 0.45 mm Acrodiscs (Gelman Scientific), with the sample flask rinsed twice with 1 ml CH_2Cl_2 each time. Approximately 100 µl of acetonitrile was added to the sample and CH_2Cl_2 was evaporated under a gentle stream of nitrogen. The final sample volume was adjusted to 1 ml with ACN. This procedure has been tested by Atkinson et al. (1988). The detailed procedure is described in the DRI SOP "Analysis of Semi-Volatile Organic Compounds by GC/MS," available on request.

The samples were analyzed by the EI (electron impact) GC/MS technique, using a Hewlett-Packard 5890 GC equipped with a 7673A Automatic Sampler and interfaced to a 5970B Mass Selective Detector (MSD) for PAH. Injections (1 µl) were made in the splitless mode onto a 60 m 5% phenylmethylsilicone fused-silica capillary column (DB-5ms, J&W Scientific). Quantification of the PAH was obtained by the multiple ion detection (MID, HP5970B MSD) technique, monitoring the molecular ion of each compound of interest and deuterated PAH, added prior to extraction as internal standards. Calibration curves for the GC/MS quantification were made for the molecular ion peaks of the PAH and all other compounds of interest using the corresponding deuterated species (or the deuterated species most closely matched in volatility and retention characteristics) as internal standards. National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 1647 (certified PAH) with the addition of deuterated internal standards and of those compounds not present in the SRM were used to make calibration solutions. A three-level calibration was performed for each compound of interest and the calibration check (using median calibration standards) was run every ten samples to check for accuracy of analyses. If the relative accuracy of measurement (defined as a percentage difference from the standard value) was less than 30%, the instrument was recalibrated. For quantification of these compounds, the deuterated PAH most closely matched in volatility and retention characteristics were used.

6.4 Results

Table 4-1 (Section 4) lists VOC quantified from the canister samples. Please note that concentrations of MTBE, ethanol, methanol and other oxygenated compounds are given in ppbC, in contrast to the 1995-1996 data, where ppbv units were used (to convert from ppbC to ppb divide by the number of carbon atoms). With the exception of methanol, ethanol and MTBE, the compound-specific calibration for species flagged as '**o**' and '**n**' are not performed, and the concentrations for these compounds are approximate only. The results of analysis of all ambient canister samples collected during SCOS97 are submitted in dBase format on two 3.5" diskettes (nos. IVand V) with this report. The files "smrpt03c" and "smrpt03u" contain hydrocarbon concentration data and their uncertainties, respectively, and "smecd03c" and "smecd03u" contain halocarbon data and their uncertainties, respectively, for the Mexican sites. Files "scrpt08c" and "scrpt08u" contain Caldecott Tunnel canister data and files "scrpt09c" and "scrpt09u" contain all remaining SCOS canister data. The following files contain carbonyl compound concentration and field data: "sccov09d" and "scfld09d" (all SCOS sites including Caldecott Tunnel), "smcov03d" and "smfld03d" (Mexicali and Rosarito), and "bacov01d" and "bafld01d" (Barstow). PAH data from Caldecott Tunnel are contained in the file "sccon08p". In summary, 194 canister samples (including 19 replicates), 232 carbonyl samples (including 26 replicates and 21 field blanks) and 9 PAH samples (including 2 replicates and 2 field blanks) were analyzed for this part of the study. The replicate and blank data for carbonyl and PAH measurements are included in the file "repblank.xls" and the replicate data for canister samples are in the file "rep_can.xls." The full list of carbonyl and canister samples is shown in the files "list_all.xls" and "list_cans.xls", respectively.

For carbonyl compounds, only the samples collected during the August 4-6, September 4-6 and September 28-29 IOP days were analyzed. The exception is Barstow — all valid carbonyl samples were analyzed. Field blank concentrations for carbonyl samples collected at the Rosarito site are high and variable; there is a possibility that actual samples and field blanks were mislabeled by the sampling crew at this site. This is the reason that the two Rosarito samples, TR97080410 and TR97080613, show zero concentrations for all carbonyl compounds after subtraction of the field blank values. Acetone concentrations at Burbank are very high; in fact they cannot be measured quantitatively, since the back-up cartridge (labeled as 2) shows nearly the same concentration of acetone as the first cartridge (labeled as 1). It was found during the site survey that the small metal shop adjacent to the Burbank station uses acetone as a degreasing agent (Dr. Fujita, personal communication). Also, in Burbank site, the concentrations of higher mw hydrocarbons measured from canisters were unusually high; it was established (Dr. Fujita, personal communication) that roofing was done at the station, just prior to the beginning of the sampling program.

7.0 REFERENCES CITED

Apel, E.C., J.G. Calvert and F.C. Fehsenfeld (1994). "The Nonmethane Hydrocarbon Intercomparison Experiment (NOMHICE): Tasks 1 and 2." *J. Geophys. Res.*, **99**, 16,651-16,664.

Atkinson, R., J. Arey, A.M. Winer and B. Zielinska (1988). "A survey of ambient concentrations of selected polycyclic aromatic hydrocarbons (PAH) at various locations in California." Final Report, prepared under Contract No. A5-185-32, for the California Air Resources Board, Sacramento, CA, by Statewide Air Pollution Research Center, University of California, Riverside, CA.

California Air Resources Board, "Clean Air Benefits." Cleaner Burning Gasoline Backgrounder I, California Air Resources Board, Sacramento, CA, 1996.

Chuang, J.C., M.R. Kuhlman and N. Wilson (1990). "Evaluation of methods for simultaneous collection and determination of nicotine and polynuclear aromatic hydrocarbons in indoor air." *Environ. Sci. Technol.*, **24**, 661-665.

Fujita, E.M., W.A. Lonneman, A. Van Arsdale and A. Oi (1996). "NARSTO-NE Hydrocarbon Laboratory Comparison." Presented at International Symposium, "Measurement of Toxic and Related Air Pollutants," Raleigh-Durham, NC, May 7-9, 1996. Air & Waste Management Association, Pittsburgh, PA.

Fujita, E.M., Z. Lu, L. Sheetz, G. Harshfield and B. Zielinska (1997). "Determination of Mobile Source Emission Source Fraction Using Ambient Field Measurements." Draft Final Report, CRC Project No. E-5a, prepared for Coordinating Research Council, Atlanta, GA, by Desert Research Institute, Reno, NV.

Fung, K., and D. Grosjean (1981). "Determination of Nanogram Amounts of Carbonyls as 2,4-Dinitrophenylhydrazones by High Performance Liquid Chromatography." *Anal. Chem.*, **53**, 168-171.

Fung, K., and B. Wright (1986). "Considerations in Aldehyde Measurements at Sub-ppb Levels with 2,4-Dinitrophenylhydrazine." Presented at 8th American Chemical Society Rocky Mountain Regional Meeting, Denver, CO, June 8-12.

Gertler, A.W., J.C. Sagebiel, and W.A. Dippel (1997a). "The Impact of California Phase 2 RFG on In-use Vehicle Emissions: Gas Phase Species." Draft Final Report, CRC Project No. E-27, prepared for Coordinating Research Council, Atlanta, GA, and South Coast Air Quality Management District, Diamond Bar, CA, by Desert Research Institute, Reno, NV.

Gertler, A.W., J.C. Sagebiel, D.N. Wittorff, W.R. Pierson, W.A. Dippel, D. Freeman and L. Sheetz (1997b). "Vehicle Emissions in Five Urban Tunnels." Final Report, CRC Project No. E-5, prepared for Coordinating Research Council, Atlanta, GA, by Desert Research Institute, Reno, NV.

Hawthorne, S.B., D.J. Miller, R.M. Barkley and M.S. Kreiger (1988). "Identification of Methoxylated Phenols as Candidate Tracers of Atmospheric Smoke Pollution." *Environ. Sci. Technol.,* **22**, 1191-1196.

Hawthorne, S.B., M.S. Krieger, D.J. Miller and M.B. Mathiason (1989). "Collection and Quantitation of Methoxylated Phenol Tracers for Atmospheric Pollution from Residential Wood Stoves." *Environ. Sci. Technol.,* **23**, 470-475.

Pasek, R., and B. Zielinska (1997). "Changes in ambient hydrocarbon concentrations in the Los Angeles area after the introduction of reformulated gasolines." Presented at Seventh CRC On-Road Vehicle Emissions Workshop, San Diego, CA, April 9-11, 1997. Coordinating Research Council, Atlanta, GA.

Rasmussen, R.A. (1992). "The ABCs of stainless steel canister clean-up and certification." Presented at the 1992 U.S. EPA/A&WMA International Symposium on Measurement of Toxic and Related Air Pollutants, Durham, NC, May 1992. Air & Waste Management Association, Pittsburgh, PA.

Sagebiel, J.C., B. Zielinska, B. (1994). "Effects of using Nafion® dryer on hydrocarbons analyzed from canisters by modified EPA Method TO-14." presented at the U.S. EPA/A&WMA International Symposium on Measurements of Toxic and Related Air Pollutants, Durham, NC. Air & Waste Management Association, Pittsburgh, PA.

Scanlon, J.T., and D.E. Willis (1985). "Calculation of flame ionization detector relative response factors using the effective carbon number concept." *J. Chromat. Sci.,* **23**, 333-340.

Shire, J.D. (1996). *Analytical Methods for the Quantification of Oxygenated Volatile Organic Compounds, Carbon Monoxide and Carbon Dioxide in Ambient Air Samples.* M.Sc. Thesis, University of Nevada, Reno.

Stoeckenius, T.E., G. Yarwood, M.P. Ligocki, J.P. Cohen, S.B. Shepard, R.E. Looker, E.M. Fujita, H.H. Main and P.T. Roberts (1995). "Feasibility Study for a 1995-1996 Southern California Air Quality Monitoring Program." Final Report SYSAPP94-94/065d, prepared for Coordinating Research Council, Atlanta, GA, by Systems Applications International, San Rafael, CA.

Yieru, R., O. Qingyu and Y. Weile (1990). "Characteristics of flame ionization detection for the quantitative analysis of complex organic matters." *Anal. Chem.,* **62**, 2063-2064.

Zielinska, B., G. Harshfield, E. Fujita, J. Sagebiel and R. Pasek (1997). "Volatile organic compound concentrations in the South Coast Air Basin (CA) during the summers of 1995 and 1996." Paper invited for presentation at 90th Annual Meeting, Toronto, Canada, June 8-13, 1997. Air & Waste Management Association, Pittsburgh, PA.

Zielinska, B., J. Shire, G. Harshfield, and R. Pasek (1997). "The concentration of oxygenated compounds in the Los Angeles, CA, area following the introduction of reformulated gasoline." Paper invited for presentation at 90th Annual Meeting, Toronto, Canada, June 8-13, 1997. Air & Waste Management Association, Pittsburgh, PA.