California Environmental Protection Agency Air Resources Board

# Air Quality Impacts of the Use of Ethanol in California Reformulated Gasoline

# Appendix C

# **Baseline and Future Air Quality Concentrations**

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# **C-1. Introduction**

This appendix discusses the methods used to estimate baseline and future air quality concentrations of important pollutants associated with the phase-out of methyl *tertiary*-butyl ether (MTBE) from gasoline. Analyses were only done for the South Coast Air Basin (SoCAB), the most populated and most polluted air basin in California and the area with the greatest wealth of air quality data. Separate sections are included on data sources, methods for establishing baseline concentrations, methods for estimating future air quality, and results.

# C-2. Data Sources Used

The criteria pollutants studied included carbon monoxide (CO), nitrogen dioxide (NO<sub>2</sub>), ozone (O<sub>3</sub>), and particulate matter (PM<sub>10</sub>). The key toxic air contaminants studied were benzene, 1,3-butadiene, MTBE, acetaldehyde, and formaldehyde. Ethanol, peroxyacetyl nitrate (PAN), and peroxypropionyl nitrate (PPN) were also studied. Some additional compounds (e.g., toluene, xylenes, isobutene, *n*-hexane, alkylates) were evaluated for baseline concentrations but were dropped from further analysis because the potential differences in concentrations due to the use of different fuels relative to risk levels would not pose a significant health concern. Ambient data for criteria pollutants in 1996-1998 were used to represent the 1997 baseline to account for natural year-to-year meteorological fluctuations while only 1996-1997 toxics data were used to represent the 1997 baseline since 1998 data were not readily available at the time of data analysis. Data from before 1996 were not used because the fuels used then did not satisfy the requirements of California Phase 2 Reformulated Gasoline (CaRFG).

Data from the following sources were used in our analysis:

- 1996-1998 Criteria Pollutant Monitoring Network in the SoCAB.
- 1996-1997 ARB Toxic Air Contaminant Network in the SoCAB (TAC data).
- 1996 SoCAB VOC Monitoring Study by Desert Research Institute (DRI data).
- 1996 Desert Research Institute Sepulveda Tunnel Study.
- 1996 and 1997 UC Berkeley Caldecott Tunnel Studies.
- 1997 ARB Emission Inventory for the SoCAB.

These data sets are described briefly below. Because 1997 Southern California Ozone Study-NARSTO (SCOS97-NARSTO) and Multiple Air Toxics Exposure Study (MATES) II data were not readily available at the time of data analysis, data from these studies were not included in our analysis. Although data from a 1999 UC Berkeley Tunnel Study were proposed to be used in the initial work plan, these data were not available at the time of our data analysis, and therefore also were not used.

# C-2.1. Criteria Pollutant Monitoring Network

Criteria pollutants are those that have national or state ambient air quality standards. The Air Resources Board (ARB), in conjunction with local districts, operates a criteria pollutant monitoring network throughout California. Currently, there are thirty-one monitoring sites in the SoCAB, monitoring one or more of the pollutants included in our analysis. Further details regarding each monitoring site can be found in the ARB State and Local Air Monitoring Network Plan (ARB, 1998a). Data from the statewide network are stored in the ARB ambient air quality database, Aerometric Data Analysis and Management (ADAM). The 1996-1998 data used in our analysis were extracted from the ADAM database in July 1999 and were used to represent our baseline year of 1997. Hence, changes to data that may have occurred since that time would not be reflected in our analysis, but these are expected to be small.

# C-2.2. Toxic Air Contaminant (TAC) Monitoring Network

The California Air Resources Board operates a toxics sampling network, which consists of twenty-one monitoring sites throughout California. This network measures sixty-four pollutants including some of the compounds used in our analysis. Twenty-four-hour toxics samples are collected on a 1-in-12-day basis. The sampling sites in the SoCAB are Burbank-West Palm Avenue, Los Angeles-North Main Street, North Long Beach, Riverside-Rubidoux, and Upland. Both 1996 and 1997 TAC data used in this study were extracted in December 1998 from ADAM and stored on a CD-ROM available to the public (ARB, 1998b). 1998 data were not available in time to use in our analysis. The exception is data for MTBE, which were not on the CD-ROM and were extracted from ADAM in July 1999.

# C-2.3. Desert Research Institute Study

Zielinska *et al.* (1999) at Desert Research Institute (DRI) undertook a study entitled "Air Monitoring Program for Determination of the Impacts of the Introduction of California Phase 2 Reformulated Gasoline on Ambient Air Quality in the SoCAB" in 1995-1996. The objective of this study was to conduct ambient measurements of speciated hydrocarbons, oxygenated organic gases, methane, carbon monoxide, and carbon dioxide during the summers of 1995 and 1996 in the SoCAB for providing data required to determine air quality impacts of CaRFG. In the study, samples were collected from two source-dominated sites (Burbank-West Palm Avenue and Los Angeles-North Main Street), a downwind receptor site (Azusa), and a background site (Santa Monica Beach) for forty-two days (six weeks) throughout the summers (i.e., from July to the end of September) of 1995 and 1996. Two three-hour samples were taken per sampling day, one in the morning (600 to 900) during rush hour traffic and one in the afternoon (1300 to 1600). Results for 1996 were used in our analysis.

# C-2.4. Los Angeles Sepulveda Tunnel Study

Gertler *et al.* (1997) at DRI conducted an impact study of California Phase 2 Reformulated Gasoline at the Los Angeles Sepulveda Tunnel in 1995-1996. The objectives of this study were to quantify automotive emission rates of CO, NMHC, speciated hydrocarbons,  $NO_X$ , and  $CO_2$  following the introduction of CaRFG. The Sepulveda Tunnel runs under part of the Los Angeles International Airport (LAX). Eighteen sampling experiments were performed in 1996 over the period of July 23 to July 25 during the hours of 0600 to 2000. One-Hour samples were collected at both ends of the tunnel and analyzed for CO, NMHC, various hydrocarbon species, and  $NO_X$ . Results from 17 of the 18 sampling experiments were reported by DRI and used in our analysis.

# C-2.5. Bay Area Caldecott Tunnel Study

Kirchstetter *et al.* (1999a; 1999b; 1999c) at the University of California at Berkeley performed a similar CaRFG air quality impact study at the Caldecott tunnel, east of San Francisco Bay on State Highway 24, during the summers of 1994 through 1997. The tunnel was heavily used during commute hours. In the study, two-hour samples were collected for analyzing speciated hydrocarbon and carbonyls during the afternoon commute period (1600 to 1800). On selected days, additional measurements were also performed earlier in the afternoon. Concentrations of  $CO_2$ , CO, and  $NO_X$  were measured continuously and each was recorded as a five-minute average concentration. The data collected from 1996 and 1997 were used in our analysis.

# C-2.6. Data Quality

The air monitoring data used in this evaluation and described above underwent various degrees of quality assurance procedures at the time the data were collected. The quality assurance procedures that apply to the data obtained from the ARB database (criteria and TAC pollutants) is described in the Quality Assurance Manual of the ARB Monitoring and Laboratory Division (ARB, 1999a). The procedures used in the special studies described above are documented in the various reports also referenced above.

# C-2.7. Emission Inventory Data

Emission inventories representing summer emissions in 1997 and 2003 for the SoCAB were extracted from the California Emission Forecasting System (CEFS) (ARB, 1999b) in late May 1999. We speciated the hydrocarbon data and produced summer inventories as described in Appendix A. Additionally, 1997 annual and winter emission inventories were extracted from CEFS in late July 1999.

# **C-3. Establishing Baseline Air Quality Concentrations**

# C-3.1. Criteria Pollutants

The criteria pollutants evaluated in this study were carbon monoxide, nitrogen dioxide, ozone and particulate matter ( $PM_{10}$ ). Baseline concentrations to represent 1997 were based on 1996-1998 data drawn from the ARB ADAM database.

# C-3.1.1. Carbon Monoxide

The maximum measured one-hour and eight-hour concentrations over the 1996-1998 period were 22.5 ppm and 17.5 ppm, respectively. Both were measured at the Lynwood monitoring station.

# C-3.1.2. Nitrogen Dioxide

The maximum measured one-hour and daily-average concentrations over the 1996-1998 period were 0.255 ppm and 0.117 ppm, respectively. The one-hour maximum was measured at the Banning monitoring station and the maximum daily-average concentration was measured at the Los Angeles-North Main monitoring station. A maximum annual-average concentration of 0.043 ppm was measured at the Pomona monitoring station.

## C-3.1.3. Ozone

The maximum measured one-hour and eight-hour concentrations over the 1996-1998 period were 0.244 ppm and 0.206 ppm, respectively. Both were measured at the Lake Gregory monitoring station.

# C-3.1.4. Particulate Matter (PM<sub>10</sub>, PM<sub>2.5</sub>)

The maximum measured daily-average concentration over the 1996-1998 period was  $227 \,\mu g/m^3$ , measured at the Banning monitoring station. The maximum annual geometric mean concentration of  $56 \,\mu g/m^3$  was measured at the Riverside-Rubidoux monitoring station. California's PM2.5 monitoring network has been deployed for less than a year and insufficient measurements are available to establish baseline air quality concentrations.

# C-3.2. Toxic Pollutants

The toxic pollutants evaluated in our analysis included benzene, 1,3-butadiene, MTBE, acetaldehyde, formaldehyde, toluene, and xylenes. Isobutene and *n*-hexane are also discussed in this section because estimates for these two compounds involve the same analytical procedures. Baseline pollutant concentrations to represent 1997 were based on 1996-1997 data drawn from the ARB toxics database, from DRI data, and from correlation analyses using these same data, tunnel study results and criteria pollutant data. Different approaches were used for different groups of toxic compounds.

### C-3.2.1. Benzene, 1,3-Butadiene, and MTBE

Two different approaches were used to estimate benzene, 1,3-butadiene, and MTBE concentrations representative of 1997. First, we used measured concentrations directly from the toxics sampling network. In addition, we developed ratios between these toxic compounds and carbon monoxide and used them to estimate concentrations at locations where there were no direct toxics measurements, but there were CO measurements. This latter approach allowed us to estimate pollutant concentrations at nineteen locations, rather than the five locations for which toxics sampling data are available. The two approaches provide a range in estimates. The next section discusses the rationale for correlating CO with other compounds. The section after that describes the method and results.

#### C-3.2.1.1. Rationale for Using Ratios of CO to Other Compounds

The concept of establishing a relationship between CO and other pollutants is based on the premise that these pollutants are principally emitted from mobile sources and that for the most part they are primary pollutants. Thus, if CO concentrations are high at a particular site, the related pollutants can be expected to be high as well. This premise is reasonably straightforward for compounds that are primary pollutants and for compounds with low reactivity. However, the relationship holds as well for 1,3-butadiene, which has much higher reactivity. In part, this is because the peak concentrations for both CO and 1,3-butadiene occur during the winter months when photochemistry is minimal. Additionally, the continual infusion of fresh emissions, the ubiquitous presence of mobile sources, and their relatively close proximity to monitoring sites means that there is little time for atmospheric reaction prior to being measured.

Ultimately, we found good correlation between CO and benzene, 1,3-butadiene, MTBE, toluene, *n*-hexane, isobutene, the three xylenes, and the alkylates. The specific application of the resulting relationships is discussed in the following sections covering the respective pollutants. Table 3.1 presents the lifetime and the maximum incremental reactivity MIR of selected compounds.

### C-3.2.1.2. Development of Ratios Between Toxic Compounds and CO

To estimate toxics concentrations at locations other than those where toxic compounds are sampled, we developed ratios between toxic compounds and CO. The general procedure for determining the ratio between a TAC and CO is described below. The same procedure was applied to all TACs except the aldehydes.

The first step was to extract the TAC and CO data from the aforementioned data sets and select sites where both TACs and CO were measured. CO was not measured at the Upland site (one of five sites in the TAC monitoring network in the SoCAB) in 1996 or 1997, so data collected at Upland were not used in the subsequent calculations. As for the DRI data set, both the AM data and the combined AM plus PM data were analyzed separately in this study to consider possible differences between the morning period of direct source contribution and overall behavior during the day.

Compound	Atmospheric Lifetime <sup>a</sup>	MIR <sup>b</sup>
·	(daylight hours)	(g ozone/g NMOG)
Acetaldehyde	11	7.25
Alkylates	13-214	1.0-2.3
Benzene	141	0.91
1.3-Butadiene	2.6	12.88
Carbon Monoxide	827	0.066
Ethanol	53	1.88
Formaldehyde <sup>c</sup>	3.6	9.27
n-Hexane	31	1.71
Isobutene	3.4	6.59
МТВЕ	59	0.88
Toluene	29	4.24
m-Xylene	7.4	11.04
o-Xvlene	13	7.87
p-Xylene	12	4.56

#### Table 3.1 Calculated Atmospheric Lifetimes and MIRs for Selected Compounds

 a. The atmospheric lifetime for each compound was calculated based on the recommended OH rate constants (Atkinson, 1994) and a 12-hr average OH radical concentration of 1.6x10<sup>6</sup> molecule/cm<sup>3</sup>.

b. Maximum Incremental Reactivity (Carter W.P.L, 1999.)

c. The atmospheric lifetime for formaldehyde is estimated based on the photolysis rate of formaldehyde, which dominates over gas-phase reaction with OH radicals.

Then we estimated representative background concentrations and subtracted them from the extracted data. The background subtraction was to facilitate development of a single basin-wide ratio between a TAC and CO. Because there was no significant natural sources for the toxic compounds studied (except aldehydes), atmospheric background for each TAC was determined to be negligible (zero). However, for CO the background was estimated to be 100 ppb, based on measurements at Santa Catalina Island, Point Conception, and San Nicholas Island during SCOS97-NARSTO.

The next step was to exclude concentrations below the level of detection (LOD) and some outliers because such values could distort the ratios being calculated. For the TAC monitoring network data set, for example, 19 benzene data values and two CO data values (out of 109 pairs of matched data values collected in the SoCAB in 1996) were below their LOD values (ARB, 1998b). As for outliers, two exceptionally high benzene concentrations, observed on July 7, 1996 (AM) and July 8, 1996 (PM) in the DRI data, were also excluded in subsequent calculations.

Finally, a least-square linear regression technique was applied to the TAC and CO data and the regression line forced through the origin. Then, the TAC to CO ratios and correlation coefficients were calculated.

The specific application of these procedures to develop ratios to CO for benzene, 1,3-butadiene, and MTBE are discussed further below.

### C-3.2.1.2.1. Benzene

Table 3.2 summarizes the ratios and correlation coefficients between benzene and CO derived from the five data sets. Ratios calculated from the emission data were based on ratios of benzene emissions to CO emissions estimated for all sources and for just on-road sources, respectively. In general, good correlation between benzene and CO data was observed, except for the 1997 Caldecott data set. No significant difference in ratios was observed between the DRI AM and AM plus PM data sets. Except for those derived from the Caldecott data sets, the benzene to CO ratios range from 0.81 to 1.21 (ppb/ppm). Statewide ratios between benzene and CO derived from TAC data collected throughout the state in 1996 and 1997 are 1.03 and 0.88 (ppb/ppm), respectively. A ratio of 1.0 (ppb/ppm) was selected as a reasonable ratio of benzene to CO.

Figure 3.1 shows a scatterplot of benzene versus CO for the SoCAB TAC samples collected in 1996. Data collected in different sites are represented by different symbols. Scatterplots of benzene versus CO for the DRI data and the Sepulveda tunnel data are shown in Figure 3.2 and Figure 3.3, respectively.

### C-3.2.1.2.2. 1,3-Butadiene

Table 3.3Table 3.2 summarizes the ratios and correlation coefficients for 1,3-butadiene to CO derived from the aforementioned data sets. Good correlation between 1,3-butadiene and CO was observed for all data sets except the two tunnel studies and Riverside data. The ratios range from 0.22 to 0.34 (ppb/ppm), except those obtained from Caldecott tunnel data. Statewide ratios calculated from TAC data collected throughout California in 1996 and 1997 are 0.29 and 0.28 (ppb/ppm), respectively. A ratio of 0.30 (ppb/ppm) was selected as a reasonable ratio of 1,3-butadiene to CO. Scatterplots of 1,3-butadiene versus CO are presented in Figure 3.4, Figure 3.5, and Figure 3.6 for 1996 TAC data, DRI data, and Sepulveda tunnel data, respectively.

### C-3.2.1.2.3. MTBE

Table 3.4 summarizes the ratios and correlation coefficients for MTBE to CO derived from the same data sets described above. Good correlation was observed for the DRI data set and the 1997 TAC data. However, correlation was poor for the Caldecott tunnel data and the 1996 Long Beach data. The ratios obtained from the TAC network data and the DRI data range from 2.6 to 4.6 (ppb/ppm), while the ratios derived from emission inventory and tunnel data are substantially lower. Based on these results, a ratio of 3.0 (ppb/ppm) was selected as a reasonable ratio of MTBE to CO. Scatterplots of MTBE versus CO are shown in Figure 3.7, Figure 3.8, and Figure 3.9 for 1996 TAC data, DRI data, and Sepulveda data, respectively.

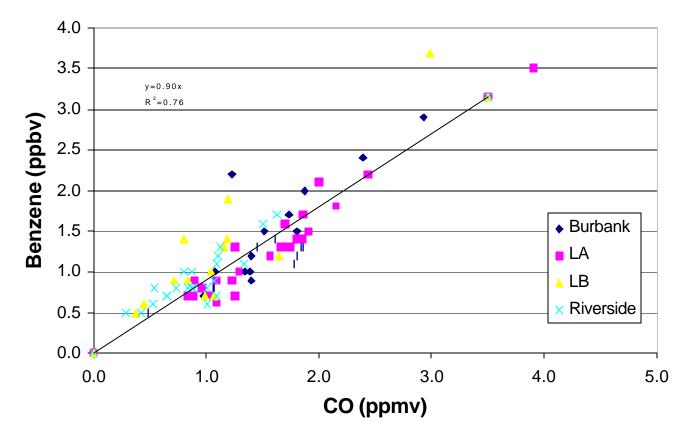
	TAC Network		DRI Data (AM)		DRI Data (AM&PM)		Tunnel Data		Emission Inventorv <sup>b</sup>	
	Ratio	R <sup>2</sup>	Ratio	R <sup>2</sup>	Ratio	$R^2$	Ratio	R <sup>2</sup>	All Sources	
1996										
California Statewide <sup>c</sup>	1.03	0.61								
South Coast Air Basin <sup>c</sup>	0.90	0.76	1.10	0.93	1.11	0.91			1.21	1.18
Burbank	0.86	0.66	1.14	0.98	1.14	0.98				
Los Angeles	0.84	0.92	1.03	0.89	1.05	0.90				
Long Beach	1.13	0.81								
Riverside	0.98	0.69								
Azusa			1.17	0.95	1.19	0.86				
Sepulveda Tunnel							1.10	0.96		
Caldecott Tunnel							0.59	0.76		
1997										
California Statewide <sup>c</sup>	0.88	0.82								
South Coast Air Basin <sup>c</sup>	0.80	0.89								
Burbank	0.78	0.84								
Los Angeles	0.82	0.95								
Long Beach	0.81	0.88								
Caldecott Tunnel							0.53	0.46		

# Table 3.2 Linear Regression Parameters for Correlations Between Ambient Concentrations of Benzene and CO<sup>a</sup>

a. Concentration units are ppmv for CO and ppbv for benzene. CO background of 100 ppb was subtracted in CO measurements. Below-LOD values were excluded in ratio calculation. Regression line was forced through zero.

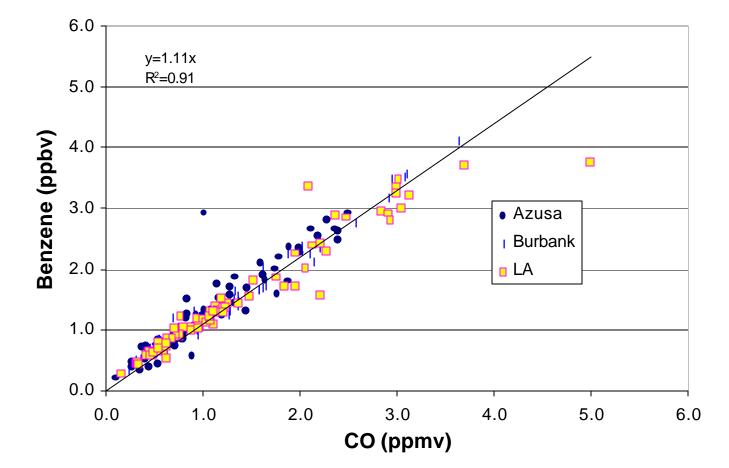
b. Emission ratios were obtained by using SoCAB emission inventory data in 1997.

c. Statewide and basin-wide ratios and correlation coefficients were calculated using the data collected statewide and in the SoCAB, respectively.



# Four TAC Sites, 1996

Figure 3.1 Benzene versus CO for SoCAB (Four TAC Sites, 1996)



# SoCAB (Three DRI Sites, 1996)

Figure 3.2 Benzene versus CO for SoCAB (Three DRI Sites, 1996)

# LA Sepulveda Tunnel (1996)

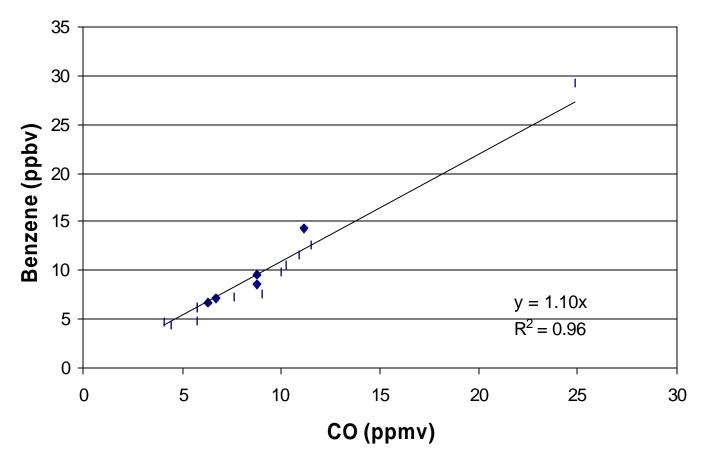


Figure 3.3 Benzene versus CO for LA Sepulveda Tunnel (1996)

	TAC N	etwork	DRI Data (AM)		DRI Data	DRI Data (AM&PM)		Tunnel Data		Emission Inventory <sup>b</sup>	
	Ratio	R <sup>2</sup>	Ratio	R <sup>2</sup>	Ratio	R <sup>2</sup>	Ratio	R <sup>2</sup>		On-road Sources	
1996											
California Statewide <sup>c</sup>	0.29	0.79									
South Coast Air Basin <sup>c</sup>	0.27	0.84	0.26	0.76	0.24	0.71			0.33	0.32	
Burbank	0.26	0.85	0.26	0.78	0.23	0.72					
Los Angeles	0.27	0.90	0.25	0.68	0.24	0.72					
Long Beach	0.34	0.68									
Riverside	0.26	0.46									
Azusa			0.27	0.83	0.22	0.64					
Sepulveda Tunnel							0.24	0.57			
Caldecott Tunnel							0.13	0.02			
1997											
California Statewide <sup>c</sup>	0.28	0.81									
South Coast Air Basin <sup>c</sup>	0.28	0.82									
Burbank	0.25	0.84									
Los Angeles	0.30	0.90									
Long Beach	0.30	0.74									
Caldecott Tunnel							0.15	0.28			

### Table 3.3 Linear Regression Parameters for Correlations Between Ambient Concentrations of 1,3-Butadiene and CO<sup>a</sup>

a. Concentration units are ppmv for CO and ppbv for 1,3-butadiene. CO background of 100 ppb was subtracted in CO measurements. Below-LOD values were excluded in ratio calculation. Regression line was forced through zero.

b. Emission ratios were obtained by using SoCAB emission inventory data in 1997.

c. Statewide and basin-wide ratios and correlation coefficients were calculated using the data collected statewide and in the SoCAB, respectively.

# SoCAB (Four TAC Sites, 1996)

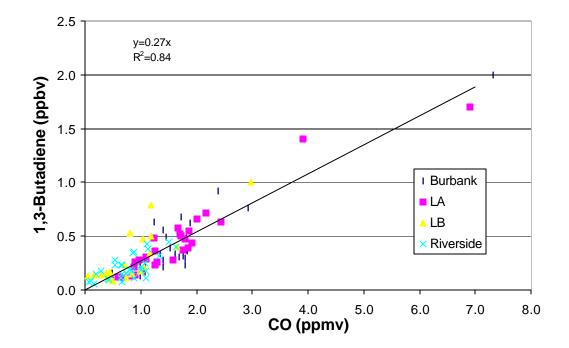
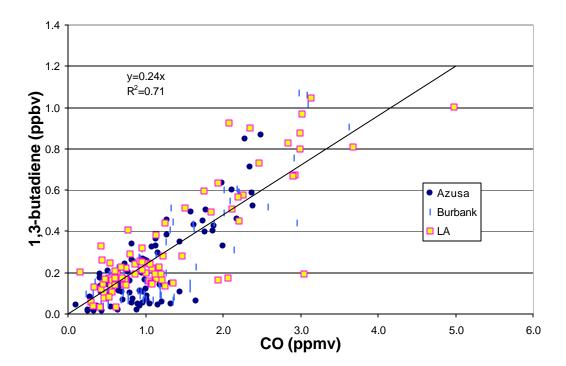


Figure 3.4 1,3-Butadiene versus CO for SoCAB (Four TAC Sites, 1996)



# SoCAB (Three DRI Sites, 1996)

Figure 3.5 1,3-Butadiene versus CO for SoCAB (Three DRI Sites, 1996)

# LA Sepulveda Tunnel (1996)

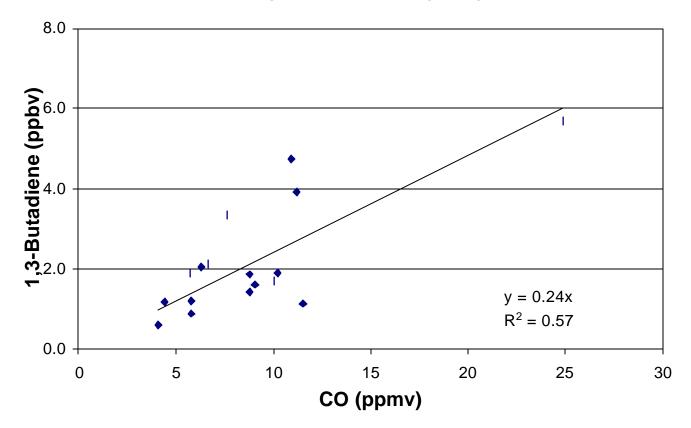


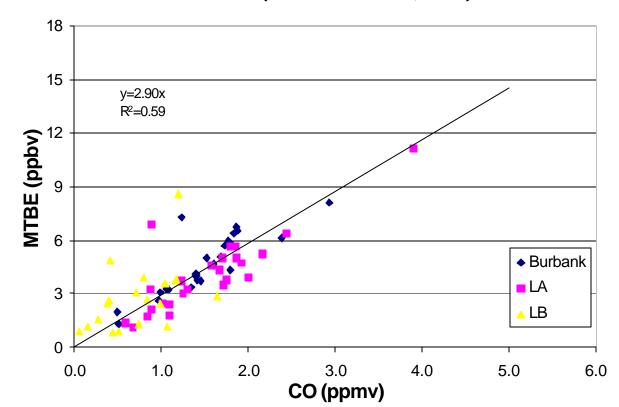
Figure 3.6 1,3-Butadiene versus CO for LA Sepulveda Tunnel (1996)

	TAC N	etwork	DRI Da	DRI Data (AM)		DRI Data (AM&PM)		Tunnel Data		Emission Inventory <sup>b</sup>	
	Ratio	R <sup>2</sup>	Ratio	R <sup>2</sup>	Ratio	R <sup>2</sup>	Ratio	R <sup>2</sup>	All Sources	<b>On-road Sources</b>	
1996											
South Coast Air Basin <sup>c</sup>	2.90	0.59	4.06	0.84	4.13	0.83			1.82	2.31	
Burbank	3.07	0.71	4.56	0.96	4.61	0.95					
Los Angeles	2.66	0.72	3.43	0.81	3.51	0.84					
Long Beach	3.37	0.10									
Riverside											
Azusa			4.45	0.90	4.59	0.79					
Sepulveda Tunnel							2.28	0.93			
Caldecott Tunnel							0.88	0.35			
1997											
South Coast Air Basin <sup>c</sup>	3.00	0.88									
Burbank	3.25	0.90									
Los Angeles	2.59	0.93									
Long Beach	3.12	0.91									
Caldecott Tunnel							0.62	0.33			

# Table 3.4 Linear Regression Parameters for Correlations Between Ambient Concentrations of MTBE and CO<sup>a</sup>

a. Concentration units are ppmv for CO and ppbv for MTBE. CO background of 100 ppb was subtracted in CO measurements. Below-LOD values were excluded in ratio calculation. Regression line was forced through zero.

b. Emission ratios were obtained by using SoCAB emission inventory data in 1997.



# SoCAB (Three TAC Sites, 1996)

Figure 3.7 MTBE versus CO for SoCAB (Three TAC Sites, 1996)



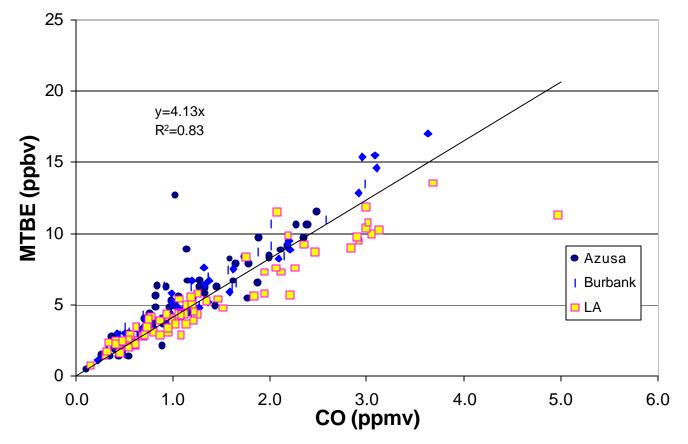


Figure 3.8 MTBE versus CO for SoCAB (Three DRI Sites, 1996)



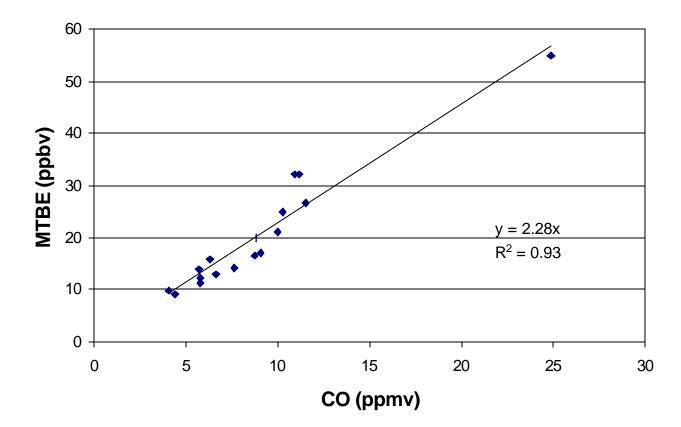


Figure 3.9 MTBE versus CO for LA Sepulveda Tunnel (1996)

### C-3.2.1.3. Estimated 1997 Concentrations

In our analyses, we estimated 1997 benzene, 1,3-butadiene, and MTBE concentrations for the maximum daily average, the maximum one-hour average, and the population-weighted annual exposure.

### C-3.2.1.3.1. Maximum Daily Average

The maximum measured daily-average benzene concentration in the SoCAB from 1996 to 1997 was 7.4 ppb, measured at Burbank on January 10, 1996. The maximum measured daily-average CO concentration in the SoCAB between 1996 and 1998 was 9.6 ppm, measured at Lynwood on November 1, 1997. Subtracting 0.1 ppm background from this and multiplying it by the benzene to CO ratio of 1.0 (ppb/ppm), the estimated maximum daily-average benzene concentration at Lynwood is 9.5 ppb.

The maximum measured daily-average 1,3-butadiene concentration in the SoCAB from 1996 to 1997 was 2.0 ppb, measured at Burbank on January 10, 1996. Multiplying the background-adjusted maximum daily-average CO concentration (9.5 ppm) by the 1,3-butadiene to CO ratio of 0.3 (ppb/ppm), the estimated maximum daily-average 1,3-butadiene concentration at Lynwood is 2.9 ppb.

The maximum measured daily-average MTBE concentration in the SoCAB from 1996 to 1997 was 13 ppb, measured at Burbank on November 24, 1997. Multiplying the background-adjusted maximum daily-average CO concentration (9.5 ppm) by the MTBE to CO ratio of 3.0 (ppb/ppm), the estimated maximum daily-average MTBE concentration at Lynwood is 29 ppb.

#### C-3.2.1.3.2. Maximum One-Hour Average

The maximum measured daily-average benzene concentration in the SoCAB from 1996 to 1997 was 7.4 ppb, measured at Burbank on January 10, 1996. The corresponding maximum one-hour and daily-average CO concentrations at Burbank on this day were 11.6 ppm and 7.43 ppm, respectively. Assuming that benzene concentrations vary during the day in proportion to CO concentrations (since they are both primarily emitted by motor vehicles and affected by the same meteorology), the estimated maximum one-hour benzene concentration at Burbank is 11.6 ppb. The maximum measured one-hour-average CO concentration in the SoCAB between 1996 and 1998 was 22.5 ppm, measured at Lynwood on January 6, 1996. Subtracting 0.1 ppm background from this and multiplying it by the benzene to CO ratio of 1.0 (ppb/ppm), the estimated maximum benzene concentration at Lynwood is 22.4 ppb.

The maximum measured daily-average 1,3-butadiene concentration in the SoCAB from 1996 to 1997 was 2.0 ppb, measured at Burbank on January 10, 1996. The corresponding maximum one-hour and daily-average CO concentrations at Burbank on this day were 11.6 ppm and 7.43 ppm, respectively. Assuming that 1,3-butadiene concentrations vary during the day in proportion to CO concentrations (since they are both primarily emitted by motor vehicles and affected by the same meteorology), the estimated maximum one-hour 1,3-butadiene concentration at Burbank is 3.1 ppb.

Multiplying the background-adjusted maximum one-hour-average CO concentration (22.4 ppm) by the 1,3-butadiene to CO ratio of 0.3 (ppb/ppm), the estimated maximum 1,3-butadiene concentration at Lynwood is 6.7 ppb.

The maximum measured daily-average MTBE concentration in the SoCAB from 1996 to 1997 was 13 ppb, measured at Burbank on November 24, 1997. The corresponding maximum one-hour and daily-average CO concentrations at Burbank on this day were 5.9 ppm and 4.03 ppm, respectively. Assuming that MTBE concentrations vary during the day in proportion to CO concentrations (since they are both primarily emitted by motor vehicles and affected by the same meteorology), the estimated maximum one-hour MTBE concentration at Burbank is 19 ppb. Multiplying the background-adjusted maximum one-hour-average CO concentration (22.4 ppm) by the MTBE to CO ratio of 3.0 (ppb/ppm), the estimated maximum MTBE concentration at Lynwood is 67 ppb.

### C-3.2.1.3.3. Population-Weighted Annual Exposure

In calculating health risks, the Office of Environmental Health Hazard Assessment (OEHHA) uses population-weighted annual pollutant exposure as an indicator of the concentration to which a typical person is exposed to toxic substances. For benzene, 1,3-butadiene, and MTBE, population-weighted annual-average exposure was calculated two ways.

The first way used available data from the five toxics monitoring sites in the SoCAB. Annual averages for 1996 and 1997 were averaged for the individual monitoring sites. Then the population-weighted annual-average concentration was estimated by interpolating between the five monitoring sites using a previously developed technique (ARB, 1993). This interpolation process starts with population data by census tract and an associated centroid. Then data for any monitoring site within 50 kilometers of the centroid is used in determining a representative concentration to which people in the In determining this representative concentration, the census tract are exposed. contribution from each monitoring site is weighted in proportion to the inverse of the square of the distance from the population centroid to the monitoring site. To determine the population-weighted exposure, the population of individual census tracts is multiplied by their representative concentration, summed over all census tracts and then divided by the total population across all census tracts. The resulting population-weighted annual-average concentrations calculated to represent the SoCAB in 1997 were 1.1 ppb for benzene, 0.34 ppb for 1,3-butadiene, and 3.9 ppb for MTBE, respectively.

The second way used an average of annual-average CO concentrations for 1996-1998 to calculate benzene, 1,3 butadiene and MTBE concentrations at nineteen monitoring locations in the SoCAB using the ratios to CO described in Section C-3.2.1.2 applied to the background-adjusted CO concentrations. Population-weighted annual-average concentrations of 1.2 ppb benzene, 0.36 ppb 1, 3-butadiene, and 3.6 ppb MTBE were calculated using the interpolation and averaging procedure described in the paragraph above.

### C-3.2.2. Acetaldehyde and Formaldehyde

Three different approaches were considered in estimating acetaldehyde and formaldehyde concentrations representative of 1997. First was the use of measured concentrations directly from the toxics sampling network. Second was the use of results from the air quality model simulations. Third was developing relationships between aldehydes and CO and oxidant so aldehyde concentrations could be estimated at many more locations than are sampled with the toxics monitoring network. Our attempt to correlate aldehydes with CO and oxidant was not considered sufficiently reliable and was abandoned. A brief discussion of that effort is presented in Section C-3.2.2.2.

### C-3.2.2.1. Estimated 1997 Concentrations

In our analyses, we estimated 1997 acetaldehyde and formaldehyde concentrations for the maximum daily average, the maximum one-hour average, and the population-weighted annual exposure.

### C-3.2.2.1.1. Maximum Daily Average

The maximum measured daily-average acetaldehyde concentration in the SoCAB from 1996 to 1997 was 5.1 ppb, measured at Upland on August 13, 1996. The maximum measured daily-average formaldehyde concentration in the SoCAB from 1996 to 1997 was 14.0 ppb, measured at Upland on August 13, 1996. In addition, the regional air quality model simulation for 1997 predicted the basin-wide maximum acetaldehyde and formaldehyde concentration predicted is lower than the maximum measured value, we considered the measured value to be more representative of the maximum concentration.

#### C-3.2.2.1.2. Maximum One-Hour Average

The maximum one-hour aldehyde concentrations were estimated three ways using three data sources.

First, three-hour DRI data were used as a basis. The maximum three-hour acetaldehyde concentration measured was 13.88 ppb at Azusa on August 28, 1996 between 1300 and 1600 PDT. Corresponding three-hour and maximum one-hour ozone concentrations for this period are 0.11 ppm and 0.14 ppm, respectively. Assuming that acetaldehyde concentrations vary in the afternoon in proportion to ozone concentrations (since both are strongly influenced by atmospheric chemical reactions at this time of day), the estimated maximum one-hour acetaldehyde concentration at Azusa is 17.7 ppb. Similarly for formaldehyde, the maximum 3-hour measurement of 18.17 ppb was in the afternoon on August 29, 1996 in Burbank. The corresponding estimated one-hour maximum is 20.3 ppb.

Second, TAC daily-average data were used. The maximum daily-average acetaldehyde concentration at Upland, measured on August 13, 1996, was 5.1 ppb. The average ratio of maximum one-hour average to daily-average ozone for monitors operating in the SoCAB on August 13, 1996 was 2.7. Assuming that acetaldehyde

concentrations at Upland in August vary in proportion to ozone concentrations (photochemical model simulations indicate that over 90% of the acetaldehyde and 85% of the formaldehyde at Upland is from atmospheric chemical reactions on high ozone days), the maximum one-hour acetaldehyde concentration estimated for Upland is 13.8 ppb. Similarly, the maximum daily-average formaldehyde concentration at Upland, measured on August 13, 1996, was 14 ppb and the corresponding estimated maximum one-hour concentration is 37.8 ppb.

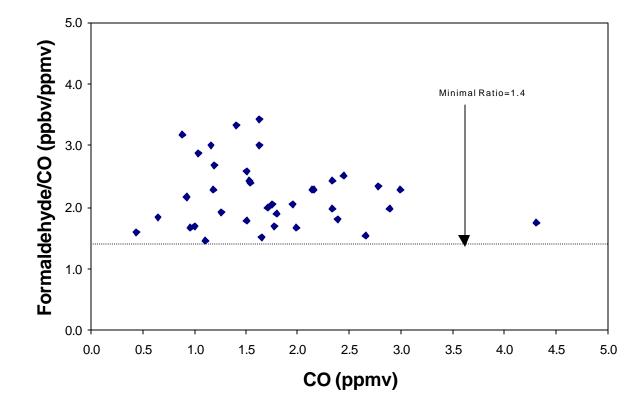
Third, the regional air quality model simulation for 1997 predicted the basin-wide maximum acetaldehyde and formaldehyde concentrations to be 9.2 ppb and 22.7 ppb, respectively. Since the model maximum one-hour acetaldehyde concentration of 9.2 ppb was less than the maximum three-hour measured value, we considered the estimates made using the measured values to be more representative of maximum concentrations.

#### C-3.2.2.1.3. Population-Weighted Annual Exposure

There are five monitoring sites in the SoCAB at which acetaldehyde and formaldehyde measurements were made between 1996 and 1997. The population-weighted annual-average concentrations were calculated using the interpolation and averaging procedure described in Section C-3.2.1.3.3 above. The resulting population-weighted annual-average concentrations calculated to represent the SoCAB in 1997 are 1.75 ppb for acetaldehyde and 4.65 ppb for formaldehyde.

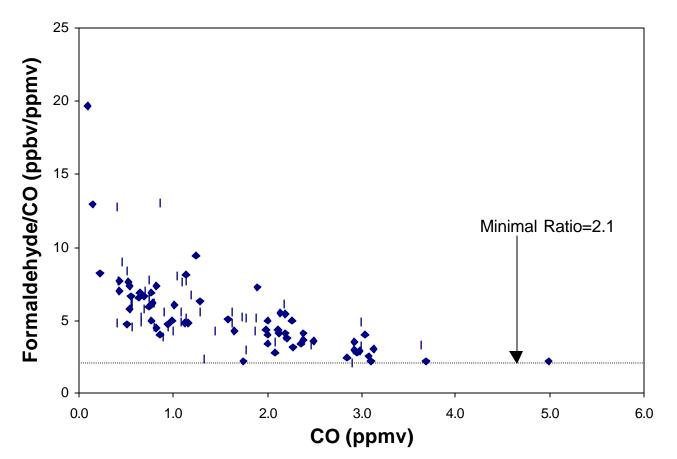
### C-3.2.2.2. Attempt to Correlate Aldehydes with CO and Oxidant

To provide a broader base of data for estimating aldehyde concentrations, an attempt was made to correlate acetaldehyde and formaldehyde concentrations with carbon monoxide and oxidant  $(O_3+NO_2)$  concentrations. CO was used as an index of primary aldehyde emissions and oxidant as an index of the secondary aldehyde produced through chemical reactions in the atmosphere. To develop a relationship with CO, we plotted aldehydes versus CO using both the TAC data and 0600 to 0900 data for 1996 from the DRI study. Because some of the measured acetaldehyde and formaldehyde may be secondary in origin, we opted to estimate a ratio between primary aldehydes and CO by plotting the aldehyde to CO ratio versus CO and identifying the minimum ratio that generally had most if not all of the points above it. For formaldehyde from the toxics monitoring network, the minimum ratio was 1.4 ppb/ppm CO (see Figure 3.10). For DRI formaldehyde data, the minimum ratio was 2.1 (see Figure 3.11). For acetaldehyde, the minimum ratio was 0.50 (see Figure 3.12) for TAC data and 0.95 (see Figure 3.13) for the DRI data. In developing these minimum ratios we first subtracted background concentrations of 0.1 ppm CO and 0.5 ppb acetaldehyde or formaldehyde from the measured values. These background concentrations were determined from measurements at Santa Catalina Island, Point Conception, and San Nicholas Island during SCOS97-NARSTO.



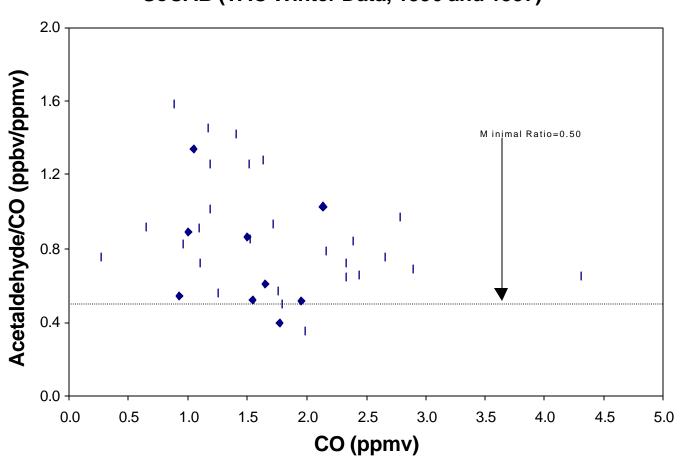
SoCAB (TAC Winter Data, 1996 and 1997)

Figure 3.10 Formaldehyde to CO Ratio versus CO for SoCAB (TAC Winter Data, 1996 and 1997)



# SoCAB (Three DRI Sites, 1996)

Figure 3.11 Formaldehyde to CO Ratio versus CO for SoCAB (Three DRI Sites, 1996)



SoCAB (TAC Winter Data, 1996 and 1997)

Figure 3.12 Acetaldehyde to CO Ratio versus CO for SoCAB (TAC Winter Data, 1996 and 1997)

# SoCAB (Three DRI Sites, 1996)

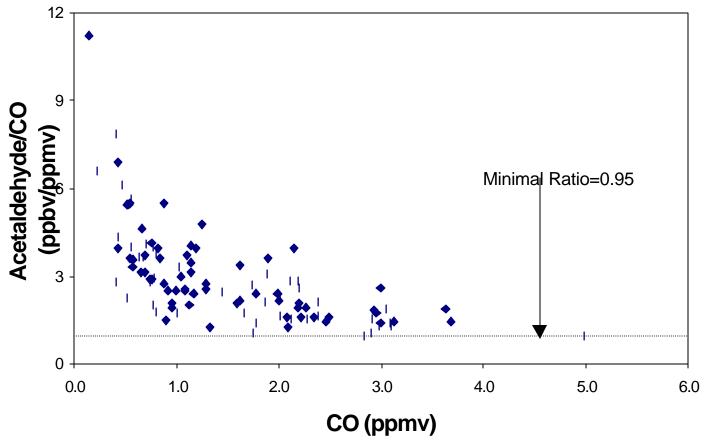


Figure 3.13 Acetaldehyde to CO Ratio versus CO for SoCAB (Three DRI Sites, 1996)

To determine a factor relating aldehydes to oxidant, we assembled carbon monoxide and oxidant  $(O_3+NO_2)$  data to match aldehyde measurements from the toxics monitoring network in the SoCAB. First, we used the aldehyde to CO ratios determined above to estimate primary acetaldehyde. Then we subtracted this from the measured aldehyde concentration to obtain a residual aldehyde amount (presumably secondary in origin). Then we plotted the residual aldehyde versus oxidant, after subtracting a background concentration of 0.03 ppm oxidant. This background concentration was determined by looking at the distribution of oxidant concentrations measured in the SoCAB between 1996 and 1998. More than 98.6 % of the measured daily-average concentrations were 0.03 ppm or higher. Using the acetaldehyde to CO ratio of 0.50, a best fit oxidant slope was determined to be 40 for the TAC data. Using the ratio of 0.95 from the DRI data, the best fit oxidant slope for TAC data was determined to be 31. Using the formaldehyde to CO ratio of 1.4, a best fit oxidant slope was determined to be 73 for the TAC data. Using the ratio of 2.1 from the DRI data, the best fit oxidant slope for TAC data was determined to be 80. For residual acetaldehyde our  $R^2$  regression coefficients were .50 to .54, depending on which slope factors were used. For residual formal ehyde our  $R^2$ regression coefficients were .12 to .37, depending on which slope factors were used. When we tried applying the CO and oxidant ratios to predict daily aldehyde concentrations, the maximum predicted concentrations at the toxics monitoring sites in the SoCAB on actual sampling days were 75% or more higher than measured maximum values. Therefore, we decided that this approach did not provide sufficiently reliable estimates to use in our analysis.

#### C-3.2.3. Toluene, Xylenes, Isobutene, and *n*-Hexane

OEHHA requested information on annual exposure and maximum one-hour concentrations for toluene, xylenes, isobutene, and *n*-hexane. In response to this, we did a sensitivity evaluation of 1997 concentrations for these compounds. A key part of the sensitivity evaluation involved developing ratios between the compounds of interest and CO. This is discussed below, followed by estimates of 1997 pollutant concentrations.

After reviewing the estimated 1997 concentrations relative to chronic Reference Exposure Levels (RELs), OEHHA concluded that even a few-fold difference in concentration from the use of one fuel over the other is not going to be a significant health concern. This was because current concentrations of these compounds are one to two orders of magnitude below their chronic RELs. Thus, airshed modeling analysis was not performed to predict future air quality concentrations of these compounds.

#### C-3.2.3.1. Ratio Between Compounds and CO

Following a procedure similar to that described in Section C-3.2.1.2, we developed ratios between the compounds of interest and CO. The results for each of the compounds evaluated follow:

### C-3.2.3.1.1. Toluene

Table 3.5 summarizes the ratios and correlation coefficients between toluene and CO derived from TAC data, DRI data, Sepulveda data, and the emission inventory. This includes ratios derived from each monitoring site as well as sites combined (basin-wide) in the same data set. In general, good correlation was observed in all cases except the Riverside site. The ratios derived from air quality data range from 2.3 to 4.6.

### C-3.2.3.1.2. Combined *meta*- and *para*-Xylenes

Table 3.6 summarizes the ratios and correlation coefficients between combined *meta*and *para*-xylene (m&p-xylene) and CO derived from the same data sets. In general, good correlation was observed for all data sets. The ratios obtained range from 1.1 to 1.9.

### C-3.2.3.1.3. *o*-Xylene

Table 3.7 summarizes the ratios and correlation coefficients between o-xylene and CO derived from the same data sets. In general, good correlation was observed for all data sets. The ratios obtained range from 0.4 to 1.8.

### C-3.2.3.1.4. Isobutene

Table 3.8 summarizes the ratios and correlation between isobutene and CO derived from DRI data, the Sepulveda tunnel study, and the emission inventory. This compound is not measured in our TAC network. In general, good correlation was observed for all data sets except Los Angeles. The ratios derived range from 0.9 to 1.6.

#### C-3.2.3.1.5. *n*-Hexane

Table 3.9 summarizes the ratios and correlation coefficients between n-hexane and CO derived from DRI data, the Sepulveda tunnel study, and the emission inventory. Like isobutene, n-hexane is not measured in our TAC network. In general, good correlation was observed for all data sets. The ratios derived range from 0.5 to 1.0.

#### C-3.2.3.2. Estimated 1997 Concentrations

We made estimates of expected maximum annual-average and maximum one-hour-average concentrations for toluene, m&p-xylene, o-xylene, isobutene and n-hexane. These were done using available measurements from the toxics monitoring network and by establishing a ratio to carbon monoxide and multiplying that ratio by maximum CO concentrations.

	TAC N	etwork	DRI Data (AM)		DRI Data (AM&PM)		Tunnel Data		Emission Inventory <sup>b</sup>	
	Ratio	$R^{2}$	Ratio	R <sup>2</sup>	Ratio	$R^2$	Ratio	R <sup>2</sup>		<b>On-road Sources</b>
1996										
South Coast Air Basin <sup>c</sup>	2.73	0.84	3.91	0.82	3.96	0.78			3.74	
Burbank	2.84	0.85	4.26	0.94	4.35	0.89				
Los Angeles	2.55	0.82	3.24	0.89	3.29	0.86				
Long Beach	2.77	0.86								
Riverside	3.11	0.31								
Azusa			4.56	0.88	4.57	0.77				
Sepulveda Tunnel							2.27	0.95		
Caldecott Tunnel										
1997										
South Coast Air Basin <sup>c</sup>	2.49	0.76								
Burbank	2.66	0.65								
Los Angeles	2.36	0.80								
Long Beach	2.55	0.75								
Caldecott Tunnel										

# Table 3.5 Linear Regression Parameters for Correlations Between Ambient Concentrations of Toluene and CO<sup>a</sup>

a. Concentration units are ppmv for CO and ppbv for toluene. CO background of 100 ppb was subtracted in CO measurements. Below-LOD values were excluded in ratio calculation. Regression line was forced through zero.

b. Emission ratios were obtained by using SoCAB emission inventory data in 1997.

	TAC Network		DRI Da	DRI Data (AM)		DRI Data (AM&PM)		Tunnel Data		Emission Inventorv <sup>b</sup>	
	Ratio	$R^{2}$	Ratio	R <sup>2</sup>	Ratio	R <sup>2</sup>	Ratio	R <sup>2</sup>		<b>On-road Sources</b>	
1996											
South Coast Air Basin <sup>c</sup>	1.29	0.93	1.83	0.87	1.76	0.85			1.33		
Burbank	1.27	0.91	1.90	0.91	1.85	0.94					
Los Angeles	1.31	0.96	1.68	0.82	1.63	0.84					
Long Beach	1.38	0.82									
Riverside	1.32	0.67									
Azusa			2.00	0.91	1.88	0.79					
Sepulveda Tunnel							1.33	0.97			
Caldecott Tunnel											
1997											
South Coast Air Basin <sup>c</sup>	1.15	0.84									
Burbank	1.16	0.62									
Los Angeles	1.15	0.92									
Long Beach	1.13	0.88									
Caldecott Tunnel											

## Table 3.6 Linear Regression Parameters for Correlations Between Ambient Concentrations of *m&p*-Xylene and CO<sup>a</sup>

a. Concentration units are ppmv for CO and ppbv for m&p-xylene. CO background of 100 ppb was subtracted in CO measurements. Below-LOD values were excluded in ratio calculation. Regression line was forced through zero.

b. Emission ratios were obtained by using SoCAB emission inventory data in 1997.

	TAC Network		DRI Da	DRI Data (AM)		DRI Data (AM&PM)		el Data	Emission Inventorv <sup>b</sup>	
	Ratio	$R^{2}$	Ratio	R <sup>2</sup>	Ratio	$R^2$	Ratio	R <sup>2</sup>		<b>On-road Sources</b>
1996										
South Coast Air Basin <sup>c</sup>	0.46	0.96	0.66	0.89	0.64	0.87			0.54	
Burbank	0.46	0.98	0.69	0.92	0.67	0.95				
Los Angeles	0.45	0.97	0.60	0.85	0.59	0.87				
Long Beach	0.48	0.87								
Riverside	0.49	0.72								
Azusa			0.73	0.92	0.70	0.83				
Sepulveda Tunnel							1.79	0.97		
Caldecott Tunnel										
1997										
South Coast Air Basin <sup>c</sup>	0.41	0.84								
Burbank	0.41	0.67								
Los Angeles	0.42	0.93								
Long Beach	0.39	0.70								
Caldecott Tunnel										

# Table 3.7 Linear Regression Parameters for Correlations Between Ambient Concentrations of o-Xylene and CO<sup>a</sup>

a. Concentration units are ppmv for CO and ppbv for o-xylene. CO background of 100 ppb was subtracted in CO measurements.

Below-LOD values were excluded in ratio calculation. Regression line was forced through zero.

b. Emission ratios were obtained by using SoCAB emission inventory data in 1997.

	TAC N	etwork	DRI Da	ta (AM)	DRI Data	(AM&PM)	Tunn	el Data	Emissi	on Inventory <sup>b</sup>
	Ratio	R <sup>2</sup>	Ratio	R <sup>2</sup>	Ratio	R <sup>2</sup>	Ratio	$R^{2}$		On-road Sources
1996										
South Coast Air Basin <sup>c</sup>			1.05	0.54	0.95	0.62			1.24	
Burbank			1.11	0.68	0.99	0.68				
Los Angeles			0.97	0.40	0.96	0.54				
Long Beach										
Riverside										
Azusa			1.10	0.58	0.89	0.61				
Sepulveda Tunnel							1.55	0.92		
Caldecott Tunnel	_									
1997										
South Coast Basin-wide										
Burbank										
Los Angeles										
Long Beach										
Caldecott Tunnel										

#### Table 3.8 Linear Regression Parameters for Correlations Between Ambient Concentrations of Isobutene and CO<sup>a</sup>

a. Concentration units are ppmv for CO and ppbv for isobutene. CO background of 100 ppb was subtracted in CO measurements. Below-LOD values were excluded in ratio calculation. Regression line was forced through zero.

b. Emission ratios were obtained by using SoCAB emission inventory data in 1997.

	TAC N	etwork	DRI Da	ta (AM)	DRI Data	(AM&PM)	Tunnel	Data	Emissi	on Inventorv <sup>b</sup>
	Ratio	$R^2$	Ratio	R <sup>2</sup>	Ratio	R <sup>2</sup>	Ratio	R <sup>2</sup>		On-road Sources
1996										
South Coast Air Basin <sup>c</sup>			0.87	0.58	0.91	0.62			1.22	
Burbank			0.96	0.73	1.02	0.65				
Los Angeles			0.70	0.60	0.74	0.71				
Long Beach										
Riverside										
Azusa			1.03	0.73	1.03	0.74				
Sepulveda Tunnel							0.49	0.92		
Caldecott Tunnel										
1997										
South Coast Air Basin <sup>c</sup>										
Burbank										
Los Angeles										
Long Beach										
Caldecott Tunnel										

#### Table 3.9 Linear Regression Parameters for Correlations Between Ambient Concentrations of *n*-Hexane and CO<sup>a</sup>

a. Concentration units are ppmv for CO and ppbv for n-hexane. CO background of 100 ppb was subtracted in CO measurements. Below-LOD values were excluded in ratio calculation. Regression line was forced through zero.

b. Emission ratios were obtained by using SoCAB emission inventory data in 1997.

#### C-3.2.3.2.1. Estimated Maximum Using Ratio to CO

We calculated ranges of maximum annual-average and one-hour toxic compound concentrations using maximum measured CO concentrations in the SoCAB for 1996-1998 and the range of ratios to CO established in Section C-3.2.3.1. The background-adjusted maximum annual-average and one-hour CO concentrations were both measured at Lynwood in 1996 and are 2.4 ppm and 22.4 ppm, respectively. The calculated maximums for the various compounds are shown in Table 3.10.

Compound	Annual Average (ppbv)	One-Hour Average (ppbv)
Toluene	6-11	52-103
<i>m&amp;p-</i> Xylene	2.6-4.6	25-43
o-Xylene	1.0-4.3	9-40
Isobutene	2.2-3.8	20-36
<i>n</i> -Hexane	1.2-2.4	11-22

# Table 3.10 Estimated Maximum Annual and One-Hour Toxics Concentrations using CO as a Surrogate

#### C-3.2.3.2.2. Maximum One-Hour Averages Extrapolated from Maximum Daily Averages

We estimated the maximum one-hour concentrations by extrapolating from measured maximum daily concentrations. For toluene and *o*-xylene the measured maximum daily concentrations for 1996-1997 in the SoCAB were 19 ppb and 3.5 ppb, respectively, and were measured at Burbank on January 10, 1996. For m&p-xylene the maximum daily concentration was 9.7 ppb, measured on January 10, 1996 at Los Angeles-North Main. We used measured CO daily and maximum one-hour CO concentrations at Burbank and Los Angeles on January 10, 1996 to extrapolate to maximum one-hour toxics concentration assuming proportionality between CO and toxics concentrations at each location. At Burbank the daily and maximum one-hour CO concentrations were 7.43 ppm and 11.6 ppm, respectively. The calculated maximum one-hour-average toluene and o-xylene concentrations are 29.7 ppb and 5.5 ppb, respectively. At Los Angeles the daily and maximum one-hour CO concentrations were 7.0 ppm and 10.3 ppm, respectively. The calculated maximum one-hour *m&p*-xylene concentration is 14.3 ppb. Isobutene and *n*-hexane are not measured as part of the TAC monitoring program, and no estimates were made for these two compounds.

#### C-3.2.3.2.3. Maximum Measured Annual Average

Based on TAC data for 1996-1997, the maximum measured annual-averages for the SoCAB were measured at Burbank in 1996 and were 5.12 ppb for toluene, 2.2 ppb for m&p-xylene, and 0.77 ppb for o-xylene.

## C-3.3. Ethanol

The only ethanol air quality data readily available were those collected by DRI in the summers of 1995 and 1996. We used the 1996 data as the basis for estimating representative population-weighted annual and maximum daily average and maximum one-hour average for 1997. The 1995 data were not used because cleaner burning gasoline was not widely available until 1996. The highest ethanol concentrations are expected in winter. Given only summer data, it was challenging to estimate concentrations in a different season. We opted to use CO as an index of mixing and dispersion to extrapolate from measured maximum ethanol concentrations in the summer to a different season.

Similar to other pollutants, we attempted to correlate ethanol with CO. The results summarized in Table 3.11 showed poor correlation. This was not surprising, given that on-road vehicles currently emit less than one percent of the estimated ethanol emissions in the SoCAB (see Appendix A). Correlations with various organic compounds (not shown) were equally unsuccessful.

#### C-3.3.1. Maximum Daily Average

The maximum daily-average ethanol concentration is expected to occur in winter, and was calculated using one procedure with two different assumptions. The general equation for calculating the maximum daily-average concentration is as follows:

					Annu	al Maximum	24hr Avg. CO
Ethanol	(Max	24hr)	= Ethanol(Hi	6hr Ave) ×		Winter CO I	Emissions hr CO Air Quality
Lununor	(ITTUA	2 m)			Summer	Matching 6	hr CO Air Quality
						Summer CO	Emission

In the equation above, the CO air quality concentrations are divided by the relevant seasonal (winter or summer) emission estimates to adjust for the effects of higher CO emissions in winter. This is because CO is being used as an index of dispersion and mixing under the assumption that CO emissions are kept constant.

This procedure was applied two ways -- once using only data for Los Angeles (the monitoring site with the highest ethanol measurements), and once using the CO data for Lynwood (the site with the highest CO concentrations) and ethanol data for Los Angeles. The latter application was made attempting to represent conditions of very limited mixing and dispersion that occur at Lynwood. A maximum daily-average ethanol concentration of 47 ppb was calculated using the Los Angeles maximum as follows:

Ethanol (Max 24hr) = 25.7 ppb× $\frac{\overline{6520 \text{ tons/day}}}{\overline{3.10 \text{ ppm}}}$  = 47 ppb

A similar calculation yielded 51 ppb using Lynwood CO data.

	TAC Ne	etwork	DRI Dat	ta (AM)	DRI Data	a (AM&PM)	Tunn	el Data	Emissio	n Inventorv <sup>b</sup>
	Ratio	R <sup>2</sup>	Ratio	R <sup>2</sup>	Ratio	R <sup>2</sup>	Ratio	$R^2$	All Sources	On-road Sources
1996										
South Coast Air Basin <sup>c</sup>			4.55	0.22	4.43	0.27			3.75	0.04
Burbank			4.25	0.12	4.32	0.23				
Los Angeles			4.37	0.17	4.34	0.23				
Long Beach										
Riverside										
Azusa			5.27	0.35	4.71	0.34				
Sepulveda Tunnel										
Caldecott Tunnel										
1997										
South Coast Air Basin <sup>c</sup>										
Burbank										
Los Angeles										
Long Beach										
Caldecott Tunnel										

#### Table 3.11 Linear Regression Parameters for Correlations Between Ambient Concentrations of Ethanol and CO<sup>a</sup>

a. Concentration units are ppmv for CO and ppbv for ethanol. CO background of 100 ppb was subtracted in CO measurements.

Below-LOD values were excluded in ratio calculation. Regression line was forced through zero.

b. Emission ratios were obtained by using SoCAB emission inventory data in 1997.

#### C-3.3.2. Maximum One-Hour Average

The maximum one-hour-average ethanol concentration is expected to occur in winter and was calculated using one procedure with two different assumptions. The general equation for calculating the maximum one-hour average is as follows:

Ethanol (Max 1hr) = Ethanol (Hi 3hr Ave.)  $\times \frac{\frac{\text{Annual Maximum 1hr Avg. CO}}{\text{Winter COEmissions}}}{\frac{\text{Summer Matching 3hr CO Air Quality}}{\text{Summer CO Emissions}}}$ 

This procedure was applied two ways -- once using only data for Los Angeles (the monitoring site with the highest ethanol measurements), and once using the maximum one-hour-average CO from Lynwood (the site with the highest CO concentrations) and the rest of the data from Los Angeles. The latter application was made attempting to represent conditions of very limited mixing and dispersion that occur at Lynwood. A maximum one-hour-average ethanol concentration of 78 ppb was calculated using the Los Angeles maximum as follows:

Ethanol (Max 1hr) = 37.0 ppb 
$$\times \frac{\frac{10.3 \text{ ppm}}{6520 \text{ tons/day}}}{\frac{3.97 \text{ ppm}}{5283 \text{ tons/day}}} = 78 \text{ ppb}$$

A similar calculation yielded 108 ppb using Lynwood CO data.

#### C-3.3.3. Population-Weighted Annual Exposure

There were three sites for which data were collected in the DRI study -- Azusa, Burbank and Los Angeles -North Main. For each site, an estimated annual-average ethanol concentration was calculated using carbon monoxide concentrations as an index of ventilation and dispersion. The following equation was used:

	Annual CO Air Quality
Ethanol (Annual) = Ethanol (Summer 1996 Avg.) $\times$	Annual COEmissions
Eutanoi (Annual) – Eutanoi (Summer 1990 Avg.) ×	Summer 1996 CO Air Quality
	Summer CO Emissions

The time period for averaging the summer 1996 CO data was 600-900 and 1300-1600 PDT for July 7, 1996 through September 29, 1996. This corresponds to the time period over which the DRI ethanol data were collected. Applying the above equation to Burbank data, we obtain:

Ethanol (Annual) = 
$$5.35 \text{ ppb} \times \frac{\frac{1.705 \text{ ppm}}{5782 \text{ tons/day}}}{\frac{1.651 \text{ ppm}}{5283 \text{ tons/day}}} = 5.04 \text{ ppb}$$

The population-weighted annual-average concentration was calculated using annual-average data for the three monitoring sites and the procedure described in Section C-3.2.1.3.3 above. The population-weighted annual-average concentration calculated to represent the SoCAB in 1997 is 5.4 ppb ethanol.

#### C-3.4. Alkylates

Similar to the analysis performed for toluene, we also did a sensitivity evaluation of 1997 concentrations for the class of organic compounds known as alkylates. Alkylates is a class of branched  $C_6$ + alkanes and branched cycloalkanes present in motor vehicle fuels. Based on the ambient measurements by DRI in the SoCAB in 1996, there were thirty-two alkylates observed in the atmosphere, which are listed in Table 3.12, together with the weight percentage of each alkylate of the total alkylates observed at each monitoring site. We used the DRI data and measured CO concentrations in 1996-1998 to estimate annual-average and maximum one-hour total alkylate concentrations, using a procedure similar to that in used Section C-3.2.3 for isobutene and *n*-hexane. Below we discuss the development of a ratio between the total alkylates and CO followed by an estimate of the 1997 pollutant concentration.

We provided the 1997 estimated pollutant data for alkylates to OEHHA. Since OEHHA concluded that there are no data that would indicate a toxicological problem with any of the alkylates, primarily due to lack of data, there was no need to model air quality concentrations for the 2003 scenarios.

#### C-3.4.1. Ratio Between Total Alkylates and CO

Following a procedure similar to that described in Section C-3.2.1.2, we developed ratios between the total alkylates and CO. Both DRI data and Sepulveda Tunnel data were used in our analysis. Alkylates are not measured in the TAC monitoring network.

Table 3.13 summarizes the ratios and correlation coefficients between total alkylates and CO derived from DRI data and Sepulveda data. Excellent correlation was observed for all data sets. The ratios obtained range from 6.5 to 9.6

Chemical Name	Azusa	Burbank	LA-North Main
2.2-Dimethylbutane	3.31%	3.20%	3.34%
2.3-Dimethylbutane	0.08%	0.11%	0.05%
2-Methylpentane	15.93%	15.35%	15.88%
3-Methylpentane	9.36%	9.13%	9.29%
Methylcyclopentane	0.00%	0.00%	0.00%
Methylcyclopentane	9.46%	9.52%	10.06%
2,4-Dimethylpentane	4.26%	4.53%	4.25%
2.2.3-Trimethylbutane	0.20%	0.19%	0.17%
3.3-Dimethylpentane	0.66%	0.62%	0.65%
2.3-Dimethylpentane	6.48%	7.31%	6.73%
1.3-Dimethylcyclopentane	2.06%	2.09%	2.18%
3-Ethylpentane	2.90%	2.78%	3.96%
2,2,4-Trimethylpentane	14.16%	12.65%	12.03%
Methylcyclohexane	6.15%	7.92%	5.78%
2,5-Dimethylhexane	1.68%	1.64%	1.51%
2.4-Dimethvlhexane	3.65%	3.61%	3.36%
2.3.4-Trimethylpentane	4.78%	4.14%	3.95%
2-Methylheptane	2.42%	2.70%	2.56%
4-Methylheptane	0.99%	1.04%	1.03%
3-Methylheptane	2.00%	2.18%	2.20%
2,2,5-Trimethylhexane	0.52%	0.52%	0.56%
1.1-Dimethylcyclohexane	0.01%	0.01%	0.02%
2.3.5-Trimethylhexane	1.51%	2.15%	3.36%
2,4-Dimethylheptane	0.13%	0.11%	0.13%
4.4-Dimethylheptane	0.48%	0.48%	0.52%
2.6-Dimethylheptane	0.63%	0.56%	0.61%
2,5-Dimethylheptane	1.75%	1.57%	1.67%
3.3-Dimethylheptane	0.95%	0.72%	0.82%
2-Methyloctane	1.39%	1.36%	1.41%
3-Methyloctane	1.20%	1.12%	1.18%
2.6-Dimethyloctane	0.17%	0.18%	0.16%
3,6-Dimethyloctane	0.73%	0.53%	0.60%
Total	100.00%	100.00%	100.00%

# Table 3.12 Weight Percentage of Each Alkylate of the Total Alkylates Observed<br/>at Each Monitoring Site

	TAC Ne	etwork	DRI Da	ta (AM)	DRI Data	(AM&PM)	Tunnel	Data	Emiss	ion Inventorv <sup>b</sup>
	Ratio	$R^{2}$	Ratio	R <sup>2</sup>	Ratio	R <sup>2</sup>	Ratio	$R^2$		<b>On-road Sources</b>
1996										
South Coast Air Basin <sup>c</sup>			8.79	0.86	8.88	0.83				
Burbank			9.49	0.96	9.64	0.91				
Los Angeles			7.77	0.82	7.90	0.85				
Long Beach										
Riverside										
Azusa			9.55	0.92	9.53	0.80				
Sepulveda Tunnel							6.53	0.95		
Caldecott Tunnel										
1997										
South Coast Air Basin <sup>c</sup>										
Burbank										
Los Angeles										
Long Beach										
Caldecott Tunnel										

#### Table 3.13 Linear Regression Parameters for Correlations Between Ambient Concentrations of Total Alkylates and CO<sup>a</sup>

a. Concentration units are ppmv for CO and ppbv for total alkylates. CO background of 100 ppb was subtracted in CO measurements. Below-LOD values were excluded in ratio calculation. Regression line was forced through zero.

b. Emission ratios were obtained by using SoCAB emission inventory data in 1997.

#### C-3.4.2. Estimated 1997 Concentrations

We made estimates of expected maximum annual-average and maximum one-hour-average concentrations for the total alkylates. These were done by using maximum measured CO concentrations in the SoCAB from 1996-1998 and the range of ratios to CO established above. The background-adjusted maximum annual-average and one-hour CO concentrations, both measured at Lynwood in 1996, are 2.4 ppm and 22.4 ppm, respectively. The calculated maximum for the total alkylates is shown in Table 3.14.

Alkylate (	Concentrations Using CO a	as a Surrogate
Compound	Annual Average (ppbv)	One-Hour Average(ppbv)
Total Alkylates	15.6-23.0	146-216

# Table 3.14 Estimated Maximum Annual-Average and One-Hour-average Alkylate Concentrations Using CO as a Surrogate

## C-3.5. PAN and PPN

Information used to establish 1997 baseline concentrations for peroxyacetyl nitrate (PAN) and peroxypropionyl nitrate (PPN) is contained in a separate document (Grosjean, 1999). Table 3.15 compares PAN and PPN measurements made at Azusa during a special study in 1993 and SCOS97-NARSTO with model predictions for the 1997 baseline scenario. The PPN model species represents higher acyl peroxy nitrates in addition to peroxypropionyl nitrate. The measured PPN concentrations should be doubled to roughly approximate the PPN modeled species (Grosjean, personal communication). Based on these data, we established the range of estimated 1997 PAN and PPN concentrations, shown in Table 3.16.

Compound	Year	Max. 1-hr Ave. (ppbv)	Max. Daily Ave. (ppbv)	Average (ppbv)
PAN	1993	9.9	5.0	3.0
	1997	4.8	2.1	0.9
	Model	1.9	1.4	-
PPN	1993	1.5	0.9	0.5
	1997	0.7	-	0.3
	Model <sup>a</sup>	0.3	0.5	-

 Table 3.15
 PAN and PPN Concentrations Measured and Modeled at Azusa

<sup>a</sup>The PPN model species represents higher acyl peroxy nitrates in addition to peroxypropionyl nitrate.

Compounds	Max. 1-hr Ave. (ppbv)	Max. Daily Ave. (ppbv)
PAN	5-10	2.5-5.0
<b>PPN</b> <sup>a</sup>	1.5-3.0	1.0-2.0

Table 3.16 Estimated Maximum 1-Hour-Average and Daily-Average 1997
PAN and PPN Concentrations

<sup>a</sup>The PPN model species represents higher acyl peroxy nitrates in addition to peroxypropionyl nitrate.

# C-4. Methods to Estimate Future Air Quality Concentrations

### C-4.1. Basic Procedure for all Pollutants

Future air quality concentrations were estimated using estimated 1997 concentrations (Section C-3) and results from the photochemical simulation model for the specific pollutant of concern in 2003. Unlike the 1997 estimates, we did not use correlations between CO and toxic compounds to estimate 2003 concentrations. Separate model simulations were made using 1997 and 2003 baseline (MTBE-based CaRFG), 2003 ethanol at 2.0 wt% oxygen, 2003 ethanol at 3.5 wt% oxygen, and 2003 non-oxygenate. Although the model simulation covered three days, the only day deemed suitable for comparison was the third day. This was because results on the first and second day are strongly affected by the choice of initial conditions. The general procedure for calculating 2003 air quality was:

2003 Air Quality for Fuel X = 1997 Air Quality  $\times \frac{\text{Modeled 2003 Air Quality for Fuel X}}{\text{Modeled 1997 Air Quality}}$ 

Departures from this basic procedure are discussed in Sections C-4.2 and C-4.3.

#### C-4.1.1. Maximum Daily and One-Hour Averages

For estimating 2003 maximum daily and one-hour-average concentrations, we normally used the maximum concentrations for the highest grid cell in the modeling region for the third day of the model simulation as the model air quality parameter in the equation above. In applying this general procedure, the grid cell with the modeled peak concentration and the time at which the peak occurred are not required to be the same in the numerator and denominator of the equation.

Notable exceptions to his general procedure are estimates for benzene, 1,3-butadiene, carbon monoxide, ethanol, and MTBE. For these, we used the modeled daily average and one-hour average for the grid cell containing Lynwood, the monitoring site with the highest measured CO concentrations. The use of the Lynwood grid cell concentrations was because these pollutants are primary pollutants and Lynwood was the site of the highest estimated concentrations for these pollutants in 1997.

#### C-4.1.2. Population-Weighted Annual Exposure

For the population-weighted annual-average exposure, we normally used the region-wide population-weighted average of the daily-average model results for the third day of the model simulation as the model air quality parameter in the equation above. This was believed reasonable for any compound that is a primary pollutant. Acetaldehyde and formaldehyde have substantial contributions from secondary reactions in the atmosphere and were treated differently as discussed below.

#### C-4.2. Special Procedures for Criteria Pollutants

Generally we followed the basic procedures for estimating 2003 air quality concentrations except as follows:

For 2003 maximum daily and maximum one-hour-average concentrations for CO, we used the model values for the grid cell containing Lynwood, as discussed above. For estimating 2003 maximum eight-hour-average ozone concentrations, we used the maximum grid cell eight-hour-average model results. For maximum eight-hour CO concentrations, we used model values for the grid cell containing Lynwood.

#### C-4.3. Special Procedures for Toxic Pollutants

Generally we followed the basic procedures for estimating 2003 air quality concentrations except as follows:

For maximum daily and maximum one-hour-average concentrations for benzene, 1,3-butadiene, ethanol and MTBE, we used the model values for the grid cell containing Lynwood, as discussed above.

For ethanol, the maximum daily and maximum one-hour-average concentrations for Los Angeles-North Main were calculated using model values from the grid cell containing the Los Angeles-North Main monitoring site.

For acetaldehyde and formaldehyde, we used the basic procedure for the maximum daily and maximum one-hour averages. This was deemed reasonable because in 1997 the maximum daily and maximum one-hour concentrations occurred in August, the month of the model simulation. For calculating the maximum daily and maximum one-hour-average concentrations, we used total aldehyde concentrations from the model. For the population-weighted annual-average, a different procedure was needed because the contribution from primary emission sources versus secondary formation in the atmosphere was expected to be different in different seasons of the year. The basic equation for estimating 2003 aldehydes was as follows:

2003 Air Quality = 0.5 ppb background

$\pm 1997$ Primary Air Quality $\times \frac{N}{N}$	Indeled 2003 Primary Air Quality           Indeled 2003 Primary Air Quality				
+ 1997 Thinking All Quality $\wedge \frac{1}{N}$	Iodeled 1997 Primary Air Quality				
+ 1997 Secondary Air Quality $\times$	Modeled 2003Secondary Air Quality				
	Modeled 1997 Secondary Air Quality				

This requires that the amount of primary and secondary aldehyde be known for 1997 and for the model results. The model was set up so secondary aldehydes were tracked separately from primary aldehydes. The 1997 Primary Air Quality and 1997 Secondary Air Quality were determined from 1996-1997 aldehyde and CO data using the following procedure:

- 1. Determine primary aldehyde to CO ratio representative of 1997 -- this was done in Section C-3.2.2.2.
- 2. Determine average CO for month using all CO measurements at each monitoring site, adjusted to remove 0.1 ppm background.
- 3. Determine average CO for each site-month combination using just aldehyde sampling days, adjusted to remove 0.1 ppm background.
- 4. Determine average aldehyde (acetaldehyde or formaldehyde) for site-month combination, adjusted to remove 0.5 ppb background.
- 5. Estimate average primary aldehyde by month =  $\#1 \times \#2$  unless this exceeds  $(\#4 / \#3) \times \#2$ , in which case substitute  $(\#4 / \#3) \times \#2$ .
- 6. Estimate average secondary aldehyde by month =( ( #4 ( #1 x #3 ) ) / #3) x #2; unless #1 x #2 exceeds (#4 / #3) x #2, in which case substitute zero.
- 7. Estimate annual-average primary aldehyde = #5 averaged over 12 months of the year.
- 8. Estimate annual-average secondary aldehyde = #6 averaged over 12 months of the year.

This procedure was applied separately to the DRI based and TAC Network based aldehyde-to-CO ratios developed in Section C-3.2.2.2. The resulting estimated 1997 annual-average primary and secondary aldehyde concentrations are listed in Table 5.1 for acetaldehyde and Table 5.2 for formaldehyde. To obtain population-weighted results, 2003 aldehyde concentrations were estimated for the four monitoring locations shown in the tables, and then these values were weighted by population.

## C-5. Results

The resulting air quality estimates for 1997 and the different fuel scenarios in 2003 are shown in Table 5.3. In general, the table shows the estimated population-weighted annual exposure, maximum daily average, and maximum one-hour average for benzene, 1,3-butadiene, acetaldehyde, formaldehyde, carbon monoxide, nitrogen dioxide, ozone,  $PM_{10}$ , ethanol, MTBE, PAN, and PPN. In some cases the pollutant averaging times are adjusted to show different averaging times. For example, maximum eight-hour averages instead of maximum daily averages are included for carbon monoxide and ozone since there are eight-hour standards for these two pollutants. In addition, the maximum predicted one-hour-average and daily-average concentrations for nitric acid are also included for 1997 and the various 2003 fuel scenarios. A column on the table indicates whether each row of the table was used (Y) or was not used (N) in producing summaries

of the estimated maximum pollutant concentrations. Two reasons that a particular row may not have been used in a summary are that it reflected summer concentrations and winter concentrations were higher, or that it reflected 1997 model results that were lower than estimated 1997 maximum concentrations.

Location / Ratio Source	Acetaldehyde to CO Ratio	Estimated Background	Estimated Primary	Estimated Secondary	Total Acetaldehyde
		-		•	-
Burbank					
TAC Data	0.50	0.50	0.82	0.98	2.30
DRI Data	0.95	0.50	1.36	0.44	2.30
Los Angeles - North Main					
TAC Data	0.50	0.50	0.65	0.92	2.07
DRI Data	0.95	0.50	1.10	0.47	2.07
North Long Beach					
TAC Data	0.50	0.50	0.44	0.38	1.32
DRI Data	0.95	0.50	0.71	0.11	1.32
Riverside - Rubidoux					
TAC Data	0.50	0.50	0.33	0.90	1.73
DRI Data	0.95	0.50	0.57	0.65	1.73

Table5.1	Estimated	1997	Annual-Average	Primary	and	Secondary	
Acetaldehyde Based on Different Ratio Assumptions (Concentrations in ppb)							

Table 5.2Estimated 1997Annual-averagePrimaryandSecondaryFormaldehyde Based on Different Ratio Assumptions (Concentrations in ppb)

Location / Ratio Source	Formaldehyde to CO Ratio	Estimated Background	Estimated Primary	Estimated Secondary	Total Formaldehyde	
Burbank						
TAC Data	1.40	0.50	2.31	4.01	5.33	
DRI Data	2.10	0.50	3.34	2.91	5.33	
Los Angeles - North Main						
TAC Data	1.40	0.50	1.95	3.95	5.14	
DRI Data	2.10	0.50	2.85	2.99	5.14	
North Long Beach						
TAC Data	1.40	0.50	1.25	2.56	3.51	
DRI Data	2.10	0.50	1.88	2.02	3.51	
Riverside - Rubidoux						
TAC Data	1.40	0.50	1.03	3.15	4.02	
DRI Data	2.10	0.50	1.53	2.57	4.02	

## Table 5.3 Estimated Pollutant Concentrations for 1997 and 2003 in the SoCAB

	Used for	1997	2003	2003	2003	2003	Commonto
Benzene, ppbV	Range?	MTBE	MTBE	Et2.0%	EI3.5%	NonOxy	Comments
Population Weighted Annual Exposure							
Based on Measured Values	Y	1.07	0.72	0.70	0.73	0.69	
Projected Level based on CO levels	Ý	1.19	0.80	0.78	0.81	0.76	
Model Output Pop Wt Summer Daily	N	0.82	0.55	0.54	0.56	0.53	Summer
Maximum Daily Average							
Measured Daily Max.	Y	7.4	5.3	5.1	5.3	4.9	
Projected Maximum based on CO levels	Y	9.5	6.8	6.5	6.8	6.4	
Model Output - Lynwood	N	0.69	0.49	0.47	0.49	0.46	Summer
Maximum from Model Output	N	1.72	1.10	1.09	1.10	1.06	Summer
Maximum One-hour Average							
Extrapolated from Measured Daily Max.	Y	11.6	7.4	7.4	7.4	7.4	
Projected Maximum based on CO levels	Y	22.4	14.3	14.3	14.3	14.3	-
Model Output - Lynwood	N	1.1	0.7	0.7	0.7	0.7	Summer
Maximum from Model Output	Ν	3.4	1.9	1.9	2.0	1.9	Summer
1,3-Butadiene, ppb							
Population Weighted Annual Exposure							
Based on Measured Values	Y	0.34	0.19	0.19	0.19	0.19	
Projected Level based on CO levels	Y	0.36	0.20	0.20	0.20	0.20	
Model Output Pop Wt Summer Daily	N	0.074	0.042	0.041	0.041	0.041	Summer
Maximum Daily Average							
Measured Daily Max.	Y	2.0	0.8	0.8	0.8	0.8	
Projected Maximum based on CO levels	Y	2.9	1.2	1.2	1.2	1.2	
Model Output - Lynwood	N	0.5	0.2	0.2	0.2	0.2	Summer
Maximum from Model Output	N	0.88	0.87	0.87	0.87	0.87	Summer
Maximum One-hour Average							
Extrapolated from Measured Daily Max.	Y	3.1	1.6	1.6	1.6	1.6	
Projected Maximum based on CO levels	Y	6.7	3.4	3.4	3.4	3.4	-
Model Output - Lynwood	N	0.2	0.1	0.1	0.1	0.1	Summer
Maximum from Model Output	Ν	3.0	3.0	3.0	3.0	3.0	Summer
Acetaldehyde, ppbV							
Population Weighted Annual Exposure							
Based on Measured Values							
TAC Based Value and Projection	Y	1.75	1.59	1.60	1.74	1.58	
DRI/TAC Based Projection	Y		1.55	1.58	1.79	1.54	
Model Output Pop Wt Summer Daily	N	3.23	2.81	2.81	2.93	2.78	Summer
Maximum Daily Average							
Measured Daily Max.	Y	5.1	5.1	5.1	5.1	5.1	
Maximum from Model Output	Y	6.2	6.2	6.2	6.2	6.2	
Model Output - Upland	N	4.43	3.83	3.86	3.99	3.83	
Maximum One-hour Average							
Extrapolated from DRI Measured Three-hour Max.using O3	Y	17.7	16.7	16.9	17.1	16.9	
Extrapolated from Measured Daily Max.using O3	Y	13.8	13.1	13.2	13.4	13.2	
Maximum from Model Output	N	9.2	8.7	8.8	8.9	8.8	
Model Output - Upland	Ν	6.4	5.6	5.5	5.7	5.5	
Formaldehyde, ppbV							
Population Weighted Annual Exposure							
Based on Measured Values							
TAC Based Value and Projection	Y	4.65	4.22	4.06	4.14	4.04	
DRI/TAC Based Projection	Y		4.12	3.97	4.04	3.95	
Model Output Pop Wt Summer Daily	N	6.85	5.95	5.74	5.86	5.70	Summer
Maximum Daily Average							
Measured Daily Max.	Y	14.0	12.2	11.8	12.1	11.7	
Maximum from Model Output	N	11.35	9.90	9.57	9.79	9.49	
Model Output - Upland	N	9.13	7.96	7.73	7.90	7.66	
Maximum One-hour Average							
Extrapolated from DRI Measured Three-hour Max.using O3	Y	20.3	20.6	20.3	20.5	20.3	
Extrapolated from Measured Daily Max.using O3	Y	37.8	38.3	37.8	38.1	37.8	
Maximum from Model Output	Y	22.7	23.0	22.7	22.9	22.7	
Model Output - Upland	N	13.9	11.8	11.5	11.6	11.4	
	C-47						

	Used for	1997	2003	2003	2003	2003	
Carbon Monoxide, ppmV	Range?	MTBE	MTBE	Et2.0%	Et3.5%	NonOxy	Comments
Maximum Eight-hour Average							
Measured Eight-hour Max.	Y	17.5	14.3	14.3	13.4	14.7	
Model Output - Lynwood	Ν	1.010	0.828	0.828	0.773	0.846	Summer
Maximum from Model Output	Ν	2.43	1.82	1.82	1.66	1.87	Summer
Maximum One-hour Average							
Measured One-hour Max.	Y	22.5	19.2	19.2	18.0	19.7	
Model Output - Lynwood	Ν	1.11	0.95	0.95	0.89	0.97	Summer
Maximum from Model Output	Ν	3.02	2.19	2.19	1.97	2.26	Summer
Nitrogen Dioxide, ppmV							
Maximum Annual Average Exposure							
Based on Measured Values	Y	0.043	No signi	ficant diffe	erence ex	pected ar	mong 2003 scenarios
Maximum Daily Average							
Measured Daily Max.	Y	0.117	0.098	0.097	0.097	0.097	•
Maximum from Model Output	Ν	0.073	0.061	0.060	0.060	0.060	Summer
Maximum One-hour Average	V	0.055	0.005	0.005	0.005	0.005	
Measured One-hour Max. Maximum from Model Output	Y N	0.255 0.105	0.235 0.097	0.235 0.097	0.235 0.097	0.235 0.097	Summer
Maximum nom Model Output	IN	0.105	0.097	0.097	0.097	0.097	Summer
Ozone, ppbV							
Maximum Eight-hour Average							
Measured Eight-hour Max.	Y	0.206	0.196	0.196	0.196	0.196	
Maximum from Model Output	Ν	0.187	0.178	0.178	0.178	0.178	
Maximum One-hour Average							
Measured One-hour Max.	Y	0.244	0.230	0.228	0.228	0.228	
Maximum from Model Output	Ν	0.236	0.222	0.220	0.220	0.220	
Particulate Matter (10 μm or less). μα/m <sup>3</sup>							
Maximum Annual Geometric Mean							
Based on Measured Values	Y	56	No siani	ficant diffe	erence ex	pected ar	mong 2003 scenarios
Maximum Daily Average							g
Measured Daily Max.	Y	227	No signi	ficant diffe	erence ex	pected ar	mong 2003 scenarios
Ethanol, ppbV							
Population Weighted Annual Exposure							
Estimated from Summer Measurements	Y	5.4	5.1	7.6	8.8	5.1	Whole Year
Model Output Pop Wt Summer Daily	Ν	2.05	1.95	2.87	3.35	1.94	Summer
Maximum Daily Average							
Extrapolated Daily Summer Max.	Ν	21	20	29	33	20	Summer
Estimated Daily Winter Max.							
Lynwood	Y	51	49	71	81	49	Winter
LA-N Main	Y	47	45	64	75	45	Winter
Model Output	NI	4.00	4 77	0.50	0.00	4 77	0
Lynwood	N	1.86	1.77	2.58	2.96	1.77	Summer
LA-N Main Maximum from Madel Output	N N	4.60	4.40	6.29	7.30	4.38	Summer Summer
Maximum from Model Output Maximum One-hour Average	íN	19.1	17.3	17.9	18.1	17.4	Summer
Extrapolated One-hour Summer Max.	Ν	42	39	56	64	39	Summer
Estimated One-hour Winter Max.	IN IN	42	55	50	04	55	Summer
Lynwood	Y	108	101	145	165	101	Winter
LA-N Main	Y	78	74	143	140	74	Winter
Model Output	·					• •	
Lynwood	Ν	3.2	3.0	4.3	4.9	3.0	Summer
LA-N Main	N	5.7	5.4	8.3	10.2	5.4	Summer
Maximum from Model Output	Ν	45.6	41.4	42.3	42.8	41.4	Summer

	Used for	1997	2003	2003	2003	2003	0
	Range?	MTBE	MTBE	Et2.0%	Et3.5%	NonOxy	Comments
MTBE, ppbV							
Population Weighted Annual Exposure							
Based on Measured Values	Y	3.9	3	0	0	0	
Projected Level based on CO levels	Y	3.6	2.4	0	0	0	
Model Output Pop Wt Summer Daily	Ν	1.09	0.72	0	0	0	Summer
Maximum Daily Average							
Measured Daily Max.	Y	13	9	0	0	0	
Projected Maximum based on CO levels	Y	29	20	0	0	0	
Model Output - Lynwood	Ν	0.97	0.67	0	0	0	Summer
Maximum from Model Output	Ν	2.63	1.67	0	0	0	Summer
Maximum One-hour Average							
Extrapolated from Measured Daily Max.	Y	19	13	0	0	0	
Projected Maximum based on CO levels	Y	67	46	0	0	0	
Model Output - Lynwood	Ν	1.6	1.1	0	0	0	Summer
Maximum from Model Output	Ν	6.1	3.9	0	0	0	Summer
PAN, ppbV							
Maximum Daily Average							
Upper Baseline	Y	5.0	4.8	4.8	4.9	4.7	
Lower Baseline	Y	2.5	2.4	2.4	2.4	2.4	
Maximum from Model Output	Ν	2.12	2.03	2.02	2.06	2.00	
Maximum One-hour Average							
Upper Baseline	Y	10.0	9.5	9.3	9.5	9.1	
Lower Baseline	Y	5.0	4.8	4.7	4.8	4.5	
Maximum from Model Output	Ν	4.4	4.2	4.1	4.2	4.0	
"Model PPN", ppbV							
Maximum Daily Average							
Upper Baseline	Y	2.0	2.0	2.0	2.0	2.1	
Lower Baseline	Y	1.0	1.0	1.0	1.0	1.0	
Maximum from Model Output	Ν	0.579	0.575	0.588	0.571	0.600	1
Maximum One-hour Average							
Upper Baseline	Y	3.0	3.0	3.0	3.0	3.0	
Lower Baseline	Y	1.5	1.5	1.5	1.5	1.5	
Maximum from Model Output	Ν	1.4	1.4	1.4	1.4	1.4	
Nitric Acid, ppb (Model Output Only)							
Population Weighted Summer Daily Exposure							
From Model	Y	12.4	11.0	11.0	11.0	11.0	
Maximum Daily Average							
Maximum from Model Output	Y	36.7	32.4	32.3	32.2	32.3	

# C-6. References

- ARB (Air Resources Board) (1993) "Guidance for Using Air Quality-Related Indicators in Reporting Progress in Attaining the State Ambient Quality Standards," Resolution 93-49, Technical Support Division, July.
- ARB (Air Resources Board) (1998a) "California State and Local Air Monitoring Network Plan," Report TSD 98-005, Planning and Technical Support Division, Air Quality Data Branch, October (<u>http://www.arb.ca.gov/aqd/namslams/namslams.htm</u>).
- ARB (Air Resources Board) (1998b) "California Ambient Air Quality Data 1980-1997,"
   CD Number: PTSD-98-010-CD, Planning and Technical Support Division, Air Quality Data Branch, Client Support Services Section, December.
- ARB (Air Resources Board) (1999a) "Air Monitoring Quality Assurance Manual," Monitoring and Laboratory Division, June (http://www.arb.ca.gov/aaqm/qmosqual/qamanual/qamanual.htm).
- ARB (Air Resources Board) (1999b) "California Emission Inventory Data," Planning and Technical Support Division, Emission Inventory Branch, July (http://www.arb.ca.gov/emisinv/emsmain/emsmain.htm).
- Atkinson, R. (1994) "Gas-Phase Tropospheric Chemistry of Organic Compounds," Journal of Physical and Chemical Reference Data, Monograph No. 2.
- Carter, W.P.L. (1999) "Documentation of the SAPRC-99 Chemical Mechanism for VOC Reactivity Assessment," Draft Report to California Air Resources Board, Contract 92-329 and 95-308, September.
- Gertler A.W., J.C. Sagebiel, W.A. Dippel, J.A. Gillies, F. Gofa, and C.M. O'Connor (1997) "Comparison of 1995 and 1996 Emissions at the Los Angeles Sepulveda Tunnel Including the Impact of California Phase 2 RFG," Final Report to Coordinating Research Council, Inc. and South Coast Air Quality Management District, Contract No. E-27, October.
- Grosjean D. (1999) "Ambient Levels of Peroxyacetyl Nitrate in Southern California," Draft Report to California Air Resources Board, September.
- Grosjean, D. (1999) Personal Communication, October.
- Kirchstetter T.W. and R.A. Harley (1999a) "Impact of Reformulated Fuels on Particle and Gas-Phase Emissions from Motor Vehicle," Final Report to California Air Resources Board, Contract No. 95-330, March.
- Kirchstetter T.W., B.C. Singer, R.A. Harley, G.R. Kendall, and M. Traverse (1999b)
  "Impact of California Reformulated Gasoline on Motor Vehicle Emissions: 1. Mass Emission Rates," *Environmental Science & Technology*, 33: 318-328.
- Kirchstetter T.W., B.C. Singer, R.A. Harley, G.R. Kendall, and M. Traverse (1999c)
  "Impact of California Reformulated Gasoline on Motor Vehicle Emissions
  2. Volatile Organic Compound Speciation and Reactivity," *Environmental Science & Technology*, 33: 329-336.

Zielinska B., J. Sagebiel, G. Harshfield, and E. Fujita (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 SoCAB," Final Report to California Air Resources Board, Contract No. 94-322, February.