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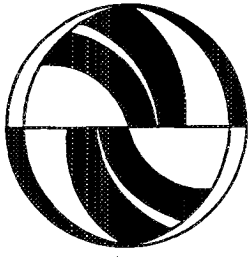
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**Impacts of Oxygenated Gasoline Use on  
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Reprint  
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**The University of California  
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# Impact of Oxygenated Gasoline Use on California Light-Duty Vehicle Emissions

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Light-duty vehicle emissions were measured at the Caldecott Tunnel in August and October 1994. In the interval between these two periods, the average oxygen content of gasoline sold in the San Francisco Bay area increased from 0.3 to 2.0% by weight. Compared to the August (low-oxygenate) sampling period, measured pollutant emission rates during the October (high-oxygenate) sampling period for CO and VOC decreased by  $21 \pm 7$  and  $18 \pm 10\%$ , respectively, while  $\text{NO}_x$  emissions showed no significant change. Formaldehyde emissions increased by  $13 \pm 6\%$ , acetaldehyde emissions did not change significantly, and benzene emissions decreased by  $25 \pm 17\%$ . Speciated VOC emission profiles show that the use of oxygenated gasoline resulted in higher MTBE and lower aromatic hydrocarbon emissions, higher isobutene, and lower aromatic aldehydes. The normalized reactivity of NMOG emissions did not change significantly between the low-oxygenate and high-oxygenate sampling periods. VOC exhaust speciation profiles for vehicles operating in the hot-stabilized mode at the Caldecott Tunnel match the speciation profile for cold-start emissions from new vehicles as measured in the Auto/Oil program. California's motor vehicle emission factor model, EMFAC7F, accurately predicts the VOC/ $\text{NO}_x$  ratio measured at the Caldecott Tunnel in August, but underpredicts the observed CO/ $\text{NO}_x$  ratio by a factor of 1.5–2.2 over the range of vehicle speeds observed at the tunnel.

## 1. Introduction

Motor vehicles are an important source of air pollution. The Environmental Protection Agency estimates that, in 1990, on-road motor vehicles accounted for 29% of the total volatile organic compound (VOC) emissions, 33% of the total oxides of nitrogen ( $\text{NO}_x$ ) emissions, and 65% of all carbon monoxide (CO) emissions nationwide (1). In urban areas, motor vehicle emissions typically account for even

larger fractions of total anthropogenic air pollutant emissions (2). Estimates for the San Francisco Bay area indicate that on-road vehicles contributed 75% of all CO emissions, 58% of all  $\text{NO}_x$  emissions, and 38% of all reactive organic gas (ROG) emissions in 1990 (3).

To reduce motor vehicle emissions, the Clean Air Act amendments of 1990 mandate the use of reformulated and oxygenated gasolines. Starting in 1995, reformulated gasoline has been required in nine areas with serious ozone air quality problems; oxygenated gasoline has been required since 1992 during the wintertime in ~40 CO nonattainment areas. A minimum fuel oxygen content of 2.7% by weight is required for all gasoline sold in CO nonattainment areas during the high-CO portion of the year. Most large urban areas in California, including the San Francisco Bay area, are required to sell oxygenated gasoline. However, in California, the required oxygen content has been set at a lower level of 1.8–2.2% by weight because of concerns of increased  $\text{NO}_x$  emissions.

The effects of oxygenated gasoline use on vehicle emissions have been studied by several researchers (4–14) as summarized in Table 1. Bishop and Stedman (8) used remote sensing to obtain more than 117 000 vehicle exhaust measurements during the Colorado oxy-fuels program. Results showed that CO emissions decreased by  $16 \pm 3\%$  following an increase in gasoline oxygen content from 0 to 2% by weight. The measured reduction in emissions was dominated by vehicles having exhaust CO concentrations above 1%; these high-emitting vehicles comprised only 25% of the vehicle fleet. Dynamometer studies indicate that an increase in oxygenates such as methyl *tert*-butyl ether (MTBE) from 0 to 2% or more oxygen by weight results in reduction of CO emissions by 15–20%, reduction of HC emissions by 8%, and no significant change in  $\text{NO}_x$  emissions from light-duty vehicles (4, 11, 12). An increase of  $5.1 \pm 4.1\%$  in  $\text{NO}_x$  emissions was found when fuel ethanol was increased from 0 to 3.5% oxygen by weight (6). Other oxygenates such as MTBE examined in the same study at levels of 2.7% oxygen by weight were not found to increase  $\text{NO}_x$  emissions significantly (6).

Dynamometer studies usually achieve a high degree of control over test conditions and fuel composition variables. However, the test procedure is time-consuming and costly, and as a result, the number of vehicles tested in most of the studies listed in Table 1 is small. Moreover, most of the vehicles tested had correctly functioning emissions control equipment. It is now well-established that a small minority of vehicles contribute the majority of CO and HC tailpipe emissions (15). Emissions from seven high-emitting vehicles were measured as a function of fuel composition during phase II of the Auto/Oil program (7), but these vehicles behaved erratically during dynamometer tests, and this variability masked the fuel effects under study. As mentioned above, Bishop and Stedman (8) measured CO emissions from a large number of in-use vehicles. However, the remote sensors used at the time were not capable of measuring VOC or  $\text{NO}_x$  emissions. Thus, the overall effects of oxygenated gasoline on in-use vehicle emissions remain uncertain.

Motor vehicle emissions in California and the rest of the United States are estimated using emission factor models,

TABLE 1

## Previous Research on the Impact of Oxygenated Gasoline Use on Vehicle Emissions

study	vehicles observed	comments
Auto/Oil, phase I (4, 5)	20 light-duty vehicles, model year 1989 14 light-duty vehicles, model years 1983–1985	dynamometer testing; studied effects on emissions of fuel variables including aromatics, MTBE, olefins, and $T_{90}$
Auto/Oil, phase I (6)	20 light-duty vehicles, model year 1989	dynamometer testing; studied effects of RVP and fuel oxygenates (ethanol, MTBE, and ETBE) on emissions
Auto/Oil, phase II (7)	7 high-emitting vehicles	dynamometer testing; variability in air/fuel ratio masked fuel effects under study
Bishop and Stedman (8)	over 117 000 measurements of in-use vehicles	remote sensing of CO emissions during the 1988–1989 wintertime oxygenated fuel program in Denver
ARB (9)	13 California vehicles, model years 1973–1991	dynamometer testing; measured effects of MTBE, ETBE, and ethanol content on emissions
EPA (10)	3 pre-1985 light-duty passenger cars	dynamometer testing; measured effects of adding MTBE at various ambient temperatures
Chevron (11, 12)	19 light-duty vehicles, model years 1970–1990	dynamometer testing using a reformulated premium grade gasoline containing 2.1% oxygen by weight
ARCO (13)	20 nontalyst light-duty vehicles, model years 1970–1979	dynamometer testing; measured regulated emissions and exhaust reactivity using a reformulated gasoline containing 1% oxygen by weight
Dolislager (14)	analysis of wintertime ambient air measurements in CO-nonattainment area in California	used $NO_x$ as an indicator of meteorological dispersion to quantify effects of oxygenated fuel program in California

EMFAC and MOBILE, respectively, together with information on vehicle populations and activity. Measurements of pollutant concentrations in roadway tunnels and in ambient air (16, 17) have raised questions about the accuracy of emission factor model predictions. In 1987, on-road vehicle emissions were measured in the Sherman Way tunnel in Van Nuys, CA, by Ingalls et al. (18). Comparisons between emission factor model predictions and results from the Van Nuys Tunnel study suggested that EMFAC (version 7C) was underestimating the emissions of CO and HC by factors of ~3 and 4, respectively (16). Since the Van Nuys tunnel study in 1987, the EMFAC and MOBILE models have been revised several times. In addition, there has been a significant turnover in the motor vehicle population since 1987; new vehicles have entered the fleet, and numerous older vehicles have been scrapped.

Motor vehicle emission rates were measured by Pierson et al. (19) in 1992 in the Fort McHenry Tunnel, near Baltimore, MD, and in the Tuscarora Tunnel on the Pennsylvania turnpike. At the Fort McHenry Tunnel, the MOBILE5 model accurately predicted the measured light-duty vehicle emissions of CO and non-methane hydrocarbons (NMHC) and overpredicted  $NO_x$  emissions by a factor of 1.6. MOBILE5 overpredicted light-duty vehicle emission rates of both CO and NMHC by a factor of ~2.5 and overpredicted  $NO_x$  emissions by a factor of 4.2 at the Tuscarora Tunnel. The findings of these studies differ from the earlier results of the Van Nuys Tunnel study, where emission factor models significantly underpredicted CO and HC emission rates.

In addition to quantifying total VOC mass emission rates accurately, it is important to know the chemical composition of VOC emissions. Speciation profiles, which specify weight fractions of individual compounds relative to the total mass of VOC emitted, are needed to assess the atmospheric reactivity of VOC emissions. An accurate speciation profile for motor vehicle hydrocarbon emissions is also necessary in source apportionment studies that use speciated ambient concentration data together with source fingerprints to calculate the contributions of individual sources to total

pollutant concentrations at a receptor (20). Finally, determination of hazardous organic air pollutants in source samples is needed to compile accurate emission inventories for these compounds.

Speciated hydrocarbon emissions from motor vehicles have been measured in California in two recent on-road studies. Ingalls and Smith (21) reported measurements of methane, ethylene, ethane, acetylene, propylene, propane, benzene, toluene, ethylbenzene, and xylenes in the Sherman Way Tunnel in Van Nuys. The relative standard deviations in the speciation profile derived from these data are 50% or higher because the Sherman Way Tunnel is short (220 m) and measured hydrocarbon concentrations at the tunnel exit were comparable to concentrations at the entrance. Zielinska and Fung (22) measured speciated non-methane hydrocarbons and semivolatile hydrocarbons in the Caldecott Tunnel, located in the San Francisco Bay area. Their measurements reflect composite hydrocarbon emissions from a mix of light- and heavy-duty vehicles.

Significant changes to California gasoline properties occurred in 1992 with the introduction of oxygenated and phase I reformulated gasolines. These changes affect the speciation of VOC emissions from motor vehicles. Addition of oxygenates such as MTBE to gasoline affects the speciation as well as the total mass of VOC emissions (12). California phase I reformulated gasoline specifications limit the summertime Reid vapor pressure (RVP) of gasoline to 7.8 psi, whereas prior to 1992, the summertime RVP limit was 9.0 psi. To reduce RVP, the lightest hydrocarbons such as butanes and pentanes must be reduced or eliminated from gasoline. This fuel change may affect the speciation of exhaust emissions as well as reducing evaporative emissions. Therefore, new VOC speciation profiles for light-duty vehicle emissions are needed.

The main objectives of this study were (1) to measure the changes in light-duty vehicle emissions of CO,  $NO_x$ , and VOC that result from the use of oxygenated gasoline, (2) to compare measured CO/ $NO_x$  and VOC/ $NO_x$  ratios with estimates from the latest version of California's mobile source emission factor model (EMFAC7F), and (3) to

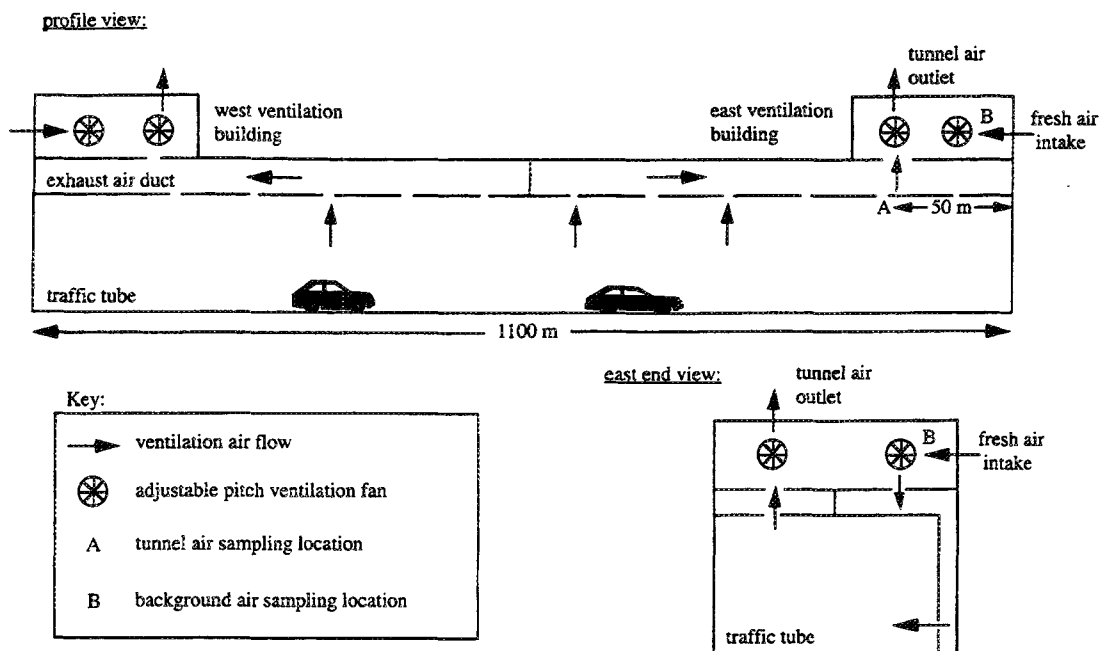


FIGURE 1. Schematic diagram of the Caldecott tunnel showing ventilation air flows and air sampling locations (figure not drawn to scale).

develop representative speciation profiles for VOC emissions from light-duty vehicles.

## 2. Experimental Section

Vehicle emissions were measured in the Caldecott Tunnel, located in the San Francisco Bay area on state highway 24. The tunnel runs a distance of 1100 m through the Berkeley Hills between Oakland and Orinda, CA. The tunnel consists of three two-lane traffic bores, running uphill in the eastbound direction at a constant roadway grade of 4.2%. Weekday traffic through the center bore is switched from westbound (downhill) during morning hours to eastbound during the afternoon. The Caldecott Tunnel has fully transverse ventilation provided by adjustable pitch fans housed in ventilation buildings at the east and west ends of the tunnel. A schematic of the tunnel is shown in Figure 1. Measurements of CO concentrations along the length of the tunnel showed that pollutant concentrations are higher at the east end of the tunnel during uphill driving events, due to the prevailing westerly winds and the motion of vehicles traveling through the tunnel. Thus, the east end of the center bore (bore 2) was selected as the sampling location for this study.

In the San Francisco Bay area, oxygenated gasoline was required at service stations from October 1 to January 31. Pollutant concentrations were measured during 1994 from August 22 to September 2, prior to the phase-in of oxygenated gasoline, and from October 18 to October 28, while the summertime fuel volatility limits were still in effect. Measurements were made on weekdays during the afternoon peak period between 1600 and 1800 h, when traffic traveled in the uphill direction.

Air temperature was measured on all sampling days with a mercury thermometer. Average temperatures inside the tunnel during the August and October periods were  $21 \pm 2$  and  $18 \pm 1$  °C, respectively. Average temperatures measured from 1600 to 1800 h at a meteorological station located nearby at the Oakland sewage treatment plant were  $19 \pm 1$  °C during the August sampling period and  $18 \pm 2$  °C in October.

**2.1. Traffic Monitoring.** The vehicle fleet traveling through the center bore was almost entirely light-duty vehicles; heavy-duty vehicles are only permitted in the outer bores of the tunnel. Due to the remote location of the tunnel, vehicles traveling through the center bore were operating in hot-stabilized mode. There are two nearby on-ramps that serve highway 24, at distances of 0.3 and 1.0 km from the western end of the tunnel. The nearer on-ramp is close enough to allow some vehicles to enter the tunnel while operating in cold-start mode, but this on-ramp directs traffic into the southernmost bore (bore 1) of the tunnel, not the center bore where our measurements were made. Vehicles merging onto highway 24 via the further on-ramp are exiting highway 13 and were therefore already operating in hot-stabilized mode.

A video camera was used to record continuously the traffic leaving the tunnel. In addition, visual vehicle counts were performed at least four times per day with separate counts for different vehicle classes (cars, pickups and small vans, and heavy-duty trucks and buses). Similar traffic flows of  $4260 \pm 240$  and  $4320 \pm 280$  vehicles per hour were measured during the August and October sampling periods, respectively. On average, the traffic in the center bore comprised 70% passenger cars and 30% pickups and small vans, with only 0.2% heavy-duty trucks and buses. The mix of vehicles was the same in both sampling periods: for example, cars comprised  $69 \pm 4\%$  of total vehicles in August and  $70 \pm 3\%$  in October. There was little opportunity for fleet turnover because the two sampling periods were separated by only two months. Many of the same commuter vehicles would have traveled through the tunnel every day both in August and October.

A hand-held radar gun was used to measure vehicle speeds exiting the tunnel. Typically, traffic flowed steadily at speeds of 40–50 mph. Traffic conditions near the exit of the tunnel were most relevant to our measurements because transverse mechanical ventilation removed air from the lower end of the tunnel using separate ducts and ventilation fans, as shown in Figure 1. Stop-and-go driving occurred regularly on highway 24 approaching the tunnel

where rush hour traffic entering via on-ramps had to merge with through traffic. Having already passed this bottleneck, vehicles were traveling at speeds of 25–40 mph upon entering bore 2 of the tunnel and accelerated gradually while traveling through the tunnel. It was rare to see any backup in traffic flow downstream of the tunnel, as expected given the bottleneck caused by traffic entering from on-ramps upstream of the tunnel. Variations in traffic flow were evident in bore 1, where heavy trucks moving slowly on the uphill grade reduced traffic speeds and flows. Traffic flow was smoother in bore 2 because very few heavy trucks were present.

On Thursday September 1, there was a stall in the tunnel at ~1730 h. A Caltrans tow truck rescued the stalled vehicle and emerged at the east end of the tunnel at 1738 h, and traffic flow was back to normal by ~1740 h. No other major disruptions in traffic flow were observed, although brief backups in traffic downstream of the tunnel were noted on 2 days in the August sampling period and 5 days in October. Since all of these events were of brief duration, 2-h average pollutant concentrations were not significantly affected.

**2.2. Pollutant Measurements.** Continuous measurements of CO, CO<sub>2</sub>, and NO<sub>x</sub> were made in the tunnel exhaust air at position A on Figure 1. Gas analyzers were housed in the east ventilation building and tunnel air samples were drawn through a 48-m Teflon sample line (inner diameter of 1.3 cm), which carried sample air to the instruments. An air flow rate of 16 L min<sup>-1</sup> ensured a short residence time of 23 s within the sample line. Background concentrations of CO and NO<sub>x</sub> were measured in the fresh air injected into the tunnel by the mechanical ventilation system (sampling location B on Figure 1) using a 5-m Teflon line. Carbon monoxide concentrations were measured using Thermo Environmental Instruments (TECO) Model 48 gas filter correlation spectrometers. Nitrogen oxide concentrations in the tunnel were measured using a TECO Model 42 chemiluminescent analyzer. A Bendix Model 8101-C chemiluminescent analyzer was used to measure NO<sub>x</sub> in the ventilation intake air. A TECO Model 41H gas filter correlation analyzer was used to monitor CO<sub>2</sub> concentrations in the tunnel air. Background CO<sub>2</sub> concentrations of 345 ppm were measured in the ventilation intake air at the start of each 2-week sampling period and on occasion during the sampling period. Although background CO<sub>2</sub> concentrations were not monitored continuously, measured CO concentrations remained below 2 ppm at the ventilation air intake during all sample periods. Therefore, recirculation of vehicle exhaust back to the ventilation intake was minimal during these experiments, and CO<sub>2</sub> levels should have remained near the background value. All instruments were calibrated daily immediately prior to each afternoon sampling period.

Two-hour integrated air samples were collected in 6-L stainless steel canisters for subsequent analysis by gas chromatography to quantify hydrocarbon concentrations. Samples were drawn from the tunnel exhaust air using XonTech model 910A air samplers that were housed in the ventilation duct next to the louver at position A in Figure 1. Similarly, 2-h integrated tunnel air samples were collected using DNPH-impregnated silica cartridges for subsequent analysis by high-performance liquid chromatography (HPLC) to quantify carbonyl concentrations. Hydrocarbon and carbonyl samples were also collected at the ventilation air intake (at position B in Figure 1). A coiled copper tube, coated on the inside with potassium iodide,

was placed upstream of the silica cartridge for the ventilation intake air samples. This was done to remove ozone from the sample air stream since ozone interferes with the quantification of carbonyl concentrations (23). An ozone scrubber was not needed for the tunnel samples because any ozone drawn into the tunnel was removed rapidly by reaction with nitric oxide. All hydrocarbon and carbonyl samples were collected concurrently with measurements of CO, NO<sub>x</sub>, and CO<sub>2</sub> concentrations.

At the end of each 2-week sampling period, the stainless steel canisters were delivered to the Bay Area Air Quality Management District's laboratory in San Francisco for analysis. Hydrocarbon samples were preconcentrated using a Nutech Model 8548 cryogenic concentrator and injected into a Perkin Elmer Model 8500 gas chromatograph (GC) equipped with a flame ionization detector (FID). The DB-1 column used in the GC was 30 m long, with an inner diameter of 0.32 mm and a 5- $\mu$ m film thickness. Following sample injection, the column temperature was held at -51 °C for 5 min, then increased at 5 °C min<sup>-1</sup> to 100 °C, at 3 °C min<sup>-1</sup> to 160 °C, at 5 °C min<sup>-1</sup> to 200 °C, and held at that temperature for 7 min. This method was used to quantify speciated hydrocarbons in the C<sub>5</sub>–C<sub>10</sub> range. A GS-alumina column, 50 m long by 0.53 mm inner diameter, was used to speciate and quantify the C<sub>2</sub>–C<sub>4</sub> hydrocarbons. Methane was quantified separately by direct injection of samples into a Perkin Elmer Model 8500 GC equipped with a FID and a 3.7 m long by 3.2 mm inner diameter stainless steel column packed with Chromosorb 102, 100–120 mesh. All analyses were completed within 2 weeks of sample delivery to the laboratory.

Immediately after each 2-h sampling period, the DNPH cartridges were eluted with 5 mL of acetonitrile and the extracted samples were stored in tightly capped glass vials in a refrigerator (*T* ~5 °C). At the end of each 2-week sampling period, the extracted samples were delivered to Chevron Research and Technology Co. in Richmond for analysis. The carbonyl derivatives were analyzed by HPLC using a procedure nearly identical to that developed for the Auto/Oil Air Quality Improvement Research Program (24). The HPLC column was a 150 mm by 4.6 mm 5- $\mu$ m Deltabond-AK C18, with integral guard column. The mobile phase flow rate and gradient conditions were identical to the Auto/Oil conditions, but the injection volume was somewhat larger—10 vs 5  $\mu$ L.

**2.3. Quality Assurance.** On August 23, the Quality Assurance Section of the Air Resources Board (ARB) conducted performance audits of the CO analyzers and of the NO<sub>2</sub> channels on the NO<sub>x</sub> analyzers. It was found that the CO analyzers were accurate to within 2% and that the NO<sub>2</sub> measurements were accurate to within 5%. ARB followed the same audit procedures used for ambient air monitoring stations throughout California, in accordance with standard EPA protocols. On September 2 and October 27, the Source Test Section of the Bay Area Air Quality Management District (BAAQMD) made independent measurements of CO and NO<sub>x</sub> concentrations in the tunnel air concurrently with our measurements. On September 2, the ratio of our measurements to the measurements of the Source Test Section for CO and NO<sub>x</sub> were 0.97 and 0.99, respectively. Similarly, the ratios for the October 27 intercomparison were 0.92 and 0.93 for CO and NO<sub>x</sub>, respectively.

Measured total NMHC and speciated hydrocarbon concentrations were compared with independent analyses



of three extra samples that were collected in parallel with tunnel air samples. Samples collected on October 21 and 24 were analyzed by the Monitoring and Laboratory Division of the ARB (25). A third sample, collected on December 7, was analyzed by BRC/Rasmussen (26). Total NMHC concentrations reported for our samples were 1.07 times higher than the value reported by Rasmussen for December 7, and 1.28 and 1.19 times higher than the values reported by ARB for October 21 and 24, respectively. Measured concentrations of most individual hydrocarbons were in good agreement. In most cases, measured values agreed within  $\pm 30\%$  for species concentrations above 20 ppb C. The agreement was best for alkanes. The measured concentration of MTBE on December 7 was 1.28 times higher than the value reported by Rasmussen; MTBE was not quantified by ARB in the October 21 and 24 samples. Measured cyclohexane concentrations were greater than 3 times higher than values reported by ARB for the October 21 and 24 samples and the December 7 sample analyzed by Rasmussen. A large 2-methylhexane peak was reported by ARB and Rasmussen. The identification of the cyclohexane peak in our samples was therefore changed to 2-methylhexane, consistent with results of ARB and BRC/Rasmussen analyses. Measured 2,2,4-trimethylpentane concentrations were 1.5–1.6 times higher than values reported by ARB and Rasmussen. Two canister samples were collected on October 20 and both were analyzed by the BAAQMD laboratory in San Francisco. Total NMHC and individual hydrocarbon concentrations were in excellent agreement. The difference in total NMHC was 10%; most of the major peaks were within 5% or better.

Measured concentrations of 1,3-butadiene were found to depend on the time interval between sample collection and analysis. For a single sample collected on December 7, the measured 1,3-butadiene concentration was 14.0 ppb C when analyzed on December 8, 4.0 ppb C on December 16, and 1.2 ppb C on January 9. Calibration standards of butadiene in air were observed to be stable in stainless steel canisters over the same time period. Rasmussen reported similar losses of butadiene in another Caldecott tunnel sample collected on December 7. It is likely that losses of 1,3-butadiene occurred in the August and October hydrocarbon samples since canisters were stored at the Caldecott Tunnel for up to 2 weeks followed by an additional 1–2 weeks at the laboratory in San Francisco.

**2.4. Gasoline Sampling.** Gasoline samples from service stations located throughout the San Francisco Bay area were collected by the ARB as part of their fuels inspection program, using a standardized sampling procedure (27). Gasoline samples were analyzed for sulfur and oxygen content using X-ray spectrometry and gas chromatography, respectively (28, 29). Reid vapor pressure was determined using an automated vapor pressure test instrument (30). ARB provided analyses of 65 gasoline samples collected between August 24 and 28, and 54 samples collected between October 24 and 28 (31). Complete chemical composition profiles for liquid gasoline were determined using gas chromatography for 3 individual gasoline samples collected in August and for four samples collected in October.

### 3. Results

**3.1. Gasoline Properties.** Average fuel properties for the August and October sampling periods are summarized in Table 2. Oxygen content of 65 fuel samples collected in

TABLE 2

Properties of Gasoline Sold in the San Francisco Bay Area during 1994

fuel property <sup>a</sup>	sampling period	
	August (low oxygenate)	October (high oxygenate)
oxygen content (wt %)	0.3 $\pm$ 0.4	2.0 $\pm$ 0.2
sulfur (ppm by wt)	54 $\pm$ 47	90 $\pm$ 53
Reid vapor pressure (psi)	7.2 $\pm$ 0.2	7.7 $\pm$ 0.3
paraffins (vol %)	47–54	38–46
aromatics (vol %)	34–43	26–35
olefins (vol %)	0.4–7.3	4.3–13.4
naphthenes (vol %)	2.9–10.4	4.1–9.6
benzene (vol %)	1.7–5.1	1.0–3.6

<sup>a</sup> Gasoline samples (65 during the August sample period and 54 during the October sample period) from service stations throughout the San Francisco Bay area were collected and analyzed by the ARB. The average oxygen and sulfur content and RVP are reported here. Detailed fuel speciation analysis was performed on three gasoline samples collected in August and four samples collected in October; the range of measured values for the additional parameters are shown here.

August was 0.3  $\pm$  0.4 wt %. Of these samples, 34 had oxygen content below the detection limit of 0.02% and four had oxygen content of greater than 1% by weight. MTBE was the only oxygenate detected in the August samples. Oxygen content increased to an average value of 2.0  $\pm$  0.2 wt % during the October sampling period. On an oxygen weight basis, 80% of the oxygenate was MTBE and 20% was ethanol. Of the 54 October samples, 34 contained MTBE as the sole oxygenate and five samples contained ethanol exclusively. The RVP increase between August and October was largely due to ethanol use: average RVP of samples with greater than 1% by weight ethanol was 8.0 psi, whereas the average RVP of samples without ethanol (MTBE only) was 7.55 psi. Sulfur content also increased between August and October, whereas paraffin and aromatic content decreased.

**3.2. Effects of Oxygenated Gasoline.** Daily average concentrations of CO, CO<sub>2</sub>, NO<sub>x</sub>, and NMOC measured at the Caldecott tunnel are given in Table 3. Since natural and mechanical ventilation rates varied, absolute concentrations of individual pollutants were not constant from day to day. The sample probe used in the tunnel was moved from point A in Figure 1 into the exhaust duct above point A for 4 days (August 30 through September 2) to examine integrated emissions over the upper half of the tunnel. Because air in the exhaust duct is drawn from points further from the tunnel exit, measured concentrations were lower on these sampling days as shown in Table 3. During both the August and October sample periods, concentrations of CO and NO<sub>x</sub> in the tunnel were  $\sim 25$  times higher than in background air; non-methane hydrocarbon concentrations in the tunnel were  $\sim 10$  times higher than background levels.

Emission factors for the August and October sample periods are reported as grams of pollutant emitted per unit volume of gasoline burned, calculated using the following equation:

$$E_p = \left( \frac{\Delta[P]}{\Delta[\text{CO}_2] + \Delta[\text{CO}] + \Delta[\text{VOC}]} \right) \left( \frac{w_c}{12\rho_f} \right) \text{MW}_p \quad (1)$$

where  $E_p$  is the emission factor for pollutant  $p$ ,  $\Delta[P]$  is the increase in the concentration (ppm) of pollutant  $p$  above background levels,  $\text{MW}_p$  is the molecular weight of pollutant  $p$ ,  $w_c$  is the carbon weight fraction in the fuel, and  $\rho_f$  is the

TABLE 3

## Measured Pollutant Concentrations at the Caldecott Tunnel

date	background concn <sup>a</sup>			tunnel concn <sup>b</sup>			
	CO (ppm)	NO <sub>x</sub> (ppb)	NMOC (ppm C)	CO (ppm)	NO <sub>x</sub> (ppm)	NMOC (ppm C)	CO <sub>2</sub> (ppm)
22 Aug	1.0	n/a <sup>c</sup>	n/a	n/a	n/a	3.14	953
23 Aug	1.4	84	n/a	34.4	n/a	3.51	948
24 Aug	1.1	64	n/a	33.9	2.14	3.36	1020
25 Aug	1.3	90	0.28	36.3	2.21	3.61	998
26 Aug	1.2	73	n/a	34.3	1.92	3.31	938
29 Aug	1.1	62	0.35	37.8	2.26	3.69	1056
30 Aug	1.2	63	0.25	30.3	1.76	2.83	839
31 Aug	0.7	45	0.33	30.8	1.83	3.25	917
1 Sep	0.7	45	0.19	28.6	1.62	2.93	848
2 Sep	1.7	87	0.30	29.5	1.69	3.17	812
17 Oct	1.6	80	n/a	29.5	2.35	n/a	n/a
18 Oct	1.1	38	0.29	32.4	2.68	3.16	1034
19 Oct	1.3	56	n/a	30.7	2.31	n/a	1009
20 Oct	1.5	72	0.35	33.0	2.44	3.50	1106
21 Oct	1.2	50	0.22	33.4	2.50	3.33	1079
24 Oct	1.7	81	0.22	28.8	1.94	2.64	1010
25 Oct	1.4	59	0.20	28.1	2.08	2.90	972
26 Oct	1.8	98	0.33	31.8	n/a	3.28	1076
27 Oct	1.2	55	0.30	32.1	2.22	3.31	1060
28 Oct	1.0	45	0.23	27.0	1.72	2.72	895

<sup>a</sup> Measured pollutant concentrations at the fresh air ventilation intake (point B on Figure 1). <sup>b</sup> Measured pollutant concentrations in the tunnel air (point A on Figure 1). <sup>c</sup> Measurement not available due to sampler malfunction, power failure, or instrument not on-line. When background NMOC concentrations were not available, the average background level from other sampling days was used.

fuel density. Industry average gasoline properties were used for  $\rho_f$  and  $w_c$ : a density of 750 g L<sup>-1</sup> and carbon weight fraction of 0.87 were used to calculate emission factors for the August sample period (32). A carbon weight fraction of 0.853 was used to account for the increased fuel oxygen content during the October period. Following standard emission inventory practice, NO<sub>x</sub> emission factors are reported as nitrogen dioxide (i.e., a molecular weight of 46 was used in eq 1 for NO<sub>x</sub> calculations), even though NO constituted 99% of the NO<sub>x</sub> measured in the tunnel. VOC emission factors were computed using eq 1, measured total NMOC concentrations in units of ppm C, and a molecular weight of 14. Methane and formaldehyde emissions were calculated separately, using appropriate molecular weights for these species, and added to obtain total VOC emissions.

Emission factors computed using eq 1 and the data from Table 3 are presented in Table 4. Compared to the August (low-oxygenate) sampling period, measured pollutant emission rates during the October (high-oxygenate) sampling period for CO and VOC decreased by 21 ± 7 and 18 ± 10%, respectively. NO<sub>x</sub> emissions showed no change between the two sample periods. Similarly, formaldehyde emissions increased by 13 ± 6%, acetaldehyde emissions did not change significantly, and benzene emissions decreased by 25 ± 17%. As discussed previously, 1,3-butadiene was unstable in the stainless steel canisters and is therefore not reported in Table 4.

**3.3. Comparison with EMFAC7F.** Average CO/NO<sub>x</sub> and VOC/NO<sub>x</sub> mass ratios measured at the Caldecott tunnel during the August sampling period are presented in Table 5. Also shown in Table 5 are the ratios as predicted by the EMFAC7F model as a function of vehicle speed. EMFAC7F ratios were calculated using the model's tabulated emission factors for 1994 summertime conditions that correspond

TABLE 4

Calculated Light-Duty Vehicle Emission Factors for Uphill Traffic in the Caldecott Tunnel<sup>a</sup>

species	August <sup>b</sup> (low oxygenate) (g L <sup>-1</sup> )	October <sup>c</sup> (high oxygenate) (g L <sup>-1</sup> )	% change <sup>d</sup>
regulated emissions			
CO	78.2 ± 4.8	61.6 ± 2.9	-21 ± 7
VOC	4.17 ± 0.37	3.41 ± 0.16	-18 ± 10
NO <sub>x</sub>	7.56 ± 0.34	7.53 ± 0.71	0 ± 10
hazardous organics			
formaldehyde	58.9 ± 2.4	66.3 ± 2.6	+13 ± 6
benzene	235 ± 37	176 ± 13	-25 ± 17
acetaldehyde	13.7 ± 1.1	14.3 ± 2.4	+4 ± 19

<sup>a</sup> Emission factors normalized to fuel consumption, computed using eq 1 and data from Table 3. <sup>b</sup> The average gasoline oxygen content during the August sample period was 0.3% by weight. <sup>c</sup> The average gasoline oxygen content during the October sample period was 2.0% by weight. <sup>d</sup> Percent change = 100(E<sub>Oct</sub> - E<sub>Aug</sub>)/E<sub>Aug</sub>. The uncertainty  $\sigma$  shown in this column is computed as  $\sigma = 100(\sigma_{Aug}^2 + \sigma_{Oct}^2)^{1/2}/E_{Aug}$ .

TABLE 5

## Measured Pollutant Ratios and Comparison with EMFAC7F Predictions

	vehicle speed (mph)	pollutant mass ratio <sup>a</sup>	
		CO/NO <sub>x</sub>	VOC/NO <sub>x</sub>
Caldecott Tunnel	40-50	10.3 ± 0.4	0.55 ± 0.05
EMFAC7F	40	6.8	0.71
	45	5.6	0.54
	50	4.7	0.41
Caldecott/EMFAC7F	40	1.5	0.8
	45	1.8	1.0
	50	2.2	1.3

<sup>a</sup> The pollutant ratios shown here were measured during the August (low-oxygenate) sample period. VOC emissions include hot-stabilized exhaust emissions and running loss evaporative emissions.

to the vehicle types and driving conditions observed in the center bore of the Caldecott Tunnel. Only running exhaust and running loss evaporative emissions were included in the EMFAC analysis. As previously mentioned, vehicles in the center bore were not operating in cold-start mode. Resting loss emissions were also neglected due to the short amount of time that vehicles spend inside the tunnel. Since medium- and heavy-duty trucks and buses accounted for only 0.2% of the traffic in the middle bore, these vehicle classes were neglected in the calculation of fleet emission factors. Vehicle technology type (i.e., catalyst, noncatalyst, or diesel) could not be distinguished visually, so this information was obtained from the BURDEN7F model (33). EMFAC7F emission factors were calculated for vehicle speeds of 40, 45, and 50 mph to span the observed range of vehicle speeds in the Caldecott Tunnel.

As shown in Table 5, the VOC/NO<sub>x</sub> mass ratio measured in the Caldecott Tunnel is well predicted by EMFAC7F; the model ratio predicted for a vehicle speed of 45 mph is equal to the measured ratio. However, the measured CO/NO<sub>x</sub> mass ratio is underpredicted by a factor of 1.5-2.2, depending on the vehicle speed used in the EMFAC calculation.

**3.4. VOC Speciation.** Concentrations of individual organics measured in the tunnel were typically 10 times

TABLE 6

Speciation Profiles for VOC Emissions from Light-Duty Vehicles<sup>a</sup>

species	concn (wt % of total VOCs)		species	concn (wt % total VOCs)	
	August (low oxygenate)	October (high oxygenate)		August (low oxygenate)	October (high oxygenate)
methane	9.9 ± 2.3	11.0 ± 3.5	toluene	8.8 ± 0.7	7.2 ± 0.4
ethane	7.8 ± 0.9	7.2 ± 0.5	2,3-dimethylhexane	0.24 ± 0.22	0.47 ± 0.15
acetylene	2.8 ± 0.3	2.6 ± 0.2	2-methylheptane	0.30 ± 0.08	0.28 ± 0.08
ethane	1.3 ± 0.2	1.2 ± 0.3	<i>n</i> -octane	0.16 ± 0.08	0.12 ± 0.06
propene	3.5 ± 0.4	3.3 ± 0.1	ethylbenzene	1.38 ± 0.08	1.11 ± 0.07
propane	0.25 ± 0.03	0.23 ± 0.15	<i>m</i> - <i>p</i> -xylene	5.7 ± 0.3	4.4 ± 0.2
isobutane	0.49 ± 0.06	0.34 ± 0.06	styrene	0.38 ± 0.08	0.30 ± 0.04
isobutene	1.4 ± 0.2	2.6 ± 0.1	<i>o</i> -xylene	2.35 ± 0.14	1.72 ± 0.07
1-butene	0.48 ± 0.06	0.43 ± 0.02	<i>n</i> -propylbenzene	0.25 ± 0.06	0.21 ± 0.02
1,3-butadiene <sup>b</sup>	0.33 ± 0.22	0.36 ± 0.17	<i>m</i> -ethyltoluene	1.70 ± 0.22	1.42 ± 0.15
<i>n</i> -butane	1.8 ± 0.2	1.9 ± 0.3	<i>p</i> -ethyltoluene	0.76 ± 0.18	0.59 ± 0.04
<i>trans</i> -2-butene	0.27 ± 0.13	0.36 ± 0.11	<i>o</i> -ethyltoluene	0.54 ± 0.12	0.41 ± 0.03
<i>cis</i> -2-butene	0.16 ± 0.07	0.40 ± 0.16	1,2,4-trimethylbenzene	2.36 ± 0.10	1.86 ± 0.07
isopentane	8.0 ± 0.6	6.9 ± 0.7	1,2,3-trimethylbenzene	0.39 ± 0.06	0.33 ± 0.05
1-pentene	0.16 ± 0.07	0.20 ± 0.05	<i>o</i> -diethylbenzene	0.28 ± 0.07	0.26 ± 0.05
2-methyl-1-butene	0.23 ± 0.13	0.34 ± 0.05	<i>m</i> -diethylbenzene	0.13 ± 0.09	0.19 ± 0.04
<i>n</i> -pentane	2.1 ± 0.2	2.4 ± 0.3	<i>p</i> -diethylbenzene	0.44 ± 0.04	0.36 ± 0.06
<i>trans</i> -2-pentene	0.23 ± 0.13	0.36 ± 0.12	<i>n</i> -butylbenzene	0.66 ± 0.09	0.55 ± 0.05
<i>cis</i> -2-pentene	0.11 ± 0.03	0.18 ± 0.07	other C <sub>5</sub> -C <sub>9</sub> hydrocarbons	2.4	2.5
2-methyl-2-butene	0.43 ± 0.06	0.48 ± 0.06	other C <sub>10</sub> + aromatics	1.2	1.1
2,2-dimethylbutane	0.59 ± 0.18	0.38 ± 0.13	C <sub>10</sub> + paraffins	1.4	1.1
cyclopentene	0.14 ± 0.06	0.16 ± 0.04	unidentified hydrocarbons	4.2	5.7
2,3-dimethylbutane <sup>c</sup>	1.0 ± 0.2	0.56 ± 0.14	formaldehyde	1.42 ± 0.15	1.97 ± 0.11
2-methylpentane	2.4 ± 0.4	2.3 ± 0.2	acetaldehyde	0.33 ± 0.04	0.43 ± 0.08
3-methylpentane	1.3 ± 0.2	1.2 ± 0.1	acetone	0.13 ± 0.08	0.19 ± 0.08
1-hexene	0.11 ± 0.06	0.16 ± 0.05	acrolein (propenal)	0.08 ± 0.01	0.10 ± 0.01
<i>n</i> -hexane	1.2 ± 0.5	1.3 ± 0.2	propionaldehyde	0.04 ± 0.01	0.12 ± 0.11
methylcyclopentane	1.5 ± 0.4	1.4 ± 0.1	crotonaldehyde (butenal)	0.04 ± 0.01	0.03 ± 0.01
benzene	5.6 ± 0.7	5.2 ± 0.3	methyl ethyl ketone	0.04 ± 0.01	0.04 ± 0.02
methyl <i>tert</i> -butyl ether	ND <sup>d</sup>	3.3 ± 0.3	methacrolein	0.06 ± 0.01	0.09 ± 0.01
2-methylhexane <sup>e</sup>	1.0 ± 0.2	1.0 ± 0.1	butyraldehyde	0.15 ± 0.02	0.21 ± 0.02
2,3-dimethylpentane	0.42 ± 0.12	0.35 ± 0.03	benzaldehyde	0.39 ± 0.04	0.19 ± 0.03
3-methylhexane	0.94 ± 0.17	0.87 ± 0.09	tolualdehyde	0.59 ± 0.06	0.39 ± 0.04
2,2,4-trimethylpentane	1.2 ± 0.1	1.2 ± 0.1	other aromatic aldehydes	0.40 ± 0.04	0.30 ± 0.09
<i>n</i> -heptane	0.59 ± 0.09	0.72 ± 0.11			
methylcyclohexane	0.36 ± 0.07	0.63 ± 0.12	total VOC (g L <sup>-1</sup> )	4.17 ± 0.37	3.41 ± 0.16
2,3,4-trimethylpentane	0.34 ± 0.04	0.30 ± 0.11	normalized reactivity <sup>f</sup> (g O <sub>3</sub> /g NMOC)	3.83	3.75

<sup>a</sup> These speciation profiles are based on VOC measurements made during 1994 in the Caldecott tunnel as part of the present study. <sup>b</sup> The numbers shown here are lower limits because 1,3-butadiene was not stable in the stainless steel canisters (see text). <sup>c</sup> 2,3-Dimethylbutane and cyclopentane coeluted in these hydrocarbon analyses. All of the measured mass is shown as 2,3-dimethylbutane in this table. <sup>d</sup> Not detected. <sup>e</sup> This peak was initially identified as cyclohexane (see text). <sup>f</sup> Normalized reactivity is computed as  $\sum_{i=1}^n (\text{MIR})_i w_i$ , where (MIR)<sub>i</sub> is the maximum incremental reactivity for species *i* (39) and *w<sub>i</sub>* is the weight fraction of species *i* in total NMOC emissions.

higher than concentrations of the same species measured in fresh air at the ventilation intake. Methane was a significant exception to the general pattern; background methane concentrations of 1.8 ppm were measured at the fresh air intake, and concentrations of methane measured in the tunnel were between 2.0 and 2.3 ppm. In addition, background concentrations of propane in the fresh air intake were comparable to propane concentrations measured in the tunnel.

The absolute concentrations of individual organic species measured in the tunnel varied significantly among individual canister samples. However, when individual species concentrations were normalized to the measured total VOC concentrations, the relative amounts of individual species were remarkably consistent in each sample period, as shown in Table 6. In addition to the overall reduction in the mass of VOC emitted (see Table 4), the use of oxygenated gasoline caused changes to the relative abundances of some individual organic species, as shown in Table 6. MTBE, isobutene, and formaldehyde weight fractions increased significantly; aromatic hydrocarbons and aromatic aldehydes decreased as a fraction of total

VOC emissions, while weight fractions of combustion-derived C<sub>1</sub>-C<sub>3</sub> hydrocarbons showed no change.

## 4. Discussion

**4.1. Effects of Oxygenated Gasoline.** The changes in light-duty vehicle emissions measured at the Caldecott Tunnel between the August and October sampling periods are consistent with results of previous studies. A similar reduction in CO emissions ( $-16 \pm 3\%$ ) was measured during the Colorado oxy-fuels program (8), resulting from an increase in fuel oxygen content approximately equal to the increase observed during this study. In both studies, the vehicle fleets observed were in-use fleets, operating in hot-stabilized mode. During phase I of the Auto/Oil program, an increase in fuel oxygen content from 0 to 2.7% by weight reduced stabilized CO emissions by  $23 \pm 7\%$  for 1989 model year vehicles and  $16 \pm 12\%$  for 1983-1985 model year vehicles (4). The reduction in VOC emissions ( $-18 \pm 10\%$ ) and the insensitivity of NO<sub>x</sub> emissions to fuel oxygen content also is consistent with results reported elsewhere (4, 9, 11, 12).

MTBE and ethanol have lower energy contents than conventional gasoline, and there is concern that fuel economy may decrease with oxygenated gasoline use. Results presented in Table 4 are expressed per unit volume of fuel burned and are not explicitly adjusted for possible changes in fuel economy. Note, however, that a lower carbon weight fraction ( $w_c=0.853$ ) was used in eq 1 for the October sampling period. The energy content of MTBE ( $35 \text{ kJ g}^{-1}$ ) and ethanol ( $27 \text{ kJ g}^{-1}$ ), as measured by their lower heating values (34), is certainly less than the energy content of conventional gasoline ( $44 \text{ kJ g}^{-1}$ ). However, the energy content of oxygenated gasoline, in this case a mixture of 8.6% MTBE, 1.1% ethanol, and 90.3% by weight conventional gasoline, is only 2% lower than the energy content of conventional gasoline. Bishop and Stedman (8) also argued that the decrease in fuel economy is small for gasoline containing 2% by weight oxygen as MTBE – on the order of 3%. In any case, the changes in emissions of CO and VOC reported here are much larger than the likely change in fuel economy associated with the use of oxygenated gasoline.

The oxygen content of gasoline increased significantly between the August and October sampling periods. This was the only change in gasoline properties that was required by law. Nevertheless, oxygenate usage alone may not provide a complete explanation of the experimental results, since oxygenate content was not the only fuel property that changed. As shown in Table 2, the sulfur content and RVP of gasoline increased between August and October. The change in sulfur content was not statistically significant. Furthermore, sulfur in gasoline affects the performance of catalytic converters (35) but would not affect engine-out emissions of noncatalyst or malfunctioning vehicles. In the absence of the fuel sulfur changes, one would expect lower emission levels during the October sampling period and, therefore, even larger reductions associated with the use of oxygenated gasoline. The increase of 0.5 psi in RVP shown in Table 2 and the decrease of  $2^\circ\text{C}$  in ambient temperature from August to October were both small changes and had opposing effects on running loss evaporative emissions. Although Table 2 suggests that olefin content increased between August and October, the number of gasoline samples analyzed for olefin content was small, so this change may not be statistically significant. As shown in Table 6, no large increases were measured in the weight fractions of individual olefins in vehicle exhaust, with the exception of isobutene formed as a partial oxidation product of MTBE.

Measurements at the Caldecott Tunnel observed vehicles operating in a hot-stabilized mode. Most CO nonattainment areas are required to sell oxygenated gasoline during the winter months, when cold-start emissions are a significant fraction of the total inventory. In the San Francisco air basin, wintertime cold starts are estimated to contribute more than half of the total light-duty vehicle exhaust CO and HC emissions (33). In other cities with lower wintertime temperatures, cold-start emissions should be even more significant. Hence, the effects of oxygenated gasoline use on cold-start emissions must be investigated to assess completely the emission impacts of oxygenated gasoline.

**4.2. Comparison with EMFAC.** As shown in Table 5, EMFAC7F underpredicts the measured CO/ $\text{NO}_x$  ratio over the range of vehicle speeds observed at the Caldecott tunnel. This result is similar to the findings of the Van Nuys study,

where version 7C underpredicted the CO/ $\text{NO}_x$  ratio by a factor of 2.5 (16), but the discrepancy between the measured ratio and the model prediction is smaller for the Caldecott/EMFAC7F comparison. The good agreement between the VOC/ $\text{NO}_x$  ratio measured at the Caldecott Tunnel (see Table 5) and the ratio predicted by EMFAC7F contrasts with the findings of the Van Nuys tunnel study, where EMFAC7C underpredicted the measured HC/ $\text{NO}_x$  ratio by a factor of 3.8 (16).

Since EMFAC does not account for roadway grade in its emission factor predictions, it is debatable whether EMFAC model predictions should agree with measurements of pollutant concentrations in the Caldecott Tunnel. While it is true that gram per mile emission factors are higher for uphill driving, emission factors normalized to fuel consumption rather than distance traveled fluctuate less as a function of driving conditions (19). Since engine air flow, fuel consumption, and gram per mile emission factors all increase for uphill driving, ratios of emission factors measured in the tunnel may still match corresponding ratios of emission factors predicted by EMFAC, even though EMFAC predictions were not corrected for the increase in engine load.

**4.3. VOC Speciation.** As discussed previously, the addition of oxygenates such as MTBE to gasoline affects both the total mass rate and the detailed chemical composition of VOC emissions from motor vehicles. Leppard et al. (36) have shown that unreacted gasoline contributes a significant fraction (30–50%) of tailpipe hydrocarbon emissions. Therefore, the increase in MTBE and decreases in aromatic hydrocarbon weight fractions shown in Table 6 are expected given the changes in fuel composition shown in Table 2.

Measurements in the Caldecott Tunnel confirm that emissions of formaldehyde and isobutene, formed as partial oxidation products of the MTBE added to gasoline, increase as reported by Hoekman (12). Lower emissions of aromatic aldehydes such as benzaldehyde and tolualdehyde are consistent with the reductions in the aromatic content of gasoline shown in Table 2. Acetaldehyde is formed as a partial oxidation product of ethanol (6), analogous to the formation of formaldehyde from MTBE, but no increase in the weight fraction of acetaldehyde was found (see Table 6). Such a change could be more evident if a larger fraction of the fuel oxygen content was supplied using ethanol.

The weight fractions of light ( $\text{C}_1\text{--C}_3$ ) hydrocarbons in vehicle exhaust did not change significantly following the introduction of oxygenated gasoline. However, the total mass emissions of these and most other species declined in proportion to the general reduction in VOC emissions shown in Table 4.

As shown at the bottom of Table 6, the normalized reactivity of non-methane organic gas emissions does not change significantly when oxygenates are added to gasoline. Although MTBE has a lower atmospheric reactivity than the hydrocarbons present in gasoline, the low reactivity of MTBE is offset by increases in emissions of isobutene and formaldehyde, which have high reactivity. Therefore, in this case, the overall ozone-forming potential of VOC emissions is reduced in proportion to the reduction in total VOC mass emissions shown in Table 4. Note that the maximum incremental reactivity (MIR) scale used here is deliberately determined under conditions where ozone formation is maximally sensitive to VOC emissions (37).

TABLE 7

# Comparison of Selected Hydrocarbons in Caldecott Tunnel<sup>a</sup> and Auto/Oil<sup>b</sup> Exhaust Emission Speciation Profiles

species	conc'n (wt % of total VOCs)		
	Caldecott Tunnel	Auto/Oil cold start (bag 1)	Auto/Oil stabilized (bag 2)
methane	9.9 ± 2.3	8.5 ± 3.1	54 ± 18
ethene	7.8 ± 0.9	8.2 ± 1.5	0.9 ± 1.5
acetylene	2.8 ± 0.3	3.7 ± 1.4	0
propene	3.5 ± 0.4	4.1 ± 0.8	0.09 ± 0.31
n-butane	1.8 ± 0.2	3.6 ± 0.8	5.3 ± 4.2
isopentane	8.0 ± 0.6	2.9 ± 0.6	4.5 ± 2.8
benzene	5.6 ± 0.7	5.0 ± 0.7	4.8 ± 4.7
toluene	8.8 ± 0.7	7.6 ± 1.4	4.0 ± 4.0
total VOC	4.17 ± 0.37 g L <sup>-1</sup>	0.61 g mi <sup>-1</sup>	0.05 g mi <sup>-1</sup>

<sup>a</sup> Measured during the August sampling period. <sup>b</sup> Exhaust speciation profiles for Auto/Oil current fleet vehicles tested using industry average gasoline (4, 38).

Addition of oxygenates to gasoline will not reduce ozone in locations where ozone formation is NO<sub>x</sub>-limited.

Speciation profiles for vehicle exhaust emissions typically have been developed based on dynamometer emission test results for small numbers of individual vehicles. Each 2-h integrated sample obtained in this study represents composite emissions from ~8600 light-duty vehicles. In Table 7, the speciation profile for summertime conditions developed in the present study is compared with speciation profiles computed for cold-start and hot-stabilized exhaust emissions from 1989 model year vehicles in the Auto/Oil test program (4, 38). Comparisons with Auto/Oil data for older vehicles show similar results. The tunnel-derived speciation profile for vehicle emissions agrees with cold-start speciation from Auto/Oil but does not agree with the hot-stabilized speciation profile. The Auto/Oil hot-stabilized profile indicates a much higher methane fraction, and much lower ethylene, acetylene, and propylene fractions, compared to measured data from the Caldecott tunnel. Concentrations of *n*-butane measured in the Caldecott tunnel were lower than those reported previously (22), consistent with reduction of the gasoline RVP limit from 9.0 to 7.8 psi. Weight fractions of *n*-butane in August 1994 gasoline samples ranged from 0.7 to 1.0% by weight, a level that is much lower than the *n*-butane content of 3.3% by weight reported for liquid gasoline with an RVP limit of 9.0 psi (20). Isopentane represents a higher fraction of total hydrocarbon emissions in the tunnel than it does in exhaust emission data from the Auto/Oil program, possibly due to running loss evaporative emissions that are present in tunnels but are not captured during tailpipe emission sampling.

Because of the location of the Caldecott Tunnel on a major highway between cities, the vehicles measured in this study are not likely to be in cold-start mode. Instead, our results suggest that the vehicles that emit significant amounts of hydrocarbons during stabilized operating mode are operating under similar conditions to new vehicles in cold-start mode: with reduced or nonexistent catalytic converter activity and lacking closed-loop control of air/fuel ratio.

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## Literature Cited

- (1) National air pollutant emission trends, 1900–1992. Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, NC, 1993.
- (2) Final 1991 air quality management plan, South Coast Air Basin. South Coast Air Quality Management District and Southern California Association of Governments, El Monte, CA, 1991.
- (3) Emission Inventory—1990. Technical Support Division, California Air Resources Board, Sacramento, CA, 1993.
- (4) Hochhauser, A. M.; Benson, J. D.; Burns, V.; Gorse, R. A.; Koehl, W. J.; Painter, L. J.; Rippon, B. H.; Reuter, R. M.; Rutherford, J. A. *SAE Tech. Pap. Ser.* 1991, No. 912322.
- (5) Gorse, R. A.; Benson, J. D. J.; Hochhauser, A. M.; Koehl, W. J.; Painter, L. J.; Reuter, R. M. *SAE Tech. Pap. Ser.* 1991, No. 912324.
- (6) Reuter, R. M.; Benson, J. D.; Burns, V. R.; Gorse, R. A.; Hochhauser, A. M.; Koehl, W. J.; Painter, L. J.; Rippon, B. H.; Rutherford, J. A. *SAE Tech. Pap. Ser.* 1992, No. 920326.
- (7) Knepper, J. C.; Koehl, W. J.; Benson, J. D.; Burns, V. R.; Gorse, R. A.; Hochhauser, A. M.; Leppard, W. R.; Rapp, L. A.; Reuter, R. M. *SAE Tech. Pap. Ser.* 1993, No. 930137.
- (8) Bishop, G. A.; Stedman, D. H. *Environ. Sci. Technol.* 1990, 24, 843–847.
- (9) Born, G. L.; Lucas, S. V.; Scott, R. D.; DeFries, T. H.; Kishan, S. Effect of use of low oxygenate gasoline blends upon emissions from California vehicles. Automotive Testing Laboratories, East Liberty, OH, and Radian Corp., Austin, TX, 1994.
- (10) Stump, F. D.; Knapp, K. T.; Ray, W. D.; Siudak, P. D.; Snow, R. F. *J. Air Waste Manage. Assoc.* 1994, 44, 781–786.
- (11) Gething, J. A. *SAE Tech. Pap. Ser.* 1991, No. 910382.
- (12) Hoekman, S. K. *Environ. Sci. Technol.* 1992, 26, 1206–1216.
- (13) Cohu, L. K.; Rapp, L. A.; Segal, J. S. EC-1 emission control gasoline. ARCO Products Co., Anaheim, CA, 1989.
- (14) Dolislagar, L. J. Did the wintertime oxygenated fuels program reduce carbon monoxide concentrations in California? Presented at the 10th International Symposium on Alcohol Fuels, Colorado Springs, CO, 1993.
- (15) Stedman, D. H.; Bishop, G. A.; Beaton, S. P.; Peterson, J. E.; Guenther, P. L.; McVey, I. F.; Zhang, Y. On-road remote sensing of CO and HC emissions in California. University of Denver, Denver, CO, 1994.
- (16) Pierson, W. R.; Gertler, A. W.; Bradow, R. L. *J. Air Waste Manage. Assoc.* 1990, 40, 1495–1504.
- (17) Fujita, E. M.; Croes, B. E.; Bennett, C. L.; Lawson, D. R.; Lurmann, F. W.; Main, H. H. *J. Air Waste Manage. Assoc.* 1992, 42, 264–276.
- (18) Ingalls, M. N.; Smith, L. R.; Kirksey, R. E. *Measurement of on-road vehicle emission factors in the California South Coast air basin. Volume I: regulated emissions*; Southwest Research Institute: San Antonio, TX, 1989.
- (19) Pierson, W. R.; Gertler, A. W.; Robinson, N. F.; Sagebiel, J. C.; Zielinska, B.; Bishop, G. A.; Stedman, D. H.; Zweidinger, R. B.; Ray, W. D. In *Fourth CRC on-road vehicle emissions workshop*; CRC: San Diego, CA, 1994; pp 6-1–6-24.
- (20) Harley, R. A.; Hannigan, M. P.; Cass, G. R. *Environ. Sci. Technol.* 1992, 26, 2395–2408.
- (21) Ingalls, M. N.; Smith, L. R. *Measurement of on-road vehicle emission factors in the California South Coast air basin. Volume II: unregulated emissions*; Southwest Research Institute: San Antonio, TX, 1990.
- (22) Zielinska, B.; Fung, K. *Composition and concentrations of semi-volatile hydrocarbons*; Desert Research Institute: Reno, NV, 1992.
- (23) Arnts, R. R.; Tejada, S. B. *Environ. Sci. Technol.* 1989, 23, 1428–1430.

- (24) Siegl, W. O.; Richert, J. F. O.; Jensen, T. E.; Schuetzle, D.; Swarin, S. J.; Loo, J. F.; Prostak, A.; Nagy, D.; Schlenker, A. M. *SAE Tech. Pap. Ser.* 1993, No. 930142.
- (25) Poore, M. Monitoring and Laboratory Division, California Air Resources Board, Sacramento, CA. Personal communication, 1994.
- (26) Rasmussen, R., Oregon Graduate Institute, Beaverton, OR. Personal communication, 1994.
- (27) California Code of Regulations, Title 13, section 2296.
- (28) American Society for Testing and Materials, Method D2622-87, 1987.
- (29) American Society for Testing and Materials, Method D4815-93, 1993.
- (30) California Code of Regulations, Title 13, section 2297.
- (31) Pasek, R., Research Division, California Air Resources Board, Sacramento, CA. Personal communication, 1994.
- (32) Pahl, R. H.; McNally, M. J. *SAE Tech. Pap. Ser.* 1990, No. 902098.
- (33) Predicted California on-road motor vehicle emissions (BURDEN7F). Mobile Source Emission Inventory Branch, California Air Resources Board, Sacramento, CA, 1993.
- (34) Heywood, J. B. *Internal combustion engine fundamentals*; McGraw-Hill: New York, 1988; p 915.
- (35) Benson, J. D.; Burns, V. R.; Gorse, R. A. J.; Hochhauser, A. M.; Koehl, W. J.; Painter, L. J.; Reuter, R. M. *SAE Tech. Pap. Ser.* 1991, No. 912323.
- (36) Leppard, W. R.; Rapp, L. A.; Burns, V. R.; Gorse, R. A.; Knepper, J. C.; Koehl, W. J. *SAE Tech. Pap. Ser.* 1992, No. 920329.
- (37) Carter, W. P. L. *J. Air Waste Manage. Assoc.* 1994, 44, 881-899.
- (38) Pollack, A. K.; Cohen, J. P.; Noda, A. M. Auto/Oil Air Quality improvement research program: description of working data set. Systems Applications International, San Rafael, CA, 1990.
- (39) California exhaust emission standards and test procedures for 1988 and subsequent model passenger cars, light-duty trucks, and medium-duty vehicles. California Air Resources Board, Sacramento, CA, 1993.

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