

# Impact of California Reformulated Gasoline on Motor Vehicle Emissions. 1. Mass Emission Rates

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This paper addresses the impact of California phase 2 reformulated gasoline (RFG) on motor vehicle emissions. Phase 2 RFG was introduced in the San Francisco Bay Area in the first half of 1996, resulting in large changes to gasoline composition. Oxygen content increased from 0.2 to 2.0 wt%; and alkene, aromatic, benzene, and sulfur contents decreased. Gasoline density and  $T_{50}$  and  $T_{90}$  distillation temperatures also decreased. Light-duty vehicle emission rates were measured in a Bay Area roadway tunnel in summers 1994–1997. Vehicle speeds and driving conditions inside the tunnel were similar each year. The average model year of the vehicle fleet was about one year newer each successive summer. Large reductions in pollutant emissions were measured in the tunnel over the course of this study, due to a combination of RFG and fleet turnover effects. Between summers 1994 and 1997, emissions of carbon monoxide decreased by  $31 \pm 5\%$ , non-methane volatile organic compounds (VOC) decreased by  $43 \pm 8\%$ , and nitrogen oxides ( $\text{NO}_x$ ) decreased by  $18 \pm 4\%$ . It was difficult to separate clearly the fleet turnover and RFG contributions to these changes. Nevertheless, it was clear that the effect of RFG was greater for VOC than for  $\text{NO}_x$ . The RFG effect on vehicle emissions of benzene was estimated to be a 30–40% reduction. Use of RFG increased formaldehyde emissions by about 10%, while acetaldehyde emissions did not change significantly. RFG effects reported here may not be the same for other driving conditions or for other vehicle fleets. RFG effects on evaporative emissions are also important. The combined effect of phases 1 and 2 of California's RFG program was a 20% reduction in gasoline vapor pressure, about one-fifth of which occurred following the introduction of phase 2 RFG.

## Introduction

Motor vehicles are a significant source of air pollution, and efforts to control vehicle emissions have been ongoing since the 1960s. Increasingly stringent vehicle emission standards have led to the deployment of control technologies, such as positive crankcase ventilation, exhaust gas recirculation, and the catalytic converter (1, 2). Today's new cars emit about

one-tenth as much carbon monoxide (CO), volatile organic compounds (VOC), and nitrogen oxides ( $\text{NO}_x$ ) compared to cars sold 25 years ago. Despite this progress, increased vehicle travel and poor vehicle maintenance have offset some of the expected air quality benefits. To achieve acceptable air quality, additional motor vehicle pollution control measures are needed. In recent years, there has been considerable interest in reformulating gasoline to make it a cleaner-burning fuel.

Use of reformulated and oxygenated gasoline was mandated in the 1990 Clean Air Act Amendments (4). Oxygenated compounds such as methyl *tert*-butyl ether (MTBE) and ethanol have been added to gasoline during winter months to reduce CO emissions. Numerous studies reporting on the emission impacts of oxygenated gasoline programs have been reviewed by Howard et al. (3). Further reformulation of gasoline composition to reduce emissions of ozone precursors (VOC and  $\text{NO}_x$ ) is required in areas with severe ozone air pollution problems. While reformulated gasoline (RFG) use is currently required in only three areas in California (San Diego, Los Angeles, and Sacramento air basins), a statewide reformulated gasoline program has been implemented by the California Air Resources Board.

In phase 1 of the California program, effective 1992, the maximum allowed Reid vapor pressure (RVP) of gasoline sold during summer months was reduced from 9.0 to 7.8 psi, the use of lead in gasoline was eliminated, and the use of detergent additives to control engine deposits was required (5). Phase 2 of the California program took effect in the first half of 1996 and required more extensive changes to gasoline properties (6, 7). These changes included further reduction of summertime RVP to 7.0 psi maximum; reduction of benzene, total aromatic, olefin, and sulfur contents in gasoline; addition of oxygenates; and reductions in distillation temperatures,  $T_{50}$  and  $T_{90}$ . Refiners can choose either to produce gasoline with a prescribed formula, as indicated in Table 1, or to use a predictive model to establish alternative gasoline formulations that result in equivalent or greater emissions reductions (7). Estimates of the effect of phase 2 RFG on vehicle emissions, including cold-start, running exhaust, and evaporative emissions, are reductions of VOC by 17%,  $\text{NO}_x$  and CO by 11%, and toxic air contaminants by 30% in its first year of use (7).

The Auto/Oil Air Quality Improvement Research Program (8–10) demonstrated through laboratory testing that vehicle emissions can be reduced by modifying fuel properties. Tests were conducted using a stop-and-go urban dynamometer driving cycle, and gasoline composition was carefully controlled in each test. Individual and combined effects of changes in gasoline properties on exhaust emissions were examined. However, fuel effects were determined for only a small number of well-maintained, low-emitting vehicles, whereas on-road emissions are dominated by small numbers of gross-polluting vehicles (11). Since the effects of fuel changes on emissions from gross-polluting vehicles could not be characterized definitively (12), the Auto/Oil results may not be indicative of RFG effects for the in-use vehicle fleet (3).

To complement the results of dynamometer studies, the effects of changes in fuel composition on vehicle emissions can be determined in on-road settings. For example, remote sensing (13, 14) and tunnel (15, 16) studies have investigated the impact of modifying fuel properties on exhaust emissions from thousands of in-use vehicles, including gross-polluters, driven under real-world conditions. Tunnel studies, in particular, are well-suited for measuring the effects of

**TABLE 1. Average ( $\pm 1$  Standard Deviation) Properties of Gasoline Sold in the San Francisco Bay Area during Summers 1994–1997<sup>a</sup> Compared with California Phase 2 RFG Specifications**

gasoline property	1994	1995	1996	1997	phase 2 RFG <sup>b</sup>
RVP (psi)	7.4 $\pm$ 0.1	7.4 $\pm$ 0.1	7.0 $\pm$ 0.1	7.1 $\pm$ 0.1	7.0 <sup>c</sup>
sulfur (ppmw)	131 $\pm$ 41	81 $\pm$ 36	16 $\pm$ 9	12 $\pm$ 11	40
oxygen (wt %)	0.5 $\pm$ 0.3	0.2 $\pm$ 0.2	2.0 $\pm$ 0.3	1.6 $\pm$ 0.6	1.8–2.2
MTBE (vol %)	2.7 $\pm$ 1.7	1.0 $\pm$ 0.9	10.7 $\pm$ 1.7	8.2 $\pm$ 3.7	
alkane (vol %)	57.4 $\pm$ 4.8	56.6 $\pm$ 5.1	62.6 $\pm$ 2.5	65.4 $\pm$ 3.7	
alkene (vol %)	7.9 $\pm$ 4.4	8.8 $\pm$ 3.5	3.3 $\pm$ 0.9	3.4 $\pm$ 1.2	6.0
aromatic (vol %)	31.9 $\pm$ 2.1	33.7 $\pm$ 3.3	23.5 $\pm$ 1.4	22.7 $\pm$ 1.4	25
benzene (vol %)	1.6 $\pm$ 0.4	1.5 $\pm$ 0.4	0.4 $\pm$ 0.1	0.4 $\pm$ 0.1	1.0
T <sub>50</sub> (°F)	214 $\pm$ 8	218 $\pm$ 4	199 $\pm$ 4	200 $\pm$ 3	210
T <sub>90</sub> (°F)	334 $\pm$ 8	341 $\pm$ 8	300 $\pm$ 4	299 $\pm$ 6	300
density (g L <sup>-1</sup> )	761 $\pm$ 8	760 $\pm$ 4	743 $\pm$ 2	741 $\pm$ 5	

<sup>a</sup> Measured properties of ~35 regular, mid-, and premium grade gasoline samples collected in Concord and San Francisco during July and August of each summer. Composite properties were computed for each brand of gasoline according to the market share of each gasoline grade: 58% regular, 20% mid, and 22% premium (41). Average gasoline properties were computed by averaging together all brand composites with equal weighting. <sup>b</sup> The phase 2 RFG specifications shown here are flat limits; refiners may also comply with average limits. Gasoline sold in California should not exceed flat limits unless refiners use the California predictive model to establish alternative RFG specifications that provide equivalent or greater emissions reductions (7). <sup>c</sup> The limit on fuel volatility applies only during summer months, defined as April 1–October 31 for the Bay Area.

reformulated gasoline because many pollutants can be measured, including CO, VOC, NO<sub>x</sub>, and individual toxic compounds.

The objective of this study was to determine the emission impact of California phase 2 RFG. Vehicle emissions were measured in a San Francisco Bay Area roadway tunnel during the summers prior to and after the introduction of RFG. Each summer, the composition of gasoline sold in the Bay Area was determined. The impact of RFG on mass emission rates is examined here. The effect of RFG on the speciation and reactivity of exhaust and evaporative VOC emissions is addressed in a companion paper (17).

## Experimental Section

**Gasoline Sampling and Analysis.** Gasoline sold in the San Francisco Bay Area was collected and analyzed by Southwest Research Institute. Measured gasoline properties included RVP; density; aromatic, alkene, alkane, oxygenate, sulfur, and benzene contents; and distillation temperatures including T<sub>50</sub> and T<sub>90</sub>. For this study, fuel survey data were obtained for regular, mid-, and premium grade gasoline samples collected during summers 1994–1997 (18). Each year, about 35 gasoline samples of major gasoline brands were collected at service stations in Concord and San Francisco in July and August, respectively.

**Field Site.** Vehicle emissions were measured at the Caldecott tunnel during summers 1994–1997. Located east of San Francisco Bay on state highway 24, the Caldecott tunnel is heavily used during commute hours. It runs in the east–west direction connecting cities in Contra Costa County with Oakland, Berkeley, and San Francisco. The tunnel comprises three two-lane traffic bores, is 1100 m long, and has a roadway grade of +4.2% in the eastbound direction. Forced transverse ventilation along the length of the tunnel is provided by adjustable pitch fans housed in portal buildings above the entrance and exit. Additional longitudinal ventilation is induced by the flow of vehicles and by prevailing westerly winds. A schematic of the Caldecott tunnel is available elsewhere (15).

Traffic direction is always westbound in the northernmost bore and always eastbound in the southernmost bore. To accommodate large traffic volumes during weekday rush hour periods, the center bore of the tunnel carries westbound traffic toward San Francisco in the morning and eastbound traffic in the afternoon. Field sampling was conducted in the center bore during afternoon hours when vehicles traveled in the eastbound (uphill) direction toward Contra Costa

County. Traffic was monitored, and pollutant concentrations were measured during the afternoon commute period from 1600 to 1800 h on 10 or more days in each summer from 1994 through 1997. On 3 days in summer 1996 and 4 days in summer 1997, additional measurements were made earlier in the afternoon, starting at 1300 h, before the afternoon peak traffic period.

**Traffic Monitoring.** The vehicle fleet traveling through the center bore of the Caldecott tunnel was monitored on all days when emissions were measured. Visual counts were used to determine traffic volumes and composition. Vehicles were assigned to one of three categories: cars; light-duty trucks including pickups, sport utility vehicles, and small vans; and heavy-duty vehicles. License plate surveys were conducted to determine the age distribution and the fuel type of the vehicles being monitored. License plates were recorded using a Hi-8 format video camera and were later matched with vehicle registration data. Driving conditions inside the tunnel were monitored by following traffic with a chase car. Average vehicle speed was determined using the tunnel length and measured transit time for each “drive-through”. Two hundred fifty drivethroughs were conducted during summers 1995–1997. In addition, an instrumented vehicle that logged speed at 1-s intervals was used in summer 1996 to measure the speed profile inside the tunnel. Finally, a video camera was used each summer to record a wide view of all traffic exiting the tunnel.

**Pollutant Measurements.** Pollutant concentrations were measured in the traffic tube ~50 m before the tunnel exit and in the clean background air which was injected into the tunnel by the ventilation fans. Concentrations of CO<sub>2</sub>, CO, and NO<sub>x</sub> were measured continuously. CO<sub>2</sub> and CO concentrations were quantified using infrared gas filter correlation spectrometers, and NO<sub>x</sub> concentrations were measured by chemiluminescence. Continuous air monitoring data were recorded as 5-min average concentrations. Using traceable gas standards, zero and span checks were performed several times a week on each analyzer.

Two-hour integrated air samples were collected in 6-L stainless steel canisters for subsequent analysis to quantify MTBE and hydrocarbon concentrations. Similarly, 2-h integrated samples were collected using DNPH-impregnated silica cartridges for subsequent analysis to quantify carbonyl concentrations. Since ozone has been shown to interfere with the quantification of carbonyl concentrations (19), a potassium iodide ozone scrubber was placed upstream of the silica cartridge used to collect carbonyl samples from the

ventilation intake air. This was not necessary when collecting carbonyl samples in the tunnel because any ozone drawn into the tunnel is rapidly removed by reaction with nitric oxide. Hydrocarbon and carbonyl samples were collected only during the 1600–1800 h sampling periods.

Air samples collected in the canisters were analyzed with a Perkin-Elmer Model 8500 GC equipped with FID to determine total nonmethane hydrocarbon (NMHC) concentrations. Samples were preconcentrated using a Nutech Model 8548 cryogenic concentrator and injected into the GC. An analytical column was not used. The oven temperature was held at 105 °C for 5 min. Total NMHC in the sample was determined by comparison of peak area to that of an NIST certified propane standard. Methane, MTBE, and speciated NMHC concentrations were determined following the procedure outlined in Kirchstetter et al. (17).

During the 1994 field campaign, it was found that 1,3-butadiene was unstable in tunnel hydrocarbon samples when canisters were stored for several weeks prior to analysis (15). Therefore, no measurements of butadiene concentrations are reported for 1994. In summers 1995–1997, canisters were usually analyzed in the laboratory within 24 h of sample collection to minimize loss of 1,3-butadiene.

After each 2-h sampling period, DNPH-cartridges were eluted with 5 mL of acetonitrile, and the extracted samples were stored in tightly capped glass vials in a refrigerator. All elutions were completed within a few hours of sample collection. At the end of each year's sampling program, the extracted samples were analyzed by high-performance liquid chromatography (HPLC) using a procedure nearly identical to that developed for the Auto/Oil Air Quality Improvement Research Program (20). Carbonyl samples were analyzed by Hoekman and co-workers (21–23) at Chevron Research and Technology Co. from 1994 to 1996 and by Fung (24) in 1997.

**Quality Assurance.** Each summer, the Quality Assurance Section of the California Air Resources Board (ARB) conducted performance audits of the CO and NO<sub>x</sub> analyzers used at the Caldecott tunnel. In all cases, the analyzers were found to operate well within ARB's ±15% control limits. Tunnel CO and NO<sub>x</sub> analyzers were always accurate within ±2 and ±5%, respectively.

Measured total NMHC concentrations were compared with independent analyses of tunnel air samples collected in parallel. Independent analyses were performed by the Monitoring and Laboratory Division of the ARB (25, 26), Desert Research Institute (27), and Rasmussen (28). Six comparisons were made in summers 1995–1997. Total NMHC concentrations reported for samples collected in this study were between 1 and 9% higher than the values reported by the other investigators.

## Results

**Gasoline Properties.** Average San Francisco Bay Area gasoline properties derived from fuel survey data for summers 1994–1997 are shown in Table 1. Also shown are the flat limits for California's phase 2 RFG program, which took effect in the first half of 1996. As expected, significant changes to gasoline occurred between summers 1995 and 1996. Large changes included decreases in benzene, olefin, and aromatic contents and an increase in oxygen content to 2.0 ± 0.3 wt %. Distillation temperatures, *T*<sub>50</sub> and *T*<sub>90</sub>, and gasoline density also decreased between 1995 and 1996. Gasoline properties shown in Table 1 did not change between summers 1994 and 1995, or between summers 1996 and 1997, with the exception of changes to sulfur and oxygen content discussed below.

A trend toward lower sulfur content in gasoline was already evident in summer 1995. The magnitude of the reduction in sulfur content was comparable between 1994 and 1995 and

1995–1996. In the earlier two years, there was large brand-to-brand variability in gasoline sulfur levels, whereas by 1996 all gasoline samples had low sulfur content (<40 ppmw).

Oxygen content in gasoline was low in summers 1994 and 1995 and then rose dramatically in 1996, as indicated in Table 1. Compared to 1996 levels, average oxygen content decreased to 1.6 ± 0.6 wt % in 1997 and showed greater variability across gasoline brands and grades, with some gasoline samples having very low oxygen content. Presumably, Bay Area refiners used California's predictive model (7) to determine modifications to other fuel properties to compensate for reduced use of oxygenate in summer 1997.

The predominant oxygenate found in gasoline was MTBE. Small amounts of *tert*-amyl methyl ether (TAME) and methanol, typically < 0.1 vol %, were detected in some 1996 gasoline samples. In 1997, some gasoline samples contained greater amounts of TAME, which contributed about 5% of the oxygen content found in gasoline overall. The remaining 95% of the fuel oxygen content continued to be supplied in the form of MTBE.

**Fuel Economy.** The volumetric energy content of gasoline is a good predictor of fuel economy (29). Reformulation may decrease fuel economy by lowering the energy content of gasoline. For example, the energy content of MTBE (26 MJ L<sup>-1</sup>), as measured by its lower heating value (LHV), is less than that of conventional gasoline (33 MJ L<sup>-1</sup>). To estimate the effect of phase 2 RFG on fuel economy, heating values were computed using the detailed chemical composition of regular and premium grade gasolines collected at high-volume service stations in Berkeley (17). Heating values were calculated using the following equation

$$\text{LHV} = - \left[ \sum_{i=1}^n (\Delta h_{c,i} \cdot w_i) \right] \cdot \rho_f \quad (1)$$

where LHV is the lower heating value (J L<sup>-1</sup>),  $\rho_f$  is the density of gasoline (g L<sup>-1</sup>),  $w_i$  is the weight fraction of compound *i* in gasoline, and  $\Delta h_{c,i}$  is the enthalpy of combustion of compound *i* (J g<sup>-1</sup>). Enthalpies of combustion for each compound in gasoline were calculated from tabulated enthalpies of formation (30) assuming complete combustion to carbon dioxide and water vapor, and are reported as Supporting Information in ref 17.

Overall, the LHV of gasoline decreased from 32.8 MJ L<sup>-1</sup> in 1995 to 31.7 MJ L<sup>-1</sup> in 1996, mainly due to a decrease in gasoline density and addition of MTBE. This decrease in the volumetric energy content of gasoline corresponds to a ~3% decrease in fuel economy for most vehicles (29).

**Traffic Characteristics.** Attributes of the traffic that traveled through the Caldecott tunnel from 1600 to 1800 h are presented in Table 2. The number of vehicles traveling through the tunnel, ~8400 during each 2-h sampling period, was consistent on all sampling days across all four summers. Traffic consisted of light-duty vehicles almost exclusively because heavy-duty vehicles were required to use other tunnel bores. Heavy-duty trucks comprised <0.3% of the vehicles in the center bore in each year. About two-thirds of the vehicles were cars, and the remainder were pickups, sport utility vehicles, and small vans. A gradual increase was seen between 1994 and 1997 in the fraction of light-duty trucks, as indicated in Table 2.

Each summer, the average vehicle model year was about one year newer. The average vehicle age was ~7 years in all cases. Pre-1980 model year vehicles comprised about 4% of the fleet; pre-1975 vehicles comprised 2% or less of the fleet each summer. The light-duty fleet was almost entirely gasoline-powered; the fraction of vehicles identified as diesel-fueled ranged from 1 to 2%. Therefore, >95% of the vehicles in the tunnel were originally equipped with catalytic converters.

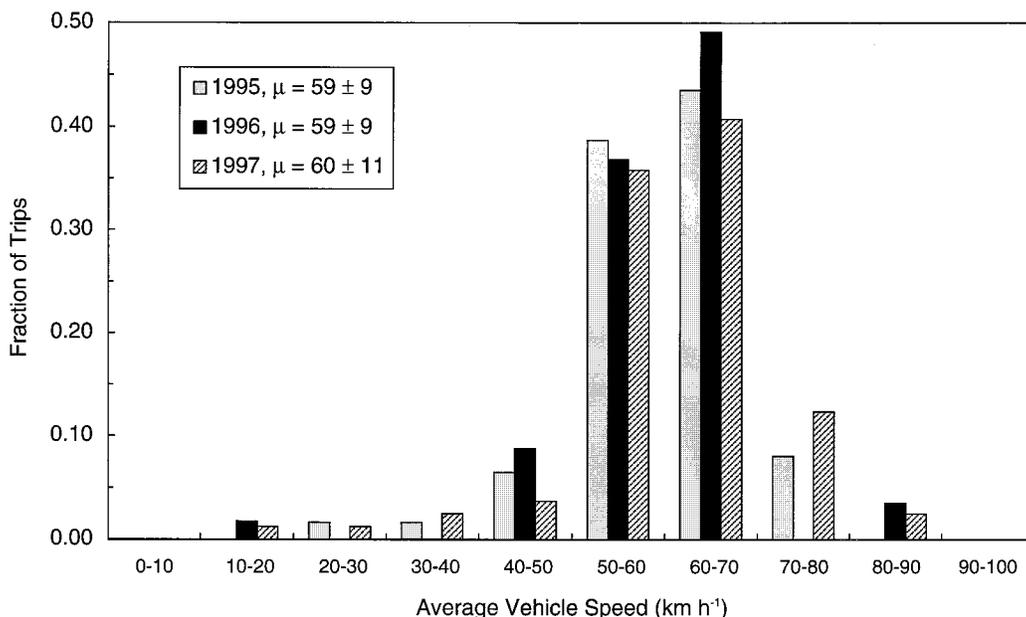
**TABLE 2. Attributes of Vehicles Using the Center Bore of the Caldecott Tunnel (1600–1800 h)**

	1994	1995	1996	1997
volume (no. h <sup>-1</sup> )	4260 ± 240	4220 ± 260	4220 ± 220	4220 ± 170
cars (%)	69	67	66	65
LD trucks <sup>a</sup> (%)	31	33	34	35
HD vehicles <sup>b</sup> (%)	0.2	0.2	0.3	0.2
mean model year	n/a <sup>c</sup>	1989.3	1990.1	1990.9
LD diesel <sup>d</sup> (%)	n/a	1.0	1.5	1.8

<sup>a</sup> Light-duty trucks included pickups, sport utility vehicles, and small vans. <sup>b</sup> Heavy-duty vehicles included large delivery trucks (i.e., UPS delivery vans and larger vehicles). <sup>c</sup> Not available. <sup>d</sup> The fraction of cars and light-duty trucks that were diesel-fueled, as determined from vehicle registration information.

The distributions of average vehicle speeds measured during 200 tunnel drivethroughs that took place between 1600 and 1800 h are shown in Figure 1. Average vehicle speeds of 60 km h<sup>-1</sup> were typical, and no major changes in driving conditions were observed from one year to the next. Eighty-six percent or more of the drivethroughs in each summer had average speeds between 50 and 80 km h<sup>-1</sup>. Slower speeds resulted from an occasional disruption in traffic flow, such as a vehicle stall inside the tunnel or heavy congestion downstream of the tunnel. Stalled vehicles were cleared rapidly from the tunnel by Caltrans personnel.

Instrumented vehicle measurements conducted in 1996 provided additional information about driving conditions. Figure 2 shows the average speed profile of the instrumented vehicle measured during 26 trips through the tunnel from 1600 to 1800 h. Average speed was 52 km h<sup>-1</sup> at the entrance and 69 km h<sup>-1</sup> at the exit of the tunnel. Speeds were slower at the entrance because heavy congestion during the afternoon peak traffic period resulted in a queue of vehicles ahead of the tunnel entrance. Vehicle speeds beyond the middle of the tunnel were more uniform than in the first half of the tunnel. The driving pattern depicted in Figure 2 was very repeatable. Heavy accelerations and stop-and-go driving were seldom observed.



**FIGURE 1. Histogram of average vehicle speeds measured during 200 drivethroughs in the Caldecott tunnel from 1600 to 1800 h.**

Figure 3 shows the instantaneous speeds and accelerations of the instrumented vehicle while driving through the tunnel. To account for the increase in engine load when driving on the 4.2% uphill grade inside the tunnel, an acceleration of  $g \cdot \sin \theta = 0.41 \text{ m s}^{-2}$ , where  $\sin \theta \approx \tan \theta = 0.042$ , has been added to the measured vehicle acceleration. The speed/acceleration domain of the LA-4 city driving cycle used in the Federal Test Procedure (FTP) is shown in Figure 3 for comparison with the driving conditions in the tunnel. Most of the driving in the tunnel occurred within a small range of speeds and accelerations, which were largely within the FTP domain. Nearly all points that were outside of this domain were due to higher accelerations. For some vehicles, this may lead to enrichment of the air/fuel mixture.

Driving conditions earlier in the afternoon differed from those observed from 1600 to 1800 h. Traffic volume from 1300 to 1500 h averaged  $2740 \pm 660$  and  $2620 \pm 520$  vehicles per hour in 1996 and 1997, respectively, which was about 60% of the 1600–1800 h volume. Since traffic was lighter, there was no queue of vehicles waiting to enter the tunnel. Vehicles typically entered, traveled through, and exited the tunnel at about the same speed. Vehicle speeds measured from 1300 to 1500 h during 50 additional drivethroughs were  $79 \pm 7$  and  $81 \pm 7 \text{ km h}^{-1}$  in summers 1996 and 1997. These were  $\sim 20 \text{ km h}^{-1}$  faster than typical vehicle speeds observed from 1600 to 1800 h.

Traffic volume was lower and vehicle speeds were higher during the 1600–1800 h sampling period on August 6, 1996 relative to conditions observed on other days due to a closure of multiple lanes on the San Francisco–Oakland Bay bridge, which is located to the west of the tunnel. Average traffic volume during this sample period was  $3910 \pm 210$  vehicles per hour; the average speed was  $71 \pm 11 \text{ km h}^{-1}$ , about  $10 \text{ km h}^{-1}$  faster than usual. Therefore, measurements of vehicle emissions on August 6 were excluded from the calculation of summer 1996 emission factors.

The vehicles observed in this study were operating in a warmed-up, or 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 of the tunnel, not the center bore where measurements for this study were made. Vehicles

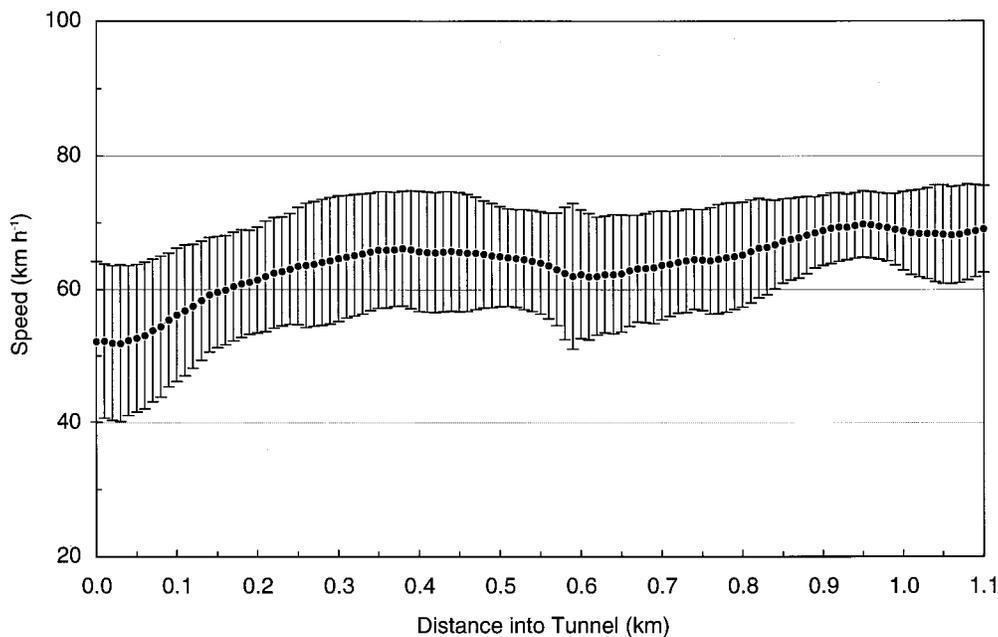


FIGURE 2. Average ( $\pm 1$  standard deviation) speed profile in the Caldecott tunnel measured during 26 trips with an instrumented vehicle from 1600 to 1800 h in summer 1996.

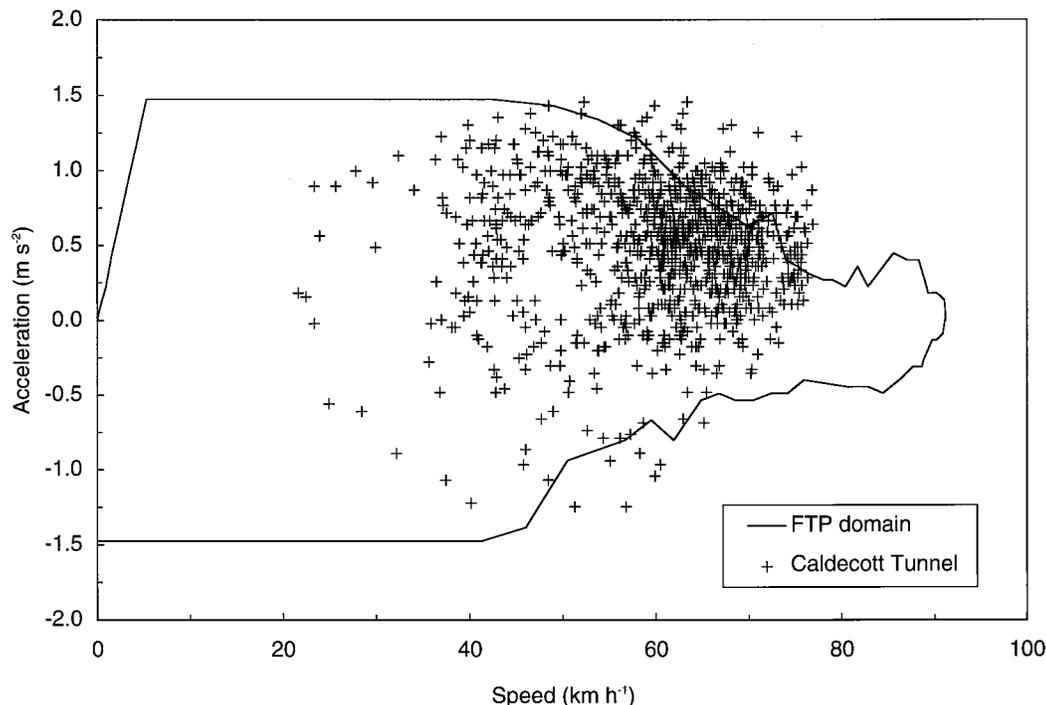


FIGURE 3. Second-by-second acceleration vs speed plot for driving inside the Caldecott tunnel during summer 1996 (1600–1800 h). Accelerations have been increased to account for the 4.2% uphill grade (see text). Also shown is the outer boundary of the domain of driving conditions experienced during the Federal Test Procedure (FTP) emissions certification test.

merging onto highway 24 via the further on-ramp are exiting another highway and are therefore already warmed-up. Moreover, the overwhelming majority of vehicles that use the tunnel during the afternoon commute travel longer distances before entering the tunnel.

**Pollutant Concentrations.** Background-subtracted pollutant concentrations measured during summers 1994–1997 at the Caldecott tunnel are presented in Table 3. Pollutant concentrations measured inside the tunnel were much higher than in background air. Concentrations of CO, NO<sub>x</sub>, and NMHC were typically 25, 30, and 10 times higher in the tunnel air compared to background air. In all years, background

concentrations of CO and NO<sub>x</sub> were very low and indicated that there was little or no recirculation of tunnel exhaust air back to the ventilation intake. For example, background CO concentrations were typically less than 2 ppm. Measured background CO<sub>2</sub> concentrations in summers 1996 and 1997 were  $383 \pm 36$  and  $380 \pm 13$  ppm, respectively. In 1994 and 1995, background CO<sub>2</sub> concentrations were not monitored continuously, so a typical concentration of 380 ppm was used to compute background-subtracted values of CO<sub>2</sub> shown in Table 3 for these summers.

**Emission Factors.** Vehicle emission factors were calculated from the measured pollutant concentrations shown in

**TABLE 3. Background-Subtracted Pollutant Concentrations<sup>a</sup> Measured from 1600 to 1800 h in the Center Bore of the Caldecott Tunnel**

date	CO (ppm)	CO <sub>2</sub> (ppm)	NO <sub>x</sub> (ppm)	NMHC (ppmC)	benzene (ppbC)	formaldehyde (ppbC)	acetaldehyde (ppbC)	1,3-butadiene (ppbC)	MTBE (ppbC)
Summer 1994									
Aug 22	n/a <sup>b</sup>	573	n/a	2.86	202	24.0	7.1	n/a	n/a
Aug 23	33.0	568	n/a	3.22	154	23.5	6.6	n/a	n/a
Aug 24	32.8	640	2.08	3.08	190	26.4	8.6	n/a	n/a
Aug 25	34.9	618	2.12	3.33	233	25.6	7.9	n/a	n/a
Aug 26	33.1	558	1.85	3.03	241	23.7	7.4	n/a	n/a
Aug 29	36.7	676	2.20	3.34	233	27.2	8.6	n/a	n/a
Aug 30	29.1	459	1.70	2.58	176	17.4	5.7	n/a	n/a
Aug 31	30.1	537	1.79	2.91	211	21.3	7.9	n/a	n/a
Sep 01	27.9	468	1.57	2.73	209	18.2	5.8	n/a	n/a
Sep 02	27.8	432	1.61	2.87	200	18.3	6.0	n/a	n/a
Summer 1995									
Jul 31	30.2	631	1.99	n/a	n/a	23.1	6.8	n/a	n/a
Aug 01	33.8	696	2.02	n/a	n/a	25.3	7.1	n/a	n/a
Aug 02	33.7	720	2.16	n/a	n/a	28.0	8.4	n/a	n/a
Aug 03	32.6	681	2.04	3.84	193	25.8	7.9	27.7	14.5
Aug 07	34.0	700	1.97	4.03	222	25.5	7.9	19.5	27.0
Aug 08	34.4	711	2.32	3.23	198	24.5	7.1	24.2	17.5
Aug 09	33.5	702	2.24	3.38	199	26.8	8.2	18.3	15.5
Aug 10	31.6	676	2.08	3.49	191	26.3	7.8	26.6	21.1
Aug 11	32.2	656	1.92	3.17	198	29.1	7.4	18.4	19.0
Aug 14	32.6	688	2.08	3.10	186	22.6	6.4	16.5	14.5
Aug 15	28.4	623	1.86	2.80	168	21.2	5.3	27.2	20.0
Aug 16	28.9	618	1.91	2.66	170	23.0	5.4	22.9	18.5
Aug 17	35.8	773	2.35	3.94	257	30.0	8.5	18.5	22.5
Summer 1996									
Jul 29	24.3	637	1.78	2.19	84.9	21.4	5.1	12.0	93.0
Jul 30	26.8	664	1.77	2.38	91.9	25.5	4.8	11.2	99.0
Jul 31	26.5	677	1.89	2.76	101.6	24.9	7.4	12.5	123.7
Aug 01	25.0	658	1.91	2.70	91.7	28.9	6.0	11.7	136.0
Aug 05	22.0	603	1.68	2.13	77.9	27.2	5.7	17.0	79.0
Aug 06 <sup>c</sup>	23.2	504	1.52	1.59	74.8	23.3	4.4	9.0	68.5
Aug 07	26.4	669	1.98	2.45	96.5	28.6	5.8	12.2	104.0
Aug 08	27.0	627	1.86	2.66	95.7	27.4	5.7	11.9	125.5
Aug 12	27.7	699	2.05	2.65	97.0	24.1	5.8	18.3	155.0
Aug 13	25.2	626	1.74	2.42	85.2	22.5	6.4	10.0	119.5
Aug 14	25.1	633	1.82	2.22	84.9	24.5	5.6	9.6	91.7
Aug 15	26.4	686	2.18	2.67	94.6	25.0	5.8	18.2	131.0
Summer 1997									
Jul 31	26.4	633	1.83	1.99	83.0	11.8	3.9	15.0	72.5
Aug 01	24.8	605	1.76	1.97	78.3	14.2	4.0	14.8	65.0
Aug 04	25.6	678	1.90	1.59	67.0	13.6	3.7	12.4	63.5
Aug 05	27.6	723	2.02	2.02	80.7	15.4	4.5	14.4	92.5
Aug 06	26.3	676	1.87	2.26	89.3	14.1	3.0	18.0	102.5
Aug 07	28.2	701	1.89	2.37	94.4	15.7	5.7	17.2	96.9
Aug 11	24.7	597	1.70	1.60	65.6	10.1	4.0	12.8	50.0
Aug 12	25.5	621	1.73	1.78	79.7	15.8	4.8	18.0	68.3
Aug 13	28.4	710	2.05	2.69	104.7	21.4	6.3	20.8	98.5
Aug 14	27.4	718	1.98	2.47	92.0	21.6	6.3	18.4	97.1

<sup>a</sup> Pollutant concentrations were measured in the tunnel air and in the background air injected into the tunnel by the ventilation fans. Shown here are background-subtracted values. <sup>b</sup> Not available. <sup>c</sup> Traffic speeds were unusually high on August 6, 1996 during the 1600–1800 h sampling period, so pollutant concentrations measured on this day were excluded from the calculation of emission factors.

Table 3. Emission factors were computed as mass of pollutant emitted per unit volume of gasoline burned using the following equation

$$E_p = \left( \frac{\Delta[\text{CO}_2] + \Delta[\text{CO}] + \Delta[\text{VOC}]}{\Delta[\text{P}]} \right) \left( \frac{\text{MW}_p}{\text{MW}_c} \right) w_c \rho_f \quad (2)$$

where  $E_p$  is the emission factor for pollutant P ( $\text{g L}^{-1}$ ),  $\Delta[\text{P}]$  is the increase in the concentration of pollutant P above background levels (ppm),  $\text{MW}_p$  is the molecular weight of pollutant P ( $\text{g mol}^{-1}$ ),  $\text{MW}_c = 12 \text{ g mol}^{-1}$  is the molecular weight of carbon,  $w_c$  is the carbon weight fraction in gasoline, and  $\rho_f$  is the density of gasoline ( $\text{g L}^{-1}$ ).  $\text{NO}_x$  emission factors are reported as  $\text{NO}_2$  (i.e., a molecular weight of 46 was used in eq 2), even though NO constituted ~99% of the  $\text{NO}_x$

measured in the tunnel. Since the FID is known to give a partial response to MTBE, equal to 86% of propane's response on a per-carbon basis (31), NMHC concentrations reported in Table 3 include a small contribution from MTBE. True NMHC concentrations were calculated by subtracting 86% of the directly measured MTBE concentrations (ppbC) from reported total NMHC concentrations measured by FID. NMHC emission factors were then computed assuming 14 g per mol of C. Non-methane organic carbon (NMOC) emission factors were calculated as the sum of NMHC, MTBE, and formaldehyde emission factors. Additional contributions to total NMOC mass from other aldehydes and ketones were negligible. Gasoline densities used in eq 2 were obtained from fuel survey data shown in Table 1. Carbon weight fractions for summers 1994–1995 and summers 1996–1997

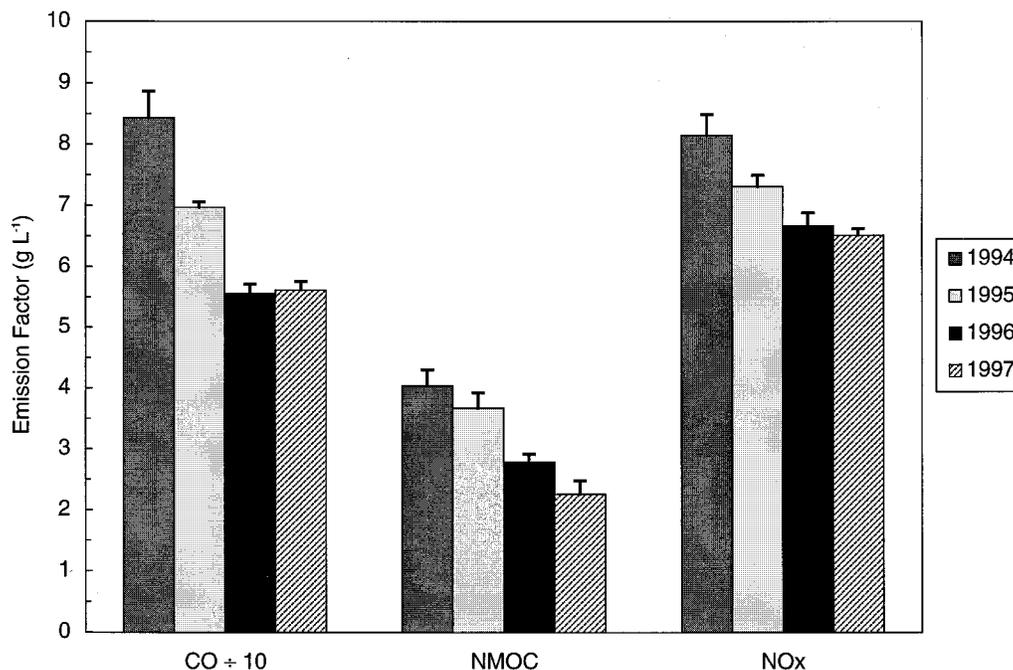


FIGURE 4. Average (+95% C.I.) light-duty vehicle emission factors for regulated pollutants measured in the Caldecott tunnel during summers 1994–1997. Emission factors are expressed per unit volume of fuel burned (see text).

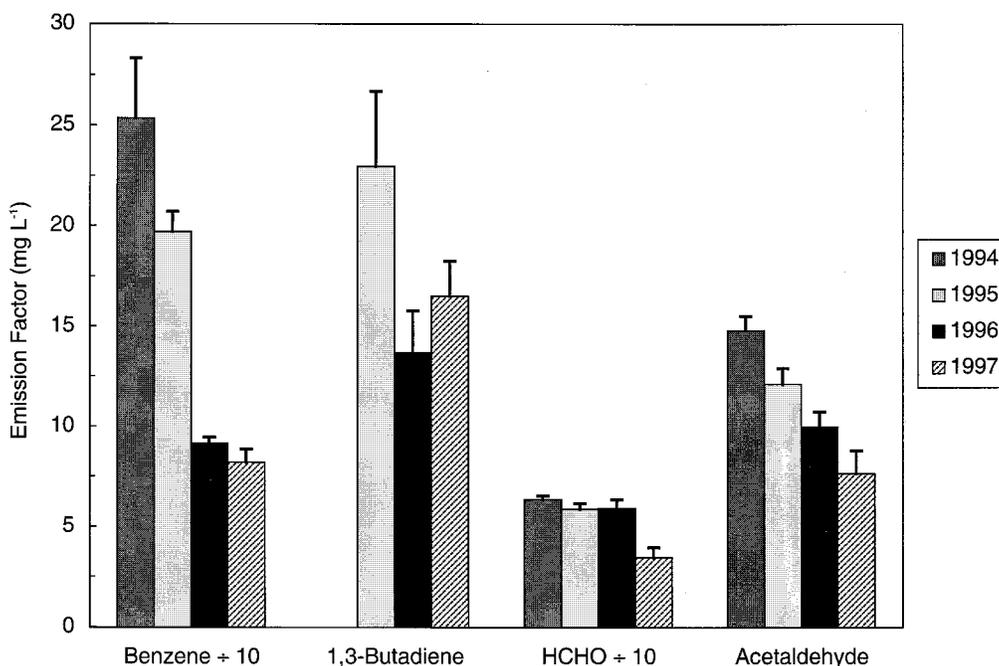


FIGURE 5. Average (+95% C.I.) light-duty vehicle emission factors for toxic pollutants measured in the Caldecott tunnel during summers 1994–1997. Emission factors are expressed per unit volume of fuel burned (see text).

were 0.87 and 0.85, respectively. The lower carbon weight fraction for the more recent summers is a result of having ~2% oxygen by weight in gasoline.

**Emission Trends.** Average emission factors of regulated and toxic air pollutants measured each summer are shown in Figures 4 and 5. Note that emission factors for CO, benzene, and formaldehyde (HCHO) shown in these figures have been divided by a factor of 10. Within each year, emission factors were consistent from one day to the next, as reflected by the confidence intervals shown on the figures. This day-to-day consistency was expected because driving conditions were similar, and many of the same commuter vehicles traveled through the tunnel each day. Emission factors for butadiene,

which was found to be unstable in stainless steel canisters during tunnel sampling in 1994 (15), showed larger day-to-day variability.

Year-to-year and overall changes in emission factors from 1994 to 1997 are reported in Table 4. Whereas vehicle emissions shown in Figures 4 and 5 are expressed per unit volume of fuel burned and have not been adjusted to account for the 3% decrease in fuel economy due to RFG use, changes in vehicle emission rates reported in Table 4 do account for changes in fuel economy. Measured emission factors for 1996 and 1997 were multiplied by 1.03 to account for the 3% decrease in fuel economy relative to 1994 and 1995. Thus, values shown in Table 4 are representative of changes in

**TABLE 4. Percent Changes between Summers<sup>a</sup> in Vehicle Emissions (g km<sup>-1</sup>) Measured during the 1600–1800 h Sampling Period**

pollutant	% change in vehicle emissions			
	1994–1995	1995–1996	1996–1997	overall 1994–1997
CO	-17 ± 4	-18 ± 2	+1 ± 4	-31 ± 5
NMOC	-9 ± 8	-22 ± 7	-19 ± 8	-43 ± 8
NO <sub>x</sub>	-10 ± 4	-6 ± 4	-2 ± 3	-18 ± 4
benzene	-22 ± 11	-52 ± 5	-10 ± 7	-67 ± 11
1,3-butadiene	n/a <sup>b</sup>	-39 ± 17	+21 ± 10	-26 ± 17 <sup>c</sup>
formaldehyde	-8 ± 5	+4 ± 8	-41 ± 10	-44 ± 8
acetaldehyde	-18 ± 7	-15 ± 9	-23 ± 13	-47 ± 8

<sup>a</sup> 95% confidence intervals for changes in vehicle emission factors calculated using eq 2. Emission factors shown in Figures 4 and 5 for 1996 and 1997 have been multiplied by 1.03 to account for the 3% decrease in fuel economy that occurred between 1995 and 1996. Thus, values reported here are representative of emission changes per kilometer of vehicle travel. <sup>b</sup> Not available. <sup>c</sup> The overall change in 1,3-butadiene reported here is the change between 1995 and 1997, discounted for the decrease in fuel economy between 1995 and 1996.

emissions per kilometer of vehicle travel.

As indicated in Figures 4 and 5, and in Table 4, vehicle emissions were significantly lower in 1997 than in 1994. Over the course of this study, emissions (per km of vehicle travel) decreased by 18% for NO<sub>x</sub>; 31% for CO; ~45% for NMOC, HCHO, and acetaldehyde; and 67% for benzene. Butadiene was not measured in 1994; however, the emission factor for butadiene in 1997 was 26% lower than in 1995. For all pollutants except formaldehyde, a significant portion of the overall decrease in emissions occurred between 1995 and 1996, which is when most of the changes to gasoline composition occurred. Emission factors also changed between 1994 and 1995 and 1996–1997, when most gasoline properties were comparatively stable. For example, decreases in CO and NO<sub>x</sub> between 1994 and 1995 were comparable to decreases between 1995 and 1996.

**Temperature Effect.** Ambient air temperature may influence vehicle emissions. For instance, greater use of air conditioning on hotter days increases engine load. Average 1600–1800 h temperatures in Berkeley, near the Caldecott tunnel, were 18, 20, 20, and 19 °C during sampling periods in summers 1994–1997, respectively (32). The differences from year to year were negligible. In fact, afternoon temperatures varied much more from day to day within each summer than they did from one summer to the next. For example, the maximum and minimum afternoon temperatures during sampling in summer 1995 were 27 and 15 °C, but there was no correlation between air temperature and emission factors (normalized to fuel consumption) measured at the tunnel. It is unlikely that air temperature had any effect on year-to-year changes in emissions measured in this study.

**Emissions vs Driving Condition.** Emission factors for CO and NO<sub>x</sub> are plotted as a function of time of day in Figures 6 and 7. For both pollutants, emission factors decreased steadily during the course of the afternoon. Average CO and NO<sub>x</sub> emission factors measured from 1300 to 1500 h were about 40 and 20% higher, respectively, than from 1600 to 1800 h. This trend is attributed to the decrease in vehicle speeds during the course of the afternoon. As noted above, vehicle speeds were ~20 km h<sup>-1</sup> faster from 1300 to 1500 h compared to the later 1600–1800 h sampling period.

Vehicle speeds during the 1600–1800 h sample period on August 6, 1996 were about 10 km h<sup>-1</sup> higher than usual. Measured CO and NO<sub>x</sub> emission factors for this period were 15 and 4% higher, respectively, than the average 1600–1800 h emission factors measured on all other days in 1996. These

changes are consistent with emissions trends during the period from 1300 to 1800 h described above. NMOC emissions on August 6 were 15% lower than the average for the other sampling days in summer 1996.

The CO emission factor exhibited a more pronounced trend than did the NO<sub>x</sub> emission factor, indicating that CO emissions were more sensitive to changes in engine load and air/fuel ratio. Fuel enrichment was probably more common from 1300 to 1500 h and during the high-speed event of August 6, 1996 than during the typical 1600–1800 h period when most of the driving occurred within the domain of the FTP city driving cycle (see Figure 3). The same decreasing trend in CO and NO<sub>x</sub> emissions factors was observed over the course of the afternoon in both 1996 and 1997 and was expected since the same pattern of increasing traffic volume and decreasing average speeds from 1300 to 1800 h was observed in both years.

## Discussion

Vehicle emissions were measured during four consecutive summers, 1994–1997, to quantify emission changes between summers 1995–1996 which spanned the transition to phase 2 RFG use, and to measure the impact of fleet turnover on vehicle emissions between summers 1994–1995 and 1996–1997 when gasoline composition was expected to be relatively stable. It was anticipated that changes in emissions between summers 1995–1996 would express the combined effects of RFG use and fleet turnover and that the RFG effect could be separated using measurements of the effect of fleet turnover alone.

Replacement of older vehicles with newer ones that have more robust emission controls and meet increasingly stringent emissions standards reduces fleet-average emissions. This is supported by a study of long-term vehicle emission trends in highway tunnels prior to the introduction of reformulated gasoline, which indicates that fleet turnover is the primary cause for reductions in on-road light-duty vehicle emissions (33). Light-duty vehicle emissions of CO decreased an average of 8.5% per year over the period from 1981 to 1992 (33). The vehicle fleet traveling in the Caldecott tunnel was newer during each successive summer that measurements were conducted (see Table 2). Thus, it is expected that fleet turnover contributed to the measured changes in emission factors.

Although it was expected in this study that changes in emission factors between 1994–1995 and 1996–1997 would be the result of fleet turnover alone, it appears that changes in fuel composition also may have been important. Assuming, for example, the 17% decrease in CO emissions measured at the Caldecott tunnel between 1994 and 1995 was due entirely to fleet turnover would be inconsistent with long-term trends in vehicle emissions measured in other tunnels (33). Additionally, California's motor vehicle emission factor model, EMFAC version 7F, predicts only a 5–7% reduction in running exhaust emissions of CO, VOC, and NO<sub>x</sub> due to fleet turnover between 1993 and 1994 when fuel properties were stable.

Gasoline sulfur content decreased by about 50 ppm between 1994 and 1995 (see Table 1). Experiments conducted during the Auto/Oil program indicate that reductions in gasoline sulfur content alone can have a significant impact on emissions, even when sulfur content is already low (34). Average hot-stabilized NMHC, CO, and benzene emissions from ten 1989 model year vehicles decreased by 32, 29, and 57% when gasoline sulfur content was reduced from 138 to 44 ppm. Average stabilized formaldehyde and acetaldehyde emissions also decreased significantly in the same test, and NO<sub>x</sub> emissions remained about the same. Therefore, changes in gasoline sulfur content may have affected emissions measured in the tunnel between 1994 and 1995, although

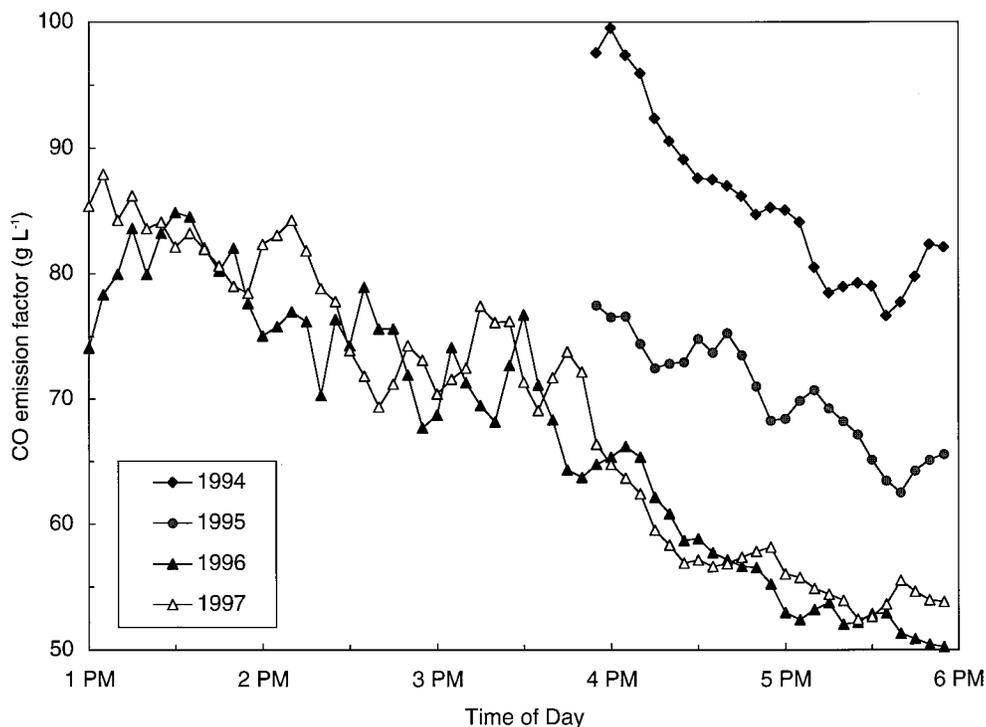


FIGURE 6. Fifteen-min running average light-duty CO emission factors measured in the Caldecott tunnel.

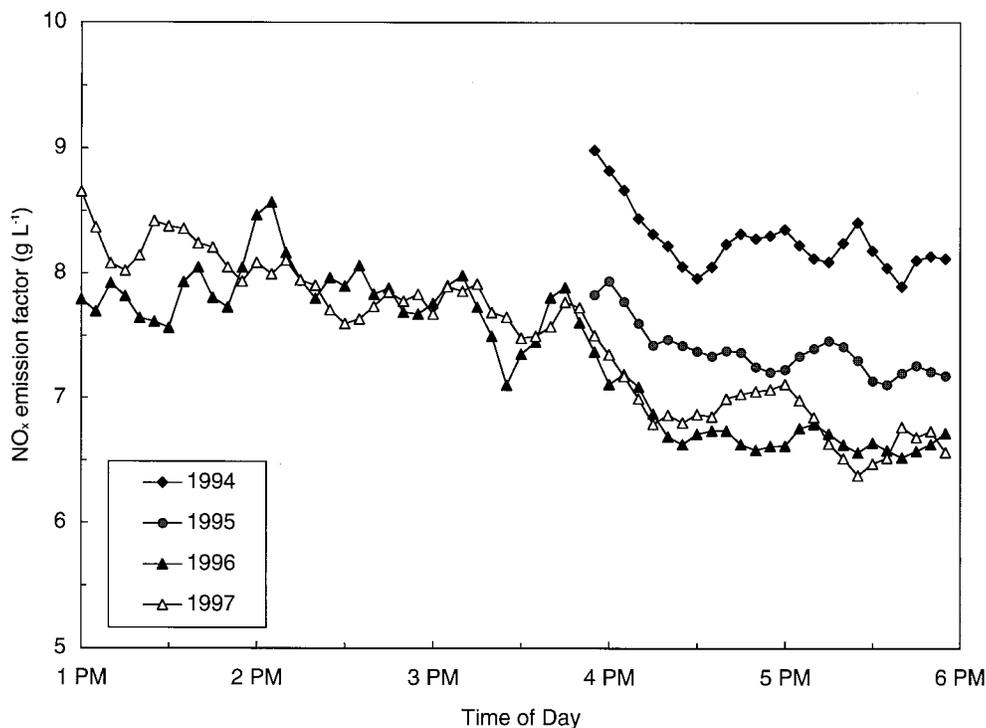


FIGURE 7. Fifteen-min running average light-duty NO<sub>x</sub> emission factors measured in the Caldecott tunnel.

the magnitude of the sulfur effect on the in-use fleet is uncertain.

Between summers 1996 and 1997, gasoline oxygen content decreased from  $2.0 \pm 0.3$  to  $1.6 \pm 0.6$  wt %; MTBE content decreased by about 2.8 vol %, whereas alkane content in gasoline increased by about the same amount. Previous on-road studies indicate that addition of oxygenates to gasoline, in combination with other changes to fuel properties such as a decrease in aromatics content, led to reduced CO and NMOC emissions (13–15). In the Caldecott tunnel, Kirchstetter et al. (15) measured decreases in CO and NMOC

emissions of about 12 and 11%, respectively, per wt % increase in gasoline oxygen content. NO<sub>x</sub> emissions were not affected (15). The decrease in Bay Area gasoline oxygenate content between 1996 and 1997 may have affected emissions, but since other fuel properties such as sulfur and aromatics content did not change much during this period, the impact was likely less than a 4–5% increase in CO and NMOC emissions, offsetting some of the potential reductions due to fleet turnover. This may explain why CO emissions did not change between these years. It is unclear, however, why measured NMOC emissions decreased over the same period.

In conclusion, emission changes between summers 1994–1995 and 1996–1997 may be the result of both fleet turnover and changes to gasoline composition. Thus, it would be inappropriate to use emissions changes during these periods to estimate the pure effect of fleet turnover. Use of emissions changes between 1994 and 1995 as an estimate of the fleet turnover effect could negatively bias an estimate of the RFG effect if reduced gasoline sulfur content between 1994 and 1995 decreased emissions in the Caldecott tunnel. Any decrease in emissions between 1994 and 1995 due to reduced sulfur content should be included in, not subtracted from, estimates of the RFG effect. Similarly, use of emissions changes between 1996 and 1997 as an estimate of the fleet turnover effect may lead to an overestimation of the RFG effect. More precise estimates of the impacts of RFG would be possible if the fleet turnover effect was better understood.

**Impact of Phase 2 RFG.** Despite the uncertainties mentioned above, it was possible to reach several conclusions about the effects of RFG on vehicle emissions. For example, the impact of RFG was larger for NMOC than for  $\text{NO}_x$ . NMOC and  $\text{NO}_x$  showed similar decreases between 1994 and 1995, whereas NMOC decreased nearly four times more than  $\text{NO}_x$  between 1995 and 1996. A clear benefit of RFG use is reduced benzene emissions. Given the emissions changes reported in Table 4, the estimated impact of RFG on benzene emissions was a 30–40% reduction. The large reduction in butadiene emissions between 1995 and 1996 also suggests a significant RFG impact. It is not clear why butadiene emissions increased between 1996 and 1997. The overall reduction in butadiene from 1995 to 1997 ( $26 \pm 17\%$ ) is likely a lower bound estimate of the RFG benefit. Acetaldehyde emissions decreased about the same amount between each summer, indicating that there was no significant effect of RFG on acetaldehyde. An increase in acetaldehyde emissions would be expected if ethanol or ethyl *tert*-butyl ether (ETBE) were used instead of MTBE (35).

Formaldehyde emissions increased between 1995 and 1996 despite the overall decrease in NMOC emissions, consistent with the increase in gasoline MTBE content (36). As shown in Table 4, formaldehyde emissions decreased substantially between 1996 and 1997. This decrease was due in part to the reduction in NMOC emissions and to lower MTBE levels in 1997 gasoline as well (see Table 1). In addition, use of different DNPH-impregnated cartridges in 1997 led to less stable sample air flow rates which may have biased 1997 carbonyl measurements. Using the change in formaldehyde emissions between 1994 and 1995 as an estimate of the fleet turnover effect, the estimated RFG effect was a 12% increase.

Vehicle emissions of MTBE increased due to the introduction of reformulated gasoline. The emission factor calculated using eq 2 and MTBE concentrations shown in Table 3 increased from  $26 \pm 4 \text{ mg L}^{-1}$  in 1995 to  $160 \pm 20 \text{ mg L}^{-1}$  in 1996 and then decreased to  $110 \pm 10 \text{ mg L}^{-1}$  in 1997. The decrease in 1997 was the result of lower MTBE content in gasoline. Given that MTBE contributed 11 and 8% of gasoline mass in 1996 and 1997, respectively, and that gasoline density was  $\sim 740 \text{ g L}^{-1}$ , then it follows that only 0.2% of MTBE in gasoline escaped combustion during tunnel driving.

RFG effects reported here do not apply to the entire California vehicle fleet. In this study, emissions were measured from on-road vehicles operating in a warmed-up mode, under loaded conditions, traveling at moderate steady speeds. The effects of RFG on emissions under cold-start or stop-and-go city driving conditions and on other vehicle fleets may differ from those reported here and thus should be studied to assess more completely the impacts of RFG. For example, Gertler et al. (16) measured vehicle emissions in the Sepulveda tunnel in southern California in 1995 and 1996. The vehicle fleet in that tunnel was about 3 years older, on

average, than vehicles observed traveling through the Caldecott tunnel in the present study.

**Evaporative Emissions.** The combined effect of phases 1 and 2 of California's RFG program is a reduction of gasoline vapor pressure by  $\sim 20\%$ . About one-fifth of the overall reduction occurred between 1995 and 1996; most of the reduction occurred in 1992 in accordance with phase 1 RFG specifications. Refueling and diurnal evaporative VOC emissions are expected to be reduced due to reductions in gasoline vapor pressure.

While use of RFG is expected to reduce evaporative emissions, it should be noted that, with the exception of running losses, evaporative emissions are not captured or reflected in the results from tunnel sampling reported in this study.

**Implications for Air Pollution Control.** A major objective of California's RFG program is to reduce toxic compound and ozone precursor emissions from motor vehicles. Motor vehicles contribute about 90% of all benzene emissions in the San Francisco Bay Area (37). Use of RFG led to much lower benzene exhaust emissions. Consistent with the large benzene reductions measured in the Caldecott tunnel, average benzene concentrations in Bay Area ambient air decreased 56% between summers 1995 and 1996 (37).

Despite difficulties in separating the effect of RFG from fleet turnover, this study indicated that RFG is more effective in reducing VOC emissions than it is in reducing  $\text{NO}_x$  emissions. Additional benefits of RFG were found when the reactivity of evaporative VOC emissions was considered (17). When coupled with the fact that diesel engines contribute half or more of mobile source  $\text{NO}_x$  emissions (38–40), we conclude that California's RFG program is most attractive as an ozone control strategy in situations where ozone formation is VOC-limited. The RFG program is effective in reducing benzene emissions regardless of whether ozone formation is VOC or  $\text{NO}_x$ -limited.

Substantial reductions in vehicle emissions were measured over a three-year period at the Caldecott tunnel. Both fleet turnover and RFG contributed to these reductions. Continued on-road surveillance is needed to track long-term trends in vehicle emissions. Determination of long-term emission trends would aid in the evaluation of emission control programs, such as new-vehicle emission standards and use of reformulated fuels.

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