

Impact of California Reformulated Gasoline on Motor Vehicle Emissions. 2. Volatile Organic Compound Speciation and Reactivity

THOMAS W. KIRCHSTETTER,
BRETT C. SINGER, AND
ROBERT A. HARLEY*

*Department of Civil and Environmental Engineering,
University of California, Berkeley, California 94720-1710*

GARY R. KENDALL AND
JAMES M. HESSON

*Technical Services Division, Bay Area Air Quality
Management District, 939 Ellis Street,
San Francisco, California 94109*

This paper addresses the impact of California phase 2 reformulated gasoline (RFG) on the composition and reactivity of motor vehicle exhaust and evaporative emissions. Significant changes to gasoline properties that occurred in the first half of 1996 included an increase in oxygen content; decreases in alkene, aromatic, benzene, and sulfur contents; and modified distillation properties. Vehicle emissions were measured in a San Francisco Bay Area roadway tunnel in summers 1994–1997; gasoline samples were collected from local service stations in summers 1995 and 1996. Equilibrium gasoline headspace vapor composition was calculated from measured liquid gasoline composition. Addition of methyl *tert*-butyl ether (MTBE) and reduction of alkenes and aromatics in gasoline between summers 1995 and 1996 led to corresponding changes in the composition of gasoline headspace vapors. Normalized reactivity of liquid gasoline and headspace vapors decreased by 23 and 19%, respectively. Ozone formation should be reduced because of both lower gasoline vapor pressure, which leads to lower mass emissions, and reduced reactivity of gasoline vapors. The reactivity of on-road emissions measured in the tunnel decreased by 8% or less. The reduction in reactivity of on-road emissions was less than that of evaporative emissions because of increased weight fractions of highly-reactive isobutene and formaldehyde in vehicle exhaust, which resulted from the increased use of MTBE in gasoline. On-road vehicle emissions of volatile organic compounds in the tunnel appear to be dominated by vehicles that have reduced catalytic converter activity.

Introduction

In California, major efforts have been made to reformulate gasoline to make it cleaner-burning. Phase 1 of California's reformulated gasoline (RFG) program began in 1992 and required reduced gasoline vapor pressure during the summer ozone season, use of detergent additives to control engine deposits, and elimination of lead-based antiknock additives (1). Phase 2 of the California RFG program took effect in the first half of 1996 and required more extensive changes to

gasoline properties (2, 3). Changes to gasoline included an increase in oxygen content; decreases in alkene, aromatic, benzene, and sulfur contents; a reduction in volatility; and decreases in distillation temperatures T_{50} and T_{90} .

Use of California RFG is intended to reduce summertime ozone air pollution by reducing emissions of ozone precursors: volatile organic compounds (VOC) and nitrogen oxides (NO_x). RFG is also intended to reduce emissions of carbon monoxide and toxic organic compounds. In addition to expected reductions in vehicle exhaust mass emission rates, changes to gasoline composition can affect the speciation and reactivity of VOC emissions. The replacement of high-reactivity compounds such as alkenes with low-reactivity compounds such as methyl *tert*-butyl ether (MTBE) in gasoline is expected to result in corresponding changes in the composition of VOC emissions. Hoekman (4) reported significant changes to the speciation of exhaust VOC emissions when vehicles were fueled with a reformulated gasoline.

While tailpipe exhaust emissions of VOC are important, significant additional emissions of VOC are associated with gasoline evaporation (5–7). Evaporative emissions occur, for example, due to vehicle fuel system leaks, during refueling, during the "hot soak" period immediately following vehicle operation, and over the course of a diurnal temperature cycle, which causes pressure changes in the vapor space above liquid fuel in gasoline tanks. Depending on the mechanism by which evaporative VOC are emitted, the chemical composition may resemble either whole liquid gasoline or gasoline headspace vapors. The composition of whole fuel provides a good description of liquid leak emissions, and headspace vapors describe certain refueling emissions. The compositions of diurnal, hot-soak, and running loss emissions lie somewhere between these extremes.

The goal of this study was to determine the impacts of California phase 2 RFG on the speciation and reactivity of exhaust and evaporative VOC emissions. To this end, motor vehicle emissions were measured in a roadway tunnel, and gasoline samples were collected from service stations, prior to and after the introduction of RFG. The impacts of phase 2 RFG on mass emission rates are reported in a companion paper (8).

Methods

Gasoline Sampling and Analysis. Regular and premium grade gasoline samples were collected from high-volume service stations located in Berkeley in August 1995 and 1996. The service stations represented the top five gasoline brands in northern California. Composite liquid samples for each gasoline grade were prepared by mixing measured amounts of individual samples in a low-temperature bath. The resulting regular and premium grade composites were sales-weighted mixtures of the individual brand samples (9). In the Bay Area, regular, mid-, and premium grade gasolines represent 58, 20, and 22% of total market sales, respectively (9). Therefore, analytical results for the regular and premium grade composite gasoline samples were combined in proportions of 68 vol % regular and 32% premium to estimate the composition of the overall gasoline pool.

Detailed liquid gasoline speciation was determined for the composite gasoline samples by gas chromatography (10). Analyses were run on a Hewlett-Packard Model 5890 II GC equipped with dual flame ionization detectors (FID) and electric flow control. Primary analysis was performed using a 60 m DB-1 capillary column of 0.25 mm ID and 0.25 μm stationary phase thickness. Secondary analysis was performed in parallel using a 60 m DB-5 capillary column of 0.25 mm

ID and 0.25 μm stationary phase thickness. Where the primary DB-1 analysis suffered from coelutions, the secondary DB-5 analysis was used to resolve the coeluting peaks. Each run was temperature programmed from subambient to approximately 250 °C. Peak identifications were based on spiking of authentic samples or corroborated by GC-MS identifications. Oxygenate response factors were based on direct calibration with weighed standards.

Headspace Vapors. The composition of gasoline headspace vapors was predicted using the measured composition of liquid gasoline. Comparisons between predicted and measured headspace vapor composition are presented below. Equilibrium headspace partial pressure for each compound identified in gasoline was predicted as

$$P_i = \gamma_i x_i P_i^0 \quad (1)$$

where P_i denotes the equilibrium partial pressure of species i in headspace vapor [atm], γ_i is the activity coefficient of species i in liquid gasoline, x_i denotes the measured mole fraction of species i in liquid gasoline, and P_i^0 is the vapor pressure of pure species i . Ideal solution behavior ($\gamma_i = 1$) was assumed in the application of eq 1. This assumption is reasonable for hydrocarbon and MTBE mixtures but is not valid for ethanol-gasoline mixtures (11).

Individual compound vapor pressures were determined using the Wagner equation

$$\ln P_r^0 = \frac{a\tau + b\tau^{1.5} + c\tau^3 + d\tau^6}{T_r} \quad (2)$$

where $P_r^0 = P_i^0/P_c$ is reduced vapor pressure, $T_r = T/T_c$ is reduced temperature, P_c and T_c are critical point pressure [atm] and temperature [K], $\tau = 1 - T_r$, and constants a , b , c , and d are tabulated for numerous organic compounds in Appendix A of Reid et al. (12). Organic compound vapor pressures were predicted for $T = 311$ K (38 °C), the standard temperature for Reid vapor pressure determination. Parameters used in eq 2 to predict individual compound vapor pressures are provided in the Supporting Information accompanying this paper.

It has been noted (12) that extrapolation of the more widely used Antoine equation to temperatures outside the range for which Antoine coefficients were determined may lead to serious errors in calculated vapor pressures. The Wagner equation is more robust and gives the correct shape of a vapor pressure curve over a wider range of temperatures, from $T_r = 0.5$ to $T_r = 1.0$ (12). Only the heaviest constituents of gasoline have critical point temperatures above 600 K, so the Wagner equation provides accurate vapor pressure estimates for all of the lighter compounds that are important contributors to gasoline headspace vapor composition and reactivity.

Field Sampling Site. Vehicle emissions were measured in the center bore of the Caldecott tunnel. The Caldecott tunnel is a heavily used commuter tunnel located in the San Francisco Bay Area. Field measurements were conducted at the tunnel on 10 or more days during each summer from 1994 through 1997. Specific dates for each summer sampling season and a description of the tunnel are provided in a companion paper (8). Field sampling was conducted during the afternoon commute period from 1600 to 1800 h when traffic volume was high. At this time of day, vehicles traveled through the tunnel in the eastbound direction, on an uphill grade of 4.2%.

Emissions measured during this study at the Caldecott tunnel are representative of vehicles operating in a warmed-up mode. The nearest on-ramp providing access to the center bore of the tunnel is located more than 1 km away, and most

vehicles using the tunnel during the afternoon commute travel longer distances before entering the tunnel.

Vehicle Attributes. Vehicles traveling in the center bore of the Caldecott tunnel were monitored to determine fleet characteristics and to compare fleet characteristics in each summer sampling season. Fleet composition and volume were determined from visual traffic counts, average speed inside the tunnel was measured by repeated drivethroughs, instantaneous speeds and accelerations inside the tunnel were measured using an instrumented vehicle, and vehicle age and fuel type were determined from license plate surveys. The main attributes of the traffic that traveled through the tunnel are summarized below. More detailed discussion of traffic characteristics is provided in ref 8.

The number of vehicles traveling through the tunnel was ~8400 during each 2-h sampling period and was consistent on all sampling days across all four summers. In all summers, vehicles traveled through the tunnel at average speeds of ~60 km h⁻¹. Traffic consisted almost exclusively of light-duty vehicles, about two-thirds of which were cars and one-third were a combination of pickups, sport utility vehicles, and small vans. Heavy-duty trucks comprised <0.3% of the vehicles in the center bore in each year. The average vehicle age was about 7 years in all four summers, and the average vehicle model year was about one year newer each summer. The light-duty fleet was almost entirely gasoline-powered. The fraction of light-duty vehicles identified as diesel-fueled ranged from 1 to 2%, and pre-1975 model year vehicles always comprised 2% or less of the vehicle fleet. Therefore, >95% of the vehicles traveling in the tunnel were originally equipped with catalytic converters.

VOC 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 ventilation fans. Background concentrations were subtracted from pollutant concentrations measured inside the tunnel to determine vehicle emissions. Two-hour integrated air samples were collected in 6-L stainless steel canisters for subsequent analysis to quantify hydrocarbon and MTBE concentrations. Similarly, 2-h integrated samples were collected using DNPH-impregnated silica cartridges for subsequent analysis to quantify carbonyl concentrations. A potassium iodide ozone scrubber was placed upstream of the silica cartridge used to collect carbonyl samples from the ventilation intake air because ozone has been shown to interfere with the quantification of carbonyl concentrations (13). A scrubber was not used when collecting carbonyl samples from tunnel air. Ozone drawn into the tunnel by ventilation is rapidly removed by reaction with nitric oxide and therefore does not interfere with carbonyl measurement.

Hydrocarbon concentrations in air samples collected in the canisters were determined by GC. Samples were pre-concentrated using a Nutech Model 8548 cryogenic concentrator and injected into a Perkin-Elmer Model 8500 GC equipped with FID. The DB-1 column used in the GC was 30 m long with an inner diameter of 0.32 mm and a 5 μm film thickness. Following sample injection, the column temperature was held at -51 °C for 5 min, then increased at 5 °C per minute to 100 °C, at 3 °C per minute to 160 °C, at 5 °C per minute to 200 °C, and held at that temperature for 7 min. This method was used to quantify speciated hydrocarbons in the C₅-C₁₀ range. A GS-alumina column, 50 m long by 0.53 mm inner diameter, was used to speciate and quantify the C₂-C₄ hydrocarbons. For summer 1997 analyses only, a Nutech Model 3550A cryogenic concentrator was used to pre-concentrate samples, and a DB-1 column was used to quantify all C₂-C₁₀ hydrocarbons.

Methane was quantified separately by direct injection of samples into a Perkin-Elmer Model 8500 GC equipped with FID and a 3.7 m long by 3.2 mm inner diameter stainless

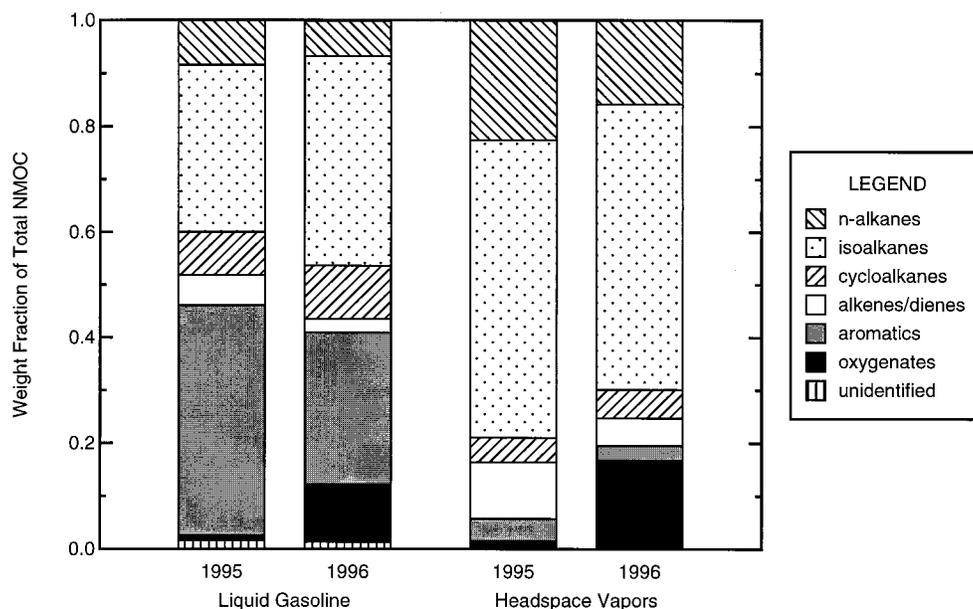


FIGURE 1. Composition of whole liquid gasoline and gasoline headspace vapors. Measured compositions of regular and premium grade gasolines were averaged according to the market share of each gasoline grade. Headspace vapor composition was predicted from measured liquid composition using eq 1.

steel column packed with Chromosorb 102, 100–120 mesh. MTBE concentrations were determined using a Varian Model 3400 GC equipped with PID/ECD in series. Samples were preconcentrated using a Tekmar 5010 Automatic Desorber and a Tenax trap. The column used in the GC was packed with 1% SP1000/Carbopack B, 60/80 mesh; was 4 m long; and had an inner diameter of 0.32 cm. Following sample injection, the oven temperature was increased at 2 °C per minute from 85 to 125 °C and held at that temperature for 15 min. MTBE concentrations were not quantified in summer 1994 samples.

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 2 h 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 (14). Carbonyl samples were analyzed by Hoekman and co-workers (15–17) in 1994, 1995, and 1996 and by Fung (18) in 1997.

Reactivity. The maximum incremental reactivity (MIR) scale developed by Carter (19) was used to calculate the reactivity of whole liquid gasoline, gasoline headspace vapors, and on-road nonmethane organic carbon (NMOC) emissions. The MIR scale is defined under conditions where VOC control is most effective in reducing ozone. Published MIR values (20) were combined with detailed chemical composition profiles developed in this study. Reactivity was expressed per unit mass of NMOC emissions using the following equation

$$R = \sum_{i=1}^n (\text{MIR})_i w_i \quad (3)$$

where R is the normalized reactivity [g of O₃ formed per g of NMOC emitted], $(\text{MIR})_i$ is the maximum incremental reactivity for species i [g of O₃ formed per g of species i emitted], and w_i is the weight fraction of species i in total NMOC emissions. MIR values used here are included in the Supporting Information to this paper.

Quality Assurance. Measured NMOC concentrations were compared with independent analyses of tunnel air samples collected in parallel in summers 1995–1997. Independent analyses were performed by the California Air Resources Board (21, 22), Desert Research Institute (23), and Rasmussen (24).

Measured concentrations of most individual hydrocarbons were in good agreement with independent analyses. In almost all cases, measured values agreed to within ±30% for species concentrations above 20 ppbC (total NMOC concentrations in the tunnel were typically 2 to 4 ppmC). Measured MTBE concentrations were in good agreement with measurements by Rasmussen but were 30% higher than values reported by Desert Research Institute. MTBE was not quantified in tunnel samples analyzed by the Air Resources Board.

Normalized reactivity was computed for each hydrocarbon sample using the speciation profile reported by each laboratory and eq 3. Computed normalized reactivity (R) for each collocated sample pair agreed within ±5%.

Results

Liquid Gasoline. As shown in summary form in Figure 1, the composition of the gasoline pool in 1996 differed markedly from that measured in 1995. Aromatic hydrocarbons constituted 44% of gasoline mass in 1995 and decreased to 29 wt % in 1996. Benzene content (included with aromatics in Figure 1) decreased from 2.0 to 0.6 wt %. Alkene content decreased from 5.7 to 2.6 wt %, mainly due to a reduction of C₅ and C₆ compounds, which comprised about two-thirds of gasoline alkene mass. These decreases were offset by increases in gasoline oxygenate and isoalkane content. The increase in oxygenate content from 1 to 11 wt % was due almost entirely to addition of MTBE to gasoline. Small amounts of *tert*-amyl methyl ether (TAME), typically less than 0.1 wt %, were present in some gasoline samples in both summers. Isoalkane content increased from 32 to 40 wt % between 1995 and 1996. Notable contributors to the increase in isoalkane content were highly branched, high-octane alkanes such as 2,2,4-trimethylpentane and 2,3,4-trimeth-

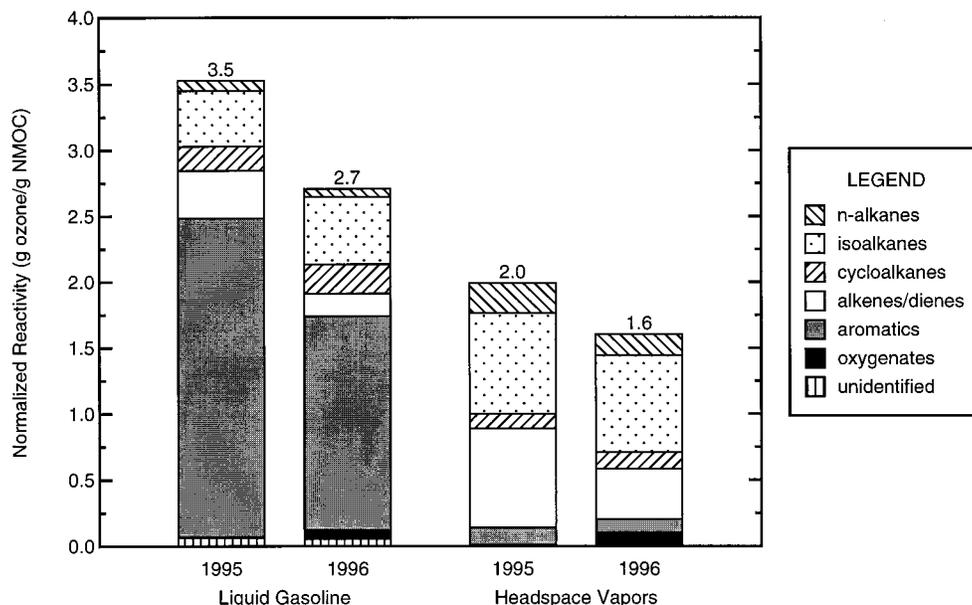


FIGURE 2. Contributions of organic compound groups to total normalized reactivity of whole liquid gasoline and gasoline headspace vapors.

ylpentane which increased from 0.92 and 0.43 wt % in 1995 to 3.6 and 1.7 wt % of gasoline in 1996, respectively. Full liquid gasoline speciation profiles are included as Supporting Information accompanying this paper.

Figure 2 shows the contributions of NMOC groups to the total normalized reactivity of liquid gasoline. As indicated, aromatic hydrocarbons dominate the reactivity of unburned gasoline. Comparison of Figures 1 and 2 illustrates that aromatics and alkenes contribute more to gasoline reactivity than to gasoline mass, whereas alkanes and MTBE contribute much less to gasoline reactivity than to gasoline mass. Compared to unburned liquid gasoline in 1995, the reactivity of RFG was lower by 23%. The decrease in gasoline reactivity was due primarily to the decrease in gasoline aromatic content. The replacement of aromatic compounds in gasoline with MTBE was partly responsible for the decrease in gasoline reactivity because MTBE has low reactivity compared to most high-octane gasoline hydrocarbons. The reduction in alkene content also contributed to the reduction in gasoline reactivity.

Headspace Vapors. Headspace vapor composition profiles for 1995 and 1996 gasoline predicted using eq 1 are shown in Figure 1. The composition of headspace vapors is heavily weighted toward the lowest boiling components of gasoline. Low molecular weight alkanes are abundant; *n*-butane, *n*-pentane, and isopentane together accounted for about 50% of total headspace vapor mass for both 1995 and 1996 gasoline. Lighter aromatics, namely benzene and toluene, comprised more than 70% of the total aromatic hydrocarbon mass in headspace vapors. Consistent with changes in liquid gasoline composition between 1995 and 1996, the weight fractions of alkenes and aromatics in headspace vapors decreased, as shown in Figure 1. A large reduction of benzene in headspace vapors, from 1.2 to 0.4 wt %, contributed more than half of the reduction in aromatics. The weight fraction of MTBE in headspace vapors rose dramatically from 1.5 to 16.8%. Full headspace vapor speciation profiles are included as Supporting Information to this paper.

As indicated in Figure 2, the reactivity of gasoline headspace vapors in 1996 was 19% lower than that of 1995 gasoline. This decrease was mostly due to the reduction of C₄ and C₅ alkenes in gasoline. Overall, headspace vapors are

less reactive than liquid gasoline (see Figure 2). Normal and isoalkanes, which dominate headspace vapor mass, have low reactivity. Also, compared to liquid gasoline, headspace vapors are depleted in the heaviest and most reactive aromatics, such as xylenes and trimethylbenzenes.

Predicted headspace vapor concentrations for the regular and premium grade gasoline samples were compared to those measured at 38 °C with a Reid vapor pressure test apparatus and a GC. GC analyses included determination of individual *n*-alkanes, isobutane, isopentane, 3-methylpentane, 3 cycloalkanes, 6 aromatic hydrocarbons, and MTBE. Other alkanes and aromatics, and all alkenes, were grouped by carbon number, e.g. total C₅ alkenes. As shown in Table 1, gasoline headspace vapor composition predicted using eq 1 agreed with measured values.

Whereas a fixed temperature of 38 °C was used to measure and predict headspace vapor composition, a range of temperatures are relevant when considering evaporative emissions to the atmosphere. However, since vapor pressures of all gasoline components increase with temperature, the relative abundance of individual VOC in headspace vapors varies much less with temperature than absolute gasoline vapor pressure. This was demonstrated by repeating the analysis (eqs 1 and 2) of headspace vapor composition using a lower temperature of 24 °C. While the total vapor pressure of gasoline decreased, predicted headspace vapor composition did not change significantly.

On-Road Emissions. The composition of NMOC emissions measured in the Caldecott tunnel in summers 1994–1997 is summarized in Figure 3 and given in full detail in the Supporting Information. Changes to the composition of NMOC emissions between summers 1995 and 1996 were consistent with changes in gasoline composition that occurred over the same period. Weight fractions of total aromatics and benzene in tunnel NMOC emissions decreased from 33 to 26% and 5.4 to 3.3%, respectively, whereas MTBE increased from 0.7 to 5.5 wt %. Consistent with the addition of MTBE to gasoline, isobutene (included with alkenes in Figure 3) increased from 1.4 to 3.3 wt %, and formaldehyde (included with carbonyls) increased from 1.6 to 2.2 wt %. Other changes in on-road NMOC emissions between 1995 and 1996 included increases in the weight fractions of isoalkanes and cycloalkanes and a decrease in the unidenti-

TABLE 1. Measured and Predicted Gasoline Headspace Vapor Composition for Regular and Premium Grade Gasoline Samples

compound	wt% of total VOC							
	1995 regular		1995 premium		1996 regular		1996 premium	
	meas ^a	pred ^b	meas	pred	meas	pred	meas	pred
n-butane	9.1	9.3	10.8	11.3	6.2	6.4	6.0	6.0
isobutane	2.8	3.0	3.7	3.8	1.3	1.4	1.2	1.2
n-pentane	10.5	10.4	7.1	7.0	7.5	7.6	6.0	6.5
isopentane	38	37	40	38	38	34	39	37
n-hexane	2.2	2.1	1.4	1.4	1.7	1.7	0.6	0.8
benzene	1.5	1.3	1.3	1.1	0.5	0.4	0.4	0.3
toluene	2.1	1.8	2.6	2.2	1.2	1.6	1.9	1.6
MTBE	0.0	0.1	4.5	4.8	14.9	16.0	21.6	18.7
total C ₄ alkenes	1.6	1.6	0.8	0.7	1.1	1.1	1.3	1.4
total C ₅ alkenes	6.8	7.1	4.3	4.9	2.5	2.8	2.8	3.0
total C ₆ alkenes	2.4	2.2	1.0	1.0	0.8	0.6	1.1	1.1

^a Headspace vapor concentrations measured at 38 °C with a Reid vapor pressure test apparatus and a GC. ^b Equilibrium headspace vapor concentrations predicted using measured composition of liquid gasoline samples and eq 1 (see text).

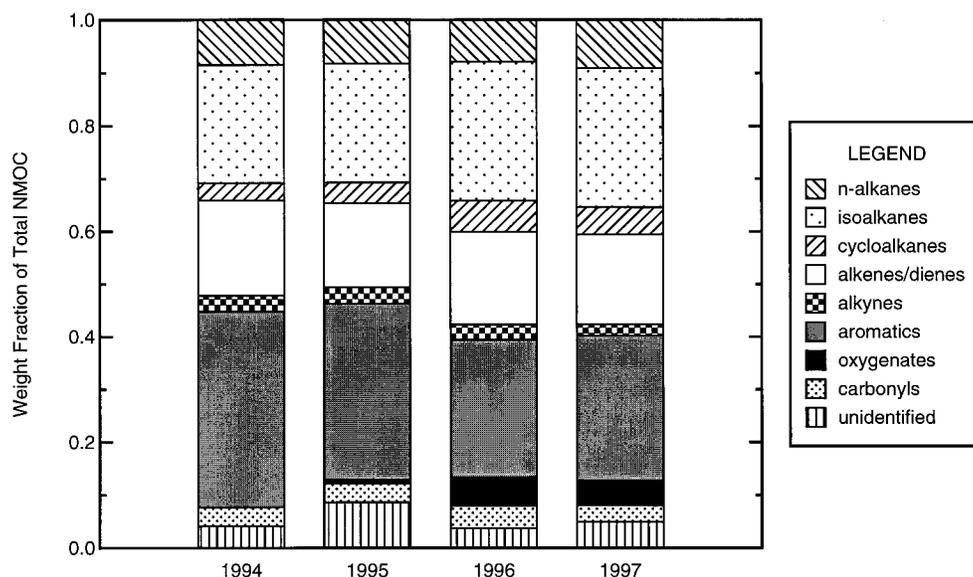


FIGURE 3. Composition of motor vehicle nonmethane organic compound emissions measured in the Caldecott tunnel.

fied mass from 8.6 to 3.7 wt % of total NMOC. Increases in weight fractions of trimethylpentanes accounted for about half of the increase in total isoalkane content.

Changes in the composition of NMOC emissions between 1995 and 1996 resulted in an 8% decrease in reactivity, as shown in Figure 4. This reduction was less than the reductions found for liquid gasoline and headspace vapors because of increased weight fractions of combustion-derived isobutene and formaldehyde, which have high reactivity. While tailpipe exhaust is expected to contribute the majority of NMOC emissions in the tunnel, the 8% decrease in the reactivity of tunnel NMOC emissions may be due in part to changes in the reactivity of running evaporative emissions. Gertler et al. (25) apportioned NMOC emissions in the Fort McHenry and Tuscarora Mountain tunnels and found that exhaust emissions comprised 85%, and evaporative emissions comprised 15%, of total NMOC emissions in both tunnels.

The composition and reactivity of NMOC emissions in the Caldecott tunnel was similar in summers 1994–1995 and in summers 1996–1997, as indicated in Figures 3 and 4. This was expected since the major changes to the properties of Bay Area gasoline occurred between summers 1995 and 1996 (8). Gasoline MTBE content decreased from 11 to 8% between 1996 and 1997 (8), and consistent with this decrease, weight fractions of MTBE, isobutene, and formaldehyde in on-road NMOC emissions also decreased.

Figure 5 compares the abundance of individual organic compounds in whole gasoline and tunnel NMOC. A distinctive feature of this figure is the linear relationship between the weight fractions of many individual compounds in tunnel NMOC and in whole gasoline. This relationship suggests that the origin of a significant fraction of NMOC in the tunnel is unburned gasoline. Combustion-derived species not present in gasoline, such as formaldehyde, ethene, propene, and isobutene, contribute significantly to NMOC mass and influence the overall reactivity of NMOC emissions. Taken together, C₁–C₃ organics plus isobutene contribute 20% of tunnel NMOC mass and 35% of tunnel NMOC reactivity. Compounds present in gasoline and found in tunnel NMOC at levels higher than expected due to emission of unburned gasoline alone suggest a contribution from running loss evaporative emissions. As discussed above, *n*-butane, *n*-pentane, isopentane, benzene, and toluene are abundant in headspace vapors. Benzene emissions may also be higher than expected due to formation of benzene during combustion, and because benzene may escape oxidation to a greater degree than other gasoline constituents. The abundance of MTBE in tunnel NMOC is lower than expected based on its concentration in gasoline, indicating that MTBE may be preferentially oxidized compared to other fuel constituents. This is consistent with findings reported by Hoekman (1992).

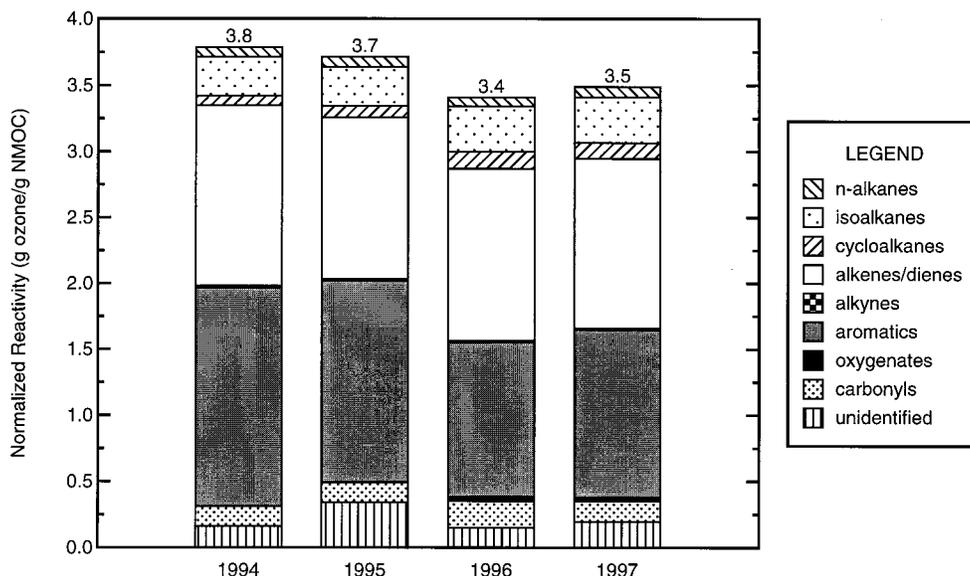


FIGURE 4. Contributions of organic compound groups to total normalized reactivity of vehicle emissions measured in the Caldecott tunnel.

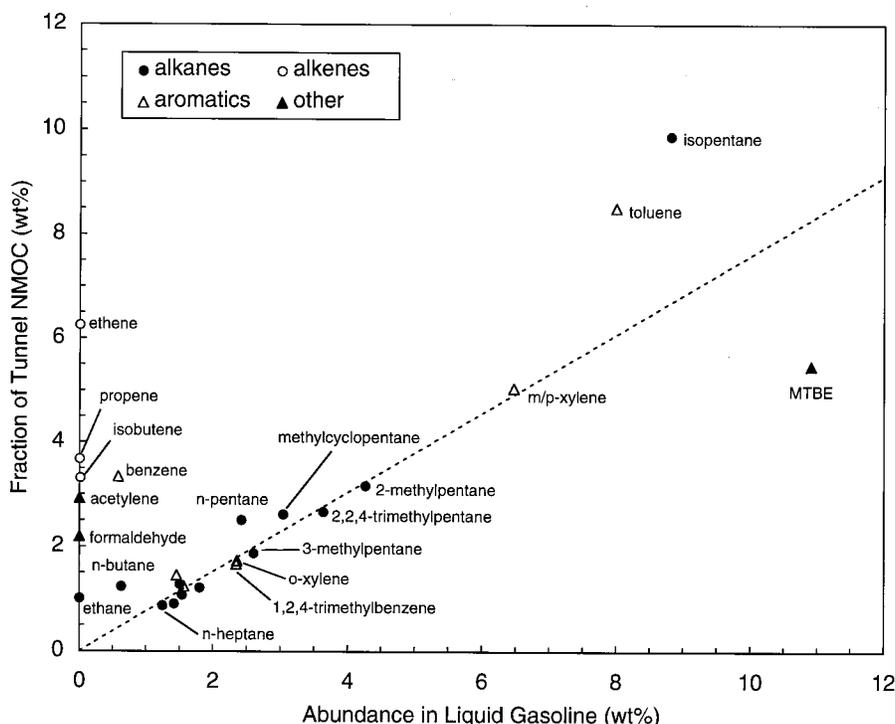


FIGURE 5. Comparison of concentrations of individual organic compounds in tunnel NMOC emissions with their abundance in liquid gasoline. Based on summer 1996 fuel and tunnel air samples; only compounds accounting for >1 wt % of tunnel NMOC are shown.

Discussion

Fleet Turnover. As previously noted in 1994 (26), the VOC speciation profile measured in the Caldecott tunnel for vehicles operating in a hot-stabilized mode more closely resembled cold start exhaust than hot-stabilized emissions from well-maintained vehicles tested during the Auto/Oil program (27, 28). In particular, Caldecott tunnel and cold-start NMOC emissions were abundant in ethene and acetylene but depleted in methane. This suggested that on-road emissions were dominated by vehicles that lacked control of air/fuel ratio and had reduced catalytic converter efficiency. As reported here, the composition of on-road NMOC emissions changed in response to changes in gasoline composition. However, fleet turnover did not have a large impact on the speciation of NMOC emissions, as indicated

by the similarity of tunnel NMOC emissions in summers 1994–1995 and summers 1996–1997 (see Figure 3 and Appendix Table 3 (Supporting Information)). The weight fraction of acetylene in tunnel NMOC was similar from 1994 to 1996, decreased from 2.9 to 2.2% between summers 1996 and 1997, and was still much higher in 1997 than measured in new vehicle exhaust during the Auto/Oil study (26). The most recent VOC species profile measured in the tunnel in summer 1997 still closely resembles Auto/Oil cold start emission profiles (27, 28).

Impact of Phase 2 RFG. Significant changes in the composition of gasoline occurred between 1995 and 1996 as a result of California's phase 2 RFG program. As reported here for the San Francisco Bay Area, speciation profiles for exhaust and evaporative emissions changed significantly due

to changes in gasoline composition. Liquid gasoline and headspace vapors now contain smaller amounts of compounds with high reactivity, such as alkenes and C₈⁺ aromatics. Emissions of headspace vapors that occur during refueling and emissions of whole gasoline that result from liquid leaks will therefore be less reactive. The reactivity of diurnal, hot-soak, and running loss evaporative emissions that have compositions lying between whole gasoline and gasoline headspace vapors also will be reduced. Thus, part of the air quality benefit of phase 2 RFG will be reductions on the order of 20% in the reactivity of evaporative emissions.

Inventory estimates for the Bay Area indicate that vehicle exhaust emissions comprised two-thirds, and evaporative emissions comprised one-third, of summertime NMOC emissions from on-road motor vehicles before the introduction of RFG (29). Evaporative emissions that occur during gasoline distribution and refueling also contribute significantly to total NMOC emissions (30). Therefore, the reactivity changes reported in this study for evaporative emissions do affect a significant fraction of total NMOC emissions, but smaller reductions in reactivity are expected for exhaust, which is the larger contributor to total vehicle-related NMOC emissions.

The magnitude of the decrease in the reactivity of tunnel NMOC emissions is uncertain because part of the decrease was due to reduced unidentified mass between 1995 and 1996, as shown in Figures 3 and 4. Not counting the change in reactivity due to the decrease in unidentified mass, the net effect of the other speciation changes in tunnel NMOC emissions was a 3% decrease in reactivity. This suggests the decrease in reactivity of on-road NMOC emissions due to RFG is likely between 3 and 8%. Alternatively, the effect of RFG on the reactivity of running emissions can be assessed by comparing NMOC composition measured in summers 1994 and 1996 since most gasoline properties were stable between summers 1994 and 1995, and the unidentified fraction of tunnel NMOC was the same in 1994 and 1996 (see Figure 3). Between 1994 and 1996, the reactivity of tunnel NMOC emissions decreased by 10%.

Reductions in gasoline vapor pressure (8) due to use of RFG will reduce some types of evaporative emissions. For example, refueling and diurnal evaporative emissions will be reduced given reductions in gasoline vapor pressure. The ozone-forming potential of evaporative emissions therefore will be reduced both because of lower mass emission rates and because of reduced reactivity. Note however, that not all categories of evaporative emissions are sensitive to fuel vapor pressure. For example, evaporative emissions due to fuel spillage and leaks depend on the volume of liquid escaping, not the vapor pressure.

Implications for Ozone Control. The reactivity scale (MIR) used here is defined under conditions where VOC control is most effective in reducing ozone. Reactivity changes reported here are not applicable to conditions where ozone formation is NO_x-limited. Rather than focus on the absolute values of the calculated reactivities shown in Figures 2 and 4, it is more meaningful to consider the changes in reactivity relative to 1995 baseline values. Relative changes in reactivity are less sensitive than absolute values to environmental conditions, model assumptions, and NO_x availability (19). To illustrate this point, reactivity calculations for gasoline headspace vapors were repeated using the maximum ozone incremental reactivity (MOIR) scale (19), under conditions where ozone formation is less sensitive to VOC emissions. Absolute reactivities were 1.01 and 0.87 g of O₃ per g of NMOC in 1995 and 1996, respectively. While the calculated reactivities for headspace vapors using the MOIR scale are much lower than corresponding values based on the MIR scale (see Figure 2), the relative changes in reactivity between 1995 and 1996 are still similar: -19% based on MIR values and

-14% based on the MOIR scale. Thus, changes to the speciation of evaporative emissions due to RFG use should lead to a less reactive mix of VOC emissions over a wide range of atmospheric conditions.

Acknowledgments

The authors gratefully acknowledge the many people who supported this work. In particular, we thank Graham Scovell, Mike Traverse, and Rudy Zerrudo of the Bay Area Air Quality Management District; Greg Noblet of UC Berkeley; Bart Croes, Michele Dunlop, Herman Lau, Mike Miguel, Jim Pederson, and Fred Schmidt of the California Air Resources Board; Don Gilson, Kent Hoekman, David Kohler, and Andrea Tiedemann of Chevron; Kochy Fung of Atmospheric Assessment Associates; Rei Rasmussen of Oregon Graduate Institute; John Sagebiel of Desert Research Institute; and Caltrans staff at the Caldecott tunnel. This research was funded by the UC Transportation Center from 1994 to 1995 and by the California Air Resources Board (Contract 95-330) from 1996 to 1997. The statements and conclusions in this paper are those of the authors and not necessarily those of the funding agencies.

Supporting Information Available

Appendix 1 (measured composition of whole liquid gasoline samples), Appendix 2 (composition of gasoline headspace vapor predicted using eq 1), Appendix 3 (composition of NMOC emissions measured in the Caldecott tunnel), Appendix 4 (variables used to predict organic compound vapor pressures) (31 pages). Ordering information is given on any current masthead page.

Literature Cited

- (1) Reformulated gasoline: proposed phase 1 specifications. California Air Resources Board, Sacramento, CA, 1990.
- (2) Proposed regulations for California phase 2 reformulated gasoline. California Air Resources Board, Sacramento, CA, 1991.
- (3) Proposed amendments to the California phase 2 reformulated gasoline regulations, including amendments providing for the use of a predictive model. California Air Resources Board, Sacramento, CA, 1994.
- (4) Hoekman, S. K. *Environ. Sci. Technol.* **1992**, *26*, 1206-1216.
- (5) Brooks, D. J.; Peltier, R. J.; Baldus, S. L.; Reuter, R. M.; Bandy, W. J.; Sprik, T. L. *SAE Tech. Pap. Ser.* **1995**, paper no. 951007.
- (6) Reuter, R. M.; Benson, J. D.; Brooks, D. J.; Dunker, A. M.; Gorse, R. A.; Koehl, W. J. *SAE Tech. Pap. Ser.* **1994**, paper no. 941965.
- (7) Burns, V. R.; Reuter, R. M.; Benson, J. D.; Gorse, R. A.; Hochhauser, A. M.; Koehl, W. J.; Painter, L. J. *SAE Tech. Pap. Ser.* **1992**, paper no. 920323.
- (8) Kirchstetter, T. W.; Singer, B. C.; Harley, R. A.; Kendall, G. R.; Traverse, M. Impact of California Reformulated Gasoline on Motor Vehicle Emissions: 1. Mass emission rates. *Environ. Sci. Technol.* **1999**, *33*, 318-328.
- (9) Gilson, D. Chevron Products Co., San Francisco, CA, Personal communication, 1995.
- (10) Kohler, D. A. Chevron Research and Technology Co., Richmond, CA, Personal communication, 1997.
- (11) Bennett, A.; Lamm, S.; Orbey, H.; Sandler, S. I. *J. Chem. Eng. Data* **1993**, *38*, 263-269.
- (12) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The properties of gases and liquids*, 4th ed.; McGraw-Hill Book Co.: New York, 1987; pp 212-215.
- (13) Arnts, R. R.; Tejada, S. B. *Environ. Sci. Technol.* **1989**, *23*, 1428-1430.
- (14) Siegl, W. O.; Richert, J. F. O.; Jensen, T. E.; Schuetzle, D.; Swarin, S. J.; Loo, J. F.; Probst, A.; Nagy, D.; Schlenker, A. M. *SAE Tech. Pap. Ser.* **1993**, paper no. 930142.
- (15) Hoekman, S. K. Chevron Research and Technology Co., Richmond, CA, Personal communication, 1994.
- (16) Hoekman, S. K. Chevron Research and Technology Co., Richmond, CA, Personal communication, 1995.

- (17) Hoekman, S. K. Chevron Research and Technology Co., Richmond, CA. Personal communication, 1996.
- (18) Fung, K. Atmospheric Assessment Associates Inc., Calabasas, CA. Personal communication, 1997.
- (19) Carter, W. P. L. *J. Air Waste Manage. Assoc.* **1994**, *44*, 881–899.
- (20) 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.
- (21) Poore, M. Monitoring and Laboratory Division, California Air Resources Board, Sacramento, CA. Personal communication, 1996.
- (22) Poore, M. Monitoring and Laboratory Division, California Air Resources Board, Sacramento, CA. Personal communication, 1997.
- (23) Sagebiel, J. C. Desert Research Institute, Reno, NV. Personal communication, 1996.
- (24) Rasmussen, R. Oregon Graduate Institute, Beaverton, OR. Personal communication, 1995.
- (25) Gertler, A. W.; Fujita, E. M.; Pierson, W. R.; Wittorff, D. N. *Atmos. Environ.* **1996**, *30*, 2297–2305.
- (26) Kirchstetter, T. W.; Singer, B. C.; Harley, R. A.; Kendall, G. R.; Chan, W. *Environ. Sci. Technol.* **1996**, *30*, 661–670.
- (27) 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**, paper no. 912322.
- (28) 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.
- (29) Emission Inventory—1993. Technical Support Division, California Air Resources Board, Sacramento, CA, 1995.
- (30) DeLuchi, M. A. *J. Air Waste Manage. Assoc.* **1993**, *43*, 1486–1495.

Received for review April 15, 1998. Revised manuscript received September 17, 1998. Accepted October 20, 1998.

ES980374G