

AIR RESOURCES BOARD

Draft Report

**A SUMMARY OF THE STAFF'S ASSESSMENT REGARDING
THE EFFECT OF ETHANOL IN CALIFORNIA GASOLINE ON
EMISSIONS**

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I. INTRODUCTION

This report is a summary of staff's assessment regarding the impact of ethanol in California reformulated gasoline (CaRFG) on the emissions of hydrocarbons (HC), oxides of nitrogen (NO_x), and carbon monoxide (CO).

This report is divided into 4 sections:

- Introduction and Summary
- The effects of ethanol on permeation and evaporative HC emissions,
- The effects of ethanol on NO_x emissions, and
- The effects of ethanol on CO emissions.

II. SUMMARY

In 1999, because of concerns of methyl tertiary butyl ether (MTBE) potential impact on ground and surface water, California's governor determined that MTBE should be phased out of the State's gasoline. The California Air Resources Board (Board or ARB) was directed to modify its fuels regulations to accomplish this phase out, and did so in 1999. At the ARB public hearing in 1999, staff presented their assessment of the impact of MTBE phase-out and ethanol use on vehicle emissions. Because there was considerable emissions uncertainty associated with ethanol use in California gasoline, the Board directed staff to conduct further study. A summary of these efforts, so far, is presented below.

A. Permeation Impacts of Ethanol

The presence of ethanol in gasoline results in a significant increase in the permeation of gasoline constituents through a motor vehicle's fuel system soft components. This increases evaporative hydrocarbon emissions by about 45 tons per day (tpd) on a typical ozone day or 75 tpd on a high-ozone day from on-road motor vehicles statewide in 2004.

B. NO_x Emissions

The addition of oxygenates to CaRFG3 to comply with the federal 2 percent oxygen requirement results in about 3 percent higher NO_x emissions than a non-oxygenated CaRFG3 or about 21 tpd NO_x increase from on-road motor vehicles statewide in 2004.

C. CO Emissions

The addition of oxygen into gasoline reduces CO emissions. The removal of oxygen from gasoline will, unless other properties are concurrently modified, increase the exhaust emissions of CO and hydrocarbons. The CaRFG3 regulations require that any increase in exhaust hydrocarbons associated with the removal of oxygen be offset before a fuel can be certified as an alternative formulation using the CaRFG3 Predictive Model. The fuel property changes necessary to reduce hydrocarbons also reduce the

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emissions of CO. As a result, these changes significantly lessen the magnitude of any CO emissions increase associated with the removal of oxygen from CaRFG3, by about half, to 3 percent.

On a reactivity-adjusted basis such an increase in CO will have relatively little impact on ozone. The reactivity of CO is 0.057 using the Maximum Incremental Reactivity (MIR) scale developed by Carter¹, where the average reactivity of exhaust hydrocarbons in gasoline is 3.35. As a comparison, the MIR of methane and ethane are 0.01 and 0.31, respectively.

D. Impact of These Changes on California Air Quality

Table 1 presents the impact of oxygen in gasoline on criteria pollutant emissions for the South Coast Air Basin (SCAB) on a high ozone day in 2004, the first year when CaRFG3 regulations were fully implemented. The results for CO are presented on a mass equivalent emission basis to permeation. This is to provide a basis for comparison and assessment of the likely impact on ozone. Although CO increase will affect ozone formation, the effect is likely to be insignificant since CO is much less reactive compared to hydrocarbons. On a reactivity basis, the increase in CO is compensated for by about twenty times the decrease in HC permeation emissions, as shown in the table below.

Table 1. Estimated Change in Emissions Associated with Non-Oxygenated Gasoline Use in the SCAB on High Ozone Day

(2004)

Pollutant	Emissions Change	
	(%)	(tpd)
HC (Permeation)	-16.9	-27.4
CO (in Evaporative HC Equivalent)	2.7	1.4
NOx	-3.0	-6.7

(2010)

Pollutant	Emissions Change	
	(%)	(tpd)
HC (Permeation)	-16.9	-21.2
CO (in Evaporative HC Equivalent)	2.7	0.9
NOx	-3.0	-4.5

¹ Based on amendments to the tables of Maximum Incremental Reactivity (MIR) values as approved by the Board on December 3, 2003.

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The impact of non-oxygenate fuel on ozone precursor pollutants, HC and NO_x, is significant. In 2004, the use of non-oxygenate gasoline in the SCAB would reduce HC emissions from permeation by about 26 tpd, on ozone reactivity basis, taking into account CO emissions increase. To put this number into perspective, in 2004 this reduction is equivalent to the total HC emissions from all oil refineries and fuel distribution systems in the SCAB. Similarly, NO_x emissions reduction from non-oxygenated gasoline is more than the NO_x emissions from the above two source categories. In 2010, the use of non-oxygenate gasoline would reduce the emissions of ozone forming pollutants, HC plus NO_x, by about 25 tpd in the SCAB.

III. INCREASES IN PERMEATION EMISSIONS

A. Background

In 1999, because of concerns regarding methyl tertiary butyl ether (MTBE) and its potential impact on ground and surface water, California's governor directed that MTBE be phased out of California gasoline. In response to the directive, in December 1999, the Air Resources Board (ARB/Board) adopted the California Phase 3 Reformulated Gasoline (CaRFG3) regulations.

The reformulated gasoline provisions of the federal Clean Air Act require that gasoline sold in the smoggiest areas of the country contain at least 2.0 percent oxygen by weight. Together, this requirement and the MTBE phase-out effectively require that at least 90 percent of California's reformulated gasoline must contain at least about 5.7 percent ethanol by volume. In 1999, as part of the efforts to obtain additional emission reductions from CaRFG3 and to provide additional flexibility to refiners, California's Governor also requested that the United State's Environmental Protection Agency (U.S. EPA) grant a waiver from the federal Clean Air Act provisions requiring that most of California's gasoline contain oxygenates.

At the ARB Board Hearing on CaRFG3 in December 1999, staff presented its assessment of the impact on emissions associated with the implementation of the CaRFG3 regulations and the phase-out of MTBE. At that hearing, it was recognized that ethanol in gasoline will increase evaporative emissions through a process known as permeation². The presence of ethanol in gasoline increases this permeation, and will result in an increase in evaporative emissions³. However, in 1999 the magnitude of this effect was not well understood. To better understand the increase in evaporative emissions due to ethanol being added to California gasoline, the Board directed staff to provide an assessment of the potential increases in hydrocarbon evaporative emissions associated with the use of ethanol in gasoline. At that time, the ARB staff estimated that the use of ethanol in CaRFG would increase permeation emissions on the order of about 13 tpd, statewide.

B. CRC Ethanol in Gasoline Permeation Study

To better understand the permeation effect, the ARB and the Coordinating Research Council (CRC) initiated a permeation test program to investigate the impact ethanol will have on evaporative emissions from motor vehicles. The CRC is a non-profit organization that directs, through committee action, engineering and environmental studies on the interaction between automotive equipment and petroleum products. The

² Permeation occurs when the hydrocarbon compounds found in gasoline migrate through the soft fuels system components of motor vehicles.

³ Evaporative emissions increase could also result from mixing a CaRFG3 containing ethanol and a non-oxygenated gasoline in a vehicle fuel tank. The potential impact of commingling has been fully accounted for by adjusting the Reid's vapor pressure (RVP) limit of the CaRFG3 regulations (<http://www.arb.ca.gov/fuels/gasoline/oxy/attch4.pdf>).

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Sustaining Members of CRC are the American Petroleum Institute (API), the Society of Automotive Engineers (SAE) and automobile manufacturers.

The objective of the permeation study was to evaluate evaporative emissions of gasoline compounds that migrate through soft fuel system components. Ten vehicles were selected to represent, by age and fuel system type, approximately equal percentiles of California's vehicle fleet. The study compared each vehicle's fuel system evaporative emissions from two oxygenated CaRFG3 gasolines – containing MTBE and ethanol respectively – and one non-oxygenated CaRFG3 gasoline.

Two types of tests were conducted. The first followed the same protocol as the California two-day diurnal test and the second was a series of two steady-state temperature tests of evaporative emissions conducted at 85°F and 105°F. In order to determine permeation emissions from a vehicle's fuel system as accurate as possible inside a SHED (Sealed Housing for Evaporative Determination), a specially designed rig was used to hold the fuel system components as they were found in the vehicle in their relative positions. These fuel system components had to be carefully removed from the vehicle body to preserve their original conditions. Emissions from other sources, such as the fuel-tank's charcoal canister and the fuel cap, were either vented or completely sealed. Because of these carefully designed and constructed set-ups, only fuel compounds migrating through the soft/non-metallic fuel system components were evaluated.

The results of the study show that all test vehicles experienced higher evaporative emissions when tested with gasoline containing ethanol than when tested with gasoline containing MTBE. Similar results were shown in nine out of ten vehicles when the ethanol gasoline was compared to non-oxygenated gasoline. On average, ethanol blends increase permeation by about 65 percent or 1.4 grams per vehicle per day higher relative to the MTBE fuel; and 45 percent or 1.1 grams per vehicle per day more than the non-oxygenated fuel. The results from the two steady-state tests indicated that permeation emissions are very sensitive to temperature. Results indicate that permeation emissions about double for each 10°C (18°F) increase in temperature. All these results are statistically significant, and consistent with findings from earlier studies.

The CRC oversight committee for this study was comprised of members from the oil and refining industry, automotive industry, ethanol industry, and the ARB. Harold Haskew, an experienced automobile emissions researcher, under an ARB research contract, independently designed the study. The data from this study was independently reviewed, and found acceptable by all members of the CRC oversight committee before it was submitted to the main CRC review group for their approval. In September 2004, the main CRC group approved the final report for public release. This report represents one of the most detailed and refined investigations in to the permeation emissions process and the effect ethanol will have on evaporative emissions in California. The results of this report were presented to the ARB at the

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November 2004 Board Hearing. A copy of this report can be found through the ARB’s website at: www.arb.ca.gov/fuels/gasoline/permeation/permeation.htm.

C. Permeation Emissions Assessment

The CRC permeation test program was designed to estimate the impact of ethanol for the diurnal heating process. However, this is only one of several processes during which permeation results in evaporative emissions. In order to estimate the total impact of increased fuel permeation emissions on other evaporative emission processes, such as resting loss, running loss, and hot soak, the results of the study must be applied to these processes. Vehicle activity and ambient temperature data must be integrated to provide an appropriate temporal and spatial distribution of emissions. This type of analysis is best performed using the EMFAC mobile source emissions inventory model.

Based on the results of the CRC study, staff used EMFAC2002 model to estimate on-road vehicles permeation increase in 2004. Table 2 presents this estimate on a typical ozone day associated with ethanol in 2004, the first year when CaRFG3 regulations were fully implemented. The details of this analysis are provided in Appendix.

Table 2. Estimated Increase in Evaporative Emissions Due to Ethanol in CARFG3 Based on EMFAC2002⁴ on Typical Ozone Day, 2004 (tpd)

Permeation Emissions	South Coast Air Basin	Sacramento County	San Joaquin Valley Air Basin
With Ethanol	139.2	15.3	35.3
Without Ethanol	121.8	12.9	29.8
Emissions Increase With Ethanol ⁵	17.4 (14%)	2.4 (19%)	5.5 (18%)

As mentioned above, the CRC study demonstrates that permeation emissions are very sensitive to temperature. The temperature profile used for the typical summer ozone day in the EMFAC assessment is the average hourly temperature for 10 high ozone days during the period 1987-1989⁶. The increase in evaporative emissions from permeation would be higher on a hot or high ozone day. The impacts on such a day are of great importance because the state’s clean air strategy must be based on reducing emissions under such conditions. To understand this effect staff identified high ozone

⁴ These calculations are based on the current motor vehicle emissions inventory model, EMFAC2002, version 2.2, April 23, 2003.

⁵ The percent increase varies because permeation rates are a function of temperature that is basin dependent in EMFAC.

⁶ The official EMFAC2002 ozone episodic temperature profiles, Section 7.8 at: http://www.arb.ca.gov/msei/on-road/doctable_test.htm

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days for the SCAB⁷, Sacramento County⁸, and the San Joaquin Valley Air Basin (SJVAB)⁹ and recalculated the expected increase in permeation emissions. Table 3 compares the average daily temperatures for a typical summer ozone day and for a higher temperature high-ozone day.

Table 3. Average Daily Temperatures for Ozone Non-Attainment Areas (°F)

Episode	SCAB	Sacramento County	SJVAB
High Ozone Day	84.3	82.6	87.0
Typical Ozone Day	71.4	73.4	74.6
Temperature Difference	12.9	9.2	12.4

The increased temperatures associated with the high ozone day were then used with the EMFAC model results to produce revised emissions estimates. Higher temperatures resulted in a significant increase in permeation emissions. Table 4 presents staff’s estimates for the increase in emissions due to the presence of ethanol for the typical ozone day and a higher temperature high-ozone day. On average the higher temperatures result in an increase in permeation emissions of about 65 percent. To illustrate this difference, the two temperature profiles for the SCAB are presented in Figure 1.

As can be seen from Figure 1, the 24-hour temperature profile for the high ozone day is significantly higher than the typical ozone temperature day profile.

Table 4. Estimated Permeation Emissions Increase, Ozone Non-Attainment Areas High Ozone Day, 2004 (tpd)

Episode	SCAB	Sacramento County	SJVAB
High Ozone Day	30.0	3.5	8.6
Typical Ozone Day	17.4	2.4	5.5
Emissions Increase on High Ozone Day	12.6 (72%)*	1.1 (48%)*	3.1 (55%)*

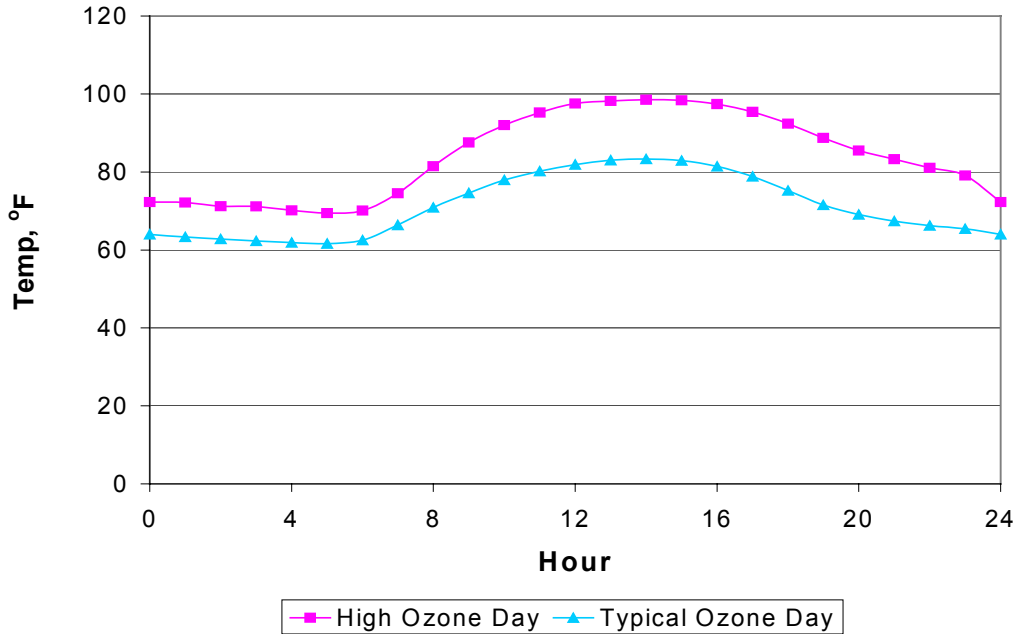
*Relative to the corresponding typical ozone day emissions

⁷ Source: The South Coast Ozone Study, August 5, 1997.

⁸ Source: the Central California Ozone Study, August 5, 2000.

⁹ Source: the Central California Ozone Study, August 5, 2000.

Figure 1. Temperature Profiles Comparison, SCAB



D. Non Motor Vehicle Permeation Emissions

Permeation emissions are not limited to motor vehicles. Two other studies have investigated the impact of ethanol on permeation from portable fuel containers and small off-road engines. Currently, there is very little information available from permeation studies of other non-road sources, such as off-road motor vehicles, portable engines, and watercraft.

In 2001, the ARB completed a study entitled, “Evaporative Emissions from Off-road Equipment.” This study estimated the impact of ethanol gasoline on evaporative emissions from small engines such as lawnmowers, blowers, chainsaws, and other lawn and garden equipment. Test results from five lawn mowers using commercial California gasoline containing 6 percent ethanol, showed that evaporative emissions increased, on average, by about 49 percent due to increased permeation from ethanol blends.

Also in 2001 the ARB completed a second study entitled, “Test Protocol and Results for the Determination of Permeation Rates from High Density Polyethylene Containers and Barrier Surface Treatment Feasibility Study.” This study investigated the permeation emissions associated with storing CaRFG in portable fuel containers. The test results indicated that the presence of about 5.25 percent volume ethanol in gasoline increases permeation emissions from untreated containers by about 45 percent.

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When the information from these studies is integrated into the statewide inventory for these sources¹⁰, the use of ethanol in gasoline is estimated to increase permeation emissions statewide by about 10 and 5 tpd from small off-road engines and portable fuel containers, respectively.

E. Overall Statewide Permeation Emissions

To estimate the total overall expected statewide increase in hydrocarbon emissions due to ethanol in gasoline, staff used the weighted average percent increase for the 3 areas (about 15 percent) on a typical ozone day presented in Table 2 and applied that percent increase to the statewide evaporative emissions inventory for gasoline powered motor vehicles (302 tpd). This 15 percent increase results in approximately 45 tpd in evaporative emissions due to the permeation effect of ethanol.

Add this to the about 15 tpd from other non-motor vehicle sources described above and the total increase in evaporative emissions due to an increase in permeation is about 60 tpd. It should be noted that there are no data currently available for other off-road motor vehicles, portable engines, and watercrafts. These categories account for about 50 tpd of evaporative hydrocarbon emissions statewide. Assuming the increase in permeation rates associated with the use of ethanol from these sources is similar that estimated for motor vehicle, about 15 percent, the use of ethanol gasoline could potentially add another 8 tpd statewide.

Table 5 presents the estimated increase in evaporative hydrocarbon emissions from the impact of ethanol on permeation emissions. On a high ozone day, the emissions increase will be even greater.

**Table 5. Estimated Statewide Permeation Emissions Increase, All Sources
Typical Ozone Day, 2004 (tpd)**

Emissions Source	HC Emissions Increase
On-Road Motor Vehicles ¹	45
Small Off-Road Engines	10
Portable Containers	5
Other Sources ²	n/a
Total	60

¹ Calculated from the weighted-average percentage (15%) in Table 2 applied to the 2004 statewide on-road motor vehicle total HC emissions (302 tpd).

² Other offroad engines and watercrafts could potentially add another 25 tpd.

¹⁰ California Air Resources Board, "Proposed California Phase 3 Reformulated Gasoline Regulations: Initial Statement of Reasons," Staff Report, October 22, 1999, Appendix M, Table K3, page M-6.

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Based on an EMFAC assessment, emissions are expected to increase by over 60 percent on a high ozone day. As a result, the statewide permeation increase could be significantly higher than what is shown in Table 5.

IV. THE IMPACT OF ETHANOL ON THE EMISSIONS OF NOx

A. Background

Reductions in NOx emissions are critical to California’s efforts to attain the State and federal ambient air quality standards for ozone and particulate matter. Adding oxygen to gasoline tends to increase emissions of NOx because the presence of oxygen leans-out the combustion process. Lean combustion, where oxygen is in excess in the combustion process, increases the efficiency of the oxidation of hydrocarbons in the fuel; decreasing the emissions of hydrocarbons and carbon monoxide and increasing emissions of NOx.

This effect has been documented in a number of studies. The most important of which is the Auto/Oil Air Quality Improvement Research Program (Auto/Oil) studies conducted through the 1990s. These are still the definitive studies relating gasoline properties to emissions from motor vehicles

B. Impact of Fuel Oxygen Content on the Emissions of NOx

Hydrocarbons are not the only important pollutant that is affected by the fuel oxygen content. Relief from the federal oxygen requirement would also result in a decrease in NOx emissions. Staff has calculated that, on average, CaRFG3 non-oxygenate would result in about a 3 percent decrease¹¹ of NOx emissions or about 21 tpd statewide NOx reduction from motor vehicles in 2004, or about 8 tpd in the South Coast. Table 6 presents CaRFG3 flat limits and an example of non-oxygenated fuel specification produced using the Predictive Model.

Table 6. CaRFG3 Flat Limits and Non-Oxygenated Fuel Specification

Fuel Properties	CaRFG3	
	Flat Limits	Non-Oxygenated Fuel**
RVP	7.0 or 6.9*	6.8
T50 (°F)	213	210
T90 (°F)	305	305
Aromatic Content (%vol.)	25.0	25
Olefin (%vol.)	6.0	6
Oxygen (%wt.)	1.8-2.2	0
Sulfur (ppmw)	20	10
Benzene (%vol.)	0.8	0.6

*The 6.9 psi RVP applies when the evaporative emissions model of the predictive Model is used.

**“Addition Material Supporting California’s Request For A Waiver Of The Federal RFG Year-Round Oxygen Mandate,” December 24, 1999, Attachment 1, Table 3.

¹¹ California Air Resources Board, “Proposed California Phase 3 Reformulated Gasoline Regulations: Final Statement of Reasons,” Staff Report, June 2000.

V. THE EFFECT OF OXYGEN IN GASOLINE ON CO EMISSIONS

The available engine tests data show that adding oxygen to gasoline tends to reduce CO and exhaust hydrocarbon emissions. As a result the removal of oxygen from CARFG3 is expected to increase the emissions of CO.

The addition of oxygenate to reformulated gasoline reduces the emissions of CO. The removal of oxygen from gasoline will, unless other properties are concurrently modified, increase the emissions of CO and hydrocarbons in the exhaust. The CaRFG3 regulations require any increase in exhaust hydrocarbons associated with the removal of oxygen be offset before a fuel can be certified as an alternative formulation using the CaRFG3 Predictive Model. The fuel property changes necessary to reduce hydrocarbons, sulfur and T50, also reduce the emissions of CO. These fuel property changes significantly lessen the size of any CO emissions increase associated with the removal of oxygen. The net effect of these changes on CO emissions is presented in Table 6. As can be seen in the table, to comply with the CaRFG3 Predictive Model flat limits, the HC increase must be offset with reductions in both sulfur and T50, about 10 ppmw and 5°F, respectively. As a result, the estimated net CO emissions increase would be about 2.7 percent.

Table 6. Estimated CO Emissions Increase from Non-Oxygenated CARFG3

Fuel Property Reduction	CO Emissions Change (%)
Oxygen (-2 %Wt)	4.6
Sulfur (-10 ppmw)	- 1.0
T50 (-5 °F)	- 0.9
Net CO Emissions Increase	2.7

Table 7 presents the impact of non-oxygenated gasoline on exhaust CO and evaporative hydrocarbon emissions from permeation for the SCAB in 2004 and 2010. In 2004, a 2.7 percent increase in CO emissions¹² from on-road gasoline powered vehicles would be equivalent to about 75 tpd. However, the impact of this CO increase on ozone is small compared to the same impact from the permeation or evaporative emissions decrease. The MIR factor for CO is about 0.057.¹³ For comparison, the MIR factors for methane and ethane are 0.01 and 0.31, respectively.

Based on the finding of the CRC test results the average MIR factor for the permeation emissions from CaRFG3 is approximately 3.27. As a result, a ton of CO has much less

¹² Based on EMFAC2002 (Ver. 2.2, April 23, 2003), total CO emissions from gasoline powered motor vehicles in the SCAB are 2771 tpd.

¹³ The latest MIR values, as approved by the ARB in 2004: <http://pah.cert.ucr.edu/~carter/reactdat.htm>

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impact on ozone than a ton of evaporative hydrocarbons. On a MIR basis, a ton of non-oxygenated gasoline permeation emissions is equivalent to about 57 tons of CO. To compare the relative impacts of the change in emissions on ozone, these emissions are converted into permeation evaporative hydrocarbons equivalent emissions. As can be seen in the table, the permeation emissions reduction associated with non-oxygenated gasoline is more than offset the increase in CO emissions.

The use of non-oxygenated gasoline would still result in a net of evaporative HC equivalent emissions reduction of more than 16 and 13 tpd in 2004 and 2010, respectively.

**Table 7. HC Emissions Change of Non-Oxygenated Gasoline
SCAB, Typical Ozone Day
(2004)**

Pollutant	Emissions Change		Evaporative HC Equiv. (tpd)
	(%)	(tpd)	
CO	2.7	74.8	1.3
HC: Exhaust*	1.8	2.4	2.5
Evaporative*	-2.2	-2.7	-2.7
Permeation	-14	-17.4	-17.4
Total Evaporative HC Emissions Change			-16.3

(2010)

Pollutant	Emissions Change		Evaporative HC Equiv. (tpd)
	(%)	(tpd)	
CO	2.7	43	0.8
HC: Exhaust*	1.8	1.6	1.6
Evaporative*	-2.2	-2.1	-2.1
Permeation	-14	-13.5	-13.5
Total Evaporative HC Emissions Change			-13.2

*These emissions change are the net results of running CaRFG3 Predictive Model for the two percent oxygen and non-oxygenated gasolines as presented in "Addition Material Supporting California's Request For A Waiver Of The Federal RFG Year-Round Oxygen Mandate," December 24, 1999, Attachment 1, Table 4.