Change in Air Quality Impacts Associated with the Use of E15 Blends Instead of E10

LCA.6091.94.2014
July 2014

Prepared by:

Stefan Unnasch
Ashley Henderson

DISCLAIMER

ACKNOWLEDGEMENT

Life Cycle Associates, LLC performed this study under contract to Americans United for Change.

Contact Information:

Stefan Unnasch
Life Cycle Associates, LLC
1.650.461.9048
unnasch@LifeCycleAssociates.com
www.LifeCycleAssociates.com

Recommended Citation: Unnasch, S. and A. Henderson, (2014). Air Quality Impacts Associated with the Use of E15 Blends Instead of E10. Life Cycle Associates Report LCA.6091.94.2014. Prepared for Americans United for Change.

Contents

Tables

Figures

Terms and Abbreviations

ARB	California Air Resources Board
Btu	British thermal unit
CA	California
EPA	Environmental Protection Agency

This page is intentionally blank

Executive Summary

Introduction

Ethanol is a renewable fuel that can be produced from a range of feedstocks, such as cornstarch, sugar cane, or cellulosic crop residues. Over 95% of the gasoline sold in the United States currently contains a low level blend of ethanol of 10% by volume. In 2010 and 2011, in response to a waiver application submitted by Growth Energy, the Environmental Protection Agency (EPA) passed regulations to allow the use of 15% ethanol blends (E15) in passenger vehicles and light-duty trucks of model years 2001 and later.

As a result of this new Federal regulation, many retailers, marketers, and localities are considering how to increase their offerings of E15 into their fueling systems. Life Cycle Associates examined factors affecting air quality related to changing from ethanol blends of 10% to 15%. Studies testing vehicles on a range of fuel blends were reviewed and aggregated to assess changes in the emissions profile from E15 tailpipe and evaporative emissions compared to currently used E10 fuel. The following factors affecting emissions impacts were considered:

- Ethanol blend composition and properties;
- Vehicle tailpipe emissions;
- Storage and fueling with ethanol blends;
- Changes in evaporative and exhaust emissions resulting from a change from E10 to E15;
- Human health impacts associated with toxic air contaminants;
- Ozone potential of hydrocarbons; and
- Life cycle greenhouse gas emissions

Methodology

A literature review of previous work was performed, and data available from prior studies (Haskew, 2011; Karavalakis, 2012; Karavalakis, 2014; Knoll, 2009) was used to perform a meta-analysis of the changes in emissions that may occur when approved vehicles are fueled with E15 instead of E10.

This study examines emissions of

- nitrogen oxides,
- carbon monoxide,
- particulate matter,
- non-methane hydrocarbons,
- ozone potential, and
- cancer risk from toxic air contaminants.

Emissions were examined on a gram per mile basis. The ratio of pollutant emissions from the same car tested with different ethanol blends provided the basis for estimating the change from E10 to E15. First, the normalized comparison of gram per mile emissions was examined for all of the available data. The likelihood that changes in emissions from one fuel blend to the next were statistically significant was examined using a Student's T test.

In order to isolate changes in emissions that result only from the change in ethanol blend level, results were normalized to E10. The data points for a given car at different ethanol blend levels were divided by the emissions of that car running on E10, the current standard blend level in most areas. In instances with no E10 data, the change in emissions from the closest blend levels was estimated by interpolation. The ratio of the two data points enables a comparison of changes in emissions across different cars since the relative change from the baseline reflects the effect of changing fuels.

The most significant changes from a change from E10 to E15 include a reduction in cancer risk from vehicle exhaust and evaporative emissions, a reduction in the potential to form ozone or photochemical smog, and a reduction in greenhouse gas (GHG) emissions.

Cancer Risk

Several toxic air contaminants found in vehicle exhaust are listed as carcinogens by the U.S. EPA and other health regulators. The toxic emissions of acetaldehyde, formaldehyde, benzene, and 1,3 butadiene were combined into one weighted unit risk factor. They are weighted by their relative cancer potency as estimated in the toxicity database of California's Office of Environmental Health Hazard Assessment, the agency tasked with regulating toxic emissions for the protection of public health.

$$\textit{Weighted Toxin}_i = \textit{Mass Toxin}_1 \times \textit{Unit Risk Toxin}_1 + \textit{Mass Toxin}_2 \times \textit{Unit Risk Toxin}_2 \ldots.\textit{Toxin}_i$$

This approach for weighting toxic air contaminants was previously reviewed by toxicologists as part of a study performed for the California Air Resources Board (Unnasch, 2001).

Figure S.1 shows the weighted toxic emissions broken down by the percent contribution from each toxin from a Coordinating Research Council (CRC) study that included cars running on E5.7 and E32 (Haskew, 2011). With these data, a decrease in cancer risk is observed with the increase in ethanol content. This effect is likely due to ethanol displacing aromatics and precursors to 1-3 butadiene in the fuel, since gasoline contains aromatic compounds but ethanol does not. Aromatics tend to have relatively high cancer causing potential. While ethanol may cause an increase in the emissions of formaldehyde and acetaldehyde, it causes a decrease in benzene, toluene, 1,3-butadiene, and other aromatic emissions that have more potent cancer toxicity risk than that of aldehydes.

Results are shown for the FTP cycle test in the CRC emissions study, where the data was most complete. These data show that benzene and 1-3 butadiene make up 29% and 68% of the cancer risk from the four toxic air contaminants shown here for the baseline E5.7 vehicles, meaning that in combustion of E5.7 fuels, formaldehyde and acetaldehyde emissions make up only 3% of the cancer causing impact potential. The cancer risk associated with acetaldehyde increased by 1% with a change from E5.7 to E32, which is much smaller than the increased risk from benzene and 1,3 butadiene.

A Student's T-test was performed to determine the statistical significance of the difference in cancer risk from each vehicle's emissions. The two-tailed P value equals 0.031. By conventional criteria, this difference is considered to be statistically significant. As shown in Figure S.1, the mean of the difference between normalized weighted toxics for E5.7 and E32 is an 18.8% reduction. The 95% confidence interval of this difference is a 2.0% to 35.6% reduction in cancer risk.

Extrapolating these results to a change from E10 to E15 shows a projected 6.6% reduction in contribution to cancer risk. This outcome is disproportionate to the change in ethanol in the fuel blend and may depend upon how the fuel blends for emission testing are formulated.

Moving from E10 to E15 also reduced the toxicity impact of evaporative emissions and fuel spills. Fuels contain essentially no 1-3 butadiene and acetaldehyde and formaldehyde are products of combustion not fuel evaporation. Displacing 5% of the gasoline components with ethanol would result in a proportional reduction in cancer risk from fugitive benzene emissions for fuels that are blended from gasoline blendstocks with the same benzene content.

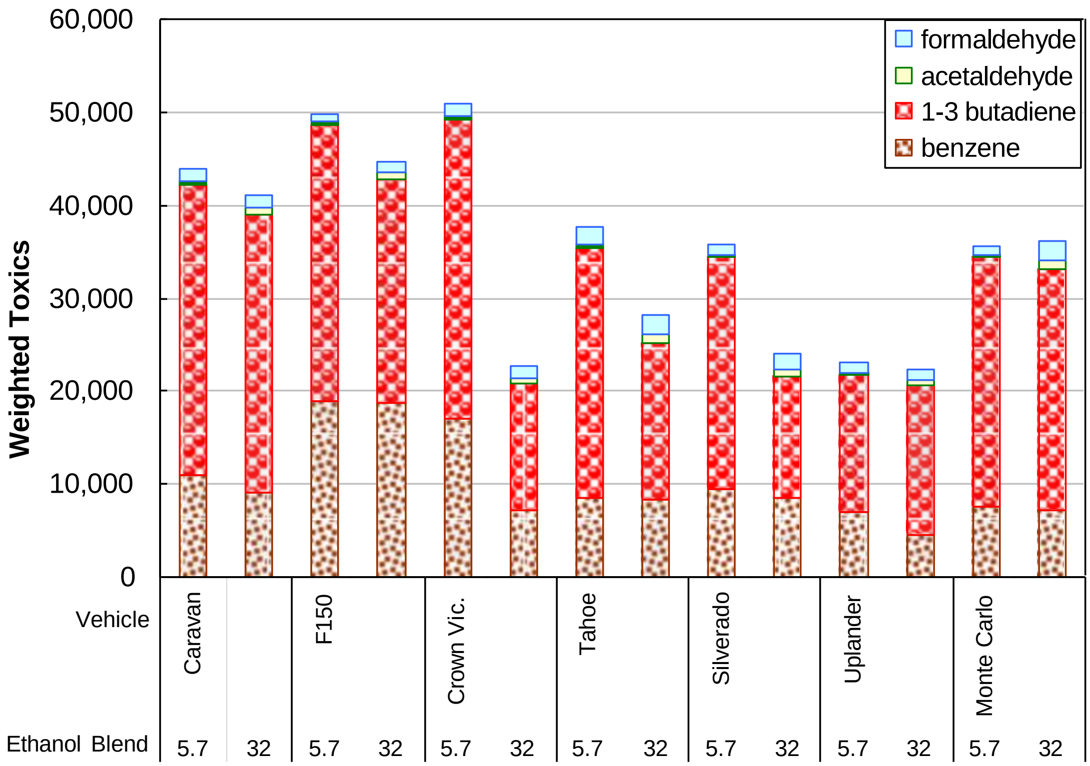


Figure S.2. Weighted cancer risk from vehicle exhaust emissions with E5.7 and E32 fuels.

Ozone Precursors

The individual components that make up vehicle exhaust and evaporative emissions were also examined in terms of their potential to form ozone or photochemical smog. The ozone potential for categories of hydrocarbons was combined with incremental ozone potential factors to evaluate the change in ozone potential when switching from E10 to E15.

The change in ozone potential due to a change from E10 to E15 fuel depends on the composition of the fuels and the photochemical reactivity rating of their constituents. The inputs to this analysis were the vehicle exhaust hydrocarbon emissions, fugitive emissions from refueling, and fuel composition. Mass-based emission estimates of the speciated hydrocarbon emissions were multiplied by factors that represent the ozone formation potential of each hydrocarbon (Carter 2009). The same approach was followed in a study of reactivity weighted emissions from alternative fuel options for the California Air Resources Board (Unnasch, 1996).

Many factors affect the potential ozone impacts of a change to E15 including, exhaust emission rates, fuel composition, and the photochemical reactivity of the exhaust components. The distribution of ozone potential outcomes shows a predicted reduction in precursors for smog formation.

Greenhouse Gas Emissions

The ethanol component of E15 results in lower GHG emissions than that of the gasoline blending component. The GHG emissions from ethanol have been examined extensively by the U.S. EPA, California Air Resources Board, European Commission, as well as independent researchers (EPA, 2010; ARB, 2009; Dunn, 2013). The GHG emissions depend on the fuel for ethanol plant operation, agricultural inputs, and indirect land use emissions. Emissions from crude oil based petroleum production have also increased over the years (Boland, 2014). Taking into account the changes in corn ethanol technology, crude oil production, and revised estimates of land use emissions, corn ethanol results in a 32% reduction in GHG emissions compared to conventional gasoline.

A change from E10 to E15 results in a 1.5% reduction in GHG emissions. The reduction in GHG emissions corresponds to the weighted contribution of corn ethanol fuel and gasoline blending components. Every billion gallons of E15 fuel would reduce GHG emissions by 180,000 metric tonnes compared to the comparable sale of E10 fuel.

These numbers are based on the existing supply of ethanol, which is almost entirely derived from corn. However, advanced biofuels such as cellulosic ethanol are now entering commercial production. These fuels can achieve lifecycle GHG reductions of 85 percent relative to regular gasoline. As these new, advanced biofuel technologies begin to penetrate the market for renewable fuels, the GHG advantages of E15 will be even larger.

Other Pollutants

The effect of ethanol on the other 3 pollutants studied was found to be very limited. . The properties of ethanol affect many aspects of engine operation and emissions but the effects are dampened or eliminated by the existing control standards. Ethanol has a higher oxygen content than gasoline, so ethanol-gasoline blends are more highly oxygenated than pure gasoline. Higher fuel oxygen levels promote more complete combustion, resulting in lower emissions of pollutants such as carbon monoxide and unburnt hydrocarbons. However, oxygenation standards have been in place for many years, and most of the gains in combustion efficiency from increased oxygen levels have already become commonplace. Any potential negative effects on the air to fuel ratio resulting from ethanol are eliminated with oxygen sensors on modern cars, therefore, NO_x and CO emissions do not change significantly with changes in ethanol blend level. Ethanol also displaces aromatics that contribute to the formation of polycyclic aromatic hydrocarbons (PAH), which have the higher contribution to cancer risk among vehicle emissions. PM was not a major focus of the studies from which data was taken, so this effect was not quantified in this particular study; however, there is a great deal of other work in this area to show ethanol's significant contribution to the reduction of particulate emissions.

Results

Table S.1 summarizes the quantity and significance of the estimated reduction in weighted cancer risk and ozone potential resulting from a change from E10 to E15.

Table S.1. Estimated Emission Reductions from a Change from E10 to E15.

Pollutant	Estimated Reduction	Likelihood of Reduction
Weighted cancer risk[a]	6.6%	95% confidence interval: 2% to 35.6% reduction in weighted toxic impact 80% confidence interval from Monte Carlo simulation[b]: 0 to 14% reduction
Ozone Potential	4%	60% confidence interval from Monte Carlo simulation: -2 to 9% reduction
Greenhouse Gases[c]	1.5%	Almost all ethanol plants reduce GHG emissions by more than 20%. Estimates vary with technology and analysis method

[a] Includes acetaldehyde, benzene, 1, 3 butadiene, formaldehyde.
[b] Includes PAH in particulate.
[c] GHG emissions correspond to weighted change in GHG emissions from ethanol and petroleum blendstock.

Conclusions

A meta-analysis of available data provides support for several conclusions.

- Ethanol displaces the cancer causing components benzene and 1-3 butadiene from gasoline. Ethanol also displaces aromatics, which are precursors to cancer causing polycyclic aromatic hydrocarbons (PAHs). These changes in fuel composition affect both the vehicle exhaust as well as refueling evaporative emissions and evaporated spilled fuel. Therefore the weighted cancer effect from E15 is lower than that for E10.
- 67.5% of the cancer risk is due to lower 1-3 butadiene, and 75% of vehicles showed a reduction in this pollutant. 29% of the cancer risk is due to lower benzene emissions, and 88% of vehicles showed a reduction in this pollutant. Acetaldehyde emissions increased with higher ethanol blend levels. Changes in acetaldehyde result in a predicted 0.3% increase in cancer risk while the risk from other listed carcinogens drops by 6.9%, resulting in a net decrease of 6.6%.

- Ethanol present in the vehicle exhaust displaces higher smog forming potential hydrocarbons that result from gasoline components; therefore, for a given amount of NOx and NMHC emissions, the smog forming potential for E15 blends is lower.
- Ethanol results in a 1.5% reduction GHG emissions, which is proportional to amount of ethanol in the fuel.

It is important to remember that changing from E10 to E15 involves a change of only 5% of the total fuel content. The estimated changes in toxic risk and ozone potential observed in the emission test results examined here are of a comparable magnitude.

1. Introduction

Ethanol is a renewable fuel that can be produced from a range of feedstocks such as cornstarch, sugar cane, or cellulosic crop residues. Ethanol is routinely blended with gasoline to improve its quality and provide a renewable source of liquid fuel for on-road vehicles. The ethanol serves to oxygenate the fuel and reduce air pollution from incomplete fuel combustion (Alternative Fuels Data Center, 2014). Ethanol blending has become so standard that over 95% of the gasoline sold in the U.S. currently contains a blend of 10% ethanol by volume (E10) (Karavalakis et al., 2014; Knoll et al., 2009).

1.1 Energy Policies

The Clean Air Act Amendments of 1990 required that gasoline producers reformulate gasoline to conform to new pollution standards. Use of oxygenates such as ethanol was key to meeting the CO emission regulations (CAAA, 1990). U.S. consumption of ethanol as an oxygenate exceeded consumption of MTBE, another oxygenate, for the first time in 2004 (U.S. Energy Information Administration, 2011). The 2007 Energy Independence and Security Act (EISA), which mandated the use of 36 billion gallons of biofuels in the transportation fuel pool by 2022, accelerated the rate of ethanol use and production in the US and provided a boost to the ethanol blend market (Karavalakis et al., 2014). Since 2007, use of ethanol in the US has increased from 6,886 million gallons to 13,176 million gallons in 2013 (U.S. Energy Information Administration, 2011). The market for E10 fuels was approaching saturation in 2009 since the volume of ethanol was increasing but the maximum allowed blending percentage remained only 10% ethanol.

In 2010 and 2011, in response to a waiver application submitted by Growth Energy, the Environmental Protection Agency (EPA) passed regulations to allow the use of 15% ethanol blends (E15) in 2001 and later model years (MYs) of passenger vehicles and light-duty trucks. The first partial waiver, passed in October of 2010, allowed for the use of E15 in MYs of 2007 and later light-duty motor vehicles, including passenger cars, light duty trucks, and medium duty cars (Environmental Protection Agency, 2010). The second partial waiver, granted in January of 2011, extended this allowance to light-duty motor vehicles from MYs 2001-2007 (Environmental Protection Agency, 2011).

1.2 Study Objectives

As a result of this new Federal regulation, many retailers, marketers, and localities are considering how to increase their offerings of E15 into their fueling systems. A City of Chicago ordinance has been proposed to require all self-service vehicle fueling stations to offer E15. This report reviews many of the considerations related to a change from ethanol blends of 10% to 15%. Prior emissions studies are reviewed and aggregated for insight about potential changes in the emissions profile from vehicle combustion of E15, and relevant issues are considered, including:

- Ethanol blend composition and properties;
- Storage, transport, and fueling with ethanol blends;
- Typical vehicle tailpipe emissions;

- Human health impacts of vehicle combustion products; and
- Possible changes in evaporative and exhaust emissions as a result of changing from E10 to E15.

1.3 Ethanol Blend Research

Researchers have been testing the effect of ethanol blends on passenger car exhaust and evaporative emissions since the early 90's, when ethanol blends began to be more widespread. Many early studies were motivated by the development of reformulated gasoline, and numerous combinations of ethanol, MTBE, ETBE, and a range of gasoline parameters were tested (Auto/Oil, 1993). Many of these studies tested cars that were from years prior to 2001. Since these cars would not be allowed to run on E15 under current regulations, they were not examined here.

This study considers recent trends in ethanol use, predicted changes in emissions, and the results of previous studies that looked at changes in the tailpipe and evaporative emissions that result from a change in ethanol blend level from 10% (E10) to 15% (E15) in different on-road vehicles. Table 1.1 summarizes the original research studies that were considered in this review. A meta-analysis was performed by Life Cycle Associates on data derived from five of the studies to determine whether strong overall trends can be observed across a wider, combined data set that is focused on an E10 to E15 change.

Table 1.1 Summary of Prior Ethanol Blending & Emissions Research

Author	Year	Fuels	Vehicle Models	Model Years
Guerreri, Caffrey, & Rao (EPA)	1995	E10, E12, E14, E17, E20, E25, E30, E35 and E40	Ford Taurus, Honda Accord, Pontiac Bonn., Chevy Cavalier, Pontiac 6000, Ford Victoria	1990 to 1992
Haskew & Liberty (CRC)	2011	E5.7, E45.5, E85	Dodge Grand, Ford Victoria, Chevy Tahoe, Ford F-150, Chevy Silverado, Chevy Uplander, Chevy Monte Carlo	2006 to 2007
Knoll & Theiss (NREL, Oak Ridge)	2009	E0, E10, E15, & E20	Toyota Camry, GM LeSabre, Ford F150, Ford Taurus, Nissan Altima, Honda Accord, Chrysler T&C, GM Silverado, Honda Civic, VW Golf, Ford Vic., Toyota Corolla, Chrysler PT Cruiser	1999 to 2007
West et. al (Oak Ridge)	2012	E0, E10, E15, & E20	Honda Accord, Chevy Silverado, Nissan Altima, Ford Taurus, Dodge Caravan, Chevy Cobalt, Dodge Caliber, Jeep Liberty, Ford Explorer, Honda Civic, Toyota Corolla, Toyota Tundra, Chevy Impala, Ford F150	2000 to 2009
Karavalakis, Durbin, Shrivastava et. al. (CE-CERT)	2012	CARB2, CARB3, E10, E20, E50, E85	Toyota Pickup, Nissan Truck, Ford Explorer, Ford Festiva, Honda Accord, Toyota Camry, Chevy Silverado	1984 to 2007
Karavalakis, Short, Vu.et al. (CE-CERT)	2014	E10, E15, E20	Kia Optima, Chevrolet Impala	2012

1.4 Approach

This study evaluated the effect of a change from E10 to E15 fuel in Chicago in all legally allowable cars. The study consisted of the following steps:

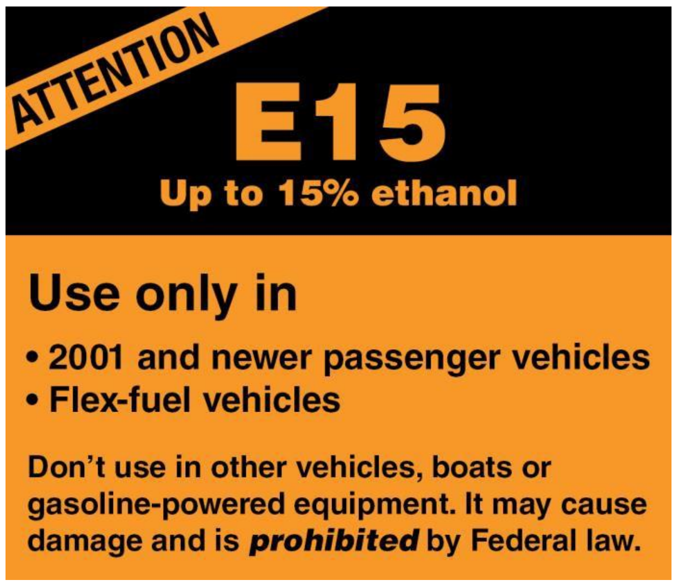
- Reviewed literature on emission effects of ethanol blends and identified emissions data available from public sources.
- Summarized criteria pollutant and air toxic emissions by vehicle type, MY, and test. In some cases, multiple tests were performed. All studies included the Federal Test Procedure (FTP).
- Examined and compared trend in emissions as a function of ethanol blend as reported in literature.
- Analyzed available data across studies to identify wider trends in emissions resulting from ethanol blend increase.

- Evaluated emission impacts from fuel spillage
- Determined weighted cancer unit risk factors for toxic emissions.
- Calculated combined toxic impacts from cancer causing components, weighted by potency, as a function of fuel composition.
- Examined variability in emissions
    - Used Student's T test to determine significance of changes in exhaust emissions and weighted cancer risk for emission test data.
    - Developed Crystal Ball TM model to factors affecting weighted cancer risk and ozone potential from hydrocarbon emissions.

2. Background: Fueling with E15

2.1 What is E15?

Ethanol is an alcohol, made up of carbon, oxygen, and hydrogen atoms (C_2H_5OH). It is a clear, colorless liquid that is fully water soluble. The energy content of pure ethanol is 76,300 Btu per gallon compared to 116,300 Btu per gallon for gasoline with no ethanol in it.



The vapor pressure of ethanol at 100˚F is 2.3 psi compared to an average of 7 psi for the mix of gasoline blending components. However, adding small amounts of ethanol to gasoline results in an initial rise in vapor pressure. This effect declines at higher ethanol blend levels. Fuel blenders take the vapor pressure effects into account when blending E10 or E15.

Ethanol has an octane rating of 113, a higher octane number than gasoline. This means it can withstand greater compression and reduces the problem of knocking in gasoline engines, i.e. the premature ignition of fuel. Ethanol molecules also contain more oxygen than gasoline, so it can be used as an oxygenate and results in a leaner air to fuel mixture that burns more cleanly and produces fewer carbon monoxide molecules.

Error! Reference source not found. displays an overview of ethanol's chemical properties and describes how they differ from those of gasoline.

Table 2.1. Description of Ethanol Properties

Property	Comment
Molecular weight	Vapors are denser than air and about half the density of gasoline vapors.
Solubility in Water	Ethanol is completely soluble in water and extremely hydroscopic (i.e., attracts water).
Energy Content	For identical volumes, pure ethanol contains approximately 30% less energy than gasoline.
Flame Visibility	A fuel ethanol flame is less bright than a gasoline flame but is easily visible in daylight.
Specific Gravity	Ethanol is slightly denser than gasoline.
Conductivity	Ethanol has higher conductivity than gasoline.
Impact on Air-Fuel Ratio	Ethanol has a higher oxygen content than gasoline, which means the air to fuel ratio is lower for an ethanol blend than it is for gasoline.
Toxicity	Unlike gasoline, pure ethanol is not considered toxic or carcinogenic.
Flammability limits, volume in air	Ethanol vapors are flammable in a wider range of concentrations that gasoline vapors.

(DOE: Office of Energy Efficiency and Renewable Energy, 2013)

Prior to transport to a retail facility, ethanol must be denatured by adding 2% gasoline to render the product unsafe for human consumption (DOE: Office of Energy Efficiency and Renewable Energy, 2013).

2.2 Transport of E15

Ethanol is primarily delivered via tanker truck or rail, when coming from refineries in the Midwest, or by barge when coming from the Gulf Coast. About 30% of U.S. ethanol is transported by truck, 60% is transported by rail, and 10% is transported by barge (U.S. Department of Agriculture, 2007). In order to accommodate ethanol, infrastructure may require installation of segregated storage tanks, railroad spurs, or special truck loading equipment (Fang, Powders, & Aabakken, 2002).

2.3 Storage and Dispensing of E15

The same equipment that is used to store gasoline can be used to store ethanol. Retailers have already changed the materials in their fueling systems to be in keeping with current ethanol blend levels of 10 and 15 percent. In addition, the materials used are usually compatible with an even higher range of ethanol blends in anticipation of increasing blend levels over time (DOE: Office of Energy Efficiency and Renewable Energy, 2013).

The blending of ethanol with gasoline typically occurs at the refining terminal. However, it is also an option to have gasoline and ethanol tanks at the fueling station and blend the two onsite. This reduces the number of storage tanks needed at the retail location, and allows for greater flexibility of blending, allowing fuel providers to mix either E10 or E15 blends as needed in what is referred to as on-site multi-product dispensing (MPD) (Fang et al., 2002). Retailers may have an E15 dedicated hose (DOE: Office of Energy Efficiency and Renewable Energy, 2013). Another likely scenario is that they may sell E15 at midgrade pumps.

Figure 2.1 displays a diagram of a typical on-site storage and fueling system.

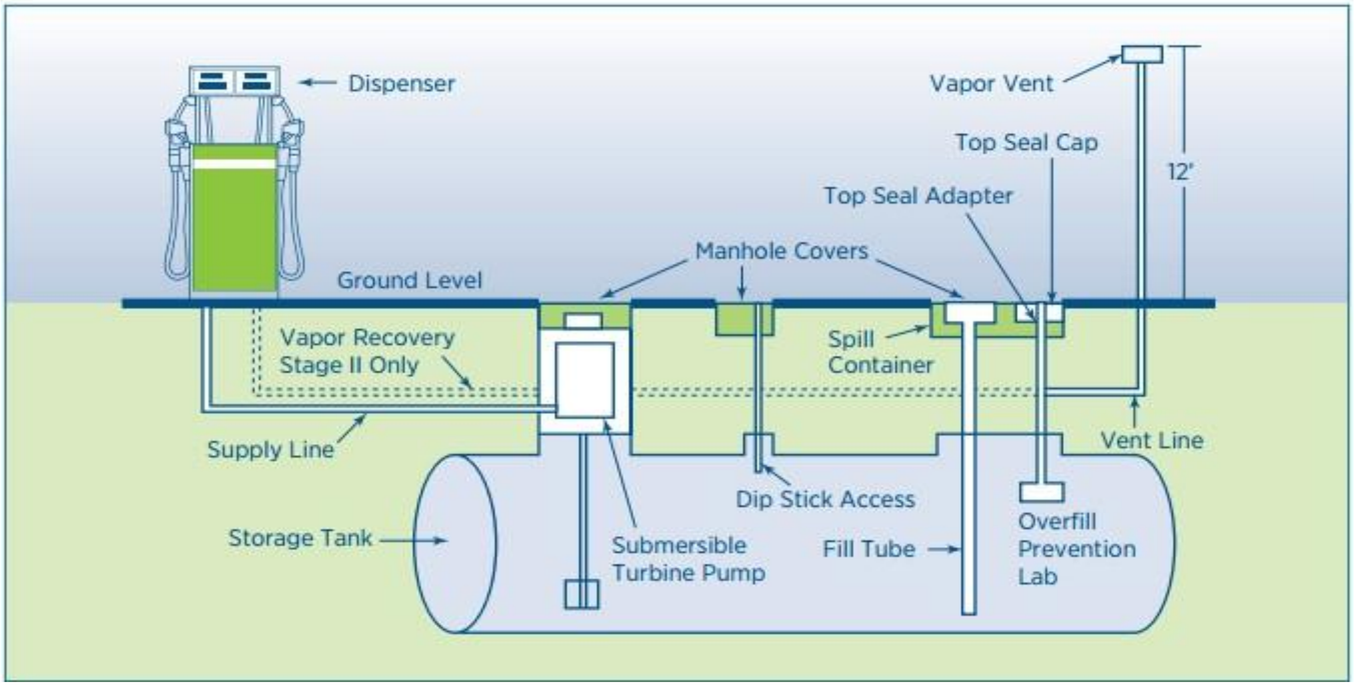


Figure 2.1. Ethanol Storage and Fueling

(DOE: Office of Energy Efficiency and Renewable Energy, 2013)

2.4 What vehicles can use E15?

Nearly all gasoline-fueled passenger cars and light-duty trucks manufactured in the last forty years are intended to handle E10 fuels. Teflon coated materials are used instead of plastics and rubbers, and stainless steel instead of metals that could rust. Most cars in the U.S. are already compatible with ethanol blends of at least E10, since this blend is widely prevalent at fueling stations nationwide (Fang et al., 2002; International Energy Agency, 2004).

One of the concerns raised about use of ethanol blends in traditional engines is that they will not be able to adjust to the higher oxygen content of ethanol. However, most vehicle models years currently on the road (MY of approximately 1999 and on) have the ability to recalibrate their air to fuel ratios based on the oxygen level of the fuel (Fang et al., 2002). Another category of vehicle, flexible fuel vehicles (FFVs), is specially designed to run on variable ethanol blends of up to E85. They are able to detect the concentration of ethanol in the fuel using an oxygen sensor, and calibrate their engines accordingly (DOE: Office of Energy Efficiency and Renewable Energy, 2013).

Another concern that has been considered is the potential for water phase separation of the ethanol from the gasoline in the fuel. This is far less of a problem in more modern vehicles with fuel injection systems and emissions controls that circulate fuel near the tank, which tends to keep the fuel well mixed (Fang et al., 2002). In fact, phase separation reduces in likelihood with increasing ethanol blend levels. E10 blends can tolerate twice as much water as E5, so it stands to reason that E15 can tolerate even higher water content (Fang et al., 2002).

Figure 2.2 shows the light duty vehicle (LDV) mix of US vehicles in operation at any given time for the years 2005-2030. As of 2011, most LDVs manufactured in 2001 and later are approved for fueling with E15. Gasoline hybrid electric vehicles (HEVs) are also approved for use of E15. Flexible fuel vehicles (FFVs) have always been compatible with ethanol blends of up to E85. The graph clearly shows that as time passes and older cars are retired from the vehicle fleet, cars that are incompatible with E15 will become increasingly scarce.

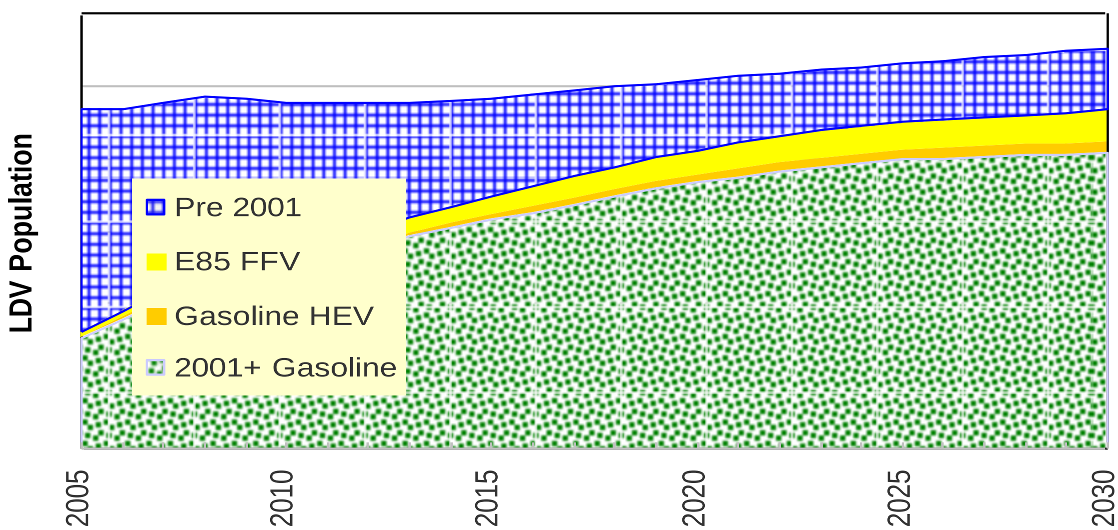


Figure 2.2. Ethanol blend compatibility of US vehicle fleet over time
(Argonne National Laboratory, 2013)

2.5 Drivability Testing

The Minnesota Center for Automotive Research tested fifteen standard, unmodified vehicles over a year of running on E30, and found no drivability or compatibility problems (Bonnema, Jones, & Ready, 1999). In Brazil, cars that have been slightly modified have been using blends of 20% to 25% ethanol since 1994 with few ill effects (International Energy Agency, 2004). A Department of Energy (DOE) study that is still ongoing has so far observed no drivability problems in 16 non-flex fuel vehicles operated on blends of E10, E15, and E20 over at least 100 miles (Knoll et al., 2009).

3. Vehicle Air Emissions and Related Health Impacts

Combustion of fuel in an internal combustion engine always results in a number of air emissions, some of which are pollutants that have significant health impacts. The most commonly regulated and studied pollutants associated with vehicle fuel combustion are:

- Carbon Monoxide (CO)
- Hydrocarbons (HC)
- Oxides of Nitrogen (NOx)
- Particulate Matter (PM)
    - Polycyclic Aromatic Hydrocarbons (PAH)
- Volatile Organic Carbon (VOCs):
    - Benzene
    - 1,3 butadiene
    - Acetaldehyde
    - Formaldehyde
- Ground-level Ozone (a secondary pollutant)
- Greenhouse Gases

3.1 How do exhaust emissions form?

Some emissions are a product of the combustion reaction, and some are the result of incompletely combusted components of the fuel itself. It is helpful to understand the origin of pollutants when considering their emission from vehicles and possible methods for controlling them.

3.1.1 Carbon Monoxide (CO)

Carbon monoxide molecules are caused by incomplete combustion of fuel in an engine. This usually occurs when the air to fuel ratio is too low in air, resulting in incomplete oxygenation of the carbon needed to convert all the carbon to CO_2. This can also be the result of inadequate mixing of fuel and air, leading to under oxygenated pockets in the engine (Bioethanol for Sustainable Transport, 2008).

3.1.2 Hydrocarbons (HC)

Incomplete combustion can also result in the release of hydrocarbons from the unburned fuel. Hydrocarbon emissions are usually related to the movement of fuel mixtures, cylinder speed, or cylinder misfiring (Bioethanol for Sustainable Transport, 2008).

3.1.3 Nitrogen Oxides (NO_x)

Nitrogen oxides include both nitric oxide (NO) and nitrogen dioxide (NO_2). Nitric oxide is formed from nitrogen and free oxygen atoms at high temperatures. Its rate of formation increases exponentially with temperature (Bioethanol for Sustainable Transport, 2008).

3.1.4 Particulate Matter (PM)

Particulate matter forms as a combination of soot carbon particles, lubricating oil, and ash-forming fuel and oil additives. Aromatics, which are contained in gasoline, are more likely to form particulate than are ethanol molecules. Polycyclic aromatic hydrocarbons (PAHs) are highly carcinogenic, can become attached to particulate matter.

3.1.5 Toxic Pollutants

Benzene is emitted in engine exhaust when fuel components escape the combustion process. 1,3 butadiene is another pollutant that results from partial combustion of hydrocarbons. Aldehydes form as intermediate products in the oxidation of alcohols, meaning they are more likely to be emitted by fuels containing ethanol. Polycyclic aromatic hydrocarbons (PAHs) can be either the result of PAHs emitted directly from fuels or can be formed during combustion from other molecules (Bioethanol for Sustainable Transport, 2008).

3.1.6 VOCs and Ground Level Ozone

Volatile organic compounds are defined by the EPA as any compound containing carbon and having a low enough boiling point that they have a tendency to vaporize near room temperature (U.S. Environmental Protection Agency, n.d.-b). VOCs contain many classes of compounds including hydrocarbons, alcohols, ketones, aldehydes, which are found in vehicle exhaust and other compounds such as vinyl chloride and solvents that are not related to vehicle operation. Ozone, or photochemical smog, is formed when NOx and VOCs react in the presence of heat and sunlight (U.S. Environmental Protection Agency, n.d.-a). Ground level ozone is an important component of smog. Since many classes of VOCs can contribute to ozone formation, the term VOC is often applied to the hydrocarbons that contribute to smog.

Ozone formation depends on the concentration of chemical species in the atmosphere, the air temperature, the presence of sunlight, and many other factors. The photochemical reactivity of individual hydrocarbons is often used as a measure of their smog forming potential (Carter, 2009). Compounds that react rapidly in the atmosphere, like olefins, branched aromatics, and aldehydes have a high smog forming potential. Other compounds, such as alkanes, methane, and ethanol, have a low smog forming potential.

Air quality managers have measured the incremental photochemical reactivity of hydrocarbon in smog chambers (Carter, 1994, 2009). The maximum incremental reactivity has been used by air quality managers to assess the ozone potential of different fuel options (Unnasch, 1996; Carter, 2009).

3.1.7 Greenhouse Gases

Greenhouse gases include such vehicle emissions as CO_2 and CH_4. These form when the hydrocarbon chains of a fuel are broken by combustion, allowing for the oxygenation of C and the formation of new molecules.

3.2 Air Pollutant Human Health Impacts

California's Office of Environmental Health Hazard Assessment (OEHHA) is required to develop guidelines for conducting health risk assessments under the Air Toxics Hot Spots Program (Health and Safety Code Section 44360(b)(2)). They maintain a database of acute and chronic non-cancer and cancer impact factors. Non-cancerous health impacts are reported in terms of Reference Exposure Levels (RELs), the exposure levels at or below which no harm would be expected over a given exposure time (Salmon, 2008). Cancerous impacts are inherently chronic and occur over the long term. OEHHA reports them in terms of unit risk, which refers to the likelihood that a certain dose of a chemical will cause a cancerous response in a human over his or her lifetime. This is typically expressed in terms of a reciprocal air concentration with units of $(\mu g/m^3)^{-1}$ (Budroe, Brown, Collins, & et al, 2009).

In order to more easily compare the impact factors of different toxins, the OEHHA cancer impact ratings of all chemicals considered in this study are expressed in Table 3.1 in normalized terms. Normalized impacts are calculated here in terms of the equivalent amount of acetaldehyde emission that would have the same impact. The calculated values are given the unit of $(\mu g/m^3)^{-1}$ acetaldehyde equivalents (Acet-eq.).

While CO and NO_x can have acute health impacts, their concentration in vehicle exhaust emissions is unlikely to reach levels high enough to cause acute impacts, except in enclosed spaces such as garages. CO, NO_x, and ozone may have cancerous impacts, but they have not been assigned OEHHA cancer potential toxicity factors. Therefore, their potential health impacts are described in Table 3.1, but they are not assigned quantitative impact factors.

Table 3.1. Air Emission Human Health Impacts

Species	Formula	Short Term Health Effects	Long Term Health Effects	Cancer (Unit Risk, $(\mu g/m^3)^{-1}$ Acetalehyde-eq.) OEHHA
Nitrogen Oxides (NO_x)	NO, NO_2	Airway inflammation Respiratory symptoms in people with asthma	Decreased immunological function Mutagenic effects	N/A
Carbon Monoxide	CO	Reduces oxygen delivery to organs Respiratory and cardiovascular morbidity	Cardiovascular changes Birth outcomes and development	N/A
Ground-level Ozone	O_3	Shortness of breath Coughing, sore throat Airway inflammation	Increased frequency of asthma attacks Lungs more susceptible to infection	N/A
Acetaldehyde	C_2H_4O	Irritation of eyes, skin, & respiratory tract Erythema, coughing, pulmonary edema, & necrosis	Potential developmental toxin Changes in nasal mucosa and trachea	1.00
Formaldehyde	CH_2O	Irritation of respiratory tract and eyes Asthma	Probable carcinogen Developmental teratogen	2.22
1,3 Butadiene	C_4H_6	Irritation of respiratory tract and eyes Blurred vision, fatigue, headache, and vertigo	Cardiovascular diseases Carcinogen Developmental and reproductive effects	62.96
Benzene	C_6H_6	Affects blood forming, nervous, and immune systems Drowsiness, dizziness, headaches, vomiting, and unconsciousness Irritates skin, eyes, and upper respiratory tract	Blood disorders Possible reproductive and developmental effects Carcinogen, esp. leukemia	10.74
Polycyclic Aromatic Hydrocarbons (PAHs) (e. g. benzo[a]-pyrene)	CH in aromatic rings	Lung and skin irritation	Carcinogen Possible reproductive and developmental effects Respiratory, liver, skin, and kidney	407.41
Ethanol	C_2H_5OH	None at ppm levels	None at ppm levels	N/A

Many different speciated hydrocarbons are considered PAHs. The health impact factor for benzo[a]pyrene is shown as an example since it is one of the PAHs of greatest concern for human health, although some PAHs have much lower toxicity potentials.

The EPA has been calculating toxicity potentials for air pollutants in terms of unit risk factors for many years, and the methodology has not changed greatly. The EPA's Integrated Risk Information System (IRIS) contains human health information about more than 550 chemicals, many of which have not changed since 1991 despite continual review. Table 3.2 shows the unit risk factors for some of the chemicals considered in this study, normalized to the toxicity of Acetaldehyde. Like the OEHHA factors, these are based only on toxin potency. These factors are not used in this study, but are presented for comparison purposes. As in the OEHHA factors, 1, 3 butadiene is the toxin with the highest toxicity.

The OEHHA factors are used in this study because they were revised in 2009, and because the OEHHA factors are typically more conservative than the IRIS factors, which means they provide greater public health protection. Table 3.2 provides a comparison of the raw unit risk factors as well as the normalized risk factors of the IRIS and OEHHA databases.

Table 3.2. EPA IRIS and OEHHA Unit Risk Factors

	Cancer Unit Risk Factor $(\mu g/m^3)^{-1}$		**Normalized Cancer Unit Risk Factor to Acetaldehyde = 1**	
Compound	EPA IRIS	OEHHA	EPA IRIS	OEHHA
Acetaldehyde	2.20×10^{-6}	2.70×10^{-6}	1.00	1.00
Formaldehyde	1.30×10^{-5}	6.00×10^{-6}	5.91	2.22
1,3 Butadiene	3.00×10^{-5}	1.70×10^{-4}	13.64	62.96
Benzene	2.20×10^{-6} 7.8×10^{-6}	2.90×10^{-5}	1.00 3.55	10.74

(Salmon, 2008; US Environmental Protection Agency, 2014)

4. Changes in Emissions from Use of Ethanol Blended Fuels

A key question with respect to the increasing use of ethanol is how the additional ethanol will change the emissions of the vehicle. Will they increase, decrease, or remain relatively unchanged? One prior analysis of sixteen different emission studies from 1995 to 2003 concluded that, under different circumstances, both increases and decreases were observed in some major pollutants, indicating that fuel composition was not the only factor at play (Bioethanol for Sustainable Transport, 2008).

Some external factors that may affect the pollutants emitted from a vehicle include characteristics of the vehicle, such as design and emission control features, characteristics of the fuels, such as their chemical components and physical properties, and the blending techniques and testing approaches used in a given study. An understanding of these factors allows us to predict some of the changes that can be expected given a change in fuel blend content, and to isolate the changes that are a result of ethanol blend level from those that are actually a consequence of outside factors.

4.1 Age of vehicle

Changes in emissions from ethanol increase may be dwarfed by the impact of the engine technology of the vehicles being studied. Newer vehicles are likely to be equipped with much better pollutant control technologies than older vehicles. Technological improvements, such as three way catalysts, direct injection combustion, and other aspects of driving cycle appear to be more significant factors of most regulated emissions than is fuel composition, especially at the low level of change that is being considered in a switch from E10 to E15. An EU Joint Research Council (JRC) study that looked at NOx, CO, PM, and total hydrocarbons found that "the impact of the driving cycle and engine technology on regulated emissions appears to be much more important than the variation in fuel properties that were tested here," (Martini et al., 2013).

Numerous control technologies can affect the exhaust emissions of a vehicle, many of which have become standard issue in modern cars. For example, in 2012, half of all U.S. vehicles manufactured had direct injection engines. The total percentage of cars with direct injection engines is expected to increase to 48% by 2016 and 93% by 2025 (Karavalakis et al., 2014).

Federal regulations do not specify what technologies vehicles should use, but they do set emissions limits that cars must comply with. Some examples of the possible features manufacturers incorporate to ensure their cars meet those limits include, but are not limited to, those listed in Table 4.1. Emissions standards have tended to become increasingly strict over time. Current emission limits are shown in Appendix A.

Table 4.1. Emission control technologies and design features

Pollutant Emission	Control Technology or Design Features
Carbon Monoxide	• Precise control of air: fuel ratio • Multi-point injection • Compact combustion chambers • Precise ignition timing • Catalytic converters
Hydrocarbons	• Crankcase ventilation systems • Evaporative emission sealing • Ignition timing • Catalytic converters
Nitrogen Oxides	• Exhaust gas recirculation • Combustion chamber shape alteration in combination with reduced compression ratios • Engine designed to operate on weak mixture • Computer-controlled ignition timing • Optimized valve timing • Fitting intercoolers to turbocharged engines • Three-way catalytic converters

(Bioethanol for Sustainable Transport, 2008)

Modern vehicle emission control systems adjust for the oxygen content of fuel, so increases in oxygen content from E15 fuel are detected with the oxygen sensor and the engine operates at its designed air fuel ratio.

4.2 Fuel Composition

Fuel composition is an important factor in determining the emissions from gasoline and ethanol blends. While ethanol is a pure substance made up of one type of molecule, gasoline is made up of many different molecules, and its exact composition can vary from sample to sample based on distillation and finishing techniques and the original crude. However, the general properties of gasoline are well known, and it must meet ASTM standards in order to be sold for use as a fuel.

Table 4.2. Fuel Properties of Pure Ethanol vs. Pure Gasoline

Property	Ethanol	Gasoline Blending Component
Chemical Formula	C_2H_5OH	C4 to C12 Hydrocarbons
Octane Number ((R + M)/2)[a]	113	86-94
Lower Heating Value (Btu/gal)	76,300	116,300 to 116,900
Heat of Vaporization (kJ/kg)	841	320
Reid Vapor Pressure (psi)	2.3	7 to 16
Ignition Point—Fuel in Air (%) Temperature (approx.) (°F)	3 to19 850	1 to 8 495
Specific Gravity	0.789	0.745
Air-Fuel Ratio (by weight)	9	14.7
Hydrogen-Carbon Ratio	3.0	1.85

(DOE: Office of Energy Efficiency and Renewable Energy, 2013); ANL, GREET)
[a]Research + Motor

Table 4.3 shows a comparison of the chemical and physical properties of different fuels and ethanol blends. CARB2 is a gasoline-based fuel containing 11% MTBE. CARB3 is a gasoline ethanol blend with 5.7% ethanol. As can be seen in the discrepancies between the CARB2 and CARB3 composition profiles, since several components that would be expected to decrease from CARB2 to CARB3 actually increase, a different gasoline base was used in the CARB2 fuel than in the other 4 blends, all of which were based on the E5.7 base and had increasing amounts of ethanol blended into them.

Nonetheless, a number of things are evident in this table. For one, it shows that RVP increases in blends up to E10, and then decreases again, as would be expected based on previous studies. The ethanol blends all have lower levels of benzene, ethylbeneze, xylene, and olefins than CARB2 fuels. Oxygen levels increase with increased ethanol blends, as would be expected. Trends across the E5.7 to E50 blends are relatively directionally consistent.

Table 4.3. Fuel Composition and Chemical Properties of Gasoline/Ethanol Blends

Property	CARB2	E5.7	E10	E20	E50
Sulfur content (µg/kg)	30.9	20.7	16.6	15.9	<10
API Gravity, 15^{0}C	60.1	59.1	58.3	56.8	51
Net heating value (MJ/kg)	42.58	42.27	41.21	39.79	33.34
Distillation					
Initial Boiling Point	336	100.5	319.5	330.7	328.3
50 %	518.9	520	520.5	520.6	521
90 %	608.6	611.3	546.4	546.3	547.5
95 %	635.1	639	552.6	553.3	554.4
FBP	661.7	662.4	569.6	564.7	569.1
Research Octane Number (RON)	97.4	96.2	98.4	101	101.2
Motor Octane Number (MON)	88.8	87.8	88.8	89.8	91.7
Reid vapor pressure (psi)	6.65	6.67	7.2	6.92	6.57
Benzene (wt.%)	1.1	0.86	0.76	0.73	0.43
Toluene (wt.%)	6.45	11.28	9.97	8.56	5.46
Ethylbenzene (wt.%) p/m	5.46	1.54	1.36	1.78	0.85
Xylenes (wt.%)	5.55	5.12	4.53	4.27	2.56
o-Xylene (wt.%)	0.58	1.03	0.91	0.78	0.51
>C9 Aromatics (wt.%)	9.62	12.08	10.66	9.53	5.87
Total aromatics, (wt.%)	28.76	31.9	28.2	25.65	15.67
Ethanol (wt.%)	<0.1	6.63	11.33	17.19	43.54
MYBE (wt.%)	11.54	<0.1	<0.1	1.48	0.18
Total oxygen (wt.%)	2.09	2.3	4.16	6.86	17.12
Olefins (wt.%)	5.5	5	4.8	4.2	2.8

(Karavalakis et al., 2012)

4.2.1 Oxygen Content

Ethanol has a higher oxygen content than gasoline, so ethanol-gasoline blends are more highly oxygenated than pure gasoline. Higher fuel oxygen levels promote leaner and more complete combustion, resulting in lower emissions of pollutants such as carbon monoxide and unburnt hydrocarbons. Operating at slightly leaner conditions results in higher combustion temperatures, which can result in increased in NOx emissions (Bioethanol for Sustainable Transport, 2008).

However, the leaning effect of ethanol is eliminated with oxygen sensors on modern cars. Newer vehicles are equipped with three-way catalysts and oxygen sensors to simultaneously reduce NOx and hydrocarbon emissions. The oxygen sensor makes the engine run at its intended air/fuel ratio. Thus, the effect of ethanol on NOx should be minimal. Furthermore, the effect of ethanol on NOx is not always consistent, and is usually only minimal when an increase in NO_x is observed (International Energy Agency, 2004). With new vehicle technologies, the primary impact of ethanol blends would be a change in the composition of toxic air contaminants on smog forming hydrocarbons.

4.2.2 Heat of Vaporization

Ethanol has a higher heat of vaporization than gasoline. In modern engines, fuel is injected into intake manifolds. Older engines use throttle body injection or carburetors. With all of these fuel delivery mechanisms, fuel starts to vaporize while it enters the combustion chamber with the intake valves open. A fuel with a higher heat of vaporization cools the surrounding air more as it evaporates than a fuel with a lower heat of vaporization. This charge air cooling has several effects on engine operation. Cooler air is denser than hot air, so the engine can intake more air fuel mixture with a cold charge and produce higher power. Reducing the charge density also reduces the suction or pumping energy needed to draw the air fuel mixture into the engine. The net effect depends on driving behavior. For the same power output, the charge air cooling effect of ethanol results in reduced power expended by the engine for pumping, and reduced fuel consumption.

4.2.3 Octane Number

The octane number of a fuel represents how well the fuel resists pre-ignition or knock in an internal combustion engine. Fuels with low octane numbers will not operate properly in engines with high compression ratios, and the pre-ignition will affect vehicle performance. Fuels with higher octane can operate with more advanced spark timing or higher compression ratio engines.

Testing of traditional engines running on ethanol blends has shown that cars do not automatically adjust to the lower energy content and higher octane levels of oxygenated fuels. Instead, volumetric fuel consumption was found to increase in direct proportion to the fuel's volumetric energy content (Martini et al., 2013).

However, cars can be equipped with a sensor that allows them to accommodate higher octane levels. Some modern engines equipped with knock sensors can take advantage of higher octane in the fuel or conversely protect the engine from low octane fuels by adjusting ignition timing. If the sensor detects knock, spark ignition is retarded. Without knock, the engine can advance the spark timing. The effect of a slight increase in spark timing can be improved power and higher efficiency.

4.2.4 Vapor Pressure

The vapor pressure of ethanol gasoline blends varies in a non-linear fashion as shown in Figure 4.1 The vapor pressure of pure ethanol is 2.3 psi but the resultant ethanol gasoline blend increases in vapor pressure at low levels (Guerrieri, Caffrey, & Rao, 1995). The initial bump in vapor pressure is caused the formation of azeotropes that have a higher vapor pressure than the linear mixture predicted by Raoult's law. Blending of ethanol into gasoline at 10 volume percent causes the RVP to increase by about 1 psi despite the fact that fuel grade ethanol has a lower vapor pressure than gasoline.

As the ethanol content rises vapor pressure drops. As ethanol content changes from 10 to 15%, a slight drop in vapor pressure is predicted in Figure 4.1. A study from NREL shows no change in vapor pressure for changes from E10 to E15 (McCormick & Yanowitz, 2013).

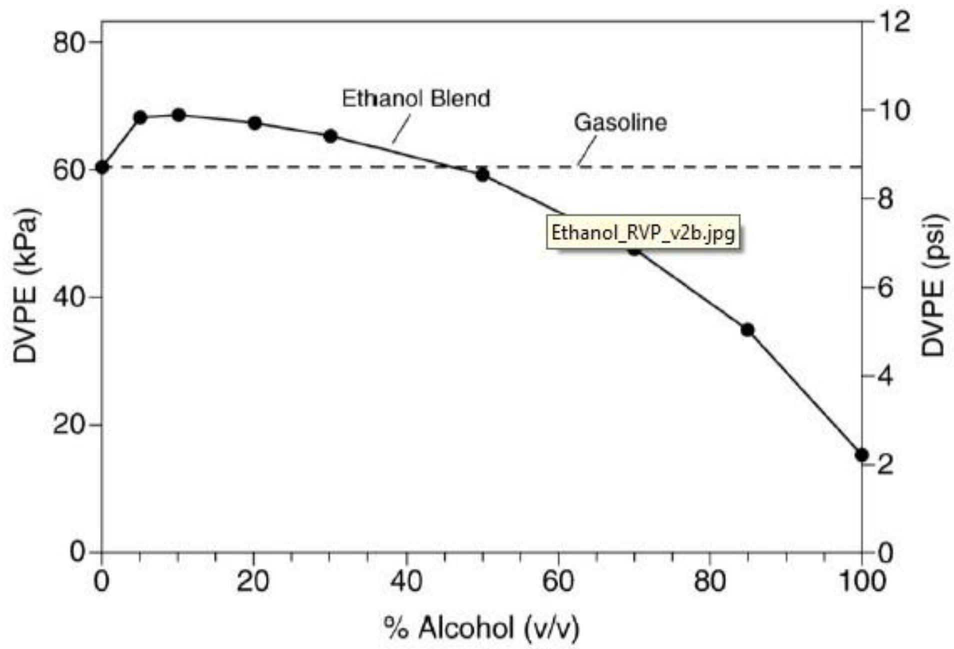


Figure 4.1. Effect of ethanol on vapor pressure of gasoline.

Ethanol has a lower vapor pressure than gasoline, and when ethanol is mixed with gasoline, the hydrocarbons of the gasoline weaken the hydrogen bonds of the ethanol and increase the volatility of the mixture. This effect is most noticeable at low concentrations of ethanol blends. A 2% by volume ethanol blend has been shown to increase the vapor pressure of gasoline by as much as 6 to 8 kPa, which could potentially put the mixture above the volatility standards for gasoline (Rose, 2009).

However, because the volatility of the ethanol blends increases for the first few percent, then levels off and decreases at the 10% blend level, this effect is more significant when changing from E0 to a low blend level of ethanol than it is in going from E10 to E15 (Guerrieri et al., 1995). Blends of 2%, 5%, 10%, and 15% have very little difference in their effect on VOCs, although there is an increase from 0% to 2% (International Energy Agency, 2004). In fact, ethanol blends of about 25% have the same RVP as pure gasoline.

4.3 Blending Technique

Another factor that can affect the results of an emissions study is the blending technique used to create different ethanol blends. There are two main techniques for mixing ethanol and gasoline blends, match blending and splash blending. Match blending involves mixing ethanol into a base fuel that has been altered in some way to meet certain specifications, such as octane level, boiling point, or vapor pressure. This may be done by using heavier cuts of the crude oil than would typically be in retail gasoline to balance out the high octane and low boiling point of ethanol. Splash blending involves mixing a base ethanol and retail gasoline to meet a certain volume % specification without altering the other properties of the fuels. In splash blending, octane level and vapor pressure may vary (West, Sluder, Knoll, Orban, & Feng, 2012). The choice between these two blending techniques, and also the approach used if match blending, can affect emission profiles in a given study.

Fuel producers can blend fuels to take account the octane number of each component. The match blending approach will take advantage of the properties of ethanol and effectively increase the efficiency of the oil refinery (MathPro Inc., 2012).

Some air emissions are directly related to the concentration of the emitted pollutant in the fuel being combusted. Ethanol has no olefins, aromatic hydrocarbons, or sulfur, some of the most important pollutants that are emitted during combustion due to the composition of gasoline. An increase in ethanol volume in the fuel will result in a corresponding decrease in these fuel components (Bioethanol for Sustainable Transport, 2008).

4.4 Evaporative Emissions

Ethanol and gasoline are volatile fuels with significant potential to emit evaporative emissions. Evaporative emissions are the vapors that escape from a vehicle's fuel system into the atmosphere during engine operation, after a hot engine is turned off (referred to as "hot-soak"), during venting after expansion of gas due to temperature increases, or through resting losses from permeation of rubber or plastic components of the fuel system. Evaporative losses are also likely to occur during refueling, when fuel vapors are displaced from the engine and released to the atmosphere (Unnasch, Browning, & Kassoy, 2001; US Environmental Protection Agency, 2012). Evaporative emissions correspond to 1.2 lb of vapor per 1000 gal of fuel transferred to the vehicle.

4.5 Spills

Fuel spillage occurs during vehicle refueling and hose transfers from delivery trucks. Most spillage during refueling consists of a few drops every 4 to 10 gallon fuel fill. Some larger spills, as shown in Figure 4.1 occur infrequently. EPA estimates the incidence of all fuel spills in an emission factor of 0.7 lb per 1000 gal of fuel dispensed (US Environmental Protection Agency, 2012). Fuel spills correspond to about one fourth of hydrocarbon emissions, with the balance being exhaust and evaporative emissions.

Virtually all of the fuel that is spilled during fueling and fuel transfers evaporates. The composition of the evaporated hydrocarbons matches the fuel composition. On average, spilled fuel contributes to 0.3 gram per gallon of fuel used. Most spills result from small drips during fueling.

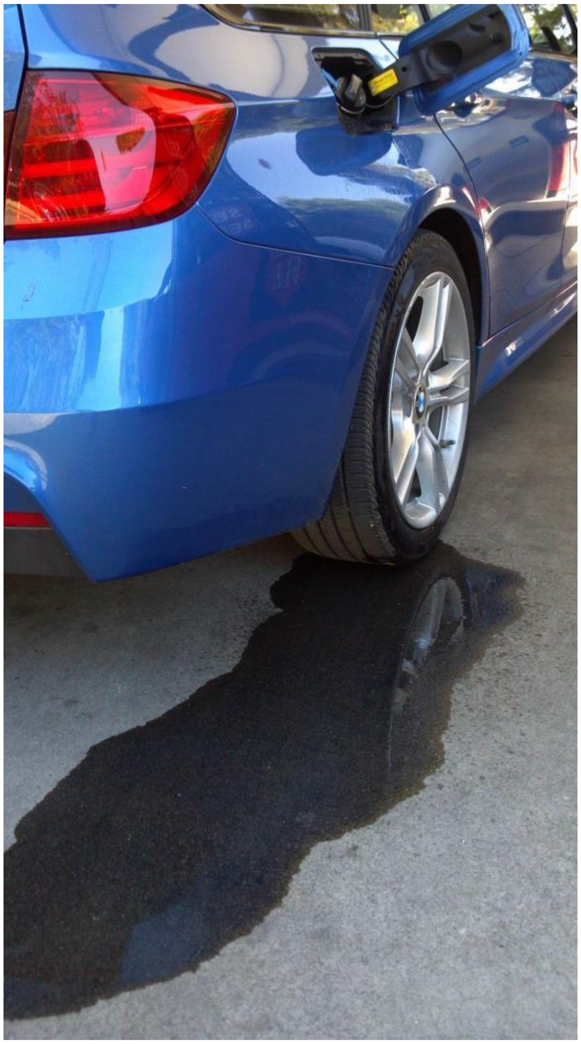


Figure 4.2. Accidental Fuel Spillage

4.6 Fuel Economy Impacts

As shown in Table 4.4, the energy content of pure ethanol is about a third lower than that of gasoline on a percent volume basis. The lower heating value represents how much energy is available to power the vehicle, so vehicles with the same efficiency would use the same amount of energy on a lower heating value basis. Table 4.4 shows the numbers input to calculate the energy content of different ethanol gasoline blends, and Table 4.5 shows the resulting energy content of different ethanol blends. Energy content decreases proportionally with increasing ethanol blend content by volume. Increasing the ethanol blend level results in a decrease in the total fuel mixture's lower heating value (LHV).

Table 4.4. Calculation of Ethanol Blend Energy Content

Blending Component	Ethanol	Gasoline Component	Denatured Ethanol	Denatured Ethanol	Gasoline Component	Finished Gasoline
Volume, (vol %)	98%	2%		15%	85%	
LHV (Btu/gal)	76,330[a]	116,300[a]	77,129	77,129	116,300	110,424
v × LHV	74,803	2,326		11,569	98,855	
Energy Fraction	0.9698	0.0302		0.1048	0.8952	

[a]Source: GREET

Table 4.5. Energy Content of Ethanol Blends

	E0	E5.7	E10	E15
Volume Fraction	0%	5.7%	10%	15%
Energy Fraction (Btu ethanol / Btu fuel blend)	0.00%	3.85%	6.86%	10.48%
LHV (Btu/gal)	116,300	114,067	112,383	110,424

On the other hand, ethanol has a higher octane number and heat of vaporization than gasoline (Anderson, DiCicco, Ginder, Kramer, & Al, 2012). Higher octane fuels can resist greater levels of compression, and increase engine efficiency by decreasing knock, the pre-ignition tendencies in the engine. The heat of vaporization refers to the amount of heat required to cause the fuel to change from a liquid to a gas. A high heat of vaporization allows the fuel to absorb energy from the surrounding air, allowing more air and fuel to enter the engine and resulting in greater efficiency and power output (Curtis, Owen, Hess, & Egan, 2008). These factors work in the opposite direction as the lower energy content of ethanol to balance the fuel economy effects of adding ethanol to gasoline.

Current practices involve blending ethanol with a lower octane gasoline so that the net octane level remains the same as it has historically been with pure gasoline. However, the potential exists to increase fuel economy and thermal efficiency by modifying cars to take advantage of the higher octane content of ethanol (Anderson et al., 2012). Measures such as adjusting engine timing and increasing compression ratios can result in engines that burn E20 more efficiently than E10 by several percentage points (International Energy Agency, 2004).

5. Findings of Existing Studies of Ethanol Blend Exhaust Emissions

This meta-analysis reviewed a number of exiting studies of ethanol blend emissions, five of which performed original research by testing passenger vehicles on different blends of gasoline and ethanol and measuring the emissions and fuel economy. Their findings are summarized in the following sections.

5.1 Carbon Monoxide Findings

Use of a 10% ethanol blend has been shown to achieve a reduction of 25% or greater in CO emissions in older (International Energy Agency, 2004). In a 1995 study, researchers found a 50% decrease in CO levels when switching from E0 to E42 in 6 vehicles from MYs 1990 to 1992 (Guerrieri et al., 1995).

However, this effect seems to have disappeared with more modern vehicles. A study of vehicles from 2006 and 2007 by the CRC found no relationship between CO emissions and ethanol blend level (Haskew & Liberty, 2011). Karavalakis et. al (2012) found a significant decrease in CO emissions when looking at older vehicles, as much as a 72.2% decrease in CO emissions from a 1984 Toyota when comparing vehicle emissions running on E20 to those from CARB2 gasoline (Karavalakis et al., 2012). However, they found no significant effects when looking at later model vehicles (2000 and 2007). These findings provide further support for the conclusion that vehicle age and engine design features are more important factors in CO emissions than ethanol blend level.

5.2 Nitrogen Oxide Findings

A study by CRC found no relationship between NOx emissions and ethanol blend level (Haskew & Liberty, 2011). Karavalakis et. al found in their 2012 study that NOx effects of ethanol content varied by vehicle. Older vehicles (a 1984 Toyota pickup truck, 1985 Nissan pickup, and 1993 Ford Festiva) showed an increase in NOx emissions with higher ethanol blends, with up to a 24.6 increase with use of E20 in the 1993 Ford Festiva. On the other hand, later models (1996 Honda Accord, 2000 Toyota Camry, 2007 Chevrolet Silverado) did not show any significant effects, although the trend was towards a decrease in NOx emissions with higher ethanol blends (Karavalakis et al., 2012). The Karavalakis et al., 2014, study found little difference in NOx emissions between blends of E10, E15, and E20 in a Kia Optima and Chevrolet Impala, both direct injection vehicles from MY 2012 (Karavalakis et al., 2014). Here, again, previous studies seem to support the conclusion that improvements in vehicle technology have eliminated the effect of ethanol blends on NOx emissions.

5.3 Carbonyl Findings

Acetaldehyde and formaldehyde emissions occur as by-products of incomplete combustion. Some studies have found that these emissions may increase with ethanol blends because ethanol contains pre-cursors to these carbonyls while gasoline typically does not.

Karavalakis, 2012 found carbonyl emissions in only 2 out of 7 vehicles, the 1996 Honda Accord and the 2007 Chevrolet Silverado. Formaldehyde, acetaldehyde, and acetone were the most prominent carbonyl compounds for both of the vehicles in which it they were present

(Karavalakis et al., 2012). Acetaldehyde emissions increased in the 1996 Honda Accord by 71% and 98% comparing E10 to CARB2 and CARB3, respectively. E20 increased 202% and 251%. However, with the 2007 Chevy Silverado, emissions of acetaldehyde increased when running on E85 (by 1097% and 1430%), but decreased when running on E10 (by -39% and -23%). In general in the other five cars, carbonyl emissions were lower for ethanol blends than the CARB 2 or 3 fuels, except in the case of E85.

Karavalakis et. al, 2014, found that formaldehyde and acetaldehyde emissions decreased from E10 to E15 in both vehicles studied. The 2012 Chevrolet Impala saw an increase in emissions of these two compounds when switching from E15 to E20, but it was not significant. In the 2012 Kia Optima, formaldehyde emissions decreased by 88% when switching from E10 to E20, and acetaldehyde emissions decreased by 82% (Karavalakis et al., 2014). Guerrieri, 1995, found that formaldehyde was only minimally affected by ethanol blend levels, but acetaldehyde emissions increased with increasing ethanol blends (Guerrieri et al., 1995). In the CRC, 2011, study, the aldehyde emissions, an in particular acetaldehyde, showed a trend of increasing with increasing ethanol levels (Haskew & Liberty, 2011).

5.4 Aromatic Compounds

On the other hand, benzene, toluene, and xylene emissions have been shown to decrease in ethanol blends. This is because these molecules are naturally occurring in petroleum but are not present in ethanol, and their emission to air is a direct result of fuel composition. These kinds of aromatic hydrocarbons have been shown to be more potently toxic than the carbonyls and aldehydes that could be increased with ethanol blending (Budroe et al., 2009; International Energy Agency, 2004).

Karavalakis et. al, 2012, found that increases in ethanol resulted in lower benzene, toluene, xylene, and 1,3 butadiene emissions (Karavalakis et al., 2012). 1,3 butadiene did not show any significant trends in Karavalakis et. al, 2014 (Karavalakis et al., 2014).

5.5 Particulate Matter

Particulate matter emissions have been repeatedly shown to decrease with increasing ethanol levels. Higher oxygenate fuels, such as those with ethanol blends, have been shown to result in lower particulate matter emissions (He, Ireland, Ratcliff, & Knoll, 2011; Karavalakis et al., 2014). PM was not a major focus of the studies from which data was taken, and for this reason it is not shown in Table 5.1. However, various other studies have also found as a general trend that particulate emissions decrease with increasing ethanol content (Magara-Gomez, Olson, McGinnis, Zhang, & Schauer, 2014; Storey, Barone, Norman, & Lewis, 2010). Storey et. al found up to a 42% decrease in PM emissions when comparing E20 to E10.

Table 5.1 displays a summary of the six studies considered as potential data sources for this meta-analysis, and shows their sample size, vehicle ages, and findings with respect to different air pollutants.

Table 5.1. Summary of Individual Emission Study Results

Study	Guerreri, 1995	Karavalakis, 2012	Karavalakis, 2014	CRC, 2011	Knoll, 2009	West et al, 2012
Sample Size (#cars)	6	7	2	7	16	26
Car MYs	1990-1992	1984-2007	2012	FFVs 2006-2007	1999-2007	2000-2009
Commonly Regulated Air Pollutants						
CO	-	- for older, no effect for younger	no effect	no effect	-	-
NOx	+	no effect	no effect	no effect	no effect	+
Particulate matter			-			
Toxic/Other Pollutants						
Acetaldehyde	+	+	-	+	+	+
Benzene		-	+			
1,3 Butadiene		-	+			
Formaldehyde	no effect	+	-	+ for some	+	+
Toluene		-	no effect			
Xylene		-	no effect			
Total Hydrocarbons	-	-	+			
NMHC				-	-	-
NMOG					no effect	no effect
Fuel economy	-		-		-	-
Ethanol						+

Decrease indicated by "-."
Increase indicated by "+."

6. Meta-analysis of Emission Test Data

In order to gain further insight into the quantitative trends across different studies and vehicles, Life Cycle Associates adapted data from five different studies and performed a meta-analysis of their data. In the cases of CRC study E-80 and Oak Ridge, 2012, emissions measurements were publically available (Haskew & Liberty, 2011; West et al., 2012). For the other three studies, data was taken from graphically presented results (Karavalakis et al., 2012, 2014; Knoll et al., 2009). The Guerrieri study data was not used here because all the cars studied in it were of MYs prior to 2000.

The CRC data included emissions from seven MY 2007 flexible fuel vehicles running on E5.7, E45.5, and E85. The Oak Ridge study considered 27 cars from MY 2000-2009, but only 16 contained measurements for the match blended test fuels (the rest were focused on aging effects), so only these 16 were included in this analysis. Cars were tested on E10, E15, and E20. The first Karavalakis study included cars from MY 1984-2007, but only the post-2000 MY cars were included in this meta-analysis. The included data were for a traditional passenger vehicle from 2000, and an FFV from 2007, running on blends of CARB2, a gasoline fuel with an MTBE oxygenate, E5.7, E10, E20, E50, and E85. The second Karavalakis study included two passenger cars from MY 2012 running on E10, E15, and E20. The Knoll study included 12 traditional passenger vehicles and 1 flex fuel vehicle, all from years 2001-2007. These were run on E0, E10, E15, and E20. In total, emissions data from 29 different vehicles was analyzed in the meta-analysis.

This study considers the emissions of CO, NOx, non-methane hydrocarbons (NMHCs), acetaldehyde, formaldehyde, benzene, and 1,3-butadiene from cars of MY 2000 and later, to the extent the data was available in each study. All test data used in this meta-analysis was taken from previous studies. Additional analysis was performed on the data to determine the weighted cancer potential from toxic emissions and the total ground level ozone potential based on change in photochemical reactivity. Greenhouse gases (GHGs) were not a focus of the studies in Table 5.1. However, many studies have been done on the effect of ethanol on greenhouse gas emissions. The results of these studies and their implications for a change from E10 to E15 were reviewed as part of this analysis, although no data was modeled with respect to GHGs.

6.1 Normalization

Change in ethanol blend level is not the only factor that has the potential to affect vehicle emissions. Emissions are also related to vehicle type and design. Control technologies tend to improve with time, meaning later models are likely to have lower emission profiles in general than older models. Many different vehicle types and model years are reported in the different studies, and while all of the studies performed FTP testing, some of the studies also performed other tests in addition.

In order to isolate changes in emissions that result from the change in ethanol blend level from those resulting from vehicle type, model year, and any other inter-study or inter-vehicle differences, most results were normalized to an E10 baseline. This means that all data points for a given car were divided by the emissions of that car running on E10, the current standard blend level in most areas. The ratio of the two data points allows us to compare changes in emissions across different cars since only the relative change from the baseline is being considered.

6.2 Toxicity Air Contaminants

The emissions of the air toxics acetaldehyde, formaldehyde, benzene, and 1,3 butadiene were combined into one weighted unit risk factor. They are weighted by their relative cancer potency as estimated by OEHHA in its toxicity database and calculated as one score for each vehicle at each blend level.

$$Weighted\ Toxin_i = Mass\ Toxin_1 \times Unit\ Risk\ Toxin_1 + Mass\ Toxin_2 \times Unit\ Risk\ Toxin_2 \ldots. Toxin_i$$

Unlike previous studies, this analysis included the impacts of emissions from fuel spillage. Since this is fuel that has not been combusted but evaporates completely, the composition of the original fuel is not changed. Therefore, in the case of an increase in ethanol blend level from E10 to E15, the evaporation of ethanol increases by 5% and the evaporation of gasoline's various components decreases by 5%. This study assumes a fuel spillage rate of 1 gram per gallon of fuel consumed (US Environmental Protection Agency, 2012).

This approach was also used in an assessment of life cycle emissions from transportation fuels preformed for the California Air Resources Board. After considerable review from toxicologists and other experts, the OEHHA factors were selected as the best representative of cancer risk. While other components in vehicle exhaust may result in adverse health effects, they are not listed carcinogens.

6.2.1 Polycyclic Aromatic Hydrocarbons (PAHs)

Very little data on PAH emissions were reported. PAH was examined parametrically as a small percentage by mass of the particulate emissions. Further information on new vehicles would provide more insight into the effect of ethanol blends on PAH emissions. Since aromatics are precursors to PAHs, the displacement of aromatics with ethanol would reduce PAH precursors.

6.2.2 Ozone Potential

Ground level ozone is not emitted directly but is formed from the emission of precursor chemicals VOCs and NO_x, which combine in the presence of sunlight to form O_3. Ozone potential, otherwise known as photochemical reactivity, refers to the likelihood that a certain VOC will react with NO_x and sunlight to create O_3 in the lower atmosphere. The level of NOx available in the air is often a limiting factor for the amount of ozone that can be produced (Carter, 1994).

There are several different methods for estimating the reactivity of a specific hydrocarbon. The method currently used by the CARB in its assessment of ozone precursors is the Maximum Incremental Reactivity (MIR) scale. In the MIR scenarios, the NOx inputs are adjusted so that the base reactive organic gas mixture has the highest incremental reactivity. The MIR scale is based on calculations of relative ozone impacts, expressed as mass of additional ozone formed per mass of VOC added to the emissions. MIR scenarios represent NOx conditions where emissions of VOCs have the greatest effect on ozone formation, and where NOx has the strongest ozone inhibiting effect (Carter, 1994, 2009).

The composition of evaporative emissions and spilled fuel allows for an assessment of the toxics impact (Unnasch 2001) and the effect on photochemical reactivity (Unnasch, 1996). These studies performed for the California ARB examined the weighted impacts with different alternative fuels.

Individual chemical's MIR ratings were multiplied by the % concentration of these molecules in different fuel mixtures to generate a weighted photochemical reactivity rating. Fuel compositions were taken from Carter, 2009. Speciated hydrocarbons were estimated based on several studies (Carter, 2009; Haskew & Liberty, 2011; Unnasch, Huey, & Browning, 1996).

The CRC's E-80 study also calculated a weighted cumulative ozone potential based on MIR reactivity. The study also found that ozone potential decreased with increasing ethanol levels (Haskew & Liberty, 2011).

Table 6.1. Ozone potential for selected chemicals

Chemical	MIR
Paraffins	1.5
Olefins	4
Ethanol	1.46
Other Hydrocarbons	1.5
Other Aromatics	3
Xylenes	7.5
> C9 Aromatics	5
Toluene	3.88
Ethyl Benzene	2.93
Benzene	0.69
Acetaldehyde	6.34
Formaldehyde	9.24
1, 3 Butadiene	12.21

(Carter, 2009)

6.3 Results

Table 6.2 displays the average emissions across all cars running on E10 for each study. This table highlights the variability that exists between different studies. For example, the Karavalakis, 2014 emissions are the lowest across the board, while the Karavalakis, 2012, study had the highest emissions across the board, except in emissions of CO, which is by far largest in the Oak Ridge study by West et al. The Knoll, 2014, and West, 2012 studies do not include a weighted toxics inventory in this study because their toxic emissions measurements were either incomplete or non-existent for the four toxics being considered in this analysis.

Table 6.2 also gives a sense of the relative magnitude of the baseline emissions. Direct exhaust emissions from E15 would be expected to be about 5% higher or lower, at most, than E10 emissions of the pollutants considered.

Table 6.2. Average E10 Mass Emissions by Study

Study	CRC, 2011	Karavalakis, 2012	Karavalakis, 2014	Knoll et al, 2014	West et al, 2012
NOx (g/mi)	0.053	0.168	0.007	0.060	0.041
NMHC (g/mi)	0.045	0.165	0.006	0.042	0.055
CO (g/mi)	0.766	0.173	0.006	0.233	1.025
Weighted Toxics (µg/mi)	34,079	238,679	1,431	N/A	N/A

6.3.1 NO_x, CO, and NMHC

Mass Based Emissions

Figure 6.1 through Figure 6.3 present study results in terms of absolute emissions by year or ethanol level for NOx, CO, and NMHC. Emissions are reported as a function of vehicle MY for the ethanol blend E10. In studies that did not measure vehicle emissions for a 10% ethanol blend, emissions were interpolated from surrounding data points. E10 is used as a baseline in this study due to its existing national prevalence.

Figure 6.1 shows NOx emissions (grams per mile) from vehicles running on E10, with model years ranging from 2000 through 2012. A clear decreasing trend can be seen in NOx emissions as vehicles become younger.

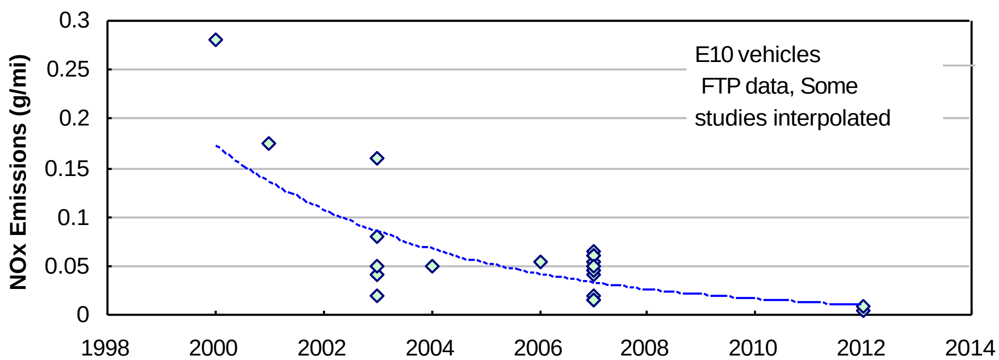


Figure 6.1. NOx emissions as a function of vehicle MY

Figure 6.2 shows CO emissions from E10 fuel as a function of vehicle of model year. In this case, the data is fairly widespread but the trend line still shows a decrease in emissions over time.

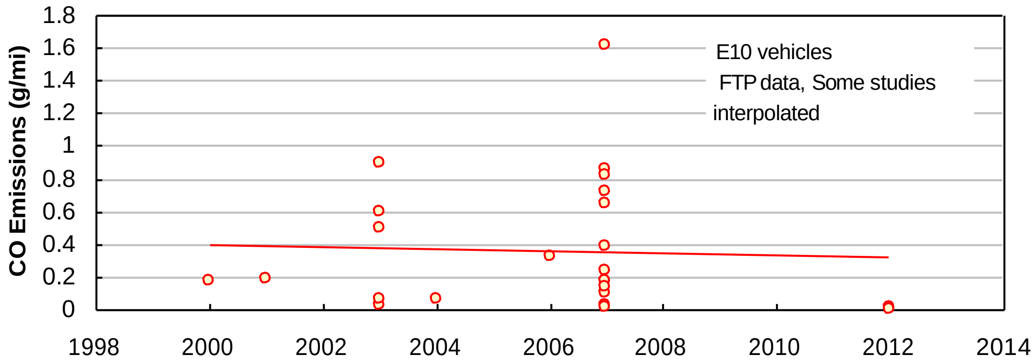


Figure 6.2. CO emissions as a function of vehicle MY

Figure 6.3 shows NMHC emissions from vehicles of MY 2000-2012 running on E10 fuel. As with NOx, a clear decrease over time can be seen in hydrocarbon emissions as vehicle technology evolves.

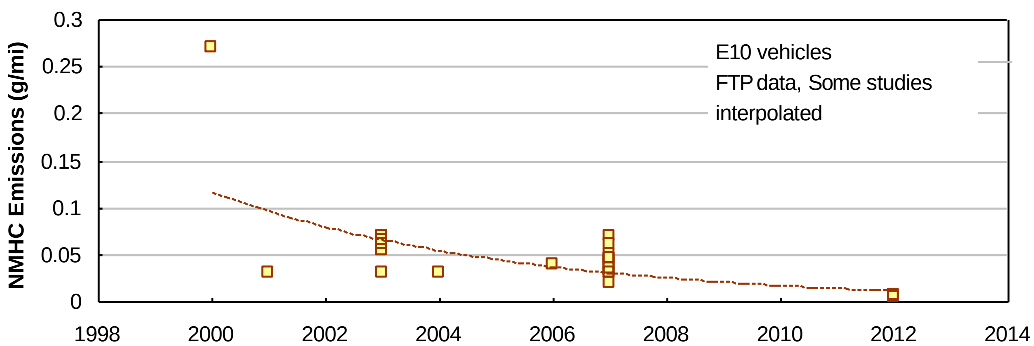


Figure 6.3. NMHC emissions as a function of vehicle MY

Together, these three graphs of absolute mass emissions demonstrate that a large amount of the variability in emissions can be attributed to underlying differences in vehicle type, MY and, in some cases, test type. As can clearly be seen in the graphs, emissions of NOx, CO, and NMHC have been going down over time in accordance with improvements in engine design and control technology and increasingly strict air pollution standards. These trends have the potential to obscure the difference in emissions between E10 and E15.

Normalized Emissions

The next section isolates the variable of ethanol blend level from vehicle variability by presenting normalized results. In these results, the change in emissions is reported for each individual vehicle, reducing the problem of inter-vehicular variability as a confounding factor. E15 emissions are divided by the emissions of the same vehicle running on E10 fuel. Therefore, E10 results are equal to 1, and this serves as our baseline. If the normalized result for another blend level was 1, this would mean the emissions had not changed from E10. If the normalized result was less than 1, it would mean the emissions had decreased, and if great than 1, that they had increased.

Figure 6.4 displays normalized emissions of NOx, CO, and NMHCs from every vehicle considered in the study, allowing for a comparison across both pollutants and vehicles. Each vehicle is assigned a different symbol, so that its individual trend across pollutants can be seen. The horizontal line in each column displays the average of all the data points for that pollutant. As can be seen in the chart, all the normalized emissions are fairly evenly distributed between being above and below 1, and the average of each column is close to 1, although CO is slightly above and NMHC is slightly below. This indicates a relatively random distribution with respect to the relative emissions of these three pollutants in a change from E10 to E15, which is confirmed in the statistical analysis findings of no significant effect for these three pollutants.

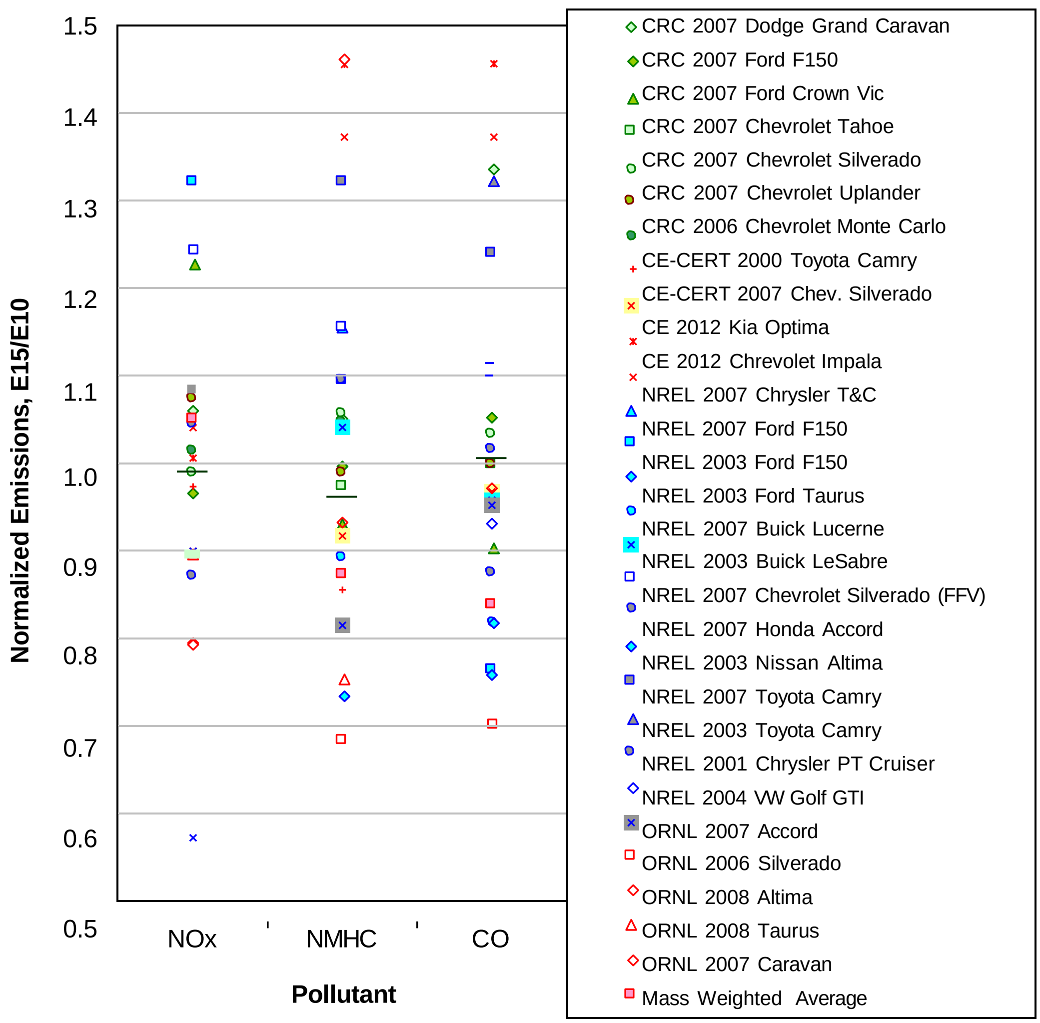


Figure 6.4. Normalized NOx, NMHC, and CO emissions by vehicle

6.3.2 Weighted Toxic Emissions

The weighted cancer causing toxics from the CRC study are shown in Figure 6.5. This chart shows the product of the OEHHA normalized unit risk factors and the mass emissions for each vehicle test. Results are shown for the FTP cycle, where the data was most complete. This analysis shows that benzene and 1-3 butadiene make up 29% and 68% of the cancer risk from the pollutants shown here for the baseline E5.7 vehicles. The cancer risk for acetaldehyde increased by 1% with a change from E5.7 to E32.

The ratio of weighted cancer risk for each vehicle was calculated and a Student's T test was performed to determine the statistical significance of the result. The two-tailed P value equals 0.031. By conventional criteria, this difference is considered to be statistically significant. The mean of the difference between normalized weighted toxics for E5.7 and E32 is a 18.8% reduction. The 95% confidence interval of this difference is a 2.0 to 35.6% reduction in toxic risk.

Extrapolating these result to a change from E10 to E15 results in a 6.6% reduction in toxic risk. This outcome is disproportionate to the change in ethanol in the fuel blend, and is driven by the fact that these impact findings are based on potency as well as mass based emission. The reduction in 1,3 butadiene and benzene produces a decrease in impacts that is greater than their relative decrease in mass emissions.

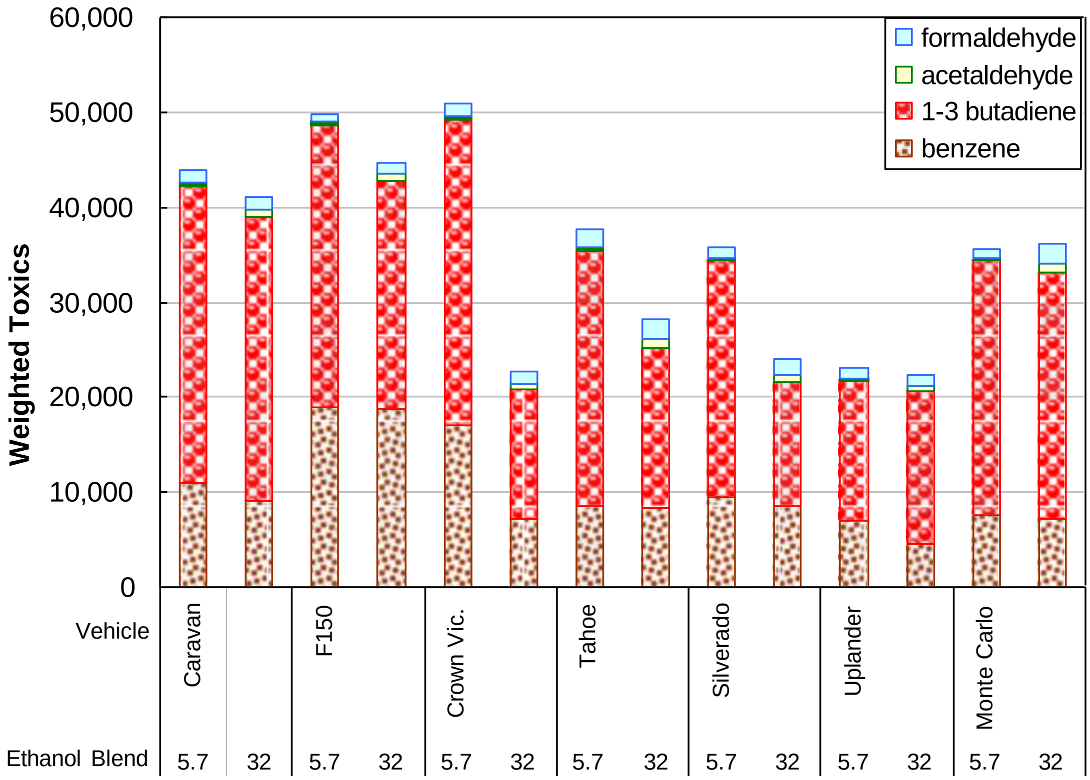


Figure 6.5. Weighted Toxics Contribution and Reduction

Moving from E10 to E15 also reduced the toxics impact of evaporative emissions and fuel spills. Fuels contain essentially no 1-3 butadiene and acetaldehyde and formaldehyde are products of combustion. Displacing 5% of the gasoline component with ethanol would result in a proportional reduction in cancer risk from fugitive benzene emissions. The relative contribution towards total hydrocarbon emissions of evaporative emissions and spills increases over time as exhaust emissions decline with the roll in of new vehicle technology.

6.3.3 Greenhouse Gas Emissions

Greenhouse gas emission estimates were taken from a study performed by Life Cycle Associates for the Renewable Fuels Association (Boland & Unnasch, 2014). E10 and E15 GHG emissions were weighted based on energy content of the fuels. The upstream energy inputs are shown in terms of Btu/mmBtu of fuel, and in the lower half of the table, the g/mmBtu of each pollutant are shown. Total GHGs are shown in terms of g CO_2 equivalent, and are also shown on a per MJ of fuel basis.

Table 6.3. Changes in Energy Content and GHG Emissions with Ethanol

Fuel Blend	Ethanol Fraction (Energy)	LHV (Btu/gal)	CI (g CO_2e/MJ) Corn Ethanol	CI (g CO_2e/MJ) Stover Ethanol
E0	0.00%	116,090	98.0	98.0
E5.7	3.85%	114,067	96.4	94.9
E10	6.86%	112,383	95.2	92.4
E15	10.48%	110,424	93.8	89.5
E100	100.00%	76,330	56.8	15.0
E10 to E15 Reduction		1.74%	1.54%	3.16%

As can be seen above in Table 6.3, corn-based E100 results in a 32% reduction in GHG emissions compared to conventional gasoline. Corn stover-based E100 results in an even greater reduction from pure gasoline of 85%.

Assuming corn-based ethanol, which is currently the dominant production approach, a change from E10 to E15 results in a 1.54% reduction in GHG emissions. The reduction in GHG emissions corresponds to the weighted contribution of corn ethanol fuel and gasoline blending components. Every billion gallons of E15 fuel that replaces an equivalent amount of E10 fuel would reduce GHG emissions by 180,000 metric tonnes.

6.3.4 Statistical and Uncertainty Analysis

A statistical analysis was performed in the modeling program Crystal Ball to assess the probability of results based on a Monte Carlo simulation. Monte Carlo analysis is a statistical method for assessing the likelihood of obtaining certain results by doing many simulations of randomly sampling the existing data.

Student T-Tests were also performed to assess whether the emissions from E10 versus those for E15 for each pollutant were significantly different. Table 6.4 displays the results of the t-tests.

Table 6.4. T-Test Results

	# of Pairs	2-Tailed P-value	95% Confidence Interval	Significant at $p < 0.05$
NOx	38	0.774	-0.08 – 0.06	No
NMHC	38	0.289	-0.08 – 0.03	No
CO	38	0.185	-0.03 – 0.14	No
Weighted Toxics	7	0.031	0.02 – 0.36	Yes

Charts corresponding to this analysis can be found in Appendix C. The results of the analysis are summarized below. In sum, changing approved vehicles from E10 to E15 will have the following impacts:

- **Weighted Toxics:** Weighted toxics are estimated to drop by 6.6% with a change from E10 to E15 based on the speciated emission data that was examined. This effect is primarily driven by a 9% reduction in 1,3 butadiene in the exhaust emissions. This change is statistically significant.

- **Ozone Potential:** There is a 70% chance of a reduction in ozone potential, with a predicted decrease value of 3.41%. It was not possible to do a t-test to determine the significance of this effect because there were too many variables.

- **NMHC:** This change is not statistically significant.

- **NOx:** This change is not statistically significant.

- **CO:** This change is not statistically significant.

7. Discussion and Conclusions: Net Effects of Changing from E10 to E15

In most of the categories of vehicle air emissions that were considered in this study, changing a vehicle's fuel from E10 to E15 resulted in either a decrease in emissions or it had little to no effect on emissions. In the case of ozone potential, weighted toxic emissions, and greenhouse gases, the switch resulted in a decrease in impacts. The changes in NMHC, CO, and NOx emissions were not significant.

Ozone Precursors

The change in ozone potential due to a change from E10 to E15 fuel depends on the composition of the fuels and the photochemical reactivity rating of their constituents. The inputs to this analysis were the vehicle exhaust hydrocarbon emissions, fugitive emissions from refueling, and fuel composition. Mass-based emission estimates of the speciated hydrocarbon emissions were multiplied by factors that represent the ozone formation potential of each hydrocarbon (Carter 2009). The same approach was followed in a study of reactivity weighted emissions from alternative fuel options for the California Air Resources Board (Unnasch, 1996).

Many factors affect the potential ozone impacts of a change to E15 including, exhaust emission rates, fuel composition, and the photochemical reactivity of the exhaust components. The distribution of ozone potential outcomes shows a predicted reduction in precursors for smog formation.

Greenhouse Gas Emissions

The ethanol component of E15 results in lower GHG emissions than that of the gasoline blending component. The GHG emissions from ethanol have been examined extensively by the U.S. EPA, California Air Resources Board, European Commission, as well as independent researchers (EPA, 2010; ARB, 2009; Dunn, 2013). The GHG emissions depend on the fuel used for ethanol plant operation, agricultural inputs, and indirect land use emissions. Emissions from crude oil based petroleum production have also increased over the years (Boland, 2014). Taking into account the changes in corn ethanol technology, crude oil production, and revised estimates of land use emissions, corn ethanol results in a 32% reduction in GHG emissions compared to conventional gasoline on a pure blending component basis. Corn stover based ethanol results in over 85% reduction in GHG emissions.

A change from E10 to E15 results in a 1.5% reduction in GHG emissions with current corn ethanol technology. The reduction in GHG emissions corresponds to the weighted contribution of corn ethanol fuel and gasoline blending components. Every billion gallons of E15 fuel would reduce GHG emissions by 180,000 metric tonnes, compared to the comparable sale of E10 fuel.

These numbers are based on the existing supply of ethanol, which is almost entirely derived from corn. However, advanced biofuels such as cellulosic ethanol are now entering commercial production. These fuels can achieve lifecycle GHG reductions of 85 percent relative to regular gasoline. As these new, advanced biofuel technologies begin to penetrate the market for renewable fuels, the GHG advantages of E15 will be even larger. The GHG savings is 3% with corn stover based ethanol. Table 7.1 shows the weighted carbon intensity (CI) for different ethanol blend levels with both corn starch and corn stover based ethanol.

Other Pollutants

The effect of ethanol on the other 3 pollutants studied (CO, NOx, and NMHC) was found to be very limited. The properties of ethanol affect many aspects of engine operation and emissions but the effects are dampened or eliminated by the existing control standards. Ethanol has a higher oxygen content than gasoline, so ethanol-gasoline blends are more highly oxygenated than pure gasoline. Higher fuel oxygen levels promote more complete combustion, resulting in lower emissions of pollutants such as carbon monoxide and unburnt hydrocarbons. However, oxygenation standards have been in place for many years, and most of the gains in combustion efficiency from increased oxygen levels have already become commonplace. Any potential negative effects on the air to fuel ratio resulting from ethanol are eliminated with oxygen sensors on modern cars, therefore, NO_x and CO emissions do not change significantly with changes in ethanol blend level. Ethanol also displaces aromatics that contribute to the formation of polycyclic aromatic hydrocarbons (PAH), which have the higher contribution to cancer risk among vehicle emissions. Test data on particulate emissions is limited; so, this effect was not quantified in the study.

Table 7.1 summarizes the quantity and significance of the estimated reduction in weighted cancer risk and ozone potential resulting from a change from E10 to E15.

Table 7.1 Estimated Emission Reductions for E10 to E15

Pollutant	Estimated Reduction	Likelihood of Reduction
Weighted cancer risk[a]	6.6%	95% confidence interval: 2% to 35.6% reduction in weighted toxic impact 80% confidence interval from Monte Carlo simulation[b]: 0 to 14% reduction
Ozone Potential	4%	60% confidence interval from Monte Carlo simulation: -2 to 9% reduction
Greenhouse Gases[c]	1.5%	Almost all ethanol plants reduce GHG emissions by more than 20%. Estimates vary with technology and analysis method

[a] Includes acetaldehyde, benzene, 1, 3 butadiene, formaldehyde.
[b] Includes PAH in particulate.
[c] GHG emissions correspond to weighted change in GHG emissions from ethanol and petroleum blendstock.

Conclusions

A meta-analysis of available data provides support for several conclusions.

- Ethanol displaces the cancer causing components benzene and 1-3 butadiene from gasoline. Ethanol also displaces aromatics, which are precursors to cancer causing polycyclic aromatic hydrocarbons (PAHs). These changes in fuel composition affect both the vehicle exhaust as well as refueling evaporative emissions and evaporated spilled fuel. Therefore the weighted cancer effect from E15 is lower than that for E10.
- 67.5% of the cancer risk is due to lower 1-3 butadiene, and 75% of vehicles showed a reduction in this pollutant. 29% of the cancer risk is due to lower benzene emissions, and 88% of vehicles showed a reduction in this pollutant. Acetaldehyde emissions increased with higher ethanol blend levels. Changes in acetaldehyde result in a predicted 0.3% increase in cancer risk while the risk from other listed carcinogens drops by 6.9%, resulting in a net decrease of 6.6%.
- Ethanol present in the vehicle exhaust displaces higher smog forming potential hydrocarbons that result from gasoline components; therefore, for a given amount of NOx and NMHC emissions, the smog forming potential for E15 blends is lower.
- Ethanol results in a 1.5% reduction GHG emissions, which is proportional to amount of ethanol in the fuel.

It is important to remember that changing from E10 to E15 involves a change of only 5% of the total fuel content. The estimated changes in toxic risk and ozone potential observed in the emission test results examined here are of a comparable magnitude.

Appendix A. Federal Emission Standards

Table A.1 Light-Duty Vehicle and Truck Emissions Standards, 50,000 Miles

	Vehicle Type	Emission Category	Vehicle Useful Life						
			5 Years / 50,000 Miles						
			THC[a, b, c] (g/mi)	NMHC[d](g/mi)	NMOG (g/mi)	CO[c, e]	NOx (g/mi)	PM[f](g/mi)	HCHO (g/mi)
Federal	LDV[h, i, j]	Tier 0	0.41	0.34[l]	-	3.4	1	0.20[n]	-
		Tier 1	0.41[k]	0.25	-	3.4	0.4[m]	0.08	-
	LDT1[h, i, j]	Tier 0[p]	-	-	-	-	-	-	-
		Tier 1	-	0.25	-	3.4	0.4[m]	0.08	-
	LDT2[h, i, j]	Tier 0[p]	-	-	-	-	-	-	-
		Tier 1	-	0.32	-	4.4	0.7[q]	0.08	-
Federal NLEV	LDV[i, r, s]	TLEV	0.41[k]	-	0.125[u, v]	3.4	0.4[w]	0.08	0.015
		LEV[t]	0.41[k]	-	0.075[u, v]	3.4	0.2[w]	0.08	0.015
		ULEV[t]	0.41[k]	-	0.040[u, v]	1.7	0.2[w]	0.08	0.008
		ZEV[t]	0	0	0	0	0.0[w]	0	0
	LDT1[i, r, s]	TLEV	-	-	0.125[u, v]	3.4	0.4[w]	0.08	0.015
		LEV[t]	-	-	0.075[u, v]	3.4	0.2[w]	0.08	0.015
		ULEV[t]	-	-	0.040[u, v]	1.7	0.2[w]	0.08	0.008
		ZEV[t]	0	0	0	0	0.0[w]	0	0
	LDT2[i, r, s]	TLEV	-	-	0.160[u, v]	4.4	0.7[w]	0.08	0.018
		LEV[t]	-	-	0.100[u, v]	4.4	0.4[w]	0.08	0.018
		ULEV[t]	-	-	0.050[u, v]	2.2	0.4[w]	0.08	0.009
		ZEV[t]	0	0	0	0	0.0[w]	0	0
Federal CFV	LDV[h, i, s]	LEV	0.41[k]	-	0.075[z]	3.4	0.2[w]	-	0.015
		ILEV[y]	0.41[k]	-	0.075	3.4	0.2[w]	-	0.015
		ULEV	0.41[k]	-	0.040[z]	1.7	0.2[w]	-	0.015
		ZEV[t]	0	0	0	0	0.0[w]	0	0
	LDT1[h, i, s]	LEV	-	-	0.075[z]	3.4	0.2[w]	-	0.015
		ILEV[y]	-	-	0.075	3.4	0.2[w]	-	0.015
		ULEV	-	-	0.040[z]	1.7	0.2[w]	-	0.008
		ZEV[t]	0	0	0	0	0.0[w]	0	0
	LDT2[h, i, s]	LEV	-	-	0.100[z]	4.4	0.4[w]	-	0.018
		ILEV[y]	-	-	0.1	4.4	0.4[w]	-	0.018
		ULEV	-	-	0.050[z]	2.2	0.4[w]	-	0.009
		ZEV[t]	0	0	0	0	0.0[w]	0	0

(U.S. Environmental Protection Agency, 2014)

Table A.2 Light-Duty Vehicle and Truck Emissions Standards, 100,000 Miles

		Emission Category	Vehicle Useful Life						
			10 Years / 100,000 Miles						
	Vehicle Type		THC[a, b, c] (g/mi)	NMHC[d](g/mi)	NMOG (g/mi)	CO[c, e]	NOx (g/mi)	PM[f](g/mi)	HCHO (g/mi)
Federal	LDV[h, i, j]	Tier 0	-	-	-	-	-	-	-
		Tier 1	-	0.31	-	4.2	0.6[o]	0.1	-
	LDT1[h, i, j]	Tier 0[p]	0.8	0.67[l]	-	10	1.2	0.26[n]	-
		Tier 1	0.80[k, p]	0.31	-	4.2	0.6[o]	0.1	-
	LDT2[h, i, j]	Tier 0[p]	0.8	0.67[l]	-	10	1.7	0.13[n]	-
		Tier 1	0.80[k, p]	0.4	-	5.5	0.97	0.1	-
Federal NLEV	LDV[i, r, s]	TLEV	-	-	0.156[u, v]	4.2	0.6[w]	0.08[x]	0.018
		LEV[t]	-	-	0.090[u, v]	4.2	0.3[w]	0.08[x]	0.018
		ULEV[t]	-	-	0.055[u, v]	2.1	0.3[w]	0.04[x]	0.011
		ZEV[t]	0	0	0	0	0.0[w]	0	0
	LDT1[i, r, s]	TLEV	0.80[k, p]	-	0.156[u, v]	4.2	0.6[w]	0.08[x]	0.018
		LEV[t]	0.80[k, p]	-	0.090[u, v]	4.2	0.3[w]	0.08[x]	0.018
		ULEV[t]	0.80[k, p]	-	0.055[u, v]	2.1	0.3[w]	0.04[x]	0.011
		ZEV[t]	0	0	0	0	0.0[w]	0	0
	LDT2[i, r, s]	TLEV	0.80[k, p]	-	0.200[u, v]	5.5	0.9[w]	0.10[x]	0.023
		LEV[t]	0.80[k, p]	-	0.130[u, v]	5.5	0.5[w]	0.10[x]	0.023
		ULEV[t]	0.80[k, p]	-	0.070[u, v]	2.8	0.5[w]	0.05[x]	0.013
		ZEV[t]	0	0	0	0	0.0[w]	0	0
Federal CFV	LDV[h, i, s]	LEV	-	-	0.090[z]	4.2	0.3[w]	0.08[aa]	0.018
		ILEV[y]	-	-	0.09	4.2	0.3[w]	0.08[aa]	0.018
		ULEV	-	-	0.055[z]	2.1	0.3[w]	0.04[aa]	0.011
		ZEV[t]	0	0	0	0	0.0[w]	0	0
	LDT1[h, i, s]	LEV	0.80[k,p]	-	0.090[z]	4.2	0.3[w]	0.08[aa]	0.018
		ILEV[y]	0.80[k,p]	-	0.09	4.2	0.3[w]	0.08[aa]	0.018
		ULEV	0.80[k,p]	-	0.055[z]	2.1	0.3[w]	0.04[aa]	0.011
		ZEV[t]	0	0	0	0	0.0[w]	0	0
	LDT2[h, i, s]	LEV	0.80[k,p]	-	0.130[z]	5.5	0.5[w]	0.08[aa]	0.023
		ILEV[y]	0.80[k,p]	-	0.13	5.5	0.5[w]	0.08[aa]	0.023
		ULEV	0.80[k,p]	-	0.070[z]	2.8	0.5[w]	0.04[aa]	0.013
		ZEV[t]	0	0	0	0	0.0[w]	0	0

(U.S. Environmental Protection Agency, 2014)

Notes:

Tests Covered:	Federal Test Procedure (FTP), cold carbon monoxide (CO), highway, and idle
Effective Model Year:	1981 - 1993, Tier 0
	1994 - 1999, Tier 1
	1999 - 2003, NLEV
	1999 - Present, CFV

a Total hydrocarbon equivalent (THCE) for methanol vehicles.

b Does not apply to compressed natural gas (CNG) vehicles.

c Certification short test emissions from gasoline vehicles shall not exceed 100 parts per million (ppm) HC or 0.5 percent exhaust gas CO at idle and 2500 revolutions per minute (rpm) at 4,000 miles; compliance statement allowed in lieu of data.

d THCE for Tier 0 methanol vehicles, non-methane hydrocarbon equivalent (NMHCE) for other alcohol vehicles.

e Cold CO emissions for gasoline fueled vehicles shall not exceed 10.0 grams per mile (g/mi) for light-duty vehicles (LDV) and light-duty trucks 1 [LDT1], or 12.5 g/mi for LDT2, LDT3, & LDT4 at 50,000 miles.

f Particulates compliance statement allowed for non-diesel cycle vehicles (in lieu of supplying acutal test data).

g Idle CO emissions from gasoline, methanol, CNG, and liquified petroleum gas trucks shall not exceed 0.50 percent exhaust gas at 120,000 miles or 11 years; compliance statement allowed in lieu of actual test data.

h Federal On-board diagnostics (OBD) system required beginning with 1994 model year vehicles.

i Tier 1, NLEV & CFV vehicles must meet Tier 1 emission standards at high altitude; Tier 0 vehicles must meet special high altitude standards; compliance statement allowed in lieu of actual test data.

j Tier 0 and Tier 1 emission standards do not apply to ethanol vehicles.

k Total hydrocarbon (THC); compliance statement allowed in lieu of acutal test data.

l CNG vehicles only.

m 1.0 for diesel-fueled vehicles through 2003 model year.

n Diesel-fueled vehicles only.

o 1.25 for diesel-fueled vehicles through 2003 model year.

p Standards apply at a useful life of 11 years or 120,000 miles.

q Does not apply to diesel-fueled vehicles.

r California OBD-II system required.

s NLEV and CFV (LDV, LDT1, LDT2) vehicles must meet special 50 degrees Fahrenheit emission standards at 4,000 miles (not applicable to diesel, CNG, or hybride electric vehicles).

t Special interim in-use emission standards apply to 1999 Low Emission Vehicles (LEV) and 1999-2002 Ultra-Low Emission Vehicles (ULEV).

u Non-methane hydrocarbon (NMHC) for diesel cycle vehicles.

v Dual and flexible fuel vehicles may meet less stringent non-methane organic gas (NMOG) standard when operating on gasoline.

w Highway nitrogen oxides (NOx) emissions shall not exceed 1.33 times the applicable FTP (city) NOx standards.

x 0.10 g/mi particulate matter (PM) standard applies to non-diesel vehicles.

y Special evaporative requirements apply (5.0 grams maximum with the evaporative system disconnected).

z Special NMOG standards apply to dual and flexible fuel vehicles.

aa Diesel-fueled vehicles only.

Appendix B. Normalized Emissions

Figure B.1 displays normalized NOx emissions with vehicles running on ethanol blends from E0 to E85. No clear trend in emissions as a function of ethanol content was observed in these data.

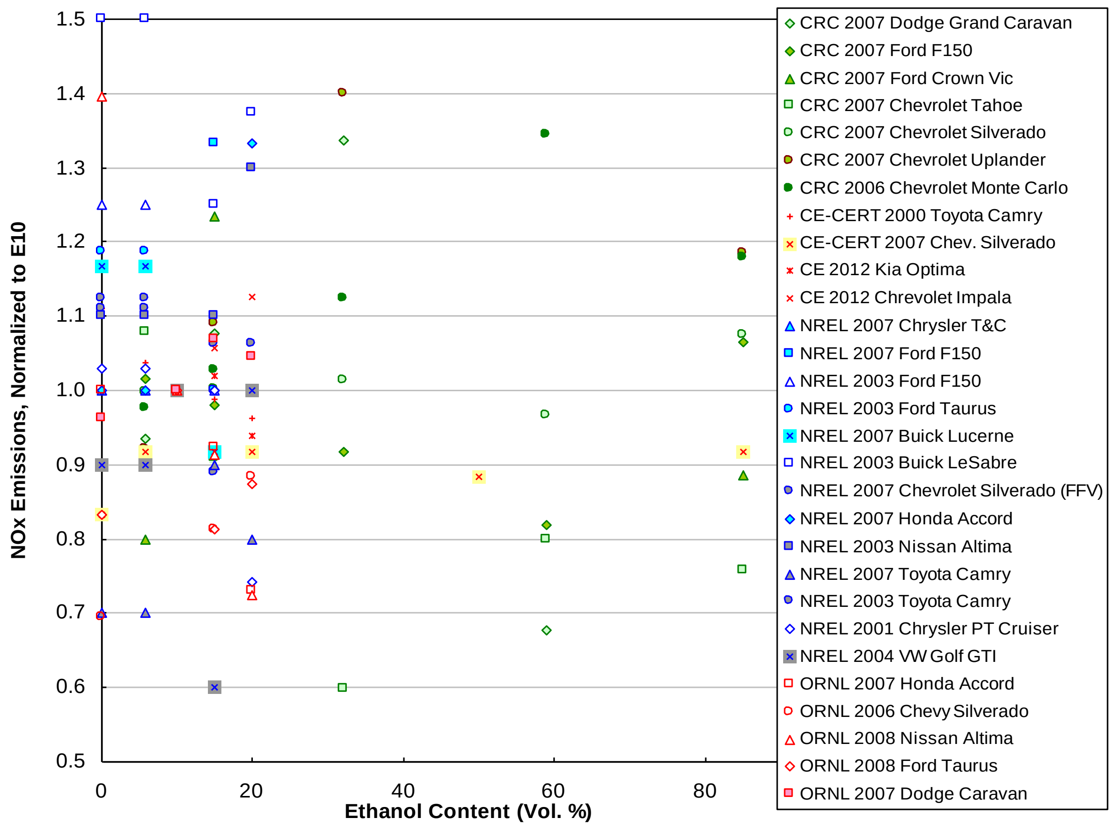


Figure B.1 Normalized NOx emissions as a function of ethanol content

Figure B.2 shows normalized CO emissions from all vehicles running on ethanol blends ranging from E0 to E85. No trend is observed in the normalized data as a function of ethanol content.

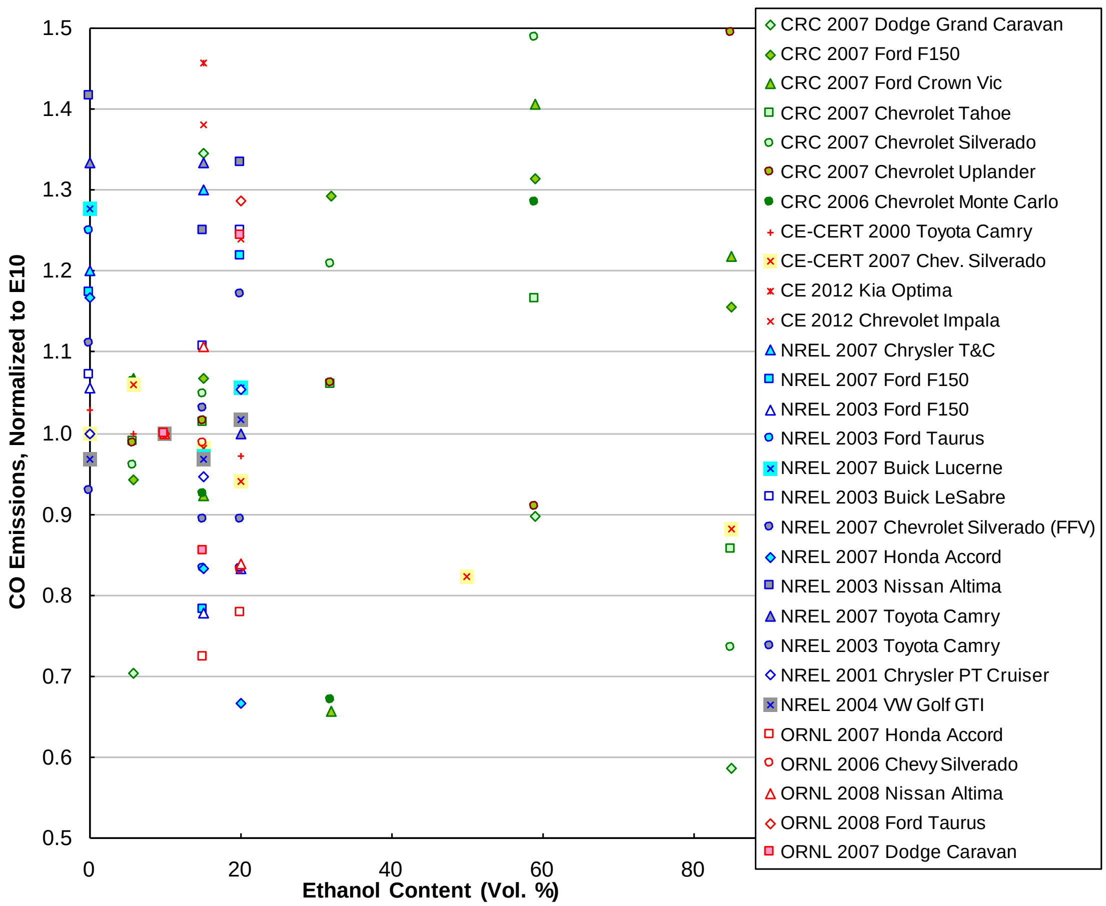


Figure B.2 Normalized CO emissions as a function of ethanol content

Figure B.3 shows normalized NMHC emissions from all vehicles running on ethanol blends ranging from E0 to E85. Unlike the absolute emissions of NMHC over time, no trend is observed in the normalized data as a function of ethanol content.

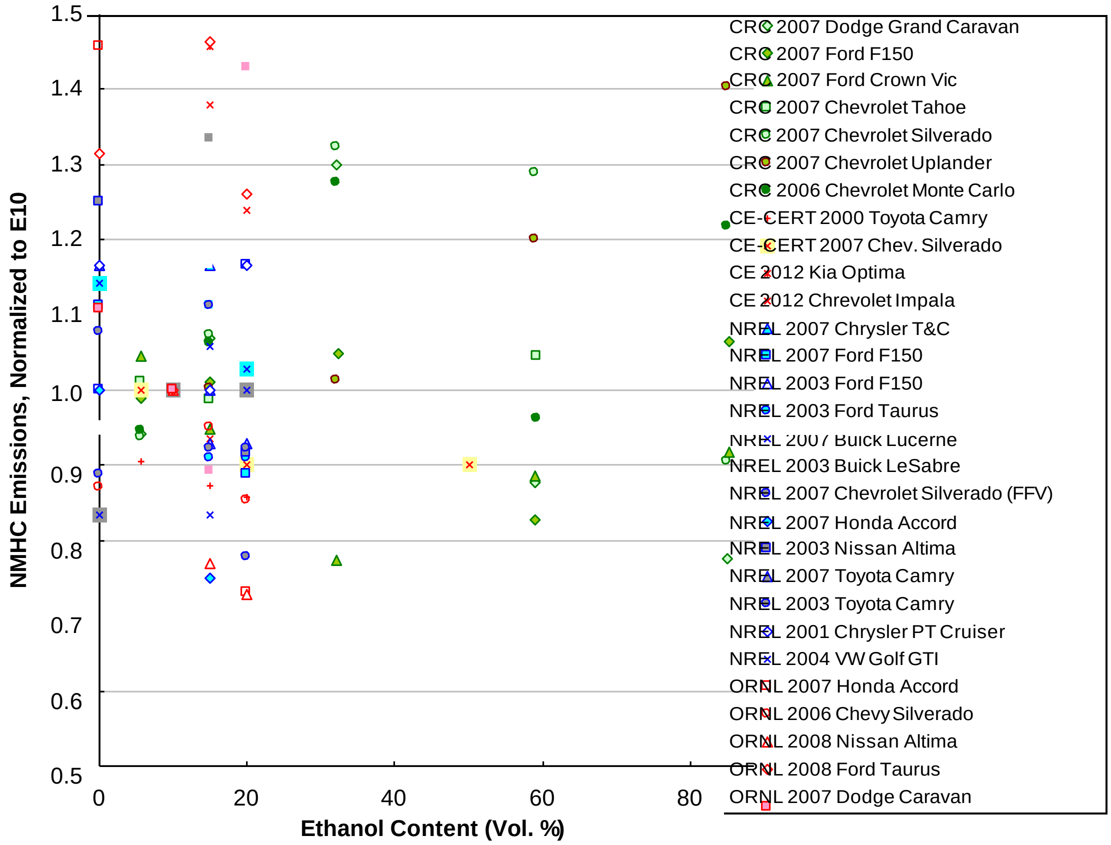


Figure B.3 Normalized NMHC emissions as a function of ethanol content

Appendix C. Uncertainty Analysis

The following charts were generated by a Monte Carlo analysis performed in the Crystal Ball software. The blue bars indicate probability area under which emissions will reduce with a change from E10 to E15. The central number on the x-axis indicates the mean of the points on the graph.

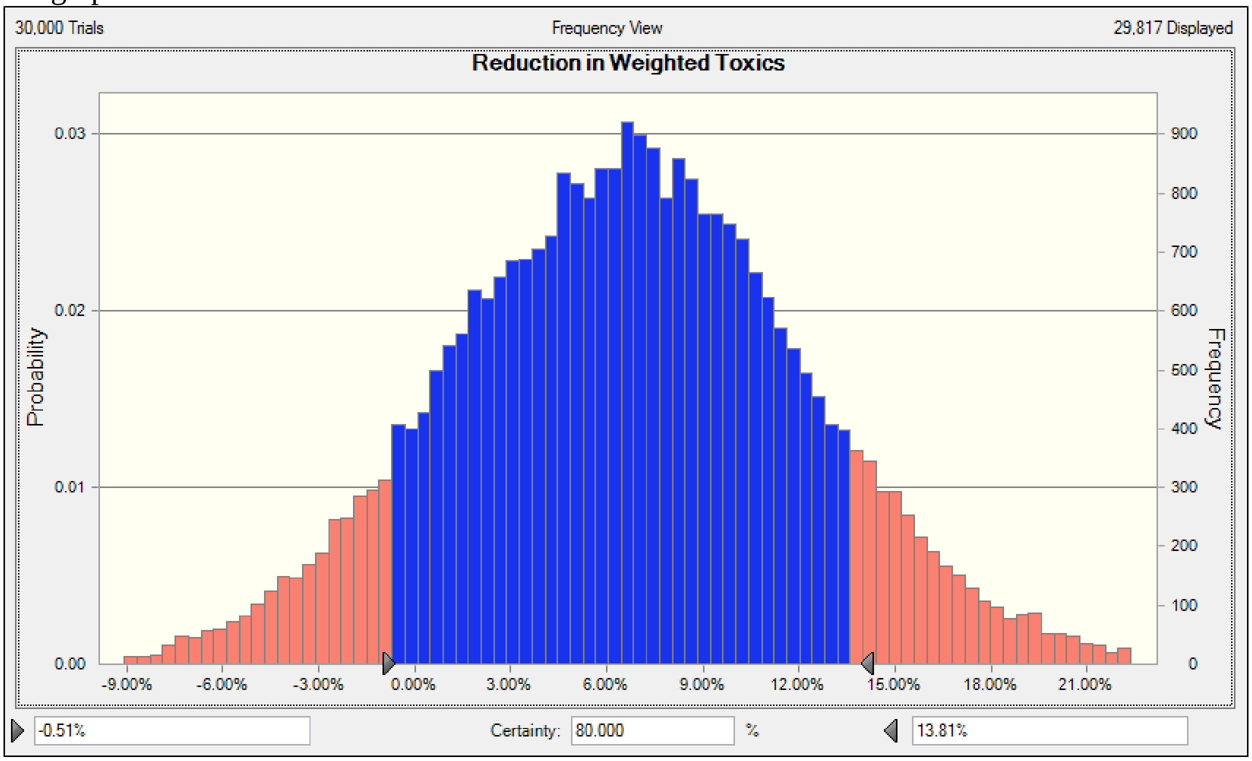


Figure C.1. Monte Carlo Simulation of Change in Weighted Toxics

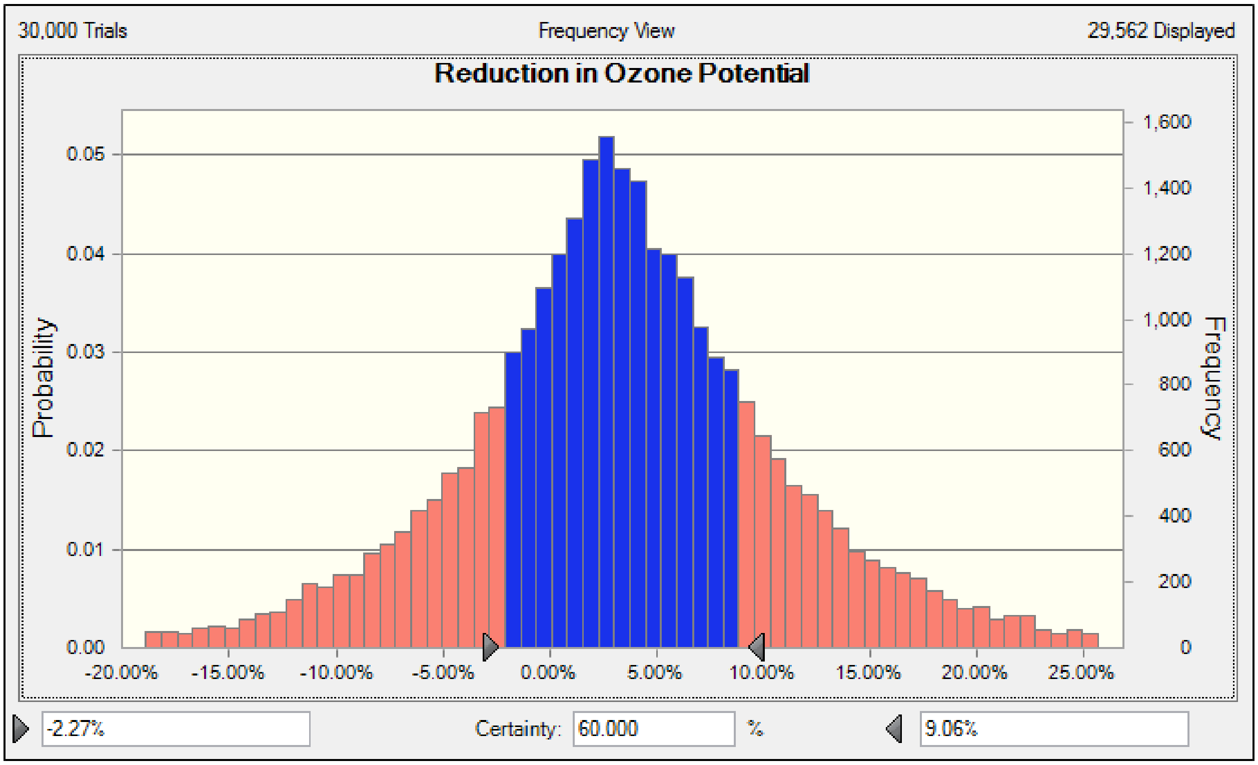


Figure C.2. Monte Carlo Simulation of Change in Ozone Potential

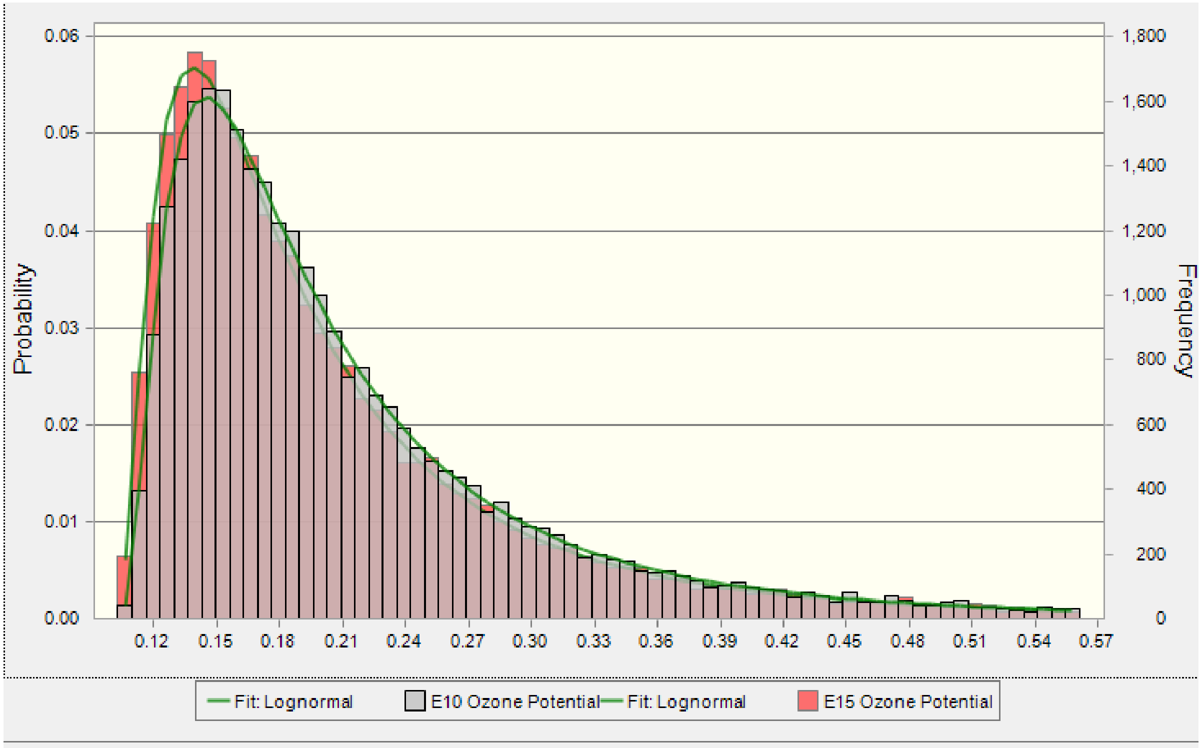


Figure C.3 Ozone Potential Overlay Comparison E15/E10

References

Alternative Fuels Data Center. (2014). *Ethanol Fuel Basics*. *afdc.energy.gov/*. Retrieved June 06, 2014, from http://www.afdc.energy.gov/fuels/ethanol_fuel_basics.html

Anderson, J. E., DiCicco, D. M., Ginder, J. M., Kramer, U., & Al, E. (2012). High octane number ethanol-gasoline blends: Quantifying the potential benefits in the United States. *Fuel*, *97*, 585–594.

Argonne National Laboratory. (2013). VISION 2013 AEO Base Case.

Auto/Oil. (1993). *Air quality improvement research program, Technical Bulletin No. 12*.

Bioethanol for Sustainable Transport. (2008). *Review of fuel ethanol impacts on local air quality*. London.

Boland, S., & Unnasch, S. (2014). *Carbon Intensity of Marginal Petroleum and Corn Ethanol Fuels. Life Cycle Associates Report LCA.6075.83.2014, Prepared for Renewable Fuels Association.*

Bonnema, G., Jones, B., & Ready, K. L. (1999). *Use of mid-range ethanol/gasoline blends in unmodified passenger cars and light duty trucks*.

Budroe, J., Brown, J., Collins, J., & et al. (2009). *Technical Support Document for Cancer Potency Factors*.

Carter, W. P. L. (1994). Development of ozone reactivity scales for volatile organic compounds. *Journal of the Air & Waste Management Association*, *44*, 881–899.

Carter, W. P. L. (2009). *Updated maximum incremental reactivity scale and hydrocarbon bin reactivity for regulatory applications*.

Curtis, S., Owen, M., Hess, T., & Egan, S. (2008). *Effect of Ethanol Blends on a Spark Ignition , 4-Stroke , Internal Combustion Engine By*. Provo, UT.

DOE: Office of Energy Efficiency and Renewable Energy. (2013). *Handbook for Handling , Storing , and Dispensing E85 and Other Ethanol-Gasoline Blends*. doi:DOE/GO-102013-3861

Environmental Protection Agency. (2010). Partial Grant and Partial Denial of Clean Air Act Waiver Application Submitted by Growth Energy To Increase the Allowable Ethanol Content of Gasoline to 15 Percent. *Code of Federal Register (CFR)*, *75*(13). doi:EPA–HQ–OAR–2009–0211

Environmental Protection Agency. (2011). Regulation To Mitigate the Misfueling of Vehicles and Engines With Gasoline Containing Greater Than Ten Volume Percent Ethanol and Modifications to the Reformulated and Conventional Gasoline Programs; Final Rule. *Code of Federal Register (CFR)*, *76*(142). Retrieved from http://www.gpo.gov/fdsys/pkg/FR-2011-07-25/pdf/2011-16459.pdf

Fang, J., Powders, M., & Aabakken, J. (2002). *Issues Associated with the Use of Higher Ethanol Blends*.

Guerrieri, D., Caffrey, P., & Rao, V. (1995). Investigation into the Vehicle Exhaust Emissions of High Percentage Ethanol Blends. *SAE Technical Paper*, *950777*.

Haskew, H., & Liberty, T. (2011). *CRC Report E80: Exhaust and evaporative emissions testing of flexible-fuel vehicles study*. doi:CRC Report No . E-80

He, X., Ireland, J. C., Ratcliff, M. A., & Knoll, K. E. (2011). Impacts of mid-level biofuel content in gasoline on SIDI engine-out and tailpipe particulate matter emissions.

International Energy Agency. (2004). *Biofuels for Transport: An International Perspective*.

Karavalakis, G., Durbin, T. D., Shrivastava, M., Zheng, Z., Villela, M., & Jung, H. (2012). Impacts of ethanol fuel level on emissions of regulated and unregulated pollutants from a fleet of gasoline light-duty vehicles. *Fuel*, *93*, 549–558. doi:10.1016/j.fuel.2011.09.021

Karavalakis, G., Short, D., Vu, D., Villela, M., Russell, R., Jung, H., … Durbin, T. (2014). Regulated Emissions, Air Toxics, and Particle Emissions from SI-DI Light-Duty Vehicles Operating on Different Iso-Butanol and Ethanol Blends. *SAE International Journal of Fuels and Lubricants*, *7*(1). doi:10.4271/2014-01-1451

Knoll, K., West, B., Clark, W., Graves, R., Orban, J., Przesmitzki, S., & Theiss, T. (2009). *Effects of Intermediate Ethanol Blends on Legacy Vehicles and Small Non-Road Engines , Report 1 – Updated Prepared by*.

Magara-Gomez, K. T., Olson, M. R., McGinnis, J. E., Zhang, M., & Schauer, J. J. (2014). Effect of Ambient Temperature and Fuel on Particle Number Emissions on Light-Duty Spark-Ignition Vehicles. *Aerosol and Air Quality Research*, *14*(5), 1360–1371.

Martini, G., Manfredi, U., Krasenbrink, A., Stradling, R., Zemroch, P. J., Rose, K. D., … Maas, H. (2013). *Effect of oxygenates in gasoline on fuel consumption and emissions in three Euro 4 passenger cars*. doi:10.2790/1136

MathPro Inc. (2012). *Analysis of the refining costs and associated economic effects of producing 92 AKI gasoline in the U.S. refining sector*.

McCormick, R. L., & Yanowitz, J. (2013). *Discussion Document – Effect of Ethanol Blending on Gasoline RVP. Prepared by National Renewable Energy Laboratory and Ecoengineering, Inc.*

Rose, K. D. (2009). Ethanol / Petrol Blends : Volatility Characterisation in the Range 5-25 vol % Ethanol Final Report, *698*.

Salmon, A. (2008). *Risk Assessment Guidelines For the Derivation of Noncancer Reference Exposure Levels*.

Storey, J. M., Barone, T., Norman, K., & Lewis, S. (2010). Ethanol Blend Effects On Direct Injection Spark-Ignition Gasoline Vehicle Particulate Matter Emissions, 1–18. doi:10.4271/2010-01-2129

U.S. Department of Agriculture. (2007). *U.S. Ethanol Transportation Backgrounder: Expansion of U.S. Corn-based Ethanol from the Agricultural Transportation Perspective*. *ams.usda.gov*. Retrieved June 30, 2014, from http://www.ams.usda.gov/AMSv1.0/getfile?dDocName=STELPRDC5063605&acct=atpub

U.S. Energy Information Administration. (2011). *EIA Annual Energy Revue*. *eia.gov*. Retrieved June 30, 2014, from http://www.eia.gov/totalenergy/data/annual/index.cfm

U.S. Environmental Protection Agency. (n.d.-a). *Nitrogen Dioxide, Health*. *epa.gov*. Retrieved June 06, 2014, from http://www.epa.gov/airquality/nitrogenoxides/health.html

U.S. Environmental Protection Agency. (n.d.-b). *Volatile Organic Compunds, Technical Overview*. *epa.gov*. Retrieved June 26, 2014, from http://www.epa.gov/iaq/voc2.html#definition

U.S. Environmental Protection Agency. (2014). *Light-Duty Vehicle and Light-Duty Truck -- Tier 0, Tier 1, National Low Emission Vehicle (NLEV), and Clean Fuel Vehicle (CFV) Exhaust Emission Standards*. *epa.gov*. Retrieved July 11, 2014, from http://www.epa.gov/otaq/standards/light-duty/tiers0-1-ldstds.htm

Unnasch, S., Browning, L., & Kassoy, E. (2001). *Refinement of Selected Fuel-Cycle Emissions Analyses*. Sacramento, California. doi:Final Report to the California Air Resources Board under Contract No. 98-338

Unnasch, S., Huey, S., & Browning, L. (1996). *Evaluation of Fuel Cycle Emissions on a Reactivity Basis. Prepared for ARB under Contract A166-134*.

US Environmental Protection Agency. (2012). *Development of Evaporative Emissions Calculations for the Motor Vehicle Emissions Simulator MOVES2010 Final Report*.

US Environmental Protection Agency. (2014). *Integrated Risk Information Assessment*. *cfpub.epa.gov*.

West, B. H., Sluder, C. S., Knoll, K. E., Orban, J. E., & Feng, J. (2012). *Intermediate Ethanol Blends Catalyst Durability Program*. Oak Ridge National Laboratory, Department of Energy.