California Multimedia Evaluation of E11 - E15 Gasoline-Ethanol Blends
Tier I Report

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RENEWABLE FUELS ASSOCIATION

growth energy™
America's Ethanol Supporters

Executive Summary

The California Health and Safety Code (CHSC) requires that a multimedia evaluation be conducted and reviewed by the California Environmental Policy Council (CEPC) before specifications for new motor fuels can be adopted by the California Air Resources Board.[1] The purpose of the multimedia evaluation is to enable CEPC to determine whether a new fuel would create any significant new environmental or public health impacts.

In 1999, the State of California performed a multimedia evaluation regarding the use of ethanol in gasoline and approved the use of blends of up to ten percent ethanol in gasoline (E10). Today, virtually all gasoline sold in California is E10. In addition, based on action taken by the California Air Resources Board in 1992, eighty-five percent ethanol blends (E85) can be sold in California. Given that gasoline-ethanol blends have a long history of being used successfully in California and that ethanol is a renewable fuel with low carbon intensity, increasing the content of ethanol in blends with gasoline is one way in which California can make progress towards achieving its goals regarding greenhouse gas emissions. In addition, increased use of ethanol in blends with gasoline has a number of other potential benefits, including reduced dependence on petroleum.

At present, the most practical short-term approach to increasing ethanol use in California would be to approve the use of gasoline-ethanol blends above E10 up to 15 percent ethanol (E15). E15 has been approved at the federal level. U.S. EPA issued a waiver in 2010 approving the use of E15 in 2007 model year and newer light-duty vehicles.[2] In 2011, U.S. EPA issued a second waiver extending the approval to 2001 model year and newer light-duty vehicles.[3,4]

In light of the above, Growth Energy and the Renewable Fuels Association (RFA)[5] have undertaken a multimedia evaluation for E15 gasoline-ethanol blends based on the addition of denatured fuel ethanol with California Reformulated Gasoline Blendstocks for Oxygenate Blending (CARBOBs) that are approved for use in producing E10 blends under the California Reformulated Gasoline Regulations for Model Year 2001 and newer California vehicles. This is intended to be the Tier 1 Report for those fuels.

This report summarizes the evidence for the following conclusions:

- Ethanol can be produced from a variety of feedstocks using well-established commercial procedures. Although additional capacity to produce ethanol may be needed to supply the additional ethanol required for E15 in California, that capacity is expected to use the same processes that have already been approved by California and that are already being used to supply the existing California market. Thus, to the extent any currently-approved processes are used, such processes would not create environmental or health impacts that are not already known. Increased use of ethanol in the fuel pool would have the added benefit of reducing demand for petroleum-derived CARBOB. Ethanol production is highly regulated on the Federal and State levels. The Federal Renewable Fuel Standard provides environmental safeguards by defining renewable biomass as planted crops and crop residue harvested from existing agricultural land cleared or cultivated prior to December 19, 2007 and that was non-forested and either actively managed or fallow on December 19, 2007.

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[1] HSC Section 43830.8

[2] 75 Federal Register 68094. November 4, 2010.

[3] 76 Federal Register 4662. January 26, 2011.

[4] These waivers all E15 use in all model years of FFVs and expressly prohibit the use of E15 in heavy-duty vehicles, motorcycles and non-road applications.

[5] Growth Energy, with headquarters at 701 8th St NW, Suite 450, Washington, DC 20001, is a trade association representing the operators of more than 90 U.S. ethanol biorefineries. http://GrowthEnergy.org. RFA is headquartered at 16024 Manchester Rd, Suite 101, Ellisville, MO 63011, and is an ethanol trade association comprised of more than 45 individual ethanol companies, in addition to feedstock and supply chain partners. https://ethanolrfa.org

- E11 – E15 gasoline-ethanol blends must be stored, transferred and dispensed from equipment appropriate for these fuels. However, that equipment is currently readily available in California. Listing by Underwriters Laboratories (UL), which tests for compatibility, is available for all the different kinds of fuel-handling equipment necessary for storage, dispensing and transport of fuels except for certain California-specific vapor recovery equipment. A process for review and approval of such equipment can be developed to assure E15 is stored and distributed in a safe and compliant manner.

- Testing of California specific vapor recovery equipment with E11 – E15 fuels may be necessary to ensure an adequate range of approved equipment for higher ethanol blends.

- Current California regulations restrict the availability of E11-E15 blending at retail sites using blender pumps because of concerns about the resulting ethanol-fuel blends meeting California quality requirements, in particular if the E85 blendstock contains natural gasoline rather than CARBOB. Currently there are no fuel quality standards for E11-E15 blends made by using E85 and E10 blendstocks and blended at retail sites with blender pumps. This Tier 1 report therefore contemplates E11-E15 blending only using currently-approved processes at terminal sites with CARBOB blendstock. Additional regulatory changes may be needed to accommodate E11-E15 blending other than at terminal sites.

- The existing California UST database shows that a significant percentage of tanks are already compatible for use with E11 - E15 fuel-ethanol blends, and the vast majority of tanks built, UL-certified, and installed in 1989 or later in California are compatible with E11-E15 storage. Facilities with older equipment that is not UL listed for higher concentration ethanol fuels will need to upgrade to handle E11 – E15 fuels.

- Fire safety requirements for fuel-handling equipment that would be applicable to gasoline-ethanol blends in the E11 – E15 range are already included in the 2016 California Fire Codes for alcohol-blended fuels. Alcohol-resistant aqueous film-forming foam (AR-AFFF) is recognized as the most effective method for controlling ethanol-blended fuel fires, whether the fuel is E10 or in the E11 – E15 range.

- The existing emissions data suggest that use of gasoline blends up to E15, as allowed by U.S. EPA in existing 2001 and later model-year vehicles and FFVs, will not result in any increase in vehicle exhaust emissions of organic compounds or their ozone-forming potential, oxides of nitrogen, carbon monoxide, particulate matter, or cancer potency-weighted toxic air contaminants relative to E10. However, as the testing did not compare E15 results to California Phase 3 RFG E10 fuels additional exhaust emissions testing will be needed to ensure that splash blending of additional ethanol (up to E15) in fuels permitted in California will not adversely affect air quality. The Tier II test plan will be designed to evaluate potential exhaust emissions impacts from the use of splash blended E15 compared to E10 (using the same CARBOB).

- E15 is expected to have a slightly lower vapor pressure than E10. Existing research strongly supports that evaporative emissions will not increase with the use of E15 compared to E10, however literature lacks evaporative emissions data comparing E15 to California gasoline.

- The increased use of ethanol in fuel will likely lead to a proportional increase in the quantity of ethanol released to the environment, with a roughly equivalent decline in the amount of petroleum released. Ethanol is readily biodegraded. Thus, the most significant pollutants in surface and subsurface releases of gasoline-ethanol blends are benzene, toluene, ethylbenzene, and xylene (BTEX) all of which are from the petroleum fraction. Although higher concentration ethanol blends will lead to smaller amounts of BTEX released, ethanol will increase the solubility of these compounds in water, and via ethanol competition for electron acceptors, reduce the rate of biodegradation of BTEX.

- Modeling efforts by Gomez and Alvarez (2009) to evaluate the effect of ethanol content in different blended fuel releases on the lifespan and maximum length of benzene plumes suggest that ethanol has a significant elongation effect on benzene plume lengths relative to a baseline regular gasoline spill. The elongation effect is most pronounced for E10–E20 blends. However, the modeled difference in benzene plume elongation relative to baseline between E10 and E20 (and thus E10 and E15) appears to be a fraction of a percent. The benzene plume life span (time until plume is degraded below MCL) decreases almost linearly as ethanol content in the blend increases. Therefore, the natural attenuation time for an E15 release is expected to be less than a similar volume release of E10.

- Due to the increased microbial activity associated with ethanol releases and degradation, there is the potential for higher concentrations of ethanol to generate significant quantities of methane. Should methane ebullition and flux be significant enough to create advective flow, explosion risks to subsurface receptors may be an issue. Additional monitoring of the methane in soil or groundwater can be addressed with existing procedures and tools.

- As with E10, E15 would have the potential to be released into the environment affecting land, groundwater, surface water, and from there into drinking water supplies, and allowing receptors to be exposed via ingestion, dermal exposure and inhalation. Such releases have the potential to impact drinking water supplies such as surface water and groundwater. E15 provides potential for inhalation exposures to exhaust and evaporative emissions, and to soil vapors entering indoor air. Other human and ecological risks associated with E15 blends would not be significantly different than those present from the widespread use of E10.

- The use of gasoline-ethanol blends of up to E15 in all vehicles for which U.S. EPA has approved its use would at worst result in very small increases in upstream emissions of air pollutants relative to the current widespread use of E10. However, overall, reductions in emissions would be reduced in response to reduced refinery operations resulting from lower demand for CARBOB. In addition, both overall GHG emissions and GHG emissions occurring in California would be reduced relative to use of E10.

Existing data shows that E15 will provide a reduction in greenhouse gas emissions relative to E10 and the additional ethanol from E15 further reduces the use of fossil fuels. Many other factors, including environmental and human exposure risks, are approximately equal for E10 and E15. This Tier I study shows to complete the multimedia evaluation that additional research is warranted for further study of exhaust and evaporative emissions on California vehicles using California RFG E10 gasoline to splash blend E15 in Model Year 2001 and newer California vehicles. During the Tier II, there will be an assessment of other identified data gaps to determine whether additional testing is warranted.

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1 Introduction

1.1 Scope and Purpose

The California Health and Safety Code (CHSC) requires that a multimedia evaluation be conducted and reviewed by the California Environmental Policy Council (CEPC) before specifications for new motor fuels can be adopted by the California Air Resources Board.[6] The purpose of the multimedia evaluation is to enable CEPC to determine whether the proposed fuel specification presents any significant new environmental or public health impacts.

The CHSC multimedia evaluation process involves three tiers. Tier I is a summary of what is known about the new fuel and the identification of any knowledge gaps that would preclude the completion of the multimedia evaluation based on the currently available data and information. Tier II is focused on the development of additional information required to complete the multimedia evaluation. Tier III is a risk assessment that identifies any potentially significant adverse impacts on the environment or public health.

Utilizing this process, CEPC, in 2000, approved the use of blends of up to 10 percent by volume of denatured fuel grade ethanol (DFE) in California Reformulated Gasoline (E10).[7,8] Such blends currently constitute substantially all the gasoline sold for use in light-duty vehicles in California. Additionally, it should be noted that in April 1992, prior to the adoption of the CHSC provisions requiring multimedia evaluations, the California Air Resources Board (CARB) adopted commercial fuel specifications for nominal 85 percent blends of ethanol and gasoline (E85). In fact, E85 has been sold in California since the 1990s.[9]

Given that ethanol is a renewable fuel with low carbon intensity, increased use of ethanol is one way in which California can make progress towards achieving its goals regarding climate change. In addition, increased use of ethanol has a number of other potential benefits, including reduced dependence on petroleum. The most effective way to begin to realize the benefits of expanded use of ethanol in California would be for CARB to adopt fuel specifications allowing gasoline-ethanol blends above E10 and up to E15 for Model Year 2001 and newer California vehicles. Given that the main purpose of this multimedia evaluation is to assess whether blends up to E15 would create any significant new environmental or public health impacts, it should be noted at the outset that blends of up to E15 have already been approved at the federal level. U.S. EPA issued a waiver in 2010 approving the use of E15 in 2007 model year and newer light-duty vehicles.[10] In 2011, U.S. EPA issued a second waiver extending the approval to 2001 model year and newer light-duty vehicles.[11,12]

In performing the multimedia evaluation of E15 gasoline-ethanol blends, the potential for environmental and public health impacts in the following areas were addressed:

- Ethanol production, basic properties, and fuel specifications;
- Storage and distribution of E15 gasoline-ethanol blends;
- Use of gasoline-ethanol blends of up to E15 in 2001 MY and later vehicles;

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[6] HSC Section 43830.8

[7] Transcripts of the California Environmental Policy Hearing, Meeting to Consider Staff Reports on the Environmental Fate and Transport and Potential Health Effects of Using Ethanol in California Reformulated Gasoline. January 18, 2000. https://www.arb.ca.gov/fuels/gasoline/Meeting/2000/0118Trns.doc

[8] California RFG meeting the requirements of this approval is produced as a blend of CARBOB with 10 percent by volume of denatured fuel grade ethanol. CARBOB is defined in the California Code of Regulations at 13 CCR 2266.5 and is unique from Federal Reformulated Blendstock for Oxygenate Blending (RBOB), defined at 40 CFR 80 Subparts D and E.

[9] https://www.arb.ca.gov/fuels/multimedia/meetings/ethanolelevatedfuelblends_tier%20iii_mar2016.pdf

[10] 75 Federal Register 68094. November 4, 2010.

[11] 76 Federal Register 4662. January 26, 2011.

[12] These waivers allow E15 use in all model years of FFVs and expressly prohibit the use of E15 in heavy-duty vehicles, motorcycles and non-road applications.

- Release scenarios for E15 gasoline-ethanol blends;
- Environmental fate and transport;
- Human and ecological risks; and
- Lifecycle impacts associated with E15 gasoline-ethanol blends.

In all areas, insofar as possible, the multimedia evaluation was predicated on the with assumption that the gasoline component of E15 blends would be California Reformulated Gasoline Blendstock for Oxygenate Blending (CARBOB) that complies with the requirements of the California Reformulated Gasoline regulations, and the appropriate reference fuel is E10 that complies with those same regulations. The proposed use of E15 would be used only in terminal blending, with Model Year 2001 and newer California vehicles, and utilize only underground storage tanks with listed compatibility.

For emissions testing and comparisons, the candidate fuels and reference fuel would necessarily be blended with the same CARBOB. Vehicles to be used in emissions testing and comparisons will be certified to the California emissions standard applicable to their model year.

1.2 History of Gasoline-Ethanol Blends as Vehicle Fuels

Historical use of ethanol as a fuel for spark-ignited engines dates to the Model T Ford originally produced in 1909. This usage diminished with improving cost and availability of petroleum-based gasoline. More modern use of gasoline-ethanol blends for light-duty vehicles in the U.S. dates to the oil price shocks of the 1970s where blends of 10 percent by volume of denatured fuel ethanol (often labeled as “gasohol”) were produced as a low-cost volume extender for increasingly costly gasoline. U.S. EPA granted a Section 211(f) waiver (the Gasohol Waiver) permitting the use of E10 in all light-duty vehicles effective December 16, 1978.[13] With the issuance of the Gasohol Waiver, ethanol blending grew slowly, primarily in the U.S. Midwest, based on ethanol’s value as an octane improver and a volume extender.

The federal Clean Air Act Amendments of 1990[14] recognized that changes in fuel composition, in coordination with vehicle emission requirements, can be a cost-effective route to reducing emissions of criteria air pollutants. This led to the establishment of the Oxygenated Fuels (OxyFuels) Program, which mandated inclusion of oxygenates at a minimum of 2.7 percent oxygen by mass[15] during winter months in regions which were in non-attainment of Federal ambient carbon monoxide standards. For regions in non-attainment of Federal ambient ozone standards, this led to establishment of the Reformulated Gasoline (RFG) program which included a 2.0 percent oxygen by mass[16] minimum year-round. In California, pursuant to the California Clean Air Act, the California Phase 2 Reformulated Gasoline (“CARB Gasoline”) program promulgated in 1991 and implemented in 1996 created a state-wide gasoline requirement which included a 1.8 to 2.2 percent oxygen by mass flat limit requirement (2.7 percent oxygen by mass cap).[17] Under these programs, ethanol was the predominant oxygenate used in the Midwest and MTBE was the predominant oxygenate used in the rest of the country, including California.

By the late 1990s, incidents of MTBE contamination of drinking water supplies in Santa Monica and elsewhere led then-California Governor Gray Davis, in March 1999,[18] to order a ban on the use of MTBE to take effect in 2002.[19] The CARB Gasoline program was updated to Phase 3 standards as part of the implementation of the MTBE ban and the gasoline supply transitioned to, initially, a 5.7 percent by volume ethanol content. Amendments to the CARB Phase 3 gasoline program finalized in 2007 enabled a

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[13] 44 Federal Register 2077. April 6, 1979.

[14] www.epa.gov. 1990 Clean Air Act Amendment Summary. https://www.epa.gov/clean-air-act-overview/1990-clean-air-act-amendment-summary

[15] Corresponding to 15% by volume of MTBE or 7.8% by volume of ethanol.

[16] Corresponding to 11% by volume of MTBE or 5.7% by volume of ethanol.

[17] Under the California RFG program, fuel producers have the option of complying on either a per gallon basis (in which case the flat limits apply) or on an annual average basis (in which the cap represents the maximum permissible level in any given batch of fuel).

[18] Executive Order D-5-99 on March 25, 1999.

[19] This was subsequently delayed to 2003 to provide refiners with required time to implement the required transition to ethanol blending.

transition to E10 in California; this transition was complete by 2010. Substantially all gasoline currently sold in California is E10.

Federal concerns over the continued use of MTBE ultimately led to the removal of the per-gallon oxygen requirement of the Reformulated Gasoline (RFG) program with the enactment of the Energy Policy Act of 2005 (EPACT 2005). This Act also established the Renewable Fuel Standard (RFS) which created annually increasing requirements for the use of renewable fuels, including ethanol, beginning in 2007. These changes resulted in the effective discontinuation of MTBE usage nationally and replacement with ethanol, primarily in E10 blends. Amendments to the RFS program (RFS2) contained in the Energy Independence and Security Act of 2007 (EISA 2007) quickly led to the current situation where nearly all gasoline sold in the U.S. is E10.

E15 has been available in the U.S. since 2011 following U.S. EPA granting partial waivers[20] permitting the use of E15 in all 2001 and newer model year light-duty vehicles.[21] Retail availability across the U.S. remains limited, and concentrated in the Midwest,[22] but it is growing steadily as automakers have warranted an increasing share of new vehicles if they use E15[23] and consumers have become increasingly aware of the product. As noted above, E15 is not currently permitted in California; completion of this multimedia evaluation is a required first step to attain such approval.

Going forward, the Federal RFS2 program and the California LCFS program effectively compel further increases in the renewable content of gasoline as these programs seek to reduce greenhouse gas (GHG) emissions in the transportation sector. Increasing the inclusion of ethanol, with its low cost and high octane, in the fuel supplied to suitably-designed vehicles can be a low-cost way to meet the GHG reduction goals of the LCFS and RFS2 programs.

1.3 Ethanol Commercial Specifications

1.3.1 Specifications for of Denatured Fuel Ethanol

Ethanol use for gasoline blending (denatured fuel ethanol or DFE) is commonly specified by ASTM D4806 Standard Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark-Ignition Engine Fuel. The incorporation of minimum 2 percent by volume of denaturant is required by U.S. Department of Treasury regulations to assure that it is unfit for beverage use and, therefore, exempt for excise taxes applicable to beverage-grade ethanol.

ASTM allows only natural gasoline, gasoline blendstocks or unleaded gasoline to be used as denaturants. California regulation further restricts the blendstocks by requiring that the DFE contain a maximum of 10 mg/kg of sulfur, a maximum of 0.06 percent by volume of benzene, a maximum of 0.5 percent by volume of olefins and a maximum of 1.7 percent by volume of aromatics.

ASTM further specifies the following properties for DFE:

TABLE 1. ASTM D4806 SPECIFICATIONS FOR DFE

Property	Limit	ASTM Test Method
Ethanol, % by volume, min	92.1	D5501
Methanol, % by volume, max	0.5	D5501
Solvent-washed gum content, mg/100 mL, max	5.0	D381
Water, % by volume (% by mass), max	1.0 (1.26)	E203, E1064 or D7923
Inorganic Chloride, mg/kg (mg/L), max	6.7 (5)	D7319 or D7328

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[20] 75 Federal Register 68094. November 4, 2010 and 76 Federal Register 4662. January 26, 2011.

[21] Use of E15 is also permitted in all FFVs and is prohibited in motor cycles, heavy-duty vehicles and non-road applications.

[22] www.e85prices.com currently reports 990 stations in 665 cities offering E85. The highest concentrations of stations are in Minnesota and Iowa, both of which have policies encouraging adoption of E15 and higher concentration gasoline-ethanol blends.

[23] According to recent analysis by the Renewable Fuels Association (RFA), approximately 93% of 2019 model year vehicles have manufacturer's approval for use of E15. https://ethanolrfa.org/wp-content/uploads/2018/10/Copy-of-2019MY-Table.pdf

Copper, mg/kg, max	0.1	D1688
Acidity (as acetic acid CH_3COOH) mg/kg (% by mass) [mg/L], max	70 (0.0070) [56]	D7795
pHe	6.5 to 9.0	D6423
Sulfur, mg/kg, max	10.	D2622, D3120, D5453 or D7039
Existent sulfate, mg/kg, max	4	D7318, D7319 or D7328

1.3.2 Specifications for Gasoline-Ethanol Blends

Commercial standards for gasoline-ethanol blends have also been developed and maintained by ASTM. Standard specifications relevant to the gasoline-ethanol above E10 and up to E15 are listed below in Table 2. Standard Specification for E15 of particular note is ASTM D4814, which establishes commercial specifications for gasoline-ethanol blends of up to E15 that could be enforced by CARB and the California Department of Food and Agriculture, Division of Measurement Standards.

TABLE 2. STANDARD SPECIFICATION FOR E15

ASTM Standard	Title	Scope
D4814	Standard Specification for Automotive Spark-Ignition Engine Fuel	Finished gasoline blends (E0 to E15)

2 Production of Ethanol and Gasoline-Ethanol Blends

Approval of gasoline-ethanol blends in the E11 – E15 range for use in California would likely increase the quantity of ethanol used in gasoline-type fuels sold in the state. Presently, about 15 to 20 percent of ethanol consumed in California is produced in-state with the remaining 80 to 85 percent produced elsewhere in the U.S. There are also infrequent imports of ethanol from Brazil. Sources of additional ethanol for use in California will depend on factors such as transportation costs and the carbon intensity (CI) values.

There are presently over 200 approved LCFS pathways for ethanol production with CI values ranging from 7.18 to 88.9 g/MJ. The average CI for ethanol supplied to California during 2018 was 67.[24]

The central process for production of ethanol is the fermentation of sugar molecules to ethanol. This reaction is catalyzed by a yeast organism (*Saccharomyces Cerevisea*) and can be represented by the chemical reaction

$$C_6H_{12}O_6\ (glucose) \rightarrow 2\ CH_3CH_2OH\ (ethanol) + 2\ CO_2$$

Lignocellulosic ethanol (also referred to as cellulosic ethanol) processes also convert C_5 sugars, primarily xylose and arabinose to ethanol through the following net chemical reaction

$$3\ C_5H_{10}O_5\ (xylose, arabinose) \rightarrow 5\ CH_3CH_2OH\ (ethanol) + 5\ CO_2$$

Feedstocks potentially utilized for production of lignocellulosic ethanol include switchgrass and corn stover. These are either crop waste materials or crops which can be grown successfully with minimal agricultural inputs. Lignin produced as a by-product from the deconstruction of the lignocellulosic biomass can be used as boiler fuel as an alternative to natural gas. While these benefits of low inputs and use of biomass (lignin) to provided process energy can be partially offset by increased energy requirements for processing into ethanol, they offer the promise of providing a lower carbon intensity ethanol source from a wide diversity of feedstocks which can be produced in regions of varying climates and soil composition.

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[24] Analysis by Stillwater Associates, June 2019.

To date, the technology for production of lignocellulosic ethanol remains in the early stages of commercial production and available volumes are limited.

2.1 Feedstocks

In principle, renewable ethanol can be produced by any renewable feedstock which can be economically processed to yield fermentable sugars. This includes sugar crops (e.g., sugarcane and sugar beet), grains (e.g., corn and grain sorghum) and lignocellulosic matter (e.g., switch grass, corn stover and corn kernel fiber). Small amounts of ethanol are produced from low-cost sugar-containing waste streams (e.g., brewery waste and dairy waste).

Nearly all the ethanol currently consumed in California is derived from corn starch with smaller amounts produced from grain sorghum starch. Other grains, such as wheat, are capable of being utilized for ethanol but their lower starch contents and higher cost generally makes them non-economical as feedstocks.

Ethanol imported from Brazil is produced from sugarcane. While sugarcane is also grown in year-round frost-free regions of the U.S., there is presently no known production of denatured fuel ethanol (DFE) from domestic sugarcane. The value of domestically-produced sugar in the U.S. receives substantial support from the Federal production quota system; this has historically raised prices to levels which deter investment in domestic sugar-based ethanol production. Sugar beet is grown in colder regions of the U.S. (primarily Idaho, North Dakota, Minnesota and Michigan) but there is no present U.S. ethanol production from sugar beet. There are several sugar beet ethanol plants in commercial operation in Europe with their product consumed in their local markets. There is currently a sugar beet ethanol plant under construction in North Dakota with an indicated intent of producing for the California market.[25]

While the potential cellulosic ethanol production has received considerable attention in recent years, current commercial production is extremely limited. Additionally, a number of corn ethanol producers are implementing production of ethanol from corn kernel fiber. This process produces ethanol from this cellulosic material concurrently with fermentation of starch and the two ethanol types are commingled in production.

2.2 Production Methods

2.2.1 Grains

While there are several grain ethanol technologies in commercial practice, Figure 1 below provides a generic overview typical of U.S. corn-based and grain sorghum-based production.

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[25] Gibson, Lisa. Ethanol Producer Magazine. Red River Biorefinery breaks ground in North Dakota August 22, 2018. http://ethanolproducer.com/articles/15552/red-river-biorefinery-breaks-ground-in-north-dakota

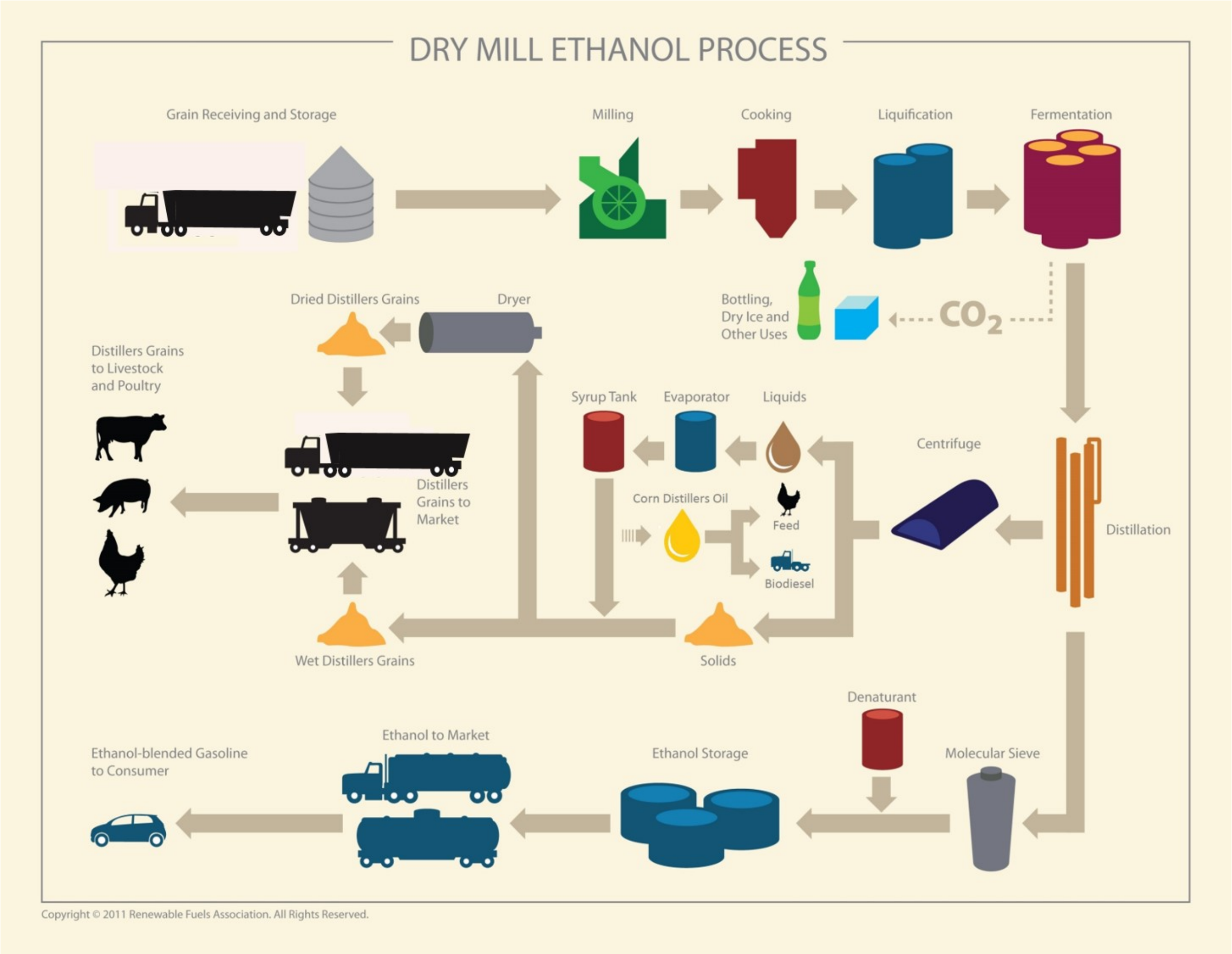

FIGURE 1: DRY MILL ETHANOL PROCESS

Reviewing the key steps in the process –

- **Milling** – the grain kernels are ground into flour, typically with a hammer mill, and the resultant flour is sieved to remove contaminants and provide the desired particle size distribution.

- **Cooking** – the flour produced in the mill is mixed with water to form the mash and heated. The water is a mix of recycled water recovered later in the process and fresh water makeup as required.

- **Liquefaction** – alpha-amylase enzyme is added to the mash to begin the process of converting the starches contained in the grain into water-soluble sugars. This step converts the long chains of polymerized sugars in the starch into shorter chains known as dextrins.

- **Fermentation** – the liquefied mash is further diluted and mixed with glucoamylase enzymes, yeast and nutrients. The glucoamylase breaks down the dextrins into simple sugars and the yeast organism ferments the simple sugars into ethanol. The fermentation is most commonly a batch process which is timed to end when nearly all the sugar has been fermented. Plants typically have several fermenters operating in a cycle to enable continuous production. Carbon Dioxide produced during fermentation may be captured for food and industrial use or vented to the atmosphere after removal of entrained ethanol and other volatile organics.

- **Distillation** – the distillation section of the plant recovers the dilute ethanol present in the fermentation broth and purifies it. At the end of the fermentation cycle, the ethanol-containing broth called beer is transferred to the beer well and from there to the beer column.
    - The beer column is designed to send all the ethanol overhead along with some of the water. The remaining water and all the solids present in the broth, known as whole stillage, are recovered out of the bottom of the beer column.
    - The beer column overhead is sent to the rectifier column which further concentrates this stream to the ethanol-water azeotrope (95% ethanol, 190 proof).
    - The 190-proof ethanol is further processed to reduce the water content to DFE requirements utilizing molecular sieve technology. This dehydration system consists of vessels containing beads that trap water molecules, while allowing ethanol to pass through.

  The residual whole stillage from the bottom of the distillation tower is further processed by a centrifuge which separates the coarse grains and thin stillage. These are further processed by evaporation and drying into a concentrated valuable high protein animal feed products. Stillage also can be further centrifuged to remove distillers corn oil which can be used as an animal food or as a feedstock for biodiesel.

- **Denaturing** – Ethanol needs to be combined with 2 percent by volume denaturant in order to be exempt for beverage ethanol taxes and meet government and commercial specifications for DFE. Natural gasoline is the most commonly used denaturant (hydrocarbon gasoline, BOBs and gasoline blendstocks are also permissible denaturants). This denaturant may be added prior to transferring the produced ethanol to bulk storage or at the time of product shipment.

- **Shipment** – DFE may be loaded onto road tank trucks if it is being used in local markets, or railcars if being used in more distant markets. For long-distance markets, unit trains consisting of 50 to 120 railcars are often employed and plants require adequate rail sidings and rail switching capabilities. Plants in the Midwest located near navigable waterways may also ship product via barge.

2.2.2 Sugar Crops

The most advanced technology for production of sugarcane ethanol is presently practiced in Brazil. The description in this section is based on practices typically employed in Brazil.

An important difference from grain-based ethanol production is the storage lifetime of the feedstock. While corn dried to an appropriate moisture content can be stored in silos for extended periods of time, sugarcane must be processed expeditiously following harvest, ideally within 24 to 48 hours. Longer storage of sugarcane results in lost sugar content due to the effects of bacterial action. This makes planning and scheduling of planting and harvest a key element in the operation of the ethanol facility. Agronomic practice for sugarcane has developed to not only improve yield and lower required inputs but also extend the harvest season as a means of maximizing the number of days of production each year. Currently, mills in South-Central Brazil are able to manage their sugarcane crops to enable up to about 200 days per year of operation.

Once the cane stalks are delivered to the ethanol facility, it is washed to reduce excess dirt and debris and then processed. Two different technologies are in common use for extraction of the sugar juice from the cane stalks. The more common technology is a rolling mill where the cane stalks are crushed between gear teeth; four to five stages of crushing are typical. Water flows counter-current to the stages of the mill to dissolve the cane juice as it is squeezed out of the stalks. The less common technology is a diffuser. With a diffuser, the cane stalks are first shredded to increase surface area and the shredded stalks are then transported through a counter-current water flow with sugar juice dissolving in the water flow via diffusion.

The processing of the sugar juice extracted via either process depends on the plant configuration. Most plants produce a mix of raw sugar and ethanol and have some flexibility to adjust the ratio of these products with market conditions. For plants producing sugar, some or all of the sugar juice is processed through one or more stages of crystallization. The crystallization process entails evaporating some of the water from the sugar juice until sugar crystals begin to form. The sugar crystals are then separated from the supernatant liquid, known as molasses. At the end of the sugar processing, the remaining molasses is combined with any unprocessed sugar juice for use in ethanol production. The combined sugar juice/molasses stream is transported to a fermenter where it is diluted with water to a desired sugar content and mixed with yeast and required nutrients. This mixture is then allowed to ferment for a scheduled time. At the end of the fermentation period, the broth is centrifuged to separate the yeast, and the liquid centrate goes on to the distillation section. Unlike a dry-grind grain process, the recovered yeast is rejuvenated and reused in subsequent fermentations.

The liquid recovered from fermentation is distilled to recover the ethanol from the water. This distillation concentrates the ethanol to the ethanol:water azeotrope (95% ethanol or 190 proof). This product, known as hydrous ethanol, is marketable directly in Brazil for use in the FFVs which constitute the bulk of the domestic light-duty vehicle fleet. Many mills further process the hydrous ethanol to produce anhydrous ethanol, suitable for use in the Brazilian gasoline market (currently a 27 percent by volume blend of ethanol with gasoline) or export sales. The most common process for production of anhydrous ethanol in Brazil is an azeotropic distillation where a co-solvent (most commonly mono-ethylene glycol, MEG) is combined with the hydrous ethanol to enable an anhydrous ethanol stream to be distilled off. A minority of plants producing anhydrous ethanol use molecular sieves, similar to what is commonly practiced at U.S. grain ethanol plants.

For sugar beet ethanol production, the harvested sugar beets are chopped into small pieces known as cossettes. The cossettes are mechanically crushed in the presence of wash water to recover the contained sugar juice. The diluted sugar juice is then mixed with yeast and nutrients in a fermenter. The ethanol-rich broth at the end of the fermentation process then undergoes distillation processes generally similar to other ethanol production processes.

2.2.3 Lignocellulosics

Stover and Switchgrass: Production of ethanol from lignocellulosic feedstocks, such as corn stover and switch grass, is an area of emerging technology, so only a general overview can be provided. Generally, the key differences from sugarcane technology discussed above are in the pre-treatment and hydrolysis steps prior to fermentation. Production of cellulosic ethanol from corn kernel fiber has some important differences and will be discussed separately.

A high-level summary of the required steps follows (this listing is conceptual, different technology providers may combine or further divide some of these steps):

- **Cleaning** – Removal of dirt, stones and other debris which can adversely impact the rest of the process. A typical approach is to water-wash the feedstock with some mechanical agitation.

- **Sizing** –Following the cleaning step, the feedstock needs to be mechanically reduced to smaller, more uniform size particles to facilitate further treatment. This may be affected by chopping, shredding, grinding or other similar processes.

- **Pre-treatment** – A variety of strategies are employed to improve the accessibility of the contained cellulose (a relatively simple polymer composed of C_6 sugar units) and hemicellulose (a more complex polymer containing both C_5 and C_6 sugar units) by pulling them away from the enveloping lignin molecules (a complex, non-fermentable, organic material). Proposed strategies for this stage include treatments with enzymes, chemicals (strong acids or bases) and steam.

- **Hydrolysis** – Treatment, typically with enzymes, to hydrolyze the cellulose and hemicellulose into their constituent sugar monomers.

- **Fermentation** – Dilute the hydrolysates with water, add yeast and required nutrients and ferment for enough time to achieve desired conversion of the sugars into ethanol. This stage can be more complex than is the case for corn starch or sugarcane technologies, as the processes required for pre-treatment may leave behind chemicals which can inhibit yeast performance.

- **Separation** – Following fermentation, the yeast and other solids present in the broth are separated from the liquid and the liquid is distilled to produce the ethanol:water azeotrope (95% ethanol or 190 proof). The azeotropic mixture is then dehydrated with molecular sieves to reduce the water content to meet commercial requirements.

- **Denaturant** is added prior to shipment.

Corn Kernel Fiber: In a standard dry-grind plant, fiber present in the corn kernel is not converted and is, instead, recovered in the distillers grain product. Production of cellulosic ethanol from corn kernel fiber has begun to enter commercial practice in the U.S. Quad County Corn Processors in Iowa was the first plant to implement this technology using an internally developed process. Commercial technology licensors include Edeniq and ICM and their technologies have significant differences. Pacific Ethanol's Stockton, CA plant has implemented the Edeniq technology. A recent article in Ethanol Producer Magazine provides a high-level description of the processes and the regulatory approvals.[26] Key points are that this technology is being implemented as a "bolt-on" to existing dry grind ethanol plant, effectively increasing the amount of ethanol which can be produced from each kernel of corn through conversion of cellulose and hemicellulose contained in the fiber. This incremental ethanol is commingled with the conventional starch-derived ethanol produced at these plants and the regulatory approvals require specific procedures to assure that the amount of cellulosic ethanol produced in this manner is properly quantified. As the early adopters of this pathway demonstrate success in both achieving the required regulatory approvals and demonstrate reliable commercial operation, it can be expected that many additional dry-grind plants will invest in this technology.

2.3 Co-Products of Ethanol Production

All ethanol fermentations produce carbon dioxide. This carbon dioxide can be readily captured and purified to food-grade standards (commonly used in carbonated beverages). Economics for capture of this carbon dioxide depend on the size of the plant and local demand. Capture and sequestration of this concentrated carbon dioxide stream is a potential option for further reductions in the CI of ethanol production.[27]

2.3.1 Grains

Distillers Grains: Traditional dry-grind processing of grains (primarily corn and grain sorghum) to produce ethanol converts most of the starch in the grain kernel into ethanol. This leaves a small amount of unconverted starch plus the other components of the kernel (primarily protein, corn/sorghum oil and fiber) to be recovered with the spent yeast as distillers grains. As the distillers grains are high in protein, they compete with soy meal as livestock feed. Over the past decade, most U.S. plants have installed equipment to separate and recover a portion of the distillers corn oil to be sold as a separate product. More recently, plants have begun to install equipment to convert some of the fiber into ethanol as described above in section 2.2.3. Depending on the targeted markets, some or all of the distillers grains

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[26] Retka Schill, Susanne. Ethanol Producer Magazine. A Straighter, Shorter Pathway. January 22, 2018 http://ethanolproducer.com/articles/14946/a-straighter-shorter-pathway

[27] ADM has demonstrated technical feasibility at their Decatur, IL ethanol plant, https://www.adm.com/news/news-releases/adm-begins-operations-for-second-carbon-capture-and-storage-project-1

may be dried. The drying process requires a significant amount of heat; thus the extent of drying is a major source of variation in the carbon intensity of ethanol produced by different plants.

- Wet Distillers Grains (with solubles) (WDG(S)) has a limited safe storage life, typically 24 to 72 hours. Accordingly, production of WDG primarily occurs at plants in close geographic proximity to livestock feeding facilities.

- Dry Distillers Grains (with solubles) (DDG(S)) can be safely stored long-term and shipped to international markets. The drying, to 10-12% moisture content is typically done through the use of a rotary dryer employing steam as the heat source.

- Modified Distillers Grains (with solubles) (MDG(S)) refers to a partially-dried product with a moisture content intermediate between WDG(S) and DDG(S), typically 50 to 55 percent. This reduced moisture content provides a shelf life of approximately three weeks. This enables the product to be shipped further and stored longer than WDG(S) while still consuming less energy than required for production of DDG(S)[28].

Corn/Sorghum Distillers Oil: Most dry-grind ethanol plants recover some of the oil contained in the grain as they are generally able to sell it at a higher price than what it would receive if left in the distillers grains. The oil recovered at these plants is non-food grade and is primarily sold as feedstock for biodiesel or renewable diesel production. As this oil is similar in composition to soybean oil, biodiesel and renewable diesel producers can readily utilize it as an alternative feedstock. A portion of the recovered oil is also sold as animal food.

2.3.2 Sugar Crops

The available co-products from sugarcane-based ethanol production include:

- **Bagasse**: The remnants of the sugarcane stalks after removal of the sugar juice (bagasse) are utilized by the plant as boiler fuel. Older sugarcane plants in Brazil typically had low-pressure boilers coupled with generators designed to consume the bagasse and provide all the steam and power required by the plant. With liberalization of Brazil’s power markets, mills are installing high-pressure boilers which, with modern steam turbine generators enable the plant to export significant quantities of power to the local grid as well as provide the steam and power requirements of the plant.

- **Vinasse**: The residual water at the end of the sugar and ethanol process (vinasse) is rich in the minerals needed to fertilize the growth of the sugarcane. The vinasse is diluted with fresh water and applied to the cane fields as fertilizer, reducing the amount of additional fertilizer the plant operator needs to purchase to sustain their crop.

- **Spent Yeast**: The sugarcane ethanol process has a key difference from the dry-grind grain ethanol process in that the yeast is the only solid present in the fermentation broth. As a result, the yeast can be recovered at the end of the process, rejuvenated and re-used. Any yeast recovered that is not viable for continued use in fermentation is allowed to dry and gets sold as a high-protein animal food.

In the sugar beet ethanol process, the pulp left after crushing and recovery of the sugar juice is generally sold as animal food.

2.3.3 Lignocellulosics

Unlike grain and sugar-based ethanol production, lignocellulosic ethanol production has not yet matured to the extent that the co-products are standardized. In general, however, the lignin which is left after

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[28] Green Plains Renewable Energy, http://www.gpreinc.com/products-and-services/distillers-grains/

extraction of the desired cellulose and hemicellulose content of the feedstocks is available for use as boiler fuel. Spent yeast may be available for sale as a high protein animal food.

2.4 Summary of Findings

Ethanol can be produced from a variety of feedstocks using well-established commercial procedures. Although additional capacity for the production of ethanol may be needed to supply the additional ethanol required for E15 in California, that capacity is expected to use the same processes that have already been approved by California and that are already being used to supply the existing California market. Thus, to the extent any currently-approved processes are used, such processes would not create environmental or health impacts that are not already known. Increased use of ethanol in the fuel pool would have the added benefit of reducing demand for petroleum-derived CARBOB. Ethanol production is highly regulated on the Federal and State levels. The Federal Renewable Fuel Standard provides environmental safeguards by defining renewable biomass as planted crops and crop residue harvested from existing agricultural land cleared or cultivated prior to December 19, 2007 and that was non-forested and either actively managed or fallow on December 19, 2007.

3 Storage and Distribution of E11 – E15 Blends

3.1 Material Compatibility

The most commonly used method for identifying underground storage equipment in California and its compatibility with different fuel types is California's Underground Storage Tank (UST) database. RFA has done extensive research with this state-supported information source, which is far superior to most other states. The age of the infrastructure, the type (double wall vs single wall) of equipment, and the manufacturer can all be determined from the UST database. Further research will continue in Tier II to develop a comprehensive resource that identifies underground storage tank equipment organized by equipment manufacturer, model, and model year manufactured that is or is not compatible with E15.

The California UST law was established in 1984 prior to Federal regulations. The State rule is the more stringent of the two. California required USTs and piping to be double walled. In addition, 90% of UST systems in California have secondary containment and continuous leak detection monitoring on systems that alert the operator of a leak. Data shows only 8 - 9% of UST inventory is single walled.[29]

California's current UST infrastructure is superior to that of most states so is likely highly compatible for the introduction of E15. Some findings in the database include:

- More than 99% of the piping installed in California post-1989 are double walled.
- More than 99% of the underground storage tanks installed in California post-1989 are double walled.
- Of the over 30,000 UST records provided by the California Water Board, 78% have been installed post-1989

When gasoline-ethanol blends in the E10 range were first introduced in the 1970s, some problems were reported with interactions between E10 and materials used in vehicles and the gasoline distribution and dispensing system. Since that time considerable testing has been done to ensure compatibility of ethanol blends with all materials used in fuel handling. The most recent studies that have evaluated the impacts

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[29] https://www.waterboards.ca.gov/ust/adm_notices/final_accessibility_california_ust_leak_prevention_report-Jan-June2019.pdf

of gasoline-ethanol blends on materials compatibility include those performed by the Minnesota Center for Automotive Research[30,31,32] and Oak Ridge National Laboratory.[33]

These studies have assessed the impacts of increasing ethanol concentration on individual materials in three distinct categories: (1) elastomers, (2) metals, and (3) plastics. Not all materials are appropriate for all fuels and not all vehicles or fuel-handling equipment designed to run on gasoline are compatible with E15. However, compatible materials for all fuel-handling equipment and vehicle fuel systems needs to have been tested and used for flex-fuel vehicles and E85 fuel infrastructure. This equipment has successfully handled all ethanol blends between E10 and E85 for many years. Flex-fuel vehicle owners can and do switch between E85 and E10, thus exposing their fuel systems to ethanol concentrations between 10% and 85%. Not all existing vehicles or infrastructure are appropriate for E11-E15 ethanol-gasoline blends, but compatible materials have been identified and are readily available for use in vehicles and the fuel-handling infrastructure in California.

Materials Selection for Compatibility Tests

As part of Tier II work, the E15 study group will develop and provide a more comprehensive material compatibility list. There is no comprehensive register of every material used in contact with fuels. However, the Minnesota Center for Automotive Research (MnCAR)[34,35,36] examined literature reviews, manuals, and recommendations from fuel system and engine manufactures to generate a list of materials to be tested. Materials previously approved for use in fuel-flex vehicles (FFVs) were removed from the list, and the list was then peer reviewed by OEM engineers and Tier I and II suppliers.[37] In addition to the MnCAR analysis, this multimedia evaluation includes the findings of a study conducted by the Oak Ridge National Laboratory (ORNL)[38] for materials intended for use in fuel storage and transfer, many of which overlap with use in vehicles. The procedures used by OEMs to ensure material acceptability for use in vehicles are not known and may be more or less stringent than the standard test methods referenced here.[39]

Control Fuel for Compatibility Tests

The control fuel used in testing should be selected to represent the baseline market condition. As all the fuel currently sold in the state of California is E10, where possible, we have compared test fuels to this control. The balance of commercially offered ethanol blended fuels is a specialized petroleum hydrocarbon blendstock for oxygenate blending (BOB). BOBs must be produced so that when mixed with ethanol, the American Society for Testing and Materials (ASTM) Standard for Automotive Spark-Ignition Engine Fuel D4814 requirements are met. For some of the studies reviewed here, BOBs are represented by Reference Fuel C (equal parts iso-octane and toluene as representative hydrocarbons) to standardize the testing and allow for more accurate repeatability. However, it is not clear that Reference Fuel C

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[30] Mead, G., B. Jones, P. Stevens, C. Connors, The Effects of E20 on Elastomers Used in Automotive Fuel System Components, 2/22/2008, http://cset.mnsu.edu/aet/facilities/msu_e20_elastomers_material_compatibility_study_2-22-08_final.pdf .

[31] Mead, G., B. Jones, P. Stevens, The Effects of E20 on Plastic Automotive Fuel System Components, 2/21/2008, http://cset.mnsu.edu/aet/facilities/msu_e20_plastic_material_compatibility_study_2-21-08_final.pdf

[32] Jones, B., G. Mead, P. Steevens, M. Timanus, The Effects of E20 on Metals Used in Automotive Fuel System Components, 2/22/2008, http://cset.mnsu.edu/aet/facilities/msu_e20_plastic_material_compatibility_study_2-21-08_final.pdf.

[33] Kass, M.D., Theiss, T.J., Janke, C.J., Pawel, S.J., Lewis, S.A. “Infrastructure Materials Compatibility Study: Elastomers, Metals, and Sealants” ORNL/TM-2010/326, March 2011

[34] Mead, G., B. Jones, P. Stevens, C. Connors, The Effects of E20 on Elastomers Used in Automotive Fuel System Components, 2/22/2008

[35] Mead, G., B. Jones, P. Stevens, The Effects of E20 on Plastic Automotive Fuel System Components, 2/21/2008, https://www.leg.state.mn.us/docs/2008/mandated/080342.pdf.

[36] Jones, B., G. Mead, P. Steevens, M. Timanus, The Effects of E20 on Metals Used in Automotive Fuel System Components, 2/22/2008

[37] A Tier 1 supplier is an automotive parts manufacturer that provides products directly to the vehicle manufacturer (Ford, GM, Honda, etc.) without a middleman. Tier 2 suppliers are manufacturers in the automotive parts industry that sell to intermediate producers or suppliers.

[38] Kass, M.D., Theiss, T.J., Janke, C.J., Pawel, S.J., Lewis, S.A. “Infrastructure Materials Compatibility Study: Elastomers, Metals, and Sealants” ORNL/TM-2010/326, March 2011

[39] 2013 NREL E15 - https://ethanolrfa.3cdn.net/b378858ac325c6e165_sgm6bknd4.pdf

appropriately represents the material compatibility effects that would be seen with a more realistic CARBOB.

Test Fuel for Compatibility Tests

Relevant testing was done by the ORNL with Aggressive TF10 (10% ethanol), Aggressive TF17 (17% ethanol, used as a proxy for E15), and Aggressive TF25 (25% ethanol) and by the MnCAR with Aggressive TF10 (10% ethanol) and Aggressive TF20 (20% ethanol). These fuels adhere to the J1681 Society for Automotive Engineers (SAE) Standard for Gasoline, Alcohol, and Diesel Fuel Surrogates for Materials Testing, established by the automotive industry in an effort to standardize materials testing fluids. The ethanol included in these blends is labeled “aggressive” due to the J1681 mandated addition of water, sodium chloride, sulfuric acid, and glacial (anhydrous) acetic acid. Historically, trace amounts of these additives have been found in either ethanol production processes or fuel distribution and transport systems[40] but are primarily included to represent the worst-case scenario and are present in quantities well beyond the allowable limits of modern fuel grade ethanol. For metals testing, the result of one study comparing non-aggressive fuels[41] with their aggressive counterparts is discussed and suggests the impact of these additives is large.

3.1.1 Elastomers

Elastomers, also known as pipe dope or thread sealants, are generally used to seal together non-threaded joints. Liquid tight seals at joints in the UST system are essential in preventing releases of regulated substances to the environment. The pipefitter spreads the paste-like dope completely over the threaded ends of a section of pipe before screwing it into place. Soon, the dope cures and provides a tight seal.

Due to the nature and potential interactions with fuel in these uses, volume swell is considered the most relevant physical property,[42] although hardness, elongation, permeation, and tensile strength are also studied. Many compounds present in elastomeric materials may chemically react with, or be dissolved by, both ethanol and gasoline. Because of the differing properties between pre-wetted and wetted elastomers most materials compatibility testing includes measurements both prior and subsequent to submersion. The degree of crosslinking, copolymers, plasticizers, and other additives can be different in elastomers with the same name, so varying studies may be testing similar elastomers with the same name but with somewhat different properties.

According to a number of studies conducted in the 1980s and 1990s, the effect of increased ethanol concentration was most prominent between 10% and 35%.[42,43,44] In an early study, of a few elastomers (fluorocarbon, fluorosilicone, polyurethane and nitrile rubber), Adu-Isa[45] observed a significant association between increasing ethanol content and volume swell. The study concluded that the largest physical changes were observed between E10 and E25. These results suggest that materials which are appropriate for E10 should not automatically be considered appropriate for higher ethanol concentrations, such E11-E15. They suggest further that E11-E15 fuels should only be stored, dispensed and transported through equipment made from materials that have been specifically tested and selected for use with these higher ethanol content fuels.

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[40] Harrigan, M.J., Banda, A., Bonazza, B., Graham, P., Slimp, B. “A Rational Approach to Qualifying materials for Use in Fuel Systems” SAE Technical Paper No. 2000-01-2013.

[41] Jafari, H., “EIS study of corrosion behavior of metallic materials in ethanol blended gasoline containing water as a contaminant,” Fuel, 90, 1181-1187, 2011.

[42] Nerasian, A. “Compatiability of Fuel-Handling Rubbers with Gasoline/Alcohol Blends,” Elastomer Chemicals Dept., DuPont Technical Bulletin No. 1, June 1980, cited in Yuen et al., 2010.

[43] Gatcomb, G.L. “Performance of FAIRPRENE Fuel Pump Diaphragm Materials in ASTM Fuel C and ASTM FuelC/Alcohol Blends,” DuPont, Technical Bulletin No. 1, June 1980, no longer available but cited in Yuen, P.K. et al. 2010.

[44] Fiedler, L.D., Knapp, T.L, Norris, A.W., and Virant, M.S., “Effect of Methanol/Gasoline Blends at Elevated Temperatures on Fluorsilicone Elastomers,” Dow Corning Corporation, March 1990.

[45] Abu, Isa, I. A., “Effects of Mixtures of Gasoline with Methanol and with Ethanol on Automotive Elastomers” SAE Technical Paper No. 800786.

In contrast, a more recent Oak Ridge National Laboratory (ORNL) study[35] focused on elastomers utilized in fuel infrastructure: fluorocarbons, flourosilicone, nitrile rubbers (NBRs), polyurethane, neoprene, styrenebutadiene rubber (SRB), and silicone. The greatest amount of swell was observed in both Aggressive TF10 and Aggressive TF17 and the discrepancies between the two fuels were less than 15% in all cases. If silicone, SRB, and polyurethane are excluded from this analysis only a 5% difference was detected and according to the Parker O-Ring Handbook, both SRB and silicone (as well as neoprene) are not deemed to be acceptable for use with standard gasoline and so are likely to be problematic whether the fuel used is E0, E10 or E15.

In its study the Minnesota Center for Automotive Research (MnCAR) submerged eight different elastomers in both Aggressive TF10 and Aggressive TF20 for 500 hours at 55 °C[33] to measure appearance, volume swell, weight, tensile strength, elongation, and hardness. Each trial was repeated five times and measurements were taken before and after submersion. Materials testing included: acrylic rubber, epichlorohydrin homopolymer, epichlorohydrin ethylene oxide copolymer, polychloroprene, nitrile rubber with medium and high acrylonitrile (ACN) content, nitrile/PVC blend, and fluoroelastomer Viton A. The weight and size of all elastomers increased in both fuels. The only material that swelled to a noticeably larger size in Aggressive TF20 than Aggressive TF10 was epichlorohydrin ethylene oxide copolymer. Additionally, the only one that increased to a noticeably higher weight in Aggressive TF20 than Aggressive TF10 was acrylic rubber. Following a dry out period, all elastomers returned to their original size, except for the fluoroelastomer, which retained its increased weight and size. Increase in ethanol content had no effect on tensile strength or hardness. In both the ORNL and MnCAR studies, the type of fuel had a far smaller impact on the measured properties than the type of material tested.

In another study, various fluoroelastomers were submerged for 168 hours and tested for volume swell, hardness, elongation, and tensile strength.[46] Observed changes were most significant in E25.

Elastomers' use in underground tanks has become the topic of debate with regards to underground infrastructure due to a common misconception of where the elastomers are located and how they can be accessed.
Figure 2 below shows a typical fuel station configuration as well as the areas where pipe dope / thread sealant may need to be addressed. Areas where pipe dope is relevant are easily accessible via a manhole or with a minor concrete cut. The process can be completed by most service organizations with very little downtime.[47]

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[46] Stevens, R.D., "Fuel and Permeation Resistance of Fluoroelastomers to Ethanol Blends, " presented at the Fall 170th Technical Meeting of the Rubber Division, ACS, Cincinnati, OH, October 12, 2006

[47] North America Corporation http://www.sourcena.com/sourceline/equipment-guide-understanding-importance-thread-sealant/

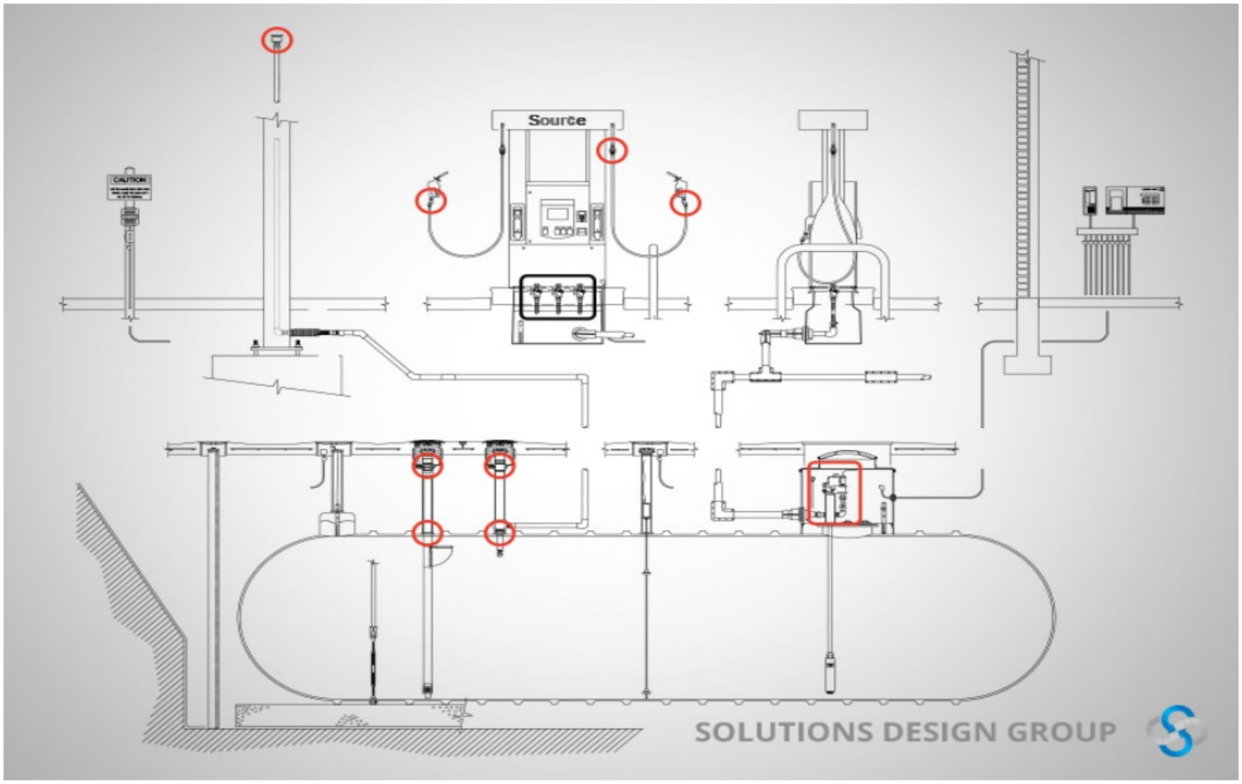

FIGURE 2: ELASTOMER LOCATIONS IN FUEL INFRASTRUCTURE

For years petroleum equipment installers have been mindful of the level of ethanol that is present in systems and have made proper concessions in order to construct compatible sites. There are only a small handful of petroleum equipment thread sealant manufacturers in the marketplace and the most recognized and distributed is Gasoila.[48]

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[48] FEDPRO https://www.fedprobrands.com/products/pipe-thread-sealants.html

Based on the fuels in the market today the sealant blends that are most often used are the “blue paste” and the “green paste”. As noted in Figure 3, both combinations are fully compatible for ethanol blends above 10%.

- Soft-setting, PTFE paste.
- Provides a positive seal on pipe threads, joints, fittings, hoses, nozzles, LPG cylinders, pump assemblies, oil burners, hydraulics, compressors, engines, motors, housings, plugs, fuel lines, couplings and more.
- Use on brass, copper, stainless steel, aluminum, black pipe, tin, galvanized, ABS, CPVC, PVC plastics, nylon, polyethylene, polypropylene, polybutylene and more.
- Excellent resistance to gasoline (up to 20% alcohol and petroleum blends), petroleum solvents, kerosene, diesel oil, propane, butane, LPG, cutting oils, ammonia, aliphatic solvents, acids, steam, potable water, compressed air and more. NOT for use on oxygen.
- Remains pliable in cold temperatures.
- Temperature Range: -100°F to 600°F (-74°C to 315°C).
- Pressure Range: To 10,000 psi sealing liquids; to 3,000 psi sealing gases.
- One year shelf life when stored at 40°F to 80°F (5°C to 27°C).
- For alcohol blended gasoline ethanol see E-Seal.

Gasoila® Soft-Set Thread Sealant with PTFE

- Soft-setting, non-toxic, PTFE paste.
- Provides a positive seal on pipe threads, joints, fittings, hoses, nozzles, LPG cylinders, pump assemblies, oil burners, hydraulics, compressors, engines, motors, housings, plugs, fuel lines, couplings and more.
- Use on brass, copper, stainless steel, aluminum, black pipe, tin, galvanized, ABS, CPVC, PVC plastics, nylon, polyethylene, polypropylene, polybutylene and more.
- Excellent resistance to gasoline (up to 20% alcohol and petroleum blends), petroleum solvents, kerosene, diesel oil, propane, butane LPG, cutting oils, ammonia, aliphatic solvents, acids, steam, potable water, compressed air and more.
- NOT for use on oxygen.
- Remains pliable in cold temperatures.
- Temperature Range: -100°F to 600°F (-74°C to 318°C).
- Pressure Range: To 10,000 psi sealing liquids; to 3,000 psi sealing gases.
- One year shelf life when stored at 40°F to 80°F (5°C to 27°C).
- For alcohol blended gasoline (ethanol), see E-Seal.

Gasoila® E-Seal Thread Sealant

- Non-hardening, non-toxic, opaque, dark green paste designed specifically for ethanol blended gasoline including E10 and E85 (for 100% ethanol or 100% methanol applications - use Gasoila 100).
- Provides a positive seal on pipe threads, joints, fittings, hoses, nozzles, pump assemblies, oil burners, hydraulics, bolts, compressors, engines, motors, fuel lines and couplings.
- For use on brass, copper, stainless steel, aluminum, black pipe, tin and galvanized pipe.
- Excellent resistance to gasoline, ethanol blended gasoline such as E10 and E85, petroleum solvents, kerosene diesel oil, BioDiesel propane, jet fuels, butane, LPG, cutting oils, ammonia, aliphatic solvents, acids, steam and potable water.
- NOT for use on oxygen.
- Temperature Range: -100°F to 600°F (-74°C to 318°C).
- Pressure Range: Up to 10,000 psi when sealing liquids and up to 3,000 psi with gases.
- One year shelf life.

FIGURE 3. COMMON SEALANTS WITH MARKETED COMPATIBILITY FOR E15

3.1.2 Metals

Due to the higher content of dissolved oxygen present in ethanol, it is potentially more corrosive to metals than gasoline.[49] In order to determine the effects of increasing ethanol concentration on metals, the

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[49] German, J, Malins, C, Sanchez F.P., Searle, S. “Technical Barriers to the Consumption of Higher Blends of Ethanol”. The International Council on Clean Transportation. February 2014. https://www.theicct.org/sites/default/files/publications/ICCT_ethanol_revised_02_03_format.pdf

Minnesota Center for Automotive Research tested 19 metals.[36] To quantify the results it was reasoned that if the lifespan of a vehicle is 20 years, then a corrosion rate of 0.0025 mm/year (0.1 mil/year) would not be significant over that time frame. Except for a thin lead-tin alloy coated steel sheet, terne plate, and Zamak 5, none of the seventeen other metals showed a significant corrosion rate. During the 2160 hours of testing the solution was changed weekly to minimize any bulk solution changes. In Aggressive TF20 a 0.0036 mm/year corrosion rate was observed for terne plate but in Aggressive E10 the rate was below the researcher's level of significance (0.0025 mm/year). However, to limit the environmental impact of the manufacturing process of terne plate, its use in automobiles has been phased out since the 1990s. In both Aggressive TF10 and Aggressive TF20 the Zamak 5 exhibited large mass loss and corrosion rates. Zamak 5 is not anticipated to be a problem as it was only used in a small amount of OEM and aftermarket carburetors that have not been utilized in U.S. vehicles since the mid-1990's.

For the purposes of this discussion, it is not assumed the reaction is zeroth rate, but rather that the concentration of ethanol in the solution and the metal plate is effectively constant over the course of the testing, and in the real-life conditions it is intended to represent. A zeroth order reaction occurs at a rate that is independent of the concentration of the reactants. During the testing the test solution was changed weekly (a dozen times over the 2016 hours of the test) to minimize bulk solution changes. In real life, fuel in a tank is replenished periodically – perhaps once a week - not enough time for these relatively slow corrosion reactions to significantly affect the concentration of ethanol in the mixture.

The surface conditions on the metal plate itself might reduce the exposed area of pure metal, slowing down the reaction rate which is proportional to the surface area, as an oxidized "crust" can form on some metals minimizing the contact area between the fluid and the unoxidized metal – that however would reduce the corrosion rate at the surface over the long exposure in real life, and not including that effect in these estimates is conservative.

The Oak Ridge National Laboratory conducted a similar study[50] in which low corrosion levels were considered to be below 0.030 mm/year (approximately 1 mil/year). The result was no correlation between yearly corrosion rate and ethanol concentration for any metal. In Aggressive TF17, cartridge brass, phosphor bronze, zinc-plated galvanized steel, lead-plated (terne) steel displayed detectable corrosion rates, but all were below 0.01 mm/year. For both Aggressive TF10 and Aggressive TF17 in 1020 mild steel, 1100 aluminum, 201 nickel, and 304 stainless the corrosion rates were too low to be calculated.

Non-Aggressive fuel testing measured corrosion rates of less than 1.0E-4 mil/year (mpy) for both E10 and E15 via electrochemical impedance spectroscope.[41] In the same study, the effect of water on the conductivity of hydrocarbon-ethanol blends were tested. The inclusion of water had the most pronounced effect on the medium-carbon steel transferring tube bolt. In E10 the observed corrosion rate of this material increased over 43% with 1% water and in E15 it increased 91%. While water inclusion was found to influence corrosion rates, neither E10 nor E15 exhibited rates exceeding 1.5E-4 mpy.[38]

3.1.3 Plastics

Plastics have become a common replacement for traditionally metal automobile components due to their light weight. While most are designed to sufficiently store higher alcohol fuels,[51] sulfonation or fluorination treatments were used in older fuel tanks and have not been endorsed to work with alcohol fuels. It is

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[50] Kass, M.D., Theiss, T.J., Janke, C.J., Pawel, S.J., Lewis, S.A. "Infrastructure Materials Compatibility Study: Elastomers, Metals, and Sealants" ORNL/TM-2010/326, March 2011.

[51] Yuen, P.K., Beckett, J., Villaire, W. "Automotive Materials Engineering Challenges and Solutions for the Use of Ethanol and Methanol Blended Fuels" SAE Technical Paper No. 2010-01-0729.

common for fuel level floats to contain polybutylene terephalate or polyurethane foam, both of which are affected by increasing concentrations of alcohol.[51]

The Minnesota Center for Automotive research conducted a study of the effect of increasing ethanol concentration on volume, weight appearance, impact resistance, tensile strength, and ultimate elongation of eight different plastics. Overall the difference between the results obtained via submersion in Aggressive TF10 and Aggressive TF20 was insignificant. It was concluded polyamide 6 (PA6)[Nylon 6], polyamide 66 (PA66)[Nylon 66], polyethylene terephthalate (PET), and polyetherimide 1010 moldable (PEI), can be used with any ethanol blend fuel up to 20%. The rest of the plastics, acrylonitrile butadiene styrene (ABS), polyurethane 55D90Adurameter hardness (PUR), and polybutylene terephthalate (PBT) cannot be used in cooperation with any fuel containing ethanol, except for polyvinyl chloride flexible version (PVC), which has some problems with ethanol concentration but is not wholly inoperable.

3.1.4 Material Compatibility Summary

The aggressive ethanol blends used in material compatibility testing are intended to amplify the potential adverse effects caused by increasing ethanol concentration and thus are not expected to exactly represent real-world, commercially available fuel. Because of this, any material approved with aggressive test fuel is considered to be acceptable for use with its respective commercial grade fuel, with a significant safety factor. However, corrosion rates observed between separate studies indicate a decrease of several orders of magnitude when non-aggressive ethanol blends are substituted for aggressive ones, no one study has quantified an acceleration factor to confirm the exact relationship.

Of all the metals tested only Zamak 5 and terne plate, both materials no longer used in the manufacturing of automobiles, exhibited marginally larger than acceptable corrosion rates (0.1mil/year) and neither material was significantly affected by a change from Aggressive TF10 and Aggressive TF20. All metals tested in non-aggressive ethanol blends exhibited corrosion rates of less than 10^{-3} mil/year for both E10 and E15. Certain elastomers and plastics did demonstrate quantifiable differences in volume swell with increasing ethanol content. Difference in material was found to have more effect than difference in fuel. The ORNL study showed changes in swell from Aggressive TF10 and Aggressive TF20 (used to represent E15) were less than 5% if materials already rejected for use with modern gasoline were omitted; and the MnCAR study only found epichlorohydrin ethylene oxide copolymer to have swelled significantly larger in Aggressive TF20 than Aggressive TF10.

Many materials, including elastomers, plastics, and metals, have been tested on E15 and E20 with the results published in the studies described here. While not all materials are appropriate for all fuels, vehicle OEMs and manufacturers of fueling infrastructure components have been able to select appropriate materials for flex-fuel vehicles and the E85 fuel infrastructure that have successfully handled all ethanol blends between E10 and E85 for many years. E11-E15 ethanol-gasoline blends must be stored, transferred, and used in equipment appropriate for these fuels, but these materials are readily available for use in vehicles and in the fuel-handling infrastructure and a significant portion of the existing underground storage infrastructure, installed after 1989, readily meet current materials compatibility requirements for E15.

3.2 Ethanol Transport and Distribution

The transport of ethanol to marketing terminals in California is dependent upon the production location.

- Ethanol produced in California is transported to marketing terminals by road tanker trucks.
- Domestic ethanol produced outside of California is loaded onto railcars at the production plants and these railcars are typically transported to the state as unit trains.[52] These unit trains go to one of a small number of hub terminals where ethanol can be transloaded onto road tankers for delivery to marketing terminals. Some marketing terminals located outside of the major metropolitan areas can directly receive manifest rail cargos of ethanol.
- Waterborne imports of ethanol (e.g., from Brazil) are offloaded at the port of entry into shore tankage and then loaded onto road tankers for delivery to marketing terminals.

Once received at marketing terminals, the ethanol is stored in dedicated tanks. These tanks are generally shared by all marketers offering gasoline at the terminal, thus all sources of ethanol are typically commingled at this point. The bulk ethanol is then on-line blended with CARBOB into a road tanker to produce finished product (currently E10) for delivery to retail stations.

If approved for sale in California, gasoline-ethanol blends in the E11 - E15 range would be produced at marketing terminals in a similar manner as E10. In the future, alternatively, marketers could choose to ship only E10 and E85 to retail stations and then produce E15 blends at retail stations using blender pumps. The use of retail blender pumps to produce E15 and other intermediate blends is a common practice in states where those fuels are currently offered. California E85 fuel quality regulations are currently under review and once established can better understand how to offer at retail using a blender pump.

3.3 Infrastructure Compatibility

Equipment for distribution, blending, storage and dispensing of fuel, compatible with up to E15 and up to E85 is widely available for all commonly expected fuel-handling uses. However, should E11-E15 fuels be permitted in California, all fuel-handling equipment will need to be checked, and updated as necessary to ensure compatibility with any new fuels.

3.3.1 Misfueling Mitigation

The U.S. EPA has required each fuel ethanol manufacturer to submit a misfueling mitigation plan (MMP) in order to ensure that E15 is not mistakenly used by pre-2001 model year (MY) vehicles that may not be properly designed to use higher content ethanol blends.[53] Nationally, any station selling E15 fuel is required to prove implementation of a misfueling mitigation plan,[54] which would include displaying an EPA E15 label on each E15 providing dispenser, providing transfer documentation regarding delivery for all fuel intended for E15 use, and use of an officially sanctioned hose/dispenser arrangement.[55] In addition, each station must participate in a fuel quality survey designed to ensure that fuels offered for sale meet EPA requirements, and are properly labeled.[56] Most, if not all, U.S. service stations offering E15 meet this requirement by participating in the RFG Survey Association,[57] which conducts the sample collection

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[52] Unit trains, composed of 50 to 120 cars of the same commodity are transported directly from origin to destination. Smaller parcels, known as manifest cargos may be switched between different trains one or more times as they are moved from origin to destination. Unit trains offer lower costs and more reliable delivery schedules than manifest cargos.

[53] E15 Notices & Regulations. EPA. http://www.epa.gov/otaq/regs/fuels/additive/e15/e15-regs.html

[54] E15 MISFUELING MITIGATION PLAN. Renewable Fuels Association, 12 March 2012. https://www.epa.gov/sites/production/files/2015-09/documents/rfa-model-e15-misfueling-mitigation-plan.pdf

[55] E15 Retail Advisory. Renewable Fuels Association. January 2013. http://www.epa.gov/otaq/regs/fuels/additive/e15/documents/rfa-e15-retail-advisoryaddendum.pdf

[56] https://www.epa.gov/sites/production/files/2015-09/documents/420f15043.pdf

[57] http://rfgsa.org/

and analysis on their behalf. Results of the survey are compiled by the EPA.[58] The misfuelling mitigation requirements would be applicable in California, and a model mitigation plan has been approved by the U.S. EPA for use by all retailers.[54]

3.3.2 Underwriters Laboratories

Underwriters Laboratories (UL) is an independent engineering firm responsible for certification of refueling equipment. UL establishes standards via consensus with its industry partners and then tests equipment to ensure those standards are met. Many governing bodies require UL certification of equipment used with flammable fluids, such as fuels, via building or fire codes. Historically, UL has had fuel equipment standards that were only for gasoline, and later only for E10. However, with the legalization of higher ethanol blends, standards have been developed that allow refueling equipment to be certified for use with fuels up to E25, and, in many cases, all ethanol-gasoline blends between E0 and E100. Further information about UL standards, the years fuels were tested, and manufacturer products will be further developed in Tier II. The E15 study group will examine versions of the UL standards, both past and present, to understand what fuel rating existed for each version and identify which manufactured products were tested for blends above E10. Relevant refueling UL standards for E11-15 blends are in Table 3 below.

TABLE 3. CURRENT REFUELING EQUIPMENT UL STANDARDS

UL Testing Standard	Equipment Covered	Listing for Ethanol Blends
UL 58	Underground steel tanks	Does not list for specific fuels
UL 1746	External Corrosion Protection Systems for USTs	Option up to E100 (non-aggressive test fluids)
UL 1856	Underground Fuel Tank Internal Retrofit Systems	All fuels (including E25 and E85) as of June 14, 2017. Prior to this: option up to E100.
UL 142	Aboveground Flammable Liquid Tanks	Does not list for specific fuels
UL 1316	Underground fiberglass tanks	Option up to E100 (non-aggressive test fluids)
UL 971	Pipes and pipe fittings non-metallic	Option up to E100 (non-aggressive test fluids)
UL 971A	Pipes and pipe fittings metallic	Option up to E100 (non-aggressive test fluids)
UL 2447	*Sumps*: tank, dispenser, transition, fill/vent (spill buckets) *Sump fittings*: penetration, termination, internal, test and monitoring *Sump accessories*: cover, frame, brackets, chase pipe	E85 (non-aggressive test fluids for current listings). The new Standard 2447 requires testing with aggressive E25 and E85. Manufacturers must have been recertified by June 2016.
UL 2039	Flexible Connectors	All fuels (including E25 and E85)
UL 2583	*Part I Vapor Control Products*: emergency vents, pressure vacuum vents, fill and vapor adaptors, and monitor well caps	Part I and Part II require testing with aggressive E25, E85, B25, and Reference Fuel F.

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[58] https://www3.epa.gov/otaq/fuels1/gasolinefuels/rfg/properf/perfmeth.htm

	Part II Liquid Control Products: overfill protection (or prevention) valves, ball float vent valve (or flow restriction device), drop tubes, extractor tee, jack screw kit, face seal adaptor (or threaded riser adaptor), fill cap and adaptors	
UL 87	Power-operated dispensing devices for petroleum products	E10 (non-aggressive test fluid)
UL 87A	Power-operated dispensing devices for gasoline and gasoline–ethanol blends with nominal ethanol concentrations up to 85% (E0 – E85)	E25 and/or E85 (tests with aggressive test fluids)
UL 25	Meters for flammable and combustible liquids and LP-gas	E10 (non-aggressive test fluid)
UL 25A	Meters for gasoline and gasoline–ethanol blends with nominal ethanol concentrations up to 85% (E0 – E85)	E25 and/or E85 (tests with aggressive test fluids)
UL 79	Power-operated pumps for petroleum dispensing products	E10 (non-aggressive test fluid)
UL 79A	Power-operated pumps for gasoline and gasoline–ethanol blends with nominal ethanol concentrations up to 85% (E0 – E85)	E25 and/or E85 (tests with aggressive test fluids)
UL 330	Hose and hose assemblies for dispensing flammable liquids	E10 (non-aggressive test fluid)
UL 330A	Outline for hose and hose assemblies for use with dispensing devices dispensing gasoline and gasoline–ethanol blends with nominal ethanol concentrations up to 85% (E0 – E85)	E25 and/or E85 (tests with aggressive test fluids)
UL 331	Strainers for flammable fluids and anhydrous ammonia	E10 (non-aggressive test fluid)
UL 331A	Strainers for gasoline and gasoline– ethanol blends with nominal ethanol concentrations up to 85% (E0 – E85)	E25 and/or E85 (tests with aggressive test fluids)
UL 428	Electrically operated valves	E10 (non-aggressive test fluid)
UL 428A	Outline for electrically operated valves for gasoline and gasoline–ethanol blends with nominal ethanol concentrations up to 85% (E0 – E85	E25 and/or E85 (tests with aggressive test fluids)

UL 567	Emergency breakaway fittings, swivel connectors and pipe-connection fittings for petroleum products and LP-gas	E10 (non-aggressive test fluid)
UL 567A	Emergency breakaway fittings, swivel connectors and pipe-connection fittings for gasoline and gasoline–ethanol blends with nominal ethanol concentrations up to 85% (E0 – E85)	E25 and/or E85 (tests with aggressive test fluids)
UL 842	Valves for flammable fluids	E10 (non-aggressive test fluid)
UL 842A	Valves for gasoline and gasoline–ethanol blends with nominal ethanol concentrations up to 85% (E0 - E85)	E25 and/or E85 (tests with aggressive test fluids)
UL 2586	Hose nozzle valves	E10 (non-aggressive test fluid)
UL 2586A	Hose nozzle valves for gasoline and gasoline–ethanol blends with nominal ethanol concentrations up to 85% (E0 – E85)	E25 and/or E85 (tests with aggressive test fluids)

Some equipment currently in use in California is UL listed only to E10. Equipment with a UL listing of E10 could be considered compatible with E15 with a manufacturer’s statement of compatibility, however research and previous requests show that not all manufacturers will provide this document for blends above E10. Single-walled systems are currently forbidden to contain any blend greater than E10 without a UL certification. This is a very high bar that no known single walled system has achieved. There are thousands of pieces of equipment that are E15 compatible and carry both a UL listing and CARB certification.

California maintains robust information in its UST database. This database shows the names of manufacturers, which was used to determine the UL listing associated with the tanks being manufactured. RFA reviewed an initial set of 5,132 records from January 1, 2003 to the present and have provided UL information for 97% of these records in a separate memo to the State Water Board. RFA and Growth Energy intend to continue working with the Water Board to update the database on an ongoing basis based on field data.

Equipment compatibility is important to ensure safe fueling with E15. UL is an independent safety laboratory that has developed standards for listing refueling equipment. Many standards allow the option to list with specific ethanol blends. All fueling equipment manufacturers offer equipment that is UL listed for E10; many manufacturers offer equipment that is UL listed for use with blends up to E25 and/or equipment listed for use with blends up to E85. California underground storage tank (UST) regulations (23 California Code of Regulations [CCR] § 2640.1) allow UST owners to meet compatibility standards by using independent laboratory-certified equipment (UL) or by providing a written affirmative statement from the equipment manufacturer.[59]

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[59] https://govt.westlaw.com/calregs/Document/I9EFF2BB6E3F74B4DA9BBBB1D0BBF7656?originationContext=document&transitionType=StatuteNavigator&needToInjectTerms=False&viewType=FullText&contextData=%28sc.Default%29

A service station consists of many interconnected pieces of refueling equipment necessary to fuel vehicles effectively and safely, including approximately 60 pieces of equipment designed to handle fuel and fuel vapor. The equipment that delivers fuel to a vehicle includes tanks, pipes, a submersible turbine pump, a dispenser, and hanging hardware.[60]

The remainder and majority of the service station refueling equipment is used to receive and store fuel and prevent, detect, and contain releases. This equipment includes an overfill protection device, a leak detection device, shear valves, fill and vapor caps and adaptors, containment sumps, and all associated fittings and accessories. Equipment that is compatible for use with ethanol blends above E10 is available in every category from multiple manufacturers. Above-ground equipment must be UL listed for the fuel dispensed. Below-ground equipment, which must be compliant with federal code, must either be UL listed for the fuel it dispenses or must have a letter from the manufacturer stating its compatibility with specific ethanol content.

Most existing tanks in California are UL-listed as compatible with ethanol blends up to 100%. All existing companies that manufacture steel tanks to store transportation fuels have issued signed letters stating their compatibility to store ethanol blends up to E100, making them compliant with federal code. All steel tank manufacturers have a UL 58 listing for flammable fuels, which includes all transportation fuels. Fiberglass tank compatibility depends on the manufacturer, the year the tank was built, and the type of tank (single or double wall). Both existing fiberglass tank companies, Xerxes and Containment Solutions, have maintained a UL Standard 1316 listing for E100 for many years. Containment Solutions issued a letter stating that all tanks it has manufactured are with compatible all ethanol blends.[61] Xerxes and Owens Corning (which no longer manufactures tanks) have stated that compatibility depends on the tank wall type and the year it was manufactured.

Several dispenser manufacturers offer products for blends above E10 including UL listed E25 and E85 dispensers with blender pump options.

Hanging hardware includes hoses, nozzles, breakaways, and swivels. Both Husky and OPW offer UL listed E25 and E85 nozzles, swivels, and breakaways. Veyance offers UL listed E25 and E85 hose. Shear valves are an important piece of safety equipment that stop the flow of fuel from the underground storage tank to the dispenser. They prevent fuel release in the event of an accident dislodging the dispenser or a fire. UL listed E85 shear valves are available from Franklin Fueling and OPW.

Submersible turbine pumps draw fuel from the tank and into the piping that delivers the fuel to the dispenser. Both Veeder-Root and Franklin Fueling offer UL listed E85 pumps. Wayne Fueling Systems' standard dispenser is UL listed for E25. Wayne also offers E85 dispensers as an option on multiple models. Gilbarco offers both UL listed E25 and E85 dispensers, and Bennett offers UL listed E85 dispensers.

All pipe currently being manufactured meets UL 971 listing for ethanol blends up to E100. To comply with federal code, other underground equipment manufacturers have either UL listed their equipment up to E85 or have stated approval in writing for specific model types with blends above E10. Other underground equipment includes overfill protection, leak detection, shear valves, fill and vapor caps, adaptors, containment sumps, and all associated fittings and accessories.

For lists of UL E10+ listed tanks, pipe, underground fuel handling equipment, dispensers, hanging hardware, shear valves, and submersible turbine pumps, please refer to the US Department of Energy's *Handbook for Handling, Storing, and Dispensing E85 and Other Ethanol-Gasoline Blends*.[62] There are several additional resources retailers can use to determine if their equipment is compatible:

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[60] Alternate Fuel Data Center, U.S. Department of Energy. https://afdc.energy.gov/fuels/ethanol_equip_options.html

[61] http://containmentsolutions.com/assets/biofuel-compatibility.pdf

[62] U.S. Department of Energy, *Handbook for Handling, Storage, and Dispensing E85 and other Ethanol-Gasoline Blends*. https://afdc.energy.gov/files/u/publication/ethanol_handbook.pdf

Petroleum Equipment Institute – www.pei.org
The Petroleum Equipment Institute is a trade association whose members manufacture, distribute and service petroleum marketing and liquid handling equipment. Founded in 1951, PEI represents more than 1,600 member companies in all 50 states and more than 80 countries. Members include manufacturers, sellers and installers of equipment used in service stations, terminals, bulk plants, fuel, oil and gasoline delivery, and similar petroleum marketing operations. PEI offers a variety of industry-related items covering technical and regulatory information of special concern to manufacturers, sellers, installers and users of petroleum marketing equipment. These items are designed to help you navigate tricky regulatory issues and federal compliance issues. In 2015 EPA published guidance regarding compatibility of underground storage tank (UST) systems with biofuel blends. The guidance discusses how owners and operators who wish to store gasoline containing more than 10 percent ethanol or diesel containing more than 20 percent biodiesel in their UST systems may demonstrate compliance with the compatibility requirement in 40 CFR 280.32 Compliance letters issue by manufacturers can be found here: https://www.pei.org/ust-component-compatibility-library

Steel Tank Institute - https://www.steeltank.com
Since 1916, the Steel Tank Institute has been a creator of cutting-edge storage tank technology, consulting with government and third-party agencies to advocate for the highest standards. STI/SPFA is now identified by federal and state government, the broader steel industry, third-party agencies, and consumers as the organization best representing the steel fabrication industry. We are recognized for our leading tank technologies, storied history, active advocacy, and prominent activities and programs.

Fiberglass Tank and Pipe Institute – www.fiberglasstankandpipe.com
This site provides information on the Fiberglass Tank & Pipe Institute - Member Companies. General information, applicable fiberglass standards, fiberglass products, published Institute white papers, direct links to company members and information on how to contact the Institute. The nonprofit institute was incorporated in 1987. Member companies must meet certain criteria – including standard UL listing as a

National Renewable Energy Laboratory (NREL) - https://www.nrel.gov/docs/fy15osti/64156.pdf
"*E15 and Infrastructure*" looks at compatibility of E15 through a literature review of published works by refueling equipment manufacturers, industry groups and federal agencies. The paper also includes a summary of applicable codes and standards, review of equipment manufacturer products, and verification with manufacturers regarding which ethanol blends work with their products.

3.3.3 California Vapor Recovery Regulations

The California Air Resources Board (CARB) mandates vapor recovery requirements for gasoline dispensing facilities (GDF), tanker trucks, bulk plants and terminals that are different than those required federally or by UL. In order to meet their unique requirements, CARB has developed its own test procedures for vapor recovery equipment. Phase I certifications are in place to control gasoline vapors emitted during the refueling of storage tanks and Phase II controls gasoline vapors emitted during the refueling of vehicle tanks. The complete system requiring approval includes the following: all associated dispensers, piping, nozzles, couplers, processing units, underground tanks, and any other components needed at GDF for vapor control. A comprehensive list of all Phase I and Phase II vapor recovery standards and specifications can be found in CARB's *Vapor Recovery Certification Procedure.*[63] None of these requirements are fuel specific; they simply provide limits for efficiencies, leakage and permeation rates, pressure settings, and collaborating equipment functions.

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[63] Vapor Recovery Certification Procedure. Certification Procedure for Vapor Recovery Systems at Gasoline Dispensing Facilities. California Environmental Protection Agency Air Resources Board, 23 April, 2015. https://www.arb.ca.gov/testmeth/vol2/CP201_april2016.pdf?_ga=2.237389191.64282148.1538405565-1092939258.1537286554

After CARB testing, if the equipment is approved, CARB issues an executive order delineating the specific makes and models that have been certified. In the executive orders CARB may use the following language:

> "….[the equipment] shall be compatible with gasoline in common use in California at the time of certification. Any modifications to comply with future California gasoline requirements shall be approved in writing by the Executive Officer or his delegate."

In other cases, CARB specifies the use of specific fuels (for example including E85 in Executive Order VR-101-Q; or fuels no greater than 15% ethanol in Executive Order VR-201-W). The language is in some cases ambiguous as to higher fuel concentrations including E15 and will need to be clarified to determine if E15 can be used in the equipment. The most up-to-date listing of CARB Enhanced Vapor Recovery (EVR) approved equipment, with the allowable fuels specified, was published by the National Renewable Energy Laboratory (NREL) in 2016.[64] Components not approved by CARB at higher ethanol levels will need to be evaluated by CARB for use with E15. However, this process, which is initiated by the component manufacturers, will likely not occur until it is clear that E15 will be marketed in California so that manufacturers can justify the cost of going through the approval process.

The Office of the State Fire Marshall also promulgates Laws and Regulations for Vapor Recovery[65] specific to California; these do not specify ethanol blend level and so will not be impacted by any change in the allowable ethanol concentration.

3.3.4 Storage Equipment

Components associated with underground and aboveground storage tanks must be compatible with the stored fuel: including (but not limited to) the tank itself (including the tank lining), piping, line leak detector, flexible connectors, drop tube, spill overflow equipment, submersible turbine pumps (STPs), sealants (pipe dope, thread sealant, fittings, gaskets, O-rings, bushings, couplings, boots), containment sumps, release detection floats, sensors/probes, and fill and riser caps.

California requires that that any underground tank systems (including the tank) be made from or lined with materials compatible with the stored liquid (Title 23, DIVISION 3, CHAPTER 16, § 2631.1). This requirement can be met by UL listing (or by other recognized, independent laboratory certification).

All steel tanks currently manufactured are listed under UL 58 for use with all flammable liquids.[64] UL listing, confirming compatibility with E11-E15, is assumed for equipment certified with E85 or E100. Fiberglass storage tanks have varying compatibility depending on the year and manufacturer. Owens Corning, a company which no longer manufactures tanks, produced single and double wall tanks between 1965 and 1994. Single (manufactured between 1965 and 1994) and double (manufactured between 1965 and July 1, 1990) wall tanks are approved to store up to E10. Double wall tanks manufactured between July 2, 1990 and December 31, 1994 are approved up to E100. Containment Solutions has manufactured UL certified tanks approved up to E100 since January 1, 1995. Single wall fiberglass tanks manufactured by Xerxes before 1981 are not approved for any ethanol blend. Xerxes single wall tanks manufactured between February 1981 and June 2005 are approved for up to E10 and from July 2005 to the present are UL listed and approved to E100. Double wall fiberglass tanks manufactured by Xerxes before April 1990 are approved for E10 and from April 1990 to the present are UL listed and approved to E100.

The additional components present at retail stations, either underground or in-tank, to assist in fuel deliveries and to prevent, detect, and contain leaks have their own compatibility standards. A list of manufacturers, models, and their associated ethanol level approvals can be found in the U.S. Department of Energy's *Handbook for Handling, Storing, and Dispensing E85 and Other Ethanol-Gasoline Blends*.

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[64] Moriarty, K. and Yanowitz, J. E15 and Infrastructure. National Renewable Energy Laboratory. May 2015. https://ethanolrfa.org/wp-content/uploads/2017/07/E15-Infrastructure_Moriarty-Yanowitz_2015.pdf

[65] Vapor Recovery Program. Department of Forestry and Fire Protection Office of the State Fire Marshal Fire Engineering Division. Laws and Regulations for Vapor Recovery. 2011. http://osfm.fire.ca.gov/strucfireengineer/strucfireengineer_vaporrecovery.php

3.3.5 Distribution and Blending Equipment

3.3.5.1 Approaches to Gasoline-Ethanol Blending

Ethanol blends of E10 or E15 are not currently shipped by pipeline, nor are they expected to be shipped by pipeline in the future. Typically, gasoline and denatured ethanol are transported to a terminal where they are blended to appropriate concentration levels and shipped by tanker truck to individual retail stations.

Pipes used for transport in-terminal or at the retail station are typically either flexible plastic or fiberglass. All pipe currently being manufactured meets UL 971 listing for ethanol blends up to E100. According to NREL, National Oilwell Varco (NOV) is currently the only manufacturer of fiberglass piping and in 1990 all its products obtained E100 approval. The company offers a 30-year warranty, while a typical flexible pipe warranty is 10 years. Because of a large market switch in the 1990s to accommodate flexible plastic pipes, some initial developmental issues occurred with a company called Total Containment. The company is no longer operating, and while its piping is thought to be almost entirely replaced it is possible some retail stations still function with this piping and the compatibility of these pipes with any ethanol blend is unknown. A complete list of the ethanol compatibility of UST equipment associated piping is available in the U.S. Department of Energy's *Handbook for Handling, Storing, and Dispensing E85 and Other Ethanol-Gasoline Blends.*

For those tanks with low ethanol blend certifications, the U.S. Environmental Protection Agency's (EPA's) Office of Underground Storage Tanks (OUST) issued Guidance – Compatibility of UST Systems with Biofuels Blends in 2011 to enable alternative compliance with federal code as UST systems are in use for decades. This guidance allowed tank manufacturers to issue letters stating the compatibility of their tanks with specific ethanol blends. All existing tank manufacturers have issued such letters, and most installed tanks are compatible with E15. Additionally, all existing pipe manufacturers have Underwriters Laboratories (UL) listing for E100.[66]

Underground Piping UL 971 "Underground Piping for Flammable Liquids" standard applies to primary and secondary containment non-metallic pipe and fittings intended for use underground to transfer petroleum-based flammable and combustible liquids, alcohols, and alcohol-blended fuels.

EPA requires that methanol blends exceeding 5% methyl alcohol meet hazardous substance storage and piping requirements and be secondarily contained. Thus, all double wall fiberglass tanks and piping have been manufactured for storage of 100% ethyl and methyl alcohol since 1988 for piping and 1990 for tanks. While E10 ethanol entered the marketplace in 1978, Underwriters Laboratory (UL) did not include gasohol and methanol fuels in their material compatibility testing protocol, until later. As a result, the UL Listing for fiberglass tanks and piping included ethanol in 1983 and 1988 respectively (i.e., UL 1316 and UL 971).

- Fiberglass Piping: Underground fiberglass piping and fittings installed in service stations have been compatible with up to E100 for over 40 years.
- 1988 – UL began listing underground fiberglass piping for E100 under UL971
- 2013 – Oak Ridge National Laboratory published study results on increasing E10 to E15 and if it would cause an increase in UST failures. For resins introduced in 1990 or later in tanks & piping "…the risk associated with leaking when switching from E10 to E15 will be low".[67]

Since 1988 all fiberglass piping systems have been listed under UL971 however there was another type of piping system to hit the market in the mid 90's known as Flexible Piping. The E15 study group will

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[66] Fiberglass Tank and Pipe Institute / http://www.fiberglasstankandpipe.com/piping/

[67] U.S. Environmental Protection Agency. https://www.epa.gov/sites/production/files/2014-03/documents/flexpip4.pdf

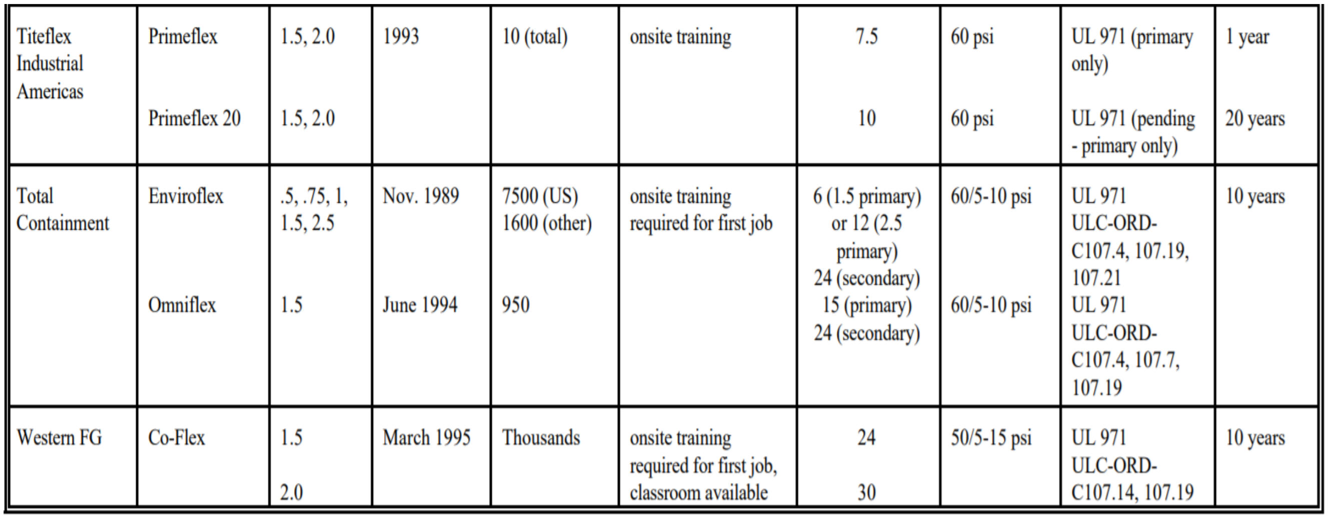
assess whether pre-1990 compatibility study is required during the Tier II based on proposed limits to E15 in California.

Flexible piping technology has come into widespread use for dispensing motor fuels. Since 1995, the flexible piping industry has seen an approximately 50 percent increase in the number of system installations. With the increasing use of MTBE, several flexible piping manufacturers have performed product testing for MTBE, and some manufacturers have requested and received UL and/or ULC testing for MTBE. To date, problems with flexible piping systems have been limited to fungal decay of first generation polyurethane coated piping. The fungal decay is mostly cosmetic and does not cause product failure, however, one manufacturer (Total Containment) has changed its outer layer construction to polyethylene and is in the process of replacing the polyurethane piping. Most manufacturers are now marketing third and fourth generation products. Problems with these systems have been infrequent, and manufacturers have stood by their products. From an environmental protection standpoint, the performance of this technology to date has been excellent.

Between the years of the 1989 to 1998 there were 14036 tank records in the California UST database. Of note 83% are noted as double wall fiberglass. The remaining 2408 records contained data on flexible piping and steel piping. Table 4 below shows that all manufacturers have carried a UL listing except for the manufacturer Buffalo who was in business one year with less than 300 total US installs.

TABLE 4: UL LISTING FOR FLEXIBLE PIPING

Company	Product	Diameter (Inch)	First Installation	Number of Installations	Installer Training	Minimum Bend Radius (Inches)	Test Pressure: Primary/ Secondary	Listing	Materials Warranty
Advanced Polymer Technology	Poly-Tech	.5, .75, 1, 1.5, 1.75, 2, 3	May 1992	2500 world wide (65-70% US)	on-site training required for first job, video training aids available	24 (1.5" pipe)	60/10 psi (1.5")	UL 971 ULC-ORD-C107.14, 107.19, 107.21 (see text for specific listings)	10 years
Ameron	Dualoy 3000/FLX II	1.5 2.0	April 1995	70	on-site training required for first job. Classroom training and slide program also available	24 30	50/10-15 psi	UL 971	10 years
	Dualoy 3000/FLX III	1.5 2.0	June 1996	50		24 30	50/10-15 psi	UL 971	10 years
Buffalo[1]	*Bufflex II*	*1, 1.5, 2*	*1989-90*	*300 (US)* *700 (other)*	*on-site training required for first job*	*15*	*60/5-15 psi*	*ULC-ORD-C107.4, 107.19, 107.21*	*30 years + pollution liability insurance*
Containment Technologies	Perma-Flexx	.75, 1.65, 2	March 1993	1200 (75% North America, 25% South America)	training video; onsite training is optional	36	60/5 psi	UL 971 (primary only) ULC-ORD-C107.14, 107.19, 107.21	10 years
Environ	GeoFlex-S GeoFlex-D	.75, 1.5, 2, (3" -Spr. '97)	June 1992	Thousands worldwide	onsite training required for first job	24	60/10 psi	UL 971 ULC-ORD-C107.14, 107.19, 107.21	10 years 30 year system



Titeflex Industrial Americas	Primeflex	1.5, 2.0	1993	10 (total)	onsite training	7.5	60 psi	UL 971 (primary only)	1 year
	Primeflex 20	1.5, 2.0				10	60 psi	UL 971 (pending - primary only)	20 years
Total Containment	Enviroflex	.5, .75, 1, 1.5, 2.5	Nov. 1989	7500 (US) 1600 (other)	onsite training required for first job	6 (1.5 primary) or 12 (2.5 primary) 24 (secondary)	60/5-10 psi	UL 971 ULC-ORD-C107.4, 107.19, 107.21	10 years
	Omniflex	1.5	June 1994	950		15 (primary) 24 (secondary)	60/5-10 psi	UL 971 ULC-ORD-C107.4, 107.7, 107.19	
Western FG	Co-Flex	1.5	March 1995	Thousands	onsite training required for first job, classroom available	24	50/5-15 psi	UL 971 ULC-ORD-C107.14, 107.19	10 years
		2.0				30			

As a tool for recognizing compatibility, RFA has a reference guide available for retailers to help identify what piping may be installed at their locations. Product specific details are included for the following manufacturers:

- Advanced Polymer Technologies
- Ameron
- Brugg Pipe Systems
- Buffalo Environmental Products*
- Containment Technologies*
- Environ Products, Inc*
- Innovative Petroleum Products
- Kungsor Plast
- NUPI
- OPW
- Omegaflex
- Petrofuse ZP
- Petrotechnik
- Smith Fibercast
- Total Containment, Inc*
- Western Fiberglass, Inc

3.3.5.2 Piping

Pipes used for transport in-terminal or at the retail station are typically either flexible plastic or fiberglass. All pipe currently being manufactured meets UL 971 listing for ethanol blends up to E100.[68] According to NREL, National Oilwell Varco (NOV) is currently the only manufacturer of fiberglass piping and in 1990 all of its products obtained E100 approval. The company offers a 30-year warranty, while a typical flexible pipe warranty is 10 years. Because of a large market switch in the 1990s to accommodate flexible plastic pipes, some initial developmental issues occurred with a company called Total Containment. The company is no longer operating, and while its piping is thought to be almost entirely replaced it is possible some retail stations still function with this piping and the compatibility of these pipes with any ethanol blend is unknown. A complete list of the ethanol compatibility of UST equipment associated piping is available in the U.S. Department of Energy's *Handbook for Handling, Storing, and Dispensing E85 and Other Ethanol-Gasoline Blends*.

3.3.6 Retail Site Equipment

There are many pieces of equipment designed to move, store and control fuel at a typical service station. This section will focus on the aboveground components not previously analyzed in the storage or distribution and blending sections. These components include dispensers, hanging hardware (breakaways, hoses, nozzles and swivels), shear valves, and STPs. Several options exist to dispense ethanol blends above E10. Veeter-Root (Gilbarco) sells an E25 UL-listed retrofit kit to convert an existing dispenser. It is also possible to purchase a UL-listed E25 dispenser with minimal cost over a traditional E10 dispenser or a UL-listed E85 blender pump dispenser at a higher cost than an E10 dispenser but with more fuel offering options. OPW has an E25 listing for a conventional swivel and breakaway, as well as a UL-listed E85 nozzle. Husky manufactures UL-listed E25 and E85 nozzles. Veyance produces UL-listed E85 hoses and, along with EMCO, Wheaton, and IRPCO, hoses warrantied at E15. STPs bring fuel from the storage tank to the dispenser and the purpose of a shear valve is to stop this flow of fuel in case of accidental dislodging of the dispenser or fire. Both Franklin Fueling and OPW provide UL listed E85 shear valves, and both Veeder-Root (Gilbarco) and Franklin Fueling offer UL listed E85 STPs.

As of June 30, 2016 new containment sumps, fittings and accessories are in compliance with an updated UL 2447 and are approved for all automotive fuels, including E25 and E85.[64] However, many older sumps will need to be replaced to ensure compatibility with E15. For further information regarding dispenser, hanging hardware, shear valve, and STP manufacture compatibility, consult the U.S. Department of Energy's *Handbook for Handling, Storing, and Dispensing E85 and Other Ethanol-Gasoline Blends*.[68]

3.3.7 Infrastructure Compatibility Summary

Although not all equipment in current fuel handling and storage use in California is appropriate for use with higher ethanol blends, newer versions of equivalent equipment have been tested and approved by Underwriters Laboratories (UL) for use with ethanol blends up to E25, and in many cases up to E100. Much of this equipment is already in wide use throughout the country and in California. In other locations, older equipment or equipment for which the owner cannot determine whether the components are compatible will need to be replaced with equipment that is certified for use with higher ethanol content blends. Some UL standards will need to be updated in order to allow certification for up to E15, where it is uneconomical to use equipment manufactured for use with E85.

Much as when ethanol replaced MTBE in the fuel supply in the early years of this century, appropriate safeguards must be in place to ensure that new fuels are placed only in equipment that has been approved for use with those fuels. In order to ensure that all necessary equipment is verified to be compatible with E11-E15, the state of California could benefit from offering official guidance for retailers to refer to throughout the process. For example, the Wisconsin Department of Agriculture, Trade, and Consumer Protection provides an Alternative Fuel Storage Tank System and/or Dispenser Installation/Conversion Application which has a comprehensive checklist for determining equipment compatibility and other necessary preparatory actions.[69]

3.4 Evaporative Emissions from Infrastructure

California requires fuels to be stored, transported and dispensed using systems that control emissions. Despite this, there is a limited potential for vented vapor emissions and leaks from infrastructure.

No testing on the relative vapor emission rates of different ethanol-gasoline fuels in infrastructure has been made, however it can reasonably be estimated that evaporative emissions of organics via venting are roughly proportional to the concentration of volatile organics in the vapor phase. Concentration of

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[68] Handbook for Handling, Storing, and Dispensing E85 and Other Ethanol-Gasoline Blends. U.S. Department of Energy. Energy Efficiency & Renewable Energy. February 2016. https://www.afdc.energy.gov/uploads/publication/ethanol_handbook.pdf

[69] E15: What Retailers and Service Companies Need to Know. Presented by: Judy Cardin. Bureau of Weights and Measurements. Wisconsin Department of Agriculture, Trade, and Consumer Protection. https://www.wpmca.org/assets/ethanol/E15_What_Retailers_Need_to_Know.pdf

organics in the vapor phase over a liquid fuel is the vapor pressure of the fuel divided by the ambient pressures. Since the vapor pressure of E11- E15 will be less than or equal to that of E10 (see Section 4.3.2), the evaporative emissions of these fuels from infrastructure should be less than or equal to those from E10.

This estimate does not consider the potential that permeation emissions may be affected by chemical interactions between the fuel and elastomers used in the infrastructure system. The applicable evidence of this comes from vehicles, which likely use many of the same elastomeric materials for fuel handling in a vehicle that are used in fuel handling infrastructure. These tests are discussed in greater detail in Section 4 and showed no impact of higher ethanol contents on permeation emissions at levels of up to E20.

3.5 Fire Safety

This section explores the differences between gasoline-ethanol blends in the E11 – E15 range and currently available E10 products to determine if, and to what extent, E11 – E15 fuels pose additional fire safety risks should they become widely available in California. It also discusses whether these potential risks warrant implementation of risk mitigation measures and emergency response procedures beyond those currently used to manage E10 fire hazards.

3.5.1 Fuel Properties

Like gasoline, ethanol-blended fuels are highly flammable and volatile, due in part to their relatively low flash points, low Lower Explosive Limits (LELs), and relatively high vapor pressures. The ways in which blending higher percentages of ethanol with gasoline affect these characteristics are detailed below.

Vapor Pressure: An ethanol-blended fuel's vapor pressure, or the pressure exerted by the gaseous phase when in thermodynamic equilibrium with its liquid phase at a given temperature within a closed system, is directly related to the fuel's overall volatility. Fuels with higher vapor pressures are more volatile, and within the context of fire safety, can pose greater risks of catching fire or producing explosive atmospheres.

Blending gasoline with up to 10% ethanol has been shown to initially increase fuel vapor pressure, increasing the gasoline's baseline vapor pressure by approximately 0.5-1.3 pounds per square inch (psi). When gasoline is blended with ethanol in excess of 10%, vapor pressure steadily decreases as the percentage of ethanol increases, as shown in Figure 4. E15 is expected to have a slightly lower vapor pressure than E10. Initial vapor pressures and total decreases in vapor pressure measurements have been shown to vary widely based on temperature, fuel grade, and fuel vapor pressure/distillation class.[70]

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[70] American Petroleum Institute (API), *Determination of the Potential Property Ranges of Mid-Level Ethanol Blends.* (2010).

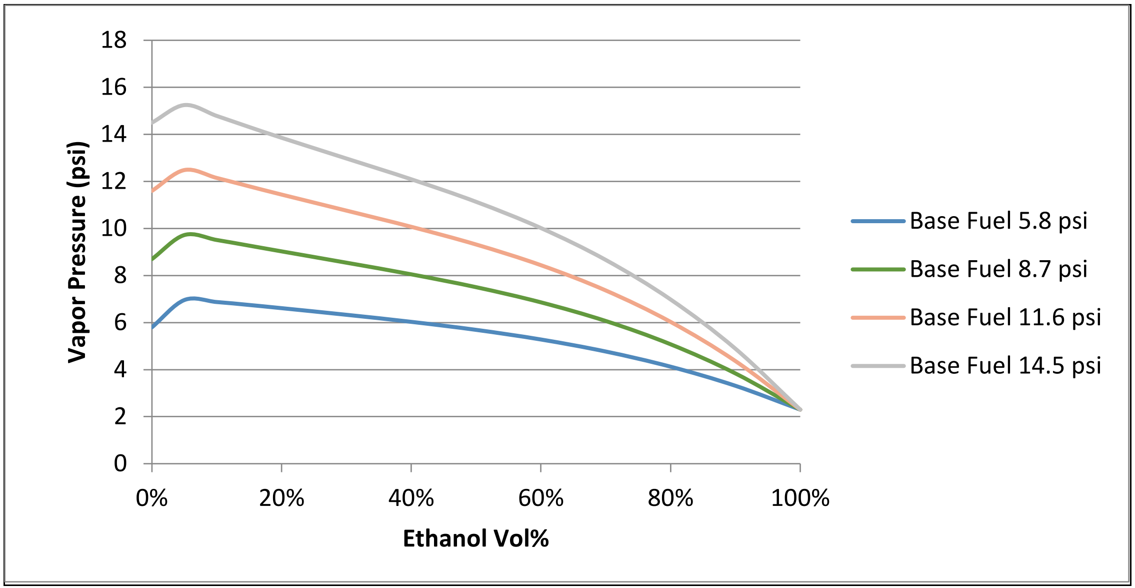

FIGURE 4. PREDICTED EFFECT OF ETHANOL BLENDING ON VAPOR PRESSURE OF GASOLINE FOR BLENDSTOCKS OF DIFFERENT VAPOR PRESSURE.[71]

Flash Point: Flash point is defined as the lowest temperature at which fuel vapors will ignite upon introduction of an ignition source. The lower the flash point, the easier it is to ignite the material. Flash points for neat ethanol is 55°F, denatured fuel ethanol and E10 are 19.4°F and -45°F, respectively.

Lower Explosive Limits: LELs, which are also referred to as Lower Flammability Levels (LFLs), are the minimum vapor concentrations, reported by percentage, required to create an explosive or flammable atmosphere at ambient temperatures and pressures. Baseline LELs for ethanol and gasoline are 3.3% and 1.4%, respectively. E10's LEL is 1.6%, indicating the addition of ethanol increases LEL, or raises threshold at which an atmosphere becomes explosive but is still like that of gasoline and is normally too rich to burn in a tank headspace.

Upper Explosive Limits: UELs, also referred to as Upper Flammability Levels (UFLs) or the maximum fuel vapor concentrations for which atmospheres remain explosive, for ethanol and gasoline are 19% and 7.6%, respectively. Once blended, E10's UEL is 8.7% (Reddy, 2011; NREL, 2011).[72] [73] The UFL of ethanol is higher than gasoline, which makes ethanol-containing vapor ignitable at higher concentrations and higher temperatures.

Blending gasoline with a percentage of ethanol greater than 10% appears to result in decreases in volatility, and though relatively small, a presumed increase in corresponding risk of fire or explosion. Gasoline-ethanol levels in the E11 – E15 range do not appear to pose new or significantly increased risks of fire or explosion.

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[71] Reddy, S.R., "A Model for Estimating Vapor Pressures of Commingled Ethanol Fuels," SAE Paper 2007-01-4006, 2007

[72] Reddy, S., *Mathematical Prediction of Flammaility of Ethanol-Containing Fuels* (CRC Report No. 661). Coordinating Research Council (CRC). (2011).

[73] National Renewable Energy Laboratory (NREL), Gardiner, D.P., Bardon, M.F., Clark, W., *Experimental and Modeling Study of the Flammability of Fuel Tank Headspace Vapors from Ethanol/Gasoline Fuels Phase 3: Effects of Winter Gasoline Volatility and Ethanol Content on Blend Flammability; Flammability Limits of Denatured Ethanol* (NREL/TP-5400-52043). National Renewable Energy Laboratory. (2011).

3.5.2 Mitigation of Fire Risks

Fire safety requirements that would be applicable to gasoline-ethanol blends in the E11 – E15 range with respect to dispensing, transportation, storage, and handling are outlined in the 2016 California Fire Codes (CFC) promulgated in California Code of Regulations Title 24, Part 9.[74] Fire codes in California are largely based on the 2015 International Fire Code (IFC) and National Fire Protection Association (NFPA) standards. Provisions specifically intended to reduce the likelihood of fires involving the storage, handling, use or transportation of flammable and combustible liquids such as gasoline and ethanol-blended fuels are found in Chapter 57, "Flammable and Combustible Liquids." Provisions regulating fuel storage at and dispensation from motor fuel-dispensing facilities are provided in Chapter 23, "Motor Fuel-dispensing Facilities and Repair Garages." Fire suppression and emergency response-related provisions found in these chapters and in CFC Chapter 9, "Fire Protection Systems," are addressed below in subsection 3.5.3 of this E15 multimedia evaluation.

Chapters 23 and 57 of the CFC include the following regulations designed to mitigate fire risks posed by "motor fuels" and "flammable and combustible liquids," respectively, at facilities in which they are stored, dispensed, or handled, such as fuel terminals and gas stations, and in situations in which they are transported and used:

- Minimum design standards and location restrictions for fuel storage tanks, piping, dispensing equipment, tanker trucks, and railcars, including restrictions on proximity to potential ignition sources, combustible materials , and other structures, construction standards prescribed by NFPA and promulgated by Occupational Safety and Health Administration (OSHA), physical protective barriers requirements, fuel compatibility requirements, and installation of equipment with emergency disconnects, emergency controls, breakaway hoses, dispensation quantity limitation equipment, vapor recovery systems, leak detection, and overfill alarms/protection;
- Fire and/or explosion hazard communication requirements, including installation of warning labels and signs visible to all personnel within the vicinity of fuel storage tanks, piping, dispensing equipment, tanker trucks, and railcars; and/or
- Spill prevention provisions, including required secondary containment, ventilation, fire extinguishing systems, routine inspections and maintenance requirements, onsite storage quantity limits, and established procedures for safe fuel delivery and offloading.

Although regulations listed in CFC 2306.8, "Alcohol-blended Fuel-Dispensing Operations," include equipment compatibility requirements for retailers of "alcohol-blended fuels," the regulations in Chapters 23 and 57 do not identify E10, E85, or any other ethanol-blended products as fuels warranting fuel-specific fire risk mitigation considerations beyond those provided for all flammable and combustible motor fuels. It therefore appears unlikely gasoline blends in the E11 – E15 range would or should warrant new or revised fire safety considerations within codified CFCs relative to E10.

3.5.3 Fire Suppression and Emergency Response

In the event fire safety provisions outlined in the previous subsection fail to prevent an ethanol-blended fuel-related fire emergency, onsite fire suppression equipment and emergency response procedures required under CFC Chapter 9, "Fire Protection Systems," and previously-mentioned Chapters 23 and 57, are designed to extinguish these fires and minimize the adverse effects to onsite personnel and property. Chapters 9, 23, and 57 include the following fire suppression and emergency response requirements for facilities engaged in fuel dispensation, transportation, storage, and handling activities:

- Develop an emergency response plan, prominently post and/or train onsite personnel on emergency response procedures, and provide contact information for emergency responders;
- Install, inspect, test, and maintain automatic fire detection systems, fire alarm systems, and emergency communication equipment; and/or

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[74] Accessible at: https://www.citymb.info/Home/ShowDocument?id=28089

- Install, inspect, test and maintain CFC-compliant fire suppression equipment, including portable fire extinguishers and foam fire protection systems.

As a polar solvent, ethanol is water soluble. The gasoline with which it is blended, however, is not water soluble, and introduction of water to burning ethanol-blended fuel may cause separation resulting in two different fire types in need of suppression. Safety Data Sheets (SDSs) for E10 products list water fog, alcohol-resistant foam, dry chemical, or carbon dioxide extinguishers as effective firefighting methods for ethanol-blended fuel fires, and state that water jets should not be used.

Of these methods, application of alcohol-resistant aqueous film-forming foam (AR-AFFF) is recognized as the most effective method for controlling ethanol-blended fuel fires. Once applied to a polar solvent fuel fire, a polymer precipitates out of the AR-AFFF foam, forming a physical barrier between the fuel surface and foam blanket. The barrier prevents the polarity of the ethanol from destroying the foam blanket, allowing it to effectively extinguish the fire. CFC 906.2 specifically prohibits use of traditional AFFFs and film forming fluoroprotein- (FFFP) foams, which can be broken down by polar solvents like ethanol, unless approval for such use is specifically referenced on the product label.

While the introduction of gasoline-ethanol blends in the E11 – E15 range, it may further underscore the importance of using AR-AFFFs for extinguishing ethanol-blended fuel fires and accelerate the transition away from less effective firefighting methods, there appears to already be a consensus amongst policy makers and emergency responders alike that these products should be included in existing onsite fire suppression systems and utilized by emergency responders. Therefore, there does not appear to be a need for development of new or improved firefighting processes, procedures, or technologies to effectively respond to E15 related fire emergencies, relative to E10.

3.6 Summary of Findings

E11 – E15 gasoline-ethanol blends must be stored, transferred and dispensed from equipment appropriate for these fuels. However, that equipment is currently readily available in California. Listing by Underwriters Laboratories (UL), which tests for compatibility, is available for all the different kinds of fuel-handling equipment necessary for storage, dispensing and transport of fuels except for certain California-specific vapor recovery equipment. A process can be developed to assure E15 is stored and distributed in a safe and compliant manner.

Testing of California specific vapor recovery equipment with E11 – E15 fuels may be necessary to ensure an adequate range of approved equipment for higher ethanol blends.

The existing California UST database shows that a significant percentage of tanks are already compatible with E11 - E15 storage, and the vast majority of tanks built, UL-certified, and installed in 1989 or later in California are compatible with E11 - E15 storage as well. Facilities with older equipment that is not UL listed for higher concentration ethanol fuels will need to upgrade to handle E11 – E15 fuels.

Current California regulations restrict the availability of E11 - E15 blending at retail sites using blender pumps because of concerns about the resulting ethanol-fuel blends meeting California quality requirements, in particular if the E85 blendstock contains natural gasoline rather than CARBOB. Currently there are no fuel quality standards for E11 - E15 blends made by using E85 and E10 blendstocks and blended at retail sites with blender pumps. This Tier 1 report therefore contemplates E11-E15 blending only using currently-approved processes at terminal sites with CARBOB blendstock. Additional regulatory changes may be needed to accommodate E11 - E15 blending other than at terminal sites.

Fire safety requirements for fuel-handling equipment that would be applicable to gasoline-ethanol blends in the E11 – E15 range are already included in the 2016 California Fire Codes. Alcohol-resistant aqueous film-forming foam (AR-AFFF) is recognized as the most effective method for controlling ethanol-blended fuel fires, whether the fuel is E10 or in the E11 – E15 range.

4 Use of Gasoline-Ethanol Blends in Vehicles

As discussed in Section 1.2, since 2010, virtually all fuel sold in the United States, and all California RFG, has been E10 and few if any ill effects have been observed in the existing vehicle fleet. Given this, California E10 rather than E0 is the appropriate basis for comparison with gasoline-ethanol blends in the E11 – E15 range. Since only 2001 and later model-year light-duty vehicles are approved to use gasoline-ethanol blends above E10 by U.S. EPA, older vehicles and non-vehicular engines, motorcycles, heavy-duty vehicles, as well as off-road vehicles such as boats and snowmobiles, which are prohibited by U.S. EPA from using higher ethanol content fuels than E10 are not considered here. Some portion of the flexible fuel vehicles (FFVs), which comprise between 5% and 10% of the on-road fleet (more than 20 million on the road in the United States[75]) that operate primarily on E10, may begin to operate on E15.

It is proposed that approval of E15 would initially be for a product created using a CARBOB that would meet all California requirements for an E10 BOB. Longer term, we anticipate that other BOBs could also be permitted as long as the E15s produced meet emission standards, in the same way that CARB currently permits variability in the BOBs produced for E10. This approach allows refiners to minimize refinery costs, while maintaining air quality.

4.1 Vehicle Compatibility

4.1.1 Vehicle design

In 2007, EPA approved E15 for the use of all MY2001 and later light-duty vehicles. And since 2012, automakers have increasingly warranted their vehicles for use with E15 such that nearly 90 percent of 2019 MY U.S. vehicles are now warrantied for such E15 (see Section 4.2),which ensures material compatibility of the fuel system and that all emissions requirements are met when new and at full useful life. However, to determine whether older vehicles (MY 2000-2009) are also compatible with higher gasoline-ethanol blends, two programs have tested relatively large numbers of older vehicles for extended times on E15 and E20 and found relatively few issues.

A study undertaken in 2006 at the University of Minnesota,[76] for example, included 40 pairs of vehicles, model years 2000-2006, with matched usage patterns. One of each pair used commercially available E0, while the second was fueled with E20, made from commercially available E10 splash blended with additional ethanol. During the test period, only two vehicles in the program had maintenance issues, with only one being fuel related, and that was in an E0-fueled vehicle. Thus, the data from this program suggest that these older vehicles (in this case, MY 2000-2006) would not have increased maintenance issues associated with the use of gasoline-ethanol blends above E10 and up to E20.

A far more intensive program[77], overseen by the Oak Ridge National Laboratory, included 82 MY 2000-2009 vehicles. Eighteen vehicle models (each represented by three matched vehicles) were aged with E0, E15 and E20; five vehicle models (each represented by four matched vehicles) were aged with E0, E10, E15 and E20; and four vehicle pairs were aged with E0 and E15. The E0 was TOP-TIER^{TM}[78] retail E0 fuel, into which ethanol was splash blended to produce the other test fuels. Each vehicle was aged the equivalent of 50,000 to more than 100,000 miles on each test fuel. The testing was conducted at three

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[75] https://www.afdc.energy.gov/vehicles/flexible_fuel.html, accessed August 23, 2018.

[76] Kittleson, D., A. Tan, D. Zarling, B. Evans, C. Jewitt, Demonstration and Driveability Project to Determine the Feasibility of Using E20 as a Motor Fuel, November 2008.

[77] West, B., Sluder, C.S., Knoll, K., Orban, J., Feng, J., Intermediate Ethanol Blends Catalyst Durability Program, ORNL/TM-2011/234, February 2012.

[78] TOP-TIER^{TM} is a fuel quality specification created and enforced by automakers. It is primarily intended to ensure that the fuel includes adequate level of detergents to avoid deposits on critical engine parts. More information can be found on the program website: www.toptiergas.com.

different facilities, the Southwest Research Institute (SwRI), the Transportation Research Center (TRC) and Environmental Testing Corporation (ETC). ETC is located in the Denver area and was included to assess the potential for altitude-related effects.

Unscheduled maintenance was recorded, and the affected equipment was removed and analyzed for potential fuel effects. Failures of certain components, including the transmission, spark plug and radiator which had no contact with the fuel, are not included here. Fuel system repairs that were required over the course of the testing included an evaporative emissions hose, believed to be made of nitrile rubber, which split on a 2002 Dodge Durango. No differences could be detected between the inside and the outside of the hose, so the failure was attributed to general aging, rather than fuel effects. Two fuel pumps in 2006 MY vehicles (plus a fuel pump and a fuel level sender in a 2000 MY vehicle) were replaced when they failed, although the researchers determined that the failures were unrelated to fuel. In addition, all three (E0, E15 and E20) 2006 Chevrolet Impalas experienced canister vent solenoid failures.

Finally, a tear-down study[79] of the engines in eighteen of the vehicles (six makes and models from model years 2006 to 2008, each run on E0, E15 and E20) showed an increase in intake valve deposits (IVD) in the E15 vehicles, relative to the E0 vehicles. The vehicles aged with E20 also showed an increase relative to both E15 and E0, although the results were not as consistent. The authors hypothesize that the increase was due to the dilution of the normal detergent additives which are present in TOP TIER™ gasoline. However, these deposits were not found to result in either operational problems or increases in emissions.

Evaporative emission canister working capacities showed a slight decreasing trend with higher concentration ethanol blends for one-third of the six different models. The emissions systems of the eighteen aged vehicles were pressure checked, and all were found to have maintained their integrity. No fuel related differences were found in valve seat width, valve surface contours, fuel tanks, fuel lines and evaporative emissions lines. Fuel injector flow rates were equivalent to within +/- 3%. There were no statistically significant differences in oil consumption attributed to the ethanol level in the fuel.[80]

Emissions were measured using EPA certification E0 fuel on all vehicles at the start of the project, at one or two points, and at the end of scheduled aging. No discernible difference in aging effects from the different fuels could be found except that on those vehicles tested by ETC which showed slightly less catalyst deterioration with higher ethanol blends. One hypothesis suggested by the researchers was that the sulfur content of the fuel was lowered as the result of dilution by ethanol as the ethanol level increased, although this impact was not seen in other vehicle sets. Largely based on these test results, which showed no degradation in emissions at gasoline-ethanol blend levels up to E20, EPA has permitted the use of gasoline-ethanol blends of up to E15 in all 2001+ MY vehicles.

The CRC has conducted studies focused on finding and testing vehicles and components suspected of being most susceptible to damage from E15 and E20. One pump, identified only as Pump N, was shown to have a greater failure rate with E15 in comparison to standard E10.[81] However, confidentiality rules which limit CRC's ability to divulge the make and model of the pump, as well as the materials of which it is made, limit the usefulness of this information to the general scientific community.

In addition, the Minnesota Center for Automotive Research conducted a 30-day static soak test[82] followed by 4000-hour endurance tests[83] for eight different models of fuel pumps and three different models of

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[79] Shoffner, B., Johnson, R., Heimrich, M., Lochte, M., Powertrain Component Inspection from Mid-Level Blends Vehicle Aging Study, ORNL/TM-2011/65, November 2010.

[80] West, B., Sluder, C.S. "Lubricating Oil Consumption on the Standard Road Cycle", SAE Technical Paper No. 2012-01-0884.

[81] CRC, Durability of Fuel Pumps and Fuel Level Senders in Neat and Aggressive E15, CRC Contract No AVFL-15a, January 2013.

[82] Mead, G., B. Jones, P. Steevens, N. Hanson, T. Devens, C. Rohde, A. Larson, The Effects of E20 on Automotive fuel Pumps and Sending Units, Minnesota Center for Automotive Research, February 21, 2008.

[83] Mead, G., B. Jones, P. Steevens, N. Hanson, J. Harrenstein, An Examination of Fuel Pumps and Sending Units During a 4000 Hour Endurance Test in E20, Minnesota Center for Automotive Research, March 25, 2009.

sending units[84] using E20, E10, and E0 (a total of 24 pumps and 9 sending units). No fuel effects were identified during the soak test, but during the 4000 -hour endurance testing, four pumps out of the twenty-four failed – two using E10 and two using E0. The commutators[85] of several of the pumps tested in E0 wore substantially more than those tested in either E10 or E20. No evidence of negative effects of use of E20 on fuel pumps was found. All of the sending units failed during the 4000-hour endurance testing, regardless of fuel. The units were not checked between the start and end of the experiment. Since all the units had failed, the authors reported no significant differences in performance or failure between the sending units as a function of test fuel.

One engine durability study was considered in this review[86] although its results were disregarded because of significant problems with its methodological and statistical approach. This study, and what we view as its methodological problems, is extensively discussed elsewhere.[87]

4.2 Manufacturer Warranty Limitations

FFVs are warrantied for the use of all levels of ethanol in fuel. Warranty information for use of gasoline-ethanol blends of up to E15 in non-FFVs is summarized in Figure 5 below. Other than the BMW Mini (warrantied for gasoline-ethanol blends up to E25), no past or current production vehicles have warranties allowing the use of fuels above E15.

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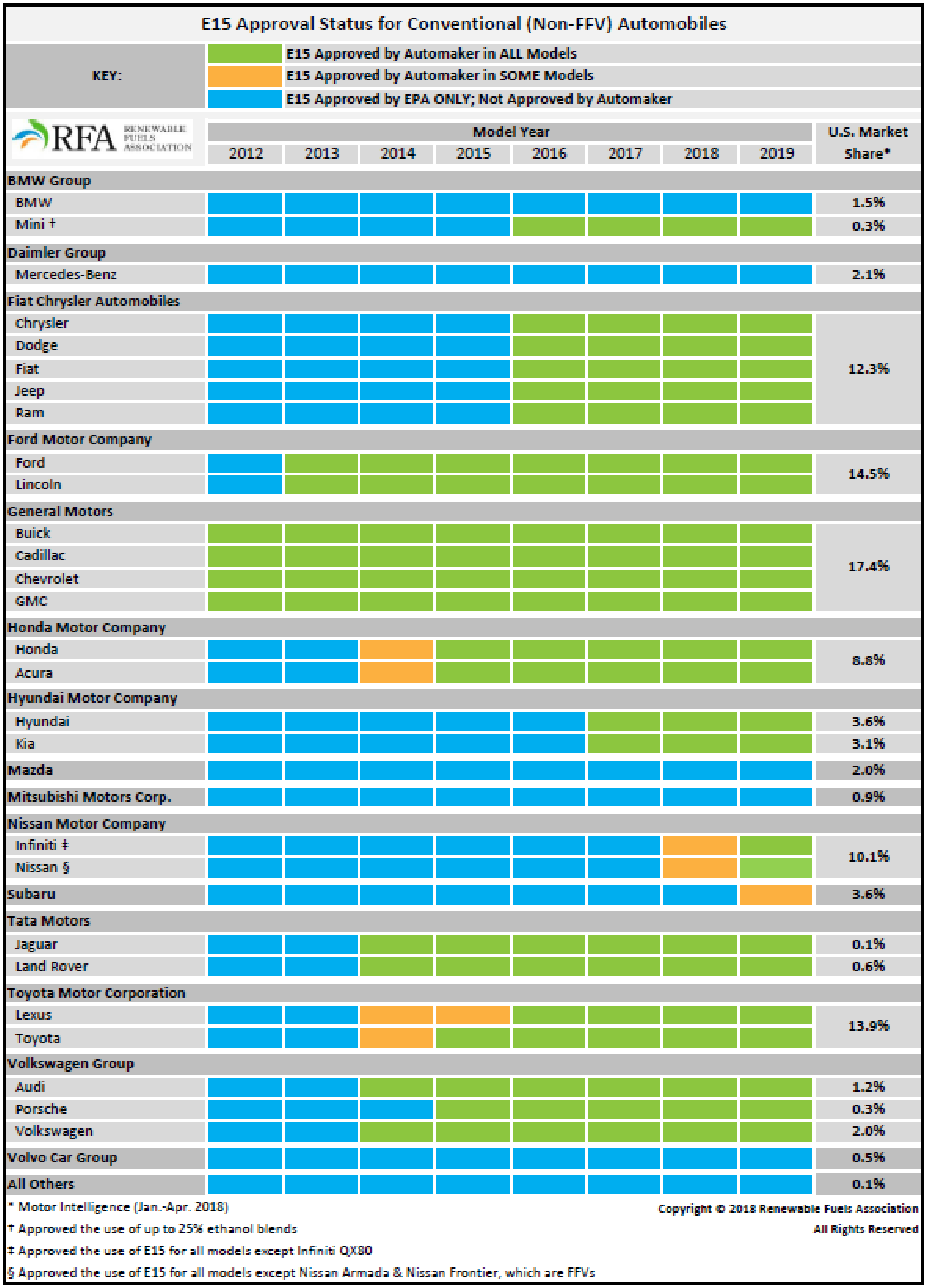
[84] The fuel sending unit is installed inside of the fuel tank. Its purpose is to measure the fuel level and send that information to the fuel gauge.

[85] A commutator is a moving part in certain types of electric motors or generators that can convert alternating current into direct current.

[86] CRC, Intermediate-Level Ethanol Blends Engine Durability Study, CRC Project CM-136-09-1B, April 2012.

[87] McCormick, R.L, j. Yanowitz, M. Ratcliff, B. Zigler, Review and Evaluation of Studies on the Use of E15 in Light-Duty Vehicles, https://ethanolrfa.3cdn.net/b378858ac325c6e165_sgm6bknd4.pdf, accessed September 18, 2018.



E15 Approval Status for Conventional (Non-FFV) Automobiles

KEY:
- 🟩 E15 Approved by Automaker in ALL Models
- 🟧 E15 Approved by Automaker in SOME Models
- 🟦 E15 Approved by EPA ONLY; Not Approved by Automaker

	Model Year								U.S. Market Share*
	2012	2013	2014	2015	2016	2017	2018	2019	
BMW Group									
BMW	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	1.5%
Mini †	🟦	🟦	🟦	🟦	🟩	🟩	🟩	🟩	0.3%
Daimler Group									
Mercedes-Benz	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	2.1%
Fiat Chrysler Automobiles									
Chrysler	🟦	🟦	🟦	🟦	🟩	🟩	🟩	🟩	12.3%
Dodge	🟦	🟦	🟦	🟦	🟩	🟩	🟩	🟩	
Fiat	🟦	🟦	🟦	🟦	🟩	🟩	🟩	🟩	
Jeep	🟦	🟦	🟦	🟦	🟩	🟩	🟩	🟩	
Ram	🟦	🟦	🟦	🟦	🟩	🟩	🟩	🟩	
Ford Motor Company									
Ford	🟦	🟩	🟩	🟩	🟩	🟩	🟩	🟩	14.5%
Lincoln	🟦	🟩	🟩	🟩	🟩	🟩	🟩	🟩	
General Motors									
Buick	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	17.4%
Cadillac	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	
Chevrolet	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	
GMC	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	
Honda Motor Company									
Honda	🟦	🟦	🟧	🟩	🟩	🟩	🟩	🟩	8.8%
Acura	🟦	🟦	🟧	🟩	🟩	🟩	🟩	🟩	
Hyundai Motor Company									
Hyundai	🟦	🟦	🟦	🟦	🟦	🟩	🟩	🟩	3.6%
Kia	🟦	🟦	🟦	🟦	🟦	🟩	🟩	🟩	3.1%
Mazda	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	2.0%
Mitsubishi Motors Corp.	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	0.9%
Nissan Motor Company									
Infiniti ‡	🟦	🟦	🟦	🟦	🟦	🟦	🟧	🟩	10.1%
Nissan §	🟦	🟦	🟦	🟦	🟦	🟦	🟧	🟩	
Subaru	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟧	3.6%
Tata Motors									
Jaguar	🟦	🟦	🟩	🟩	🟩	🟩	🟩	🟩	0.1%
Land Rover	🟦	🟦	🟩	🟩	🟩	🟩	🟩	🟩	0.6%
Toyota Motor Corporation									
Lexus	🟦	🟦	🟧	🟧	🟩	🟩	🟩	🟩	13.9%
Toyota	🟦	🟦	🟧	🟩	🟩	🟩	🟩	🟩	
Volkswagen Group									
Audi	🟦	🟦	🟩	🟩	🟩	🟩	🟩	🟩	1.2%
Porsche	🟦	🟦	🟦	🟩	🟩	🟩	🟩	🟩	0.3%
Volkswagen	🟦	🟦	🟩	🟩	🟩	🟩	🟩	🟩	2.0%
Volvo Car Group	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	0.5%
All Others	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	0.1%

* Motor Intelligence (Jan.-Apr. 2018)

† Approved the use of up to 25% ethanol blends

‡ Approved the use of E15 for all models except Infiniti QX80

§ Approved the use of E15 for all models except Nissan Armada & Nissan Frontier, which are FFVs

FIGURE 5. WARRANTY INFORMATION FOR USE OF E15 IN U.S. VEHICLES

4.3 Detailed Properties of Gasoline-Ethanol Blends Relevant to Use in Vehicles

The addition of ethanol to hydrocarbon gasoline changes the properties of the fuel, including its energy density, vapor pressure, octane, distillation properties and its impact on materials. Material compatibility of gasoline-ethanol blends with metals, elastomers and plastics that are used in vehicles and fuel infrastructure has been discussed in Section 3 above.

As noted in Section 1, ASTM Standard D4814-18d, specifies the properties of spark-ignition fuel and used by the Division of Measurement Standards (part of the California Department of Food and Agriculture) to set requirements for such fuels.[88] As present, this specification addresses blends up to E15 fuels, so no changes would be required for CARB to approve fuels specifications covering those fuels.

The analysis of vapor pressure and octane below is based on results of a study in which the American Petroleum Institute (API) has tested a variety of fuel properties on 71 different gasolines with widely variant properties. Each gasoline was then blended with 10%, 12.5%, 15%, 20% and 30% ethanol and retested. Some of the gasolines were petroleum blendstocks intended to be used to make gasoline-ethanol blends (blendstocks for oxygenate blending or BOBs), others were intended for use without the addition of ethanol. These fuels were not selected to be representative of typical or average fuels, but rather to show the expected range of changes in properties that could occur due to the addition of ethanol to hydrocarbon fuels.

4.3.1 Energy Density

Ethanol has about two-thirds of the energy of gasoline on a volumetric basis.[89] Because the energy density of ethanol is lower than gasoline, fuel economy tends to decrease as the ethanol content in blends increases. Modern engines can take advantage of higher-octane fuels to be slightly more efficient. A gallon of E15 has roughly 98% of the energy content of E10.

4.3.2 Vapor Pressure

As noted in Section 3.5.1, at E10, the Reid Vapor Pressure (RVP) of the blended fuel is about 1 psi higher than that of the blendstock but is expected to decrease as the ethanol content increases as is shown in Figure 4.

As shown in Figure 6, the measured RVP at E15 was indistinguishable from that of an E10 using the same base gasoline blendstock using ASTM methods.

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[88] https://www.cdfa.ca.gov/dms/

[89] California Air Resources Board, Low Carbon Fuel Standard and Alternative Diesel Fuels Regulation 2018, Final Regulation Order, posted September 17, 2018, https://www.arb.ca.gov/regact/2018/lcfs18/fro.pdf accessed November 13, 2018.

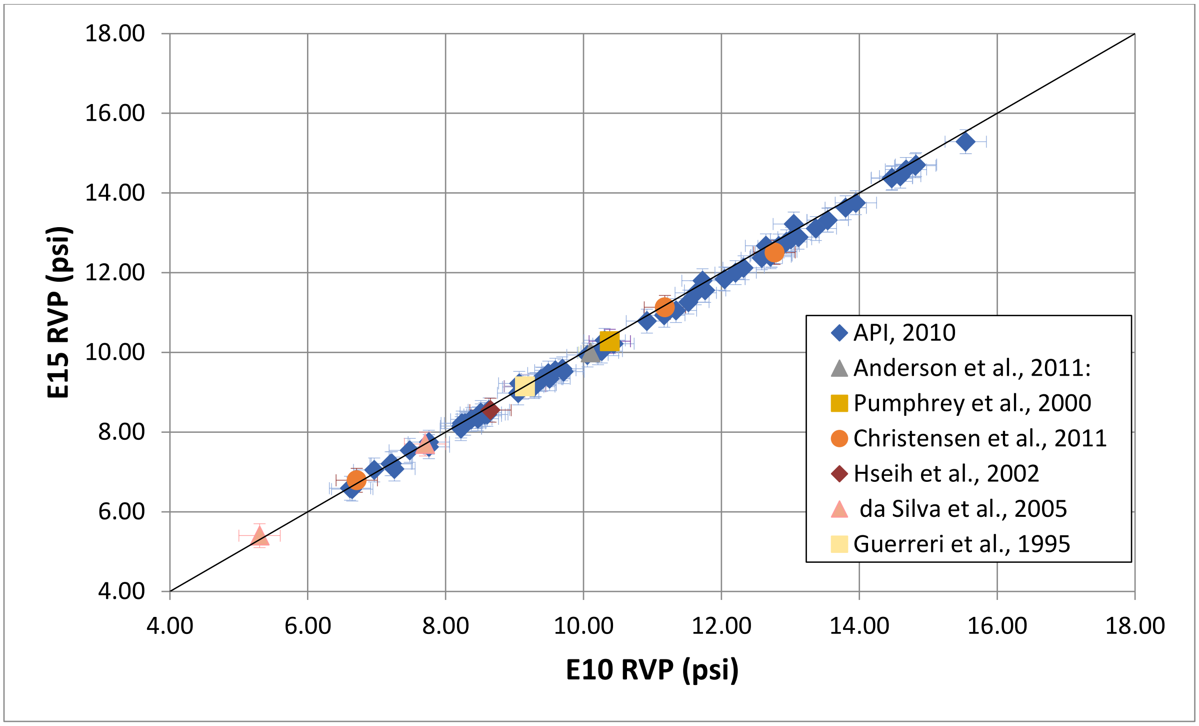

FIGURE 6. THE VAPOR PRESSURES OF E15 AND E10 BLENDS MADE USING THE SAME BASE GASOLINE BLENDSTOCK. THE ERROR BARS SHOW THE REPEATABILITY OF THE ASTM METHOD D5191 USED TO MEASURE REID VAPOR PRESSURE.

4.3.3 Octane

Inside the cylinder of an internal combustion engine the air/fuel mixture should ignite at a precise time in the piston's stroke. Engine knock occurs when pockets of the air/fuel mixture ignite earlier than they should. A minimum octane in fuel is required to prevent engine knocking. In comparison to retail gasoline, ethanol has a high-octane number. Its AKI[90] (antiknock index) is 114 while gasoline is typically sold with an octane number of between 85 and 91. Adding additional ethanol to gasoline increases the octane number, as shown in Figure 7. As mentioned above, higher octane levels of ethanol blend fuels can also reduce fuel consumption in those vehicles which optimize fuel economy by advancing ignition timing to just below the knock limit offsetting to some degree the impacts of the lower energy content of those blends.

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[90] AKI is equal to the average of the research octane number and the motor octane number, which are two different ways of measuring octane. The octane number posted at the retail fuel station is the AKI.

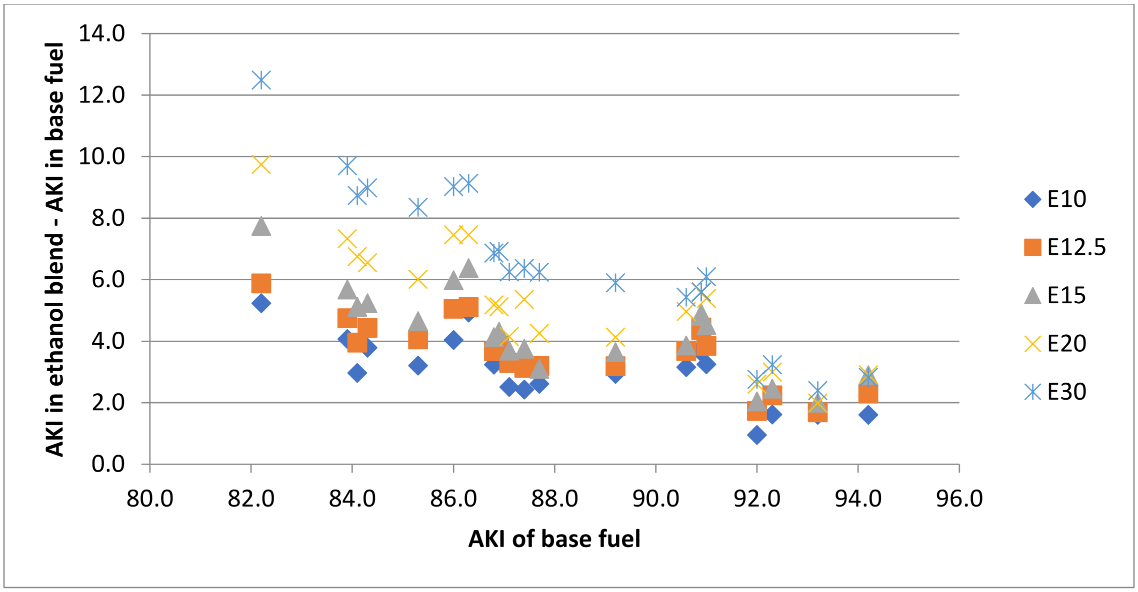

FIGURE 7. IMPACT OF INCREASING ETHANOL CONTENT ON 71 DIFFERENT BASE FUELS.[91]

4.3.4 Distillation Curve

Gasoline and oxygenate blendstocks are complex mixtures of hydrocarbon compounds with a range of boiling points. As a result, the distillation curves of these fuels typically rise steadily upward as temperature increases and individual compounds volatilize. As shown in Figure 8, the distillation curves of ethanol-containing blends start in the same way as pure hydrocarbon gasoline, but then plateau, at a relatively constant temperature as the azeotropes[92] that form between ethanol and various hydrocarbons distill. When the ethanol is gone, the curve shoots upward to rejoin the distillation curve of the base hydrocarbon fuel, thus T10 and T90 are largely unchanged by the addition of ethanol below 30 percent by volume. At higher ethanol concentrations, the length of the plateau increases, and typically impacts T50.

The American Petroleum Institute (API) testing a range of U.S. gasolines and BOBs found that the T50 of E15s were, on average, 10 °C lower than that of E10s made with the same base fuel, and 27 °C less than that of the base fuel which contained no ethanol. In contrast, a more recent analysis by CARB[93] on the effect of ethanol addition, CARB found the T50 depression of E15s averaged more than 22 °C lower than E10s made from the same CARBOBs, but only 31 °C lower than the CARBOB itself. Thus, the primary difference between the two datasets seems to be their impact on the T50 of E10, perhaps because the CARB fuels were all intended to be used to create E10s (blendstocks for oxygenate blending, BOBs) while only 13 of the 71 samples in the API study were BOBs. The variability of the API dataset was far greater than CARB's, and roughly one-fourth (17) of the 71 fuels tested had a difference in T50 between E10 and E15 of greater than 20 °C, that is, a level comparable to that of the typical fuel in the CARB analysis. The set of fuels with high disparity in T50 between E15 and E10 included many, but not all, of the BOBs that API tested. Because CARB Phase 3 gasoline regulations set a maximum allowable T50 value for the E10 blended fuel, it is hypothesized that CARBOBs are specifically designed with additional levels of those gasoline components which will form an azeotrope with ethanol at the appropriate

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[91] American Petroleum Institute, Determination of the Potential Property Ranges of Mid-Level Ethanol Blends, Final Report, April 23, 2010 https://www.api.org/~/media/Files/Policy/Fuels-and-Renewables/2016-Oct-RFS/The-Truth-About-E15/E10-Blending-Study-Final-Report.pdf

[92] An azeotrope is a mixture of two or more liquids that have the same concentration in the liquid and vapor phase and so cannot be separated by distillation.

[93] Results of distillation testing performed from August 17 through September 21, 2017, by CARB FAMES for Project No. 17F01, Test Plan for RVP and Distillation Analysis of Ethanol Blends with CARBOB Samples from 10 Different California Refineries and One Importer, July 11, 2017.

temperature to minimize the T50 of the E10 blend. If California E15s are formed using existing CARBOBs then we would expect that the T50 of those blends might average 22 °C lower than that of current E10s. However, if E15 should become ubiquitous, it is possible that the same economic and technological factors which have driven the T50 of E10s higher, will likely also impact E15s.

ASTM D4814-18d allows for the expected lower T50 with E15. Higher ethanol content (i.e., above E15) fuels will not result in significantly lower T50s.

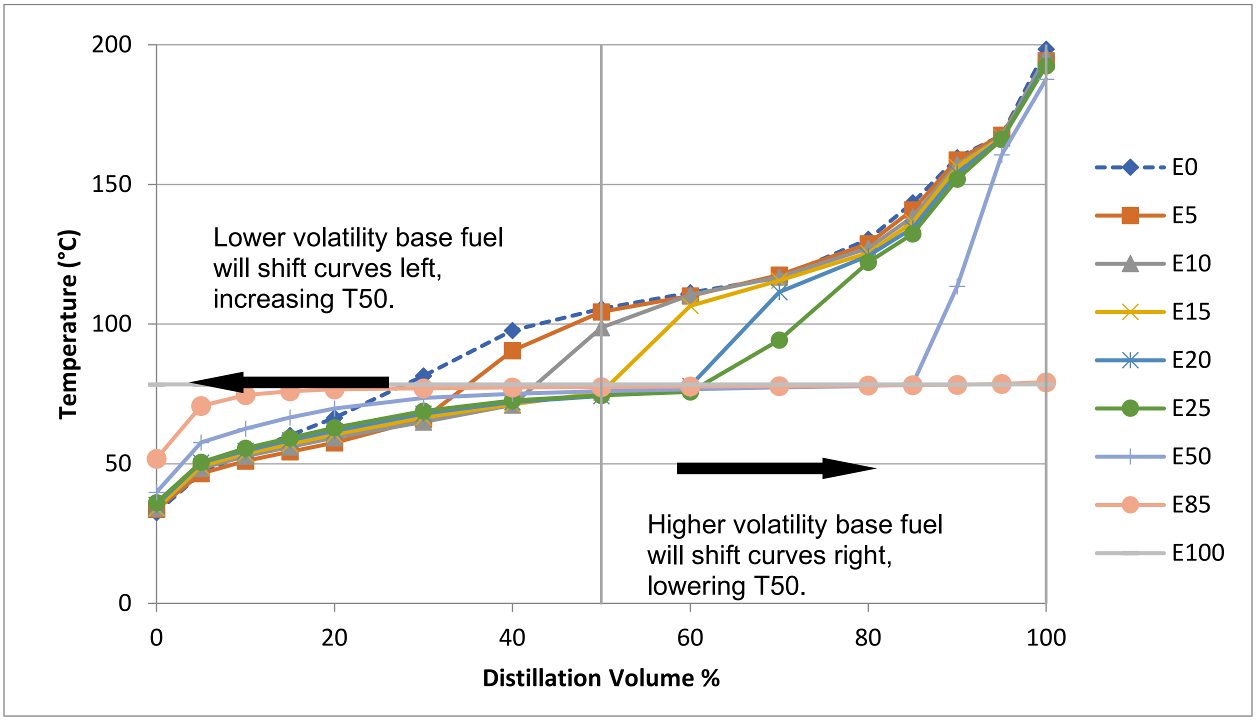

FIGURE 8. DISTILLATION CURVES OF ETHANOL IN CERTIFICATION GASOLINE FROM ANDERSON (2010)[94]

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[94] V. F. Andersen, J. E. Anderson, T. J. Wallington, S. A. Mueller And O. J. Nielsen, Distillation Curves For Alcohol−Gasoline Blends, Energy Fuels, 2010, 24 (4), Pp 2683–2691.

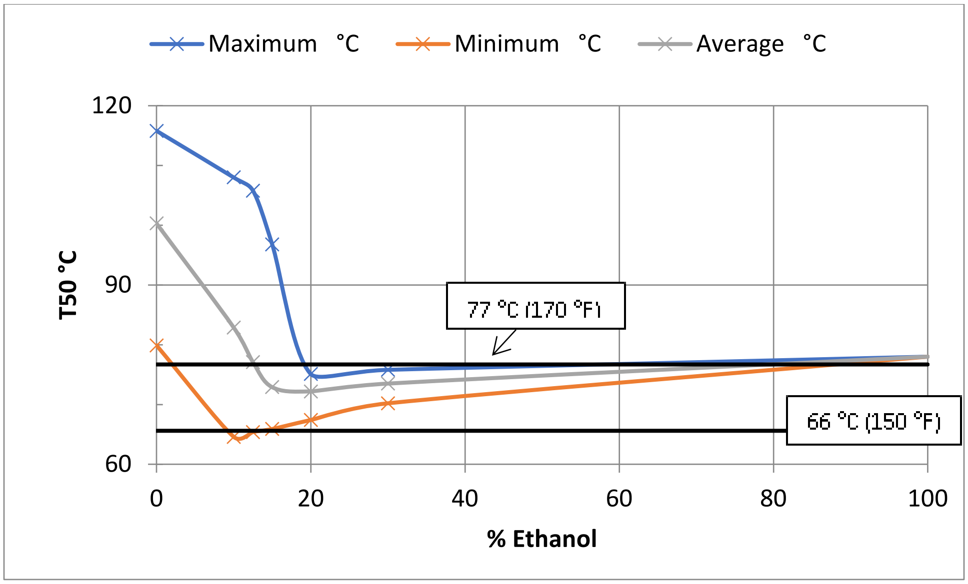

FIGURE 9. T50 RANGE FOR A VARIETY OF GASOLINES AT VARIOUS ETHANOL CONCENTRATIONS[95]

TABLE 5. T50 FOR A VARIETY OF GASOLINES, INCLUDING SOME BOBS, BLENDED WITH BETWEEN 10% AND 15% ETHANOL, AND EXTRAPOLATED TO BOILING POINT OF ETHANOL.[95]

T50 °C (°F)	E0 (straight gasoline)	E10	E12.5	E15	E100 (straight ethanol)
Average °C	100.3	82.9	77.1	72.9	78
°F	(212.6)	(181.2)	(170.8)	(163.2)	(173)
Std. Dev. °C	7.6	14.7	11.2	5.4	0
°F	(13.6)	(26.4)	(20.2)	(9.8)	(0)
Minimum °C	79.9	64.6	65.4	65.9	78
°F	(175.9)	(148.2)	(149.8)	(150.7)	(173)
Maximum °C	115.8	108.0	105.8	96.8	78
°F	(240.5)	(226.4)	(222.5)	(206.3)	(173)

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[95] From data in American Petroleum Institute, Determination of the Potential Property Ranges of Mid-Level Ethanol Blends, Final Report, April 23, 2010 https://www.api.org/~/media/Files/Policy/Fuels-and-Renewables/2016-Oct-RFS/The-Truth-About-E15/E10-Blending-Study-Final-Report.pdf

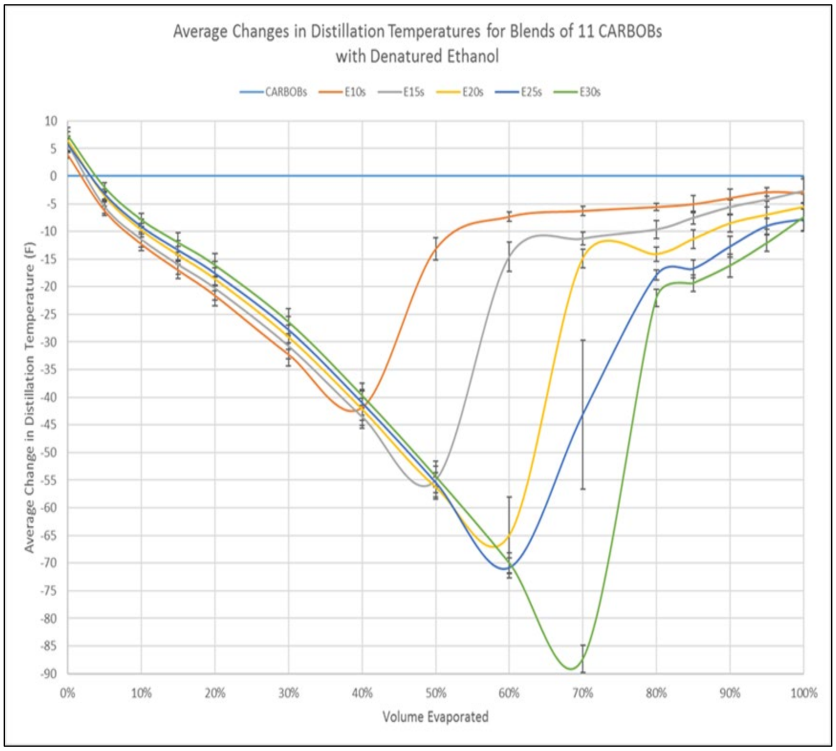

FIGURE 10. CARB ANALYSIS OF AVERAGE CHANGES IN T50 FOR ETHANOL

4.4 Additive Requirements for Gasoline-Ethanol Blends

The U.S. EPA and CARB (California Title 13, Chapter 5, Article 1 section 2257) require detergent additives to be added to gasoline to control deposit formation at a minimum dosing rate. The detergents are tested using ASTM D5598 and ASTM D5500 to ensure that they perform adequately. Detergent is generally considered necessary for the purposes of reducing intake valve and fuel injector deposits from the hydrocarbon portion of the fuel. In approving blends up to E15, U.S. EPA concluded that no changes were required relative to levels required for use with E10.[96] Given this, and the available data described above, use of additive levels consistent with those that apply in California for E10 may also be effective for blends of up to at least E15. However, California's gasoline deposit control additive formulations possibly have not been tested or certified for use with E15 per California regulations, so it is likely that additional certification testing could be required.

4.5 Vehicle Emissions

This section evaluates the available emissions test data to assess the impacts of ethanol blends in the E11 – E15 range on air quality. Impacts on greenhouse gas emissions (GHGs) are addressed in Section 8. Since only vehicles that have been built since MY 2001 are permitted to use E15 under EPA regulations (in addition to specially designed FFVs which are permitted to use any ethanol concentrations of up to 85%) only data from testing of these vehicles are considered here and impacts are assessed relative to E10.

4.5.1 Test Fuels

All blends of ethanol and gasoline up to E10 sold in California must comply with CARB's California Reformulated Gasoline (CaRFG) regulations. This requirement imposes limits on the allowable properties

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[96] US Government Accountability Office, BIOFUELS Challenges to the Transportation, Sale, and Use of Intermediate Ethanol Blends, June 2011.

of petroleum blendstocks for oxygenate blending (CARBOBs) used in preparing these compliant blends. The analysis presented below is focused on assessing the emission impacts associated with use of gasoline-ethanol blends above E10 that are created via splash blending of ethanol into a CARBOB that complies with CARB regulations for E10. Because of the limited number of studies done comparing nominal E15 (and in some cases E20) blends to E10, this review will also describe testing performed to compare E15 and E20 to E0. Inclusion of these studies is conservative given that any observed differences in emission between E15 and E20 relative to E0 should be larger than those expected to exist between E15 and E20 relative to E10.

Further, the analysis also uses data from some studies involving what is known as “match blending” instead of splash blending. In match blending, the properties of the CARBOB or other blendstock are intentionally altered such that the properties of the blends being compared, E10 and E15, for example, are as close as possible except for the difference in ethanol content. The match characteristics vary but frequently include vapor pressure, and/or aromatic content and/or T50. Splash blending, by contrast, employs the same base hydrocarbon fuel for each blend regardless of ethanol content. Studies which employ splash blending are more representative than match blending studies of the changes that would occur should E11-E15 fuels be blended with the same CARBOBs that are used for E10, as is proposed for these new fuels in this Multimedia Evaluation.

There are many issues that need to be considered when using data from match blending studies to evaluate impacts of splash blending. These include:

- match blending for multiple fuel properties is difficult and rarely perfectly successful, because it is impossible to change one property without changing many of the other properties;
- despite extensive study it is not clear which fuel properties are most important with respect to emissions because the effects of correlated properties cannot be easily separated from each other by statistical analysis; and
- there are numerous properties that could conceivably have an impact on emissions[97] such that no match blending study could control for changes in all properties that could impacts emissions.

Given the differences in match and splash blending, it is not surprising that there are differences in the results from studies using the two approaches to evaluate the impact of ethanol content on emissions.

Of the studies considered only one,[98] by Karavalakis and colleagues at UC Riverside, used a base or test fuel that was specifically described as “CARB” fuel. In that case, the base CARB fuel included 6.6% ethanol by volume and was diluted to create E10 and E20 blends while maintaining constant RVP, and the fuel was tested on only one MY 2001+ vehicle. In other work conducted at UC Riverside [99] the fuel was described as follows:

> “The ethanol fuels were blended …………to represent ethanol fuels that would be utilized in California, in terms of properties such as aromatic content, Reid vapor pressure (RVP), and other properties.”

RVP and other fuel volatility parameters were matched within certain limits. The E10 fuel in the UC Riverside-1 Study did meet all requirements for California RFG3. A third study, also conducted by Karavalakis and his colleagues at the UC Riverside, did not employ fuel that was selected based on compliance with CARB regulations and included both splash blended and match blended fuels.

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[97] See for example, “Analysis of EPAct Emission Data Using T70 as an Additional Predictor of PM emissions from Tier 2 Gasoline Vehicles,” (Darlington, T. et al. SAE 2016-01-0996).

[98] Karavalakis, G., T. Durbin, M. Shrivasastava, Z. Zheng, M. Villela, H. Jung. “Impacts of ethanol fuel level on emissions of regulated and unregulated pollutants from a fleet of gasoline light-duty vehicles,” *Fuel* 93 (2012) 549-558.

[99] Karavalakis, G., D. Short, D. Vu, R. Russell, A. Asa-Awuku, T. Durbin, “A Complete Assessment of the Emissions Performance of ethanol blends and Iso-Butanol blends from a fleet of Nine PFI and GDI Vehicles,” SAE 2015-01-0957, (2015).

4.5.2 Criteria Pollutants

The criteria pollutants considered include nitrogen oxides, (NOx), carbon monoxide (CO), particulate matter (PM) and organic compounds. Organic compounds result from both combustion as well as fuel evaporation and can be characterized in a number of ways: total hydrocarbons (THC – which includes all hydrocarbons); non-methane hydrocarbons (NMHC – which includes all hydrocarbons except methane which is relatively non-reactive and thus not a significant predictor of ozone);or non-methane organic gases (NMOG – which include NMHC plus gases that may have an oxygen molecule, like ethanol, acetaldehyde or formaldehyde). In this document, we report the organic emissions, in whatever form they were published in the relevant studies. The emissions data considered in this analysis are compiled in Appendix 2.

Emissions of organic compounds and NOx react in the atmosphere to form ozone, the primary component of smog in the presence of sunlight. Different organic molecules differ in their reactivity in the production of ozone. The total amount and composition of organic compounds emitted can be analyzed to provide a rough gauge of their ozone-forming potential. Thus, studies which speciated or otherwise considered the reactivity of the specific organic compounds emitted during testing form a more reliable basis for assessing changes in the ozone- forming potential of changes in the ethanol content of blends.

4.5.3 Toxic Air Contaminants

In assessing emissions of toxic air contaminants (TACs) from spark-ignition vehicles, U.S. EPA and CARB have long focused on emissions of formaldehyde, acetaldehyde,1,3-butadiene and benzene. Based on extensive research, the state of California has developed risk factors for exposure to these and other compounds.[100] These risk factors have been used by CARB to evaluate the relative toxic cancer “potency” of the four compounds listed above for the purpose of assessing the relative risk in changes in fuel composition on overall exposure to air toxics. CARB’s Predictive Model has assigned the weighting factors listed in Table 6 to these pollutants, based on their relative toxicity. Naphthalene does not list a weighting factor because the naphthalene cancer inhalation unit risk (IUR) was established by OEHHA after CARB developed the Predictive Model. The Predictive Model has not been updated to include the naphthalene IUR. For each pollutant listed, the potency-weighted toxicity is calculated as the sum of the concentration of each of these pollutants’ times the weighting factor.

TABLE 6. CARB TOXIC AIR CONTAMINANT CANCER POTENCY-WEIGHTING FACTORS

Pollutant	Weighting Factor
Benzene	0.170
1,3-butadiene	1.000
formaldehyde	0.035
acetaldehyde	0.016
acrolein	
naphthalene	

4.5.4 Statistical Analysis

Because test procedures were different, each dataset was analyzed independently. All emissions are presented on a weight/mile basis and were transformed logarithmically prior to the statistical analysis to equalize the impact of high and low emitting vehicles in determining the statistical significance of changes. Logarithmic transform of data is common with emissions data. Results were considered to be statistically significant for $p<=0.05$ and marginally significant if p fell between 0.05 and 0.1.

Extensive statistical analyses were also performed by the researchers and reported in these studies. In many cases the original researchers analyzed overall impacts between E0, and the highest ethanol blend considered, assuming linear effects. Where possible the statistical analysis performed here was limited to consider only emission differences between E10 and the higher gasoline-ethanol blends, given E10 as

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[100] CARB, California Procedures for Evaluating Alternative Specifications for Phase 3 Reformulated Gasoline Using the California Predictive Model, Last Amended August 24, 2012.

the reference point for this evaluation. Ethanol impacts on other fuel properties that are often thought to impact emissions (T50 and RVP) are clearly non-linear between E0, E10 and higher ethanol blends.

In addition, in the UC Riverside-3 study, the scientists apply the Tukey-Kramer correction to their analyses of the statistical significance of pairwise t test comparison of the eight different fuels they consider. This correction is intended to account for the increased probability of a Type 1 error (false positive showing statistically significant difference where none exists) when conducting multiple pairwise comparisons. For eight different fuels, and the resultant 28 different pairwise comparisons, this correction is quite large, resulting in p-values almost ten times the uncorrected value. However, this correction was not made in this statistical evaluation, since only four pairwise comparisons were made, with markedly less potential for false positives. Thus, in contrast to the original study report, the statistical analysis presented here found a marginally significant decrease in NOx emissions, and significant decrease in NMHC, as well as some significant changes in toxic emissions that were not identified in the original report. This type of finding also applies to differences in results presented here versus those presented in other original studies. Where statistical results differ, this is not due to errors in either analysis, but to differences in analytical approaches.

The older studies (CRC E74b and the DOE Study on Legacy Vehicles) did not report any repeated test runs. The DOE Catalyst Study reported the minimum, maximum and average of the repeated tests, but not every test result. Three to four repeats were made for all test runs in the UC Riverside-1 and -3 studies. The only study which tested the same vehicles on different test cycles was UC Riverside-1. A measure of the magnitude of the variability between repeat runs was calculated by dividing the standard deviation of repeat runs by the average value of the measured emissions for each set of repeats. This parameter did not differ in a statistically significant manner between different test cycles for any of the pollutants reported in this paper (p (paired, two-sided) was greater than 0.3 for CO, NOx, THC) suggesting that neither test cycle would be more likely to result in repeatable results.

4.5.5 Tailpipe Emissions

The total dataset considered here includes tailpipe emissions from a total of 61 vehicles, including one FFV. Twenty-five vehicles were tested on E10 and E15; twenty-four were tested on E0 and E15; twenty-three were tested on E10 and E20; twenty-four were tested on E0 and E20 (there were a number of vehicles that fell into multiple categories). There are no published data on the impact of blends above E20 on tailpipe emissions. A summary of the results is included in Table 7 and Table 8 and a more detailed summary of the average emissions from each vehicle/test cycle/fuel are included in Appendix 2.

FFVs are vehicles designed and permitted to use any ethanol fuel level up to E85, but many may fill up with conventional fuel and so may be impacted by a change in the availability of E15 in place of E10. According to IHS Automotive[101] there are nearly 20 million FFVs on US roads today, or somewhere around one-tenth of the total number of vehicles on the road. Only one has been tested on E15 and E10, and the results of that test are included in this analysis.

Table 7 (E15) and Table 8 (E20) summarize the results of our analyses of the individual studies which directly compared the air emissions impacts of higher and lower ethanol concentrations in hydrocarbon fuel. None of the E15 studies, whether done on California fuels or other US fuels, found a statistically significant increase in any criteria pollutant. NOx, CO, PM mass emissions, or organic emissions (NMOG, THC, or NMHC depending on the study) were measured. Statistically significant decreases were found for NMHC, CO and potency weighted toxics, along with a marginally significant decrease in NO_x emissions, due to increases in ethanol content in the fuel as compared with E0 – E10.

For E20, organic emissions are reduced in several studies by a significant or marginally significant amount. A statistically significant reduction in CO is also found in one study and a marginally significant reduction in another study. A significant increase in NOx for E20 was found in a single study.

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[101] Cited by the US DOE, https://www.afdc.energy.gov/vehicles/flexible_fuel.html, accessed March 2, 2018.

The results of the EPAct[102] study, a large EPA study of 15 vehicles and 27 fuels, is not explicitly included in this analysis because it does not provide emissions data for a set of lower and higher ethanol content fuels that are either match blended or splash blended, that could be analyzed in the manner we used for the other studies. The experimental design of the EPAct study included 27 different fuels, by blending for 5 specific properties in such a way that the full reasonable range of each property was explored, but not all the possible different combinations (which would have required 240 different fuels). EPA's analysis of the results of their emissions data suggest that the emissions of total hydrocarbon (THC), NMOG, NMHC, CH4, NOx, PM would increase, and CO would decrease with increasing ethanol content (between E0 and E20) should aromatic content, T50, T90 and vapor pressure be held constant. However, Section 4.3.4, shows that T50 is inversely correlated with ethanol content, as is aromatic content by simple dilution. Increasing aromatic content and T50 are also correlated with increasing THC, NMOG, NMHC, NOx, PM emissions, potentially confounding any increase in emissions due to ethanol alone. In contrast, the California Predictive Model shows that decreasing T50 correlates with increasing NOx emissions. This disparity should be addressed in the testing conducted for E15 approval.

4.5.6 Description of Studies

4.5.6.1 Coordinating Research Council Study E74-B

The Coordinating Research Council (a consortium of car and petroleum companies) conducted a study[103] in 2009 which included 15 vehicles, model years 1994 to 2006, tested over the Federal Test Procedure (FTP) cycle. The study was intended to separate the effects of vapor pressure, ethanol content and test temperature on CO exhaust emissions, but THC and NO_x emissions were also reported. Seven match blended[104] E0, E10 and E20 fuels were tested at several different vapor pressures. Because their study included vehicles older than the 2001 MY cutoff, and E0 fuels, the CRC statistical analysis is not considered directly applicable. Instead, for this analysis, the dataset has been limited to tests conducted on post 2001 MY vehicles, the E20 fuel and the only E10 fuel with the same vapor pressure.

The results showed that for vehicles using both E20 and E10, the higher ethanol content fuel yielded an increase in NO_x in 6 out of the 11 vehicles at 75 °F, and for 7 out of 11 vehicles at 50 °F. The 2006 Ford Taurus seemed to show an especially large sensitivity to ethanol content in both tests. However, when the wide variability between vehicles is taken into account, the change in NO_x is not statistically significant (p=0.38) and could be due to chance alone. Similarly, there was a decrease in THC emissions for E20 in 8 out of 11, and 6 out of 11 vehicles in the 75 °F and 50 °F tests respectively. For the 75 °F test, the difference between THC emissions using the two different fuels is statistically significant at the 95% level (p <=0.05), but not for the 50 °F test. When the datasets at the two temperatures are combined, the reduction in THC is marginally significant (p=.051). Finally, for CO, 6 of the 11 vehicles saw a decrease at 75 °F, 7 out of 11 saw a decrease at 50 °F, but, statistically, this difference was not significant at either temperature.

Overall, there is little apparent difference in emissions between E10 and E20 from later model vehicles (MY 2001+) for these criteria pollutants; given that differences between E10 and E15 should be smaller, the impact of changing from E10 to E15 would likely not cause any increase in emissions in these vehicles.

4.5.6.2 The Department of Energy (DOE) Study of Intermediate Blends on Legacy Vehicles

This study[105] included a number of vehicles older than 2001 and therefore the statistical analysis which accompanied the study is not applicable. Instead, the data from the 2001+ MY vehicles were extracted

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[102] EPA, Assessing the Effect of Five Gasoline properties on Exhaust Emissions from Light-Duty Vehicles Certified to Tier 2 Standards: Analysis of Data from EPAct Phase 3 (EPAct/V2/E-89), Final Report, April 26, 2013. https://www.epa.gov/moves/epactv2e-89-tier-2-gasoline-fuel-effects-study, accessed September 23, 2018.

[103] CRC E74-B, Effects of Vapor Pressure, Oxygen Content and Temperature on CO Exhaust emissions, May 2009.

[104] The fuels were blended to match four distillation points, octane values, and aromatic, benzene, olefin and sulfur content as close as practicable. For the E20 fuel, especially, a tight match was not possible.

[105] Knoll,K., B. West, W. Clark, R. Graves, J.Orban, S. Przesmitzki, T. Theiss , Effects of Intermediate Ethanol Blends on Legacy Vehicles and Small Non-Road Engines, Report 1 – Updated February 2009, NREL/TP-540-43543.

and analyzed. The base hydrocarbon fuel used was certification gasoline, and ethanol was fuel-grade per ASTM D4806. In this case, we were able to compare splash-blended E15 with E10 and found NO_x increased in 7 out of 13 of 2001+ MY vehicles, and NMHC and CO decreased in 7 out of 13 vehicles, and 8 out of 13 vehicles, respectively. In comparison to the variability between the vehicles, the paired t-test conducted for each of these pollutants finds that the difference between the E15 results and the E10 results is not significant.

The same vehicles were tested on splash-blended E20. These showed a large (30%) and statistically significant increase in NOx (11 out of 13 vehicles), a marginally significant decrease of -5% in NMHC (9 out of 13 vehicles) and no statistically significant impact on CO emissions.

4.5.6.3 DOE Catalyst Study

The purpose of this study[106] was to determine if the use of higher ethanol content fuels for the full useful life of a vehicle (as defined in the EPA emissions standards) would adversely affect the emissions control systems and result in emissions which exceeded the EPA emissions standards. Retail top-tier E0 fuel was splash blended with ASTM D4806 ethanol to produce E10, E15 and E20 blends. This was the largest study and included 24 matched (make, model and approximate starting mileage) sets of vehicles which accumulated mileage on E0, E10, E15 or E20 and then were tested on different ethanol fuels. The vehicles aged on E15 were tested on E15 and E0, and the vehicles aged on E20 were tested on E0 and E20. No vehicle sets were tested on both E10 and E15, or E10 and E20 in this program.

Average emissions in the DOE Catalyst study show significant reductions in CO between E15 and E0 (-13%), and changes which are not statistically significant in NMOG and NO_x. The same make and model vehicles tested on E20 versus E0 showed no statistically significant change in NOx, and large significant reductions in NMOG (-16%) and CO (-22%). It is not clear how much of the difference between E0 and E15 occurs between E0 and E10 and what is due to the change between E10 and E15, or E10 and E20. However, the implication of this study is that changes in NOx emissions are likely to be non-detectable in these vehicles, and there is an apparent reduction in CO and NMOG.

4.5.6.4 UC Riverside-1 and UC Riverside-2

A total of seven standard vehicles and one FFV MY 2001+, were tested by Karavalakis and his colleagues at UC Riverside using E10, E15 and E20 fuels that would likely be permissible in California should the higher ethanol fuels be legalized. Those results were reported in three different papers[107], and an extensive statistical analysis of the results from seven of those vehicles was made in a 2015 SAE paper. In addition, a single FFV, a 2007 Chevrolet Silverado, will be considered independently of the other vehicles because it is a different type of vehicle and also because it was not tested on E15 but was tested on E20 and E10. The data was provided in graphical form in the published papers, but this analysis of the seven standard vehicles was based on the data in Excel form provided to us courtesy of Dr. Karavalakis. The graphic presentation of the Chevrolet Silverado results was on such a small scale that magnitude could not be accurately gauged and only the direction of change can be reported.

Considering only both E20, E15 and E10 emissions from the seven vehicles, Karavalakis and his colleagues found there were no significant differences in the weighted (cold start and running) emissions for PM, THC, NMHC, CO and NO_x emissions, although the cold start emissions were slightly higher for both THC and NMHC for E15, and the difference was statistically significant. They did not report any significant changes in PM mass and total particle number, between E15 and E10. Our analysis, in Table 7 generally supports these conclusions, although we found a marginally significant decrease in CO between E20 and E10. In addition, we calculated potency-weighted toxicity for the 7 vehicles and found

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[106] West, B.H., C. S. Sluder, K.E. Knoll, J.E. Orban, J. Feng, Intermediate Ethanol Blends Catalyst Durability Program, February 2012, ORNL/TM-2011/234.

[107] Karavalakis, G., D. Short, D. Vu, R. Russell, A. Asa-Awuku, T. Durbin, " Evaluating the regulated emissions, air toxics, ultrafine particles, and black carbon from SI-PFI and si-di vehicles operating on different ethanol and iso-butanol blends," *Fuel* 128 (2014), 410-421.

no significant difference between these pollutants at either E15 or E20 and E10. The study also reported extensively on other pollutants including methane, carbon dioxide and a number of individual VOCs.

The single FFV (MY 2007) showed small reductions in all pollutants including CO, THC, NMHC and NO_x for E20 in comparison to E10, although none appear to be statistically significant in comparison to the standard deviations of the measurements as shown on the graph. Tests on higher ethanol concentrations suggest the trend is for reductions in CO, THC and NMHC at E20 and higher ethanol concentrations for this FFV.

Taken together these CARB fuel studies show no evidence for any increase in emissions for potency-weighted toxicity, PM, CO, THC, NMHC or NO_x, if E15 replaces E10 fuel in California.

The UC Riverside team performed an analysis for emissions from two 2012 model year vehicles and found that the ozone reactivity for emissions from E15 was less than that for emissions from E10, as shown in the figure below.

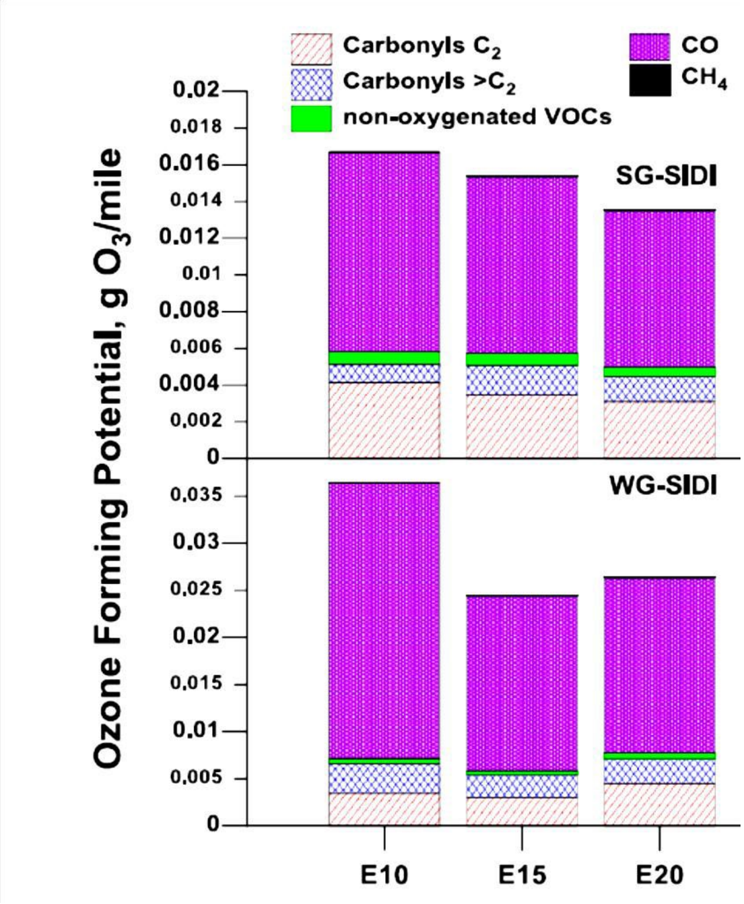

FIGURE 11. OZONE-FORMING POTENTIAL OF TAILPIPE EMISSIONS FROM VEHICLES USING E10, E15 AND E20.[108]

Because of the extremely limited data on the ozone-forming potential of E15 versus E10, the impact of both higher and lower ethanol contents on ozone-forming potential will be briefly mentioned, although this may not be representative of the change between E15 and E10. In their extensive study of FFV vehicle

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[108] Karavalakis, G., D. Short, D. Vu, R. Russell, A. Asa-Awuku, H. Jung, K.C. Johnson, T. Durbin, “The impact of ethanol and iso-butanol blends on gaseous and particulate emissions from two passenger cars equipped with spray-guided and wall-guided direct injection SI (spark ignition) engines,” *Energy* 82 (2015) 168-179.

emissions from E6, E32, E59 and E85 fuels, the CRC[109] found that the average ozone-forming potential decreased with increasing ethanol content of the fuels on the cold start FTP. There were mixed results on the US06 and Unified Cycle tests. Wang and colleagues[110] in China found a slight reduction in ozone-forming potential calculated from MIR values when E10 was compared to E0 in a Euro 4 vehicle. Taken together, these results suggest that there will be no increase in ozone-forming potential with higher ethanol content fuel.

4.5.6.5 UC Riverside-3

In another study conducted by UC Riverside,[111] five 2016 and 2017 MY vehicles were tested on match-blended (E0, E10 and E15, at both high and low aromatic content) and splash-blended (E10, E15 and E20) fuels. The results of the study found that the splash-blended E15 caused significant reductions in NMHC, THC and potency weighted-toxics, and marginally significant reductions in NOx. However, reductions were not found in the splash-blended E20 when compared to E10. The vehicles tested with match-blended E10 and E15 showed no statistically significant differences at either low or high aromatic content.

In addition, the tailpipe emissions from one vehicle tested on the eight different fuels were injected into an atmospheric chamber to determine the potential for these emissions to form secondary aerosols in the environment. Secondary aerosol formation showed a weak negative correlation with increased ethanol content from E0 to E20, suggesting that higher concentrations of ethanol in fuel will lead to less secondary aerosols.

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[109] CRC E-80, Exhaust and Evaporative Emissions Testing of Flexible-Fuel Vehicles, Final Report, August 2011.

[110] Wang, X, Y. ge, C. Zhang, J. Liu, Z. Peng, H. Gong., Estimating Ozone Potential of Pipe-out Emissions from euro-3 to euro-5 Passenger cars Fueled with gasoline, Alcohol-Gasoline, Methanol and Compressed Natural Gas, SAE 2010-01-1009.

[111] Karavalakis, G, T.D. Durbin, J. Yang, P. Roth, Impacts of Aromatics and Ethanol Content on Exhaust Emissions from Gasoline Direct Injection (GDI) Vehicles, April 2018.

TABLE 7. TAILPIPE EMISSIONS STUDIES ON E15 VERSUS EITHER E10 OR E0 AS BASE FUEL[112]

Study Name	Test Cycle	No. of Vehicles	Vehicle Model Years	Base Fuel and Blending Strategy	NO_x	Organic Emissions	CO	PM mass emissions	Potency Weighted Toxics[113]
DOE Intermediate Fuel Blends	LA-92	13	2001-2007	E10 splash blend	No significant difference	No significant difference[114]	No significant difference	Not tested	Not tested
DOE Catalyst Study	FTP	24	2003-2009	E0 splash blend	No significant difference	No significant difference[115]	⬇	Not tested	Not tested
UC Riverside -1	UC and FTP	7	2007-2012	E10 match blend	No significant difference	No significant difference[116]	No significant difference	No significant difference	No significant difference
UC Riverside -3	LA-92	5	2016-2017	E10 low aromatics splash	⇩	[114] ⬇	No significant difference	No significant difference	⬇
UC Riverside -3	LA-92	5	2016-2017	E10 low aromatics match blend	No significant difference	No significant difference[114]	No significant difference	No significant difference	No significant difference
UC- Riverside-3	LA-92	5	2016-2017	E10 high aromatics match blend	No significant difference	No significant difference[114]	No significant difference	No significant difference	No significant difference
All Data (no. of datapoints for each pollutant in parentheses)	Various		2001-2017	Various	No significant difference (66)	NMHC:No significant difference (42) THC:No significant difference (29) NMOG:No significant difference (24)	⬇ (66)	No significant difference (24)	No significant difference (22)

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[112] Solid arrows represent p values <.05, textured arrows represent p values between 0.05 and 0.1, for paired, two-tailed t-test.

[113] Calculated using CARB factors in California Procedures for Evaluating Alternative Specification for Phase 3 Reformulated Gasoline Using the California Predictive Model, Last Amended August 24, 2012

[114] Non-methane hydrocarbons, NMHC

[115] Non-methane organic gases, NMOG

[116] Total hydrocarbon and non-methane organic gases, THC and NMHC both measured with same statistical conclusion

TABLE 8. TAILPIPE EMISSION STUDIES ON E20 EITHER E10 OR E0 AS BASE FUEL[117]

Study Name	Test Cycle	No. of Vehicles	Vehicle Model Years	Fuels	NO$_x$	Organic Emissions	CO	PM mass emissions	Potency Weighted Toxics[118]
CRC E74B	FTP	11 (at two different temps)	2001-2006	E10 match blend	No significant difference	[119] ⇩	No significant difference	Not tested	Not tested
DOE Intermediate Fuel Blends	LA-92	13	2001-2007	E10 splash blend	⬆	[120] ⇩	No significant difference	Not tested	Not tested
DOE Catalyst Study	FTP	24	2003-2009	E0 splash blend	No significant difference	[121] ⬇	⬇	Not tested	Not tested
UC Riverside-1	UC and FTP	7	2007-2012	E10 match blend	No significant difference	No significant difference[122]	⇩	No significant difference	No significant difference
UC Riverside-2	FTP	1 FFV	2007	E10 match blend	E20 emissions less than E10	E20 emissions less than E10[120]	E20 emissions less than E10	Not tested	Reported on graph, E20 is slightly less than E10
UC Riverside -3	LA-92	5	2016-2017	E10 low aromatics splash	No significant difference	No significant difference[120]	No significant difference	No significant difference	No significant difference
All Data (no. of datapoints for each pollutant in parentheses)	Various		2001-2017	Various	⇧ (77)	NMHC: No significant difference (32) THC: No significant difference (41) NMOG: (24) ⬇	⬇ (78)	No significant difference (15)	No significant difference (12)

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[117] Solid arrows represent p values <.05, textured arrows represent p values between 0.05 and 0.1, for paired, two-tailed t-test.

[118] Calculated using CARB factors in California Procedures for Evaluating Alternative Specification for Phase 3 Reformulated Gasoline Using the California Predictive Model, Last Amended August 24, 2012

[119] Total hydrocarbon, THC

[120] Non-methane hydrocarbons, NMHC

[121] Non-methane organic gases, NMOG

[122] Total hydrocarbon and non-methane organic gases, THC and NMHC both measured with same statistical conclusion

4.5.7 Evaporative Emissions

Evaporative emissions are volatile organic compounds which escape from the fuel system of the vehicle. Fuel systems are designed to prevent fuel evaporation and direct venting to the atmosphere, although emissions can occur due to system liquid leaks, vapor leaks through the air emissions control system and permeation of vapors through the materials that make up the fuel lines and other components of the fuel system.

Liquid leaks are rare but can result in large quantities of emissions. They are due to poorly maintained vehicles, or carelessness when fueling. The composition of the fuel is not believed to have any impact on the number of liquid leaks.

Because this study is intended to evaluate E11-E15 generated from the blending of fuels into the same CARBOBs used for E10, California E10 and E15 fuels would be expected to have roughly the same or slightly lower vapor pressures.

The quantity of evaporative emissions vented to the emissions control system, and the amount which escapes would be expected to be roughly the same for fuels with the same vapor pressure, thus we do not expect any differences due to splash blended E15 versus E10. However, permeation emissions, in which fuels move through the fuel system materials are chemical specific and could be different for fuels with different chemical compositions. Two Coordinating Research Council studies were conducted to determine if higher ethanol content would affect permeation emissions. A detailed summary of the results of those studies (and other evaporative emissions related issues) has been performed by Air Improvement Resource[123] and highlights of the results of these two studies are presented below.

Evaporative emissions of benzene are also of concern, but it should be noted that the other TACs of concern besides benzene are only of concern with respect to exhaust emissions. Unfortunately, no measurement of benzene emissions were reported in either of these two studies of E20 evaporative emissions. It seems likely that since benzene comes from the hydrocarbon portion of the ethanol-gasoline blend, diluting the hydrocarbon portion with additional ethanol would likely decrease the amount of benzene emissions by a roughly proportional amount.

In an auto company 2007 study[124] of materials representative of those used in older plastic fuel tanks showed that permeation in absence of ethanol was strongly linked to aromatic content, with a 35% increase in permeation with every 10% increase in fuel aromatic content. This study also presented limited data indicating that increasing ethanol content decreased permeation emissions at constant aromatic content Based on this study, it would appear that a move from E10 to E15 would reduce permeation both because of increased ethanol content as well as reduced aromatic content.

CARB conducted a permeation study[125] on three hoses in 2008 using E6.1 (6.1% ethanol fuel). For one of the hoses, the chemical composition of the fuel was tested before and after the permeation study and ethanol was found to have preferentially permeated the hose. All the ethanol had permeated, while only 14.4% of the overall fuel mass had left the hose. This could be due to the fact that when there is evaporation from ethanol-gasoline blends, ethanol will evaporate at a faster rate than other hydrocarbon components of the blend.[126] Alternatively, it could be because ethanol more readily permeates through the hoses tested. However, since there is no statistically significant evidence that fuel permeation increases between E10 and slightly higher ethanol content fuels (E20) (see data in

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[123] Air Improvement Resource, “Effects of E15 Ethanol Blends on HC, CO, and NOx Regulated Emissions from On-Road 2001 and Later Model Year Motor Vehicles” (2011).

[124] Reddy, S. Understanding Fuel Effects on Hydrocarbon Permeation through Vehicle Fuel System Materials, SAE 2007-01-4089.

[125] CARB, Gasoline Dispensing Facility (GDF)Balance Hose Permeation Study, June 19, 2008.

[126] Aulich, T., X. He, A. Grisant, C.K., Knudson, “Gasoline Evaporation-Ethanol and Nonethanol Blends,” *J. Air & Waste Manage. Assoc*. 44:1004-1009, 1994.

Table 9 from the CRC studies referenced above) this result suggests if ethanol permeates at a higher rate it is balanced out by lower permeation emissions of other hydrocarbons if the vapor pressure of the two tested fuels are the same.

TABLE 9. EVAPORATIVE EMISSION STUDIES ON E20

Study Name	Test Cycle	No. of Vehicles	Vehicle Model Years	Fuels	Organic Emissions	Ozone forming potential
CRC E-65-3	Diurnal	4	2001-2005	E10 match blend	No significant difference	No significant difference
CRC E-65-3	Steady-state	4	2001-2005	E10 match blend	No significant difference	No significant difference
CRC E-77-2	Static	6	2001-2006	E10 match blend	No significant difference	Not tested
CRC E-77-2	Running Loss	6	2001-2006	E10 match blend	No significant difference	Not tested
CRC E-77-2	Hot Soak	6	2001-2006	E10 match blend	No significant difference	Not tested
CRC E-77-2	Diurnal (3-day)	6	2001-2006	E10 match blend	No significant difference	Not tested

4.5.7.1 Description of Studies

4.5.7.1.1 Coordinating Research Council Study E-65-3

CRC E-65-3[127] was conducted using a number of fuels (E0, E6, E6 high aromatics, E10, E20 and E85), and five vehicles, but only the results of E10 and E20 (matched aromatic content) conducted on the four post 2001 MY vehicles are considered here. E15 was not tested. The fuel systems were removed from the vehicles and the fuel rigs were tested over the 24-hour diurnal test in a Variable Temperature Sealed Housing for Evaporative Determination (VT-SHED) using the California Enhanced Evaporative Testing rules. The fuel tanks and the canisters were vented to the outside of the SHED to limit measured emissions to permeation emissions alone. Test results in mg/day for the four vehicles are shown in Table 3 of the study. Two of the vehicles showed increases comparing E20 to E10, and two showed decreases, and the net change is not considered statistically significant. The specific reactivity of the emissions was measured, and the ozone-forming potential was calculated. The result, in Table A- 8 of the study, shows that the ozone-forming potential of the permeation emissions from the two fuels were not statistically distinguishable.

4.5.7.1.2 Coordinating Research Council Study E-77-2

Similar permeation testing was conducted by Coordinating Research Council[128] in 2010 on six vehicles that were 2001+ MY. Again, the testing was conducted in a SHED to capture permeation emissions, with all of the emissions from the vehicle's activated carbon canister vented to the outside. The vehicles were tested on two E10 fuels, with vapor pressures of 7 psi and 10 psi, and a single match-blended E20 fuel (aromatic content held constant between the fuels) with a nominal vapor pressure of 9 psi, but which actually had a vapor pressure of 8.5 psi. The 10 psi E10 fuel was created from the 7 psi E10 fuel by

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[127] CRC E65-3 Fuel Permeation from Automotive Systems: E0, E6, E10, E20 AND E85, Final Report, December 2006.
[128] CRC E77-2 Enhanced Evaporative Emission Vehicles, March 2010.

adding butane. In order to equalize any impact of vapor pressure, the emissions results of the two E10 fuels were averaged to roughly estimate the emissions of an 8.5 psi fuel.

Measurements were made for the following tests:

- Static permeation: fuel system pressurized and monitored for vapor and fuel leaks at 86 °F
- Running loss: two cycles of the LA-92 test at 86 °F
- Hot soak: one hour immediately following LA-92 test
- Diurnal test: California 3-day test, in which temperature is varied between 65 °F and 105 °F.

None of the tests resulted in a statistically significant difference between the average of the E10 7 and 10 psi fuel results and the E20 8.5 psi fuel. Two of the tests showed an average emission increase in the higher ethanol content fuel, one showed almost no change, and one found a decrease.

Taken together, these results suggest that there is no trend in permeation emissions between E10 and E20 in these studies. There are no data specific to permeation emissions from E15 fuel, but these results suggest that they will not be significantly different than E10 emissions.

Another important factor that needs to be considered is that the vehicles tested in the two CRC studies ranged from MY1996 to 2006 with most being certified to the original enhanced evaporative test procedures as opposed to the considerably more stringent LEV II near- and zero-emission standards which apply to SULEVs or comparable the LEV III evaporative emissions standards that apply to all 2015 and later model-year vehicles. These more stringent standards lead to lower evaporative emissions in general and are also expected to reduce permeation emissions – particularly the zero-emission and LEV III standards.

Vehicles certified to these more stringent standards dominate the 2001 and later model-year vehicle fleet that would use E15. This can be seen from a recent CRC study which showed, based on vehicle registration data, that more than about 50% of California passengers cars were certified to LEV II or the more stringent zero or LEV III standards beginning with the 2004 model-year increasing to virtually all vehicles by the 2007 and later model-years. Light-duty trucks reached the greater than 50% level during the 2005 model-year and all vehicles by the 2007 and later model years.

It should also be noted the LEV III regulations, adopted in 2012, also changed the test fuel used for determining evaporative emissions to an E10 blend and that CARB staff noted at that time that (page 53 of the LEV III ISOR):

"…most vehicles currently contain low-permeation materials because manufacturers must design for the commercial fuel in California, which contains up to 10 percent ethanol. Therefore, staff does not expect manufacturers to make significant changes to the fuel system to accommodate the proposed test fuel, nor does staff expect any impact on fleet evaporative emissions due to the change."

Overall, all of the above supports a finding that there is no reason to expect that going from E10 to E15 will increase permeation emissions.

4.5.8 Combined Analysis of All Emissions Data

Taken independently, these studies show no consistent, measurable difference between E10 and E15 or even E10 and E20 tailpipe emissions of NO_x, organics, PM or toxic weighted potency, although a number of studies showed a tendency of lowered CO and organic compound emissions with both E15 and E20. One study showed a statistically significant increase in NOx emissions with E20. Combining the data from all of the studies (Table 6 in Appendix 2) shows a statistically significant decrease in CO with both E15 (-7%, p value = 0.0009), and E20 (-9%, p value =0.0002), and a marginally significant increase (+11%, p value = 0.07) in NOx with E20. There is limited evidence that the organic compounds emitted from the tailpipe will have a lower ozone forming potential with E15 in comparison to E10, based on California-specific fuels and other test fuels in the US and China.

The total mass of permeation emissions and the ozone-forming potential of those emissions from E20 and E10 are statistically indistinguishable, suggesting that the use of E15 in place of E10 will have no impact on permeation emissions. There has been no reported testing on benzene evaporative emissions. It seems likely that benzene emissions would decrease at higher ethanol content, since benzene is only present in the hydrocarbon portion of ethanol-gasoline blends.

These results are derived from tailpipe emissions data from 61 vehicles and permeation emissions data from 10 vehicles.

4.6 Summary of Findings

The existing emissions data suggest that use of gasoline blends up to E15, as allowed by U.S. EPA in existing 2001 and later model-year vehicles and FFVs, will not result in any increase in vehicle exhaust emissions of organic compounds or their ozone-forming potential, oxides of nitrogen, carbon monoxide, particulate matter, or potency-weighted toxic air contaminants relative to E10. However, as the testing did not compare E15 results to California Phase 3 RFG E10 fuels additional exhaust emissions testing will be needed to ensure that splash blending of additional ethanol (up to E15) in fuels permitted in California will not adversely affect air quality. The Tier II test plan will be designed to evaluate the exhaust emissions impacts and determine emissions equivalence with a high level of statistical significance.

E15 is expected to have a slightly lower vapor pressure than E10 and the research strongly support that evaporative emissions will not increase with the use of E15 compared to E10. A Multimedia Tier II will test whether the same is true for evaporative emissions when utilizing California RFG.

California will need to determine if currently acceptable levels of detergent additives are acceptable for E15.

4.7 Additional Testing Required to Evaluate Ethanol Blends Above E10

In 2012, the California Air Resources Board adopted the California Test Procedures for Evaluation Substitute Fuels and New Clean Fuels in 2015 and Subsequent Years.[129] These test procedures will be used for guidance on the additional testing required to evaluate vehicle exhaust and evaporative emissions impacts of ethanol blends above E10 for Model Year 2001 and newer California vehicles. The authors of this multimedia evaluation propose that the statistical methods in this Test Procedure, particularly the value of gamma, be reevaluated on the basis of the variability of recently conducted repeat testing. Test vehicles will be chosen as described under Section VI, Test Vehicles.

The test-program reference fuels will be E10 CaRFG3, and the candidate fuel will be E15. The candidate fuel will be blended with the same CaRFG3 CARBOB as the reference fuel, or splash blended up with denatured ethanol from the E10 reference fuel to E15. Alternative petroleum blendstocks for the E15 may also be considered during the emissions test program, in order to optimize refinery economics, while minimizing emissions. In all cases testing will be conducted using the E10 CaRFG3 as the reference fuel. Alternative E15 blendstocks which meet emissions standards will be approved based on the specific fuel properties of the test fuel.

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[129] https://ww3.arb.ca.gov/regact/2012/leviiighg2012/lev12.pdf

5 Release Scenarios

Releases of ethanol-blended fuels have the potential to impact air, soil, groundwater, and surface water, resulting in exposures to both human and environmental receptors. This section presents the scenarios in which E15 would or could be released into the environment to determine if, and to what extent, these fuels pose release-related hazards beyond those of E10, the baseline reference fuel for this multimedia evaluation.

Ethanol-blended fuel release scenarios outlined in this section are categorized as either “normal” releases, which are routine releases anticipated during standard production, storage, distribution, dispensation, and use, and “off-normal” releases, which are generally accidental and unplanned releases resulting from human error or equipment failure. Examples of recent off-normal ethanol-blended fuel releases are then presented to illustrate the anticipated environmental impacts of these types of scenarios.

5.1 Normal Releases

Normal release scenarios for E11 - E15 blended fuels (referred to as E15 in this chapter) are the same as those of E10, as the processes by which E15 is produced, stored, distributed, dispensed, and used are expected to be the same as those of E10. There are three general scenarios in which E10 is, and E15 would be routinely released into the environment under normal circumstances:

- Temperature increases drive increases in evaporation and vapor pressure, resulting in emissions to the atmosphere via ventilation systems or fill pipe openings;
- Fuels introduced to tank enclosures displace fuel vapors within, resulting in emissions to the atmosphere via ventilation systems or fill pipe openings; and
- Fuels are not completely consumed during combustion process in vehicles, vessels, and equipment engines, resulting in discharge of fuel vapor or liquid fuel to the air, land, or water via the exhaust system.

Temperature increases frequently result in vapor emissions from tanks used to blend fuels at the terminal, from tanker trucks and railcar tanks used to transport the fuels, from fuel retailers’ tanks, and from fuel tanks in consumers’ vehicles or vessels. While vapors exiting these tanks via ventilation systems are often diverted to vapor recovery systems, temperature-driven fugitive emissions often reach the atmosphere while fuel is stored.

Vapor emissions also escape when ethanol-blended fuels and blended fuel components are introduced to these tanks during normal fuel blending, tank filling, and vehicle/vessel fueling processes, resulting in vapor displacement and discharge via the same tank ventilation systems and via tank fill pipes and valves. While terminals, trucks, retailer tanks, and most motor vehicles are now equipped with vapor recovery systems and/or vapor flares designed to capture fugitive fuel vapor emissions, opportunities for normal releases of displaced vapors into the atmosphere exist during normal blending, distribution, and dispensation processes.

Normal releases of ethanol-blended fuels in both vapor and liquid phases occur when fuel injected into an engine is not completely combusted, resulting in discharge, or “rainout,” of fuel via the associated exhaust system. These vehicle, vessel, and equipment tail pipe emissions can result in impacts to the air, ground, and in the case of vessels, surface water. Residual heat from a recently-operated engine can also evaporate liquid fuel within a fuel system, resulting vapor emissions to the atmosphere after engine use has ceased.

Table 10 provides location, equipment, and process-specific details related to normal release scenarios from the point at which E15 fuels are blended, which could occur at a fuel terminal or at a retail station, to the point at which the fuels are purchased and utilized by consumers.

TABLE 10. NORMAL RELEASE SCENARIOS

Normal Release Scenarios				
Release Scenario	**Cause(s) of Release**	**Affected Media**	**Volume of Release**	**Likelihood**
Vapor emissions exit storage tank via ventilation system	1. Ethanol-blended fuel components enter blending tank and displace vapors. 2. Increase in ambient temperature results in increased vapor pressure and evaporation.	Impact to ambient air quality.	Potential volume limited to capacity of tank. Actual release volume likely to be significantly lower.	High likelihood of occurrence. Low likelihood of significant environmental impacts. Facilities are required to account vapor emissions during permitting process. Significant quantities require control.
Vapor emissions exit tanker truck via ventilation system	1. Ethanol-blended fuel enters truck tank during loading and displaces vapors. 2. Increase in ambient temperature results in increased vapor pressure and evaporation.	Impact to ambient air quality.	Potential volume limited to capacity of tank. Actual release volume likely to be significantly lower.	High likelihood of occurrence. Low likelihood of significant environmental impacts. Displaced vapors are often diverted to recovery systems that condense vapors or a flare system that burn off vapors prior to reaching atmosphere.
Vapor emissions exit rail car tank via ventilation system	1. Ethanol-blended fuel enters railcar tank during loading and displaces vapors. 2. Increase in ambient temperature results in increased vapor pressure and evaporation.	Impact to ambient air quality.	Potential volume limited to capacity of tank. Actual release volume likely to be significantly lower.	High likelihood of occurrence. Low likelihood of significant environmental impacts. Displaced vapors are often diverted to recovery systems that condense vapors or a flare system that burn off vapors prior to reaching atmosphere.
Vapor emissions exit retailers' storage tank via ventilation system	1. Ethanol-blended fuel enters railcar tank during refilling and displaces vapors. 2. Increase in ambient temperature results in increased vapor pressure and evaporation.	Impact to ambient air quality.	Potential volume limited to capacity of tank. Actual release volume likely to be significantly lower.	High likelihood of occurrence. Low likelihood of significant environmental impacts. Vapors displaced by offloading are often diverted back into head space of tanker truck's tank.

Normal Release Scenarios (continued)				
Release Scenario	**Cause(s) of Release**	**Affected Media**	**Volume of Release**	**Likelihood**
Vapor emissions exit vehicle/vessel fuel tank via fill pipe.	1. Ethanol-blended fuel enters vehicle/vessel fuel tank during refueling and displaces vapors. 2. Increase in ambient temperature results in increased vapor pressure and evaporation.	Impact to ambient air quality.	Potential volume limited to capacity of tank. Actual release volume likely to be significantly lower.	High likelihood of occurrence. Low likelihood of significant environmental impacts due to low release volume.
Vapor emissions exit vehicle/vessel engine.	1. Residual heat from recently-operated engine evaporates fuel within the fuel line.	Impact to ambient air quality.	Potential volume limited to capacity of tank. Actual release volume generally limited to less than one ounce per occurrence.	High likelihood of occurrence. Low likelihood of significant environmental impacts due to low release volume.
Liquid fuel and vapor emissions exit vehicle/vessel via tailpipe (rain out)	1. Liquid fuel and fuel vapor not consumed during engine's combustion process is discharged via the exhaust system.	Vapor emissions result in impact to ambient air quality. Liquid fuel impacts ground (possibly soil) and surface water.	Potential volume limited to capacity of tank. Actual release volume generally limited to less than one ounce per occurrence.	High likelihood of occurrence. Low likelihood of significant environmental impacts due to low release volume.

5.2 Off-normal Releases

Off-normal releases of E15 resulting in impacts to the environment may occur during blending, storage, distribution, transportation, handling, dispensation and use of these products. Off-normal release scenarios for E15 are the same as those of baseline fuel E10, as E15 would presumably be blended, stored, distributed, transported, handled, dispensed, and used by the same people and processes currently managing E10. Accidental releases of E10 have occurred, and releases of E15 are expected to occur, under two primary circumstances:

- Equipment failure results in a loss of containment; or
- Human error or negligence results in a spill.

Common off-normal release scenarios involving equipment failures include leaks and spills from above and below ground storage tanks, tanker trucks, rail cars, pipes, hoses, or valves caused by corrosion, manufacturing defects, equipment malfunctions, physical damage from weather events, and other inadvertent impacts such as train derailments or vehicle/vessel accidents not caused by human error. Equipment-related off-normal releases have the potential to impact soil, groundwater, surface water, and air if leaks and spills are not contained.

Common off-normal release scenarios involving human errors and negligence include spills from overfilling tanks; leaks due to physical damage to tanker trucks, rail cars, storage tanks, fuel pumps, and other vehicles, vessels, and equipment; spills resulting from failure to follow proper hose connection and disconnection protocols; and other general instances of improper equipment installation and operation. Like equipment-related off-normal leaks and spills, human error- and negligence-related off-normal releases have the potential to impact soil, groundwater, surface water, and air if they are not contained.

In above ground storage tanks, risks to the environment and human health posed by E10 and E15 fuel spills/releases are largely mitigated by secondary containment requirements included in Spill Prevention, Control, & Countermeasure (SPCC) provisions promulgated in 40 Code of Federal Regulations (CFR) 112. As stated in 40 CFR 112.8(c)(2)[130], facilities storing petroleum-based fuel products above ground are required to “construct all bulk storage container installations so that you provide a secondary means of containment for the entire capacity of the largest single container and sufficient freeboard to contain precipitation.” Provisions listed in 40 CFR 112.8(c)(4-8)[131] include additional requirements for tank corrosion prevention, scheduled tank integrity testing, implementation of fuel level monitoring procedures, and installation of high liquid level alarms and pump cutoff devices to prevent accidental releases.

Additional safeguards against E15 releases via leaking underground storage tanks (LUSTs) include underground storage tank regulations listed in 40 CFR 280.32-34, which require tank owners and operators to notify their implementing agency and make additional fuel compatibility verifications before storing ethanol-blended fuels in excess of 10% ethanol onsite. California has State regulations that generally follow the federal regulations for SPCC with some additional requirements for petroleum storage tanks. The California Aboveground Petroleum Storage Act (APSA) regulates facilities with aggregate aboveground petroleum storage capacities of 1,320 gallons or more, which include aboveground storage containers or tanks with petroleum storage capacities of 55 gallons or greater.[132] The State Water Board oversees the Underground Tanks Regulations.[133] Adherence to these pollution prevention standards provide safeguards against these release scenarios, which will help reduce the overall number of releases.

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[130] 40 CFR 112.8(c)(2)

[131] 40 CFR 112.8(c)(4-8)

[132] Health and Safety Code (HSC) Division 20. Chapter 6.67. Aboveground Storage of Petroleum [25270 - 25270.13] http://leginfo.legislature.ca.gov/faces/codes_displayText.xhtml?lawCode=HSC&division=20.&title=&part=&chapter=6.67.&article=

[133] Title 23. California Code of Regulations, Division 3. State Water Resources Control Board and Regional Water Quality Control Boards, Chapter 16. Underground Tank Regulations https://govt.westlaw.com/calregs/Browse/Home/California/CaliforniaCodeofRegulations?guid=I1EB45220D45B11DEA95CA4428EC25FA0&originationContext=documenttoc&transitionType=Default&contextData=(sc.Default)

Table 11 provides additional details related to off-normal release scenarios from the point at which E15 fuels are blended to the point at which the fuels are purchased and utilized by consumers.

TABLE 11. OFF-NORMAL RELEASE SCENARIOS

Off-normal Release Scenarios				
Release Scenario	**Cause(s) of Release**	**Affected Media**	**Volume of Release**	**Likelihood**
Release from fuel storage tanks at blending facility	1. Equipment Failure: Tank, pump, piping, or valve failure. 2. Operator Error: Valves left open or tank overfilled during blending.	Limited to evaporative emission impacts to air quality if fuel tanks are located within proper secondary containment.	Potential volume limited to capacity of storage tank (18,000 to 3,000,000 gallons). Actual release volume likely to be significantly lower.	Low likelihood of environmental impacts. Facilities required to provide secondary containment for bulk fuel storage.
Release while loading tanker truck or rail car	1. Equipment Failure: Tank, pump, piping, hose, or valve failure. 2. Operator Error: Valve left open, tanker overfilled, improper hose connection, or release during hose disconnection.	Limited to evaporative emission impacts to air quality if loading is performed within proper secondary containment.	Potential volume limited to capacity of storage tank (>1 million gallons). Actual release volume likely to be significantly lower.	Low likelihood of environmental impacts. Facilities required to provide secondary containment for fuel loading/unloading processes.
Release from tanker truck as a result of a traffic accident	1. Impact resulting in fuel tank puncture.	Impacts will vary based on volume and location of release. Impacts to soil, groundwater, surface water, and air possible.	Volume limited to capacity of tanker truck (Approx. 5,000-15,000 gallons).	Moderate likelihood of occurrence.
Release from train tanker car as a result of an accident or derailment	1. Impact resulting in fuel tank puncture.	Impacts will vary based on volume and location of release. Impacts to soil, groundwater, surface water, and air possible.	Volume limited to capacity of train's tanker cars (Approx. 20,000-35,000 gallons per car).	Moderate likelihood of occurrence.

Off-normal Release Scenarios (continued)				
Release Scenario	**Cause(s) of Release**	**Affected Media**	**Volume of Release**	**Likelihood**
Release while off-loading fuel from tanker truck to retailer's tank	1. Equipment Failure: Tank, pump, piping, hose, or valve failure. 2. Operator Error: Tank overfilled, truck valve left open, improper hose connection, or release during hose disconnection.	Immediate impact to air and paved surfaces, with possible accumulation of free product in in soil and groundwater if release is of sufficient volume. Potential discharge to surface waters via stormwater runoff.	Volume limited to capacity of tanker truck or compartment of tanker truck in use (Approx. 1,000-15,000 gallons).	Moderate likelihood of occurrence.
Release while off-loading fuel from train tanker car	1. Equipment Failure: Tank, pump, piping, hose, or valve failure. 2. Operator Error: Tank overfilled, valve left open, improper hose connection, or release during hose disconnection.	Immediate impact to air and surface soil, with possible accumulation of free product in in subsurface soil and groundwater if release is of sufficient volume. Potential discharge to surface waters via stormwater runoff.	Volume limited to capacity of train's tanker car (Approx. 20,000-35,000 gallons).	Moderate likelihood of occurrence.
Release from fuel retailer's leaking storage tank	1. Equipment Failure: Tank leaks due to corrosion or puncture.	Impact to subsurface soil. Impact to groundwater possible if present and release is of sufficient volume.	Volumes of releases from leaking tanks vary widely. Volumes depend on rate of release and length of time over which release occurs.	Moderate likelihood of occurrence. Likelihood decreasing as retailer's transition to tanks with corrosion-resistant coatings, secondary containment, and leak detection mechanisms.

Off-Normal Release Scenarios (continued)

Release Scenario	Cause(s) of Release	Affected Media	Volume of Release	Likelihood
Release while fueling consumer vehicle	1. Fuel Dispensing Equipment Failure: Automatic shutoff malfunction, hose or nozzle leak. 2. Operator Error: Auto fuel tank or container overfill or dispensing/spilling outside of tank or container.	Impacts often limited to paved surfaces and evaporative impacts to air quality, Accumulation of free product in soil and groundwater possible if spills are of sufficient frequency and volume. Potential discharge to surface waters via stormwater runoff.	Generally less than 50 gallons, with most spills less than one gallon.	High likelihood of occurrence with low likelihood of significant environmental impact – Low volume releases resulting from operator errors during consumer dispensing are common.
Release from consumer vehicle as a result of a traffic accident	1. Impact resulting in fuel tank puncture.	Impacts will vary based on volume and location of release. Immediate impact to air and paved surfaces, with possible impacts to soil, groundwater, surface water, and air.	Volume limited to capacity of vehicle's fuel tank (<50 gallons).	Moderate likelihood of occurrence.
Release of fuel-contaminated water from secondary containment basin	1. Equipment Failure: Basin leaks due to degradation or puncture, or pump, piping, or valve failure causing loss of containment. 2. Operator Error: Basin drained despite presence of fuel. 3. Severe Weather: Significant rain or flooding event causing basin to overfill.	Impacts will vary based on volume and location of release. Impacts to surface water possible if discharged to stormwater retention pond or storm drain.	Volumes of releases from secondary containment basins vary widely. Volumes depend on volume of initial release. Releases often consist of mostly water with slight surface sheen.	High likelihood of low volume releases with limited environmental impact due to operator error. Low likelihood of release due to equipment failure or significant rain event.

5.3 Human and Environmental Exposures

Normal and off-normal releases of ethanol-blended fuels can result in adverse impacts to humans and the environment. Opportunities for and the likelihood of biological impacts from E15 fuel releases are expected to be the same as those of E10.

5.3.1 Exposures to Human Receptors

Risk of human exposure posed by normal releases is generally limited to fuel vapor inhalation. While ventilation and vapor recovery systems largely prevent the accumulation of high concentrations of fuel vapors in ambient air, there exists the potential for personnel working in and around fuel terminals and retail stations to breath air containing relatively low concentrations of ethanol-blended fuel vapors. Vapor concentrations in and around areas subject to normal releases of E15 are expected to be similar, if not less than those of E10, as vapor pressure and overall volatility of ethanol-blended fuels decrease as ethanol concentrations in excess of 10% are increased in fuel.

Off-normal releases pose greater risks for human exposure. In addition to the potential for vapor inhalation, accidental releases and subsequent control and cleanup efforts present opportunities for eye and dermal absorption, and releases to potable water sources present opportunities for ingestion. The resulting risks to human health are expected to be similar, if not less severe than those associated with E10 spills, as an increase in the ethanol concentration in the fuel to which humans are exposed should produce a proportional decrease in total exposure to benzene, the primary human carcinogen found in gasoline.

Symptoms of exposure include skin and eye irritation, dullness of memory and concentration, impaired motor skills, drowsiness, stupor, and coma. Prescribed treatments for individuals displaying symptoms of exposure include moving away from fuel vapors to fresh air, removing contaminated clothing, washing contacted areas with soap and water, and contacting medical personnel, if necessary.[134]

Potential impacts to human health are discussed in greater detail in Section 7: Scientific Discussion on Human/Ecological Risk.

5.3.2 Exposures to Environmental Receptors

Releases into the environment can result in impacts to several biological receptors. Aquatic ecosystems are particularly vulnerable to ethanol-blended fuel releases due to ethanol's high oxygen demand, which can rapidly decrease the amount of dissolved oxygen (DO) within impacted water bodies. Ethanol-blended fuel spills can cause fish kills and have adverse effects on amphibians, reptiles, and mammals living in and around the affected area. Ethanol concentrations of 0.5 ug/L can injure crustaceans.[135]

Once ethanol concentration in water is diluted below approximately 1%, the natural biodegradation process begins. Ethanol's expected half-life in surface water ranges from 3 to 5 days. Much of the remaining gasoline floats in surface waters and evaporates within a few hours. However, the more soluble chemical constituents of gasoline, such as BTEX, may persist in impacted surface and groundwater. [135] Potential environmental impacts are discussed in greater detail in Section 7: Scientific Discussion on Human/Ecological Risk.

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[134] United States Department of Energy, *Handbook for Handling, Storing, and Dispensing E85 and Other Ethanol-Gasoline Blends, DOE/GO-102016-4854*. (2016).

[135] National Response Team (NRT), NRT Quick Reference Guide: Fuel Grade Ethanol Spills (including E85). (2010).

5.4 Field Studies of Ethanol-Blended Fuel Releases

Publicly available field study literature produced in response to two off-normal bulk fuel releases are summarized below to illustrate environmental impacts of ethanol-blended fuel release scenarios presented in Sections 5.1 and 5.2. The case studies involve accidental releases of denatured fuel ethanol (E95) and E85 fuels.

5.4.1 Train Derailment Field Study

A train derailment in November 2006 in Cambria, Minnesota resulted in a release of approximately 25,000 gallons of denatured ethanol, or E95. Approximately 12,000 gallons of ethanol and ethanol-impacted water pooled in nearby drainage ditches and tank cars was collected immediately following the release, while the remaining ethanol soaked into the ground. Ethanol impacts were noted in the topsoil and underlying sand and silty sand soils in the surrounding area. No benzene, toluene, ethylbenzene, and xylenes (BTEX) or ethanol was detected above method detection limits in five series of surface water samples collected from the adjacent Little Cottonwood River immediately following the release. Potable water wells at four nearby residences were sampled four times each. No concentrations of volatile organic compounds (VOCs) or ethanol above method detection limits were detected in any of the samples.

A total of 20 groundwater monitoring wells were installed in 2006 and 2007. Groundwater impacts detected on and around the derailment site were primarily ethanol and benzene, which both naturally declined over time, with ethanol concentrations declining the fastest. Samples from a monitoring well installed onsite had an ethanol concentration of 400,000 micrograms per liter (ug/l) in the initial sampling event and 637,000 ug/l in May 2009, before rapidly declining to 130 ug/l by June 2010. Toluene concentrations of 260 ug/l and 350 ug/l, which exceeded the 20 ug/l Health Risk Limit (HRL) were detected in two onsite wells in October 2009; however, toluene concentrations in these wells were back below the HRL by the next sampling event in June 2010. Concentrations of methane in groundwater, which is released during the degradation of ethanol, were also monitored throughout the process. Methane concentrations in groundwater varied widely but mostly increased in the summer sampling events. The highest concentrations were generally in the same wells which showed the highest benzene concentrations. Soil gas monitoring points were installed to measure methane and VOCs vapors. Soil gas concentrations generally decreased over time, with no compound detections in excess of 10 times their intrusive screening value (ISV) by June 2010.

Though initial onsite benzene concentrations in excess of 500 ug/L steadily declined over time, benzene concentrations were consistently detected in excess of the 2 ug/L HRL in five of the monitoring wells, primarily concentrated in the spill area. Benzene concentrations remained above HRLs when the reviewed field study report was prepared in December 2010.[136]

5.4.2 Leaking Underground Storage Tank Field Study

A gas station in Hastings, Minnesota detected a leak from its underground storage tank (UST) in February 2009. The tank had historically been used to store gasoline and later E85. A subsurface investigation revealed that steel UST developed a leak due to corrosion, resulting in releases of unknown quantities of gasoline and E85 into the surrounding soil and groundwater. Impacted soils were removed, and five groundwater monitoring wells were installed. Samples were analyzed for BTEX, diesel range organics (DRO), gasoline range organics (GRO), ethanol, methane, and acetate. Although benzene concentrations in excess of the HRL for drinking water were periodically detected in wells down-gradient

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[136] Pinnacle Engineering, Inc., *Minnesota Pollution Control Agency Annual Monitoring Report, DM&E Railroad Derailment, Highway 68, Cambria, Minnesota, Spill 68733*. (Pinnacle). (2010).

of the site, no drinking water receptors were identified, and no evidence of elevated soil gas was found during field screening.

Initial ethanol concentrations detected in onsite monitoring wells topped out at 270,000 ug/L in July 2010, but then rapidly dropped below the 160 ug/L detection limit by 2012. Benzene, however, was consistently detected in on- and off-site wells. Benzene concentrations detected during the October 2015 sampling event, which was the last documented sampling event before the site was closed and monitoring ceased, were found to be 3.0 ug/L onsite and 14.3 ug/L in a down-gradient well, indicating the plume was migrating offsite. The 2015 Annual Monitoring Report prepared for the site attributed the persistence and migration of benzene to the preferential utilization of ethanol under both aerobic and anaerobic conditions, resulting in rapid biodegradation of ethanol at the expense of significantly slower biodegradation rates for BTEX.[137]

Additional details related to specific instances in which ethanol-blended fuels have been released into environmental, the manner in which these fuels interact with various media including volatilization, solubility, and liquid phase partitioning, and the anticipated outcomes of these fuel impacts are discussed in greater detail in Section 6: Environmental Fate and Transport.

5.5 Emergency Response and Release Management Procedures

The U.S. National Response Team (NRT), which is responsible for coordinating federal emergency responses to releases of oil and hazardous substances, recommends the following actions immediately following a release of fuel-grade ethanol:

- Stop leak if it is safe to do so;
- Contact emergency responders;
- Prevent fuel from entering soil, groundwater, surface water, drains, and ditches;
- Eliminate all ignition sources in the immediate area;
- Ensure the area is well-ventilated;
- Ensure all equipment used around the release is grounded and intrinsically safe;
- Restrict access to the area surrounding release;
- Apply vapor-suppressing alcohol-resistant foam to reduce vapors and limit fire risks; and
- Remediate impacted media.

Once the spill source is controlled and conditions at site are stable, the extent of onsite impacts can be investigated. Initial characterization of affected media (e.g., soil, surface water, and groundwater) can be achieved via visual and olfactory inspections, screening with field instrumentation such as a photoionization detector (PID), and sample collection with associated laboratory analyses. Soils, groundwater, and surface water found to contain concentrations of contaminants in excess of applicable regulatory thresholds must be identified and reported to appropriate agencies. Due to the potential for recovered liquids and impacted soils excavated from the release site to exhibit the hazardous waste characteristic of ignitability, NRT recommends managing and disposing of release-related wastes as hazardous waste, as required by 40 CFR 260-262.[135]

NRT's emergency response and release management documents do not make ethanol concentration-specific recommendations, so the responses prescribed for releases of E15 are presumed to be the same as those used for E10 releases.

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[137] Pinnacle Engineering, Inc (Pinnacle), *Minnesota Pollution Control Agency Annual Monitoring Report, Miller & Holmes, Inc. Convenience Store, 1402 Vermillion Street, Hastings, Minnesota, Leak 17529*. (2015).

5.6 Data Gaps and Data Sufficiency

No case studies involving off-normal bulk E10 or E15 fuel releases were identified during preparation of this multimedia evaluation, presumably because these fuels are most often blended at retail facilities as they are sold to consumers in small batches or blended at fuel terminals as they are loaded into tanker trucks, eliminating opportunities for bulk releases from pipelines, train derailments, and terminal storage tanks. In the event bulk E10 and E15 fuel releases occur in the future and field study data becomes publicly available, additional review may be warranted.

Groundwater monitoring data collected during the field studies included in Sections 5.4.1 and 5.4.2 demonstrate that ethanol is preferentially biodegraded in both aerobic and anaerobic environments, and that the primary contaminant of concern is benzene from gasoline. While field study data specifically related to off-normal releases of E15 fuels to soil, surface water, and groundwater were not available for review, the existing body of data is sufficient to determine that fuels released into the environment with ethanol concentrations greater than that of E10 will result in releases of a greater percentage of easily biodegradable ethanol, and a lesser percentage of benzene-containing gasoline.

5.7 Summary of Findings

The use of E15 would not result in any release, or human or environmental impact scenarios, different from those that occur with current ethanol containing fuels approved for use in California.

6 Environmental Fate and Transport

6.1 Introduction

As with E10 fuels already approved in California, there is the potential for releases into the environment during the production, distribution, and use of blends in the E11 – E15 range. If a spill or leak of these blends occurs, the higher ethanol content in the fuel can influence the fate and transport characteristics of fuel constituents in the mixture relative to E10.

Environmental and human health impacts associated with releases of E11 – E15 blends are similar to those associated with E10. Primary migration pathways include:

- Volatilization to atmosphere;
- Releases to surface water bodies;
- Migration from surface soils to subsurface soils;
- Migration of volatile organic compounds to soil vapor (including the generation of methane vapors); and,
- Migration to groundwater.

The following sections confirm the reference fuel used, establish the relevancy of previous ethanol fuel multimedia studies to this study, summarize ethanol, ethanol blend feedstock and E15 fuel properties, and discuss the various principles of partitioning and phase interface relationships and how they relate to E15 fate and transport relative to the reference fuel.

6.1.1 Reference Fuel

As discussed previously, E10 meeting the current California Reformulated Gasoline requirements is the recommended reference fuel for this multimedia evaluation of E11 – E15. Also noted previously, U.S. EPA has approved blends up to E15 for use in light-duty conventional vehicles of model year 2001 and newer, and it should be noted that E15 is currently available at 1,400 stations in 29 states across the country.[138] To understand the environmental fate and transport of E11 – E15 blends, a discussion and comparison to E10 is needed.

6.1.2 Relevance to draft E85 Multimedia Study to E11 – E15 Blends

A substantial amount of information regarding the fate and transport of ethanol, denatured ethanol, and ethanol blended fuel is provided in the *Health and Environmental Assessment of the Use of Ethanol as a Fuel Oxygenate* report to the California Environmental Policy Council in response to executive order D-5-99 (OEHHA, 1999) and the draft *California Multimedia Evaluation of Elevated Ethanol Fuel Blends for Flexible-Fuel Automotive Spark-Ignition Engines*.[139] [140] This report was not reviewed or approved by California's Multimedia Working Group, but still contains valuable data as reference for E15 use. The draft E85 Multimedia Evaluation document synthesizes a large volume of more current research on ethanol, denatured ethanol, and ethanol blended fuel, with emphasis on E10 and E85 blends. As is the case here, the draft E85 Multimedia Evaluation used E10 as the reference fuel.

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[138] Alternative Fuels Data Center, *E15*. U.S. Department of Energy (AFDC). Retrieved November 29, 2018, from https://afdc.energy.gov/fuels/ethanol_e15.html

[139] Office of Environmental Health Hazard Assessment (OEHHA), Rice, D. & Cannon, G. (Eds.), *Health and Environmental Assessment of the Use of Ethanol as a Fuel Oxygenate* (UCRL-AR-135949) (1999). https://www.arb.ca.gov/fuels/multimedia/1999_mme_ethanolfueloxygenate.pdf

[140] The University of California, Davis & The University of California, Berkeley (UC), *California Multimedia Evaluation of Elevated Ethanol Fuel Blends for Flexible-Fuel Automotive Spark-Ignition Engines Tier I Report*. (2016).. https://www.arb.ca.gov/fuels/multimedia/meetings/ethanolelevatedfuelblends_tier%20i_mar2201.pdf

The compositional differences between equal volumes of E10 and a E11 – E15 blends are generally the proportional difference of greater ethanol mass and volume, and less gasoline component mass and volume for the E11 – E15 blend vs E10.[135 70] Therefore, the environmental fate and transport differences between E10, and E11 – E15 blends has more to do with the effects of the differences in ethanol concentrations on the environment and on the risk-driving toxic constituents of the gasoline portion of the fuel mixture (e.g., benzene, and to a lesser extent toluene, ethylbenzene, and xylenes). As such, data, interpretations, fate and transport theory, models, and in some cases empirical data observed in the draft E85 Multimedia Evaluation are relevant to E11 – E15 blends. Given this, the environmental fate and transport information summarized for E11 – E15 blends in this document draws heavily from the draft E85 Multimedia Evaluation. Where possible, new or pertinent information specific to environmental behavior of E11 – E15 ethanol blends in the E11 - E15 range relative to E10 is included.

Critical to understanding the relative risk of E11 – E15 releases versus E10 releases along these pathways is knowing the physical and chemical properties of ethanol, and of E11 – E15 fuel blends relative to E10.

6.1.3 Chemical and Physical Properties of Ethanol

Ethanol is a clear, colorless, flammable liquid alcohol made by fermenting and distilling some types of vegetation, such as corn. It is a polar solvent, and has a vinous, wine-like odor. Additionally:

- Ethanol is completely miscible in water, meaning that it will mix without limits (in all amounts) with water to form a homogenous mixture;
- Ethanol is hygroscopic, i.e., it has a tendency to absorb moisture either from aqueous interfaces or from humid air interfaces.
- Ethanol and water form an azeotrope (a mixture of two liquids that has a constant boiling point and composition throughout distillation).

Table 12 below summarizes key chemical properties of ethanol important for evaluating environmental fate and transport.

TABLE 12. ETHANOL PROPERTIES

Property	Value and Units	Source
CAS No.	64-17-5	(1)
Molecular Formula	C_2H_6O or C_2H_5OH	(1)
Molecular Weight	46.069 g/mol	(1)
Specific Gravity	0.794 @ 25°F	(2)
Vapor Density (Relative to Air, Air = 1)	1.59	(1)
Boiling Point	78 – 79 °C	(2)
Water Solubility (mg/L)	Infinite (miscible with water)	(1)
Vapor Pressure	49 – 56 mm Hg @ 25 °C	(2)
	50 mm Hg @ 25 °C (77 °F)	(1)
	5.8 kPa @ 20 °C	(1)
	17 kPa @ 100 °F	(2)
Reid Vapor Pressure	2.3 psi	(2)
Henry's Law Constant	6.17×10^{-6} atm-m^3/g-mole	(2)
	5.13×10^{-6} atm-m^3/g-mole	(2)
	6.29×10^{-6} atm-m^3/g-mole	(2)
Henry's Law Constant (Dimensionless)	2.522 x 10-4	(2)
	2.097 x 10-4	(2)
	2.571 x 10-4	(2)
Log Koc	1.21, 0.2	(2)

Log Kow	-0.16, -0.31	(2), (1)
Viscosity	1.074 mPa @ 20 ^{o}C	(1)
Surface Tension	21.97 mN/m @ 25 ^{o}C	(1)
Flash Point	55 ^{o}F	(1)
Lower Explosive Limit	3.3%	(3)
Upper Explosive Limit	19%	(3)
Half Life in Air	0.5 – 5 days	(2), (4)
Half Life in Surface Water	<1 – 39 days	(2), (3)

Sources:
(1) https://pubchem.ncbi.nlm.nih.gov/compound/ethanol#section=Top
(2) OEHHA[139]
(3) Shaw, 2011[141]
(4) ODOH, 2016[142]

6.1.4 Chemical and Physical Properties of CARBOB, California Reformulated Gasoline (E10), California Reformulated Gasoline (E15), and Denatured Fuel Ethanol

Table 13 below summarizes chemical and physical specifications (when available) regarding California Reformulated Gasoline (CaRFG3)/E10, Denatured Fuel Ethanol (DFE), and California Reformulated Gasoline Blendstock for Oxygenate Blending (CARBOB) approved in California. These specifications are provided in Title 13, California Code of Regulations (CCR), Sections 2262 for CaRFG3/E10, 2262.9 for denatured fuel ethanol, and 2266.5 for CARBOB.[143] Where property values are listed on the table but not in the specifications in the code, data is inferred from other listed sources, such as safety data sheets for equivalent fuel. Data shown for CA E15 blend assumed to be a proportional value based on blend of E10.

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[141] Shaw's Environmental and Infrastructure Group, *Large Volume Ethanol Spills – Environmental Impacts & Response Options*. (Shaw). (2011). https://www.mass.gov/files/2017-08/ethanol-spill-impacts-and-response-7-11.pdf

[142] Ohio Department of Health (ODOH), Bureau of Environmental Health and Radiation Protection, *Ethanol Answers to Frequently Asked Health Questions*. (2016). https://www.odh.ohio.gov/-/media/ODH/ASSETS/Files/eh/Chemical-Fact-sheets/014-Ethanol.pdf?la=en

[143] California Air Resources Board (CARB), *The California Reformulated Gasoline Regulations, Unofficial electronic version, Title 13, California Code of Regulations, Sections 2250-2273.5.* (2014).

TABLE 13. CHEMICAL AND PHYSICAL PROPERTIES OF CARBOB AND VARIOUS ETHANOL FUEL BLENDS

Gasoline Parameter	CARBOB	CA E10 (RFG 3)	CA E15[144]	DFE
Ethanol Content (assumed % volume)	0	10	15	92.1
Aromatic HC Content (% volume)	38.7[a]	35.0[a]	*33.19*	1.7[a]
Benzene Content (% volume)	1.22[a]	1.10[a]	*1.04*	0.06[a]
Distillation, T50 (°F)	RVP: 232 Non-RVP: 237[a]	220[a]	xx	NA
Distillation, T90 (°F)	335[a]	330[a]	xx	NA
MTBE Content (% volume)	NA[a]	0.05[a]	*0.075*	0
Olefin Content (% volume)	11.1[a]	10.0[a]	*9.49*	0.5[a]
Oxygen Content (% weight)	NA[a]	3.5[a]	*3.6 - 5.x*	*34*
Oxygen Content (total, other than EtOH & MTBE) (% weight)	NA[a]	0.06[a]	*0.09*	NA
RVP (psi)	5.99[a]	6.40 - 7.20[a]	xx	~2.3
DVPE (psi) (avg. value)	5.79[b]	6.98[c]	7.055[b]	xx
Sulfur Content (ppm)	21[a]	20[a]	*20*	10[a]
Deposit Control Additive	NA[a]	NA[a]	NA	NA
Lead Content (mg/L)	13.21[a]	13.21[a]	*12.40*	NA
Manganese Content	NA[a]	NA[a]	NA	NA
Phosphorus Content (mg/L)	1.32[a]	1.32[a]	*1.24*	NA
Specific Gravity (Range)	0.7453-0.7482[b]	0.7494-0.7540[b]	0.7515-0.7532[b]	0.794[c]
Vapor pressure	5.5-15 psi[d]	6.5-15 psi[e]	5-16 psi[f]	48 mm Hg[g]
Vapor density	3-4[d]	3-4[e]	--	1.5[g]
Relative Density	0.70 - 0.76[d]	0.70 - 0.76[e]	0.76[h]	~0.8[g]
Boiling Point (°C)	24 - 210[d]	24 - 210[e]	38[f]	77[g]
Flash Point (°C)	-43[d]	-43[e]	-40[f]	15.5[g]
LEL (% air volume)	1.4[d]	1.4[e]	1.5[f]	3.3[g]
UEL (% air volume)	7.6[d]	7.6[e]	7.6[f]	18[g]
pHe	NA[d]	NA[e]	NA[f]	6.5-9.0[a]
Viscosity	NA[d]	NA[e]	NA[f]	NA[g]

Footnotes and Abbreviations:
[a] CARB, 2014a and 2014b; value represents maximum allowable content
[b] API, 2010
[c] USDOE, 2016
[d] Marathon, 2018a
[e] Marathon, 2018b
[f] Sunoco, 2014
[g] Fisher, 2014
Italic font: value calculated from proportions of CA RFG 3 (E10)

HC: hydrocarbon
CARBOB: California Reformulated Gasoline Blendstock for Oxygenate Blending
CA: California
RFG 3: Reformulated Gasoline Phase 3
EtOH: denatured ethanol
°F: degrees Fahrenheit
MTBE: methyl tertiary butyl ether
RVP: Reid Vapor Pressure
psi: pounds per square inch
ppm: parts per million
DVPE: Dry Vapor Pressure Equivalent

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[144] Information denoted as “xx” to be populated within Tier II.

Gasoline Parameter	CARBOB	CA E10 (RFG 3)	CA E15[144]	DFE
Vapor Density (relative to air, air = 1) kPa: kilopascals mmHg: millimeters of mercury LEL: lower explosive limit UEL: upper explosive limit SUS: Sabolt universal seconds cm^2/s: square centimeters per second				

6.1.5 Volatilization, Solubility, and Partitioning Between Water, Fuel and Soil

Available information on actual fate and transport characteristics of E11 – E15 blends is generally limited but can be inferred or extracted from the information presented in the draft E85 Multimedia Study.[140] A thorough literature review and evaluation on the principles of partitioning and phase interface relationships was presented in the draft E85 Multimedia Evaluation, including the following principles:

- Volatilization
- Liquid to Liquid Phase Partitioning (ethanol-gasoline-water mixtures)
  - Solubility
  - Light Non-Aqueous Phase Liquid (LNAPL)-Water Partitioning
- Surface/Interfacial Tension and Capillary Forces
- Wettability
- Sorption, and
- Cosolvency

The following discussions summarize information presented in previous literature and, again, draws heavily from the draft E85 Multimedia Evaluation.[140] Where possible, specific information pertaining to E11 – E15 blends is gleaned from previous studies to determine the net environmental effect from the E11 – E15 blends.

6.2 Volatilization

6.2.1 Volatility of Ethanol Blended Fuels

Ethanol is a volatile organic compound, meaning it has an elevated tendency to evaporate under room temperatures. The RVP of pure ethanol is much less than that of typical gasolines. However, when ethanol is blended with typical gasoline, the resulting blend has a much higher RVP because the mixture forms a non-ideal solution (Figure 4).

Figure 12 below provides a review of the impact of aging on vapor pressure for a range of ethanol blended fuels as part of an evaluation of permeation for fuel tank components, (NREL, 2016).[145] Changes over time indicate losses which occur as a result of volatilization.

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[145] National Renewable Energy Laboratory (NREL), Christensen, E. D. & McCormick R. L., *Water Uptake and Weathering of Ethanol-Gasoline Blends in Humid Environments*, NREL TSA 14-665. Renewable Fuels Association (2016). https://ethanolrfa.org/wp-content/uploads/2016/09/Evaluation-of-Water-Uptake-by-Ethanol-RFA-09-16.pdf

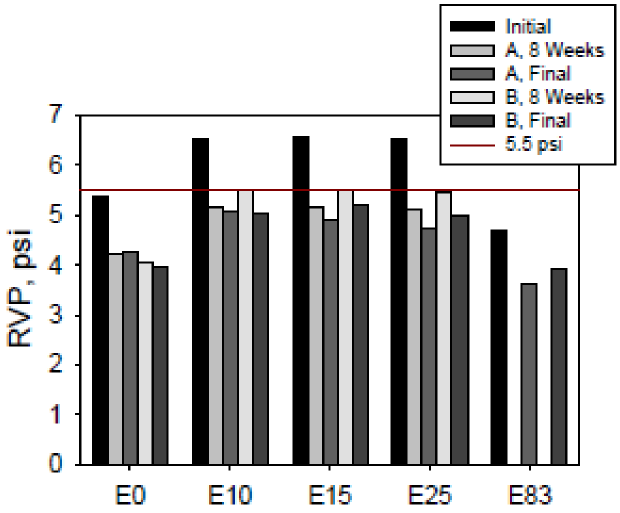

FIGURE 12. VAPOR PRESSURES OF BLENDS BEFORE, DURING, AND AFTER THE THREE MONTHS OF EXPOSURE FOR TWO TYPES OF TANKS (TANKS A AND B). ADAPTED FROM (NREL 2016).[145]

Evaporative losses for E11 – E15 fuels will be of similar magnitude to the evaporative losses for E10.[146,145]

6.2.2 *Volatilization from Releases to the Environment*

6.2.2.1 Volatilization from Releases to the Surface

If a release occurs on the surface, open to the atmosphere, components of the ethanol blended fuel volatilize quickly. Ethanol has a vapor density of 1.59 and gasoline has a vapor density between 3 and 4. This indicates that it is heavier than air and there is the potential for vapors to accumulate in low lying areas.[147]

Volatilized ethanol is degraded in the atmosphere by a reaction with photo chemically-produced hydroxyl radicals.[141]

6.2.2.2 Volatilization Concerns from Subsurface Impacts

Releases of blended ethanol fuels to the subsurface have the potential to occur as a result of failures in subsurface infrastructure (i.e., pipelines, underground storage tanks, etc.) or as a result of downward migration from spills at the surface.

If an ethanol blended fuel is released to the subsurface, just like traditionally formulated gasoline, volatile components in the released fuel can migrate through permeable subsurface features/ preferential pathways, into indoor air environments, or accumulate in enclosed spaces. In the subsurface, due to the Henry's constant, studies show that ethanol will completely dissolve in water, and once in solution, volatilization and adsorption are not likely to be significant transport pathways.[141] The primary risk driver associated with an ethanol blended fuel release for long term vapor intrusion is the benzene component of the gasoline in E11 – E15 blended fuels.

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[146] Unnasch, S. & Henderson, A., *Change in Air Quality Impacts Associated with the Use of E15 Blends Instead of E10*. (2014). http://cleartheairchicago.com/files/2014/09/E15-Clean-Air-Benefits-Study.pdf

[147] Renewable Fuels Association (RFA), *The Impact of Accidental Ethanol Releases on the Environment*. (2015). https://ethanolrfa.org/wp-content/uploads/2016/02/The-Impact-of-Accidental-Ethanol-Releases-on-the-Environment.pdf

As a strategy for evaluating risks due to petroleum releases, Interstate Technology & Regulatory Council (ITRC) has established a vertical screening distance for vapor control in petroleum vapor intrusion scenarios, which provide an indication of when releases to the subsurface might result in unacceptable risks to receptors. Vertical screening distances for several contaminant distribution scenarios are displayed below in Table 14.[148]

TABLE 14. VERTICAL SEPARATION SCREENING DISTANCES BY SOURCE (ITRC, 2014)[148]

Dissolved-Phase Sources	LNAPL Sources (Petroleum UST/AST sites)	LNAPL Sources (Petroleum Industrial Sites)
5 feet	15 feet	18 feet

According to ITRC, there are uncertainties regarding applicability of the vertical screening distances including its application to sites containing lead scavengers, high-ethanol content fuel (i.e., greater than 10%), sites with preferential pathways, sites containing large building foundations (e.g., industrial sites) and sites containing either high organic-rich or excessively dry soils due to insufficient soil gas data available to evaluate these scenarios. Additional study on sites involving E15 releases would provide insight in the applicability of these screening distances for subsurface impacts involving E15 fuels.[148]

An additional factor for vapor intrusion associated with E15 fuel releases to the subsurface is the increased potential for methane generation if natural bio attenuation occurs under anaerobic conditions and is discussed further in Section 6.5.2.

6.2.2.3 Atmospheric Washout

Indirect impacts of ethanol in air emissions washing out of the atmosphere as a result of precipitation and contributing negatively to surface water is expected to be minimal.[140]

6.2.2.4 Volatilization from Releases to Rivers and Streams

The air-to-water partitioning behavior of ethanol is governed by Henry's Law and described by the Henry's Law constant, which represents the equilibrium ratio of a contaminant's concentration in the air to its concentration in the water. The value of the dimensionless Henry's Law constant for ethanol is approximately 2.5×10^{-4} at 25 degrees C (°C).[140] As a result, ethanol volatilization from surface water is not likely to be a significant transport pathway.[141] It is noted, however, that the affinity for ethanol to partition into the vapor phase will increase with increasing temperatures.

Once ethanol reaches a surface water body, ethanol is not expected to volatilize quickly. While volatilization from water surfaces does occur, the estimated volatilization half-lives for a model river and model lake are 3 and 39 days, respectively, which are significantly longer than the biodegradation rates for ethanol in water (few hours to a day).[141]

The salinity of marine water is expected to have limited effects on the fate and transport of the ethanol. Environmental degradation in salt water may be slower than freshwater. For ethanol blended fuels, the higher salinity of marine waters will tend to further reduce the solubility of the gasoline components, allowing the gasoline components to float on water.[141]

6.3 Solubility and Partitioning Between Water, Fuel, and Soil

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[148] Interstate Technology & Regulatory Council (TRC), *Petroleum Vapor Intrusion Fundamentals of Screening, Investigation, and Management.* (2014). http://www.itrcweb.org/PetroleumVI-Guidance/

6.3.1 Liquid Phase Partitioning

Water and gasoline are immiscible, but small amounts of each are soluble in the other. Typical water contents of gasoline are on the order of 0.01%.[149] Ethanol, on the other hand, is completely miscible with water and with gasoline. Because ethanol is a polar compound it has a higher affinity to water than gasoline, therefore interactions between water and ethanol blended fuels becomes important as the ethanol content of a blend increases, the amount of water that can be accommodated in the fuel increases. As a result, the capacity of E15 to adsorb water before phase separation occurs increases slightly with increasing ethanol content and will be slightly higher than with E10. However, phase separation represents the limit for water adsorption. Ethanol partitioning among liquid phases of water and gasoline is commonly represented in a ternary-phase diagram, as shown in Figure 13. The diagram graphically depicts the ratios of three variables – gasoline weight percent, ethanol, weight percent, and water weight percent – as positions in an equilateral triangle which sum to a constant of 100%

The mass fraction of gasoline, water and ethanol for any point on the interior of the diagram can be determined using the three axes. Any point within the triangle is interpreted as follows:

- "The gasoline content is read diagonally from the gasoline side to the ethanol side with a line parallel to the water side. Where the line intersects the gasoline side is the gasoline content in weight percent;
- The ethanol content is read horizontally from the ethanol side to the water side, with a line parallel to the gasoline side. Where the line intersects the ethanol side is the ethanol content in weight percent;
- The water content is read diagonally from the water side to the gasoline side with a line parallel to the ethanol side. Where the line intersects the water side is the water content in weight percent.

The shaded area in the ternary-phase diagram indicates the range of water, gasoline, and ethanol mass fractions where the three components exist in two distinct liquids – an aqueous (phase where water is the primary component) and a gasoline phase where gasoline is the primary component - and ethanol is dissolved in each. The non-shaded (white) region corresponds to the single gasoline/ethanol/water phase, with no separate aqueous phase." The curve that separates the shaded and unshaded regions in the ternary phase diagram, referred to as the binodal curve, is the cut-off point where gasoline, ethanol and water will exist as a single phase. For example, as long as the ethanol present in the entire system exceeds 70% (by weight), a single phase will exist in all relative combinations of water and gasoline.

The transecting lines crossing the shaded area where both phases exist. These lines connect two points on the binodal curve. These two points give the equilibrium concentration of the "aqueous" phase (left-hand point) and the "gasoline" phase (right-hand point). The downward slope of the transecting lines indicates the preferential partitioning of ethanol into the aqueous phase.

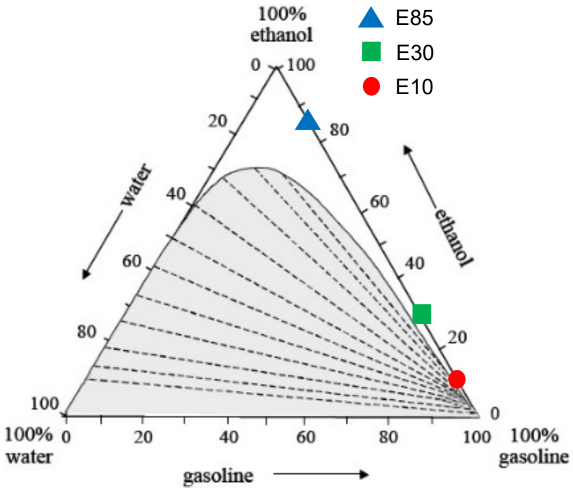

FIGURE 13. TERNARY PHASE DIAGRAM FOR GASOLINE-ETHANOL-WATER SYSTEM AT 25°C. AXES INDICATE %TOTAL MASS. NOTE THAT BECAUSE THE DENISTY OF ETHANOL IS CLOSE TO GASOLINE, THE MASS PERCENT OF ETHANOL IS SIMILAR TO THE VOLUME PERCENT OF ETHANOL IN VARIOUS ETHANOL-GASOLINE BLENDS. (ADAPTED FROM UC, 2016)[140]

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[149] Weaver, J. W., Skaggs, S. A., Spidle, D. L., & Stone, G. C., *Composition and Behavior of Fuel Ethanol, EPA/600/R-09/037.* (2009). https://cfpub.epa.gov/si/si_public_file_download.cfm?p_download_id=492615

Assuming there is no water in the system, E10, E30 and E85 fuel blends are represented by the labeled marks on Figure 13.

An increase in the water content will move the marks on the diagram towards the two-phase state. As shown, it does not take much water to create phase separation for E10 (~ 1% water by mass) relative to E85 (~ 20% by mass). Christensen and McCormick noted phase separation for aliquots of E10, E15 and E25 at 0.4 to 0.5%, 0.75 to 0.9%, and 1.8 to 1.9% water by mass respectively during a water uptake study in humid environments.[145] Weaver et al. observed that between 15 to 20% water by volume must be added to an E85 fuel mix before the beginning of phase separation and existence of a separate aqueous phase occurs. [149] [140]

Water tolerance of a blend is dependent on temperature as well as ethanol concentration (i.e. at higher temperatures, the blend can dissolve a greater amount of water than at lower temperatures before phase separation occurs).[145] Ethanol is hygroscopic, meaning it has a tendency to absorb moisture either from aqueous interfaces or from humid air. The water uptake study of ethanol-gasoline blends in humid environments conducted by Christensen and McCormick included a test using two different small engine fuel tanks (Tank A & Tank B) constructed of different plastics. [145] Results of that study indicated that moisture uptake rates were very similar for E0, E10, and E15 between Tanks A and B, which resulted in nearly the same water concentration at the end of three months.

- An underground storage tank (UST) storing E10 will experience phase separation with the presence of 1% volumetric fraction of water. This separated water phase, which is heavier than gasoline, falls to the bottom of the tank. Although the UST is approved by Underwriters Laboratory (UL) that the materials of the tank are compatible with 10% ethanol fuel, the materials may be incompatible with bottom water that contains a higher percentage of ethanol. Fuel lines and engines in automobiles taking in two separate phases instead of a blend of ethanol and gasoline could become an issue for the automotive industry.
- With E15, more water can be absorbed than for E10 before phase separation occurs, but that water will have higher concentrations of ethanol than E10 phase-separated water.
- Fuel transporters and dispensers take measures to reduce water exposure of ethanol blends, and phase separation in the marketplace up to the point of retail dispensing is rate.[145]

6.3.1.1 Partitioning Behavior in the Environment

Ethanol in blended fuels released to the surface will absorb moisture, and if enough moisture is present, the ethanol will partition from the gasoline. Less moisture is needed to be absorbed for ethanol to partition from E10 blends than for E15. The bulk mass from small incidental spills of E15 to the surface is expected to evaporate at similar rates to incidental spills of E10 (See Section 5.2).

Spills to surface water bodies will almost certainly lead to partitioning of ethanol into surface water within a very short period of time, leaving behind a floating gasoline layer.[135] The rate of phase separation will depend on the mixing energy and size and depth of the receiving water body. The major differences between a release to surface water bodies of E10 than a similar volume release of higher midlevel blends are proportional increases in ethanol volume dissolved into the surface water body, and proportional decreases in gasoline volume left on the water surface. The cosolvent effects of ethanol will allow higher concentrations of gasoline constituents to dissolve in the water (see subsequent sections). Also, the increased biological oxygen demand (BOD) of the larger volumes of ethanol partitioned into surface water bodies from midlevel blends as opposed to E10 may be of concern for aquatic life. Ethanol in surface water is readily biodegraded once the ethanol fraction becomes diluted to below approximately 1%.[135] The risks to aquatic life will be dependent on the volumes released and the nature and condition of the water body.

The extent and rate of partitioning behavior of E15 blends in the subsurface will be site specific, but generally determined by the ethanol content and volume of the spill, as well as the subsurface conditions (e.g., soil type, moisture content, groundwater depth and flow conditions, etc.). Following a spill, ethanol will absorb vadose-zone water within the blended fuel mixture until cumulative water content reaches the level where an aqueous phase would form, according to Figure 13. Whether the phase separation happens quickly or is delayed, and whether it occurs in the vadose zone or at the capillary fringe will be dictated by site conditions and the quantity released.

6.3.1.2 Solubility and NAPL-Water Partitioning

Ethanol fuel blends are complex mixtures of ethanol and the multi-constituent hydrocarbons of gasoline. Ethanol is completely miscible with gasoline. Ethanol is also hygroscopic, and completely miscible in water. As discussed above, because ethanol is a polar compound, it has a higher affinity for water than for gasoline. Water will cause ethanol to phase separate from an ethanol blended fuel to the aqueous phase.

Because gasoline is a compound mixture, the solubility of a constituent of gasoline into water will be less than the solubility of the pure phase constituent into water assuming no cosolvent is present. Assuming no cosolvency or mixture effects, the solubility of a constituent of gasoline into water can be approximated using an analog of Raoult's Law where "the aqueous phase concentration is equal to the aqueous phase solubility of the constituent in equilibrium with the pure constituent phase, multiplied by the mole fraction of the constituent in the oil phase".[140]

$$C_w = X_m S_p$$

Where,

C_w = concentration of constituent in water (aqueous phase)
X_m = mole fraction of constituent in gasoline
S_p = solubility in water of constituent in equilibrium with pure phase constituent

The solubility of gasoline constituents into the aqueous phase also correlates with the constituent's octanol-water partition coefficient (K_{ow}) - the ratio of a chemical's concentration in the octanol (organic) phase to its concentration in the aqueous phase at equilibrium of a two-phase octanol/water system at a specific temperature. The log of K_{ow} is often used as measure of a compound's hydrophobicity, or tendency to not mix with water – the larger the value, the more hydrophobic the compound. Values for log K_{ow} are shown for ethanol and select gasoline constituents in Table 15.

A similar measure of a constituent's tendency to partition from organic phase to aqueous phase is the light non-aqueous phase liquid (LNAPL)-water partition coefficient (K_o). A larger K_o value indicates that a higher concentration of the constituent will exist in the LNAPL phase versus the aqueous phase. The K_o values of the typical traditional gasoline mixtures are provided in Table 15. Data in Table 15 shows that benzene is more soluble and less hydrophobic than the other gasoline constituents listed. Ethylbenzene and xylenes are significantly less soluble and more hydrophobic than benzene and toluene.

TABLE 15. SOLUBILITIES AND K_O VALUES FOR COMMON GASOLINE COMPONENTS

Gasoline Component	Pure-Phase Aqueous Solubility[1] (mg/L @ 25° C)	Octanol/Water Partition Coeff. (Log(K_{ow}))[1, 2]	Average K_o Value[2]
Ethanol	Infinite	-0.16, -0.31	
Benzene	1,790	2.13	350
Toluene	526	2.73	1,250
Ethylbenzene	170	3.15	4,500
m-, p-xylene	160-165	3.15-3.20	4,350
o-xylene	180	3.12	3,630

NOTES:
MG/L = MILLIGRAMS PER LITER
1 = DATA FROM https://pubchem.ncbi.nlm.nih.gov/compound/[150]
2 = TAKEN FROM UC, 2016[140]

6.3.1.3 Ethanol Effects on Solubility and LNAPL-Water Partitioning

Because ethanol is a polar, organic solvent it can increase the solubility of non-polar organic compounds such as BTEX into the aqueous phase as it phase-separates into water. Recent ethanol fate and transport models have included alternatives or modifications to Raoult's law to account for the cosolvent effects of ethanol (See Section 6.5.3).

Figure 25 in Section 6.5.3 shows a comparison by Gomez et. al (2009) between a linear-log-linear cosolvency model and Raoult's Law equation results for estimating equilibrium benzene concentrations at the water-LNAPL interface for various ethanol concentrations in ethanol blended fuel.[151] The models show similar results for the higher ethanol blend fuels but diverge as ethanol concentrations in the fuel go down (and benzene concentrations in the fuel goes up). Higher ethanol blended fuels have less benzene, so the increasing potential of cosolvency effects in these blends due to higher ethanol concentrations is generally offset to a degree by the decrease in benzene mass.

6.3.2 Surface/Interfacial Tension and Capillary Forces

In the subsurface just above the groundwater table, groundwater rises in pore spaces in proportion to the interfacial tension of the water, and inversely with the diameter of the pore, which is known as capillary action. The subsurface layer in which groundwater rises up to fill pore spaces from a water table by capillary action is called the capillary fringe.

Interfacial tension (or "surface tension" when the term is used for liquid in contact with vapor) is defined as the surface energy at the interface of two immiscible fluids that results from differences in the forces of molecular attraction within the fluids and at the interface and is expressed in units of energy per unit

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[150] National Center for Biotechnology Information (NCBI),.. *PubChem Compound Database CID=702.* (n.d.). *CID=702*, https://pubchem.ncbi.nlm.nih.gov/compound/702

[151] Gomez, D. E. & Alvarez, P. J. J., *Modeling the natural attenuation of benzene in groundwater impacted by ethanol-blended fuels: Effect of ethanol content on the lifespan and maximum length of benzene plumes. Water Resources Research, 45(3).* (2009). https://doi.org/10.1029/2008WR007159

area.[152] Higher values of interfacial tension generally indicate a more stable interface and is an important factor affecting wettability (see below).

Powers and McDowell (2001) shows that increases in ethanol concentrations have significant effects on capillary forces in the subsurface, including:[153]

- An almost linear decrease in the interfacial tension with increasing ethanol content from ethanol in a reformulated gasoline. Data show an almost 50% decrease in interfacial tension when the volumetric fraction of ethanol is increased from 10% to 30%.
- An almost linear to first order decrease in surface tension with increasing volume fractions of ethanol in the aqueous phase (Figure 14 bottom).
- A continuous decrease in unsaturated zone hydraulic conductivity with increasing volume of ethanol (see Figure 14 top) attributed to the increase in viscosity of water with increasing volume of ethanol.
- A direct relationship between capillary pressure and the height of the capillary fringe to ethanol content in capillary water.

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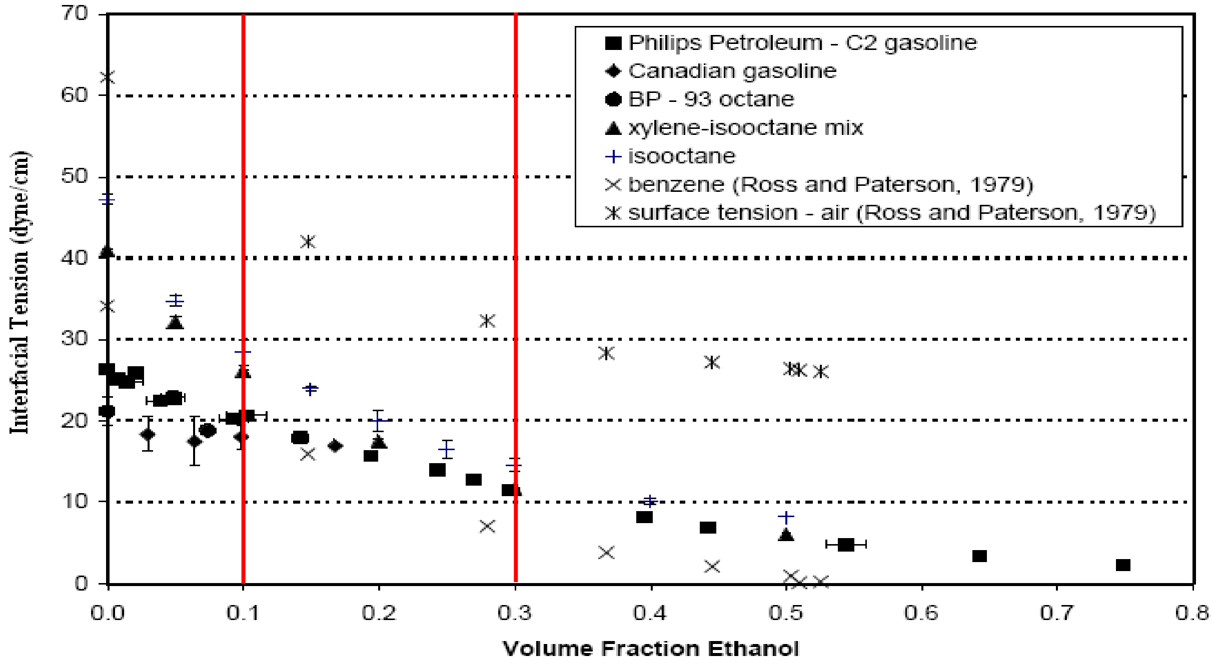
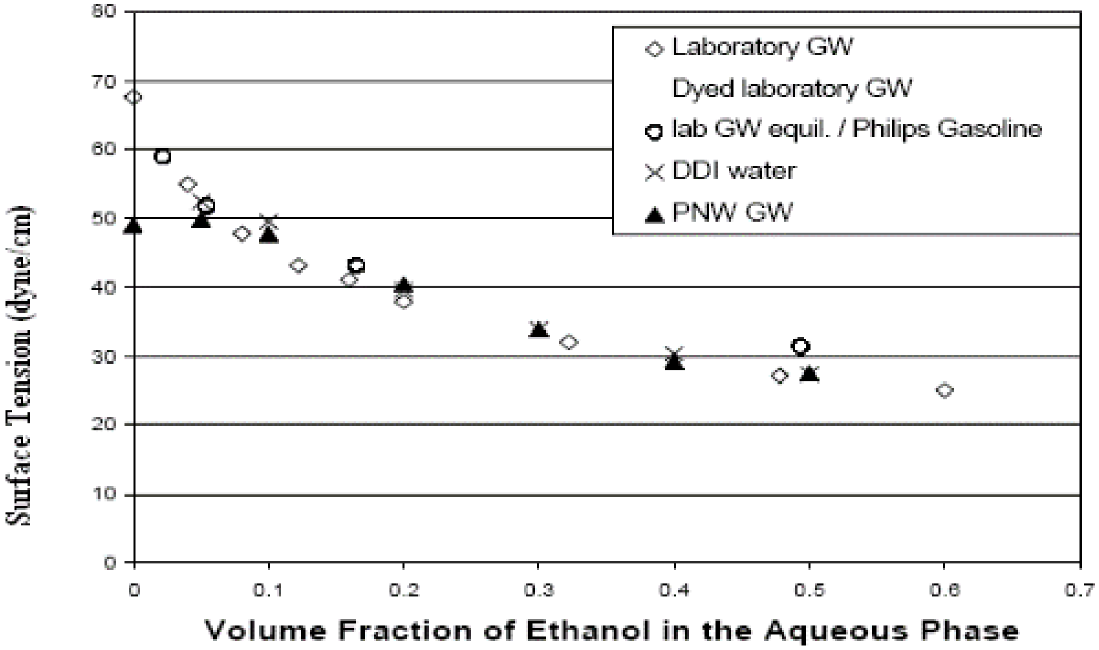
[152] Newell, C. J., Acree, S. D., Ross, R. R., Huling, S. G., *Light Nonaqueous Phase Liquids, EPA/540/S-95/500.* (1995). https://www.epa.gov/remedytech/light-nonaquaeous-liquids

[153] Powers, S. E., & McDowell, C. J., *Mechanisms affecting the infiltration and distribution of ethanol-blended gasoline in the vadose zone.* (2001). https://doi.org/10.1021/es0259761


Interfacial Tension (dyne/cm)
70
60
50
40
30
20
10
0
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
Volume Fraction Ethanol
■ Philips Petroleum - C2 gasoline
◆ Canadian gasoline
● BP - 93 octane
▲ xylene-isooctane mix
+ isooctane
× benzene (Ross and Paterson, 1979)
⁎ surface tension - air (Ross and Paterson, 1979)


Surface Tension (dyne/cm)
80
70
60
50
40
30
20
10
0
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
Volume Fraction of Ethanol in the Aqueous Phase
◇ Laboratory GW
Dyed laboratory GW
○ lab GW equil. / Philips Gasoline
× DDI water
▲ PNW GW

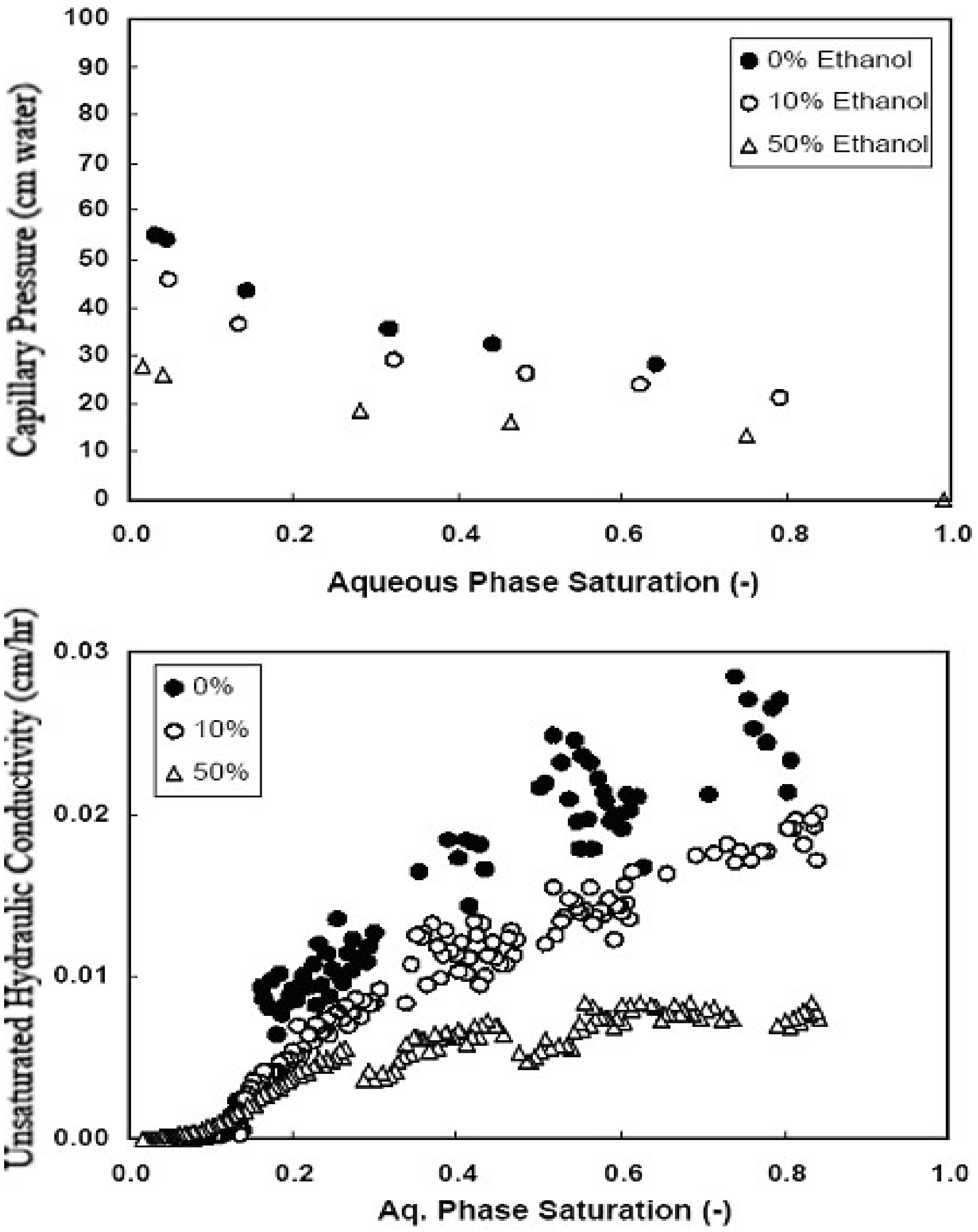


FIGURE 15. CAPILLARY PRESSURE (TOP) AND UNSATURATED HYDRAULIC CONDUCTIVITY (BOTTOM) RESULTS FROM MULTI-STEP OUTFLOW EXPERIMENTS (TAKEN FROM UC, 2016).[140]

6.3.3 Wettability

Wettability is described as the tendency of a fluid to spread on a particular solid surface in the presence of another immiscible fluid.[140]

In a three-phase system with water, air and non-aqueous phase liquid (NAPL), water is typically the wetting fluid, air the non-wetting fluid, and NAPL has intermediate wettability.[154] Wettability is a qualitative indicator useful to understanding the general transport behavior of NAPL in multi-phase systems. In an NAPL-wet system, the organic phase coats the soil grain and occupies the smallest of pore spaces as opposed to a water wetting system where the smallest pore spaces are occupied by water. Under increasing oil-wetting conditions, biodegradation rates can be decreased due to reduced bioavailability of the hydrocarbons.

Powers and McDowell were able to show visually that a significant change in wettability occurred due to increased ethanol concentrations. As the percent volume of ethanol in solution increases, quartz and sand grains were coated by LNAPL.[153] In a sample with 40% ethanol, LNAPL was not able to separate from sand grains when water was added compared to the sample with 10% ethanol where separation occurred.

6.3.4 Sorption

Sorption is a generic term used to encompass the processes of absorption, which implies penetration of a contaminant into the bulk mass of a substance, and adsorption, which refers to retention of a contaminant on the surface of a substance. Sorption of petroleum hydrocarbons constituents to soil particles in the subsurface is an important process that limits transport of those contaminants. Sorption tendency can be described by the ratio of a chemical’s sorbed concentration to the dissolved concentration at equilibrium. This ratio is the distribution coefficient (K_d).

For organics, K_d is calculated by multiplying a chemical’s soil organic carbon-water partition coefficient (K_{oc}) by the mass fraction of soil organic carbon content (f_{oc}). Values of f_{oc} are site-dependent but are typically low at sites posing the most risk associated with subsurface transport (e.g. sandy soils).

$$K_d = K_{oc} \times f_{oc}$$

K_{OC} indicates the relative mobility of organic soil contaminants; higher K_{OC} values correlate to less mobility while lower values correlate to more mobility. K_{OC} values for ethanol are low relative to values of the more toxic fractions of gasoline such as BTEX.

The presence of ethanol in a fuel mixture exerts a cosolvency effect on hydrocarbons which results in changes to the distribution coefficient. Increasing ethanol content results in less sorption tendency and higher mobility of the hydrocarbons variations. The distribution coefficient (K_d) is used in equations that take ethanol concentrations and the cosolvency effect into account to calculate a retardation factor (R). Equations and assumptions for calculation of R are presented in Gomez et. al, 2009.[151]

The low KOC values for ethanol result in a retardation factor for ethanol that approaches unit. As such, ethanol will generally migrate at the velocity of groundwater.

The retardation factor for BTEX components decreases as the water phase ethanol fraction increases, which Gomez et al. (2009) hypothesizes could be a factor in longer BTEX plumes (Figure 16).[151] The more hydrophobic BTEX components xylene and ethylbenzene are the most influenced by cosolvency with a 2% decrease in retardation for E10, 5 to 7% for E50, and 8 to13% for E85. Benzene, on the other hand, has a change in retardation of ~0.4% for E10, ~1.8% for E50, and 3% for E85 considering a sandy

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[154] Charbeneau, R. J., Groundwater Hydraulics and Pollutant Transport. (2000). https://doi.org/10.1115/1.1451232

soil with 2% organic matter. Interpolating the benzene results suggest that there will be a 0.58% decrease in benzene retardation for E15.

6.4 Cosolvency

Ethanol is miscible in both water and gasoline. The oxygen atom in ethanol makes this molecule more polar than other petroleum hydrocarbons, and it is this polarity that makes ethanol extremely hydrophilic.

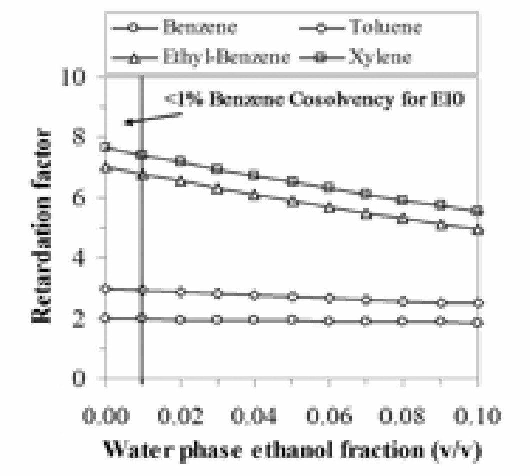


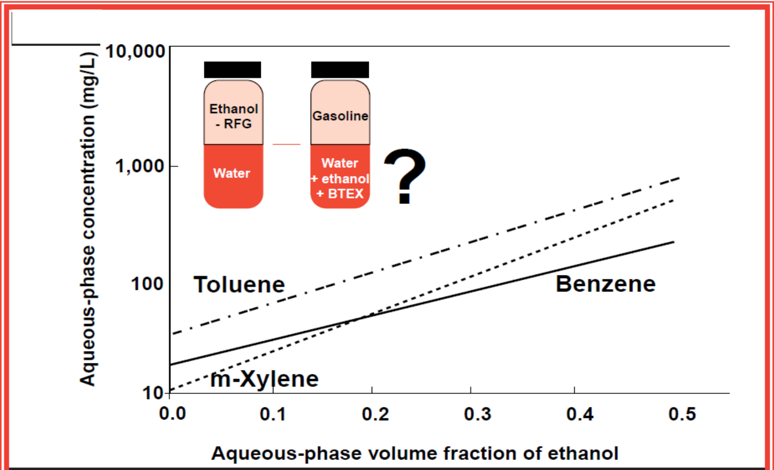
FIGURE 16. RETARDATION FACTOR FOR BENZENE, ETHYLBENZENE, XYLENE, AND TOLUENE FOR DIFFERENT FRACTIONS OF ETHANOL IN THE WATER PHASE FOR A SANDY SOIL WITH 2% ORGANIC MATTER.

Ethanol is also hygroscopic, meaning it has a tendency to absorb moisture either from aqueous interfaces or from humid air interfaces.

When an ethanol-blended fuel is mixed with an adequate amount of water, ethanol will partition favorably into the water (aqueous phase) (see Section 6.3.1). Because ethanol is an organic solvent, it attracts other organic materials. Therefore, depending on the volume fraction of ethanol in the gasoline and the relative volumes of gasoline and water that are mixed - the resulting aqueous-phase concentrations of ethanol will increase aqueous-phase concentrations of generally hydrophobic petroleum compounds, such as benzene. In other words, if an ethanol blended fuel impacts groundwater, dissolved BTEX concentrations will likely exceed concentrations from an ethanol-free fuel release because the solubility of BTEX is higher in ethanol-water mixtures than in plain water - this is known as “cosolvency”.

The cosolvency effect is a function of the amount of ethanol in the aqueous phase. Figure 17 illustrates the approximate logarithmic increase in dissolved phase BTEX concentrations with increasing aqueous phase ethanol concentrations in water equilibrated with ethanol-blended gasoline.

Increased concentrations of dissolved-phase BTEX, and particularly benzene, arising from ethanol-blended fuel releases or from neat or denatured ethanol intersecting pre-existing petroleum impacts, are a concern due to the toxic and/or carcinogenic effects of these compounds. Fortunately, as shown in Figure 17, the smallest percentage increase (smallest slope) was observed for benzene, the least hydrophobic and most toxic of the BTEX compounds.



The presence of ethanol can increase concentrations of BTEX species in an aqueous phase equilibrated with ethanol-blended RFG. This drawing of vials illustrates experiments conducted to determine the cosolvency effect. RFG with a range of ethanol concentrations is mixed in a small vial with water. Following mixing to equilibrate, the aqueous-phase concentrations of ethanol and BTEX are analyzed. Results plotted illustrate that contaminant concentrations increase in a generally logarithmic relation with increasing volume fraction of ethanol in the aqueous phase (data from Heermann and Powers, 1999).

Spills of neat ethanol could result in very high ethanol concentrations in a localized area, and potentially cause order of magnitude increases in BTEX concentrations near the source area due to cosolvent effects, if released over a previously contaminated soil with petroleum product. However, from the models, batch and pilot scale studies, field studies and observations from actual ethanol releases presented below, it is unlikely that cosolvent-related increases in BTEX concentrations will be significant at the field scale following spills of E15 versus E10. Researchers suggest that the volume fraction of the dissolved ethanol in groundwater systems is predicted to be less than or equal to 15% (i.e., ~119,000 mg/L), and at these relatively low ethanol volume fractions, BTEX concentrations in the aqueous phase near a gasoline spill are predicted to increase by approximately 20 to 50 percent.

6.4.1 Cosolvency Predictive Models

Several models have been presented to approximate the effect of cosolvency in ethanol-fuel-water systems. These models have included:

- Simple log-linear cosolubility models:
  - Corseuil et. al. (2004) presented a simple log-linear model to predict cosolvency effect of ethanol on the aqueous solubility of mono- and polycyclic aromatic hydrocarbons under equilibrium conditions.[155] A linear relationship between cosolvency energy (or power) is used to predict this effect under equilibrium conditions. As the hydrophobicity (log K_{ow}) of a particular organic compound increases, the cosolvency power of it increases linearly, and thus cosolvency will exert a greater effect on that compound’s solubility (i.e., the relatively

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[155] Corseuil, H. X., Kaipper, B. I. A. & Fernandes, M., *Cosolvency effect in subsurface systems contaminated with petroleum hydrocarbons and ethanol*. (2004). https://doi.org/10.1016/j.watres.2003.12.015

more hydrophobic compounds ethylbenzene and xylene will be more soluble compared to the relatively less hydrophobic benzene and toluene compounds).

  - The simple log-linear cosolvency model described above and enhanced with extrapolated cosolvency power coefficients was utilized to evaluate E10 and E85 cosolvency effects in the draft E85 Multimedia Evaluation.[139] Multiphase (air, water, and soil) equilibrium partitioning calculations modified to include cosolvency effects the long-linear model in the evaluation. The analysis provides a review of cosolvency theory and partitioning with equations and examples derived primarily from Chen et al, (2008), Corseuil et al. (2004), and Charbeneau (2000).[156] [155] [154]That suggests that while increased ethanol concentrations induce a significant increase in benzene solubility in the aqueous phase, the reduced mass fraction of benzene in E85 compared to E10 offsets the effect.

- A thermodynamic model to estimate activity coefficients of each component in each phase which are then used in a set of equations that equate the chemical activities of a species between the two phases (these models include the UNIQUAC (universal quasi chemical) model for multicomponent liquid-liquid equilibrium problems, or the modified UNIQUAC - the UNIFAC (UNIQUAC functional-group activity coefficients) model, which allows the necessary parameters to be estimated from the number and type of functional groups that comprise the chemical species (Powers et. al., 2001).[157]
- A linear-log-linear (LLL) cosolvency model developed by Heermann and Powers, (1998) with a linear relationship for low ethanol contents (approximately 25% or less) and a log-linear relationship for higher ethanol contents.[158] In developing the model, data were fit to a surrogate gasoline consisting of eight compounds and then used to predict BTEX concentrations for commercial gasoline and varying ethanol volume fractions in the aqueous phase.

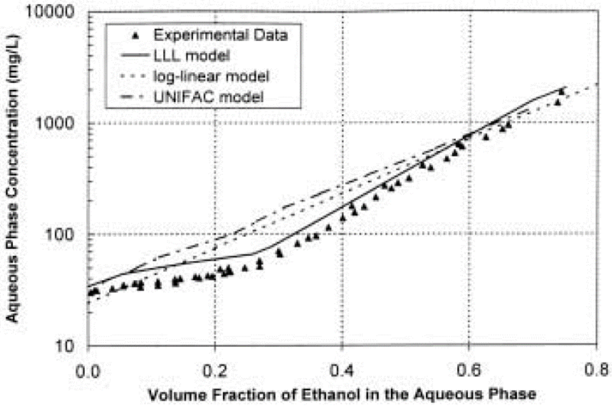

FIGURE 18. PREDICTION OF BENZENE CONCENTRATIONS THAT HAD BEEN EQUILIBRATED WITH "C2" GASOLINE AND ADDITIONAL ETHANOL. "LLL" INDICATES THE PIECEWISE LINEAR-LOG-LINEAR COSOLVENCY MODEL. (TAKEN FROM POWERS ET. AL., 2001)[157]

As shown in Figure 18, the LLL model was found to most accurately reflect the differences in solubilization mechanisms at low versus high cosolvent concentrations.[157]

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[156] Chen, C. S., Lai, Y. W. & Tien, C. J., Partitioning of aromatic and oxygenated constituents into water from regular and ethanol-blended gasolines. (2008). https://doi.org/10.1016/j.envpol.2008.05.012

[157] Powers, S. E., Hunt, C. S., Heermann, S. E., Corseuil, H. X., Rice, D., Alvarez, P. J. J. (2001). The Transport and Fate of Ethanol and BTEX in Groundwater Contaminated by Gasohol. *Critical Reviews in Environmental Science and Technology, 31*(1), 79-123. https://doi.org/10.1080/20016491089181

[158] Heermann, S. E. & Powers, S. E., Modeling the Partitioning of BTEX in Water-Reformulated Gasoline Systems Containing Ethanol. (1998). https://doi.org/10.1016/S0169-7722(98)00099-0

The LLL model was used in a subsequent ethanol fate and transport model developed by Gomez et al., 2009 which is described in more detail in the discussion (see Section 6.5.3).[151]

As mentioned above from prior modeling efforts, as the amount of ethanol increases, so does the cosolvency effect, but this effect is balanced by the decline in benzene mass with higher ethanol content fuels. Weaver et al. applied the LLL model developed by Heermann and Powers to a hypothetical mixture of blendstock containing 1% benzene and denatured fuel ethanol which was assumed to be denatured with 2% gasoline which itself contained 1% benzene.[149 158] Results of their calculations indicated that at ethanol contents below 25% by volume, there is no increase in benzene solubility for this mixture. The aqueous benzene concentration peaks at about 85% ethanol before sharply declining.

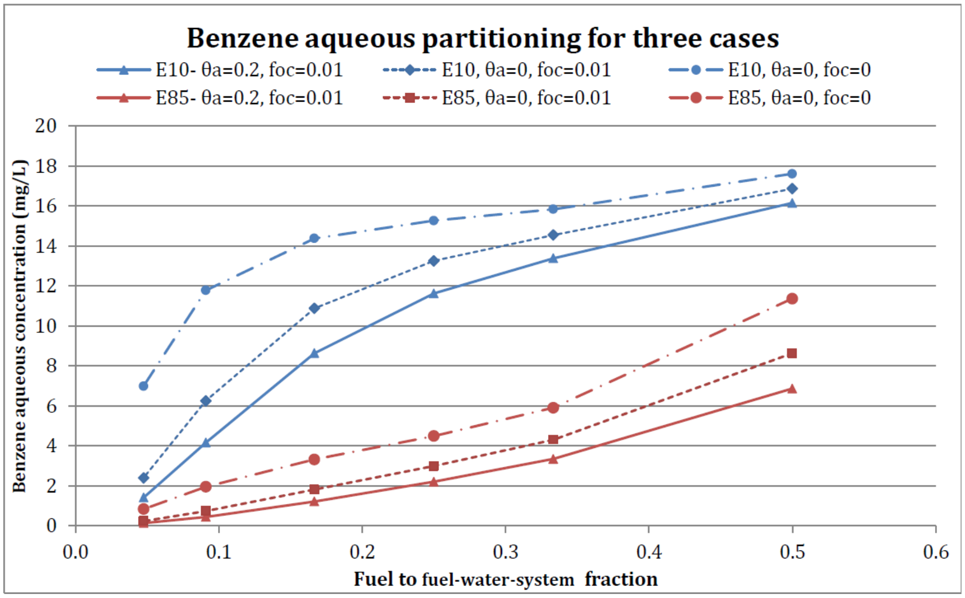

FIGURE 19. BENZENE AQUEOUS PARTITIONING FOR THREE CASES INCLUDING AIR AND ORGANIC SOLID FRACTION, NO AIR AND YES ORGANIC SOLID FRACTION, AND NO AIR AND NO ORGANIC SOLID FRACTION, AS A FUNCTION OF FUEL TO FUEL-WATER SYSTEM FRACTIONS (CORRESPONDING TO RATIOS OF 0:1 ETHANOL TO WATER UP TO 1:1 ETHANOL-WATER. (TAKEN FROM UC, 2016).[140]

6.4.2 Previous Literature Review, Laboratory and Field Scale Experiments of the Cosolvency Effect on Various Ethanol Blends

Conclusions from a critical review of research material at the time by Powers et al. include the following:[157]

- Concentrations of ethanol in water equilibrated with ethanol blended fuels ranging from E10 or less are expected to be low (<15% by volume). At this low aqueous ethanol concentration, aqueous BTEX concentrations will increase by less than 50% over concentrations from ethanol-free fuel due to the cosolvent effect. The extent of the increase in concentration is least for benzene, which is the least hydrophobic and most toxic petroleum hydrocarbon in gasoline.
- Higher ethanol concentrations in water would be expected for a neat ethanol spill.
- Unless there is a neat ethanol spill, aqueous phase ethanol concentrations are unlikely to exceed 10% in contaminated sites. Therefore, it is unlikely that cosolvent related increases in BTEX concentrations will be significant at the field scale.[153]

Rixey, et al (2005) conducted batch equilibrium and continuous flow column experiments to assess the enhancement of BTX and other hydrocarbon concentrations in groundwater near ethanol releases. The experiments were conducted to approximate worst-case scenarios in which either E15 or E95 comes in direct contact with groundwater.[159] Results indicate the following:

- Aqueous BTX and other hydrocarbon concentrations significantly increase when ethanol concentrations in the aqueous phase are greater than 10% by volume. Benzene concentrations were enhanced by a factor of 1.2 at an ethanol concentration of 10% by volume.
- Column experiments with E15 produced a maximum aqueous ethanol concentration of 34,700 mg/L (< 5% by volume), and aqueous BTX concentration enhancement factors of 1.3 to 1.4.

An experimental cosolvency study conducted in 1999 evaluated the effective solubility's of BTX compounds in water equilibrated with a Brazilian commercial gasoline containing 22% ethanol (E22).[157]

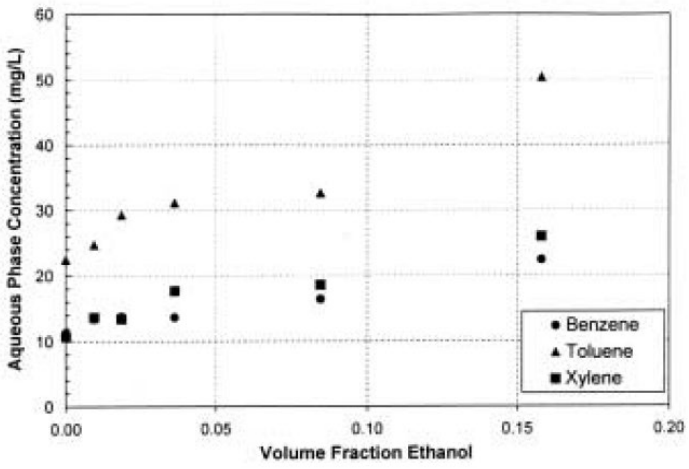

FIGURE 20. CONCENTRATION OF BTX COMPOUNDS IN WATER EQUILIBRATED WITH A BRAZILIAN GASOLINE CONTAINING 22% ETHANOL (DATA FROM CORSEUIL AND FERNANDES, 1999). (TAKEN FROM POWERS ET. AL., 2001)[157]

A range of ethanol concentrations in the aqueous phase was achieved in the batch experiments by varying the volume ratio of water to gasoline, and the maximum volume fraction of ethanol in the aqueous phase was on the order of 15%. Over the range of aqueous phase ethanol volume fractions observed, BTX concentrations in the aqueous phase that was equilibrated with the ethanol-free gasoline generally increased by approximately 20 to 50%. (Figure 20) The relative magnitude of this effect increased with the hydrophobicity of the compound as discussed above (e.g., xylene had a larger percentage increase in aqueous phase concentration than benzene).

Corseuil et al. conducted batch experiments with BTX and varying percentages of pure ethanol, and with an ethanol-free gasoline and a Brazilian ethanol blended fuel with 22% (E22) ethanol by volume to investigate the cosolvency effect of ethanol on the aqueous solubility of mono- and polycyclic aromatic hydrocarbons, including benzene, toluene and other components of gasoline and diesel.[155] Experiments with E22 were conducted with gasoline to distilled water rations of 1:1, 1:2, 1:5, 1:10 and 1:20, which

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[159] Rixey, W. G. He, X., & Stafford, B. P., *The Impact of Gasohol and Fuel-Grade Ethanol on BTX and Other Hydrocarbons in Ground Water: Effect on Concentrations Near a Source Results from Bench-Scale Partitioning and Column Studies.* (2005). https://www.api.org/~/media/Files/EHS/Clean_Water/Bulletins/23_Bull.pdf

corresponded to ethanol aqueous volume fractions of 15.8 %, 8.47%, 3.62%, 1.81% and 0.93%.

- Results of the BTX-only experiment showed that in the presence of 10% ethanol volumetric fraction in water, the aqueous solubility of benzene, toluene, and o-xylene increased by 20%, 40% and 50% respectively.
- Results showed that an ethanol fraction of 15.8% in water compared to that of 0.93% in the aqueous phase will show an increase of 67%, 89%, and 90% for benzene, toluene, and xylene respectively.
- The authors note that's spills or leaks of ethanol blended fuels and /or simultaneous releases of neat ethanol and petroleum hydrocarbons in the subsurface may increase the effective solubility of hydrocarbons in groundwater, but the effect is more pronounced for aqueous ethanol concentrations above 10%. The authors conclude the following:
  - For minor spills of ethanol blended fuels (e.g., <E10 – E22), it is not expected that concentrations of ethanol in groundwater will reach 10%;
  - Cosolvency may be critical in large spills of gasoline -ethanol blends or neat ethanol with other fuels.

Results of a controlled release field experiments of 100 Liters of an E24 gasoline-ethanol blend in a sandy aquifer which indicated that the highest observed ethanol concentration in groundwater near the source zone was 1% by volume.[155] Stafford et al. (2009) conducted a pilot scale experiment consisting of releasing neat ethanol into the upper capillary zone in a large (8.2 m^3) continuous-flow (groundwater velocity 0.75 m/day), sand-packed aquifer tank that contained a residual LNAPL that extended from the capillary zone to 10 cm below the water table.[160] Results included:

- Maximum aqueous concentrations of ethanol were 20% by volume (~158,000 mg/L) in the capillary zone and 0.08% by volume (~600 mg/L) in the saturated zone.
- The difference between the capillary zone and groundwater ethanol concentrations observed is consistent with advective-dispersive limited mass transfer from the capillary to the saturated zone in the absence of rapid water table fluctuations.
- The authors infer that "spills of highly concentrated ethanol will be largely confined to the capillary zone due to its buoyancy, and ethanol concentrations in near-source zone groundwater will be controlled by mass transfer limitations and hydrologic conditions."
- Concentrations of BTX in the capillary zone were less than a factor of 2 higher than effective water solubilities from the LNAPL due to the cosolvent effect, and these results are consistent with previous equilibrium studies for the maximum level of ethanol (20%) observed.

A summary of several case studies of bulk neat or denatured ethanol releases is provided in Section 5.5. Although these case studies do not include information on mid to low range ethanol fuel blends, the bulk concentration of ethanol observed in groundwater, and the relative degree of benzene impacts should be noted, namely:

- The highest ethanol concentrations observed in groundwater from the large volume neat or denatured ethanol releases shown in Table 16 was at the Tacoma Washington Site at 81,000 mg/L, which corresponds to an aqueous ethanol volume concentration of roughly 10% (assuming no volume contraction of the mixture).
    - This result is consistent with what has generally been predicted or observed by researchers - that the volume fraction of the dissolved ethanol in groundwater systems is

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[160] Stafford, B. P., Cápiro, N. L., Alvarez, P. J. J., & Rixey W. G., *Pore Water Characteristics Following a Release of Neat Ethanol onto Pre-existing NAPL.* (2009). https://doi.org/10.1111/j.1745-6592.2009.01243.x

predicted to be less than or equal to 15% (Powers & Rice, 2000,).[161] [153]

- Benzene concentrations were noted to be over an order of magnitude higher within the immediate vicinity of the ethanol release area of the Tacoma, Washington Site than they were prior to the release, and the high concentrations have persisted. The area had been impacted by petroleum in the past.

In previous studies it has been suggested that the cosolvent effect of raising the effective solubilities of petroleum hydrocarbons in groundwater may become significant or more pronounced when the aqueous ethanol volume fractions are greater than 5-10%.[162] [155] With ethanol concentrations at ~ 10% in groundwater at the Tacoma Site, the increased benzene concentrations noted are not surprising.

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[161] Powers, S. E. & Rice, D., *Oxygenates, The Subsurface Fate of Ethanol, A Look at the Emerging Oxygenate Alternative to MTBE.* (2000) https://www.epa.gov/sites/production/files/2015-03/documents/ll36eth.pdf

[162] Schwarzenbach, R. P., Gschwend, P. M., & Imboden, D. M. (2003). *Environmental Organic Chemistry (2nd Ed.)*. John Wiley & Sons.

TABLE 16. SUMMARY OF LARGE-SCALE ETHANOL RELEASE SITES (CASE STUDIES)

Summary of Large-Scale Ethanol Release Sites (Case Studies)

Site	Release Date	Released Fuel	Volume Released (gal)	Previous Contamination Present (Y/N)	Maximum Ethanol Concentration Observed in GW (mg/L)	Concentrations of Benzene in GW before Release (mg/L)	Max Benzene Concentration in GW After Release (mg/L)	Methane Observed (Y/N)	Time to Ethanol Clean-up (months)	Source
Bulk Storage Terminal - Tacoma, WA	Sep-92	denatured ethanol	17,740	Yes - PHC LNAPL, BTEX	81,000	0.88	10 - 20	No Data	60	UC, 2016
Bulk Storage Terminal - Pacific Northwest	March-99	neat ethanol	19,000	Yes - PHC	16,000			Yes - up to 30 mg/L in GW 2 years after release	27	UC, 2016; Shaw, 2011
Balaton, MN	28-Jul-04	E95, soybean oil	40,000	No	41,000	No Contamination Present	3.4	Yes	Does not specify	UC, 2016; Spalding et. al., 2011
Rail collision between Montreal and Ottawa, Canada	2-May-05	denatured ethanol	27,000		46,000			Yes	33	Shaw, 2011

Summary of Large-Scale Ethanol Release Sites (Continued)

Site	Release Date	Released Fuel	Volume Released (gal)	Previous Contamination Present (Y/N)	Maximum Ethanol Concentration Observed in GW (mg/L)	Concentrations of Benzene in GW before Release (mg/L)	Max Benzene Concentration in GW After Release (mg/L)	Methane Observed (Y/N)	Time to Ethanol Clean-up (months)	Source
South Hutchinson, KS	30-Aug-05	Natural Gasoline - denatured E95	24,888	No	2,500 in GW; ~71,460 (9%) in vadose zone pore water	No Contamination Present	0.56	YES - delayed by 1-2 years after release	Does not specify	Spalding et. al., 2011
Cambria, MN	22-Nov-06	E95	24,877	No	~50,000	No Contamination Present	5.3	YES - delayed by 1-2 years after release	Does not specify	Spalding et. al., 2011
South Hutchinson, KS	30-Aug-05	Natural Gasoline - denatured E95	24,888	No	2,500 in GW; ~71,460 (9%) in vadose zone pore water	No Contamination Present	0.56	YES - delayed by 1-2 years after release	Does not specify	Spalding et. al., 2011
Cambria, MN	22-Nov-06	E95	24,877	No	~50,000	No Contamination Present	5.3	YES - delayed by 1-2 years after release	Does not specify	Spalding et. al., 2011

Notes:
gal: gallon
mg/L: milligrams per liter
GW: groundwater
PHC: Petroleum Hydrocarbons
LNAPL: Light Non-Aqueous Phase Liquid
BTEX: Benzene, Toluene, Ethylbenzene, Xylenes
BToX: Benzene, Toluene, o-Xylene
*Time to Benzene Clean-up was omitted due to lack of specifications in case studies

6.4.3 Cosolvency Effects Summary

Models, laboratory and field studies, and models, batch and pilot scale studies, field studies and observations from actual ethanol releases evaluated to date indicate that it is unlikely that cosolvent-related increases in BTEX concentrations will be significant at the field scale following spills of E15 as compared to E10. The following observations from the literature support this assertion:

- There was little to no difference noted in BTEX concentration enhancements due to co-solvent effects from water equilibrated from various ethanol blended fuels ranging from E10 to E24. The general range from each fuel blend observed was between 20 to 50% enhancements of BTEX concentrations, with ethanol water volume fractions observed to be less than 10%.[153] [159] [155]
- Researchers suggest that the volume fraction of the dissolved ethanol in groundwater systems is predicted to be less than or equal to 15% (i.e., ~119,000 mg/L), and at these relatively low ethanol volume fractions, BTEX concentrations in the aqueous phase near a gasoline spill are predicted to increase by approximately 20 to 50 percent.[153]
- Weaver et al. concluded that with ethanol contents below about 25 volume %, there is no increase in benzene solubility for this mixture.[149]
- Dissolved ethanol concentrations are not expected to be higher than 15% and likely won't exceed 10% by volume for E15 released to the environment.[153] [159] [155]
- Several case studies of neat or denatured ethanol spills show that ethanol concentrations in groundwater were observed to be approximately 10% by volume (~81,000 mg/L).
- Higher concentrations of ethanol from neat ethanol spills are likely to be observed in the capillary fringe (up to 20% by volume) as opposed to the groundwater due to buoyant forces and advective-dispersive limited mass transfer from the capillary to the saturated zone in the absence of rapid water table fluctuations.[160]

6.5 Biodegradation

Ethanol is known to be highly biodegradable under both aerobic and anaerobic conditions in the environment.[141] Aerobic and anaerobic biodegradation of petroleum hydrocarbons released to the environment is also well documented in the literature.

When ethanol blended fuel is released to the environment, there is a growing body of evidence showing that ethanol will be preferentially degraded over petroleum hydrocarbon compounds (such as BTEX). The resulting depletion of electron acceptors will inhibit the natural attenuation of the petroleum compounds until ethanol is degraded and electron acceptors are replenished. The inhibition of the natural attenuation of the petroleum hydrocarbons can lead to greater BTEX plume lengths and increased BTEX plume longevity and may also create avenues for increased risk of vapor intrusion.[148] [163] The degree of the effects of natural attenuation inhibition on BTEX plumes will depend on the hydrogeological and geochemical conditions at the site and the volume, duration and ethanol content of the blended fuel released.[164] [165] [166]

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[163] Minnesota Pollution Control Agency (MPCA), *Investigation Requirements for Ethanol-Blended Fuel Releases*. (2010). https://www.pca.state.mn.us/sites/default/files/c-prp4-21.pdf

[164] Corseuil, H. X., Schneider, M. R., & Rosário, M., *Weathering of Ethanol-Blended Gasoline in Aquifers – A Field Experiment.* (2005). http://rema/ufsc.br/wp-content/uploads/2014/10/2005_congres_CORSEUIL-et-al.pdf

[165] Corseuil, H. X., Gomez, D. E., Schambeck, C. M., Ramos, D. T., & Alvarez, P. J. J., *Nitrate addition to groundwater impacted by ethanol-blended fuel accelerates ethanol removal and mitigates the associated metabolic flux dilution and inhibition of BTEX degradation [Abstract].* (2015). https://doi.org/10.1016/j.jconhyd.2014.12.004

[166] Steiner, L. V., Ramos, D. T., Liedke, A. R., Serbent, M. P., & Corseuil, H. X., *Ethanol content in different gasohol blend spills influences the decision-making on remediation technologies.* (2018). https://doi.org/10.1016/j.jenvman.2018.01.071

The sections below summarize biodegradation concepts as well as studies and modeling efforts that evaluate the effects of increasing ethanol content in blended fuel releases on biodegradation mechanisms and plume dynamics.

6.5.1 Aerobic Biodegradation

In most release scenarios, oxygen is generally plentiful in the subsurface in soil moisture, soil vapor, and groundwater environment. Thus, initial degradation pathways for petroleum hydrocarbons generally proceed via aerobic biodegradation.

Existing indigenous bacteria can utilize oxygen to its advantage to degrade both ethanol and petroleum constituents including BTEX. Hydrocarbon biodegradation routes generally involve an initial oxidation step, various metabolism steps and intermediates, and finally the process of β-oxidation to produce constituents that can then participate in the tricarboxylic acid cycle (TCA) cycle. The TCA cycle is a series of enzyme-catalyzed chemical reactions that form a key part of aerobic respiration in cells. This process is also known as the Krebs cycle or the citric acid cycle. This process is the key set of reactions for aerobic cellular respiration that breaks down hydrocarbon (ethanol) molecules into carbon dioxide, water, and energy. Due to ethanol's physical and chemical properties, including being a polar solvent and extremely soluble in water, it can be rapidly degraded in the environment by aerobic microorganisms. Typically, the half-life of ethanol in the environment ranges from 0.5-5 days, and in surface water, a shorter half-life is possible.[141] Table 17 displays the biodegradation rates and fate of ethanol in differing media.

TABLE 17. FATE AND BIODEGRADATION RATE (HALF LIFE) OF ETHANOL IN DIFFERING MEDIA[137]

Fate of Ethanol After Major Release		
Media	**Biodegradation Rate**	**Ethanol Fate**
Soil	0.1 – 2.1 days	• Ethanol is rapidly biodegraded in soil
Surface Water	0.25 – 1 day	• Neat Ethanol rapidly mixes with water • Ethanol is rapidly biodegraded in surface water
Groundwater	0.1 – 2.1 days	• Ethanol is rapidly biodegraded in groundwater
Air	0.5 – 5 days	• Ethanol vapor is denser than air and tends to settle in low areas • Ethanol vapor disperses rapidly after release
Storm/sanitary sewers	0.5 – 5 days	• Ethanol will volatilize and rapidly biodegrade

The process of aerobic biodegradation for ethanol is facilitated by several naturally occurring enzymes – alcohol dehydrogenase and acetaldehyde dehydrogenase. The pathway is initiated by the oxidation of ethanol to acetaldehyde, an intermediate before forming acetate, and then acetyl coenzyme A (acetyl CoA). Acetyl CoA then joins the TCA cycle, which releases carbon dioxide at various stages and generates energy and other metabolites (Figure 21).

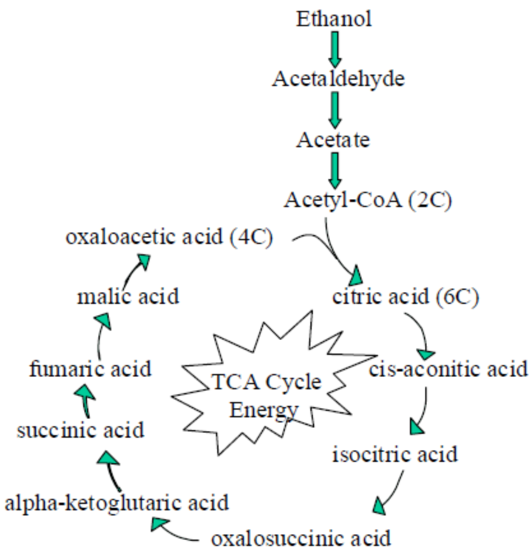

FIGURE 21. AEROBIC ETHANOL METABOLISM PATHWAY (ULRICH, 1999)[167]

As of 1999, there have been 363 strains of bacteria identified capable growing on 1.5% ethanol (Ulrich, 1999).[167] Specific to ethanol-blended fuels, there has been documented potential preferential degradation of ethanol over BTEX constituents. This preferential degradation could deplete the oxygen supply for degradation of BTEX constituents, which may persist in the environment longer than predicted, resulting in other negative effects. If large amounts of ethanol are released, the production of acetic acid and hydrogen may overwhelm and limit the overall biodegradation processes of ethanol and BTEX constituents. Preferential degradation of ethanol also depletes the dissolved sulfate, which leads to the aforementioned acetogenic conditions. This process also results in methanogenic conditions, which is discussed in the anaerobic biodegradation section.

6.5.2 Anaerobic Biodegradation

Anaerobic biodegradation is rarely the initial pathway of petroleum hydrocarbon biodegradation, but after oxygen is depleted, anaerobic biodegradation may take place. Anaerobic biodegradation of both petroleum hydrocarbons and ethanol utilize other electron acceptors, such as nitrate (NO_3^-), manganese (Mn_2^+), iron (Fe^{3+}), sulfate (SO_4^{2-}), and carbon dioxide, hydrogen or other sources in methanogenesis.

The source zone of a recent release may have too much ethanol and/or petroleum hydrocarbon mass initially that biodegradation of either ethanol or petroleum is inhibited (i.e. the source zone may include NAPL and/or very high concentrations of ethanol and/or petroleum hydrocarbons that are toxic to microbes). The area immediately surrounding the source zone of a mature release site typically has depleted oxygen and low electron acceptor availability due to preferential aerobic and anaerobic biodegradation of ethanol. This area can become methanogenic, and adjacent zones of increasing oxidation-reduction potential form progressively moving away from the spill – a sulfate-reducing zone, iron-reducing zone, a nitrate and manganese reducing zone, and finally an aerobic zone (Figure 22).

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[167] Ulrich, G., *The Fate and Transport of Ethanol-Blended Gasoline in the Environment A Literature Review and Transport Modeling.* (1999). https://ethanolrfa.org/wp-content/uploads/2017/06/Fate-Transport-of-Ethanol-Blended-Gasoline-in-the-Environ_Ulrich_1999.pdf

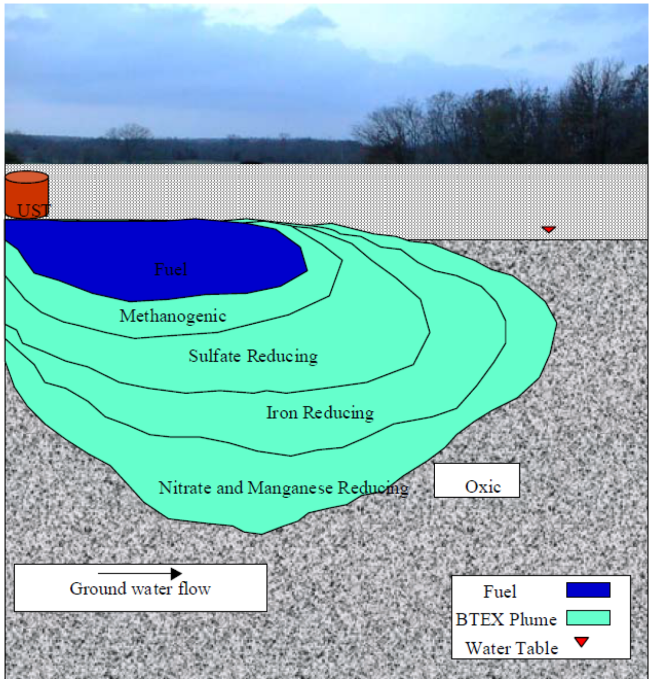

FIGURE 22. ELECTRON-ACCEPTING REGIONS IN HYDROCARBON-CONTAMINATED GROUNDWATER[167]

Typical ethanol release sites transition from initial aerobic to lasting anaerobic conditions. The anaerobic biodegradation pathway for ethanol involves the fermentation of ethanol (and organic acids) to form acetate and hydrogen, which eventually results in a net production of carbon dioxide and methane (Figure 23).

Anaerobic biodegradation possesses the potential for high levels of methane to be produced, and thus constitute a potential safety and explosion risk. Based on the stoichiometry of ethanol degradation chemical equations under methanogenic conditions, up to 75% methane gas could be produced. Sites impacted by ethanol-blended fuels have been recently studied, confirming high methane concentrations in groundwater at a range of 23-47 mg/L and in subsurface deep soil gas at 68%.[168] [169]Methane production and accumulation yields an explosion hazard, which is especially true in confined spaces and poorly ventilated areas. These harmful gases have the potential to migrate and result in vapor intrusion and/or an exceedance of the flammable limits. The various sites in this analysis provide evidence of rapid degradation of high initial ethanol concentrations. However, the analysis also provided evidence of detected ethanol persistence (at low concentrations) at multiple sites up to 4 to 5 years after the release.[169]

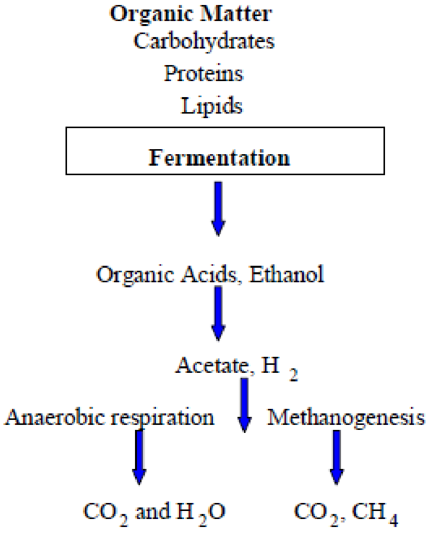

FIGURE 23. ANAEROBIC ETHANOL BIODEGRADATION[167]

Indigenous methanotrophs will also further deplete any available oxygen to consume the produced methane in these anaerobic conditions. Additionally, there is potential for acetic acid accumulation, which can inhibit other degradation compounds from being produced. Reportedly, this concentration is around 2 g/L.[167]

Regarding petroleum hydrocarbons, the biodegradation pathway relies on the type and complexity of the hydrocarbons. Aromatic hydrocarbons will undergo hydroxylation to form intermediates, until the ring is cleaved and is able to progress onto β-oxidation and then glycolysis and the TCA cycle, similar to steps in the aerobic biodegradation process. The success of the anaerobic

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[168] Ma, J., Rixey, W. G., DeVaull, G. E., Stafford, B. P., & Alvarez, P. J. J., *Methane Bioattenuation and Implications for Explosion Risk Reduction along the Groundwater to Soil Surface Pathway above a Plume of Dissolved Ethanol.* (2012). https://dx.doi.org/10.1021/es300715f

[169] Spalding, R. F., Toso, M. A., Exner Spalding, M., Hattan, G., Higgins, T.M., Sekely, A.C., et al., *Long-Term Groundwater Monitoring Results at Large, Sudden Denatured Ethanol Releases.* (2011). https://doi.org/10.1111/j.1745-6592.2011.01336.x

biodegradation process depends heavily on the electron acceptor availability in the existing environment, and if those electron acceptors are supplemented in-situ (or potentially ex-situ as well).

6.5.3 Ethanol Effect on Benzene Plumes

As discussed, ethanol is preferentially degraded in comparison to gasoline hydrocarbons in the natural environment, which leads to degradation inhibition of the hydrocarbons. Since benzene is a well-established human carcinogen, studies on benzene releases, exposures, and overall persistence are critical in attempt to mitigate human health risks and detrimental ecological results. Slower biodegradation rates, elongation of plume length, faster migration, and an increased risk of exposure to down-gradient receptors are possible results of this preferential degradation. Following are results of laboratory studies and field scale studies on the effect of ethanol on the biodegradation/natural attenuation of BTEX from controlled ethanol blend releases, and the results of ethanol and BTEX plume modeling efforts that take selective biodegradation into account.

Deeb et al. (2002) conducted laboratory studies using a pure culture microbial community indigenous to a gasoline contaminated aquifer to evaluate the effect of ethanol on the rate of benzene biodegradation under aerobic conditions, and developed a two-dimensional model derived from the Domenico solution to quantify the impact of ethanol plume lengths using weighted-average aerobic and anaerobic biodegradation rates for benzene in the presence and absence of ethanol.[170]

- Results from the microbial studies indicated that the biodegradation of 25 mg/L benzene mixed with 25 mg/L ethanol was severely inhibited relative to benzene alone;
  - Results for toluene, ethylbenzene and xylene experiments were similar to those of benzene – severe inhibition in the presence of ethanol;
  - Ethanol alone was very rapidly degraded by the benzene-grown culture;
- Model simulations of initial ethanol concentrations in groundwater of 4,000 mg/L (assumed to be a 5% by volume ethanol blend (E5) with a 10-fold water dilution factor) and benzene concentrations 8 mg/L indicated increased benzene plume lengths ranging from 17 to 34% relative to similar benzene concentrations and site conditions without ethanol present
  - The simulations assumed the aquifer material to be a porous media and the plume length was assumed to be the distance from the source to the point where the benzene concentration falls below 0.001 mg/L (the primary MCL for California).
  - In the absence of ethanol, benzene biodegradation was assumed to follow first order kinetics.
  - In the presence of ethanol, ethanol biodegradation was assumed to follow first order kinetics. The benzene biodegradation rate constant for benzene was assumed to be zero when the concentration of ethanol is over 3 mg/L.
    - This assumption was based on batch studies conducted by others that suggested that, when ethanol and BTEX are mixed in solution, benzene is not likely to degrade at a significant rate until ethanol concentrations decrease below a threshold limit;
    - When ethanol concentrations fall below 3 mg/L, the benzene biodegradation rate was assumed to follow the first order kinetics as before;
- Deeb et. al. provided an overview of past published modeling efforts (1996 – 2002) to assess the impact of ethanol on benzene plume lengths.[170]
  - Five models were identified, three of which were 2-D (x, y) transport models, and two of which included three-dimensional transport.
  - Four of the models included an element of biodegradation (either using first order decay kinetics or Monod kinetics). Estimated increase in benzene plume lengths in the presence of ethanol relative to plumes without ethanol indicated ranges from 7 to 150%.

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[170] Deeb, R. A., Sharp, J. O., Stocking, A., McDonald, S. West, K. A., Laugier, M., …Alvarez-Cohen, L., *Impact of Ethanol on Benzene Plume Lengths: Microbial and Modeling Studies.* (2002). http://dx.doi.org/10.1061/(ASCE)0733-9372(2002)128:9(868)

    - One model focused solely cosolvency and interphase mass transfer (no biodegradation). The results of this modeling effort (for xylene only) showed an increase in plume length of < 10% in the presence of ethanol.

Ahsanuzzaman et. al. (2008) developed screening model software for the EPA for estimating the area of a plume produced from gasoline containing ethanol.[171] The software is called "FOOTPRINT" and is available for download at https://www.epa.gov/water-research/footprint-screening-model-estimating-area-plume-produced-gasoline-containing-ethanol.

- The conceptual model used in FOOTPRINT is an extension of the model proposed by Deeb, et. al. described above.[170]
- The software uses the Domenico model modified to allow the option of zero-order decay for either ethanol or BTEX compounds.
- The software can be used to estimate the surface area of the plume or the concentration at any given point down-gradient from the source and can be used to estimate the behavior of the chemical of concern with or without ethanol present.
- Model simulations using Footprint were run with conditions assumed to simulate releases of similar volumes of E10 and E15 created with CaRFG3 and DFE meeting California specifications (i.e. with benzene concentrations proportional to the end members used to make the mixture). Similar first order decay rates were assumed from both ethanol and benzene. Results suggest a minimal 4% increase in benzene plume length with E15 vs E10.

The effect of BTEX weathering from a controlled release of 100 liters of E24 at an experimental farms site in Brazil.[155] Multi-level monitoring wells were installed in a grid pattern around and downgradient (to groundwater flow) of the 2-meter wide x 1-meter long source area. The study source area was excavated and E24 was "spilled" within source area approximately at the water table. Source weathering was evaluated using a mass flux approach. The study area was monitored for 5.7 years. Results of the study included the following:

- Ethanol was still present near the source zone 3 years following the release and BTEX flux was still increasing after that time period.
- BTEX flux reduction occurred only after complete depletion of ethanol, due to the preferential biodegradation of ethanol.
- BTEX flux reduction and increased rates of BTEX weathering was not observed until nine months after ethanol was degraded from the source zone and favorable geochemical conditions were re-established.
- Benzene mass flux was reduced by 93% from its peak and was nearly completely attenuated five and a half years after the controlled release.

Mackay et al. (2006) conducted a field scale evaluation of the impact of ethanol on the natural attenuation of benzene, toluene, and o-xylene (BToX) in a sulfate reducing aquifer, relative to BToX-only. BToX and ethanol were co-injected to concentrations similar to what would be expected of an E10 spill in one "lane", and BToX-only was injected at similar BToX concentrations in an adjacent "lane".[172] Results indicated the following:

- The biodegradation rate of BToX components decreased due to depletion of sulfate as a result of preferred biodegradation of ethanol.
- "Methanogenic conditions were shown to develop only in the lane "with ethanol" due to the depletion of sulfate by the biodegradation of the ethanol".[140]

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[171] Ahsanuzzaman, A. N., Wilson, J. T., Wang, M., & Earle, R. C., *FOOTPRINT, A Screening Model for Estimating the Area of a Plume Produced from Gasoline Containing Ethanol, Version 1.0, EPA/600/R-08/058.* (2008). https://www.epa.gov/water-research/footprint-screening-model-estimating-area-plume-produced-gasoline-containing-ethanol

[172] Mackay, D. M., Desieyes, N. R., Einarson, M.D., Pappas, A. A., Wood, L., Jacobson, L. G., et al., *Impact of Ethanol on the Natural Attenuation of Benzene, Toluene, and o-Xylene in a Normally Sulfate-Reducing Aquifer.* (2006).

- Biodegradation of benzene "with ethanol" decreased to 5% the rate of the "no ethanol lane."
- Under steady-state conditions, benzene, toluene and o-xylene migrated further in the "with ethanol lane" that the "without ethanol lane".
- The longevity of the benzene plume was greater in the "with ethanol lane" than the "without ethanol lane."

Freitas et. al. (2011) performed a field test where gasoline (E0), E10, and E95 were released below the water table.[173] Mass discharge rates of BTEX, trimethylbenzenes and naphthalene were simulated with the BIONAPL/3D numerical model and compared to the field study monitoring results. Results were as follows:

- Ethanol dissolved rapidly and migrated downgradient as a short slug;
- Similar first order decay rates determined from the mass discharge of the hydrocarbons from the E0 and E10 source areas were similar, suggesting that E10 had no impact of hydrocarbon degradation relative to E0.
- Estimated hydrocarbon decay rates were significantly lower in the E95 source area.
- When assuming partial degradation of the hydrocarbons to intermediate compounds, a better match between the numerical model and the field data was obtained.
- The authors conclude that hydrocarbon degradation in the presence of ethanol depends on the ethanol concentration and on the availability of electron acceptors.
- A field study of two controlled 100-liter spills of similar gasoline-ethanol blends (E24 and E25) to evaluate and compare monitored natural attenuation (MNA) versus nitrate biostimulation.[165] Groundwater concentrations of ethanol and BTEX were measured 2 meters downgradient of the source zones. The authors noted the following: Measurable BTEX degradation only occurred after the ethanol fraction was substantially degraded.
- Ethanol degradation was faster in the nitrate amended plot (1.4 years) than the MNA plot (3.0 years), which led to faster BTEX degradation.
- The fate and transport of ethanol and benzene were accurately simulated in both releases using a model similar to Gomez, et. al, (2008, 2009 and 2010) (see below).
- The authors suggest that the initial cleanup efforts of ethanol blended fuel releases (after free product recovery) should be to stimulate the biodegradation of ethanol so that the on-set of BTEX degradation can be expedited.

Completed evaluations and comparisons of two controlled releases of E10 and E25 under MNA and nitrate biostimulation, respectively to evaluate the efficacy of those remedial approaches for ethanol blended fuel releases, and to assess the most effective remediation strategy for each release.[166] The study presented two long-term field experiments of a controlled 100-liter E25 release at the water table and under nitrate biostimulation monitored over an 11-year period, and a controlled 100-liter E10 release at the water table and monitored over a 6-year period for natural attenuation. Injections of 5 liters of 4 g/L solutions of $NaNO_3$ were initiated two months after the controlled E25 release and conducted three times per week over a period of 9 months. Results indicated the following:

- Ethanol was preferentially biodegraded in both release plots.
- The on-set of BTEX biodegradation was observed only after ethanol depletion.
- Ethanol was substantially degraded in the both plots in less than 1 year and was essentially depleted by year 2.
- Initial BTEX concentrations were significantly higher in the E10 plot but began to show signs of degradation shortly after year 1 compared to shortly after year two for the E25 plot.
- Gasoline-ethanol blends with higher concentrations of ethanol require a greater stoichiometric electron acceptor demand. A theoretical biological oxygen demand (BOD) for ethanol

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[173] Freitas, J. G., Mocanu, M. T., Zoby, J. L. G., Molson, J. W., & Barker, J. F., *Migration and fate of ethanol-enhanced gasoline in groundwater: A modelling analysis of a field experiment.* (2011*).* https://doi.org/10.1016/j.jconhyd.2010.08.007

biodegradation suggested that the BOD would be proportionally higher for the higher ethanol blends relative to the lower ones (i.e. The theoretical BOD for E25 is 2.5 times higher than for E10).

- The authors conclude that natural attenuation can be an effective strategy to deal with releases of gasoline-ethanol blends of lower ethanol content (e.g. E10 or less) due to the lower BOD exerted by releases of these blends vs. higher blends.
- The ethanol content of the released fuel and the groundwater geochemical characteristics of the site are paramount to determining whether an MNA strategy alone will effectively manage releases of ethanol blended fuels.

Gomez et. al. (2008) developed a mathematical model to evaluate the effect of ethanol on benzene fate and transport in ethanol blended fuel-contaminated groundwater, and to discern the most influential benzene plume elongation mechanisms.[174] The model was enhanced in 2009 to include cosolvency and microbial toxicity exerted by high ethanol blends near the source zone and to evaluate the effect of ethanol content in gasoline on the natural attenuation of benzene plumes.[151] The model was used to evaluate how the varying concentrations of ethanol in reformulated gasoline blended fuels including midlevel blends, affects the length and longevity of benzene plumes in groundwater.

A description of the model follows:

- The model calculations were based on a combination of the MT3DMS/MODFLOW (USGS) groundwater flow and reactive transport models combined with an advanced computer module (designated the General Substrate Interaction Module (GSIM)) developed to incorporate substrate interactions (benzene/ethanol) and the resulting microbial metabolic and population shifts that influence the natural attenuation of ethanol blended fuel releases and the resulting benzene plume length.

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[174] Gomez, D. E., de Blanc, P. C., Rixey, W. G., Bedient, P. B., & Alvarez, P. J. J., *Modeling benzene plume elongation mechanisms exerted by ethanol using RT3D with a general substrate interaction module.* (2008). http://dx.doi.org/10.1029/2007WR006184

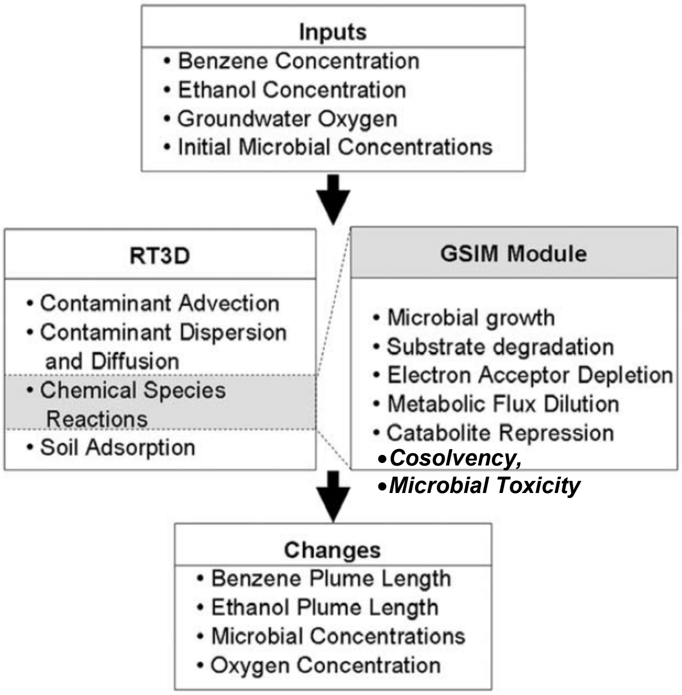

FIGURE 24. PROCESSES CONSIDERED BY RT3D AND GSIM FOR THE SIMULATION OF BENZENE AND ETHANOL FATE AND TRANSPORT.COSOLVENCY AND MICROBIAL TOXICITY EXERTED BY HIGH ETHANOL BLENDS WERE BUILT INTO THE GSIM MODEL AS DISCUSSED IN GOMEZ ET. AL, 2009.ERROR! BOOKMARK NOT DEFINED.

The GSIM was developed for use with the Reactive Transport in 3 Dimensions (RT3D) model, and considers common fate and transport processes, (advection, dispersion, adsorption, aerobic and anaerobic biodegradation, and depletion of molecular oxygen and other electron acceptors during biodegradation), substrate interactions that decrease the specific utilization rate of benzene due to metabolic flux dilution and/or catabolite repression, and LNAPL source dissolution dynamics.

Initial model simulations included two types of source zones that were assumed to originate from a spill of LNAPL: a constant concentration source scenario with an ethanol concentration of 1,000 mg/ and a benzene concentration of 10 mg/L assumed to exist at the source as a result of a relatively large LNAPL release; and a decreasing source concentration scenario where concentrations of benzene and ethanol in the groundwater directly in contact with the source LNAPL were estimated using the API LNAPL Dissolution and Transport Screening Tool (LNAST) model.[175] For this scenario a release of 2,000 kg of an E10 blend of ethanol and benzene mixture was considered. Results of the simulations indicated the following:

- Benzene plume elongation for E10 vs a regular ethanol-free gasoline was on the order of 40% for a constant source of E10 gasoline which compares favorably to field observations made by others.
- For low benzene concentrations (<1 mg/L), oxygen depletion during ethanol degradation was the principal mechanism hindering benzene natural attenuation.

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[175] Huntley and Beckett, *Persistence of LNAPL sources: relationship between risk reduction and LNAPL recovery*. Department of Geological Sciences, San Diego State University, (2002).

- For higher benzene concentrations metabolic flux dilution was the dominant plume elongation process.
- If oxygen were not limiting, model simulations suggest that microbial growth on ethanol could offset negative substrate interactions and enhance benzene degradation, resulting in shorter plumes than baseline conditions without ethanol.

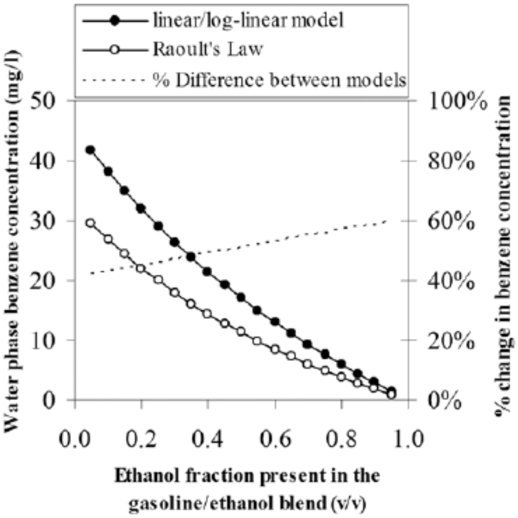

FIGURE 25. EQUILIBRIUM BENZENE CONCENTRATIONS AT THE WATER-LNAPL INTERFACE CONSIDERING HEERMANN AND POWERS' [1998] LINEAR/LOG LINEAR MODEL FOR GASOLINE-ETHANOL BLENDS AND TAKING INTO ACCOUNT FUGACITY AND COSOLVENCY AND RAOULT'S LAW (WITHOUT COSOLVENCY) FOR A RANGE OF ETHANOL BLENDS.
(TAKEN FROM GOMEZ ET. AL., 2009)[151]

Gomez et. al. (2010) evaluated the effect of ethanol on the natural attenuation of benzene using the models discussed above and a probabilistic sensitivity analysis.[176] The model was used to evaluate similar E10 and E85 fuel releases relative to regular gasoline. Model simulations were run for a 30-gallon LNAPL source in a homogenous sandy aquifer, and results inferred maximum benzene plume elongation relative to a regular gasoline release of 26% for E10 and 25% for E85.

Simulations considering decaying LNAPL sources of 85 kg each of E5 through E95 ethanol fuel blends in a fine to medium-grained sand aquifer with a groundwater seepage velocity of 9 cm/day.[151] The maximum benzene plume length for the different ethanol contents in the released fuel for the simulations was defined as the maximum down-gradient distance from the spill source to the EPA maximum contaminant level (MCL) for benzene in drinking water of 5 ug/L (note that the current MCL for benzene in California is 1 ug/L). Results of the simulations and follow-up analyses are as follows:

- Figure 25 shows the different calculated equilibrium concentrations of benzene at the water-LNAPL interface for different ethanol fractions in ethanol blended fuels. Results for both the LLL cosolvency model[158] and for simple Raoult's law equations are presented. Results show that ethanol increases the aqueous concentration of benzene, because of its cosolvent effects by more than 40% when considering an E5 spill and up to 60% when E95 is considered. However,

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[176] Gomez, D. E. & Alvarez, P. J. J., *Comparing the effects of various fuel alcohols on the natural attenuation of Benzene Plumes using a general substrate integration model.* (2010). http://dx.doi.org/10.1016/j.jconhyd.2010.02.002

as the ethanol content in the blended fuel increases, the mass of benzene available for dissolution is reduced resulting in decreasing dissolved benzene concentrations

- Considering a sandy soil with 0.2% organic matter, calculations show that increasing ethanol fractions in the water phase causes a decrease in retardation for BTEX (i.e. a decrease in the degree of sorption to soil). The more hydrophobic and most cosolvent-impacted BTEX compounds – xylene and ethylbenzene – had greater decreases in retardation than was observed for benzene and toluene (xylene and ethylbenzene had a ~2% decrease in retardation for E10, 5 to 7% for E50, and 8 to 13% for E85. Benzene had a change in retardation of ~0.4% for E10, 1.8% for E50). Reduced retardation could lead to longer plume lengths.
- Figure 26 presents the simulated effects that ethanol content had on benzene plume lengths and longevity. The largest plume lengths are observed for E10 to E30 blends, with a maximum plume length change of 59% for E20 relative to simulated ethanol-free benzene plume length.

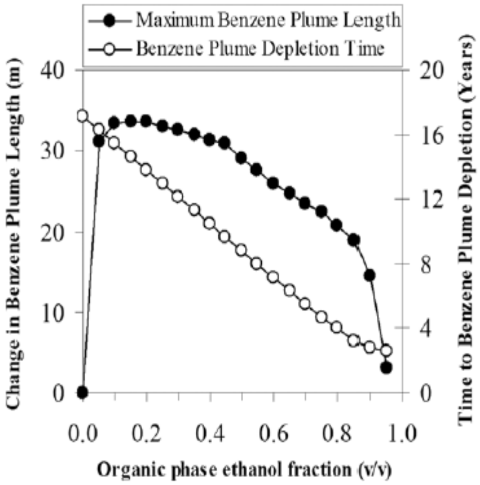

FIGURE 26. MAXIMUM BENZENE CENTERLINE PLUME LENGTH (TO 5 PPB CONTOUR) CHANGE (% OF BASELINE) AND TIME TO BENZENE PLUME DEPLETION FOR BLENDED FUELS WITH VARYING ETHANOL FRACTIONS (VOL/VOL ORGANIC PHASE).[151]

- Benzene plume elongation was due to depletion of dissolved oxygen during ethanol degradation and to a lower specific rate of benzene utilization caused by metabolic flux dilution and catabolite repression.
- Simulations show that the lifespan of benzene plumes decreases with increasing ethanol concentrations and is shorter for all ethanol blends compared to regular gasoline (e.g., 17 years for regular gasoline, 15 years for E10, 9 years for E50, and 3 years for E85) (Figure 26). The authors attribute the reduced benzene plume lifespans on the less benzene mass for higher ethanol blends and on "increased microbial activity associated with fortuitous growth of benzene degraders on ethanol". Site-specific conditions will determine actual benzene plume length and longevity.

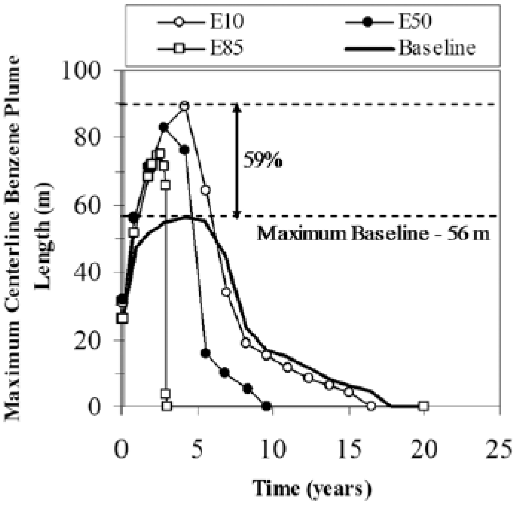

FIGURE 27. EFFECT OF ETHANOL VOLUMETRIC CONTENT IN RELEASED FUEL ON RESULTING BENZENE PLUME LIFE CYCLE COMPARED TO REGULAR GASOLINE WITHOUT ETHANOL (BASELINE).

- "As the ethanol content increases, processes that hinder the natural attenuation of benzene because of the presence of ethanol are accentuated, such as electron acceptor depletion, metabolic flux dilution, and catabolite repression.[174] At the same time, the mass of benzene available for dissolution decreases for higher-ethanol blends because of the higher content of ethanol, resulting in lower benzene concentrations. Furthermore, higher ethanol concentrations result in larger overall microbial populations that contribute to benzene degradation.[151]
- As shown in Figure 27, the simulated benzene plume lengths are similar for ethanol blends between E10 and E25. In this range plume elongation and attenuation processes are in relative balance. "Beyond E45 ethanol content, a decrease in the mass of benzene released and increased biodegradation dominate, and the maximum plume length decreases more abruptly".

A summary of plume lifespans from the 2009 model simulations by Gomez et. al. (2009) is provided in Table 18.

TABLE 18. BENZENE PLUME LIFE-SPANS OF BIOFUEL BLENDS VIA MATHEMATICAL MODELING (GOMEZ ET AL., 2009)[151]

Benzene Plume Life-Spans			
Regular Gasoline	**E10**	**E50**	**E85**
17 years	15 years	9 years	3 years

Results indicate that benzene plume life-span decreased as the percentage of ethanol in the fuel increased. Overall, blends with 50% ethanol or more were more likely to possess a shorter benzene plume life, and also displayed a decrease in plume elongation.[151] These results indicate a greater potential for natural attenuation in high percentage ethanol fuels such as E85. Blends with a larger percentage of ethanol inherently possess less benzene and overall hydrocarbon constituents due to ethanol maintaining the largest percentage of the blend. Thus, benzene plumes are smaller and may attenuate quicker than lower ethanol blends such as E10.[140 151] Due to this correlational relationship between benzene plume life-span and ethanol content of fuel, there may be an advantage in transporting blends of higher ethanol percentage rather than lower, at least when considering potential environmental release risks.

6.5.4 Implications on the Vapor Intrusion Pathway

Biodegradation processes of ethanol blended fuels have important implications on the fate and transport characteristics. Risks due to oxygen depletion, subsequent methane generation, and the associated potential for vapor intrusion into enclosed spaces of benzene or methane may be a result of high ethanol-blend fuel releases (greater than E10). The critical considerations are summarized in the Minnesota Pollution Control Agency's (MPCA) *Investigation Requirements for Ethanol-Blended Fuel Releases*:

- Ethanol degradation in the subsurface has the potential to produce large quantities of methane gas that could lead to explosive conditions. Methane generation may be delayed for months to years after a release and may persist for years after the ethanol is no longer present in groundwater. At some sites, methane might be the primary contaminant of concern and the risk driver for corrective action (safety issue) or long-term monitoring.[163]
- Elongated petroleum plumes in groundwater may serve as a vapor source and present increased risk for the vapor intrusion pathway.[163] As discussed in Section 6.2.2, currently accepted vapor intrusion screening distances are based on 'traditional' petroleum vapor intrusion risks (i.e., incorporating data from fuels ranging from E0 to E10), and the applicability to E15 blends requires validation.[148]
- The increased production of methane and carbon dioxide may strip petroleum hydrocarbons from groundwater and provide a pressure gradient to move vapor into receptors.[163]

6.6 Discussion

Gasoline-ethanol blends up to E15 have been used in the U.S. since partial waivers were approved for E15 by the EPA in 2010. E15 is currently available at 1,400 stations in 29 states across the US.[138] In Brazil, ethanol was used as a fuel starting in the 1970s, was used as nearly the sole source of fuel in 1985 and has been used in ethanol blends up to E24 since the 1990s.[153] Current commercial gasoline in Brazil has a mandatory ethanol blending percentage of 27% (E27).[166]

Actual case studies on E15 spills are lacking. Two statistical analyses have been conducted on actual leak site data for ethanol blends up to E10 to determine estimated BTEX plume elongation relative to sites without ethanol. These analyses are summarized below.

Ruiz-Aguilar et. al. (2003) conducted a statistical review of benzene and toluene plume lengths for 217 Iowa sites impacted with ethanol-free gasoline to 29 Kansas sites impacted with E10 ethanol-blended gasoline.[177] Results of the study included the following:

- The presence of ethanol in E10 ethanol blended fuel impacted sites resulted in mean benzene plume lengths that were approximately 36% longer than mean benzene plume lengths for sites with ethanol-free gasoline impacts.
- The mean toluene plume length was only slightly longer in the presence of ethanol (14% longer); this difference was not statistically significant.
- The authors suggest that benzene may be more sensitive than toluene to the depletion of electron acceptors caused by ethanol degradation, and that the presence of ethanol in gasoline can lead to longer benzene plumes.
- Buscheck (2003) cautions that while the mean benzene plume length was somewhat longer at the ethanol-blended gasoline sites, it is still within the expected range of stable benzene plume lengths and should not hinder the application of natural attenuation as a remediation strategy.[178]

O'Reilly et. al (2016) mined and analyzed data from leak sites with and without ethanol detections in groundwater from the State of California's GeoTracker Database to evaluate relative plume lengths, to evaluate the hypothesis that ethanol affects attenuation of petroleum hydrocarbons, and to determine whether the use of ethanol blended fuel alters the applicability of monitored natural attenuation (MNA).[179] Data from over 2,000 fuel release sites in California were utilized in the study.

- Ethanol was detected at 22% of the sites analyzed and only 1.4% of those sites had a maximum concentration exceeding 500 mg/L ethanol. The median concentration was 0.31 mg/L.
- Median hydrocarbon plume lengths at sites with ethanol detections were statistically longer than those without ethanol detections (19% longer for benzene an 20% longer for toluene).
- No relationship was observed between detecting ethanol at a site and elevated methane concentrations, when comparing methane concentrations at sites with and without ethanol.
- The authors indicate that the results suggest that for most biodegrading release sites, methane concentrations are currently too low to result in off-gassing into the vadose zone, regardless of ethanol detection.
- The authors conclude that results were generally more similar than different at sites with and without ethanol detections, and that the continued use of ethanol blended fuel did not alter the attenuation of hydrocarbon compounds or require changes in site risk management strategies.

The above results are consistent with previous studies that suggest low level ethanol blend releases (E5 – E10) may impart a slight increase in BTEX plume lengths relative to fuel releases without ethanol, but the overall fate and transport risk from these blends is low.

Comparative analyses of the E15 with E10 have been inferred from the various reviews of partitioning theory and model calculations, laboratory bench and pilot scale studies, and field studies (when available)

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[177] Ruiz-Aguilar, G. M. L., O'Reilly, K., & Alavarez, P. J. J., *A Comparison of Benzene and Toluene Plume Lengths for Sites Contaminated with Regular vs. Ethanol-Amended Gasoline.* (2003). https://doi.org/10.1111/j.1745-6592.2003.tb00782.x

[178] Buscheck, T., *Answers to Frequently Asked Questions About Ethanol Impacts to Groundwater.* (2003) https://www.api.org/~/media/Files/EHS/Clean_Water/Bulletins/20_Bull.pdf

[179] O'Reilly, K., Devine, C. E., Sihota, N., & North, K., *An Empirical Evaluation of the Influence of Ethanol on Natural Attenuation of Gasoline Constituents.* (2016). https://doi.org/10.1111/gwmr.12165

of volatilization, liquid phase partitioning, cosolvency effects, and biodegradation conducted to date. The single most significant fate and transport effect of additional ethanol in E15 compared to E10 is related to a proportional increase in BOD and/or electron acceptor demand during biodegradation of released fuel. The preferential degradation of ethanol and the depletion of oxygen and/or available electron acceptors will inhibit petroleum hydrocarbon degradation until ethanol has been adequately degraded. Case studies suggest that as little as 10% ethanol in gasoline will increase benzene plume lengths by up to 40%, and this is likely due to preferential degradation of ethanol and initial inhibition of petroleum hydrocarbon degradation.[177] [179] [172] However, with increasing ethanol contents, there is a proportional decrease in gasoline (and hence BTEX) mass, and models developed by Gomez et. al. (2008, 2009) suggests that the differences between benzene plume lengths and longevity between E10 and E15 blends may be negligible.[174] [151]

6.7 Summary of Findings

Increased use of ethanol in fuel will likely lead to a proportional increase in the quantity of ethanol released to the environment, with a roughly equivalent decline in the amount of petroleum released. Ethanol is readily biodegraded.

The most significant pollutants in surface and subsurface releases of gasoline-ethanol blends are benzene, toluene, ethylbenzene, and xylene (BTEX) all of which are from the petroleum fraction. Although higher concentration ethanol blends will lead to smaller amounts of BTEX released, ethanol will increase the solubility of these compounds in water, and via ethanol competition for electron acceptors, reduce the rate of biodegradation of BTEX.

Modeling efforts by Gomez and Alvarez (2009) to evaluate the effect of ethanol content in different blended fuel releases on the lifespan and maximum length of benzene plumes suggest that ethanol has a significant elongation effect on benzene plume lengths relative to a baseline regular gasoline spill. The elongation effect is most pronounced for E10–E20 blends. However, the modeled difference in benzene plume elongation relative to baseline between E10 and E20 (and thus E10 and E15) appears to be a fraction of a percent. The benzene plume life span (time until plume is degraded below MCL) decreases almost linearly as ethanol content in the blend increases. Therefore, the natural attenuation time for an E15 release is expected to be less than a similar volume release of E10.

Due to the increased microbial activity associated with ethanol releases and degradation, a concern with higher concentrations of ethanol in blended fuels released to the subsurface is generation of methane. Several of the case studies of neat or denatured ethanol releases discussed above have indicated soil vapor concentrations of methane above the lower explosive limit. Should methane ebullition and flux be significant enough to create advective flow, explosion risks to subsurface receptors may be an issue.[168] [169] Additional monitoring of the methane in soil or groundwater can be addressed with existing procedures and tools.

Currently accepted vapor intrusion screening distances are based on ‘traditional’ petroleum vapor intrusion risks (i.e., incorporating data from fuels ranging from E0 to E10), and the applicability to E15 requires validation. To our knowledge, there have been no cases of methane risk to receptors from releases of gasoline-ethanol blends up to E15. Additional study on sites involving E15 releases would provide insight in the applicability of vapor intrusion screening distances for subsurface impacts.

7 Scientific Discussion of Human/Ecological Risk

There are risks to human health and the environment inherent in the use of gasoline-ethanol blends that are related primarily to the complex mixture of volatile hydrocarbons that make up the gasoline blendstock. The main purpose of this section is an evaluation of the potential for risks associated with blends above E10 and up to E15 in comparison to E10. The evaluation is focused on the increased ethanol component in addition to primary hydrocarbon risk drivers (BTEX), and, where available, effects due to exposures to mixtures and transformation byproducts (via biodegradation, or combustion) such as acetaldehyde, formaldehyde, and 1,3-butadiene and benzene.

As discussed in Section 4, emissions testing of vehicles on E15 indicates equal or reduced emissions of potency weighted toxic air contaminants relative to E10.

7.1 Oral, Dermal, and Inhalation Toxicity

7.1.1 Toxicity Information

Table 19 provides a summary of available carcinogenic and non-carcinogenic toxicity data for key chemicals of concern.

TABLE 19. TOXICITY DATA FOR PRIMARY CONSTITUENTS OF CONCERN

Analyte	**Carcinogenic**			**Non-Carcinogenic**		
	OEHHA Oral CSF (mg/kg-day)	EPA IRIS (ug/m^3)$^{-1}$	OEHHA (ug/m^3)$^{-1}$	RfD$_O$ (mg/kg-day)	RfC$_i$ (ug/m^3)	OEHHA REL (ug/m^3)
Ethanol	--	--	--	--	--	--
Benzene	1×10^{-1}	2.2×10^{-6} 7.8×10^{-6}	2.9×10^{-5}	4.0×10^{-3}	30	3
Toluene	--	--	--	8.0×10^{-2}	5000	300
Ethylbenzene	1.1×10^{-2} (EPA data)	--	--	1.0×10^{-1}	1000	2000
Xylenes	--	--	--	2.0×10^{-1}	100	700
Acetaldehyde	1×10^{-2}	2.2×10^{-6}	2.7×10^{-6}	--	9.0	140
Formaldehyde	2.1×10^{-2}	1.3×10^{-5}	6.0×10^{-6}	2.0×10^{-1}	9.8	9
1,3-Butadiene	3.4 (EPA data)	3×10^{-5}	1.7×10^{-4}	--	2.0	2
Acrolein	--	--	--	5.0×10^{-4}	0.02	0.35
Naphthalene	1.2×10^{-1}	--	3.4×10^{-5}	2.0×10^{-2}	3.0	9

OEHHA: Office of Environmental Health Hazard Assessment of the California Environmental Protection Agency Chemical database
EPA: U.S. Environmental Protection Agency
Oral CFS: Oral Cancer Slope Factor
RfD$_O$: Chronic Oral Reference Dose
mg/kg-day: milligrams per kilogram-day
(ug/m^3)$^{-1}$: (microgram per cubic meter)$^{-1}$
RfC$_i$: Chronic Inhalation Reference Concentration
REL: Chronic Reference Exposure Level; OEHHA
ug/m^3: micrograms per cubic meter

7.1.2 Oral Toxicity Review

Increased ethanol concentrations in gasoline-ethanol blends result in minimal direct human health effects, although adverse impacts associated with the hydrocarbon fraction of the blend remain.

Ethanol is used widely in substances intended for human contact or consumption, including alcoholic drinks, lotions, soaps, hairsprays, industrial solvents, vinegar production, scents, flavorings, colorings, and medicines.[134] Literature on the effects of alcohol consumption reflects a consensus that ethanol occurs in many foods and the toxicity of ethanol is not considered a critical issue. Pure ethanol in small amounts is not toxic and is not considered carcinogenic; however, fuel ethanol and ethanol/gasoline blends must be treated as toxic and carcinogenic due to the addition of hydrocarbons and gasoline.[134]

Ethanol is widely available for human consumption at levels significantly higher than those estimated to occur in the environment during the use of ethanol in fuel.[140] Health impacts due to low level contamination of drinking water as a result of releases would be driven by risks due to benzene, primarily. Table 20 summarizes health assessment values, for oral exposures via the drinking water pathway.

TABLE 20. HEALTH ASSESSMENT VALUES – ORAL EXPOSURES FROM DRINKING WATER

Compound	EPA MCL, (mg/L)	OEHHA Value, (mg/L)	Source [date]
Ethanol	--	1,100	Former Draft HPC [1999][181]
Benzene	0.005	0.00015	PHG [2001][180]
Toluene	1	0.15	PHG [1999][181]
Ethylbenzene	0.3	0.3	PHG [1997][182]
Xylenes	1.8	1.8	PHG [1997][182]
Acetaldehyde	--	--	--
Formaldehyde	--	--	--
Acrolein	--	--	--
Naphthalene	--	--	--
Total Petroleum Hydrocarbons	--	100 ug/L	CA RWQCB [2007][183]

--: no screening value available
EPA: US Environmental Protection Agency
MCL: Maximum Contaminant Level
OEHHA: Office of Environmental Health Hazard Assessment
mg/L: milligrams per liter
HPC: Health Protective Concentration
PHG: Public Health Goal

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[180] McDonald, T. A. (2001). *Public Health Goal for Benzene in Drinking Water*. Pesticide and Environmental Toxicology Section Office of Environmental Health Hazard Assessment California Environmental Protection Agency. Retrieved October 9, 2018, from https://oehha.ca.gov/media/downloads/water/chemicals/phg/benzenefinphg_0.pdf

[181] Parker, T. (1999). *Public Health Goal for Toluene in Drinking Water*. Pesticide and Environmental Toxicology Section Office of Environmental Health Hazard Assessment California Environmental Protection Agency. Received October 9, 2018, from https://oehha.ca.gov/media/downloads/water/chemicals/phg/toluf_0.pdf

[182] Faust, J. (1997). *Public Health Goal for Ethylbenzene in Drinking Water*. Pesticide and Environmental Toxicology Section Office of Environmental Health Hazard Assessment California Environmental Protection Agency. Retrieved October 9, 2018, from https://oehha.ca.gov/media/downloads/water/public-health-goal/etbx2c.pdf

*Source: *OEHHA, 1999*[139]
CA RWQCB: California Regional Water Quality Control Board[183]

Table 21 demonstrates the wide range of acceptable regulated concentrations of ethanol in drinking water, which illustrates uncertainties and no general regulatory agency consensus in potential quantitative toxicity characteristics. The California (i.e., OEHHA) and New Hampshire levels included above are based on exposure to ethanol in food and beverages. The New York value is generic for oxygenates and is not specific to ethanol. The New England Interstate Water Pollution Control Commission (NEIWPCC) level is based on a drinking water concentration that is unlikely to result in an increased ethanol concentration in blood and incorporates an uncertainty factor to account for sensitive individuals.

The odor detection threshold in water is approximately 6 ppm (mg/L) ethanol in water and is characterized by a wine-like odor.[135]

The increased ethanol content in E15 does not significantly change the risk profile with respect to oral toxicity, compared to E10. The current body of knowledge provides sufficient evidence that use of E15 will not produce any unique risks or exposure scenarios necessary for consideration with respect to human health compared to the baseline fuel, E10.

TABLE 21. DRINKING WATER HEALTH PROTECTIVE CONCENTRATIONS-ETHANOL (SHAW, 2011)[141]

Drinking Water	
1,100 mg/L	California Draft Value based on the minimum reporting concentration for ethanol in food (0.5%)
6,500 mg/L	NH did not develop drinking water value, but provided value equivalent to drinking 1 beer (13,000 mg ethanol)
0.4 mg/L	NEIWPCC value for comparative purposes, unlikely to increase ethanol in blood over baseline blood concentrations of about 10 mg/L
0.05 mg/L	New York state standard for oxygenates

7.1.3 Dermal Toxicity Review

Direct contact with E10 as well as E15 are expected to cause skin irritation and serious eye irritation.

Human health exposures to ethanol and/or gasoline-ethanol blends during spill situations could occur by contact with the skin, or ingestion if ethanol reaches water supplies (surface water intakes or groundwater). According to *Large Volume Ethanol Spills – Environmental Impacts and Response Options*, acute ingestion of ethanol in doses of 0.1 to 0.5 grams per kilogram (g/kg) body weight are considered the threshold for central nervous system effects.[141]

Acute ingestion of ethanol can cause headache, nausea, vomiting, drowsiness, fatigue, impaired judgment, lack of coordination, stupor, unconsciousness, and coma. Inhalation can cause eye and upper

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[183] California Regional Water Quality Control Board (CA RWQCB). (2007). *Screening For Environmental Concerns at Sites with Contaminated Soil and Groundwater*. Retrieved from https://www.waterboards.ca.gov/rqqcb2/water_issues/available_documents/esl.pdf

respiratory tract irritation, fatigue and headache. Dermal contact can result in irritation of skin, with prolonged contact leading to dry skin, cracking, peeling, and itching.

TABLE 22. FIRST AID TREATMENTS FOR EXPOSURE TO FUEL ETHANOL, EXCERPTED FROM USDOE, 2016, HANDBOOK FOR HANDLING, STORING, AND DISPENSING E85 AND OTHER ETHANOL-GASOLINE BLENDS.[134]

First Aid Treatments for Exposure to Fuel Ethanol		
Symptoms of Exposure • Dullness of memory and concentration • Impaired motor coordination • Drowsiness, stupor, and coma.		
Exposure	First Aid Treatment	Treatment Compared to Gasoline Exposure
Skin Absorption	Immediately wash skin with soap, and flush skin with plenty of water for at least 15 minutes. Remove contaminated clothing and contact medical personnel.	Same
Eye Absorption	Immediately flush eyes with plenty of water for at least 15 minutes and contact medical personnel.	Same

The dermal contact considerations for fuel ethanol (denatured ethanol) and gasoline are the same, providing an indication that there are not known increased risks due to increased ethanol content in E15 compared to E10 from a dermal contact hazard perspective. Recent research on the toxicological effects on the dermal exposure pathway for E15 (or E10) was not identified during this evaluation.

In a literature review published in 2008, contradictory evidence about the safety of topical applications of alcohol [ethanol] were identified by Lachenmeier.[184] The study identified a lack of evidence to associate topical ethanol use with an increased risk of skin cancer. Limited and conflicting epidemiological evidence is available on the link between the use of ethanol in the oral cavity in the form of mouthwashes or mouth rinses and oral cancer. Some studies pointed to an increased risk of oral cancer due to locally produced acetaldehyde, operating via a similar mechanism to that found after alcoholic beverage ingestion.

The study identified that topically applied ethanol can act as a skin penetration enhancer and may facilitate the transdermal absorption of xenobiotics. Ethanol use is associated with skin irritation or contact dermatitis, especially in humans with an aldehyde dehydrogenase (ALDH) deficiency.

After regular application of ethanol on the skin (e.g., in the form of hand disinfectants) relatively low but measurable blood concentrations of ethanol and its metabolite acetaldehyde may occur, which are, however, below acute toxic levels. Only in children, especially through lacerated skin, can percutaneous toxicity occur. The study identified a need for further independent research focused on the chronic toxic

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[184] Lachenmeier, D. W., *Safety evaluation of topical applications of ethanol on the skin and inside the oral cavity.* (2008). https://doi.org/10.1186/1745-6673-3-26

effects of ethanol and acetaldehyde at the point of impact, with special regard to children and individuals with genetic deficiencies in ethanol metabolism.

Chronic exposures to ethanol are unlikely to occur as a result of a spill, due to volatilization (especially in the presence of wind and/or higher air temperatures) and due to the rapid biodegradation of ethanol. Additional study on high-concentration acute exposures would likely have relevance for these exposed in an occupational setting, such as in an ethanol production facility.

The increased ethanol content of E15 is not likely to significantly change the risk profile with respect to dermal toxicity, compared to E10. The current body of knowledge provides sufficient evidence that use of E15 will not produce any unique risks or exposure scenarios necessary for consideration with respect to human health compared to the baseline fuel, E10.

7.1.4 Inhalation Toxicity Review

Evaporative emissions of ethanol blended fuels usually occur primarily during refueling activities, from spills, and directly from vehicles.

The differences in health risks between evaporative emissions of E10 compared to E15 are based predominantly on a reduced benzene concentration and an increased ethanol concentration.

Exposure to evaporative emissions is most likely to occur in an occupational setting associated with transportation, loading, and spill response operations. However, there is some applicability to exposures to the public at retail service stations.

Exhaust emissions include unburned fuel and other products of incomplete combustion. Many of these products, particularly emissions of hydrocarbons and nitrogen oxides (NOx), together are critical precursors in the formation of ozone and other atmospheric transformation products. The compounds determined to be the most important in terms of public health risks for the purpose of this multimedia evaluation are:

- Ethanol;
- Benzene; and,
- Combustion byproducts including air toxics 1,3-butadiene, formaldehyde, and acetaldehyde.

Benzene and the combustion byproducts 1,3-butadiene, formaldehyde, and acetaldehyde are all potential human carcinogens, but non-cancer health effects are also possible.

Health effects associated with formaldehyde exposure have been studied extensively in people, laboratory animals, and in vitro systems with a variety of study designs. Formaldehyde is ubiquitous in indoor and outdoor air, and everyone is exposed to formaldehyde at some concentration daily. Non-cancer effects due to formaldehyde exposure include sensory irritation (eye, nose, and throat), upper respiratory tract pathology, decreased pulmonary function, increased asthma and allergic sensitization, and reproductive and developmental toxicity.[185]

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[185] National Research Council Committee to Review EPA's Draft IRIS Assessment of Formaldehyde (NRC), *Reference Concentrations for Noncancer Effects and Unit Risks for Cancers.* (2011). https://ncbi.nlm.nih.gov/books/NBK208227/pdf/Bookshelf_NBK208227.pdf

Non-cancer effects of chronic acetaldehyde intoxication in humans resemble those of alcoholism. In hamsters, chronic inhalation exposure to acetaldehyde has produced changes in the nasal mucosa and trachea, growth retardation, slight anemia, and increased kidney weight.[186]

Reproductive and developmental effects have been observed in mice exposed to 1,3-butadiene by inhalation, however there are no human data on reproductive or developmental effects.[187]

Table 23 provides a summary of some of the key thresholds and standards for evaluating inhalation exposure risks due to benzene and ethanol.

TABLE 23. EXPOSURE THRESHOLDS FOR ETHANOL AND BENZENE

Ethanol	
100 ppm	Odor Threshold[213]
1,000 ppm	STEL.[188] No significant neuromotor effects .[141]
1,000 ppm	OSHA: The legal airborne permissible exposure limit (PEL) is 1000 parts per million (ppm) averaged over an 8-hour workshift.
1,000 ppm	NIOSH: The recommended airborne exposure limit (REL) is 1000 ppm averaged over a 10- hour workshift.
3,000 ppm	Headaches and early signs of intoxication.[141]
5,000 – 10,000 ppm	Irritating to eyes and respiratory system.[141]
Benzene	
1.5 ppm	Odor Threshold (*EPA, 2012*)
5 ppm	OSHA STEL[189]
1 ppm	OSHA TWA [189]
0.0083 ppm	Acute REL[190]
0.00092 ppm	Chronic REL [190]
ppm: parts per million STEL: short-term exposure limit TWA: time-weighted average REL: reference exposure level	

Toxicological studies indicate that ethanol, (e.g., alcoholic beverages) is known to change the metabolism of benzene and toxicity of benzene.[191] Greater understanding of the enhancement of health effects of benzene by ethanol represents an area where more study may be warranted, especially with respect to

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[186] Environmental Protection Agency (EPA), *Acetaldehyde Hazard Summary, 75-07-0*. (2000). https://www.epa.gov/sites/production/files/2016-09/documents/acetaldehyde.pd f

[187] Environmental Protection Agency (EPA), *Integrated Risk Information System (IRIS) Chemical Assessment Summary, 1,3-Butadiene; CASRN 106-99-0*. (2002). https://cfpub.epa.gov/ncea/iris/iris_documents/documents/subst/0139_summary.pdf#nameddest=rfc

[188] International Labor Organization and World Health Organization (ILO/WHO). (2000). *Ethanol (Anhydrous), ICSC: 0044*. Retrieved October 9, 2018, from http://www.inchem.org/documents/icsc/icsc/eics0044.htm

[189] *29 CFR 1910.1028*

[190] Office of Environmental Health Hazard Assessment (OEHHA). (2014). *Benzene.* Retrieved October 11, 2018, from https://oehha.ca.gov/air/chemicals/benzene

[191] Agency for Toxic Substances and Disease Registry (ATSDR), Wilbur S., Keith, S., Faroon, O., Wohlers, D., Stickney, J., Paikoff, S., et al. (2007). *Toxicological Profile for Benzene*. U.S. Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry. Retrieved from https://www.atsdr.cdc.gov/toxprofiles/tp3.pdf

occupational exposures. However, OEHHA (1999) found that ethanol toxicity issues are not likely to be significant at expected ambient air levels.[139]

7.1.5 Comparative Studies – Toxicological Evaluations of Ethanol Blended Fuels

A literature review was conducted to identify toxicological studies which compare E15 blends to E10. Each study was designed with specific objectives and often evaluate a wide range of concentrations of ethanol in gasoline, including gasoline without ethanol (E0) as well as blends up to E85. Evaluating a range of dose-response relationships as a function of ethanol concentration allows for quantitative comparison so that the toxicity of any blend can be estimated.[192] The following provides a summary of relevant research for evaluating potential toxicological effects relevant to increased ethanol concentrations blended with gasoline.

7.1.5.1 Toxicological assessments of rats exposed prenatally to inhaled vapors of gasoline and gasoline-ethanol blends.[192]

A study published by Bushnell, et. al., compared the toxicity to vapors of E0, E15, and E85.[192]Pregnant rats were exposed to vapors at relatively high concentrations of 3000, 6000 or 9000 ppm in order to permit characterization of observed effects.

No concentration-related changes in neurobehavioral development, immune function or glucose homeostasis were observed in the offspring of pregnant rats exposed to concentrations up to 9000 ppm. Pregnant rats exposed to E0 and E85, but not E15, consumed less food while maintaining a normal trajectory of weight. Fuel vapor exposure did not affect litter size/weight, or postnatal weight gain in the offspring. Tests revealed an increase in vertical activity counts in the 3000- and 9000-ppm groups in the E85 experiment, suggesting a Lowest Observed Effect Level (LOEL) of 3000 ppm of E85 for vertical activity, LOELs of 9000 ppm of E0 and E85 for maternal food consumption, and No Observed Effect Levels (NOELs) of 9000 ppm for the other endpoints assessed in the study. The study concluded that ethanol content of the vapors did not consistently alter the pattern of behavioral, immunological, or physiological responses to the fuel vapors. Note that the results related to cognitive function performed under the same experimental conditions are reported by Oshiro, et. al, (2015), and are discussed below.[193]

The researchers concluded that the concentrations used in the study (3000 to 9000 ppm [8.0 x 10^6 ug/m3 to 2.4 x10^7 ug/m3]) were 4-6 orders of magnitude higher than typical exposure levels encountered by the public. Typical exposures to volatile organic compounds in ambient air cited by the authors ranged from 5.18 ug/m3 and 44.5 ug/m3) in urban settings. Occupational exposure limits for hydrocarbon vapors are higher (100 to 500 ppm) for 8-hour exposures.

Because of the lack of differences in the results between the effects of exposure to E0, E15, and E85, this study provides evidence that increased toxicity due to the inhalation of evaporative emissions will not be observed as a result of E15 use compared to E10.

7.1.5.2 Prenatal exposure to vapors of gasoline-ethanol blends causes few cognitive deficits in adult rats

The Oshiro et. al. study reported the results of an assessment of cognitive function in adult offspring of pregnant rats exposed to vapors of gasoline blended with a range of ethanol concentrations (E0, E15,

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[192] Bushnell, P. J., Beasley, T. E., Evansky, P. A., Martin, S. A., McDaniel, K. L., Moser, V. C. Rogers, J. M. (2015). *Toxicological assessments of rats exposed prenatally to inhaled vapors of gasoline and gasoline-ethanol blends. Neurotoxicology and Teratology, 49,* 19-30. http://dx.doi.org/10.1016/j.ntt.2015.02.004

[193] Oshiro, W. M., Beasley, T. E., McDaniel, K. L., Evansky, P. A., Martin, S. A., Moser, V. C.,… Bushnell, P. J. (2015). *Prenatal exposure to vapors of gasoline-ethanol blends causes few cognitive deficits in adult rats. Neurotoxicology and Teratology, 49,* 59-73. http://dx.doi.org/10.1016/j.ntt.2015.04.001

and E85).[193] The research extended on the existing knowledge gained through published reproductive and developmental studies on inhaled vapors of gasoline and gasoline blended with 10% ethanol (E10, Gray et al., 2014) to include neurocognitive tests in offspring exposed in utero to fuel vapors.[194] [195] Few deficits were detected in test of learning memory and attention. It was concluded that where effects were observed, they were likely due to a combination of hydrocarbons in the mixtures rather than the ethanol component. Regardless, the observed effects occurred at levels 4-6 orders of magnitude higher than typical residential and occupational exposure levels.[193] Because of the lack of differences in the results between the effects of exposure to E0, E15, and E85, this study provides evidence that increased toxicity due to the inhalation of evaporative emissions will not be observed as a result of E15 use compared to E10.

7.1.5.3 Health assessment of gasoline and fuel oxygenate vapors: Subchronic inhalation toxicity[196]

In this study, rats were exposed via inhalation to vapor condensates of either gasoline or gasoline combined with various fuel oxygenates to assess whether their use in gasoline influences the hazard of evaporative emissions. Test substances included vapor condensates prepared from an EPA described ‘‘baseline gasoline’’, or gasoline combined with ethanol or other oxygenates at concentrations up to 20,000 mg/m3. The researchers concluded that results provided evidence that use of the studied oxygenates [including ethanol] are unlikely to increase the hazard of evaporative emissions during refueling, compared to those from gasoline alone. The ethanol fraction of the fuel tested was not presented but is presumed to be E10. The lack of increased hazard potential due to the use of E10 compared to gasoline (E0) provides an indication that use of E15 would not result in an increased hazard compared to E10.

7.1.5.4 Health assessment of gasoline and fuel oxygenate vapors: Neurotoxicity Evaluation[197]

This research was conducted under the same experimental conditions as the study listed above. Rats were exposed via inhalation to vapor condensates prepared from a “baseline gasoline’’, or gasoline blended with ethanol or other oxygenates at concentrations up to 20,000 mg/m3, and then evaluated for neurotoxicity. The exception is response of rats exposed to G/EtOH (gasoline blended with ethanol). Increases in glial fibrillary acidic protein (GFAP) levels were seen in several brain regions in male rats with a concentration-related increase seen over all doses in the cerebellum although the high dose dropped back below the increases at lower dose levels. These increases in the cerebellum were in the 30% range and indicated minor gliosis. This finding is consistent with positive GFAP results reported from oral treatment of ethanol alone.[198]

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[194] Roberts, L., White, R., Bui, Q., Daughtrey, W., Koschier, F., Rodney, S., Newton, P., *Developmental toxicity evaluation of unleaded gasoline vapor in the rat.* (2001). *Reproductive Toxicology, 15,* 487-494. https://doi.org/10.1016/S0890-6238(01)00150-2

[195] Gray, T. M., Steup, D., Roberts, L. G., O’Callaghan, J. P., Hoffman, G., Schreiner, C. A., & Clark, C. R., *Health assessment of gasoline and fuel oxygenate vapors: Reproductive toxicity assessment.* (2014). *Regulatory Toxicology and Pharmacology, 70,* S48-S57. https://doi.org/10.1016/j.yrtph.2014.04.014

[196] Clark, C. R., Schreiner, C. A., Parker, C. M., Gray, T. M., & Hoffman, G. M., *Health assessment of gasoline and fuel oxygenate vapors: Subchronic inhalation toxicity.* (2014). *Regulatory Toxicology and Pharmacology, 70,* S18-S28. http://dx.doi.org/10.1016/j.yrtph.2014.07.003

[197] O’Callaghan, J. P., Daughtrey, W. C., Clark, C. R., Schreiner, C. A., & White, R. (2014). Health assessment of gasoline and fuel oxygenate vapors: Neurotoxicity evaluation. *Regulatory Toxicology and Pharmacology, 70,* S35-S42. http://dx.doi.org/10.1016/j.yrtph.2014.05.002

[198] Franke, H., Kittner, H., Berger, P., Wirkner, K., & Schramek, J. (1997). The reaction of astrocytes and neurons in the hippocampus of adult rats during chronic ethanol treatment and correlations to behavioral impairments. *Alcohol, 14,* 445-454. https://doi.org/10.1016/S0741-8329(96)00209-1

7.1.5.5 Hazard identification of exhausts from gasoline-ethanol fuel blends using a multi-cellular human lung model[199]

The aim of this study was to investigate the possible toxic effects of exhaust components produced from a passenger car with ethanol blended fuels ranging from E0, E10, and E85 and to correlate the emissions with possible effects in a multi-cellular human lung model. The lung cells were exposed to the exhaust and assessed for effects on biological endpoints such as cytotoxicity, pro-inflammation, oxidative stress, and mutagenicity. Researchers determined that the tested exhausts from a flex-fuel gasoline vehicle using different ethanol-gasoline blends (E0, E10, and E85) did not induce adverse cell responses in an acute exposure. The same experiment resulted in significant adverse effects associated with exposures to diesel exhaust. Because of the lack of differences in the results between the effects of exposure to E0, E10, and E85, this study provides evidence that increased acute toxicity due to the inhalation of ethanol blended fuel exhaust will not be observed as a result of E15 compared to E10.

7.1.5.6 Effects of gasoline and ethanol-gasoline exhaust exposure on human bronchial epithelial and natural killer cells in vitro[200]

This study, which used human cells to avoid potential translation difficulties from animal data, evaluated effects of exhausts from E0 and E85. The study involved a comparison of effects due to exposure to the whole exhaust mixture, including gaseous and particulate components, which more closely represents typical exposure conditions. The authors found no toxic effects after exposure to E0 or E85 compared to air controls. Comparison between E0 and E85 exposure showed a weak association for less oxidative DNA damage after E85 exposure compared to E0.

7.1.5.7 Transcriptional response to organic compounds from diverse gasoline and biogasoline fuel emissions in human lung cells[201]

This study characterized gasoline exhaust particles produced by gasoline (E0) and its blends with 15% ethanol (E15), 25% n-butanol (n-But25) and 25% isobutanol (i-But25). The results of the study indicated that i-But25 resulted in less severe genotoxic effects, but relevant to this evaluation are the study results which did not identify significant differences between the effects of E0, E15 and/or n-But25. Tests involving E0, E15 and n-But25 resulted in persistent stress signaling including DNA damage response MAPK signaling, oxidative stress, metabolism of PAHs or pro-inflammatory response. These results support other scientific studies which do not identify significant differences between gasoline and gasoline-ethanol blends, providing another line of evidence that an increased toxicity will not be observed based on the exposure to E15 compared to E10.[192] [193]

There are a number of recent studies involving inhalation exposures to ethanol (i.e. E100) concentrations, but these literature reviews were not considered as relevant as those directly evaluating vapors and exhausts of ethanol blended fuels.[202] [203] [195]

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[199] Bisig, C., Roth, M., Müller, L., Comte, P., Heeb, N., Mayer, A., Rothen-Rutishauser, B. (2016). Hazard identification of exhausts from gasoline-ethanol fuel blends using a multi-cellular human lung model. *Environmental Research, 151,* 789-796. http://dx.doi.org/10.1016/j.envres.2016.09.010

[200] Roth, M., Usemann, J., Bisig, C., Comte, P., Czerwinski, J., Mayer, A., …Müller, L. (2017). Effects of gasoline and ethanol-gasoline exhaust exposure on human bronchial epithelial and natural killer cells in vitro. *Toxicology in Vitro, 45,* 101-110. http://dx.doi.org/10.1016/j.tiv.2017.08.016

[201] Libalova, H., Rossner, P., Jr., Vrbova, K., Brzicova, T., Sikorova, J., Vojtisek-Lom, M., … Topinka, J. (2018). Transcriptional response to organic compounds from diverse gasoline and biogasoline fuel emissions in human lung cells. *Toxicology in Vitro, 48,* 329-341. https://doi.org/10.1016/j.tiv.2018.02002

[202] Beasley, T. E., Evansky, P. A., Martin, S.A., McDaniel, K. L., Moser, V. C., Luebke, R. W., …Bushnell, P. J. (2014). Toxicological outcomes in rats exposed to inhaled ethanol during gestation. *Neurotoxicology and Teratology, 45,* 59-69. https://doi.org/10.1016/j.ntt.2014.07.002

[203] Boyes, W. K., Degn, L., Martin, S. A., Lyke, D. F., Hamm, C. W., & Herr, D. W. (2014). Neurophysiological assessment of auditory, peripheral nerve, somatosensory, and visual system function after developmental exposure to ethanol vapors. *Neurotoxicology and Teratology, 43,* 1-10. https://doi.org/10.1016/j.ntt.2014.02.006

7.1.6 Comparative Studies – Relative Differences in Emissions of Ethanol Blended Fuels

Numerous models have been utilized to evaluate the potential risks due increased ethanol blended fuels. Comparisons of predicted emissions from E10 and E20 ethanol blended fuels to E0 provide an indication of the relative health risk impacts for using E15. To provide insight on the effect of the use of increasing ethanol proportions in gasoline, relative emissions of these compounds have been evaluated using 1) comparative toxicological dose-response studies, 2) studies on air emissions data, and 3) studies on predicted air emissions using models.

The following provides a summary of relevant literature providing a comparison between the baseline fuel E10 and higher ethanol blends:

Increased use of ethanol-blended fuels has been key to significantly reducing air pollution in the state of California, in accordance with a study published in 2018.[204] In the report titled, "*Gasoline-Related Air Pollutants in California: Trends in Exposure and Health Risk*," OEHHA assessed risks using air emissions data collected from 1996 to 2014, which spans the time before and after the removal of methyl t-butyl ether (MTBE) from gasoline.[204] Beginning in 1996, MTBE was used as a gasoline oxygenate. After significant environmental concerns associated with MTBE were identified, MTBE was voluntarily phased out between 2000 and 2003, and was banned from California gasoline beginning in 2004. Ethanol replaced MTBE as the preferred gasoline oxygenate.

The report provides valuable insight into potential health concerns associated with the changing gasoline formulation, which is backed by data collected by CARB, rather than emissions predicted by models. The data show that emissions from automobile use have declined over the past recent decades due to the use of ethanol blended cleaner burning gasoline, as well as improvements in vehicle emission controls.[204]

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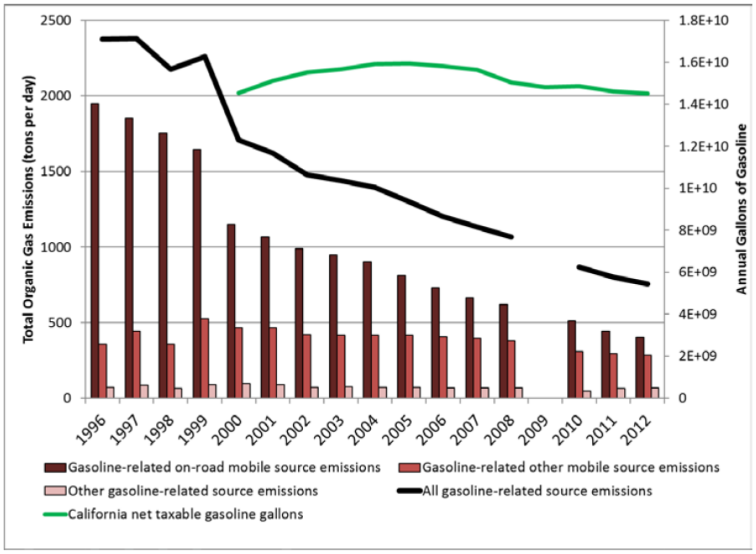
[204] Office of Environmental Health Hazard Assessment (OEHHA), Sultana, D. & Hoover, S. (2018). *Gasoline-Related Air Pollutants in California Trends in Exposure and Health Risk 1996 to 2014*. Safer Alternatives Assessment and Biomonitoring Section, Reproductive and Cancer Hazard Assessment Branch, Office of Environmental Hazard Assessment, California Environmental Protection Agency. https://oehha.ca.gov/media/downloads/air/report/oehhagasolinereportjanuary2018final.pdf



Data from CARB Emission Inventory and State Board of Equalization. Mobile source emissions estimates not available for 2009.

FIGURE 28. CALIFORNIA STATEWIDE TRENDS IN GASOLINE-RELATED EMISSIONS AND GASOLINE USE[204]

As shown in Figure 28, a steep decline in total organic emissions occurs between 1999 and 2004, which is attributable, in part, to the switch from MTBE to ethanol as an oxygenate.[204] The data illustrate the health risk benefits of increasing ethanol fractions in gasoline. According to the OEHHA study, in 2004, California gasoline contained about 5.7% ethanol by volume, but that percentage increased over time to the maximum allowed percentage of 10%, (E10).[204] Increasing use of E15 has the potential to further reduce the total organic emissions in the state of California.

According to a study completed by the University of Illinois at Chicago, (UIC) the blending of ethanol at 10% and 15% (E10 and E15) in conventional gasoline, and at higher blends in FFVs, has been accompanied by a dramatic reduction in air emissions throughout all driving seasons based on air quality data.[205]

Combustion chemistry shows that the oxidation of ethanol produces an increased amount of acetaldehyde and formaldehydes, however, it does not produce benzene or 1,3 – butadiene. Therefore, increased use of ethanol in fuel blends increases aldehyde emissions and decreases benzene and 1,3-butadiene emissions. When factoring the relative toxicity levels of these compounds, the weighted sum risk of all four compounds is less with ethanol-blended fuel.[205]

Figure 29 below, which shows cancer risk due to air toxics including benzene, 1,3-butadiene, formaldehyde, and acetaldehyde in California, demonstrates that the increase in acetaldehyde concentrations due to increased ethanol use did not result in increased risk as ethanol was phased in after 1999. The calculations take into account early-in-life sensitivity to carcinogens.

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[205] University of Illinois at Chicago (UIC), Mueller, S., Unnasch, S., Keesom, B., Mohan, S., & Goyal, L. (2018). *The Impact of Higher Ethanol Blends Levels on Vehicle Emissions in Five Global Cities*. The University of Illinois at Chicago Energy Resource Center. Retrieved October 9, 2018, from http://www.erc.uic.edu/assets/pdf/UIC5cities_FINAL.pdf

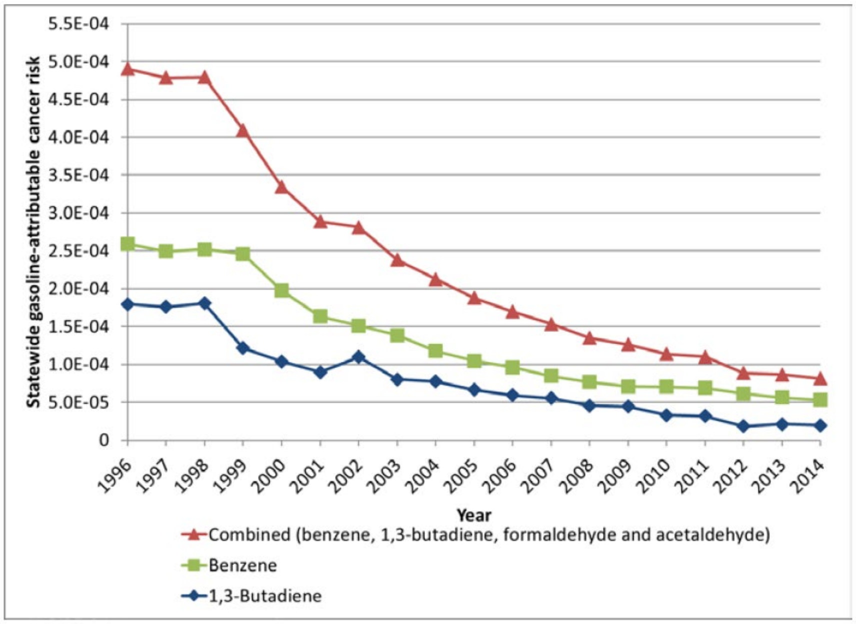


FIGURE 29. STATEWIDE CANCER RISKS FOR SELECTED VOCS BASED ON GASOLINE-ATTRIBUTABLE POPULATION-WEIGHTED ANNUAL AVERAGE AMBIENT AIR CONCENTRATIONS[204]

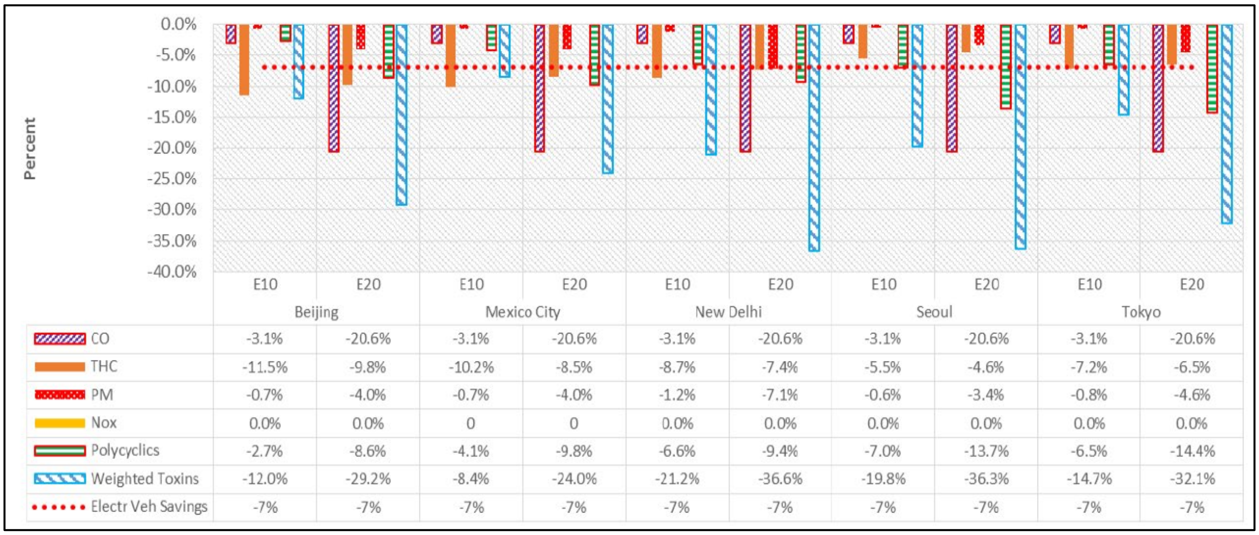
"*The Impact of Higher Ethanol Blend Levels on Vehicle Emissions in Five Global Cities*", (UIC, 2018) This study provides an examination of differences between emissions of current gasoline use without ethanol (E0) compared to higher ethanol blends including E10 and E20 in five international cities.[205]The UIC report provides an updated summary of some of the key ethanol-gasoline vehicle emissions studies detailed in the literature. UIC concluded that the results showed generally consistent decreases for total hydrocarbons (THC) and non-methane hydrocarbons (NMHC), consistent decreases for carbon monoxide (CO) for the higher ethanol blends, with higher uncertainties for NOx reflected in the literature. Increased acetaldehyde emissions expected with increased ethanol blended fuels are reflected in the summary of average emissions factors obtained from the literature below but need to be considered in light of its potency relative to benzene, 1,3 butadiene and formaldehyde.

TABLE 24. SUMMARY OF AVERAGE EMISSIONS FACTORS, COMPARED TO E0, BASED ON LITERATURE [205]

Compound	E10	E20
THC/NMHC	-21.9%	-21.5%
CO	-3.0%	-23.4%
NOx	-11.80%	-17.1%
Benzene	-32.0%	-36.0%
1,3-butadiene	-18.0%	-56.0%
Formaldehyde	-24.90%	-36.0%
Acetaldehyde	83.3%	101.0%

While significant increases in acetaldehyde emissions (101%) are for the use of E20 compared to E0, the increased exposure to acetaldehyde emissions associated with E15 use is anticipated to be less than 20% compared to the baseline fuel, E10.

The UIC study also evaluated emissions benefits from adopting higher ethanol blends including E10 and E20 in light of current and predicted fuel demand in five global cities (Figure **30**). The cities studied are Beijing, Mexico City, New Delhi, Seoul, and Tokyo, all of which face major air quality challenges. The study provides some insight to support additional risk reduction as a result of using ethanol blends containing >10% ethanol, primarily through reductions in emissions of CO.



	Beijing		Mexico City		New Delhi		Seoul		Tokyo	
	E10	E20	E10	E20	E10	E20	E10	E20	E10	E20
▨ CO	-3.1%	-20.6%	-3.1%	-20.6%	-3.1%	-20.6%	-3.1%	-20.6%	-3.1%	-20.6%
▬ THC	-11.5%	-9.8%	-10.2%	-8.5%	-8.7%	-7.4%	-5.5%	-4.6%	-7.2%	-6.5%
▦ PM	-0.7%	-4.0%	-0.7%	-4.0%	-1.2%	-7.1%	-0.6%	-3.4%	-0.8%	-4.6%
▬ Nox	0.0%	0.0%	0	0	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
▭ Polycyclics	-2.7%	-8.6%	-4.1%	-9.8%	-6.6%	-9.4%	-7.0%	-13.7%	-6.5%	-14.4%
▨ Weighted Toxins	-12.0%	-29.2%	-8.4%	-24.0%	-21.2%	-36.6%	-19.8%	-36.3%	-14.7%	-32.1%
•••••• Electr Veh Savings	-7%	-7%	-7%	-7%	-7%	-7%	-7%	-7%	-7%	-7%

FIGURE 30. PREDICTED EMISSIONS REDUCTIONS BY CITY AND ETHANOL BLEND[205]

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

Another study, titled, "Change in Air Quality Impacts Associated with the Use of E15 Blends Instead of E10," provides a comparison of weighted cancer risks from vehicle exhaust emissions with E5.7 and E32 Fuels.[146] The study included a literature review and meta-analysis of changes in emissions that may occur when approved vehicles are fueled with E15 instead of E10.[146] The analysis incorporated a weighted relative cancer potency to evaluate changes in emissions. The study indicated a decrease in cancer risk observed with an increase in ethanol content, due to the ethanol replacement of aromatics and precursors to 1,3-butadiene. Moving from E10 to E15 also reduced the toxicity impact of evaporative emissions from fuel spills, the study found.[146] The following Figure 31 shows weighted toxics, for a variety of vehicle types for vehicle exhaust emissions with E5.7 and E32 fuels.

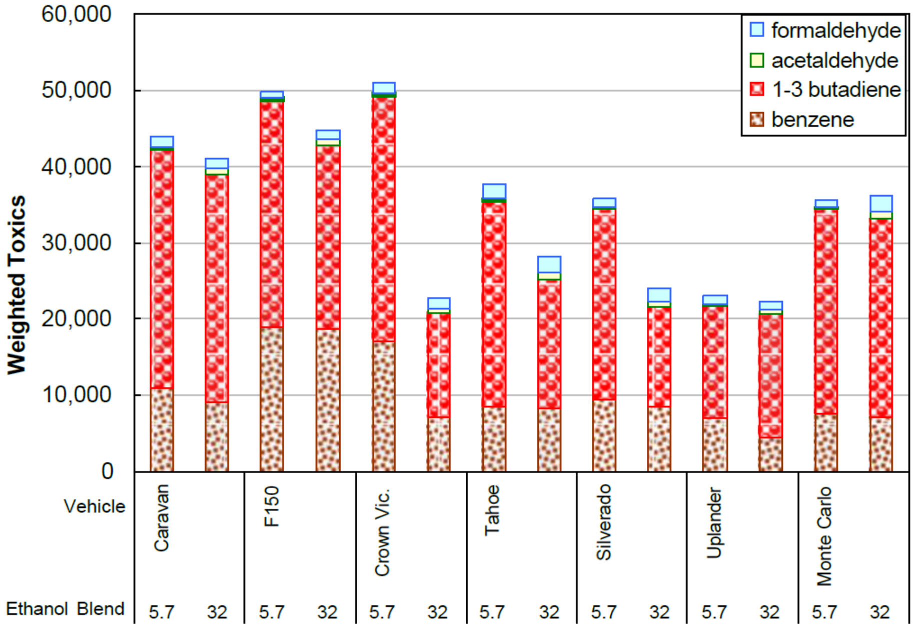


FIGURE 31. WEIGHTED CANCER RISK FROM VEHICLE EXHAUST EMISSIONS WITH E5.7 AND E32 FUELS

The comparative emissions analyses are based on the results of mathematical models and vehicle use predictions, which inherently have underlying assumptions and uncertainties in the methods and results. The data presented here reflects a review of the literature, and future developments may warrant re-evaluation based on new knowledge.

High-end exposure relationships of volatile air toxics and carbon monoxide to community-scale air monitoring stations in Atlanta, Chicago, and Houston (2015)
Evaporative and exhaust mobile source air toxic (MSAT) emissions of total VOCs, carbon monoxide, BTEX, formaldehyde, acetaldehyde, butadiene, MTBE, and ethanol were measured in vehicle-dominated microenvironments (ME) (e.g., garages, during refueling) under worst-case conditions plausibly simulating the >99th percentile of inhalation exposure concentrations. Measurements were performed in Atlanta (baseline gasoline), Chicago (ethanol-oxygenated gasoline), and Houston (methyl tertiary butyl ether-oxygenated gasoline) during winter and summer seasons. With the exception of vehicle refueling operations, the results indicate that evaporative emissions are a minor component of high-end MSAT exposure concentrations.

7.2 Carbon Monoxide, NOx, and PM

The effect of increasing ethanol in fuel blends on other air pollutants such as NOx, CO, and PM are less well understood, however, reductions in CO and PM emissions are anticipated.[146 204] Regardless of whether E11 – E15 blends contribute to significant differences in these air pollutants, according to Unnasch, “while CO and NOx 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, NOx, and ozone may have cancerous impacts, but they have not been assigned OEHHA cancer potential toxicity factors”.[146]

In a study comparing various ethanol blends and diesel fuel, average particle numbers were 6×10^2 #/cm3 (E0), 1×10^5 #/cm3 (E10), 3×10^3 #/cm3 (E85), and 2.8×10^6 #/cm3 (diesel).[199] Compared to E10, particle emissions from E15 use should be less.

7.3 Atmospheric Transformation Products

In general, there are currently limitations for the analysis of transformation products in the atmosphere.[204] However, decreases in air toxics emissions and fuel volatility associated with greater percentages of ethanol-blended fuels should have a positive effect on ozone formation.[206] In a study evaluating the *Change in Air Quality Impacts Associated with the Use of E15 Blends Instead of E10*, indicated that changes in ozone formation potential depends on a number of factors including exhaust emission rates, fuel composition, and the photochemical reactivity of the exhaust components. However, the estimated reduction of ozone potential is 4%.[146]

7.4 Toxicity in Aerated Soil

Ethanol has a short half-life in soil. Aerated soil should theoretically provide enough oxygen for indigenous microorganisms' aerobic biodegradation and terrestrial plants' photosynthesis. Plants utilize oxygen as the terminal electron acceptor in the electron transport chain portion of photosynthesis. In the event of a biofuel and/or ethanol release, the existing oxygen may be consumed faster than it can diffuse into the soil, due to the large increase in carbon source for microorganisms. In response to poor aeration, anaerobic metabolism may commence, yielding potentially toxic acetic acid and other byproducts including methane. Without the necessary oxygen for plant growth, there is a reduction in photosynthesis, as well as natural abatement attempts by the plant such as inhibition of shoot growth, leaf, flower, or fruit abscission, enhanced root exudation. Eventually these conditions will lead to death of the exposed plant(s).

Regarding biofuel blends, the combination of ethanol and hydrocarbons causes the hydrocarbons to mobilize (see Section 6.2), which allows them to infiltrate smaller pore spaces and adsorb to soil particles. The fraction of components that are not retained will progress to the groundwater.[141] Terrestrial system exposure regarding an ethanol release is unlikely, due to the high biodegradability and volatilization. However, more risks are present with the combined effect of hydrocarbons and ethanol (see Section 6). Some reported wildlife effects due to ethanol are reported in Table 25.

TABLE 25. EFFECTS OF ALCOHOL ON WILDLIFE/PLANTS

Organism	Effect
Douglas fir Seedlings (*Pseudotsuga menziesii*)	Applied EtOH concentrations of 10% + lethal within a week, effects observed at 5% and 1% solutions [141]
Japanese Quail (*Coturnix japonica*)	EtOH at 2% in drinking water had effects on blood, brain weight and growth after 7-day exposure[141]
Honey Bees (*Apus spp.*)	Bees fed solutions of EtOH 5% + showed behavioral effects, and mortality at 50% EtOH [141]
Little Brown Bat (*Myotis lucifugus*)	LD_{50} of 3.9 – 4.4 g/kg (*Shaw, 2011*)[141]
Lettuce (*Lactuca sativa*)	Seed germination inhibited by 50% at 390 mg/L 1-butanol [210]
Cucumber (*Cucumis sativus*)	Seed germination inhibited by 50% at 2500 mg/L 1-butanol[210]

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[206] National Renewable Energy Laboratory (NREL), Hammel-Smith, C., Fang, J., Powders, M., & Aabakken, J. (2002). *Issues Associated with the Use of Higher Ethanol Blends (E17-E24)* (NREL/P-510-32206). National Renewable Energy Laboratory. Retrieved October 9, 2018, from https://www.afdc.energy.gov/pdfs/32206.pdf

1-butanol, a comparable chemical to ethanol due to the presence of two additional carbons in its chain, was used as a substitute in a terrestrial ecotoxicity study. This study revealed that common terrestrial plants are not likely to be detrimentally affected by spills and leaks, particularly because they are generally to subsurface soil. The effect of ethanol was also studied in pea plants up to a concentration of 2.1 mol/m^3 and displayed no ill effect to the plant. Even concentrations one hundred times greater showed little to no effect.[207] In terms of a neat ethanol release, there may be effects directly in the spill area, though significant exposure is unlikely.

The toxicity data regarding microorganisms is critical due to its direct relationship to biodegradation of released chemicals, in this case, ethanol. The toxicity of ethanol in relation to biodegradation of biofuel from releases to the environment is addressed in Section 6.5. As discussed, in the event of an ethanol or biofuel release, ethanol will volatilize and degrade rapidly. Regarding biofuel blends, an increase in gasoline percentage could result in an inhibited biodegradation plume after preferential degradation of ethanol. The toxicity of ethanol regarding microbial activity is based upon the chain length and hydrophobicity of the alcohol. Short-chain alcohols such as ethanol (as it only possesses two carbon atoms) are less toxic or inhibitive than the longer-chain alcohols. However, it is well-documented that microbial activity can be inhibited by large concentrations of ethanol. This is particularly true in the presence of petroleum co-contaminants, which are degraded after ethanol due to preferential degradation.

Ethanol microbial toxicity studies that have been conducted reported various toxic results, including multiple toxic concentrations of ethanol, as well as evidence for microbial stimulation or enhancement of certain types of degradation. There are uncertainties associated with the body of evidence collected to date, and further evaluation will help determine scientific consensus on the issue. Some reported toxic concentrations of ethanol and other documented effects are reported in Table 26.

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[207] Jackson, M. B., Herman, B., & Goodenough, A. (1982). An examination of the importance of ethanol in causing injury to flooded plants. *Plant, Cell & Environment*. https://doi.org/10.1111/1365-3040.ep11571590

TABLE 26. EFFECTS OF ETHANOL ON MICROBIAL ACTIVITY

Toxic Concentrations of Ethanol		
Reported Value	**Media**	**Source**
5-20 mg/L	Groundwater	*Adair et. al., 2012*[208]
40 g/L (4% by weight)	--	*UC, 2016*[140]
5% EtOH	Soil	*Araújo, 2000*[209]
Few species showed growth at 100 g/L	Soil	*UC, 2016*[140]
Ethanol as Microbial Activity Enhancer		
Reported Value	**Media**	**Source**
0.5-3% EtOH	Soil	*Araújo, 2000*[209]
1 mg/L EtOH (increased benzene removal)	--	*UC, 2016*[140]

--: media not specified
EtOH: ethanol
mg/L: milligrams per liter
g/L: grams per liter

In reference to the previously mentioned 1-butanol study, in soil and water media, butanol was actually found to *enhance* the biodegradation of gasoline and did so more efficiently than ethanol, as has been reported in certain concentrations.[210]

7.5 Aquatic Ecological Toxicity

Aquatic systems are generally at more risk than terrestrial systems in the event of an ethanol or ethanol blended fuel release. Ethanol is acutely toxic to many organisms present in these types of ecosystems, especially when they are localized at the release location. Effects of ethanol on water quality and different aquatic species have been extensively studied. Sensitive crustaceans can be affected when exposed to 0.5 ppm ethanol for 72 hours, while most crustaceans exposed to ethanol concentrations of 1 part per thousand for 24 hours will result in injury.[135]

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[208] Adair, C., J. Wilson, H. White, R. Howard, & D. Forrer. (2012). *Effect of Ethanol and Ethanol Biodegradation Products on Prospects for Natural Anaerobic Biodegradation of Benzene at Gasoline Spill Sites* [PDF file]. Presented at 23rd National Tanks Conference and Expo, March 19 - 21, 2012. Retrieved from https://cfpub.epa.gov/si/si_public_file_download.cfm?p_download_id=507772&Lab=NRMRL

[209] Araújo, D. (2000). *Effect of Fuel Ethanol on Subsurface Microorganisms and its Influence on Biodegradation of BTEX Compounds*. UWSpace. Available from University of Waterloo, UWspace website, http://hdl.handle.net/10012/1224

[210] DuPont, ButamaxTM Advanced Biofuels, LLC, BP. (2010). *California Biobutanol Multimedia Evaluation Tier I Report*. California Environmental Protection Agency Multimedia Working Group. Retrieved October 9, 2018, from https://www.arb.ca.gov/fuels/multimedia/020910biobutanoltierI.pdf

TABLE 27. ETHANOL TOXICITY CONCENTRATIONS IN VARIOUS AQUATIC SPECIES[140]

Aquatic Ethanol Toxicity		
Test Organism	**Exposure**	**LC_{50} (mg/L)**
Daphnia magna (Water flea)	48 hours	9,248
Ceriodaphnia dubia (Water flea)	48 hours	8,808
Hyalella azteca (Scud)	216 hours	454
Pimephales promelas (Fathead Minnow)	96 hours	14,740

For many fish species present in aquatic ecosystems, a general LC_{50} for ethanol has been identified to range from 9,000 to 11,000 mg/L.[211] For biofuel blends, the amount of ethanol present in a release would be decreased compared to a neat ethanol release, and thus there would be even less exposure of ethanol to the ecosystem. However, gasoline components must also be considered when evaluating toxicity of biofuel releases. Table 28 displays the 48-hour LC50 results and relative toxicity from a bioassay of freshwater Cladocera, an order of small crustaceans, more commonly known as water fleas.

TABLE 28. COMMON GASOLINE HYDROCARBON TOXICITY VALUES[140]

Compound	48-hr LC50 (mg/L)	Relative Toxicity
Alkanes		
Hexane	3.9	2.4
Octane	0.37	1.8
Decane	0.028	1.9
Cycloalkanes		
Cyclohexane	3.8	145
Methyl Cyclohexane	1.5	9.3
Monoaromatics		
Benzene	9.2	195.6
Toluene	11.5	44.8
Ethylbenzene	2.1	72.4
p-xylene	8.5	21.8
m-xylene	9.6	16.9
o-xylene	3.2	54.7
1,2,4-trimethylbenzene	3.6	15.8
1,3,5-trimethylbenzene	6	16.2
Cumene	0.6	83.3
1,2,4,5-tetramethylbenzene	0.47	7.4
Polyaromatics		
1-methylnaphthalene	1.4	20.2
2-methylnaphthalene	1.8	17.8
Biphenyl	3.1	6.8
Phenanthrene	1.2	5.5

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[211] Hollenbone, B. (2009). *Biofuels in the Environment A Review of Behaviors, Fates and Effects & Remediation Techniques*. Presented at Freshwater Spills Symposium. Retrieved on October 9, 2018, from https://archive.epa.gov/emergencies/content/fss/web/pdf/hollebonebiofuels.pdf

Anthracene	3.0	2.0
9-methylanthracene	0.44	2.0
Pyrene	1.8	1.6

Comparing gasoline hydrocarbons and ethanol, ethanol has a low aquatic toxicity. As seen in Table 28, hydrocarbons have a much lower LC_{50} of common gasoline components, including BTEX constituents. When considering biofuel blends at the E15 level, there is less aquatic toxicity due to the ethanol component in blended fuels (in comparison to gasoline hydrocarbons). This low percentage in conjunction with the high LC_{50} concentrations and rapid degradation and/or volatilization properties reveals ethanol will not likely pose a direct toxicity risk. However, in the lower ethanol blends, there is a higher percentage of gasoline hydrocarbons which possess lower LC_{50} values and initially degrade via aerobic degradation, therefore raising toxicity concerns. See Section 6.5 for more information on biodegradation. Despite the direct potential toxicity of ethanol blended fuels to an aquatic environment, there is an even larger concern regarding the dissolved oxygen of an aquatic system.

Dissolved oxygen (DO) is a critical component in determining the toxicity of ethanol in aquatic ecosystems. Typical dissolved oxygen concentrations are variable depending on the time of year, temperature, and even on the day.
Figure 32 shows the general fluctuation of DO values.

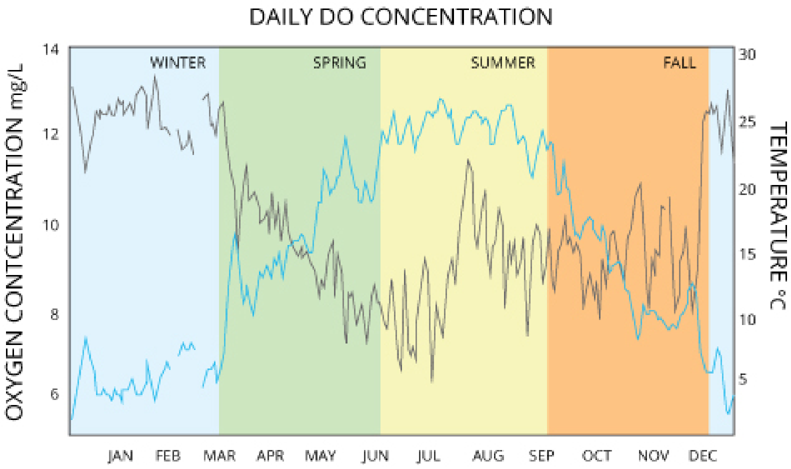

FIGURE 32. DAILY DO CONCENTRATION AND TEMPERATURE BY SEASON[212]

As mentioned in the biodegradation section, aerobic biodegradation is the initial pathway of degrading both hydrocarbons and ethanol. Because of this, oxygen can be depleted rapidly, especially in the proximity of a fresh release. The depletion of oxygen in an aquatic system can have a much greater detrimental impact on the aquatic system than the toxicity of ethanol. Biodegradation also generates methane, often in high levels, which is an explosion risk. Once aerobic biodegradation has depleted the DO in result of a fresh release, conditions become anaerobic and methanogenesis occurs. Existing methanotrophs will work to break down the methane produced, but will do so by utilizing oxygen, exacerbating the issue of available oxygen.

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[212] Fondriest Environmental. (2013). *Fundamentals of Environmental Measures, Dissolved Oxygen* Retrieved October 15, 2018, from https://www.fondriest.com/environmental-measurements/parameters/water-quality/dissolved-oxygen/#8

Oxygen depletion results in hypoxic, and possibly anoxic conditions, which causes dead zones and fish kills, possible release of other toxic substances normally targeted by affected microbial and chemical processes, inhibited degradation of co-solvent constituents, and losses in biodiversity, ecosystem function, and ecosystem services. Fish kills as a result of depleted DO content of an aquatic system may persist up to 30-40 miles downstream in flowing streams.[135] Oxygen depletion can vary depending on the type of aquatic system, as shown in
Table 29.

TABLE 29. INSTREAM ETHANOL CONCENTRATIONS REQUIRED TO DEPLETE DISSOLVED OXYGEN ACCORDING TO STREETER-PHELPS MODEL (NEIWPCC, 2001)[213]

Ethanol Concentrations to Deplete Stream Dissolved Oxygen	
Small Stream	56 mg/L
Average River	32 mg/L
Large River	13 mg/L

These concentrations are based on the Streeter-Phelps Model, which incorporates a number of associated assumptions, including estimating the initial DO concentration at 7 mg/L. Based on this model, a large river is more susceptible to oxygen depletion than both an average size river and small stream, as it possesses the lowest ethanol concentration (13 mg/L) of the three modeled systems. This is due to the re-aeration rate of a large body of water being much larger than the rate of a small body of water. However, a large water body would be less impacted by the release due to the sheer volume of water and dilution factor of a larger system in comparison to a smaller one.

Another concern is bioconcentration or bioaccumulation in indigenous species and their tissues. Ethanol was determined to be unlikely to accumulate in tissues due to the rapid rate of metabolism and its octanol/water partition coefficient, which indicates its fatty tissue affinity.[141] See Section 6.3 for more information on partitioning.

7.6 Exposures

Table 30 provides a summary of the potential differences between exposures to releases as a result of E15 use compared to E10. Based on the similarities between E15 and E10, the use of blends up to E15 are not expected to be a greater hazard to human health and the environment than E10.

7.7 Summary of Findings

As with E10, E15 would have the potential to be released into the environment affecting land, groundwater, surface water, and from there into drinking water supplies, and allowing receptors to be exposed via ingestion, dermal exposure and inhalation. Such releases have the potential to impact drinking water supplies such as surface water and groundwater. E15 provides potential for inhalation exposures to exhaust and evaporative emissions, and to soil vapors entering indoor air. Other human and ecological risks associated with E15 blends would not be significantly different than those present from the widespread use of E10.

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[213] New England Interstate Water Pollution Control Commission (NEIWPCC). (2001). *Health, Environmental, and Economic Impacts of Adding Ethanol to Gasoline in the Northeast States, Volume 3. Water Resources and Associated Health Impacts*. New England Interstate Water Pollution Control Commission. Retrieved October 9, 2018, from https://www.nescaum.org/documents/health-environmental-and-economic-impacts-of-adding-ethanol-to-gasoline-in-the-northeast-states/ethanol3.pdf/

TABLE 30. POTENTIAL DIFFERENCES BETWEEN EXPOSURES TO RELEASES AS A RESULT OF E15 USE COMPARED TO E10

Exposed Population	Exposure Scenario	Exposure Route	Exposure Pathway	Exposure Media	Chronic/Acute	Potential Differences Between Baseline Fuel [E10] and E15[1]
Residential/ Public	E15 released to groundwater or surface water	Ingestion (Oral)	Impacted drinking water source (groundwater or surface water)	E15 fuel dissolved in water	Most likely short-term (Acute) based on regulatory environment, potential acute exposures, (e.g., in the event of a surface water drinking water supply intake is affected by catastrophic release)	Risks to drinking water sources would be similar for E15 compared to E10, except for the possibility of plume configuration changes (longer benzene plumes),
Residential/ Public	Direct Contact with Fuel, during vehicle refueling	Dermal Contact	Direct contact with fuels due to incidental spills on skin (hands) during refueling	Direct contact with fuel	Acute	Differences are not expected to be significant between E10 and E15, (USDOE, 2016)[134]
Residential/ Public	Inhalation of vapor emissions (evaporative emissions) during refueling and use	Inhalation	Inhalation of vapor emissions to ambient air for a short duration	Ambient Air	Acute	No differences between E10 and E85, therefore no difference between E10 and E15 expected for concentrations typical of residential exposures[2,3]
Residential/ Public	Inhalation of the vapors as a result of volatilization from high concentration soil and groundwater sources (i.e., vapor intrusion)	Inhalation	Soil/groundwater volatilization to Soil Vapor and migration to Indoor Air	Indoor Air	Chronic (VOCs)/Acute (methane)	Longer benzene plumes may require review and update of LNAPL exclusion distances for vapor intrusion as E15 soil and groundwater impacts are studied, also increased monitoring for methane if E15 is spilled, (ITRC, 2014)[148] See Section 6.5.3.
Residential/ Public	Catastrophic release of blended fuel or fuel feed stocks from infrastructure	Inhalation	Inhalation of the vapors as a result of a release to surface (soil) or surface water body	Ambient Air	Acute	No differences between E10 and E85, therefore no difference between E10 and E15 expected
Residential/ Public	Vehicle Exhaust Emissions	Inhalation	Inhalation of Ambient Air in areas	Ambient Air	Chronic	Differences between E10 and E15 expected to be small, overall risk due

Exposed Population	Exposure Scenario	Exposure Route	Exposure Pathway	Exposure Media	Chronic/Acute	Potential Differences Between Baseline Fuel [E10] and E15[1]
			of concentrated vehicle use (e.g., urban environments with concentrated vehicle use)			to emissions is expected to be less considering potency weighting[4,5,6]
Industrial/ Workers	Dermal Contact with fuel during occupational exposures, (including release scenarios as described in Tables 2.1 and 2.2)	Dermal Contact	Direct contact with fuels	fuel	Acute	Differences are not expected to be significant between E10 and E15, (USDOE, 2016)[134]
Industrial/ Workers	Vapor Emissions from fuel and fuel component production, storage, distribution and use	Inhalation	Inhalation of ambient air in high-concentration environments	Ambient Air	Acute and chronic	Differences between E10 and E15 not expected to be significant[2,3]
Ecological Receptors	Catastrophic release of blended fuel or fuel feed stocks from infrastructure to surface water bodies	NA	NA	Surface Water	Acute	While unique considerations relative to ethanol releases to surface water bodies exist for ecological receptors (See Section 6.5), risks due to E15 use vs. E10 are not materially different

1: E15 (E11-E15)
2: Bushnell et. al., 2015[192]
3: Oshiro et. al., 2015[193]
4: OEHHA, 2018[204]
5: UIC, 2016[205]
6: Unnasch, 2014[146]

8 Estimated Changes in GHG Emissions and Upstream Emissions of Air Pollutants from Expanded Use of Ethanol in California

8.1 Introduction

This section addresses the potential changes in “upstream emissions” that would occur in the state of California with expanded ethanol use that would result from approval of higher-level blends such as E15. These changes would result from the import of greater amounts of ethanol and from decreased use and potentially reduced production of gasoline. Upstream activities associated with ethanol that generate emissions include feedstock farming, feedstock transport, ethanol production, and ethanol transport. For gasoline, upstream activities that generate emissions include recovery, transport, and storage of crude oil, as well as refining and the storage, transport and distribution of gasoline. It should be noted that the analysis presented in this section focuses only on upstream emissions that occur in California which are smaller than the total upstream emissions for both ethanol and gasoline.

The latest version of the California GREET model (CaGREET3.0) was used in the analysis to estimate changes in upstream emissions of the air pollutants VOC, CO, NOx, PM2.5, SOx as well as greenhouse gases associated with increased ethanol use. The California GREET model was developed by ARB in support of the California Low Carbon Fuel Standard (LCFS) and is based on the Argonne GREET2016.[214] The model outputs emissions for a fuel in units of grams of pollutant or CO2 equivalent GHG per mega joule of fuel energy (g/MJ) associated with the upstream activities related to the production and delivery of the fuel for use in vehicles.

For purposes of this analysis, upstream emissions impacts associated with a complete transition from E10 to E15 for those vehicles approved for E15 use under the U.S. EPA waiver were estimated.

This section is organized into the following subsections:

- Potential impacts of expanded ethanol use on volumes of ethanol and gasoline used in California;
- Impacts of reduced use of gasoline on upstream emissions of air pollutants;
- Impacts of increased use of ethanol on upstream emissions of air pollutants; and
- Impacts of increased use of ethanol on total and California specific GHG emissions.

Details regarding the methodology and calculations used to generate the results presented here can be found in Appendix 3.

8.2 Changes in Ethanol and Gasoline Volumes with Expanded Use of Ethanol

This section examines the changes in ethanol and gasoline fuel consumption in the state if use of ethanol is expanded. Expanded ethanol will in turn decrease demand for gasoline blend stocks (CARBOB); however, the volume reduction in gasoline blend stock use will be somewhat lower on a volumetric basis than the increase in ethanol due to the energy density differences between the fuels.

EPA’s waiver for E15 applies to 2001 and later model-year light-duty automobiles (LDA) light-duty trucks (LDT1 and LDT2), and medium-duty passenger vehicles (MDV) given that the waiver does not apply for light heavy duty trucks, heavy duty gasoline vehicles, motorcycles, or off-road sources.[215] In light of the above, CARB’s EMFAC2017 model was used to estimate daily and annual fuel consumption rates for

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[214] https://www.arb.ca.gov/fuels/lcfs/ca-greet/ca-greet.htm

[215] https://www.epa.gov/gasoline-standards/e15-fuel-partial-waivers

E10 for calendar year 2018.[216] The results are shown in Table 31. As shown, California is expected to consume about 13.1 billion gallons of E10 in 2018 for the vehicle types listed below.

TABLE 31. ESTIMATED E10 CONSUMPTION VEHICLES APPROVED TO USE E15 IN CALENDAR YEAR 2018 BASED ON EMFAC2017

Vehicle Type	Fuel Volume (1000s of gallons per day)	Fuel Volume (billion gallons per year)
LDA	18,643	6.8
LDT1	1,892	0.7
LDT2	8,064	2.9
MDV	7,315	2.7
Total	35,912	13.1

To estimate the ethanol volume that would have been used in calendar year 2018 by vehicles approved for E15 use had that been possible, the total fuel volume in Table 31 was first multiplied by 10%. This puts the ethanol volume at E10 at 1.3 billion gallons per year. Multiplying this value by 1.5 yields the ethanol volume at E15 of 1.95 billion gallons per year - an increase of 0.65 billion gallons per year relative to E10. Since the energy density of ethanol is approximately a third less than that of gasoline, the reduction in gasoline consumption would be about a third less than the increase in ethanol volumes, or about 0.44 billion gallons per year.[217] The estimated fuel consumption for both E10 and E15 for E15 approved vehicles is shown in Table 32. As shown, with E15, total fuel volume increased by 0.21 billion gallons per year (or 1.5%) from E10 to E15, due to the lower energy density of ethanol.

TABLE 32. ESTIMATED ETHANOL AND GASOLINE VOLUMES AT E10 AND E15 FOR E15 APPROVED VEHICLES IN 2018 (BILLIONS OF GALLONS PER YEAR)

Fuel	E10	E15	Change
Gasoline Blendstock	11.8	11.36	-0.443
Ethanol	1.3	1.95	+0.65
Total	13.1	13.31	+0.21

This estimated shift in gasoline and ethanol volumes in the state will, in turn, impact upstream emissions associated with the production of both fuels. A reduction in gasoline consumption by vehicles approved to use E15 would result in lower gasoline upstream emissions if the state's many refineries chose to operate at lower crude input levels and cut production. However, it is possible that instead of cutting production, refiners instead opt to leave refinery operations at current levels and export the excess gasoline. This analysis examines the upstream impacts of both possibilities.

The increase in ethanol volume would result in more ethanol imported from out-of-state, affecting some components of upstream ethanol emissions in California, such as ethanol transportation. Overall, given that total fuel volume is estimated to increase by 1.8%, upstream fuel distribution emissions resulting from moving fuel via truck from blending terminals to service stations will increase proportionally by 1.8%.

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[216] https://www.arb.ca.gov/msei/msei.htm

[217] CaGREET3.0 indicates that denatured ethanol has an energy density of 81.51 MJ/gal, and CARBOB has an energy density of 119.53 btu/gal, thus, the energy density of ethanol is 2/3 that of CARBOB (0.682). This analysis conservatively assumes that this energy density difference should be taken into account in estimating fuel volumes, but this energy density adjustment is not a foregone conclusion in real world operation. If E15 is made by splash-blending additional ethanol into E10, then octane will increase from today's levels, because ethanol has very high-octane levels. Modern vehicles may be able to take advantage of this improved octane, and run more efficiently, thereby compensating for the loss of energy density.

8.3 Impacts on Upstream Air Pollutant Emissions Associated with Reduced Gasoline Use

The California GREET3.0 models upstream emissions associated with gasoline blend stock (e.g. CARBOB) production and distribution of gasoline blend stocks and finished gasoline (e.g. E10 or E15) from the following processes:

1. Crude oil recovery;
2. Transportation of crude oil to California refineries;
3. Crude oil storage;
4. Gasoline Blend stock Refining;
5. Gasoline Blend stock Transportation;
6. Gasoline Blend stock Distribution;
7. Gasoline Distribution; and
8. Gasoline Storage.

The first four processes deal with gasoline production from crude oil. Processes five and six address blend stock transportation and the last two distribution of finished gasoline (e.g. E10 or E15).

Approximately a third of all crude oil used for gasoline production in the state is recovered in California, while the rest is imported from outside the state by pipeline and by ship.[218] California has 16 refineries producing California gasoline; 8 of these refineries are in the Los Angeles area, and 8 are in the San Francisco Bay Area and North Central California.[219] After producing gasoline and other products (e.g., diesel fuel, jet fuel), these refineries transport gasoline to blending terminals mainly by pipeline but also by truck, where the blend stocks are mixed with ethanol and then transported via truck to service stations. Some gasoline is exported outside of California (to Arizona and some to South America).

As discussed above, two possible responses to increased ethanol in gasoline may be no change in refinery operations or a reduction in refinery operations directly proportional to the gasoline displaced by ethanol moving from E10 to E15. Under the first response, there will be little or no change in upstream emissions. However, if reduce refinery operations, upstream emissions will be reduced. In addition, diesel and jet fuel upstream emissions could also decline as well, although it is difficult to predict by how much,[220] therefore, this analysis will only examine the reduction in gasoline upstream emissions.

As noted above, if all vehicles approved to use E15 did so in 2018, gasoline blend stock consumption in the state would decline by 0.443 billion gallons per year. Using criteria pollutant emission rates from CaGREET3.0 for upstream gasoline blend stock and finished gasoline processes upstream air pollutant emissions impacts occurring in California were estimated for full E15 use in vehicles for which it is approved as well as on a per gallon basis for each gallon of ethanol substituted for gasoline blend stock. These results are shown in Table 33.

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[218] https://www.wspa.org/resources/california-fuel-facts/

[219] *West Coast Transportation Fuels Markets*, U.S. Energy Information Agency, September, 2015.

[220] Energy Information Agency information indicates that out of a barrel of crude oil, the yield is about 20 gallons of gasoline, 12 gallons of distillate of which the majority is sold as diesel fuel, 4 gal of jet fuel, and the remainder other products https://www.eia.gov/energyexplained/index.php?page=oil_refining . Refiners have many options to either change the crude inputs or change the output mix, or both.

TABLE 33. REDUCTIONS IN UPSTREAM EMISSIONS IN CALIFORNIA ASSOCIATED WITH REDUCED GASOLINE USE MOVING FROM E10 TO E15

Pollutant	Emission Reduction (tons per year)	Emission Reduction (grams / gal of increased ethanol use)
VOC	1,414	1.97
CO	813	1.14
NOx	1,306	1.82
PM2.5	59	0.08
SOx	1,225	1.71

8.4 Impacts on Upstream Air Pollutant Emissions Associated with Increased Ethanol Use

As noted above, the California GREET3.0 models upstream emissions associated with ethanol production and distribution from the following processes:

1. Feedstock farming;
2. Feedstock transportation;
3. Ethanol plant;
4. Ethanol transportation;
5. Ethanol distribution; and
6. Land use.

However, unlike most of the processes associated with gasoline blend stock and production and distribution of finished gasoline, not all of the ethanol related processes result in upstream emissions that occur in California. Feedstock farming, for example, takes place outside of California, even for feedstock delivered to California ethanol plants. These plants generally use corn that is transported from out-of-state. Indirect land use change emissions also take place outside of California. All of the other upstream emission processes take place in California for the California ethanol plants. For ethanol sourced outside of California, only ethanol transport emissions to blending terminals, and from blending terminals to service stations, take place within California.

Ethanol is transported from the Midwest to California in unit trains that deliver ethanol to the blending terminals. As explained earlier, ethanol is then blended with gasoline at the terminals and transported to service stations in heavy-duty tanker trucks. Some ethanol is also imported from Brazil. This ethanol travels from Brazil to the Caribbean, where it is denatured with a small amount of gasoline and transported further to California ports.

California has five ethanol plants with nameplate ethanol capacity of 200 million gallons. Since the amount of ethanol used in the state far exceeds the capacity at these plants, additional ethanol must come from outside the state, and the emissions from the California ethanol plants will not change. This analysis assumes that the additional 0.650 billion gallons per year of ethanol resulting from E15 is sourced from the Midwest. This ethanol would arrive at blending terminals in northern and southern California via unit train. Rail transport of ethanol is one source of additional emissions of E15 in California. And, as noted above, total fuel volume in California was estimated to increase by 0.210 billion gallons per year. Thus, a second source of emissions is the transport of the additional finished fuel volume from blending terminals to service stations in the state. The total upstream emissions impact is the sum of these two sources.

The increase in upstream emissions of air pollutants associated with use of E15 in all vehicles for which it has been approved are shown in Table 34. Emission increases range from 4.4 tons per day for PM2.5 to 166 tons per day for NOx all of which are very small compared to total statewide emissions of these pollutants.

TABLE 34. INCREASE IN UPSTREAM EMISSIONS IN CALIFORNIA ASSOCIATED WITH INCREASED ETHANOL USE MOVING FROM E10 TO E15

Pollutant	Emission Increase (tons per year)	Emission Increase (grams per gallon ethanol increase)
VOC	9.08	0.013
CO	28.4	0.040
NOx	165.5	0.231
PM2.5	4.41	0.006
SOx	4.78	0.007

Overall, if refinery operations stay constant, the values in Table 34 represent the increases in upstream emissions that would occur in California from increased ethanol use. However, if refinery operations decrease due to decreased demand for gasoline in proportion to the increased use of ethanol resulting from use of E15 in all vehicles for which it is approved, the overall impact will be a net decrease in emissions of air pollutants in California as shown in Table 35. As shown, the reductions in emissions associated with reduced gasoline production are much greater than the increase in emissions associated with E15 use. Given this, even a very small reduction in refinery operations is likely to provide a reduction in upstream emissions of air pollutants in California. Also shown in Table 35 is the overall impact per gallon of increased use of ethanol in California.

TABLE 35. UPSTREAM EMISSIONS IN CALIFORNIA ASSOCIATED WITH INCREASED ETHANOL REDUCED USE MOVING FROM E10 TO E15 IF REFINERY OPERATIONS ARE REDUCED

Pollutant	Decrease due to Reduced Gasoline Use (tons per year)	Increase Due to Increased Ethanol Use (tons per year)	Overall Impact (tons per year)	Overall Impact (grams per gallon ethanol increase)
VOC	-1,414	+9.08	-1,405	-1.963
CO	-813	+28.4	-785	-1.096
NOx	-1,306	+165.5	-1,141	-1.593
PM2.5	-59	+4.41	-55	-0.076
SOx	-1,225	+4.78	-1,220	-1.705

Impacts of Increased Ethanol Use on Overall and California Specific GHG Emissions

The current carbon intensity value of gasoline blend stocks under the California Low Carbon Fuel Standard (LCFS) is 100.82 gCO2e/MJ.[221] Based on second quarter LCFS data reported by CARB the current CI of corn ethanol is 70 gCO2e/MJ. The overall impact of expanded ethanol use on GHG emission as characterized by the example of using E15 in all vehicles for which it has been approved can be calculated as follows:

$$\text{GHG reduction} = \text{Volume} \times (\text{CI}_{\text{Gasoline}} - \text{CI}_{\text{ethanol}}) \times \text{Energy Density}_{\text{ethanol}} / 1{,}000{,}000$$

Where:

GHG reduction is in metric tons per year

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[221] LCFS 2018 Final Regulation Order, https://www.arb.ca.gov/regact/2018/lcfs18/fro.pdf

Volume = increased volume of ethanol 0.65 billion gallons per year in gallons
$CI_{gasoline}$ = carbon intensity of CARBOB in g/MJ
$CI_{ethanol}$ = carbon intensity of ethanol in g/MJ
Energy $density_{ethanol}$ = 81.51 MJ/gallon
1,000,000 = conversion factor from grams to metric tons

This calculation indicates that expanded ethanol associated with use of E15 in all vehicles capable of using it would result in an overall reduction in GHG emissions of 1.6 million metric tons per year. Alternatively, for each additional gallon of ethanol used in California, GHG emissions would be reduced by 2.5 kilograms.

However, the above calculation fails to account for GHG emissions associated with need to distribute the additional 0.210 billion gallons of fuel per year under this scenario. The equation for estimating additional GHG from fuel deliveries is:

$$\text{GHG increase} = \text{Volume} \times EF_{trans} \times ED_{E15} / 1{,}000{,}000$$

Where:

GHG = increase in GHG emissions in tons per year
Volume = increased volume fuel delivered per year in gallons
ED_{E15} = energy density of E15 in MJ/gal (113.827 MJ/gal)
EF_{trans} = CaGREET3.0 emission factor fuel transportation in g/MJ (0.199 g/MJ)
1,000,000 = conversion factor from grams to metric tons

Based on the above expression, the GHG emissions associated with increased fuel distribution are 0.005 million metric tons per year or 0.01 kilograms per additional gallon.

The net overall reduction in GHG emissions from expanded use of ethanol where E15 is used in all vehicles for which it is approved is presented in Table 36.

TABLE 36. NET OVERALL REDUCTION IN GHG EMISSIONS FROM EXPANDED ETHANOL USE IN CALIFORNIA

	Emission reduction (metric tons per year)	Emission reduction (kg/gallon of increased ethanol use)
Increased Ethanol Use	1,632,890	2.55
Increased Fuel Transport	-4,756	-0.01
Net Reduction	1,628,134	2.54

Putting the 1.6 million metric ton net reduction in perspective, in 2018, lifecycle emissions from on-road gasoline vehicles were about 171 million metric tons for the year in California. The 1.63 million metric ton reduction due to E15 is therefore a reduction of about 1% of lifecycle greenhouse gases.[222]

Although GHG emissions are important on a global scale, an analysis of the impacts of increased ethanol use on GHG emissions occurring in California was also performed by adjusting the life-cycle CI values from the CaGREET3.0 model for both gasoline and ethanol to only account for in-state emissions.

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[222] EMFAC2017 was used to estimate fuel consumption of 43.4 million gallons per day in California. Using an E10 energy density per gallon of 115.7 MJ/gal and the 2018 LCFS carbon intensity of 95.33 g/MJ, the result is 171 million metric tons per year for total lifecycle GHG emissions from on-road fuel consumption in 2018.

The major change to the CI value of 100.82 gCO2e/MJ for gasoline blendstock is the use of California crude only CI value for the "crude recovery and transport" emissions component resulting in an overall California-specific blendstock CI of 105.65 gCO2e/MJ. For ethanol, all emissions other than ethanol transportation to blending terminals occur outside of California and the resulting CI value for ethanol is 2.28 gCO2e/MJ. The "California-only" difference in lifecycle emissions between gasoline blendstock and ethanol is therefore 105.65 minus 2.28, or 103.37 gCo2e/MJ. Repeating the above calculations and again accounting for increased fuel transportation yields the California specific impacts on GHG reductions shown in TABLE 37. As shown, the reduction in California-specific GHG reductions are much larger than the overall GHG reductions owing to the fact that most GHG emissions associated with ethanol occur outside of California.

TABLE 37. CALIFORNIA-SPECIFIC REDUCTION IN GHG EMISSIONS FROM EXPANDED ETHANOL USE IN CALIFORNIA

	Emission reduction (metric tons per year)	Emission reduction (kg/gallon of increased ethanol use)
Increased Ethanol Use	5,470,182	8.416
Increased Fuel Transport	-4,756	-0.023
Net Reduction	5,465,426	8.408

8.5 Summary of Findings

The use of gasoline-ethanol blends of up to E15 in all vehicles for which U.S. EPA has approved its use would at worst result in very small increases in upstream emissions of air pollutants relative to the current widespread use of E10. However, overall, reductions in emissions would be reduced in response to reduced refinery operations resulting from lower demand for CARBOB. In addition, both overall GHG emissions and GHG emissions occurring in California would be reduced relative to use of E10.

9 Summary of Tier 1 Findings

As documented above and by California's current approval of E10, ethanol gasoline blends are well-known and have been extensively studied fuels. This multimedia evaluation has assessed the potential for significant new environmental or public health impacts from the expanded use of ethanol in California for blends of up E15. The findings of the evaluation demonstrate approval of blends up to E15 will yield environmental benefits and decrease public health risks relative to a continuation of the current E10 limit. More specifically, the evaluation shows:

- Ethanol can be produced from a variety of feedstocks using well-established commercial procedures. Although additional capacity for the production of ethanol may be needed to supply the additional ethanol required for E15 in California, that capacity is expected to use the same processes that have already been approved by California and that are already being used to supply the existing California market. Thus, to the extent any currently-approved processes are used, such processes would not create environmental or health impacts that are not already known. Increased use of ethanol in the fuel pool would have the added benefit of reducing demand for petroleum-derived CARBOB. Ethanol production is highly regulated on the Federal and State levels. The Federal Renewable Fuel Standard provides environmental safeguards by defining renewable biomass as planted crops and crop residue harvested from existing agricultural land cleared or cultivated prior to December 19, 2007 and that was non-forested and either actively managed or fallow on December 19.

- E11 – E15 gasoline-ethanol blends must be stored, transferred and dispensed from equipment appropriate for these fuels. However, that equipment is currently readily available in California. Listing by Underwriters Laboratories (UL), which tests for compatibility, is available for all the different kinds of fuel-handling equipment necessary for storage, dispensing and transport of fuels except for certain California-specific vapor recovery equipment. A process can be developed with respect to the approval of such equipment to assure E15 is stored and distributed in a safe and compliant manner.

- Testing of California specific vapor recovery equipment with E11 – E15 fuels may be necessary to ensure an adequate range of approved equipment for higher ethanol blends.

- Current California regulations restrict the availability of E11-E15 blending at retail sites using blender pumps because of concerns about the resulting ethanol-fuel blends meeting California quality requirements, in particular if the E85 blendstock contains natural gasoline rather than CARBOB. Currently there are no fuel quality standards for E11-E15 blends made by using E85 and E10 blendstocks and blended at retail sites with blender pumps. This Tier 1 report therefore contemplates E11-E15 blending only using currently-approved processes at terminal sites with CARBOB blendstock. Additional regulatory changes may be needed to accommodate E11-E15 blending other than at terminal sites.

- The existing California UST database shows that a significant percentage of tanks are already compatible for use with E11-E15 fuel-ethanol blends, and the vast majority of tanks built, UL-certified, and installed in 1989 or later in California are compatible with E11-E15 storage. Facilities with older equipment that is not UL listed for higher concentration ethanol fuels will need to upgrade to handle E11 – E15 fuels.

- Fire safety requirements for fuel-handling equipment that would be applicable to gasoline-ethanol blends in the E11 – E15 range are already included in the 2016 California Fire Codes for alcohol-blended fuels. Alcohol-resistant aqueous film-forming foam (AR-AFFF) is recognized as the most effective method for controlling ethanol-blended fuel fires, whether the fuel is E10 or in the E11 – E15 range.

- The existing emissions data suggest that use of gasoline blends up to E15, as allowed by U.S. EPA in existing 2001 and later model-year vehicles and FFVs, will not result in any increase in vehicle exhaust emissions of organic compounds or their ozone-forming potential, oxides of nitrogen, carbon monoxide, particulate matter, or potency-weighted toxic air contaminants relative to E10. However, as the testing did not compare E15 results to California Phase 3 RFG E10 fuels additional exhaust emissions testing will be needed to ensure that splash blending of additional ethanol (up to E15) in fuels permitted in California will not adversely affect air quality. The Tier II test plan will be designed to evaluate the exhaust emissions impacts and determine emissions equivalence with a high level of statistical significance.

  E15 is expected to have a slightly lower vapor pressure than E10 and the research strongly support that evaporative emissions will not increase with the use of E15 compared to E10.

- The use of gasoline-ethanol blends in the E11 – E15 range would not result in any release scenarios or human or environmental impacts different from those that already occur with existing fuels.

  The increased use of ethanol in fuel will likely lead to a proportional increase in the quantity of ethanol released to the environment, with a roughly equivalent decline in the amount of petroleum released. Ethanol is readily biodegraded. Thus, the most significant pollutants in surface and subsurface releases of gasoline-ethanol blends are benzene, toluene, ethylbenzene, and xylene (BTEX) all of which are from the petroleum fraction. Although higher concentration ethanol blends will lead to smaller amounts of BTEX released, ethanol will increase the solubility of these compounds in water, and via ethanol competition for electron acceptors, reduce the rate of biodegradation of BTEX.

Modeling efforts by Gomez and Alvarez (2009) to evaluate the effect of ethanol content in different blended fuel releases on the lifespan and maximum length of benzene plumes suggest that ethanol has a significant elongation effect on benzene plume lengths relative to a baseline regular gasoline spill. The elongation effect is most pronounced for E10–E20 blends. However, the modeled difference in benzene plume elongation relative to baseline between E10 and E20 (and thus E10 and E15) appears to be a fraction of a percent. The benzene plume life span (time until plume is degraded below MCL) decreases almost linearly as ethanol content in the blend increases. Therefore, the natural attenuation time for an E15 release is expected to be less than a similar volume release of E10.

- Due to the increased microbial activity associated with ethanol releases and degradation, there is the potential for higher concentrations of ethanol to generate significant quantities of methane. Should methane ebullition and flux be significant enough to create advective flow, explosion risks to subsurface receptors may be an issue. Additional monitoring of the methane in soil or groundwater can be addressed with existing procedures and tools.
- As with E10, E15 would have the potential to be released into the environment affecting land, groundwater, surface water, and from there into drinking water supplies, and allowing receptors to be exposed via ingestion, dermal exposure and inhalation. Such releases have the potential to impact drinking water supplies such as surface water and groundwater. E15 provides potential for inhalation exposures to exhaust and evaporative emissions, and to soil vapors entering indoor air. Other human and ecological risks associated with E15 blends would not be significantly different than those present from the widespread use of E10.
- The use of gasoline-ethanol blends of up to E15 in all vehicles for which U.S. EPA has approved its use would at worst result in very small increases in upstream emissions of air pollutants relative to the current widespread use of E10. However, overall, reductions in emissions would be reduced in response to reduced refinery operations resulting from lower demand for CARBOB. In addition, both overall GHG emissions and GHG emissions occurring in California would be reduced relative to use of E10.

In summary, the potential for significant new environmental and public health impacts associated with gasoline-ethanol blends up to E15 has been generally well-examined and clearly documented. The evidence suggests environmental benefits and decreased risks associated with E15 relative to E10. Section 10 identifies the knowledge gaps that currently exist with respect to the potential impacts of increasing the ethanol content of California gasoline from 10 percent to 15 percent.

10 Identification of Knowledge Gaps

This section identifies the knowledge gaps found in Tier I of this multimedia evaluation.

As documented in the previous sections of this report, much general information exists regarding the potential use of higher ethanol blends in gasoline. Therefore, the knowledge gaps are primarily specific to the scope of this multimedia evaluation and its applicability to California, California gasoline, and California vehicles. No changes can be made to California’s motor vehicle fuel regulations with respect to increasing the allowable ethanol content without first identifying and, if possible, quantifying the environmental and health impacts of the changes.

Knowledge gaps exists within the available literature and studies to compare motor vehicle exhaust and evaporative emissions for E15 using California Reformulated Gasoline. Further technical evaluation and Tier II testing is essential to support the proposed regulatory changes.

Appendix 1: Regulatory and Legislative Standards, Approvals and Incentives for Biofuel Use

1 Overview of Regulations and Standards

In the United States, fuels are regulated at both the Federal and State level. Additionally, commercial standards play a key role as much of the fuel supply and distribution networks are composed of common-carrier assets utilizing commingled storage.

At the Federal level, U.S. EPA regulates fuels and fuel additives to control air emissions and assure compatibility with emission control aspects of motor vehicles. EPA also administers the RFS which seeks to improve U.S. energy independence and security and reduce GHG emissions through displacement of petroleum-derived gasoline and diesel with renewable fuels. The Federal Trade Commission regulates dispenser labeling as a means to provide consistent information on fuel products to consumers. The Department of Treasury issues regulations to assure the payment of fuel excise taxes and to assure that ethanol designated for fuel use is not inappropriately diverted into more highly-taxed beverage use. The Department of Transportation regulates transport of fuels by pipeline, marine vessel, railcar and road tanker to assure safety and avoid the environmental and health consequences of accidental spillage.

Most states in the U.S. set fuel specifications and pump labeling standards within, and in addition to, Federal requirements. These state specifications are generally managed by the states' Weights and Measures Department with a goal of protecting consumers. Under the Federal Clean Air Act, California has special authority to regulate transportation fuels to protect air quality. With respect to gasoline, the California Air Resources Board (CARB) regulates criteria pollutant emissions though the Reformulated Gasoline Program (CaRFG or CARB Gasoline) currently in Phase 3. California also seeks to regulate GHG emissions associated with the consumption of gasoline, diesel and certain other fuels through the Low Carbon Fuel Standard (LCFS).

Many jurisdictions have regulations aimed to increase the renewable content of transportation fuels. For gasoline supplied into California, both the Federal Renewable Fuel Standard and the California Low Carbon Fuel Standard are applicable. While both programs encompass a wide range of options for renewable fuels (and other low carbon fuels in California) used to substitute for petroleum-derived gasoline and diesel, the use of ethanol in gasoline is the most widely utilized compliance option. This is a result of ethanol's wide availability, low cost, high octane and other favorable fuel properties.

Commercially, consensus standards for fuels are developed and maintained by ASTM. ASTM, a voluntary consensus standards organization works through a membership drawn from fuel producers, automakers, Federal and State regulators and other interested parties. Standard specifications relevant to the gasoline-ethanol blends to be covered by this Multimedia Evaluation are listed below.

TABLE 38. STANDARD SPECIFICATIONS RELEVANT TO GASOLINE-ETHANOL BLENDS

ASTM Standard	Title	Scope
D4814	Standard Specification for Automotive Spark-Ignition Engine Fuel	Finished gasoline blends (E0 to E15)
D4806	Standard Specification for Denatured Fuel Ethanol for Blending with Gasoline for Use as Automotive Spark-Ignition Engine Fuel	Denatured Fuel Ethanol (DFE) for use in gasoline blends
D5798	Standard Specification for Ethanol Fuel Blends for Flexible Fuel Automotive Spark-Ignition Engines	E85 (blends with 51 to 85 percent by volume of DFE)
D7794	Standard Practice for Blending Mid-Level Ethanol Fuel Blends for Flexible-Fuel Vehicles with Automotive Spark-Ignition Engines	Preparation Gasoline-Ethanol blends with 16 to 50 percent by volume of ethanol

D8076	Standard Specification for 100 Research Octane Number Test Fuel for Automotive Spark-Ignition Engines	Potential basis for future E30 blends for high-compression engines designed to deliver high fuel economy/low GHG emissions

ASTM also develops and maintains a suite of Standard Test Methods designated for use in the determination of the specified properties of these fuels. Most Federal and state fuel regulations adopt specifications, practices and test methods developed by ASTM. The use of ASTM standards by commercial entities facilitates commerce by standardizing the qualities of products traded in the market. Pipeline companies also set specifications for commodities accepted for shipment and storage; these specifications are based on ASTM, relevant federal and state regulations and, often, are slightly more stringent to assure the ultimate delivery of compliant product to retail customers.

2 Approvals for Gasoline-Ethanol Blends

U.S. EPA's statutory authority to regulate fuel composition is based on Section 211 of the Clean Air Act, codified as 42 U.S. Code § 7545. Under paragraph (f)(1)(B) of this section:

> *Effective upon November 15, 1990, it shall be unlawful for any manufacturer of any fuel or fuel additive to first introduce into commerce, or to increase the concentration in use of, any fuel or fuel additive for use by any person in motor vehicles manufactured after model year 1974 which is not **substantially similar** to any fuel or fuel additive utilized in the certification of any model year 1975, or subsequent model year, vehicle or engine under section 7525 of this title.* (emphasis added)

EPA has authority to waive this prohibition under terms of paragraph (f)(4) of this section:

> *The Administrator, upon application of any manufacturer of any fuel or fuel additive, may waive the prohibitions established under paragraph (1) or (3) of this subsection or the limitation specified in paragraph (2) of this subsection, if he determines that the applicant has established that such fuel or fuel additive or a specified concentration thereof, and the emission products of such fuel or fuel additive or specified concentration thereof, will not cause or contribute to a failure of any emission control device or system (over the useful life of the motor vehicle, motor vehicle engine, nonroad engine or nonroad vehicle in which such device or system is used) to achieve compliance by the vehicle or engine with the emission standards with respect to which it has been certified pursuant to sections 7525 and 7547(a) of this title. The Administrator shall take final action to grant or deny an application submitted under this paragraph, after public notice and comment, within 270 days of the receipt of such an application.*

U.S. EPA generally approves the use of C_2 through C_8 aliphatic alcohols and ethers, a category which includes ethanol, at levels of up to 2.0 percent oxygen by weight (corresponding to about 5.7 percent by volume of ethanol) under the Substantially-Similar ("SubSim") rule. As referenced earlier in the report, EPA issued a waiver (commonly referred to as a Section 211(f) waiver) approving the use of E10 on December 16, 1978. Partial waivers issued by EPA in 2010 and 2011 collectively approve the use of E15 in 2001 and newer model year light-duty vehicles while prohibiting its use in older, non-FFVs, motorcycles, heavy-duty vehicles and non-road applications. EPA has approved the use of E85 (defined as 51 to 85 percent by volume of ethanol) as an alternative fuel for use in FFVs. EPA proposed regulations covering E16-E50 in the "REGS Rule" in November 2016[223] but has not yet finalized this proposal. To provide the objective data required to inform EPA's decision on granting a Section 211(f)(4) waiver for E15, the corrosion and solvent interactions of E15 with a wide range of materials commonly

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[223] 81 Federal Register 80828, November 16, 2016.

utilized in automotive fuel systems and gasoline dispensing systems was extensively studied by Oak Ridge National Laboratories (ORNL) and Underwriters Laboratories (UL).[224]

The UL study concluded, in part --

> *Various pieces of new and used dispensing equipment demonstrated compliant results. Shear valve and flow limiter test items produced compliant results, the submersible turbine pump performed well, and hoses generally yielded compliant results.*[225]

EPA found these data sufficient to support their decisions granting the partial waivers permitting E15 blends federally. More detailed discussions on the material compatibility of E15 blends with retail infrastructure vehicles are presented in Sections 3 and 4 of this report.

The State of California currently approves the use of up to 10 percent by volume of ethanol in CaRFG. California has also approved the use of E85 (defined as 70 to 85 percent by volume of ethanol) as an Alternative Fuel for use in FFVs.

2.1 California Low Carbon Fuel Standard

The Low Carbon Fuel Standard (LCFS) is a program designed to lower the Carbon Intensity (CI, measured in grams of CO_2 equivalents per Megajoule of fuel energy) of transportation fuels marketed in California. The program sets decreasing annual CI targets for gasoline and diesel fuels and substitutes. Deficits are generated for fuels with CIs above the annual target and credits are generated for fuels with CIs below the annual target. Refiners and other parties in the supply chain supplying high carbon intensity fuels, such as petroleum-derived gasoline, to the market in California are Deficit Generators (DG). To comply with the LCFS regulation, DGs retire a like amount of credits generated from blending or supplying low CI fuels, credits purchased from others, or unused credits from prior periods in the annual compliance report.

The CI of each fuel is a function of its pathway (defined as the feedstocks, production process and transport to market) and determined via lifecycle analysis (LCA) of the GHG emissions associated with the production of each element of the pathway. Currently, the LCFS has over 500 approved fuel pathways, including over 200 pathways for ethanol production. During 2017, ethanol utilized in the LCFS had an average CI of 71.1 g/MJ, accounted for 32 percent of all credits generated and accounted for 73 percent of credits attributable to gasoline-type fuels.[226]

DGs can increase the number of credits which they generate through their gasoline and diesel marketing by reducing the CI of the fuels they produce and by increasing the proportion of their fuel mix coming from low CI fuels. With respect to gasoline-type fuels, substantially all gasoline sold in California is E10 with limited sales of E85. While ethanol producers have been able to steadily lower the CI of ethanol supplied to California, further reductions in ethanol CI are increasingly challenged as material volumes of cellulosic ethanol are not expected to become available in the near future.

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[224] Boyce, Kenneth, J. Thomas Chapin. Dispensing Equipment Testing With Mid-Level Ethanol/Gasoline Test Fluid: Summary Report . Underwriters Laboratories, Inc. report, November 2010; M. D. Kass, T. J Theiss, C. J. Janke. S. J Pawel, and S. A. Lewis, Sr., Intermediate Ethanol Blends Infrastructure Materials Compatibility Study: Elastomers, Metals, and Sealants. ORNL/TM-2010/326, March 2011; M. D. Kass, T. J Theiss, C. J. Janke. and S. J Pawel. Compatibility Study for Plastic, Elastomeric, and Metallic Fueling Infrastructure Materials Exposed to Aggressive Formulations of Ethanol-blended Gasoline. ORNL/TM-2012/88, July 2012; M. D. Kass, T. J Theiss, C. J. Janke. and S. J Pawel. Analysis of Underground Storage Tanks System Materials to Increased Leak Potential Associated with E15 Fuel. ORNL/TM-2012/182, July 2012 (Report for U.S. EPA Office of Underground Storage Tanks); M. D. Kass, C. J. Janke, S. J. Pawel, J. K. Thomson, H. Meyer, and T. J. Theiss. Compatibility Study for Plastic, Elastomeric, and Metallic Fueling Infrastructure Materials Exposed to Aggressive Formulations of Isobutanol-blended Gasoline. ORNL/TM-2013/243, August 2013.

[225] Boyce, Kenneth and J. Thomas Chapin, ibid, p16.

[226] Analysis by Stillwater Associates, November 2018.

2.2 Federal Renewable Fuel Standard

The Renewable Fuel Standard (RFS) was originally established by Congress through provisions of the Energy Policy Act of 2005 (EPAct05) and substantially amended and expanded through provisions of the Energy Independence and Security Act of 2007 (EISA). The goals of the RFS are to improve the energy independence and security of the U.S. and decrease GHG emissions through displacement of petroleum-derived gasoline and diesel with increasing volumes of renewable fuels meeting specified GHG reduction thresholds.

The RFS establishes four nested categories of renewable fuels:

- Renewable Fuels – fuels produced from approved feedstocks utilizing a production pathway which achieves a GHG reduction of at least 20 percent. Production facilities in operation or under construction at the time of enactment of EISA are grandfathered into this category even if they do not meet the minimum GHG reduction.
- Advanced Biofuels – A subset of Renewable Fuels which achieve a GHG reduction of at least 50 percent; ethanol produced from corn starch is explicitly excluded from this category.
- Biomass-Based Diesel (BBD) – A subset of Advanced Biofuels which are used to displace diesel fuel, heating oil or jet fuel. Biodiesel and Renewable diesel generally fall within this category.[227]
- Cellulosic Biofuels – A subset of Advanced Biofuels which are produced from approved lignocellulosic feedstocks and which achieve a GHG reduction of at least 60 percent. Renewable natural gas (RNG) from qualifying feedstocks is currently the largest source of Cellulosic Biofuels utilized for RFS compliance.

The term “Conventional Biofuels” refers to Renewable Fuels which are not Advanced Biofuels; corn starch ethanol constitutes nearly all the biofuels classified in this category. The term “Undifferentiated Advanced Biofuels” refers to Advanced Biofuels which are not BBD or Cellulosic Biofuels; sugarcane ethanol falls within this category. All biofuel production pathways are placed into one of the four statutory categories based on its feedstock, GHG reduction and application as assessed by EPA.

EISA defines refiners and importers of finished gasoline and diesel as obligated parties (OP). The statute sets out an annual schedule of total volumes required to be achieved in each of the four categories. These four annual volumes are each allocated to OP’s annually by dividing the annual volume requirement by the estimated total demand for petroleum-derived gasoline and diesel in the 49 states participating in RFS.[228] This creates a percentage obligation, known as the Renewable Volume Obligation (RVO) for each of the four categories. EPA publishes the RVOs through an annual rulemaking process with a proposed rule typically published in June of the preceding year leading to a final rule published in November of the preceding year. Each OP multiplies their total petroleum-derived gasoline and diesel production for the calendar year by each of the four RVOs to calculate their volume obligation for each category each year.

Ethanol used to satisfy RFS obligations can be derived from corn and other grains, sugarcane or lignocellulosic feedstocks. Corn starch ethanol, limited by statute to be a Conventional Biofuel, is the largest volume biofuel used to satisfy RFS obligations. Small volumes of ethanol produced from other grains (primarily sorghum) can be classified as either Conventional or Advanced depending on the pathway approval secured by the individual production plant. Small amounts of Brazilian sugarcane ethanol are imported to the U.S. and qualify as Advanced Biofuels. Production of cellulosic ethanol

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[227] The GHG reduction of certain BBD feedstocks, such as palm oil, do not meet the 50% threshold and those fuels are classified as Conventional Biofuels.

[228] EISA requires that the 48 continental states participate, and Alaska and Hawaii were given the option of participating. Hawaii opted in to RFS and Alaska has not opted in.

remains very limited; some corn ethanol plants are beginning to secure EPA approval for cellulosic ethanol produced from corn kernel fiber in conjunction with their starch-derived production.

The annual RVOs under RFS are now sufficiently high that they exceed what can be achieved with E10 blending in all U.S. gasoline. Some additional ethanol is utilized in E85 and a small but increasing volume of ethanol is utilized in E15 blends. BBD blending in excess of its RVO is used to close the gap despite its significantly higher cost. Continuing annual increases in RFS RVOs serve as an incentive to increase retail availability, and thus, sales of E15 and higher ethanol blends.

Appendix 2: Tailpipe and Evaporative Pollutant Emissions Data

Coordinating Research Council Study E74-B

Table 1-a. CRc E74-B Study Criteria pollutants Tailpipe emissions on ftp cycle at 75 °F (TOP) and 50 °F (Bottom) using E10 and E20.

Vehicle	$\mathrm{NO_x}$ Emissions, g/mi			THC Emissions, g/mi			CO Emissions, g/mi		
	E10	E20	Change	E10	E20	Change	E10	E20	Change
2001 Corolla	0.176	0.139	-21%	0.071	0.064	-10%	0.99	1.04	5%
2002 Altima	0.182	0.176	-3%	0.049	0.051	4%	1.94	1.54	-21%
2001 Caravan	0.296	0.506	71%	0.066	0.051	-23%	0.57	0.35	-39%
2002 Trail Blazer	0.182	0.185	2%	0.084	0.058	-31%	0.52	0.44	-15%
2004 Stratus	0.048	0.058	21%	0.036	0.023	-36%	0.36	0.28	-22%
2004 Impala	0.045	0.027	-40%	0.054	0.044	-19%	0.50	0.52	4%
2004 Camry	0.046	0.037	-20%	0.024	0.024	0%	0.15	0.18	20%
2006 Taurus	0.046	0.089	93%	0.030	0.023	-23%	0.23	0.06	-74%
2004 Ram 1500 SLT	0.099	0.110	11%	0.054	0.056	4%	0.68	0.66	-3%
2004 Escape	0.048	0.057	19%	0.037	0.034	-8%	0.20	0.17	-15%
2004 Highlander	0.055	0.050	-9%	0.024	0.026	8%	0.14	0.23	64%
Average			11%			-12%			-9%
p value (two tail) of log transformed values			0.61			0.023			0.25

Table 1-b. CRc E74-B Study criteria Pollutants Tailpipe emissions on ftp cycle at 75 °F (TOP) and 50 °F (Bottom) using E10 and E20.

Vehicle	$\mathrm{NO_x}$ Emissions, g/mi			THC Emissions, g/mi			CO Emissions, g/mi		
	E10	E20	Change	E10	E20	Change	E10	E20	Change
2001 Corolla	0.158	0.136	-14%	0.085	0.111	31%	1.63	1.48	-9%
2002 Altima	0.263	0.278	6%	0.085	0.078	-8%	1.98	1.79	-10%
2001 Caravan	0.42	0.33	-21%	0.078	0.067	-14%	0.59	0.6	2%
2002 Trail Blazer	0.192	0.197	3%	0.089	0.078	-12%	0.55	0.52	-5%
2004 Stratus	0.061	0.087	43%	0.057	0.045	-21%	0.39	0.34	-13%
2004 Impala	0.035	0.035	0%	0.078	0.076	-3%	1.53	1.37	-10%
2004 Camry	0.047	0.052	11%	0.06	0.063	5%	0.2	0.26	30%
2006 Taurus	0.025	0.119	376%	0.046	0.044	-4%	0.47	0.29	-38%
2004 Ram 1500 SLT	0.142	0.114	-20%	0.091	0.091	0%	0.99	0.95	-4%
2004 Escape	0.081	0.119	47%	0.061	0.067	10%	0.4	0.67	68%
2004 Highlander	0.042	0.055	31%	0.033	0.039	18%	0.24	0.28	17%
Average			8%			0%			2%
p value (two tail) of log transformed values			0.44			0.84			0.93
Average of results at both temperatures			10%			-6%			-3%

Removed from data analysis as outlier as determined by Chauvenet's Criterion

p value (two tail) of log transformed values of results at both temperatures	0.38			0.051			0.27

The Department of Energy (DOE) Study of Intermediate Blends on Legacy Vehicles

Table 2-a. doe intermediate blend study criteria Pollutants tailpipe emissions on la92 cylce using e10 and e15.

	NO_x Emissions, g/mi			**NMHC Emissions, g/mi**			**CO Emissions, g/mi**		
Vehicle	E10	E15	Change	E10	E15	Change	E10	E15	Change
2001 PT Cruiser	0.171	0.171	0%	0.021	0.019	-10%	1.89	1.76	-7%
2003 Le Sabre	0.034	0.042	24%	0.019	0.022	16%	0.25	0.32	28%
2003 F150	0.016	0.016	0%	0.063	0.054	-14%	0.92	0.78	-15%
2003 Taurus	0.078	0.079	1%	0.048	0.042	-13%	0.5	0.41	-18%
2003 Altima	0.042	0.051	21%	0.049	0.072	47%	0.52	0.65	25%
2003 Camry	0.154	0.164	6%	0.048	0.043	-10%	4.95	5.07	2%
2004 Golf GTI	0.042	0.028	-33%	0.018	0.017	-6%	0.53	0.49	-8%
2007 Lucerne	0.058	0.056	-3%	0.034	0.031	-9%	1.86	1.81	-3%
2007 Silverado	0.039	0.035	-10%	0.035	0.039	11%	1.4	1.32	-6%
2007 T&C	0.017	0.034	100%	0.023	0.028	22%	1.02	1.23	21%
2007 F150	0.008	0.012	50%	0.038	0.042	11%	2.21	1.87	-15%
2007 Accord	0.009	0.009	0%	0.01	0.006	-40%	0.18	0.14	-22%
2007 Camry	0.037	0.032	-14%	0.015	0.016	7%	0.13	0.16	23%
Average			11%			1%			0%
p value (two tail) of log transformed values			0.34			0.84			0.84

Table 2-b. doe intermediate blend study criteria Pollutants Tailpipe emissions on la-92 cylce using e10 and e20.

	NO_x Emissions, g/mi			**NMHC Emissions, g/mi**			**CO Emissions, g/mi**		
Vehicle	E10	E20	Change	E10	E20	Change	E10	E20	Change
2001 PT Cruiser	0.171	0.126	-26%	0.021	0.025	19%	1.89	1.93	2%
2003 Le Sabre	0.034	0.051	50%	0.019	0.021	11%	0.25	0.37	48%
2003 F150	0.016	0.017	6%	0.063	0.054	-14%	0.92	0.8	-13%
2003 Taurus	0.078	0.121	55%	0.048	0.044	-8%	0.5	0.42	-16%
2003 Altima	0.042	0.064	52%	0.049	0.044	-10%	0.52	0.69	33%
2003 Camry	0.154	0.163	6%	0.048	0.045	-6%	4.95	5.81	17%
2004 Golf GTI	0.042	0.047	12%	0.018	0.019	6%	0.53	0.55	4%
2007 Lucerne	0.058	0.059	2%	0.034	0.029	-15%	1.86	1.91	3%

2007 Silverado	0.039	0.044	13%	0.035	0.031	-11%	1.4	1.31	-6%
2007 T&C	0.017	0.027	59%	0.023	0.024	4%	1.02	0.97	-5%
2007 F150	0.008	0.018	125%	0.038	0.033	-13%	2.21	2.73	24%
2007 Accord	0.009	0.014	56%	0.01	0.008	-20%	0.18	0.12	-33%
2007 Camry	0.037	0.028	-24%	0.015	0.014	-7%	0.13	0.12	-8%
Average			30%			-5%			4%
p value (two tail) of log transformed values			0.03			0.097			0.78

Table 2-c. DOE INTERMEDIATE BLEND STUDY toxic POLLUTANTS tailpipe EMISSION ON LA-92 CYLCE USING E10 AND E15.

Vehicle	**Acetaldehyde, g/mi**			**Formaldehyde, g/mi**		
	E10	E15	Change	E10	E15	Change
2001 PT Cruiser	0.00070	0.00090	29%	0.00090	0.00105	17%
2003 Le Sabre	0.00070	0.00090	29%	0.00115	0.00115	0%
2003 F150	0.00035	0.00051	46%	0.00052	0.00045	-13%
2003 Taurus	0.00030	0.00040	33%	0.00045	0.00035	-22%
2003 Altima	0.00028	0.00048	71%	0.00035	0.00045	29%
2003 Camry	0.00080	0.00120	50%	0.00080	0.00073	-9%
2004 Golf GTI	0.00099	0.00080	-19%	0.00070	0.00049	-30%
2007 Lucerne	0.00052	0.00076	46%	0.00070	0.00075	7%
2007 Silverado	0.00024	0.00026	8%	0.00048	0.00035	-27%
2007 T&C	0.00075	0.00145	93%	0.00085	0.00070	-18%
2007 F150	0.00015	0.00020	33%	0.00030	0.00050	67%
2007 Accord	0.00010	0.00011	10%	0.00051	0.00030	-41%
2007 Camry	0.00048	0.00070	46%	0.00045	0.00055	22%
Average			37%			-1%
p value (two tail) of log transformed values			0.0004			0.51

Table 2-d. DOE INTERMEDIATE BLEND STUDY TOXIC POLLUTANTS tailpipe EMISSIONS ON LA-92 CYLCE USING E10 AND E20.

Vehicle	**Acetaldehyde, g/mi**			**Formaldehyde, g/mi**		
	E10	E20	Change	E10	E20	Change
2001 PT Cruiser	0.00070	0.00110	57%	0.00090	0.00080	-11%
2003 Le Sabre	0.00070	0.00103	47%	0.00115	0.00113	-2%
2003 F150	0.00035	0.00065	86%	0.00052	0.00052	0%
2003 Taurus	0.00030	0.00055	83%	0.00045	0.00040	-11%
2003 Altima	0.00028	0.00047	68%	0.00035	0.00045	29%
2003 Camry	0.00080	0.00140	75%	0.00080	0.00060	-25%

2004 Golf GTI	0.00099	0.00123	24%	0.00070	0.00063	-10%
2007 Lucerne	0.00052	0.00060	15%	0.00070	0.00060	-14%
2007 Silverado	0.00024	0.00033	38%	0.00048	0.00055	15%
2007 T&C	0.00075	0.00090	20%	0.00085	0.00080	-6%
2007 F150	0.00015	0.00030	100%	0.00030	0.00033	10%
2007 Accord	0.00010	0.00013	30%	0.00051	0.00030	-41%
2007 Camry	0.00048	0.00072	50%	0.00045	0.00055	22%
Average			53%			-3%
p value (two tail) of log transformed values			0.000003			0.37

DOE Catalyst Study

Table 3-a. doe catalyst study Criteria Pollutants tailpipe Emissions on ftp cycle using e0 and e15 at full useful life.

	NO_x Emissions, g/mi			**NMOG Emissions, g/mi**			**CO Emissions, g/mi**		
Vehicle	E0	E15	Change	E0	E15	Change	E0	E15	Change
2007 Accord	0.016	0.024	50%	0.024	0.0184	-23%	0.24	0.13	-46%
2006 Silverado	0.036	0.035	-3%	0.035	0.0574	64%	0.99	0.76	-23%
2008 Altima	0.051	0.053	4%	0.053	0.0545	3%	0.62	0.62	0%
2008 Taurus	0.009	0.013	44%	0.013	0.0275	112%	0.42	0.45	7%
2007 Caravan	0.036	0.047	31%	0.047	0.0385	-18%	1.56	1.12	-28%
2006 Cobalt	0.026	0.027	4%	0.027	0.0409	51%	0.45	0.47	4%
2007 Caliber	0.059	0.059	0%	0.059	0.0769	30%	4.3	3.61	-16%
2009 Liberty	0.056	0.045	-20%	0.045	0.0448	0%	1.77	1.16	-34%
2009 Explorer	0.031	0.028	-10%	0.028	0.0585	109%	1.18	1.04	-12%
2009 Civic	0.03	0.043	43%	0.043	0.0333	-23%	0.46	0.33	-28%
2009 Corolla	0.056	0.047	-16%	0.047	0.0528	12%	0.6	0.57	-5%
2005 Tundra	0.039	0.035	-10%	0.035	0.0545	56%	1.17	0.94	-20%
2006 Impala	0.038	0.039	3%	0.039	0.0471	21%	1.4	1.44	3%
2005 F150	0.089	0.06	-33%	0.06	0.0901	50%	2.56	2.23	-13%
2006 Quest	0.036	0.04	11%	0.04	0.0694	74%	1.08	1.02	-6%
2009 Outlook	0.022	0.016	-27%	0.016	0.0341	113%	0.62	0.43	-31%
2009 Camry	0.046	0.052	13%	0.052	0.0348	-33%	0.23	0.25	9%
2009 Focus	0.058	0.062	7%	0.062	0.0275	-56%	0.77	0.67	-13%
2009 Odyssey	0.044	0.039	-11%	0.039	0.0278	-29%	0.22	0.2	-9%
2002 Frontier	0.216	0.102	-53%	0.102	0.0933	-9%	3.92	4.02	3%
2002 Durango	0.391	0.462	18%	0.462	0.1523	-67%	2.55	2.34	-8%
2003 Camry	0.118	0.084	-29%	0.084	0.0436	-48%	0.64	0.72	13%
2003 Taurus	0.137	0.155	13%	0.155	0.062	-60%	0.59	0.35	-41%

2003 Cavalier	0.092	0.085	-8%	0.085	0.0608	-28%	0.71	0.56	-21%
Average			1%			13%			-13%
p value (two tail) of log transformed values			0.68			0.93			0.0006

Table 3-b. DOE CATALYST STUDY CRITERIA POLLUTANTS TAILPIPE EMISSIONS ON FTP CYCLE USING E0 AND E20 AT FULL USEFUL LIFE.

	NO_x Emissions, g/mi			**NMOG Emissions, g/mi**			**CO Emissions, g/mi**		
Vehicle	E0	E20	Change	E0	E20	Change	E0	E20	Change
2007 Accord	0.022	0.019	-14%	0.0314	0.019	-39%	0.27	0.14	-48%
2006 Silverado	0.05	0.038	-24%	0.0674	0.0516	-23%	0.84	0.64	-24%
2008 Altima	0.044	0.042	-5%	0.0628	0.0516	-18%	0.56	0.47	-16%
2008 Taurus	0.008	0.014	75%	0.0229	0.0237	3%	0.37	0.27	-27%
2007 Caravan	0.086	0.046	-47%	0.0479	0.0617	29%	2.37	1.63	-31%
2006 Cobalt	0.075	0.119	59%	0.0458	0.0356	-22%	0.82	0.43	-48%
2007 Caliber	0.059	0.064	8%	0.0703	0.0689	-2%	3.54	2.23	-37%
2009 Liberty	0.057	0.044	-23%	0.0849	0.0427	-50%	1.66	0.89	-46%
2009 Explorer	0.029	0.028	-3%	0.0654	0.076	16%	1.26	1.09	-13%
2009 Civic	0.025	0.035	40%	0.0443	0.0255	-42%	0.51	0.48	-6%
2009 Corolla	0.043	0.046	7%	0.0535	0.0487	-9%	0.61	0.48	-21%
2005 Tundra	0.038	0.039	3%	0.0571	0.073	28%	0.88	0.88	0%
2006 Impala	0.041	0.019	-54%	0.0504	0.0487	-3%	1.69	1.46	-14%
2005 F150	0.059	0.061	3%	0.0582	0.0564	-3%	2.32	1.95	-16%
2002 Frontier	0.131	0.117	-11%	0.1026	0.1203	17%	4.17	4.57	10%
2002 Durango	0.605	0.701	16%	0.1554	0.1454	-6%	2.54	2.23	-12%
2003 Camry	0.286	0.267	-7%	0.1709	0.1716	0%	2.6	2.65	2%
2003 Taurus	0.064	0.122	91%	0.0762	0.0528	-31%	0.64	0.38	-41%
2003 Cavalier	0.091	0.092	1%	0.0983	0.1027	4%	1.06	0.68	-36%
2007 Accord	0.022	0.019	-14%	0.0314	0.019	-39%	0.27	0.14	-48%
2002 Durango	0.391	0.462	18%	0.462	0.1523	-67%	2.55	2.34	-8%
2003 Camry	0.118	0.084	-29%	0.084	0.0436	-48%	0.64	0.72	13%
2003 Taurus	0.137	0.155	13%	0.155	0.062	-60%	0.59	0.35	-41%
2003 Cavalier	0.092	0.085	-8%	0.085	0.0608	-28%	0.71	0.56	-21%
Average			4%			-16%			-22%
p value (two tail) of log transformed values			0.88			0.004			0.00001

UC Riverside - 1

Table 4-a. uc riverside study -1 criteria Pollutants tailpipe Emissions on uc and ftp cycles using e10 and e15.

Vehicle	Test Cycle	NO_x Emissions, g/mi			NMHC Emissions, g/mi			CO Emissions, g/mi			THC Emissions, g/mi			PM Emissions, g/mi		
		E10	E15	Change	E10	E15	Change	E10	E15	Change	E10	E15	Change	E10	E15	Change
2007 Civic	**UC**	0.006	0.009	54%	0.017	0.015	-12%	0.330	0.275	-17%	0.020	0.018	-9%	#DIV/0!	#DIV/0!	
2007 Ram	**UC**	0.164	0.158	-4%	0.069	0.069	-1%	2.728	2.539	-7%	0.092	0.093	2%	#DIV/0!	#DIV/0!	
2012 Camry	**UC**	0.012	0.011	-13%	0.003	0.005	35%	0.030	0.028	-9%	0.005	0.006	14%	0.075	0.294	290%
2012 Optima	**UC**	0.006	0.007	11%	0.006	0.010	55%	0.121	0.071	-41%	0.007	0.010	46%	4.133	6.320	53%
2012 Impala	**UC**	0.007	0.009	22%	0.005	0.006	15%	0.148	0.136	-8%	0.006	0.007	5%	3.062	2.784	-9%
2012 Mercedes Benz	**UC**	0.026	0.027	4%	0.015	0.011	-24%	0.220	0.173	-21%	0.022	0.018	-17%	0.298	0.417	40%
2012 Mazda 3	**UC**	0.011	0.009	-21%	0.007	0.007	-4%	0.624	1.083	73%	0.008	0.008	10%	2.534	2.003	-21%
2007 Civic	**FTP**	0.010	0.012	21%	0.029	0.026	-10%	0.284	0.252	-11%	0.031	0.029	-8%	#DIV/0!	#DIV/0!	
2007 Ram	**FTP**	0.053	0.047	-11%	0.069	0.073	7%	1.488	1.360	-9%	0.087	0.092	6%	#DIV/0!	#DIV/0!	
2012 Camry	**FTP**	0.010	0.009	-17%	0.004	0.005	44%	0.024	0.025	2%	0.005	0.006	22%	-0.029	-0.080	
2012 Optima	**FTP**	0.005	0.005	5%	0.007	0.010	48%	0.055	0.070	27%	0.007	0.011	56%	4.327	4.302	-1%
2012 Impala	**FTP**	0.009	0.009	6%	0.005	0.007	26%	0.159	0.149	-6%	0.007	0.009	22%	3.202	3.294	3%
2012 Mercedes Benz	**FTP**	0.009	0.009	0%	0.013	0.010	-25%	0.195	0.173	-12%	0.016	0.012	-23%	0.090	0.380	320%
2012 Mazda 3	**FTP**	0.008	0.007	-17%	0.007	0.008	16%	0.570	0.458	-20%	0.009	0.010	10%	2.743	1.921	-30%
Average				3%			12%			-4%			10%			72%
p value (two tail) of log transformed values				0.81			0.18			0.29			0.17			0.18

Table 4-b. UC RIVERSIDE STUDY -1 CRITERIA POLLUTANTS TAILPIPE EMISSIONS ON UC AND FTP CYCLES USING E10 AND E20.

Vehicle	**Test Cycle**	**NO$_x$ Emissions, g/mi**			**NMHC Emissions, g/mi**			**CO Emissions, g/mi**			**THC Emissions, g/mi**			**PM Emissions, g/mi**		
		E10	E20	Change	E10	E20	Change	E10	E20	Change	E10	E20	Change	E10	E20	Change
2007 Civic	**UC**	0.006	0.010	62%	0.017	0.017	-3%	0.330	0.245	-26%	0.020	0.020	0%			
2007 Ram	**UC**	0.164	0.137	-16%	0.069	0.053	-23%	2.728	2.429	-11%	0.092	0.074	-19%			
2012 Camry	**UC**	0.012	0.011	-7%	0.003	0.005	56%	0.030	0.034	11%	0.005	0.007	39%	0.075	0.147	94%
2012 Optima	**UC**	0.006	0.008	26%	0.006	0.009	43%	0.121	0.091	-25%	0.007	0.011	46%	4.133	3.618	-12%
2012 Impala	**UC**	0.007	0.007	-2%	0.005	0.005	-2%	0.148	0.111	-25%	0.006	0.006	-2%	3.062	1.520	-50%
2012 Mercedes Benz	**UC**	0.026	0.028	7%	0.015	0.007	-53%	0.220	0.179	-19%	0.022	0.012	-43%	0.298	0.447	50%
2012 Mazda 3	**UC**	0.011	0.013	16%	0.007	0.007	-7%	0.624	0.724	16%	0.008	0.008	7%	2.534	0.682	-73%
2007 Civic	**FTP**	0.010	0.013	36%	0.029	0.022	-24%	0.284	0.228	-20%	0.031	0.025	-22%			
2007 Ram	**FTP**	0.053	0.045	-15%	0.069	0.071	3%	1.488	1.498	1%	0.087	0.088	2%			
2012 Camry	**FTP**	0.010	0.011	8%	0.004	0.005	32%	0.024	0.022	-8%	0.005	0.006	19%	-0.029	-0.055	92%
2012 Optima	**FTP**	0.005	0.005	-3%	0.007	0.013	85%	0.055	0.075	36%	0.007	0.014	92%	4.327	4.049	-6%
2012 Impala	**FTP**	0.009	0.010	12%	0.005	0.006	13%	0.159	0.166	5%	0.007	0.008	13%	3.202	1.606	-50%
2012 Mercedes Benz	**FTP**	0.009	0.008	-10%	0.013	0.008	-38%	0.195	0.153	-21%	0.016	0.010	-39%	0.090	0.336	272%
2012 Mazda 3	**FTP**	0.008	0.009	6%	0.007	0.006	-10%	0.570	0.362	-37%	0.009	0.009	-6%	2.743	1.229	-55%
Average				9%			5%			-9%			6%			26%
p value (two tail) of log transformed values				0.21			0.92			0.07			0.91			0.61

Table 4-C. UC RIVERSIDE STUDY-1 Toxic POLLUTANTS TAILPIPE EMISSIONS ON FTP1 CYCLE USING E10 AND E15.

Vehicle	Test Cycle	Acetaldehyde Emissions, ug/mi			Formaldehyde Emissions, ug/mi			1,3-butadiene Emissions, mg/mi			Benzene Emissions, mg/mi			Potency Weighted Toxics (mg of 1,3 butadiene/mi equivalent)		
		E10	E15	Change	E10	E15	Change	E10	E15	Change	E10	E15	Change	E10	E15	Change
2007 Honda Civic	FTP 1	432.0	822.0	90%	595.6	847.0	42%	18.4	15.2	-17%	54.0	48.0	-11%	27.6	23.4	-15%
2007 Dodge Ram	**FTP 1**	863.3	1168.3	35%	1159.4	1103.7	-5%	33.3	26.4	-21%	155.4	126.1	-19%	59.8	47.9	-20%
2012 Toyota Camry	**FTP 1**	440.2	374.2	-15%	383.6	422.5	10%	1.1	1.2	13%	10.0	14.3	43%	2.8	3.7	31%
2012 Kia Optima	**FTP 1**	336.1	94.3	-72%	463.2	119.6	-74%	1.6	3.0	81%	23.4	36.6	56%	5.6	9.2	63%
2012 Chevrolet Impala	**FTP 1**	247.3	182.8	-26%	232.2	91.3	-61%	1.3	0.7	-45%	10.3	17.4	69%	3.1	3.7	20%
2012 Mercedes-Benz E350 coupe	**FTP 1**	156.1	350.3	124%	222.4	280.2	26%	2.7	1.5	-43%	65.7	29.2	-56%	13.8	6.5	-53%
2012 Mazda Mazda3	**FTP 1**	183.9	196.3	7%	235.8	182.9	-22%	2.4	1.2	-49%	44.1	27.2	-38%	9.9	5.8	-41%
Average				21%			-12%			-12%			6%			-2%
p value (two tail) of log transformed values				0.97			0.30			0.25			0.83			0.56

Table 4-c1. UC RIVERSIDE STUDY -1 additional TOXIC POLLUTANTS TAILPIPE EMISSIONS ON FTP1 CYCLE USING E10 AND E15.

Vehicle	Test Cycle	Toluene Emissions, mg/mi			Ethylbenzene Emissions, g/mi			m,p-Xylene Emissions, mg/mi			0-Xylene Emissions, mg/mi		
		E10	E15	Change	E10	E15	Change	E10	E15	Change	E10	E15	Change
2007 Honda Civic	FTP1	123.4	128.8	4%	25.1	22.8	-9%	80.1	82.4	3%	25.6	26.8	5%
2007 Dodge Ram	**FTP1**	377.9	303.4	-20%	72.7	52.8	-27%	264.7	197.5	-25%	84.5	64.9	-23%
2012 Toyota Camry	**FTP1**	27.9	28.4	2%	4.0	4.6	15%	9.5	12.5	31%	2.5	4.3	68%
2012 Kia Optima	**FTP1**	28.1	79.5	183%	4.4	7.1	61%	13.0	29.8	129%	3.9	10.4	165%
2012 Chevrolet Impala	**FTP1**	19.9	16.8	-15%	3.2	3.0	-6%	10.8	7.7	-29%	3.2	2.5	-23%
2012 Mercedes-Benz E350 coupe	**FTP1**	62.5	65.5	5%	9.1	12.3	36%	31.4	30.7	-2%	10.4	9.3	-10%

2012 Mazda Mazda3	**FTP1**	46.4	52.1	12%	9.3	9.3	0%	23.8	22.7	-4%	6.9	7.5	9%
Average				24%			10%			15%			27%
p value (two tail) of log transformed values				0.46			0.55			0.70			0.44

Table 4-d. UC RIVERSIDE STUDY-1 TOXIC POLLUTANTS TAILPIPE EMISSIONS ON FTP1 CYCLE USING E10 AND E20.

		Acetaldehyde Emissions, ug/mi			**Formaldehyde Emissions, ug/mi**			**1,3-butadiene Emissions, mg/mi**			**Benzene Emissions, mg/mi**			**Potency Weighted Toxics (mg of 1,3 butadiene/mi equivalent)**		
Vehicle	**Test Cycle**	E10	E20	Change	E10	E20	Change	E10	E20	Change	E10	E20	Change	E10	E20	Change
2007 Honda Civic	FTP 1	432.0	402.3	-7%	595.6	485.7	-18%	18.4	10.3	-44%	54.0	41.9	-22%	27.6	17.4	-37%
2007 Dodge Ram	**FTP 1**	863.3	1729.2	100%	1159.4	1339.6	16%	33.3	29.6	-11%	155.4	134.5	-13%	59.8	52.5	-12%
2012 Toyota Camry	**FTP 1**	440.2	203.7	-54%	383.6	436.1	14%	1.1	2.1	94%	10.0	13.1	32%	2.8	4.4	55%
2012 Kia Optima	**FTP 1**	336.1	59.4	-82%	463.2	55.6	-88%	1.6	6.1	274%	23.4	53.1	127%	5.6	15.1	169%
2012 Chevrolet Impala	**FTP 1**	247.3	397.1	61%	232.2	413.9	78%	1.3	1.1	-16%	10.3	10.1	-1%	3.1	2.8	-7%
2012 Mercedes-Benz E350 coupe	**FTP 1**	156.1	310.9	99%	222.4	218.9	-2%	2.7	2.2	-18%	65.7	22.3	-66%	13.8	6.0	-57%
2012 Mazda Mazda3	**FTP 1**	183.9	298.4	62%	235.8	263.9	12%	2.4	1.1	-52%	44.1	36.9	-16%	9.9	7.4	-25%
Average				26%			2%			32%			6%			12%
p value (two tail) of log transformed values				0.93			0.58			0.93			0.72			0.44

Table 4-d1. UC RIVERSIDE STUDY-1 Additional TOXIC POLLUTANTSTAILPIPE EMISSIONS ON FTP1 CYCLE USING E10 AND E20.

Vehicle	**Test Cycle**	**Toluene Emissions, mg/mi**			**Ethylbenzene Emissions, g/mi**			**m,p-Xylene Emissions, mg/mi**			**0-Xylene Emissions, mg/mi**		
		E10	E20	Change	E10	E20	Change	E10	E20	Change	E10	E20	Change
2007 Honda Civic	FTP1	123.4	105.3	-15%	25.1	20.3	-19%	80.1	77.2	-4%	25.6	21.0	-18%
2007 Dodge Ram	**FTP1**	377.9	357.0	-6%	72.7	71.3	-2%	264.7	298.0	13%	84.5	82.8	-2%
2012 Toyota Camry	**FTP1**	27.9	22.7	-19%	4.0	3.9	-2%	9.5	11.1	17%	2.5	2.8	11%
2012 Kia Optima	**FTP1**	28.1	73.7	162%	4.4	15.9	264%	13.0	51.1	292%	3.9	14.1	260%
2012 Chevrolet Impala	**FTP1**	19.9	21.8	9%	3.2	3.4	7%	10.8	11.9	10%	3.2	3.0	-6%
2012 Mercedes-Benz E350 coupe	**FTP1**	62.5	37.9	-39%	9.1	6.5	-28%	31.4	26.0	-17%	10.4	7.4	-29%
2012 Mazda Mazda3	**FTP1**	46.4	54.6	18%	9.3	12.2	31%	23.8	33.4	40%	6.9	9.0	31%
Average				16%			36%			50%			35%
p value (two tail) of log transformed values				0.82			0.49			0.22			0.49

UC Riverside-3

Table 5-a. UC Riverside Study-3 Criteria Pollutants of Splash blended low aromatics on la92 cycle using e10 and e15.

Splash Blended Low Aromatics		NO$_x$ Emissions, g/mi			NMHC Emissions, g/mi			CO Emissions, g/mi			THC Emissions, g/mi			PM Emissions, g/mi		
Vehicle	Test Cycle	E10	E15	Change	E10	E15	Change	E10	E15	Change	E10	E15	Change	E10	E15	Change
Honda Accord	LA92	0.00485	0.00365	-25%	0.00835	0.00775	-7%	0.07565	0.0506	-33%	0.00985	0.0089	-10%	0.56	0.715	28%
Chevrolet Impala	LA92	0.0045	0.00435	-3%	0.0038	0.0033	-13%	0.18125	0.1562	-14%	0.0043	0.0038	-12%	5.715	2.69	-53%
VW Jetta	LA92	0.0172	0.0164	-5%	0.00465	0.00415	-11%	0.05025	0.04765	-5%	0.00655	0.0058	-11%	0.3615	0.315	-13%
Kia Optima	LA92	0.0146	0.0121	-17%	0.00355	0.0033	-7%	0.12585	0.1213	-4%	0.0044	0.004	-9%	1.59	0.9	-43%
Ford Fusion	LA92	0.0099	0.00535	-46%	0.00425	0.0033	-22%	0.13265	0.17935	35%	0.006	0.0044	-27%	2.75	2.44	-11%
Average				-19%			-12%			-4%			-14%			-19%
p value (two tail) of log transformed values				0.09			0.02			0.61			0.02			0.21

Table 5-B. UC RIVERSIDE STUDY -3 CRITERIA POLLUTANTS OF SPLASH BLENDED LOW AROMATICS ON LA92 CYCLE USING E10 AND E20.

Splash Blended Low Aromatics		NO$_x$ Emissions, g/mi			NMHC Emissions, g/mi			CO Emissions, g/mi			THC Emissions, g/mi			PM Emissions, g/mi		
Vehicle	Test Cycle	E10	E20	Change	E10	E20	Change	E10	E20	Change	E10	E20	Change	E10	E20	Change
Honda Accord	LA92	0.00485	0.00605	25%	0.00835	0.0088	5%	0.07565	0.0483	-36%	0.00985	0.0102	4%	0.56	0.515	-8%
Chevrolet Impala	LA92	0.0045	0.00405	-10%	0.0038	0.00495	30%	0.18125	0.14165	-22%	0.0043	0.0054	26%	5.715	4.96	-13%
VW Jetta	LA92	0.0172	0.0161	-6%	0.00465	0.00405	-13%	0.05025	0.0428	-15%	0.00655	0.0058	-11%	0.3615	0.21	-42%
Kia Optima	LA92	0.0146	0.0136	-7%	0.00355	0.0029	-18%	0.12585	0.12035	-4%	0.0044	0.00375	-15%	1.59	4.305	171%
Ford Fusion	LA92	0.0099	0.0105	6%	0.00425	0.00495	16%	0.13265	0.21215	60%	0.006	0.0069	15%	2.75	3.045	11%
Average				2%			4%			-3%			4%			24%

p value (two tail) of log transformed values				0.91			0.78			0.61			0.76			0.81

Table 5-c. UC RIVERSIDE STUDY-3 CRITERIA POLLUTANTS OF match BLENDED LOW AROMATICS ON LA92 CYCLE USING E10 AND E15.

Match Blended Low Aromatics		**NO_x Emissions, g/mi**			**NMHC Emissions, g/mi**			**CO Emissions, g/mi**			**THC Emissions, g/mi**			**PM Emissions, mg/mi**		
Vehicle	**Test Cycle**	E10	E15	Change	E10	E15	Change	E10	E15	Change	E10	E15	Change	E10	E15	Change
Honda Accord	**LA92**	0.00485	0.0054	11%	0.00835	0.00685	-18%	0.07565	0.0415	-45%	0.00985	0.00785	-20%	0.56	0.54	-4%
Chevrolet Impala	**LA92**	0.0045	0.0066	47%	0.0038	0.00365	-4%	0.18125	0.17915	-1%	0.0043	0.0042	-2%	5.715	2.7	-53%
VW Jetta	**LA92**	0.0172	0.01735	1%	0.00465	0.0041	-12%	0.05025	0.0424	-16%	0.00655	0.00585	-11%	0.3615	0.325	-10%
Kia Optima	**LA92**	0.0146	0.01575	8%	0.00355	0.0042	18%	0.12585	0.1146	-9%	0.0044	0.00465	6%	1.59	1.865	17%
Ford Fusion	**LA92**	0.0099	0.0103	4%	0.00425	0.0047	11%	0.13265	0.2212	67%	0.006	0.00645		2.75	4.29	56%
Average				14%			-1%			-1%			-4%			1%
p value (two tail) of log transformed values				0.14			0.79			0.70			0.44			0.78

Table 5-d. UC RIVERSIDE STUDY -3 CRITERIA POLLUTANTS OF match BLENDED high AROMATICS ON LA92 CYCLE USING E10 AND E15.

Match Blended High Aromatics		**NO_x Emissions, g/mi**			**NMHC Emissions, g/mi**			**CO Emissions, g/mi**			**THC Emissions, g/mi**			**PM Emissions, mg/mi**		
Vehicle	**Test Cycle**	E10	E15	Change	E10	E15	Change	E10	E15	Change	E10	E15	Change	E10	E15	Change
Honda Accord	**LA92**	0.0036	0.0029	-19%	0.0085	0.00905	6%	0.06895	0.0682	-1%	0.00965	0.0099	3%	1.54	1.725	12%
Chevrolet Impala	**LA92**	0.00495	0.0045	-9%	0.0049	0.0041	-16%	0.2088	0.2351	13%	0.00525	0.00465	-11%	7.535	5.74	-24%
VW Jetta	**LA92**	0.0148	0.0139	-6%	0.0054	0.00585	8%	0.06405	0.0429	-33%	0.007	0.0074	6%	0.61	0.555	-9%
Kia Optima	**LA92**	0.0204	0.0183	-10%	0.00445	0.00395	-11%	0.13135	0.13565	3%	0.00515	0.00485	-6%	2.71	6	121%
Ford Fusion	**LA92**	0.00945	0.01435	52%	0.0042	0.0053	26%	0.1938	0.1225	-37%	0.0056	0.00685	22%	4.835	5.265	9%
Average				1%			3%			-11%			3%			22%

p value (two tail) of log transformed values	0.91			0.84			0.29			0.73			0.53

Table 5-e. UC RIVERSIDE STUDY-3 toxic POLLUTANTS OF SPLASH BLENDED LOW AROMATICS ON LA92 CYCLE USING E10 AND E15.

Splash Blended Low Aromatics		**Acetaldehyde Emissions, ug/mi**			**Formaldehyde Emissions, ug/mi**			**1,3-butadiene Emissions, mg/mi**			**Benzene Emissions, mg/mi**			**Potency Weighted Toxics (mg of 1,3 butadiene/mi equivalent)**		
Vehicle	**Test Cycle**	E10	E15	Change	E10	E15	Change	E10	E15	Change	E10	E15	Change	E10	E15	Change
Honda Accord	**LA92**	3.805	5.31	40%	1.61	0.785	-51%	0.025	0.01	-60%	0.485	0.315	-35%	0.108	0.064	-41%
Chevrolet Impala	**LA92**	2.31	2.735	18%	0.91	1.805	98%	0	0	0%	0.22	0.19	-14%	0.037	0.032	-14%
VW Jetta	**LA92**	2.845	2.505	-12%	1.2	1.595	33%	0.025	0.01	-60%	0.96	0.83	-14%	0.188	0.151	-20%
Kia Optima	**LA92**	1.925	2.105	9%	1.285	1.53	19%	0.03	0.01	-67%	0.29	0.185	-36%	0.079	0.042	-48%
Ford Fusion	**LA92**	3.165	2.985	-6%	3.715	2.285	-38%	0.055	0.045	-18%	0.335	0.3	-10%	0.112	0.096	-14%
Average				10%			12%			-41%			-22%	-27%	-27%	-27%
p value (two tail) of log transformed values				0.38			0.96			0.05			0.03			0.03

Table 5-e1. UC RIVERSIDE STUDY-3 Additional toxic POLLUTANTS OF SPLASH BLENDED LOW AROMATICS ON LA92 CYCLE USING E10 AND E15.

Splash Blended Low Aromatics		**Toluene Emissions, mg/mi**			**Ethylbenzene Emissions, g/mi**			**m,p-Xylene Emissions, mg/mi**			**0-Xylene Emissions, mg/mi**		
Vehicle	**Test Cycle**	E10	E15	Change	E10	E15	Change	E10	E15	Change	E10	E15	Change
Honda Accord	**LA92**	0.615	0.65	6%	0.075	0.085	13%	0.195	22%	0.128205	0.085	0.085	0%
Chevrolet Impala	**LA92**	0.24	0.22	-8%	0.015	0.015	0%	0.01	2%	0.5	0.01	0.01	0%
VW Jetta	**LA92**	0.645	0.5	-22%	0.05	0.045	-10%	0.15	13%	-0.16667	0.075	0.055	-27%
Kia Optima	**LA92**	0.6	0.51	-15%	0.065	0.045	-31%	0.175	11%	-0.4	0.045	0.03	-33%
Ford Fusion	**LA92**	0.735	0.435	-41%	0.12	0.03	-75%	0.3	6%	-0.81667	0.125	0.02	-84%

Average			-16%			-20%			-15%			-29%
p value (two tail) of log transformed values			0.27			0.27			0.36			0.21

Table 5-F. UC RIVERSIDE STUDY -3 TOXIC POLLUTANTS OF SPLASH BLENDED LOW AROMATICS ON LA92 CYCLE USING E10 AND E20.

Splash Blended Low Aromatics		**Acetaldehyde Emissions, ug/mi**			**Formaldehyde Emissions, ug/mi**			**1,3-butadiene Emissions, mg/mi**			**Benzene Emissions. mg/mi**			**Potency Weighted Toxics (mg of 1,3 butadiene/mi equivalent)**		
Vehicle	**Test Cycle**	E10	E20	Change	E10	E20	Change	E10	E20	Change	E10	E20	Change	E10	E15	Change
Honda Accord	**LA92**	3.805	6.37	67%	1.61	1.265	-21%	0.025	0.025	0%	0.485	0.36	-26%	0.108	0.086	-20%
Chevrolet Impala	**LA92**	2.31	4.44	92%	0.91	1	10%	0	0.01		0.22	0.24	9%	0.037	0.051	36%
VW Jetta	**LA92**	2.845	4.01	41%	1.2	1.5	25%	0.025	0.02	-20%	0.96	0.825	-14%	0.188	0.160	-15%
Kia Optima	**LA92**	1.925	2.355	22%	1.285	1.025	-20%	0.03	0.02	-33%	0.29	0.205	-29%	0.079	0.055	-31%
Ford Fusion	**LA92**	3.165	3.42	8%	3.715	3.335	-10%	0.055	0.05	-9%	0.335	0.27	-19%	0.112	0.096	-14%
Average				46%			-3%	0.027	0.025	-7%			-16%			-9%
p value (two tail) of log transformed values				0.03			0.60			0.13			0.07			0.35

Table 5-f1. UC RIVERSIDE STUDY-3 Additional TOXIC POLLUTANTS OF SPLASH BLENDED LOW AROMATICS ON LA92 CYCLE USING E10 AND E20.

Splash Blended Low Aromatics		**Toluene Emissions, mg/mi**			**Ethylbenzene Emissions, g/mi**			**m,p-Xylene Emissions, mg/mi**			**0-Xylene Emissions, mg/mi**		
Vehicle	**Test Cycle**	E10	E20	Change	E10	E20	Change	E10	E20	Change	E10	E20	Change
Honda Accord	**LA92**	0.615	0.605	-2%	0.075	0.08	7%	0.195	0.2	3%	0.085	0.085	0%
Chevrolet Impala	**LA92**	0.24	0.33	38%	0.015	0.025	67%	0.01	0.065	550%	0.01	0.03	200%
VW Jetta	**LA92**	0.645	0.505	-22%	0.05	0.035	-30%	0.15	0.1	-33%	0.075	0.045	-40%

Kia Optima	**LA92**	0.6	0.245	-59%	0.065	0.025	-62%	0.175	0.035	-80%	0.045	0.015	-67%
Ford Fusion	**LA92**	0.735	0.465	-37%	0.12	0.055	-54%	0.3	0.075	-75%	0.125	0.035	-72%
p value (two tail) of log transformed values				0.27			0.32			0.65			0.45

Table 5-g. UC RIVERSIDE STUDY-3 TOXIC POLLUTANTS OF match BLENDED LOW AROMATICS ON LA92 CYCLE USING E10 AND E15.

Match Blended Low Aromatics		**Acetaldehyde Emissions, ug/mi**			**Formaldehyde Emissions, ug/mi**			**1,3-butadiene Emissions mg/mi**			**Benzene Emissions mg/mi**			**Potency Weighted Toxics (mg of 1,3 butadiene/mi equivalent)**		
Vehicle	**Test Cycle**	E10	E15	Change	E10	E15	Change	E10	E15	Change	E10	E15	Change	E10	E15	Change
Honda Accord	**LA92**	3.805	4.38	15%	1.61	1.83	14%	0.025	0.015	-40%	0.485	0.245	-49%	0.108	0.064	-41%
Chevrolet Impala	**LA92**	2.31	3.41	48%	0.91	1.35	48%	0	0	0%	0.22	0.205	-7%	0.037	0.032	-14%
VW Jetta	**LA92**	2.845	2.69	-5%	1.2	0.85	-29%	0.025	0.015	-40%	0.96	0.915	-5%	0.188	0.151	-20%
Kia Optima	**LA92**	1.925	3.8	97%	1.285	0.955	-26%	0.03	0.02	-33%	0.29	0.19	-34%	0.079	0.042	-48%
Ford Fusion	**LA92**	3.165	3.79	20%	3.715	2.495	-33%	0.055	0.05	-9%	0.335	0.64	91%	0.112	0.096	-14%
Average				35%			-5%			-24%			-1%			-11%
p value (two tail) of log transformed values				0.10			0.54			0.03			0.63			0.36

Table 5-G1. A UC RIVERSIDE STUDY-3 Additional TOXIC POLLUTANTS OF MATCH BLENDED LOW AROMATICS ON LA92 CYCLE USING E10 AND E15.

Match Blended Low Aromatics		**Toluene Emissions, mg/mi**			**Ethylbenzene Emissions, g/mi**			**m,p-Xylene Emissions, mg/mi**			**0-Xylene Emissions, mg/mi**		
Vehicle	**Test Cycle**	E10	E15	Change	E10	E15	Change	E10	E15	Change	E10	E15	Change
Honda Accord	**LA92**	0.615	0.52	-15%	0.075	0.075	0%	0.195	0.18	-8%	0.085	0.06	-29%
Chevrolet Impala	**LA92**	0.24	0.29	21%	0.015	0.02	33%	0.01	0.015	50%	0.01	0.01	0%
VW Jetta	**LA92**	0.645	0.65	1%	0.05	0.06	20%	0.15	0.175	17%	0.075	0.06	-20%

Kia Optima	**LA92**	0.6	0.365	-39%	0.065	0.045	-31%	0.175	0.14	-20%	0.045	0.04	-11%
Ford Fusion	**LA92**	0.735	0.855	16%	0.12	0.125	4%	0.3	0.325	8%	0.125	0.085	-32%
Average				-3%			5%			9%			-19%
p value (two tail) of log transformed values				0.64			0.81			0.56			0.04

Table 5-H. UC RIVERSIDE STUDY-3 TOXIC POLLUTANTS OF MATCH BLENDED high AROMATICS ON LA92 CYCLE USING E10 AND E15.

Match Blended High Aromatics		**Acetaldehyde Emissions, ug/mi**			**Formaldehyde Emissions, ug/mi**			**1,3-butadiene Emissions mg/mi**			**Benzene Emissions mg/mi**			**Potency Weighted Toxics (mg of 1,3 butadiene/mi equivalent)**		
Vehicle	**Test Cycle**	E10	E15	Change	E10	E15	Change	E10	E15	Change	E10	E15	Change	E10	E15	Change
Honda Accord	**LA92**	3.7	7.025	90%	0.675	1.44	113%	0.035	0.045	29%	0.475	0.59	24%	0.116	0.145	26%
Chevrolet Impala	**LA92**	3.93	4.215	7%	1.38	1.255	-9%	0.02	0.01	-50%	0.305	0.285	-7%	0.072	0.059	-19%
VW Jetta	**LA92**	3.635	4.53	25%	1.835	1.13	-38%	0.015	0.03	100%	1.21	1.635	35%	0.221	0.308	40%
Kia Optima	**LA92**	2.585	3.05	18%	2.255	1.495	-34%	0.03	0.01	-67%	0.32	0.355	11%	0.085	0.070	-17%
Ford Fusion	**LA92**	2.5	4.505	80%	3.455	4.585	33%	0.045	0.07	56%	0.375	0.45	20%	0.109	0.147	35%
Average				44%			13%			13%			17%			13%
p value (two tail) of log transformed values				0.04			0.97			0.83			0.08			0.47

Table 5-h1. UC RIVERSIDE STUDY-3 Additional TOXIC POLLUTANTS OF MATCH BLENDED HIGH AROMATICS ON LA92 CYCLE USING E10 AND E15.

Match Blended High Aromatics		**Toluene Emissions, mg/mi**			**Ethylbenzene Emissions, g/mi**			**m,p-Xylene Emissions, mg/mi**			**0-Xylene Emissions, mg/mi**		
Vehicle	**Test Cycle**	E10	E15	Change	E10	E15	Change	E10	E15	Change	E10	E15	Change
Honda Accord	**LA92**	0.865	0.985	14%	0.125	0.15	20%	0.365	0.475	30%	0.085	0.1	18%
Chevrolet Impala	**LA92**	0.675	0.465	-31%	0.075	0.045	-40%	0.23	0.095	-59%	0.055	0.02	-64%

VW Jetta	**LA92**	0.965	1.305	35%	0.085	0.095	12%	0.325	0.495	52%	0.08	0.12	50%
Kia Optima	**LA92**	0.705	0.55	-22%	0.1	0.055	-45%	0.31	0.155	-50%	0.1	0.035	-65%
Ford Fusion	**LA92**	0.685	0.93	36%	0.09	0.12	33%	0.255	0.24	-6%	0.055	0.06	9%
Average				6%			-4%			-6%			-10%
p value (two tail) of log transformed values				0.88			0.60			0.50			0.42

Table 6. combined analysis of all data

Fuels		**NO_x**	**Organic Emissions**			**CO**	**PM mass emissions**	**Potency Weighted Toxics**
			NMHC	**THC**	**NMOG**			
E15 vs. E10 or E0	**Average**	3%	3%	2%	13%	-7%	28%	-2%
	p value (two tail) of log transformed values	0.93	0.72	0.90	0.93	0.0009	0.48	0.23
	No. of datapoints	66	42	29	24	66	24	22
E20 vs. E10 or E0	**Average**	+11%	1%	-1%	-16%	-9%	25%	4%
	p value (two tail) of log transformed values	0.07	0.60	0.35	0.004	0.0002	0.72	0.57
	No. of datapoints	77	32	41	24	78	15	12

Coordinating Research Council Study E-65-3

Table 6-A. CRC study E65-3 of Diurnal VOC evaporative Permeation emissions.

Vehicle	Diurnal VOC Permeation Emissions (mg/day)			Ozone-Forming Potential of Diurnal VOC permeation emissions (Ozone g/Day)		
	E10	E20	Change	E10	E20	Change
2001 Tacoma	468	508	9%	1.42	1.63	15%
2004 Taurus	123	102	-17%	0.29	0.24	-15%
2004 Sebring	64	75	17%	0.18	0.22	20%
2005 Tahoe	466	360	-23%	1.42	1.21	-15%
Average			-4%			1.3%
p value (two tail) of log transformed values			0.65			.999

Table 6-b. CRC STUDY E65-3 OF Steady-state VOC EVAPORATIVE PERMEATION EMISSIONS.

Vehicle	Steady-state VOC Permeation Emissions (mg/hour)			Ozone-Forming Potential of Steady-State VOC permeation emissions (ozone g/hour)		
	E10	E20	Change	E10	E20	Change
2001 Tacoma	35.2	43.4	23%	0.107	0.139	30%
2004 Taurus	6.36	5.42	-15%	0.015	0.013	-12%
2004 Sebring	4.65	5.38	16%	0.013	0.016	19%
2005 Tahoe	29.8	27.6	-7%	0.091	0.093	2%
Average			4%			10 %
p value (two tail) of log transformed values			0.75			0.42

Coordinating Research Council Study E-77-2[229]

Table 8-a. cRC study e-77-2 of static and cycle la92 running loss permeation using e10 at 7 and 10 psi and e20 at 8.5 psi.

	Static Permeation					**Running Loss Permeation**				
Vehicle	E10 7 psi (mg/ hr)	E10 10 psi Mg/hr	E10 Average between 7 and 10 psi (mg/hr)	E20 8.5 psi (mg/hr)	Difference between average E10 and E20	E10 7 psi (mg/ hr)	E10 10 psi (mg/ hr)	E10 Average between 7 and 10 psi (mg/hr)	E20 8.5 psi (mg/hr)	Difference between average E10 and E20
2001 Corolla	59.6	41.6	50.6	46.2	-9%	232.8	191.6	212.2	169.7	-20%
2001 Caravan	64.4	78.7	71.6	88.2	23%	812.2	858.1	835.2	1028.2	23%
2004 Escape	23.9	24.4	24.2	16.8	-30%	105.7	133.1	119.4	139.4	17%
2004 Highlander	12.2	10.4	11.3	19.3	71%	97.9	71.9	84.9	102.5	21%
2004 Camry	9.4	19.9	14.7	55.8	281%	56.3	138.3	97.3	410.6	322%
2006 Taurus	21.8	10.6	16.2	4.7	-71%	201.2	148.9	175.1	116.8	-33%
Average					44%					55%
p value (two tail) of log transformed values					0.86					0.43

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[229] Descriptions of each test are as follows:

- Static permeation: fuel system pressurized and monitored for vapor and fuel leaks at 86 °F.
- Running loss: two cycles of the LA-92 test at 86 °F.
- Hot soak: one hour immediately following LA-92 test.
- Diurnal test: California 3-day test, in which temperature is varied between 65 °F and 105 °F.

Table 8-b. CRC STUDY E-77-2 OF hot soak ANd diurnal (3-day) PERMEATION USING E10 AT 7 AND 10 PSI AND E20 AT 8.5 PSI.

Vehicle	**Hot Soak Permeation**					**Diurnal Permeation (3 Day)**				
	E10 7 psi (mg/ hr)	E10 10 psi (mg/ hr)	E10 Average between 7 and 10 psi (mg/hr)	E20 8.5 psi (mg/hr)	Difference between average E10 and E20	E10 7 psi (mg)	E10 10 psi (mg)	E10 Average between 7 and 10 psi (mg)	E20 8.5 psi (mg)	Difference between average E10 and E20
2001 Corolla	71.9	29.5	50.7	60.3	19%	5022.3	5266.7	5144.5	5145.4	0%
2001 Caravan	122.2	237.7	180.0	0	-100%	2722.1	3894.5	3308.3	4278.7	29%
2004 Escape	32.9	57.4	45.2	56	24%	1316	12705.2	7010.6	1662.7	-76%
2004 Highlander	0	1.6	0.8	0	-100%	723.9	816.4	770.15	1282.2	66%
2004 Camry	13.8	0	6.9	0	-100%	611.9	781.7	696.8	709.2	2%
2006 Taurus	0	0	0.0	4.9	NA	360.8	315	337.9	289.3	-14%
Average			47.3	20.2	-57%[230]			2878.0	2227.9	1%
p value (two tail) of log transformed values					0.86					0.65

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[230] Normally this percentage is calculated as the average of the column above, but it is not possible when there is a datapoint in which the base fuel emissions are 0. Instead in this case percentage change was calculated from the average emissions for each fuel.

Appendix 3: Estimated Changes in GHG Emissions and Upstream Air Pollutants from Expanded Use of Ethanol in California

Methodology and Calculations

1. Calculate Upstream Air Pollutant Emission Changes Due to Reduced Gasoline Use

The following expression was used to estimate the upstream gasoline emissions impact of E15:

Impact (tons per year) = Volume * $ED_{blendstock}$* EF * CF

Where:

Volume = reduction in gasoline volume (0.443 bgy)
$ED_{blendstock}$ = energy density of blendstock (119.53 MJ/gal)
EF = emission factor in g/MMBtu (see Table A1)
CF = conversion factor for MJ to MMBtu (947.82 MMBtu/MJ) and from grams to short tons (908,000 g/ton)

Table 1 a shows criteria pollutant emission rates from CaGREET3.0 for gasoline blendstock refining, blendstock transportation and distribution, and gasoline (+ethanol) distribution. Note that CaGREET3.0 does not have criteria pollutant emissions for crude oil extraction and crude oil transport, thus those components are omitted. Total emissions are shown in the last column.

Table 1 a. Gasoline Blendstock Upstream Emissions (g/MMBtu)

Pollutant	Refining: Feed Inputs	Refining: Intermediate Product Combustion	Refining: Non-Combustion Emissions	Transportation and Distribution	Gasoline Distribution	Total
VOC	3.41	0.25	2.30	0.083	0.075	25.9*
CO	10.6	2.57	1.15	0.280	0.257	14.9
NOx	15.3	5.84	1.36	0.734	0.686	23.9
PM2.5	0.51	0.38	0.16	0.012	0.008	1.07
SOx	6.97	10.8	4.40	0.171	0.052	22.4

* Includes 6.667 g/mmBTU from bulk terminal and 13.082 g/mmBTU from refueling stations.

Using emission factors in Table A1 and the energy densities and conversion factors identified in the formula above, the resulting air pollutant emissions impacts were calculated and summarized in Table 1 b for VOC, CO, NOx, PM2.5, and SOx.

Table 1 b. Reductions in Upstream Emissions in California Associated with Reduced Gasoline Use Moving from E10 to E15

Pollutant	Emission Reduction (tons per year)	Emission Reduction (grams per gallon of increased ethanol use)
VOC	1,414	1.98
CO	813	1.14
NOx	1,306	1.82
PM2.5	59	0.08
SOx	1,225	1.71

2. Calculate Upstream Air Pollutant Emission Changes Due to Increased Ethanol Use

As discussed in Section 8, the air pollutant emission impacts due to increased ethanol use are depended on (1) upstream ethanol transport emissions to blending terminals, and (2) finished fuel transport emissions to service stations.

The following expression was used to estimate the upstream ethanol emissions impact of E15 due to additional ethanol transport:

Impact (tons per year) = Volume * ED_{EtOH}* EF * CF

Where:

Volume = increase in ethanol volume (0.65 bgy)
ED_{EtOH} = energy density of ethanol (81.51 MJ/gal)
EF = emission factor in g/MMBtu (see Table A3)
CF = conversion factor for MJ to MMBtu (947.82 MMBtu/MJ) and from grams to short tons (908,000 g/ton)

Table 1 c shows rail emission rates for ethanol transport from the CaGREET3.0 model for an estimated average transport distance of 1,400 miles.[231] The approximate distance from the Arizona border to Los Angeles via rail is 220 miles. This analysis conservatively assumes 220 miles as the rail transport distance for the additional ethanol volumes coming from the Midwest, as the distance from the California border to the blending terminals at either northern or southern California. The emissions in the far right column adjust the emissions in the middle column for this distance.

Table 1 c. Emission Rates for the Transport of Ethanol From the Midwest by Rail

Pollutant	Emission Rate (g/MMBtu) to Transport Ethanol 1,400 miles	Emission Rate (g/MMBtu) to Transport Ethanol 220 miles within California
VOC	0.844	0.133
CO	2.564	0.403
NOx	16.94	2.661
PM2.5	0.497	0.078
SOx	0.405	0.064

Using emission factors in Table 1 c and the energy densities and conversion factors identified in the formula above, the resulting air pollutant emissions impacts associated with additional ethanol transport to blending terminals were calculated and summarized in Table 1 d for VOC, CO, NOx, PM2.5, and SOx.

Table 1 d. Increase in Upstream Emissions Due to Additional Ethanol Transport to Blending Terminals

Pollutant	Emission Increase (tons per year)	Emission Increase (grams per gallon of increased ethanol use)
VOC	7.22	0.0101
CO	21.9	0.0306
NOx	144.8	0.2023
PM2.5	4.23	0.0059
SOx	3.47	0.0048

The following expression was used to estimate the upstream ethanol emissions impact of E15 due to additional finished fuel transport:

Impact (tons per year) = Volume * ED_{E15}* EF * CF

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[231] 1,400 miles is the default transport distance in CaGREET3.0 for ethanol from the Midwest to California.

Where:

Volume = increase in finished fuel volume (0.21 bgy)
ED_{E15} = energy density of ethanol (107,780 Btu/gal)
EF = emission factor in g/MMBtu (see Table A5)
CF = conversion factor from grams to tons (908,000 g/ton)

The transport mode for finished E15 fuel from blending terminals to service stations is by heavy-duty truck. Table 1 e shows HDT transport emission rates in g/MMBtu for finished gasoline blended with ethanol from CaGREET3.0.

Table 1 e. Emission Rates for the Transport of Fuel from Blending Terminals to Service Stations

Pollutant	Emissions (g/MMBtu)
VOC	0.075
CO	0.257
NOx	0.686
PM2.5	0.008
SOx	0.052

Using emission factors in Table 1 e and the energy densities and conversion factors identified in the formula above, the resulting air pollutant emissions impacts associated with additional finished fuel transport to service stations were calculated and summarized in Table 1 f for VOC, CO, NOx, PM2.5, and SOx.

Table 1 f. Increase is Upstream Emissions Due to Additional Fuel Transport to Service Stations

Pollutant	Emission Increase (tons per year)	Emission Increase (grams per gallon ethanol increase)
VOC	1.86	0.0026
CO	6.42	0.0090
NOx	20.7	0.0289
PM2.5	0.18	0.0003
SOx	1.31	0.0018

Assuming refinery operations stay constant, total air pollutant emission impacts due to increased ethanol use are shown in Table 1 g.

Table 1 g. Total Increase in Upstream Emissions in California Associated with Increased Ethanol Use Moving from E10 to E15

Pollutant	Ethanol Transport (tons per year)	Additional Finished Fuel Transport (tons per year)	Total (tons per year)	Total (grams per gallon ethanol increase)
VOC	7.22	1.86	9.08	0.013
CO	21.9	6.42	28.4	0.040
NOx	144.8	20.7	165.5	0.231

PM2.5	4.23	0.18	4.41	0.006
SOx	3.47	1.31	4.78	0.007

If refinery operations decrease due to decreased demand for gasoline, the overall impact will be a net decrease in emissions of air pollutants in California. Table 1 h shows the overall emissions impacts after accounting for emissions benefits of reducing California CARBOB production by 443 million gallons as calculated above and shown in Table 1 b

Table 1 h. Upstream Emissions in California Associated with Increased Ethanol Use Moving from E10 to E15 if Refinery Operations are Reduced

Pollutant	Decrease due to Reduced Gasoline Use (tons per year)	Increase Due to Increased Ethanol Use (tons per year)	Overall Impact (tons per year)	Overall Impact (grams per gallon ethanol increase)
VOC	-1,414	+9.08	-1,405	-1.963
CO	-813	+28.4	-785	-1.096
NOx	-1,306	+165.5	-1,141	-1.593
PM2.5	-59	+4.41	-55	-0.076
SOx	-1,225	+4.78	-1,220	-1.705

3. Calculate Overall GHG Emissions Changes Due to E15

The GHG emission impacts of E15 are directly related to additional ethanol use, as well as increased total finished fuel transport to service stations. Thus, the following equation summarizes the net GHG calculation:

Net GHG Reduction = GHG Reduction from Increased Ethanol Use – GHG Increase from Additional Finished Fuel Transported to Service Stations

The following expression was used to estimate GHG emissions reduction of E15 due to additional ethanol use:

$$\textbf{GHG Impact (tons per year)} = \text{Volume}*(CI_{Gasoline}-CI_{ethanol})*ED_{ethanol}/CF$$

Where:

Volume = increase in ethanol volume (0.65 bgy)
$CI_{gasoline}$ = carbon intensity of CARBOB (100.82 gCO2e/MJ)[232]
$CI_{ethanol}$ = carbon intensity of ethanol (70.0 gCO2e/MJ)[233]
$ED_{ethanol}$ = 81.51 MJ/gallon
CF = 1,000,000 grams/metric ton

The following expression was used to estimate GHG emissions reduction of E15 due to additional finished fuel transport:

$$\textbf{GHG Impact (tons per year)} = \text{Volume}*EF_{trans}*ED_{E15}/CF$$

Where:

Volume = increase in finished fuel volume (0.21 bgy)
ED_{E15} = energy density of E15 (113.83 MJ/gal)
EF_{trans} = CaGREET3.0 emission factor for fuel transport (0.199 g/MJ)
CF = 1,000,000 grams/metric ton

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[232] LCFS 2018 Final Regulation Order, https://www.arb.ca.gov/regact/2018/lcfs18/fro.pdf
[233] Q2, 2018 LCFS Data Summary. https://www.arb.ca.gov/fuels/lcfs/lrtqsummaries.htm

The net overall reduction in GHG emissions from expanded use of ethanol where E15 is used in all vehicles for which it is approved is presented in Table 1 i.

Table 1 i. Net Overall Reduction in GHG Emissions from Expanded Ethanol Use in California

	Emission reduction (metric tons per year)	Emission reduction (kg/gallon of increased ethanol use)
Increased Ethanol Use	1,632,890	2.512
Increased Fuel Transport	-4,756	-0.023
Net Reduction	1,628,134	2.505

4. Calculate California-Specific GHG Emissions Changes Due to E15

The approach can be used to estimate California-specific GHG emissions reduction. While the volumes of increased ethanol and finished fuel are the same, the relative carbon intensities (CIs) of gasoline and ethanol must be adjusted to account for emissions that occur in California only. For ethanol, the only California-specific emissions component is ethanol transport that occurs within the state boundaries.[234] According to CaGREET3.0, ethanol transport emissions are approximately 3% of total Midwest corn ethanol average CI as shown in Table 1 j. CARB reported that the average ethanol CI as of Quarter 2, 2018 of the Low Carbon Fuel Standard program was 70.0 gCO2/MJ. This means that California-specific ethanol transport emissions are 2.28 gCO2/MJ.

Table 1 j. Ethanol Carbon Intensity by Process

Process	Carbon Intensity (gCO2e/MJ)
Feedstock Farming	3.0
Chemicals, N_2O in soil	25.16
Feedstock Transport	8.84
Ethanol Production	28.92
Co-product Credit	-14.14
Ethanol Transport	2.44
Land Use	19.8
Denaturant	0.97
Total	75.0
CA Average Total	**70.0**
California-Specific Ethanol Transport	**2.28**

For gasoline, California-specific crude recovery and transport CI should be used. According to OPGEE 2.0, this value was slightly higher than the California crude oil average mix and is shown in Table 1 k along with GHG emissions for the rest of CARBOB production processes.

Table 1 k. CARBOB Carbon Intensity by Process

Component	Carbon Intensity (gCO2e/MJ)
Crude Recovery and Transport (California Crude Average)	11.78
Refining	15.10
Exhaust	73.94

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[234] California-located ethanol plant emissions should not be counted, because they are not expected to provide the “marginal” ethanol needed to meet E15.

Total CA Crude Average	100.82*
Crude Recovery and Transport (California Crude Only)	**16.61**
Total CA-Specific	**105.65**

* Does not include CARBOB Transport and Distribution CI of 0.33 gCO2/MJ available in CaGREET3.0.

Thus, the difference in California-specific CIs between gasoline and ethanol is 105.65-2.28 = 103.37 CO2e/MJ. The difference in CIs for the global GHG impact analysis described in Step 3 above is 100.82-70.0= 30.82 gCO2/MJ. The California-specific GHG emission benefits of increased ethanol use are 103.37/30.82 or 3.35 times greater than the GHG total benefits. Therefore, California only GHG benefits can be estimated by multiplying total benefits due to increased ethanol use by a factor of 3.35 as shown in Table 1 l. The emission increase due to additional fuel transport is as calculated above.

Table 1 l. California-Specific Reduction in GHG Emissions from Expanded Ethanol Use in California

	Emission reduction (metric tons per year)	Emission reduction (kg/gallon of increased ethanol use)
Increased Ethanol Use	5,470,182	8.416
Increased Fuel Transport	-4,756	-0.023
Net Reduction	5,465,426	8.408