Technical/Regulatory Guidance

Biofuels: Release Prevention, Environmental Behavior, and Remediation

September 2011

Prepared by
The Interstate Technology & Regulatory Council
Biofuels Team

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BIOFUELS-1

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ITRC (Interstate Technology & Regulatory Council). 2011. *Biofuels: Release Prevention, Environmental Behavior, and Remediation.* BIOFUELS-1. Washington, D.C.: Interstate Technology & Regulatory Council, Biofuels Team. www.itrcweb.org.

ACKNOWLEDGEMENTS

The members of the Interstate Technology & Regulatory Council (ITRC) Biofuels Team wish to acknowledge the individuals, organizations, and agencies that contributed to this technical and regulatory guidance document.

As part of the broader ITRC effort, the Biofuels Team effort is funded by the U.S. Department of Energy, U.S. Department of Defense, and the U.S. Environmental Protection Agency and through ITRC's Industry Affiliates Program.

Current members of the Biofuels Team are listed in Appendix F. The Biofuels Team wishes to recognize the efforts of specific team members who provided valuable input during the development of this document. The team recognizes the efforts of the following state environmental personnel who contributed to the development of this guidance document:

- Team Leader Bill Gidley, Nebraska Department of Environmental Quality
- William Burns, Florida Department of Environmental Protection
- Cassandra Jobe, Kentucky Department of Environmental Protection
- Tom Higgins, Adam Sekely, and Mark Toso, Minnesota Pollution Control Agency
- Valerie Garrett, Missouri Department of Natural Resources
- Michael Verchick, Nevada Division of Environmental Protection
- David Leavitt, Oklahoma Corporation Commission
- Marcy Kirk, Oregon Department of Environmental Quality
- Ramesh Belani, Gregory Bowman, Michael Maddigan, Jeff Painter, and Lisa Wilt, Pennsylvania Department of Environmental Protection
- Alison Hathcock, South Carolina Department of Health and Environmental Control
- Steve Mueller, formerly of the Wisconsin Department of Commerce
- Mark Thiesse, Wyoming Department of Environmental Quality

The team recognizes the valuable contributions to the development of the document by the following stakeholder, academic representatives, and local government representatives:

- Iona Black, Tribal Stakeholder
- Sat Mellacheruvu, Broward County Pollution Prevention
- Jeff Short, ITRC Stakeholder
- Roy Spalding, University of Nebraska at Lincoln

The team also recognizes the contributions of the following federal agency personnel, who provided valuable comments, input, and suggestions for this document’s improvement during its development and draft reviews:

- Andrea Barberry, Kirby Biggs, and Scott Jacobs, USEPA
- Marshall Williams, U.S. Army

Finally, the team would like to recognize the efforts and contributions of the following consultants and industry representatives:

- Bruce Bauman, American Petroleum Institute
- Tim Buscheck, Catalina Espino Devine, Ravi Kolhatkar, and Amy Wormsley, Chevron
- Dora Chiang, AECOM
- Denice Nelson, Arcadis
- Brent Stafford, Shell Projects and Technology
- David Tsao, British Petroleum

The Biofuels Team also wishes to acknowledge the hard work and dedication of Stacey Kingsbury, ITRC Program Advisor, whose efforts made immeasurable contributions to the quality of the document.

EXECUTIVE SUMMARY

Biofuels are a relatively new category of renewable transportation fuels whose manufacture and consumption are increasing due, in part, to usage mandates and incentives, both in the United States and abroad. In the United States, federal mandates have increased the volume of renewable fuel required to be blended into U.S. transportation fuels from 9 billion gal in 2008 to 36 billion gal in 2022 (Public Law 110-140). Biofuels are expected to account for a large proportion of the renewable fuel increase. A number of U.S. states have passed mandates on the use of biofuels or biofuel blends and/or have producer or retailer incentive programs, labeling requirements, or state fleet fuel purchase/use requirements. Other countries and the European Union have also adopted renewable fuel use targets and offer biofuel tax credits for use of biofuels in the transportation sector.

Definitions of “biofuels” in current use vary. The ITRC Biofuels Team defines the term as liquid fuels and blending components produced from renewable biomass feedstocks used as alternative or supplemental fuels for internal combustion engines. Biofuels are often blended with a conventional petroleum-based fuel to form a biofuel blend, such as E85 (approximately 85% ethanol, 15% gasoline) and B20 (approximately 20% biodiesel, 80% diesel).

The introduction and expanded use of any new transportation fuel poses challenges with respect to understanding its potential impacts to the environment; biofuels are no exception. Except for low-percentage biofuel blends (such as E10, approximately 10% ethanol, 90% gasoline), biofuels differ from conventional fuels with respect to their physical, chemical, and biological properties. Because of the different properties of biofuels and the biofuel component of higher-percentage biofuel blends, these fuels exhibit either known or reasonably projected differences in environmental behavior in comparison to conventional fuels.

The differences in biofuel properties, and therefore environmental behavior, can be evaluated using a multimedia approach. Multimedia evaluations gauge the potential human health and environmental impacts of contaminants in a given fuel or fuel additive. Such an approach was first proposed and recommended by an independent Blue Ribbon Panel convened to advise the U.S. Environmental Protection Agency on the impacts of methyl tertiary-butyl ether–blended gasoline on the environment (USEPA 1999a). To develop regulatory and technical guidance, the ITRC Biofuels Team focused on selected regulatory aspects of biofuel releases using the multimedia evaluation approach as a framework. This framework can be used for both currently commercially available and future biofuels and incorporates a risk-based approach to release characterization and remediation strategies.

An assessment of the potential frequency of biofuel releases depends on the likely release points within the biofuel supply chain infrastructure coupled with consumption (current and future projections). Once the fuels are manufactured, the supply chains for biofuel and petroleum differ primarily with respect to bulk fuel transportation from manufacturing facilities to bulk depots/supply terminals. For example, bulk biofuels (such as denatured fuel ethanol and biodiesel) are transported from manufacturing facilities mostly by tanker truck, railcar, and tank barges, as compared to petroleum, which is transported from refineries to bulk depots/supply

terminals mostly through pipeline networks. Therefore, an increased likelihood of releases from transportation accidents for biofuels exists.

Additional release scenarios arise from the use of incompatible materials in equipment within the supply chain, such as storage tanks, hosing, piping, dispensers, etc. For example, the solvent nature of biofuel can scour the sediment, sludge, rust, and scale built up in an underground storage tank system deposited from previously stored conventional fuels. Furthermore, leak detection equipment may fail if not compatible with the biofuel being stored. Methods to prevent these releases include the use of compatible materials and adjusting management practices.

Once released into the environment, short-term response strategies generally focus on containment and recovery of released biofuel, elimination of any immediate threats, and prevention of transport to sensitive receptors such as waterways and conduits such as sewer lines. If the released biofuel is not contained and recovered, its fate and transport depend highly upon site conditions, the release scenario, and the fraction of biofuel in the release. Nonetheless, some key biofuel properties—including physical-chemical properties, biodegradation, and interactions with other potential contaminants—can provide insight into their fate, transport, and potential impacts to the environment.

The physical and chemical properties of biofuels offer insight into their mobility in different environmental media. Physical properties of fuels, such as the specific gravity and viscosity, can play a role in determining the extent of impact to soil and water. Chemical properties can significantly influence the persistence of volatile fuels in ground and surface waters. For example, fuels with high Henry's law constants (the ratio of vapor pressure to aqueous solubility) tend to easily partition from the aqueous phase into the atmosphere. Hydrophilic fuel components with high aqueous solubility, low Henry's law constant, and low sorptivity (e.g., ethanol) are dissolved in the aqueous phase and transported at rates similar to that of flowing groundwater. Conversely, hydrophobic fuel components (e.g., benzene) preferentially partition to organic materials and are transported at rates much lower than that of water.

Biodegradation rates are affected by several factors, including contaminant concentration, complexity of the chemical structure, the presence of microorganisms, and bioavailability. Biofuels, such as biodiesel, ethanol, and butanol, have simple structures and are readily biodegradable under both aerobic and anaerobic conditions (Corseuil et al. 1998; Lovanh, Hunt, and Alverez 2002; Feris et al. 2008). The relatively rapid and ubiquitous biodegradation of biofuels in soil and groundwater induces changes to the biological and geochemical environments, including stimulation of microorganisms, exertion of oxygen demand, and production of biomass/exudates and methane.

Methane can be produced at petroleum sites, but the volumes are often small, and any methane in soil gas typically degrades rapidly. In contrast, biofuels and biofuel blends have the potential for producing significantly more methane due to their biodegradable nature, but it may not be detected until months after the release. The accumulation of methane in some scenarios can represent a potentially high-risk situation that may require emergency mitigation measures or the use of engineering controls (ITRC 2007b). Methane can become a risk driver for a biofuel release investigation, requiring additional site characterization and longer-term monitoring to assess delayed generation. Biofuel release site conceptual models should therefore consider potential methane accumulation and methane vapor migration pathways (Jewell and Wilson 2011). In addition, an evaluation for potential remobilization of preexisting contamination following a biofuel release should be considered.

Site characterization following a biofuel release may include monitoring for biofuel-related parameters such as methane and methane precursors, specific biofuel contaminants, and the potential dissolved oxygen depletion in surface water. The physical properties of biofuels may require some changes to a site investigation design, such as the use of wire-wrapped or shorter well screens for groundwater monitoring and the use of material-compatible equipment, sampling for additional parameters, and the use of additional field screening equipment (meters).

Once characterized, development of a long-term response strategy for a biofuel release requires consideration of a number of factors, including the type of biofuel, extent and magnitude of the release, regulatory threshold contaminants, and source receptor pathways. A risk-based approach to remediation can be followed to tailor responses to site-specific conditions and risks, as allowed by state policies. These long-term response strategies may include any or all of the following: monitored natural attenuation (MNA), controls (institutional or engineered), and/or contaminant source reduction through implementation of an active remedy.

Because of the biodegradable nature of current widely used biofuels (ethanol and biodiesel), MNA may be an amenable remediation strategy. Under some scenarios, accumulation of methane from biofuel biodegradation may require special attention when MNA is used because of a potential explosive hazard risk. Additionally, because of the potential lag time before methane may be generated, long-term monitoring and/or engineering controls should be evaluated as part of a site management strategy.

In some cases, an active remedy may be desired as part of the response strategy. However, few case studies involving active remediation for biofuels currently exist. Therefore, the ITRC Biofuels Team conducted a detailed analysis of remedial technologies that have been used or are likely to be used when the remediation driver is a biofuel or biofuel degradation product or may be used when petroleum contaminants are the remediation driver but biofuel remediation is also desired. Evaluated technologies include those that have been documented in biofuel release case studies and those identified by states as having been used for biofuel remediation. These technologies were then evaluated with respect to their ability to exploit the physical, chemical, and biological properties of biofuels to achieve remedial goals. For site-specific remediation projects, a technology evaluation and selection process was developed based on considerations for evaluating expected effectiveness, such as the targeted medium; contaminant of concern; and the physical, chemical, or biological property of the contaminant of concern targeted for remediation.

Stakeholder concerns associated with the release prevention, environmental behavior, and remediation of accidental biofuel releases generally depend on the location and timing of the incident, emergency response, and long-term management. In most cases, chronic, small total volume releases impact fewer stakeholders unless the situation is not addressed for an extended period of time. However, the other extreme of sudden catastrophic, large total volume releases can be of immediate and enduring concern to stakeholders.

Response to different biofuel release scenarios, from emergency response to longer-term site management, differ somewhat from well-established petroleum release response procedures. Because of the different biological, chemical, and physical properties of biofuels, the release causes and fate and transport in the environment vary somewhat, with consequences for site characterization considerations and longer-term response strategy development. These property differences provide insight into the differences between biofuels and petroleum fuels, providing a framework for not only currently available biofuel, but also emerging biofuels.

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1. INTRODUCTION

Environmental issues related to releases of conventional transportation fuels are generally understood. However, the introduction of new fuels poses challenges with respect to understanding the potential impacts to the environment. For example, methyl tertiary-butyl ether (MTBE) was blended with gasoline in the United States beginning in 1979, initially as an octane booster and subsequently as an oxygenate. The volume of MTBE produced and blended with gasoline increased over the years in response to the requirements of the U.S. Environmental Protection Agency (USEPA) Clean Air Act Amendments for oxygenated fuels. However, impacts of releases of MTBE-blended gasoline from leaking underground storage tanks (USTs), surface spills, and other sources caused unanticipated groundwater impacts (ITRC 2005).

Biofuels are a relatively new category of transportation fuels whose manufacture and consumption have increased recently and are projected to continue increasing. Releases of biofuels to the environment have occurred and may potentially increase in frequency as the manufacture and consumption of biofuels increases. Since their physical, chemical, and biological properties differ from those of conventional fuels, release scenarios, environmental impacts, and remediation of biofuel releases also differ in some respects. Because of the potential impact to the environment, the Interstate Technology & Regulatory Council (ITRC) Biofuels Team was convened to provide technical and regulatory guidance on issues related to releases of biofuels.

The Biofuels Team has used a multimedia evaluation approach in developing this guidance. A multimedia approach to evaluating new fuels and fuel additives was first proposed and recommended by an independent Blue Ribbon Panel convened to advise USEPA on the impacts of MTBE-blended gasoline on the environment (USEPA 1999a). Multimedia evaluations are used to evaluate the potential human health and environmental impacts of contaminants of concern (COCs) in a given fuel or fuel additive and to assess how they may interact with the flora, fauna, and natural resources within different environmental media (air, water, land).

A full-scale multimedia evaluation is a comprehensive review of a number of different related topics encompassing the expertise of a wide variety of professions. For example, California has instituted a multimedia evaluation process for new fuels (see www.arb.ca.gov/fuels/multimedia/multimedia.htm). For this document, the ITRC Biofuels Team has focused on selected aspects of biofuel releases of regulatory concern using this multimedia evaluation approach as a framework.

1.1 Definition of Key Terms

For the purposes of this document, the term “biofuel” is applied to liquid fuels and blending components produced from renewable biomass feedstocks used as alternative or supplemental fuels for internal combustion engines (ICEs). In addition, “biofuel blend” describes a biofuel that has been mixed with a conventional petroleum-based fuel.

Federal agencies and states may have different definitions of "biofuels." For example, the U.S. Energy Information Administration (EIA) defines "biofuels" as liquid fuels and blending components produced from biomass feedstocks used primarily for transportation (EIA 2010). State regulatory definitions of biofuel vary based on blend percentage. For example, some states consider fuels with 10% ethanol (E10) a biofuel, and others do not. Out of 25 states responding to the ITRC Biofuels Team survey conducted in 2009, ten states defined fuels with 10% ethanol or greater as a biofuel, six states defined blends greater than E10 as a biofuel, one state defined fuels with 85% ethanol (E85) or greater as a biofuel. Biodiesel blends are considered biofuel by 15 states responding to the survey, two states define blends above a specified percentage as a biofuel, and one state defines only 100% biodiesel (B100) as a biofuel.

Biofuels are considered a subset of renewable fuels, which are renewable energy sources that can be replenished in a short period of time. Biofuels currently in use or expected to be in use in the near future are addressed in this document and include alcohols, such as ethanol and biobutanol, and biodiesel.

Biofuels not currently in widespread use as transportation fuels and therefore not covered in this document include the following:

- some alcohols—such as propanol
- ethers—alkyl ethers (e.g., ethyl tertiary-butyl ether [ETBE]) derived from biologically produced alcohols (see ITRC 2005 for more information on ethers)
- methane (natural gas)—biologically produced in landfills, manure digesters, etc.; can be liquefied and/or compressed and used directly in ICEs or processed into other biofuels and blending agents
- biomass-to-liquids (BTLs)—renewable gasoline or diesel fuel made through gasification of carbon-based biomass into bio-oil and/or synthesis gas (syngas), followed by conversion of the bio-oil or syngas to the final biofuel and chemically indistinct from petroleum fuels
- others—including 2,5-dimethyl furan (DMF), dimethoxymethane (DMM, or methylal), and a host of other bioproducts that can be used as drop-in fuels and/or blended with petroleum fuels

Other terms often used when discussing biofuels include the following:

- additives—Provide or enhance various performance features related to the satisfactory operation of engines, as well as to minimize fuel handling and storage problems (ASTM 2009).
- alternative fuels—In the United States, EIA (www.eia.gov) defines "alternative fuels" as fuels not substantially petroleum that yield substantial energy security and environmental benefits. The term does not include alcohol or other blended portions of primarily petroleum-based fuels used as oxygenates or extenders, i.e., MTBE, ETBE, other ethers, and the 10% ethanol portion of E10.
- biomass-based diesel—Renewable fuel that is a biodiesel as defined in Section 312(f) of the Energy Policy Act of 1992 (42 U.S. Code 13220[f]), which according to USEPA is a diesel fuel substitute produced from nonpetroleum renewable resources that meets the registration

requirements for fuels and fuel additives established by USEPA under Section 7545 of the Clean Air Act.

- cellulosic biofuels—Any renewable fuel, not necessarily ethanol, derived from any cellulose, hemicellulose, or lignin, each of which must originate from renewable biomass (40 Code of Federal Regulations Part 80 [40 CFR §80]).
- conventional gasoline—A mixture of compounds, called "hydrocarbons," refined from petroleum crude, plus additives to improve its stability, control deposit formation in engines, and modify other characteristics. Conventional gasoline also may contain oxygenates, such as MTBE and ethanol to meet octane needs (American Petroleum Institute [API] website, www.api.org).
- fossil fuel—A general term for any hydrocarbon that may be used for fuel: chiefly petroleum, natural gas, and coal (Bates and Jackson 1987).
- natural gasoline—A natural gas liquid with a vapor pressure intermediate between condensate and liquefied petroleum gas. This liquid hydrocarbon mixture is recovered at normal pressure and temperature and is much more volatile and unstable than commercial gasoline (Oilfield Glossary, www.glossary.oilfield.slb.com).
- oxygenates—An oxygen-containing, ashless compound, such as an alcohol or ether, that can be used as a fuel or fuel supplement (ASTM 2009).
- petroleum (Greek, meaning "rock oil")—A naturally occurring complex liquid hydrocarbon (a.k.a. "crude oil"), which after distillation and removal of impurities yields a range of combustible fuels, petrochemicals, and lubricants. Also used as a general term for all naturally occurring hydrocarbons, whether gaseous, liquid, or solid (Bates and Jackson 1987).

1.2 Document Scope

The focus of this guidance is on biofuels and the biofuel component of blends. Instances when the biofuel component of a blend affects the behavior of the petroleum component of the blend are noted. The scope is generally limited to biofuels where the physical, chemical, and biological properties are distinct from those exhibited by petroleum fuels and therefore will exhibit either known or reasonably projected differences in environmental behavior in comparison to petroleum fuels. While this document is intended to be applicable to commercially available or pending biofuels, ethanol and biodiesel are used most often as examples in the document.

In most cases, low-percentage biofuel blends (such as E10 and B5) do not exhibit physical, chemical, and biological properties distinct from petroleum fuels when released to the environment and therefore are not discussed in detail in this document. However, where relevant, this document addresses considerations for these types of biofuel blends.

Because of the different uses of the term "biofuel," it is also important to identify fuels that are *not* addressed in this document:

- Substances not legally recognized as motor vehicle fuels, such as neat vegetable oils and recycled greases (also called "waste cooking oil" or "yellow grease").
- Fuels indistinguishable from petroleum-based fuels. For example, renewable diesel is a broad class of non-ester-based diesel fuels derived from nonpetroleum resources that can be

processed in conventional refineries either separately or along with petroleum stocks using hydrotreating methods. Renewable diesel is chemically indistinguishable from petroleum diesel (i.e., meets the ASTM D975 petroleum diesel fuel standard). The environmental issues related to renewable diesel and other fuels indistinguishable from petroleum-based fuels are already well understood and therefore are not covered.

Two states currently have published guidance on ethanol-related releases (MassDEP 2011, MPCA 2010). This document is focused in scope to meet the greatest needs identified by state environmental regulatory agencies on the topic of biofuels based in part on the results of a 2009 survey of ITRC member states conducted by the ITRC Biofuels Team. Of the 25 states that responded, the highest-ranked topics of interest in biofuels were identified as follows (more than one choice was allowed):

- site investigation/characterization (20 states)
- remediation technologies (19 states)
- release response scenarios and case studies (15 states)
- regulatory guidance (14 states)
- biofuels storage and distribution facilities (14 states)
- biofuels production facilities (12 states)
- pollution prevention (11 states)

The guidance in this document is intended to meet the needs identified in the survey by providing a framework and recommendations for evaluating the causes and prevention of post-manufacture biofuel releases; impacts to soil, sediment, surface water, and groundwater; characterization methods; and remedial responses to releases to these media. In addition, potential stakeholder concerns pertinent to biofuel releases as scoped in this document are presented.

A number of issues regarding biofuels could not be adequately addressed in one guidance document. These issues include the following:

- sustainability
- manufacturing processes
- end-user considerations
- biofuel policies
- air quality

Sustainability issues in particular are often raised with respect to the manufacture and use of biofuels. The concept of “sustainability” has been defined by the World Commission on Environment and Development as “meeting the needs of the present without compromising the ability of future generations to meet their own needs.” The sustainability of biofuels is an important and currently debated topic. More information on sustainability issues associated with biofuels is available from other sources, including a number of reference documents are available (e.g., FAO 2008 and GAO 2009). Applicable sustainability criteria and indicators may include but are not limited to the following:

- net energy balance (total fuel input vs. energy yield)
- greenhouse gas and other air emissions
- surface and groundwater quality impacts from fertilizer and pesticide usage
- ecotoxicity, biodegradability, and bioavailability
- water resource impacts
- agricultural and land use impacts
- by-products/waste generation and recycling/reuse
- use of genetically modified organisms for feedstocks and production
- inputs into production processes (renewable sources)

Environmental issues associated with the manufacturing processes for biofuels include a variety of regulatory concerns, including waste and air quality issues. Addressing these issues would be best covered in a separate guidance document; therefore, this document discusses manufacturing processes as a point in the fuel supply chain. However, because of the potential significance of the environmental issues associated with manufacture, Appendix A provides a summary of the manufacturing processes.

1.3 Intended Audience

The primary audience for this guidance document is state regulators who have responsibility for the following potential aspects associated with biofuel:

- regulatory responsibility related to biofuel storage, distribution, releases, or release prevention
- inspections at production facilities (with respect to releases of end product)
- inspections of storage and dispensing systems
- site investigation and characterization
- spill response and remediation

Other audiences include other regulators, potentially responsible parties, contractors, and stakeholders. This guidance provides these audiences with a common understanding of the causes and prevention of releases; potential environmental impacts to soil, surface water, and/or groundwater; and appropriate methods for site characterization and remediation, as well as an understanding of regulatory expectations.

1.4 Biofuel Summary Descriptions

Currently, the two most widely used biofuels are ethanol/ethanol blends and biodiesel/biodiesel blends. Biofuels are the subject of active research and development, and additional, future-generation biofuels may become commercially available. Summary descriptions of these biofuel types are provided as follows.

1.4.1 Ethanol and Ethanol-Blended Fuels

Ethanol (also called ethyl alcohol, or C_2H_5OH) is typically made by fermenting the sugar derived from a variety of feedstocks such as corn, sugar cane, beet, and grain sorghum, among others. In the United States, corn is used almost exclusively as an ethanol feedstock (EIA 2007).

Following ASTM D4806-11, *Standard Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark-Ignition Engine Fuel* (ASTM 2011b), the following terminology is used in this document:

- fuel ethanol—ethanol with impurities common to its production, including water but not denaturants
- denaturant—a material added to fuel ethanol to make it unsuitable for beverage use
- denatured fuel ethanol (DFE), also known as E95—ethanol made unfit for beverage use by the addition of 2%–5% hydrocarbon denaturants

Some ethanol fuel mixtures, such as E10 and E85, have "E" numbers that describe the approximate percentage of ethanol in the mixture by volume. ASTM standards apply to some ethanol fuel blends, while others, such as E85 and E15, do not have standards (Table 1-1). E85 was previously defined by ASTM standards (D5798-10a, ASTM 2010c) as consisting of 70%–85% DFE and 30%–15% hydrocarbons by volume. However, ASTM standards have been revised to facilitate blending of ethanol fuel blends that meet seasonal vapor pressure requirements by establishing a new, lower minimum ethanol content. It should be noted, however, that the Energy Policy Act of 1992 defines alternative fuels as blends of 85% or more alcohol (or such other percentage, but not less than 70%). Therefore, not all ethanol fuel blends for flexible-fuel vehicles meet current alternative fuel requirements.

Table 1-1. Ethanol fuel blends description and standards

Fuel	Description	ASTM standard
E85	A commercial trade name representing an alternative fuel consisting of 70%–85% DFE by volume as defined in the Energy Policy Act of 1992	No adopted ASTM standard
Ethanol fuel blends for flexible-fuel vehicles	Fuel produced for use in ground vehicles equipped with flexible-fuel spark-ignition engines containing 51%–83% ethanol; may be referred to at retail as "ethanol flex-fuel"	D5798-11
Intermediate ethanol blends	Intermediate blends of DFE and gasoline >E10 and <E51	No adopted ATSM standard
E10	Gasoline with up to 10% DFE by volume	D4814-10 (standard for gasoline)

Producers of ethanol for use in fuel in the United States do not distribute their product in a nondenatured form because of federal regulations; therefore, DFE is the typical ethanol fuel stock distributed from manufacturing locations to bulk storage locations. Typical denaturants used in the United States include natural gasoline, gasoline components, and unleaded gasoline. Other denaturants are used around the world and may or may not be required. For example, 1%

methanol and 10 parts per million (ppm) denatonium benzoate (Bitrex) are used in the United Kingdom as a denaturant (Denatured Alcohol Regulations 2005).

At bulk storage locations, ethanol is blended with gasoline before transportation to dispensing locations (such as retail gas stations). The currently most widely used ethanol blends within the United States are E10 and E85. E10 blends can be used in the ICEs of most modern automobiles and light-duty vehicles without need for any modification of the engine or fuel system. However, higher blends can be used only in specially designed vehicles known as flexible-fuel vehicles (FFVs). Ethanol-blended fuels may also contain additives such as metal deactivators, corrosion inhibitors, oxygenates, and antioxidants.

1.4.2 Biodiesel and Biodiesel-Blended Fuels

Biodiesel can be defined as fatty acid monoalkyl esters (FAMEs), transesterified oils derived from vegetable oils or animal fats, blended with or used in place of conventional diesel fuels that conform to ASTM D6751 specifications (ATSM 2011a). This definition is consistent with U.S. federal and state laws and the original equipment manufacturer guidelines. FAME also refers specifically to methylated esters, as opposed to the more general monoalkyl esters. The terms "FAME" and "biodiesel" are often used interchangeably because fatty acid methyl esters are the most common biodiesel produced. Fatty acid ethyl esters (FAEE) are another type of biodiesel, but FAME is the most common form of biodiesel currently produced.

Biodiesel is similar to petroleum diesel fuel and can be used in the same applications, but it has different chemical, handling, and combustion characteristics. Biodiesel feedstocks are typically derived from virgin or waste vegetable oils such as soybean, sunflower, palm, and rapeseed oil. The U.S. biodiesel industry relies almost exclusively on soybean oil as a feedstock, whereas other countries use other feedstocks such as rapeseed oil in Europe and palm oil in Indonesia. Current research in biodiesel includes the production of oils from nonfood crops.

Biodiesel and biodiesel blends are described by "B" numbers to designate the percentage of biodiesel in a mixture by volume. Biodiesel can be blended in any ratio with petroleum diesel. Table 1-2 provides examples of and standards for biodiesel and biodiesel blends.

Table 1-2. Biodiesel and biodiesel blends descriptions and standards

Fuel	Description	ASTM standard
B100	Biodiesel fuel blend stock; legally registered as a fuel and fuel additive with USEPA under Section 211(b) of the Clean Air Act	D6751-11
>B20 to <B100	A blend of petroleum-distillate and biodiesel fuel that contains between 21% and 99% biodiesel	No standard adopted
>B5 to B20	A blend of petroleum-distillate and biodiesel fuel that contains between 6% and 20% biodiesel	D7467-10
Up to B5	Fuel blends of up to 5% biodiesel fuel are considered a fungible component of conventional petroleum-based diesel fuel	D975 (same as petroleum diesel standard)

Before the adoption of ASTM D7467, the U.S. Department of Defense (DOD) developed its own specifications for B20 biodiesel blends, as defined in the "Commercial Item Description: Diesel Fuel, Biodiesel Blend (B20)" (CID-A-A-59693A, January 15, 2004). According to this specification, B20 must consist of 20±1% (by volume) of biodiesel conforming to ASTM D6751, and the balance of #1 or #2 diesel fuel conforming to ASTM D975 or to the military specification A-A-52557. B20 that meets DOD requirements has been approved for use in Army engines and vehicles other than combat and tactical vehicles (DOD 2009).

B20 is used chiefly by vehicle fleets, which receive credit for using alternative-fuel vehicles (AFVs) without having to purchase new vehicles. B20 is also available to individual consumers with diesel vehicles. Biodiesel requires a variety of additives to address issues such as oxidative instability, cold-flow limitations, microbial contamination, increased water affinity, and increased NO_x emissions. These additives create a broad range of chemical variations in the biodiesel blend stock or final fuel.

1.4.3 Future Generation Biofuels

Current liquid biofuels based on sugar and starch crops (for ethanol) and oilseed crops (for biodiesel) are generally referred to as first-generation biofuels. Future-generation biofuels, also known as advanced biofuels, are categorized as follows:

- current biofuels (ethanol, biodiesel) produced through new methods
- new molecules produced through existing methods
- new molecules produced through new methods

Research on a number of advanced biofuels is currently under way. The two most likely advanced biofuels to become commercially available in the near future are lignocellulosic (LC) ethanol and biobutanol because continuing research is developing more efficient and cost-effective ways of producing them. A number of pilot and demonstration plants are either operating or under development around the world.

LC biomass can include dedicated biofuel crops (e.g., switchgrass, *Miscanthus* spp., *Pennisetum* spp., and other high-biomass-producing crops) or agricultural residue (corn stalks, sugarcane bagasse, wood wastes, and other sources). Ethanol can be produced from LC biomass but requires a more complex first step of saccharification, which enzymatically converts lignin, cellulose, and/or hemicellulose into sugars. Once converted, the subsequent fermentation and separation processes more closely follow traditional corn-based ethanol production, although different impurities may be encountered. Once processed into ethanol, however, the physical, chemical, and biological properties of the final product from LC biomass are indistinguishable from sugar- or starch-based ethanol, and therefore guidance in this document pertaining to ethanol is applicable to LC-derived ethanol.

Similarly, biobutanol is an alcohol that can be produced conventionally by fermenting the sugars derived from domestically grown crops, such as corn and sugar beets, and other LC biomass, such as fast-growing grasses and agricultural waste products. However, only three of the four isomers of butanol (1-butanol, 2-butanol, and isobutanol) can be produced through fermentation. Like ethanol, biobutanol can be blended as a fuel oxygenate to meet USEPA Clean Air Act requirements. In addition, the physical, chemical, and biological properties of butanol are similar to those of ethanol; therefore, guidance in this document specific to ethanol is generally applicable to butanol.

1.5 Current and Projected Volumes of Biofuels

1.5.1 Biofuel Mandates and Other Use Requirements

The Energy Policy Act of 2005 (Public Law 109-58) established the first Renewable Fuel Standard (RFS) program. The original RFS program increased the volume of renewable fuel to be blended into gasoline to 7.5 billion gal by 2012. The RFS applies to transportation fuel sold or introduced into commerce in the 48 contiguous states. However, the USEPA Administrator is authorized, upon a petition from Alaska or Hawaii, to allow the RFS to apply in that state(s). Hawaii petitioned USEPA to opt into the RFS, and the Administrator approved that request. Therefore, statements that the RFS applies to U.S. transportation fuel refer to the 48 contiguous states and Hawaii.

Under the Energy Independence & Security Act (EISA) of 2007 (Public Law 110-140), the RFS program was expanded by increasing the volume of renewable fuel required to be blended into U.S. transportation fuel from 9 billion gal in 2008 to 36 billion gal in 2022. Each November, EISA requires USEPA to set renewable fuel standards for cellulosic biofuel, biomass-based diesel, advanced biofuel, and total renewable fuel that must be used in transportation fuel for the following year. These standards are based on gasoline and diesel projections from the EIA and assessments of production capability for cellulosic biofuel from industry. The regulatory requirements for RFS apply to domestic and foreign producers and importers of renewable fuel used in the U.S. (USEPA 2010a).

The 36 billion gallon renewable fuel goal for 2022 can include up to 15 billion gal of conventional biofuels, while the balance (at least 21 billion gal) must be composed of advanced biofuels. Of the 21 billion gallon advanced biofuels target, EISA requires that at least 16 billion gal be produced from cellulosic feedstocks. However, advanced biofuels are at the earliest stages of being commercially produced in the United States, and a number of logistical and technical challenges must still be overcome before they are economically viable (GAO 2009).

In addition to mandates, energy objectives for federal fleets with 20 or more vehicles have been established as required in the Energy Policy Acts of 1992 and 2005 (first two bullet items below) and Executive Order 13423 (remaining three bullet items below). Federal agencies are to do the following:

- acquire AFVs as 75% of all new light-duty vehicle acquisitions
- use only alternative fuel in AFVs, unless granted a waiver
- increase overall alternative fuel use by 10% annually
- reduce petroleum consumption by 2% annually through 2015
- purchase plug-in hybrid electric vehicles when available and at a reasonable cost

These requirements apply to all light-duty vehicles that weigh ≤8500 pounds; however, certain law enforcement, emergency, and military tactical vehicles are exempt (DOD 2009). Federal agencies are permitted to meet up to 50% of their AFV acquisition requirements by using biodiesel (Title XII of Section 101(a) of the Omnibus Consolidated and Emergency Supplemental Appropriations Act of FY 1999 [Public Law 105-277]).

A number of U.S. states have passed renewable fuel standards and mandates on the use of biofuels or biofuels blends (Table 1-3). In addition, some states have one or more of the following: producer or retailer incentive programs, labeling requirements, or state fleet fuel purchase/use requirements. Additional information on state RFS policies is available in published documents (such as Brown, Cory, and Arent 2007 and NRC 2010) and the EIA's Alternative Fuels and Advanced Vehicles Data Center website (www.afdc.energy.gov).

Industrial Use of Biofuels

While not mandated, some industries are using or exploring the use of biofuels, such as the airline industry (Commercial Aviation Alternative Fuels Initiative, www.caafi.org) and the railroad industry (IAIS 2009).

In addition to the United States, some countries and the European Union have adopted mandatory and nonmandatory targets for use of biofuels in the transportation sector. For example, Brazil has required the use of ethanol in gasoline since 1976. Similarly, in 2003, the European Commission adopted Directive 2003/30/EC, which is aimed at promoting the use of biofuels and other renewable fuels in the transportation sector and setting nonmandatory biofuels targets. Along with usage mandates, biofuel tax credits are also common worldwide to promote the use of biofuels (Kojima, Mitchell, and Ward 2007).

1.5.2 Current and Projected Consumption of Biofuels

Ethanol is currently the most widely used biofuel in the United States (Table 1-4) and worldwide, most notably Brazil, where vehicles run on either hydrous ethanol or an ethanol-blended fuel (E20 or E25). Biodiesel is used to a much lesser extent than ethanol in the United States, although it is the most commonly used biofuel in the European Union (FAO 2008). The consumption of ethanol and biodiesel is projected to increase worldwide (Figures 1-1 and 1-2).

1.6 Biofuel Toxicity

Chemical-specific toxicity data may be used to assess risk to human health and the environment posed by releases of biofuel to the environment. Available toxicity information for the two most widely used biofuels (ethanol and biodiesel) and isobutanol is summarized below; future generation biofuels may require additional research to establish toxicity. Biofuel additives may be toxic; however, many of these additives are proprietary, and toxicity data are generally not publicly available.

Ethanol toxicity has been established based on exposure for its use as an industrial chemical (UNEP 2004a). Ethanol has been found to be a human health hazard only at doses associated with consumption of alcoholic beverages. In the environment, ethanol has a low hazard profile based on its biodegradability and volatility. Acute aquatic toxicity data indicate 96-hour lethal concentration 50 (LC_{50}) values for fish (*Pimephales promelas* and *Salmo gairdneri*) in the order of 11,000–14,000 mg/L and for invertebrates consistently over 1,000 mg/L.

Table 1-3. State renewable fuels standards and mandates as of August 2011

State	Status	Ethanol	Biodiesel	Comments
FL	Current	9%–10%		
HI	Current	10%		At least 85% of unleaded gasoline must be E10
LA	Within 6 months of DFE production meeting or exceeding a minimum annual volume of 50 million gal and the price equal to or below average wholesale price of conventional gasoline for a period of not less than 60 days	2%		Requirement for total fuel sold by volume
	Within 6 months of cumulative monthly production meeting or exceeding 10 million gal		2%	Requirement for total fuel sold by volume
MA	Implementation may be delayed due to lack of supply, lack of blending facilities, or unreasonable cost; as of June 2010, the formal requirement suspended on grounds of unreasonable cost		2% 3% 4% 5%	July 1, 2010 July 1, 2011 July 1, 2012 July 1, 2013
MN	Current May 1, 2012 (April to October only) May 1, 2015 (April to October only)		5% 10% 20%	2012 and 2015 use mandates may be effective year-round if an ASTM specification or equivalent federal standard exists to adequately address cold-weather technical issues
	Current August 30, 2013	10% 20%		2013 requirement may be waived based on USEPA approval of higher-blend usage
MO	Current	10%		Premium gasoline exempt; potential waivers based on price
MT	Within 1 year after in-state production of 40 million gal maintained for at least 3 months	10%		Potential waivers based on in-state production levels
NM	July 1, 2012		5%	Potential waivers based on price
OR	Current	10%		High-octane gasoline exempt; potential suspension based on supply
	Current		5%	
PA	Within 1 year after in-state production of 350 million gal of cellulosic ethanol	10%		
	Within one year of in-state production of: • 40 million gal of biodiesel • 100 million gal of biodiesel • 200 million gal of biodiesel • 400 million gal of biodiesel		 2% 5% 10% 20%	
WA	Current	2%	2%	Requirement for total fuel sold by volume
	180 days after in-state feedstocks and oil-seed crushing capacity can meet a 3% requirement		5%	Requirement for total fuel sold by volume

Source: U. S. Department of Energy, Alternative Fuels and Advanced Vehicles Data Center, www.afdc.energy.gov/afdc.

Table 1-4. Fuel ethanol, biodiesel, and gasoline consumption in the United States

Year	**Consumption (millions of gallons)**			
	Gasoline	**Ethanol**	**Diesel**	**Biodiesel**
2004	138,283	3,552	62,258	27
2005	138,723	4,059	63,165	91
2006	140,146	5,481	62,192	261
2007	140,646	6,886	63,210	358
2008	134,644	9,683	58,262	316
2009	137,924	11,037	52,731	339
2010	138,491	13,189	N/A	222

Sources: U.S. Dept. of Energy (ethanol and biodiesel) (www.afdc.energy.gov/afdc/data/fuels.html), EIA 2010 (gasoline and diesel) (http://tonto.eia.doe.gov/energyexplained).

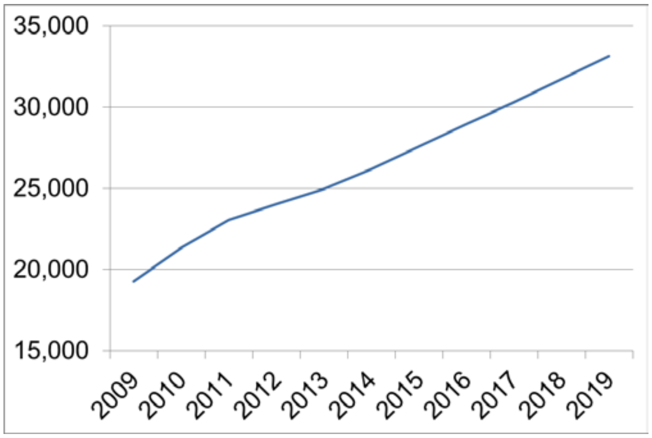

Figure 1-1. World ethanol production projections, 2009–2019. *Source*: FAPRI 2010.

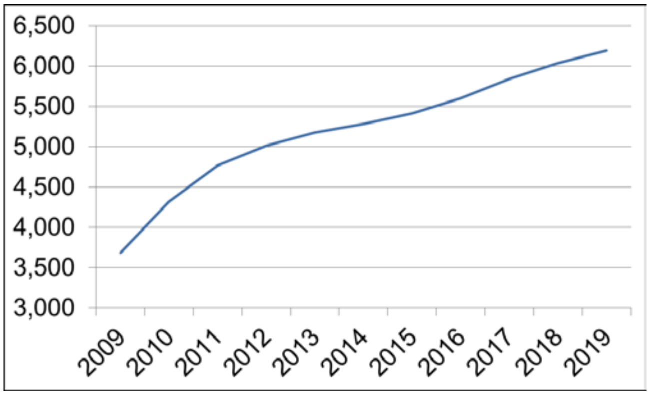

Figure 1-2. World biodiesel production projections, 2009–2019. *Source*: FAPRI 2010.

Chronic toxicity data indicate LC_{50} values above 100 mg/L in fresh water and marine invertebrates (UNEP 2004a). Microorganisms have been shown to be more resistant to ethanol toxicity, where inhibition in the presence of ethanol has been observed at high concentrations ranging 6%–10% (vol/vol) [60g/L to 100 g/L]) (Nelson, LaPara, and Novak 2010; Heipieper and deBont 1994). However, at nontoxic levels, ethanol can stimulate rapid growth of microorganisms that can result in the depletion of dissolved oxygen (DO) in surface water and lead to potentially detrimental impacts to aquatic life (Section 3.5.2).

Biodiesel toxicity is still the subject of research. Biodiesel (B100, without additives) has very low mammalian toxicity with lethal dose 50 (LD_{50}) values greater than 5000 mg/kg when administered orally to rats (Peterson and Moller 2005). Biodiesel has been shown to be less toxic than diesel for soil microorganisms, toxic at concentrations up to 12% w/w as compared to diesel fuel, which exhibits toxic properties at concentrations higher than 3% w/w (Lapinskiene, Martinkus, and Rebzdaite 2006). Recent experimental investigations for the California Tier II Risk Assessment for biodiesel included a series of aquatic toxicity tests conducted on seven fuel types (Ginn et al. 2010), including neat biodiesel (B100) derived from two feedstocks; B20 blends from both feedstocks; both B20 blends with an antioxidant additive; and ultralow-sulfur diesel (ULSD) as a reference for comparison. The conclusions reached included the following:

- The biodiesel test materials without the antioxidant additive (neat biodiesels [B100] and their B20 mixtures) were not shown to produce detectable toxicity in some species (mysid, topsmelt, and fathead minnow) but did cause toxicity in others (algae cell growth, water flea survival and/or reproduction, and abalone shell development).
- Biodiesel blends exhibited somewhat increased toxicity to subsets of tested species as compared to ULSD.
- Biodiesel blends with the antioxidant additive exhibited increased toxicity for a smaller subset of tested species.[1]

Isobutanol toxicity has low acute toxicity by all routes and is rapidly metabolized to isobutyraldehyde and isobutyric acid in rodents and humans. Isobutanol is not persistent in the environment and is not likely to bioaccumulate in food webs. Acute aquatic toxicity data indicate 96-hour LC_{50} values for fish (*Pimephales promelas*) of 1430 mg/L and for invertebrates of 1100–1300 mg/L (UNEP 2004b).

1.7 Summary and Document Overview

Releases of biofuels to the environment have occurred and may potentially increase in frequency based on projected increases in the manufacture and use of biofuels. The physical, chemical, and biological properties of biofuels can influence the frequency of releases, magnitude of impact, and response actions related to their release. Because this document is intended to be applicable to both currently available and future biofuels, these considerations are presented with respect to physical, chemical, and biological properties. Therefore, this document provides biofuel-specific guidance for both current and future biofuels for the following:

- an assessment of potential release scenarios and release prevention measures (Section 2)
- evaluation of fate and transport in the environment (Section 3)
- considerations for site characterization of a biofuel release (Section 4)
- long-term response strategies (Section 5)

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[1] Note: Additives other than the one tested may have different effects on toxicity.

- potential stakeholder concerns (Section 6)
- appendices for additional information, a checklist, case studies, and tables for supplementary information and guidance

2. BIOFUEL RELEASES

This section covers the potential frequency of biofuel releases, short-term release response considerations, and recommendations for preventing biofuel releases. As the projected usage of biofuel increases due to mandates (as discussed in Section 1), the potential frequency of releases may increase due to higher handling and transfer requirements. The potential frequency of biofuel releases is assessed in this section by first describing the general biofuel supply chain and then evaluating the supply chain infrastructure with respect to potential release points, release causes, potential media impacts, and materials compatibility issues. Recommendations for preventing biofuel releases summarize the differential impact that biofuels pose on the frequency of fuel releases. This section also describes planning and emergency procedures specific to biofuel release response, which must account for the different behaviors of biofuels.

2.1 Release Scenarios along the Biofuel Supply Chain

The supply chains for biofuel (Figure 2-1) and petroleum (Figure 2-2) differ primarily with respect to the type of manufacturing facility and the modes of bulk fuel from the manufacturing facility to the bulk depot/supply terminal transport. Although not shown on Figure 2-1, a secondary supply chain is also required to provide denaturant to ethanol manufacturing facilities prior to bulk transport of DFE. The differences in the two supply chains are relevant when considering the overall potential frequency for releases due to the increased handling and transfer associated with managing the supply chain.

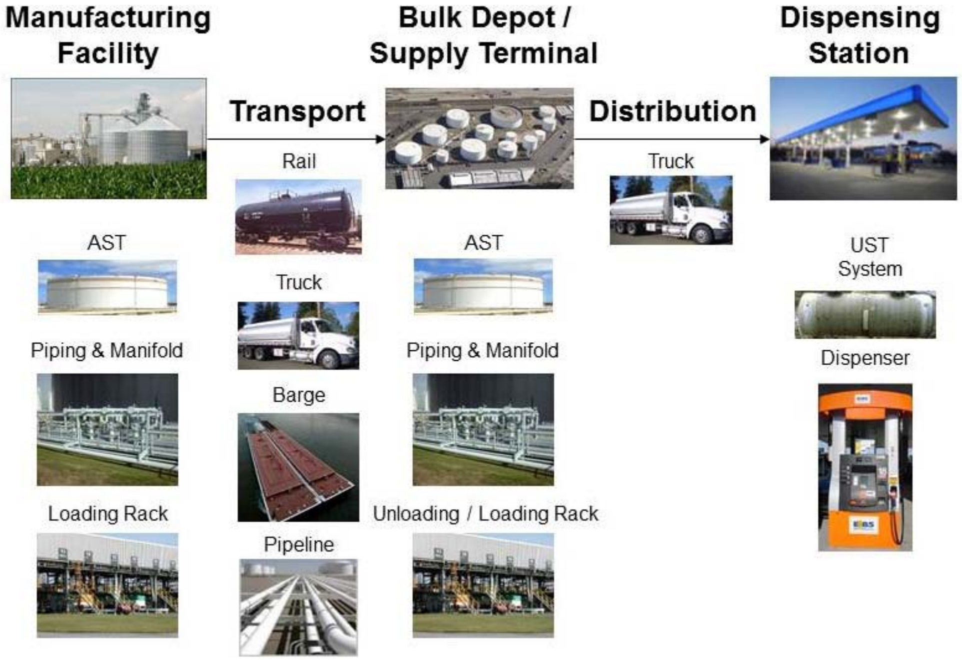


Figure 2-1. Generic biofuel supply chain.

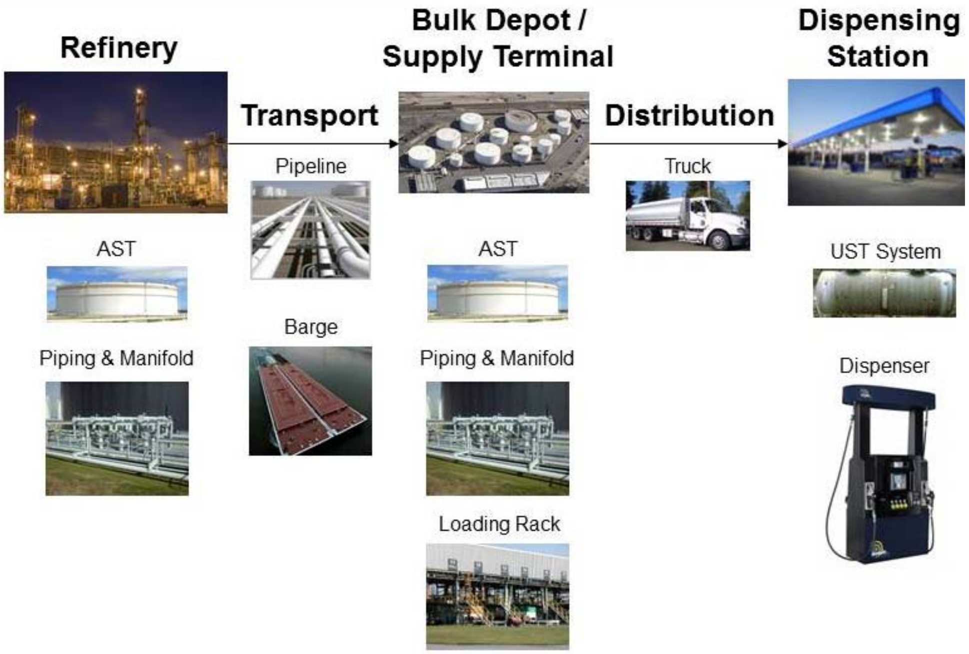


Figure 2-2. Generic petroleum supply chain.

Table 2-1 provides for each point in the biofuel supply chain a summary of the fuel types, geographic locations, potential release scenarios, and potential release frequency. Release scenarios were evaluated based on Biofuel Team members' evaluation of historic petroleum releases compared to the potential for release of biofuel. Release scenarios, including the type of biofuel released, location, volume, and site characteristics, influence the fate and transport of the biofuel once released into the environment, as discussed later in Section 3.

2.1.1 Biofuel Manufacturing Facilities

Biofuel manufacturing facilities, also known as biorefineries, have several unifying traits:

- Feedstock inputs include biological materials (e.g., corn, lignocellulose, oilseeds).
- Processes include physical (e.g., mechanical, thermal, separation), chemical (e.g., acids, bases, reagents), and/or biological (saccharification, fermentation) steps.
- Manufactured outputs include bulk biofuel (e.g., ethanol, biodiesel) and other bioproducts (e.g., animal feed, glycerine).
- Waste streams include air emissions (e.g., CO_2, NO_x, SO_x, particulate matter), wastewater (e.g., biochemical oxygen demand [BOD], total suspended solids, vinasse, distillers' grains with solubles), and/or solid waste (e.g., corn stover, bagasse).
- General locations are in and around agricultural regions to reduce feedstock transportation costs.

Appendix A provides more information on the manufacturing process of biofuels.

Table 2-1. Biofuel supply chain release scenarios, volumes, and throughput or frequency statistics

Supply chain point	Scenarios	Potential volume	Throughput or frequency statistics
Bulk biofuel			
Manufacturing facility produces bulk biofuels from agricultural feedstocks. Facilities often concentrated in agricultural regions.[a]	Minor accidents or chronic releases from equipment (e.g., piping and manifold system, loading rack)	Small volumes to large volumes accumulated over time.	Total U.S. production capacity of current biofuels equals approximately 0.93 million barrels (1 U.S. barrel = 42 U.S. gal) of fuel ethanol and 0.17 million barrels of biodiesel per day (2010 data).[b]
	Catastrophic storage tank failure, typically aboveground storage tanks (ASTs), less commonly USTs	ASTs: broad range of sizes ranging up to 11 million gal or more; USTs: up to 35,000 gal; partial to full storage capacities possible, depending on the conditions of the incident and response activities to contain and recover product.	
Transportation of bulk biofuels from manufacturing facility to bulk depots, within the supply network, and/or to the supply terminal. Releases likely to occur in proximity to the manufacturing facility or bulk depot/supply terminal, or within the transportation (roadway) supply routes.	Tanker truck accident	Tanker trucks: ~8,000–10,000 gal (DOE n.d., “Ethanol Distribution”); partial to full transport capacities possible, depending on the conditions of the accident (i.e., degree of damage, fire, etc.) and emergency response to contain and recover product.	The number of tanker truck accidents resulting in a material release of automotive fuels (flammable liquids) has averaged just over 1,000 per year (DOT 2010), which equates to a frequency of 1 in 25,000 fuel deliveries in the United States. This statistic includes both bulk transport and blended biofuel distribution. Approximately 1,250 tanker trucks carrying bulk biofuels would be required per day to produce the current volume of E10 and B5 blended biofuels.[c]

Supply chain point	Scenarios	Potential volume	Throughput or frequency statistics
Bulk biofuel			
Transportation of bulk biofuels from manufacturing facility to bulk depots, within the supply network, and/or to the supply terminal. Releases likely to occur in proximity to the manufacturing facility or bulk depot/supply terminal, or within the transportation (railway) supply routes.	Train car derailment	Railcars: ~25,000–30,000 gal per railcar (DOE n.d., "Ethanol Distribution"); unit trains of up to 70–100 railcars possible. Partial to full transport capacities possible, depending on the conditions of the accident (i.e., degree of damage, fire, etc.) and emergency response to contain and recover product.	Over a 10-year time frame, train derailments averaged just over 2,000 per year (DOT n.d.), although the severity and whether material releases (including whether the material included petroleum or biofuels) resulted from the incidents was not investigated. Approximately 415 train cars carrying bulk biofuels would be required per day to produce the current volume of E10 and B5 blended biofuels.
Transportation of bulk biofuels from manufacturing facility to bulk depots, within the supply network, and/or to the supply terminal. Releases likely to occur on waterways in proximity to the manufacturing facility or bulk depot/supply terminal, or within the transportation supply routes.	Tank barge incident	Tank barges: 420,000–630,000 gal barges typical; 1.26 million gal barges possible (USDA 2007). Partial to full transport capacity releases possible, depending on the conditions of the accident (i.e., degree of damage, fire, etc.) and emergency response to contain and recover product.	Tank barge spill results in an average of 200,000 gal of oil products released into waterways annually (Venosa 2010). The average oil spill rate (1997–2003) is 2.16 gal per 1 million gal moved by tank barge (American Waterways Operators 2004). Approximately 20 barges carrying bulk biofuels would be required per day to produce the current volume of E10 and B5 blended biofuels.

Supply chain point	Scenarios	Potential volume	Throughput or frequency statistics
Bulk or blended biofuel			
Bulk depot/supply terminal network historically developed for handling, storing, and distributing petroleum, most often interconnected by petroleum pipelines. Same network is now used to also receive bulk biofuels through various transportation avenues and create blended biofuels for distribution.	Minor accidents or chronic releases from equipment (e.g., piping and manifold system, loading/unloading racks)	Small volumes to large volumes accumulated over time.	The estimated number of bulk depots and supply terminals in the United States as of 2010 is 1,350 (IRS n.d.). Any or all of these facilities are likely to be handling and transferring bulk biofuel, bulk petroleum, and blended fuel based on widespread use of E10.
	Catastrophic storage tank failure, typically ASTs, less commonly USTs	ASTs: broad range of sizes ranging up to 11 million gal or more; USTs: up to 35,000 gal. Partial to full storage capacities possible, depending on the conditions of the incident and response activities to contain and recover product.	
Blended biofuel			
Distribution of blended biofuels from supply terminals to dispensing stations. Releases likely to occur in proximity to the supply terminal or within the distribution (roadway) supply routes to dispensing facilities.	Tanker truck accident	Tanker trucks: ~8,000–10,000 gal (DOE n.d., "Ethanol Distribution"). Partial to full transport capacities possible, depending on the conditions of the accident (i.e., degree of damage, fire, etc.) and emergency response to contain and recover product.	The number of tanker truck accidents resulting in a material release of automotive fuels (flammable liquids) has averaged just over 1,000 per year (DOT 2010), which equates to a frequency of 1 in 25,000 fuel deliveries in the United States. This statistic includes both bulk transport and blended biofuel distribution. An average of 10–15 tanker trucks per month is required to provide E10 to one retail site.[d] Distribution of higher-blend alcohol fuels and biodiesel is expected to increase as the number of dispensing stations offering these biofuels increases.

Supply chain point	Scenarios	Potential volume	Throughput or frequency statistics
Blended biofuel			
Dispensing stations are locations where blended fuels are received from distribution tanker trucks, stored, and dispensed to consumers. Widespread distribution, especially in population centers and along interstate roadways.	Minor accidents or chronic releases from equipment (e.g., UST system, dispenser system) or customer accidents/ spills	Small volumes to large volumes accumulated over time.	In 2009, there was an estimated 160,000 standard automotive dispensing stations in the United States; the average volume of sales of all grades of gasoline is estimated at 118,000 gal per month (NACS 2010). Minnesota has the greatest number of E85 retail stations (349 sites in 2010) averaging over 4,000 gal per month sold per site (Minnesota Department of Commerce 2011). The numbers of B20 and E85 dispensing sites in the United States are updated monthly by DOE, Alternative Fuels and Advanced Vehicles Data Center (DOE n.d., "Ethanol: Equipment"). Other dispensing stations include facilities for marine craft, public transportation, agricultural cooperatives, military bases, etc. and may expand to include airplane and rail fuel dispensing stations. The numbers of biofuel dispensing stations may be expected to increase.
	Catastrophic storage tank failure, typically USTs, less commonly ASTs	USTs: typically 15,000 gal up to 35,000 gal at large truck stops; ASTs: 1,000 and 3,000 gal per tank (DOE n.d., "Alternative"). Partial to full storage capacities possible, depending on the conditions of the incident and response activities to contain and recover product.	

[a] Ethanol and domestic biodiesel manufacturing refineries are concentrated in the upper Midwest (GAO 2007) although concentration is less pronounced for biodiesel refineries (NBB n.d.). Cellulosic manufacturing facilities are likely to be concentrated in the southeast United States.

[b] Production rates calculated from data as follows: commercial corn ethanol facilities produce 0.4–160 (average 67, n = 213) million gal per year (Nebraska Energy Office n.d.); commercial biodiesel facilities produce 0.03–160 (average 18, n = 142) million gal per year (NBB n.d.).

[c] For this and all subsequent such estimates: 2.2 million barrels of bulk gasoline represents 90% of 2.4 million barrels of E10 fuel; therefore, 0.24 million barrels of bulk ethanol are needed. 0.24 million barrels = 10.26 million gal of bulk ethanol. To transport 10.26 million gal of bulk ethanol, 1,026 tanker trucks are required (assuming 10,000-gal capacity per truck). Similarly, this number becomes 342 railcars (30,000-gal capacity) or 16 barges (630,000-gal capacity). 1.0 million barrels of bulk diesel represents 95% of 1.053 million barrels of B5 fuel; therefore, 0.053 million barrels of bulk biodiesel are needed. 0.053 million barrels = 2.21 million gal of bulk biodiesel. To transport 2.21 million gal of bulk biodiesel, 221 tanker trucks are required (assuming 10,000-gal capacity per truck). Similarly, this number becomes 73 railcars (30,000-gallon capacity) or 4 barges (630,000-gal capacity). 1,026 + 221 = 1,247 tanker trucks (rounded to 1,250). 342 + 73 = 415 railcars. 16 + 4 = 20 barges.

[d] Based on the average gross throughput at a typical neighborhood gasoline retail station of 120,000 gal/month and the typical capacity of a tanker truck of 8,000–10,000 gal.

Regardless of the biofuel being produced, biofuel manufacturing facilities typically employ similar equipment. In addition to ASTs, biorefineries have distribution piping and a manifold leading to a loading rack where biofuel is offloaded onto a transport such as a truck, railcar, or barge. At ethanol production facilities in the United States, multiple ASTs (or less commonly, USTs) store nondenatured ethanol, denaturant, and DFE. Aboveground distribution piping and a control manifold typically connect the storage tanks.

Bulk Transportation

Rail

Truck

Barge

Pipeline

Bulk Depot and Supply Terminal

AST

Piping & Manifold

Unloading / Loading Rack

DFE is typically created by directly blending the nondenatured ethanol and denaturant in the storage tank in a process known as splash blending. Alternatively, denaturant can be introduced into the nondenatured ethanol in the distribution piping itself prior to either storage or loading onto a bulk transport in a process known as ratio blending.

2.1.2 Bulk Transportation

Possible transportation methods for bulk biofuels (i.e., DFE or B100) from the manufacturing facility to a bulk depot/supply terminal include tanker truck, railcar, and tank barges. In general, existing pipelines have not been used to transport biofuels until only very recently because of the physical/chemical properties of biofuels. For example, the hygroscopic characteristic of ethanol and potential to increase pipe corrosion has made transport via pipeline impractical (API 2007). However, a pipeline was retrofitted with ethanol-compatible materials and opened in 2009 in Florida for DFE transport; other ethanol-compatible pipelines are in various stages of consideration, construction, and/or operation in the United States, Brazil, and other countries. In contrast, almost all petroleum products are transported from the refinery to the bulk depot/supply terminal through pipeline networks. In the United States, this network is estimated to span 95,000 miles (Pelsoci 2005).

2.1.3 Bulk Depot and Supply Terminal

From the manufacturing facility, bulk biofuels are transferred to a network of bulk depots and supply terminals. These facilities are fed by offloading the bulk biofuels from tanker trucks, railcars, or barges, depending on accessibility. Typically, depots contain an unloading rack (at the roadway, rail spur, or waterway), a truck loading rack, aboveground distribution piping and manifold system, and several ASTs.

These intermediate "transloading" stops are used to supply bulk biofuels to terminals downstream in the network. These intermediate transloading stops employ unloading racks at rail spurs or waterways, aboveground distribution piping and manifold to control the flow, ASTs to store the bulk biofuel, and a tank truck loading rack. Supply terminals are similar in design to depots except that terminals are where bulk biofuels are blended with petroleum to create the blended biofuels that are distributed to dispensing stations.

The use of bulk depots in biofuel supply chain differs from their use in the petroleum supply chain in two respects: (a) in the petroleum supply chain, transfers are typically via pipeline, and (b) bulk depots typically transport, store, and distribute only fungible fuel without additives.

Like bulk depots, supply terminals employ unloading racks for tanker trucks and/or similar equipment for rail cars or barges if fed through those transport routes. Furthermore, terminals have separate ASTs (or USTs in a few cases) for storing the bulk biofuel (i.e., DFE or B100) and bulk petroleum (i.e., E0 or B0) prior to blending. Terminals also typically contain many storage tanks, aboveground distribution piping and manifolds, and one loading rack.

The distribution piping is often dedicated to either the bulk biofuel or the bulk petroleum. Splash blending (simultaneous feeds) or sequential blending (fed one after the other at high rates to induce mixing) usually occurs directly into a tanker truck at a loading rack fed through the dedicated distribution piping. However, in some cases, additional ASTs at the terminal are used to store blended biofuels splash-blended through dedicated distribution piping. Biofuel blends are loaded onto tanker trucks at loading racks and distributed to nearby dispensing stations.

2.1.4 Distribution

The distribution of biofuels from bulk depots and supply terminals to dispensing stations is mostly through tanker trucks. From bulk depots, the tanker trucks distribute bulk biofuels (i.e., DFE or B100) to secondary supply terminals. These tanker trucks generally have a single compartment and are dedicated to a specific fuel type. Tanker trucks leaving supply terminals distribute blended biofuels to dispensing stations. These tanker trucks often contain multiple compartments to accommodate various fuel grades (e.g., regular unleaded or premium gasoline) and/or blends (e.g., E85 or B20).

Distribution

Truck

Dispensing Station

2.1.5 Dispensing Station

Once a tanker truck carrying blended biofuel reaches a dispensing location, the truck offloads the product into a UST or AST, depending on the type of station. Most common neighborhood gasoline retail dispensing stations contain multiple USTs accommodating different conventional fuel grades. However, additional USTs may also be dedicated biofuels. On rare occasions, these common retail gasoline stations use an AST, particularly for biodiesel.

Once stored in the UST (or AST), the biofuel is accessed by the customer (or attendant) through a dispenser connected by product piping to the UST. Dedicated dispenser lines are used for each UST. Furthermore, UST systems are typically equipped with a vapor recovery unit (VRU) to capture volatilized fuel. In addition, various sumps or spill buckets are located throughout the dispensing infrastructure from the UST fill port to the dispenser itself to collect small-volume fuel releases. Figure 2-3 illustrates the typical infrastructure associated with a dispensing station.

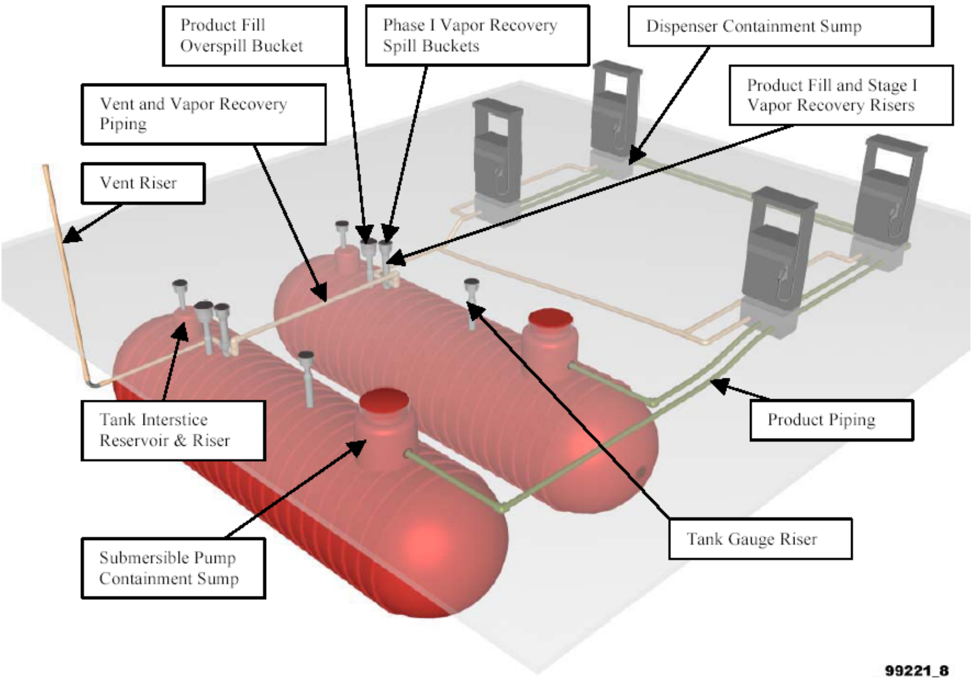


Figure 2-3. Illustration of a common dispensing station. *Source:* Shell Oil Products.

2.2 Release Causes

Each step in the supply chain contains various pieces of equipment that are potential release points for biofuels. These releases can be caused by multiple reasons, including incompatible materials, equipment failures, inappropriate management practices, human error, and accidents. Table 2-2 summarizes biofuel-specific release causes by equipment in the supply chain.

2.2.1 Aboveground Storage Tanks

ASTs are used to store petroleum products, and most biofuels and are primarily regulated under 40 CFR §112. Most ASTs are constructed of stainless steel, cold-finished steel, or fiberglass, although plated metal tanks are generally not recommended for high-blend ethanol fuels due to material incompatibility issues (DOE 2010), as discussed in Section 2.3.1.

Aboveground Storage Tanks

Table 2-2. Leak detection issues and release causes by equipment type

Equipment type	Potential volume	Leak detection	Release causes
Aboveground storage tanks (Section 2.2.1) are common at manufacturing facilities and bulk depots/supply terminals, less common at dispensing stations.	Small-volume or chronic releases that can become large occur over an extended period of time.	May be within the error of volume reconciliation estimates or may go unnoticed until next inspection. Materials used in engineering controls (ECs) for monitoring for releases may be incompatible with biofuels.	Increased rates of permeation through common rubbers, plastics, and elastomers or deterioration of seals and gaskets used at joints and connections. Increased rates of corrosion and stress corrosion cracking (SCC) (API 2007) particularly in tank floors and other internal components, possibly also at the tank skirt or where connections to distribution piping occur.
	Acute, large-volume release; however, emergency response actions, including rapid containment, surface recovery, and excavation (where feasible), may minimize impact to the environment.	Typically detected either by direct observation or through automated volume reconciliation accounting.	
Distribution piping and manifold systems (Section 2.2.2) are common at facilities with ASTs such as at manufacturing facilities and bulk depots/supply terminals.	Small-volume or chronic releases that can become large occur over an extended period of time.	Abnormal pressure or flow readings.	Partially or completely blocked filters (particularly for biodiesel) may cause pressure buildup that can lead to additional leaks in seals, gaskets, or pressure-relief devices. In rare cases, complete blockages of filters can cause catastrophic ruptures in the piping or other equipment. Increased rates of deterioration of seals and gaskets, permeation of materials, and increased corrosion at valve joints and in pumps in the manifold.
	Acute, large-volume release; however, emergency shutoff systems and emergency response actions, including rapid containment, surface recovery, and excavation (where feasible) may minimize impact to the environment.	Loss of pressurization or flow.	

Equipment type	Potential volume	Leak detection	Release causes
Loading/unloading racks (Section 2.2.3) are used at facilities where bulk or blended biofuels are transferred from or to tanker trucks, railcars, or barges such as at manufacturing facilities and bulk depots/supply terminals. Also used at manufacturing facilities to unload denaturant.	Small-volume or chronic releases that can become large occur over an extended period of time.	Depending on the location of the component, may go unnoticed for an extended period or until next inspection or operation and maintenance event; otherwise, direct observation.	Overfills or incorrect connections to the transport or distribution vehicle. Increased rates of permeation through common rubbers, plastics, and elastomers or deterioration of seals and gaskets used at joints and connections. Increased corrosion and SCC in pipes. Loss of integrity in sumps and/or oil-water separator due to solvent effect of biofuels to scour sludge, sediment, rust, and scale.
	Acute, large-volume releases; however, emergency shutoff systems and emergency response actions, including rapid containment, surface recovery, and excavation (where feasible), may minimize impact to the environment.	Direct observation or loss of flow.	
Tanker trucks, railcars, and barges (Section 2.2.4) are used for transporting bulk biofuels; tanker trucks are used solely for distributing blended biofuels.	Acute, large-volume releases; however, emergency response actions, including rapid containment, surface recovery, and rapid excavation (where feasible) may minimize impact to the environment.	Direct observation.	Accidents.
Underground storage tank systems (Section 2.2.5) are common to dispensing stations but may also be present at manufacturing facilities and bulk depots/supply terminals.	Small-volume or chronic releases that can become large occur over an extended period of time.	Commercial leak detection equipment may be incompatible with certain blends of biofuels.	Materials used in older UST system components may not be compatible with biofuels, including sealing and jointing materials for pipe runs and turns. The solvent nature of biofuels can scour the sediment, sludge, rust, and scale built up in the UST system from conventional fuels.
	Acute, large volume releases; however, rapid excavation (where feasible) may minimize impact to the environment.	Detected through automated volume reconciliation accounting.	

Equipment type	Potential volume	Leak detection	Release causes
Dispensers (Section 2.2.6) are common at dispensing stations.	Small-volume or chronic releases that can become large occur over an extended period of time.	Depending on the location of the component, may go unnoticed until next inspection or operation and maintenance event.	Materials used in older dispenser system components (e.g., meters, hoses, nozzles) may not be compatible with biofuels, including sealing and jointing materials for pipe connections from UST. Inappropriate filters used for biofuel (DOE 2010) or frequency of filter changeouts not sufficient.

ASTs can be either single- or double-walled, depending on local regulatory requirements. Double-walled tanks may contain an interstitial fluid for leak detection. ASTs have either a fixed or floating roof, where floating roofs may be internal or external. Roofs may also be domed. Fill pipes structures are placed to minimize jetting corrosion or wear on internal structures, may contain a splash plate, are supported to minimize physical movement, and contain an in-line check valve to prevent backflow. In addition, some ASTs may be equipped with internal heating coils or stirrers, of particular relevance for storing biodiesel in colder climates where gelling can become an issue. Due to the more corrosive nature of some biofuels, the materials used to construct these various AST components need to be compatible with biofuels.

The subsurface support underneath the AST is usually concrete. All ASTs are required to be contained within a bermed, diked, bunded, or secondarily contained area with sufficient volume to capture 110% of the contents should the tank have a release (NFPA 2008). These containment structures are usually made of concrete or compact clay with a specific permeability to prevent infiltration. If more than one fuel is stored in a containment area, the fuels must be compatible with each other. Precipitation captured in the containment area is also controlled prior to discharge. This step is particularly important for ethanol-based fuels and other more soluble biofuels since these may preferentially partition into aqueous solution (see Section 3.2).

Many releases from ASTs are due to galvanic or pitting corrosion, particularly in the tank floor and other internal components, but possibly at the tank skirt or where connections to distribution piping occur (Figure 2-4). The physical, chemical, and biological properties of some biofuels, including ethanol and biodiesel, can exacerbate this occurrence by promoting or enhancing the rate of corrosion. These properties include the hygroscopic ability to attract water; biological growth; higher electrical conductivity than petroleum; and scouring capabilities to solubilize rust, scale, and sediment. In addition, biofuels tend to have a higher rate of permeation through common rubbers, plastics, and elastomers used at joints and connections.

Figure 2-4. Corrosion in an AST storing a biodiesel blend: tank wall (left) and tank floor (right). *Source*: BP.

In addition to these material or equipment issues, potential releases from ASTs are managed by at least one of several ECs, such as high liquid level alarms or cutoff devices, direct signal communications, digital fast response systems, or personal observation while the tank is being filled (FedCenter n.d.). Since most of these devices operate on the physical liquid level regardless of the type of liquid, there should be general compatibility with biofuels. Furthermore, standard operation and maintenance procedures are conducted regularly, which include testing the ECs; visual inspection of the supports and foundations; and observing for signs of deterioration, discharges, or accumulation of oil in the secondary containment area. Hydrostatic testing, radiographic testing, ultrasonic testing, acoustic emissions testing, or another system of nondestructive shell integrity testing must be conducted periodically by qualified personnel (40 CFR §112). Again, these are independent of the stored liquid type and should therefore be compatible with biofuels even though the materials they are designed to test may not be as compatible with biofuels as petroleum. Similarly, standard operation and maintenance also include monitoring internal heating coils and return steam lines should these be present in the AST. These too are relatively independent of the fuel type, but the coils themselves have different material compatibilities with biofuels compared to petroleum. Therefore, inspection frequencies may need to be adjusted to account for the differences in material compatibilities with biofuels.

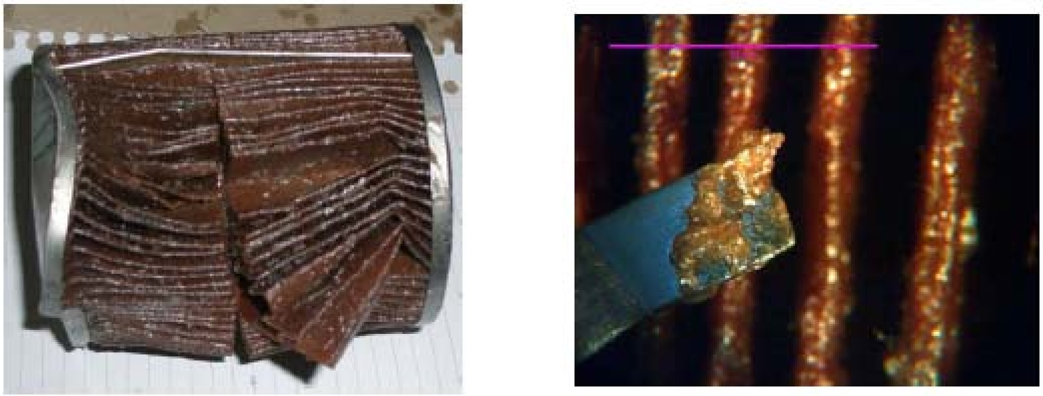
2.2.2 Distribution Piping and Manifold

Distribution piping and a manifold are common to any facility with ASTs, including manufacturing facilities, bulk depots, and supply terminals. This interconnecting piping is usually constructed of steel and generally must be cathodically protected and coated to prevent corrosion. While most of this piping is aboveground, some piping runs and typically road crossings occur underground.

Distribution Piping and Manifold

Common releases from the piping itself can be due to corrosion caused by failed cathodic protection, accidental line punctures and breaks from ground disturbance activities, and failures in seals and gaskets. Biofuels can cause additional or more frequent releases due to their physical, chemical, and biological properties contributing to enhanced corrosion, stress cracking, and advanced deterioration in seals and gaskets. The latter may be a result of applying management practices suitable for petroleum, yet inappropriate or inadequate for biofuels.

To control the flow of product through the various distribution piping, a control manifold (or pump station) is usually placed in a common area where all product piping at a facility is routed. The manifold is a series of in-line valves, flow meters, filters, and pumps that are used to manage the distribution and flow of product. This equipment is usually constructed of steel or ductile iron. Common releases from the manifold can be a result of malfunctioning valves, filters, or pumps; worn seals and gaskets; or incomplete or incorrect maintenance. Biofuels may increase the rate of deterioration of seals and gaskets, permeate the materials faster, and increase corrosion at valve joints and in pumps. In addition, partially or completely blocked filters may cause pressure buildup that can lead to additional small leaks in seals, gaskets, or pressure-relief devices that can become chronic issues if they go unchecked. In rare cases, complete blockages can cause catastrophic ruptures in the piping or other equipment. Blocked filters are especially relevant with biodiesel (Figure 2-5) and may require more frequent changeouts than standard practice.



30 micron diesel pump filter element covered in gel like material

Close up of gel removed from filter

Figure 2-5. Blocked filter caused by biodiesel. Filter changeout frequency was increased to weekly. *Source*: BP.

2.2.3 Loading/Unloading Racks

Loading and unloading racks are used for transfer of bulk or blended biofuels; unloading racks are also used to transfer denaturants at biorefineries. Central to the operation of loading and unloading racks is the distribution piping and manifold that provides or receives fuel at the proper blending mixture, rate of flow, and loading position in the rack.

Loading/Unloading Rack

Transportation vehicles typically queue for an open bay where they are "connected" to the rack. For purposes of this discussion, tanker truck loading racks are described, but other types of rack and transport combinations are generally similar. Trucks are maneuvered into a rack bay, and the swing arm or other loading equipment correctly positioned to minimize any chance of spillage. Variations in truck designs and fill ports may constitute the need for different equipment in different truck bays to accommodate these variations. The truck must be properly grounded to prevent sparks, and both the VRU and overfill protection units must be in place. Once readied and verified, the proper valves and pumps commence transferring the biofuel product either through electronic preset or other automated controllers. This process often involves inline ratio, splash, or sequential blending into the tanker truck of the petroleum, biofuel, and/or additives. The transfer must be performed quickly to speed turnaround but not so quickly that excessive static electricity is generated. This is less of a problem for biofuels that have higher conductive properties compared to petroleum and thus are less susceptible to static buildup. Once the tank truck is filled, the loading equipment, ground connection, and vapor recovery and overfill protection equipment are removed from the truck, which then departs.

Releases from the unloading and loading racks can occur as a result of a multitude of operational or equipment issues. However, in most cases, biofuels do not represent a change in the maintenance activities although material compatibilities, such as flexible rubber or plastic materials, should be checked to determine whether the frequency should be adjusted. Small to very small releases may occur with greater frequency due to the lower compatibility with common materials used in the construction of gaskets, connectors, and seals on the transports themselves. This issue is particularly relevant for loading and unloading higher blend or bulk biofuels (i.e., E85, DFE, B100).

Most releases during the operation of the rack for tanker truck and railcars are captured by a sump system. These racks are often built on concrete pads that contain the sump collection system to capture spillage as well as storm water. The collection sump may be routed to an oil-water separator where the carryover fuel is routed to a recycle tank and the underflow aqueous phase is routed to the wastewater collection system. Depending on the residence time and amount of water collected in the sump, holding tank, and/or oil-water separator, the biofuel component may partially separate into the aqueous phase. Likewise, small amounts of water may be pulled into the organic phase, rendering any petroleum fuel contaminated with water. However, the loss of integrity of the sump and/or the oil-water separation system, both of which are usually partially or wholly subsurface, may result in severe chronic releases. These may or may not result in significant biofuel components entering the environment, depending on where the loss of integrity occurs.

2.2.4 Transports

As discussed previously, the transportation method varies depending on the point in the supply chain; bulk biofuels are transported by rail, truck, or barge transports, while blended biofuels are mostly transported by tanker truck (Table 2-2).

The causes of both tanker truck and train accidents (Figure 2-6) are tracked by DOT (DOT 2010, n.d.). Typical causes include human error (both tanker trucks and trains), unbalanced loads (primarily tanker trucks), and equipment malfunctions (primarily trains). For tank barges, releases are generally a result of collisions or groundings but may also be a result of equipment malfunctions.

Transports

Rail

Truck

Barge

2.2.5 Underground Storage Tank Systems

A UST system is a complex set of parts, including the underground tank, connected underground piping, underground ancillary equipment, and containment system (40 CFR §280.12). Individual UST systems should be dedicated for the biofuel type and must be compatible with the specific fuel blend stored.

UST System

Figure 2-6. Tanker truck incident in Lanesboro, Minnesota, resulting in 3000 gal of DFE released.
Source: Minnesota Pollution Control Agency.

One of the most common modes of operation for filling USTs is as follows: operators position tanker trucks near the fill containment vault (also known as a "fill port"). The operator then connects the tanker truck to the UST system using suction hoses carried on the tanker truck. These can be single-point (coaxial) or dual-point connections; one for liquid transfer and the other for vapor recovery. These hoses are constructed of rubber and are fitted with crimped-on aluminum or brass cam and groove fittings. Once properly connected, the tanker truck "drops" the biofuel into the UST through the fill pipe. As the fuel is entering the UST, the displaced headspace vapors are vented through the vapor recovery system, where the vapors are routed back into the tanker truck, eventually returned to the supply terminal for condensation and recovery. Furthermore, since December of 1998, USTs have been required to have some form of overfill protection to minimize and eliminate the chances of delivering more product to a tank than the capacity of the tank allows. The three options for overfill protection to comply with state and federal requirements include shutoff devices, alarms, and float restrictors.

Product piping connects the storage tank to the dispenser. Product piping can be constructed of several materials, including steel, fiberglass-reinforced plastic, and flexible plastic. In addition, double-walled piping is typically required.[2] Two basic types of piping systems are used: pressurized and suction. Different management practices are required to properly operate and maintain these two types of piping systems. Pressurized piping systems use a submersible turbine pump (STP) to draw fuel from inside the tank, through the underground piping, to the dispenser. The pump itself is located in a sump vault on top of the UST that is accessible at the surface, while a draw tube on the pump inlet penetrates into the tank down to a few inches above the bottom of the UST. Federal UST regulations require two forms of release detection for pressurized piping. The first targets catastrophic releases on a frequent basis (such as pressure drop measurements). The second is performed on a more periodic basis (for example, tightness testing). The other type of piping system is suction systems, which use pumps within the dispenser to draw fuel out of the tank. Typically, these systems use a check valve at the dispenser to control the suction and limit fuel losses such that the UST and product piping are maintained under negative pressures, where leaks would be drawn back into the system rather than released. Continuous leak detection (such as pressure rise measurements) and other precautions are employed.

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[2] Secondary containment and leak monitoring is required for new or replaced USTs or piping within 1000 feet of any existing community water system or any existing potable drinking water well (2005 Energy Policy Act, Title XV, Ethanol and Motor Fuels, Subtitle B, UST Compliance, Section 1530).

Typical causes of releases of biofuels from older UST systems often depend on the age, construction, operation and maintenance practices, and historic use. For example, tanks previously used to store conventional fuel converted to store E85 may fail if they have not gone through a proper recertification process to check whether compatible materials and components are in use. Unless the materials and components are checked ahead of time or management plans are altered to accommodate for the different physical, chemical, and biological behaviors of the newly introduced biofuel, the likelihood of a release can increase. Appendix B provides an example of a process checklist for tank system conversions and installations.

2.2.5.1 Leak detection

Automatic tank gauge (ATG) systems are widely used to detect releases and to determine the ingress of water into a UST. However, ATG systems were traditionally designed to detect water infiltrating into a conventional hydrophobic gasoline, where the water would remain as a separate phase. With the hygroscopic nature and the higher to complete solubility of biofuels with water, most ATG systems present in existing USTs are rendered nonfunctional or lead to erroneous or confusing results. Inspectors have reported issues with leak detection equipment and other components used in storage systems (Figure 2-7). Representative examples are as follows (Biofuels Team members Alison Hathcock, South Carolina Department of Health and Environmental Control, and Valerie Garrett, Missouri Department of Natural Resources, personal communication):

- dissolved ATG probe in E85 UST
- external corrosion of metallic components in STP sump attributable to degradation products of ethanol vapors (observed in both E10 and E85 USTs)
- corrosion of an ATG riser in an E10 UST

Figure 2-7. (*l. to r.*) Corroded ATG in an E85 UST, corrosion in an E85 STP sump likely caused by degradation products of ethanol vapors, and corrosion in E85 STP sump.
Sources: South Carolina Department of Health and Environmental Control (left and right), Delaware Department of Natural Resources and Environmental Control (center).

2.2.5.2 UST system regulation and guidance

New UST systems, if properly installed with compatible components, should minimize releases if they conform to standards established in the United States by USEPA, Underwriters Laboratories (UL), Petroleum Equipment Institute, and API. By federal regulation, UST systems must be compatible with the fuel stored and must have functional leak detection equipment.

A number of federal codes, regulations, standards, and other recommended practices exist for UST systems that apply to biofuels, including the following:

- regulations requiring owners and operators to use a UST system made of or lined with materials that are compatible with the substance stored in the UST system (40 CFR §280.32)
- regulations to control water quality impacts from spills or leaks of biofuel products and by-products through the spill prevention, control, and countermeasure (SPCC) rule
- owners and operators of regulated UST systems must comply with requirements for financial responsibility, corrosion protection, leak detection, and spill and overfill prevention under the Resource Conservation and Recovery Act

USEPA provides a compendium website (www.epa.gov/oust/altfuels/bfcompend.htm) that provides information regarding storing ethanol and biodiesel fuels and has developed guidance for UST owners to use in complying with the federal compatibility requirement (40 CFR §280.32) for UST systems storing gasoline containing >10% ethanol or diesel containing >20% biodiesel (USEPA 2011).

In addition to federal regulations and guidance, some states provide biofuel storage guidance or require application processes for approval of storing biofuels in storage systems. USEPA highlights a number of states with available guidance or application processes specific to storing biofuels in UST systems at www.epa.gov/oust/altfuels/states.htm. Appendix B provides an example of a process checklist for tank system conversions and installations. Other countries have similar governing bodies that set equipment standards and/or require certification of the equipment for service.

2.2.6 Dispensers

Dispensers

Another complex system primarily associated with dispensing stations is the dispensers themselves. These can be of different constructs but generally provide the customer with choices of different fuel types and/or grades. Most dispensers offer standard, middle, and premium grades of gasoline. Specific or dedicated dispensers are often used for biofuel blends. Some locations offer the choice of custom blending through "blender pumps" where the customer can select the blending concentration.

The major components in the fuel pathway from the UST system to the dispenser system include a sump where the product piping feeds in, individual pumps that control the fuel flow, filters to protect the pumps and other internal components, and flexible hoses with nozzles where the customer accesses the supply.

The fuel dispensing components should be compatible with the fuel type being dispensed. For example, E85 dispensers should use iron, unplated steel, or stainless steel in the fuel path. In the case of vane-type pumps, impellers made from soft metals (zinc, brass, lead, aluminum) should be avoided, and all fittings, connectors, and adapters in contact with the fuel blend should be made of materials like stainless steel (best choice), black iron, or bronze to avoid degradation. If aluminum or brass fittings are used, they should be nickel-plated to avoid any contact between the bare metal and the fuel ethanol.

2.3 Release Prevention and Recommendations

Release prevention efforts specific to biofuel should focus on the physical, chemical, and biological properties of biofuels. The increased conductivity of biofuels, compared to that of petroleum hydrocarbons, can cause corrosion of metals, such as galvanic or pitting corrosion. Similarly, the solvent nature of biofuels compared to conventional fuels can scour sediment, sludge, rust, and scale that have built up over time. In addition to potentially clogging filters and pipes and damaging and/or contaminating fuels, this scoured material may expose previously plugged pinholes in storage tanks formed as a result of corrosion (Figure 2-8). Release prevention measures specific to biofuels include the use of appropriate and compatible equipment and adapting management practices.

Figure 2-8. Corrosion in an E85 tank previously used to store E10. *Source*: Iowa Department of Natural Resources.

2.3.1 Material Compatibility

Use of compatible metallic and nonmetallic materials for the different supply chain infrastructure points helps to prevent potential release causes such as degradation of materials in system equipment and corrosion of metals in the presence of biofuels. General examples of compatibility issues include the following:

- Zinc, brass, lead, and aluminum are sensitive to high-blend alcohol fuels.
- Plated steel (referred to as “terne-plated,” a lead-tin alloy) and lead-based solder are not compatible with E85.
- Natural rubber, cork, leather, polyurethane, polyvinyl chloride (PVC), polyamides, methyl-methacrylate plastics, and some types of thermoset and thermoplastic polymers may degrade in high-blend alcohol fuels.
- Certain elastomers, metals, and plastics are not compatible with B100, whereas biodiesel blends of 20% or lower generally have a much smaller effect on these materials (NREL 2009).

The use of compatible materials includes equipment in each part of the supply chain infrastructure as described in Section 2.2, including but not limited to storage systems, product and distribution piping, pipe thread sealant, dispenser systems, etc. It should be noted that UL standards for evaluating compatibilities continue to evolve for different biofuels. In general, as long as the materials themselves are compatible with the biofuel, releases from system components should be minimal.

A number of guidance documents are available for ethanol and biodiesel material compatibility:

- DOE (U.S. Department of Energy). 2010. *Handbook for Handling, Storing, and Dispensing E85*. DOE/GO-102010-3073. www.afdc.energy.gov/afdc/pdfs/48162.pdf.
- DOE. 2009. *Biodiesel Handling and Use Guide.* NREL/TP-540-43672. www.nrel.gov/vehiclesandfuels/pdfs/43672.pdf.
- Kass, M. D., T. J. Theiss, C. J. Janke, S. J. Pawel, and S. A. Lewis. 2011. *Intermediate Ethanol Blends Infrastructure Materials Compatibility Study: Elastomers, Metals, and Sealants*. ORNL/TM-2010/326. Oak Ridge, Tenn.: Oak Ridge National Laboratory. http://info.ornl.gov/sites/publications/files/Pub27766.pdf.
- API (American Petroleum Institute). 2010. *Storing and Handling Ethanol and Gasoline-Ethanol Blends at Distribution Terminals and Filling Stations,* 2nd ed. www.api.org/Standards/new/rp-1626.cfm.
- NBB (National Biodiesel Board). n.d. "Materials Compatibility." www.biodiesel.org/pdf_files/fuelfactsheets/Materials_Compatibility.pdf.
- NREL (National Renewable Energy Laboratory). 2010. *Dispensing Equipment Testing with Mid-Level Ethanol/Gasoline Test Fluid*. www.nrel.gov/docs/fy11osti/49187.pdf.

In addition, UST-specific links to resources are provided by the USEPA Office of Underground Storage Tanks Biofuels (www.epa.gov/oust/altfuels/biofuels.htm), as well as by guidance for UST owners to use in complying with federal compatibility requirements (USEPA 2011).

Research, development, and demonstration programs on existing transportation fuel distribution infrastructure and new alternative distribution infrastructure are currently ongoing, with implications for material compatibility and biofuel release prevention.

2.3.2 Management Practices

Management practices specific to biofuel release prevention include the following:

- use of compatible materials and proper documentation of equipment
- increased frequency of filter changeouts
- increased frequency of inspections for corrosion
- use of appropriate leak detection equipment

Adapting management practices prevents potential release causes such as the use of incompatible materials. The frequency of filter changeouts to prevent clogging of filters and ensuring operability and inspections for corrosion should be reviewed and increased as necessary. In addition, seals and joints of long piping runs, at pipe turns, or connections to either a dispenser or UST sump should be inspected as leaks can form over time, generally as low-volume, chronic releases. Furthermore, the continual pressure or suction these piping networks are under, exacerbated by clogs or fouling from sediment, sludge, rust or scale scoured from older UST systems deposited in the piping, can result in weakening of the seals or joints.

Leak detection equipment, such as ATG systems used in USTs, may not detect releases if not designed for the biofuel being stored. These systems not only have to be made of compatible materials; they also need to function properly in biofuel. Similarly, materials used in ECs for monitoring for releases in ASTs may be incompatible with biofuels. Therefore, compatibility and functionality should be reviewed for leak detection equipment.

2.4 Response Planning

2.4.1 Facility Response Plans

The oil pollution prevention regulation (40 CFR §112) requires plans to prevent, prepare, and respond to oil discharges to navigable waters or adjoining shorelines. The regulation includes two sets of requirements.

The first set of requirements is the SPCC rule, which is the basis of USEPA's oil spill prevention program. The SPCC rule requires specific facilities to prepare, amend, and implement SPCC plans. The SPCC rule applies to facilities that have aboveground aggregate storage capacity for oil or oil products (including biodiesel and E85) or a completely buried storage capacity greater than 42,000 U.S. gal and a reasonable expectation of an oil discharge into or upon navigable waters of the United States or adjoining shorelines.

The second set of requirements is the facility response plan (FRP) rule. FRP requirements are designed to ensure that certain facilities have adequate oil spill response capabilities. Facilities that could reasonably be expected to cause substantial harm to the environment by discharging oil into or on navigable waters or adjoining shorelines must prepare and submit to USEPA plans to respond to a worst-case discharge of oil and to a substantial threat of such a discharge (40 CFR §112.20–21). These regulations apply to biofuel facilities meeting the applicability criteria. While not required, FRPs are recommended for facilities not meeting the applicability criteria.

2.4.2 Emergency Planning and Response

Releases of biofuel or the biofuel component of blends may require additional emergency response considerations in addition to those required for a petroleum release. Additional planning and preparation may be warranted and could include an evaluation of the following:

- locations of potential releases, such as manufacturing facilities, supply depots, terminals, etc. specific to biofuels or biofuel blends
- types of biofuel or biofuel blends manufactured, stored, transported, or dispensed (for example, ethanol or biodiesel refineries, locations of E85 stations, etc.)
- biofuel release preparedness considerations, such as availability of appropriate firefighting foam and foam application techniques for alcohol-based fuels (EERC 2009, DOT 2008)
- emergency alert notification and evacuation procedures for biofuel releases, when warranted
- potential for transport of biofuel to sensitive receptors

Emergency response concerns relevant specifically to biofuels may include the increased potential for fire hazards, such as the fire risk associated with alcohol fuel releases. For example, fires involving biofuel blends containing >10% alcohol should be treated differently than traditional petroleum fires because these mixtures are polar/water-miscible flammable liquids and degrade the effectiveness of non-alcohol-resistant firefighting foam (EERC 2009). Additional guidance is available in the *Emergency Response Guidebook* Guide 127 (DOT 2008) for transportation-related release response procedures. In the United States, first responders must be trained regarding the use of the guidebook according to the requirements of the U.S. Department of Labor's Occupational Safety and Health Administration (OSHA, 29 CFR §1910.120), and regulations issued by USEPA (40 CFR §311). In addition, Massachusetts has guidance on response options for large-volume ethanol releases (MassDEP 2011).

If possible, first responders should institute initial containment measures with particular attention to sensitive receptors. For example, storm and sanitary sewer conveyances that can transfer the biofuel to the local wastewater treatment facility can impact wastewater treatment systems by harming the microbial systems (i.e., activated sludge) used to process wastewater. In addition, releases to surface water should be avoided due to potential ecological impacts (Section 3.5.2).

Compatibility of biofuels with absorbent booms should be evaluated with respect to potential release scenarios. For example, absorbent booms used for petroleum releases are designed to pick up oil-type substances. They pick up ethanol in ethanol-blended fuel as long as no water is present. However, if water is present, the water/ethanol solution phase-separates and requires a water-absorbing boom or absorbent (EERC n.d.).

3. FATE AND TRANSPORT OF BIOFUELS IN THE ENVIRONMENT

3.1 Introduction

Because biofuels, such as the biodiesel in B20 or ethanol in E85, have chemical properties significantly different from those of conventional (petroleum) fuels, the environmental behavior of these biofuels differs from that of conventional fuels following a release. This chapter provides a comparison of the differing properties and implications for evaluating the fate and transport of biofuels.

The conceptual model of a conventional petroleum release to the subsurface is generally understood. As petroleum fuel migrates vertically from the release point, some is trapped in the unsaturated zone. Simultaneously, some of its components partition to the surrounding media (soil, organic material, air, water). Depending on the release scenario (e.g., spill volume, geology, etc.), the petroleum may approach the water table and spread laterally around it (Figure 3-1) with some vertical migration if a sufficient light, nonaqueous-phase liquid (LNAPL) head is present. Following a release, the LNAPL eventually stops spreading laterally, and the footprint becomes stable. Within the LNAPL boundary, or "footprint," LNAPL may move and redistribute itself with water table fluctuations (ITRC 2009; Huntley and Beckett 2002). Figure 3-1 presents an illustrative conceptual model of the migration of LNAPL and partitioning of fuel components to media along the migration pathway.

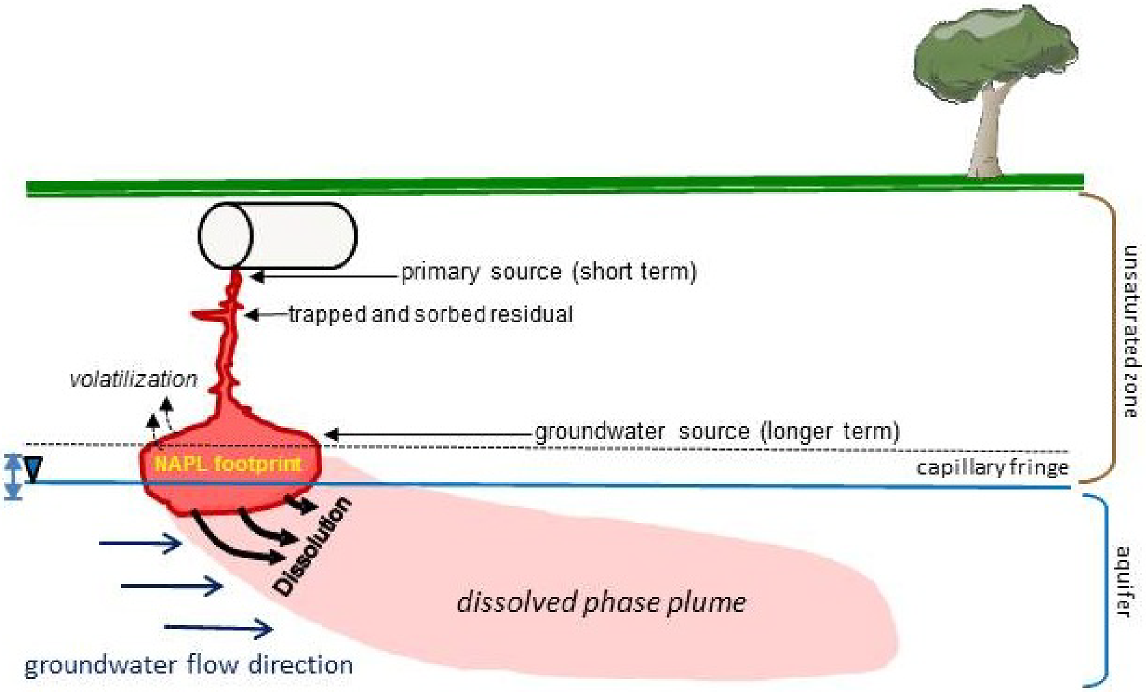

Figure 3-1. Illustrative conceptual model of a UST release showing the influences on fuel and fuel constituent fate and transport in soil and groundwater.

Fate and transport of biofuel in the environment are highly dependent on site conditions, volume and rate of the release, and the fraction of biofuel in the released products. Nonetheless, some key properties of biofuel can provide insight into their fate, transport, and their potential adverse impacts to the environment. These include the following:

- physical-chemical properties
- biodegradation potential
- interactions with other contaminants

While evaluations of biofuel fate and transport offer insight into the mobility, attenuation, and chemical interactions in the environment, they do not incorporate assessments of risk. Although beyond the scope of this document, evaluations of potential risks in the environment entail assessments of chemical toxicity, pathways for exposure, and identified receptors. In the development of site conceptual models (SCMs), fate and transport assessments are best formulated in conjunction with risk evaluations (ASTM 2010a, ITRC 2008b).

3.2 Physical and Chemical Properties of Biofuels

The physical and chemical properties of biofuel components offer insight into their mobility in different environmental media. Phase transfer depends on contact *with* and partitioning *from* one media to another (air, water, soil). Fuel components with high vapor pressures tend to rapidly evaporate into the atmosphere. Vapor pressure and Henry's law constant (tendency to partition into vapor phase from dissolved phase) significantly influence the persistence of volatile fuels in ground and surface waters. Fuels with high Henry's law constants tend to easily partition from the aqueous phase into the atmosphere. In addition, hydrophilic fuel components with high aqueous solubility and low sorptivity (e.g., ethanol) are dissolved in the aqueous phase and transported at rates similar to that of flowing water. Conversely, hydrophobic fuel components (e.g., benzene) preferentially partition to organic materials and are transported at rates much lower than that of water. Physical properties of fuels such as the specific gravity and viscosity can also play a role in determining the extent of impact to soil and water.

Table 3-1 lists some physical and chemical properties and biodegradation potential of selected biofuels with benzene and diesel for comparison (see also Appendix C). Also provided in Table 3-1 are brief descriptions of the potential implications of key properties. An analysis of fate and transport implications for biofuels not listed should consider the physical and chemical properties of these fuels in a similar manner.

3.3 Biodegradation

3.3.1 Biodegradation of Biofuels

The capacity of a compound to be biologically degraded is affected by several factors, including the concentration, complexity of the chemical structure, the presence of suitable electron acceptors, and bioavailability. Chemical structure features that can negatively affect biological degradation rates include branching, degree of saturation, and high hydrophobicity (Watts 1996). Most hydrocarbons in conventional fuels are characterized by these properties. In contrast, biofuels, such as FAMEs, ethanol, and butanol, have simple structures and are readily biodegradable under both aerobic and anaerobic conditions (Corseuil et al. 1998; Lovanh, Hunt, and Alvarez 2002; Feris et al. 2008) (Table 3-1). Therefore, dilute concentrations of biofuels in groundwater exhibit smaller plumes with shorter longevity than plumes associated with conventional fuel components.

3.3.2 Secondary Effects from Biofuel Biodegradation

The relatively rapid and ubiquitous biodegradation of biofuels in soil and groundwater induces changes to the biological and geochemical environments. Stimulation of microorganisms, available electron acceptors, and production of biomass/exudates and methane are discussed further in this section.

3.3.2.1 Microbial stimulation

Biofuels such as ethanol, butanol, and biodiesel are more readily degradable via microbial processes when compared to petroleum hydrocarbons at equivalent aqueous concentrations. High concentrations of ethanol can inhibit biodegradation, with reported inhibitory levels from microcosm studies ranging 6%–10% (vol/vol) (Ingram and Buttke 1984; Heipieper and deBont 1994; Nelson, LaPara, and Novak 2010). Once biofuel concentrations are diluted to below these levels, they are metabolized, although factors such as nutrient limitation, available electron acceptors, and thermodynamic inhibition resulting from the buildup of some metabolites (Corseuil et al. 2011a) can affect the efficiency and subsequent biological decay rate of biofuels. These effects can cause a delay in the generation of methane for months to years following the release.

Table 3-1. Comparison of selected fuel component properties

	Density (ρ) (g/cm^3)	Aqueous solubility (25°C, mg/L)	Henry's law constant, H (unitless)	Log K_{ow}[a]	Vapor pressure at 25°C (mm Hg)	Biodegradation potential	Implications
Ethanol	0.79	Infinite	2.1E-4 to 2.6E-4	-0.16 to -0.31	59	Aerobic: days-weeks Anaerobic: weeks-months	Readily partitions to water and dilutes according to water availability. Rapidly biodegradable.
Butanol	0.81	7.4E+4 to 8.7E+4	3.7E-4 to 5.0E-4	0.83 to 0.88	0.42 to 11.8	Aerobic: days-weeks Anaerobic: weeks-months	Low volatility from water phase. Rapidly biodegradable.
Benzene	0.88	1.8E+3	0.22	2.13	75	Aerobic: weeks-months Anaerobic: years	Readily partitions to vapor phase from nonaqueous-phase liquid and from aqueous phase.
Biodiesel (FAMEs)	0.84 to 0.90	1.2E-3 to 2.1E-2	6.4E-3 to 1.3	6.29 to 8.35	8.63E-6 to 3.74E-4	Aerobic: days-weeks Anaerobic: weeks-month	Low mobility in soil/ sediment. Low volatilization from surface releases. Readily biodegradable.
Diesel	0.87 to 0.95	5.0	2.4E-3 to 3.0E+2	3.3 to 7.06	2.12 to 26.4	Aerobic: weeks-months Anaerobic: years	Moderate volatility from aqueous phase. Low mobility in soil/sediment.

[a] Octanol-water partition coefficient, representing the degree to which an organic substance preferentially dissolves in water vs. an organic solvent.

The microbial degradation of biofuel compounds can result in complete mineralization to methane or carbon dioxide. This process is complex and involves the interactions of several different groups of bacteria (Schink 1997) that can generate several different metabolites such as volatile fatty acids (VFAs), which include acetate, propionate, butyrate and lactate (Madigan and Martinko 2006). As an example, Figure 3-2 is a schematic showing the anaerobic fermentation of ethanol and possible degradation products. Depending on the buffering capacity of the aquifer, production of VFAs can potentially lower the pH. Microbial activity can become inhibited when the pH is <6 (Madigan and Martinko 2006).

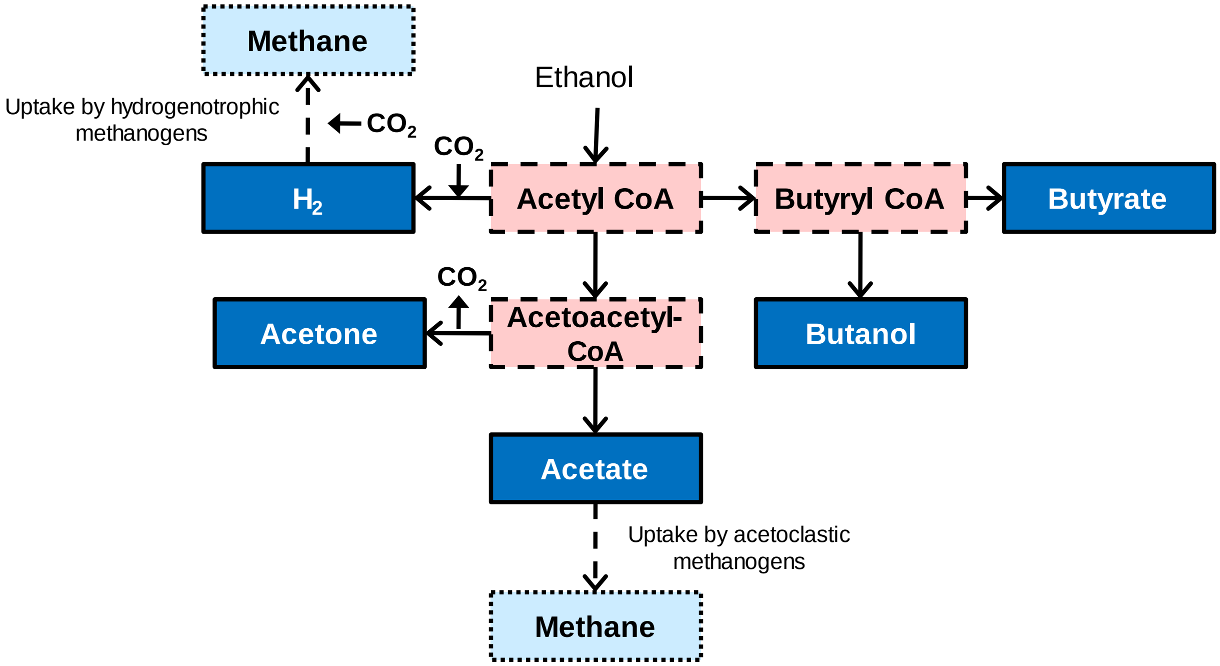

Figure 3-2. Major routes of the anaerobic fermentation of ethanol. Pink boxes indicate enzyme-mediated reaction steps. Solid outline and blue shading indicates dominant fermentation products. Dashed arrows and light blue shading depict secondary processes by other organisms. NOTE: Not all steps are shown in metabolic pathways, and dominant metabolites can undergo additional degradation via secondary processes. *Source*: Adapted from Madigan and Martinko (2006).

3.3.2.2 Biochemical oxygen demand

The release of a readily degradable biofuel to soil or water results in the rapid consumption of oxygen. This can be particularly detrimental in surface waters where low oxygen levels can adversely affect biological communities. The impact of a highly biodegradable fuel on the system is strongly dependent on the ability of the receiving water to dilute the load. In release scenarios where a highly soluble and highly biodegradable biofuel reaches groundwater, rapid biodegradation induces anaerobic conditions. During this time, other compounds such as nitrate, iron, sulfate, and carbon dioxide serve as electron acceptors. Metabolites of biofuel biodegradation may also exert their own oxygen demand, such as methane from ethanol biodegradation. Near source zones, this added oxygen demand can reduce bioattenuation rates of petroleum hydrocarbons in saturated and unsaturated environments, which can potentially allow petroleum vapors to migrate further, both horizontally and vertically (Jewel and Wilson 2011).

3.3.2.3 Biomass and exudate production

Where biofuels are rapidly metabolized by aerobic and anaerobic organisms, ethanol releases to shallow groundwater are likely to produce dark-colored slimes that contain microbial exudates near the water table (Ghose and Bhadra 1985, Constantin and Fick 1997, Khan and Spalding 2003). These slimes have been noted in soil cores following DFE releases and may encapsulate high concentrations of ethanol in the capillary fringe, preserving them for several years (Spalding et al. 2011). The presence of biomass indicates a high density of organisms growing in the source zone, likely leading to reduced transport of ethanol and degradation products in groundwater.

3.3.2.4 Generation of methane

Biological degradation of biofuels produces compounds such as acetate and hydrogen that are used by methanogenic bacteria to produce methane under anaerobic conditions (Schink 1997). Methane can be produced at petroleum sites and can present an explosive risk for large releases under some scenarios. However, for most petroleum sites, biodegradation rates are insufficient to generate methane vapor at rates that would not be rapidly attenuated beyond the source zone. In contrast, biofuels and biofuel blends have the potential for producing significantly more methane as compared to petroleum releases due to the biodegradable nature of biofuel. Biological degradation of both biodiesel and ethanol in groundwater can result in significant dissolved methane, as shown in both laboratory and field studies (Buschek et al. 2011; Mackay et al. 2006; Feris et al. 2008; Ma et al. 2011; Nelson, LaPara, and Novak 2010; Westway and Cambria case studies in Appendix D).

As discussed in Section 3.3.2.1, the appearance of methane can be delayed for months to years after the initial biofuel release and has been observed at ethanol release sites (Spalding et al. 2011). Furthermore, methane generation can also continue for years after the apparent disappearance of the source biofuel in groundwater. Long-term monitoring may be required to assess potential methane generation and persistence.

Equilibrium methane concentrations in the soil-pore gas phase are strongly dependent on average groundwater temperatures; in warmer groundwater temperatures the potential for methane in soil gas is greater (Figure 3-3). Henry's law constant (H) for a volatile compound is derived by dividing its vapor pressure by its aqueous solubility. Since vapor pressure increases faster with temperature than solubility, both H (the slope) and gas-phase levels dramatically increase with relatively small increases in water temperature. In Figure 3-3 the temperature dependence was calculated using the relationship described in Sander (1999).

At most sites, accumulation of methane near the surface is unlikely as methane is highly biodegradable in normally well-oxygenated soil. However, for shallow vadose zones where a significant volume of biofuel has been released, methane may not be completely attenuated in soil, as found in a recent investigation with a surface soil gas sampler (see Cambria case study, Appendix D). Generation of methane and carbon dioxide from biofuel releases can induce pressure gradients that may in some scenarios allow for advective migration of methane and other gases towards potential receptor structures (Amos and Mayer 2006). In environments where dilution and/or methane oxidation cannot occur (e.g., shallow depth to groundwater) and structures are present that allow gas accumulation, steps should be made to evaluate soil gas methane concentrations (Section 4.1.1) and mitigate if necessary (Section 5). The lower explosive limit (LEL) of methane is ~5% by volume (5000 ppmv); the upper explosive limit is ~15% in air (Figure 3-4). Methane concentrations above 10% of the LEL present a potentially high-risk situation and may require emergency mitigation measures.

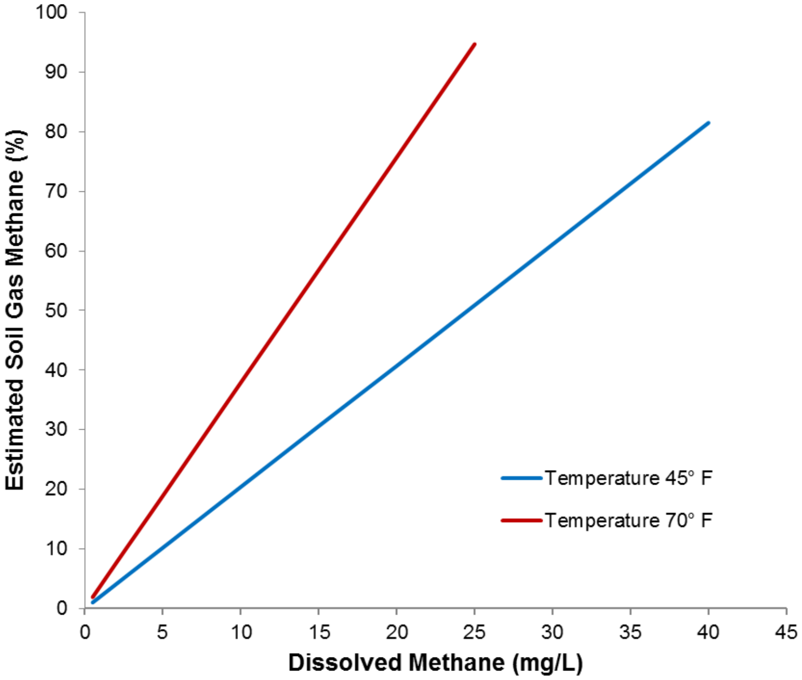

Figure 3-3. Estimated soil gas levels from dissolved (aqueous) concentrations in groundwater.
Source: Spalding et al. 2011.

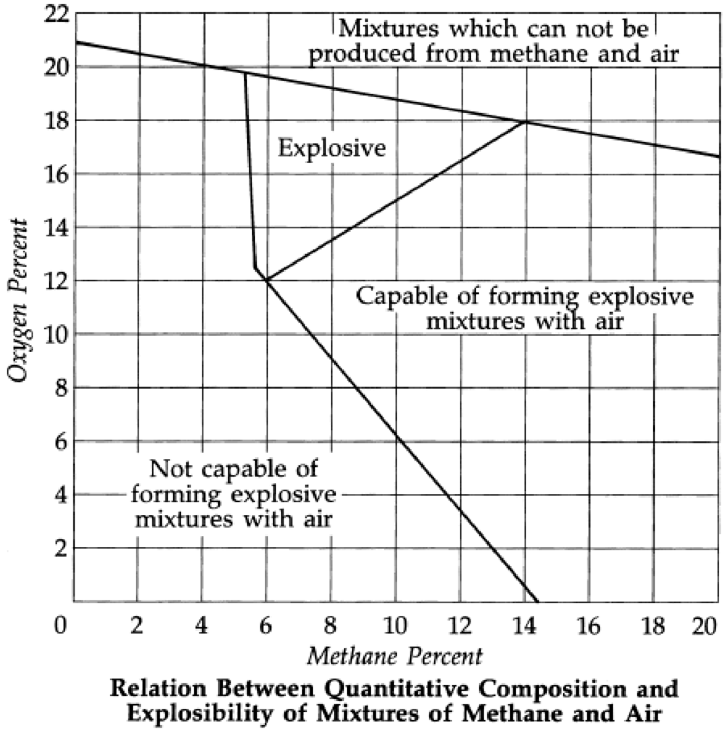

Figure 3-4. Explosive potential of methane.
Source: 30 CFR 57.22003.

3.4 Biofuel Interactions with Petroleum Fuels

In general, the higher the fraction of the biofuel in a blend, the lower the content of petroleum hydrocarbons in the environment. Nonetheless, the presence of some petroleum hydrocarbons in released fuels can potentially impact soil or water, and their fate and transport can be influenced by the presence of the biofuel. Below are brief discussions describing the influence of biofuels on other potential contaminants.

3.4.1 Enhanced Solubilities of Petroleum Hydrocarbons

Concentrations of petroleum hydrocarbons in water are limited by the fraction of the hydrocarbon in the fuel and the individual hydrocarbon's solubility according to Raoult's law. When present in water at high enough concentrations, some biofuels (e.g., ethanol) may act as a cosolvent and enhance these solubility limits. In the case of ethanol, aqueous ethanol concentrations must be >20% to see significant enhancements in aqueous concentrations of gasoline hydrocarbons, including benzene, toluene, ethylbenzene, and xylenes (BTEX) (Heerman and Powers 1998; Rixey, He, and Stafford 2005). Due to retention of ethanol and hydrocarbons in the capillary fringe, these enhancements may be temporarily observed within this narrow zone following releases of high-percentage blend ethanol onto preexisting LNAPL contamination (He, Stafford, and Rixey 2011). However, laboratory and field evidence has shown that ethanol concentrations in the saturated zone are unlikely to occur at levels greater than a few percent even for large spills of high concentration ethanol (Spalding et al. 2011). Consequently, cosolvency effects within hydrocarbon plumes are not expected at most release sites.

3.4.2 Influence of Biofuels on Transport and Distribution of Preexisting Hydrocarbons in Soil

Large volumes of biofuels are often stored in industrial areas such as bulk depots and supply terminals (as discussed in Section 2.1). In many cases, these sites have had prior hydrocarbon releases and may contain residual-phase (nonmobile) hydrocarbons in the subsurface. Thus, preexisting residual hydrocarbons could mobilize following a biofuel release.

At very high concentrations (30%–70%, depending on the biofuel), highly water-soluble biofuels with solvent properties (e.g., ethanol) can dissolve separate-phase hydrocarbons and mobilize these dissolved components as a migrating bulk phase. For example, for ethanol-water-hydrocarbon mixtures >70% ethanol, the mixture exists as a single phase with properties very similar to neat ethanol (Weaver et al. 2009). Therefore, for a spill of considerable ethanol volume that encounters residual nonaqueous-phase liquid (NAPL), the hydrocarbons are dissolved by the ethanol and migrate with the bulk fuel until the ethanol dilutes to <70%. At this point, the hydrocarbons phase-separate from the bulk fuel. Mobilization of preexisting hydrocarbons has been shown to occur vertically in the vadose zone (McDowell, Buscheck, and Powers 2003; see Pacific Northwest Terminal case study in Appendix D) and laterally (Stafford et al. 2009), and distributions can be influenced by changing hydraulic conditions near the water table (Stafford and Rixey 2011).

3.4.3 Preferential Biodegradation of Biofuels

Because many biofuels are readily degradable, preferential degradation of biofuels over other hydrocarbons (e.g., BTEX) in aquifers is a concern. Preferential degradation can result in limitations of available electron acceptors, causing lower rates of petroleum hydrocarbon degradation and potentially increasing the lengths of hydrocarbon plumes. Ethanol has been the subject of more research than biodiesel in this area. Current knowledge for these biofuels is summarized below.

Some laboratory and field studies have shown the presence of ethanol to negatively impact the biological degradation of petroleum hydrocarbons such as BTEX (Corseuil et al. 1998; Lovanh, Hunt, and Alvarez 2002; Feris et al. 2008). Groundwater modeling efforts that assume a continuous source of ethanol to groundwater suggest that the presence of ethanol increases hydrocarbon plume length (Molson et al. 2002, Gomez and Alvarez 2010) compared to releases without ethanol. However, other research suggests no plume elongation (Freitas et al. 2010) or shortening of plumes due to increased microbial capacity for biodegradation (Cápiro et al. 2008, Corseuil et al. 2011a, Kline et al. 2011) and lower fractions of petroleum hydrocarbons in the fuel (Gomez and Alvarez 2010). Although elongation of the hydrocarbon plumes may be predicted, the impact of ethanol is expected to be temporary, and these diluted and elongated plumes may have shorter lifetimes because of the lower concentration of petroleum hydrocarbons in ethanol-blended fuel plumes compared to conventional hydrocarbon fuel plumes.

Research has established that, similar to ethanol, biodiesel is preferentially biodegraded compared to petroleum hydrocarbons (DeMello et al. 2007, Owsianiak et al. 2009, Mariano et al. 2008). However, there is a lack of consensus in current literature whether the preferential biodegradation of biodiesel depresses the rate of petroleum hydrocarbon biodegradation during natural attenuation (Corseuil et al. 2011b; Owsianiak et al. 2009; Pasqualino, Montane, and Salvado 2006).

3.4.4 Mobilization of Metals

A shift from oxidizing to reducing conditions can occur in a plume when a spill of either conventional fuel or biofuel reaches the groundwater. The rate at which the redox shift occurs, however, may be more rapid for a biofuel spill because biofuels contain more readily degradable constituents. The shift towards more reducing conditions can result in the localized mobilization of naturally occurring redox-sensitive metals such as iron, manganese, and arsenic near the release location where conditions remain anaerobic (Brown et al. 2010).

3.5 Physical Transport

Provided below are brief descriptions of the differing behavior of some biofuels in the environment. The potential for media impacts by release scenarios is presented in Table 3-2 and discussed below, categorized by environmental media. Note that the conclusions presented below are based on limited field investigation data.

3.5.1 Surface Spills, Overland Flow, and Runoff

The initial fate of surficial biofuel releases is largely controlled by vaporization of the product(s), consumption by fire, infiltration, surface drainage, and surface water dilution. Ignition of vapors can be catastrophic and are the greatest concern for first responders at large alcohol-based fuel release sites (see Section 2.4.2). Unless precautions are taken, biofuel not consumed by fire may be more rapidly transported to nearby lakes, rivers, and streams due to firefighting efforts.

Table 3-2. Potential media impacts by equipment type

Equipment type	Potential media impacts
Aboveground storage tanks (Section 2.2.1) are common at manufacturing facilities and bulk depots/supply terminals, less common at dispensing stations.	Soil impacts; groundwater impacts possible for large-volume releases due to pressure heads that can cause percolation down to the water table. Biofuels released onto a preexisting hydrocarbon plume may also lead to cosolvency issues; particularly relevant for bulk depots and supply terminals where historic hydrocarbon plumes may exist directly beneath a biofuel AST.
Distribution piping and manifold systems (Section 2.2.2) are common at facilities with ASTs, such as at manufacturing facilities and bulk depots/supply terminals.	In most cases, result in impacts to soil. Less likely are impacts to groundwater since this infrastructure is primarily aboveground and sufficient driving force to cause the biofuel to percolate downward is generally absent. Distribution piping and manifold are typically positioned away from water bodies, making direct surface water and sediment impacts unlikely. Potential for large-volume biofuel releases to reach a receiving water body through storm-water routes, although control systems may prevent this occurrence.
Loading/unloading racks (Section 2.2.3) are used at facilities where bulk or blended biofuels are transferred to or from tanker trucks, railcars, or barges, such as at manufacturing facilities and bulk depots/supply terminals. Also used at manufacturing facilities to unload denaturant.	Racks are often built on concrete pads that contain a sump collection system to capture spillage as well as storm water and may be routed to an oil-water separator routed to a wastewater collection system. Depending on the residence time and amount of water collected in the sump, holding tank, and/or oil-water separator, the biofuel component may partially separate into the aqueous phase. Small amounts of water may be pulled into the organic phase, rendering any petroleum fuel contaminated with water. However, the loss of integrity of the sump and/or the oil-water separation system may result in severe chronic releases, with potential impacts depending on where the loss of integrity occurs. Barge transfers from a rack system can contaminate surface water.
Tanker trucks, railcars, and barges (Section 2.2.4) are used for transporting bulk biofuels; tanker trucks are used solely for distributing blended biofuels.	Tanker truck and railcar accidents can release partial to full transport capacities. Potential impacts to soil, sediment, surface water, and groundwater depend on release volumes and site-specific characteristics of release location. Barge accidents can result in surface water and sediment impacts.
Underground storage tank systems (Section 2.2.5) are common to dispensing stations but may also be present at manufacturing facilities and bulk depots/supply terminals.	Media immediately impacted from a UST release is the surrounding backfill in the UST "pit." Depending on the size or duration of the biofuel release, the soil around the UST pit is generally likely to be impacted as well. Groundwater impacts depend on the proximity of the water table to the UST as well as a sufficient driving force to cause the biofuel to percolate to depth. Soil is likely to be impacted by a release from underground product piping. Only under rare circumstances where groundwater is very shallow do impacts from product piping occur. Regardless of the location of the release, should groundwater be impacted by biofuel, cosolvency issues may be present if historic petroleum releases have occurred at the same location.
Dispensers (Section 2.2.6) are common at dispensing stations.	Surface releases, soil contamination if under-dispenser containment not present.

When low-density biofuels such as ethanol and butanol are released into surface water bodies, their lower specific gravities initially cause them to be buoyant as they mix in the upper water column. However, this buoyancy is not expected to last, as dilution and mixing by waves and currents are likely to be rapid. Hydrocarbons from the gasoline fraction quickly phase-separates, generating LNAPL on the biofuel's contact and dilution with water. For low hydrocarbon fractions, such as the 2%–5% in DFE, LNAPL is not likely to be observed due to rapid dispersion, spreading, and the evaporation of the relatively small quantities of hydrocarbons. For higher hydrocarbon fractions (e.g., E50 or E85), LNAPL and/or sheens are expected to result from the turbulent mixing of the ethanol fuel and surface waters, as long as the amount of water exceeds the amount that can be held within the fuel. Since butanol has a vapor pressure of 7 mm Hg and is highly volatile, loss by vaporization from the LNAPL phase is significant. In addition, because the vapor density of butanol is 2.6 (Appendix C), the vapors are heavier than air and can accumulate in low-lying areas. Because the explosive range for butanol in air is 1.4%–11.2% (as compared to 5%–15% for ethanol), vaporization from surface spills could quickly result in conditions favorable for combustion.

3.5.2 Surface Water Fate and Transport

Surface waters include rivers, lakes, ponds, wetlands, estuaries, etc. Under a variety of release scenarios (Table 3-2), biofuels can enter surface water directly or through conveyances, such as storm drains and ditches. Site-specific characteristics of the water body and the physical, chemical, and biological properties of the biofuel released influence the significance of the fate and transport mechanisms.

In stagnant or lower-energy or surface water systems, alcohol releases can form temporary, buoyant, concentrated layers that disperse within the water column. Under these conditions, vaporization could be a significant attenuation mechanism. In higher-energy, fast-flowing waters or with significant wave action, alcohols are quickly diluted and attenuation may primarily occur by biodegradation, which places a significant oxygen demand on the water body. Under these conditions, attenuation rates depend on the influx of atmospheric oxygen.

Biodiesel is expected to behave similarly to petroleum at surface water release sites. Like alcohols, biodiesel has a fuel density <1.0; unlike alcohols, biodiesel has a high interfacial tension and mostly floats on the water surface (University of California 2008) making recovery easier. Relatively insoluble biofuels that exist as an LNAPL, such as biodiesel, are likely to attenuate more slowly.

Releases of biofuel can have immediate short-term impacts on surface water biota; this impact can be due to highly water-soluble biofuels (alcohol biofuels) that can potentially disperse throughout the entire water column or that, in the case of relatively insoluble biofuel such as biodiesel, can coat shorelines and vegetation. In general, alcohols may impact larger volumes of surface water than equivalent petroleum releases due to their higher solubilities and the inability to capture separate-phase product. Recovery of biodiesel LNAPL from the water surface can be completed using the same techniques as petroleum recovery to limit environmental impacts.

Biodegradation is an important fate process for biofuels in aquatic environments. Compared to aquifers, surface water environments have a greater capacity to rapidly decrease concentrations of dissolved organic compounds through biodegradation and dilution. Sudden large biofuel releases can result in surface water zones with large BOD loadings, resulting in enhanced and rapid bacterial growth. The increased biological activity is due in part from exposure to sunlight, wind, and atmospheric oxygen. DO drives microbial processes, resulting in rapid biological transformation. DO depletion is reflected in oxygen sag curves, decay curves modeled using a differential equation containing BOD rates, oxygen depletion rates, and flow rates (Tchobanoglous and Schroeder 1985). The rate of DO depletion depends on the rates of biodegradation and volatilization. For example, the half-life due to volatilization of butanol in streams (2.4 hours) and lakes (125 days) may result in DO depletion as great or greater than that following an ethanol release of similar size. DO depletion can cause significant fish kills, as has been observed in the case of several large train derailments of DFE (South Hutchinson, Kansas; Rockford, Illinois; and New Brighton, Pennsylvania).

3.5.3 Vadose Zone Fate and Transport

The vadose zone includes the soil between the land surface and the water table and includes the capillary fringe and permanent or temporary perched water zones. Unsaturated zone soil pores contain both air and water. The degree of saturation within soil pores is generally low except in zones of perched water and in the capillary fringe. The capillary fringe differs from the water table in that its pore water pressure is less than atmospheric pressure, while pore water pressure at and below the water tables is at or greater than atmospheric pressure. Recent studies offer key insight into the transport of ethanol in the vadose zone. For other biofuels, much of the state of the knowledge is based on limited laboratory experiments and property-based predictions.

Ethanol may readily partition into pore water along its migration pathway or migrate as a bulk fuel (Figure 3-5). As ethanol reduces the surface tension in the pores, increased drainage can occur. However, much of the ethanol is expected to be retained in soil with low conductivities as reported at the South Hutchinson, Kansas, derailment site (Spalding et al. 2011). Due to density differences, ethanol is retained above the water table where it can be trapped or can migrate horizontally within the capillary fringe (McDowell, Buscheck, and Powers 2003; Freitas and Barker n.d.; Stafford, O’Reilly, and Mackay n.d.). Water table fluctuations promote mixing of groundwater with capillary zone ethanol, but most of the ethanol migrates in sync with the water table (Stafford and Rixey 2011). The likelihood of ethanol overcoming this unsaturated zone retention capacity and reaching the aquifer depends on the release scenario.

The mechanisms controlling the entry of a biofuel to groundwater under different site conditions are not fully understood; however, laboratory and field investigations have provided some insight into important properties and variables that influence downward transport. For large releases of DFE, ethanol has been detected in source zone groundwater soon after the release except in cases where deep-soil excavation occurred immediately following the release (Roy Spalding, University of Nebraska at Lincoln, personal communication). In shallow groundwater areas, large DFE releases appear capable of creating sufficient head pressures to quickly transport 1%–5% of the ethanol beneath the water table (Buscheck et al. 2001, Spalding et al. 2011). These releases have an immediate impact on the geochemistry and biodegradation reactions in the source zone. Ethanol has been reported to also enter groundwater over much longer time frames via a slow diffuse transport from the capillary fringe following episodic releases such as the South Hutchinson, Kansas, and Cambria, Minnesota, sites (Spalding et al. 2011).

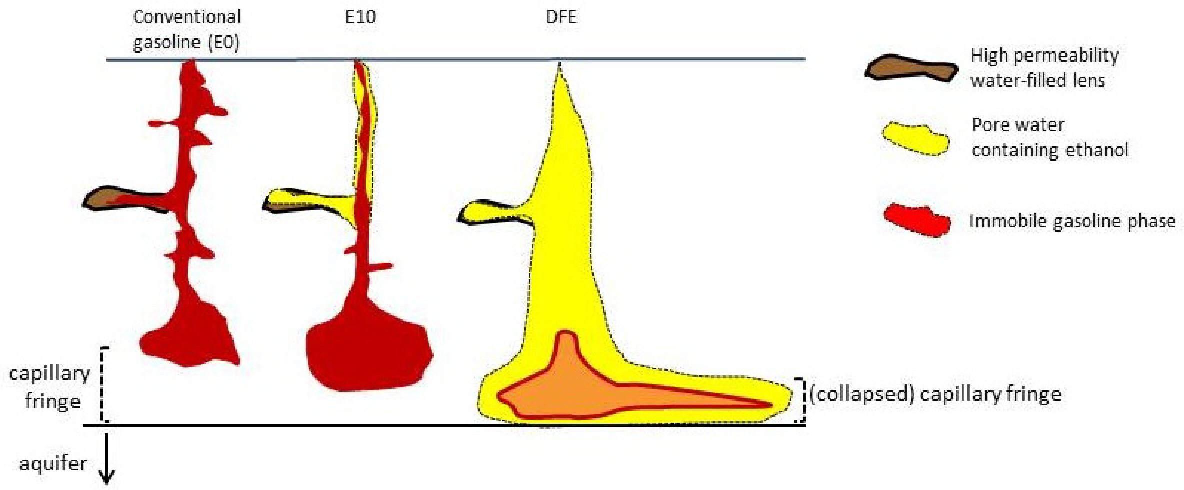

Figure 3-5. Illustration depicting relative behaviors and NAPL distributions of conventional gasoline, E10, and DFE for approximately equal-volume releases. Darker red shading indicates greater NAPL pore saturations; yellow indicates the extent of detectable ethanol prior to dilution and attenuation. *Source*: Adapted from Stafford et al. (2011).

Hydrocarbon constituents are slowly released to groundwater according to their solubility and mass fraction in the hydrocarbon phase if a sufficient mass of hydrocarbon from the fuel mixture remains as a residual LNAPL source near the water table (Raoult's law, see Appendix C). The longevity of residual LNAPL as a source of hydrocarbons (BTEX) to groundwater is on the scale of years to decades. Because biofuel blends have lower fractions of petroleum hydrocarbons than conventional fuels, concentrations of aromatic hydrocarbons are expected to be lower, and the longevity of LNAPL as a continuing source to groundwater is expected to be shorter.

Biodiesel is predicted to be highly adsorbed to vadose soil organic matter. The log K_{ow} values for some biodiesel FAMEs are higher than those for diesel (Table 3-1), indicating that groundwater impacts will mostly be limited to large releases on excessively well-drained soil with a shallow depth to groundwater.

Anaerobic degradation of biofuels can lead to significant generation of gases such as methane and carbon dioxide in the bioreactive zones within the capillary fringe or by generation in groundwater and partitioning or bubbling (i.e., ebullition) to the unsaturated zone. In either case, these gases can accumulate in soil and be advectively transported rapidly within the unsaturated zone. Large volumes of biogenic gases may also strip petroleum volatile organic compounds (VOCs) from the groundwater and induce the advective transport of VOC vapors leading to potentially greater vapor intrusion risks (Toso 2010). Conversely, vapors from petroleum sources are transported mainly by diffusion (Buscheck et al. 2001; Reisinger, Raming, and Hayes 2001; Amos and Mayer 2006).

3.5.4 Saturated Zone Fate and Transport

The saturated zone is defined as the area below the water table where all pore spaces are filled with water under pressure equal to or greater than that of the atmosphere. For chemicals to adversely impact groundwater, contaminants must enter the aquifer, reach concentrations of concern, and persist long enough to be a concern for potential receptors (such as a drinking water supply well or surface water discharge).

Ethanol in groundwater has been investigated at several experimental sites and a few DFE release sites. At these sites, the concentration of ethanol in groundwater ranged 220–55,000 mg/L (Zhang, Kahn, and Spalding 2006; McDowell, Buscheck, and Powers 2003; Cambria case study in Appendix D). Reported zero-order rates of ethanol decay range from 2.9 mg/L/day (Corseuil et al. 2000) to >500 mg/L/day in a sulfate-reducing aquifer (Mackay et al. 2006). The most commonly reported ethanol decay rates are 20–70 mg/L/day (McDowell, Buscheck, and Powers 2003; Zhang, Kahn, and Spalding 2006).

A downgradient groundwater ethanol plume was delineated at only one of several DFE release sites (Tousignant, Evrard, and Campin 2011). At this site, the local geology consisted of very coarse-textured, excessively well-drained materials, including rail line ballast, cobbles, and gravel. The biofuel was released directly into a railway ditch hydraulically connected to the cobble-filled ballast. The result was limited retention above the water table and mixing of the fuel with flowing groundwater developing a downgradient ethanol plume. For other DFE release scenarios, it is unlikely that downgradient ethanol plumes could occur due to the capillary fringe effects noted above, and any dissolved concentrations are expected to quickly decrease to below detection limits. Investigated DFE sites where ethanol plumes did not develop are also characterized by fine-textured soil horizons in the vadose zones and the presence of a large capillary fringe. For scenarios with finer-textured vadose zones where biofuels can be retained in the unsaturated zone above the water table, groundwater concentrations beneath the source zone may increase months to years later due to slow diffusive releases to groundwater and/or infiltration or water table fluctuation events (Spalding et al. 2011).

The most frequent release scenarios are small releases of fuel with low percentages of ethanol biofuel (E10). These are not expected to produce a detectable plume downgradient of the source zone due to retention of ethanol above the water table, rapid biodegradation, and low initial ethanol concentrations. Ethanol that does reach the saturated zone may temporarily influence the biodegradation potential of coexisting hydrocarbons as discussed above, but these effects are expected to be minor. Therefore, E10 releases are expected to behave similarly to E0 (i.e., nonblended petroleum fuel).

Butanol and biodiesel have not been as extensively studied as ethanol; therefore, limited data have been published to date that provide decay rate ranges. Isobutanol was shown to follow an apparent first-order decay curve, with rates dependent on redox conditions, ranging from 0.098 to 0.22 per day under nitrate-reducing conditions, 0.022 per day under sulfate-reducing conditions, and 0.064 per day under methanogenic conditions (Schaefer et al. 2010). Biodiesel has also been shown to follow first-order decay rate trends ranging 0.004–0.05 per day (Lapinskiene and Martinkus 2007, Corseuil et al. 2011b).

3.6 Summary

The differing properties of biofuel from those of conventional fuels influence their fate and transport in the environment. Below are key considerations for SCM development following a biofuel release:

- Following a release, highly soluble biofuels quickly partition to water encountered along their migration pathways.
- Highly soluble and highly biodegradable biofuels released to surface waters significantly impact DO levels as they disperse according to the flow regime of the water body.
- Ethanol has been shown to be retained above the water table, limiting mass transfer to the underlying saturated zone and creating longer-term and diffuse source zones.
- Enhanced petroleum hydrocarbon concentrations from cosolvency effects of ethanol are expected to be limited to the capillary fringe and for large DFE releases.
- Biodegradation of biofuels can generate significant levels of methane in the capillary fringe and shallow groundwater that can then also be transported by advection in the unsaturated zone.
- The generation of large volumes of biogenic gases may strip petroleum VOCs from groundwater and induce the advective transport of VOC vapors, leading to potentially greater vapor intrusion risks.
- Metabolites of biofuel biodegradation can exert a large oxygen demand, which can reduce bioattenuation rates of petroleum hydrocarbons in saturated and unsaturated environments. This effect can extend petroleum plume lengths and allow petroleum vapors to migrate farther.
- The potential impact of ethanol on a groundwater BTEX plume is expected to be temporary and minimal for releases of low ethanol content blends (e.g., E10).
- The longevity of LNAPL generated from gasoline fractions in biofuel blends following a release will be shorter than for equal volume releases of conventional fuels.

4 BIOFUEL RELEASE SITE CHARACTERIZATION

As discussed in Section 3, the physical, chemical, and biological properties of biofuels and their fate and transport in the environment differ from those of conventional petroleum fuels. Consequently, the monitoring, sampling, and analytical methods used to characterize the extent, magnitude, and temporal changes of contamination from biofuel releases also differ.

Site characterization is essential for a robust SCM and includes evaluations of the following:

- release scenario (volume, location, type of biofuel, percentage of biofuel, etc.)
- potentially contaminated media and migration pathways
- potential human and ecological targets or receptors

For biofuel releases, the SCM should also include evaluations preexisting contamination that may be remobilized by the biofuel release and potential for methane generation and gas migration pathways. Initial SCM results assist in the determination of the appropriate level of investigation and the risk factors associated with sources, pathways, and receptors. Risk factors are those aspects of sources, pathways, and receptors that significantly influence the potential for adverse effects. In addition, the SCM is used to determine an appropriate long-term response and, when necessary, justify an active remedy (Section 5).

This section describes considerations beyond those normally included in petroleum release investigations for developing a SCM through a characterization and monitoring program. Because relatively few biofuel release investigations have been conducted to date, only limited experience and published guidance related to biofuel releases are currently available.[3] Therefore, information and recommendations to characterize a biofuel release presented in this section are primarily derived from an evaluation of available case studies, laboratory tests, and controlled-release experiments. However, it should be noted that recommendations based on laboratory or controlled-release experiments may not apply in all field situations.

4.1 Characterization and Monitoring

Characterization and monitoring programs for biofuel releases should consider the following in addition to typical site-specific characteristics (such as geology, release volume, etc.):

- percentage of biofuel component released (for blends)
- biofuel-specific SCM considerations
- material compatibility concerns for wells and other sampling devices (Section 2)

The characterization program for a biofuel release may include monitoring for biofuel-related parameters such as methane and methane precursors; specific biofuel contaminants such as ethanol and biodiesel; and potential DO depletion in surface water. Considerations for monitoring of each are provided below for guidance in development of characterization programs.

4.1.1 Methane and Methane Precursors

Methane gas can accumulate in structures, utilities, or other enclosed places and create an explosive hazard. Because methane is odorless, its presence may be less obvious than that of other contaminants.

As discussed previously, accumulation of methane where ignitable conditions exist can present an explosive hazard (Section 3.3.2). Methane concentrations above 10% of the LEL in enclosed spaces under these conditions present a potentially high-risk situation (see Figure 3-4) and may require emergency mitigation measures (OSHA regulations, 29 CFR §1910) if receptors are present and conditions warrant. Therefore, biofuel releases may need to be initially evaluated for explosive conditions based on site conditions and field gas measurement instruments such as handheld explosimeters or methane gas meters. Methane appearance at sites can be delayed for months to years, suggesting extended monitoring where risks are present (Buscheck et al. 2011). Monitoring data should be sufficient to assess potential methane generation, persistence, and effects on the stability of the petroleum fraction (if present) in groundwater and soil gas. Additional vapor intrusion monitoring may be required due to the possible advection of petroleum vapor by methane and other biogenic gases produced by biofuel degradation (Toso 2010).

Methane may be sampled for in soil gas or in the dissolved phase in groundwater. Because of the dynamic nature of flowing surface water systems, methane and methane precursors are not typically sampled for in surface water. Dissolved methane in groundwater may be more reliable

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[3] Minnesota has developed guidance specifically for ethanol-blended fuel site investigations (MPCA 2010).

for detecting methane than soil gas because of the potential influence of barometric pressure fluctuations on the transport of atmospheric gas into the vadose zone (Massmann and Farrier 1992). However, groundwater monitoring alone should not be used to assess risks to structures from methane vapor intrusion.

Methane precursors may also be sampled for in groundwater to evaluate the potential for methane generation (Section 3.3.2). Acetate, a biodegradation product, can migrate and may produce methane away from the source zone. An alternative method to evaluate potential for methane generation is to analyze for dissolved organic carbon (DOC) or total organic carbon (TOC) in groundwater, rather than acetate.

4.1.1.1 Methane in groundwater

Because methane can move with groundwater and result from intermediate degradation products, dissolved methane is likely to be found in the absence of the source biofuel (such as ethanol or biodiesel). Therefore, methane monitoring should be considered whenever a potential risk exists whether or not the source has been detected in groundwater.

Groundwater monitoring for methane can be conducted to assess the long-term trends in methane generation and the potential for vapor intrusion issues. However, the presence of methane in groundwater does not always imply a soil gas accumulation risk. In theory, methane as low as 2 mg/L in water can produce 5% methane in soil gas based on Henry's law. However, the risk to receptors from these very low dissolved methane concentrations is remote; additionally, distance to receptors and amount of overlying soil can rapidly diminish methane levels in soil gas. Methane generated in the capillary fringe or shallow groundwater may be transported to the soil gas by ebullition (bubbling) at very high production rates. Methane levels above 25 mg/L in groundwater indicate saturated levels, where ebullition may be occurring. Ebullition can occur at lower observed methane concentrations and in the presence of other gasses such as carbon dioxide. Buildup of methane and carbon dioxide in soil gas can produce pressure gradients leading to advective transport that may put structures at risk at greater distances than would be typical for a petroleum release site (Toso 2009).

Methane in groundwater is usually characterized using standard monitoring wells as in typical petroleum release investigations. Caution should be used when interpreting methane risk based on groundwater concentrations as monitoring well screen lengths may have an effect on the detected methane concentrations. Longer screen lengths may not be as representative as shorter screen lengths due to the effect of dilution.

4.1.1.2 Methane in soil gas

In general, monitoring soil gas for methane is needed to evaluate only the potential risk to receptors, if present. If potential vapor or explosive risks associated with a site are not present, methane soil gas monitoring may not be necessary even when methane concentrations in groundwater are high.

The initial site characterization phase of a biofuel investigation may use push probes or temporary wells for soil gas monitoring. However, permanent soil gas monitoring points are recommended for long-term monitoring due to the potential for delayed methane generation and potential for atmospheric effects on soil gas samples. Direct-push wells can be used where appropriate and allowed by the controlling regulatory agency for long-term monitoring (ITRC 2006b).

The location and number of monitoring points needed to adequately characterize methane in soil gas depends on a number of factors, including the following:

- extent of groundwater and soil contamination
- depth to groundwater
- site geology
- access restrictions
- location and distance to potential receptors such as buildings, utilities, etc.

If potential receptors are present, a minimum of one monitoring point should be placed within the release area to monitor the potential for methane accumulation in soil gas over time. The location and construction of methane monitoring points are very similar to those for a typical soil vapor investigation for a petroleum release (ITRC 2007b). Procedures should follow state-specific guidance. Methane monitoring can also be accomplished using existing monitoring wells that have a portion of the well screen in the vadose zone (Jewell and Wilson 2011).

4.1.2 Ethanol and Other Alcohols

Ethanol can be monitored in the vadose zone, capillary fringe, or in groundwater. Surface water may also be monitored for the presence of ethanol, although oxygen depletion is often the primary focus for surface water monitoring (Section 4.1.4). Because alcohols are infinitely miscible in water, ethanol is not likely to be detected in sediment; therefore, sediment sampling is not recommended. Other alcohols, such as butanol, are expected to behave similarly to ethanol, and therefore recommendations applied to monitoring for ethanol should generally apply to butanol and other alcohols as well.

4.1.2.1 Vadose zone and capillary fringe monitoring

Ethanol in the vadose zone can reside in soil gas or within the soil pore space water. Soil gas in the vadose zone can be quantified along with other VOCs as part of a standard soil gas sampling program using USEPA Method TO-15 (USEPA 1999c).

Because of the behavior of ethanol in the subsurface, source zone delineation requires monitoring of the capillary fringe for ethanol, although this has not typically been done as ethanol can also be monitored with properly constructed monitoring wells. However, the levels of ethanol detected in groundwater are likely to be significantly lower than those in the capillary fringe. Caution should be exercised in interpreting monitoring well data for potential vapor intrusion risk from methane and other VOCs, as the absence of ethanol in groundwater is not an absolute indicator of its absence in the capillary fringe. Methane monitoring should be required regardless of ethanol concentrations in groundwater at sites where vapor intrusion is a risk. If necessary, capillary fringe monitoring can be accomplished using lysimeters and/or continuous cores (Freitas and Barker n.d., Spalding et al. 2011).

4.1.2.2 Groundwater

In most cases ethanol can be sufficiently delineated using shorter-screened monitoring wells to capture ethanol draining and/or leaching from the capillary fringe. Because of ethanol's vadose zone retention (see Section 3.5.3), the highest ethanol concentrations in groundwater are found right at the water table interface. Water table fluctuations dictate the screen length needed, but in general these are 1–5 feet in length. Samples from longer-screened wells may not be as representative of conditions as shorter-screened wells due to the effect of dilution.

Because of ethanol's retention above the water table and its rapid degradation at dilute concentrations in groundwater, ethanol is not typically found beyond the original source zone, even for large (>20,000 gal) releases of DFE (Spalding et al. 2011). However, ethanol biodegradation products, including methane and methane precursors, may be found along the groundwater flow path.

4.1.3 Biodiesel

To date, only a limited number of laboratory experiments and release investigations have been reported for biodiesel and biodiesel blends, and therefore limited information is available on environmental fate and transport. From the available information, site investigation strategies for biodiesel releases require additional considerations compare to those for petroleum diesel fuels.

The methyl esters in biodiesel are highly degradable and, like ethanol-blended fuel, may extend petroleum plumes in groundwater due to preferential degradation and may also produce significant quantities of methane (J. T. Wilson 2010). Although the longevity of methane production in biodiesel degradation is poorly understood, methane generation may, like ethanol, be a principal risk driver at a biodiesel release (Adair and Wilson 2010).

Although the biodiesel component of blends (such as B20) may also be investigated, the petroleum fraction of blends is likely to dictate the investigation requirements. Detection of biodiesel-based LNAPL and FAME in soil or groundwater may be possible for biodiesel releases, as discussed below. As with ethanol blends, the potential for increased vapor intrusion risks exists due to methane generation stemming from biodiesel degradation.

B100 is relatively insoluble and, like biodiesel blends, has a density less than water and therefore forms a LNAPL in groundwater. The interaction of a biodiesel-based LNAPL and groundwater is poorly understood at present. Although biodiesel LNAPL has a higher viscosity than ULSD, it should behave similarly to petroleum diesel (Ginn et al. 2010). Because of this higher viscosity, the design of a groundwater monitoring program for biodiesel should include materials that help facilitate the entry of higher-viscosity LNAPL into monitoring wells. For example, the use of wire-wrapped monitoring well screens, as opposed to traditional slotted screens, provides a greater open area for the higher-viscosity LNAPL, facilitating the entry of LNAPL into the well.

Monitoring a B100 release or the FAME component of a biodiesel blend can be problematic as no standard procedures for analyzing biodiesel or FAMEs in soil or groundwater currently exist. In addition, FAMEs are readily hydrolyzed to fatty acids in soil and groundwater and therefore are not detectable as FAMEs. Because the risk driver for a biodiesel blend is likely to be the petroleum fraction (BTEX and naphthalene), generally these parameters can be used to track the extent of the release in soil or groundwater. For a B100 release the general analytical parameters TOC/DOC and chemical oxygen demand (COD) can be used to quantify the dissolved biodiesel fraction in groundwater. TOC can also be used to quantify the amount of FAME in soil. These surrogate methods can be useful to evaluate the potential methane generation risk. Short-chain fatty acids (acetate, butyrate) have been found in groundwater at a B100 release but have not been shown to reliably track the dissolved organic plume in one case study in Minnesota (Westway case study, Appendix D).

A new technology for assessing biodiesel releases is the Tar-specific Green Optical Screening Tool, or TarGOST®, developed by Dakota Technologies. This direct-reading ultraviolet fluorescence instrument was effective at delineating free-phase B100 in subsurface soil (Westway case study, Appendix D).

4.1.4 Surface Water Monitoring

Depletion of oxygen is the primary concern associated with releases of soluble biofuel to surface water. The potential of DO depletion is especially true for ethanol, which is completely miscible with water. DO levels may be measured directly in the field. Alternately, BOD and COD may be analyzed to assess the potential oxygen consumption load. DOC and/or TOC can also be used to determine the total organic loading and thus the oxygen depletion potential due to a surface water release.

Biofuel and typical petroleum parameters can be sampled concurrently with surface water sampling for DO depletion potential, depending on the sampling objectives and fuel composition. Standard methods for collecting water quality data should be followed (USGS n.d.). In general, DO levels above 5 mg/L are necessary to protect most forms of aquatic life. Specific DO and COD levels to support fish and other aquatic life depend on temperature and other considerations; consult the appropriate wildlife agency.

4.2 Sampling and Analytical Methods

Sampling and analysis of the biofuel component, such as ethanol and biodiesel, and potential breakdown products, such as methane and methane precursors, depend on investigative goals and potential risk to receptors. For biofuel blends, the petroleum component should be investigated in accordance with regulatory agency requirements or as described in USEPA SW-846.

This section describes the sampling and analytical field and laboratory methods specific to biofuel or the biofuel component of blends typically used, based on the site-specific monitoring plan. Table 4-1 summarizes the constituents that could be sampled and analyzed for currently available biofuels and biofuel blends.

Table 4-1. Field and laboratory analytical methods for biofuel analytes

Analyte	Environmental media	Analytical methods
Field methods		
Methane	Soil gas	Infrared landfill gas meter
Methane (LEL)	Soil gas	Explosimeter
Ethanol/butanol	Soil gas	Photoionization detector
DO	Surface water	Field meter, kit, or titration
BOD	Surface water	Field meter or kit
Laboratory methods		
Methane	Soil gas	USEPA 3C, ASTM D1946
Dissolved methane	Groundwater	RSK 175
Acetate	Groundwater	Ion chromatography
DOC, TOC	Surface water, soil, groundwater	Standard Method 5310C, ASTM D513-6, USEPA 415.3
BOD, COD	Surface water	USEPA Methods 405.1(BOD), 410.1 #DR/3000 Procedure Code 0.9 (COD), or similar
Ethanol/butanol	Soil	USEPA 8260B with a heated purge trap unit
Ethanol/butanol	Soil gas	USEPA Method TO-15
Ethanol/butanol	Groundwater	USEPA 8260B with heated purge trap (recommended), USEPA 8260, USEPA 8015c USEPA 8261A

4.2.1 Methane

4.2.1.1 Soil gas

Methane in soil gas can be detected with either portable field meters or laboratory methods following active soil gas sampling techniques. Active soil gas sampling techniques typically involve the withdrawal of soil gas from the vadose zone into an appropriate container for analysis, such as laboratory-supplied evacuated canisters or tedlar bags. The ITRC guidance document *Vapor Intrusion Pathway, A Practical Guideline* (ITRC 2007b) contains a description of active soil sampling techniques.

Soil gas samples can be submitted for laboratory analysis for methane and other fixed gases (oxygen and carbon dioxide) using USEPA Method 3C (USEPA n.d.) or ASTM D1946 (ASTM 2006a). These methods require a Summa canister or equivalent for collecting the sample. Required purging of soil gas monitoring points can be done with a field methane gas meter. This method can be advantageous in that real-time data are collected.

Explosive potential includes the presence of methane above levels that could produce an explosive mixture when exposed to oxygen in atmospheric air (see Figure 3-4).

Portable landfill gas meters can be used to measure methane and other fixed gases (oxygen, carbon dioxide) in lieu of laboratory sampling for routine measurements if a good correlation between consecutive laboratory and field measurements can be demonstrated (MPCA 2010). When using a landfill gas meter, care must be taken to avoid interference with petroleum VOCs. An in-line activated carbon filter can be used to remove

VOCs so that the meter reports only methane (Jewell and Wilson 2011). Methane can also be indirectly measured using an explosimeter, although the use of an explosimeter to quantify methane is limited as this type of meter may not be able to read methane in excess of the LEL (approximately 5% or 50,000 ppm). In addition, in the absence of oxygen, explosimeters do not detect explosive potential. Therefore explosimeters are recommended to assess only for current explosive conditions, not methane levels or explosive potential.

4.2.1.2 Groundwater

Special care for sampling methane in groundwater is critical to avoid the loss of methane due to volatilization. Samples should be carefully collected to avoid agitation of the sample and air bubbles within the bottle, which can dramatically lower results. Sampling methods should be well documented to help evaluate the quality of results in case discrepancies arise. Dissolved methane is quantified in groundwater using headspace analysis techniques (RSK 175), which are commonly used in landfill investigations (Missaoui et al. 2009).

4.2.2 Acetate

Both ion chromatography and gas chromatography methods may be used to quantify total dissolved acetate. The detection limits for acetate may vary between the two methods and should be evaluated to ensure they are sufficient to meet site-specific objectives.

4.2.3 DOC and TOC

Standard analytical methods are recommended for the analysis of DOC and TOC (Standard Method 5310C, ASTM D513-6, and USEPA 415.3). Field meters may are available and may be applicable for biofuel releases.

4.2.4 DO, BOD, and COD

DO in surface waters may be measured directly in the field either using a field meter or kit or by titration. For measuring oxygen demand, COD analysis is typically preferred over BOD for assessing current DO conditions because COD can be quantified using portable, handheld field meters. BOD may be applicable for regulatory purposes, but the length of time needed for analysis (minimum of five days) precludes an assessment of current conditions. Standard laboratory methods for BOD and COD analysis are available.

4.2.5 Ethanol

4.2.5.1 Soils

Soil sampling methodologies are similar to those used for conventional petroleum release investigations. Analysis is completed using USEPA Method 8260B. Detection limits are based on one of the laboratory preparation methods described in USEPA Method 5035.

4.2.5.2 Soil gas

Soil gas samples from the vadose zone can be collected using active soil gas sampling techniques (ITRC 2007b). Passive soil gas sampling techniques are not recommended as the absorbent materials used are not suitable for methane and fixed gases. Ethanol in soil gas samples can be quantified using USEPA Method TO-15.

4.2.5.3 Water

Sampling methodologies for ethanol should follow the same procedures as for petroleum. Passive diffusion bag samplers should be verified with the manufacturer for applicability with ethanol (ITRC 2006a). Several laboratory analytical techniques for analyzing ethanol in water exist, but in general, USEPA Method 8260B with heated purge trap is recommended. Without employing a heated purge trap the MDLs are in the 100 µg/L range, which is generally sufficient for site investigation purposes. With the heated purge trap, ethanol MDLs can be as low as 5 µg/L by using a calibration mixture of ethanol in water versus a standard methanol calibration mixture. Other methods which have higher MDLs, such as USEPA Methods 8015C and 8261A, can be used to quantify ethanol in groundwater.

4.3 Fate and Transport Modeling

Data collected as part of the site-specific monitoring program can be used to build fate and transport models for predicting environmental behavior and decision making. Models specific to the fate and transport of biofuels released to the environment have been developed. Generally, these models use standard input parameters characterizing the impacted media, such as hydraulic conductivity, hydraulic gradient, and porosity along with the physical, chemical, and biological properties of the constituents, including solubility, partitioning, biodegradability, etc. (Sections 3.2 and 3.3). Furthermore, these models can be one- to three-dimensional in nature and can range from simple screening models to complex numerical solutions.

Other biofuel models have also been developed that consider the overall environmental footprint with perspectives on water resources, greenhouse gases, land usage, feedstock productivity, etc. These are generally outside the scope of this document.

In most cases, these models consider not only the fate and transport of the biofuel fraction but also the effects that the biofuel has on the blended petroleum constituents as well. For example, the FOOTPRINT model (USEPA 2008) specifically considers the effects that ethanol can have on the area of a BTEX plume when released as a blended biofuel. As a hypothetical worst-case scenario, this model presumes a given ethanol concentration within the groundwater near the source zone and a biodegrading ethanol plume emanating from the source. The model software uses a modified Domenico equation to approximate the advective-dispersive solute transport equation with first-order decay. Similarly, the General Substrate Interaction Module (GSIM) is an “add-on” to the general Reactive Transport in Three Dimensions (RT3D) and Modular Three-Dimensional Finite Difference Groundwater Flow (MODFLOW) models (Gomez et al. 2008). Specifically, RT3D and MODFLOW can be used to model the natural attenuation processes (e.g., advection, dispersion, dilution, adsorption, etc.) for biofuels and/or petroleum compounds using the physical and chemical properties of both the media and the constituents. The advantage of RT3D is that reactive mechanisms within natural attenuation, such as biodegradation, are based on user-defined inputs. Therefore, GSIM can then be added to incorporate degradation, electron acceptor substrate interactions, microbiological changes, and toxicity into the reactive portion of the simulations. This particular modeling approach has been done to examine the effects of different blend concentrations of ethanol, methanol, 1-propanol, 1-butanol, and isobutanol on benzene plume characteristics (Gomez and Alvarez 2010).

4.4 Conclusions and Recommendations

In general, site characterization and risk assessment for biofuels and biofuel blends follow standard petroleum release procedures. However, because of the physical, chemical, and biological properties of biofuels, characterization of a biofuel or biofuel component of a blend differs in some respects. The following conclusions and recommendations specific to biofuel release characterization are based on the best available information to date:

- Methane in soil gas can be a risk driver for a biofuel release, and site closure may require longer-term monitoring to assess methane risks due to delayed methane generation.
- The physical properties of biofuels may require some changes to a site investigation design, such as the use of wire-wrapped or shorter well screens for groundwater monitoring.
- Sampling for additional parameters is likely needed.
- Additional field screening equipment (meters) may be required.
- Site investigation and analysis techniques for biofuels other than ethanol and biodiesel should be based on physical, chemical, and biological properties of the biofuel. For example, the behavior of butanol is similar to that of ethanol, and therefore site investigation and analysis techniques would be expected to be similar.
- Additional vapor intrusion monitoring may be required due to the possible stripping of petroleum VOCs from groundwater and advection of petroleum vapor by methane and other biogenic gases produced by biofuel degradation. Methane can also exert a large oxygen demand, which can reduce bioattenuation rates and allow petroleum vapors to migrate further.

Active research on biofuel releases continues to evolve understanding of the fate and transport of biofuels in the environment and therefore the characterization, sampling and analytical methods for investigation of a release. In addition, potential emerging characterization technologies, such as geophysics, isotopic analysis, and environmental molecular diagnostics, may advance the investigative capabilities for biofuel.

5. LONG-TERM RESPONSE STRATEGIES FOR BIOFUEL RELEASES

Short-term response strategies generally focus on containment and recovery of released biofuel, elimination of any immediate threats, and prevention of transport to sensitive receptors such as waterways and sewer lines, as discussed in Section 2.4. Long-term response strategies for a biofuel release require consideration of a number of factors, including the following:

- type of biofuel
- extent and magnitude of the release
- regulatory threshold for a COC

- risk to identified receptors

In this document, long-term decision making follows a risk-based approach—a decision-making process for the assessment and response to a release based on the protection of human health and the environment. As with petroleum releases, sites with biofuel releases vary greatly in terms of complexity; physical, chemical, and biological characteristics; and the risk that they may pose to human health and the environment. This risk-based approach tailors responses to site-specific conditions and risks and can be applied to the variety of release scenarios. A similar tiered approach has been standardized for petroleum releases by ASTM Standard E1739-95(2010)e1 (ASTM 2010a). However, state guidance and policy may vary and should be consulted and followed regarding the use of a risk-based approach.

Figure 5-1 depicts a generalized model of the risk-based decision-making process. The process begins when sufficient site characterization data and an accurate SCM are available to determine whether a regulatory threshold triggering a response has been exceeded. If contamination does not exceed any applicable threshold, no further action may be appropriate. However, if contaminant levels are above regulatory thresholds or a potential hazard exists (such as explosive risk due to methane), a site-specific risk assessment should be completed. The results of the risk assessment can be used to determine whether the risk is acceptable and manageable through monitoring and/or control measures or may require implementation of an active remedy. Remedial end points for active remedies or closure requirements must be met before proceeding to site closure.

Following this approach, a number of strategies may be implemented to achieve site closure and may include any or all of the following: monitored natural attenuation (MNA), controls (institutional or engineered), and/or contaminant source reduction through implementation of an active remedy. This section discusses implications for risk assessment and the strategic options for risk reduction for biofuel releases. Few case studies involving active remediation for biofuels exist. Therefore, a methodology for evaluating and selecting a remedial technology was developed by gauging current remedial technologies' ability to exploit the physical, chemical, and biological properties of biofuels to achieve remedial goals.

5.1 Regulatory Thresholds and/or Potential Hazards

Regulatory thresholds triggering a long-term response could be a state-specific target level (e.g., maximum contaminant level, toxicity level, water quality level, etc.) or a predefined Tier 1 (or screening level) assessment look-up table value for a COC(s). In addition, other factors such as an explosive risk hazard may trigger a long-term response. If regulatory thresholds are not exceeded and no other risk hazards are present, additional remedial action may not be necessary other than maintaining the land use in accordance with the exposure assumptions. The framework for making risk-based management decisions differs from state to state, and some states may not have thresholds relevant to biofuel releases. Therefore, regulatory guidance should be evaluated on a state-by-state basis.

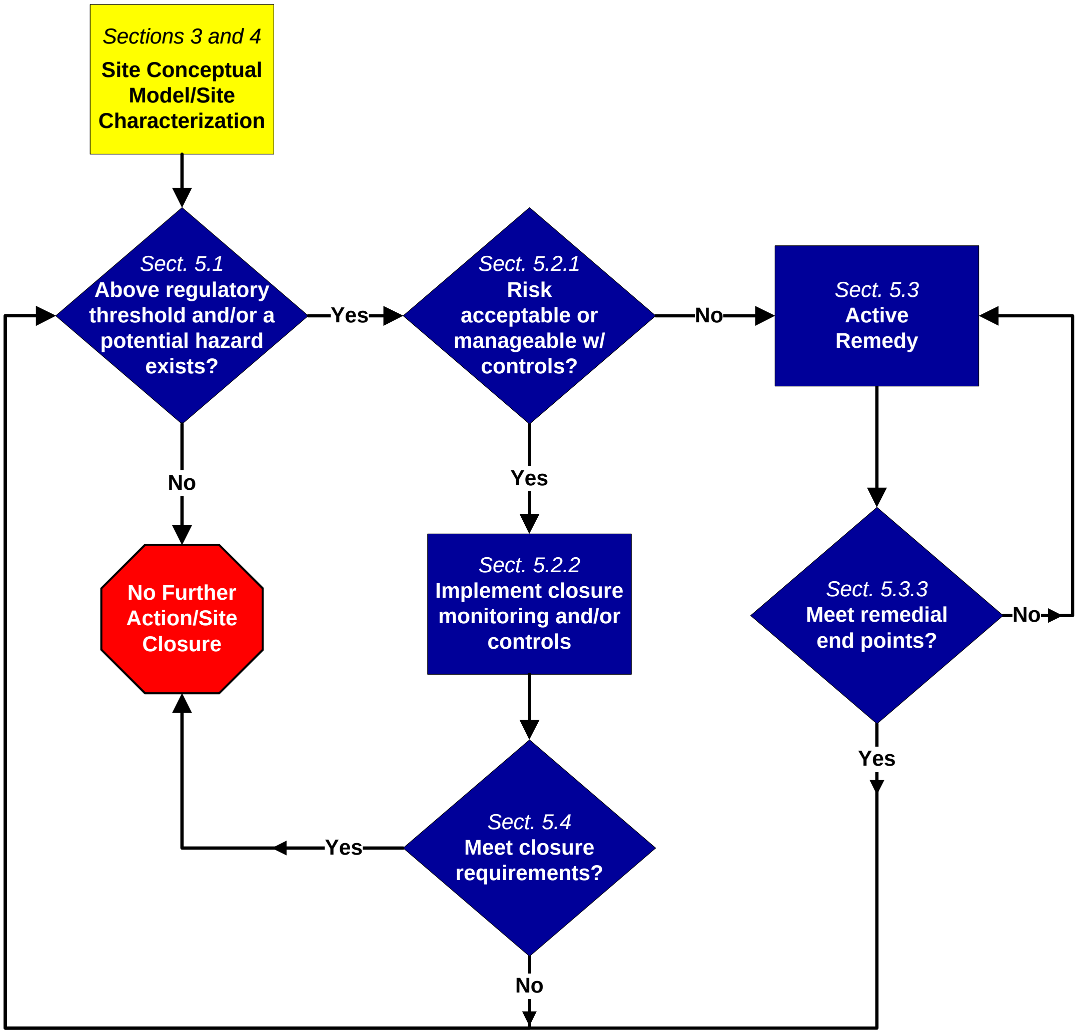


Figure 5-1. Generalized framework for risk-based management of biofuel releases.

For tiered risk-based approaches to remediation, a Tier 1 assessment is composed of an analysis of potential receptor exposure to contaminants at or migrating from the release site. This assessment compares COC concentrations measured in site media to defined regulatory screening levels based on land use and conservative exposure assumptions. The Tier 1 screening levels are used to identify which, if any, contaminants and environmental media may warrant additional evaluation or remediation to protect human health and the environment.

COCs at a biofuel release may be one or several of the following in one or multiple phases (e.g., aqueous and/or vapor phase) in soil, sediment, groundwater, or surface water:

- the biofuel (including the biofuel component of a blend)
- a degradation product (such as methane)
- a biofuel additive or denaturant
- the petroleum component of a biofuel blend

While some states may have standards for one or more biofuels (most likely for ethanol), others may not. Therefore, the remediation driver may be something other than the biofuel, such as the petroleum component of a blend, an additive, or denaturant. As discussed previously in Sections 3 and 4, the biodegradation of biofuels can result in methane generation, which presents an explosive hazard. Therefore, the presence of methane in soil gas or dissolved in groundwater or the presence of methane precursors may require mitigation of the methane and/or the source biofuel. Biofuel additives, if known, may also present a risk, although screening levels may not exist. In some cases remediation of the biofuel component of a blend may need to proceed before remediation of the petroleum fraction due to preferential biodegradation of the biofuel component (Section 5.3.2).

5.2 Risk Assessment and Management

Risk assessment allows for site-specific management decisions to be made. Detailed information on risk assessment is available in a number of published guidance documents (ITRC 2008b, USEPA 1991), as is information on risk-based decision making (ITRC 2004, 2007a; DOE 2008; NAVFAC 2008; ASTM 2010a). This section provides a general overview of risk assessment and management as these processes can be applied to biofuel releases, with a focus on how risk-based decisions affect long-term response strategies.

If a regulatory threshold is exceeded, some level of risk management is usually involved in decision making based on the following:

- evaluation of site-specific risk assessment results
- determination of whether the risk can managed through MNA and/or land use controls alone or whether an active remedy for source reduction is needed
- evaluation and selection of potential long-term remedial technologies for source reduction (if warranted)

5.2.1 Site-Specific Risk Assessment

Site-specific risk assessments may be conducted if a regulatory threshold or Tier 1 look-up value is exceeded. If methane generation is a concern, the physical component of risk should be evaluated, which is typically not included in a Tier 1 risk assessment. Under a tiered risk-based approach, the site-specific risk assessment is typically a Tier 2 assessment that relies on site-specific information, including land or water use determinations. Site contaminant concentrations are compared against Tier 2 screening levels to determine whether individual contaminants or mixtures of contaminants pose a potential risk. A Tier 3 assessment, based on more complex modeling using site-specific data, may be necessary in cases where remediation to Tier 2 screening levels is not feasible or when site conditions require a unique approach to site investigation and setting remedial goals. The site-specific risk assessment can be used to develop closure criteria. Site-specific risk assessments incorporate the following:

- toxicity assessment
- analysis of potential receptor exposures to contamination at or migrating from the release site
- site characterization data analysis

Chemical-specific toxicity data may be used to derive regulatory thresholds and/or to develop site-specific screening levels. More information on biofuel toxicity can be found in Section 1.6. For methane generation, regulatory thresholds and site-specific screening levels are typically based on explosive risk, as discussed in Section 3.3.2.4.

Biofuel exposure pathways are not expected to differ markedly from petroleum fuels (as described in Section 3). The process of building and updating the SCM (Section 4) can be used to identify potential receptors and evaluate contaminant concentrations to determine exposure potential, including potential generation of biofuel degradation products of concern (e.g., methane).

Proper site characterization, as discussed in Section 4, is critical for evaluating exposure. Ideally, identifying potential receptors should be intertwined with site characterization activities to expeditiously and thoroughly evaluate exposure pathways. If sufficient site characterization data are not available, additional characterization is likely to be needed before deciding on a long-term response strategy.

Based on the toxicity assessment, evaluation of potential exposure pathways, and site characterization data, risk assessment conclusions inform risk-based site management decisions. Depending on state regulations, risks may be manageable with MNA or institutional or engineering controls. Impacts requiring an active remedy are generally associated with human and ecological receptors, such as inhabitants of an impacted structure, users of an impacted water supply well, and aquatic and terrestrial organisms. An active remedy may also be driven by planned or future land use, explosive or dangerous conditions, or other state-specific regulatory requirements.

5.2.2 Managing Risk Through Ongoing Monitoring

MNA relies on a variety of physical, chemical, and biological processes that reduce the toxicity, mobility, or concentration of contaminants in soil, soil gas, and groundwater (USEPA 1998b). MNA may be an applicable alternative to an active remedy. MNA takes advantage of the ability of biofuels to readily dissolve and biodegrade, although it also has some limitations (Table 5-1).

Table 5-1. Benefits and limitations of MNA for biofuel remediation

Benefits	Limitations
Dissolved biofuel is readily biodegradable without additional enhancement.	• High concentrations of some dissolved biofuel constituents (e.g., ethanol) can be toxic to microorganisms. • Delayed biodegradation of more recalcitrant contaminants via preferential biodegradation of the biofuel. • Does not address immediate risks. • High potential for methane generation. • Does not address LNAPL, although microbial processes can enhance dissolution in groundwater. • Surface water may become anoxic, impacting aquatic species and habitat.

The use of MNA has been documented in several biofuel release sites following physical treatment of the source zone through soil excavation. Case studies in Appendix D evaluate MNA results over time for a large-volume DFE release (Cambria, Minnesota) and for a biodiesel release (Westway Biodiesel). The Cambria case study demonstrates the spatial variability in attenuation, which can be accounted for with an adequate monitoring well network. In addition, the presence of methane, as identified in the DFE and biodiesel case studies, may be detected in monitoring wells after the biofuel is no longer detectable. Therefore, the presence of methane may require additional mitigation measures. For example, at a third case study site, Pacific Northwest Terminal (Appendix D), MNA was conducted for ethanol; however, for methane, active remediation using soil vapor extraction (SVE) was used. Furthermore, because of the potential for delayed methane generation (Section 3.3.2.4), monitoring should continue for some period of time after the biofuel is no longer detected as well, and consideration should be given to monitoring methane precursors (such as acetate or TOC) to evaluate the potential for methane generation (see also Section 4.2).

5.2.3 Managing Risk Through Control Measures

Control measures provide protection from exposure to contaminants that exist or remain on a site and include institutional (administrative and/or legal) controls (ICs) and engineering (physical) controls (ITRC 2008a). USEPA defines ICs as "non-engineering measures, such as administrative and/or legal controls, that help to minimize the potential for human exposure to contamination and/or to protect the integrity of a remedy by limiting land or resource use" (EDSC 2006). ECs are barriers or systems that control migration, infiltration, or natural leaching/ migration of contaminants through the subsurface over time.

The determination as to the type and duration of a specific control and whether an IC is sufficient or both an IC and an EC are needed depends on regulatory requirements and site-specific conditions. Additional guidance and examples on applying these controls can be found in a number of published guidance documents (ITRC 2008a, USEPA 2010b, ASTM 2005).

5.3 Active Remedy Evaluation and Selection

Active remedies focus on reducing or eliminating the remediation driver, or COC, until risk reduction or elimination has been achieved. Selection of a remedial technology takes this goal, as well as other factors (such as timeliness, cost, stakeholder concerns, etc.), into consideration when evaluating potential technologies.

Because of the limited experience in active remediation of biofuel releases at this writing, a detailed analysis was conducted of remedial technologies that have been used or are likely to be used when the remediation driver is a biofuel or biofuel degradation product or when petroleum contaminants are the remediation driver but biofuel remediation is also desired (Section 5.3.1). These technologies include those that have been documented in case studies (Appendix D) and those identified by states responding to the ITRC Biofuels Team state survey. Next, a site-specific remedial technology evaluation and selection process was developed that draws upon the technologies analysis (Section 5.3.2). Last, general considerations for remedy implementation and monitoring (Section 5.3.3) and site closeout (Section 5.3.4) are provided.

5.3.1 Process for Selecting Applicable Remedial Technologies for Evaluation

Identification of applicable remedial technologies was limited to an initial evaluation of the known or expected ability to remediate a biofuel or biofuel component with respect to physical, chemical, or biological properties of the biofuel. Appendix E provides brief descriptions of the technologies selected in this document, divided into in situ and ex situ categories, with references to additional technology-specific information.

The in situ and ex situ remedial technologies were further classified according to the dominant biofuel property (i.e., physical, chemical, or biological) that the remediation technology can be expected to act on and the applicable environmental media (categorized as soil/sediment and surface water/groundwater). The selected technologies were evaluated based on their expected benefits and limitations specific to biofuel remediation (Tables 5-2 and 5-3). The benefits and limitations were evaluated based on general technology considerations for a variety of release scenarios, for example, whether the technology addresses LNAPL for separate-phase biofuels (e.g., butanol or biodiesel) or the potential for methane generation.

Table 5-2. Selected remedial technologies for soil/sediment impacts

Technology		Benefits	Limitations
In situ treatment	***Biological***		
	Enhanced aerobic biodegradation *Bioventing—soil*	Can result in rapid elimination of dissolved constituents and increase in dissolution and subsequent biodegradation of residual NAPL. Promotes methane oxidation. Likely inhibits formation of anaerobic conditions and methane generation.	Does not directly address LNAPL. High concentrations of some dissolved biofuel constituents (e.g., ethanol) can be toxic to microorganisms.
	Chemical		
	Chemical oxidation *Soil and sediment*	Rapid destruction of all constituents.	Does not directly address LNAPL; high potential for rebound (if LNAPL is present).
	Surfactant enhancement/ cosolvent flushing *Soil only*	Removal of LNAPL over a short time frame.	Requires hydraulic control or other remedial technique to protect groundwater beneath targeted treatment zone and to prevent plume expansion.
	Physical		
	SVE *Soil*	Rapid removal of readily strippable compounds (constituents with a high Henry's law constant, vapor pressure, and/or biodegradability). Promotes aerobic biodegradation of biofuels and methane oxidation (if present).	Not effective for constituents with a low Henry's law constant, vapor pressure, and/or biodegradability. May require ex situ vapor treatment.
	Containment *Capping—soil, lining—sediment*	Removes human and/or ecological health risk. Can prevent leaching into groundwater (soil) or further contact with benthic organisms (sediment).	Does not directly destroy or remove biofuel constituents. May require periodic replacement; possible methane mitigation.
Ex situ treatment[a]	***Biological***		
	Landfarming, composting, biopiling	Destruction/removal of biofuel constituents via biodegradation and volatilization.	Requires intensive manipulation/handling of media.
	Chemical		
	Soil washing	Rapid removal of all constituents.	Disposal of washing fluid required.
	Physical		
	Thermal (desorption incineration)	Complete destruction of constituents; rapid time frame.	May require dewatering of soil/sediment.
	Landfilling	Immediate removal/disposal of constituents.	Requires transportation and disposal.

[a] Ex situ treatment of excavated source material in soil and sediment.

Table 5-3. Selected remedial technologies for groundwater/surface water impacts

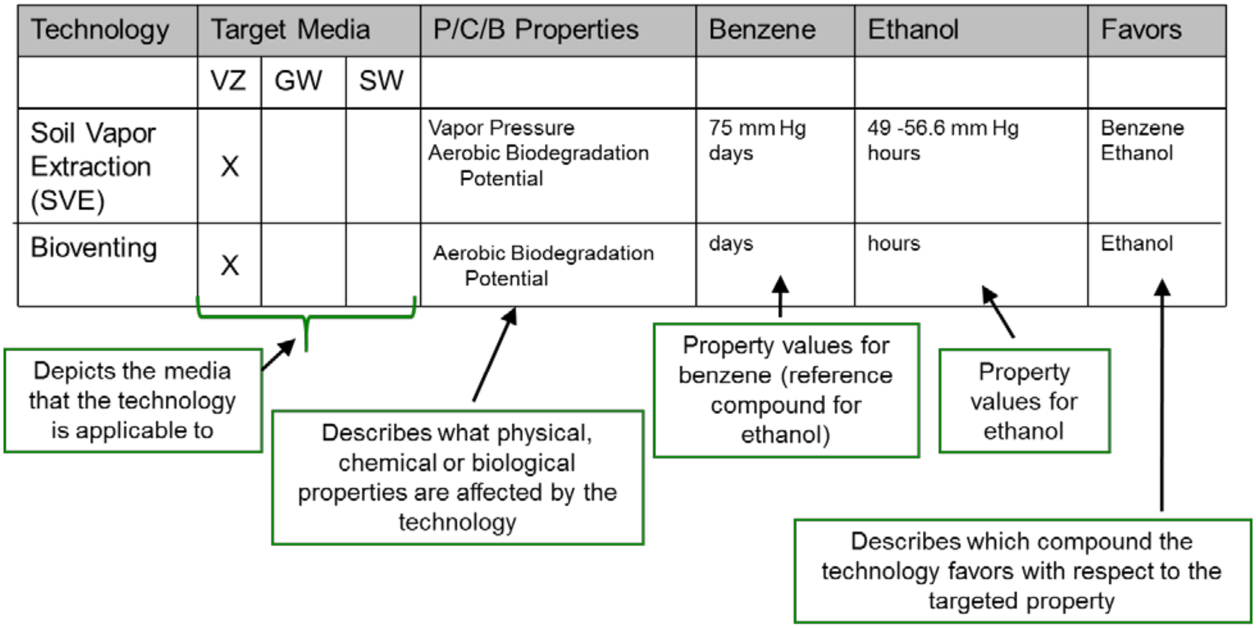
	Technology	Benefits	Limitations
In situ treatment	***Biological***		
	Enhanced aerobic biodegradation *Aeration (surface water); biosparging, oxygen diffusion, etc. (groundwater)*	Aerobic biodegradation can result in rapid elimination of dissolved biofuel constituents, likely to inhibit formation of anaerobic conditions and methane generation, can increase dissolution and subsequent biodegradation of immobile (residual) LNAPL.	High concentrations of some dissolved biofuel components (e.g., ethanol) can be toxic to microorganisms. May be difficult to satisfy oxygen demand stemming from dissolved biofuel. Does not directly address LNAPL.
	Enhanced anaerobic biodegradation *Anaerobic electron acceptor addition (groundwater only)*	Anaerobic biodegradation of dissolved-phase biofuel constituents can readily occur under alternative (anaerobic) electron-accepting processes, may inhibit methane generation, can increase dissolution and subsequent biodegradation of residual LNAPL.	Does not address immediate risks. Does not directly address mobile LNAPL. Some risk of methane generation (dependent on the type of electron acceptor addition). High concentrations of some dissolved biofuel constituents (e.g., ethanol) can be toxic to microorganisms.
	Chemical		
	Chemical oxidation *Groundwater*	Rapid destruction of biofuels, inhibits methane generation, may indirectly address residual LNAPL (dependent on oxidant kinetics).	Does not directly address mobile LNAPL. High potential for rebound (if LNAPL is present).
	Surfactant enhancement/ cosolvent flushing *Surfactant/dispersant (surface water and groundwater); cosolvent addition (groundwater only)*	Removal of LNAPL over a short time frame (groundwater), dispersal/breakup of LNAPL to aid and allow for biodegradation processes (surface water).	Hydraulic control required to prevent plume expansion. Does not directly address dissolved plume (some removal via hydraulic control may occur). Methane generation likely if dissolved biofuels remain following remedy completion (groundwater).
			Increases risk of anaerobic conditions, which would negatively affect aquatic species and habitat (surface water).

Technology		**Benefits**	**Limitations**
In situ treatment	***Physical***		
	Air sparging *Surface water and groundwater*	Rapid removal of readily strippable/biodegradable compounds (those containing a high Henry's law constant, vapor pressure and/or biodegradability). Promotes aerobic biodegradation, inhibits formation of anaerobic conditions and methane generation.	Not effective for constituents with a low Henry's law constant, vapor pressure, and/or biodegradability. May require subsurface vapor capture and ex situ vapor treatment.
	Physical or hydraulic containment *Surface water and groundwater*	Source and mobile NAPL control (surface water and groundwater). Prevention of plume expansion (groundwater).	Management/treatment of extracted fluid. Methane generation in aquifer likely. Formation of anaerobic conditions and methane generation during hydraulic containment (groundwater).
			Increases risk of anaerobic conditions, which would negatively affect aquatic species and habitat (surface water).
	Sorbents/skimmers *Surface water*	Removal of mobile LNAPL.	Does not address dissolved plume. Limited to removal of mobile LNAPL. Methane generation likely in dissolved portion of the plume if not addressed using another remedial technology.
	Multiphase extraction *Groundwater*	Physical removal of mobile LNAPL. Removal of volatile fractions of residual LNAPL. Removal of dissolved-phase biofuel constituents. Promotes aerobic biodegradation. Likely to inhibit methane generation.	Ex situ management/treatment of extracted liquids and vapors. Need to extract excessive volume of groundwater to address the dissolved plume.
	Thermal treatment *Electrical resistance/ thermal conductive heating, steam sparging (groundwater); pyrolysis (surface water)*	Short time frame. Enhanced LNAPL recovery and/or destruction of dissolved biofuel constituents (groundwater). Complete destruction of NAPL (surface water).	Requires hydraulic control. Ex situ management/ treatment of extracted fluid (groundwater).
			Hazards associated with burning. Requires safety precautions. Does not address dissolved-phase biofuel constituents. Does not prevent anaerobic conditions from forming (surface water).

Technology		**Benefits**	**Limitations**
Ex situ treatment[a]	***Biological***		
	Bioreactor	Biodegradation of biofuel constituents. No introduction or emissions of hazardous substances.	Management of solids. Biofouling. Media replacement.
	Constructed wetlands	Removal of biofuel constituents via multiple mechanisms, including biodegradation, phytoremediation, photolysis, and volatilization (direct and indirect via plant uptake).	Large footprint. High potential for methane generation under anaerobic system design.
	Chemical		
	Advanced oxidation	Rapid destruction of all constituents.	High energy requirements. LNAPL, metals, and turbidity affect performance.
	Physical		
	Air stripping	Rapid removal of readily strippable compounds (constituents with a high Henry's law constant and vapor pressure).	Not effective for constituents with a low Henry's law constant and/or vapor pressure. May require vapor treatment.
	Discharge to sewer/ wastewater plant	Removal of all biofuel constituents.	Sewerage costs. Permitting.

[a] Ex situ treatment of excavated source material in soil and sediment.

A detailed evaluation of each technology based on the ability of the technology to influence the physical, chemical, and biological properties of potential contaminants (ethanol, biodiesel, butanol, and methane) was also conducted (Tables 5-4a, b, c, and d). This series of tables is organized by base technology (e.g., air sparging), and where applicable also shows additional treatment technologies that can be used in conjunction with the base technology (e.g., SVE). For clarity, the companion technologies are indented under the base technology and preceded by a "+." For this evaluation, the effectiveness of ethanol, butanol, and biodiesel were normalized to reference compounds. For ethanol and butanol, the reference compound was benzene; for biodiesel, the reference compound was petroleum diesel. Indications are provided to denote whether the contaminant is expected to be either more or less susceptible to remediation than the reference compound based on comparison of relevant physical, chemical, and/or biological properties, such as volatility, solubility, biodegradability, sorption, etc. For example, SVE in the vadose zone enhances the biodegradation of ethanol. Figure 5-2 shows an extract of Table 5-4a to explain each column in the technology tables.



Technology	Target Media			P/C/B Properties	Benzene	Ethanol	Favors
	VZ	GW	SW				
Soil Vapor Extraction (SVE)	X			Vapor Pressure Aerobic Biodegradation Potential	75 mm Hg days	49 -56.6 mm Hg hours	Benzene Ethanol
Bioventing	X			Aerobic Biodegradation Potential	days	hours	Ethanol

Depicts the media that the technology is applicable to

Describes what physical, chemical or biological properties are affected by the technology

Property values for benzene (reference compound for ethanol)

Property values for ethanol

Describes which compound the technology favors with respect to the targeted property

Figure 5-2. Extract from Table 5-4a describing each column in the technology selection Tables 5-4a through 5-4c.

As shown, the properties affecting a specific technology were compared with respect to the reference compounds; accordingly, an overall scoring of a technology is not provided. Technologies are shaded if they are not applicable for remediation of a biofuel. For example, multiphase extraction would not be used on ethanol since it is a completely miscible compound. Appendix C provides the references for the properties depicted in the tables.

Table 5-4a. Ability of selected remedial technologies to influence the physical, chemical, and biological properties of ethanol as normalized to benzene in the vadose zone (VZ), groundwater (GW), and surface water (SW)

Technology	Target media			Physical, chemical, biological properties	Benzene	Ethanol	Generally favors
	VZ	GW	SW				
Excavation	x			Sorption (log K_{oc}) Surface tension Density Capillary rise	1.98 (unitless) 28.88 dyn/cm 0.879 g/cm^3 0.14 cm	0.21 to 1.21 (unitless) 22.1 dyn/cm 0.789 g/cm^3 0.12 cm	Benzene Benzene Benzene Benzene
+ Landfarming, composting, biopiling	x			Vapor pressure Aerobic biodegradation potential Anaerobic biodegradation potential	75 mm Hg Weeks-months Years	49 to 56.6 mm Hg Days-weeks Weeks-months	Benzene Ethanol Ethanol
+ Soil washing	x			Solubility Interfacial tension	1.8E+3 mg/L 35.5 dyn/cm	Infinite None (miscible)	Benzene Benzene
+ Thermal (desorption incineration)	x			Vapor pressure Boiling point	75 mm Hg 80.1°C	49 to 56.6 mm Hg 78.3°C	Benzene Ethanol
Soil vapor extraction	x			Vapor pressure Aerobic biodegradation potential	75 mm Hg Weeks-months	49 to 56.6 mm Hg Days-weeks	Benzene Ethanol
Bioventing	x			Aerobic biodegradation potential	Weeks-months	Days-weeks	Ethanol
Natural attenuation (biodegradation)	x	x		Aerobic biodegradation potential Anaerobic biodegradation potential	Weeks-months Years	Days-weeks Weeks-months	Ethanol Ethanol
Anaerobic bioremediation	x	x		Anaerobic biodegradation potential	Years	Weeks-months	Ethanol
Aerobic bioremediation	x	x	x	Aerobic biodegradation potential	Weeks-months	Days-weeks	Ethanol
Air sparging, oxygen sparging	x	x		Henry's law constant Solubility Aerobic biodegradation potential	0.22 (gas/aq) 1.8E+3 mg/L Weeks-months	2.1E-4 to 2.6E-4 (gas/aq) Infinite Days-weeks	Benzene Benzene Ethanol
+ Soil vapor extraction	x	x		Vapor pressure Aerobic biodegradation potential	75 mm Hg Weeks-months	49 to 56.6 mm Hg Days-weeks	Benzene Ethanol
In situ chemical oxidation	x	x		Hydroxyl rate	1.95E-12 cm^3/mol-sec	3.6E-12 cm^3/mol-sec	Ethanol
In situ thermal treatment	x	x		Vapor pressure Viscosity Boiling point	75 mm Hg 0.649 cp 80.1°C	49 to 56.6 mm Hg 1.074 cp 78.3°C	Benzene Benzene Benzene
Physical containment (in situ wall/barrier)		x		Solubility	1.8E+3 mg/L	Infinite	Ethanol

Technology	**Target media**			**Physical, chemical, biological properties**	**Benzene**	**Ethanol**	**Generally favors**
	VZ	**GW**	**SW**				
Fluid extraction	x	x	x	Solubility	1.8E+3 mg/L	Infinite	Ethanol
+ Product pumping, skimming, separation		x	x	Partitioning (log K_{ow}) Solubility	2.13 (unitless) 1.8E+3 mg/L	-0.16 to -0.31 (unitless) Infinite	Benzene Benzene
+ Multiphase extraction, dual-phase extraction, vacuum-enhanced recovery	x	x		Vapor pressure Viscosity	75 mm Hg 0.649 cp	49 to 56.6 mm Hg 1.074 cp	Benzene Benzene
+ Surfactant flushing, cosolvent flushing		x	x	Solubility Interfacial tension	1.8E+3 mg/L 35.5 dyn/cm	Infinite None (miscible)	Benzene Benzene
+ Air stripping		x	x	Henry's law constant	0.22 (gas/aq)	2.1E-4 to 2.6E-4 (gas/aq)	Benzene
+ Advanced oxidation		x	x	Hydroxyl rate	1.95E-12 cm^3/mol-sec	3.6E-12 cm^3/mol-sec	Ethanol
+ Bioreactor		x	x	Aerobic biodegradation potential	Weeks-months	Days-weeks	Ethanol
+ Constructed wetlands		x	x	Sorption (log K_{oc}) Henry's law constant Aerobic biodegradation potential Anaerobic biodegradation potential	1.98 (unitless) 0.22 (gas/aq) Weeks-months Years	0.21- 1.21 (unitless) 2.1E-4 to 2.6E-4 (gas/aq) Days-weeks Weeks-months	Ethanol Benzene Ethanol Ethanol
+ Discharge to sewer or wastewater plant		x	x	Henry's law constant Aerobic biodegradation potential Anaerobic biodegradation potential	0.22 (gas/aq) Weeks-months Years	2.1E-4 to 2.6E-4 (gas/aq) Days-weeks Weeks-months	Benzene Ethanol Ethanol
Surface booms/barriers			x	Partitioning (log K_{ow}) Solubility	2.13 (unitless) 1.8E+3 mg/L	-0.16 to -0.31 (unitless) Infinite	Benzene Benzene
+ Sorbents/skimmers			x	Sorption (log K_{oc})	1.98 (unitless)	0.21 to 1.21 (unitless)	Benzene
+ Aeration, agitation (air/ oxygen sparging)			x	Henry's law constant Aerobic biodegradation potential	0.22 (gas/aq) Weeks-months	2.1E-4 to 2.6E-4 (gas/aq) Days-weeks	Benzene Ethanol

Table 5-4b. Ability of selected remedial technologies to influence the physical, chemical, and biological properties of butanol as normalized to benzene in the vadose zone (VZ), groundwater (GW), and surface water (SW)

Technology	**Target media**			**Physical, chemical, biological properties**	**Benzene**	**Butanol**	**Generally favors**
	VZ	**GW**	**SW**				
Excavation	x			Sorption (log K$_{oc}$)	1.98 (unitless)	1.86 to 2.05 (unitless)	Both
				Surface tension	28.88 dyn/cm	22.98 to 24.93 dyn/cm	Benzene
				Density	0.879 g/cm^3	0.81 g/cm^3	Benzene
				Capillary rise	0.14 cm	0.12 cm	Benzene
+ Landfarming, composting, biopiling	x			Vapor pressure	75 mm Hg	0.42 to 11.8 mm Hg	Benzene
				Aerobic biodegradation potential	Weeks-months	Days-weeks	Butanol
				Anaerobic biodegradation potential	Years	Weeks-months	Butanol
+ Soil washing	x			Solubility	1.8E+3 mg/L	7.4E+4 to 8.7E+4 mg/L	Benzene
				Interfacial tension	35.5 dyn/cm	1.8 to 2.0 dyn/cm	Benzene
+ Thermal (desorption incineration)	x			Vapor pressure	75 mm Hg	0.42 to 11.8 mm Hg	Benzene
				Boiling point	80.1°C	108 to 118°C	Benzene
Soil vapor extraction	x			Vapor pressure	75 mm Hg	0.42 to 11.8 mm Hg	Benzene
				Aerobic biodegradation potential	Weeks-months	Days-weeks	Butanol
Bioventing	x			Aerobic biodegradation potential	Weeks-months	Days-weeks	Butanol
Natural attenuation (biodegradation)	x	x		Aerobic biodegradation potential	Weeks-months	Days-weeks	Butanol
				Anaerobic biodegradation potential	Years	Weeks-months	Butanol
Anaerobic bioremediation	x	x		Anaerobic biodegradation potential	Years	Weeks-months	Butanol
Aerobic bioremediation	x	x	x	Aerobic biodegradation potential	Weeks-months	Days-weeks	Butanol
Air sparging, oxygen sparging	x	x		Henry’s law constant	0.22 (gas/aq)	3.73E-4 to 5.0E-4 (gas/aq)	Benzene
				Solubility	1.8E+3 mg/L	7.4E+4 to 8.7E+4 mg/L	Benzene
				Aerobic biodegradation potential	Weeks-months	Days-weeks	Butanol
+ Soil vapor extraction	x	x		Vapor pressure	75 mm Hg	0.42 to 11.8 mm Hg	Benzene
				Aerobic biodegradation potential	Weeks-months	Days-weeks	Butanol
In situ chemical oxidation	x	x		Hydroxyl rate	1.95E-12 cm^3/mol-sec	6.9E-12 to 8.6E-12 cm^3/mol-sec	Butanol
In situ thermal treatment	x	x		Vapor pressure	75 mm Hg	0.42 to 11.8 mm Hg	Benzene
				Viscosity	0.649 cp	2.54 to 4.70 cp	Benzene
				Boiling point	80.1°C	108 to 118°C	Benzene
Physical containment (in situ wall/barrier)		x		Solubility	1.8E+3 mg/L	7.4E+4 to 8.7E+4 mg/L	Butanol

Technology	**Target media**			**Physical, chemical, biological properties**	**Benzene**	**Butanol**	**Generally favors**
	VZ	**GW**	**SW**				
Fluid extraction	x	x	x	Solubility	1.8E+3 mg/L	7.4E+4 to 8.7E+4 mg/L	Butanol
+ Product pumping, skimming, separation		x	x	Partitioning (log K_{ow}) Solubility	2.13 (unitless) 1.8E+3 mg/L	0.83 to 0.88 (unitless) 7.4E+4 to 8.7E+4 mg/L	Benzene Benzene
+ Multiphase extraction, dual-phase extraction, vacuum-enhanced recovery	x	x		Vapor pressure Viscosity	75 mm Hg 0.649 cp	0.42 to 11.8 mm Hg 2.54 to 4.70 cp	Benzene Benzene
+ Surfactant flushing, cosolvent flushing		x	x	Solubility Interfacial tension	1.8E+3 mg/L 35.5 dyn/cm	7.4E+4 to 8.7E+4 mg/L 1.8 to 2.0 dyn/cm	Benzene Benzene
+ Air stripping		x	x	Henry's law constant	0.22 (gas/aq)	3.73E-4 to 5.0E-4 (gas/aq)	Benzene
+ Advanced oxidation		x	x	Hydroxyl rate	1.95E-12 cm^3/mol-sec	6.9E-12 to 8.6E-12 cm^3/mol-sec	Butanol
+ Bioreactor		x	x	Aerobic biodegradation potential	Weeks-months	Hours	Butanol
+ Constructed wetlands		x	x	Sorption (log K_{oc}) Henry's law constant Aerobic biodegradation potential Anaerobic biodegradation potential	1.98 (unitless) 0.22 (gas/aq) Weeks-months Years	1.86 to 2.05 (unitless) 3.73E-4 to 5.0E-4 (gas/aq) Days-weeks Weeks-months	Both Benzene Butanol Butanol
+ Discharge to sewer or wastewater plant		x	x	Henry's law constant Aerobic biodegradation potential Anaerobic biodegradation potential	0.22 (gas/aq) Weeks-months Years	3.73E-4 to 5.0E-4 (gas/aq) Days-weeks Weeks-months	Benzene Butanol Butanol
Surface booms/barriers			x	Partitioning (log K_{ow}) Solubility	2.13 (unitless) 1.8E+3 mg/L	0.83 to 0.88 (unitless) 7.4E+4 to 8.7E+4 mg/L	Benzene Benzene
+ Sorbents/skimmers			x	Sorption (log K_{oc})	1.98 (unitless)	1.86 to 2.05 (unitless)	Both
+ Aeration, agitation (air/oxygen sparging)			x	Henry's law constant Aerobic biodegradation potential	0.22 (gas/aq) Weeks-months	3.73E-4 to 5.0E-4 (gas/aq) Days-weeks	Benzene Butanol

Table 5-4c. Ability of selected remedial technologies to influence the physical, chemical, and biological properties of biodiesel as normalized to diesel in the vadose zone (VZ), groundwater (GW), and surface water (SW)

Technology	**Target media**			**Physical, chemical, biological properties**	**Diesel**	**Biodiesel**	**Generally favors**
	VZ	**GW**	**SW**				
Excavation	x			Sorption (log K$_{oc}$) Surface tension Density Capillary rise	3 to 5.7 (unitless) 28.0 dyn/cm 0.87 to 0.95 g/cm^3 0.11 cm	6 to 8.21 (unitless) 25.3 to 31.0 dyn/cm 0.84 to 0.9 g/cm^3 0.14 cm	Biodiesel Biodiesel Biodiesel Biodiesel
+ Landfarming, composting, biopiling	x			Vapor pressure Aerobic biodegradation potential Anaerobic biodegradation potential	2.12 to 26.4 mm Hg Weeks-months Years	8.63E-6 to 3.74E-4 mm Hg Days-weeks Weeks-months	Diesel Biodiesel Biodiesel
+ Soil washing	x			Solubility Interfacial tension	5 mg/L 7.4 dyn/cm	1.2E-3 to 2.1E-2 mg/L 10.1 to 13.5 dyn/cm	Biodiesel Biodiesel
+ Thermal (desorption incineration)	x			Vapor pressure Boiling point	2.12 to 26.4 mm Hg 160 to 360°C	8.63E-6 to 3.74E-4 mm Hg 352 to 417°C	Diesel Diesel
Soil vapor extraction	x			Vapor pressure Aerobic biodegradation potential	2.12 to 26.4 mm Hg Weeks-months	8.63E-6 to 3.74E-4 mm Hg Days-weeks	Diesel Biodiesel
Bioventing	x			Aerobic biodegradation potential	Weeks-months	Days-weeks	Biodiesel
Natural attenuation (biodegradation)	x	x		Aerobic biodegradation potential Anaerobic biodegradation potential	Weeks-months Years	Days-weeks Weeks-months	Biodiesel Biodiesel
Anaerobic bioremediation	x	x		Anaerobic biodegradation potential	Years	Weeks-months	Biodiesel
Aerobic bioremediation	x	x	x	Aerobic biodegradation potential	Weeks-months	Days-weeks	Biodiesel
Air sparging, oxygen sparging	x	x		Henry’s law constant Solubility Aerobic biodegradation potential	2.4E-3 to 3.0E+2 (gas/aq) 5 mg/L Weeks-months	6.4E-3 to 1.3 (gas/aq) 1.2E-3 to 2.1E-2 mg/L Days-weeks	Diesel Biodiesel Biodiesel
+ Soil vapor extraction	x	x		Vapor pressure Aerobic biodegradation potential	2.12 to 26.4 mm Hg Weeks-months	8.63E-6 to 3.74E-4 mm Hg Days-weeks	Diesel Biodiesel
In situ chemical oxidation	x	x		Hydroxyl rate	1E-11 to 1E-10 cm^3/mol-sec	1.3E-12 to 1.8E-10 cm^3/mol-sec	Biodiesel
In situ thermal treatment	x	x		Vapor pressure Viscosity Boiling point	2.12 to 26.4 mm Hg 1.1 to 3.5 cp 160 to 360°C	8.63E-6 to 3.74E-4 mm Hg 324 to 480 cp 352 to 417°C	Diesel Diesel Diesel
Physical containment (in situ wall/barrier)		x		Solubility	5 mg/L	1.2E-3 to 2.1E-2 mg/L	Diesel

Technology	Target media			Physical, chemical, biological properties	Diesel	Biodiesel	Generally favors
	VZ	GW	SW				
Fluid extraction	x	x	x	Solubility	5 mg/L	1.2E-3 to 2.1E-2 mg/L	Diesel
+ Product pumping, skimming, separation		x	x	Partitioning (log K_{ow}) Solubility	3.3 to 7.06 (unitless) 5 mg/L	6.29 to 8.35 (unitless) 1.2E-3 to 2.1E-2 mg/L	Biodiesel Biodiesel
+ Multiphase extraction, dual-phase extraction, vacuum-enhanced recovery	x	x		Vapor pressure Viscosity	2.12 to 26.4 mm Hg 1.1 to 3.5 cp	8.63E-6 to 3.74E-4 mm Hg 324 to 480 cp	Diesel Diesel
+ Surfactant flushing, cosolvent flushing	x	x	x	Solubility Interfacial tension	5 mg/L 7.4 dyn/cm	1.2E-3 to 2.1E-2 mg/L 10.1 to 13.5 dyn/cm	Biodiesel Biodiesel
+ Air stripping		x	x	Henry's law constant	2.4E-3 to 3.0+E2 (gas/aq)	6.4E-3 to 1.3 (gas/aq)	Diesel
+ Advanced oxidation		x	x	Hydroxyl rate	1E-11 to 1E-10 cm^3/ mol-sec	1.3E-12 to 1.8E-10 cm^3/ mol-sec	Biodiesel
+ Bioreactor		x	x	Aerobic biodegradation potential	Weeks-months	Days-weeks	Biodiesel
+ Constructed wetlands		x	x	Sorption (log K_{oc}) Henry's law constant Aerobic biodegradation potential Anaerobic biodegradation potential	3 to 5.7 (unitless) 2.4E-3 to 3.0+E2 (gas/aq) Weeks-months Years	6 to 8.21 (unitless) 6.4E-3 to 1.3 (gas/aq) Days-weeks Weeks-months	Diesel Diesel Biodiesel Biodiesel
+ Discharge to sewer or wastewater plant		x	x	Henry's law constant Aerobic biodegradation potential Anaerobic biodegradation potential	2.4E-3 to 3.0+E2 (gas/aq) Weeks-months Years	6.4E-3 to 1.3 (gas/aq) Days-weeks Weeks-months	Diesel Biodiesel Biodiesel
Surface booms/barriers			x	Partitioning (log K_{ow}) Solubility	3.3 to 7.06 (unitless) 5 mg/L	6.29 to 8.35 (unitless) 1.2E-3 to 2.1E-2 mg/L	Biodiesel Biodiesel
+ Sorbents/skimmers			x	Sorption (log K_{oc})	3 to 5.7 (unitless)	6 to 8.21 (unitless)	Biodiesel
+ Aeration, agitation (air/ oxygen sparging)			x	Henry's law constant Aerobic biodegradation potential	2.4E-3 to 3.0+E2 (gas/aq) Weeks-months	6.4E-3 to 1.3 (gas/aq) Days-weeks	Diesel Biodiesel

Table 5-4d. Ability of selected remedial technologies to influence physical, chemical, and biological properties with respect to methane remediation and potential for methane generation in the vadose zone (VZ), groundwater (GW), and surface water (SW)

Technology	Target media			Physical, chemical, biological properties	Methane remediation	Methane generation
	VZ	GW	SW			
Excavation	x			Sorption (log K_{oc})	N/A	N/A
				Surface tension	N/A	N/A
				Density	N/A	N/A
				Capillary rise	N/A	N/A
+ Landfarming, composting, biopiling	x			Vapor pressure	N/A	N/A
				Aerobic biodegradation potential	N/A	N/A
				Anaerobic biodegradation potential	N/A	N/A
+ Soil washing	x			Solubility	N/A	N/A
				Interfacial tension	N/A	N/A
+ Thermal (desorption incineration)	x			Vapor pressure	N/A	N/A
				Boiling point	N/A	N/A
Soil vapor extraction	x			Vapor pressure	Applicable	N/A
				Aerobic biodegradation potential	Applicable	Inhibits
Bioventing	x			Aerobic biodegradation potential	Applicable	Inhibits
Natural attenuation (biodegradation)	x	x		Aerobic biodegradation potential	Applicable	Inhibits
				Anaerobic biodegradation potential	N/A	May promote
Anaerobic bioremediation	x	x		Anaerobic biodegradation potential	N/A	May promote
Aerobic bioremediation	x	x	x	Aerobic biodegradation potential	Applicable	Inhibits
Air sparging, oxygen sparging	x	x		Henry’s law constant	Applicable	N/A
				Solubility	N/A	N/A
				Aerobic biodegradation potential	Applicable	Inhibits
+ Soil vapor extraction	x	x		Vapor pressure	Applicable	N/A
				Aerobic biodegradation potential	Applicable	Inhibits
In situ chemical oxidation	x	x		Hydroxyl rate	Applicable	N/A
In situ thermal treatment	x	x		Vapor pressure	Applicable	N/A
				Viscosity	N/A	N/A
				Boiling point	N/A	N/A
Physical containment (in situ wall/barrier)		x		Solubility	N/A	N/A

Technology	**Target media**			**Physical, chemical, biological properties**	**Methane remediation**	**Methane generation**
	VZ	**GW**	**SW**			
Fluid extraction	x	x	x	Solubility	N/A	N/A
+ Product pumping, skimming, separation		x	x	Partitioning (log K_{ow}) Solubility	N/A N/A	N/A N/A
+ Multiphase extraction, dual-phase extraction, vacuum-enhanced recovery	x	x		Vapor pressure Viscosity	Applicable N/A	Inhibits N/A
+ Surfactant flushing, cosolvent flushing	x	x	x	Solubility Interfacial tension	N/A N/A	N/A N/A
+ Air stripping		x	x	Henry's law constant	Applicable	Inhibits
+ Advanced oxidation		x	x	Hydroxyl rate	Applicable	Inhibits
+ Bioreactor		x	x	Aerobic biodegradation potential	Applicable	Inhibits
+ Constructed wetlands		x	x	Sorption (log K_{oc}) Henry's law constant Aerobic biodegradation potential Anaerobic biodegradation potential	N/A Applicable Applicable N/A	N/A N/A Inhibits May promote
+ Discharge to sewer or wastewater plant		x	x	Henry's law constant Aerobic biodegradation potential Anaerobic biodegradation potential	Applicable Applicable N/A	N/A Inhibits May promote
Surface booms/barriers			x	Partitioning (log K_{ow}) Solubility	N/A N/A	N/A N/A
+ Sorbents/skimmers			x	Sorption (log K_{oc})	N/A	N/A
+ Aeration, agitation (air/ oxygen sparging)			x	Henry's law constant Aerobic biodegradation potential	Applicable Applicable	N/A Inhibits

It should be noted that some parameters influence the success of a specific technology more than others and therefore will have a greater impact on the technology's applicability to the biofuel. In addition, a parameter's score as less susceptible with respect to a technology does not necessary mean that the technology is not still applicable for the biofuel. For example, the volatility of ethanol is lower than that of benzene, but ethanol can still be successfully addressed via soil vapor extraction. It should also be noted that this analysis was performed on the properties of either ethanol or biodiesel and therefore did not consider how the properties of a gasoline-ethanol or diesel-biodiesel blend would impact the analysis. The relative differences shown on the table with respect to the properties of ethanol and biodiesel in comparison to their reference compound would be less significant if blended.

The evaluation of methane was conducted on two different aspects: methane remediation and potential for methane generation (Table 5-4d). For methane remediation, values were ascribed to the technology for its ability to remediate methane based on its expected ability to successfully influence the described property. For methane generation, an evaluation of whether the technology could promote or inhibit the generation of methane was conducted. These detailed evaluations are intended to be used along with the benefits and limitations table for the site-specific evaluation and selection of remediation technologies.

5.3.2 Site-Specific Evaluation and Selection of Remedial Technologies

When an active remedy is needed, the evaluation and selection of applicable technologies is based on a number of considerations, including but not limited to the remedial goal, expected effectiveness, cost, etc. A number of guidance documents are available for further information on risk-based approaches to technology selection for remediation (ITRC 2011, 2007a; DOE 2008; NAVFAC 2008). Additional considerations based on potential stakeholder concerns are presented in Section 6.

Because the remedial goal will have already been decided and other factors, such as cost, are largely site-specific, the remainder of this section discusses a method for evaluating expected technology effectiveness for site-specific biofuel release scenarios. In general, the following are considerations for evaluating expected effectiveness:

- targeted medium
- COC, contaminant phase
- physical, chemical, or biological property of the COC targeted for remediation

Implementing this evaluation method depends in large part on review of the technology evaluation information presented in Tables 5-2 through 5-4 in conjunction with site-specific characterization information and the SCM. In addition, the potential co-occurrence of a petroleum release (released as a component of a biofuel blend) or the release of a biofuel into a previously petroleum-impacted area may require evaluating the same technology for remediating both components. If biological remedies are considered, a delay in the biodegradation of the petroleum fraction may occur (Section 3.5.2); therefore, they should be considered in the overall remedial time frame.

For a site-specific technology evaluation using the information presented in this document, the first consideration is to identify the targeted medium that remedial efforts will be focused on, which may involve more than one medium. For example, if LNAPL is the targeted contaminant phase and it exists above and below the water table, the active remedy may consist of dewatering to below the base of the LNAPL, followed by treatment in the vadose and dewatered zones. Similarly, excavation below the water table may require dewatering, thus leading to ex situ treatment of both soil and groundwater. Tables 5-2 and 5-3 can be used to narrow the selection by medium, but some technologies can be used in multiple applications. For example, multiphase extraction can be used in the example above to dewater and then aerate the dewatered zone. In this case, the technology is applied to soil and groundwater, with the application of the technology to soil being equivalent to SVE.

The second consideration is the targeted COC and/or contaminant phase. Tables 5-2 and 5-3 present significant limitations and benefits of each technology. Some technologies are more applicable to one phase than another and may be applied only to COCs with specific properties. Once the targeted media and the COC and/or contaminant phase are identified, technologies can be further evaluated using Tables 5-2 and 5-3 to select likely alternatives.

The third consideration is the nature of the targeted COC, specifically its physical, chemical, or biological properties. This may also be considered when considering the targeted COC and/or contaminant phase. Table 5-4 can be used to evaluate the comparative effectiveness of a technology to remediate the chosen COC within a specific medium to a representative petroleum counterpart as described in Section 5.3.1. For example, excavation as a possible alternative to remediate a biodiesel release may be more effective than when applied to petroleum diesel due to biodiesel having a greater affinity for soil organic matter, higher capillary rise, and higher viscosity than petroleum diesel. Subsequent treatment of removed soil, however, may be affected by other properties. For example, thermal treatment of biodiesel may not be a practical ex situ treatment technology because of biodiesel's high boiling point and low vapor pressure compared to those of petroleum diesel. If the fuel is a biodiesel blend, the relative percentages of biodiesel and petroleum diesel need to be considered when evaluating the potential effectiveness of a technology.

Application of technologies commonly used for petroleum releases can be successful in consideration of the physical, chemical, and biological properties of the targeted fuel or fuel component. Because there is a greater biodegradation potential for biofuels than for petroleum, biofuels remediation may focus on adapting existing petroleum remediation strategies to remediate the petroleum component that exists in the presence of the more degradable biofuel, or at best, preventing or eliminating risk of methane generation resulting from the biodegradation of the biofuel.

5.3.2.1 Soil/sediment

When the targeted medium is soil or sediment and the targeted COC is a biofuel, technologies that enhance aerobic biodegradation, such as bioventing, are likely to be effective in hastening biodegradation of the released fuel and preventing or minimizing methane production. Similarly, ex situ treatment of biofuel-impacted soil or sediment through biological processes are likely to be effective.

Physical- and chemical-based technologies are more restrictive with respect to biofuel remediation. For example, SVE may be used to target pure-phase ethanol in the vadose zone (sufficiently high vapor pressure) but may not physically remove the aqueous-phase ethanol present within the pore water because aqueous-phase ethanol does not readily partition from the aqueous-phase to the vapor phase (low Henry's law constant). SVE could, however, increase the aerobic biodegradation of aqueous-phase ethanol, thus using both physical and biological strategies for overall remediation in the vadose zone. SVE could also be used to directly remove methane from the vadose zone and minimize its production by promoting aerobic conditions within the soil.

Similar to petroleum diesel, biodiesel's physical and chemical properties limit the effectiveness of technologies that rely on volatility and are used mainly to remediate gasoline contaminants. In situ physical removal of biodiesel LNAPL is more restrictive than that of petroleum diesel due to its low volatility and higher viscosity and may be practical only through use of a surfactant or cosolvent.

5.3.2.2 Groundwater/surface water

As with soil and sediment remediation, technologies that use a biological strategy are likely to be effective for groundwater remediation. Enhancing aerobic or anaerobic biodegradation through subsurface injection of air, oxygen, or other terminal electron receptors can hasten degradation rates and minimize or prevent methane generation.

Physical removal of alcohol biofuels (e.g., as ethanol and biobutanol) from groundwater is impractical as alcohols typically have low Henry's law constants and therefore do not readily partition from the aqueous phase to the vapor phase. Air sparging may not be an effective technology for groundwater remediation in terms of physical removal, but it may be an effective technology for enhancing aerobic biodegradation, as previously mentioned. This is an important consideration if the targeted COC is petroleum related but is present with ethanol. Limitations of physical removal of alcohols may also be important for ex situ treatment of contaminated groundwater. Air strippers and activated carbon treatment are likely to be ineffective, with biological treatment methods being the most applicable.

Biodiesel is relatively insoluble and not expected to generate large, aqueous-phase plumes but may persist as an LNAPL in the subsurface. Recovery is possible with standard petroleum LNAPL recovery methods, but soy-based FAMEs are more viscous, and recovery success may improve with thermal enhancement. Because FAMEs are immediately biodegradable, natural source zone depletion of the LNAPL may be an acceptable alternative to active recovery.

5.3.3 Meeting Remedial End Points

Remedial end points and goals will have been determined prior to remedy implementation. The remedial end point is reached when contaminant concentrations are below regulatory thresholds at the point of compliance. The location of the point of compliance should be based on an evaluation of fate and transport expectations, the SCM, and identified receptors. If the remedial goal is above the regulatory threshold, then MNA or control measures (such as methane vapor mitigation measures) may be required prior to proceeding to site closure.

5.4 Closure Requirements

Site closure follows state- or program-specific regulatory requirements. In general, once it can be demonstrated that all identified risks have been mitigated, closure can be granted. Site closure may result in no further regulatory oversight if permanent risk reduction has been achieved. In cases where engineered or institutional controls are used to mitigate risk, additional long-term stewardship measures (i.e., control monitoring and/or maintenance) may be required to demonstrate continued risk reduction, which may or may not involve continued regulatory oversight.

5.5 Summary and Recommendations

As presented in this section, long-term response strategies are driven by the risk a release poses to human health and the environment. Using the risk-based approach presented in this section, management decisions are based on an evaluation of the risk presented by the biofuel, the petroleum component of a biofuel blend, and/or biodegradation products such as methane. Depending on the risk, multiple strategies are available to manage the release and achieve site closure. If the risk evaluation warrants additional action, MNA and/or land use controls may be sufficient response strategies. Otherwise, active remedies may be warranted. Depending on site-specific concerns, strategies might employ both active remedies for source reduction and MNA and/or controls, such as vapor mitigation measures for methane.

Current widely used biofuels (ethanol and biodiesel) are readily biodegradable; therefore, MNA may be a viable strategy. Methane production from biofuel biodegradation, however, may require special attention when MNA is used as it could pose an explosive hazard risk. Additionally, because of the potential lag time before methane may be generated, long-term monitoring and/or ECs should be evaluated as part of the response strategy.

When an active remedy is chosen as a response strategy, a method for evaluating and selecting a remedial technology for biofuels was presented. Technologies were initially selected by evaluating their likelihood of effectively remediating ethanol and biodiesel with respect to their physical, chemical, and biological properties. The technology evaluation information presented in this section can be used along with site-specific considerations to identify those technologies likely to be effective for a variety of release scenarios. These scenarios include the potential for remediation of the biofuel component of blends, which can potentially include the selection of the same technology as for remediation of the petroleum component of the blend. Regardless of the scenario, however, a thorough evaluation of the benefits and limitations of applicable technologies is recommended.

The technology evaluation and selection method was developed to assist in technology selection based on site-specific information, including the targeted environmental medium, the targeted contaminant phase (e.g., LNAPL, aqueous, vapor), and the biofuel’s properties. This process can be also be applied to future biofuels to identify technologies expected to be effective based on their physical, chemical, and biological properties. With today’s most widely used biofuels, technologies that take advantage of their biodegradability have the most promise for success.

6. STAKEHOLDER CONCERNS

Stakeholders affected by biofuel releases include people in communities, indigenous peoples, local governments, and various nongovernmental organizations, as well as state and federal agencies (e.g., environmental regulators, fish and wildlife, land management, natural resources, etc.). Within the scope of this document, stakeholder concerns associated with the prevention, environmental behavior, and remediation of accidental biofuel releases generally depend on the location and timing of the incident, emergency response, and long-term management and cleanup.

As summarized in Section 2, different types of incidents (measured by magnitude or volume of release along with the duration) occur depending on the situation (see Table 2-3). In most cases, chronic, small total volume releases such as from distribution piping and manifolds and unloading/loading racks at bulk depots and supply terminals impact fewer stakeholders unless the situation is not addressed for an extended period of time. However, the other extreme of sudden, catastrophic, large total volume releases such as from a tanker truck accident or train derailment can be of immediate and enduring concern to stakeholders. In general, this section discusses stakeholder concerns associated with the latter scenario.

6.1 Location of the Incident

Tanker truck accidents and train car derailments involving biofuels can occur just about anywhere since the associated transportation routes traverse highly populated cities, suburban communities, rural agricultural regions, ecologically sensitive areas, and other places of interest. As with any other release, stakeholder concerns associated with biofuel releases depend on the proximity of the incident in relation to these interests, which can also include tribal, cultural, spiritual, rights of way, subsistence, economic, historical, archeological, and recreational interests, among others. The primary issues that stakeholders may be most concerned about specifically related to biofuel releases are as follows:

- human health and ecological risks associated with the depletion of oxygen in receiving water bodies due to the rapid biodegradation of the biofuel (see Section 3.5.2).
- vapor intrusion risks associated with the generation of methane in the subsurface in proximity to structures (see Section 3.3.2.4).

Releases occurring in or near a surface water body can potentially have environmental impacts, such as DO depletion negatively affecting aquatic species. Impacts to possible beneficial uses of these water bodies, such as recreational, economic, tribal, or subsistence uses, can be immediate and extend into the short term. Potential long-term impacts may depend on the behavior of the biofuel in the environment. In most cases, ethanol and other alcohol-based biofuels do not persist in an open water body as they tend to rapidly vaporize, volatilize, and biodegrade (Section 3.5). Furthermore, these constituents are known not to bioaccumulate. Similarly, if biodiesel impacts a water body, biodegradation significantly reduces the concentration such that the natural resources may likely recover. However, long-term impacts to natural resources may occur if a biodiesel LNAPL is allowed to persist such that it penetrates into the sediment.

In some cases, water bodies are also used as potable water supply reservoirs. If a biofuel release impacts these resources, the drinking water supply will likely need to be taken out of service until the risks associated with the biofuel or the petroleum components in a blend are assessed and mitigated. In these situations, public notifications need to be conducted along with other communications updating stakeholders on mitigation progress. In addition, another potential water-bearing receptor that should be of concern to stakeholders are storm and sanitary sewers that might receive the released biofuel. Depending on the biofuel load and the sewer outfall, these sewer conveyances may impact surface waters or wastewater treatment facilities. For example, the microbial systems (i.e., activated sludge) used to process wastewater at a wastewater treatment facility may become “poisoned” by the biofuel, rendering the wastewater treatment plant inoperable. Similarly, potable water supply wells may be impacted by a biofuel release if conditions exist at the release site that allow the biofuel to transport into the groundwater (see Section 3). In these cases, water purveyors and communities relying on those water supplies need to be informed and periodically updated.

For situations where a biofuel release occurs near a structure or building, stakeholders may be concerned about the short-term impacts to livelihood from the incident and emergency response actions (see Section 6.2) and should also understand the long-term potential for the generation of methane from the release (see Section 3.3.2.4). To ensure that stakeholders understand the explosive or other hazardous conditions stemming from methane, an adequate communications plan may need to be implemented. This plan should include information on the explosive limits; health effects; and other physical, chemical, and biological behaviors of methane. Furthermore, this plan may need to be supplemented with a monitoring program (see Section 4.2.1) to track methane generation in the subsurface. If persistent methane generation and other vapor intrusion risks are shown to exist, mitigation systems (see Section 5.2.3) may also need to be included and communicated with stakeholders.

In cases where historical, archeological, cultural, or other long-term interests may be impacted, stakeholders not only may be concerned about the human health, ecological, and safety risks associated with these locations but also may be disrupted by emergency response and long-term remediation activities (see Sections 6.2 and 6.3, respectively), which may restrict access to the release area.

6.2 Timing and Duration of the Incident and Emergency Response

During a sudden, catastrophic incident (minutes to hours) or while the emergency response actions are occurring (up to weeks afterwards), stakeholder concerns differ as the situation evolves. Initial concerns are the immediate threats to human health and safety from explosions, fires, vapors, etc. In addition, notification of appropriate officials and emergency response personnel is of primary importance. Depending on the proximity of the incident to populated areas, stakeholders may need to be evacuated from the area. Furthermore, care for elderly, domestic animals, and persons with special needs are of concern. For stakeholders displaced by the incident due to evacuation or damage to dwellings, concerns are likely to regard the duration and time frame of the inconvenience.

While these concerns and actions are no different from those of any other environmental release, stakeholders such as facility managers, transport operators, and tank owners of the biofuel supply chain (see Section 2.1) should make sure first responders are aware of the chemicals they are dealing with in the biofuel release so they can respond accordingly. For example, fires involving biofuel blends containing more than 10% alcohol should be treated differently than traditional petroleum fires because alcohols are polar/water-miscible flammable liquids that degrade the effectiveness of non-alcohol-resistant firefighting foam. Therefore, first responders require appropriate firefighting foam and foam application techniques for ethanol-based fuels (EERC 2009, DOT 2008). Additional guidance is available in the *Emergency Response Guidebook* Guide 127 (DOT 2008) for transportation-related release response procedures. In the United States, first responders must be trained regarding the use of the guidebook according to the requirements of the U.S. Department of Labor's OSHA (29 CFR §1910.120) and regulations issued by USEPA (40 CFR §311).

In cases where the incident does not result in an immediate explosion or fire, the impacted area needs to be tightly controlled by law enforcement or other responders. Of particular concern are low-lying areas, sewers, underground conveyances, and other collection points where the spilled biofuel can pool and potentially lead to an explosive atmosphere. Furthermore, since biofuels can have additional detrimental effects on water bodies compared to petroleum, first responders and other stakeholders should try to minimize these impacts where possible. This effort may include actions to isolate storm drains and sewers, dam storm water conveyances, or create diversion channels to minimize runoff of the biofuels into water bodies. These collection approaches can be used to contain the bulk of the released biofuel during the emergency response, which can subsequently be removed once the situation is under control. Depending on the situation, this may include the use of sorbents, controlled burns, skimming and vacuuming, and other spill response countermeasures available to the incident commander.

In some situations, however, the biofuel may seep in significant quantities into the soil, which may require excavation equipment and other actions to remove. These activities may last for days, weeks, or even longer. In these situations, the concerns associated with the release are on worker safety, exposure of vapors from the soil, development of any explosive conditions in excavations, etc. Furthermore, interim response actions may employ soil vapor, dual-phase, or multiphase extraction techniques (see Section 5.3) that are effective at removing liquid and gaseous constituents in the subsurface resulting from a biofuel release (see Appendix D, Pacific Northwest Terminal case study).

6.3 Timing and Duration of the Long-Term Response

Long-term impacts to natural resources and/or land use associated with a long-term response to a biofuels release may be of concern to stakeholders. Potential stakeholder concerns with respect to long-term impacts may include the implementation and/or effectiveness of a selected remedial technology; land-use impacts, such as access restrictions or loss of property value; or economic impacts. A community relations plan can be incorporated into the remedial process to address these concerns and can be critical to the success of the project where stakeholder interest is high.

Remedial technology effectiveness concerns are usually first and foremost in the public's mind. Remedial effectiveness concerns include but are not limited to issues such as protectiveness of human health, water supplies, and ecological resources. These issues should be addressed during the remedy selection and remedial design components of a project. Implementation concerns include but are not limited to issues such as the timing and duration of remedial activities and exposure, noise, odor, or visual impacts associated with the implementation of the technology. Timing and duration concerns may be most pronounced for MNA (see Section 5.2.2), which may require affected communities to coexist with some residual level of contamination for a period of time versus active remedy technologies. Active remedy technologies that may be more susceptible to stakeholder implementation concerns include landfarming/composting/biopiling, which may have issues associated with aesthetic value or odor/vapor concerns, and capping/lining, which may require a large spatial area and therefore may carry a site access or cultural impact concern. A project risk management approach may be useful in the various stages of a project to include these concerns in decision making (ITRC 2011).

Land use is an extremely important issue to stakeholders, especially local governments, tribes, citizens, and organizations of all types. In general, communities typically favor remediation strategies that lead to unrestricted land use. If the long-term response includes the use of ICs, such as land use restrictions, they should be minimized to the extent possible. Most states track and monitor ICs at some level. Tools available for tracking the status of IC implementation and maintenance may include long-term inspections, registries, state one-call systems, and third-party notification systems (ITRC 2008a). These controls could be maintained in a searchable database accessible to stakeholders.

Potential economic impacts associated with the long-term response to a biofuels release can include the loss of property value due to land-use impacts, loss of access to natural resources during the remediation process, and commercial restrictions during the remediation process. The potential for economic impacts should be evaluated during the remediation process and minimized to the extent possible.

7. REFERENCES

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Appendix A

Biofuel Manufacture

BIOFUEL MANUFACTURE

Currently, biofuels are produced at biomass-based refineries, or “biorefineries.” These biorefineries have several unifying traits:

- use one or more biomass feedstocks
- use mechanical, thermal, chemical, and/or biological processes to convert the biomass feedstocks to desired end product
- produce biofuels and other bioproducts

Integrated biorefineries can be very simple with few inputs and outputs or very complex with multiple inputs, conversion steps, and product(s). Technical, resource, and economic factors reduce the likely production possibilities to a manageable number of pathways and products.

U.S. ethanol manufacturing facilities are concentrated in the upper Midwest (GAO 2007); Iowa, Minnesota, and Wisconsin together have 35% of the total U.S. capacity for producing ethanol (NRC 2010).[4] Domestic biodiesel manufacturing facilities are concentrated in the eastern half of the United States (NBB n.d.) but are more evenly distributed than ethanol manufacturing facilities.

A.1 ETHANOL MANUFACTURE

The production of ethanol used for fuel involves four basic steps:

1. extraction of fermentable carbohydrates from a carbonaceous feed stock (grinding and liquifaction)
2. saccharification and fermentation of carbohydrate to ethanol
3. distillation and recovery of ethanol
4. drying and processing of by-products

A.1.1 Ethanol Feed Stocks

A wide variety of biologically based feed stocks can theoretically be used for ethanol production. Several research and development studies are currently being conducted on the use of wood, grasses, sugar cane and sugar cane bagasse, corn stover, and the organic fraction of municipal solid waste. At this writing, the primary feed stock for ethanol production is corn kernels. This discussion uses corn-based ethanol production as an example of one method. Regardless of the carbon source, the production process is the same once the glucose (dextrose) is developed from the feed stock.

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[4] For updated information on geographic distribution of ethanol refineries, see www.ethanolrfa.org/industry/locations.

A.1.2 Dry Grind Milling Method of Ethanol Production

Dry grind milling is the most common method of preparing grains for the liquefaction and fermentation steps in fuel ethanol production. Dry grind milling is simply putting the whole feed stock grains through a hammer mill or other mechanical crushing device and reducing the grain size to produce desirable size particles with optimum surface area for the enzymatic reactions that follow. Dry grind milling takes less energy than wet milling, but fractionation of the grain into the component parts of endosperm, germ, and bran is more difficult. Fractionated components can be used to produce vegetable oil, high-protein distillers' grains, and fuel.

Liquefaction

The starch in the corn endosperm is composed of about 80% amylopectin and 20% amylose. These long-chain carbohydrates are the primary target for fermentation. Dry ground grains are mixed with water and heated to swell and unravel the starch granules into long carbohydrate chains. This process, called "gelatinization," is done in a slurry tank under agitation. Gelatinized slurry is quite viscous. Alpha-amylase is added to reduce viscosity so the mash can be pumped from one part of the process to another. This step in the mash production is done at 182–185°F and a pH of 5.6–5.8. Alpha-amylase also cleaves the amylopectin and amylose chains into shorter dextrin chains that yeast can later metabolize into alcohol. The mash viscosity can be further reduced and the alpha-amylase inactivated by passing the mash through a "jet cooker" that mechanically shears the starch and raises the temperature. After the mash is passed through the jet cooker, alpha-amylase is added to the mash again, and the mash is pumped to a series of liquefaction tanks to allow further breakdown of long-chain starches into shorter chains.

Saccharification and fermentation

Saccharification and fermentation are simultaneous processes in ethanol production. Saccharification is the breakdown of long-chain carbohydrates to simple sugars such as glucose. Fermentation is the conversion of glucose to ethanol and carbon dioxide. The mash slurry is cooled, mixed with yeast and glucoamylase, and placed in fermentation tanks. The proper temperature for fermentation is 90–93°F with a pH range of 3.8–5.0. The enzyme glucoamylase breaks the dextrin chains into glucose molecules ready for fermentation by the yeast organisms. Ethanol production is based on yeast (S*accharomyces cerevisiae*). As part of its metabolic process, the yeast uses glucose for an energy source and produces ethanol and carbon dioxide as by-products. For each pound of simple sugars, a healthy population of yeast can produce about ½ pound of ethanol (0.15 gal) and ½ pound of CO_2.

Distillation and recovery

When most of the sugar has been converted to ethanol and CO_2, the mash is transferred to a beer well and then into distillation columns. The beer is 10%–15% ethanol. The distillation columns separate the ethanol from the whole stillage and produce a 190 proof ethanol product. The distilled alcohol is forced through a molecular sieve to remove the remaining water and produce 200 proof (100%) ethanol.

Drying and drying and processing of by-products

The whole stillage left over after distillation consists of approximately 15% solids and residual liquids. The whole stillage is then fed to centrifuges, which produce wet distillers' grains with solubles (WWDGS) and thin stillage. WWDGS may be sold without further removal of moisture (approximately 65% moisture) or may undergo further drying in a drum or ring dryer to reduce moisture to meet customer demand. Modified distillers grains with solubles (MWDGS) or dry distillers grains with solubles (DDGS) are two products created after additional drying of WWDGS. Thin stillage (~4% solids) is recycled into the plant and fed into evaporators to reduce the water content to approximately 20%–25% solids. After the water content is reduced, the product is called "syrup." Syrup may be added back onto the WWDGS, MWDGS, and DDGS or may also be sold to customers as an additive for livestock feed.

Ethanol product blending and load out

After distillation, 200 proof ethanol is blended with approximately 5% denaturant (unleaded gasoline) to make the product unfit for human consumption. Also, a corrosion inhibitor is added to the final product. The denatured ethanol is loaded onto tanker trucks or rail car tankers for shipment off site.

A.1.2 Wet Milling Method of Ethanol Production

The corn wet milling process is designed to separate the corn kernel into various fractions to make separate products. Ethanol is one of the final products made from the corn starch. Wet milling has an advantage over dry milling in that the mill operator can change the emphasis on the final products in response to market demands and remain profitable. The disadvantage of corn wet milling is the cost of the extra energy demand required by this production method.

Wet milling begins with steeping the corn kernels in a solution of water and sulfur dioxide. In most facilities, this initial soak lasts for 20–36 hours while the corn kernels double in size. The swelling of the corn kernel allows the corn germ to loosen and separate after the first grinding.

After steeping, the corn is coarsely ground into slurry. The germ is separated from the slurry in a hydro cyclone, relying on the lower density of the germ to facilitate the separation. The germ contains the corn oil, making it less dense than the rest of the kernel. The germ is dried and sent to be processed further to obtain corn oil, usually at a separate centralized facility.

The slurry that remains after the germ is separated is finely ground and screened to free as much starch and gluten from the fiber as possible. The fiber is washed to recover the maximum amount of starch and gluten. The fiber is dewatered, and steep water from the beginning of the process is added. The mixture is dried and sold as corn gluten feed for cattle and other animals.

The starch and gluten are separated next. Starch has a higher density than gluten, so centrifugation is used for the separation process. The gluten is dewatered and dried to produce corn gluten meal, another animal feed that is commonly used in poultry production.

The remaining corn starch slurry can then be processed and used in the production of a wide range of products from food stuffs and paper making to uses in plastics manufacturing and well drilling. When used for ethanol production, the starch is treated the same as the dry milled corn, similarly undergoing saccharification, fermentation, and distillation.

A.2 BIODIESEL MANUFACTURE

A wide variety of oils and fats feedstocks can theoretically be used for biodiesel production (Figure A-1). In the United States, almost all biodiesel production uses soybean oil as a feedstock. Three basic routes to biodiesel production from oils and fats currently exist:

Figure A-1. Biodiesel production plant.
Source: Nebraska Department of Environmental Quality.

- base-catalyzed transesterification of the oil
- direct acid-catalyzed transesterification of the oil
- conversion of the oil to its fatty acids and then to biodiesel

Use of acid or base catalyst in the transesterification process is determined by the free fatty acid content in the feedstock. A base catalyst is used for feedstocks with free fatty acid levels around 1%, such as soybean oil. Therefore, base-catalyzed reactions are most commonly used to produce biodiesel, and this production process is the one described here. Small biodiesel manufacturing facilities generally use batch reactors, while those producing over 1 million gal per year tend to use continuous-flow processes with plug-flow reactors or continuous-stirred tank reactors (NBB 2007).

Base-Catalyzed Transesterification

Mixing of alcohol and catalyst

The base catalyst (typically sodium hydroxide [NaOH] or potassium hydroxide [KOH]) is dissolved in a short-chain alcohol (usually methanol, but sometimes ethanol) using a standard agitator or mixer. One hundred pounds of feedstock reacted with 10 pounds of alcohol in the presence of the catalyst produces 10 pounds of glycerin and 100 pounds of biodiesel.

Reaction

The alcohol/catalyst mix is charged in a closed reaction vessel and the oil or fat added. The system from here on is totally closed to the atmosphere to prevent the loss of alcohol. The reaction mix is kept just above the boiling point of the alcohol (around 160°F) to speed the reaction. Recommended reaction time varies 1–8 hours, and some systems recommend the reaction take place at room temperature. Excess alcohol is normally used to ensure total conversion of the feedstock to its esters.

In commercial-scale production systems, this reaction is often done in two steps. First, approximately 80% of the alcohol and catalyst are added to the oil in the reaction vessel. The reacted product is separated from the glycerin and sent to a second reaction vessel, where the remaining 20% of the alcohol and catalyst are added. This system causes a very complete reaction with the use of less alcohol (NBB 2007).

Separation

Once the reaction is complete, two major products exist: glycerin and biodiesel. The glycerin phase is much more dense than the biodiesel phase, and the two can be gravity separated. In some cases, a centrifuge is used to separate the two materials faster.

Alcohol removal

Alcohol removal can take place either before or after the separation step and is achieved by distillation or by a flash evaporation process. Most often, the alcohol is removed after glycerin separation because the transesterification process is reversible and the methyl esters may recombine with glycerine to form monoglycerides.

Glycerin neutralization

The glycerin by-product contains unused catalyst and soaps that are neutralized with an acid and sent to storage as crude glycerin. The acid splits the soaps into free fatty acids and salt. In most cases, the salt is left in the glycerin, but it can also be recovered for use as fertilizer if specific acids (phosphoric acid) and catalysts (potassium hydroxide) are used in the process. Free fatty acids separate from the glycerin and are removed. Water and alcohol are removed to produce 80%–88% pure glycerin that is ready to be sold as crude glycerin. The crude glycerine could be characterized as an ignitable hazardous waste if the alcohol were not removed. When distilled to 99% or higher purity, the glycerin can be sold to the cosmetic and pharmaceutical markets. Purified glycerin can also be “cracked” into syngas and synthesized into methane and possibly other biofuels.

Methyl ester wash

Once separated from the glycerin, biodiesel is stripped of any remaining methanol in a mechanical methanol stripper. Acid is added to the biodiesel to neutralize residual catalyst and split any soap into free fatty acids and water-soluble salt. The biodiesel is then purified by washing with water to remove residual catalyst, soaps, and color before being sent to storage.

Product quality and registration

Prior to use as a commercial fuel, the finished biodiesel must be analyzed to ensure it meets ASTM specification D6751-09. Biodiesel produced must be registered with USEPA under 40 CFR §79.

A.3 OTHER BIOFUELS PRODUCTION METHODS

A number of conversion technologies can potentially be used by biorefineries to draw on a variety of biomass feedstocks to produce fuels, chemicals, and other products. Many of these technologies are the subject of current research and development efforts. The DOE Office of

Energy Efficiency and Renewable Energy's Biomass Program (www1.eere.energy.gov/biomass/about.html) focuses on research, development, and demonstration of biomass feedstocks and conversion technologies geared toward the development of integrated biorefineries for biofuels production.

Cellulosic ethanol is currently the leading candidate for replacing a large portion of U.S. petroleum use, and several commercial cellulosic ethanol production plants are under construction. Intensive research and development are rapidly advancing the state of cellulosic ethanol technology for the breakdown of hemicellulose into cellulose and the breakdown of cellulose into the simple sugar glucose. Once glucose is developed from a feedstock, the alcohol production process is similar to that described above. For more information on cellulosic ethanol production, see NREL (2007). In addition to cellulosic ethanol, other potential production methods are being researched and show promise, such as technologies for the production of algae-based biofuels for both ethanol and biodiesel manufacturing (USEPA 2010).

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Appendix B

UST Installation Application/Conversion Notification Checklist Example for Biofuel

UST INSTALLATION APPLICATION/CONVERSION NOTIFICATION CHECKLIST EXAMPLE FOR BIOFUEL

INSTRUCTIONS: This form is to be submitted to the Department along with the Application for the Permit to Install for new installations, or submitted independently for conversions of existing systems from conventional motor fuels to blends greater than E10 as well as all biodiesel blends greater than B20. For existing tank systems, submit this form prior to the conversion.

Part I

1. OWNER INFORMATION	**2. FACILITY INFORMATION**	**3. CONTRACTOR INFORMATION**
Name	Facility ID#	Contractor Name
Mailing Address	Facility Name	Mailing Address
City, State, Zip Code	Facility Address	Contact Person
Telephone Number ( )	Telephone Number ( )	Telephone Number ( )
Email:		Email:
4. Tank Information		

Tank Size:___________(gallons) ☐ New Tank ☐ Existing Tank **Fuel to be Stored**: ____________

Is tank lined: ☐ Yes ☐ No **Note**: **Tanks with interior lining will not be approved for E85 storage**

Tank leak detection method: ☐ Automatic tank gauging ☐ Vapor/Groundwater monitoring ☐ Interstitial monitoring ☐ Statistical Inventory Reconciliation (SIR)

Component:	**Manufacturer**	**Model/Brand**	**UL Listed or Verified by Manufacturer for Fuel to be Stored**	**Comments**
If manufacturer or model/brand cannot be determined, write "UNK" in the corresponding box. In the Comment area, write "UNK" if compatibility cannot be determined; write "NA" if system does not have the component listed, write "HC" and the treatment material if a hard-coat treatment is used to achieve compatibility.				
Configuration: ☐ Single wall ☐ Double wall **Type:** ☐Steel ☐Steel clad ☐ Fiberglass				
Tank construction material			☐ Listed ☐ Verified	☐ PE ☐Installer __ Initials
Spill bucket			☐ Listed ☐ Verified	☐ PE ☐Installer __ Initials
Overfill/drop tube shutoff/ball float vent valve/pressure/ vacuum valves			☐ Listed ☐ Verified	☐ PE ☐Installer __ Initials
Drop tube			☐ Listed ☐ Verified	☐ PE ☐Installer __ Initials
Submersible pump			☐ Listed ☐ Verified	☐ PE ☐Installer __ Initials
Leak detection probes			☐ Listed ☐ Verified	☐ PE ☐Installer __ Initials
Sump sensors			☐ Listed ☐ Verified	☐ PE ☐Installer __ Initials
Vapor balance equipment			☐ Listed ☐ Verified	☐ PE ☐Installer __ Initials
5. Pipe Information **Is sump present for submersible / pipe connections:** ☐ Yes ☐No				
Configuration: ☐ Single wall ☐ Double wall **Type:** ☐ Steel ☐ Fiberglass ☐ Flexible ☐ Other (*Specify*):				
Pipe construction material			☐ Listed ☐ Verified	☐ PE ☐Installer __ Initials
Gaskets/seals			☐ Listed ☐ Verified	☐ PE ☐Installer __ Initials
Pipe sealant/adhesive			☐ Listed ☐ Verified	☐ PE ☐Installer __ Initials
Flex connector			☐ Listed ☐ Verified	☐ PE ☐Installer __ Initials
Line leak detector			☐ Listed ☐ Verified	☐ PE ☐Installer __ Initials
Containment sump			☐ Listed ☐ Verified	☐ PE ☐Installer __ Initials
Vent piping			☐ Listed ☐ Verified	☐ PE ☐Installer __ Initials
Riser piping			☐ Listed ☐ Verified	☐ PE ☐Installer __ Initials

6. Dispenser Information		**Blending dispenser:** ☐ Yes ☐No		**Is sump present under dispenser:** ☐ Yes ☐No
Dispenser piping			☐ Listed ☐ Verified	☐ PE ☐Installer __ Initials
Gaskets/seals			☐ Listed ☐ Verified	☐ PE ☐Installer __ Initials
Dispenser sump			☐ Listed ☐ Verified	☐ PE ☐Installer __ Initials
Check valve			☐ Listed ☐ Verified	☐ PE ☐Installer __ Initials
Nozzle(s)/swivel(s)			☐ Listed ☐ Verified	☐ PE ☐Installer __ Initials
Hose(s)			☐ Listed ☐ Verified	☐ PE ☐Installer __ Initials
Break-away device			☐ Listed ☐ Verified	☐ PE ☐Installer __ Initials
Fuel filters			☐ Listed ☐ Verified	☐ PE ☐Installer __ Initials
Emergency valve			☐ Listed ☐ Verified	☐ PE ☐Installer __ Initials
Sump sensor			☐ Listed ☐ Verified	☐ PE ☐Installer __ Initials
Stage II vapor processor			☐ Listed ☐ Verified	☐ PE ☐Installer __ Initials
Fittings			☐ Listed ☐ Verified	☐ PE ☐Installer __ Initials

I certify by signature that I have personally examined and/or am familiar with the information submitted to verify system compatibility, and the information is true, accurate, and complete.

Signature of Authorized Party

Date

REFERENCE

South Carolina Department of Health and Environmental Control. 2006. “Underground Storage Tank Alternative Fuel Installation Application/Conversion Notification.” DHEC 3885 (06/2006). www.scdhec.gov/environment/lwm/forms/d-3885.pdf.

Appendix C

Fuel Component Properties

FUEL COMPONENT PROPERTIES

Parameter	**Ethanol**	**Butanol**[a]	**Benzene**	**Biodiesel**	**Diesel**[b]
CAS number	64-17-5	78-83-1 and 71-36-3	71-43-2	—	—
Molecular formula	C_2H_5OH	$C_4H_{10}O$	C_6H_6	Soy FAMEs	Fuel No. 2
Molecular weight (g/mole)[c]	46.07	74.1	78.11	—	—
Boiling point (°C)[c]	78.3	108 to 118	80.1	352 to 417	160 to 360
Density (g/cm^3)[c]	0.79	0.81	0.88	0.84 to 0.90	0.87 to 0.95
Surface tension (dynes/cm)[d, e, f]	22.1 (20°C)	22.98 to 24.93 (20°C)	28.88	28.4 to 30 (25°C)	25 (20°C)
Interfacial tension (dynes/cm)	Miscible	1.8 to 2.0	35.5	10.1 to 13.5	7.4
Vapor pressure (mm Hg @ 25°C)[g, h]	59	0.42 to 11.8	75	8.63E-6 to 3.74E-4	2.12 to 26.4 (21°C)
Water solubility (mg/L @ 20°C)[c, g, h, i, j, k]	Infinite	7.4E+4 to 8.7E+4	1.8E+3	1.2E-3 to 2.1E-2	5.0
Dynamic viscosity (cp @ 25°C)	1.074[l]	2.54 to 4.70	0.649 (20°C)[l]	324 to 480	1.1 to 3.5 (40°C)
Henry's law constant (gas/aq)[g, j]	2.1E-4 to 2.6E-4	3.73E-4 to 5.0E-4	0.22	6.4E-3 to 1.3	2.4E-3 to 3.0E+2
Log K_{oc}[m, n, o]	0.20 to 1.21	1.86 to 2.05	1.98	6.14 to 8.21[i]	3.0 to 5.7
Log K_{ow}[g, h, m]	-0.16 to -0.31	0.83 to 0.88	2.13	6.29 to 8.35	3.3 to 7.06
Estimated aerobic biodegradation potential in groundwater	Days-weeks	Days-weeks	Weeks-months	Days-weeks	Weeks-months
Estimated anaerobic biodegradation potential in groundwater	Weeks-months	Weeks-months	Years	Weeks-months	Years
Hydroxyl radical oxidation (in atmosphere) (cm^3/molecule-sec)[a]	3.5763E-12	6.9E-12 to 8.6E-12	1.9498E-12	1.27E-12 to 180E-12	10E-12 to 100E-12

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Appendix D

Case Studies

CASE STUDIES

This case study appendix provides three case studies, including two case studies of DFE releases and one biodiesel (B100) release. In addition, a table of selected biofuel releases (Table D-2) is provided following the case study narratives. This table provides more information on a number of releases, including release scenarios, analytes, contaminants of concern, and responses.

The first case study, Cambria Denatured Fuel Ethanol Release (Section D.1), provides information on the investigation of a November 2006 train derailment that released approximately 25,000 gal of DFE. The site was selected as a study site for evaluating MNA for DFE and high-concentration ethanol releases. Monitoring wells and soil gas probes were used to delineate the extent of groundwater impacts and evaluate vapor-phase methane concentrations. This site demonstrates the potential for delayed generation of methane and for ethanol to be resident in the capillary fringe.

The second case study, Pacific Northwest Terminal Denatured Fuel Ethanol Release (Section D.2), provides information on the investigation and remediation of a March 1999 19,000-gal release of DFE from an AST at a bulk fuel terminal. This case study discusses the bioremediation of the ethanol release and the impacts to a preexisting dissolved hydrocarbon (NAPL) plume that was present at the site.

The third case study, Westway Terminal Biodiesel Release (Section D.3), describes the investigation of a 29,000-gal release of B100 from a large AST located along the Mississippi River in St. Paul, Minnesota. Because no current analytical methods directly measure aqueous-phase biodiesel, some common analytical methods were used as a surrogate during the investigation of this release. High levels of DOC, TOC, and carbonaceous biochemical oxygen demand detected at the site indicate a high concentration of organic matter in groundwater that were attributed to the B100 release. This high level of organic loading resulted in an anoxic and methane-generating groundwater plume.

D.1. CAMBRIA DENATURED FUEL ETHANOL RELEASE CASE STUDY

Adam Sekely, Minnesota Pollution Control Agency

D.1.1 Introduction

In November 2006, a train derailment in south central Minnesota resulted in the release of approximately 25,000 gal of denatured fuel ethanol. The release occurred in a low-lying area south of the railroad tracks near the Little Cottonwood River. Soils in the release area consist of fine to coarse, poorly sorted sands and silty sands. Groundwater is encountered 0.5–3 feet below grade in the release area, as deep as 12 feet in upslope areas adjacent to the release, and 1–4 feet in the downgradient area northeast of the railroad tracks.

The immediate response to the release consisted of recovering 11,600 gal of liquid product, including an unknown amount of water; no soil was removed from the site. This action was followed by installation of monitoring wells MW-1 to MW-6 and several soil test pits in December 2006 and January 2007 to evaluate the remaining contamination. Visual and olfactory observations from test pits revealed that unrecovered DFE that had not evaporated had infiltrated into the subsurface, with a January 2007 groundwater sample from MW-1 indicating ethanol had reached the water table.

This initial site assessment identified a potential risk to the nearby river based on residual petroleum hydrocarbons originating from the DFE denaturant. This risk, however, was determined to be low, as contaminant concentrations did not exceed applicable surface water standards at wells located between the release area and the river. Subsequently, the site was selected as a study site for evaluating MNA for DFE and high-concentration ethanol releases.

D.1.2 Investigation to Assess Natural Attenuation

Following selection for MNA evaluation, temporary wells and soil gas probes (B-1 to B-7) were drilled in June 2007 to further delineate the extent of groundwater impacts and evaluate vapor-phase methane concentrations, respectively. Monitoring wells MW-7 to MW-11, along with permanent soil gas monitoring points VP-7 to VP-11 and surface gas samplers SG-1 to SG-3, were installed in November 2007 to monitor for natural attenuation. In July 2008, monitoring wells MW-12 and MW-13 and soil gas monitoring points VP-12 and VP-13 were installed as the aqueous-phase methane plume migrated beyond the monitoring network. In November 2008, six prepacked monitoring wells with 1-foot screens were installed within the release area as well nests MW-16 and MW-17 to better characterize the vertical distribution of ethanol. Top-of-screen depths for each three-well nest were approximately 1 (A), 4 (B), and 7 (C) feet below the water table at the time of installation. Figures D-1 and D-2 show sampling locations.

Groundwater samples were analyzed for petroleum VOCs, ethanol, acetate, methane, and several inorganic parameters used to assess biodegradation, including DO, nitrate-nitrogen, ferrous iron, and sulfate. In addition, groundwater temperature and pH were collected during well stabilization prior to sampling. Soil gas and surface gas samples were analyzed for petroleum VOCs, ethanol, methane, oxygen, and carbon dioxide. Additional details of the release site and data analysis can be found in Spalding et al. (2011).

D.1.3 Results

Aqueous-Phase Ethanol And Methane

In June 2007, seven months after the release, ethanol concentrations in groundwater exceeded 5% (55,000,000 µg/L) in the release area (B-5), whereas aqueous-phase methane concentrations remained relatively low (Figure D-1). By December 2007, the groundwater methane plume had expanded in both magnitude and extent (Figure D-2). Quarterly monitoring was initiated in December 2007, followed by semiannual monitoring beginning in October 2009.

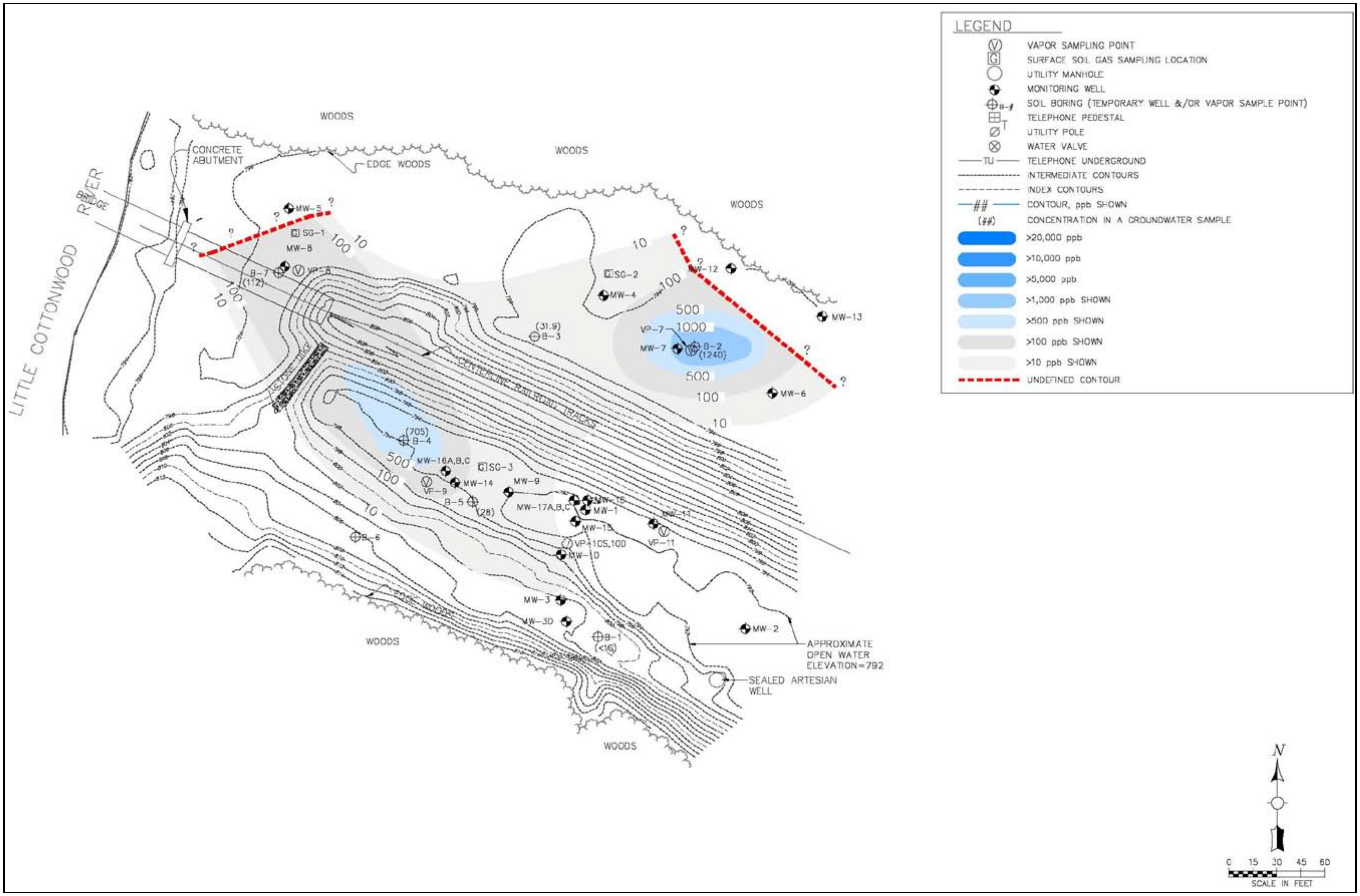

Figure D-1. Aqueous-phase methane concentrations (μg/L) from temporary monitoring well samples (B-1 to B-5, B-7) collected in June 2007, approximately seven months after the release.

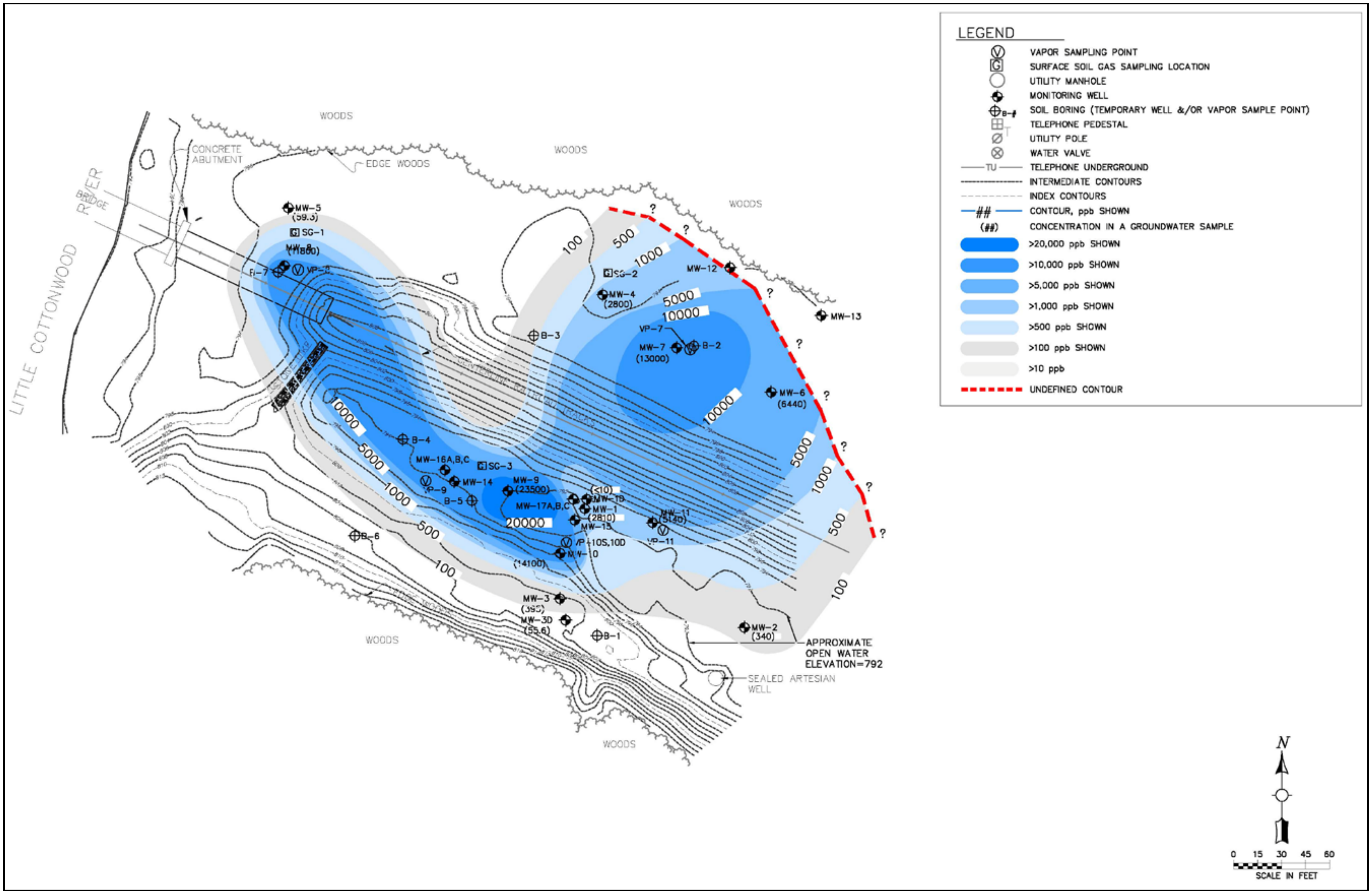

Figure D-2. Aqueous-phase methane concentrations (µg/L) from monitoring well samples (MW-1 to MW-11) collected in December 2007, approximately 11 months after the release.

Figures D-3 through D-5 show ethanol and methane concentrations over time for three different monitoring wells within (MW-1 and MW-9) and near (MW-11) the release area. Figure D-6 shows methane concentrations in downgradient wells. No ethanol has been detected above laboratory reporting limits (100 µg/L) in the downgradient wells. There is little evidence to indicate that a groundwater ethanol plume migrated from the release area. Although referred to as a near-source area well, MW-11 may have been drilled in an area that had been impacted directly by the release but not observed prior to initial response actions or by ethanol that migrated within the rail ballast.

Release-area monitoring wells show distinctly different trends in methane, with MW-1 showing persistent high methane concentrations and no currently detectable ethanol and MW-9 showing decreasing methane concentrations that mirror the ethanol concentrations. Despite no currently detectable ethanol in MW-1 and MW-9, which are constructed similarly to wells used for petroleum releases, ethanol is still present in the release area. Recent samples from short-screened MW-16A had ethanol concentrations near the water table of 9,000,000 and 3,600,000 µg/L in October 2009 and June 2010, respectively. Conversely, ethanol has not been detected in groundwater samples from MW-16B and MW-16C, suggesting ethanol may be residing in the capillary fringe. The variability in detecting ethanol in monitoring wells makes methane sampling for the purposes of MNA of greater importance because methane is more consistently measured in groundwater.

Methane concentrations in downgradient wells MW-6 and MW-13 (Figure D-6) reached their peak in May 2009, which correlates to peak ethanol concentrations in MW-1 and MW-11. Downgradient methane concentrations have steadily decreased since May 2009, which correlates to decreasing acetate (not shown) and ethanol concentrations in MW-1 and MW-11. The correlations suggest aqueous-phase methane production has reached its peak and that residual contamination in the release area is attenuating. MW-12 is more side-gradient to the release and near the groundwater plume edge, which may account for a slight dissimilar trend over time.

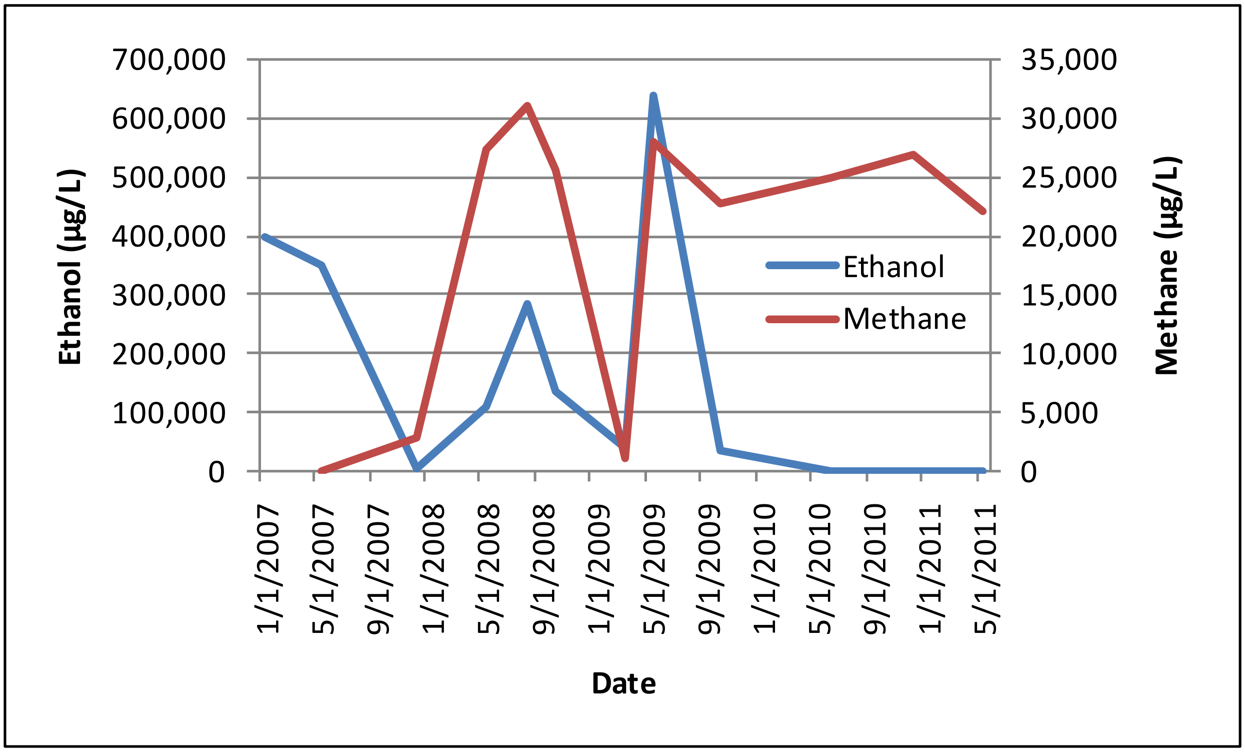

Figure D-3. Aqueous-phase ethanol and methane concentrations in MW-1, a release-area monitoring well.

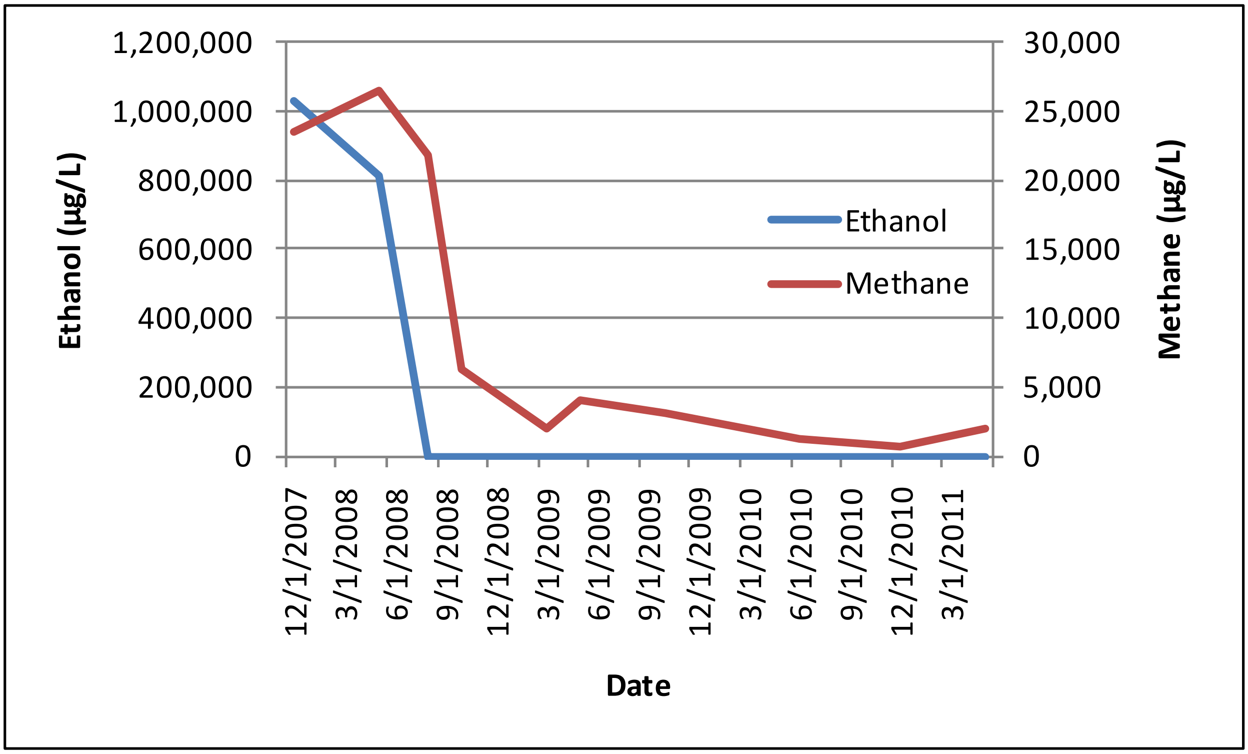

Figure D-4. Aqueous-phase ethanol and methane concentrations in MW-9, a release-area monitoring well.

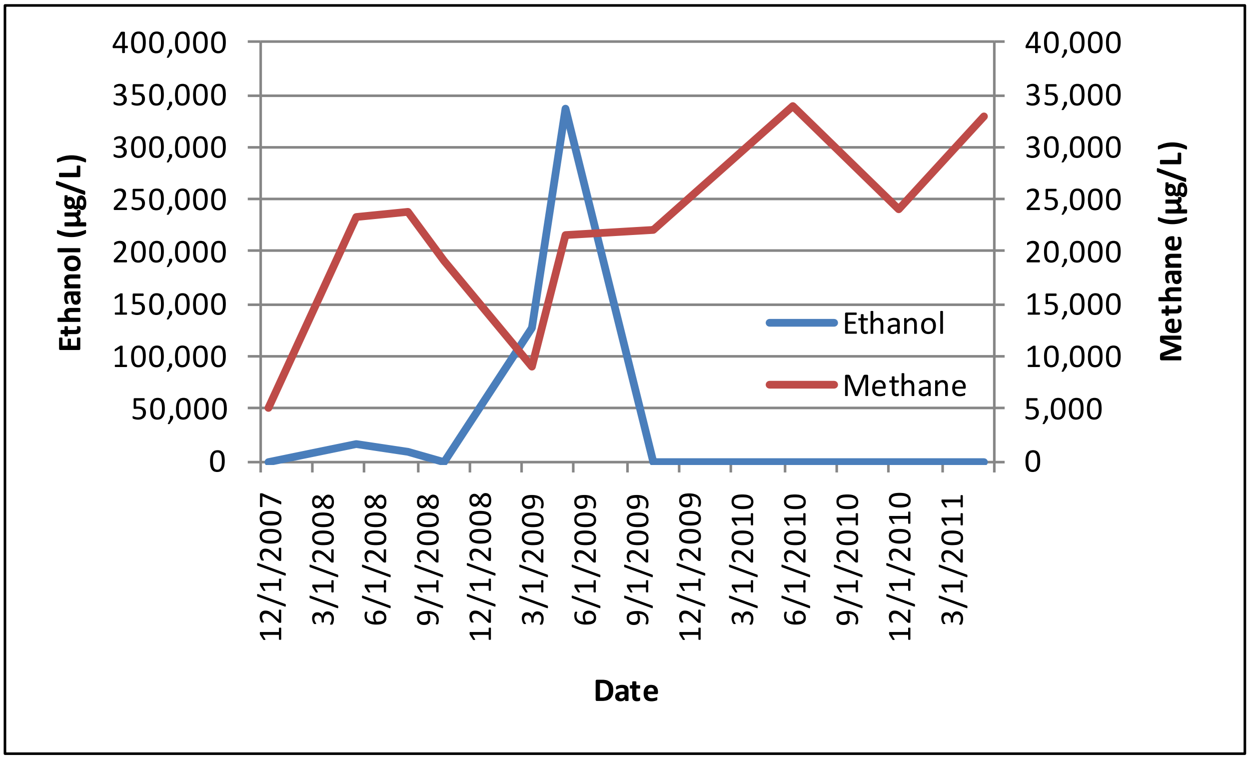

Figure D-5. Aqueous-phase ethanol and methane concentrations in MW-11, a near release-area monitoring well.

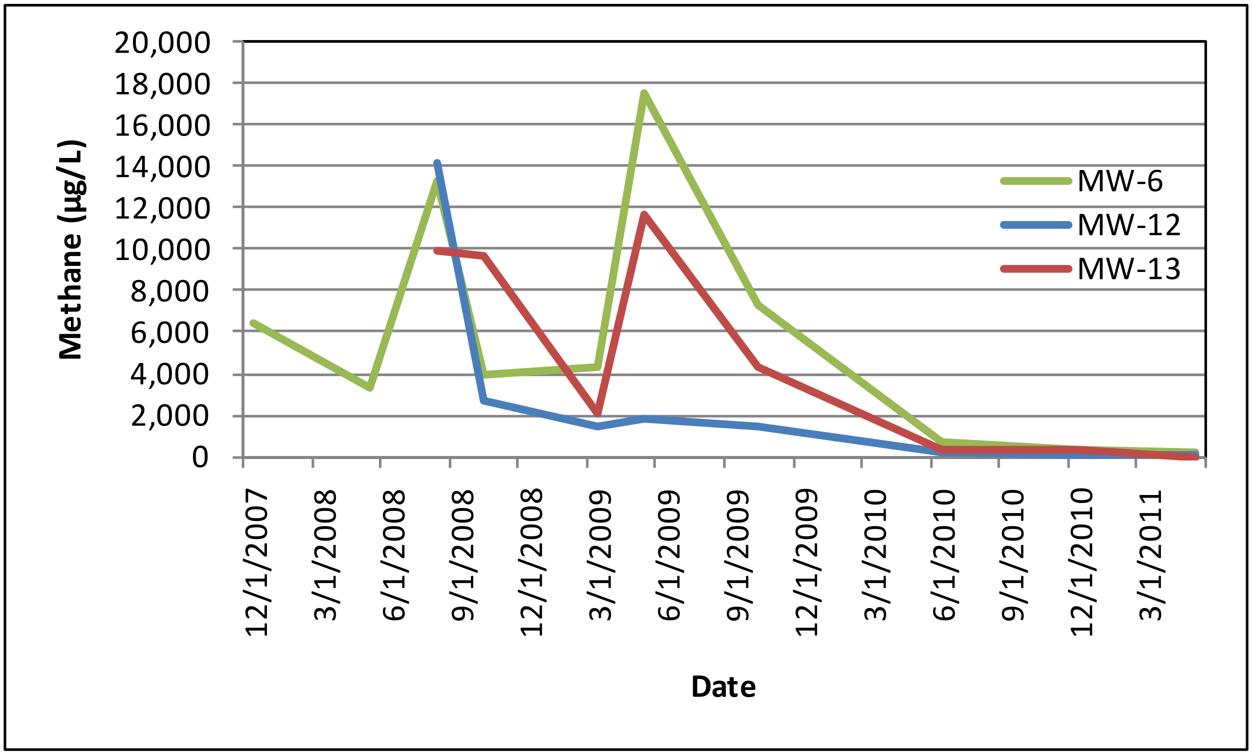

Figure D-6. Aqueous-phase methane concentrations in downgradient monitoring wells.

Aqueous-Phase Benzene

Figures D-7 and D-8 show benzene concentrations in release-area monitoring wells and downgradient wells, respectively. In MW-1, the benzene concentration was initially stable but steadily rose over a seven-month period to a high of 910 µg/L in October 2008, where it has since steadily decreased over an approximate three-year period. The rise in benzene and its peak corresponds to the rise and peak of methane and acetate (not shown) in MW-1. Additionally, acetate has continued to decrease along with benzene, suggesting that benzene degradation may have been hindered when ethanol and acetate consumption was at its highest. Although initial petroleum hydrocarbon concentrations were low relative to a gasoline release, they have persisted longer than might be expected at these concentrations.

Benzene concentrations in the downgradient wells displayed a decreasing trend similar to MW-1 but starting three months after MW-1 benzene concentrations began to decrease. Benzene has not been detected in MW-6 and MW-13 since June 2010 and October 2009, respectively. Benzene has never been detected in MW-12 above laboratory reporting limits (1.0 µg/L) despite observed methane concentrations above 10,000 µg/L. Decreasing trends in benzene concentrations, along with the aforementioned decreasing downgradient methane concentrations, indicate the groundwater plume is attenuating despite continued high ethanol, acetate, and methane concentrations in the release area.

Vapor-Phase Methane

Vapor-phase methane concentrations were initially assessed in June 2007 and measured up to 5% by volume (v/v) in the release area (B-5). In December 2007, methane was detected near 1% v/v in release-area soil gas monitoring points VP-9 and VP-10, with surface gas methane concentrations up to 1.6% v/v in SG-3. There has been no methane detected above laboratory reporting limits (~1%–2% v/v) in soil gas monitoring points or surface gas samplers since December 2007 and May 2008, respectively. Because the monitoring point screens are set at a shallow depth (2.5–3 feet below grade), some locations have not been routinely sampled due to either submerged screens or frozen subsurface conditions. No soil gas samples were collected in December 2010 because of frost or in May 2011 because of submerged screens.

Vapor-phase methane concentrations do not show a relationship to aqueous-phase concentrations, although there is no monitoring point or surface sampler near MW-1 in the main release area. MW-1 lies in the lowest area of the release where the shallow water table and periodic standing water prevent installation of a monitoring point and surface sampler. Oxygen concentrations in soil gas samples are typically above 10% v/v and often near expected atmospheric concentrations. The lack of a relationship may be explained by the inability to collect consistent and reliable samples because of the shallow water table and the shallow screen depth. In addition, methane oxidation rates in the vadose zone may be sufficient to maintain concentrations below laboratory reporting limits.

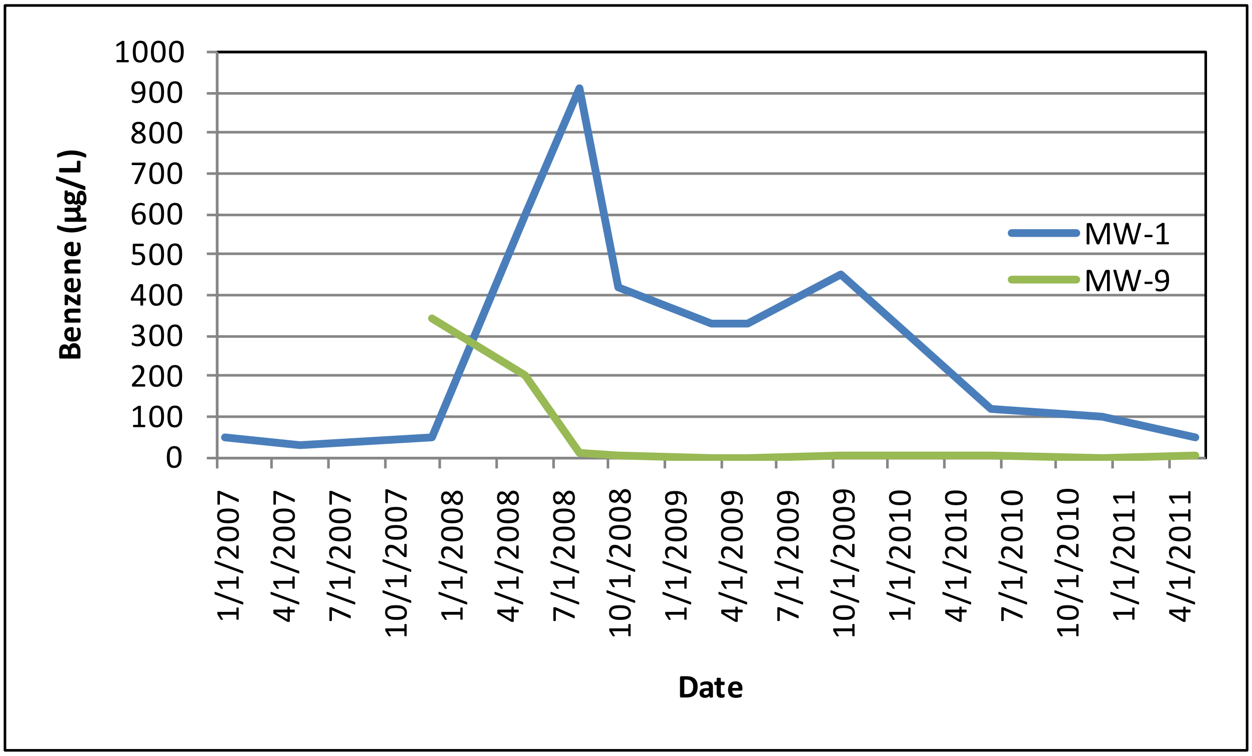

Figure D-7. Aqueous-phase benzene concentrations in release-area monitoring wells.

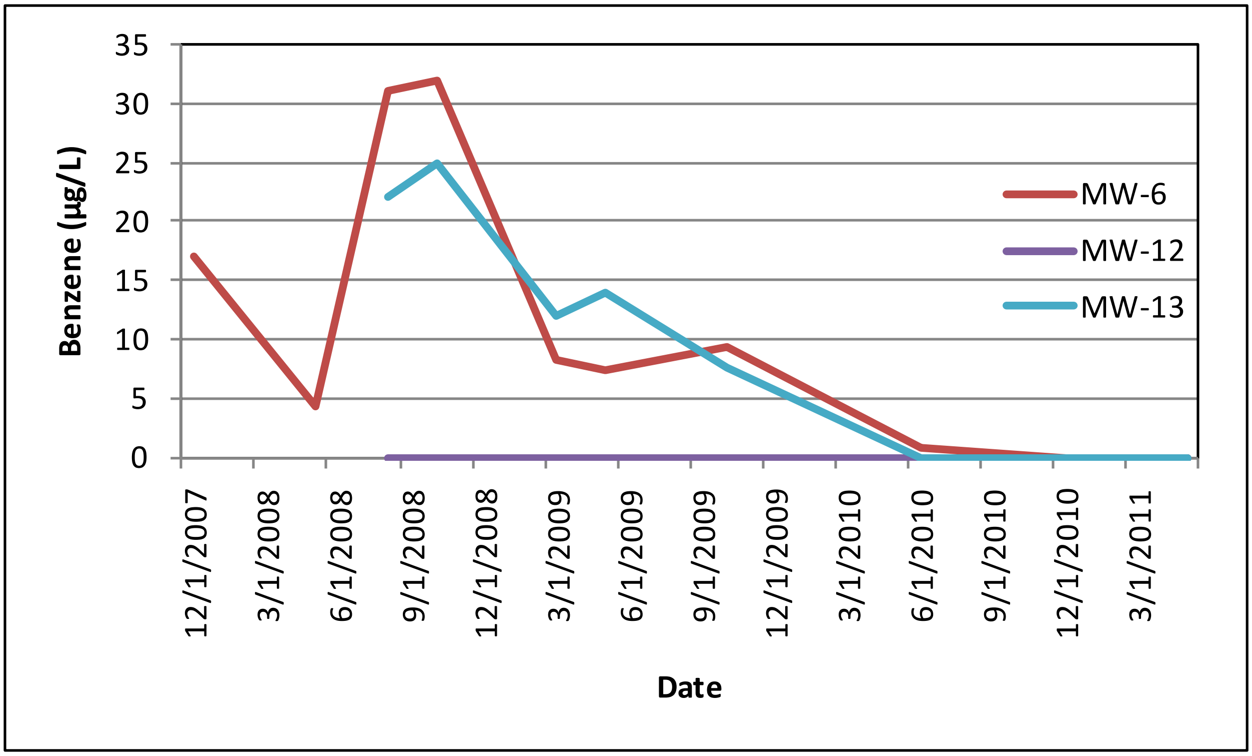

Figure D-8. Aqueous-phase benzene concentrations in downgradient monitoring wells.

D.1.4 Conclusions

The Cambria site demonstrates that an MNA management strategy can be viable following a DFE release when site conditions allow. The unique behavior of ethanol in the subsurface and the potential for significant methane production following a DFE release may warrant investigation, monitoring, and sampling methods different from those following typical petroleum releases. For example, as ethanol is often undetectable in standard monitoring wells, methane measurements provide evidence of ethanol attenuation and can assist in determining whether methane poses a potential risk.

Cambria will continue to be used as a study site for MNA. Groundwater monitoring will focus on assessing ethanol, acetate, and methane concentrations as well as their vertical distribution within the aquifer via MW-16 and MW-17. Additionally, soil probes will be completed in the release area to evaluate the presence and distribution of residual ethanol in the capillary fringe. Soil gas samples will be collected in soil gas monitoring points when possible, while additional research is being conducted using flux chambers to measure the occurrence and magnitude of soil gas methane flux to the atmosphere.

D.1.5 Reference

Spalding, R. F., M. A. Toso, M. E. Exner, G. Hattan, T. M. Higgins, A. C. Sekely, and S. D. Jensen. 2011. “Long-Term Groundwater Monitoring Results at Large, Sudden Denatured Ethanol Releases,” *Ground Water Monitoring and Remediation* **31**(3): 69–81, DOI 10.1111/j.1745-6592.2011.01336.x.

D.2 PACIFIC NORTHWEST TERMINAL DENATURED FUEL ETHANOL RELEASE CASE STUDY

Amy Wormsley and Tim Buscheck, Chevron

D.2.1 Introduction

In March 1999, a 19,000-gal release of DFE occurred from an AST at a bulk fuel terminal located in the northwest United States (“Pacific Northwest Terminal”). This case study discusses the bioremediation of the ethanol release and the impacts to a preexisting dissolved hydrocarbon plume (NAPL) that was present at the site. Additional information is available from Buscheck et al. (2001).

The hydrogeologic setting of the Pacific Northwest Terminal is a layer of alluvium overlain by a layer of sand and silty sand fill. The fill and the alluvium are hydraulically connected, and groundwater flows to a river at approximately 0.01 ft/ft. The fill layer is the primary zone for the occurrence of hydrocarbons, and the less permeable underlying alluvium may provide an aquitard (K. Kline, KHM Environmental Management, Inc., personal communication, 2001).

Water levels beneath the site are influenced by annual precipitation cycles and by river stage fluctuations. The depths to water typically range 2–14 feet below grade. Based on field tests, the groundwater velocity within the fill material is estimated to be 300–400 feet per year (K. Kline, KHM Environmental Management, Inc., personal communication, 2001).

D.2.2 Site Characterization

Historical groundwater monitoring data were available from existing monitoring wells to delineate the preexisting dissolved hydrocarbon plume. After the ethanol release, 18 additional monitoring wells were installed, and groundwater samples were analyzed for BTEX, total petroleum hydrocarbons (TPH), and ethanol (USEPA Method 8260).

In May 2000, the groundwater sampling protocol was expanded to include analytes for in situ bioremediation. The analytes included DO, methane, nitrate, sulfate, CO_2, acetate, and dC^{13} (carbon-13 isotope for CO_2). The dC^{13} data were not used in the final analysis but are now understood to be important when distinguishing the origin of methane emissions (Freitas et al. 2010). In addition, a field soil gas survey was conducted in June/July 2001, and Summa canister samples were collected and analyzed for methane in the laboratory. Table D-1 summarizes media sampling conducted at the site.

Table D-1. Summary of media sampling at the Pacific Northwest Terminal

Sampled media	Samples
Soil	BTEX, TPH
Groundwater	Ethanol analyzed by USEPA 8260b Analytes for in situ bioremediation (DO, NO_3, SO_4, CH_4, CO_2, acetate, dC13) BTEX, TPH
Soil vapor	Field and laboratory methane
Surface water	Not applicable
NAPL characterization	A laboratory analysis designed to understand the apparent increase in NAPL mobility at the site. The tank experiments investigated density, viscosity, and surface tension (McDowell, Buscheck, and Powers 2003).

D.2.3 Fate and Transport

In the presence of ethanol, biodegradation of BTEX in groundwater may be inhibited and may potentially increase hydrocarbon plume lengths. At the Pacific Northwest Terminal, elevated benzene concentrations in one well after the ethanol release suggest a possible cosolvent effect and lower benzene transformation rates resulting from the presence of ethanol. However, ethanol concentrations at UST release sites (<10% ethanol in ethanol-gasoline mixtures) are not likely to have the same impact on a hydrocarbon plume.

An increase in the apparent NAPL thickness was also observed in two monitoring wells following the ethanol release. Laboratory tank experiments designed to understand the increase in NAPL mobility indicated that the addition of ethanol to preexisting gasoline contamination reduced surface and interfacial tensions. This event resulted in changes to the size, shape, and saturation of the gasoline pool. Some smearing of the gasoline into the saturated zone also occurred as the capillary fringe was depressed. The final gasoline pool occupied a smaller area but had a higher saturation (McDowell, Buscheck, and Powers 2003).

Although ethanol can be degraded in both aerobic and anaerobic environments, microbial aerobic respiration in hydrocarbon-contaminated aquifers can quickly deplete oxygen, suggesting ethanol is likely to be degraded under anaerobic conditions at field sites. Microorganisms that can ferment ethanol are ubiquitous, and ethanol is a common intermediate in the anaerobic food chain (Alvarez and Hunt, 1999). Anaerobic microbial degradation of ethanol generates a variety of metabolic intermediates and end products (Alvarez and Hunt 1999). In the third stage of ethanol fermentation, methanogens mineralize acetate to CO_2 and CH_4 (Alvarez and Hunt 1999).

There is evidence for ethanol biodegradation under methanogenic conditions at the Pacific Northwest Terminal. Dissolved methane concentrations in groundwater increased to their highest levels in mid-2001 and have declined since. A soil gas survey conducted in June/July 2001 measured methane concentrations that exceeded 150,000 ppm-v above groundwater containing elevated dissolved methane concentrations.

Within six months of the ethanol release, dissolved ethanol was detected 250 feet downgradient, but shortly afterward the plume appeared to attenuate. Over the first 18 months, ethanol concentrations significantly declined in two monitoring wells directly downgradient of the ethanol release, but in December 2000 and April 2001, ethanol concentrations increased, suggesting some residual ethanol remained in the vadose zone. In July 2001 ethanol was not detected above a practical quantification limit of 20 µg/L. Since 2001 ethanol has been detected intermittently at concentrations very close to the practical quantification limit.

D.2.4 Remediation

The release of ethanol at the Pacific Northwest Terminal created a strongly anaerobic groundwater system, demonstrated by low or nondetectable DO, depleted sulfate and nitrate, and elevated methane concentrations (as high as 30,000 µg/L). There is evidence for ethanol biodegradation under methanogenic conditions, indicated by elevated methane concentrations and declining ethanol concentrations throughout the plume.

In 2002, an SVE system was installed to safely remove methane vapors from the subsurface. In 2009, it was determined that SVE at the Pacific Northwest Terminal had reached asymptotic levels, and a plan for SVE system shutdown and rebound monitoring was approved by state regulators.

D.2.5 Regulatory Issues

The investigation at the Pacific Northwest Terminal demonstrates that ethanol in groundwater can impact a preexisting hydrocarbon plume in four ways:

- Reduction of interfacial tension can enhance NAPL mobility and increase apparent NAPL thickness.
- Cosolvent effects can lead to increased dissolved benzene concentrations.
- Depletion of electron acceptors can decrease benzene intrinsic biodegradation rates (and potentially result in longer benzene plumes).
- Strongly reducing, methanogenic conditions can cause elevated methane concentrations in groundwater and vapor phases.

D.2.6 References

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Buscheck, T. E., K. T. O'Reilly, G. Koschal, and G. O'Regan. 2001. "Ethanol in Groundwater at a Pacific Northwest Terminal," pp. 55–66 in *Proceedings of the Petroleum Hydrocarbons and Organic Chemicals in Ground Water Conference*, National Ground Water Association/ API, Nov. 14–16, Houston.

Freitas, J. G., B. Fletcher, R. Aravena, and J. F. Barker. 2010. "Methane Production and Isotopic Fingerprinting in Ethanol Fuel Contaminated Sites," *Journal of Ground Water* **48**(6): 844–57.

McDowell, C. J., T. Buscheck, and S. E. Powers. 2003. "Behavior of Gasoline Pools Following a Denatured Ethanol Spill," *Ground Water* **41**(6): 746–57.

D.3 WESTWAY TERMINAL BIODIESEL RELEASE CASE STUDY

Mark Toso, Minnesota Pollution Control Agency

D.3.1 Introduction

In August 2007, approximately 29,000 gal of soy-based neat biodiesel (B100) was released through corrosion holes in the bottom of a large AST located along the Mississippi River in St. Paul, Minnesota. The release amount was based on inventory records. Initial response actions included hand-digging shallow trenches along the tank to recover product and the installation of monitoring wells. Up to 1.87 feet of LNAPL was subsequently found in a monitoring well.

The site is located adjacent to the Mississippi River in the flood plain. Soils consist of fill and sandy flood plain deposits over sand and gravel glacial outwash deposits several hundred feet thick. The fill appears to consist, in part, of bar screen material from the nearby metropolitan wastewater treatment plant. The water table is approximately 12 feet below grade but is highly influenced by the river stage. Groundwater flows toward the river but may be reversed during periods of very high river levels.

D.3.2 Site Investigation

The initial remedial investigation resulted in the installation of six monitoring wells using hollow-stem augers. All wells were constructed using 2-inch PVC casing and 10-foot-long wire-wrapped screens set with the bottom approximately 5 feet below the water table, since the density of B100 is less than that of water. Only one well was found to contain LNAPL.

Additional LNAPL delineation was conducted using the Tar-specific Green Optical Screening Tool (TarGOST®). This is a new laser-induced fluorescence instrument attached to a standard push probe. The B100 exhibited a positive fluorescence response to the laser, and the TarGOST appeared to delineate an LNAPL smear zone of limited aerial extent. Based on these results, an additional monitoring well was installed. LNAPL was not detected in this well, but groundwater was highly impacted.

Currently, there are no analytical methods for directly measuring aqueous-phase biodiesel, but it was thought that some common analytical methods could be used as a surrogate. Groundwater samples were analyzed for VOCs, diesel-range organics (DRO), FAME, sulfates, nitrate/nitrite, ammonia, dissolved iron, carbonaceous biochemical oxygen demand (CBOD), DOC, TOC, dissolved inorganic carbon, and methane.

Low-level VOCs not associated with the site were detected, as was DRO (6.6 mg/L), but the chromatographic profiles did not match typical petroleum product patterns.

Observational, geochemical, and inorganic parameters in groundwater indicate a highly reduced environment with methane levels approaching saturation (up to 19,200 µg/L). Very high levels of ammonia were also found (up to 790 mg/L). It is suspected that the source of ammonia might be from nitrogen-based additives in the B100 or possibly from the wastewater treatment plant–derived fill. High levels of DOC, TOC, and CBOD were also detected.

FAME analysis by gas chromatography/flame ionization detector was for methyl esters of six fatty acids (linoleic, oleic, palmitic, stearic, a-linolenic, and y-linolenic). These were selected because they are thought to represent the primary fatty acids in the original soybean oil. None of these compounds was detected.

D.3.3 Results and Conclusions

Immediately following the release, LNAPL was detected in one monitoring well up to 1.87 feet in thickness, but this essentially disappeared after an initial bail-down test. LNAPL has not been observed at the site since April 2008, which includes the additional monitoring well installed after the TarGOST investigation.

Based on investigation results, the high levels of DOC, TOC and CBOD indicate a high concentration of organic matter in groundwater attributed to the B100 release. This high level of organic loading resulted in an anoxic and methane-generating groundwater plume. The environmental risk of this release is still unknown, but beyond the production of methane and potential organic loading to surface waters, it is believed to be minor.

Biodiesel is practically nontoxic for human oral and dermal exposure; however, the degradation compounds in groundwater has not been well studied. Despite the lack of standards, the groundwater is obviously impacted based on color, odor, and off-gassing, which would prohibit consumption.

Quantification of aqueous-phase contamination will continue primarily using TOC, and methane levels will be monitored until they subside. Closure criteria will likely be based on potential impacts to the Mississippi River using CBOD and ammonia standards.

Additional anticipated work will involve determining the source of ammonia and providing samples to USEPA’s Robert S. Kerr Environmental Research Center for their development of a total biodiesel analysis.

Table D-2. Selected biofuel releases information

Release site	Release date	Release scenario	Approximate release volume (gal)	Analytes	Contaminant of concern	Response
Denatured fuel ethanol						
Pacific Northwest Terminal, Oregon	1999	AST release	19,000	BTEX, TPH, ethanol, methane, MNA parameters, dC13, acetate	Methane	Long-term: MNA, SVE
Maxville, Ontario	2005	Derailment	26,000	BTEX, ethanol, methane	BTEX, ethanol, methane	Short-term: containment and removal of approximately 20,000 gal, soil removal; long-term: in situ bioremediation
Balaton, Minnesota	2004	Derailment	60,000	Ethanol, methane, acetate, VOCs, MNA parameters	BTEX, ethanol, methane	Short-term: soil excavation; long-term: MNA
South Hutchinson, Kansas	2005	Derailment	28,000	BTEX, ethanol, methane, acetate	BTEX, ethanol, methane	Short-term: soil excavation; long-term: MNA
Cambria, Minnesota	2006	Derailment	25,000	Ethanol, methane, acetate, VOCs, MNA parameters	BTEX	Short-term: soil excavation; long-term: MNA
New Brighton, Pennsylvania	2006	Derailment	Unknown[a]	BTEX and ethanol in soil	BTEX, ethanol	Short-term: soil excavation; long-term: not needed
Storrie, California	2007	Derailment	30,000	Ethanol, VOCs, TPH, methane, MNA parameters, major ions	BTEX, ethanol, methane, and TPH	Short-term: fire suppression, surface water diversion, streambed cleaning; long-term: SVE and biosparging, passive vent wells for methane
Rockford, Illinois	2009	Derailment	55,000–75,000[b]	2-butanone, acetaldehyde; acetone; ethanol	BTEX and TPH	Short-term: 1,400 tons soil excavated/ removed; long-term: TBD
Wood River, Nebraska	2009	Loading to railcar	20,000	BTEX, ethanol	BTEX, ethanol	Short-term: dry distillers grain placed on the spill area to absorb the ethanol, soil excavated from area of spill; long-term: TBD
Williams County, Ohio	2010	Derailment	80,000	Groundwater: BTEX; ethanol; surface water: DO, BOD, COD	DO depletion	Short-term: 104,000 gal of ethanol/water mixture pumped out of creeks, aerators in creeks to increase DO levels, very limited soil excavation; long-term: TBD

Release site	**Release date**	**Release scenario**	**Approximate release volume (gal)**	**Analytes**	**Contaminant of concern**	**Response**
E85						
Rice, Minnesota	2008	UST	700	Ethanol, methane, acetate, VOCs, MNA parameters	Ethanol	Short-term: SVE for 6 weeks immediately following release; long-term: MNA.
Hastings, Minnesota	2009	UST	800	Ethanol, methane, acetate, VOCs, MNA parameters	Methane, BTEX	Long-term: MNA
Biodiesel (B100)						
Westway, Minnesota	2007	AST	29,000	DOC, TOC, COD, DRO, VFA, methane, FAME	Methane, COD	Short-term: fluid recovery; long-term: MNA

[a] 485,283 gal released, most assumed to have been consumed by fire immediately following release.

[b] Approximately 360,000 gal consumed by fire immediately following release.

Appendix E

Remediation Technology Descriptions

REMEDIATION TECHNOLOGY DESCRIPTIONS

Technology		**Description**	**References**
In situ treatment	***Biological***		
	Enhanced aerobic biodegradation	Promotes the growth of aerobic microorganisms capable of degrading organic contaminants in water, soil, sludge, and solids through addition of oxygen or air.	USEPA 2004, 2006b
	Enhanced anaerobic biodegradation	Promotes the growth of anaerobic bacteria capable of degrading organic contaminants through addition of alternate terminal electron acceptors such as nitrate, iron, manganese, sulfate, or carbon dioxide.	Anderson and Lovely 2000; Cunningham et al. 2001
	Chemical		
	Chemical oxidation	Injection of a chemical oxidant to destroy targeted contaminants. Common chemical oxidants include permanganate, persulfate, peroxide, and ozone.	USEPA 2004, 2006a, 2006c; ITRC 2005b
	Surfactant enhancement/ cosolvent flushing	Involves the injection and subsequent extraction of surfactants or cosolvents to solubilize and/or mobilize NAPL, coupled with immediate extraction.	USEPA 1995, ITRC 2003b
	Physical		
	Air sparging	Injection of air into groundwater to strip VOCs/semivolatile organic compounds (SVOCs) into the gaseous phase, thereby removing them from groundwater. Usually implemented in conjunction with SVE. Can also enhance aerobic biodegradation of contaminants.	USACE 2008, USEPA 2004, ITRC 2005a
	Physical or hydraulic containment	Construction of a physical (sheet piling, slurry wall) or hydraulic (pumping) subsurface barrier to impede migration of NAPL and/or dissolved contaminants.	USEPA 2005b, ITRC 2005a
	Thermal treatment	The addition of heat to the subsurface to increase the contaminant mass transfer from NAPL to vapor phase by lowering the NAPL viscosity and increasing its vapor pressure. Requires coupling to a SVE system or multiphase extraction system.	ITRC 2000
	Product pumping/ skimming/separation	Physical removal of LNAPL from the top of a water surface.	ITRC 2009
	Soil vapor extraction	Application of a vacuum to the vadose zone to remove VOCs and some SVOCs from soil through volatilization.	USACE 2002; USEPA 1990, 2004
	Containment (capping/ lining)	Placement of clean material or an impermeable barrier over contaminated soil or sediment to prevent adverse harm to human or ecological health.	USEPA 2005a
	Multiphase extraction	Use of a vacuum system or a combination vacuum and pumping system to remove combinations of contaminated groundwater, LNAPL, and vapors from the subsurface. Requires treatment of the extracted material.	USEPA 1997b, 1999, 2004; USACE 1999

Technology		Description	References
Ex situ treatment	***Biological***		
	Bioreactor	An engineered reactor designed to retain a high quantity of biomass to metabolize COCs within a targeted retention time.	USEPA 2005a
	Constructed wetlands	Artificial wetlands constructed to remove various types of contaminants that may be present in water that flows through them.	ITRC 2003a
	Landfarming/ composting/biopiling	Application of contaminated soil onto a surface (landfarming) or mixed with amendments and placed into an engineered enclosure (composting/biopiling) aerated through either engineered venting or periodic turning/mixing of the soil.	USEPA 2004
	Chemical		
	Advanced oxidation	Includes the use of ultraviolet radiation, ozone, and/or hydrogen peroxide to destroy organic contaminants through a treatment system/tank.	USEPA 2005a
	Soil washing	Removal of contaminants sorbed onto soil surfaces using wash water amended with surfactant or chelating agent or through pH adjustment.	USEPA 1997a
	Physical		
	Air stripping	Removal of VOCs/SVOCs in water through volatilization into vapor phase. Aeration methods include packed towers, diffused aeration, tray aeration, and spray aeration.	USEPA 2005a
	Discharge to sewer/ wastewater plant or to a discharge point via NPDES permit	Disposal of extracted ground/surface water to the sanitary sewer/wastewater treatment plants or to a surface water or other discharge point through a National Pollution Discharge Elimination System (NPDES) permit	USEPA 2005a
	Excavation	Removal of contaminated soil by digging, cutting, and/or scooping soil. The excavated material can be either treated on site or transported to an off-site disposal facility.	USEPA 1993
	Thermal	Use of heat to destroy or volatilize organic chemicals sorbed onto excavated soil surfaces.	USEPA 1997a; ITRC 1996, 2000
	Landfilling	Disposal of contaminated material to a permitted off-site treatment and/or disposal facility. Some pretreatment of the contaminated material may be required to meet land disposal restrictions.	USEPA 2004

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Appendix G

Glossary

GLOSSARY

additives—Chemical additions to fuels that provide or enhance various performance features related to the satisfactory operation of engines, including minimizing fuel handling and storage problems.

biobutanol—Alcohol that can be produced conventionally by fermenting the sugars derived from domestically grown crops, such as corn and sugar beets, and other lignocellulosic biomass, such as fast-growing grasses and agricultural waste products. Only three of the four isomers of butanol (1-butanol, 2-butanol, isobutanol) can be produced through fermentation.

biodegradation—Biological degradation, or transformation of a chemical through biological processes.

biodiesel—FAME derived from vegetable oils or animal fats that conforms to ASTM D6751 specifications.

biofuel—For the purposes of this document, the term "biofuel" is applied to liquid fuels and blending components produced from renewable biomass feedstocks used as alternative or supplemental fuels for internal combustion engines.

biofuel blend—As used in this document, a biofuel blend is a biofuel and conventional petroleum-based fuel mixture.

biomass-based diesel—Renewable fuel that is biodiesel as defined in Section 312(f) of the Energy Policy Act of 1992. According to USEPA, biomass-based diesel is a diesel fuel substitute produced from nonpetroleum renewable resources that meets the registration requirements for fuels and fuel additives established by USEPA under Section 7545 of the Clean Air Act.

biomass-to-liquids (BTL)—Renewable gasoline or diesel fuel made through gasification of carbon-based biomass into bio-oil and/or synthesis gas (syngas), followed by conversion of the bio-oil or syngas to the final biofuel and chemically indistinct from petroleum fuels.

biorefineries—Biofuel manufacturing facilities.

BTEX—Acronym for the monoaromatic compounds benzene, toluene, ethylbenzene, and xylenes.

bulk biofuel—Biofuel (such as denatured ethanol or B100) transported in large quantities from biorefineries to bulk depots/supply terminals.

capillary fringe—Zone of soil immediately above the water table in which groundwater seeps up from a water table by capillary action to fill soil pores. The height of the capillary fringe varies according to the sediment grain size.

cellulosic biofuel—Any renewable fuel, not necessarily ethanol, derived from any cellulose, hemicellulose, or lignin, each of which must originate from renewable biomass (40 CFR §80).

cellulosic ethanol—See *lignocellulosic ethanol.*

contaminant of concern (COC)—Material detected at a site which has been determined to adversely affect receptors due to its concentration, distribution, and/or risk.

contaminant of potential concern (COPC)—Material detected at a site which has the potential to adversely affect receptors due to its concentration, distribution, and/or risk.

conventional fuel—Mixture of compounds, called "hydrocarbons," refined from petroleum crude, plus additives to improve its stability, control deposit formation in engines, and modify other characteristics. Conventional gasoline also may contain oxygenates, such as MTBE and ethanol, to meet octane needs (American Petroleum Institute).

denaturant—A material added to fuel ethanol to make it unsuitable for beverage use.

denatured fuel ethanol (DFE)—Ethanol made unfit for beverage use by the addition of 2%–5% hydrocarbon denaturants.

engineering controls—Barriers or systems that control downward migration, infiltration, or seepage of surface runoff and rain or natural leaching/migration of contaminants through the subsurface over time.

ethanol—Ethyl alcohol, or C_2H_5OH.

fatty acid ethyl esters (FAEE)—One of the types of esters known as "biodiesel." These esters are less commonly produced industrially than FAMEs.

fatty acid monoalkyl ester (FAME)—Transesterified oils derived from vegetable oils or animal fats, blended with or used in place of conventional diesel fuels. In many instances, the acronym "FAME" also refers specifically to methylated esters as opposed to the more general monoalkyl esters. The terms "FAME" and "biodiesel" are often used interchangeably because fatty acid methyl esters are the most common biodiesel produced.

fossil fuel—A general term for any hydrocarbon that may be used for fuel: chiefly petroleum, natural gas, and coal (Bates and Jackson 1987).

half-life—Time required for the concentration of a given chemical to become half its initial concentration through either biotic or abiotic processes.

Henry's law constant (H)—Ratio of vapor pressure to aqueous solubility.

institutional controls—Nonengineering measures, such as administrative and/or legal controls, that help to minimize the potential for human exposure to contamination and/or to protect the integrity of a remedy by limiting land or resource use (USEPA definition).

K_{ow}—See *octanol-water partition coefficient*.

lignocellulosic ethanol—Ethanol produced from lignocellulosic biomass (such as switchgrass, *Miscanthus* spp., *Pennisetum* spp., and other high-biomass producing crops) or agricultural residue (corn stalks, sugarcane bagasse, wood wastes, and other sources).

LNAPL—Light, nonaqueous-phase liquid. The free-product, or nondissolved, portion of the contaminants.

methane—CH_4. As a potential fuel, methane can be biologically produced in landfills, manure digesters, etc.; liquefied and/or compressed and used directly in internal combustion engines; or processed into other biofuels and blending agents. As a contaminant, methane presents an explosive hazard when it accumulates in structures, utilities, or other enclosed places.

monitored natural attenuation—Reliance on processes (within the context of a carefully controlled and monitored site cleanup approach) to achieve site-specific remediation objectives within a time frame that is reasonable compared to that offered by other more active methods. The "MNA processes" at work in such a remediation approach include a variety of physical, chemical, or biological processes that, under favorable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil or groundwater. These in situ processes include biodegradation;

dispersion; dilution; sorption; volatilization; radioactive decay; and chemical or biological stabilization, transformation, or destruction of contaminants (USEPA definition).

multimedia evaluation—Methods used to evaluate the potential human health and environmental impacts of contaminants of potential concern in a given fuel or fuel additive.

natural attenuation—Intrinsic capacity of soil and groundwater to reduce the toxicity, mobility, or concentration of contaminants in soil, soil gas, and groundwater. Natural attenuation processes are biodegradation, dilution, adsorption, and abiotic degradation.

natural gasoline—A natural gas liquid with a vapor pressure intermediate between condensate and liquefied petroleum gas. This liquid hydrocarbon mixture is recovered at normal pressure and temperature and is much more volatile and unstable than commercial gasoline ("Oilfield Glossary" definition).

neat biodiesel—100% biodiesel, designated as B100.

neat ethanol—100% ethanol, designated as E100.

octanol-water partition coefficient (K_{ow})—Represents the degree to which an organic substance will preferentially dissolve in water vs. an organic solvent.

oxygenate—An oxygen-containing, ashless compound, such as an alcohol or ether, that can be used as a fuel or fuel supplement.

petroleum—A naturally occurring complex liquid hydrocarbon (a.k.a. "crude oil"), which after distillation and removal of impurities yields a range of combustible fuels, petrochemicals, and lubricants.

ratio blending—Denaturant can be introduced into the nondenatured ethanol in the distribution piping itself prior to either storage or loading onto a bulk transport.

remedial threshold—Risk- or technology-based standard against which contaminant levels are compared to make a determination that (a) risk to public health and welfare and environment are reduced to an acceptable level or (b) cleanup goals have been met. Similar or synonymous terms include cleanup level; cleanup goal; and remedial standard, level, requirement, or goal.

renewable diesel—A broad class of non-ester-based diesel fuels derived from nonpetroleum resources that can be processed in conventional refineries either separately or along with petroleum stocks using hydrotreating methods.

renewable fuels—Renewable energy sources that can be replenished in a short period of time.

risk-based approach—Approach to decision making in investigation and remedial action. Based primarily on evaluations of risks posed to human health and the environment. Other aspects considered in this approach include planned property use, a preference for detoxification and treatment, and minimization of cross-media transfer of contaminants.

risk management—A decision-making process whereby policies or regulations related to political, social, historical, and economic factors are integrated with risk assessment.

source zone—Soil or groundwater contamination origination area.

splash blending—Directly blending nondenatured ethanol and denaturant into the denatured ethanol AST (or UST).

stakeholder—May include people in communities, indigenous peoples, local governments, various nongovernmental organizations, as well as state and federal agencies.

stress corrosion cracking (SCC)—Unexpected sudden failure of normally ductile metals or tough thermoplastics subjected to a constant tensile stress in a corrosive environment.

Tier 1 assessment—Analysis of potential receptor exposure to contaminants at or migrating from the release site comparing COC concentrations measured in site media to defined regulatory screening levels or Tier 1 look-up values based on land use and conservative exposure assumptions. The Tier 1 screening levels are used to identify which, if any, contaminants and environmental media may warrant additional evaluation or remediation to protect human health and the environment.

Tier 2 assessment—Under a tiered risk-based approach, a Tier 2 assessment is a site-specific risk assessment that relies on site-specific information, including land or water use determinations. Site contaminant concentrations are compared against Tier 2 screening levels to determine whether individual contaminants or mixtures of contaminants pose a potential risk.

Tier 3 assessment—Under a tiered risk-based approach, a Tier 3 assessment is based on more complex modeling using site-specific data; may be necessary in cases where remediation to Tier 2 screening levels is not feasible or when site conditions require a unique approach to site investigation and setting remedial goal.

total organic carbon (TOC)—Carbon fraction of the total organic matter of sediment or groundwater. It is the portion of the sample that comes from biologically derived compounds composed primarily of nitrogen, carbon, oxygen, and phosphorous.

vadose zone—The unsaturated zone between the land surface and the water table. Includes the root zone, intermediate zone, and capillary fringe. The pore spaces contain water at less than atmospheric pressure, as well as air and other gases.

volatilization—Conversion of all or part of a liquid or solid to a vapor or gas.

Appendix H

Acronyms

ACRONYMS

AFV	alternative-fuel vehicle
API	American Petroleum Institute
AST	aboveground storage tank
ASTM	ASTM International, formerly American Society for Testing and Materials
ATG	automatic tank gauge
BOD	biochemical oxygen demand
BTEX	benzene, toluene, ethylbenzene, and xylenes
BTL	biomass-to-liquid
CBOD	carbonaceous biochemical oxygen demand
CFR	Code of Federal Regulations
COC	contaminant of concern
COD	chemical oxygen demand
DFE	denatured fuel ethanol
DMF	2,5-dimethyl furan
DMM	dimethoxymethane
DO	dissolved oxygen
DOC	dissolved organic carbon
DOD	U.S. Department of Defense
DOE	U.S. Department of Energy
DRO	diesel-range organic
EC	engineering control
EERC	Ethanol Emergency Response Coalition
EIA	Energy Information Administration
EISA	Energy Independence and Security Act
ETBE	ethyl tertiary-butyl ether
FAEE	fatty acid ethyl ester
FAME	fatty acid monoalkyl ester
FAO	Food and Agriculture Organization
FAPRI	Food and Agricultural Policy Research Institute
FFV	flexible-fuel vehicle
FRP	facility response plan
GAO	Government Accountability Office
GSIM	General Substrate Interaction Module
IC	institutional control
ICE	internal combustion engine
ITRC	Interstate Technology & Regulatory Council
LC	lignocellulosic
LC_{50}	lethal concentration 50
LD_{50}	lethal dose 50
LEL	lower explosive limit
LNAPL	light, nonaqueous-phase liquid
MNA	monitored natural attenuation
MODFLOW	Modular Three-Dimensional Finite Difference Groundwater Flow

MPCA	Minnesota Pollution Control Agency
MTBE	methyl tertiary-butyl ether
NAPL	nonaqueous-phase liquid
NRC	National Research Council
NREL	National Renewable Energy Laboratory
OSHA	Occupational Safety and Health Administration
ppm	parts per million
PVC	polyvinyl chloride
RFS	Renewable Fuel Standard
RT3D	Reactive Transport in Three Dimensions
SCC	stress corrosion cracking
SCM	site conceptual model
SPCC	spill prevention, control, and countermeasure
STP	submersible turbine pump
SVE	soil vapor extraction
SVOC	semivolatile organic compound
syngas	synthetic gas
TOC	total organic carbon
TPH	total petroleum hydrocarbons
UL	Underwriters Laboratories
ULSD	ultralow-sulfur diesel
UNEP	United Nations Environment Programme
USACE	U.S. Army Corps of Engineers
USEPA	U.S. Environmental Protection Agency
UST	underground storage tank
VFA	volatile fatty acid
VOC	volatile organic compound
VRU	vapor recovery unit