

Welcome – Thanks for joining this ITRC Training Class



Biofuels



Biofuels: Release Prevention, Environmental Behavior, and Remediation

Sponsored by: Interstate Technology and Regulatory Council (www.itrcweb.org)
Hosted by: US EPA Clean Up Information Network (www.cluin.org)

Biofuels and biofuel blends are a new category of transportation fuels and are defined as liquid fuels and blending components produced from renewable biomass feedstocks used as alternative or supplemental fuels for internal combustion engines. Their manufacture and consumption are increasing, in part, due to usage mandates and incentives both in the United States and abroad. This expanded use of biofuel and biofuel blends increases the potential frequency of releases due to the increased manufacture, transportation, storage, and distribution. Because biofuels differ from conventional fuels with respect to their physical, chemical, and biological properties, their introduction poses challenges with respect to understanding the potential impacts of releases to the environment. Specifically, once released into the environment, these fuels will exhibit different environmental behaviors as compared to conventional fuels.

This training, which is based on the ITRC's *Biofuels: Release Prevention, Environmental Behavior, and Remediation* (Biofuels-1, 2011), focuses on the differences between biofuels and conventional fuels specific to release scenarios, environmental impacts, characterization, and remediation. The trainers will define the scope of the potential environmental challenges by introducing biofuel fundamentals, regulatory status, and future usage projections. Participants will learn how and when to use the ITRC biofuels guidance document for their projects. They will understand the differences in biofuel and petroleum behavior; become familiar with the biofuel supply chain, potential release scenarios and release prevention; be able to develop an appropriate conceptual model for the investigation and remediation of biofuels and select appropriate investigation and remediation strategies; and be prepared to assess the behavior of new biofuels when alternatives come on the market.

ITRC (Interstate Technology and Regulatory Council) www.itrcweb.org

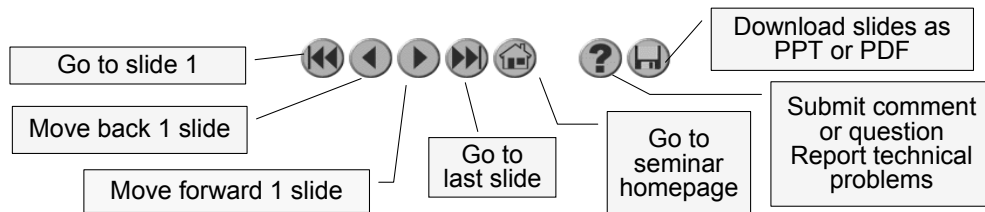
Training Co-Sponsored by: US EPA Technology Innovation and Field Services Division (TIFSD)
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Housekeeping



- ▶ Course time is 2¼ hours
- ▶ Question & Answer breaks
 - Phone - unmute #6 to ask question out loud
 - Simulcast - ? icon at top to type in a question
- ▶ Turn off any pop-up blockers
- ▶ Move through slides
 - Arrow icons at top of screen
 - List of slides on left
- ▶ Feedback form available from last slide – **please** complete before leaving
- ▶ This event is being recorded



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Although I'm sure that some of you are familiar with these rules from previous CLU-IN events, let's run through them quickly for our new participants.




We have started the seminar with all phone lines muted to prevent background noise. Please keep your phone lines muted during the seminar to minimize disruption and background noise. During the question and answer break, press *6 to unmute your lines to ask a question (note: *6 to mute again). Also, please do NOT put this call on hold as this may bring unwanted background music over the lines and interrupt the seminar.

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For a state to be a member of ITRC their environmental agency must designate a State Point of Contact. To find out who your State POC is check out the “contacts” section at www.itrcweb.org. Also, click on “membership” to learn how you can become a member of an ITRC Technical Team.

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Meet the ITRC Trainers



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Mike Maddigan is an environmental chemist with the Pennsylvania Department of Environmental Protection's (PADEP) Land Recycling Program (Act 2) in Harrisburg, PA. Since 2008, Mike has worked at PADEP focusing on human health and ecological risk assessment, vapor intrusion and the Uniform Environmental Covenants Act (UECA). Mike provides technical support for the administration of the Land Recycling Program (PA's voluntary cleanup program) and has performed human health and ecological risk assessment reviews in support of Act 2 remediation projects throughout Pennsylvania. Mike also provides support with the administration of UECA, the development of an environmental covenant registry and the development of PADEP's vapor intrusion guidance. Before joining PADEP, Mike served as an environmental scientist for 11 years with Gannett Fleming, Inc. in Camp Hill, PA. Mike's duties at Gannett Fleming included managing projects for a variety of environmental investigations and site assessment projects along with performing human health and ecological risk assessment reviews and numerous field projects. Mike joined the ITRC Biofuels team in early 2009 and has served as the Fate and Transport Section subteam leader. This is Mike's first experience working with ITRC. Mike earned a bachelor's degree in environmental resource management from Penn State University in 1993 in University Park, Pennsylvania and a master's degree in environmental pollution control in 1998 from Penn State University's Harrisburg, Pennsylvania campus.

Dr. David Tsao is a technical specialist for the Remediation Engineering & Technology group in BP's Remediation Management function at their Naperville, IL office. In response to the Deepwater Horizon incident, David was Strike Team Leader evaluating biological and chemical agents for the long term remediation and restoration of Gulf Coast shorelines and wetlands. Concurrent with these responsibilities, David has been leading BP's evaluation of the potential environmental impacts of current and future biofuels and other fuel oxygenates since 1997. He is responsible for providing general technical support to a broad range of contaminated sites around the globe by developing site conceptual models, selecting appropriate remedies, and optimizing the performance of engineered remediation systems. David specializes in the development, advocacy, and implementation of bioremediation, phytotechnologies, treatment wetlands, ecosystem restoration, and other natural systems technologies. He has actively participated and taught these technologies through the Interstate Technology and Regulatory Council since 2000 (Phytotechnologies-1, Constructed Wetlands, Mitigation Wetlands, Ecological Land Reuse, Phytotechnologies -2). David was also involved on the MTBE and Mining Wastes teams, and is active on the Biofuels, Sediment Remediation, and Biochemical Reactors for Mine-Influenced Waters teams. He is a three-time chemical engineering graduate of Purdue University earning his baccalaureate degree in 1988, Masters in 1990, and Doctorates in 1997. His research theses included plant biotechnology, phytochemical and pharmaceutical production, plant nutrition, and plant biomass production for zero-gravity (NASA) applications.

Dr. Denice Nelson is a Principal Remediation Engineer with ARCADIS-US, and is located in the Minneapolis, Minnesota office. Since 2000 she has focused on the application and optimization of injection-based bioremediation technologies including enhanced reductive dechlorination, anaerobic biological oxidation of petroleum hydrocarbons, metals precipitation, and explosives remediation. Denice's current responsibilities include leading the In Situ Bioremediation Services group within ARCADIS-US which entails providing technical assistance, strategy development, and engineering oversight on several contaminated sites undergoing bioremediation. Through this role, she also manages a team of technical staff whose responsibilities include ensuring high quality and consistent design standards are applied to bioremediation sites throughout the United States. Denice has been an active member of the ITRC Biofuels team since 2010. She became involved with the team through her PhD research where she focused on quantifying the effect of ethanol-based fuel input on the indigenous microbial communities in groundwater, focusing on the effects that a low concentration E85 input had on methane-producing organisms and subsequent methane production, the type and quantity of fermentation products, and the structure of the groundwater aquifer microbial community. Denice routinely presents at national conferences, has taught several short courses on bioremediation, and has also authored several technical publications. Denice earned a bachelor's degree in Civil Engineering in 1998, a master's degree in Environmental Engineering in 2001, and a doctoral degree in Environmental Engineering in 2009 from the University of Minnesota in Minneapolis. Denice is a registered professional engineer in Minnesota.

Mark Toso is a hydrogeologist at the Minnesota Pollution Control Agency in St Paul, MN. Working in the MPCA's remediation division since 1992, his responsibilities include technical oversight of investigation and remediation at petroleum and chemical tank storage facilities, biofuel production facilities, RCRA and superfund sites, and pipeline releases. He also provides technical assistance for the emergency response program. Mark is a registered Professional Geologist in Minnesota and Wisconsin. Prior to his work as a regulator he spent 5 years as a geologist in the private sector. Mark has been a member of the ITRC Biofuels team since its inception. Mark earned a bachelor's of science degree in geology from the University of Wisconsin in Madison in 1985 and since then has completed graduate level coursework within the University of Wisconsin system.

Biofuels and the Environment



- ▶ What are biofuels and why are they important?
- ▶ Are there equipment compatibility issues associated with biofuels?
- ▶ How do biofuel releases impact the environment?
- ▶ Do biofuels behave differently in the environment than petroleum-based fuels?
- ▶ How should biofuels releases be cleaned up?



- Manufacture and usage have increased in recent years in an effort to reduce dependence on fossil fuels.
- The mention of “Biofuels” evokes a variety of questions and no shortage of opinions regarding the “big picture” of energy use, global warming and sustainability. But what about their direct impact on the environment?
- These questions and more will be answered during this training.

What You Will Learn



- ▶ Scope of potential environmental challenges
- ▶ Differences between biofuel and petroleum fuel behavior
- ▶ Biofuel supply chain, potential release scenarios, and release prevention
- ▶ How to develop an appropriate conceptual model for the investigation and remediation of biofuels
- ▶ Appropriate investigation and remediation strategies
- ▶ How to assess the behavior of new biofuels when alternatives come on the market

This training is designed to help you get the most out of the ITRC biofuels document.

Training Roadmap



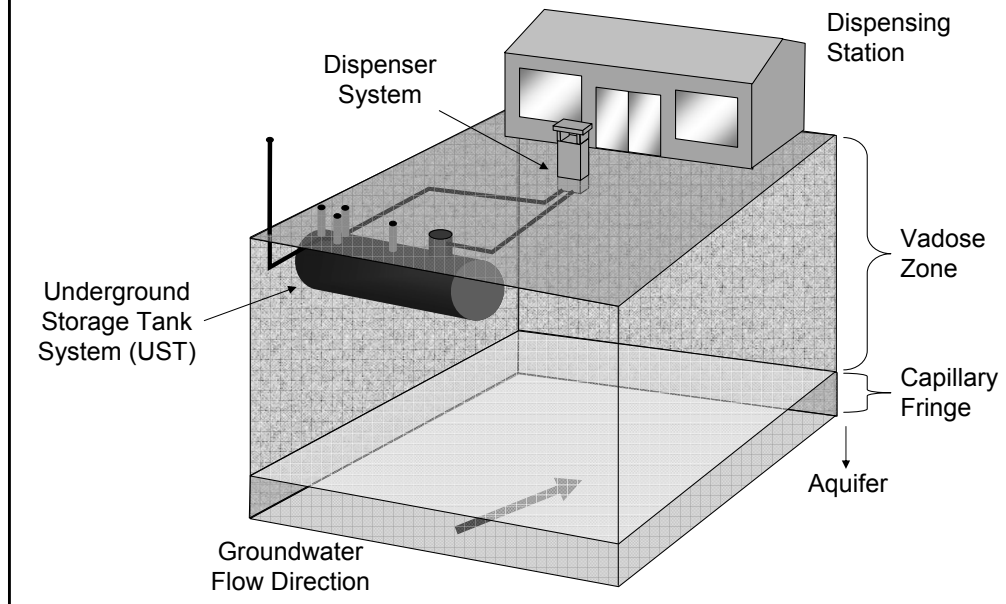
- ▶ Introduction
- ▶ Releases
- ▶ Fate and Transport
- ▶ Q&A Session #1
- ▶ Site Investigation
- ▶ Long-Term Response Strategies
- ▶ Summary
- ▶ Q&A Session #2

★ = hypothetical case study

These "Roadmap" slides are shown when we change topics during the training.

The red star indicates we're discussing the hypothetical case study used to better illustrate specific points.

Our Hypothetical Case Study



This case study will serve as a visual aid throughout the training and will be building upon the case study as we progress through the training.

What Are Biofuels?



- For the purposes of this training, 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.



"Biofuels" is a relatively general term and it is defined differently depending on who you ask. Biofuels can be in the form of solid and gas as well as liquid fuel.

Important Terms



- ▶ Denatured Fuel Ethanol (DFE) – fuel ethanol made unfit for beverage use by the addition of a denaturant; also called E95.
- ▶ FAME (Fatty Acid Mono-alkyl or Methyl Esters) – Transesterified oils derived from vegetable oils or animal fats, blended with or used in place of conventional diesel fuels.
- ▶ Biofuel Blend – Mixture of biofuel and conventional petroleum-based fuel.
- ▶ Conventional Fuel – 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.

See Glossary (Appendix G) for complete list of terms used in the document.
<http://www.itrcweb.org/guidancedocument.asp?TID=76>

In this training, conventional fuels include lower-percentage biofuel fuel blends, such as E10 and B5.

Why be Concerned with Biofuel Releases?



- ▶ Catastrophic impact of large releases
 - Large releases from tank car train derailments
 - Massive fires
- ▶ Smaller releases
 - Slow leaks can go undetected (such as in storage tanks)
 - Large volume - severe environmental impacts



2009 train derailment in Rockford, IL resulting in 435,000-gallon DFE release.



Scorched rail cars after fire in the Rockford, IL release.

Photos from NTSB

Most biofuel releases occur during transport and handling, such as the transport of DFE by train derailments. Smaller releases can be caused by slow leaks can lead to substantial releases over time and can be caused by equipment incompatibility or faulty valves/connections. Sometimes these smaller releases are detected by observing unexpected changes in nearby ongoing petroleum remediation. Appendix D of the document provides a table of selected case studies that provides release scenarios, including volumes and fuel types.

•<http://www.itrcweb.org/guidancedocument.asp?TID=76>

Petroleum vs. Biofuel Releases



- ▶ Behave differently in the environment
 - Site characterization and remediation strategy
 - Safety risks
 - Potential release points
- ▶ For more info on LNAPL training go to <http://www.itrcweb.org>



Biofuel releases behave differently than petroleum in the environment

Site characterization and remediation strategy

Safety risks

Potential release points

Objectives of site characterization and remediation strategies for biofuel releases may be different from petroleum releases.

Methane generation at biofuel spill locations can pose a safety risk during site investigation activities.

Most petroleum is transported via pipeline while biofuels are transported via truck or rail. Increased handling and transfer of biofuels poses a higher potential frequency of releases.

ITRC LNAPL Training and Documents

ITRC's 2-day classroom training on LNAPLs, **Light Nonaqueous-Phase Liquids: Science, Management, and Technology**, will enable you to develop and apply an LNAPL Conceptual Site Model (LCSM), understand and assess LNAPL subsurface behavior, develop and justify LNAPL remedial objectives including maximum extent practicable considerations, select appropriate LNAPL remedial technologies and measure progress, and use ITRC's science-based LNAPL guidance to efficiently move sites to closure. More information is available from <http://www.itrcweb.org/crt.asp>

ITRC also offers Internet-based training on LNAPLs. More information and registration from <http://www.itrcweb.org/ibt.asp>

LNAPL Part 1: An Improved Understanding of LNAPL Behavior in the Subsurface

LNAPL Part 2: LNAPL Characterization and Recoverability

LNAPL Part 3: Evaluating LNAPL Remedial Technologies for Achieving Project Goals

ITRC LNAPL team products are available from <http://www.itrcweb.org/LNAPLs>

Federal Renewable Fuel Mandates



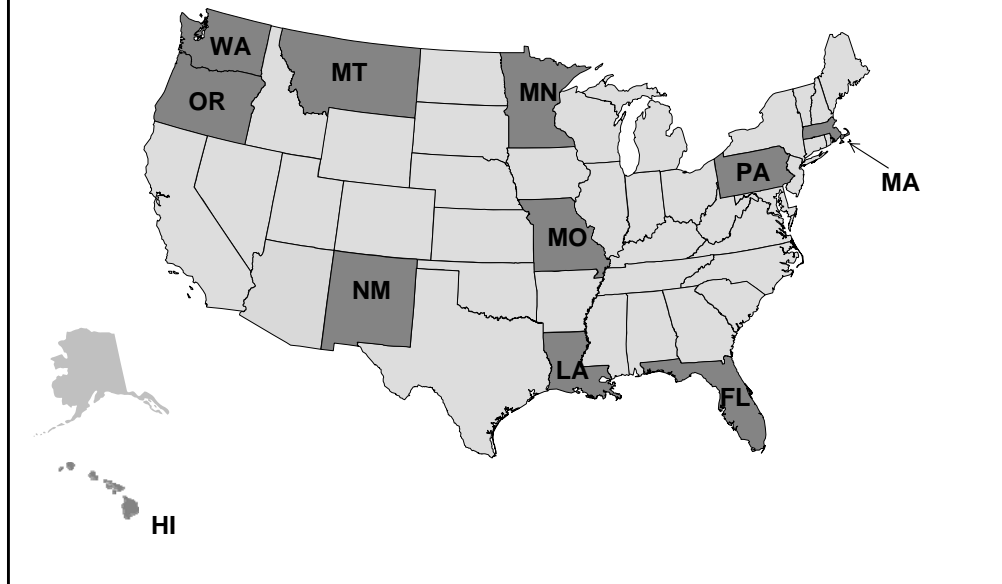
- ▶ Energy Policy Act of 2005
 - First Renewable Fuel Standard (RFS) program
 - Required 7.5 billion gallons of renewable fuel to be blended into gasoline by 2012
- ▶ Energy Independence & Security Act of 2007
 - Renewable fuel requirements increased
9 billion gallons (2008) ➡ 36 billion gallons (2022)
- ▶ Additional alternative fuel objectives for federal Alternative Fuel Vehicle (AFV) fleets

Biofuel production and use goals increase from 7.5 billion gallons in 2012 (EPAAct) to 36 billion gallons in 2022 (EISA)

These biofuel use and production mandates will likely lead to an increase in releases.

State Renewable Fuel Mandates

Table 1-3



As of April 2011, eleven U.S. states have passed mandates on the use of biofuels or biofuel blends. (Table 1-3 in document).

- Florida*
- Hawaii
- Louisiana
- Massachusetts*
- Minnesota
- Missouri
- Montana
- New Mexico
- Oregon
- Pennsylvania
- Washington

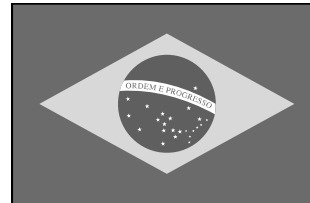
* As of June 2010, Massachusetts has suspended the formal requirement on grounds of unreasonable cost. As of July 1, 2013, Florida has repealed the state's renewable fuel standard on the grounds that it is a duplication of the Federal Renewable Fuel Standard and that it is inconsistent with efforts to reduce the regulatory burden on Floridians.

Some states have one or more of the following mandates:

- Producer or retailer incentive programs
- Labeling requirements
- State fleet fuel purchase/use requirements

International Mandates

- ▶ **European Union**
 - Directive 2003/30/EC
 - Promotes biofuels use in transportation sector
 - Proposes non-mandatory biofuels use targets
- ▶ **Brazil**
 - Has required the use of biofuels since 1976

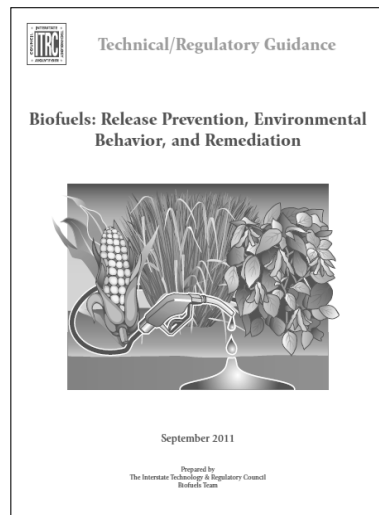


International mandates – EU and Brazil

16 **ITRC Guidance: *Biofuels: Release Prevention, Environmental Behavior, and Remediation***



1. Biofuel basics
2. Release prevention and response planning
3. Fate & transport (F&T) of biofuels in the environment
4. Characterizing release sites
5. Long-term response strategies
6. Stakeholder concerns



ITRC document *Biofuels: Release Prevention, Environmental Behavior, and Remediation*. Released in September 2011.

Stakeholder concerns are addressed in the document in Section 6. Stakeholder concerns are associated with the prevention, environmental behavior, and remediation of accidental biofuel releases and generally depend on the location and timing of the incident, emergency response, and long-term management and cleanup. In this training, stakeholder concerns are incorporated into each section of the training. For example, fish kills as described in the fate and transport and site investigation section are a significant potential stakeholder concern. Methane generation and the explosive hazard it presents is another significant concern discussed throughout the training.

What is Not Covered



- ▶ Vegetable oils, recycled greases, and fuels indistinguishable from petroleum-based fuels
- ▶ Air quality
- ▶ Sustainability
- ▶ Detailed information on manufacturing processes
- ▶ End-user considerations
- ▶ Biofuel policies
- ▶ Fuel additives



Not an “all encompassing” biofuels document. It focuses mainly on ethanol and biodiesel, and biobutanol in some places due to a lack of information available regarding other emerging biofuels.

Multimedia approach of document can be applied to emerging biofuels not discussed in this document.

Bio-butanol is mentioned in document but not in detail.

Use multi-media approach and/or technology tables in document to evaluate specific fuel additives and emerging biofuels.

Applying the ITRC Document Before a Release



- ▶ Release prevention
 - Ensure materials compatibility
 - Update best management practices
- ▶ Release response planning
 - Fire/explosion threats
 - Rapid containment



Prevention: Can prevent chronic releases (slow leaks) caused by high corrosion rates and high permeation rates of incompatible materials. Updating BMPs can help prevent releases from inadequate equipment inspection and/or maintenance.

Response: Potential for catastrophic releases necessitate up to date emergency response procedures including rapid containment methods (e.g. prevent releases to surface water bodies).

Applying the ITRC Document After a Release



- ▶ Site characterization, sampling, F&T modeling
 - Physical, chemical, and biological properties
 - Developing Site Conceptual Model (SCM)
- ▶ Long-term responses
 - Determining remediation strategy
 - Assessing hazards and risks
- ▶ Stakeholder concerns
 - Location of incident
 - Timing of response
- ▶ Emerging biofuels
 - Multi-media evaluation process



Site Characterization, Sampling, F&T Modeling: Biofuel physical, chemical and biological properties differ from conventional fuels so they will behave differently in the environment. Examples of different considerations in Site Conceptual Model (SCM) include remobilization of pre-existing contamination and potential for methane production.

Long-Term Response: Remediation strategies will depend on physical, chemical and biological characteristics of biofuel released and site characteristics. Hazards and risks will be different from conventional fuel releases.

Stakeholder Concerns: As with any release, need to consider the sensitiveness of the location of the incident and the timing of the response. Remediators and regulators also need to be sensitive to the potential impact of any lingering or residual contamination on stakeholders.

Emerging Biofuels: Multi-media approach evaluates the potential HH and environmental impacts of a release of a given fuel or fuel additive and assesses how contaminants may interact with the flora, fauna, and natural resources within different environmental media. This approach can be used with emerging fuels not addressed in this document.

Ethanol Fuel Blends (Table 1-1)



Fuel	Description	ASTM Standard
E85	A commercial trade name representing an alternative fuel consisting of 70%–85% DFE by volume as defined in the EPAct of 1992	No adopted 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 standard
E10	Gasoline with up to 10% DFE by volume	D4814 (standard for gasoline)

“Neat Ethanol” (E100) is non denatured ethanol

ASTM has set the naming standard for biofuels.

The “E” number is generally the percentage of ethanol in the fuel mixture.

Neat ethanol (E100) is ethanol with no denaturant.

Biodiesel and Biodiesel Blends (Table 1-2)



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% to 99% biodiesel	No standard adopted
>B5 to B20	A blend of petroleum-distillate and biodiesel fuel that contains between 6% to 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 standard)

"Neat Biodiesel" is biodiesel not blended with petroleum-based diesel and is designated as "B100"

ASTM has set the naming standard for biofuels.

The "B" number is the percentage of biodiesel in the fuel mixture.

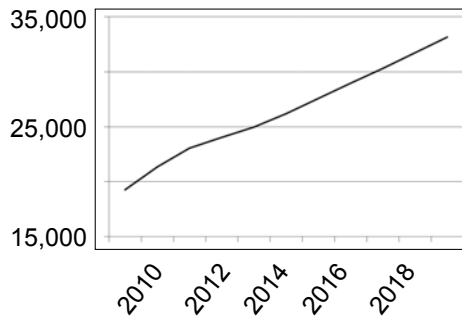
Neat biodiesel (B100) is biodiesel with no petroleum denaturant.

Biodiesel is defined as mono-alkyl, but often referred to as methyl esters interchangeably

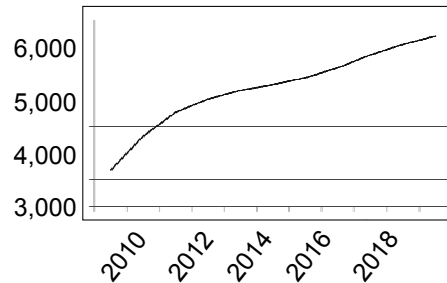
Biofuel Production Projections (Figures 1-1 and 1-2)



**World Ethanol Production Projections
(millions of gallons)**



**World Biodiesel Production Projections
(millions of gallons)**



Historic biofuel use in US

- Ethanol: 277% increase in US consumption from 2004 to 2010 [3.5 billion gallons in 2004 to 13.2 billion gallons in 2010 (EIA 2010)].
- Biodiesel: 722% increase in US consumption from 2004 to 2010 [27 million gallons in 2004 to 222 million gallons in 2010 (EIA 2010)].

Projected biofuel use worldwide

- Ethanol \approx 55% increase in worldwide consumption projected from 2010 to 2018 [22 billion gallons in 2010 to 34 billion gallons by 2018 (FAPRI 2009)].
- Biodiesel \approx 31% increase in worldwide consumption project from 2010 to 2018 [4.2 billion gallons in 2010 to 5.5 billion gallons by 2018 (FAPRI 2009)].

Opportunities to Use this Document in Your State



- ▶ Connection to your state vapor intrusion regulations or guidance
 - Fate & transport modeling
 - Indoor air modeling
- ▶ Equipment compatibility requirements
 - Storage tank programs
 - Bulk transport requirements
- ▶ Facility response plans
 - Emergency response
 - Spill Prevention Control and Countermeasures (SPCC) plans

The biofuels document can be used in concurrence with ITRC's *"Vapor Intrusion Pathway: A Practical Guide"* and *"Vapor Intrusion Pathway: Investigative Approaches for Typical Scenarios"* both published in January 2007 and available at <http://www.itrcweb.org/guidancedocument.asp?TID=49>.

Training Roadmap



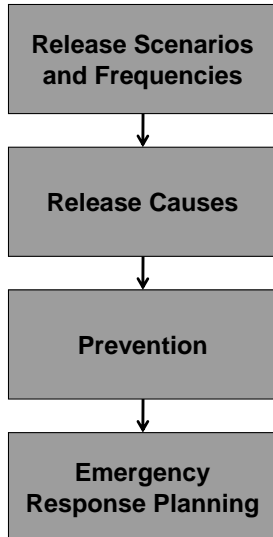
- ▶ Introduction
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- ▶ Q&A Session #2

No associated notes.

Biofuel Releases (Section 2)



This section will cover



Evaluated based on the differences between petroleum and biofuel supply chains



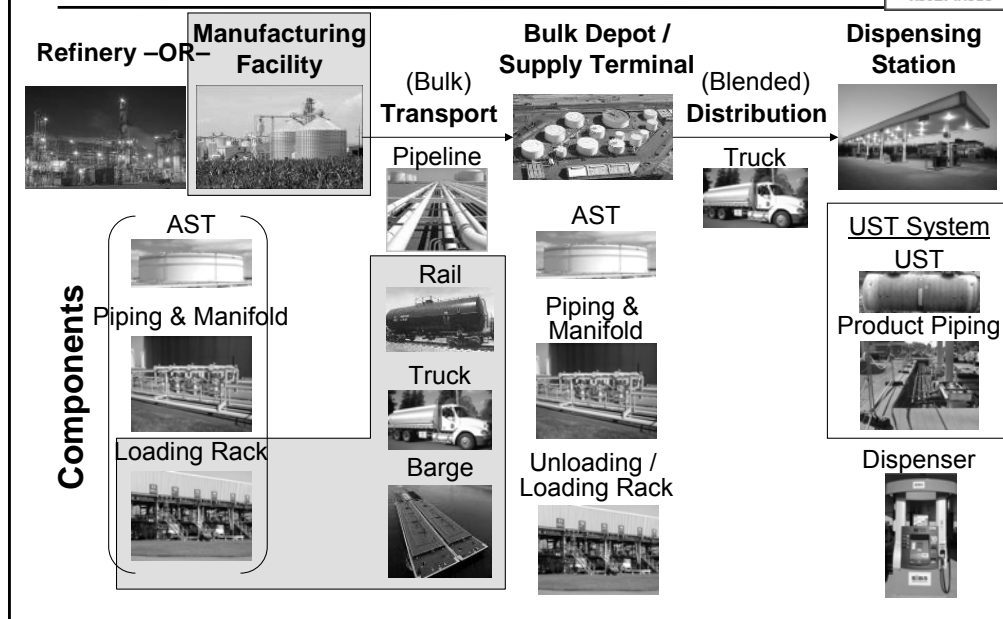
Section includes information collected on:

Release Scenarios and Frequencies - based on an analysis of statistics from NTSB, DOT, petroleum industry

Release Causes and Prevention - based on incident root cause analyses and inspection best management practices

Emergency Response Planning - based on petroleum industry response plans, SPCC, fire fighting associations

Petroleum vs. Biofuel Supply Chains (Combined Figures 2-1 and 2-2)



This combined figure is meant to represent generalized supply chains for petroleum and biofuels. The current (2010 data) production moving through these chains per day:

0.93 million barrels fuel ethanol vs. 4.9 million barrels gasoline
0.17 million barrels biodiesel vs. 4.1 million barrels diesel

The major differences from petroleum supply chain: type of manufacturing facility and modes of transport to bulk depot/supply terminal. Everything from the bulk depot/supply terminal and downstream are the same for both supply chains.

There are exceptions to these generalizations such as many petroleum refineries also contain loading racks to transport bulk petroleum via barges. Similarly, 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.

Release Scenarios and Incidents (Section 2.1)



Transport



Pipeline



Volume and Incident Frequencies (Table 2-1):

Potential Volume	Incident Frequency
Railcars: ~25,000 to 30,000 gallons per railcar; unit trains 70-100 cars	2,000 derailments per year (severity not specified)
Tanker trucks: ~8,000 to 10,000 gallons per truck	1,000 road accidents per year (1 in 25,000 deliveries)
Tank barges: ~420,000 to 630,000 gallons per barge typical	2.16 gallons spilled per 1 million gallons moved

- If all bulk gasoline and diesel currently transported was used to produce E10 and B5, then bulk biofuels transport needs would be:

- 1,250 tanker trucks,
- 415 railcars, or **PER DAY**
- 20 tank barges

Distribution Truck



Section 2.1 tries to paint a picture of how frequently biofuel releases may occur and how much volume can potentially be released with each incident. It also attempts to provide projections of future frequencies of releases depending on the point in the supply chain. Increased production, transport, storage, distribution, and dispensing through mandates implies an increased potential for, or frequency of, releases.

Table 2-1 summarizes the typical release scenarios based on the point in the supply chain...Manufacturing Facility, Bulk Transportation, Bulk Depot/Supply Terminal, Distribution, Dispensing Station. Furthermore, Table 2-1 compares potential volumes that may be released to the throughput at the point in the supply chain (i.e. number of gallons spilled vs. total number of gallons moved at that point in the supply chain). Alternatively, the frequency of incidents resulting in a release at that point in the supply chain are provided from tracking statistics.

The projection on tanker truck, railcar or barges needed for bulk biofuel transport based on 2.2 million barrels of bulk gasoline and 1.0 million barrels of bulk diesel currently sent through pipeline and the calculations below.

For ethanol:

- 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 needed to blend all bulk gasoline to make E10.
- 0.24 million barrels = 10.26 million gallons of bulk ethanol.
- To transport 10.26 million gallons of bulk ethanol, 1,026 tanker trucks required (assuming 10,000 gallon capacity per truck). Similarly, this number becomes 342 railcars (30,000 gallon capacity) or 16 barges (630,000 gallon capacity).

For biodiesel:

- 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 needed.
- 0.053 million barrels = 2.21 million gallons of bulk biodiesel.
- To transport 2.21 million gallons of bulk biodiesel, 221 tanker trucks required (assuming 10,000 gallon capacity per truck). Similarly, this number becomes 73 railcars (30,000 gallon capacity) or 4 barges (630,000 gallon capacity).

Total transport needs for bulk biofuel (ethanol + diesel) if all bulk gasoline and diesel blended to make E10 and B5:

- 1,026 (for ethanol transport) + 221 (biodiesel transport) = 1,247 tanker trucks needed total (rounded to 1,250)
- 342 (for ethanol transport) + 73 (for biodiesel transport) = 415 railcars needed total
- 16 (for ethanol transport) + 4 (for biodiesel transport) = 20 barges needed total

Release Causes (Section 2.2)



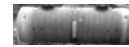
Leak Detection Issues, Release Causes (Table 2-2):

Dispensing Station



Equipment	Detection	Causes
Underground Storage Tank (UST) System	Small volume or chronic releases may not be detected if commercial leak detection equipment is incompatible	Incompatible materials; solvent nature of biofuels scouring sediment, sludge, rust, and scale built up in tank previously storing conventional fuels
	Acute, large volume releases detected through automated volume reconciliation accounting	
Dispenser System	Small volume or chronic releases detected through standard inspections	Incompatible materials; filters plugging due to insufficient rate of changeouts

UST System



Product Piping



Dispenser



Section 2.2 delves into the root cause analyses conducted on known incidents of biofuel releases. Appendix D contains additional information on various case studies.

Table 2-2 discusses the common causes of releases occurring with various pieces of equipment used throughout the supply chain and how the releases are commonly detected. In addition to UST and Dispenser Systems, Table 2-2 also contains subsections for ASTs, Piping & Manifold, Loading/Unloading Racks, Transports

Items relevant to our case study are highlighted.

Selected Biofuel Release Information (Table D-2, Appendix D)



Site	Fuel	Volume in gallons (Section 2.1)	Causes (Section 2.2)
PNW Terminal, OR	DFE	19,000	AST release
Maxville, Ontario	DFE	26,000	Derailment
Balaton, MN		60,000	
South Hutchinson, KS		28,000	
Cambria, MN		25,000	
Storrie, CA		30,000	
Rockford, IL		55,000 – 75,000	
Williams County, OH		80,000	
Wood River, NE	DFE	20,000	Loading railcar
Rice, MN	E85	700	UST release
Hastings, MN		800	
St. Paul, MN	Biodiesel	29,000	AST release

See Appendix D: fate and transport evaluation (Section 3), analytes investigated (Section 4), and response activities conducted (Section 5)

Appendix D, Table D-2 contains information on the specific site where the biofuel release occurred, release date, type of biofuel, volume, cause of the release, analytes investigated, contaminants driving risk, and response activities conducted.

Furthermore, Appendix D contains full write ups on several select case studies, 2 case studies of DFE (E95) releases from derailments and one case study of a biodiesel (B100) release from an AST.

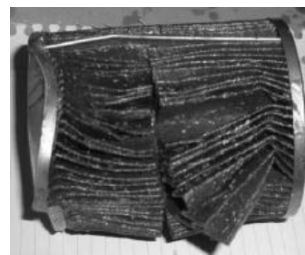
Release Prevention (Section 2.3)



- ▶ Compatible materials and equipment
 - Plastics, polymers, and elastomers
 - Metal components and solders
 - Commercial leak detection equipment
- ▶ Management practices
 - Changing out filters more frequently can prevent clogging issues
 - Proper Operations & Maintenance and frequency on leak detection equipment prevents undetected releases
- ★ ▶ Appendix B (checklist) provides guidance on compatibility of UST systems for biofuels



ITRC, Biofuels-1, Figure 2-7



ITRC, Biofuels-1, Figure 2-5

Several published guidance documents provide ethanol and biodiesel material compatibility information (listed in ITRC BIOFUELS-1)

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 thermo and thermoset plastics may degrade in high—blend alcohol fuels
- B100 is not compatible with certain elastomers, metals, and plastics; generally biodiesel blends of 20% or lower have a much smaller effect on these materials (NREL 2009).

Pictures are figures provided in the document. 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. Figure 2-5. Blocked filter caused by biodiesel. 30 micron diesel pump filter element covered in gel like material. Filter changeout frequency was increased to weekly. *Source:* BP.

General changes in management practices needed for biofuels 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

See also the example tank conversion checklist (Appendix B)

Emergency Response Planning (Section 2.4)



- ▶ Applicable plans
 - Spill Prevention Control and Countermeasures (SPCC) regulations (40 CFR 112)
 - Facility Response Plans (FRP)
- ▶ Additional Emergency Response considerations
 - Common fire-fighting foams – less effective
 - Appropriate foams – less available
 - Sorbent booms – miscibility, sorption, etc.
 - Impacts to sensitive receptors – oxygen demand, biodegradability, etc.

SPCC regulations (40 CFR 112) apply for biofuels for aboveground aggregate storage capacity for oil or oil products (including biodiesel and E85) greater than 1,320 gallons

Facility Response Plan (FRP) requirements apply depending on storage capacity total oil storage capacity greater than 1 million gallons

Additional Emergency Response considerations

Common fire-fighting foams are less effective on alcohol-based fuels; appropriate foams are less available or not stocked in large quantities

Sorbent booms should be evaluated with respect to biofuels physical and chemical properties (e.g. miscibility, sorption, etc.)

Impacts to sensitive receptors are different due to biological properties (e.g. oxygen demand, biodegradability)

Our Case Study: The Release

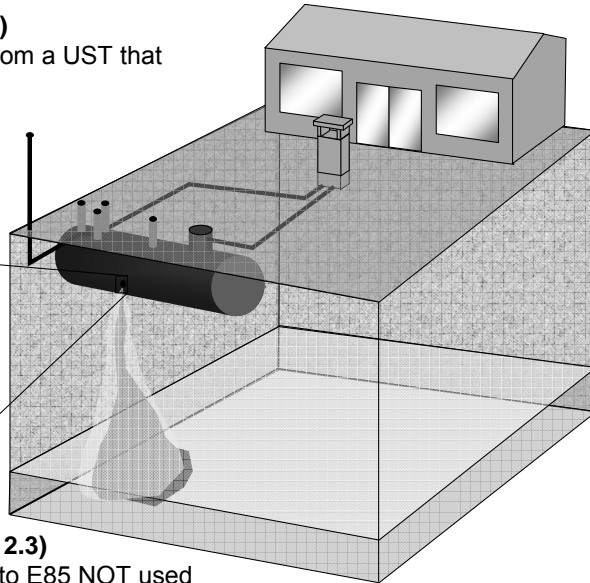
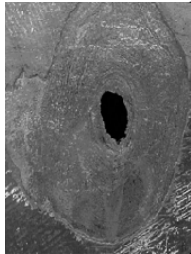


Release Volume (Section 2.1)

10,000 gallons E85 released from a UST that was switched from storing E10

Release Cause (Section 2.2)

E85 scoured the sludge, rust, sediment, & scale



Release Prevention (Section 2.3)

Guidance on converting tanks to E85 NOT used

160,000 dispensing stations in the U.S. (2009)

Average 120,000 gallons per month volume sales from one station (2009)

Shifting product slate: information on current stations dispensing B20 and E85 updated at:
http://www.afdc.energy.gov/afdc/fuels/stations_counts.html

We will build our case study during this presentation so that it contains the same information as the case studies provided in Appendix D.

Biofuel Releases Summary (Section 2)



- ▶ Biofuel releases will occur somewhere along the supply chain
- ▶ Current case studies (Appendix D) indicate they occur more often in association with bulk transport or during storage
- ▶ Frequency is likely to increase as storage and handling increases
- ▶ Root causes are often materials compatibility and management practices associated with equipment
- ▶ Can be addressed to prevent releases such as using the tank conversion checklist (Appendix B)
- ▶ Resources for emergency response preparedness are also available

No associated notes.

Training Roadmap

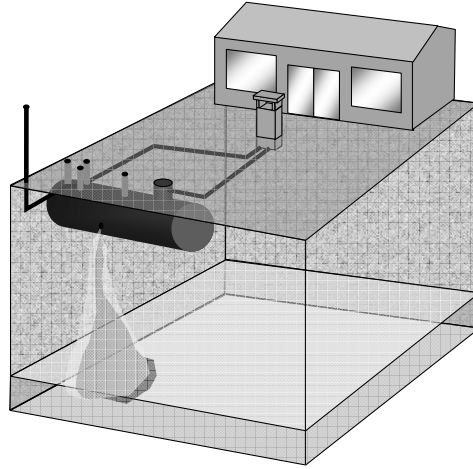
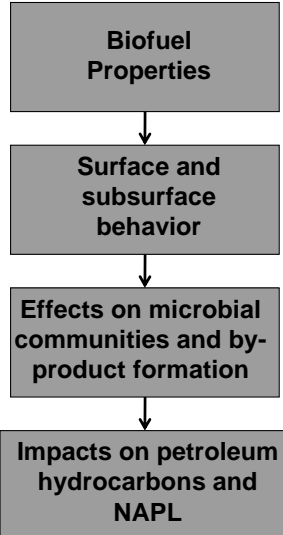


- ▶ Introduction
- ▶ Releases
- ▶ Fate and Transport
- ▶ Q&A Session #1
- ▶ Site Investigation
- ▶ Long-Term Response Strategies
- ▶ Summary
- ▶ Q&A Session #2

No associated notes.

Fate and Transport (Section 3)

This section will cover:



Use of the hypothetical case study to help illustrate key points

No associated notes.

Properties of Selected Fuel Components (Table 3-1)



	Solubility (mg/L)	Henry's Law Constant (unitless)	Vapor Pressure (mm Hg)	Biodegradation Potential	Implications
Ethanol	Infinite	2.1E-4 to 2.6E-4	59	Aerobic: hours to days Anaerobic: days to weeks	Readily partitions to water and dilutes according to availability. Rapidly biodegradable
Benzene	1,800	0.22	75	Aerobic: days to months Anaerobic: years	Readily partitions to vapor phase from NAPL and from water
<p>► Summary of some of the more pertinent properties of biofuels and reference compounds (benzene and diesel)</p> <ul style="list-style-type: none"> • Provides a generalized summary of implications relating to these properties • Expanded property table available in Appendix C of the document <p>► Table excerpts provided for the E85 case study ★</p>					

Expanded property table available in Appendix C of the document

Behavior in Surface Spills (Section 3.5.1 and 3.5.2)



- ▶ Initial fate can be controlled by
 - Vaporization
 - Ignition and consumption by fire
 - Surface drainage
 - Surface water dilution



- ▶ Immediate short-term impacts on surface water biota
 - Aquatic species toxicity (Section 1.6)
 - Ethanol and isobutanol: aquatic toxicity values range from 1,000 mg/L to > 14,000 mg/L
 - Biodiesel: numerical values currently not available (area of research)
 - Dissolved oxygen depletion
 - Can result in detrimental impacts to aquatic life (i.e. fish kills)

No associated notes.

Behavior in the Subsurface: Petroleum Hydrocarbons (Figure 3-1)



ITRC LNAPL guidance and training available for additional information on LNAPL distribution – www.itrcweb.org/LNAPLs

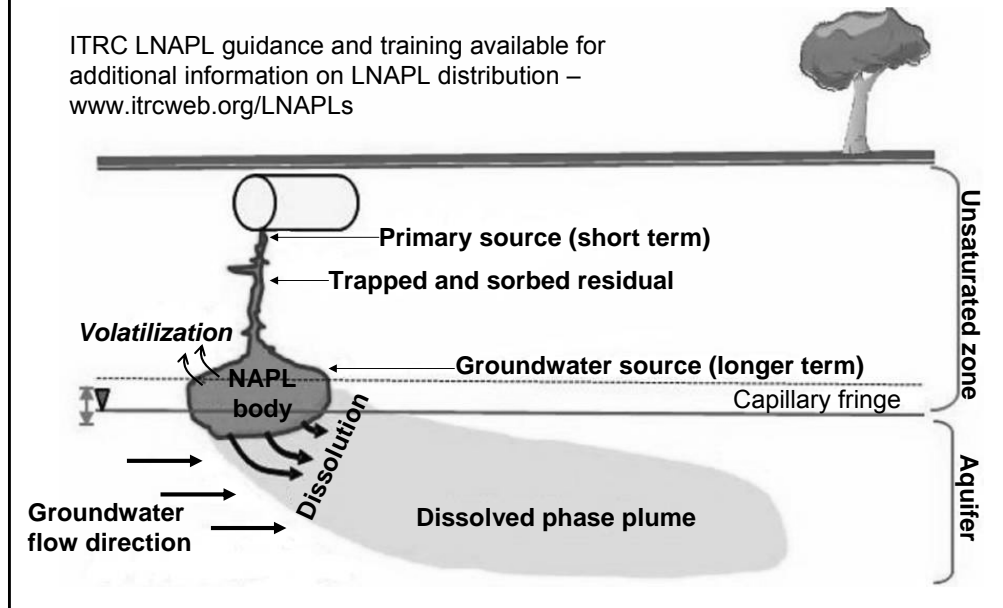
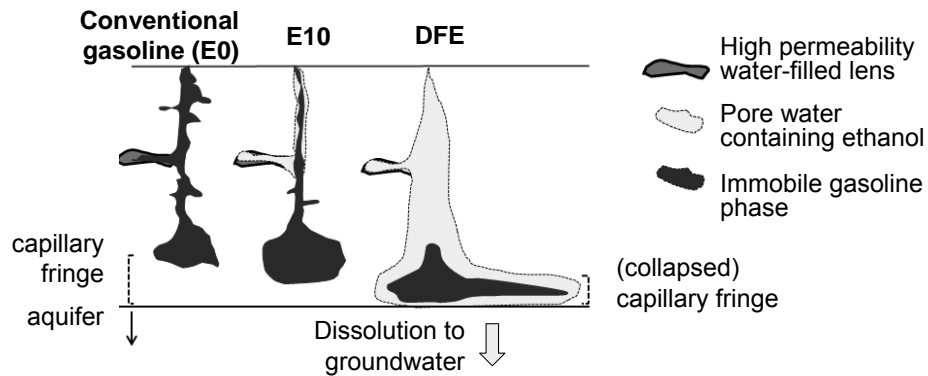


Figure 3-1 is an illustrative conceptual model of a UST release showing the influences on fuel and fuel constituent fate and transport in soil and groundwater. For more information on this topic, the ITRC has LNAPL guidance and training available (see www.itrcweb.org/LNAPLs).

Behavior in the Subsurface: Ethanol Blends (Figure 3-5)



- Ethanol blends behave differently than low solubility biofuels or petroleum compounds

- ★
 - Ethanol fraction will partition into soil moisture present within the vadose zone and capillary fringe
 - Once in contact with groundwater, will migrate
 - Likelihood of ethanol reaching groundwater is dependent on release scenario (large spills more likely to reach water table)

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).

Potential Media Impacts by Equipment Type (Table 3-2)



- ▶ Table objective: provide information regarding potential release points, release volumes and media that can be affected by release
- ▶ Example for E85 case study (UST release) ★

Equipment Type	Potential Media Impacts
Underground storage tank systems (Section 2.2.5) <ul style="list-style-type: none"> • Dispensing stations • May be present at manufacturing facilities and bulk depots/supply terminals 	<ul style="list-style-type: none"> • Surrounding backfill and soil in the UST “pit” • 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 • If groundwater is impacted, cosolvency issues may be present if historic petroleum releases have occurred at the same location

Example of information presented in Table 3-2 in the document. In this example, the longer version of potential media impacts as provided in Table 3-2 are as follows: 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.

Biochemical Oxygen Demand (Section 3.3.2.2)

- ▶ Release of biofuel into an aqueous environment will result in rapid consumption of dissolved oxygen (DO)
- ▶ In groundwater, rapid biodegradation will induce anaerobic conditions



Dead paddlefish resulting from a release of Wild Turkey Bourbon

Release of biofuel into an aqueous environment will result in rapid consumption of oxygen; this is particularly detrimental in surface water. The Impact on dissolved oxygen (DO) in surface water is strongly dependent on receiving water. This can be particularly detrimental in surface waters where low oxygen levels can adversely affect biological communities.

In groundwater, rapid biodegradation will induce anaerobic conditions. Once oxygen is depleted, alternate electron acceptors such as nitrate, ferric iron, sulfate and carbon dioxide will be utilized by anaerobic organisms during the breakdown of the biofuel.

Biofuel Biodegradation (Figure 3-2)

► Biofuels more readily biodegradable

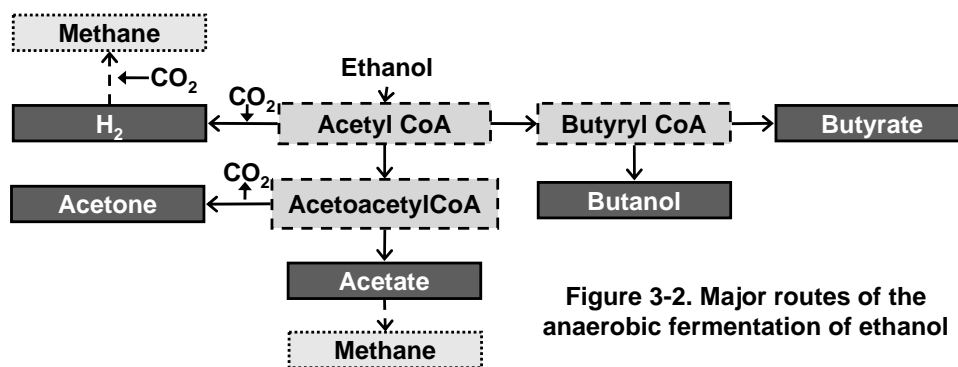


Figure 3-2. Major routes of the anaerobic fermentation of ethanol

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 that can generate several different metabolites such as volatile fatty acids (VFAs), which include acetate, propionate, butyrate and lactate. As an example, Figure 3-2 is a schematic showing the 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.

In the figure, the major routes of the anaerobic fermentation of ethanol are shown. 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, M. T., and J. M. Martinko. 2006. *Brock Biology of Microorganisms*, 11th ed. Upper Saddle River, N.J.: Pearson/Prentice Hall.

Factors Affecting Biodegradation



- ▶ Inhibition of biological degradation at high concentrations (6% - 10% ethanol)
- ▶ Rate affected by
 - Available electron acceptors
 - Nutrients
 - pH (optimal = 6-8)
 - Production of volatile fatty acids during metabolism can lower pH

Once biofuel concentrations are diluted to below inhibitory levels, they are metabolized, although factors such as nutrient limitation, available electron acceptors, and thermodynamic inhibition resulting from the buildup of some metabolites can affect the efficiency and subsequent biological decay rate of biofuels. These effects cause delays in methane generation to significant levels.

Depending on the buffering capacity of the aquifer, production of volatile fatty acids can potentially lower the pH. Microbial activity can become inhibited when the pH is <6.

Methane Hazards (Figure 3-4)



- Methane is a flammable gas



- ★ • Lower explosive limit (LEL) = 5% in atmosphere
• Upper explosive limit (UEL) = 15% in atmosphere
- LEL equivalent concentration in groundwater
- 1 - 2 mg/L
 - Dependent on temperature

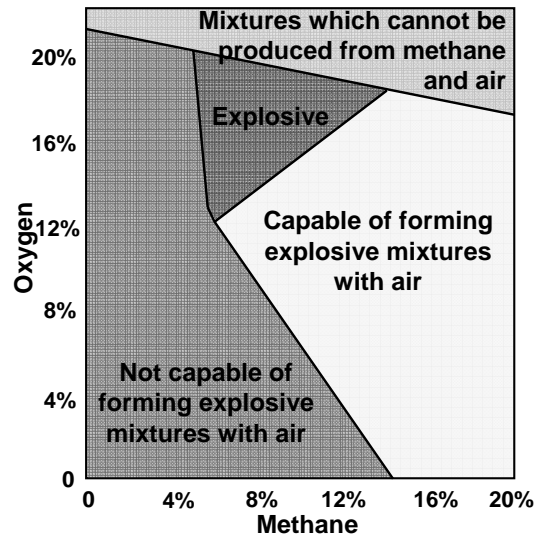


Figure source:
30 CFR 57.22003

Relationship Between Quantitative Composition
and Explosivity of Mixtures of Methane and Air

Methane LEL equivalent concentration in groundwater (based on Henry's Law) is between 1 and 2 mg/L (dependent on temperature). The methane solubility limit is approximately 25 mg/L (also temperature dependent).

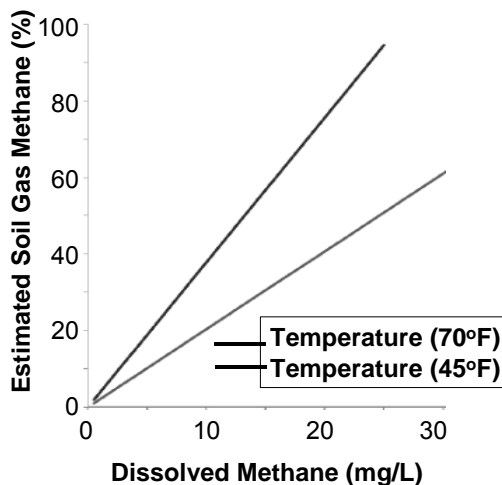
The OSHA action level for methane in the atmosphere is 0.5%, or 50,000 ppm (10% of the LEL) .

The lower explosive limit (LEL) for gasoline is 1.4% and the upper explosive limit (UEL) is 7.6%.

Generation of Methane (Figure 3-3)



- ▶ Methanogens utilize acetate and hydrogen
 - Partitioning between dissolved and gaseous methane concentrations
 - Dissolved methane concentration dependent on groundwater temps
- ▶ Delays (months to years) in methane production have been observed in both lab and field studies
- ▶ Methane soil gas may undergo attenuation in the vadose zone



The same factors affecting biofuel degradation (nutrient limitation, available electron acceptors, and thermodynamic inhibition resulting from the buildup of some metabolites) can also delay the onset of significant methane production. The Cambria Case Study (Appendix D) describes delayed methane production at a large release site in Minnesota. Methane will also be generated at sites with conventional fuel spills (including E10), but the rate and extent of methane production is typically much lower than that of biofuel sites.

A recent laboratory study was released evaluating the role of methanotrophs (aerobic organisms that consume methane) in the attenuation of methane soil gas in the vadose zone. The study indicated that even though dissolved methane concentrations in groundwater reached saturation levels (20 to 23 mg/L), methane in soil gas did not reach an explosive level at the ground surface as significant attenuation (up to 99%) occurred within the vadose zone. It should be noted that this observation may not hold true at all sites, as the level of attenuation is affected by several parameters such as the thickness of the vadose zone, the presence of oxygen in the vadose zone, etc. For example, methane was found at the ground surface at concentrations exceeding 1.5% (and within the vadose zone at 8%) at the Cambria Site which has a shallow depth to groundwater, and likely contains an anoxic vadose zone as portions of the site are submerged during the year. Nevertheless, the ability of methane to attenuate within the vadose zone is something that should be considered when designing and sampling for soil gas at ethanol sites.

For more information on the laboratory study referenced above, please refer to: Ma, J., Rixey, W., DeVaul, G., Stafford, B., Alvarez, P. "Methane Bioattenuation and Implications for Explosion Risk Reduction along the Groundwater to Soil Surface Pathway above a Plume of Dissolved Ethanol" *Environ. Sci. Technol.*, **2012**, 46 (11), pp 6013–6019

Preferential Biodegradation of Biofuels Over COCs (Section 3.4.3 and 3.4.4)



- ▶ Readily degradable nature of biofuels can result in preferential biodegradation of biofuels over COCs
- ▶ Plume elongation expected to be temporary
- ▶ Elongated plumes may have shorter lifetimes because of lower concentrations of petroleum hydrocarbons and buildup up biomass
- ▶ Redox changes in the subsurface may lead to changes in the mobilization of metals

Plume elongation may be predicted by modeling studies, however, other research has indicated that no plume elongation, or shortening of plume occurs because of increased biomass stimulated by biofuel presence. Any plume elongation is expected to be temporary and elongated plumes may have shorted lifetimes because of lower concentrations of petroleum hydrocarbons (from denaturant) than a petroleum hydrocarbon release.

Mobilization of Metals (Section 3.4.4.) 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 (see Brown, R.A., K.E. Patterson, M.D. Zimmerman, and G.T. Ririe. 2010. Attenuation of Natural Occurring Arsenic at Petroleum Hydrocarbon-Impacted Sites. Proceedings: Seventh International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, CA 2010.)

Enhanced Solubility of Petroleum (Section 3.4.1)



- ▶ Some biofuels can act as cosolvent
 - High concentrations (> 20% ethanol)
 - May occur within capillary fringe
 - Unlikely to occur in groundwater
- ▶ Releases of highly soluble biofuels (e.g. ethanol) onto prior hydrocarbon releases
 - May result in mobilization of pre-existing residual separate phase hydrocarbons
 - Section 3.4.2

Some biofuels can act as a cosolvent when present in water at high enough concentrations

Aqueous concentrations must be greater than 20% (ethanol) to enhance solubility limits of petroleum hydrocarbons

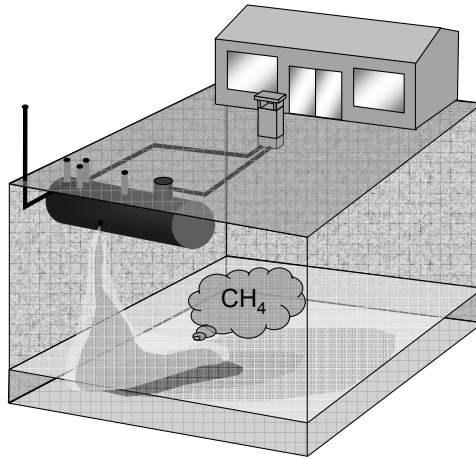
May occur within capillary fringe

In groundwater, biofuels concentrations unlikely to occur at levels greater than a few percent – making cosolvency unlikely in groundwater

Releases of highly soluble biofuels (e.g. ethanol) onto prior hydrocarbon releases may result in mobilization of pre-existing residual separate phase hydrocarbons (Section 3.4.2)

Our Case Study: Fate & Transport ★

- ▶ Media impacts to vadose zone, capillary fringe and groundwater
 - Capillary fringe can act as a lingering source area for ethanol
- ▶ Groundwater will become anaerobic, possibly leading to methane generation



No associated notes.

Fate and Transport Summary



Property differences between biofuels and petroleum fuels influence fate and transport in the environment

- ▶ Highly soluble biofuels readily partition into water
- ▶ Biodegradable nature of biofuels significantly impacts dissolved oxygen concentrations
- ▶ Ethanol can be retained in the capillary fringe (lingering source)
- ▶ Cosolvency effects likely limited to capillary fringe and large E95 releases
- ▶ Potential for significant methane generation
- ▶ Temporary plume elongation

- Highly soluble biofuels will partition into water encountered along migration pathway (e.g., soil moisture)
- Biodegradable nature of biofuels will significantly impact dissolved oxygen concentrations in surface water
- Ethanol can be retained above water table (capillary fringe) limiting mass transfer to saturated zone (lingering source)
- Enhanced solubility of hydrocarbons from cosolvency effects of biofuels are likely limited to capillary fringe, and large E95 releases
- In groundwater, significant methane can be generated, with potential for transport into the vadose zone
- Plume elongation resulting from biofuels expected to be temporary

Training Roadmap



- ▶ Introduction
- ▶ Releases
- ▶ Fate and Transport
- ▶ Q&A Session #1
- ▶ Site Investigation
- ▶ Long-Term Response Strategies
- ▶ Summary
- ▶ Q&A Session #2

No associated notes.

Training Roadmap

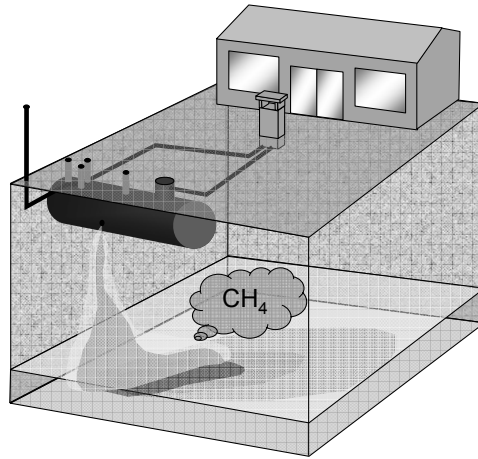
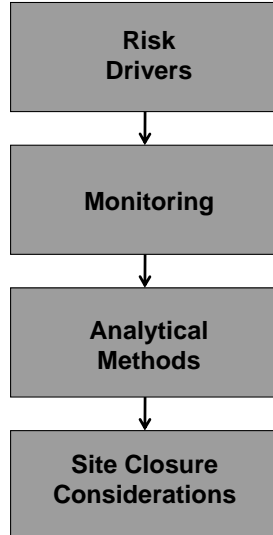


- ▶ Introduction
- ▶ Releases
- ▶ Fate and Transport
- ▶ Q&A Session #1
- ▶ Site Investigation
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- ▶ Summary
- ▶ Q&A Session #2

No associated notes.

Site Investigation (Section 4)

This section will cover:



Use of the hypothetical case study to help illustrate key points

Site investigation considerations – what's different from a typical petroleum release

Emphasis on new potential risk drivers

Risk Drivers for Site Investigation

- ▶ Surface water
 - Ethanol can not be recovered due to solubility; biodiesel can be recovered like petroleum
 - Dissolved oxygen depletion – risk to aquatic species a significant new concern
- ▶ Vadose zone
 - Explosive risk from increased methane production – NO ODOR
 - Potential increased vapor intrusion (VI) risk for petroleum VOCs
- ▶ Groundwater
 - Risk to drinking water supplies due to plume elongation
 - Biofuel degradation can produce taste and odor issues in drinking water supplies

No associated notes.

July 2008 – Lanesboro, MN
3,000 gals E95



No associated notes.

Our Case Study: Site Investigation (Section 4)

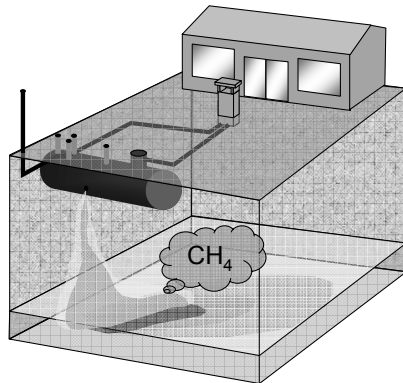


► Site investigation strategy:

- Dependent on age, volume, composition of release →
- Potential risk receptors →

Case study:

- Recent E85 spill
- Dispensing station building and surrounding residential area



The receptors are the same as a typical petroleum release, but the risks are not.

Site Investigation – What's Different



- ▶ Different chemical and physical properties of biofuels require changes to investigation design
 - Monitoring well screen length and type ★
 - Additional analytical parameters
- ▶ Additional vapor risk assessment for VOCs and methane (if receptors are present) ★
- ▶ Time factor
 - Longer monitoring duration needed to assess risk

Based on what was discussed in Section 3, the different chemical and physical properties of biofuels require a different approach to Site Investigation.

Typical UST investigation: 3-5 water table monitoring wells, 10' long screens. Shorter-screened wells are recommended for biofuel investigations.

VI investigation typically one time snapshot. However, this will not work for biofuels because of the potential for delayed methane generation.

The time factor is important, may not be able to close out sites as quickly or with limited investigation.

Methane Monitoring (Section 4.1.1)



- ▶ Biofuels have the potential to generate significantly more methane than petroleum
- ▶ Initial evaluation should determine if explosive conditions exist
- ▶ Methane appearance may not be immediate, suggesting extended monitoring when receptors are present
 - Low or no initial methane may not mean no future risk
 - May appear without detection of source biofuel
- ▶ Subsurface methane may be sampled in:
 - Soil gas using push probes or vapor points
 - Groundwater using push probes or wells for dissolved methane



Biofuels, such as ethanol, butanol, and biodiesel are more readily degradable via microbial processes when compared to petroleum hydrocarbons at equivalent aqueous concentrations. As discussed in the previous section, methane generation can be delayed and 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.

The potential for methane generation presents a significant concern. Methane has no odor. OSHA action level of 10% LEL is 0.5%, or 50,000 ppm.

Case study sites, such as the Balaton DFE release (Appendix D, Table D-2), have shown 2.7% methane in surface gas samplers with over 12' of vadose zone. Cambria case study (Appendix D) shows that the methane flux is about the same as a municipal solid waste landfill.

Methane usually degrades in a very short distance once oxygen is encountered in the subsurface, but the flux at biofuel sites is too great and overwhelms the system.

Soil gas sampling methods for methane same as vapor intrusion methods.

Methane Monitoring (Section 4.1.1)



► Groundwater

- Generally more reliable than soil gas for detection
- Well screen lengths may affect concentrations
- Must closely follow QA/QC sampling procedures
 - Methane is easily lost during sampling
- Levels above 25 mg/L indicate saturated levels where ebullition (bubbling) may be occurring

► Soil gas

- Sampling points and procedures same as VOCs (ITRC 2007, Vapor Intrusion Pathway: A Practical Guideline)
- If potential receptors are present at least one vapor monitoring point should be placed in the release area



Soil gas has variables related to weather that can impact results, so groundwater is a more stable and reliable indicator. If methane is present in groundwater, it will also be present in soil gas.

Longer screens may result in lower concentrations from the effects of dilution. Shorter-screen lengths sampling at the water table interface is most important because methane is produced at the water table interface.

Methane can be easily lost from the water sample, therefore, close adherence to proper sampling methods is needed.

Ebullition can also transport the VOCs further away from the source zone than in a typical petroleum release.

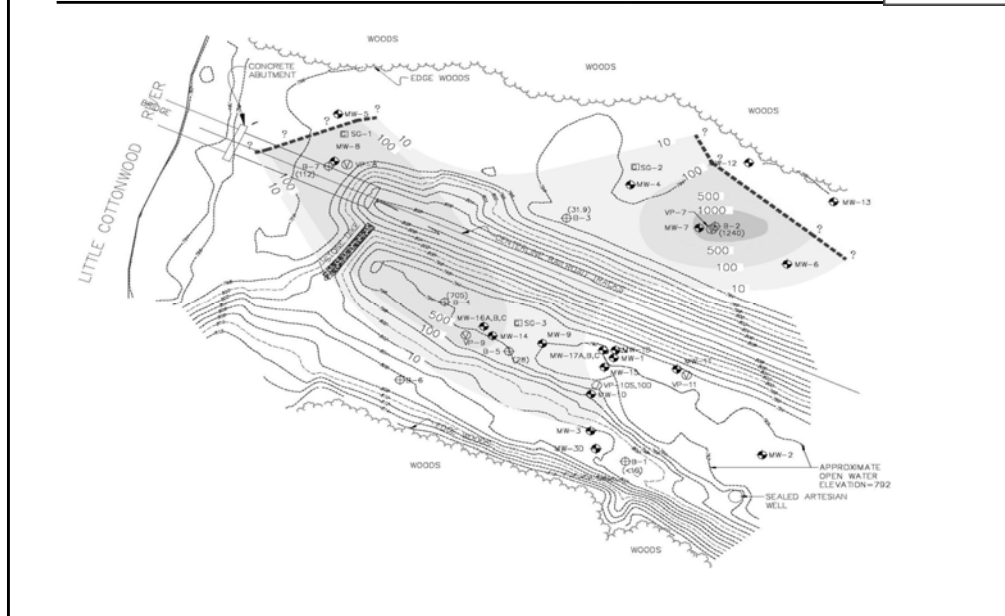
59

November 2006 - Cambria, MN 25,000 gals DFE (E95)



No associated notes.

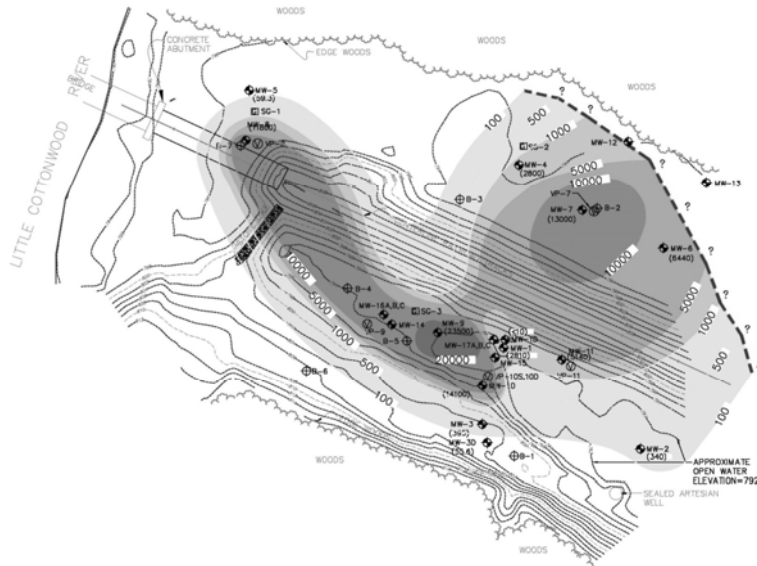
Delayed Methane Generation: Cambria, MN Case Study July 2007 (Appendix D)



In November 2006, a train derailment in south central Minnesota resulted in the release of approximately 25,000 gal of denatured fuel ethanol. This site was selected as a study site for evaluating monitored natural attenuation (MNA) for denatured fuel ethanol (E95). Monitoring wells and soil gas probes were used to delineate the extent of groundwater impacts and evaluate vapor phase methane concentrations.

The initial investigation results (June 2007) showed ethanol concentrations in groundwater exceeding 5% (55,000,000 µg/L) in the release area, whereas aqueous-phase methane concentrations were detected, but remained relatively low (Figure D-1).

Delayed Methane Generation: Cambria, MN Case Study December 2007 (Appendix D)



By December 2007, the groundwater methane plume had expanded in both magnitude and extent. We think this demonstrates a classic delay in methane generation from toxicity and microbial stimulation. Further details on this case study are available in Appendix D of the document.

Ethanol Monitoring (Section 4.1.2)



- ▶ Vadose zone
 - Soil gas monitoring same as VOCs
 - Soils can be sampled using standard VOC methodology
- ▶ Capillary fringe
 - Lysimeters have been used, but sampling capillary fringe not necessary
- ▶ Groundwater
 - Shorter monitoring well screens recommended to capture ethanol draining, and/or leaching from the capillary fringe ★
 - Multi-level wells may be needed
 - Detection of ethanol in groundwater should not be used alone for methane risk assessment

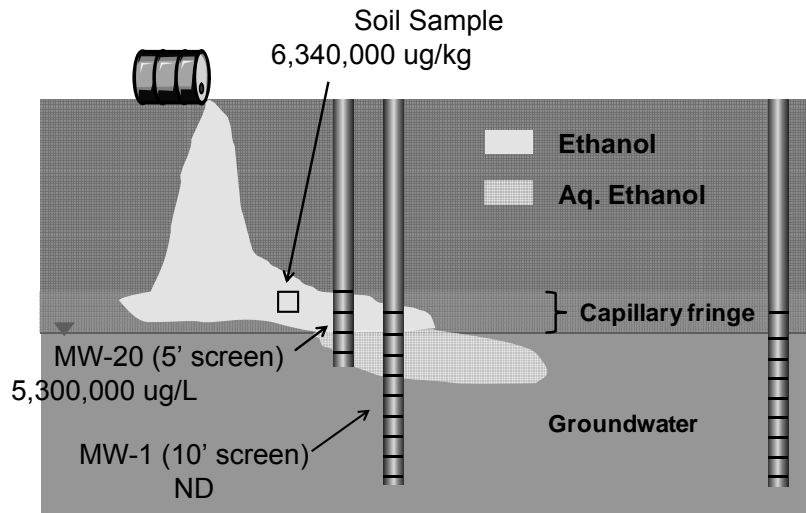
The subsurface behavior of ethanol discussed in Section 3 have an impact on monitoring for ethanol.

Short well screens intersecting the water table has been shown to detect ethanol residing in the capillary fringe. Ethanol concentrations in groundwater wells is not equivalent to concentrations detected in the capillary fringe.

Highly variable water table elevations may require several wells.

Methane can still be generated in the apparent absence of the source biofuel, even years after the source biofuel is gone. Therefore, the presence or absence of the source biofuel alone should not be used to determine potential risks or for site closure.

Cambria, MN Case Study



Note: Not in ITRC document

Geology also plays a factor, MW-1 taps a more transmissive zone at depth

MW-1 Screen 3'-13'

MW-20 screen 2'-7'

Biodiesel Monitoring (Section 4.1.3)



- ▶ Biodiesel forms a LNAPL on groundwater
 - Wire wrapped screens are recommended to help facilitate the entry of higher viscosity biodiesel LNAPL into monitoring wells
 - TarGOST (LIF) has been shown to effectively map B100 NAPL
- ▶ No standard analytical methods for biodiesel in soil or groundwater exist but surrogates can be used
 - Bugs immediately hydrolyze FAMES to fatty acids
 - TOC/DOC and COD to quantify dissolved fraction in groundwater
 - TOC can also be used to quantify biodiesel in soil
 - Degradation products (e.g. short chain fatty acids)
 - Surrogates do not directly quantify the concentration of biodiesel, but are useful to evaluate groundwater impact and methane generation potential

Biodiesel monitoring recommendations based on case study of a B100 release (see Westway Biodiesel case study in Appendix D). At that site, 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. TarGOST was used to delineate B100 product as B100 fluoresces. A number of analytes sampled for, including surrogates. In collaboration with EPA, TOC found to be most useful. The standard total petroleum analysis DRO did not detect anything, but at other sites, the petroleum compounds in biodiesel blends will likely drive risks and investigations.

Wire wrapped screens have a much greater open area than slotted screens.

Biodiesel Monitoring (Section 4.1.3)



- ▶ Biodiesel (B100) produces a lot of methane (and CO₂)
- ▶ Like ethanol ebullition (bubbling) may increase methane risks, and VI risks for blended fuels
- ▶ 1.4L FAME → 662 L methane
- ▶ Biodiesel also has a taste/odor/appearance impact on water quality →
- ▶ Petroleum fraction of blends may be the risk driver for biodiesel blends; however methane may still be an issue for higher percentage blends



At the Westway site, high levels of DOC, TOC and CBOD indicated 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. Soil gas in monitoring wells comprised of 67% methane, 33% CO₂.

FAME → methane gas is almost a 500x expansion factor

Picture is from Westway biodiesel case study site, note foam. Also contained particles of biomass. Bugs immediately hydrolyze FAMES to fatty acid which at pH >5.5 forms alkanates (soap)

Surface Water Monitoring (Section 4.1.4)

- ▶ Depletion of dissolved oxygen and the affect on aquatic life is primary concern with soluble biofuels (e.g. ethanol)
- ▶ DO may be measured directly in the field
- ▶ COD, DOC and/or TOC may be used to assess the potential oxygen consumption load



2000 Wild Turkey bourbon spill into Kentucky river impacted wildlife for 66 river miles and killed 228,000 fish.

2009 Rockford IL E95 spill (Table D-2) is suspected of causing large fish kill (72,000 fish).

Field Screening Methods (Table 4-1)



Table for Sampling and Analytical Methods (Table 4-1) ★

Analyte	Environmental Media	Analytical Methods
<i>Field Methods</i>		
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

Most useful was the GEM landfill gas meter for measuring methane in soil gas. Note – need to use a carbon filter to remove VOCs if present, otherwise you will have false high readings.

Analytical Laboratory Methods (Table 4-1)



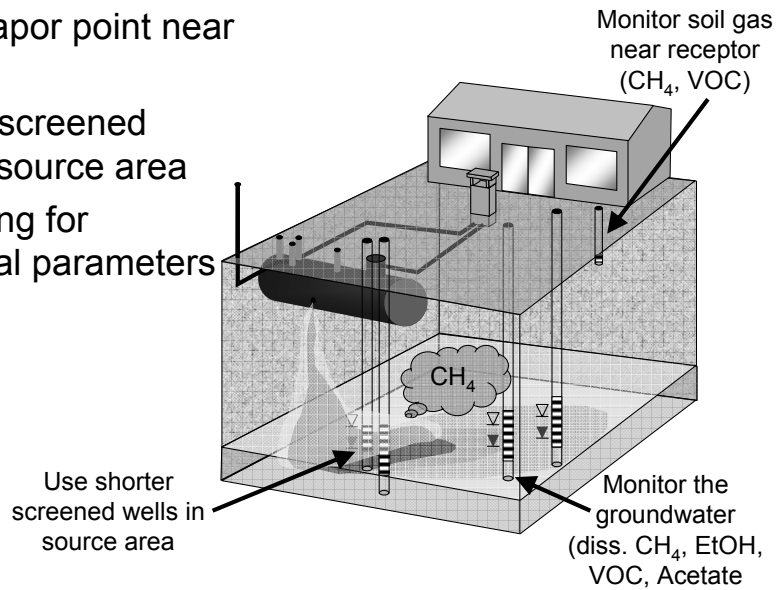
Analyte	Environmental Media	Analytical Methods
Methane	Soil Gas	USEPA 3C; ASTM D1946
Dissolved Methane	Groundwater	RSK-175
Acetate	Groundwater	Ion chromatography, other
DOC/TOC	Surface Water, Soil, Groundwater	Standard Method 5310C; ASTM D513-6; USEPA 415.3
BOD/COD	Surface Water	USEPA Methods 405.1 (BOD); 410.1 #DR/3000 (COD), or similar
Ethanol/butanol	Soil	USEPA 8260B
Ethanol/butanol	Soil Gas	USEPA Method TO-15
Ethanol/butanol	Groundwater	USEPA 8260B; USEPA 8260; USEPA 8015C; USEPA 8261A

USEPA Method 8260B with a heated purge trap unit recommended for lower detection limits for ethanol. There is a question of the usefulness of a very low DL. When present ethanol will be seen at normal detectable levels.

Our Case Study: Site Investigation ★



- Install vapor point near receptor
- Shorter-screened wells in source area
- Monitoring for additional parameters



Now that we know more about these concepts, how do they apply to our hypothetical case study?

Risk to receptors from methane:

- evaluate by groundwater sampling
- one vapor point near receptor to evaluate whether emergency condition exists

Shorter monitoring well screen to detect ethanol and methane.

Additional analytical parameters may be needed.

Longer monitoring duration.

Site Investigation Summary (Section 4)



- ▶ Methane in soil gas = likely risk driver
- ▶ Physical properties of biofuels may require some changes to a site investigation design, such as monitoring wells
- ▶ Sampling for additional parameters will likely be required
- ▶ Additional field screening equipment may be required
- ▶ Additional VI monitoring may be required due to
 - Stripping of petroleum VOCs from groundwater and advection of petroleum vapor by methane and other biogenic gases
 - Methane exerts a large oxygen demand which can allow petroleum vapors and methane to migrate further
- ▶ Site investigation of other or new biofuels should be based on the physical, chemical, and biological properties of the biofuel

Methane is a key difference for site investigation of biofuel releases. Additional VI monitoring may be required due to methane and other biogenic gases, which can strip petroleum VOCs from groundwater and from advection of petroleum vapor. Methane exerts a large oxygen demand, which can allow petroleum vapors to migrate further.

Site investigation for biofuels other than ethanol and biodiesel should be based on the same approach used in the ITRC document (i.e. based on the physical, chemical, and biological properties of the biofuel).

Site Closure Considerations



- ▶ Was the site investigation adequate for a biofuel release?
- ▶ Have all groundwater and vapor risks been identified?
- ▶ Are degradation products still present in groundwater (e.g. methane, acetate)
- ▶ Has monitoring adequately accounted for delayed methane generation?
- ▶ If elevated risks and hazardous conditions exist, remediation may be required

All states are different, but these are key items to consider beyond a typical petroleum release.

If the site investigation follows a standard petroleum investigation, you maybe missing out on significant risks to receptors.

Don't rely on just detection of the biofuel, look for degradation products.

Time is very important, especially for UST releases where you may not know where you are at in the lifecycle, so err on the side on greater monitoring.

Training Roadmap

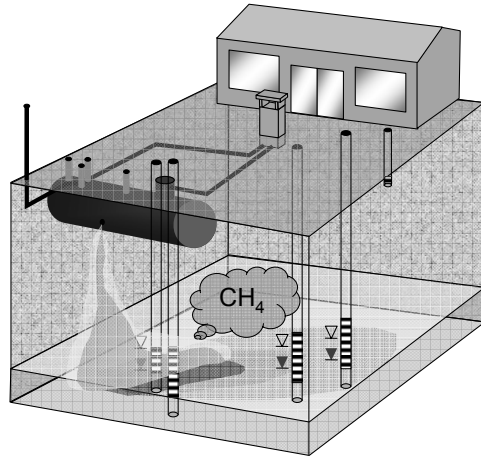
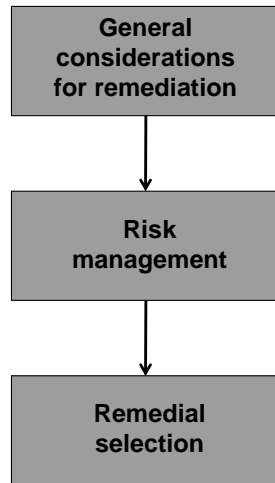


- ▶ Introduction
- ▶ Releases
- ▶ Fate and Transport
- ▶ Q&A Session #1
- ▶ Site Investigation
- ▶ Long-Term Response Strategies
- ▶ Summary
- ▶ Q&A Session #2

No associated notes.

Long-Term Response Strategies (Section 5)

This section will cover:



Use of the hypothetical case study to help illustrate key points

Long-term response strategies for a biofuel release require consideration of a number of factors, including the following:

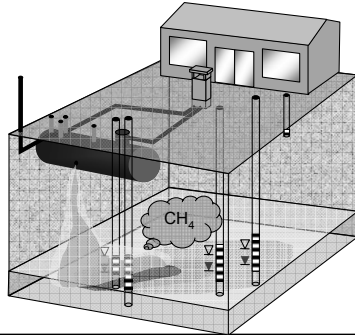
- Type of biofuel
- Extent and magnitude of the release
- Regulatory threshold for a COC
- Risk to identified receptors

Our Case Study: Long-Term Response Strategies (Section 5)



Requires consideration of:

- Type of biofuel →
- Extent and magnitude of the release →
- Regulatory threshold for a COC(s) →
- Risk to identified receptors →

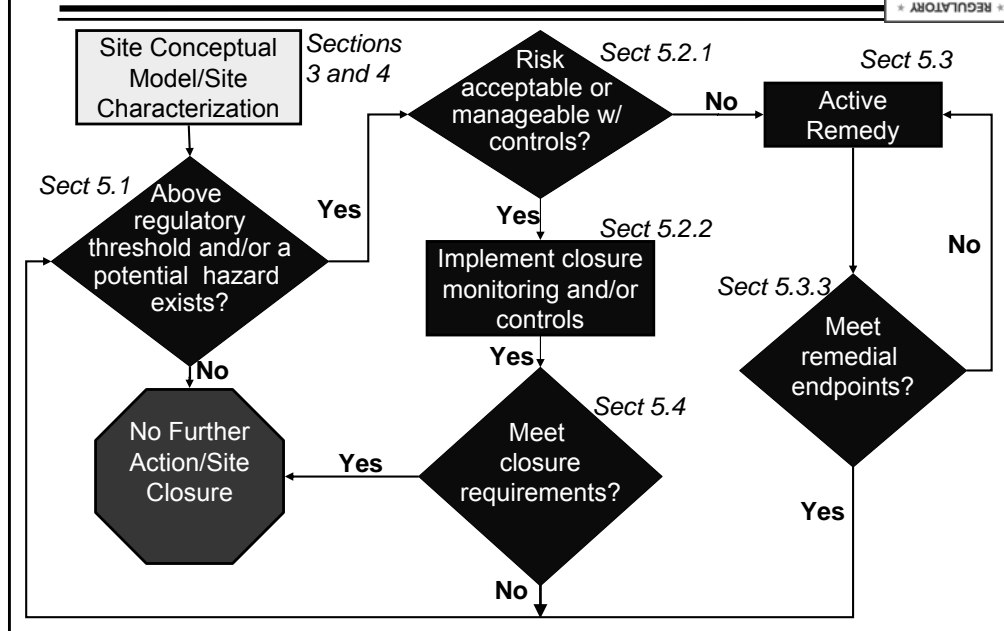


Case study:

- E85 spill
- Media impacted:
 - Vadose zone
 - Capillary Fringe
 - Groundwater
- State regulations applicable to gasoline components
- Dispensing station building and surrounding residential area

At this hypothetical site, state regulations are applicable to gasoline components (no regulatory thresholds established for ethanol, methane or other degradation products)

Generalized Framework (Figure 5-1)



Rectangular shapes denote when an action is required such as development of the site conceptual model (SCM), implementation of an active remedy or closure monitoring.

This is 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.

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. This methodology will be explained in the following slides as well examples of how to use the information presented in the document.

Risk Management (Section 5.2.1; Table 5-1)



- ▶ Management of risk through long-term monitoring
- ▶ Controls (institutional or engineering)
 - Provide protection from exposure to contaminant(s) that exist or remain on a site

Implement closure
monitoring and/or
controls



Benefits	Limitations
Dissolved biofuel is readily biodegradable without additional enhancement	<ul style="list-style-type: none"> • High concentrations of some dissolved biofuel constituents (i.e., 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

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.

Monitored natural attenuation (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. 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).

The Pacific Northwest Terminal case study in Appendix D of the document utilized MNA and an active remedy together in the remediation process.

Selection of Remedial Technology (Tables 5-2 and 5-3)



- ▶ Active remedy
 - Eliminate or reduce the remediation driver or COC
- ▶ Remedial technologies
 - Soils/Sediment (Table 5-2)
 - Groundwater/Surface water (Table 5-3)
- ▶ Categorized as in situ or ex situ
- ▶ Subdivided within each category by dominant remedial mechanism
 - Biological technologies (e.g. enhanced aerobic biodegradation)
 - Chemical (e.g. chemical oxidation)
 - Physical (e.g. soil vapor extraction)
- ▶ Provides discussion on overall benefits and limitations of each technology to help guide selection

Active
Remedy

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. 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.

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, 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.

The document includes a sites specific remedial technology evaluation and selection process was developed that draws upon the technologies analysis in Section 5.3.2.

Remedial Technology (Soils Example) Table 5-2



- Examples applicable to E85 impacts to vadose zone/capillary fringe ★

Active
Remedy

Technology		Benefits	Limitations
In Situ Treatment	<i>Physical</i>		
	Soil vapor extraction (SVE)	Rapidly removes 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.
	<i>Soil</i>		
	<i>Biological</i>		
	Enhanced Aerobic Biodegradation	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.
	<i>Bioventing - soil</i>		

This slide provides examples of two technologies as provided in Table 5-2. This table provides benefits and limitations of technologies with some level of expected effectiveness for biofuel remediation, addressing expected benefits and limitations for each technology.

Detailed Remedial Technology Tables (Tables 5-4a through 5-4c)



- ▶ Biofuels evaluated
 - Ethanol (Table 5-4a)
 - Butanol (Table 5-4b)
 - Biodiesel (Table 5-4c)
- ▶ Identifies targeted environmental media
- ▶ Evaluates technology by specific property (e.g. solubility) and provides numerical values
- ▶ Compares efficiency to a reference petroleum hydrocarbon compound
- ▶ Summarizes which compound (biofuel or reference hydrocarbon) is favored by the remedial technology

Active
Remedy

Target environmental media breakdown in tables:

- Vadose zone
- Groundwater
- Surface water

Reference compounds for each evaluated biofuel:

- Ethanol (reference = benzene) – Table 5-4a
- Butanol (reference = benzene) – Table 5-4b
- Biodiesel (reference = diesel) – Table 5-4c

Example Table 5-4a (Figure 5-2)



Expanding on the examples selected from Table 5-2 as ★
applicable to vadose zone remediation of the E85 case study:

Active
Remedy

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

In this example from Table 5-4a, Soil Vapor Extraction applies to ethanol in the vadose zone by acting on ethanol's vapor pressure and aerobic biodegradation potential properties. The reference for ethanol is benzene. Comparison of the property values for benzene and ethanol for vapor pressure and aerobic biodegradation potential show that SVE favors benzene with respect to vapor pressure and ethanol with respect to ethanol. Similarly, bioventing will affect the aerobic biodegradation potential of ethanol and will favor ethanol over benzene.

Example Table 5-4d (Methane)



Evaluates technology effectiveness on methane remediation versus methane generation ★

Active
Remedy

Technology	Target Media			P/C/B Properties	Methane Remediation	Methane Generation
	VZ	GW	SW			
SVE	X			Vapor Pressure	Applicable	N/A
				Aerobic Bio Potential	Applicable	Inhibits
Bioventing	X			Aerobic Bio Potential	Applicable	Inhibits

Depicts the media that the technology is applicable to

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

Evaluates whether technology can remediate methane, and by which P/C/B property

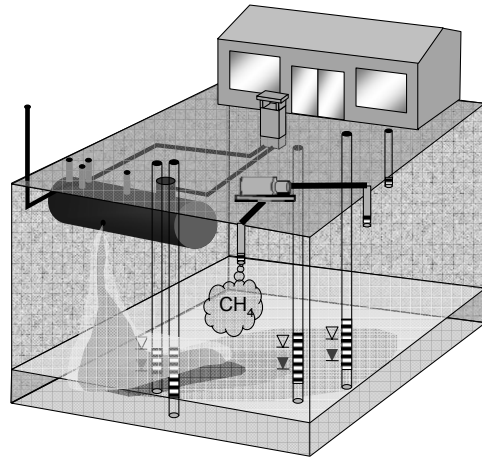
Specifies whether technology inhibits methane generation, and by which P/C/B property

In this example from Table 5-4d, the table shows that both SVE and bioventing may be applicable for methane remediation and will inhibit methane generation.

Our Case Study: Long-Term Response Strategies ★



- ▶ Application of SVE for vadose zone:
 - Physical removal
 - Enhanced biodegradation
- ▶ Long-term monitoring for both soil gas and dissolved plume to assess and re-evaluate risk
- ▶ Additional technologies can be evaluated/implemented



Approach presented for the hypothetical case study is similar to that taken at the Pacific Northwest Terminal Case Study presented in Appendix D.

Application of SVE for vadose zone:

Physically remove regulated compounds, ethanol, and methane (if present); addresses explosive risk

Biologically enhance degradation of ethanol, regulated compounds, and methane

Long-Term Response Strategies Summary



- ▶ Response strategies should be based on risks presented by biofuel release
- ▶ MNA may be a viable response strategy
- ▶ If methane is a concern, longer-term monitoring and/or engineering controls may be warranted
- ▶ Technology evaluation process can be applied to biofuels, the petroleum component of the blend, and future biofuels

Current widely used biofuels (ethanol and biodiesel) are readily biodegradable; therefore, MNA may be a viable strategy.

The technology evaluation and selection process can be also be applied to future biofuels based on their physical, chemical, and biological properties.

Training Roadmap



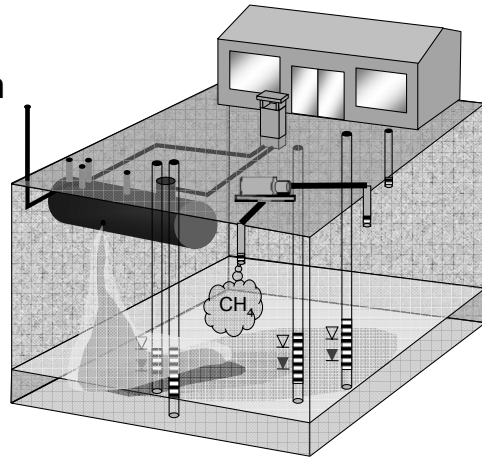
- ▶ Introduction
- ▶ Releases
- ▶ Fate and Transport
- ▶ Q&A Session #1
- ▶ Site Investigation
- ▶ Long-Term Response Strategies
- ▶ Summary
- ▶ Q&A Session #2

No associated notes.

Our Case Study: Summary



- ▶ Equipment compatibility issues
- ▶ Biofuels fate & transport in the environment
- ▶ Methane gas generation
- ▶ Site investigation design
- ▶ Monitoring in environmental media
- ▶ Long-term response strategies
- ▶ Risk management



The hypothetical case study was used to illustrate all of these points and also how biofuel releases, investigations and remediation strategies differ from petroleum releases.

Overall Summary



- ▶ Biofuel production and consumption is increasing
 - = increase in potential frequency of releases
 - = potential for environmental impacts

- ▶ By using the ITRC document, you will be prepared and able to:
 - Build a better Site Conceptual Model (SCM)
 - Understand fate & transport in the environment
 - Know how to investigate a biofuel release site
 - Formulate a better response strategy

- The use of biofuels has increased and is expected to continue increasing with a concurrent expected increase in biofuel releases
- Differences in the supply chain of biofuels from conventional fuels have implications for potential release scenarios
- The physical, chemical, and biological properties of biofuels influence their fate and transport in the environment
- Characterization of biofuel releases based on the site conceptual model and can include monitoring for methane and methane precursors
- Long-term response strategies may include the use of monitored natural attenuation and/or active remediation technologies, depending on remediation goals
- Use remediation technology tables to evaluate potential technologies for remediation
- Future biofuels may be evaluated using a similar multi-media approach

Thank You for Participating



- ▶ 2nd question and answer break
- ▶ Links to additional resources
 - <http://www.cluin.org/conf/itrc/biofuels/resource.cfm>
- ▶ Feedback form – *please complete*
 - <http://www.cluin.org/conf/itrc/biofuels/feedback.cfm>

Need confirmation of your participation today?

Fill out the feedback form and check box for confirmation email.

Links to additional resources:

<http://www.cluin.org/conf/itrc/biofuels/resource.cfm>

Your feedback is important – please fill out the form at:

<http://www.cluin.org/conf/itrc/biofuels/feedback.cfm>

The benefits that ITRC offers to state regulators and technology developers, vendors, and consultants include:

- ✓ Helping regulators build their knowledge base and raise their confidence about new environmental technologies
- ✓ Helping regulators save time and money when evaluating environmental technologies
- ✓ Guiding technology developers in the collection of performance data to satisfy the requirements of multiple states
- ✓ Helping technology vendors avoid the time and expense of conducting duplicative and costly demonstrations
- ✓ Providing a reliable network among members of the environmental community to focus on innovative environmental technologies

How you can get involved with ITRC:

- ✓ Join an ITRC Team – with just 10% of your time you can have a positive impact on the regulatory process and acceptance of innovative technologies and approaches
- ✓ Sponsor ITRC's technical team and other activities
- ✓ Use ITRC products and attend training courses
- ✓ Submit proposals for new technical teams and projects