



# **Denatured Fuel Ethanol: Guideline for Release Prevention & Impact Mitigation**

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## Chapter 1 – Introduction

### A. Introduction

This document provides a comprehensive discussion of best practices for preventing releases of denatured fuel ethanol into the environment, understanding the potential impacts of such releases, and implementing effective mitigation techniques. It is intended to serve as a practical resource for fuel producers, ethanol transporters, and emergency and environmental responders, including Local Emergency Planning Committees (LEPCs). The information is presented in an actionable format that supports decision-making at facilities and during transport operations, both proactively and in response to incidents. Prepared by engineers with extensive experience in the ethanol industry, this guide draws on real-world expertise in managing denatured fuel ethanol releases. It consolidates essential regulatory and scientific principles into a practical framework of best practices, recognizing that each release scenario requires a tailored response. Originally published in March 2013 and revised in July 2016, this updated edition incorporates the latest advancements in enhanced bioremediation and addresses developments in the expanding rail transportation sector. Additional details and references can be found in the Appendices.

- Appendix A provides further explanation of Federal requirements for biofuel production facilities and shipments.
- Appendix B references the technical document *Biofuels: Release Prevention, Environmental Behavior, and Remediation*, which offers comprehensive and detailed insights into the topics addressed in this guide. This document includes in-depth technical information and case studies of ethanol releases, providing valuable context and practical illustrations of the concepts discussed.
- Appendix C contains case study excerpts from *Large Volume Ethanol Spills-Environmental Impacts and Response Options*. The extensive document provides additional case studies and useful references that describe the fate and transport of ethanol in the environment.
- Appendix D contains an article published in *Ground Water Monitoring and Remediation*. The article highlights the effect of denatured ethanol on ground water from three sites.

### B. Ethanol is Different than Crude Oil, Gasoline, and Other Traditional Hydrocarbon Fuels

Ethanol acts differently in the environment than gasoline and other traditional hydrocarbon fuels. Hydrocarbon fuels generally have similar characteristics, whether flammable or combustible liquids. Gasoline is a hydrocarbon fuel produced from crude oil by fractional distillation. It is hydrophobic, or non- water soluble, and has a flash point of approximately -45°F. Gasoline has a vapor density between 3 and 4. Therefore, as with all products with a vapor density greater than 1, gasoline vapors will seek low levels or remain close to ground level. Gasoline has a specific gravity of 0.7 – 0.8 which indicates it will float on top of water since it is also insoluble. Gasoline’s auto-ignition temperature is between 536°F and 847°F, and it has a boiling point between 102°F and 400°F depending on fuel composition. Gasoline is not considered a poison but does have harmful effects after long-term and high-level exposure that can lead to respiratory failure. Much of the adverse health effects of gasoline exposure are due to aromatic hydrocarbons which comprise 20 - 50% of the mixture, 0.5 - 2.5% of which is benzene. Smoke from burning gasoline is black and has toxic components. Finished gasoline typically contains more than 150

separate natural and additive compounds serving to improve function, stability, and emissions. Crude oils, the parent of gasoline, differ further still from ethanol and contain compounds ranging widely in structure, toxicity, and carbon number <sup>22</sup>.

Ethanol is a renewable fuel produced through fermentation and distillation processes. In the United States, corn remains the predominant feedstock for ethanol production, accounting for 98% of the total output in recent years. This utilization represents a significant portion of domestic corn use, with ethanol plants projected to consume approximately 5.45 billion bushels of corn during the 2023-2024 marketing year, marking a notable increase from previous years. <sup>15</sup> However, ethanol can also be produced from other sources such as sugar cane, switchgrass, and other biomass conducive to the fermentation and distillation process. Ethanol is a polar solvent that is water-soluble and has a 55°F flash point. It has a vapor density of 1.59, indicating that it is heavier than air; consequently, ethanol vapors, like gasoline vapors, tend to settle in lower areas. Ethanol's specific gravity is 0.79, meaning it is lighter than water; however, due to its water solubility, it mixes thoroughly with water. The auto-ignition temperature of ethanol is 685°F, and it has a boiling point of 173°F. Ethanol is less toxic than gasoline and does not contain carcinogenic compounds. <sup>18</sup> In its pure form, ethanol burns with a hard-to-see blue flame and does not produce visible smoke; when denatured, it may produce a slight orange flame with little to no smoke.

The most significant distinction between ethanol and hydrocarbon fuels, including crude oils, lies in its water solubility. This characteristic fundamentally influences ethanol's behavior in environmental contexts, particularly in surface water, groundwater, and soil interactions.

### **C. Managing Ethanol Risks: Key Considerations and Definitions**

As ethanol production continues to expand, the handling and transportation of ethanol will inevitably increase. Even in well-managed operations, the potential for environmental releases remains a persistent risk. Producers and transporters must remain vigilant regarding the hazards associated with ethanol releases and understand their behavior and transport dynamics in air, surface water, soil, and groundwater.

The first step in effective ethanol management is to identify and implement actions that:

- Prevent releases, and
- Enable decisive mitigation of environmental impacts in the event of a release.

Ethanol facilities are required by both federal and state regulations to develop and maintain emergency response and environmental mitigation plans. These plans are designed to identify potential risks and enhance facility preparedness. It is essential that ethanol plant personnel are thoroughly trained on these plans and are equipped to respond effectively in the event of a release. Beyond planning, implementing engineering controls can further minimize the likelihood of incidents, enhancing overall operational safety and environmental protection.

Transporters, primarily railroads, are required by federal regulations to maintain response plans based on the volume capacity of their vessels or rail tank cars. Over the past ten years, railroads have significantly enhanced their engineering controls, internal safety standards, and infrastructure in response to increased demands from domestic crude oil shipments. <sup>3,4</sup>

It is crucial to recognize that swift action is essential to minimize environmental impacts in the event of release.

Ensuring that plant personnel are well-informed about their responsibilities, knowing whom to contact, and having response contractors readily available can significantly mitigate the environmental consequences of a release. Beyond environmental concerns, other critical issues include immediate safety risks and potential impacts on the surrounding community. Regulatory agencies must be promptly notified, and relevant information shared with all stakeholders. The management of the response process plays a key role in determining the effectiveness of the outcome and in minimizing costs and reputational risks to the company. With advancements in knowledge and practices in recent years, there are now numerous strategies available to prepare for, prevent, and effectively respond to such incidents.

The ethanol products under discussion in this guideline are defined as follows:

E10 is a common fuel consisting of gasoline mixed with up to 10% ethanol. This fuel is widely available all over the United States. This fuel is commonly shipped as gasoline (DOT placard: UN1203).

E15 is a common fuel consisting of gasoline mixed with up to 15% ethanol. This fuel is shipped as a gasoline and ethanol mixture (DOT placard: UN3475).

Mid-level blends (MLBs), such as E20, E30, and E40, consist of 20%, 30%, and 40% ethanol blended with gasoline, respectively. These blends are designed for use in flex-fueled vehicles (FFVs). MLBs do not have unique placard numbers; instead, any gasoline blend containing more than 10% ethanol is classified under the DOT placard UN3475.<sup>23</sup>

Flex fuel (also known as E85) is a fuel intended for flexible fuel vehicles only that consists of gasoline blended with 51% to 83% ethanol. This fuel is shipped as a gasoline and ethanol mixture (DOT placard: UN3475).

Denatured fuel ethanol is a high-ethanol-content fuel additive with a small percentage of hydrocarbons added during manufacturing. In the United States, a small amount of gasoline (typically 2% to 5%) is mixed with ethanol to render it unfit for human consumption and exempt it from excise taxes on beverage alcohol. The most transported ethanol product by rail is E98, which contains approximately 2% gasoline.<sup>6</sup> Denatured fuel ethanol is typically shipped from ethanol producers to fuel blending terminals, where it is combined with gasoline in specified ratios before being distributed to retail stations and ultimately to consumers. In the United States, denatured ethanol is classified as “Alcohol, not otherwise specified” (N.O.S.) and transported under the DOT placard UN1987.

## Chapter 2 – Why are there releases?

### **A. Like the petroleum industry, the production, storage, and transportation of ethanol involve inherent risks.**

These risks are particularly prominent during product transfers and transportation. Ethanol is routinely moved across the United States via cargo tank trucks, rail tank cars, barges, and pipelines. Much like petroleum facilities and pipelines, even well-designed and carefully managed systems are susceptible to failure. Mechanical components may malfunction, human errors can occur, and automated systems are not immune to malfunction. While ethanol production facilities are engineered and operated with a strong emphasis on safety and environmental protection, maintaining an awareness of potential accidents is a critical aspect of any industrial process.

At production facilities, there are several points in the process that create the possibility of a release:

- Storage in tanks,
- Movement in piping systems, and
- During transfer to rail tank car and cargo tank truck,

The likelihood of a release can be heightened by failures in transfer mechanisms, accidental overfilling, or limitations in containment system design. While historical releases at production facilities are typically of a smaller scale, large-scale incidents have occurred due to catastrophic events such as fires caused by lightning strikes.

### **B. During transportation, the potential for large-scale releases is heightened, particularly in the following scenarios.**

- Incidents during transloading from rail tank car to cargo tank truck
- Cargo tank truck traffic accidents
- Rail tank car derailments

The increasing demand for transporters, especially railroads, has led to a rise in unit train shipments of biofuels and gasoline precursors, which has, in turn, contributed to several high-profile derailments involving these flammable fuels. Despite this increased demand, derailment rates have been on a downward trend, decreasing by 5.8% annually from 2000 to 2012.

## Chapter 3 – What should facilities and transporters do to prevent and minimize releases?

### A. Federal Regulations for Facilities

Federal regulations applicable to most ethanol facilities mandate the development of comprehensive plans aimed at promoting awareness, preventing releases, and mitigating their potential impacts. These federal regulations are noted below and discussed in detail in Appendix A.

1. Facility Response Plan (FRP)
2. Spill Prevention, Control and Countermeasures Plan (SPCC)
3. Risk Management Program (RMP)
4. Process Safety Management (PSM)
5. Emergency Action Plan (EAP)
6. Storm Water Pollution Prevention Plan (SWPPP)
7. Oil Spill Prevention and Response Plans (SRP)

Each of these plans serves as a framework for preventing releases and effectively managing them if they occur. Ethanol facilities are responsible for identifying the applicable plans and ensuring their proper implementation, providing valuable resources and guidance in the event of a release incident.

### B. Federal Regulations for Transporters

Federal regulations governing transporters, primarily railroads, are overseen by the Department of Transportation (DOT), the Federal Railroad Administration (FRA), and agencies such as the Pipeline and Hazardous Materials Safety Administration (PHMSA). These regulatory bodies introduced enhanced rail tank car standards for the transportation of ethanol and crude oil. Rail tank cars carrying crude oil were required to be retrofitted by 2017, while ethanol, classified as a medium-hazard liquid, was given until 2023 to comply with upgrades such as improved pressure relief valves, thermal protection, and additional shielding. The May 2015 rule also provided specific guidance on transporting hazardous materials, addressing factors such as speed limits in high-risk areas and braking system capacities<sup>25</sup>.

Railroads implement rigorous internal training programs and regulations to ensure the safe handling and transportation of ethanol. Contractors involved in emergency response efforts are required to adhere to railroad safety and procedural policies. However, the awareness and risk management practices emphasized by ethanol facility personnel in this section are equally applicable to both railroad staff and contractors

### C. State and Local Requirements for Facilities

Many state regulations align with federal requirements; however, numerous states and local governments have introduced additional provisions related to release prevention and response. Some general guidelines regarding state and local requirements include the following:

- State-specific regulations are typically more stringent than federal regulations, including having more stringent reporting thresholds.

- Some state and local agencies require that copies of the plans referenced in Chapter 3.A be provided to local responders to facilitate preparedness in the event of an emergency.
- In certain cases, states hold primary enforcement responsibility (primacy) over the EPA for implementing regulations. One example is the National Pollutant Discharge Elimination System (NPDES), which includes Storm Water Pollution Prevention Plans (SWPPPs). Facilities required to develop SWPPPs must ensure compliance with state-specific SWPPP requirements for release prevention when creating these plans.

While the prevention of all releases is always the goal, unforeseen circumstances may require a response. State release reporting requirements vary significantly, and facilities must be familiar with these requirements and prepared well in advance of any incident. Both federal and state regulations should be thoroughly addressed in release prevention plans. During an emergency, these plans are essential resources for ensuring compliance with all applicable regulations. A review of release reporting highlights the following categories that often differ across states:

- The amount of a material constituting a reportable release
- The amount of time before a facility must contact state and/or local agency for a reportable release
- Specific requirements associated with communicating the release to the news media
- Whether or not an onsite release to an impermeable surface (i.e. within secondary containment) meets reportable criteria
- The agencies that must be notified for different types of releases

Despite variations in reporting requirements, most states maintain a 24/7 environmental emergency response hotline for the immediate reporting of releases. When contacting these hotlines, states typically require callers to provide specific information to their dispatchers, including the following:

- Responsible party
- Name or identity of the substance involved in the release, including whether it is classified as hazardous
- Quantity of substance released
- Date, time, and duration of release
- Location of release
- Medium into which the release occurred (i.e. land, water, air)
- Risks to community (i.e. health risks requiring medical attention)
- Actions/Notifications/Precautions needed (i.e. evacuation)
- Name and phone number of facility's contact person

The information provided in this section is not exhaustive. To ensure compliance, individual facilities are advised to consult with their respective regulatory agencies to confirm the applicability of state-specific release prevention and response requirements

#### **D. Beyond regulations – what else can I do?**

Response plans are only truly effective when employees have a thorough understanding of their content, integrate them into daily operations, and are prepared to respond appropriately during an actual release. Training programs should ensure that all personnel know their specific roles and responsibilities, as well as the procedures to follow in the event of an incident. Incorporating these plans into regular drills and operational workflows helps reinforce their importance and prepares staff to act swiftly and decisively when necessary. Prompt actions taken by facility personnel to contain a release are critical, as they can significantly reduce both the environmental impact and financial costs associated with the incident. Beyond contingency planning, implementing additional measures such as enhanced communication protocols, readily accessible spill containment resources, and fostering collaboration with local emergency responders can greatly improve the effectiveness of response plans. By focusing on these proactive steps, facilities can strengthen their overall preparedness and ensure that response plans are not just documents but living frameworks that guide real-world action:

##### Awareness

- Employees must be trained and understand the critical importance of their actions. Quick responses within the first hour of a release can contain spills, enabling faster cleanup and reducing environmental harm.
- What heavy equipment is available at or near the facility? For example, a front-end loader can be used to construct dikes and berms for emergency containment.
- What spill control products are readily accessible on-site? A well-stocked spill kit can make the difference between containing an incident on-site and allowing it to spread off-site.
- Who are the local authorities, and how will they respond? Facilities must make required notifications under state and federal law during a spill. Establishing relationships with local responders beforehand ensures they are familiar with the facility and its risks—waiting until an emergency to build these relationships is not ideal.
- Are appropriate contractors pre-identified to respond? Contractors can supply additional manpower and essential equipment to recover lost product quickly, reducing environmental risks. Establishing working relationships with contractors in advance is essential.

##### Site Specifics

- The site's geology directly influences how a release impacts the environment.
- Nearby surface waters and pathways to those waters must be identified and mapped in advance.
- Soil type and proximity to groundwater must also be understood beforehand.
- What are your state's cleanup standards for ethanol releases? These standards will shape the remediation strategy and methods.

## Prevention

- Many spills can be prevented or contained through improved systems and facilities.
- Engineering controls and upgrades can exceed regulatory requirements and focus on process improvements. Such controls often pay for themselves by preventing costly releases.
- Review transfer and containment systems. For instance, secondary containment for rail transfer may meet volume requirements, but the conveyance piping may be inadequately sized for larger releases, limiting its effectiveness.
- Process Safety Management is critical for release prevention. Are storage, piping, and process systems properly inspected and maintained for the associated hazards?
- Drills and training exercises, mandatory under some regulations, are also the best practice for the industry. Inviting local responders, such as fire departments and police, to participate enhances preparedness. Post-exercise debriefings often identify gaps, enabling improved prevention strategies moving forward.

### **E. Summary**

Chapter 3 highlights the critical steps that facilities and transporters must take to prevent and minimize ethanol releases, focusing on regulatory compliance, state-specific requirements, and proactive measures beyond regulations. Federal regulations provide a robust framework for developing comprehensive response plans, while state and local requirements emphasize tailored strategies to meet region-specific needs. Awareness, training, and preparedness are essential for both facilities and transporters to mitigate environmental and financial risks effectively. Additionally, understanding site-specific factors and implementing prevention strategies, such as engineering controls and regular drills, enhances overall readiness. By integrating these measures into their operations, facilities and transporters can ensure compliance, safeguard the environment, and maintain the highest standards of safety and operational excellence

## Chapter 4 - What happens to ethanol released to the environment?

This chapter explores the physical properties of ethanol and their influence on environmental media, including air, soil, surface water, and groundwater. Additionally, Chapter 5 will address the actions to take in response to a release, emphasizing the potential impacts on various media.

### A. Key Physical Properties of Ethanol

- **Appearance:** Ethanol is a clear, colorless liquid. Denatured fuel ethanol includes approximately 2% petroleum hydrocarbons, typically gasoline, as a denaturant.
- **Solubility:** Ethanol is fully soluble in water, meaning any release that reaches surface, or groundwater will completely dissolve and will not separate once dissolved.
- **Volatility:** Ethanol has sufficient vapor pressure to volatilize readily from liquid to vapor, either in its pure form or when mixed with denaturants. However, ethanol dissolved in water exhibits much lower volatility due to its low Henry's Law constant.
- **Soil Mobility:** Ethanol demonstrates low soil mobility, tending to remain in soil until it meets moisture or groundwater.
- **Flammability:** Ethanol is highly flammable, with a Lower Explosive Limit (LEL) of 3.3%, an Upper Explosive Limit (UEL) of 19%, and a flashpoint of 55°F. Even when diluted to 50% with water, the flashpoint of denatured ethanol remains 78°F. Ethanol is classified as a flammable liquid in solutions diluted to as little as 20%.<sup>21</sup> As a polar solvent, ethanol conducts electricity, presenting an ignition hazard.
- **Health and Safety:** The OSHA Permissible Exposure Limit (PEL) for ethanol is 1,000 ppm, with health effects such as eye irritation and headaches observed above this level. The Immediate Danger to Life or Health (IDLH) threshold is 3,300 ppm, which equates to 10% of the LEL.
- **Denaturants**
  - **Composition:** The most common denaturants are petroleum products, such as gasoline and natural gasoline.
    - Adding denaturants (e.g., E98) lowers the flashpoint of ethanol from 55°F to 19.4°F. Colder temperatures further reduce flammability by decreasing vapor pressure.
    - Ethanol preferentially biodegrades in the presence of petroleum hydrocarbons, including denaturants or existing contaminants in soil and groundwater. The interaction of ethanol, denaturants, and site-specific conditions must be carefully evaluated.
  - **Properties:** Denaturants differ chemically and physically from ethanol, necessitating consideration during investigation and remediation. For example, gasoline has lower solubility and may form a light non-aqueous phase liquid (LNAPL) at high concentrations. Gasoline constituents may absorb soil materials and degrade more slowly than ethanol.

By understanding these properties, facilities and responders can better anticipate ethanol's behavior in the environment and tailor mitigation and remediation strategies accordingly

## B. How do these physical properties impact environmental media?

- **Air**

Ethanol spills on the ground or within containment areas pose a significant flammability risk. Under windy and sunny conditions, ethanol readily volatilizes into the air. Ethanol vapors are toxic to humans but generally only under extreme conditions where concentrations are high. However, precautions are necessary due to the potential for ethanol vapors, which are denser than air, to displace breathable air. Once ethanol dissolves in water, evaporation from its aqueous state is significantly reduced and unlikely to contribute substantially to mass balance calculations <sup>21</sup>.

- **Surface Water**

Ethanol's complete solubility in water means that any release into surface water leads to rapid dispersion, rendering recovery as a product unfeasible. Ethanol biodegrades quickly in surface water, but its concentration may exert toxic effects on aquatic organisms. Often, however, the depletion of dissolved oxygen caused by biodegradation has a more pronounced impact on fish and aquatic ecosystems. Ethanol's low bio-concentration factor indicates that it will not bioaccumulate within the ecological food chain <sup>21</sup>.

- **Soil**

The mobility of ethanol in soil depends on the volume of the spill, the soil's conductivity, and its moisture profile. Due to density differences between ethanol and water, ethanol tends to be retained above the water table unless significant hydraulic head pressures drive it downward. Ethanol contacting soil moisture will disperse and migrate downward toward groundwater. As bacteria metabolize ethanol, intermediate products such as acetate are formed, which eventually degrade into carbon dioxide and water, provided sufficient oxygen is present. In anaerobic conditions, methanogenic bacteria degrade ethanol compounds, producing methane as a byproduct. The accumulation of methane in soil represents a potential hazard, with peak methane levels often occurring months or years after the initial release. Additionally, ethanol-water mixtures mobilize existing petroleum contamination in the soil by increasing the solubility of gasoline constituents <sup>21</sup>.

- **Groundwater**

Upon reaching groundwater, ethanol dissolves and disperses. Lower concentrations, such as those found in E10, degrade rapidly in the presence of oxygen. Higher concentrations persist and migrate with groundwater, degrading slowly due to limited oxygen availability. In oxygen-deficient environments, other compounds, such as iron, nitrate, and sulfate, may facilitate ethanol degradation, albeit at a slower rate. As with soil, anaerobic conditions may result in significant methane production over time, requiring an understanding of vapor pathways to mitigate risks of methane accumulation. Notably, methane production may peak at one to two years post-release. Furthermore, ethanol interacting with existing petroleum contamination can significantly increase BTEX plume size and concentration, with BTEX levels rising to tenfold as ethanol mobilizes these compounds <sup>8,21</sup>.

Chapter 4 examines ethanol's behavior in air, soil, surface water, and groundwater, emphasizing its solubility, volatility, and biodegradability. These properties, combined with its flammability and interactions with contaminants, underscore the need for informed mitigation and remediation strategies.

## Chapter 5 – What do I do if a release occurs?

This chapter focuses on what to do if a release of denatured fuel ethanol to the environment occurs.

### A. Know the available resources.

Understand in advance who to contact and what equipment to mobilize if an ethanol spill occurs:

- Public safety and emergency officials – Often assist with evacuation and safety issues. These officials have limited resources and are not a substitute for cleanup personnel.
- Contractors – Emergency response should begin within hours, not days from the spill event. Knowing which contractor to call is essential. A rapid response by a contractor may be hours away.
- Staff – In the first few hours, staff personnel may need to take the initial actions to contain the release. Part of the development of emergency response plans is to train toward this need for initial containment.

### B. In the first 24 hours:

- Prevent the ethanol from reaching surface water. Quick action is essential to prevent release from reaching surface water. Potential containment methods, such as diking, should be understood in advance (i.e. Where? Who? What material? How?). Additionally, staff should understand the emergency response and containment products and equipment that are available at the facility, as well as at nearby facilities and the community.
- Collect liquid ethanol that has been contained or is pooled on the surface of the soil. Identify in advance where to find the containment equipment such as adsorbent pads, diking material, portable pumps, and any other response equipment. Some bioremediation products act as absorbent material as well, functioning like oil-dry, while degrading contaminants.
- Evaluate immediate response and remediation options. Appropriate response actions with implementing criteria should be planned prior to the release. Quickly evaluate site characteristics such as soil type, likelihood of underground utilities present, potential receptors, and estimated depth of contamination. These characteristics should guide the choice of remediation strategy.

For example, immediate excavation might be preferable as an immediate threat to public health or safety. Such as if the impacted area is free of utilities, of a porous sandy soil type, and shallow groundwater is within a wellhead protection area. Excavation is a viable method when risk to groundwater or surface water contamination is high.

Conversely, if no receptors are under immediate threat, or safety and utilities impede efficient excavation of impacted soil, then in-situ options are preferred. In-situ remediation methods are viable and flexible methods used to treat soil, groundwater, and soil vapor given appropriate duration. The first 24-hours is crucial when choosing to excavate ethanol-impacted soil, however, if another remediation option is selected, drafting a data collection plan to refine remediation strategies is recommended.



### **C. In the first week:**

- Emergency response efforts will likely continue for several days.
- Determine with public officials the degree of impact and likelihood of aquatic toxicity. There are actions that can be taken to add oxygen to the water to limit this impact.
- Continue with the chosen response/remediation strategy. This often involves confirming the extent of impacts, including a groundwater investigation as mentioned below. Begin data collection for relevant in-situ soil and/or groundwater remediation parameters and develop a work plan. Large scale excavation operations can be assisted by field screening the active excavation areas as well as adjacent soil boring investigations.
- Determine if groundwater impacts have occurred. This may be conducted in connection with the soil excavation. Denatured or neat ethanol in contact with certain types of utility lines may compromise the material over time. Review material susceptibility charts for utility line and joint gasket components.
- Conduct a vapor survey to determine the potential for vapor migration that could impact utility corridors and adjacent buildings or houses. The potential for both ethanol vapors, and methane generation and migration should be considered.

### **D. After the emergency response:**

- Next actions will depend on the type of release, temperature, and the effectiveness of the emergency response efforts in recovering the product.
- Interfacing with the regulatory agency in charge may be required when ongoing soil and groundwater investigations might drastically change the scope of the response/remediation strategy. Collection of shallow surface samples, deeper soil samples and groundwater samples through geo-probing, and installation of groundwater wells are common practices. These techniques can also be utilized for further site monitoring. Groundwater monitoring wells are a crucial need when impacts to groundwater have been confirmed, as groundwater flow direction and speed needs to be determined.
- Industry literature provides detailed information on potential remedial technologies for treatment of surface water, soil, soil vapor, and groundwater media along with a description of the benefits and limitations of each technology. A brief discussion of typical response actions is provided below.

## E. Remediation

As with all remediation projects, actions should be discussed and approved by the appropriate authority before commencing any work. With respect to the expansion of denatured fuel ethanol shipments by rail, remediation options for denaturants, in particular BTEX compounds were evaluated alongside ethanol for each environmental media.

### Soil impacts

Soils may be treated in-situ or ex-situ. The decision to treat in place or to treat following removal via excavation typically is based on the type of soils impacted, the depth of contamination, the presence of subsurface structures (e.g., utilities), and the proximity of the contamination to buildings. Ultimately the decision on whatever soil remediation technique is used will depend upon the circumstances of the site and the regulatory authority. Often there is no clear ‘silver-bullet’ solution. The techniques used are usually a compromise between the health and safety of the public and environmental receptors, the volume of the spill, and the physical characteristics of the site.

Common in-situ treatment technologies are biological (e.g., bio-augmentation) or physical (e.g., soil vapor extraction or SVE). Ex-situ treatment technologies that can be effectively implemented following excavation include biological, physical, or chemical methods such as bio-piling, thermal or electrical heating (ERH), and chemical oxidation. Additionally, excavated soils can also be disposed of off-site, depending on contaminant concentrations and receipt of disposal approvals, at a permitted landfill or land-farming facility.

#### ➤ Biological Treatment Methods

In general, there are two branches of bioremediation techniques, bio-stimulation and bio-augmentation. Bio-stimulation relies on the indigenous organisms to perform biodegradation reactions, while supplying the proper nutrient blend in-situ to promote microbiological growth and drive reactions to completion. Because oxygen is crucial for rapid ethanol biodegradation, this technique is often paired with bioventing, as discussed below. Bio-augmentation is the practice of introducing cultured microorganisms selected for breaking down a particular contaminant. These injections are often comprised of a community of several naturally occurring bacteria which serve cooperative roles in the degradation process. With both techniques, the nutrient and bacterial communities are often supplied in a dehydrated, highly concentrated form and require mixing with clean water prior to administration. Sourcing the proper water and nutrient amendments is crucial. The water must be free of chlorine (e.g., non-tap water, etc.) and other organic materials. The nutrient amendments cannot contain urea-based nitrogen. These compounds will either kill the bioremediation bacteria or be a competing molecule in biodegradation processes. In general, ethanol is one of the most readily biodegraded hydrocarbons, due to its chemical structure and lack of double bonds.

Enhanced aerobic biodegradation otherwise known as bioventing in soils is an in-situ remediation technology that uses indigenous microorganisms to biodegrade organic constituents in the unsaturated zone. Soil in the capillary fringe (located above the groundwater surface) and the saturated zone (groundwater) are not affected by this technique. In bioventing, the activity of the indigenous bacteria is enhanced by inducing air flow into the unsaturated zone using extraction or injection wells and, if necessary, by adding nutrient amendments. Bioventing can result in rapid elimination of dissolved

constituents in pore water above the groundwater table and subsequent biodegradation of residual ethanol product. It also promotes methane oxidation and likely inhibits formation of anaerobic conditions and methane generation. Note that if the soil contains significant amounts of ethanol, this type of treatment may take longer to effectively treat the soil.

Land farming, composting, and bio-piling are all forms of biological ex-situ treatment used to treat constituents. These technologies provide destruction/removal of biofuel constituents via biodegradation and volatilization. These forms of treatment require intensive handling of media (e.g., continuous tilling of the soil), especially if significant amounts of ethanol are contained in the soil. While also applicable to in-situ remediation of soil or groundwater, bio-augmentation and a nutrient blend is commonly used alongside ex-situ treatment cells, primarily because the intensive handling and mixing of the soil required serves as a necessary and effective mechanism for delivering the amendments.

Bio-augmentation is sometimes necessary or preferred to stimulate indigenous organisms due to circumstances which sterilize the indigenous communities within contaminated soil. Severe ethanol pool fires or persisting liquid products may sterilize soil environments. Most microorganisms' experience cell membrane destruction at ethanol concentrations above 15%, but are inhibited in some way between 1% and 10% (v/v) <sup>1</sup>.

Bio-augmentation cultures commonly selected for ethanol degradation are the same as utilized for more persistent and diverse crude oil compounds. A recommended nutrient amendment blend for microorganisms with access to oxygen is comprised of inorganic salts of nitrogen, phosphorus, and potassium in the ratio of 21:10:10, in addition to trace minerals such as boron, copper, chelated iron, and manganese <sup>13</sup>. Introduction of microbial communities in soil requires regulatory approval, but their limited mobility in soil often does not pose concerns when seeking approval. Nutrient amendments can support rapid plant and algae growth and in soil generally are not of concern unless storm water runoff discharges to a nearby waterway.

#### ➤ Chemical Treatment Methods

Chemical oxidation can be used to treat soil and sediment providing rapid destruction or flushing of all constituents. With sufficient contact time with the organic contaminants, chemical oxidants may be capable of converting the contaminant mass to carbon dioxide and water. This treatment method does not directly address ethanol and there is high potential for rebound if significant amounts of ethanol are present. The BTEX compounds present in denatured ethanol are less susceptible to rapid chemical oxidation and may require further treatment.

For soils with significant amounts of ethanol, surfactant enhancement/co-solvent flushing can be used for the removal in a short time frame. The water solubility of many organic contaminants is the controlling removal mechanism, so additives are used to enhance efficiencies. The high solubility of ethanol makes this technology potentially feasible, with water serving as the solvent. Note that the use of this technology in-situ requires the collection and removal of ethanol and its constituents from the underlying groundwater through treatment of the groundwater in-situ or hydraulic control (i.e., groundwater pumping) to reduce groundwater contamination and prevent plume expansion.

Soil washing is a form of chemical ex-situ treatment used for the rapid removal of all constituents. This type of contaminant mass transfer treatment does create a large amount of fluid washing that will require treatment or disposal.

In co-solvent flushing and ex-situ soil washing of denatured ethanol impacted soils, ethanol and a fraction of BTEX compounds will yield to flushing with water, yet less mobile, hydrophobic, and potentially organically adsorbed BTEX compounds will likely remain and require additional remediation strategies to address <sup>14</sup>.

### ➤ Physical Treatment Methods

Soil Vapor Extraction (SVE) technology is an in-situ remedial technology that reduces concentrations of volatile constituents, such as ethanol in the unsaturated soil zone. In this method, a vacuum is applied through wells near the source of contamination in the soil. Volatile constituents of the contaminant mass "evaporate" and the vapors are drawn toward the extraction wells. SVE can be effective with ethanol remediation because ethanol is more volatile than water and will more readily evaporate. Extracted vapor is then treated as necessary (commonly with carbon adsorption or a thermal oxidizer) before being released into the atmosphere. SVE also promotes aerobic biodegradation of biofuels and methane oxidation (if present). The moisture content of the soil can dramatically influence ethanol recovery rates because once ethanol is dissolved in water (i.e., pore water), partitioning to air is greatly reduced. The BTEX compounds may require longer vapor extraction times. When compared to ethanol's volatility, only benzene evaporates more easily, with slower rates for toluene, ethylbenzene, and xylenes <sup>21, 16, 17, 19, 20</sup>.

In-situ thermal treatment methods involve applying energy into contaminated soil and/or groundwater, raising the temperature of ethanol and other volatile compounds and encouraging them to volatilize. There are several ways to deliver heat to the contaminant mass. Heat can be applied directly by injecting steam into the subsurface. Heat can be delivered indirectly through electrical current, also known as electrical resistance heating (ERH). This method involves placing subsurface electrodes throughout the contaminant mass and in proper phase alignment as to create current between them. The resistance through poorly conductive soil creates large amounts of heat, which aid in volatilizing contaminants. The final common way heat can be delivered is chemically through exothermic reactions (reactions which give off heat) of injected reagents. This method is technically feasible if injection of additional fluids or chemicals will not destabilize the contaminant perimeter. Injection of reagents such as Fenton's agents or persulfates can yield heat in the subsurface and may be paired with other injection strategies for co-contaminants or to enhance biological amendments.

While the above in-situ thermal treatment methods are effective ex-situ, costs often prohibit excavation in addition to treatment. However, these methods may be ideal when soil reuse is a goal or sensitive areas need to be removed or immediately backfilled, such as near utilities or cathodic protection sites. The most rapid ex-situ treatment method, but most cost-prohibitive is soil incineration. This removed contaminated soil may require dewatering prior to treatment. Once prepared, a permitted soil incineration system can be mobilized to the site or conversely hauled to an off-site permitted facility. All compounds in denatured ethanol respond similarly to thermal treatments.

When treating soil ex-situ, providing containment using liners and covers is another way to remove human and/or ecological health risk. The containment can prevent leaching into groundwater, and control of soil vapor conditions beneath structures. Liners and covers may require periodic replacement and stockpiles may require methane monitoring.

Landfilling provides immediate transfer and off-site disposition of constituents, but is usually the most cost prohibitive and prevents soil reuse or other sustainable initiatives. This requires

transportation and disposal at a facility permitted to accept the soil, after regulatory approval of the profiled soil.

### Soil Vapor

As discussed in Chapter 5, Section C. a soil vapor survey is a critical action item shortly following emergency response protocol. Soil vapor originating from highly volatile contaminants such as ethanol and BTEX compounds or from degradation products such as methane can migrate through any preferential pathway within the subsurface. A thorough soil vapor survey involves identifying:

- a contaminant mass capable of generating appreciable levels of impacted soil vapors,
- all potential migration and accumulation routes and spaces between the subsurface and the ground surface, and
- all potential exposure pathways to humans, including structures and spaces which might be occupied by humans for any length of time.

Many state regulatory agencies provide guidance on conducting a complete vapor intrusion (VI) survey. Common exposure routes by vapor intrusion include unsealed or compromised foundations within basements in habited structures, floor drains, sumps, underground utility corridors, and elevator shafts.

If complete exposure pathways exist, action is required to eliminate the pathway, either by removing the source contaminant mass or by installing engineering controls which mitigate the vapor before entering the occupied space or prevent vapor from entering the space. Many of the remediation technologies discussed above, particularly in-situ technologies, acts to remove volatile contaminants and in some cases all soil vapors. In-situ methods which generate methane, such as anaerobic biodegradation, are not recommended if vapor intrusion is a risk at the site.

Human health risk from ethanol vapors is very low, as very high concentrations are required before regulatory and health standard thresholds are exceeded. Methane generation is the primary concern with ethanol-related vapor intrusion issues. However, permanent and temporary vapor intrusion mitigation systems are available for structures when vapor risks are present. Due to the high susceptibility of ethanol to biodegradation, temporary vapor intrusion could be installed while in-situ amendments remove contaminants.

### Surface water impacts

The effective treatment of surface water and thus the chosen remediation methods, depend on several factors. These factors may include the amount of ethanol released, whether the impacted surface water is a lake or a flowing stream, the classification of the water body (i.e. is it used as a drinking water source), meteorological conditions (i.e., wind speed, temperature, etc.), and whether the response can capture the ethanol before it dissipates.

As noted, ethanol is infinitely soluble in water (it dissolves completely). When released into surface water bodies, ethanol may initially float as a light nonaqueous phase liquid (LNAPL) as it is mixed near the

surface. This is a short-term condition; dilution and mixing by waves and currents will rapidly dissolve ethanol into the water column. Typical physical treatment methods such as use of boom and absorbents are not effective unless LNAPL is present<sup>21</sup>.

An effective treatment method to address ethanol release in surface water is enhanced aerobic biodegradation. This treatment methodology adds oxygen to water, increasing the number and vitality of indigenous microorganisms performing biodegradation. Aerator technologies (e.g., floating aerators) or agitation (e.g., fountain sprayers) may be used in smaller water bodies. Aeration treatment will inhibit the formation of anaerobic conditions and methane generation. The addition of oxygen may also restore dissolved oxygen levels to mitigate some of the impacts to fish and other aquatic organisms.

Beyond or in addition to aeration techniques, commercial oxygen releasing compounds (ORC) are available which supply a rapid, or steady, source of dissolved oxygen into the water column. Products can be a quickly reacting oxidizer. These chemicals are supplied in powder form and can be distributed into stagnant wetlands, ponds, lakes, or groundwater where traditional mechanical aeration is infeasible. These products have been commonly used in treating large BTEX and ethanol groundwater plumes<sup>21</sup>.

In general, bio-stimulation (e.g., nutrient amendment), bio-augmentation, and chemical oxidants are generally not recommended nor approved by regulatory authorities for surface water remediation. Particularly in flowing systems (e.g., rivers, streams, etc.), the introduction of these amendments have the potential to create unintended consequences outside of the contaminated zone such as algal blooms or pH shifts. In addition, some commercial bio-augmentation products remain largely untested for long-term ecological effects in non-impacted areas by EPA and remain on the EPA's National Contingency Plan (NCP) Product Schedule for emergency response uses. However, while EPA's NCP Product Schedule does not equate to an approval or recommendation for use, independent testing on many of these products is readily available in the NCP Product Schedule and shows they are pathogen-free, non-mutagenic, and effective<sup>24</sup>.

## Groundwater impacts

### ➤ Biological Treatment Methods

Persistent concentrations of ethanol (and potentially BTEX) are often found in groundwater plumes due to the increased difficulty of treatment resulting from inaccessibility and oxygen demand. As discussed below, ex-situ groundwater treatment methods are often cost-prohibitive. In Pinnacle's experience once impacts have reached a groundwater aquifer amendment, injections of bio-stimulation, bio-augmentation, and chemical oxidation are much more likely to be approved by regulatory authorities, particularly if the contamination plume is likely to migrate.

Enhanced aerobic biodegradation is the simplest form of in-situ treatments harnessing indigenous organisms. This treatment often utilizes air sparging (AS) to add oxygen to groundwater and the capillary fringe, and like surface water or soil treatments, the AS stimulates the growth and vitality of indigenous organisms performing biodegradation. The diffusion of oxygen into the groundwater and capillary fringe will inhibit the formation of anaerobic conditions and methane generation as well as the dissolution of pure ethanol product. Like surface water aeration, this treatment methodology is

limited because high concentrations of ethanol can be toxic to microorganisms. The limitations of this technique include difficulty satisfying biological oxygen demand using only injected air, or when oxygen is sufficient, other essential nutrients may be depleted and halt biodegradation <sup>21</sup>. Augmentation with additional organisms, nutrients, and chemical-based oxygen release agents are discussed in subsequent sections and may be paired with this technology for improved biodegradation efficiencies.

Bio-stimulation of the groundwater involves the injection of soluble nutrients which restore or increase existing biodegradation rates by indigenous organisms. The blend of nutrients required to enhance aerobic biodegradation in groundwater is the same as used in other environmental media. For petroleum hydrocarbons and denatured fuel ethanol, the blend is often solid inorganic salts in a ratio of 21:10:10 nitrogen, phosphorus, potassium respectively, plus various trace minerals. This is the same nutrient amendment blend previously discussed for soil remediation. Numerous field and laboratory studies have shown how crucial the addition of nitrogen and phosphorus are in driving biodegradation quickly and completely to non-toxic endpoints, even with temperatures around 4°C and on more recalcitrant petroleum hydrocarbons <sup>7, 11, 5</sup>. Depending on the size and concentration of the contamination plume, multiple injections may be required during the life of the remediation project.

Bio-augmentation of the groundwater may be required if indigenous microbial communities do not have the capability to degrade a particular set of constituents or toxicity has inhibited bacterial populations or metabolism. Estimated lethal ethanol concentrations to bacterial populations in groundwater are approximately 100,000 mg/L <sup>14</sup>. More often than not, the proper microbes for degrading a contaminant naturally exist within the saturated or unsaturated zone, but may demonstrate an 'acclimation period' during which microbial populations experience a dramatic shift in response to the new environment <sup>7, 11</sup>. If monitoring reveals nutrients and oxygen are present, biodegradation is not progressing, bio-augmentation may be necessary. Many commercial products exist for augmenting the microbial community, and many also contain nutrients. As discussed above, microbes suited for petroleum hydrocarbons are sufficient for degradation of ethanol and BTEX compounds. If the aquifer is a drinking water source, bio-augmentation and/or bio-stimulation may not be recommended, as bio-stimulation treatments may surpass drinking water nitrate standards and the introduction of non-native bacterial populations may not be permitted.

Enhanced aerobic biodegradation can also be conducted ex-situ as part of a groundwater extraction and treatment system. Bioreactors or tanks are commercially available and are equipped with aeration and nutrient injection systems. The size and scale of the treatment systems depend on the contaminant loading and groundwater extraction rates necessary to achieve groundwater hydraulic control.

In contrast to aerobic biodegradation discussed above, another form of treatment is enhanced anaerobic biodegradation, which occurs naturally after the preferred final electron acceptor (oxygen) has been depleted. Anaerobic biodegradation of ethanol will continue, however more slowly than aerobic activities, until all alternative electron acceptors have been consumed (nitrate, iron, and sulfate). Once these have been consumed, methane generation will begin, the details of which are discussed below in monitored natural attenuation methods.

Enhanced anaerobic biodegradation is preferred when access to groundwater or remote site conditions limit the feasibility of managing an active aerobic remediation system which often requires consistent electricity, increased monitoring, and well maintenance (due to mineral precipitation in

well screens). In-situ amendments delivered to groundwater often include emulsified vegetable oil (to stimulate anaerobic

and reducing conditions) with an electron acceptor source. The table below reflects the preferential utilization of electron acceptors by microbes, with aerobic respiration proceeding the quickest and methanogenesis the slowest.

Process	Electron Acceptor	Metabolic Products	Relative Potential Energy
Aerobic Respiration	O <sub>2</sub>	CO <sub>2</sub> , H <sub>2</sub> O	High
Denitrification	NO <sup>3-</sup>	CO <sub>2</sub> , N <sub>2</sub>	
Iron reduction	Fe <sup>3+</sup>	CO <sub>2</sub> , Fe <sup>2+</sup>	
Sulfate reduction	SO <sub>4</sub> <sup>2-</sup>	CO <sub>2</sub> , H <sub>2</sub> S	
Methanogenesis	CO <sub>2</sub>	CO <sub>2</sub> , CH <sub>4</sub>	Low

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Site geochemistry may be more important than relative potential energy when evaluating which electron acceptor to supply groundwater. Typical examples of amendments include fertilizers (NO<sup>3-</sup>), suspended small-particle iron (Fe<sup>3+</sup>), and soluble sulfate products. Many commercial products are available and tailored to each degradation pathway that can be mixed and delivered easily as a low to medium viscosity liquid. Injection amendments under these conditions and degradation are expected to persist in groundwater anywhere from 1 to 30 years and should be approved as part of a remediation plan submitted to regulatory authorities. Aquifer type and groundwater migration may greatly influence applicability of this remediation method.

Monitored natural attenuation (MNA) is a strategy best chosen in sites with no risks to receptors, environmental or human, from methane or ethanol and approved as part of a monitored natural attenuation plan submitted to regulatory authorities. While the toxicity of ethanol is very low relative to crude oils, mobility of the ethanol plume and methane generation poses the greatest risk when choosing to forgo an active remediation program. As shown in the table above, methane generation will only begin by methanogenic bacteria after other electron acceptors are depleted. Plumes of ethanol may undergo several types of degradation at once throughout different plume zones which have access to contrasting nutrients and oxygen. However, methane generation from purely methanogenic conditions ranges from approximately 20 to 60 mg/L per day. Field and laboratory studies have shown a lag time of 6 to 10 weeks for methane generation from time of the release, while peak methane generation can occur anywhere between 3 to 8 months following a release<sup>21</sup>. Methane typically will reside in soil gas or utility corridors until it is degraded in the presence of oxygen, creating a further depression of oxygen above the plume. In addition to vapor intrusion risks, methane poses an explosion hazard if allowed to accumulate between concentrations of 5 and 15%<sup>21</sup>.

Denatured fuel ethanol has additional considerations in remediation strategies due to the presence of less-soluble denaturants, particularly BTEX compounds. As discussed in previous sections above, ethanol can increase the aqueous concentration of BTEX compounds due to a co-solvent effect<sup>14</sup>. Despite this effect, some BTEX compounds will likely remain in upper layers of soil due to affinity for soil particles and incomplete solubility. BTEX compounds have about twice the affinity for oil than water. In gasohol spills (gasoline with 5-20% ethanol), experimental data has shown at 80% ethanol in groundwater, aqueous BTEX concentrations increased from 30 mg/L to 1100 mg/L (a 36-fold

increase)<sup>14</sup>. In denatured fuel ethanol spills, however, co-solvency equilibrium is expected to be reached before an effect of this magnitude. Secondly, ethanol consumes oxygen and nutrients preferentially over BTEX compounds during biodegradation, therefore suppressing normally expected BTEX biodegradation rates in aerobic conditions. A similar effect can be expected under anaerobic conditions, with slower overall biodegradation rates. Continuing with aerobic bioremediation techniques beyond the removal of ethanol will ensure all BTEX compounds are completely mineralized into non-toxic endpoints.

Constructed wetlands may be used as a form of ex-situ biological treatment. This technique provides treatment of extracted groundwater via multiple mechanisms, including biodegradation, phytoremediation, photolysis, and volatilization (direct and indirect via plant uptake). Once harvested groundwater is placed back into an aerobic environment, biodegradation of ethanol is expected to proceed quickly. Constructed wetlands have value when denaturant composition is the dominant threat to receptors. A pilot-study of gasoline contaminated groundwater pumped to a constructed wetland using subsurface aeration lines could remove 88% of total BTEX compounds during one year of operation<sup>2</sup>. Constructed wetlands require a large amount of land, especially if ethanol requires dilution with water to reduce toxicity to plant life.

#### ➤ Chemical Treatment Methods

Chemical oxidation is a form of in-situ treatment that uses a variety of chemical oxidants and application techniques to bring oxidizing materials into contact with subsurface contaminants and to remediate the contamination. With sufficient contact time this technology can provide for the rapid destruction of biofuels, inhibits methane generation, and may indirectly address residual ethanol free product which is dependent on oxidant kinetics.

Surfactant enhancement, co-solvent flushing, and surfactant dispersant addition are other methods that can be used for in-situ treatment of constituents. Surfactant enhancement is a form of chemical remedial technology used for the dispersal/breakup of free product to aid and allow for biodegradation processes. Like in surface water, the application of surfactants can enhance remediation in three ways: by increasing contaminant solubility to improve pump-and-treat performance; by decreasing the mobility of contaminants to prevent their migration; and to speed the rate of biodegradation of contaminants. Surfactant based treatments are tailored towards hydrophobic contaminants such as gasoline used as denaturant, as ethanol readily dissolves.

Co-solvent flushing consists of a network of injection and extraction wells designed to hydraulically sweep the targeted volume of an aquifer that is contaminated with free ethanol product. Because of the high solubility of ethanol, water is an effective solvent for flushing. Methane generation is likely if dissolved ethanol remains following completion of the treatment.

#### ➤ Physical Treatment Methods

Air sparging is also an in-situ physical treatment method that injects contaminant-free air into the subsurface saturated zone, enabling a phase transfer of contaminants from a dissolved state to a vapor phase. The air is then vented through the unsaturated zone. This technology is typically coupled with soil vapor extraction to remove the vapors from the soil (AS/SVE), including any methane that may be generated. As discussed in the soil section, vapors may require treatment above ground. This form of treatment is not effective for constituents with low Henry's Law constant, low vapor pressure, and/or low biodegradability, such as BTEX compounds. The biggest advantage of this technology for ethanol is to promote aerobic biodegradation, inhibiting formation of anaerobic conditions and methane generation.

Multiphase extraction (MPE) is a technology that simultaneously extracts volatile compounds in soil vapor and groundwater. This method provides the physical removal of mobile ethanol, volatile fractions of residual ethanol, and dissolved-phase fuel constituents. This treatment promotes aerobic biodegradation and is likely to inhibit methane generation. The ex-situ management and treatment of extracted liquids and vapors can be expensive. It is often necessary to extract an excessive volume of groundwater to address the dissolved plume. Discharge permits are often required when handling large volumes of water and should be considered in a remediation feasibility study. These permits are often National Pollutant Discharge Elimination System (NPDES) permits sought from state governmental units which manage pollution control or discharging to a local publically owned treatment works (POTW).

Air stripping is an ex-situ physical treatment process consisting of forcing air through extracted groundwater to provide removal of readily strippable compounds (constituents with a high Henry's law constant and vapor pressure such as ethanol). Because of the solubility of ethanol, batch processing or utilization of two or more air stripping units in series may be required, along with the heating of the water prior to stripping. Treatment of vapors from the air stripper may also be required, and an air permit may be required when exhausting to ambient air. These permits are often described as general De Minimis permits and are often issued by the same agencies which issue water discharge permits.

## Chapter 6– Summary: Am I prepared?

Ethanol production and transportation is expected to increase in the coming years. As the knowledge base grows, it is important to share information widely to establish a sound system of requirements and actions moving forward.

- ✓ Review the required contingency plans already in place and establish any additional ones to help prepare.
  
- ✓ Decide whether the staff/personnel are properly trained. Will they know what type of action to take in an emergency?
  
- ✓ Assess the situation regarding facilities and transport operations. Consider an audit of the physical systems, process safety management, and maintenance programs. Are they safe and reliable?
  
- ✓ Implement engineering controls and improvements that have been identified to reduce the likelihood that problems will occur or lessen the impacts if the unplanned does occur.
  
- ✓ Seek additional information. The appendices contain case studies that may uncover the potential for a release in daily operations, as well as additional information that can be used.

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## Appendix A – Federal Regulations and How They Impact Ethanol Facilities

There are numerous federal regulations intended to prevent ethanol releases to the environment and keep the public safe. The list of regulations discussed below is for educational purposes and not intended to be an all-inclusive list.

### 1. Facility Response Plan

Under the Oil Pollution Act of 1990 and Section 311 of the Clean Water Act, owners or operators of tank vessels, offshore facilities, and certain onshore facilities must prepare and submit “A plan for responding, to the maximum extent practicable, to a worst-case discharge, and to a substantial threat of such a discharge, of oil or a hazardous substance.” This plan is the Facility Response Plan or “FRP.” This requirement applies to all offshore facilities and any onshore facility with a total storage capacity that is greater than 1 million gallons that “because of its location, could reasonably be expected to cause substantial harm to the environment by discharging into or on the navigable waters, adjoining shorelines, or the exclusive economic zone.”

It should be noted that U.S. Environmental Protection Agency (USEPA) has adopted a very conservative definition of “navigable waters”. Effectively onshore facilities that meet the storage capacity criteria are required to prepare and submit FRPs regardless of location or proximity to navigable waters. Facilities are required to submit their FRPs to the U.S. EPA for review and approval.

Ethanol is included in Oil Pollution Act of 1990 because gasoline is an oil; tanks storing ethanol denatured with gasoline are considered oil tanks and the shell capacity of such tanks must be included in the facility’s total oil storage capacity when determining applicability under 40 CFR Part 112, including the FRP requirements. (*Nov. 7, 2006, Letter from Susan Parker Bodine of EPA to Mr. Bob Dinneen of Renewable Fuels Association*).

### 2. Spill Prevention, Control and Countermeasures Plan (SPCC)

Originally published in 1973 under the authority of Section 311 of the [Clean Water Act](#), the Oil Pollution Prevention regulation sets forth requirements for prevention of, preparedness for, and response to oil discharges at specific non-transportation-related facilities in 40 CFR Part 112. To prevent oil from reaching navigable waters and adjoining shorelines, and to contain discharges of oil, the regulation requires facilities storing 1,320 gallons in aboveground storage or more than 42,000 gallons of oil in underground storage to develop and implement Spill Prevention, Control, and Countermeasure (SPCC) Plans. The SPCC Plan must establish procedures, methods, and specify equipment requirements for oil spill prevention, preparedness, and response procedures. The Plan is intended to prevent oil discharges to navigable waters and adjoining shorelines. As noted under FRP applicability, since ethanol is denatured with gasoline—an oil—the volume of denatured ethanol storage capacity counts toward the 1,320-gallon threshold.

### 3. Risk Management Program (RMP)

Under the authority of section 112(r) of the [Clean Air Act](#), the [Chemical Accident Prevention Provisions](#) require facilities that produce, handle, process, distribute, or store certain chemicals to develop a Risk

Management Program, prepare a Risk Management Plan (RMP), and submit the RMP to EPA. Covered facilities were initially required to comply with the rule in 1999, and the rule has been subsequently amended on several occasions, most recently in 2004. The plans must be reviewed, updated, and resubmitted every five years or as the facility makes changes.

For ethanol plants, the RMP threshold triggers may include:

- Ammonia: Anhydrous 10,000 lbs. or >20% Aqueous 20,000 lbs.
- Denaturant
- Chemical with an NFPA 4 rating: 10,000 lbs.

The Risk Management Program includes:

- Hazard assessment that details the potential effects of an accidental release, an accident history of the last five years, and an evaluation of worst-case and alternative accidental releases.
- Prevention program that includes safety precautions and maintenance, monitoring, and employee training measures; and
- Emergency response program that establishes emergency health care, employee training measures and procedures for informing the public and response agencies (e.g. the fire department) should an accident occur.

The Risk Management Program is about reducing chemical risk at the local level. This information helps local fire, police, and emergency response personnel (who must prepare for and respond to chemical accidents), and is useful to citizens in understanding the chemical hazards in their communities.

#### 4. Process Safety Management (PSM)

To help ensure safe and healthful workplaces, OSHA has issued the Process Safety Management (PSM) of Highly Hazardous Chemicals standard ([29 CFR 1910.119](#)), which contains requirements for the management of hazards associated with processes using highly hazardous chemicals. OSHA's PSM standard emphasizes the management of hazards associated with highly hazardous chemicals and establishes a comprehensive management program that integrates technologies, procedures, and management practices.

For ethanol plants, the PSM threshold triggers may include:

- Ammonia: Anhydrous - 5,000 lbs. or >44% Aqueous - 15,000 lbs.
- Flammable Mixtures: Any flammable liquid or gas – 10,000 lbs.

#### 5. Emergency Action Plan (EAP)

OSHA requires that every employer with 10 or more employees must maintain a written emergency action plan (29 CFR 1910.38), kept in the workplace, and available to employees for review.

An emergency action plan must include procedures for reporting a fire or other emergency, procedures

for emergency evacuation; including type of evacuation and exit route assignments; procedures to be followed by employees who remain to operate critical plant operations before they evacuate; procedures to account for all employees after evacuation; procedures to be followed by employees performing rescue or medical duties; and the name or job title of every employee who may be contacted by employees who need more information about the plan or an explanation of their duties under the plan.

An employer must review the emergency action plan with each employee covered by the plan. The emergency action plan must be reviewed when the plan is developed or the employee is assigned initially to a job, the employee's responsibilities under the plan change, or the plan is changed.

## 6. Storm Water Pollution Prevention Plan (SWPPP)

The Clean Water Act (Section 402(p)) requires that operators of “discharges associated with industrial activity” obtain a National Pollutant Discharge Elimination System (NPDES) permit to control storm water discharges associated with eleven categories of industrial activity. EPA regulations (40 CFR 122.26) define the categories of industrial activity required to obtain NPDES permits, and specify the application requirements for these permits. To regulate storm water discharges from these industrial activities, EPA and authorized States issue NPDES general permits.

Most industrial storm water discharges are covered under general NPDES permits, as opposed to individual NPDES permits, although States and USEPA can and do issue individual NPDES permits to some facilities for storm water discharges based on site-specific or industry-specific concerns. General permits are used primarily to avoid the need to issue multiple permits, and instead only require a single permit to cover a large number of industrial facilities performing similar types of activities. To be covered under a general permit, an eligible operator of an industry must read the general permit, typically develop a SWPPP, comply with any special eligibility provisions, and submit a notice of intent (NOI) or permit application to the permitting authority.

Ethanol manufacturing falls under NPDES Standard Industrial Classification Major Group 28 (Industrial Organic Chemicals), and, thus, requires coverage under an industrial storm water permit and the development of a SWPPP.

## 7. Oil Spill Prevention and Response Plans

As provided in 49 CFR 130, this rule, administered by the Department of Transportation, adopts requirements for packaging, communication, spill response planning and response plan implementation intended to prevent and contain spills of oil during transportation, including an analysis of a worst-case discharge. It requires comprehensive response plans, known as Spill Response Plans (SRP), for oil shipments in bulk packaging (i.e., cargo tank trucks, rail tank cars, and portable tanks) in a quantity greater than 42,000 gallons per packaging and for petroleum oil shipments in bulk packaging of 3,500 gallons or more. The SRP is applicable to ethanol transported with petroleum in a concentration by weight greater than 10 percent.

## Appendix B – Selected Case Studies ITRC



### Technical/Regulatory Guidance

## Biofuels: Release Prevention, Environmental Behavior, and Remediation



September 2011

Prepared by  
The Interstate Technology & Regulatory Council  
Biofuels Team

Public document available with permission of the ITRC (Interstate Technology & Regulatory Council) 2011.Washington, D.C.: Interstate Technology & Regulatory Council, Biofuels Team  
<https://itrcweb.org/wp-content/uploads/2024/09/biofuels-1.pdf>

## Appendix C – Selected Case Studies MassDEP

### LARGE VOLUME ETHANOL SPILLS – ENVIRONMENTAL IMPACTS AND RESPONSE OPTIONS

*Prepared for:*



*Prepared by:*



*Shaw's Environmental and Infrastructure Group  
11 Northeastern Boulevard  
Salem, New Hampshire 03079*

*July 2011*

Public document available at the Massachusetts Department of Environmental Protection  
<https://www.mass.gov/doc/large-volume-ethanol-spills-environmental-impacts-response-options/download>

## Appendix D – Groundwater Monitoring Reference

Ground Water  
Monitoring & Remediation

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# Long-Term Groundwater Monitoring Results at Large, Sudden Denatured Ethanol Releases

by Roy F. Spalding, Mark A. Toso, Mary E. Exner, Gregory Hattan, Tom M. Higgins, Adam C. Sekely, and Shane D. Jensen

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### Abstract

Hundreds of groundwater samples were collected at E95 (95% ethanol, 5% gasoline) train derailment spills in Balaton and Cambria, Minnesota and South Hutchinson, Kansas. Most samples were analyzed for benzene, toluene, ethylbenzene, and xylenes (BTEX), ethanol, methane, acetate, terminal electron acceptors, and field parameters. At each site, maximum groundwater ethanol concentrations at percent levels were restricted to the release area and downgradient ethanol transport was not detected. A shallow, anaerobic groundwater zone characterized by the absence of dissolved oxygen, low nitrate (less than 1 mg N/L), high Fe<sup>+2</sup>, and high dissolved methane (more than 10,000 µg/L) and BTEX formed and spread downgradient from each release area. BTEX appeared to be persistent. Methane appeared to be generated within the capillary fringe and very shallow groundwater and migrate laterally. Methane's high oxygen demand promotes anaerobic conditions within the shallow groundwater. Estimated and measured methane soil gas concentrations exceeded the lower explosive limit. Long-term monitoring at South Hutchinson and Cambria using 1 to 5-foot (0.3 to 1.5 m) well screens straddling the capillary fringe and the shallow water table effectively demonstrated the presence of high ethanol (~1%) and benzene (more than 250 µg/L) concentrations 5 years after the release. The wells appear impacted by long-term ethanol inputs from the vadose zone where ethanol has persisted for years after the initial release. Toxicity, volatile fatty acids, excess hydrogen production, and/or exudate coatings could be responsible for ethanol's preservation. High acetate and hydrogen concentrations at South Hutchinson indicated that fermentation was actively occurring in the very shallow groundwater and/or in the lower capillary fringe. Short-screened (1 to 5 feet; 0.3 to 1.5 m) nested wells were pivotal to improving our understanding of ethanol's behavior.

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Ground Water Monitoring & Remediation  
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NGWA.org

Public document available at the University of Nebraska-Lincoln: <http://digitalcommons.unl.edu/natrespapers/328/>

## Appendix E – Acknowledgment & Revision History

### Acknowledgment

This guideline was originally developed in 2016 by Pinnacle Engineering, Inc. for the Renewable Fuels Association to provide technical and regulatory guidance for preventing and mitigating releases of denatured fuel ethanol.

The 2025 revision was comprehensively updated by Justin Schultz, Director of Environment, Health and Safety, Renewable Fuels Association, to reflect current industry practices, regulatory updates, and scientific advances in spill prevention, response, and remediation.

The Renewable Fuels Association recognizes Pinnacle Engineering’s foundational contribution to the original edition and gratefully acknowledges the continued input of ethanol producers, safety professionals, and emergency response partners whose experience informs this living document.

### Revision History

<b>Version / Year</b>	<b>Prepared By</b>	<b>Summary of Changes</b>
March 2013 (Original Publication)	Pinnacle Engineering for RFA	First edition summarizing ethanol release prevention and mitigation guidance.
July 2016 (1st Revision)	Pinnacle Engineering for RFA	Updated with additional case studies and expanded regulatory discussion.
December 2024 (5th Revision) → Published January 2025	Justin Schultz, Director EH&S, RFA	Comprehensive modernization: updated regulatory citations, enhanced bioremediation and remediation sections, current EIA/PHMSA data, and new best-practice guidance for facilities and transporters.

### Document Control

This manual is maintained by the Renewable Fuels Association (Environment, Health & Safety Department). For questions, comments, or future revisions, please contact:

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