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Denatured Fuel Ethanol: Guideline for Release Prevention & Impact Mitigation

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Chapter 1 – Introduction

A. Introduction

This updated document is a discussion of the best practices for preventing releases of denatured fuel ethanol to the environment, the likely impacts if a release does occur, and the mitigation techniques to address a release. This information may be useful to fuel producers and transporters of ethanol, as well as emergency and environmental responders like Local Emergency Planning Committees (LEPC). The information is presented in a practical format that a producer or transporter can use to take action at facilities and transport operations, both prior to and after releases. The document has been prepared by engineers who work in the ethanol industry utilizing real world experiences as responders to denatured fuel ethanol releases. The important regulatory and scientific concepts are gathered here as a guideline of best practices. Each release is different so no one response strategy will be adequate for every situation. This document has been expanded from its original publication in March 2013 to include current information on enhanced bioremediation and the growing rail transportation industry. Additional details and references are presented in the Appendices.

- Appendix A provides further explanation of Federal requirements for biofuel production facilities and shipments.
- Appendix B is a reference to an excellent technical document called *Biofuels: Release Prevention, Environmental Behavior, and Remediation*. The document provides more detailed technical information on subjects covered in this guide and case studies of ethanol releases that help illustrate the information discussed in this guide.
- 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 [22].

Ethanol is a renewable fuel that is produced by a fermentation and distillation process. The most common source of ethanol in the United States in 2013 was overwhelmingly corn, accounting for 98%. This quantity equates to less than 3% of global grain supplies [15]. However, it can be produced from other products such as sugar cane, saw grass, and other natural products that are conducive to the fermentation / distillation process. Ethanol is a polar solvent that is water-soluble and has a 55°F flash point. Ethanol has a vapor density of 1.59, which indicates that it is heavier than air. Consequently, ethanol vapors do not rise, similar to vapors from gasoline, which seek lower altitudes. Ethanol's specific gravity is 0.79, which indicates it is lighter than water; however, it is water-soluble and therefore will thoroughly mix with water. Ethanol has an auto-ignition temperature of 685°F and a boiling point of 173°F. Ethanol is less toxic than gasoline. Carcinogenic compounds are not present in ethanol [18]. In a pure form, ethanol does not produce visible smoke and has a hard-to-see blue flame. In a denatured form, there is little to no smoke, but a slight orange flame may be visible.

The biggest difference between ethanol and hydrocarbon fuels (including crude oils) is the water solubility. This property changes how ethanol will react in the environment, including surface and ground water, and soils.

C. Key Issues & Definitions

As the production of ethanol continues to increase, handling and transportation of ethanol will also increase. Even in well-managed operations, the chance for releases to the environment is always present. Producers and transporters should be aware of the risks and concerns associated with ethanol releases, and of the fate and transport of ethanol in air, surface waters, soil, and groundwater.

The first step is to be aware of the actions that can be taken to prepare facilities and transportation operations to:

- ✓ prevent releases, and
- ✓ make decisive actions to mitigate the impact of a release to the environment.

At ethanol facilities, two types of plans including emergency response and environmental mitigation plans are required by both Federal and state regulations to identify potential problems and increase facility preparedness. Ethanol plant personnel should be well trained in these plans, and should know what to do in the event of a release. Beyond plans, there are engineering controls that can be implemented to reduce the chance that problems will occur.

Transporters, largely railroads, are required by Federal regulations to have response plan contingent upon volume capacity of the vessel or rail tank car. Railroads' extensive engineering controls and internal safety standards along with infrastructure improvement have been increasing in the last five years due to domestic crude oil shipment demands [3, 4].

Next is to realize that if a release occurs, quick action can minimize the impact to the environment.

Knowing what plant personnel can do, who to call, and having response contractors lined up is important and can greatly mitigate the environmental impact of a release. There are many issues beyond the environmental impacts, such as immediate safety concerns and potential community impacts. Regulators must be notified. Information will need to be provided to all of these stakeholders. The management of the process will determine the effectiveness of the outcome, and will limit the potential cost and negative exposure to the company. The knowledge base has increased significantly in the past few years and there are many options available to prepare, prevent, and take action.

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 with 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 the most popular E20, E30, and E40 blends are rapidly growing products for flex-fueled vehicles (FFVs), comprised of 20%, 30%, and 40% ethanol within gasoline, respectively [15]. MLBs do not have unique placard numbers, as any gasoline blend comprising more than 10% ethanol receives the DOT placard UN3475 [23].

Flex fuel (formerly 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 amount of hydrocarbon added at the manufacturing location. For ethanol shipments in the United States, a small amount of gasoline (2% - 5%) is added to ethanol to make the ethanol un-drinkable and avoid the required excise taxes on beverage alcohol. The most common ethanol product shipped by rail is called E98 and contains approximately 2% gasoline [6]. Denatured fuel ethanol is usually shipped from ethanol producers to fuel blending terminals where it is mixed with gasoline in the ratios discussed above prior to delivery to the retail station and ultimately consumers. In the United States denatured ethanol is shipped as “Alcohol, not otherwise specified” (N.O.S.) (DOT placard: UN1987).

Chapter 2 – Why are there releases?

A. Just as in the petroleum industry, the production, storage, and transport of product create risk.

Those risks are highest during transfers and during transport. Ethanol is moved via cargo tank truck, rail tank car, barge, and pipeline across the U.S. every day. Just as with petroleum facilities and pipelines, even thoughtful and carefully managed systems can fail. Mechanical components break, human error occurs, and malfunction of automated systems is always a possibility. Ethanol facilities are designed and operated with safety and environmental protection in mind, but awareness of the potential for an accident is an important part of any process or industry.

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 potential for a release is heightened by failure of transfer mechanisms, accidental overfilling, and the design capability of containment. Historical releases at production facilities are typically of a smaller scale, though large releases have occurred as a result of catastrophic anomalies, such as fire from a lightning strike.

B. During transport, the potential is higher for large-scale releases.

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

Demand on transporters, particularly railroads; have resulted in increased unit train shipments of biofuel and gasoline precursors and subsequently several large-profile derailments of these flammable fuels. Despite this demand, derailment rates have been declining, dropping 5.8% per year from 2000 to 2012 [9].

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

A. Federal Regulations for Facilities

Federal regulations that apply to the majority of ethanol facilities require the preparation of several plans designed to create awareness, prevent releases, and minimize the impact of releases. 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 provides a means whereby releases can be prevented and appropriately managed should they occur. Ethanol facilities are responsible for determining which plans are applicable and properly implementing all aspects of the required plan, which in turn will serve as a great asset and resource in the event that a release incident should occur.

B. Federal Regulations for Transporters

Federal regulations that apply to transporters, primarily railroads, are largely regulated by the Department of Transportation (DOT) and the Federal Railroad Administration, as well as satellite departments such as The Pipeline and Hazardous Materials Safety Administration. This particular group of regulatory authorities has recently released an enhanced rail tank car standard for the transportation of ethanol and crude oil. While rail tank cars carrying crude oil must be retrofitted by as soon as 2017, ethanol was placed in a separate category as a medium hazard liquid and has until 2023 to update rail tank cars to include such items as improved pressure relief valves, thermal protection, and additional shielding. Specific guidance on transporting hazardous materials including speed limits across varying risk areas and braking capacity were addressed in the May 2015 rule [25].

Railroads have strict internal training programs and rules which make the handling and transport of ethanol as safe as possible. Contractors assisting emergency response efforts must comply with railroad safety and procedural policies, but awareness and risk management skills encouraged by ethanol facility personnel in this section wholly apply to all railroad personnel and contractors.

C. State and Local Requirements for Facilities

Many state regulations mirror the requirements established by the federal regulations, however, many states and some local governments have also implemented additional requirements in regards to release prevention and response. Some general rules of thumb with regards to 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 ask that copies of the aforementioned plans (see Chapter 3.A) be provided to local responders in the case of an emergency.
- In some instances, states have primary enforcement responsibility (primacy) over EPA for implementing regulations. One such instance includes the National Pollutant Discharge Elimination System (NPDES), which encompasses SWPPPs. Facilities requiring SWPPPs must be aware of state permitted SWPPP requirements for release prevention when developing those plans.

While it is preferred to prevent all releases from occurring, unforeseen circumstances necessitate responding to a release. State release reporting requirements widely vary and facilities must be familiar with and prepare for these well in advance of an incident. Both federal and state requirements should be accurately addressed in any required release prevention plans. In an emergency, these plans become a great asset and resource to facilitate compliance with all applicable federal and state regulations. In a review of release reporting, the categories that tend to vary the most from state to state include the following:

- 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
- Special requirements associated with the media to which the release occurred
- Whether or not an onsite release to an impermeable surface (i.e. within secondary containment) is considered reportable
- Which agencies must be notified for different kinds of releases

Despite these variations in reporting, each state generally has an environmental emergency response hotline available 24 hour hours per day 365 days per year used for reporting releases immediately. When reporting to one of these hotlines, states often require information to be provided to their dispatchers including the following:

- Responsible party
- Material name or identity of substance involved in release and whether or not it is 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 contact person

The information contained in this section is by no means comprehensive and, to maintain compliance, individual facilities should check with their regulatory agencies to verify the applicability of state release prevention and response regulations.

D. Beyond regulations – what else can I do?

Response plans are effective only if they are well understood by employees, implemented during regular operations, and educated reactions are taken in the event of an actual release. Quick actions taken by facility personnel to contain a release can be extremely effective at mitigating the environmental impact and financial cost of the release. Contingency planning is important, but additional steps should be taken to make plans more effective:

Awareness

- Employees should be trained and made aware of the importance of their actions. Especially in the first hour after a release, quick action can contain the spill, which allows for faster cleanup and reduces the environmental impact.
- What type of heavy equipment is available at, or nearby, the facility? A front-end loaded used at the facility can be used to create dikes and berms for emergency containment.
- What kinds of spill control products are available on site? A well-stocked spill kit can mean the difference in an incident contained onsite to one that is released offsite.
- Who are the local authorities and how will they respond? In the event of a spill, notifications in accordance with state and federal law must be made. Facilities should establish relationships with the local responders so that the local responders are familiar with the facility and the risks. In the midst of an emergency is not the best time to first establish a relationship with local responders.
- Are there appropriate contractors lined up to respond? Contractors can provide additional man-power and key equipment used to quickly recover lost product reducing the risk of environmental impact. Facilities should establish working relationships with available contractors.

Site Specifics

- The specific geology of the site will affect how a release impacts the environment.
- Nearby surface waters and the pathways to those waters should be understood and mapped in advance.
- Soil type and distance to groundwater should be understood in advance.
- What are my state's cleanup standards for ethanol released into the environment? These standards will dictate the remediation strategy and methods.

Prevention

- Many spills are preventable or can be contained with improved systems and facilities.
- Engineering controls and improvements can go beyond the regulations and focus on the process itself. An engineering control quickly pays for itself if it prevents a costly release.
- Transfer and containment systems should be reviewed. In some cases, rail transfer secondary containment is sufficient to hold the required amount of ethanol, but in a larger release the secondary containment conveyance piping might not be properly sized to completely convey the release to containment.
- Process Safety Management is an important component of release prevention. Are the process, storage, and piping systems properly inspected and maintained for the hazards involved?
- Drills and training exercises are mandatory under some regulatory programs, and are generally a best operating practice for the industry. Consider inviting your local responders (fire department, police) to participate in your drills and training exercises. Debriefs following these exercises often leads to improved prevention by identifying gaps that can be addressed moving forward.

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

This chapter will discuss the physical properties of ethanol and how these properties affect environmental media – air, soil, surface water and groundwater. Chapter 5 will discuss the actions to take if a release does occur, knowing the likely impact to various media.

A. The key physical properties of ethanol [21]

- Ethanol is a clear, colorless liquid. Denatured fuel ethanol is denatured with petroleum hydrocarbons, typically gasoline at about 2%.
- Ethanol is infinitely soluble in water, which means that any release that reaches surface or groundwater will fully dissolve and will not separate once dissolved.
- Ethanol has sufficient vapor pressure to readily volatilize from a liquid to a vapor as a pure product or mixed with denaturant. With a low Henry's Law constant, ethanol dissolved in water will be much less volatile.
- Ethanol has a low soil mobility, which means that it tends to remain in soil until it contacts moisture in the soil or groundwater.
- Ethanol is highly flammable. The Lower Explosive Limit (LEL) is 3.3% and the Upper Explosive Limit (UEL) is 19%, with a flashpoint of 55°F. Even at 50% dilution with water, the flashpoint of denatured fuel ethanol is 78°F. Ethanol is still considered a flammable liquid in solutions as dilute as 20%. Because ethanol is a polar solvent it will conduct electricity, which creates an ignition hazard.
- The OSHA Permissible Exposure Level is 1,000 ppm. Health impacts such as eye irritation and headaches have been observed above this level. The Immediate Danger to Life or Health (IDLH) threshold is 3,300 parts per million, or 10% of the LEL.
- Denaturants. The most common denaturants are gasoline and natural gasoline, which are petroleum products.
    - The addition of denaturant (E98) significantly lowers the flashpoint from 55°F to 19.4°F. Colder temperatures will further depress the flammability by reducing vapor pressure.
    - Ethanol will preferentially biodegrade in the presence of petroleum hydrocarbons used as denaturants or already present in the soil and groundwater. Consideration of the extent of ethanol, denaturant and existing conditions must be taken into account.
    - Denaturants have chemical and physical properties different from ethanol, which should be considered during the scoping and implementation of investigation and remediation programs. For example, gasoline has a lower solubility and may float as a light aqueous phase liquid (LNAPL) when present at a high enough concentration. Gasoline constituents can have an affinity for carbon and may adsorb to both unsaturated and saturated soil materials. Gasoline constituents, while biodegradable, may degrade more slowly than ethanol.

B. How do these physical properties impact environmental media?

Air [21]

- An ethanol spill on the ground or in a containment area can create an immediate danger of flammability. Especially in windy and sunny conditions, much of the ethanol will volatilize into the air.
- Ethanol vapors are toxic to humans but only in extreme conditions where concentrations are high. Still, caution must be exercised against the potential for vapors to displace air because ethanol is heavier than air.
- Once ethanol dissolves, evaporation from the aqueous state is greatly reduced and unlikely to be a significant factor in mass balance calculations.

Surface water [21]

- The complete solubility of ethanol in water means that if a release reaches surface water, the ethanol will rapidly disperse and can no longer be recovered as a product.
- Ethanol in surface water will rapidly biodegrade. The concentration of ethanol can create a toxic effect on aquatic organisms, though frequently the depletion of dissolved oxygen caused by biodegradation has a greater impact to fish and aquatic organisms.
- Ethanol has a low bio-concentration factor, which indicates ethanol in impacted aquatic organisms will not bio-accumulate within the ecological food chain.

Soil [21]

- The mobility of ethanol in soil is dependent on the volume spilled, the conductivity of the soil, and the moisture of the soil profile. Due to density differences between ethanol and water, ethanol will tend to be retained above the water table although hydraulic head pressures caused by significant releases can quickly transport ethanol downward beneath the water table surface. Additionally, as the ethanol contacts moisture in the soil, it will disperse, and will also migrate downward towards groundwater.
- As bacteria begin to consume the ethanol, ethanol molecules will be broken, typically first into intermediate products like acetate and eventually into carbon dioxide and water if there is sufficient oxygen present. The presence or absence of oxygen can be a significant factor. In the absence of oxygen, methanogenic bacteria will degrade the various compounds and produce methane as a product.
- The accumulation of methane in the soil is a potential hazard that must be addressed. Degradation occurs over time, so the buildup of methane may reach a peak in months or years after the initial release.
- Denatured fuel ethanol and ethanol water mixtures moving through soil pores can mobilize existing petroleum contamination present in soil due to the increased solubility of gasoline constituents in aqueous ethanol.

Groundwater [21]

- As the ethanol reaches groundwater, the ethanol will dissolve in the groundwater.
- Lower concentrations of ethanol, such as in E10, will degrade rapidly, especially in the presence of oxygen.
- Higher concentrations of ethanol will persist and typically move with the groundwater. Degradation will continue to occur but be limited by the absence of oxygen; the presence of oxygen will be defined by the geochemistry of the groundwater. In the absence of oxygen, other compounds such as iron, nitrate and sulfate will assist the degradation process but typically in a slower timeframe and with different products.
- Just as with ethanol degradation in soil, under some conditions, a significant amount of methane will be generated, especially over time, as oxygen is depleted and the plume migrates with groundwater. Again, the presence of vapor pathways must be understood, because the hazard of methane accumulation is a risk factor that must be considered. The fact that the methane accumulation may not peak for one or two years after the release is one of the lessons learned from the study of previous spills [21].
- As discussed further in Chapter 5, if ethanol encounters existing petroleum contamination, plumes of BTEX can greatly increase in size and concentration. BTEX concentrations can increase up to 10-fold as ethanol mobilizes and dissolves more BTEX into solution [8].

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 of initial containment.

B. In the first 24 hours:

- Prevent the ethanol from reaching surface water. Quick action is essential to prevent a 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, and portable pumps, and any other response equipment. Some bioremediation products act as absorbent material as well, functioning similar to 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 in 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.

<u>Soil impacts</u>

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 particular 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 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 material. 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. Soils 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 product 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) [1].

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 [13]. 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 washing fluid 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 [14].

- 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 to 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 [21, 16, 17, 19, 20].

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 volatize. 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 volatizing 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 stock piles 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 are very low, as very high concentrations are required before regulatory and heath 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 use 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 [21].

An effective treatment method to address an 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. The 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 [21].

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 show they are pathogen-free, non-mutagenic, and effective [24].

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 similar to 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. Similar to 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 become depleted and halt biodegradation [21]. 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 [7, 11, 5]. 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 [14]. 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 [7, 11]. If monitoring reveals nutrients and oxygen are present, but 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 require 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_2	CO_2, H_2O	High
Denitrification	NO^{3}-	CO_2, N_2	
Iron reduction	Fe^{3+}	CO_2, Fe^{2+}	
Sulfate reduction	SO_4^{2-}	CO_2, H_2S	
Methanogenesis	CO_2	CO_2, CH_4	Low

[10]

Site geochemistry may be more important than relative potential energy when evaluating which electron acceptor to supply to groundwater. Typical examples of amendments include fertilizers (NO^{3-}), suspended small-particle iron (Fe^{3+}), 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 range 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 [21]. 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% [21].

Denatured fuel ethanol has additional considerations in remediation strategies due to the presence of less-soluble denaturants, in particular BTEX compounds. As discussed in previous sections above, ethanol can increase the aqueous concentration of BTEX compounds due to a co-solvent effect [14]. Despite this effect, some BTEX compounds will likely still 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) [14]. 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 was capable of removing 88% of total BTEX compounds during one year of operation[2]. 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, inhibit 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 in order 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 is properly trained. Will they know what type of action to take in an emergency situation?

- ✓ Assess the situation at 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.

References Cited

[1] Araujo, D. B. (2000). *Effect of Fuel Ethanol on Subsurface Microorganisms and its Influence on Biodegradation of BTEX Compounds* (Unpublished master's thesis). University of Waterloo, Waterloo, Ontario, Canada.

[2] Bedessem, M. E., Ferro, A. M., & Hiegel, T. (2007). Pilot-Scale constructed wetlands for petroleum-contaminated groundwater. *Water Environmental Resources*, *79*(6), 581-586.

[3] Congressional Research Service. (2014). *U.S. Rail Transportation of Crude Oil: Background and Issues for Congress*. Retrieved from https://www.fas.org/sgp/crs/misc/R43390.pdf

[4] *eCFR — Code of Federal Regulations*. (2016). Retrieved from http://www.ecfr.gov/cgi-bin/ECFR?page=browse

[5] Evans, F. F., Rosado, A. S., Sebastian, G. V., Casella, R., Machado, P., Holmstrom, C., … Kjelleberg, S. (2004). Impact of oil contamination and biostimulation on the diversity of indigenous bacterial communities in soil microcosms. *FEMS Microbiology Ecology*, *49*, 295-305.

[6] Franklin Regional Council of Governments. (2014). *Ethanol Response Plan*. Retrieved from http://frcog.org/wp-content/uploads/2014/04/Ethanol-Response-Plan.pdf

[7] Heiser, D. (1999). Bioremediation of Petroleum Pollutants in Cold Environments. *Restoration and Reclamation Review*, *5*(2).

[8] Lawrence Livermore National Laboratory. (1999). *Health and Environmental Assessment of the Use of Ethanol as a Fuel Oxygenate, Report to the California Environmental Policy Council in Response to Executive Order D-5-99*.

[9] Liu, X. (2015). Change of U.S. Freight-Train Derailment Rate From 2000 to 2012. San Jose, CA.

[10] Malcolm Pirnie, Inc. (1998). *Evaluation of the Fate and Transport of Ethanol in the Environment*. American Methanol Institute.

[11] Margesin, R., & Schinner, F. (2001). Biodegradation and Bioremediation of Hydrocarbons in Extreme Environments. *Applied Microbiology and Biotechnology*, *56*, 650-663.

[12] Nyendu, G. C. (2011). *Storability of modified wet distiller's grains with solubles* (Doctoral dissertation). Retrieved from http://lib.dr.iastate.edu/cgi/viewcontent.cgi?article=1553&context=etd

[13] Oppenheimer Biotechnology. (n.d.). *Oppenheimer Nutrient Blend Label*.

[14] Powers, S. E., Hunt, C. S., Heermann, S. E., Corseuil, H. X., Rice, D., & Alvarez, P. J. (2001). The Transport and Fate of Ethanol and BTEX in Groundwater Contaminated by Gasohol. *Critical Reviews in Environmental Science and Technology*.

[15] Renewable Fuels Association. (2014). *2014 Pocket Guide to Ethanol*. Retrieved from http://www.ethanolrfa.org/wp-content/uploads/2015/09/2014-Pocket-Guide-to-Ethanol.pdf

[16] ScienceLab. (2013, May 21). *Benzene MSDS*. Retrieved from http://www.sciencelab.com/msds.php?msdsId=9927339

[17] ScienceLab. (2013, May 21). *Ethylbenzene MSDS*. Retrieved from http://www.sciencelab.com/msds.php?msdsId=9923958

[18] ScienceLab. (2013, May 21). *MSDS of 200 Proof Ethyl Alcohol*. Retrieved from http://www.sciencelab.com/msds.php?msdsId=9923955

[19] ScienceLab. (2013, May 21). *Toluene MSDS*. Retrieved from http://www.sciencelab.com/msds.php?msdsId=9927301

[20] ScienceLab. (2013, May 21). *Xylenes MSDS*. Retrieved from http://www.sciencelab.com/msds.php?msdsId=9927646

[21] Shaw Environmental and Infrastructure Group. (July 2011). *Large Volume Ethanol Spills – Environmental Impacts and Response Options*. Massachusetts Department of Environmental Protection.

[22] U.S. Department of Health and Human Services, Agency for Toxic Substances and Disease Registry. (1995). *Toxicological Profile for Automotive Gasoline*. Retrieved from http://www.atsdr.cdc.gov/toxprofiles/tp72.pdf

[23] U.S. Department of Transportation, Pipeline and Hazardous Materials Safety Administration. (2012). *Emergency Response Guidebook*. Neenah, WI: J.J. Keller and Associates.

[24] U.S. EPA National Contingency Plan Subpart J. NCP Product Schedule (March 2016). Retrieved from https://www.epa.gov/emergency-response/national-contingency-plan-subpart-j#schedule.

[25] Voegel, E. (2015, May 5). Ethanol Producer Magazine – The Latest News and Data About Ethanol Production. Retrieved from http://www.ethanolproducer.com/articles/12189/dot-rule-includes-new-tank-car-standards-retrofit-schedule

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 education 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 SPR 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 http://www.itrcweb.org/documents/biofuels/BIOFUELS-1.pdf

Appendix C – Selected Case Studies MassDEP

LARGE VOLUME ETHANOL SPILLS – ENVIRONMENTAL IMPACTS AND RESPONSE OPTIONS

Prepared for:

MassDEP
Commonwealth of Massachusetts
Department of Environmental Protection

Prepared by:

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July 2011

Public document available at the Massachusetts Department of Environmental Protection
http://www.mass.gov/eea/docs/dep/cleanup/laws/ethanol-spill-impacts-and-response-7-11.pdf

Appendix D – Groundwater Monitoring Reference

Ground Water Monitoring&Remediation

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

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^{+2}, 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.

Ground Water Monitoring & Remediation

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

Appendix E – About Pinnacle Engineering

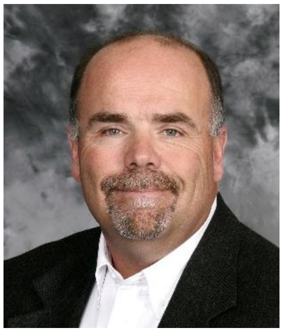
Celebrating 25 years of excellence, Pinnacle Engineering, Inc. (Pinnacle) was formed in 1991 to serve the expanding environmental needs of industrial and manufacturing businesses.

As an environmental engineering and consulting company, Pinnacle provides a full range of environmental, industrial, civil engineering, renewable fuels, and remedial field services -- serving the expanding environmental needs of railroad, industrial, commercial, utility, manufacturing, and renewable energy clientele.

Our staff is a multi-disciplined team of mechanical, civil, chemical, and geological engineers, supported by hydrologists, geologists, and natural resource scientists, who are focused on providing the professional expertise our clients have come to expect. Pinnacle takes pride in our systematic and common sense approach to the issues clients face – achieving compliance without duplication of effort. Pinnacle also employs

Pinnacle has grown steadily through our development of long term client relationships. Historically, over 90% of our revenue has been generated from past clients of the firm. Our loyal client relationships are the cornerstone to our strong and steady growth. We will continue to partner with our clients to build strong relationships - resulting in effective, innovative solutions.

Pinnacle is based in Minneapolis, MN, with offices in Rochester, MN; Omaha, NE; and Bismarck, ND. For additional information about us and contact information, please visit our home page at www.pineng.com



Jim Holland, PE - CEO/President

In 1991, Jim founded Pinnacle Engineering, Inc., and he has served as CEO since the company's inception. Jim's tireless efforts and leadership have been the primary catalyst for growth and change within Pinnacle Engineering. His experience spans the realm of service offerings. For the past ten plus years, Jim has focused his practice on the Rail and Infrastructure industries. Jim is a trusted partner that Rail and Industrial clientele call on in times of emergencies that need immediate response. He typically provides the role of "Regulatory Representation" for clients during Emergency Response services. In this role, Jim is called upon to provide an immediate assessment of the environmental impacts of the situation and to relate this assessment to corporate management and to the regulatory community. Jim has responded to over 25 large scale environmental releases in the upper Midwest. Most recently, he served as Lead Engineer for a "Crude Oil to Rail" facility in western ND that is valued at over $50M. Jim has a Bachelor of Science Degree in Mechanical Engineering from the University of Minnesota.

Steve Schleicher - Vice President, Industrial Services

Steve has over 19 years of experience in environmental and occupational health and safety management experience. This combined experience has been derived through assisting clientele in the broad areas of regulatory compliance and due diligence. Steve is a client manager and also leads the business development efforts for our Industrial and Renewable Fuel groups. Steve is knowledgeable in comprehensive industrial environmental compliance including CAA, CWA, RCRA, EPRCA, SPCC, RMP/PSM, P2, GHG, compliance auditing and self-disclosure, regulatory agency interaction and negotiation, permitting and compliance program development. Steve has a Bachelor of Science Degree in Environmental and Public Health from the University of Wisconsin.

Matt Henry, PE – Manager - Midwest Operations

With over 10 years of experience in the field of environmental compliance and permitting, Matt specializes in the air quality compliance support to industrial facilities and the renewable fuels industry. Matt is the Midwest Operations Manager out of our Omaha, NE office and prepares various reports, environmental plans and applications, and compliance programs associated with chemical manufacturing projects. Matt's project experience includes preparing and negotiating air quality construction/operating permit applications, managing stack test events, evaluating and implementing leak detection and repair programs, and providing annual operation and compliance services to the renewable fuel industry.

Jeff Powell – Staff Scientist, GIS Lead

Jeff is a Staff Scientist and GIS lead with extensive knowledge of surface/groundwater chemistry, aquatic ecology, ESRI's ArcGIS, and bioremediation techniques. Jeff's project experience includes work on several large scale derailments for Canadian Pacific and BNSF Railways, where he provided support in contractor management, soil and water sampling, bioremediation implementation, storm water control, GPS/GIS mapping services, and associated reporting.