Assessment and Remediation of Bio-Blended Fuels and Additives

Presented by Jon Berntsen, P.G. • November 3, 2015
Background on Bio-Fuel
**What is Bio-Fuel**

- Fuel derived from biological materials (i.e. – plants, animals)
- Two widely available forms
  - Ethanol
    - fermented corn / sugar cane
  - Biodiesel
    - vegetable or animal oil
What is Bio-Fuel

- Ethanol and Ethanol Fuel Blends
  - Typically Corn Ethanol (US)
  - E-10 – Currently Available Blend
  - Intermediate Ethanol Blends (E11-E50)
  - Ethanol for Flex Fuel Vehicles (E51-E83)
  - E85 (Actually E70-E85)
  - Denatured Fuel Ethanol (E95)
  - E100 – Pure (Neat) Ethanol
Background

- What is Bio-Fuel
  - Biodiesel
    - Biodiesel Blend B5 to B20
      - Anything below B5 is considered conventional fuel
    - B100 – Biodiesel fuel blend stock
Why Bio-Fuels

- **Energy Policy Act of 2005**
  - First Renewable Fuels Standard (RFS) Program
    - Required 7.5 Billion Gallons of renewable fuel by 2012.
- **Energy Independence & Security Act of 2007**
  - Renewable Fuels Requirements Increased
    - 9 Billion Gallons of renewable fuel by 2008
    - 36 Billion Gallons of renewable fuel by 2022
    - Expanded the RFS to include diesel in addition to gasoline
    - Provided additional alternative fuel objectives for federal Alternative Fuel Vehicle fleets
Alternative Fuels Are Catching On

U.S. Alternative Fueling Stations by Fuel Type

Number of Stations

- Electric
- Propane
- Methanol (M85)
- LNG
- Hydrogen
- Biodiesel
- CNG
- E85

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Eleven states currently have adopted renewable fuel programs for part of or all of the state.
Releases to the Environment
Releases to Environment

- Biofuels enter the environment via the following:
  - During Transport
    - Rail – 2,000 derailments per year (25,000 gal)
    - Tanker Trucks – 1,000 accidents per year (1 per 25,000 deliveries) (8,000-10,000 gallons)
    - Tank Barges – 2.16 gallons spilled per 1 million gallons moved. (500,000 gallons)
  - For reference – daily biofuel transport needs
    - 1,250 tanker trucks, 415 rail cars, 20 barges
Releases to Environment

- **UST Systems**
  - Small Volume or Chronic Releases
    - Not detected by leak detection equipment if the equipment is incompatible with ethanol.
  - Large releases detected through volume reconciliation.

- **Dispenser Systems**
  - Small Volume or Chronic Releases detected through standard inspections

- Caused by incompatible materials, the solvent nature of biofuels which scour sediment, sludge, rust and scale
Releases to Environment

30 micron diesel pump filter element covered in gel like material

Close up of gel removed from filter

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Releases to Environment

- Biofuels enter the environment via the following:
  - AST Systems
    - Small volume releases that can become large over an extended period of time
    - Releases caused by permeation through common rubbers, plastics, and elastomers.
    - Deterioration of Gaskets and Seals at Joints and Connections
    - Corrosion and Stress Cracking in Tank Floors or at the Tank Skirt where connections to distribution piping occur
Releases to Environment

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Release Prevention

- **Proper Construction**
  - Compatible Materials and Equipment
    - Plastics, polymers, elastomers
    - Metal components and solders
  - Appropriate Commercial Leak Detection Equipment

- **Management Practices**
  - Proper O&M on Leak Detection Equipment
  - Filter Change Outs
  - STP Sump Maintenance (ethanol fuels)
Petroleum Release Model

- Typical Petroleum Release

Diagram:
- Primary source (short term)
- Trapped and sorbed residual
- Groundwater source (longer term)
- Capillary fringe
- NAPL body
- Dissolution
- Groundwater flow direction
- Dissolved phase plume
- Unsaturated zone
- Aquifer
Ethanol Release Models

- Ethanol/Blend Release

![Diagram showing Ethanol Release Models with conventional gasoline (E0), E10, and DFE phases, and associated groundwater dissolution and capillary fringe details.]

- High permeability water-filled lens
- Pore water containing ethanol
- Immobile gasoline phase
- (collapsed) capillary fringe
Fuel Grade Ethanol Release

- Many FGE facilities are located where previous hydrocarbon releases occurred
- Residual NAPL may be present in vadose zone
- FGE release will remobilize NAPL if present.

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## Behavior in Environment

### Behavior of Bio-Fuels

- **Ethanol**
  - Often Compared against Benzene for Fate and Transport

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solubility in Water</th>
<th>Biodegradation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>1,800 mg/L</td>
<td>Aerobically – Days to Months</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Anaerobically – Years</td>
</tr>
<tr>
<td>Ethanol</td>
<td>Infinite</td>
<td>Aerobically – Hours to Days</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Anaerobically – Days to Weeks</td>
</tr>
</tbody>
</table>
Behavior in Environment

- Ethanol will behave significantly different than petroleum-related hydrocarbons compounds
  - Ethanol will be drawn out into soil moisture, creating a trail of ethanol-enriched soil moisture
  - Bulk fuel becomes depleted in ethanol as it migrates through the vadose zone
  - At capillary fringe, remaining ethanol partitions into aqueous phase – may collapse capillary fringe (high conc.)
  - Little ethanol gets beyond capillary fringe unless water table is shallow.
Behavior in Environment

- Ethanol partitioning into water resulting in higher solubility of hydrocarbons because of cosolvency.
- Effect increases with ethanol concentration
- Significant effects not seen until ethanol concentrations in water exceed 10%
- More BTEX compounds will be retained above the water table due to ethanol in vadose zone moisture
Biodegradation

- Ethanol Biodegradation is Rapid and ever present
- Results in changes to biological and geochemical environments
  - Stimulation of microorganisms
  - Influences electron acceptor availability
  - Results in the production of methane
- High concentrations of ethanol (6-10%) can inhibit biodegradation as the condition will rapidly turn environment anaerobic
Biodegradation

- Ethanol depletes the attenuative capacity of groundwater in immediate vicinity of discharge
  - Results in less degradation of BTEX compounds
  - Higher source concentrations
  - Larger plume footprints
Biodegradation of Ethanol in shallow groundwater are likely to produce biomass exudates (fluid excretions) – dark colored slimes

- Exudates may encapsulate higher concentration ethanol sources preserving them for years
Biodegradation produces acetate and hydrogen that are used by methanogenic bacteria to produce methane under anaerobic conditions.
Biodegradation

- For some large release scenarios, especially with shallow groundwater, methane generation can lead to explosive risk.
- Dissolved methane of 1-2% can lead to lower explosive limit concentrations in soil gas.
- Methane production can be delayed for months or even years at some sites as site conditions evolve.
- Methane generation may strip petroleum VOCs from groundwater and induce advective transport – leading to greater vapor intrusion risk.

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Biodegradation

- Biofuels will preferentially degrade over hydrocarbons
- Causes lower rates of petroleum hydrocarbon degradation in source areas
- Longer Plumes likely to exist following discharge
- Rapid shift in groundwater geochemistry can result in localized mobilization of iron, manganese and arsenic
Assessment and Remediation
Site Assessment Considerations

- Site assessment techniques are generally similar to petroleum releases.
Site Assessment Considerations

- Site assessment techniques are generally similar to petroleum releases.
- With blended fuels, the petroleum hydrocarbon component will dictate the majority of the investigation requirements.
- Additional parameters required for investigation include
  - methane (dissolved and soil gas)
  - DO depletion (groundwater)
Site Assessment Considerations

- Methane can typically be monitored in groundwater using standard monitoring wells as in typical petroleum release investigations
  - “Water Table” well with 10 foot screen length

- Methane in soil gas can be measured in soil headspace samples or monitored over time using soil gas monitoring points.
  - Permanent points recommended due to potential for delayed methane generation
Site Assessment Considerations

- Groundwater Investigation
  - Shorter monitoring well screens recommended to capture ethanol draining and/or leaching from capillary fringe.
  - Multiple wells may be needed
Site Assessment Considerations

- Groundwater Investigation
  - Use of Proper Sampling Points Critical to Assessment
Site Assessment Considerations

Additional Parameters to be Considered

• Groundwater
  • Methane – soil gas
  • Acetate
  • Dissolved Organic Carbon / Total Organic Carbon
  • Ethanol/Butanol

• Soil Gas
  • Methane and Methane LEL
  • Ethanol/Butanol

• Soil
  • Ethanol/Butanol
Site Assessment Considerations

- Biodiesel
  - Groundwater
  - Wire wound screens recommended to facilitate higher viscosity biodiesel LNAPL into wells
Site Assessment Considerations

- Biodiesel
  - Soil
    - Laser Induced Fluorescence has been shown effective to map B100
Site Assessment Considerations

- Biodiesel
  - Soil
    - Laser Induced Fluorescence has been shown effective to map B100
Long Term Strategy

Long Term Response Strategy will depend on:

- Type of biofuel
- Extent and magnitude of the release
- Regulatory thresholds for contaminants of concern
- Risk to identified receptors
Long Term Strategy

Assessment and Management of Risk is Key

- Monitored Natural Attenuation is applicable alternative
- Takes advantage of propensity of biofuels to dissolve and degrade without enhancement
- Limitations
  - High concentrations of some constituents toxic (ethanol)
  - Does not address immediate risk
  - High potential for methane generation
  - Delayed biodegradation of recalcitrant petroleum compounds
Active Remediation

- Limited area of expertise due to emerging issue
- Goal is to reduce risk to human health and environment
- Traditional technologies have merits when addressing biofuel
  - Excavation
  - Soil vapor extraction
  - Air sparging
  - Groundwater extraction
Active Remediation

- Excavation

High degree of certainty. Removes source.
Active Remediation

- **Soil Vapor Extraction**
  - Favorable technology for removing ethanol and gasoline compounds from subsurface.
  - Oxygen introduced into vadose zone will promote biodegradation
  - Secondary benefit of methane venting from subsurface
Active Remediation

- **Air Sparging**
  - Will strip petroleum compounds from groundwater
  - Little stripping of ethanol
  - Will remove dissolved methane
  - Introduces oxygen which will stimulate biodegradation of ethanol and acetate
  - Growth of ethanol degrading bacteria may result in fouling of screens
Active Remediation

- Air Sparging/Soil Vapor Extraction
Active Remediation

Groundwater Extraction

- Will be effective at plume capture
- Impacts likely to water treatment system
  - Biofouling if oxygen introduced (air stripper)
  - Ethanol may induce corrosion or degradation of treatment components
  - Ethanol may not completely strip out of aqueous phase
- Biodiesel may not flow readily via gravity to extraction points
Active Remediation

- Dual Phase Extraction
  - Technology will work to extract petroleum and ethanol from subsurface
  - Mixing of ethanol into groundwater phase may result in additional recovery of LNAPL
  - Presence of ethanol may interfere with oil/water separation
  - Oxygenation of recovered liquid stream will promote biofouling
  - Ethanol removal from aqueous phase can be challenging
Active Remediation

- Dual Phase Extraction

  - High viscosity biodiesel may emulsify if single pump system is employed
  - Separation of emulsions difficult in aboveground treatment
  - May require additional treatment train
Active Remediation

- Solutions?
  - Bioreactors
  - Resins and polymers for adsorption
  - Area for continued academic and industry research
Additional Challenges
Other Challenges

- Diesel Exhaust Fluid
  - 67.5% water
  - 32.5% ultra pure urea

- Commonly sold in small quantities (2.5 and 5 gallon)

- Increasing occurrence in bulk storage at high volume facilities
Other Challenges

- Diesel Exhaust Fluid
  - Stored in USTs
  - Increased incidents of discharge
  - Urea is nitrogenous fertilizer
  - Will react and convert to ammonia
  - Ammonia is very difficult to remove from aqueous stream
Summary
Summary

Releases to Environment caused by

- Incompatible Materials
- Solvent Scouring Properties of Biofuels
- Poor Maintenance
Summary

Best Release Prevention Measures

• Proper Construction
  • Compatible Materials
  • Appropriate Equipment Selection

• Proper Management Practices
  • Proper O&M on Equipment
  • Filter Change Outs
  • STP Sump Maintenance
Summary

Ethanol in Environment

- Ethanol behaves differently than petroleum hydrocarbon compounds
- Introduction of ethanol to environment changes behavior of petroleum hydrocarbon compounds
- Ethanol depletes the attenuative capacity of aquifer in close proximity to release site
  - Results in potential for higher source concentrations and larger plume footprints
Summary

- Biodegradation of Biofuels
  - Primary metabolic byproduct is Methane
  - Biofuels will preferentially degrade vs. hydrocarbons
  - Longer contaminant plumes likely to exist
  - Causes lower rates of petroleum hydrocarbon degradation
Summary

Site Assessment

- Additional parameters required for characterization
  - Methane
  - Acetate
  - Ethanol/Butanol
- Biodiesel (B100) difficult to assess
  - If blend, need to look at typical petroleum markers
Summary

- Long Term Strategy and Remediation
  - Manage Risk and Behavior in Subsurface
  - Remediation of Biofuels
    - Emerging Practice
    - Traditional Technologies have merits with respect to biofuel
    - Limitations due to ethanol removal and treatment in ex-situ liquid streams
    - Biodiesel viscosity can complicate total fluids recovery/separation
Summary

- Additional Challenges
  - Diesel Exhaust Fluid
  - Urea-to-Ammonia Conversion
  - Ammonia Toxicity
  - Difficulty of Removal
Questions?

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