Characterization of #2 Fuel Oil Spills

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Today’s Agenda
- Nature and Scope of Problem
- Conceptual Site Model
- NAPL
- Soil
- Groundwater
- Indoor Air

Nature and Scope of Problem

Fate and Transport Characteristics of Home Heating Oil Releases Based Upon a Review of Empirical Data from Actual Releases

Jonathan Kitchen & Joseph Salvetti
27th Annual International Conference on Soils, Sediments, Water and Energy
October, 2011

Sites that were Evaluated
- 100 residential oil spills, 1993 – 2011
- 53% of sites had known/est. spill quantities
- 98% of sites reported soil impacts
- 65% of sites reported groundwater impacts
- 32% of sites reported concentrations of hydrocarbons in GW above standards

Towns Where Sites were Located
Cause of Residential Fuel Oil Spills

- Natural cause: 3%
- Filter: 6%
- Delivery error: 11%
- UST: 19%
- Fuel Line: 24%
- AST: 19%
- Pile/low: 3%
- Unknowns: 3%

Kitchen/Salvetti, 2011

Quantity of Oil Spilled

- 401-1000 Gals: 13%
- 201-400 Gals: 11%
- 101-200 Gals: 27%
- 51-100 Gals: 15%
- 1-50 Gals: 32%
- > 1000 Gals: 2%

Kitchen/Salvetti, 2011

Soil Removal

- 98% of sites had soil impacts
- 87% of sites had some soil removal
- Average Removal in GW-1 Area was 160 tons
- Average Removal in non-GW-1 Area was 90 tons

Kitchen/Salvetti, 2011

Groundwater Plume

- Gallons of Fuel Spilled vs. Plume Length (ft)

Kitchen/Salvetti, 2011

Visible NAPL was observed at 30 out of the 100 sites.

Out of those 30 sites, 60% reported groundwater contaminant levels greater than one or more groundwater standard.

Kitchen/Salvetti, 2011

Indoor Air

Only 10 sites reported an indoor air impact detected.

Only 3 sites required (or elected) additional remedial action, the remaining 7 attenuated to background conditions with time and ventilation.

Kitchen/Salvetti, 2011
Soil Closure/Remediation Drivers

GW-1 areas:
- 2-methylnaphthalene (72% of time)
- C₉-C₁₈ Aliphatic HC (16% of time)
- C₉-C₁₀ Aromatics (8% of time)

Non GW-1 Areas:
- C₉-C₁₈ Aliphatic Hydrocarbons

GW Closure/Remediation Drivers

GW-1 areas:
- C₁₁-C₂₂ Aromatic HC (~60% of time)
- 2-methylnaphthalene (23%)
- C₉-C₁₀ Aromatic HC (12%)

Non GW-1 Areas:
- C₉-C₁₈ Aliphatic Hydrocarbons

Time to Closure

Conceptual Site Model

“Knowledge is Good”

Emil Faber

Typical Scenarios

Fate

Sorption Volatilization Release

Groundwater Contamination
**#2 Fuel Oil**

- **Gasoline**
- **Jet Fuel**
- **#2 Diesel Oil**
- **Lube Oils**

- Mostly C₂₂ to C₉⁶
- Boiling Range 200 to 350°C
- Density 0.90 to 0.95 g/mL

- 69°C to 449°C

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**Hydrocarbon Chemistry of Fresh #2 Fuel Oil**

- **Aliphatics**
  - C₅₋C₆ Aliphatics: 60%
  - C₁₂₋C₂₀ Aliphatics: 10%
  - C₁₁₋C₂₂ Aromatics: 25%
  - N-Alkanes = 10-20%
  - Iso-Alkanes = 20-30%
  - Cyclo-Alkanes = 30-35%

- **Aromatics**
  - <C₆: 5%

- 2-Methylnaph = 0.9%
- Naphthalene = 0.3%
- Benzene = 0.03%

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**#2 Fuel Oil Chromatogram (Fresh)**

- n-C₆ to n-C₂₂

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**#2 Fuel Oil Evaporation Rate**

- Approx 230 mg/hr/ft² first week avg
- Approx 1 gal/100 ft² (1 week vent)
- Avg Flux first week

(Kaplan et. al., 1993)

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**Discharge to Concrete Floors**

- Pooled Oil
- Depth of Penetration 0.6”
- Sorption
- Saturation 4% wt/wt
- Crack
**Sorption of Oil into Concrete**

Very Rough Rule of Thumb:

\[ \text{Sorption} = 0.04 \text{ gallons/ft}^2 \times \text{spill area} \]

**Bulk Movement of Separate Phase Oil Through Environmental Media**

**Release of Fuel Oil**

Vadose Zone

Saturated Zone

**The Battleground**

- Sorption On/Into Soil
- Organic Carbon Dissolution Into Pore Water
- Volatilization Into Soil Pore Air

**Partitioning/Residual NAPL for #2 Fuel Oil in Soil**

<table>
<thead>
<tr>
<th>Soil Type</th>
<th>Porosity $\theta_p$</th>
<th>Pore Water $\theta_w$</th>
<th>Fraction OC $F_{oc}$</th>
<th>Theoretical Partitioning Saturation</th>
<th>Concentration (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coarse Gravel</td>
<td>0.28</td>
<td>0.02</td>
<td>0.001</td>
<td>2</td>
<td>2000 +/-</td>
</tr>
<tr>
<td>Coarse Sand &amp; Gravel</td>
<td>0.35</td>
<td>0.03</td>
<td>0.002</td>
<td>4</td>
<td>4000 +/-</td>
</tr>
<tr>
<td>Med to Coarse Sand</td>
<td>0.39</td>
<td>0.04</td>
<td>0.003</td>
<td>5</td>
<td>8000 +/-</td>
</tr>
<tr>
<td>Fine to Med Sand</td>
<td>0.41</td>
<td>0.043</td>
<td>0.005</td>
<td>9</td>
<td>13,000 +/-</td>
</tr>
<tr>
<td>Silt to Fine Sand</td>
<td>0.44</td>
<td>0.045</td>
<td>0.01</td>
<td>18</td>
<td>22,000 +/-</td>
</tr>
</tbody>
</table>

(API, 2000)
NAPL Flavors and Concerns

Micro-Scale Mobility

Direct-Contact Human Health Risk

Breakout to subsurface structures/utilities

Breakout to surface water

Non-Stable NAPL

Macro/Site-Scale Mobility

Stable NAPL

Vapor Intrusion

Dissolved Phase Transport

Micro-Scale NAPL Mobility?

Yes if

- NAPL Visible in a monitoring well
- NAPL Visible in an excavation

Maybe if

- Hydrocarbons in Soil > Residual Saturation

Macro-Scale NAPL Mobility?

Yes if

- NAPL Discharge to Drains/Water Bodies
- NAPL Movement in Preferred Flow Path

Maybe if

- Very High Hydrocarbons in Soil
- Elevated NAPL thickness in Wells

Example of Monitoring Well Criteria

British Columbia Protocol 17 (Golder Assoc.)

<table>
<thead>
<tr>
<th>Soil Type</th>
<th>Characteristic Fraction</th>
<th>Percent Fines (silt/clay)</th>
<th>LNAPL Thickness (m) (inches)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coarse sand/gravel</td>
<td>&gt; 20% Coarse sand</td>
<td>&lt; 3</td>
<td>0.03 (1.2 inches)</td>
</tr>
<tr>
<td>Coarse sand/gravel</td>
<td>&gt; 20% Coarse sand</td>
<td>3-10</td>
<td>0.05 (2 inches)</td>
</tr>
<tr>
<td>Medium sand</td>
<td>Medium sand</td>
<td>&lt; 10</td>
<td>0.1 (4 inches)</td>
</tr>
<tr>
<td>Fine sand</td>
<td>Fine sand</td>
<td>&lt; 10</td>
<td>0.2 (7.9 inches)</td>
</tr>
<tr>
<td>Silty sand</td>
<td>Sand</td>
<td>&gt; 10</td>
<td>0.3 (12 inches)</td>
</tr>
</tbody>
</table>

1If present at this thickness over more than 50 m²

Implications

Micro-Scale NAPL Mobility:

- Concern with Vapor Intrusion Pathway
- Concern with direct human contact risks
- May require AUL

Macro-scale NAPL Mobility:

- Requires Remedial Measures

Federal/Proposed MCP Requirements:

Recover LNAPL to the Extent Feasible
**LNAPL Transmissivity (T_n)**

The quantity of LNAPL that will flow through a unit aquifer width in a unit time for a unit gradient

Function of:
- LNAPL Properties
- Degree of LNAPL Saturation
- Formation Properties

Empirically determined via LNAPL bail-down or recovery operations

**LNAPL Transmissivity (T_n)**

Hydraulic Recovery of LNAPL to the Maximum Extent Feasible?

Current thinking:

- To a $T_n$ value of 0.1 to 0.8 ft$^2$/day

(ITRC, 2009)

**Generic Approach**

API LNAPL Interactive Guide, 2004, for up to 5 inches Apparent Well Thickness

**Soil Contamination**

**NAPL Continuum**

Typical Chemistry of #2 Fuel Oil

EPH Soil Data

MassDEP Evaluation of 378 EPH Data Reports from 23 Sites where Fuel Oil #2 was Spilled (2007)
Typical Chemistry of #2 Fuel Oil

EPH Soil Data
378 Samples from 23 Sites

Relative Percentage

C9-C18 Aliphatics
C19 - C36 Aliphatics
C11-C22 Aromatics
Target PAH Analytes

%RSD = 30

Soil Sampling at #2 Fuel Oil Sites
VPH/EPH Implementation Policy, 2002

EPH Target Analytes:
- Acenaphthene
- Naphthalene
- 2-Methylnaphthalene
- Phenanthrene

Total EPH (TPH) vs Acenaphthene
(137 Samples)

Total EPH (TPH) vs Naphthalene
(299 Samples)

Total EPH (TPH) vs 2-Methylnaphthalene
(298 Samples)

Total EPH (TPH) vs Phenanthrene
(137 Samples)
More Data = Better Characterization

PID Headspace = Cheap & Effective
EPH Data for Confirmation

MassDEP Jar Headspace Procedure

#WSC-94-400 (1994)

- Half fill 8-16 oz glass jar
- Apply aluminum foil/cap
- Shake twice for 15 seconds over 10 minute period
- Puncture foil and obtain reading

Jars are Old School - Plastic Bags are easier…..

Plastic “Ziploc” Type Bags have been Replacing Glass Jars for headspace testing

Preliminary Studies – MassDEP – 2012

By Intern

- Evaluated Glass Jar, Plastic Baggies, Plastic Jars, Foil Lined Bags
- Short and Long term, Static and Dynamic Headspace Development
- Water and Soil, mostly gasoline contaminants
Why are Headspace Data so Poor for Baggies?

Preliminary Indications:
- Poor Dis-aggregation of wet/cohesive soils
- Sorption of Hydrocarbons on the LDPE
- Permeation Through the LDPE

Headspace Chemistry (GC/MS)

Headspace Chemistry (GC/MS)

Time to Bag the Bag!
Interpreting (Jar) Headspace Data

Jar Headspace vs Total EPH (i.e., TPH)

0 2 4 6 8 10

222/224 samples with <10 ppmV Headspace were < 1000 mg/kg Total EPH

MassDEP, 2007

= 0.0413

C9-C18 Aliphatic Hydrocarbons

C19-C36 Aliphatic Hydrocarbons

C11-C22 Aromatic Hydrocarbons

Utility of Soil Headspace Screening

For most sites where #2 Fuel oil was spilled, soils with < 10 ppmV Jar Headspace values will likely meet S-1 Cleanup Standards for EPH fractions.

May still have problems meeting S-1 standards for Naphthalene and 2-Methylnaphthalene

Final Word on Testing Soils for #2 Fuel Oil Contamination – 3 Letters

V PH
Soil Sampling at #2 Fuel Oil Sites

**VPH/EPH Implementation Policy, 2002**

- Fresh” Contamination (≥100 ppmV Headspace)
  - EPH and VPH
- Weathered” Contamination (<100 ppmV Headspace)
  - Just EPH

Excessive VPH Testing

From 2007 File Review Project, 141 soil samples tested for both VPH and EPH, including 110 samples where soil headspace < 100 ppmV

Of this universe of 110:
- All VPH Target Analytes << S-1/GW-1 Standards
- All C9-C12 Aliphatics < S-1/GW-1 Standard
- 97% C5-C8 Aliphatics < S-1/GW-1 Standard
- 91% C9-C10 Aromatics < S-1/GW-1 Standard (and rest exceeded C11-C22 Standard)

Dissolution

**Solubility of #2 Fuel Oil and Key Constituents (Raoult’s Law)**

<table>
<thead>
<tr>
<th>Constituent</th>
<th>In Fresh Fuel Oil #2</th>
<th>Water in Contact w/ #2 Fuel</th>
<th>MCP GW-1</th>
<th>MCP GW-2</th>
<th>MCP GW-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acenaphthene</td>
<td>100-600</td>
<td>0.04-0.014</td>
<td>0.02</td>
<td>NA</td>
<td>6</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>350-1500</td>
<td>0.08-0.3</td>
<td>0.14</td>
<td>1</td>
<td>20</td>
</tr>
<tr>
<td>2-Methylnaphthalene</td>
<td>3500-9000</td>
<td>0.18-0.34</td>
<td><strong>0.01</strong></td>
<td>2</td>
<td>20</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>100-1500</td>
<td>0.15-0.025</td>
<td>0.04</td>
<td>NA</td>
<td>10</td>
</tr>
</tbody>
</table>

**Total Maximum Solubility of #2 Fuel Oil = 2 - 6 mg/L**

Estimated Maximum Solubility of #2 Fuel Oil Hydrocarbon Fractions

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Concentration [mg/L]</th>
<th>Likely Upper Limit of Solubility</th>
<th>MCP GW-1</th>
<th>MCP GW-2</th>
<th>MCP GW-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>C&lt;sub&gt;9&lt;/sub&gt;–C&lt;sub&gt;18&lt;/sub&gt; Aliphatics</td>
<td>0.5 – 1.0</td>
<td>0.7</td>
<td>5</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>C&lt;sub&gt;19&lt;/sub&gt;–C&lt;sub&gt;28&lt;/sub&gt; Aliphatics</td>
<td>&lt; 0.01</td>
<td>14</td>
<td>NA</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>C&lt;sub&gt;11&lt;/sub&gt;–C&lt;sub&gt;22&lt;/sub&gt; Aromatics</td>
<td>1 – 3</td>
<td>0.2</td>
<td>50</td>
<td>5</td>
<td></td>
</tr>
</tbody>
</table>

Why Do So Many Sites Exceed GW Standards?

- Soil Particle Residual NAPL
Example – Fuel Oil Spill in Peabody, MA

Groundwater EPH data from well in tank grave – sampled with bailer

Exceeds MCP GW Standards

Surrogate @ C_{20}

Aliphatic FID Chromatogram

Recommendations for GW Sampling

Per VPH/EPH Implementation Policy, filtering of samples is NOT preferred. Low Stress/Low Flow Sampling is recommended, at least in source areas with likely past history of mobile NAPL

Do NOT use bailers or other high-stress/high flow techniques, at least in source areas

Request and view Chromatograms!

Pathway(s)

Vapor Intrusions/Indoor Air
Lines of Evidence

Indoor Air Data
Sub-Slab Soil Gas Data
Sample Chemistry – Obtain and Review Chromatograms!

Air-Phase Petroleum Hydrocarbons (APH)

GC/MS Procedure
Total Ion Chromatogram used to Quantify Aliphatic Fractions
Extracted Ions (120 and 134 m/z) used to Quantify Aromatic Fraction
Characteristic and Quant ions used to identify and quantify Target Analytes

Air-Phase Petroleum Hydrocarbons (APH)

Like VPH and EPH, APH test method has built-in assumptions that are designed to provide a positive (health-protective) bias. This is disclosed in the method.

APH bias is more problematic than VPH/EPH test, given “background” stuff in indoor air:
- Fuel Oil if still stored/used on-site
- Common household chemicals

Air-Phase Petroleum Hydrocarbons (APH)

Table 7 of the Method

<table>
<thead>
<tr>
<th>Potential Non-APH Compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₅-C₈ Aliphatic Hydrocarbons</td>
</tr>
<tr>
<td>C₉-C₁₀ Aliphatic Hydrocarbons</td>
</tr>
<tr>
<td>C₉-C₁₀ Aromatic Hydrocarbons</td>
</tr>
</tbody>
</table>

Example – Fuel Oil Spill in Westfied, MA

Basement Air – APH Total Ion Chromatogram

C₅-C₈ Hydrocarbons
p/m Xylenes
Very Low Fuel Oil Hydrocarbons

Example – Fuel Oil Spill in Westfied, MA

Basement Air – APH Total Ion Chromatogram

Ethanol
Ethyl Acetate
Freons
C₅-C₈ Hydrocarbons
MEK
PCE
And Similar Chromatogram for Second Floor
Example – Fuel Oil Spill in Westfied, MA

More Lines of Evidence – Soil Gas Chromatogram

Once analytes not associated with Vapor Intrusion Pathway were subtracted from the APH data, site could be closed out.

Take Home Message – Assemble Lines of Evidence and always ask for the Total ion Chromatograms!

Questions?