An Introduction to Biogenic Hydrocarbon Issues At Federal Contaminated Sites

June 4, 2015
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Overview

Hydrocarbons are one of the most common contaminants at federal sites. Naturally occurring hydrocarbons can result in false exceedances. Overestimation of soil impacts could have serious cost implications.
Acknowledgements

► David Rae, Erin Smith and Jeff Braun (Amec Foster Wheeler)
Definitions

► Biogenic:
  ► Produced or brought about by living organisms
  ► Naturally occurring
  ► Constituents or secretions of plants or animals
  ► Examples include pearls, silk, coal

► Phytogenic:
  ► Derived from or formed by plants
Definitions

► Petrogenic:
  ► Produced by incomplete combustion or releases of petroleum products
  ► Examples include spills of gas, diesel, oil, etc.

► Anthropogenic:
  ► Originating from human activity
Background

Regulatory Requirements

► Remediation driven by need to meet regulated levels of petroleum hydrocarbons (PHC) in soil established by Canadian Council of Ministers of the Environment (CCME)

► Canada-Wide Standards (CWS) for Petroleum Hydrocarbons in Soil are organized into four carbon range fractions:
  ► F1 (C6-C10)
  ► F2 (C10-C16)
  ► F3 (C16-C34)
  ► F4 (>C34)
Background

Regulatory Requirements

► CCME reference method provides chemical analysis protocols for generating accurate and reproducible PHC results across Canada.

► Hexane, acetone and dichloromethane solvents can co-extract naturally occurring biogenic organic compounds (BOCs) from organic soils.
Background

Biogenic Organic Compounds

- Organic compounds biosynthesized by living organisms:
  - Alkanes
  - Sterols, sterones
  - Fatty acids and fatty alcohols
  - Waxes and wax esters

- Sources:
  - Plants
  - Algae
  - Bacteria
  - Animals

Plants and algae produce BOCs as protective wax coatings that are released back into the soil at the end of their life cycle.
Relevance to Federal Sites

- BOC interference can cause false exceedances of PHC:
  - Mainly F3, but also F2 and F4
  - Overestimation of impact
  - Increased project complexity
  - Increased cost
  - Increased site disturbance

- Particular concern at sites with peaty soils:
  - High organic content
  - Northern, remote sites
Alternatives

Chromatogram Interpretation

► Sun Rose Former Uranium Exploration Site:
Alternatives

Chromatogram Interpretation

Background Soil

Background Sediment

Soil Under Empty Drum
Alternatives

Silica Gel Treatment
Alternatives

Silica Gel Treatment

► Highway #1 Drum Dump:
Silica Gel Treatment

► CWS protocol includes silica gel treatment step:
  ► Removes polar BOCs from final extract
  ► Developed on mineral/loam soils with <5% total organic content
  ► Standard 5 g silica gel treatment step becomes oversaturated by highly organic soils (35%-60% organics)
  ► Excess BOCs that cannot be contained by 5 g of silica gel become part of final PHC extract
Alternatives

Silica Gel Treatment

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<th>Parameters</th>
<th>Analytical Results - µg/L</th>
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<td>AEC 4</td>
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<td>DP-6</td>
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<td>SM478-DP-06</td>
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<td>17-Sep-14</td>
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<tr>
<td>F1 (C6 - C10) - BTEX</td>
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</tr>
<tr>
<td>F2 (&gt;C10 - C16)</td>
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<tr>
<td>F3 (&gt;C16 - C34)</td>
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<tr>
<td>F4 (&gt;C34)</td>
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Groundwater Results
1x Silica Gel Treatment

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Groundwater Results
5x Silica Gel Treatment
Alternatives

Kelly-Hooper et al. (2013)
Alternatives

Kelly-Hooper et al. (2013)

- Results quantified PHC F3 subfractions:
  - F3a (C16-C22)
  - F3b (C22-C34)

- Impacts determined by F2:F3b ratio:
  - Clean peat F2:F3b ratio <0.1
  - Crude oil spiked samples ≥0.1

- Developed equation to adjust F3 concentrations in peat:
  \[
  \text{Petrogenic F3} = \text{Measured F3a} + \left( \text{Measured F3a} \times \frac{\text{F3b in contaminated sand}}{\text{F3a in contaminated sand}} \right)
  \]
  Assumed to be petrogenic
  Petrogenic portion of F3b
Alternatives

Amec Foster Wheeler Study (2015)

- Based on Kelly-Hooper et al. (2013):
  - Clean peat
  - PHC impacted peat
  - PHC impacted sand

- Analyses:
  - F1, F2, F3a, F3b, F4
  - F1, F2, F3a, F3b, F4 with 3x silica gel treatment

- Results:
  - F2, F3a, F3b and F4 detected in clean peat sample
  - F3b and F4 non-detect in all impacted sand samples
Alternatives

Amec Foster Wheeler Study (2015)

► Site-specific modifications to approach of Kelly-Hooper et al. (2013) required for application at 5 Wing Goose Bay:
  ► Assumed F4 to be biogenic
  ► Calculated ratios for clean reference peat:
    ► F4:F1
    ► F4:F2
    ► F4:F3a
    ► F4:F3b

► For contaminated peat samples:
  ► Biogenic F1, F2, F3a and F3b calculated based on above ratios
  ► Petrogenic PHCs calculated after accounting for biogenic interference
Alternatives

Amec Foster Wheeler Study (2015)

► Conclusions:
  ► Modified Kelly-Hooper approach provided more consistent and predictable results than 3x silica gel treatment
  ► F4 and a significant portion of F3 in test site samples were biogenic and do not require remediation
Biogenic organic compounds can falsely elevate PHC results
Overestimation of PHC impacts adds significant cost and complexity
Should consider potential effects of BOCs when planning site assessments

Alternatives available to address issue:
- Chromatogram interpretation
- Silica gel treatment
- Kelly-Hooper et al. approach
- Site-specific modification of Kelly-Hooper et al. approach