Toluene in Peatlands and Wetlands

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Overview

- Peatland and wetland characteristics
- Reason for studies
- Sources of petrogenic and biogenic toluene in the environment
- Proposed forensic approach
- Case studies
- Next steps and conclusions
Peatlands and Wetlands

• Highly saturated (> 75% moisture)
• High in organic matter and biogenic hydrocarbons are common
• Sensitive ecosystem
  – Peat-forming wetlands can take up to 10,000 years to form, so reducing the disturbance in these areas is important.
  – Cost of remediation high, both financially and environmentally.
Why did Matrix do these studies?

- Toluene measured at concentrations greater than guidelines in soil and water from peatlands and wetlands
- Areas of potential impact extended off-lease into undisturbed areas
Literature Search - Sources of Toluene

Petrogenic
- Deep subsurface
  - Petroleum generation

Biogenic
- Surface and near-surface
  - Plant growth (atmosphere)
  - Microbial metabolism (hydrosphere)

Pyrogenic
- Thermal
  - Combustion of organic matter
- Ambient
  - Combustion of fuels from urban areas
Literature Search - Sources of Biogenic Toluene

Plant Growth

- Toluene emitted to atmosphere by plants under stress
- New England study demonstrates that summer pattern of atmospheric toluene does not follow benzene
  - Biogenic toluene up to 7% of total toluene measured in air

Microbial Metabolism

- A bacterium isolated from anoxic lake waters produces toluene from phenyl precursor
- Biogenic toluene documented in sludge bioreactor
Routine Analytical Approach

• Analysis of BTEX, F1 using GC/MS in selective ion mode

• Analysis of F2 to F4 PHCs using GC/FID
  – Method also extracts biogenic organic compounds (BOCs)
  – Soil extract subjected to silica gel clean-up to remove contribution from biogenic hydrocarbons present in organic soils
New Approach Needed

- Contacted lab:
  - Was there a way to determine if the toluene measured in samples is biogenic or petrogenic?
  - Could they come up with an analytical approach to solve the problem?
Forensic Approaches

• Forensic approaches to date
  – most forensic approaches look only at extractable hydrocarbons

• Forensic approach taken for this work
  – In conjunction with an extractable hydrocarbon evaluation, applied a forensic approach looking at the volatile organic carbon (VOC) fraction
  – C13:C12 isotope characterization
Determination of “True Biogenic” Samples - F3 Fraction

Obvious unresolved complex mixture (UCM) present

Largest n-alkane within C13-C18

Elevated sulphur

C10-C19 alkanes with Carbon Preference Index (CPI) ~1 or C19-C32 alkanes with CPI ~1

All false?

One or more are true?

True Biogenic

Yes

Petrogenic Impact

Yes
Decision Process for Biogenic F3 Encountered in Organic Soil

Pre-screening requires chromatogram interpretation expertise

Pre-screening

Tier 1 Evaluation

Does the GC-FID pattern in the peat sample match the GC-FID pattern(s) in the contamination source and/or background soil?

Yes

No

Exclude sample from evaluation

Do the F2 and/or F4 concentrations in the soil sample exceed soil standards?

Yes

Management required

No

Does the contamination source have an F2:F3b ratio of ≥0.10?

Yes

Do not proceed with evaluation

No

Excluding sample from evaluation

Tier 2 Evaluation

Does the F3 concentration in the soil sample exceed the soil standard?

Yes

Management required

No

Does the F2:F3b ratio in the soil sample exceed 0.10?

Yes

Management not required

No

Does the soil sample biomarker and/or PAH analysis indicate PHC presence?

Yes

Management required

No

Management not required

Adapted from Kelly-Hooper et al. 2013

Decision Process for Biogenic F3 Encountered in Organic Soil
Proposed Decision Process for Biogenic Toluene

1. Petrogenic Impact
   - Process indicates petrogenic?
     - True
     - Petrogenic markers present?
       - True
       - Matches contaminated source?
         - True
         - Isotopic carbon δC13 analysis
           - Matches biogenic material?
             - True
             - Conclusions need to be consistent with field observations
           - Matches biogenic organic compounds (BOCs) present?
             - True
             - Biogenic markers absent or trace?
               - True
               - True Biogenic
               - For selected samples and only if required for burden of proof
             - True
             - Harris and Bright (2006) and/or Kelly Hooper et al. (2013) processes
               - If F2 to F4 exceedances

2. Process indicates biogenic?
   - True
   - Requires specialized testing lab services
Carbon Isotopes

• Isotopes: atoms of the same element with different amount of neutrons, but equal number of protons in their nuclei

• Carbon isotopes include:
  – C12 – stable and predominant
  – C13 – stable
  – C14 – radioisotope

• The approximate ratio of C13 to C12 is 1:99
Carbon Isotope Analysis

• Analysis of stable isotopes for specific compounds is done by Isotope Ratio, Mass Spectrometer (IRMS)—known as Compound Specific Isotope Analysis (CSIA)

• Results expressed relative to a benchmark standard of C13

\[ \delta^{13}\text{C} = \left( \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1000 \text{ expressed as } \% \]

or per mil, and

\[ R = \frac{^{13}\text{C}}{^{12}\text{C}} \]
Case Study Applications

• Selected sites that had the following:
  – Toluene in organic soils from remedial excavations
  – Toluene measured in soil and surface water from peatlands and wetlands from undisturbed areas

• In collaboration with local laboratories, tested analytical process to distinguish between petrogenic and biogenic toluene
  – Case Study 1 – Peatland
  – Case Study 2 – Boreal Forest Wetlands
Case Study 1: Assessment, delineation and remediation of hydrocarbon impacts within peatlands at an abandoned well site
West – East Cross Section

- Clay Pad
- Silty Clay
- Organic
- Weathered Sandstone

Elevation (masl)

Distance (m)
Soil Quality Results

Toluene, LEPH, HEPH (Background)

Xylenes, VPH, LEPH,

Benzene, Toluene, LEPH, HEPH

Benzene, Toluene

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Soil Quality Results

Contaminants of concern
- benzene
- toluene
- LEPH ($C_{10}$-$C_{19}$)
- HEPH ($C_{19}$-$C_{32}$+)

- Toluene concentration range 1 to 22.8 mg/kg

Extent of impact large if lab results were used as received (no interpretation)
Soil Quality Results

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- benzene
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Parameters Exceeding Regulatory Standards

- Benzene
- HEPH ($C_{19}-C_{32}$)
- Toluene
- LEPH ($C_{10}-C_{19}$)
- Analyzed - No Exceedance
Soil Quality Results

Contaminant of concern
- benzene

Extent of impact much smaller

- Minimizes disturbance to sensitive undisturbed peat land

Parameters Exceeding Regulatory Standards
- Benzene
- Analyzed - No Exceedance
VOC scan – Petrogenic Markers

- m, p-xylenes
- C3-benzenes
- ethyl toluenes
- other aromatic hydrocarbons
VOC Biogenic Markers

Toluene major VOC detected
VOC Biogenic Markers

VOC Scans – Example Biogenic Markers
- camphene
- pinene
- carene
Case Study 1 – Carbon Isotopes

\[\delta C_{13} \text{ toluene signature in petrogenic source range from -22 to -30‰} \]

\[\delta C_{13} \text{ of Refined Gasoline or Crude} \]

\[\delta C_{13} \text{ of Peatlands and Wetlands} \]

\[\delta C_{13} \text{ of Flare Pit} \]

\[\delta C_{13} \text{ of Suspected Biogenic Toluene} \]
Case Study 2: Background Wetlands Study

• Former Gas Plant and Active Compressor Station in green zone, west Alberta
• Gas Plant (south part of site) is part of a regulatory decommissioning project as per the EPEA Approval requirements
• Decade-long soil remedial program nearly complete
• Surface water monitoring program at site (9 locations)
Site Wetlands Monitoring

• Applied *Environmental Quality Guidelines for Alberta Surface Waters* (ESRD 2014)

• Regulatory exceedances encountered:
  – Acidic pH (one location)
  – Toluene (five locations)
  – Total metals – As, Cd, Cr, Co, Cu, Pb, Ag, Zn
  – Dissolved metals – Al, Fe

• Question: Are exceedances natural or introduced?
Site Surface Water Monitoring
Background Wetland Study

- 15 sites from area sampled
- Sites classified by Alberta Wetland Inventory classification system
Background Wetland Study - Methods

• Field
  – Wetland descriptions and classification
  – In situ water chemistry (temperature, dissolved oxygen, pH, conductivity and turbidity)

• Lab Analysis
  – Routine chemistry
  – Dissolved hydrocarbons by headspace analysis
  – 5 of 15 samples had detectable toluene
  – These 5 samples - open scan purge and trap dissolved hydrocarbon analysis including full VOC scan
  – 1 of the 5 samples submitted for toluene carbon isotope analysis
Background Wetlands Study - Results
Toluene Concentrations at Site and Background Surface Water

- **Active Site Deciduous Swamp**
- **Active Site Marsh**
- **Background Deciduous Swamp**
- **Background Marsh**
- **Background Shallow Open Water**

**Toluene Aquatic Life Guideline:** 0.0005 mg/L

- Toluene Concentrations at Site and Background Surface Water
• VOC chromatograms indicated both compounds understood to be biogenic (BOCs) and those potentially anthropogenic (?)
  – toluene (?)
  – hexanal (BOC)
  – heptanal (BOC)
  – trimethylbenzene (?)
  – 3-octanone (BOC)
  – o/m/p-cymene (BOC)
  – eucalyptol (BOC)
VOCs Biogenic Markers

VOC Scan – Example

Biogenic Markers
- Hexanal
- O/M/P – Cymene
- Eucalyptol

spiking solution contains: nC6, benzene, toluene, ethylbenzene and xylenes

Sample + Spike

Time
Abundance
Sample
Blank

Toluene Spike
Hexanal
O/M/P - Cymene
Eucalyptol
Case Study 2 Carbon Isotope Result

δC13 toluene signature in petrogenic source range from -22 to -30‰.

- Refined Gasoline or Crude
- Flare Pit
- Petrogenic Toluene Spikes
- Peatlands and Wetlands
- Suspected Biogenic Toluene

Case Study 2 Result
Both case studies were able to establish presence of true biogenic toluene.
Challenges

- Presence of both petrogenic and biogenic markers
  - More work is required to develop approaches for addressing this
  - Need better characterization of source and background materials

- Lab analysis packages for biogenic toluene evaluations are needed
Conclusions

• If you are doing work in peatlands and wetlands, and suspect that you need to do these evaluations:
  – Need extra sample bottles
  – Always run two or more background samples in open scan mode to determine biomarkers for your site
  – In BC, you should also do silica gel clean up for extractable hydrocarbons (done automatically in Alberta)
  – If you anticipate needing additional evidence (i.e. biomarkers, carbon isotopes) – plan in advance

• Use targeted analyses for characterization - no need to analyze all samples

• Talk to the lab in advance
Thank You

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Maxxam
Apache

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References


References


