



Accurate and Quantifiable Characterization of Biogenic vs. Petrogenic Hydrocarbons in Soil

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Alberta Tier 1 PHC Soil and Groundwater Remediation Guidelines (AEP, 2016)

Biogenic Organic Compounds (BOCs) can be falsely detected as PHCs in uncontaminated organic soils and composts.

Slightly contaminated soils may exceed Tier 1 guidelines for F3.



Chromatogram review by a Qualified Person may be employed to help distinguish false exceedances due to BOC from true petroleum releases.

Background:

- BOCs can be falsely detected as PHCs in uncontaminated organic soils and compost materials.
- They can also cause slightly contaminated soils to exceed the Tier 1 guidelines for F3 PHCs.

Peat BOCs are a Significant Source of Organic Interference in Alberta

Title:	BIC Scale for Delineating Petroleum Hydrocarbons in Organic Soils and Compost
Number:	AEP Land Policy 2018-1
Program Name:	Land Conservation and Reclamation Policy
Effective Date:	April 3, 2018
This document was updated on:	

Purpose

This Information Letter describes the Biogenic Interference Calculation (BIC) Scale and regulatory requirements for its use in Alberta. The BIC Scale is a mathematical tool for identifying false exceedances of the Alberta Tier 1 soil guidelines (AEP, 2016) for petroleum hydrocarbons (PHCs) due to the presence of natural biogenic organic compounds (BOCs). However, the BIC Scale does not quantify true PHC concentrations. Plants and animals biosynthesize BOCs (e.g. tissues, wastes, etc.) which are integral components of organic soils and compost. By definition, organic soils contain greater than 17% total organic carbon (TOC), with peat soils containing greater than 40% TOC. Compost typically ranges from 50% to 60% TOC.

This Information Letter provides guidance on analytical and reporting requirements when using the BIC Scale for closure at sites regulated by Alberta Environment and Parks or the Alberta Energy Regulator.

Scope

Detailed instructions are provided for applying PHC F2 (C10-C16) and sub-fraction PHC F3s (C22-C34) concentrations to the BIC Scale, in order to determine if organic samples have falsely exceeded the Alberta Tier 1 soil guidelines for PHC F3 (C16-C34).

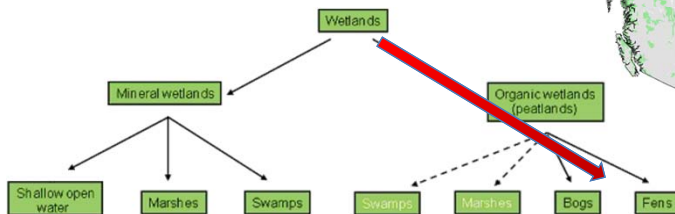
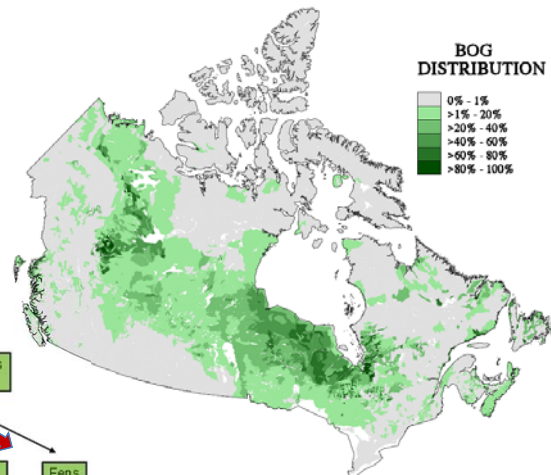
Introduction

The Canada-wide Standard (CWS) for PHCs in Soil (CCME, 2008) provides the protocols and primary technical basis for the Alberta Tier 1 PHC Soil and Groundwater Remediation Guidelines (AEP, 2016). These guidelines are established for the following four carbon ranges/fractions: F1 (C8-C10), F2 (C10-C16), F3 (C16-C34), and F4 (C34-C50). The reference method for the Canada-Wide Standard (CWS) for petroleum hydrocarbons (PHC) in soil provides laboratory methods for generating accurate and reproducible soil analysis results (CCME, 2001).

The CWS PHC analytical methods quantify PHC F1, F2, F3 and F4 concentrations for light to heavy PHC products, such as diesel, crude oil, bitumen, asphalt, motor oil, etc. However, BOCs can be falsely detected as PHCs in uncontaminated organic soils and compost materials. They can also cause slightly

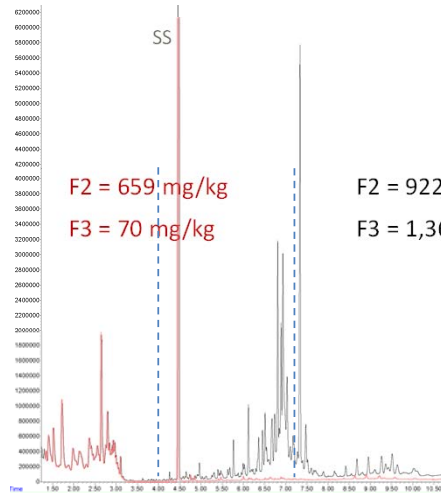
90% of Canadian Wetlands are Peat

- 113.6 million hectares across Canada.
- Bogs and Fens are the dominant Alberta peatland classes.
- Swamps and marshes can accumulate peat.



<http://www.hww.ca/en/wild-spaces/peatlands.html>

Petrogenic or Biogenic?? Is F3 a True Exceedance?

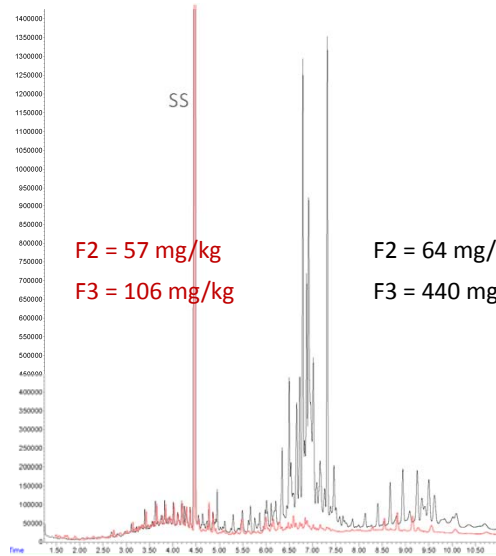


F2 = 659 mg/kg
F3 = 70 mg/kg

F2 = 922 mg/kg
F3 = 1,361 mg/kg



Petrogenic or Biogenic?? Is F3 a True Exceedance?



F2 = 57 mg/kg
F3 = 106 mg/kg

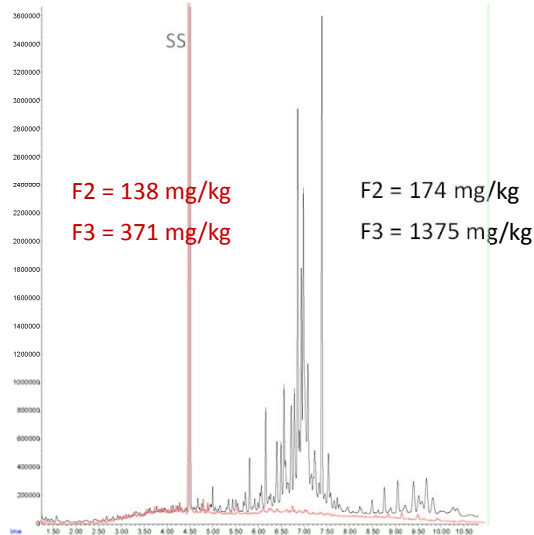
F2 = 64 mg/kg
F3 = 440 mg/kg



Petrogenic or Biogenic?? Is F3 a True Exceedance?



Maxxam
A Business Services Group Company

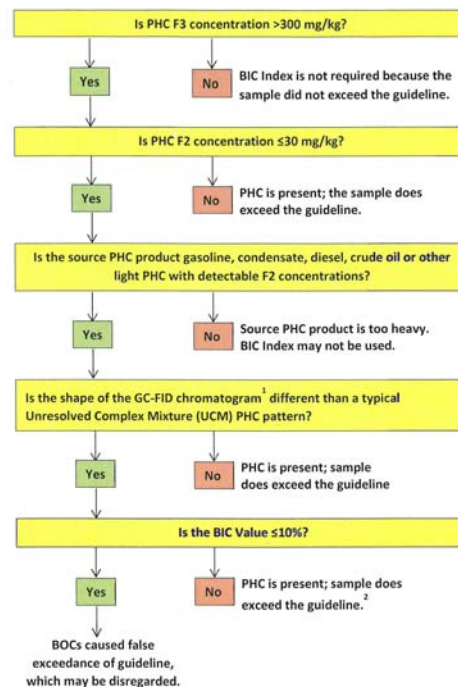


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BIC Scale

Overview

- Adopted by Alberta Government April 2018
- Mathematical tool for identifying false exceedances of AT1 soil guidelines for PHC due to presence of natural Biogenic Organic Compounds (BOC).
- Does not quantify true PHC.



BIC Value Calculation

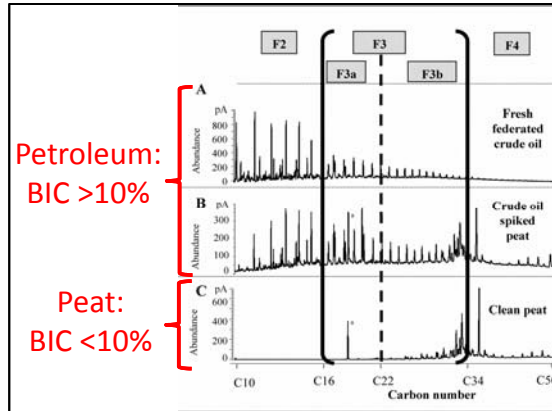
F3 region (C16-C34) of hydrocarbon scan divided into two segments:

- F3a: C16-C22
- F3b: C22-C34

- In peat profiles, F2 and F3a are ND
- In most petroleum products, hydrocarbons seen in both F2 and F3a.

BIC Value distinguishes peat biogenics from PHC through ratio of F2 and F3b:

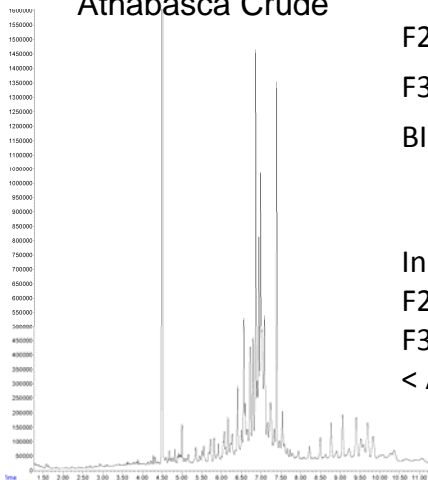
$$BIC\ Value = \frac{[PHC\ F2]}{[PHC\ F2] + [PHC\ F3b]}$$



F. Kelly-Hooper et al. *Envir. Toxicol. Chem.* 2013, 32, 2197-2206.

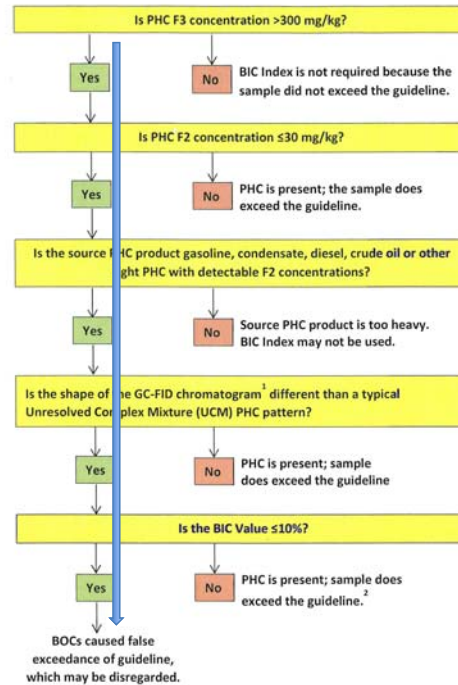
BIC Application

30% Peat, 100 mg/kg
Athabasca Crude



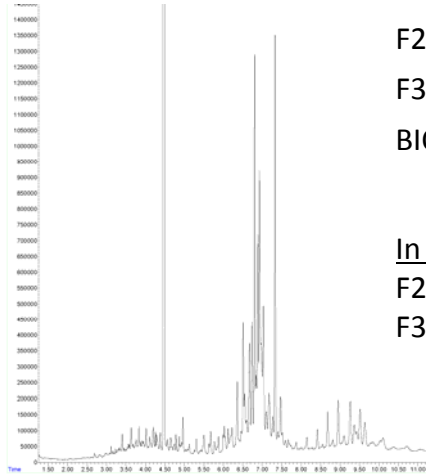
F2 = 19
F3 = 418
BIC = 5%

In mineral soil:
F2 = 0
F3 = 80
< AT1 Guideline



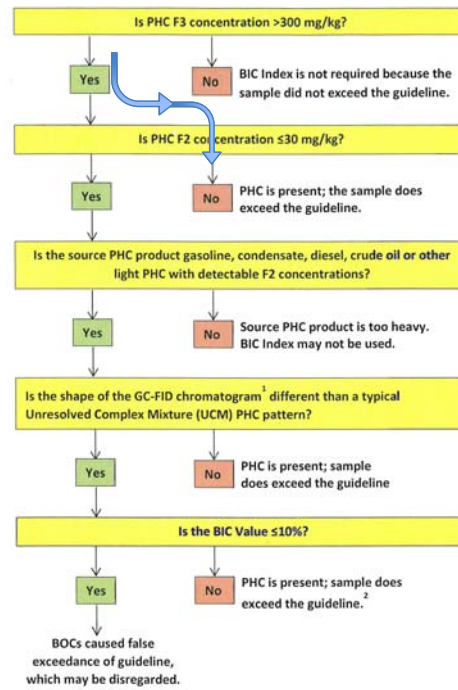
BIC Application

100 mg/kg Diesel, 30% Peat



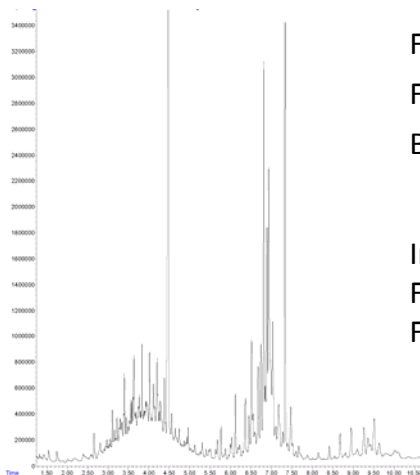
F2 = 64
F3 = 440
BIC = 15%

In mineral soil:
F2 = 57
F3 = 106



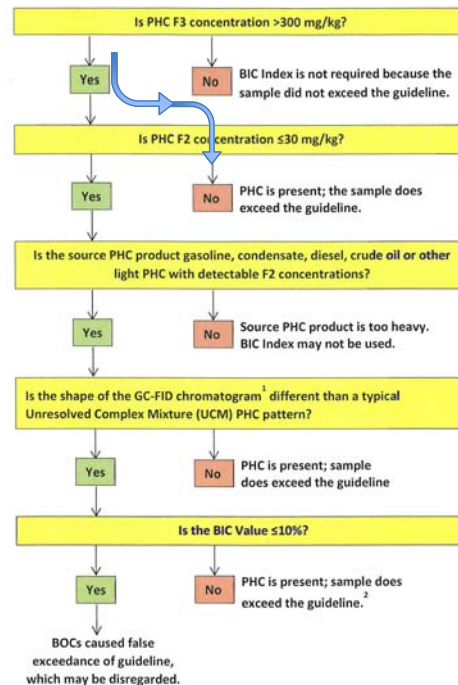
BIC Application

1,000 mg/kg Diesel, 30% Peat



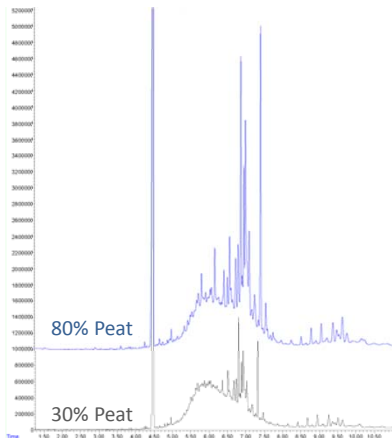
F2 = 681
F3 = 830
BIC = 54%

In mineral soil:
F2 = 615
F3 = 476



BIC Application

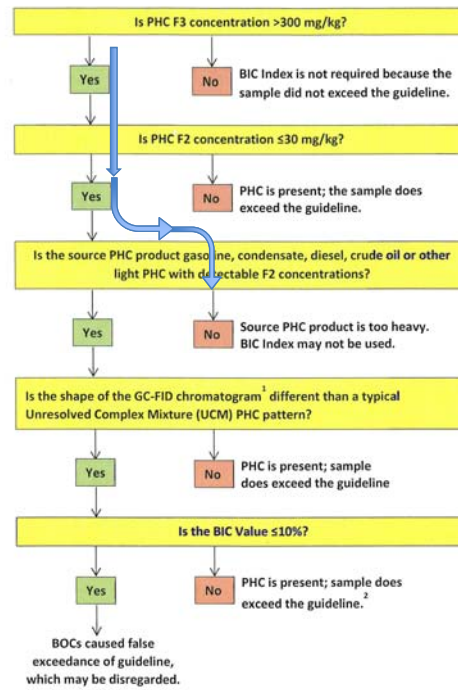
1,000 mg/kg Motor Oil



In mineral soil:
F2 = nd
F3 = 1,080

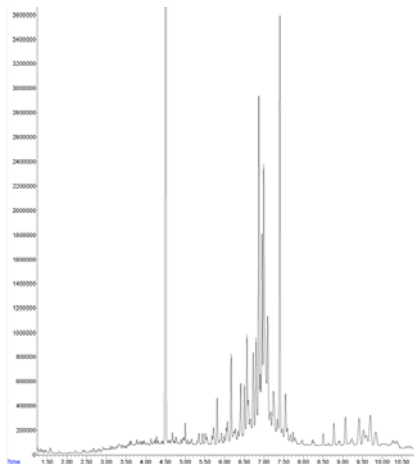
F2 = 21
F3 = 2,346

F2 = 11
F3 = 1,374



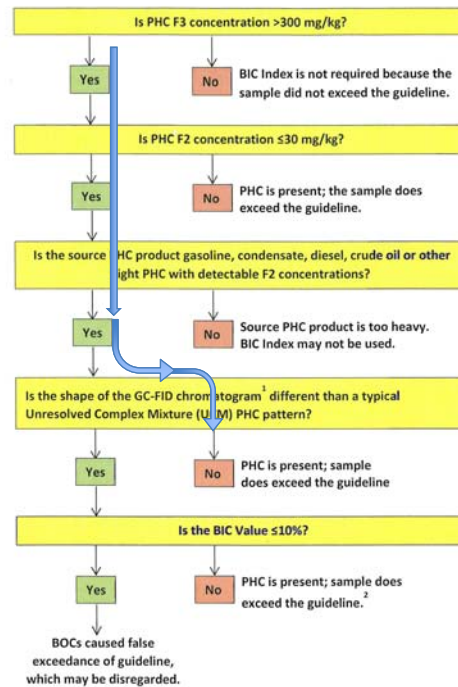
BIC Application

100 mg/kg Athabasca Crude



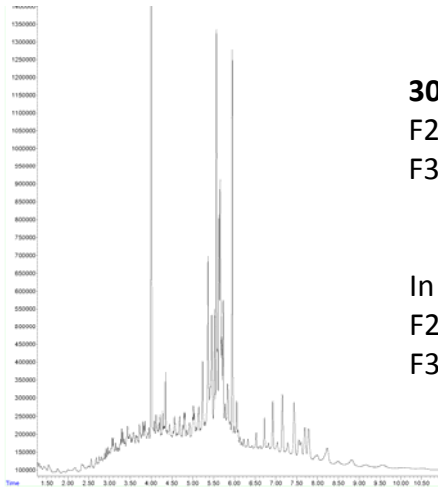
30% Peat
F2 = 19
F3 = 418
BIC = 19%

In mineral soil:
F2 = 16
F3 = 96



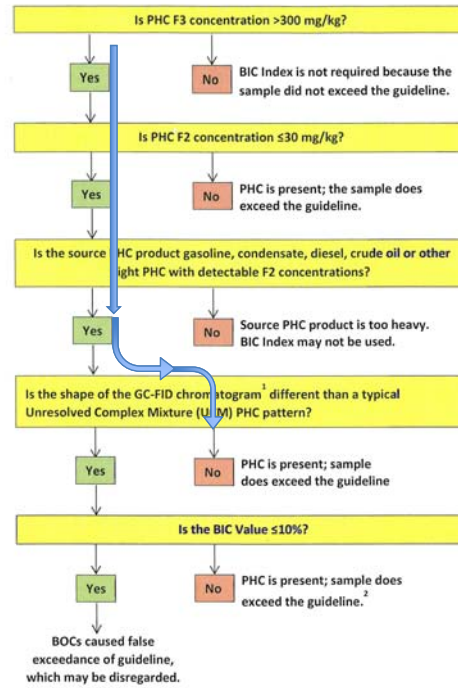
BIC Application

1,000 mg/kg Athabasca Crude



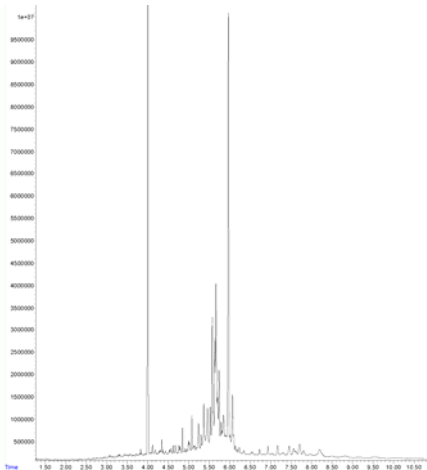
30% Peat
F2 = 165
F3 = 678

In mineral soil:
F2 = 132
F3 = 357



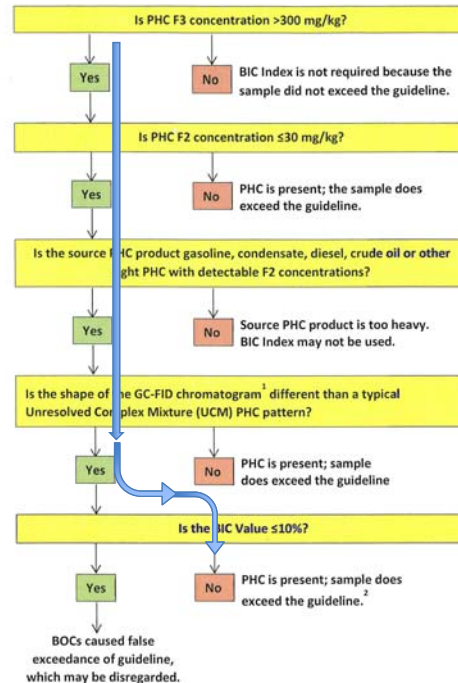
BIC Application

1,000 mg/kg Athabasca Crude



80% Peat
F2 = 174
F3 = 1,375
BIC = 12%

In mineral soil:
F2 = 138
F3 = 371



CCME: PHCs in Soils and Sediment, Section 4.1.9

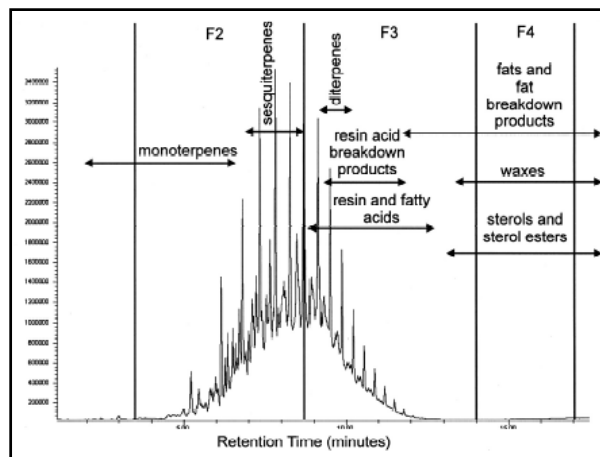
The organic extract is dried using sodium sulphate and **treated with silica gel** ... either *in situ* or by **column chromatography** to remove polar material (50:50 dichloromethane/hexane).

Soils and sediment with **high organic content such as peat may exceed the capacity of the silica gel** to remove non-petroleum hydrocarbons.



What are Biogenic Interferences?

- This is a well documented old issue, but a clear solution is not available
- Biogenic Organic Compounds (BOCs) such as sterols, fatty acids and fatty alcohols although highly polar are partially extracted in the hexane:acetone solvent mix.
- Mainly elute in the F3 (C16-34) and some in the F4 (C34-C50) fraction.



Can Column Clean-up be Tailored to Peat Soils?

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 Zhendi Wang¹
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 Mike Landriault¹

¹Emergencies Science and Technology Section (ESTS), Science and Technology Branch, Environment Canada, Ottawa, ON, Canada

Research Article

Method development for fingerprinting of biodiesel blends by solid-phase extraction and gas chromatography-mass spectrometry J. Sep. Sci. 2011, 34, 3253-3264.



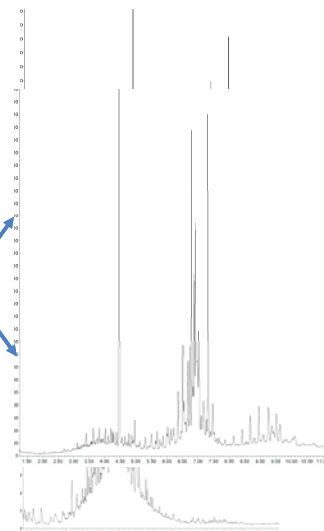
Extract with (double) solvent. Standard CCME surrogate.



Put extract on column for fractionation.
 ⊖
 Additional surrogates to monitor fractionation.
 ⊖
 Collect separate PHC and BOC fractions.



Analyse by GC/FID.

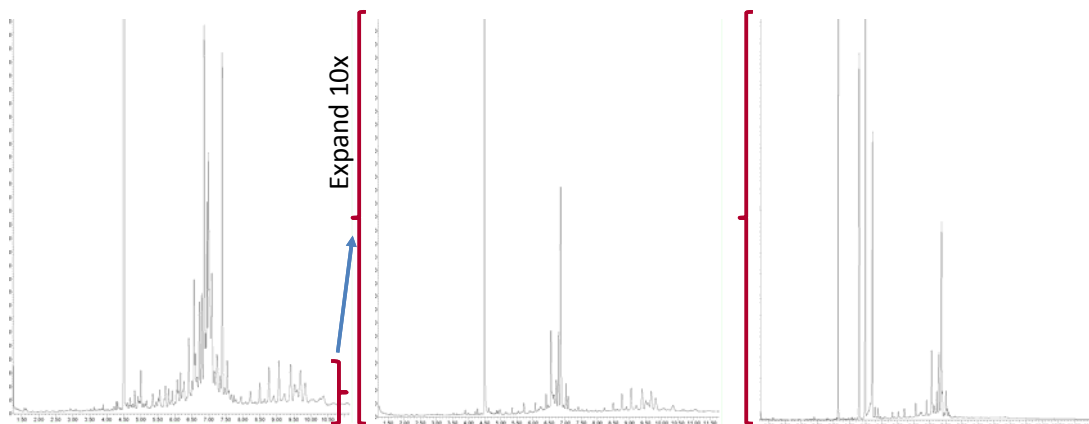


30% Peat Soils

In Situ Silica Clean-up

Silica Column Clean-up

Fractionation Column



30% Peat, 100 mg/kg Diesel

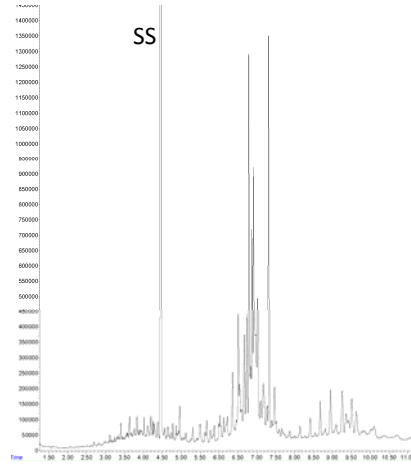
In mineral soil:

- F2 = 57, F3 = 106 (< AT1 guideline)

In 30% Peat:

- F2 = 64; F3 = 440
- BIC = 14%

Decision Tree deems it to exceed guideline, requiring chromatogram review.



30% Peat, 100 mg/kg Diesel

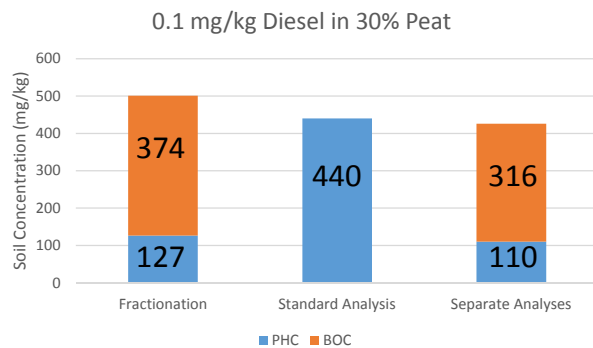
In mineral soil:

- F2 = 57, F3 = 110 (< AT1 guideline)

In 30% Peat:

- F2 = 64; F3 = 440
- BIC = 14%

Decision Tree deems it to exceed guideline, requiring chromatogram review.



30% Peat, 1,000 mg/kg Athabasca Crude

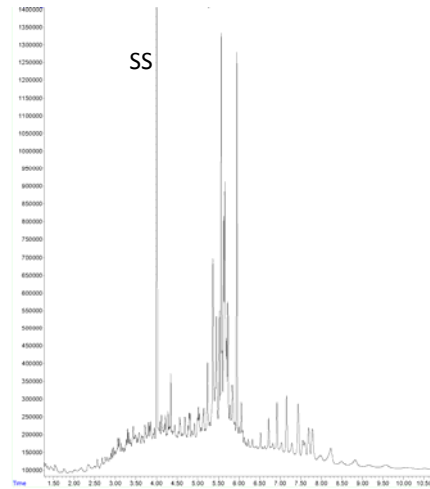
In mineral soil:

- F2 = 138, F3 = 371 (> AT1)

In 30% Peat:

- F2 = 167; F3 = 764
- BIC = 19%

Decision Tree deems it to exceed guideline requiring chromatogram review.



30% Peat, 1,000 mg/kg Athabasca Crude

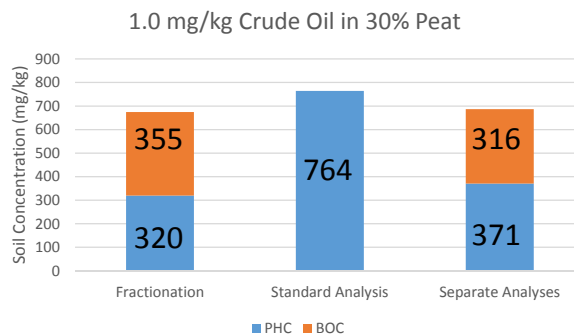
In mineral soil:

- F2 = 138, F3 = 371 (> AT1)

In 30% Peat:

- F2 = 167; F3 = 764
- BIC = 19%

Decision Tree deems it to exceed guideline requiring chromatogram review.

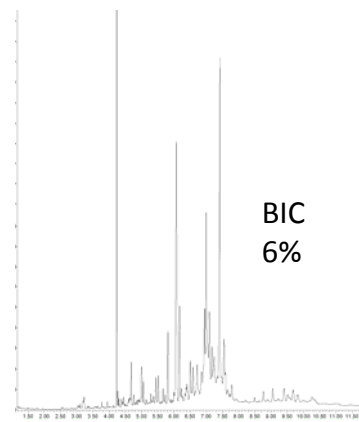
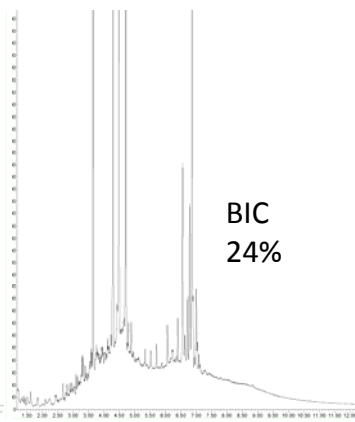
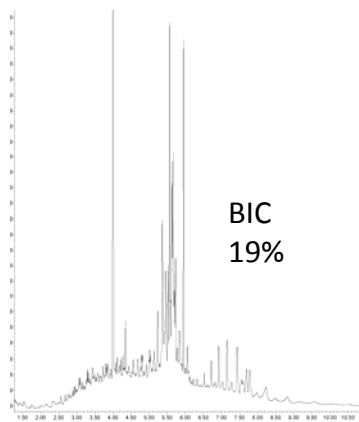


Athabasca Crude in 30% Peat Soils

In Situ Silica Clean-up

Fractionation Column PHCs

Fractionation Column BOC

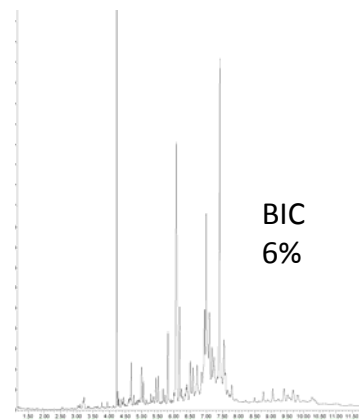
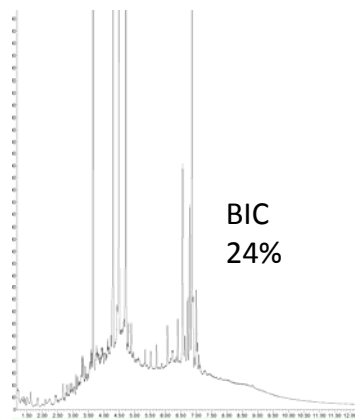
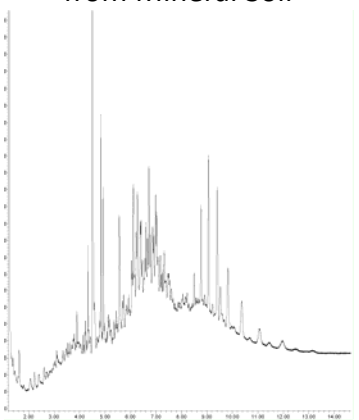


Athabasca Crude in 30% Peat Soils

In Situ Silica Clean-up
from Mineral Soil

Fractionation Column PHCs

Fractionation Column BOC



80% Peat, 1,000 mg/kg Motor Oil

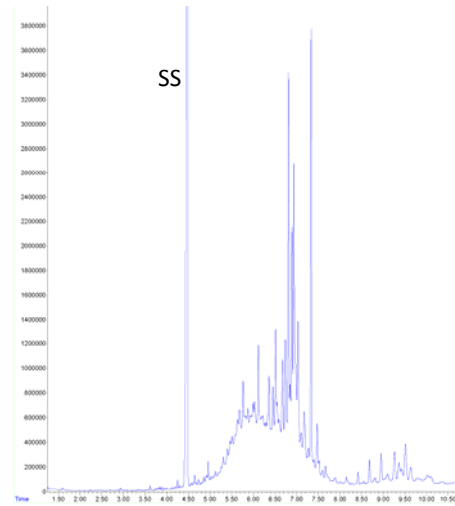
In mineral soil:

- F2 = nd, F3 = 1,080 (> AT1)

In 30% Peat:

- F2 = 21; F3 = 2,346
- BIC = 1%

Decision Tree cannot be used.



80% Peat, 1,000 mg/kg Motor Oil

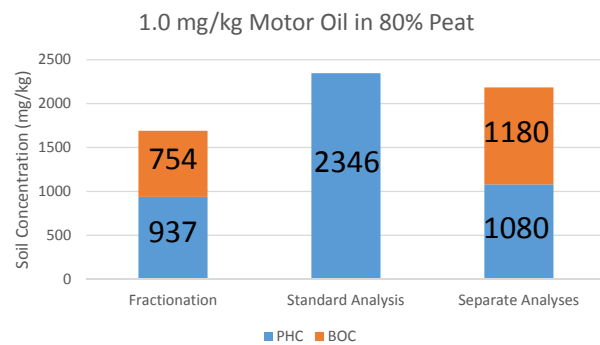
In mineral soil:

- F2 = nd, F3 = 1,080 (> AT1)

In 30% Peat:

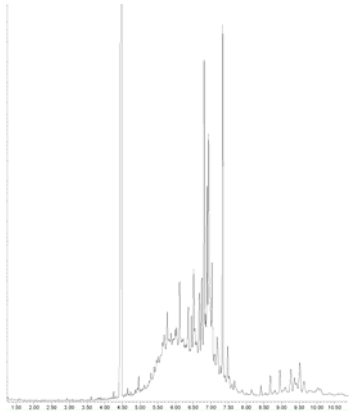
- F2 = 21; F3 = 2,346
- BIC = 1%

Decision Tree cannot be used.

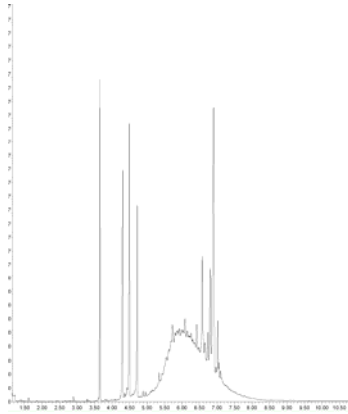


Motor Oil in 80% Peat Soils

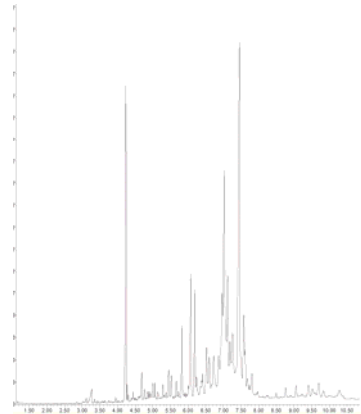
In Situ Silica Clean-up



Fractionation Column PHCs



Fractionation Column BOC



Column Fractionation Overview

1. Samples extracted with double amount of solvent
2. Standard CCME F2-F4 surrogate added to monitor PHC recovery
3. Additional recovery surrogates added after extraction, prior to fractionation, to monitor fractionation efficiency:
 - PHC Surrogates:
 - aliphatic + aromatic (PAH)
 - BOC Surrogates:
 - moderate + high polarity
4. Column eluted with a series of solvents with increasing polarity.
5. Fractions containing PHCs combined and quantified
6. Fractions containing BOC combined and quantified

Summary of Quantitative PHC/BOC Method

- Provides quantitative reporting of the separate petroleum (PHC) and biologic (BOC) extractable concentrations in a high organic soil.
- Both petroleum and biologic components are calibrated to the same petroleum calibration standards used for a regular F2-F4 analysis.
 - i.e. BOC concentration is expressed in petroleum-equivalents.
- PHC fraction obtained is similar to PHC fraction from a regular column clean-up of a F2-F4 extract.
- Extraction processes and instrumentation are identical to a regular F2-F4 analysis.
- Additional lab recovery surrogates used with each sample verify efficiency of separation of PHC and BOC components.
- Isolation of BOC from petroleum fraction allows for easier compound identification in chromatogram review or through GC/MS analysis.



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Thank You

Comments and Questions:
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