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

Heather Lord, Lusine Khachatryan, Alicia Rahamat

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.

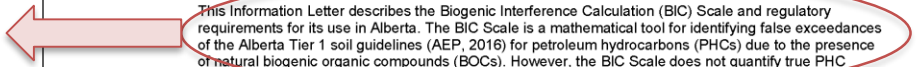
Slightly contaminated soils may exceed Tier 1 guidelines for F3.

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

2018: BIC Scale

- Guide to requirements for use of BIC Scale in Alberta.
- Mathematical tool for identifying false exceedances of AT1 soil guidelines for PHCs due to presence of BOC.
- Does not quantify true PHC.

Samples not identified as false exceedances may still require chromatogram review



Alberta Government Guide

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

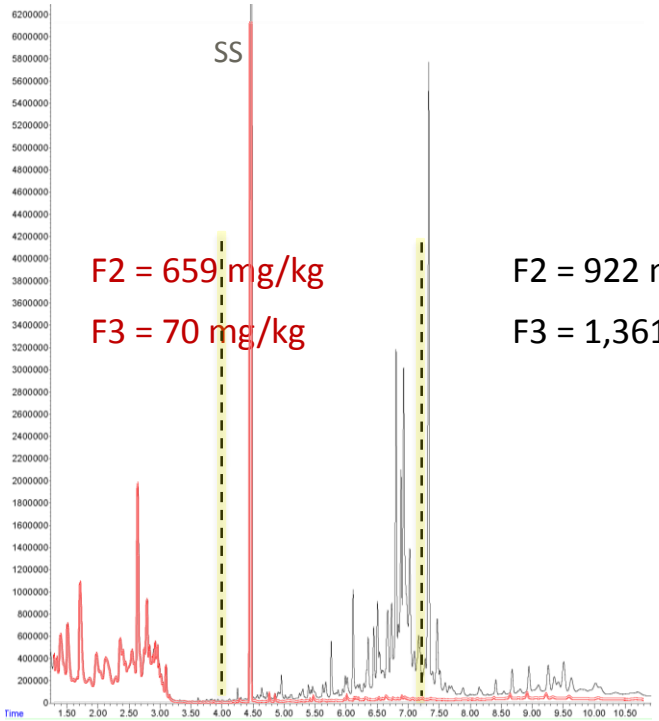
Detailed instructions are provided for applying PHC F2 (C10-C16) and sub-fraction PHC F3b (C22-C34) concentrations to the BIC Scale, in order to determine if organic samples have falsely exceeded the Alberta Tier 1 soil guidelines for PHC F3 (C16-C34).

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 (C6–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

Petrogenic or Biogenic?? Is F3 a True Exceedance?



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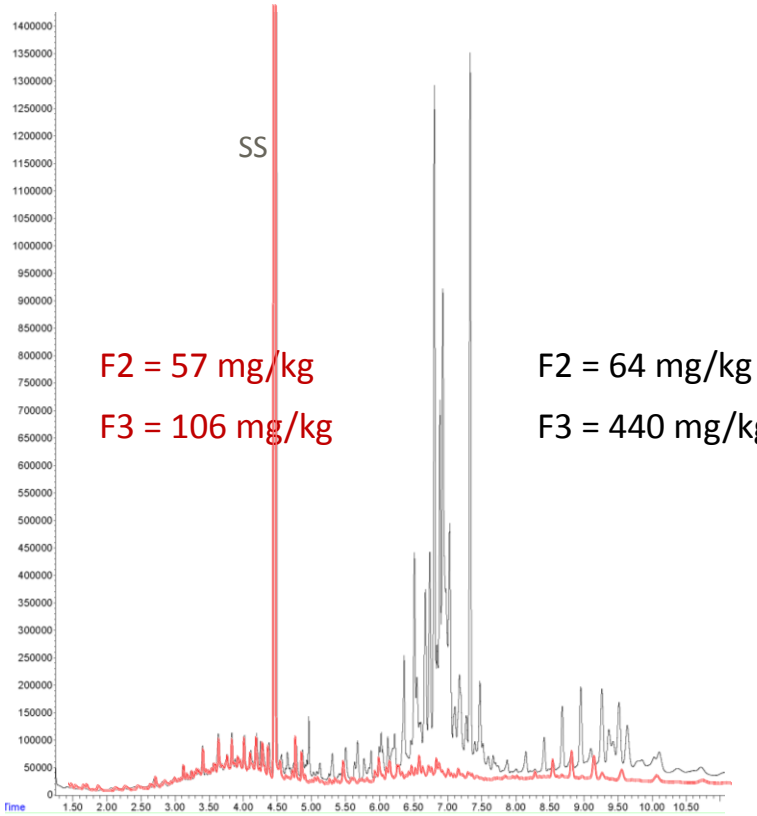

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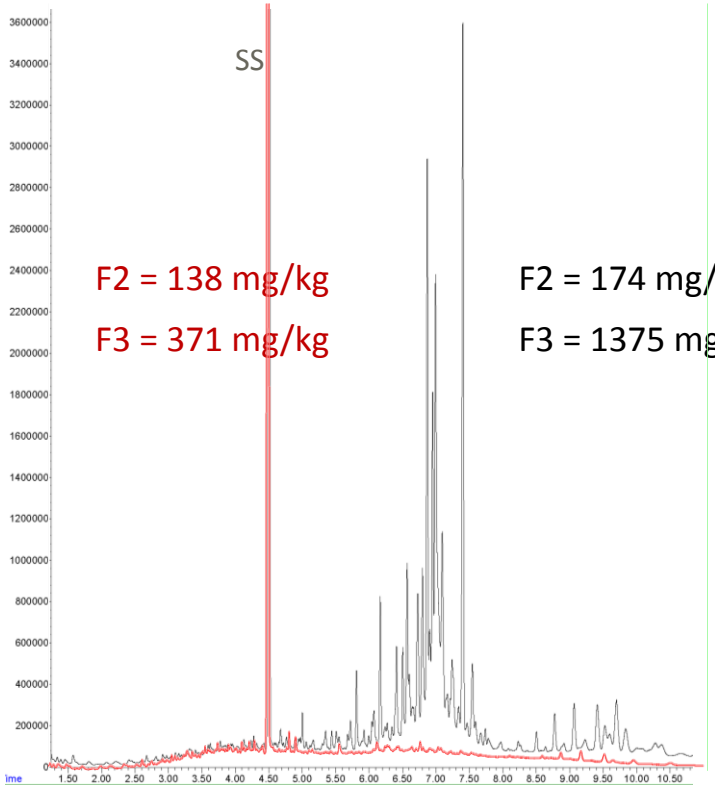

F2 = 138 mg/kg

F3 = 371 mg/kg

F2 = 174 mg/kg

F3 = 1375 mg/kg

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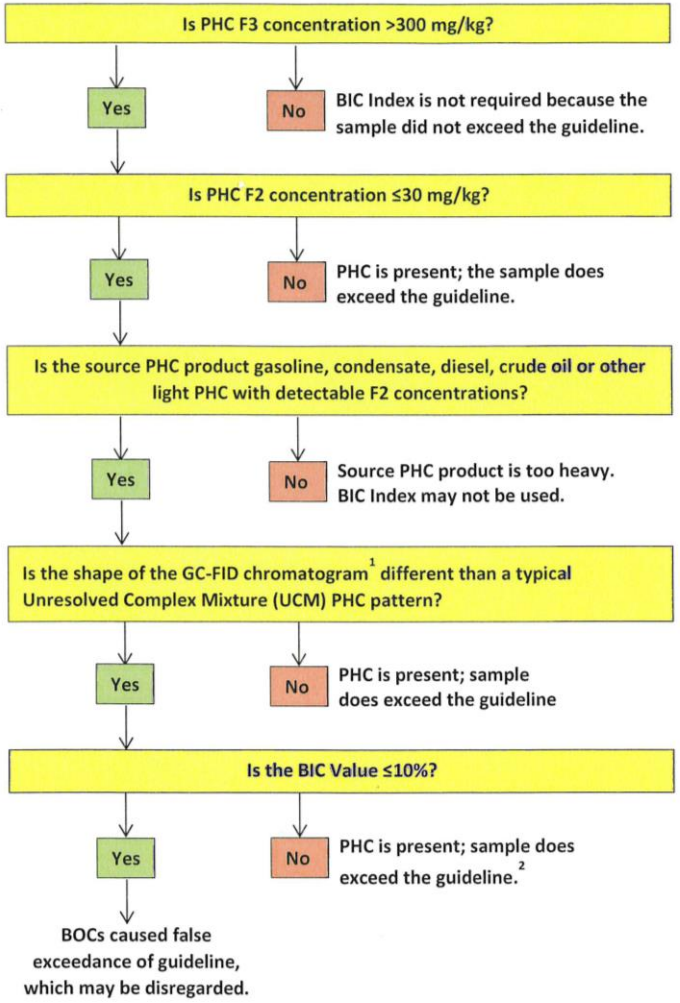
BIC Scale

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

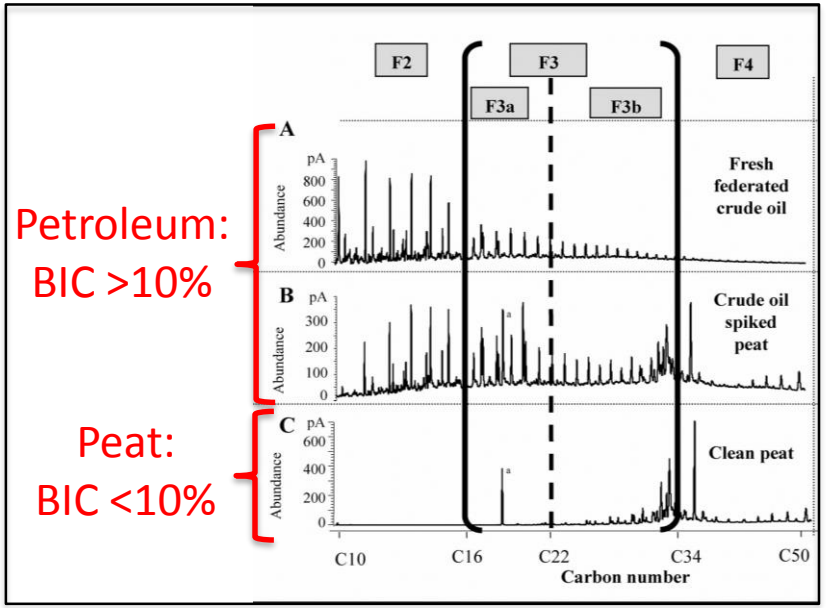
F3 region (C16-C34) of hydrocarbon scan divided into two segments:

- 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:

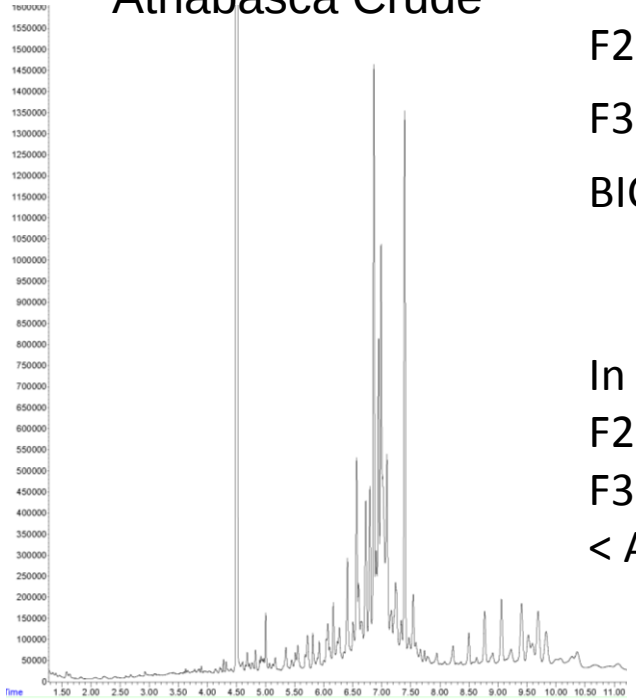
$$BIC\ Value = \frac{[PHC\ F2]}{[PHC\ F2] + [PHC\ F3b]}$$



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

BIC Application

30% Peat, 100 mg/kg
Athabasca Crude

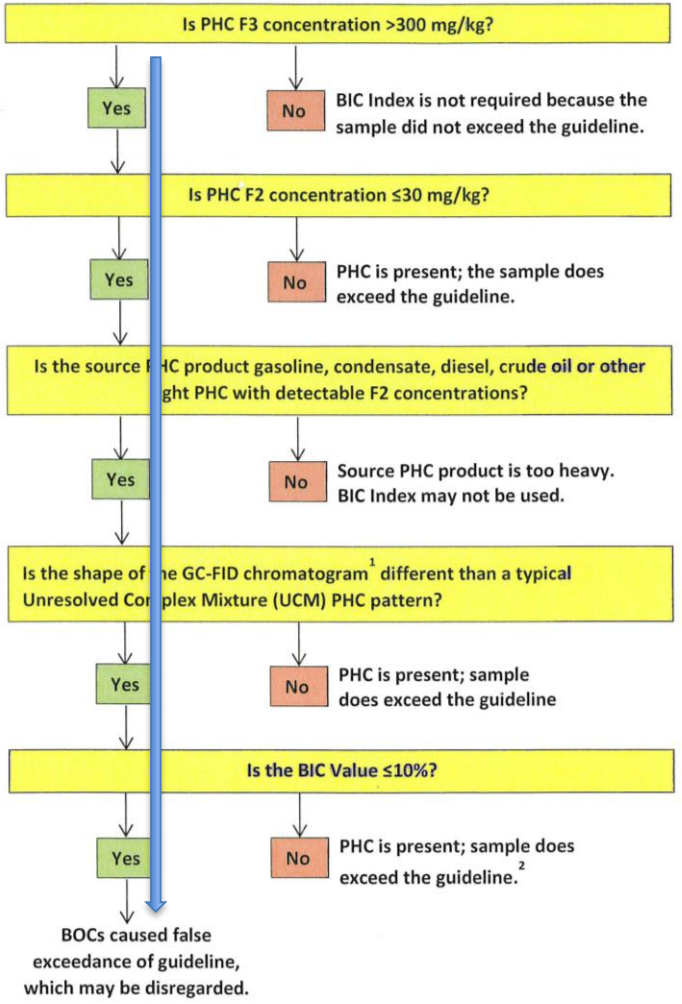


F2 = 19

F3 = 418

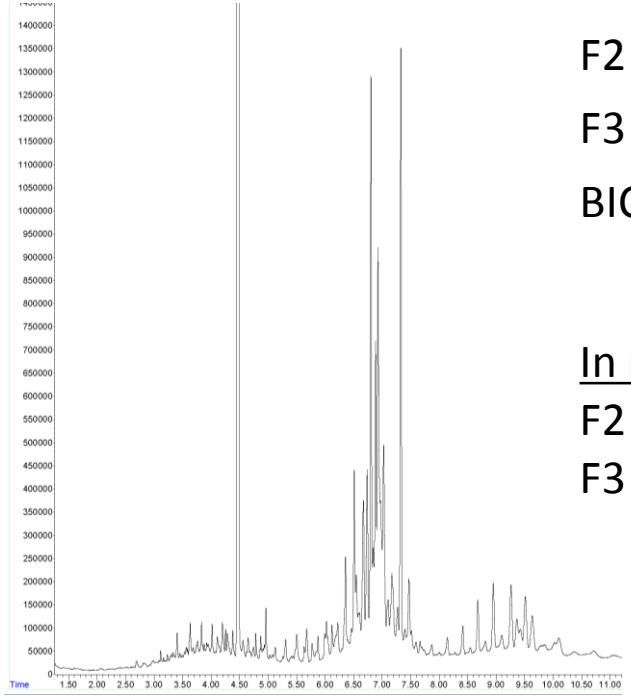
BIC = 5%

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



BIC Application

100 mg/kg Diesel, 30% Peat



F2 = 64

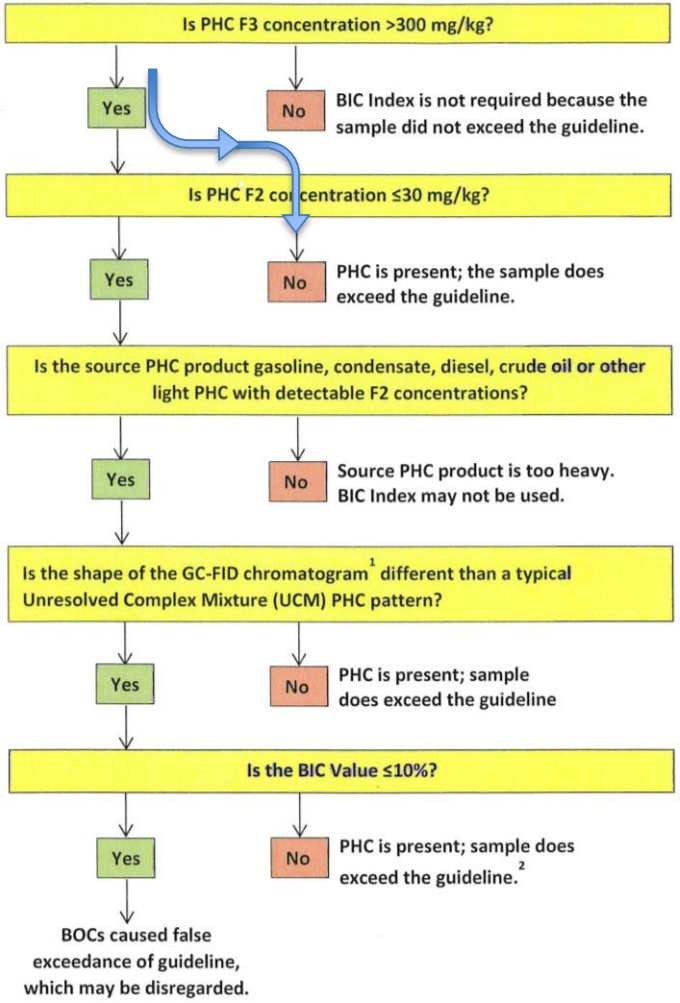
F3 = 440

BIC = 15%

<u>In mineral soil</u>:

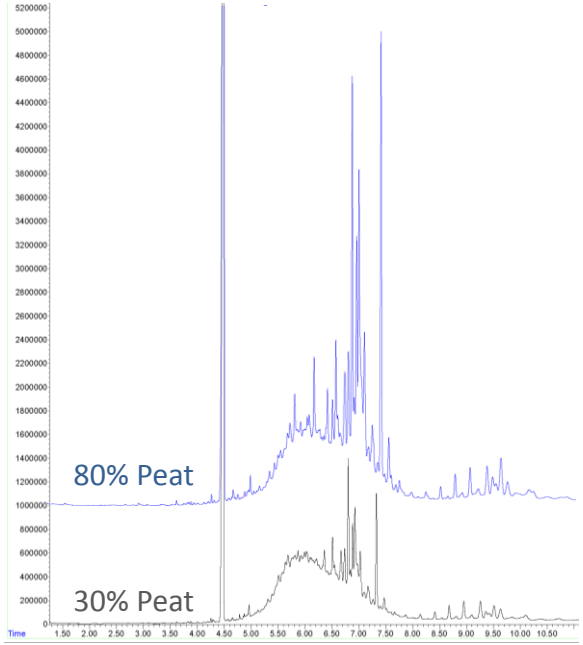
F2 = 57

F3 = 106



BIC Application

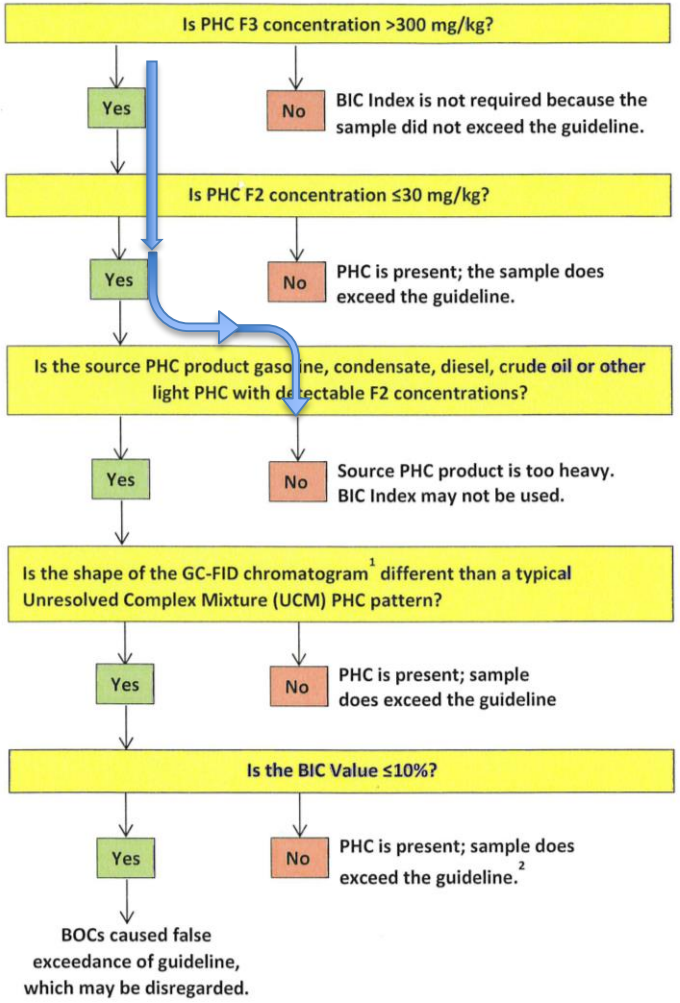
1,000 mg/kg Motor Oil



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

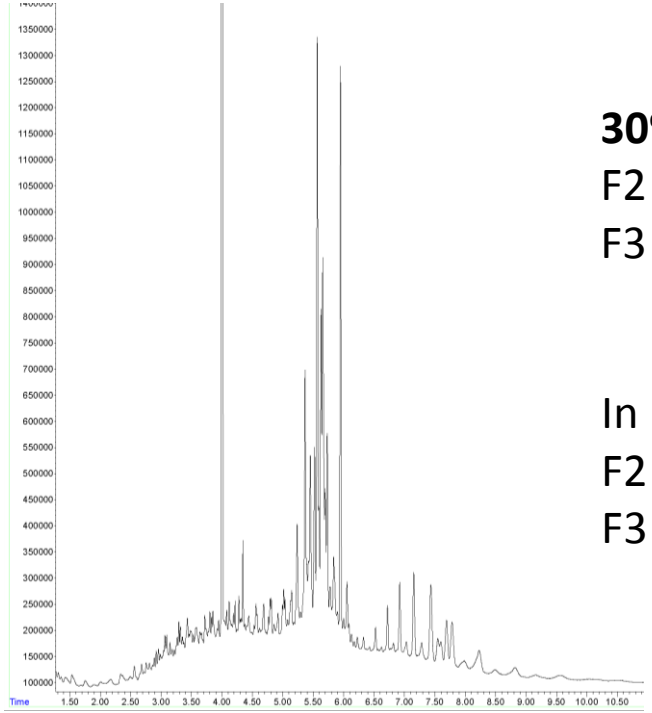
F2 = 21
F3 = 2,346

F2 = 11
F3 = 1,374



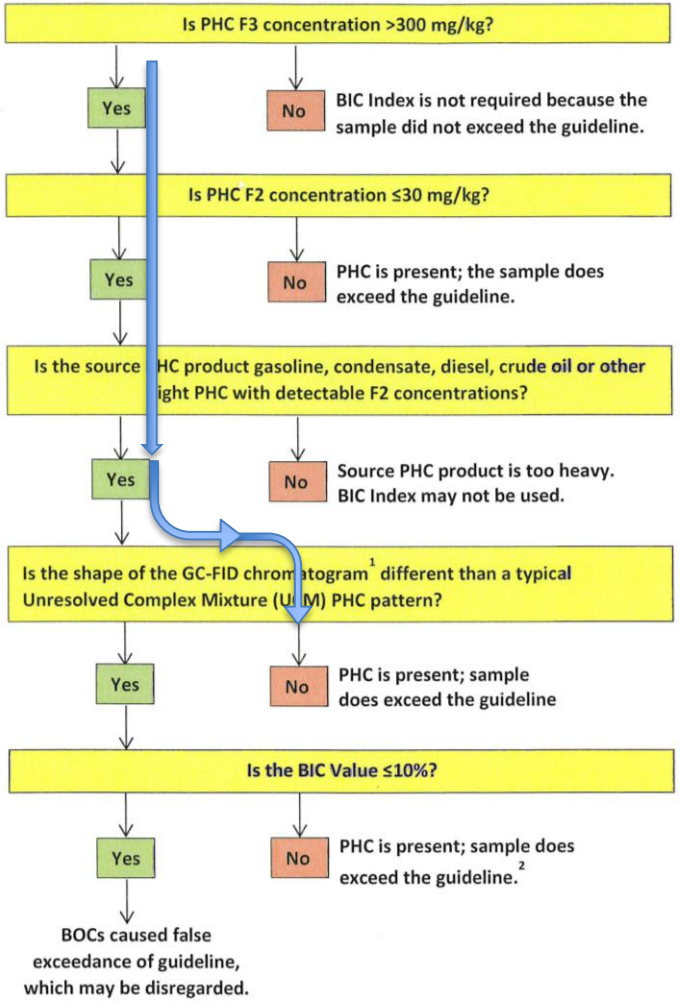
BIC Application

1,000 mg/kg Athabasca Crude



30% Peat
F2 = 165
F3 = 678

In mineral soil:
F2 = 132
F3 = 357



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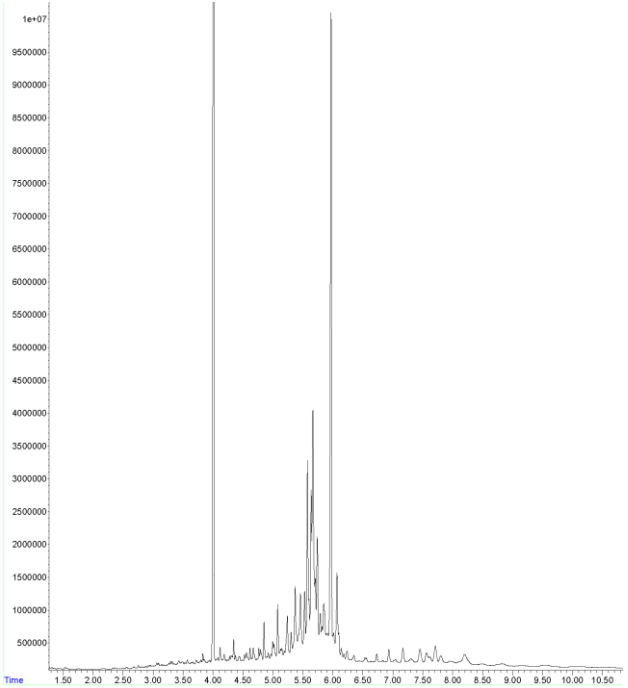
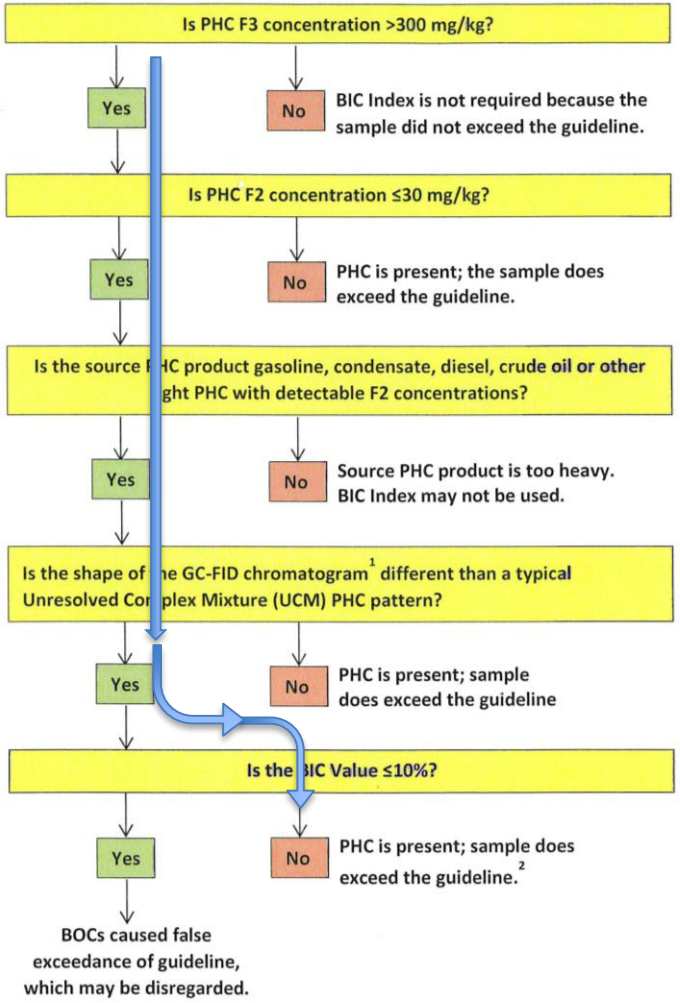


80% Peat
F2 = 174
F3 = 1,375
BIC = 12%

In mineral soil:
F2 = 138
F3 = 371



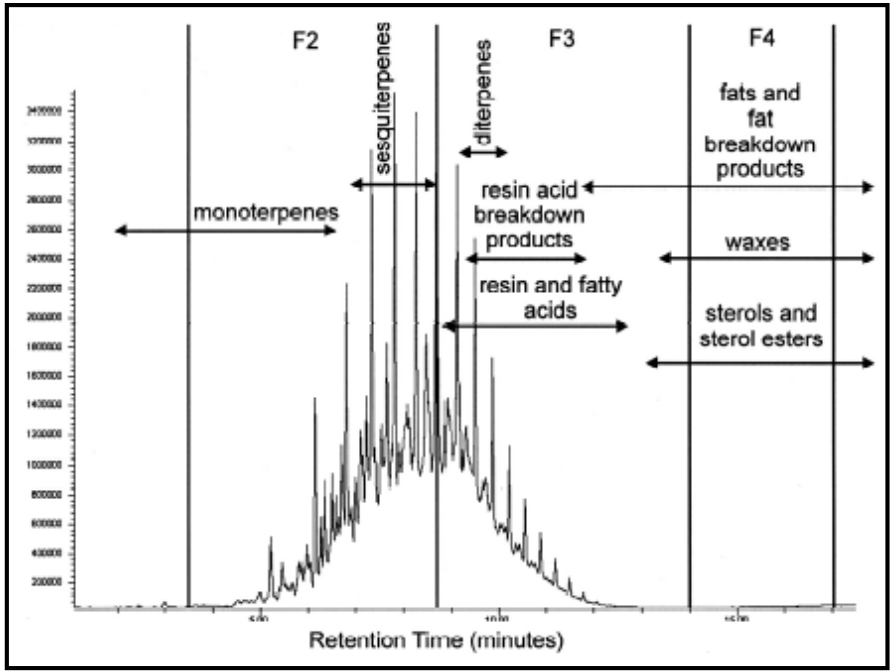
CCME: PHCs in Soils and Sediment, Section 4.1.9

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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Bruce P. Hollebone[1]
Zhendi Wang[1]
Chun Yang[1]
Mike Landriault[1]

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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.

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Additional surrogates to monitor fractionation.

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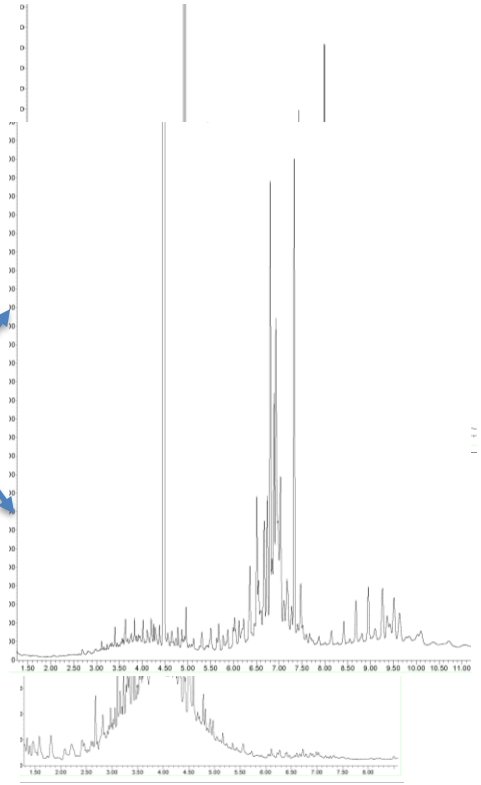
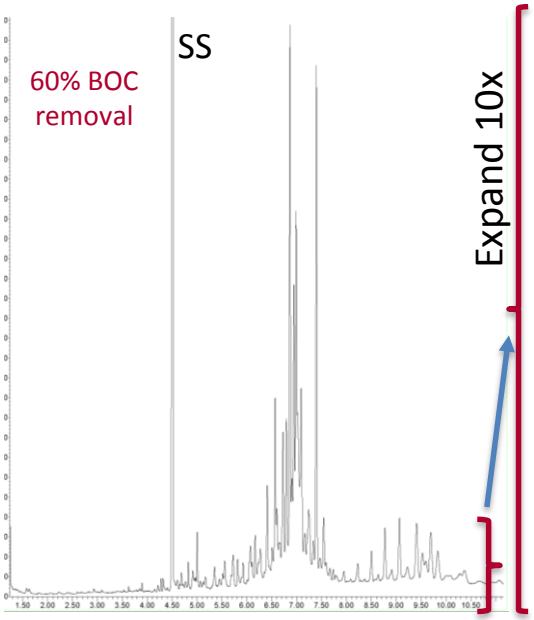
Collect separate PHC and BOC fractions.

Analyse by GC/FID

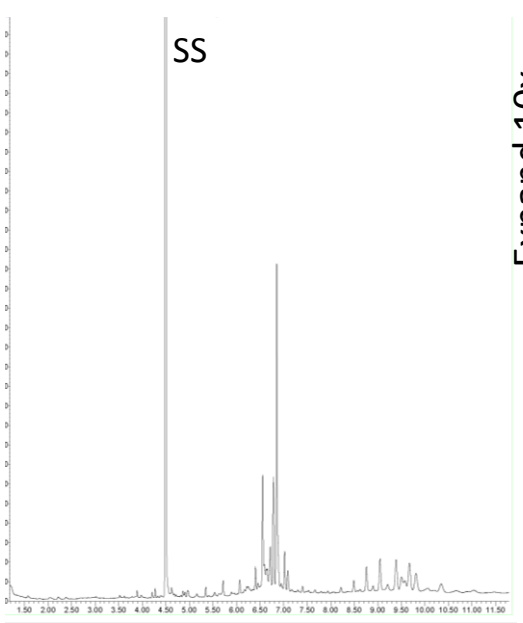


30% Peat Soils

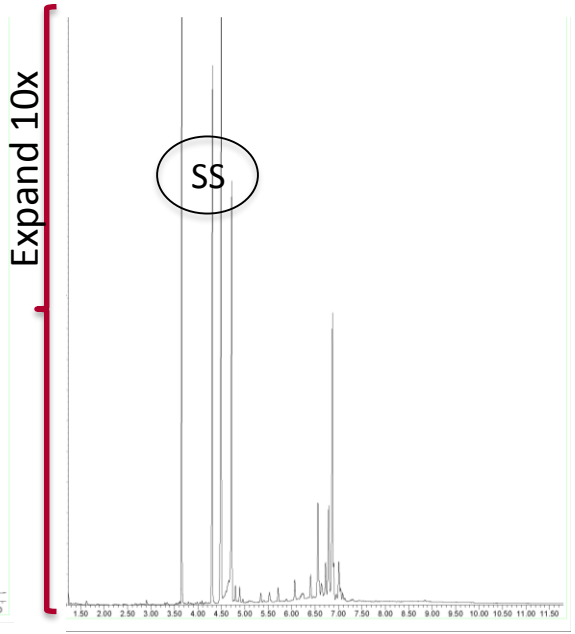
In Situ Silica Clean-up



Silica Column Clean-up



Fractionation Column



30% Peat, 100 mg/kg Diesel

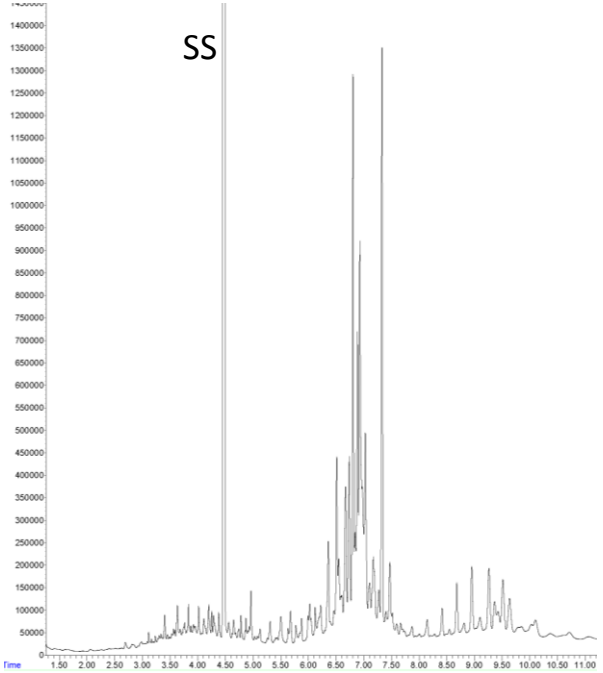
In 30% Peat:

- F3 = 440
- BIC = 14%

In mineral soil:

- F3 = 110 (< AT1 guideline)

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



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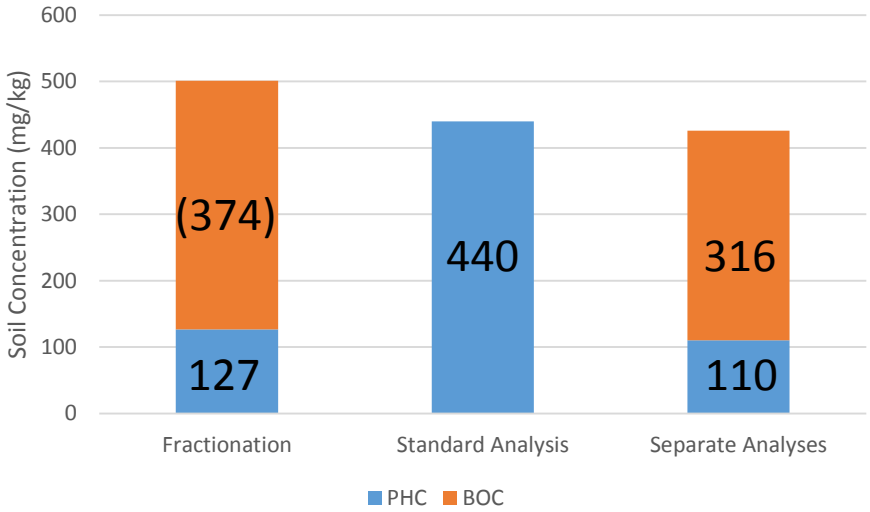


30% Peat, 1,000 mg/kg Diesel

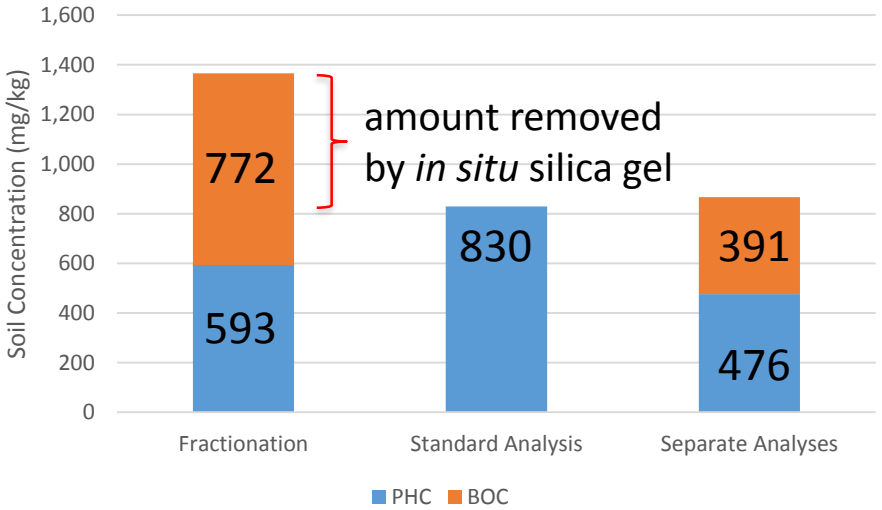
In 30% Peat:

- F3 = 830
- BIC = 54%

In mineral soil:

- F3 = 476 (< AT1 guideline)

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



80% Peat, 1,000 mg/kg Diesel

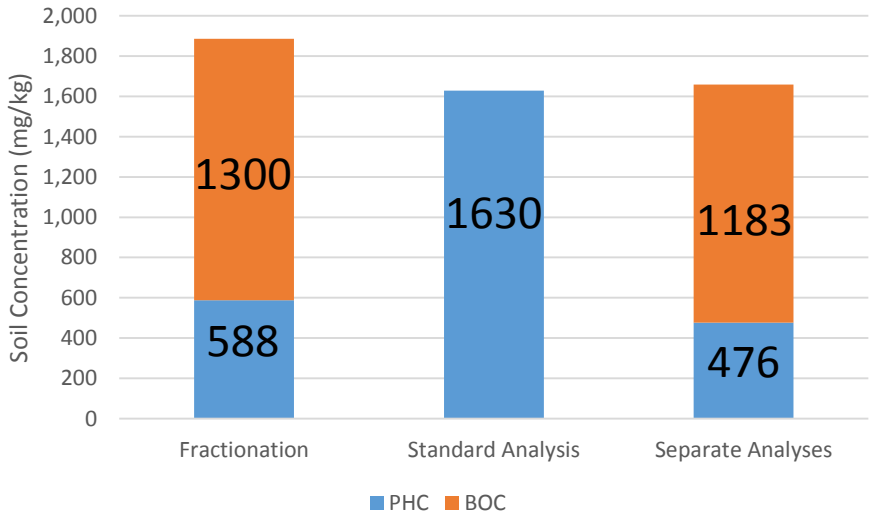
In 80% Peat:

- F3 = 1630
- BIC = 38%

In mineral soil:

- F3 = 476

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



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

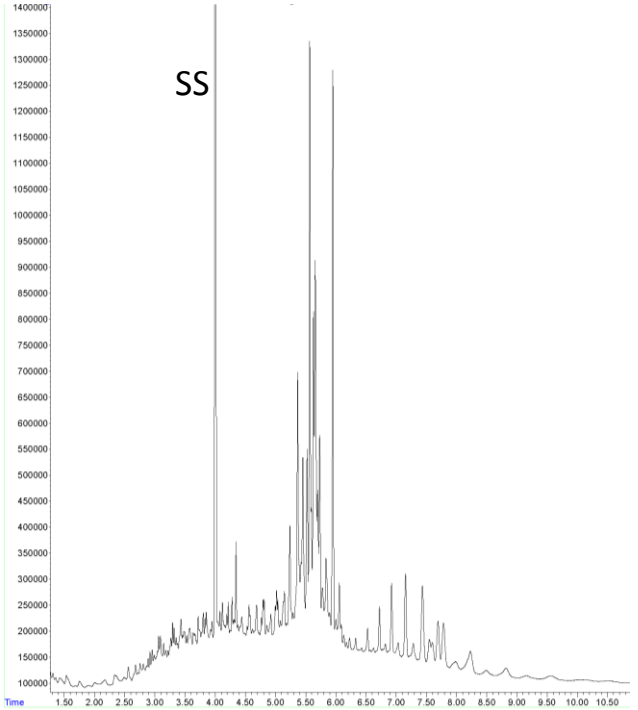
In 30% Peat:

- F3 = 764
- BIC = 19%

In mineral soil:

- F3 = 371 (> AT1)

Decision Tree deems it to exceed guideline requiring chromatogram review.



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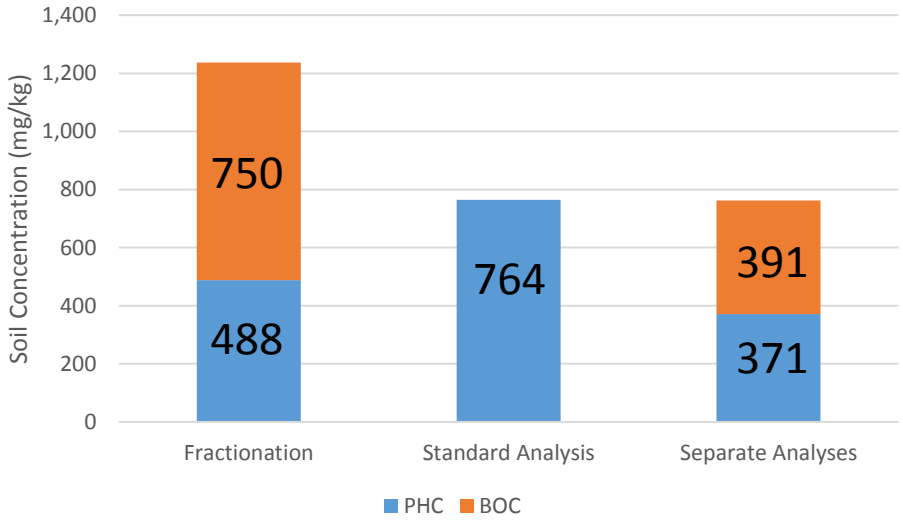

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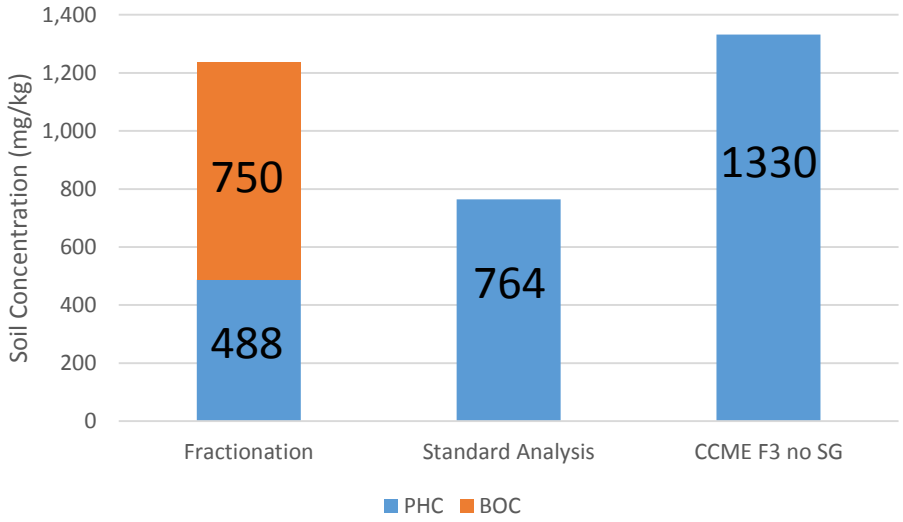
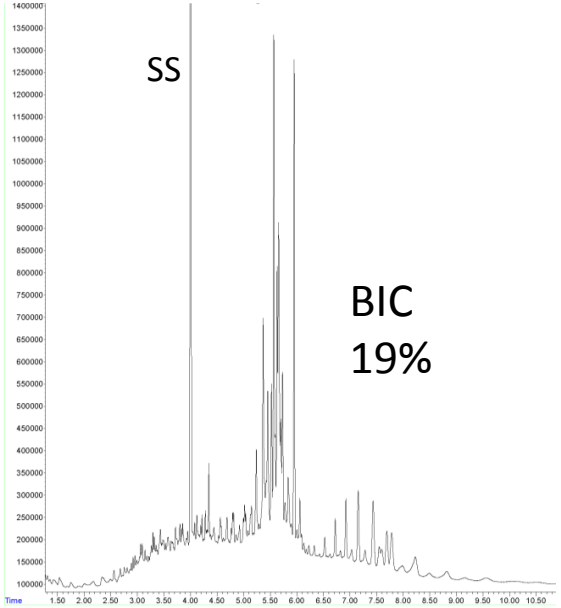
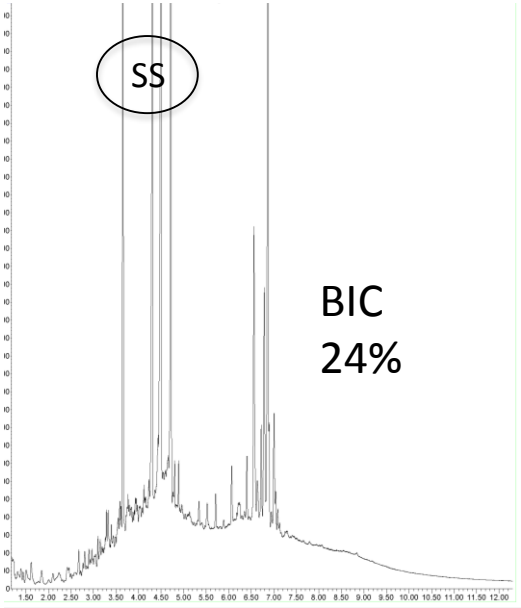


Athabasca Crude in 30% Peat Soils

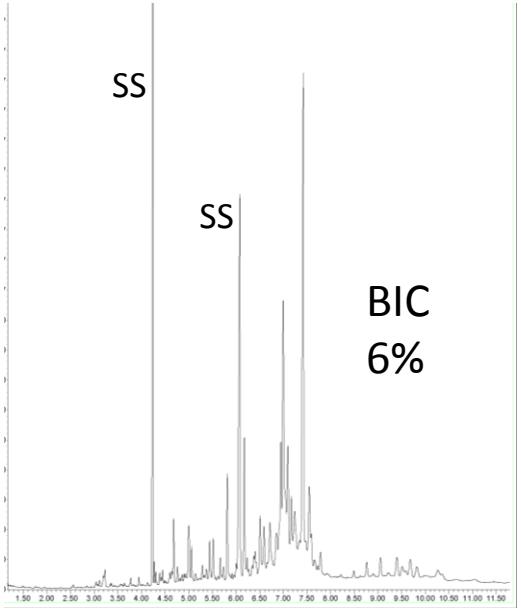
Standard F2-F4 Analysis



Fractionation Column PHC

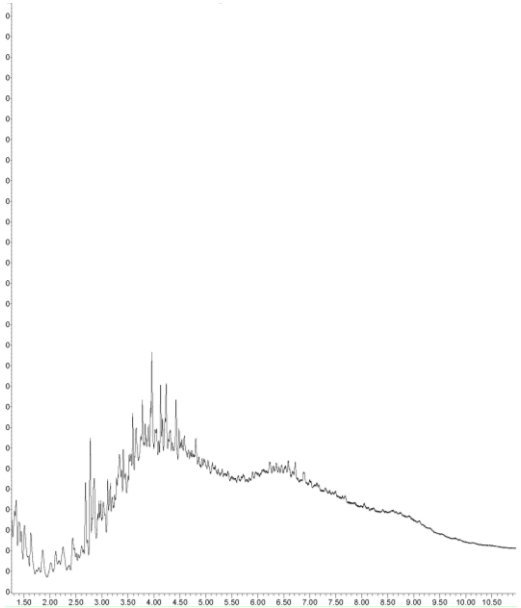


Fractionation Column BOC

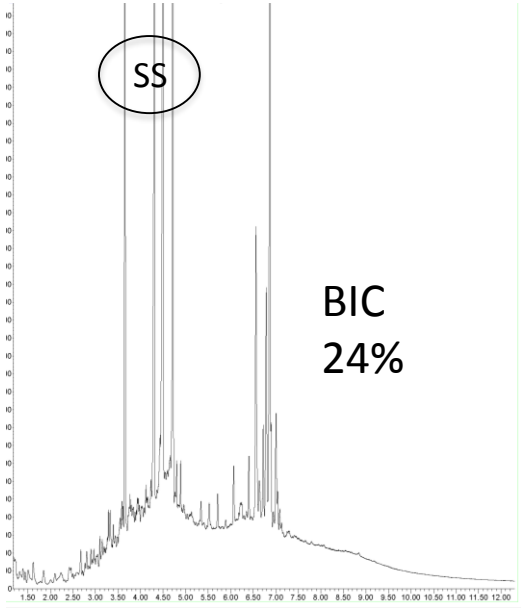


Athabasca Crude in 30% Peat Soils

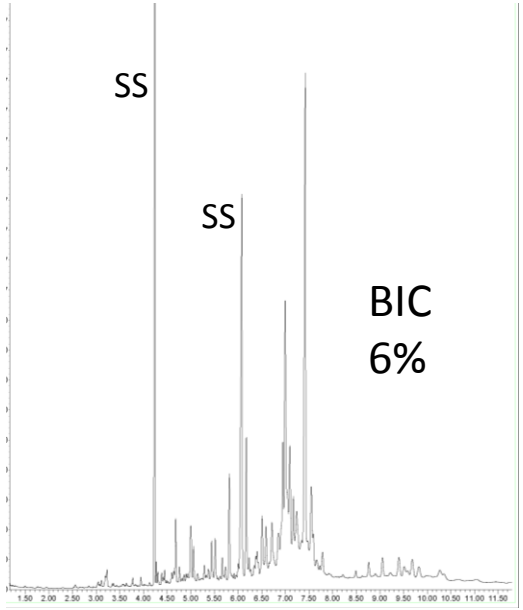
Athabasca Crude



Fractionation Column PHC



Fractionation Column BOC



Column Fractionation Overview

1. Larger volume of sample extracted with double amount of solvent in larger vials – compensates for high moisture and low dry weight.
2. Standard CCME F2-F4 surrogate added to monitor PHC recovery
3. Additional recovery surrogates added after extraction, prior to fractionation, to monitory 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 BOCs combined and quantified

Next Steps

- Finalize surrogate selection and concentrations.
- Compensate for *in situ* silica bias between standard F2-F4 and polar fraction results.
- Method validation.

- **Stress Test the Method:**

  Analyse as many ‘nasty’ samples as possible prior to full roll-out!

Summary of Quantitative PHC/BOC Method

- Quantitative reporting of both petroleum (PHC) & biologic (BOC) contents of high organic soils.
- Chromatogram review simplified.
- 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.
- Extraction processes and instrumentation are identical to a regular F2-F4 analysis.
- Easier compound identification by GC/MS analysis for both PHC and BOC.
- PHC fraction is similar to PHC fraction from a regular column clean-up of a F2-F4 extract.
- Additional lab recovery surrogates used with each sample verify efficiency of PHC / BOC separation.

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Thank You

Comments and Questions:

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