

REPORT

Review of Analytical Methodologies and Interpretation of Analytical Results in Peat

Prepared for

Society of
Contaminated Sites
Approved
Professionals of
British Columbia



June 30, 2017



CH2M HILL Canada Limited
Metrotower II, Suite 2100
4720 Kingsway
Burnaby, BC V5H 4N2



SLR Consulting (Canada) Ltd.
Suite 200
1620 West 8th Avenue
Vancouver, BC V6J 1V4

Contents

| Section | Page |
|--|------------|
| Acronyms and Abbreviations..... | v |
| 1. Introduction | 1-1 |
| 1.1 Background | 1-1 |
| 1.2 Objective | 1-1 |
| 1.3 Scope of Work..... | 1-1 |
| 2. Definitions and Characteristics of Peat | 2-1 |
| 2.1 Definitions..... | 2-1 |
| 2.2 Peat Characteristics | 2-1 |
| 2.3 Issues with Definition of Peat | 2-3 |
| 3. Peat Analysis Issues and Biases | 3-1 |
| 3.1 Field Sampling of Peat | 3-1 |
| 3.2 Wet Weight Concentration..... | 3-1 |
| 3.3 Naturally Occurring Background Concentrations | 3-2 |
| 3.3.1 Metals | 3-2 |
| 3.3.2 Hydrocarbons..... | 3-2 |
| 3.4 Laboratory MDLs, Blanks, and Duplicates | 3-3 |
| 3.5 Soil Standards versus Bioavailability..... | 3-3 |
| 4. Regulatory Framework and Issues for Peat Assessment | 4-1 |
| 4.1 BC Regulatory Numeric Standard Derivation for Soil | 4-1 |
| 4.2 BC Regulatory Risk Assessment Guidance for Soil..... | 4-1 |
| 5. Review of Limitations and Research Completed for Three Parameter Groups | 5-1 |
| 5.1 Metals | 5-1 |
| 5.2 Extractable Petroleum Hydrocarbon | 5-3 |
| 5.2.1 Silica Gel Column Cleanup Procedure – Strengths and Limitations | 5-3 |
| 5.2.2 BIC Index for Resolving False Petroleum Hydrocarbon Detections in Clean Peat Soils | 5-4 |
| 5.3 Salinity Parameters..... | 5-7 |
| 5.3.1 Saturated Paste Method for Salinity Parameter Analysis..... | 5-7 |
| 5.3.2 Salinity Standards | 5-8 |
| 6. Recommendations..... | 6-1 |
| 6.1 Interim “Quick Fix” | 6-1 |
| 6.2 Long-term Recommendations | 6-1 |
| 7. Limitations..... | 7-3 |
| 8. References..... | 8-1 |

Tables

| | |
|-----|---|
| 2-1 | Peat vs. Mineral Soil (Sand) Characteristics |
| 5-1 | Preliminary HWS vs. Saturated Paste Boron for Various Alberta Sites |
| 5-2 | ALS Silica Gel Cleanup Results for Peat Soils |

5-3 Comparison of CSR VPH and EPH Carbon Ranges to CCME PHC Carbon Ranges

Figures In Text

5-1 Identifying Site Impacts with Saturated Paste Boron

5-2 BIC Index Decision Tree

Appended Figures

- 1 LEPH and HEPH Carbon ranges and GC-FID Chromatograms for Petroleum Sources and Clean Peat
- 2 Comparison of CCME CWS F2 and F3 PCH Concentrations for Soil Samples Treated Separately with In Situ and Column Silica Gel Cleanups
- 3 CCME CSW PHC Sub-Fractions F3a and F3b Distributions in Petroleum Sources and Clean Peat
- 4 Example BIC Index Calculations for Identifying False Exceedances of CCME CWS F3 PHC Soil Standards by Clean Peat Soils

Appendices

- 1 SynergyAspen Graphical Presentation of Dry Weight vs. Wet Weight Concentration in High Moisture Content Soils

Acronyms and Abbreviations

| | |
|-------------------|--|
| AB | Alberta |
| AEP | Alberta Environment and Parks |
| AER | Alberta Environment Regulators |
| AP | Approved Professional |
| AUPRF | Alberta Upstream Petroleum Research Fund |
| BC | British Columbia |
| BC MoE | British Columbia Ministry of Environment |
| BC OGC | BC Oil and Gas Commission |
| BC OGRIS | BC Oil and Gas Research and Innovation Society |
| BFT | Bioavailability Factor Testing |
| BIC | Biogenic Interference Calculation |
| BOC | biogenic organic carbon |
| BTEX | benzene, toluene, ethylbenzene and xylene |
| CAPP | Canadian Association of Petroleum Producers |
| CCME | Canadian Council of Ministers of the Environment |
| CH2M | CH2M HILL Canada Limited |
| cm | centimetre |
| CSAP | Contaminated Sites Approved Professionals |
| CSR | Contaminated Sites Regulation |
| CSST | Contaminated Sites Soil Taskgroup |
| CWS | Canadian Wide Standards |
| DL | detection limits |
| EPA | Environmental Protection Agency |
| EPH | extractable petroleum hydrocarbons |
| EC | effects concentration |
| EC-NL | non-lethal Effects Concentration |
| Eco-SSL | Ecological Soil Screening Levels |
| F2 | CCME F2 fraction C16-C34 carbon range |
| F3 | CCME F3 fraction C10-C16 carbon range |
| F4 | CCME F4 fraction C10-C16 carbon range |
| f _{oc} | fraction of organic carbon |
| g | gram |
| g/cm ³ | grams per cubic centimetre |

ACRONYMS AND ABBREVIATIONS

| | |
|--------|---|
| GC/FID | Gas Chromatography Flame Ionization Detection |
| ha | hectare |
| HEPH | heavy extractable petroleum hydrocarbon |
| HWS | Hot Water Soluble |
| ICPMS | Inductively Coupled Plasma with Mass Spectrometer |
| IRIS | Integrated Risk Information System |
| Kd | partition coefficient |
| L/kg | litres per kilogram |
| LC | lethal concentration |
| LEPH | light extractable petroleum hydrocarbon |
| m | metre |
| MDL | method detection limits |
| mg/kg | milligram/kilogram |
| mg/L | milligram per litre |
| mm | millimetre |
| NEBC | Northeastern British Columbia |
| OM | organic matter |
| PAH | polyaromatic hydrocarbon |
| PERD | Program for Energy Research and Development |
| pH | potential of hydrogen |
| PHC | petroleum hydrocarbon |
| PTAC | Petroleum Technology Alliance of Canada |
| SALM | Strong Acid Leachable Method |
| SGC | silica gel cleanup |
| SLR | SLR Consulting (Canada) Ltd. |
| TEPH | total extractable petroleum hydrocarbon |
| TRV | toxicity reference value |

Introduction

1.1 Background

During several meetings in 2015 and 2016, between the Society of Contaminated Sites Approved Professionals of British Columbia (CSAP) and British Columbia Ministry of Environment (BC MoE), the issue of analytical methodologies and interpretation of results within peat was reviewed. Difficulties are arising during regulatory instrument submissions by Approved Professionals (APs) for adequate investigation and remediation of peat material. Based on discussions with BC MoE, this was an identified area that requires greater understanding and guidance.

CH2M HILL Canada Limited (CH2M) and SLR Consulting (Canada) Ltd. (SLR) have completed on behalf of CSAP a joint review of Peat Analytical Methodologies and Interpretation of Analytical Results in Peat (the Project).

1.2 Objective

The objective of this Project is to provide understanding and guidance to BC MoE and CSAP APs regarding peat material, limitations of current analytical methodologies when analysing for peat, a review of works being completed by practitioners in British Columbia (BC) and other jurisdictions, and identification of recommendations for potential changes within the BC regulatory regime to address peat material. It is the understanding that the final report will be presented to the BC MoE for their review and consideration.

1.3 Scope of Work

To meet the objective of this Project, the following tasks were completed:

- Review definitions and characteristics of peat.
- Review basis of current soil standards applicable to peat.
- Review analytical methodologies and their limitations with respect to peat characteristics for parameters of interest.
- Review works completed to date for various contaminants of concern.
- Final written report, including recommendations.

Definitions and Characteristics of Peat

2.1 Definitions

In BC MoE Procedure 8 (BC MoE 2015), the following definitions are identified:

- **Organic soil** – any soil containing at least 30 percent by weight and includes most of the soils commonly known as peat, muck, or bog soils.
- **Soil** – includes (a) unconsolidated mineral or organic material.
- **Muskeg** – a boreal wetland bog, fen, or permanent marsh as classified by the Canadian Wetland Classification System 1 and is characterized, without limitation, by a surface or near-surface water table and a preponderant presence of peat, Sphagnum mosses and sedges.

The following are additional definitions for peat:

- **Oxford Dictionary:** A brown material consisting of partly decomposed vegetable matter forming a deposit on acidic, boggy, ground, which is dried for use in gardening and as fuel.
- **International Peatland Society:** Peat is a heterogeneous mixture of more or less decomposed plant (humus) material that has accumulated in a water-saturated environment and in the absence of oxygen. Its structure ranges from more or less decomposed plant remains to a fine amorphous, colloidal mass. The warmer the climate, the quicker the plant material will decompose.

The rate of accumulating plant material is greatest in areas where the temperature is high enough for plant growth but too low for the vigorous microbial activity that breaks down the plant material. Such conditions are found more frequently in the northern hemisphere.

- **“Wise Use of Mires and Peatlands” (Clarke and Joosten 2002):** Peat is sedentarily accumulated material consisting of at least 30 percent (dry mass) of dead organic material.
- **Tarnocai, 1980:** Peatland (such as, muskeg) is defined as containing more than 40 centimetres (cm) of peat accumulation on which organic soils develop

2.2 Peat Characteristics

Peat is an interesting matrix as it comprises of two distinct media, organics and water, which is considerably different from the mineral soil sample, which forms the basis of the soil media standards in the BC Contaminated Sites Regulation (CSR).

Table 2-1 compares the characteristics of peat in comparison to a mineral soil, Fraser River sand, which has been used by BC MoE for the Contaminated Sites Soil Taskgroup (CSST).

Peat land covers 113 million hectares (ha) of Canada (approximately 13 percent of land surface), which is about 35 percent of World peatland. Within Canada, 11 million ha are located in Alberta (AB) and 6 million ha in BC (Tarnocai 2011).

Table 2-1. Peat vs. Mineral Soil (Sand) Characteristics*Review of Analytical Methodologies and Interpretation of Analytical Results in Peat*

| Characteristic | Peat ^a | Mineral Soil – Fraser River Sand ^b |
|-----------------------------------|---|--|
| Moisture content | <ul style="list-style-type: none"> • Range: 50 to 95 percent • Average: 87 percent | <ul style="list-style-type: none"> • Average: 20 percent |
| Organic matter content | <ul style="list-style-type: none"> • Average: 91.6 percent | <ul style="list-style-type: none"> • Average: < 1 percent |
| Total organic carbon ^c | <ul style="list-style-type: none"> • Average 43 percent • Range: 20 to 60 percent | <ul style="list-style-type: none"> • < 1 percent |
| Water retention | <ul style="list-style-type: none"> • 20 times its weight in water • 0.3 water filled porosity | <ul style="list-style-type: none"> • Porosity 30 percent, with only 10 percent of pore volume filled with water |
| Bulk density | <ul style="list-style-type: none"> • 0.114 g/cm³ | <ul style="list-style-type: none"> • 1.75 g/cm³ |
| pH | <ul style="list-style-type: none"> • 4.5 to 7 | <ul style="list-style-type: none"> • Neutral |

Notes:^a Data source (Tarnocai, 1984)^b Fraser River sand characteristics (BC MoE, 1996)^c Carbon content greater than 17 percent by weight (Tarnocai, 1984)g/cm³ = grams per cubic centimetre

pH = potential of hydrogen

BC peats are generally composed of the following types of peat: sedge, sphagnum, and woody. A description of each is as follows:

- Sedge peat is moderately decomposed and matted with large amounts of very fine roots. Extremely acid to neutral pH 4.5 to 7.
- Woody peat is composed of dominantly woody materials derived from both coniferous and deciduous trees. Wood fragments are easily identifiable but moderately to well decomposed. Strong to slightly acidic (pH 5.0 to 6.5).
- Sphagnum peat is usually undecomposed (fibric), loose and spongy with the entire sphagnum plan being identifiable. The pH is the lowest of all peat materials.

According to the Tarnocai (Tarnocai 1984) study of peatlands in BC, and mapped by Maynard (1988), the north trending core of the BC Interior Plateau, west of the Fraser River between Williams Lake and Prince George, has the highest concentration of organics and comprise of mainly fens, other sedges, or brown-moss dominated organics. The largest peat deposits occupying extensive tracts of level or depressional grounds are in the Peace River and Fort Nelson low lands. In Fort Nelson area, they comprise of partially decomposed fibric mosses overlying moss, sedge, and woody peat. The Fort St. John-Dawson Creek area features clusters of isolated bogs and fens, compared to the vast level areas of continuous bogs in the Fort Nelson area. The third area in BC is the central and north coast area, located on the Queen Charlotte lowland, flat mid-coast islands, in the Nootka sound area and near Prince Rupert. They are typically thin surficial cover of sphagnum moss overlying sedge dominated peat. In the Lower Fraser Valley, the organic deposits are sedge dominated except near the floodplains and deltas of the Fraser and Pitt Rivers, which are sphagnum bogs which vary in size.

2.3 Issues with Definition of Peat

Based on the characteristics described in the previous paragraphs, does peat in its natural definition constitute a soil? It is a combined matrix of organics and water, more like tissue. Consideration should be given to consider it as its own media or a subset media of soil.

Options for classification of organic soils could be based on:

- Percentage of organic matter (OM) present in the sample, per Huang et al (2009) geotechnical study. Mineral soils were classified as less than 3 percent OM, mineral soil with organics as > 3 to 15 percent OM, organic soil as > 15 to 30 percent OM. (Huang et al. 2009); and
- Moisture content of the material. Currently practitioners in BC use a classification of soil with presence of organic with a moisture content of >50 percent is considered a peat/organic material.

As part of a BC Oil and Gas Research and Innovation Society (BC OGRIS) funded research project, Hemmera is reviewing the definition of peat.

Peat Analysis Issues and Biases

The following is a summary of several issues and biases that have been identified by both BC practitioners and analytical laboratories.

3.1 Field Sampling of Peat

In their presentations, SynergyAspen (2016 and 2015a) identify the inherent bias for analysing muskeg samples, which occurs even before samples arrive at the lab: Field sample collection. Other BC consulting firms, including Hemmera, and Navus (Graham 2014) have also identified similar shortcomings.

As there is no current prescribed methodology for muskeg sample collection by BC MoE, two issues can arise:

- As water is a major part of muskeg, particularly if it is visibly over-saturated with standing water, a volume of water (and potential dissolved contaminants) is lost during the placement of a sample within laboratory jars.
- There are still practitioners that squeeze out the water from muskeg or peat samples when placing in laboratory jars. This intentionally biases analytical results, particularly for salinity parameters which are miscible in water. Consequently, this is not a recommended practice.

As there are no prescriptive field sampling methodologies for peat material, the variability in method can underestimate the true in-situ concentrations of contaminants. This is definitely an issue with salinity parameters, given that the partition coefficient (Kd) is virtually zero for salinity parameters and that salinity is highly water soluble – water is easily lost from sampling methods, thereby biasing concentrations determined by laboratory procedures.

3.2 Wet Weight Concentration

Currently, some BC practitioners have used a multiple lines of evidence approach and professional judgement, when interpreting analytical results of intrusive investigation assessments in peat material, particularly at the oil and gas sites for supporting Certificate of Restoration submissions to the BC Oil and Gas Commission (BC OGC) for low risk sites. The multiple line of evidence approach can include:

- Use of wet weight concentrations being compared to milligram/kilogram (mg/kg) standard.
- Use of chromatogram interpretation to determine biogenic vs. petrogenic patterns.
- Comparing background soil sample concentrations to on-site concentrations.

For the wet weight concentration, for salinity parameters, this is calculated in milligram per litre (mg/L) by the laboratory as part of the saturated paste methodology. For other parameters, the following calculation, is used (Equation 1):

$$\text{Concentration}_{\text{wet weight}} (\text{mg/kg}) = \text{Concentration}_{\text{dry weight}} \times (1 - \text{moisture content})$$

SynergyAspen (SynergyAspen 2013a) presented the “wet weight” concentration concept which identifies over estimation of analyte concentration in peat material compared to mineral soils. Consider in simple terms (Equation 2):

$$\text{Concentrations of Analyte} = \frac{\text{Mass of contaminant}}{\text{Mass of dry soil}}$$

As discussed in Section 2, peat is a material with two matrices: organics and water. SynergyAspen argues that by only accounting for the mass of the dry organics in Equation 2 in the denominator, and not the water component of the peat material, this will grossly overestimate the actual concentration of an analyte. SynergyAspen identified that this overestimation can be up to 20 times when using only the dried component of the peat material. Analytical methods, for metals for example, require that samples are dried with the analysis completed on the dry weight of the sample. By not accounting for the water mass in Equation 2, as noted, grossly biases the concentration at the onset. Using Equation 1 takes into consideration the weight of the water component of the muskeg, providing a closer representation of field conditions and of the analyte concentration in the peat sample. Use of this comparison to the CSR dry weight standards on its own is not deemed acceptable; however, consideration as part of a line of evidence may be acceptable to regulators, in the absence of updated analytical methodologies or peat specific standards.

3.3 Naturally Occurring Background Concentrations

3.3.1 Metals

There are issues regarding naturally occurring background concentrations for analytes, particularly metals, in peat environment. The current BC MoE Protocol 4 soil background concentrations were derived using only mineral soils samples. Given the nutrient rich composition of peat, as well as its natural low pH range, it would tend to have higher background concentrations in metals compared to mineral soils.

Based on practitioner experience (particularly in the upstream oil and gas industry in northeastern British Columbia [NEBC]) common metal parameters are frequently observed to be greater than CSR standards and BC MoE Protocol 4 background concentrations.

It has been found in peat material in background non-anthropogenic locations metals that exceed CSR standards include:

- Arsenic
- Cadmium
- Chromium
- Selenium
- Titanium
- Vanadium

For work in the oil and gas industry in NEBC, many practitioners advance background boreholes as standard practice for Stage 2 preliminary site investigation (PSI) or Detailed Site Investigation (DSI) as part of completing a barite site investigation according to BC MoE Protocol 14 (BC MoE, 2008) and for assessing local background concentrations of metals. These practitioners and BC OGC (within supporting documents of Certificate of Restoration [COR] applications) would have valuable metals background data to supplement the existing limited provincial database for naturally occurring background concentrations of metals in the Omenica Peace Region for peat material (and mineral soils).

3.3.2 Hydrocarbons

The authors have noted during their years of practice that there are detectable toluene concentrations in peat soil and groundwater outside of hydrocarbon impacted areas, and where no additional benzene, toluene, ethylbenzene and xylene (BTEX) compounds have been detected. Published studies have found that microbes can also synthesize biogenic toluene in anaerobic aquatic sediment environments (Zargar, et al. 2016; Juttner, 1991). However, the toxicity risk for toluene is the same regardless of its derivation – biogenic organic compounds or petrogenic, petroleum hydrocarbons (PHCs). Discussions with Alberta

Environment Regulators (AER) have indicated that elevated toluene concentrations have been found to occur in muskeg peat that has been affected by soil compaction type human activities, such as the placement of concrete slabs and the running of construction equipment. However, conclusive links between elevated toluene concentrations and soil compaction have not been established at present.

3.4 Laboratory MDLs, Blanks, and Duplicates

Due to elevated (> 50 percent) moisture content in peat materials, it is not uncommon to require elevated method detection limits when completing laboratory analysis of analytes. This is not usually problematic for parameters with elevated standards, but can be problematic where low level detection limits (DLs) are required, such as BTEX parameters that have low concentration standards.

Practitioners have identified that lab blanks may have various chromatographic patterns and to look for similarity of these within the sample chromatograms. This is to ensure there is no cross-contamination that may have occurred, particularly if an analyte concentration exceeds a standard.

Ontario (Riley, 1986) carried out testing analytical methods for the analysis of peat in 1986. It included “test peat” samples incorporated as blind replicates. They stated that it is unlikely that a true “reference material” for peat can be found. The study also found that the reproducibility of results is highly variable in peat material. This is related to the heterogeneity of the media which includes organic matter of varying sizes and varying high water content.

3.5 Soil Standards versus Bioavailability

The BC extractable petroleum hydrocarbons (EPH) soil analysis methods are designed to extract all EPH concentrations from the entire soil sample. The EPH soil standards assume that reported concentrations are fully bioavailable. However, highly organic soils such as peat will adsorb/absorb portions of the EPH, making it less bioavailable for uptake by living organisms. Under these circumstances, the EPH soil standards may overestimate the true risks associated with contaminated peat soils.

One approach currently used in several US states, but not currently accepted as a standard method by any Canadian province regulatory body is Bioavailability Factor Testing (BFT). BFT provides an approach to characterizing true bioavailability in peat soils. The BFT using milder solvents (for example, cyclodextrin) to extract only mobile (labile) EPH concentrations. More specifically, BFT mimics the ability of the living organism gut (such as, human or earthworm) to absorb EPHs from a soil sample. Canadian regulators can be open to scientific arguments such as these and can use their discretion in considering BFT results in weight-of-evidence risk assessments to determine if soil standards may be lowered to reflect true bioavailability risks.

Regulatory Framework and Issues for Peat Assessment

This section reviews the basis for regulatory standard derivation, site specific standard derivation, and how it relates to peat assessment.

4.1 BC Regulatory Numeric Standard Derivation for Soil

Recent BC regulatory standard changes for the Stage 10 Omnibus amendments outlined how a regulatory standard was derived for human and ecological receptors for soil media (Odense & Fox 2016). Generally, for human receptors toxicological data from the US Environmental Protection Agency (EPA) (Integrated Risk Information System [IRIS]) or Health Canada and defined exposure values were used to derive a standard. For humans, the toxicity of a chemical exposure is generally not related to soil type.

Generally, for ecological receptors, the standard was based on a review of toxicological studies and benchmarks and calculation of a linear regression line for each chemical. Thereafter, calculating from the regression line a standard based on an Effects Concentration (EC) on a percentage of the population depending on land use (ECx). If this calculation was not possible due to a limited dataset, then the ECs would be estimated using the geometric mean of the combined non-lethal effects concentration (EC-NL) and lethal concentration (LC) data. The toxicological databases used for obtaining these EC values are mainly based on mineral soil data and a terrestrial environment that does not represent a peat ecosystem (see Section 4.2). For ecological receptors, soil type may influence the toxicological results.

Alternatively, a site-specific soil standard can be derived for a site using BC MoE Protocol 2 (BC MoE 1998). Protocol 2 allows for site-specific values for default parameters used in the CSST model. The CSST model is used for deriving numeric standards for the groundwater flow exposure pathway soil standards. The fraction of organic content (f_{oc}) value can be changed from the default value of 0.06 percent used in the model to any site-specific value within the range of 0.01 to 2 percent. This change in f_{oc} has been found to significantly change the site-specific standard for organic contaminants. However, the allowable f_{oc} range (up to 2 percent) is still much less than a peat or organic soil f_{oc} value which can range up to 30 percent.

4.2 BC Regulatory Risk Assessment Guidance for Soil

When deriving ecological risk based standards within the risk assessment framework in BC, the ECs are used to derive Toxicity Reference Values (TRV) for risk assessments. A TRV is a receptor-specific concentration of a chemical, above which adverse effects might occur, and below which there is a low likelihood that adverse effects will occur.

BC MoE Technical Guidance 7 recommends that the preferential use US EPA Ecological Soil Screening Levels (Eco-SSL). As well, the US EPA ECOTOX database (<https://cfpub.epa.gov/ecotox/>) can be used to develop terrestrial ecological TRVs.

A TRV is then used to develop site-specific risk based standards. The ECOTOX database does not sort the toxicological data based on percentage of organic content or type of soil, however, a word search in the reference title may locate studies with organic soils. The ECOTOX database includes few studies with organic content above 6 percent.

The US EPA guidance document (US EPA 2003) related to development of Eco-SSLs states the limitations for evaluating terrestrial ecological risk for contaminants in high organic content media:

*“Eco-SSLs are appropriate to all sites where key soil parameters fall within a certain range of chemical and physical parameters. The Eco-SSLs for plants and soil invertebrates were derived to apply to soils where the pH is greater than or equal to 4.0 and less than or equal to 8.5, and **the organic matter content is less than or equal to 10%.** Based on these stated parameters, it is expected that there are certain soils or situations to which Eco-SSLs do not apply. These situations included (but may not be limited to) wetland soils that are regularly flooded (i.e., sediments), sewage sludge amended soils where the organic matter content is > 10%, and waste types where the pH is < 4.0.”* (emphasis added)

Therefore, the ecological TRVs are mainly mineral soil based and would not be directly applicable and may be considerably more conservative when used in a peat soil based environment. Also, the ecological receptors used in toxicity testing may not be representative of ecological receptors found in a peat environment.

Some efforts have been made to develop new Canadian Council of Ministers of the Environment (CCME) standards for peat soils. In 2012, the University of Waterloo received funding from the Petroleum Technology Alliance of Canada (PTAC) to conduct benchscale ecotoxicity tests on crude oil spiked peat soils. The study followed the Environment Canada biological test methods for earthworm (*Eisenia fetida*) and springtail (*Orthonychiurus folsomi*) invertebrate species. These commonly used terrestrial species were selected in the absence of recognized muskeg test species. The organisms thrived in the standard artificial soil mixture, which was characteristic of a terrestrial soil quality. However, the spiked peat results were inconclusive because the organisms did not thrive in either the clean peat control treatment or in the spiked treatment. After sharing these results with Environment Canada, it was concluded that the existing test methods should be expanded to include species that are indigenous to muskeg habitats.

Review of Limitations and Research Completed for Three Parameter Groups

The Project focussed on three main parameter groups: metals, hydrocarbons, and salinity. The following sections detail some of the specific issues with analysis of peat for each parameter group as well as a review of existing literature and research work being completed in the industry by laboratories and practitioners. An informal questionnaire was sent to several BC accredited analytical laboratories with the following questions in the context of the BC regulatory regime:

1. What is your labs method for silica gel cleanup? What have you noted to be limitations to silica gel clean up? Do you use any other method to remove natural hydrocarbons from soil and water samples prior to analysis?
2. What method and instrumentation do you use for metals analysis and do you use a different method or instrumentation if the sample is high in organic content?
3. What is your experience in the limitations, if any, of current methodology(ies) for analysis of high organic content soil?

5.1 Metals

For BC CSR purposes, the BC Laboratory Manual requires the BC Strong Acid Leachable Method (SALM) digestion method. The method is 100 percent prescriptive, which means that there are no individual variations allowed. The BC SALM digestion method is effective and appropriate for peat soils, which are dried prior to digestion. It is found by one laboratory that the SALM digestion destroys most organics and the addition of butanol in the analysis process eliminates interferences from any residual organics. One laboratory uses collision cell Inductively Coupled Plasma with Mass Spectrometer (ICPMS), which they consider the best practice for the elimination or reduction of ICPMS interferences. They surmise that non-collision cell ICPMS can be subject to interferences from polyatomic species, which could potentially cause interferences on peat soils. Another laboratory also found no limitations to the methodology except when responding to the request for “an accurate analysis for metals concentrations in the peat matrix”. At that time, the laboratory suggested that the peat samples would need to be digested using the Tissue and Vegetation method which uses hydrogen peroxide to dissolve the organic material and the samples should not be sieved to 2 millimetre (mm) as some of the organic material would be removed by this process.

An example of the sensitivity of laboratory method for metal concentration in peat is found in the derivation of boron standards for Alberta Environment and Parks (AEP) (AEP, 2016). Three different methods were evaluated, Hot Water Soluble (HWS), saturated paste and acid digest. The difference in concentrations is given in Table 5-1 (AEP, 2016).

Furthermore, identification of soil impacts from boron is difficult in dissimilar media with different analytical methods. As shown in Figure 5-1 (AEP, 2015), there are differences based on soil type and methodology.

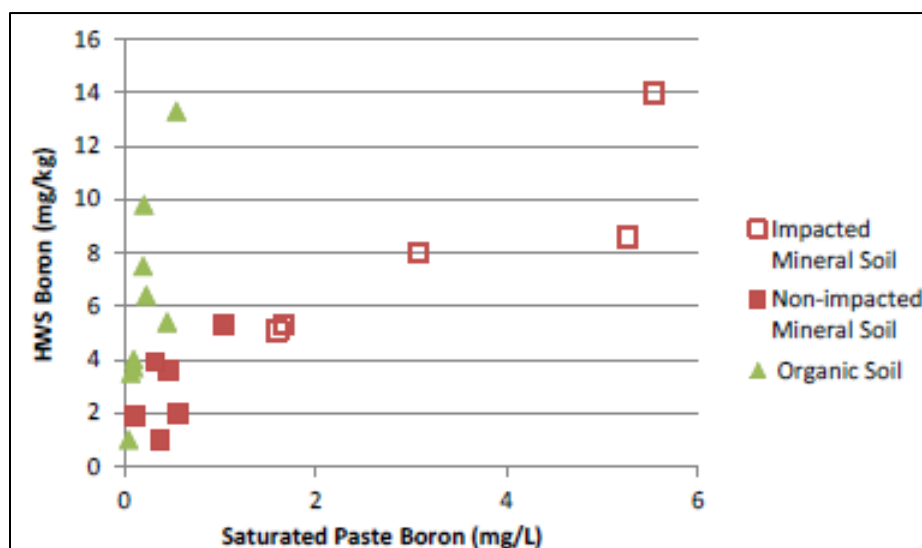
Based on the research into methods for boron, AEP selected the saturated paste method for measuring boron for regulatory compliance.

Table 5-1. Preliminary HWS vs. Saturated Paste Boron for Various Alberta Sites*Review of Analytical Methodologies and Interpretation of Analytical Results in Peat*

| Location | HWS Boron (mg/kg) | Acid Digest Boron (mg/kg) | Organic Matter % | Clay % | Saturated Paste Boron | | | K _d (L/kg) |
|----------------|-------------------|---------------------------|------------------|--------|-----------------------|---------------|--------------|-----------------------|
| | | | | | Saturation % | Boron (mg/kg) | Boron (mg/L) | |
| Control A | 1.0 | 54.7 | – | – | 52 | 0.2 | 0.38 | 2.1 |
| Peat A | 1.0 | – | – | – | 196 | 0.1 | 0.05 | 17.6 |
| Veg scar A | 1.9 | – | 9.7 | 11.6 | 77 | 0.1 | 0.11 | 16.2 |
| On-site A | 2.0 | 52.4 | – | – | 72 | 0.4 | 0.56 | 2.9 |
| Peat B | 3.5 | – | – | – | 682 | 0.5 | 0.07 | 40.9 |
| Veg scar B | 3.6 | – | 5.7 | 25.2 | 75 | 0.3 | 0.46 | 7.2 |
| Peat C | 3.7 | – | – | – | 659 | 0.7 | 0.10 | 29.8 |
| Slough edge | 3.9 | – | 11.8 | 24.6 | 86 | 0.3 | 0.33 | 11.1 |
| Peat D | 4.0 | – | – | – | 418 | 0.4 | 0.10 | 37.6 |
| Site impact B | 5.1 | 85.8 | – | – | 75 | 1.2 | 1.60 | 2.4 |
| Site impact C | 5.3 | – | 4.5 | 25.6 | 57 | 0.9 | 1.67 | 2.6 |
| Veg scar C | 5.3 | – | 7.0 | 19.2 | 72 | 0.7 | 1.04 | 4.3 |
| Slough | 5.4 | – | 23.0 | 10.6 | 130 | 0.6 | 0.45 | 10.6 |
| Peat control A | 6.4 | – | – | – | 316 | 0.7 | 0.23 | 24.5 |
| Peat E | 7.5 | – | – | – | 700 | 1.4 | 0.20 | 30.5 |
| Site impact D | 8.0 | – | 3.9 | 19.6 | 55 | 1.7 | 3.08 | 2.1 |
| Site impact E | 8.6 | 91.0 | – | – | 76 | 4.0 | 5.26 | 0.9 |
| Peat control B | 9.8 | – | – | – | 486 | 1.0 | 0.21 | 42.8 |
| Slough center | 13.3 | – | 29.3 | 9.2 | 194 | 1.1 | 0.55 | 22.2 |
| Site impact F | 14.0 | – | 3.6 | 33.6 | 71 | 3.9 | 5.54 | 1.8 |

Notes:

L/kg = litres per kilogram

**Figure 5-1. Identifying Site Impacts with Saturated Paste Boron**
AEP, 2016

5.2 Extractable Petroleum Hydrocarbon

The BC EPH analysis of soils by Gas Chromatography Flame Ionization Detection (GC/FID) method measures the aggregate concentration of EPH in solids, divided into two boiling point ranges, each quantitated against eicosane (nC₂₀), as noted in Table 5-2. The EPH parameter concentrations are used in the calculation of LEPH and HEPH concentrations. In addition, the EPH method also produces GC/FID chromatograms. As shown in Figure 1, chromatograms can be used to visually identify signature patterns for a variety of different EPH sources. The C₁₀-C₃₂ EPH carbon range captures the full range of many petroleum products such as diesel fuel, jet fuel, and kerosene. Some heavier products such as crude oil, bitumen, and motor oil would not be completely captured by the EPH range. For example, Figure 1 provides chromatograms for diesel fuel, crude oil, engine oil, bitumen, and clean peat. These chromatograms demonstrate that the entire diesel pattern and most of the fresh crude oil was captured by the LEPH and HEPH carbon ranges. However, substantial portions of the engine oil and bitumen extended beyond the C₃₂ limit. The peat chromatogram and biogenic organic carbon (BOC) interference are discussed in Section 5.2.2.

The EPH method extracts soil samples in a 50:50 mixture of hexane and acetone solvents to target all EPH compounds. However, these solvents can inadvertently extract non-PHC BOCs. The natural life cycles of all plants and animals produce many BOCs such as lipids plant oil/waxes, tannins, lignins, animal fats, proteins, humic acids, fatty acids, and resin acids. All peat soils are naturally enriched with polar and non-polar BOCs, which can be falsely detected as PHCs. For example, ALS Environmental conducted a background EPH study on five clean peat samples. Three of the five clean peat samples exceeded the CSR EPH 19-32 soil standard, with concentrations that ranged from 953 to 1,690 mg/kg (see Table 5-2). None of the EPH 10-19 concentrations exceeded the soil CSR standard.

Table 5-2. ALS Silica Gel Cleanup Results for Peat Soils

Review of Analytical Methodologies and Interpretation of Analytical Results in Peat

| Sample ID | Pre-Cleanup | | Post-Cleanup | | Qualitative Evaluation |
|-------------|--------------|---------------|--------------|----------------|-----------------------------|
| | EPH 10-19 | EPH 19-32 | EPH 10-19sg | EPH 19-32sg | |
| Peat #1 | 610 | 1,690 | 128 | 383 | No evidence of PHC |
| Peat #2 | 318 | 1,120 | 104 | 351 | No evidence of PHC |
| Peat #2 dup | 356 | 1,190 | 138 | 277 | No evidence of PHC |
| Peat #3 | 248 | 953 | < 100 | 262 | No evidence of PHC |
| Peat #4 | 130 | 995 | < 100 | 229 | No evidence of PHC |
| Peat #5 | 125 | 1,260 | < 100 | 290 | No evidence of PHC |
| Peat #6 | 201 | 1,550 | < 100 | 338 | No evidence of PHC |
| Peat #7 | 880 | 2,420 | 438 | 979 | Moderately PHC contaminated |
| Peat #8 | 6,780 | 12,700 | 6,080 | 10,9000 | Highly PHC contaminated |

Note:

Bold = greater than CSR AL/PL/RL Standard

5.2.1 Silica Gel Column Cleanup Procedure – Strengths and Limitations

The EPH method includes an optional silica gel column cleanup procedure (BC MoE 2004), which is intended to irreversibly retain polar BOCs in the polar silica gel. However, the method only allows silica

gel cleanup (SGC) when, “there is good reason to suspect that naturally occurring organics are present at a site, to an extent where EPH results would likely be significantly elevated” (BC MoE 2004). Silica gel excludes BOCs from the final EPH extract, which can effectively eliminate false exceedances of the BC soil standards. For example, ALS Environmental conducted a pre- and post-SGC study for clean peat and peat that was contaminated by weathered crude oil. The study showed that the column cleanup eliminated false EPH 19-32 soil standard exceedances for all three of the clean peat samples (see Table 5-2). The ALS data also included one peat sample (Peat #7) that was marginally contaminated by highly weathered crude oil. The pre-cleanup EPH 19-32 concentration of 2,420 mg/kg exceeded the CSR soil standard. However, the post-cleanup concentration of 979 mg/kg did not exceed the soil standard. Peat #8 shows that the true PHC concentrations in this highly contaminated sample exceeded the CSR soil standards in the pre- and post-cleanup samples for both carbon ranges.

Although the column cleanup can be highly effective at quantifying true PHC concentrations, it has several limitations. For example:

- Silica gel cannot remove non-polar BOCs, which would falsely elevate EPH concentrations.
- The EPH method allows 1 gram (g) of activated silica gel to be used for each sample extract. Highly organic samples can oversaturate this amount of silica gel, with the unretained BOCs falsely elevating EPH concentrations. The current BC Silica gel methodology does not allow for running a sample twice through silica gel analysis.
- It is possible for silica gel to retain non-BOC organics if they are sufficiently polar (for example, some polyaromatic hydrocarbons [PAHs] and bacterial metabolites of PHCs), which can reduce true EPH concentrations.
- Although the method is prescriptive, there are no spike test validation requirements. This introduces vulnerabilities to individual laboratory variabilities, potentially creating a range of results between samples and laboratories.

To illustrate the last point, the Kelly-Hooper data (Kelly-Hooper 2014) presented in Figure 2 bar chart compares CCME F2 fraction C16-C34 carbon range (F2) and CCME F3 fraction C10-C16 carbon range (F3) concentrations in extracts that were treated separately with an in situ and a column SGC. The data included six clean peat samples and five samples contaminated with diesel and crude oil. As previously discussed, F2 concentrations should be non-detectable or very low in clean soils. Elevated F2 indicates the presence of true PHCs. As expected, the F2 concentrations in the clean peat samples were non-detectable, with the exception of one slight concentration of 37 mg/kg. However, the in situ versus column SGC F2 concentrations in the contaminated samples were highly variable. This study did not include data for samples that had not been treated with SGC. However, the existing data indicates that true PHCs were affected by the SGC treatments.

5.2.2 BIC Index for Resolving False Petroleum Hydrocarbon Detections in Clean Peat Soils

The Biogenic Interference Calculation (BIC) Index is a mathematical approach to resolving false PHC detections in organic materials, such as peat. AEP is currently drafting an Information Letter to support its use in AB by practitioners when completing investigations in organic materials. The BIC Index was developed during a 7-year PhD study, which included two 300-day microcosm experiments, numerous contaminated site studies, and a Canadian background PHC soil field survey of 34 sites (Kelly-Hooper, et al. 2014; Kelly-Hooper, et al. 2013). The study results determined that natural organic matter, including peat, had distinctive carbon ranges and chromatogram patterns. For example, the chromatograms shown in Figure 1 show signature patterns for clean peat and four EPH/PHC products. Three peat samples are shown, with one treated with a column SGC, one treated with an in situ SGC, and one that did not receive any SGC treatment. All three peat samples dominated the heavier carbon range with

HEPH composing over 90 percent of the total EPH concentrations. The carbon distribution patterns shown in these chromatograms are consistent with the Canadian background PHC soil survey results as well. In contrast, the unweathered diesel sample was dominated by the light carbon range, with a low HEPH of 14 percent. Unweathered crude oil also had a moderate HEPH of 62 percent. Unweathered bitumen had a higher HEPH of 82 percent and the engine oil was 100 percent HEPH. These calculations show that carbon ranges can be used to quantitatively distinguish clean peat from LEPH products, but not heavy products.

5.2.2.1 Overview of the CCME Canadian Wide Standards PHC Method and Soil Standards

The BIC Index was specifically developed to resolve false exceedances of the CCME Canadian Wide Standards (CWS) (CCME 2008) soil standards for F3 PHCs. Understanding the premise for this method is essential to understanding how it can be potentially applied to the BC EPH method as well. The BC and CCME methods have some similarities. Both methods extract soils in 50:50 hexane and acetone solvent mixture, which is why both methods are prone to BOC interference issues. However, BC and CCME use different SGC methods. The BC method only allows SGC when, “there is good reason to suspect that naturally occurring organics are present at a site, to an extent where EPH results would likely be significantly elevated” (BC MoE 2004). In contrast, the CCME method applies SGC to all soil samples and allows either the column or in situ methods to be used. For example, the in situ method is most commonly used in AB. The column cleanup is similar to the BC column cleanup method while the in situ method mixes sample extracts with silica gel in a beaker, which causes the adhered polar compounds to settle out of the solution. The “cleaned” overlying extract is then decanted and submitted for GC/FID analysis.

The BC and CCME methods analyse EPH/PHC extracts by GC/FID, which generates data that are used to calculate concentrations for specific carbon ranges. The BC method subtracts specified PAH from the EPH concentration, which are then reported as two carbon ranges (see Table 5-3).

In contrast, the CCME CWS method reports total PHC concentrations as four carbon ranges, as presented in Table 5-3. CCME F2 and F3 carbon ranges are similar to the BC CSR LEPH and HEPH carbon ranges, respectively.

Table 5-3. Comparison of CSR VPH and EPH Carbon Ranges to CCME PHC Carbon Ranges
Review of Analytical Methodologies and Interpretation of Analytical Results in Peat

| Hydrocarbon Designation | Carbon Range |
|-------------------------|-----------------------------------|
| CCME F1 | C6-C10 |
| CSR VPH | C6-C10 |
| CCME F2 | C10-C16 |
| CSR LEPH | C10-C19 |
| CCME F3 | C16-C34 |
| CSR HEPH | C19-C32 |
| CCME F4 | C34-C50 |
| CSR | Hydrocarbons > C32 not considered |

LEPH and HEPH concentration risks are evaluated by the BC CSR soil standards. The most stringent standards are 1,000 mg/kg for both LEPH and HEPH, which apply to agricultural/residential/park land use types. F2-F4 PHC concentration risks are evaluated by the CCME CWS PHC soil standards. For the purposes of this discussion, we have only referenced the standards that apply to F2 and F3, which are most similar to the LEPH and HEPH carbon ranges. The most stringent standards, 150 mg/kg for F2, and 300 mg/kg for F3, apply to agricultural/residential/parkland land use types.

5.2.2.2 Overview of BIC Index Method

The BIC Index uses a simple mathematical approach to identifying false F2, F3, and F4 PHC detections and false exceedances of CCME Tier 1 F3 PHC guideline exceedances in organic soils. The previously mentioned Kelly-Hooper PhD study (Kelly Hooper 2013, 2014) documented predictable carbon range and chromatogram patterns in clean soils and in petroleum products (see Figure 3). The BIC Index is based on the following four characteristics of uncontaminated organic soils:

- F2 (C10-C16) concentrations are less than 20 mg/kg and do not exceed the CCME Tier 1 guidelines;
- F3 (C16-C34) concentrations are detectable and may exceed the CCME Tier 1 guidelines;
- F4 (C34-C50) concentrations are detectable but do not exceed the CCME Tier 1 guidelines; and
- Greater than 85 percent of the total F3 range occurs within the F3b (C22-C34) range.

The BIC Index is as follows (Equation 3):

$$\text{BIC Index} = [F2 / (F2 + F3b)] \times 100$$

Where:

F2 = the C10-C16 concentration

F3b = the C22-C34 concentration

Samples that exceed the 300 mg/kg F3 soil CCME guideline, but have < 10 percent BIC Index are identified as false PHC exceedances. Samples with ≥ 10 percent BIC Index are identified as true F3 PHC exceedances. Figure 5-2 provides a decision tree and screening criteria for indicating if biogenic interferences have caused false exceedances of the 300 mg/kg F3 PHC coarse soil guideline.

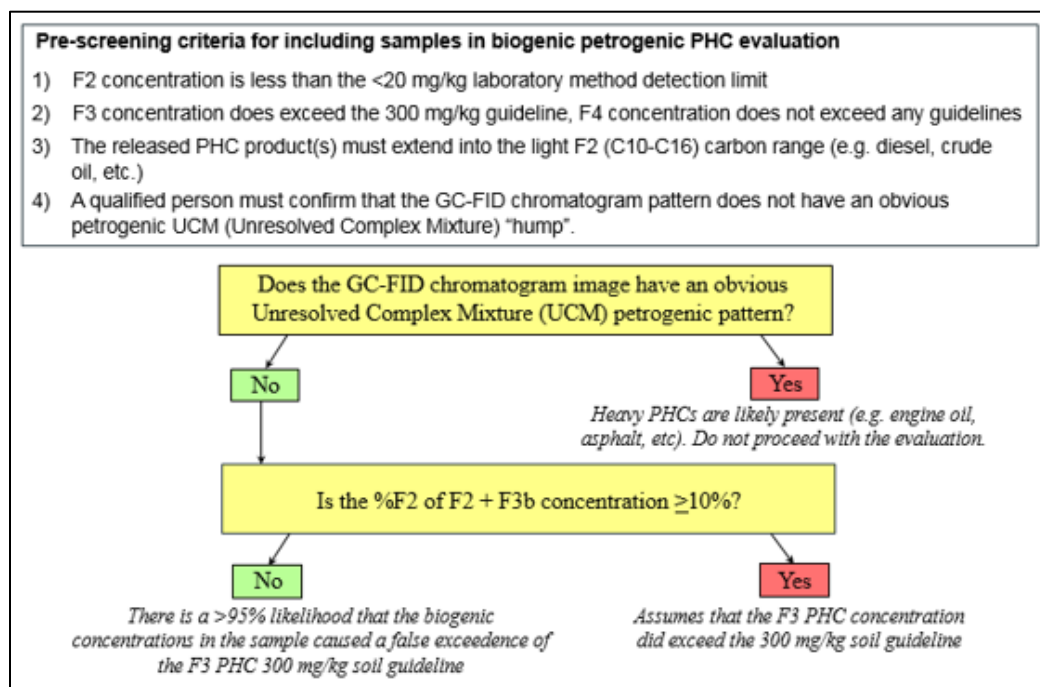


Figure 5-2. BIC Index Decision Tree
(Kelly-Hooper 2013)

Figure 4 provides examples of BIC Index calculations to identify false exceedances, for a clean peat and a contaminated peat with diesel.

5.2.2.3 Relevance of the BIC Index to the BC EPH Methods and Soil Standards

The BIC Index was designed to resolve false exceedances of the CCME CWS PHC F3 soil standards. There are some similarities and differences between the CCME and BC methods and standards that require consideration for managing peat soils.

- The F2 and LEPH carbon ranges are similar. The F3 and LEPH carbon ranges are also similar. Slight adjustments to the BIC Index calculation may allow it to be applied to the BC EPH method as well to identify false exceedances.
- The BC method only allows SGC application when there is a reasonable expectation that organic materials are present in a soil sample. Unless samples are analysed for organic matter content, determining if a sample warrants a SGC treatment introduces some uncertainty to the analytical process. Standard application of an adapted BIC Index could quantitatively identify those samples that warrant a SGC treatment in a timely and cost effective manner.

5.3 Salinity Parameters

5.3.1 Saturated Paste Method for Salinity Parameter Analysis

The BC MoE saturated paste (BC MoE, 2013) analytical laboratory method was intended for mineral soils. The saturated paste procedure, as a general description is to dry the “as received” sample, grind, saturate, extract the liquid, analyse, and then convert the mg/L obtained back to mg/kg using the calculated percent saturation. The percent saturation is a biased value based on a chemist’s subjective interpretation of saturation. The traditional saturated paste application is derived by agronomic researchers to determine natural soil salinity and reported results in mg/L.

The BC MoE saturated paste method (BC MoE, 2013) defines saturation as follows:

“Add sufficient deionized water while mixing to saturate the soil sample. At saturation, the soil paste glistens, flows slightly when the container is tipped, and slides cleanly from a spatula. A trench carved in the soil surface will readily close upon jarring the container.”

The BC Environmental Laboratory Manual (BC MoE 2009) also states: “The moisture content of soils, sediments, sludge and plant tissue can vary significantly and, while the analysis is more appropriately performed on the sample ‘as received’, it affords a more consistent basis for interpretation of results if they are reported on a ‘dry weight’ basis.”

This statement has now been proven debatable when it comes to peat material, as discussed below.

The alternate “as-received” method put forth in the BC MoE method, is for soils that are over-saturated in their “as-received” state. This was an allowance for “over-saturated” soils (generally high moisture content soils), but the over-saturated is defined by BC MoE¹ as having “freeboard” water on top of the soil. In speaking with practitioners and laboratories, the alternate “as received” method was not used for the majority of peat containing materials due to its inherent properties of behaving like a sponge, thus no “freeboard” was present. The percent saturation of a peat material can be up to 300 to 700 percent, which affects the conversion of salinity dry weight concentration by grossly overestimating it by up to twenty times.

This overestimation was presented in 2013 by Hugdahl (Hugdahl 2013). As salinity is highly soluble, it tends to exist in the dissolved phase, which differs significantly from other parameters (metals and

¹ BC MoE’s definition of over-saturation:

organics) which tend to adsorb to soils. Hugdahl demonstrated the difference in conversion factors between different types of mineral soils vs. peat – the mineral soil factor was < 1 percent, compared to 7 percent for peat, converting to 10 to 20 times the concentrations in peat than mineral soils for a given pore water concentration. SynergyAspen (SynergyAspen 2013b) demonstrated this overestimation graphically as presented in Appendix I.

As industry is accepting the limitations of presenting salinity concentrations as mg/kg for peat material, SynergyAspen received a grant through BC OGC through the BC Oil and Gas Research and Innovation Society to review and recommend changes to the BC MoE prescribed saturated paste method for sodium and chloride analysis, specifically for muskeg material. Using muskeg samples collected in NEBC in the oil and gas fields, SynergyAspen worked in collaboration with Maxxam Analytics and CARO Analytical Services to evaluate variations of the saturated paste method and provide data to confirm that the use of saturated paste grossly overestimates the dry weight concentrations of salinity parameters for peat materials.

The following is a brief description of the three alternatives:

- **“Wet-weight method” (M2)** – This method is based on work completed by Mark Hugdahl of ALS and considered accepted by industry as an alternative to dry weight for salinity parameters, when used with other lines of evidence. It uses the derived mg/l concentration in the saturated paste method to be compared directly to the soil standard, instead of converting it back to an over-estimated dry weight concentration.
- **As-received “squeeze and analyse” (M3)** – This method is the suggested BC MoE saturated paste method for soils that are over-saturated in their as-received state. The alternative was designed for high moisture content soil having a “freeboard” of water on top of the soil, which as noted above is not the case. However, this method is using the alternative laboratory on peat *regardless if there is no freeboard*.
- **Intentional over-saturation (M4)** – This method was a by-product of method M3, for samples that could not readily be squeezed using analytical instruments and required a controlled saturation to a pre-determined moisture content before being squeezed and analyzed. “Drier” samples with a moisture content between 60 and 70 percent could not be readily squeezed and required the intentional over saturation before squeezing.

In their conclusions, SynergyAspen confirm through laboratory testing of their field collected muskeg from NEBC, what others also have, that the current BC regulated laboratory standard saturated paste method greatly overestimates the sodium and chloride concentrations in a muskeg sample when reported as mg/kg. SynergyAspen recommends the “intentional over-saturation” method, which targets the miscible analytes in the water portion of the muskeg and reporting it in mg/L would eliminate the gross overestimation, and in turn, reduce the falsely identified contamination identified at many oil and gas sites located within a muskeg setting in BC. The “intentional over-saturation” method is within the currently prescribed BC MoE saturated paste methodology. The change required would be in the definition of “over-saturated soil” to include peat materials, regardless of the presence or absence of freeboard. SynergyAspen identified this methodology would remove two biases – the effect of moisture content in expressing salinity concentrations in mg/kg, and the limitations in field sampling muskeg, particularly in high water table, visible saturated conditions.

5.3.2 Salinity Standards

Bright and Addison (Bright and Addison 2002) identified that the environmental concern with salinity is predominantly toxic to plants and provided first toxicity based specific ion salt standards in Canada. These led to the introduction of BC CSR matrix standards for sodium and chloride in January 2009. However, even the basis for the research and standards was road salt and oil and gas site produced

water release issues, in mineral soil deposit environments. They identified that plants were more sensitive to salt than soil invertebrates, based on data from mineral soils. Toxicity thresholds used to derive the salinity standards for both plant and soil invertebrates was relevant to only coarse mineral soils and not for peat containing soils. Conclusions identified that soil type has a profound influence on toxicity and that correlation between toxicity and standards would be better across all soil types if mg/L saturated paste concentrations were used instead of mg/kg concentrations. Hugdahl also presented the effect of soil type assumption on the CCST groundwater model, which assumed Fraser River sand as the soil type, which is vastly different from peat.

Based on his laboratory evidence and Bright and Addison toxicity research, Hugdahl's provided strong evidence to support a solution based salt standard (mg/L) for sodium and chloride in peat samples and conclusion this would eliminate the bias from soil types if soil standards for salinity were expressed as mg/L (soil solution) instead of mg/kg (soil dry weight).

Bright and Addison (Bright and Addison 2002) toxicity data evaluation identified a plant toxicity threshold of EC 4.6 deciSiemens per metre (dS/m), which correlates to approximate 1,480 mg/L chloride as saturated paste (Chemical Rubber Company [CRC] Handbook). This is in comparison to the Alberta Environment Salt guidelines of EC 2-4 = 625 to 1,280 mg/L EC 3-5 = 950 to 1,610 mg/L and the PTAC peatland salinity field study of EC 3-4 = 950 to 1,280 mg/L chloride (sat paste). Based on these studies, an ecological protective threshold for chloride of 600 to 1,500 mg/L would be a target range for a soil standard for chloride in peat. This is shown in graphical format by Bright and Addison in Attachment B.

Hemmera has been commissioned by BC OGRIS to derive an alternative suite of salt ion numerical standards for use within the CSR framework for peat type materials in wetland environments, compared to terrestrial upland soil systems. As noted in Hemmera's BC OGRIS Project Profile (Hemmera 2014), based on recent practitioner and laboratory work for site assessments in the NEBC, the following insight has been gained:

- True effects on wetland mesofauna, plant roots, and other biota is likely to be better correlated with the soil salt solution results than analytical results expressed on a dry soil mass basis for soils (based in turn on saturated paste extract methods) that are almost completely saturated in their native state.
- The standardized CSR assumptions for back-calculation of soil chloride and sodium concentrations protective of aquatic life based on a groundwater-mediated transport scenario are likely overly conservative for the vast majority of wetland systems.

The Hemmera project will include:

- Developing guidance on when it would be appropriate to use alternative CSR wetland soil standards for salt, expressed in mg/L.
- Derive alternative CSR solution-based wetland salt soil standards based on two major lines of evidence:
 - Interpretation of pre-existing ecotoxicity data collected by Bright during the PTAC/Canadian Association of Petroleum Producers (CAPP)/Alberta Upstream Petroleum Research Fund (AUPRF)/ Program for Energy Research and Development (PERD) *Peatland Salinity Project* (2008–2011); and
 - New scientific data from manipulation field trials in fen-type and marsh-type sites near Fort St. John.
- Derive alternative set of wetland soil standards for salt to protect aquatic life based on groundwater-mediated transport assumptions geared for boreal wetland ecosystems (especially in bogs and fens).

- Develop for consideration by the BC Government for possible incorporation in the CSR, Schedule 5, matrix soil standards for salt, new wetland “Toxicity to soil invertebrates and plants” and “Groundwater flow to surface water used by aquatic life” solution-based matrix soil standards; along with detailed proposed technical guidance or protocol for appropriate use of the above-mentioned new wetland solution-based matrix soil standards for salt.

Results from the Hemmera project are expected to be published in June 2017. Interim results on toxicity indicated that the new protocol for derivation of BC CSR soil matrix standards (BC MoE, 2016), may have short-comings and may be an impediment to deriving alternative standards for peatlands, since peat matrix is not a “soil” per se. Therefore, this puts into question whether BC MoE policies developed for soil invertebrate and plant soil matrix standards apply to peat matrix. This may assist in further development of peat specific matrix standards, particularly for salinity. In regards to sampling of muskeg, Hemmera’s first preference is to sample standing water within upper 1.0 metres (m) of peatland and measure major ions including chloride and sodium directly (mg/L). Where it is not possible to obtain water from the peat, Hemmera recommends methodology for analysing the salt analytes. Options for developing an ecotoxicity threshold were also provided within the project, including lab toxicity testing rather than field testing.

Recommendations

In completing the literary research and discussions with practitioners and analytical laboratories, there are common issues for biases occurring for peat media sample analysis, but then there are also very specific issues related to each different parameter groups researched, namely salinity, metals, and organics.

The following recommendations are subdivided into two main categories: interim quick fix and long-term recommendations.

6.1 Interim “Quick Fix”

The following are general interim “quick fix” recommendations pertaining to peat media, that BC practitioners have successfully utilized in their practice:

- Request from laboratory to complete an extra concentration step to obtain a lower method detection limits (MDLs) for peat samples for low standard parameters. This is not a standard lab approach, but it can be requested for high-moisture content soils, such as peat.
- Identify adequate sampling practices for peat sample collection. It is not a recommended practice to intentionally squeeze out the water from a muskeg sample (which has been done by practitioners). This is critical for salinity, which is miscible in water.
-
- Use a screening level risk assessment and multiple lines of evidence when presenting rationale for interpretation of anomalous concentrations during intrusive investigation work in peat media, including wet weight concentrations, advancement of background borehole for sample collection and comparison of data to onsite data, and chromatogram review for biogenic peaks.
- Obtain background release for detectable metals greater than Protocol 4 (BC MECCS, 2010) concentrations, particularly for arsenic in upstream oil and gas sites.
- If working on a site where both provincial and federal regulatory regimes apply, consider applying the Biogenic Interference Calculation (BIC) index calculation for petroleum hydrocarbon (PHC) concentrations greater than applicable Canadian Council of Ministers of the Environment (CCME) guidelines to confirm whether true exceedances exist or not.

6.2 Long-term Recommendations

The following are recommendations for consideration by BC MECCS to implement changes in the regulatory regime for successful characterization of peat materials and to reduce unnecessary remediation of perceived contaminated peat materials:

- **Field methodology:**
 - Provide a standardized peat sample collection methodology.
- **Standards:**
 - Identify peat either as its own media or as a subcategory of soil, allowing specific standards to be derived for peat media.

- Re-evaluate soil standards for peat media based on toxicity data for specific peatland ecosystem receptors (plant and soil invertebrates). Use appropriate soil invertebrates specific to a peat environment and not a terrestrial environment. These would likely demonstrate that higher standards could be warranted for this matrix, as more representative risks would be determined; in part, due to lower bioavailability for uptake by living organisms.
- Derive salt standards as milligrams per litre (mg/L), which would eliminate variability across soil types due to water-holding capacity differences.
- **Analytical methodologies:**
 - Review analytical laboratory methods for applicability and sensitivity to peat soils, including:
 - Recommend alternate method for use in peat media, including peat samples to be digested using the current BC MECCS laboratory method for tissue and vegetation analysis
 - Do not allow peat samples to be sieved to 2 millimetres (mm), as some of the organic material would be removed by this process
 - Use inductively coupled plasma mass spectrometry (ICP-MS) for metals analyses
 - Allow for the alternate “as-received” saturated paste extraction methodology (BC MECCS, 2015) for all soils containing organics; and avoid the standard dry, grind, and analyze saturated paste extraction method (BC MECCS, 2015) for soils with peat, even if there is no freeboard, as defined by oversaturated soil.
 - Review and update the BC MECCS silica-gel methodology (BC MECCS, 2004) by completing a multi-lab study for variability in silica-gel methodology and results. Francine Kelly-Hooper’s PhD experiments spiked 34 clean peat samples with fresh crude oil, which was placed into muskeg microcosm tanks and allowed to weather over 300 days (Kelly-Hooper et al., 2013). Portions of these original peat samples are currently preserved and frozen. Upon an agreement with Dr. Kelly-Hooper, these samples could be contributed to a round-robin laboratory study, in which duplicate samples are provided to laboratories for silica gel analysis, and the results are compared between the laboratories for variances.
- **Regulatory guidance:**
 - Allow for fraction of organic carbon (f_{oc}) values greater than 2 percent for calculation of site-specific standards under Protocol 2 (BC MECCS, 1998).
 - Allow for more than one site-specific standard per site for both soil and peat media, if present, similar to varying pH concentrations within the BC *Contaminated Sites Regulation* (CSR) and more than one numeric standard per site.
 - Complete a background study of peat materials to determine background concentrations for metals and biogenic hydrocarbons, and update the Protocol 4 background concentrations to include peat media. Obtain background study data either by completing new field work or seeking input from Canadian Association of Petroleum Producers members and practitioners for existing background data in muskeg.
 - The previously discussed Canadian background PHC peat soil survey samples (34 in total) (Kelly-Hooper et al., 2014) remain in frozen storage. Upon Dr. Kelly-Hooper’s permission, these peat samples could be contributed to a BC background soil survey, which would build on the existing published research.
 - Provide further guidance as to when silica-gel clean-up is to be implemented.

Limitations

This Report was prepared jointly by CH2M and SLR for CSAP. It is intended for the sole and exclusive use of CSAP for its stated purpose. Third parties cannot rely upon the findings and conclusions presented nor copy or distribute the Report without express written consent of CH2M, SLR, and CSAP through an extension of reliance using a reliance letter signed by all parties.

The Report has been prepared in accordance with the scope of work and agreements between CSAP, CH2M, and SLR. CH2M and SLR accept no responsibility for damages, if any, incurred by any third party as a result of decisions made or actions based on this Report.

The information, opinions, and recommendations of the Report are based solely on the extent of information gathered and recorded by CH2M and SLR at the time the work was conducted and are intended only for CSAP purposes, locations, time frames and project parameters as outlined in the scope or work and agreement between CH2M, SLR, and CSAP. The data reported, findings, observations, and conclusions expressed are limited by the scope of work. All findings and recommendations stated in this Report are based on facts and circumstances as they existed during the time that the work was conducted. This is a technical Report and is not a legal representation or interpretation of environmental laws, rules, regulations, or policies of governmental agencies.

CH2M and SLR believe this report to be accurate; however, disclaim any warranty of the completeness or accuracy of information supplied to CH2M or SLR that was relied upon in the preparation of this report or accurate beyond current environmental engineering consulting standards. Any changes in fact or circumstances upon which the summary was based may change the findings reported. CH2M and SLR are not responsible for the impacts of any changes in environmental standards, practices, or regulations subsequent to performance of services.

References

- Alberta Environment and Parks (AEP). 2016. Soil Remediation Guidelines for Boron: Environmental and Human Health. Land Policy Branch, Policy and Planning Division.
- BC Ministry of Environment (BC MoE). 2016. Extractable Petroleum Hydrocarbons (EPH) in Solids by GC/FID. PBM/Hydrocarbon. July 14.
- BC Ministry of Environment (BC MoE). 2015. Procedure 8: Definitions and Acronyms for Contaminated Sites. November 20.
- BC Ministry of Environment (BC MoE). 2013. Environmental Monitoring, Reporting and Economics, Sampling, Methods and Quality Assurance, British Columbia Environmental Laboratory Manual.
- BC Ministry of Environment (BC MoE). 2008. Protocol 14: Requirements for Determining Barite Sites. December 10.
- BC Ministry of Environment (BC MoE). 2004. Silica Gel Cleanup of Extractable Petroleum Hydrocarbons. May 6.
- BC Ministry of Environment (BC MoE). 1998. Protocol 2: Site-Specific Numerical Soil Standard. February 11.
- BC Ministry of Environment (BC MoE). 2010. Protocol 4: for Contaminated Sites, Determining Background Soil Quality. Prepared pursuant to Section 64 of the Environmental Management Act. October 12.
- BC Ministry of Environment (BC MoE). 2015. "Section B: Physical, Inorganic and Miscellaneous Constituents." *Saturated Paste Extraction for Soils, BC Environmental Laboratory Manual*. March 31.
- BC Ministry of Environment (BC MoE). 1996 Overview of CSST Procedures for the Derivation of Soil Quality Matrix Standards for Contaminated Sites. January 31.
- Bright and Addison. 2002. Derivation of Matrix Soil Standards for Salt under the British Columbia Contaminated Sites Regulation. Applied Research Division, Royal Roads University, Victoria, BC. June.
- Canadian Council of Ministers of the Environment (CCME). 2008. Canada-Wide Standard (CWS) for Petroleum Hydrocarbons (PHC). Winnipeg, Canada. January 2008.
- Clarke and Joosten. 2002. Wise Use of Mires and Peatlands – Background and Principles. International Mire Conservation Group and International Peat Society. November.
- Gorsic, SynergyAspen, Novak, CARO. 2015a. A Case for Matrix Specific Methods for Peat Characterization. Presented at 5th Annual SAB Conference on Contaminated Sites. September 24.
- Gorsic, SynergyAspen. 2016. Review and Recommended Changes to the Saturated Paste Method to Determine Concentrations of Sodium and Chloride in Muskeg. Presented at REMTECH 2016. October 12.
- Graham et al. 2014. Site Specific Investigation for Salt Contaminated Site in Northeast BC. Presented at the 4th Annual SAB Conference on Contaminated Sites. September.
- Hemmera. 2014. Adapting Contaminated Sites Approach for Produced Water Releases to Wetlands. BCOGRIS Project Profile. October.
- Huang, Pao-Tsung, M. Patel, M. Santagata, and A. Bobet. 2009. FHWA/IN/JTRP-2008/2 Classification of Organic Soils. Joint Transportation Research Program, Project No. C-36-36TT, File No. 6-14-45, SPR-3005, Purdue University and Indiana Dept. of Transportation and Federal Highway Administration. September.

Hugdahl, M., ALS. 2013. Issues with BC CSR Salt Standards in Peat Soils Related to Saline Produced Water. Presented at the WaterTECH conference. April 10 2013.

International Peatland Society. <http://www.peatociety.org/peatlands-and-peat>

Juttner, F. 1991. "Formation of Toluene by Microorganisms from Anoxic Freshwater Sediments." *Fresenius' Journal of Analytical Chemistry*. October 1991, Volume 339, Issue 10, pp 785–787

Kelly-Hooper, F., A.J. Farwell, G. Pike, J. Kennedy, Z. Wang, E.C. Grunsky, and D.G. Dixon. 2013. "Is it Clean or Contaminated Soil? Using Petrogenic Versus Biogenic GC-FID Chromatogram Patterns to Mathematically Resolve False Petroleum Hydrocarbon Detections in Clean Organic Soils: A Crude Oil Spiked Peat Microcosm Experiment." *Environmental Toxicology and Chemistry*. 32: 2197-2206.

Kelly-Hooper, F., A.J. Farwell, G. Pike, J. Kennedy, Z. Wang, E.C. Grunsky, and D.G. Dixon. 2014. "Field Survey of Canadian Background Soils: Implications for a New Mathematical Gas Chromatography – Flame Ionization Detection Approach for Resolving False Detections of Petroleum Hydrocarbons in Clean Soils." *Environmental Toxicology and Chemistry*. 33: 1754-1760

Maynard, Dennis Edward. 1989. Peatlands Inventory of British Columbia, Mineral Resource Division, Geologic Survey Branch, Victoria, BC., March.

Oxford Dictionary. <https://en.oxforddictionaries.com/definition/peat>

Remi Odense & Glyn Fox. 2016. CSR OMNIBUS UPDATING: Protocol Summary - Amendments to Schedule 5 Environmental Protection, Matrix Soil Standards. February.

Riley, J.L. 1986. Laboratory Methods for Testing Peat – Ontario Peatland Inventory Project

SynergyAspen. 2013a. Regulatory and Assessment Challenges for High Moisture and Organic Content Soil in Northeast BC. Presented at Environmental Management Association Meeting. September 25.

SynergyAspen. 2013b. Regulatory Assessment Challenges for Muskeg Soil at Oil and Gas Sites in Northeast BC. Presented at the Annual Northeast BC Producer's Group Meeting. October.

SynergyAspen. 2015b. Review and Recommended Changes to the Saturation Paste Method to Determine Concentrations of Sodium and Chloride in Muskeg. Prepared for BC Oil and Gas Research and Innovation Society. November 23.

Tarnocai, C. 1980. Canadian wetland registry. In: C.D.A. Rubec and F.C. Pollett (eds.), *Proceedings, Workshop on Canadian Wetlands*. Lands Directorate, Environment Canada. Ecological Land Classification Series No. 12. Ottawa, Ontario. pp. 9-39.

Tarnocai. 1984. Peat Resources of Canada. Land Resources Research Institute, Research Branch, Agriculture Canada. October.

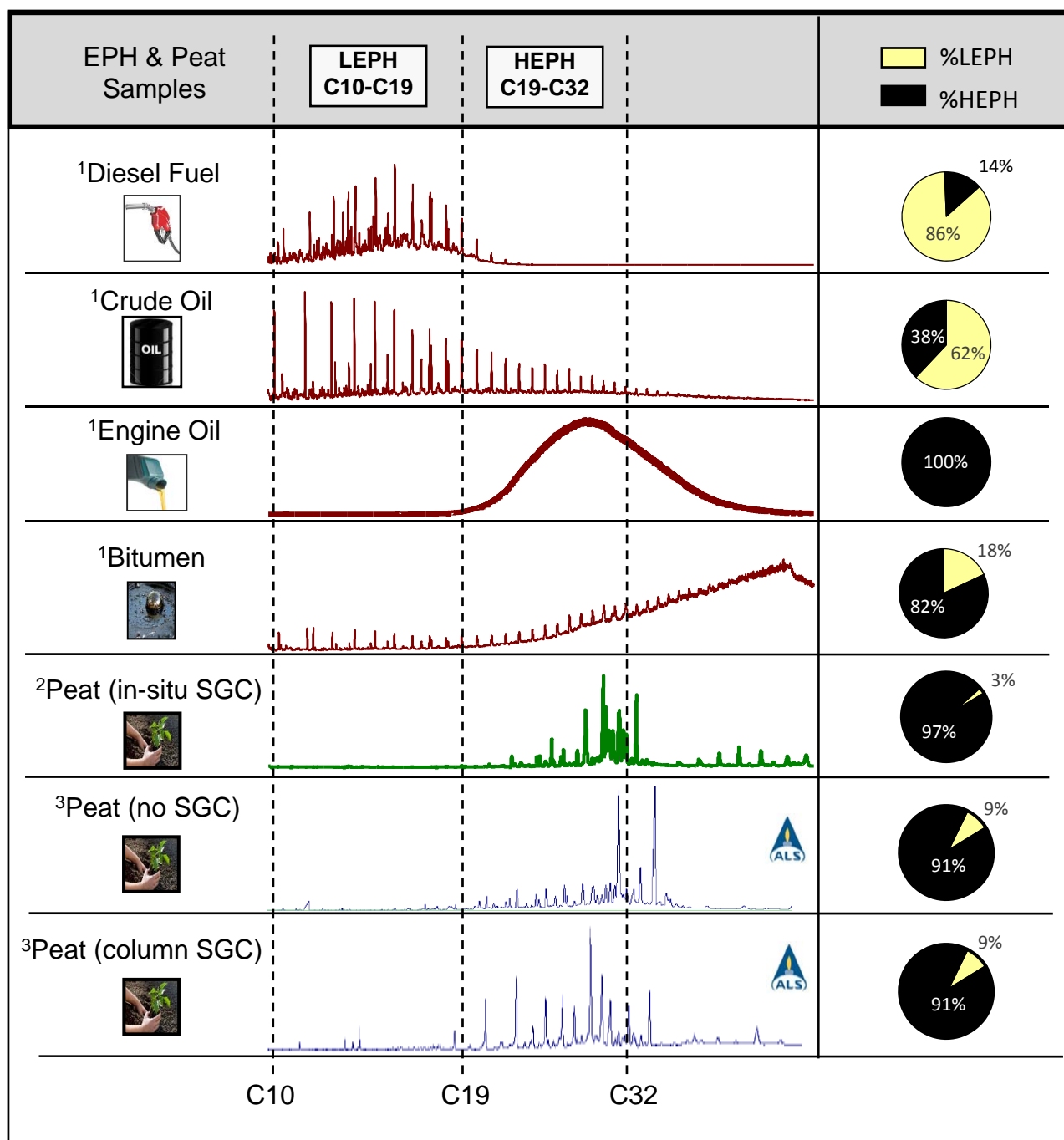
Tarnocai, Kettles, & Lacette. 2011. Peatlands of Canada. Geological Survey of Canada. Open File 6561

United States Environmental Protective Agency. 2003. Guidance for Developing Ecological Soil Screening Levels (Eco-SSLs). OSWER Directive 92857-55. Department of Solid Waste and Emergency Response. Washington, DC. November.

Zargar K, Saville R, Phelan RM, Tringe SG, Petzold CJ, Keasling JD and Beller Hr. 2016. "In Vitro Characterization of Phenylacetate Decarboxylase, a Novel Enzyme Catalyzing Toluene Biosynthesis in an Anaerobic Microbial Community." *Scientific Reports*. 6:31362

Figures

Figure 1: LEPH and HEPH Carbon Ranges and GC-FID Chromatograms for Petroleum Sources and Clean Peat



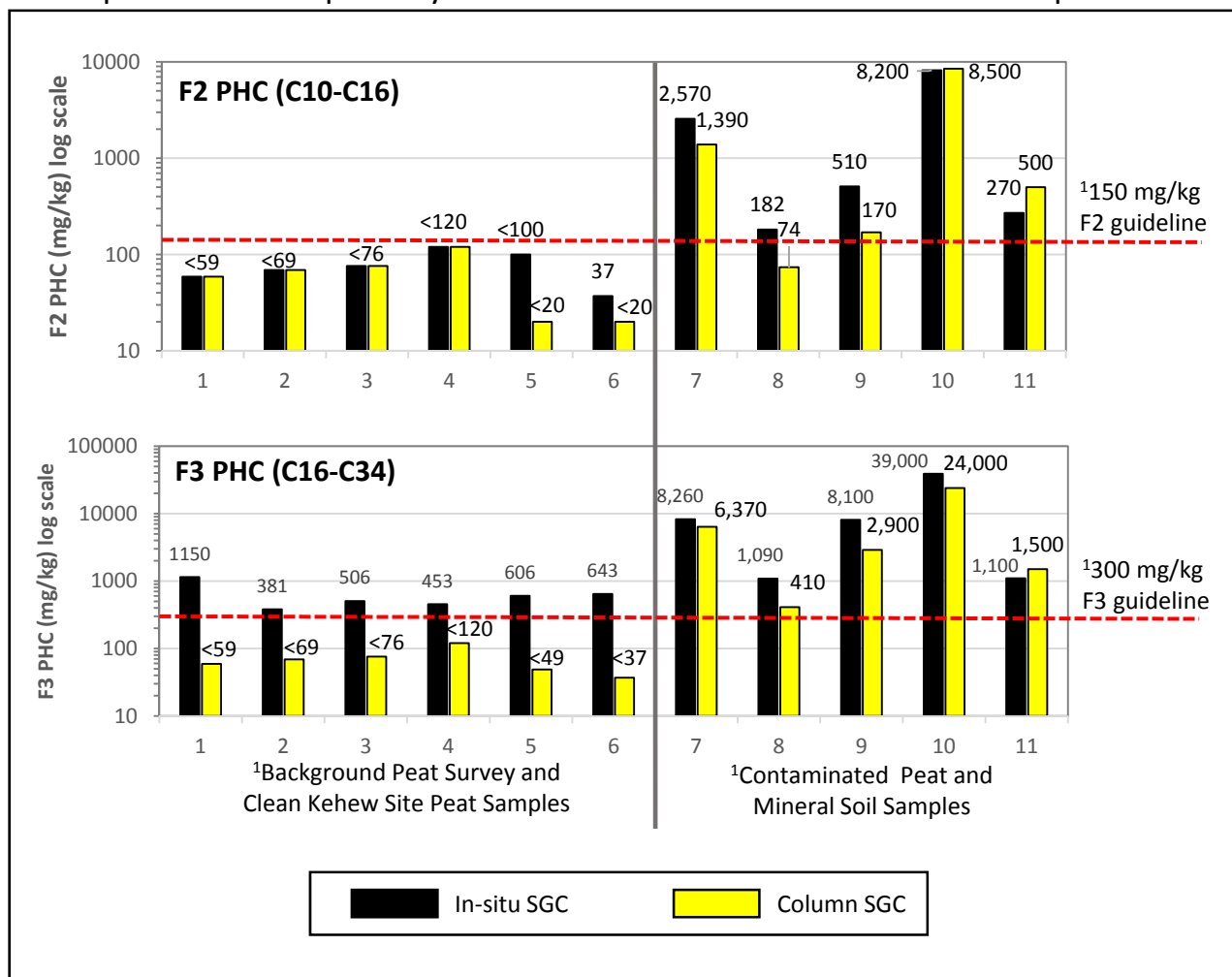
¹Unweathered EPH products were analyzed in their neat forms without any extractions

²Clean peat was analyzed by the CCME CWS PHC method, including an insitu silica gel cleanup

³Clean peat was analyzed by the BC EPH method, excluding silica gel cleanup

⁴Clean peat was analyzed by the BC EPH method, including a column silica gel cleanup

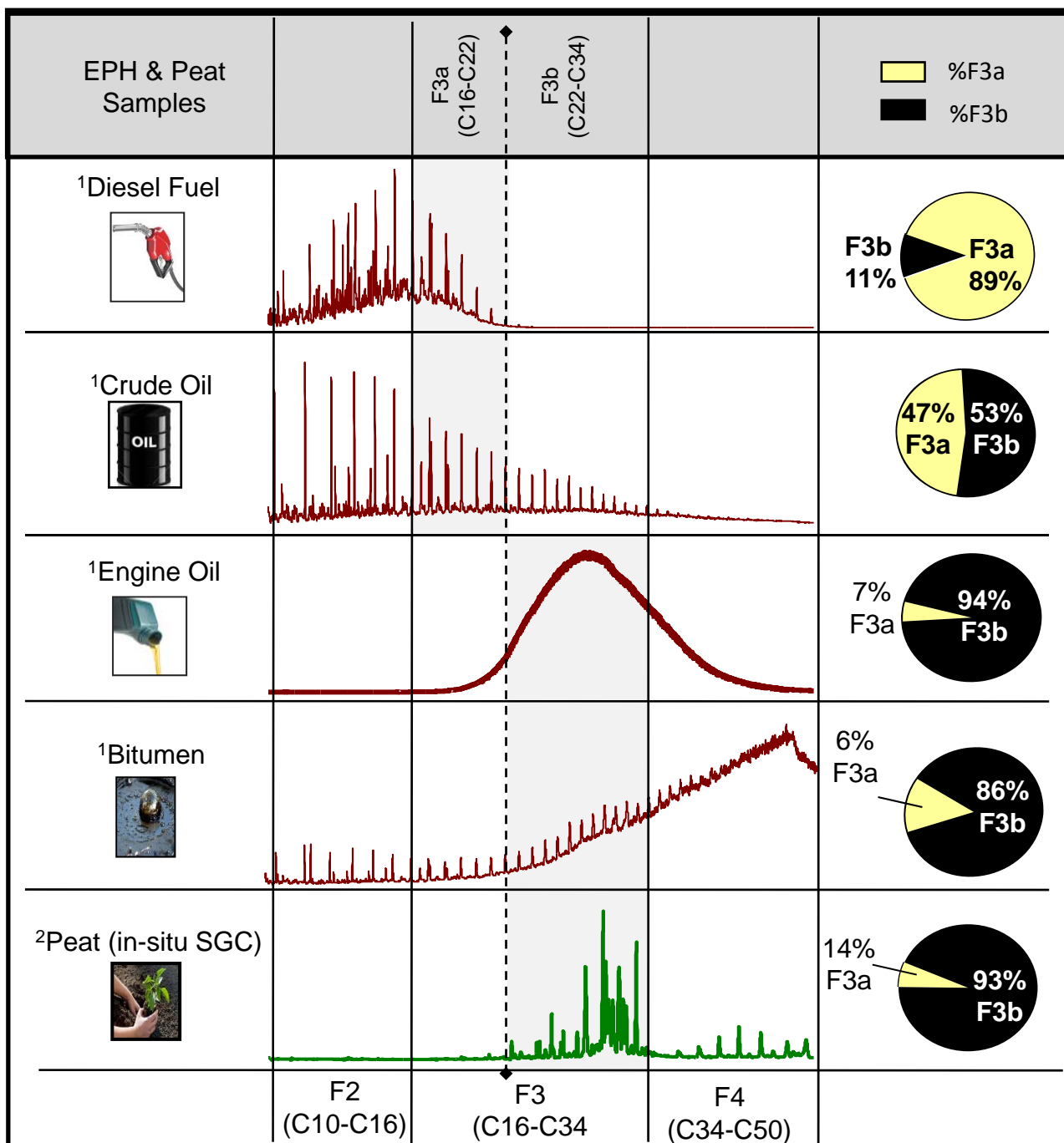
Figure 2: Comparison of CCME CWS F2 and F3 PHC Concentrations for Soil Samples Treated Separately with In-situ and Column Silica Gel Cleanups



¹Alberta Tier 1, natural area, coarse surface soil PHC guidelines

*Sample extracts were treated separately with insitu and column silica gel cleanups.

Figure 3: CCME CWS PHC Sub-fractions F3a and F3b Distributions in Petroleum Sources and Clean Peat


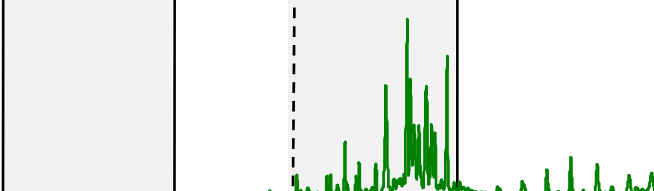
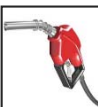
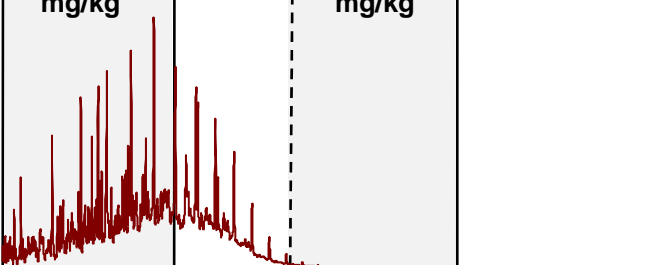
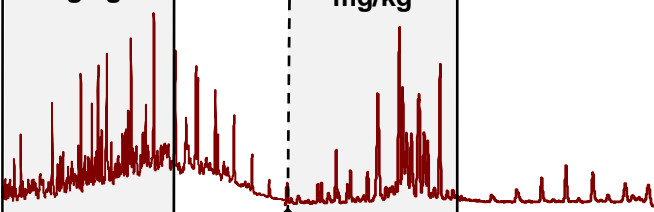


¹Unweathered EPH products were analyzed in their neat forms without any extractions

²Clean peat was analyzed by the CCME CWS PHC method, including an insitu silica gel cleanup

Figure 4: Example BIC Index calculations for Identifying False Exceedences of CCME CWS F3 PHC Soil Standards by Clean Peat Soils

*The BIC Index may be adapted to identify false exceedences of BC EPH soil standards

| Peat, Diesel & Contaminated Peat Samples | F2 (C10-C16) F2 (C10-C16) | F3 (C16-C34) F3b (C22-C34) | F4 (C34-C50) | BIC Index [F2/F2+F3b] x 100 <10% = true F3 petroleum concentration was less than 300 mg/kg |
|--|------------------------------------|-------------------------------------|--|---|
| | | | | |
| Peat  | F2 = 10 mg/kg | F3b = 1,395 mg/kg |  | 1% = True F3 PHC/EPH concentration was less than 300 mg/kg |
| Diesel Fuel  | F2 = 823 mg/kg | F3b = 371 mg/kg |  | 69% = True F3 PHC/EPH concentration was higher than 300 mg/kg |
| Diesel Contaminated Peat | F2 = 613 mg/kg | F3b = 2,816 mg/kg |  | 33% = True F3 PHC/EPH concentration was higher than 300 mg/kg |

Appendix 1
SynergyAspen Graphical Presentation
of Dry Weight vs. Wet Weight
Concentration in High Moisture
Content Soils

Substance Concentration Comparison:

Dry Weight Concentration Derived from Soil Moisture Content and
100 mg/kg Wet Weight Concentration Constant

