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1 INTRODUCTION

Petroleum hydrocarbon (PHC) soil contamination is a globally recognized environmental issue. The Canadian Federal Contaminated Sites inventory list identifies over 18,000 sites, 55% of which are contaminated by PHCs. $3.5 billion has been allocated to reducing federal contaminated site risks by the year 2020 (Treasury Board of Canada, 2007). A substantial portion of these funds will be dedicated to PHC contaminated sites. The Canadian petroleum industry is expected to spend $40.6 billion on the remediation of existing privately owned sites as well (CAPP, 2009).

Effective site evaluations and remediation strategies rely on accurate delineations of PHC contamination boundary zones. However, currently PHC soil extraction and chemistry analysis techniques misidentify natural biogenic organic compounds (BOCs) as originating from petroleum sources. “BOC” is a general term used to describe mixtures of biological organic compounds such as alkanes, sterols, sterones, fatty acids, fatty alcohols, waxes and wax esters (Wang, Z. et. al. 2009). BOCs are biosynthesized by plants and animals during their life cycles and are integral components of peat and manure. Standard PHC analysis of highly organic soils such as peat and remediation materials such as manure could trigger false toxicity criteria exceedences, resulting in unnecessary site remediation and/or landfill disposal requirements.

2 RESEARCH OBJECTIVE

The primary objective of this research is to develop a new approach to resolving false PHC soil criteria exceedences in uncontaminated and marginally contaminated soils and compost materials.

3 2009 AND 2010 RESEARCH ACTIVITY SUMMARY

This study focuses on the following two scenarios, which are highly relevant to the petroleum industry: crude oil pipeline spills in muskeg peat and composted manure biopile remediation of diesel invert contaminated drilling waste.

Two laboratory scale experiments were conducted over two consecutive 300 day periods. The first experiment was completed in November 2009 and focused on crude oil contaminated peat. The second ongoing experiment will be completed in February 2010 and focuses on diesel drilling invert contaminated manure biopiles.

A background PHC soil field survey was also conductd in 2009. A total of 34 soil samples were collected from 34 background sites located in the provinces of Alberta, British Columbia and Newfoundland. Additional soil samples will also be collected during the 2010 field season.

The 2009 research activities also included the PHC chemistry analysis of 13 fresh crude oils.

4 PART I AND PART II REPORT DESCRIPTION

This Part I draft report discusses how standard PHC extraction methods can be combined with alternative data calculations to offset false criteria exceedences for crude oil contaminated peat and diesel invert contaminated manure biopiles. This report includes the PHC F2, F3, F3a, F3b and F4 results for the following completed studies:

i) Preliminary F2, F3, F3a, F3b and F4 PHC analysis of biogenic and petrogenic source materials used in the 300 day crude oil contaminatd peat and diesel invert contaminated manure biopile experiments;

ii) F2, F3, F3a, F3b and F4 PHC data for the Day 0, 150 and 300 crude oil contaminated peat experiments;

iii) F2, F3, F3a, F3b and F4 PHC analysis of 13 crude oils; and

iv) F2, F3, F3a, F3b and F4 PHC and priority polyaromatic hydrocarbon (PAHs) analysis of 34 background soil samples.

The subsequent Part II report will include the Day 0, 150 and 300 diesel invert contaminated manure biopile experiment results. It will also demonstrate how current forensics techniques were used to identify petroleum sources and weathering stages for aged and/or “mystery” spill sites. The Phase II report will include the following data:

i) F2, F3, F3a, F3b and F4 PHC results for the 300 day diesel invert experiments;

ii) Petroleum biomarker forensics data for the Day 0, 150 and 300 crude oil and diesel invert experiments; and

iii) Petroleum biomarker forensics data for at least 8 of the 34 background soil samples.

5 CANADA-WIDE TIER-1 PHC SOIL ANALYSIS STANDARDS AND TOXICITY CRITERIA

The Canada-Wide Standard (CWS) for PHCs in Soil is an intergovernmental agreement developed under the Canadian Council of Ministers of the Environment (CCME) Canada-wide Environmental Standards Sub-Agreement). The CWS is a 3-tiered, risk-based remedial standard developed for a variety of common land uses (see Table 1) (CCME, 2001).

Contaminated site evaluations typically begin by analyzing soil samples in accordance with the CWS Reference Method for PHCs in Soil – Tier 1 Method. Under this method, PHC data is categorized into four different carbon fractions. The term “fraction” refers to the following equivalent normal straight-chain hydrocarbon boiling point ranges:

i) Fraction 1: C6-C10;
ii) Fraction 2: C10-C16;
iii) Fraction 3: C16-C34;
iv) Fraction 4: >C34

Each of the four fractions have dedicated CWS Tier-1 PHC soil criteria, as indicated in Table 1. (CCME, 2008). These criteria are based upon the likelihood that petroleum constituents within a given fraction could produce a potential environmental or human health risk. The criteria are suited to a variety of land uses, groundwater potability and soil texture conditions. "Coarse" refers to soils with a median grain size of >75 µm, such as sand and gravel. “Fine” refers to soils with a median grain size of <75 µm, such as peat, silt and clay.

Table 1: Summary of Tier 1 criteria (mg/kg soil) for PHCs in surface soils[1] (CCME, 2008a)

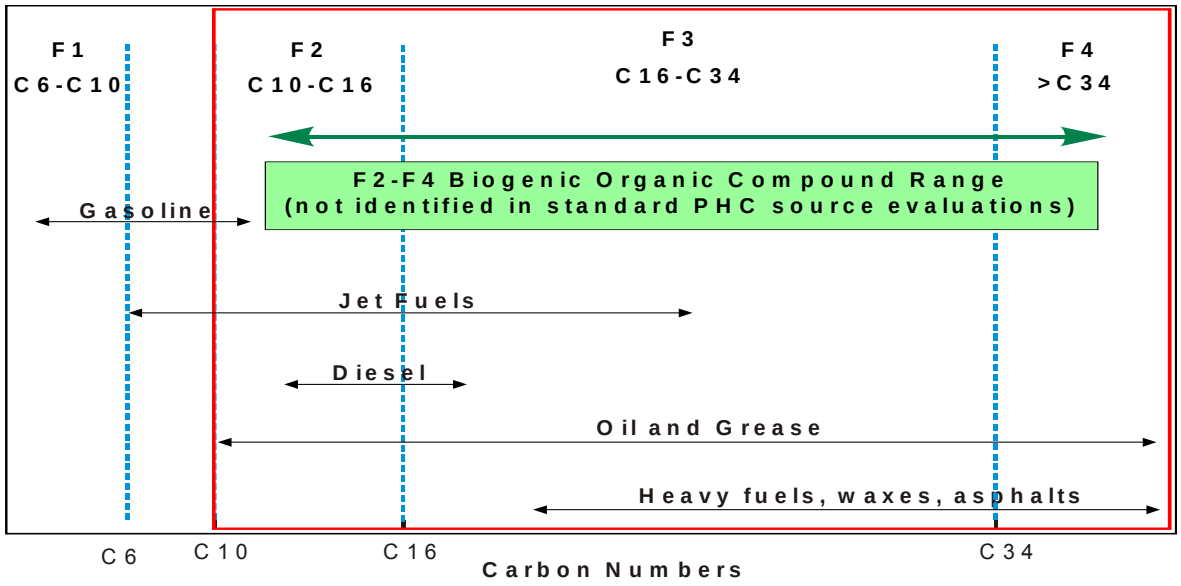
Land Use	Soil Texture	Fraction 1	Fraction 2	Fraction 3	Fraction 4
Agricultural	Course-grained soil	30[3]	150	300	2,800
	Fine-grained soil	210 (170[2])	150	1,300	5,600
Residential/ Parkland	Course-grained soil	30[3]	150	300	2,800
	Fine-grained soil	210 (170[2])	150	1,300	5,600
Commercial	Course-grained soil	320 (240[2])	260	1,700	3,300
	Fine-grained soil	320 (170[2])	260 (230[2])	2,500	6,600
Industrial	Course-grained soil	320 (240[2])	260	1,700	3,300
	Fine-grained soil	320 (170[2])	260 (230[2])	2,500	6,600

[1] Additional Tier 1 levels are presented in Technical Supplement (CCME, 2009).
[2] - Where applicable, for protection of potable groundwater.
[3] - Assumes contamination near residence
Note: Agricultural/Residential/Parkland levels are most relevant to contamination scenarios included in this study (Sources: Personal communications with petroleum industry managers).

6 CWS SUGGESTED SOLUTION TO FALSE PHC CRITERIA EXCEEDENCES

Figure 1 illustrates that various petroleum products and BOCs overlap between the F2, F3 and F4 carbon ranges. The results of this study supports the general perception that false CWS PHC soil criteria exceedences occur only in the F3 carbon range C16-C34.

Figure 1: Petroleum and Biogenic Source Carbon Ranges



The CWS suggested solution to false PHC criteria exceedences is to measure and subtract background F2, F3 and/or F4 concentrations from contaminated soil concentrations. While this approach can be helpful, background concentrations can be highly variable. To illustrate this point, uncontaminated peat samples were collected from Lakeland Provincial Park located 250 km northeast of the City of Edmonton, Alberta (see Figure 4 location map). Two peat samples were collected from depths of 0-5 cm and 11-15 cm and extracted in accordance with the CWS PHC F2-F4 standards (see Methods Section 12.2). The respective F3 concentrations of 3,020 mg/kg and 2,160 mg/kg exceeded the CWS PHC 1,300 mg/kg fine soil criteria. Just as importantly, there was a significant difference of 860 mg/kg between replicate samples collected within the 0-15 cm sample zone.

This type of variability could lead to the under- or over-estimation of true petroleum concentrations and perceived toxicity risks. False PHC criteria exceedences could trigger unnecessary remediation and/or disposal requirements resulting in the waste of valuable landfill space and unnecessary disturbances to uncontaminated natural habitat areas.

7 RELEVANCE TO COMMON PETROLEUM INDUSTRY SCENARIOS

This research focuses on the following two scenarios, which are highly relevant to the petroleum industry: crude oil pipeline spills in muskeg peat and composted manure biopile remediation of diesel invert contaminated drilling waste.

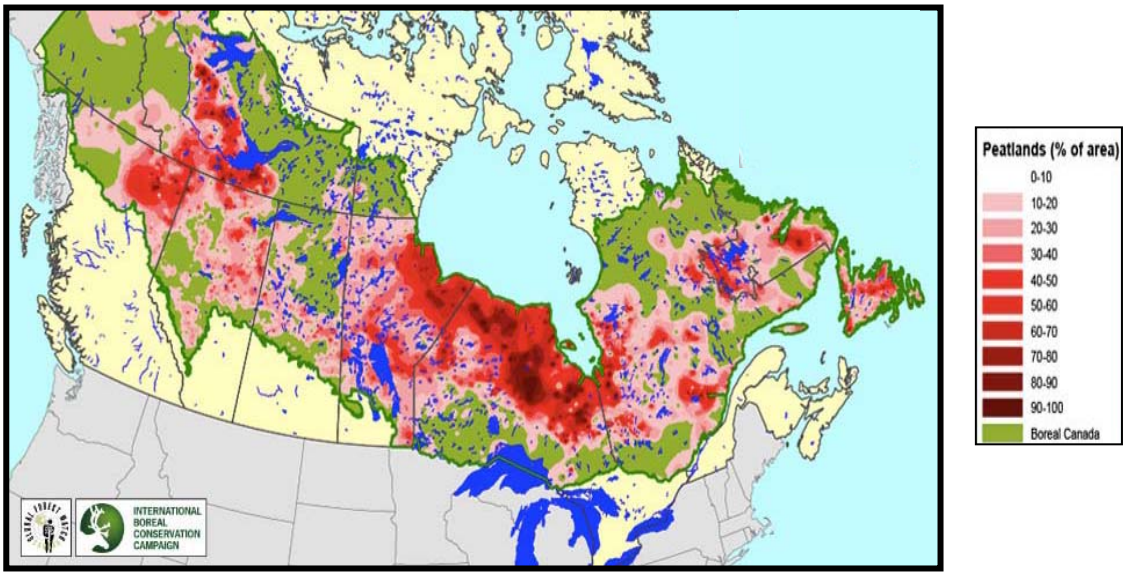
7.1 Crude Oil Spills in Muskeg Peat Soils

The term “muskeg” refers to a type of wetland with highly organic peat soils created from partially decomposed plant remains that have accumulated in deep layers over time. Canada has the largest muskeg areas in the world, encompassing 12% of the nation’s land area (Natural Resources Canada, 2002). Canadian muskegs extend from the west coast to the east coast and into the Northwest Territories (see Figure 2 map).

The 36,033 km Canadian crude oil pipeline network extends through large muskeg areas (see Figure 3 map). The majority of the pipeline (50% or 18,125 km) extends through Alberta (CAPP, 2009), with muskegs covering 20% of the total land area (Alberta Environment, 2003) (see Figure 4 map). Over time, internal pipeline corrosion can create pipeline failures, causing crude oil to spill into surrounding peat soils. Pipeline corrosion accounts for 43% of the 6,600 m^3 of PHCs that are spilled into the Alberta environment each year (Alberta Energy and Utilities Board 2006). In spill situations, the delineation of contaminated vs uncontaminated boundary lines is critical to the site remediation process. This however can be very difficult when the contaminated areas are surrounded by highly organic peat soils.

For the purposes of this study, uncontaminated peat was extracted and analyzed by CWS F2-F4 PHC standards (see Methods Section 12.2 of this report). Figure 5a illustrates two Gas Chromatography Flame Ionization Detector (GCFID) chromatograms of an uncontaminated peat sample and a fresh federated crude oil sample. These chromatograms illustrate that the biogenic and petrogenic sources extended to varying degrees from the F2 to F4 carbon ranges. The uncontaminated peat sample had an F2 concentration of 78 mg/kg and F4 concentration of 2,890 mg/kg F4, which did not exceed the 150 mg/kg and 5,600 mg/kg fine soil criteria (respectively). However, the 2,567 mg/kg F3 concentration did exceed the 1,300 mg/kg fine soil criteria. Cases such as this would prevent background, marginally contaminated and/or bioremediated soils from meeting the F3 criteria.

Figure 2: Canadian muskeg (peatland) areas

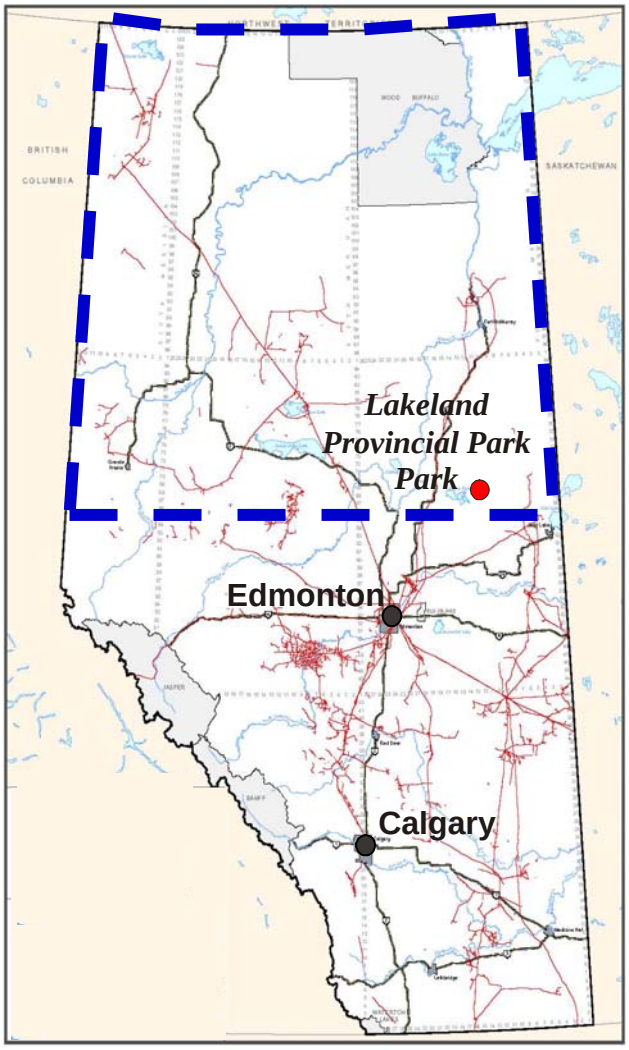


Map Source: Natural Resources Canada, 2002

Figure 3: Crude oil pipelines managed by the National Energy Board of Canada

Map Source: National Energy Board of Canada, 2008.

Figure 4: - Alberta Crude Oil Pipelines located within Muskeg Areas
- Lakeland Provincial Park (Fen Peat Sampling Location)



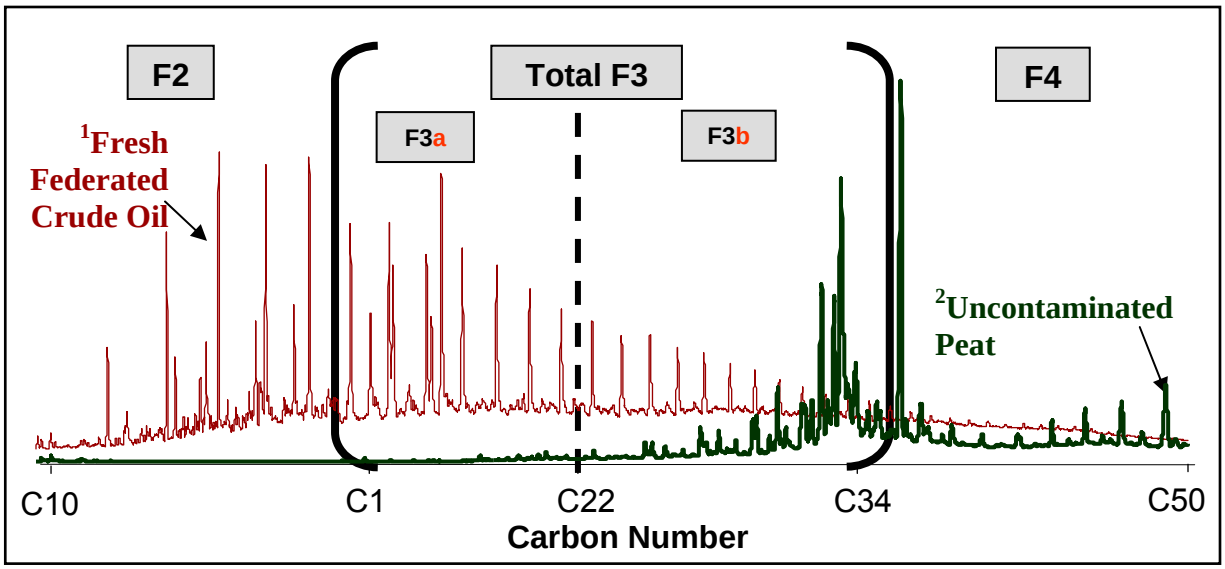
Sources:
- Oil pipeline map: Alberta Energy and Utilities Board, 2004.
- Muskeg boundary zone: Alberta Environment, 2003

Approximate area of largest muskeg coverage within Alberta

Crude oil pipeline

Figure 5: Example GCFID Chromatogram Carbon Range Distribution Patterns in Petrogenic vs. Uncontaminated Biogenic Sources

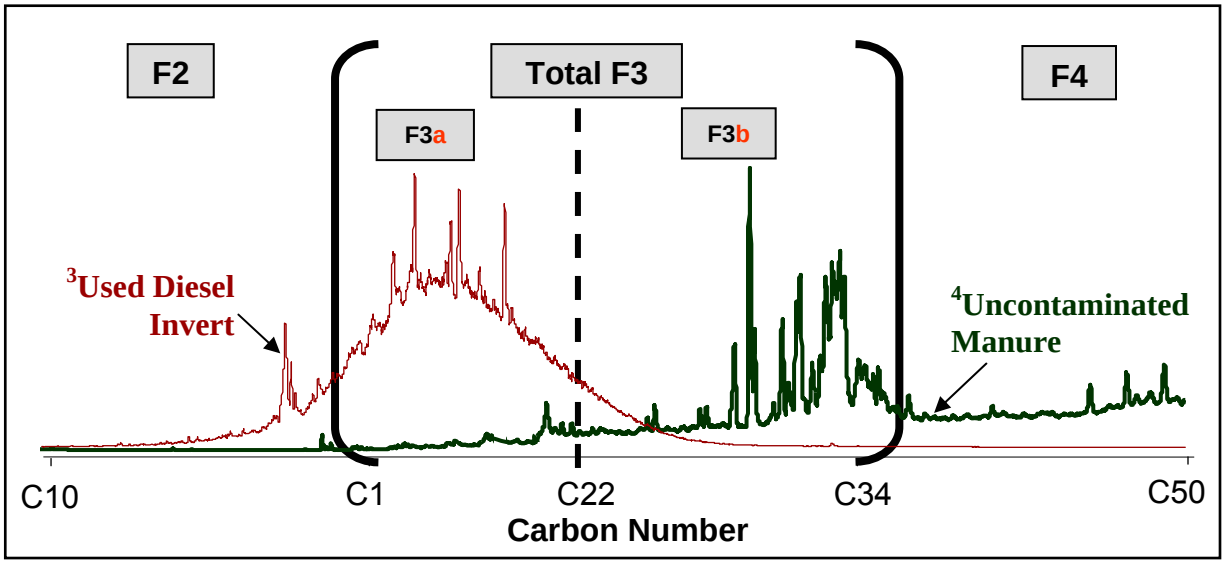
Figure 5a: Overlayed chromatograms of fresh federated crude oil and uncontaminated peat



[1]Crude Oil concentrations: 432 mg/kg F2; 1,204 mg/kg F3; 284 mg/kg F4

[2]Uncontaminated peat concentrations: 78 mg/kg F2; 2,567 mg/kg F3; 2,890 mg/kg F4

Figure 5b: Overlayed chromatograms of used diesel invert and uncontaminated manure



[3]Used diesel invert concentrations: 852 mg/kg F2; 3,160 mg/kg F3; 340 mg/kg F4

[4]Uncontaminated manure concentrations: 38mg/kg F2; 816 mg/kg F3; 590 mg/kg F4

7.2 Manure Biopile Remediation of Diesel Invert Contaminated Drilling Waste

Drilling waste management is an important component of petroleum and gas industry exploration and production activities. Approximately 482,939 oil and gas wells were drilled in Canada during the time period of 1981 to 2008. 73% (350,846) of these wells are located within the province of Alberta (CAPP, 2009).

The most common drilling process is based on the movement of a rotating drill bit through rock. A fluid called "drilling mud" is pumped into the drill hole to lubricate the bit, stabilize drill hole walls and circulate rock cuttings back to the surface. Drilling muds may contain various combinations of water, diesel invert or synthetic fluids mixed with colloidal matter such as organophilic clay, bentonite, barite and other additives (J.A. McDonald, 2003). In recent years, environmentally innocuous synthetic muds have been used whenever possible. However, diesel invert mud is still used under difficult drilling conditions.

During the drilling process, used mud is recovered from the drill hole and poured into a mechanical shaker which strains the fluid from the rock cuttings. The drilling mud is reused again and the rock cutting waste material may be either bioremediated and/or sent to a registered landfill facility.

The term "biopile" refers to a bioremediation composting technology that mixes diesel invert contaminated cuttings with materials such as manure, straw, nutrients, minerals and water. The mixture is heaped into piles with forced aeration to stimulate microbial activity. Over time, naturally occurring microbes convert diesel PHCs into carbon dioxide and water (Rojas-Avelizapa, et. al., 2007). Although PHC concentrations can be effectively reduced by this method, background BOCs in the manure can elevate F3 concentrations to levels that create false soil criteria exceedence issues, ultimately resulting in unnecessary landfill disposal requirements.

For the purposes of this study, uncontaminated manure was extracted by CWS PHC F2-F4 methods (see Methods Section 12.2 of this report). Figure 5b illustrates two GCFID chromatograms of a used diesel invert sample and an uncontaminated composted manure sample. The chromatograms illustrate that both biogenic and petrogenic sources were present to varying degrees within the F2, F3 and F4 carbon ranges. The 38 mg/kg F2 concentration and the 340 mg/kg F4 concentration in the uncontaminated composted manure sample did not exceed the 150 mg/kg and 5,600 mg/kg fine soil criteria (respectively). Although the 816 mg/kg F3 concentration did not exceed the 1,300 mg/kg criteria, it would falsely elevate perceived petroleum concentrations in biopiles that may have otherwise met the true PHC bioremediation requirements.

8 CRUDE OIL EXPERIMENT SAMPLE SOURCES AND COLLECTION METHODS

8.1 Reference Peat, Sand and Crude Oil Sources

The crude oil contamination experiments utilized peat that originated from a fen muskeg and a bog muskeg. "Fens" are defined as peat-accumulating wetlands that are predominantly groundwater fed with obvious inflow and outflow hydrology. The waters are nutrient rich with pH ranges from 4.5 to greater than 7. Vegetation may include mosses, sedges, grasses, reeds, shrubs and trees with moderately acidic to neutral pH requirements. "Bogs" are defined as peat-accumulating wetlands that are predominantly rain fed with no significant inflows or

outflows. The waters are nutrient poor and very acidic with pH values of less than 4.5. Vegetation may include acidic pH tolerant combinations of mosses, shrubs and trees (Mitsch, W.J. et. al., 1993).

The following describes the soil and petroleum sources that were used in these experiments.

i) Fen peat and overlying vegetation collected from Lakeland Provincial Park in Alberta

The University of Waterloo collaborated with the Alberta Parks and Protected Parklands Division for the purpose of selecting a muskeg site and facilitating sample collections. Aerial photo analysis, helicopter and ground surveys were used to identify a fen located within the Lakeland Provincial Park as the most suitable site (see Appendix B map and photographs). The park is located approximately 250 km northeast of the City of Edmonton (see Figure 4 map). The sampling site was located 11 km from the nearest access road and at least 20 km from the nearest oil or gas pipeline. The sampling location did not have a known history of contamination problems.

75 L of uncontaminated peat and overlying vegetation were collected and couriered overnight to ALS Laboratories in Waterloo, Ontario. The peat and vegetation samples were transplanted into 70 L aerated aquarium tanks fitted with full spectrum lighting to enhance plant growth.

ii) *Commercial* Bog Peat

Premier Sphagnum Peat Moss is a commercial brand of Canadian bog peat that was used in this study. Commercial bog peat is one component of the artificial soil mixture that was used to develop the CWS PHC Tier-1 soil criteria (Environment Canada, 2004, 2005, 2007).

iii) Silica Sand

Chemically inert silica sand was purchased from the *U.S. Silica Company* for use in this study.

iv) Crude Oil Source Used for Soil Spiking Treatments

Whole federated crude oil was provided by the Environment Canada Emergencies Science and Technology Oil Research Laboratory for use in this study. Federated crude oil is a typical light, sweet crude oil from Alberta. Its density and viscosity at 15 ^{0}C are 0.8298 g/mL and 5 mPa.s, respectively with a pour point and flash point of -22 ^{0}C and -26 ^{0}C respectively. This particular crude oil was also used to generate CWS PHC Tier-1 soil criteria (CCME, 2001).

8.2 Crude Oil Experiment Design

The crude oil contamination experiment was designed to simulate the full spectrum lighting and saturated soil conditions of a natural muskeg environment. Sub-soil aeration stones were used to prevent the peat and sand treatments from becoming anoxic. Twenty-one rectangular 70 L glass aquarium tanks were pre-washed with mild detergent, rinsed with deionized water and rinsed again with a 50:50 acetone:hexane solvent. Two aeration stones measuring 10 cm in length were placed on opposite ends of each tank in addition to one 20 cm stone that was placed at the centre. The sand and peat treatments were placed on top of the stones at approximate depths of 20 cm. Deionized water was then added to each tank until the water levels were approximately 1 cm above the soil surface. Deionized water was routinely added to

each tank during the entire study period in order to maintain the same 1 cm water level. Each tank was fitted with full spectrum lighting hoods that remained on for 24 hours each day. All of the microcosm experiments were maintained at room temperature in an indoor laboratory facility (See Appendix C photographs).

8.3 Experiment Treatments

The experiment treatment concentrations were selected to study false exceedences of the CWS PHC F3 soil criteria. Moderate F3 concentrations of 1,500 mg/kg were expected to bioremediate below the 1,300 mg/kg fine soil criteria within the first 150 days. In contrast, higher F3 concentrations of 10,000 mg/kg were expected to remain above the criteria by the end of the 300 day study period (Baas et al. 2000; Perusetti et al., 2005; Pollard et al., 1999; Wang et al., 2006; (Yunker et al., 1995).

Six triplicate soil contamination treatments plus one triplicate blank were included in this study (See Appendix C photographs). The following treatment concentrations are reported as dry weights.

- Treatment #P1: *Commercial bog peat spiked with whole federated crude oil concentrations of: TPH = 19,608 mg/kg, F3 = 10,000 mg/kg.*

  The 10,000 mg/kg F3 PHC contamination treatment was selected as a concentration that far exceeded the 1,300 mg/kg CWS fine soil criteria. This concentration was expected to remain above the criteria for the entire study period

- Treatment #P2: *Lakeland fen peat spiked with whole federated crude oil concentrations of: TPH = 2,942 mg/kg, F3 = 1,500 mg/kg*

  The 1,500 mg/kg F3 PHC contamination treatment was selected as a concentration that slightly exceeded the 1,300 mg/kg CWS fine soil criteria. It was expected that this concentration would bioremediate below the criteria by the end of the study period.

- Treatment #P3: *Uncontaminated commercial bog peat*

  Day 0 analysis of the uncontaminated bog peat determined that the mean biogenic F3 concentration of 2,273 mg/kg did exceed the CWS PHC F3 criteria. It was however unknown if the biogenic F3 concentrations would remain high enough to create false exceedence issues by the end of the study period.

- Treatment #P4: *Uncontaminated Lakeland fen peat*

  Day 0 analysis of the uncontaminated fen peat determined that the mean biogenic F3 concentration of 1,480 mg/kg did exceed the F3 criteria. It was also unknown if the biogenic F3 concentrations would remain high enough to create false exceedence issues by the end of the study period.

- Treatment #S5: *Sand spiked with bacteria broth, inorganic nutrients and whole federated crude oil concentrations of: TPH = 2,942 mg/kg, F3 = 1,500 mg/kg*

  The #S5 sand treatment was designed to monitor PHC bioremediation patterns in the virtual absence of biogenic compounds. The sand was amended to match the contaminated fen (#P2) nutrient and bacteria components as closely as possible. As a course grain soil however, the 1,500 mg/kg F3 PHC concentration was five times higher than the 300 mg/kg

F3 PHC course soil criteria. The absence of peat BOCs was expected to increase bacteria bioremediation efficiencies, ultimately reducing the PHCs to below the contaminated peat concentrations by the end of the study period.

The sand was amended with the following inorganic nutrients to match the concentrations that were detected in the fen peat: calcium, potassium, iron, magnesium, nitrate and phosphorus. In addition, total heterotrophic plate counts (HPC) determined bacteria concentrations in the peat to be 10^9 cfu/gas as compared to non-detectable concentrations in the sand. The three dominant peat bacteria species were cultured into an inorganic broth and added to the sand tanks at concentrations of 10^9 cfu/g HPC.

- Treatment #S6: *Uncontaminated Sand Spiked with Bacteria Broth and Inorganic Nutrients*

  Treatment #S6 was identical to Treatment #S5 with the exception that crude oil was not added. The purpose of Treatment #S6 was to monitor possible BOC additions from bacteria populations over time.

- Treatment #S7: *Untreated Sand Blank*

  The purpose of control Treatment #S7 was to monitor the presence or absence of biogenic F3 concentrations in an untreated inorganic soil.

8.4 Crude Oil Spiking Procedure

The oil spiking equipment included laboratory grade glass syringes, aluminum bowls, trays, spoons and electric mixers. All equipment was pre-washed with a mild detergent and thoroughly rinsed with deionized water. Glass syringes were also pre-rinsed with 50:50 acetone:hexane. The oil spiking procedure was very time consuming, with several small batches prepared over a period of several weeks. It was therefore necessary to freeze each batch as it was produced so that the entire volume could be thawed and placed into the experiment tanks on the same day. All of the contaminated and uncontaminated peat and sand treatments were frozen and subsequently thawed on the same day at room temperature for sample continuity purposes.

Glass syringes were used to spike treatments #P1, #P2 and #S5 with pre-determined crude oil volumes. The first step in the spiking process was to calculate the volumes of whole crude oil that were needed to achieve final F3 dry weight concentrations of 1,500 mg/kg in the #P2 and #S5 treatments and 10,000 mg/kg in the #P1 treatment. A 60 cm X 40 cm aluminum tray was first placed onto a laboratory scale and zeroed. Uncontaminated peat or sand was placed onto the tray until a pre-determined weight was reached. The soil was manually smoothed into a uniform 2 cm deep layer and a 2 cm X 2 cm grid pattern was pressed lightly into the soil. A glass syringe was used to drop pre-set quantities of crude oil onto the grid-patterned soil. The contaminated soil was then scooped into an aluminum bowl and thoroughly homogenized with an electric mixer. The spiked soil was then transferred to pre-labeled food grade plastic bags and immediately placed into a freezer at a temperature of minus twenty degrees celcius.

8.5 Experiment Sample Collection Procedures

Seven sampling spoons, bowls and electric mixers were dedicated to each of the seven treatments in order to reduce cross contamination risks. All of the Day 0, 150 and 300 samples were immediately frozen until they were subsequently extracted and analyzed as one large group.

i) Commercial Bog Peat Treatments #P1, #P3 and Sand Treatments #S5, #S6 and #S7

Aluminum spoons were used to transfer approximately 400 mls of peat or sand from the centre of each tank to aluminum mixing bowls, which was then thoroughly homogenized with an electric mixer. The contents of each bowl were then divided into four 100 ml wide-mouth amber replicate jars and immediately stored at minus twenty degrees celcius for future analysis. The peat and sand that remained in each tank was then homogenized with electric mixers.

ii) Vegetated Lakeland Fen Peat Treatments #P2 and #P4

Prior to sampling, the vegetation layer from each tank was carefully removed and layed onto temporary aluminum holding trays. The exposed peat was then sampled from the centre of each tank in the same manner as described for the unvegetated peat and sand treatments. The remaining peat in the glass tanks was then homogenized with electric mixers before the vegetation was placed back onto the peat surface.

9 DIESEL INVERT MANURE BIOPILE EXPERIMENTS

The laboratory scale diesel invert manure biopile experiment descriptions will be included in a subsequent report once the 300 day study period has been completed in February 2010.

10 BACKGROUND PHC SOIL FIELD SURVEY

As part of the North America Soil Geochemical Landscapes Project (NASGLP), the Geological Survey of Canada has undertaken to define natural geochemical background variations for Canada as a reference framework for environmental and human health protection. In 2008, the University of Waterloo entered into a collaborative arrangement with the Geologic Survey of Canada and Natural Resources Canada. Financial and field sampling support was provided to the University of Waterloo for the purpose of expanding the existing Geological Survey of Canada's chemistry analysis list to include the standard CWS PHC analysis in addition to PHC vs BOC research evaluations.

10.1 Sampling Locations

The Geologic Survey of Canada field crew collected 34 soil and vegetation samples from 34 sites during the months of September and October 2008. The samples were collected from the following three provinces:

i) Alberta – 15 sites;

ii) British Columbia – 10 sites; and

iii) Newfoundland – 9 sites.

10.2 Field Sampling, Processing and Storage

Vegetation cover and underlying topsoil samples were collected with an aluminum spade and placed in labelled food grade plastic sample bags. The samples were stored in chilled coolers and shipped by overnight courier to ALS Laboratories in Waterloo, Ontario. The samples were then unpacked and photographed by individual site numbers (see Appendix D photographs). Representative plant samples were pressed between sheets of paper, left to dry for one week and transferred to plant collection binders for future research studies. The soil samples were placed into 250 ml wide-mouth amber glass jars and immediately frozen at minus twenty degrees celcius for future analysis.

11 CRUDE OIL SURVEY

Petroleum industry partners provided the following 13 fresh crude oil samples representing light to heavy oils which are produced and/or refined in Canada:

- Cook Inlet
- Troll
- Arabian Heavy
- Federated
- IFO-180
- Imperial Heavy
- Pembina
- Mava
- Rainbow
- Syncrude
- Peace Sour
- Peace Sweet
- South Lousiana

12 CHEMISTRY ANALYSIS METHODS

12.1 General List of Analytes

i) PHC Fractions F2, F3 and F4;

ii) Fractions F3a (C16-22) and F3b (C22-C34) percentage distributions;

iii) 16 priority polyaromatic hydrocarbons (PAHs); and

iv) Petroleum biomarkers (e.g. hopanes, steranes, terpanes, etc.)

12.2 F2, F3, F3a, F3b, F4 PHC Analysis Methods

ALS Laboratories conducted the F2-F4 extraction and analysis of the Day 0, 150 and 300 samples. The ALS methods adhered to the *Canada-Wide Standard (CWS) for Petroleum Hydrocarbons in Soil – Tier 1 Method* (CCME 2001). Ten grams of each soil sample were mixed with celite for de-watering purposes. O-terphenyl surrogate was added to each sample before they were soxtech extracted in a 50:50 acetone:hexane solvent. The extracts were

solvent exchanged to 50:50 hexane:dichloromethane and treated insitu with 6 g activated silica gel to remove BOCs and other polar compounds. The treated extracts were then concentrated to 10 mls. Octacosane is the current surrogate standard that ALS routinely uses to measure extraction efficiency. However, o-terphenyl was chosen over octacosane for this study, as octacosane is an n-alkane of interest in the study. 5-α-androstane was also added post extraction/clean up, as an internal standard that could be used for future comparison purposes, but was not used to quantify the F2-F4 concentrations in this study. The concentrated extracts were analyzed by GCFID chromatography and integrated for the F2, F3, F3a, F3b and F4 concentrations. Soil criteria exceedences were evaluated by comparing the dry weight concentrations to the CWS PHC Tier 1 levels for Agricultural/Residential/Parkland land uses in potable groundwater conditions.

12.3 PHC Sub-fractions F3a (C16-C22) and F3b (C22-C34) Analysis – Calculation for Estimating Maximum Possible F3 Concentrations from Crude Oil or Diesel Invert in Uncontaminated Peat and Composted Manure

University of Waterloo PhD Candidate, Francine Kelly-Hooper, re-integrated the ALS F2, F3 and F4 GCFID chromatograms to determine PHC sub-fraction F3a and F3b concentrations and distribution patterns.

12.3.1 Baseline Biogenic vs Petrogenic F3a:F3b Distribution Survey

Although F3a and F3b subfractions are not included in the CWS PHC Tier-1 Standard, this research study has identified biogenic and petrogenic signature patterns that can be used to resolve false F3 criteria exceedence issues. Baseline F3a:F3b distribution data were generated for 36 uncontaminated soil samples, 1 uncontaminated manure sample, 13 crude oils and 1 diesel invert sample. The 13 fresh crude oils included federated, which was used in the crude oil contaminated peat and sand experiments. The single diesel invert sample was obtained from the same product that was used in the biopile contamination experiments.

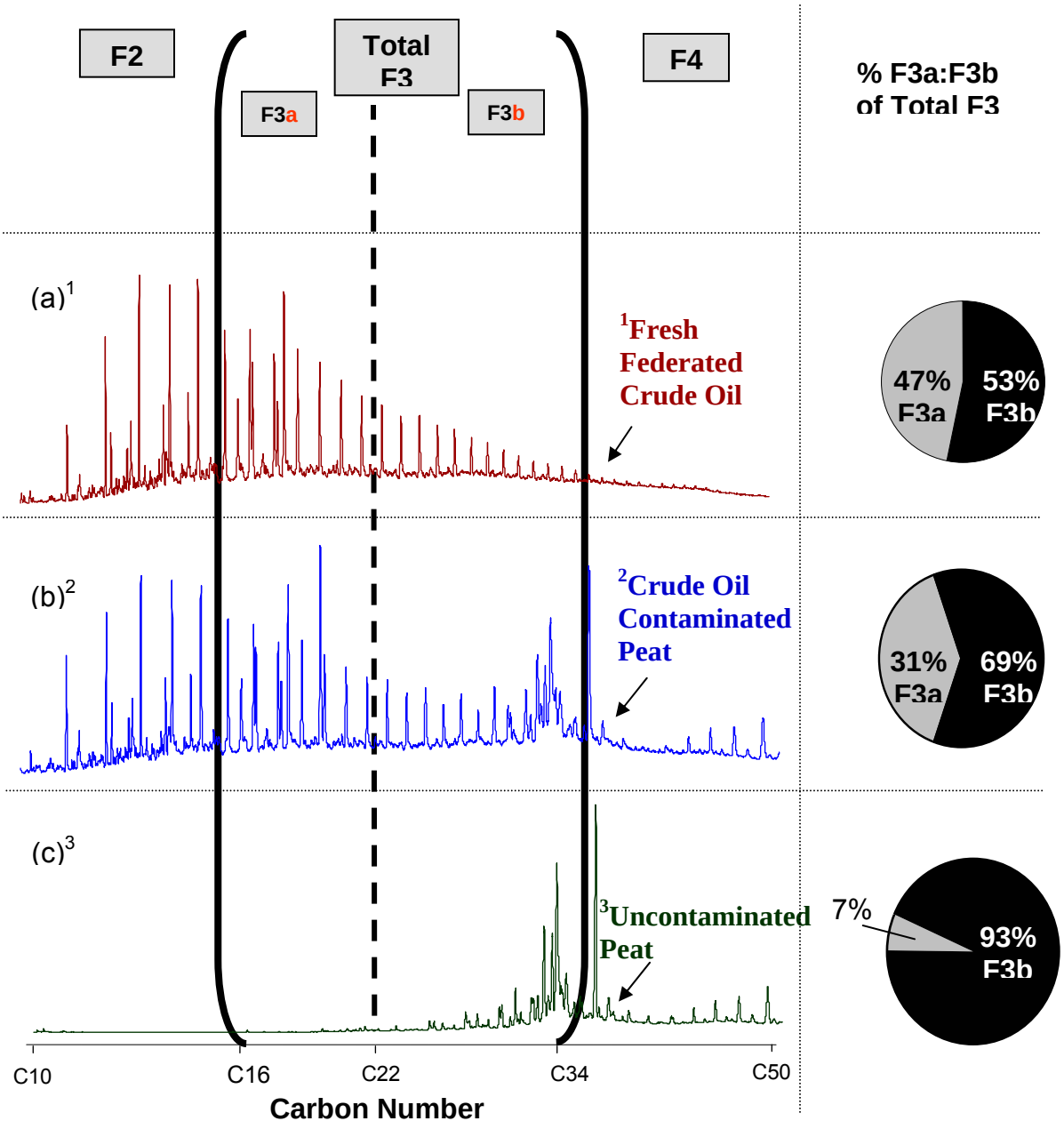
The baseline data determined that the uncontaminated soils and composted manure were stongly dominated by the F3b range. The median F3a:F3b background soil distributions were 7%:93% and the manure distributions were 16%:84%. In contrast, the fresh crude oils had virtually equal distributions with median F3a:F3b values of 49%:51%. The diesel invert sample was strongly dominated by F3a with F3a:F3b distributions of 89%:11%. (See Figures 6 and 7)

12.3.2 Rationale and Formula for Calculating Petrogenic F3 in Contaminated Soils and Manure Biopiles

The maximum possible F3 petroleum concentration calculation is based on the premise that measured F3a concentrations can be used to estimate F3b concentrations if the petroleum source F3a:F3b percentage distributions are known.

Baseline PHC and BOC chemistry data was generated to demonstrate the effectiveness of this approach. The PHC and BOC sources included peat, manure, crude oil and diesel drilling invert. The chemistry data indicated that the F3a range was dominated by petrogenic sources, with relatively little contributions from biogenic sources. Figures 6a and 6c illustrate that the F3a:F3b distributions were 47%:53% in the fresh federated crude oil and 7%:93% in the uncontaminated peat. The Figure 6b contaminated peat GCFID

Figure 6: Example GCFID chromatogram comparisons of F2-F4 and F3a:F3b distributions in fresh federated crude oil, contaminated peat and uncontaminated peat.

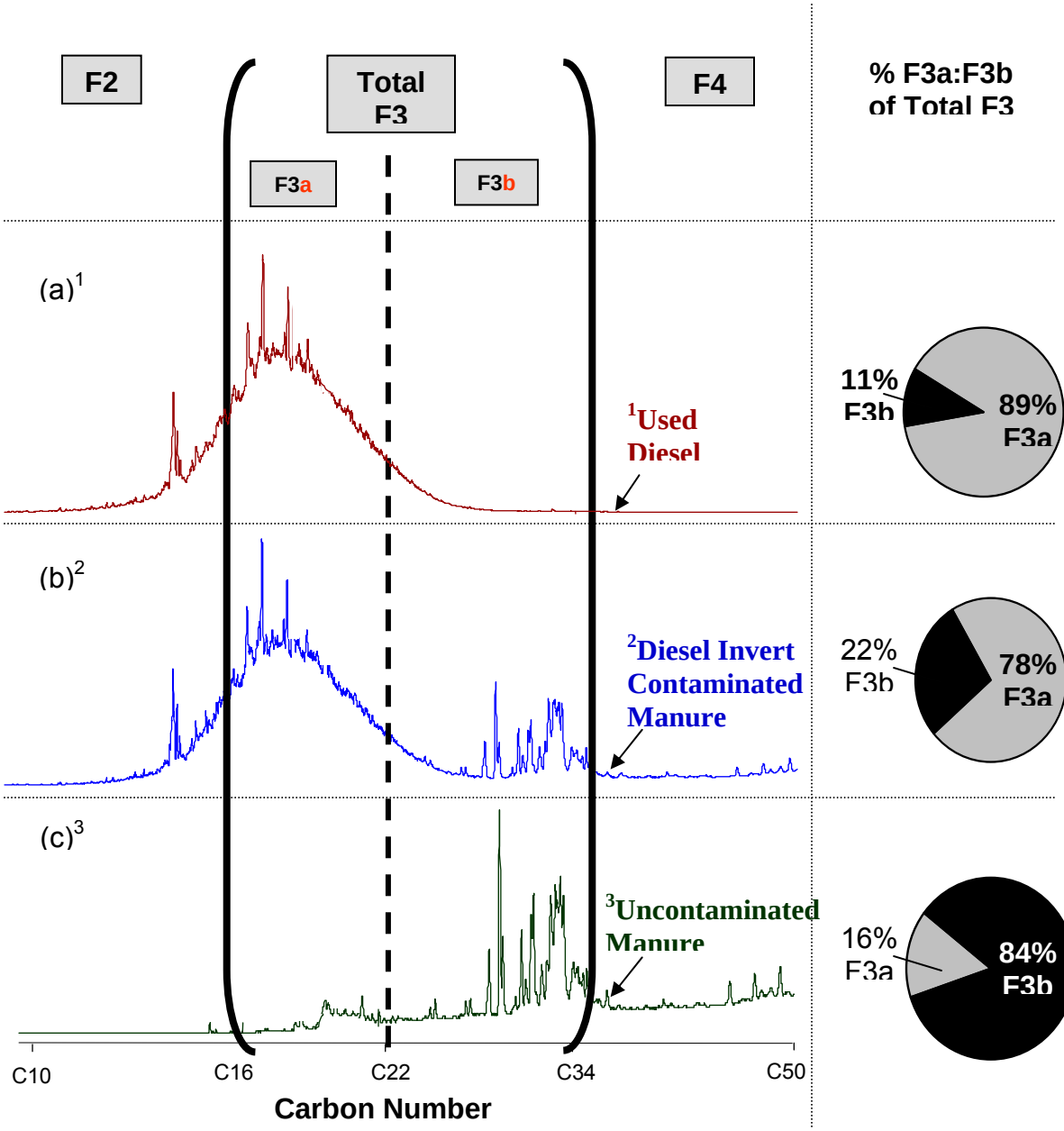


[1]Crude Oil concentrations: F2 432 mg/kg; F3 1,204 mg/kg; F3a 566 mg/kg; F3b 638 mg/kg; F4 284 mg/kg

[2]Contaminated peat concentrations: F2 3,494 mg/kg; F3 10,035 mg/kg; F3a 3,713; F3b 6,322; F4 5,400 mg/kg

[3]Uncontaminated peat concentrations: F2 78 mg/kg; F3 2,567 mg/kg; F3a 128 mg/kg; F3b 2,439 mg/kg; F4 2,890 mg/kg

Figure 7: GCFID chromatogram comparisons of F2-F4 and %F3a:F3b distributions in used diesel invert, contaminated manure and uncontaminated manure



[1]Used diesel invert concentrations: F2 852 mg/kg; F3 3,160 mg/kg; F3a 2,749 mg/kg; F3b 411 mg/kg; F4 340 mg/kg

[2]Contaminated manure concentrations: F2 610 mg/kg; F3 2,850 mg/kg; F3a 2,081 mg/kg; F3b 770 mg/kg; F4 300 mg/kg

[3]Uncontaminated manure concentrations: F2 38 mg/kg; F3 816 mg/kg; F3a 122 mg/kg; F3b 694 mg/kg; F4 590 mg/kg

chromatogram clearly shows both the petrogenic and biogenic carbon signature patterns with intermediate F3a:F3b distributions of 31%:69%.

Figures 7a and 7c illustrate that the F3a:F3b distributions were 89%:11% in the diesel invert and 16%:84% in the uncontaminated manure. The Figure 7b contaminated manure GCFID chromatogram also shows both the petrogenic and biogenic carbon signature patterns. However, F3a was dominant with F3a:F3b distributions of 78%:22%.

Formula #1: Calculation of Maximum Possible F3 Concentrations from Crude Oil or Diesel Invert

[(a x b/c] + a

a = Measured F3a concentration in peat or manure sample

b = Measured and/or documented %F3b of total F3 in crude oil or diesel invert source

c = Measured and/or documented %F3a of total F3 in crude oil or diesel invert source

Example Calculation #1: ***Fresh Crude Oil Contaminated Peat (Measured Total F3 = 10,035 mg/kg)*** *(see Figures 6 and 8 graphs)*

[3,713 x 0.53/0.47)] + 3,713 = 7,900 mg/kg

a = Measured soil sample F3a concentration 3,713 mg/kg

b = Measured federated crude oil petroleum source F3b 53%

c = Measured federated crude oil petroleum source F3a 47%

Calculated maximum possible Total F3 concentration from federated crude oil = 7,900 mg/kg

Example Calculation #2: ***Uncontaminated Peat (Measured Total F3 = 2,567 mg/kg)*** *(see Figure 6 and 8 graph)*

[128 x 0.53/0.47)] + 128 = 272 mg/kg

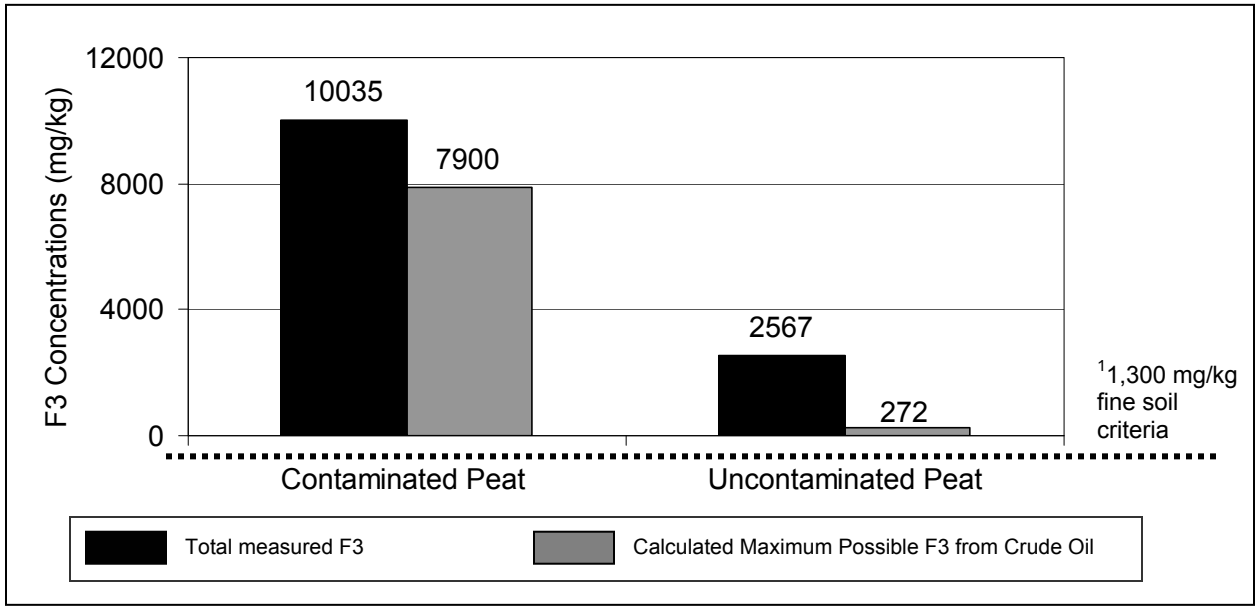
a = Measured soil sample F3a concentration 128 mg/kg

b = Measured crude oil petroleum source F3b 53%

c = Measured crude oil petroleum source F3a 47%

Calculated maximum possible Total F3 concentration from crude oil = 272 mg/kg

Figure 8: Example of Calculated Maximum Possible Fresh Crude Oil F3 Concentrations in Contaminated and Uncontaminated Peat



[1]CCME Canada Wide Standard for PHC in Soil, Tier 1 fine surface soil criteria for agricultural/residential/parkland land uses in potable groundwater conditions (CCME 2008a)

Example Calculation #3: ***Diesel Invert Contaminated Manure (Measured Total F3 = 2,850 mg/kg)*** *(see Figures 7 and 9 graphs)*

[2,081 x 0.11/0.89)] + 2,081 = 2,338 mg/kg

a = Measured soil sample F3a concentration 2,081 mg/kg

b = Measured diesel invert petroleum source F3b 11%

c = Measured diesel invert petroleum source F3a 89%

Calculated maximum possible Total F3 concentration from diesel invert = 2,338 mg/kg

Example Calculation #4: ***Uncontaminated Manure (Measured Total F3 = 816 mg/kg)*** *(see Figures 7 and 9 graphs)*

[122 x 0.53/0.47)] + 122 = 260 mg/kg

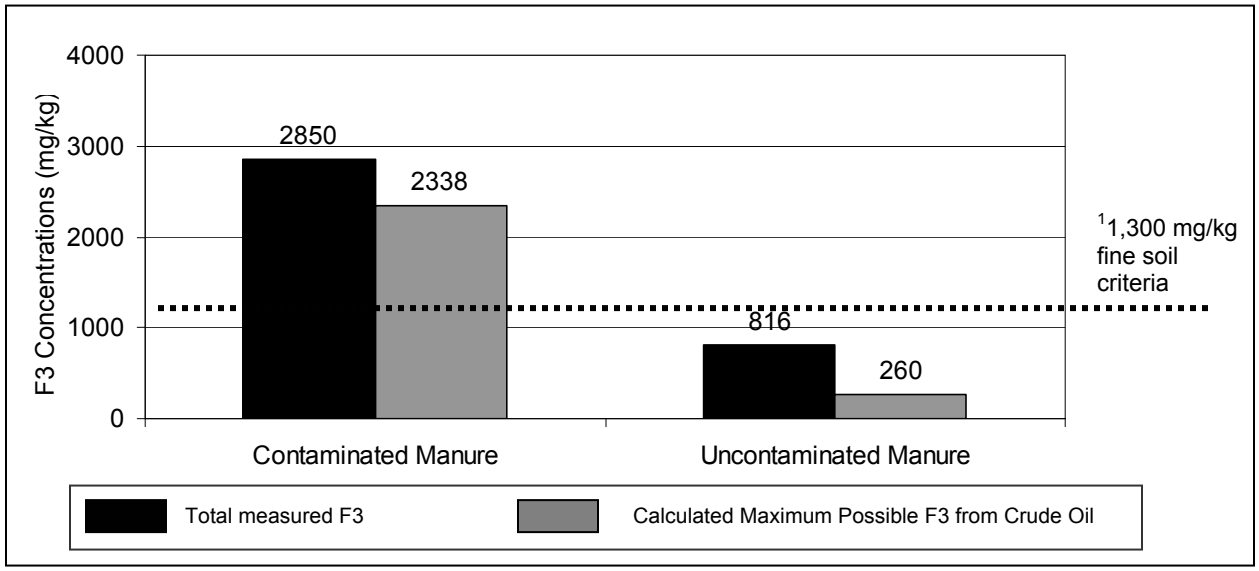
a = Measured soil sample F3a concentration 122 mg/kg

b = Measured diesel invert petroleum source F3b 11%

c = Measured diesel invert petroleum source F3a 89%

Calculated maximum possible Total F3 concentration from crude oil = 260 mg/kg

Figure 9: Example of Calculated Maximum Possible Diesel Invert F3 Concentrations in Contaminated and Uncontaminated Manure Compost



[1]CCME Canada Wide Standard for PHC in Soil, Tier 1 fine surface soil criteria for agricultural/residential/parkland land uses in potable groundwater conditions (CCME 2008a)

12.3.3 Petroleum Weathering and Biodegradation Considerations

Fresh crude and diesel oils are subject to natural weathering (e.g. evaporation, photo oxidation) and microbial degradation processes. Within periods of days, weeks and months, these processes can significantly reduce PHC concentrations while also transforming chemical signatures (Pollard, R. et al., 1999; Wang, Z. et al. 2006). In fresh spills, evaporation of F1 and F2 fractions is the single most important weathering process. Microbial degradation is another process that represents one of the primary mechanisms by which aged PHCs are naturally eliminated from the environment. Fresh versus aged petroleum spills can therefore produce very different chemical signatures.

To our knowledge, no studies have been conducted specifically on F3a:F3b distributions in fresh or aged PHCs. The 300 day crude oil and diesel invert experiments were designed to document these changes over time. The median F3a:F3b distributions in the crude oil contaminated sand treatments shifted from 47%:53% on day 0 to 38%:62% on day 150, to 31%:69% on day 300. The different day 0, 150 and 300 distributions in the contaminated sand were used to calculate the estimated crude oil F3 concentrations in the contaminated treatments. This same approach will be used upon completion of the Day 300 diesel invert experiments as well.

12.4 Polyaromatic Hydrocarbons (PAH)

Polyaromatic hydrocarbon (PAH) is a common term for high molecular weight, aromatic hydrocarbons, which range from two rings (e.g. naphthalene) to six rings (e.g. benzo(g,h,i) perylene). PAHs are utilized as sensitive indicators of petroleum contamination from the following two sources:

i) Petrogenic (Petroleum sources) – Primarily generated from the geochemical alteration of organic matter into liquid petroleum products and is therefore an indicator of petroleum spills (Yunker 1995).

ii) Pyrogenic (Petroleum and Biogenic Sources) – PAH from petroleum sources are created by the incomplete combustion of fossil fuel products, which are released into the atmosphere and eventually settle into terrestrial and/or aquatic environments. Pyrogenic PAHs can also be created by the combustion of biogenic materials such as wood. Relatively small concentrations of certain PAHs are also known to be produced by microbial activities as well (Yunker 1995).

PAHs can have either parent or alkylated chemical structures. Parent PAHs consist of benzene rings fused together and are generally associated with atmospheric deposition from pyrogenic sources. Standard analytical techniques include 16 parent PAHs as listed in Section 12.4.1 of this report.

Conversely, alkylated PAHs have various levels of alkyl substitutions added to the fused ring structure and they are typically found in oils and petroleum products. The analysis of alkylated PAHs is considered to be a specialized field that is not currently considered a routine analysis.

12.4.1 ALS Laboratory PAH Analysis Method

ALS Laboratories analyzed all 34 background PHC soil samples for the following 16 parent PAHs: acenapthene, acenapthylene, anthracene, benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(g,h,I)perylene, benzo(k)fluoranthene, chrysene, dibenzo(ah)anthracene, fluoranthene, fluorene, indeno(1,2,3-cd)pyrene, naphthalene, phenanthrene and pyrene. The ALS list of analytes also included the following two alkylated PAHs as well: 1-methylnaphthalene and 2-methylnaphthalene.

10 g soil samples were mixed with sodium sulphate, and deuterated surrogate standards were added. A solvent mixture was added to the sample, and the soil:solvent mixture was agitated on a paint shaker to thoroughly break up the soil and provide adequate solvent exposure. After a solvent exchange to toluene, an aliquot was removed and internal standard was added. The extract was analyzed by Gas chromatography-mass spectrometry (GC/MS) in selected ion monitoring mode (SIM).

12.4.2 Environment Canada Emergencies Science and Technology Oil Research Lab PAH Analysis Methods

The Oil Research Laboratory, Emergencies Science and Technology of Environment Canada is currently conducting parent and alkylated PAH analysis on the Day 0 and 300 crude oil contaminated treatments P1, P2, P3, P4 and S5. The same analysis will be conducted for the Day 0 and 300 diesel invert contaminated biopile experiment samples as well. Parent and

alkylated PAH analysis will also be conducted on at least 8 of the 34 background PHC soil samples.

A primary objective of this analysis is to determine, through PAH analysis, if petroleum was absent in the uncontaminated peat treatments P3 and P4, and present in the crude oil spiked treatments P1, P2 and S5. The methods used for this analysis are described in Wang, et. al., 2007. A detailed forensics report will be prepared once the ongoing analysis has been completed.

12.5 Petroleum Biomarker Forensics Analysis Methods

Petroleum biomarkers are complex molecules that have been formed during millions of years of sedimentary burial and geochemical alteration of biogenic materials such as plants, animals and bacteria. Biomarkers are one of the most important hydrocarbon groups used for chemical fingerprinting of petroleum products. Several classes of typical biomarkers include: pristane, phytane, steranes, diasteranes and hopanes. Although biomarker concentrations represent a very small portion of total PHC concentrations (1%), they are very useful for tracing specific petroleum sources (Wang, Z. et. al., 2007; Yunker, M.B. et. al. 1995).

Biomarkers can be detected in low quantities (ppm and sub-ppm level) in the presence of a wide variety of petroleum types by the use of GC-MS. Relative to other hydrocarbon groups such as alkanes and most aromatic compounds, biomarkers are highly resistant to weathering and biodegradation. The detection of petrogenic biomarkers in soils is a clear indication of petroleum contamination. Conversely, no detection of petroleum biomarker compounds often indicates the absence of petroleum contamination.

The Environment Canada Emergencies Science and Technology Oil Research Laboratory is currently conducting petroleum biomarker analysis on the Day 0 and 300 crude oil contaminated treatments P1, P2, P3, P4 and S5. Biomarkers will be analyzed for the Day 0 and 300 diesel invert contaminated biopile experiment samples in addition to at least 8 of the 34 background PHC soil samples.

13 CRUDE OIL CONTAMINATION EXPERIMENT - F2, F3, F3a, F3b, F4 PHC RESULTS

13.1 Source Material PHC Evaluation Results

i) *Uncontaminated Commercial Bog Peat*

The biomarker forensics analysis indicated an absence of petroleum hydrocarbons in the commercial bog peat. The day 0 PHC analysis detected average concentrations of 62 mg/kg F2; 2,273 mg/kg F3; and 2,210 mg/kg F4. The average F3a and F3b distributions were 7% and 93% respectively, of the total average F3 concentration.

ii) *Uncontaminated Lakeland Fen Peat*

The biomarker forensics analysis indicated an absence of petroleum hydrocarbons in the Lakeland fen peat. The Day 0 PHC analysis detected average concentrations of 68 mg/kg F2; 1,480 mg/kg F3; and 765 mg/kg F4. The average F3a and F3b distributions were 14% and 86% respectively, of the total F3 concentration.

ii) *Uncontaminated Silica Sand*

The biomarker forensics analysis indicated an absence of petroleum hydrocarbons in the silica sand. The Day 0 PHC analysis detected average concentrations of 2 mg/kg F2; 13 mg/kg F3; and 24 mg/kg F4. The average F3a and F3b distributions were 23% and 73% respectively of the total average F3 concentration.

iii) *Federated Crude Oil*

Biomarker forensics analysis data will confirm the presence of federated crude oil in the contaminated peat and sand treatments. The fresh federated crude oil source had a petroleum hydrocarbon concentration of 179,000 mg/kg F2; 432,000 mg/kg F3; and 64,000 mg/kg F4. The F3a and F3b distributions were 49% and 51% respectively of the total F3 concentration.

13.2 Crude Oil Experiment Treatment Results – F2, F3, F4 Concentrations

(see Figure 10 graphs, Appendix Table A-1 and Appendix E GCFID chromatograms)

- Treatment #P1: *Commercial Bog Peat + 19,608 mg/kg F2, F3, F4 Whole Crude Oil F2-F4 Results*

The Day 0 F2 concentration was 3,897 mg/kg, which was 26X higher than the CWS PHC fine soil criteria. On Day 300 the concentration had decreased by 68% to 1,227 mg/kg, which was 8X higher than the CWS PHC fine soil criteria.

On Day 0, the F3 concentration of 11,292 mg/kg was 9X higher than the criteria. This concentration had decreased by 45% to 6,256 mg/kg on Day 300, which was 4X higher than the criteria.

The F4 concentration on Day 0 was 4,503 mg/kg, which did not exceed the criteria. On Day 300, the F4 concentration had decreased by 35% to 2,927 mg/kg.

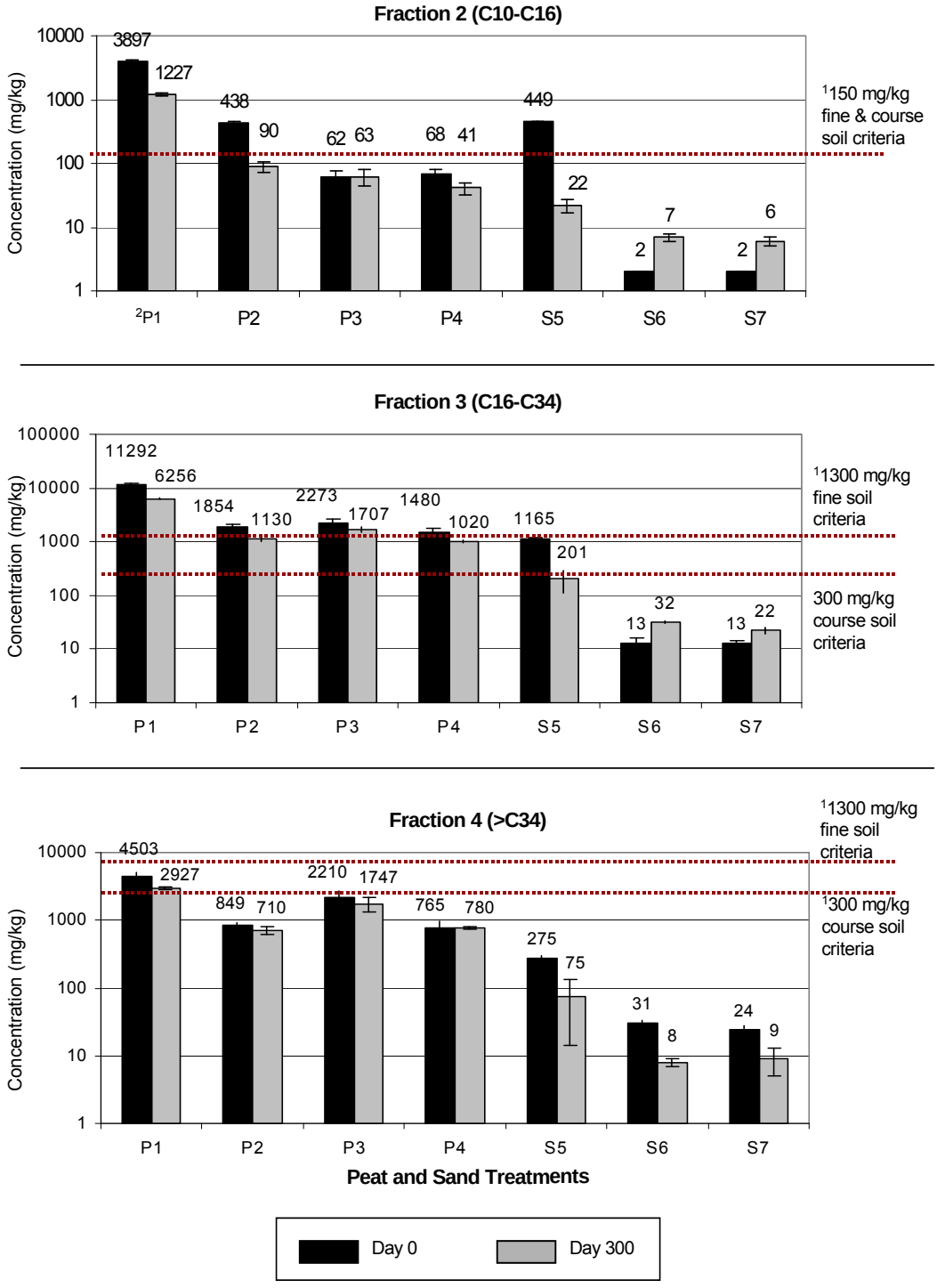
- Treatment #P2: *Lakeland Fen Peat + 2,942 mg/kg F2, F3, F4 Whole Crude Oil – F2-F4 Results*

The F2 concentration on Day 0 was 438 mg/kg, which was 3X higher than the CWS PHC fine soil criteria. On Day 300 the concentration had decreased by 79% to 90 mg/kg, which did not exceed the criteria.

On Day 0, the F3 concentration of 1,854 mg/kg was 1.4X higher than the criteria. This concentration had decreased by 39% to 1,130 mg/kg on Day 300, which did not exceed the criteria.

The F4 concentration on Day 0 was 849 mg/kg, which did not exceed the criteria. On Day 300, the F4 concentration had decreased by 16% to 710 mg/kg.

Figure 10: Crude Oil Contaminated Peat and Sand Experiments – Day 0 and Day 300 F2, F3, F4 Concentrations and CCME Soil Standard Compliance Results



[1]CCME Canada Wide Standard for PHC in Soil, Tier 1 fine surface soil criteria for agricultural/residential/parkland land uses in potable groundwater conditions (CCME 2008)

- Treatment #P3: *Uncontaminated Commercial Bog Peat – F2-F4 Results*

  The F2 concentration on Day 0 was 62 mg/kg, which did not exceed the CWS PHC fine soil criteria. F2 remained stable with a Day 300 concentration of 63 mg/kg.

  On Day 0, the F3 concentration of 2,273 mg/kg was 1.8X higher than the criteria. The Day 300 1,707 mg/kg concentration had decreased by 25% but remained above the criteria.

  The Day 0 F4 concentration of 2,210 mg/kg did not exceed the criteria. The Day 300 concentration decreased by 21% to 1,747 mg/kg.

- Treatment #P4: *Uncontaminated Lakeland Fen Peat – F2-F4 Results*

  The uncontaminated fen peat F2 to F4 concentrations remained relatively stable during the study period. The Day 0 and 300 F2 concentrations did not exceed the CWS PHC fine soil criteria with concentrations of 68 mg/kg and 41 mg/kg respectively.

  On Day 0, the F3 concentration of 1,480 mg/kg was 1.1X higher than the criteria. The Day 300 concentration decreased to below the criteria with a concentration of 1,130 mg/kg.

  The Day 0 and 300 F4 concentrations were well below the soil criteria with respective levels of 765 mg/kg and 780 mg/kg.

- Treatment #S5: *Sand + 2,942 mg/g F2, F3, F4 Whole Crude Oil + Bacteria – F2-F4 Results*

  The PHC concentrations in the contaminated sand decreased substantially over the 300 day study period. The 449 mg/kg F2 concentration on Day 0 was 3X higher than the CWS PHC course soil criteria. On Day 300 however, F2 had decreased by 95% to a concentration of 22 mg/kg, which was well below the soil criteria,

  On Day 0, the F3 concentration of 1,165 mg/kg was 4X higher than the criteria. This concentration had decreased by 83% to 201 mg/kg on Day 300, which did not exceed the criteria.

  The average F4 concentration on Day 0 was 275 mg/kg, which did not exceed the criteria. On Day 300, the F4 concentration had decreased by 73% to 75 mg/kg.

- Treatment #S6: *Uncontaminated Sand + Bacteria – F2-F4 Results*

  The uncontaminated sand plus bacteria F2 to F4 concentrations remained relatively stable and did not exceed the CWS PHC course soil criteria at any time during the study period. The F2 concentrations on Day 0 and 300 were 2 mg/kg and 7 mg/kg respectively. The Day 0 F3 concentration of 13 mg/kg increased to 32 mg/kg on Day 300. The Day 0 F4 concentration of 31 decreased to 8 mg/kg on Day 300.

- Treatment #S7: *Uncontaminated Sand Blank – F2-F4 Results*

  The uncontaminated sand F2 to F4 concentrations remained relatively stable did not exceed the CWS PHC course soil criteria at any time during the study period. The F2 concentrations on Day 0 and 300 were 2 mg/kg and 6 mg/kg respectively. The Day 0 F3 concentration of 13 mg/kg increased to 22 mg/kg on Day 300. The Day 0 F4 concentration of 24 decreased to 9 mg/kg on Day 300.

13.3 Percentage F3a:F3b Distribution Results

(See Figure 11 graphs, Appendix Table A-1 and Appendix E GCFID Chromatograms)

F3a:F3b percentages of the total F3 concentrations were calculated for all seven treatments including replicates for Days 0, 150 and 300. The following discussion includes the average distributions for the seven treatments. As discussed in Section 13.1, the Federated Crude Oil had virtually equal F3a:F3b distributions of 49%:51%. In contrast, F3b dominated the uncontaminated bog peat, fen peat and silica sand with respective F3a:F3b distributions of 7%:93%, 14:86% and 23%:77%. These source material distribution patterns are relevant to changes that occur as contaminated soils bioremediate over time.

- Treatment #P1: *Commercial Bog Peat + 19,608 mg/kg F2, F3, F4 Whole Crude Oil*
  %F3a:F3b Results

  F3b maintained the dominant percentage of at least 61%, which increased steadily during the 300 Day study period. On Day 0, the F3a:F3b distributions of 39%:61% shifted to 32%:68% on Day 150 and 26%:74% on Day 300.

- Treatment #P2: *Lakeland Fen Peat + 2,942 mg/kg F2-F4 Whole Crude Oil*
  %F3a:F3b Results

  F3b maintained the dominant percentage of at least 72% throughout the entire study period. The Day 0 F3a:F3b distributions were 28%:72%, which shifted to 17%:83% on Day 150 and 19%:81% on Day 300.

- Treatment #P3: *Uncontaminated Commercial Bog Peat*
  %F3a:F3b Results

  The F3a and F3b distributions remained stable during the study period, with F3b dominating with a minimum percentage of 93%. The F3a:F3b distributions were 7%:93% on Day 0; 5%:95% on Day 150; and 7%:93% on Day 300.

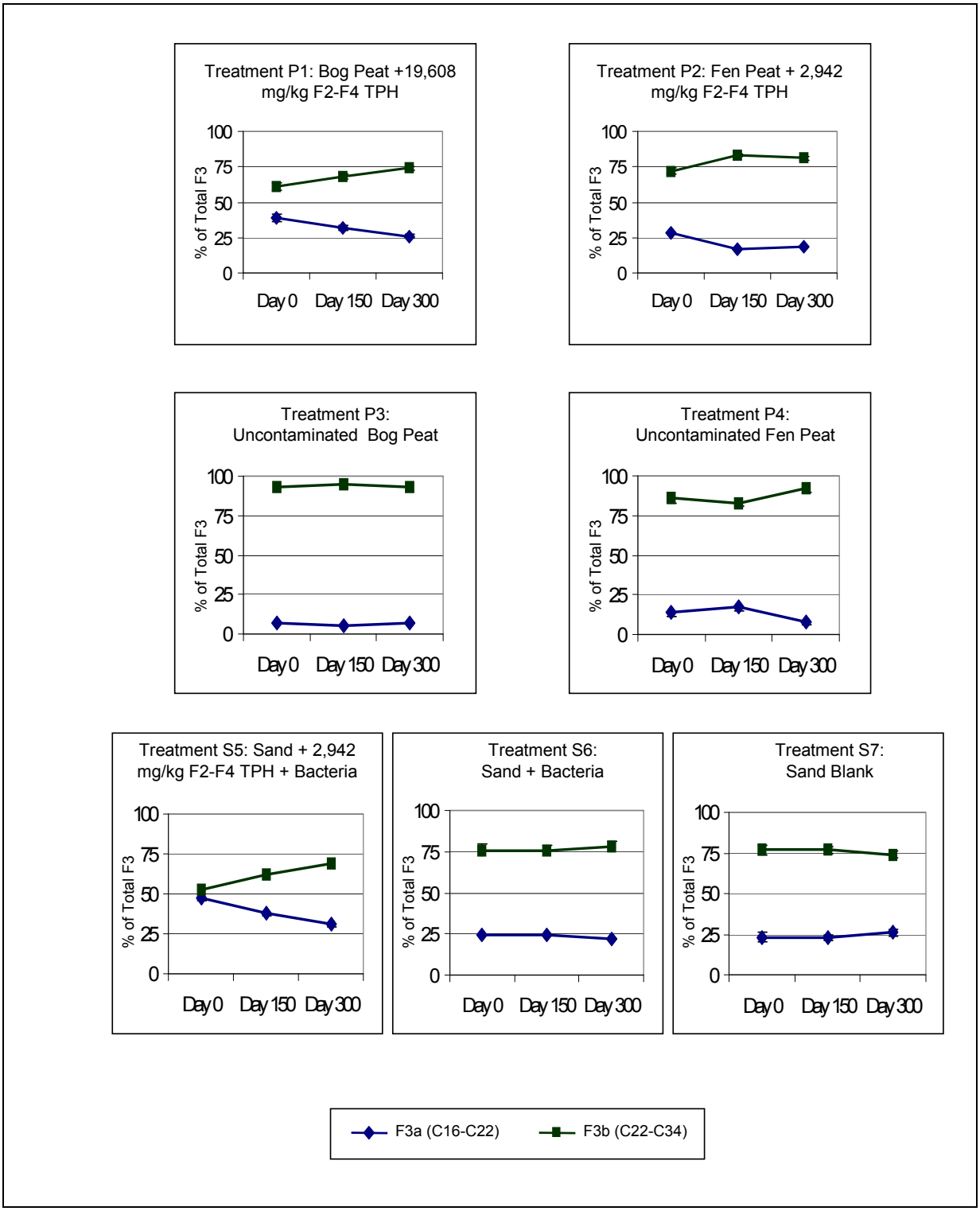
- Treatment #P4: *Uncontaminated Lakeland Fen Peat*
  %F3a:F3b Results

  F3a:F3b fluctuated in the uncontaminated Lakeland fen peat, with F3b maintaining the dominant percentage of at least 83%. The F3a:F3b distributions were 14%:86% F3b on Day 0, 17%:83% on Day 150 and 8%:92% on Day 300.

- Treatment #S5: *Sand + 2,942 mg/g F2-F4 Crude Oil + Bacteria*
  %F3a:F3b Results

  In comparison to the other six treatments, the contaminated sand had the lowest F3b percentage of 53%. The F3b percentages did however steadily increase during the 300 day study period. The F3a:F3b distributions were 47%:53% F3b on Day 0, 38%:62% on Day 150 and 31%:69% on Day 300.

Figure 11: Crude Oil Contaminated Peat and Sand Experiments - F3a:F3b Percentages of Total F3 Concentrations Over Time



- Treatment #S6: *Uncontaminated Sand + Bacteria*
  %F3a:F3b Results

F3b dominated the uncontaminated sand plus bacteria treatment during the entire study period, with percentages of at least 76%. The F3a:F3b distributions were 24%:76% on Day 0, 24%:76% on Day 150 and 23%:77% on Day 300.

- Treatment #S7: *Uncontaminated Sand Blank*
  %F3a:F3b Results

F3b dominated the uncontaminated sand blank treatment during the entire study period, with percentages of at least 74%. The F3a:F3b distributions were 23%:77% on Day 0, 23%:77% on Day 150 and 22%:78% on Day 300.

13.4 Corrections of False Petroleum Hydrocarbon Criteria Exceedences

(See Figure 12 graphs and Appendix Table A-1)

- Treatment #P1: *Commercial Bog Peat + 19,608 mg/kg F2-F4 Whole Crude Oil*
  - calculated maximum possible F3 concentrations from crude oil

The P1 treatment was spiked with whole crude oil with a target F3 PHC concentration of 10,000 mg/kg. This was the only one of the seven treatments with measured total F3 and calculated F3 PHC concentrations that exceeded the 1,300 mg/kg CWS PHC fine soil criteria during the entire study period. The Day 0 total F3 concentration was 11,292 mg/kg with a calculated F3 PHC concentration of 9,468 mg/kg. The Day 300 total F3 concentration was 6,256 mg/kg and the calculated F3 PHC concentration was 5,180 mg/kg.

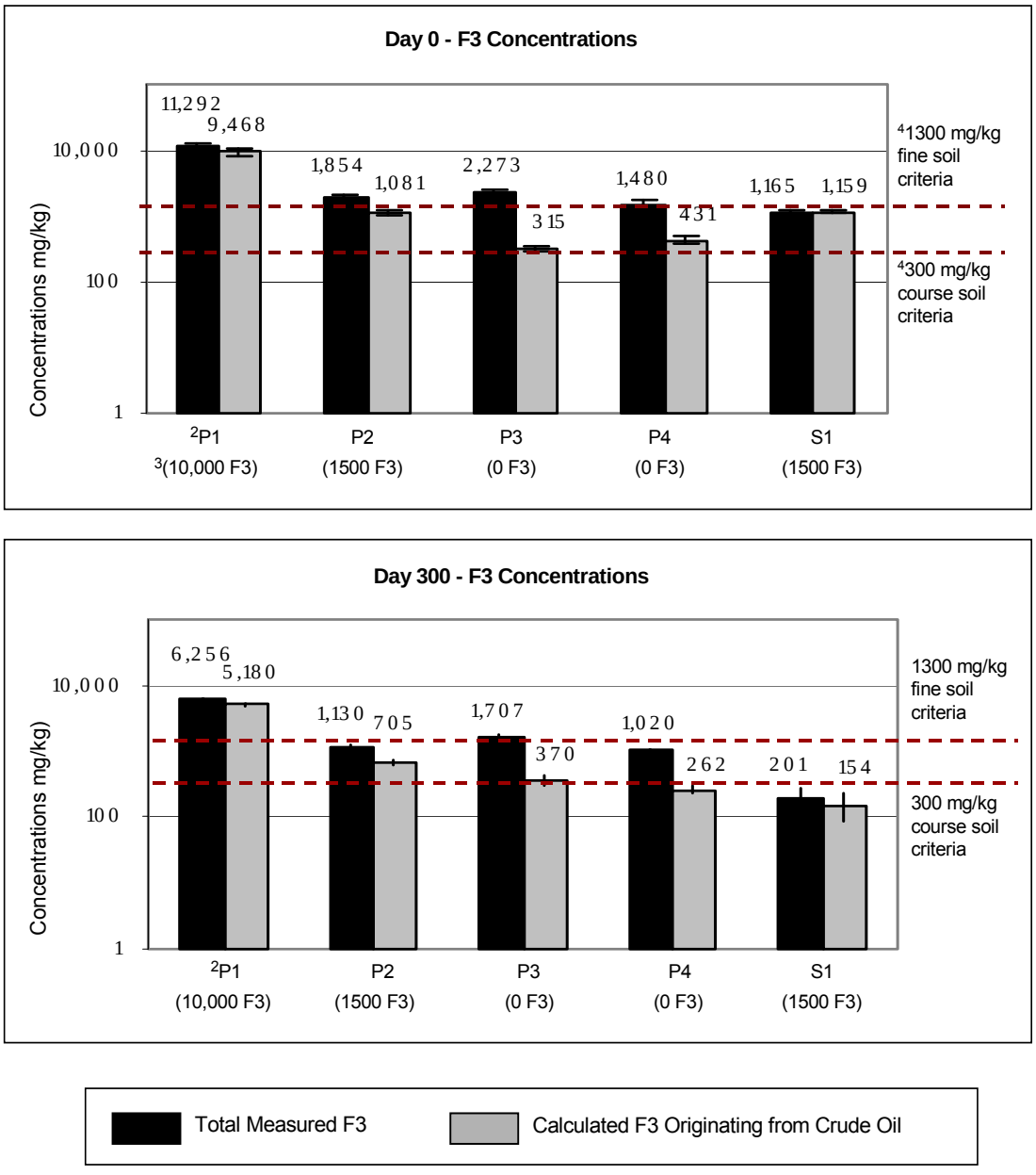
- Treatment #P2: *Lakeland Fen Peat + 2,942 mg/kg F2-F4 Whole Crude Oil*
  – calculated maximum possible F3 concentrations from crude oil

The P2 treatment was spiked with whole crude oil with a target F3 PHC concentration of 1,500 mg/kg. The CWS PHC fine soil criteria was exceeded only by the Day 0 total F3 concentration of 1,854 mg/kg. The Day 0 calculated F3 PHC concentration was slightly below the criteria with a concentration of 1,081 mg/kg. Although the Day 300 total F3 concentration of 1,130 mg/kg was slightly below the criteria, the calculated 705 mg/kg F3 PHC concentration was approximately half the limit.

- Treatment #P3: *Uncontaminated Commercial Bog Peat*
  – calculated maximum possible F3 concentrations from crude oil

On Day 0 and 300, the total F3 in the uncontaminated commercial bog peat exceeded the CWS PHC fine soil criteria with respective concentrations of 2,273 mg/kg and 1,707 mg/kg. However, the Day 0 and 300 calculated F3 PHC concentrations were at a level one quarter of the criteria with respective concentrations of 315 mg/kg and 370 mg/kg.

Figure 12: Crude Oil Contaminated Peat and Sand Experiments – Comparisons of Total Measured F3 vs Calculated F3 Concentrations Originating from Crude Oil



[1]CCME Canada Wide Standard for PHC in Soil, Tier 1 fine surface soil criteria for agricultural/residential/parkland land uses in potable groundwater conditions (CCME 2008)

[2]P1-commercial bog peat + 19,608 mg/kg TPH oil; P2-Lakeland fen peat + 2,942 mg/kg TPH oil; P3-uncontaminated commercial bog peat; P4-uncontaminated Lakeland fen peat; S5-sand + 2,942 mg/kg TPH oil + bacteria broth; S6-uncontaminated sand + bacteria broth; S7-uncontaminated sand blank

[3]Nominal crude oil F3 concentrations (mg/kg) spiked into soil treatments on Day 0

[4]The 1300 mg/kg fine soil guideline applies to P1, P2, P3, P4. The 300 mg/kg course soil guideline applies to S5.

- Treatment #P4: *Uncontaminated Lakeland Fen Peat*
  – calculated maximum possible F3 concentrations from crude oil

  The uncontaminated Lakeland fen peat total F3 was slightly above the CWS PHC fine soil criteria on Day 0 and slightly below the criteria on Day 300 with respective concentrations of 1,480 mg/kg and 1,020 mg/kg. The respective Day 0 and Day 300 calculated F3 PHC concentrations of 431 mg/kg and 262 mg/kg were one quarter and one third of the criteria.

- Treatment #S5: *Sand + 2,942 Whole Crude Oil*
  – calculated maximum possible F3 concentrations from crude oil

  The S5 treatment was spiked with whole crude oil with a target F3 PHC concentration of 1,500 mg/kg. The Day 0 total F3 and corrected F3 PHC concentrations were 1,165 mg/kg and 1,159 mg/kg respectively. These concentrations were 4 times higher than the 300 mg/kg CWS PHC course soil criteria. The Day 300 total F3 and corrected F3 PHC respective concentrations of 201 mg/kg and 154 mg/kg did not exceed the criteria.

14 BACKGROUND SOIL SURVEY CHEMISTRY RESULTS

The following discussion focuses primarily on the F2, F3, F3a, F3b and F4 results. The PAH and petroleum biomarker results, however are briefly touched upon with greater detail to be included in future reports.

14.1 Petroleum Presence/Absence Screening

Priority PAH analysis was conducted on all 34 background samples (see Appendix Table A-2). The PAH concentrations were non-detectable in every sample except for minimal concentrations found in background sample NFL 08. These detectable PAHs included: chrysene (0.06 mg/kg), fluoranthene (0.12 mg/kg) and phenanthrene (0.08 mg/kg). The chrysene and fluoranthene concentrations were insignificant in comparison to the CWS PHC soil criteria. There is no soil criteria for phenanthrene.

The Environment Canada Oil Research Laboratory is conducting ongoing forensics analysis of selected soil samples to be published at a later date.

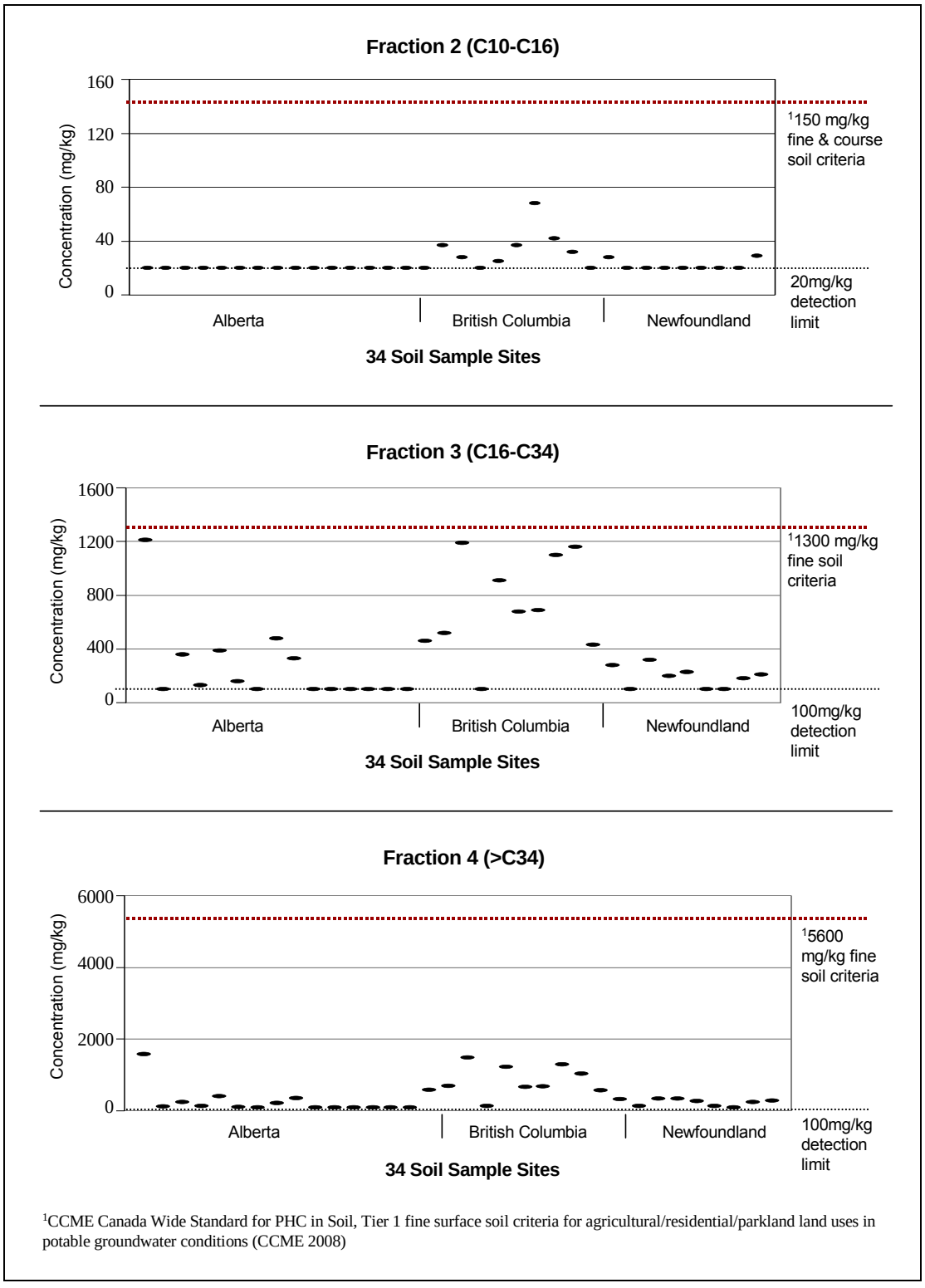
14.2 CWS PHC Tier 1 Soil Criteria Compliance Results

All 34 background soil samples were in compliance with the CWS PHC fine soil criteria (see Figure 13 graphs and Appendix Table A-2).

i) F2 (C10-C16)

All of the samples were lower than the CWS PHC F2 soil criteria of 150 mg/kg. The concentrations ranged from a minimum of <20 mg/kg to a maximum of 68 mg/kg. The median concentration was <20 mg/kg, with a standard deviation of 10 mg/kg.

Figure 13: Background PHC Soil Survey – Compliance with CCME CWS PHC Tier 1 Soil Criteria



[1]CCME Canada Wide Standard for PHC in Soil, Tier 1 fine surface soil criteria for agricultural/residential/parkland land uses in potable groundwater conditions (CCME 2008)

ii) F3 (C16-C34)

80% of the samples were less than half of the 1,300 mg/kg CWS PHC F3 fine soil criteria. The remaining 20% of the samples ranged from 690 mg/kg to 1280 mg/kg. The median concentration was 220 mg/kg, with a standard deviation of 355 mg/kg.

iii) F4 (>C34)

All of the samples were lower than the 5,600 mg/kg CWS PHC F4 fine soil criteria. The concentrations ranged from a minimum of <100 µg/g to a maximum of 1,580 mg/kg. The median concentration was 260 mg/kg, with a standard deviation of 427 mg/kg.

14.3 Percentage F3a:F3b Distribution Results

(see Figure 14 graphs and Appendix Table A-3)

The F3a concentrations ranged from a minimum of 7 mg/kg to a maximum of 85 mg/kg. The median concentration was 15 mg/kg with a standard deviation of 25 mg/kg. The F3b concentrations ranged from a minimum of 93 mg/kg to a maximum of 1125 mg/kg. The median concentration was 205 mg/kg, with a standard deviation of 325 mg/kg.

All 34 samples contained at least 90% F3b and no more than 10% F3a. The median percentage F3a:F3b distribution was 7%:93%.

15 CRUDE OIL CHEMISTRY SURVEY – Percentage F3a:F3b DISTRIBUTION RESULTS (See Figure 14 and Appendix Table A-4)

A total of 13 crude oils were evaluated for F3a:F3b percentage distributions. The percentage F3a:F3b distributions ranged from 41%:59% to 52%:48% with a median value of 51%:49%.

16 CONCLUSIONS

General conclusions are as follows:

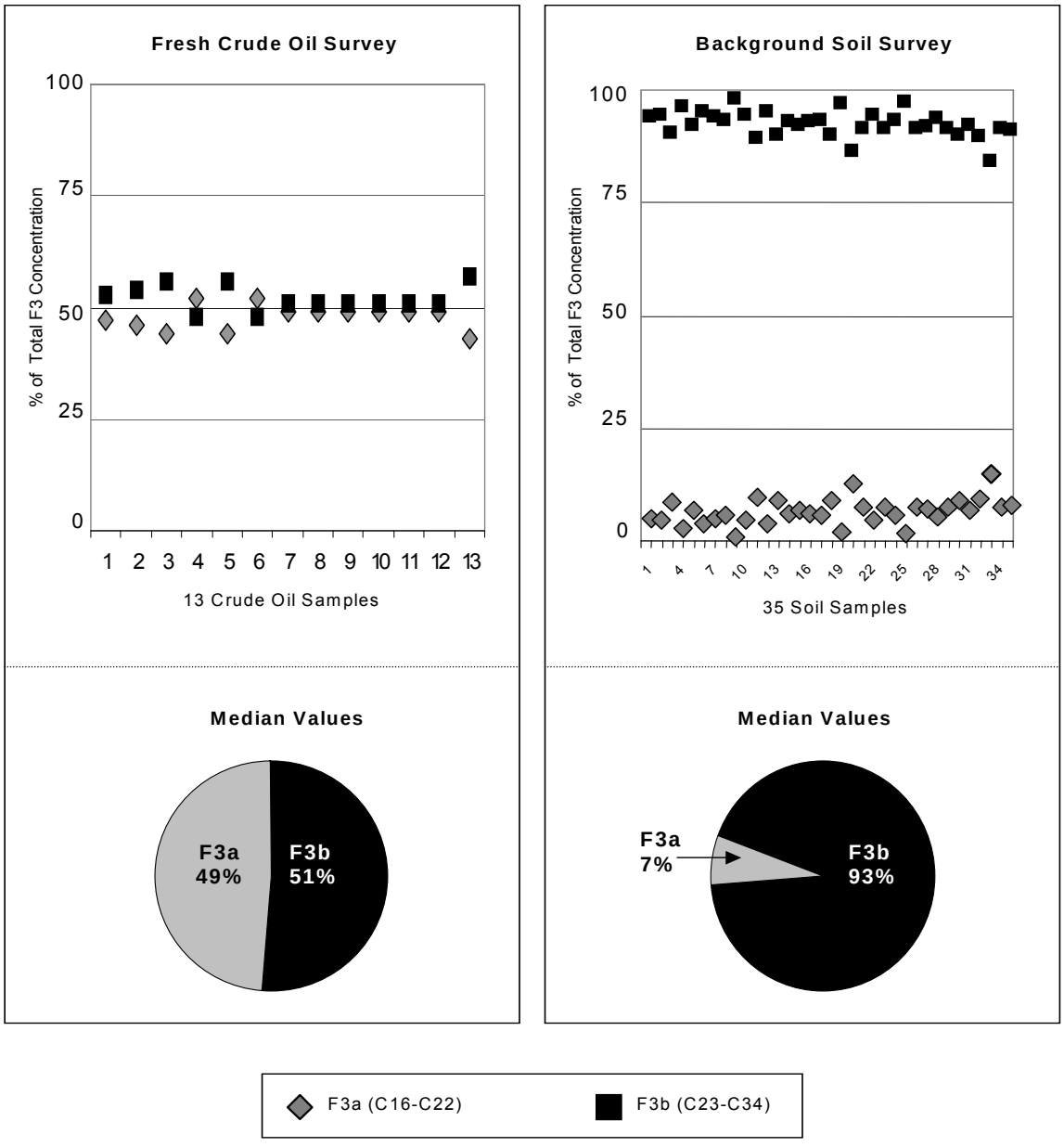
i) The maximum possible F3 petroleum calculation can be applied to petroleum products such as diesel and crude oils because they do not heavily dominate the F3b carbon range.

ii) The calculation can only be applied if the F3a:F3b distributions are known for the petroleum spill source.

iii) Degree of weathering is an important factor that can increase F3b percentage distributions in crude oils. Diesel oil weathering and biodegradation patterns will be discussed in the subsequent Part II report.

iv) Specialized forensics testing would be necessary to identify petroleum sources and/or weathering stages in undocumented and/or older spill sites.

Figure 14 - Percentage F3a:F3b Distributions in 13 Fresh Crude Oils vs 34 Background Soils



16 CONCLUSIONS (cont'd)

16.1 Crude Oil Contaminated Peat and Sand Experiments

The crude oil experiments confirmed that the total F3 concentrations in the uncontaminated peat falsely exceeded the PHC soil criteria. The crude oil F3a:F3b signature patterns were successfully used to reduce the maximum possible crude oil concentrations to levels that were less than one third of the F3 criteria.

The maximum possible F3 concentration from crude oil calculation is most easily applied to fresh spill sites where the petroleum source product can be analyzed for F3a:F3b distribution patterns. However, the contaminated sand treatments demonstrated that the F3b distributions became more dominant over time. The contaminated sand treatment degraded from 1,165 mg/kg on Day 0 to 201 mg/kg on Day 300. During that time, the F3a:F3b distributions in the contaminated sand shifted from 47%:53% to 31%:69%. This data demonstrates that understanding F3a:F3b distributions in degraded crude oils is essential to evaluating older spill sites.

The F3 petroleum concentration calculation could only be applied to abandoned contaminated sites if preliminary forensics testing is able to conclusively identify the petroleum product and stage of weathering. These results will be included in the Part II report.

16.2 Background Soil Survey

The background soil survey identified a wide range of F2, F3 and F4 concentrations. Only the F3 concentrations approached the CWS PHC fine soil criteria with a range of 26 to 1,431 mg/kg. Regardless of the concentrations, F3b dominated with distributions ranging from 80% to 99%. These data indicate that the calculated F3 PHC method could be effectively used to eliminate false F3 soil criteria exceedences in crude oil and diesel contaminated sites.

16.3 Fresh Crude Oil Survey

The F3a:F3b distributions were relatively equal in the thirteen fresh crude oils, with median values of 46%:54% and a standard deviation of 3%. The F3b distributions ranged from 48% to 59%, which indicates that the F3 petroleum concentration calculation could be effectively used for the 13 fresh crude oils. Additional research is needed to document the effects of weathering on the F3a:F3b distributions in crude oils.

16.4 Preliminary Diesel Invert and Manure Biopile Evaluation

The biopile evaluation determined that the 816 mg/kg F3 concentration in the uncontaminated manure was elevated but did not exceed the CWS PHC fine soil criteria. The F3a:F3b distributions were 16%:84% in the uncontaminated manure and 89%:11% in the diesel invert. These data indicate that the F3 petroleum concentration calculation could be used to reduce false criteria exceedence issues in marginally contaminated biopiles.

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EXECUTIVE SUMMARY

Petroleum hydrocarbon (PHC) soil contamination is a globally recognized environmental issue. The Canada-Wide Standard (CWS) for Petroleum Hydrocarbons (PHCs) in Soil is an intergovernmental agreement developed under the Canadian Council of Ministers of the Environment (CCME) Canada-wide Environmental Standards Sub-Agreement (CCME, 2001).

The CWS is a 3-tiered, risk-based remedial standard developed for a variety of common land uses. Contaminated site evaluations typically begin by analyzing soil samples in accordance with the CWS Reference Method for PHCs in Soil – Tier 1 Method. Under this method, PHC data is categorized into four different carbon fractions. The term "fraction" refers to the following equivalent normal straight-chain hydrocarbon boiling point ranges:

i) Fraction #1: C6-C10;
ii) Fraction #2: C10-C16;
iii) Fraction #3: C16-C34;
iv) Fraction #4: >C34

Each of the four fractions have dedicated CWS Tier 1 PHC soil criteria, as indicated in Table 1. (CCME, 2008a). These criteria are based upon the likelihood that petroleum constituents within a given fraction could produce a potential environmental or human health risk. Effective site evaluations and remediation strategies rely on accurate delineations of PHC contamination boundary zones. However, currently PHC soil extraction and chemistry analysis techniques misidentify natural biogenic organic compounds (BOCs) as originating from petroleum sources. "BOC" is a general term used to describe mixtures of biological organic compounds such as alkanes, sterols, sterones, fatty acids, fatty alcohols, waxes and wax esters (Wang, Z. et. al. 2009). BOCs are biosynthesized by plants and animals during their life cycles and are integral components of peat and manure. Standard PHC analysis of highly organic soils such as peat and remediation materials such as manure could trigger false PHC soil criteria exceedences, resulting in unnecessary site remediation and/or landfill disposal requirements.

Table 1: Summary of Tier 1 criteria (mg/kg soil) for PHCs in surface soils[1] (CCME, 2008a)

Land Use	Soil Texture	Fraction 1	Fraction 2	Fraction 3	Fraction 4
Agricultural	Course-grained soil	30[3]	150	300	2,800
	Fine-grained soil	210 (170[2])	150	1,300	5,600
Residential/ Parkland	Course-grained soil	30[3]	150	300	2,800
	Fine-grained soil	210 (170[2])	150	1,300	5,600
Commercial	Course-grained soil	320 (240[2])	260	1,700	3,300
	Fine-grained soil	320 (170[2])	260 (230[2])	2,500	6,600
Industrial	Course-grained soil	320 (240[2])	260	1,700	3,300
	Fine-grained soil	320 (170[2])	260 (230[2])	2,500	6,600

[1] Additional Tier 1 levels are presented in Technical Supplement (CCME, 2009).
[2] - Where applicable, for protection of potable groundwater.
[3] - Assumes contamination near residence
Note: Agricultural/Residential/Parkland levels are most relevant to contamination scenarios included in this study (Sources: Personal communications with petroleum industry managers).

RESEARCH OBJECTIVE

The primary objective of this research is to develop a new approach to resolving false PHC soil criteria exceedences in uncontaminated and marginally contaminated soils and compost materials.

2009 AND 2010 RESEARCH ACTIVITY SUMMARY

This study focuses on the following two scenarios, which are highly relevant to the petroleum industry: crude oil pipeline spills in muskeg peat and composted manure biopile remediation of diesel invert contaminated drilling waste.

Two laboratory scale experiments were conducted over two consecutive 300 day periods. The first experiment was completed in November 2009 and focused on crude oil contaminated peat. The second ongoing experiment will be completed in February 2010 and focuses on diesel drilling invert contaminated manure biopiles.

A background PHC soil field survey was also conductd in 2009. A total of 34 soil samples were collected from 34 background sites located in the provinces of Alberta, British Columbia and Newfoundland. Additional soil samples will be collected during the 2010 field season.

The 2009 research activities also included the PHC chemistry analysis of 13 fresh crude oils.

PART I AND PART II REPORT DESCRIPTION

This Part I draft report discusses how standard PHC extraction methods can be combined with alternative data calculations to offset false criteria exceedences for crude oil contaminated peat and diesel invert contaminated manure biopiles. This report includes the PHC F2, F3, F3a, F3b and F4 results for the following completed studies:

i) Preliminary F2, F3, F3a, F3b and F4 PHC analysis of biogenic and petrogenic source materials used in the 300 day crude oil contaminatd peat and diesel invert contaminated manure biopile experiments;

ii) F2, F3, F3a, F3b and F4 PHC data for the Day 0, 150 and 300 crude oil contaminated peat experiments;

iii) F2, F3, F3a, F3b and F4 PHC analysis of 13 crude oils; and

iv) F2, F3, F3a, F3b and F4 PHC and priority polyaromatic hydrocarbon (PAHs) analysis of 34 background soil samples.

The subsequent Part II report will include the Day 0, 150 and 300 diesel invert contaminated manure biopile experiment results. It will also demonstrate how current forensics techniques were used to identify petroleum sources and weathering stages for aged and/or “mystery” spill sites. The Phase II report will include the following data:

i) F2, F3, F3a, F3b and F4 PHC results for the 300 day diesel invert experiments;

ii) Petroleum biomarker forensics data for the Day 0, 150 and 300 crude oil and diesel invert experiments; and

iii) Petroleum biomarker forensics data for at least 8 of the 34 background soil samples.

CWS SUGGESTED SOLUTION TO FALSE PHC CRITERIA EXCEEDENCES

The CWS suggested solution to false PHC criteria exceedences is to measure and subtract background concentrations from contaminated soil concentrations. While this approach can be helpful, background concentrations can be highly variable. To illustrate this point, uncontaminated peat samples were collected from Lakeland Provincial Park located 250 km northeast of the City of Edmonton, Alberta. Two peat samples were collected from depths of 0-5 cm and 11-15 cm and extracted in accordance with the CWS PHC F2-F4 standards (CCME, 2001). The respective F3 concentrations of 3,020 mg/kg and 2,160 mg/kg exceeded the CWS PHC 1,300 mg/kg fine soil criteria. Just as importantly, there was a significant difference of 860 mg/kg between replicate samples collected within the 0-15 cm sample zone.

This type of variability could lead to the under- or over-estimation of true petroleum concentrations and perceived toxicity risks. False PHC criteria exceedences could trigger unnecessary remediation and/or disposal requirements resulting in the waste of valuable landfill space and unnecessary disturbances to uncontaminated natural habitat areas.

ALTERNATIVE F3a:F3b APPROACH To CALCULATING MAXIMUM PETROGENIC F3 In ORGANIC MATERIALS

Although F3a (C16-C22) and F3b (C22-C34) subfractions are not included in the CWS PHC Tier-1 Standard, this research study has identified biogenic and petrogenic signature patterns that can be used to resolve false F3 PHC criteria exceedence issues. The total F3 concentrations for all of the research samples were divided into subfractions F3a and F3b. The F3a:F3b percentage distributions of the total F3 concentrations were then calculated. The results determined that although the soils, manure, diesel and crude oils all overlapped within the same F3 carbon range, only the soils and manure heavily dominated the F3b range.

Figure 1 illustrates these patterns in 34 uncontaminated background soils and 13 fresh crude oils. The background soils had a median F3a:F3b distribution of 7%:93%, with a standard deviation of 4%. In contrast, the crude oils had a median F3a:F3b distribution of 49%:51%, with a standard deviation of 3%.

The GCFID chromatograms illustrated in Figures 2 and 3 demonstrate that petrogenic vs. biogenic patterns remain visually distinct even when different sources are mixed together. The F3a concentrations predominantly originate from petrogenic sources only. However, the F3b petrogenic concentrations may be calculated only if the F3a:F3b signature distributions in the source petroleum product are known.

Formula #1: Calculation of Maximum Possible F3 Concentrations from Crude Oil or Diesel Invert

[(a x b/c] + a

a = Measured F3a concentration in peat or manure sample

b = Measured and/or documented %F3b of total F3 in crude oil or diesel invert source

c = Measured and/or documented %F3a of total F3 in crude oil or diesel invert source

Figure 1: Percentage distributions in 13 fresh crude oils and 34 background soils

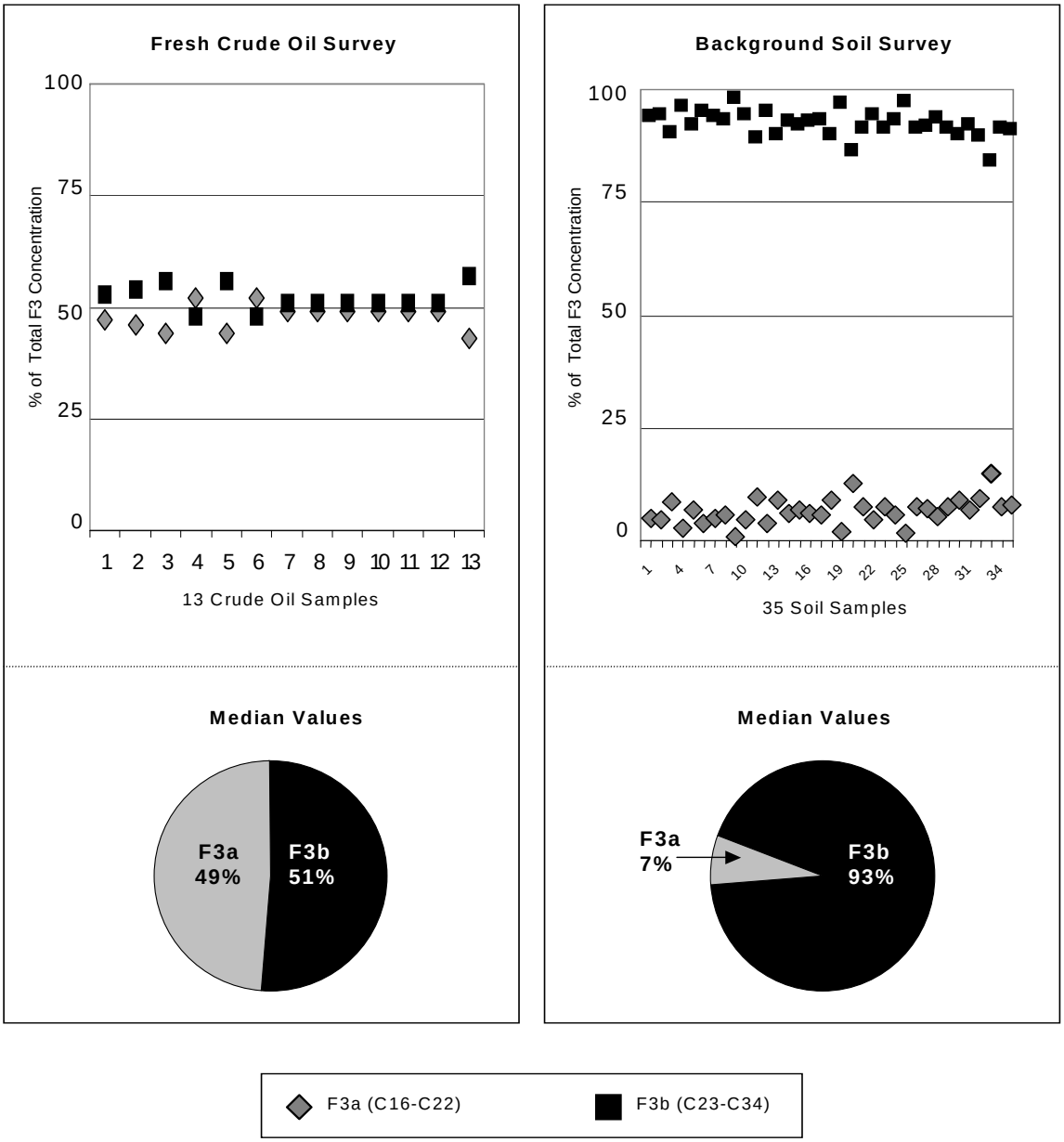
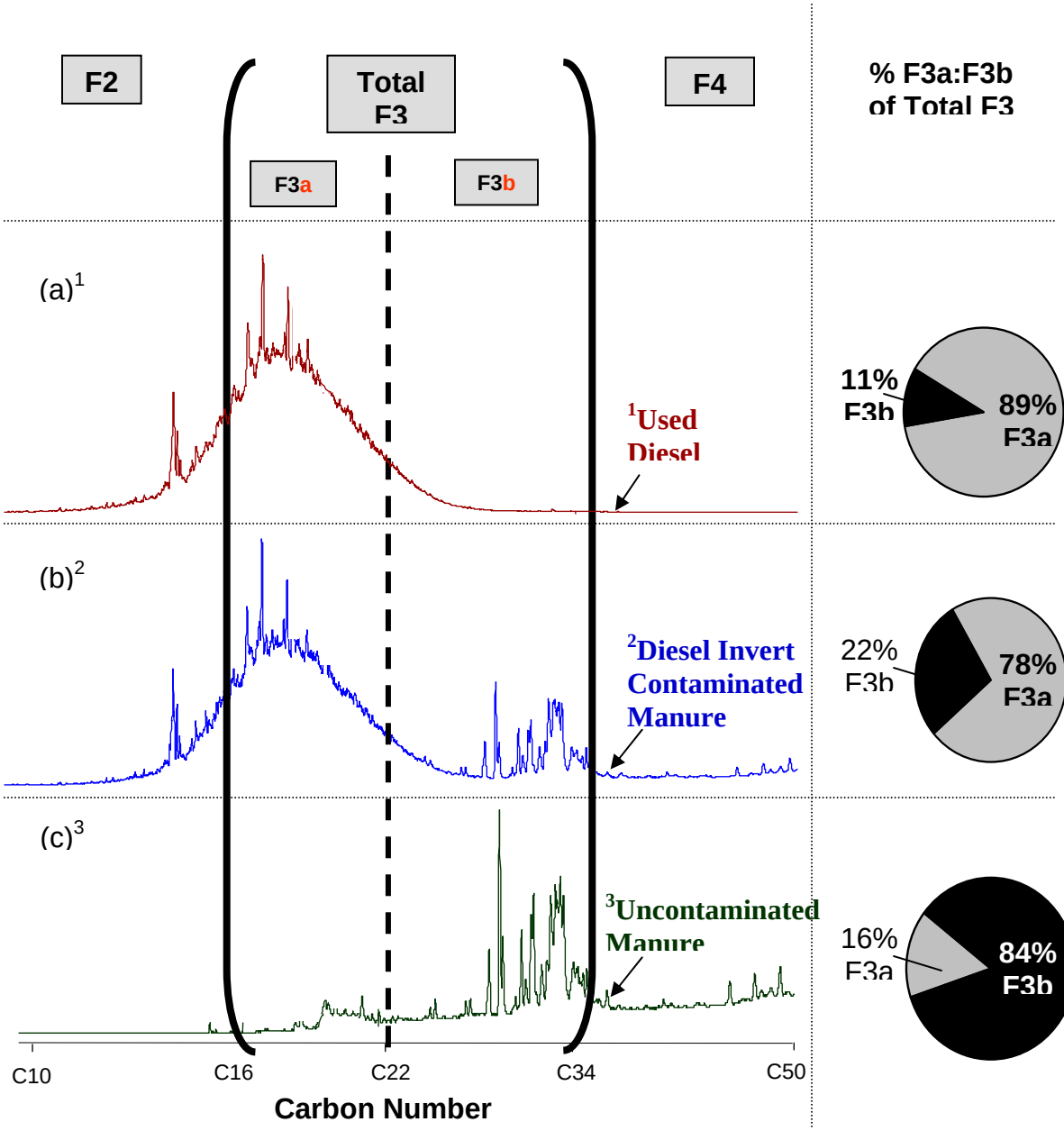


Figure 2: Example GCFID chromatogram comparisons of F2-F4 and F3a:F3b distributions in fresh federated crude oil, contaminated peat and uncontaminated

Dr. D.G. Dixon, VP of Research, Professor of Biology, University of Waterloo, dgdixon@uwaterloo.ca

Figure 3: GCFID chromatogram comparisons of F2-F4 and %F3a:F3b distributions in used diesel invert, contaminated manure and uncontaminated manure



[1]Used diesel invert concentrations: F2 852 mg/kg; F3 3,160 mg/kg; F3a 2,749 mg/kg; F3b 411 mg/kg; F4 340 mg/kg

[2]Contaminated manure concentrations: F2 610 mg/kg; F3 2,850 mg/kg; F3a 2,081 mg/kg; F3b 770 mg/kg; F4 300 mg/kg

[3]Uncontaminated manure concentrations: F2 38 mg/kg; F3 816 mg/kg; F3a 122 mg/kg; F3b 694 mg/kg; F4 590 mg/kg

Example Calculation #1: ***Fresh Crude Oil Contaminated Peat (Measured Total F3 = 10,035 mg/kg)*** *(see Figure 2)*

[3,713 x 0.53/0.47)] + 3,713 = 7,900 mg/kg

a = Measured soil sample F3a concentration 3,713 mg/kg

b = Measured federated crude oil petroleum source F3b 53%

c = Measured federated crude oil petroleum source F3a 47%

Calculated maximum possible Total F3 concentration from federated crude oil = 7,900 mg/kg

Example Calculation #2: ***Uncontaminated Peat (Measured Total F3 = 2,567 mg/kg)*** *(see Figure 2)*

[128 x 0.53/0.47)] + 128 = 272 mg/kg

a = Measured soil sample F3a concentration 128 mg/kg

b = Measured crude oil petroleum source F3b 53%

c = Measured crude oil petroleum source F3a 47%

Calculated maximum possible Total F3 concentration from crude oil = 272 mg/kg

Example Calculation #3: ***Diesel Contaminated Manure (Measured Total F3 = 2,850 mg/kg)*** *(see Figure 3)*

[2,081 x 0.11/0.89)] + 2,081 = 2,338 mg/kg

a = Measured soil sample F3a concentration 2,081 mg/kg

b = Measured diesel invert petroleum source F3b 11%

c = Measured diesel invert petroleum source F3a 89%

Calculated maximum possible Total F3 concentration from diesel invert = 2,338 mg/kg

Example Calculation #4: ***Uncontaminated Manure (Measured Total F3 = 816 mg/kg)*** *(see Figure 3)*

[122 x 0.53/0.47)] + 122 = 260 mg/kg

a = Measured soil sample F3a concentration 122 mg/kg

b = Measured diesel invert petroleum source F3b 11%

c = Measured diesel invert petroleum source F3a 89%

Calculated maximum possible Total F3 concentration from crude oil = 260 mg/kg

Petroleum Weathering and Biodegradation Considerations

Fresh crude and diesel oils are subject to natural weathering (e.g. evaporation, photo oxidation) and microbial degradation processes. Within periods of days, weeks and months, these processes can significantly reduce PHC concentrations while also transforming chemical signatures (Pollard, R. et al., 1999; Wang, Z. et al. 2006). In fresh spills, evaporation of F1 and F2 fractions is the single most important weathering process. Microbial degradation is another process that represents one of the primary mechanisms by which aged PHCs are naturally eliminated from the environment. Fresh versus aged petroleum spills can therefore produce very different chemical signatures.

To our knowledge, no studies have been conducted specifically on F3a:F3b distributions in fresh or aged PHCs. The 300 day crude oil and diesel invert experiments were designed to document these changes over time. The median F3a:F3b distributions in the crude oil contaminated sand treatments shifted from 47%:53% on day 0 to 38%:62% on day 150, to 31%:69% on day 300. The different day 0, 150 and 300 distributions in the contaminated sand were used to calculate the estimated crude oil F3 concentrations in the contaminated treatments. This same approach will be used upon completion of the Day 300 diesel invert experiments as well.

CRUDE OIL EXPERIMENTS: Day 0 and 300 petrogenic correction results

(see Figure 4)

The 300 day crude oil contamination experiment was designed to simulate full spectrum lighting and saturated soil conditions of a natural muskeg environment. Seven different treatments including three replicates were placed into 70 L glass aquarium tanks and monitored monthly for 300 days (see Appendix C photographs). The experiment treatment concentrations were selected to study false exceedences of the CWS PHC F3 soil criteria. (Baas et al. 2000; Perusetti et al., 2005; Pollard et al., 1999; Wang et al., 2006; (Yunker et al., 1995).

- Treatment #P1: *Commercial Bog Peat + 19,608 mg/kg F2-F4 Whole Crude Oil*

  The P1 treatment was spiked with whole crude oil with a target F3 PHC concentration of 10,000 mg/kg. This was the only one of the seven treatments with measured total F3 and calculated F3 PHC concentrations that exceeded the 1,300 mg/kg CWS PHC fine soil criteria during the entire study period. The Day 0 total F3 concentration was 11,292 mg/kg with a calculated F3 PHC concentration of 9,468 mg/kg. The Day 300 total F3 concentration was 6,256 mg/kg and the calculated F3 PHC concentration was 5,180 mg/kg.

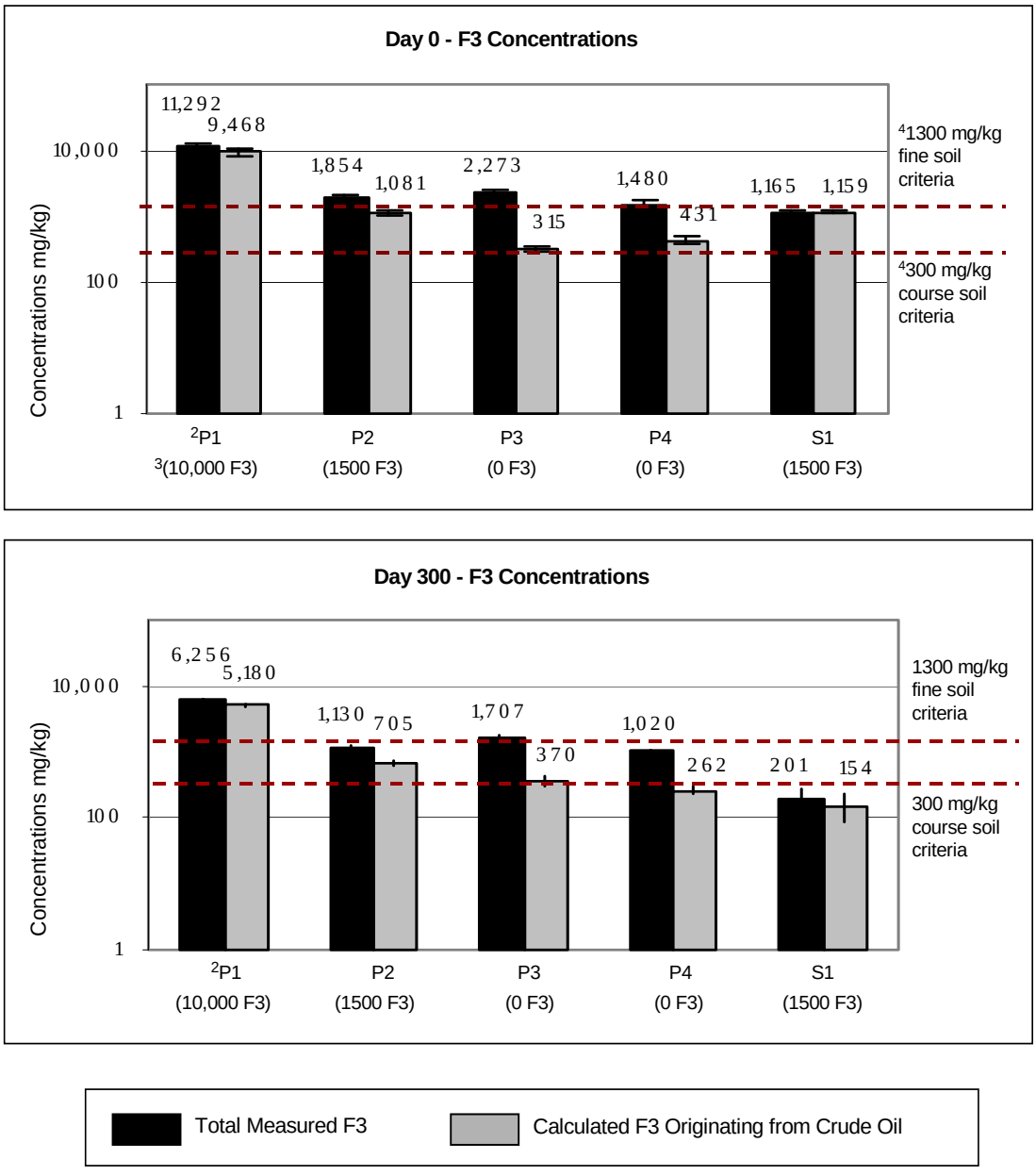
- Treatment #P2: *Lakeland Fen Peat + 2,942 mg/kg F2-F4 Whole Crude Oil*

  The P2 treatment was spiked with whole crude oil with a target F3 PHC concentration of 1,500 mg/kg. The CWS PHC fine soil criteria was exceeded only by the Day 0 total F3 concentration of 1,854 mg/kg. The Day 0 calculated F3 PHC concentration was slightly below the criteria with a concentration of 1,081 mg/kg. Although the Day 300 total F3 concentration of 1,130 mg/kg was slightly below the criteria, the calculated 705 mg/kg F3 PHC concentration was approximately half the limit.

- Treatment #P3: *Uncontaminated Commercial Bog Peat*

  On Day 0 and 300, the total F3 in the uncontaminated commercial bog peat exceeded the CWS PHC fine soil criteria with respective concentrations of 2,273 mg/kg and 1,707 mg/kg. However, the Day 0 and 300 calculated F3 PHC concentrations were at a level one quarter of the criteria with respective concentrations of 315 mg/kg and 370 mg/kg.

Figure 4: Crude oil contaminated peat and sand experiments – Comparisons of total measured F3 vs. calculated concentrations originating from crude oil



[1]CCME Canada Wide Standard for PHC in Soil, Tier 1 fine surface soil criteria for agricultural/residential/parkland land uses in potable groundwater conditions (CCME 2008)

[2]P1-commercial bog peat + 19,608 mg/kg TPH oil; P2-Lakeland fen peat + 2,942 mg/kg TPH oil; P3-uncontaminated commercial bog peat; P4-uncontaminated Lakeland fen peat; S5-sand + 2,942 mg/kg TPH oil + bacteria broth; S6-uncontaminated sand + bacteria broth; S7-uncontaminated sand blank

[3]Nominal crude oil F3 concentrations (mg/kg) spiked into soil treatments on Day 0

[4]The 1300 mg/kg fine soil guideline applies to P1, P2, P3, P4. The 300 mg/kg course soil guideline applies to S5.

- Treatment #P4: *Uncontaminated Lakeland Fen Peat*

  The uncontaminated Lakeland fen peat total F3 was slightly above the CWS PHC fine soil criteria on Day 0 and slightly below the criteria on Day 300 with respective concentrations of 1,480 mg/kg and 1,020 mg/kg. The respective Day 0 and Day 300 calculated F3 PHC concentrations of 431 mg/kg and 262 mg/kg were one quarter and one third of the criteria.

- Treatment #S5: *Sand + 2,942 Whole Crude Oil + Bacteria Broth + Inorganic Nutrients*

  The S5 treatment was spiked with whole crude oil with a target F3 PHC concentration of 1,500 mg/kg. The Day 0 total F3 and corrected F3 PHC concentrations were 1,165 mg/kg and 1,159 mg/kg respectively. These concentrations were 4 times higher than the 300 mg/kg CWS PHC course soil criteria. The Day 300 total F3 and corrected F3 PHC respective concentrations of 201 mg/kg and 154 mg/kg did not exceed the criteria.

CONCLUSIONS

General conclusions are as follows:

i) The maximum possible F3 petroleum calculation can be applied to petroleum products that do not heavily dominate the F3b carbon range, such as diesel and crude oils.

ii) The calculation can only be applied if the F3a:F3b distributions are known for the petroleum spill source.

iii) Degree of weathering is an important factor that can increase F3b percentage distributions in crude oils. Diesel oil weathering and biodegradation patterns will be discussed in the subsequent Part II report.

iv) Specialized forensics testing would be necessary to identify petroleum sources and/or weathering stages in undocumented and/or older spill sites.

Crude Oil Contaminated Peat and Sand Experiments

The crude oil experiments confirmed that the total F3 concentrations in the uncontaminated peat falsely exceeded the PHC soil criteria. The crude oil F3a:F3b signature patterns were successfully used to reduce the maximum possible crude oil concentrations to levels that were less than one third of the F3 criteria.

The maximum possible F3 concentration from crude oil calculation is most easily applied to fresh spill sites where the petroleum source product can be analyzed for F3a:F3b distribution patterns. However, the contaminated sand treatments demonstrated that the F3b distributions became more dominant over time. The contaminated sand treatment degraded from 1,165 mg/kg on Day 0 to 201 mg/kg on Day 300. During that time, the F3a:F3b distributions in the contaminated sand shifted from 47%:53% to 31%:69%. This data demonstrates that understanding F3a:F3b distributions in degraded crude oils is essential to evaluating older spill sites.

The F3 petroleum concentration calculation could only be applied to abandoned contaminated sites if preliminary forensics testing is able to conclusively identify the petroleum product and stage of weathering. These results will be included in the Part II report.

Background Soil Survey

The background soil survey identified a wide range of F2, F3 and F4 concentrations. Only the F3 concentrations approached the CWS PHC fine soil criteria with a range of 26 to 1,431 mg/kg. Regardless of the concentrations, F3b dominated with distributions ranging from 80% to 99%. These data indicate that the calculated F3 PHC method could be effectively used to eliminate false F3 soil criteria exceedences in crude oil and diesel contaminated sites.

Fresh Crude Oil Survey

The F3a:F3b distributions were relatively equal in the thirteen fresh crude oils, with median values of 46%:54% and a standard deviation of 3%. The F3b distributions ranged from 48% to 59%, which indicates that the F3 petroleum concentration calculation could be effectively used for the 13 fresh crude oils. Additional research is needed to document the effects of weathering on the F3a:F3b distributions in crude oils.

Preliminary Diesel Invert and Manure Biopile Evaluation

The biopile evaluation determined that the 816 mg/kg F3 concentration in the uncontaminated manure was elevated but did not exceed the CWS PHC fine soil criteria. The F3a:F3b distributions were 16%:84% in the uncontaminated manure and 89%:11% in the diesel invert. These data indicate that the F3 petroleum concentration calculation could be used to reduce false criteria exceedence issues in marginally contaminated biopiles.