



Resolving False PHC Detections in Crude Contaminated Amazon Rainforest Peat Soils

Application of Canadian BIC Index Principles



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Authors:

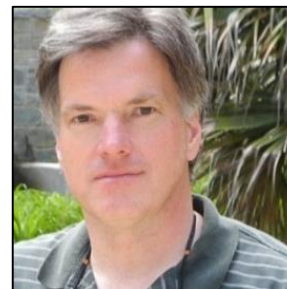
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J. Bishop



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V. Ucar



Historical Crude Oil Contamination in Peruvian Rainforest Organic Peat/Turba Soils



Rhino
Beetle





2015 Contaminated Site Study Overview

- 30 years of crude oil extraction activities contaminated a 721 hectare (ha) rainforest area.
- 17,132 soil samples were analyzed for total petroleum hydrocarbons (PHC/TPH)
- Most of the 5,569 clean and contaminated peat soil samples exceeded Peruvian PF3 (C28-C40) regulatory limit of 3000 mg/kg

What is Peat/Turba?

Peat (English); Turba (Spanish)

Saturated Soil and
Decayed Plants



+

Thousands of
Years



=

Peat/Turba



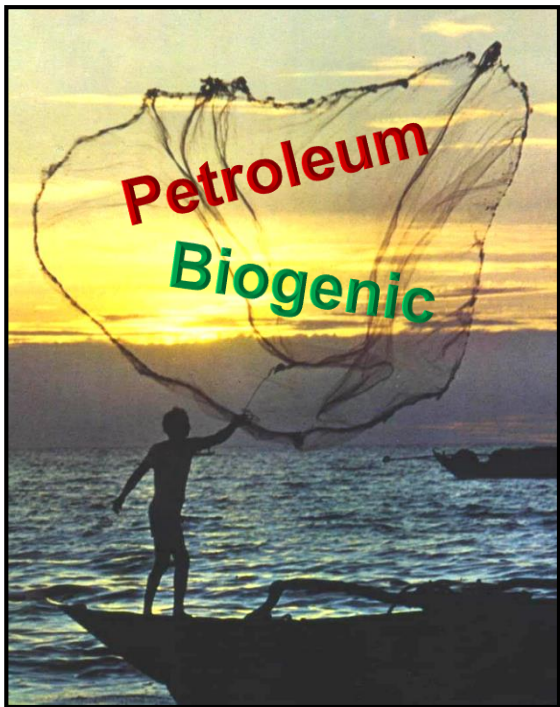
- Typically has >40% total organic carbon (TOC) content
- Natural Biogenic Organic Compounds (BOCs) are often falsely detected as Petroleum Hydrocarbons (PHCs)

Biogenic Organic Compounds are the Building Blocks of Life



- ❖ Natural carbon-based compounds biosynthesized by living organisms.
- ❖ BOC groups contain alkanes, lipids, carbohydrates, proteins, etc.

Why are Biogenic Organic Compounds Falsely Detected as PHC/TPH?



- Peruvian and Canadian laboratories use organic hexane, acetone and DCM solvents to extract PHC/TPH.
- However, background BOCs can be inadvertently extracted as well.
- Polar cleanups (e.g. silica gel) are used to reduce BOC concentrations, but they can be ineffective if oversaturated by highly organic materials such as peat (>20% total organic carbon).



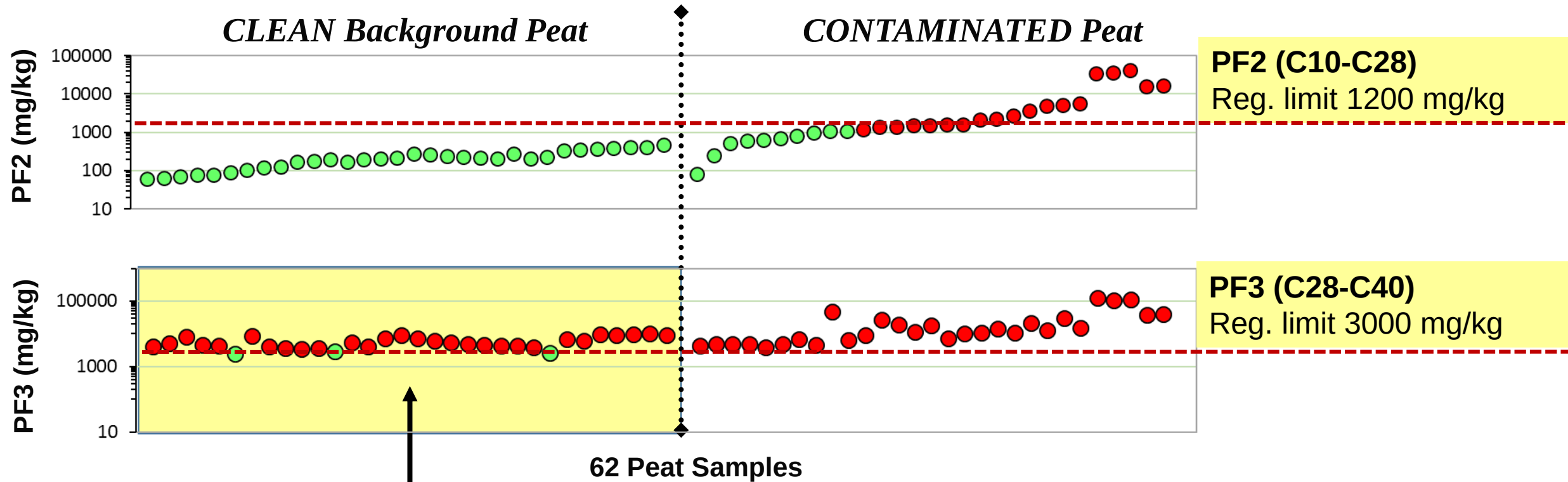
Peruvian Soil PHC/TPH Analysis Method

Adaptation of USEPA SW846 8015 Method

- Microwave extraction in acetone, hexane and dichloromethane solvents
- Silica gel cartridge cleanup of polar (biogenic) compounds
- PHC/TPH concentrations quantified by Gas Chromatography-Flame Ionization Detector (GC-FID) on a 3 minute run
- Peruvian PF2 (C10-C28) regulatory limit 1,200 mg/kg
- Peruvian PF3 (C28-C40) regulatory limit 3,000 mg/kg



Peru Soil Data Examples: True and False Exceedences of Regulatory Limits in Clean and Contaminated Peat Soils



Clean Peat Samples – Only PF3 exceedences; No PF2 exceedences

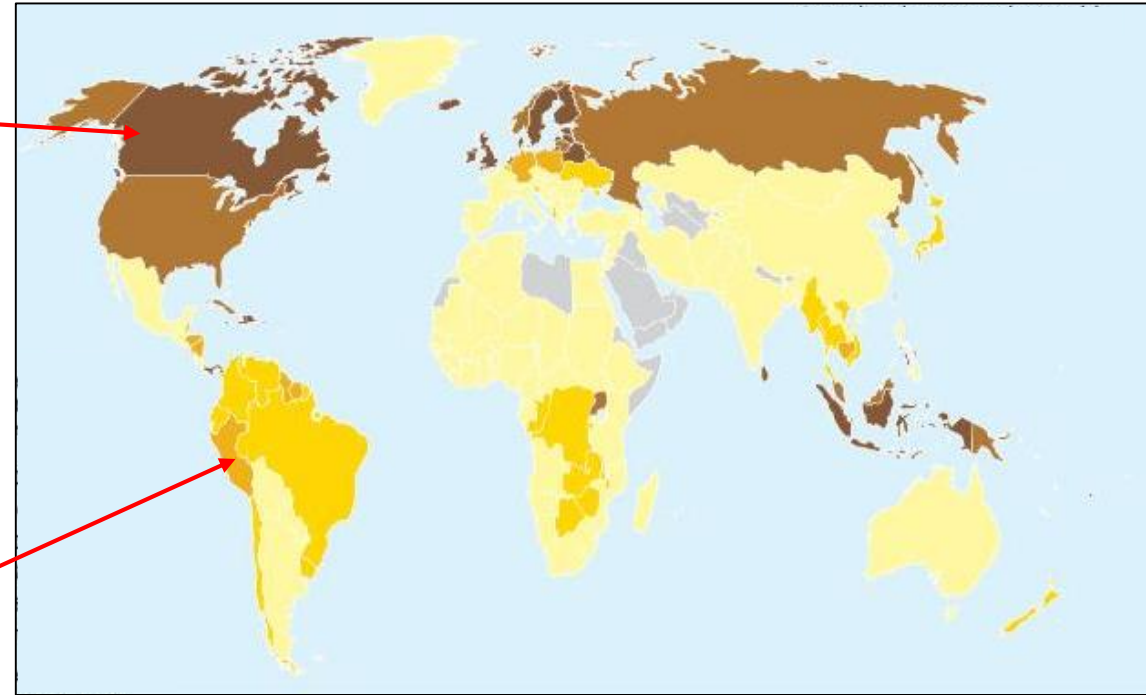
Peat Soils are Distributed Throughout the World

Canadian
Peat



*Same Carbon Distribution
Patterns Provided the Basis of
the Peru Study Approach*

Peruvian
Peat



Source: Parish et al. 2008

 <0.5%

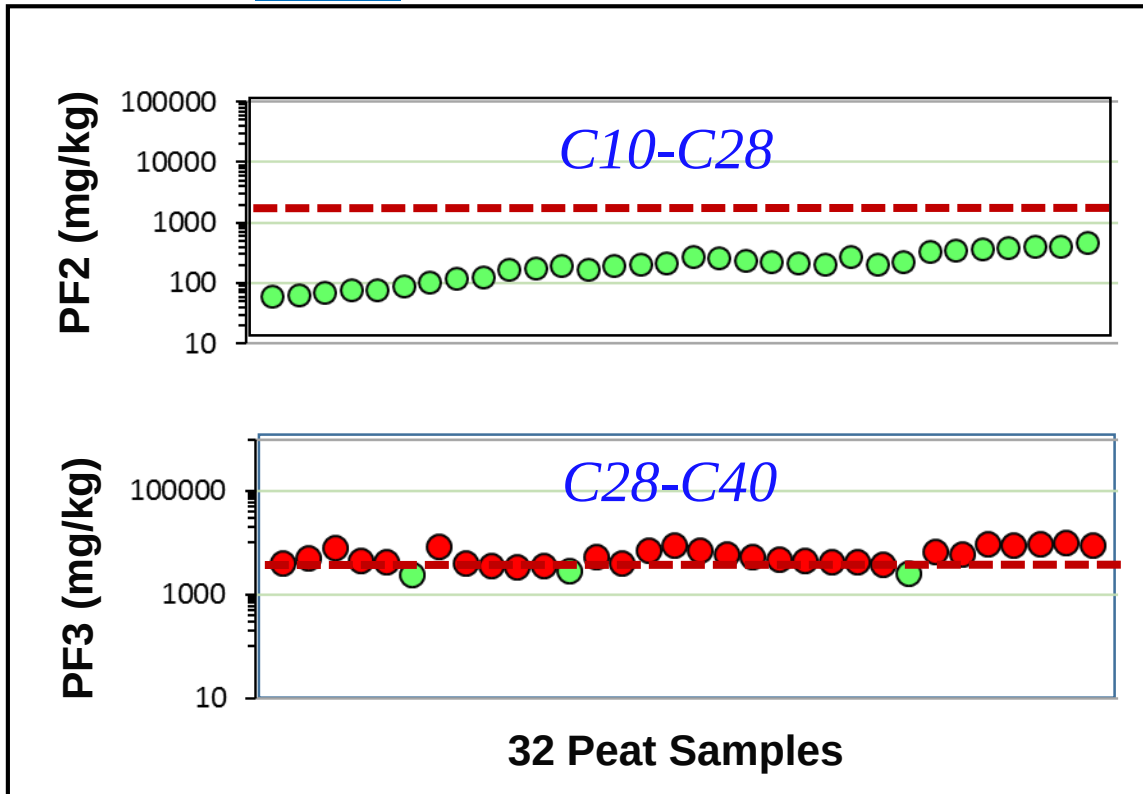
 0.5-5%

 5%->10%

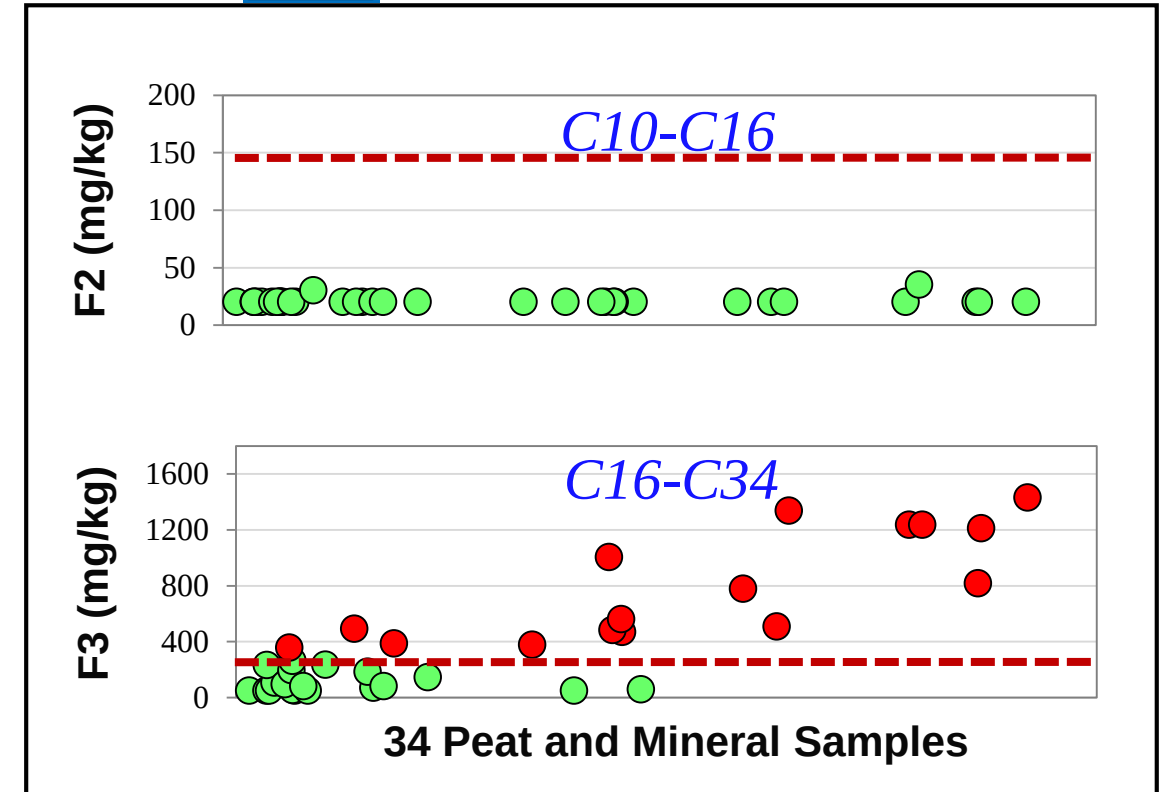
Comparison Of Peruvian and Canadian Clean Soil Exceedences of Regulatory TPH/PHC Limits



Clean Peruvian Peat



Clean Canadian Peat



● Does not Exceed Regulatory Limit

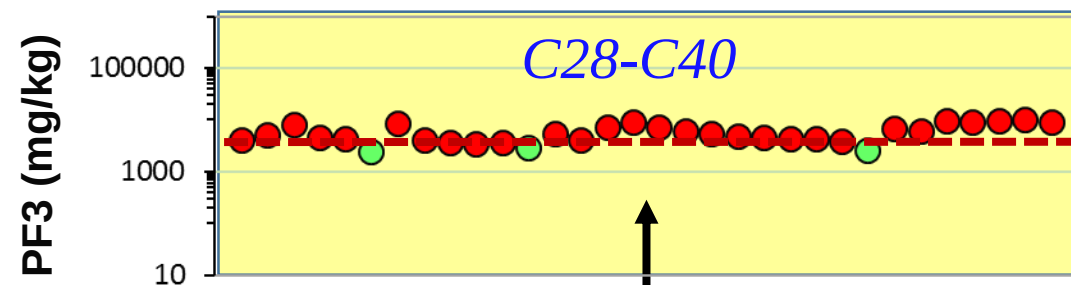
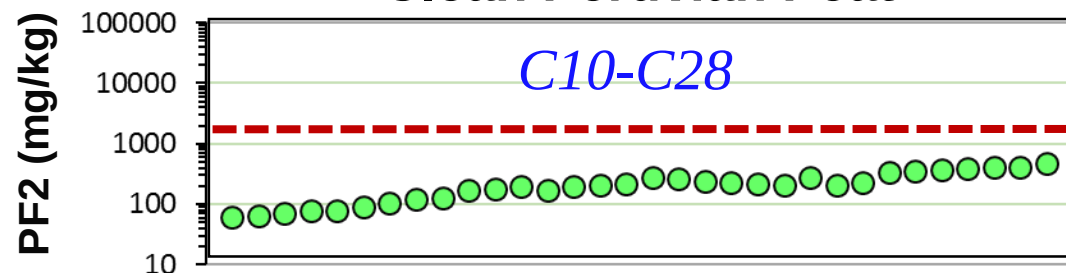
● Exceeds Regulatory Limit



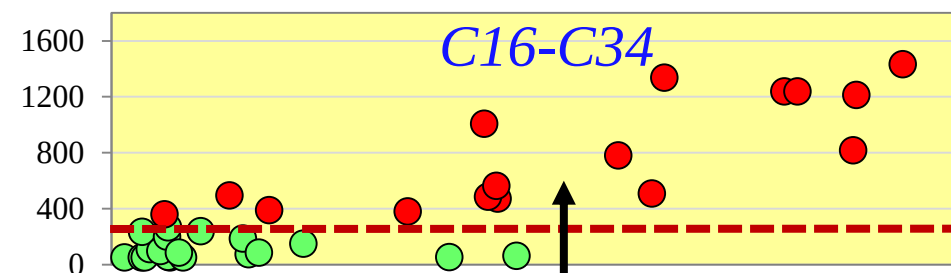
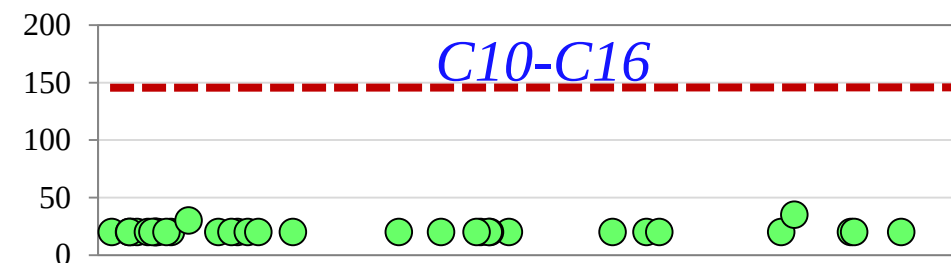
Comparison Of Peruvian and Canadian Clean Peat Exceedences of Regulatory TPH/PHC Limits



Clean Peruvian Peat



Clean Canadian Peat



Only heavy carbon ranges exceeded regulatory limits

Resolution of Peruvian False Exceedences through Canadian BIC Index Principles



What is the Biogenic Interference Calculation (BIC) Index?



Pronounced “BIC” like the pen

- ❖ A calculation for determining if biogenic interferences have caused organic (peat) samples to falsely exceed the Canadian Council of Ministers of the Environment (CCME) F3 PHC 300 mg/kg F3 PHC soil guideline.
- ❖ CCME Fractions: F2 (C10-C16), F3 (C16-C34), F4 (C34-C50); BIC Index Sub-fraction F3b (C22-C34)
- ❖ $[F2/(F2+F3b)] \times 100$
- ❖ $<10\%$ = **false** PHC exceedence
- ❖ $\geq 10\%$ = **true** PHC exceedence

Biogenic Interference Calculation (BIC) Index Research & Development History



Developed Through 7-Year PhD Study

2007-2010

Contamination Experiments



2007-2015

Clean Background Soil Surveys



2005-2017

Contaminated Site Studies



Publications



Environmental Toxicology and Chemistry, Vol. 32, No. 10, pp. 2197–2206, 2013
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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

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ERIC C. GRUNSKY,^{||} and D. GEORGE DIXON[†]



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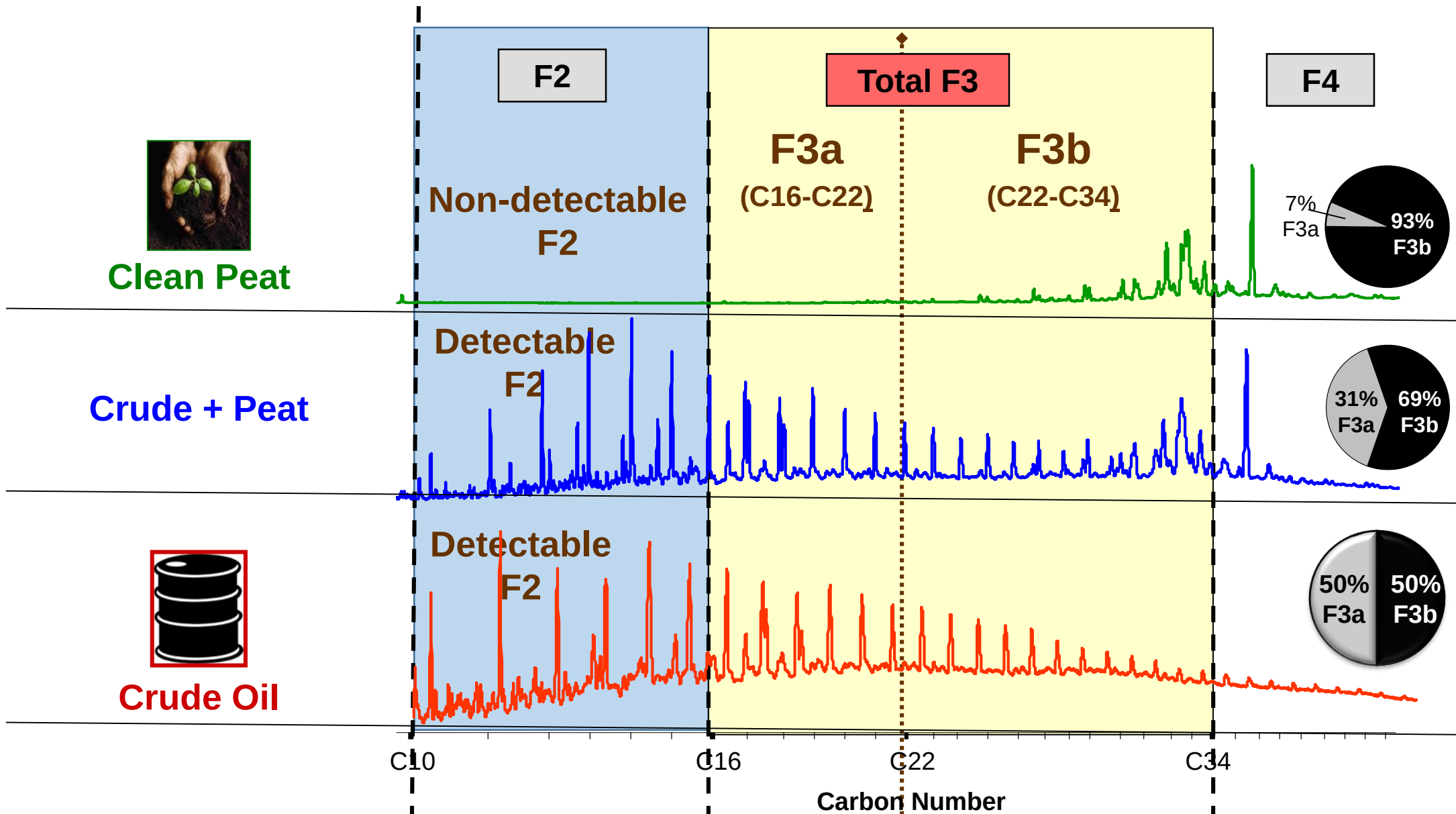
Environmental Chemistry

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

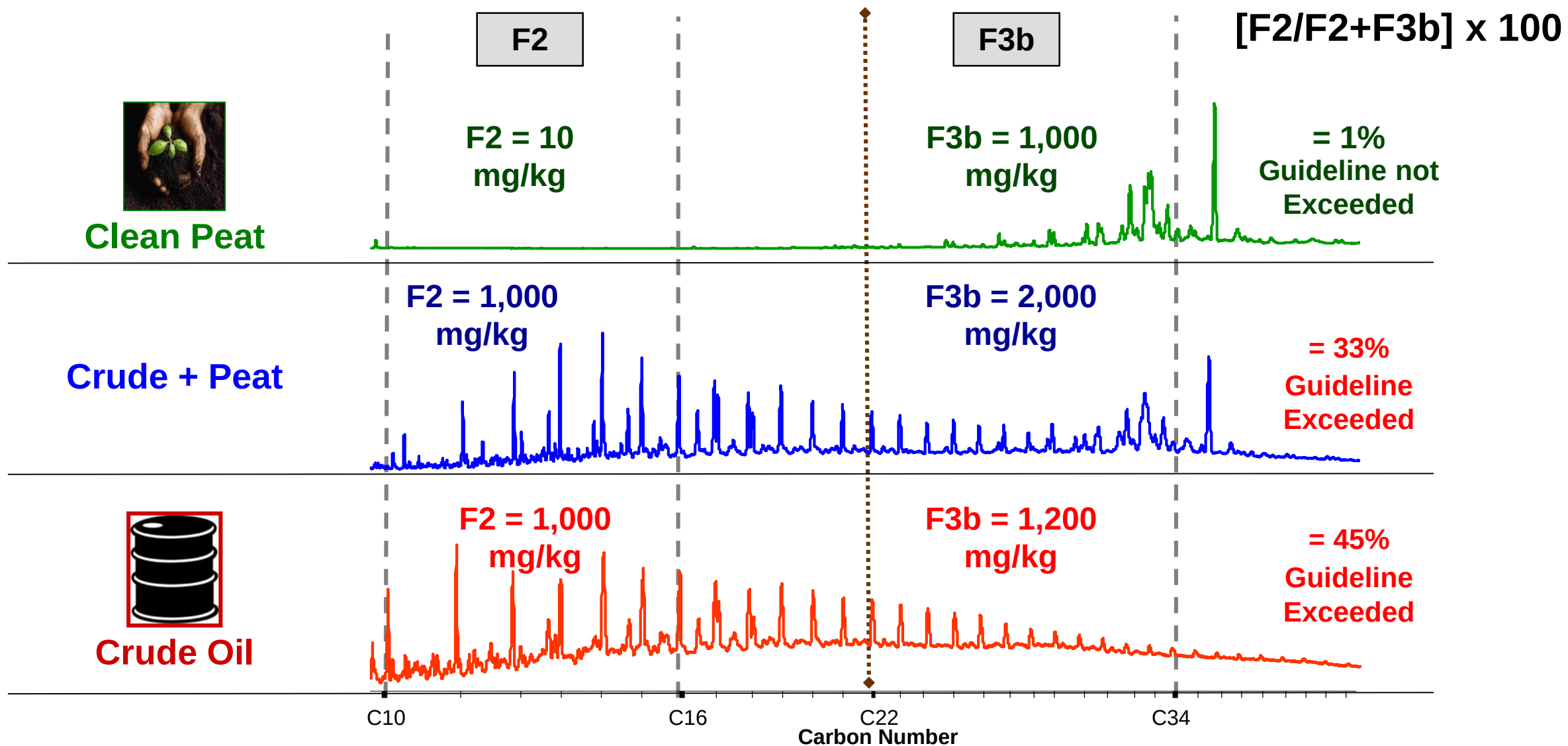
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Primary BIC Index Principle:

Clean Soils Have Negligible F2 (C10-C16) and High F3b (C22-C34)



Example of BIC Index Calculation for Crude Oil PHCs





Comparison of Canadian and Peruvian GC-FID Chromatograms





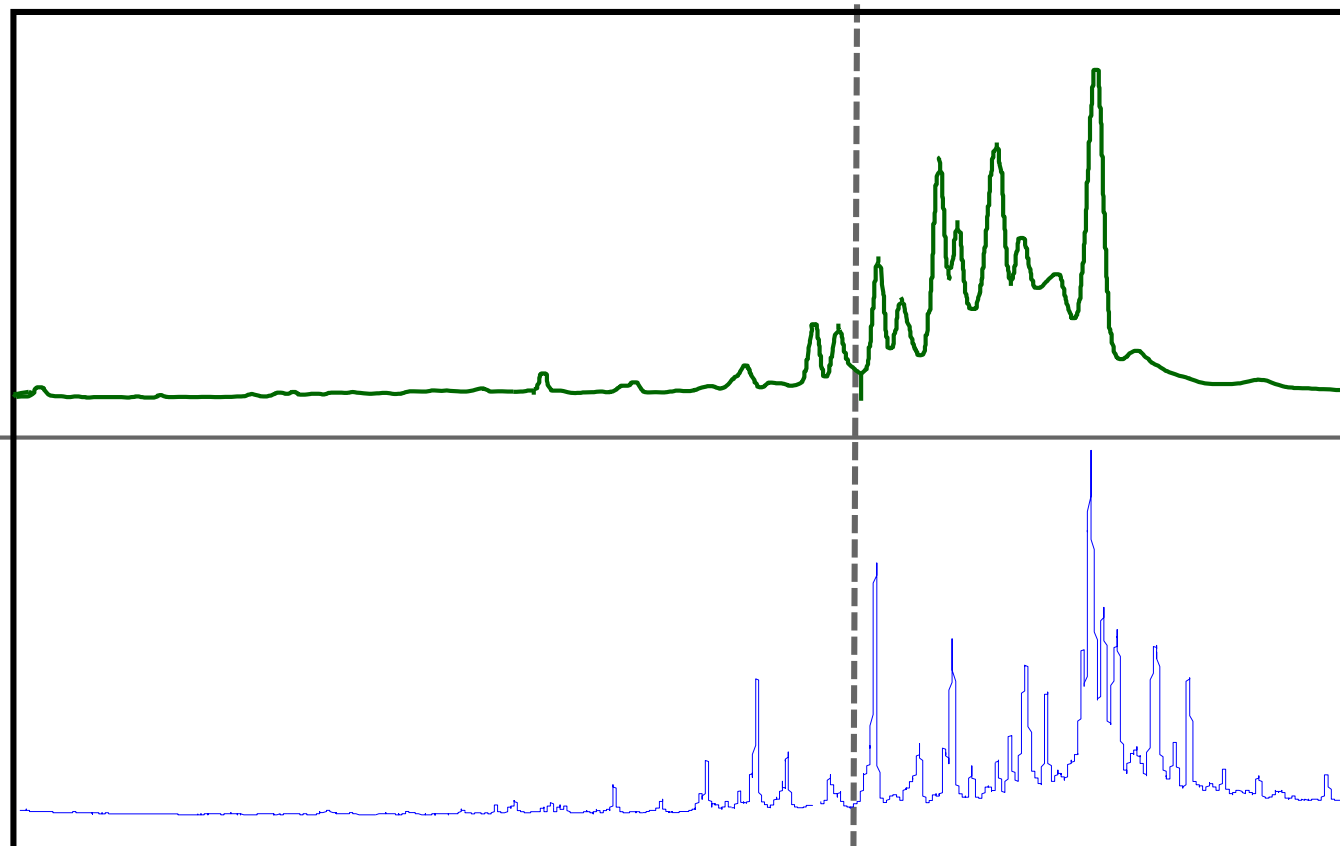
Peru versus Canadian Samples – Similar Clean Peat GC-FID Patterns

Peru



PF2 (C10-C28)

PF3 (C28-C40)



Less defined due to
3 minute run time

Alberta Canada



More defined due to
18 minute run time

C10

C28

C40

Carbon Range



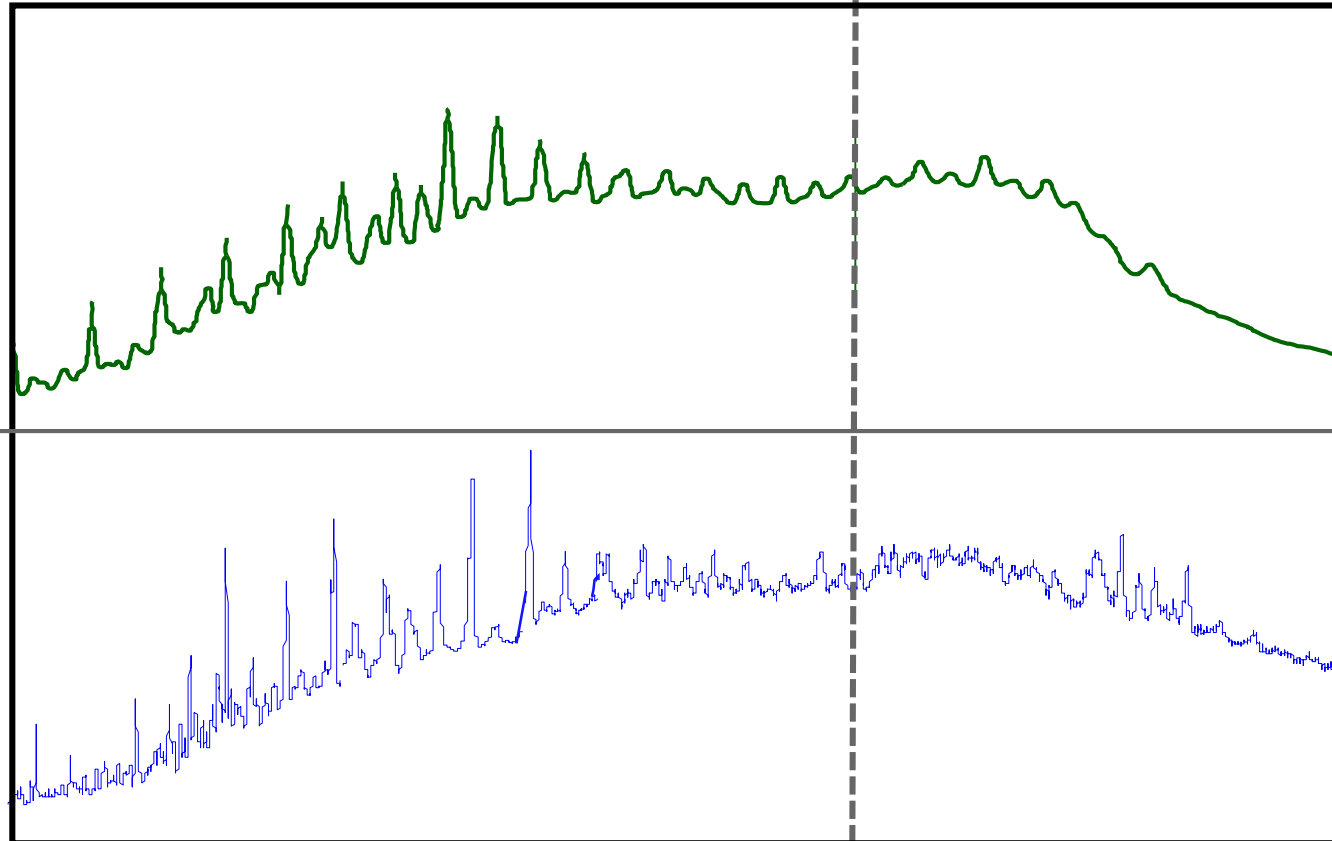
Peru versus Alberta Samples – Similar Weathered Crude Oil Patterns

Peru



PF2 (C10-C28)

PF3 (C28-C40)



Less defined due to
3 minute run time

Alberta Canada



More defined due to
18 minute run time

C10

C28

C40

Carbon Range

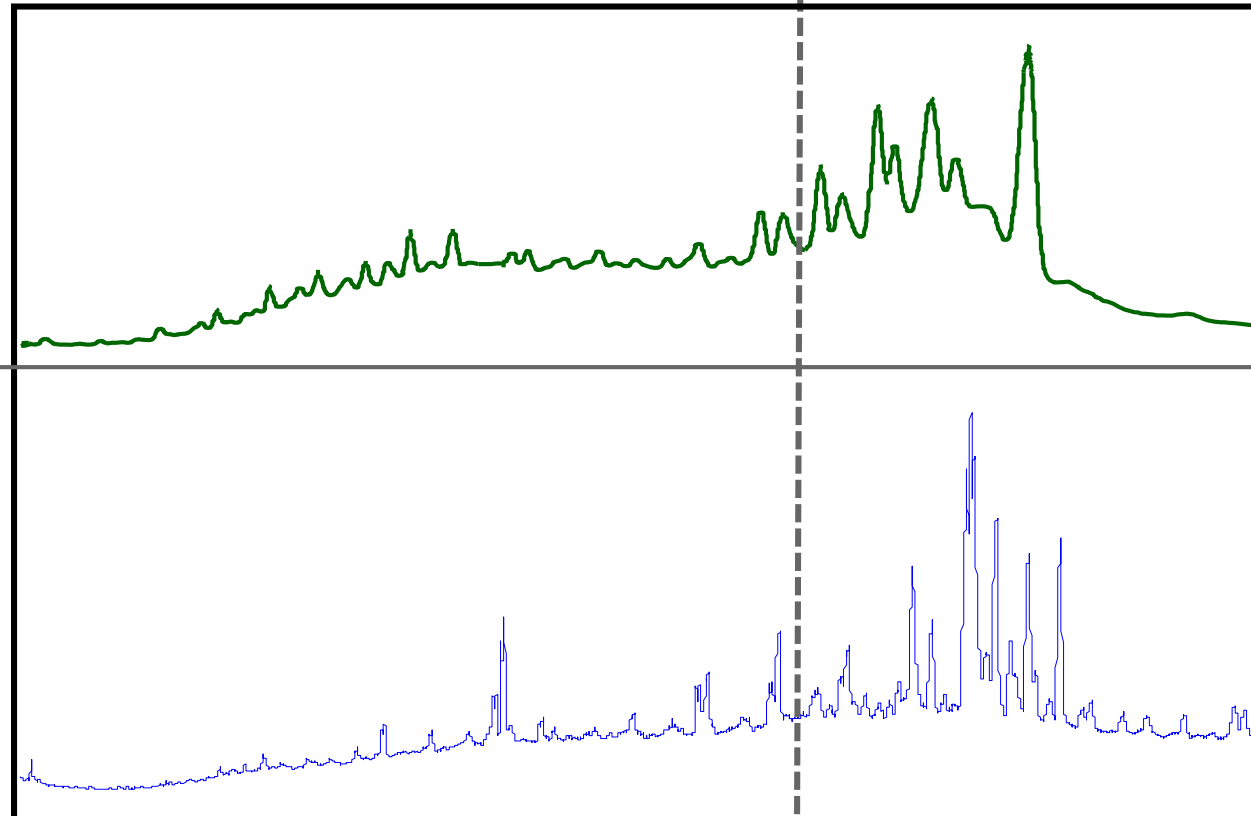
Peru versus Alberta Samples – Similar Crude Oil Contaminated Peat GC-FID Patterns

Peru



PF2 (C10-C28)

PF3 (C28-C40)



Less defined due to
3 minute run time

Alberta Canada



C10

C28

C40

Carbon Range

More defined due to
18 minute run time



Challenges of Applying Canadian BIC Index to Peruvian Peat Samples



- Different Canadian and Peruvian carbon ranges and regulatory limits
- Electronic chromatograms were essential to finding the correct Canadian BIC Index F3b sub-fraction carbon range.
- Electronic chromatograms were not available for the Peruvian samples. CH2M developed an alternative graphics software technique for calculating false exceedences of Peruvian regulatory limits.

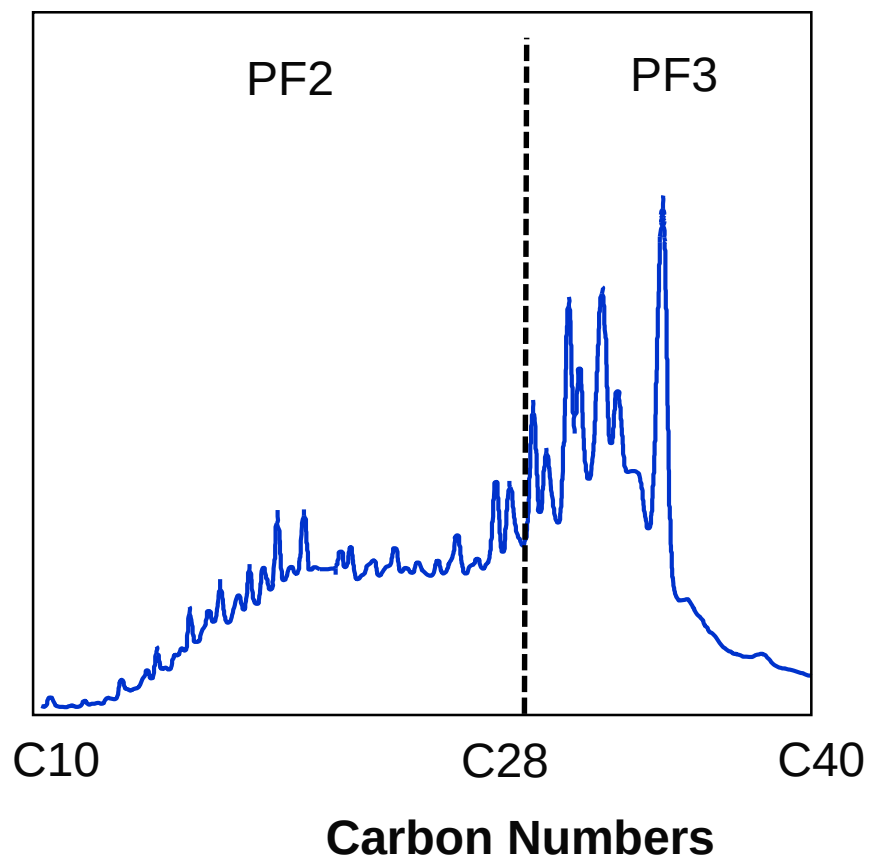
Peru Results



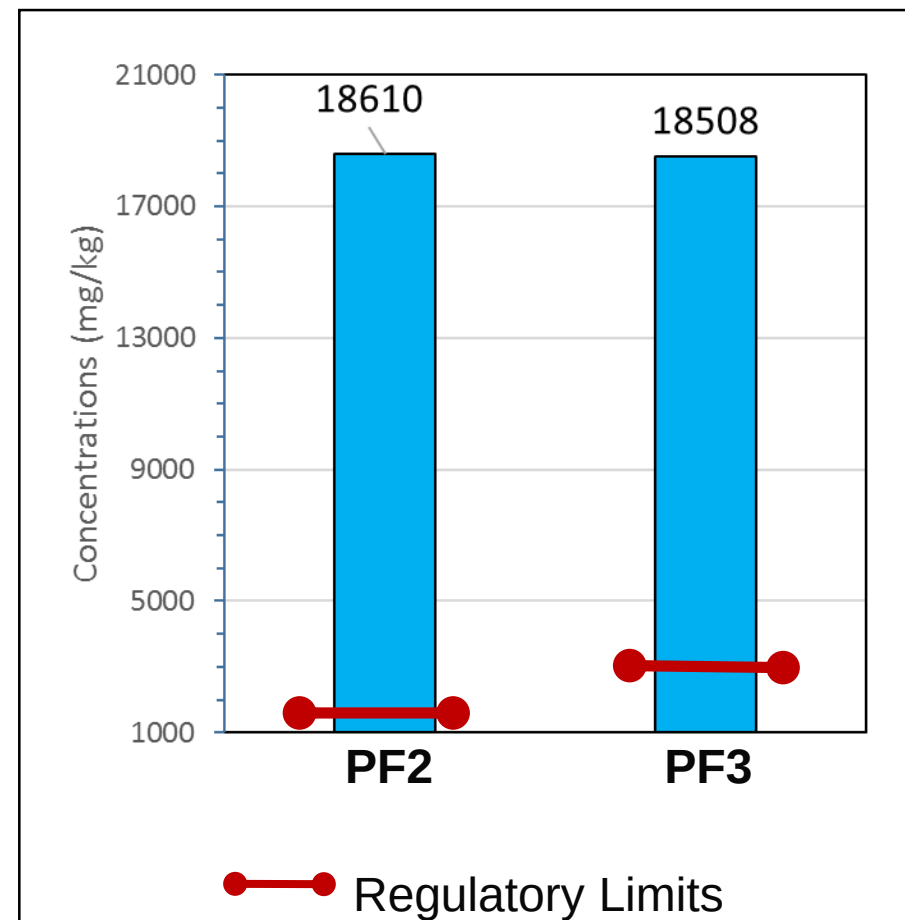


Highly Contaminated Peat

GC-FID Chromatogram



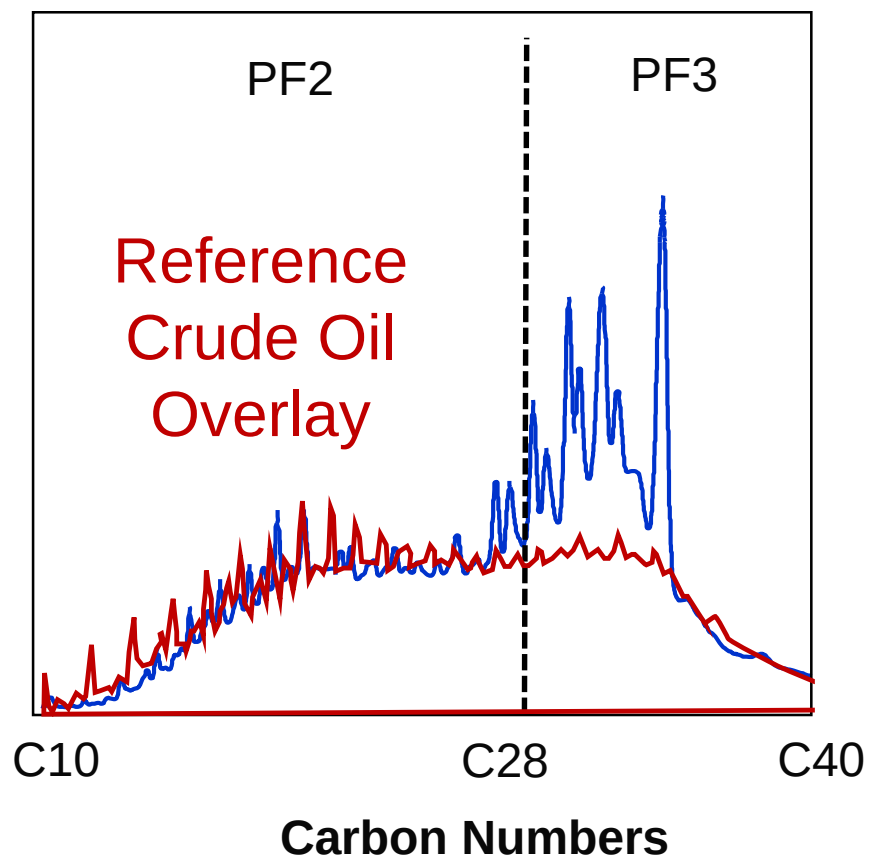
PF2 and PF3 Concentrations



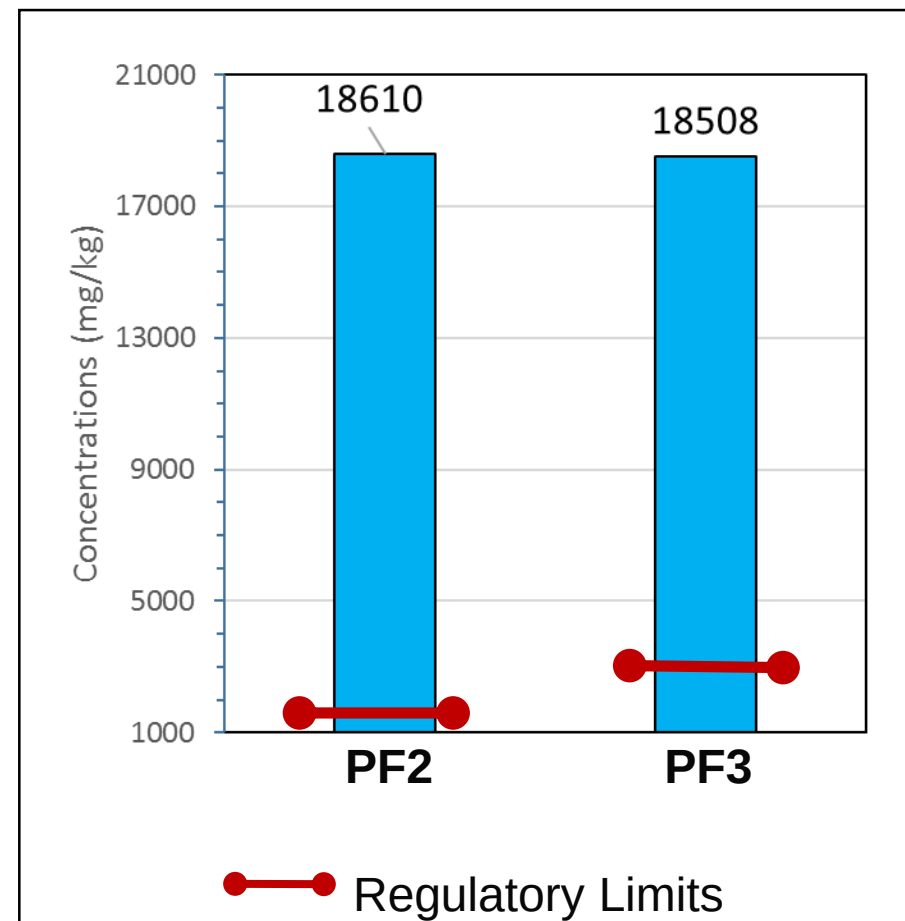


Highly Contaminated Peat

GC-FID Chromatogram



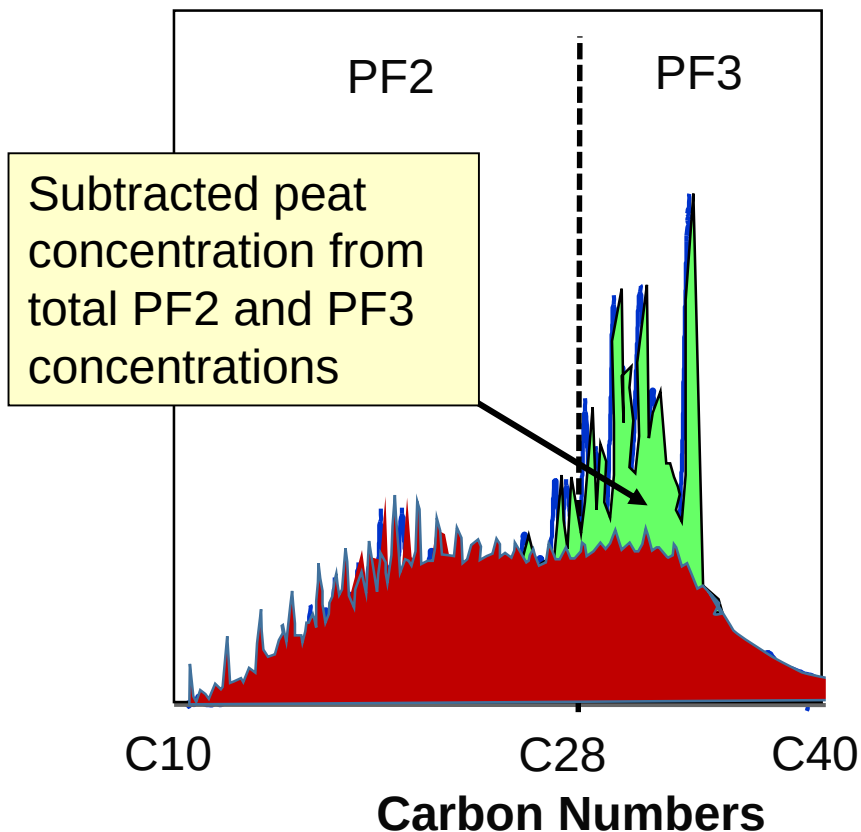
PF2 and PF3 Concentrations



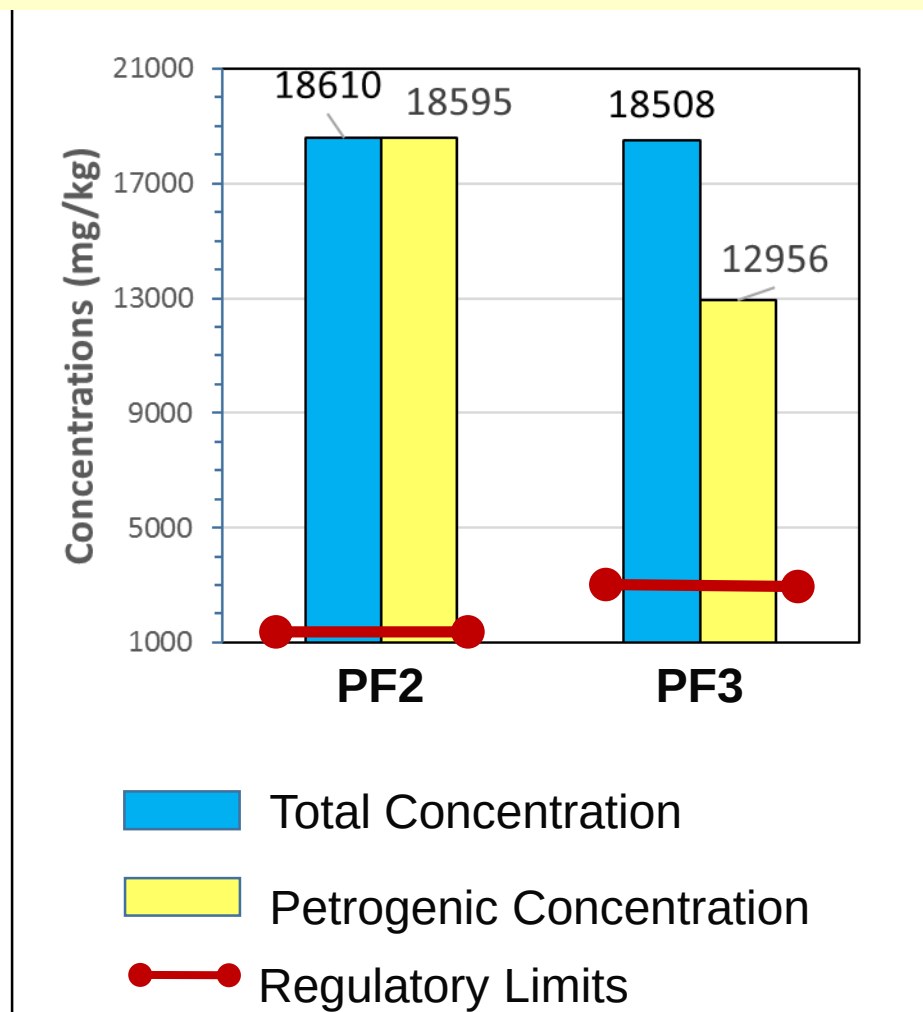


Contaminated Peat

GC-FID Chromatogram



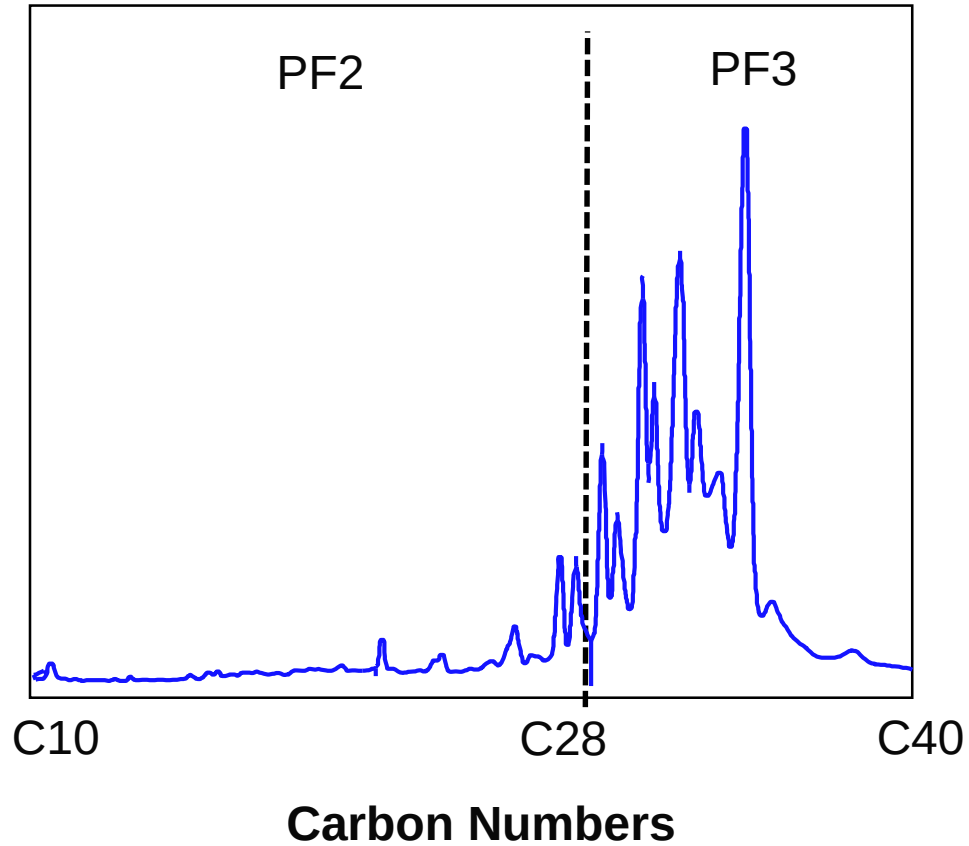
True Exceedences of Regulatory Limits



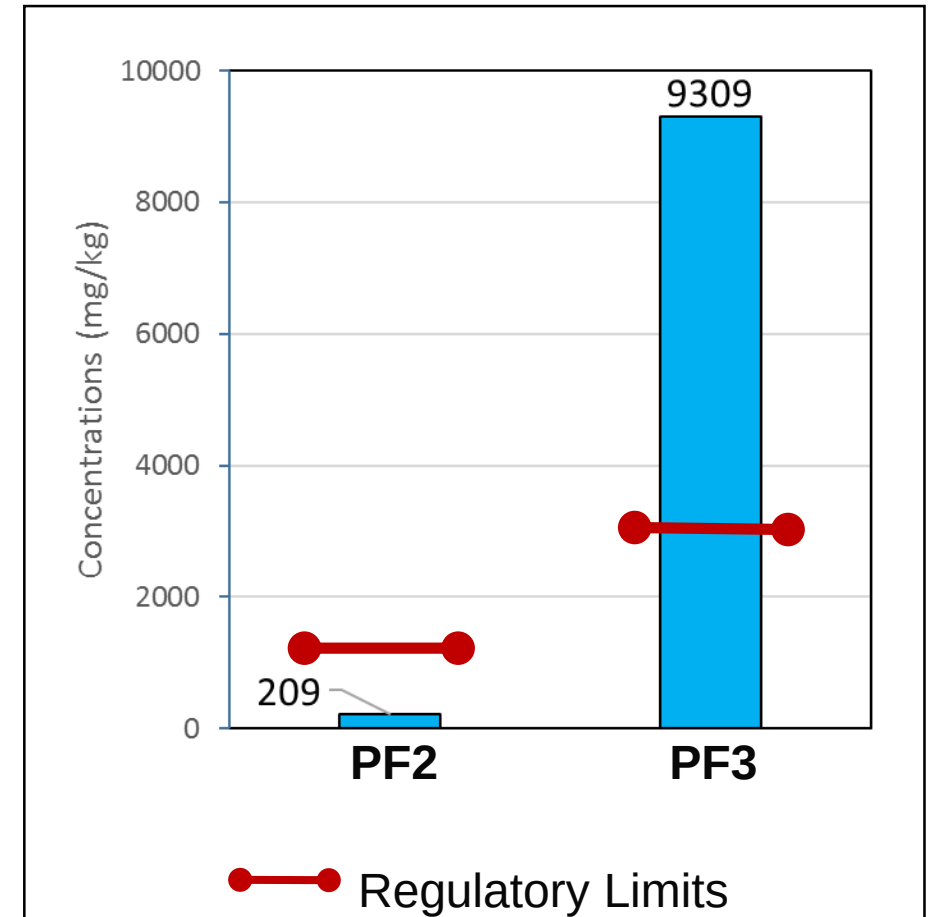


Clean Peat

GC-FID Chromatogram



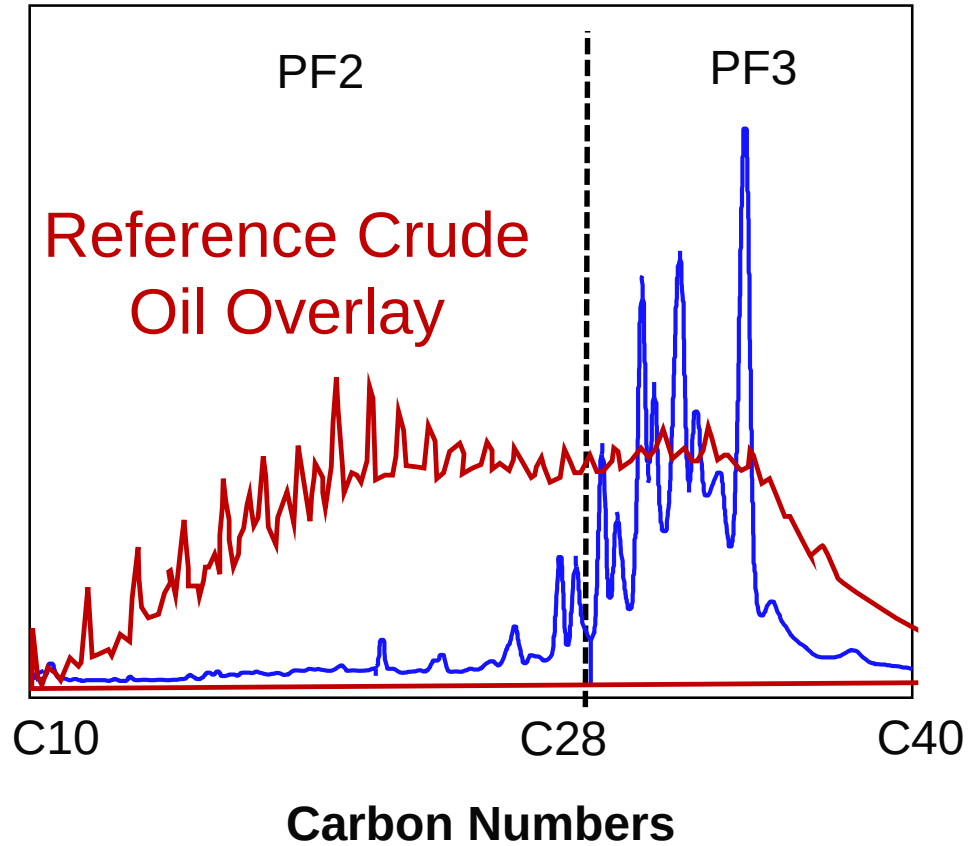
PF2 and PF3 Concentrations



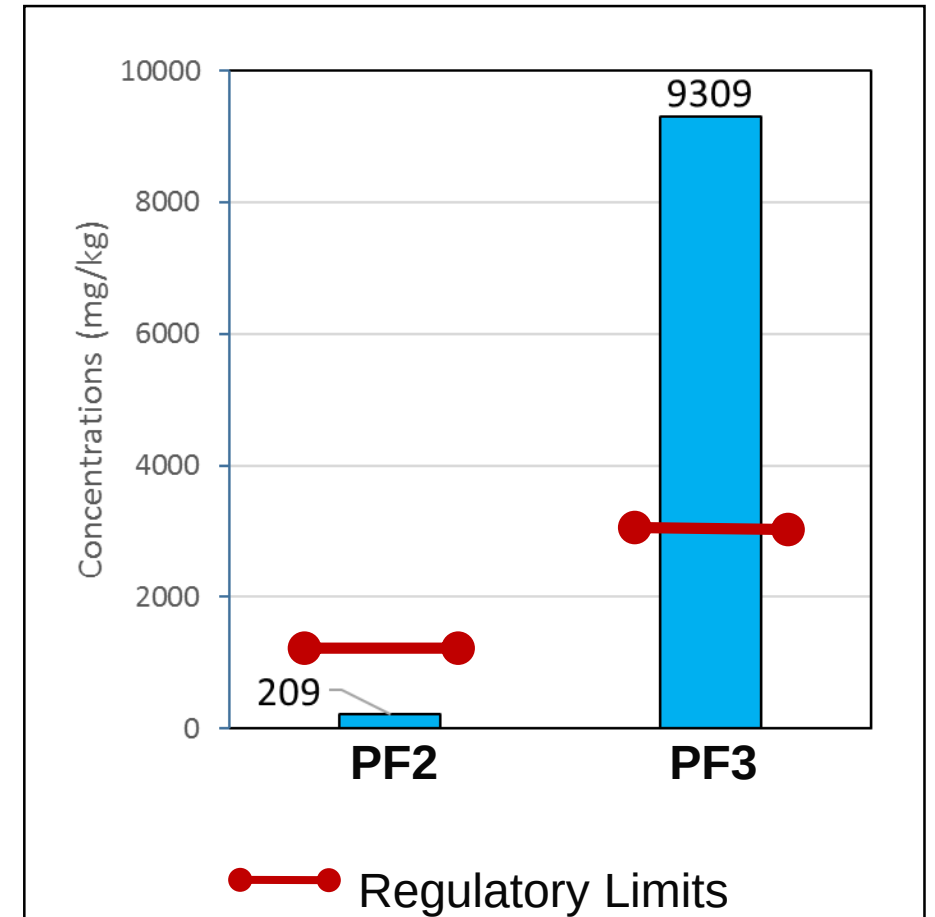


Clean Peat

GC-FID Chromatogram



PF2 and PF3 Concentrations

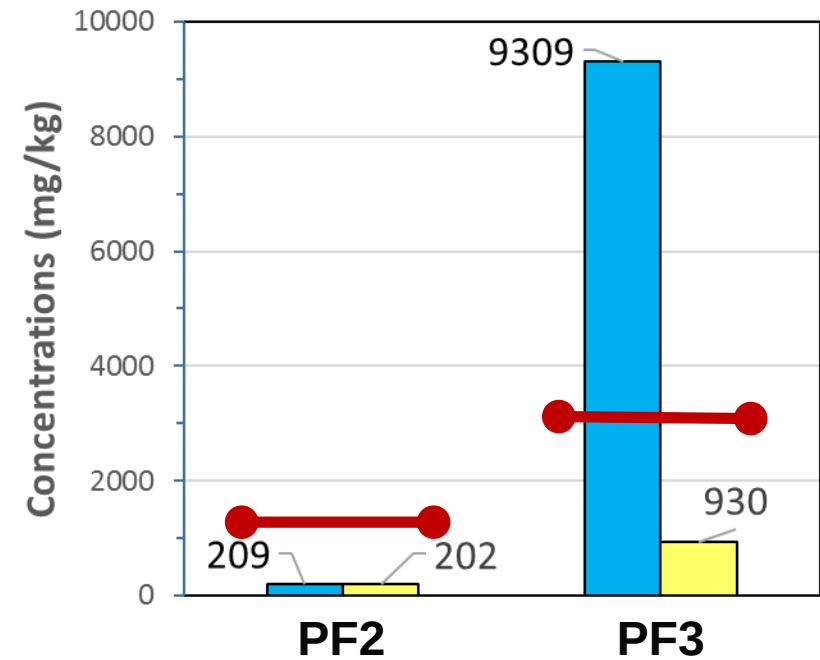
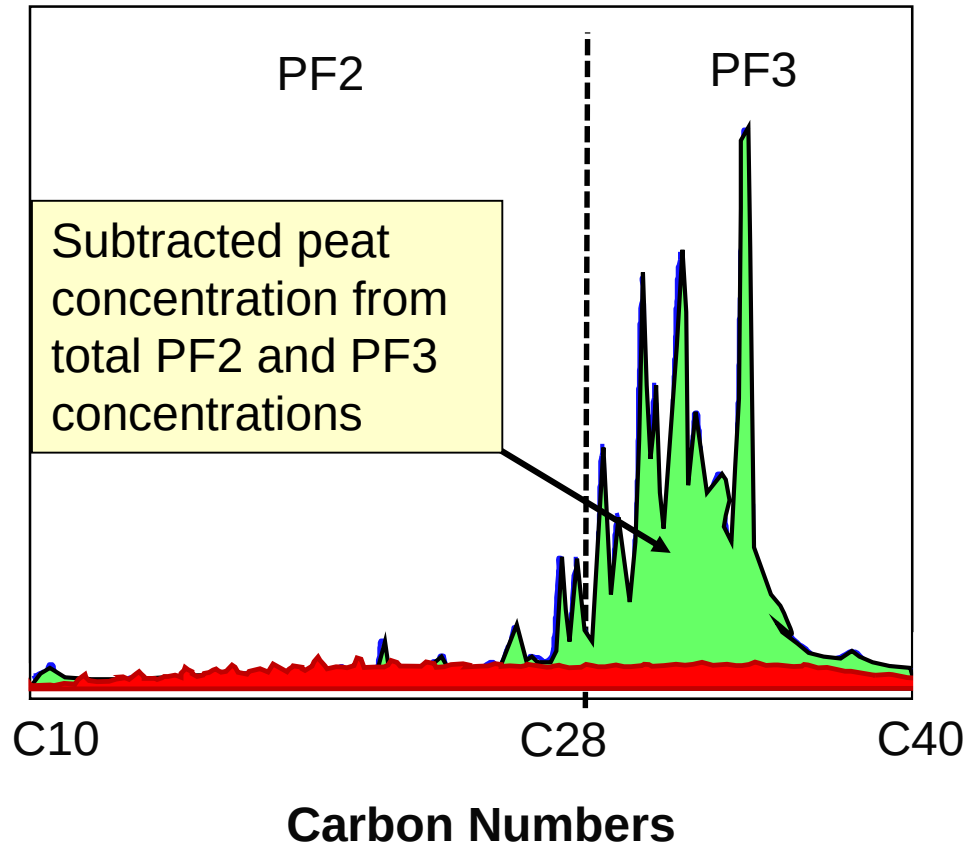




Clean Peat

False Exceedence of PF3 Regulatory Limit

GC-FID Chromatogram

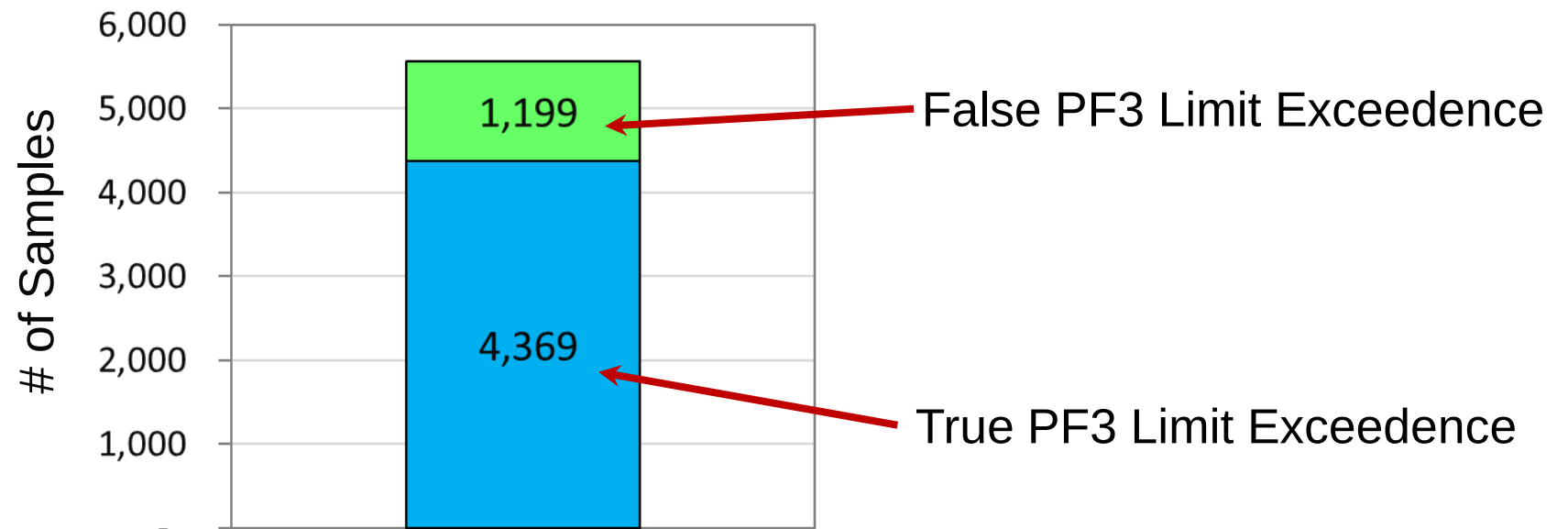


- Total Concentration
- Petrogenic Concentration
- Regulatory Limits



Summary of All Results

1,199 (22%) of 5,568 contaminated soil samples were identified as falsely exceeding the F3 regulatory limit due to background peat



Thank You

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