

# Phantom PHCs?

Using the F2:F3b ratio to eliminate false  
PHC detections in clean soils

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CH2M HILL Canada



# Research Partners



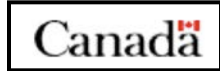
Alberta Parks and Protected Areas Division



ALS Laboratory Group



Canadian Association of Petroleum Producers, Petroleum Technology Alliance of Canada



Environment Canada Oil Spills Research Centre



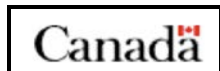
Geological Survey of Canada



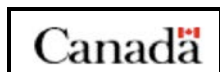
Husky Energy



Imperial Oil



Natural Sciences and Engineering Research Council



Natural Resources Canada



Orphan Well Association

- Spiked peat with crude oil to study biogenic vs petrogenic carbon patterns over a 300 day period.



- Spiked composted manure and sand with diesel oil and studied biogenic vs petrogenic carbon patterns over a 300 day period.





# 2009: Background PHC survey of 34 sites located in Alberta, BC and Newfoundland

- **Canadian Geologic Survey collected soils samples and shipped them to ALS Laboratories in Waterloo for PHC, PAH and grain size analysis.**



# What are biogenic organic compounds?



BOCs are carbon-based compounds that are naturally biosynthesized by living organisms. BOCs are ubiquitous throughout the environment.

BOC groups containing C, H and O include: lipids, carbohydrates, proteins and nucleic acids.

BOC hydrocarbon groups containing only C and H include n-alkanes.

# Why are BOCs confused as PHCs?



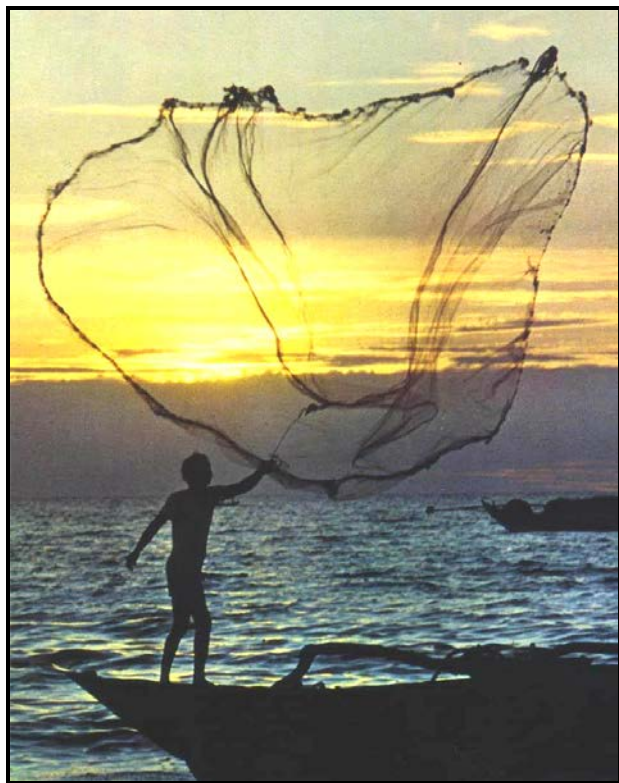
# Canadian Council of Ministers of the Environment (CCME) *Reference Method for the Canada-Wide Standard (CWS) for Petroleum Hydrocarbons (PHC) in Soil*



Methods can produce false positives in uncontaminated organic materials (e.g. peat, manure, etc.).



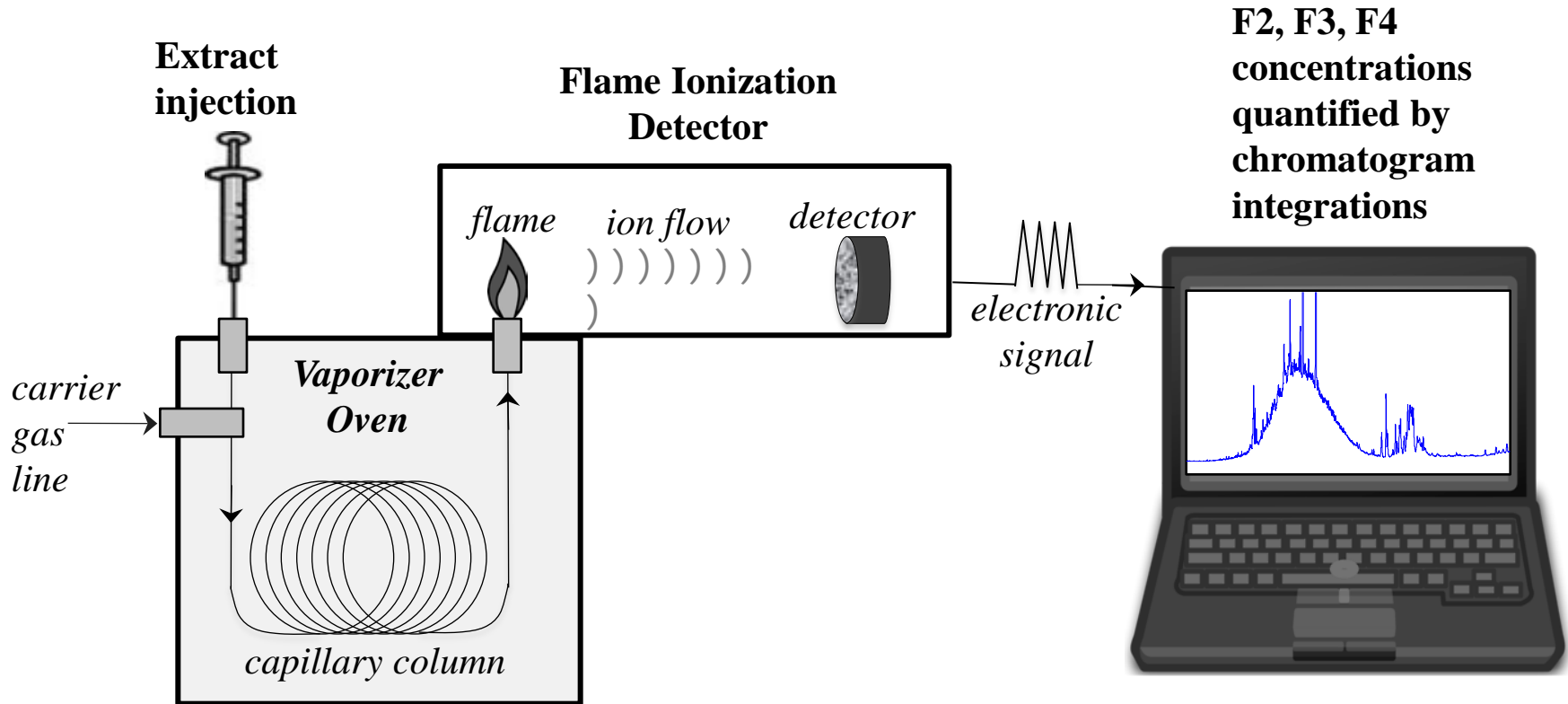
The problem is that the hexane and acetone solvents indiscriminately extract all carbon from petroleum and biological sources.



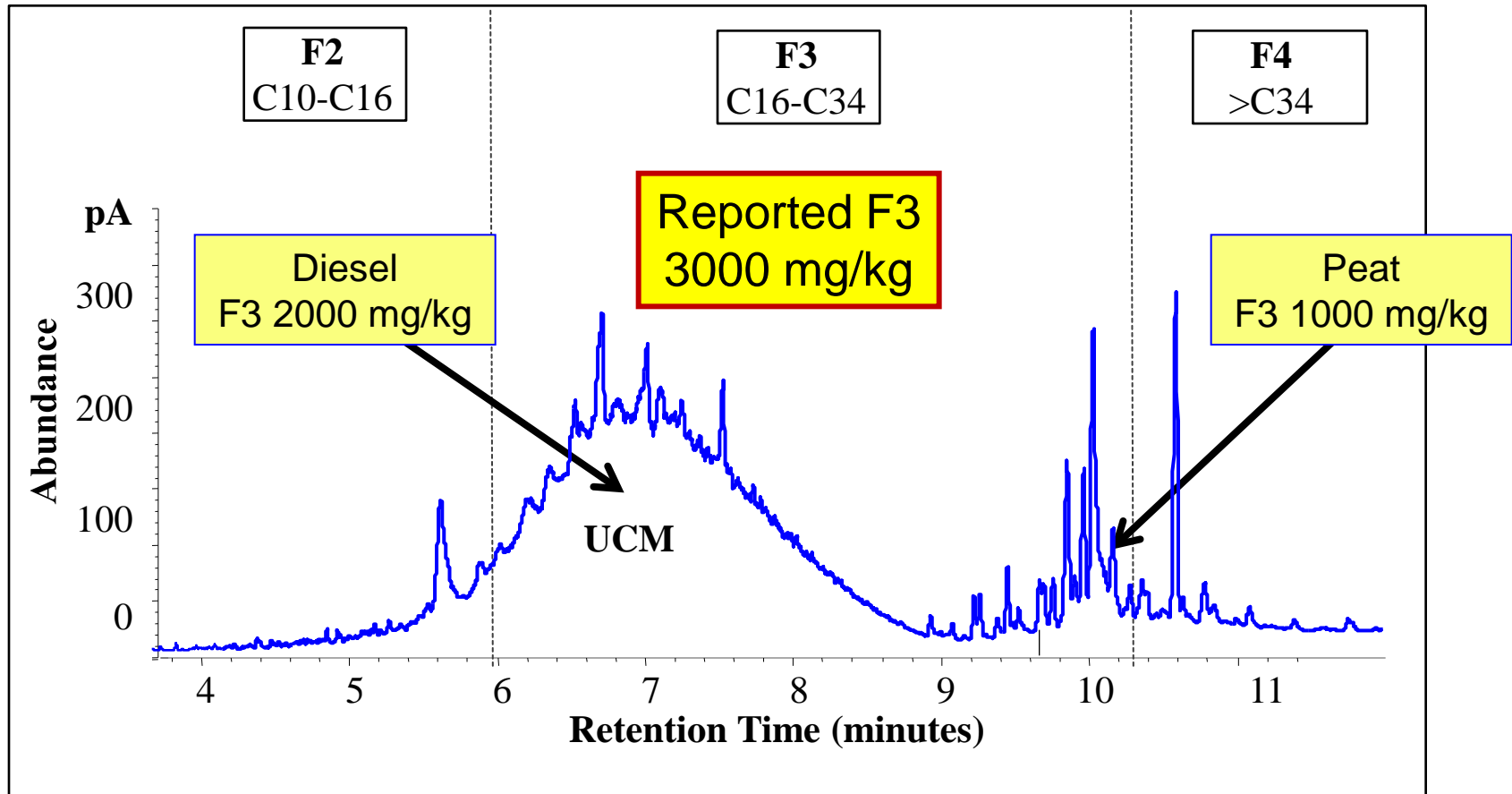
Source: thedatingangle.com

The goal is to “catch” petroleum hydrocarbons. However, background biogenic organic compounds are inadvertently “caught” as well.

# GC-FID Analysis of Sample Extract

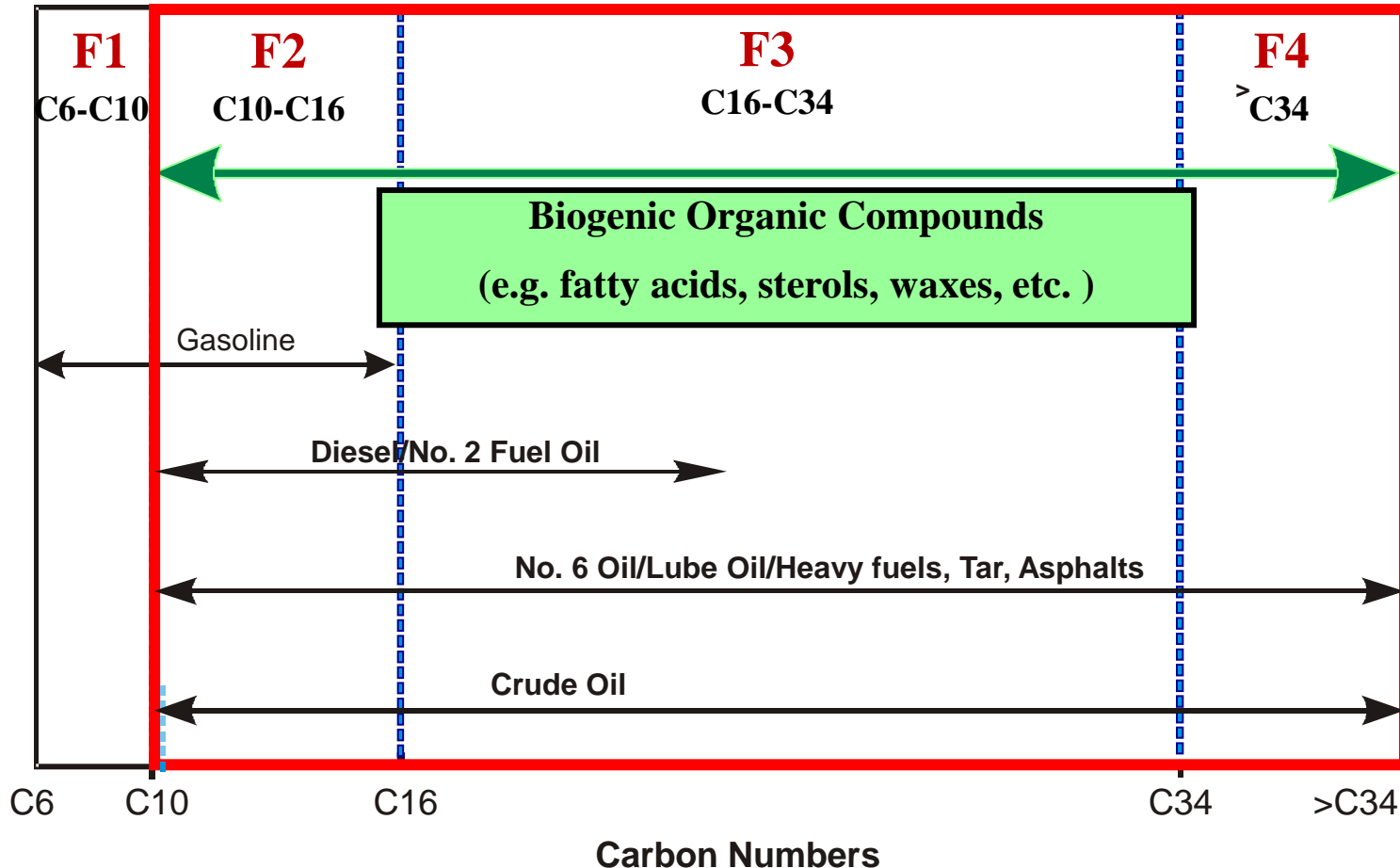


# Diesel-Spiked Peat GC-FID Chromatogram



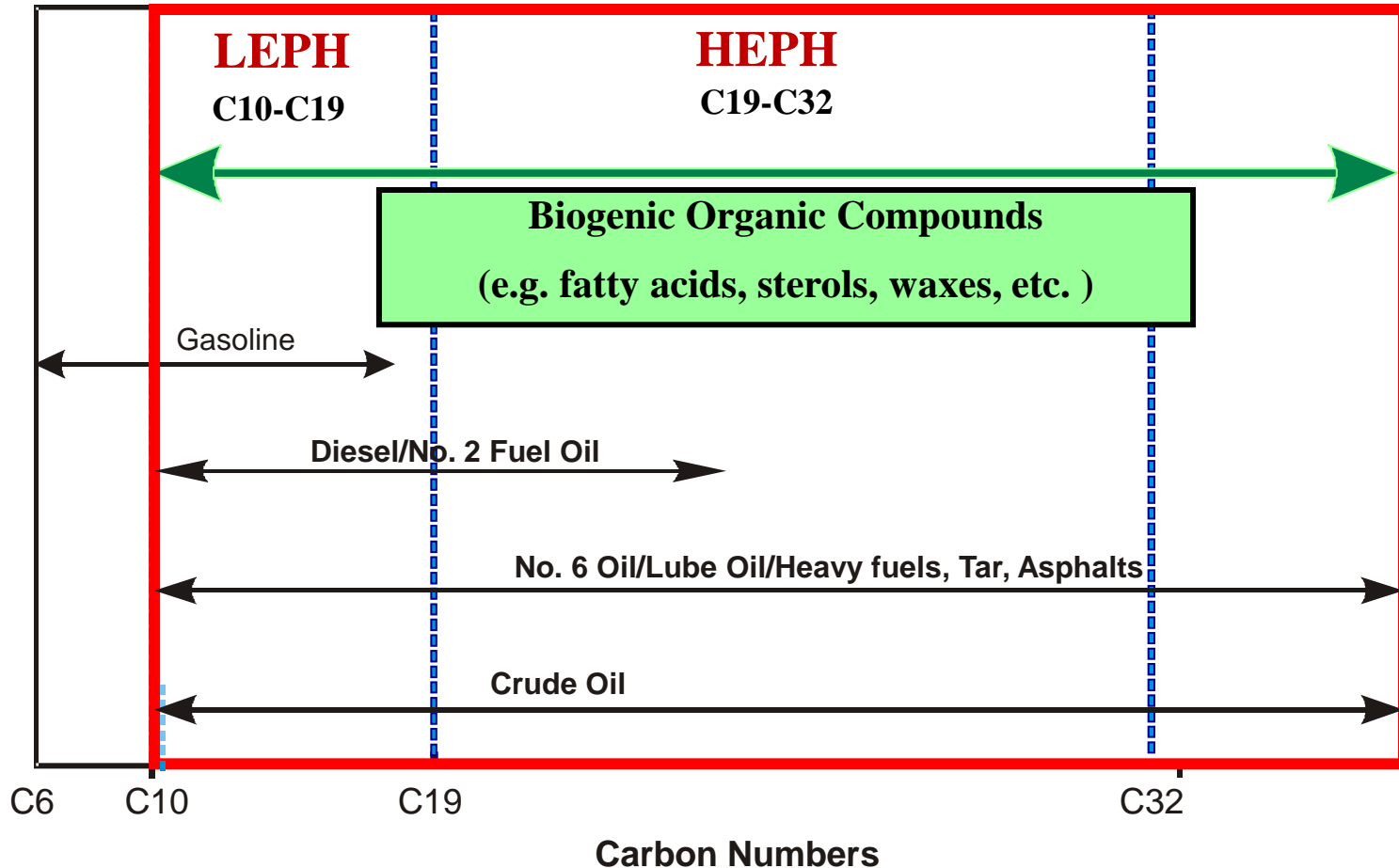
# Classification of Petroleum Hydrocarbon Sources by Carbon Number Range

## CCME Fractions F1 to F4



# Classification of Petroleum Hydrocarbon Sources by Carbon Number Range

## LEPH and HEPH Ranges

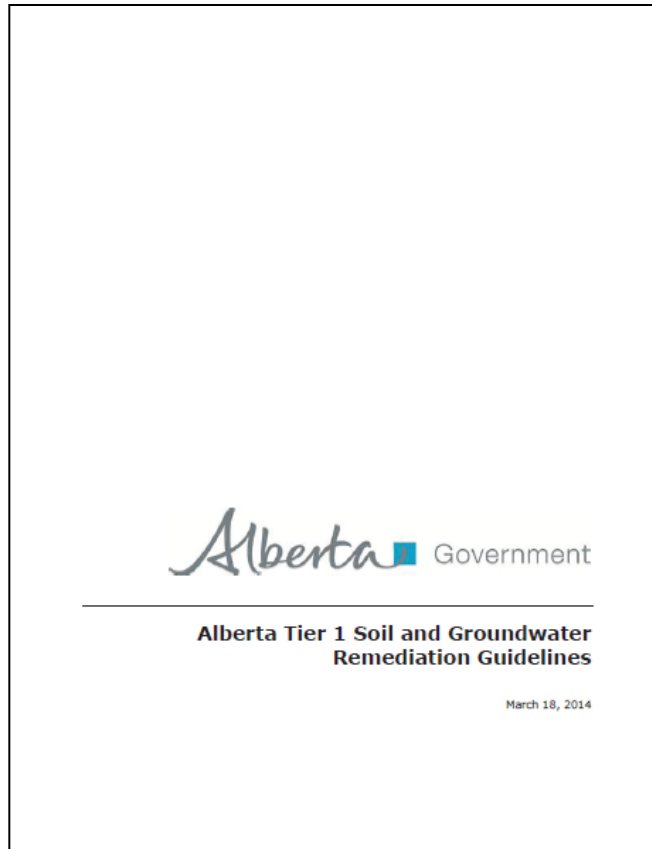




# Comparison of Background Soil Survey Results to Alberta Tier 1 Soil and Groundwater Remediation Guidelines



# Alberta Tier 1 Soil and Groundwater Remediation Guidelines – March 18, 2014

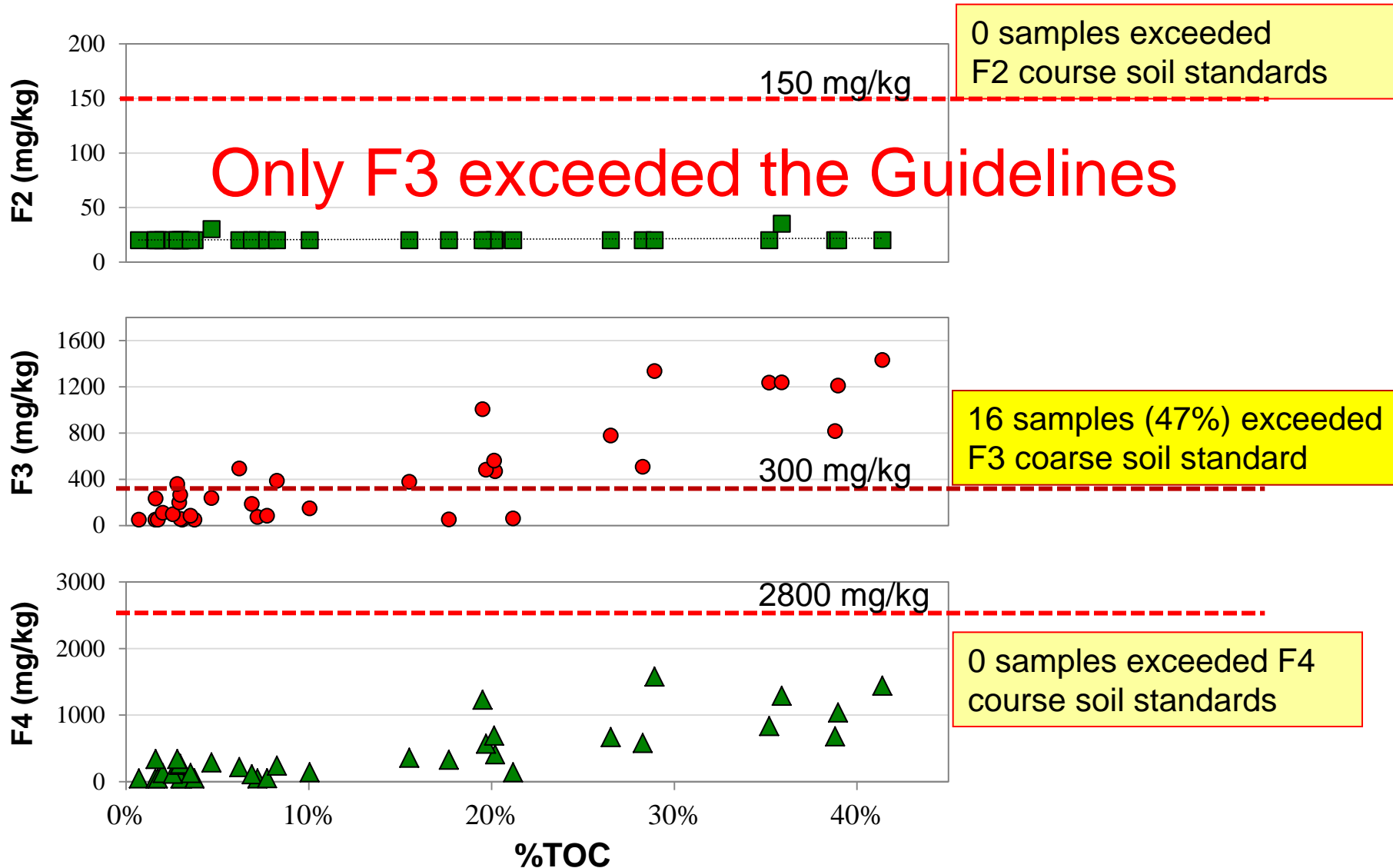


*“Coarse textured soil and groundwater remediation guidelines may be used for organic contaminants in organic soils”*

# 34 Background Soil Samples: AB, BC, NL

Comparisons of F2, F3, F4 Concentrations to AB Tier 1 Soil Remediation Guidelines

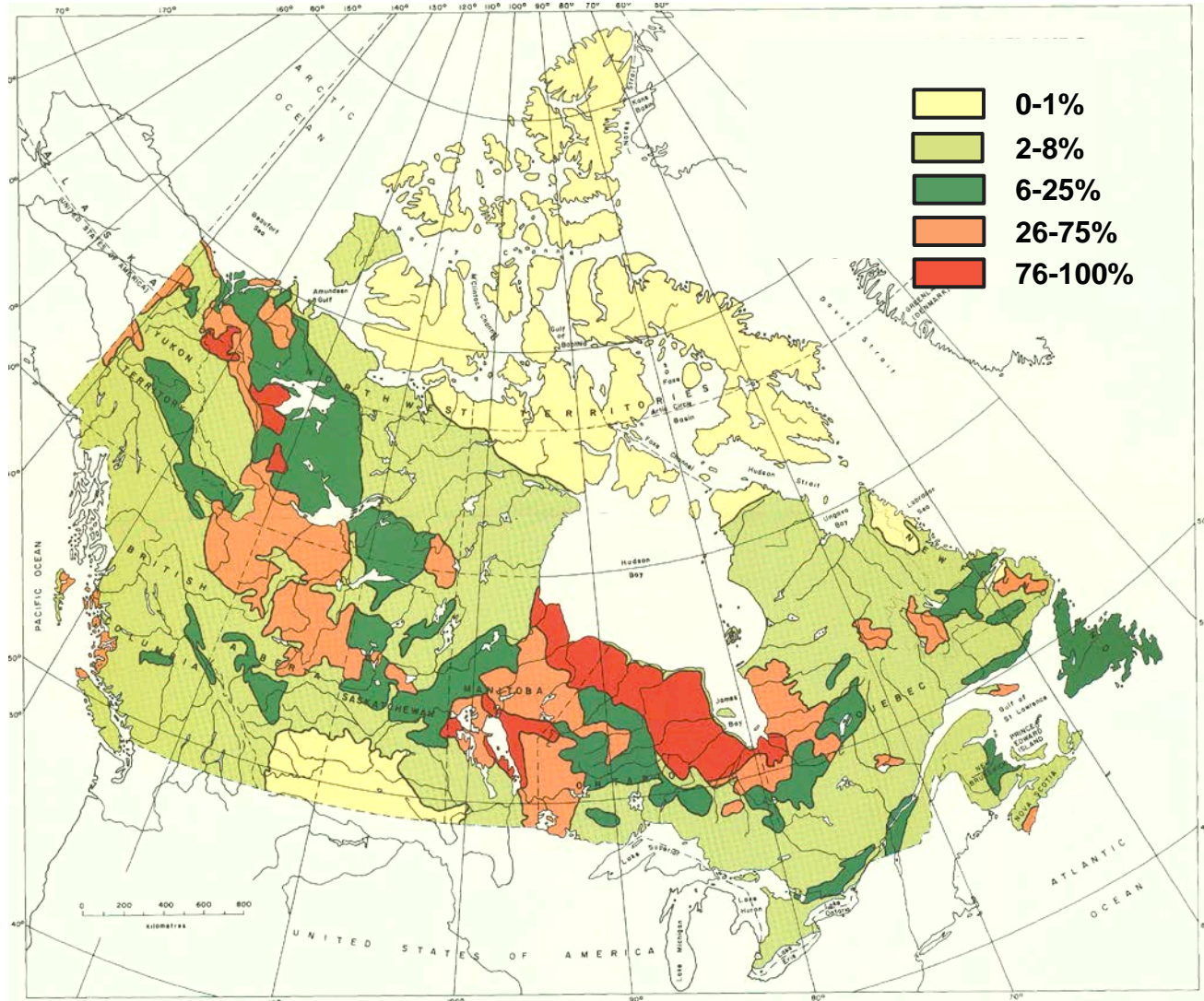
Surface Soils Natural/Agr/Resid/Parkland Guidelines



- All soils with  $>28\%$  TOC exceeded the F3 coarse soil standards
- Peat soils have  $>40\%$  TOC



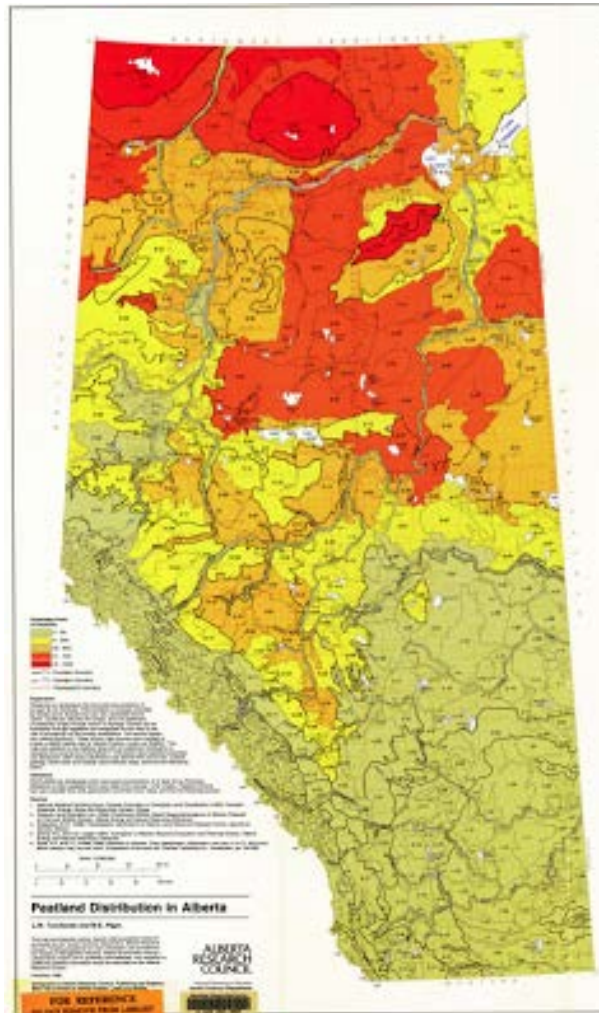
# Peat soils cover 11% of Canada



source: Peatland Resources of Canada



# Peat soils cover 18% of Alberta



source: Alberta Geological Survey

But there is a light at the end of the tunnel!



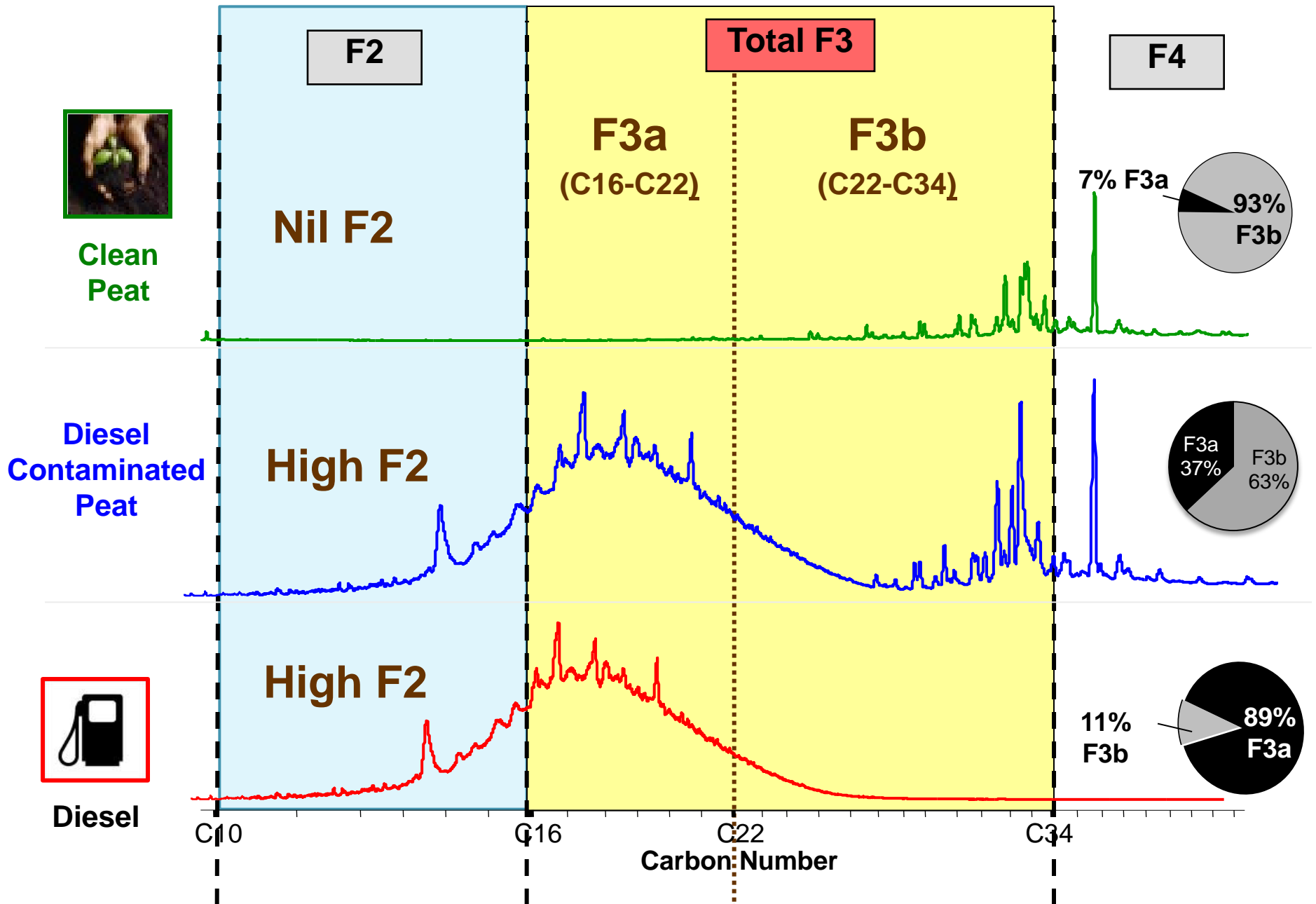


# F2:F3b presence vs absence ratio

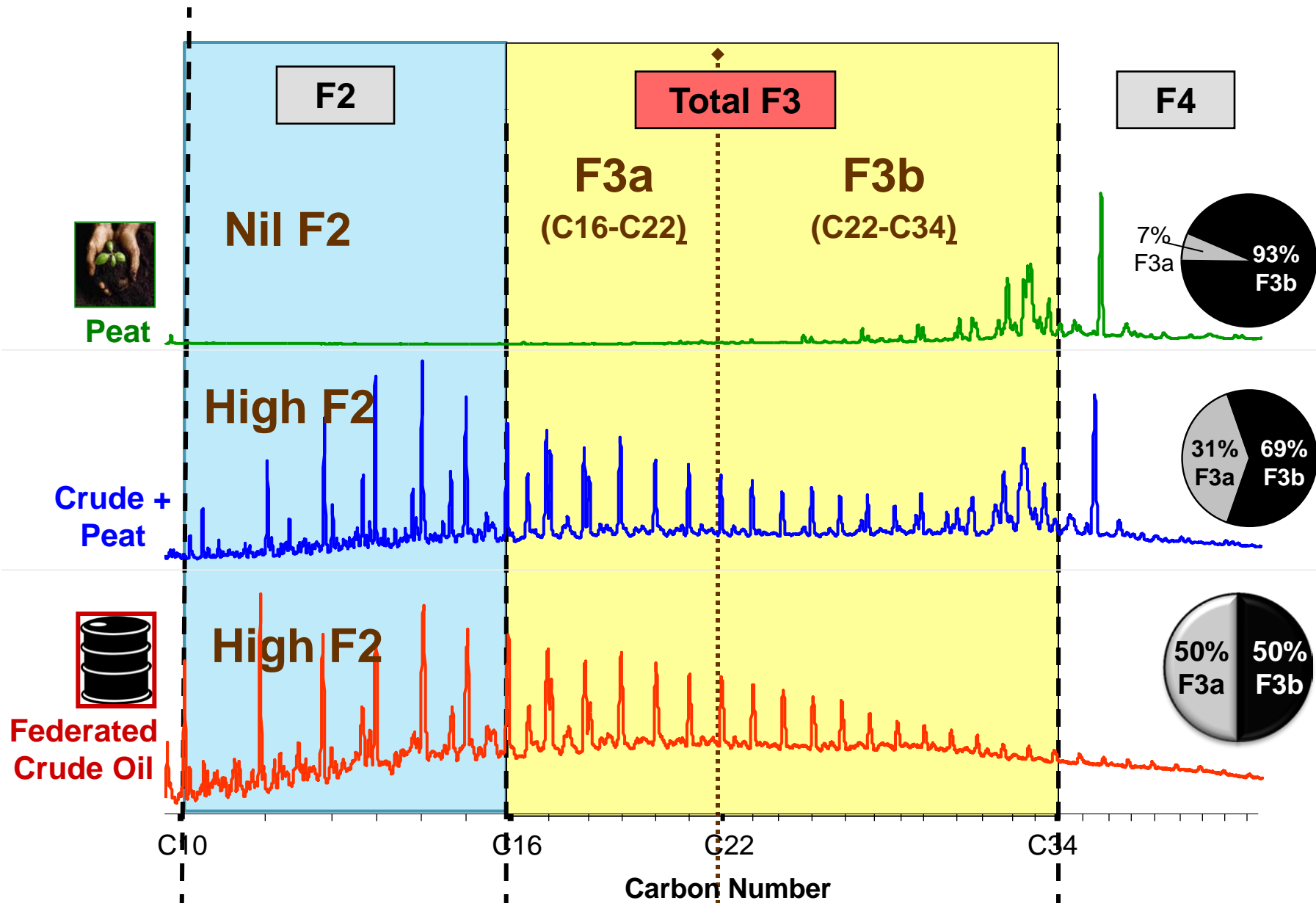
Ratio  $\geq 0.10$  = PHC presence (contaminated)

Ratio  $< 0.10$  = PHC absence (clean)

# F3a (C16-C22) and F3b (C22-C34) Distributions in Diesel and Clean Peat



# F3a (C16-C22) and F3b (C22-C34) Distributions in Crude Oil and Clean Peat

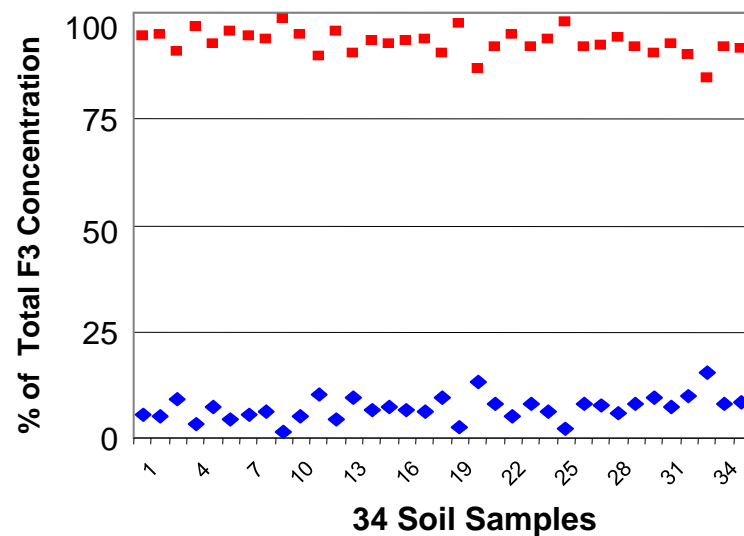
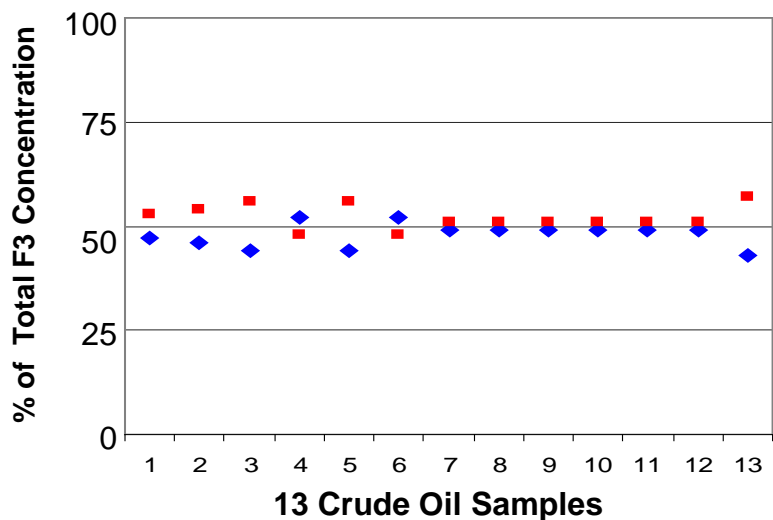
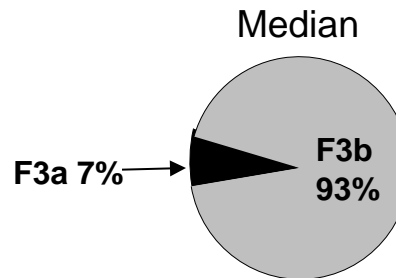
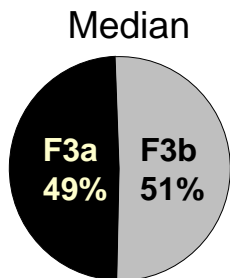






# 13 Fresh Crude Oil Samples

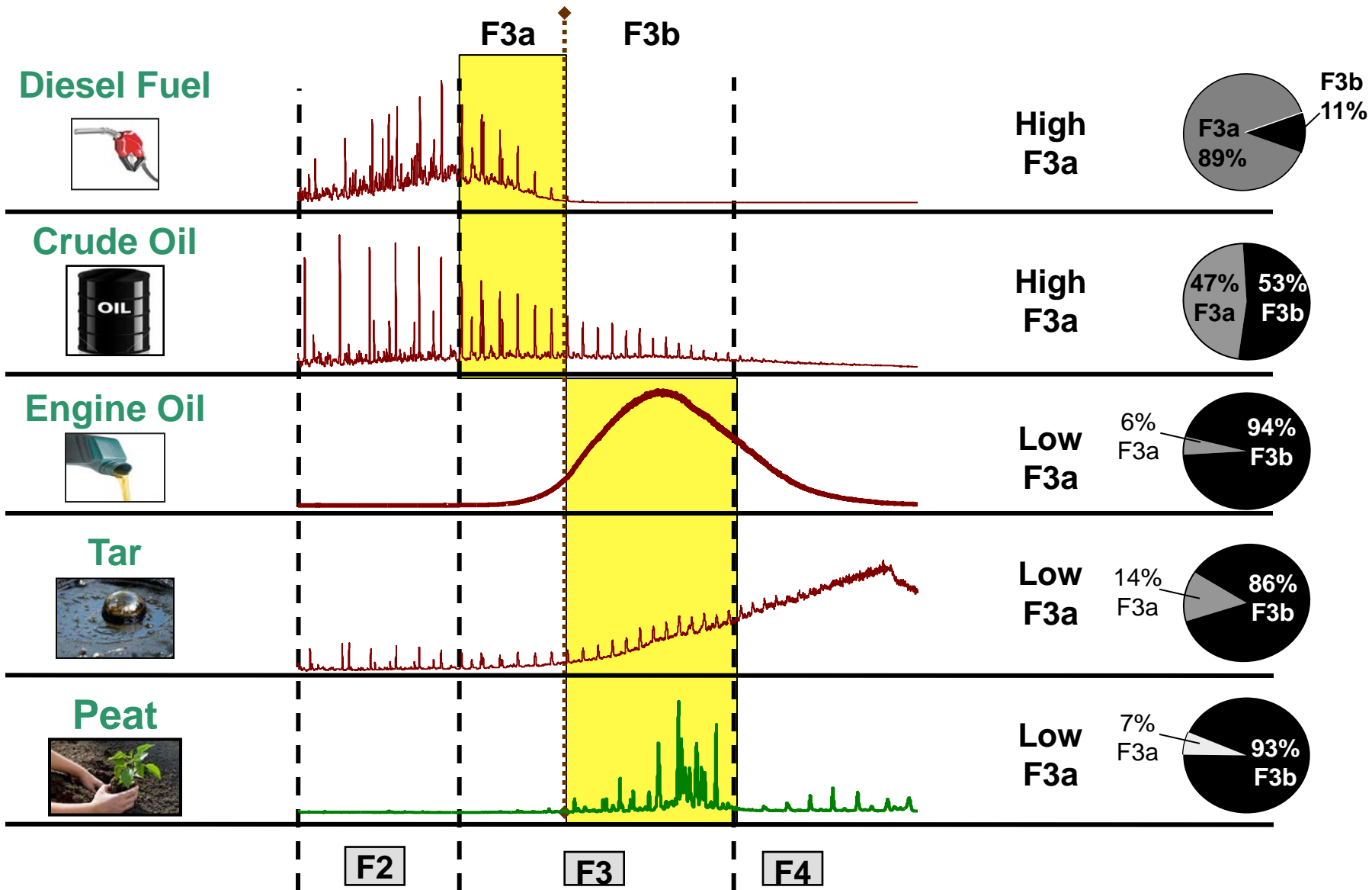
# 34 Background Soil Samples



◆ F3a (C16-C22)    ■ F3b (C23-C34)

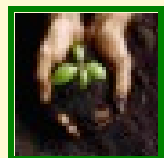
◆ F3a (C16-C22)    ■ F3b (C23-C34)

# Heavy PHC sources such as engine oil and tar have high F3b percentages as do clean soils, manure and biosolids



# F2:F3b Ratio

Diesel PHC Presence Value is  $>0.10$



Clean Peat

F2

F2 = 10 mg/kg

F3b

F3b = 1,395 mg/kg

F2:F3b Ratio

= 0.01  
ABSENT

Diesel Spiked Peat

F2 = 613 mg/kg

F3b = 2,816 mg/kg

= 0.79  
PRESENT



Diesel

F2 = 823 mg/kg

F3b = 371 mg/kg

= 2.22  
PRESENT

C10

C16

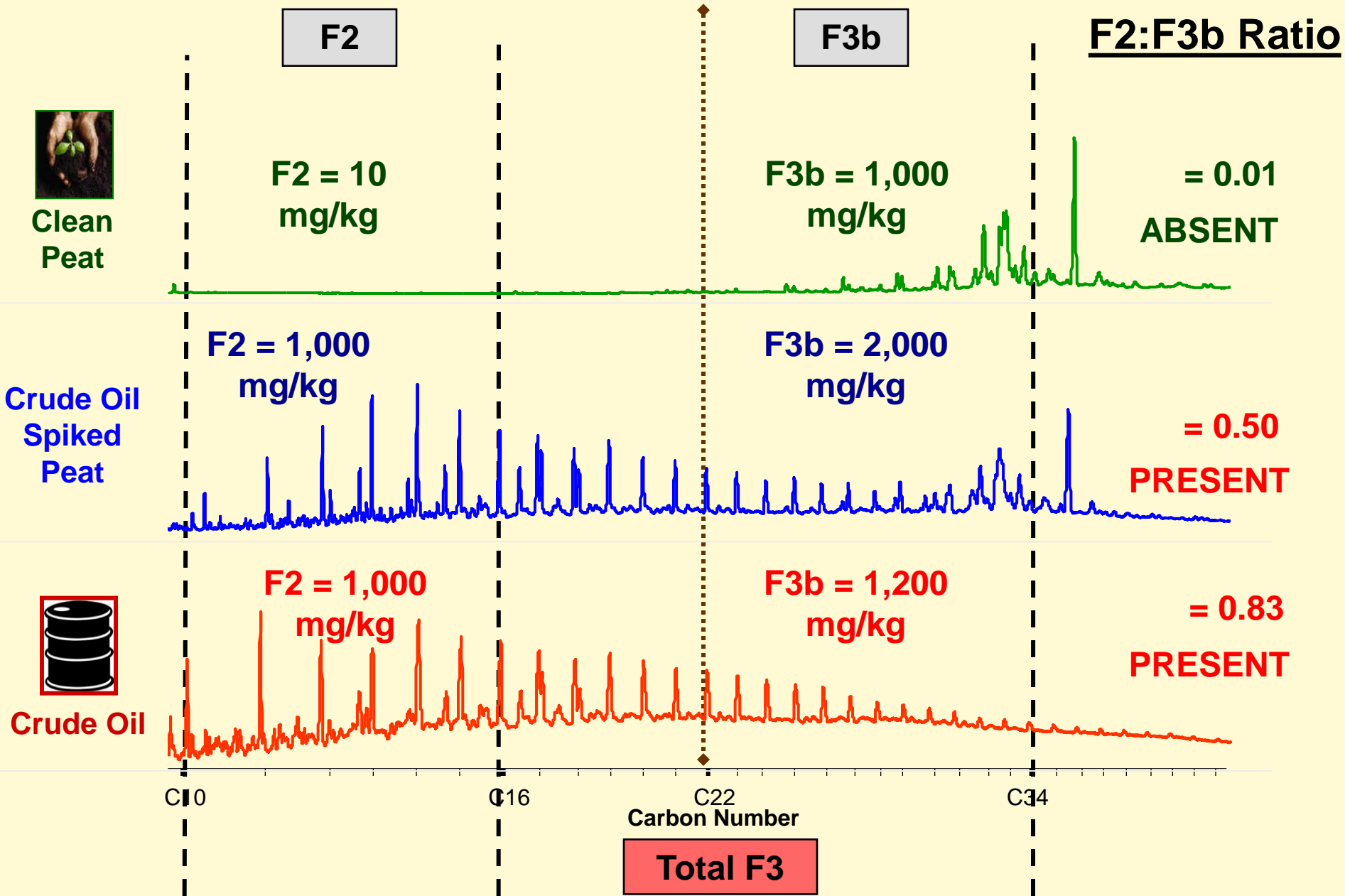
C22

C34

Carbon Number

# F2:F3b Ratio

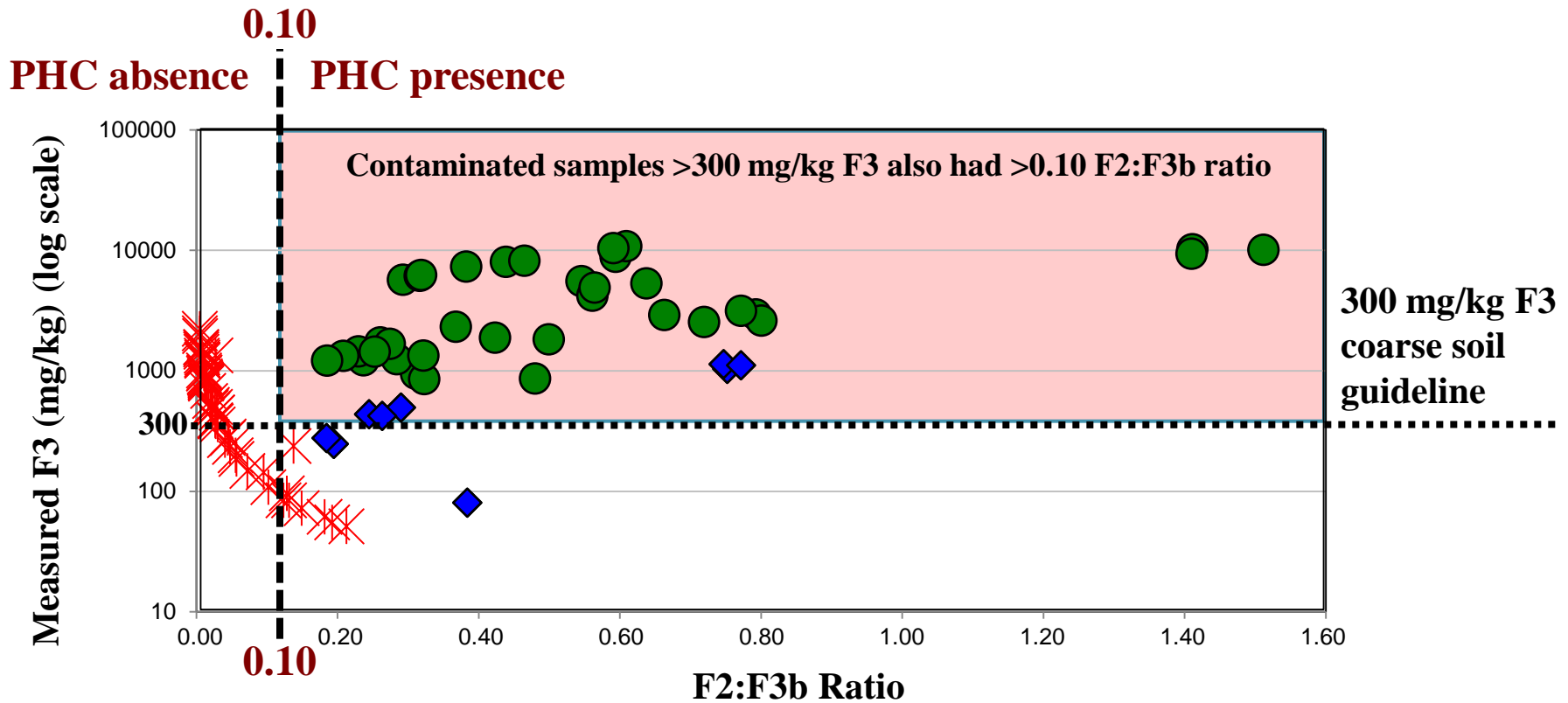
Crude Oil PHC Presence Value is  $\geq 0.10$



# F2:F3b Ratios and F3 Concentrations

Clean Manure Compost and Background Soil Survey Samples

Manure Compost, Peat and Sand Spiked with Diesel and Crude Oil – Day 0 & Day 300 Samples



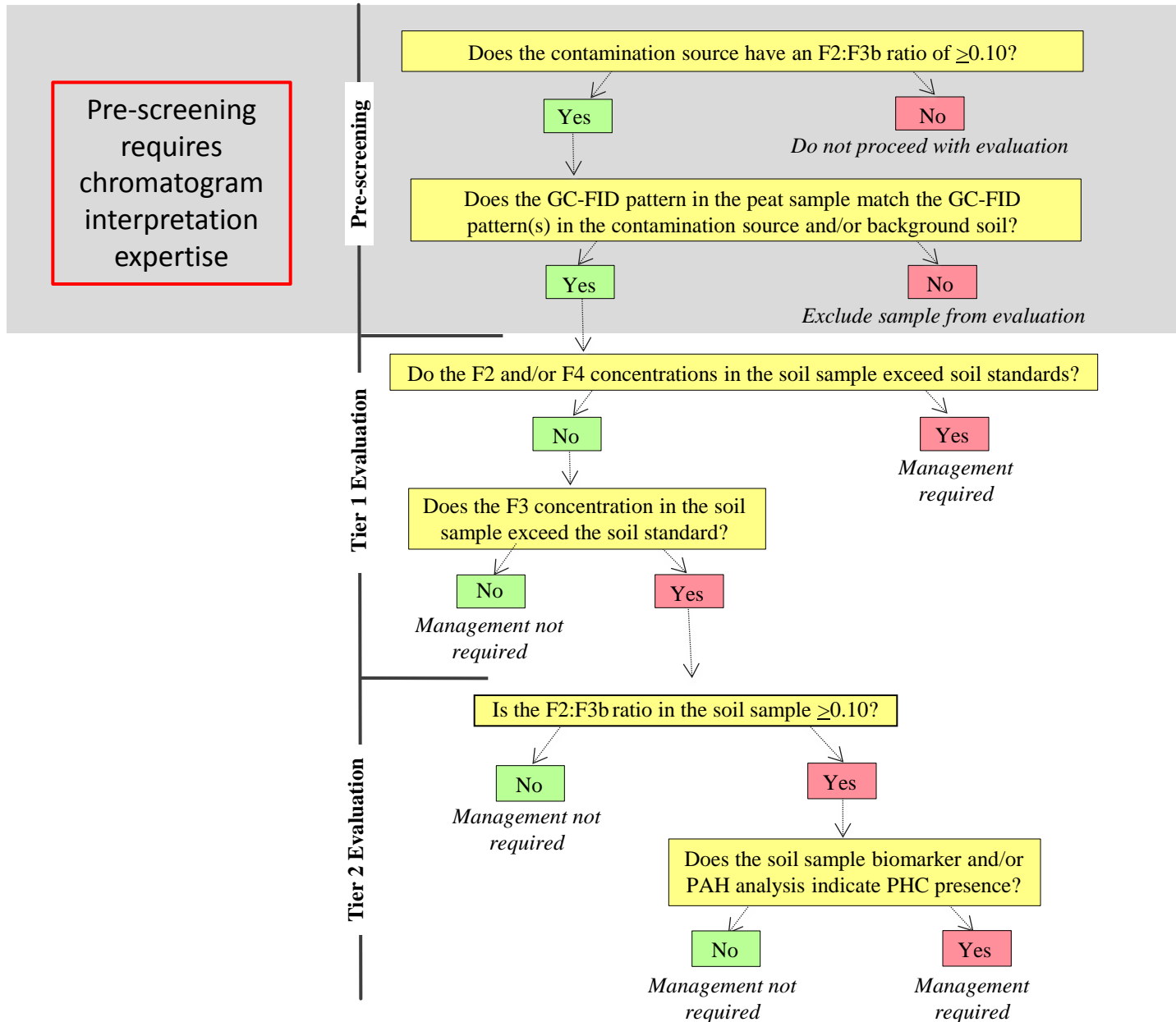
× clean soils/compost

● contaminated soil/compost

◆ contaminated sand



# Biogenic vs Petrogenic Decision Tree





# Rules of Thumb for Practical Applications

- Cannot be used to assess soils contaminated by heavy PHC products (e.g. motor oil, tar, asphalt, etc.)
- PHC contamination source must have an F2:F3b ratio of greater than or equal to 0.10
- Chromatograms must be studied for every soil sample to ensure that all contaminated samples have the same PHC source.
- Clean samples are identified by non-detectable F2 concentrations combined with the absence of PHC UCMs.



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