Application of CEN Methodology in Evaluating Sources of Multiple Land-Based Fuel Spills in Alberta

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The Issue

- Between 1975 and 2012 a large number of crude oil spills (28,666) occurred in Alberta (Young, 2013, Global News).
- Spillage from well pads, pipelines, batteries, and spills resulting from train derailments and tanker accidents can and do release petroleum. Amounts < 2000 L not included in the numbers above.
- Areas affected: farmland, forests, muskeg and into waterbodies such as creeks, rivers, ponds and lakes.
- Report commissioned by First Nations raised concerns about under-reporting of spills by the Alberta Energy Regulator as well as inadequate cleanup following spill events (Nikiforuk, 2017).

The Challenge

- This information suggests that investigations following petroleum and chemical spills can result in surprises, *i.e.* detection of hydrocarbons from one or more sources, or from past spill events in the same area.
- Because the cost of cleanup can be expensive, it is in the interest of governments and industry to determine the extent of the reported spill as well as evaluate the potential environmental damage. It is also important to determine if other mitigating factors exist, such as the discovery of previous spills which may have been inadequately cleaned or have been unreported.

Tools Required for Petroleum Forensics

Multidisciplinary team:

- Laboratory experienced with the processes and familiar with the Centre for European Norms method (CEN, 2012).
- Participation in international round robin forensic studies.
- Field and laboratory staff experienced with handling legal evidence.
- Legal support familiar with environmental prosecution and defense.
- Consultant familiar with all aspects as well as participation in international round robin studies and litigation experience.

Forensic Team

- Newalta – legal sample collection - remediation
- Laboratory – Life Science Forensics and Paracel Laboratories, Calgary
- Legal council – Susan McRory – former head of special prosecutions, Alberta Justice
- Deib Birkholz, consultant, over 40 years of practical experience including extensive litigation experience.

Forensic Technology

- Existing oil spill fingerprinting protocols, designed to identify sources of spilled oil, are either qualitative or quantitative in nature (Stout, 2016).
- Qualitative methods rely on visual comparison of chromatograms obtained following GC/FID or GC/MS analyses.
- GC/MS relies on comparisons of extracted ion profiles for PAHs or petroleum biomarkers.
- These qualitative protocols have been formalized in two standards of the American Society for Testing and Materials (ASTM 1995, 2000).

Forensic Technology

Quantitative methods such as the technical guideline prepared by the Centre of European Norms (CEN, 2012) rely on a tiered approach that include:

- A qualitative assessment of GC/FID or GC/MS chromatograms to assess the overall character of oil in a samples or potential source,
- A quantitative comparison of diagnostic ratios of PAHs and petroleum biomarkers in a sample and source, as well as weathering assessments, and
- A post analysis synthesis of the data to confirm resulting scientific conclusions.

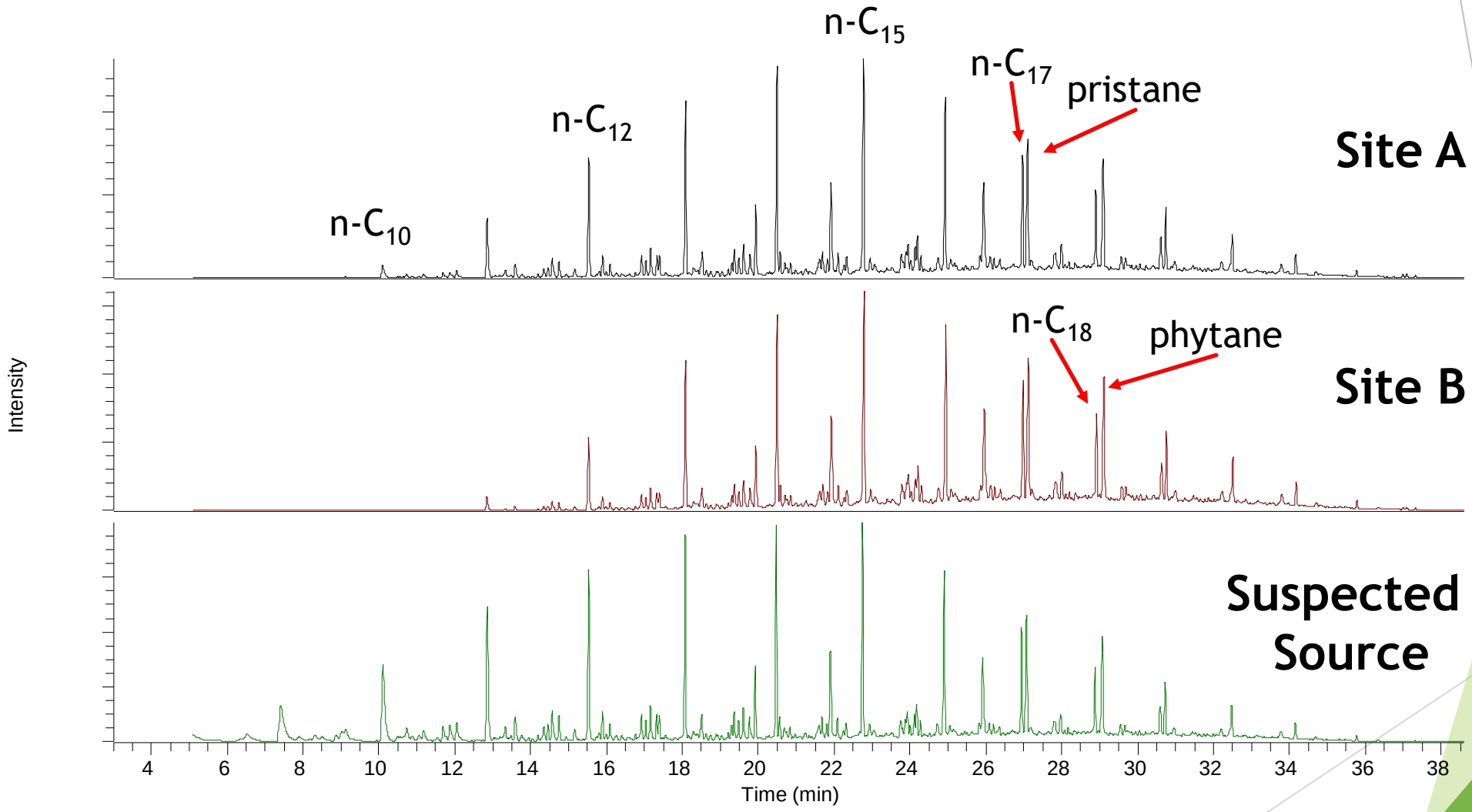
Methods

- Soil samples are mixed with anhydrous sodium sulfate and subjected to extraction via Soxhlet, shake or ultrasound.
- Extracts are concentrated, dried and cleaned up using alumina/silica or neutral alumina.
- Crude oil, or heavy oil samples are deasphaltened prior to alumina cleanup.
- Final extracts concentrated and analyzed using GC/FID, GC/MS (scanning and SIM).

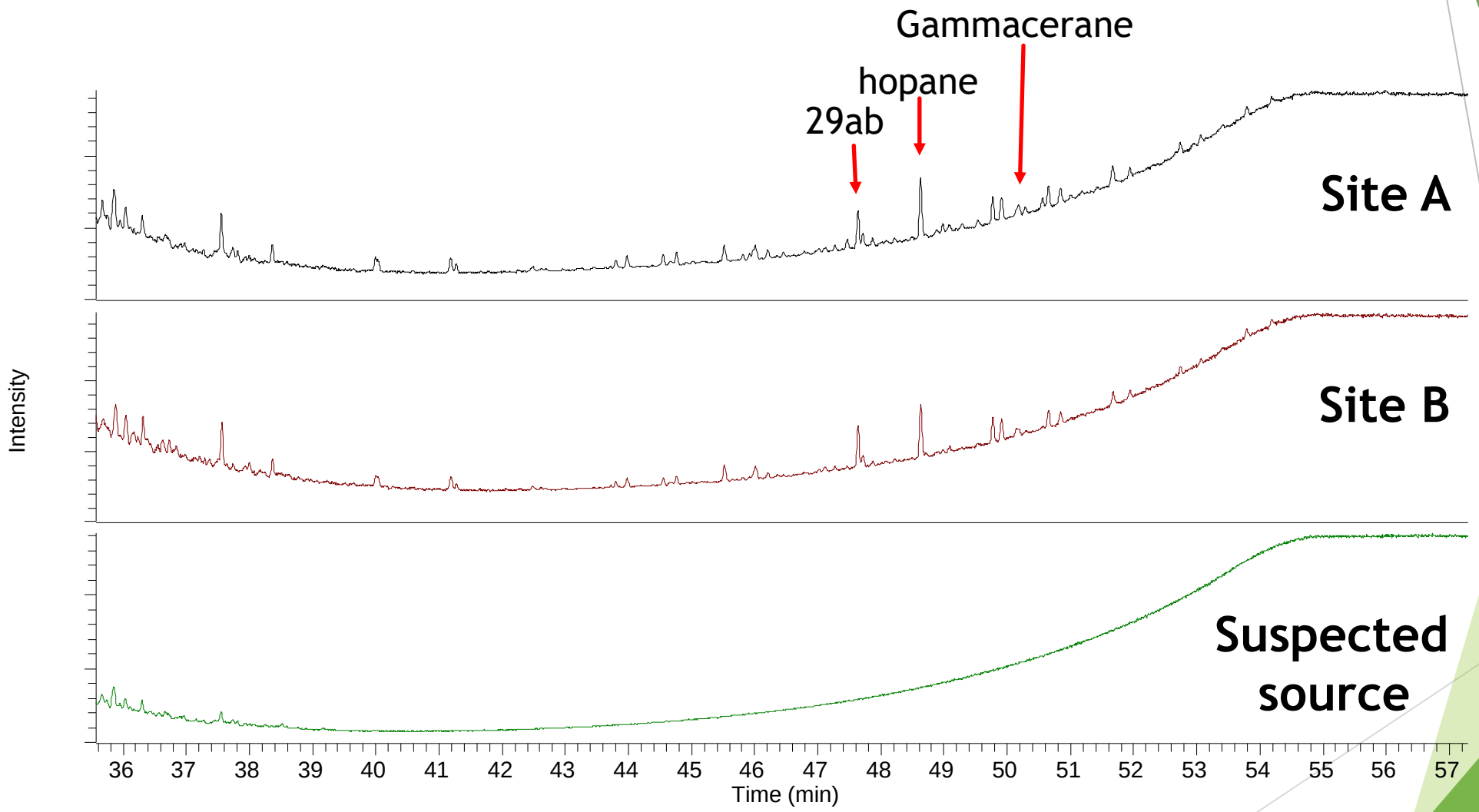
Case Study 1

- Fuel spill detected in various parts of a large industrial site.
- Based upon vehicle logs and tare weights indication was that spill was due to a leaking on-site fuel tanker.
- FID Chromatograms suggested this was likely the cause.
- Alkane/isoprenoid ratios (n-C_{17}/pristane, n-C_{18}/phytane and pristane/phytane) supported this conclusion, which was reported by a consultant.

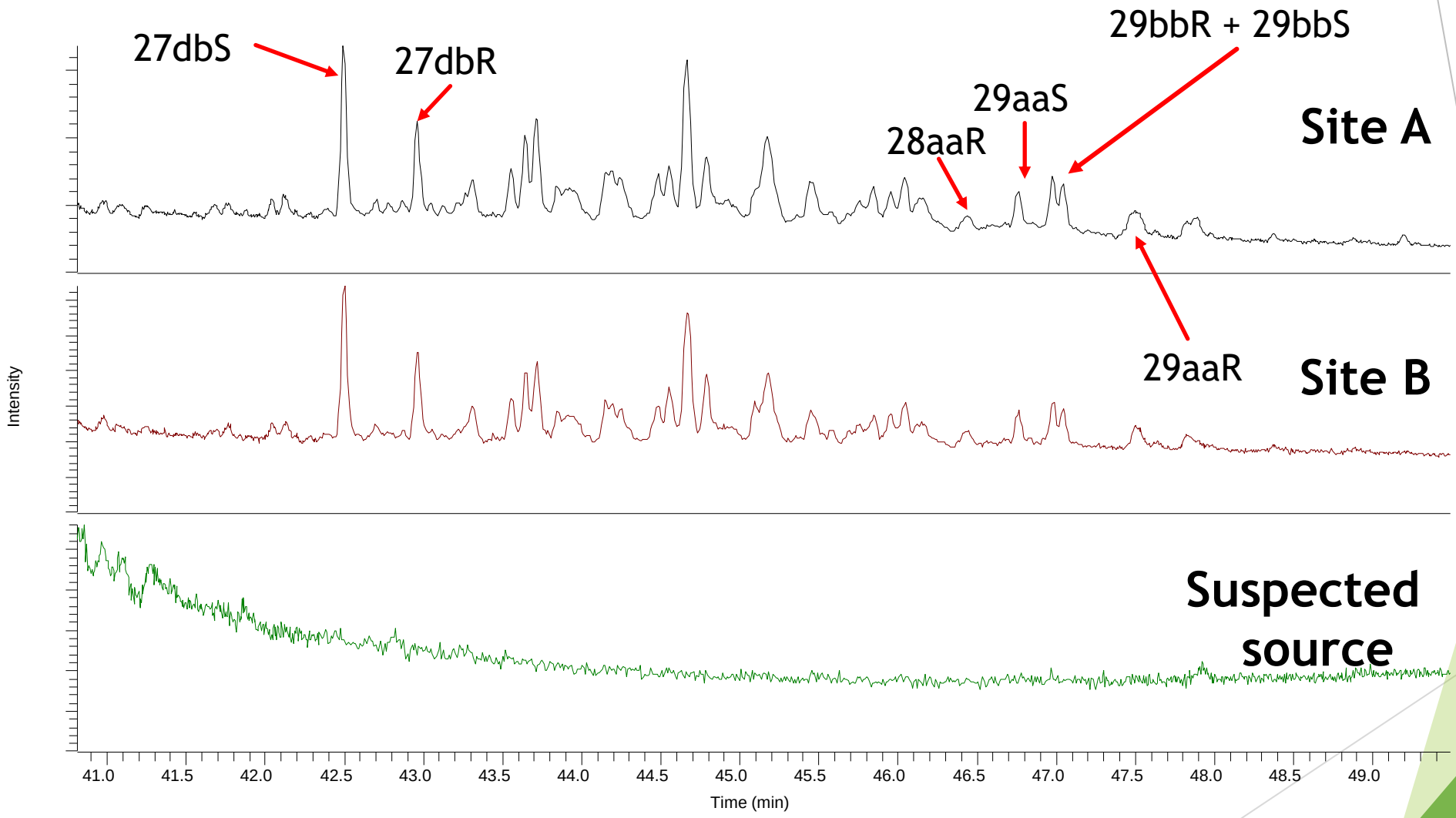
FID Chromatograms



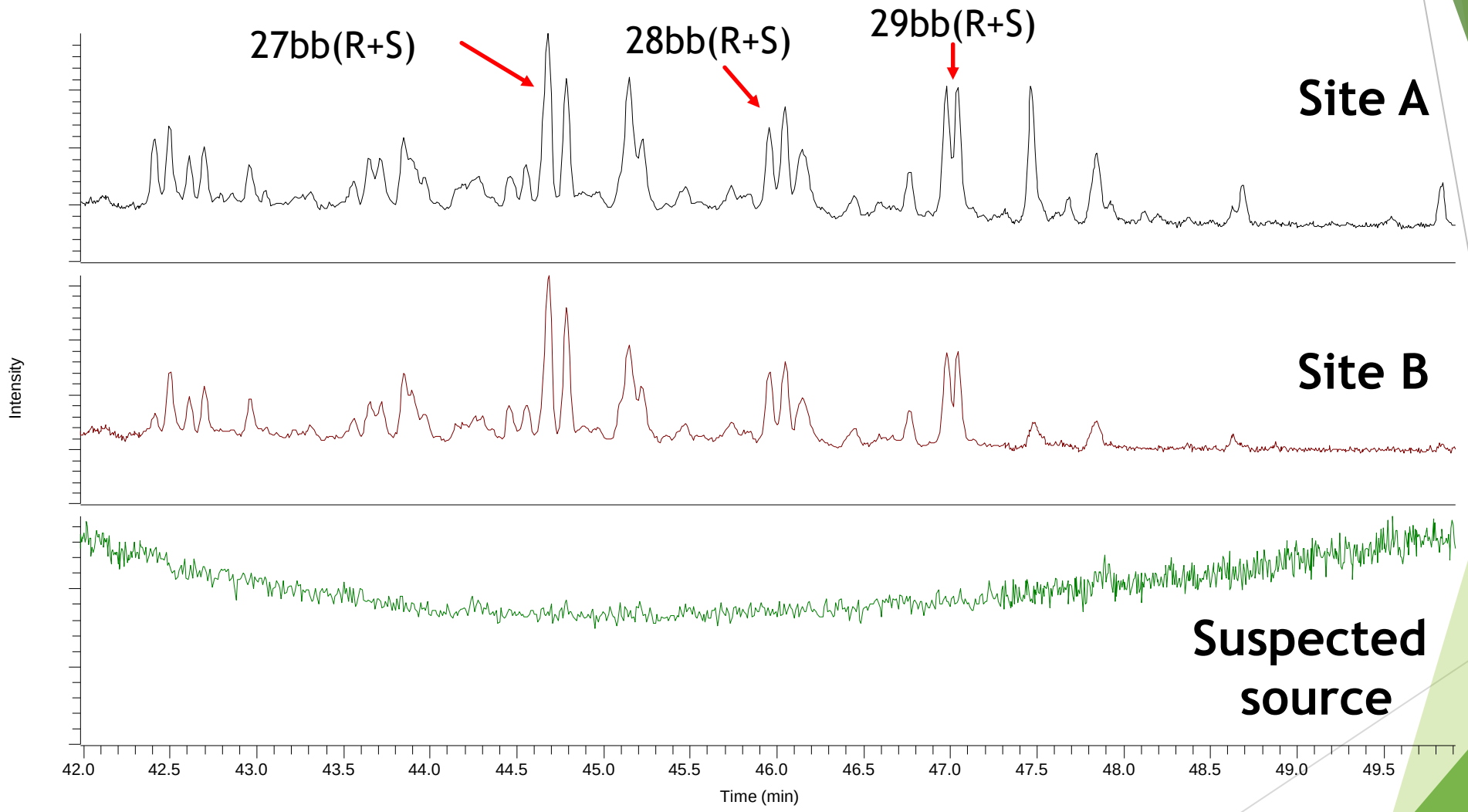
GC/MS – Tricyclic terpanes and hopanes



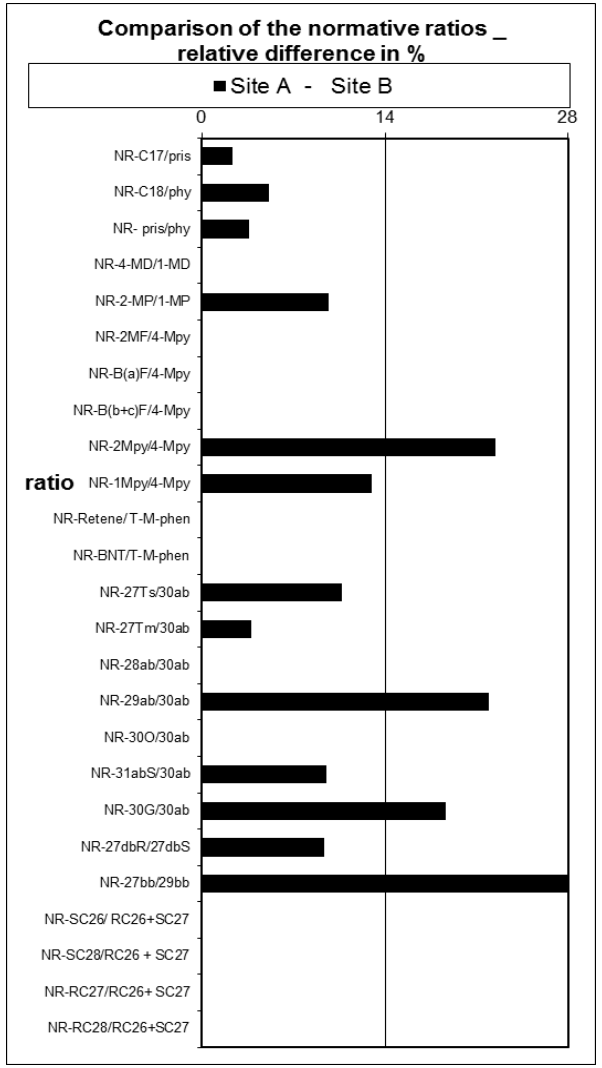
GC/MS – Diasteranes and ααα-Steranes

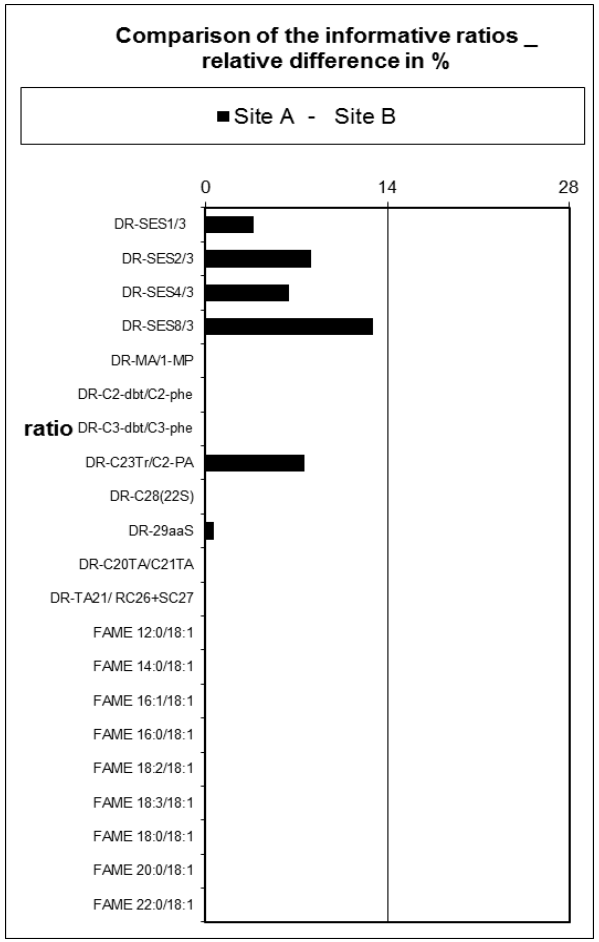


GC/MS – αββ-Steranes



Ratio comparison – Site A vs. Site B





Ratios indicating a non-match

DR – 2-Mpy/4-Mpy *
DR – 29ab/30ab **
DR – 30G/30ab **
DR - 27bb(S+R)/29bb(S+R) **

* Explained by photo-oxidation
** Stable ratios

Case Study 1 - Conclusions

- Application of CEN (2012) revealed a number of biomarkers that were present in the contaminated soil but not in the suspected source fuel. This suggested that the tanker truck was not the source of contamination.
- Data was collected for 19 petroleum biomarker ratios, four of which exceeded 14% RPD when the two soil samples were compared. This suggests a non-match scenario.
- One ratio exceedance (2-Mpy/4-Mpy) could be explained by weathering (photo-oxidation) and as such is dismissed. However, the other three ratios were derived from stable compounds which are generally not affected by weathering.
- It was concluded that the soil was contaminated with differing sources not related to the suspected tanker truck.

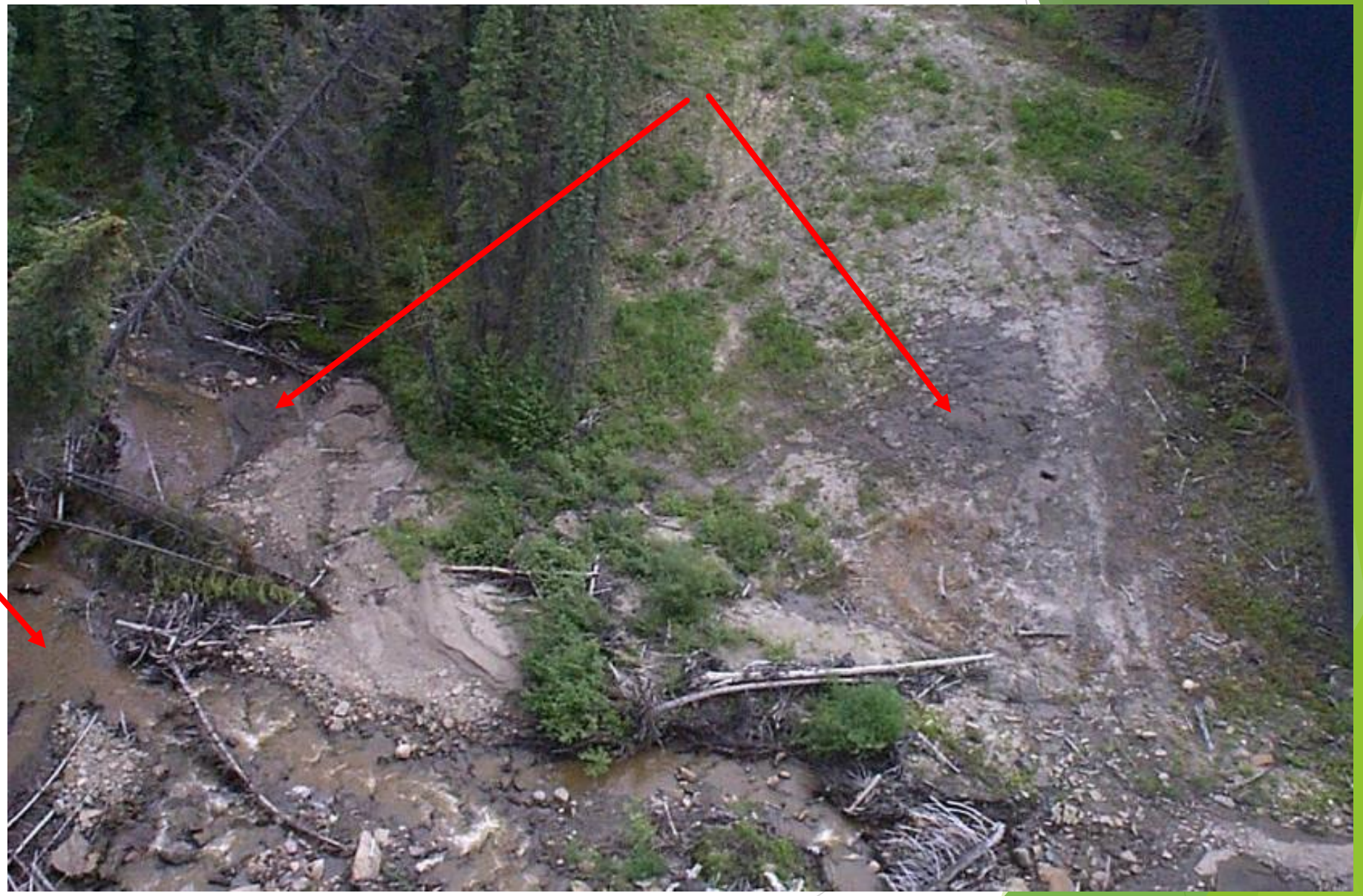
Case Study 2

- Crude oil pipeline fracture in remote area.
- Cleanup well underway when investigators arrived.
- Pipeline purged and cleaned prior to sampling.
- Only other source sample available was from vacuum truck.
- This product was compared to four contaminated soil samples taken from the spill site.

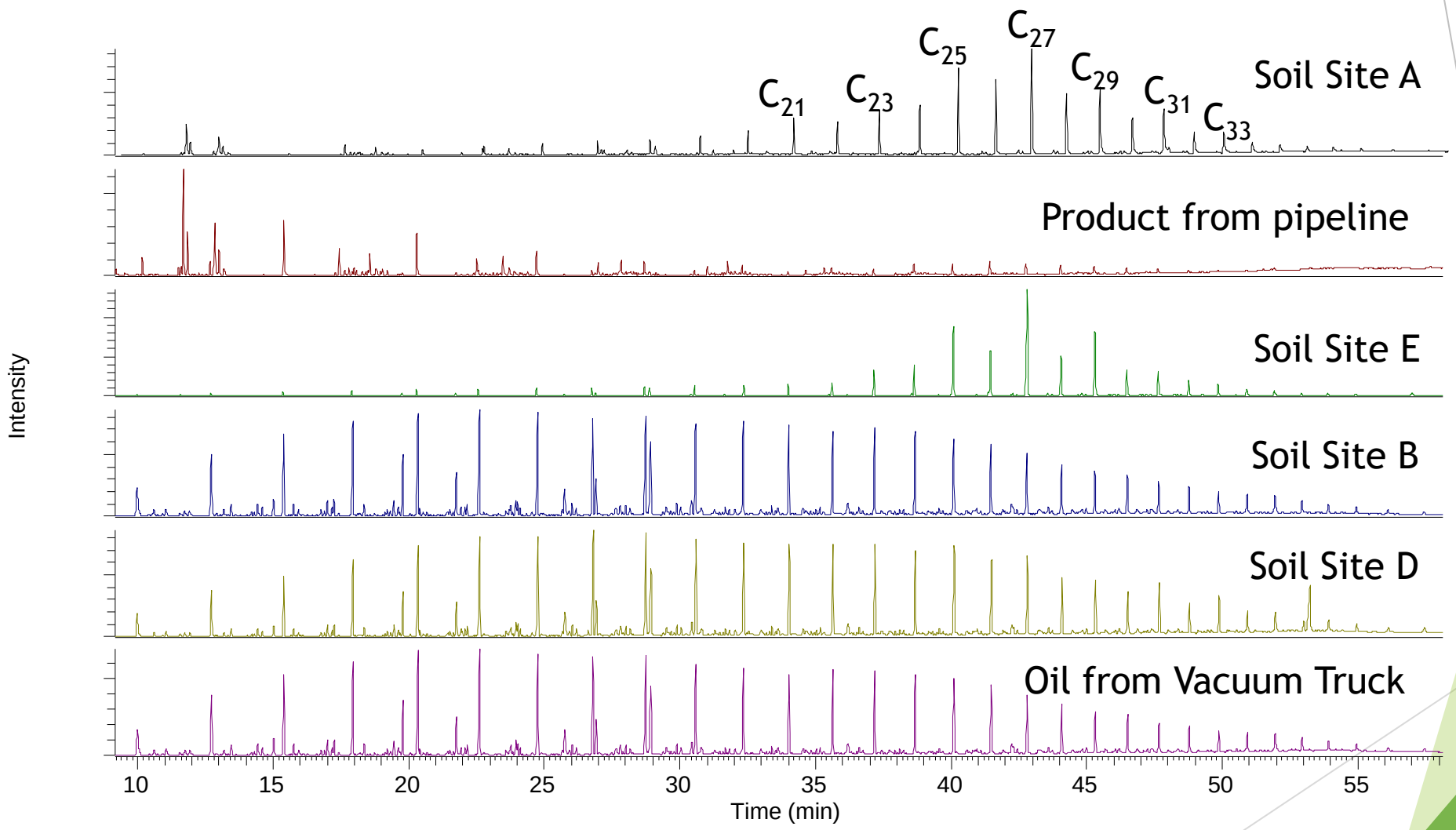
What is it? Where did it come from?

Is this a fish bearing stream or fish habitat?

Is this stuff toxic? Could we be dealing with Fisheries Act charges?



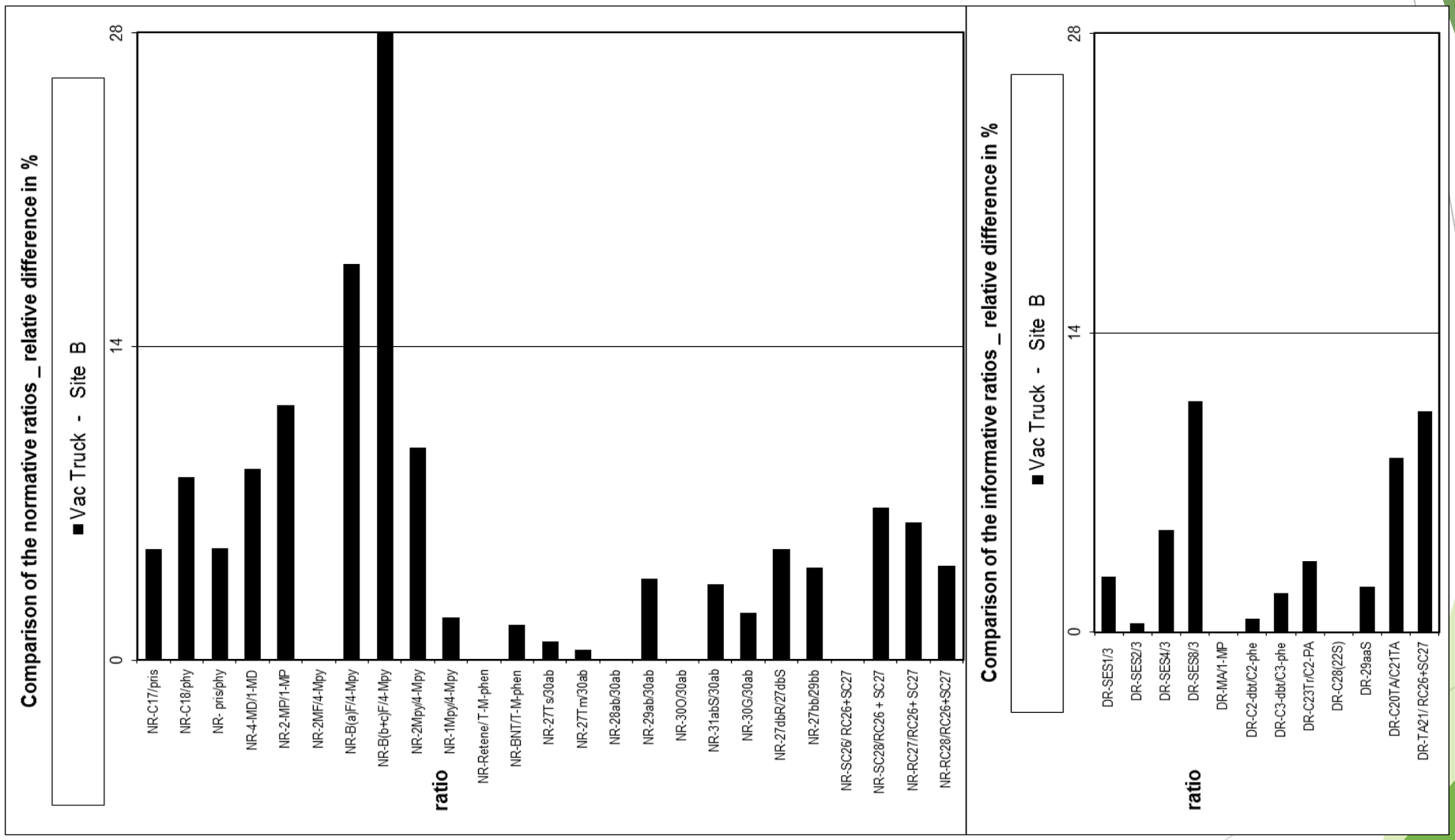
FID Chromatograms



Chromatographic interpretation

- Product from pipeline is unusual. Not similar to soils. Pattern inconsistent with crude oil.
- Sites A and E different from vacuum truck or sites B and D. Dominated by odd-numbered n-alkanes which are associated with naturally occurring plant waxes found in soil and vegetation. Crude oil if, is present in minor concentrations, if at all.
- Product from vacuum truck consistent with evaporated crude oil and similar to product found at sites B and D.

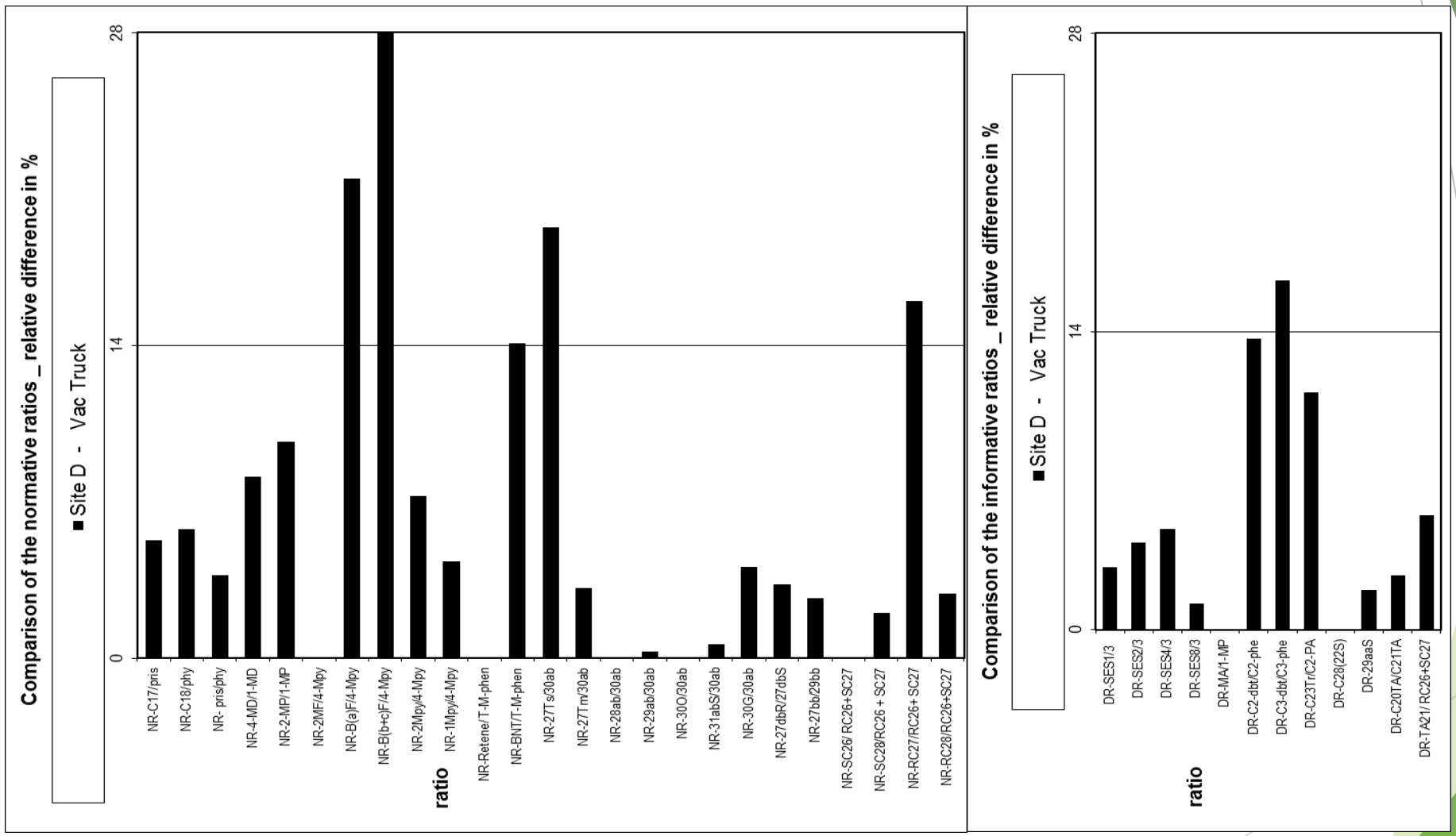
Ratio Comparison – Vac. Truck vs. Site B



Ratio Comparison – Vac. Truck vs. Site B

- Two ratios observed to have RD >14% suggesting a no match scenario: BaF/4Mpy and B(b+c)F/4Mpy.
- Pyrenes are very sensitive to photo oxidation because they are very efficient absorbents of UV-radiation and it is reasonable that crude oil spilled from the pipeline experienced UV exposure on the site surface.
- Ratio exceedances can be explained by weathering through photo oxidation.
- Therefore, it is concluded that the product taken from the vacuum truck and soil from site B were a positive match.

Ratio Comparison – Vac. Truck vs. Site D



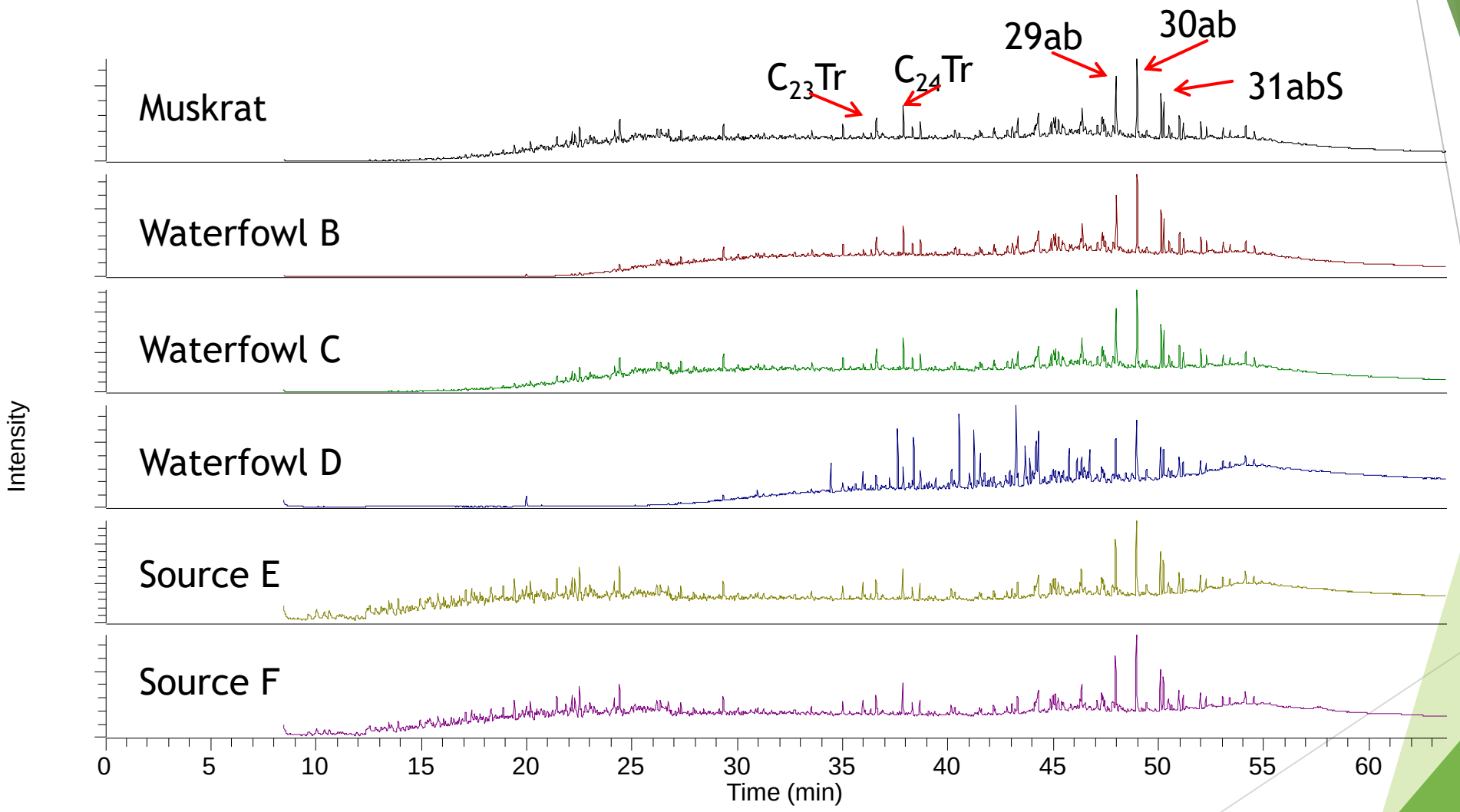
Ratio Comparison – Vac. Truck vs. Site D

- Six ratios exceed 14% RD: B(a)F/4-Mpy, B(b+c)F/4-Mpy, BNT/T-M-Phe, 27Ts/30ab, RC27/RC26+SC27 and C_3-DBT/C_3-Phe.
- Pyrene ratios influenced by photo-oxidation.
- Sulphur-containing ratios influenced by water solubility (pipeline was flushed before sampling).
- Stearanes are generally stable and even those that are photo-oxidizable were not affected, suggesting a non-match.
- Therefore, it was concluded that the spill material from Site D did not match the product in the vacuum truck.

Case Study 3

- Large heavy oil spill observed and reported.
- Sometime after, carcasses of waterfowl and a muskrat were found and removed from the area.
- Since waterfowl and muskrats can migrate after exposure to oil but prior to death, the issue at hand was whether the oil found on the deceased waterfowl and muskrat came for the reported heavy oil spill or from another source such a holding pond, sump, other spill, etc.

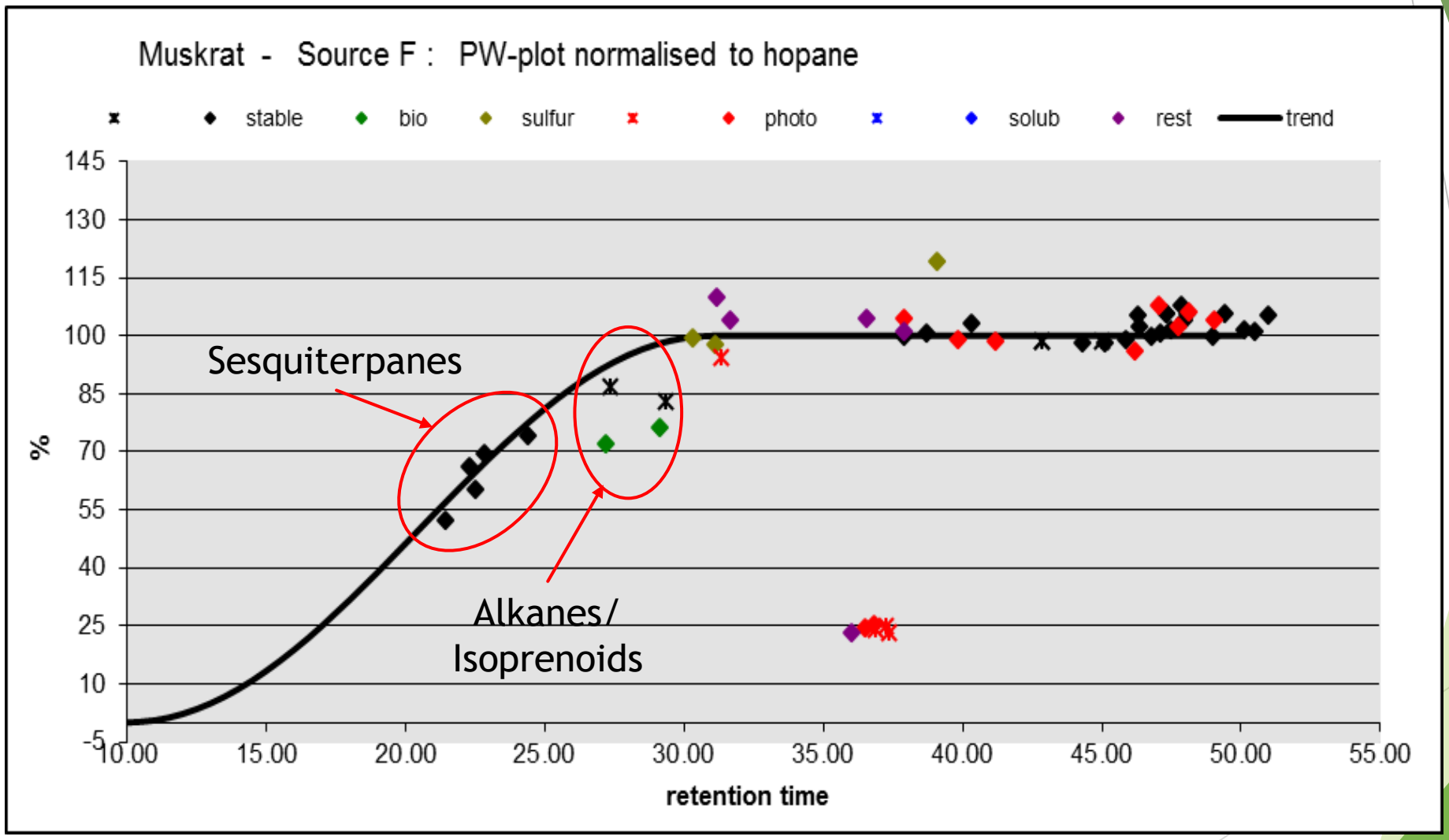
FID Chromatograms



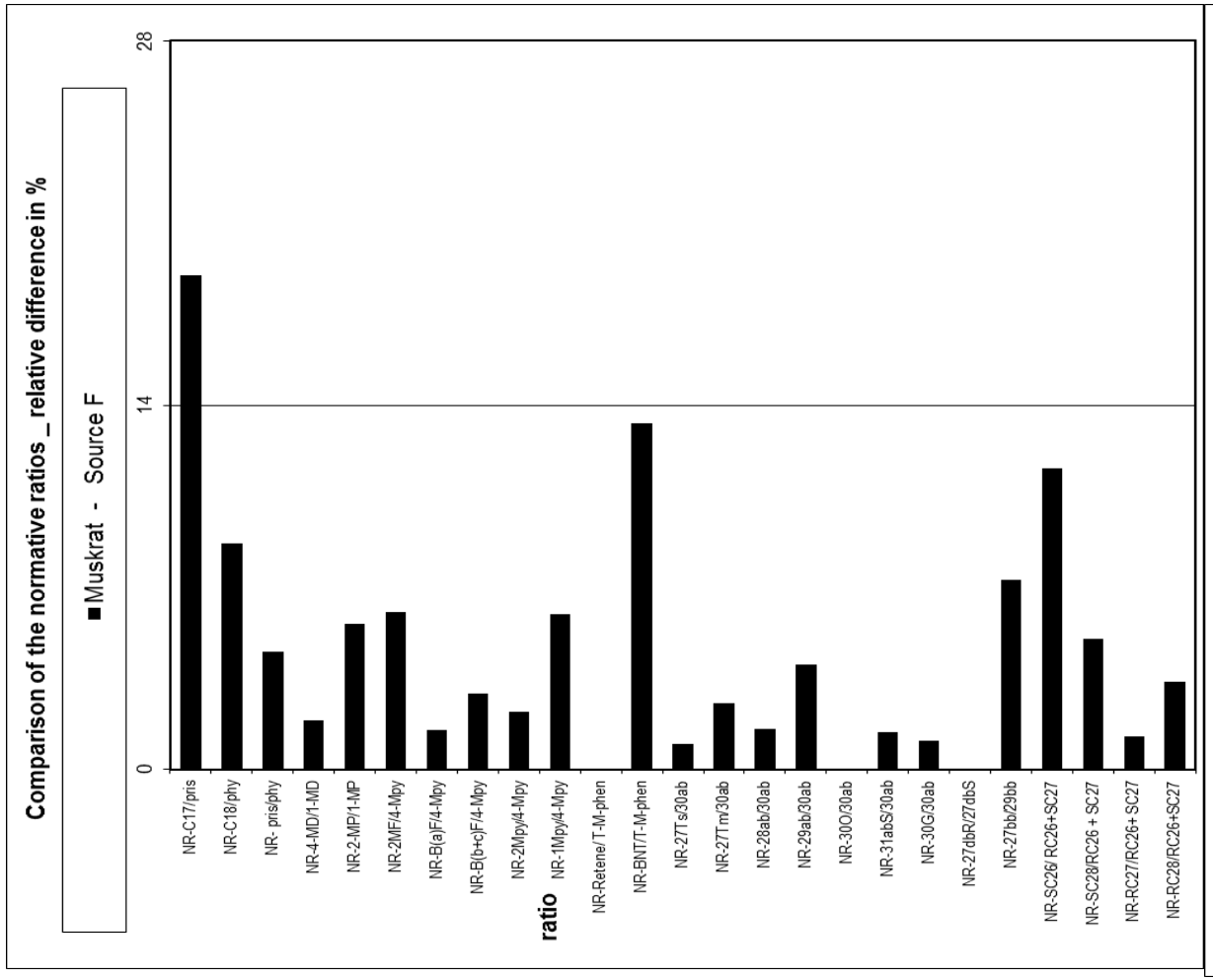
Chromatographic Interpretation

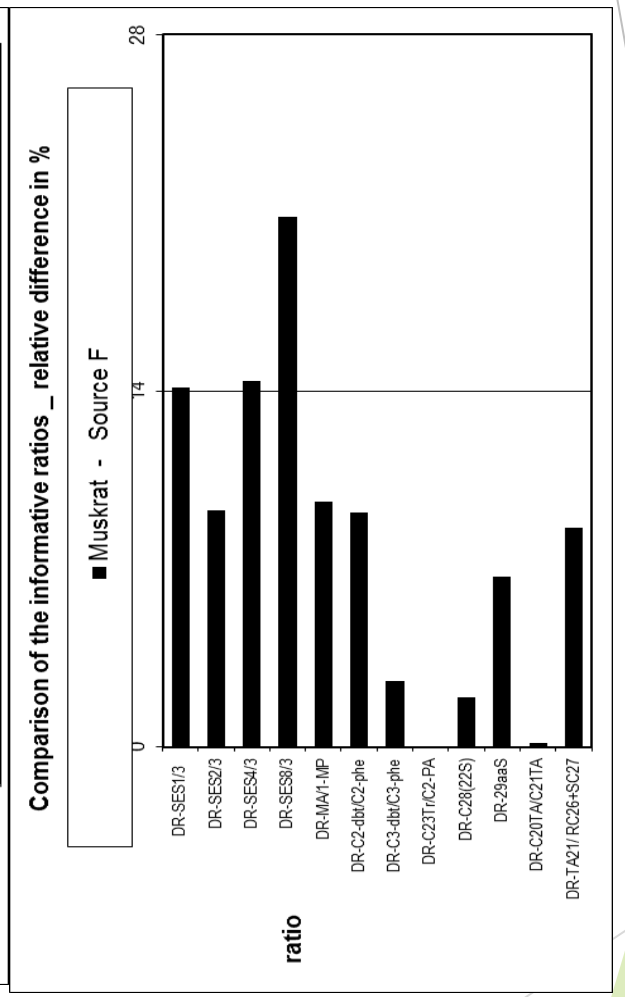
- Identification of heavy oil is obvious: presence of tricyclic diterpanes (C23Tr and C24Tr), as well as norhopanes, hopane, and homohopanes (29ab, 30ab, and 31abS). Lack of n-alkanes is associated with conventional petroleum.
- Two source samples appear similar (E and F) as well as muskrat and waterfowl B and C.
- Waterfowl D appears different owing to prominent additional peaks.

PW-plot – Muskrat vs. Source F



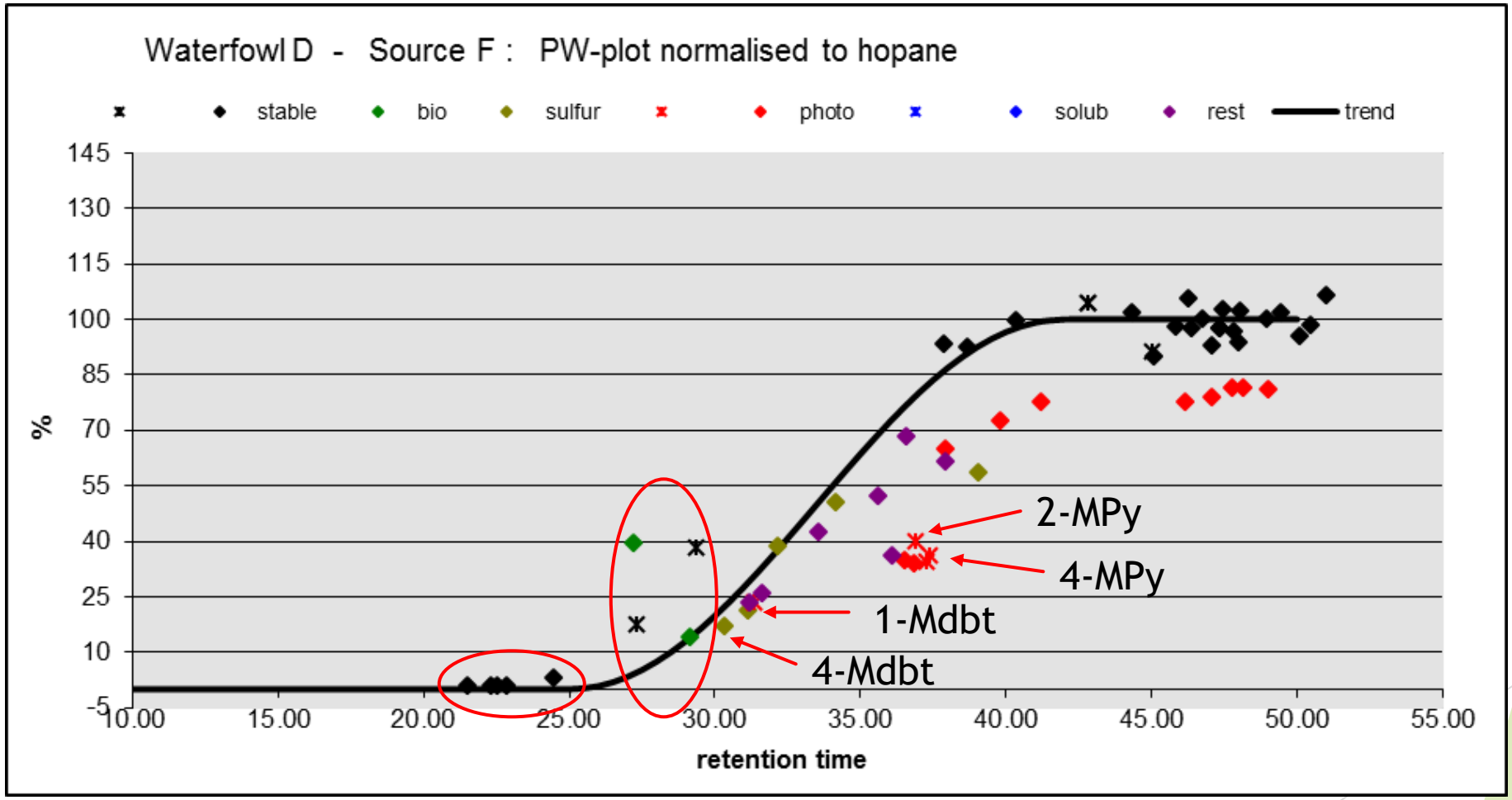
Ratio Comparison – Muskrat vs. Source F



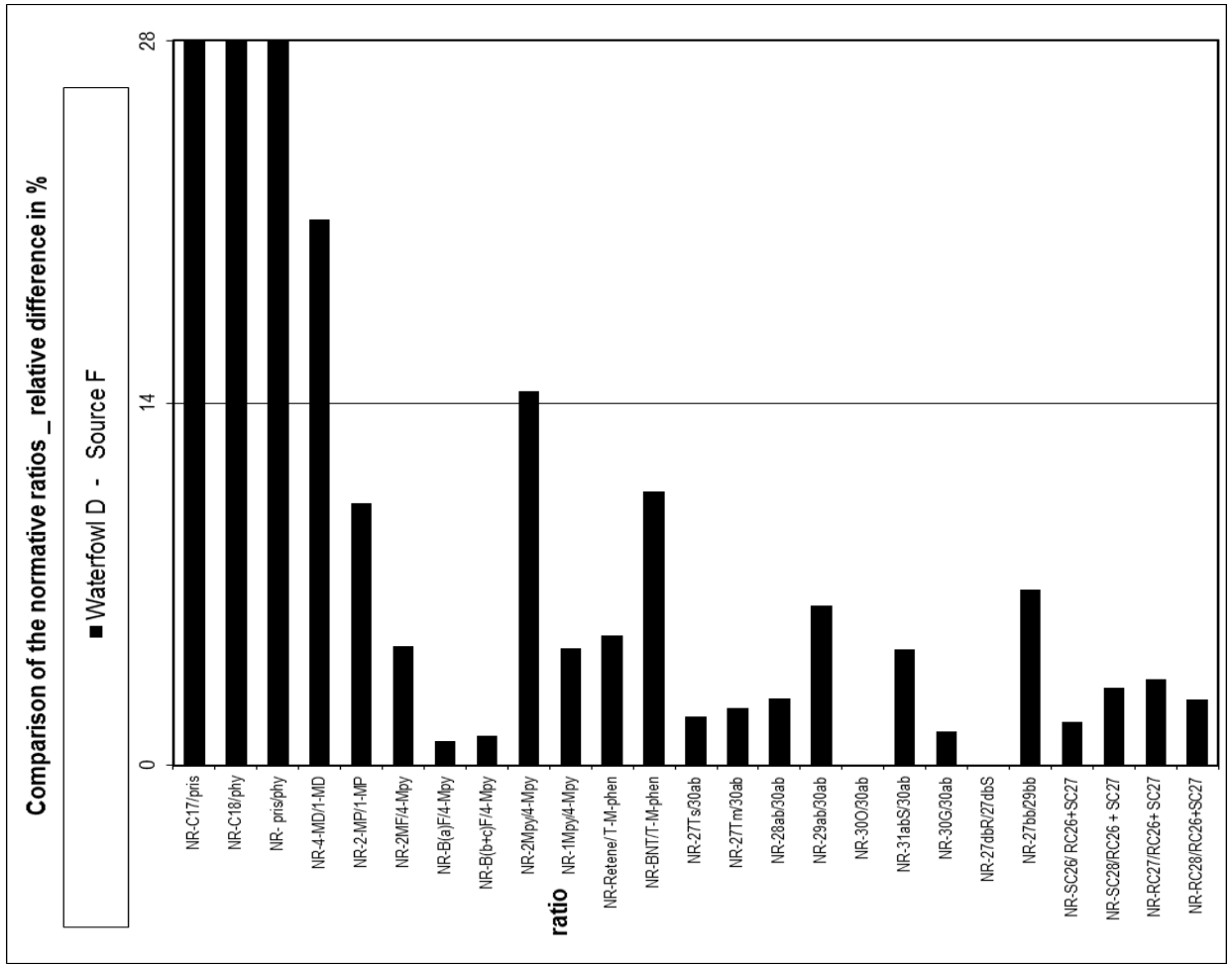


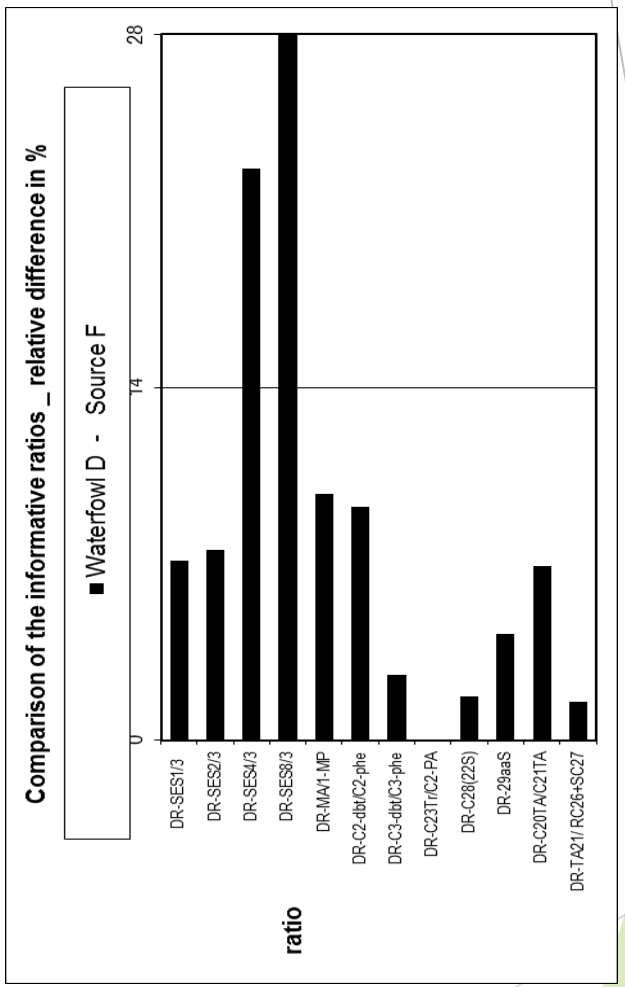
Four failures explained through weathering: positive match

PW-Plot – Waterfowl D vs. Source F



Ratio Comparison – Waterfowl D vs. Source F





All failing ratios explained through weathering: positive match

Conclusions

- The CEN (2012) method was applied in comparing environmental and potential source samples. Caution has to be taken to address co-extractives and biogenic material. Proper sample preparation is critical.
- Consideration of mixing of spilled material with unreported or uncleaned petroleum from previous spills (Case Study 2).
- Weathering assessments of DRs and chromatograms are particularly useful when comparing spilled material with impacted environmental samples.
- The necessity of collecting a large amount of information (chromatograms and DRs) as prescribed by CEN (2012) has been illustrated in the three case studies discussed.
- Weathering assessments are critical to determine which data are pertinent for sample and source comparisons and which are not.

Acknowledgements

- Newalta Corporation, Calgary, Alberta. Sample collection, litigation protocol.
- Dr. Milan Ralitsch, Paracel Laboratories, Calgary, Alberta. Forensic chemical analyses following litigation protocol.

NEW BOOK: Oil Spill Environmental Forensics Case Studies, Ed. Z. Wang and S. Stout, Elsevier, Inc.

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