APPLICATION OF CEN METHODOLOGY IN EVALUATING SOURCES OF MULTIPLE LAND-BASED FUEL SPILLS IN ALBERTA

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The Issue

- Global news report that between 1975 and 2012 a large number of spills (28,666) occurred in Alberta (Young, 2013).
- Spillage from well pads, pipelines, batteries, and spills resulting from train derailments and tanker accidents can an do release petroleum.
- Areas affected include: 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).

- Young, L. (2013). Crude Awakening: 37 Years of Oil Spills in Alberta, May 22, 2013, Global News
- Nikiforuk, A. (2017). On Oil Spills, Alberta Regulator Can’t Be Believed: New Report. The Tyre News, Culture Solutions.

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.

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

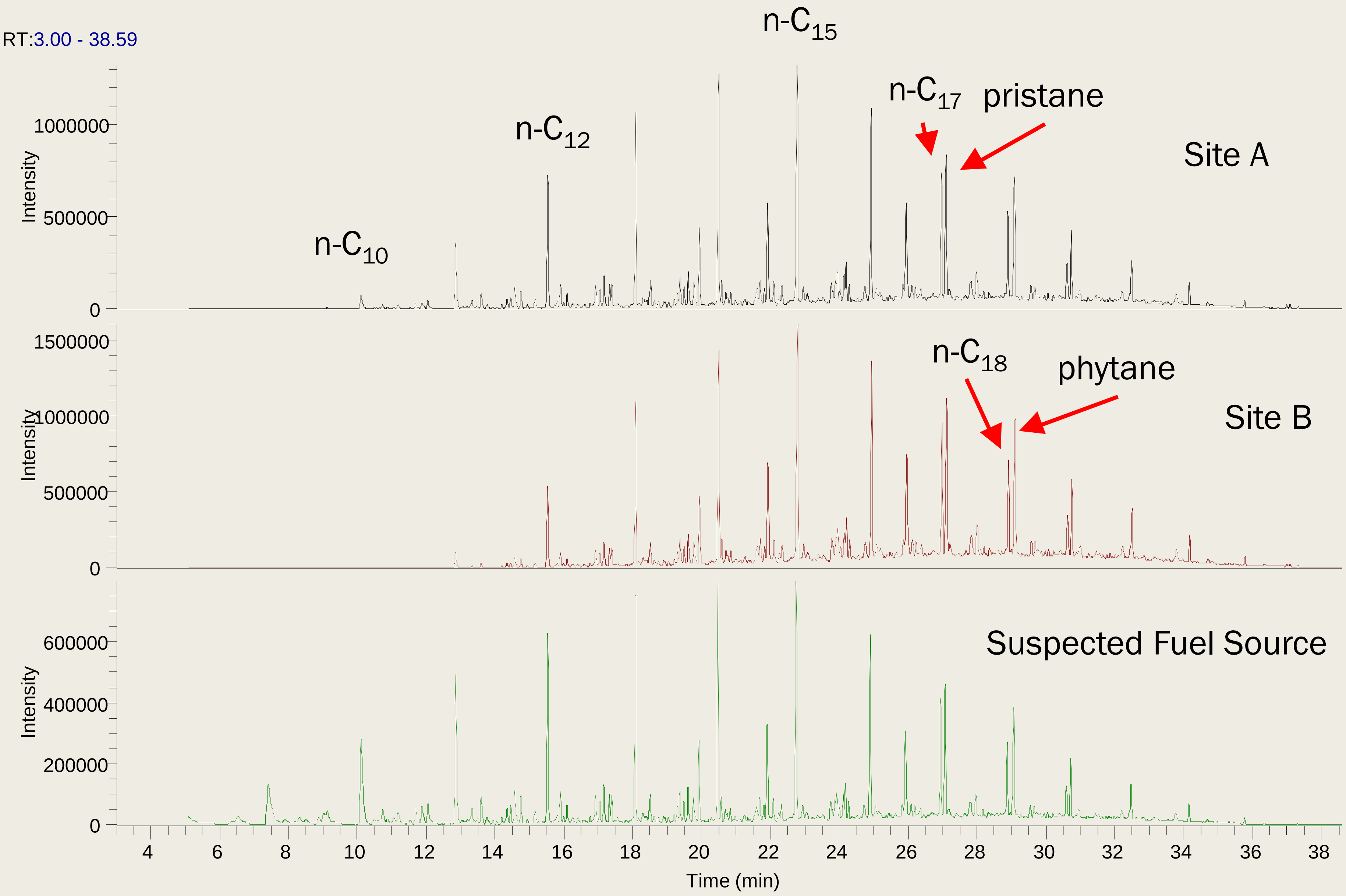
- Quantitative methods such as the technical guideline prepared by the Centre of European Norms (CEN, 2012) relies on a tiered approach that includes: (1) a qualitative assessment of GC/FID or GC/MS chromatograms to assess the overall character of oil in a samples or potential source (2) a quantitative comparison of diagnostic ratios of PAHs and petroleum biomarkers in a sample and source, as well as weathering assessments, and (3) a post analysis synthesis of the data to confirm resulting scientific conclusions.

Methods

- Soil samples (6 – 50 g) are mixed with anhydrous sodium sulfate and subjected to extraction via Soxhlet, shake or ultrasonic extraction.
- Resulting 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.
- Cleanup is performed on 20 – 50 mg of extract material to prevent overloading cleanup column.
- Final extracts concentrated and analyzed using GC/FID, GC/MS (scanning and SIM).

Case Study 1

- Fuel spill was 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
- Chromatograms indicated 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.



RT:3.00 - 38.59
n-C10
n-C12
n-C15
n-C17
pristane
Site A
n-C18
phytane
Site B
Suspected Fuel Source
Intensity
Intensity
Intensity
1000000
500000
0
1500000
1000000
500000
0
600000
400000
200000
0
4
6
8
10
12
14
16
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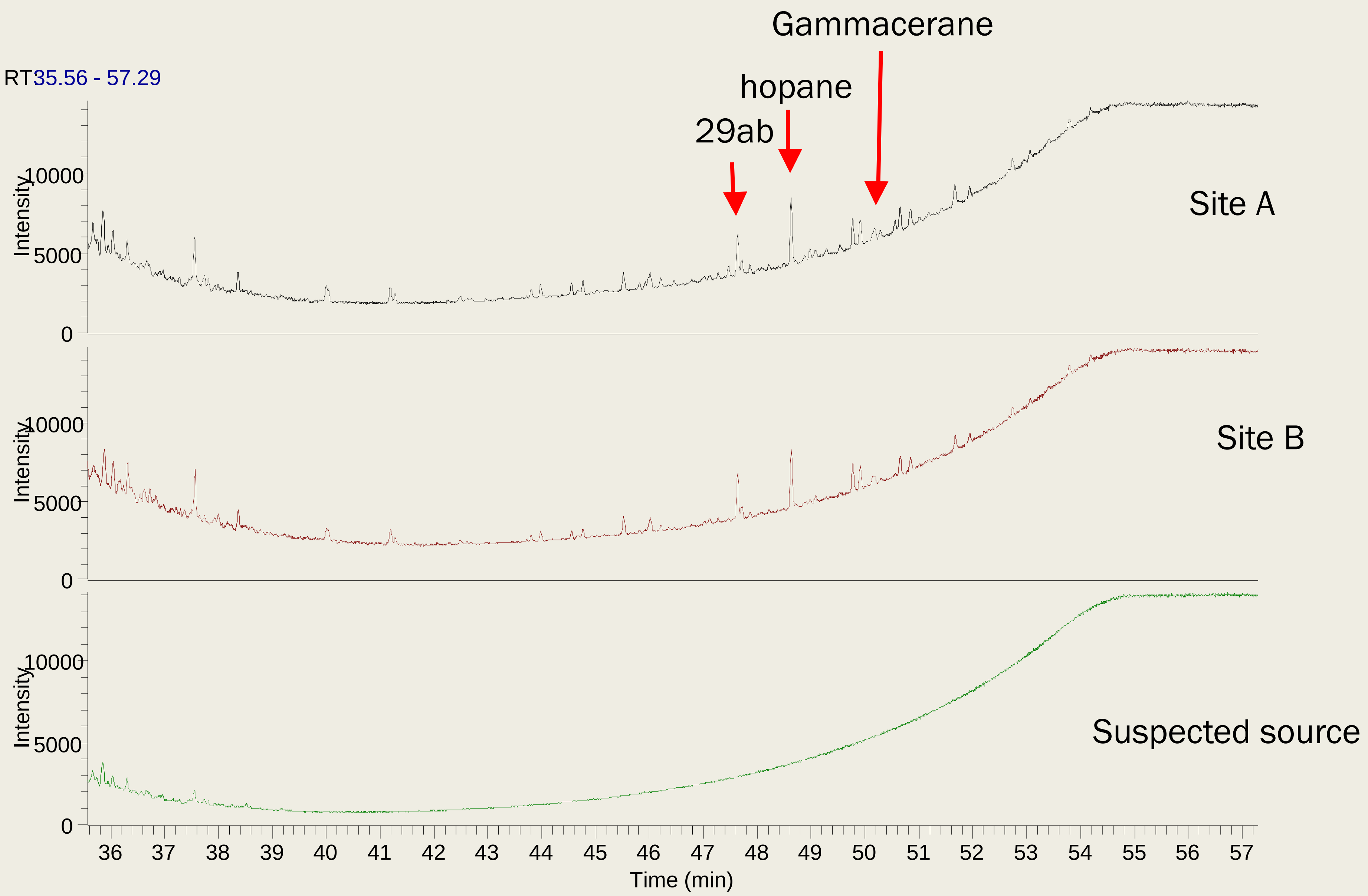
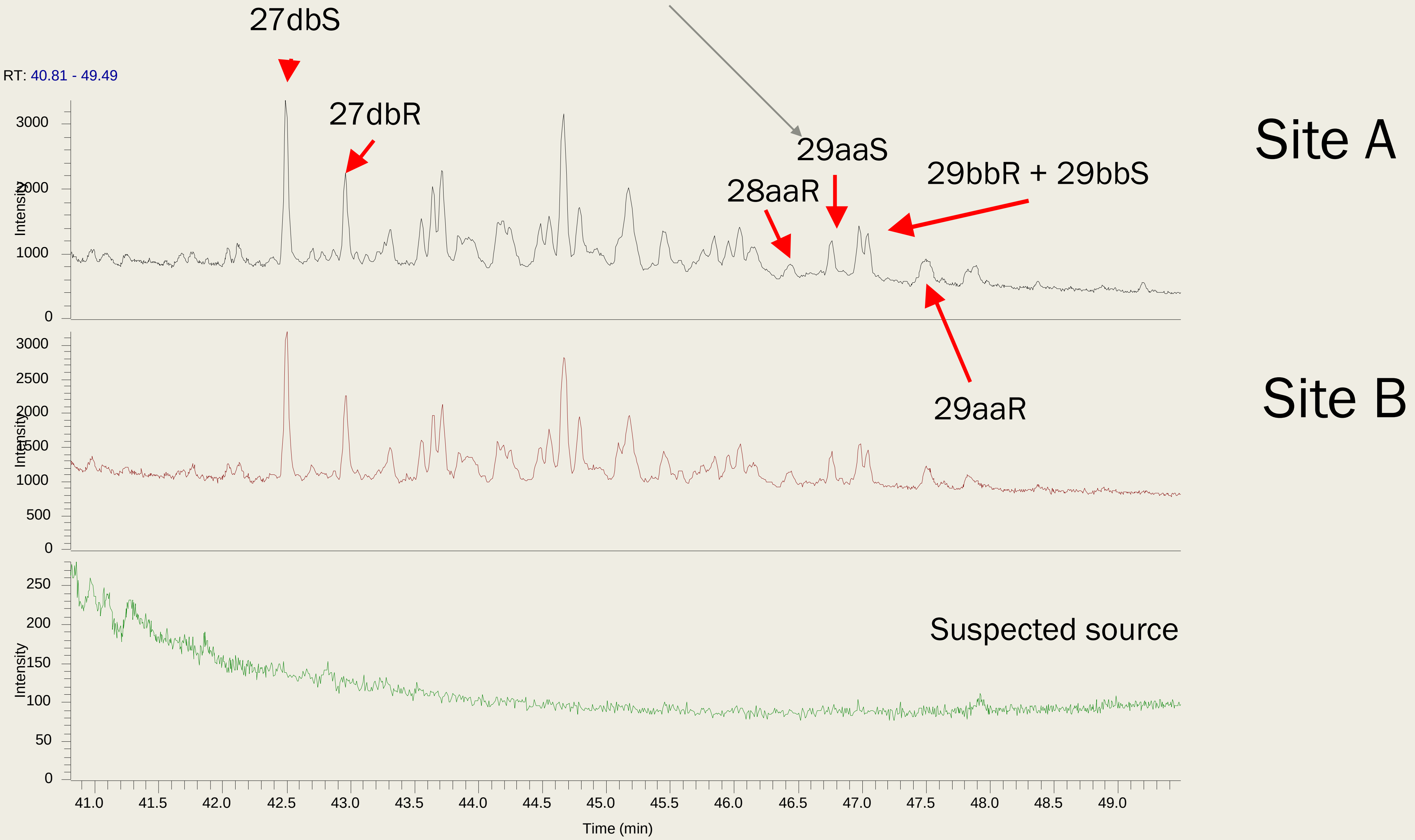
32
34
36
38
Time (min)

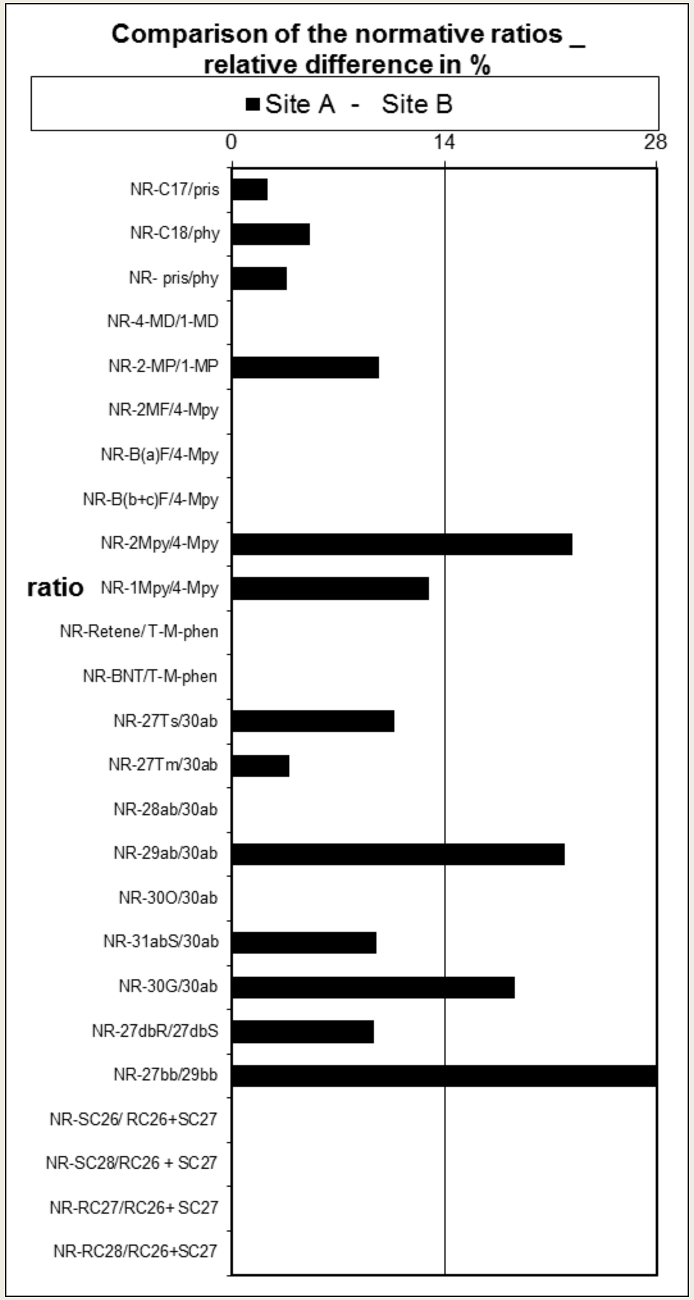


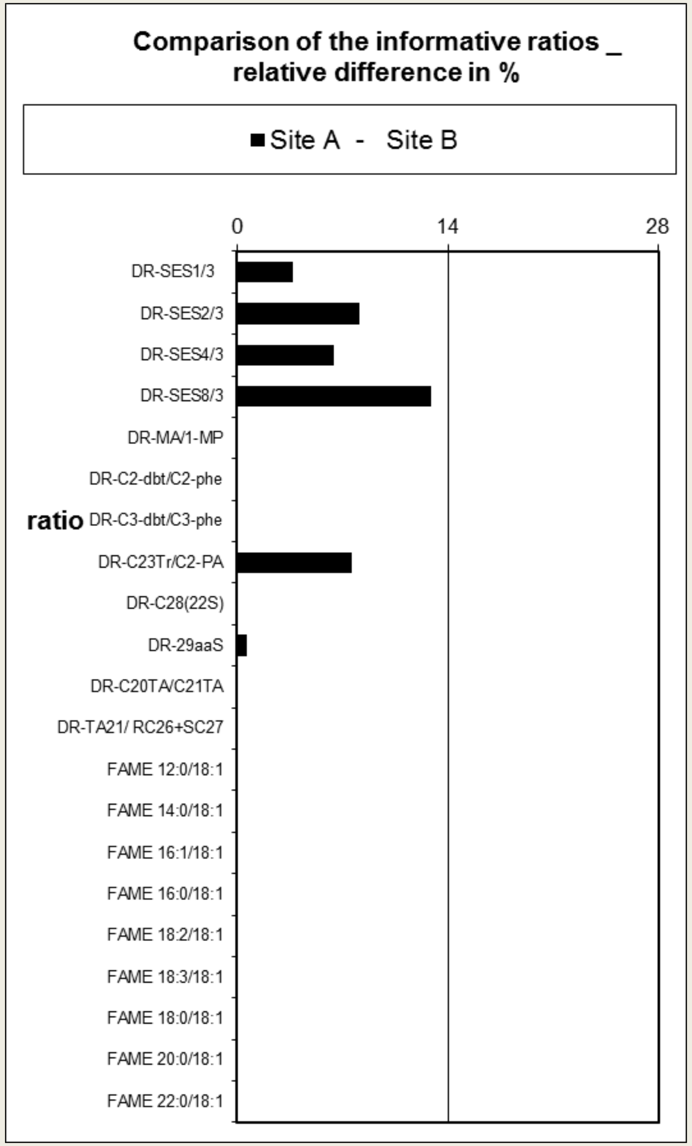
Tricyclic terpanes and hopanes



Diasteranes and ααα-Steranes

αββ - Steranes





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

Comparison of spill sites

Case 1 - Conclusions

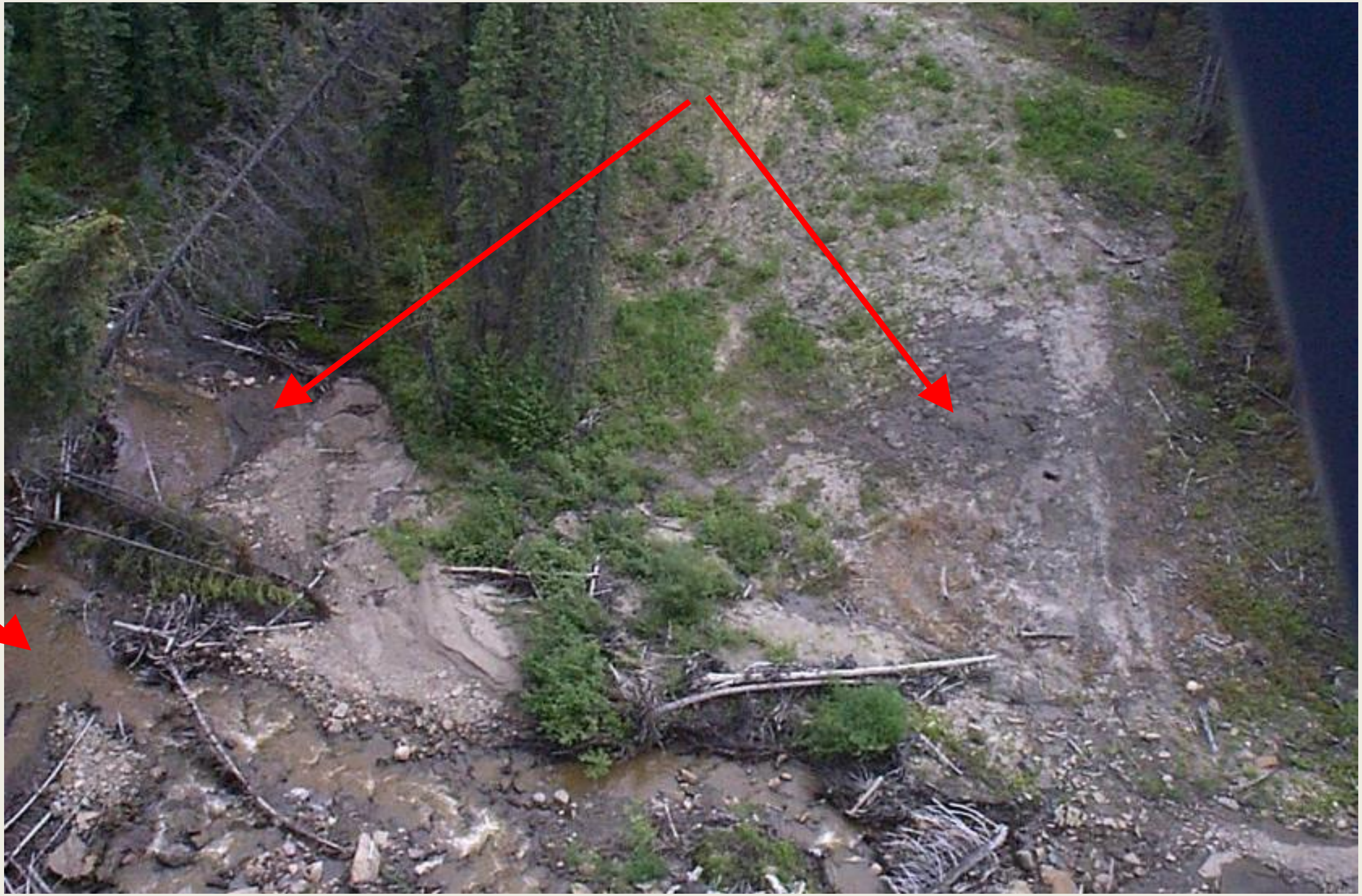
- Application of CEN (2012) revealed that tricyclic terpanes, hopanes as well as ααα- and ααβ-steranes were present in the contaminated soil but not in the suspected source fuel. This suggested the tanker truck was not the source of contamination.
- Our analysis did not stop there, we collected data for 19 petroleum biomarker ratios, and found four ratios exceeded 14% relative difference when we compared the two soil samples. 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 (CEN, 2012; Stout, 2016).
- This finding suggested that the soil was contaminated with differing sources and neither related to the suspected tanker truck.

CASE STUDY 2

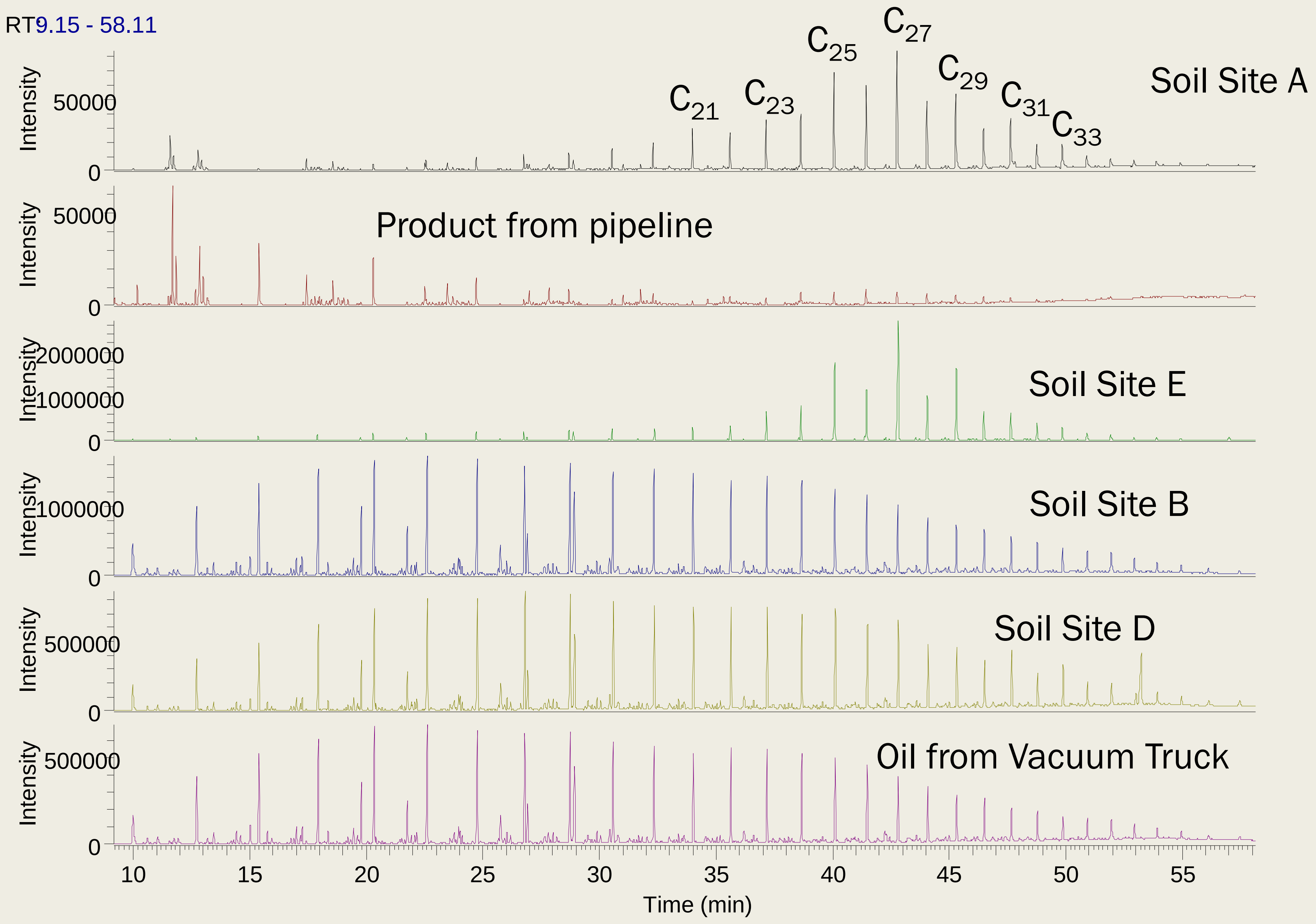
- Crude oil pipeline fracture in remote area.
- Cleanup well underway when investigators arrived
- Pipeline purged and cleaned prior to sampling
- Only other source sample available from vacuum truck
- This product compared to four contaminated soil samples taken from the spill site.

What is it? Where did it come from?

Is this a fish bearing
stream or fish habitat?

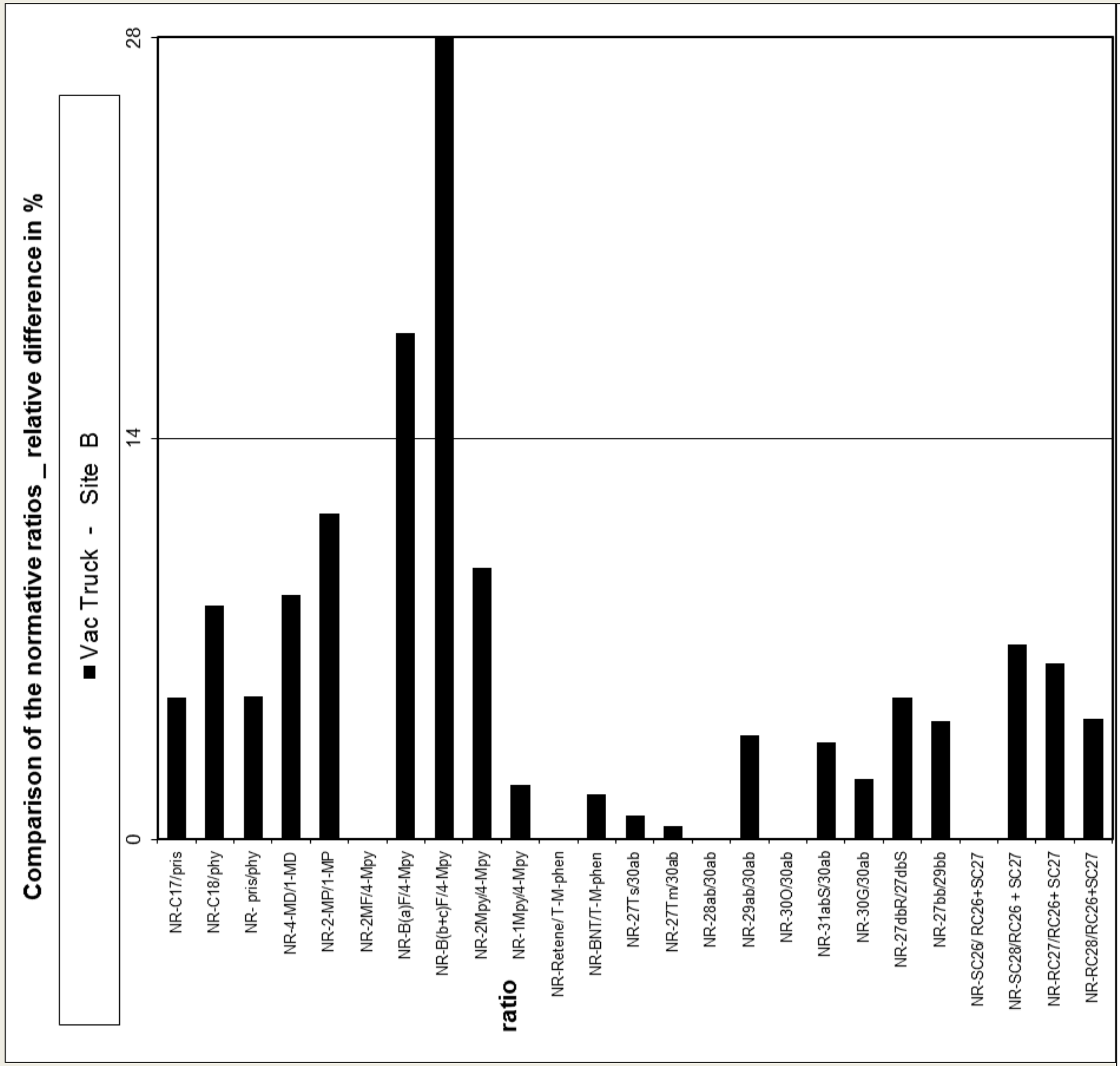


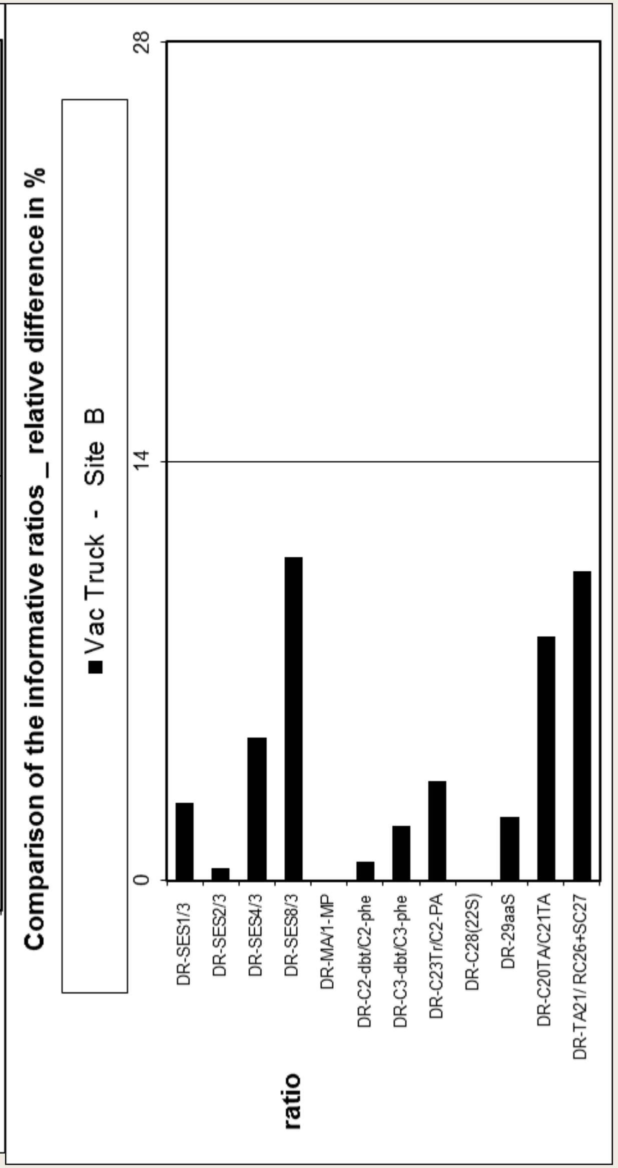
Is this stuff toxic?
Could we be dealing
With Fisheries Act charges?


RT9.15 - 58.11
Soil Site A
C21
C23
C25
C27
C29
C31
C33
Product from pipeline
Soil Site E
Soil Site B
Soil Site D
Oil from Vacuum Truck
Intensity
50000
0
2000000
1000000
500000
10
15
20
25
30
35
40
45
50
55
Time (min)

Chromatographic interpretations

- Product from pipeline is unusual not readily comparable to soils. Pattern inconsistent with crude oil.
- Product from vacuum truck consistent with evaporated crude oil and similar to oil found at sites B and D.
- Site A and E does not appear similar to vacuum truck or site 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 present at all is present in minor concentrations





Comparison of Vaccum Truck and Site B

Normative and Informative Ratios Interpretation

Normative and informative ratios obtained following ***comparison of the vacuum truck product and soil sample from Site B.***

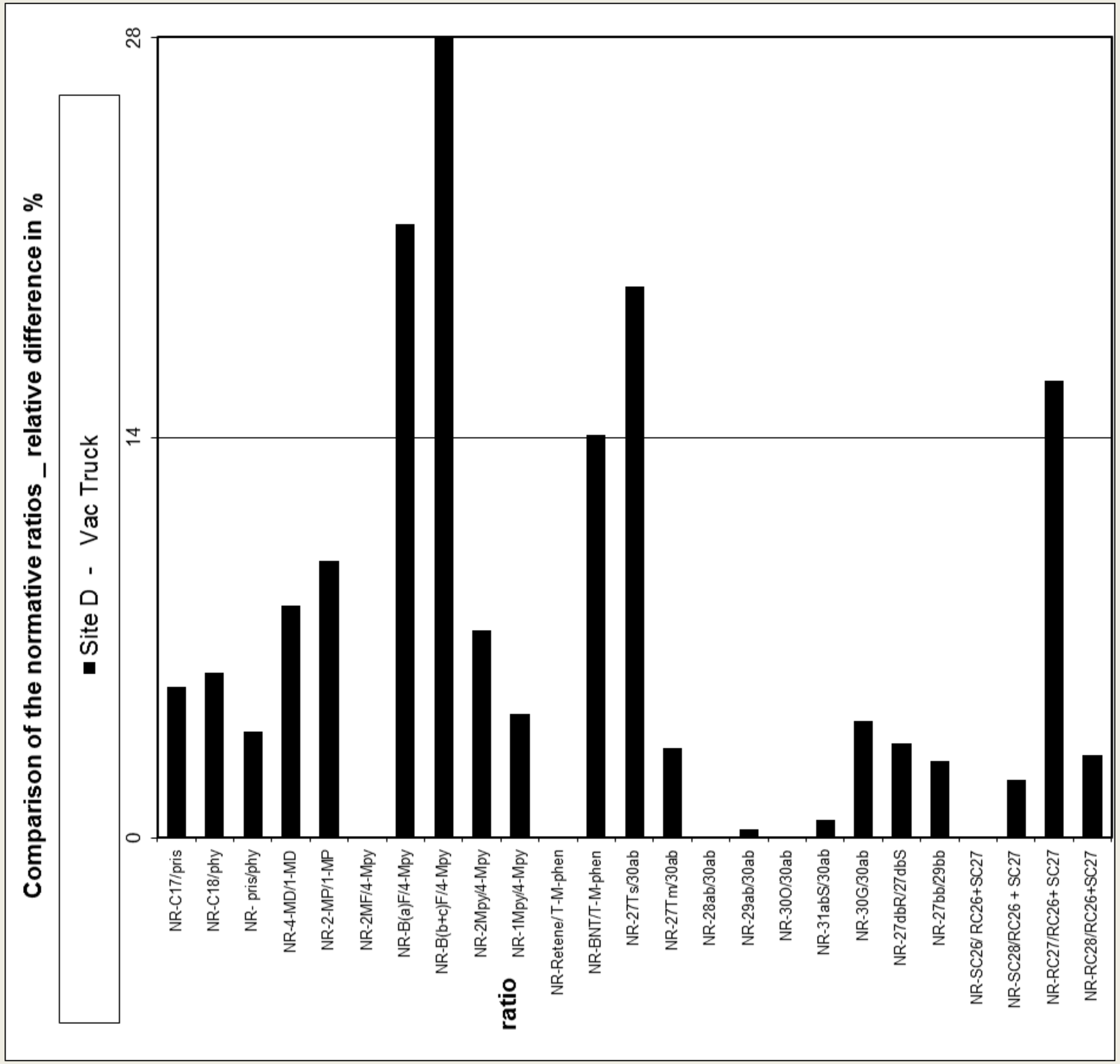
Two ratios observed to have a %RD greater than 14% indicating a no match scenario.

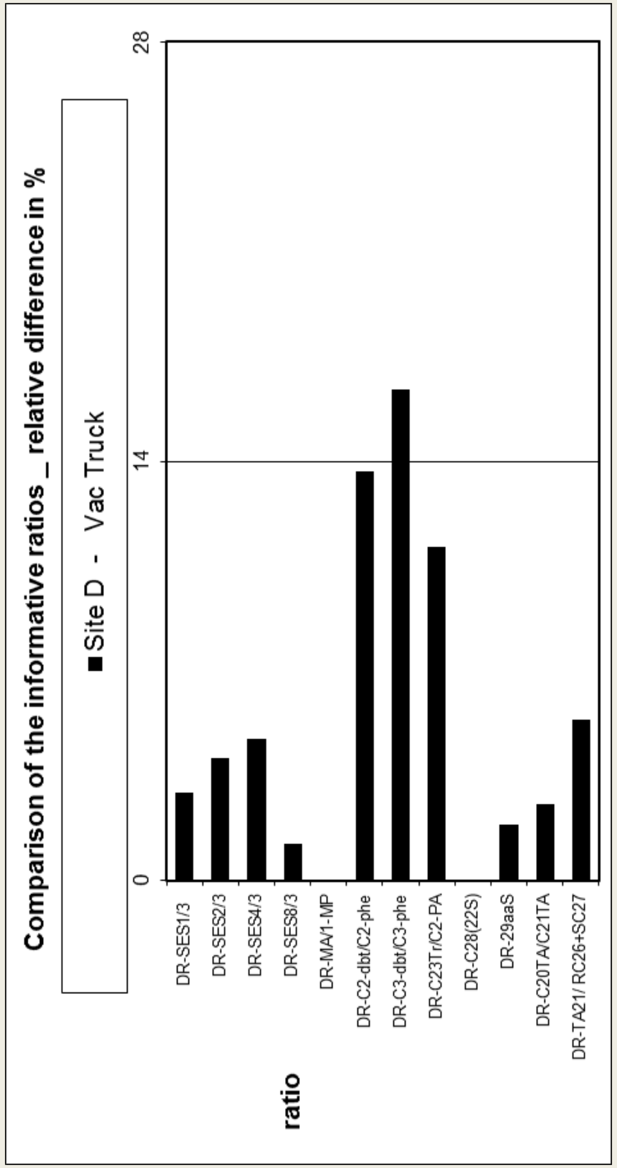
These ratios include: benzo(a)fluorine/4-methy-pyrene (BaF/4-Mpy) and benzo(b+c)fluorine/4-methyl-pyrene (B(b+c)F/4-Mpy.

These ratio exceedances of 14% RD can be explained by weathering through photo oxidation.

Peri-condensed structures such a 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 after spillage to the site surface

Because these two ratio exceedances can be explained by weathering (photo oxidation) it is concluded that the product taken from the vacuum truck and soil from site B were a positive match.





Comparison of Vacuum Truck and Site D

Vaccum Truck and Site D

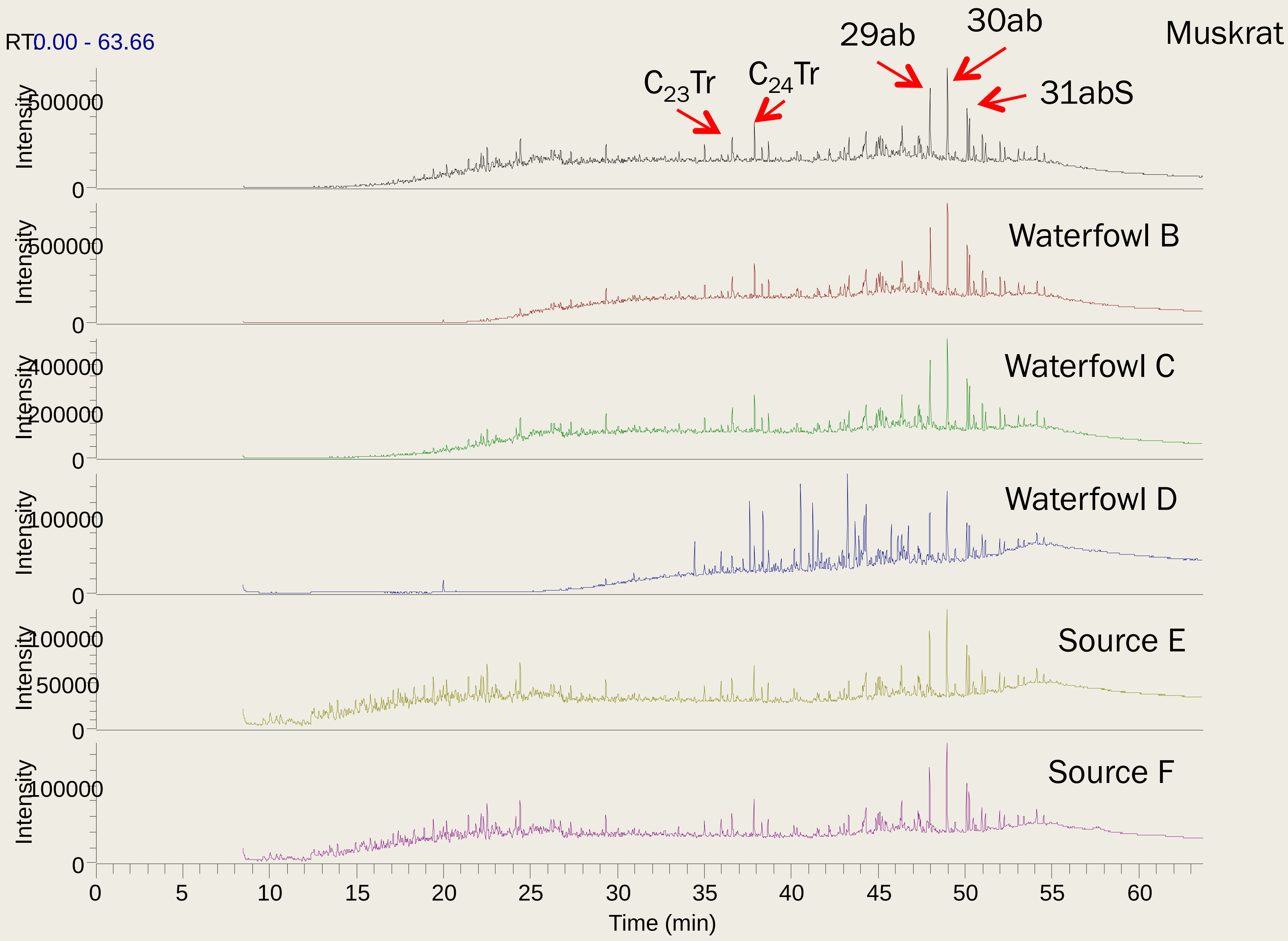
- *Ratios which exceed 14% RD*
- B(a)F/4-MPy (benzo(a)fluorine/4-methy-pyrene)
- B(b+c)F/4-Mpy (benzo(b+c)fluorine/4-methyl-pyrene)
- BNT/T-M-Phe (benzo(b)naphtha(1,2-d)thiophene/tetra-methyl-phenanthrene)
- 27Ts/30ab (18α(H)-22,29,30-trisnorhopane/17α(H),21β(H)-hopane)
- RC27/RC26+SC27 (C_{27}-20R-triaromatic sterane/C_{26}-20R- + C_{27}-20S-triaromatic steranes)
- C_3-DBT/C_3-Phe (C_3-dibenzothiophenes/C_3-phenanthrenes)

Data Interpretation

- B(a)F/4-MPy – influenced by weathering, namely photo oxidation
- B(b+c)F/4-MPy – influenced by weathering, namely photo oxidation
- BNT/T-M-Phe – influenced by dissolution in water because of sulphur presence
- C_3-DBT/C_3-Phe – influenced by dissolution in water because of sulphur presence
- Pipeline flushed with water prior to repair therefore dissolution is a reasonable mechanism
- RC27/RC26+SC27. Triaromatic steranes generally stable but can photo oxidize. However, more susceptible triaromatic steranes such as C21TA/RC26+SC27 and RC28/RC26+SC27 were not affected. Therefore, results is considered valid and is evidence for a non-match
- 27Ts/30ab is stable and not subject to weathering. Further evidence for a non-match conclusion.
- Conclusion: 4-ratio failures can be explained by weathering (photo oxidation and water dissolution). Two cannot be explained therefore Site D is a non-match with the vacuum truck

Case Study 3

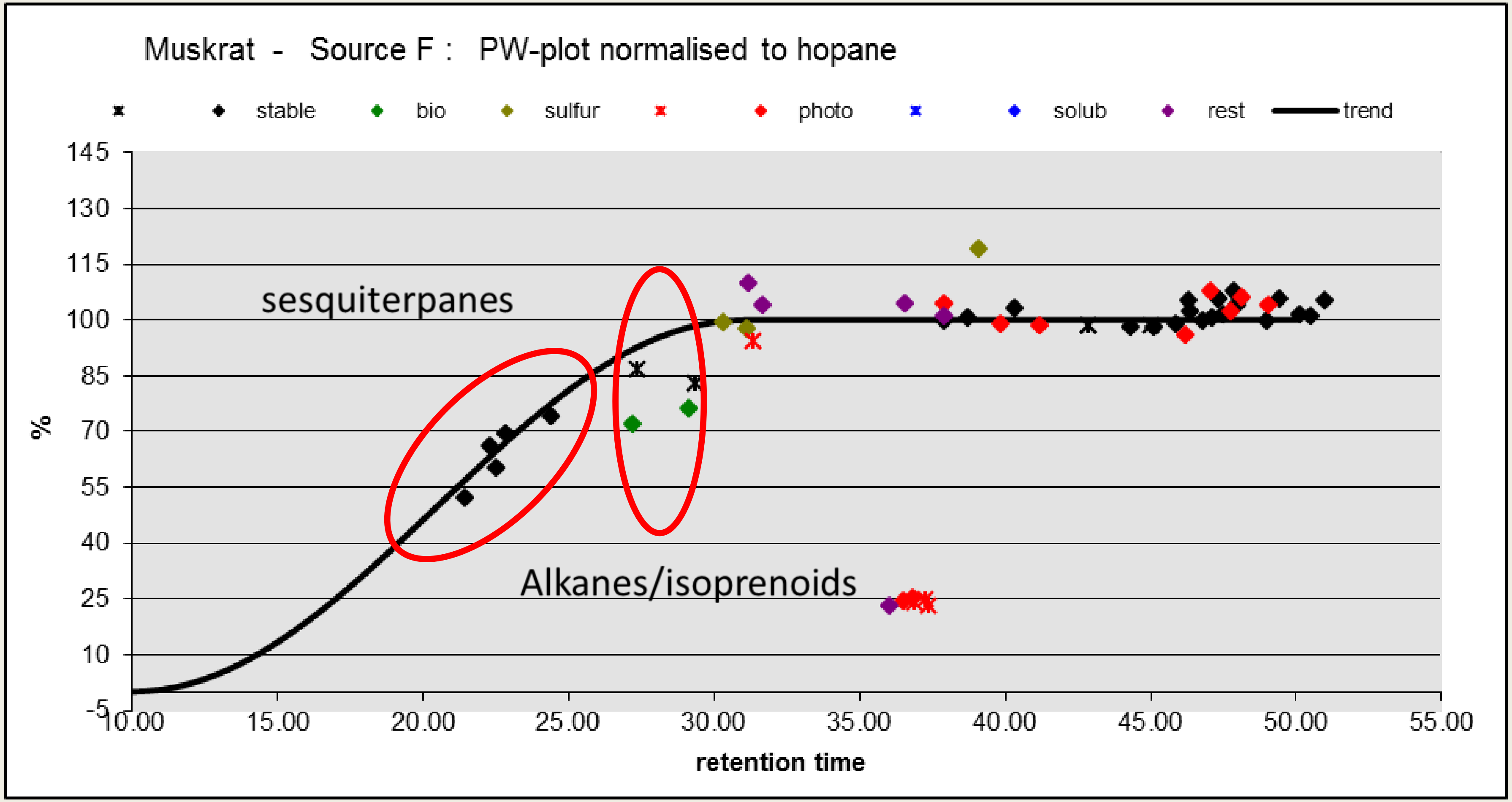
- Large heavy oil spill observed and reported.
- Sometime after carcasses of waterfowl, and a muskrat found removed from the area.
- Since waterfowl and muskrats can migrate after exposure to oil but prior to death, the issue at hand was whether the oil found on the deceased waterfowl and muskrat came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



RT0.00 - 63.66
Muskrat
$C_{23}Tr$
$C_{24}Tr$
29ab
30ab
31abS
Waterfowl B
Waterfowl C
Waterfowl D
Source E
Source F
Intensity
500000
400000
200000
100000
50000
0
0
5
10
15
20
25
30
35
40
45
50
55
60
Time (min)

Interpretation of Chromatograms

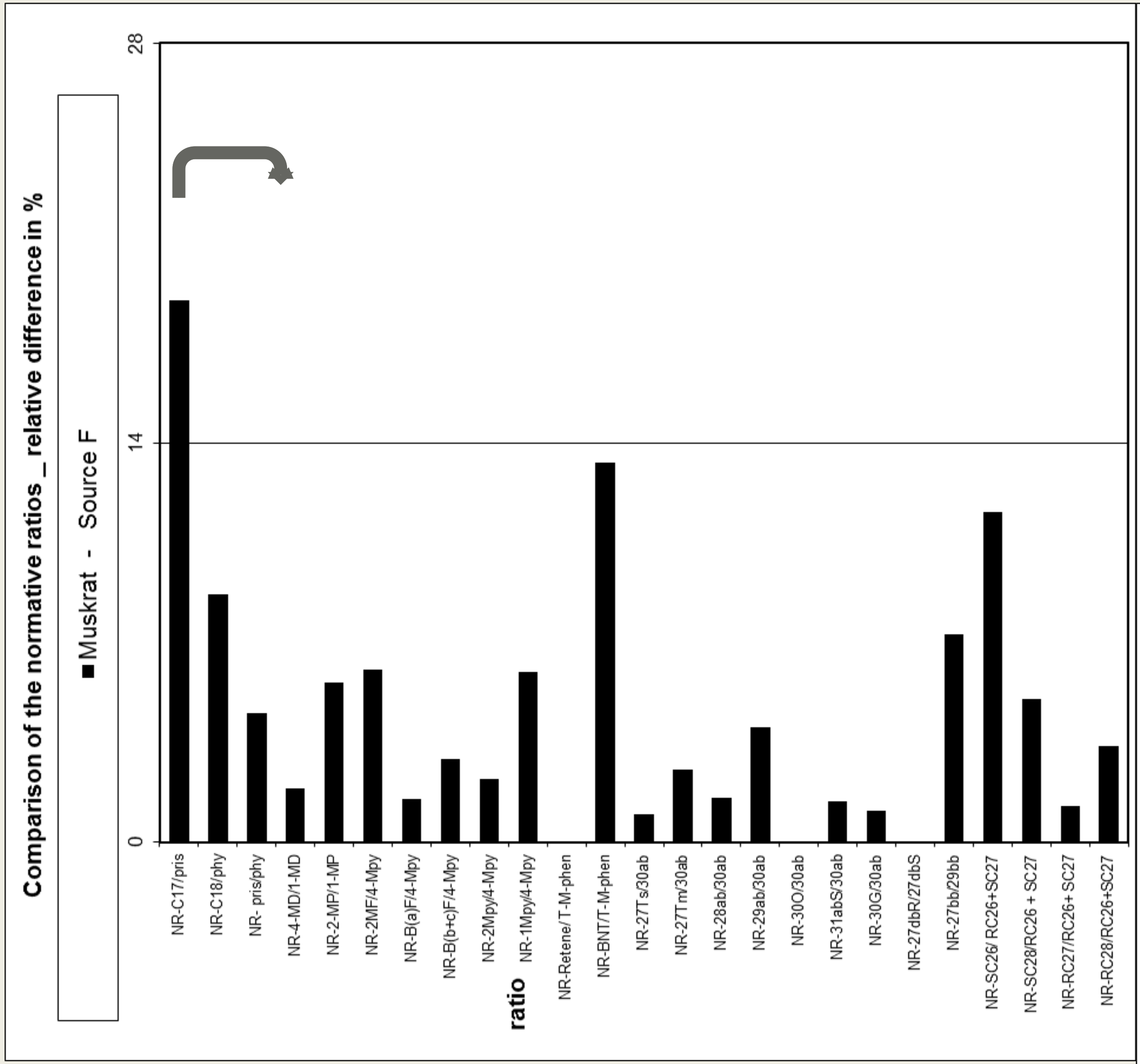
- Identification heavy oil is obvious. Tricyclic diterpanes (C23Tr and C24Tr), as well as norhopanes, hopane, and homohopanes (29ab, 30ab, and 31abS). Lack of n-alkanes which is associated with conventional petroleum
- Two source samples appear similar (E and F) as well as muskrat and waterfowl (B and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

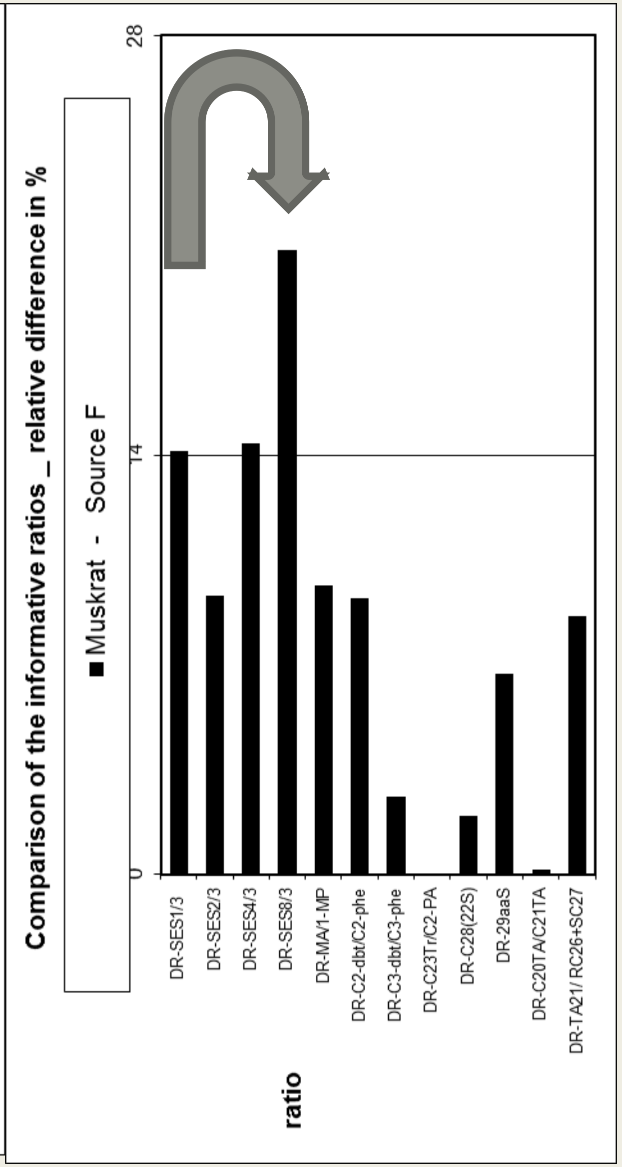


Data for 59 petroleum biomarkers collected

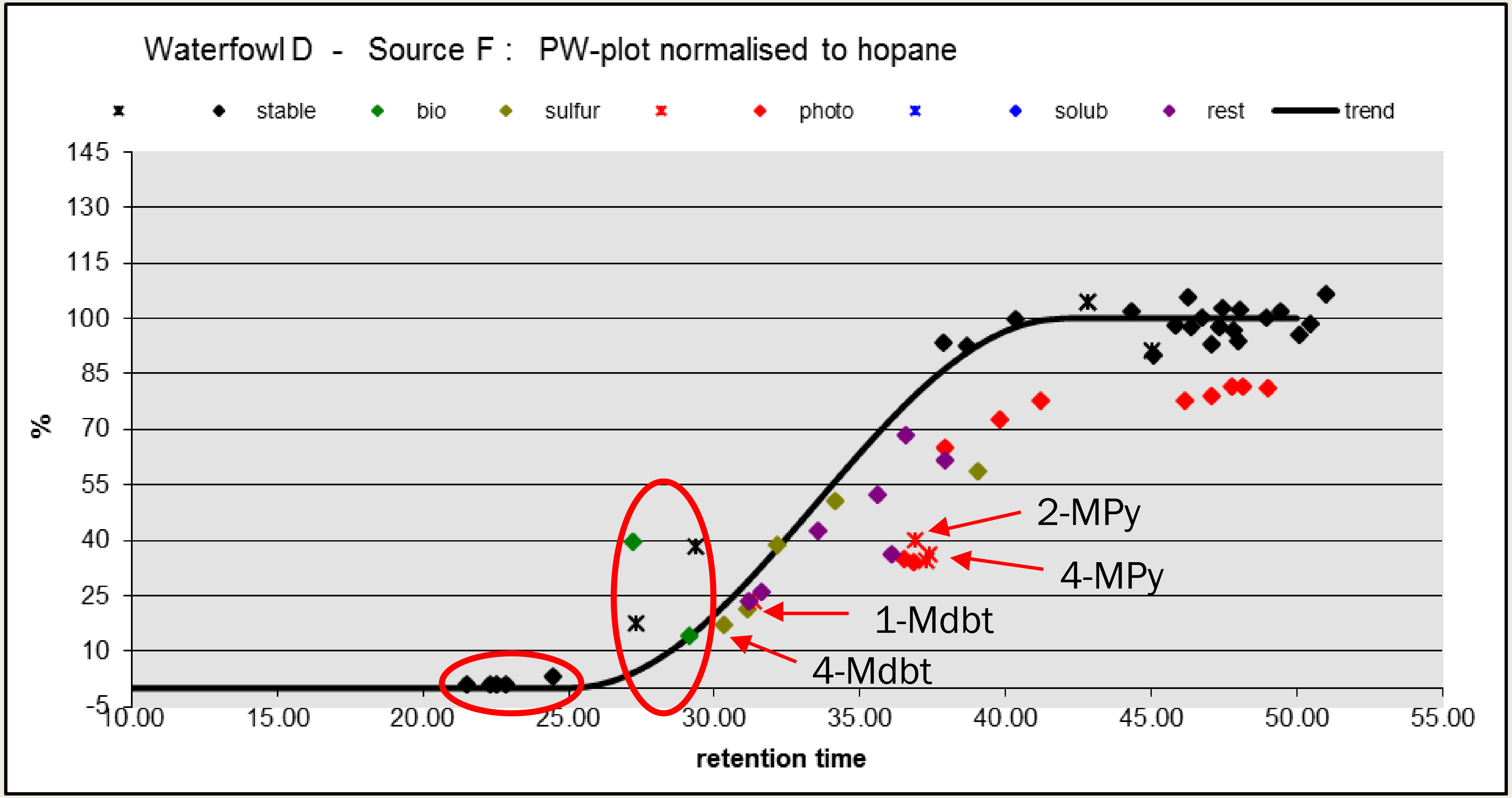
Alkanes/isoprenoids

Sesquiterpanes

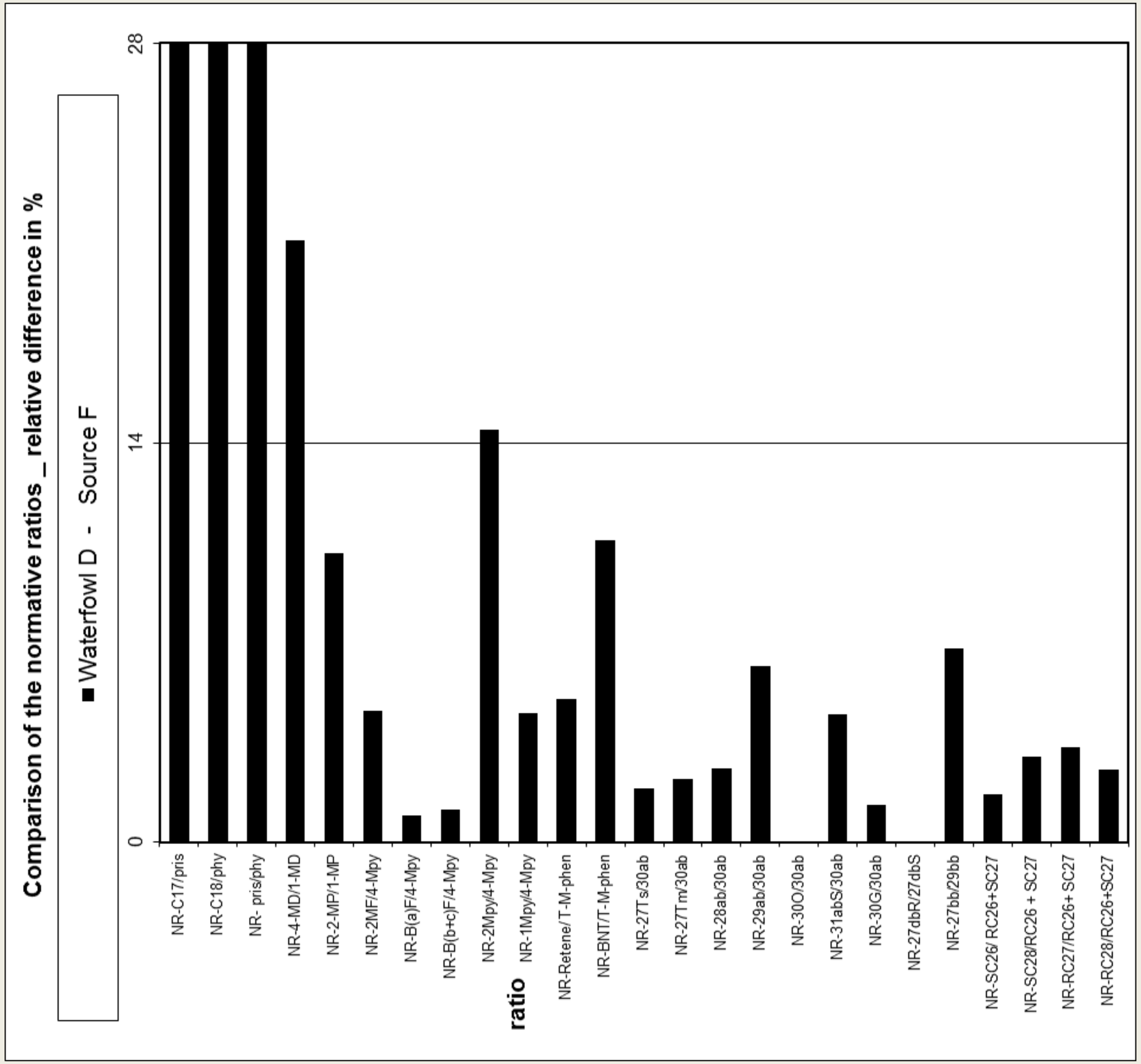


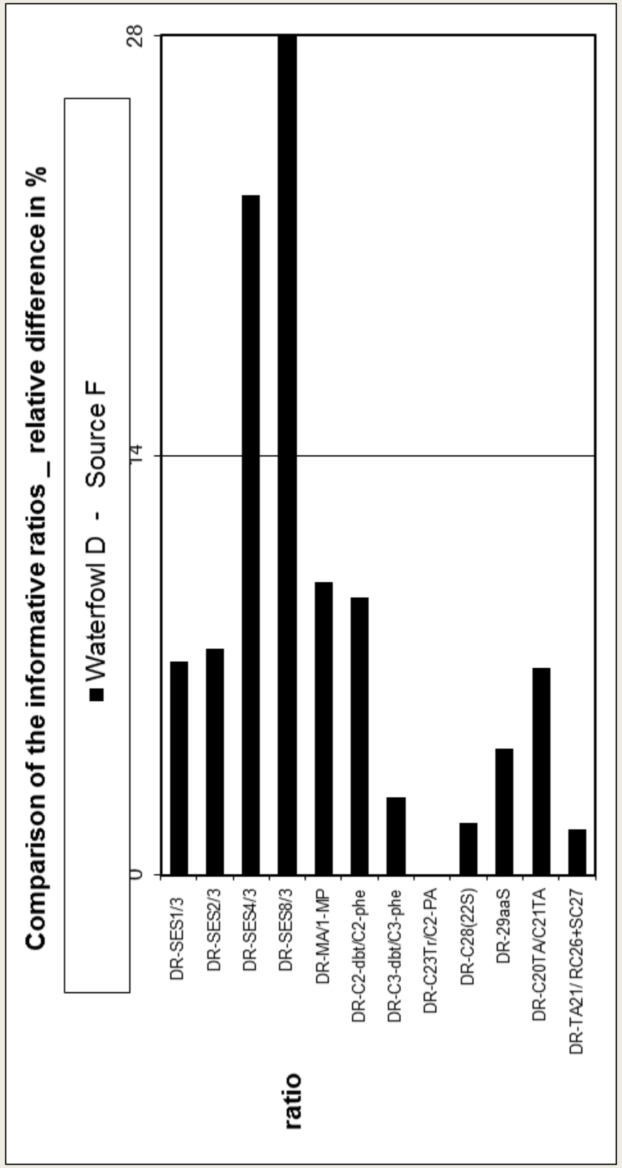


Four failures explained through weathering, therefore positive match



Waterfowl D - Source F : PW-plot normalised to hopane
stable
bio
sulfur
photo
solub
rest
trend
%
145
130
115
100
85
70
55
40
25
10
-5
10.00
15.00
20.00
25.00
30.00
35.00
40.00
45.00
50.00
55.00
retention time
2-MPy
4-MPy
1-Mdbt
4-Mdbt





All failing ratios explained through weathering, therefore positive match

Conclusions

- Muskrat and waterfowl samples a positive match with source oil. Differences explained by weathering.
- We applied the CEN (2012) method in comparing environmental and potential source samples. Caution has to be taken to address co-extractives and biogenic material. Proper sample preparation is critical.
- Furthermore 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.
- Furthermore, weathering assessments are critical to determine which data are pertinent for sample and source comparisons and which are not.

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

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