REM TECH 2012

Environmental

Challenges in the Source Identification and Aging of Extremely Weathered Petroleum Contaminated Soil Samples

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Geochemistry Metallurgy Mine Site Inspection Coal Oil & Gas Asset Care Tribology Environmental Food & Pharmaceutical

RIGHT SOLUTIONS RIGHT PARTNER

Private Labs

- Modus operandi is to analyze client submitted samples for hydrocarbons
- Apply the reference method for the Canada-Wide Standard for Petroleum Hydrocarbons in Soil – Tier 1 Method (Canadian Council of Ministers of the Environment, CCME, 2001)
- Delineate compliance or non-compliance following provincial regulations

Challenges

- When exceedences are observed reclamation is usually in order, and there may be substantial costs incurred.
- This generates a host of questions, usually spurred by insurance underwriters, including:

1. Type of petroleum product?
2. Potential sources?
3. Age of the product?

Question 3 is particularly important because we are in an era of property transfers and and shifting liability

Challenges

- Some clients expect these questions to be answered by simply studying the CCME Tier 1 hydrocarbon chromatograms which they paid for.
- Considering we are dealing with a likely litigation situation this is not possible
- Need to apply a forensic approach and good science based upon weight of evidence.

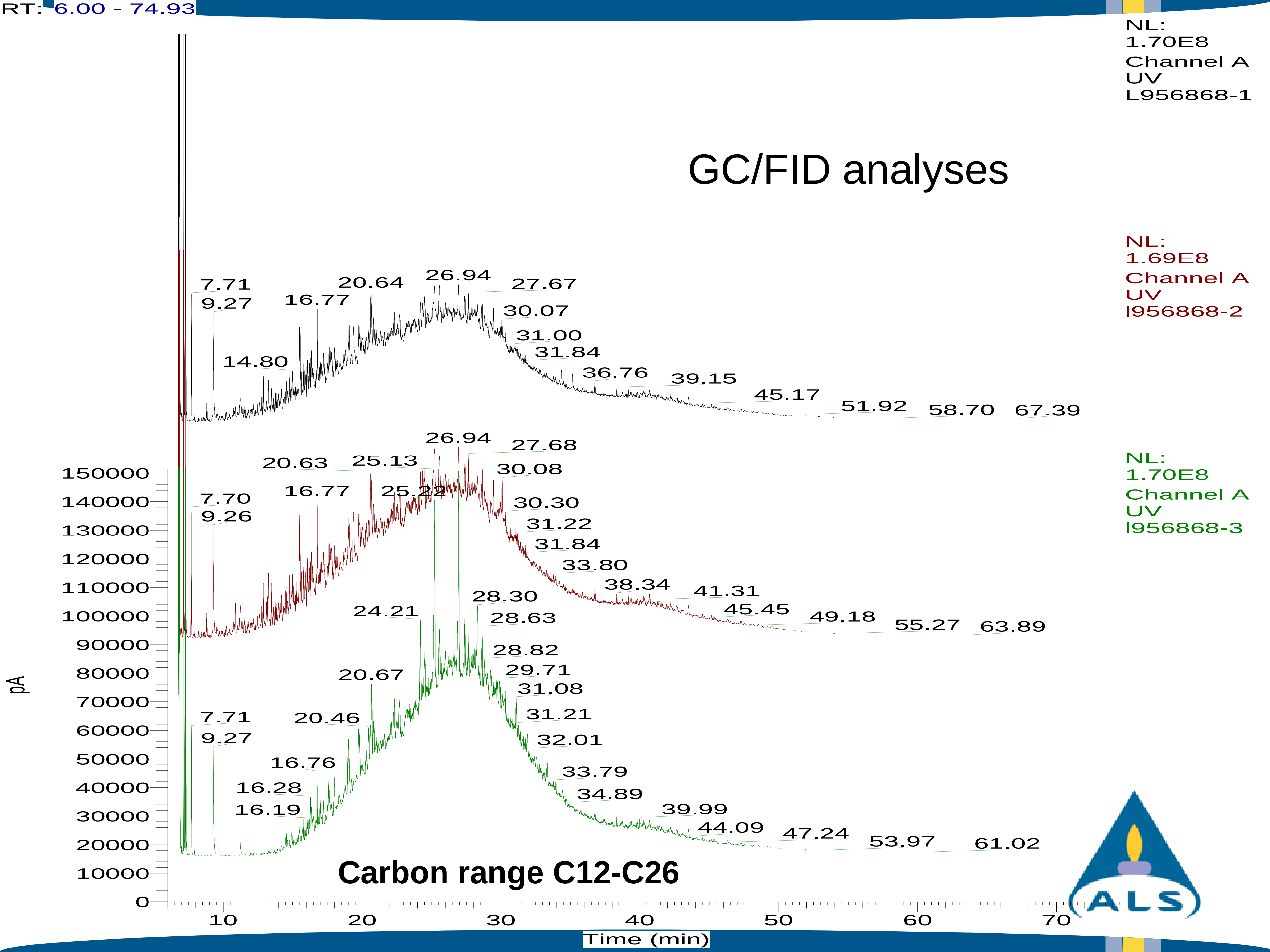
Background

- Received three soil samples from client
- CCME Tier 1 analyses revealed the presence of hydrocarbons above acceptable levels.
- Client requested information on nature of the petroleum, age and whether the samples were related, i.e. common source

Methods

- Soil samples (10 g) were mixed with sodium sulfate, and after the addition of labeled PAHs (internal standards) were subjected to Soxhlet extraction overnight with dichloromethane (DCM).
- Extract concentrated and cleaned up using neutral alumina/silica.
- Saturates removed with pentane and aromatics eluted with DCM.
- Analyses performed by GC/FID and GC/MS (SIM and scanning).

GC/FID analyses



Carbon range C12-C26

GC/FID Data

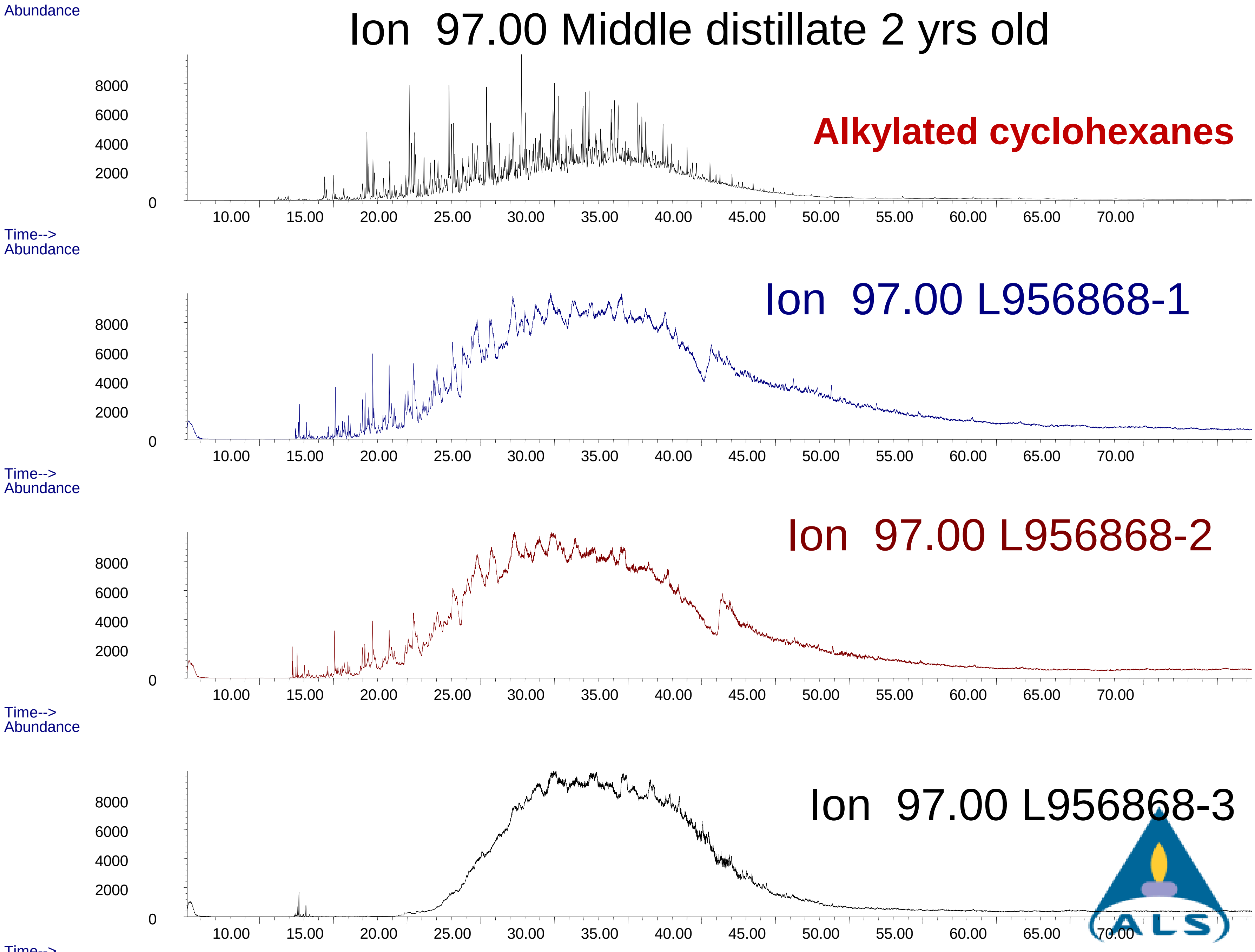
Sample	Pristane/ Phytane	n-C_{17}/pristane	Age (years)
Fresh	1.61	From Oudijk, 2009	
Moderate	1.73		
Degraded	1.59		
Very degraded	1.18		
L956868-1	0.978	0.559	15.1 ± 2
L956868-2	0.979	0.610	14.7 ± 2
L956868-3	0.946	0.504	15.6 ± 2
L956868-3	rep anal.	0.348-0.660	12.3-18.9

Christensen and Larson Method (1993)

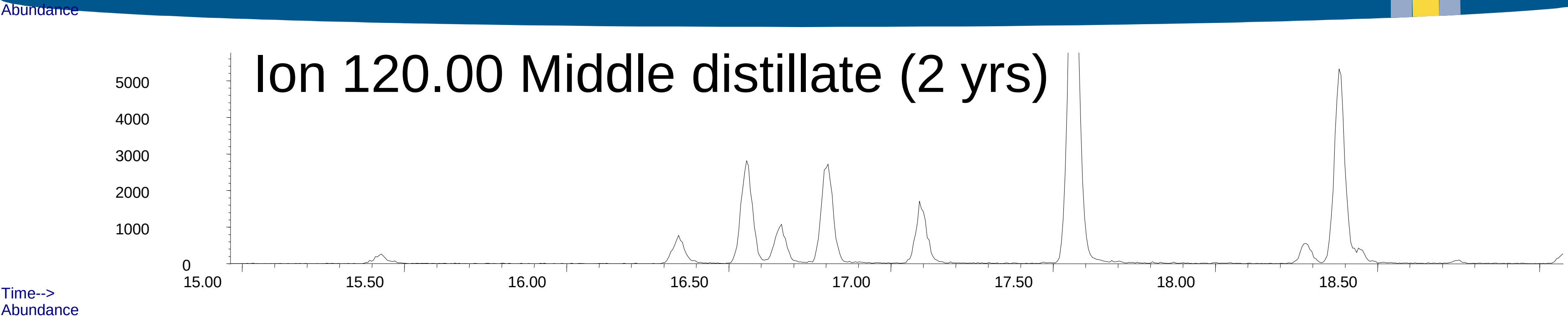
- Applies to middle distillates (heating oil)
- T (years) = -8.4 (n-C_{17}/pristane) + 19.8 (Kaplan 1997)
- Error is ± 2 years (Oudijk, 2009).
- Error is ± 1.5 years under optimal conditions and ± 5 years under the worst case conditions (Hurst and Schmidt (2005)
- Accepted by the courts in New Jersey and Massachusetts
- Is a viable method <u>if it is used within prescribed limitations.</u>
- Cannot be used anywhere and everywhere
- Literature cites many cases where this method does not apply
- Ref: Oudijk et al, 2006; Oudijk, 2009

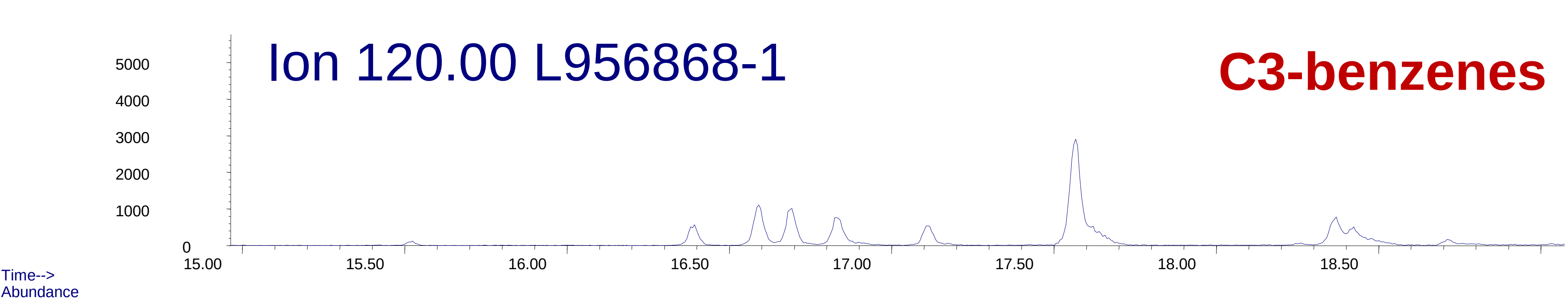
Age of Product

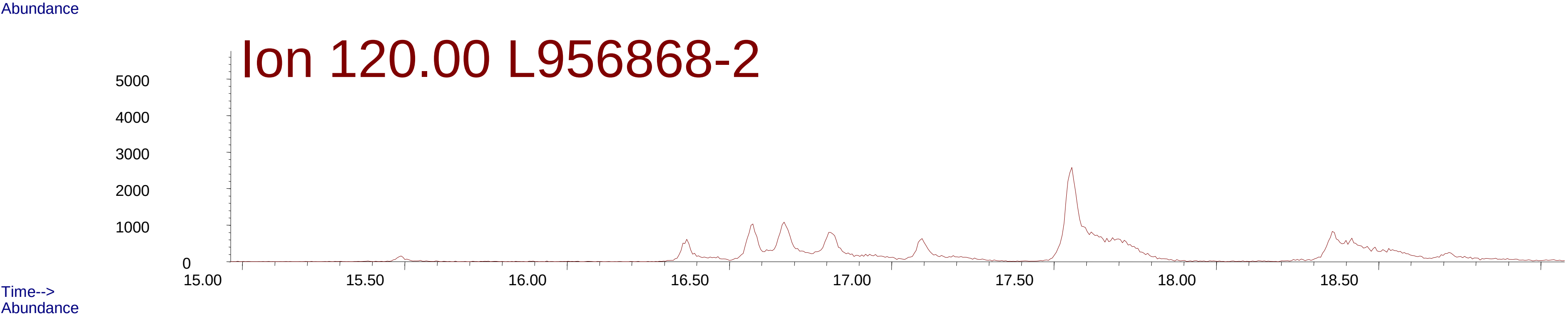
- Need more than just Christensen and Larsen method to determine age.
- Considering <u>possible litigation</u>, it would be risky to just use this method
- Another approach follows the depletion of select chemical classes as a function of soil type
- This approach provides a weight of evidence approach and age range.
- Ref: Oudijk (2009).

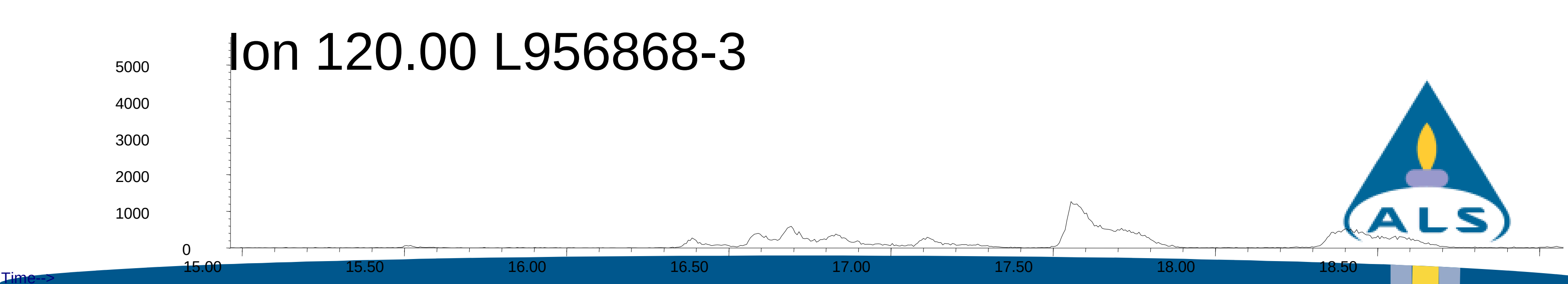

Ion 97.00 Middle distillate 2 yrs old
Alkylated cyclohexanes
Ion 97.00 L956868-1
Ion 97.00 L956868-2
Ion 97.00 L956868-3
Abundance
8000
6000
4000
2000
0
Time-->
10.00
15.00
20.00
25.00
30.00
35.00
40.00
45.00
50.00
55.00
60.00
65.00
70.00

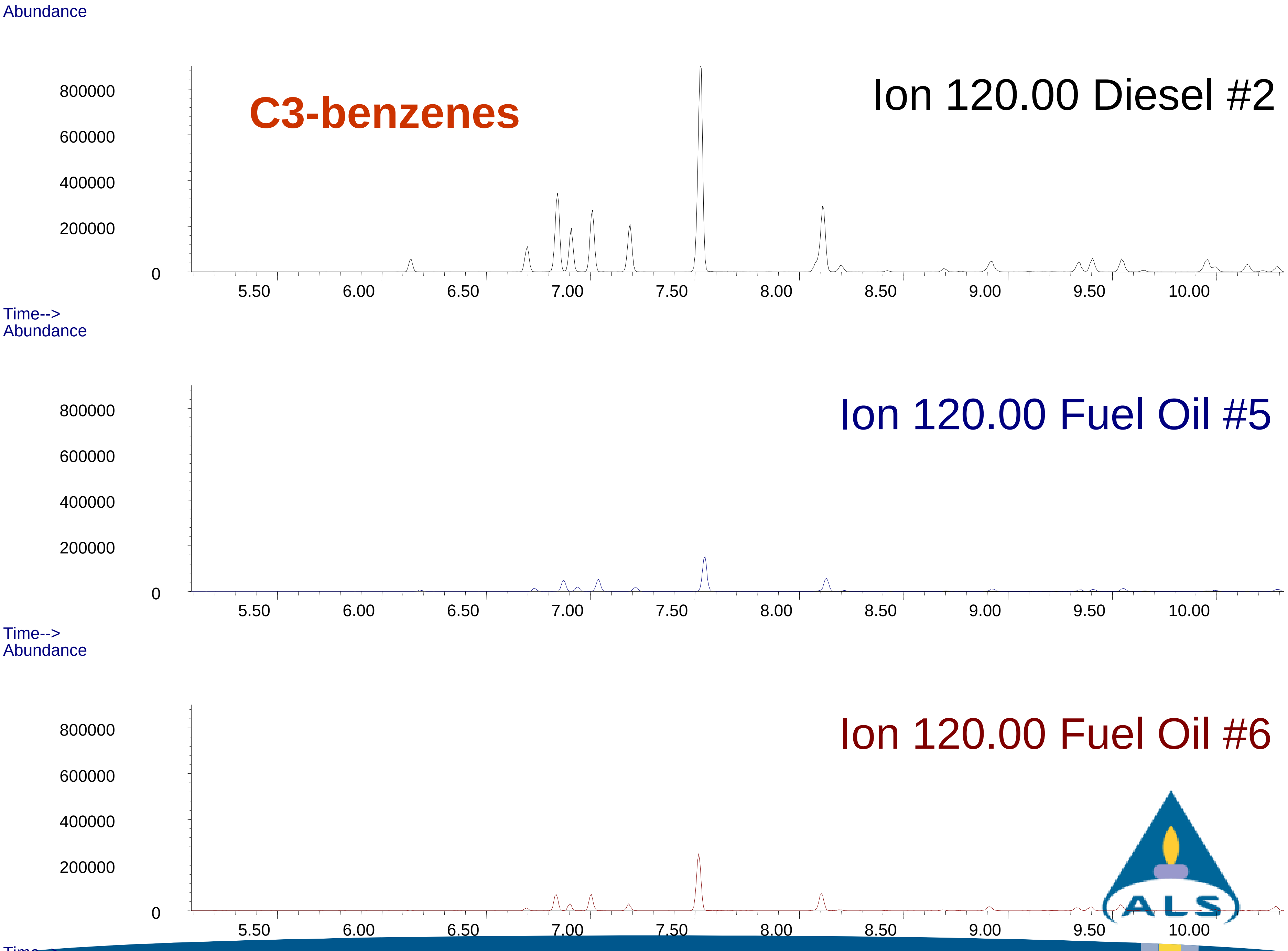
C3-benzenes

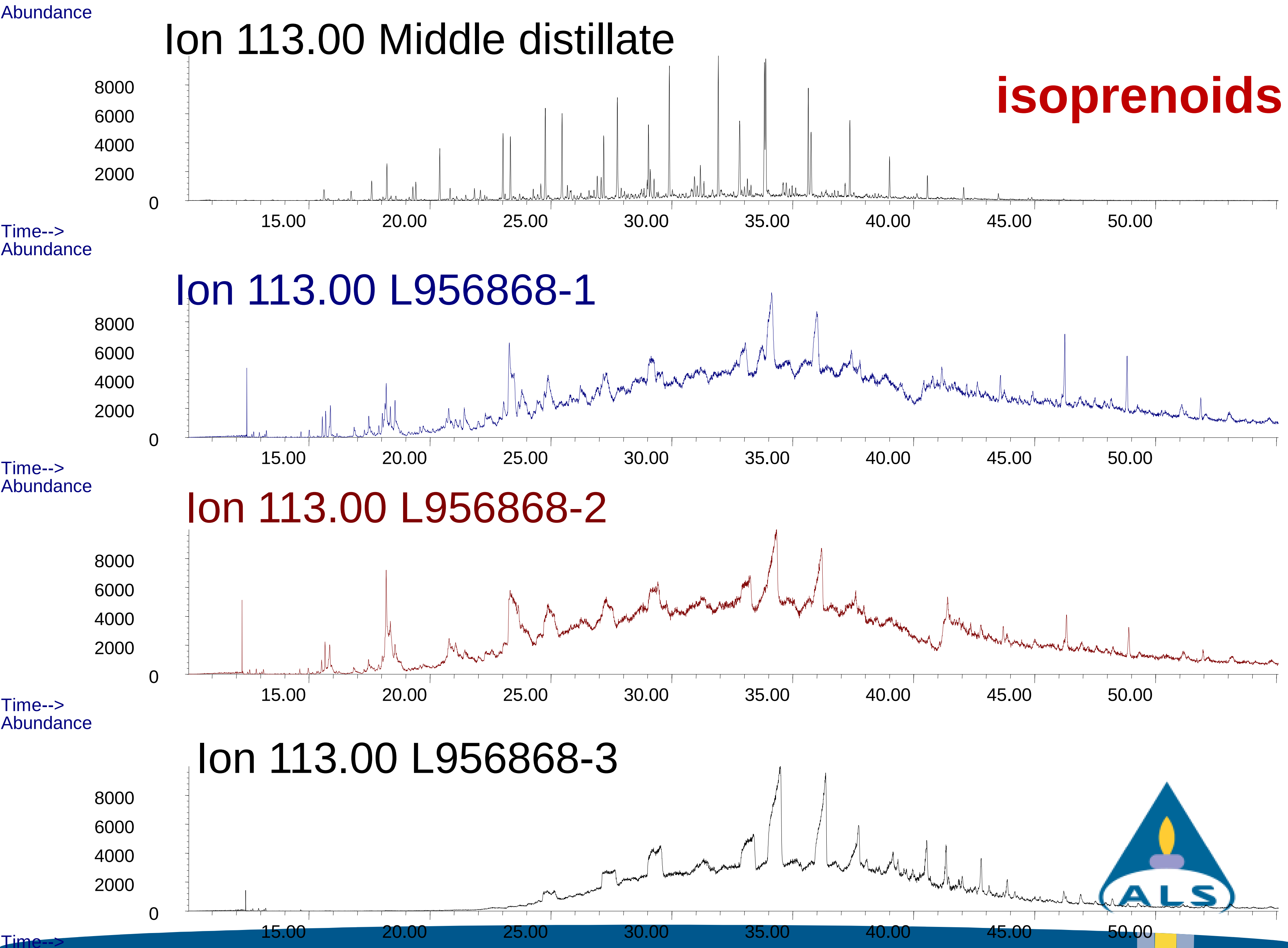

Abundance
Ion 120.00 Middle distillate (2 yrs)
5000
4000
3000
2000
1000
0
15.00
15.50
16.00
16.50
17.00
17.50
18.00
18.50
Time-->


Abundance
Ion 120.00 L956868-1
5000
4000
3000
2000
1000
0
15.00
15.50
16.00
16.50
17.00
17.50
18.00
18.50
Time-->

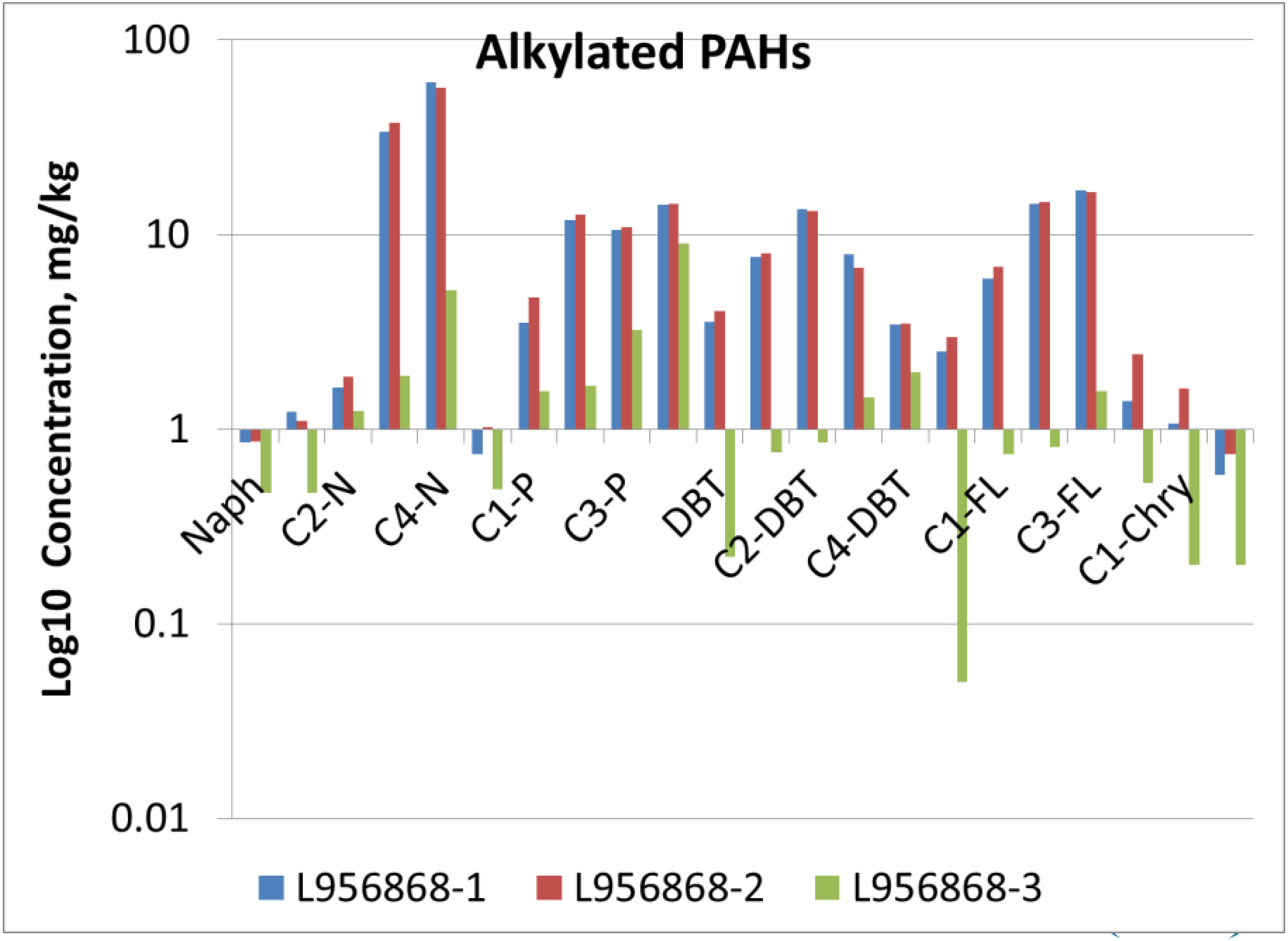

Abundance
Ion 120.00 L956868-2
5000
4000
3000
2000
1000
0
15.00
15.50
16.00
16.50
17.00
17.50
18.00
18.50
Time-->


Abundance
Ion 120.00 L956868-3
5000
4000
3000
2000
1000
0
15.00
15.50
16.00
16.50
17.00
17.50
18.00
18.50
Time-->


C3-benzenes
Ion 120.00 Diesel #2
Ion 120.00 Fuel Oil #5
Ion 120.00 Fuel Oil #6
Abundance
800000
600000
400000
200000
0
Time-->
5.50
6.00
6.50
7.00
7.50
8.00
8.50
9.00
9.50
10.00
ALS



Abundance
Ion 113.00 Middle distillate
isoprenoids
8000
6000
4000
2000
0
Time-->
15.00
20.00
25.00
30.00
35.00
40.00
45.00
50.00
Abundance
Ion 113.00 L956868-1
8000
6000
4000
2000
0
Time-->
15.00
20.00
25.00
30.00
35.00
40.00
45.00
50.00
Abundance
Ion 113.00 L956868-2
8000
6000
4000
2000
0
Time-->
15.00
20.00
25.00
30.00
35.00
40.00
45.00
50.00
Abundance
Ion 113.00 L956868-3
8000
6000
4000
2000
0
Time-->
15.00
20.00
25.00
30.00
35.00
40.00
45.00
50.00


Alkylated PAHs
Log10 Concentration, mg/kg
100
10
1
0.1
0.01
Naph
C2-N
C4-N
C1-P
C3-P
DBT
C2-DBT
C4-DBT
C1-FL
C3-FL
C1-Chry
L956868-1
L956868-2
L956868-3

Summary

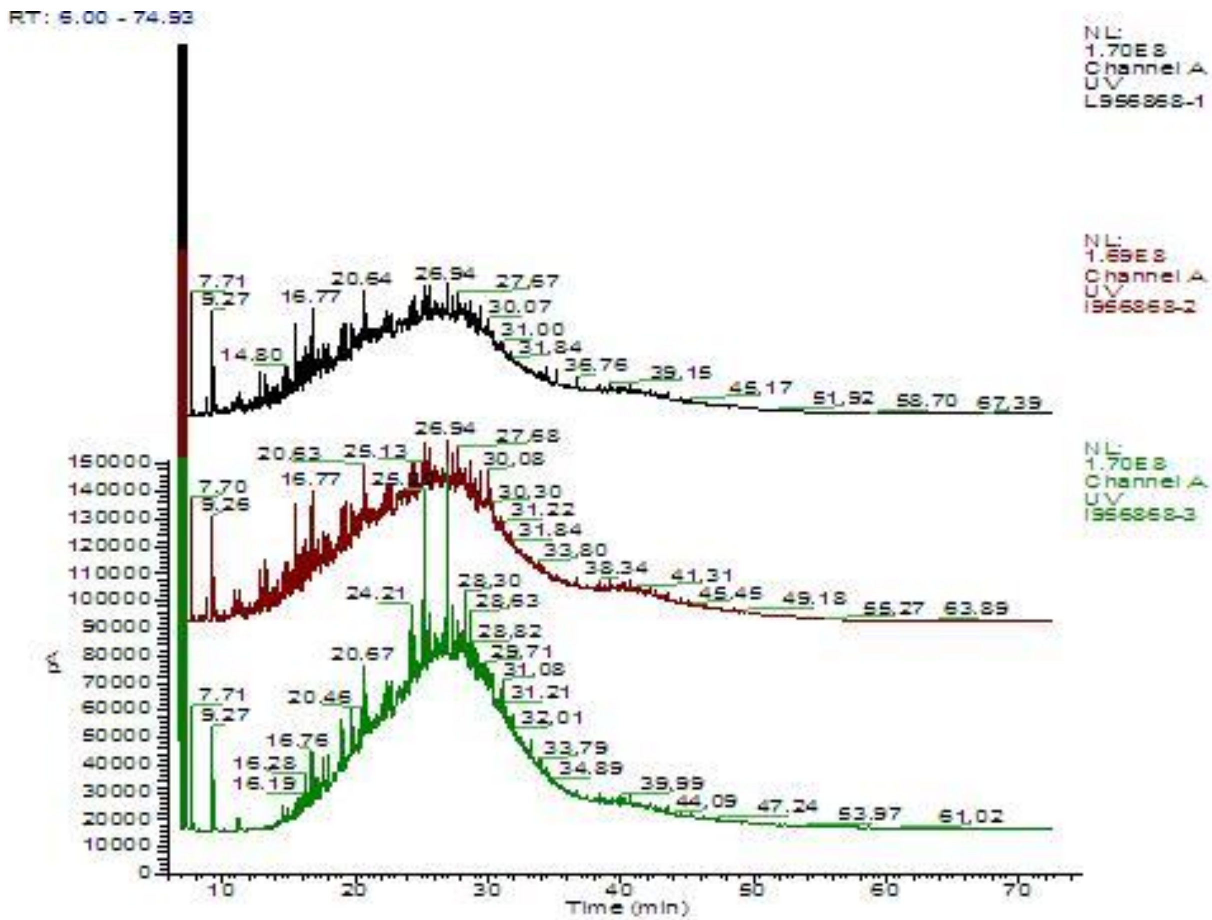
- Alkanes, cycloalkanes, alkylated benzenes, and isoprenoids significantly reduced
- Assuming a moderate soil, fuels are 20-24+ years old (Oudijk, 2009).
- Significant reduction in C_1- and C_2-naphthalenes – represents a stage 6 biodegradation in a moderate soil. Therefore at least 20 years old. (Oukijk, 2009)
- Predominance of two and three ring PAHs (naphthalenes, phenanthrenes, dibenzothiophenes, fluorenes) as well as low amount of high molecular weight PAHs (e.g. alkylated chrysenes) provides further evidence for a middle distillate (Wang et al, 2001)
- Presence of C3-benzenes in severely weathered samples provides further evidence for middle distillate

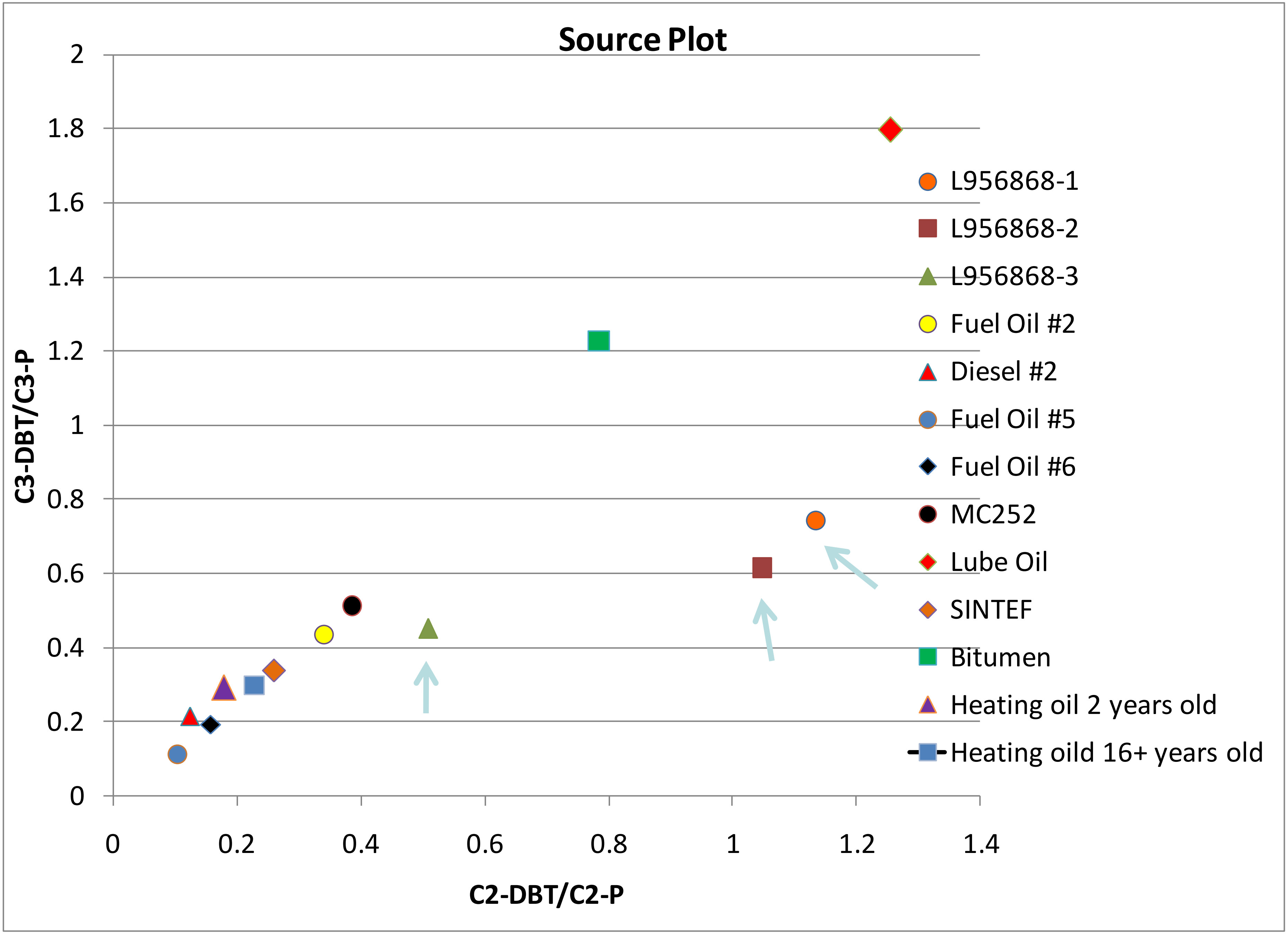
Source

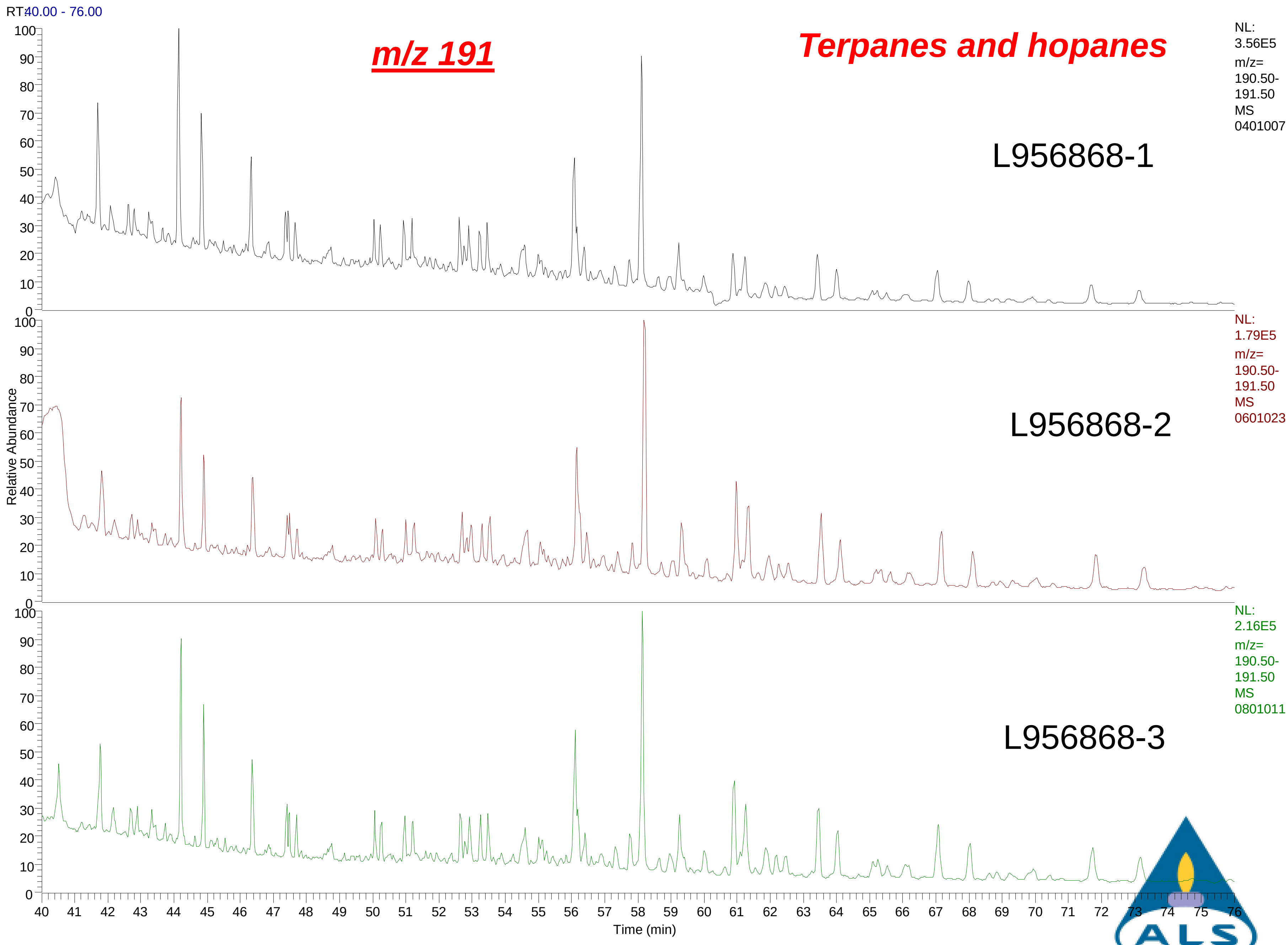
Are these sources of petroleum from a common source?

Are they different?

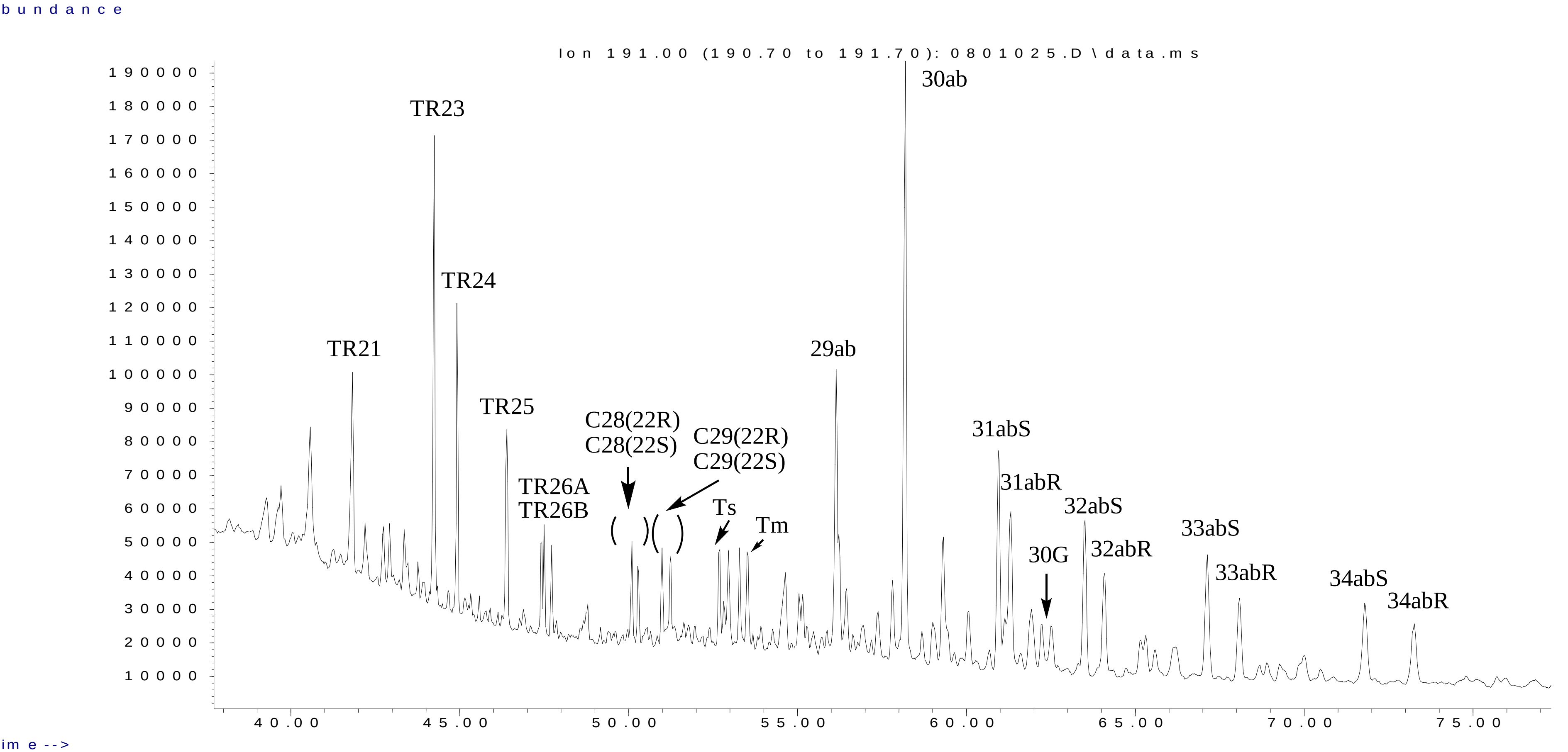
Petroleum biomarkers best suited to answer these questions.



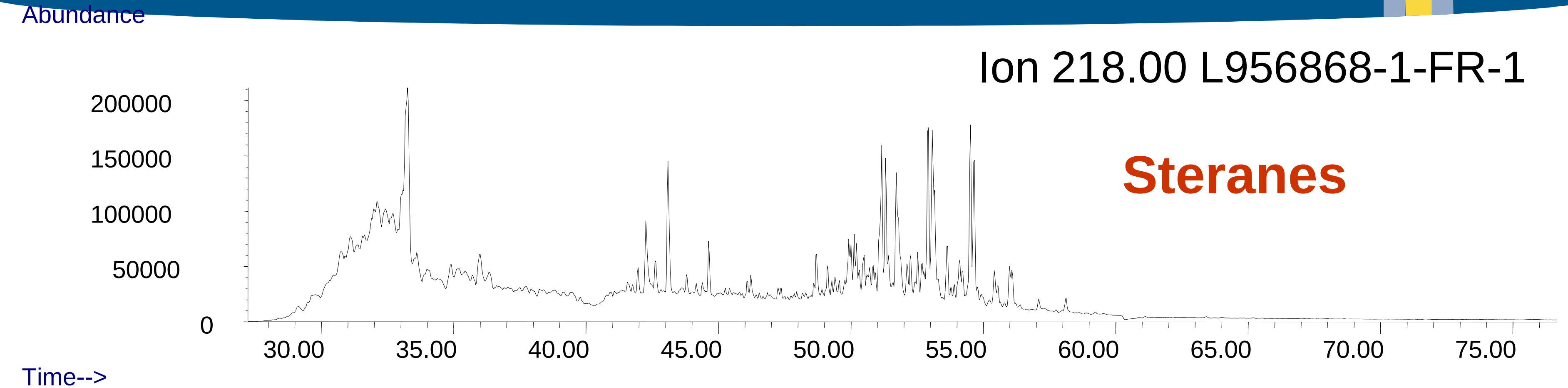

Source Plot
C3-DBT/C3-P
C2-DBT/C2-P
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2
0
0.2
0.4
0.6
0.8
1
1.2
1.4
L956868-1
L956868-2
L956868-3
Fuel Oil #2
Diesel #2
Fuel Oil #5
Fuel Oil #6
MC252
Lube Oil
SINTEF
Bitumen
Heating oil 2 years old
Heating oild 16+ years old

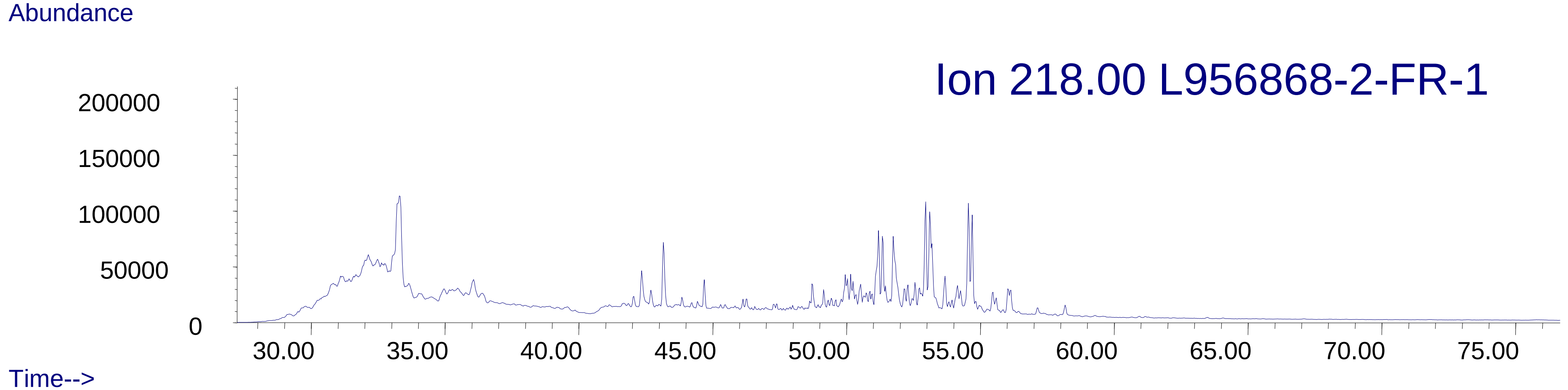


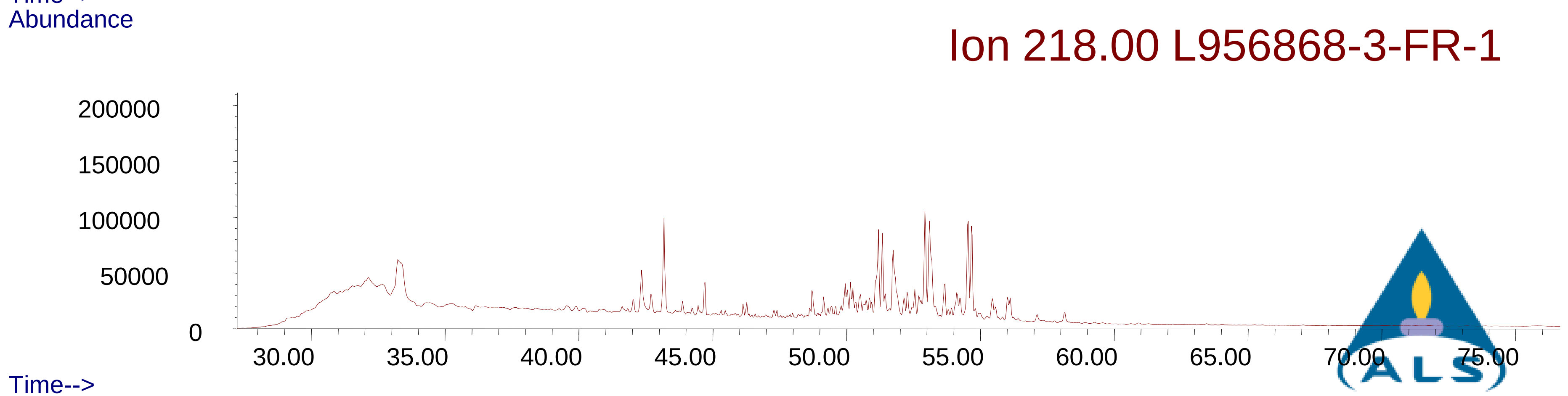
RT: 40.00 - 76.00
m/z 191
Terpanes and hopanes
NL: 3.56E5
m/z= 190.50-191.50
MS 0401007
L956868-1
NL: 1.79E5
m/z= 190.50-191.50
MS 0601023
L956868-2
NL: 2.16E5
m/z= 190.50-191.50
MS 0801011
L956868-3
Relative Abundance
Time (min)
ALS

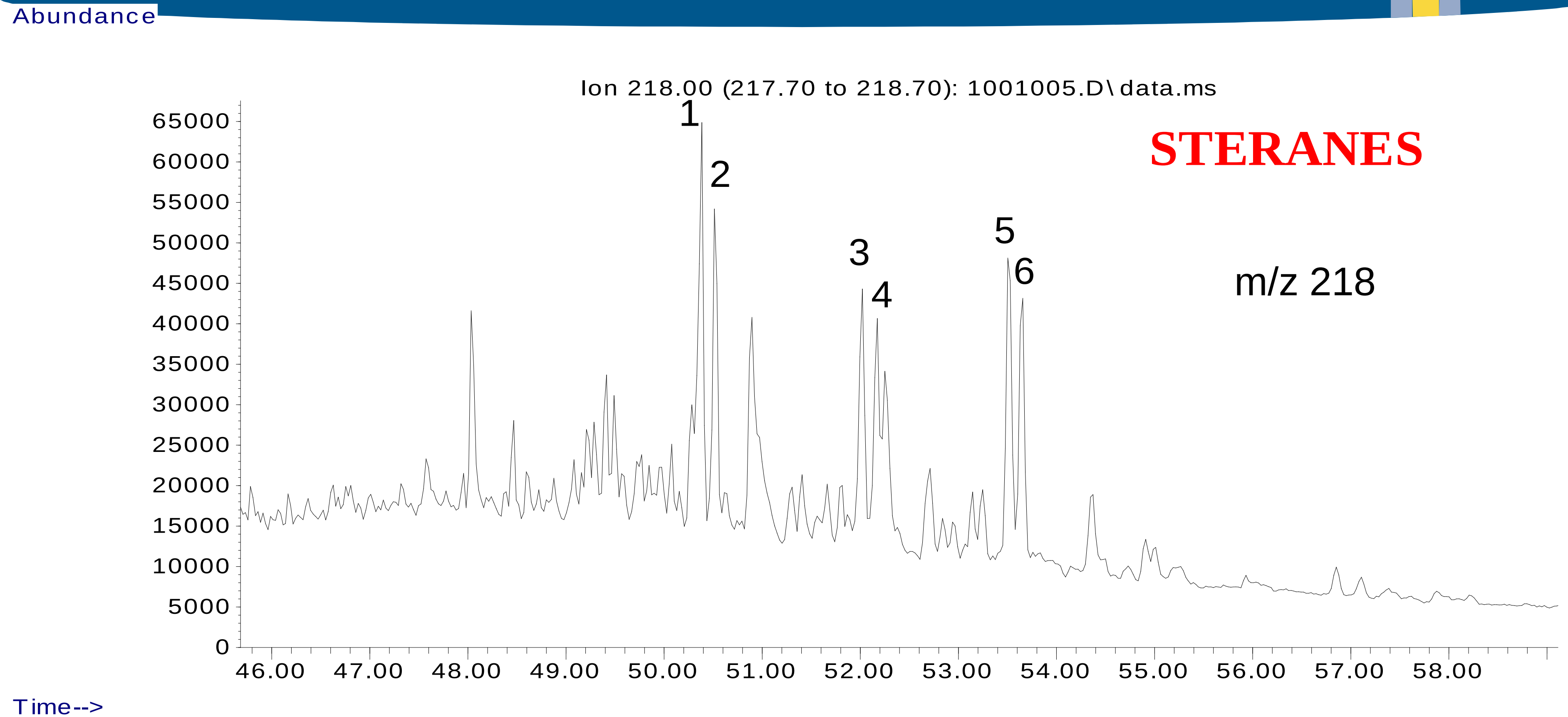

bundance
Ion 191.00 (190.70 to 191.70): 0801025.D\data.ms
190000
180000
170000
160000
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
40.00
45.00
50.00
55.00
60.00
65.00
70.00
75.00
ime -->
TR21
TR23
TR24
TR25
TR26A
TR26B
C28(22R)
C28(22S)
C29(22R)
C29(22S)
Ts
Tm
29ab
30ab
31abS
31abR
30G
32abS
32abR
33abS
33abR
34abS
34abR

Steranes


Abundance
Ion 218.00 L956868-1-FR-1
200000
150000
100000
50000
0
30.00
35.00
40.00
45.00
50.00
55.00
60.00
65.00
70.00
75.00
Time-->


Abundance
Ion 218.00 L956868-2-FR-1
200000
150000
100000
50000
0
30.00
35.00
40.00
45.00
50.00
55.00
60.00
65.00
70.00
75.00
Time-->


Abundance
Ion 218.00 L956868-3-FR-1
200000
150000
100000
50000
0
30.00
35.00
40.00
45.00
50.00
55.00
60.00
65.00
70.00
75.00
Time-->



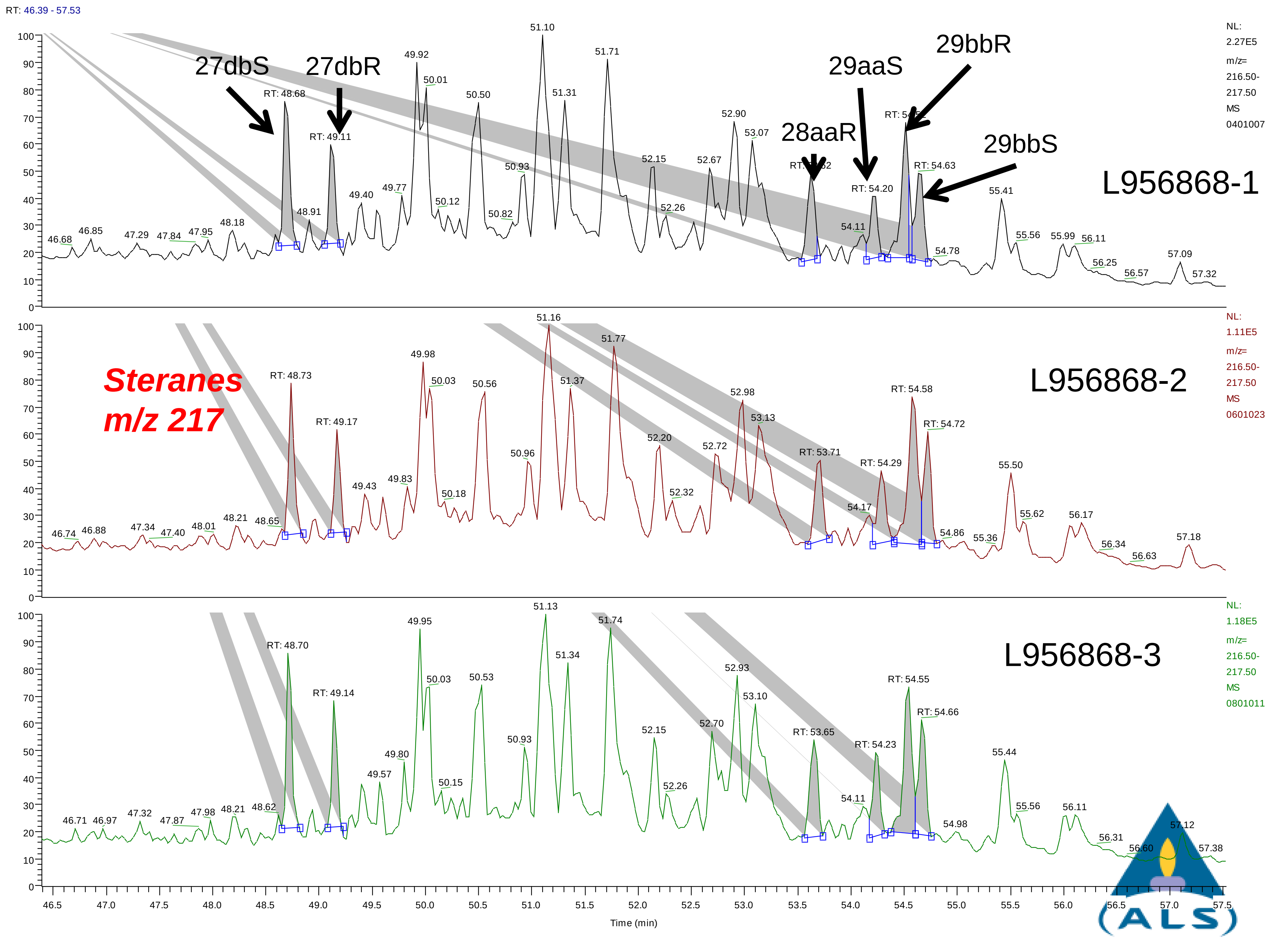
1. 5a(H), 14b(H),17b(H),20R-cholestane ***- 27bbR***
2. 5a(H), 14b(H),17b(H),20S-cholestane - ***27bbS***
3. 24-methyl-5a(H),14b(H), 17b,20R-cholestane - ***28bbR***
4. 24-methyl-5a(H),14b(H),17b,20S-cholestane- ***28bbS***
5. 24-ethyl-5a(H),14b(H)m17b,20R-cholestane - ***29bbR***
6. 24-ethyl-5a(H),14b(H),17b,20S-cholestane - ***29bbS***

Ratios

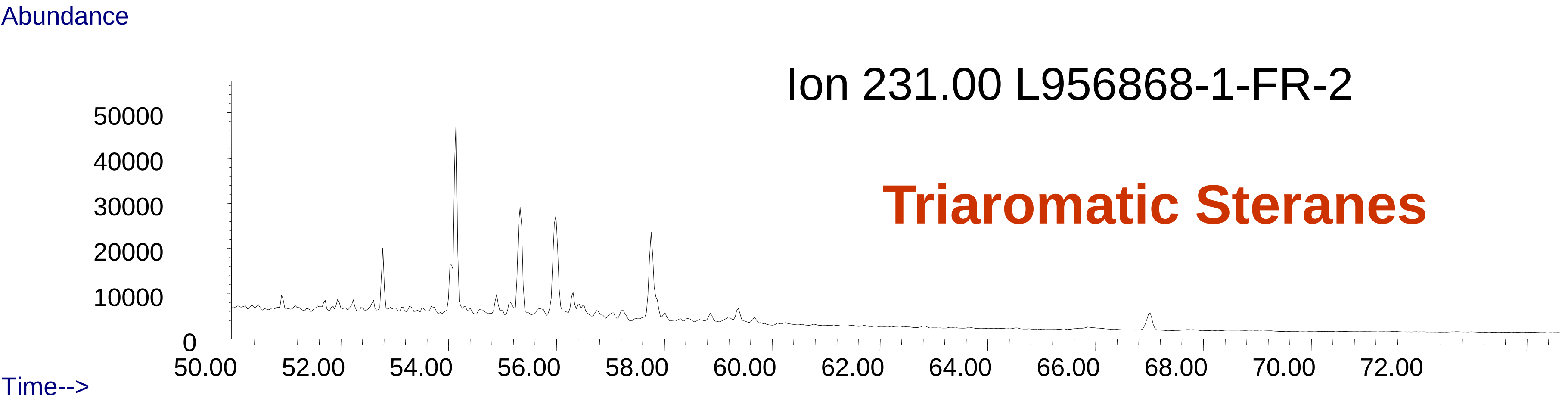
(27bbR + 27bbS)/(28bbR + 28bbS + 29bbR +29bbS)

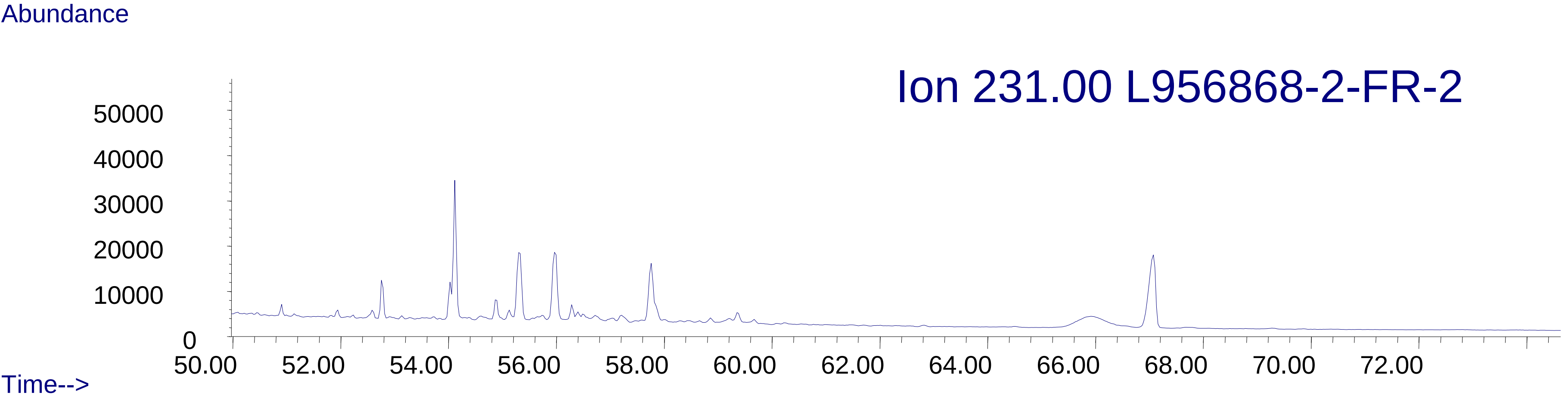
(28bbR + 28bbS)/(27bbR + 27bbS + 29bbR + 29bbS)

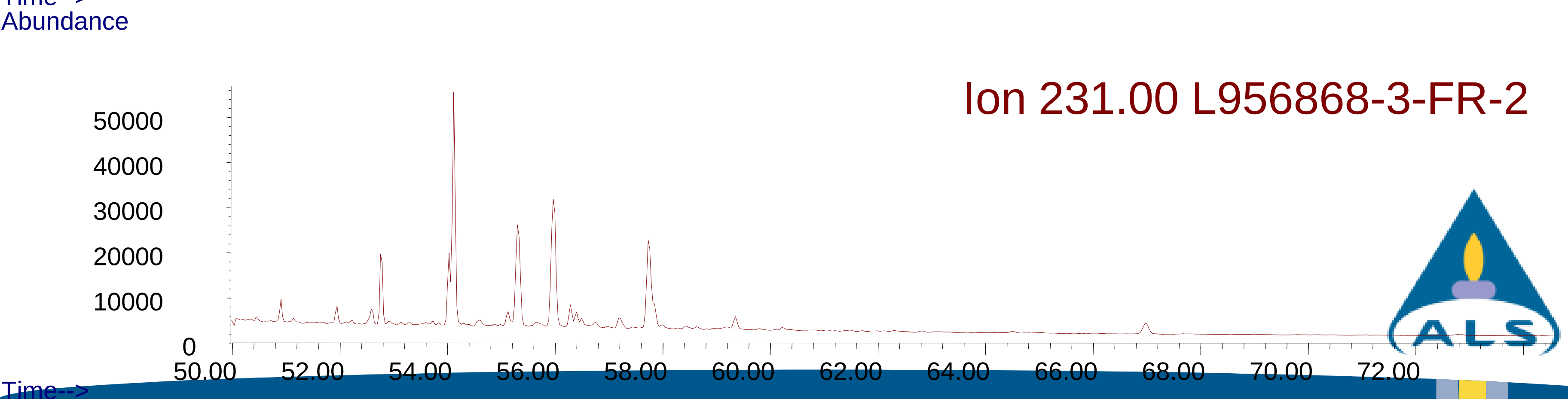
(29bbR + 29bbS)/(27bbR + 27bbS + 28bbR + 28bbS)

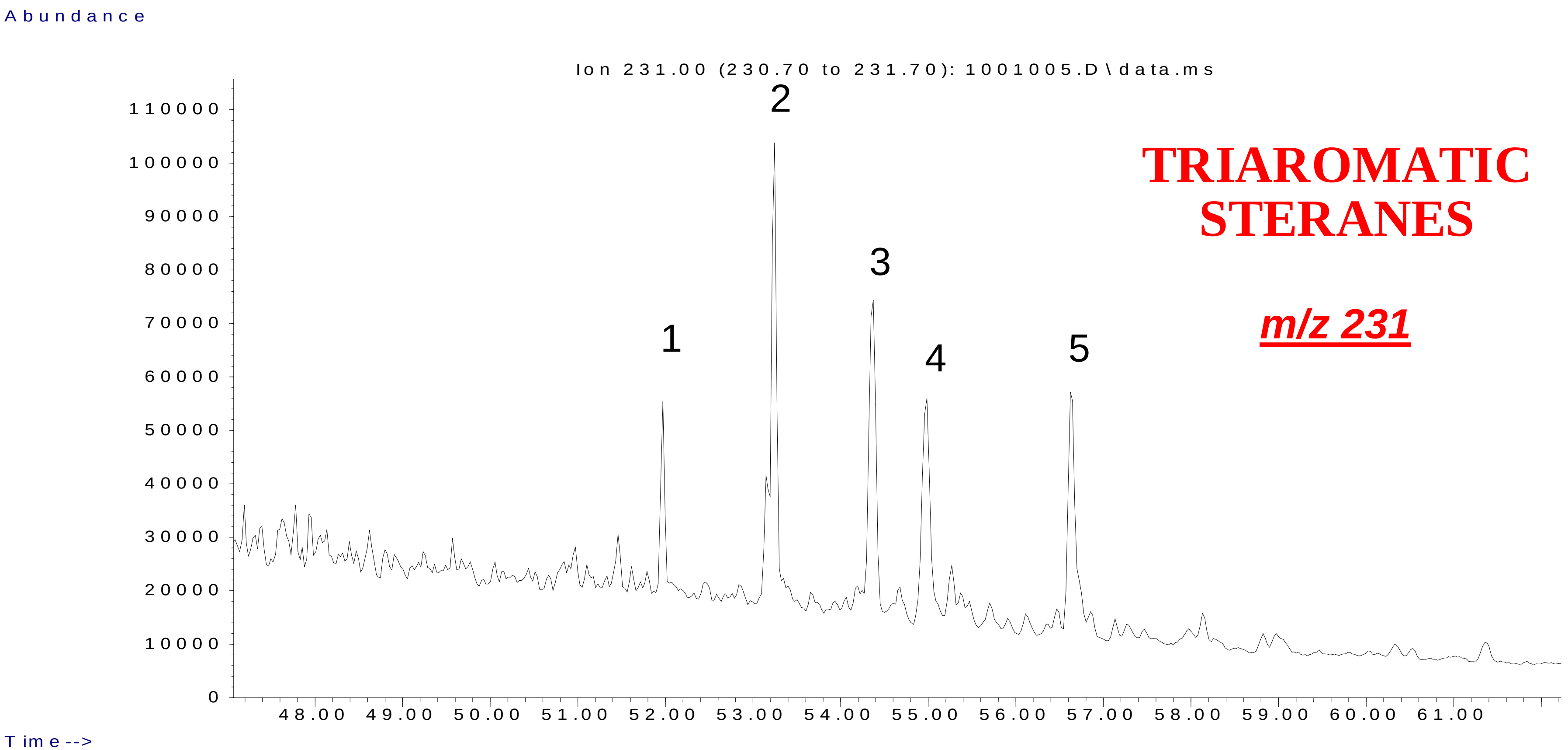

RT: 46.39 - 57.53
27dbS
27dbR
28aaR
29aaS
29bbR
29bbS
L956868-1
NL: 2.27E5 m/z= 216.50-217.50 MS 0401007
Steranes m/z 217
L956868-2
NL: 1.11E5 m/z= 216.50-217.50 MS 0601023
L956868-3
NL: 1.18E5 m/z= 216.50-217.50 MS 0801011
Time (min)

Triaromatic Steranes

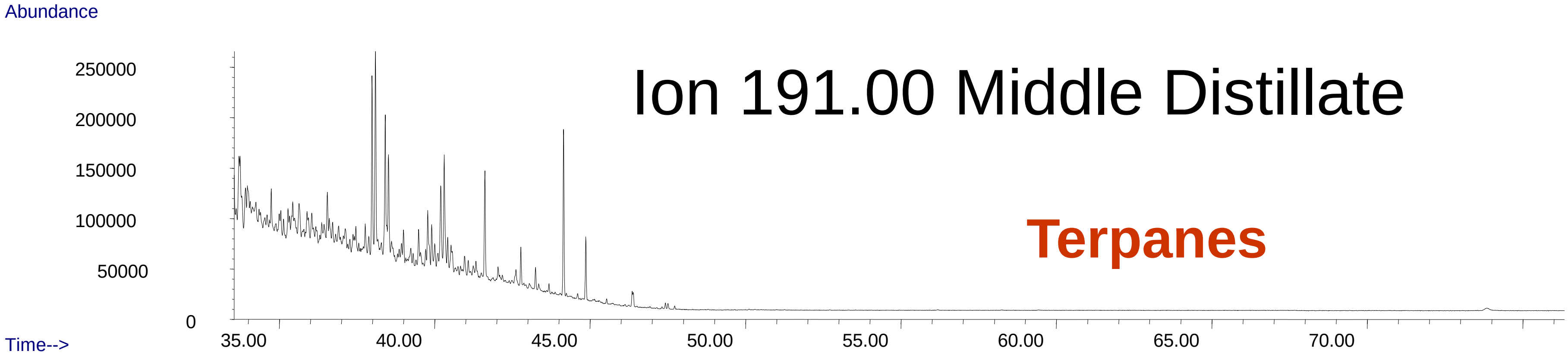




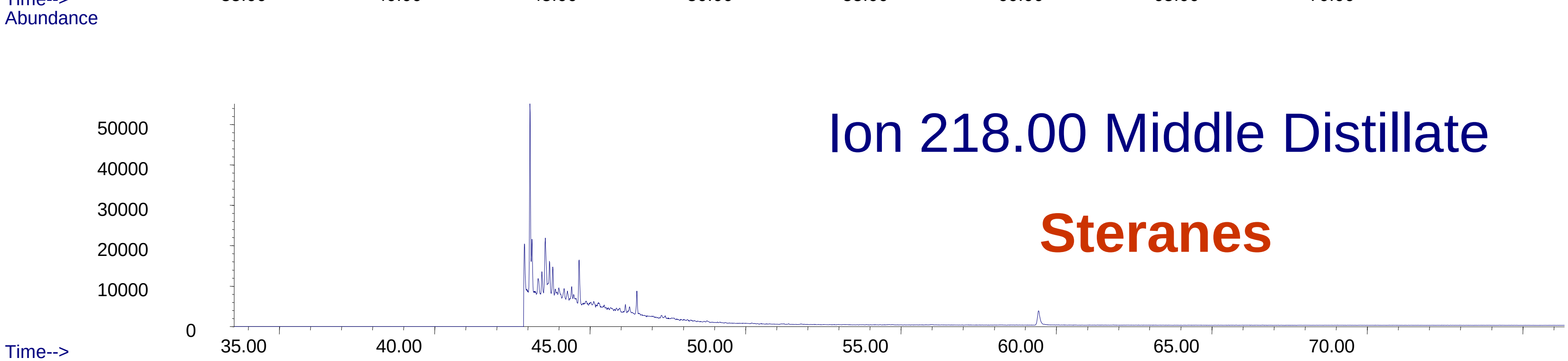




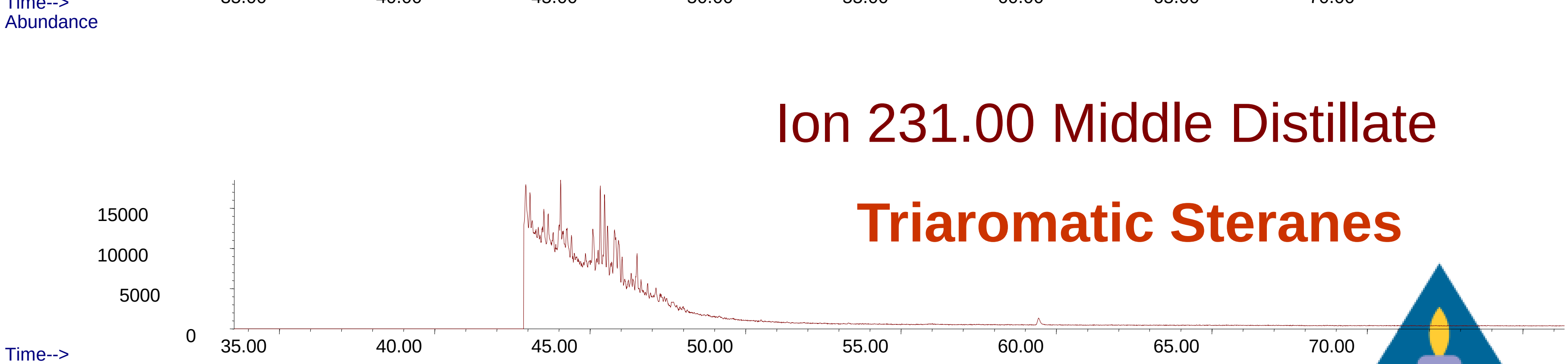
1. C26,20S-triaromatic sterane ***-C26TA(20S)***
2. C26, 20R-triaromatic sterane + C27, 20S-triaromatic sterane ***-C26TA(20R) + C27TA(20S)***
3. C28, 20S-triaromatic sterane ***-C28TA(20S)***
4. C27, 20R-triaromatic sterane ***-C27TA(20R)***
5. C28, 20R-triaromatic sterane ***-C28TA(20R)***



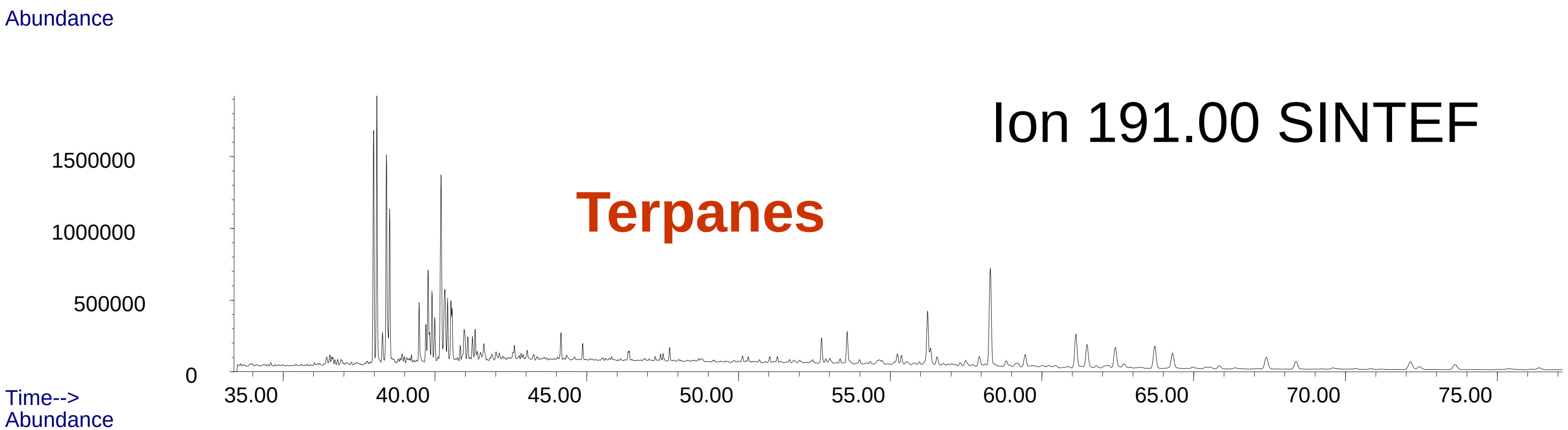
Abundance
Ion 191.00 Middle Distillate
Terpanes
250000
200000
150000
100000
50000
0
Time-->
35.00
40.00
45.00
50.00
55.00
60.00
65.00
70.00

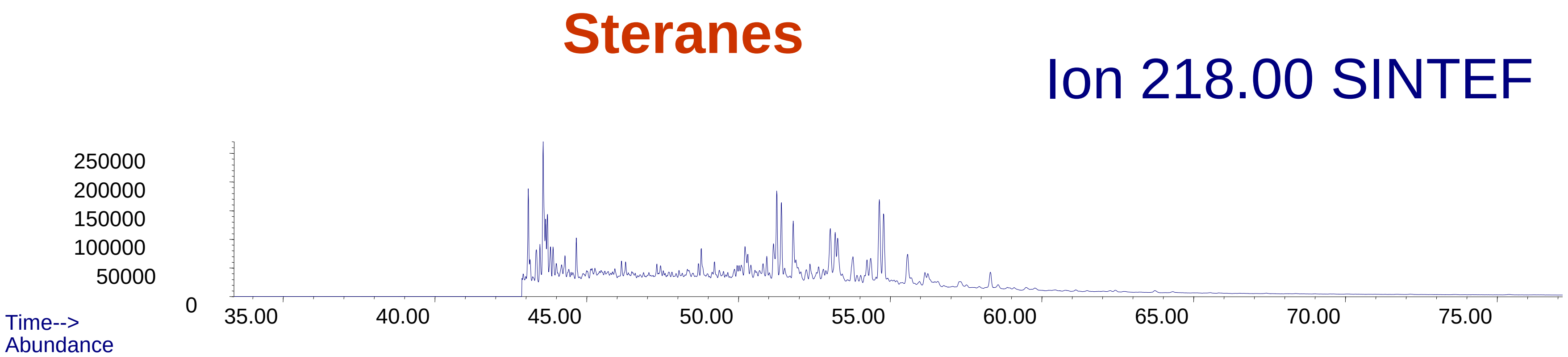


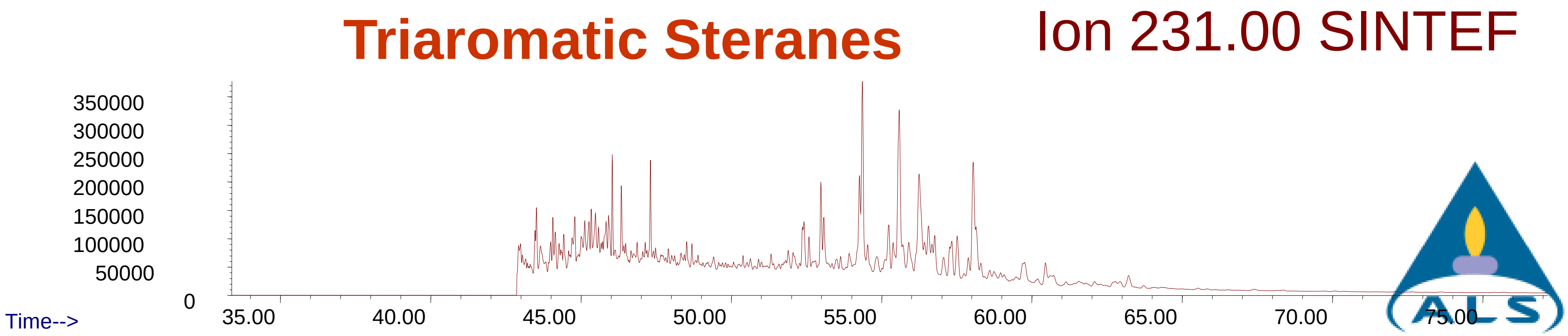
Abundance
Ion 218.00 Middle Distillate
Steranes
50000
40000
30000
20000
10000
0
Time-->
35.00
40.00
45.00
50.00
55.00
60.00
65.00
70.00



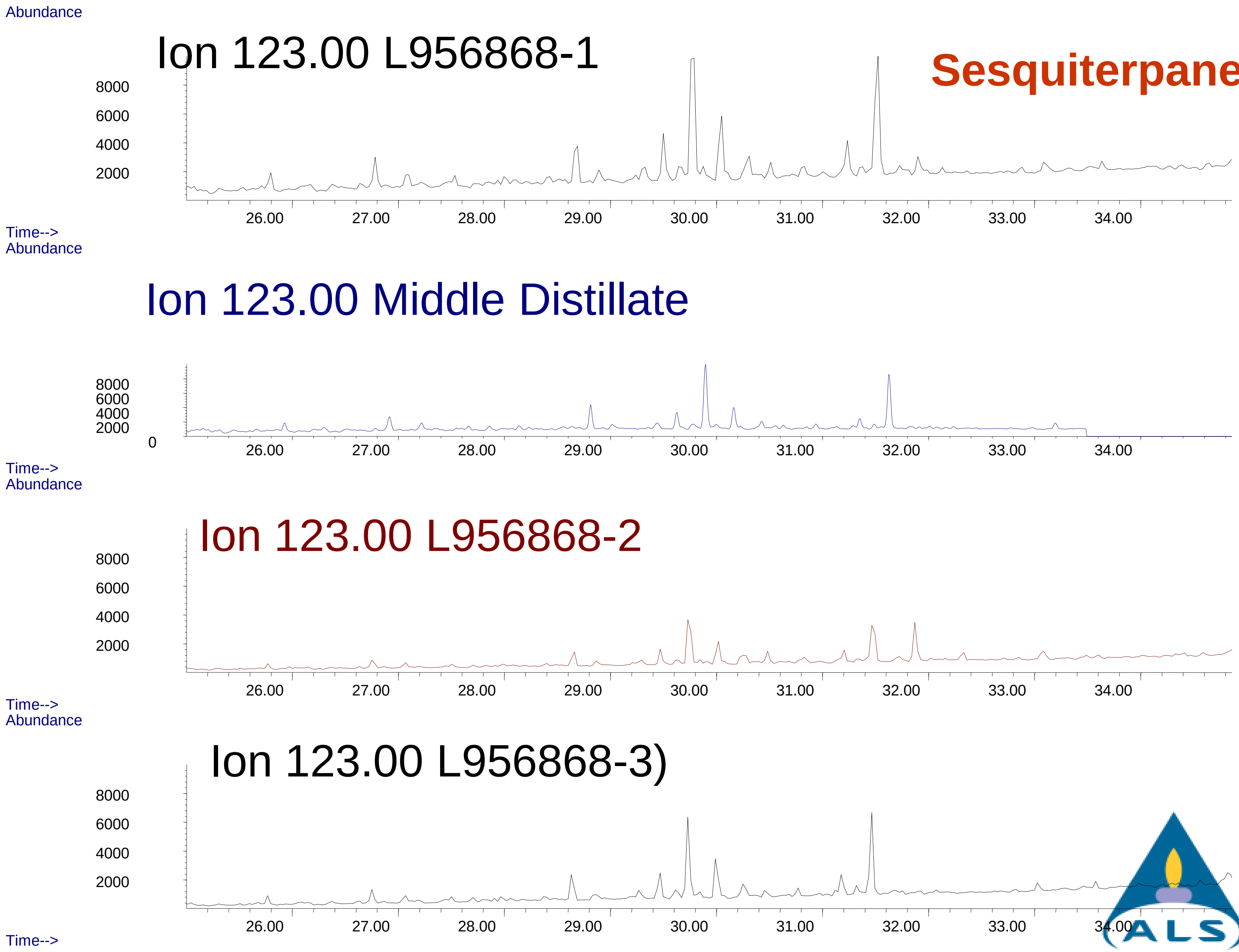
Abundance
Ion 231.00 Middle Distillate
Triaromatic Steranes
15000
10000
5000
0
Time-->
35.00
40.00
45.00
50.00
55.00
60.00
65.00
70.00

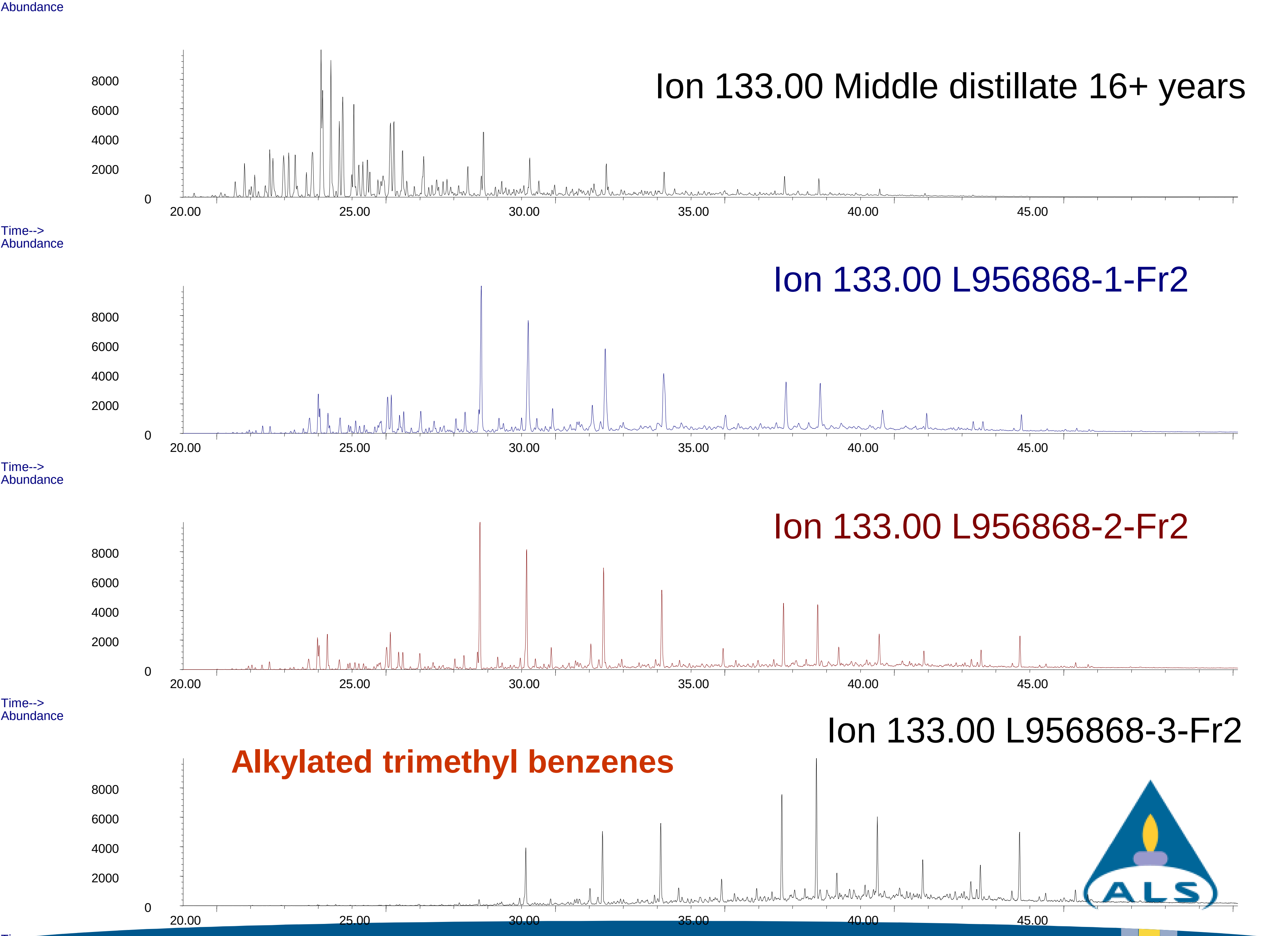

Abundance
Ion 191.00 SINTEF
Terpanes
1500000
1000000
500000
0
Time-->
35.00
40.00
45.00
50.00
55.00
60.00
65.00
70.00
75.00

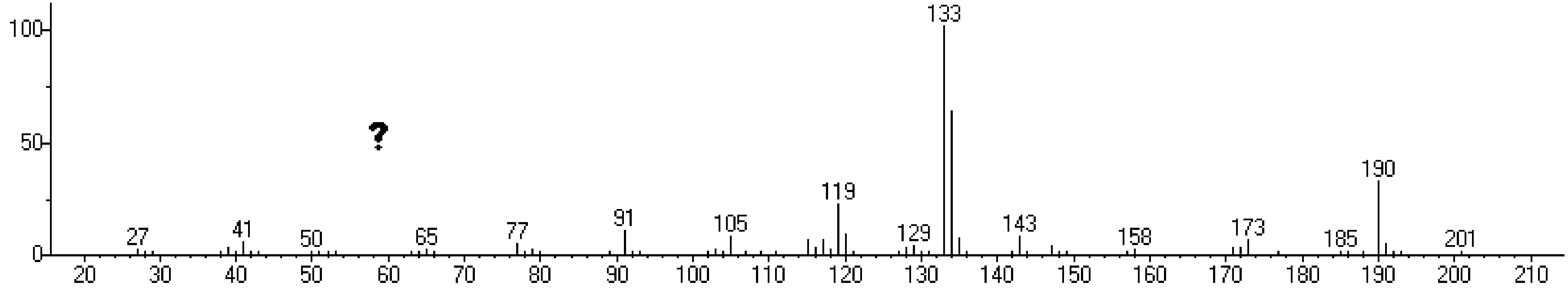

Abundance
Steranes
Ion 218.00 SINTEF
250000
200000
150000
100000
50000
0
Time-->
35.00
40.00
45.00
50.00
55.00
60.00
65.00
70.00
75.00


Abundance
Triaromatic Steranes
Ion 231.00 SINTEF
350000
300000
250000
200000
150000
100000
50000
0
Time-->
35.00
40.00
45.00
50.00
55.00
60.00
65.00
70.00
75.00

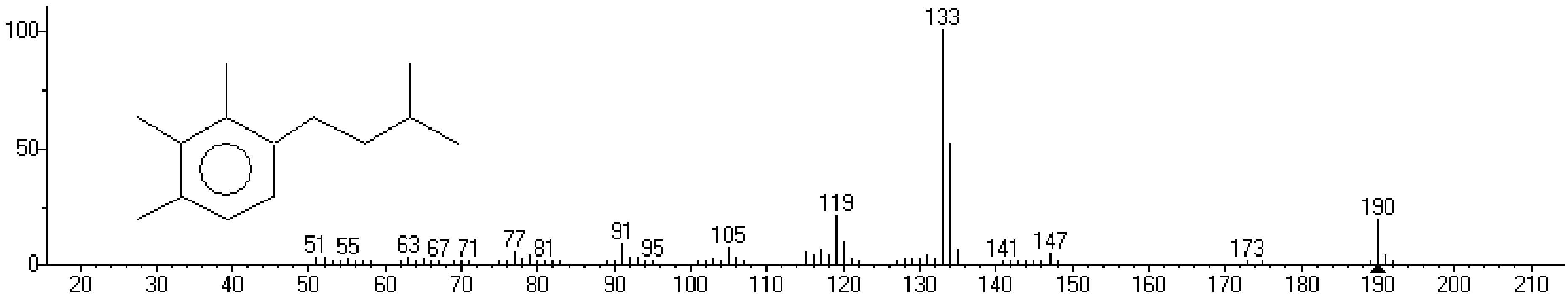
Sesquiterpanes



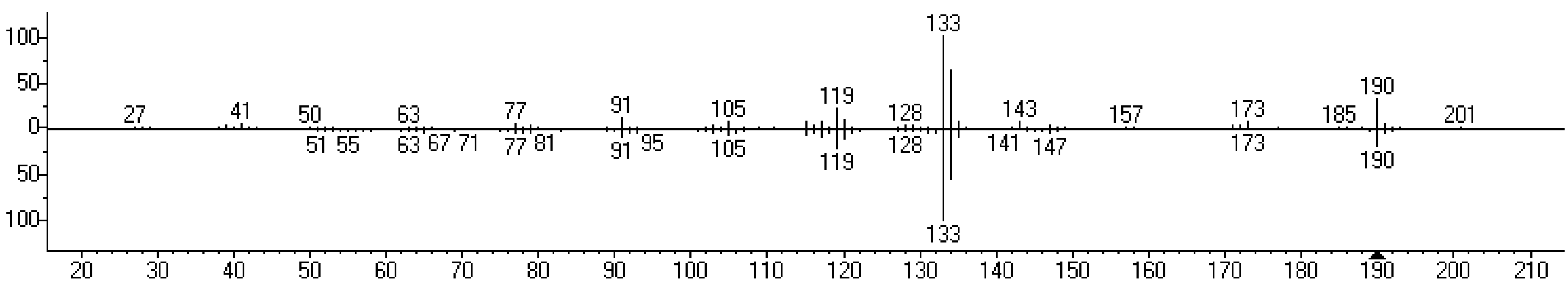

Abundance
Ion 133.00 Middle distillate 16+ years
8000
6000
4000
2000
0
20.00
25.00
30.00
35.00
40.00
45.00
Time-->
Abundance
Ion 133.00 L956868-1-Fr2
8000
6000
4000
2000
0
20.00
25.00
30.00
35.00
40.00
45.00
Time-->
Abundance
Ion 133.00 L956868-2-Fr2
8000
6000
4000
2000
0
20.00
25.00
30.00
35.00
40.00
45.00
Time-->
Abundance
Ion 133.00 L956868-3-Fr2
Alkylated trimethyl benzenes
8000
6000
4000
2000
0
20.00
25.00
30.00
35.00
40.00
45.00
Time-->



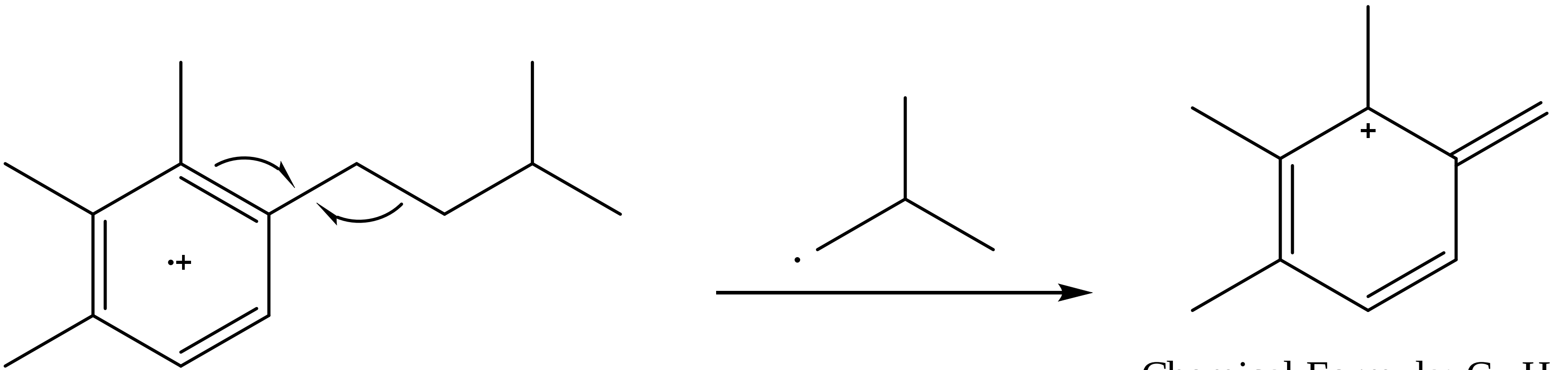
(Text File) Scan 4027 (29.197 min): 0501005.D\data.ms (-4010)



(mainlib) 1-(3-Methylbutyl)-2,3,4-trimethylbenzene



Scan 4027 (29.197 min): 0501005.D\data.ms (-4010) Head to Tail MF=770 RMF=794 1-(3-Methylbutyl)-2,3,4-trimethylbenzene



Chemical Formula: $C_{14}H_{22}$
Exact Mass: 190.17215
Molecular Weight: 190.32448

Chemical Formula: $C_{10}H_{13}^{+}$
Exact Mass: 133.10118
Molecular Weight: 133.20967

Petroleum Biomarker Ratios

Terpanes	L956868-1	L956868-2	L956868-3
27Ts/27Tm	1.127	1.099	1.045
29ab/30ab	0.505	0.457	0.519
31abS/31abR	1.119	1.279	1.344
32abS/32abR	1.484	1.508	1.461
33abS/33abR	1.440	1.499	1.488
Steranes			
(27bbR+27bbs)/(28bbR+28bbS+29bbR+29bbS)	0.424	0.362	0.418
(28bbR+28bbS)/(27bbR+27bbS+29bbR+29bbS	0.566	0.592	0.557
(29bbR+29bbS)/(27bbR+27bbS+28bbR+28bbS	0.517	0.568	0.532

Petroleum Biomarker Ratios

PAHs	L956868-1	L956868-2	L956868-3
C3-DBT/C3-Phen	1.134	1.048	0.509
C2-DBT/C2-Phen	0.742	0.616	0.452
4-MDT/1-MDT	3.075	2.436	4.61
Retene/C4-Phen	0.078	0.084	0.121
Isoprenoids			
Pristane/Phytane	0.978	0.979	0.946
Sesquiterpanes			
SES1/SES2	1.720	1.709	1.496
SES3/SES5	0.323	0.261	0.364
SES4/SES6	0.651	0.596	0.560
SES5/SES10	1.476	1.228	1.080
SES10/SES5+10	0.404	0.449	0.481

Critical Difference Analysis

Terpanes	L956868-1	L956868-2	Difference	Critical Difference	Conclusion
27Ts/27Tm	1.127	1.099	0.028	0.156	Match
C2-D/C2-P	0.742	0.616	0.126	0.095	No Match

Difference = absolute difference between pair of ratios

Critical Difference = mean between ratios * repeatability limit (14%)

Conclusions = Match if difference < than critical difference

Conclusions = No Match if difference > critical difference

Reference: Hansen et al (2007)

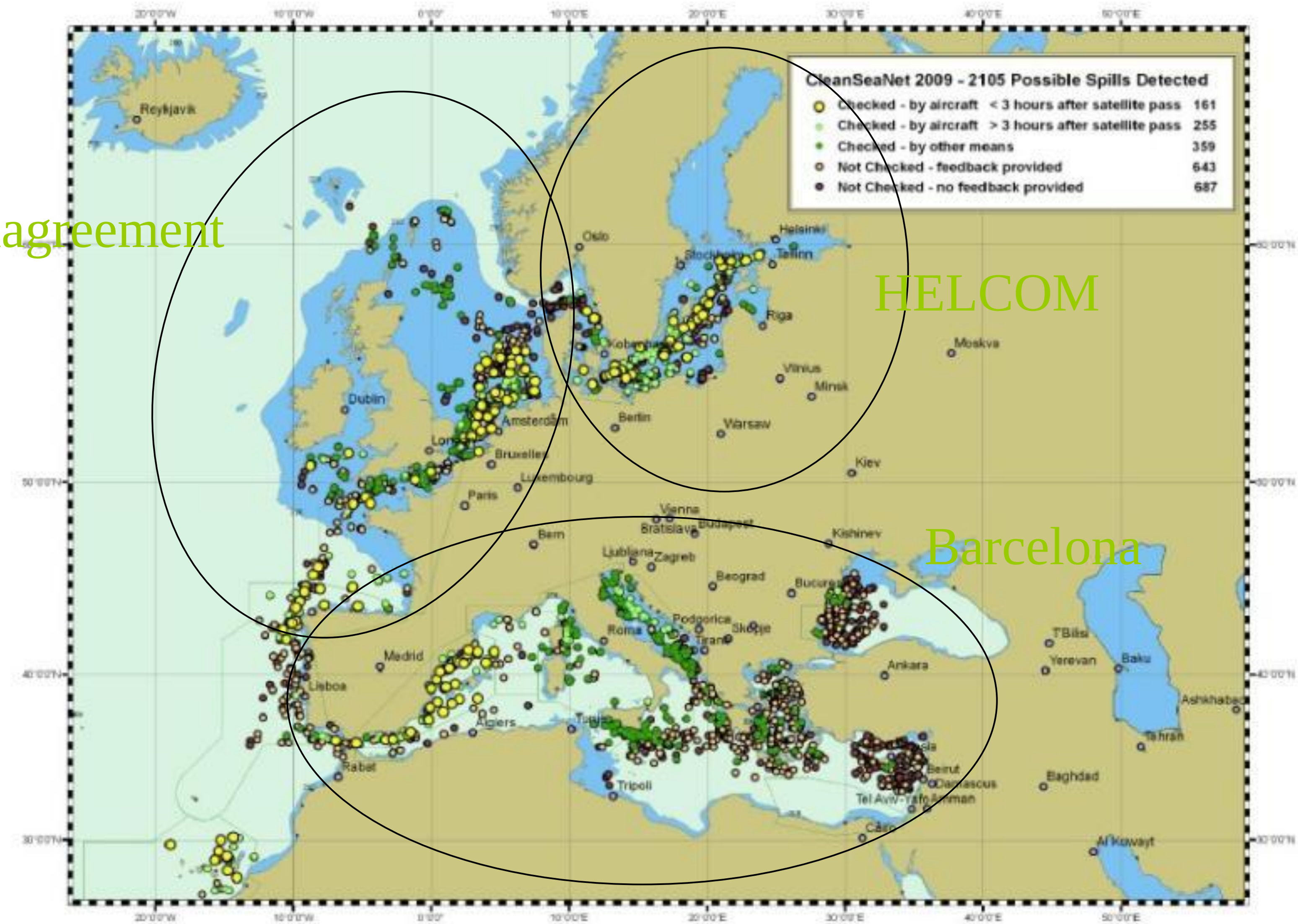
Critical Difference Analysis

L956868-1 vs -2 Match/Total	L956868-1 vs -3 Match/Total	L956868-2 vs -3 Match/Total
16/21	11/21	14/21
76%	52%	67%

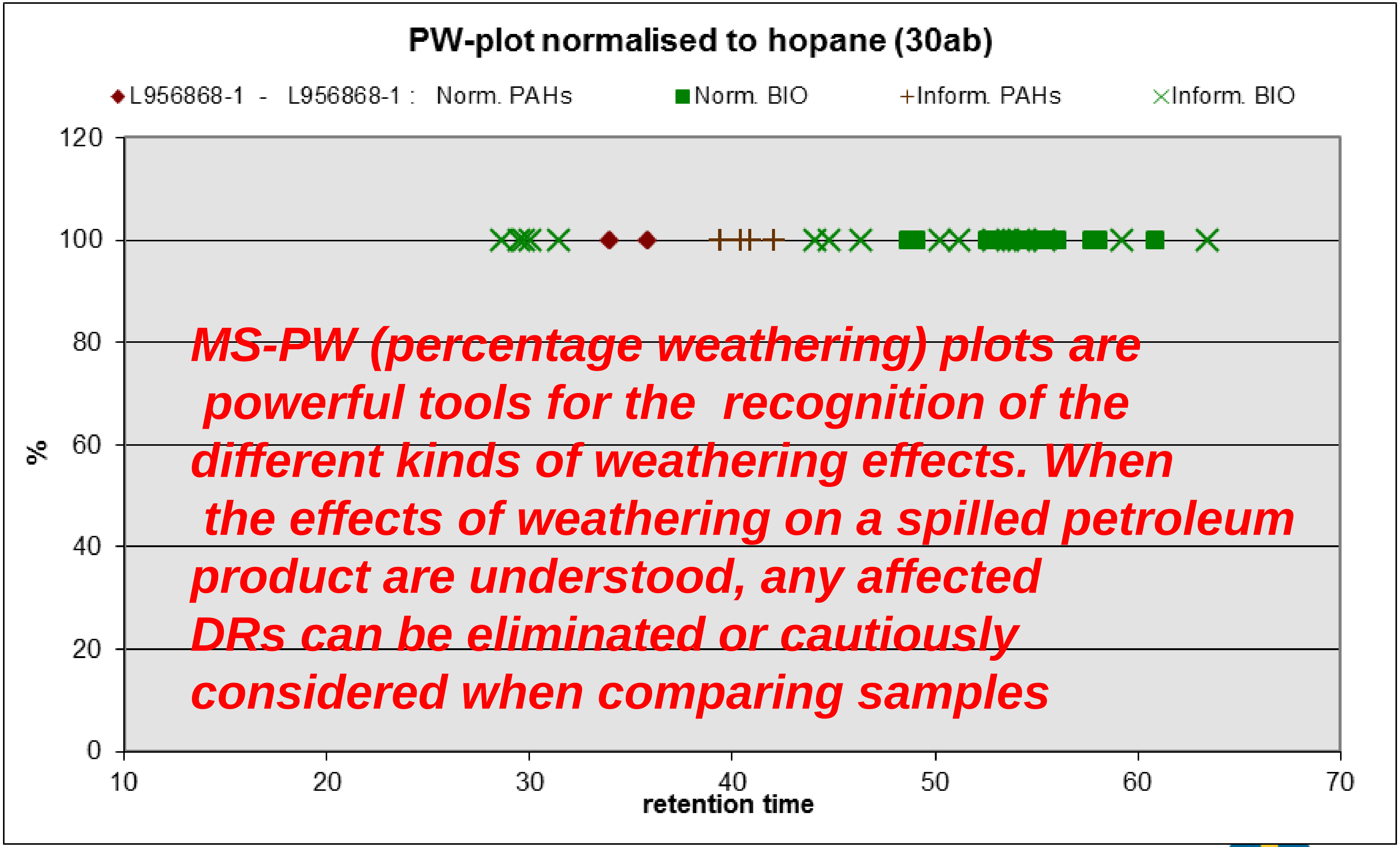
North Sea CleanSeanet EMSA

Oil Spill Identification Network of Experts – Bonn Agreement

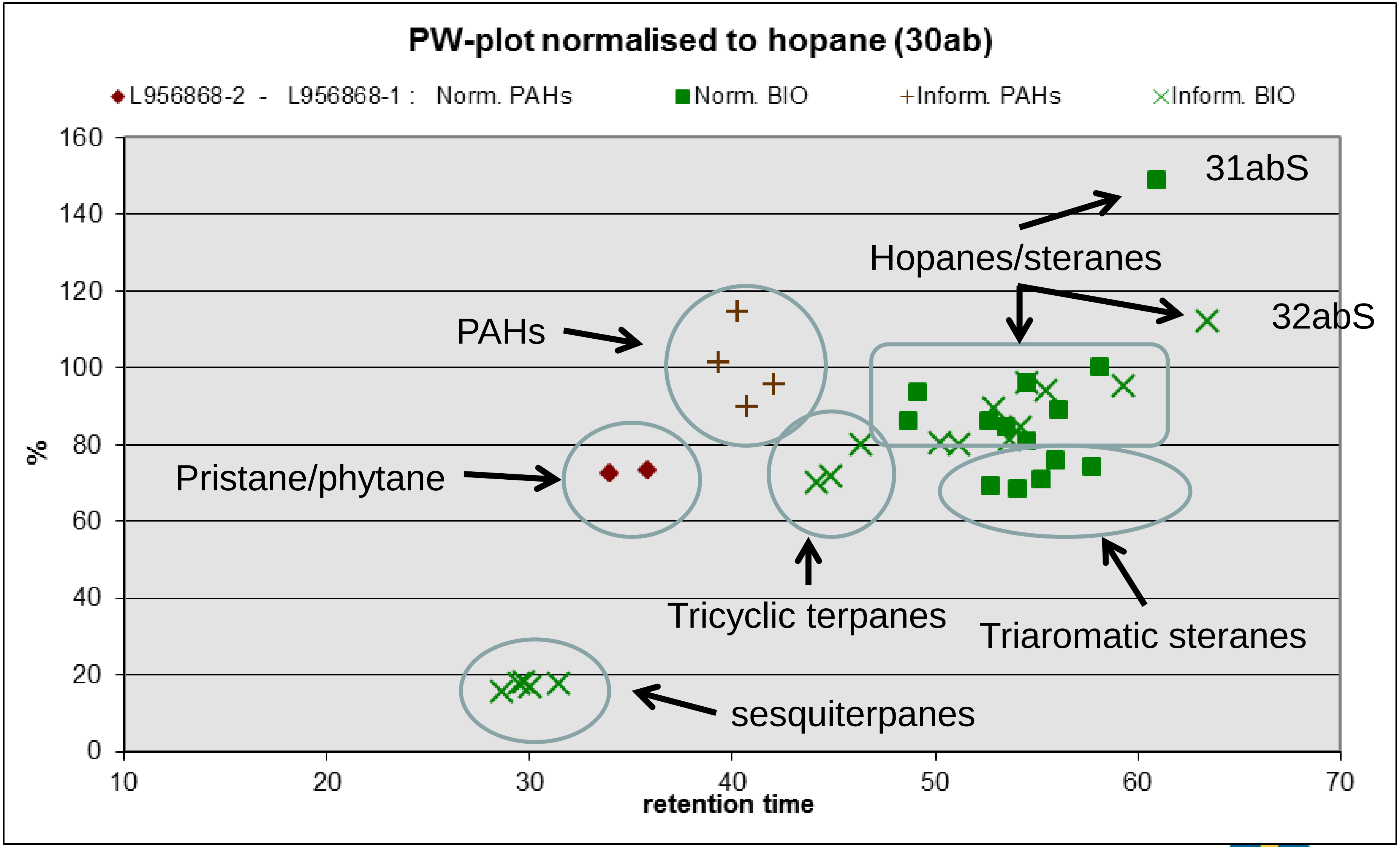
European Maritime Safety Agency **FprCEN/TR 15522-2 April 2012** Discussion paper

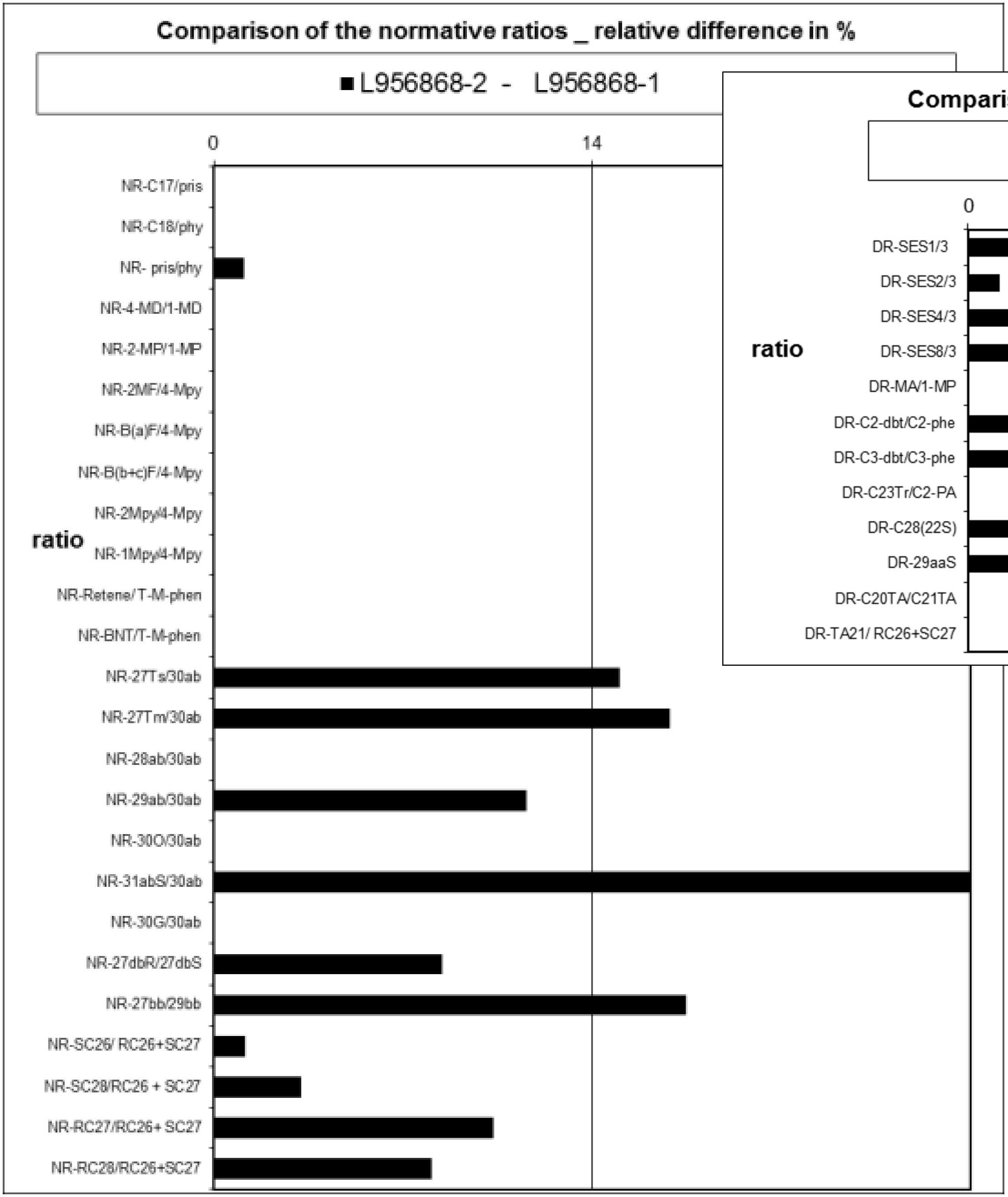


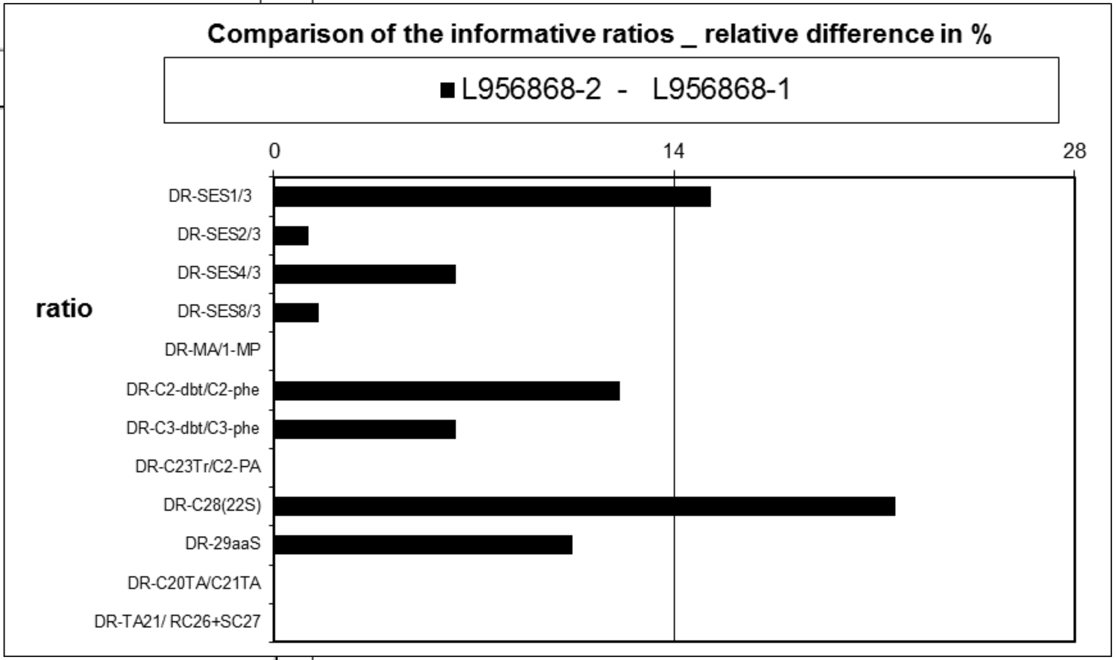
Note: Out of the 161 spills checked by aircraft less than 3 hours after satellite 51% (81) have been confirmed as being mineral oil
Out of the 614 spills not checked by aircraft or checked later than 3 hours after satellite pass, only 18 % (114) have been confirmed



MS-PW (percentage weathering) plots are powerful tools for the recognition of the different kinds of weathering effects. When the effects of weathering on a spilled petroleum product are understood, any affected DRs can be eliminated or cautiously considered when comparing samples

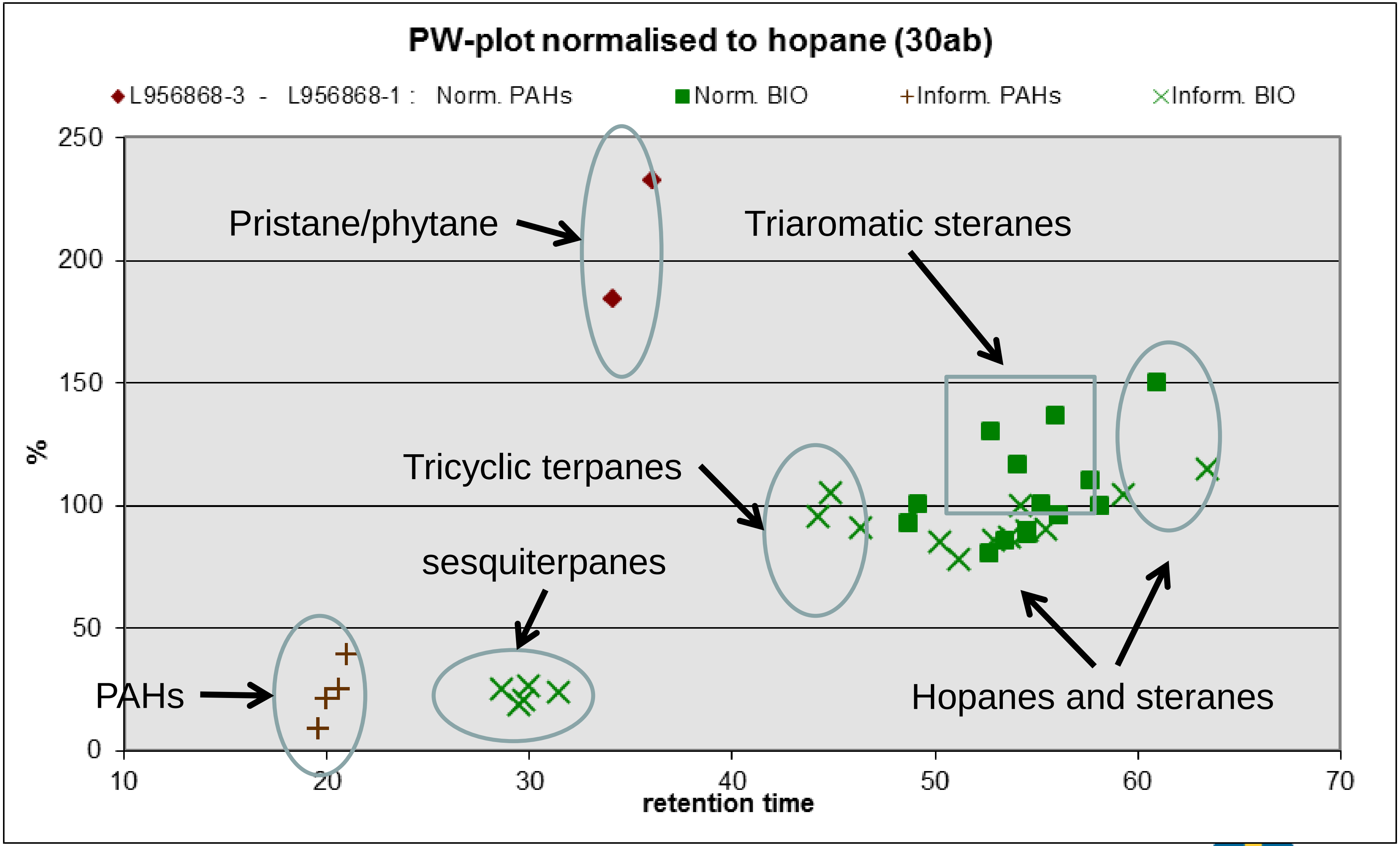

PW-plot normalised to hopane (30ab)
L956868-2 - L956868-1 : Norm. PAHs
Norm. BIO
Inform. PAHs
Inform. BIO
160
140
120
100
80
60
40
20
0
%
10
20
30
40
50
60
70
retention time
31abS
Hopanes/steranes
32abS
PAHs
Pristane/phytane
Tricyclic terpanes
Triaromatic steranes
sesquiterpanes

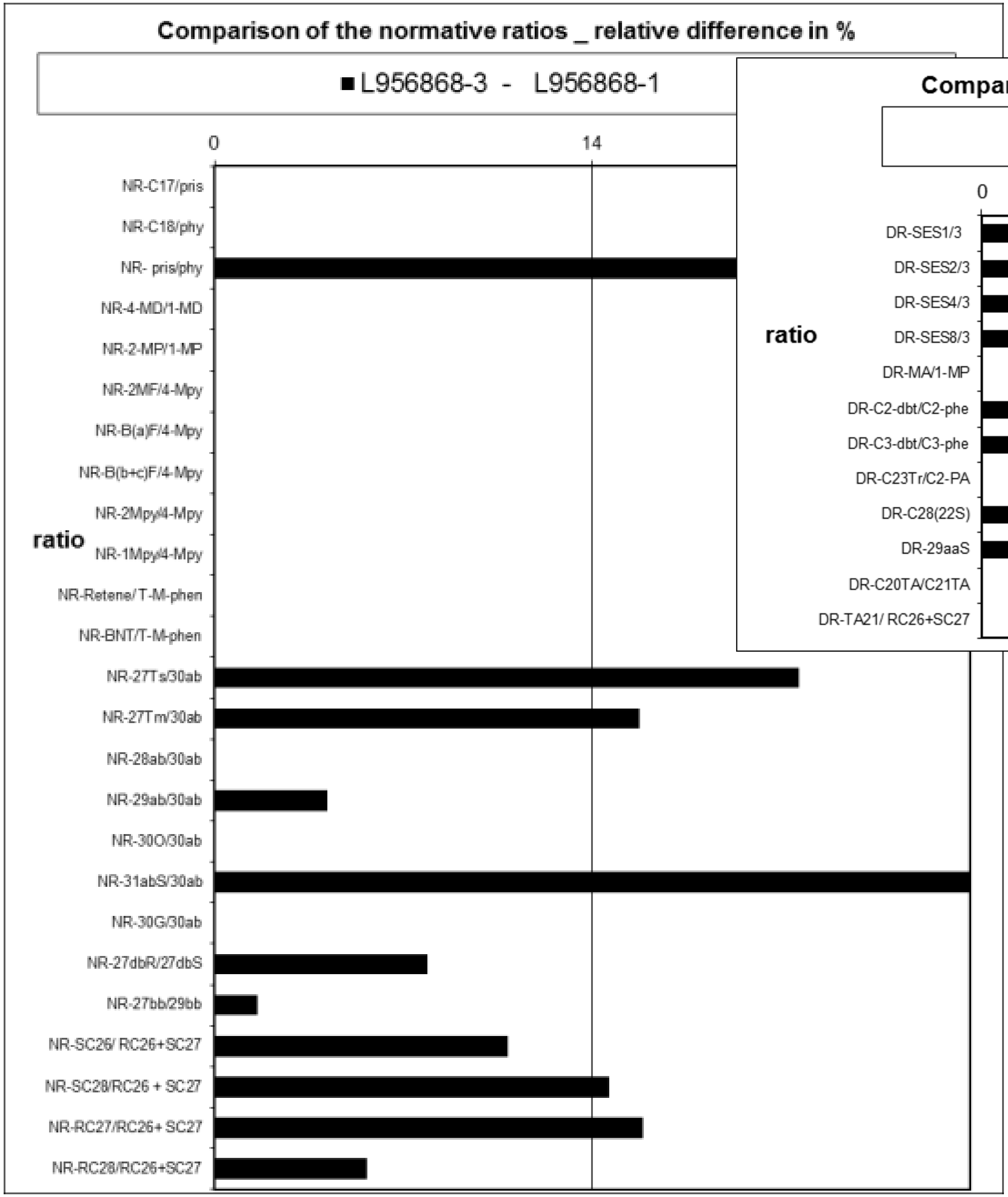


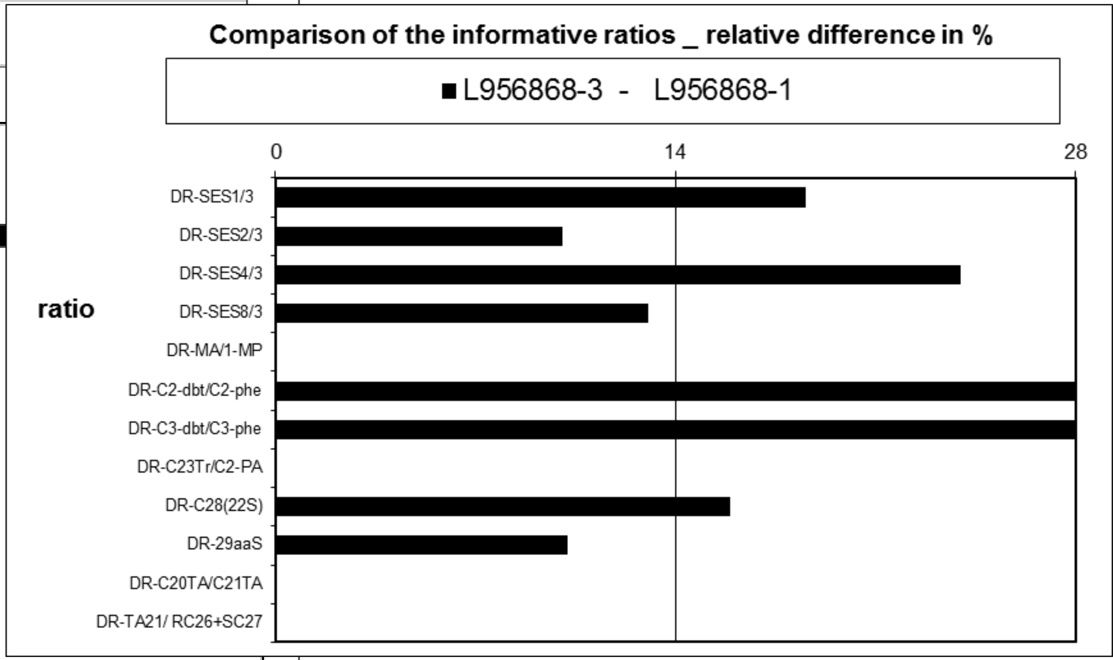


6/19 Fail
13/19 Match

Probable Match


PW-plot normalised to hopane (30ab)
L956868-3 - L956868-1 : Norm. PAHs
Norm. BIO
Inform. PAHs
Inform. BIO
250
200
150
100
50
0
%
10
20
30
40
50
60
70
retention time
Pristane/phytane
Triaromatic steranes
Tricyclic terpanes
sesquiterpanes
PAHs
Hopanes and steranes

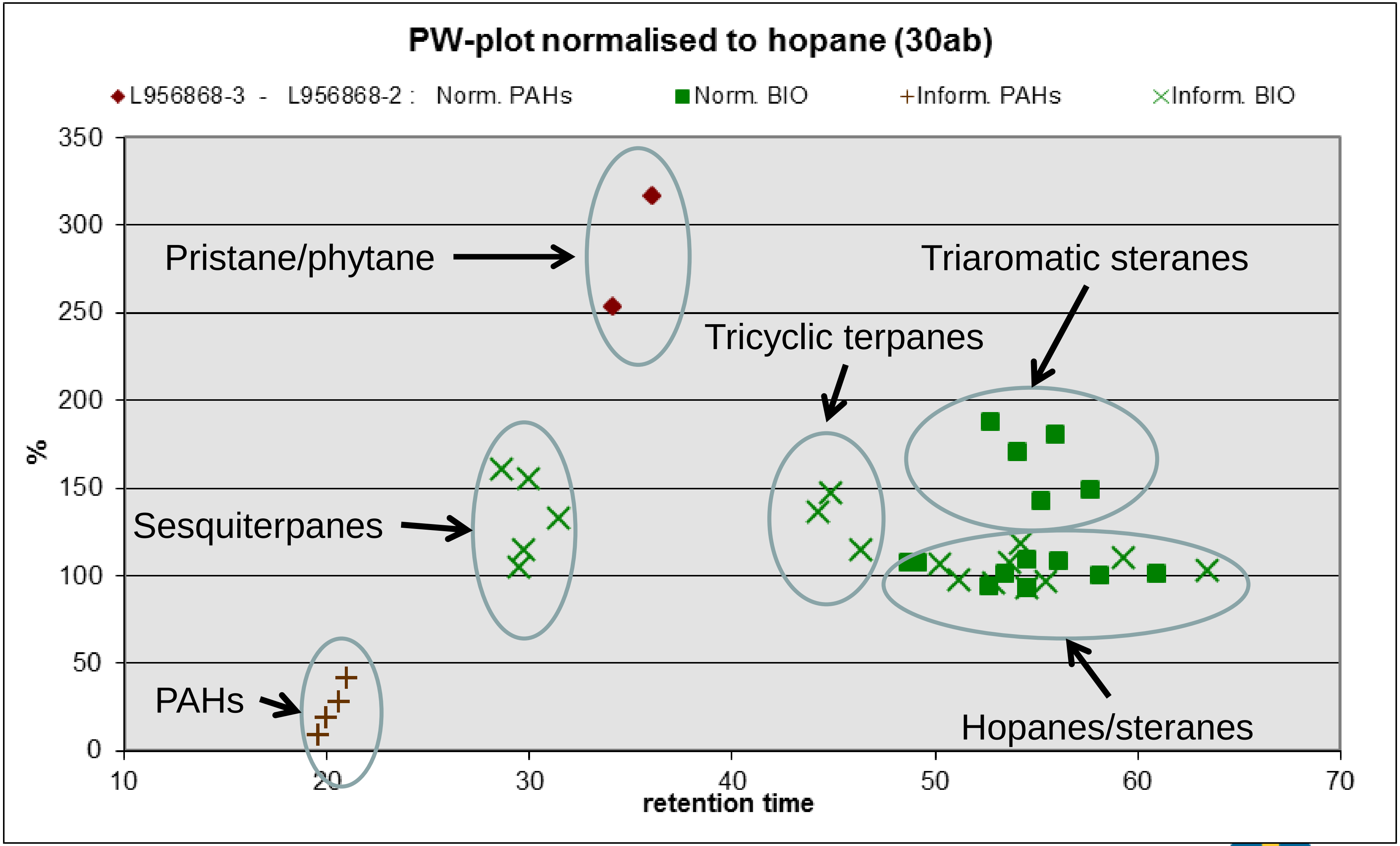


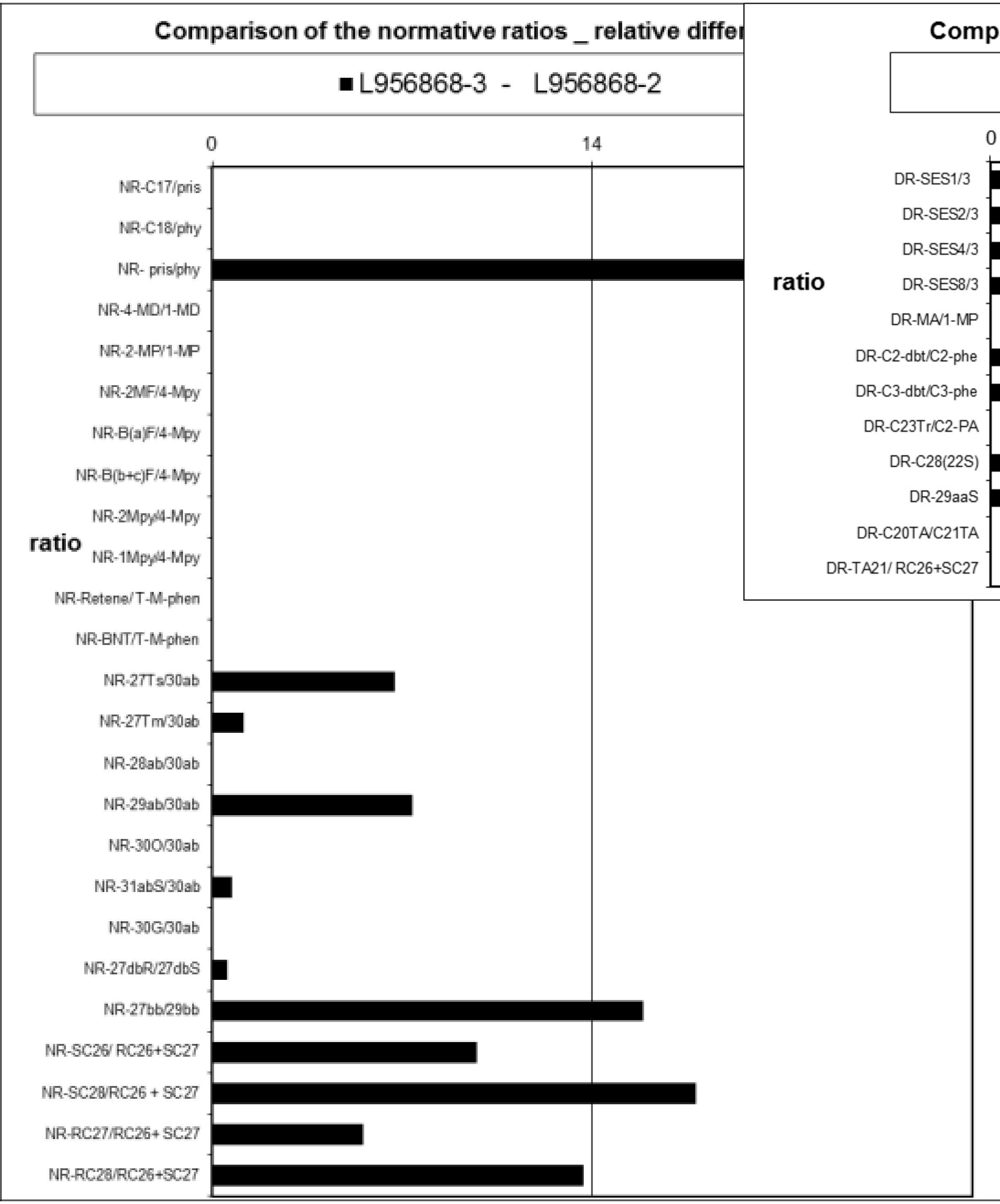


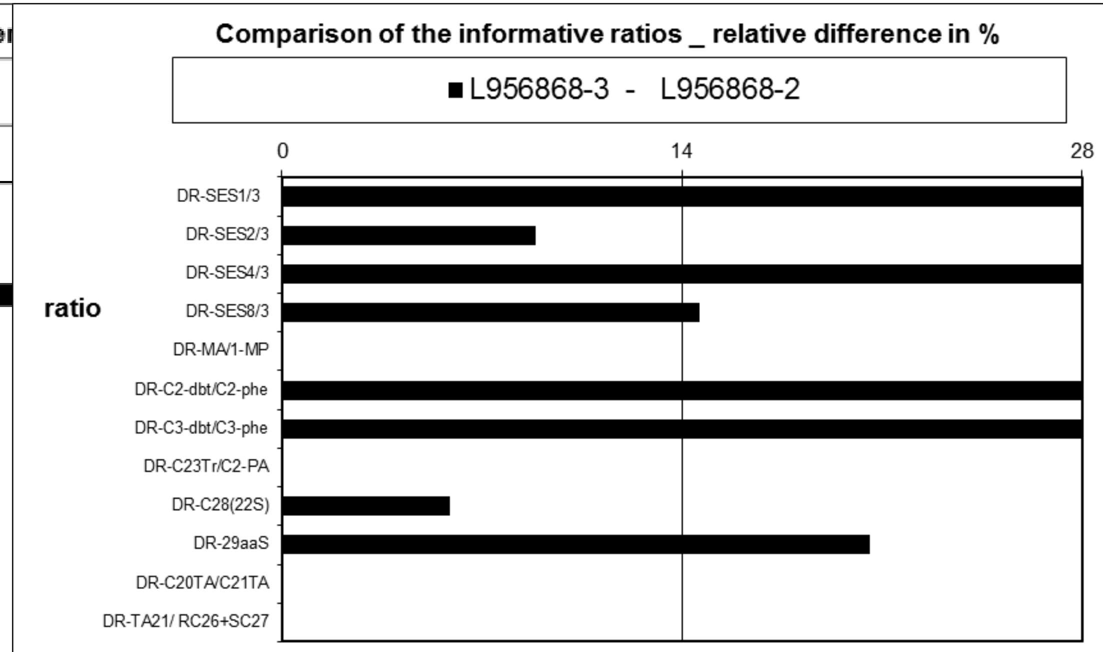
11/19 failures

Many dismissed by weathering

And concentration effects


PW-plot normalised to hopane (30ab)
L956868-3 - L956868-2 : Norm. PAHs
Norm. BIO
Inform. PAHs
Inform. BIO
Pristane/phytane
Triaromatic steranes
Tricyclic terpanes
Sesquiterpanes
PAHs
Hopanes/steranes
%
retention time
350
300
250
200
150
100
50
0
10
20
30
40
50
60
70





9/19 failures
Many dismissed by weathering
And concentration effects

Conclusions

- All samples contain middle distillate
- Supported by carbon range: $C_{12}H_{26}$-$C_{26}H_{54}$
- Supported by presence of C3-substituted benzenes
- Supported by PAH profile
- Supported by presence of sesquiterpanes
- Terpane profile similar to tar sands and it is known that Western locomotive diesel fuel is derived from heavy oil (Transport Canada)

Conclusions

- Exact age of product is difficult to determine.
- Using C&L method range is 12 – 19 years
- Using the Oudijk method range is 20 – 24+ years
- Oudijk method based upon weight of evidence
- Based upon 21 petroleum biomarker ratios the weight of evidence suggests a common source. Discrepancies likely due to extreme weathering and/or concentration differences

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