Application of Bicyclic Sesquiterpanes in Forensic Identification of Light Petroleum Products Spilled on Water

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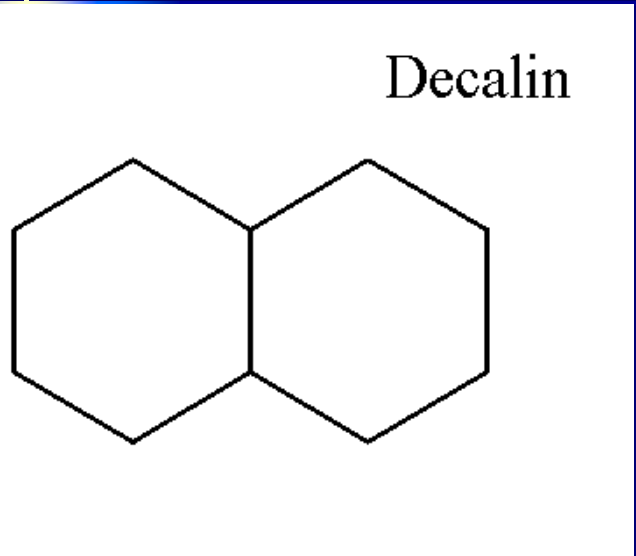
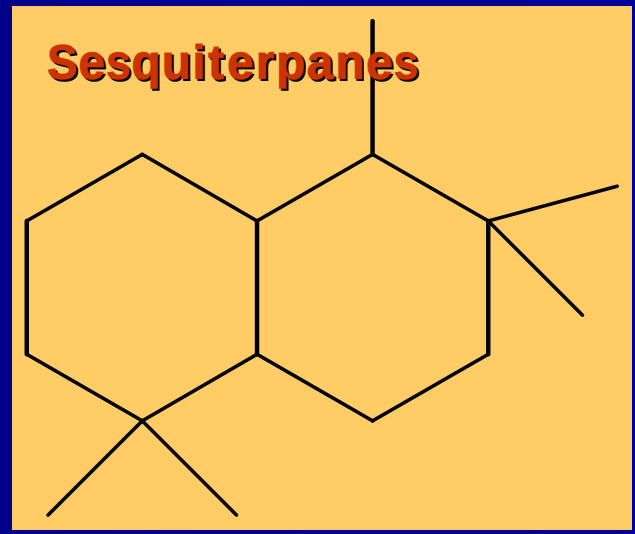
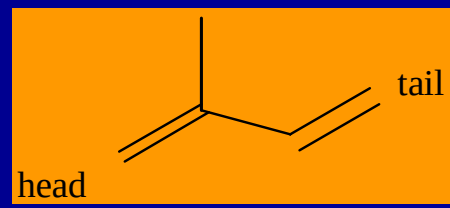
What is Bicyclic Sesquiterpanes?





- Polymethyl-substituted decalins
- Containing three isoprene subunits
- Containing two hexyl-ring (or cyclohexyl-).



What is Bicyclic Sesquiterpanes?

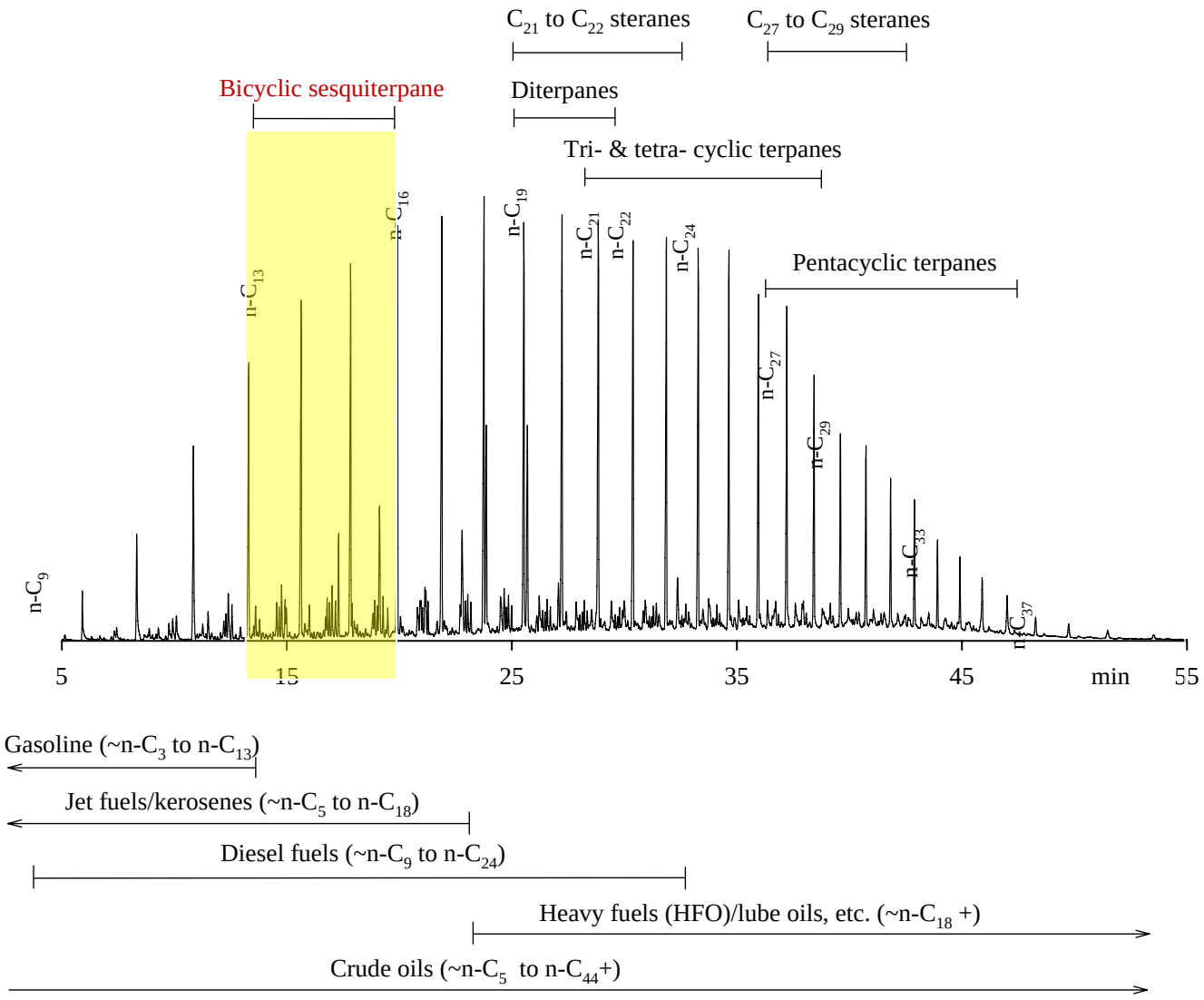
- The bicyclic biomarker sesquiterpanes with the drimane skeleton (C_{14}-C_{16}) are ubiquitous components of crude oils and ancient sediments.
- Most sesquiterpanes probably originate not only from *high plants* but also from *algae or bacteria*
- The concentration of C_{14} sesquiterpanes is higher at the immature stage, while those of C_{15} drimane and C_{16} homodrimane are relatively lower.

What is Bicyclic Sesquiterpanes?

- Early studies mainly focused on geological application of sesquiterpane compounds.
- The abundance of major compounds in the *m/z* 123 chromatograms has been employed to differentiate the organic matter input from various sedimentary environments.
- The naturally occurring bicyclic sesquiterpanes are stable in biodegradation, therefore, have potential applications in oil-source correlation and differentiation.

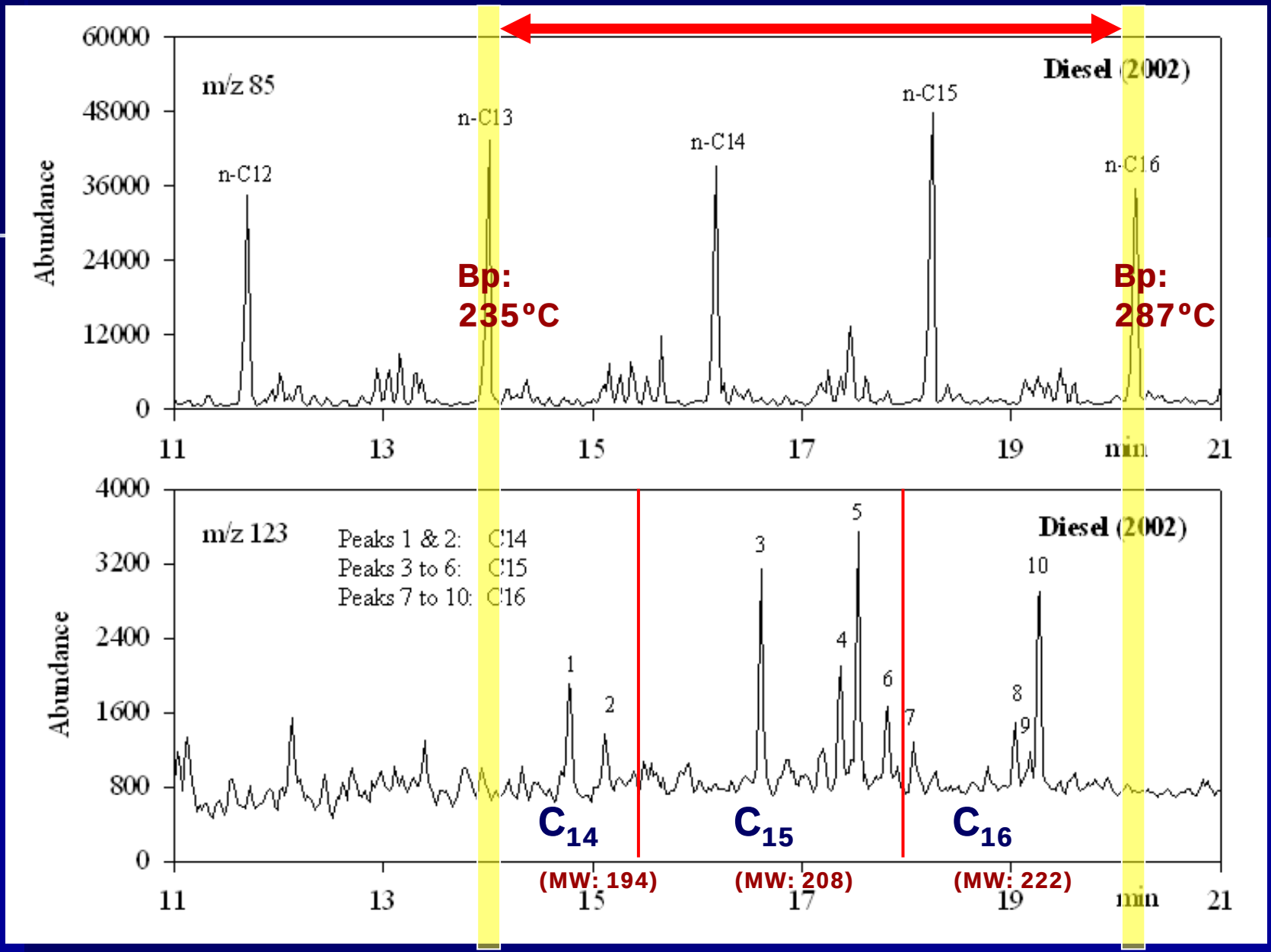
Why Sesquiterpanes?

- Biomarkers play a very important role in characterization, correlation, differentiation, and source identification in environmental forensic investigations of oil spills.
- The commonly used biomarkers include pentacyclic triterpanes (e.g., hopanes), regular and rearranged steranes, and mono- and tri-aromatic steranes.

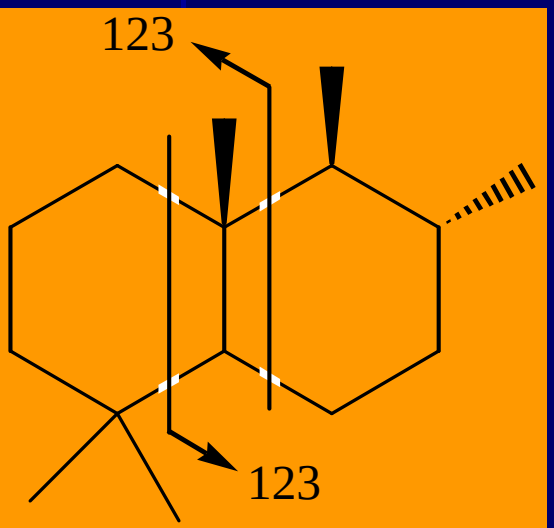

C21 to C22 steranes
C27 to C29 steranes
Bicyclic sesquiterpane
Diterpanes
Tri- & tetra- cyclic terpanes
Pentacyclic terpanes
n-C9
n-C13
n-C16
n-C19
n-C21
n-C22
n-C24
n-C27
n-C29
n-C33
n-C37
5
15
25
35
45
min
55
Gasoline (~n-C3 to n-C13)
Jet fuels/kerosenes (~n-C5 to n-C18)
Diesel fuels (~n-C9 to n-C24)
Heavy fuels (HFO)/lube oils, etc. (~n-C18 +)
Crude oils (~n-C5 to n-C44+)

Why Sesquiterpanes?

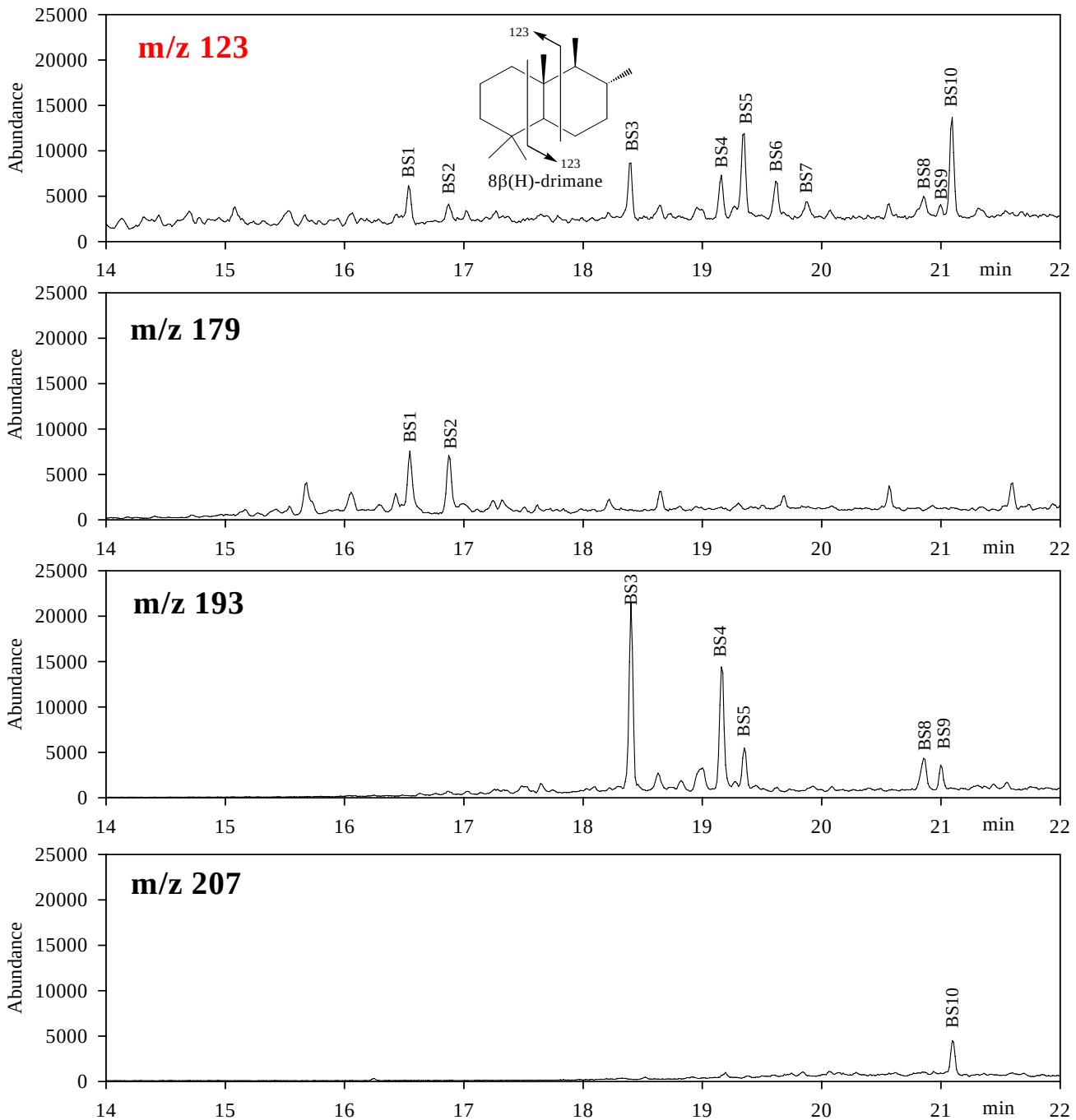
- The high MW biomarkers occur within the residual range. For lighter petroleum products like jet fuels and diesel, the refining processes remove most of these compounds from the original oil feedstock.
- The smaller bicyclic sesquiterpanes are concentrated in these products.


m/z 85
Diesel (2002)
Abundance
n-C12
n-C13
n-C14
n-C15
n-C16
Bp:
235°C
Bp:
287°C
min
m/z 123
Peaks 1 & 2: C14
Peaks 3 to 6: C15
Peaks 7 to 10: C16
Diesel (2002)
C14
C15
C16
(MW: 194)
(MW: 208)
(MW: 222)

GC/MS Determination of bicyclic sesquiterpanes



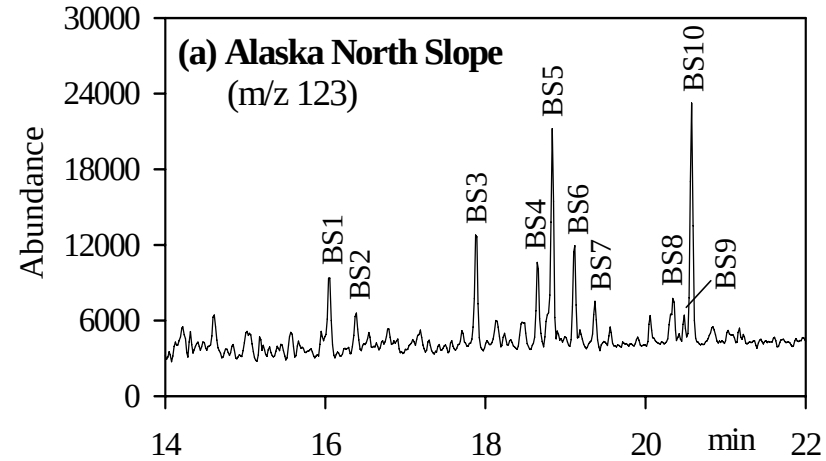
Bicyclic terpane

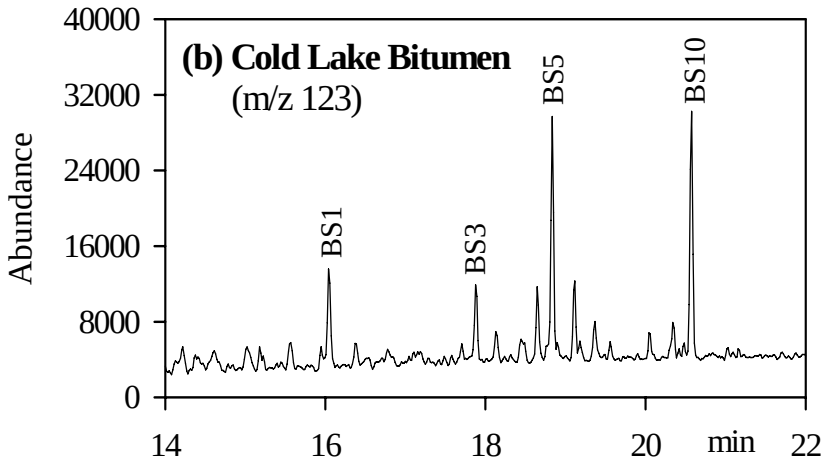


Sesquiterpanes in Crude Oils and Petroleum Products

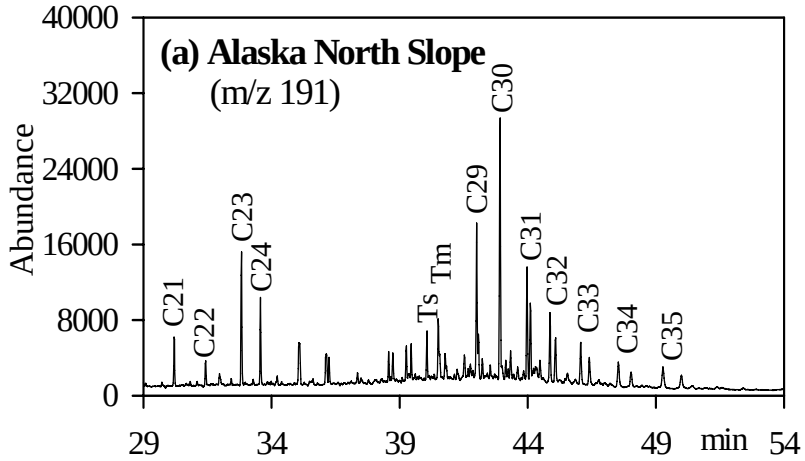
Sesquiterpanes in Crude Oils

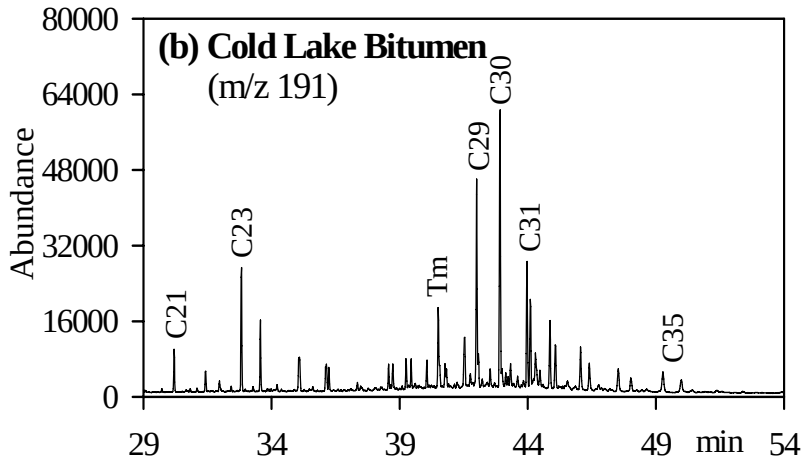
Sesquiterpanes (m/z 123)





Biomarker terpanes (m/z 191)





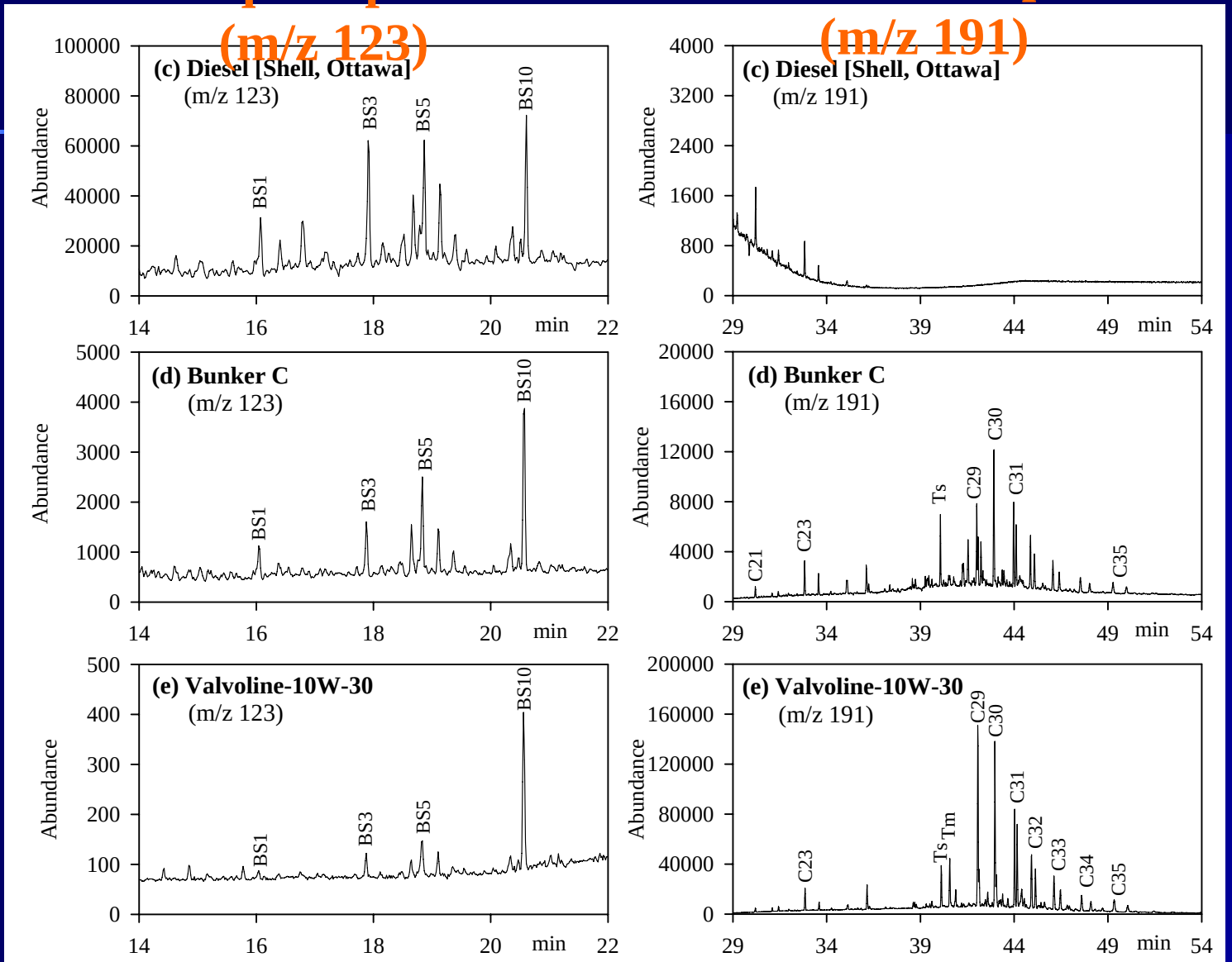
Sesquiterpanes in Crude Oils

Oil samples	**Total** (µg/g oil)
Mississippi Canyon	917
Maya	969
Mars TLP	976
West Delta Canyon	1,010
Platform Elly	1,129
Orinoco bitumen	1,302
Arabian Heavy	1,904
Cold Lake bitumen	2,124
Alaska North Slope	2,179
Cook Inlet	2,211
Prudhoe Bay	2,551
Federated	3,670
Troll	5,119
South Louisiana	5,155

Sesquiterpanes in Petroleum Products

Sesquiterpanes (m/z 123)

Biomarker terpanes (m/z 191)



Sesquiterpanes in Petroleum Products

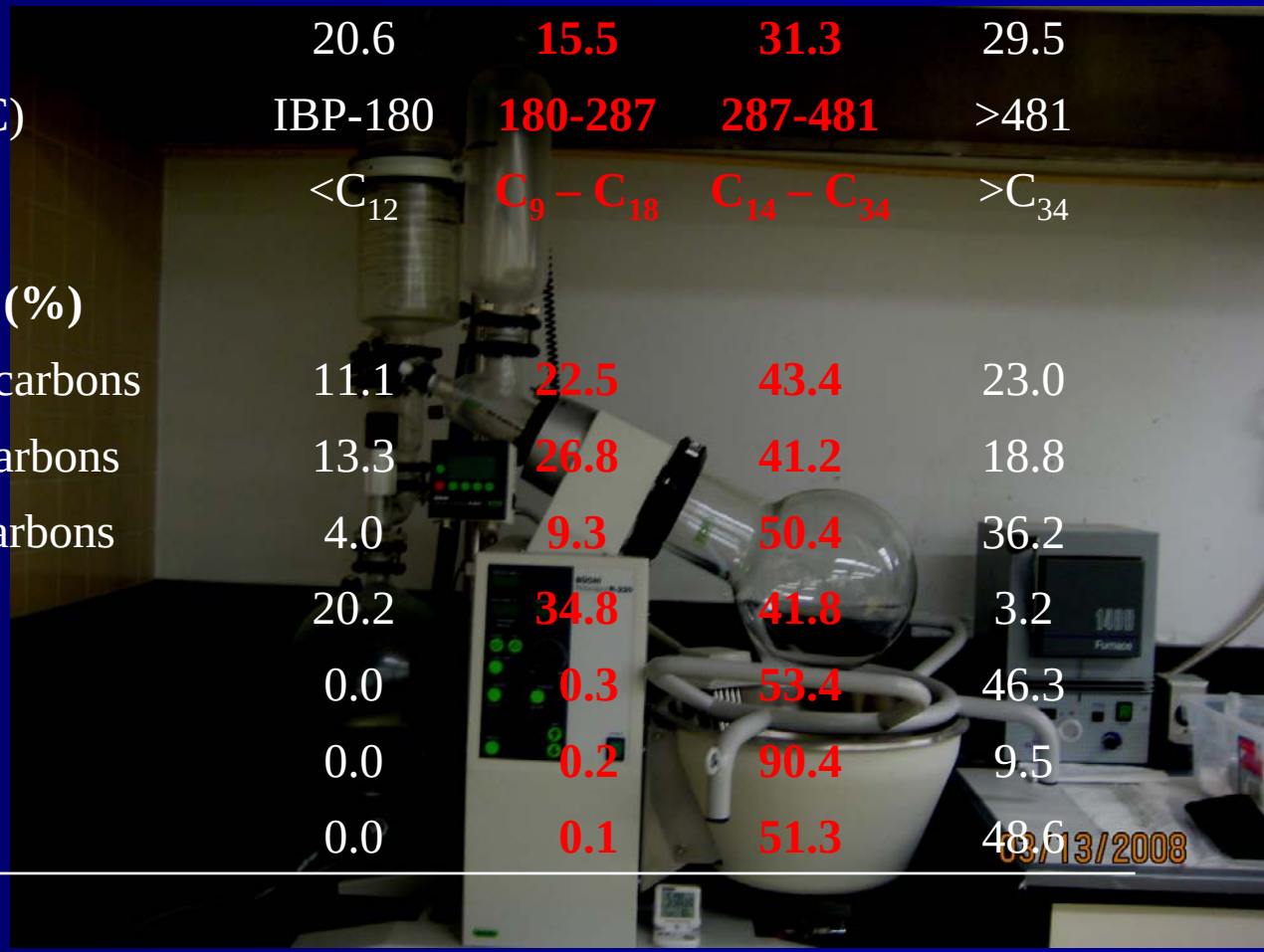
Oil samples	Total (µg/g oil)
Winter gasoline	ND
Kerosene	0.7
Aviation gasoline	30.6
Jet-A	6,770
Diesel-Pioneer	7,628
Diesel-Shell	8,703
Diesel-Stinson	8,447
Diesel-Ottawa	6,028
Korea diesel #1	7,658
Korea diesel #2	5,819
Korea diesel #3	6,129
Fuel #4	4,221
IFO-180	2,033
Fuel No. 5	1,449
Bunker C	255
Valvoline-10W-30	10.1
Pennzoil synthetic-10W-30	15.3
Extreme pressure gear	15.6

Summaries: Sesquiterpanes in Oils

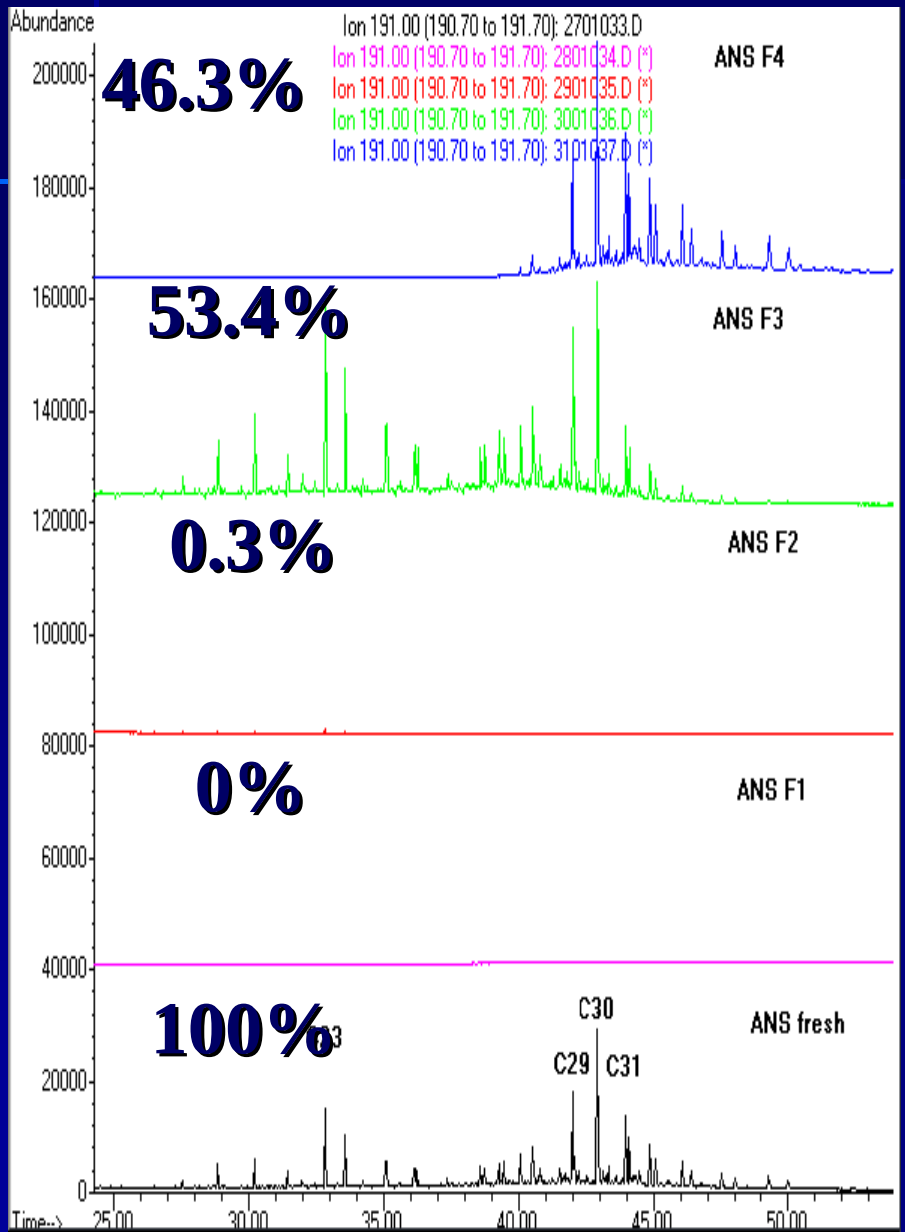
- The presence of bicyclic sesquiterpanes in crudes and petroleum products are apparent.
- The oils from different sources demonstrate differences in both the absolute concentrations and relative distribution patterns of sesquiterpanes.
- The pentacyclic triterpanes and steranes are generally absent in lighter petroleum products, but bicyclic sesquiterpanes are present in diesels and certain jet fuels with significant abundances.

Sesquiterpanes in Distillation Fractions

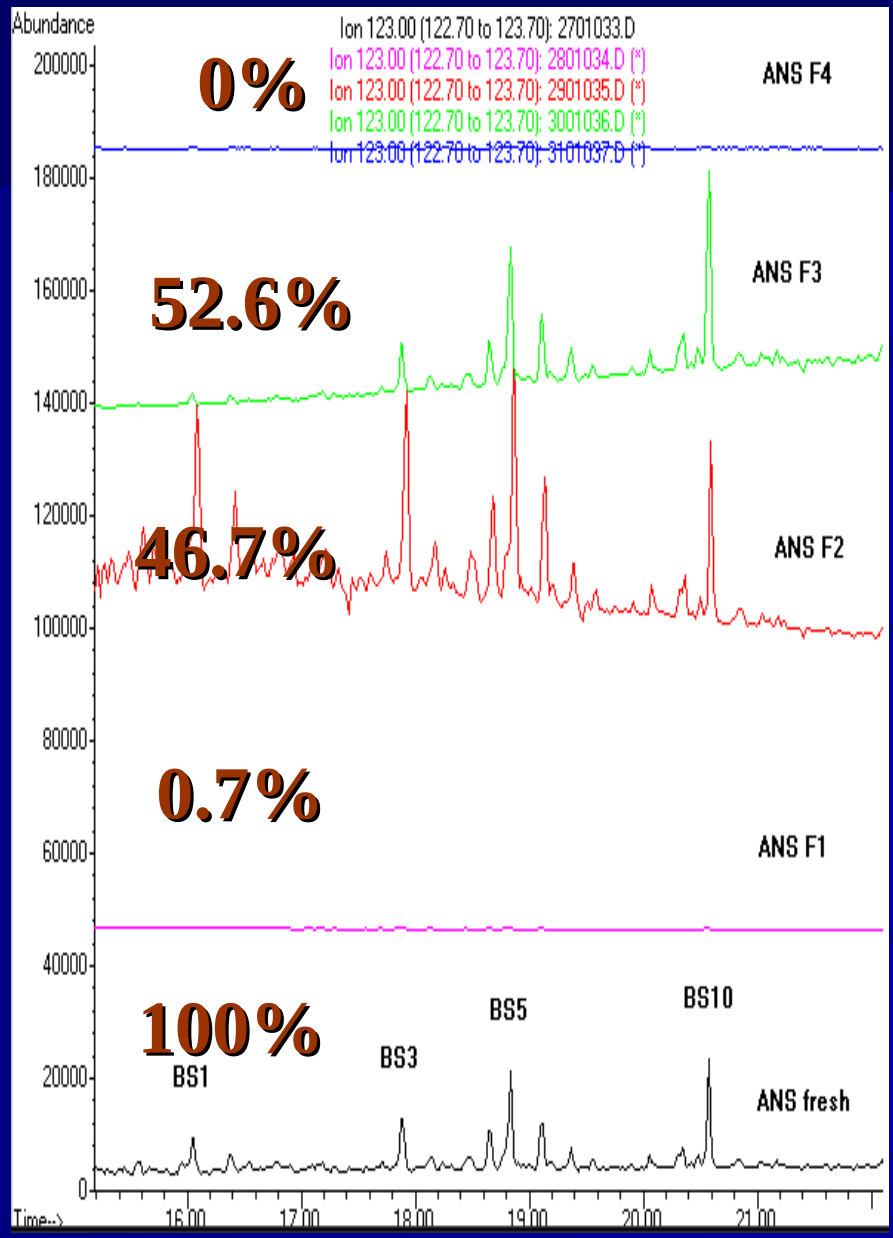
Alaska north slope crude oil	F1	F2	F3	F4
Mass (%)	20.6	15.5	31.3	29.5
Boiling point range (ºC)	IBP-180	180-287	287-481	>481
Main carbon range	$<C_{12}$	$C_9 - C_{18}$	$C_{14} - C_{34}$	$>C_{34}$
Hydrocarbon groups (%)				
Total petroleum hydrocarbons	11.1	22.5	43.4	23.0
Total saturated hydrocarbons	13.3	26.8	41.2	18.8
Total aromatic hydrocarbons	4.0	9.3	50.4	36.2
n-Alkanes	20.2	34.8	41.8	3.2
Biomarker terpanes	0.0	0.3	53.4	46.3
Biomarker steranes	0.0	0.2	90.4	9.5
C_{30} bb-Hopane	0.0	0.1	51.3	48.6



Biomarker Terpanes



Sesquiterpanes



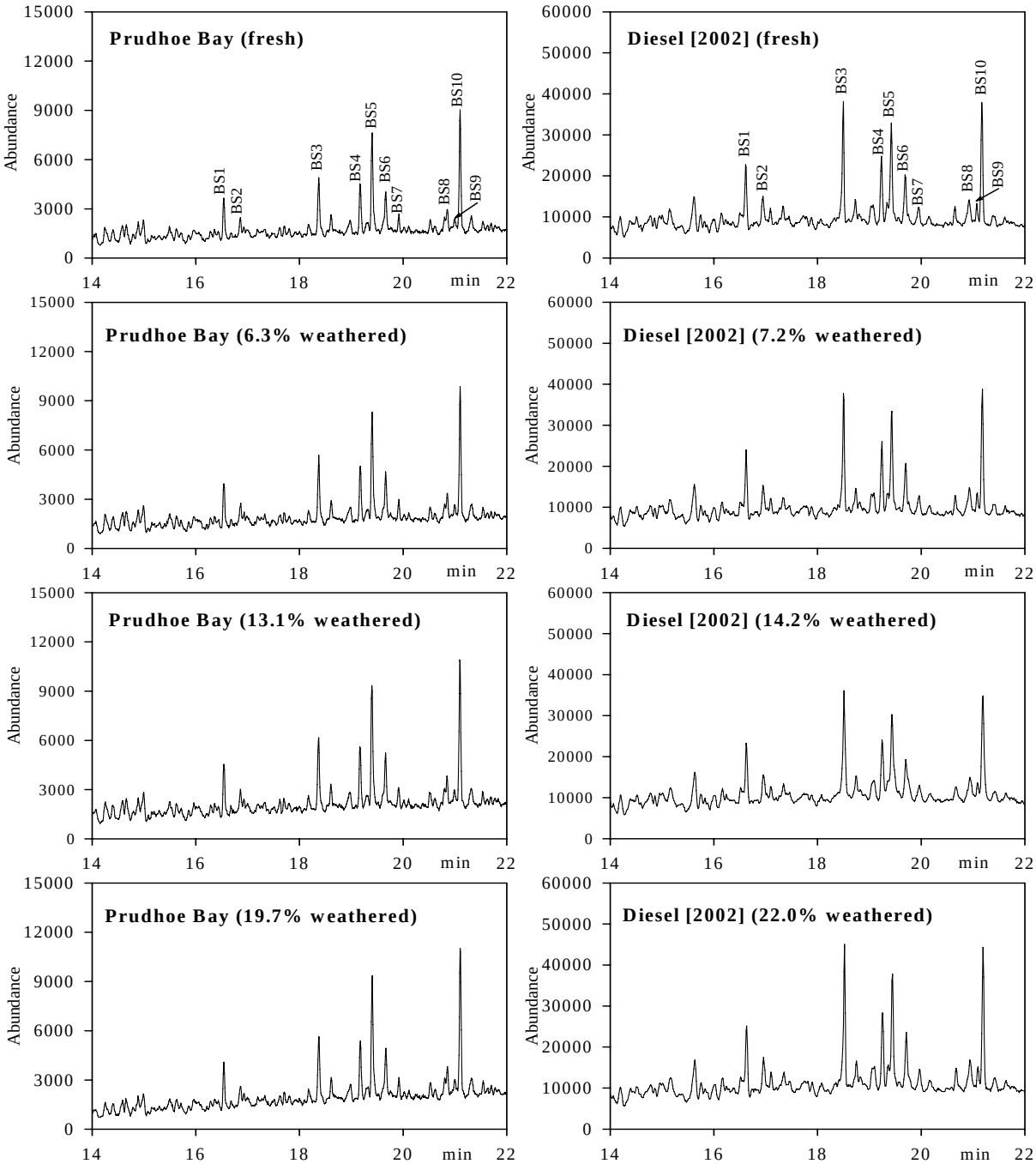
Sesquiterpanes in Distillation Fractions

Sesquiterpanes (%)	F1	F2	F3	F4
BS1	1.0	**89.4**	**9.6**	0.0
BS2	1.3	**86.6**	**12.1**	0.0
BS3	0.8	**71.3**	**28.0**	0.0
BS4	0.6	**62.5**	**36.9**	0.0
BS5	0.4	**56.1**	**43.4**	0.0
BS6	0.4	**52.6**	**47.0**	0.0
BS7	0.3	**48.4**	**51.3**	0.0
BS8	0.2	**43.5**	**56.3**	0.0
BS9	0.3	**40.4**	**59.3**	0.0
BS10	0.4	**37.5**	**62.1**	0.0

Summaries: Sesquiterpanes in Distillation Fractions

- Biomarker terpanes and steranes were found almost entirely in heavier fractions 3 and 4 due to their high boiling points
- Sesquiterpanes were largely found in fractions 2 and 3.
- For fraction 2, all ten target sesquiterpanes were concentrated up to approximately five-fold compared to the native crude oils
- Sesquiterpanes were in low concentration in the lightest fraction 1 and rarely found in the heaviest fraction 4.

Weathering Effects on Sesquiterpane Distributions



Summaries: Weathering Effects on Sesquiterpane Distributions

- In general, light to medium weathering has little effects on distribution pattern and diagnostic ratio values of sesquiterpanes.
- Smaller C_{14} sesquiterpanes (BS1 and BS2) start to be lost as oil subjected to high percentages of weathering .
- Most of sesquiterpane ratios are robust for correlation and differentiation of oil samples in that have only lightly to moderately weathered
- The most heavily weathered might result in certain changes for such ratios as BS1/BS5, BS3/BS10 and BS5/BS10.

Application of Bicyclic Sesquiterpanes in Forensic Identification of Oil Spill

Case Study:

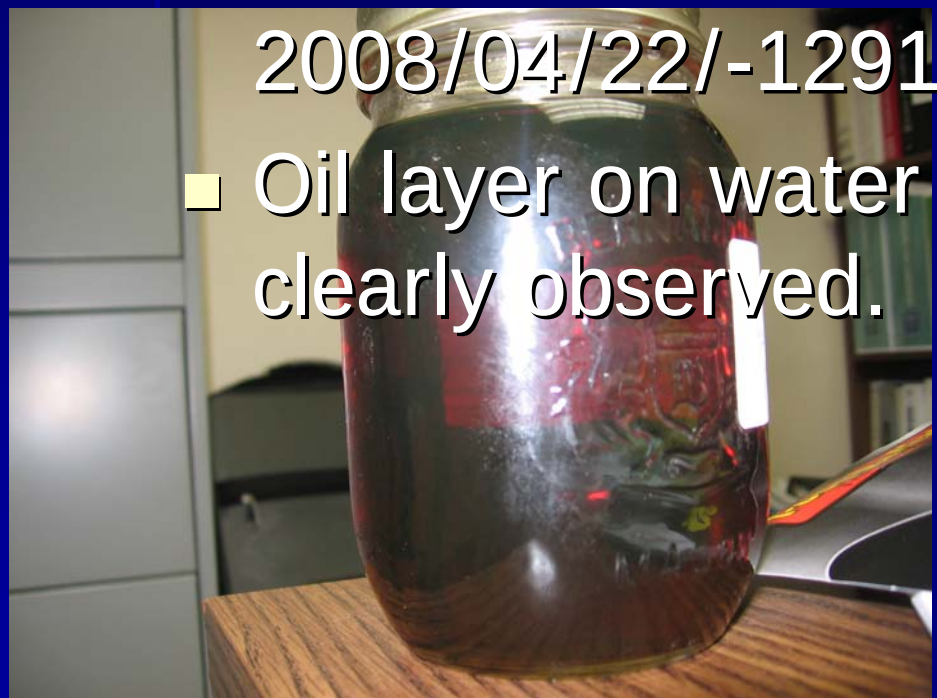
Oil Spill in Northbay, Ontario

Oil Spill in Northbay, Ontario

- In 2008, Wagg's Petroleum Equipment Ltd. was hired by the Department of National Defence (DND) and Canadian Forces Exchange System (Canex) at Canadian Force Base (CFB) at North Bay to clean up a hydrocarbon spill at one of the sites.
- The site is a fueling site for gasoline only and this site has had 3 spills; one in 1998, one in 2002 and one in 2008
- Preliminary laboratory test indicates the spilled oil is not pure gasoline, could be a mixture with other type of fuel.

Oil Spill in Northbay, Ontario

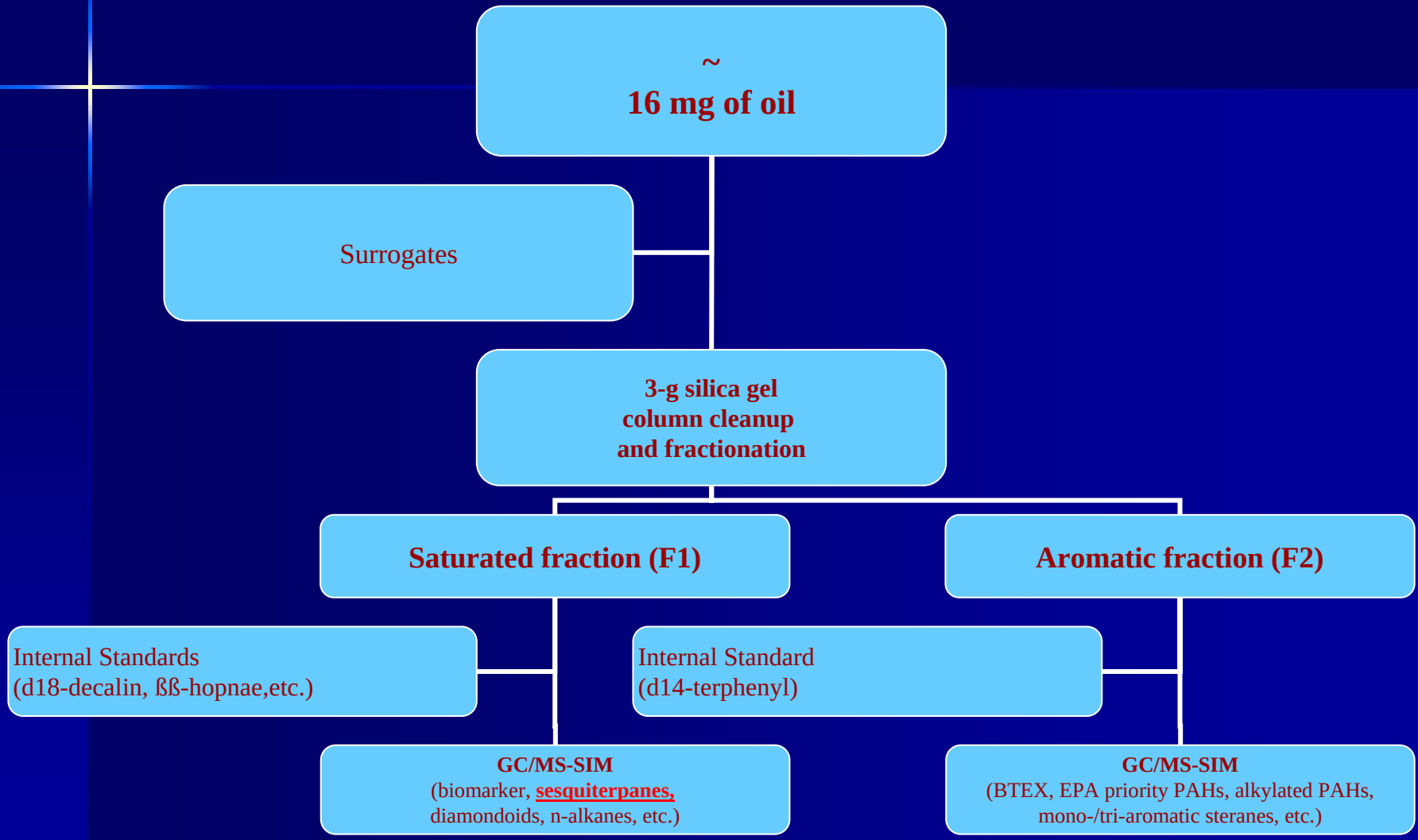
- Spill site: Northbay, Ontario
- Two water samples:
- 2008/04/22/-1290, 2008/04/22/-1291
- Oil layer on water surface was clearly observed.



Oil Fingerprinting Analysis

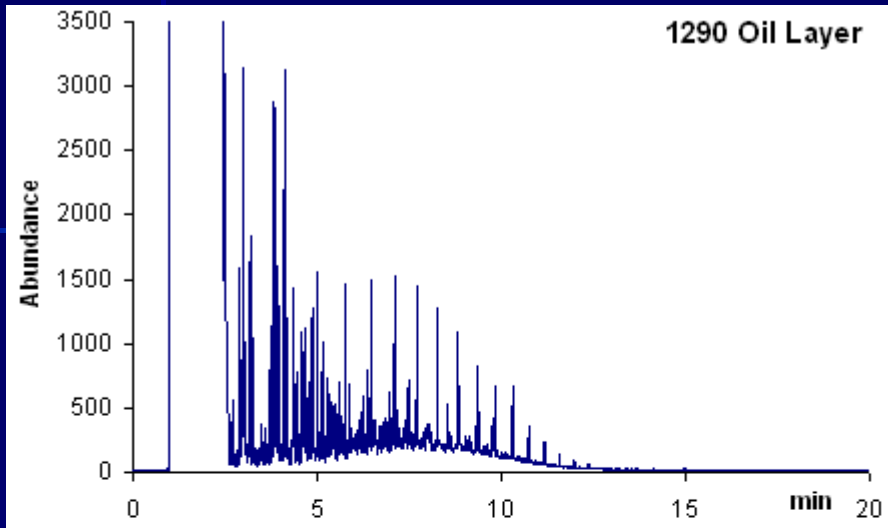
- The water samples were separated into two parts: oil phase and water phase respectively;
- **Oil layer:** Approximately 0.5 mL of oil was removed from the top oil layer of two water samples. About 16.0 mg of oil was used for fingerprinting analysis.
- **Water layer**: The water samples were weighed and then transferred to separatory funnels and extracted (liquid/liquid extraction) with dichloromethane (DCM) three times (50/50/50 mL).

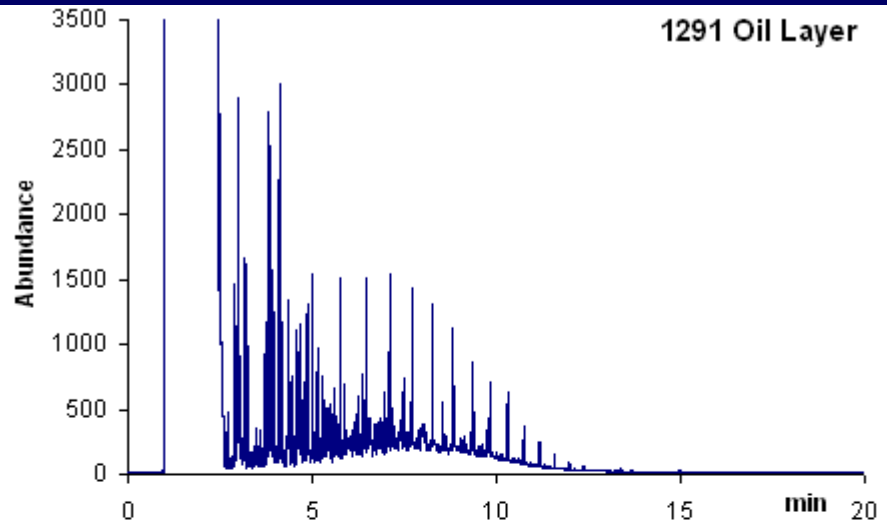
Oil Fingerprinting Analysis



Hydrocarbon Group Analysis Results

ESTD code	2008/04/22-1290Oil	2008/04/22-1290L	2008/04/22-1291Oil	2008/04/22-1291L	Diesel
Customer sample info.	Oil Layer	Water	Oil Layer	Water	**Shell [2003]**
TPH (mg/g)	768	803	805	705	957
TSH/TPH (%)	75.8	80.2	84.4	77.9	89.8
TAH/TPH (%)	24.2	19.8	15.6	22.1	13.6
Resolved/TPH (%)	57.0	53.5	53.9	52.0	22.3
∑n-Alkanes (mg/g)	72.4	77.4	76.5	67.9	128
∑EPA PAHs (mg/g)	0.24	0.30	0.25	0.27	0.61
∑APAHs (mg/g)	13.4	16.6	13.6	14.9	19.9
∑Biomarkers (mg/g)	0.052	0.067	0.060	0.060	0.014


1290 Oil Layer
Abundance
3500
3000
2500
2000
1500
1000
500
0
0
5
10
15
min
20


1291 Oil Layer
Abundance
3500
3000
2500
2000
1500
1000
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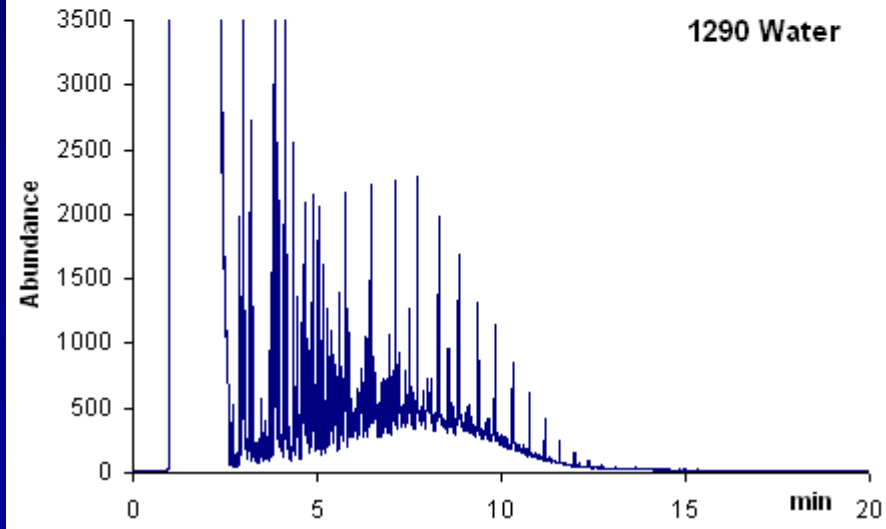
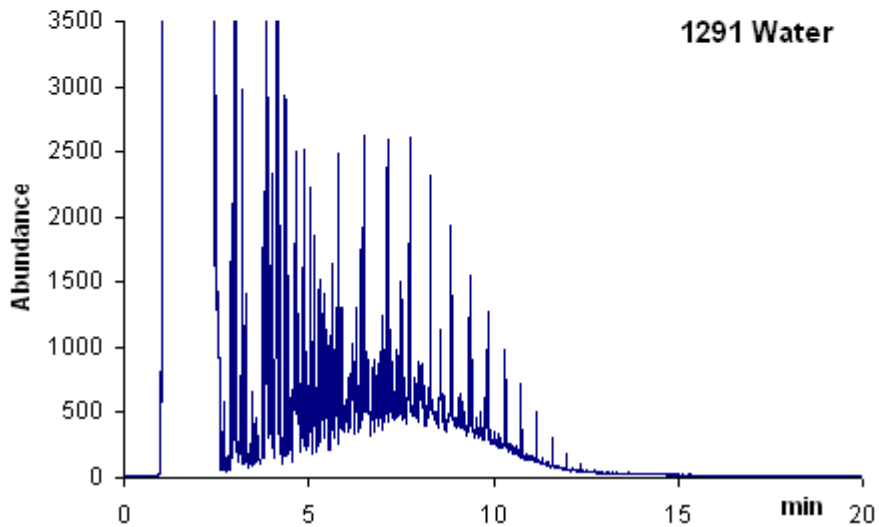
0
0
5
10
15
min
20


1290 Water
Abundance
3500
3000
2500
2000
1500
1000
500
0
0
5
10
15
min
20


1291 Water
Abundance
3500
3000
2500
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0
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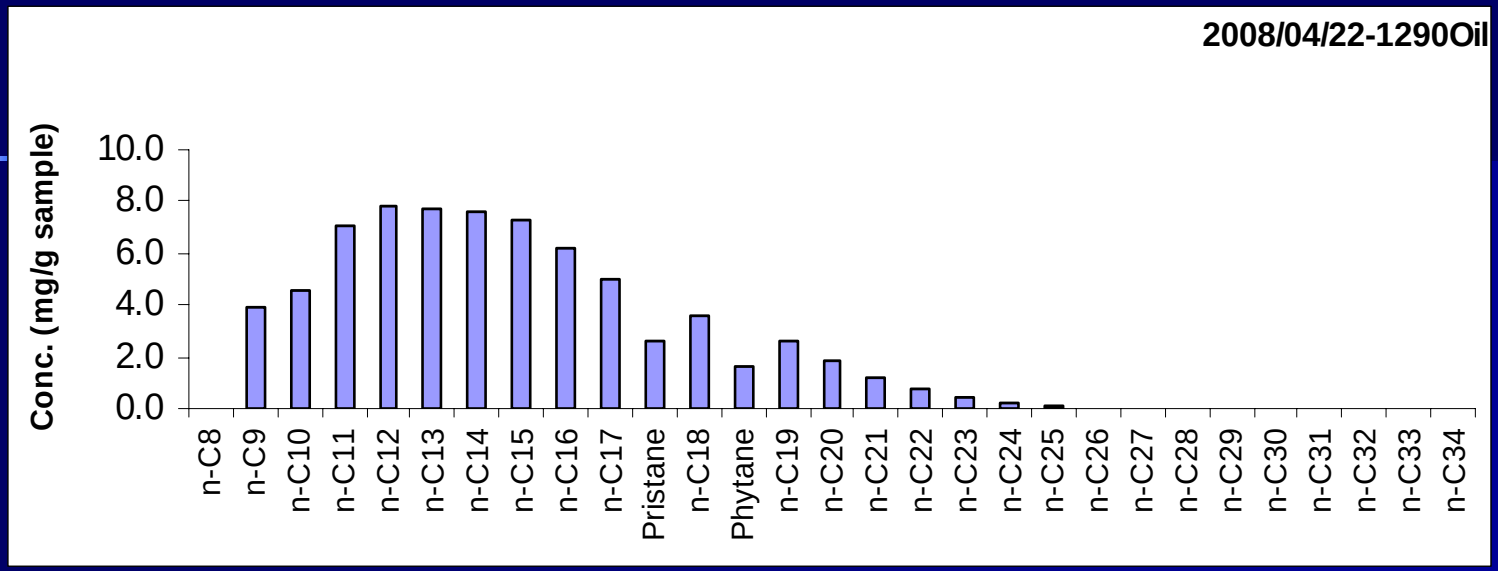
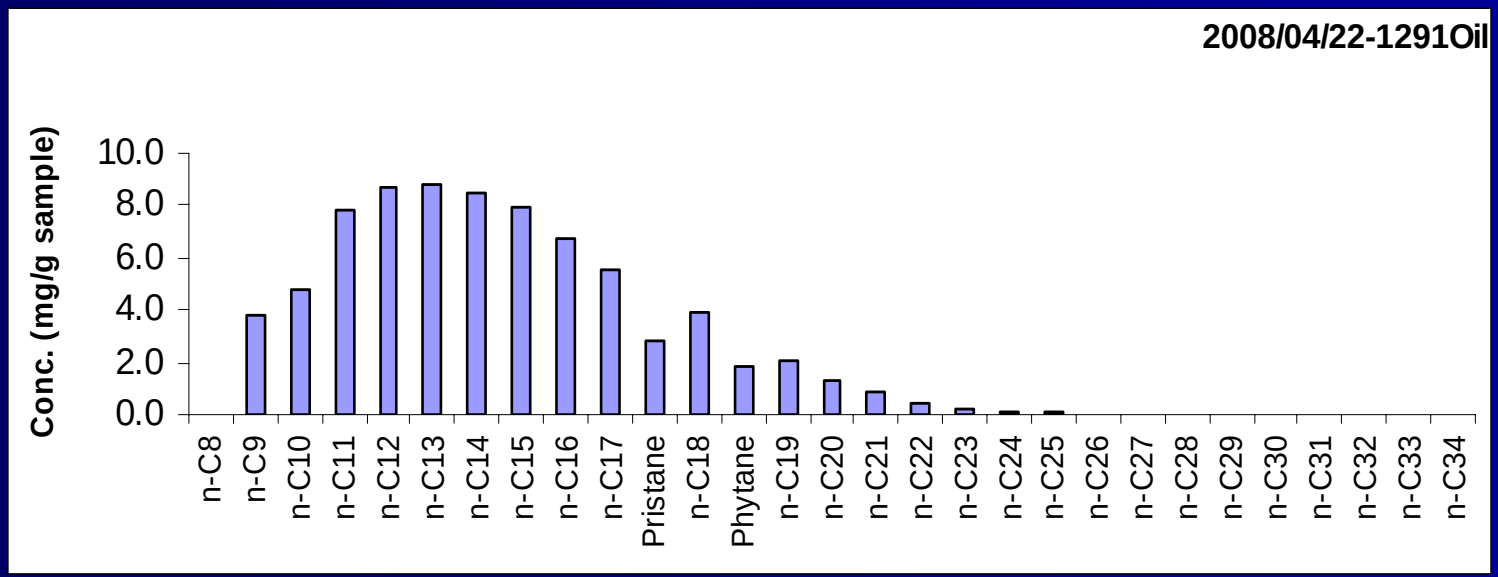
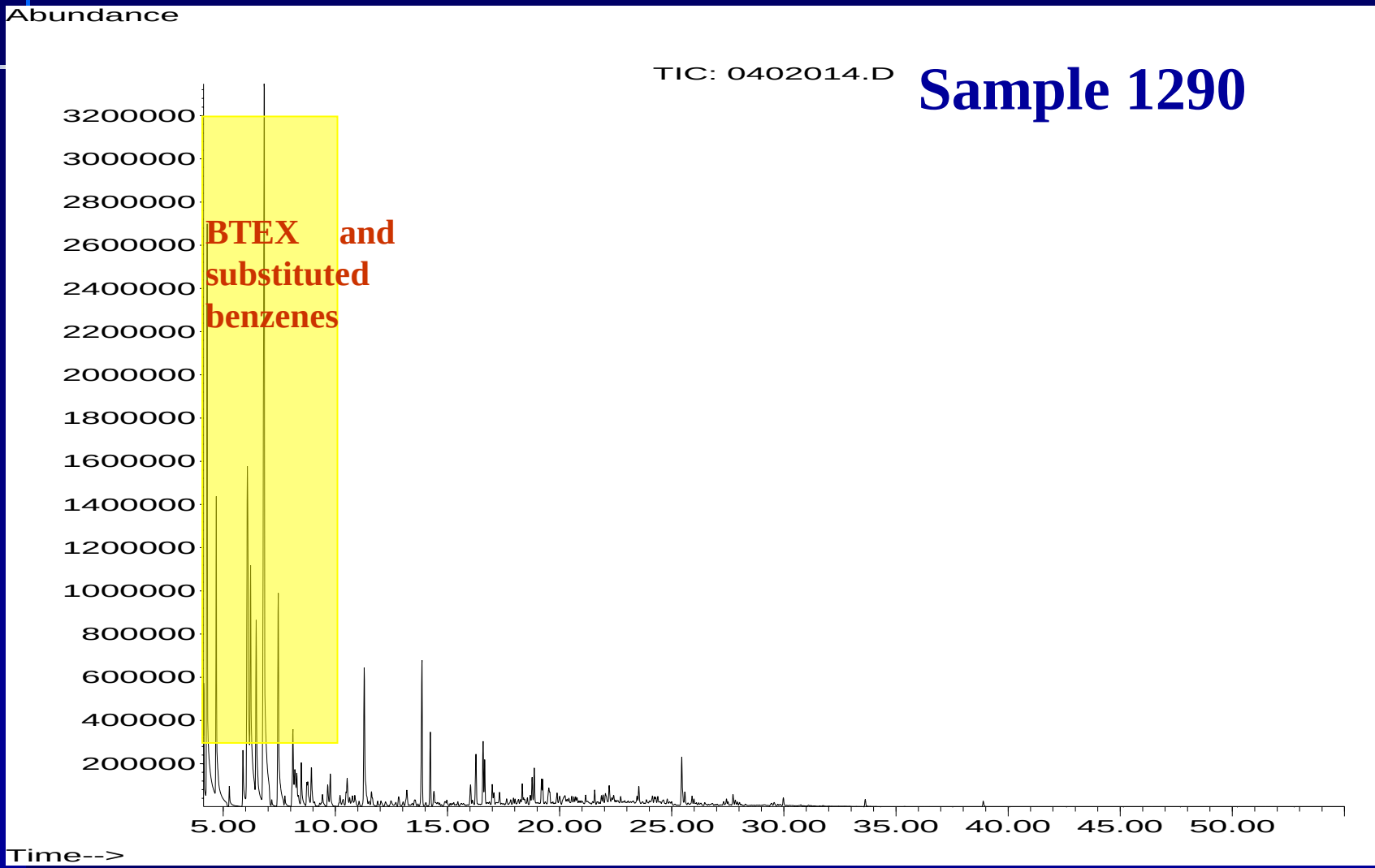
5
10
15
min
20

N-Alkane Distribution

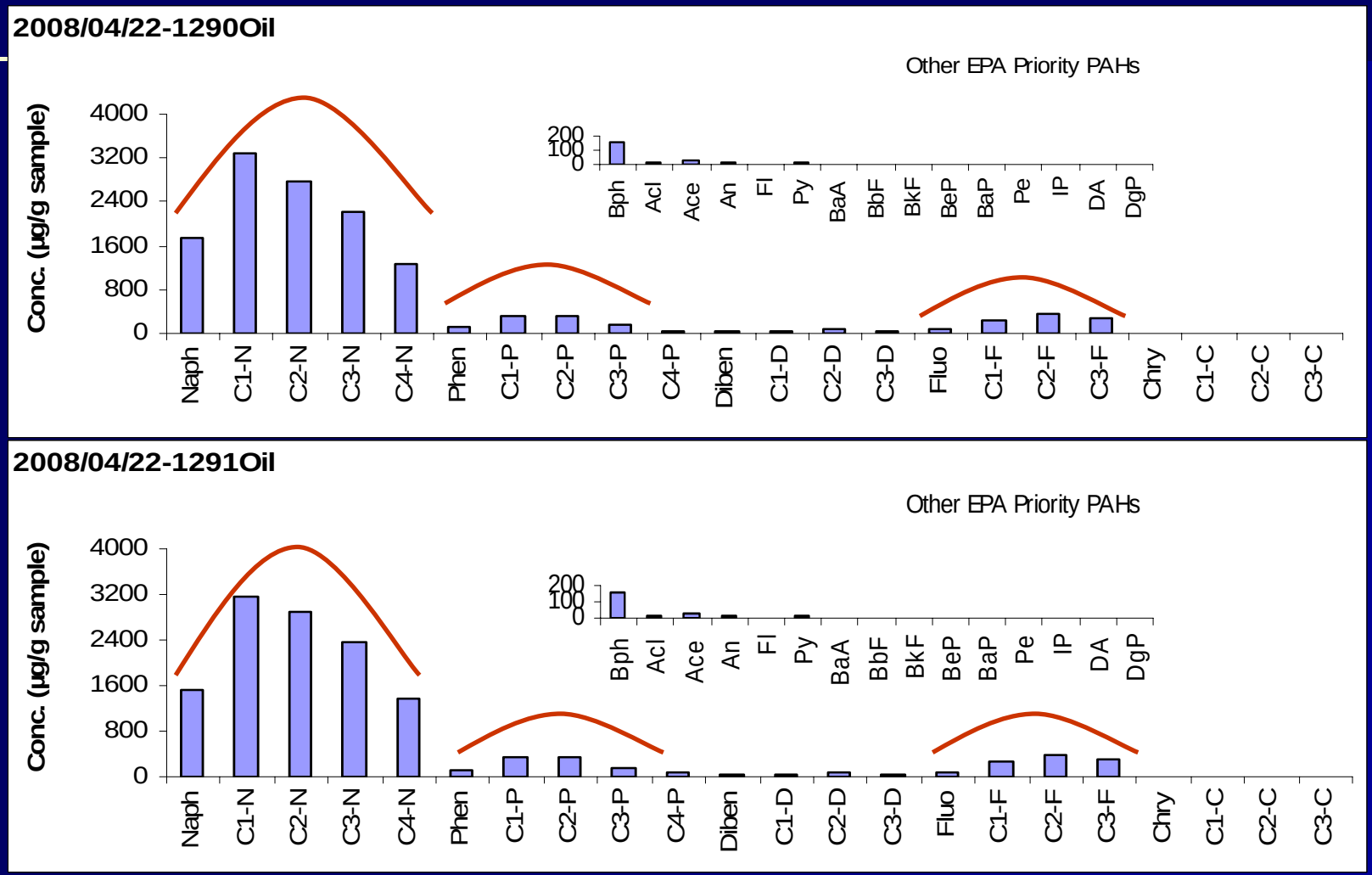




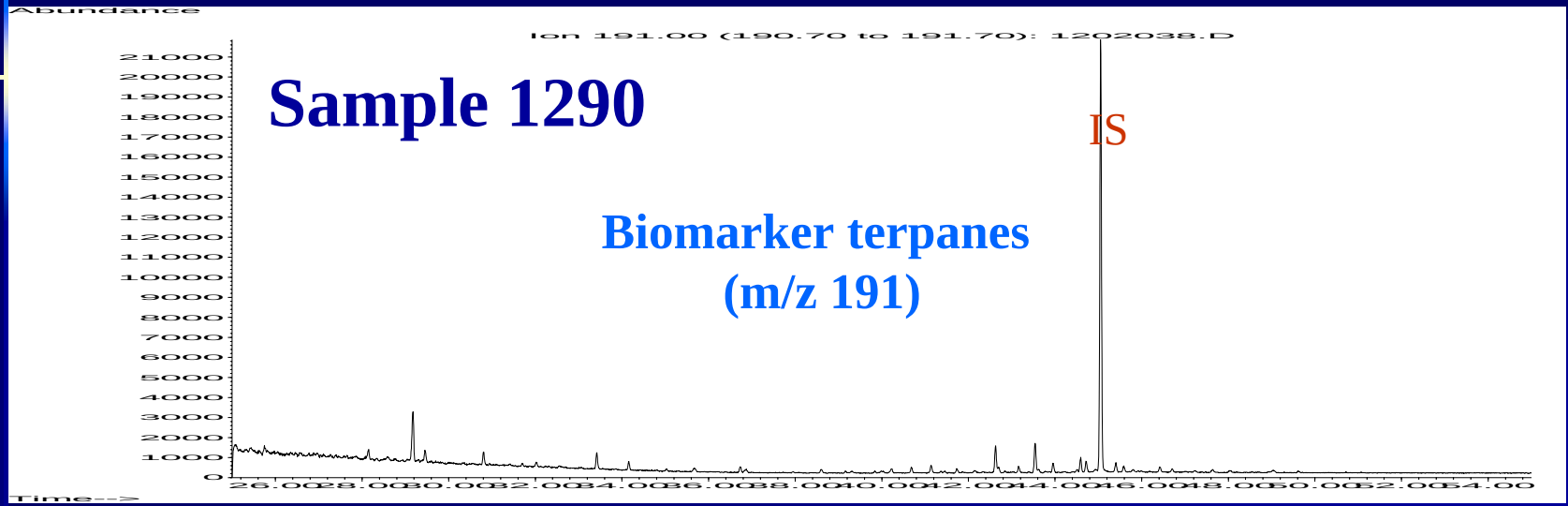
BTEX and PAHs Analysis

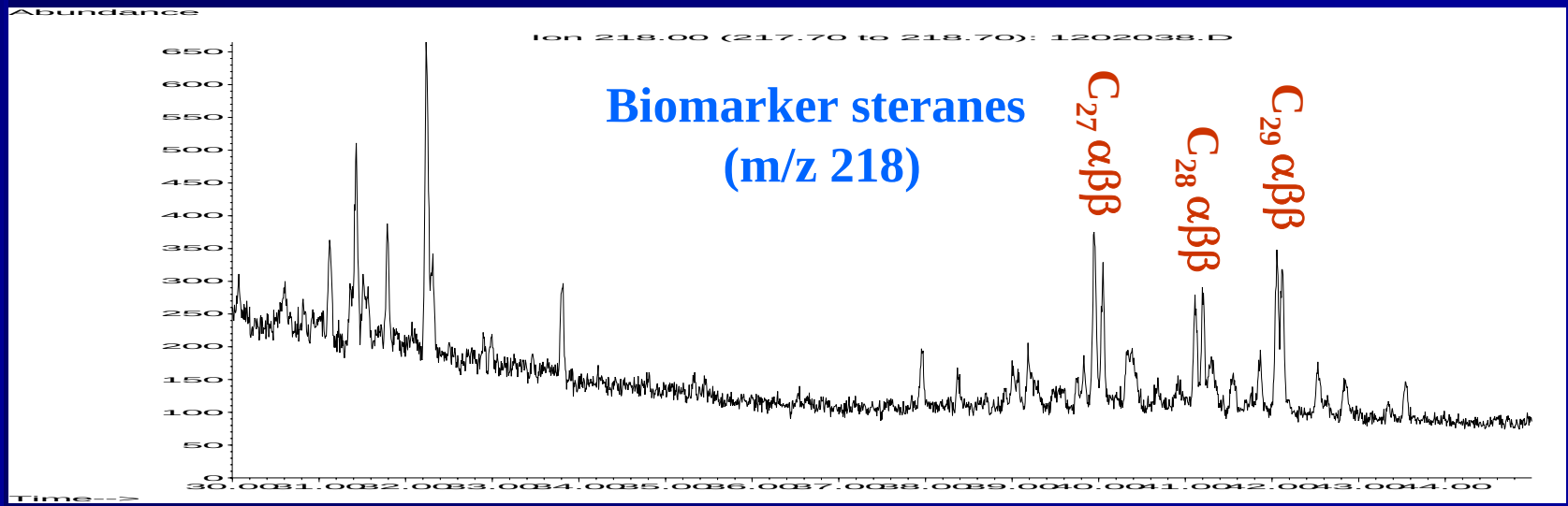


BTEX and PAHs Analysis



Biomarkers Analysis





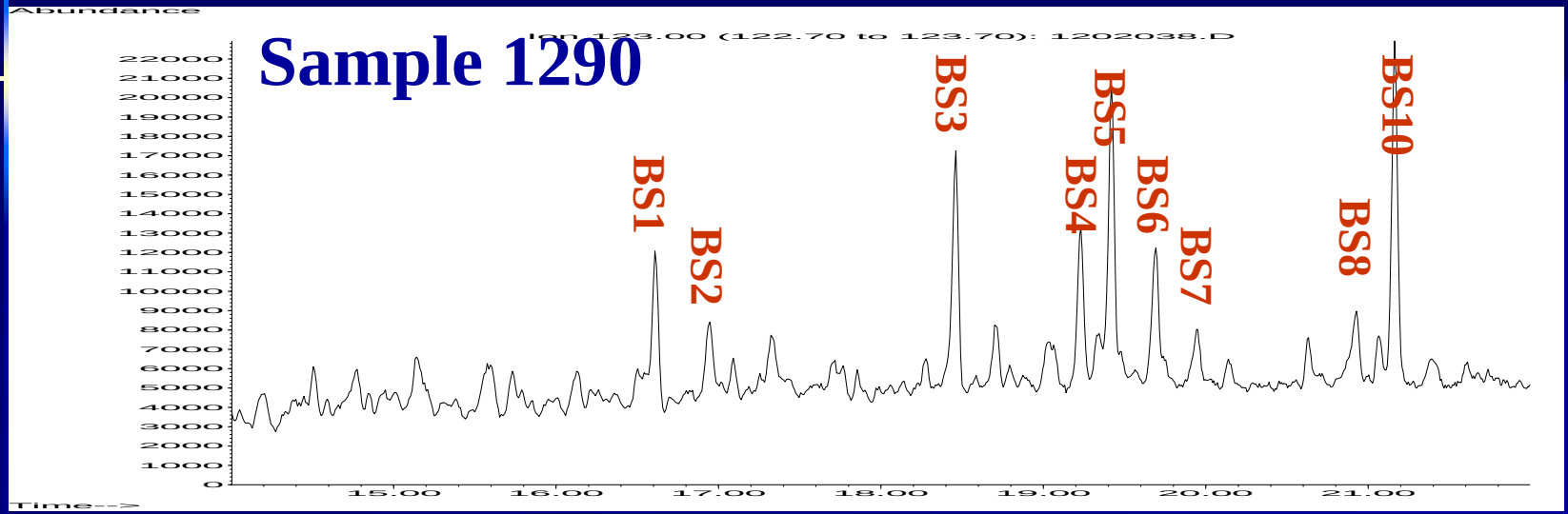
Answer

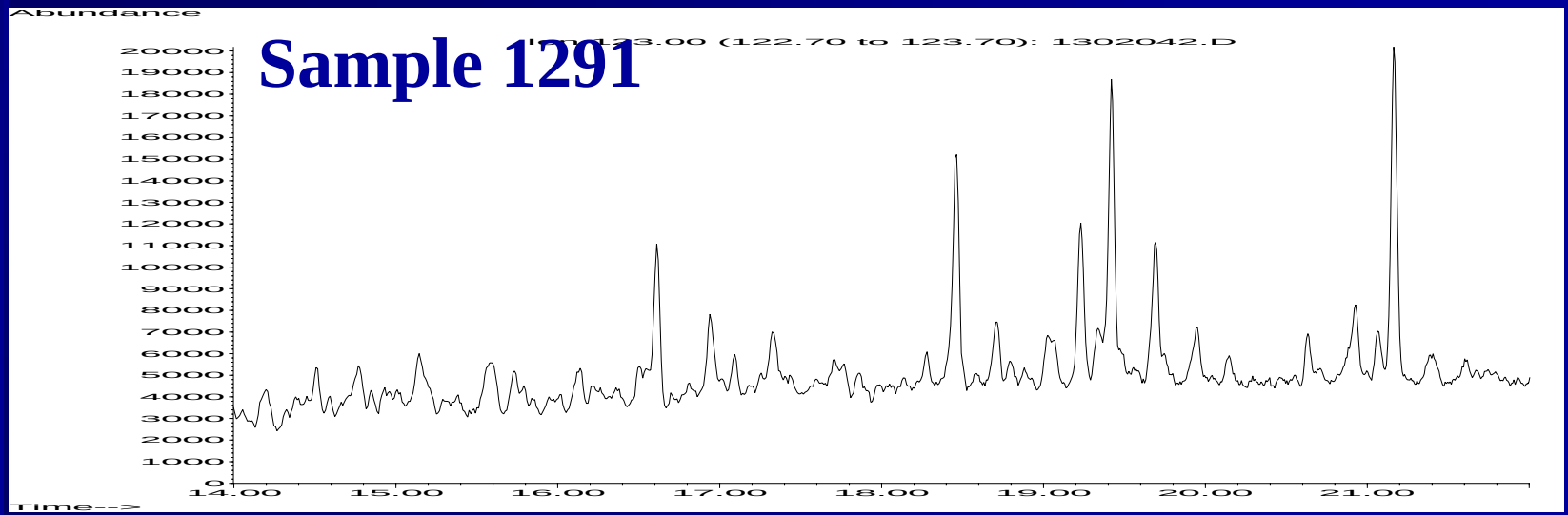
- The spilled oil is a mixture of a **Gasoline** and a **Diesel** *!!!*

Questions

- How much ***Gasoline*** **?**
- How much ***Diesel*** ?

Bicyclic Sesquiterpanes Analysis





Sesquiterpanes Analysis

Oil samples	Total (µg/g)
2008/04/22-1290 Oil	3,476
2008/04/22-1290 Water	3,973
2008/04/22-1291 Oil	4,022
2008/04/22-1291 Water	3,772
Mean	3811
Gasoline	ND
Kerosene	0.7
Diesel-Pioneer	7,628
Diesel-Shell	8,703
Diesel-Stinson	8,447
Diesel-Ottawa	6,028
Mean	7702

Answer

- The spilled oil is a mixture of a **Gasoline** and a Diesel
- Gasoline : Diesel = ~50:50 *!!!*

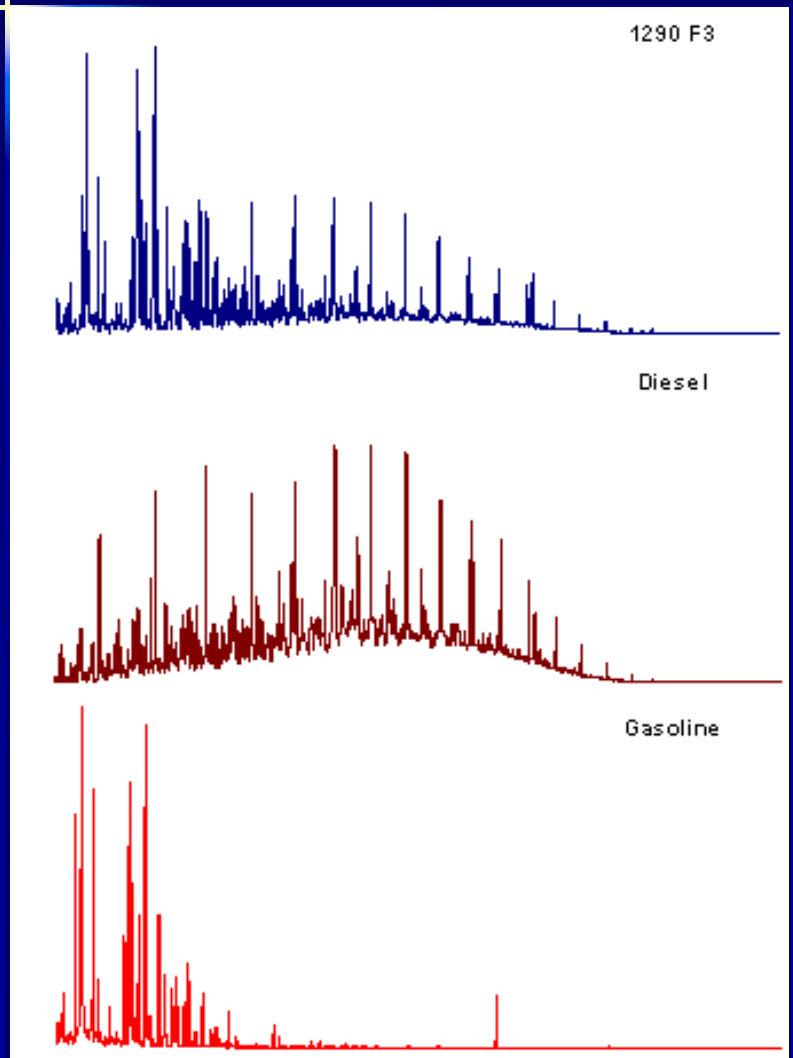
Simulation of Spilled Oils

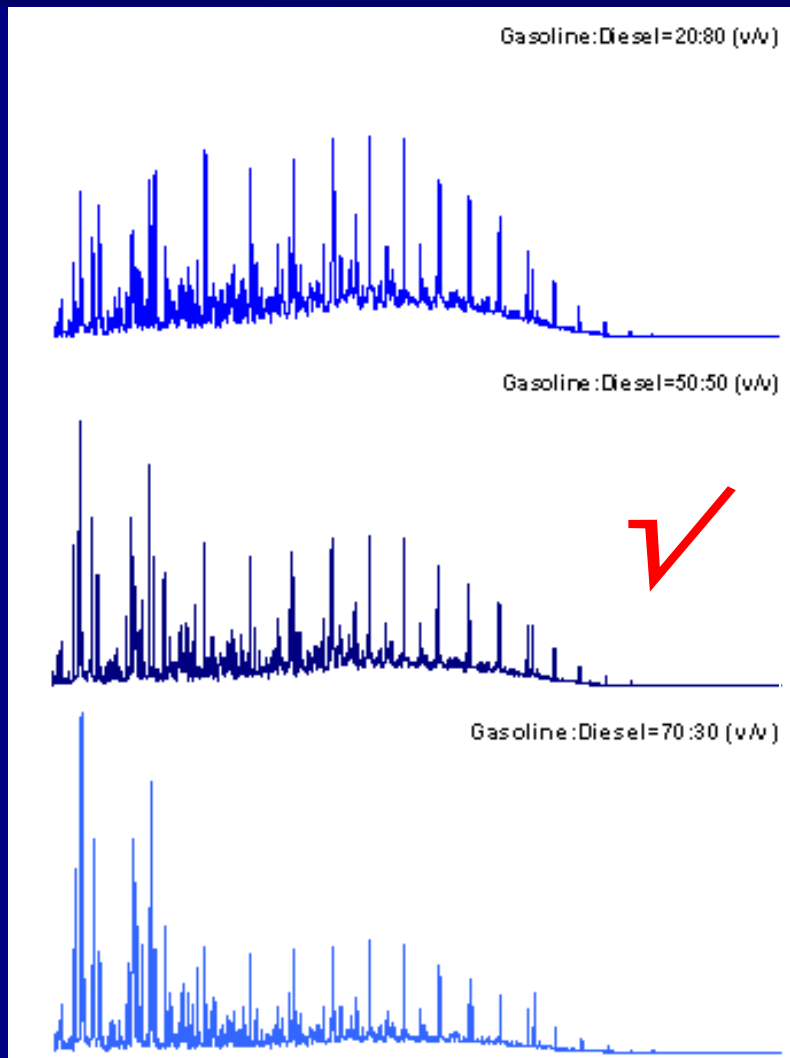
Gasoline: **from Petro Canada gas station, Ottawa**

Diesel: **from Shell gas station, Ottawa**

Gasoline : Diesel = 100:0, 90:10, …, 0:100 (v:v).

Simulation of Spilled Oils





Conclusions

- Bicyclic sesquiterpanes are widely present in crude oils and diesel range petroleum products with significant abundances.
- Sesquiterpanes offer potential criteria for both oil identification and oil-source correlation in cases where the traditional biomarkers are absent due to refining of petroleum product or environmental weathering.

Conclusions

- The oil samples are gasoline/diesel type fuel.
- The oil samples are probably mixtures of gasoline and diesel (No. 2) at an approximate ratio of 50:50 (v:v).

Thank You!