Interpretation of Bicyclic Sesquiterpane Petroleum Biomarker Results for Environmental Forensic Investigations

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How Can Bicyclic Sesquiterpanes Help To Investigate Degraded Fuel Oil Releases?

Presentation Outline

- Introduction to petroleum biomarkers and bicyclic sesquiterpanes
- Properties, degradation resistance and laboratory determination
- Uses for source determination
- Roles in forensic investigations
- Biodegradation and evaporation effects
- Case studies
- Conclusions

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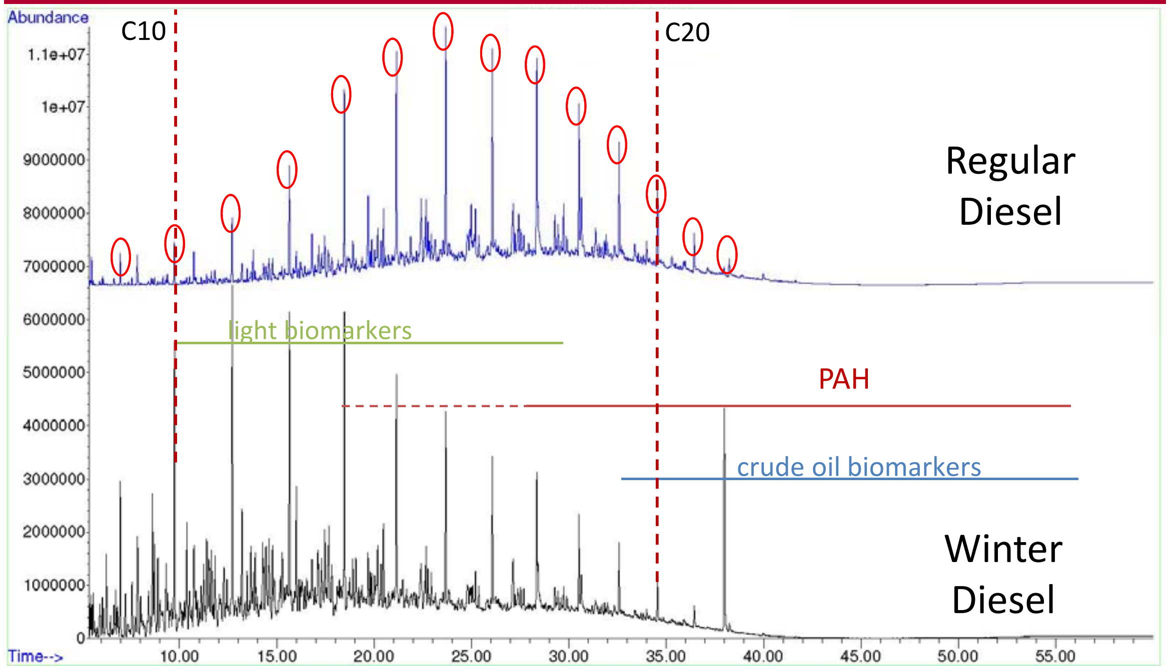
Petroleum Biomarkers

ALKANES
(e.g. C10 = decane)

Components of petroleum with a known link the biological material the deposit was derived from "Chemical Fossils". They are:

- More resistant to degradation than the alkanes that make up the bulk of petroleum.
- Used extensively in petroleum exploration.
- Used in forensic identification of <u>source</u> and <u>degree of weathering</u> for spills investigations since ~1980s.

Fresh Diesel Profiles



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Petroleum Biomarkers

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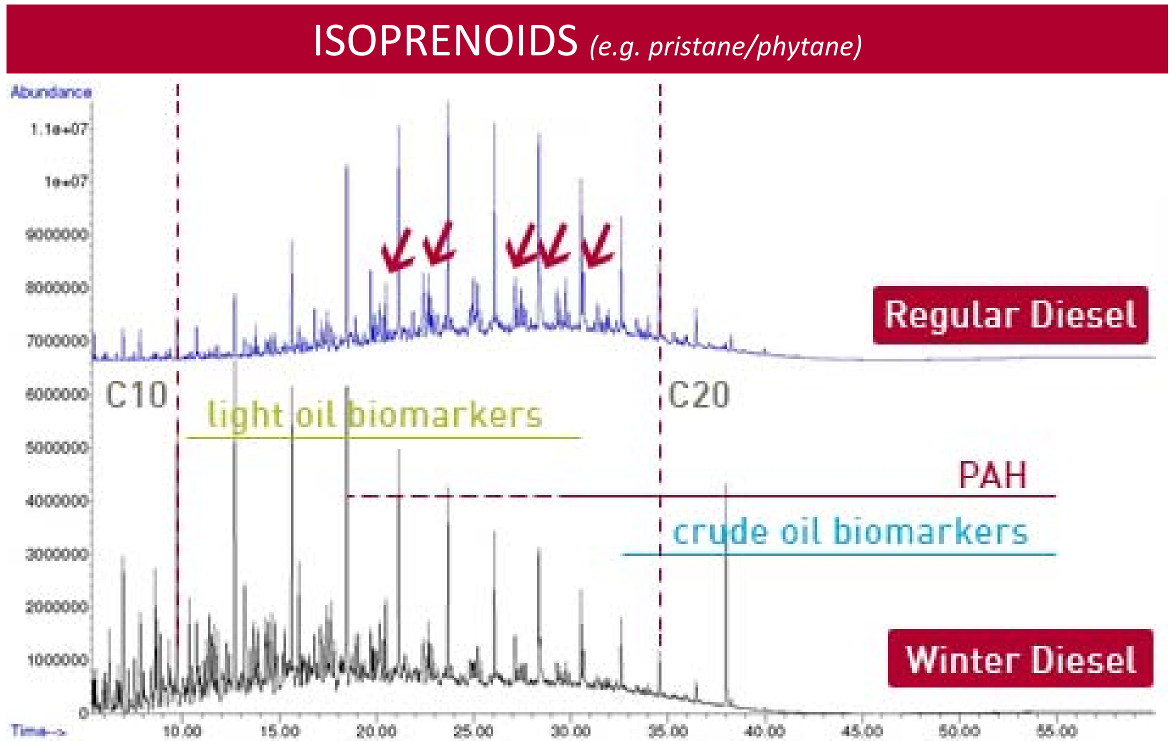

Petroleum Biomarkers

However, many biomarkers known in petroleum exploration are not present in the light distillates (e.g. diesel, heating oil) that are often spilled.

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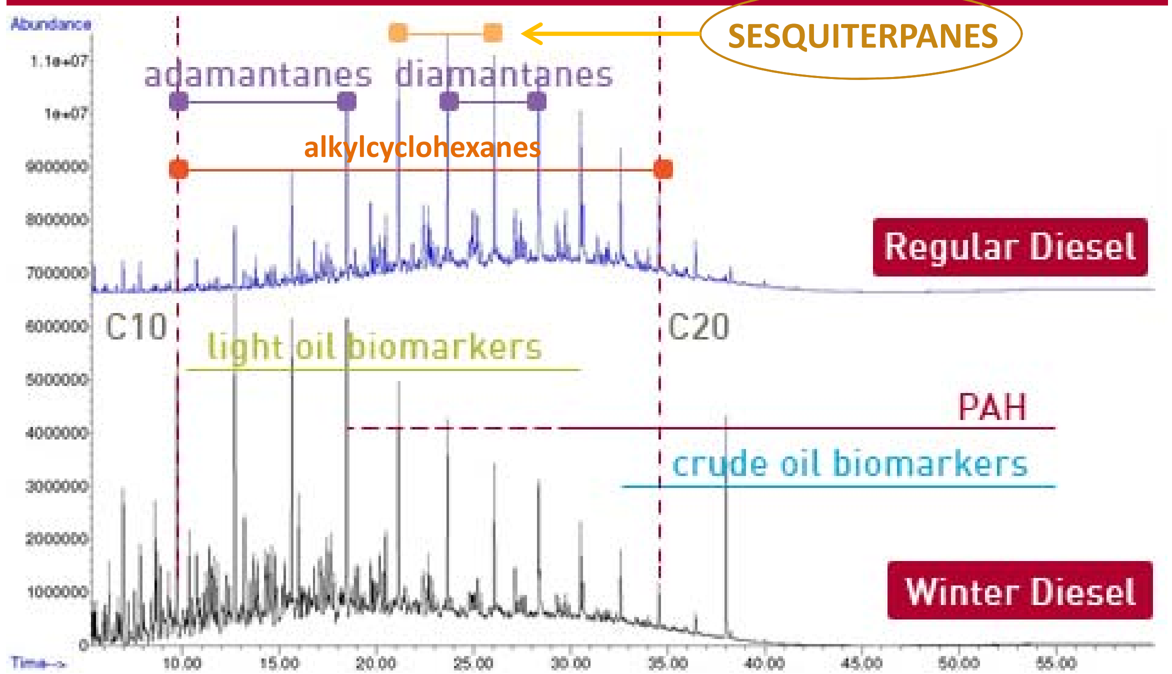
Petroleum Biomarkers

Components of petroleum with a known link the biological material the deposit was derived from "Chemical Fossils". They are:

- More resistant to degradation than the alkanes that make up the bulk of petroleum.
- Used extensively in petroleum exploration.
- Used in forensic identification of <u>source</u> and <u>degree of weathering</u> for spills investigations since ~1980s.

LIGHT BIOMARKERS CLASSES



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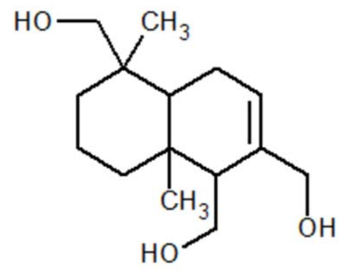
What are Bicyclic Sesquiterpanes?

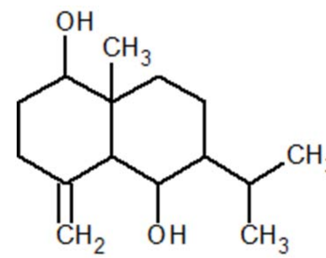
- Cyclic paraffins (naphthenes) with 14 - 16 carbons.
- Derived from microbial and plant terpenes.
- Present in all crude oils.
- Produced through thermal maturation in the petroleum reservoir through removal of oxygen and double bonds.

“Fossilization”

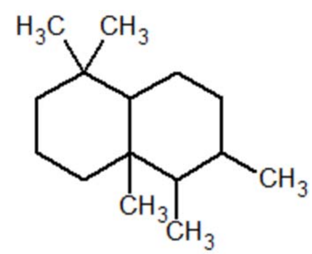
- Enriched during the distillation processes used to produce middle distillates: e.g. diesel, heating oil, kerosene.
- Immature crudes have high C14 sesquiterpanes.
- Mature crudes have high C15-C16 sesquiterpanes.



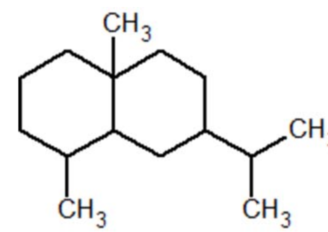
Drimene
Produced by bacteria and fungus



Eudesmene
Produced by terrestrial plants



Drimane
Found in all petroleum deposits



Eudesmane
Found in only the youngest petroleum deposits

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Properties and relative degradation resistance

- Typically the highest concentration light biomarker in diesels:
  - o Diamantanes: 0.1 mg/g
  - o Adamantanes: 1 mg/g
  - o Sesquiterpanes: 10 mg/g
- Resistant to losses by volatility or water dissolution
- Biodegradation Resistance: C16>C15>C14
- More resistant to biodegradation than isoprenoids and naphthalenes*
- In terms of the Kaplan Stages: ~6.5

*Malmborg, J. Envir. Foren., 2017, 18, 197-206.

Helpful for both source determination and weathering assessment when the typical light biomarkers have disappeared.

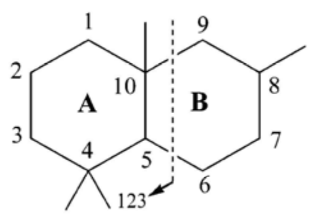
Properties and relative degradation resistance

KAPLAN DEGRADATION STAGES - Source: Kaplan et al., 1997.	
Stage	**Description**
1	Abundant *n*-alkanes, red dye still present
2	Light-end *n*-alkanes removed
3	Middle-range *n*-alkanes, benzene, toluene removed
4	More than 90% of *n*-alkanes removed
5	Alkylcyclohexanes & alkylbenzenes removed
6	Isoprenoids, C_1-naphthalenes, benzothiophene, alkylbenzothiophenes removed, C_2-naphthalenes selectively reduced
6.5	**Bicyclic sesquiterpanes**
7	Phenanthrenes, dibenzothiophenes, other PAH reduced

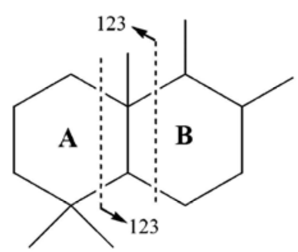
Oudijk, G. Envir. Foren., 2009, 10, 120-131.

Laboratory Determination

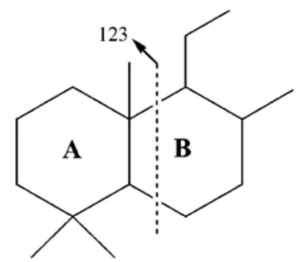
- Monitored by GC/MS using fragment ion m/z 123, which is common to all bicyclic sesquiterpanes.
    - o SIM Mode is preferred.
- Confirmation ions must also be monitored as well
    - o Other petroleum components also have m/z 123 ions.



C_{14}: C_4-decalin (peak 1)



C_{15}: 8β(H)-drimane (peak 5)



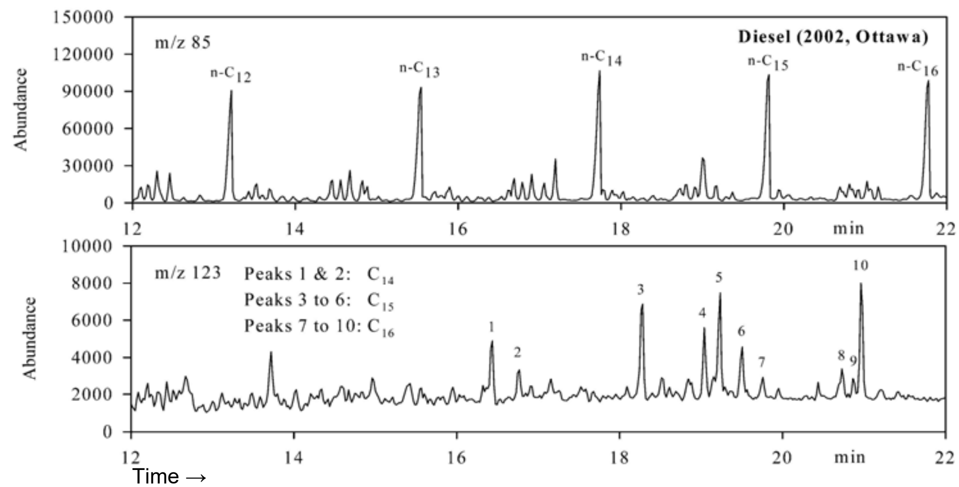
C_{16}: 8β(H)-homodrimane (peak 10)

Laboratory Determination

Solvent Extract:
- Product/water – hexane
- Soil – acetone/hexane

Column Fractionation:
- Aliphatics
- Aromatics

Aliphatic extract
analysed by GC/MS



Bicyclic Sesquiterpane Range

Wang, Z. et al. Environ. Sci. Technol. 2005, 39, 8700-8707.

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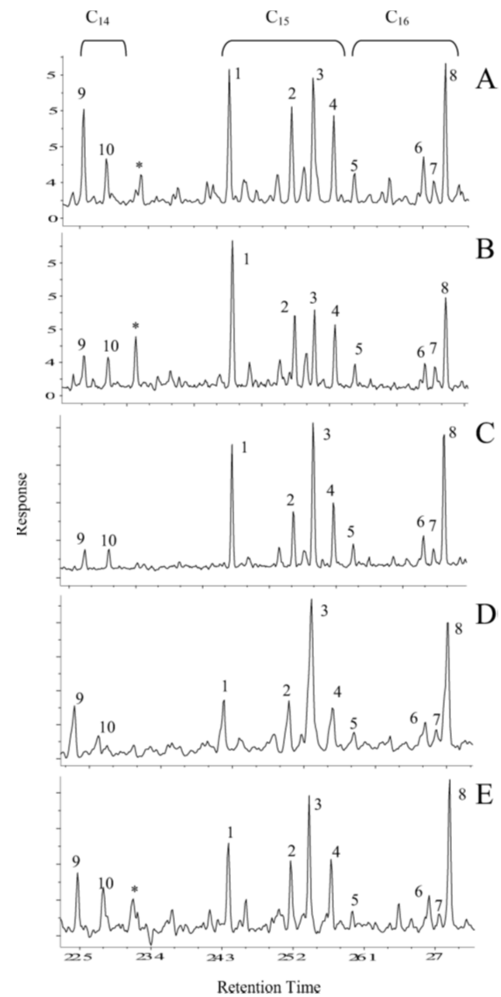
Use in source determination

Overview:

- Originally (and still) used in oil exploration.
- Chromatograms at the right are from five fresh diesels, showing typical variability the differences in biomarker patterns from different sources.
- Stout ratios were selected for comparing <u>fresh</u> diesels from different sources.



STOUT RATIOS
8/(3+8)
1/(1+3)
8/sum(5 to 8)
(2+4)/(2+4+8)
9/(9+10)
3/(3+9)

Stout, S.A. et al. Environ. Foren. 2005, 6, 241-251.

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Roles in forensic investigations

Overview:

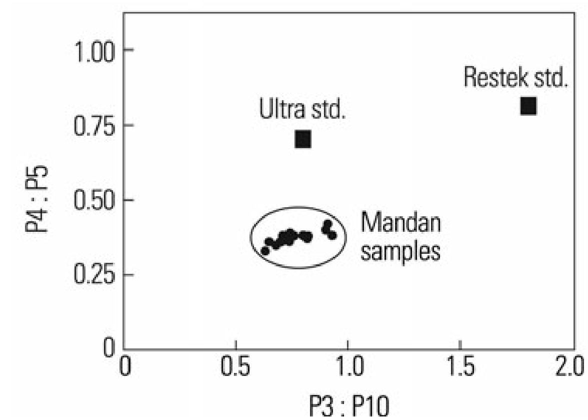
- First used in forensic oil spill investigations ~2005

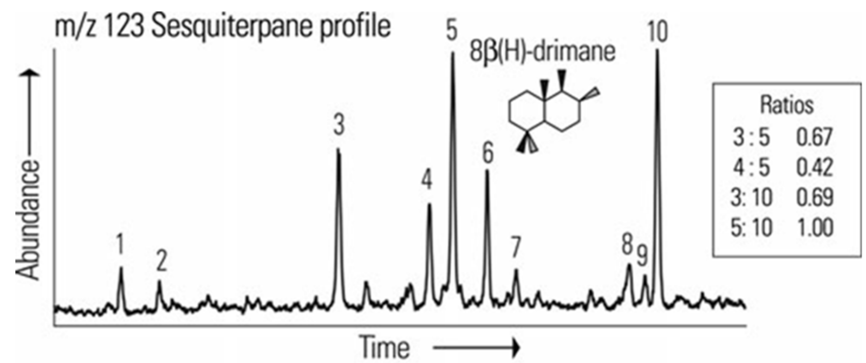
Source Determination:

- Recognized as ‘highly diagnostic’ for middle distillates (Wang et al. 2005)
- Ten bicyclic sesquiterpanes commonly used for oil source determinations: BS-1 – BS-10.
- Numerous ratios are used for comparisons.

Weathering and Source Determination:

- The same markers (BS-1 – BS-10) used.
- More care needed in ratio selection.





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Hostettler, F.D. et al. Envir. Forensics 2013, 14, 262-277.

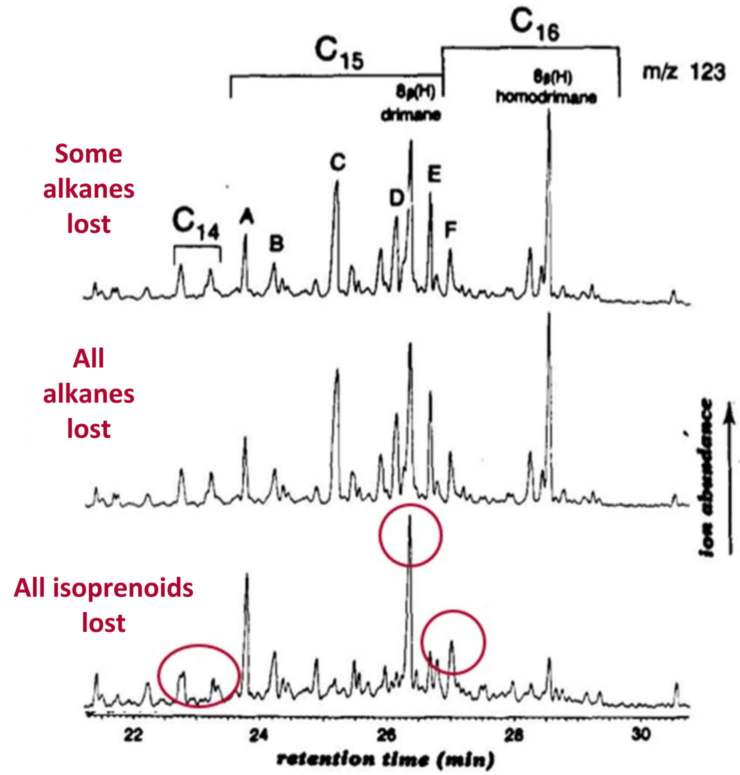
Bicyclic Sesquiterpane Biodegradation Patterns

Observations:

- No change in signature when all alkanes have degraded.
- Some peaks are conserved even when all isoprenoids have been lost.

Conclusions:

- Bicyclic Sesquiterpanes can be used for source similarity determinations when:
  - Significant alkane loss.
  - Isoprenoid biodegradation is minimal.



Williams, J.A. et al. Adv. Org. Geochem. 1986, 10, 451-461.

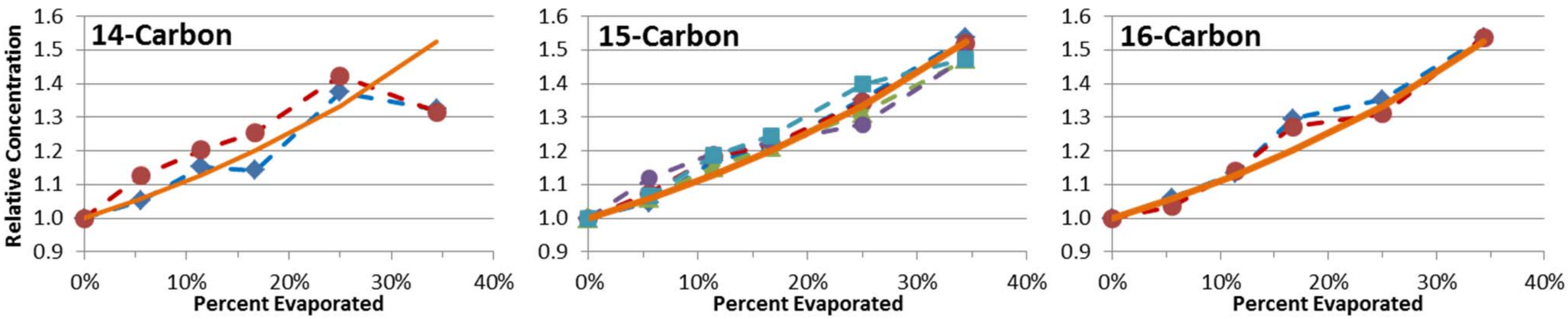
Bicyclic Sesquiterpane Evaporation

- Different crude oils evaporated between 5% and 35%.
- Concentrations of bicyclic sesquiterpanes measured in the evaporated samples.
- Relative concentrations plotted vs. percent oil evaporation.
- Orange line shows theoretical relative concentration for non-volatile components.

Findings:

14-carbon bicyclic sesquiterpanes are lost at > 25% evaporation.

15- and 16-carbon bicyclic sesquiterpanes are retained at up to at least 35% evaporation.



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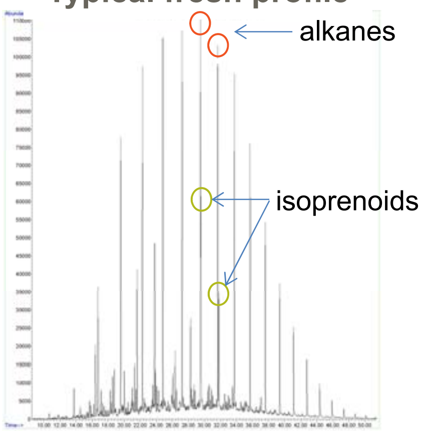
Wang, Z. et al. Environ. Sci. Technol. 2005, 39, 8700-8707.

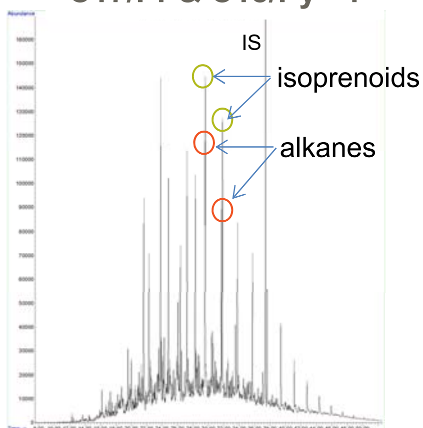
Typical Aliphatic Chromatograms:

Typical fresh profile



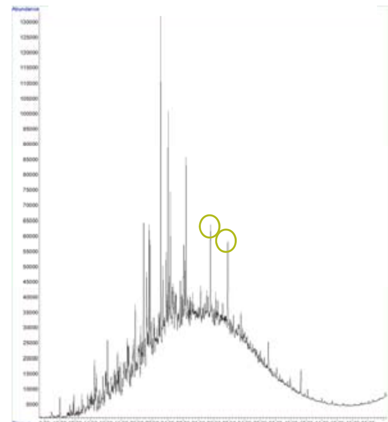
unweathered

C17/Pr & C18/Py <1



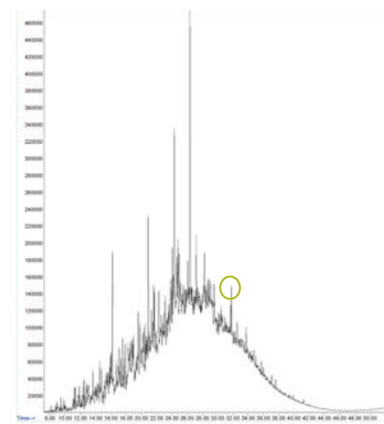
weathered

Alkanes lost

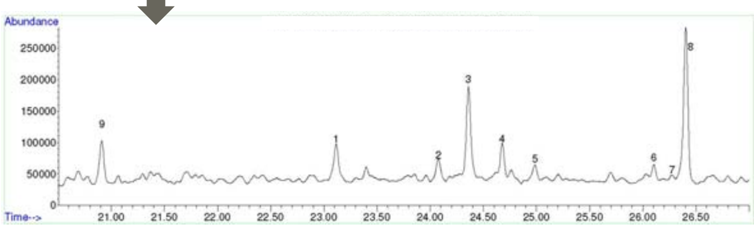


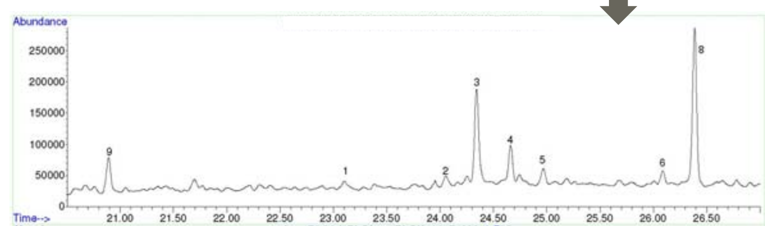
very weathered

Significant isoprenoid loss



extensively weathered





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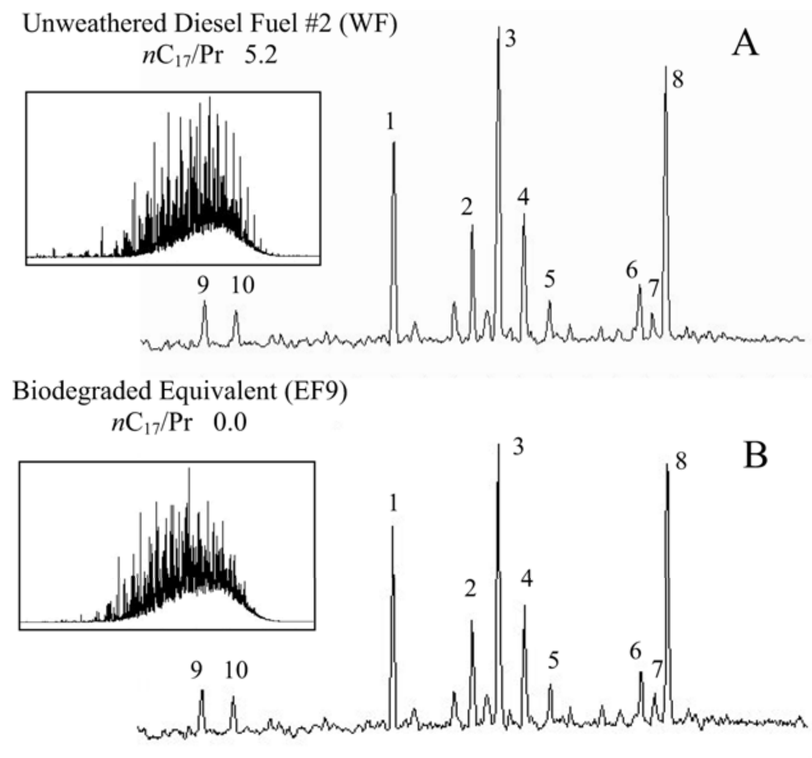
Case Study #1

Sample A: Suspected source sample
Sample B: Impacted railway soil

Sample A relatively fresh:	C17/Pr = 5.2
Sample B biodegraded:	C17/Pr = 0

Bicyclic sesquiterpane profiles are nearly identical.

Conclusion: Likely to be the same source.



Stout, S.A. et al. Environ. Foren. 2005, 6, 241-251.

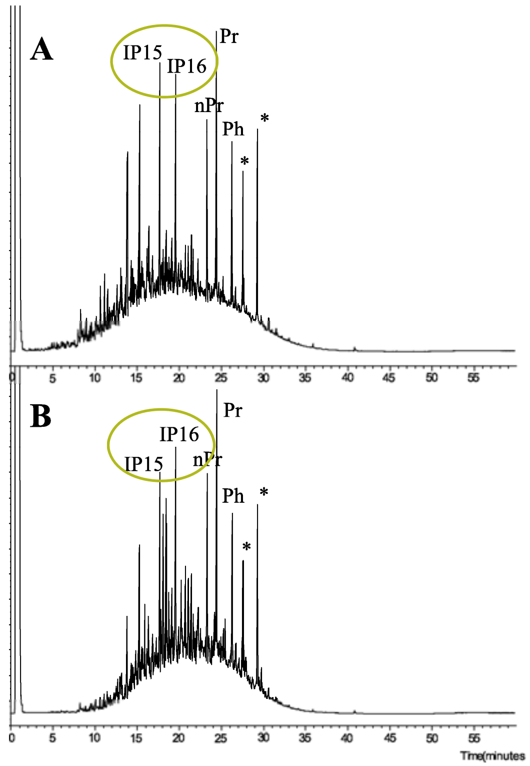
Case Study #2

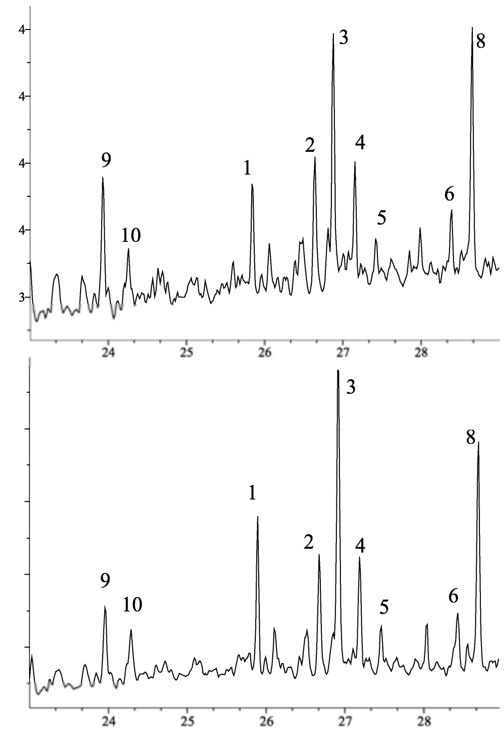
Two similarly degraded soils:

- Alkanes gone.
- Differences in light isoprenoids may be related to degradation.
- Pr/Py ratios similar.
- PAH data suggested different sources.
- Bicyclic Sesquiterpane data also suggest different sources.
- Site histories supported different sources

RATIOS	PROPERTY A	PROPERTY B	RPD
8/(3+8)	0.49	0.43	13%
8/sum(5 to 8)	0.63	0.66	5%
(2+4)/(2+4+8)	0.50	0.43	15%
9/(9+10)	0.68	0.60	14%

n=3





Evaluation only valid due to similar degradation patterns.

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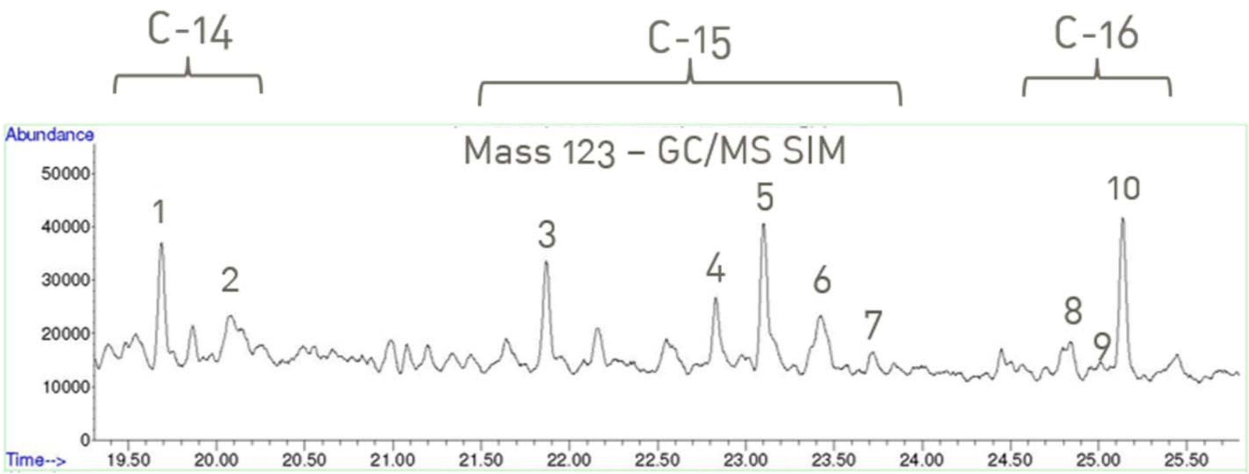
Stout, S.A. et al. Environ. Foren. 2005, 6, 241-251.

Source Determination With Variable Evaporation

Most groups have now switched to using a set of ratios that better control for evaporative losses.



C14 Ratios
1/2
C15 Ratios
3/5*
4/5*
4/6
6/5*
C16 Ratio
8/10
Intergroup Ratios
1/3
1/5
3/10
5/10*

* These four are also recommended by CEN

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Stout, S.A. et al. 2016, Standard Handbook, Oil Spill Environmental Forensics, Chapter 11.

Case Study #3

Overview:

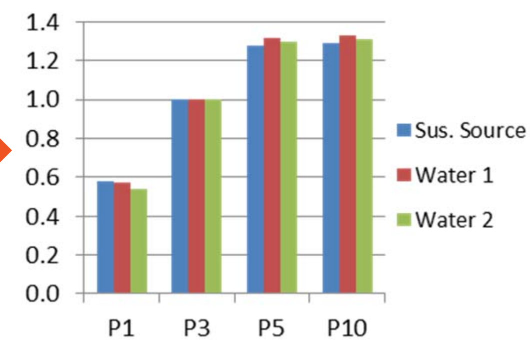
- Two water samples with diesel impacts collected at a sewer outfall.
- A diesel tank close to the outfall was the suspected source.
- Diesel in water samples was lightly weathered.
- Alkylated PAH profiles and ratios were similar among the three sources.
- Bicyclic Sesquiterpanes assessed as an additional line of evidence.

Note:

- Bicyclic sesquiterpanes have very low water solubility
- No evidence of water washing losses.

TABLE 2. Diagnostic Sesquiterpane Ratios of Two Representative 1998 Spill Diesels and One Suspected-Source Diesel

	diagnostic indices	spill sample I	spill sample II	suspected source
C15 ratio >	P5:P3	1.30	1.32	1.28
Intergroup>	P10:P3	1.31	1.33	1.29
C16 ratio >	P8:P10	0.28	0.28	0.29
C14 ratio >	P2:P1	0.48	0.47	0.50
	P1:P3:P5:P10	0.54:1.00:1.30:1.31	0.57:1.00:1.32:1.33	0.58:1.00:1.28:1.29



Spill sample results are all within 14% of the suspected source.

- CEN recommendation as criterion for determining similarity.

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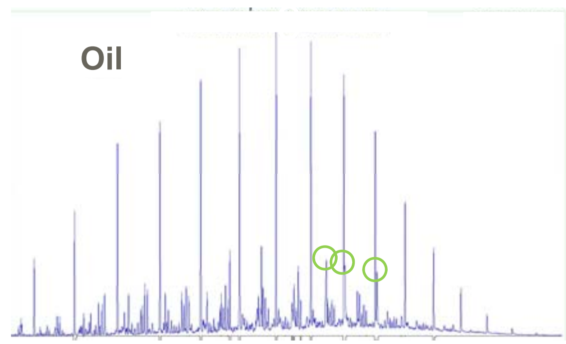
Wang, Z. et al. Environ. Sci. Technol. 2005, 39, 8700-8707.

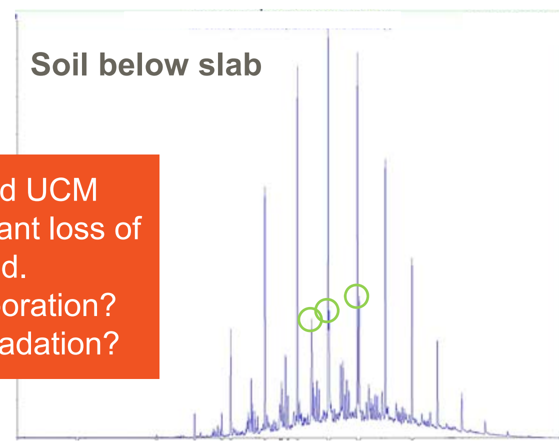
Case Study #4

- Fuel oil release in a residential basement (AST).
- Impacted soil found 6” below concrete slab.
- Fuel oil had been used for several decades.

Question: Are the soil impacts related to the current release or historic?

- Pr/Py ratios identical between oil and soil.
- C17/Pr and C18/Py different between oil and soil.





Elevated UCM
Significant loss of front end.
- Evaporation?
- Degradation?

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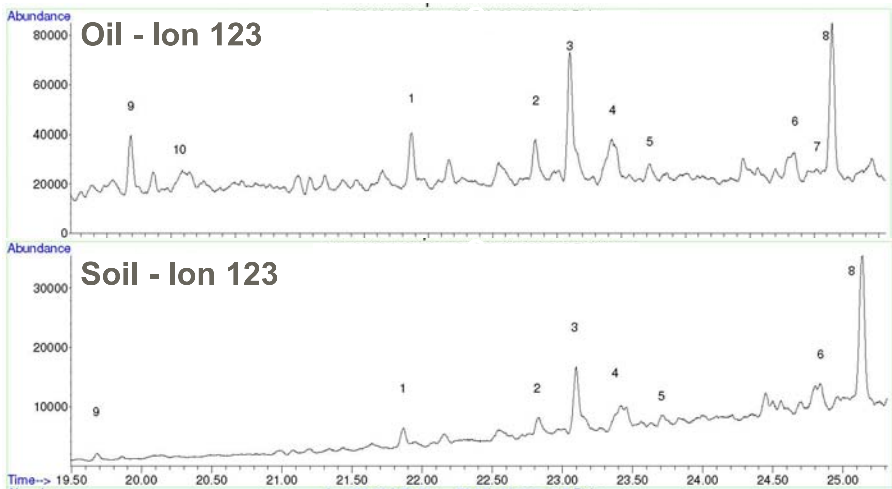
Case Study #4 Bicyclic Sesquiterpanes



ORIGINAL RATIOS	OIL	SOIL
8/(3+8)	0.50	0.65
1/(1+3)	0.25	0.17
8/sum(5 to 8)	0.80	0.84
(2+4)/(2+4+8)	0.46	0.28
9/(9+10)	0.65	n/c
3/(3+9)	0.72	0.92

NEW RATIOS	OIL	SOIL
C14 Ratios		
1/2	1.84	n/c
C15 Ratios		
3/5*	0.34	0.21
4/5*	0.29	0.22
4/6	0.52	0.45
6/5*	0.56	0.50
C16 Ratio		
8/10	0.11	0.10
Intergroup Ratios		
1/3	1.14	0.42
1/5	0.39	0.09
3/10	0.34	0.11
5/10*	0.99	0.54

Conclusion:

Even when accounting for evaporation, data suggest soil impact is from a different source.

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Case Study #5

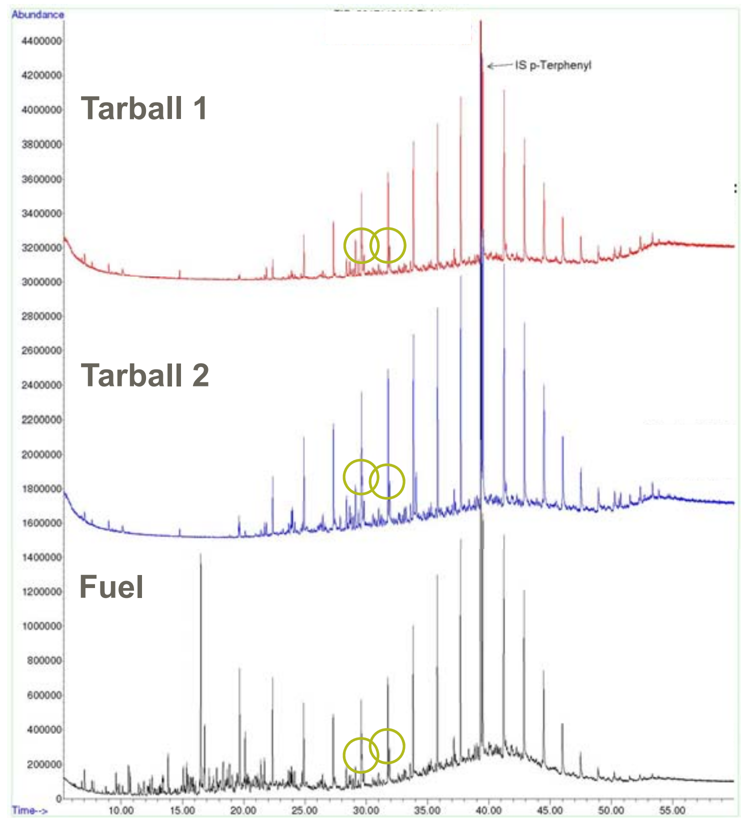
- Fuel cargo ship carrying fuel oil sank outside a harbour.
- Vessel in the harbour was undergoing repairs for a breached fuel tank.
- Tar balls appeared on nearby shorelines the next day.
- Both vessels likely using the same crude oil source.
- Tarball profile suggests evaporation of light alkanes.

Question:

Did the tar balls come from the vessel under repair?

Phenanthrenes data suggest same source.

ISOPRENOID DATA INCONCLUSIVE			
Sample	**C17/Pr**	**C18/Py**	**Pr/Py**
Oil	3.7	2.5	0.57
Tarball 1	3.7	3.1	0.72
Tarball 2	3.7	3.2	0.78



Case Study #5 Bicyclic Sesquiterpanes

Bicyclic Sesquiterpanes distribution is expected to be dependent on the refining process:

- A route to distinguish oils from the same crude source.

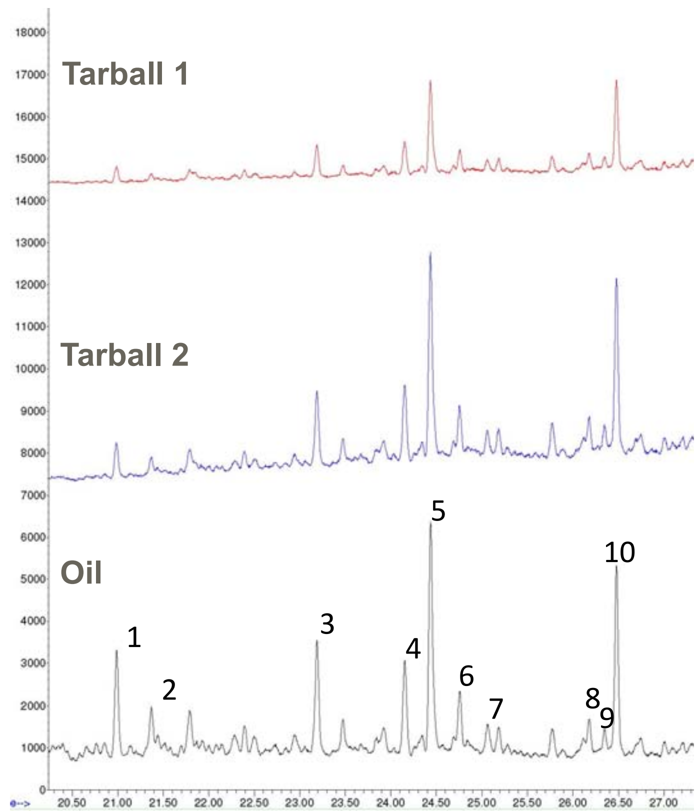
Extractable petroleum hydrocarbon results suggest >30% evaporation.

	Oil	Tarball1	Tarball 2
C15 Ratios			
3/5	0.51	0.34	0.37
4/5	0.41	0.37	0.38
4/6	1.92	1.73	1.87
6/5	0.21	0.21	0.20
C16 Ratio			
8/10	0.16	0.15	0.16
Intergroup Ratios			
3/10	0.68	0.37	0.44
5/10	1.32	1.07	1.19

Conclusion:

Forensic data could not conclusively link the tarballs with the ship in drydock.

Site information suggested the tarballs came from the sunken oil tanker.



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Conclusions

- **Bicyclic Sesquiterpanes can be used for source identification when other aliphatics have experienced significant weathering.**
  - More resistant to weathering than other aliphatic biomarkers.
  - Do not degrade until isoprenoid loss is very advanced.
  - No evidence of significant loss with water washing.
  - In cases of significant oil evaporation (> 35%) C-14 bicyclic sesquiterpanes are less reliable.

- Used since the 1980s for petroleum exploration and source determination.
- Ratios typically used for exploration should be used with caution in cases of evaporation.
- Newer ratios recommended in North America and Europe are seen to be superior for evaporated samples.

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THANK YOU

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