Forensic Evaluation in Heavily Degraded Crude and Middle Distillate Releases

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How Can Forensics Evaluations be performed on Heavily Degraded Oils?

Outline

- Introduction to petroleum biomarkers and oil degradation
- Properties, degradation resistance and laboratory determination
- Biomarkers for degraded petroleum releases
  - Source determination vs. weathering
- Case studies

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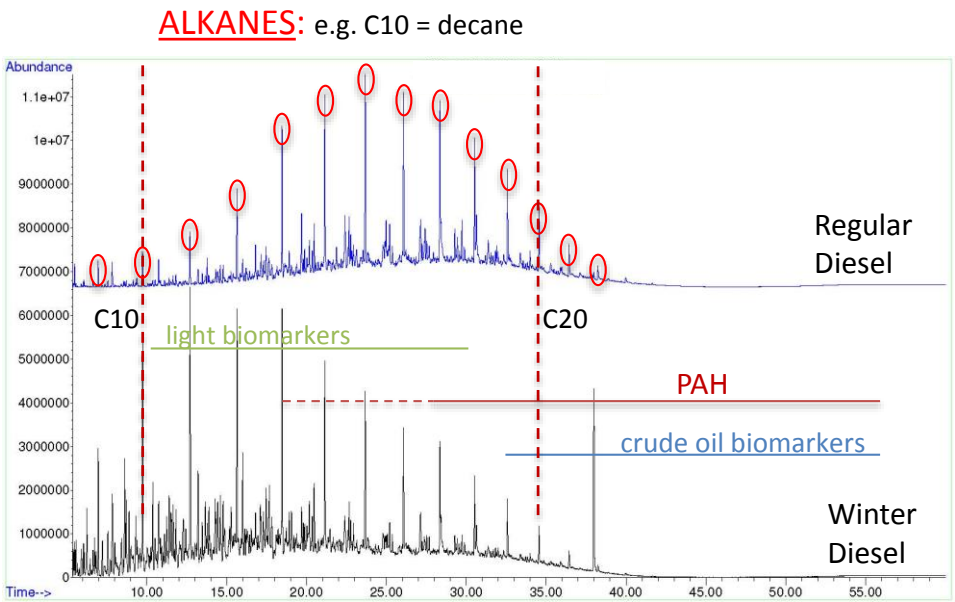
Petroleum Biomarkers

Components of petroleum with a known link the biological material the deposit was derived from

- More resistant to degradation than the paraffins (alkanes).
- Used extensively in petroleum exploration.
- Used in forensic identification of source and degree of weathering for spills investigations since ~1980s.



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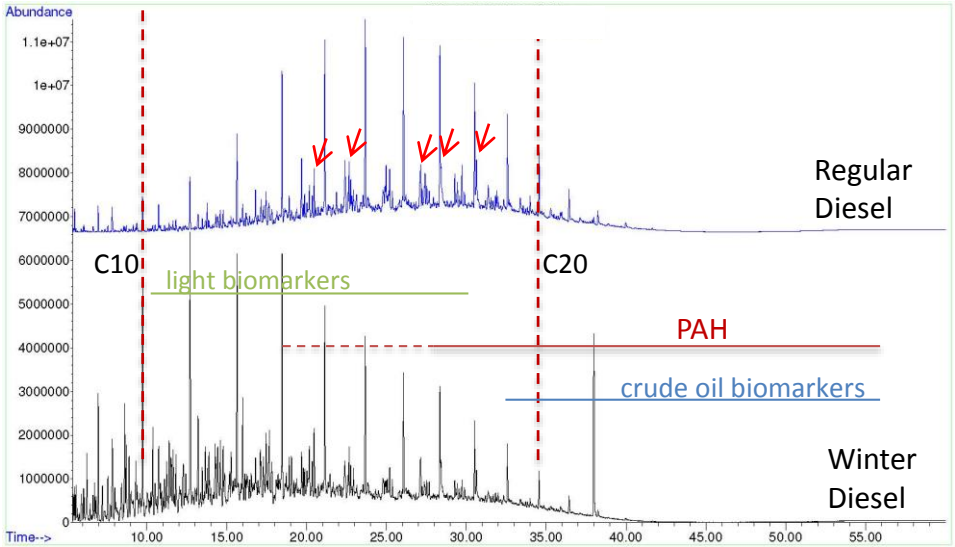
ISOPRENOIDS: e.g. pristane/phytane



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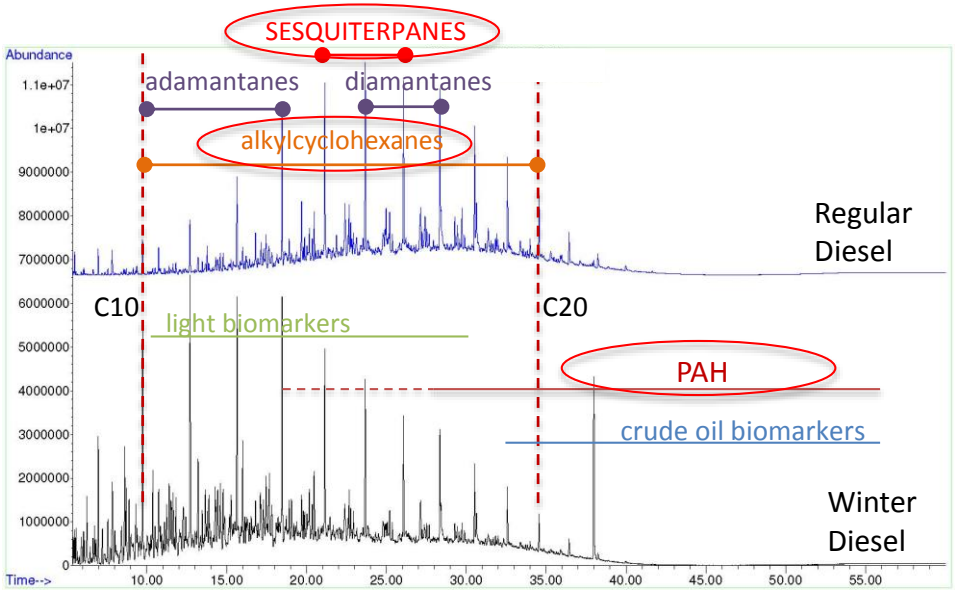

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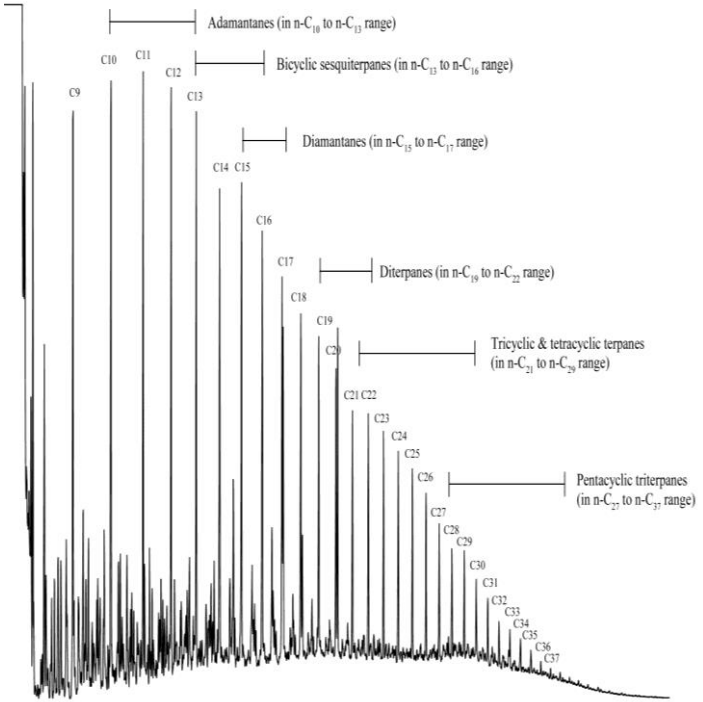
Laboratory Determination

- Monitored by GC/MS using fragment ion specific to the biomarker class.
  - SIM Mode is preferred.
- Confirmation ions must also be monitored as well
  - Other petroleum components often have the same target ion.

Solvent Extract:
product/water – hexane
soil: - acetone/hexane

Column Fractionation:
- Aliphatics
- Aromatics

Both extracts analysed by GC/MS



Wang, Z. et al. Environ. Foren. 2006, 7, 105-146.

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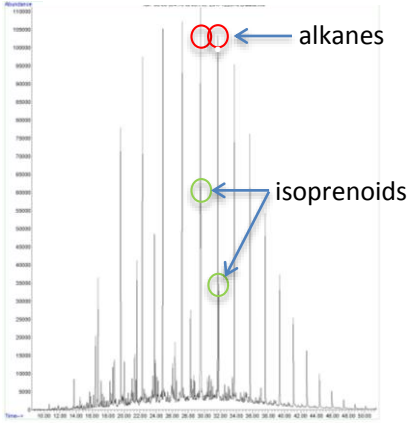
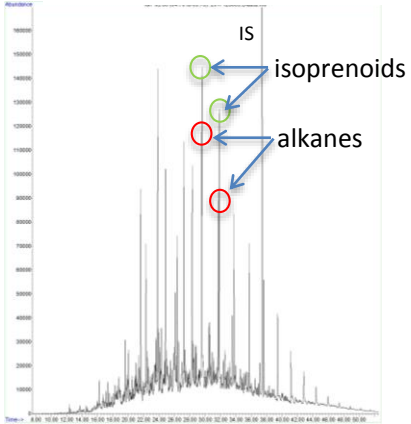
Typical Weathering Patterns

Typical fresh profile



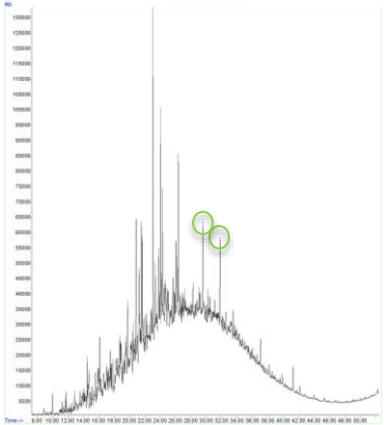
unweathered

C17/Pr & C18/Py <1



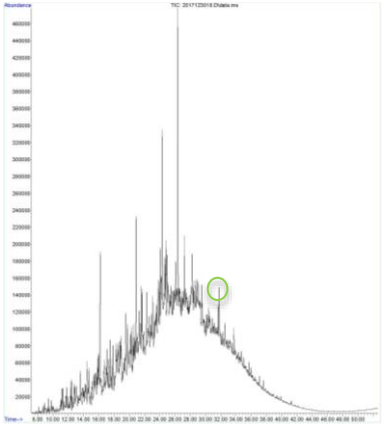
weathered

Alkanes lost



very weathered

Significant isoprenoid loss



extensively weathered

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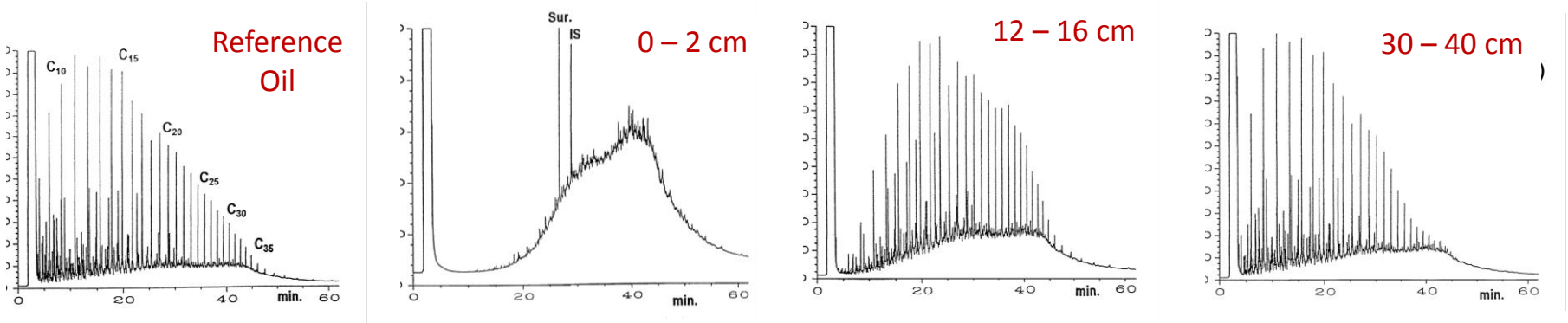
Crude Oil Weathering



25 year old oil spill.

- Oil 30-40 cm deep looks fresh: very similar to reference spilled oil.
- Oil at the surface (0-2 cm) looks either highly weathered or like fresh mature (heavy) oil

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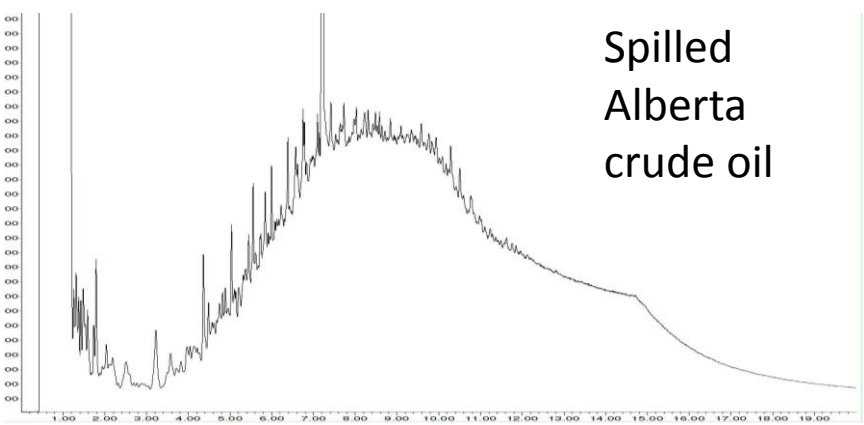
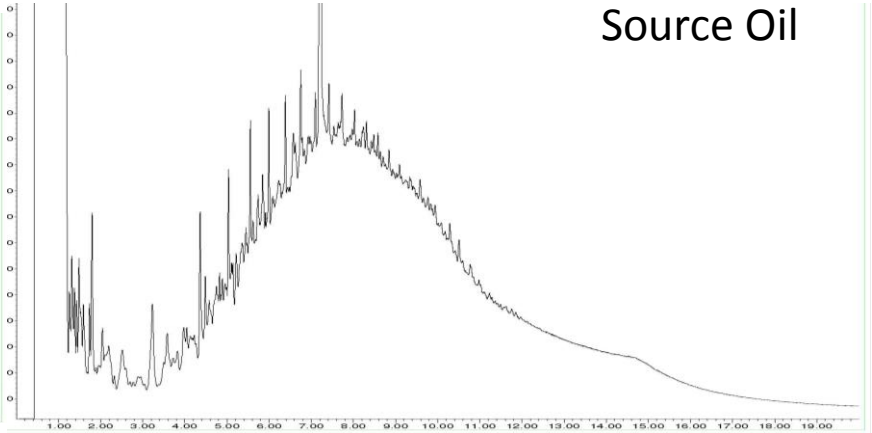
Crude Oil Profiles





- This was a heavy oil spill.
- If you hadn't seen the source oil profile, you would have thought the spilled oil was highly degraded!!
- In reality, it has only lost a bit of the light front end, consistent with a few days of sun/heat or water exposure.

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Biomarkers for Mature / Weathered Petroleum

Source and Weathering Determinations:

- Bicyclic Sesquiterpanes
- Alyklcyclohexanes
- Polycyclic Aromatic Hydrocarbons

Source Determinations:

- Diamondoids
- Terpanes
- Hopanes
- Steranes
- Monoaromatic Steranes
- Triaromatic Steranes

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Relative degradation resistance

- The ‘Kaplan stages of biodegradation’ published in 1997, are still well recognized 20 yrs later.
- Stages define the order of degradation
  - Late stage biomarkers are most resistant to degradation.
- Originally proposed for heating oil / diesel
  - Applicable to all petroleum crudes and products.

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 and alkylbenzothiophenes removed, C_2-naphthalenes selectively reduced
6.5.	**Bicyclic Sesquiterpanes**
7.	**Phenanthrenes, Dibenzothiophenes and other PAHs reduced**

Helpful for both source determination and weathering assessment once mid-range alkanes are degraded.

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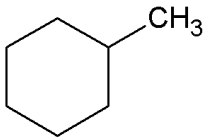
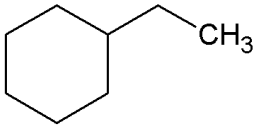
N-Alkylcyclohexanes (ACH)

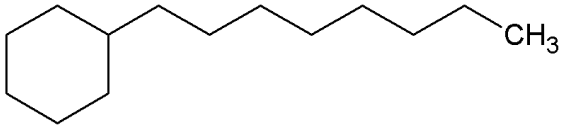
CH-1



CH-2



CH-8



- Six-carbon cyclic hydrocarbons with different numbers of alkyl side chains.
- Present in both crude oils and refined petroleum products.
- Distribution profiles in refined products is related to the refining processes.
  - i.e. before ACH degradation begins, distribution indicates the original product.
- After ACH degradation begins, peak distribution speaks to relative aggressiveness and type of weathering in the sample.

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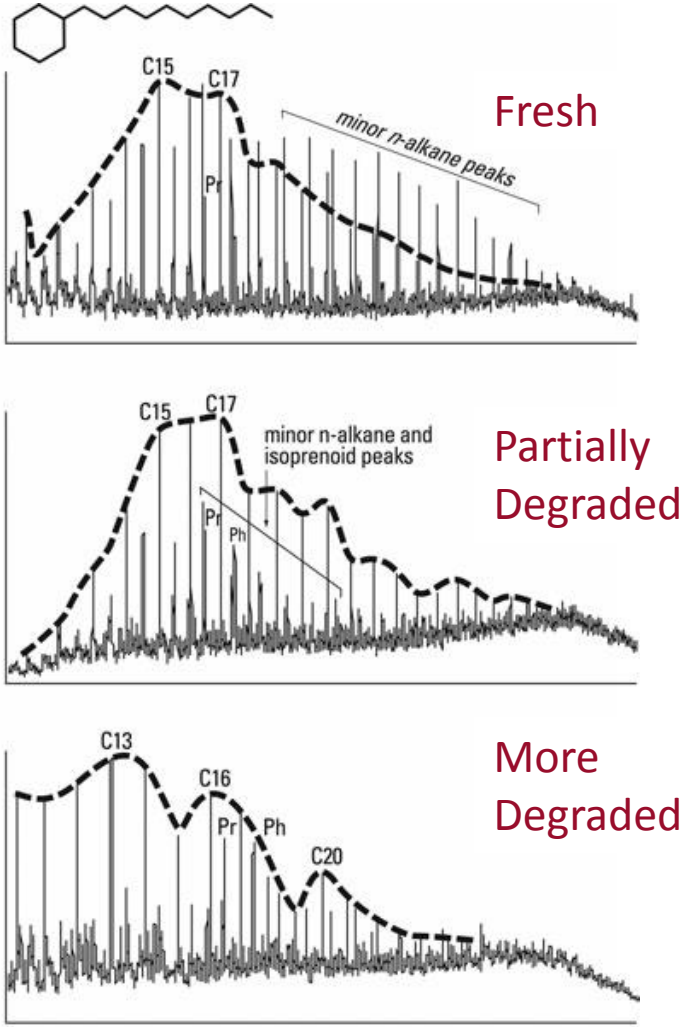
Alkylcyclohexanes

- In <u>anaerobic</u> environments, the longer-chain ACHs are lost first
  - shorter-chain ACHs appear to increase.
- In <u>aerobic</u> environments, shorter-chain ACHs are lost first.
- If the release is significantly weathered the ACH distribution from a crude may look like that of diesel.



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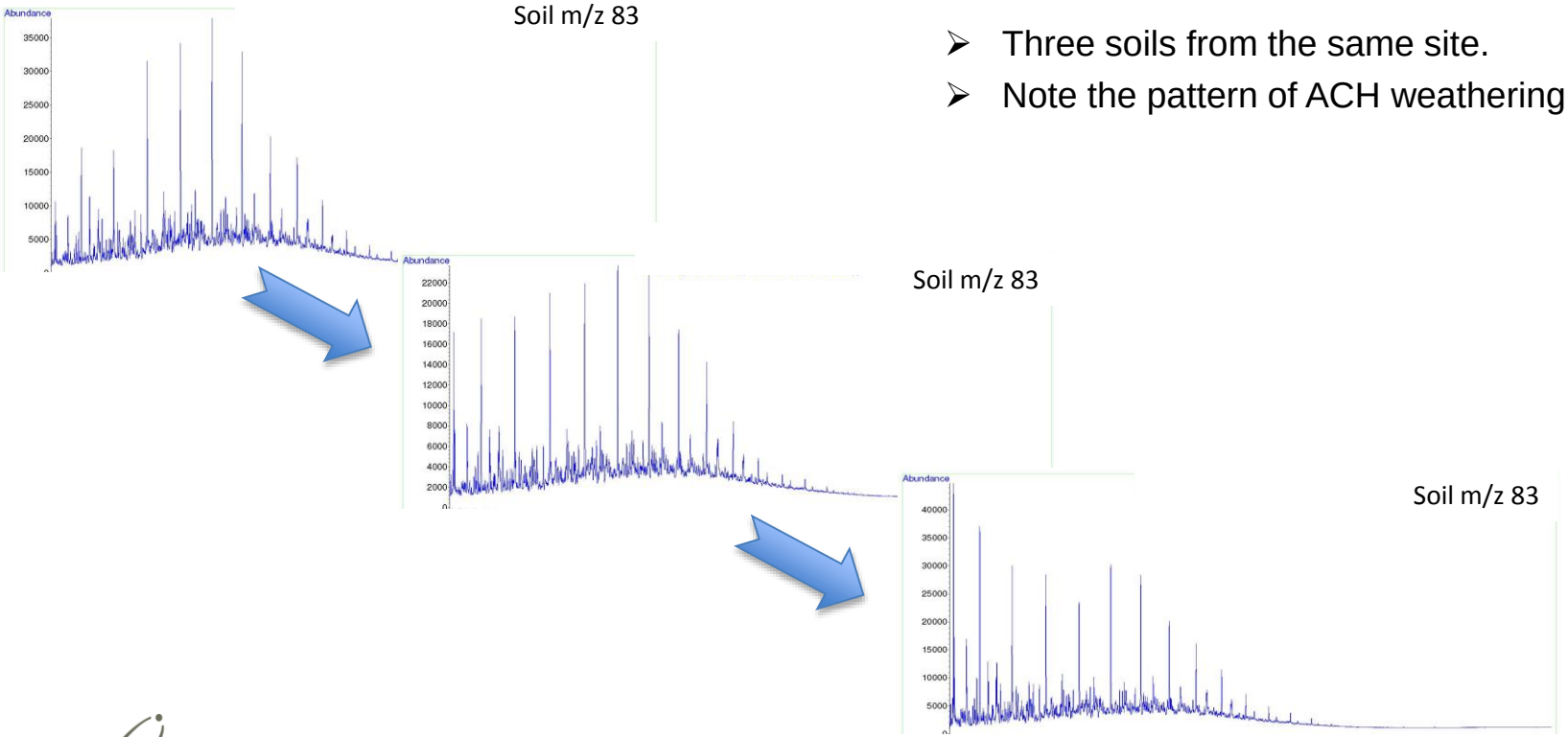
Hostettler, FD. et al. Environ. Foren. 2013, 14, 262-277.

ACH Weathering



- Three soils from the same site.
- Note the pattern of ACH weathering.

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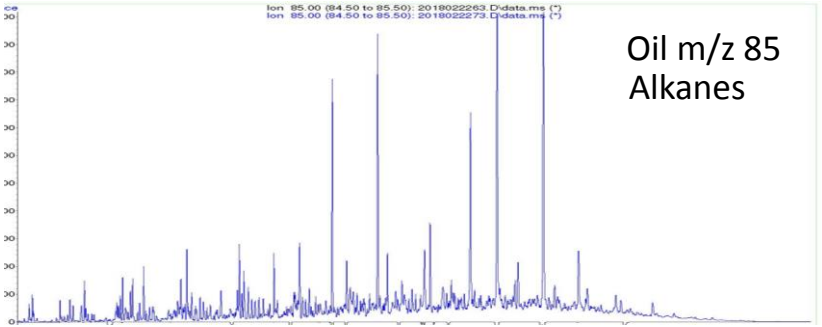
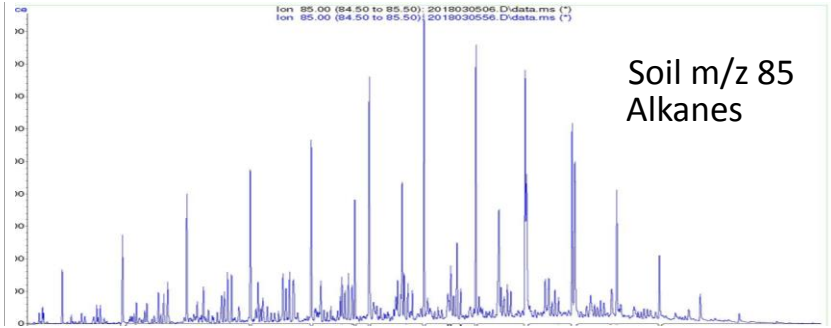
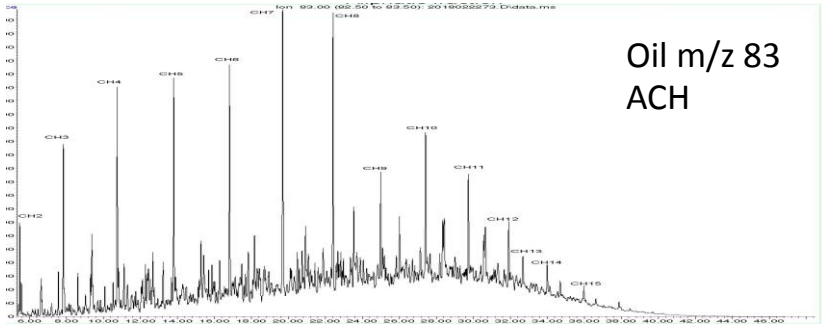
ACH Case Study



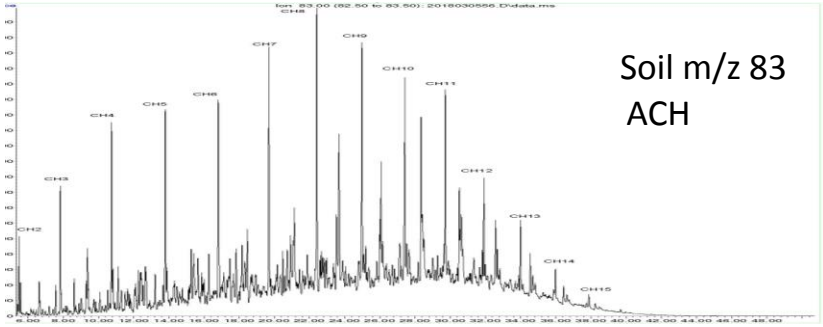
Oil m/z 85
Alkanes



Soil m/z 85
Alkanes



Oil m/z 83
ACH



Soil m/z 83
ACH

Oil collected at surface, soil collected at depth.

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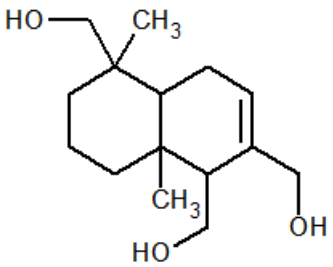
Bicyclic Sesquiterpanes

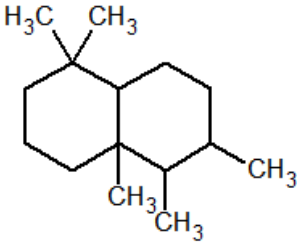
- Cyclic paraffins (naphthenes) with 14 - 16 carbons.
- Derived from microbial and plant terpenes.
- Present in all crude oils.
- Produced through thermal maturation in the petroleum reservoir through removal of oxygen and double bonds.

  "Fossilization"

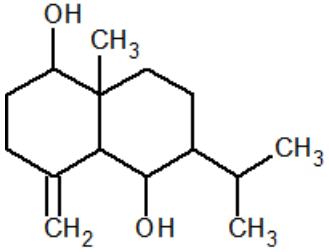
- Enriched during the distillation processes used to produce middle distillates: e.g. diesel, heating oil, kerosene
- Immature crudes have high C14 sesquiterpanes
- Mature crudes have high C15-C16 sesquiterpanes



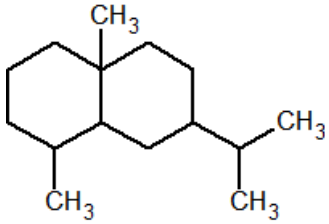
Drimene
Produced by bacteria and fungus



Drimane
Found in all petroleum deposits



Eudesmene
Produced by terrestrial plants



Eudesmane
Found in only the youngest petroleum deposits

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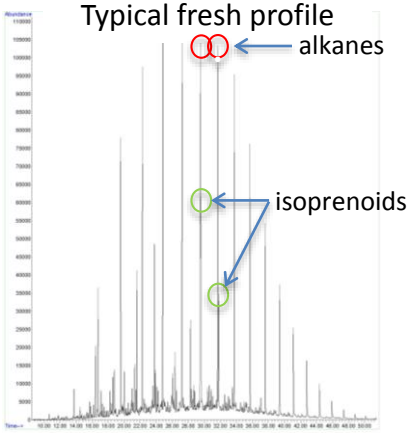
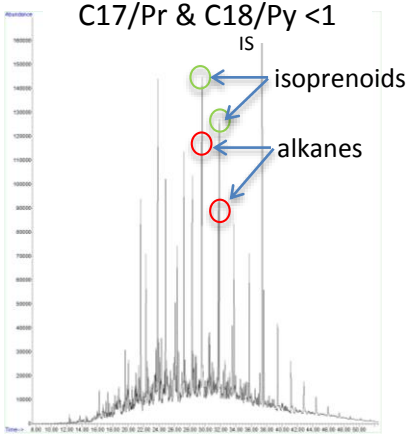
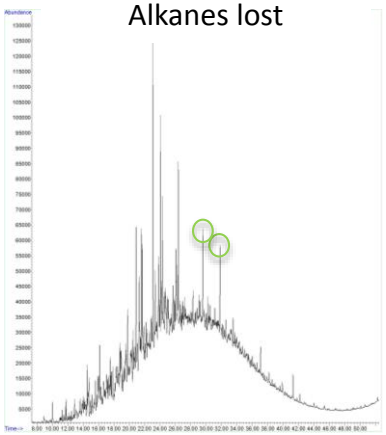
Typical Weathering Patterns



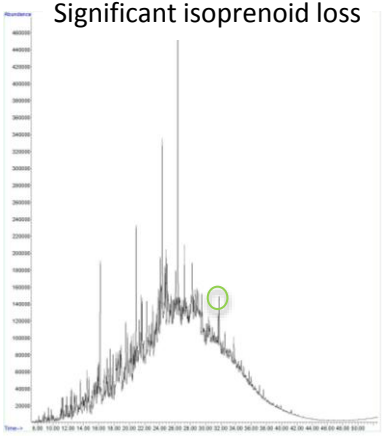
unweathered



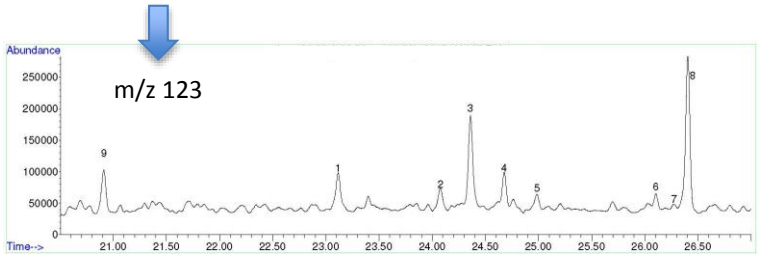
weathered

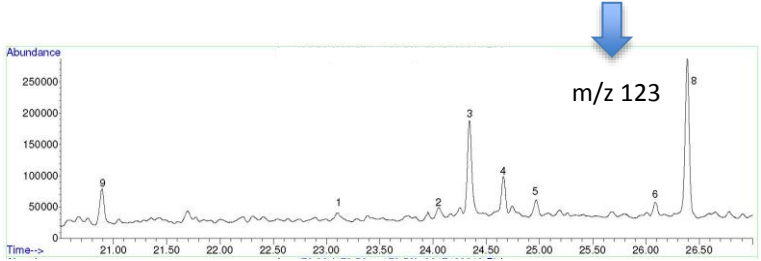


very weathered



extensively weathered





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Role(s) in forensic investigations

Overview:

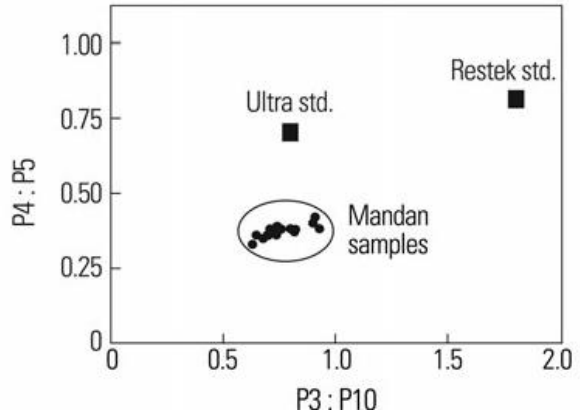
- First used in forensic oil spill investigations ~2005

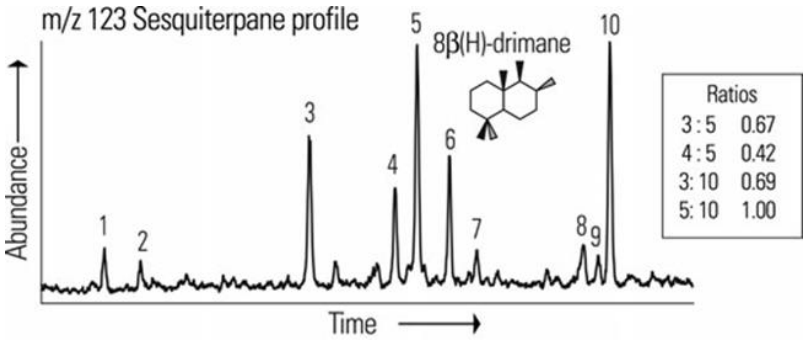
Source Determination:

- 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 Determination:

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





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

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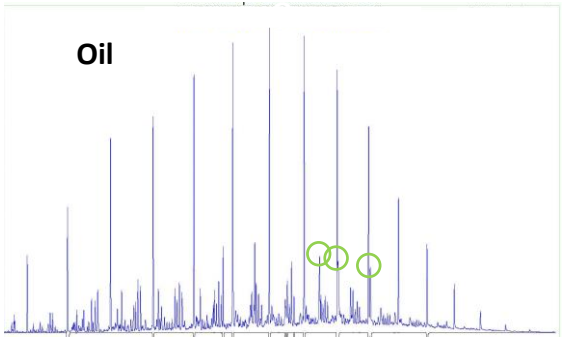
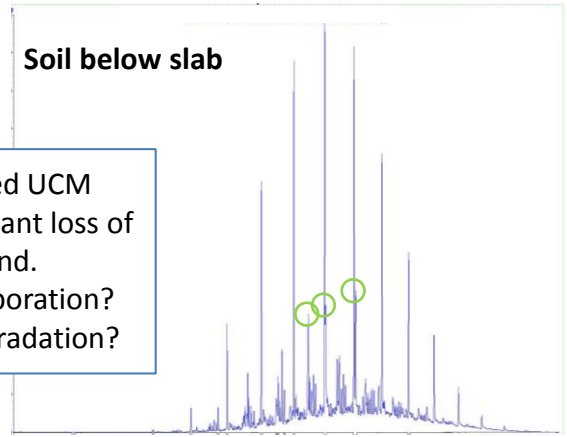
Case Study

- 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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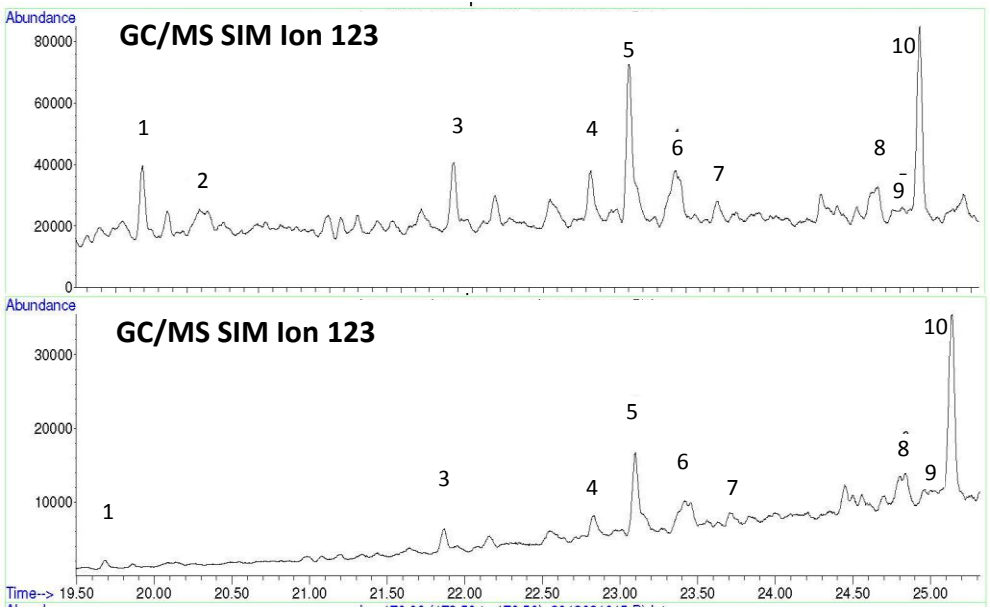
Case Study



Ratios	Oil Avg.	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

Coloured cells: RPD > 14%

Conclusion:

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

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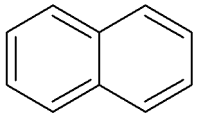
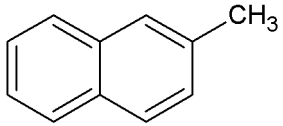
PAHs Source Determination

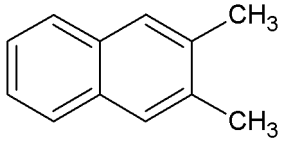
N0



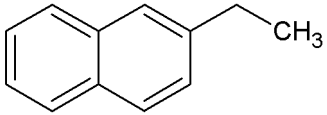
N1



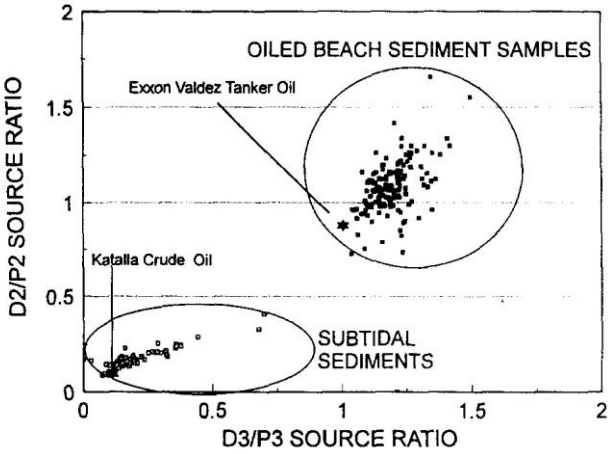
N2

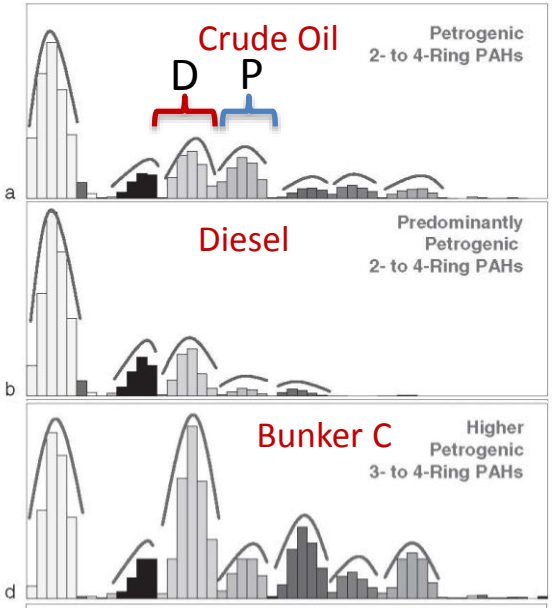


N3



Naphthalenes





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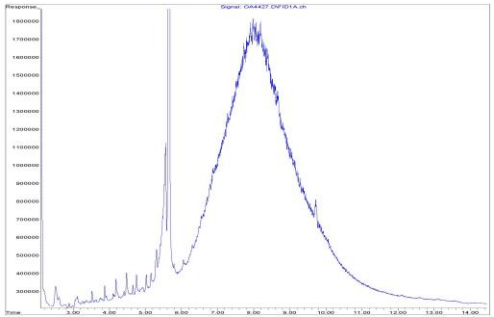
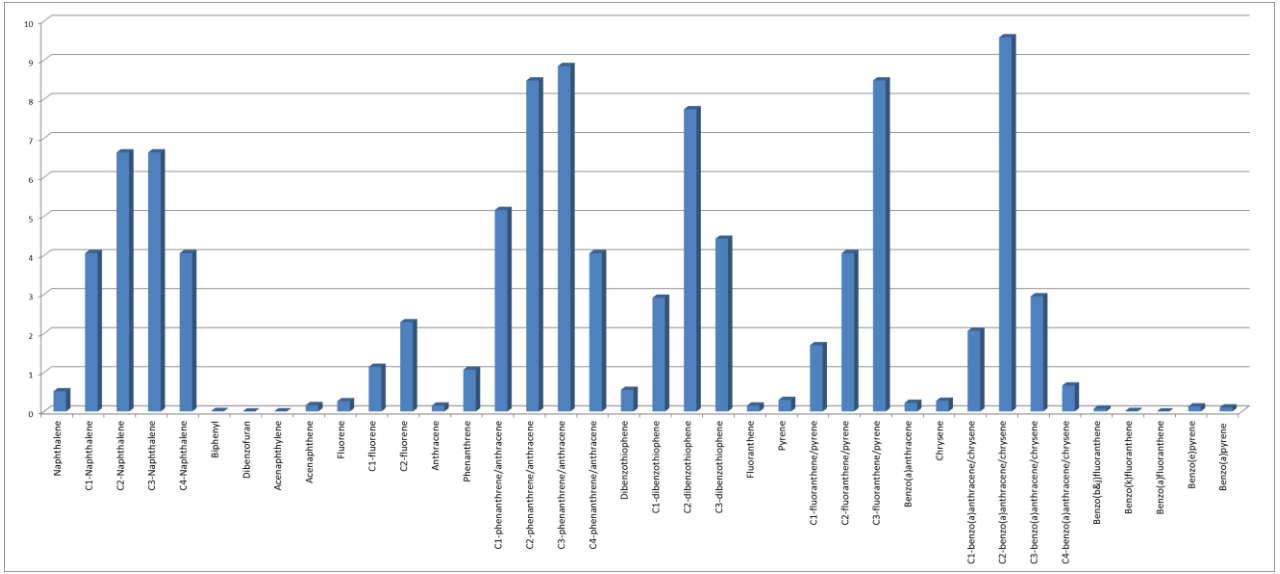
Boehm, P.D. Marine Pollut. Bull. 1997, 34, 599-613.

PAH Case Study – Source Determination



Lube oil??



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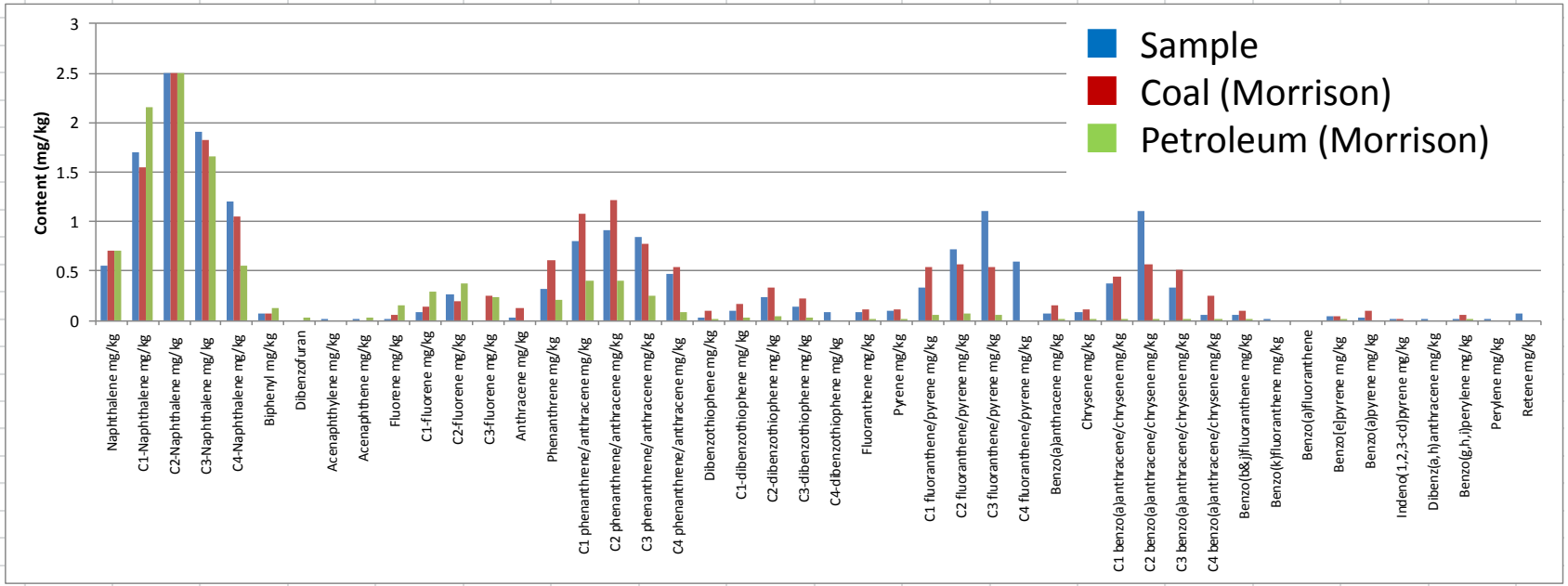
PAH Case Study 1



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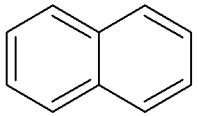
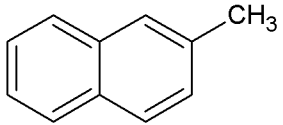
Weathered PAHs

N0



N1



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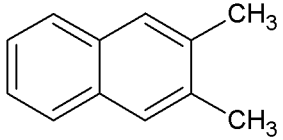

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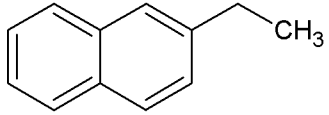
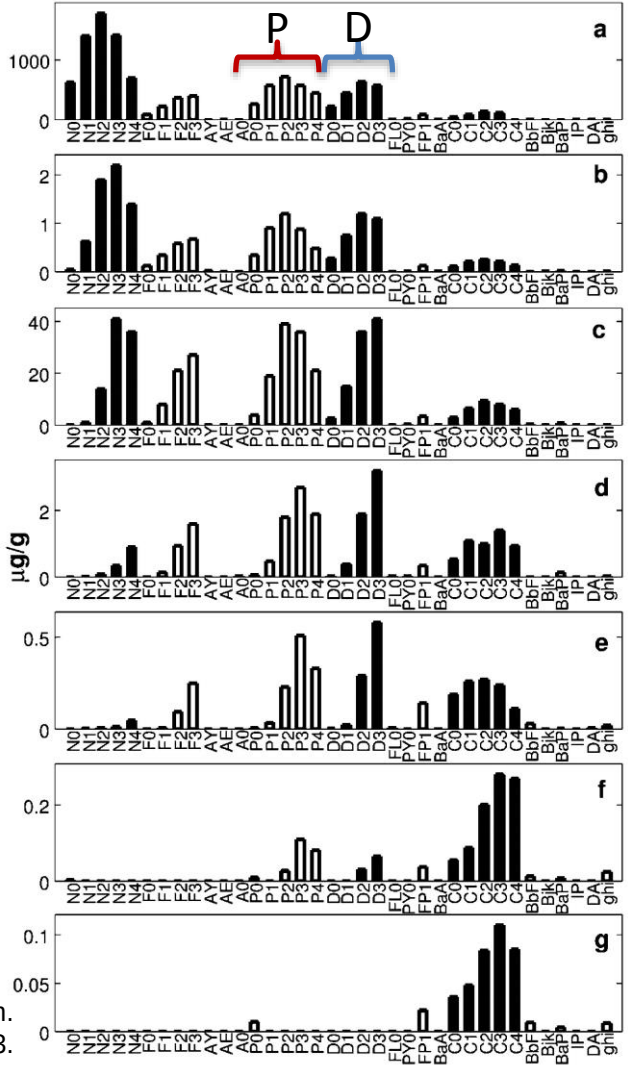


Naphthalenes



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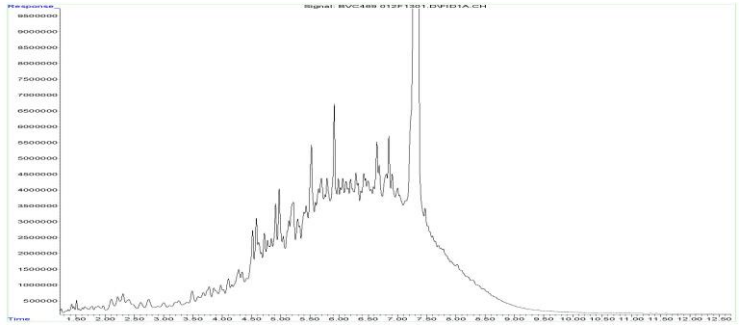
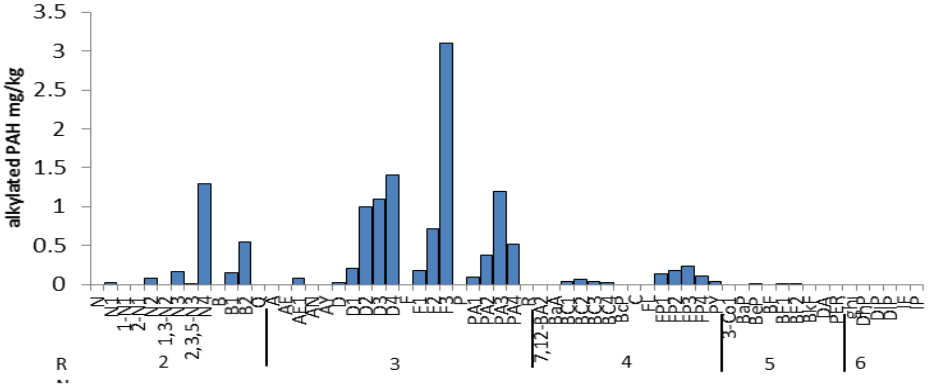
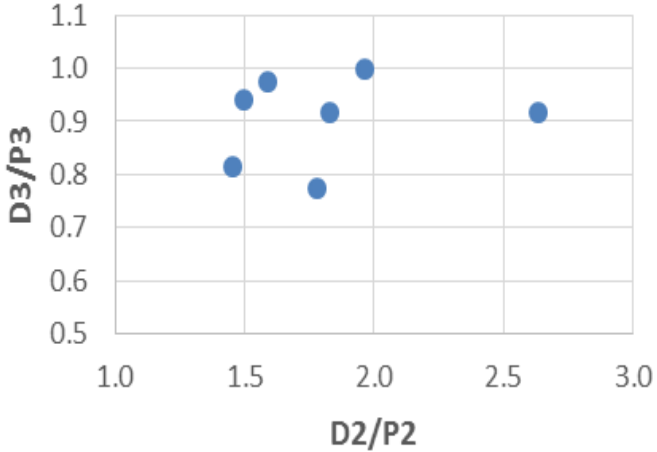
Stogiannidis, E. Rev. Environ. Contam. Toxicol. 2015, 234, 49-133.

PAH Case Study 2



- Soils, heavily degraded fuel oil, from beneath a concrete slab in a basement. Suspected to be up to several decades old.
- Is it only one source??





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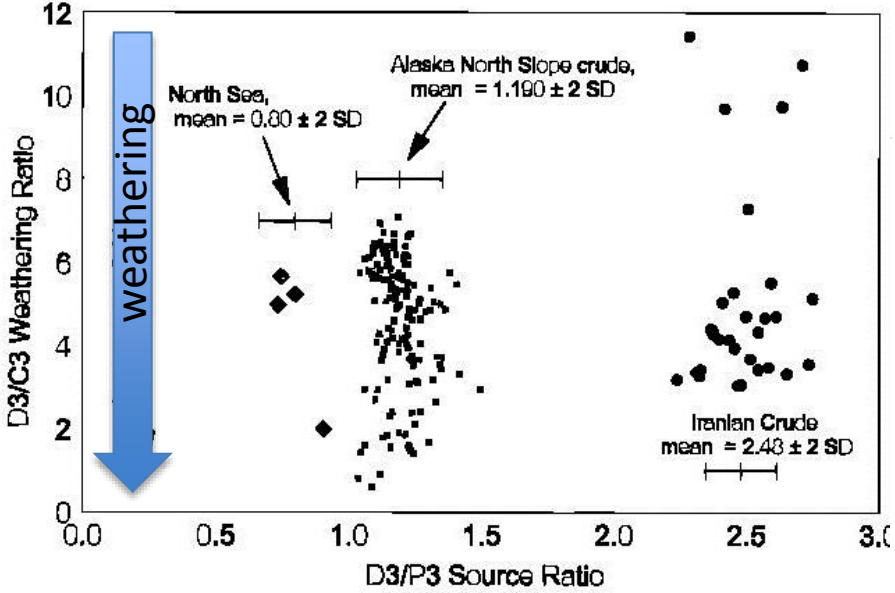
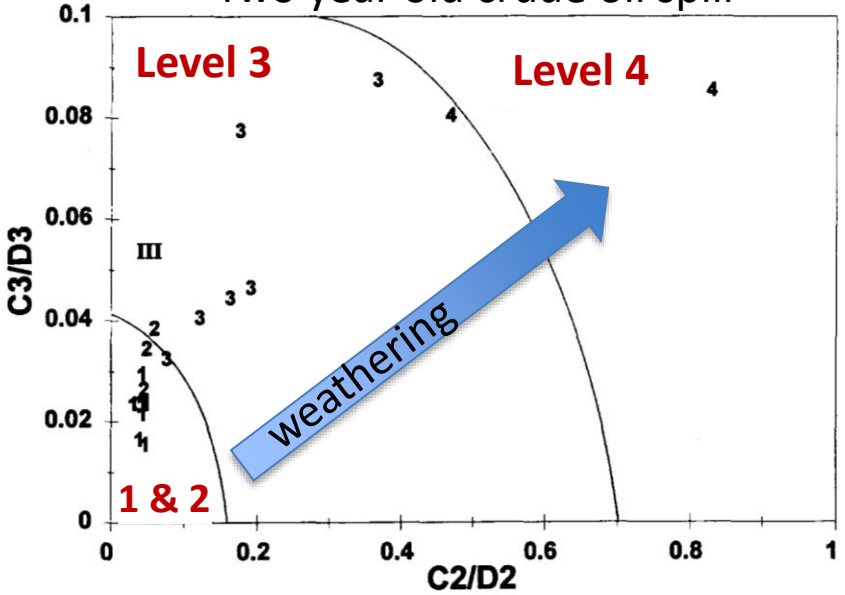
PAH Weathering Ratios – Cross Plots

Three different crudes



weathering ratio vs. source ratio

Two year old crude oil spill



two weathering ratios

Douglas, E.S., Environ. Sci. Technol. 1996, 30, 2332-2339.

Sauer, T.C. Environ. Int., 1998, 24, 43-60.

Conclusions

- **Common petroleum forensic approaches cannot be used in cases of advanced weathering.**
- **More recalcitrant and/or heavier biomarkers may be useful.**
  - Alkylcyclohexanes
  - Bicyclic Sesquiterpanes
  - Alkylated Polycyclic Aromatic Hydrocarbons
- **Consider weathering patterns of these biomarkers in all evaluations.**
  - Relative degrees of weathering indicate relative ages of impact under similar site conditions
- **Source similarity determinations should only be made from biomarkers that have not started to weather.**

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THANK YOU

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