Forensic Investigations of Petroleum Hydrocarbon Environmental Impacts: Overview & Case Studies

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A Common Request…

"How much PHC is there?"

Usually asked during compliance testing or for monitoring remediation progress – and answered with a TPH analysis

When the answer is unexpected you may want to learn why!

Common Forensic Investigative Goals:

Are there plumes co-mingling?

How old is the NAPL?

When did the contamination begin?

Is my client responsible?

Is the spill from the most recent tank nest?

Is the contamination OLDER than 1992?

Who's leaking gasoline into the street?

Is this a fresh spill?

Who can I invite to the cleanup party?

Keys to Success…

1. Understand the site and the question to be answered
    - Site History – ask lots of questions
    - Define the goal
2. Employ a tiered approach to lab analysis
    - Start with a total PHC screening test
        - CCME Hydrocarbons
    - Based on those results – select the desired analytical approach
3. Develop multiple lines of evidence to support the conclusion

Background Information: "Detective Work"

History

- Background Information
- Past use of the property or location
- Compounds of concern

Geology/Geochemistry

- What is the nature of the soil environment? Aggressive or passive?

Hydrogeology

- Groundwater flow

Where were the samples collected?

- Relative to surface
- Relative to water table
- Relative to potential sources of impact

Would additional samples allow for more solid conclusions?

- The samples in hand may have been collected for a different purpose
  - compliance monitoring
- Are they appropriate for the required investigation??

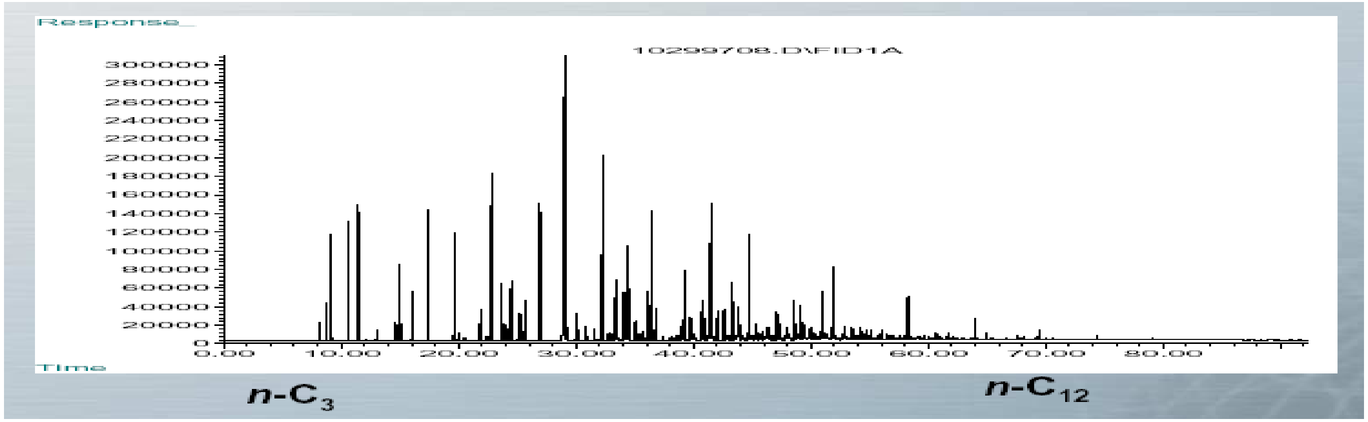
Gas Chromatography for Identification of Petroleum Products

GC remains the most widely used technique to identify petroleum products in the environment.

- Most fuels and lubricants are too complex to allow full speciation of every component.

Identification/quantification of target components

Visual inspection and target analytes are used as identification tools



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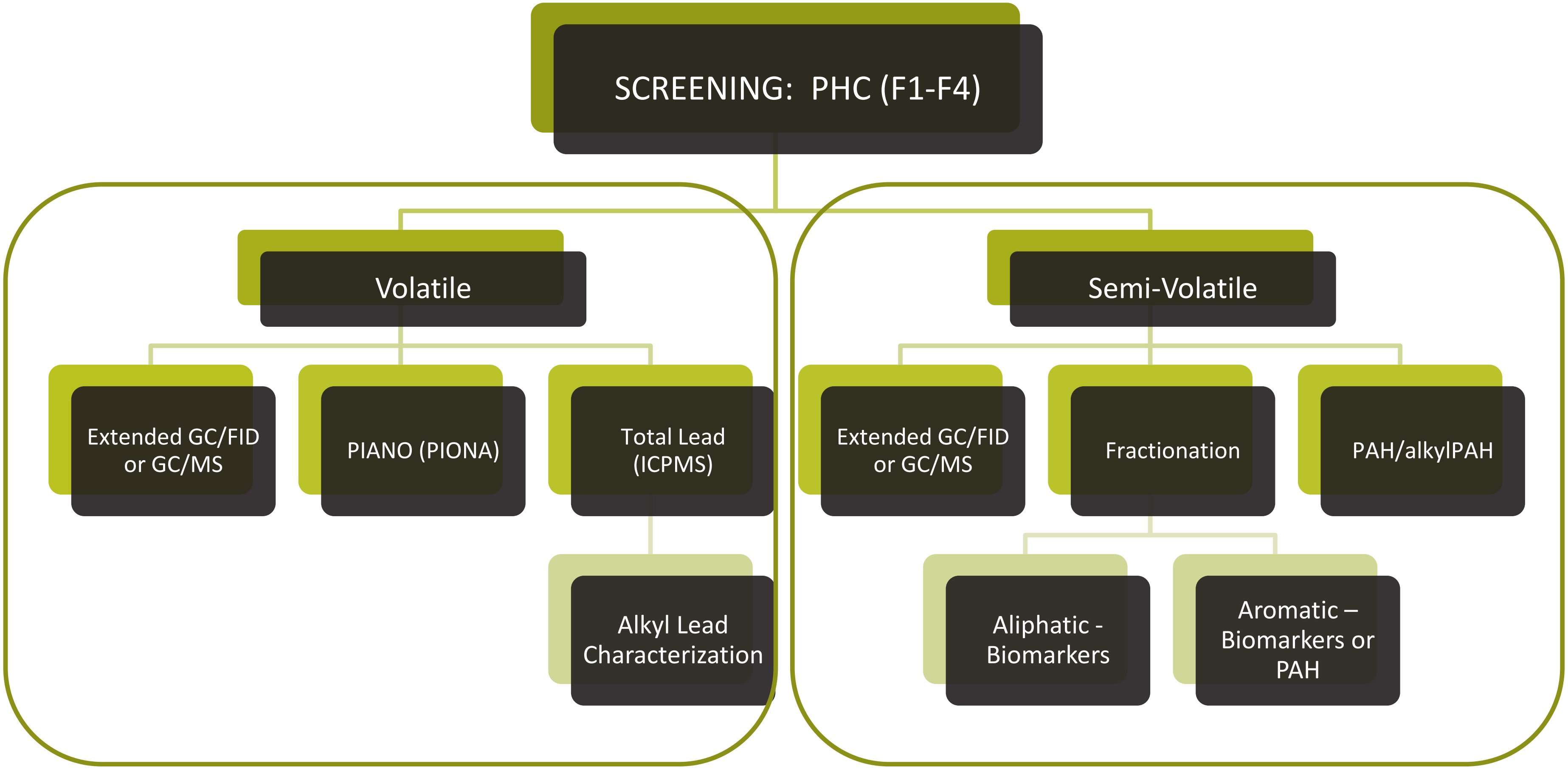
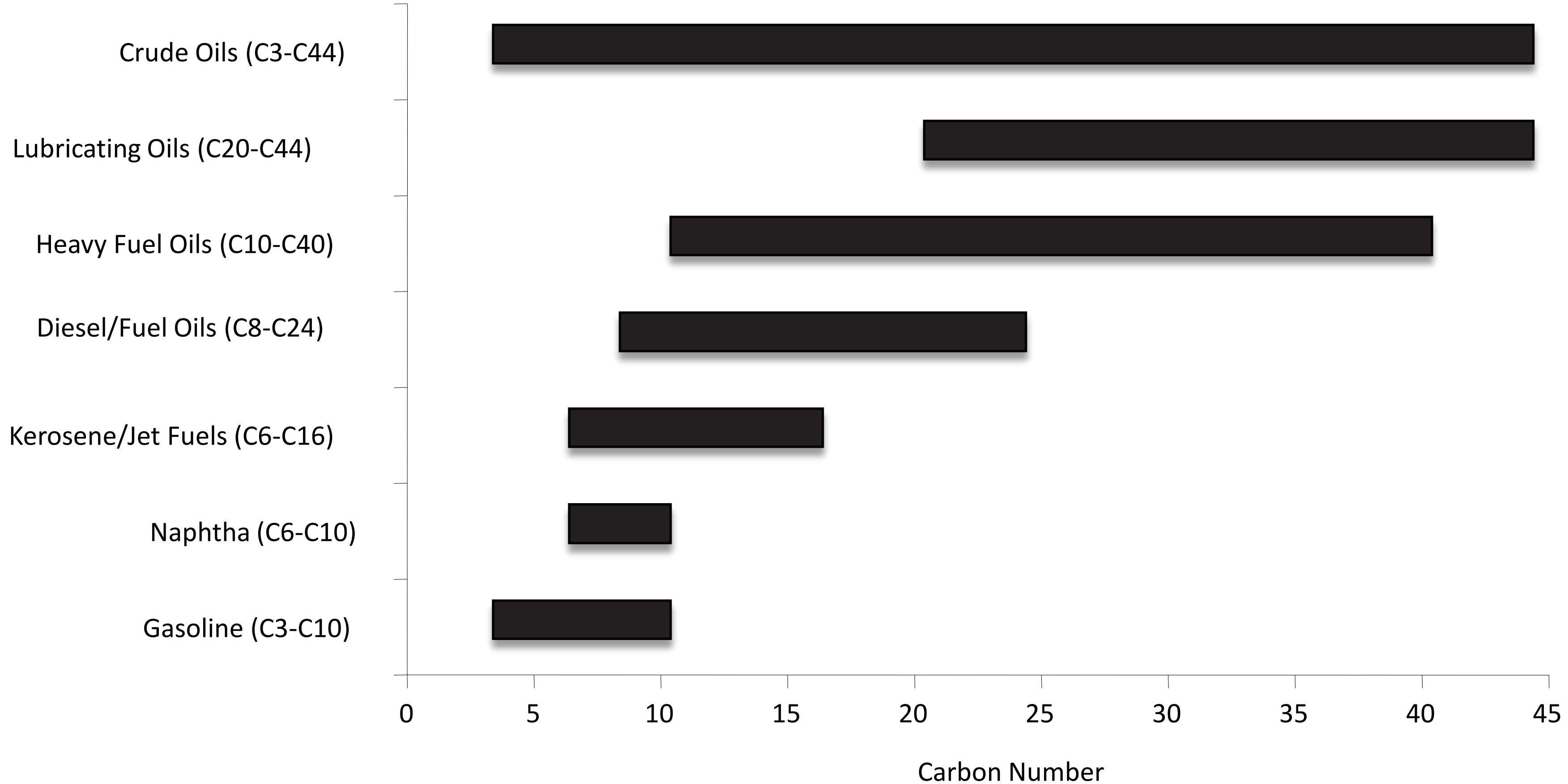
Tiered Approach to Forensic Investigations



Petroleum Products

Carbon Number Distribution



Some products may span both the Volatiles and the Semi-Volatiles

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Gasoline Forensics

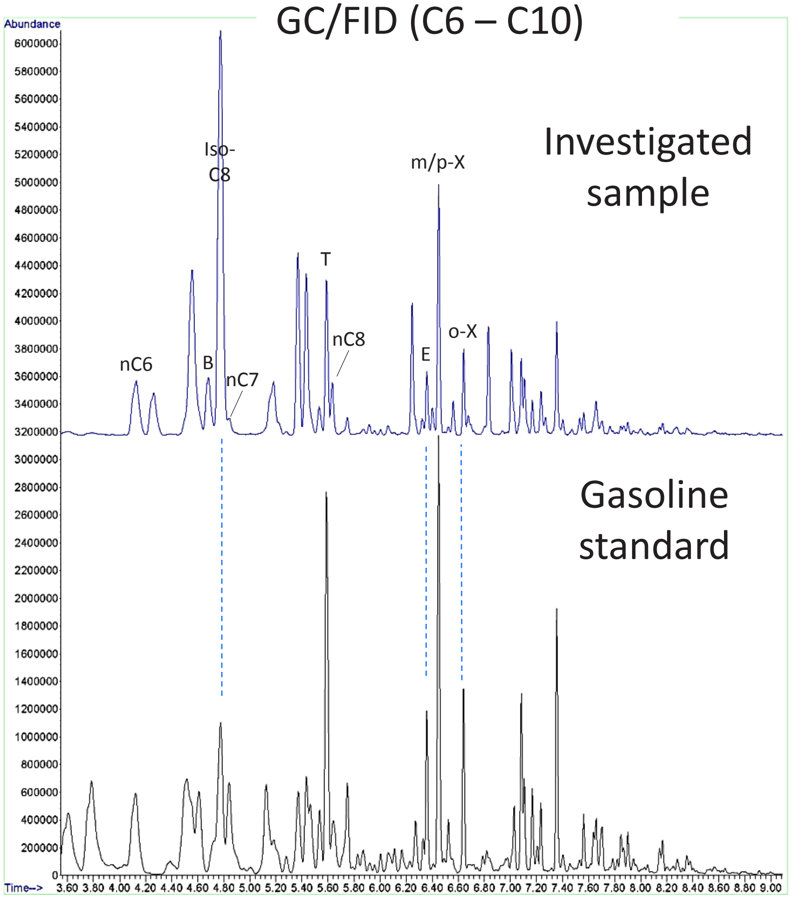
Determination of gasoline grade

History:
LNAPL collected from sump at a refinery
- evaporation & water washing expected

TPH screening identified gasoline

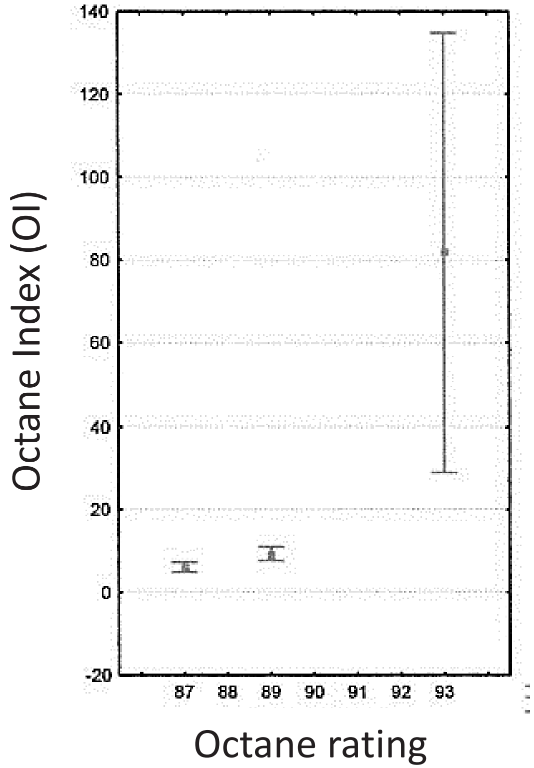
Two potential sources were identified:
- premium vs. regular gasoline

Goal:
Identify the source from limited LNAPL volume, avoid extensive excavation

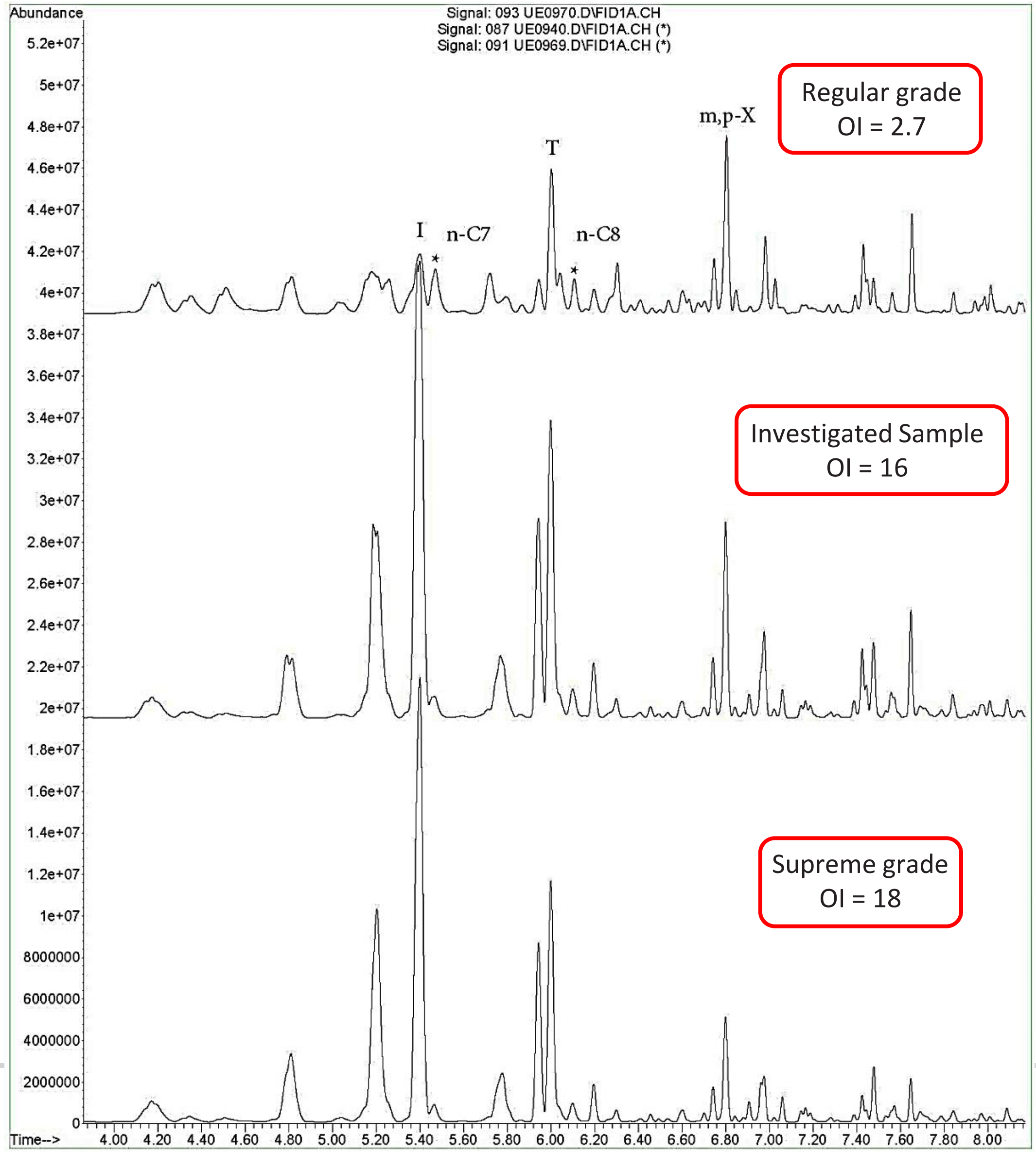


Supreme grade gas confirmed

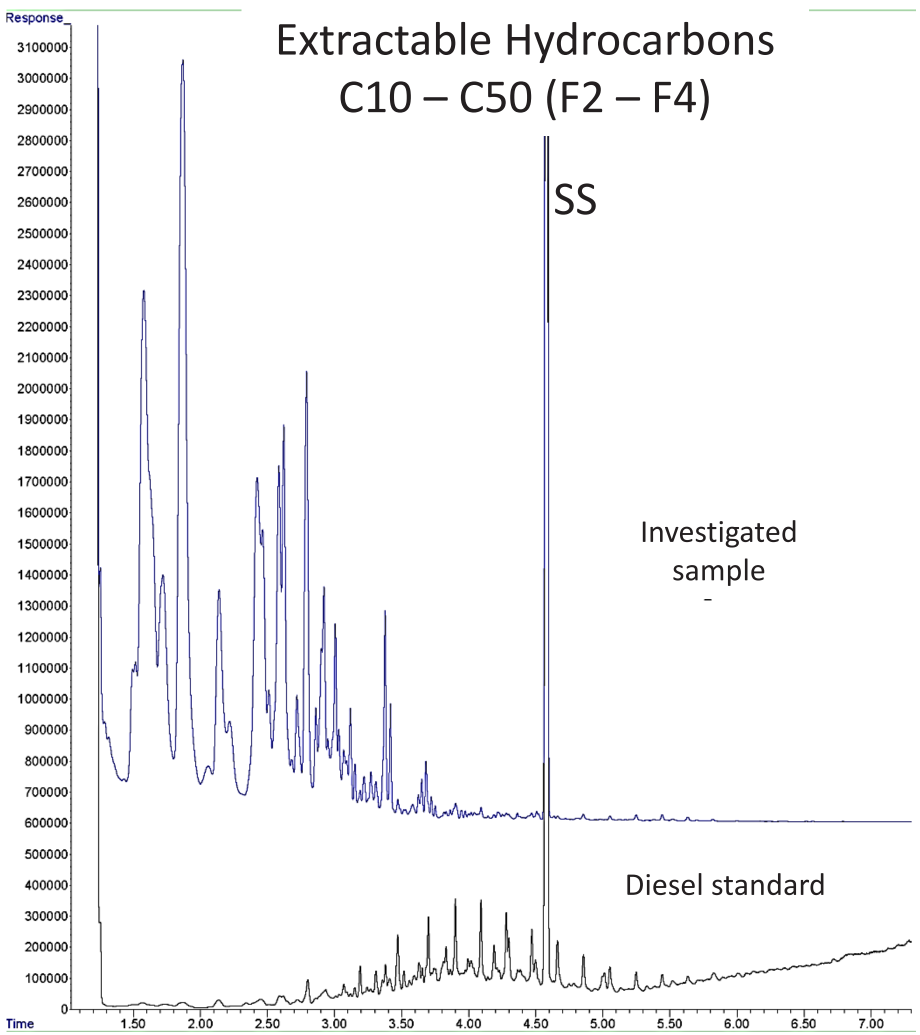
$$OI = \frac{IsoC8 + T}{nC7 + nC8}$$

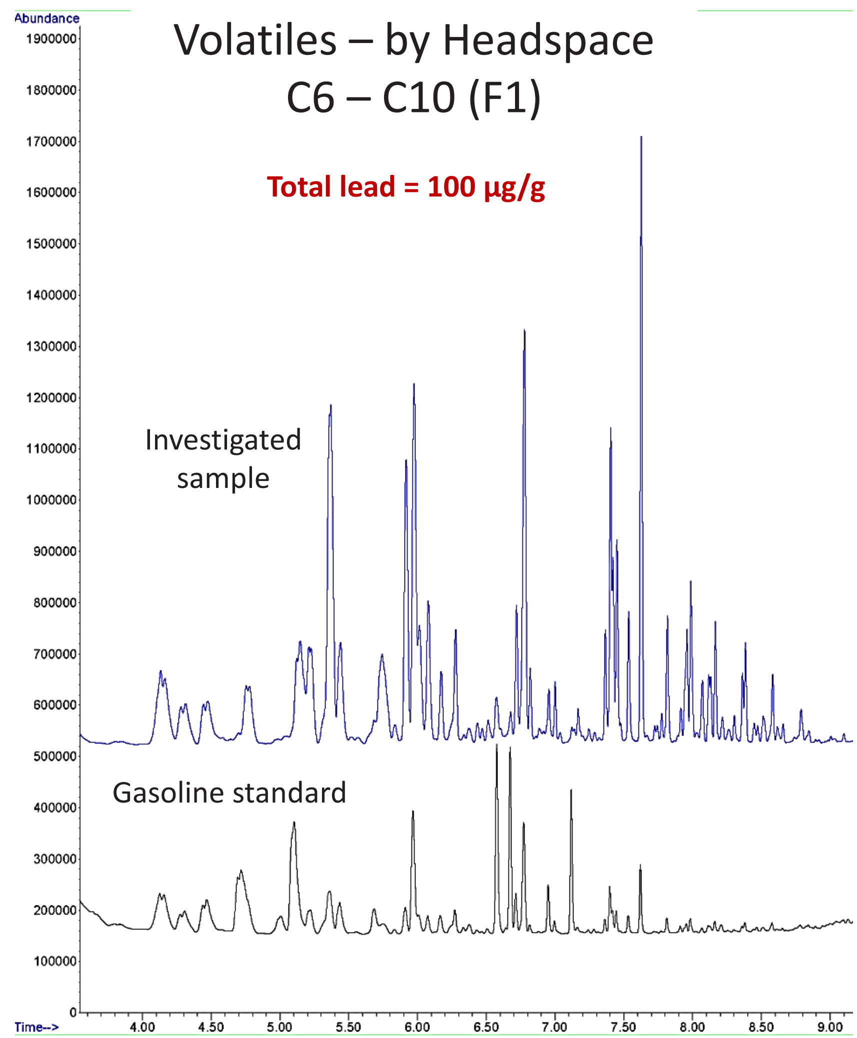


source: Schmidt et al. Environmental Forensics, 2003, 4: 75-80.



Unknown product: gasoline range confirmed





Unknown product: PIONA & Lead Results

Parameter	mass %
iso-Paraffins	43.98
Naphthenes	7.40
Paraffins	8.84
Methylcyclohexane	0.46
n-Heptane	1.75
3-Methylhexane	2.39
Benzene	0.10
Toluene	4.24
Ethylbenzene	1.39
m-Xylene	3.25
p-Xylene	1.87
o-Xylene	0.54
Cyclohexane	0.11
n-Pentane	1.10
2-Methylpentane	2.44
2-Methylheptane	1.29
2,2,4-Trimethylpentane	7.44

Parameter	mass %
n-Octane	1.32
2,2,3-Trimethylpentane	0.00
2,3,4-Trimethylpentane	4.06
2,3,3-Trimethylpentane	0.00
n-Butane	0.15
iso-Butane	0.02
n-Pentane	1.10
iso-Pentane	1.78
Naphthalene	0.02
n-Dodecane	0.05
2-Methylhexane	3.54
2,3-Dimethylpentane	0.00
3-Methylhexane	2.39
2,4-Dimethylpentane	1.03
C5 and C6 Olefins	Absent
Total Aromatics (%)	29.72
Oxygenates	None

Total Lead Analysis (ICPMS): 103 µg/g

<u>Lead Speciation Analysis:</u>

Tetraethyl lead: 150 µg/g

Triethyl lead: 0.46 µg/g

Tetramethyl lead: <1 µg/g

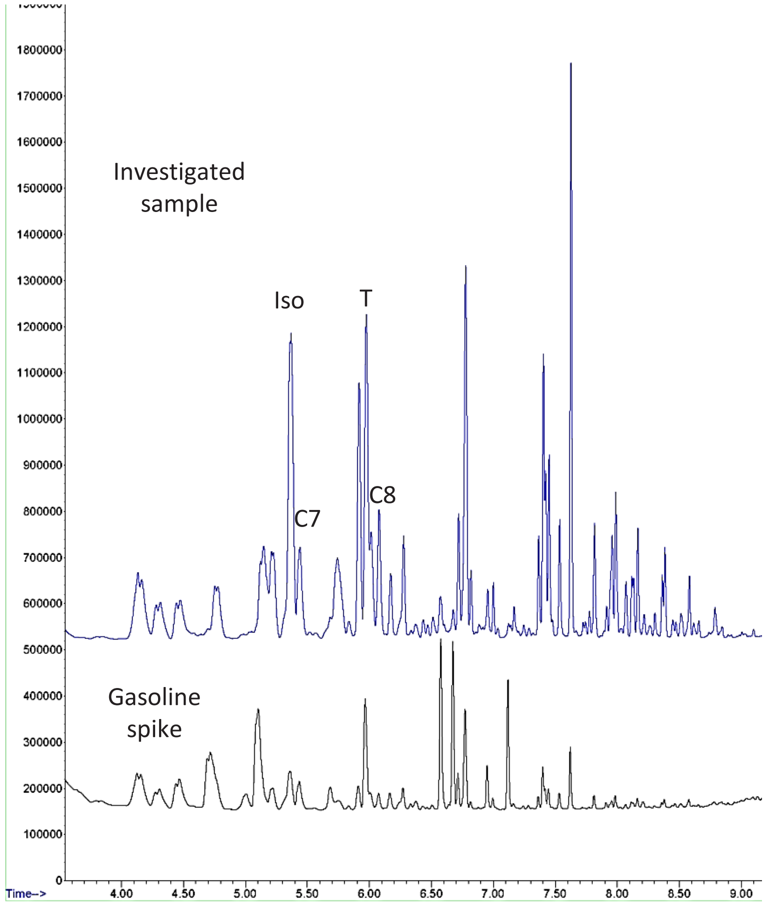
Unknown product: PIONA ratio analysis

Weathering:			
(*iso*Paraffins+Naphthenes)/Paraffins	5.81	2.0 - 8.0	Biodegradation: Ratio increases with increased biodegradation
Methylcyclohexane/n-Heptane	0.26	0.5 - 0.8	Biodegradation: Ratio increases with increased biodegradation
3-Methylhexane/n-Heptane	1.37	0.5 - 2.0	Biodegradation: Ratio increases with increased biodegradation
(Benzene+Toluene)/(Ethylbenzene+Xylenes)	0.62	0.8 - 1.1	"Waterwashing": Ratio decreases with increased dissolution
Benzene/Cyclohexane	0.91	0.5 - 2.0	"Waterwashing": Ratio decreases with increased dissolution
Toluene/Methylcyclohexane	9.22	2 - 10	"Waterwashing": Ratio decreases with increased dissolution
n-Pentane/n-Heptane	0.63	0.5 - 2.0	Evaporation: Ratio decreases with increased evaporation
2-methylpentane/2-methylheptane	1.89	3 - 8	Evaporation: Ratio decreases with increased evaporation
Refining Method:			
2,2,4-Trimethylpentane/Methylcyclohexane	16.17	2 - 3	Values >5 typically represent premium grade gasoline
(2,2,4-Trimethylpentane+Toluene)/ (n-Heptane+n-Octane)	3.80	2 - 5	Values increase with octane rating in unweathered samples
224TMP/(224TMP+223			kylation; 0.39-0.45 typically represent
Ethylbenzene/(Ethylbe			hylbenzene in unweathered samples
n-Butane/(n-Butane+*is*			butane in modern gasolines
*iso*Pentane/(*iso*Pentane+n-Pentane)	0.62	---	Isomerate blending usually results in a ratio >0.7
Naphthalene/Dodecane	0.40	1 - 3	Higher values may be indicative of gasoline reforming
(2-MH+23DMP)/(3-MH+24DMP)	1.04	---	
C5 & C6 olefins	Absent		Produced through Fluidic Catalytic Cracking (FCC)
Reformulated vs. Conventional:			
Benzene (wt %)	0.10	<1 %	Benzene content cannot exceed 1% in typical gasolines. Under aerobic conditions benzene degrades quickly
Total Aromatics (wt %)	29.72	<35%	Typically < 30% in gasolines produced after 1999; increased aromatic content may be due to the resistance of the alkylbenzenes to weathering relative to simpler, non-aromatic hydrocarbons
Oxygenates (wt. %)	None		

These indicators are suspect in weathered gasolines!!

minimal biodegradation, minimal dissolution, evaporation indicated

Unknown product: gasoline grade?



- PIONA suggested premium grade gasoline
  - Unreliable due to evaporation
- Chromatographic evaluation of grade suggested regular grade
  - OI = 2.8

Conclusion: old (pre 1992) evaporated leaded regular grade gasoline

Middle Distillate Forensics (Diesel Range)

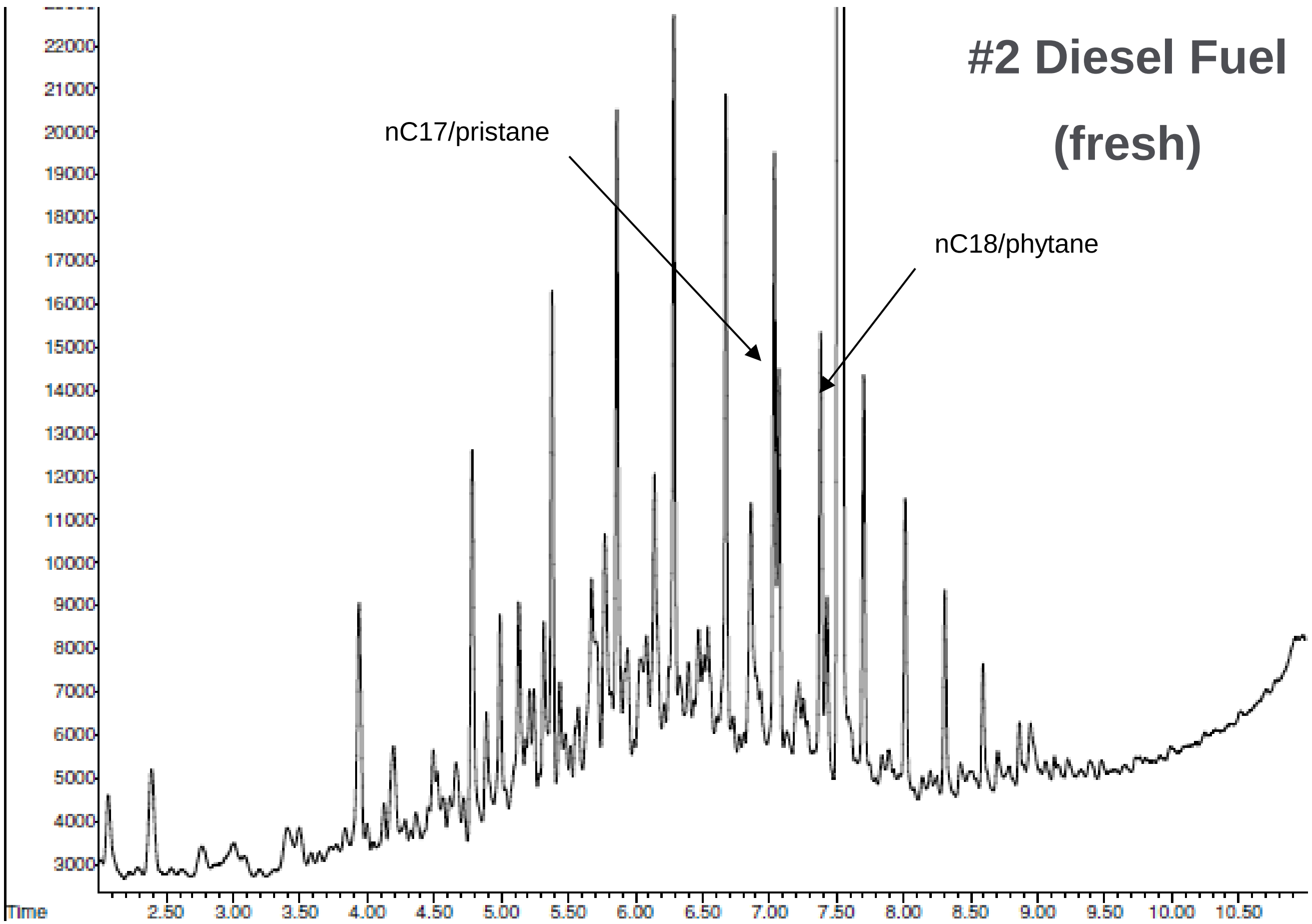
Impact of Weathering

- Light hydrocarbons
- Olefins
- N-Alkanes
- Monoaromatics
- Isoalkanes
- Parent PAH > 2-ring
- C1 alkyl PAH → C4 alkyl PAH
- Triterpanes
- Diasteranes → Aromatic Steranes
- Porphyrins

Introduction to Environmental Forensics, Murphy and Morrison

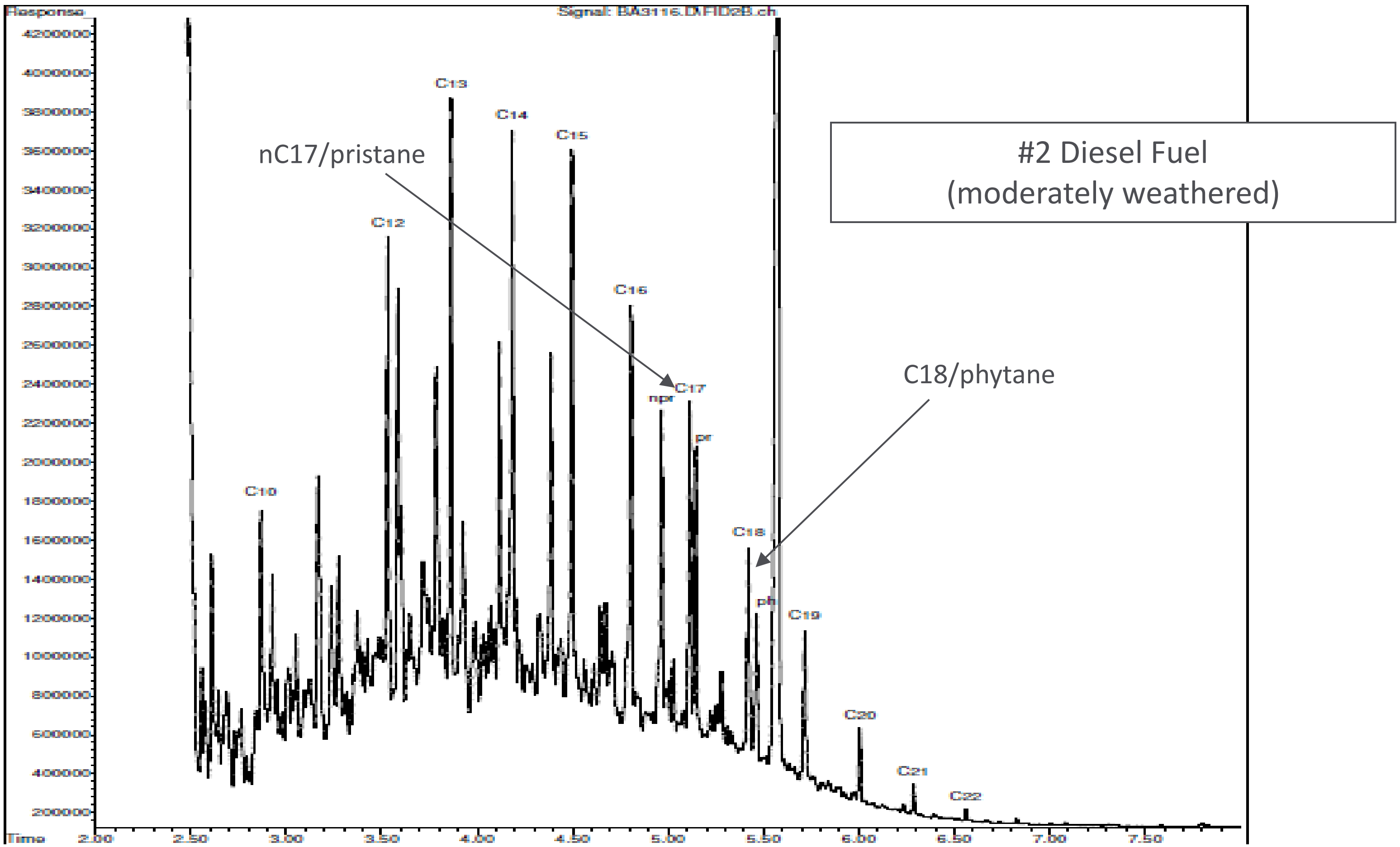
Isoprenoid Biomarkers

C17/Pristane & C18/Phytane

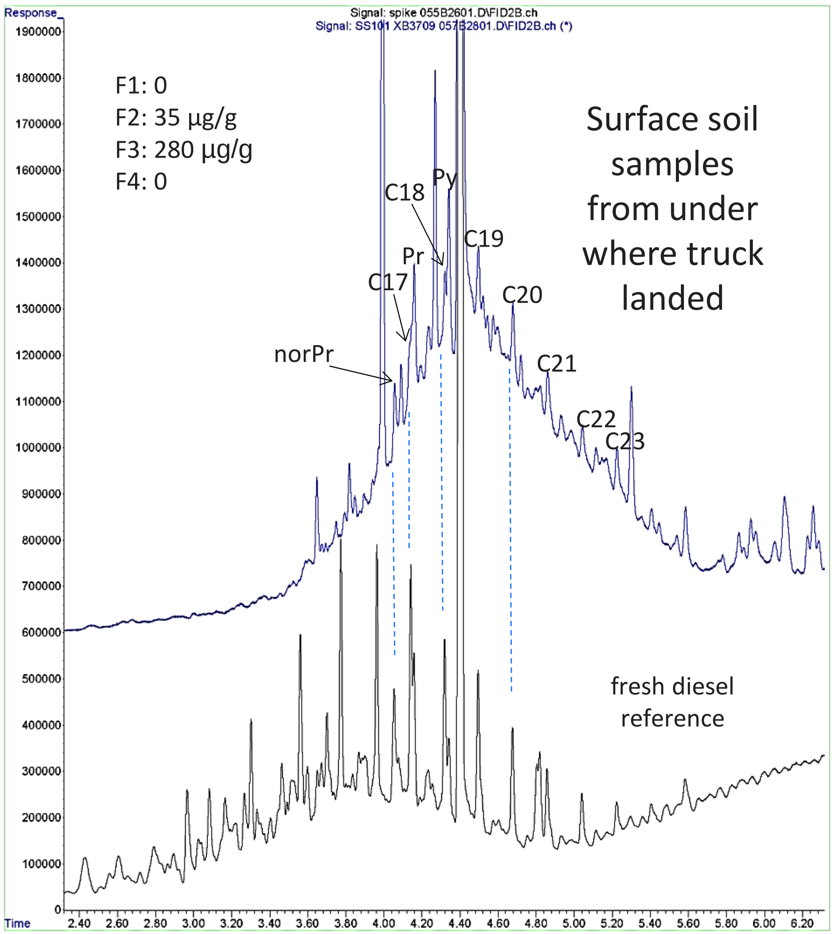


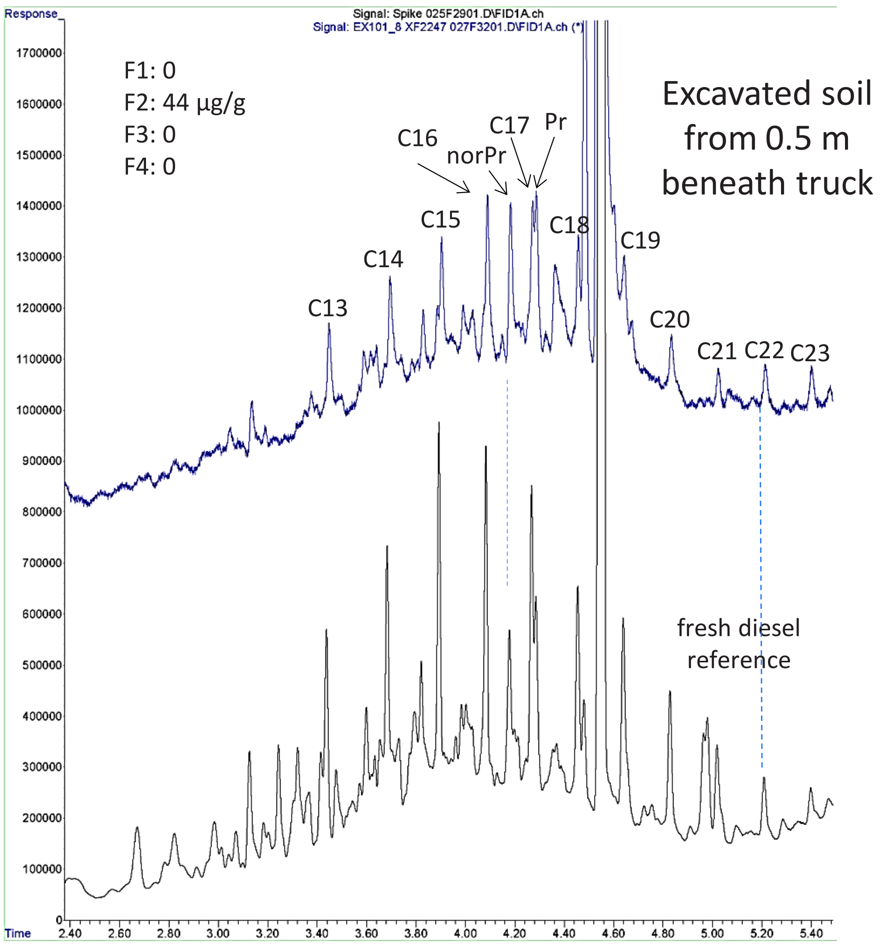
Isoprenoid Biomarkers

C17/Pristane & C18/Phytane



Highly Weathered: Site of Recent Truck Crash





Conclusion: these F2 and F3 impacts are not due to the truck crash

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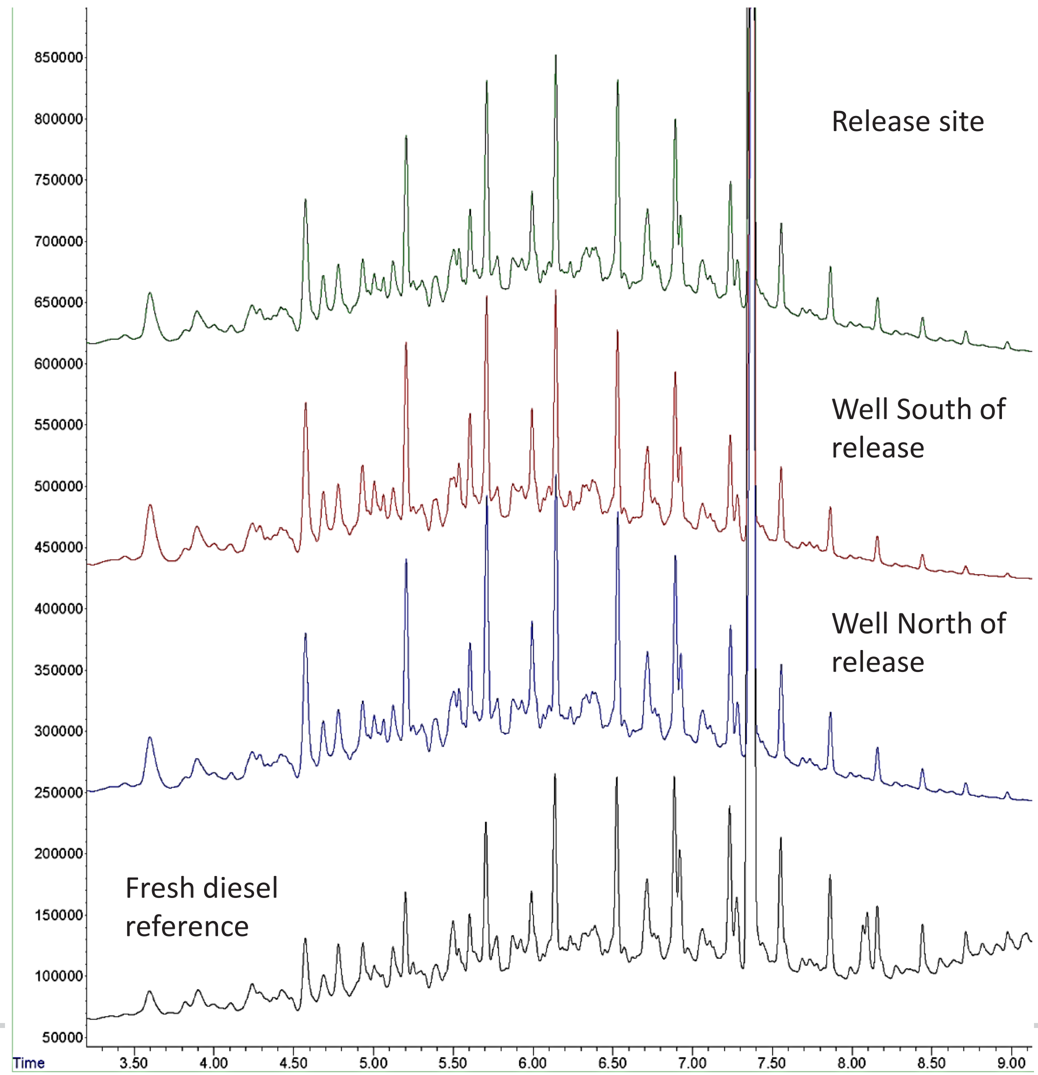
Using Weathering to Estimate Impact Age

- Using weathering as an indicator of age may be subject to considerable scrutiny/uncertainty
- Be careful with statements like "this groundwater sample contained diesel, but many of the low boiling point hydrocarbons are absent, so this is an older release"
- What impacts weathering? ("context")
  - Soil Environment
  - Volume of contaminant released
  - Time of release (one event / leak over time)
  - Depth of spill (or depth of where the sample was collected)
  - Subsurface conditions (oxygen content, microbiological populations)

Known Catastrophic Heating Oil Release in 1990

- Water wells, 60 m deep in fractured bedrock
- LNAPL layer 20 – 60 cm thick still present on top of water

From CCME F2 – F4 data all signatures look very similar and relatively <u>unweathered</u>



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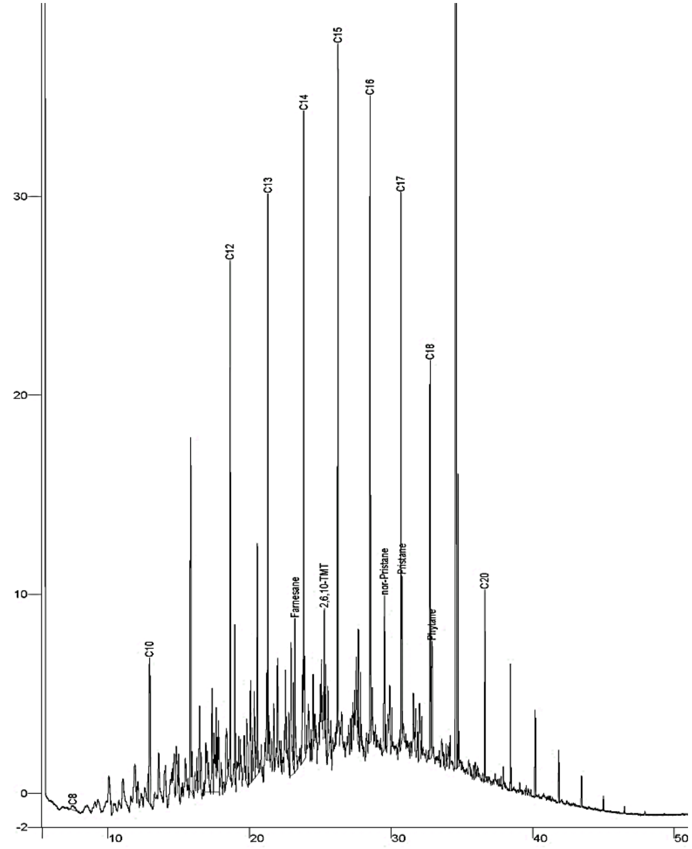
Known Catastrophic Heating Oil Release in 1990

Extended GC/FID confirms high similarity and minimal evidence of weathering

- The ratios expected to decrease with weathering trend slightly lower further from the release site
- Ratios expected to remain constant are generally consistent, confirming the same source

	Fresh Diesel	Release Site		N of release	S of release
C17/Farnesane	5.29	3.60	3.41	3.18	2.75
C17/2,6,10-tmt	4.91	4.26	4.12	3.55	3.19
C17/nor-Pr	3.37	3.60	3.49	3.32	3.29
C17/Pristane	2.18	3.38	3.21	2.90	2.65
C18/nor-Pr	2.95	2.58	2.74	2.51	2.39
C18/Phytane	3.27	3.46	3.60	3.21	3.22
Pristane/nor-Pr	1.55	1.07	1.09	1.14	1.24
Pr/Ph	1.72	1.43	1.43	1.46	1.67
Pr/2,6,10-tmt	2.26	1.26	1.28	1.22	1.21
nor-Pr/Phytane	1.11	1.34	1.31	1.28	1.35
nor-Pr/2,6,10-tmt	1.46	1.18	1.18	1.07	0.97
Pristane/Farnesane	2.43	1.07	1.06	1.09	1.04
nor-Pr/Farnesane	1.57	1.00	0.98	0.96	0.84
C10/C20	0.41	0.75	0.72	0.63	1.08



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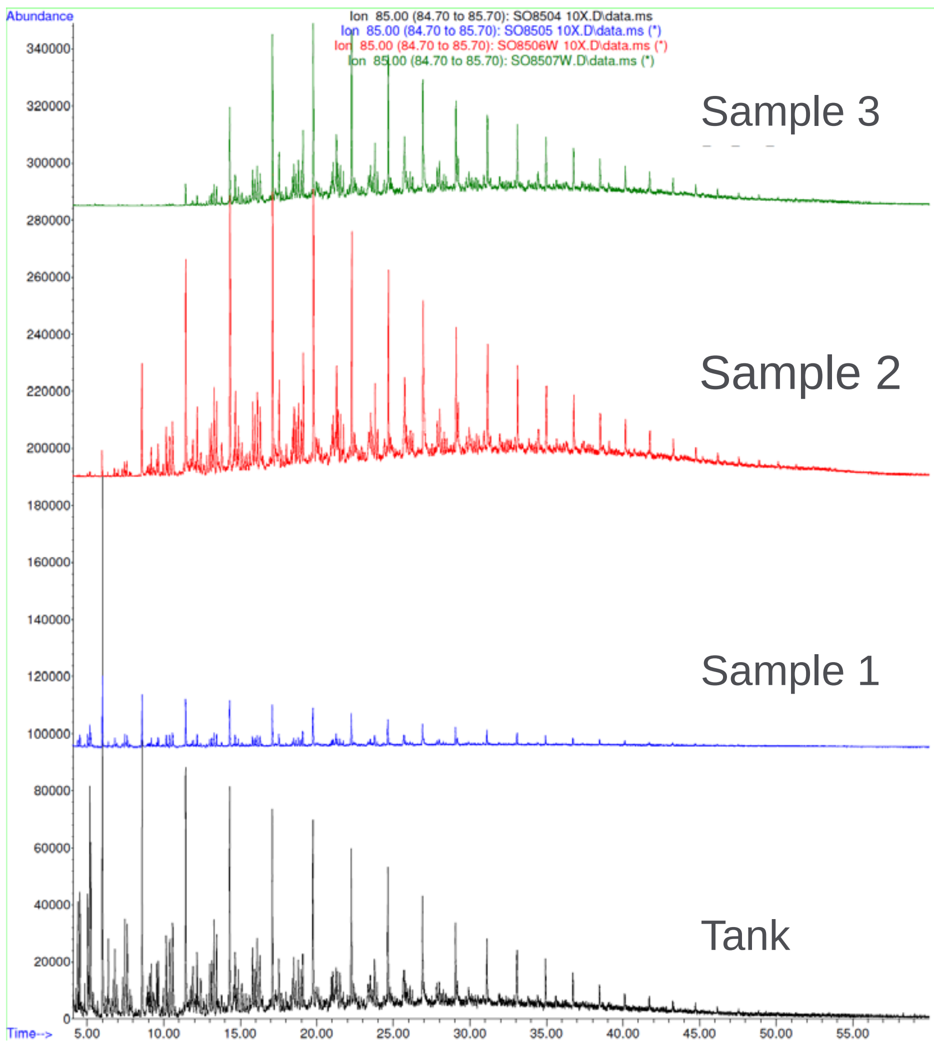
Diesel release in surface water

further from source



Heavier alkanes

GC/MS extracted ion trace: m/z = 57

- characteristic ion of alkanes

Lighter alkanes decrease with distance from source

Alkane pattern is consistent with a single source release, but are these four traces really the same product??

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GC/MS Biomarker Analysis

Biomarkers are chemical "fossils"

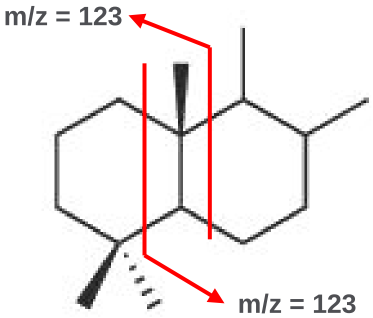
- unique tracers for petroleum contaminants
- structurally very similar to natural products; chlorophyll
- one of the last group of compounds to degrade

Isoprenoids (e.g. pristane and phytane) are considered "biomarkers"

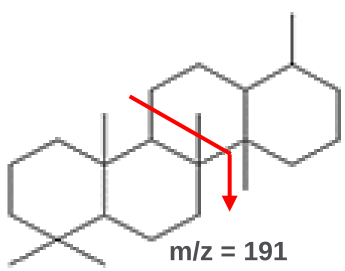
GC/MS biomarker peak patterns can be used to:

- Evaluate degree of weathering under specific soil conditions
- Differentiate petrogenic and biogenic impacts
- Identify crude oil sources

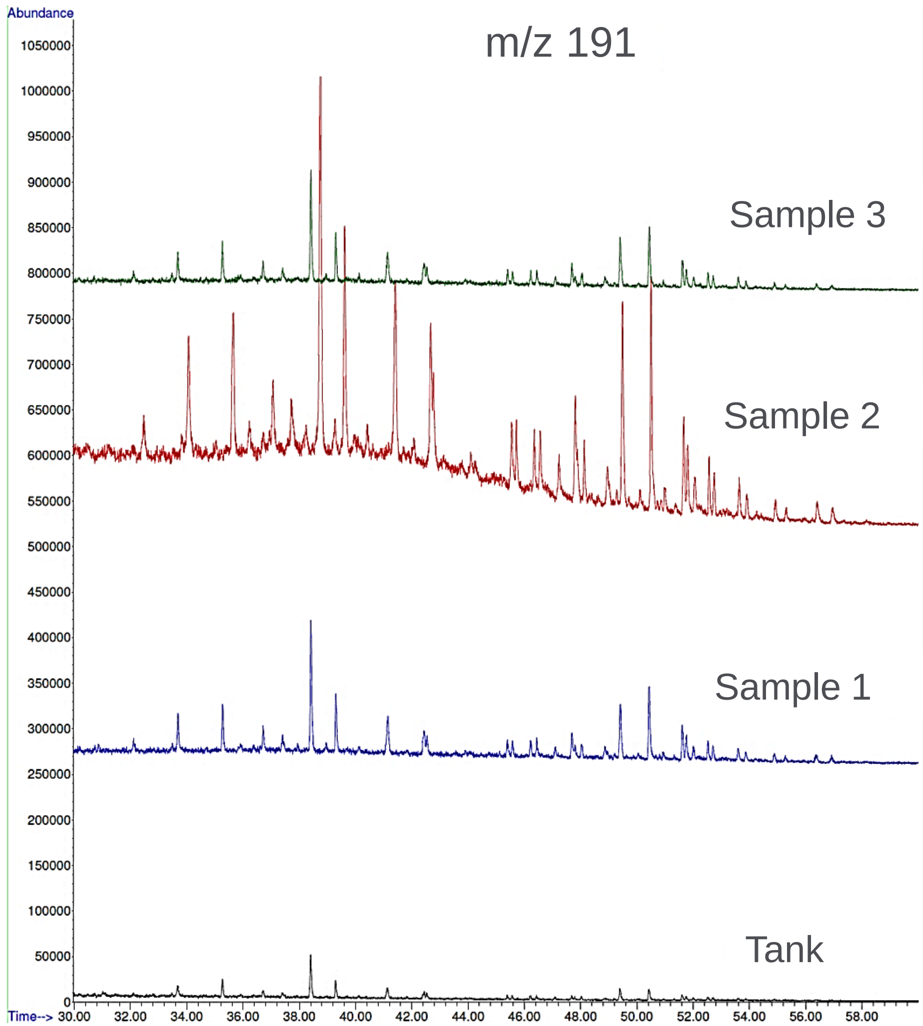
Diesel release in surface water (cont.)



sesquiterpanes



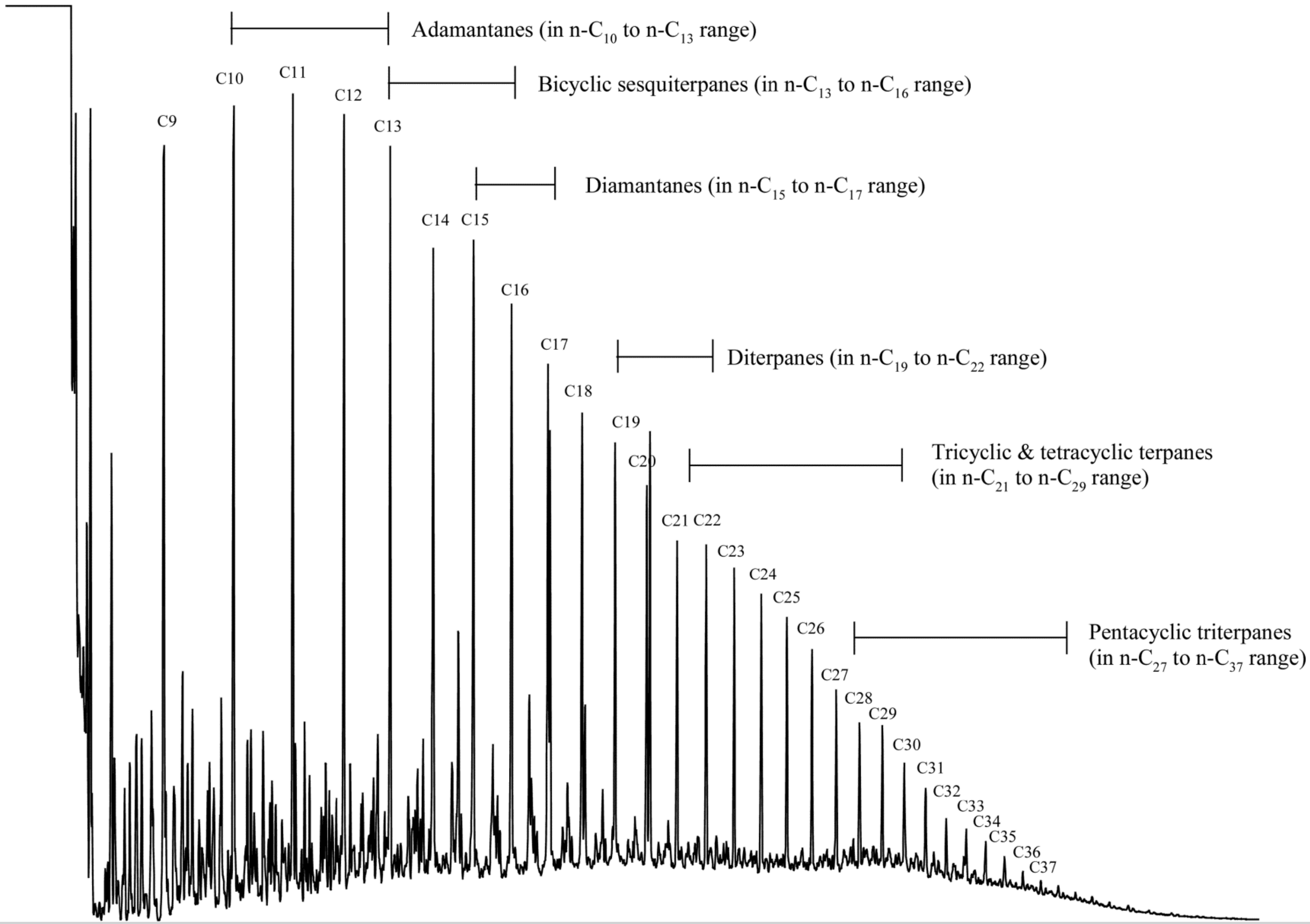
Tri- tetra- penta-cyclic terpanes (hopanes)



Hopanes Profiles Confirm Single Source

Crude Oil Characterization

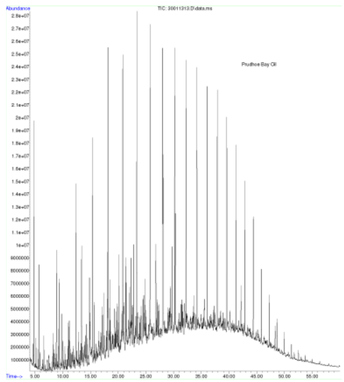
Known Biomarkers by Elution Range

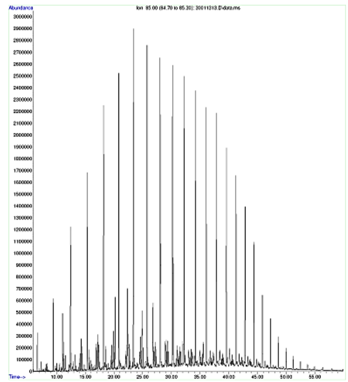


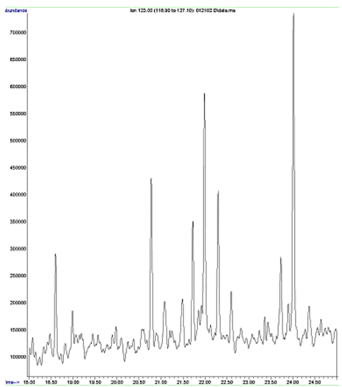
Source: Wang et al. Environmental Forensics 2006 , 7(2) 105-146

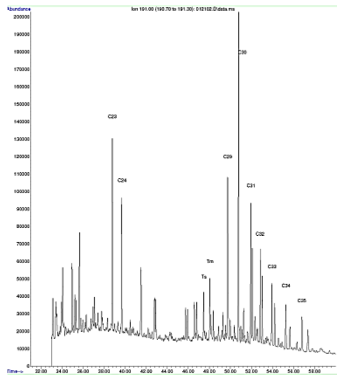
Biomarker Signatures in Crude Oils

Prudhoe Bay Oil

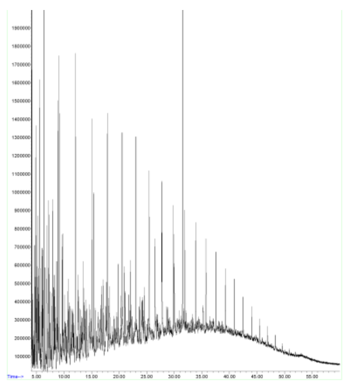


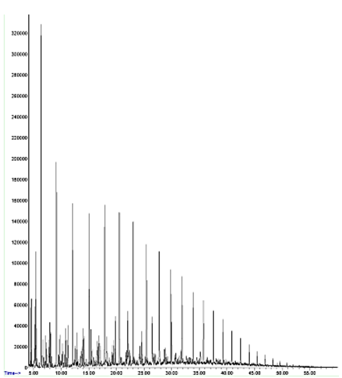


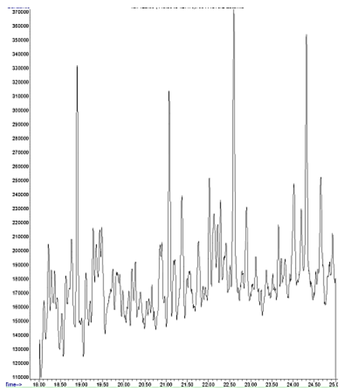


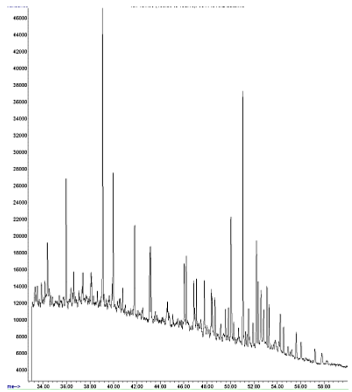


Bakken Light Crude









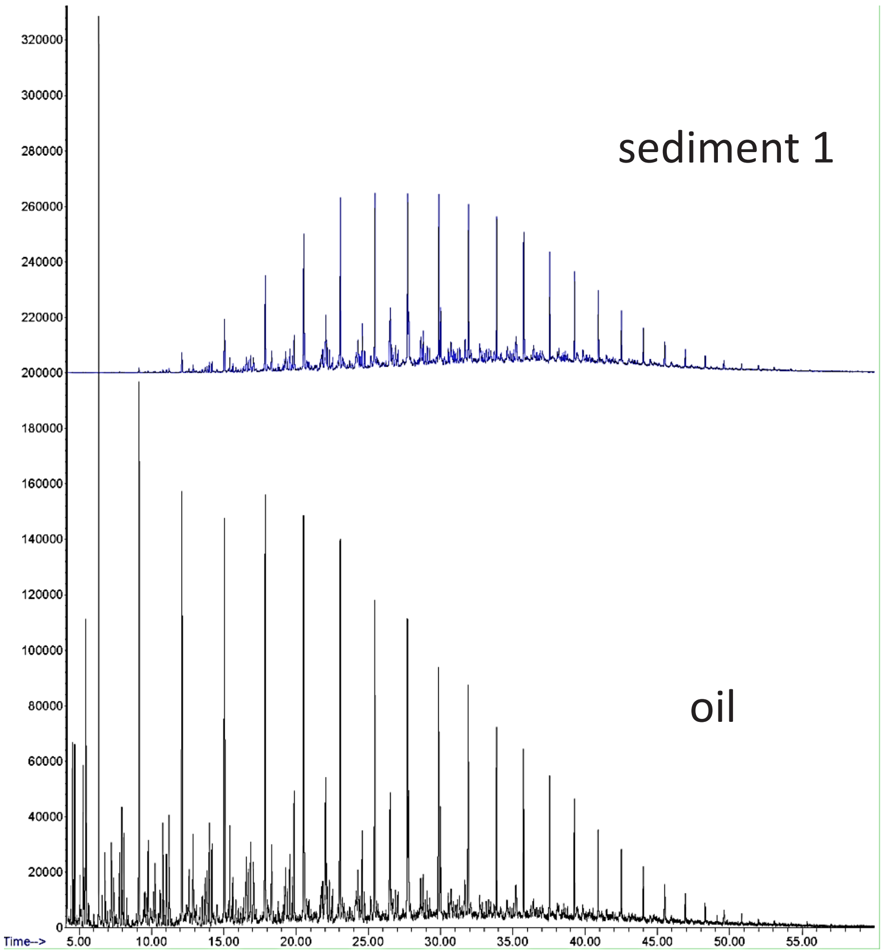
TIC (Scan)

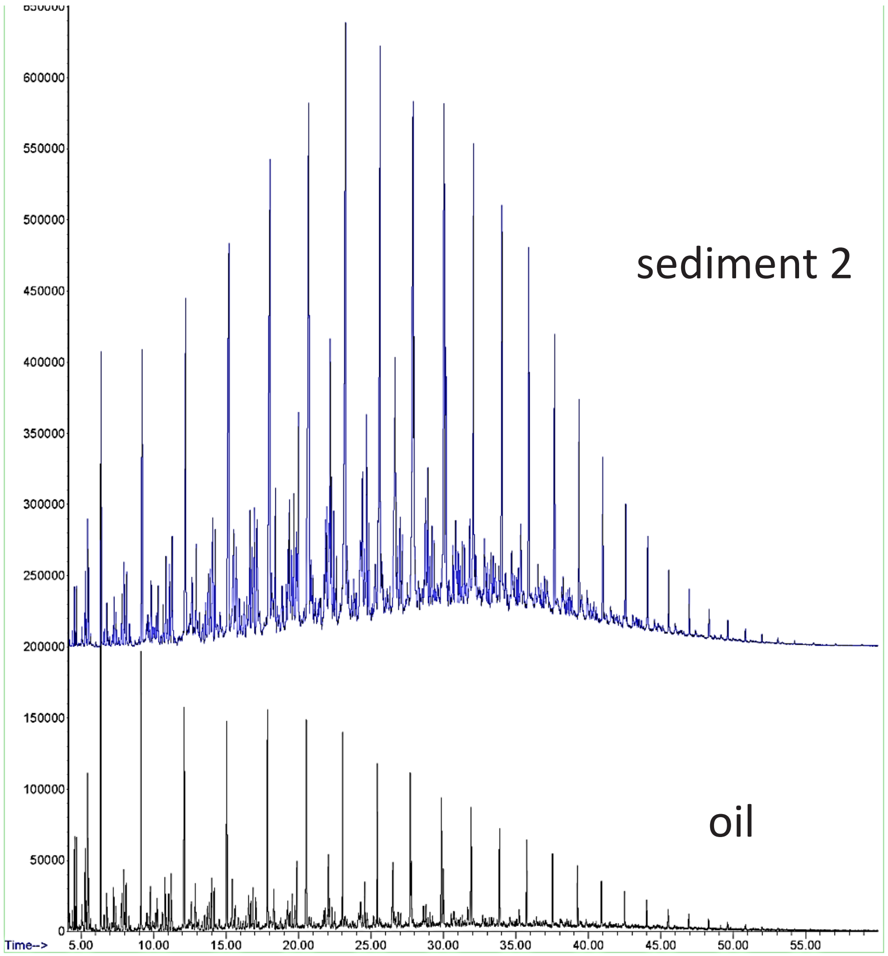
Alkanes/isoprenoids (Scan)

Bicyclic Sesquiterpanes (SIM)

Hopanes (SIM)

Light Crude Sediment Impacts

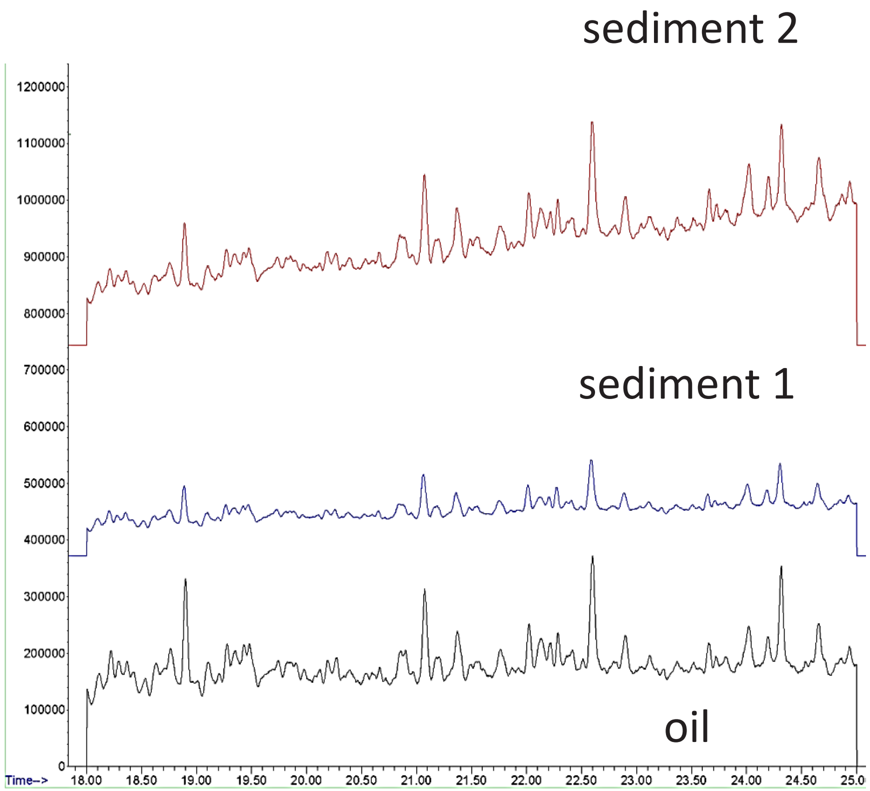




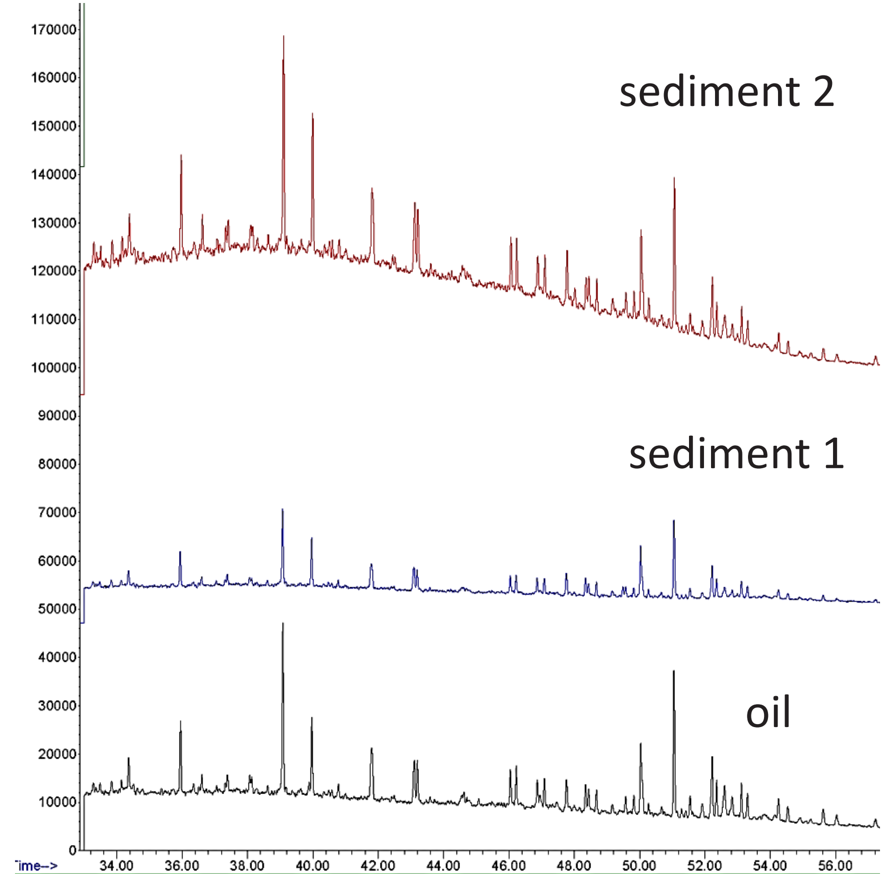
Alkanes / Isoprenoids - Good Correlations

Light Crude Sediment Impacts – cont.

Correlations Confirmed

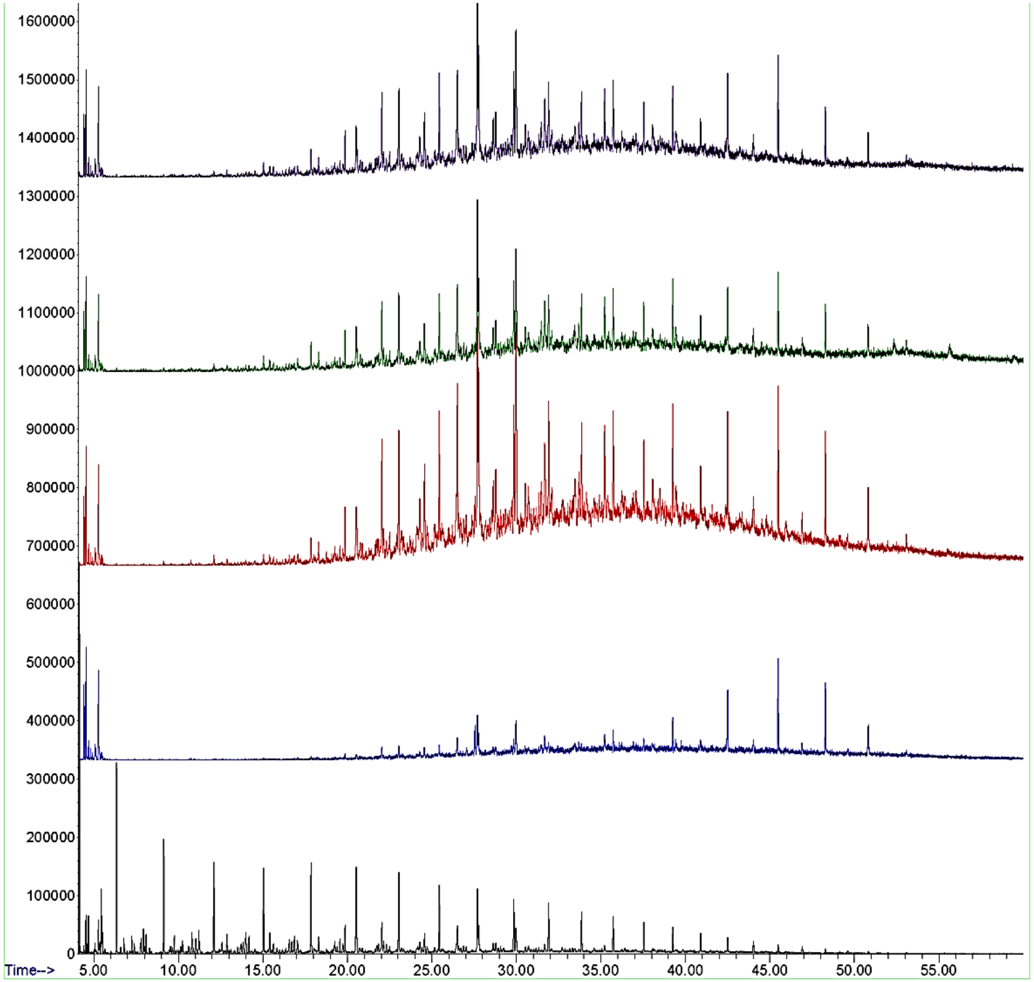


Bicyclic Sesquiterpanes



Hopanes

Additional High F2-F3 Impacted Sediments



m/z = 85
Alkanes
/Isoprenoids

Biogenic Hydrocarbon Signature

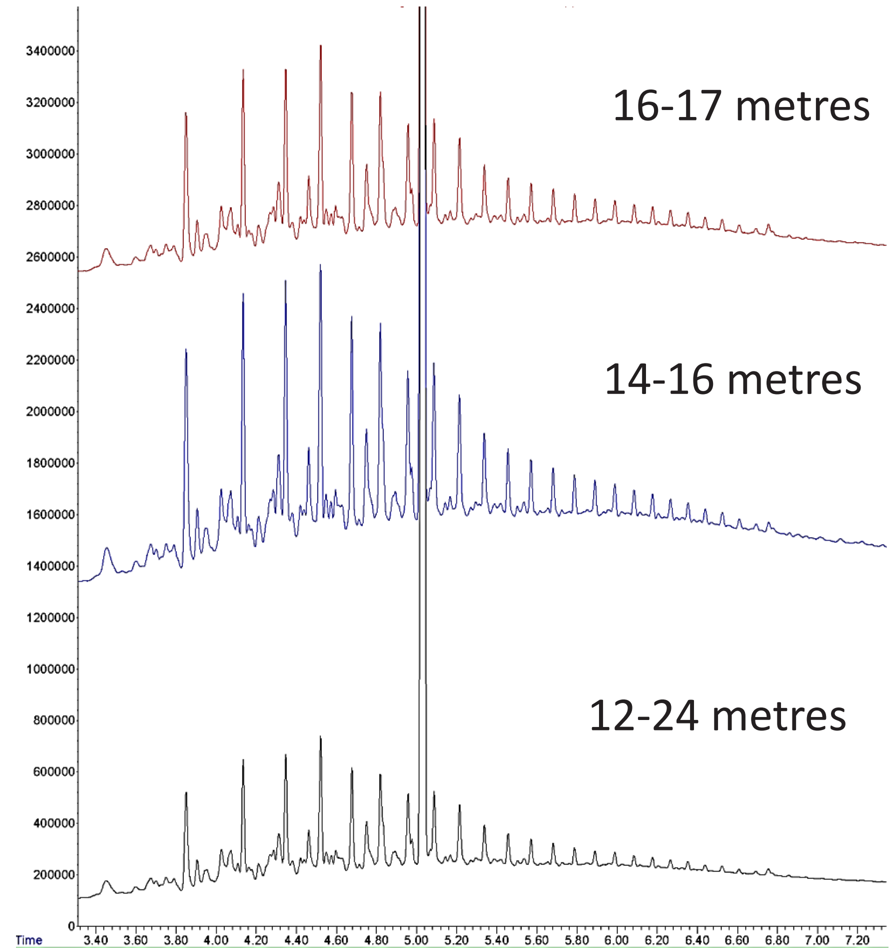
Unexpected hydrocarbons found at depth

Unexpected PHC hits found at depth

- 12-17 m below grade
- Soil at higher levels clean

Long industrial history at site but minimal PHC usage

- One long-term diesel/heating oil AST tank location



Crude Oil Signature!!

Natural Shale Oil Source!

- Literature search indicated naturally occurring crude oil deposits in the area at unusually shallow depths
- Excavated material still had to be treated as ‘hazardous’, but property owner not liable for site remediation.

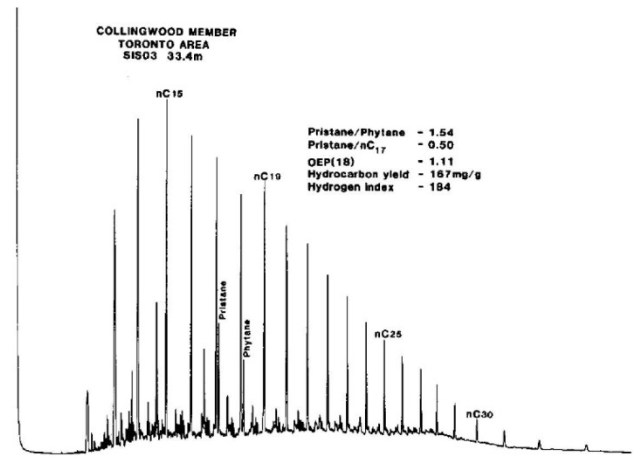


Figure 4: Saturate Fraction Gas Chromatogram – Ontario Oil Shale Formation (Collingwood Member)[6]

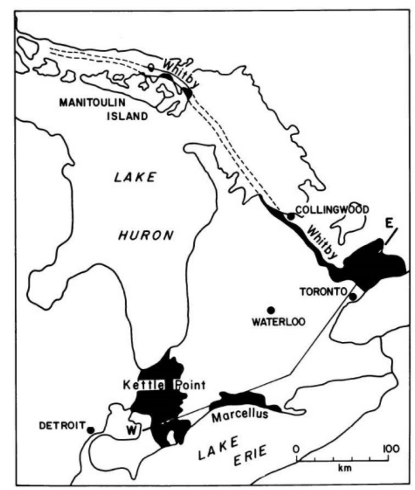


Figure 5: Locations of Paleozoic Black Shale in Ontario[7]

[6] Snowden, L.R.: *Bulletin of Canadian Petroleum Geology*. 32(3), 1984. pp. 327-334
[7] Barker, J.F. et.al.in *“Geochemistry and Chemistry of Oil Shales”*, American Chemical Society, Washington, DC, 1983. pp 119-138

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Summary

- Forensic investigations are often spurred from unexpected results during compliance monitoring (e.g. CCME hydrocarbons)
- CCME hydrocarbon test results are useful as a screening tool:
    - Reviewed in greater depth to answer some basic forensic questions
    - Point to the next appropriate forensic sampling/testing option
- In any forensic investigation, additional background information not normally collected during compliance monitoring is key to getting the best testing and data review
- Multiple lines of evidence are preferred to build a solid case in support of the investigative conclusions

Thank You!

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