



# FINGERPRINTING METHODS FOR “CSI” INVESTIGATIONS OF SPILLED OIL

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“The Reduced, The Reused, and The Recycled”  
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# OVERVIEW



- **Problem**
- **Understanding Used Oil**
- **Tiered Fingerprinting**
  - **Tier 1:** Chemical fingerprinting  
GC/FID
  - **Tier 2:** Chemical fingerprinting  
GC/MS
  - **Tier 3:** Isotopic fingerprinting
- **Case Studies**

# PROBLEM – in the World...

*“Fake car engine oil floods the market”* (Uganda)



*“A variety of fake car engine oil is being sold in shops and garages across the country, according to investigation done by oil companies.”*

***According to investigators, the fake oil is produced from waste lubricants and machine oil, which are bought cheaply from various fuel stations in Kampala and it is recycled and repackaged for sale as clean lubricants.”***

SOURCE:

TRUTH EVERYDAY

**Saturday Monitor** (Sat. March 28, 2015)

# PROBLEM – in the U.S.

## ***News12 New Jersey Honored with New York Emmy® Award Nomination for Story on "Bad Motor Oils"***

*February 17, 2015*



*“The New York Chapter of the National Academy of Television Arts and Sciences honored [News12 New Jersey](#) with 10 New York Emmy® Award nominations. One is for the excellent investigative reporting by News12's Walt Kane (Kane in Your Corner) on "[Bad Motor Oils Exposed](#).” News12 was the first station in the country to tackle this important issue. ”*



# PROBLEM — in the U.S.

## *“Illegal dumping runneth over”*



*“Illegal dumping runneth over Avon Park public safety director Jason Lister shows a motor oil bottle that was left behind in an illegal dump in Avon Park Lakes. In addition to being unsightly, dumping can be dangerous for the environment and wildlife.”*

<http://highlandstoday.com/hi/local-news/illegal-dumping-runneth-over-20150307/#sthash.kxtZVGII.dpuf>

*SOURCE: Highlands Today, March 28, 2015*

# PROBLEM - OVERVIEW

- **Illegal dumping**

- On land and water
- Frequent small chronic spillages of used lube oil worldwide (several million tons yearly)

- **Illegal activities**

- Fake, used or waste lube oils adulteration into lube oils to extend volume sold

- **Contaminated oil loads/Commingled oil**



# USED MOTOR OIL COMPOSITION

## Saturated Hydrocarbons (73-80%)

- Alkanes (Parrafins)
- Isoalkanes (Isoparrafins)
- Cycloalkanes (Naphthenes)

## Aromatic Hydrocarbons & polar compounds

- Monoaromatic (11-15%)
- PAHs (Parent and Alkylated)

## Lubrication additives (20%)

- Detergents & dispersants (2-15%)
- Zinc diaryl
- Molibdenum disulfide
- Zinc dithiophosphate
- Other organometallic compounds

## Metals

- Pb, Zn, Ca, Ba, Mg (higher)
- Fe, Na, Cu, Al, Cr, Mn, K, Ni, Sn, Si, B (lower)

## Other compounds/contaminants

- Gasoline, Diesel
- Ba, P, Cl, Br, Si
- PCBs (in the past)





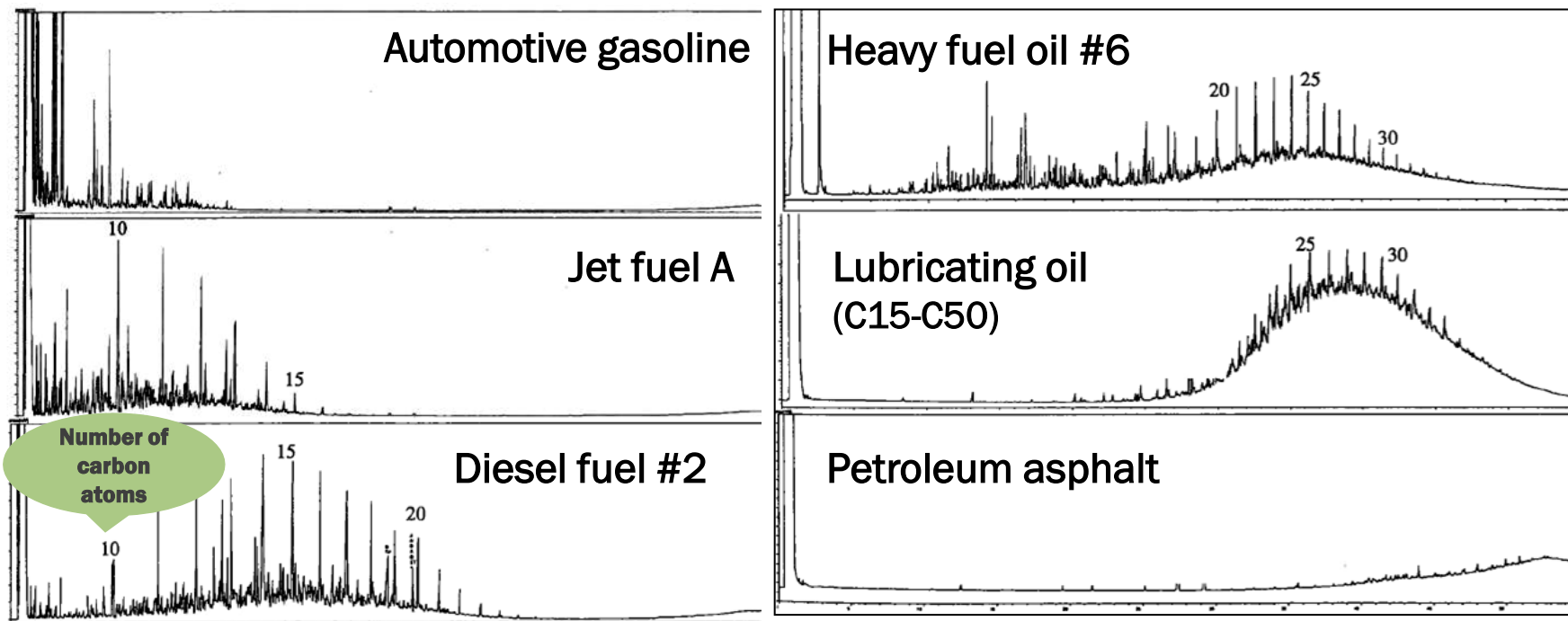
# ANALYTICAL DETECTION PRINCIPLE

## Separation Equipment coupled with/**Detector** Gas Chromatograph (GC)/ **Flame Ionization Detector (FID)** **Mass Spectrometer (MS)**

- Individual compounds are separated based on their mass fragments and elute from chromatographic column at distinct times
- The separated compounds enter in the detector unit:
  - **Tier 1** – GC/FID or GC/MS (TIC – Total Ion Mass Chromatogram): captures **all organic compounds**
  - **Tier 2** – GC/MS (Selected Ion Monitoring - SIM mode): captures **selected classes of compounds**
  - **Tier 3** – GC/IRMS (compound specific isotopic analysis): captures **isotopic signatures** of compounds – highly specialized characterization

# TIER 1 DATA

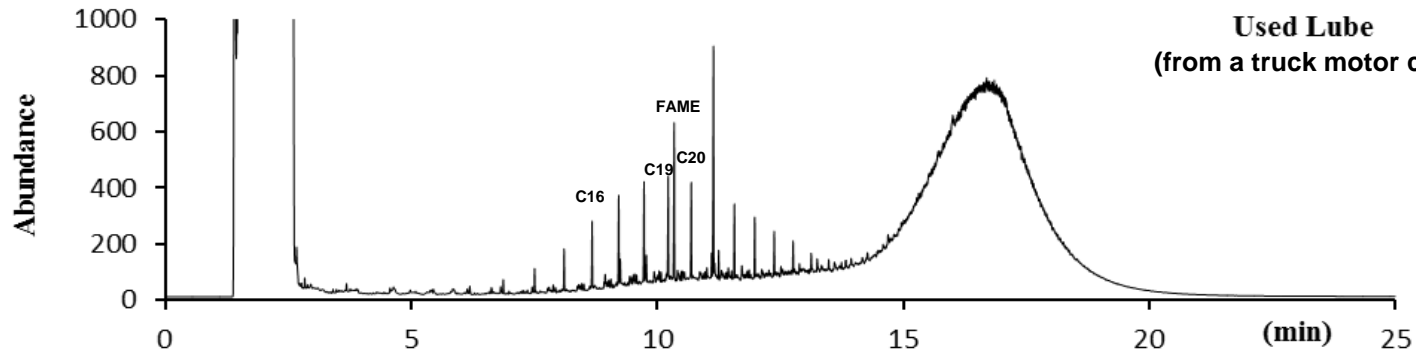
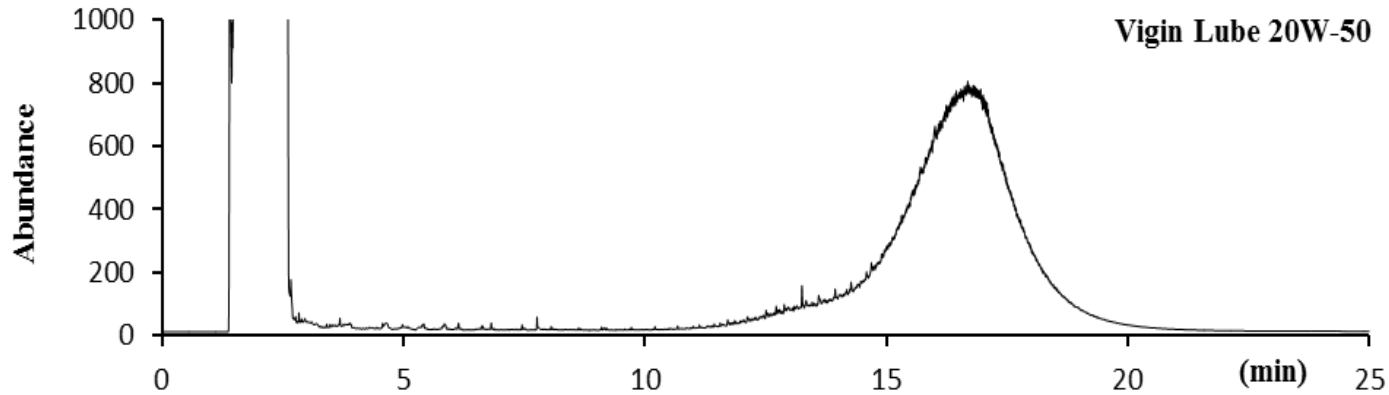
## TIC - Distinguish Between Main Types of Petroleum Products



Source: Wang, Z. and Stout, S. (Ed.) 2007. Oil Spill Environmental Forensics – Fingerprinting and Source Identification. Elsevier Academic Press, ISBN 13: 978-0-12-369523-9

# TIER 1 DATA

## TIC – Help Distinguish Between Virgin and Used Motor Oils & Provide Source Info



FAME = fatty acid methyl esters – from biodiesel engines

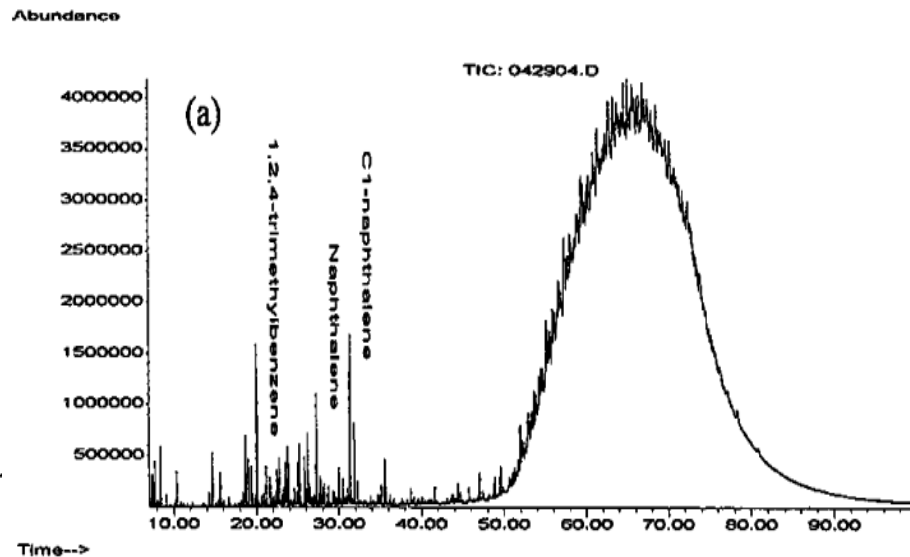
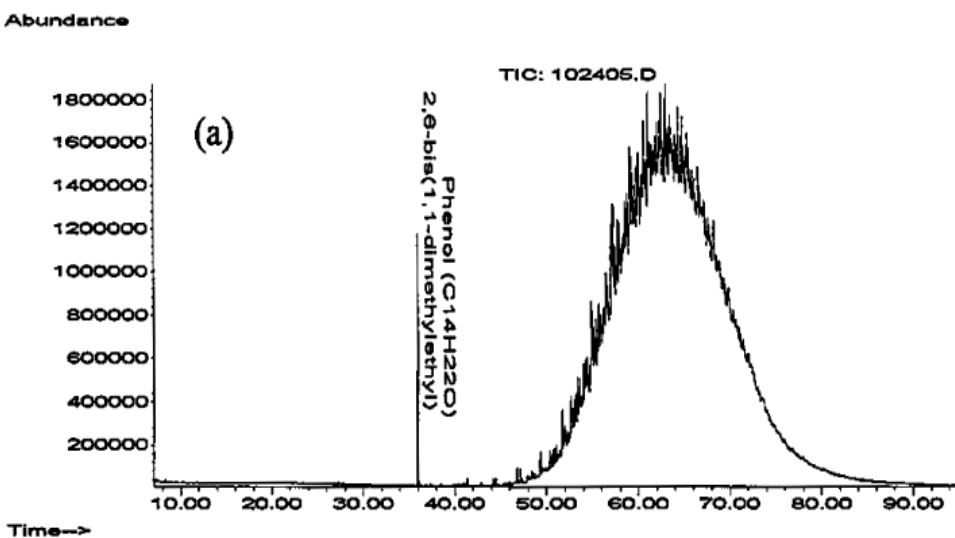
Source: Chun et al. 2015. Fingerprinting Analysis and Differentiation of Virgin and Used Lubricating Oils. AMOP 2015 Proceeding Volume

# TIER 1 DATA

## TIC - Help Distinguish Between Virgin and Used Motor Oils & Provide Source Info

*Unused Pennzoil motor oil*

*Used Pennzoil motor oil*



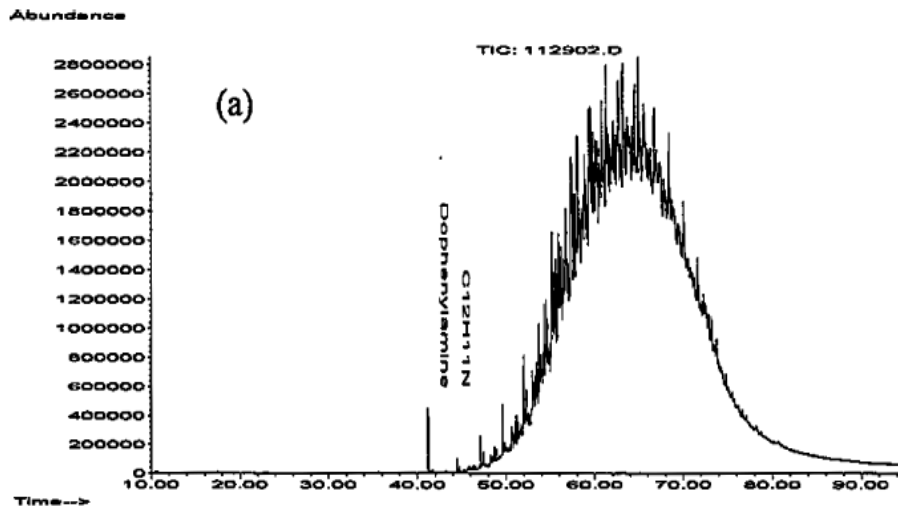
Source: Lu, S-T and Kaplan, I. 2008. Characterization of Motor Lubricating Oils and Their Oil-Water Partition, *Environmental Forensics* 9:4, 295-309.



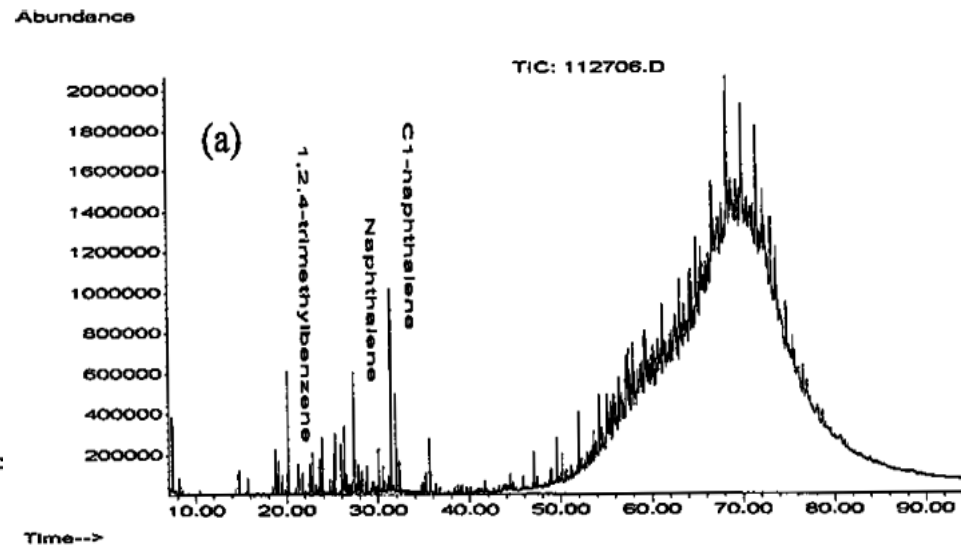
# TIER 1 DATA

## TIC - Help Distinguish Between Virgin and Used Motor Oils & Provide Source Info

*Unused Mobil motor oil*



*Used Mobil motor oil*

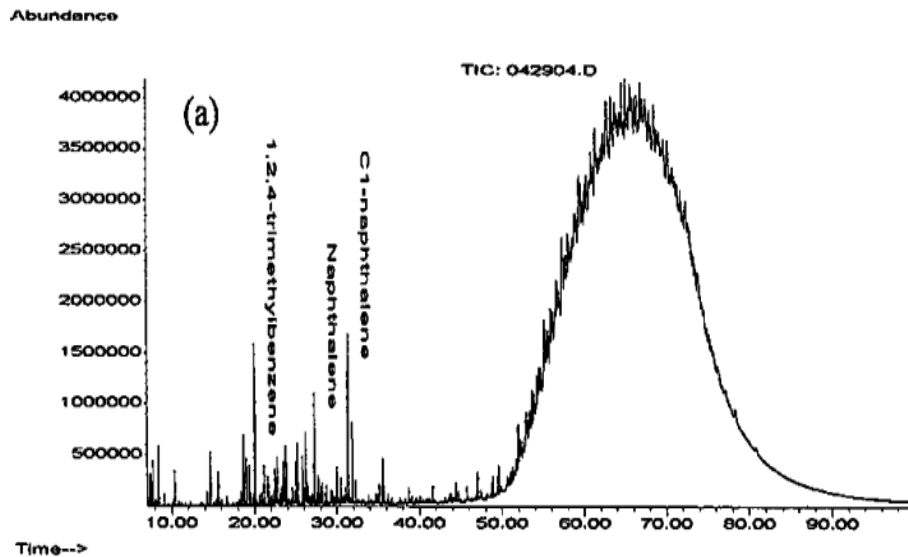


Source: Lu, S-T and Kaplan, I. 2008. Characterization of Motor Lubricating Oils and Their Oil-water Partition, *Environmental Forensics* 9:4, 295-309.

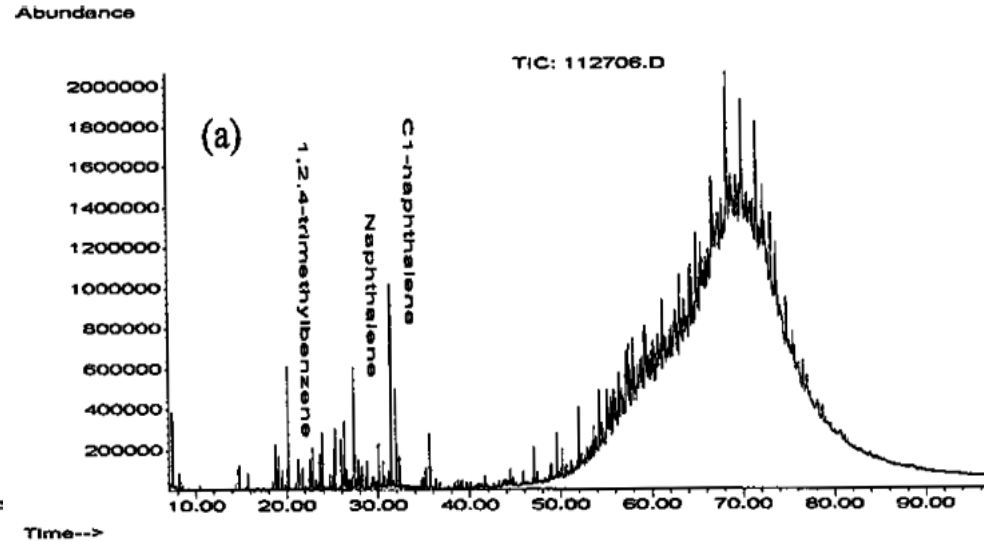
# TIER 1 DATA

## TIC - Help Distinguish Between Used Motor Oils

*Used Pennzoil motor oil*



*Used Mobil motor oil*



# TIER 2 DATA - PAHS

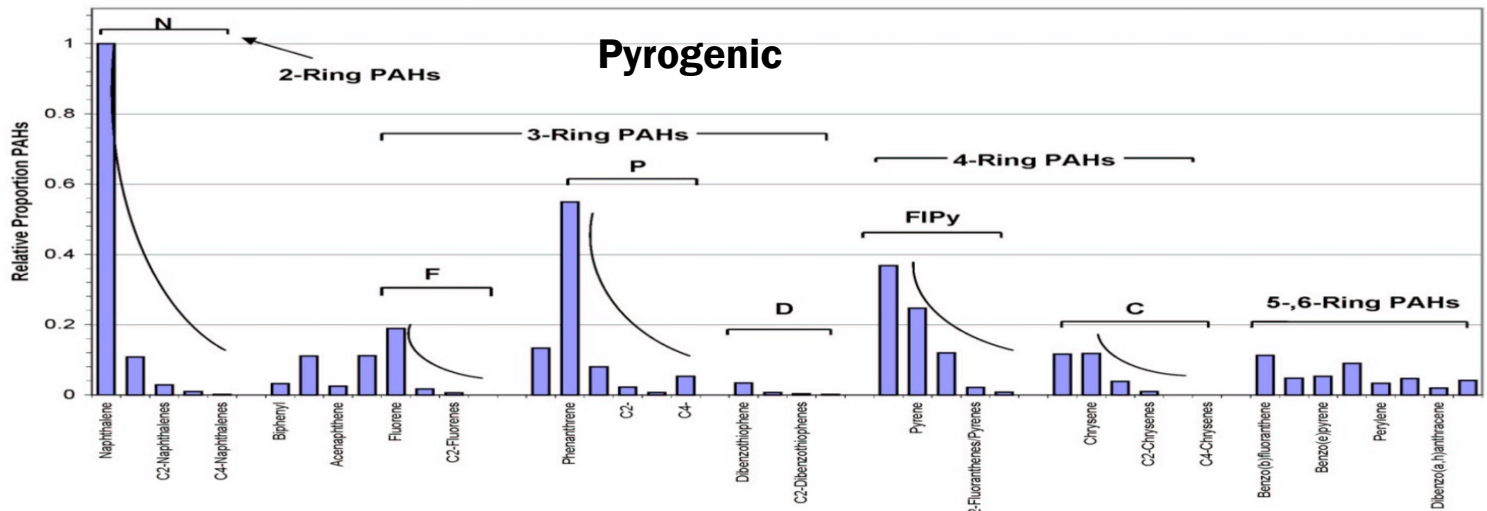
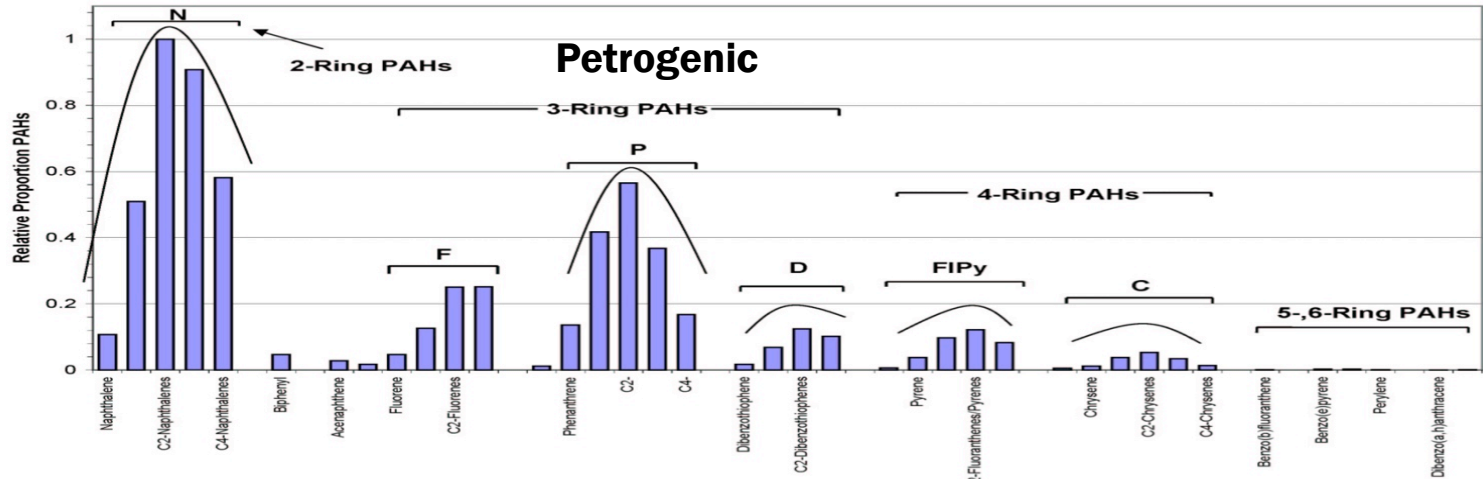
## PAHs To Be Analyzed in Forensic Investigations by GC/MS SIM

Compound Name	Abbrev	RF	Compound Name	Abbrev	RF
Decalins ( <i>cis</i> - and <i>trans</i> -)	d0	d0	Dibenzothiophene	D0	D0
C1-decalins	d1	d0	C1-dibenzothiophenes	D1	D0
C2-decalins	d2	d0	C2-dibenzothiophenes	D2	D0
C3-decalins	d3	d0	C3-dibenzothiophenes	D3	D0
C4-decalins	d4	d0	C4-dibenzothiophenes	D4	D0
Benzo(b)thiophene	BT0	BT0	Fluoranthene	FL	FL
C1-benzo(b)thiophenes	BT1	BT0	Benzo[b]fluorene	BF	BF
C2-benzo(b)thiophenes	BT2	BT0	Pyrene	PY	PY
C3-benzo(b)thiophenes	BT3	BT0	C1-fluoranthenes/pyrenes	FP1	FL
C4-benzo(b)thiophenes	BT3	BT0	C2-fluoranthenes/pyrenes	FP2	FL
Naphthalene	N0	N0	C3-fluoranthenes/pyrenes	FP3	FL
C1-naphthalenes	N1	N0	Benz(a)anthracene	BaA	BaA
C2-naphthalenes	N2	N0	Chrysene	C0	C0
C3-naphthalenes	N3	N0	C1-chrysenes	C1	C0
C4-naphthalenes	N4	N0	C2-chrysenes	C2	C0
Biphenyl	Bph	Bph	C3-chrysenes	C3	C0
Acenaphthylene	AcI	AcI	C4-chrysenes	C4	C0
Acenaphthene	Ace	Ace	Benzo(b)fluoranthene	BbF	BbF
Dibenzofuran	DdF	DdF	Benzo(j/k)fluoranthene	BjkF	BjF
Fluorene	F0	F0	Benzo(a)fluoranthene	BaF	BaF
C1-fluorenes	F1	F0	Benzo(e)pyrene	BeF	BeF
C2-fluorenes	F2	F0	Benzo(a)pyrene	BaP	BaP
C3-fluorenes	F3	F0	Perylene	Per	Per
Anthracene	AN	AN	Indeno(1,2,3-c,d)pyrene	ID	ID
Phenanthrene	P0	P0	Dibenz(a,h)anthracene	DA	DA
C1-phenanthrenes/anthracenes	P1	P0	Benzo(g,h,i)perylene	BgP	BgP
C2-phenanthrenes/anthracenes	P2	P0			
C3-phenanthrenes/anthracenes	P3	P0			
C4-phenanthrenes/anthracenes	P4	P0			

RF - response factor based upon listed compound

# TIER 2 DATA - PAHS

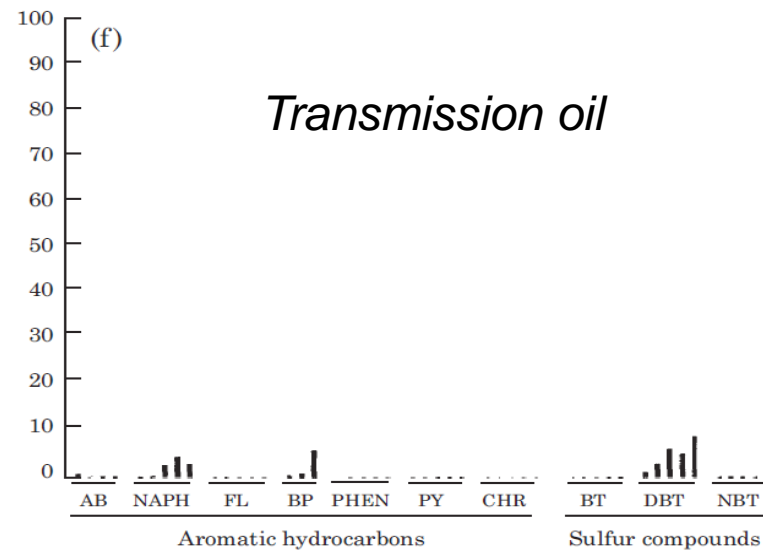
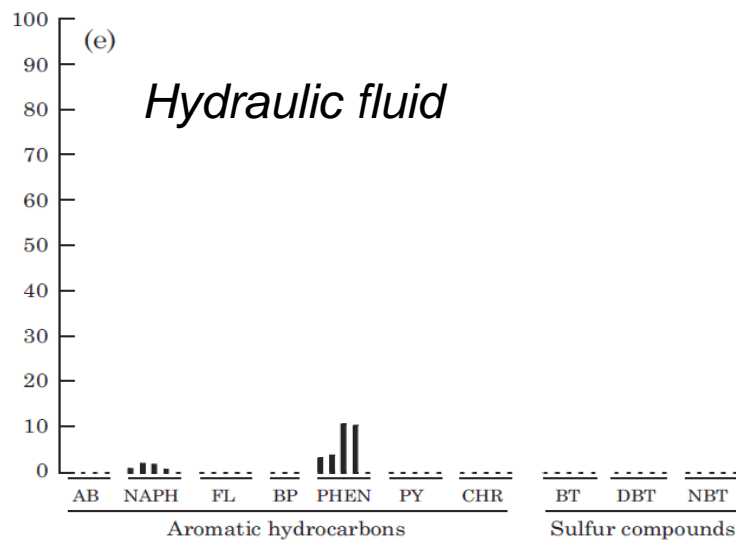
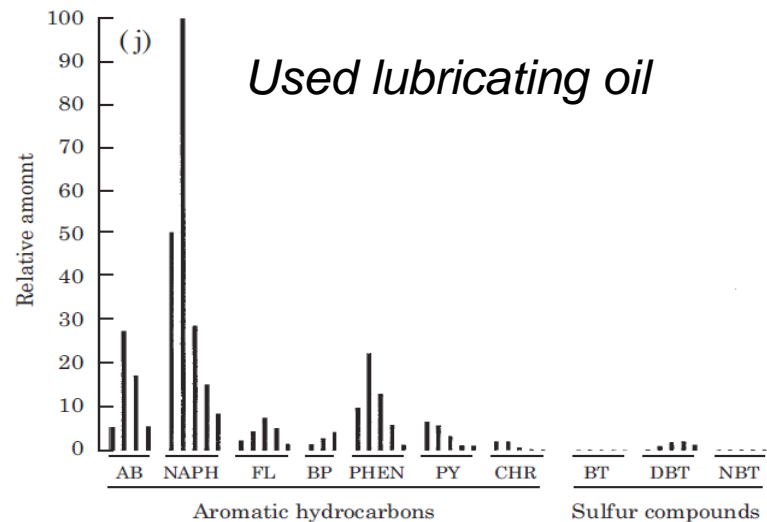
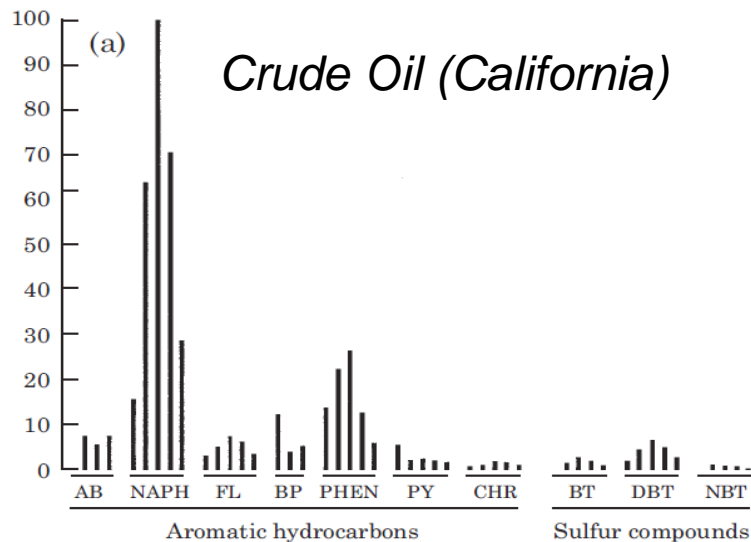
## PAH Profiles - Distinguish Petrogenic Vs. Pyrogenic Sources





# TIER 2 DATA - PAHS

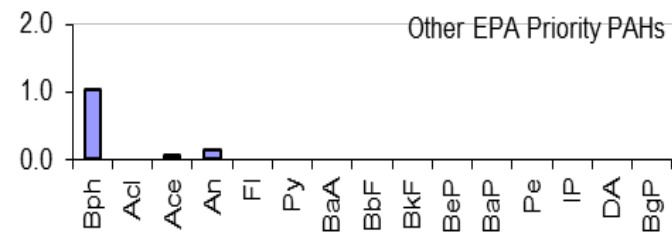
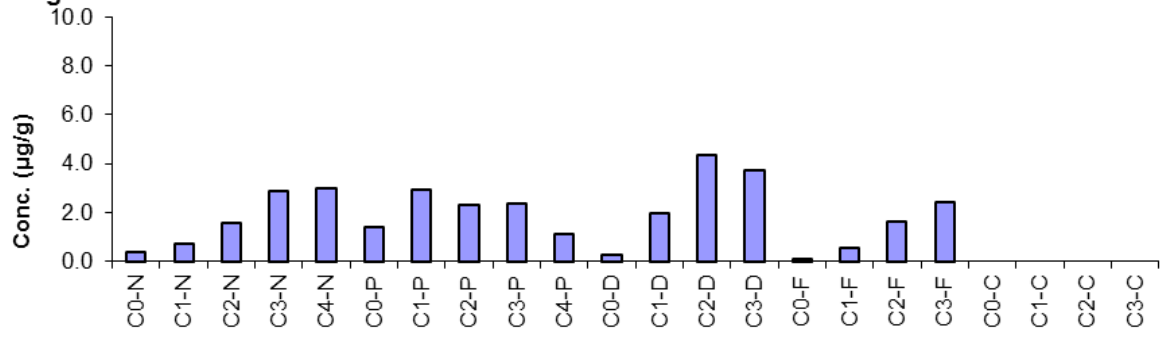
## PAH Profiles - Help Distinguish Types of Petroleum Product



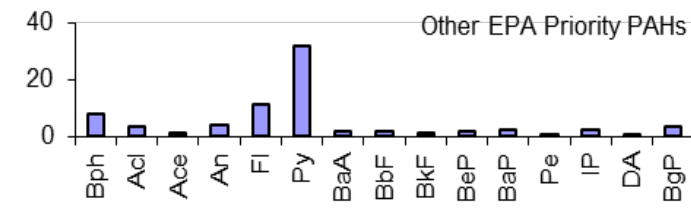
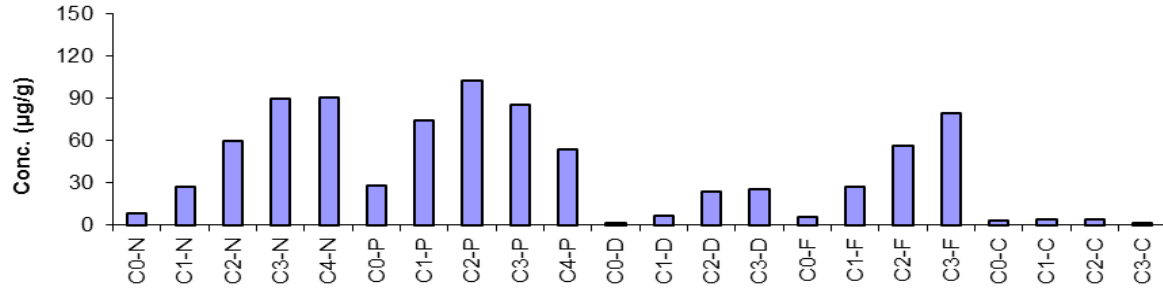
# TIER 2 DATA - PAHS

## PAH Profiles - Help Distinguish Between Virgin and Used Motor Oils

Virgin Lube



Used Lube



Source: Chun et al. 2015. Fingerprinting Analysis and Differentiation of Virgin and Used Lubricating Oils. AMOP 2015 Proceeding Volume

# TIER 2 DATA - BIOMARKERS

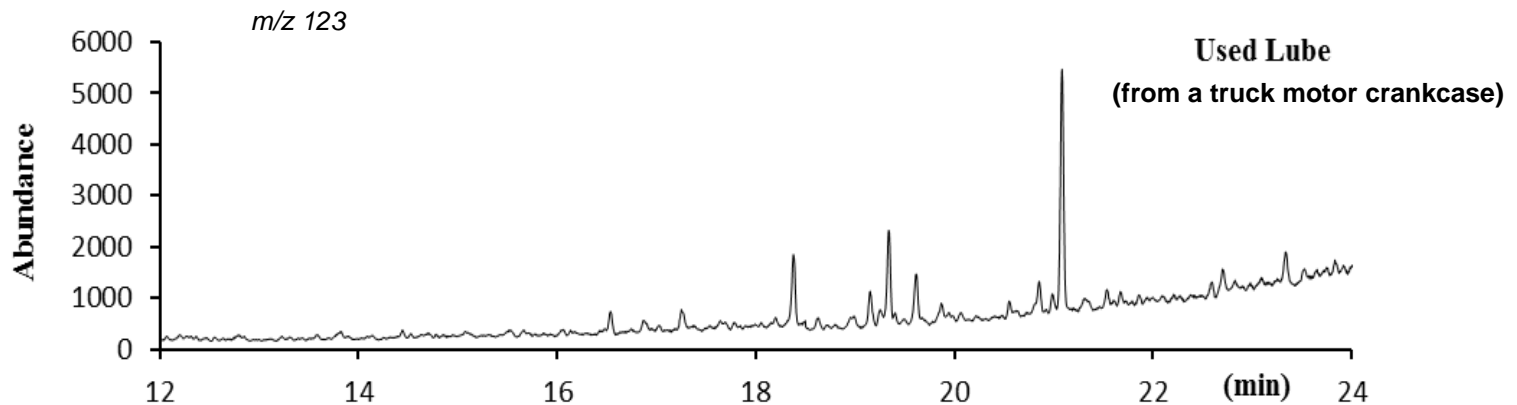
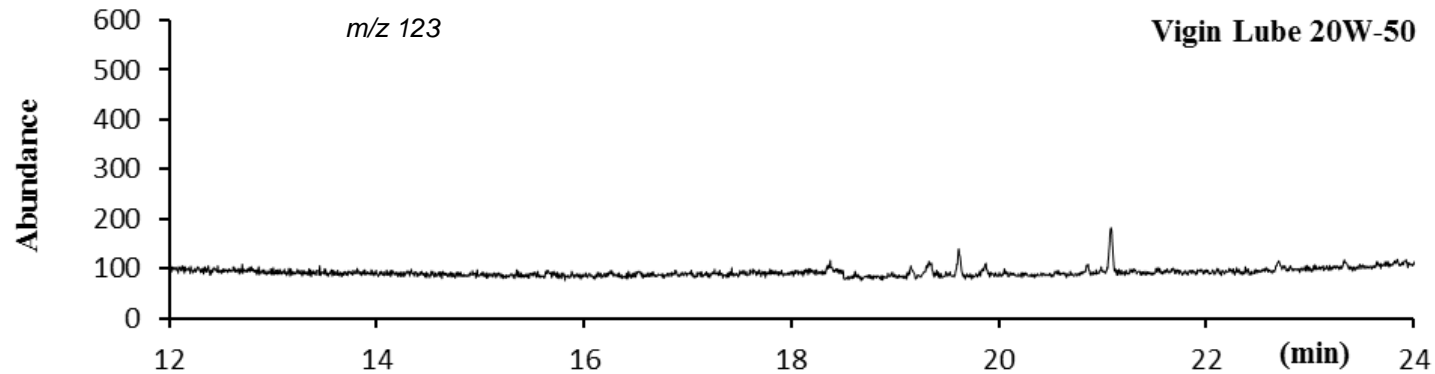
## Biomarker Classes To Be Analyzed in Forensic Investigations by GC/MS SIM

Common biomarker compound class	Approximate carbon boiling range	Mass spectral fragment ions
<i>n</i> -Alkanes	C1 to C45*	<i>m/z</i> 85
Acyclic isoprenoids	C12 to C19	<i>m/z</i> 113
Bicyclic sesquiterpanes	C13 to C17	<i>m/z</i> 123
Diterpanes	C19 to C24	<i>m/z</i> 191
Extended tricyclic terpanes	C18 to C26	<i>m/z</i> 191
Tetracyclic terpanes	C22 to C23	<i>m/z</i> 191
25-norhopanes (10-desmethylhopanes)	C25 to C33	<i>m/z</i> 177
Pentacyclic triterpanes	C26 to C34	<i>m/z</i> 191
Diasteranes	C23 to C26	<i>m/z</i> 217
Regular steranes	C25 to C29	<i>m/z</i> 217 and 218
C-Ring monoaromatic steranes	C23 to C26	<i>m/z</i> 253
Triaromatic steranes	C26 to C29	<i>m/z</i> 231

*Environmental Forensics*, 6:241–251, 2005

# TIER 2 DATA - BIOMARKERS

## Sesquiterpanes - Help Distinguish Between Some Virgin and Used Motor Oils



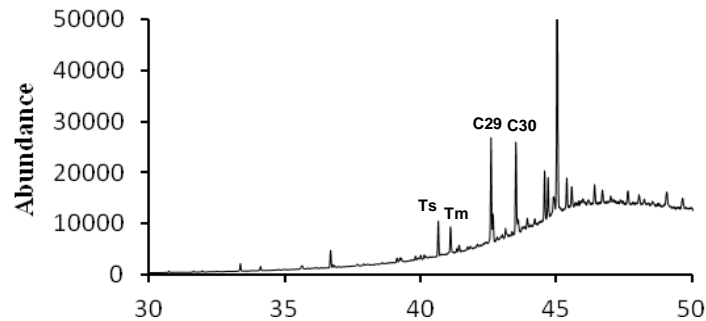
Source: Chun et al. 2015. Fingerprinting Analysis and Differentiation of Virgin and Used Lubricating Oils. AMOP 2015 Proceeding Volume



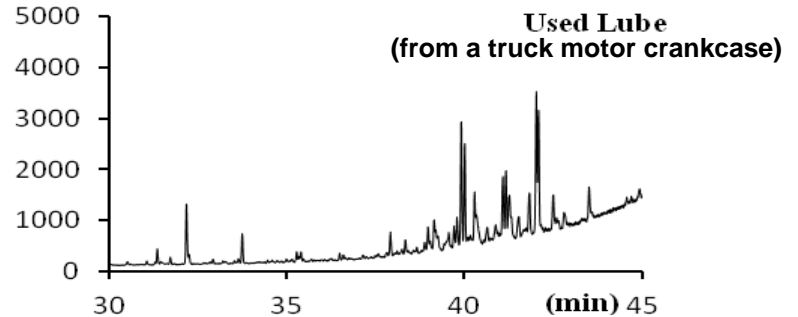
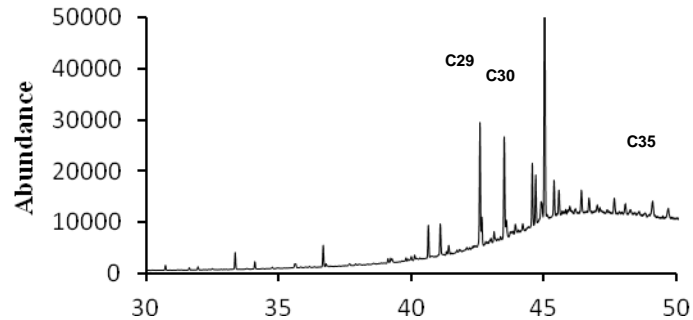
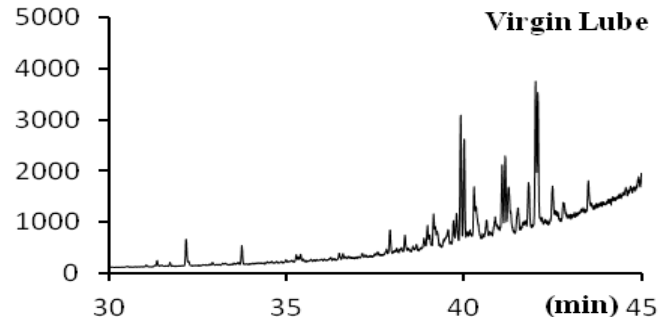
# TIER 2 DATA - BIOMARKERS

## Hopanes and Steranes - May NOT Distinguish Virgin from Used Motor Oils

Hopanes m/z 191



Steranes m/z 218

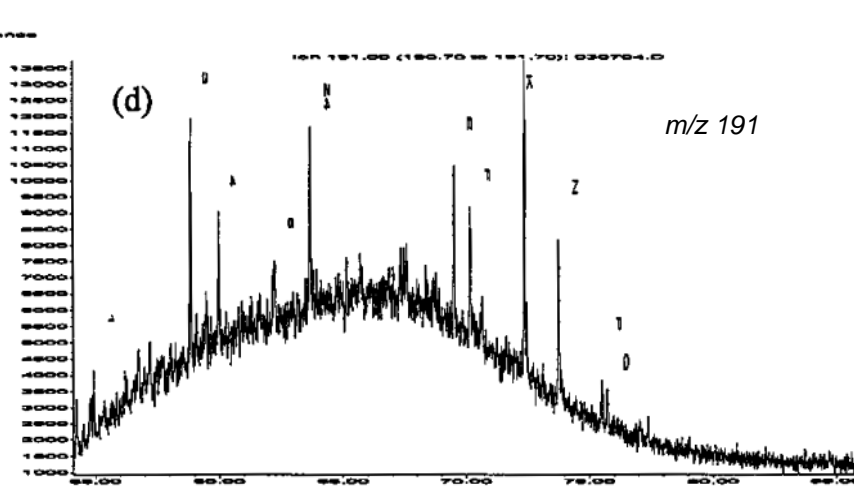


Source: Chun et al. 2015. Fingerprinting Analysis and Differentiation of Virgin and Used Lubricating Oils. AMOP 2015 Proceeding Volume

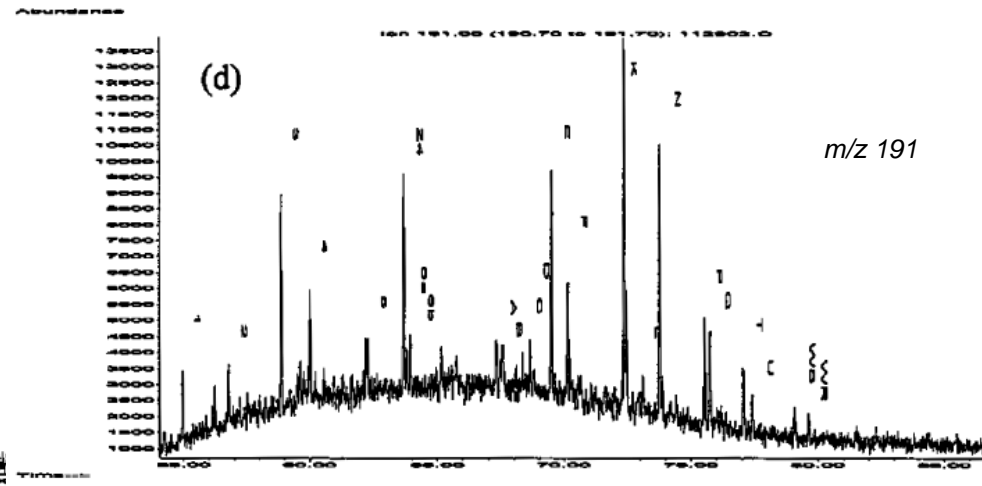
# TIER 2 DATA - BIOMARKERS

## Hopanes - Help Distinguish Between Potential Sources of Motor Oils

*Pennzoil motor oil*



*Mobil motor oil*

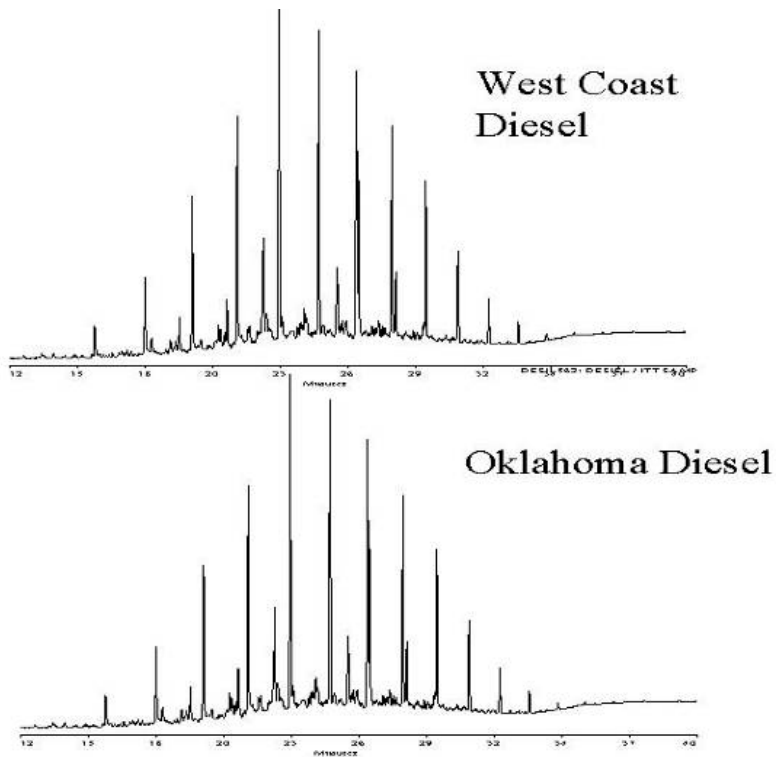


Source: Lu, S-T and Kaplan, I. 2008. Characterization of Motor Lubricating Oils and Their Oil-Water Partition, *Environmental Forensics* 9:4, 295-309.

# TIER 1 AND TIER 3 DATA

## Example - Targeted Fingerprinting

### Tier 1 Data: Chemical Fingerprinting (TIC)



### Tier 3 Data: Isotopic Fingerprinting (CSIA for isoprenoids)

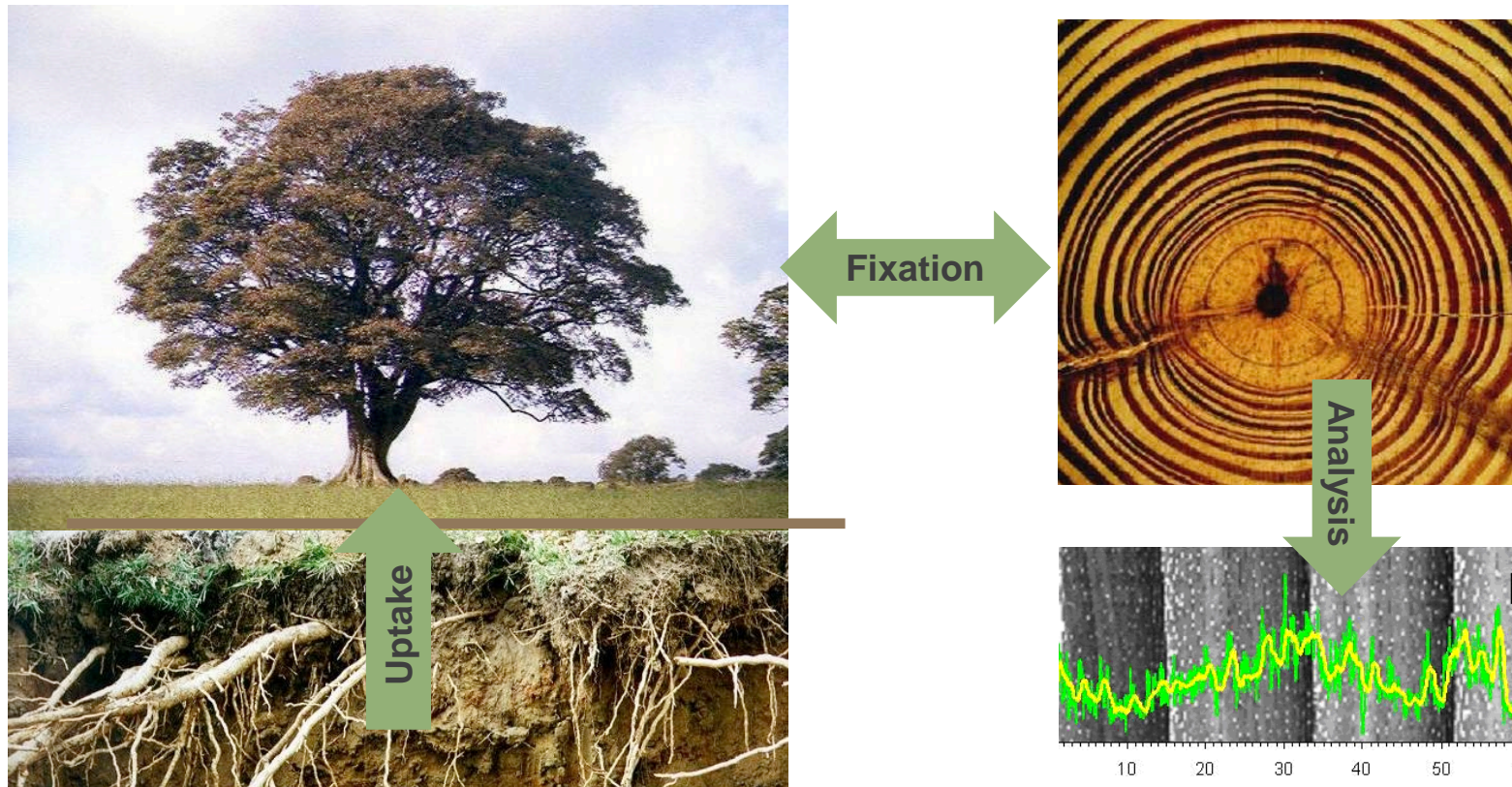


Source: EPA. 2010. Applications of Stable Isotope Analyses to Environmental Forensics (Part 3) and to Understand Degradation of Chlorinated Organic Compounds. CLU-IN Internet Seminar. Presented by Paul Philp

# TREE RING FINGERPRINTING

## Dendroecology – Tracking Contamination in the Tree Rings

Contamination in the root zone may affect both ring width and chemical composition.





# THE FORENSIC APPROACH

- Use of increment borers
- Sample is dried
- Sample is progressively sanded
- Sample is grooved on wooden block
- Sample is analyzed for:
  - Width of rings
  - Chemical element composition of rings (through EDXRF or other techniques)

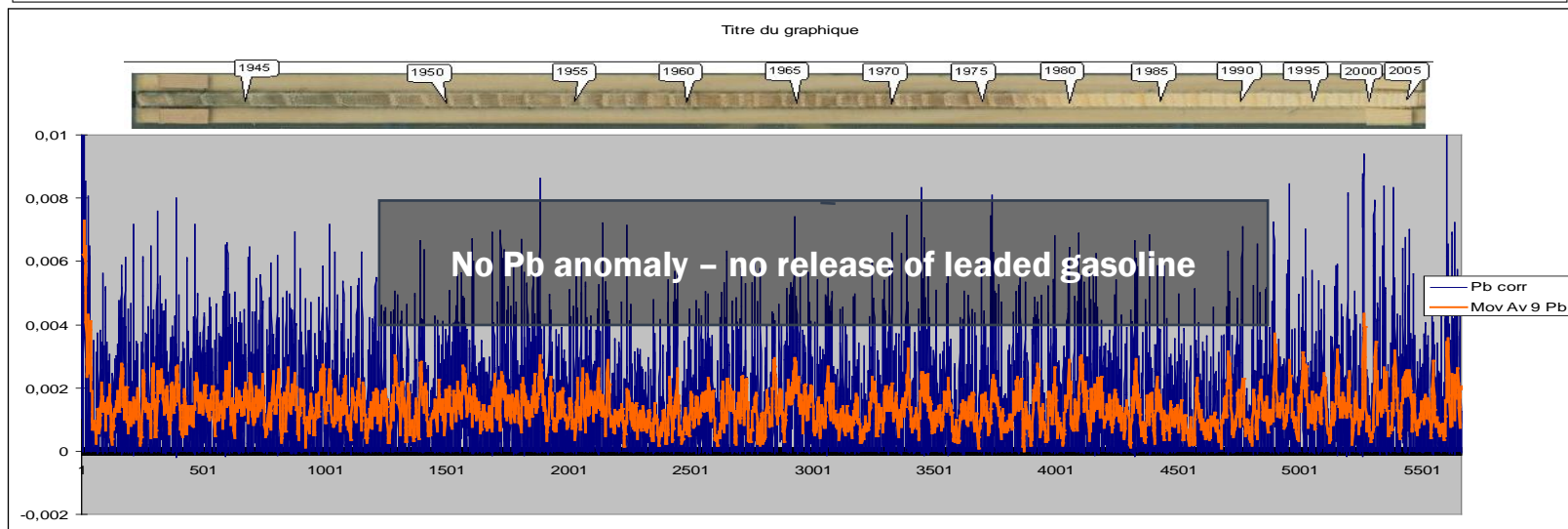
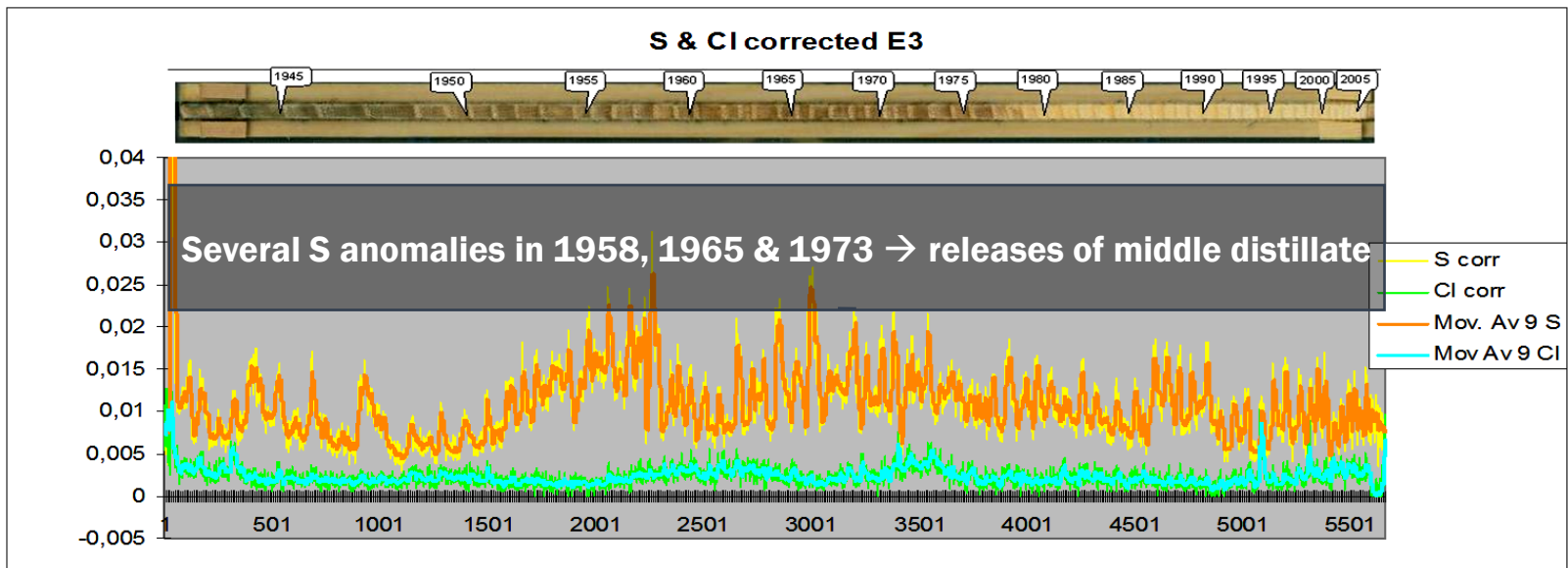


# APPLICATIONS

- Insurance cost-recovery:
  - Age-dating to the year
  - Type of release(s)
- Distinguish multiple releases
- Sustainable site characterization
- Remedial design
- **Provides information when none is available**



# RESULTS EXAMPLE-TREE WITHIN A DIESEL PLUME



# TREE RING FINGERPRINTING

*Trees and other living organisms may retain the effects of contaminants passage over a long time, providing **accurate and defensible** evidence about the environmental history of a site.*

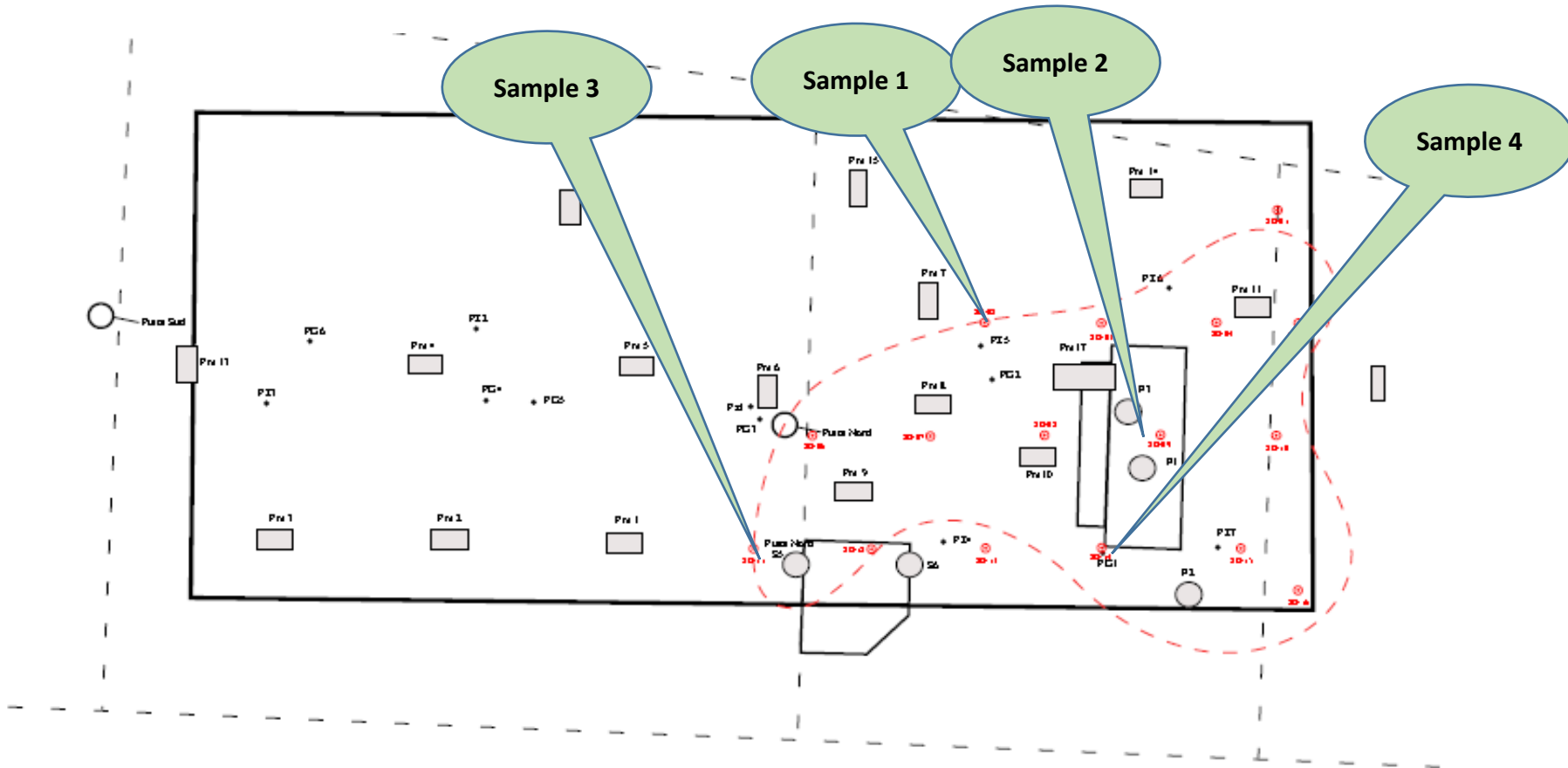


# CASE STUDY 1: INVESTIGATING THE TYPE AND SOURCE OF PETROLEUM PRODUCTS IN SOIL AT LYON AUTO PARK, LYON, FRANCE

- Site located in a redevelopment area – previously used:
  - North part - by a major oil company as service station
  - South part – by a chemical plant
- Construction of an underground parking revealed the presence of petroleum contamination in soil
- Hydrocarbons in soil ranged 11,000-46,000 mg/Kg
- An oil pipeline was discovered containing heavy (lubricating) oil
- **CHALLENGE: evaluate the sources of hydrocarbons in soil and potentially recover the costs from responsible parties**

# FORENSIC SAMPLING PLAN

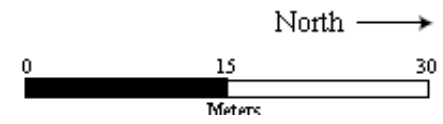
(proposed samples – in red; shown samples – selected for fingerprinting)



30m Grid (16 borings to 7m)

Potential Monitoring Well Location

Potential Soil Boring Location





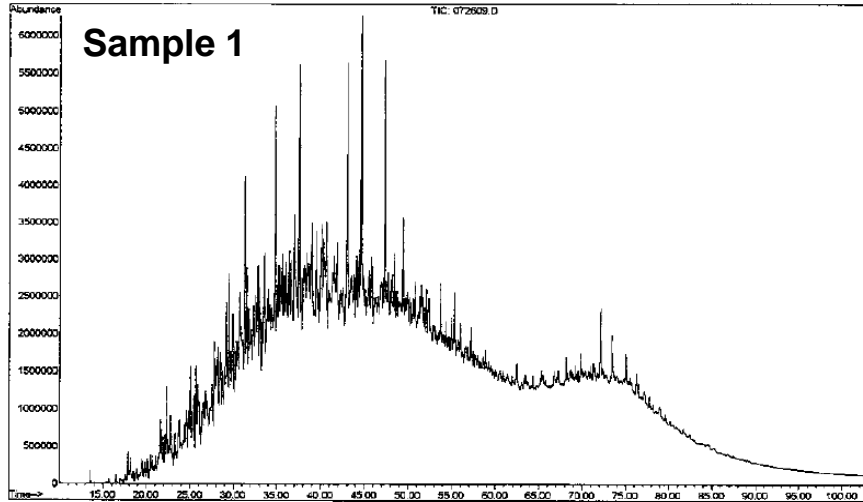
# METHODS

**Table 1. Specific chromatograms generated for fingerprinting analysis**

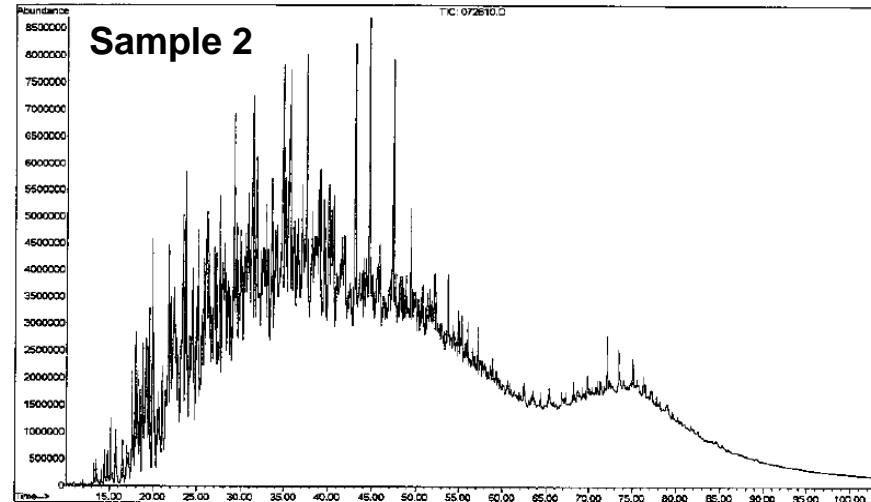
<b>ION (M/Z)</b>	<b>COMPOUND CLASS</b>
TIC	All Compounds
85	n-Alkanes
113	Iso-Alkanes and Isoprenoids
83	Alkylcyclohexanes
134	C <sub>4</sub> -benzenes
123	Bicyclanes
191	Terpanes
217	Steranes
253	Monoaromatic Steranes
231	Triaromatic Steranes
Bar Diagram	Aromatic Hydrocarbon Distribution

# TIER 1 RESULTS: TIC (TOTAL ION CHROMATOGRAM)

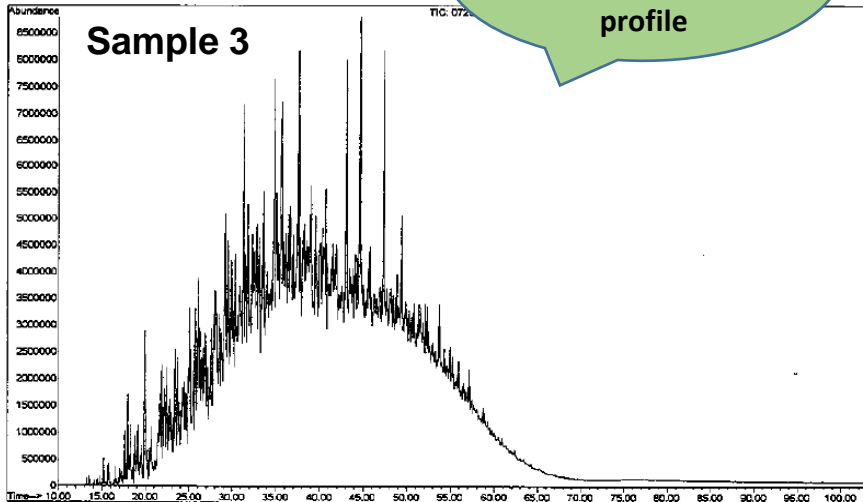
Sample Name: 6F5379-02 (40156-1) soil extract  
Misc Info : Lyon Park Auto, Adamas Law firm



Sample Name: 6F5379-19 (40156-3) soil extract  
Misc Info : Lyon Park Auto, Adamas Law firm

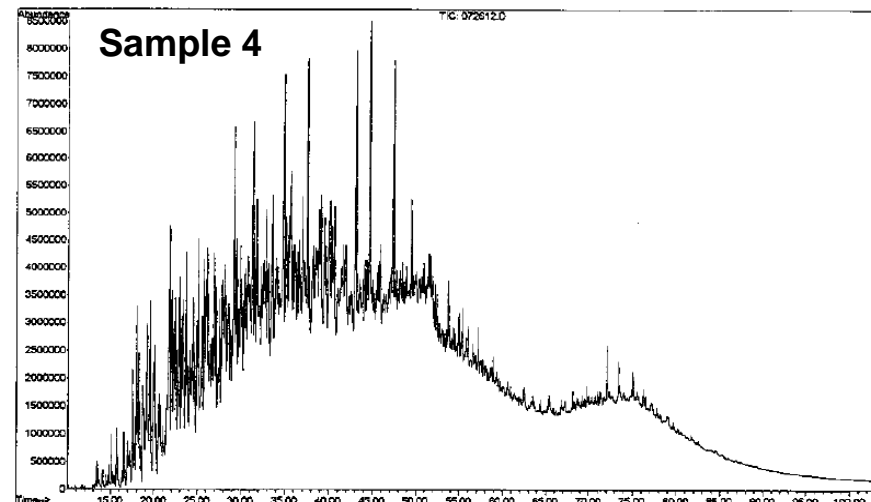


Sample Name: 6F5379-23 (40156-4) soil extract  
Misc Info : Lyon Park Auto, Adamas Law firm



This sample had a distinct chromatographic profile

Sample Name: 6F5379-34 (40156-5) soil extract  
Misc Info : Lyon Park Auto, Adamas Law firm



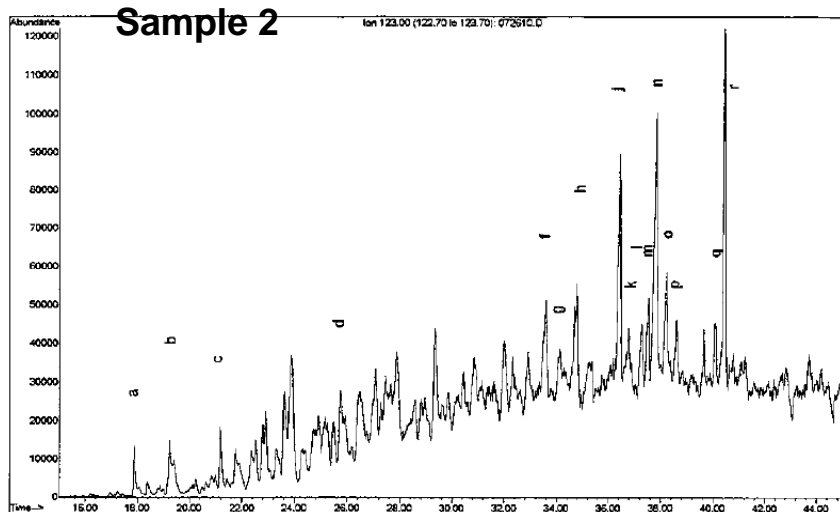
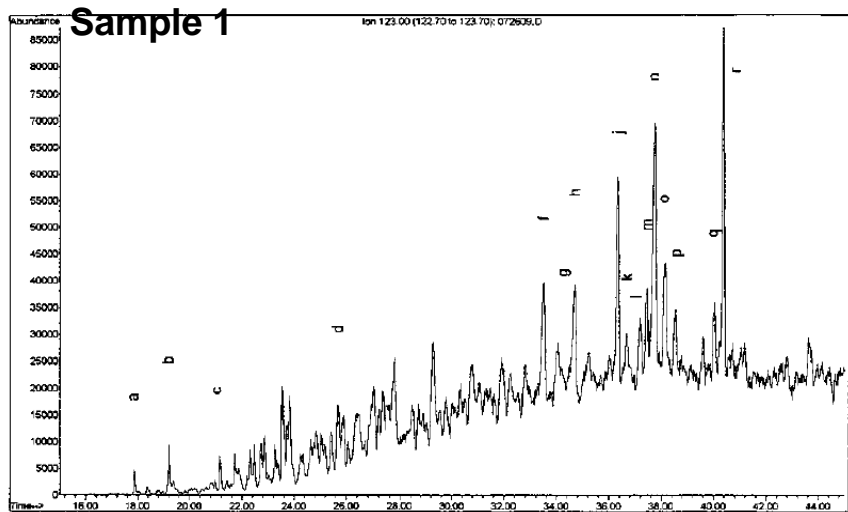
Zymax  
FORENSICS

Zymax  
FORENSICS

# TIER 2 RESULTS: BIOMARKERS (M/Z 13 – BICYCLIC SESQUITERPANES)

Sample Name: 6F5379-02 (40156-1) soil extract  
Misc Info : Lyon Park Auto, Adamas Law firm

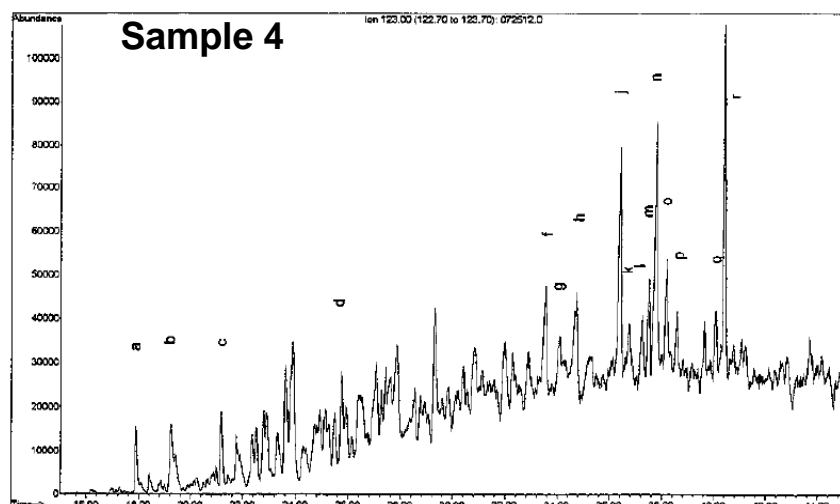
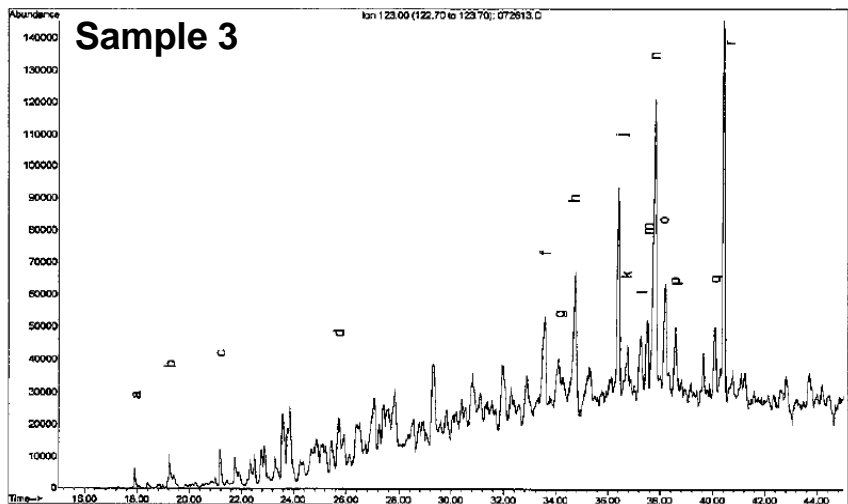
Sample Name: 6F5379-19 (40156-3) soil extract  
Misc Info : Lyon Park Auto, Adamas Law firm



Similarity of all samples indicate that there is a common source for the middle distillate component in all samples

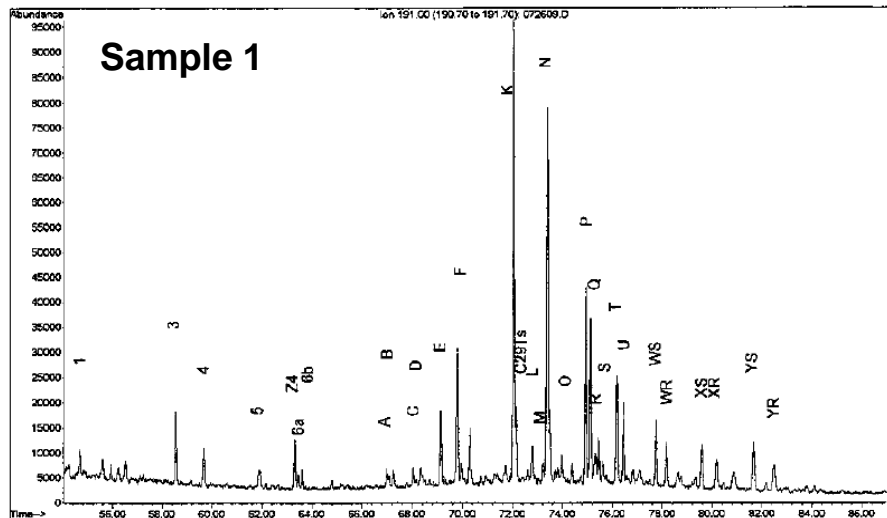
Sample Name: 6F5379-23 (40156-4) soil extract  
Misc Info : Lyon Park Auto, Adamas Law firm (1:3)

Sample Name: 6F5379-34 (40156-5) soil extract  
Misc Info : Lyon Park Auto, Adamas Law firm

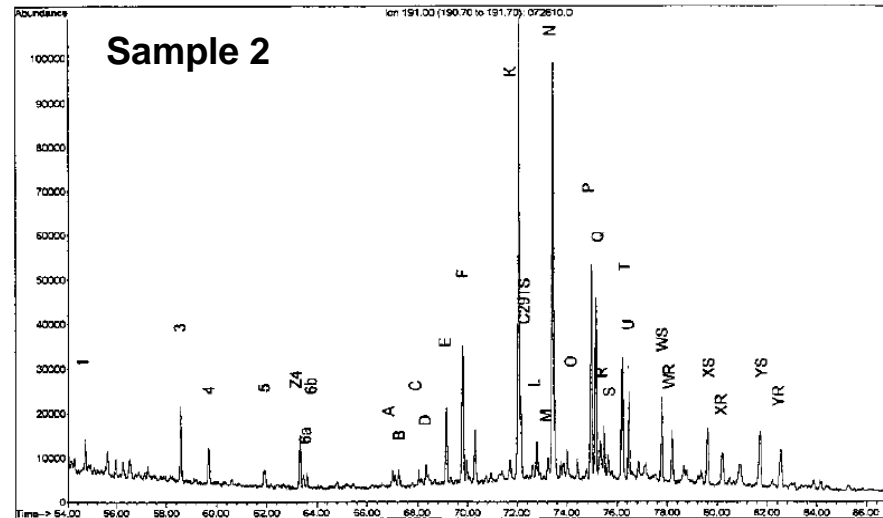


# TIER 2 RESULTS: BIOMARKERS (M/Z 191 - TERPANES)

Sample Name: 6FS379-02 (40156-1) soil extract  
Misc Info : Lyon Park Auto, Adamas Law Firm



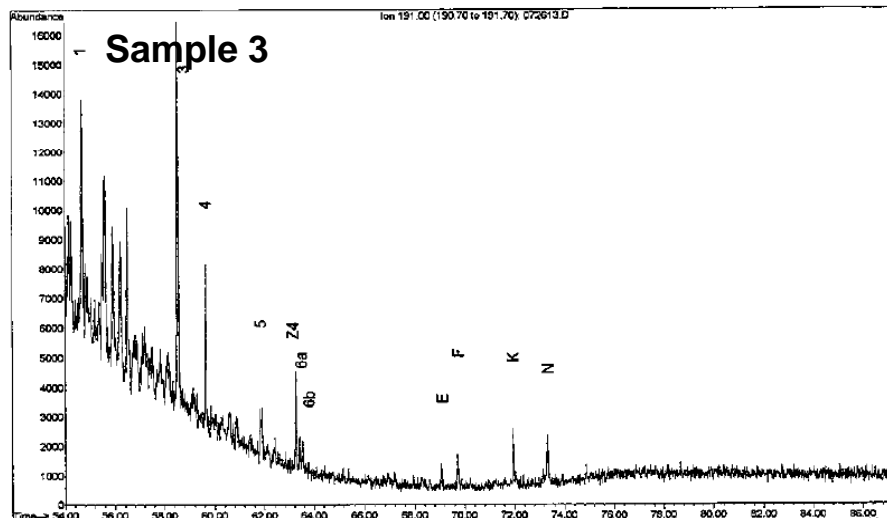
Sample Name: 6FS379-19 (40156-3) soil extract  
Misc Info : Lyon Park Auto, Adamas Law Firm



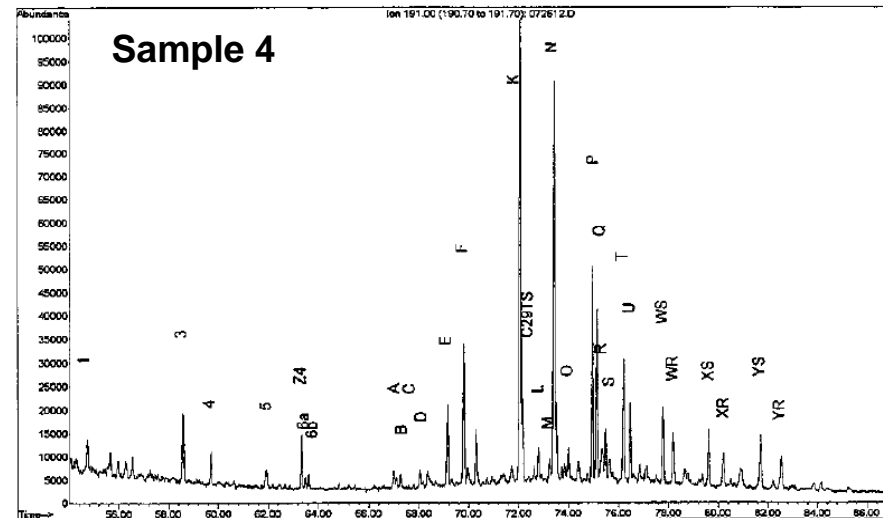
Results revealed the presence of hydraulic or lubricating oil of similar origin in samples 1, 2 and 4

Zymax  
FORENSICS

Sample Name: 6FS379-23 (40156-4) soil extract  
Misc Info : Lyon Park Auto, Adamas Law Firm (1:3)

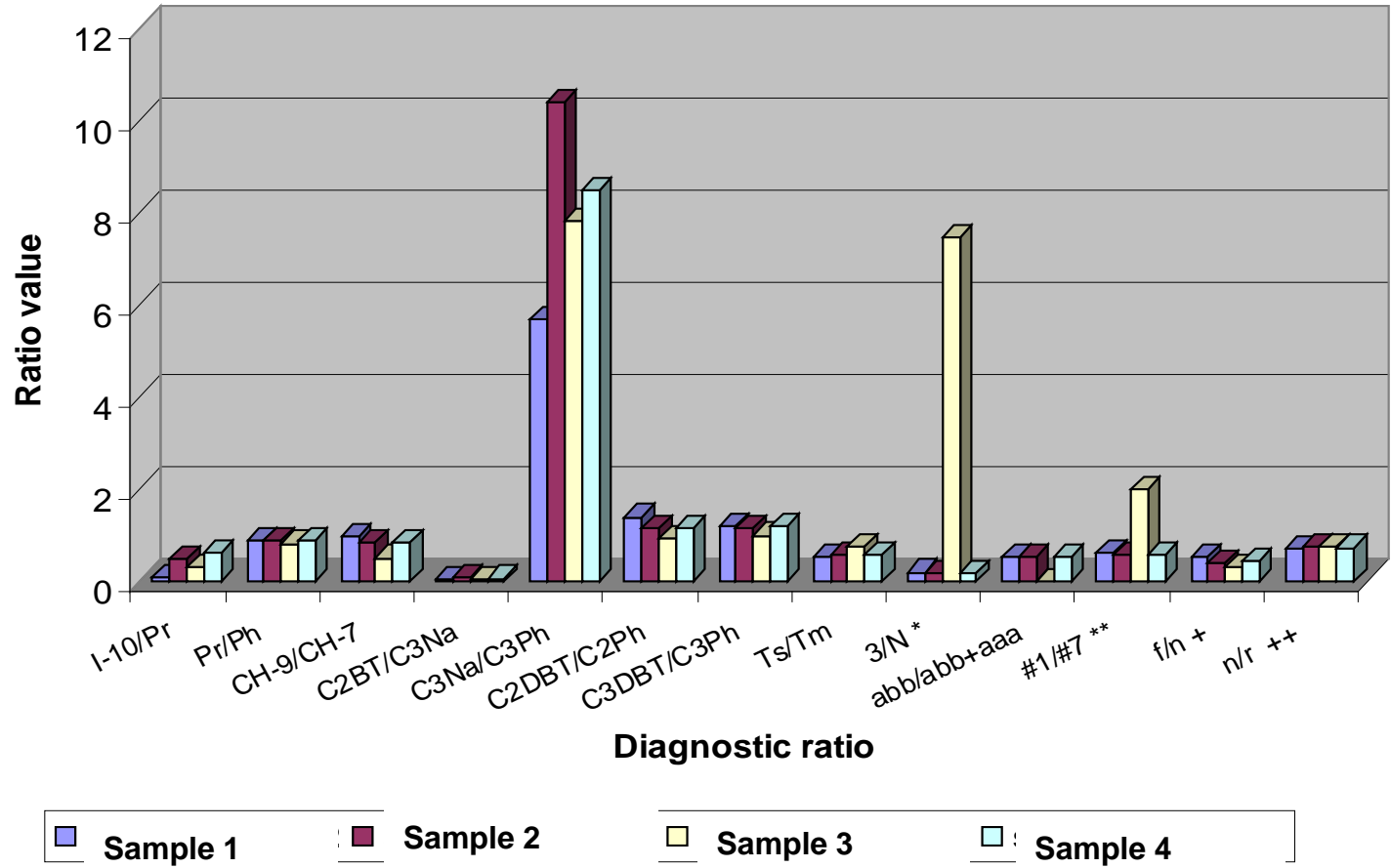


Sample Name: 6FS379-34 (40156-5) soil extract  
Misc Info : Lyon Park Auto, Adamas Law Firm



# OVERVIEW OF DIAGNOSTIC RATIOS USED

**Graph. 1 Diagnostic ratios for the soil samples with detected hydrocarbons from Lyon Auto Park**



# FINDINGS

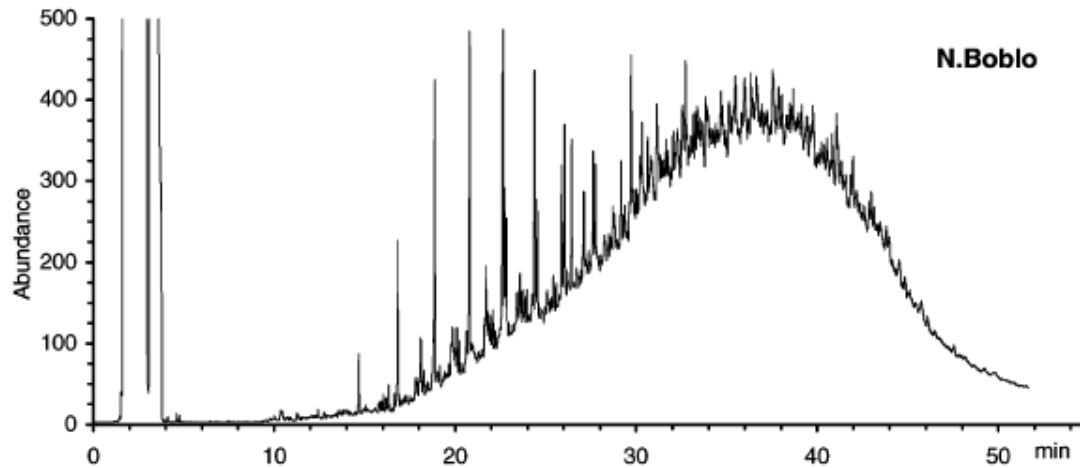
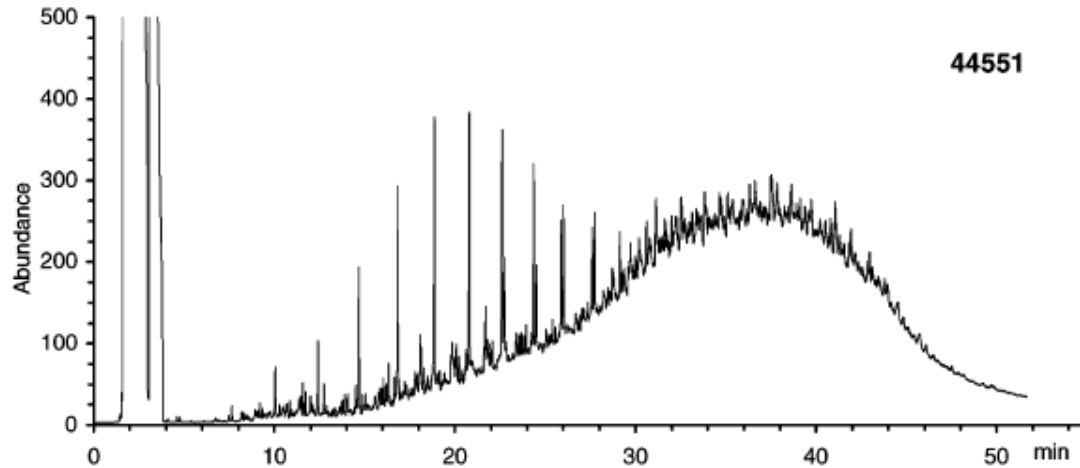
- A mixture of middle and heavy distillate (e.g., lubricating oil) was present in all soil samples except Sample 3
- The heavy distillate fingerprints were similar to product close to piping attributed to major oil company
- **The study cost was approx. \$10,000 and saved approx. \$1M in soil remediation costs**
- **Based on this investigation the case settled before litigation**



# CASE STUDY 2: DETROIT RIVER MYSTERY OIL SPILL INVESTIGATION

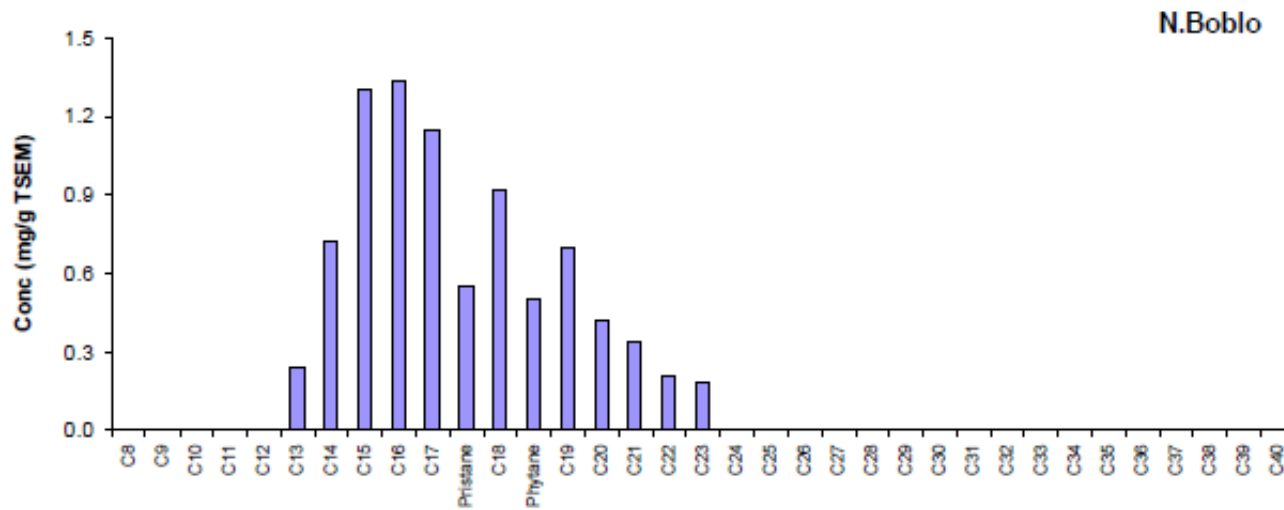
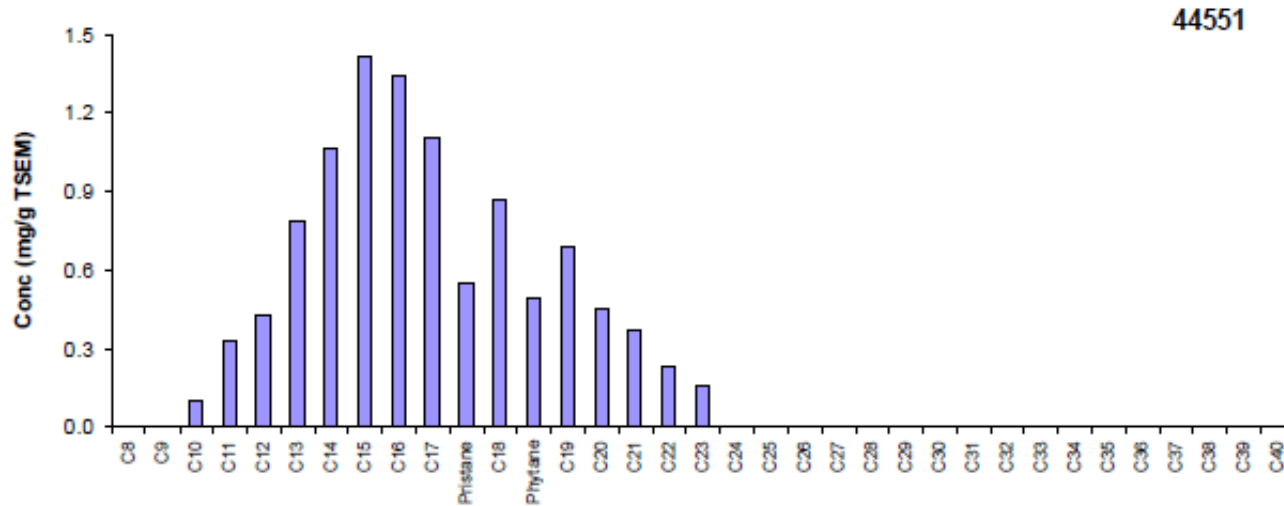
- A mystery oil spill (thousands of liters) to the Rouge River and Detroit River was discovered and reported in April 2002 → Spilled oil floated into northern Lake Erie
- Thousands of more liters spilled into Rouge River over the weekend
- 43 km of USA and Canadian shorelines were impacted
- Investigation - by Environment Canada
- 11 “emergency” spill samples – 3 selected for detailed fingerprinting
- **CHALLENGE: evaluate the type of spilled oil product and its source**

# TIER 1 (GC/FID CHROMATOGRAMS - TIC) SELECTED RESULTS



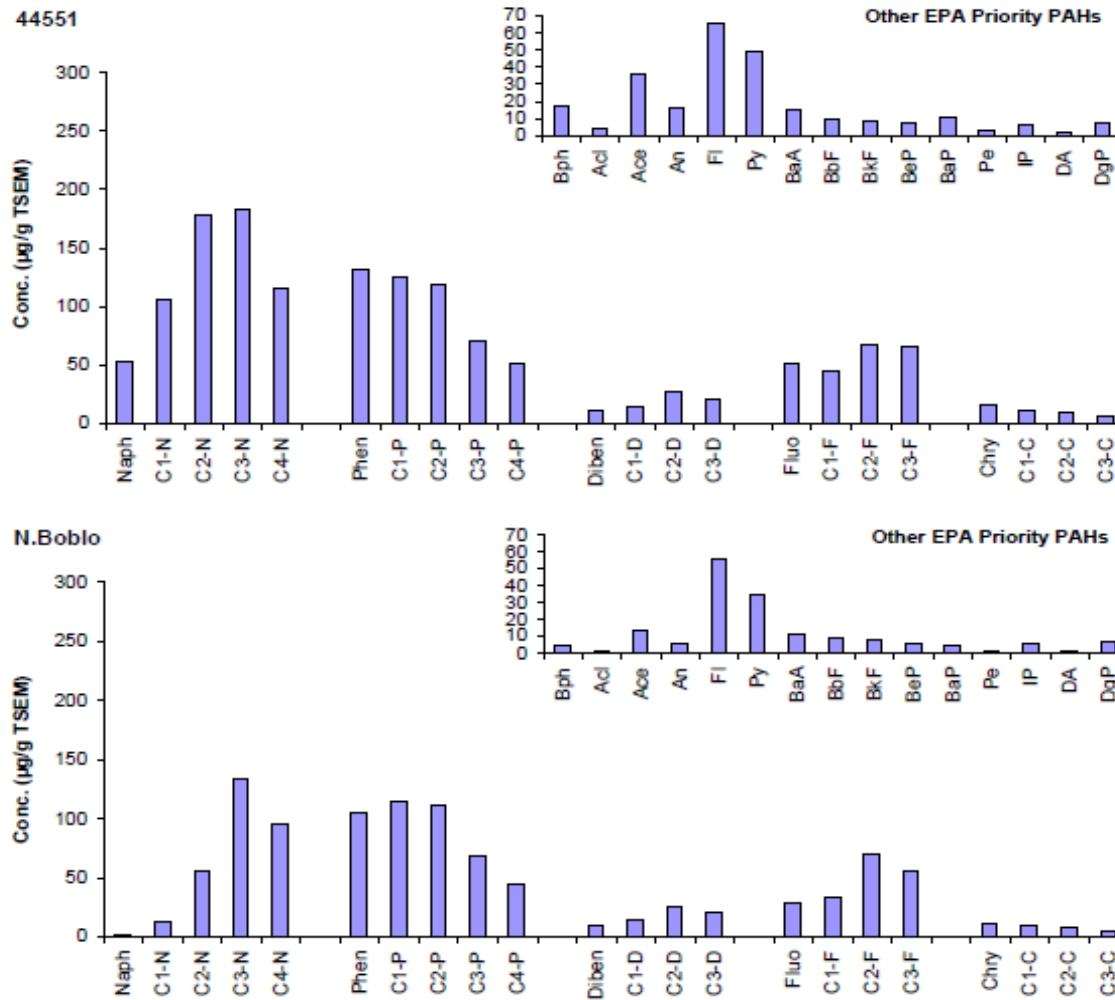
Source: Wang et al. 2004. Characterization and identification of the Detroit River mystery oil spill (2002). *Journal of Chromatography A*, 1038: 201-214.

# TIER 2 (N-ALKANES) - SELECTED RESULTS



Source: Wang et al. 2004. Characterization and identification of the Detroit River mystery oil spill (2002). *Journal of Chromatography A*, 1038: 201-214.

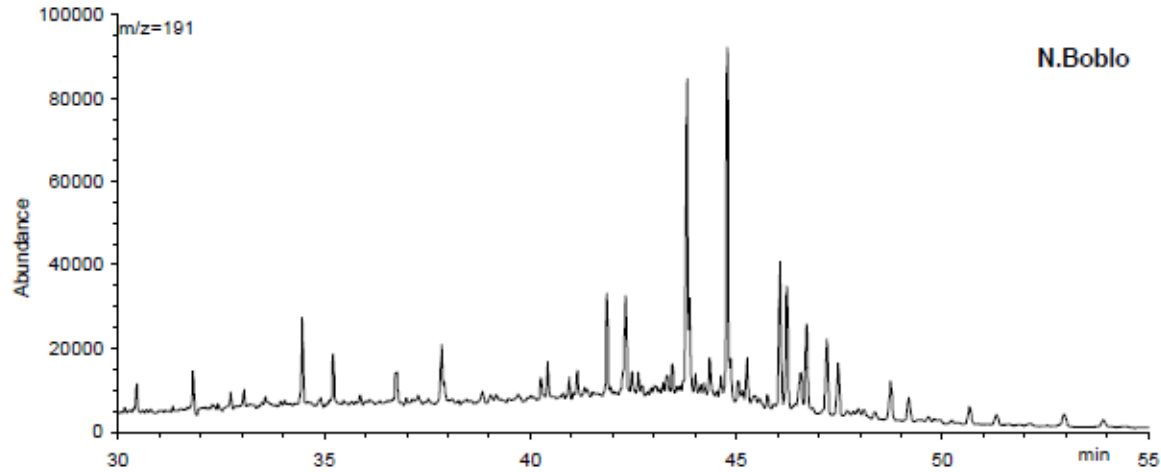
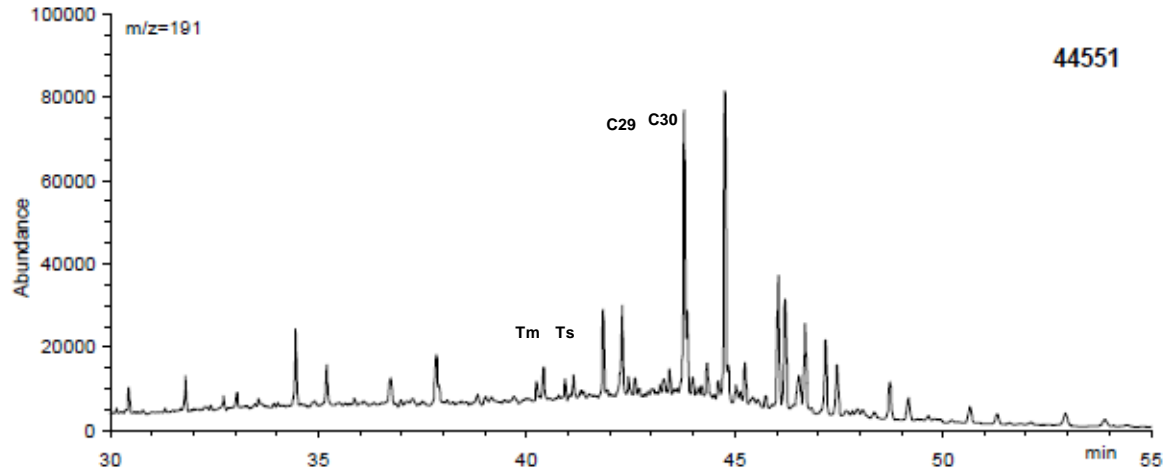
# TIER 2 (PAHS) - SELECTED RESULTS



Source: Wang et al. 2004. Characterization and identification of the Detroit River mystery oil spill (2002). *Journal of Chromatography A*, 1038: 201-214.

# TIER 2 (BIOMARKERS) - SELECTED RESULTS

## Hopanes m/z 191



Source: Wang et al. 2004. Characterization and identification of the Detroit River mystery oil spill (2002). *Journal of Chromatography A*, 1038: 201-214.

# FINDINGS

- The type of product was identified as used lubricating oil mixed with smaller portions of degraded diesel fuel
- Similar characteristics for the lube oil were observed in all samples
- **The analyzed spill samples came from the same source**

Source: Wang et al. 2004. Characterization and identification of the Detroit River mystery oil spill (2002). *Journal of Chromatography A*, 1038: 201-214.



# PROBLEMS & SOLUTIONS

PROBLEMS	SOLUTIONS
Identify fake or unsuitable motor oil	<ul style="list-style-type: none"><li>• Tier 1 (all compounds) data usually suffices</li><li>• No comparison samples needed</li></ul>
Identify source(s) of illegal dumping	<ul style="list-style-type: none"><li>• Tier 1 &amp; 2 data (biomarkers) typically needed</li><li>• Comparison samples (from suspected sources) preferred</li><li>• Metals &amp; specific additives profile may help</li></ul>
Evaluate co-mingled oils	<ul style="list-style-type: none"><li>• Tier 1, 2 &amp; 3 data (isotopic fingerprints) likely needed</li><li>• Additives and other specific contaminants help</li><li>• Comparison samples are highly desirable</li></ul>

# MORE INFORMATION ON FORENSIC FINGERPRINTING AND PRINCIPLES



## ENVIRONMENTAL FORENSICS FUNDAMENTALS

A Practical Guide



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# QUESTIONS/DISCUSSION



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