



# INTRODUCTION TO ENVIRONMENTAL FORENSICS

Fingerprinting Techniques in Support of Environmental Litigation,  
Investigations, and Remediation

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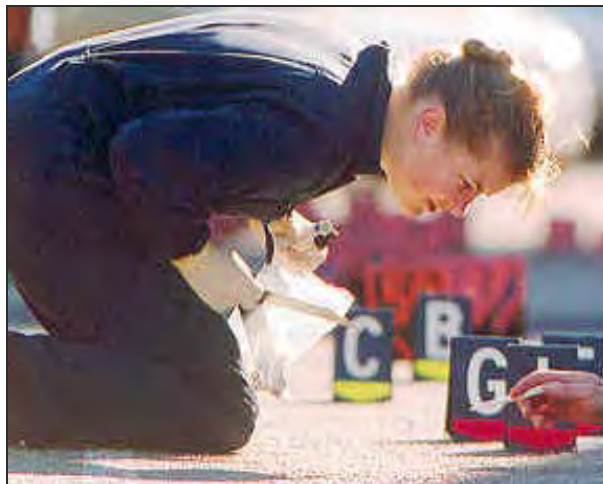
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*Innovative Solutions  
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*Presented at SAM Fall Meeting  
October 30, 2018*

# Forensic Science

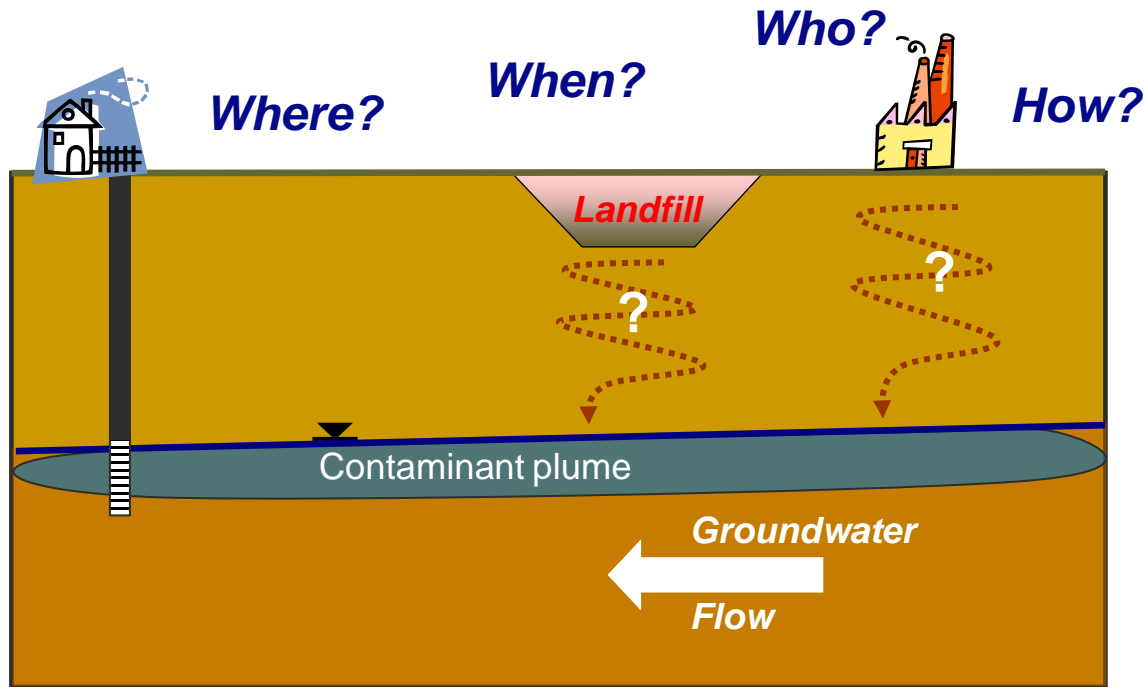
Reconstruction of past events based on the evidence that remains



Often just  
**a trace...**

*From: Horswell, J. et al. 2003. Forensic DNA Profiling of Bacterial Communities in Soil.  
Paper presented at ISEF Workshop, Taipei, Taiwan, Dec. 8-9, 2003*

# Environmental Forensics



# Applications of Environmental Forensics

- **Litigation Support / Expert Witness**
- **Site Characterization** (e.g., background evaluation)
- **Site Remediation** (e.g., reduce costs & time)
- **Monitored Natural Attenuation (MNA) Feasibility**
- Vapor Intrusion
- Consumer Products
- Sediment Age-Dating

# Environmental Forensics Techniques

Focused on <b>Contaminants</b>	Focused on <b>Contaminants within Environmental Matrix</b>	Focused on <b>“Traces”</b> Left by Contaminants in Environment
<ul style="list-style-type: none"><li>➤ <b>Chemical fingerprinting</b><ul style="list-style-type: none"><li>• Comprehensive fingerprinting</li><li>• Signature chemicals</li><li>• Chiral fingerprinting</li></ul></li><li>➤ <b>Stable isotopic fingerprinting</b><ul style="list-style-type: none"><li>• Bulk isotopic analysis</li><li>• Compound-specific isotopic analysis (CSIA)</li><li>• Position-specific isotopic analysis (PSIA)</li></ul></li><li>➤ Radioisotopic age-dating</li></ul>	<ul style="list-style-type: none"><li>➤ <b>Mineralogical fingerprinting</b></li><li>➤ Geochemical fingerprinting</li><li>➤ Statistical analysis</li><li>➤ Transport modeling</li></ul>	<ul style="list-style-type: none"><li>➤ <b>Tree-ring fingerprinting</b> (Dendroecology)</li><li>➤ DNA fingerprinting</li><li>➤ Atmospheric tracers</li></ul>

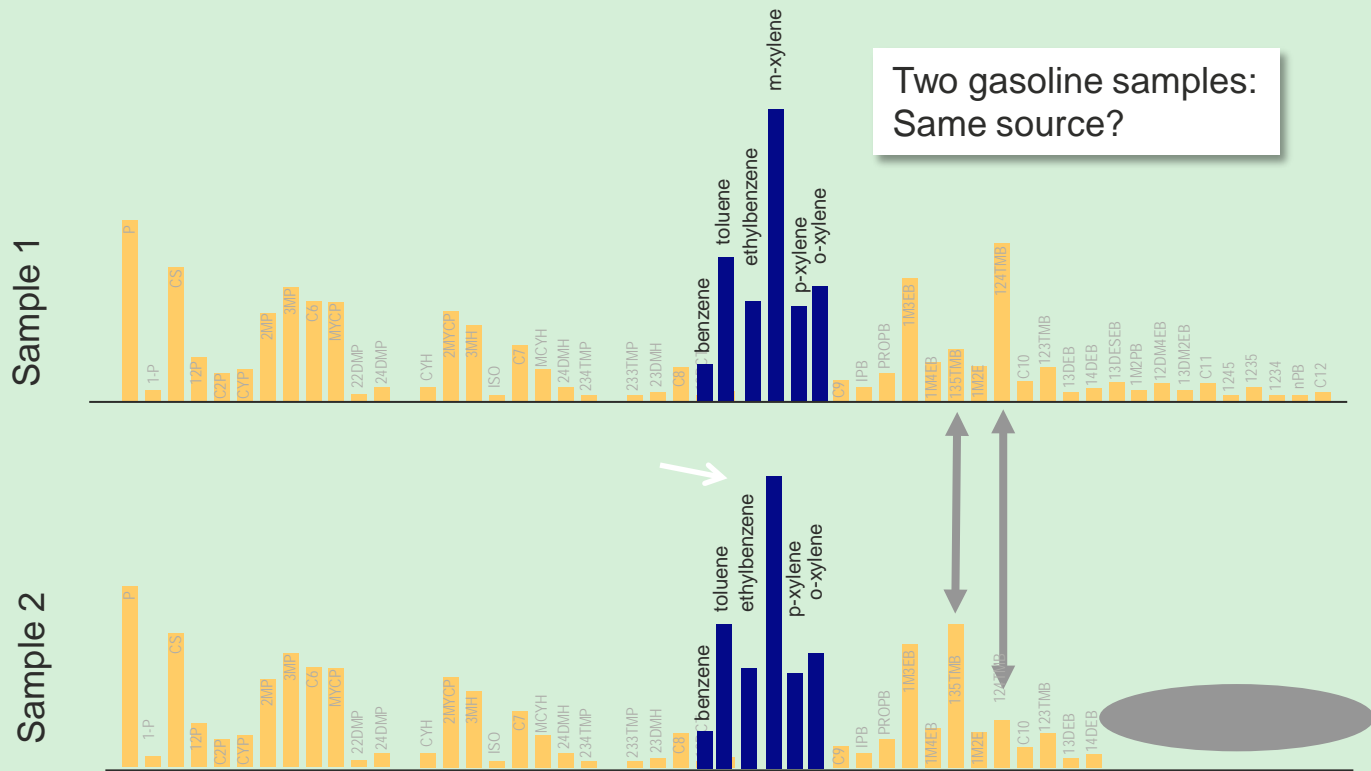
# Chemical Fingerprinting

**Principle:** Analyzing the types and chemical concentrations of contaminants in the environment and comparing the results to the types and concentrations of contaminants from suspected sources

## Applications:

- Complex mixtures (e.g., crude oil & petroleum products, PCBs, PBDEs)
- Compounds with degradation intermediates (e.g., chlorinated solvents)
- “Contaminant cocktails”
  - Waste streams
  - Runoff

# Chemical Fingerprinting □ Example

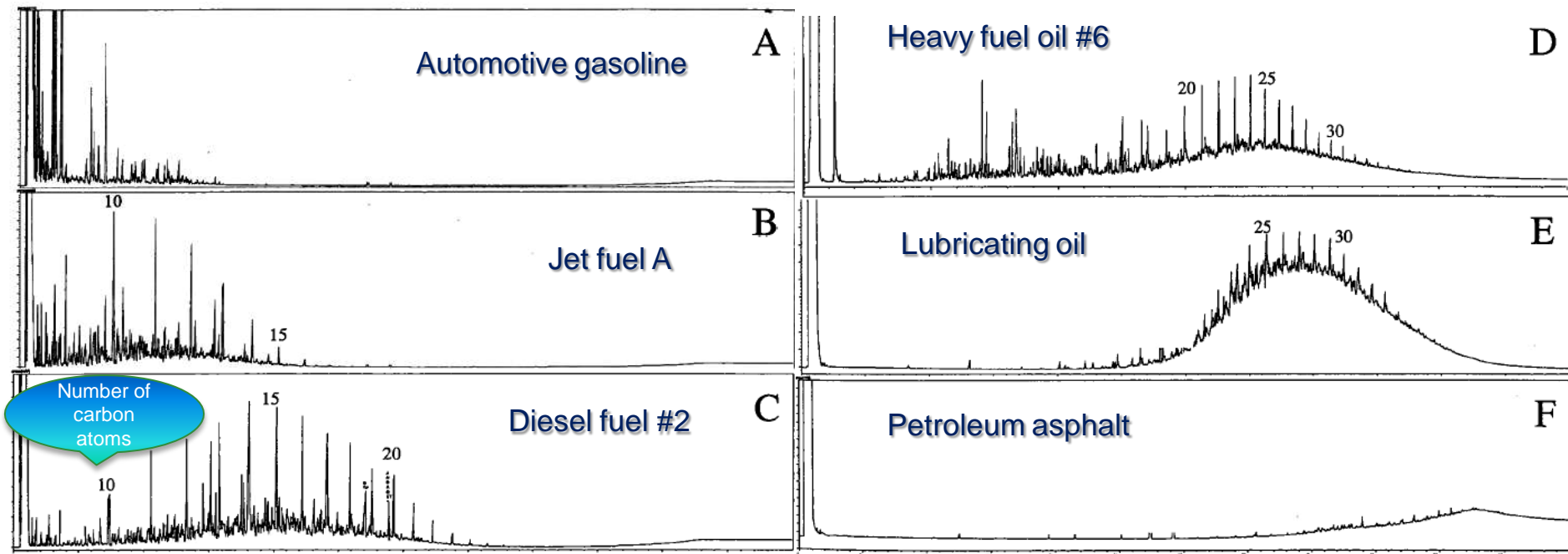


# Crude Oil & Petroleum Product Fingerprinting

- **Tier 1** □ **GC/FID or full scan GC/MS:** looking at all constituents
- **Tier 2** □ **GC/MS (SIM Mode):** “zooming in” on selected constituents
- **Tier 3** □ **GC/IRMS:** isotopic fingerprinting (bulk & compound-specific)

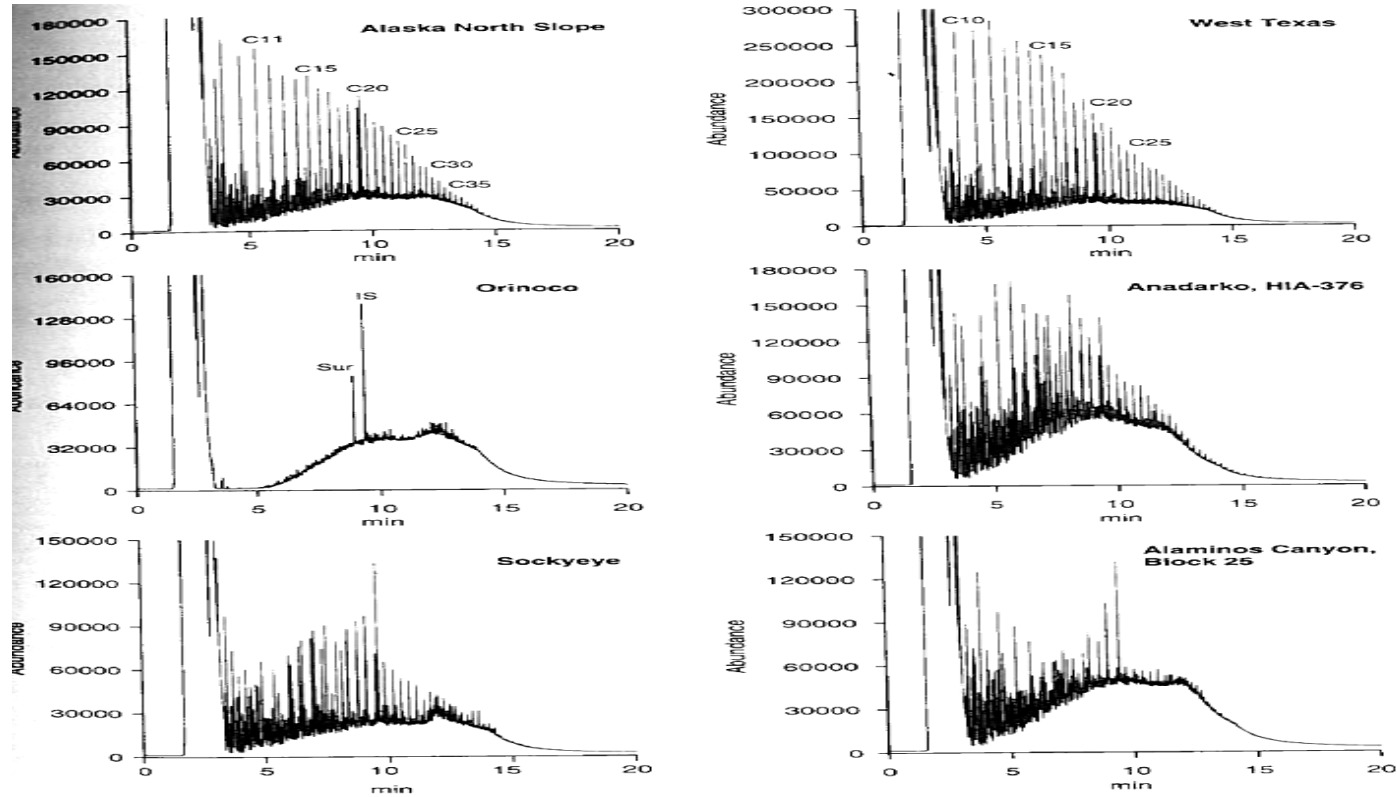


# Tier 1 □ Evaluate Product Type



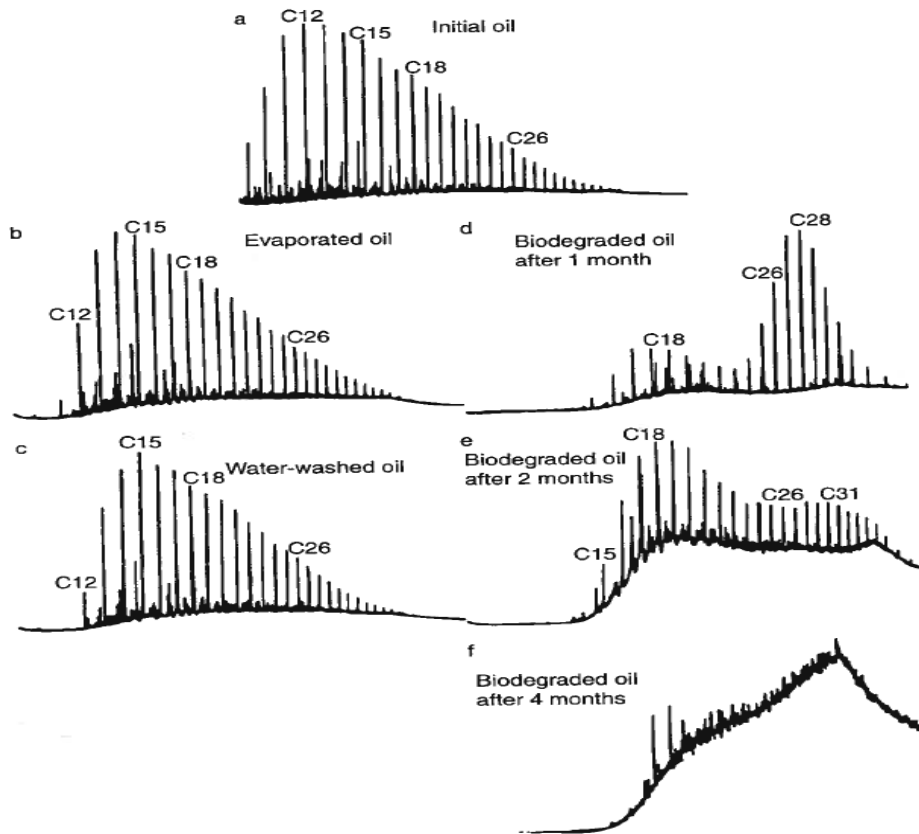
Source: Wang Z, Stout S (Eds). 2007. *Oil Spill Environmental Forensics – Fingerprinting and Source Identification*. Elsevier Academic Press, ISBN 13: 978-0-12-369523-9

# Tier 1 □ Evaluate Oil Source



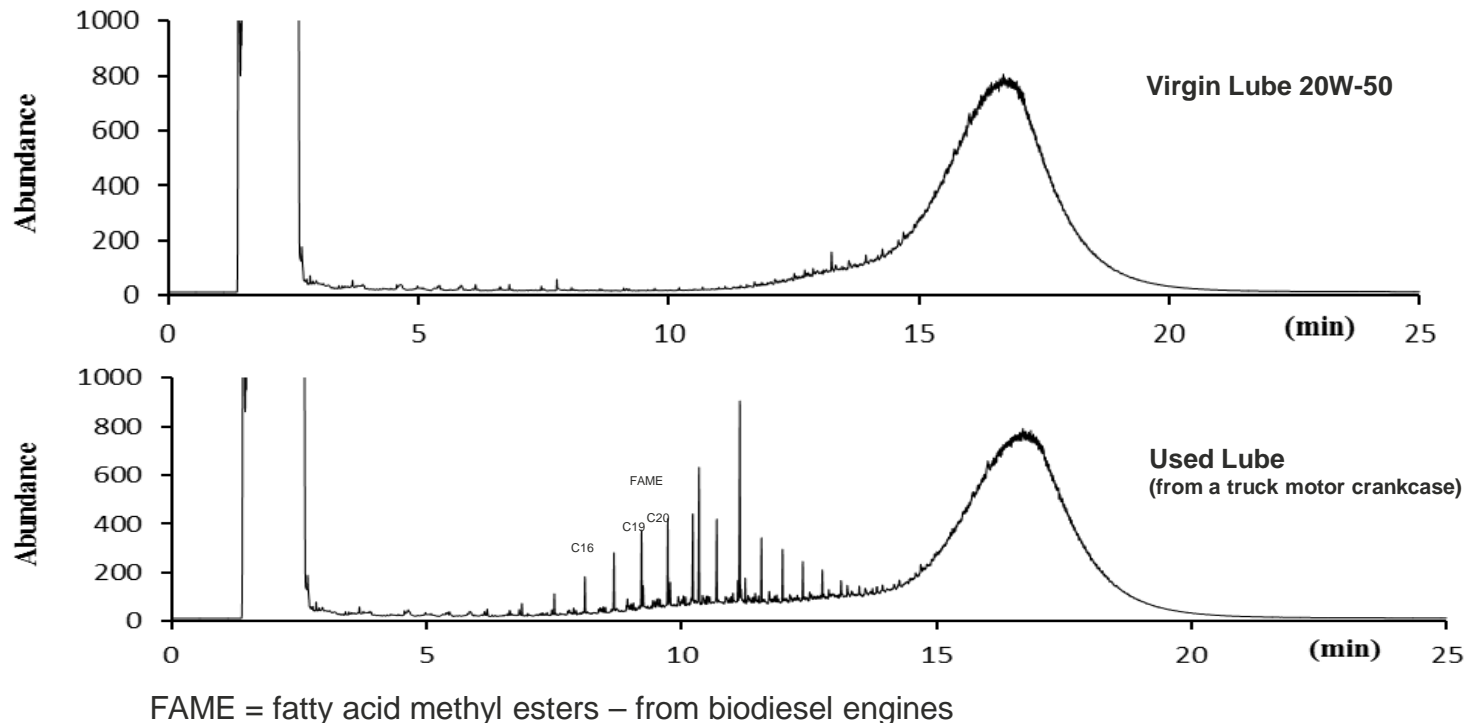
Source: Wang Z, Fingas M, Yang C, Christensen JH. 2005. Crude oil and refined product fingerprinting: Principles. In: Environmental Forensics - Contaminant Specific Guide. Morrison RD, Murphy B (Eds). Elsevier, 340-407.

# Tier 1 □ Evaluate Weathering Patterns



Source: Mansuy et al. 1997. *Environmental Science & Technology*, 31(12)

# Tier 1 □ Distinguish Virgin vs. Used Motor Oil



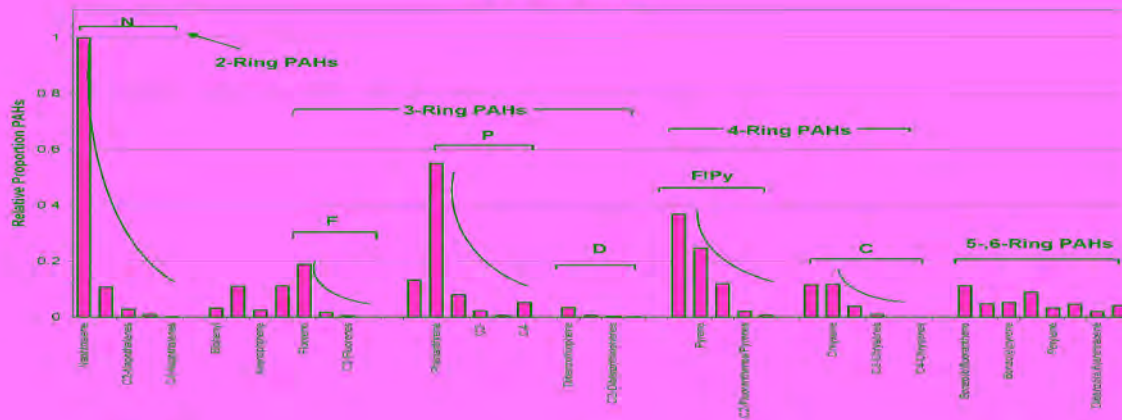
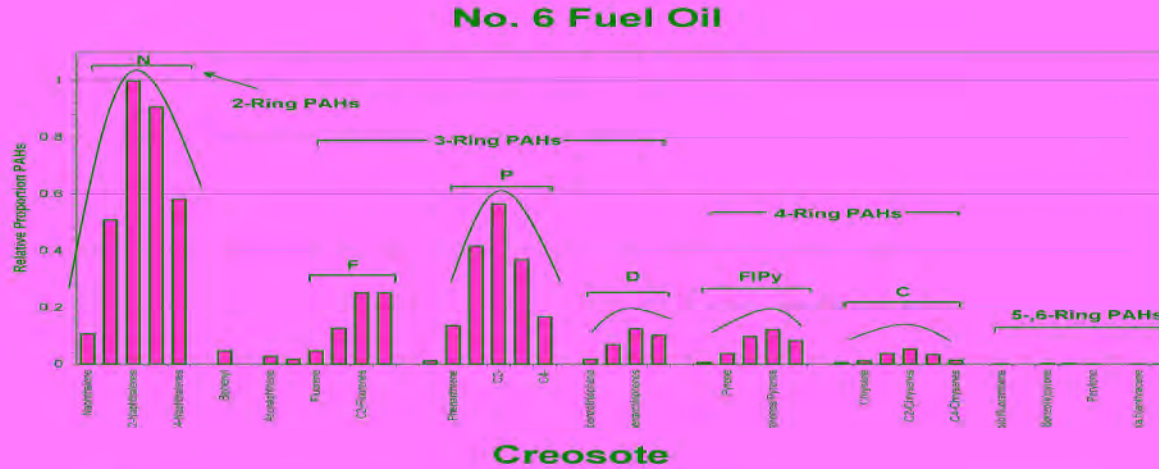
Source: Chun et al. 2015. *Fingerprinting Analysis and Differentiation of Virgin and Used Lubricating Oils*. AMOP 2015 Proceeding Volume

# Tier 2 ☐ Targeted PAHs (Extended List)

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	Acl	Acl	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

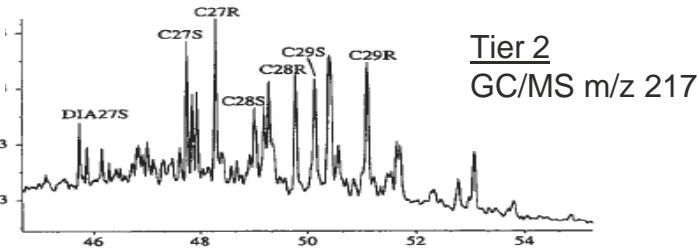
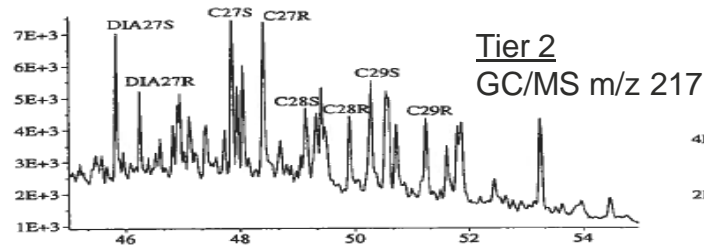
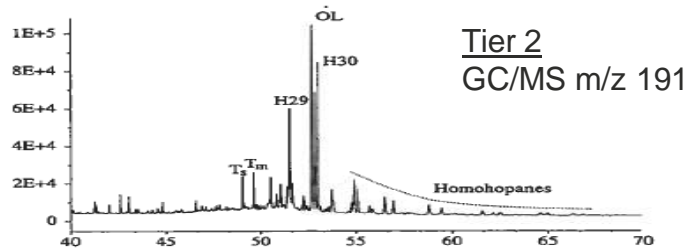
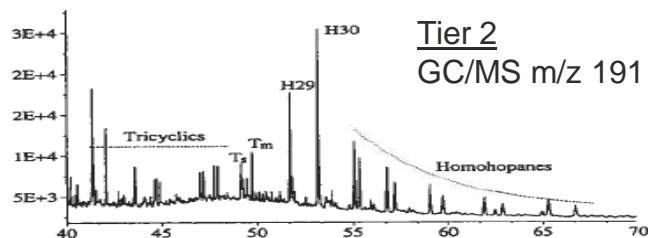
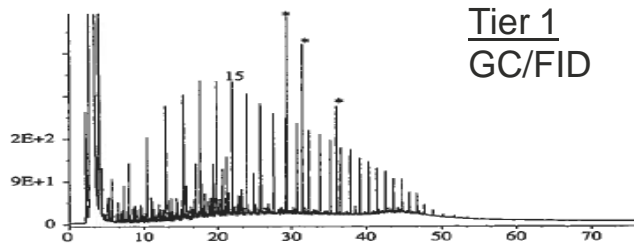
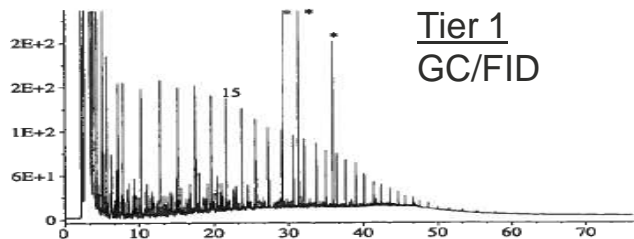
# Tier 2 ☐ PAH Patterns for Petrogenic vs. Pyrogenic Sources



## Tier 2 □ Biomarker Classes

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

# Tiers 1 & 2 □ Examples of Crude Oil Fingerprints

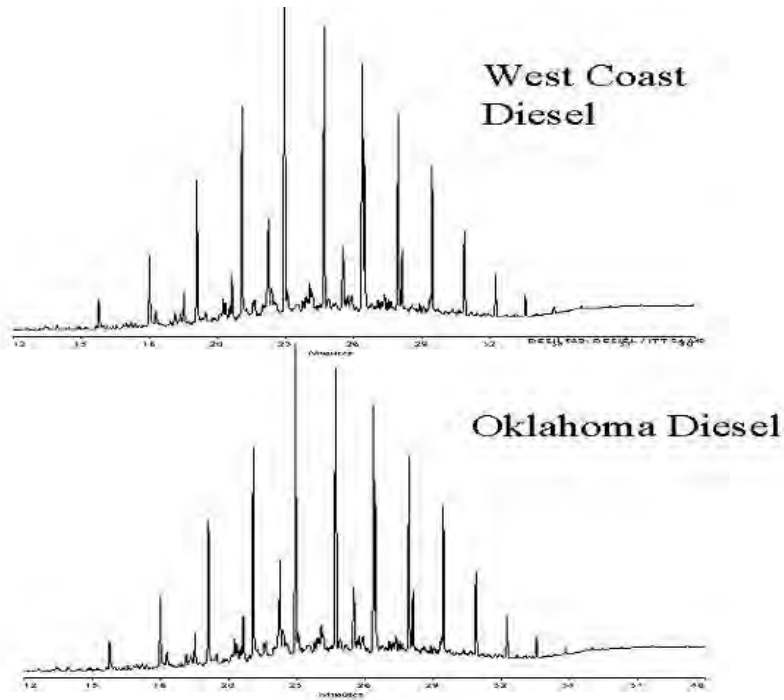


Alaska North Slope crude oil

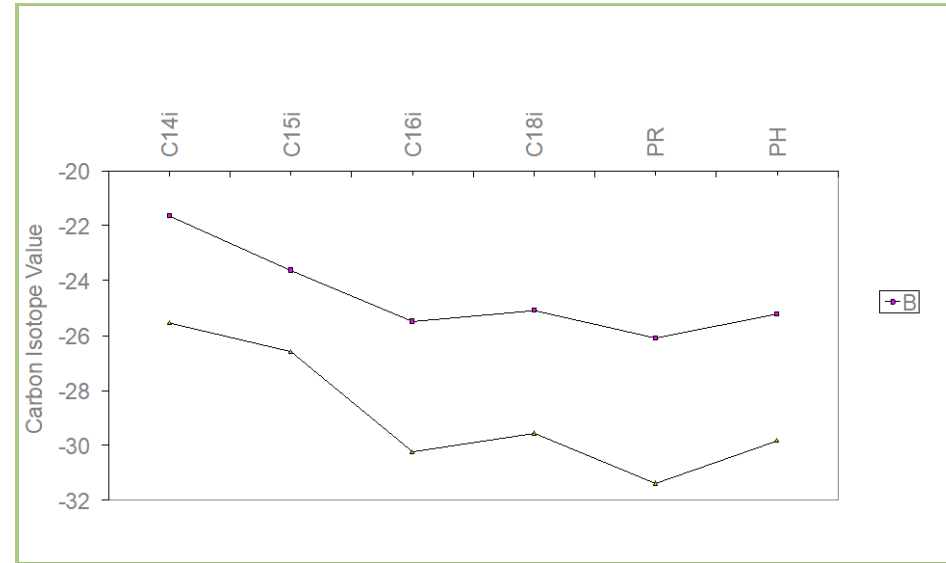
Nigerian crude oil



# Tiers 1 & 3 – Example of Diesel Fingerprints



Tier 1 Data: Chemical Fingerprinting (GC/FID)



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

## More Efficient Remediation by Differentiating Release Timing

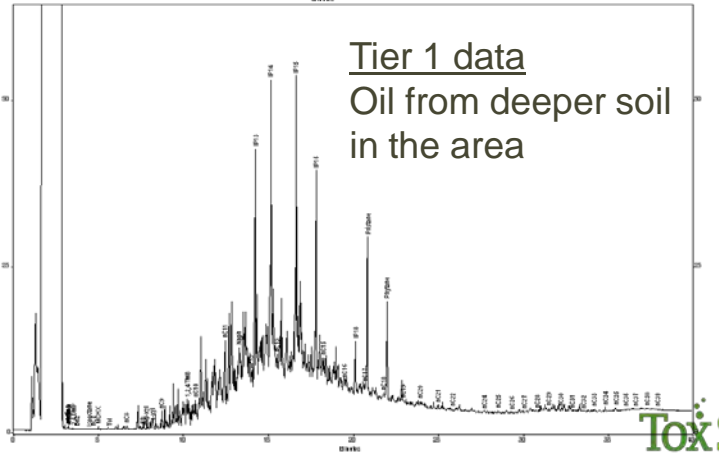
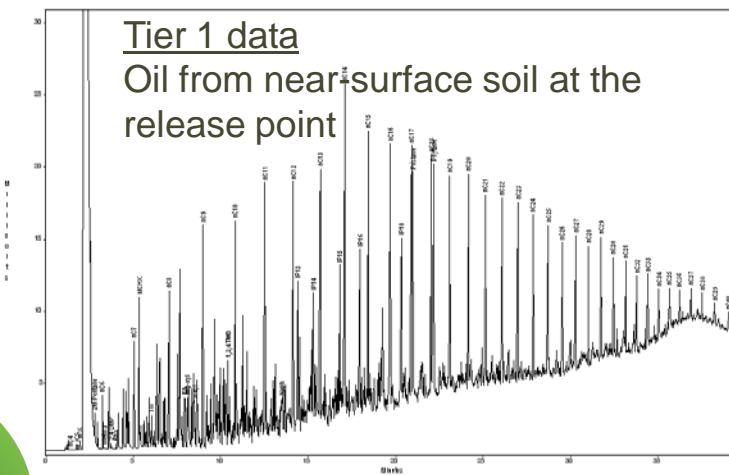
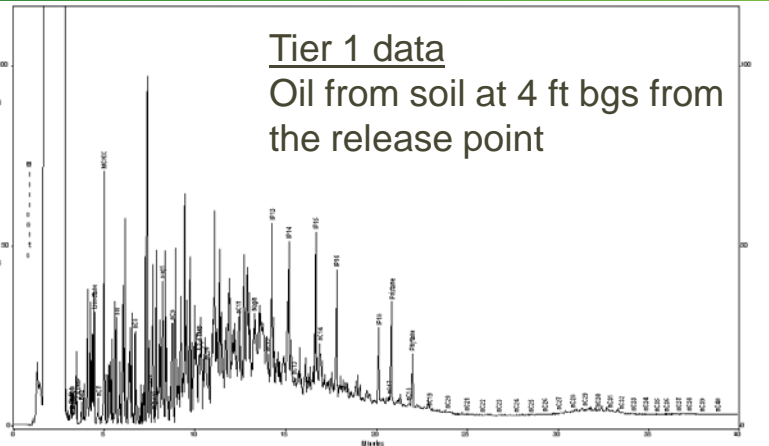
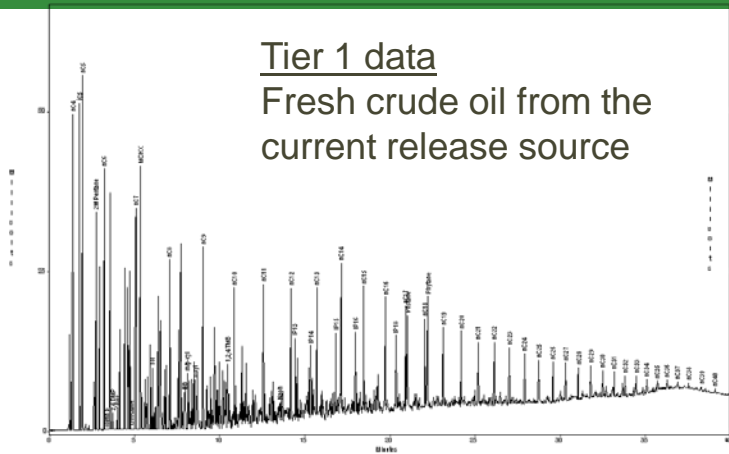
- A release occurred from a crude pipeline at a petroleum terminal
- Released oil was immediately recovered above grade
- Release occurred in an area historically contaminated with petroleum contaminants
- No litigation, but potential subsurface impacts needed delineation from historical releases due to distinct regulatory oversight
- Conventional delineation approach (TPH, BTEX, MTBE) was not working

*Source: Lu J. 2016. Use of chemical fingerprint data to enhance remedial site investigations at petroleum impacted sites. Environmental Forensics 17(1):19-26*

# Applied Forensic Tools

- Chemical fingerprinting (Tier 1 and possibly Tier 2 data) on representative soil samples at multiple depths from various locations
- Analyses proceeded from shallow to deep soil:
  - Deep soil analyzed only when overlaid by impacted shallower soil
- Fingerprinting data interpreted in the context of site setting and weathering patterns

# Results



# Outcome

- Tier 1 fingerprinting was sufficient to delineate releases:
  - Representative current releases were mostly evaporated crude oil
  - Historical releases were a mixture of weathered gasoline and kerosene
- Most samples were impacted by historical releases
- Accurate delineation of the current release area significantly reduced the remedial footprint

# Isotopic Fingerprinting

- Analyzing the isotopic composition of contaminants that contain elements with stable isotopes, and comparing the results with those of suspected sources
- Stable isotopes are atoms of the same element with different masses; same number of protons, different number of neutrons
- The values are usually reported as a ratio:

$$\left[ \frac{\left( \frac{^{34}\text{S}}{^{32}\text{S}} \right) \text{ sample}}{\left( \frac{^{34}\text{S}}{^{32}\text{S}} \right) \text{ standard}} - 1 \right] \times 1000 = \delta \text{ or } \delta \text{ (delta) } \text{‰ (per mil)}$$

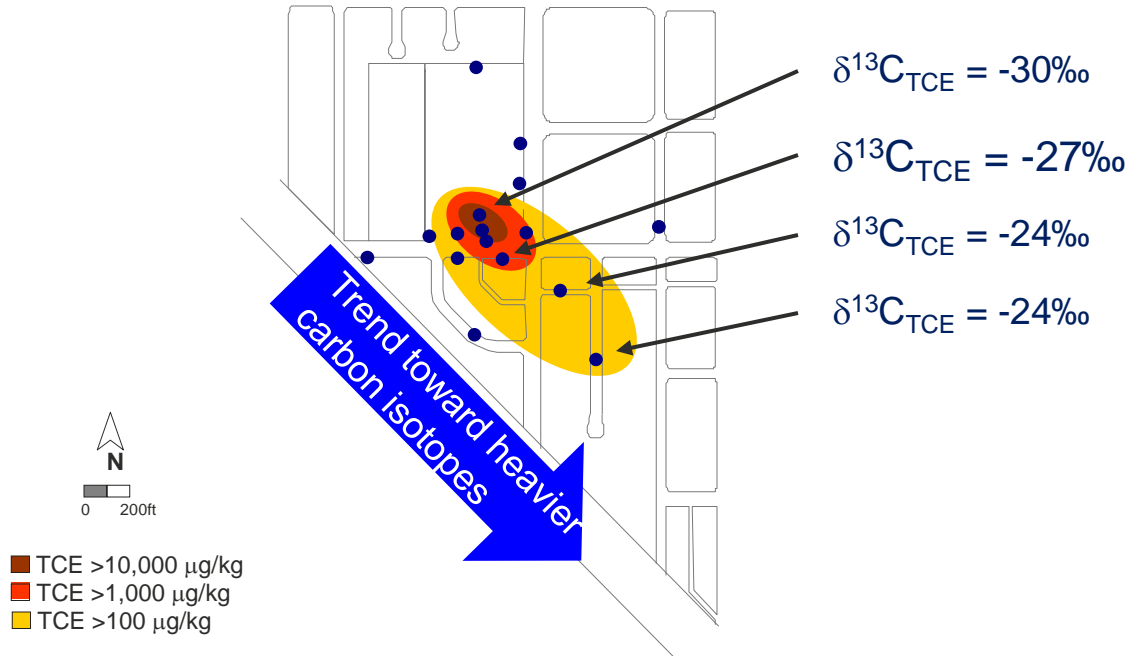
# Isotopic Fingerprinting

Principles	Applications
I. There is measurable variability in stable-isotope composition of natural materials and manufactured products	Source Identification
II. Contaminant biodegradation changes the stable-isotope composition in the degraded compound by increasing the proportion of the heavier isotope	<b>Evaluating Degradation Processes</b>

# Case Study

## Biodegradation Evaluation via Spatial Trends

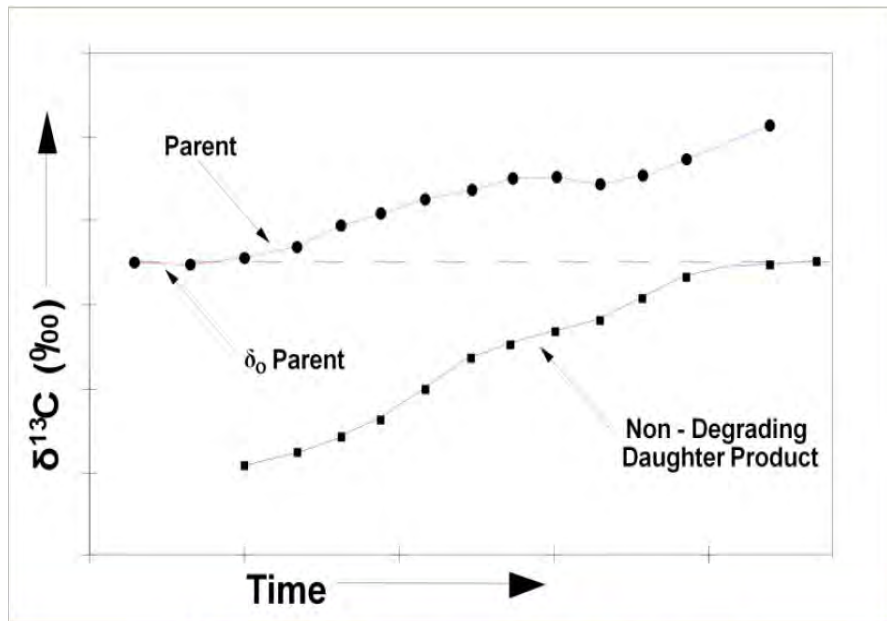
### TCE in Groundwater at a Site in Southern California



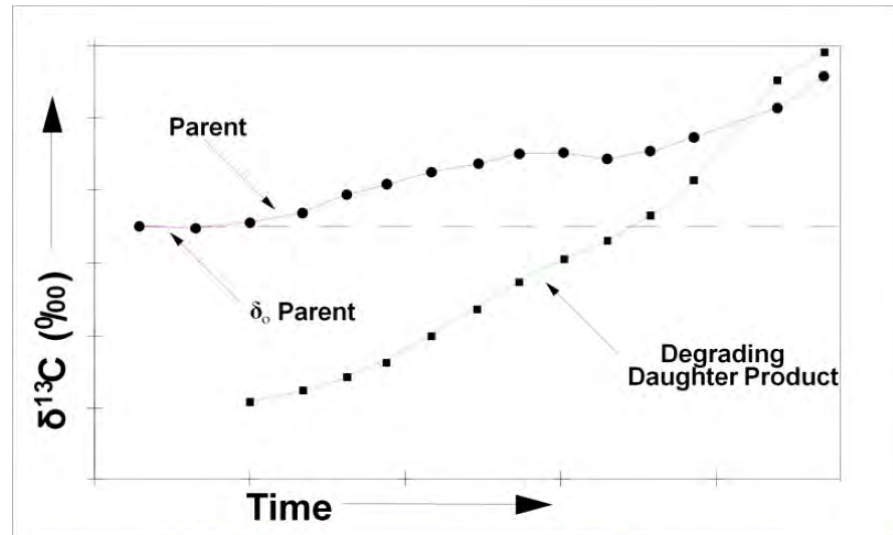


# MNA Evaluation via Temporal Trends

## Degrading vs. Non-Degrading Daughter Product



$$\delta^{13}\text{C}_{\text{non-degrading daughter product}} = \delta_0 \text{ parent}$$



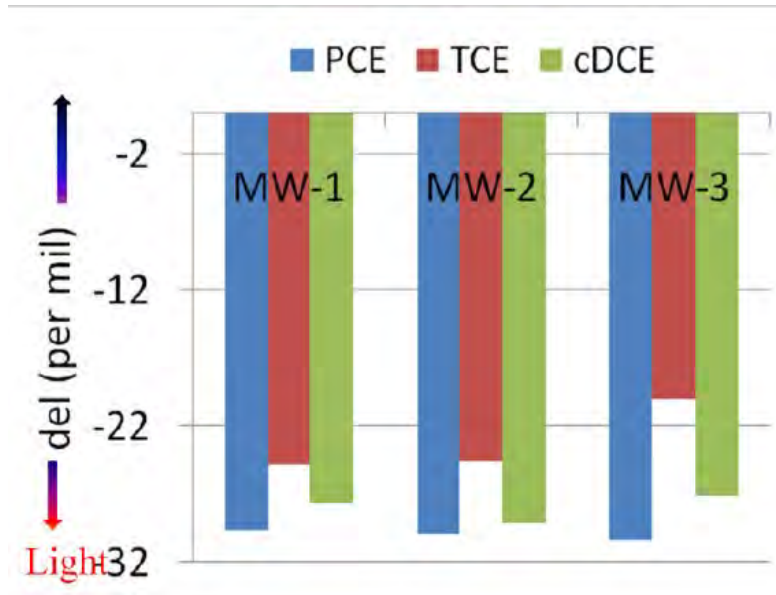
$$\delta^{13}\text{C}_{\text{daughter product}} \geq \delta_0 \text{ parent}$$

**Daughter product degrading**

Source: Pat McLoughlin, *Microseeps, Compound Specific Isotope Analysis and Solvent Case Studies: Forensic and Remedial Insights*. Presented at ITRC Meeting, Fall 2010

# Case Study □ Is MNA Feasible?

## SITE 1 □ MNA Feasible



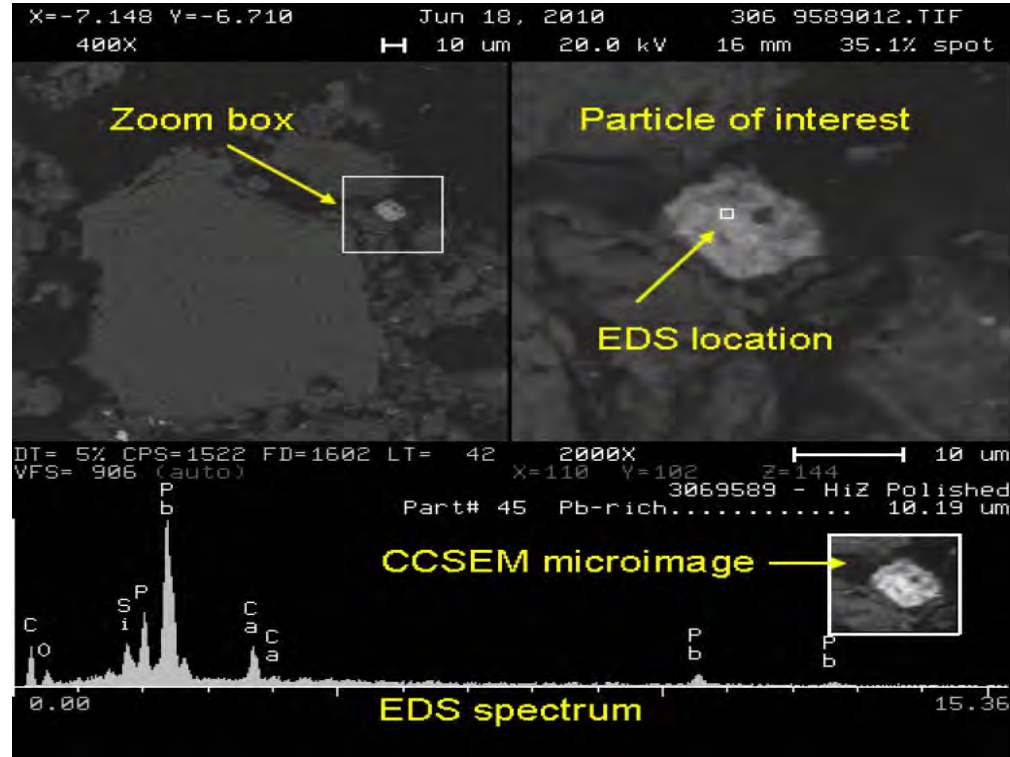
## SITE 2 □ MNA Not Feasible



Case study adapted and figure after: Pat McLoughlin, *Microseeps, Compound Specific Isotope Analysis and Solvent Case Studies: Forensic and Remedial Insights*. Presented at ITRC Meeting, Fall 2010

# Mineralogical Fingerprinting

- Consists of **identifying the size, shape, and chemical composition of particles** associated with a contaminant of concern in a solid sample
- Typically applied to metals in soil or dust samples



# Case Study: Evaluate Metal Background/Cleanup Limits at a Historical Foundry, Lyon, France

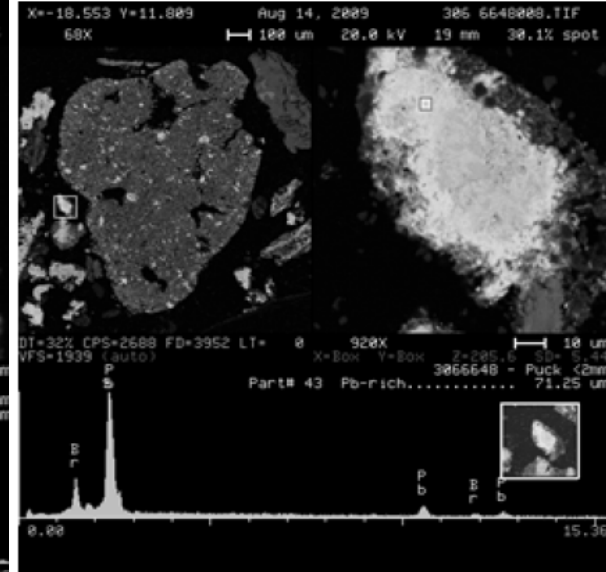
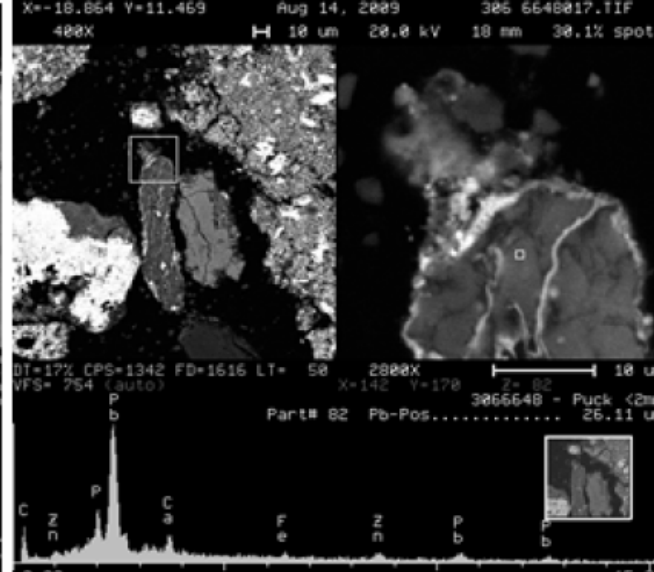
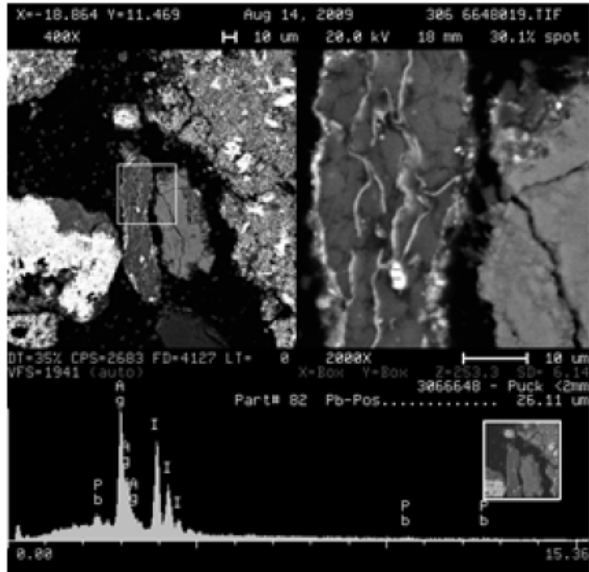


# Results □ Overview of Chemical Fingerprinting

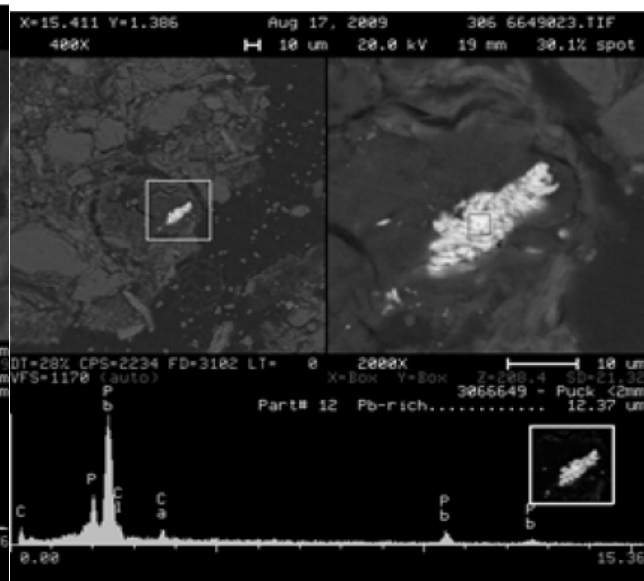
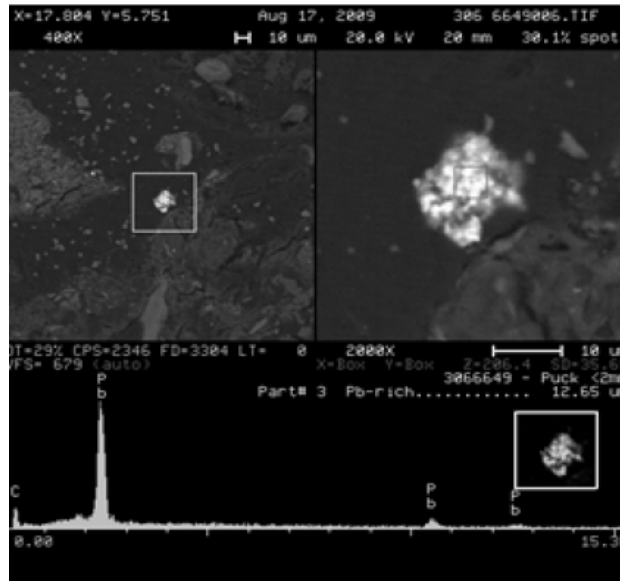
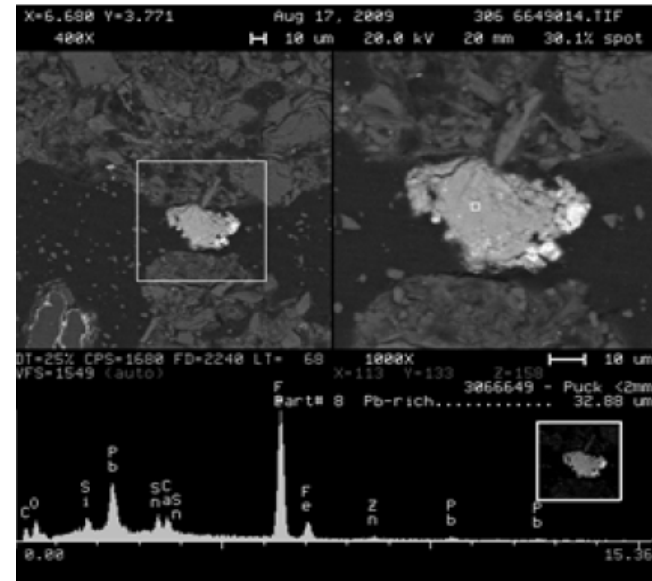
Metal	Ranges in the background samples collected off-site in 2008	Concentration ranges in top soil from site less impacted areas	Concentration ranges in deeper (0.3-0.6 m) soils from site less impacted areas	Concentration ranges in site soil from highly impacted areas	Previously proposed clean-up limits	Newly proposed clean-up limits - background values for the site soils
Lead (Pb)	15 – 490	540 - 6900	<b>230 – 2300</b>	1300 – 110000	110	<b>1100</b>
Cadmium (Cd)	<0.5 – 1.8	8.1 – 69	<b>2 – 17</b>	580 – 5300	0.9	<b>9.5</b>
Nickel (Ni)	19 – 39	18 – 26	<b>19 – 24</b>	27 – 8600	39	<b>same</b>
Mercury (Hg)	<0.1 – 0.6	0.92 – 31	<b>0.38 – 9.7</b>	1.9 – 37	0.6	<b>5</b>
Arsenic (As)	9 – 38	25 – 97	<b>31 – 73</b>	42 – 360	25	<b>52</b>
Cobalt (Co)	4 – 11	7 – 12	<b>8.1 – 10</b>	17 – 82	10	<b>same</b>
Chromium (Cr)	23 – 52	<b>22 - 33</b>	<b>23 – 32</b>		52	<b>same</b>
Tin (Sn)	Not evaluated	10 – 75	<b>9.6 - 51</b>	38 – 6200	Not applicable	
Zinc (Zn)	46 – 150	84 – 280	<b>86 - 220</b>	2400 – 29000	Not applicable	
Silver (Ag)	Not evaluated	17 – 61	<b>15 - 36</b>	93 – 310	Not applicable	
Aluminum (Al)	Not evaluated	9900 – 12000	Not available	3500 - 15000	Not applicable	
Palladium (Pd)	Not evaluated	< 10	Not available	< 10	Not applicable	
Gold (Au)	Not evaluated	< 4	Not available	< 4	Not applicable	
Platinum (Pt)	Not evaluated	< 10	Not available	< 10 - 11	Not applicable	

*Note: Association of Zn, Sn, Ag, Pd, Au, and Pt with Pb suggests site impacts*

# Results □ Representative Mineralogical Fingerprints for Highly Polluted On-Site Soils



# Results □ Representative Mineralogical Fingerprints for Less Polluted On-Site Soils



# Results □ Overview of All Mineralogical Fingerprints

On-Site Soil Sample	Pb-Bearing Particles (Pb occurrences)	Prevalence (approximation based on SEM counts)
Polluted soil	Pb associated with tin, cadmium and/or zinc matrix - Linked to foundry operations	90%
	Large particles of anglesite or susannite	< 10%
	Pb in an iron-rich phase and lead phosphate	< 10%
Less impacted top soil	Pb associated with tin, cadmium and/or zinc matrix - Linked to foundry operations	70%
	Lead phosphate	One third (approx.)
	Lead in an iron-rich phase	< 1%

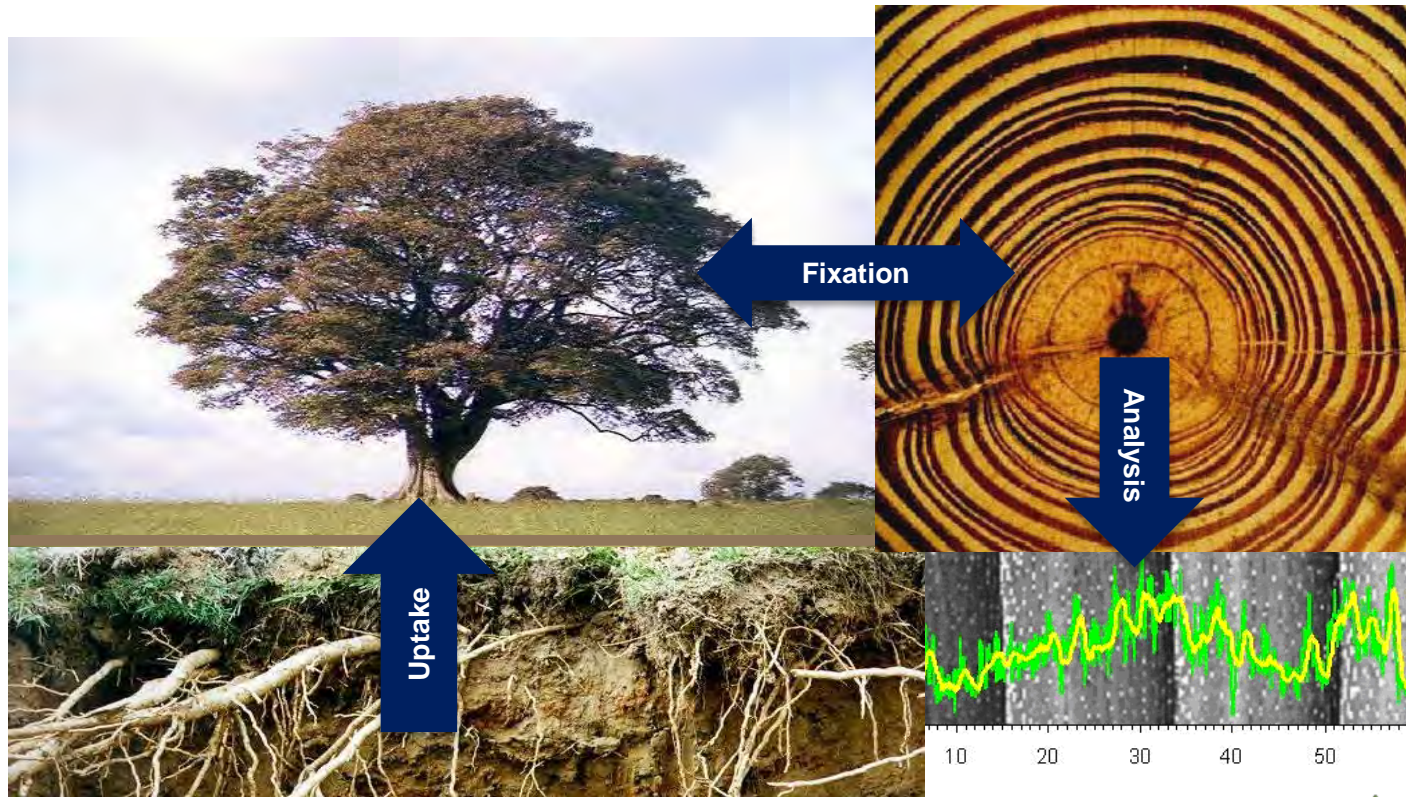
- 30% of Pb from the less impacted sample could be attributed to background
- Pb concentration in that sample was 3,300 mg/kg (ppm)
- **Pb background is approx.  $30\% \times 3,300 = 1,000$  mg/kg (ppm) result**



# Outcome

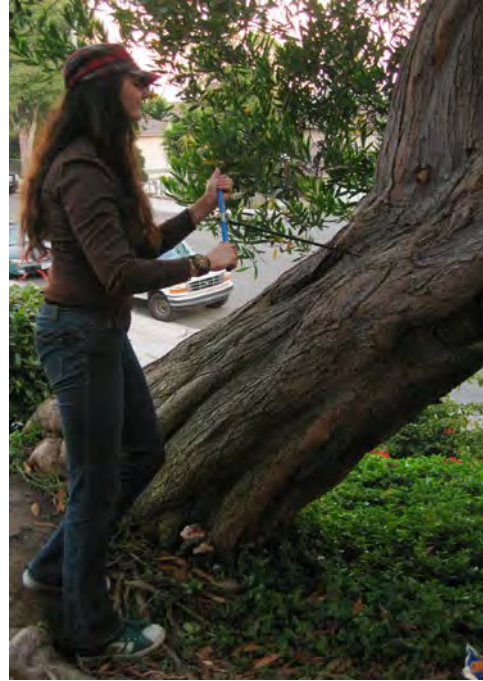
- Mineralogical fingerprinting provided on-site background value for Pb consistent with that from chemical data
- New clean-up limits for Pb were proposed equal to the determined background values
- The forensic study cost approx. **\$50K**
- The new clean-up values were accepted by the regulatory agency, resulting in **\$2.5 million in remediation savings** for the client

# Tree-Ring Fingerprinting



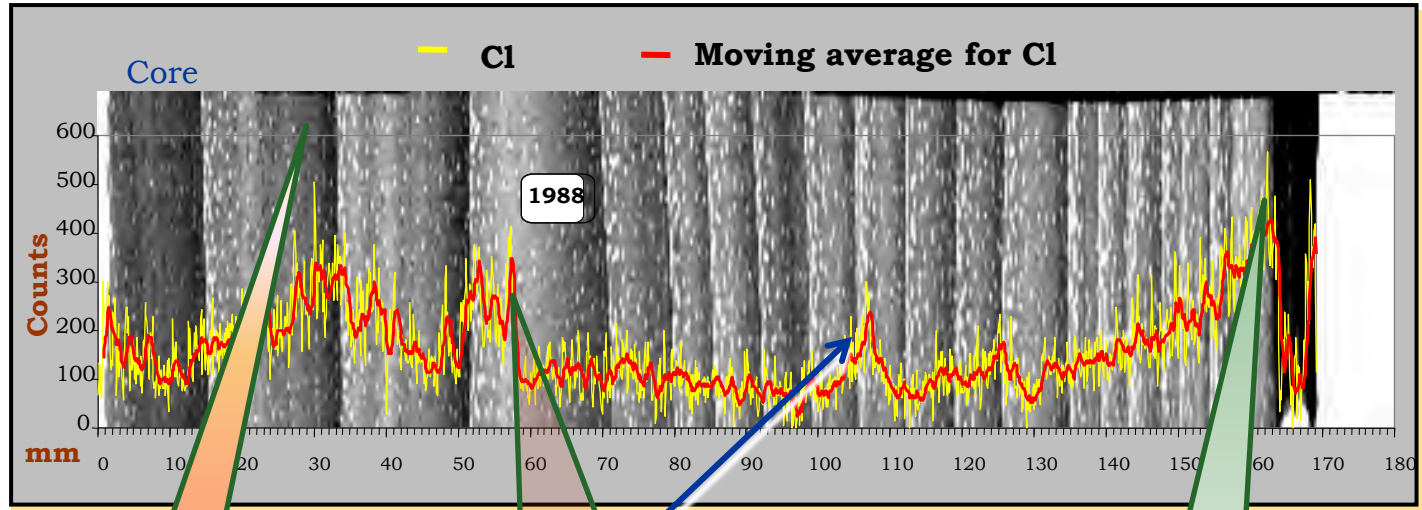
# Method

- Use of increment borers
- Sample transported in straws
- Sample is dried
- Sample is progressively sanded
- Sample is analyzed for:
  - Width of rings
  - Chemical element composition of rings (through EDXRF or other techniques)



# Case-Study Example

## Age-Dating TCE/PCE Plume at a Site in San Diego



1986 –  
Release got  
to tree

1988 & 1994 – More  
releases or worsening  
of original release

2005 -  
Sampling year

# Application as Sustainable Site Investigation Tool



Prepared in cooperation with the U.S. Environmental Protection Agency, Region VII

## Assessment of Subsurface Chlorinated Solvent Contamination Using Tree Cores at the Front Street Site and a Former Dry Cleaning Facility at the River-front Superfund Site, New Haven, Missouri, 1999–2003



Scientific Investigations Report 2004–5049

U.S. Department of the Interior  
U.S. Geological Survey

## Real-Time and Delayed Analysis of Tree and Shrub Cores as Indicators of Subsurface Volatile Organic Compound Contamination, Durham Meadows Superfund Site, Durham, Connecticut, August 29, 2006

By Don A. Vroblesky, Richard E. Willey, Scott Clifford, and James J. Murphy

Prepared in cooperation with the U.S. Environmental Protection Agency

Scientific Investigations Report 2007–5212

U.S. Department of the Interior  
U.S. Geological Survey



Prepared in cooperation with the U.S. Environmental Protection Agency  
Measurement and Monitoring for the 21st Century Initiative

## User's Guide to the Collection and Analysis of Tree Cores to Assess the Distribution of Subsurface Volatile Organic Compounds



Scientific Investigations Report 2008–5088

U.S. Department of the Interior  
U.S. Geological Survey

# USGS Case Study

## PCE in: Tree Cores (left) vs. Groundwater (right)

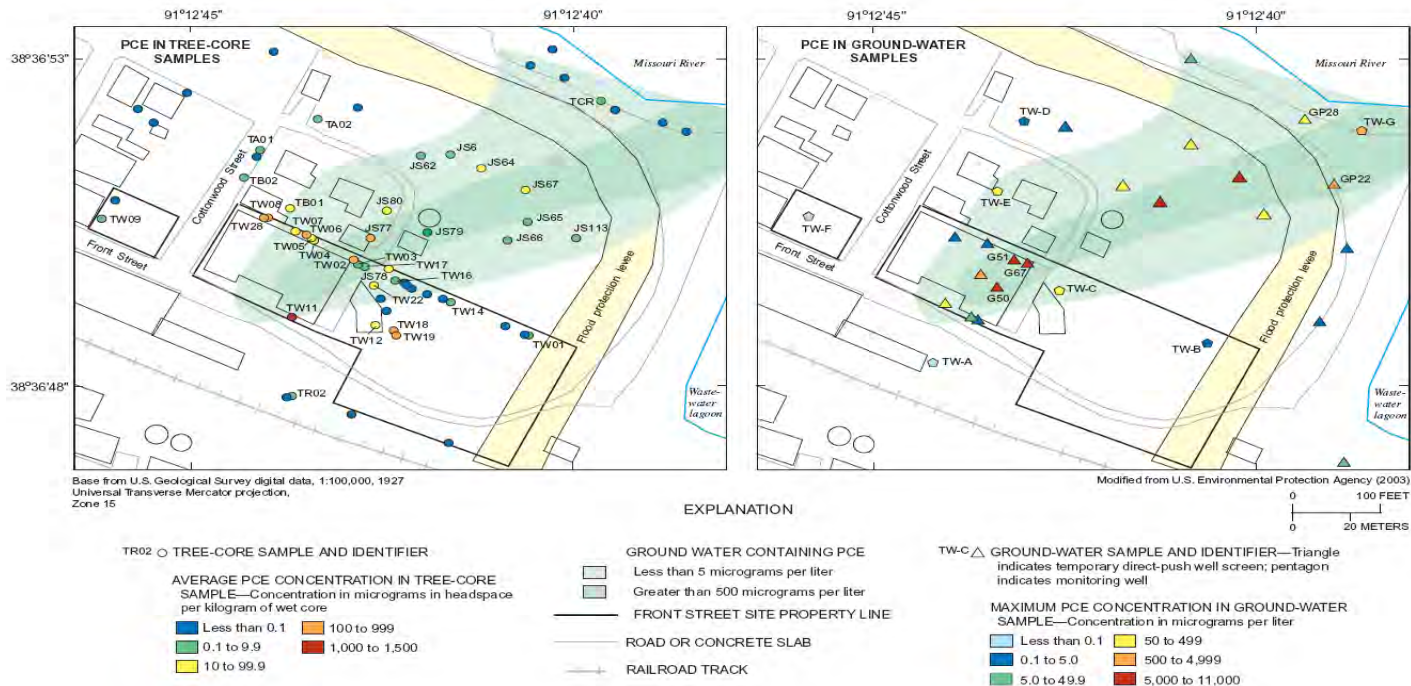
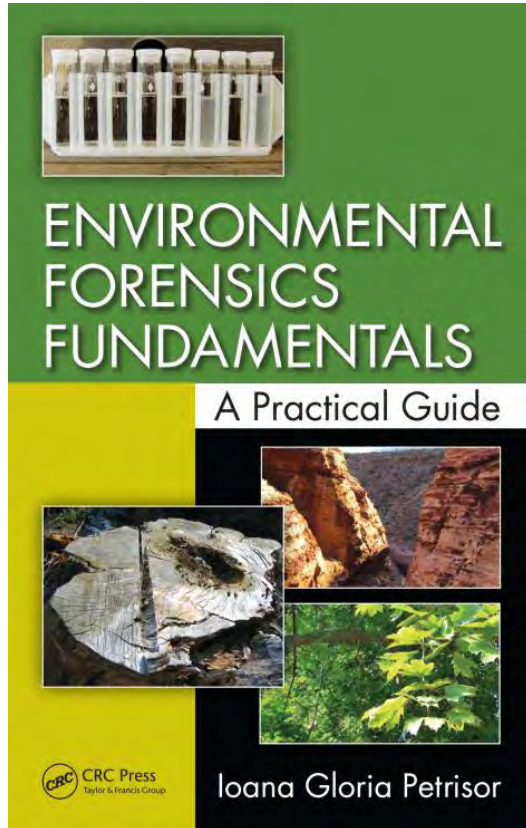


Figure 6. Relation between average tetrachloroethene (PCE) concentrations in tree-core samples and PCE concentrations in ground-water samples at the Front Street site (1999–2003).

# Additional Information, Questions, Discussion



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