Use of Forensics in Petroleum Spill Cases

NYSBA Oil Spill Symposium

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Topics for Discussion

- Introduction
- Chemical fingerprinting
- Gasoline case study
- Diesel case study
- PAH case study
- Age-dating

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Introduction

- About Alpha Analytical
  - Conventional & Specialty Laboratory Services
    - Advanced hydrocarbon analysis
      - Saturated hydrocarbons
      - Alkylated PAHs
      - Geochemical biomarkers
      - PIANO
      - PHI
- About NewFields Environmental Forensics
  - Consultants/Experts (technical and litigation)
  - Frequent collaboration with Alpha Analytical
  - Industrial and governmental clients

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Introduction to Petroleum Analysis

What's your application?

- Regulatory compliance
  - Generally a quantitative determination i.e. "TPH"
  - Lots of methods
- Risk assessment
  - Quantitative, but can have qualitative aspects
    - Risk based corrective action (RBCA)
  - ITRC TPH Workgroup
- Qualitative determinations
  - "What is it?"
    - "Routine" ("& not so routine") product identification
  - "Whose is it?"
    - Forensic / source allocation

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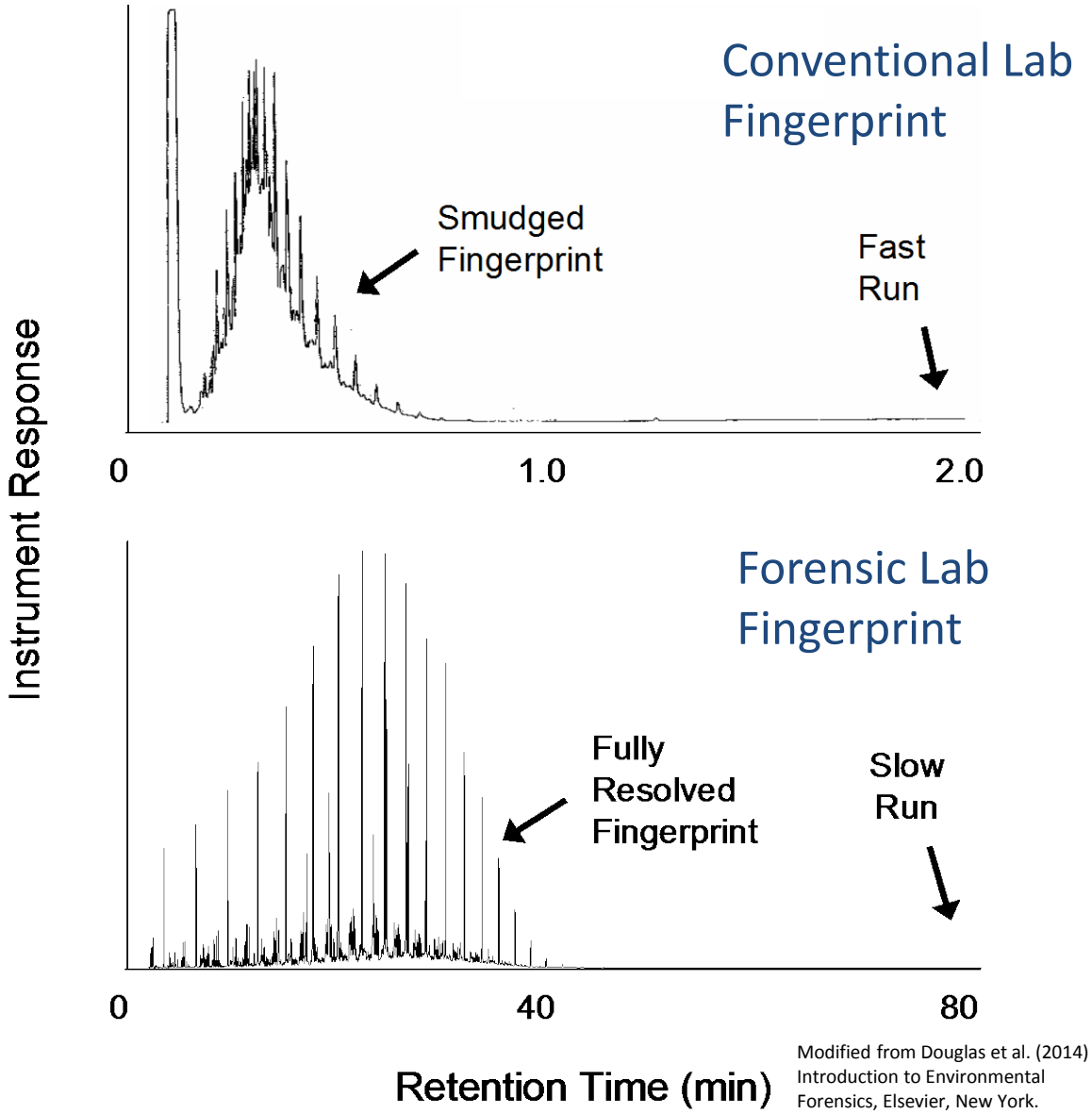
Qualitative Analysis
Routine Environmental Lab
"Fingerprinting"

- Methods can identify -
  - Presence or absence of common products
  - ID based on pattern recognition
    - "Forest vs. trees"
- Limitations
  - ~ 20 minute chromatographic run time
  - Trouble with mixtures, weathered samples
    - "Unknown product" ID

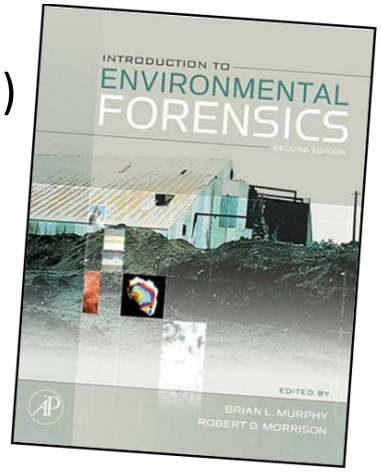


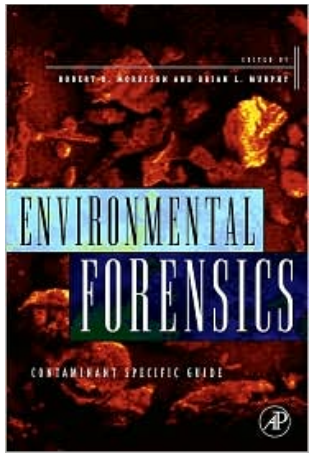
Modified from Douglas et al. (2014) Introduction to Environmental Forensics, Elsevier, New York.

Environmental Forensics

WHAT and WHERE?

- Unambiguous contaminant identification(s)
- Well-defined spatial extent of contaminant(s)



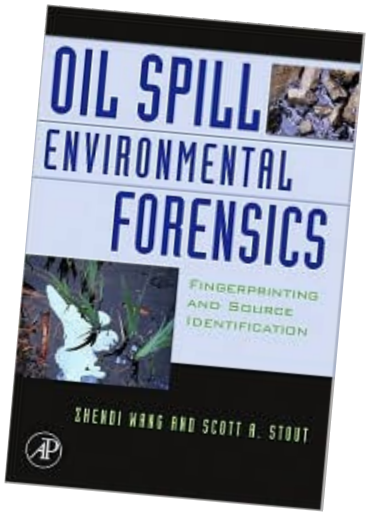


WHEN and WHO?

- Age-dating of contaminant(s)
- Defensible Allocation of Responsibility

Integrated Approach

- Chemical Fingerprinting
- Site/Regulatory History
- Process Forensics
- Geology and Hydrology
- Transport Modeling
- Numerical Analysis
- Allocation



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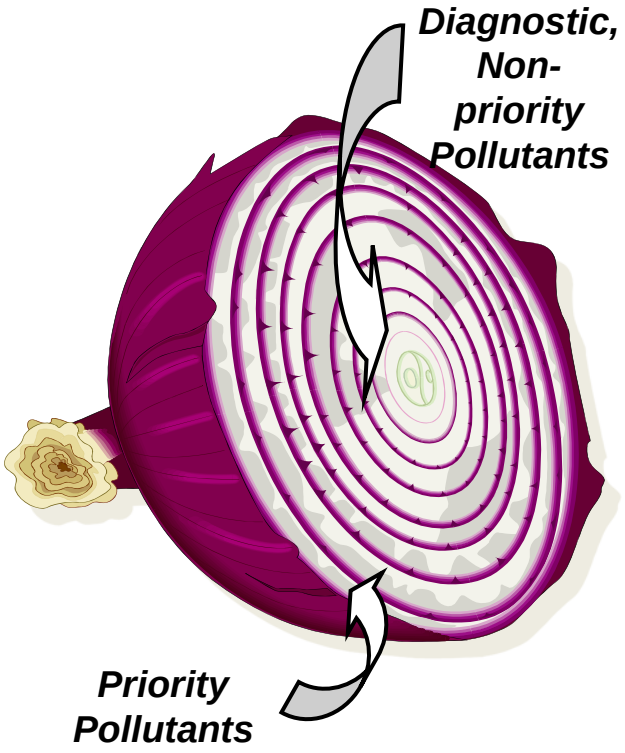
Limitations of Standard (SW-846) Methods

- Standard methods were developed to establish “nature and extent” of prescribed lists of COPCs
  - “Priority pollutant” chemicals (n=~130) are only a subset of chemicals contained in complex mixtures of products released into the environment
  - Many co-occurring, “nonpriority, pollutant” chemicals provide clues as to the source of the “priority pollutant” chemicals



Peel the Onion!

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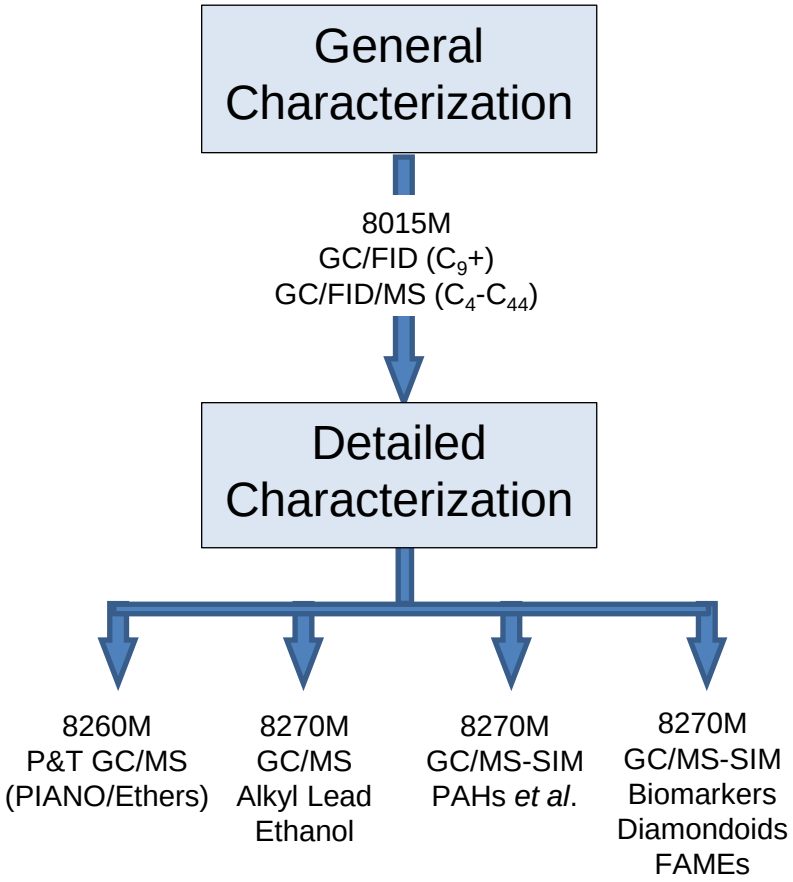
Tiered Approach to Chemical Fingerprinting of Hydrocarbons



TIER 1

High-resolution "fingerprint"
TPH, DRO, ORO, PHI

Contamination vs. Natural OM
Hydrocarbon Product ID
Overall Weathering

TIER 2

Detailed quantitative "fingerprint"
VOC: PIANO, ethers, ethanol, alkyl lead
SVOC: PAHs, Alkyl-PAHs, Sulfur-PAHs, PAH isomers, HPAHs, decalins, n-alkylcyclohexanes, biomarkers, biodiesels

Fuel, lube, waste specifics
Quantitative comparative analysis, weathering & mixture assessment

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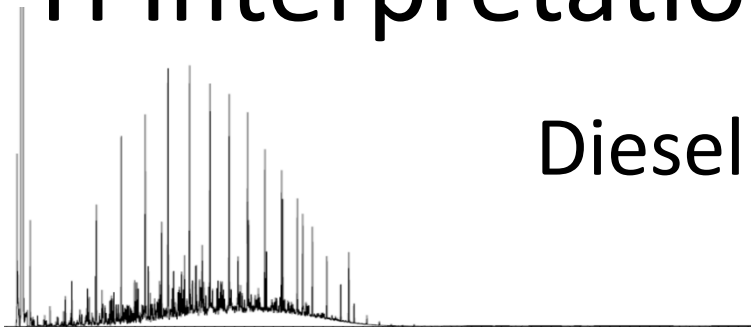
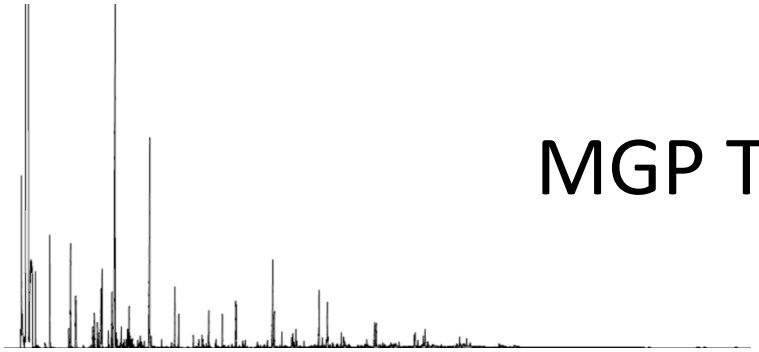
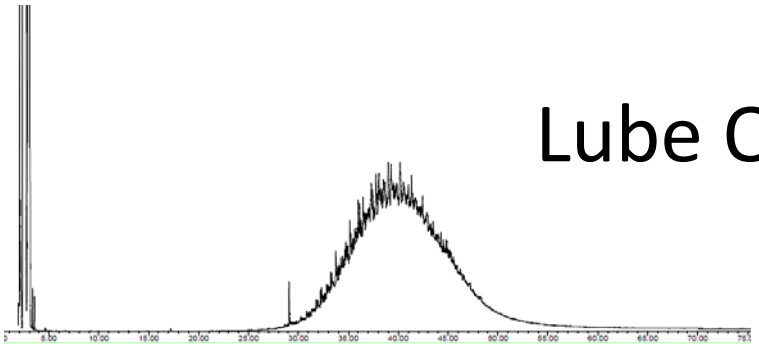
Tier 1: *What is it?*
TPH Interpretations



Diesel

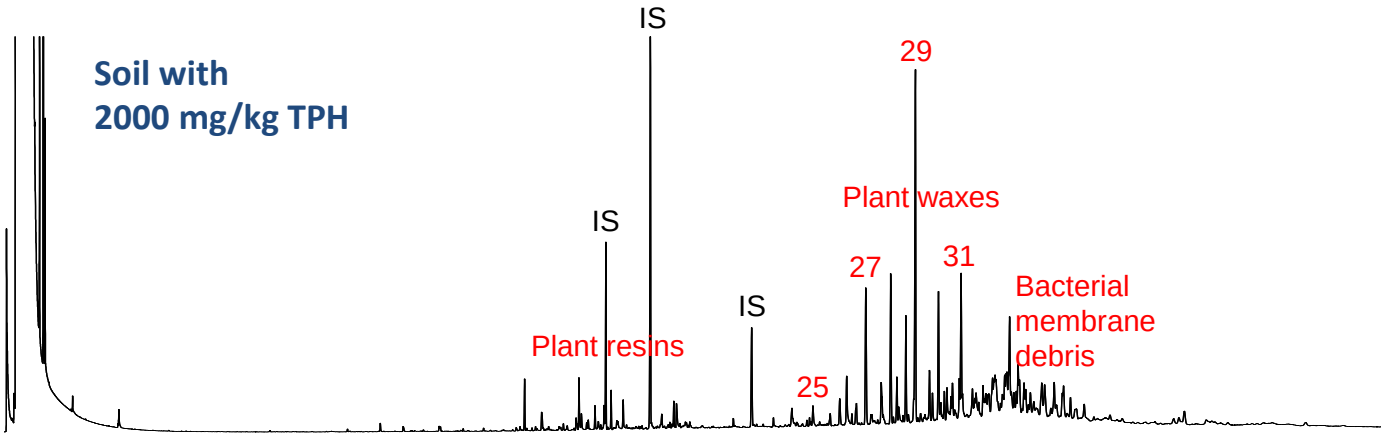


MGP Tar

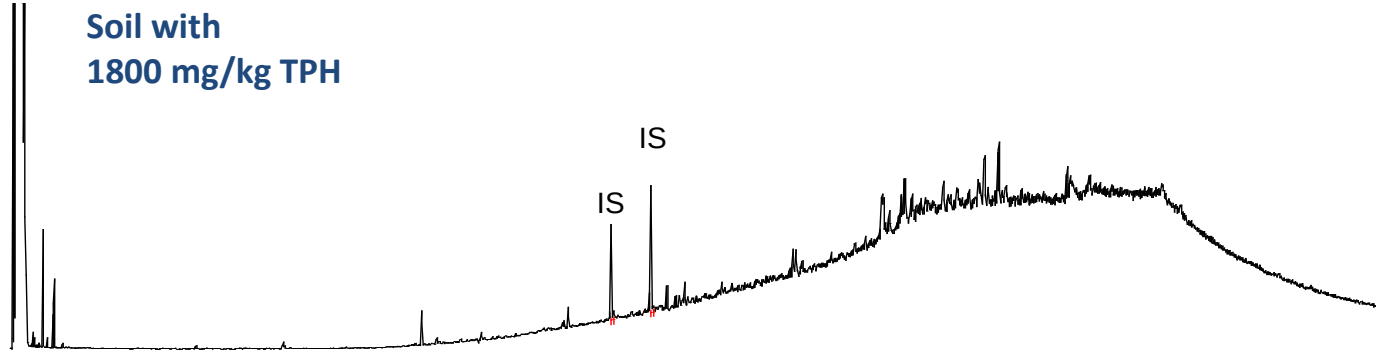


Lube Oil

Tier 1: Not all TPH is contamination



Naturally-occurring organic matter



Coal ash

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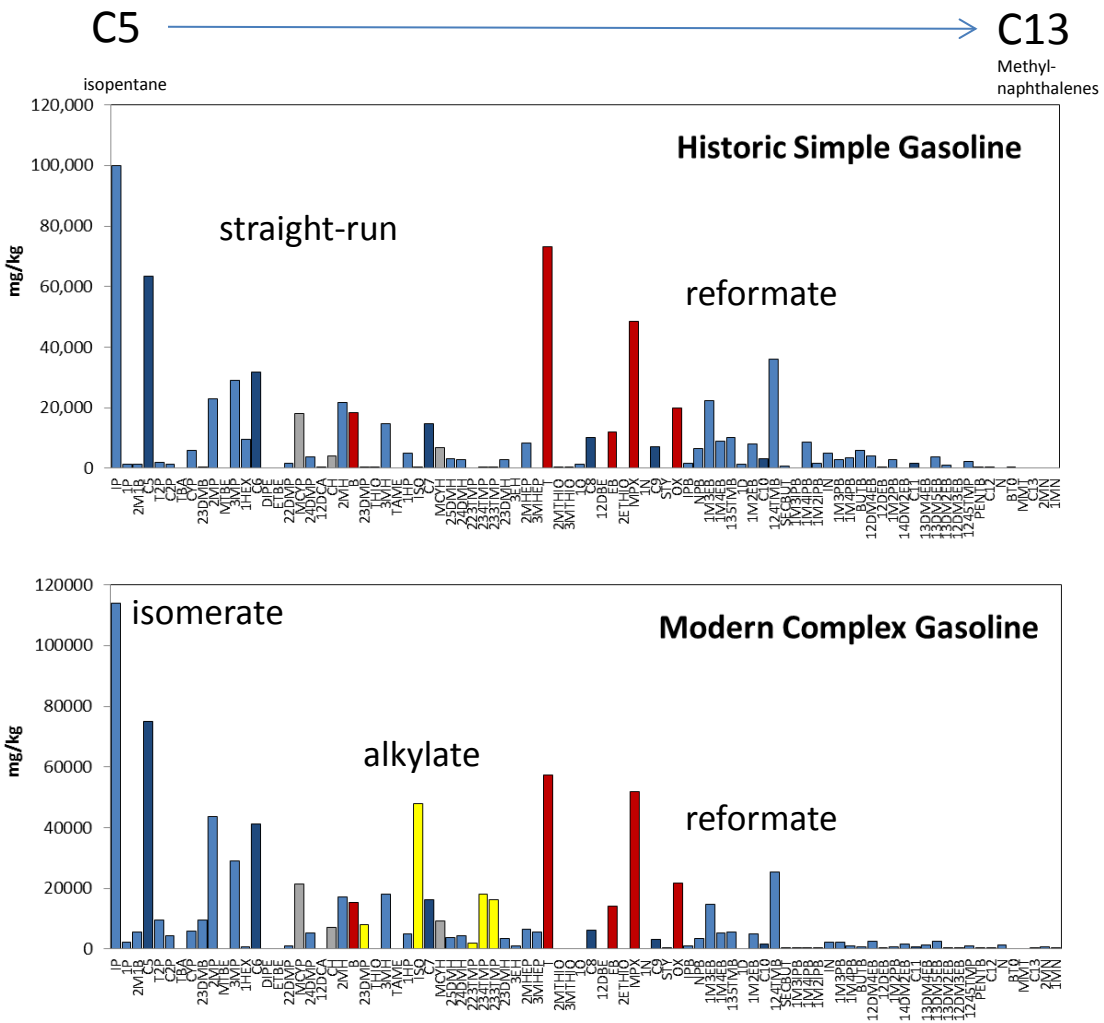
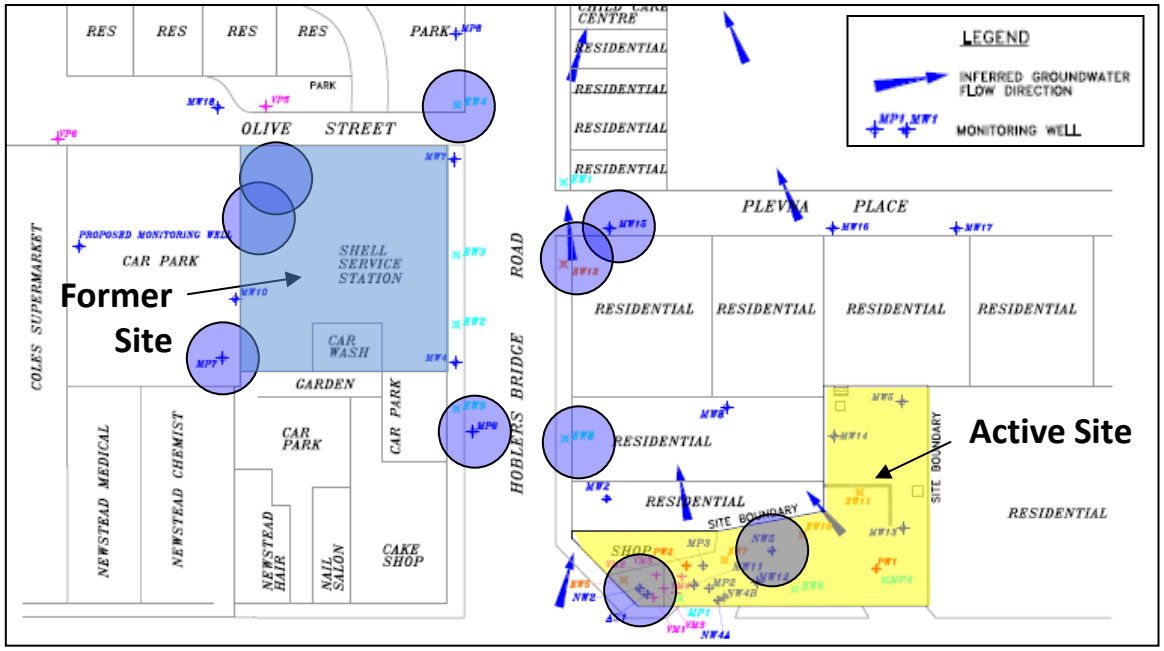
Tier 2: Gasoline/PIANO Fingerprinting

- PIANO data (~90 analytes) can reveal meaningful differences
  - Weathering
  - General and specific blending practices



Gasoline Case Study



- Former site with historic impacts observes NAPL increase; suspected impact from upgradient active site
- NAPLs (10) and active site dispensed gasolines (3) analyzed via modified EPA Methods 8015, 8260 (PIANO), and 8270 (organic lead).

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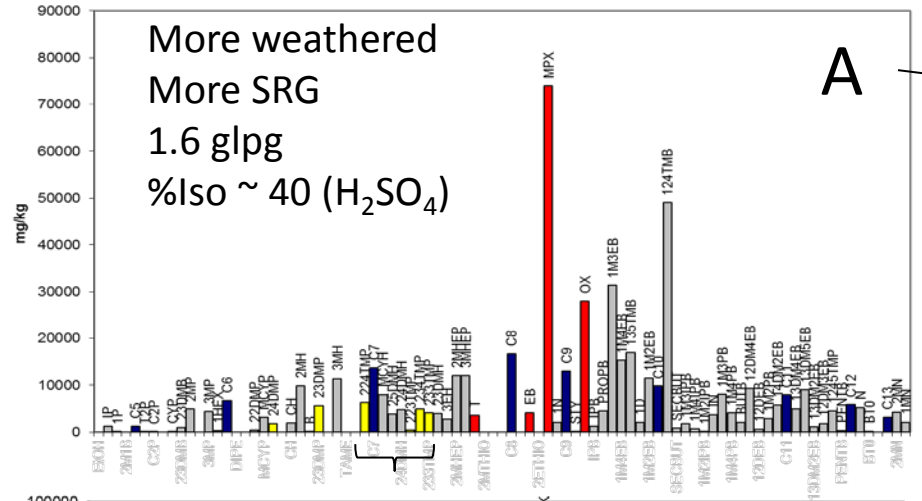
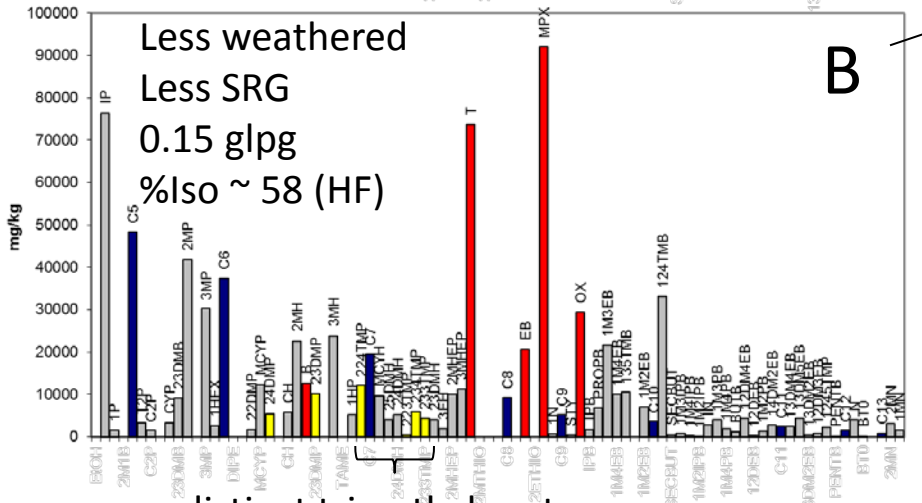
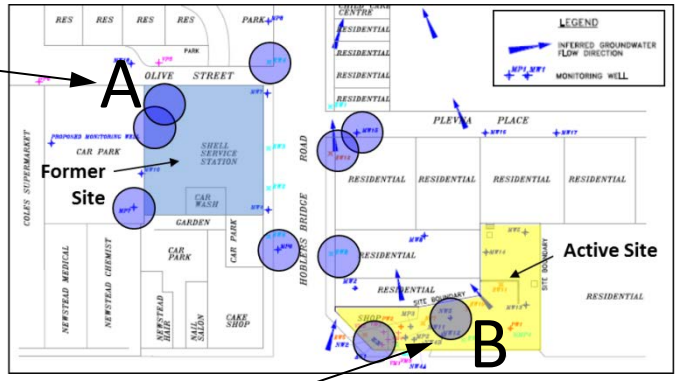
Gasoline Case Study





distinct trimethylpentane isomer patterns



- differences in degree of weathering, SRG abundance, and lead concentrations are evident
- specific alkylate type (%Iso) differences (independent of weathering) are also evident
  - alkylate type varies by refining process

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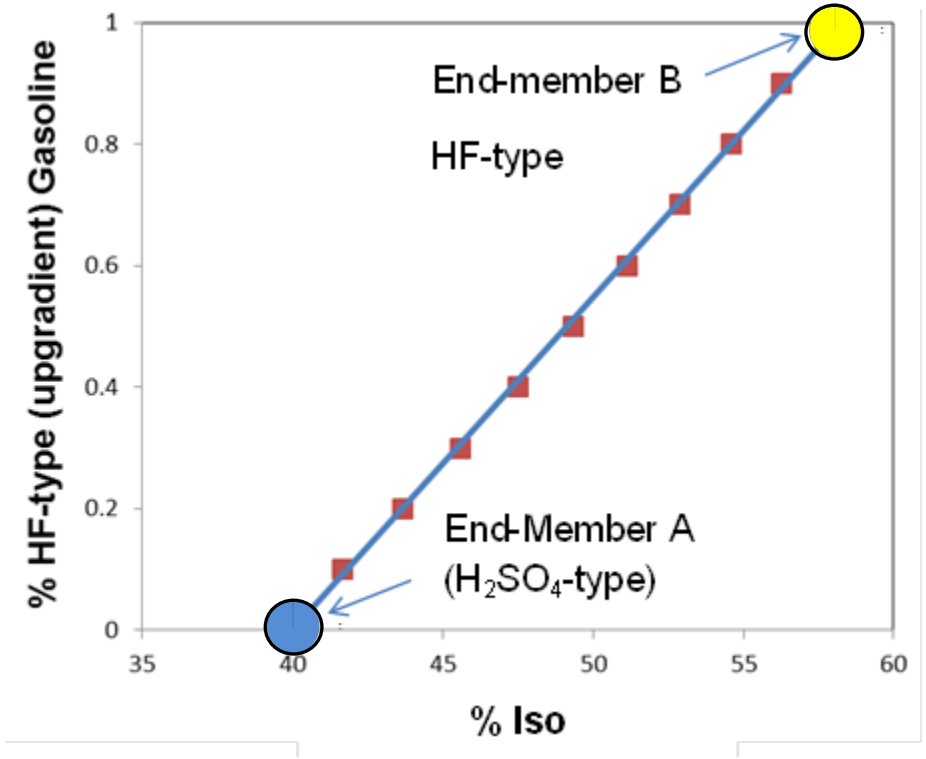
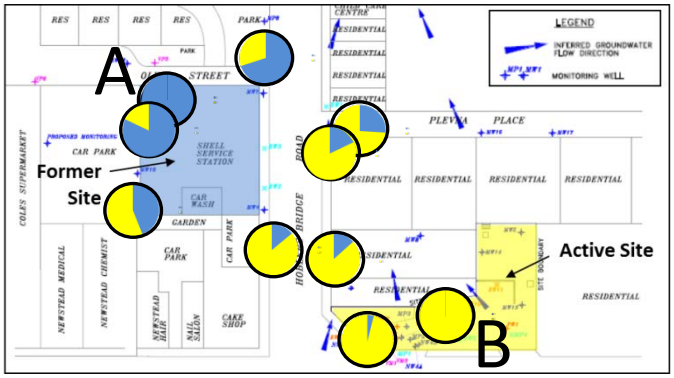
Gasoline Case Study





	End Member A	Well 1	Well 2	Well 3	Well 4	Well 5	Well 6	Well 7	Well 8	End Member B
%Iso Ratio	40	45	48	49	50	52	53	54	57	58
% Inactive	100	82	70	54	44	26	18	14	4	0
% Active	0	18	30	46	56	74	82	86	96	100

- Mixing model based on alkylate type used to estimate volume allocation

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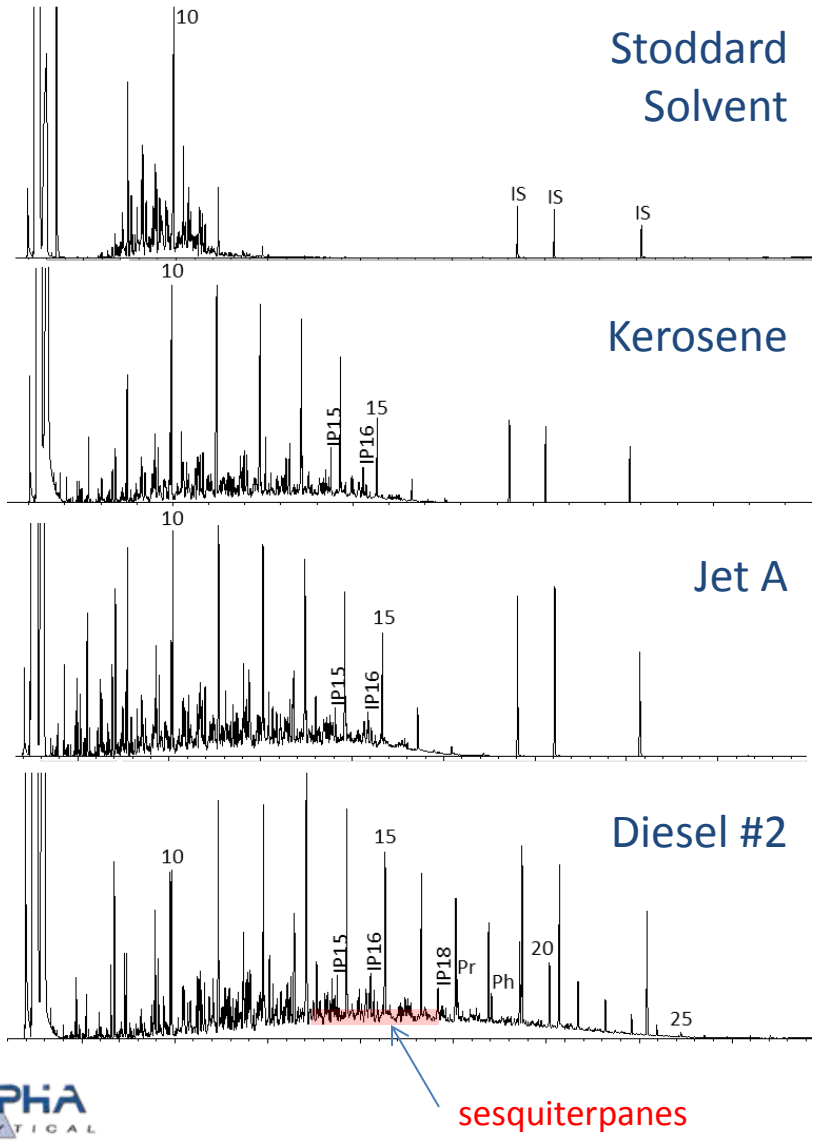
Distillate Fingerprinting



- Modified EPA Method 8015 (Tier 1)
  - whole oil and SHC
- Modified EPA Method 8270 (Tier 2)
  - Alkylated PAH
  - Sulfur-containing aromatics
  - Low boiling Biomarkers

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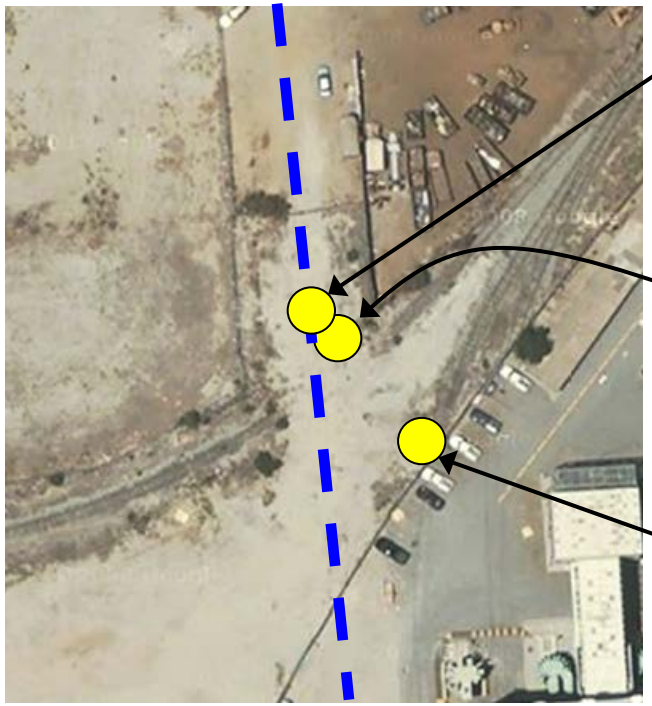
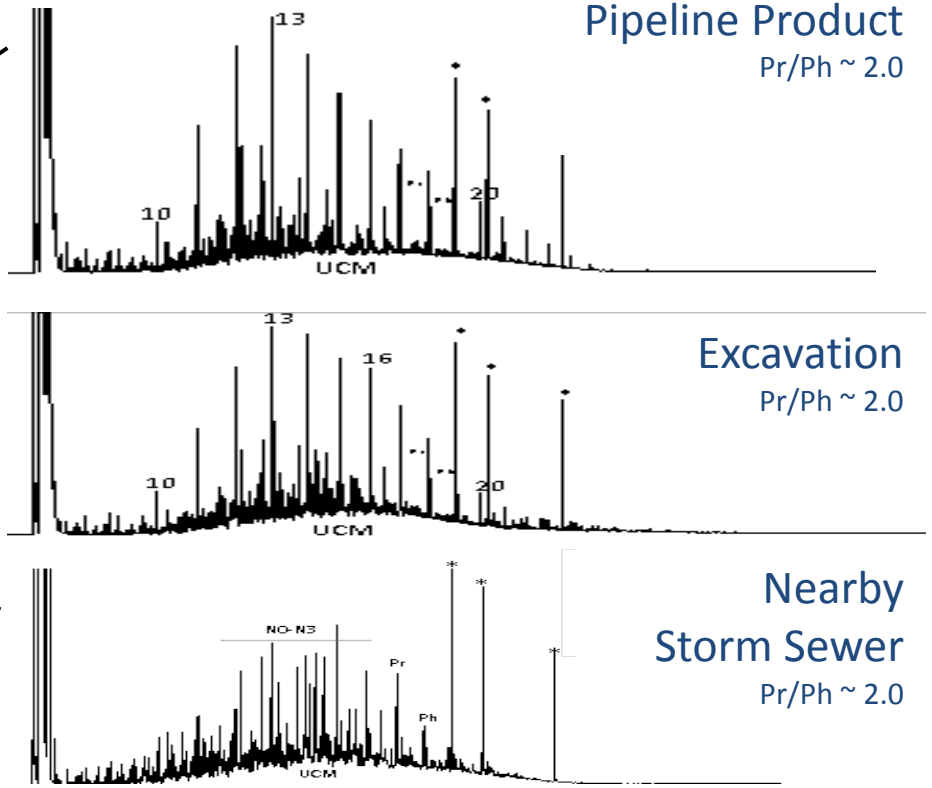
Diesel Case Study





- underground pipeline failure prompts investigation/clean-up in industrial area

Tier 1 GC/FID chromatograms (8015M)

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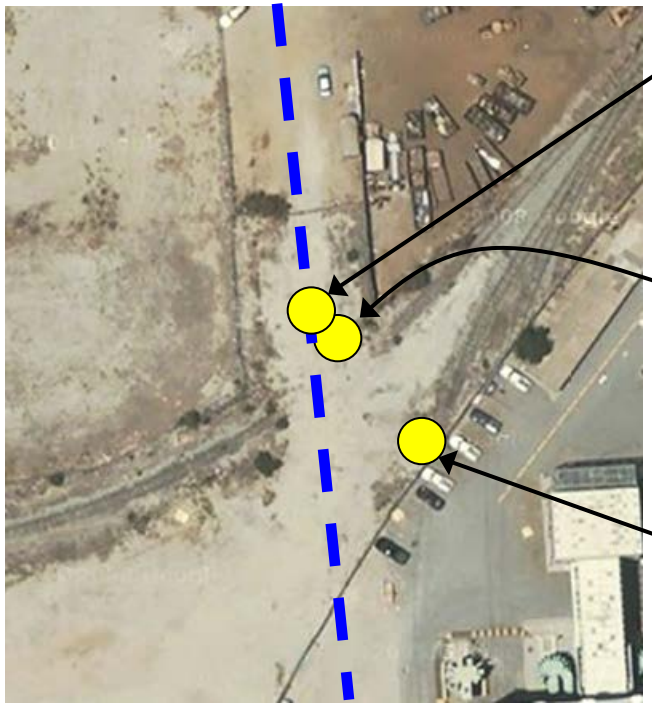
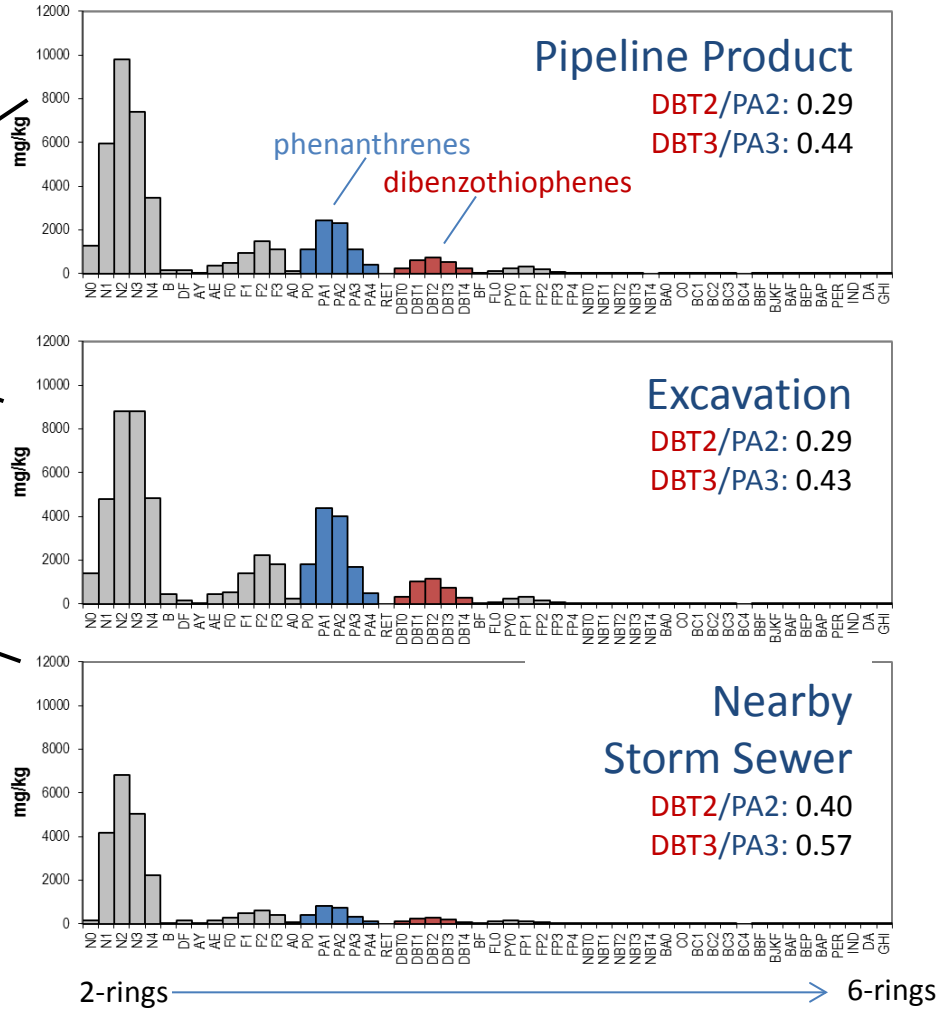
Diesel Case Study





- nearby storm sewer diesel contains higher sulfur aromatics

Tier 2: 52 PAH-related analytes (8270M)

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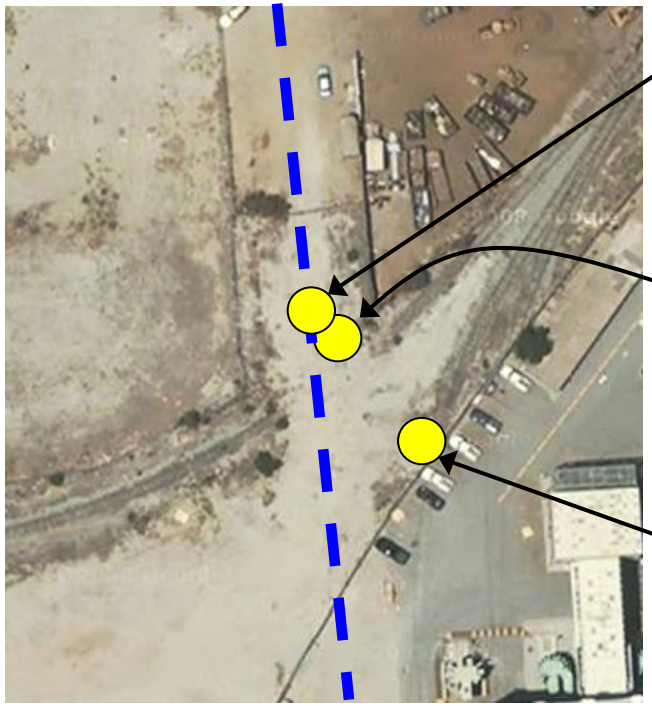
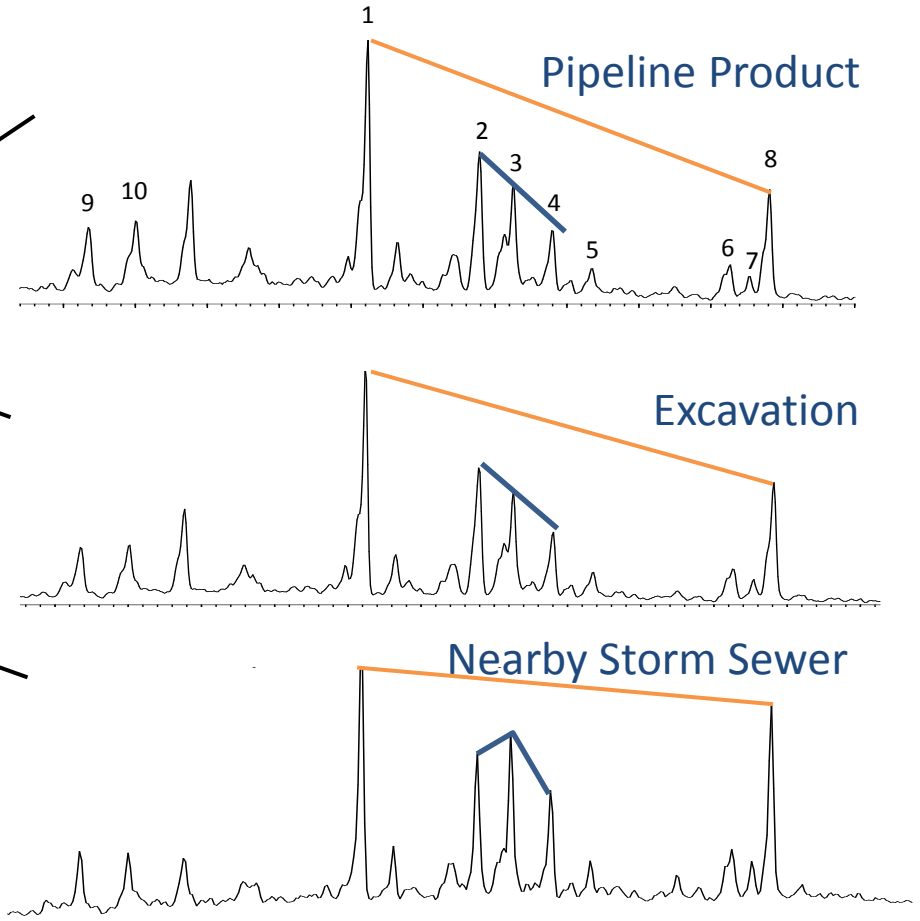
Diesel Case Study





- nearby storm sewer contains distinct sesquiterpane biomarkers

Tier 2: *m/z* 123 extracted ion profiles (8270M)

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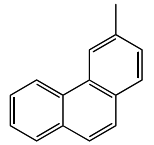
Comparison of Methods PAH-based (EPA 8270)

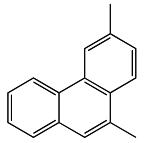
Abbrev.	Compound Name/Group	Abbrev.	Compound Name/Group
D0	cis/trans-Decalin	DBT0	Dibenzothiophene
D1	C1-Decalins	DBT1	C1-Dibenzothiophenes
D2	C2-Decalins	DBT2	C2-Dibenzothiophenes
D3	C3-Decalins	DBT3	C3-Dibenzothiophenes
D4	C4-Decalins	DBT4	C4-Dibenzothiophenes
BT0	Benzothiophene	BF	Benzo(b)fluorene
BT1	C1-Benzo(b)thiophenes	FL0	Fluoranthene
BT2	C2-Benzo(b)thiophenes	PY0	Pyrene
BT3	C3-Benzo(b)thiophenes	FP1	C1-Fluoranthenes/Pyrenes
BT4	C4-Benzo(b)thiophenes	FP2	C2-Fluoranthenes/Pyrenes
N0	Naphthalene	FP3	C3-Fluoranthenes/Pyrenes
N1	C1-Naphthalenes	FP4	C4-Fluoranthenes/Pyrenes
N2	C2-Naphthalenes	NBT0	Naphthobenzothiophenes
N3	C3-Naphthalenes	NBT1	C1-Naphthobenzothiophenes
N4	C4-Naphthalenes	NBT2	C2-Naphthobenzothiophenes
B	Biphenyl	NBT3	C3-Naphthobenzothiophenes
DF	Dibenzofuran	NBT4	C4-Naphthobenzothiophenes
AY	Acenaphthylene	BA0	Benz[a]anthracene
AE	Acenaphthene	C0	Chrysene/Triphenylene
F0	Fluorene	BC1	C1-Chrysenes
F1	C1-Fluorenes	BC2	C2-Chrysenes
F2	C2-Fluorenes	BC3	C3-Chrysenes
F3	C3-Fluorenes	BC4	C4-Chrysenes
A0	Anthracene	BBF	Benzo[b]fluoranthene
P0	Phenanthrene	BJKF	Benzo[j]fluoranthene/Benzo[k]fluoranthene
PA1	C1-Phenanthrenes/Anthracenes	BAF	Benzo[a]fluoranthene
PA2	C2-Phenanthrenes/Anthracenes	BEP	Benzo[e]pyrene
PA3	C3-Phenanthrenes/Anthracenes	BAP	Benzo[a]pyrene
PA4	C4-Phenanthrenes/Anthracenes	PER	Perylene
RET	Retene	IND	Indeno[1,2,3-cd]pyrene
		DA	Dibenz[ah]anthracene/Dibenz[ac]anthracene
		GHI	Benzo[g,h,i]perylene

Parent PAH

Alkylated PAHs



C1-



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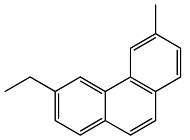
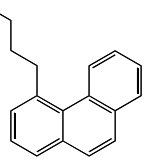


C3-



C4-

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Examples of PAH Fingerprinting

Petrogenic

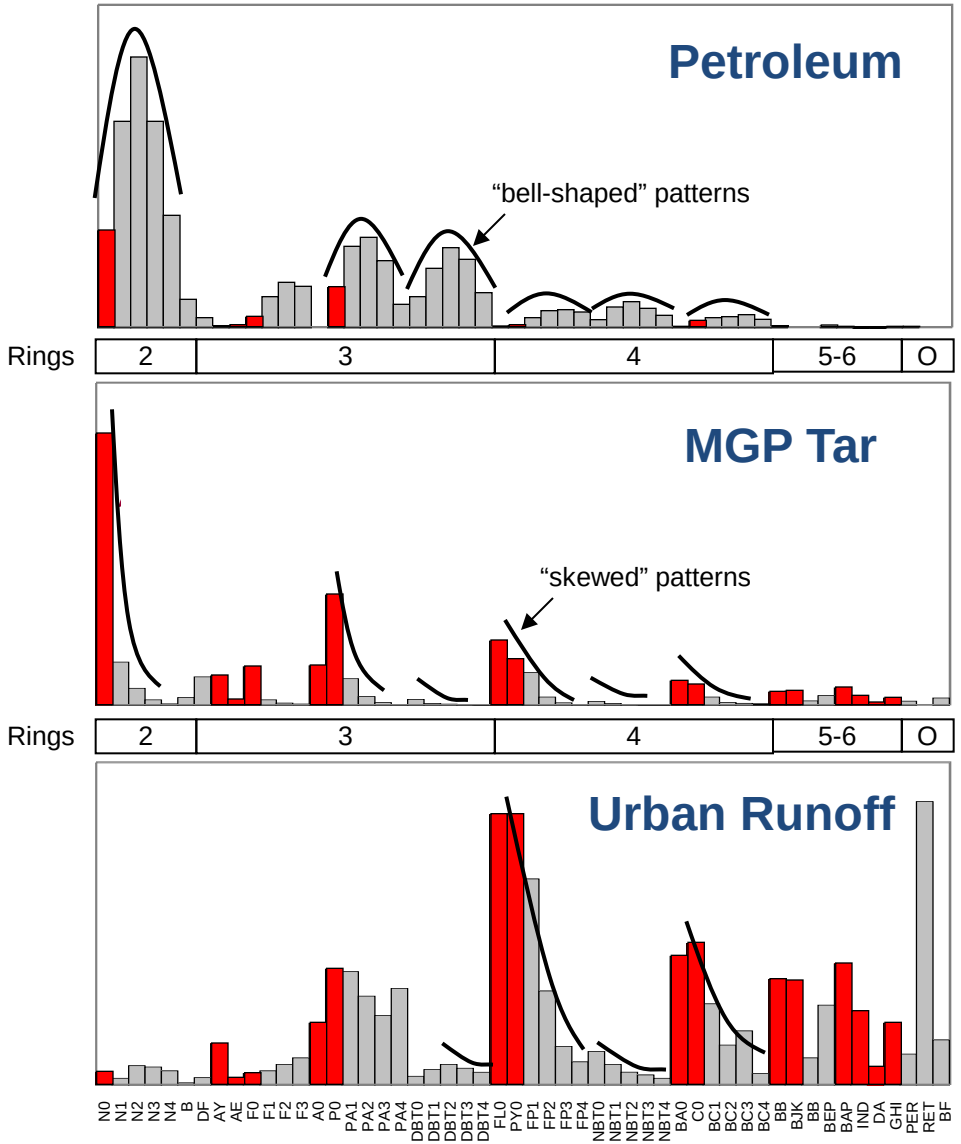
- Alkyl > Parent
- Little 4 to 6 Ring

Pyrogenic I

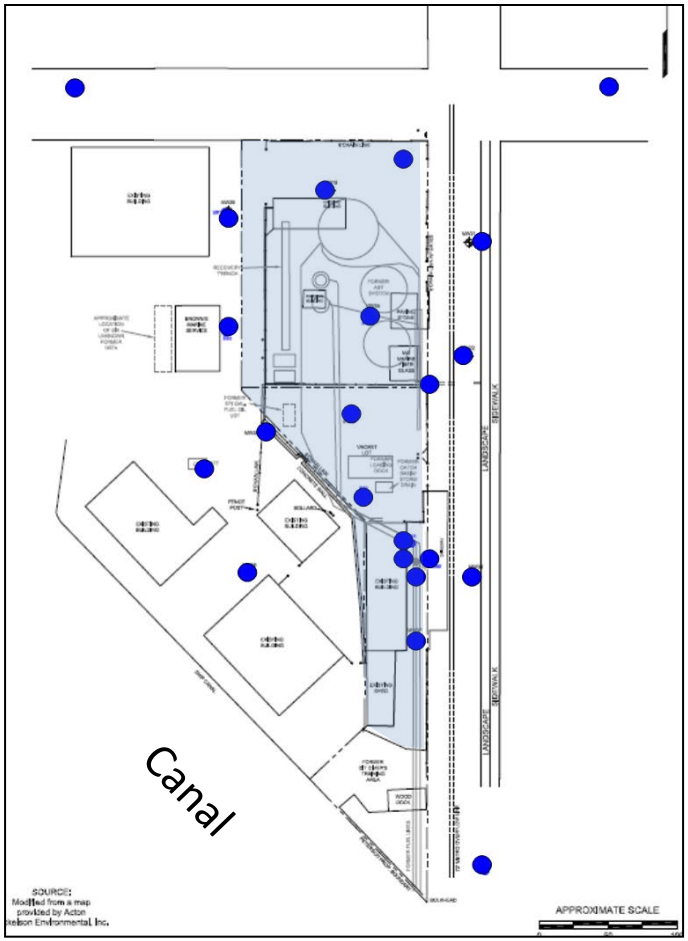
- Alkyl < Parent
- High 2 and 3 Ring

Pyrogenic II

- Alkyl < Parent
- High 4 to 6 Ring



PAH Case Study



- Former fuel storage facility located in industrial area along canal
- cPAH source(s) in surface soils elevated and attributed to spilled fuel by regulator
- Chemical fingerprinting study conducted to evaluate source(s) of PAH in surface soils
  - Tier 1: 8015M
  - Tier 2: 8270M

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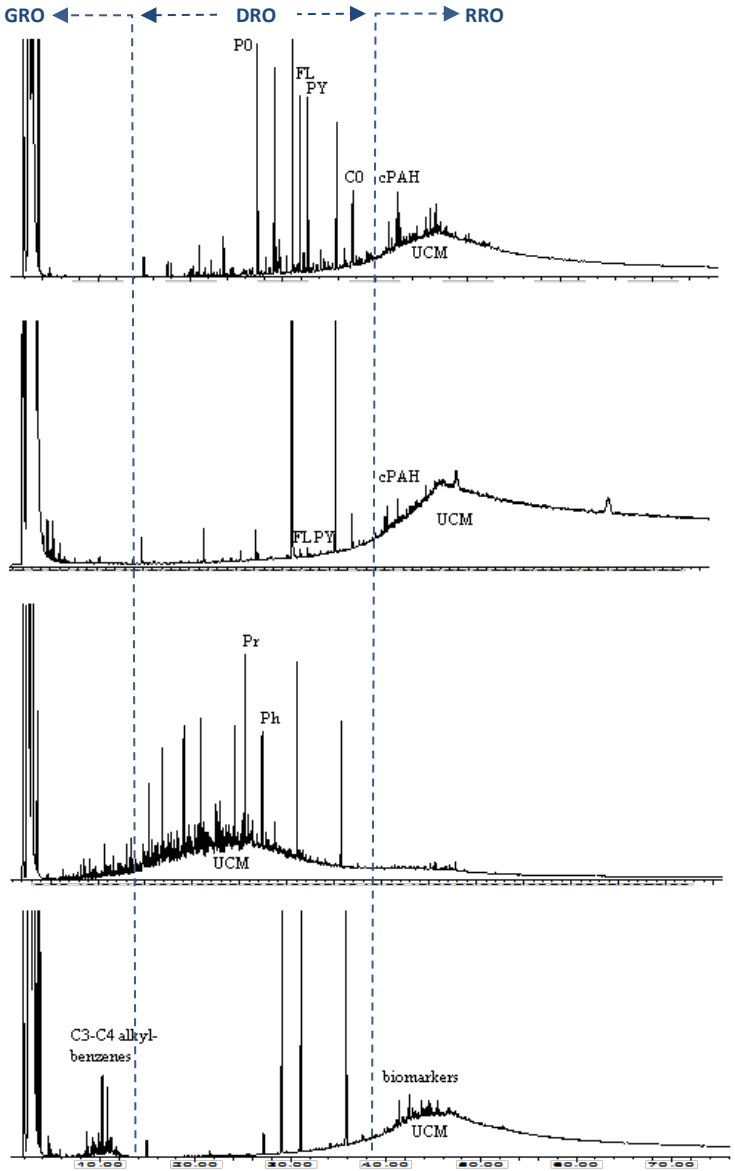
PAH Case Study



- PAHs sources can be more confidently determined when TPH is understood
- Tier 1 TPH fingerprinting via 8015M revealed four distinct hydrocarbon sources

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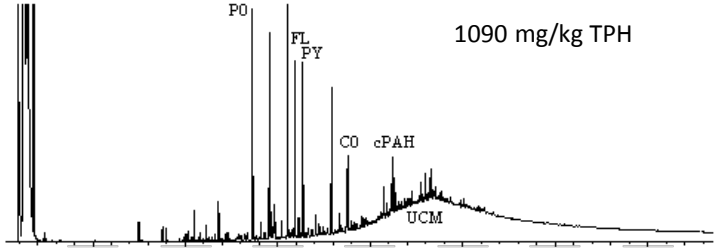
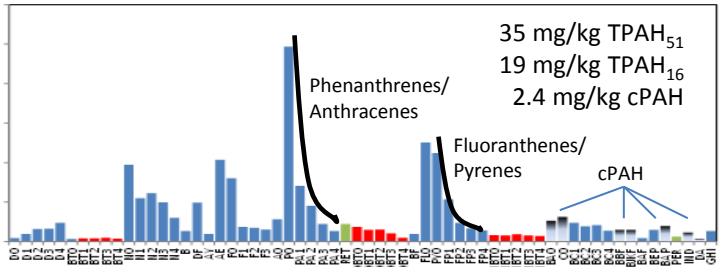
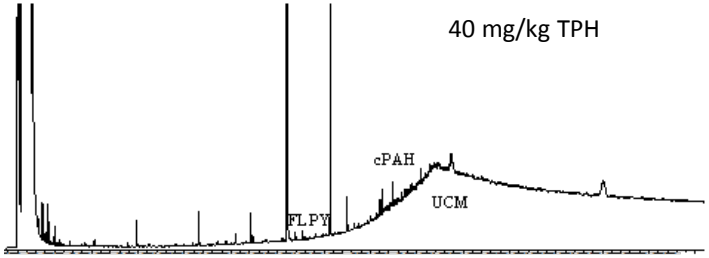
PAH Case Study



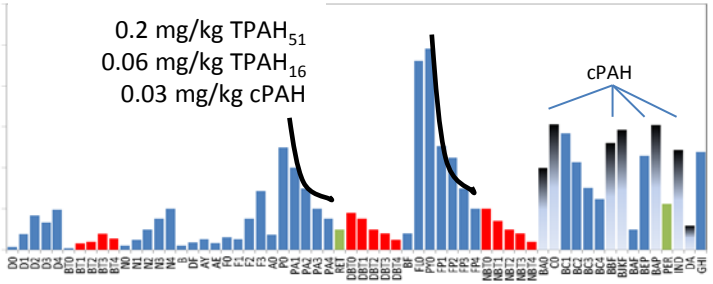
1090 mg/kg TPH



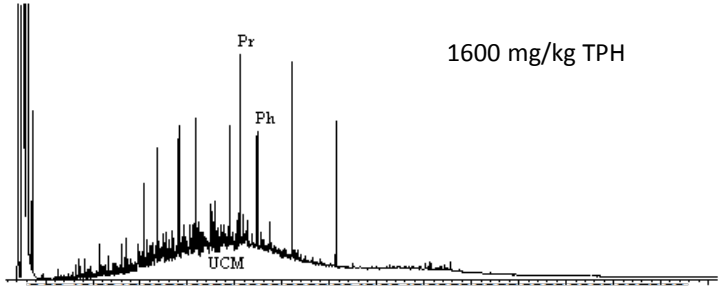
35 mg/kg $TPAH_{51}$
19 mg/kg $TPAH_{16}$
2.4 mg/kg cPAH



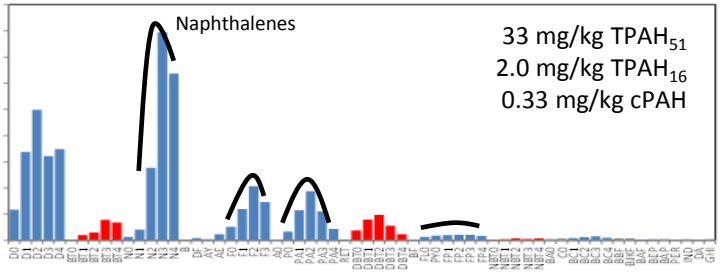
40 mg/kg TPH



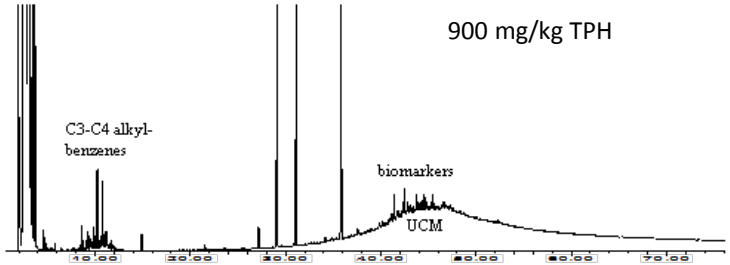
0.2 mg/kg $TPAH_{51}$
0.06 mg/kg $TPAH_{16}$
0.03 mg/kg cPAH



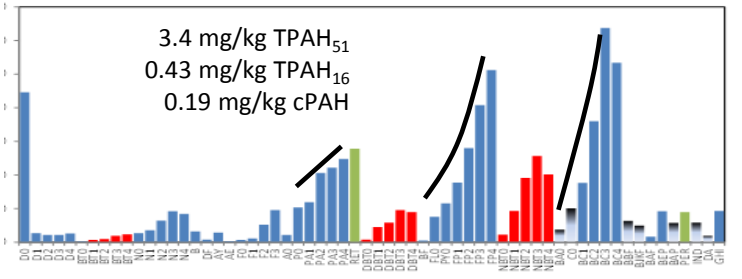
1600 mg/kg TPH



33 mg/kg $TPAH_{51}$
2.0 mg/kg $TPAH_{16}$
0.33 mg/kg cPAH



900 mg/kg TPH



3.4 mg/kg $TPAH_{51}$
0.43 mg/kg $TPAH_{16}$
0.19 mg/kg cPAH

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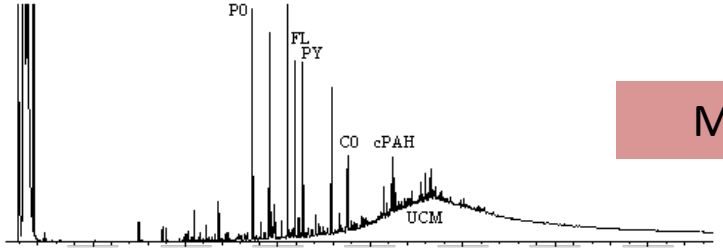
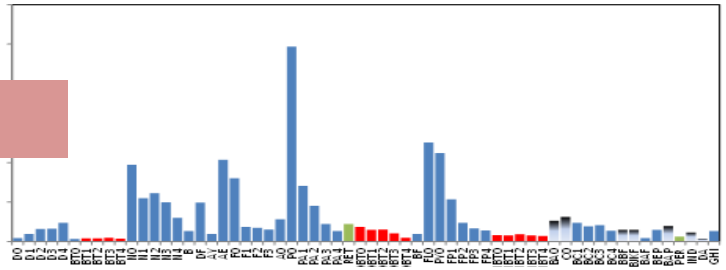
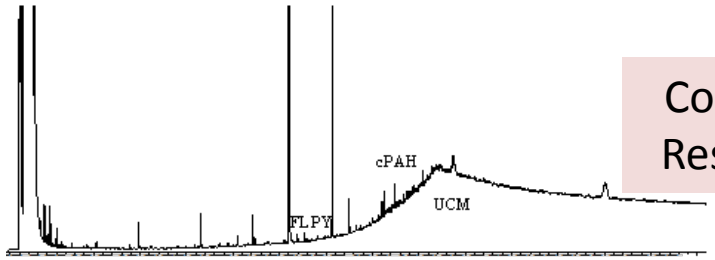
PAH Case Study

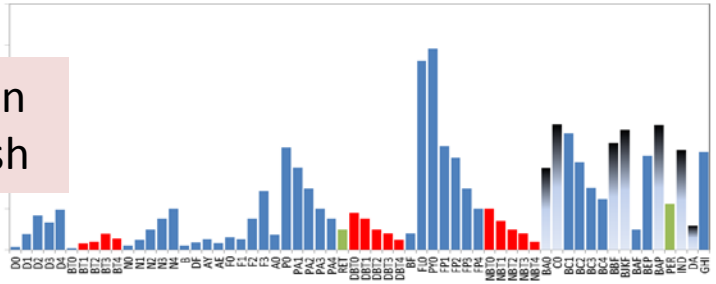


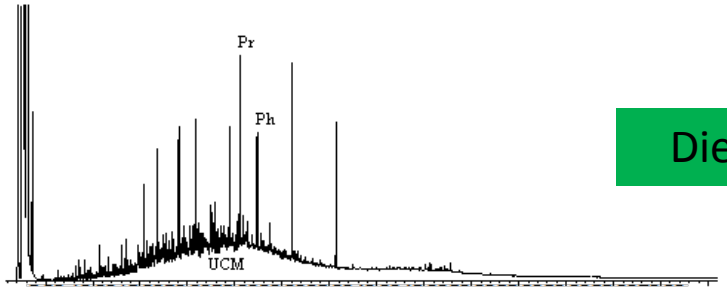
MGP Tar



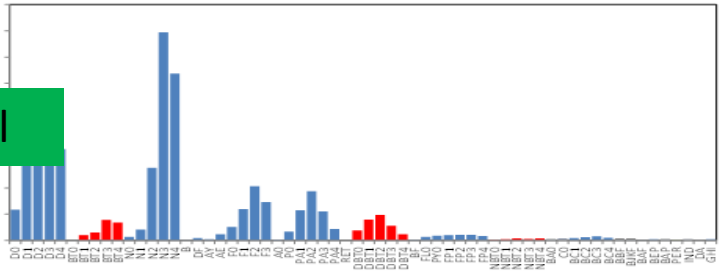


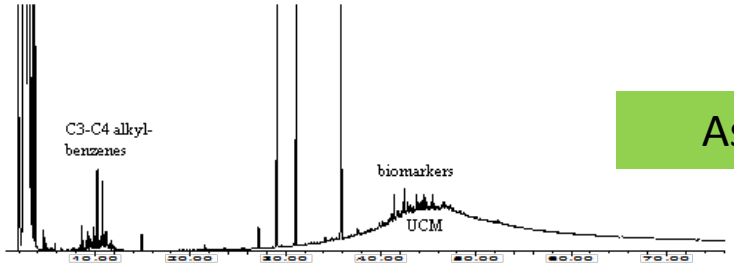
Combustion Residue/Ash



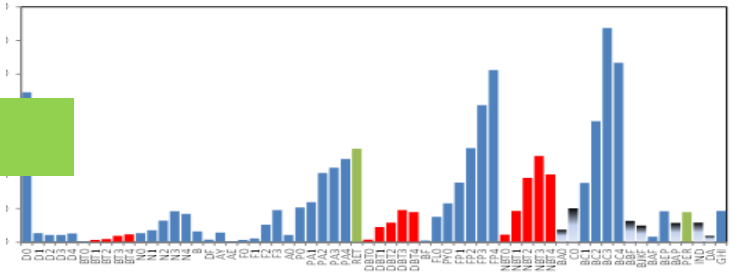


Diesel Fuel





Asphalt



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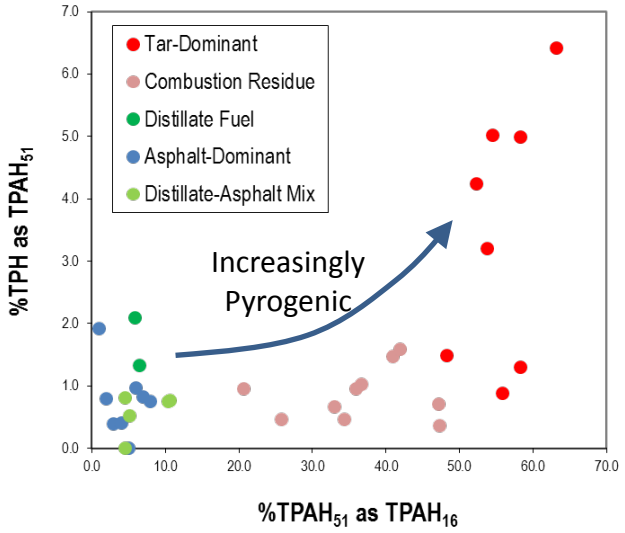
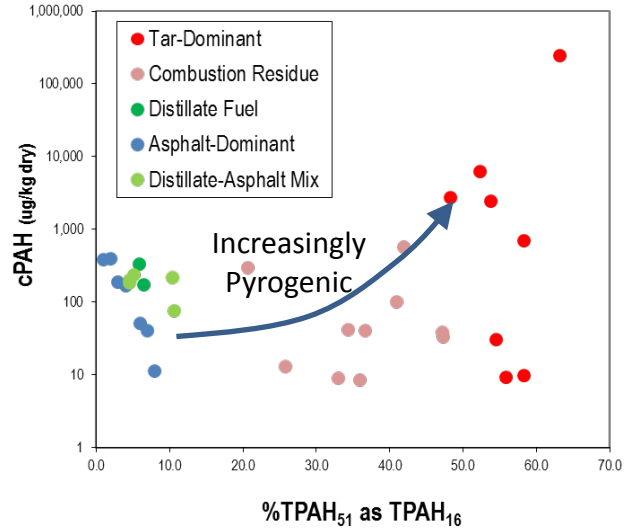
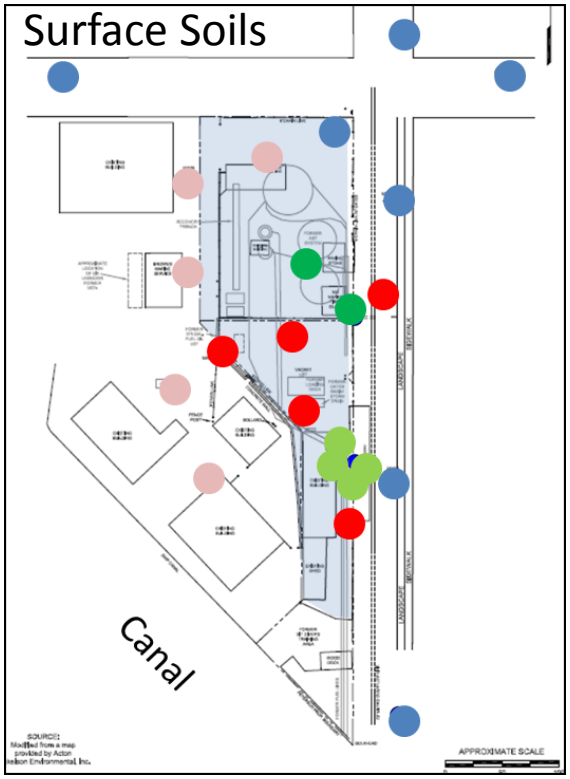
PAH Case Study







- Spilled petroleum was a limited source of cPAH
- Historic fill (MGP tar and ash) from canal dredging is dominant source of cPAH

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Age-Dating of Gasoline Contamination

- Never simple
- Mixing always confounding
- Chemistry is not 'magic'
- Constrain the age thru combination of:
  - chemistry
  - site or regulatory history
  - F&T modeling

Common Approaches

- Gasoline additives (concentration *vs.* presence/absence)
- Blending Practices
- Sulfur content
- Lead Isotopes $^{206}Pb/^{207}Pb$
- Degree of Weathering (simple ratios, volatiles)

Regulatory Limits on Lead in Gasoline

Date	United States		Regulation
	Leaded	Unleaded	
1926	3.17		Surgeon General
1959	4.23		Surgeon General
Jul-74		0.05[b]	Federal Register 38(6), Part II, Jan. 10, 1973
Oct-82	1.1[a]		Federal Register, June 8, 1977
Jul-85	0.5[a]		
Jan-86	0.1		
Jan-92	banned in CA		
Jan-96	banned nationwide		Federal Register, 1990

Date	Canada		Regulation
	Leaded	Unleaded	
Jan-76	3.0	0.05	Clean Air Act, Section 22, Canada Gazette, Part II, 108(15), Aug. 14, 1974
Jan-87	1.1		
Dec-90	banned nationwide		
Dec-90	0.1[c]		

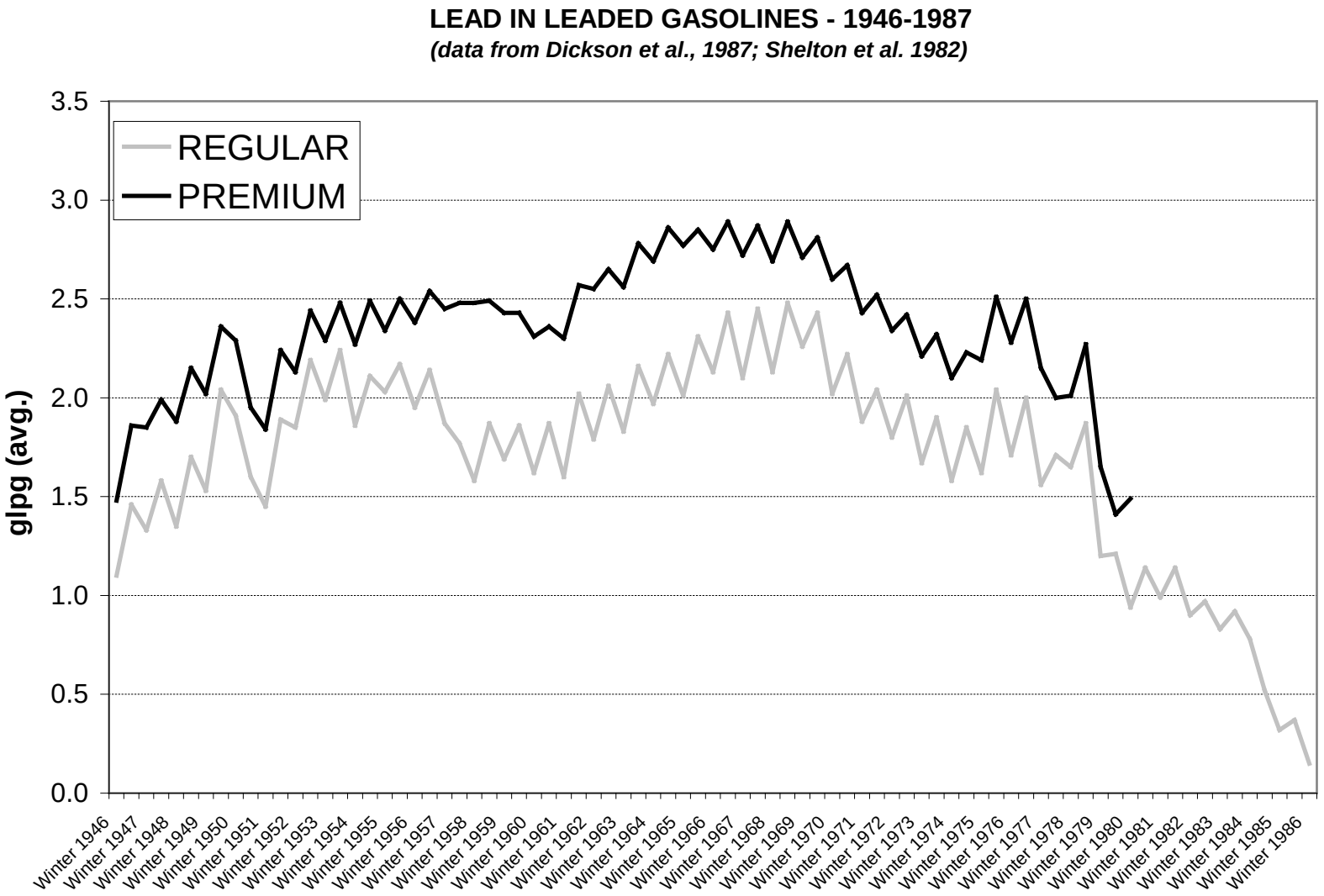
[a]average quarterly leaded gasoline production

[b]incidental lead in unleaded gasoline

[c]only permitted in off-highway and marine use

Stout et al. (2006) *Automotive Gasoline*. Environmental Forensics, Academic Press, p. 465-531.

Lead Concentration (Avg)



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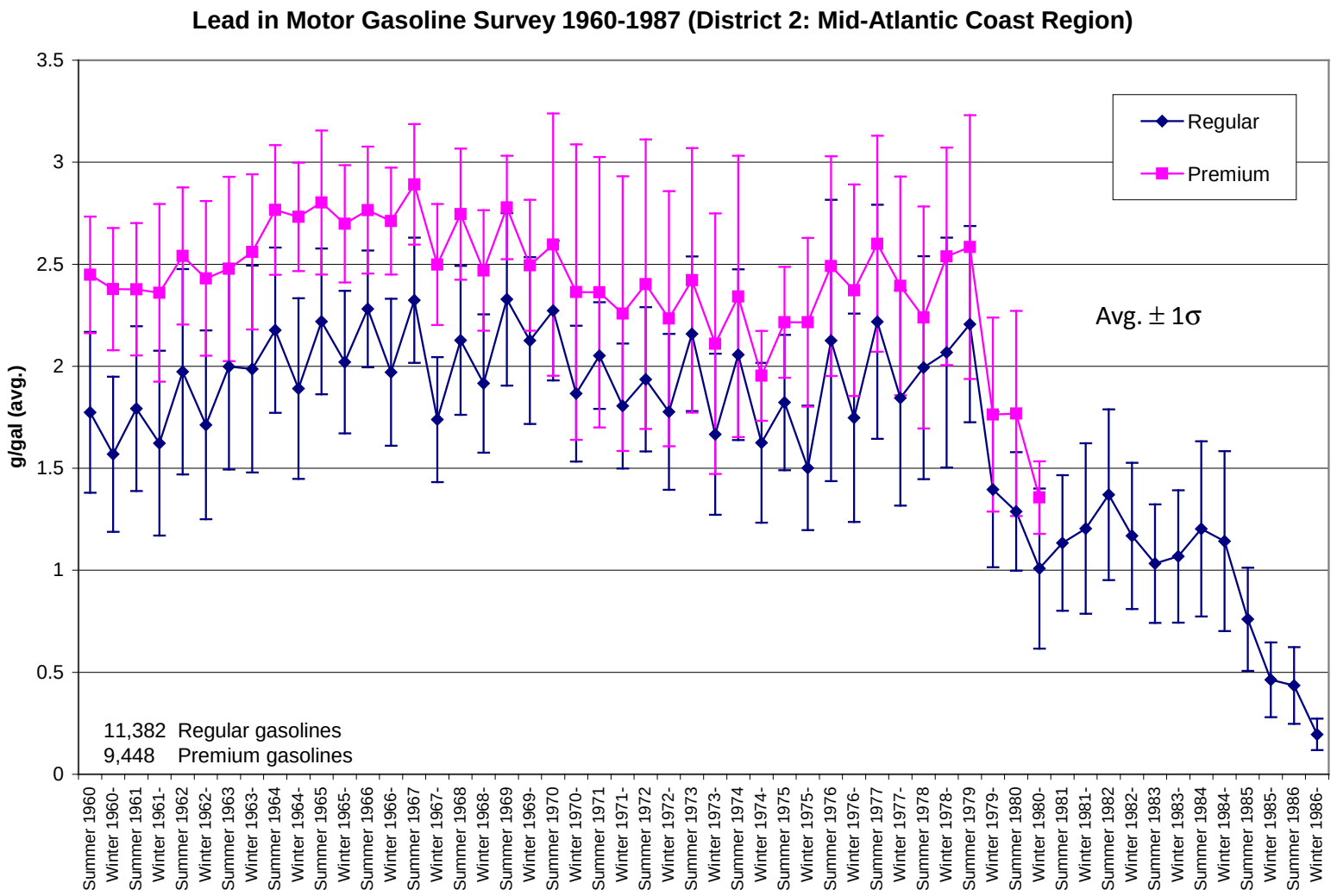
Regional Datasets show considerable ‘scatter’



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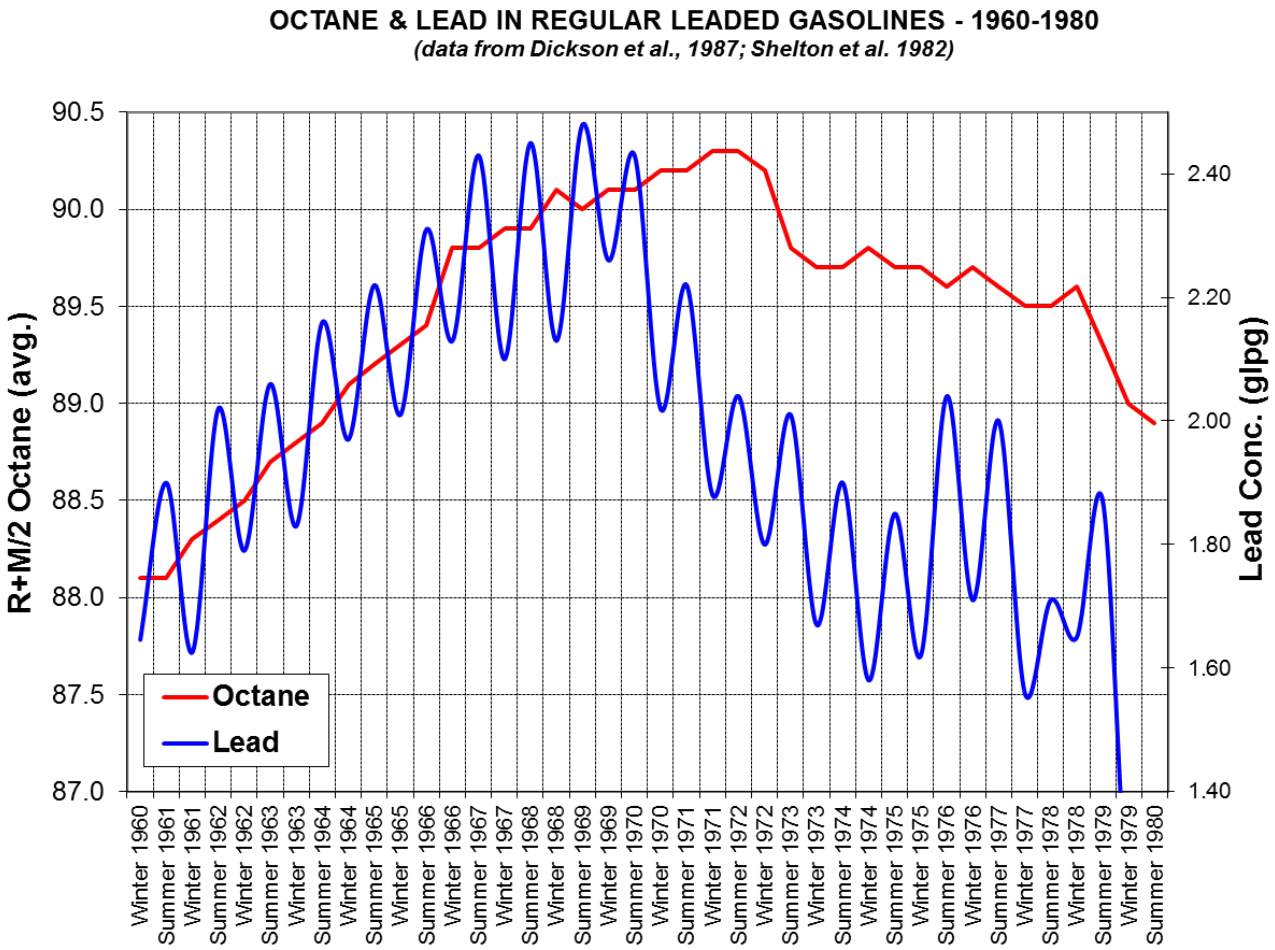
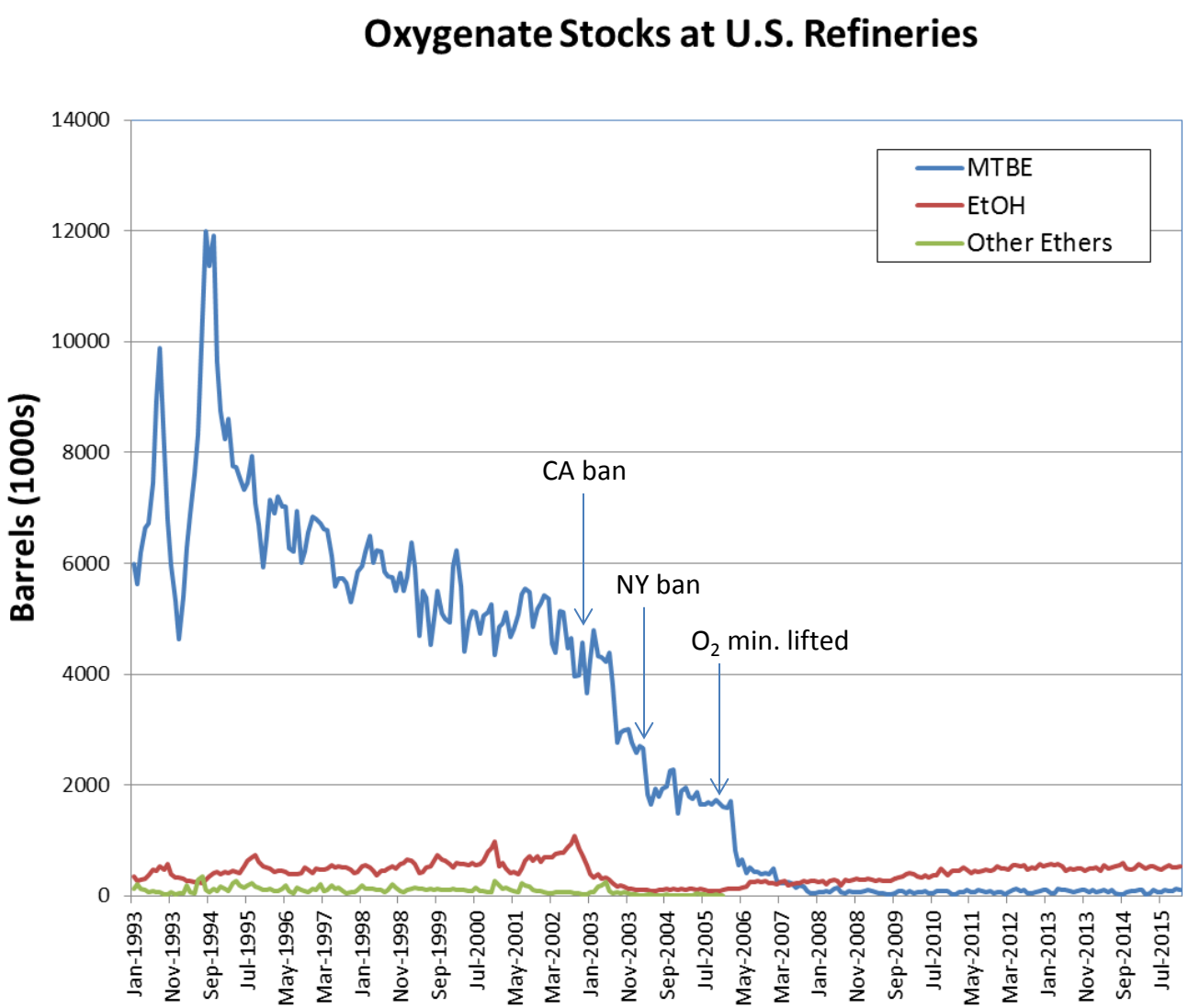
Blending and Lead Content Changes Coincident in 1970s



MTBE


Oxygenate Stocks at U.S. Refineries
Barrels (1000s)
14000
12000
10000
8000
6000
4000
2000
0
MTBE
EtOH
Other Ethers
CA ban
NY ban
O2 min. lifted
Jan-1993
Nov-1993
Sep-1994
Jul-1995
May-1996
Mar-1997
Jan-1998
Nov-1998
Sep-1999
Jul-2000
May-2001
Mar-2002
Jan-2003
Nov-2003
Sep-2004
Jul-2005
May-2006
Mar-2007
Jan-2008
Nov-2008
Sep-2009
Jul-2010
May-2011
Mar-2012
Jan-2013
Nov-2013
Sep-2014
Jul-2015

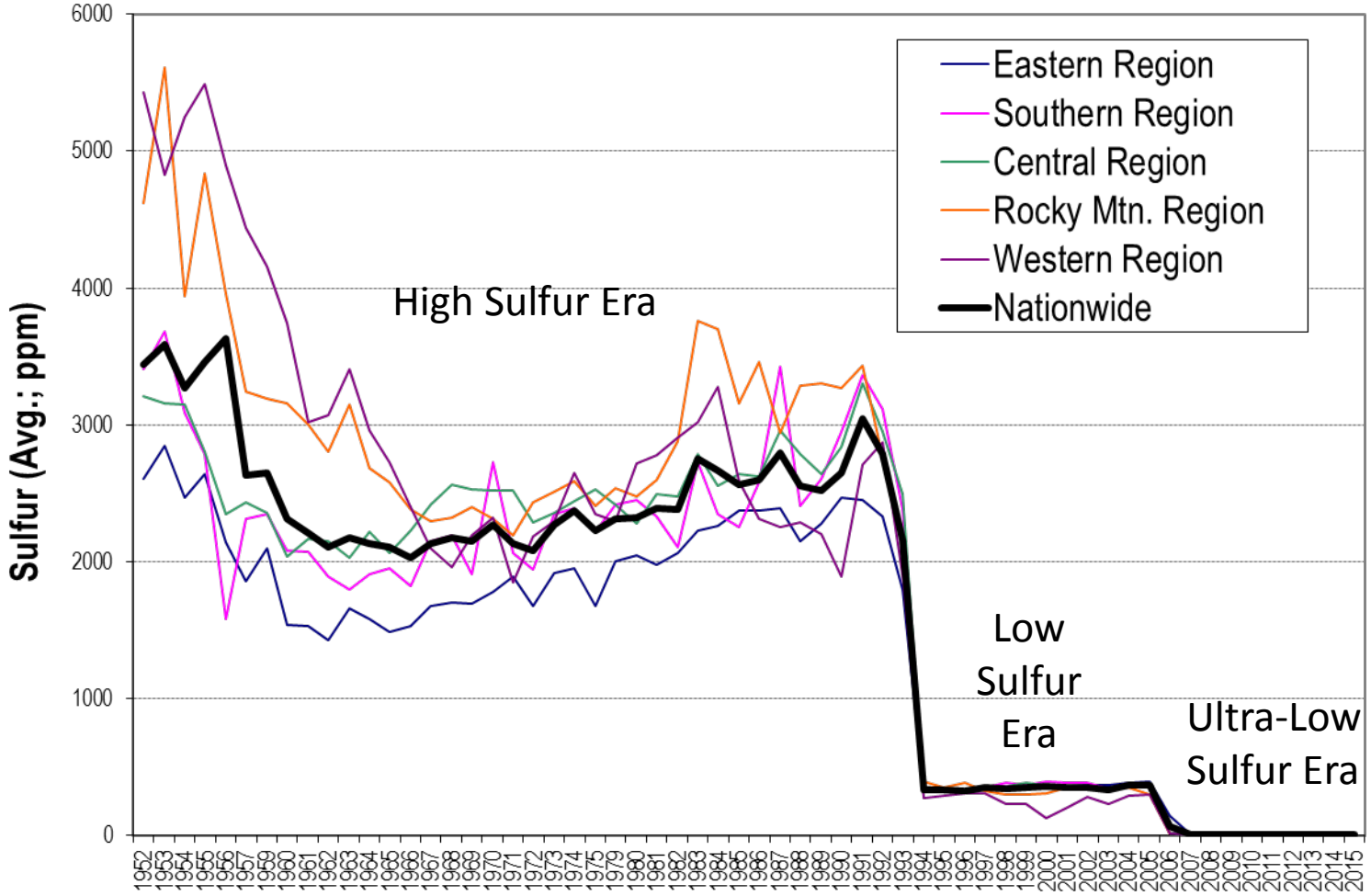
Age-Dating of Diesel Contamination

- Never simple
- Mixing always confounding
- Chemistry is not 'magic'
- Constrain the age thru combination of:
  - chemistry
  - site or regulatory history
  - F&T modeling

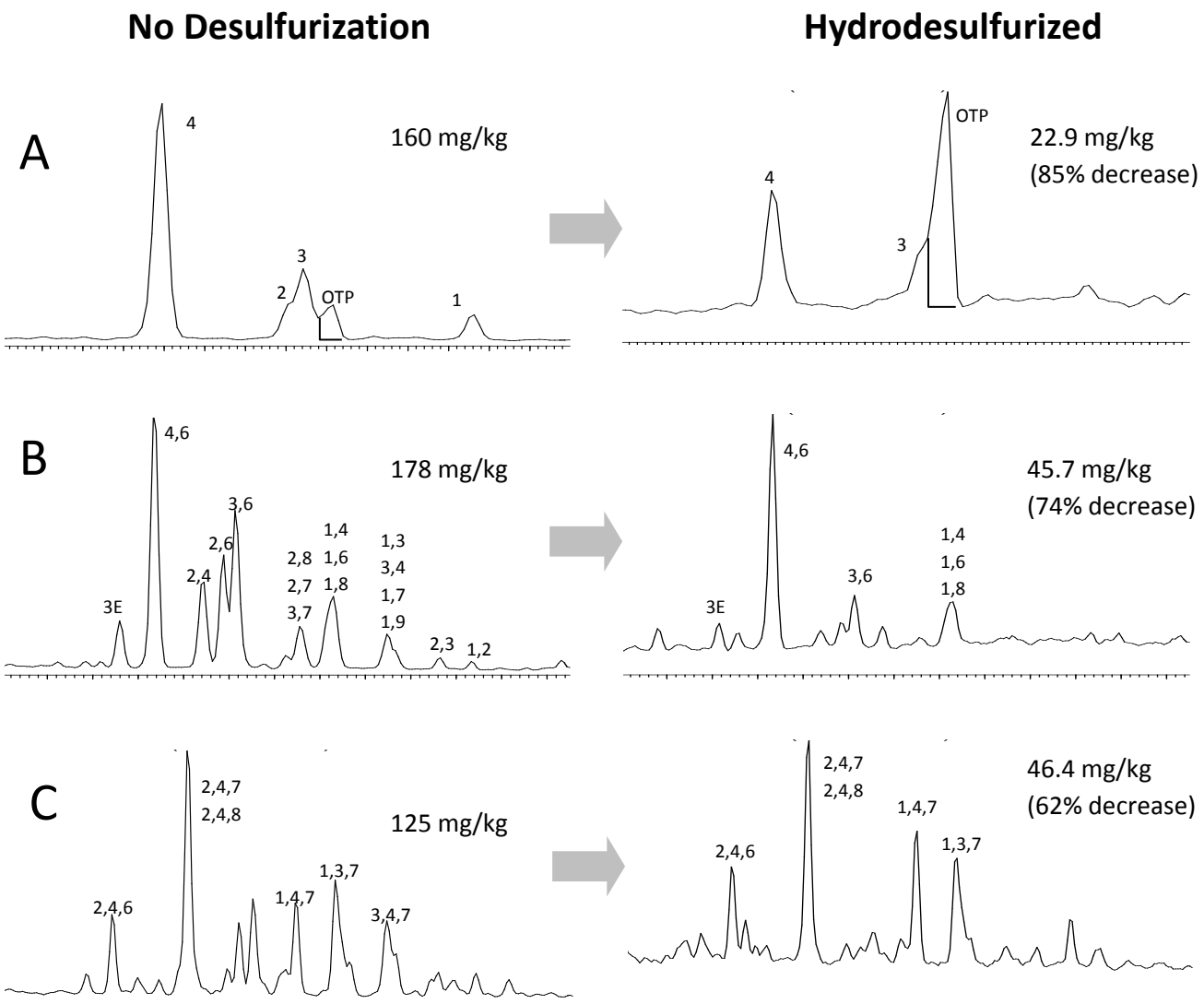
Common Approaches

- ← Blending Practices
- ← Sulfur content
- ← Hydrotreating
- ← Biodiesel
- ← Degree of Weathering (simple ratios)

Sulfur Concentration (Avg) On-Road Diesels



Distillate Hydrotreatment



Christensen & Larsen Model

- Weathering-based “age-dating” method

Table 1
Location, Type of Installation, and Age of Known Diesel Oil Spills

Location Name	Type of Installation	Age from Historical Records (Years)
Provestenen, DK	Oil Terminal	22
Hengelo, depot, NL	Oil Terminal	19
Fredericia, DK	Oil Terminal	18
Ishoj, DK	Service Station	18
Haarlem, NL	Service Station	17
Vanlose, DK	Service Station	14
Horsholm, DK	Service Station	12
Nieuwesluis, NL	Oil Terminal	11
Brunnik, NL	Service Station	9
Hengelo, loading rack, NL	Oil Terminal	9
Thisted, DK	Service Station	8
Ejby, DK	Heating Oil Tank*	0.5

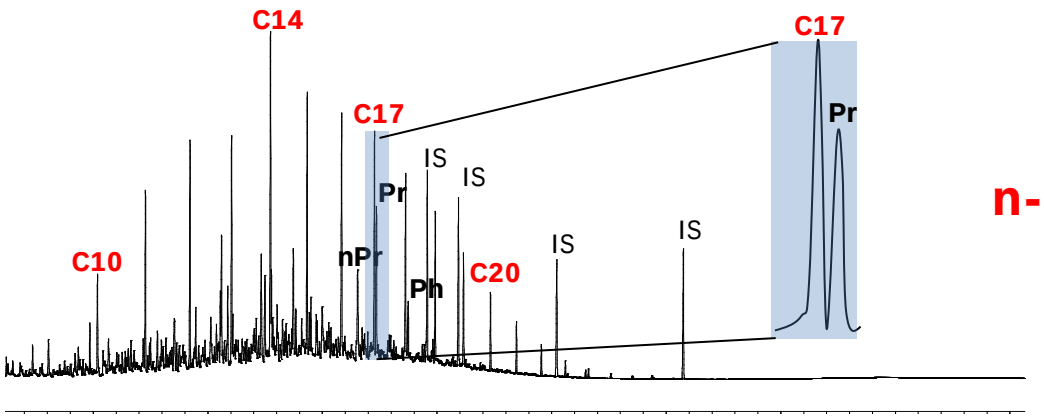
*The site was included because the location was in all respects similar to the other locations. Heating and diesel oils are basically the same, except for additives.

Christensen & Larsen (1993). Method for determining the age of diesel oil spills in the soil. *Ground Water Monitoring & Remediation*. 13(4); 142-149.

Premise to Christensen & Larsen

n-Alkanes are more susceptible to biodegradation than acyclic isoprenoids

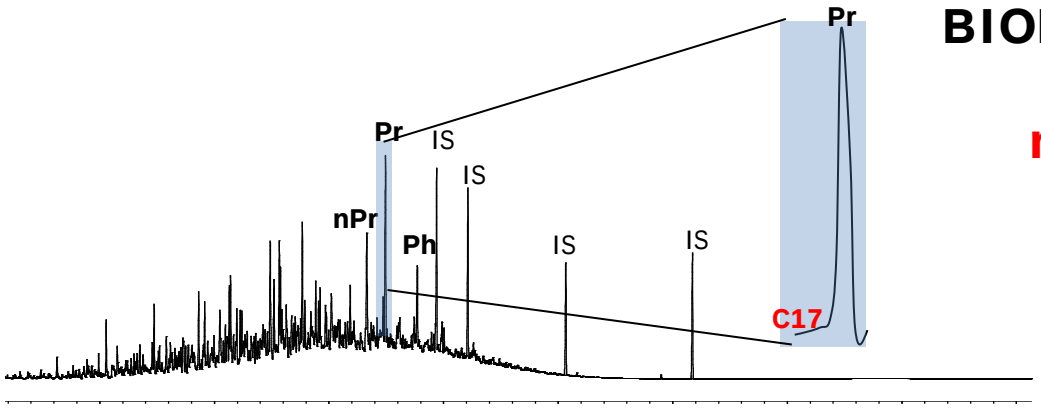
TRUE



FRESH DIESEL

abundant n-alkanes

n-C17 / Pristane ~ 1.4

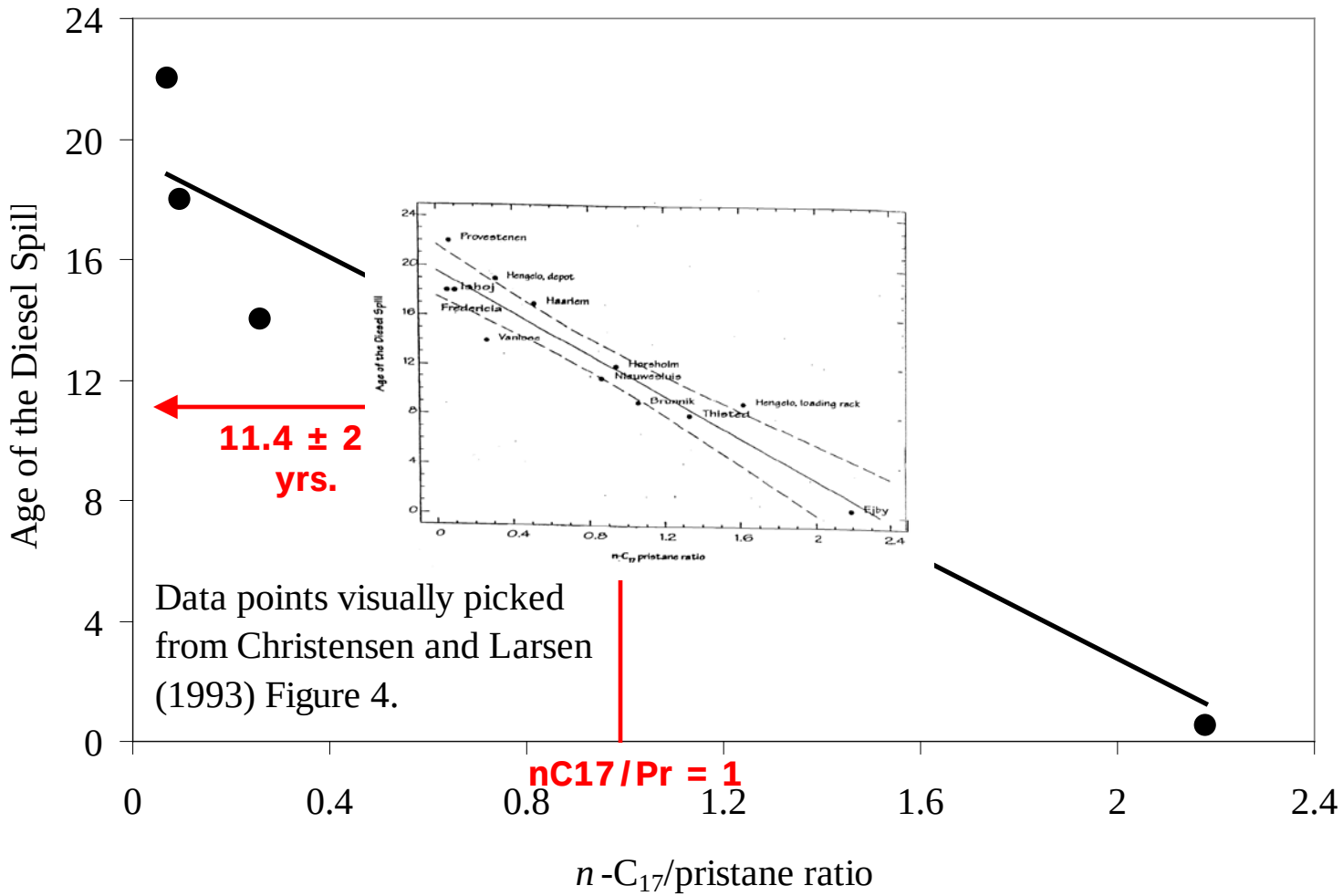


BIODEGRADED DIESEL

no n-alkanes

n-C17 / Pristane ~ 0

Christensen & Larsen Model



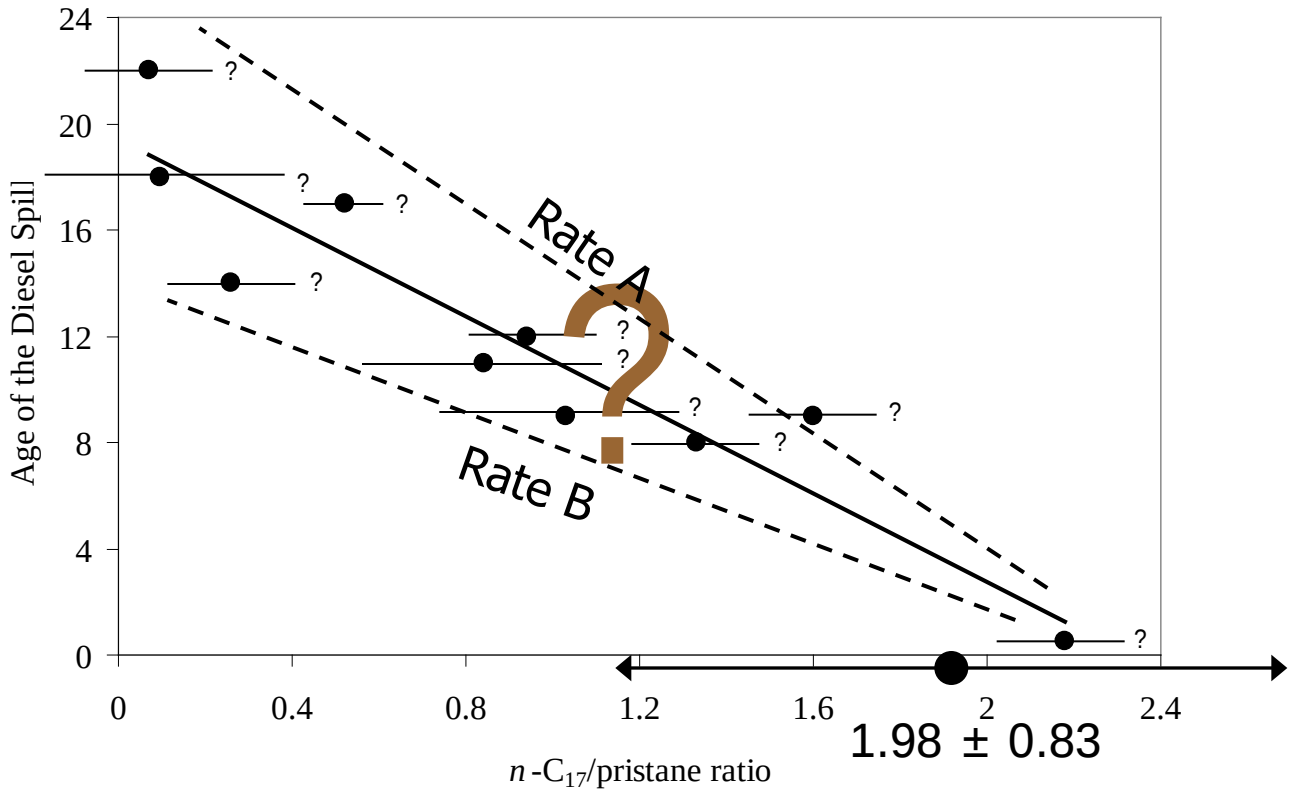
Kaplan et al. (1995). Pattern of chemical changes in fugitive hydrocarbon fuels in the Environment. SPE Paper No. 29754.

Principal Critique of C&L Model

- Too many site-specific variables control rate(s) of biodegradation to expect a single, universal rate
  - O_2, nutrient availability, etc.
  - NAPL mass/concentration
- Insufficient data presented by C&L to evaluate correlation/statistics
- Starting ratio of spilled fuels vary
- Almost never know if a single, multiple, or long-term release has occurred

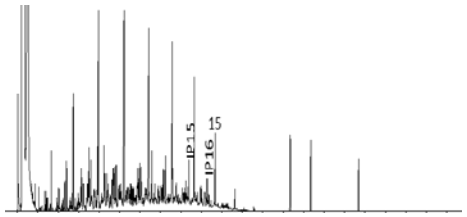
Stout et al. (2002). Invited commentary on the Christensen and Larsen Technique. *Environ. Forensics* 3:9-11.

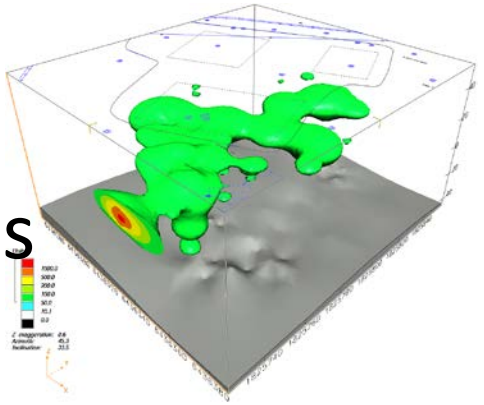
Elegantly Simple or Overly Simple



Conclusions

- Environmental forensics (*what, who, when?*) requires appropriate data and interpretation
- Tiered analytical approach whose design depends on questions/ objectives
- Integration of good data with knowledgeable interpretation yields greater defensibility in conclusions





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Questions?

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