

innovative environmental solutions

## **Environmental Forensics as a Tool for Environmental Liability Management**

**Court Sandau, PhD, PChem**

# Environmental Forensics

Environmental forensics includes investigating, interpreting and presenting evidence of source, fate, transport, composition, age, and extent of or responsibility for contamination of all environmental media (i.e. air, soil, water or biota).



**“The application of scientific methods used to identify the origin and timing of a contaminant release”**

# Alberta Environmental Protection and Enhancement Act

## Part 5 – Release of Substances

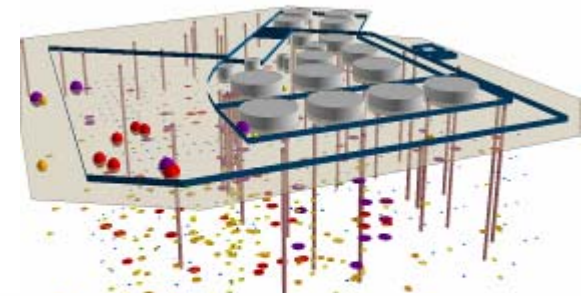
### Section 112

- (1) Where a substance that may cause, is causing or has caused an adverse effect is released into the environment, the person responsible for the substance shall, as soon as that person becomes aware of or ought to have become aware of the release,
- (a) take all reasonable measures to
    - (i) repair, remedy and confine the effects of the substance, and
    - (ii) remediate, manage, remove or otherwise dispose of the substance in such a manner as to prevent an adverse effect or further adverse effect,
  - and
  - (b) restore the environment to a condition satisfactory to the Director.

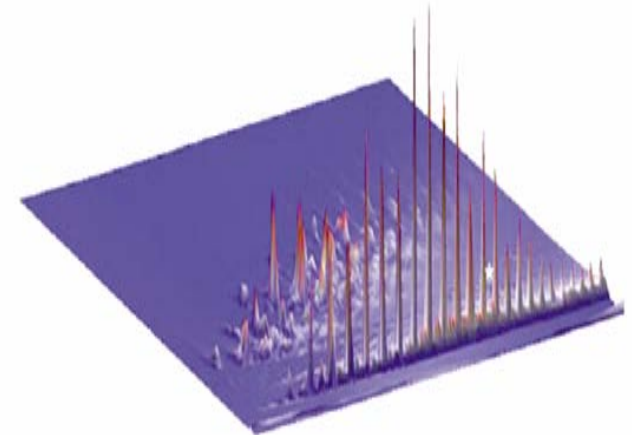
**The polluter pays...**

# Components of an Environmental Forensics Project

- Compilation of historical information
  - Chemical
  - Physical (satellite maps, GIS, geological features)
- Collection of site specific data and of current data
- Interpretation (data analysis, modelling)
- Visualization



a)

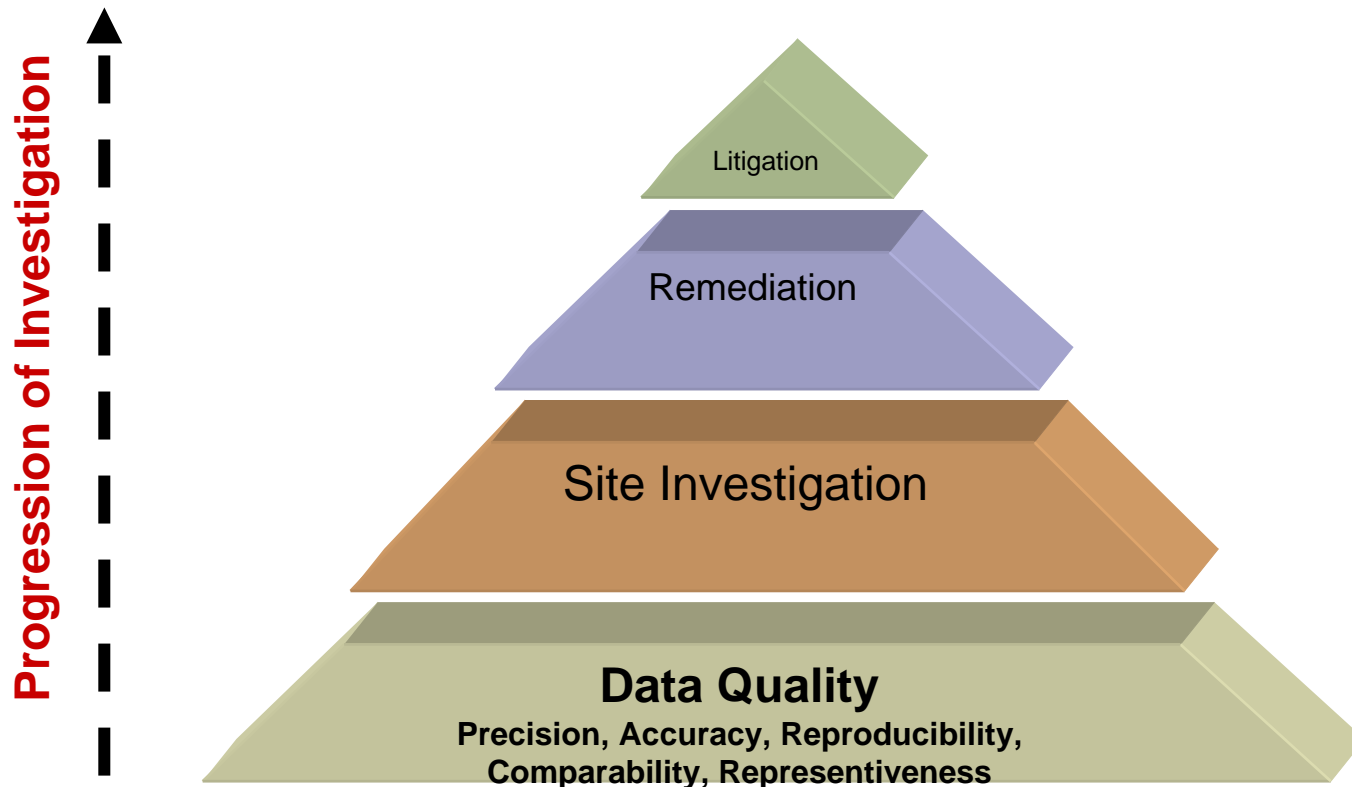


## Disciplines in Environmental Forensics

- Chemistry
- Statistics
- Environmental Engineering
- Microbiology
- Hydrogeology
- Soil Science
- Toxicology
- Biology
- Ecology
- Litigation Experience
- And others.....



# The Foundation of All Environmental Investigations



# Lifecycle of Forensics Project

- Review available data to **determine goals of investigation**
- Field sampling, investigation, data gathering, sampling strategy, QA-QC
- Choose laboratory with appropriate analyte list (non-routine)
- Develop QA-QC for external laboratory evaluation
- Data analysis and statistical assessment
- Data compilation and development of conclusion



**Forensics work is not completed in the same fashion as routine environmental investigations.**

# When to use Environmental Forensics

- When contamination may not be yours (remove liability)
- When contamination is from multiple sources (share liability)
- Insurance purposes (protect liability)

## Implicate or Vindicate?

- It may demonstrate your own responsibility
- It may show dual responsibility (share the liability)
- It may vindicate a party completely

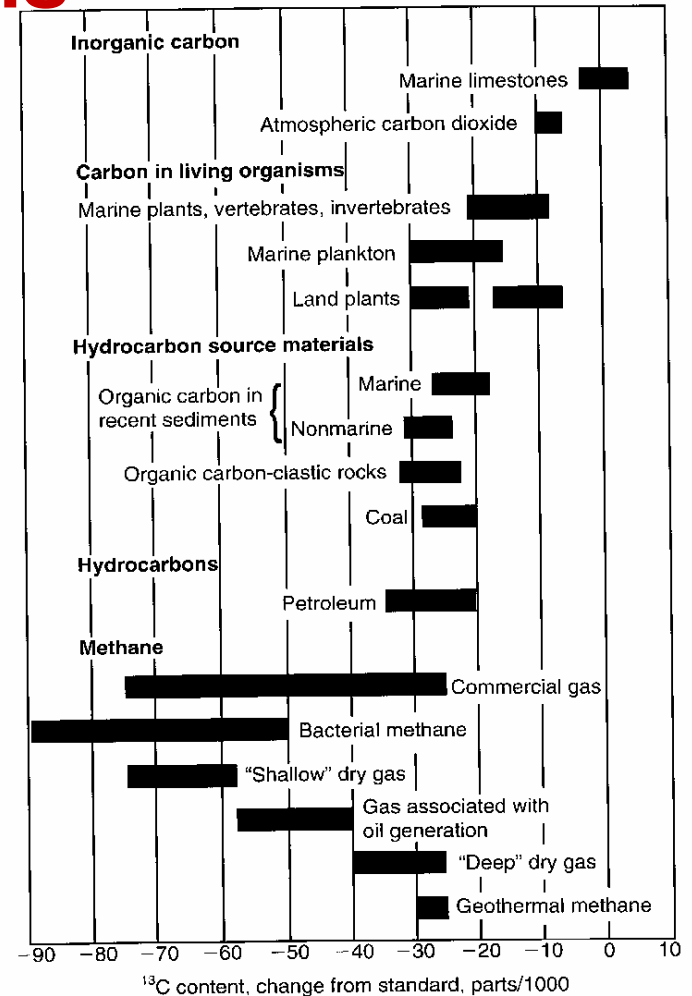


## Contaminants where Environmental Forensics can be used

- Chlorinated solvents (PERC)
- PCBs / “Dioxins&Furans”
- Pesticides (persistent/non-persistent)
- Pharmaceuticals and personal care products
- Metals (mercury, lead, chromium, arsenic etc.)
- **VOCs**
- **PAHs**
- **Methane (coal bed methane)**
- **Hydrocarbons (refined/unrefined)**

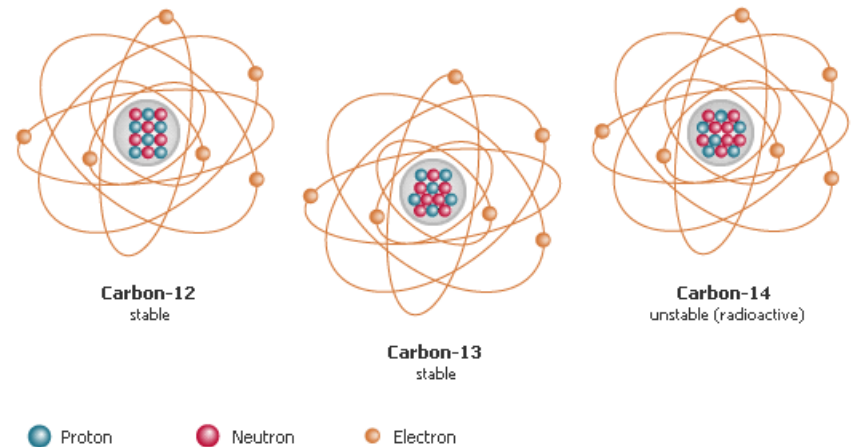
# Chemical Environmental Forensic Investigations

- Isotope analysis
- Biomarkers
- Pattern Assessment
  - chemical mixtures
  - breakdown products



# Principles of Isotope Analysis

- isotopes of an element have slightly different chemical and physical properties because of their mass differences
- mass differences are large enough for many physical, chemical, and biological processes or reactions to "fractionate" or change the relative proportions of various isotopes
- There also exists differences in synthetic versus natural chemicals

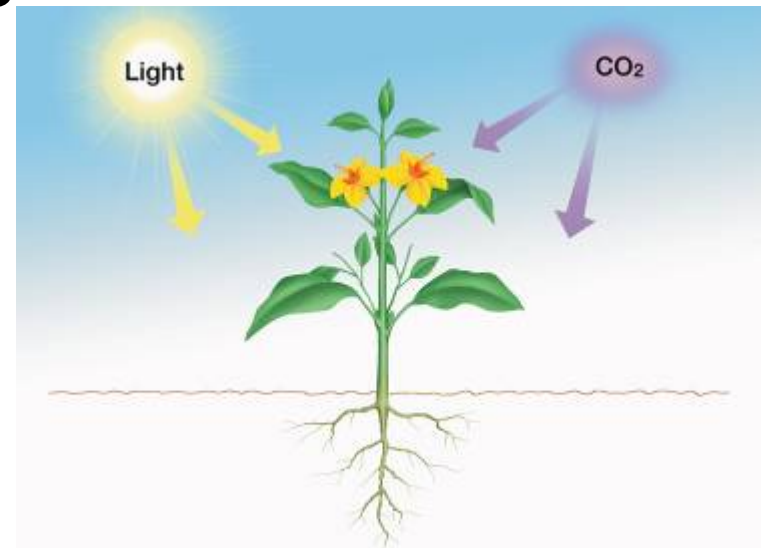


# Most Common Isotopes

<u>Element</u>	<u>Isotope</u>	<u>Abundance</u>
Carbon	$^{12}\text{C}$	98.93 %
	$^{13}\text{C}$	1.07 %
Hydrogen	$^1\text{H}$	99.9885 %
	$^2\text{H}$	0.0115 %
Oxygen	$^{16}\text{O}$	99.757 %
	$^{17}\text{O}$	0.038 %
	$^{18}\text{O}$	0.205 %
Sulfur	$^{32}\text{S}$	94.93 %
	$^{33}\text{S}$	0.76 %
	$^{34}\text{S}$	4.29 %
	$^{36}\text{S}$	0.02 %

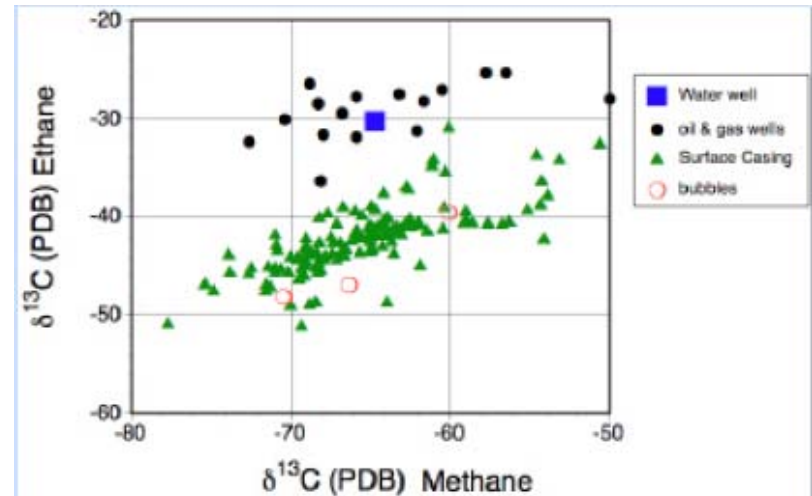
# Isotopic Carbon Differences

- Stable isotopes:  $C^{12}$  and  $C^{13}$  (99:1)
- Atmospheric carbon dioxide assimilated by plants during photosynthesis
- Preferential uptake of lighter  $C^{12}$



# Fossil Fuels, Coal, Crude, Natural Gas

- Formed from long term reactions where living organic matter dies and is deposited
- These deposited sources have characteristic isotopic signal
  - coal bed methane
  - Gasoline will have similar GC pattern but differ in isotopic pattern if from different feed stocks
- Refining does not change isotopic pattern



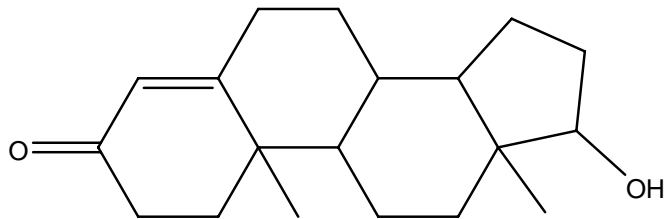
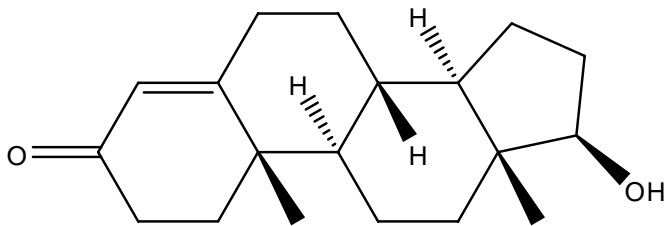
Dr. Karlis Muehlenbachs, U of A

# Isotopic Analysis

- Bulk isotopic analysis
  - All compounds in mixture measured at the same time
- Continuous flow analysis
  - Compounds separated by GC or LC, then measured separately
- Multiple isotopes or measurement of isotopes of multiple analytes can help differentiate products



## Tour de France & Floyd Landis



‰ -24 is normal

‰ -30 indicates doping

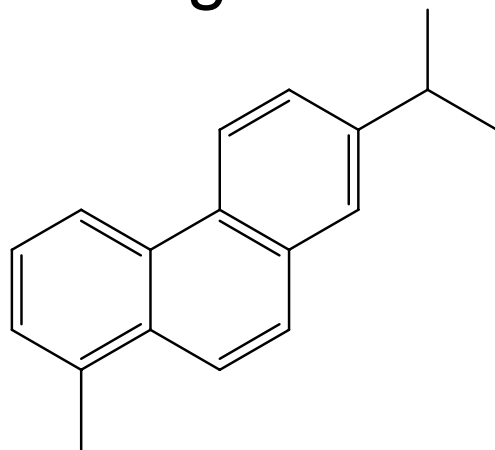
- Abnormal ratio of testosterone to epitestosterone
- “Naturally high testosterone levels”
- Natural versus synthetic isotopic pattern

# Chemical Environmental Forensic Investigations

- *Isotope analysis*
- **Biomarkers**
- Pattern Assessment

## Biomarkers

- Organic compounds in petroleum whose chemical structure can be unequivocally linked to a naturally occurring biochemical



- Indicator compounds – unique chemicals identifying the mixture or source e.g. lead for gasoline

# Biomarkers

- Biomarker assessment relatively easy
- In-depth knowledge of composition of mixtures of interest
  - Historical knowledge of additives can aid in “dating” the contamination
- Solid knowledge of stability of the biomarker of interest in the environment of concern

## Indicator Compounds

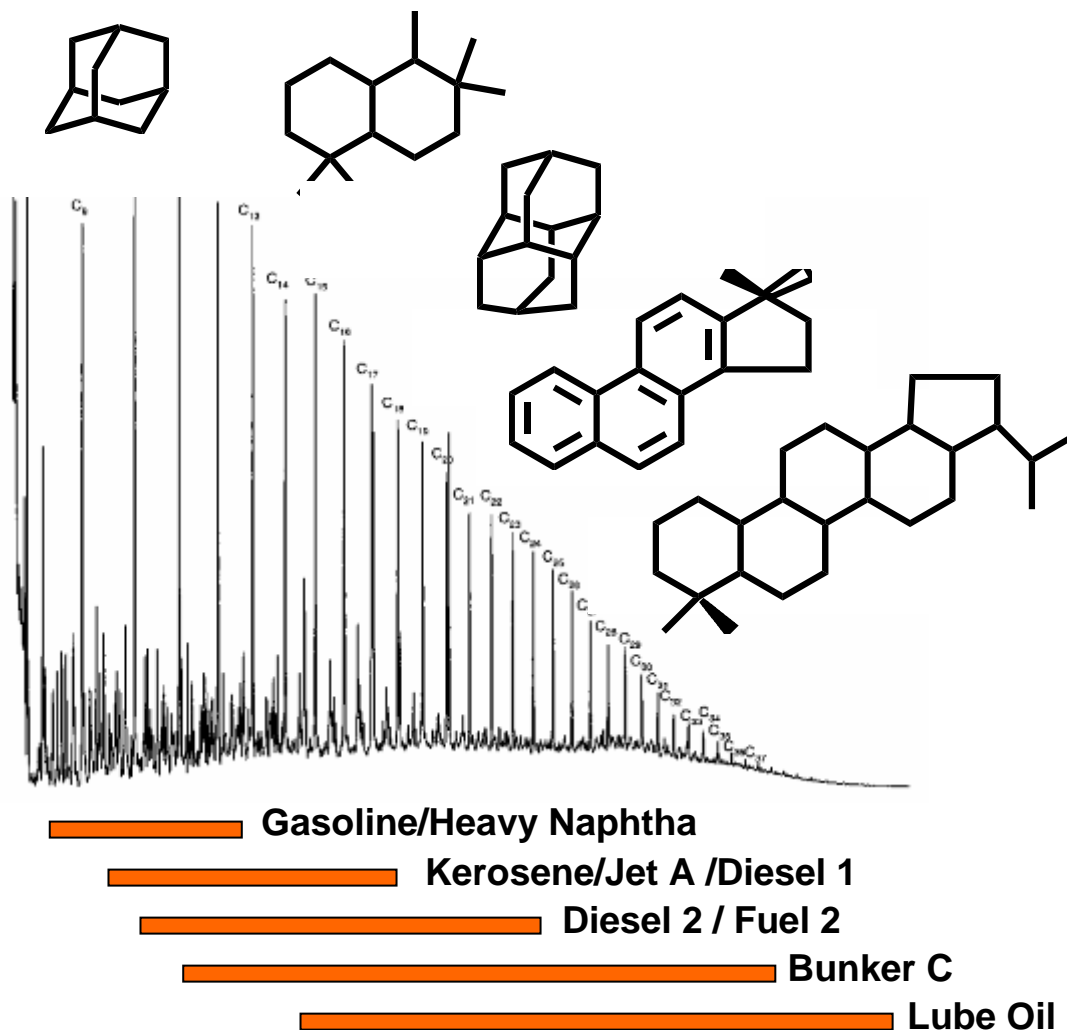
- Simple analysis – usually requiring GC or LC coupled with mass spectrometry
  - Retention time and mass spectral match
- Testing for presence or absence
  - YES or NO

# Gasoline - Additives

- Antiknock (lead based)
- Lead scavengers (dibromo/chloroethane)
- Detergents (amines, amides)
- Oxygenates (ethanol, MTBE)
- Antirust (sulfonates)
- Antioxidants (aminophenols)
- Dyes
- Anti-icing (glycols, alcohols)
- Lubricants (light mineral oils/paraffins)

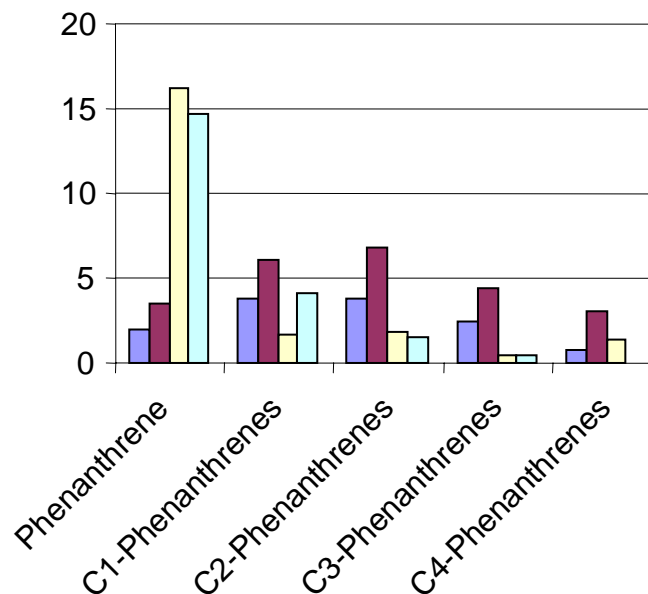
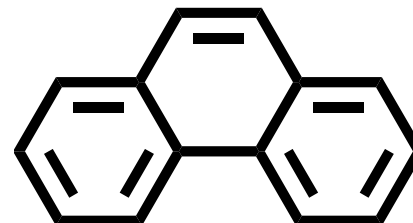
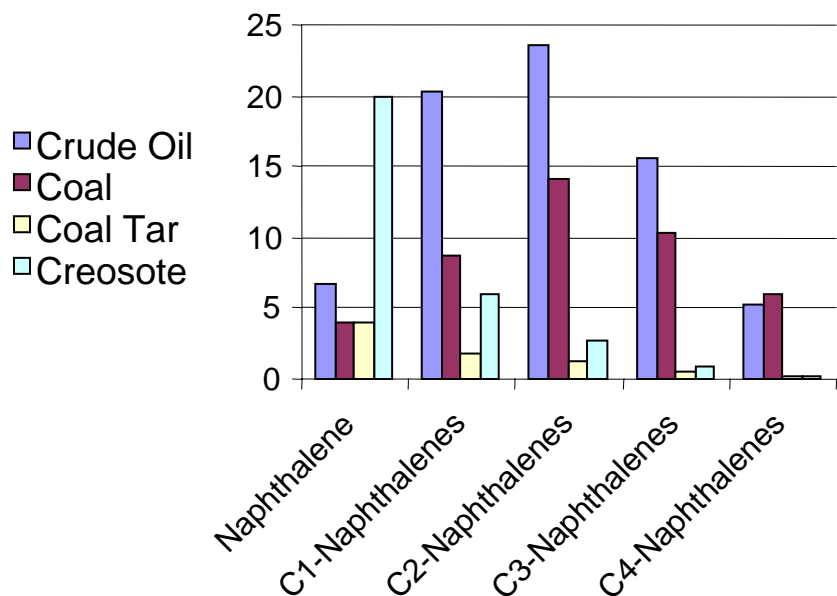
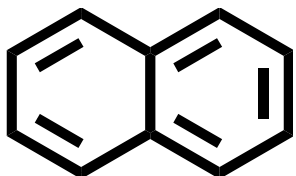
# Specific Petroleum Biomarkers

- Adamantanes
- Sesquiterpanes
- Diamantanes
- Steranes
- Hopanes



# Petrogenic versus Pyrogenic

- Higher temperature results in less alkylation
- PAH differences in products



# Chemical Environmental Forensic Investigations

- *Isotope analysis*
- *Biomarkers*
- **Pattern Assessment**
  - chemical mixtures
  - weathering products
    - Pattern matching for identification
    - Weathering pattern to determine age

# Chemical Fingerprinting

## Pattern Analysis

- Most complex forensics technique
- Requires broad knowledge of environmental studies
  - Soil microbes, physical/chemical properties
- Statistical analysis – PCA
- Ratio analysis

# Weathering

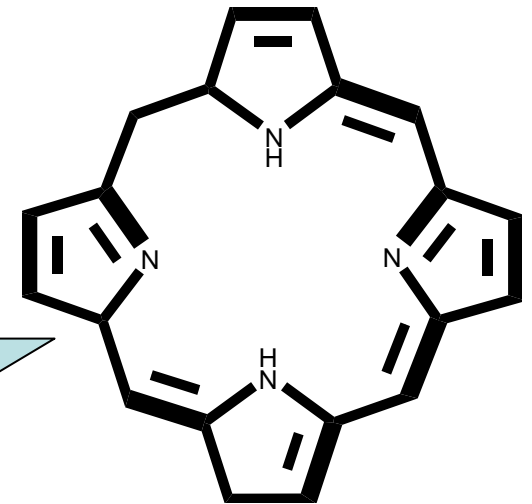
- The influence of physical, chemical and biological forces on the physical and chemical composition of contaminants in the environment
- Evaporation
- Solubilization
- Biodegradation

# Susceptibility to Biodegradation

**Most susceptible**



C<sub>5</sub>-C<sub>6</sub> Hydrocarbons  
Olefins  
n-Alkanes  
Monoaromatics  
Isoalkanes  
Parent PAH > 2 ring  
C<sub>1</sub>-alkyl PAH  
C<sub>2</sub>-alkyl PAH  
C<sub>3</sub>-alkyl PAH  
C<sub>4</sub>-alkyl PAH  
Triterpanes  
Steranes  
Diasteranes  
Aromatic Steranes  
Porphyrins



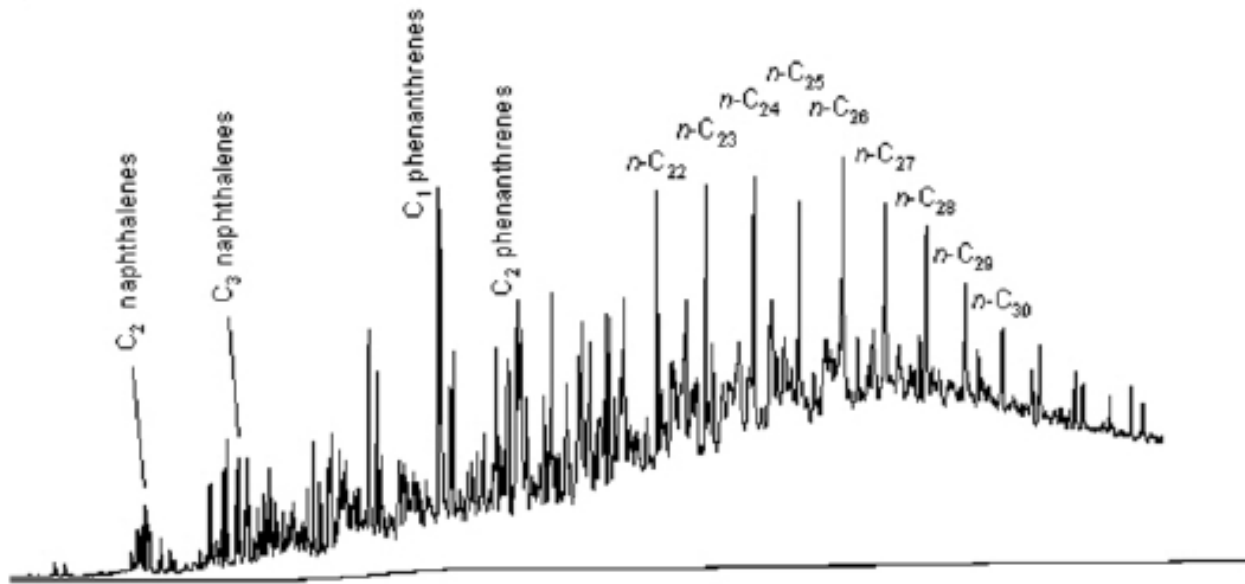
**Least susceptible**

# Weathering

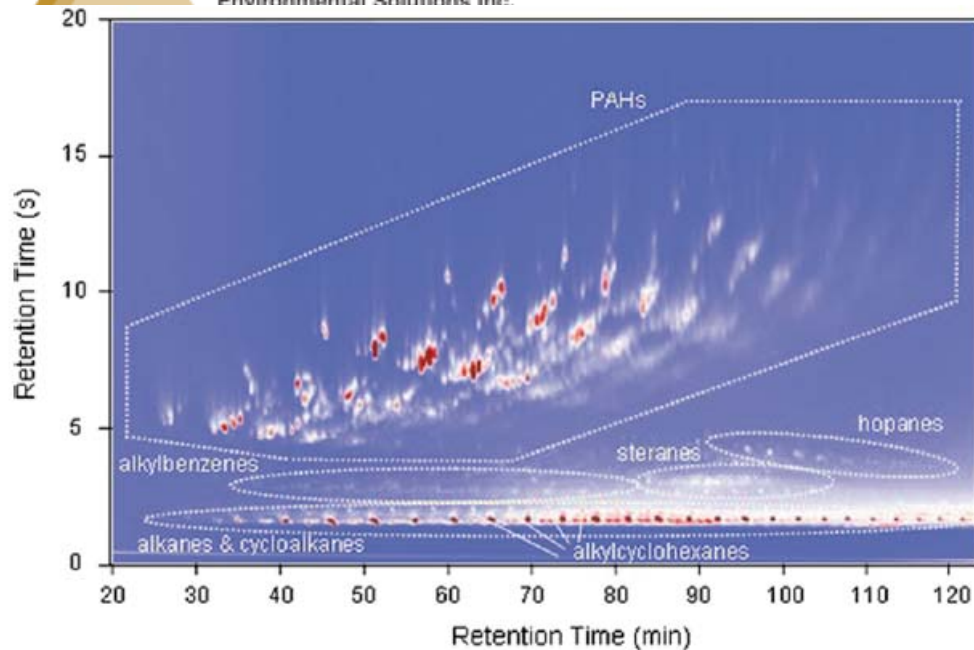
- Sometimes weathering can be used to age date the contamination
  - Model the natural attenuation
  - Approximate time of release

# Conventional GC Analysis

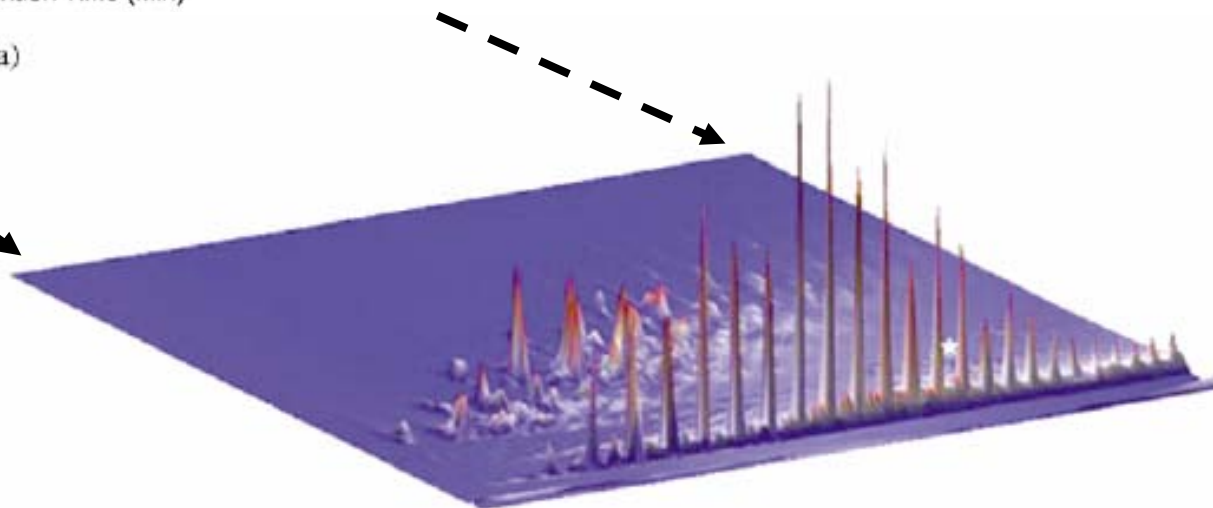
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*Nelson et al. Environmental Forensics, 7:33–44, 2006*

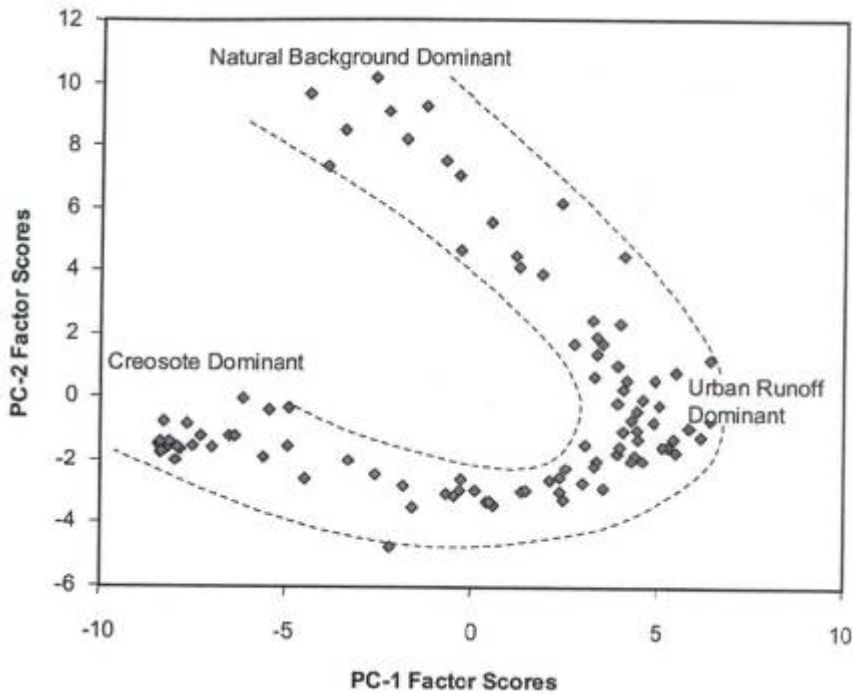


## 2D-GC-TOF

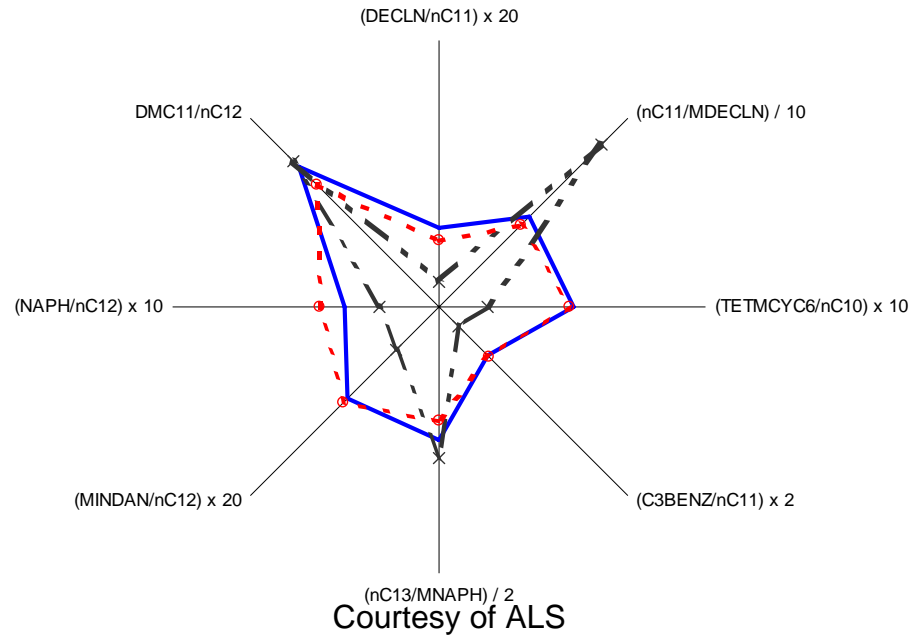


*Nelson et al. Environmental Forensics, 7:33–44, 2006*

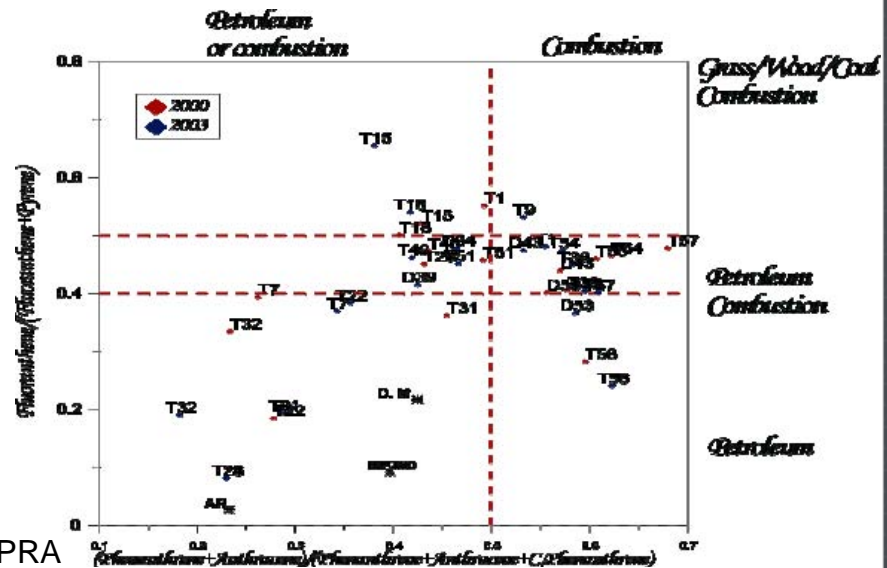
# Statistical Interpretation



Stout et al. 2002, Intro to Enviro Forensics



Courtesy of ALS

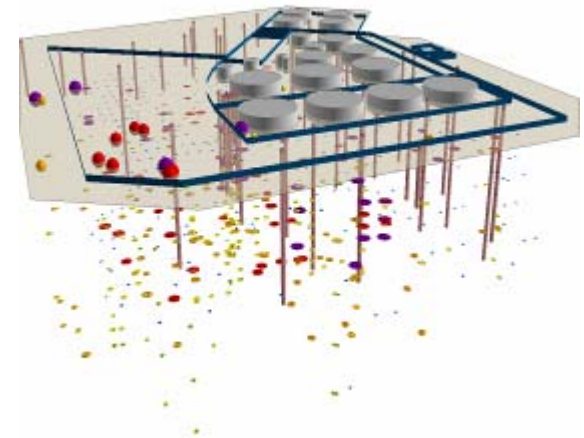


Courtesy of Zymax/DPRA

# Environmental Forensics

- Very powerful tool for your liability management toolbox...

**...if in the right hands.**



# Questions