TRIUM Environmental Solutions Inc.

TRIUM 주식회사 트리엄 코리아

Investigate Integrate Innovate

# Environmental Forensic Principals for Sources Allocation of Polycyclic Aromatic Hydrocarbons

October 2008

Presented by: Gwen O'Sullivan, Erik Martin and Court D. Sandau

TRIUM WORLD EXPERTS

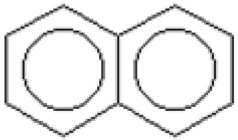
# Presentation Outline

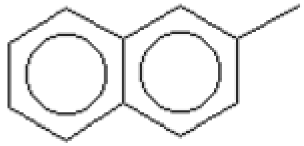
- PAHs (structure and physicochemical properties)
- Sources and sinks (fate and behavior)
- Analytical techniques (including QA/QC)
- Conventional source identification techniques
- Toxic equivalent fingerprinting
- Case study

# Polycyclic Aromatic Hydrocarbons (PAHs)

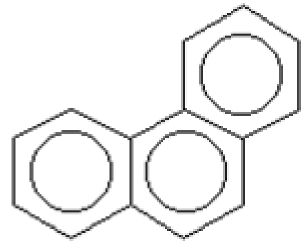
*Organic compounds which include only carbon and hydrogen with a fused ring structure containing at least two benzene (six-sided) rings but may also contain additional fused rings that are not six-sided.*

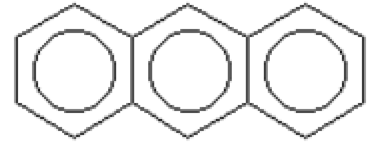
# PAHs


Naphthalene

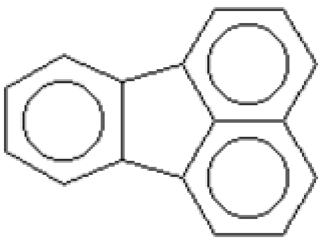

2 Methylnaphthalene

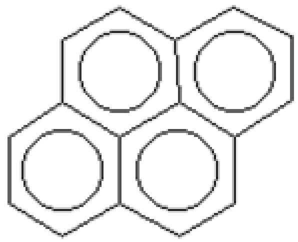
**2-Ringed PAH**


Anthracene

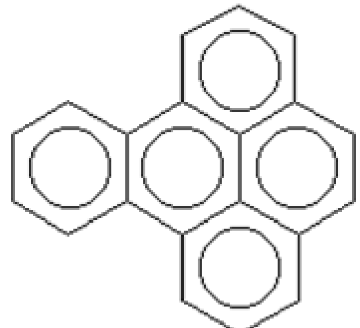

Phenanthrene

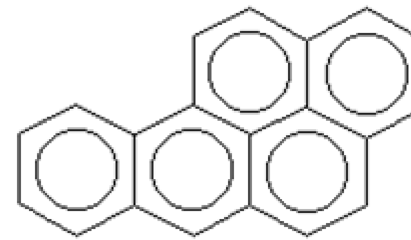
**3-Ringed PAH**


Fluoranthene

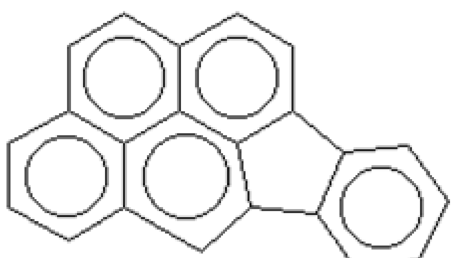

Pyrene

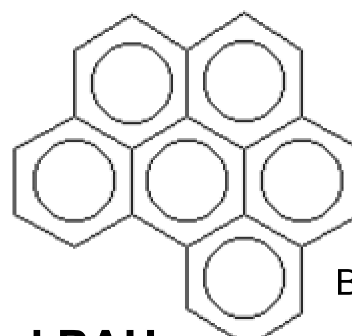
**4-Ringed PAH**


Benzo(e)pyrene


Benzo(a)pyrene

**5-Ringed PAH**


Indeno(1,2,3-cd)pyrene


Benzo(ghi)perylene

**6-Ringed PAH**

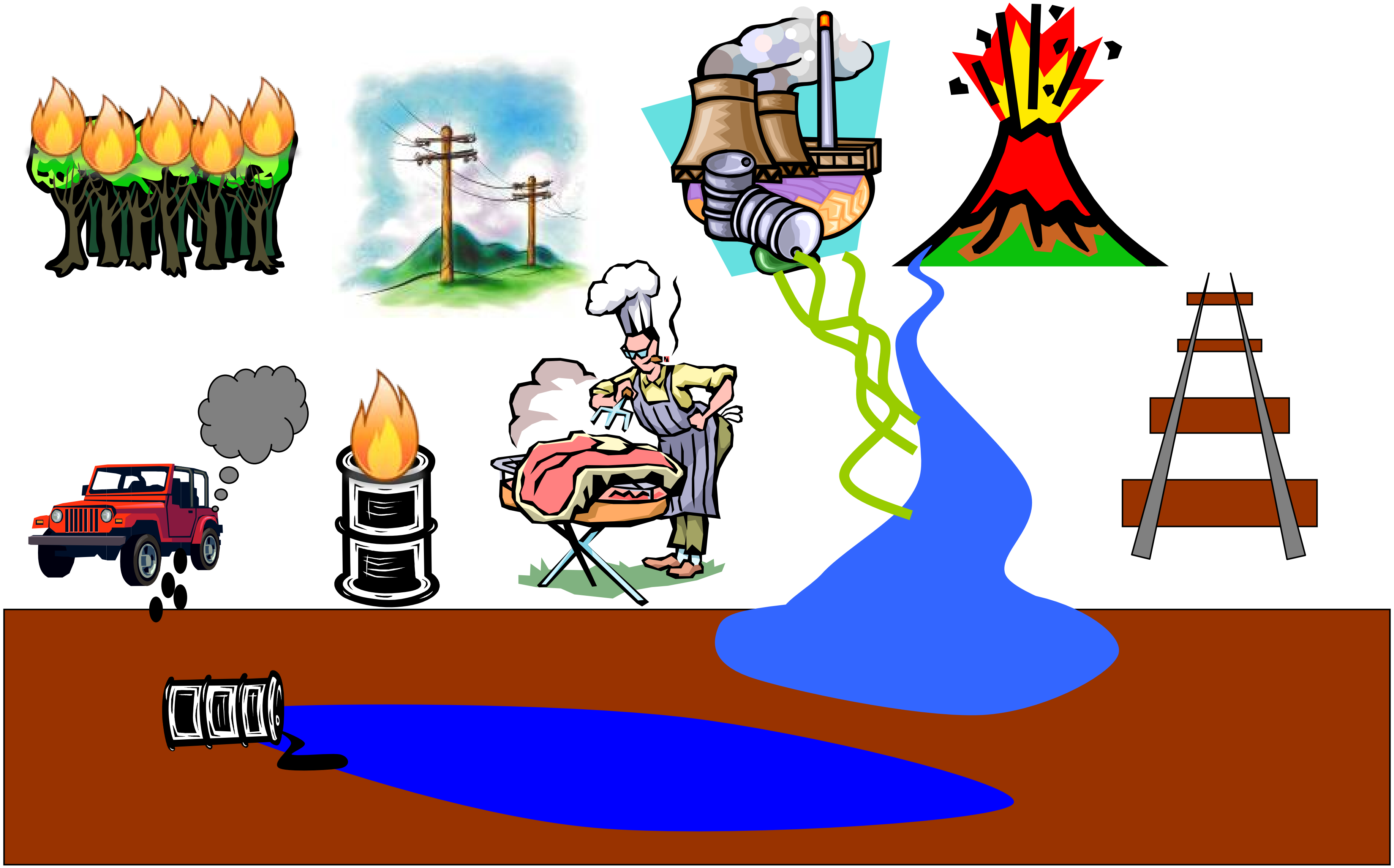
# Classification

Governed by thermodynamic properties

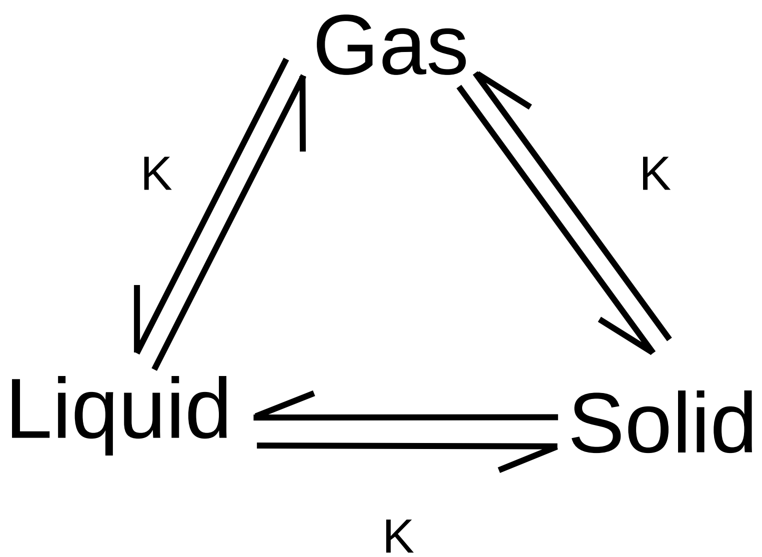
- Biogenic (transformation of natural precursors)
- Petrogenic (fossil fuels)
- Pyrogenic (burning of organic materials)

# Sources and Sinks

# Sources & Sinks



# Fate and Behavior




- Molecular weight,
- Aqueous solubility,
- $K_H$ – Henry's constant,
- Octanol-water partition coefficients [Kow]
- Gas / soil partition coefficient

# Analytical / Data Quality

# There are many variations of methods

# Method Comparison - PAHs

**<u>Low Resolution MS Method</u>**

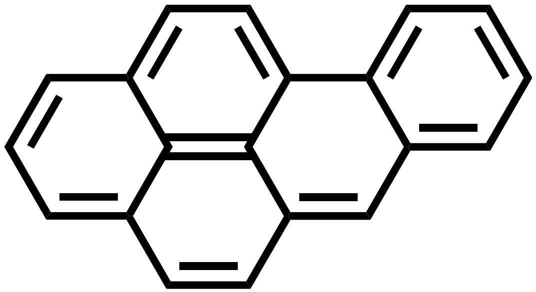
- EPA Method 8270C
- Full Scan analysis
- No confirmation ions or ratios
- Inappropriate surrogate standards

**<u>High Resolution MS Method</u>**

- Modified California Method
- IDMS quantitation
- Less likely to have interferences present
- Isotopically labeled standards
- More accurate and precise
- Better data = better decisions

# PAH Analysis

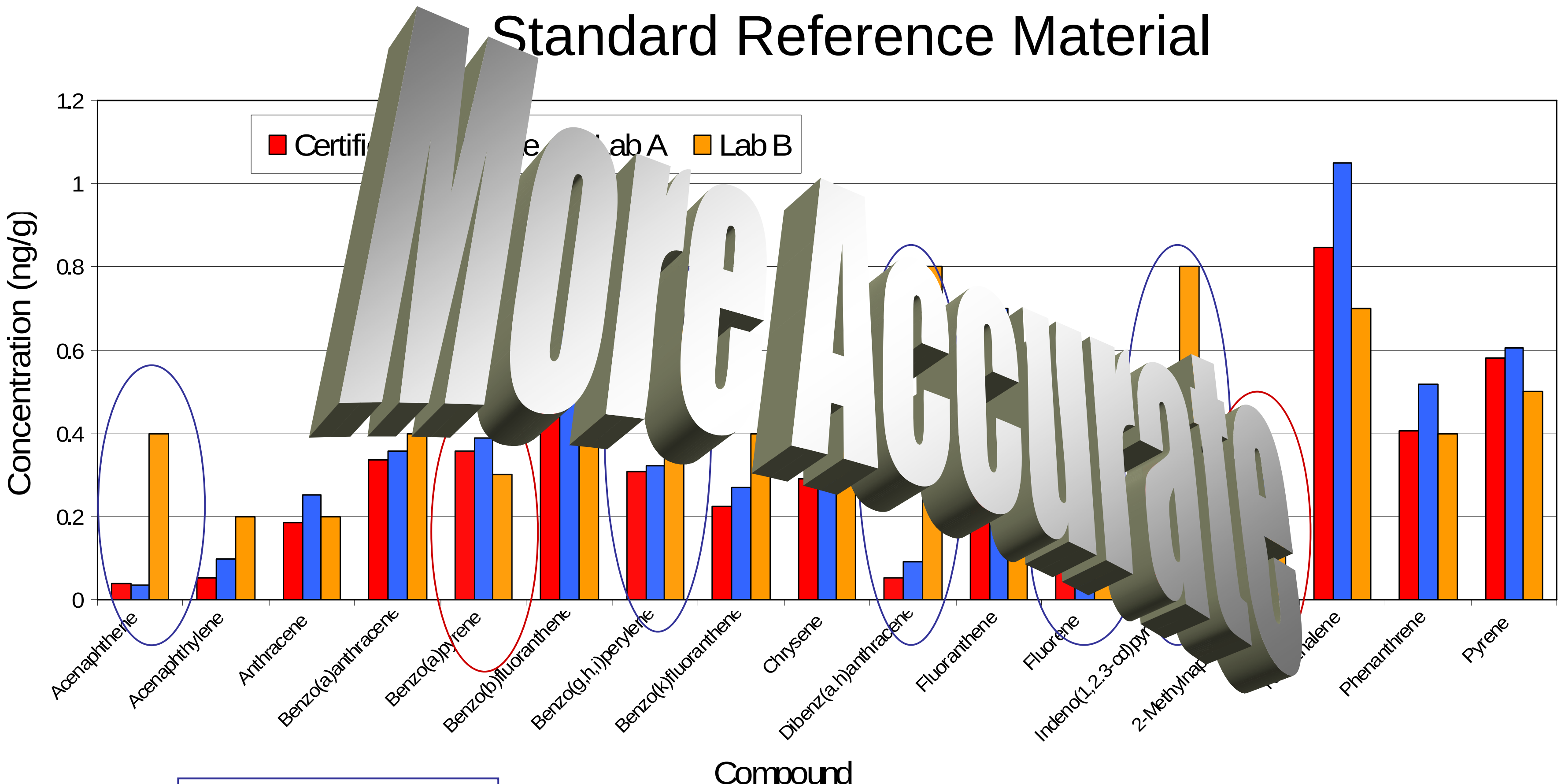
- Many interferences exist in low molecular weight range
  - Depends on matrix, clean up method
- Specificity of HRMS allows better accuracy and precision
- Comes at a cost – 4-6x the cost



Benzo(a)pyrene

Difference in measuring 252 versus 252.30928

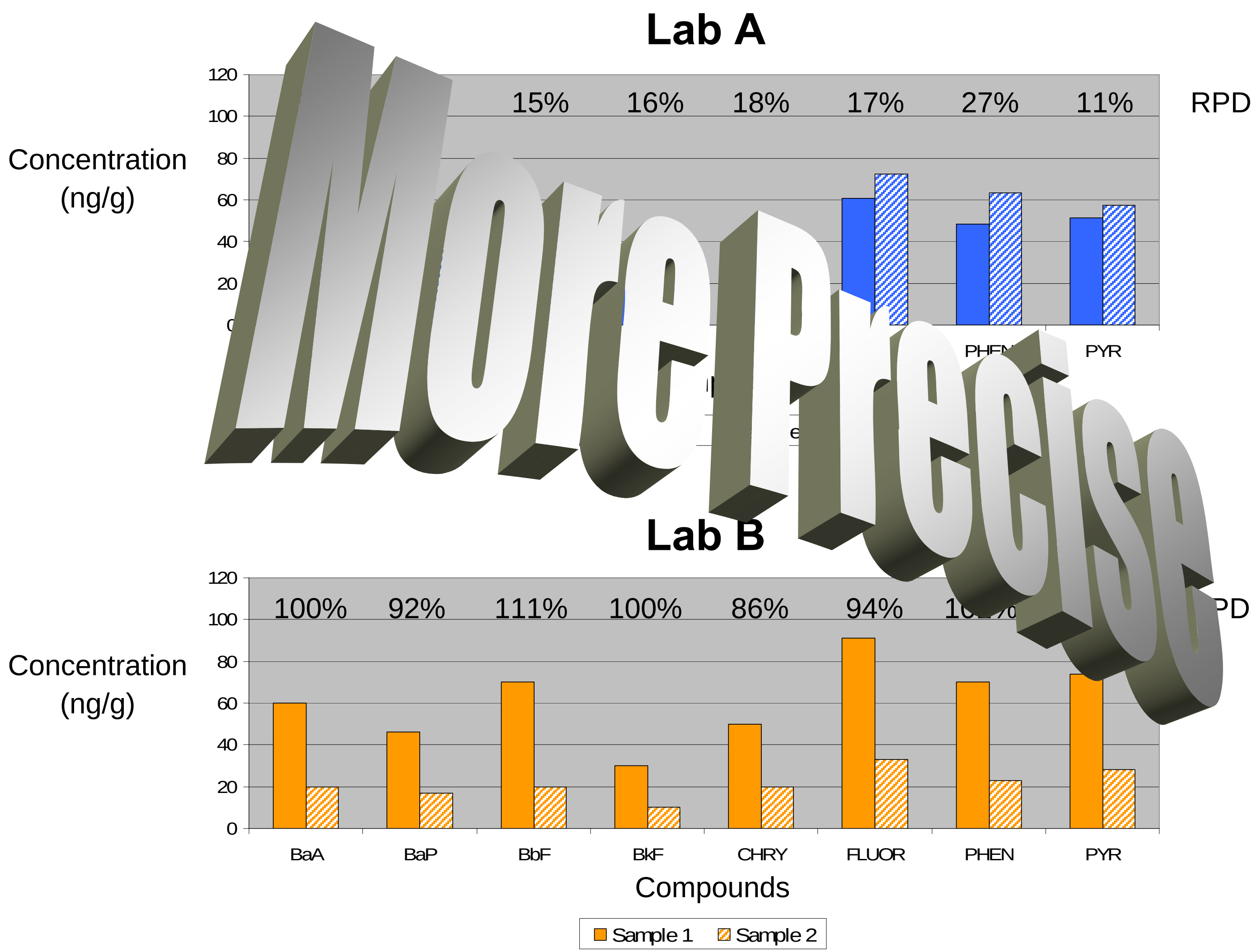
# PAH Comparisons



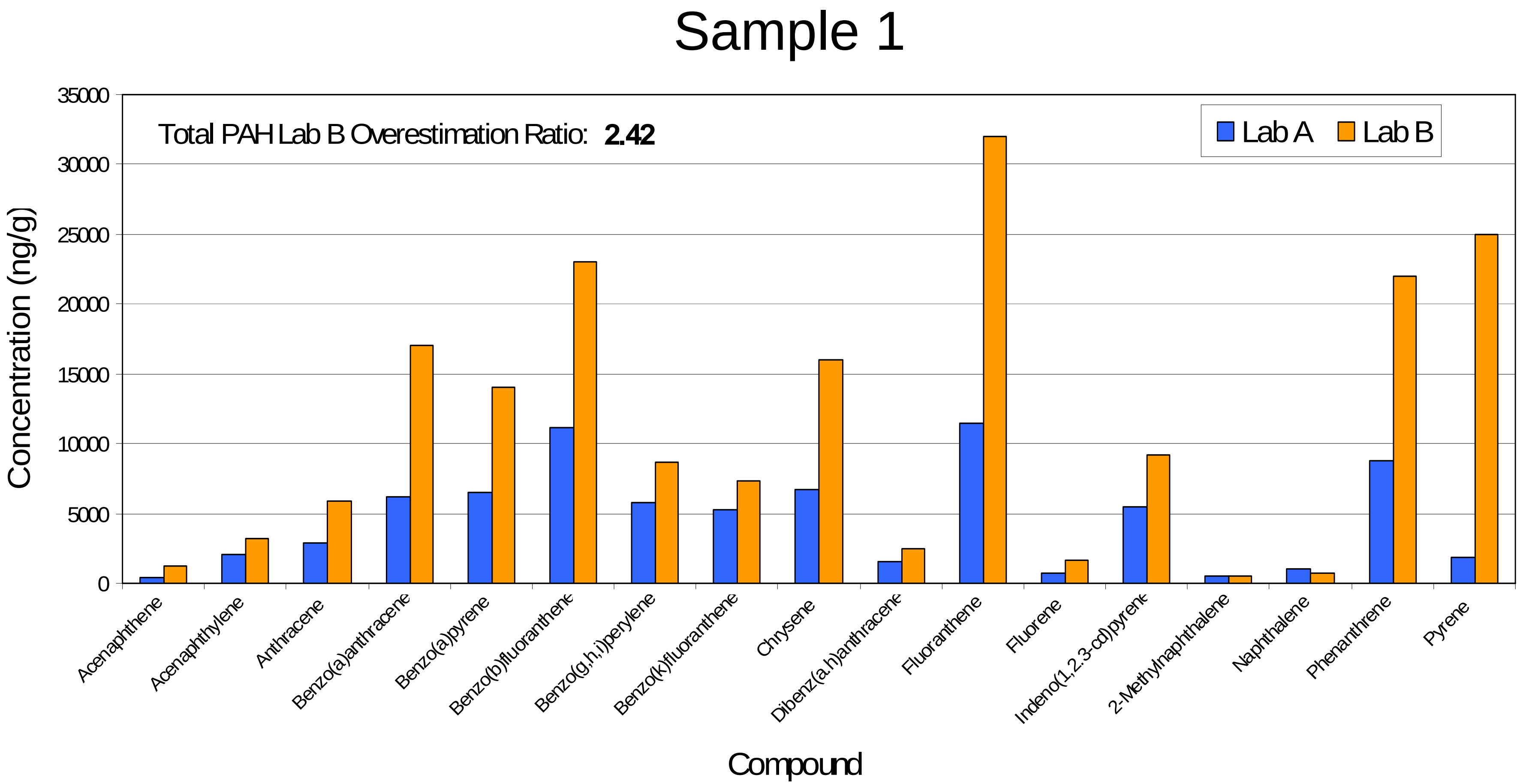

Overestimation

Underestimation – suppression

# PAH Duplicate Results



# PAH Comparisons



# Data Quality for PAHs

- Low resolution MS method for PAHs should be eliminated
- Sites driven by PAH risk require the ID-HRMS method
  - Sensitivity – for the guidelines
  - Specificity – for the interferences that are naturally present in samples
- Also important for pattern assessment

# Conventional source identification techniques

# Environmental Forensic Investigations

The systematic examination of environmental information, which may be used in litigation, to allocate responsibility for contamination

Success relies on an understanding of a variety of disciplines and knowing which tools are best suited for a particular case

# Interpretation of Data

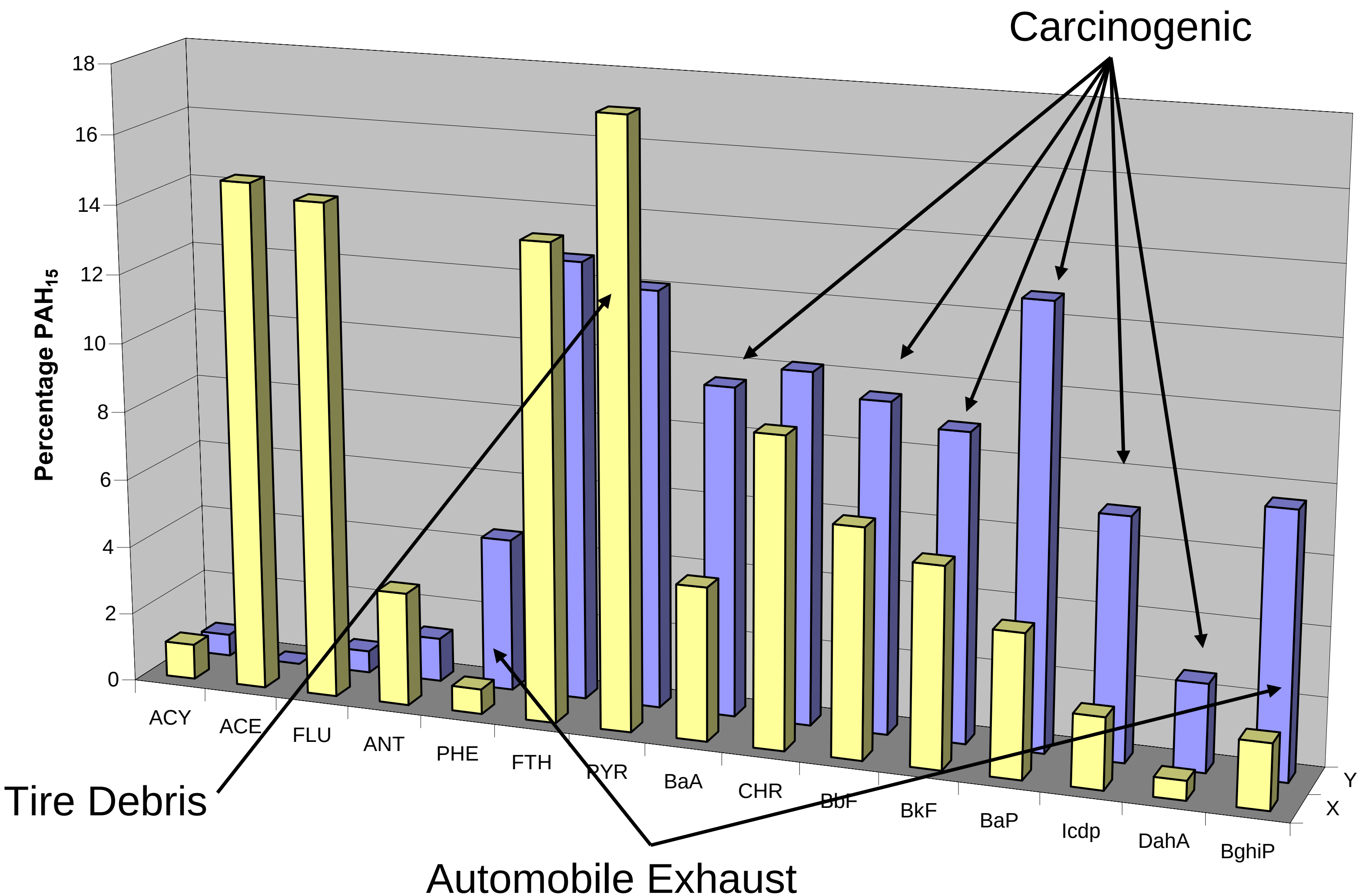
Source identification may be determined using a combination of the following techniques:

- Chemical fingerprinting
- Molecular diagnostic ratios
  - Single and double ratio plots
- Cluster analysis
- Principal component analysis

# Chemical Fingerprinting

*Chemical fingerprinting describes the use of a unique chemical signature to identify or distinguish different chemical sources*

# Chemical Fingerprinting



# Chemical Fingerprinting

Extension of chromatograph method to include both ***alkylated*** PAHs and ***dibenzothiophenes*** greatly increases the potential to differentiate sources of PAH e.g.

– petrogenic fingerprints generally exhibit low parent PAHs relative to alkylated PAHs while

– inversely pyrogenic fingerprints generally exhibit higher parent PAHs relative to alkylated PAHs.

*Murphy and Morrison 2007*

# Molecular Diagnostic Ratios

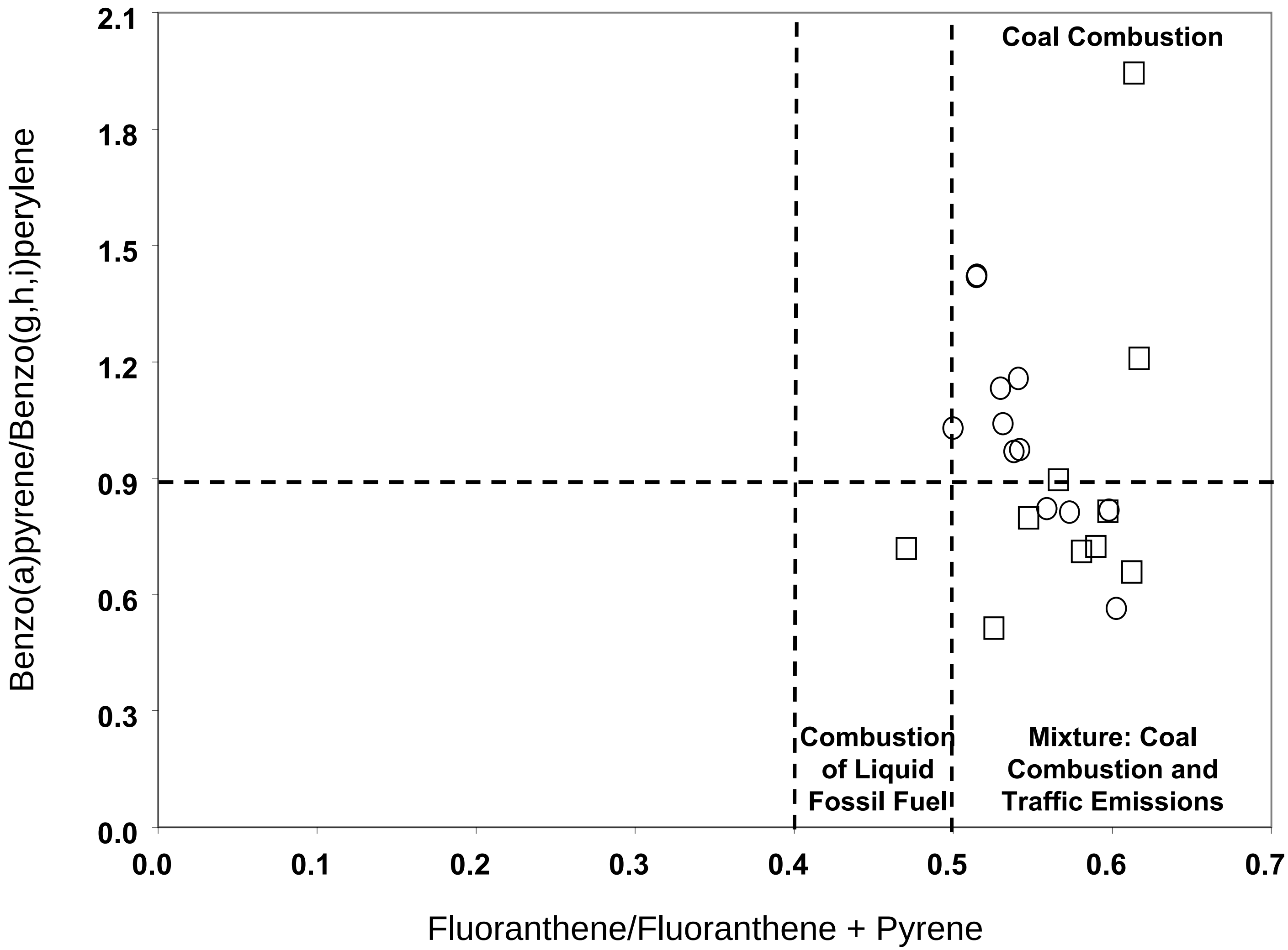
*"The principal underlying the use of paired PAH constituents as "diagnostic source ratios" is that PAHs with similar properties (e.g. molecular weight, aqueous solubilities, and octanol-water partition coefficients [Kow] typically retain the same relative concentration in residues as in their sources."*

( Costa et al 2004)

# Diagnostic Ratios

| Ratios | Values / Sources | References |
|---|---|---|
| Phenanthrene / Anthracene | < 5 = Pyrogenic; > 5 = Petrogenic | Neff et al., 2005 |
| Fluorene / Pyrene | + 1 = Pyrogenic. < 1 = Petrogenic | Neff et al., 2005 |
| indeno(1,2,3-cd)pyrene / (indeno(1,2,3-cd)pyrene + benzo(g,h,i)perylene | > 0.1 = Combustion | Motelay-Massei et al 2007; Yunker et al., 2002 |
| Fluoranthrene/ Pyrene | < 1 = Petrogenic; >1 Pyrogenic | Motelay-Massei et al 2007 |
| LMW / HMW | < 1 = Combustion | Zhang et al 2005; |
| benzo(a)pyrene / benzo(a)pyrene + chrysene | < 0.2 = Petrogenic; > 0.35 = Combustion | Zhang et al 2005; Zhang et al 2007 |

# Double Ratio Plot



# Cluster Analysis

*Cluster Analysis is a classification method which is used to arrange a set of cases into clusters. The aim is to establish a set of clusters such that cases within a cluster are more similar to each other than they are to other cases in other clusters.*

# Principal Component Analysis

*"The objective of PCA is to reduce the dimensionality of a data set in which there are a large number of interrelated (i.e.., correlated) variables."*

*"… is achieved by transforming the data to a new set of uncorrelated reference variables (principal components or PCs)."*

*Introduction to Environmental Forensics*
*(Murphy and Morrison 2007)*

# Summary

- Conventional techniques allow for the separation of sources of PAHs into broad classes pyrogenic and petrogenic

- A large number of sources of PAHs may be encompassed with the classification pyrogenic PAHs and further separation based on chemical fingerprinting, diagnostic ratios and statistical analysis have not always been conclusive.

# Toxic Equivalency Factors (TEFs)

*…Compare the relative toxicity of individual chemicals, or congeners, within a family of chemicals displaying similar chemical and physiological characteristics to a designated member (typically the most toxic) of this family of chemicals.*

# Toxic Equivalency Factors (TEFs)

Introduced to facilitate risk assessment and regulatory control of exposure to PAH, PCDD, PCDF and PCB-like mixtures

- The TEF approach has been used extensively for hazard assessment of different classes of toxic chemical mixtures.
- TEF concept applicable only to chemicals whose mechanism of action involves AhR binding and activation
- When applying the TEF concept, the toxicity of a compound(s) is determined relative to BaP
- TEFs are dependent on species and endpoints

# Toxic Equivalency Factors

Assumptions:

- The individual compounds all act through the same biological or toxicological pathway
- The effects of individual chemicals in a mixture are dose or concentration additive
- The dose-response curves for different congeners should be parallel
- The organotropic manifestations of all congeners must be identical over the relevant range of doses

# Toxic Equivalents (TEQ)

TEQs provide an estimate of the potential toxicity of a sample for risk assessment purposes

$$\mathrm{TEQ} = \sum_{n=1}^{k} C_n \times TEF_n$$

**Where:**

**$TEF_n$ = Toxic Equivalency Factor of Individual Congener**

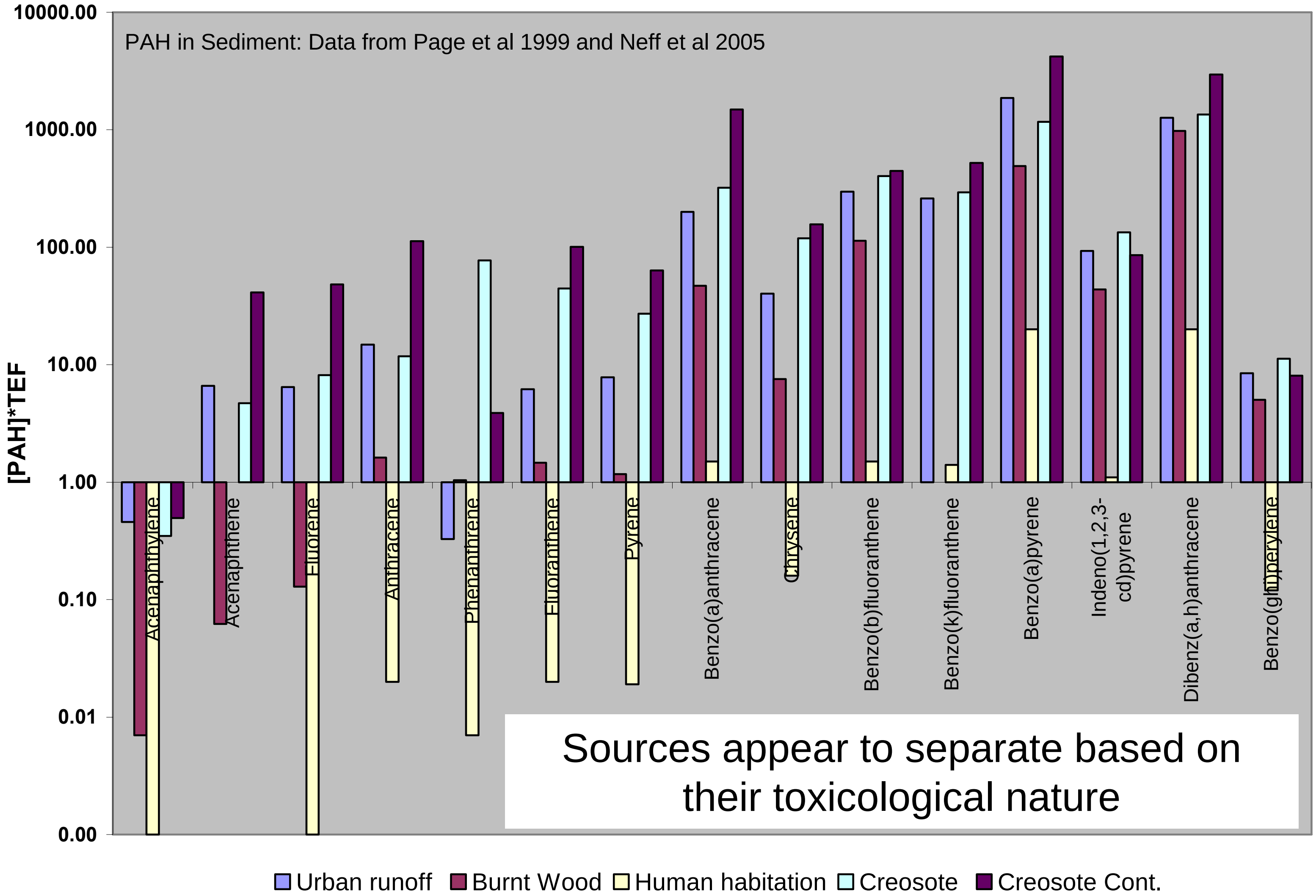
**$C_n$ = Concentration of Congener in Complex Mixture**

# TEFs and TEQ

$$TEQ = \Sigma\ ([PAH_{individual}] * TEF_{individual})$$

| PAH Compound | TEF (Nisbet and Lagoy 1992) |
|---|---|
| Acenaphthylene | 0.001 |
| Acenaphthene | 0.001 |
| Fluorene | 0.001 |
| Anthracene | 0.010 |
| Phenanthrene | 0.001 |
| Fluoranthene | 0.001 |
| Pyrene | 0.001 |
| Benzo(a)anthracene | 0.100 |
| Chrysene | 0.010 |
| Benzo(b)fluoranthene | 0.100 |
| Benzo(k)fluoranthene | 0.100 |
| Benzo(a)pyrene | 1.000 |
| Indeno(1,2,3-cd)pyrene | 0.100 |
| Dibenz(a,h)anthracene | 5.000 |
| Benzo(ghi)perylene | 0.010 |

# TEQ Fingerprint



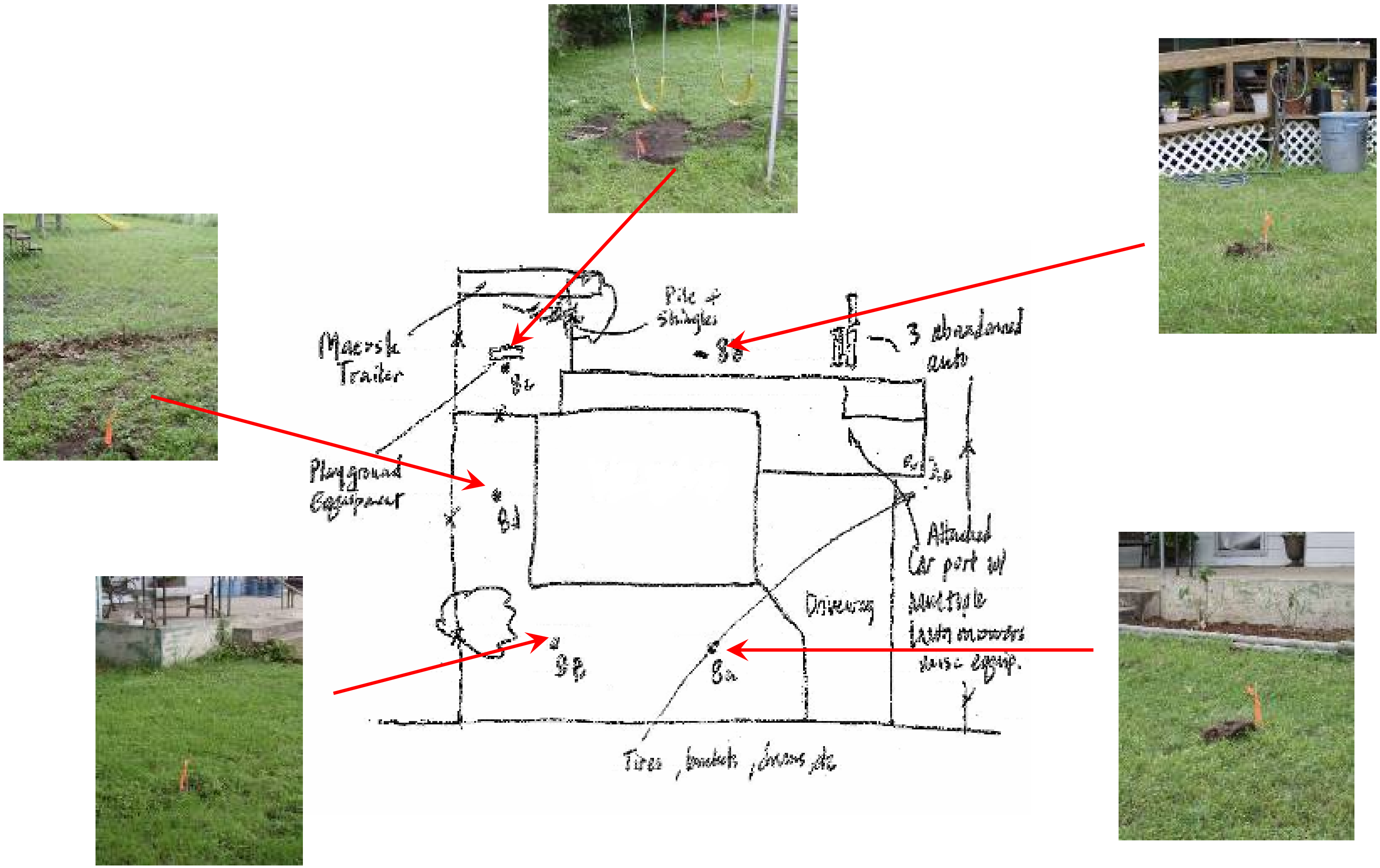
# Case Study: PAHs

*Residents have allegedly been exposed to dioxins, PAHs and metals released from a railroad tie treatment plant. Exposure pathways include inhalation of ambient air and incidental ingestion of soil*

# Investigation Objectives

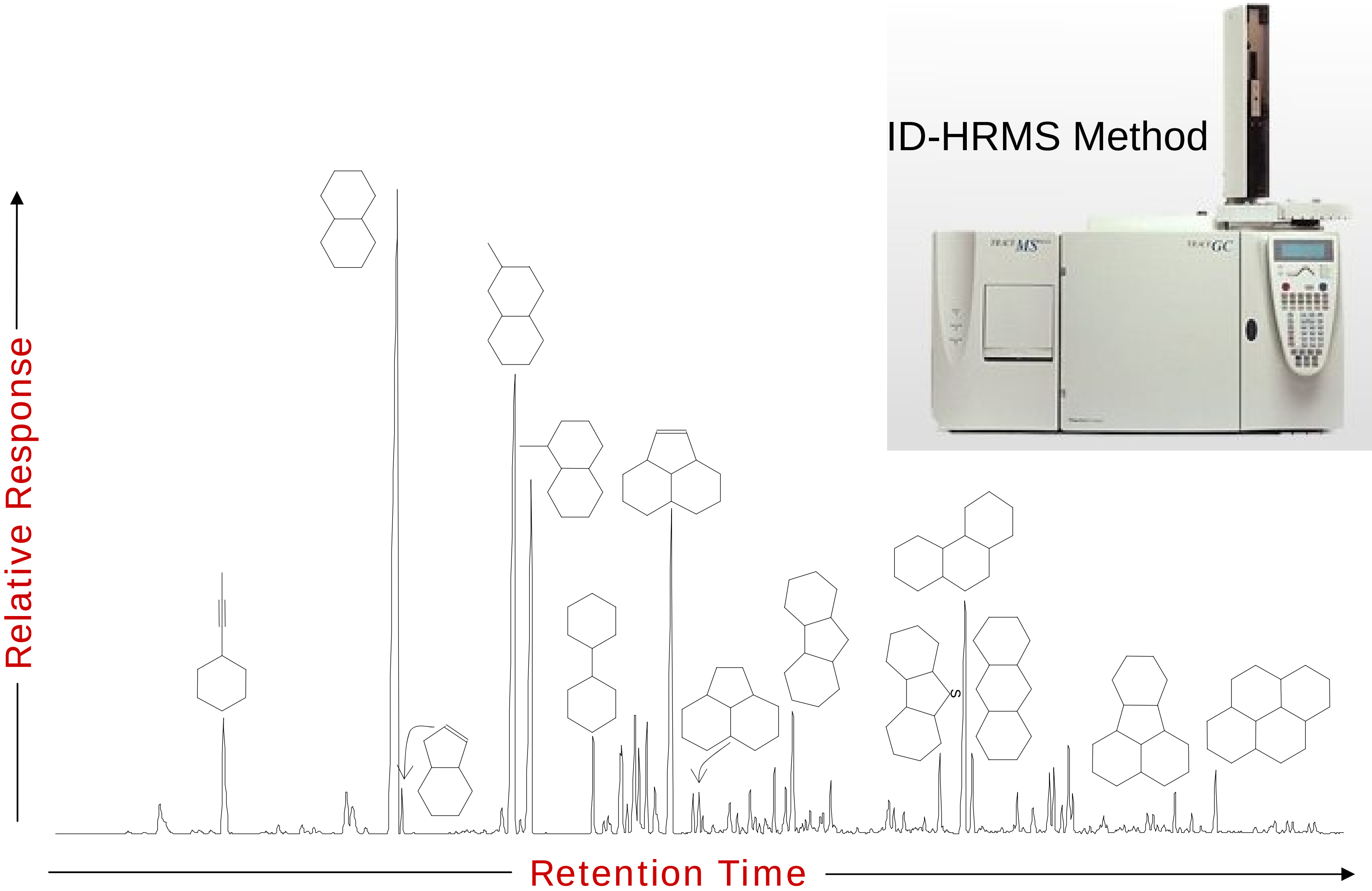
- Collection of representative samples from ‘impacted’ and background sites
- Identify potential sources
- Identify relationship, if any, between ‘impacted’ sites

# Sampling



Maersk Trailer
Pile of Shingles
3 abandoned auto
Playground Equipment
Attached Car port w/
Driveway
Tires, buckets, drums, etc

# Analysis

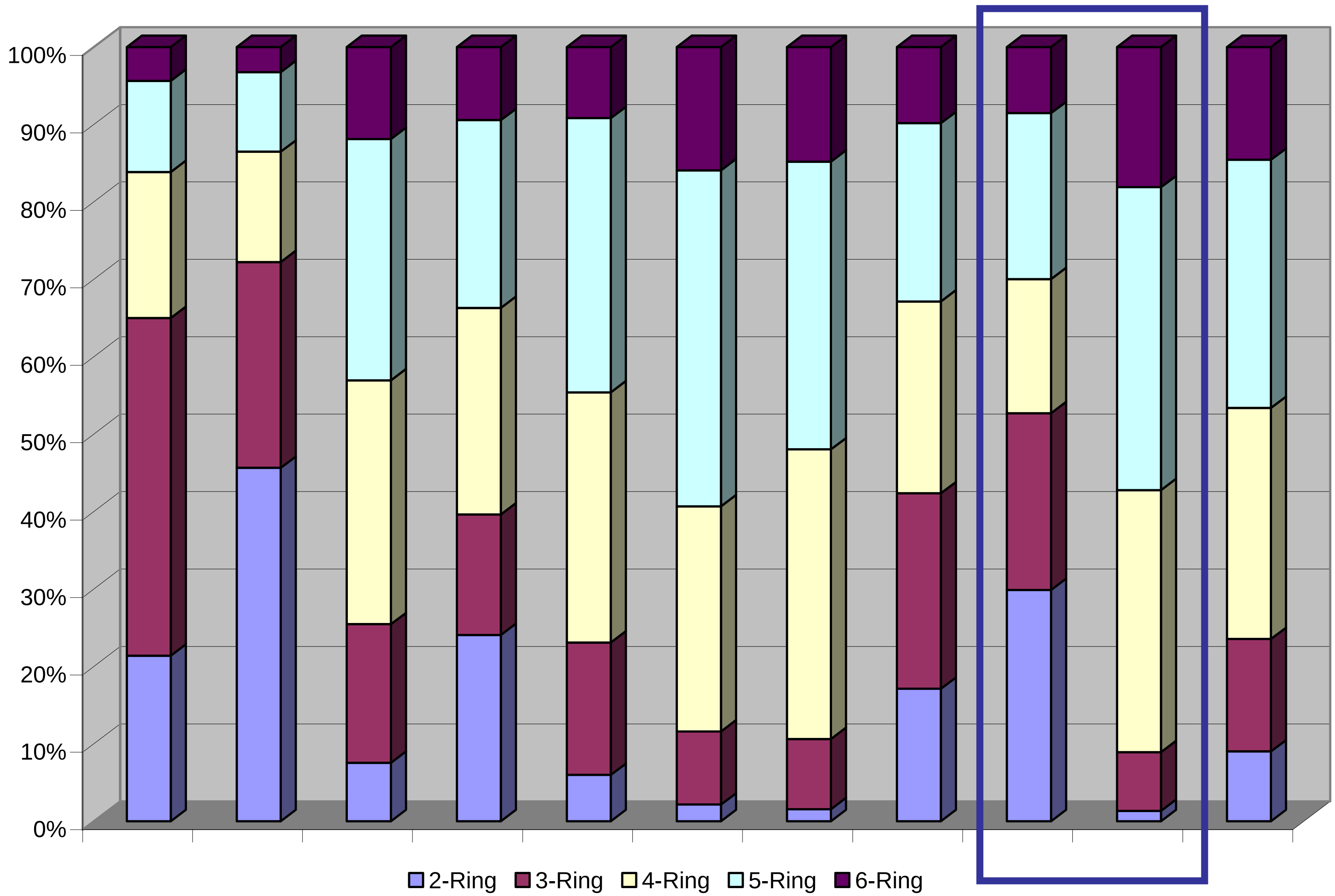


# Interpretation

A number of techniques were completed including:

– Chemical fingerprinting
– Molecular diagnostic ratios
– Cluster analysis
– Principal component analysis
– TEF fingerprinting

# Potential for multiple sources or alternatively the degradation of lighter components

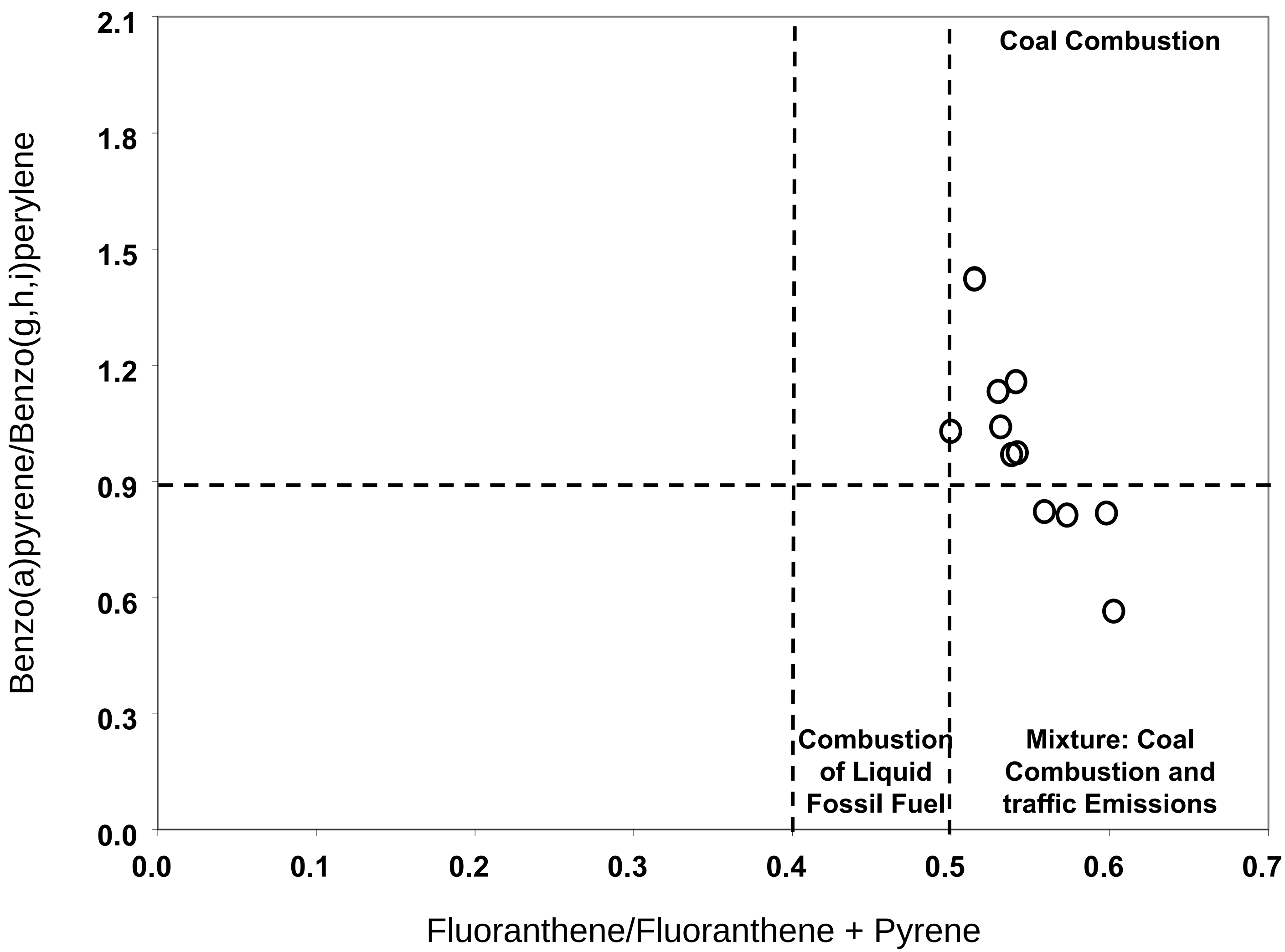


# Diagnostic Ratios

| Sample | Ph/An[a] < 5 = Py., > 5 = Pet. | Flu/Py[a] +1 =Py., <1= Pet. | IcdP/Icdp+BghiP [b,c] > 0.1 = Com. | Fth/Pyr[b] <1= Pet. >1= Py. | LW/HW[d] <1= Com. | BaA/(BaA+Chr)[d,e] <0.2= Pet; >0.35=Com. |
|---|---|---|---|---|---|---|
| **A** | 0.7 | 4.03 | 0.46 | 1.5 | 5.19 | 0.22 |
| **B** | 1.5 | 2.16 | 0.50 | 1.5 | 6.40 | 0.23 |
| **C** | 3.5 | 0.11 | 0.48 | 1.2 | 1.32 | 0.42 |
| **D** | 2.6 | 0.09 | 0.49 | 1.1 | 1.00 | 0.40 |
| **E** | 1.1 | 0.26 | 0.45 | 1.2 | 1.97 | 0.40 |
| **F** | 0.4 | 0.35 | 0.46 | 1.1 | 1.24 | 0.36 |
| **G** | 0.4 | 0.22 | 0.51 | 1.1 | 0.69 | 0.49 |
| **H** | 2.0 | 0.03 | 0.50 | 1.1 | 0.92 | 0.36 |
| **I** | 1.3 | 0.91 | 0.44 | 1.3 | 2.04 | 0.35 |
| **J** | 1.1 | 2.17 | 0.49 | 1.3 | 2.34 | 0.30 |
| **K** | 3.1 | 0.05 | 0.47 | 1.0 | 0.75 | 0.45 |
| **L** | 1.4 | 0.26 | 0.49 | 1.3 | 1.14 | 0.45 |

a: Neff et al., 2005; b: Motelay-Massei et al 2007; c: Yunker et al., 2002; d: Zhang et al 2005; e: Zhang et al 2007

# Double Ratio Plot



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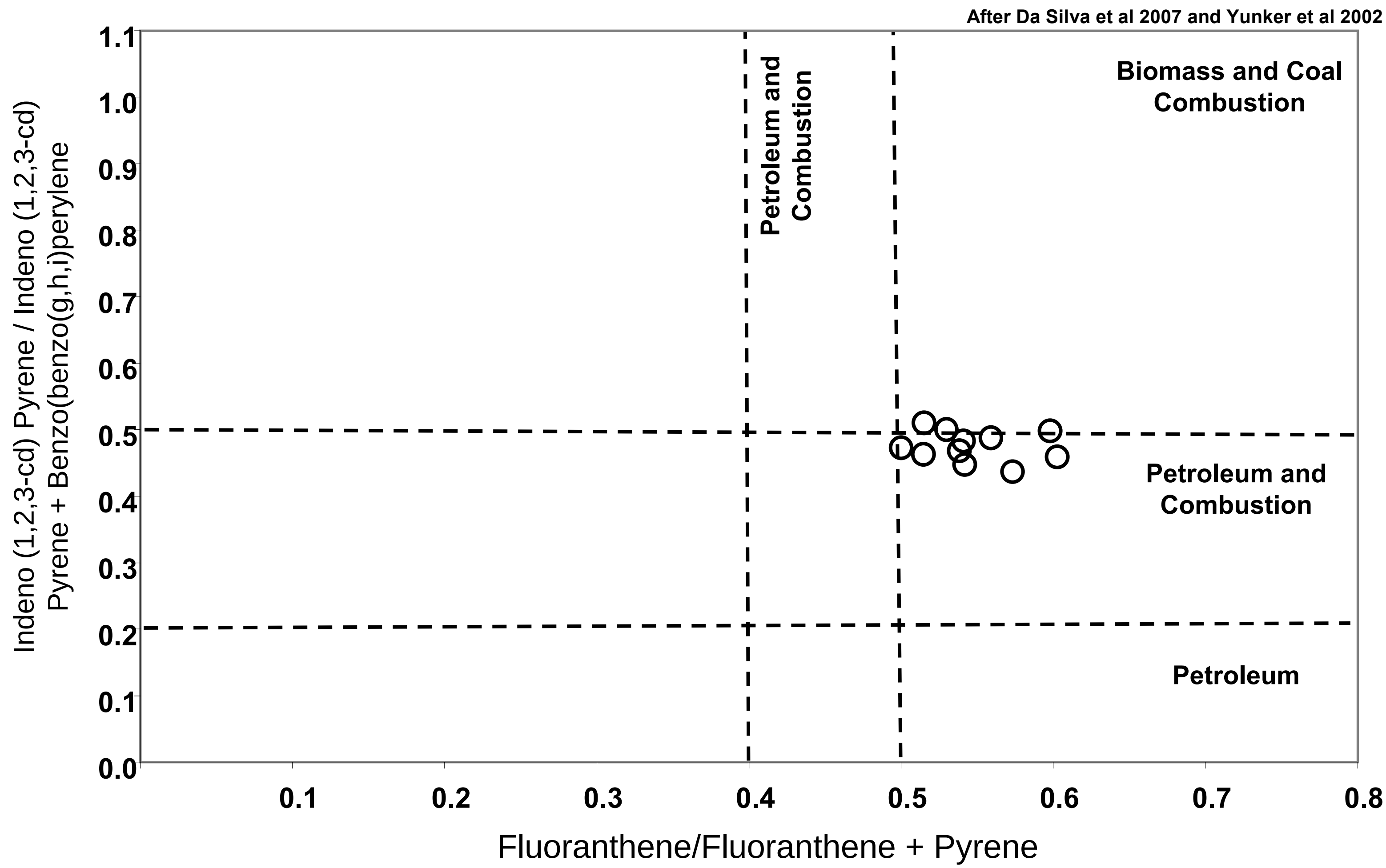
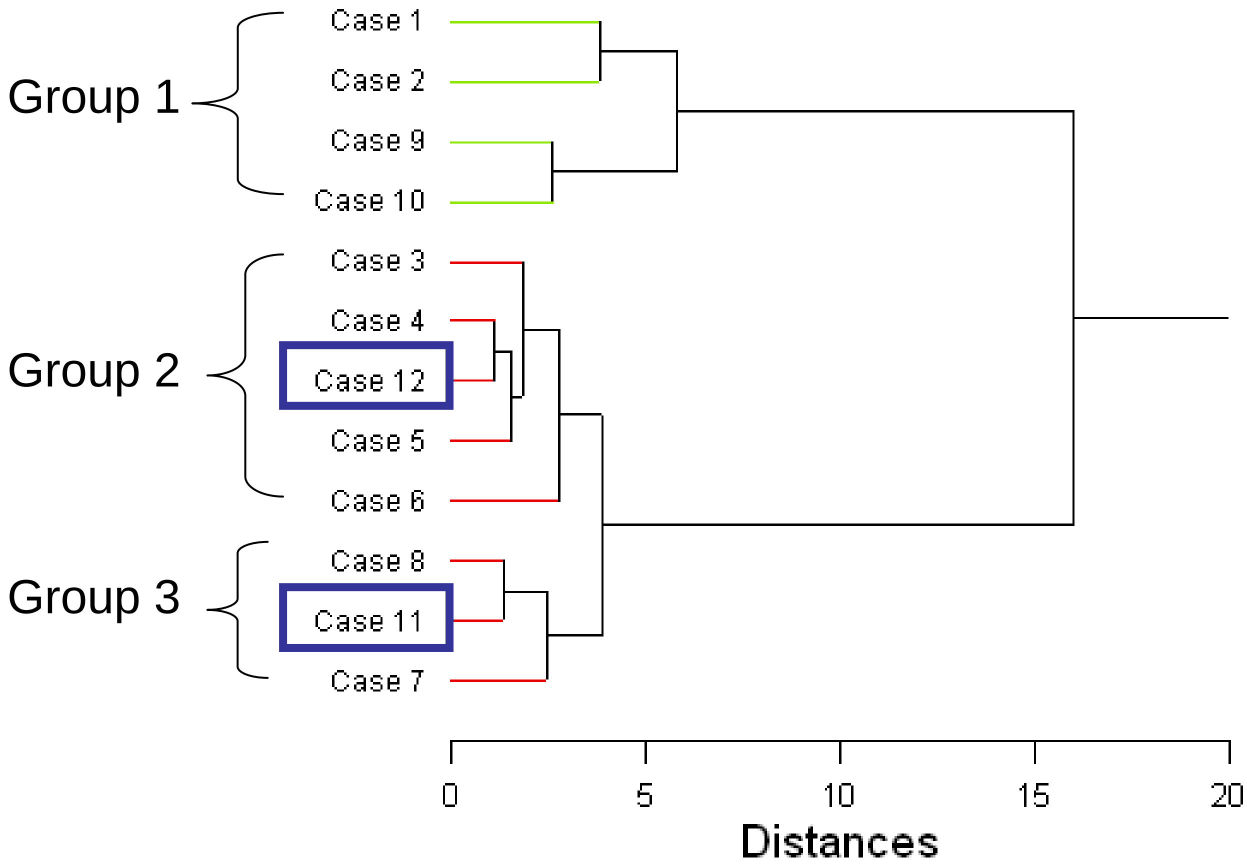


# Cluster Analysis

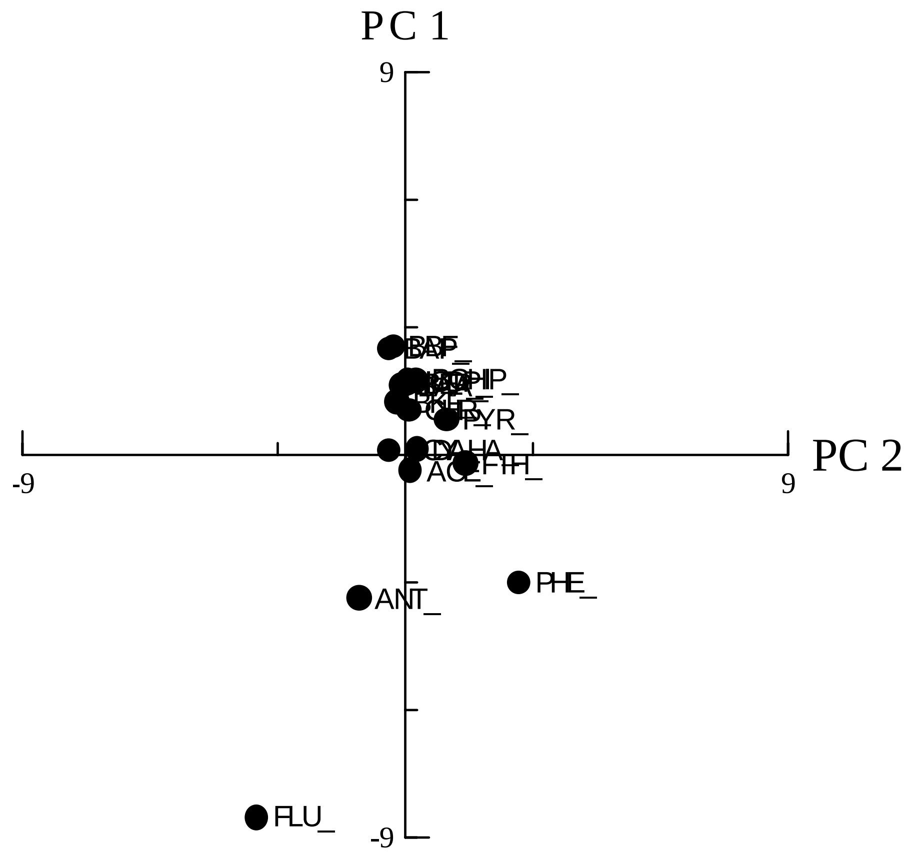



**Statistical Analysis was completed using SYSTAT 12: Ward Method with Squared Euclidean Distances**

# Principal Component Analysis

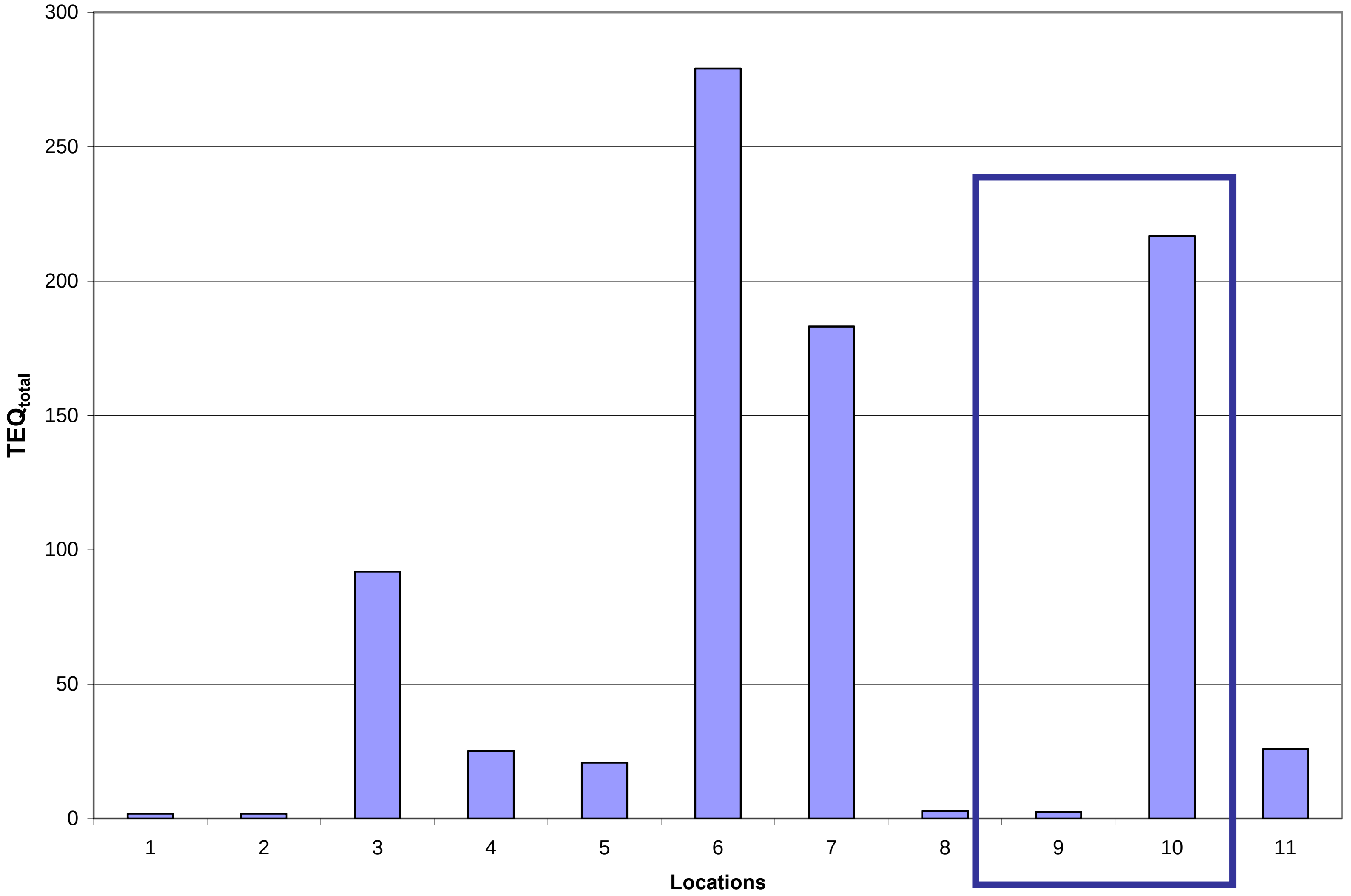
Factor 1 and 2 were responsible for total variance of 75% and 15% respectively

- Loadings were separated based on molecular weight
- The highest loadings were on Flu, Ant and Phe which are indicative of Diesel Emissions
- BaA, Chr, BbF, Bap, Icdp also loaded and may indicate influence of meat cooking

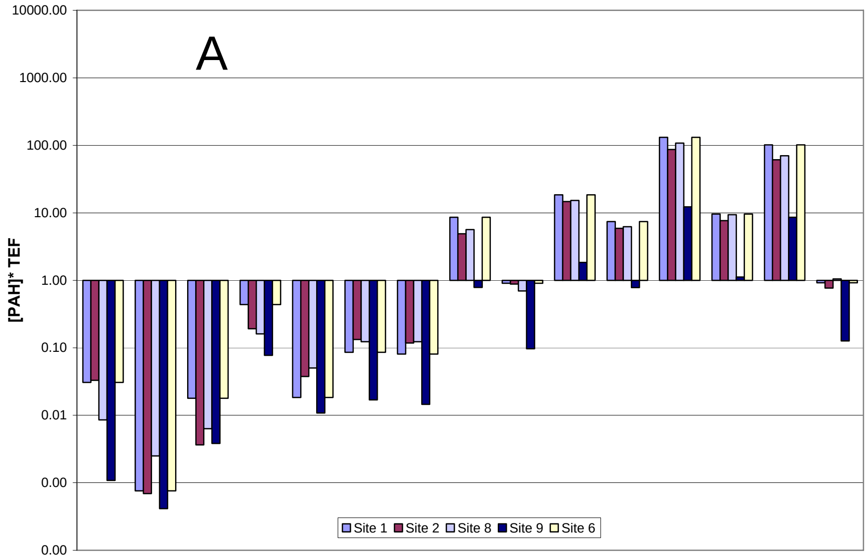


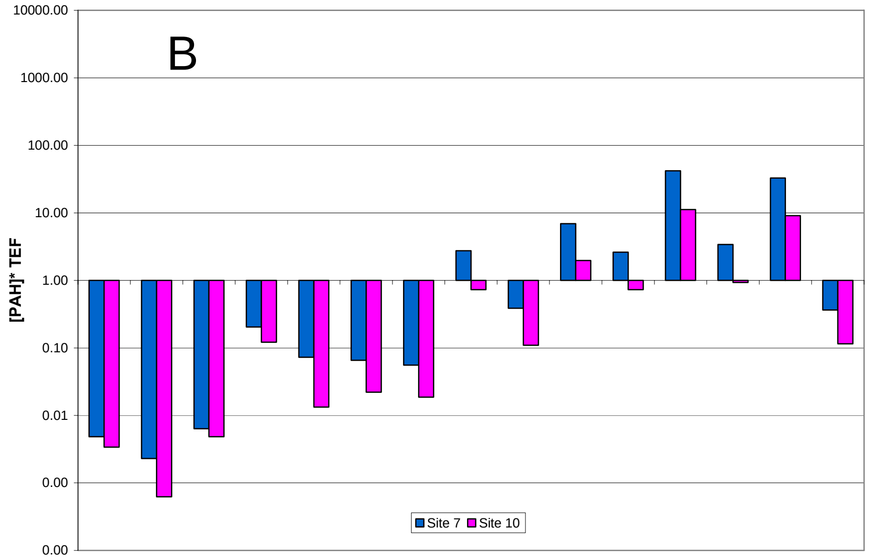

Groupings were determined using PCA with varimax rotation and principal components having eigenvalues >1

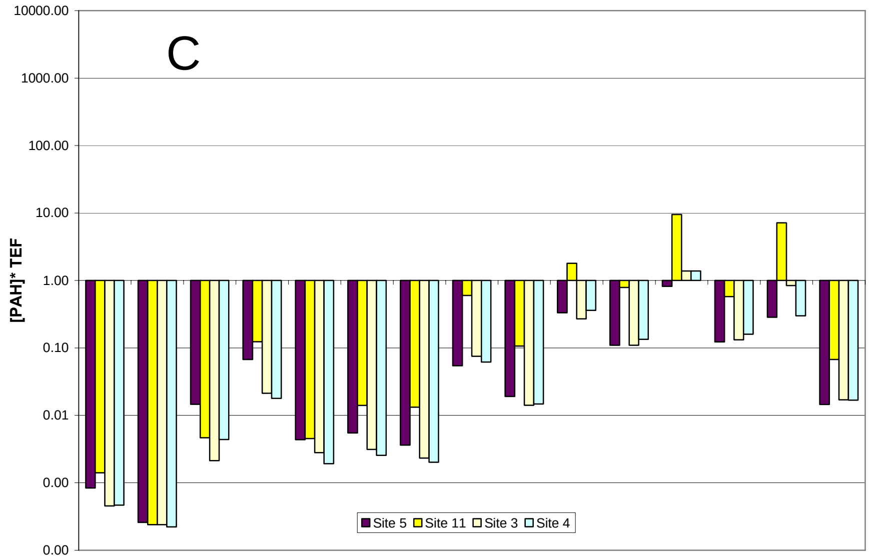
# $TEQ_{sum}$



# TEQ Fingerprint



# Summary

Interpretation of chemical fingerprints, molecular ratios, cluster analysis, PCA and TEQs suggest:

- Suspected impacted sites do not all share similar PAH signatures indicating the potential for various sources
- A number of the sites share similar signatures to background locations
- PAHs may be derived from mixed pyrogenic sources (e.g. diesel exhaust, BBQ)