

Improving Rigor in Polycyclic Aromatic Source Fingerprinting

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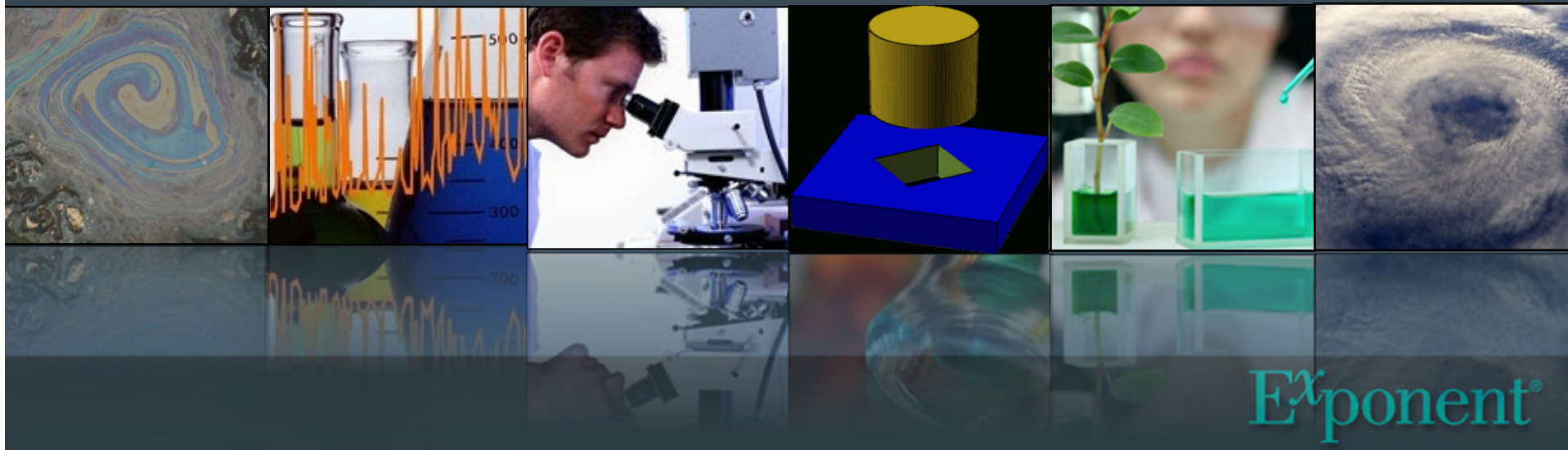
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Boehm et al. (2018) Environmental Forensics. 19:172-184



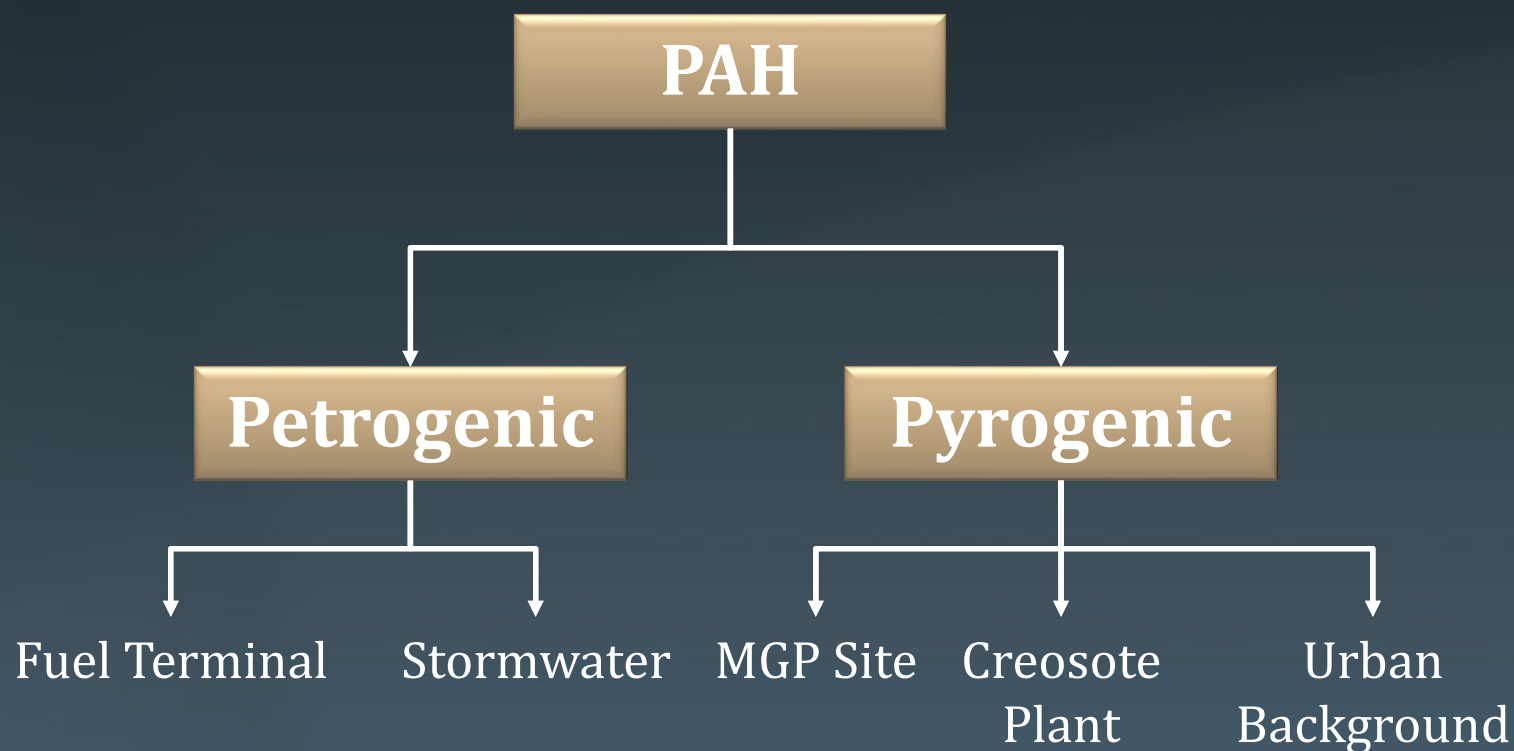
Key Message

Source identification of polycyclic aromatic hydrocarbons (PAH) in environmental samples has advanced greatly in the last 20 years. To realize potential benefits and avoid possible pitfalls, care is needed as one applies published diagnostic tools to available data sets.

Using PAH data collected for another purpose in a forensic evaluation may be like trying to fit a square peg in to a round hole.



The Challenge: Characterizing the Contribution of Multiple PAH Sources



The Problem(s)



- The Problem is rooted in suboptimal 1) sampling, 2) analytical chemistry, and 3) data analyses
- For Sites and Spills...
- **Sampling:** Samples that don't fit the question
 - Non-representative source samples
 - Literature vs. site-specific
 - Incomplete set of potential sources
 - Non-representative site samples
 - Parts of site vs. whole area in question
 - Snapshot in time vs. historical representation

The Problem(s)

- **Analytical chemistry** that falls short of adequate information
 - PAH analyte lists that are truncated
 - Detection limits that are too high
 - Inappropriate treatment of non-detects
 - Data from various labs and/or collected over time ... combined without analysis
- **Data analyses** that don't align with the questions, are based on flawed data sets, or are applied without rigor (e.g., based on someone's paper)

Sampling: The Foundation of a Good PAH Forensic Investigation

- Three key elements:
 - ❖ Source Samples
 - ❖ Representative of known sources and/or source areas in the time frame of interest
 - ❖ Site samples
 - ❖ Representative in the time frame of interest
 - ❖ Background samples
 - ❖ The chemical concentrations and compositions “but for” a release



PAH Forensic Chemistry Requires a Specific Set of Target Analytes

EPA's list of 16 PAHs may be insufficient.

- $\Sigma\text{PAH}_{16 \text{ or } 17}$ – a regulatory screening list
- $\Sigma\text{PAH}_{44 \text{ or } 50}$ – the forensics list

Table 15.4.1 Comparison of PAH Analytes Commonly Used in Environmental Forensic Investigations (ΣPAH_{50}) to the US EPA "Priority Pollutant" List (ΣPAH_{16})

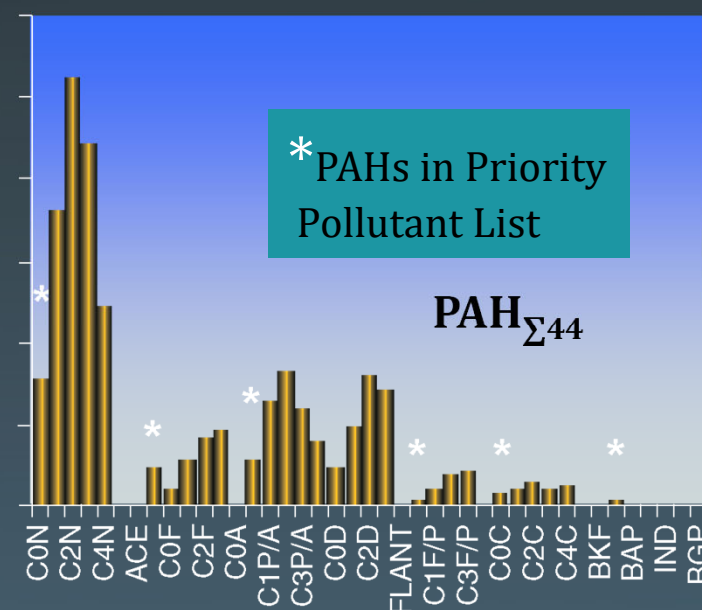
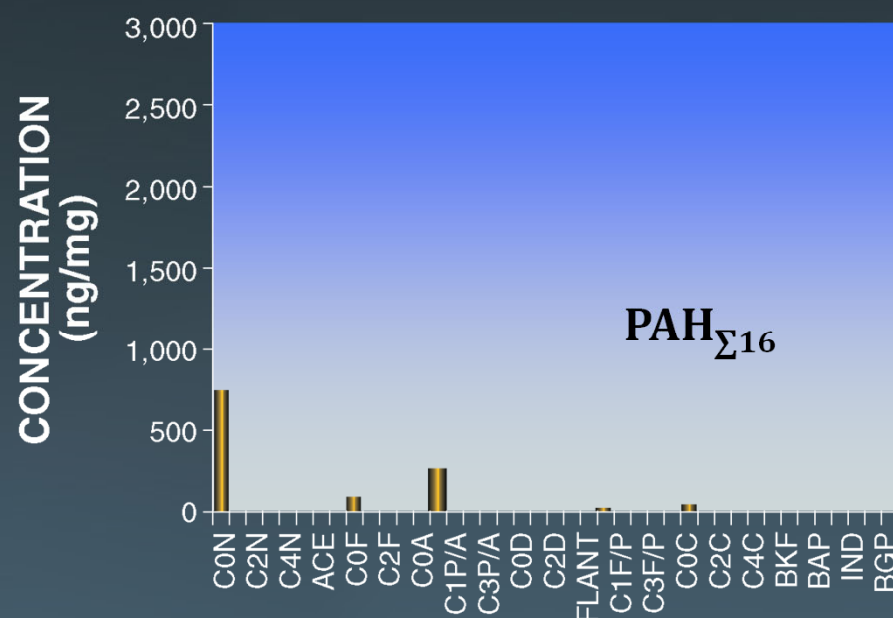
Analyte/Analyte Group	Abbr.	Analyte/Analyte Group	Abbr.
Naphthalene	N0	Pyrene	PY
C1-naphthalenes	N1	C1-fluoranthenes/pyrenes	FP1
C2-naphthalenes	N2	C2-fluoranthenes/pyrenes	FP2
C3-naphthalenes	N3	C3-fluoranthenes/pyrenes	FP3
C4-naphthalenes	N4	Benz(a)anthracene	BaA
Biphenyl	Bph	Chrysene	C0
Acenaphthylene	AcI	C1-chrysenes	C1
Acenaphthene	Ace	C2-chrysenes	C2
Dibenzofuran	DbF	C3-chrysenes	C3
Fluorene	F0	C4-chrysenes	C4
C1-fluorenes	F1	Benzo(a)fluoranthene	BaF
C2-fluorenes	F2	Benzo(b)fluoranthene	BbF
C3-fluorenes	F3	Benzo(j,k)fluoranthene	BkF
Anthracene	AN	Benzo(e)pyrene	BeP
Phenanthrene	P0	Benzo(a)pyrene	BaP
C1-phenanthrenes/anthracenes	P1	Perylene	Per
C2-phenanthrenes/anthracenes	P2	Indeno(1,2,3-c,d)pyrene	ID
C3-phenanthrenes/anthracenes	P3	Dibenzo(a,h)anthracene	DA
C4-phenanthrenes/anthracenes	P4	Benzo(g,h,i)perylene	BgP
Dibenzothiophene	D0	Dibenzo(a,e)pyrene	DeP
C1-dibenzothiophenes	D1	Dibenzo(a,h)pyrene	DhP
C2-dibenzothiophenes	D2	Dibenzo(a,l)pyrene	DlP
C3-dibenzothiophenes	D3	Dibenzo(a,i)pyrene	DiP
C4-dibenzothiophenes	D4	Dibenzo(a,e)fluoranthene	DeF
Fluoranthene	FL	Anthanthrene	A

bold - 16 Priority Pollutant PAH

(Boehm 2006)

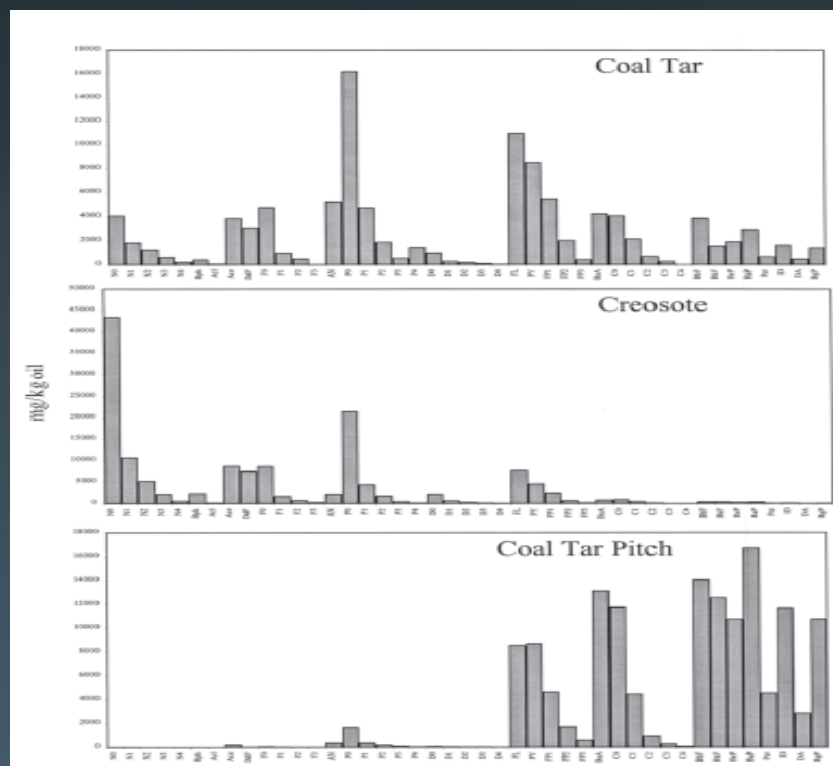
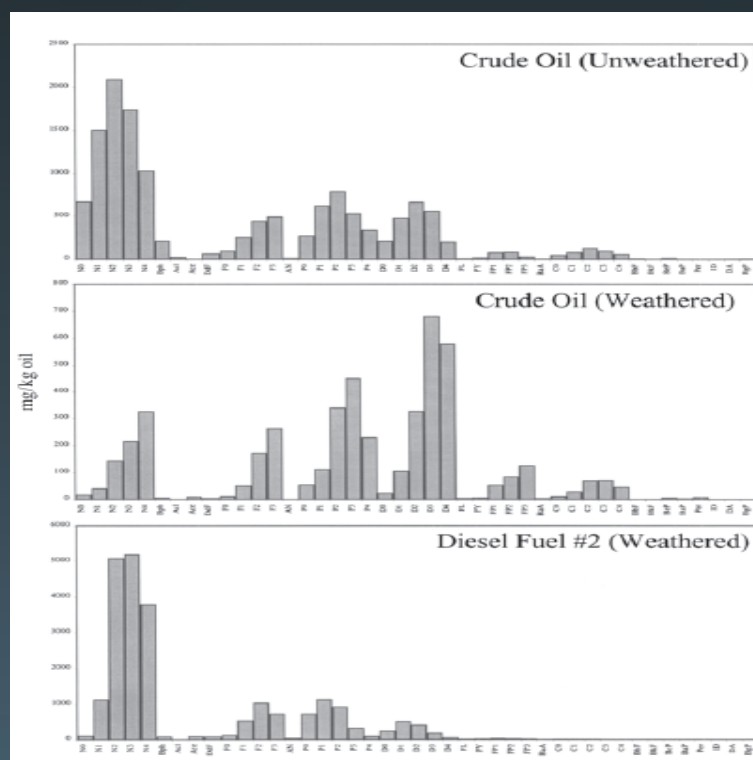
Comparison of PAH Analysis of Same Crude Oil Sample Using Two Target Lists

- Standard analysis of the EPA priority pollutant PAHs (“Regulatory List”) yields only a small fraction (10-30%) of the total PAH content
- Truncated regulatory PAH lists create vulnerabilities



PAH₄₄ Provides Foundation to Better Differentiate Petroleum and Pyrogenic PAH Source Profiles

- Unobtainable by regulatory lists (**PAH₁₇** or **PAH₃₄**)



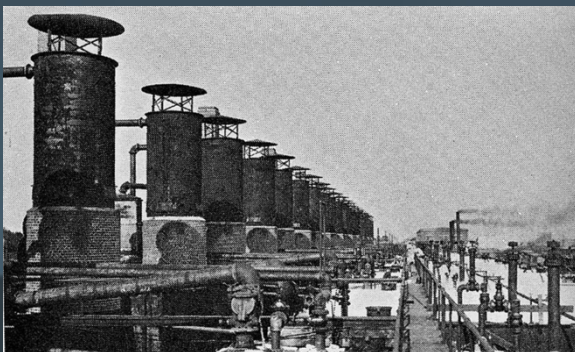
(Stout et al. 2001)

Using Literature Values for Source Types is Convenient, But Can Be Flawed.

- Use of literature derived source profiles for different categories of source types.



- Use of site specific data from potential local sources.



Problems with published PAH profiles

- PAH profiles vary with fuel type, combustion conditions, temperature, and other factors.
- Too few examples to characterize variability.
- Some historical data are available only as averages, so the actual profiles are not reviewable.
- Different averaging approaches have been used.
- Changes in profiles due to photo-oxidation and other weathering processes are ignored.

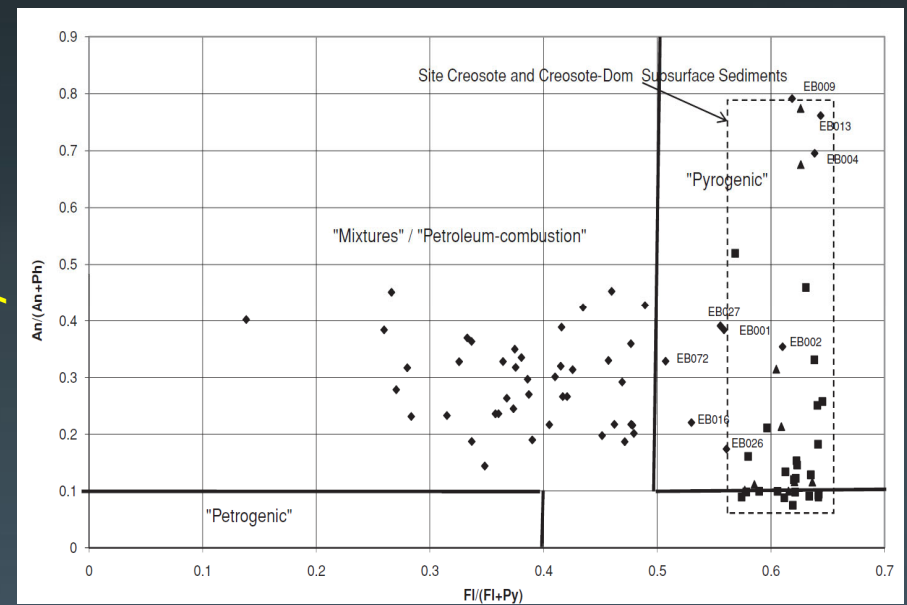
Weathering Results in Shifting PAH Profiles

- The loss of lighter more degradable PAH compounds will cause a shift in the source profile
- Can be a challenge to differentiate weathering effects from multiple sources
- Weathering will not cause a pyrogenic profile to change into a petrogenic profile.
- Solution: Run forensic evaluation methods with different combinations of PAHs, eliminating lighter ones, to assess the influence of weathering on results and interpretations.

Be Leary of Ratios of Convenience

While double ratio plots can be a useful tool for comparing samples within a sample set, comparison with published ratios has limited value for specific source identification.

An/Ph

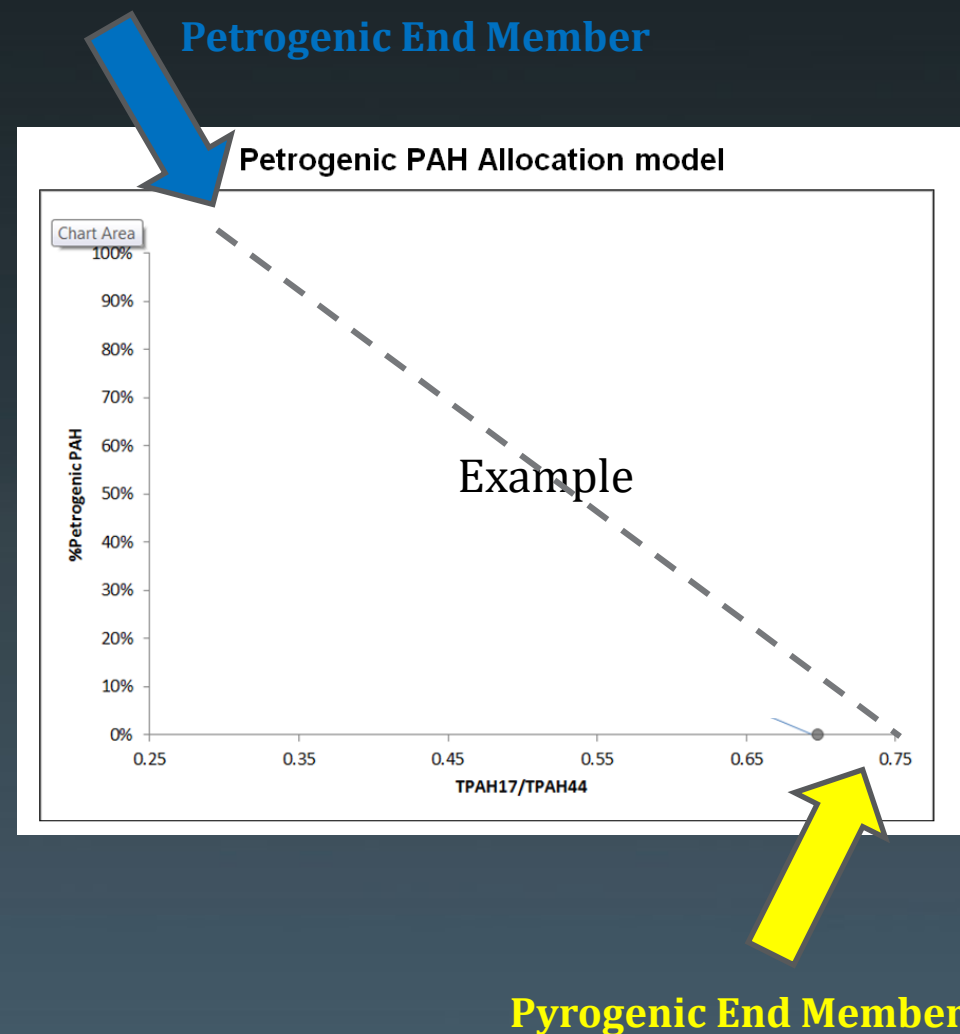


Fl/Py

From: Zemo 2009

Real Value in the Interplay of ΣPAH_{17} and ΣPAH_{44}

- Need both
- Pyrogenic PAH $\equiv \Sigma\text{PAH}_{17}$
- Petrogenic PAH $\equiv \Sigma\text{PAH}_{44}$
- Ratio $\Sigma\text{PAH}_{17}/\Sigma\text{PAH}_{44}$ is an excellent tool
- **Higher** for samples with a pyrogenic origin; and **lower** for samples of petrogenic origin



Data Analysis Issues: Problems of High Detection Limits = Non Detects



Environmental Forensics



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Cautions on the treatment of non-detect results for environmental forensics

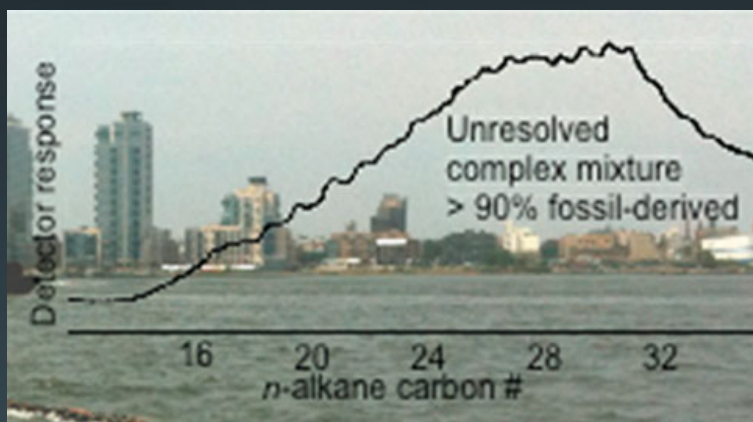
Mihai Aldea, Melanie Edwards, Jaana Pietari & Paul Boehm

Data Analysis Issues – Non Detects

- Substituting values for NDs on multivariate analyses greatly increases the potential for incorrect conclusions about the true forensic features within the data
- In some cases, removal of variables and/or samples with high degrees of censoring resolves this challenge
- But best approach is to lower detection limits

PAH Forensics is Enhanced through Other Chemical Lines of Data/Evidence

- Gas Chromatograms



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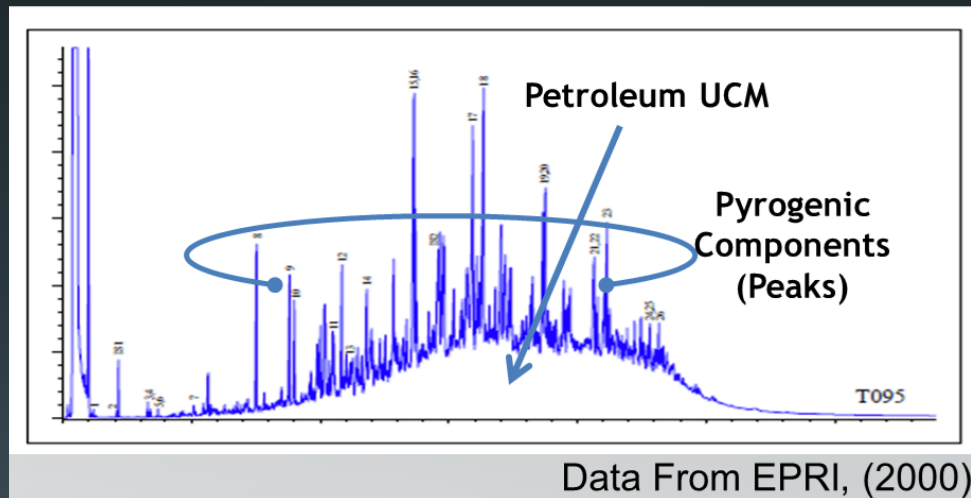
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Unresolved Complex Mixture (UCM) in Coastal Environments Is Derived from Fossil Sources

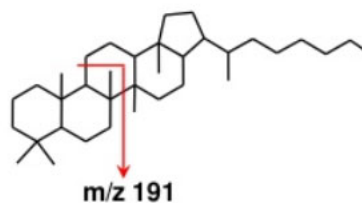
Helen K. White,^{*,†} Li Xu,[‡] Paul Hartmann,[§] James G. Quinn,^{||} and Christopher M. Reddy[⊥]

- Petroleum Biomarkers

- Petrogenic sources rich in biomarkers

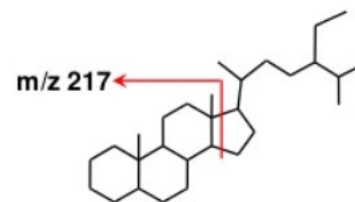


Hopanes



$M^{+} \rightarrow m/z\ 191$

Steranes

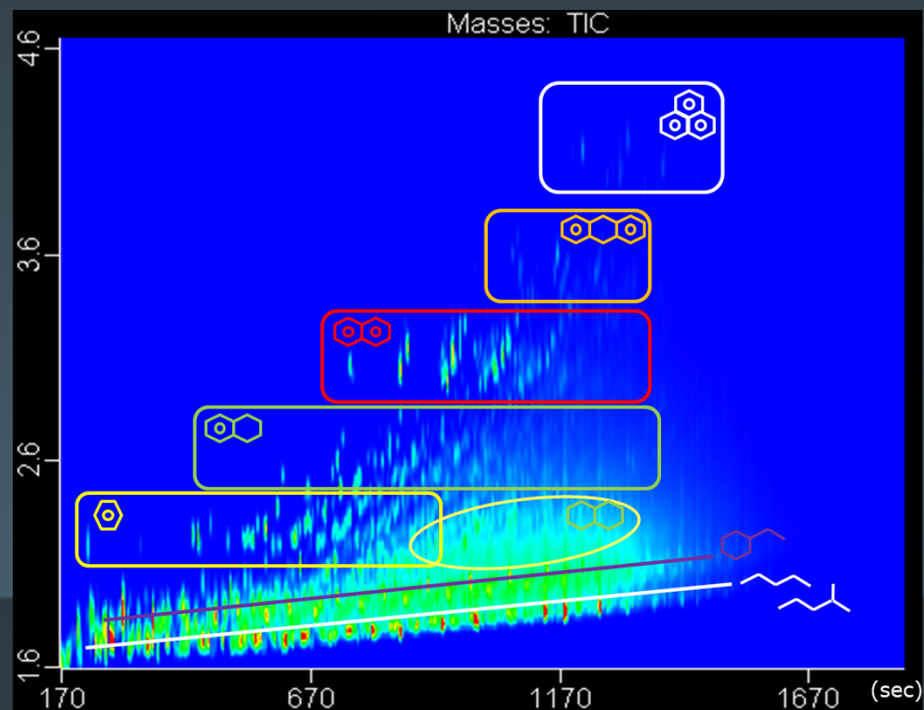
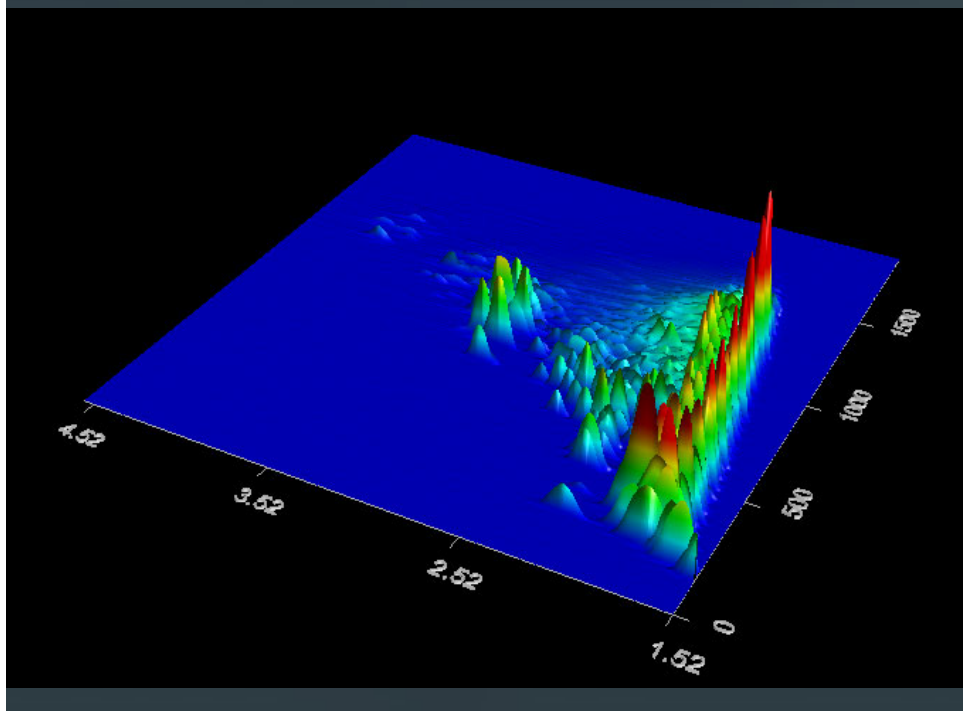


$M^{+} \rightarrow m/z\ 217$

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Analytical Advances May Improve Forensic Evaluations

- Two dimensional chromatography better separates compounds in complex mixtures.
- Rigorous methods of incorporating the results are under development.



Use of Statistical Receptor “Mixing” Models

- Receptor models are tools for characterizing potential sources and quantifying their contribution.
- Examples: CMB, PVA, UNMIX, PMF etc.
- While, powerful and versatile, careful application necessary

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Contributed Articles

Sediment PAH Allocation Using Parent PAH Proportions and a Least Root Mean Squares Mixing Model

Kurt Herman, Eric J. Wannaruker, and Gautham B. Jegadeesan

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Parsing Pyrogenic Polycyclic Aromatic Hydrocarbons: Forensic Chemistry, Receptor Models, and Source Control Policy

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Use of Receptor Models to Evaluate Sources of PAHs in Sediments

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Receptor models are mathematical procedures for resolving one or more of these parameters in a mixed chemical system: (1) the number of sources, (2) their chemical characteristics, and (3) the relative contribution of each source in environmental samples. These models are being used increasingly to evaluate sources of polycyclic aromatic hydrocarbons (PAHs) in sediments. As with any mathematical model, understanding the underlying assumptions is critical in interpreting the output. Three assumptions that raise particular challenges when applying receptor models to evaluate multiple sources of pyrogenic PAHs are (1) identification of all important sources, (2) stability of source profiles, and (3) linear independence of each profile. Variability within source types, and similarities among the PAH profiles of different sources, create uncertainties that must be considered when evaluating the results of receptor models. Various procedures for evaluating uncertainties have been applied in the literature, but validation and standardization of such methods are often lacking. Using a case study, this article demonstrates how a more detailed evaluation of model output can produce conclusions that differ from those initially published. While not eliminating uncertainty, we recommend a multiple-lines-of-evidence approach that includes both mixing and unmixing receptor models, along with other environmental forensic techniques.

Key Words: PAH, pavement sealer, receptor models, sediments, source control

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous constituents in urban sediments that are generally regulated as toxic and as potential carcinogens (1). Therefore, PAHs are of interest to both environmental scientists and policy makers. As a class of compounds with profiles that differ by source, they lend

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Do Not Ignore the Underlying Assumptions of Mixing Models

1. All potential sources have been identified
2. Source profiles are known and stable
3. The number of sources is less than the number of fitting species
4. Source profiles are linearly independent of each other
5. Measurement uncertainties are random, uncorrelated, and normally distributed.

Conclusions

- Environmental forensics provides powerful tools for characterizing and quantifying source of PAHs.
- Forensic methods are not plug and play but require technical rigor and integration of site-specific information for proper implementation.

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