The use of Poly-Aromatic Hydrocarbons (PAHs) in oil spill forensic geochemistry

By Marianne Nuzzo

The source of oils spilled in the environment is frequently unknown, and a defensible identification based on correlation to suspected sources is a critical part of oil spill assessments (Stout *et al*., 2001). Two major processes complicate the correlation of the spilled oil to its source(s): **weathering** of oil in the environment, and the forming of **mixtures** with hydrocarbon compounds from different sources (see also the IGI Technical Note #25 by Nuzzo and Gehlen, February 2021).

Poly-Aromatic Hydrocarbons (PAHs) encompass thousands of compounds formed by the fusion of two or more benzene rings. About fifty 2- to 6-ringed compounds are used in oil forensic geochemistry (Figure 1).

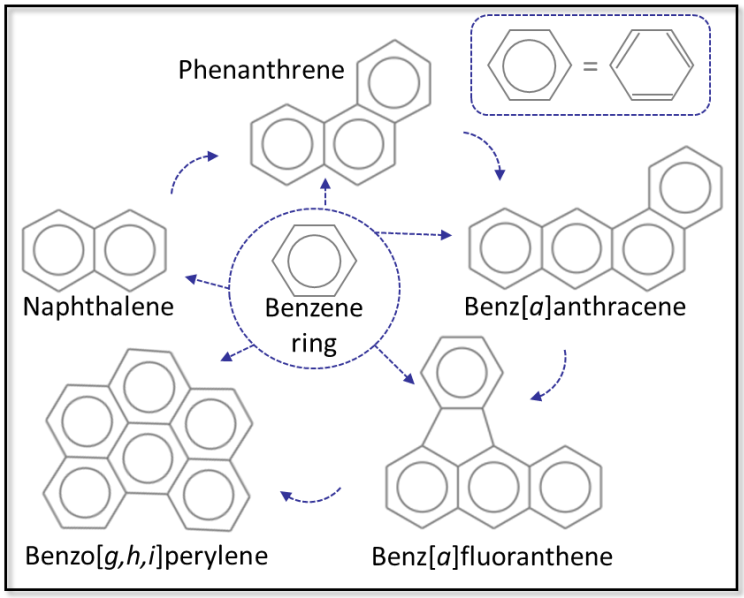

Figure 1: Examples of 2- to 6-ringed PAHs (molecular structures: webbook.nist.gov)

The PAHs also include a wide range of homologues containing alkylated[1] rings, as well as compounds in which a carbon atom in a ring is substituted, e.g. by a sulphur atom (Figure 2).

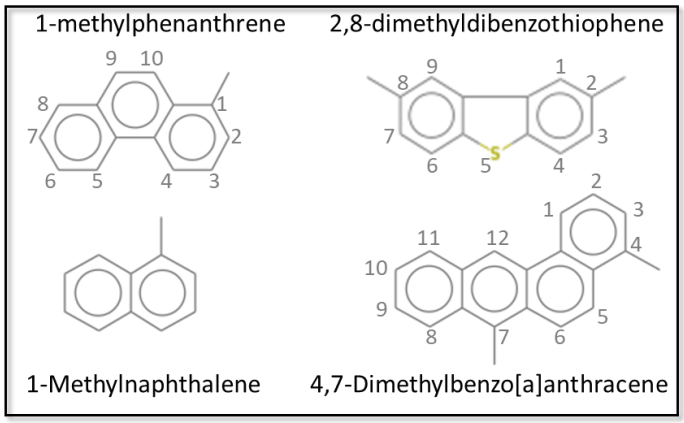

Figure 2: Examples of methylated and S-containing PAHs (molecular structures: webbook.nist.gov)

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The PAHs represent an important tool in geochemical oil spill studies (e.g. Emsbo-Mattingly and Litman, 2016) because:

1. Many PAHs are toxic to the wildlife and to humans. Their presence must therefore be detected, and their concentrations kept below specific thresholds.
2. The PAHs are highly persistent in the environment by virtue of their resistance to weathering and are therefore instrumental in the forensic investigation of the propagation of petroleum spills.

Furthermore, different groups of PAHs are representative of different types of sources, and PAHs in the environment can therefore be used to help identify oil spill sources (Figure 3). The three main types of source-associated PAHs are:

1. Parent PAHs, a group of predominantly 4- to 6-ring compounds that are typically enriched in pyrogenic and petrogenic sources. They are dominated by non-alkylated PAHs, because of the removal of alkyl substituents during refining or combustion.
2. Alkylated PAHs, mostly 2- and 3-ringed compounds, are relatively enriched in natural petroleum compared to refined products.
3. A few PAHs have a diagenetic origin, i.e. they originate from the organic matter in shallow sediments.

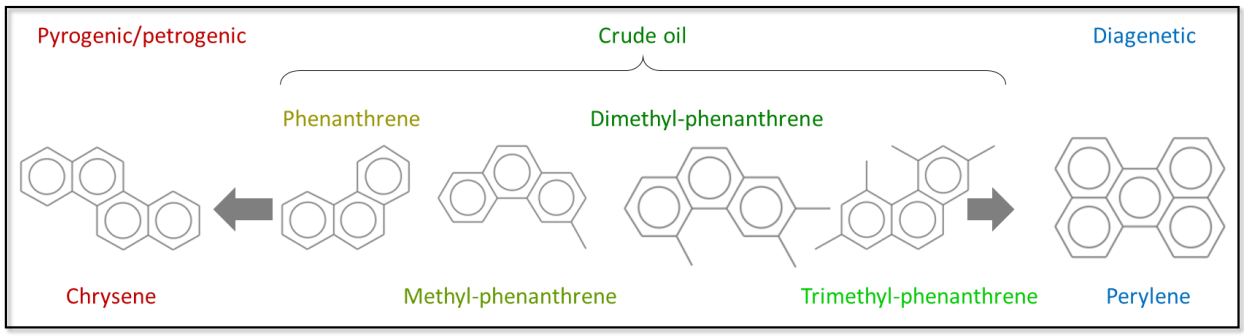

Figure 3: PAHs of pyrogenic, natural oil and diagenetic origins (molecular structures: webbook.nist.gov)

Importantly, the distribution and concentrations of PAHs in potential spill samples is key to unravelling mixtures of spilled oil and background anthropogenic components.

The PAHs exhibit chemical properties, such as molecular weight, which control their physical properties, for instance their boiling point or their solubility in water. The distinct physical properties of the different PAH compounds are thus predictable and dictate compositional changes during refining (Figure 4).

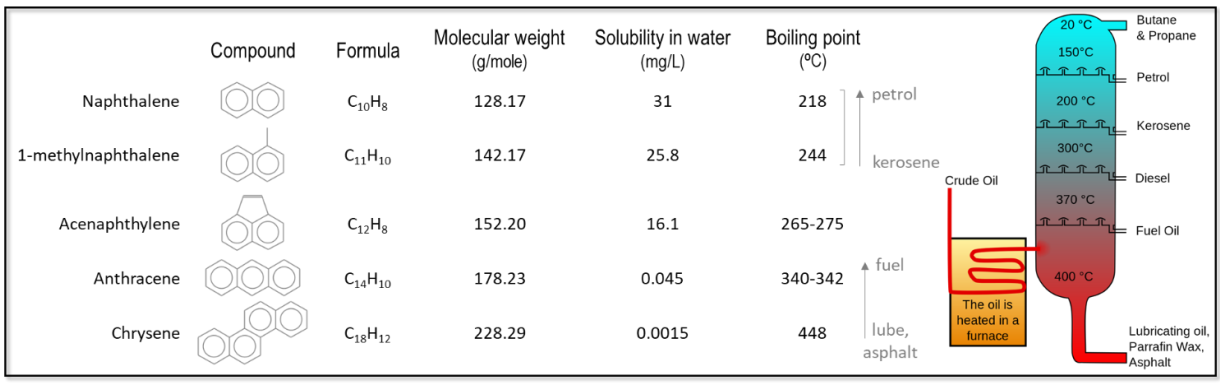

Figure 4: Principles for changes in PAH abundances and distributions in refined petroleum products (molecular structures: webbook.nist.gov and distillation tower scheme: wikipedia)

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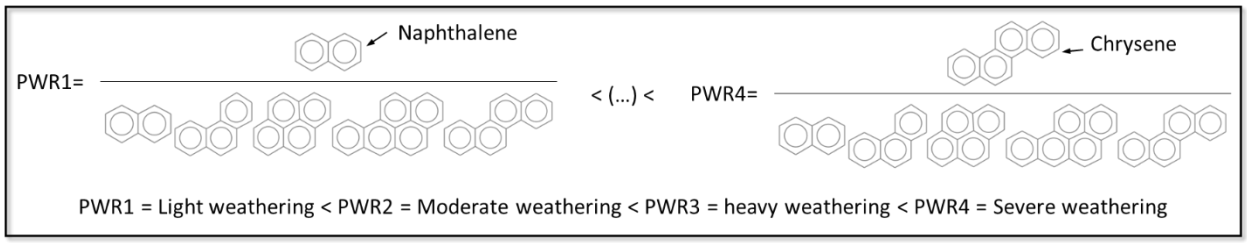
The physical-chemical properties of individual PAHs also determine changes in composition of spilled oil in response to post-spill weathering processes (Figure 5).

	C0	C1	C2	C3	C4	Parent & alkylated homologues
2-rings						Naphthalenes
3-rings						Phenanthrenes
4-rings						Benzo[*a*]anthracenes
5-rings						Benzo[*b*]fluoranthenes
6-rings						Benzo[*g,h,i*]perylene

Figure 5: Trend of increasing relative proportions of PAHs that are most resistant to the combined actions of various weathering processes (increasing towards the left and from top to bottom)

Various parameters can be computed to assess the extent of weathering or the origin of PAHs.

For weathering, these are generally ratios of PAHs that are least- to more-prone to weathering, i.e. the ratios increase with the degree of weathering. Examples of parameters used in the assessment of the degree of weathering of a sample include the PAH Weathering Ranks (PWRs), in which the dominant parent PAH compound in the numerator (e.g. naphthalene in PWR1 or chrysene in PWR4; below) reflects the magnitude of the weathering effects.



While PAHs are rarely used in the absence of other data types such as biomarkers, they have the potential to provide essential information on the source and on the degree of weathering of spill oils. Assessing the extent of weathering of spill oil is an essential component of forensic geochemistry investigations to:

- Support the interpretation of source-related characteristics and increase the degree of confidence in these parameters.
- Enable the detection of trace oil spilled a long time ago which are likely to be highly weathered, with weathering characteristics that may provide information on the processes that the spilled oil has experienced.

Furthermore, the geochemical analysis of PAHs represents one of the most efficient tools to unravel mixed oil sources in the environment (e.g. anthropogenic background *vs*. spill oil).

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[1] Alkylated = substitution of a carbon-hydrogen bond by a carbon-carbon bound, for instance a methyl group ($-CH_3$) or an ethyl group ($-CH_2-CH_3$).

References:

Emsbo-Mattingly, S. D. and Litman, E. (2016). Polycyclic aromatic hydrocarbons homolog and isomer fingerprinting. Standard Handbook Oil Spill Environmental Forensics, 255-312.

Stout, S. A., Ulher, A. D. and McCarthy, K. J. (2001). A strategy and methodology for defensibly correlating spilled oil to source candidates. *Environmental Forensics* **2**, 87-98.

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