

Source Characterization of Polycyclic Aromatic Hydrocarbons by Using Their Molecular Indices: An Overview of Possibilities

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1 Introduction

The Polycyclic Aromatic Hydrocarbons (PAHs or polyaromatic hydrocarbons) have been extensively studied to understand their distribution, fate and effects in the environment (Haftka 2009; Laane et al. 1999, 2006, 2013; Okuda et al. 2002; Page et al. 1999; Pavlova and Ivanova 2003; Stout et al. 2001a; Zhang et al. 2005). They are organic compounds consisting of conjoined aromatic rings without heteroatoms (Schwarzenbach et al. 2003). Sander and Wise (1997) list 660 parent PAH compounds (i.e., aromatic substances without alkyl groups and consisting solely of fused rings connected to each other), ranging from the monocyclic molecule of benzene (molecular weight=78) up to nine-ringed structures (MW¹ up to 478). PAHs containing one or more alkyl groups are called alkyl PAHs. Our study deals with the parent compounds (without alkyl groups and/or heteroatoms), the alkyl PAHs (denoted as PAH_{*n*}, with *n* referring to the number of methyl groups; see footnotes in Table 1), and certain heterocyclic sulfur PAHs (dibenzothiophenes). The term PAHs includes all the above, unless explicitly specified. In Table 1, we present the nomenclature of PAHs used in this paper.

The PAHs have high molecular weight (HMW), low volatility (Ou et al. 2004), and are classified as semivolatile organic contaminants (Ollivon et al. 1999). They are hydrophobic and lipophilic (Pavlova and Ivanova 2003). Their hydrophilicity and mobility decrease as the number of rings increases (Iqbal et al. 2008). In Table 2, we present the physicochemical properties of several parent PAHs. Because of their hydrophobic characteristics, PAHs tend to rapidly adsorb to particulate organic matter in sediments or soots, rather than vaporizing or dissolving in water (Bertilsson and Widenfalk 2002).

Depending on their volatility, the PAHs may be transported far from their original source, ending up in various environmental compartments, although their main environmental sink is the organic fraction of soils and sediments (Agarwal 2009; Harris et al. 2011; Morillo et al. 2008a; Stark et al. 2003). PAHs emitted from the combustion of fossil fuels are transported into marine sediments by atmospheric

¹MW: molecular weight.

Table 1 PAH (poly aromatic hydrocarbon) abbreviations used in text, figures and tables

PAH	RN ^a	Abbreviation	PAH	RN	Abbreviation
Naphthalenes	2	Nn ^b	Biphenyl	2	B
Dibenzofuran	3	DF	Acenaphthylene	3	AY
Acenaphthene	3	AE	Fluorenes	3	Fn ^b
Phenanthrenes	3	Pn ^b	Anthracenes	3	An ^b
Phenanthrenes + anthracenes	3	PAn ^b	Retene	3	RET
Dimethylphenanthrene	3	DMP	Dibenzothiophenes	3	Dn ^b
Naphthodibenzothiophenes	4	NTn ^b	Pyrenes	4	PYn ^b
Fluoranthenes	4	FLn ^b	Pyrenes + fluoranthenes	4	FPn ^b
Chrysenes	4	Cn ^b	Benz[a]anthracene	4	BaA
Chrysenes + Benz[a]anthracenes	4	BCn ^b	Benzo[b]fluorene	4	BFu
Benzo[k]fluoranthene	5	BkF	Benzo[a]fluoranthene	5	BaF
Benzo[b]fluoranthene	5	BbF	Benzo[j]fluoranthene	5	BjF
Benzo[j + k]fluoranthenes	5	Bjk	Benzo[b + j + k]fluoranthenes	5	BF
Benzo[a]pyrene	5	BaP	Benzo[e]pyrene	5	BeP
Cyclopenta[cd]pyrene	5	CP	Benzo[b]chrysene	5	BbC
Perylene	5	PER	Benzo[ghi]perylene	6	ghi
Indeno[1,2,3-cd]pyrene	6	IP	Dibenz[ah]anthracene	5	DA
Coronene	6	Cor	Dibenz[ac]anthracene	5	DcA

Parent PAH names written in the plural form denote parent and its alkylated PAHs together. In text, figures, or tables, when relevant, the position of alkylation is indicated by a number preceding the abbreviation (e.g., 1-P1 denotes 1-methylphenanthrene)

^aNumber of rings

^bn refers to the alkylation level (e.g., n=0 for the parent PAH, and so C0 stands for the parent chrysene, C1 for methylchrysenes, 1-C1 for 1-methylchrysene and so on); in such a case, PAH names written in the plural form denote all the homologues of that certain alkylation level

fallout (dry or wet deposition), riverine inflows, or discharge from urban runoff (Compaan and Laane 1992; Fabbri et al. 2003; Ollivon et al. 1999).

PAHs can be of anthropogenic or natural origin (Bertilsson and Widenfalk 2002; Morillo et al. 2008a). Natural sources include oil seeps from crude oil deposits, forest fires, volcanoes and erosion of ancient sediment (e.g., Jiao et al. 2009; Zakaria et al. 2002). Some PAHs, such as perylene, are produced naturally in the environment from chemical or biological transformation of natural organic matter, or from biological processes (Venkatesan 1988).

Anthropogenic PAHs in the environment are formed either by thermal alteration of organic matter, or its incomplete combustion (e.g., Luo et al. 2008; Ou et al. 2004). Today, the major sources of PAHs in the biosphere are human utilization of petroleum products and incomplete combustion of fossil fuels, biofuels or other forms of organic matter, which far exceed natural sources (Kim et al. 2008; Morillo et al. 2008a; Yan et al. 2006; Zakaria et al. 2002). As a result, the PAH concentrations in sediments increase at points that are near emission sources, especially near

urban and industrial areas that often have multiple point sources of release (Boll et al. 2008; Elmquist et al. 2007).

PAHs are potentially toxic and mutagenic to many living organisms, such as marine plants and animals (Boehm et al. 2007; Guo et al. 2007; Swietlik et al. 2002). The lower molecular weight PAHs (LMW PAHs) are acutely toxic but non-carcinogenic to many aquatic organisms, whereas the high molecular weight PAHs (HMW PAHs) are strongly carcinogenic and mutagenic (Karlsson and Viklander 2008; Laane et al. 2006; Ou et al. 2004). Different PAH priority lists have been compiled by different environmental or statutory bodies, such as the U.S. Environmental Protection Agency (EPA), the Dutch ministry of housing, spatial planning and the environment (VROM) and the so called “Borneff-6” PAHs (e.g., European Commission 2001; Laane et al. 1999; Table 2).

PAH source characterization defensibly links the contaminants with their sources for the purpose of finding parties that are liable for the contamination. Source apportionment quantifies the amount of contamination contributed by each party involved, so that regulators can make accountability decisions (relating to, e.g., cleanup costs, mitigation, etc.). If a strategy for characterizing PAHs is to succeed, knowledge of the sources, chemistry and fate of each individual PAH is crucial, and the PAHs to be analyzed must be carefully selected (Peters et al. 2005).




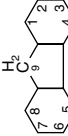
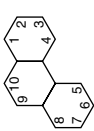

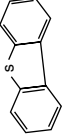
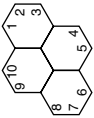
PAHs are classified according to the temperature at which they form, or their origin. An example is the threefold classification espoused by Boehm et al. (2007) and Mitra et al. (1999): i) pyrogenic PAHs, which originate from different pyrolysis substrates, such as fossil fuels and biomass, ii) petrogenic PAHs from petroleum-related sources, and iii) natural PAHs of biogenic or diagenetic origin.

In the history of determining the PAH contaminating source and the contaminants themselves, it was realized that petroleum and its products, as well as combustion byproducts, included quite complicated mixtures of PAHs (Farrington et al. 1977; Giger and Blumer 1974; Windsor and Hites 1979; Youngblood and Blumer 1975). However, it was observed that the distribution of PAHs varied among different PAH sources (Grimmer et al. 1981, 1983; Laflamme and Hites 1978; Youngblood and Blumer 1975). Since then, there has been an ongoing effort to find the proper molecular indices of a PAH distribution that would allow source characterization of contaminated areas.

Our approach on reviewing PAH molecular indices that are used for source characterization is twofold. Firstly, we review indices of a PAH distribution (ubiquitous PAH markers, PAH abundance, modes of distribution, etc.) which are characteristic for pyrogenic and petrogenic sources. The possible modifications that a PAH distribution undergoes on its way from source to receptor are also reported. Secondly, we review a selection of certain indices of a PAH distribution (PAH ratios and some of their combinations) in a quantitative way and evaluate their use in source characterization. Finally, we address the following questions in this review:

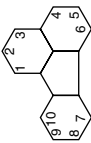
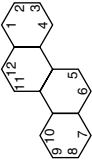
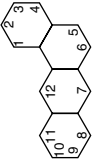
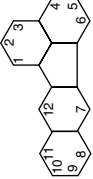
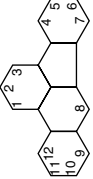
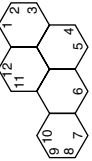
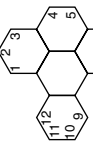
- What are the most important PAH sources in the aquatic environment, and which PAH indicators can be used to unequivocally identify them?

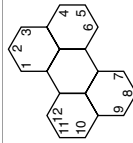
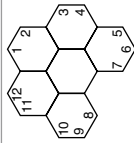
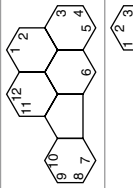
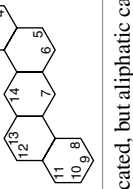
Table 2 The physicochemical properties of selected parent PAHs

PAH	Priority list ^a	Structure	MW	RN	S (mg/l)	P (Pa)	K _{ow}	bp (°C)
Naphthalene	E, U, V		128	2	32	11	3.37	218 ^b
Acenaphthylene	U		152	3	3.9	9.0×10 ⁻¹	4.1	280
Acenaphthene	U		152	3	3.9	3.0×10 ⁻²	3.9	279
Fluorene	B, U		166	3	1.9 ^c	9.0×10 ⁻²	4.18	295
Phenanthrene	U, V		178	3	1.1 ^c	2.0×10 ⁻²	4.57	340
Anthracene	E, U, V		178	3	0.05 ^c	1.0×10 ⁻³	4.54	342
Dibenzothiophene			184	3	1.0 ^b		4.49	333 ^d
Pyrene	U		202	4	0.13 ^c	6.0×10 ⁻⁴	5.18	393

(continued)

Table 2 (continued)

PAH	Priority list ^a	Structure	MW	RN	S (mg/l)	P (Pa)	K _{ow}	bp (°C)
Fluoranthene	E, U, V		202	4	0.26	1.2 × 10 ⁻³	5.22	375
Chrysene	C, U, V		228	4	0.002	1.4 × 10 ⁻⁶	5.86	448
Benz[<i>a</i>]anthracene	C, U, V		228	4	0.009–0.014	2.8 × 10 ⁻⁵	5.6	400
Benzo[<i>k</i>]fluoranthene	B, C, E, U, V		252	5	0.0007–0.008	5.2 × 10 ⁻⁸	6	480
Benzo[<i>b</i>]fluoranthene	B, C, E, U		252	5	0.0014	6.7 × 10 ⁻⁵	5.8	481
Benzo[<i>a</i>]pyrene	B, C, E, U, V		252	5	0.003 ^c	7 × 10 ⁻⁷	6.0	496
Benzo[<i>e</i>]pyrene			252	5	0.005 ^c	7.3 × 10 ^{-6,c}	6.44, 7.4	311 ^b

Perylene		252	5	0.0004	1.8×10^{-8}	6.40	503 ^f
Benzo[ghi]perylene		276	6	0.00026	$1.4 \times 10^{-8,e}$	7.1	550 ^e
Indeno[1,2,3-cd]pyrene		276	6	0.00019 ^f	1.3×10^{-8}	6.6	536
Dibenz[ah]anthracene		278	5	0.0005	3.7×10^{-8}	6.5	524

Double (or conjugated) bonds are not explicitly indicated, but aliphatic carbons are designated by associated hydrogen atoms. *MW*=molecular weight, *RN*=ring number, *S*=aqueous solubility (25 °C), *P*=vapor pressure (25 °C), *K_{ow}*=the logarithm of the octanol-water partition coefficient, *bp*=boiling point. Images and molecular weights are taken from Sander and Wise (1997). Unless otherwise specified, all solubility and *K_{ow}* data are from Irwin et al. (1997) and all vapor pressure and bp data are from Hailwood et al. (2001)

^aPriority PAH pollutant lists that enlist the specific PAH: *B* Borneff6, *C* considered carcinogenic (Stout and Emsbo-Mattingly 2008), *E* European priority pollutant as defined by the European Commission (2001), *U* U.S. EPA 16, *V* VROM 10

^bLide (2004)

^cHafika (2009)

^dDean (1999)

^eIrwin et al. (1997)

^fMackay et al. (2006)

- What are the inherent uncertainties in these indicators and how does the value of the indicator change after undergoing biogeochemical processes (i.e., photochemical oxidation, degradation, volatilization, etc.) in the aquatic environment?
- Can the Borneff-6, 16 EPA, and 10 VROM PAHs be used to calculate the proposed indicator—and, if so, which uncertainties are introduced by utilizing this approach?

2 Source Profiles of PAHs

If source inventories are lacking or incomplete, the first task is to clarify whether the known or unknown sources of PAHs are petrogenic, pyrogenic or natural. This is usually accomplished by observing PAH fingerprints that show the relative PAH abundances (Douglas et al. 2007a). For example, the relative distribution of PAHs in each homologous family is used to differentiate compositional changes during the degradation of oil spills (Wang et al. 1999a). Characteristic PAH fingerprints of petrogenic and pyrogenic sources from the literature are shown in Figs. S1–S32 (Supporting Material).

Once released to the environment, the PAHs are prone to a wide variety of degradation processes, including evaporation, dissolution, dispersion, emulsification, adsorption on suspended materials, microbial degradation (biotic or biodegradation), photo-oxidation, and interaction among the contaminants and sediments (Gogou et al. 2000; Kim et al. 2009; Page et al. 1996; Wang et al. 2004). Degradation substantively changes the physicochemical properties and relative abundances of even the highest MW PAHs, and such changes must be considered when identifying and quantifying PAH sources (Page et al. 1996; Wang et al. 2004).

2.1 *Petrogenic*

Petrogenic substances (petrogenics) are defined as the substances that originate from petroleum, including crude oil, fuels, lubricants, and their derivatives (Saber et al. 2006). Petrogenic PAHs are introduced into the aquatic environment through accidental oil spills, discharge from routine tanker operations, municipal and urban runoff, etc. (Zakaria et al. 2002). There have been no observations of widespread, and continuous (i.e., nationwide and non-accidental) input of petrogenic PAHs (Zakaria et al. 2002).

Petroleum is a complex mixture of different organic compounds formed during different geological ages and under different geological conditions. The different depositional environments during oil formation are reflected in different PAH distributions (e.g., dibenzothiophenes: D_n) in crudes from different sources

(Page et al. 1996; Wang and Fingas 2003; Wang et al. 1999a, 2001). For example, many of the monomethyl PAH derivatives are preserved in petroleum because of their low formation temperatures ($<150^{\circ}\text{C}$) (Mitra et al. 1999). The proportion of thermally stable phenanthrene isomers increases as the crude matures (Stout et al. 2002). Furthermore, the dibenzothiophene abundance in source rock, i.e., the rock in which the oil matured, is a function of anoxia (leading to reduced sulfur), and therefore reflects the type of source rock facies (Peters et al. 2005; Stout et al. 2002).

The main PAH components of a petroleum source include the EPA 16 parent PAHs and the petroleum-specific alkylated (PAH1-PAH4) homologues of selected PAHs: viz., alkylated naphthalene, phenanthrene, dibenzothiophene, fluorene, and chrysene series, which are also called “the alkylated five” or “*five target*” (Bertilsson and Widenfalk 2002; Wang et al. 1999a; Zeng and Vista 1997). These PAHs are source-specific (concentrations vary among different oils) and their abundance in sediment is taken to indicate petrogenic sources (Boll et al. 2008; De Luca et al. 2004; Stout and Wang 2007; Wang et al. 2001). For example, dibenzothiophenes, together with phenanthrenes, are widely used for PAH source apportionment because of their numerous isomers and their mild and similar degradabilities (absolute concentrations of the methyl dibenzothiophenes increase during weathering) (Page et al. 1996; Stout and Wang 2007; Wang and Fingas 1995, 2003; Wang et al. 1999a, 2001).

Figure 1a–d show that petroleum products contain mainly two- to three-ringed PAHs and only the heavier ones (Fig. 1c, d) contain significant amounts of four-ringed PAHs. In all instances (except Fig. 1e), five- and six-ringed PAHs, and occasionally compounds such as acenaphthylene (AY), anthracene (A0) and fluoranthene (FLO) (e.g., Fig. 2; Fig. S3, Supporting Material), are undetectable in crude oil and its refined products (Stout et al. 2002). For instance, benz[*a*]anthracene (BaA), benzo[*a*]pyrene (BaP), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF) and chrysene (C0) are minor constituents of petroleum products, if present at all (e.g., Irwin et al. 1997; Jiang et al. 2009; Shreadah et al. 2011; Wang et al. 2001). Figure 1e, given for comparison, shows a mixture of pyrogenic and petrogenic products, as is common in used lubricants.

In crude oil, the content of LMW PAHs (containing two or three fused aromatic rings), and especially their alkylated homologues far exceed the unsubstituted parent PAHs. The petroleum PAHs exhibit a characteristic bell-shaped pattern within their homologue series (Fig. 1a–d; Figs. S2–S5, Supporting Material): PAH3 or PAH2 alkylated PAHs predominate and amounts of PAH0-PAH2 and PAH4 homologues decrease (Douglas et al. 2007a; Stout 2007). Thus, much more information is contained in the alkylated homologue series of crude oil than in the parent PAHs, i.e., the abundance of alkylated PAHs, bell-shaped patterns and depletion of HMW PAHs (compare Figs. S1 vs. S2; Figs. S5 and S6 vs S9, Supporting Material). This information allows us to differentiate between petrogenic products and to distinguish them from pyrogenic forms, regardless of the oil formation environ-

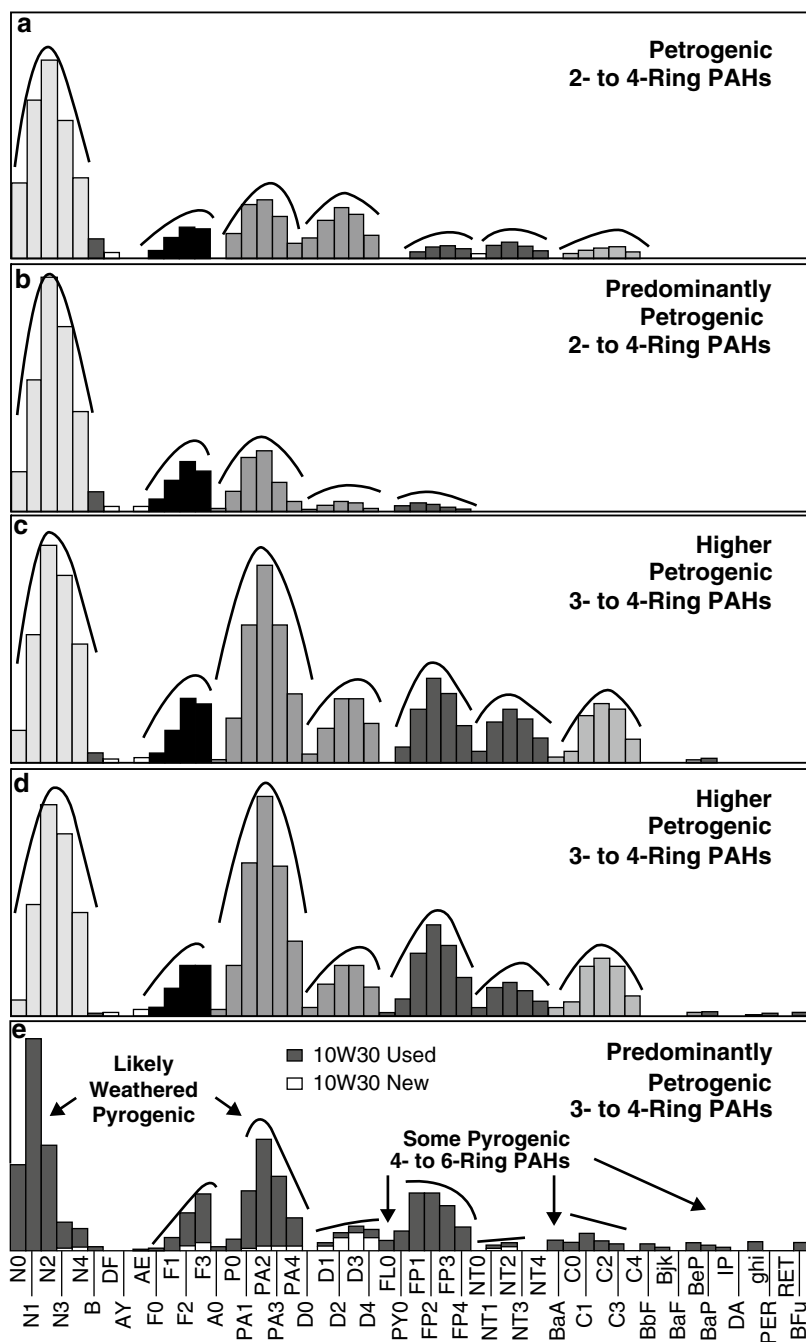


Fig. 1 Source profiles/fingerprints of characteristic petrogenic PAHs. (a) crude oil, (b) fuel oil #2, (c) fuel oil #4, (d) fuel oil #6, (e) new and used lubricating oils. See Table 1 for PAH abbreviations. Adapted from Douglas et al. (2007a), with permission, © Elsevier Academic Press

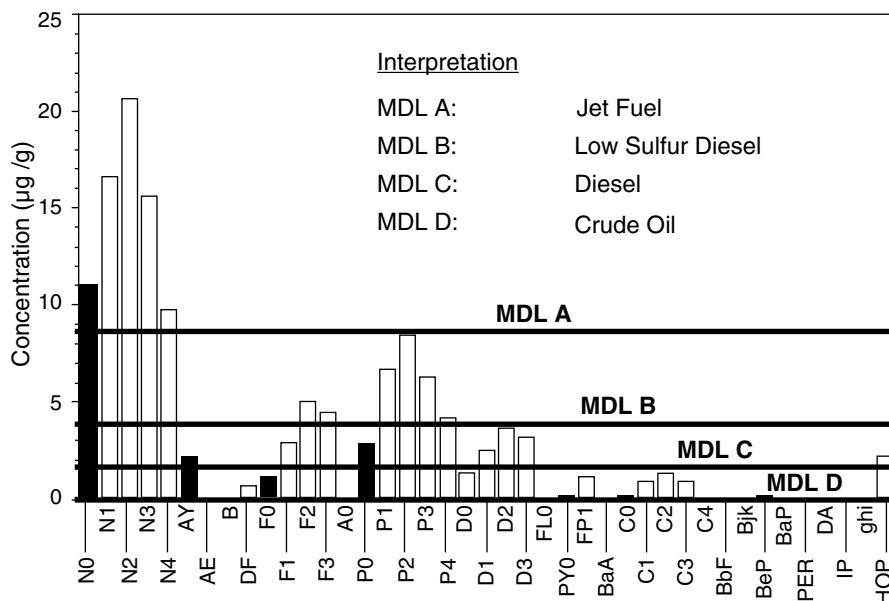


Fig. 2 How the method detection limit (MDL) affects the interpretation of fingerprinting. Shown here is a comparison of fingerprints of crude and its refined products (crude fractions). EPA16 priority PAHs are shown in *black*. See Table 1 for PAH abbreviations, except for *HOP*: hopane. Adapted from Douglas et al. (2007a), with permission, © Elsevier Academic Press

ment or the degree of degradation to which they were subjected (Ou et al. 2004; Yan et al. 2005).

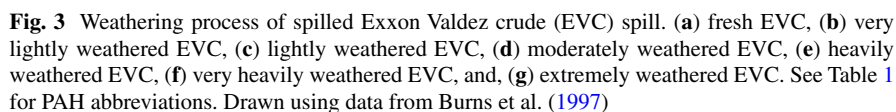
Distilling crude oil does not produce significant amounts of new PAHs in the crude fractions (Stout et al. 2001b). As a result, all refined petroleum products mainly contain PAHs that were present in the original crude oil. Nevertheless, fractionation among refined products (Fig. 2), and different crude oil feedstocks, make the PAH compositions of the refined crude products distinguishable (Stout et al. 2001b; Wang and Fingas 2003). Lighter products, such as jet fuel, tend to contain the more volatile LMW PAHs (e.g., phenanthrene). In crude and heavier fractions (higher distillation temperature), the higher MW PAHs become more abundant (Fig. 2; and note boiling points and vapor pressures of the PAHs in Table 2). For example, because methylphenanthrene isomers all boil in the same temperature range, they pass unchanged from the crude oil feedstock into a straight-run distillate (Stout and Wang 2007). Nevertheless, during the refining process, alkylated chrysenes are removed from diesel (Bence et al. 1996). Other heavily alkylated three- and four-ringed homologues are impoverished in fuel #2 PAH distributions (Figs. S3 vs. S5, Supporting Material). Similarly, the abundances and distributions of sulfur-bearing compounds, such as dibenzothiophenes, are altered during hydrodesulfurization processing of crude oil or middle distillate blending stocks (Page et al. 2006; Stout et al. 2006).

Oil degradation processes, including evaporation, dissolution, and microbial oxidation, are controlled by factors such as oil type, environmental conditions and microbiological activity (Short et al. 2007; Sicre et al. 1987; Wang et al. 1999a). The petrogenic PAHs degrade at much faster rates than pyrogenic ones, because the former are more bioavailable and associate less with carbon particles after their release, e.g., oil spills, discharges (Gogou et al. 2000; Zakaria et al. 2002). Figure 3 shows the PAH fingerprint of the spilled Exxon Valdez crude (EVC) at different states of degradation (Burns et al. 1997). The weathering largely resulted from evaporation and dissolution, which first impacted the more volatile and soluble LMW compounds (Hostettler et al. 2007; Table 2; Wang et al. 1999a).

Evaporation of the PAHs after their incorporation into sediments is not a significant process (Stout et al. 2001b), but the evaporation of PAHs before they associate with sediments or particles (e.g., oil spills) is the most important short-term (hours–days) weathering factor (Wang and Fingas 2003). The degree of loss from evaporation depends on the kind of petroleum product involved. Light products containing light PAHs evaporate readily, whereas heavier ones lose as little as 5–10% of their total volume (Philp 2007; Wang and Fingas 2003). Thereafter a PAH0<PAH1<PAH2<PAH3 profile emerges for each alkylated PAH family (Iqbal et al. 2008; Stout 2007), starting from the LMW PAHs (Fig. 3c–g).

Dissolution depends mainly on the structure of the PAHs and decreases as the ring number and alkylation level of the PAHs increases, although exceptions exist (e.g., chrysene is less soluble than its methyl and dimethyl homologues) (Stout et al. 2001b). Furthermore, the linear PAHs are less soluble than their angular equivalents (anthracene is less soluble than phenanthrene) (Stout et al. 2001b; Wang and Fingas 2003). As dissolution proceeds, biodegradation may begin to affect the distribution of individual compounds. The biodegradation rate depends on the nature of the spill and environment (O₂, pH, microbial populations, etc.) into which the oil is spilled (Philp 2007; Stout et al. 2002); biodegradation is slower and less predictable than abiotic degradation. Biodegradation can even alter the distribution of PAHs within a homologue category, because individual isomers have different susceptibilities to microbial activity (Wang et al. 1998, 1999a, 2004). Utilizing a biodegradation index for oils has been proposed to assist in evaluating their potential for biodegradation in the lab (Christensen et al. 2004; Wang et al. 1998, 2004). It is generally accepted that PAH biodegradation decreases concomitantly with increasing PAH ring numbers and alkylation (Stout et al. 2001b).

Further degradation (Fig. 3c–g) leads to the enhancement of chrysenes relative to other PAH series, and to a significant decrease in the relative ratios of the sum of naphthalenes, phenanthrenes, dibenzothiophenes, and fluorenes, to chrysenes (most stable) (Wang et al. 1998). In Fig. 3, there are two distinct and apparent features of PAH degradation. The first is the more rapid depletion of the less alkylated homologues, together with faster degradation of the parent PAH. The second is the enhancement of the more alkylated homologues at certain degrees of degradation, not only relative to the less alkylated homologues, but also in absolute terms.



The rate of petrogenic PAH degradation decreases with time and as the number of rings increases, i.e., naphthalenes > fluorenes > phenanthrenes \approx dibenzothiophenes \approx fluoranthenes/pyrenes > chrysenes (e.g., Hegazi and Andersson 2007; Page et al. 1996; Short et al. 2007). Hence, the relative ratios of phenanthrenes, dibenzothiophenes, fluorenes and naphthalenes remain very consistent as the weathering percentages increase, which makes them useful for source identification (Hegazi and Andersson 2007). Nevertheless, oil degradation is a very complex process and although different first-rate kinetic models have been developed, source apportionment of petroleum products is best dealt with case by case (Wang and Fingas 2003).

Crude oil contains significant amounts of PAHs: from 0.2% to more than 7% total PAHs (Zakaria et al. 2002). For certain crudes, only a small portion of the total PAHs are priority pollutant PAHs (Stout et al. 2007). The PAHs in crude oils decrease in concentration as their molecular weight increases (Stout 2007; Stout et al. 2001b). The HMW PAHs that may be non-detectable, or only present in minute quantities include acenaphthylene (AY), anthracene (A0), fluoranthene (FL0), pyrene (PY0), benzo[ghi]perylene (ghi), indeno[1,2,3-cd]pyrene (IP), benzo[k]fluoranthene (BkF), benzo[b]fluoranthene (BbF), perylene (PER), dibenz[ah]anthracene (DA), benzo[e]pyrene (BeP), benzo[a]pyrene (BaP) (Fig. 2 and Figs. S1–S4, Supporting Material). Many crude oils are dominated by alkyl naphthalenes (Figs. S2–S4, Supporting Material). Stout et al. (2007) observed variable environmental weathering for some crudes after their release. In most instances, weathering resulted in the loss of hydrocarbons that had boiling points below that of n-eicosane (including naphthalene and alkylated naphthalenes). Weathered crude tends to contain more PAHs than does unweathered crude (Stout et al. 2001b).

Diesel PAHs (Figs. S5–S7 and S9, Supporting Material) are largely composed of two- and three-ringed PAHs and their alkylated homologues (Douglas et al. 2007a; Wang et al. 2001). Diesels contain only extremely small amounts of anthracenes (A0) and HMW PAHs (four to six rings such as indeno[1,2,3-cd]pyrene, dibenz[ah]anthracene and benzo[ghi]perylene), because most of these are removed during refining (Wang et al. 2001). Of the *five target alkylated PAH series* of diesel, the most abundant (>55%) is alkylated naphthalene and the least abundant (<0.02%) is chrysene; thus, the absence of chrysene can be used to identify diesel or diesel soot (Wang et al. 1999a, 2001). Conversely, the presence of chrysenes or HMW PAHs possibly excludes diesel or its soot as a main PAH source (Burns et al. 1997).

Figures S8 and S10 (Supporting Material) show that naphthalene is abundant in jet B fuel (99% of total PAHs is naphthalenes), gasoline (97% of EPA priority PAHs) and diesel No.2 (86% naphthalenes, 5% phenanthrenic content and no chrysenes). In contrast, in the bunker C diesel mixture, the alkylphenanthrenes account for 35% of PAHs and chrysenes for 18% (Karlsson and Viklander 2008; Wang and Fingas 2003; Wang et al. 1999a). In the orimulsion oil (Fig. S11, Supporting Material), the phenanthrenic and dibenzothiophenic content is much higher (38% and 22% of total PAHs respectively) (Wang and Fingas 2003). PAHs having a MW greater than that of pyrene are hardly present in light distillates such as jet B fuel or gasoline, although in heavier products such as bunker C diesel and orimulsion oil they may be present in significant quantities (Figs. S5–S11, Supporting Material).

For this reason, it is suggested that highly alkylated PAHs (e.g., P4 or P3–phenanthrenes) be selected and used for identifying the source of PAHs in distilled oil products such as diesel and jet fuel samples (Wang et al. 1999a).

Some coal PAHs have been characterized, as occasionally has their contribution to sediment contamination (Achten and Hofmann 2009; Boehm et al. 2001; Dzou et al. 1995; Peters et al. 2005; Radke et al. 1982; Stout and Emsbo-Mattingly 2008). Lower rank coals (lignite and sub-bituminous coal) may contain significant amounts of perylene. Dibenzothiophenes may also be abundant in coals (Stark et al. 2003). Coal PAHs are generally not bioavailable and the concentrations at which they exist are below risk limits. However, they are of practical interest in forensic studies, and for understanding potential sources of PAHs (Stout and Emsbo-Mattingly 2008).

The PAH distribution patterns in coals seem to be a function of coal rank (Fig. S27, Supporting Material; Radke et al. 1982; Stout and Emsbo-Mattingly 2008). The higher the coal rank, the more dominant are the LMW compounds over the HMW ones (petrogenic characteristic). However, the homologous series of phenanthrenes (minus retene), fluoranthenes and chrysenes show a bell-shaped PAH profile in low rank coals (typical of petrogenic PAHs). In higher coal ranks, this bell-shaped profile shifts to a pyrogenic-like skewed pattern that is dominated by parent PAHs (Fig. S27, Supporting Material).

Leakage, spillage and dumping of fresh and used lubricating oils (Fig. 1e; Figs. S12–S15, Supporting Material) are major sources of PAHs in the aquatic environment of Malaysia (Zakaria et al. 2002). “Fresh” lubricants are severely depleted of HMW PAHs and contain small amounts of LMW PAHs, such as dibenzothiophenes (Denton 2006; Sicre et al. 1987; Wang et al. 2004; Zakaria et al. 2002). In contrast, the PAH content of used lubricating oil is three orders of magnitude higher than that of fresh lubricating oil. The “extra” PAHs are derived both from the accumulation of PAHs formed in the engine combustion chamber (Pyrogenic HMW compounds) and from the incorporation of petrogenic PAHs from unburned fuel (gasoline or diesel alkyl-homologues such as P1) into the lubricating oil (Boonyatumanond et al. 2007; Douglas et al. 2007a; Zakaria et al. 2002). For example, methylphenanthrenes are less abundant in diesel than in used lubricating oils (Boonyatumanond et al. 2007). Thus, lubricants used in fuel combustion chambers might be classified as a mixed source of PAHs that show an enhanced pyrogenic profile (Fig. 1e and Figs. S12–S15, Supporting Material).

A significant amount of liquid fuel used in vehicles or in other combustion processes may be unburned (up to 1.2%), and therefore may contain the initial petrogenic fingerprint (Fig. 4, Figs. S16, S17, Supporting Material) of the fuel as vapor (Bucheli et al. 2004; Lehnndorff and Schwark 2009; Simoneit 1985; Wang et al. 1999b; Williams et al. 1986; Zeng and Vista 1997). For example, automobile and boat engine exhausts contain both petroleum residues and incomplete combustion products (Zeng and Vista 1997). In Tokyo, Japan, alkyl PAHs and the street dust of heavily traveled roads contained a greater abundance of alkyldibenzothiophenes than the street dust from roads in residential areas (Takada et al. 1990). Diesel fuel contributes more alkylated, sulfur and three-ringed PAHs (petrogenic fingerprint) to the atmosphere than does gasoline (Hwang et al. 2003; Lehnndorff and Schwark 2009).

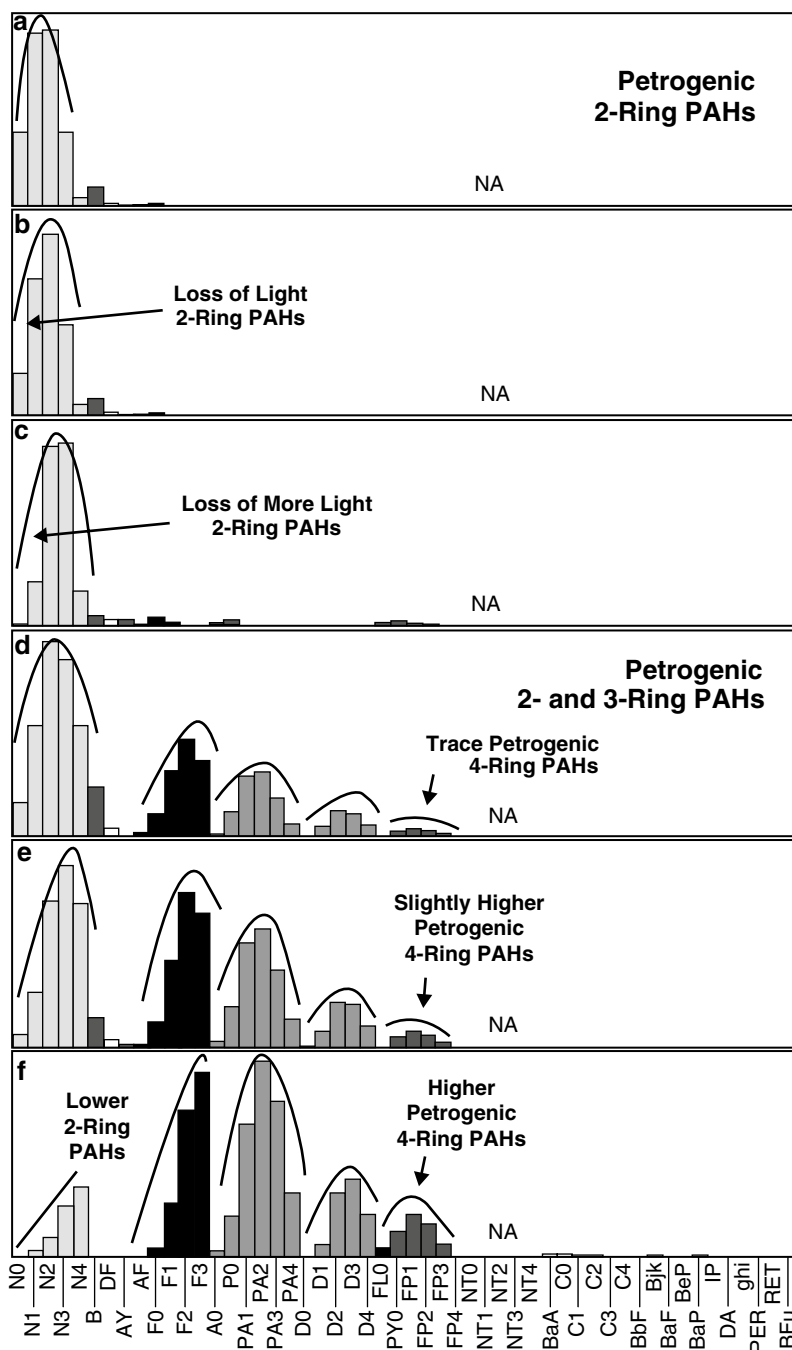


Fig. 4 PAH profiles during combustion of fossil fuels. (a) kerosene, (b) kerosene combusted 50%, (c) kerosene combustion residue, (d) middle petroleum distillate (diesel), (e) diesel combusted 50%, (f) diesel combustion residue. NA: not analyzed. See Table 1 for PAH abbreviations. Adapted from Douglas et al. (2007a), with permission, © Elsevier Academic Press

2.2 *Pyrogenic*

Pyrogenic substances are defined as organic substances produced from oxygen-depleted, high-temperature combustion of fossil fuels and biomass (e.g., incomplete combustion, pyrolysis, cracking, and destructive distillation) (Saber et al. 2006). Pyrogenic PAHs are released in the form of exhaust and solid residues, and are largely prevalent in aquatic environments (De Luca et al. 2004; Zakaria et al. 2002). Only in a limited number of locations do petrogenic PAHs dominate over pyrogenic ones (Guo et al. 2007; He and Balasubramanian 2010; Wickramasinghe et al. 2011; Zakaria et al. 2002). The HMW PAHs of pyrolytic origin reach aquatic environments by direct atmospheric deposition or via contaminated soil (Budzinski et al. 1997; Morillo et al. 2008b). LMW pyrogenic PAHs are mainly introduced to aquatic environments by rain washout (Ollivon et al. 1999).

Hailwood et al. (2001) list the main industrial processes that produce significant amounts of PAHs. Power stations may contribute less than 5% to the PAH emissions of a large city (Masclet et al. 1987). It is the mobile PAH emission sources that have sharply increased in the environment during recent decades (Hwang et al. 2003). The main pyrogenic sources in urban waterways include fuel combustion products, and discharges from aluminum smelters and manufacturing gas plant (MGP) sites (Stout et al. 2001b). Sources such as municipal and industrial waste discharges, and runoff (e.g., from farms and farmland) contain a mixture of pyrogenic, petrogenic, and natural PAHs (Van Metre and Mahler 2010; Zeng and Vista 1997). The distribution of PAHs from such sources is similar to that in pyrogenic sources (Stout et al. 2001b).

In pyrogenic PAH patterns, unsubstituted compounds predominate over their alkylated homologues. As the alkylation level increases, the PAH homologues become less abundant (i.e., a skewed pattern), whereas the HMW four- to six-ringed PAHs are more abundant than LMW two- to three-ringed PAHs (e.g., Boll et al. 2008; Ou et al. 2004; Page et al. 2006; Stout 2007; Stout et al. 2004; Wang et al. 1999a). Furthermore, the abundance of alkyl PAHs relative to parent PAHs, and also the abundance of LMW PAHs relative to HMW ones in combustion products, decrease with increasing combustion temperature (Laflamme and Hites 1978; Sporstol et al. 1983; Takada et al. 1990; Tobiszewski and Namiesnik 2012; Zeng and Vista 1997). Some researchers (Budzinski et al. 1997; Sicre et al. 1987) have noted that catacondensed PAHs (wherein no more than two rings have a carbon atom in common) are abundant in pyrolytic PAHs.

Combusting two petrogenic products (Fig. 4—kerosene and diesel) in an open flame does not create a significant amount of important five-ringed PAHs (Douglas et al. 2007a). Open-flame combustion significantly alters the distribution of naphthalene (N0) and its homologues. Simultaneously, the relative abundance of phenanthrene, fluorene, pyrene and their alkylated homologues increases. Combustion in a closed system (such as diesel engines), however, characteristically creates the pyrogenic signature of LMW and HMW PAHs and their alkylated homologues (Douglas et al. 2007a).

Wang et al. (1999b) found that emissions, residues, and soots of combusted PAH-containing liquid fuels (e.g., diesel, crude) were likely to inherit the petrogenic

bell-shaped distribution of volatilized LMW PAHs (2–4 rings). In such cases, the destruction efficiency of PAHs decreased as the MW increased. The newly diesel-combustion-generated PAHs (mainly HMW) were in the range of 0.5–1.5‰ of the destroyed/combusted PAHs (mainly LMW) (Fig. S16, Supporting Material; Wang et al. 1999b).

The most abundant pyrogenic PAHs are fluoranthene, pyrene, and, to a lesser extent, phenanthrene (Page et al. 1999). Predominance of P0, FL0 and PY0 indicates the pyrolytic origin of the contamination (Morillo et al. 2008a). Like phenanthrene, anthracene is also common to pyrogenic sources (De Luca et al. 2004; Gogou et al. 2000). In sediments, absence of IP has been interpreted as the absence of pyrogenic PAHs (De Luca et al. 2004). Moreover, it has been shown that the use of HMW PAHs (e.g., MW=252, benzo[k]fluoranthene, benzo[b]fluoranthene, benzo[a]pyrene, benzo[e]pyrene, benzo[j]fluoranthene, and perylene) is adequate to discriminate between different high-temperature processes, e.g., carbonization and coking in manufacturing gas plants, and combustion in motor vehicle engines (Boll et al. 2008; Costa and Sauer 2005; Costa et al. 2004; Ollivon et al. 1999; Stout and Graan 2010).

The HMW pyrogenic PAHs emitted at high temperatures as gases condense on particulates when cooled (Tobiszewski and Namiesnik 2012 and references therein). Accordingly, LMW pyrogenics are more abundant in the gaseous phase.

The pyrogenic PAHs (especially parent PAHs) associate with small soot-rich particles (Sicre et al. 1987; Yunker et al. 2002). As a result, pyrogenic PAHs are more often associated with sediments and become more resistant to microbial degradation than PAHs of petrogenic origin (De Luca et al. 2004). Nevertheless, weathering also causes pyrogenic products to increasingly be dominated by four- to six-ringed PAHs, producing a pattern very similar to what appears in urban runoff (see below), rendering it more difficult to identify the source (Stout et al. 2003).

The pyrogenic PAHs are subject to differential photodegradation (first order kinetics). The isomer pairs of phenanthrene-anthracene, fluoranthene-pyrene and indeno[1,2,3-*cd*]pyrene-benzo[*ghi*]perylene degrade photolytically at about the same rate in the atmosphere (Behymer and Hites 1988; Yunker et al. 2002). By contrast, BaP is photolyzed in the atmosphere at much faster rates than are its isomers (Behymer and Hites 1988; Gogou et al. 2000; Sicre et al. 1987; Yunker et al. 2002). On the other hand, Brenner et al. (2002) used BaP as a normalization constant to calculate PAH losses in a weathered creosote site. Despite not being listed as a priority pollutant (Table 2), benzo[*e*]pyrene (BeP) has been included in many studies (especially of iron and steel plant emissions) because of its chemical stability in the atmosphere and the additional information it can provide (Daisey et al. 1986; Ollivon et al. 1999; Soclo et al. 2000; Yang et al. 2002). PAH photodegradation also takes place in other environmental matrices (e.g., water), which preferentially protect certain isomers (Bertilsson and Widenfalk 2002; Tobiszewski and Namiesnik 2012).

Motor vehicles are a major source of potential carcinogenic HMW PAHs (such as benzo[*a*]pyrene, benz[*a*]anthracene, and benzo[*b*]fluoranthene), especially in highly populated areas (Dickhut et al. 2000; Simoneit 1985). Marr et al. (1999) reported unburned fuel, lubricating oil, and pyrosynthesis as possible sources for PAHs from

motor vehicle exhausts. Indeno[1,2,3-*cd*]pyrene (IP) and benzo[*ghi*]perylene (*ghi*) are indicators (e.g., correlate with the total PAHs) of combustion sources and are typical products of motor vehicle exhausts – although these HMW PAHs are not transported far from their source (Boll et al. 2008; Larsen and Baker 2003; Ollivon et al. 1999; Yunker et al. 2002). Ollivon et al. (1999) have suggested using benzo[*ghi*]perylene and pyrene as tracers of vehicle emissions in river waters. Benz[*a*]anthracene and chrysene are also considered to be automobile markers when other petroleum sources are excluded (Morillo et al. 2008b; Yunker et al. 2002). Similarly, particulate phase coronene in city centers may hypothetically be exclusively traffic-related (Larsen and Baker 2003), especially at locations far from main point sources of PAH emission (Bucheli et al. 2004 and references therein). Unlike the higher MW alkylated PAHs (i.e., alkyl-fluoranthenes, -benz[*a*]anthracenes, -chrysenes, -pyrenes), the alkylated LMW PAHs (i.e., alkyl phenanthrenes, alkyl anthracenes and alkyl naphthalenes) are usually present in higher proportions than their parent PAHs in diesel combustion soots and burn residues (Wang et al. 1999b). The bell-shaped profile of LMW PAHs in diesel combustion products accentuates the deviation from the classical pyrogenic fingerprint, which prevails in higher MW PAHs (Fig. S17, Supporting Material ; Sect. 2.1; Wang et al. 1999b; Yunker et al. 2002). Higher MW or sulfur PAHs such as coronene, BkF or benzo[*b*]naphtho[2,1-*d*]thiophene and dibenzothiophenes have been proposed as markers of diesel emissions (Dobbins et al. 2006; Larsen and Baker 2003; Marvin et al. 2000; Riddle et al. 2007; Wang et al. 1999b).

Compared with gasoline exhausts, diesel exhausts are said to be enriched in phenanthrene, fluoranthene, pyrene and chrysene (Larsen and Baker 2003; Masclet et al. 1986). Gasoline combustion produces patterns dominated by naphthalene and HMW PAHs, such as benzo[*a*]pyrene and dibenz[*ah*]anthracene (Larsen and Baker 2003; Marr et al. 1999; Miguel et al. 1998; Valle et al. 2007). Instead, cyclopenta[*cd*]pyrene and benzo[*ghi*]perylene have been proposed as markers for gasoline-fuel combustion (Dzepina et al. 2007; Larsen and Baker 2003).

Motorcycles contribute significant amounts of PAHs to atmospheric environments in some locations, such as Southeast Asia. In other parts of the world (e.g., U.S.A. and Canada), motorcycle contribution to air PAHs is insignificant compared to other traffic-related PAH emissions (Chien and Huang 2010; Oanh et al. 2013; Valle et al. 2007). Two-stroke motorcycle exhausts have been reported to contain higher amount of PAHs than four stroke or fuel injection motorcycles (Boonyatumanond et al. 2007). Different factors such as motorcycle speed, engine type and age affect the PAH patterns emitted (Chien and Huang 2010). Exhausts from motor vehicles are transported far from point sources and contribute to diffuse background levels.

The PAH concentrations decrease as the distance from traffic sources increases (Boll et al. 2008). The typical gray particle color of automobile emissions makes the particle-associated PAHs vulnerable to photodegradation (Dickhut et al. 2000 and references therein). Furthermore, automotive emissions of PAHs depend on the fuel and vehicle type and local traffic conditions (e.g., Geller et al. 2006; Lim et al. 2007; Riddle et al. 2007).

Biomass combustion occurs at relatively low temperatures and is a significant source of pyrogenic PAHs in nearshore subtidal sediments (Barra et al. 2007; Gogou et al. 2000; Oanh et al. 1999; Page et al. 1999; Tobiszewski and Namiesnik 2012). However, aerosol from wheat and rice straw burning is enriched in HMW PAHs (Ravindra et al. 2008 and references therein). Stark et al. (2003) identified three- to six-ringed parent PAH compounds as the major PAHs in fireplace soots (see also Figs. S18–S20, Supporting Material); alkylated three- and four-ringed compounds were less abundant. Stark et al. (2003) noted that when soots have high total PAH concentrations, they also contain larger amounts of three- and four-ringed parent compounds. In contrast, soots with lower total PAH concentrations show a relative increase in the amounts of five- and six-ringed PAHs.

Guillon et al. (2013) identified fluoranthene and pyrene as dominant parent PAH compounds in particulates from wood combustion, whereas the dominant parent HMW PAHs are benz[*a*]anthracene and chrysene, followed by benzo[*a*]pyrene. Cyclopenta[*a*]phenanthrene, phenylnaphthalene and either cyclopenta[*cd*]pyrene or benzo[*ghi*]fluoranthene are present in fireplace soots (O'Malley et al. 1997; Stark et al. 2003). Other HMW PAHs such as benzo[*ghi*]perylene are also produced by biomass combustion (Dzepina et al. 2007).

Under certain conditions (e.g., steady combustion and forest fires), and in contrast to HMW parent PAHs, alkylated naphthalenes, phenanthrenes, and even chrysenes may be ubiquitous biomass combustion products (Figs. S18–S20, Supporting Material; Wang and Fingas 2003). Furthermore, three-ringed alkyl PAHs such as 1-methylphenanthrene, 1,7-dimethylphenanthrene (also known as pimanthrene) and retene (1-methyl-7-isopropyl phenanthrene) are produced from abietic and pimaric acid—both present in pine wood resin—and can be used as markers for softwood combustion (Benner et al. 1995; Bucheli et al. 2004; Gogou et al. 2000; Sicre et al. 1987; Yan et al. 2005; Yunker et al. 2002). The 2,6-dimethylphenanthrene isomer is present at comparable concentrations in emissions from fossil fuel and residential wood combustion (Benner et al. 1995).

The PAHs derived from coal combustion are a concern in some regions of the world (Chen et al. 2005). Fluoranthene, pyrene, phenanthrene and anthracene dominate in coal combustion profiles (Larsen and Baker 2003 and references therein). Chrysene and benzo[*k*]fluoranthene dominance has also been suggested as an indicator of coal combustion (Ravindra et al. 2008 and references therein). Dibenzothiophenes are also abundant in coal emission condensates (Marvin et al. 2000; Sicre et al. 1987) and industrial coal emissions, and escape from most modern SO_x removal processes (Lehndorff and Schwark 2009).

Coal combustion patterns sometimes deviate from the general pyrogenic fingerprint of PAH homologues (i.e., maxima at the parent PAH), and can show maxima for the methyl or dimethyl homologues of phenanthrene and anthracene (Oros and Simoneit 2000; Yunker et al. 2002). Similarly, four-ringed methyl PAHs methylfluoranthene or methylpyrene may also show maxima in coal combustion PAH patterns (Oros and Simoneit 2000; Yunker et al. 2002). PAH emissions from coal burning depend not only on the coal rank, but also on the temperature of combustion.

Lower coal combustion temperatures (e.g., domestic stoves) yield more PAHs than do high-temperature processes, such as in coal power plants (Chen et al. 2005; Oros and Simoneit 2000). Therefore, in addition to coal content, the combustor is crucial when calculating coal PAH emissions.

Much attention has been paid to increased creosote PAH contamination in sediments, particularly in the U.S. (Brenner et al. 2002; Stout et al. 2001a, 2003). Coal tar, creosote and coal tar pitch contain very large quantities of pyrogenic PAHs (>10%). As a result, small amounts of these materials greatly influence the distribution of PAHs in sediments (Stout et al. 2001b). Two- and three-ringed PAHs are abundant in creosote. For example, parent PAHs, such as naphthalene (NO), acenaphthene (AE), fluorene (FO), phenanthrene (PO), fluoranthene (FLO) and pyrene (PYO) (see also Fig. S28a, Supporting Material), dominate over four- to six-ringed PAHs (Stout et al. 2001a and references therein).

Creosote degradation (Fig. S28b–d, Supporting Material) results in the loss of LMW PAHs and a PAH signature dominated by four to six rings (increasing abundance of benz[*a*]anthracenes, chrysenes, benzo[*fluoranthene*], benzo[*pyrene*]) (Brenner et al. 2002; Stout et al. 2003). This fingerprint is hardly distinguishable from the urban background, which contains mainly pyrolytic sources. Therefore, creosote is classified as a pyrogenic PAH source (Stout et al. 2001b).

Industrial activities such as coke and steel production have released large quantities of not only pyrogenic PAHs (Orecchio 2010; Saber et al. 2005), but also of LMW PAHs such as naphthalene (Fig. S31), and all of these PAHs eventually end up in soil or sediment (Karlsson and Viklander 2008; Morillo et al. 2008b). Distillation of tars (e.g., coal tar) alters the pyrogenic PAH composition (depending on the PAH boiling point), leading to mixtures enriched in LMW PAHs, as occurs with creosote (Neff et al. 2005). Coal tar PAHs are present in pavements and asphalt, and result from high-temperature baking of hard coal in a reducing atmosphere to produce coke and manufactured gas. These sources (i.e., those rich in PAHs such as benz[*a*]anthracene, chrysene, indeno[1,2,3-*cd*]pyrene and benzo[*ghi*]perylene), show a characteristic pyrogenic profile (Fig. 5e), and are likely to be washed out by rain and end up in sediments (Douglas et al. 2007a; Neff et al. 2005; Yunker et al. 2002).

PAH patterns in paving materials show distributions of both LMW PAHs (petrogenic) and HMW PAHs (pyrogenic) (Fig. 5). Such patterns reflect the blending that occurs with different types of heavy petroleum products (Fig. 1c, d), paving materials (Fig. 5a) and coal tar (Fig. 5e) (Douglas et al. 2007a). In general, PAHs heavier than fluoranthene or pyrene (and to a lesser extent anthracene, phenanthrene, and acenaphthene) are dominant in such materials, although coal tar pitch or tar residues may be enriched in naphthalenes, phenanthrenes, and possibly dibenzothiophenes (Figs. S29, S30; Supporting Material; Saber et al. 2006). The HMW PAH tar fingerprint is minimally changed, even after degradation (Uhler and Emsbo-Mattingly 2006), making it possible to use HMW PAHs to characterize coal tars (Costa et al. 2004).

Street dust is transported in sediments, rivers, wastewater treatment plants and estuaries via street runoff, which is an important source and pathway of how PAHs reach sediment, particularly in regions that have high and intense rainfall events

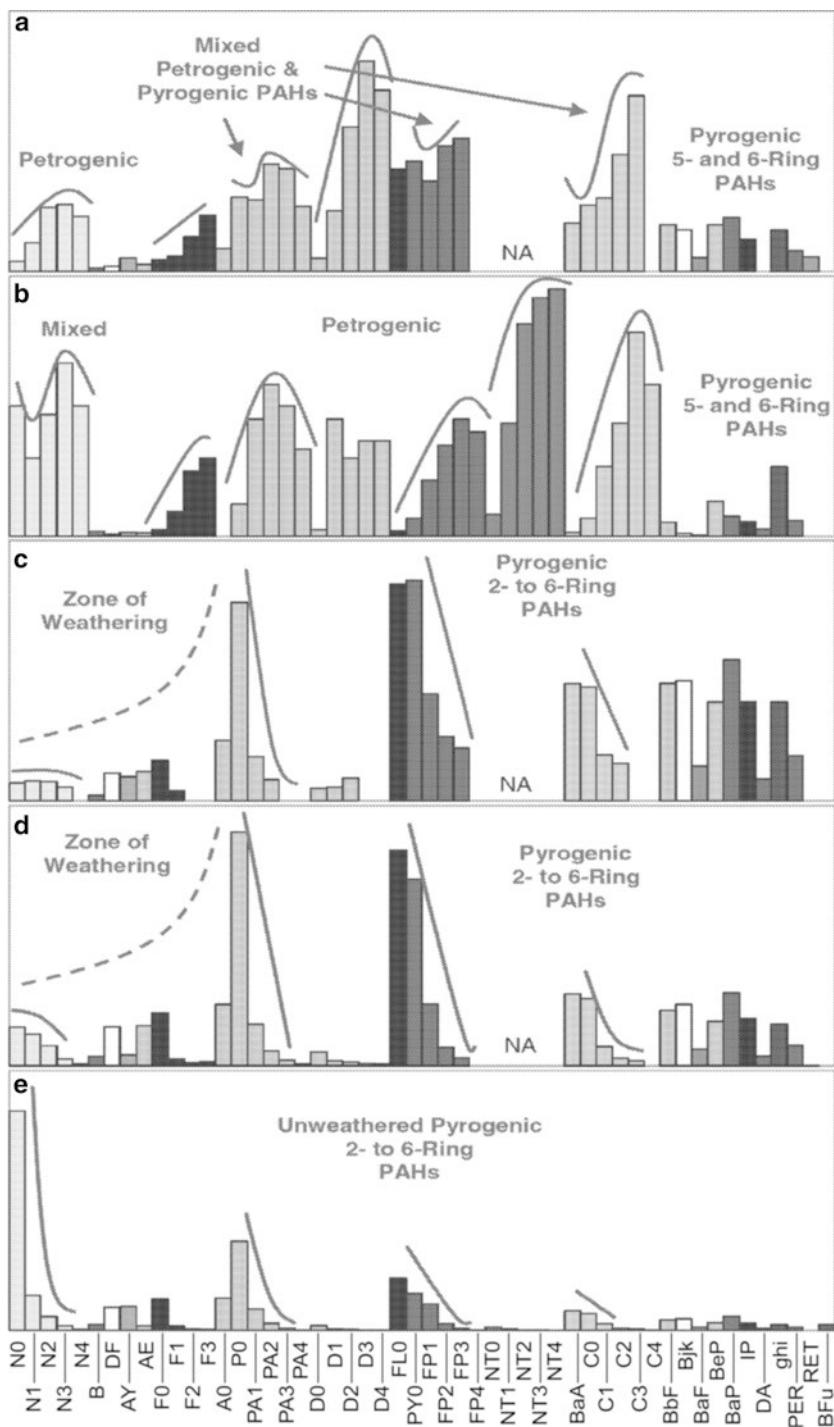


Fig. 5 Mixed PAH profiles. **(a)** hot patch (paving material), **(b)** modern (2005) roadway paving, **(c, d)** older types of roadway paving, **(e)** coal tar oil. NA: not analyzed. See Table 1 for PAH abbreviations. Adapted from Douglas et al. (2007a), with permission, © Elsevier Academic Press

(Lorenzi et al. 2011; Ollivon et al. 1999; Takada et al. 1990). Street dust is a mixture of weathered material from street surfaces, automobile exhaust, asphalt, lubricating oils, gasoline, diesel fuel, tire particles, atmospheric fallout, and soil (Breault et al. 2005; Takada et al. 1990). Figures S21–S26 (Supporting Material) show different fingerprints of sources that contribute to street dust.

Depending on the local traffic conditions, asphalt and tire particles contribute variable PAH amounts to street dusts (Boonyatumanond et al. 2007; Takada et al. 1990; Zakaria et al. 2002). Ou et al. (2004) reported only a small amount of PAHs in asphalt (0.7%). It is known that tire particles can contribute significant quantities of phenanthrenes, pyrene, and benzo[ghi]perylene to street dust (Figs. S22 and S24, Supporting Material; Zakaria et al. 2002). Chen et al. (2006) reported that indeno[1,2,3-cd]pyrene, dibenz[ah]anthracene and benzo[a]pyrene are the most dominant PAHs (>90% of total) in tire powder. In other cases, PAHs in street dust result mainly from automobile exhaust, although domestic heating emissions contribute to PAH releases as well (Takada et al. 1990; Zakaria et al. 2002).

The primary components of street dust are reported to be parent PAHs ranging from phenanthrene (three aromatic rings) to benzo[ghi]perylene (six aromatic rings) and in particular, the three- and four-ringed PAHs (i.e., phenanthrene, fluoranthene, pyrene and benzo[ghi]perylene) (Ollivon et al. 1999; Stark et al. 2003). Lower (two-ringed) and higher MW PAHs may also be present, and so may a range of parent, methylated, and substituted compounds (such as biphenyls and dibenzothiophenes) (Stark et al. 2003). If lower MW PAHs (such as dimethylphenanthrenes present in tire wear particles) are mixed with street dust, they will selectively dissolve in runoff water and will reach sediment (Mandalakis et al. 2004; Takada et al. 1990). The impact of street dust PAHs on aquatic environments can be quantified by determining the PAH contents and profiles in runoff samples from street surfaces (Karlssohn and Viklander 2008; Takada et al. 1990).

For decades, rainfall from storm events have washed PAHs from numerous non-point and point sources (e.g., urban dust/soot, used lubricants, petroleum products) into stormwater outfalls along urban waterways (Battelle Memorial Institute et al. 2003). This mix of point and non-point pollution sources usually dominates a whole area with a unique, or hardly varying fingerprint (Fig. S32a, b, Supporting Material), which is not representative of any specific PAH source, and is termed “background concentration” (Costa and Sauer 2005; Page et al. 1999; Stout et al. 2003, 2004). PAH background concentrations are highly variable and site-dependent, owing to the variable effects of dilution and transport processes in the aquatic environment (Battelle Memorial Institute et al. 2003).

“Anthropogenic background” sediment concentrations in both urban and remote locations have long exceeded the low concentrations of naturally occurring background PAHs (e.g., from forest fires, natural oil seeps, etc.) (Fig. S32a, b, Supporting Material; Page et al. 1996; Saber et al. 2005; Stout et al. 2003, 2006). Stout et al. (2004) suggested that sediments containing significantly more than 20 µg/g dry weight of any of the EPA 16 Priority Pollutant PAHs (or more than 30 µg/g of 43 parent and alkylated PAHs) is suspect for containing PAHs that are not entirely

attributable to urban background, unless site- or region-specific survey data support a different urban background concentration profile.

As with street dust, the most abundant of the 16 parent PAHs in storm water (and in urban background) are fluoranthene and pyrene, and to a lesser extent, phenanthrene and anthracene (Battelle Memorial Institute et al. 2003; Karlsson and Viklander 2008). Urban background is generally enriched in four- to six-ringed PAHs, and depleted in LMW PAHs (Battelle Memorial Institute et al. 2003). In urban runoff, the pyrogenic homologues of fluoranthene and chrysene, and to a lesser extent those of phenanthrene and anthracene exhibit the sloping pyrogenic pattern. Therefore, urban background reflects pyrogenic characteristics that are distinct from those of other pyrogenic sources. Nevertheless, weathering may alter a pyrogenic fingerprint (preferential elimination of LMW and parent PAHs over HMW and alkylated PAHs) to resemble that of urban background (Battelle Memorial Institute et al. 2003).

2.3 Biogenic/Diagenetic

Diagenetic PAHs are produced during the slow transformation of organic materials in lake sediments, whereas biogenic PAHs are produced by plants, algae/phytoplankton and microorganisms (Venkatesan 1988). Perylene (PER) is produced under several conditions: by diagenesis and biosynthesis from terrestrial precursors (e.g., perylenequinone pigment) or other organic matter; under anoxic conditions; and in soil and subtidal, marine and freshwater sediments (e.g., Boll et al. 2008; Guo et al. 2007; Venkatesan 1988; Zakaria et al. 2002). In the tropics, termite nests may act as a perylene source in soil (Barra et al. 2007; Mandalakis et al. 2004; Wilcke et al. 2002).

If perylene does not correlate with the total organic carbon, then the perylene is likely to have a natural origin (Luo et al. 2008). In such a case, perylene may not yield its source of organic matter, although it can be a useful tracer for water and for depositional conditions (Budzinski et al. 1997). For instance, assuming a biogenic perylene origin, Page et al. (1996) used perylene depth gradients to show lack of vertical mixing.

Other PAHs such as benzo[*b*]fluoranthene (BbF), phenanthrene (P0) and naphthalene (N0) can originate from vascular land plants or termite activity (Bakhtiari et al. 2009; Irwin et al. 1997; Tobiszewski and Namiesnik 2012). Benzo[*a*]pyrene can be biosynthesized by certain bacteria and plants (Peters et al. 2005). Retene (RET) can be produced from the anaerobic microbial degradation of dehydroabietic acid (present in tire particles in urban areas) in soils and sediments (Mandalakis et al. 2004).

Perylene or biogenic-diagenetic PAHs also potentially have anthropogenic sources. PER has been detected in trace amounts after pyrolytic processes (Luo et al. 2008), such as coal pyrolysis in municipal incinerator waste products and automotive emissions (Abrajano et al. 2003; Boll et al. 2008; Gogou et al. 2000).

Retene has other anthropogenic sources, such as fresh oil, diesel, exhaust emissions from heavy-duty diesel fuels, pulp/paper mill effluents, and emissions from coals (Mandalakis et al. 2004; Yan et al. 2005).

3 Factors Influencing PAH Distribution in Aquatic Systems

Sediments are sensitive indicators of natural and anthropogenic origin, such as PAH contamination (De Luca et al. 2004; Klamer et al. 1990). Variables such as OC, particle size and depositional environment are important for discovering and characterizing the source, transport and bioavailability of PAHs in sediment (e.g., Dickhut et al. 2000; Morillo et al. 2008b; Soclo et al. 2000; Wang and Fingas 2003).

In the different environmental matrices (atmosphere, water column, oil, sediments), easily degradable LMW PAHs (i.e., two- and three-ringed) are relatively soluble and predominate in the water phase, whereas the more recalcitrant and more lipophilic alkylated and/or HMW PAHs are more often associated with particulate matter, and thus are better protected from degradation (Budzinski et al. 1997; Cailleaud et al. 2007; De Luca et al. 2005; Karlsson and Viklander 2008; Page et al. 1996; Stout et al. 2001a, b). This fact has implications that need to be taken into consideration when dealing with PAH distributions:

- a. It is difficult to distinguish certain weathered pyrogenic sources (e.g., severely weathered coal tar) from urban background, which is also dominated by HMW four- to six-ringed PAHs (Battelle Memorial Institute et al. 2003).
- b. Lack of oxygen (that fosters biodegradation) in deeper sediment layers and also the physical-chemical association of PAHs with the sediment matrix can result in long-term PAH stability (Page et al. 1996, 1999; Short et al. 2007).
- c. Small molecules, such as three-ringed/LMW PAHs, are selectively depleted by physical mixing and tend to be enriched in the fine sand fraction, whereas the larger PAHs (six-ringed) are enriched in the fine silt fraction (Karlsson and Viklander 2008; Mitra et al. 1999). Partitioning of PAHs into different sediment fractions has been reported in the literature (Johnson-Restrepo et al. 2008; Magi et al. 2002; Micic et al. 2011). Sediment particle size affects the oxygenation of sediments, as well (Jeanneau et al. 2008).
- d. Climatic conditions may affect the distribution of PAHs in different environmental compartments, particularly in the atmosphere and consequently may determine what constitutes the final sink. For example, fluctuations in temperature directly affect the particle and vapor phase distributions of retene, a common softwood combustion marker (Benner et al. 1995; Gogou et al. 2000; Stout 2007; Yunker et al. 2002). Accordingly, retene's diagnostic reliability for softwood combustion in aqueous environments has been doubted (Bucheli et al. 2004; Gogou et al. 2000).
- e. The sorption and desorption of PAHs to the organic carbon (OC) content of sediments can be used to interpret the source of PAH contamination (Boehm et al. 2001, 2002; De Luca et al. 2004, 2005; Mitra et al. 1999; Morillo et al. 2008b; Zakaria et al. 2002).

4 Analytical Approach for PAH Source Characterization

It is often complicated to define the sources of PAH contamination in waterways and coastal areas that have limited water circulation, particularly where multiple point sources co-occur with persistent non-point sources (i.e., urban areas or areas that have high ambient background levels). In such situations, the potential contributions of all possible point or non-point sources should be considered (De Luca et al. 2004; O'Reilly et al. 2012, 2014; Stout et al. 2003).

The major approaches used in source identification are pattern recognition, spatial and temporal analysis (sources, historic records, etc.), source-specific diagnostic ratios of PAH analytes, and principal component analysis (PCA) or positive matrix factorization (Battelle Memorial Institute et al. 2003; Burns et al. 1997; Johnson et al. 2007; Stout and Graan 2010). If the types of sources and the relative abundances of contributing PAHs are known, then the most useful tools for distinguishing pyrogenic from petrogenic hydrocarbons are the PAH distributions (patterns, boiling ranges and fingerprints of alkylated and non-alkylated PAHs) and diagnostic ratios (Benner et al. 1995; Elmquist et al. 2007; Neff et al. 2005; Wang and Brown 2009).

Successful inference and/or differentiation of sources depends on many factors, such as sampling plan design, sample collection, chemical analysis methods and knowledge of historical industrial processes (Johnson et al. 2007). Problems often exist in establishing unique organic “tracer” compounds for a given combustion source, and such problems include variability in the composition of emissions from the same types of source, degradation of the “tracer”, and general lack of source composition data for all but a few classes of compounds (Johnson et al. 2007).

There are three main steps (tiers) in characterizing the sources of PAHs (Fig. 6). First, inexpensive rapid screening techniques like gas chromatography (GC)—flame ionization detection (FID), are applied to identify trends, background concentrations, “hotspots”, and key samples (Page et al. 2006; Stout et al. 2003; Wang et al. 1999a). Second, if initial screening results allow defensible decision-making, advanced chemical fingerprinting (e.g., GC-MS,² GC-FID, use of diagnostic ratios, etc.) helps to reveal and identify distinct source “fingerprints” (Boehm et al. 1995; Page et al. 2006; Stout et al. 2003; Wang and Fingas 2003; Wang et al. 1999a).³ Third, tier results are explored and explained by using statistical tools. In this review, we emphasize the use of molecular indices (PAH ratios) as the basis for characterizing PAH sources.

²Mass Spectrometry.

³For guidelines on how to perform a fingerprinting analysis of PAH sources (assessment of historic records, sampling considerations, climatic conditions, background pollution, quality assurance, etc.) see Christensen and Tomasi (2007), Christensen et al. (2004), Saber et al. (2006), Stout et al. (2001b, 2003), Wang et al. (1999a).

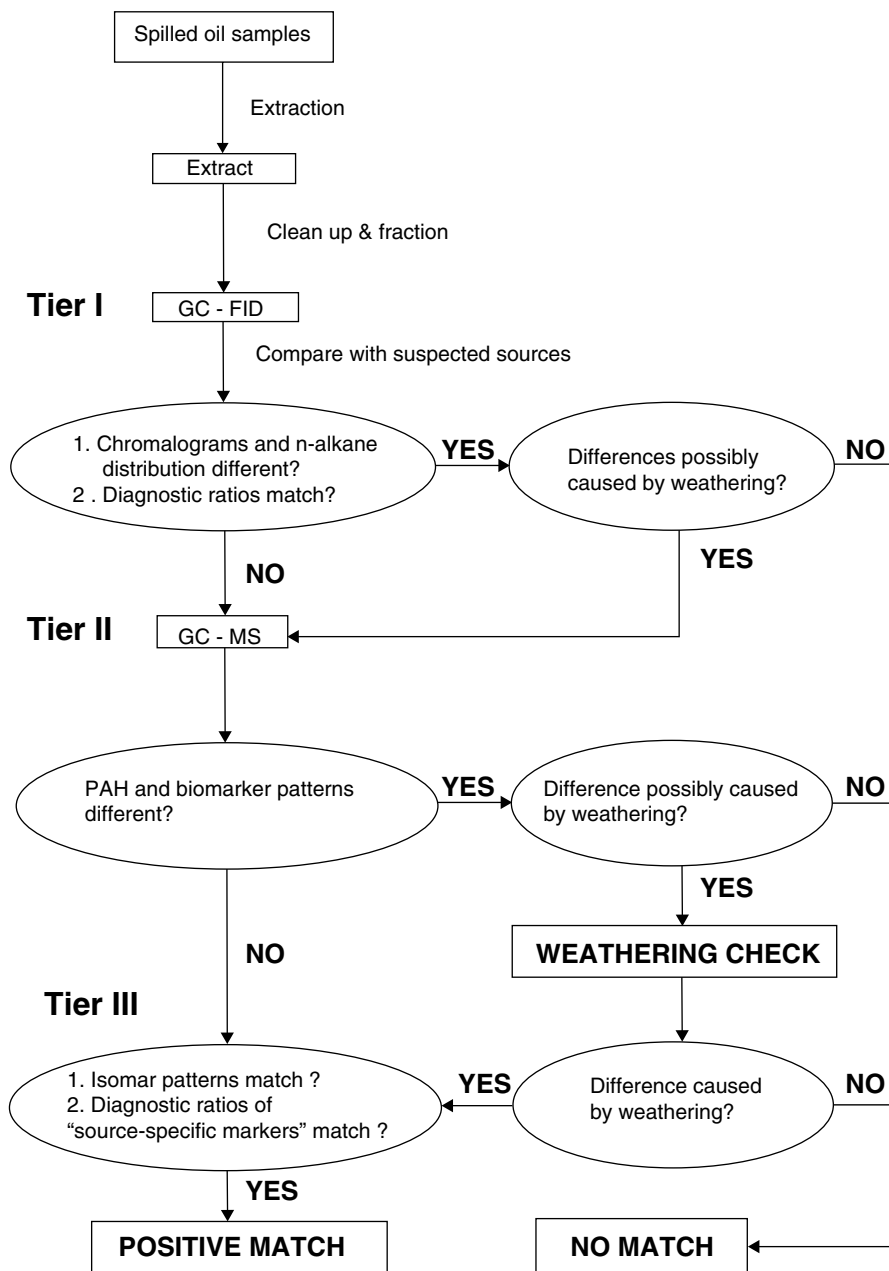


Fig. 6 Oil spill identification protocol. If significant differences in hydrocarbon fingerprints and diagnostic ratios are found at any stage during the identification process, the conclusion will be that the samples are not from the suspected source. From Wang et al. (1999a) (modified decision chart of Nordtest Method 1991), with permission, © Elsevier Science BV

5 Molecular Indices

Comparing PAH concentrations in a contaminated area with the PAH content of potential/suspected sources can produce very useful results (e.g., Boehm et al. 1995; Wang et al. 2001; Yunker et al. 2002). To evaluate compositional differences in PAH profiles, the concentrations of PAHs are usually standardized into ratios that are both source-specific and refractory (De Luca et al. 2004; Kim et al. 2008). These indices are of interest, because during PAH formation the PAH distribution is temperature-dependent (De Luca et al. 2004, 2005; Yunker et al. 2002). The PAH distribution patterns are governed by the thermodynamics of low-temperature processes (e.g., the formation of petroleum), and the kinetic factors of high-temperature processes (e.g., combustion).

Different ratios may be attributable to differences between the sources (Hwang et al. 2003; Stout et al. 2004), such as the type of substrate and the available pathways and conditions of PAH formation (Yan et al. 2005). PAH ratios can also be used as tracers of PAH transformation during transport from the PAH source to deposition and burial (Mitra et al. 1999; Stout et al. 2002). Consequently, to optimize data analysis, one should use diagnostic ratios of PAH isomers, PAHs within a homologue category, or PAHs that have similar thermodynamic stabilities (Christensen et al. 2004). The use of PAH ratios minimizes confounding factors such as differences in volatility, water solubility and adsorption (Yunker et al. 2002). Therefore, such ratios may be used in two-component mixing models⁴ for PAH sources in sediment (Page et al. 1996).

From a statistical point of view, by using diagnostic ratios the sample compositional information can be condensed into fewer variables that are less affected by analytical artifacts/errors (e.g., retention time shifts, changes in peak shapes, relative signal intensities, etc.; Christensen and Tomasi 2007). When degradation effects are factored in, a “multiple mixing model” can be developed that assists in establishing the range of contributions of different PAH sources (Gogou et al. 2000; Stout et al. 2003; Wang et al. 2001).

5.1 Practical Concepts

PAH ratios are expressed as the ratio of the thermodynamically most stable isomer (S) to the most unstable isomer (U) (e.g., S/U), or vice versa (e.g., Mitra et al. 1999; Stout 2007). Such ratios are sometimes called thermal parameters because they are

⁴A two component mixing model to estimate the “a” % contribution of the source A to the sample, where the ratio of the two isomers is “ r_s ”, given the ratios of the isomer components in the sources A and B (r_A and r_B respectively), and only sources A and B contribute, would look like:
$$a = \frac{(r_A + 1)(r_B - r_s)}{(r_s + 1)(r_B - r_A)}$$

a function of the formation temperature (e.g., Budzinski et al. 1997; Stout 2007; Yunker et al. 2002). For parent PAHs, combustion or anthropogenic input—or both—are often inferred from an increase in the proportion of the less stable, “kinetic” PAH isomer relative to the more stable, “thermodynamic” isomer, and the stability of the lighter PAH isomers has been calculated to support such interpretations (Budzinski et al. 1997; Yunker et al. 2002).

Some researchers prefer to limit the ratio to the range of 0–1 and thus report the

ratio as: $\frac{S}{S+U} = \frac{S/U}{1+S/U} = \left(1 + \frac{1}{S/U}\right)^{-1}$. In this paper, such ratios are usually

written in the form of “nominator/denominator”. For example, the formula FL0/

FL0+PY0 simplifies the form $\frac{\text{FL0}}{\text{FL0} + \text{PY0}}$ (using the molar concentrations of these

compounds). The S/S+U form results in smaller relative standard deviations (RSD) than the S/U form does, but only the RSD of the S/U form is constant and independent of the numerical values of S and U (Hansen et al. 2007 and references therein). Therefore, the use of the S/U form is recommended.

PAH ratios that are used to indicate a characteristic molecular fingerprint of a substance are sometimes called source parameters (Stout 2007). For example, the ratios of dibenzothiophenes or benzonaphthothiophenes reflect the differences in the abundance of sulfurous aromatics in crudes (Boehm et al. 2001; Dzou et al. 1995; Grimmer et al. 1983; Stout 2007; Stout et al. 2006). Consequently, knowledge of the possible source fingerprints/PAH distributions is of critical importance when utilizing PAH ratios to identify sources (Johnson et al. 2007; O'Reilly et al. 2012, 2014). Finally, PAH ratios that vary according to the degree of weathering are used as weathering parameters/indicators (e.g., the ratio of the less stable compound to the significantly more stable compound).

PAH ratios are usually shown as one or more of the following plots:

- Double ratio plots. These are the most popular (e.g., Andersson et al. 2014; Budzinski et al. 1997; Yunker et al. 2002) and display the chart as areas separated according to PAH origin (e.g., pyrolytic, petrogenic, etc.).
- Time or depth plots of the ratio. Useful for studying temporal trends of PAH sources (effects of population, combustion practices, and new sources) (e.g., Guo et al. 2007; Mitra et al. 1999; Pereira et al. 1999). Occasionally, data such as ^{137}Cs , ^{210}Pb , and $\delta^{13}\text{C}_{\text{py}}$ are plotted against PAH ratios to elucidate the source profile over time (e.g., Elmquist et al. 2007; Stout et al. 2001b; Yan et al. 2005).
- Map plots and boxplots of PAH ratios. These are used to identify point sources and hotspots (Battelle Memorial Institute et al. 2003).
- Nordtest plot. Allows researchers to examine matches between the ratios for possible sources and sediment contamination.

The basis of selecting the proper diagnostic ratios should be based on the specificity and diversity of the ratio over a range of sources, the resistance of the ratio to weathering effects and the precision of the analytical method used (Christensen and Tomasi 2007; Christensen et al. 2004; Hansen et al. 2007 and references therein).

When the PAH ratios for sources are known, the ratios can be classified according to their diagnostic power (DP), so that the most suitable ones are selected for the study area (Christensen and Tomasi 2007; Christensen et al. 2004). Christensen and Tomasi (2007) evaluated the diagnostic power of 25 PAH ratios of oil spill samples. They reported high diagnostic power for ratios such as alkylated phenanthrenes to alkylated dibenzothiophenes, fluoranthene to pyrene, methylphenanthrenes to phenanthrenes and other less common ratios.

A standardized and simple means of comparing chemical fingerprints (Fig. 6—tier III) of different oil spills is the Nordtest (Douglas et al. 2007b; Stout et al. 2005). It entails plotting several diagnostic ratios (generally accepted, or calculated for the occasion) for the source and the sample, together with the 98% and 95% confidence intervals (Fig. 7) (Stout et al. 2005).

Douglas et al. (2007b) described the Nordtest method (limited to spilled oils and refined oil products in water) in more detail and showed how to establish new candidate ratios for discriminating between two known sources. They also recommended a list of 10 diagnostic ratios for identifying oil spills. Phenanthrenes and dibenzothiophenes are included on this list because they are common in all oils. The concentrations of methylfluoranthenes, methylpyrenes and benzofluorenes also vary among different oils and are included on the list (Douglas et al. 2007b).

Principal component analysis (PCA) (Davis 2002; Luo et al. 2008) is one of the most suitable tools for identifying potential sources of PAHs. PCA allows for greater resolution among different sources and for reduced variance than does the Nordtest

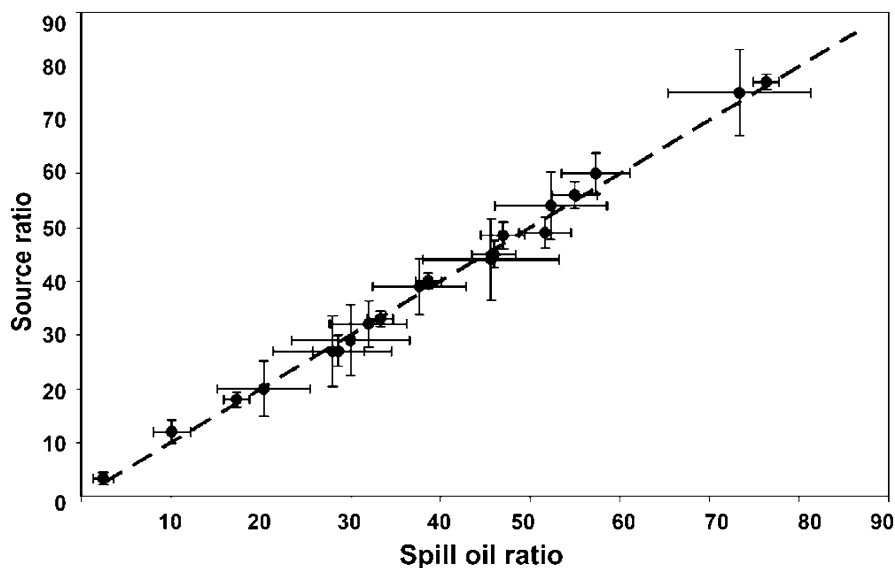


Fig. 7 The Nordtest method. All ratios match the possible source (i.e., the ratios in the sample and source are within a 95% confidence interval). Adapted from Stout et al. (2005), with permission, © Taylor & Francis Inc

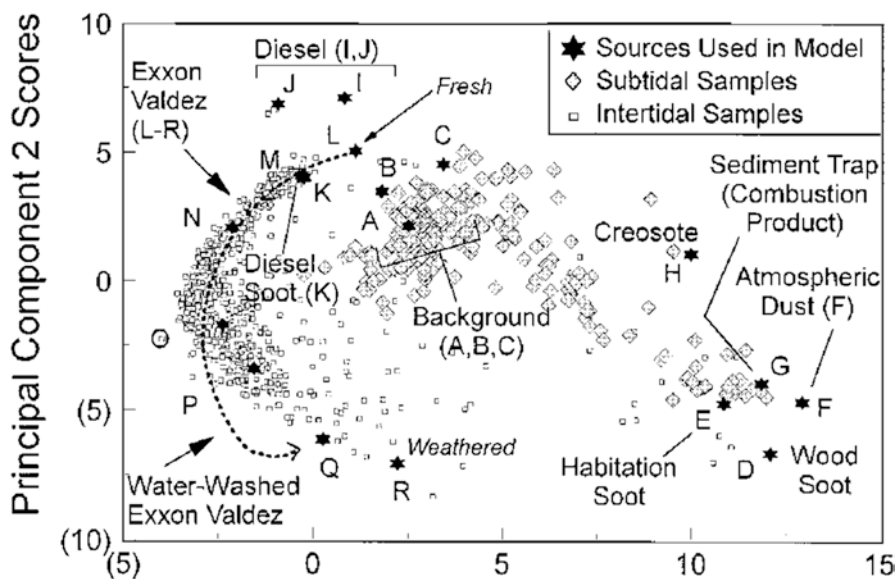


Fig. 8 PCA (principal component analysis) allocates sediment PAHs to the contributing sources by least-squares match of the PAH profile of the sample with the respective source. Adapted from Burns et al. (1997), with permission, © SETAC

method (De Luca et al. 2004; Douglas et al. 2007b; Neff et al. 2005). The first principal component accounts for the largest possible variance in the data, and each succeeding component explains as much of the remaining variability as possible (Davis 2002). If principal components can be given a meaningful explanation (i.e., pyrogenic, petrogenic or natural sources), by assigning certain compounds to a certain principal component, then it is possible to quantify the contribution of the different PAH sources (Luo et al. 2008). In a cross-plot of principal components, samples that have similar compositions will be close to each other (Fig. 8).

If there are doubts about the PAH source profiles, principal components can be used to indicate the possible sources (Burns et al. 1997). If more is known about the sources, PCA can be used to reveal the contributions of each source to the samples (Boehm et al. 2001). Because the concentrations of individual PAHs often differ by orders of magnitude in a given sample, they are usually normalized to the sum of the analytes (Boehm et al. 2001).

Burns et al. (1997) used PCA to determine the major contributions of 36 identified sources in Prince William Sound, Alaska. The sources that contributed most were then apportioned by a best-fit least square model to calculate a linear combination of contributing sources. Christensen et al. (2004) used externally normalized PAH ratios as the loading variables in PCA, providing an integrated methodology for oil spill identification similar to the tiered one presented in Fig. 6.

Basic guidelines for successful application of a PCA include adequate, good quality data (e.g., samples with higher PAH concentrations may have different origins), and the optimization of the sources and the number of principal components (Burns et al. 1997; Johnson et al. 2007; Luo et al. 2008). However, if the sources of the PAHs are strongly correlated, then other chemical compounds might have to be used.

The inherent disadvantages of the PCA method (Johnson et al. 2007) and growing interest in PAH source apportionment led to the adoption of a new analysis tool: positive matrix factorization (PMF). PMF (Comero et al. 2009) has been successfully used (sometimes in conjunction with PCA) to apportion PAH sources (Lang et al. 2013; Larsen and Baker 2003; Sofowote et al. 2008, 2011; Stout and Graan 2010). By combining multiple statistical techniques in source apportionment, Stout and Graan (2010) successfully determined the concentration of PAHs that originated from non-point sources (urban background).

An important difference between using only PAH ratios vs. a PCA/PMF approach is that ratios classify the sample into very few categories (e.g., pyrogenic, petrogenic, etc.), whereas PCA places the samples and the sources in a continuous multidimensional space. Similarities or differences among samples and sources are tracked and measured by PCA/PMF. Quantitative assessments are achieved by using the PCA/PMF approach (Luo et al. 2008) or by applying a mass balance model, in which several PAH ratios are simultaneously considered. Uncertainties in the PAH ratios may cause a sample to be misclassified, whereas employing a PCA/PMF method by itself does not misclassify the samples. Most importantly, application of a PAH ratio relies on the correlation of two variables, whereas PCA/PMF takes account of all available variables. Consequently, once they have been established through a PCA/PMF apportionment method (e.g., Luo et al. 2008; Nasher et al. 2013; Stout and Graan 2010; Stout et al. 2005), PAH ratios may prove to be a rapid and inexpensive way to infer sources and/or to develop a mixing model, albeit on a case by case basis.

The potential problem of using molecular ratios in source identification is the chemical and biological alterations of PAHs relative to each other (Galarneau 2008; Mansuy-Huault et al. 2009; O'Malley et al. 1994). It is possible to take the photodegradation effects on the ratio⁵ into account, if the kinetics of photodegradation (half-lives, first order kinetics) and the color of the particles are known (Behymer and Hites 1988; Dickhut et al. 2000; Tobiszewski and Namiesnik 2012). Therefore, the association of PAHs with particles (e.g., soot, fly ash etc.) is fundamental to understanding how photodegradation affects PAH ratios. Similarly, it is possible to

⁵ Using 1st order kinetics, the ratio r_{after} of two isomers (S and U) after photodegradation in air for time t would be: $R_{\text{after}} = R_{\text{emission}} e^{(k_U - k_S)t}$, where k is the photodegradation constant of the respective analytes for a certain particle color.

account for other kinds of degradation (biotic or abiotic), if a model describes them adequately. Several authors have evaluated the different types of degradation that affects PAH ratios (e.g., Costa and Sauer 2005; Stout et al. 2003; Uhler and Emsbo-Mattingly 2006; Wang et al. 1998). Hence, different PAH ratios may also be used as a simple means of evaluating degradation.

5.2 *Sum of PAHs*

A way to quantify the amount of pollution for a specific area, and also to take the first step in characterizing a PAH source, is to compare the sum of PAHs with the amounts released by a suspected source (Dupree and Ahrens 2007; Saber et al. 2005, 2006; Stout 2007). “Total PAHs” is commonly defined as the sum of identified three- to six-ringed parent PAH compounds, which is denoted as Σ PAH or EPA 16 (i.e., the U.S. EPA sixteen priority PAHs). To account for uncombusted petroleum sources that are rich in alkyl PAHs, TPAH is defined as the sum of all quantified parent and alkyl PAHs (Stout et al. 2003; Yan et al. 2006). Sometimes naphthalene, perylene and retene are excluded from TPAH estimation because the naphthalene is a common laboratory contaminant and perylene and retene could have a non-anthropogenic origin (Boehm et al. 2001, 2002, 2007; Gogou et al. 2000).

5.3 *Low Molecular Weight PAH Ratios*

5.3.1 *Naphthalene Indices*

Naphthalene and alkyl naphthalene ratios find several applications in source identification, as they constitute potentially useful thermal (Stout et al. 2002) or weathering parameters for crudes, coals, bitumen and other sources. Roush and Mauro (2009) used the N0/N1 ratio (parent naphthalene over methylnaphthalene) to detect coal tar residues enriched in naphthalene oil. The ratio $MNR = 2-N1/1-N1$ (2-methylnaphthalene to 1-methylnaphthalene) is unaffected by light weathering and can be used to distinguish products that have different methylnaphthalene content, such as lightly weathered distillates (Stout and Wang 2007). MNR and other alkylnaphthalenic ratios were used for the characterization of coals of different ranks (Radke et al. 1982). For minimally weathered sediments, the petrogenic background may be deduced simply from a high N0/F0 (naphthalene to fluorene) ratio (Neff et al. 2006).

In the initial weathering stages of an oil spill, the loss of naphthalene and methylnaphthalenes relative to dimethylnaphthalenes ($N0 + N1/N2$) can be used as a measure for the loss of PAHs due to dissolution (Diez et al. 2007). The N3/P3 (trimethyl naphthalenes over trimethylphenanthrenes) ratio is useful for estimating the weathering state of light crude oils (Peters et al. 2005). Heavier weathering may be evaluated by the sum of alkylated naphthalenes over TPAH or over the recalcitrant

alkylated chrysenes (e.g., N1-N4/C1-C3) (Bence et al. 1996; Boehm et al. 2008; Wang et al. 2006). After the rapid dissolution of the parent naphthalene and methyl-naphthalenes, these ratios decrease more slowly (Bence et al. 1996).

5.3.2 The Ratio of Phenanthrene to Anthracene

The ratio of parent phenanthrene to parent anthracene (P0/A0) redundant has been extensively used to differentiate between petrogenic and pyrogenic PAH pollution in sediments (e.g., Grimmer et al. 1981; Gschwend and Hites 1981; Guo et al. 2007; Lake et al. 1979; Sicre et al. 1987). Thermodynamically, this ratio is temperature-dependent (Budzinski et al. 1997 and references therein). Phenanthrene is the thermodynamically most stable triaromatic isomer, and its prevalence over A0 supports petrogenesis (Budzinski et al. 1997; De Luca et al. 2004, 2005; Gogou et al. 2000). High-temperature (800–1,000 K) processes yield low P0/A0 ratio values (4–10), usually less than 5. The slow thermal maturation of organic matter in petroleum leads to much higher P0/A0 values (50 at 373 K) (Budzinski et al. 1997; De Luca et al. 2005; Neff et al. 2005; Wang et al. 2001). However, fresh petroleum products occasionally exhibit small P0/A0 values (down to 4), whereas some combustion sources have a higher value (Budzinski et al. 1997; Colombo et al. 1989; Wang et al. 1999a).

P0/A0 ratios in different literature data sources are summarized in Fig. 9. Also shown in Fig. 9 are the P0/A0 threshold values that researchers used to distinguish petrogenic from pyrogenic sources. For example, $P0/A0 > 15$ for likely petrogenic inputs (or > 30 for negligible pyrogenic) and $P0/A0 < 15$ for the dominance of pyrolytic sources (< 5 according to Neff et al. 2005), such as fuel combustion or other high-temperature processes (Budzinski et al. 1997; De Luca et al. 2004; Morillo et al. 2008a). Yunker et al. (2002) concluded that a lowest P0/A0 boundary of 9 or 10 appears applicable for petrogenics, except that P0/A0 ratios overlap for certain sources such as diesel oils, coals, and coal emissions (Fig. 9).

In summary: i) $P0/A0 > 30$ shows crude oil contamination, but creosote and the combustion of some coals or crude occasionally exhibit high P0/A0 ratios, ii) values $30 > P0/A0 > 10$ show a mixed source profile, but if diesel and coal combustion and creosote are ruled out, then such values indicate a probable petrogenic source, iii) values $10 > P0/A0 > 5$ define a mixed source profile, and iv) values smaller than 5 indicate pyrogenic origin except for gasoline fuel, some road fingerprints, and low rank coals that exhibit $5 < P0/A0 < 9$.

The different thermodynamic stabilities of P0 and A0 allow biogeochemical processes to alter the P0/A0 value (Bucheli et al. 2004; Lake et al. 1979; Yan et al. 2006). The phenanthrenes photodegrade much more slowly than anthracenes (Behymer and Hites 1988; Hwang et al. 2003). As a result, smaller quantities of A0 are observed during the daytime in urban areas (Yunker et al. 2002). However, Zhang et al. (2005) calculated an air-to-sediment (i.e., receptor-to-source) ratio to be approximately 1 for P0/A0. This indicated that the P0/A0 ratio does not change significantly during deposition from atmospheric emissions to sediment. Nevertheless, the P0/A0 is sensitive to parameters such as molecular mobility and volatility (Zhang et al. 2005).

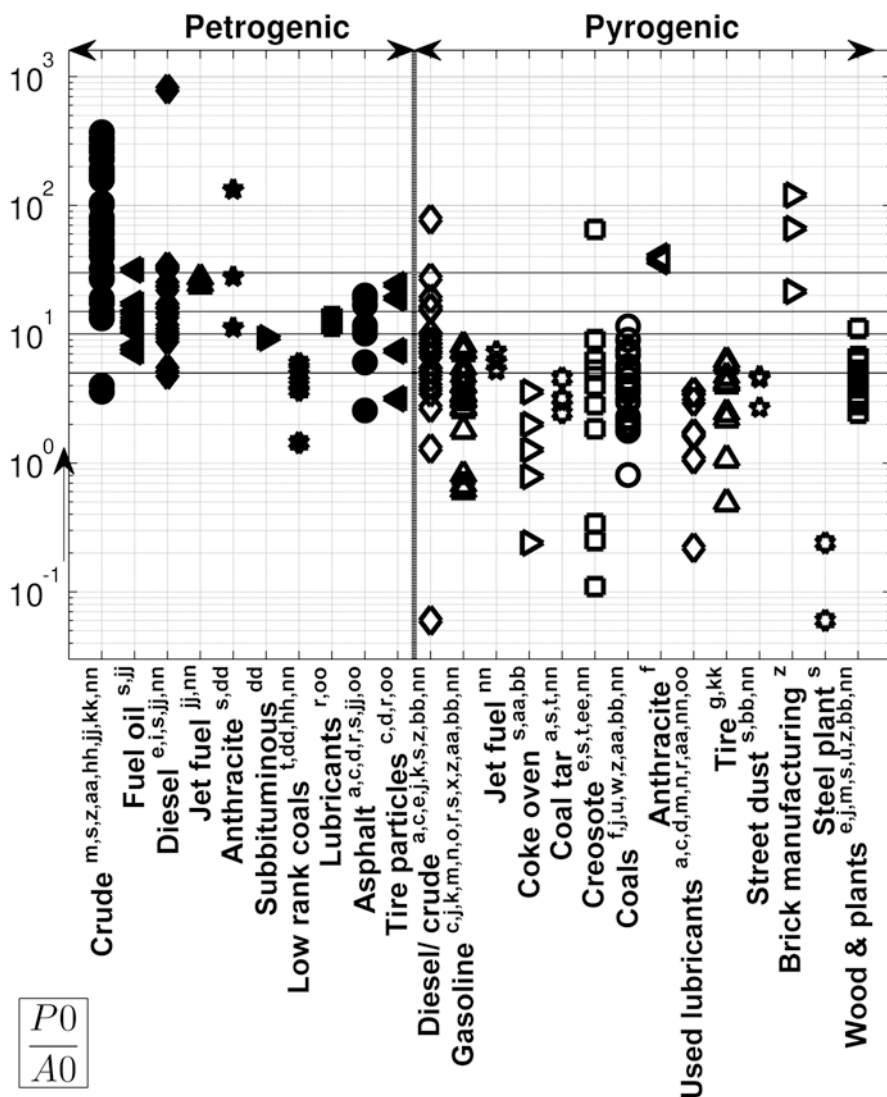


Fig. 9 Mean, maximum and minimum values of $P0/A0$ ratio (Y-axis in logarithmic scale) for different PAH sources (X-axis), as reported in the literature (see Table 5 in appendix). The vertical dashed line divides the graph into petrogenic (left) and pyrogenic (right) sources. Horizontal continuous lines indicate the thresholds used to distinguish pyrogenic and petrogenic products discussed in the text. Degradation arrow (left of graph, by the Y-axis) shows the change in $P0/A0$ with most types of degradation. However, $P0$ is more soluble than $A0$ (see text for more information)

In water, both $P0$ and $A0$ follow similar first order photodegradation kinetics when not attached to particles, although humic substances protect $P0$ but not $A0$ (Bertilsson and Widenfalk 2002). $P0$ is more soluble than $A0$ ($P0/A0$ decreases as dissolution increases) (Table 2), otherwise $A0$ is more degradable than $P0$ (ratio increases as the degradation proceeds). However, $P0$ in soils biodegrades more

readily than A0 (Tobiszewski and Namiesnik 2012 and references cited by these authors). Iqbal et al. (2008) noted that the P0/A0 ratio also depends on analytical matrix effects.

When degradation significantly changes the P0/A0 ratio, consistency with other ratios such as FL0/PY0 and P1/P0 has to be checked (Hwang et al. 2003). De Luca et al. (2004, 2005) noted that a prerequisite for the applicability of the P0/A0 is that $\Sigma\text{PAH} > 0.22 \mu\text{g/g}$ dry weight. Furthermore, when P0/A0 values are close to the pyrogenic/petrogenic thresholds, the ratio may be misleading for certain sources such as automobile exhausts (Morillo et al. 2008b). Dvorska et al. (2011) reported that the P0/A0 ratio is not very useful for distinguishing between traffic and domestic heating sources.

The P0/A0 ratio and other ratios such as FL0/PY0, BaA/C0 have been widely applied (Budzinski et al. 1997; Sicre et al. 1987; Wang et al. 2001, 2006; Yunker et al. 2002). However, caution needs to be exercised when applying the P0/A0 ratio for intermediate values (e.g., 4–15), on sediment that contains weathered PAH, or for solely pyrogenic discriminations (Bucheli et al. 2004; Dvorska et al. 2011; Hwang et al. 2003; Karlsson and Viklander 2008; Yan et al. 2005; Zhang et al. 2005). Thus, P0/A0 is more useful for petrogenic–pyrogenic discriminations.

5.3.3 The Ratio of Methylphenanthrenes to Methylanthracene

Methylphenanthrenes can be used to distinguish between petrogenic and pyrogenic sources by comparing them with methylanthracenes that are mainly products of catalytic or thermal cracking (Lake et al. 1979; Stout and Wang 2007; Uhler et al. 2007; Walker and Dickhut 2001). Such pyrolytic processes reduce the proportions of 9-, 4-, and 1-methylphenanthrenes in favor of methylanthracenes (Stout and Wang 2007). Therefore, a $\Sigma\text{P1/2-A1}$ (sum of methylphenanthrenes to 2-methylanthracene) ratio might serve as an indicator of the presence of coal tar, or of cracked gas-oil blending stock in heavy fuel oils (Uhler et al. 2007). Using this ratio it is also possible to distinguish heavy fuel oil from crude oil (Uhler et al. 2007).

Methylphenanthrenes are thermodynamically stable, and thus the $\Sigma\text{P1/2-A1}$ ratio should be high for most crudes and higher rank coals, which are produced during different geologic periods and under different heating conditions. Methylanthracenes may rapidly decompose to methylphenanthrenes (Walker and Dickhut 2001). Furthermore, the $\Sigma\text{P1/2-A1}$ ratio is sensitive to different source inputs, which may significantly alter its value (Walker and Dickhut 2001).

5.3.4 Methylphenanthrene Plus Methylanthracene Versus Their Parents

A sensitive indicator for tracing petrogenic and pyrogenic PAHs is the ratio of methylphenanthrene plus methylanthracene to the sum of parent phenanthrene plus parent anthracene: $\frac{P1+A1}{P0+A0}$, or PA1/PA0 in short (Fig. 10) (Da Silva and Bicego 2010; Mitra et al. 2009; Yan et al. 2005; Yunker et al. 2002). High PA1/PA0 ratios (>1.5) generally indicate petroleum, but occasionally PA1/PA0 is greater than 1.5

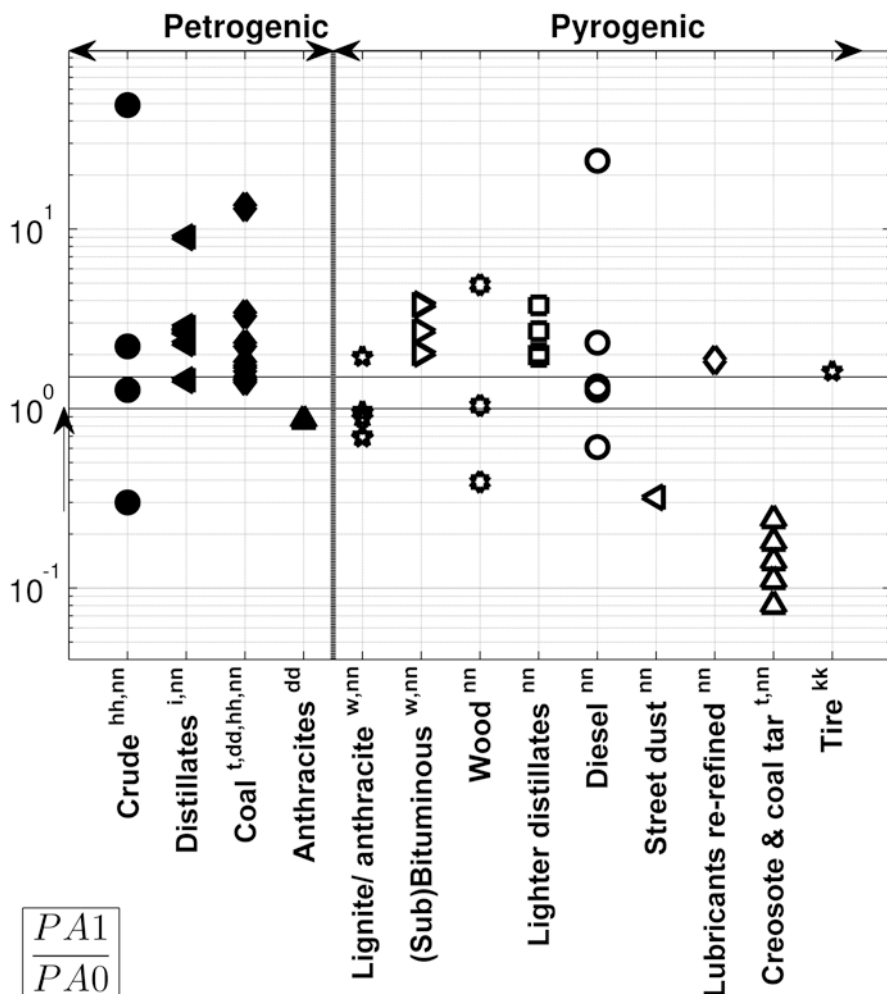


Fig. 10 The ratio of methylalkylated PAHs of PA1 to their parents. See Fig. 9 for the symbols and to the text for explanation

for combustion samples, too (Fig. 10; Yunker et al. 2002). Accordingly, $PA1/PA0 < 1$ indicates the combustion of coal or wood, or weathered urban aerosols. The $PA1/PA0$ ratio is lower (< 0.2) in creosotes or coal tar than in any other pyrogenic or petrogenic sources (Fig. 10) and seems appropriate for differentiating creosotes or coal tar from other sources (Fig. 10).

According to Yan et al. (2005), further study is required to fully exploit the potential of the $PA1/PA0$ ratio for pyrogenic PAH source apportionment. $PA1/PA0$ should preferably be used along with other ratios such as (see also Sect. 5.8): alkyl/ ΣPAH , $FP1/FP0$, $Ring456/TPAH$ (Yan et al. 2005). For petroleum products, Yunker et al. (2002) assumed that the $PA1/PA0$ ratio is more reliable than the $P0/A0$ ratio, especially if the latter has a value close to 9.

5.3.5 Ratio of Methylphenanthrenes to Phenanthrene

After carbonaceous materials are combusted at 600–1,500 °C, phenanthrene dominates over its alkylated homologues, which are negligible (Lehndorff and Schwark 2009). High ratios of methylphenanthrenes (the sum of 1- plus 2-, and optionally 3- plus 9-methylphenanthrenes) over phenanthrene (P1/P0) indicate combustion at low temperatures that preserve the petrogenic alkylation pattern, e.g., fossil fuels, products of petroleum diagenesis, inefficient combustion, etc. (Elmquist et al. 2007; Lehndorff and Schwark 2009; Luo et al. 2008; Mitra et al. 1999; Takada et al. 1990).

In petrogenic sources such as unburned fossil organic material, petroleum, oil shales, and their refined products, the P1/P0 ratio displays values over 2 (Gschwend and Hites 1981; Hwang et al. 2003; Kim et al. 2008; Luo et al. 2008; Takada et al. 1990; Zakaria et al. 2002). When $P1/P0 < 1$ (Budzinski et al. 1997; Hwang et al. 2003; Takada et al. 1990), or $0.4 < P1/P0 < 0.7$, according to Elmquist et al. (2007) a pyrogenic origin may be inferred. Indeed, in Fig. 11, the area of overlap between pyrogenic and petrogenic sources (coal, used lubricants, automobile exhausts) is mainly the interval $1 < P1/P0 < 2$. Because phenanthrene is less stable than its methyl homologues, the degradation of crude or diesel increases the P1/P0 (Burns et al. 1997).

The methylphenanthrenes to phenanthrene ratio has been used to identify pyrogenic or petrogenic hydrocarbon contaminants (e.g., Farrington et al. 1977; Guo et al. 2007; Luo et al. 2008), or, together with the dimethylphenanthrene (DMP) ratio, to trace PAH sources over time (Sect. 5.3.8) (Elmquist et al. 2007). The P1/P0 ratio has also been used to distinguish asphalt from vehicle emissions (along with the D1/P1 ratio—methyl dibenzothiophenes to methylphenanthrenes), and vehicle traffic (0.7 to 8.2) from background domestic pollution (0.7–1.2) in Tokyo (Takada et al. 1990).

Used oil or diesel emissions have both petrogenic (unburned fuel, $P1/P0 > 2$) and pyrogenic (HMW) PAH signatures (Mostafa et al. 2009; Zakaria et al. 2002). Therefore, the P1/P0 ratio is usually higher in diesel vehicle emissions than in gasoline ones (Hwang et al. 2003; Larsen and Baker 2003). Accordingly, Hwang et al. (2003) calculated the diesel and gasoline vehicle contributions to pine needles via a mass balance model. Furthermore, pyrogenic contribution from used crankcase oil could cause the P1/P0 ratio to be correlated with chrysene, benzo[*a*]pyrene, benzo[*ghi*]perylene and the total PAHs (Zakaria et al. 2002).

5.3.6 Distribution of Methylphenanthrenes

Alkylphenanthrene homologues are considered as petrogenic markers and enable petrogenic PAHs to be recognized (Gogou et al. 2000). For example, if $P2 > P1 + P0$ (dimethylphenanthrenes concentration is higher than the sum of the concentrations of methylphenanthrene plus phenanthrene), then the dominant source is petroleum (Gogou et al. 2000; Sicre et al. 1987). However, coal combustion and wood smoke may show maxima in the parent PAH, or the methyl-PAH, or the dimethyl-PAH (Sicre et al. 1987; Yunker et al. 2002). Furthermore, coal PAHs (Fig. S27, Supporting Material) do not follow the “usual” pyrogenic or petrogenic

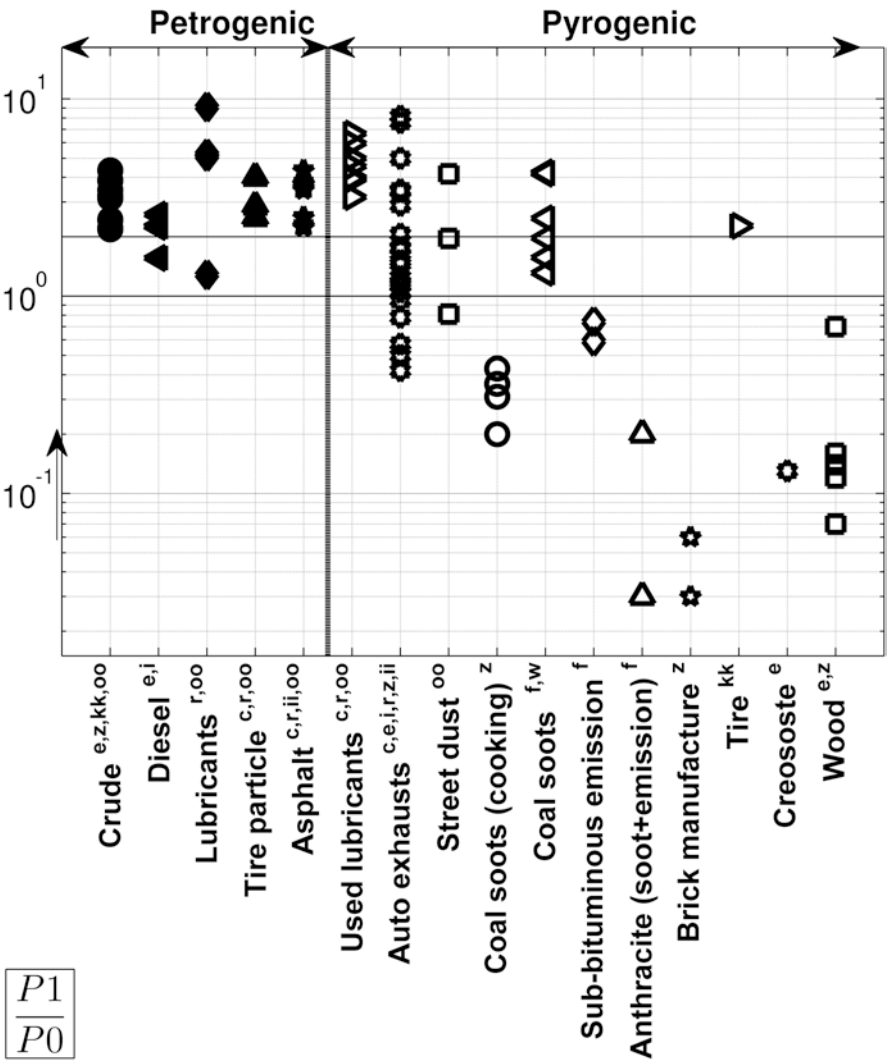


Fig. 11 The ratio of $P1/P0$ for different sources. See Fig. 9 for the symbols and to the text for explanation

distributions, and so other methylphenanthrenic indices (MPIs) such as the $MPI3 = \frac{2 - P1 + 3 - P1}{9 - P1 + 1 - P1}$ are frequently used to distinguish between coals or oils of different thermal maturity (Achten and Hofmann 2009; Boehm et al. 2001; Dzou et al. 1995; Lehnendorff and Schwark 2009; Radke et al. 1982; Stout and Emsbo-Mattingly 2008; Wang and Brown 2009).

Methylphenanthrene (1-, 2-, 3- and 9-P1) ratios of the more stable β isomers to the less stable α isomers (9-, 4- and 1-P1) have been developed for monitoring the thermal maturity of oil and middle distillate fuels (Faksness et al. 2002; Stout et al. 2002; Uhler et al. 2007). The European Committee for Standardization (CEN) includes the ratio of 2-P1/1-P1 (sometimes called the methylphenanthrene ratio or MPR) in its methods for identifying different oil products, such as IFO 380 heavy fuel oil (Hansen et al. 2007; Uhler et al. 2007). However, preferential biodegradation of 2-methylphenanthrene (Faksness et al. 2002) may reduce the value of 2-P1/1-P1, which can then be used as a biodegradation ratio (Wang and Brown 2009). In such a case, caution is necessary when utilizing this biodegradation index for bunker fuels that may represent a blend of different oils and fuels, which consequently have altered physicochemical properties (Wang and Brown 2009).

Another methylphenanthrenic ratio, the 4-P1 + 5-P1/P1, may be used to discriminate wood fires from coal combustion or asphalt (Simcik et al. 1999). Low values of this ratio have been observed for oil (0.02), which can thus be discriminated from other pyrogenic sources (Gschwend and Hites 1981).

5.3.7 Retene

The ratio of retene to chrysene (RET/C0) has been used to apportion softwood (e.g., fir and pine) combustion sources (RET/C0=4.5) and other combustion sources (RET/C0=0.35) (Bogdal et al. 2011; Mathieu and Friesse 2012; Yan et al. 2005, 2007). However, hardwood combustion may significantly reduce the RET/C0 ratio (similar to the dimethylphenanthrene ratio: Sect. 5.3.8), which is insensitive to inputs from the combustion of petroleum or of coal. It is thus recommended to use the RET/C0 ratio together with other ratios such as the DMP ratio (Yan et al. 2005). Roush and Mauro (2009) suggested that the RET/C0 ratio be used to distinguish between coal fines (high value) and coal tar or petroleum products (low value).

Other RET ratios have occasionally been used. Dupree and Ahrens (2007) used the retene to methylpyrene (RET/PY1) (three-/four-ringed alkyl PAHs) ratio to distinguish wood soot in urban runoff samples. The retene to pyrene (RET/PY0) ratio was used to trace wood combustion in air (0.25–0.4) and sediments (Bucheli et al. 2004 and references cited by these authors). The RET/P4 ratio has been used to distinguish different spilled oil products according to the CEN methodology (Hansen et al. 2007). Grimalt et al. (2004) suggested that the ratio of retene to benzo[*b*]naphtho[2,1-*d*]thiophene, can be used together with the DMP ratio to distinguish between wood combustion and sulfur pyrogenic sources such as coal combustion.

5.3.8 Dimethylphenanthrenes

The $\frac{1,7}{1,7+2,6}$ dimethylphenanthrene ratio (DMP ratio) is useful for distinguishing between vehicle emissions and wood combustion. The 1,7-dimethylphenanthrene isomer is thermally unstable relative to 2,6-dimethylphenanthrene (by 3.3 kcal/

mol). As petroleum matures, the DMP ratio decreases; softwood combustion however, is associated with high DMP values (Benner et al. 1995; Gogou et al. 2000; Yunker et al. 2002).

Yunker et al. (2002) suggested that $DMP > 0.7$ indicates strong wood combustion sources, and (Yan et al. 2005, 2007) state that a $DMP < 0.7$ indicates that vehicle/petroleum/fossil fuel or non-softwood emissions are dominant. Others (Lehndorff and Schwark 2009 and references therein) have suggested that a ratio of $DMP < 0.43$ indicates vehicle emissions exclusively. Yunker et al. (2002) point out that DMP ratios in the range of 0.45–0.7 may indicate marine or terrestrial oils, terrestrial source rocks or even a mix of vehicle emissions and wood combustion. Thus, DMP ratios in these ranges may imply multiple mixed sources.

The DMP ratio in aerial particulate matter was used to apportion softwood combustion and motor vehicle emissions (Benner et al. 1995). It has also been used to estimate the present and historic relative contributions of softwood, coal, and petroleum combustion sources to sediments (Yan et al. 2005; Yunker et al. 2002). In these studies, the DMP ratio was used together with the fluoranthene to pyrene ratio. However, for wood and coal combustion the DMP ratio is best used in conjunction with the ratio of retene to chrysene (Yan et al. 2005). The DMP ratio has been used together with the acenaphthylene to acenaphthene (AY/AE) ratio, which is a marker for MGP tars, to distinguish coal soot from coal tar or other sources such as tires, oil, or bitumen (Craig and Mauro 2012; Dupree and Ahrens 2007).

In sources other than softwood combustion, the DMP ratio has a low value and should not be applied to distinguish petroleum or its combustion products, particularly in sediments with background contamination (Bogdal et al. 2011; Yunker et al. 2002). Biodegradation increases the DMP ratio (Jimenez et al. 2006 and references therein). The DMP and RET/C0 ratios may also be compromised by hardwood emissions, which produce lower ratios than softwood emissions (Yan et al. 2005). Therefore, DMP-based source apportionment may be inaccurate in areas affected by multiple combustion sources (Elmqvist et al. 2007; Mandalakis et al. 2004). Yan et al. (2005) have argued that 7,9-dimethylphenanthrene may be used instead of 2,6 DMP to apportion PAHs from fresh bituminous coal and brown-coal smoke. These two substances are present in similar amounts in bituminous sources, although softwood combustion emissions contain much greater amounts of 1,7 DMP than 1,6 DMP.

5.4 Four-Ringed PAHs

5.4.1 The Ratio of Fluoranthene to Pyrene

Similar to the P0/A0 ratio, the fluoranthene to pyrene (FL0/PY0) ratio correlates with the temperature of formation (e.g., Budzinski et al. 1997). Thermodynamically, fluoranthene is less stable than its isomer pyrene (Yan et al. 2005). FL0 is less favored than PY0 under fossil fuel formation conditions (Iqbal et al. 2008). As a result, $FL0/PY0 < 1$ for petrogenic products, except for certain coals, crudes and diesels (Fig. 12).

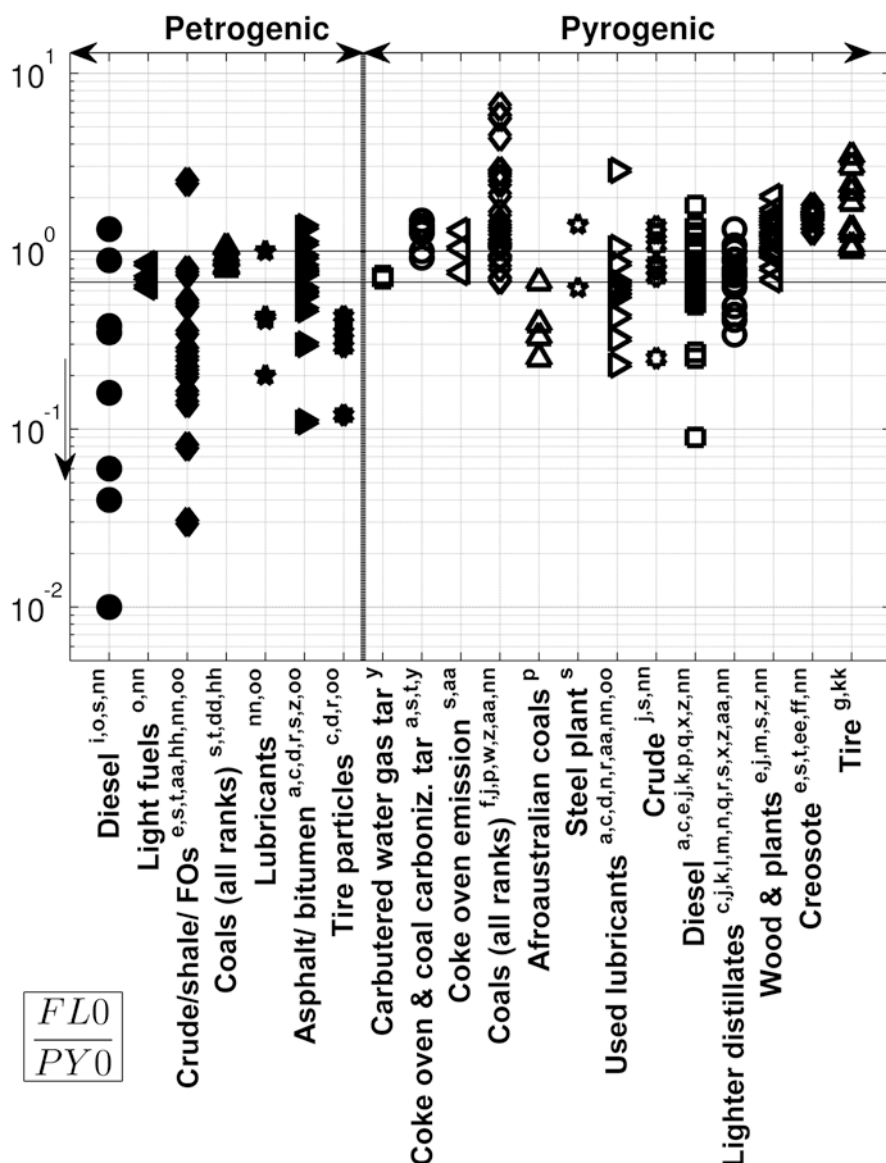


Fig. 12 The ratio of $FLO/PY0$ for different sources. Note that $PY0$ is more prone to biodegradation than FLO . See Fig. 9 for the symbols and to the text for explanation. *FO*: fuel oil

Coal combustion usually yields values of $FLO/PY0$ greater than 1 (Gschwend and Hites 1981; Sicre et al. 1987). Creosotes exhibit a narrow range of $FLO/PY0$ values (Stout et al. 2001a), which also exceed 1 (Fig. 12). Similarly, $FLO/PY0 > 1$ occur for coke oven tars and other pyrogenic materials produced at relatively high temperatures (Costa et al. 2004; Saber et al. 2006).

Pyrogenic sources that could have $FL0/PY0 < 1$ include used lubricants, emissions from automobiles and diesel trucks, and the combustion of gasoline, diesel, fuel oil and crude oil (Fig. 12; Yunker et al. 2002). Accordingly, pyrene can dominate over fluoranthene ($FL0/PY0 = 0.6\text{--}0.8$) in atmospheric urban aerosols (Budzinski et al. 1997; Sicre et al. 1987). Tars from former manufacturing gas plants operating the relatively low-temperature carbureted water gas process also have low $FL0/PY0$ ratios, which typically range from about 0.6–0.8 (Saber et al. 2006).

A relatively reliable threshold could be $FL0/PY0 \leq 0.5$ for petrogenic sources, but diesel combustion and some used lubricants can also have $FL0/PY0$ values below 0.5 (Fig. 12). Ratios between 0.5 and 1.0 are indicative of a mixed source profile, although automobile emissions are also in that interval. If $FL0/PY0 > 1$, then pyrogenic sources such as the combustion of coal or of biomass are probably predominant (Laflamme and Hites 1978; Yan et al. 2005; Yunker et al. 2002). A ratio of 1.2 was used as an upper limit for petroleum sources, depending on the reference oil used (Colombo et al. 1989; Iqbal et al. 2008; Neff et al. 2005).

The $FL0/PY0$ ratio has been used in conjunction with other PAH ratios (e.g., Budzinski et al. 1997; Morillo et al. 2008a) or PAH isotopic signatures (Stark et al. 2003; Yan et al. 2005). Yunker et al. (2002) reported differences between the $FL0/PY0$ ratios of the effluents of waste water treatment plants (WWTP) receiving stormwater and the $FL0/PY0$ ratios of WWTP effluents that did not receive stormwater. These differences (also evident for the indeno[1,2,3-*cd*]pyrene to benzo[*ghi*]perylene ratio) were attributed to the stormwater runoff that contained petrogenic PAH signatures. De Luca et al. (2004) were able to distinguish pyrogenic from petrogenic sources in harbor sediments by using both the $FL0/PY0$ and the phenanthrene to anthracene ($P0/A0$) ratios (De Luca et al. 2004, 2005; Yunker et al. 2002).

The $FL0/PY0$ ratio is more sensitive as a source indicator than the $P0/A0$ ratio (Yunker et al. 2002). The $FL0/PY0$ is probably more reliable at elevated PAH values, but caution is necessary when applying it in heavily industrialized areas that have pyrogenic sources, which exhibit a low value of this ratio (Yan et al. 2006; Yunker et al. 2002). The $FL0/PY0$ pair is more stable than the $P0/A0$ pair over large concentration ranges and in regard to degradation, because both $FL0$ and $PY0$ degrade at almost the same rate in the atmosphere and in other matrices (Behymer and Hites 1988; Budzinski et al. 1997; Costa and Sauer 2005; Saber et al. 2006; Uhler and Emsbo-Mattingly 2006; Yunker et al. 2002). Nevertheless, $FL0$ is more difficult for organisms to metabolize and is not easily photodegraded (Behymer and Hites 1988; Yunker et al. 2011), but is more prone to evaporation and dissolution than $PY0$ (Table 2). In contrast, $FL0$ biodegrades preferentially over $PY0$ in soil (Tobiszewski and Namiesnik 2012 and references therein).

5.4.2 Other Fluoranthenic and Pyrenic Ratios

For petrogenic–pyrogenic discriminations, several less common ratios use fluoranthenic (FLn) and pyrenic (PYn) isomers in conjunction with alkyl PAHs. The ratio of methylfluoranthene plus methylpyrene to pyrene ($FP1/PY0$) can be used to

distinguish pyrogenic (≈ 0.3) from petrogenic (≈ 4) sources (Bucheli et al. 2004). If multiple sources influence the P1/P0 ratio, then the FP1/FL0 ratio can be used to detect anthropogenic inputs (Gustafsson 1997; Pereira et al. 1999 and references therein); in such cases, an FP1/FL0 > 1 indicates petroleum contamination. However, such ratios (e.g., FP1/FL0) may be influenced by weathering (Neff et al. 2005).

Ratios of FP1/FP0 < 1 (Fig. 13) are said to indicate combustion (Yunker et al. 2002). Saha et al. (2009) used a more conservative upper FP1/FP0 value of 0.5 for

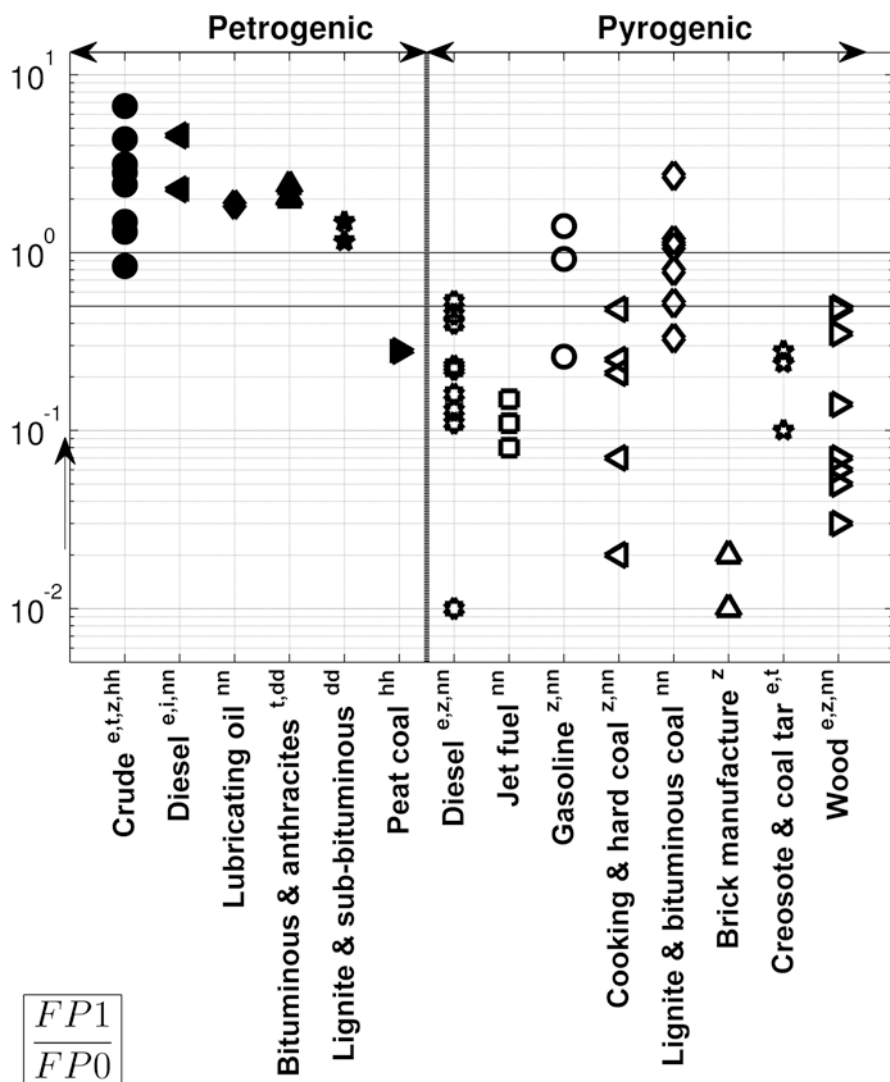


Fig. 13 The ratio of FP1/FP0 for different sources. *Degradation arrow* drawn assuming that parent PAHs are less stable than their alkylated homologues. See Fig. 9 for the symbols and the text for explanation

pyrogenic inputs, probably because $FP1/FP0 < 1$ for some petrogenic sources such as coals (Fig. 13; Yunker et al. 2002). The $FP1/FP0$ and the $PA1/PA0$ ratios may not correlate with emissions from old vehicles (Yan et al. 2006; Yunker et al. 2002). Yunker et al. (2002) suggested that the $FP1/FP0$ ratio is better used for detecting combustion and is less variable than the $PA1/PA0$.

Sporstol et al. (1983) showed that the alkyl fluoranthene plus pyrene (alkylation level: 1-3) homologue distributions of soot and oil differ significantly. The ratios of $\frac{FP0}{FP2 + FP3}$ and $\frac{BC0}{C2 + C3}$ (proportion of alkylated PAHs) were used by Stout et al. (2003) to classify pyrogenic and petrogenic sources. These thermal parameters range from 1.9 to 3.6 for pyrogenic sources, whereas petrogenic values (crudes) range from 0.05 to 0.06 (Stout 2007). In coal tars, the $\frac{FP0}{FP2 + FP3}$ ratio is more prone to changes from evaporation than from biodegradation (Uhler and Emsbo-Mattingly 2006). Thus, caution is advised when applying $FP0/FP2 + FP3$ to different matrices.

Methylpyrenes and benzofluorenes (MW 216) are relatively stable isomers that are suitable for comparing light fuel oils (e.g., gas oil), which rapidly degrade in the environment (Dahlmann 2003; Hansen et al. 2007; Uhler and Emsbo-Mattingly 2006). In addition, the ratios of benzo[*a*]fluorene/4-PY1, benzo[*b+c*]fluorene/4-PY1, 1-PY1/4-PY1 and 2-PY1/4-PY1 are recommended in the oil spill identification methodology of the European Committee for Standardization (Hansen et al. 2007).

Roush and Mauro (2009) used the benzofluorenes to methylpyrene ratio to exclude petroleum as having contaminated soils and sediments. Contamination from coal tar or creosote is possible if this ratio is >1 . Craig and Mauro (2012) reported that, in sediments contaminated with coal tar, the ratio of benzo[*b+c*]fluorene to monomethylpyrenes is little changed by weathering and can be used to discriminate sources such as coal tar (3.9) and MGP tar (1.5).

The PAH pyrogenic indicator (PPI)—not to be confused with the pyrogenic index (Sect. 5.8)—is the $\frac{P2 + P3 + P4}{FP0}$ ratio (Fig. 14). It reflects the relative abundance of petrogenic PAHs and decreases as the pyrogenic contamination increases (Bence et al. 2007; Luo et al. 2008; Page et al. 1999). According to Neff et al. (2005), the PPI is almost always higher than 9 for petrogenics (50–100 for Exxon Valdez crude at different stages of weathering) and lower than 0.3 for pyrogenic PAHs. If $TPAH > 0.1$ $\mu\text{g/g}$, and $PPI < 4$, then the PAH contamination probably has a pyrogenic component (Bence et al. 2007; Neff et al. 2006; Page et al. 1999). Values of PPI for wood burning and creosote have also been reported (Fig. 14; Neff et al. 2006; Page et al. 1999).

The PPI has been used to show that forest fire fallout contributed to PAHs in nearshore subtidal sediments (Page et al. 1999). The PPI was used to differentiate petrogenic from pyrogenic PAHs in sediments and biological samples at the site of the 1989 Exxon Valdez oil spill, and also in other cases (Neff et al. 2005, 2006; Pies et al. 2008). Bence et al. (2007) showed that PPI is unaffected by weathering.

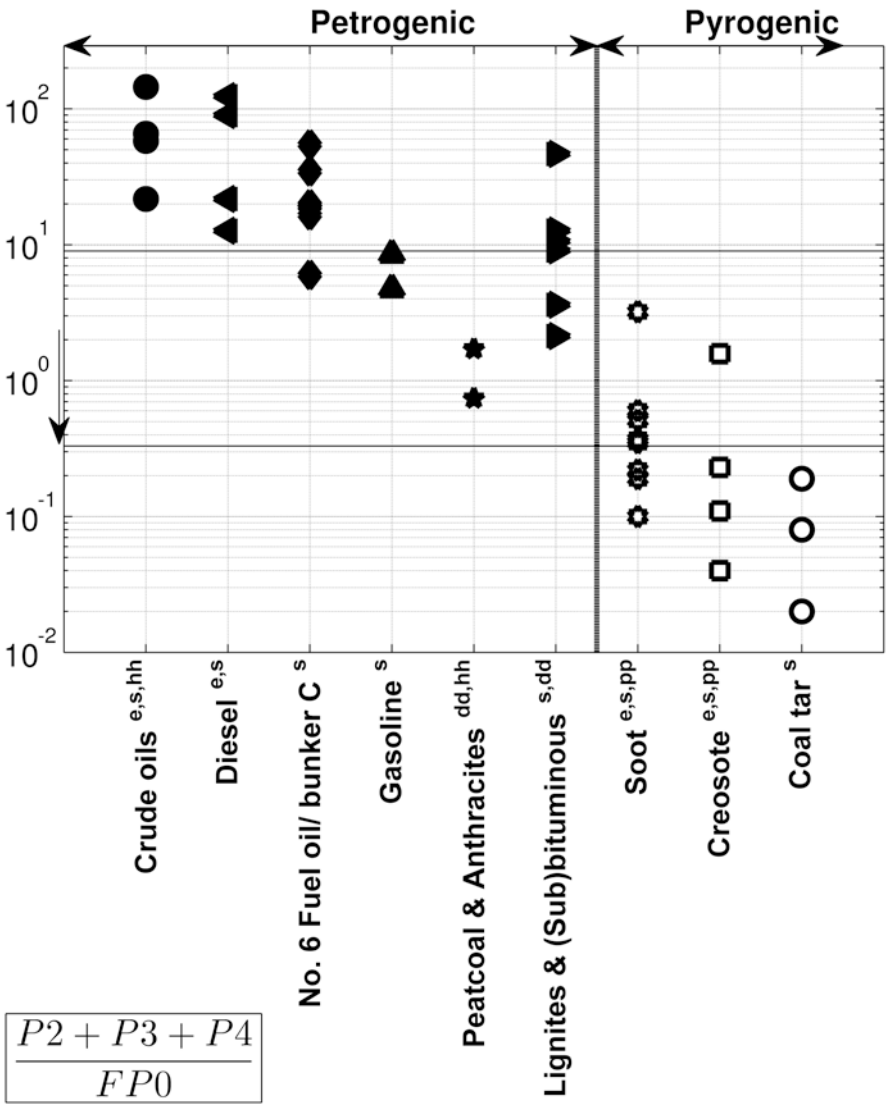


Fig. 14 The ratio of $P2 + P3 + P4 / FP0$ or PPI for different sources. See Fig. 9 for the symbols and the text for explanation

The degradation rates of FL0 and PY0 are similar to that of P4, and when mass losses of spilled oil approach 60%, the PPI is undefined (Bence et al. 2007; Neff et al. 2006). Extensively weathered oils have reduced PPI values which are higher than 5.5 (Neff et al. 2006).

5.4.3 The Ratio of Benz[*a*]anthracene to Chrysene⁶

Benz[*a*]anthracene (BaA) is preferentially produced over chrysene (C0) during the combustion of fossil fuel or of biomass (Dvorska et al. 2011; Yunker et al. 2002). Yunker et al. (2002) have suggested that $BaA/C0 < 0.25$ indicates petroleum sources, $0.25 < BaA/C0 \leq 0.5$ indicates mixed sources and $BaA/C0 \geq 0.5$ indicates combustion (e.g., vehicular emissions). In contrast, De Luca et al. (2004) have suggested that the transition point from petrogenesis to pyrogenesis is at $BaA/C0 = 1$. Nevertheless, the $BaA/C0$ ratio is well above 1 for gasoline and above 0.5 for coals (Fig. 15). Examples of pyrogenic sources below the threshold of 0.5 are creosote and the combustion of some coals, diesel and gasoline. Only anthracite combustion and some combusted diesels have $BaA/C0$ values below 0.25.

The $BaA/C0$ ratio has sometimes been used in conjunction with the IP/*ghi* ratio, to distinguish between automobile and domestic heating sources (e.g., Dvorska et al. 2011; Sofowote et al. 2008), or to apportion the contributions from coal tar and paving bitumen to urban runoff and sediments (Ahrens and Depree 2010; Dupree and Ahrens 2007). BaP/BbF (five-ringed PAHs) and $BaA/C0$ have been successfully used to differentiate Al smelter sludge from creosote pilings (Boehm and Saba 2008). The combination of A0/P0 (the inverse of P0/A0) and the $BaA/C0$ ratio can be used to distinguish between pyrogenic sources and crude oils because both ratios are higher for pyrogenic sources (Wang et al. 1999b, 2001). Sofowote et al. (2009) factorized both the A0/P0 and the $BaA/C0$ ratios into a new ratio that is more robust than both constituent ratios. Zeng and Vista (1997) found that the $BaA/C0$ ratio correlated with the P1/P0 and P0/A0 ratios. However, the $BaA/C0$ ratio correlates only weakly with the FL0/PY0 ratio (De Luca et al. 2004). Yunker et al. (2002) observed negligible amounts of BaA in wood combustion and used the $BaA/C0$ ratio plus the DMP ratio to trace wood combustion.

The $BaA/C0$ ratio is stable over different concentration ranges and aerobic degradation and evaporation conditions (Costa and Sauer 2005; Uhler and Emsbo-Mattingly 2006). However, caution is advised when only the $BaA/C0$ ratio is used to distinguish different types of creosotes in sediments, especially if influences from urban background (lower ratio) or weathering are possible (Mauro 2008; Stout et al. 2003; Yan et al. 2005, 2006). Compared with C0, BaA is more easily photolyzed and has a different environmental behavior (Dvorska et al. 2011; Tobiszewski and Namiesnik 2012; Yunker et al. 2002). Yunker et al. (2002) reported that the photolysis patterns for the $BaA/C0$ and the P0/A0 ratios were similar. Chrysene is the more stable isomer and BaA can convert to C0 during degradation (De Luca et al. 2004; Soclo et al. 2000). Therefore, the applicability of $BaA/C0$ in weathered sediments may be questionable (Stout et al. 2003; Yan et al. 2005; Yunker et al. 2002).

⁶The BaA/228 (i.e., the denominator is the sum of PAHs that have MW = 228) is sometimes used instead of $BaA/C0$, because of the coelution of triphenylene (TPh) and chrysene (e.g., Gogou et al. 2000). In this paper no discrimination is made between the two ratios.

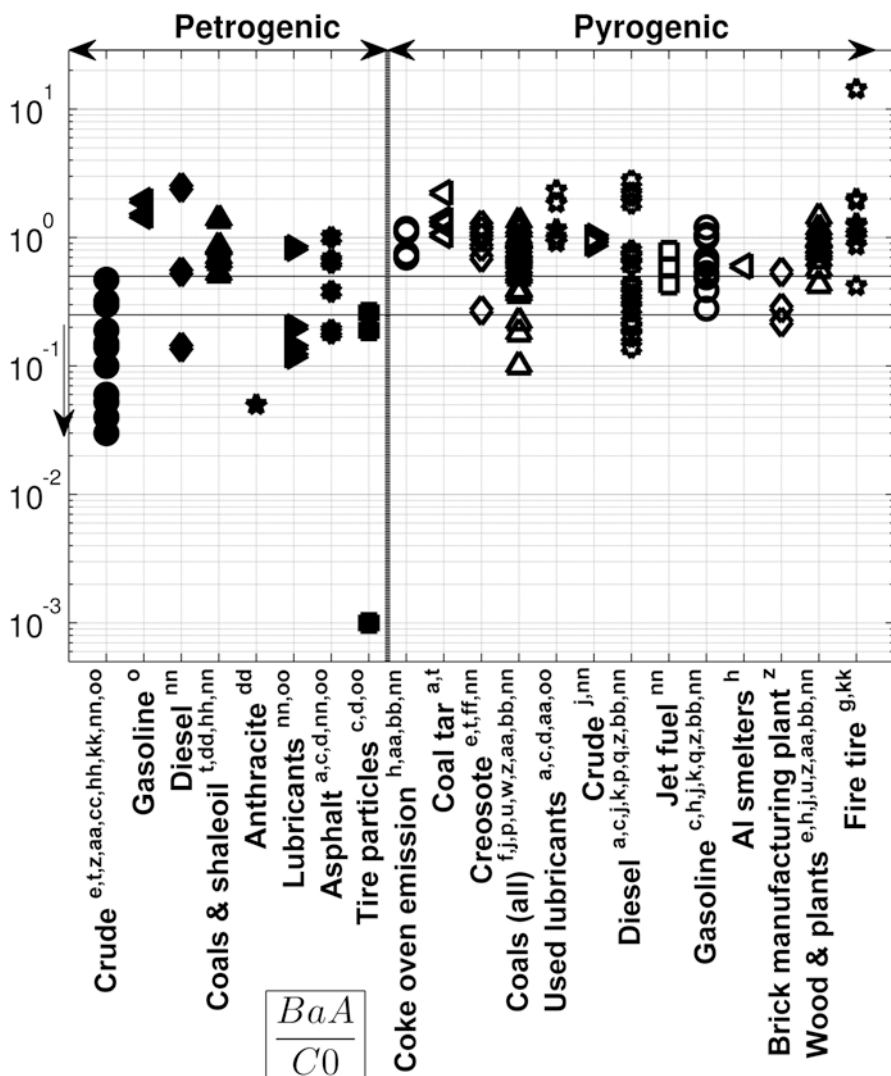


Fig. 15 The ratio of $BaA/C0$ for different sources. See Fig. 9 for the symbols and the text for explanation

5.4.4 Alkylated Chrysenes

Combustion usually yields the characteristic pyrogenic distribution ($C0 > C1 > C2 > C3$) for chrysenes in soots of diesel, wood, coal, refined petroleum products, etc. However, the dominance of parent over alkylated PAHs in diesel soots is unique for chrysenes (Wang et al. 1999b). Other LMW (2–4 ringed) PAHs volatilize and are

incorporated uncombusted into diesel soots, retaining the bell-shaped distribution (Fig. 4 and Fig. S16, Supporting Material), which readily modifies to a $PAH0 < PAH1 < PAH2 < PAH3$ profile during weathering. Furthermore, the ratio of alkylated chrysenes to the *five target alkylated PAH homologues* is significantly higher in diesel soots (0.1–0.2) or in diesel burn residues than in diesel fuel (0.001) or other weathered fuels (Wang et al. 1999b).

Urban background or pyrogenic impact on sediments can be deduced from high ratios of chrysene to dimethylchrysenes (i.e., predominance of non-alkylated parent PAHs over their dimethyl- or ethyl-alkylated equivalents) (Stout et al. 2004). This C0/C2 ratio is minimally affected by degradation, can indicate pyrogenic origin if higher than 1 (Battelle Memorial Institute et al. 2003), and can be used to distinguish between different pyrogenic sources (Roush and Mauro 2009). Similarly, Wang et al. (2001) used the relative distribution of the highly degradation-resistant alkyl (C0 to C3) chrysene series to apportion sources by using mass balance equations.

The $\frac{BC0}{C2 + C3}$ ratio is a measure of the alkylation (Stout et al. 2003) and can be used to determine pyrogenic or petrogenic origin. For example, the contribution of a petroleum component (lubricating oil) to urban background enabled Stout et al. (2003) to distinguish creosote from urban background by using the BC0/C2+C3 ratio. The measured values for the BC0/C2+C3 ratio given by Stout (2007) for contributions to sediments are 0.11–0.12 for crude, 0.28–0.27 for petrogenic and 4.11–7.86 for pyrogenic. In coal tars, the biodegradability of the BC0/C2+C3 ratio is moderate and its evaporability is negligible (Douglas et al. 2007a; Uhler and Emsbo-Mattingly 2006). Saha et al. (2009) suggested that the BC0/BC1 ratio can be used to distinguish pyrogenic (>1) from petrogenic sources. Costa et al. (2004) used the Cn/FPn double ratio plot ($n = 1, 2$) to distinguish MGP tars from background pyrogenic contamination.

Several weathering ratios that use chrysenes have been reported. Degradation increases the ratios C2/P2 and C3/P3 at a relatively constant rate (Barakat et al. 2001; Bence et al. 1996). Additionally, these ratios can assist in discriminating distillates such as diesel (when alkylated chrysenes are absent the ratios approach zero) from unweathered crude oil (Bence et al. 1996). Similarly, the ratio of the C2-C4 alkylchrysenes to the P2-P4 alkylphenanthrenes increases as the weathering proceeds, because phenanthrenes are more soluble in water and are thus removed from the oil faster (Page et al. 2003). In general, ratios of chrysenes to the more degradable two- and three-ringed PAHs can be used to ascertain the weathering state of sediments (partly because of the low solubility of chrysenes in water) (Kim et al. 2008; Page et al. 1999). Such ratios are called weathering ratios (weathering and biodegradation greatly affect them). Weathering-sensitive ratios are usually combined with ratios that are unaffected by weathering, to resolve multiple sources and the extent of weathering (Barakat et al. 2001).

5.5 Sulfur PAH Indices

5.5.1 Ratios of Alkylated Dibenzothiophenes to Alkylated Phenanthrenes

The methyl dibenzothiophene/methylphenanthrene (D1/P1) ratio is an expression of the relative abundance of alkyl-substituted dibenzothiophenes, and has been used to apportion diesel and pyrogenic sources in sediments (Wang et al. 2001). The D1/P1 was used by Takada et al. (1990) to distinguish asphalt (0.78), diesel emissions (0.40) and fuel oil soot (0.05) in street dusts. Used in conjunction with the weathering ratio N2/P2, the D1/P1 ratio was useful for source identification in groundwater samples having dibenzothiophene concentrations >0.07 ng/cm³ (Hegazi and Andersson 2007).

Among the most popular ratios in oil spill identification are the D2/P2 and D3/P3 ratios (Dn/Pn-alkyldibenzothiophene/alkylphenanthrene). They are source ratios (almost constant because the compounds degrade at the same rate). They are also called “the petrogenic source ratios” (because they distinguish different petroleum sources) and “sulfur to non-sulfur ratios” (Wang et al. 1999a). Both ratios vary among products having different sulfur contents (e.g., diesel, crude) (Fig. 16; Fig. S3a, b, Supporting Material) and are useful in identifying such oil sources (e.g., distillate fuels from sour or sweet crude) (Hegazi and Andersson 2007; Stout et al. 2006). Small differences in the crude oil supplied by a refinery may greatly change these ratios (Hostettler et al. 2007; Stout 2007).

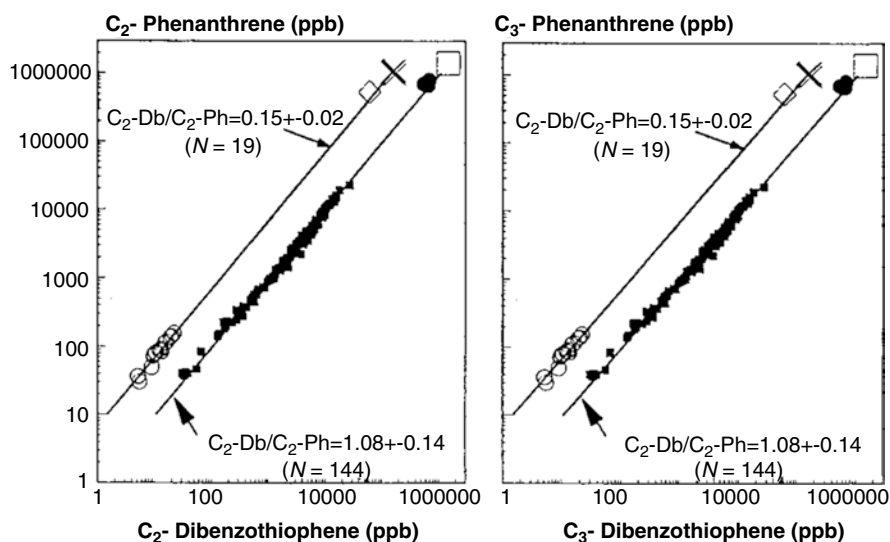


Fig. 16 The discriminating power of the Dn/Pn ratios for different crudes (filled square weathered Exxon Valdez Crude, open circle prespill cores, filled circle Exxon Valdez, multiplication sign Katalla, open square ANS diesel, open diamond Cook Inlet). Adapted from Wang et al. (1999a), with permission, © Elsevier Science BV

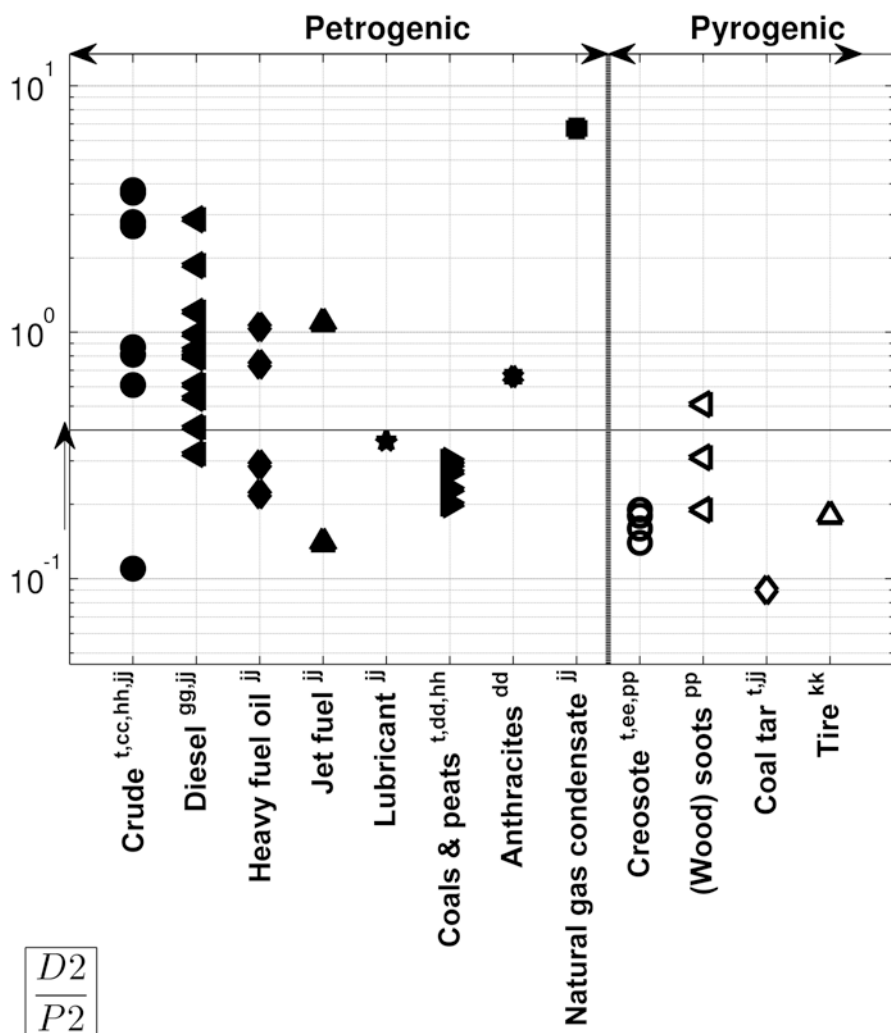


Fig. 17 The ratio of $D2/P2$. Evaporation leads to opposite *degradation arrow* direction (i.e., decreases ratio). See Fig. 9 for the symbols and the text for explanation

Using the double ratio plot of $D2/P2$ versus $D3/P3$, Wang et al. (1999b) sufficiently resolved burn products and diesel fuel. Pyrogenic sources (coal tar, creosote and fire tire wipe) have values below 0.4 for both ratios (Fig. 17; Neff et al. 1998; Stout et al. 2001a; Wang et al. 1999b, 2006). Together with other PAH markers (e.g., $D1$, $FL0$, $PY0$), the Dn/Pn ratios have been used to characterize pyrogenic products mixed with petrogenic ones (Wang et al. 1999a, 2001).

The Dn/Pn ratios have been used to identify petrogenic sources (crudes, diesels, etc.) of different origin; for example, in the studies of the Gulf War and of the 1989 Exxon Valdez oil spills and their weathering products (Hostettler et al. 2007; Kim

et al. 2008; Page et al. 1999; Stout 2007; Stout et al. 2006; Wang et al. 1999a). Page et al. (1996, 1999) applied a two-component mixing model that used both Dn/Pn ratios and apportioned petroleum and background sources. However, this model cannot discriminate a source contribution of less than 3–8%. Similarly, Stout et al. (2006) apportioned different historic oil inputs (diesels of different blends) in non-aqueous phase liquids. Douglas et al. (2007b) used the Dn/Pn ratios in combination with the Nordtest method, to rule out spilled fuel oils in tarballs and mousse samples.

The success of the Dn/Pn ratios as diagnostic tools for heavy fuel oils that contain LMW or HMW PAHs is based on the fact that these ratios are not a strong function of TPAH (Douglas et al. 2007b). However, if all sources have the same sulfur content, or their upper boiling point (bp) is below those of D2, D3, P2, P3 (e.g., kerosene), then the Dn/Pn ratios are not applicable (Stout et al. 2006).

Both Dn/Pn ratios, especially the trimethyl one, are not significantly affected by heavy (bio) degradation—up to 98% depletion of total PAHs—for a range of petrogenic products (Douglas et al. 1996; Uhler and Emsbo-Mattingly 2006). Wang et al. (1999b) noted that both combustion and heavy degradation decrease the Dn/Pn . Natural weathering, long-term biodegradation and photo-oxidation will increase the Dn/Pn ratios, but evaporation is thought to slightly decrease them, rendering them inapplicable for source characterization (Hegazi and Andersson 2007; Kim et al. 2008; Page et al. 1999; Stout et al. 2006; Uhler and Emsbo-Mattingly 2006; Wang et al. 1999a, b).

Costa et al. (2004) used a version of the Dn/Pn ratio slightly modified by the addition of the respective anthracenic homologues to the denominator to distinguish between background and petroleum contamination. The $D3/PA3$ and $D2/PA2$ (alkyldibenzothiophenes to the sum of alkylphenanthrenes and alkylanthracenes, all with the same alkylation degree) are slightly affected by weathering and biodegradation of coal tars in the laboratory, although in field samples, degradation can significantly alter such ratios (Douglas et al. 2007a; Uhler and Emsbo-Mattingly 2006).

5.5.2 Other Dibenzothiophenic Ratios

The $D3/P3$ ratio in conjunction with the Dn/Cn ($n=2, 3$) ratios has been used to describe oil depletion and identify sources in subtidal sediment data (Hegazi and Andersson 2007; Stout et al. 2002; Wang and Fingas 2003; Wang et al. 1999a). Furthermore, the double ratio plot of $P2/P3$ versus the $D2/D3$ has been used as a weathering index for oil residues from the Exxon Valdez oil spill (Hegazi and Andersson 2007 and references therein).

5.5.3 Alkyldibenzothiophene and Benzonaphthothiophene Distributions

The distribution of methyldibenzothiophenes (1-D1, 2-D1, 3-D1, 4-D1) is characteristic for particular crudes, and the methyldibenzothiophene ratios exhibit excellent consistency with weathering (so they can be used as weathering ratios), even for

burned oils (Hegazi and Andersson 2007; Wang and Fingas 1995). Wang and Fingas (1995, 2003) established a database of the methyl dibenzothiophene ratios for crudes, weathered and biodegraded oils, and other petroleum products. The ratios pair of $\frac{1-D1}{4-D1}$ versus $\frac{2-D1+3-D1}{4-D1}$ exhibits a satisfactory discriminating ability for different oils (Hegazi and Andersson 2007). Alternatively, such ratios may be used as biodegradation indicators, because 1-D1 is most affected by biodegradation, whereas 2-D1 and 3-D1 are the least affected by biodegradation (Faksness et al. 2002; Hegazi and Andersson 2007). Therefore, prior knowledge of the weathering state of a sample is necessary before the methyl dibenzothiophene ratios can be used either as source or weathering indicators (Wang and Fingas 1995). Furthermore, the 1-D1/4-D1 ratio correlates with coal vitrinite reflectance (Dzou et al. 1995; Hansen et al. 2007; Stout and Emsbo-Mattingly 2008). As the coals mature, the value of the 1-D1/4-D1 increases, because the less stable 4-D1 decreases (Dzou et al. 1995).

The dimethyl dibenzothiophenes, together with the methyl dibenzothiophene distributions, may further assist in the identification of oils (Hegazi and Andersson 2007), or to distinguish between coal combustion and automobile emissions (Allan 1999; Marvin et al. 2000 and references therein). According to these authors, the D1/D0 ratio is distinct for diesel emissions (1.6–2.9) and coal tars or coke oven condensates (0.11–0.18). Similarly, the D2/D0 ratio ranges from 2.7 to 4.2 for diesel vehicles, vs. a range of 0.03–0.04 for coal tars and coke oven condensates. Allan (1999) points out that coke oven emissions yield $D2/D0 < 2.4$. The D2/D0 ratio is increased by biodegradation, solubilization and evaporation, whereas photo-oxidation decreases it (Allan 1999).

Benzonaphthothiophenes are sometimes used for source discrimination tasks. For example, the ratio of IP to benzo[*b*]naphtho[2,1-*d*]thiophene has been used to distinguish vehicle emissions (<0.4) from urban heating sources (>0.9) in Gliwice, Poland (Bylina et al. 2005). However, this ratio is insensitive to coke oven emissions. Allan (1999) reported that the benzo[*b*]naphtho[2,1-*d*]thiophene/benzo[*b*]naphtho[2,3-*d*]thiophene is characteristic for diesel emissions (>3.2), whereas coal tar or coke oven emissions exhibit lower values of this ratio. For such sources, D0 and dibenzonaphthothiophene ratios are far superior to other PAH ratios (BeP/BaP, *ghi*/BeP, BkF/BeP, *ghi*/BaP) (Allan 1999).

5.6 HMW Five- and Six-Ringed PAHs

5.6.1 Ratio of Benzo[*e*]pyrene to Benzo[*a*]pyrene

The benzo[*e*]pyrene/benzo[*a*]pyrene (BeP/BaP) ratio is indicative of aging particles when >1, and has been used as a photodegradation indicator in atmospheric aerosols (Okuda et al. 2002; Tan et al. 2009; Tobiszewski and Namiesnik 2012). The BeP/BaP ratio is not affected by biodegradation and evaporation in sediments, tarballs, tars and in creosote-contaminated sites (Costa and Sauer 2005; Stout et al. 2003; Uhler and Emsbo-Mattingly 2006; Zakaria and Takada 2007).

Together with the FL0/PY0 ratio, the BeP/BaP has successfully been used to differentiate MGP tar residues from background contamination (Costa et al. 2004), and other combustion sources (Dickhut et al. 2000). Ahrens and Depree (2010) discriminated bitumen from coal tar in sediments by using the BeP/BaP ratio in conjunction with IP/*ghi* and BaA/C0.

The literature ratios of BeP/BaP are >1 for most petrogenic sources, except for some coals (Fig. 18). BeP/BaP is usually <2 for pyrogenic sources, and this

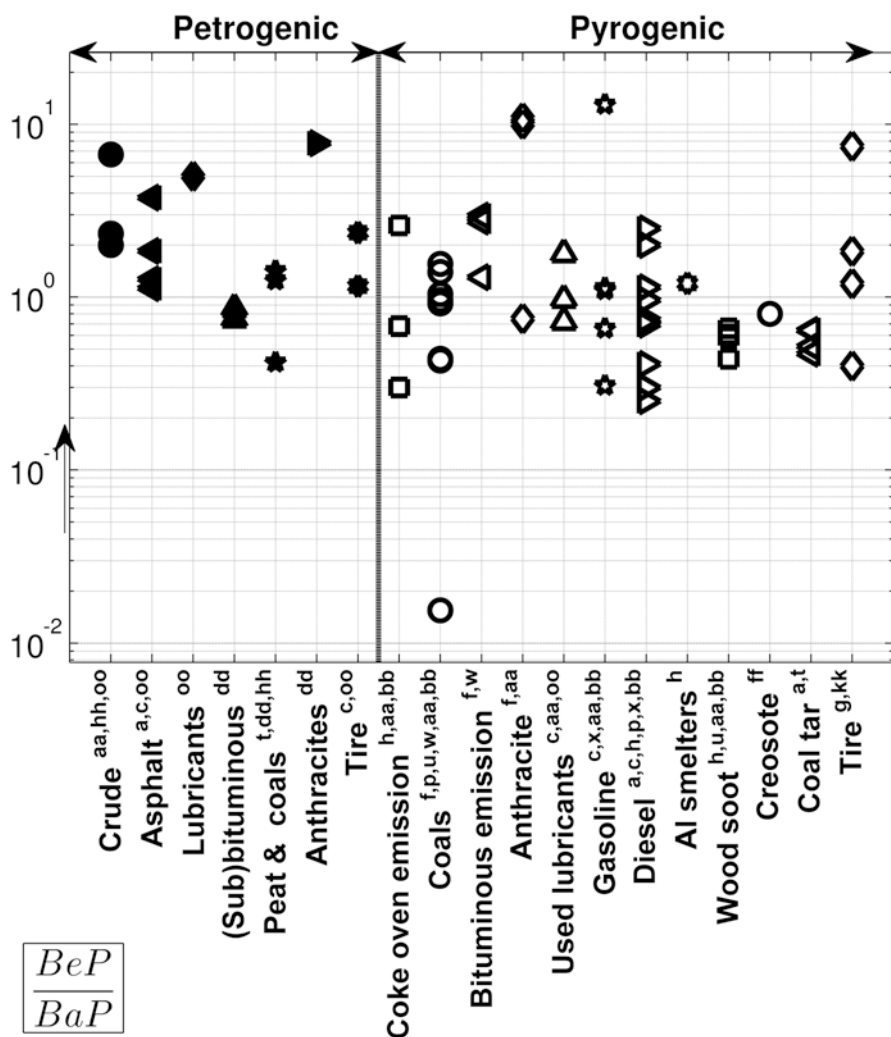


Fig. 18 The ratio of BeP/BaP for different sources. See Fig. 9 for the symbols and the text for explanation

range overlaps with the range of BeP/BaP in petrogenic sources. The combustion of bituminous and anthracite coals yields BeP/BaP ratios higher than 1.5 and 2.5, respectively. The combustion of diesel and gasoline occasionally yields higher ratios. Therefore, a limited number of sources may be discriminated by using the BeP/BaP ratio (e.g., wood soots seem to have a narrow range for BeP/BaP; Fig. 18). Further study is necessary to verify the applicability of the BeP/BaP ratio under environmental conditions, especially in regard to the reactivity of BaP in air (Abrajano et al. 2003). Thus, the BeP/BaP ratio is suitable for non-atmospheric pyrogenic characterization (BeP/BaP < 1) because of the low concentrations of these isomers in petrogenic products (e.g., fuel oils, crudes) and because sediments protect BeP and BaP from degradation to the same degree.

5.6.2 Ratio of Benzo[*b*]fluoranthene to Benzo[*k*]fluoranthene

The ratio of benzo[*b*]fluoranthene to benzo[*k*]fluoranthene (BbF/BkF) has been used to differentiate between two or more pyrogenic sources in urban soils or in sediments (e.g., Morillo et al. 2008b; Walker and Dickhut 2001). The BbF/BkF has distinct values for pyrogenic emissions for an aluminum smelter (2.5–2.9), coke oven (3.7), motor vehicles (1.3), creosote (1.2) and wood soot (0.9) (Dickhut et al. 2000; Fig. 19; Stout et al. 2003; Tobiszewski and Namiesnik 2012). BbF/BkF correlates with coal rank or with other petrogenic PAHs (Jiang et al. 2009; Stout and Emsbo-Mattingly 2008).

Weathering or urban background may limit the applicability of BbF/BkF for different creosote types (Stout et al. 2003). However, under aerobic degradation and evaporation conditions, the BbF/BkF ratio is minimally influenced (Uhler and Emsbo-Mattingly 2006).

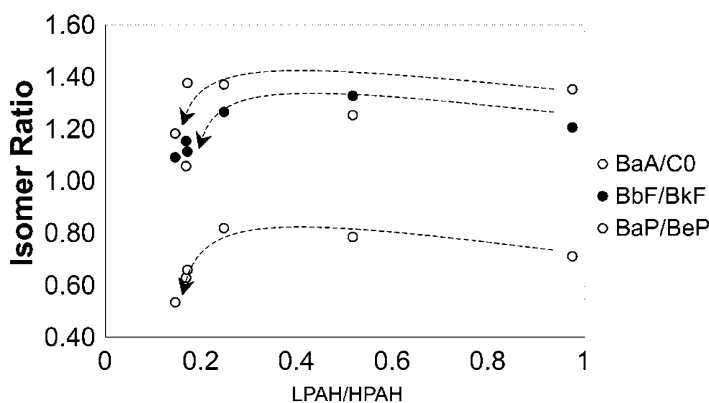


Fig. 19 LPAH/HPAH as a proxy of weathering and how certain ratios may be compromised after weathering. See Table 1 for PAH abbreviations. Adapted from Stout et al. (2003)

5.6.3 Perylene

Perylene (PER) ratios are useful for discriminating between natural and coal-derived PAHs. Low abundance of PER (<10% of TPAH, or of total five-ringed PAHs) may indicate non-natural production (Calvacante et al. 2009; Gogou et al. 2000; Wang et al. 2014). Conversely, high amounts of perylene (>10% of TPAH) indicate that the PAHs have a natural origin, and when PER is >10% of the total five-ringed PAHs, the main PER source is regarded to be diagenesis under reducing conditions (Boll et al. 2008; Calvacante et al. 2009; Fan et al. 2011; Stout et al. 2001a). The relative abundance of PER over five-ringed PAHs ($B[b+k]F + BaP + BeP + DA$) has been used to identify whether the PAH contamination in intertidal sediments in Brazil was of natural or petrogenic origin (De Fatima et al. 2007), and to estimate the contribution of fluvial PAHs to coastal sediments (Luo et al. 2008).

The PER/BeP (Gogou et al. 2000) and PER/BaP (Stout et al. 2001a) ratios can be used to identify that PAHs have a natural origin. The PER/PY0 ratio has been used by Abrajano et al. (2003) to indicate diagenetic origin for retene. If such ratios are high, the PER is from natural or petrogenic sources (e.g., coals). The PER/BaP ratio is recalcitrant under aerobic and evaporative conditions in sediments (Uhler and Emsbo-Mattingly 2006).

5.6.4 Ratio of Indeno[1,2,3-*cd*]pyrene to Benzo[*ghi*]perylene

The indeno[1,2,3-*cd*]pyrene/benzo[*ghi*]perylene (IP/*ghi*) ratio has been used by several researchers to distinguish/apportion distinct pyrolytic sources (and, specifically, automobile sources) of contamination in sediments (Agarwal 2009; Larsen and Baker 2003; Magi et al. 2002; Morillo et al. 2008b; Park et al. 2002; Sicre et al. 1987; Van Drooge et al. 2012; Zhang et al. 2005). Examples include automobile exhausts, gasoline emissions, coal-fired domestic heaters, biomass combustion and other forms of combustion. Sometimes the IP/*ghi* ratio is studied in conjunction with the dimethylphenanthrene ratio (DMP), the BaA/C0 or the FL0/PY0 ratios (Dvorska et al. 2011; Walker and Dickhut 2001; Yunker et al. 2002).

In Fig. 20, the IP/*ghi* is greater than 0.25 for most pyrogenic sources except for used lubricants and the combustion of gasoline, of jet fuel, and occasionally of diesel. If such specific sources are absent, an IP/*ghi* < 0.25 implies strong petroleum inputs (Yunker et al. 2002). If $0.25 < \text{IP}/\text{ghi} < 1$, mixed sources are possible. Ratios > 1 imply combustion sources if certain petrogenics (e.g., asphalt, tire particles, coals) are excluded. Wood and coal combustion may be discriminated by the IP/*ghi* ratio, but they sometimes yield IP/*ghi* < 1 (Fig. 20; Guillon et al. 2013). Furthermore, patterns for pyrogenic sources (e.g., automobile) are hardly distinguishable from each other in Fig. 20 because IP/*ghi* ratios for vehicle, diesel emissions and other pyrogenic sources overlap. For this reason, PAH patterns from local sources should be scrutinized before the IP/*ghi* is used as a pyrogenic indicator for atmospheric emissions.

It has been argued that there is uncertainty about the IP/*ghi* ratio, its threshold values, and its correlation with other ratios (Yunker et al. 2002). Yan et al. (2006) reported that the IP/*ghi* had little to no correlation with the $\delta^{13}\text{C}_{\text{py}}$ or with the FL0/

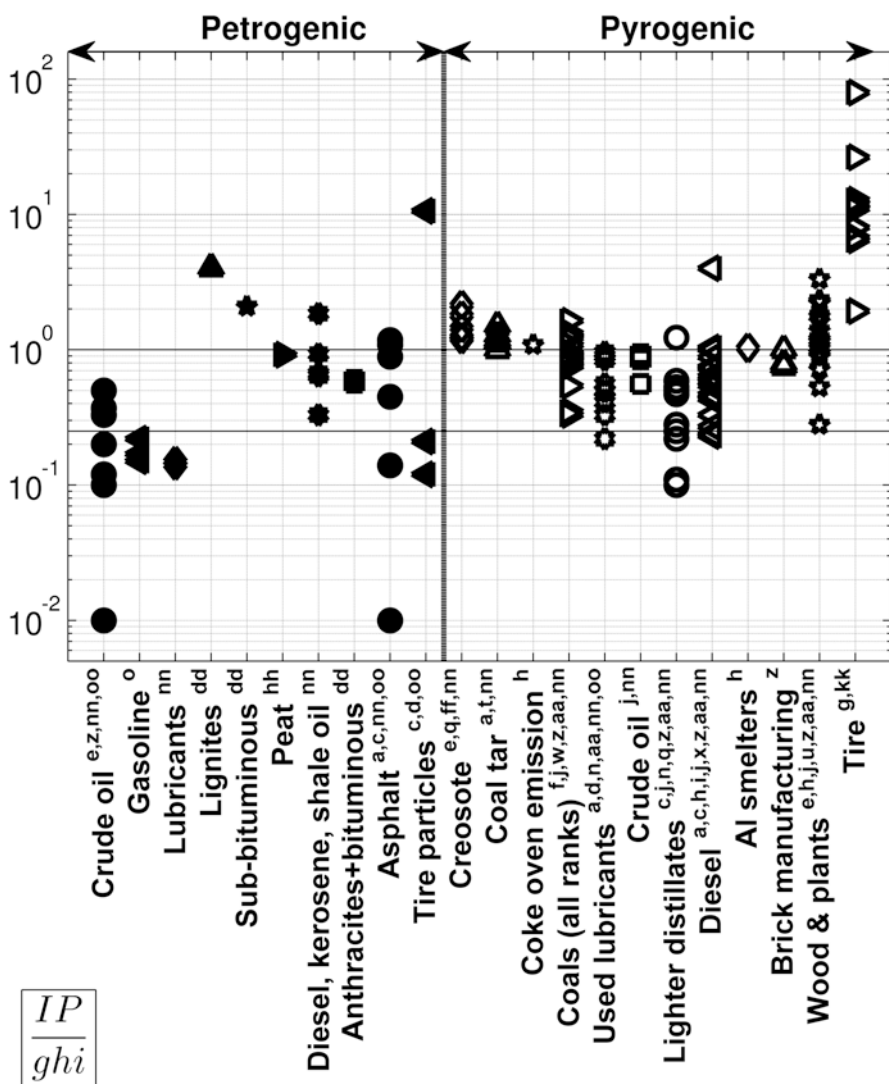


Fig. 20 The ratio of IP/ghi for different sources. Degradation depends heavily on particle color for pyrogenics and is highly variable. See Fig. 9 for the symbols and the text for explanation

PY0 in New York sediments. By means of fugacity model calculations, Zhang et al. (2005) classified the IP/ghi ratio as being superior to $FL0/PY0$, $A0/P0$, BaP/ghi , BbF/BkF and $BaA/C0$ for source apportionment in different media, when the contamination resulted from atmospheric emissions. Uhler and Emsbo-Mattingly (2006) reported that the IP/ghi ratio is stable in tar-contaminated sediment under aerobic and evaporation conditions. However, weathering and urban background may render the IP/ghi not applicable to creosote characterization (Stout et al. 2003).

A probable explanation for the uncertainty of the IP/*ghi* is the differential degradation of the two PAHs in the atmosphere. Both isomers degrade at about the same rate when they are attached to black particles, but IP attached to gray particle degrades faster than *ghi*, whereas IP attached to white particles degrades more slowly than *ghi*, and IP attached to red particles degrades more variably than *ghi* (Behymer and Hites 1988). Other studies have also suggested that particle association is very important for understanding photodegradation effects on the IP/*ghi* ratio (Tobiszewski and Namiesnik 2012 and references therein).

5.7 Non Isomer Ratios

According to Costa and Sauer (2005), when the more recalcitrant PAH isomer pairs (e.g., 4ring/4ring or 5ring/5ring) cannot provide enough resolution in double ratio plots, then non isomer ratios (e.g., five- over six-ringed PAHs) may be used. It is also possible to input non isomer ratios into a PCA/PMF model. For such a case, Christensen and Tomasi (2007) proposed an external normalization of the ratio (i.e., using a reference material).

5.7.1 Ratios of Five- to Six-Ringed PAHs

Some authors (Boitsov et al. 2009; Bucheli et al. 2004) have found that the BaP/*ghi* ratio is correlated with pyrogenic PAHs, whereas other researchers (Alam et al. 2013; Bucheli et al. 2004; Jiang et al. 2009; Ravindra et al. 2008) have investigated whether traffic sources in soils can be discriminated (e.g., by a BaP/*ghi* ratio < 0.6) from the combustion of coal, wood or oil. Jiang et al. 2009 used both the BaP/*ghi* and the IP/*ghi* ratios to identify PAHs from automobile exhausts. Lehnendorff and Schwark (2004) used the BaP/*ghi* ratio together with the FL0/PY0 ratio to investigate biomass burning (indicated by a high ratio). The BaP/*ghi* ratio is prone to photodegradation, as BaP decomposes faster in the atmosphere (e.g., Alves et al. 2009). The literature data in Fig. 21 show the low discriminating power of the BaP/*ghi* ratio. For example, the BaP/*ghi* ratio for traffic sources has intermediate values that overlap the values of other pyrogenic and petrogenic products. Nevertheless, the BaP/*ghi* ratio may be used in certain situations, for example, when PAH sources are limited and have BaP/*ghi* values in a relatively narrow range (e.g., wood combustion, some coals, etc.; see Fig. 21).

Another traffic indicator, the ratio of BeP/*ghi*, is sometimes studied together with the IP/*ghi* (Alves et al. 2009; Tan et al. 2009). In a study conducted in Malaysia (Okuda et al. 2002), BeP/*ghi* values for diesel vehicles (1.1), gasoline vehicles (0.4), wood burnings (0.9), smoke hazes (0.3) and coal burnings (2.2) were reported. Therefore, BeP/*ghi* has been used to discriminate traffic sources, specifically gasoline, from non-traffic sources such as wood burning (Jensen et al. 1993; Larsen and Baker 2003; Okuda et al. 2002).

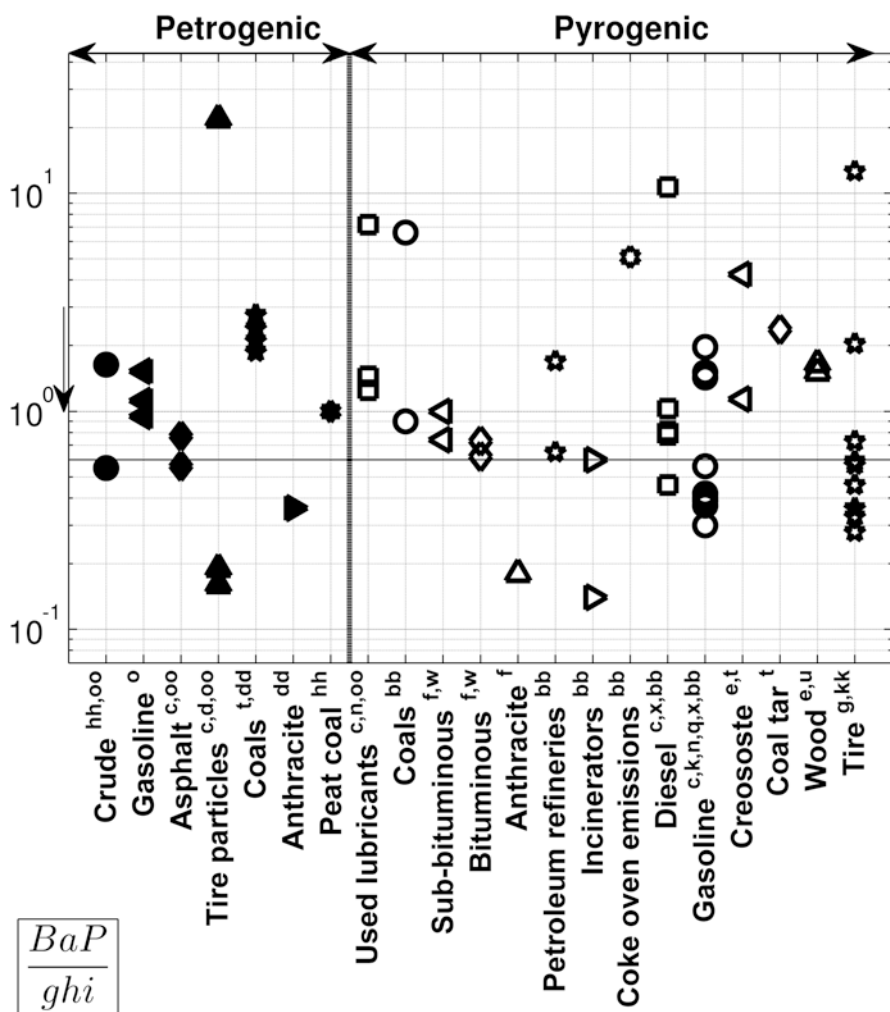


Fig. 21 The ratio of BaP/ghi for different sources. See Fig. 9 for the symbols and the text for explanation

Together with the BeP/ghi ratio, the Cor/BeP ratio (six over five rings) has been used to distinguish or apportion traffic sources (1.8) and non-traffic sources (0.3) (Daisey et al. 1986; Jensen et al. 1993; Larsen and Baker 2003 and references cited by these authors). When doing so, there are two equations to be solved simultaneously (Larsen and Baker 2003). Applying this method at different locations revealed significant differences for the Cor/BeP ratio (>20%). Thus, location-specific source inventories are required prior to application. If only the Cor/BeP is available, then it can be assumed that the excess BeP is unrelated to traffic (Larsen and Baker 2003). Alternatively, the Cor/IP ratio may be used to distinguish gasoline from wood burnings (Okuda et al. 2002).

5.7.2 Ratios of Four- to Five-Ringed PAHs

The benz[*a*]anthracene/benzo[*a*]pyrene (BaA/BaP) ratio is little influenced by photodegradation and has been used (sometimes together with the FL0/PY0 ratio) to identify enhanced industrial emissions or to distinguish diesel or wood emissions from gasoline emissions (Lehndorff and Schwark 2004; Zhu et al. 2011). The BaA/BaP ratio may be adequate to distinguish coal tar and creosote residues from urban background PAHs (Costa and Sauer 2005; Costa et al. 2004). Wood combustion has a BaA/BaP ratio of about 1 (Lai et al. 2011 and references therein).

Low pyrene/benzo[*a*]pyrene (PY0/BaP) ratios indicated a negligible contribution of terrigenous flows into the aquatic system, whereas PY0/BaP > 10 indicated petrogenic sources (De Luca et al. 2004). The PY0/BaP ratio may be used to discriminate coal from wood combustion, but may not be applied to discriminate between combustion products of different wood species (Guillon et al. 2013). PY0/BaP values have been reported for diesel (≈ 10), gasoline emissions (≈ 1) and wood combustion (≈ 0.7) (Lai et al. 2011; Ravindra et al. 2008 and articles cited by these authors).

5.8 Assignment of PAHs to Sources

One way to estimate the different source contributions to a sample is to empirically classify PAHs into pyrolytic, petrogenic or natural, even if some PAHs could have more than one origin (Page et al. 2006; Stout et al. 2004; Table 3). For instance, a typical urban background sediment containing approximately 74% of pyrogenic and 26% of petrogenic PAHs is distinctly different from some pyrogenic fingerprints (Battelle Memorial Institute et al. 2003). Assignment of PAHs to sources depends on the specific region examined (local sources) and on the analytical methods applied (number of PAH analytes), which is why the lists of PAHs assigned to sources differ between different studies (Jeanneau et al. 2008).

5.8.1 PCA/PMF Classification

PAH classification schemes occasionally emerge from a successful discriminant analysis application for a certain contamination case. The resulting compilation of PAH indices may have a local or wider applicability, and offers adequate resolution,

Table 3 PAH apportionment to sources according to Stout et al. (2004)

Pyrogenic	Petrogenic	Mixed	Biogenic
A0, FL0, PY0, FP1, BaA, C0, C1, BbF, BkF, BeP, BaP, IP, DA, ghi	N0, N1, N2, N3, N4, B, F0, F1, F2, F3, AE, AY, DF, PA2, PA3, PA4, D0, D1, D2, D3, D4, FP2, FP3, C2, C3, C4	C0, PA1	PER

See Table 1 for PAH abbreviations

particularly in non-trivial cases, e.g., when urban background has to be discriminated from a petrogenic or, more often, a pyrogenic source. Using PMF in conjunction with PCA for the EPA16 PAHs and advanced chemical fingerprinting, Stout and Graan (2010) differentiated between creosote and urban background runoff. One confounding factor contributing to PAH contamination was two four-ringed parent PAHs (FP0). The other factor was eight HMW PAHs (BaA, C0, BbF, BkF, BaP, IP, DA, *ghi*). An increase in the abundance of the eight PAHs was attributed not to weathering, but to increased urban contribution.

Walker and Dickhut (2001) intrigued by abundances of FP0 (MW=202) or of the isomer sum BbF+BkF+BeP+BaP+PER (MW=252), plotted ratios of these sums to the parent compounds that have MW=202-276 (i.e., FL0+PY0+BbF+BkF+BeP+BaP+PER+IP+DA). Using double PAH ratio plots and PCA, they showed that both isomer-sum ratios ($\Sigma\text{PAH}_{202}/\Sigma\text{PAH}_{202-276}$ and $\Sigma\text{PAH}_{252}/\Sigma\text{PAH}_{202-276}$) explained a significant proportion of the variability (1st principal component). These results show that parent PAH compilations (e.g., fluoranthene-pyrene pair and HMW PAHs) are suitable for discriminating pyrogenic sources. However, it remains important to consider the influence of weathering or urban background when interpreting the results, in order to attribute the explained variability to the correct source factor (Stout et al. 2003; Walker and Dickhut 2001).

5.8.2 Low Versus High Molecular Weight Parent PAHs

A numeric index related to the pyrogenic-petrogenic differentiation into LMW and HMW PAHs is the ratio of these PAH fractions (De Luca et al. 2004; Fig. 22; Magi et al. 2002; Soclo et al. 2000):

$$L / H = \frac{\text{PA0} + \text{FP0}}{\text{BaA} + \text{C0} + \text{BkF} + \text{BaP} + \text{IP} + \text{DA} + \text{ghi}}$$

Others (Boonyatumanond et al. 2007; Zakaria et al. 2002) add P1 to “L”, and B[b+j]F, BeP, and optionally, Cor and PER to “H”, without the DA.

In some studies (De Luca et al. 2004; Karlsson and Viklander 2008; Mathieu and Friese 2012), the EPA 16 are divided into low molecular weight (LPAH, i.e., naphthalene to anthracene, 2-3 rings) and high molecular weight PAHs (HPAH, i.e., fluoranthene to indeno[1,2,3-*cd*]pyrene, 4-6 rings):

$$\text{LPAH} / \text{HPAH} = \frac{\text{N0} + \text{AE} + \text{AY} + \text{F0} + \text{PA0}}{\text{FP0} + \text{BC0} + \text{BbF} + \text{BkF} + \text{BaP} + \text{IP} + \text{DA} + \text{ghi}}.$$

Chen and Chen (2011) add 2-P1 to the numerator. Stout et al. (2003) used all quantified compounds, including alkylated ones. The LPAH/HPAH ratio has been reported for several substances, including gasoline, diesel fuel, used lubricating oil and bitumen (Fig. 23; Karlsson and Viklander 2008). The ratio can differ for different brands of gasoline, diesel, and oil, depending on the differences in the crude oil properties and refinery processes.

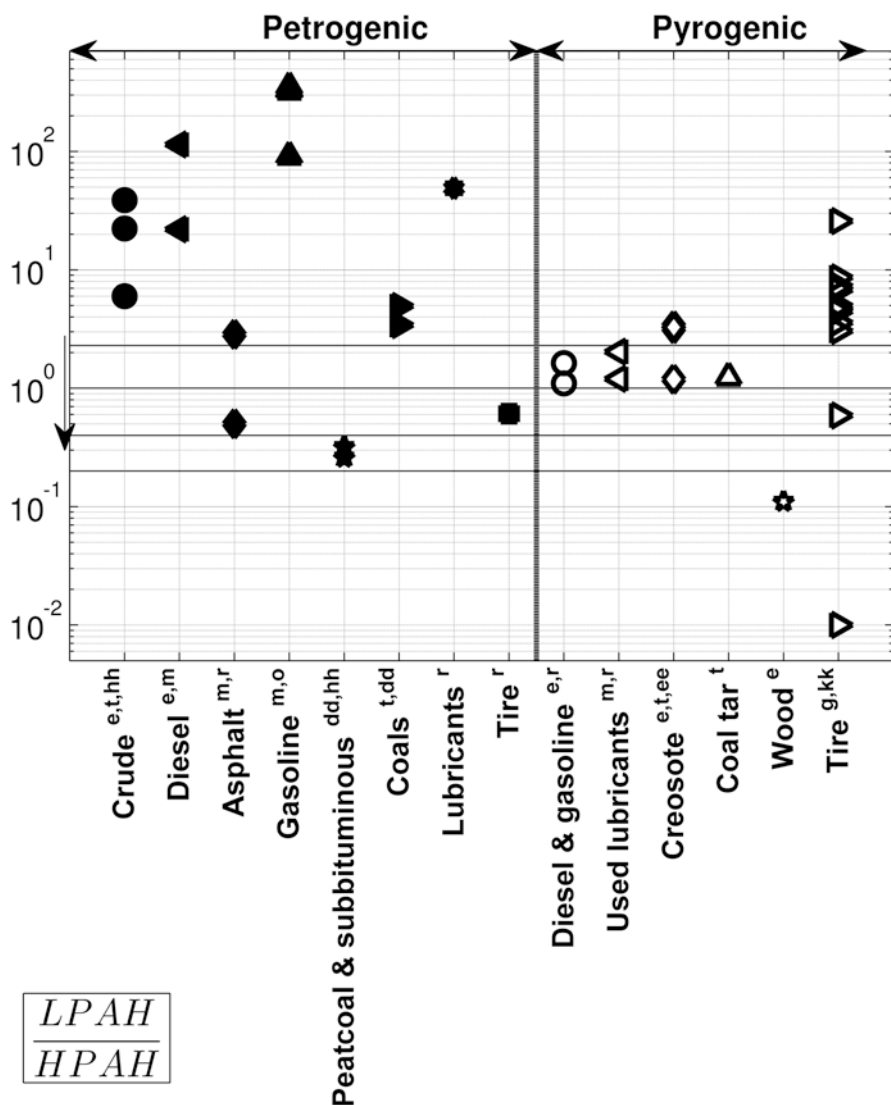


Fig. 23 The $LPAH/HPAH$ ratio for different sources. See Fig. 9 for the symbols and the text for explanation

HPAH, then: $\frac{\Sigma COMB}{\Sigma PAH} = \left(\frac{LPAH}{HPAH} + 1 \right)^{-1}$. Accordingly, pyrolytic PAHs = $\Sigma COMB /$

ΣPAH , and $\Sigma COMB / \Sigma PAH < 0.3$ (or $LPAH / HPAH \geq 2.3$) indicates petroleum. When $\Sigma COMB / \Sigma PAH > 0.7$ (or $LPAH / HPAH \leq 0.4$) a pyrolytic origin is likely (Hwang et al. 2003; Tobiszewski and Namiesnik 2012). Phenanthrene and anthracene (MW = 178) are not included in $\Sigma COMB$ because they may be of petrogenic origin, whereas perylene usually originates from natural sources (Gogou et al. 2000).

Since LMW PAHs are more susceptible to degradation (microbial, volatilization, and dissolution), sediments exhibit lower LMW/HMW ratios than the contamination source (Zakaria et al. 2002). As a workaround, De Luca et al. (2005) suggested using P0 as a possible marker of LPAH pollution in Olbia harbor (Italy). Furthermore, some combustion sources may produce LMW PAHs (Guo et al. 2007). Hence, source apportionment assignments using two- to three-ringed parent PAHs may become compromised after moderate weathering (Yan et al. 2006), rendering the LMW/HMW ratios (i.e., L/H, LPAH/HPAH) inadequate for discriminating crude oil from other major sources of sedimentary PAHs.

For the above reasons, the LPAH/HPAH ratio was used as a proxy of PAH weathering by Stout et al. (2003), who noted that if the LPAH/HPAH ratio becomes low (≈ 0.2), then the ratios of BaA/C0, BbF/BkF, BeP/BaP decrease sharply and may fail to indicate the contaminant sources (Fig. 19). However, Costa and Sauer (2005) did not observe such trends for these ratios, and used the LPAH/HPAH ratio as a weathering index. Consequently, the L/H ratio is consistent with degradation and as such it was used to interpret the degradation in oil tarballs in Malaysia (Zakaria and Takada 2007). Summarizing, if LPAH/HPAH > 2.3 , then recent input of petrogenic products is implied. Degradation or pyrogenic sources are likely when $0.2 < \text{LPAH/HPAH} < 0.4$, whereas at values of LPAH/HPAH < 0.2 , degradation is likely to have occurred.

5.8.3 Ratios of Alkyl to Parent PAHs

The sum of the parent PAHs with masses 128, 178, 202, and 228, divided by the total PAH1-PAH4 homologues of these PAHs (N0, P0, A0, FL0, PY0, BaA, C0) is called the parent to alkyl (Par/Alkyl) ratio:

$$\left(\frac{\text{N1} + \text{N2} + \text{N3} + \text{N4} + \text{PA1} + \text{PA2} + \text{PA3} + \text{FP1} + \text{FP2} + \text{BC1}}{\text{N0} + \text{PA0} + \text{FP0} + \text{BC0}} \right)$$

The Par/Alkyl ratio was used by Yan et al. (2005, 2006, 2007) to distinguish petrogenic (> 2.3 – 4) and pyrogenic (< 1) sources (e.g., in oil spills even after extensive weathering in sediments). Apportionment values for petroleum combustion (1.1) and coal combustion (0.35) have also been reported (Yan et al. 2007). The correlation of Par/Alkyl with $\delta^{13}\text{C}_{\text{Py}}$, FL0/PY0 and Ring456/TPAH (discussed below), implies that Par/Alkyl is a reliable PAH source indicator over large geographic areas or even long timespans (Yan et al. 2005, 2006).

Yunker et al. 2002 used an alkyl/ Σ PAH ratio to infer pyrogenic or petrogenic sources in sediments. In this case, Σ PAH is the $\Sigma(178$ – $278)$ parent PAHs:

$$\frac{\text{N1} + \text{N2} + \text{N3} + \text{N4} + \text{D1} + \text{D2} + \text{PA1} + \text{PA2} + \text{PA3}}{\text{PA0} + \text{FP0} + \text{BC0} + \text{BeP} + \text{BaP} + \text{BbF} + \text{BjF} + \text{BkF} + \text{ghi} + \text{IP} + \text{DA} + \text{DcA}}$$

and when alkyl/ Σ PAH ≤ 0.35 , coal is ruled out, since natural background sources (e.g., shales, coal, and bitumen) have a ratio of 2.3–3.2 (Yunker et al. 2002).

The ratio of the sum total of four- to six-ringed PAHs (including parent and alkylated homologues) to total PAHs (Ring456/TPAH) is minimally influenced by the degradation of LMW PAHs (Yan et al. 2005, 2006). Ring456/TPAH is sensitive to inputs from fresh oil spills, and thus can be used to distinguish petrogenic (<0.4) and pyrogenic (>0.5) inputs (Yan et al. 2005, 2006). In the study of Yan et al. (2006), Ring456/TPAH correlated with FL0/PY0, but weathering rendered the Ring456/TPAH insensitive to petrogenic contributions. Furthermore, the applicability of the Ring456/TPAH is currently limited because of the small amount of data available to validate this ratio, particularly for environments where petrogenic sources are dominant (Yan et al. 2006).

5.8.4 Pyrogenic Index

The pyrogenic index (PI) is the ratio of the sum of the concentrations of EPA priority unsubstituted three- to six-ring PAHs (sometimes coronene is also added: Wang et al. 2006) to the sum of the concentrations of the *five target alkylated PAH homologues* ($\Sigma 5$ alkylated: naphthalenes, fluorenes, dibenzothiophenes, phenanthrenes and chrysenes) (Wang et al. 1999b, 2001, 2014):

$$PI = \frac{AY + AE + A0 + FP0 + BaA + BbF + BkF + BeP + BaP + Per + ghi + IP + DA}{N(1-4) + P(1-4) + D(1-4) + F(0-4) + C(0-4)}$$

PI ranges from 0.8 to 2.0 for pyrogenic sources and is much lower for petrogenics: <0.01 for crudes and <0.05 for heavy oils and heavy fuels (Fig. 24; Wang et al. 1999a, b, 2001, 2009). Thus, PI can be useful for distinguishing heavy fuels from crude oils or light refined products, and soot from crude oils or petroleum products (De Fatima et al. 2007; Wang et al. 1999a, b, 2001).

Compared with other indices, PI better resolves pyrogenic and petrogenic products (combustion significantly alters the value of PI) and is more accurate and consistent (Wang et al. 1999a, b). In contrast to combustion, weathering has little effect on PI, which makes it one of the most reliable PAH indices.

5.8.5 Fossil Fuel Pollution Index

A precursor to PI for differentiating pyrogenic and petrogenic products is the fossil fuel pollution index (FFPI) (Iqbal et al. 2008; Stout et al. 2001b), defined as:

$$FFPI = \frac{N0 + N1 + N2 + N3 + N4 + D0 + D1 + D2 + D3 + \frac{1}{2}(P0 + P1) + P2 + P3 + P4}{TPAH}$$

FFPI is close to zero for most pyrogenic PAHs, whereas for sediments containing significant amounts of fossil-fuel PAH constituents, the FFPI is close to 1 (Iqbal et al. 2008). FFPI can thus be used as a method for apportioning the contribution of different PAH sources.

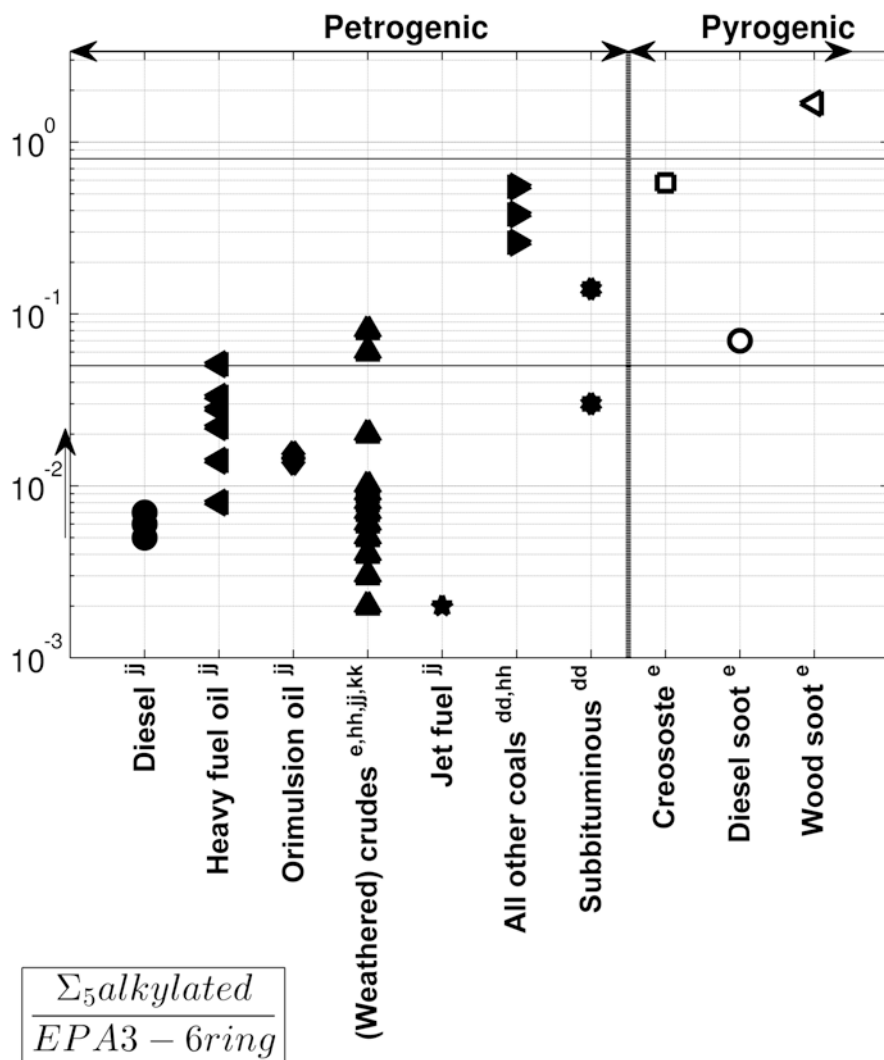


Fig. 24 The *PI* for different sources. PER was omitted for data estimations from Burns et al. (1997). Degradation arrow is assumed as inferred from EVC crude weathering data from Burns et al. (1997). See Fig. 9 for the symbols and the text for explanation

6 Discussion and Conclusions

The various PAH distributions, which differ from refinery feedstocks, refinery fractionation/processes, differential degradation/weathering, formation or combustion temperatures, provide a basis for differentiating and identifying the sources of PAHs in sediments. Below, we reproduce and answer the questions posed in the introduction section.

6.1 *What Are the Most Important PAH Sources in the Aquatic Environment and Which PAH Indicators Can Be Used to Unequivocally Identify Them?*

Thermal, source and degradation PAH indicators produce fingerprint physicochemical gradients that are developed during pyrogenic and petrogenic PAH formation, transport, and deposition. One of the most widely applicable and robust approaches to PAH source characterization is to apply different discriminant analysis techniques (e.g., ratios, PMF) to the PAH pattern of parent versus alkylated (e.g., reflected in PI, PPI), stable versus unstable isomer, and HMW versus LMW forms.

Mathematically, it is not possible to discriminate more sources (times their temporal, climatic and geographical variations) than the known variables (PAH analytes). Therefore, to limit the number of possible suspected sources, knowledge of current and historic records of contamination is helpful. PAHs are classified according to their origin or temperature of formation into three classes: pyrogenic, petrogenic, and biogenic/natural. The multitude of PAH sources in the aquatic environment, their variability and the differential fate of PAHs have resulted in a plethora of PAH indicators for the purposes of PAH source assessment.

Each class of indicator is based upon a physicochemical aspect of the contaminant (source, degradation, and thermodynamic) and has been designated to solve a particular problem, but also indicates an existing gradient in the PAH chemistry. For example, the sulfur gradient (dibenzothiophenes) was initially applied for petroleum sources, but it can also be used to discriminate pyrogenic ones. There are extensive databases for PAHs and their sources. Table 4 gives an overview of the PAH indices used to characterize or apportion the pyrogenic or petrogenic nature of a sample.

Of special importance is the spatial extent of the PAH analysis, which is ascertained by distinguishing between point and non-point sources and measuring background concentrations. Background PAH concentrations always make it necessary to proceed with caution when using PAH ratios, because some degraded PAH source fingerprints (e.g., coal tar, creosote, etc.) are similar to urban background fingerprints. PAH indices such as $N0/F0$, $C2/C0$, $FP0/(C0 + BaA + BaP + BjF + ghi + IP + D A)$ have been used to discriminate different sources that contribute to urban background. If urban background concentrations are high, it is possible to break down the composite urban background into individual sources by examining the inventory of sources contributing to it (e.g., asphalt, automobile soot, etc.).

PAH ratios are a fast and simple means to overview and understand the origin of pollution, particularly when coupled with a discriminant analysis approach. In general, two- to three-ringed PAHs (including alkylated) are good for distinguishing petrogenic contamination, whereas four- to six-ringed PAHs are appropriate for discriminating between pyrogenic sources. One of the most successful approaches for deducing the pyrogenic or petrogenic character of sedimentary contamination is the apportionment of PAHs to sources (e.g., the PI). The PPI and the $FLO/PY0$ ratio are robust and simple to use.

When petrogenic contamination is suspected, chrysenes, PAHs that are lighter than $C0$, and definitely alkylated PAHs are useful. For example, the Dn/Pn ratios are

Table 4 Safe PAH ratios and threshold values for initial screening/identification of pyrogenic and petrogenic PAHs

Ratios	Fig	List	Pyrogenic	Petrogenic	Degr ^a	Comments
P0/A0	9	U, V	<u><4-10^b</u>	>15 ^{b-30}	↑	–
P1/P0	11	–	<u><1-2</u>	>2–5	↑	–
PA1/PA0	10	–	<u><1^b</u>	>1.5 ^b	↑	–
DMP	–	–	–	–	↓	>0.7=> Softwood combustion, <0.45=> non softwood, 0.9 = softwood combustion, ~0.4 = vehicle
RET/C0	–	–	–	–	↓	4.5 = Softwood, 0.35 = other combustion sources
FLO/PY0	12	U	>1.5	<0.5 ^b	↓	–
FP1/PY0	–	–	≈0.3	≈4	↓	–
FP1/FP0	13	–	<u><0.5-1</u>	>1 ^b	↑	–
P2+P3+P4/FP0	14	–	<0.3	≥5.5–9	↓	Intermediate values indicate weathering/mixing
BaA/C0	15	U	>0.5 ^{b-1}	<0.25 ^{b-0.5^b}	↓	–
D1/P1	–	–	–	–	↑	Source ratio for crudes, 0.78 = asphalt, 0.4 = diesel emissions, 0.04 = fuel oil soot
D2/P2	17	–	<0.4	–	↑	Source ratio for crudes, up to 98% degradation
PY0/BaP	–	B, U, V	<<10	≥10	↓ ^c	–
BaP/ghi	21	B, U, V	–	–	↓	<0.6 ^b => Non traffic
BeP/BaP	18	–	≤1	–	↑	Atmospheric weathering ratio
IP/ghi	20	U	>1	<0.25	~	Degradation depends on particle color for pyrogenics
ΣPAH/Alkyl	–	–	>0.5	≤0.2–0.3	Minor ↑	–
L/H	22	U	<1	≥1	↓	Weathering ratio, extensive degradation at low values
LPAH/HPAH	23	U	<0.4–2 ^b	≥1–2.3	↓	Weathering ratio, <0.2 => extensive degradation
Pyrogenic index	24	–	>0.05 ^b	<0.05	Minor ↑	–

Most safe thresholds in **bold**. Underlined: the side (values) of the ratio that will not be compromised by degradation (opposite direction). Intermediate ratio values indicate either mixed or unclear origin. *Fig* figure in manuscript which shows the respective ratio for different sources. *List*: priority list which can be used to estimate the ratio (U U.S. EPA 16, V VROM 10, B Borneff 6)

^aDegradation effects on this ratio (↓ decrease, ↑ increase, ~ variable) based on thermodynamic assumption under “common” environmental conditions (i.e., stability of PAH isomers in the environment) but differences in environmental conditions and degradation types may differentially affect the value of the indicators

^bSerious caveat when this value of this ratio is applied (see text for more)

^cAccording to evaporation and dissolution potential as seen in Table 2

=Apportionment value (all apportionment values for one ratio refer to a single case in literature)

good for distinguishing weathered crudes, whereas C2/P2 can be used to distinguish crude from diesel, and 2-P1/1-P1 can be used to discriminate between fuel oils. For coal PAHs, the phenanthrenic ratios (MPIs), the 1-D1/4-D1, and BbF/BkF correlate with vitrinite reflectance (coal ranks). Unfortunately, little is known about the PAH composition of coals, which is geographically very variable (Achten and Hofmann 2009; Stout and Emsbo-Mattingly 2008).

Three-ringed PAHs such as Dn ($n=1,2,\dots$), P1/A1, AY/AE, F0, and the two-ringed N0 are useful for distinguishing coal-derived liquids such as unweathered creosotes and coal tars, which do not follow the usual pyrogenic/petrogenic distributions. Weathered creosotes are rich in benzo[fluoranthene], BaA, benzopyrenes, C0, FL0, PY0 (Fig. S28, Supporting Material). Ratios of four- or five-ringed (methyl) PAHs such as C0/BaA, BbF/BkF, FP0/FP2+FP3, may prove useful for distinguishing (un)weathered creosote from background contamination and other high-temperature processes.

Useful indicators of biomass combustion are alkylphenanthrenic indices such as DMPs and retene (RET/C0, RET/PY1, RET/benzo[*b*]naphtho[2,1-*d*]thiophene etc.), and PAH markers such as coronene. Of these, coronene is also a vehicle combustion marker, as are five- to six-ringed PAHs such as BeP, *ghi*, PY0, and other LMW PAHs (e.g., P1, F0, D0, benzonaphthothiophenes, etc.), which can assist in discriminating automobile-related emissions from other combustion forms (wood, coal, etc.).

Perylene, even though not of anthropogenic origin, can help yield information as to the source, depositional environment and the transport dynamics of the PAHs before or during their deposition.

In summary, a full scan analysis (all suspected sources included) should include the EPA16 parent PAHs (mostly pyrogenic discrimination), the *five target alkylated* (PI and petroleum products), the fluoranthenes/pyrenes homologues (pyrogenic/petrogenic discrimination), BeP (vehicle), PER (Biogenic), RET, and DMPs (biomass/softwood). This “initial screening” yields a set of candidate substances to be analyzed. A faster, cost-effective solution can narrow down the number of PAH analytes, but it depends on the case in question.

6.2 What Are the Inherent Uncertainties in These Indicators and How Does the Value of the Indicator Change After Undergoing Biogeochemical Processes (i.e., Photochemical Oxidation, Degradation, Volatilization, etc.) in the Aquatic Environment?

PAH degradation, background contamination, mixing of multiple sources and similarities between the PAH sources are functions of anthropogenic, environmental, and geographic conditions that differentially affect all but a few PAH molecular indices. It is possible to take these uncertainties into account by using suitable degradation/weathering PAH ratios.

Generally, HMW and alkylated PAHs are more recalcitrant than LMW and less alkylated PAHs. Furthermore, PAHs attached to particles are protected from several types of degradation (such as photodegradation and biodegradation). As a result, pyrogenic PAH distributions retain their signature better than petrogenic ones. PAH ratios such as P1/P0, 2-P1/1-P1, C0/C2, Ring456/TPAH, and the PPI are all inevitably affected by degradation. Ratios such as BbF/BkF, BaA/C0, P0/A0, FP0/FP2 + FP3, and BeP/BaP should be applicable in moderate weathering conditions, although they depend on sample matrix effects (differential weathering in air, aerobic or anaerobic conditions). More stable are the FL0/PY0 and IP/*ghi*—but only in certain compartments and substrates, not everywhere. For such ratios, the degradation effects for different matrices should be considered (e.g., empirically or by a degradation rate kinetic model) prior to application.

Differential degradation has been established for numerous ratios. The ratios of D2/D0 and P0/A0 are decreased by photo-oxidation and solubilization. Most other forms of degradation increase these ratios. Degradation does not significantly affect the alkyl/ Σ PAH and PI. By definition, source parameters such as D0/P0 ratios are constant even after severe degradation, although if these substances do not associate with particles, long-term weathering also affects them. Other ratios such as benzo-fluorenes to methylpyrenes or the 2-N1/1-N1 ratio are resistant in certain cases or at certain degradation stages. In sediments and water matrices, biodegradation (oxic or anoxic) often has opposite effects than other forms of degradation for the same PAH ratio. For example, biodegradation usually increases the values of DMP and FL0/PY0 ratios, although other forms of degradation reduce them.

Empirical and theoretical models have been used to account for the differential degradation patterns. Weathering ratios of the more stable PAHs to the less recalcitrant PAHs (e.g., LMW/HMW or alkylated/less alkylated) are often used. The methyl-dibenzothiophene isomer ratios are useful biodegradation indicators. The ratio N0 + N1/N2 can account for dissolution in oil spills. The ratios of N2 or N3 alkyl-naphthalenes to the respective phenanthrenes are used as weathering indicators at early weathering stages (dissolution and evaporation). The ratios of two- or three-ringed PAHs (naphthalenes, dibenzothiophenes, phenanthrenes) to HMW PAHs (chrysenes or TPAH) are frequently used as general-purpose degradation indicators. Ratios such as P2/P3 (or the respective alkylated dibenzothiophenes) make use of the fact that the more alkylated the isomer is, the more recalcitrant it is. Notice that certain weathering ratios such as C2/P2 and C3/P3 are also source ratios when unweathered. Both BaP and the BeP/BaP ratio are applicable as photodegradation indicators in the atmosphere. Otherwise, the L/H and the LPAH/HPAH can be used to indicate the degradation level at which other PAH ratios may fail.

The charts (Figs. 9, 10, 11, 12, 13, 14, 15, 17, 18, 20, 21, 22, 23, and 24, summary in Table 4) summarize literature values for the PAH ratios in sources and show the possibilities for source characterization. Comparing the sediment contamination with these charts can assist in deducing the nature of contamination and its uncertainty. The degradation arrow shows how degradation will change a specific ratio

and assists in finding whether the ratio is compromised by degradation. Ranges and reliable (degradation-independent) threshold values of PAH ratios can be estimated, either for individual sources or for a group of sources of interest. Because of the higher degradability of petrogenic PAHs, petrogenic assessments should take into account at least dissolution and evaporation.

6.3 Can the Borneff-6, 16 EPA, and 10 VROM PAHs Be Used to Calculate the Proposed Indicator—and, if so, Which Uncertainties are Introduced by This Approach?

All the proposed indicators contain parent PAHs only, which make it difficult to trace petrogenic sources. We believe that after a local case study has taken into account a wider range of alkylated and parent PAHs, it is possible to establish the EPA16 as an indicator of pyrogenic and petrogenic sources.

All three indicators are suitable mainly for pyrogenic sources. Specifically, Borneff-6 has only one LMW parent PAH (easily degradable), making it inadequate to detect petrogenic contamination. Even though some LMW PAHs are included in the VROM10 PAH compilation, important ones such as pyrene (useful for discriminating petrogenic/pyrogenic or different combustion sources) are omitted.

Alkylated homologues are petroleum-specific, but they cannot be measured by using the standard EPA methods. Of the three proposed PAH compilations, the most adequate for identifying pyrogenic or petrogenic sources seems to be the Σ PAH16, although it does not take into account certain important parent PAHs (e.g., N0, BeP, PER, D0) nor, most importantly, does it take account of alkylated PAHs. Under degradation conditions, the parent compounds are those that are lost first—sometimes preferentially over the alkylated ones.

Certain ratios within the Σ PAH16 (e.g., LPAH/HPAH) are able either to describe patterns, in which degradation has occurred, or in which the targets are recalcitrant. Even for very complex systems, it should be possible to establish a diagnostic set of PAH indicators (e.g., the EPA16 indicators) after implementing a full scan analysis and a tiered approach (historic records, source inventories, background concentrations, weathering check, and parent and alkylated PAHs and data analysis). If the compounds that we expect to be present or absent in the sources are empirically known, the number of analytes to be investigated can be reduced. Establishing the levels and correlations of a small subset of indicators can reduce the effort of extensive analysis of PAHs while providing adequate data analysis and resolution, which are necessary for monitoring programs. We suggest that the next step in using a small subset of all the PAHs for the source characterization in sediments would be to implement an inference protocol (e.g., a multi-valued logic, or a PMF), in which conclusions drawn from multiple PAH ratio combinations are applied to weight the Σ PAH16 ratios in a standardized manner on the basis of source composition and degradation.

7 Summary

In recent decades, an exponential increase in the concentration of anthropogenic Polycyclic Aromatic Hydrocarbons (PAHs; see Table 1 for a list of PAH abbreviations) has been observed worldwide. Regulators need to know the sources if concentrations are to be reduced and appropriate remediation measures taken. “Source characterization of PAHs” involves linking these contaminants to their sources. Scientists place PAH sources into three classes: pyrogenic, petrogenic, and natural.

In this review, we investigate the possibility of using PAH molecular ratios individually or in combination for the purpose of deducing the petrogenic or pyrogenic origin of the contamination in sediments. We do this by reviewing the characteristic PAH patterns of the sources and by taking into account the fate of PAHs in the aquatic environment. Many PAH indicators have been developed for the purpose of discriminating different PAH sources. In Table 4 we summarize the applicability of different PAH ratios and threshold values.

The analysis of two- to four-ringed alkylated PAHs offers the possibility to distinguish two or more single sources or categories of pollution in greater detail. For example, the FL0/PY0, the PPI, and P0/A0 ratios can be used to discriminate between pyrogenic and petrogenic sources of contamination. When petrogenic contamination is suspected, chrysenes, PAHs lighter than C0, and in particular, alkylated PAHs can usually be of use. For unburned coal PAHs, the methylphenanthrenic ratios (MPIs), the 1-D1/4-D1, and BbF/BkF are promising, since they are sometimes correlated with vitrinite reflectance (coal ranks). Alkylphenanthrenes can be used to detect biomass combustion. Higher molecular weight parent and alkylated PAHs are appropriate for pyrogenic discriminations. When PAH indices are coupled with discriminant analysis techniques such as PMF (positive matrix factorization), the origin of multiple sources in even the most complex environments can be traced and measured.

Even so, the most stable isomer pairs degrade differentially, depending on their thermodynamic stability, the environmental conditions, and the type of degradation. If PAH ratios are to be used, it is usually necessary to have prior knowledge of the degradation state of the matrices examined (air, sediment, etc.) and of how the PAH ratio behaves under such conditions. PAH indices (e.g., N0/C0 or LPAH/HPAH) can be applied for distinguishing differential degradation gradients (photodegradation, biodegradation, etc.). Degradation does not significantly affect the ratio of parent to alkylated PAHs and the PI. The degradation arrow in Table 4 and Figs. 9, 10, 11, 12, 13, 14, 15, 17, 18, 19, 20, 21, 22, 23, and 24 shows how the ratio usually changes with degradation.

Merely detecting the six PAHs of Borneff-6 is not enough to establish petrogenic contamination, because Borneff6 includes mainly HMW PAHs. The Σ PAH16 appears to be the most suitable for identifying pyrogenic and petrogenic sources. For more specific information on sources and their discrimination it is recommended to further take into account important parent PAHs such as N0, BeP, PER, D0, and—most importantly—alkylated PAHs.

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Appendix

Table 5 Key to literature data cited in figures

a	Ahrens and Depree (2010)	b	Benner et al. (1995)	c	Boonyatumanond et al. (2007)
d	Breault et al. (2005)	e	Burns et al. (1997)	f	Chen et al. (2005)
g	Chen et al. (2006)	h	Dickhut et al. (2000)	i	Dobbins et al. (2006)
j	Galarneau (2008)	k	Geller et al. (2006)	l	Jiao et al. (2009)
m	Karlsson and Viklander (2008)	n	Lim et al. (2007)	o	Marr et al. (1999)
p	Masclet et al. (1987)	q	Miguel et al. (1998)	r	Mostafa et al. (2009)
s	Neff et al. (2005)	t	Neff et al. (1998)	u	Oanh et al. (1999)
v	Okuda et al. (2002)	w	Oros and Simoneit (2000)	x	Riddle et al. (2007)
y	Saber et al. (2006)	z	Saha et al. 2009	aa	Sicre et al. (1987)
bb	Simcik et al. (1999)	cc	Stout (2007)	dd	Stout and Emsbo-Mattingly (2008)
ee	Stout et al. (2001a)	ff	Stout et al. (2003)	gg	Stout et al. (2006)
hh	Stout et al. (2007)	ii	Takada et al. (1990)	jj	Wang et al. (1999b)
kk	Wang et al. (2006)	ll	Yan et al. (2005)	mm	Yan et al. (2007)
nn	Yunker et al. (2002)	oo	Zakaria et al. (2002)	pp	Page et al. (1999)

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