

A Guide to Understanding, Assessment, and Regulation of PAHs in the Aquatic Environment

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Regulatory and Scientific Affairs

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A Guide to Understanding, Assessment, and Regulation of PAHs in the Aquatic Environment

1.0 Executive Summary

The American Petroleum Institute (API) has commissioned this introductory guide to understanding and assessing polycyclic aromatic hydrocarbons (PAHs) in the aquatic environment. The guide provides an overview on the chemistry, fate, and sources of PAHs, and techniques for differentiating among sources in sediments.

PAHs belong to a broad class of chemicals, but only some of these PAHs are of concern in the environment due to health impacts on humans or animals, occurrence in freshwater and marine sediments worldwide, and persistence in sediments. However, because PAHs are classified as a group, there is a tendency to view all PAHs as contaminants of concern. The impact of a particular PAH depends not only on its individual chemical characteristics, but also on environmental conditions, fate and transformation processes, and biological processes in exposed organisms. In environmental work, most analyses focus on the “16 priority pollutant” PAHs and an expanded list containing about 40 individual PAHs and PAH groups.

PAHs are composed of two or more fused aromatic hydrocarbon rings. Low molecular weight, 2- to 3-ringed PAHs are generally more soluble in water, and therefore, more toxic to aquatic life. Carcinogenicity, mutagenicity, and teratogenicity may all increase with ring number. Although PAHs bioaccumulate to some extent in aquatic organisms, because many organisms are able to metabolize PAHs, PAHs do not tend to biomagnify up the food chain.

The two major sources of PAHs are petrogenic and pyrogenic. Petrogenic PAHs are formed naturally within petroleum reservoirs and coal beds, and common sources include crude oil and refined petroleum products. Pyrogenic PAHs are formed by combustion, and common sources include fires, combustion of fossil fuels and petroleum products, and coal gasification. Because individual PAHs may be found in both petrogenic and pyrogenic sources, it is the distribution of PAHs characteristic to a source that may distinguish it from others. Petrogenic and pyrogenic PAH sources have distinctive chemical fingerprints that can be used to differentiate among the various source contributions of PAHs in sediments. Numerous studies have shown that urban runoff, primarily a source of pyrogenic PAHs, is a major and widespread contributor to PAHs in sediments. Contributions from treated refinery wastewater are generally minor and are limited to areas near the discharge point.

Analytical methods commonly used to measure PAHs in sediment are currently based on Method 8270C for semi-volatile organic compounds. Because the PAHs in Method 8270C are limited primarily to the 16 priority pollutant PAHs, advanced analytical methods have been developed (based on Method 8270C) for expanded lists of PAHs. These expanded lists provide more detailed PAH profiles to help characterize and differentiate sources of PAHs in the environment.

Because the effects of PAHs in sediments are very complex and site-specific, most states have not adopted numerical sediment criteria in their water quality regulations, instead relying on sediment quality guidelines to assess PAH contamination, list impaired water bodies, develop total maximum daily loads (TMDLs), and guide remediation efforts. The complexity of the issues involving PAHs in sediments may result in oversimplification and in turn, poor decision-making. Sediment guidelines issued in 2003 by the U.S. Environmental Protection Agency are routinely being used; however, they have their own limitations, which should be well understood before they are applied.

Site investigations involving PAHs in sediments should use a tiered approach, with initial efforts focused on identifying whether environmental impacts actually exist, and using the more simple chemical analysis methods. If further study is warranted, advanced site investigation techniques can be used, including advanced chemical fingerprinting.

2.0 Scope of This Guide

This document was designed to be an introductory guide to understanding and assessing polycyclic aromatic hydrocarbons (PAHs) in the aquatic environment (water and sediments). The American Petroleum Institute (API) commissioned this guide primarily for refinery personnel and home office environmental staff who may have to address PAH issues. In addition, this guide may also be useful to staff in regulatory agencies that work with PAHs in wastewater discharge permits, waste load allocations (TMDLs), and sediment investigation and remediation.

The guide provides an overview on the chemistry, fate, and sources of PAHs in the environment, and the regulatory implications. The guide also includes descriptions of the different sources of PAHs (petrogenic, pyrogenic, diagenic, biogenic) and techniques for differentiating these sources through their characteristic fingerprints, including straightforward ways to help identify or rule out potential sources.

3.0 Why This Guide was Developed

In the environmental field of water and sediments, there is an emerging focus on sediment quality. The United States Environmental Protection Agency (EPA) has developed the concept of sediment quality criteria, which could lead to numerical targets for contaminants in sediment similar to water quality criteria in the water column. Some states, such as California and Washington, have adopted or are adopting sediment quality standards based on such criteria. Failure of sediments to meet the criteria may result in waters being listed as impaired and/or remediation of the sediments.

There is also an emerging focus on PAHs as a family of contaminants, especially in sediments. PAHs are a class of compounds containing from 2 to more than 10 fused aromatic hydrocarbon rings, for example, naphthalene (2 rings) and ovalene (10 rings). Lower ringed compounds, such as naphthalene, are relatively soluble and biodegradable, but they can exhibit significant acute toxicity to aquatic organisms. Higher ringed compounds, such as benzo(a)pyrene (5 rings), are more persistent in the environment. Higher ringed compounds tend to exhibit lower direct toxicity, but a higher potential to be carcinogenic, mutagenic, or teratogenic to a wide range of organisms, including amphibians, fish, birds, and mammals. Often, the higher ringed PAHs are assumed to bioaccumulate more than the lower ringed PAHs; however, studies have shown that higher ringed PAHs actually bioaccumulate less in higher trophic levels.

PAHs occur naturally in trace amounts in crude oil and certain petroleum-based products such as diesel. Consequently, petroleum refineries are often blamed for PAH contamination in water or sediments. Studies have shown, however, that combustion can be a major contributor to PAHs. Recent studies have also identified pavement sealers as significant sources of PAHs.

As a family of compounds, PAHs vary in source materials by type and quantity. Consequently, many PAH sources have distinctive characteristics that provide a signature or fingerprint that can be used to identify and quantify their contribution to the total PAH content in sediments. For example, pyrogenic PAHs, whose source is combustion, present a much different signature than petrogenic PAHs, whose source is petroleum. A variety of techniques, ranging from simple to very complex, can be used to differentiate among PAHs sources reflected in sediments at a particular location.

This guide was developed to address these issues by providing basic, factual information on PAHs that affect water and sediments. This guide can be used by both refinery and regulatory personnel to understand how differences among individual PAHs relate to their environmental impacts, how to properly differentiate among sources of PAHs, and how to properly regulate PAHs in petroleum industry discharges.

API has published other reports containing useful information on PAHs, some of which has been incorporated into this guide. Interested readers will find additional information in those reports: (1) *A Guide to Polycyclic Aromatic Hydrocarbons for the Non-specialist* (2002, API Publication No. 4714); (2) *Fate and Effects of Polynuclear Aromatic Hydrocarbons in the Aquatic Environment* (1978, API Publication No. 4297); and (3) *Bioaccumulation: How Chemicals Move from the Water Into Fish and Other Aquatic Organisms* (1997, API Publication No. 4656).

4.0 Why PAHs Are Important

PAHs are nearly ubiquitous trace contaminants of freshwater and marine sediments worldwide. Some PAHs are toxic to organisms that live in the water and sediments. Some PAHs are known or suspected carcinogens, making the consumption of contaminated fish and water a concern. Concern about PAHs due to their toxicity or carcinogenicity, and their persistence in the environment, has led to regulation of PAHs under numerous environmental laws such as the Clean Air Act, Clean Water Act, Emergency Planning and Community Right-to-Know Act, Occupational Safety and Health Act, Resource Conservation and Recovery Act, and Safe Drinking Water Act.

5.0 Chemical Structure of PAHs

Polycyclic aromatic hydrocarbons, or PAHs, are a class of hydrocarbon compounds consisting of two or more fused aromatic hydrocarbon rings. PAHs may also be referred to as polynuclear aromatic hydrocarbons (PNAs) or polycyclic aromatic compounds (PACs). The hydrocarbon ring is hexagonal (six sides), with a carbon atom at each corner or point.

Although there are many individual chemicals that are PAHs, the ones most common in environmental investigations are shown in Figure 1 and Table 1. Of these PAHs, 16 are referred to as the priority pollutant PAHs because they are the PAHs on EPA's priority pollutant list. Consequently, they are the ones most commonly analyzed in environmental samples. As noted in Table 1, seven of the 16 priority pollutant PAHs are known or suspected carcinogens: benz(a)anthracene; benzo(a)pyrene; benzo(b)fluoranthene; benzo(k)fluoranthene; chrysene; dibenz(a,h)anthracene; and indeno(1,2,3-cd)pyrene.

Figure 1 shows common PAHs containing from two to six rings. Naphthalene, consisting of 2 rings, is the simplest PAH. Most PAHs found in the environment contain two to seven rings joined into a variety of shapes, although PAHs with more rings are also found. The ultimate PAH is graphite, an inert material consisting of planes of fused rings.

True PAHs are made up only of hydrogen and carbon atoms. Closely related compounds, called heterocycles, in which nitrogen, oxygen, or sulfur replaces one of the carbon atoms in a ring, are commonly found with PAHs. Figure 1 also shows examples of heterocyclic compounds such as dibenzothiophene, a sulfur heterocycle. Although not PAHs, certain nitrogen- and sulfur-containing heterocyclic compounds are frequently used for forensic PAH fingerprinting purposes.

PAHs often occur with aliphatic and non-aromatic cyclic hydrocarbons attached to the rings at one or more points. These PAHs are described as alkylated PAHs. An example of aliphatic, alkylated PAHs in Table 1 would be the C1-naphthalene group, which would include 1-methylnaphthalene and 2-methylnaphthalene. Examples in Table 1 of non-aromatic cyclic hydrocarbons attached to PAHs are acenaphthene, acenaphthylene, fluorene, and fluoranthene. The basic, unalkylated form of a PAH is called the parent PAH; all of the 16 priority pollutant PAHs are parent PAHs. For example, naphthalene would be the parent PAH of its series of alkylated forms. A parent PAH and its various alkylated homologues is called a homologous series. A homologue is a chemical that has the same basic structure as other homologues in the series, but differs in the number of repeated structural units; in this case, the alkyls. Because there are many possible locations, number, and length of alkyl chains on the parent PAH, alkylated PAHs are often classified by the number of alkyl carbons they contain. For example, 1-methylnaphthalene is a C1-naphthalene PAH and ethylpyrene is a C2-pyrene PAH.

The environmental significance of PAHs stems from their ubiquitous nature in aquatic systems as well as their perceived persistence and toxicity. Solubility, molecular weight, and structure all play important roles in assessing persistence and toxicity. The smaller, two- to three-ringed PAHs are generally more soluble in water, more available to ecological receptors, and therefore, more toxic to aquatic life than higher ringed PAHs. Other effects of exposure are also variable based on the size and structure of a given PAH. While toxicity has been shown to decrease with increasing size; carcinogenicity, mutagenicity, and teratogenicity may all increase with molecular size.

The division between low- and high-molecular weight PAHs (LPAHs, HPAHs) is somewhat arbitrary. LPAHs typically are taken to include: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, and anthracene

(2- and 3-ring parent PAHs). HPAHs typically are taken to include: fluoranthene, pyrene, benz(a)anthracene, chrysene, total benzofluoranthenes, benzo(a)pyrene, indeno(1,2,3-c,d)pyrene, dibenz(a,h)anthracene, and benzo(g,h,i)perylene (i.e., 4-, 5-, and 6-ring member parent PAHs). In general, the presence and predominance of HPAHs is a fairly good indicator of pyrogenic input to the environment.

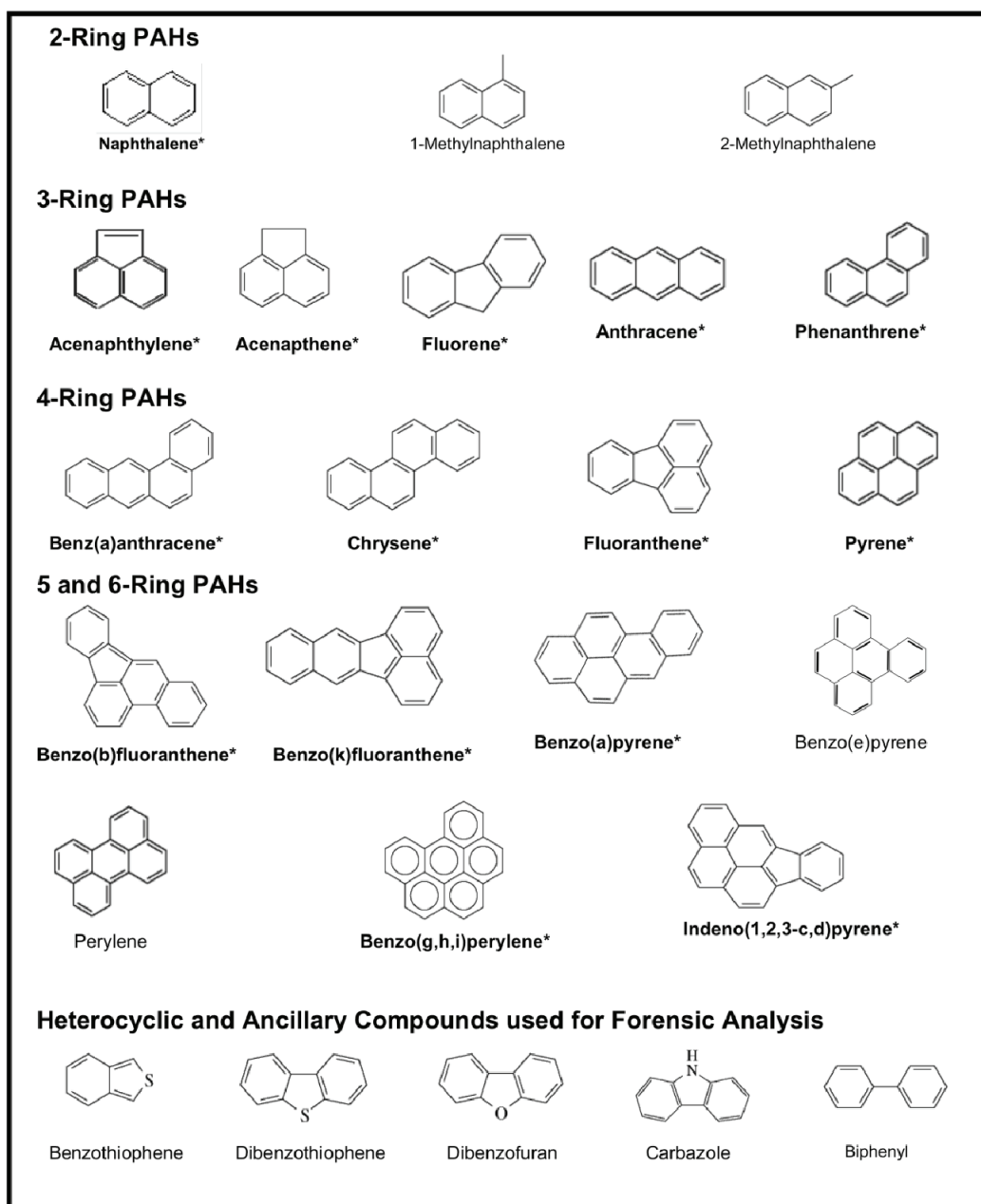


Figure 1. Representative PAH and Heterocyclic Compounds.

Note: The "priority pollutant" PAHs are marked (*); dibenz(a,h)anthracene* not shown.

Table 1. PAHs and Related Heterocyclic Compounds Commonly Used in Advanced Chemical Fingerprinting to Distinguish Among PAH Sources

Analyte/Analyte Group	Abbreviation	Rings
*EPA 16 priority pollutants †Suspected or known carcinogen		
Naphthalene*	N0	2
C1-Naphthalenes	N1	2
C2-Naphthalenes	N2	2
C3-Naphthalenes	N3	2
C4-Naphthalenes	N4	2
Biphenyl	B,Bph	2
Acenaphthylene*	AY,Acl	3
Acenaphthene*	AE,Ace	3
Dibenzofuran	DF,DbF	3
Fluorene*	F0	3
C1-Fluorenes	F1	3
C2-Fluorenes	F2	3
C3-Fluorenes	F3	3
Anthracene*	A0,AN	3
Phenanthrene*	P0	3
C1 Phenanthrenes/Anthracenes	PA1,P1	3
C2 Phenanthrenes/Anthracenes	PA2,P2	3
C3 Phenanthrenes/Anthracenes	PA3,P3	3
C4 Phenanthrenes/Anthracenes	PA4,P4	3
Dibenzothiophene	DBT0,D0	3
C1-Dibenzothiophenes	DBT1,D1	3
C2-Dibenzothiophenes	DBT2,D2	3
C3-Dibenzothiophenes	DBT3,D3	3
C4-Dibenzothiophenes	DBT4,D4	3
Fluoranthene*	FL0,FL	4
Pyrene*	PY0,PY	4
C1-Fluoranthenes/Pyrenes	FP1	4
C2-Fluoranthenes/Pyrenes	FP2	4
C3-Fluoranthenes/Pyrenes	FP3	4
Benz(a)anthracene*†	BA0,BaA	4
Chrysene*†	C0	4
C1-Chrysenes	BC1,C1	4
C2-Chrysenes	BC2,C2	4
C3-Chrysenes	BC3,C3	4
C4-Chrysenes	BC4,C4	4
Benzo(a)fluoranthene	BAF	5
Benzo(b)fluoranthene*†	BB,BbF	5
Benzo(k)fluoranthene*†	BkF	5
Benzo(j/k)fluoranthene	BJK	5
Benzo(e)pyrene	BEP,BeP	5
Benzo(a)pyrene*†	BAP,BaP	5
Perylene	PER,Per	5
Indeno(1,2,3-c,d)pyrene*†	IND,ID	6
Dibenz(a,h)anthracene*†	DA	5
Benzo(g,h,i)perylene*	GHI,BgP	6
Source: Stout <i>et al.</i> 2003b, Uhler <i>et al.</i> 2005		

6.0 Formation of PAHs

PAHs are produced by both natural processes and human activities. PAHs may be classified by the type of process by which they are formed: diagenic, petrogenic, pyrogenic, or biogenic. Diagenic refers to geologic processes after organic matter has been deposited. Petrogenic refers to geologic processes creating fossil fuels. Pyrogenic refers to combustion processes. Biogenic refers to biological processes. Petrogenic and pyrogenic sources are the most common in the environment in both number and quantity of PAHs. The lighter PAHs are present in petrogenic and pyrogenic sources.

It is important to know that a particular PAH may be created by more than one of these processes, and that sources of PAHs may be mixtures – for example, urban runoff is a mixture of both petrogenic and pyrogenic PAHs. This overlap is an important consideration when investigating multiple PAH source inputs at a particular site.

Table 2 summarizes the characteristics of PAHs of petrogenic, pyrogenic, diagenic, and biogenic origins. The following sections describe them in more detail.

Table 2. Categories of PAHs, Examples, and General Characteristics

PAH Category	Description	General Characteristics	Characteristic Sources
Petrogenic	Formed during creation of fossil fuels (petroleum, coal)	Predominately 2- to 4-ringed PAHs, homologous series of parent and alkylated PAHs, alkylated PAHs most abundant	Natural oil seeps, erosion of petroleum source rocks such as shale, spills/releases of petroleum, drips/leaks of petroleum products, primarily lubricating oils
Pyrogenic	Formed during high temperature incomplete combustion of fossil fuels and organic material such as wood and grass	Higher number ringed PAHs, typically 4-6, unalkylated PAHs most abundant	Fossil fuel burning, engine exhaust, forest/grass fires, coal tars, creosote, parking lot coal tar based sealcoats
Biogenic	Formed through biological activity, separate from diagenesis	Can form PAH precursors; however, PAH formation has not been demonstrated	Not considered a significant (direct) source
Diagenetic	Diagenesis of sediments through biological, chemical, and physical processes at low temperatures and in anaerobic environments	Relatively few types of PAHs formed through diagenesis. Examples: retene, perylene, derivatives of phenanthrene and chrysene.	Not a dominant source where sediments have formed during human activity

6.1 Petrogenic

Petrogenic PAHs are formed naturally within petroleum reservoirs and coal beds. Petrogenic PAHs are formed at higher pressures and temperatures than diagenic PAHs, but the process is still considered a low temperature one. Although hundreds to thousands of different PAHs may be found in fossil fuels, they do have some similar characteristics. Petrogenic PAHs consists primarily of two to four-ringed PAHs, most of which are alkylated (see “Chemical Structure of PAHs” in this report for an explanation of chemical structure). Examples of parent (unalkylated or unsubstituted) petrogenic PAHs are naphthalene, acenaphthylene, and fluorene. Examples of alkylated (substituted) petrogenic PAHs are methylnaphthalenes. Key characteristics of petrogenic PAHs are that homologous series of alkylated PAHs are abundant and that alkylated PAHs far exceed parent PAHs in both number and quantity.

Sources of petrogenic PAHs in the environment include natural oil seeps and erosion of petroleum source rocks such as shales, as well as spills and releases of petroleum and petroleum-based materials.

Examples of areas with natural oil seeps are the Santa Barbara Channel, the Gulf of Alaska, and the Caspian Sea. Natural oil seeps can contribute significant quantities of petrogenic PAHs to the environment. For example, in the case of Prince William Sound, the site of the *Exxon Valdez* oil spill in 1989, natural oil seep petroleum from the eastern Gulf of Alaska is carried with suspended sediment into the sound. These natural seeps, rather than spilled oil, are the dominant petrogenic hydrocarbon source in Prince William Sound sediments and the PAHs contained in them produce a significant background level of PAHs (Page *et al.* 1999).

Petrogenic PAHs may enter the environment through direct spills of crude oil and petroleum-based materials. Other sources include oil leaks and drips from vehicles on parking lots and roadways. These materials are abraded/washed off and carried by storm water into water bodies. In general, spills and releases do not account for a large fraction of PAHs entering the environment and the lighter PAHs contained in them are readily biodegradable.

6.2 Pyrogenic

Pyrogenic PAHs are created during incomplete, but high temperature combustion of organic materials such as fossil fuels and wood. Examples include the burning of diesel fuel and forest fires. Soot from incomplete combustion containing PAHs is carried by air and runoff into waterways. Urban runoff may contain a considerable amount of pyrogenic PAHs, including soot and abraded particles from tires containing carbon black. In many urban areas, the largest fractions of PAHs come from chronic, day-to-day runoff. Also included in the pyrogenic category are aluminum smelting and the products of high temperature processing of coal in the coal gasification process. Residuals of the coal gas process are *coal tars*, and they are rich in pyrogenic PAHs. A derivative of coal tar is creosote, used as a wood preservative in wood pilings and telephone poles. Coal tar emulsion sealcoats on parking lots have been shown to be a significant source of PAHs in some urban watersheds.

Characteristics of pyrogenic PAHs are higher number ringed structures and the dominance of parent, unalkylated forms. Four, five, and six rings are common. Unalkylated PAHs are more abundant because high temperature processes associated with pyrogenic PAHs preferentially remove alkyl branches. Anthracene and benzo[a]pyrene are examples of pyrogenic PAHs. Where pyrogenic PAHs are sorbed in soot particles, they are generally not available to biodegradation processes.

6.3 Biogenic

Biogenic processes refer to biological activity of bacteria, fungi, plants, or animals. Although biological processes can produce certain compounds that are precursors to PAH formation, direct biosynthesis of PAHs has not been demonstrated, suggesting that biogenesis is not a significant (direct) source of PAHs (USEPA 2003). As discussed in the next section, these precursor PAHs may be transformed by diagenic processes into certain PAHs.

6.4 Diagenetic

Diagenesis is a geologic term referring to chemical, physical, and biological processes acting on sediments after deposition. Creation of PAHs by diagenesis is a low temperature process, occurring in anaerobic environments. The exact steps in diagenic PAH formation have not been clearly identified; however, they are believed to involve microorganisms, such as bacteria, and possibly in combination with other physical and chemical processes. Relatively few types of PAHs are produced by diagenic processes. Terpenes from deposited plant material can become biogenic precursors for the formation of diagenic PAHs such as retene and derivatives of phenanthrene and chrysene (USEPA 2003). Perylene is another diagenic PAH, commonly found in sediments under anaerobic conditions. Although PAHs formed diagenically may be found in recent sediments, they are unlikely to be the main source in sediments deposited during human activity.

7.0 Distribution of PAHs

Given that PAHs arise from natural processes and many human activities that occur around the globe, there are many sources of PAHs. PAHs from these sources are widely distributed in the environment and found in all environmental media – air, water, sediments, and soils. This section discusses some of the common sources of PAHs and levels of PAHs found in the environment.

7.1 PAHs in the Environment

Although this guide focuses on PAHs in the aquatic environment, PAH concentrations for all environmental media (air, water, sediment, soil) are presented in the following sections so that there is some basis for comparison.

7.1.1 Air

PAHs are found in ambient air in both gaseous form and on particles. PAHs in gaseous phase are predominantly two- and three-ringed, in the particulate phase are PAHs with five or more rings, and those with four rings are found in both phases (ATSDR 1995). Most of the particle-phase PAHs are found on particles having aerodynamic diameters of 0.1 to 3.0 microns, such that they are easily respirable.

PAHs are ubiquitous in ambient air and are found in urban, suburban, and rural locations. PAH emissions to the atmosphere are primarily anthropogenic in origin. PAHs, particularly those of heavier molecular weight, tend to associate with particles of a size that remain in the atmosphere for several days (Baek *et al.* 1991), allowing time for dispersal into areas that may have little human activity.

More than 100 species of PAHs have been identified in the urban air of the U.S. (Baek *et al.* 1991) and concentrations vary widely. For example, background concentrations of benzo(a)pyrene in the U.S. are reported to range from 20 to 1,200 ng/m³ in rural areas and 150 to 19,300 ng/m³ in urban areas (Pucknat 1981). Urban dust, a pyrogenic PAH source, shows a preponderance of HPAHs.

7.1.2 Water

PAHs are widely found in fresh and marine surface water due to widespread dispersion and deposition of airborne PAHs, urban storm water runoff, wastewater discharges, spills, and natural oil seeps and erosion. Concentrations vary widely. For example, Menzie *et al.* (1992) reported a median concentration of 8 ng/L for total carcinogenic PAHs in surface water with a range of 0.1 to 830 ng/L.

Reported concentrations of PAHs in seawater vary widely, in part due to differences in methods of sampling and analysis. In general, PAHs in locations far offshore and away from natural oil seeps or anthropogenic releases are low or not detectable, and at higher levels in coastal and estuary areas (Manoli and Samara 1999) where sources of PAHs are more abundant.

Concentrations of two- to six-ringed PAHs in Chesapeake Bay were found typically to range between 0.1 and 2 nanograms per liter (ng/L) (Manoli and Samara 1999). In areas affected by oil seeps or spills, concentration could be greater. For example, near a seep in the Gulf of Mexico, PAHs in the water were reported at 28 ng/L, and near a shallow water seep off of southern California, PAHs in the water ranged from 150 to 520 ng/L (Neff 1997).

PAH levels in groundwater are typically lower than in surface waters. This is to be expected because suspended sediment, to which heavier PAHs tend to sorb, occurs at lower levels in groundwater, and PAHs also tend to sorb to the organic matter in soils. Menzie *et al.* (1992) reported a median value of total carcinogenic PAHs in groundwater of 1.2 ng/L with a range of 0.2 to 6.9 ng/L.

7.1.3 Aquatic Sediments

The low water solubility of PAHs with more than three rings results in higher levels of these PAHs in sediments and soils than dissolved in water. For example, Manoli and Samara (1999) report that total particulate PAH levels in the

Seine were an order of magnitude higher than dissolved levels, and that sediments in the Slave River in Canada often exceeded regulatory thresholds while dissolved levels in the water column rarely exceeded analytical detection limits.

Levels of PAHs in marine sediments span almost four orders of magnitude. National Oceanographic and Atmospheric Agency (NOAA) Status and Trends data range from 0.002 to 232 mg/kg (dry weight) for total carcinogenic PAHs, and other studies report values from 0.003 to 232 mg/kg. Highest concentrations are found in urban harbors around the U.S. Background concentrations are at the low end of these ranges with total PAHs off the southern New England coast at 0.01 to 0.02 mg/kg in sediment cores 24 to 35 cm deep (Neff 1997). The surficial sediment concentration in these cores was 0.1 mg/kg, consistent with the high end of the 0.001 to 0.1 mg/kg reported by Boehm and Farrington (1984) for sediments from Georges Bank off the Massachusetts coast.

Marine sediments in the immediate area of oil and gas production operations have higher levels of PAHs. Brooks *et al.* (1990) found near-shore coastal Texas sediments to have average PAH levels of 0.029 mg/kg. Average sediment concentrations at 10 and 25 meters from a multi-well platform were 0.494 and 1.82 mg/kg, respectively, and consisted primarily of two-ringed aromatics, indicating that the PAHs were petrogenic in origin.

The PAH background found in sediments in areas of Alaska were 0.1 to 1.0 mg/kg in the near-shore Beaufort Sea, and over 1 mg/kg in Prince William Sound (Steinhauer and Boehm 1992; Page *et al.* 1996). In Prince William Sound sediments, natural oil seep petroleum is the dominant source of petrogenic PAHs (Page *et al.* 1999).

PAHs almost never occur alone in sediments. They usually are present as complex mixtures of hundreds or even thousands of related compounds spanning a wide range of physical/chemical properties and toxicity to aquatic organisms. The composition of PAHs in sediments varies widely depending on the sources of the PAH and the extent of natural degradative processes (called weathering) they have undergone since their release into the environment.

7.1.4 Soil

Because PAHs emitted to the air are eventually deposited on the ground, they are widely distributed in soils. Concentrations of individual PAHs are typically 10 to 100 times higher in urban soils than in rural soils. This is to be expected because urban areas have larger populations and more industrial and commercial activities that generate PAHs, particularly, pyrogenic PAHs from combustion processes. Menzie *et al.* (1992) report median levels of total carcinogenic PAHs of 50, 70, and 1,100 µg/kg for forest, rural, and urban soils, respectively.

Road dust contains very high levels of carcinogenic PAHs. Menzie *et al.* (1992) reported PAH levels ranging from 8,000 to 336,000 µg/kg with a median of 137,000 µg/kg. High levels of PAHs in urban areas unaffected by industrial releases are believed to be due primarily to road dust.

At sites contaminated by PAHs from industrial operations such as wood preserving and treatment, creosote or coke production, and gas works, PAH levels in their soils may be even greater than those in road dust. Levels of individual PAHs, including naphthalene, phenanthrene, dibenz(a,h)anthracene, fluoranthene, and fluorene have been reported in the thousands of ppm (mg/kg) range (ATSDR 1995).

7.2 PAHs in Source Materials

Typical sources of PAHs of petrogenic and pyrogenic origin are described in this section, along with some data on PAH content. Examples of petrogenic sources are crude oils, fuels, and exploration and production wastes. Examples of pyrogenic sources are coal tar, coal tar pitch, coke, and creosote. Urban runoff is an example of a mixed source; it contains predominantly pyrogenic PAHs, but may contain petrogenic PAHs from minor sources such as automotive oil drippings. PAH data for refinery wastewaters, which may also contain both petrogenic and pyrogenic PAHs, are also included in this section.

It should be noted that the PAH analytical data presented here are limited to the 16 priority pollutant PAHs. Analysis for expanded lists of PAHs, including alkylated PAHs, is a more recent approach, and is generally applied only to environmental samples.

7.2.1 Crude Oils

PAHs are natural constituents of crude oil. The characteristics of PAHs in crude oil follow the petrogenic profile, that is, two- to four-ring PAHs and their alkylated forms predominate. The PAH content of crude oils varies widely; however, in typical crude oils, the PAH fraction is small compared to other hydrocarbons.

Table 3 presents PAH concentrations measured in 48 crude oils by a joint industry project to obtain data on crude oils, exploration and production (E&P) wastes, and site soils around the world. Because the data are limited to the 16 priority pollutant PAHs, it is not a comprehensive profile, but it does provide typical concentrations for these PAHs and highlights the petrogenic profile. Higher ring, heavier PAHs were generally found at lower levels or were not detected in any samples. The PAHs most frequently found, and at the highest concentrations, were naphthalene, fluorene, phenanthrene, and chrysene, all two- to four-ring PAHs and found in more than 95% of the samples. Other PAHs found in at least 50% of the samples were benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(ghi)perylene, acenaphthene, benzo(a)pyrene, dibenz(a,h)anthracene, and benz(a)anthracene. PAHs found in 25% or less of the samples were anthracene, fluoranthene, and indeno(1,2,3-cd)pyrene. Acenaphthylene, a three-ring PAH, was not found in any of these samples.

Table 3. Priority Pollutant PAHs in Crude Oil

PAH (listed in order of occurrence, most to least frequent, and number of rings)	Number of Rings	%Time Detected (out of 48 analyses)	mg/kg oil			
			Minimum	Maximum	Mean	Median
Naphthalene	2	100%	1.2	3700	427	345
Fluorene	3	100%	1.4	380	70.34	60.5
Phenanthrene	3	98%	ND	400	146	130
Chrysene	4	98%	4	120	30.36	25
Pyrene	4	96%	ND	90.2	17	13
Benzo(b)fluoranthene	5	92%	ND	14	4.08	3.35
Benzo(k)fluoranthene	5	88%	ND	1.3	0.07	ND
Benzo(ghi)perylene	6	79%	ND	1.7	0.08	ND
Acenaphthene	3	75%	ND	58	11.1	9.55
Benzo(a)pyrene	5	69%	ND	7.7	1.5	1.15
Dibenz(a,h)anthracene	5	58%	ND	7.7	1.25	0.68
Benz(a)anthracene	4	54%	ND	16	2.88	1.03
Anthracene	3	25%	ND	17	4.3	1.2
Fluoranthene	4	25%	ND	15	1.98	ND
Indeno(1,2,3-cd)pyrene	6	8%	ND	1.7	0.08	ND
Acenaphthylene	3	0%	ND	ND	ND	ND
Source: Kerr <i>et al.</i> , 1999						
ND – not detected						

7.2.2 Fuels

A summary of PAH data for various fuel oil and gasoline is presented in Table 4. This is not a comprehensive profile, but it does highlight some characteristics PAHs in fuels. In the fuels that were analyzed, naphthalene and its C1-alkylated forms account for the majority of the two- to six-ring PAHs. The totals for the two- and three-ring PAHs are much greater than the totals for the four- to six-ring PAHs, which exemplifies the petrogenic profile of petroleum-based fuels. Ratios of totals for two- to three-ring PAHs to totals for four- to six-ring PAHs range from about 5 to 1300.

Table 4. Priority Pollutant PAHs in Fuel Oils and Gasoline

PAH (listed by number of rings, low to high)	Number of Rings	mg PAH/kg oil					
		Bunker C	Diesel #2	Fuel Oil #2	Fuel Oil #4	Fuel Oil #6	Gasoline
C1-naphthalenes	2	1336	5983	8414	9280	4924	758
Naphthalene	2	108	1071	2200	982	548	2917
Acenaphthene	3	1	116	251	238	185	ND
Acenaphthylene	3	ND	ND	ND	ND	1	ND
Anthracene	3	18	ND	ND	99	156	3
Fluorene	3	112	350	620	438	280	7
Phenanthrene	3	267	612	1041	1225	1173	9
Benz(a)anthracene	4	49	ND	ND	46	547	ND
Chrysene	4	132	ND	ND	88	669	ND
Fluoranthene	4	13	ND	38	55	151	1
Pyrene	4	91	59	251	292	1081	2
Benzo(a)pyrene	5	63	ND	ND	ND	347	ND
Dibenz(a,h)anthracene	5	15	ND	ND	ND	76	ND
Benzo(b,k)fluoranthenes	5	2	ND	ND	ND	27	ND
Benzo(g,h,i)perylene	6	21	ND	ND	ND	171	ND
Indeno(1,2,3-cd)pyrene	6	4	ND	ND	ND	22	ND
Total low ring (2-3) PAH	2-3	1842	8132	12526	12262	7269	3694
Total high ring (4-6) PAH	4-6	392	59	289	481	3091	3
Ratio low/high PAH	---	4.70	137.83	43.34	25.49	2.35	1278.66
Source: Stout <i>et al.</i> 1998							
ND – Not detected							

7.2.3 Exploration and Production Wastes

As part of the same study discussed in Section 7.2.1, PAH data were obtained for tank bottoms and sludges related to oil exploration and production activities. The results of the analyses of ten oil E&P wastes are provided in Table 5. As these data show, the distribution of PAHs in E&P wastes is naturally similar to crude oils, and reflects a petrogenic profile. PAHs with the highest concentrations are two- to four-ring PAHs and include phenanthrene, naphthalene, fluorene, chrysene, acenaphthene, and pyrene. PAHs with the lowest concentrations, benzo(k)fluoranthene and indeno(1,2,3-cd)pyrene, are five- and six-ring PAHs. Acenaphthylene, which was not detected in the crude oil samples, was detected in the E&P wastes, but at a very low concentration.

Table 5. Priority Pollutant PAHs in E&P Tank Bottoms and Sludges

PAH (listed in order of concentration, high to low)	Number of Rings	mg/kg Mean of 10 Samples
Phenanthrene	3	55.53
Naphthalene	2	44.00
Fluorene	3	21.09
Chrysene	4	12.16
Acenaphthene	3	6.51
Pyrene	4	5.42
Benzo(1)anthracene	4	2.98
Fluoranthene	4	2.31
Anthracene	3	2.22
Benzo(b)fluoranthene	5	1.74
Benzo(a)pyrene	5	0.97
Benzo(ghi)perylene	6	0.73
Dibenz(a,h)anthracene	5	0.65
Acenaphthylene	3	0.29
Benzo(k)fluoranthene	5	0.28
Indeno(1,2,3-cd)pyrene	6	0.20
Source: Kerr <i>et al.</i> , 1999		

7.2.4 Pyrogenic and Mixed Sources of PAHs

A summary of PAH data for various pyrogenic sources is presented in Table 6. This is not a comprehensive profile, but it does highlight some characteristics of pyrogenic PAH sources. Ratios of totals for two- to three-ring PAHs to totals for four- to six-ring PAHs range from 0.02 to 2.55, much lower than the ratios for the petrogenic PAH fuel sources shown in Table 4. Although the coke and creosote samples are pyrogenic sources and contain significant quantities of high-ring PAHs, in this priority pollutant PAH set, they have higher percentages of low-ring PAHs, primarily naphthalene. Such differences emphasize the need to evaluate PAH sources not by a single characteristic or index. Pyrogenic and petrogenic PAH sources may be distinguished by combinations of indices, as discussed elsewhere in this report.

Table 6. Priority Pollutant PAHs in Representative Pyrogenic and Mixed Sources

PAH (listed by number of rings, low to high)	Number of Rings	Urban Runoff*	mg PAH/kg product			
		(ug PAH/kg dry soil)	Coal Tar	Coal Tar Pitch	Coke	Creosote
C1-naphthalenes	2	2	1193	2	1958	8229
Naphthalene	2	4	4044	6	67487	60274
Acenaphthene	3	3	3817	167	1680	22699
Acenaphthylene	3	3	45	1	7449	5248
Anthracene	3	17	5217	371	37074	7073
Fluorene	3	4	4761	45	12733	18774
Phenanthrene	3	100	16231	1678	9009	44572
Benz(a)anthracene	4	113	4218	13232	7811	5149
Chrysene	4	143	4032	11714	7960	4108
Fluoranthene	4	196	10988	8811	24847	29232
Pyrene	4	150	8517	8791	16664	21131
Benzo(a)pyrene	5	107	2932	16355	6040	2222
Dibenz(a,h)anthracene	5	28	469	2749	1300	208
Benzo(b,k)fluoranthenes	5	262	1525	12284	3208	2159
Benzo(g,h,i)perylene	6	92	1355	10485	2762	574
Indeno(1,2,3-cd)pyrene	6	97	1597	12474	3150	718
Total low ring (2-3) PAH	2-3	132	35308	2270	137390	166869
Total high ring (4-6) PAH	4-6	1188	35633	96894	73742	65501
Ratio low/high PAH	---	0.11	0.99	0.02	1.86	2.55
Source: Stout <i>et al.</i> 1998						
ND – Not detected						
*Primarily pyrogenic sources, but can contain some petrogenic sources (e.g., automotive fuel)						

Parking lot coal tar emulsion sealcoats have been shown to be significant contributors to urban PAHs. In a study of thirteen parking lots in Austin, TX, the mean total PAH content in particulates in simulated runoff from sealcoat lots was 3500 mg/kg, 65 times higher than that for unsealed lots (Mahler *et al.* 2005). The time of sampling after sealcoat application varied from a few weeks or months to several years. An evaluation of diagnostic ratios of key PAHs indicated that suspended sediment from the urban streams most closely matched the coal tar sealcoat group. Using the simulated runoff data, PAHs loads in storm runoff were projected for four watersheds in Texas. It was estimated that the PAH load from parking lots in the four watersheds could be reduced 5 to 11% if sealcoats were not applied.

In 1994, API evaluated the treatment efficiency of biological wastewater systems of 10 petroleum refineries. Most of the treatment systems were variations of the activated sludge process and others were high rate aeration systems (conditions to allow shorter hydraulic retention time). Over 200 parameters were measured in wastewater influents, effluents, and biological sludge, including the 16 priority pollutant PAHs. Wastewater influent sample points were after primary treatment processes such as oil/water separation, dissolved/air flotation, and equalization. PAH data from this study are summarized in Table 7. Six of the 16 priority pollutant PAHs were detected in wastewater influents prior to the biological treatment system: naphthalene (median concentration 150 µg/L), phenanthrene (23 µg/L), and fluorene (22 µg/L), acenaphthene (<20 µg/L), chrysene (<22 µg/L), and pyrene (<22 µg/L). Of these six