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

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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.

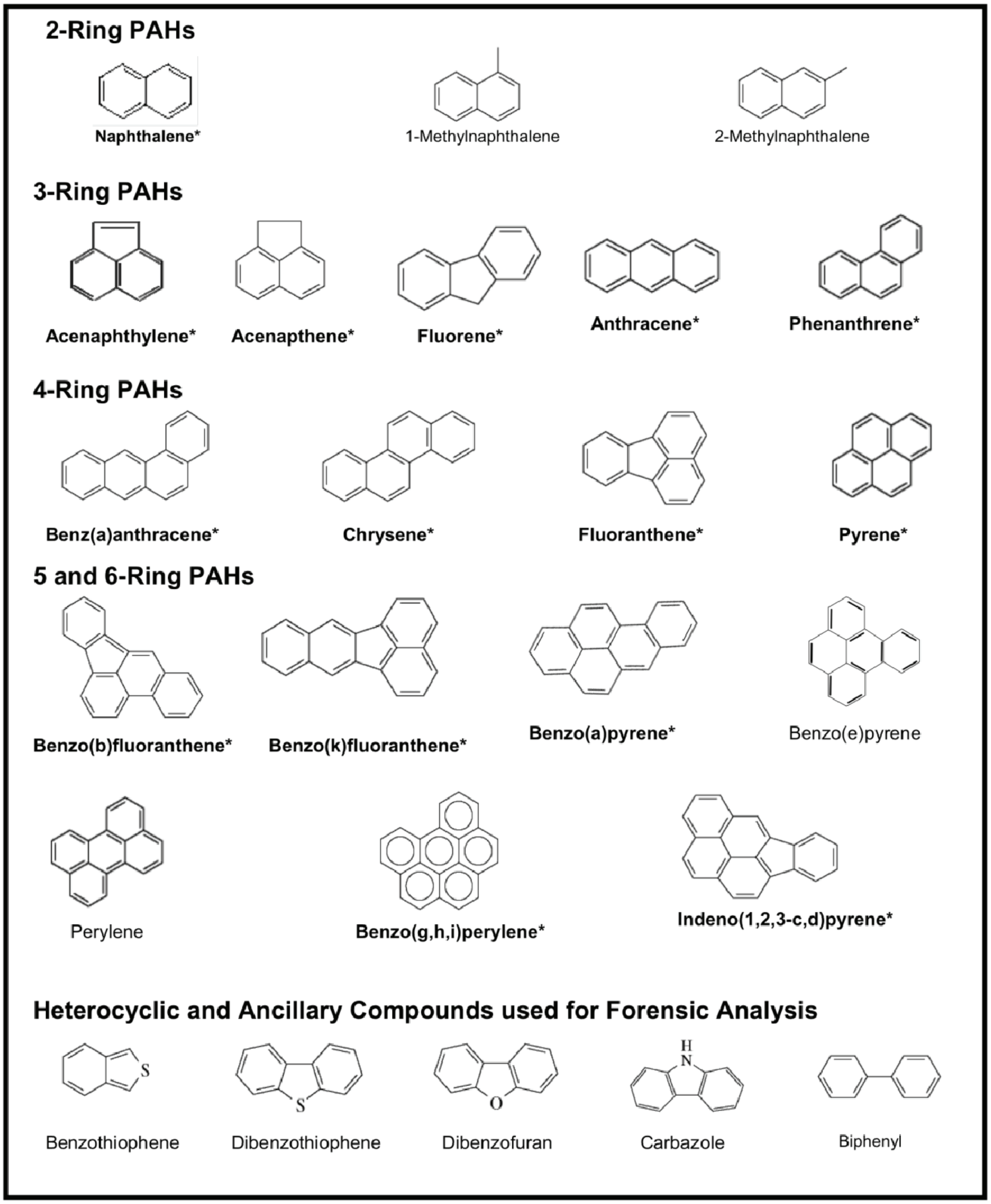

Figure 1. Representative PAH and Heterocyclic Compounds.
Note: The "priority pollutant" PAHs are marked (*); dibenz(a,h)anthracene* not shown.

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

*EPA 16 priority pollutants
†Suspected or known carcinogen

Analyte/Analyte Group	Abbreviation	Rings
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 *et al*. 2003b, Uhler *et al*. 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/m^3 in rural areas and 150 to 19,300 ng/m^3 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 *et al.*, 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 *et al*. 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
Benz(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 *et al*., 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* (ug PAH/kg dry soil)	mg PAH/kg product			
			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 *et al*. 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

PAHs, only naphthalene was detected in the wastewater effluents from biological treatment, prior to discharge to receiving waters, and it was detected in only one sample of 26 (1.8 μg/L).

Table 7. Priority Pollutant PAHs in Petroleum Refinery Biological Treatment Wastewaters

PAHs Detected in Sample*	Wastewater Influent to Biological System (μg/L)					Wastewater Effluent from Biological System (μg/L)				
	Min	Median	Max	Number of Samples	% Detections	Min	Median	Max	Number of Samples	% Detections
Acenaphthene	3.3	<20	<500	33	39%	<0.26	<10	<11	25	0%
Chrysene	1.9	<22	<500	35	20%	<0.2	<10	<11	26	0%
Fluorene	4.5	22	<200	33	55%	<0.4	<10	<11	25	0%
Naphthalene	8.5	150	600	35	89%	1.8	<10	<11	26	4%
Phenanthrene	7.3	23	290	35	69%	<0.2	<10	<11	26	0%
Pyrene	2.4	<22	<200	37	14%	<0.6	<10	<11	26	0%
*The 16 priority pollutant PAHs were included as part of the semivolatile organic analyses. Only those PAHs detected are shown.										

8.0 Environmental Fate

Although the presence of PAHs in aquatic systems provides evidence of contaminant sources, source identification is often complicated due to changes by physical, chemical, and biological processes. These processes that affect the fate and transport of PAHs are described in this section. This information is critical to evaluating the toxicity of PAH mixtures as well as their potential sources and can be used both to help estimate toxic effect levels and to identify and differentiate various PAH sources.

The bulk of PAHs in the environment are due to anthropogenic activities, including direct and indirect sources (Soclo 2002). When sediments are found contaminated with PAHs, direct sources such as chemical spills and wastewater discharges are often suspected; however, many studies have shown that indirect sources such urban runoff are major contributors. From both direct and indirect sources, PAHs enter the aquatic environment by surface water and groundwater and atmospheric deposition.

A variety of properties influence the fate and disposition of specific PAH compounds after they enter the aquatic environment, although solubility in water and vapor pressure have a major influence on PAH movement (ATSDR 1995). As a class, PAHs as are extremely hydrophobic (insoluble in water) and solubility typically decreases as molecular weight increases. For example, naphthalene, one of the most water soluble of the PAHs, has a solubility in water of about 30 mg/L compared to benzo(a)pyrene and chrysene, which have water solubility in the low parts per billion (ug/L) range (Soclo 2002). As a result, lower molecular weight PAHs (LPAHs) such as naphthalene are more amenable to biotransformation and abiotic degradation than are the higher molecular weight compounds (HPAHs) (ATSDR 1995)[1]. Also, the HPAHs formed in combustion processes are bound in soot particles, are not very water soluble, and therefore, are much less available to transformation processes.

In contrast, PAHs with 4 or 5 rings such as benzo(a)pyrene and perylene are more stable and thus, persist in sediment and the water column much longer. The processes affecting PAHs in sediment are described in the following sections.

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[1] 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 (i.e., 2- and 3-ring member 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).

8.1 PAH Partitioning

The primary characteristics affecting the partitioning of PAHs between the water column or sediment pore water and sediments are solubility in water and sorption onto organic matter. Due to their low solubilities and high affinity for organic carbon, PAHs in aquatic systems are primarily found sorbed to particles that either have settled to the bottom or are suspended in the water column. Some of the PAHs are already sorbed to particles before they enter the water, such as those attached to soot particles, which are deposited from the air or carried in storm runoff. It has been estimated that two-thirds of PAHs in aquatic systems are associated with particles while one-third is present in a dissolved form (Eisler 1987).

The octanol-water partition coefficient (K_{ow}) is used to estimate the potential for an organic chemical to move from water into lipid (oily materials, including biological membranes). The organic carbon partition coefficient (K_{oc}) indicates the chemical's potential to bind to organic carbon in soil and sediment. K_{oc} is closely correlated with K_{ow} and can be estimated from K_{ow} through regression techniques (Karickhoff 1981). LPAHs have K_{oc} values that range between 10^3 and 10^4, which indicate a moderate potential to be sorbed to organic carbon in the soil and sediments. HPAHs have K_{oc} values ranging from 10^5 to 10^6, which indicate a stronger tendency to sorb to organic carbon (Southworth 1979). It is important to note that the type of carbon (anthropogenic or natural) found in aquatic systems also has an effect on K_{oc} values.

Another chemical property that affects PAH levels in the water column is the Henry's Law Constant. The Henry's law constant is the partition coefficient that expresses the ratio of the chemical's concentrations in air and water at equilibrium and is used as an indicator of a chemical's potential to volatilize from the water into the air. Lower molecular weight PAHs can be substantially volatilized from water under conditions of high water temperatures, shallow depths, and high wind (Southworth *et al*. 1978). Southworth (1979) estimated that the volatilization half-live for anthracene was 18 hours in a stream with moderate current and wind and about 300 hours in a body of water with a depth of 1 meter and no current. Consequently, even for PAHs susceptible to volatilization, other processes such as sorption, photolysis, and biodegradation may become more significant than volatilization in slow-moving waters (ATSDR 1995).

Specific techniques to estimate and measure partitioning of PAHs in sediment and the water column are discussed in the following sections.

8.1.1 Estimation Techniques

Chemical partitioning within the sediment can be estimated as follows:

$$C_{\text{sorbed}} = f_{\text{OC}} \cdot K_{\text{OC}} \cdot C_{\text{dissolved}}$$

where C_{sorbed} represents the chemical concentration sorbed to organic carbon (milligrams organic carbon–sorbed chemical per kilogram dry sediment), f_{OC} represents the fraction of dry sediment present as organic carbon, K_{OC} represents the organic carbon–water partition coefficient (L/kg), and $C_{\text{dissolved}}$ represents the chemical concentration dissolved in pore water (mg/L) (Fuchsman 2003). This equation assumes that chemical partitioning is at equilibrium and that the amount of chemical sorbed to the non–organic carbon (mineral) component of sediment particles is negligible.

Estimating sediment concentrations or pore water concentrations using a partitioning equation has certain advantages. Results are relatively accurate if the system is at or near equilibrium. Because pore water concentrations can be calculated using sediment concentrations and partition coefficients, additional pore water extraction and analysis, which can be costly and time-consuming, is not necessary. Besides the cost and time factors, pore water extraction results can be highly variable, in part because conditions may not satisfy the assumption of equilibrium and also because the heterogeneous nature of sediments makes it difficult to get representative samples. Despite the advantages of estimation techniques and partitioning models, it is important to remember that they are only accurate if one assumes the system is in equilibrium and an appropriate organic carbon water partition coefficient is used.

8.1.2 Direct Measurement Techniques

Direct measurement techniques to determine sediment partitioning focus on the analytical measurement of PAH concentrations in sediment and in pore water. The major advantage of direct measurement techniques is that the result is a quantitative measure of conditions in the sediments from the site and the data can be directly compared and evaluated to determine the partition coefficient between sediment and pore water.

Three extraction techniques that are used in understanding sediment partitioning include mild Supercritical Fluid Extraction (SFE), Solid Phase Micro-Extraction (SPME), and Semi-Permeable Membrane Devices (SPMD). Mild SFE measures the release of the readily available fraction of PAHs in sediments. SPME measures the dissolved concentration of PAHs in sediment pore water and is a solvent-free equilibrium extraction method that, with proper calibration, can allow quantitative determinations of PAHs at very good sensitivity (usually low-to-mid parts per trillion). In the refinery sector, the use of the SPME approach gives information about the concentration of potentially accumulative substances in effluent and receiving waters, which may then be used to assess the need for further investigation. SPMD can be deployed in a water column over a long period of time, yielding an average partitioning estimate between water and sediments, or water and biological tissue.

Bioassays can also aid in understanding processes that influence partitioning and bioaccumulation of chemicals in sediments. In Norway, SPMDs and caged mussels together with in situ sampling of seawater were identified as capable methodologies for measuring average levels of produced water compounds over a certain time period (Durell *et al*. 2006). These predictions using mussels, SPMDs, and modeling were found to support and complement each other and the Norwegian surveys demonstrated that a combination of these methods are valuable tools for estimating the fate and impact of PAHs in produced waters that are discharged to the ocean. In the United States, the ASTM D19.06 subcommittee is currently assessing the method development and proof of concept, as requested by EPA.

In contrast to estimation techniques, direct measurement techniques can have significantly higher analytical and sampling costs and have not yet been well standardized for routine analysis of field samples. Despite these disadvantages, direct measurement techniques are likely to gain increasing use, particularly at more contaminated sites, since results offer a more relevant measure for the purpose of environmental risk assessment.

8.2 Transformation Processes

The most important processes contributing to the degradation of PAHs in water and sediment include photo-oxidation, volatilization, chemical oxidation, and biodegradation. How much of a PAH is degraded and what are the degradation products depends on environmental conditions such as temperature, depth, chemical quality, flow rate, and oxygen content. Degradation also depends on the exposure of a PAH to transformation processes. For example, naphthalene in fuels can degrade relatively quickly, whereas naphthalene sorbed within a soot particle is far less available to these processes.

Degradation of PAHs in water generally takes weeks to months and is primarily through microbial activity. Studies have shown that there is a two-stage curve where some PAHs degrade or transform readily during the first few weeks or months, then degrade at a very slow rate, if at all (Huesemann *et al*. 2003; Ghoshal 1996). In environmental samples, because weathering processes can alter the original source signatures, it is important to understand if and how weathering may have an effect. A pyrogenic distribution cannot weather to look like a petrogenic one and similarly, a petrogenic distribution will not weather to look like a pyrogenic one.

The rate and extent of photodegradation varies widely among PAHs and is a complex function of structure (Fasnacht and Blough 2002, 2003; Kosian *et al*. 1998; Kubicki 2005). Anthracene, phenanthrene, and benz(a)anthracene were found amenable to photodegradation in water (Nagata and Kondo 1977), but benzo(a)pyrene, chrysene, fluorene and pyrene were not (ATSDR 1995). The most common photo-reaction products are peroxides, quinones and diones (NAS 1972). As one might expect, the rate of photolysis being dependent on light penetration, decreases with increasing depth and turbidity (Zepp and Schlotzhauer 1979).

PAHs in water can be chemically oxidized by chlorination and ozonation. In general, ozonation is generally slower and less efficient than chlorination in degrading PAHs (Neff 1979) and can lead to the formation of carcinogenic peroxides. Reaction pathways for ozonation of some PAHs include benz(a)anthracene to 7,12-quinone and fluorene to fluoreneone (NAS 1972). In comparison to ozonation, a high efficiency of PAH degradation from chlorination has been reported by Harrison *et al*. (1976a,b) for both laboratory and waste-water treatment plant conditions. When tested, pyrene was the most rapidly degraded PAH when exposed to chlorination. Benzo(k)fluoranthene and fluoranthene were the most slowly degraded of the compounds tested. Oyler *et al*. (1978) identified anthraquinone and monochloro derivatives of several PAHs as products from chlorination. Mori *et al*. (1993) also found that chlorination of benz(a)anthracene in solution produced a variety of halogenated compounds.

For PAHs in sediment, biological activity is the most significant degradation pathway. Biodegradation of PAHs in sediment is affected by organic content, structure and particle size of sediment, characteristics of microbial population, the presence of toxic contaminants, and the physical and chemical properties of the PAHs (Wilson and Jones 1993). For example, sorption of PAHs to organic matter may limit the bioavailability, and thus, biodegradation of compounds that would otherwise rapidly undergo metabolism (Manila and Alexander 1991; Weissenfels *et al*. 1992). The actual source of the PAH is an important aspect of biodegradation, considering for example, that sorption to soot, a pyrogenic source of PAHs, can make even LPAHs unavailable to biodegradation.

Among varying trophic levels, biodegradation of PAHs is significantly influenced by the type of PAH, age of release, type of organic or inorganic matter substrate, and the biological community structure. Other factors that affect PAH biodegradation are water temperature and whether adapted microorganisms are present (Aamand *et al*. 1989). Biodegradation of PAHs can be significantly metabolized by microbes under oxygenated conditions; however, under anoxic conditions, degradation is extremely slow (Neff 1979). Concentrations of dissolved oxygen greater than 0.7 mg/L are adequate for biotransformation and a minimal concentration of PAHs (30 to 70 μg/L) is required for biodegradation to proceed (Borden *et al*. 1989). Herbes and Schwall (1978) investigated the rates of microbial transformation of PAHs in freshwater sediments from both pristine and oil-contaminated streams. They found that turnover times in uncontaminated sediment were 10 to 400 times greater than in contaminated sediment (ATSDR 1995) due to reduced oxygen concentrations. Herbes and Schwall (1978) also reported that turnover times in the oil-contaminated sediment increased 30 to 100 fold per additional ring from naphthalene (2-ring) through benz(a)anthracene (4-ring). Naphthalene was broken down in hours while the turnover times for benz(a)anthracene and benzo(a)pyrene were approximately 400 days and greater than 3.3 years, respectively.

Some PAHs are totally or partially degraded by some bacterial and fungal species (ATSDR 1995). The bacterial degradation pathway involves formation of cis-dihydrodiols, then oxidation to dihydroxy products. In fungi and mammalian systems, trans-dihydrodiol is produced via an arene oxide intermediate (Cemiglia and Heitkamp 1989; Neff 1979). This is significant because the arene oxides have been linked to the carcinogenicity of PAHs (ATSDR 1995). Algae have been found to transform benzo[a]pyrene to oxides, peroxides, and dihydrodiols (Kirso *et al.* 1983; Warshawsky *et al*. 1993).

Biotransformation of PAHs in fish liver can produce carcinogenic and mutagenic intermediates, and exposure to PAHs has been linked to the development of tumors in fish (Eisler 1987). Although fish and most crustaceans evaluated to date have the biological pathways required for biotransformation of PAHs, some mollusks and other aquatic invertebrates are unable to metabolize PAHs efficiently (Varanasi *et al*. 1985). Varanasi *et al*. (1985) ranked the extent of benzo(a)pyrene metabolism by aquatic organisms as follows: fish > shrimp > amphipod crustaceans > clams.

8.3 Bioaccumulation

Bioaccumulation refers to the uptake of a chemical from water, air, and ingested food or sediment. It could also include direct transfer from sediment particles or pore water through the surfaces of benthic organisms. Bioaccumulation of PAHs is an important process influencing aquatic toxicity. However, it is important to realize that many PAHs are also susceptible to metabolism, which reduces bioaccumulation. EPA concluded that PAHs were not bioaccumulative chemicals of concern (BCC) when they adopted the Great Lakes Water Quality Guidance (40 CFR 132), confirming the EPA's acceptance that bioaccumulation in aquatic food chains is not the mode of potential toxicity for PAHs in surface waters.

In this section, common terms related to bioaccumulation are briefly described. All of these terms relate in different ways to the propensity of a chemical to transfer from the ambient environment to an exposed aquatic organism. A more detailed discussion of bioaccumulation related to PAHs may be found in API Publication No. 4656, *Bioaccumulation: How Chemicals Move from the Water into Fish and Other Aquatic Organisms*.

Bioconcentration factors (BCFs) express the PAH concentration in tissues compared to PAH concentration in the water column. Eisler (1997) reported BCFs ranging from 10 to 10,000 for aquatic organisms. These BCFs were used by EPA to calculate its recommended surface water quality criteria for the 16 priority pollutant PAHs.

Sediment associated PAHs are accumulated by bottom-dwelling invertebrates and fish (Eisler 1987). The biota-sediment accumulation factor (BSAF) relates the tissue concentrations of aquatic organisms to the sediment concentration to which the organisms are exposed.

Bioaccumulation factors (BAFs) are used to calculate aquatic organism tissue concentrations from water column concentrations and food intake, assuming that the organism food source concentrations are in equilibrium with the water column concentrations. Generally speaking, bioaccumulation occurs when the rate of uptake exceeds the rate of passive elimination into the water, resulting in a net transfer into lipid-containing tissues.

Bioaccumulation can be magnified (biomagnification) through the food chain. Biomagnification refers to an increase in tissue concentrations moving up a food chain when organisms at lower trophic levels are ingested by organisms at progressively higher trophic levels. Biomagnification of PAHs has not been documented because many aquatic species, particularly fishes, are able to metabolize and eliminate them. In general, decreasing PAH concentrations are associated with increasing trophic level, most likely the result of the rapid biotransformation of the compounds. Therefore, food chain uptake has not been documented as a major source of exposure to PAHs for aquatic animals and human consumers (ATSDR 1995).

9.0 Toxicity and Health Effects

Despite low solubilities in water, PAHs have the potential to cause adverse health and environmental effects. These effects are discussed in the following sections. PAHs almost always occur in the environment as complex mixtures, and the overall toxic effect of PAHs depends on the composition of the mixture. The toxicity of individual PAHs has been widely studied in the laboratory, and the toxicity of PAH mixtures has been evaluated in both the laboratory and the field. Some PAHs have been found to exhibit carcinogenic and mutagenic effects in humans or animals, while others have not.

9.1 Human and Ecological Effects

Evidence of adverse effects to humans from exposure to PAHs comes primarily from occupational studies of workers who were exposed to PAH mixtures from coke production, roofing, oil refining, or coal gasification. Cancer associated with exposure to PAH-containing mixtures in humans occurs predominantly in the lungs following inhalation and in/on the skin following dermal contact (ATSDR 1995). Leukemia and lymphoma have also been diagnosed in humans exposed to coal tar creosote, coal tar, coal tar pitch, and coal tar pitch volatiles. Dermal effects such as skin irritation, burning, and erythema (redness) have been observed after exposure to coal tar and coal tar products. There are no reports of adverse reproductive or developmental effects in humans exposed to coal tar and coal tar products. Exposure to wood creosote, which is derived from the resin from leaves of the creosote bush, has been observed to have hepatic effects such as jaundice, abdominal pain, liver failure, acute toxic hepatitis, and elevated serum liver enzymes and dermal effects such as acute allergic reactions of the skin.

EPA has classified creosote as a Group B1 probable human carcinogen, based on sufficient evidence from animal studies and limited evidence from human studies (ATSDR 2002). USEPA is currently re-evaluating human toxicity values for benzo(a)pyrene, naphthalene, and PAH mixtures, although to-date, final chemical assessments have not been issued. EPA has not announced any pending revisions to the 2003 PAH sediment benchmark document (USEPA 2003).

Certain PAHs and PAH mixtures (i.e., coal tar products) have also been shown to induce cancer in animals (i.e., mice and rats). Similar to human studies, the site of tumor induction is generally influenced by route of exposure (i.e., stomach tumors are observed following ingestion, lung tumors following inhalation, and skin tumors following dermal exposure), although tumors can also form at other locations that are not directly related to the exposure route (e.g., lung tumors after dermal exposure) (ATSDR 1995).

Noncancerous adverse health effects associated with PAH exposure has also been observed in laboratory animals. Studies demonstrate that PAHs tend to affect proliferating tissues such as bone marrow, lymphoid organs, gonads, and intestinal epithelium (ATSDR 1995). In other laboratory studies, skin irritation and the formation of comedones have been observed following short-term dermal exposure to coal tar creosote (ATSDR 2002).

For aquatic organisms, EPA developed toxic units (a “toxic unit” (TU) is the measured sample concentration divided by the concentration that may result in toxicity) for PAH based on existing aquatic toxicity tests for many species with many hydrocarbons, and critical body burden (internal PAH concentration at which hydrocarbon narcosis occurs) (USEPA 2003). One example is the U.S. Army Corps of Engineers Environmental Residue-Effects Database (ERED), which is a compilation of data, taken from the literature, where biological effects (e.g., reduced survival, growth, etc.) and tissue contaminant concentrations were simultaneously measured in the same organism. These data indicate that biological effects have been observed in aquatic organisms exposed to PAH concentrations typically through ingestion and sorption pathways.

Research over the last decade has shown that exposure to sunlight, more specifically, the ultraviolet (UV) portion of the spectrum can greatly enhance the ecotoxicity of many PAHs. This photo-activated toxicity has been shown to cause rapid, acute toxicity to several freshwater and marine species including fish, amphibians, invertebrates, plants and phytoplankton (USEPA 2003, Lampi *et al*. 2006) at aqueous concentrations below the effects levels for non-UV-activated PAH. Depending on the organism and exposure, photo-activation can increase toxicity to certain PAHs by one to four orders of magnitude over that caused by narcosis (USEPA 2003).

9.2 Bioavailability and Influence on Toxicity

The toxicity of PAHs to humans and aquatic organisms is controlled by their bioavailability. Bioavailability is a measure of the rate and extent of uptake of a chemical, in its unaltered form, into the systemic circulation of an organism from the source of exposure (e.g., a contaminated sediment) (Hrudey *et al.* 1996). It relates directly to the toxic effects of the chemical on the organism because it determines whether the organism can absorb sufficient amounts of the chemical from its immediate environment to cause adverse effects. It is an important factor in the aquatic toxicity of PAHs because these compounds are often tightly bound to organic sediment particles, which makes them less bioavailable than if they were readily dissolved in the interstitial and overlying water.

Bioavailability of PAHs from sediments depends in part on the organic content of the sediment. It has been found that anthropogenic carbon (such as soot) binds PAHs more strongly than natural organic matter (Burgess *et al*. 2004; Cornelissen and Gustafsson 2004; Kukkonen *et al*. 2005). In another study, field data from more than 14 MGP and aluminum smelter sites indicated that toxicity to aquatic organisms was not related to the concentration of total extractable PAHs in sediments using EPA standard methods (Kreitinger *et al*. 2007). Typically both natural and anthropogenic carbons are present in sediment and therefore, the quantity of each carbon type is important in assessing PAH bioavailability in sediments at a particular site. There is currently no universally accepted method for accurately quantifying the fraction of sediment carbon that is soot (USEPA 2003), but the method proposed by Gustafsson et al. (1997) is probably the most frequently used method.

EPA’s guidance document on the development of equilibrium partitioning benchmarks for PAHs (USEPA 2003) uses organic carbon normalized PAH concentrations and median response concentrations, for specific PAH compounds, to account for bioavailability in its sediment benchmarks.

9.3 Individual Compounds Versus Mixtures

Toxicity varies among PAHs. LPAHs generally have a significant acute toxicity that is currently believed to be best described by narcosis theory, whereas some HPAHs, such as benzo(a)pyrene, are identified as having significant carcinogenic potential. EPA's report on equilibrium partitioning benchmarks for PAHs relies on narcosis theory as the primary acute toxic effect of these chemicals to benthic organisms (USEPA 2003).

The carcinogenic potential of those HPAHs identified by EPA as Class B2 human carcinogens (e.g., benzo(a)pyrene, benz(a)anthracene, chrysene) is from direct ingestion of water, fish/shellfish tissue, or by inhalation. Because of the very low solubility of these PAHs and the fact that they are metabolized by many aquatic organisms, they do not tend to bioaccumulate or biomagnify in the food chain. Also, because of the very low solubility of these PAHs in water, they are essentially never found in fresh water at concentrations that approach the drinking water criteria. Therefore, although the carcinogenic properties of certain HPAHs are important, they are rarely the controlling factor in determining the environmental risk of contaminated sediments.

PAHs almost always occur in the environment as complex mixtures. As mixtures, the toxicities of PAHs are additive or nearly additive and the combined toxicities must be considered. EPA's equilibrium partitioning benchmarks for sediment PAHs uses an extended list of PAHs (both LPAHs and HPAHs), with sediment concentrations normalized to the carbon content of the sediments, to establish total PAH sediment concentrations to protect benthic species from acute and chronic toxicity (USEPA 2003). States with sediment quality criteria or guidelines, such as Washington and Florida, also combine PAHs into classes for evaluation. Both Florida and Washington use two classes for combined PAHs in sediments, LPAH and HPAH. They also have criteria for specific individual PAHs, not limited to those that are carcinogenic.

Current research supports treating PAHs as having additive toxicity, which results in sediment concentration targets that are based on "total PAHs." How this term should be defined is still being studied. For example, should LPAH and HPAH compounds be combined into a single group, as EPA has recommended for its equilibrium partitioning sediment benchmarks, or into two classes as done by Florida and Washington, or by some other method.

10.0 Regulations, Standards, and Guidelines

10.1 Water Quality Standards

The Clean Water Act (CWA) requires states to adopt surface water quality standards to protect beneficial uses and requires EPA to approve these standards. If EPA deems that a state's standards are not sufficiently protective, EPA can promulgate all or part of the state's water quality standards.

Water quality standards have three components:

1. Designated beneficial uses of surface waters including aquatic life propagation, drinking water supply, production of fish and shellfish that are acceptable for human consumption, and contact recreation;[2]

2. Numeric water quality criteria adopted by the states to protect designated uses; and

3. Narrative water quality standards that protect designated uses with generic objectives that do not rely on numeric criteria for specific pollutants.

EPA publishes national recommended water quality criteria that states may adopt as water quality standards. These are water column criteria and include marine and fresh water criteria for the 16 priority pollutant PAHs. These criteria are based on the protection of human health from the consumption of contaminated fish and shellfish, using a bioconcentration factor and assumed cancer and non-cancer risk factors. Most states have adopted these PAH water quality criteria either directly or in modified form.

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[2] Many states have additional designated uses in their standards, but the above list is the minimum acceptable set of uses under the CWA.

10.2 Sediment Quality Standards

To date, only the state of Washington has adopted numeric sediment quality criteria for specific chemicals, including PAHs, in its state water quality standards, and these are only for Puget Sound.[3] The California State Water Resources Control Board adopted sediment quality objectives in 2008; however, these will not be numeric criteria for specific pollutants, but rather will use a multiple lines of evidence (MLOE) approach.[4] Florida has used sediment quality assessment guidelines (SQAG) in its water quality programs since the mid-1990s, but these are not adopted as part of its water quality regulations. The California and Florida sediment quality guidance values both include PAHs as individual chemicals and as LPAH and HPAH classes.

A number of states have numeric sediment quality screening levels or benchmarks in their guidance, and in some cases, regulations, for contaminated site identification and remediation. These guidelines typically include PAHs, individually or as classes, or both. Essentially all of these numeric criteria are based on the sediment quality guidelines approaches described elsewhere in this report. States may use combinations of the published guidelines to try to better represent the characteristics of their surface waters, but rarely do these guidelines include any new state-specific information. *The most important fact to remember is that these guidance levels, benchmarks, screening levels, or whatever they may be called, are not surface water quality standards as defined by the CWA.*

Notwithstanding considerable efforts by EPA and the states, numeric sediment quality criteria for PAHs are unlikely to be adopted in state or federal surface water quality standards regulations in the foreseeable future. As described in this report and elsewhere, the effects of sediment constituents on benthic organism populations are very complex and site-specific. Unlike water quality criteria that protect aquatic life in the water column, research has shown that site-specific sediment chemistry is so important that it is currently impossible to establish single number criteria for pollutants (including the PAHs) that are protective of benthic populations, but not prone to predicting false positive effects (predicting effects when there are none).

10.3 Impaired Surface Waters and TMDLs

Section 303(d) of the CWA addresses surface waters of the U.S. that states have designated as impaired. Impaired waters do not meet the applicable numeric or narrative surface water quality standards and thus, is assumed to not achieve one or more of its designated uses.

Section 303(d)(1)(C) of the CWA states that for each surface water designated as impaired, the state must calculate a total maximum daily loading (TMDL) that will assure that the water quality standards are achieved (the impairment is eliminated). This section of the CWA further requires states to have a process to identify impaired surface waters (the 303(d) list) and to prioritize them for TMDLs.

In the absence of state adopted numeric sediment quality criteria for PAHs, states rely on their narrative standards to list surface water as impaired due to sediment contaminants. Listing a surface water as having impaired sediment quality based only on screening guidelines is challengeable in the absence of site-specific data showing impaired benthic biology, and/or that there is a potential human health or wildlife risk based on PAH concentrations in tissues of shellfish and fish exposed to the sediments. All of the sediment quality screening threshold methodologies clearly state that the concentration levels are not criteria and that they may indicate impaired benthic biology when there is no impairment. Thus, screening level thresholds provide insufficient scientific evidence for a Section 303(d) listing in the absence of supporting site-specific data — typically biological data.

As discussed elsewhere in this report, PAHs do not bioaccumulate to ecologically significant concentrations in benthic organisms and do not biomagnify in the aquatic food chain. Thus, fish and shellfish tissue data typically are insufficient to justify a listing determination using surface water quality criteria for PAHs. Impaired benthic biology is the applicable basis for a listing determination due to contaminated sediments and should be demonstrated by a

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[3] Washington's sediment quality standards apply only to Puget Sound. These standards are based on the AET method using data collected in Puget Sound.

[4] Essentially, this rule will use the EPA sediment quality triad approach to identify impaired sediment ecosystems.

state agency or EPA in order to legally list a water body pursuant to Section 303(d) as having impaired sediment quality.

In the absence of state adopted numeric sediment criteria, states should always have site-specific evidence other than elevated sediment PAH concentrations to support listing a surface water segment as impaired. However, EPA and some states have placed surface water bodies on Section 303(d) lists based solely on sediment PAH concentrations that exceed thresholds in the screening methods.

Sediments that are considered contaminated with PAHs have in several instances triggered the development of TMDLs (see Table 8). In each of these cases, surface water segments were identified as impaired based upon measurements of PAHs above numeric screening guidelines such as Effects Range Median (ER-Ms) or Effects Range Low (ER-Ls). The resulting TMDLs were developed using a water quality standard or a sediment concentration as the objective. In these TMDLs, the sources of PAHs were largely attributed to storm water runoff. However, point source dischargers of PAHs in a watershed are potentially impacted because a TMDL requires that an allocation be made for each contributing source. All potential point source dischargers of PAHs, whether they currently have permit limits for PAHs or not, may be limited by a TMDL through its allocations.

The listing decisions and TMDLs for PAHs likely have deficiencies that can be administratively, and if necessary, legally, challenged. The most effective point of challenge is the Section 303(d) listing decision. States are obligated to provide the opportunity for public review and comment of their draft listing decisions. The state must provide their complete listing basis, including all supporting data and analyses.

As shown in Table 8, TMDLs for PAHs can have serious technical shortcomings. Common problems include:

- Limited or no PAH data for listing decisions;
- Limited or no PAH for the water body or source loads;
- Borrowing of PAH data from a nearby water body used when no water body-specific data are available;
- Simplistic modeling of fate and transport in the water body, little or no data to calibrate model; and
- Criteria targets that do not account for relative toxicity of individual compounds and/or sum of the compounds.

Listings of surface water bodies as impaired due to PAHs in sediments based solely on screening levels and guidance or limited data should be scrutinized, and if necessary, challenged. For example, all of the TMDLs for the Potomac River watershed shown in Table 8 were listed as impaired by PAHs based solely upon data for the Anacostia River, due to lack of data for the actual water bodies listed. This type of listing decision likely could not be sustained if challenged through the administrative process for listing impaired waters, and almost certainly could have been overturned by litigation.

Challenging a completed TMDL is much more difficult than challenging a listing decision, because state and federal regulations do not require public review and comment for this action, although most states will typically allow for public review. There are legal theories for challenging TMDLs based on specific state statutes, but it is a difficult process and beyond the scope of this discussion.

It is possible to challenge waste load allocations for a specific point source during the amendment of an NPDES permit that would establish TMDL-based limits. However, the probability of success with this approach is questionable given that the TMDL would have been formally adopted by the state and approved by EPA.

Table 8. Selected TMDLs for PAHs

Water Body	Year	Primary PAH Sources	TMDL Results	Shortcomings in TMDL Approach
Calcasieu Estuary, Louisiana	2002	Bayou Verdine - storm water runoff (but no PAH data available)	Bayou Verdine - No reductions specified; monitoring recommended for 3 industrial outfalls (no process wastewater) and instream sediments	No PAH data for source loads.
		Upper Calcasieu Estuary - point source discharges. No data to estimate urban runoff load. Atmospheric deposition considered negligible.	Upper Calcasieu Estuary - Wasteload allocation for 10 industrial dischargers greater than existing total permitted discharges. However, although only 4 dischargers had existing permitted loads, the allocation was divided among the 10, requiring reductions of some existing permitted discharges.	Modeling (WASP) was attempted but lack of data for calibration/validation made prediction impossible. Simple mass balance approach used to calculate TMDLs for two “indicator” PAHs. No PAH data for storm water loads.
Lewis Creek Watershed, Shenandoah River Basin, Virginia	2006	Storm water runoff (background and contaminated sites)	More than 70% of existing PAH load attributed to runoff from contaminated sites. Reduction required from contaminated sites >99%.	Biological impacts could not be directly linked to PAHs. No PAHs were found above their probable effects concentrations. Additive effects were considered possible; total PAHs were above the threshold effects concentration (TEC). Simplistic modeling of PAHs based on sediment loads and mass-balance approach. Assumed PAH concentrations in sediment. No site-specific soil-PAH data.
Potomac River Watershed, District of Columbia				
Anacostia River Watershed	2003	Storm water runoff	Reductions required for PAHs from 98% - 100%.	Because the only available monitoring data for PAHs were from upstream tributaries, the Northeast and Northwest Branches; those average concentrations were used to estimate PAH loads for all non-point sources. No PAH water column calibration data available, so model predictions were compared to predictions of ambient concentrations based on fish tissue data and bioaccumulation factors. Modeling predicted much lower sediment concentrations than were measured. Loads from watersheds were adjusted upwards by 50% to achieve “calibration.” Thus, no real calibration was achieved with the available data. Tributary portion of model based on simple mass balance. (*2)
Dalecarlia Tributary	2004	Storm water runoff		(*1)
				(*2) (*3) (*4)

Water Body	Year	Primary PAH Sources	TMDL Results	Shortcomings in TMDL Approach
Kingman Lake	2003	Storm water runoff, tidal inflow from Anacostia River (listed above)	Reductions for all PAH groups 98%.	(*1) (*2) (*3)
Rock Creek Tributaries	2004		Reductions required to meet water quality standards: PAH group 1 (2- to 3-ring) - 0%; PAH group 2 (4-ring) - 98%; and PAH group 3 (4- to 5-ring) - 98%.	(*1) (*2) (*4)
Washington Ship Channel and Tidal Basin,	2004	Storm water runoff	Reductions required to meet water quality standards: PAH group 1 (2- to 3-ring) - 0%; PAH group 2 (4-ring) - 95.53%; and PAH group 3 (4- to 5-ring) - 93.06%.	(*1) (*2) The water quality model could not be calibrated for organics because of a lack of data for the waterbody. In the water quality model, the organics were assumed as conservative materials and no chemical and biological reactions were considered

(*1) Because of lack of data in the water bodies of concern, organic chemicals of concern were determined from data derived from fish tissue and sediment analysis in nearby water body (Anacostia River).

(*2) Individual PAHs were grouped. The water quality standard applied for each of the 3 groups was the most stringent standard of the individual PAHs in a group.

(*3) TMDL prepared with no data showing impairment or source data.

(*4) Simple mass balance model.

10.4 Sediment Quality Guidelines

Several sediment quality guideline (SQGs) approaches have been developed for PAHs, of which the five major ones are described in the following sections. They are:

1. Equilibrium Partitioning (EqP) approach,
2. National Status and Trends (NS&T) approach,
3. Effects Levels Approach,
4. Apparent Effects Threshold (AET) approach, and
5. Triad/Weight of Evidence Method (WOE).

The EqP based ΣPAH model provides a method to address causality, account for bioavailability, consider mixtures, and predict toxicity and ecological effects using Final Chronic Values (FCVs) for individual PAHs. In contrast, the NS&T approach uses laboratory toxicity data, field studies, and model data to develop specific toxicity criteria (i.e., the Effects Range-Low (ER-L) and the Effects Range Median (ER-M)). The AET method relies on the weight of evidence from a multitude of matched chemical and biological effects data sets to develop a sediment concentration above which an adverse biological effect is always statistically observed. The WOE approach is used in conducting integrated assessments of sediment quality based on measures of chemistry, toxicity and benthos.

To help in understanding the differences among these various methods, Table 9 lists a brief description of each, including their limitations.

Table 9. Advantages and Limitations of Various Sediment Quality Guidelines

Sediment Quality Guideline	Advantages	Limitations
Equilibrium Partitioning (EqP) Approach	• Addresses causality • Accounts for bioavailability • Considers mixtures • Predicts toxicological and ecological effects • Linked to large database • Applicable across sediments	• Assumptions in model may be inaccurate for site • Applicable only to sediment >0.2% organic carbon • False positives and negatives • Lack of relevance to additional binding phases
National Status and Trends (NS&T) Approach	• Weight of evidence approach • Applicable to wide variety of chemicals and sediments	• Limited quality and compatibility of data • Cause and effect relationships cannot be inferred
Apparent Effects Threshold (AET) Approach	• Large data set of correlative effects	• False positives and negatives • Lack of causality
Sediment Quality Triad (SQT) / Weight of Evidence (WOE) Approach	• Effects based technique • Flexible • High quality data and endpoints with strongest links to sediment used as primary evidence • Assesses mixtures	• Time intensive • Site specific with limited extrapolation to other sites

10.4.1 Equilibrium Partitioning (EqP)

Equilibrium partitioning (EqP) describes the assumption that pore water and sediment organic carbon are in equilibrium and that the concentrations are related to a partition coefficient (K_{oc}). The EqP approach (Di Toro, Zarba *et al*. 1991) uses the mass fraction of organic carbon in sediment (f_{oc}) and the K_{oc} to calculate sediment quality benchmarks as follows:

$$\textit{Sediment quality benchmark} = \textit{Water quality benchmark} \times K_{oc} \times f_{oc}$$

Using this approach, EqP assumes that the bioavailable fraction of non-polar organic chemicals is equivalent to the fraction of the sediment concentration that is freely dissolved in interstitial water; and that the freely dissolved fraction is determined primarily by the extent of partitioning to organic carbon. The K_{oc} parameter is typically estimated based on octanol-water partition coefficient (K_{ow}) values.

The equilibrium partitioning approach to nonionic organic chemicals has been used extensively by EPA (2000, 2003) and is presently the EPA's preferred approach for deriving numerical chemical-specific sediment guidelines. The approach was first applied to non-ionic organic chemicals because it presented the greatest promise for generating defensible national numerical chemical specific guidelines applicable across a broad range of sediment types; that is, the EqP based Sum (Σ) PAH model provides a method to address causality, account for bioavailability, consider mixtures and predict toxicological and ecological effects (USEPA 2003).

Other advantages to the EqP method include: (1) the benchmark concentration is linked to a large water quality database; (2) the benchmark concentration recommended is applicable across sediments; (3) the theory is well understood and can be applied in a regulatory framework; and (4) the approach is based on toxicological principles (McCauley *et al*. 2000).

The EqP approach is limited in that the assumptions made are only approximately true, and therefore, the predictions from the model have an inherent uncertainty. Other limitations include limited spatial and geographical coverage (only applicable to sediment having greater than 0.2% organic carbon), the occurrence of false negatives and positives, and the lack of relevance to additional binding phases such as soot carbon and non-aqueous phase liquids like coal tar.

The EqP ΣPAH model attempts to assess the combined toxicity of a PAH mixture. EPA recommends 37 specific PAHs be used to characterize “total PAH.” The measurement of 13 or 23 PAHs will result in an excessive incidence of false positives when total PAH is estimated using the appropriate uncertainty factors (USEPA 2003; McCauley 2000).

It is important to note that EPA and the EPA Science Advisory Board (SAB) do not recommend the use of Equilibrium Sediment Guidelines (ESGs) as stand alone, pass-fail criteria for all applications (McCauley 2000).

10.4.2 National Status and Trends (NS&T)

The National Status and Trends (NS&T) approach (Long and Morgan 1991; USEPA 1992) is a correlative method in which laboratory toxicity data, field studies, and model data have been collected and analyzed. Two criterion points, the ER-L and the ER-M, have been determined for 41 contaminants (12 metals, 18 PAHs, total PCBs, and 10 other organic contaminants). Sediments with chemical concentrations below the ER-L (lower 10th percentile concentration associated with biological effects) are not expected to exhibit adverse effects. Concentrations above the ER-M (50th percentile concentration associated with biological effects) are expected to show biological effects in a majority of the benthic organisms assessed. Concentrations between the ER-L and the ER-M may exhibit effects in sensitive organisms.

Overall, the NS&T approach provides a weight-of-evidence from the available information for assessing sediment quality. In addition, it provides a framework for assessing sediment quality by organizing and summarizing data that relate concentrations of sediment-associated contaminants to specific biological effects (MacDonald 1994; CCME 1999). The NS&T approach is currently used by Environment Canada for the derivation of Canadian sediment quality guidelines. The database developed by Long and Morgan (1990) to derive SQGs for marine and estuarine sediments has been updated and expanded by Environment Canada.

There are significant limitations to the NS&T approach, specifically related to the quality and compatibility of the available data. The data evaluated in Long and Morgan (1990) consists of information collected at multiple locations (freshwater and saltwater) throughout the United States. In addition, the ER-L and ER-M values are for single chemicals, although sediments containing chemical mixtures were used for their derivation. Therefore, the degree of confidence in the ER-L and ER-M values should be considered low for PAHs and much more data are needed to support or refute this approach for all chemicals and for all types of sediment (MacDonald 1994). In addition, direct cause and effect relationships cannot be inferred from this dataset (CCME 1999). Because the NS&T is used in numerous applications, ranging from contaminated site assessment to litigation, caution should be used when evaluating conclusions based solely on this approach (MacDonald 1994).

10.4.3 Apparent Effects Threshold (AET)

The updated and revised data set discussed above in the NT&S approach section also was used by MacDonald (1994) in the Effects Levels Approach to calculate Threshold Effects Levels (TELs) and Probable Effects Levels (PELs); these data are presented by MacDonald *et al*. (1994). However, unlike the ER-Ls and ER-Ms, the TELs and PELs also incorporate chemical concentrations observed or predicted to be associated with no adverse biological effects (no observed adverse effects level data). Specifically, the TEL is the geometric mean of the 15th percentile in the effects data set and the 50th percentile in the no observed effects data set. The PEL is the geometric mean of the 50th percentile in the effects data set and the 85th percentile in the no effects data set. Therefore, the TEL represents the upper limit of the range of sediment contaminant concentrations dominated by no effects data. The PEL represents the lower limit of the range of contaminant concentrations that are usually or always associated with adverse biological effects (MacDonald 1994; Jones *et al*. 1997).

The strength of this approach includes a large database of correlative effects. Similar to the NS&T approach, limitations include the occurrence of false positives and negatives and the lack of causality.

10.4.4 Sediment Quality Triad (SQT) /Weight of Evidence (WOE)

The Sediment Quality Triad (SQT)/Weight of Evidence (WOE) approach was developed by Chapman (1990) to evaluate the degree to which contaminants are responsible for the degradation of sediment health. The SQT/WOE approach is an effects-based technique that involves three components: (1) sediment chemistry (a measure of contamination); (2) sediment toxicity testing (a measure of biological effects and bioavailability); and (3) in situ community parameters (benthic macro-invertebrate community structure). Although somewhat structured, the approach is flexible for each individual site. The highest quality data and endpoints with the strongest links to sediment are used as the primary evidence, with other endpoints used in an ancillary role. All endpoints are integrated at a given sampling location to determine the appropriate action.

The SQT/WOE approach, developed in 1990 (Long and Morgan, 1990; Long and Chapman 1985), is now widely used for conducting integrated assessments of sediment quality based on measures of chemistry, toxicity and benthos (Paine *et al*. 1996). The SQT/WOE approach offers several advantages over other methods. First, it assesses mixtures of contaminants. Second, it uses several approaches as supporting evidence to reach conclusions. Third, relevant information can be gained from each of the components. And fourth, the results are replicable. The disadvantages of this approach are that the cause of the effects may not be readily determined and data derived are site-specific, which may limit extrapolation to other sites.

11.0 Evaluating PAHs in Sediments

Individual PAH chemicals never occur alone in sediments — they are always present in complex mixtures that may complicate evaluation and remediation. In addition, sediment quality screening methods (NS&T, AET, EqP) have a high level of uncertainty when applied to a specific site. Because these methods are designed to be conservative, they tend to generate more false positive than false negative determinations of benthic organism impairment. Therefore, finding PAH concentrations in sediment above screening values by any of the available methods is not determinative that benthic organism impairment is occurring.

Equally important, PAHs as a chemical class only rarely occur as the only or even principal anthropogenic chemical contaminant in sediments. Metals and persistent and potentially bioaccumulative organic chemicals such as polychlorinated biphenyls (PCBs) and pesticides (both banned and currently used) are not uncommon co-contaminants. The co-contaminants are important because the screening level assessment methods do not adequately account for the potential toxicity to benthic organisms of other non-PAH chemicals that may be present.

A tiered approach to evaluating PAH contamination in sediments is needed in order to determine:

1. If benthic organism populations at a specific location are impaired when compared to suitable control locations;

2. If there is documented benthic population impairment, whether there are other contaminants and/or physical conditions other than PAHs that contribute to or may be the principal causes of the impairment; and

3. The most probable source(s) of the PAHs based on the types and relative quantities of PAH chemicals found in the sediments.

The source analysis itself is tiered, beginning with relatively simple and inexpensive sampling and analysis of sediments and progressing, if needed, to more complex and expensive procedures.

12.0 Site Assessments

This section provides guidance on conducting site assessments involving PAHs in sediments. A tiered approach is presented. The first tier is confirmation of impairment to the benthic community of the water body, which should be used to determine whether or not further study is warranted. The second tier is identification of the different sources of PAHs found in the sediments and their relative distribution. This tier itself is divided into two stages: the first using standard subsets of PAHs for source identification, and the second using more complex, advanced chemical fingerprinting (ACF). Several case studies using ACF are presented. Greater detail on site investigations and ACF techniques is provided in the Appendix.

12.1 Tiered Evaluation Approach

In the tiered PAH evaluation approach described here, it is assumed that potentially impacted sediments in a surface water body have been identified by chemical analysis of representative sediment samples and comparison to sediment quality screening guidelines. It is further assumed that the PAH analyses include at least the 16 priority pollutant PAHs.

12.1.1 Confirmation of Benthic Population Impairment

In the absence of adopted numeric sediment quality criteria, it is necessary to document that elevated sediment concentrations of PAHs have resulted in impaired benthic organism populations. This step involves sampling of benthic invertebrate organisms in the affected sediments and at one or more control locations, and statistically comparing the populations, as described in EPA's Sediment Classification Compendium (USEPA, 1992a). In the absence of demonstrated impacts on benthic organism populations, additional chemical sampling of sediments may not be cost-effective because the screening level thresholds have a relatively high probability of giving false positive results (i.e., predicting benthic organism impairment when it does not exist). It is essential that sediment sampling consider physical conditions such as substrate composition, epibenthic water chemistry including dissolved oxygen, and surficial water currents, to rule out contributions (all or in part) to benthic organism impairment. These factors should be addressed by selection of representative control locations.

Ideally, the biological sampling should be performed by the regulatory agency identifying a site as having potentially impaired benthic organism communities. In practice, especially at locations where there is a potential for a CERCLA or state Superfund listing, biological sampling may fall upon potentially responsible parties, which are typically identified by a regulatory agency as the industrial (and possibly municipal) direct dischargers to the affected surface water. If the regulatory agency is unable or unwilling to perform the biological sampling, then potentially affected dischargers can decide to skip this step and proceed with the second and third tiers of evaluation before conducting sediment biological sampling. If biological sampling is deferred until source identification is completed (including identification of important co-contaminants), then responsibility for the biological sampling could be allocated on an equitable basis. However, before any control or remediation actions requiring significant expenditures are taken, it is essential that biological sampling be completed to verify the presence and extent of impairment.

12.1.2 Identification of Co-Contaminants and Confounding Physical Factors

Generally, when sediment samples are collected and analyzed, a suite of potential chemical contaminants including metals, pesticides, PCBs, and other non-polar organic chemicals are measured along with PAHs. The sediment quality data for all co-contaminants present with the PAHs should be evaluated against sediment quality screening thresholds to determine which, if any, could contribute to toxicity. If any co-contaminants are present at concentrations potentially toxic to benthic organisms, then it is important that all further tiers of the site evaluation consider the effects of these co-contaminants.

Statistical methods examining correlation between multiple variables can help determining the contribution of co-contaminants and other factors, such as percent silt in sediments, to benthic organism counts and species. Multivariate methods can be used to examine databases with a number of dependent and independent variables and determine the strength of related variables. These methods are best applied by knowledgeable scientists or statisticians. They should be considered for use to determine the importance of impairment due to PAHs when sediment databases have multiple co-contaminants, and/or control locations are not essentially identical to the area of interest in terms of physical conditions and water chemistry.

12.1.2.1 Assessment of Confounding Factors – West Coast Refinery

A West Coast petroleum refinery (Refinery) utilizes a pier causeway that extends into marine waters for its refinery effluent. Under the Refinery's National Pollutant Discharge Elimination System (NPDES) permit, effluent consisting of treated process water and storm water is discharged from an outfall located about 1,700 feet from shore. Sediments in the vicinity of the pier/outfall structure were characterized as part of the Refinery's permit. In response to state agency concerns regarding these characterization studies, a sediment re-characterization study was conducted in 2006 to achieve the following objectives:

(1) Re-characterize the sediment quality conditions near the pier, outfall, and adjacent eelgrass beds; secondarily, determine sources of sediment polycyclic aromatic hydrocarbons (PAHs) in samples demonstrating toxicity.

(2) Resolve potential confounding factors on toxicity test results based on information from previous chemical and toxicity testing in these areas.

To meet the study objectives, the re-characterization study included a comprehensive sampling and analysis program designed to assess substrate conditions (i.e., shell distribution and density in the sediments surrounding the piers); evaluate the impact of the outfall discharge on area sediments by collecting surface sediment samples (0 to 10 centimeters) in the immediate vicinity of the outfall and in localized reference areas; conduct sediment toxicity tests to control for potentially adverse effects resulting from sulfides, ammonia, and grain size/shell fragments; and isolate the source of the sediment PAHs by collecting effluent-suspended solids and pier coal-tar epoxy samples and then comparing the semivolatile organic compound and extended PAH distributions to the sediment samples.

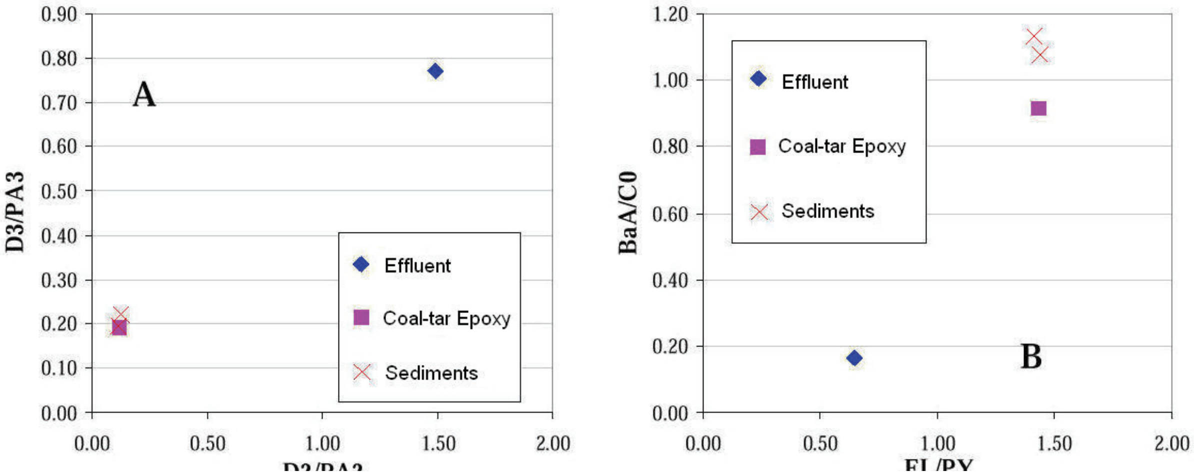
A chemical evaluation of site sediments showed that total organic carbon was consistent site-wide (average 0.5%) and averaged lower than typical marine sediments. Ammonia, total sulfide, and PAH concentrations were higher under the pier than elsewhere. Relative to the dominant outfall discharge direction, PAH concentrations were higher up gradient than down gradient. The highest total PAH concentrations were 13.56 milligrams per kilogram dry weight (1,745 milligrams per kilogram organic carbon). There were no PAH exceedances above state criteria beyond the pier footprint. However, since the outfall and coal-tar epoxy-coated pilings are both potential sources of PAHs and co-located, it was difficult to determine the source of PAHs and toxicity without further analysis. Secondly, since the pier structure supports an abundant diversity of invertebrate marine life, the receiving sediments under the pier have greater than 50% shell fragments accumulated over the last 20 years. It was difficult to determine if PAHs or anoxic, shell-dominated site conditions were causing sediment toxicity.

Previous bulk sediment samples showed significant toxicity. The state agency was uncertain whether the earlier toxicity study results indicated PAH toxicity or were byproducts of other site factors, such as increased sediment sulfide concentrations due to the thick build up of shells on the sediment surface. In the recharacterization study, the substrate assessment showed that sediments below the pier were silt with greater than 50% shell cover. The sediment toxicity tests were conducted to isolate the effects due to PAHs versus naturally occurring factors by conducting analyses of sieved and unsieved sediment samples in parallel. Using two acute tests (10-day *Rhepoxynius abronius* survival and 48-hour *Mytilus galloprovincialis* larval development) and one chronic test (20-day *Neanthes arenaceodentata* growth), only one sieved sample (shells removed) collected from under the pier had minor failures. All other sieved samples passed the toxicity testing program.

In effect, the sieved samples removed the shell fragments, which directly affected grain size (i.e., shell fragment) and indirectly influenced sulfide and ammonia concentrations. This study design demonstrated that observed toxicity was attributable to the naturally occurring factors stemming from the presence of the thick shell layer and not PAHs.

Samples were collected from the two possible PAH sources to under-pier sediments: (1) the coal-tar epoxy historically used to coat the pier pilings and (2) the Refinery effluent. Diver-collected epoxy samples were collected as composites by scraping the pilings and collecting the hard, brittle, foliated shavings. The divers noted that the pilings were corroding as the epoxy coating, designed to protect the steel pilings, weathered. Effluent solids were collected over a 48-hour period using an inline filtration system (discharge port, peristaltic suction pump filtered water through glass filters and funnels); 300 gallons of water were passed through filters, and the filters, which were changed hourly, were placed in jars on ice for subsequent testing. These samples, along with two of the under-pier sediment samples and a filter control sample, were submitted to Alpha Woods Hole Laboratory for extended, alkylated homologue PAH testing. The PAH distributions (i.e., fingerprints) of these samples were assessed through the use of histograms and double ratio plots designed to compare source or weathering effects (by Applied Geochemical Strategies Inc.). These evaluations clearly demonstrated that the sediments most closely resemble the coal-tar epoxy sample (Figure 2). The Refinery has an ongoing pile wrapping and fendering program to help prevent further deterioration of the coal-tar epoxy. This protection program, coupled with deposition of new sediment over time, essentially comprises a source control program that will gradually improve sediment PAH concentrations detected in the study area. Monitoring will continue as part of the Refinery's next 5-year NPDES permit.

Figure 2. PAH Source Indicator Double Ratio Plots



Notes:

This figure is summarized from Appendix G.

Abbreviations

D2/PA2 = C2-Dibenzothiophene / C2-Phenanthrene/anthracene
D3/PA3 = C3-Dibenzothiophene / C3-Phenanthrene/anthracene
FL/PY = Fluoranthene / Pyrene
BaA/C0 = Benz(a)anthracene / Chrysene

Summary:

A: The degradation rates between D2 vs. D3 and PA2 vs. PA3 are very similar. By using these ratios, the effects of degradation are removed, meaning that any differences are related to source differences rather than weathering effects.

B: This ratio takes advantage of the fact that the ratio parameters are isomers with the same molecular weight and thus tend to behave similarly in the environment, thereby masking any weathering effects and allowing comparison of the source ratios.

	2006 SEDIMENT RECHARACTERIZATION		PAH SOURCE INDICATOR DOUBLE RATIO PLOTS
	Date: 3/28/07	File: 18971	Figure 2

The state agency accepted these findings and intends to remove this area from a pending 303d impaired water body listing. This comprehensive study saved the Refinery from a potential sediment cleanup project and/or upgrades to its effluent treatment system.

12.2 PAH Source Identification

Because PAHs in sediments can originate from pyrogenic, petrogenic, and diagenic sources, assessing the relative contribution of these sources is important so that responsibilities can be equitably allocated and source controls will be effective at preventing future contamination. PAH source identification is practical because the chemical fingerprints of the PAH mixtures from the three types of sources are sufficiently distinctive.

An effective approach for characterization of PAHs in sediment should be a tiered evaluation approach, starting with the simple methods and proceeding to the more complex methods, if necessary. The following sections describe such a tiered approach.

12.2.1 Tier 1 — Evaluation of Existing Data

For a surface water site containing sediments of regulatory concern, a sediment quality database is usually available. As shown in the example TMDL cases presented earlier, it is important that the database include data for the actual site, and potentially responsible parties should strongly resist attempts to categorize a site as impaired in the absence of site-specific sediment data.

The database will likely cover at least the 16 priority pollutant PAHs, but not always. In some cases the sediment quality data may include an extended list of PAHs that EPA has used in its EqP methodology. These databases will often have sufficient information to qualitatively, and maybe quantitatively, estimate PAH allocations by source type (pyrogenic, petrogenic, diagenic). If an objective is to demonstrate that the bulk of the PAHs at a particular site are from pyrogenic sources, then evaluation of existing data may provide sufficient documentation. As discussed above, multivariate statistical methods may be useful for this type of analysis.

12.2.2 Tier 2 — Advanced Chemical Fingerprinting

A brief overview of a technique called advanced chemical fingerprinting (ACF) is provided here. More detailed information regarding this technique is provided in the Appendix.

ACF uses characteristic PAH profiles, relative distributions or “fingerprints,” to distinguish among different PAH sources. These chemical fingerprints are derived from detailed chemical analyses of non-alkylated (parent) PAHs and their alkylated homologues. For ACF, compounds most commonly analyzed are shown in Table 1, which include a selection of individual PAHs, PAH isomers, and related heterocyclic compounds. Chemical analysis for ACF requires modification of standard analytical methods, typically USEPA Method 8270. The analysis is significantly more expensive than analysis for the 16 priority pollutant PAHs (containing only parent PAHs) and the number of laboratories that can perform this type of analysis is limited.

The specific investigation techniques used in ACF will depend on the particular study. Typical tools include chromatographic PAH profiles, PAH concentrations of sediments and sources, and ratios of key PAHs that define characteristic fingerprints (diagnostic ratios). The large volume of data in these studies requires extensive use of data plotting and analysis techniques to distinguish among PAH sources and their distribution in the study area.

ACF will typically require that additional sediment samples be collected for the comprehensive chemical analyses. Although archived samples may be used for ACF analyses, the potential that chemical and biological action has transformed the PAHs in such samples may negate the cost-effectiveness of analyzing such samples.

12.2.2.1 Thea Foss/Wheeler-Osgood Waterways, Washington

Stout *et al*. (2003b) characterized sources of PAHs in the Thea Foss and Wheeler-Osgood Waterways in Tacoma, Washington. The Thea Foss Waterway is connected to Commencement Bay south of Puget Sound. It is a long (1.5-mile), narrow and dead-ended channel originally dredged through mud flats in the 1880s. The Wheeler-Osgood Waterway is a short, offshoot channel of the Thea Foss Waterway. Although tidally influenced, there is no fresh water inflow in the system, so flushing is poor and there is no significant sediment transport out of the waterways. Historical activities related to PAH sources in the area include mills, shipping/marine operations, petroleum product storage and distribution, asphalt plant and oil-loading wharf, railroad terminus, manufactured gas plant (MGP), tar distillation/storage, and boat traffic. The MGP operated from 1884-1926 and related tar distillation/storage operations continued into the 1970s, and these activities were located near the head of the Thea Foss Waterway. Other sources of PAHs in the waterways are urban runoff and atmospheric deposition.

Data on priority pollutant PAHs from previous studies were useful in identifying PAH trends and hotspots and selecting 42 near-surface sediment samples for more detailed analyses. The expanded analysis included 43 individual PAHs and PAH groups from Table 1, as well as total extractable hydrocarbons (THC), and total organic carbon (TOC). Other tools used in the study were PAH profiles of reference materials and principal component analysis (PCA).

Diagnostic ratios calculated from the PAH data were LPAH/HPAH, C0/C2, AN/P0, and FL/PY. These ratios are briefly described below:

- Light PAHs/Heavy PAHs (LPAH/HPAH) – The ratio of light PAHs (2- to 3-ring PAHs) to heavy PAHs (4- to 6-ring PAHs). HPAH are preferentially formed by higher temperature combustion processes characteristic of pyrogenic PAHs. In general, a ratio <1 indicates a pyrogenic source.

- C0/C2 – Ratio of chrysene (C0) (parent form) to total C2-alkylated chrysenes. Pyrogenic sources typically have C0/C2 ratios >1 because the higher temperature processes associated with combustion processes preferentially reduce alkylated forms. Although weathering tends to preferentially reduce parent PAHs, chrysene is less susceptible to weathering. C0/C2 was selected as a diagnostic ratio because it would be less influenced by post-deposition environmental variables.

- Anthracene/Phenanthrene (AN/P0) and Fluoranthene/Pyrene (FL/PY) – These two diagnostic ratios were used to plot trends of the pyrogenic PAHs going from the head of the waterway to the mouth. The ratio of AN/P0 is temperature dependent. High temperature processes such as combustion of organic matter generate PAHs characterized by a high AN/P0 ratio (>0.1), whereas the slow maturation of organic matter during catagenesis leads to much lower AN/P0 ratios (<0.1). Similarly, the ratio of FL/PY can be used to distinguish pyrogenic sources of PAHs (>1) from petroleum hydrocarbons (petrogenic sources, <1). Nevertheless, for both ratios, the limits between the two processes are not precise and the two indices must be considered together to provide a good estimate of the different PAH sources.

The study concluded that PAHs in the waterway sediments were predominantly from pyrogenic sources with the majority derived from urban runoff/atmospheric deposition. Sediments closer to the head of the waterway were found to be mostly impacted by one or more types of MGP tar or tar distillate, which was consistent with the location of historic MGP and tar processing operations.

12.2.2.2 Delaware River – Evaluation of Refinery Effluent Impacts

Uhler *et al*. (2005) describes in great detail an ACF study evaluating the potential impacts of the Motiva Delaware City Refinery's wastewater effluent on the Delaware River. The court-mandated study included over 1,000 environmental samples of refinery wastewater, refinery petroleum products, river water, sediments, and bivalve tissue. The study concluded that the majority of PAHs in the Delaware River likely originated from urban runoff and that the refinery hydrocarbon signature was evident only at moderate to low levels in the wastewater effluent channel and near-field regions. Moderate levels of PAHs from the refinery were associated with sediments in the effluent channel, whereas the river sediments reflected little or none of the refinery's fingerprint.

The refinery PAH fingerprint exhibited relatively high levels of alkylated fluoranthenes/pyrenes with C2- and C3-alkyl groups and benz(a)anthracene/chrysenes with C2 – C4 alkyl groups. The urban background fingerprint characteristics included varying levels of 2- to 3-ring PAHs, pyrogenic 4- to 6-ring PAHs from partially combusted organic material like soot, and perylene, a diagenic product of plant decomposition. The lower 2- to 3-ring PAHs represented a petrogenic component of urban runoff, likely from weathered automotive fuel, marine fuel, or bilge tank discharges.

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Appendix 1

Appendix – Site Investigation of PAH Sources Using Advanced Chemical Fingerprinting (ACF)

Situations involving PAH contamination in water and sediments can be complicated and may benefit from enhanced investigation techniques, often referred to as advanced chemical fingerprinting (ACF). ACF can be an additional tool to help quantify the nature, extent, and sources of PAHs. While ACF is applicable to all media, it is particularly useful for complex aquatic environments where it is difficult to differentiate among the sources of PAH contamination in sediments.

ACF uses characteristic PAH profiles or distributions of PAHs to distinguish among different PAH sources. These chemical fingerprints are derived from detailed chemical analyses of nonalkylated (parent) PAHs and their alkylated homologues. Table 1 in the main report includes a list of target PAHs, groups of PAHs, and selected heterocyclic compounds generally used in ACF. Chemical analyses for ACF requires modification of standard analytical methods. It is more expensive and the number of laboratories that can perform this type of analysis is limited.

The large volume of data that can be generated in these studies requires extensive use of data analysis techniques to develop PAH profiles, differentiate PAH sources, and evaluate spatial and temporal trends.

This purpose of this appendix is to outline the key steps of planning a site investigation that will be using ACF to evaluate PAH contamination. In addition to describing techniques used in ACF, it includes common elements of a site investigation such as study design and sample collection/analysis.

ACF supports site investigations in:

- Defining contaminant signatures that are site-related and that may be useful in determining responsibility under regulatory programs;
- Defining ambient/background conditions, which may influence decisions impacting a site;
- Providing insight in the fate of contaminants in sediments such as degree of weathering or biodegradation and the propensity for other attenuation mechanisms, including natural recovery;
- Providing insight to the transport of contaminants such as dispersion, re-suspension of sediments, tidal effects; and
- Providing potential benefits to regional watershed investigations with supporting evidence for cost-effective water quality management.

A.1 Steps in Site Investigation

The steps in a site investigation incorporating ACF are:

1. Evaluation of the site’s need for ACF to support a contaminant source study,
2. Development of a conceptual site model,
3. Development of a defensible study design,
4. Field sample collection,
5. Rapid sediment characterization screening,
6. Advanced chemical fingerprinting, and,
7. Synthesis and presentation of the results.

A.2 Evaluating the Need for ACF

Factors that may affect a decision to conduct a contaminant source study using ACF include:

1. Regulatory remedial action (e.g., RCRA, CERCLA),
2. Potential for natural resource injuries to be assessed,
3. Political or social pressures for action, and
4. Acceptability of ACF methods to regulators and other stakeholders.

A.3 Development of the Conceptual Site Model

A new conceptual site model (CSM) for a PAH source study may be developed, or an existing one may be modified. For example, a model developed for a baseline ecological risk assessment can be expanded to include PAH sources for the study area and the potential for transport of sediments/contaminants. The CSM should:

1. Identify all of the known or suspected sources of PAHs within the study area; and
2. Develop specific objectives to be evaluated.

When developing the CSM, it is important to review pre-existing data, not only for the study area, but possibly for nearby areas because they can provide insight into regional background issues. Pre-existing data may include the scientific literature related to earlier investigations, environmental studies conducted by local universities, and information submitted to regulatory and other agencies. These data may be useful in identifying PAH distribution, contamination hotspots, and PAH sources. It is important to recognize differences among the data sources that may limit comparison or combining of the data. For example, there may be differences in time periods, parameters that were analyzed, data quality, laboratories, analytical methods, and detection limits.

A.4 Development of a Defensible Study Design

A good study design begins with identifying the study objectives. A common objective of site investigations involving PAH sediment contamination is to estimate the relative contribution of multiple PAH sources. A relatively simple study might involve differentiating between sediments impacted by an oil spill and the general urban background. A more complex study might involve determining contamination sources, distribution, and trends resulted from a long history of manufacturing, commercial, and urban activity.

Other elements of the study design are selection of parameters to analyze or measure, sample collection, sample analyses, and ACF techniques. Because sample collection and analyses are usually a large part of the project budget, the study design will need to focus on critical data needs and obtaining data of sufficient quality to meet study objectives.

A.5 Selection of Analytes

The standard set of 16 priority pollutant PAHs is useful for screening purposes and initial assessments, and in most cases, this approach may also be sufficient to characterize site conditions. If additional assessment is needed, ACF can be considered. ACF includes an expanded PAH list to develop more detailed characteristic source profiles or fingerprints. PAHs commonly used in ACF are listed in Table 1 (main report). Most PAH source studies would involve only a subset of these compounds.

In developing source PAH characteristics, the degree of alkylation tends to be more useful than the actual individual PAHs. For example, C2-naphthalenes are listed in Table 1 (main report) rather than 1-ethylnaphthalene, 2-ethylnaphthalene, 1,2-dimethylnaphthalene, and so on.

In some instances, principally where specific sources of PAHs are suspected, it is useful to include compounds that are frequently associated with a source. This may include heterocyclic aromatic compounds and hydrocarbons associated with petroleum products. Heterocyclic compounds are similar to PAHs, but have one or more hetero atoms (typically sulfur, oxygen or nitrogen) substituted for carbon atoms in the ring structure. Examples of heterocyclic compounds are benzothiophenes and dibenzothiophenes where sulfur has substituted for carbon in the parent PAH indene and fluorene, respectively; and dibenzofuran and carbazole where oxygen and nitrogen have substituted for carbon in the parent PAH fluorene.[5] Hydrocarbons associated with petroleum include C8 to C44 normal and branched-chain hydrocarbons, n-alkyl-cyclohexanes, isoprenoid compounds such as pristane and phytane, and other high molecular weight polycyclic hydrocarbons including steranes, terpanes, and hopanes (Murphy and Morrison 2001; Ahmed *et al*., 2006).

A.6 Sampling Considerations

Designing a technically defensible sampling strategy requires balancing project (and data quality) objectives with the project budget. The design is typically based upon either some sort of a statistically-based sampling (e.g., random, systematic, stratified, cluster) and professional judgment based upon the information assembled in the CSM. Sampling designs are often site-specific and require consideration of many aspects of the study design. These types of considerations are addressed in many outside references (e.g., Gilbert 1987 and references therein).

It is also necessary to consider the representation of potential contaminant sources. In some instances at least, sampling of some properties may not be accessible, so sampling may have to be in nearby sediments, usually at some point below the mean high water line. In other instances (e.g., storm water runoff), access to sediments within a catchment basin may require a permit from the city. In any case, the sampling strategy needs to include consideration of the legal issues balanced by the best means of representing potential contamination from an inaccessible area.

Lastly, if the study is to consider historical inputs to the sediments, then the sampling design should include collection of at least some sediment cores that are intended to capture pre-industrial (natural background or at least pre-facility operations) contributions to the sediments. Such cores need to be placed in areas that have been shown (or are believed to be) areas of sedimentary deposition and that have not been dredged. Radiogenic dating of core segments using radiogenic dating techniques (e.g., ^{210}Pb or ^{137}Cs) can yield sediments from particular time intervals whose chemistry reflects conditions from those periods. This dating can be important in areas where historic (and now defunct) operations are considered to have been a significant source of PAHs to the study area.

A.7 Analytical Considerations

For site investigations involving PAH contaminated sediments and incorporating ACF, a 2-tiered approach can be cost-effective (Stout *et al*. 2003a):

1. Semi-quantitative characterization, typically using field-deployed methods, of a sufficient number of sediment samples to identify contaminant trends, hotspots, and key samples; followed by

2. ACF of a selected subset of sediments to develop distinct source chemical fingerprints using more advanced laboratory methods.

Selection of chemical analytical techniques is a balance between acquiring sufficient data to identify PAH trends (i.e., a large number of samples using screening techniques) and acquiring higher quality data (i.e., data of superior precision, accuracy, and resolution) to recognize and resolve distinct source fingerprints using advanced analytical techniques. Table 10 provides a summary of the benefits and limitations of the semi-quantitative and ACF methods.

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[5] For example, dibenzothiophene evaluation was used to differentiate between petroleum released by the Exxon Valdez and natural oil seeps in Prince William Sound (Page et al. 1996; Boehm et al. 1998).

Table 10. Comparison of Semi-quantitative and ACF Analytical Methods

	Semi-quantitative	**Advanced Chemical Fingerprinting (ACF)**
Benefits	Near real time results can guide sampling locations Potential for high data density for mapping Lower costs	Highly specialized, quantitative methods Can remove interferences Can distinguish contaminant fingerprints
Limitations	Typically non-specific Semi-quantitative Matrix sensitive	Typically reliant on blind sampling Limited availability in commercial laboratories
Cost per Sample	UV Fluorescence: \$75 Immunoassay: \$100 Bioassay (toxicity): \$200	GC/FID (THC/fingerprinting): \$275 GC/MS (full suite): \$500 - \$800 GC/IRMS (^{13}C): \$ 1,000+ GC/MS (biomarkers): \$150
Throughput	UV Fluorescence: 20 samples per day Immunoassay: 40 samples per day Bioassay: 6 – 12 samples per day	GC/FID: 30 – 60 days standard TAT GC/MS: 30 – 60 days standard TAT GC/IRMS: not widely available commercially

Source: Stout *et al*. 2003a.

Semi-quantitative, screening methods can cost-effectively provide the spatial coverage necessary to:

1. Recognize concentration gradients that relate to fate and transport processes in an area and perhaps changes in over time;

2. Recognize contaminant hotspots, which often indicate source areas;

3. Help define background/ambient conditions that will impact regulatory goals and methods; and

4. Provide supporting information to determine what samples are needed for ACF analysis.

Analytical screening methods can be conducted using various immunoassay or fluorescence techniques. In particular, screening techniques for analysis of PAHs in sediments have been adapted from methods developed for use in soils and require dewatering of the sediment to below about 30% moisture. Sample preparation, however, can be more involved and similar to standard laboratory methods, depending on project objectives. In most instances, it is appropriate to use basic preparation methods (that meet project data quality objectives) to generate analytical results in a timely manner: the dewatered sediment is extracted using a solvent followed by analysis of the extract by either immunoassay or UV fluorescence techniques. In the case of immunoassay, the extract is then treated with specific antibodies that promote a color change depending upon PAH concentration, which is measured against a PAH standard solution-calibrated spectrophotometer. Fluorescence techniques allow direct measurement of the emitted fluorescence following UV excitation of the extract. The fluorescence response is compared to that of a suite of PAH standard calibration solutions. Screening data interpretation of PAH data can significantly benefit from additional physical properties data for the sediments (e.g., grain size, total organic carbon, types of carbon) and some consideration should be given to obtaining relevant physical properties data concurrently with the screening data.

A.8 ACF Method Selection

Several analytical procedures are available for characterizing PAH concentrations in sediment and water samples. The most common for sediment analysis is USEPA (SW-846) Method 8270, which utilizes gas chromatography and mass spectrometry (GC/MS). USEPA Method 8015 is also used to provide a fingerprint analysis of samples over a broad range of non-PAH, hydrocarbon compounds. Both methods are suitable for a variety of media including water, soils, sediment, and source materials (e.g. coal, sludge, oils, etc). Descriptions of these methods are provided elsewhere in this report.

For ACF in PAH site investigations, the fundamental shortcoming of most conventional USEPA SW-846 methods is a lack of detailed measurements of those diagnostic chemicals (alkylated and hetroatomic PAH) associated with the PAH sources. Instead, these methods cover only the 16 priority pollutant PAHs. For example, Figure 2 compares the PAH profile of a crude oil developed with only priority pollutant PAH analysis and one developed with an expanded PAH list. In the priority pollutant profile, only 7 PAHs are present, compared with many more PAH groupings in the more detailed profile. These limitations may not be a problem, depending on the objectives of the site investigation. If determining whether PAHs were from a recent oil spill versus other sources, the 16-PAH profile may be adequate. However, source apportionment among many sources with a long history of inputs to a given site will require a more detailed profile.

In addition, standard SW-846 methods lack sufficient sensitivity (i.e., have higher detection limits). Figure 3 illustrates how identifying a PAH source can be skewed by the method detection limit (MDL). As the figure shows, in the case of a crude oil sample, when the MDL is the most sensitive, many PAHs are measureable and a profile typical of a crude oil is observed. As the MDL increases, smaller PAH peaks in the chromatogram drop out of the profile because they would not be detected. As the MDL increases, the profile interpretation becomes less and less accurate as the apparent profile changes from truly crude oil to diesel, then to low sulfur diesel, then to jet fuel.

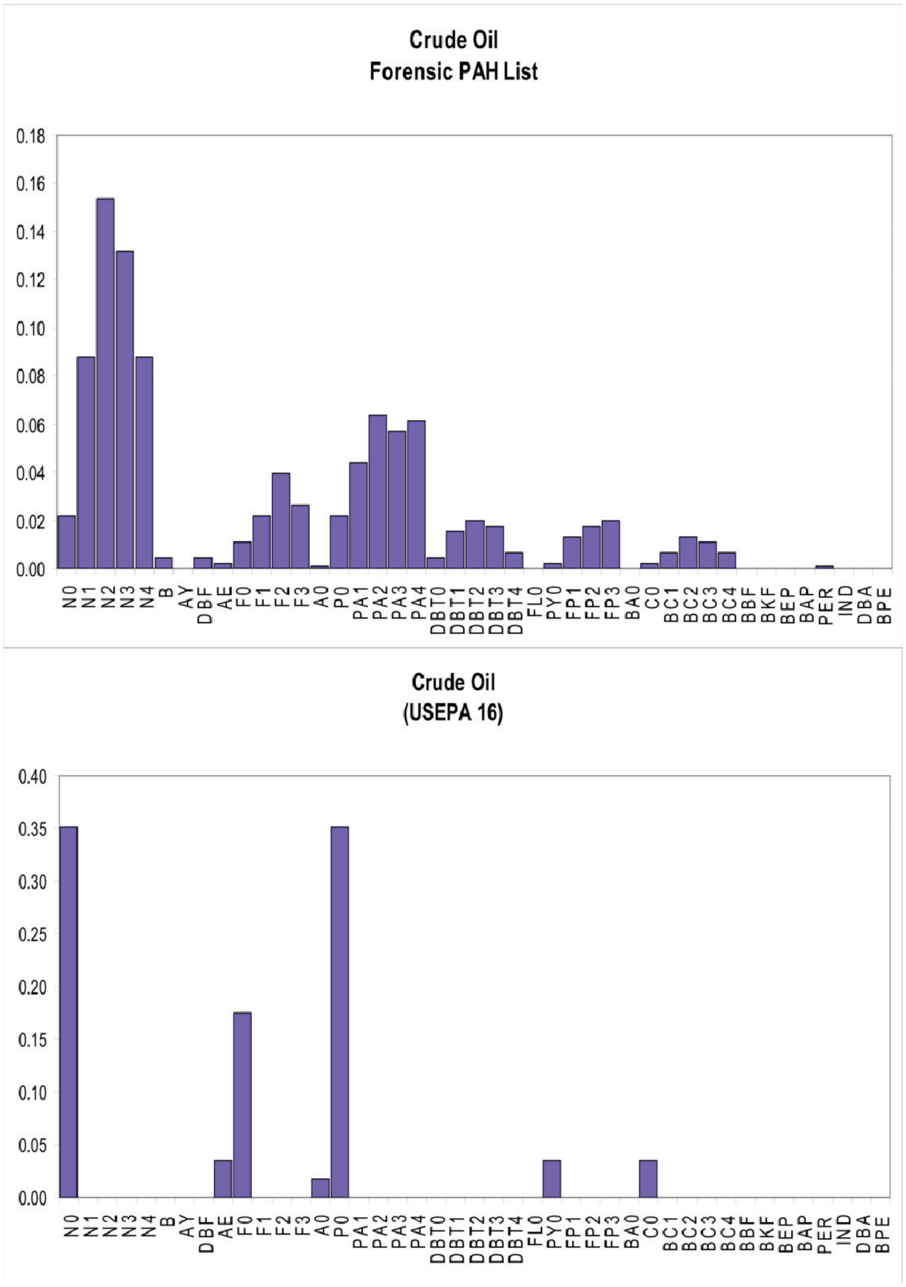

Figure 3. PAH Profile for crude oil with USEPA 16 Priority Pollutant PAHs and Forensic PAH target list.

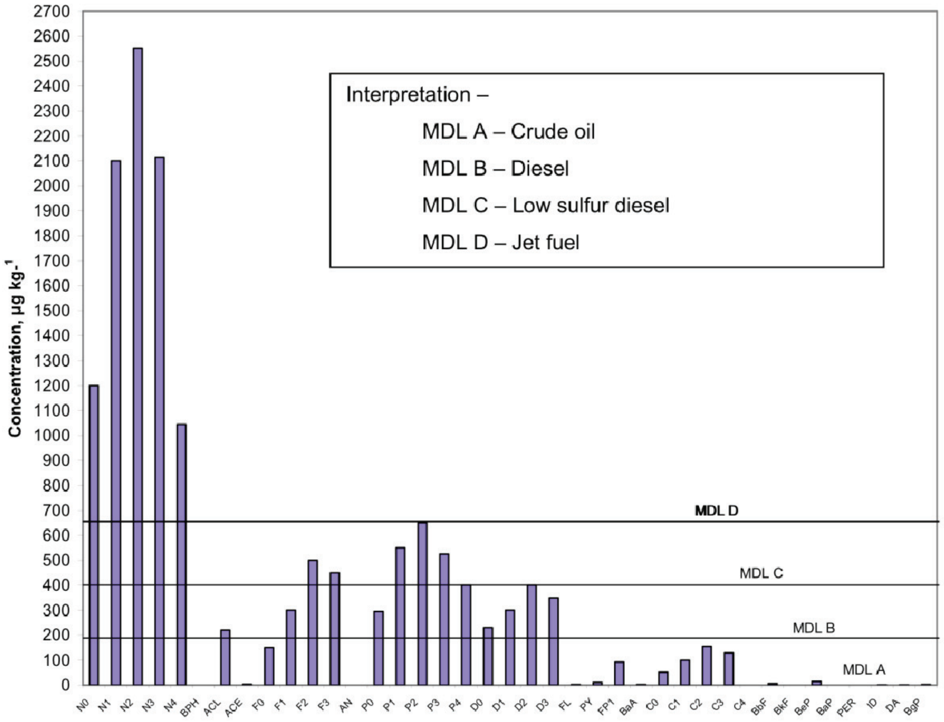

Figure 4. The ability to interpret PAH data depends on the method MDL (minimum detection limit).

ACF techniques available for the assessment of PAHs (and other diagnostic organic compounds) in sediments are all based upon high-resolution gas chromatography (HRGC), usually operated in conjunction with compound-specific detectors such as a mass spectrometer (MS). Some typical ACF methods available for fingerprinting semi-volatile organic contaminants, mostly hydrocarbons, are given in Table 11. More detailed descriptions of these methods are in Stout *et al*. (2002). Not all the target compounds listed in Table 11 are PAHs, nor even considered contaminants (e.g., petroleum biomarkers). Nonetheless, these compounds are extremely useful in characterizing different sources of PAHs (Peters and Moldowan, 1993; Stout *et al*., 2002) and when used in conjunction with PAH fingerprinting, and can be used to distinguish contaminant sources.

Table 11. Common Analytical Methods Used for Advanced Chemical Fingerprinting of PAHs

Analytical Method	Target Compounds	Utility for ACF of PAHs
Modified EPA Method 8015 High resolution gas chromatography - Flame ionization detection (GC/FID) MDL for sediment ~1 mg/kg	Total (extractable) hydrocarbons (THC) C8 to C44 normal and branched-chain hydrocarbons Resolved components versus unresolved components High resolution fingerprints	Accurate determination of THC Development of diagnostic indices Accurate product identification in the light distillate to residual petroleum products range Evaluation of the degree of weathering
Modified EPA Method 8270 High resolution gas chromatography – mass spectrometer detection (GC/MS) Multiple types of MS detection systems available Selected ion monitoring Quadrapole Ion trap MDL for sediment ~1 µg/kg	Priority pollutant PAH (16 compounds) Alkyl homologues of priority pollutant PAHs (35 compounds) Sulfur containing PAHs (8) Nitrogen containing PAHs n-alkyl-cyclohexanes (~20) Biomarkers (~40)	Optimized for low level analysis of sediments Detailed chemical indices used for evaluation of PAH sources Mixing and allocation Degree of weathering

A description of several analytical methods including characterization of compound-specific isotope ratios is provided in the following sections. In addition to Method 8270, there are several other analytical methods available. These methods can provide supporting information from historical compliance monitoring programs, which may be of use in the overall project. These include USEPA Methods 525.2, 625, and 8310. USEPA Methods 525.2 and 625 use technology similar to Method 8270. USEPA Method 8310 uses high performance liquid chromatography (HPLC) with an ultraviolet and/or fluorescence detector, and can be used to evaluate sludge, oils, and water samples. The utility of such analyses should not be discounted on the basis of method alone, but rather should be evaluated on a case-by-case basis. The limitations of these methods should be incorporated in any discussion of findings.

A.8.1 Method 8270 GC/MS

The basic USEPA 8270 GC/MS method allows for chromatographic separation of PAHs, followed by verification of the compound by mass spectra. This method is most commonly used for identification and quantification of the 16 priority pollutant PAHs and is offered by commercial laboratories. The principal advantages of this method are that it is a well established protocol that provides excellent specificity (proper identification of compounds) and that the method can be modified to incorporate an expanded range of compounds to include alkylated PAHs and heterocyclic compounds. The principal disadvantage of the method is that the quantification limit of 300 to 500 µg/kg (ppb) dry weight may not provide the sensitivity needed to detect low concentrations of target compounds.

A.8.2 Method 8015 GC/FID

USEPA Method 8015 utilizes gas chromatography with a flame ionization detector (FID). Although this method can be used to quantify PAHs, it is most commonly used in forensic evaluations to evaluate the overall distribution of hydrocarbons and associated compounds in a given sample. The resulting chromatogram is commonly referred to as a fingerprint of the sample and can be very useful in identifying the general categories and overall distribution of PAHs and other compounds in the sample. These fingerprints can then be used to determine if the contaminants are consistent with various sources such as crude oil, refined petroleum products, creosote, coal tar, lubricating or waste oils, or urban background.

A.8.3 Modified Method 8270 GC/MS SIM

Method 8270 GC/MS SIM method utilizes similar equipment and analysis protocols as the standard 8270 method, with the exception that the instrument is operated in selected ion mode (SIM) rather than total ion mode. The advantage of SIM analysis is that only selected ion masses are monitored during the analysis. Each target compound (including PAHs) has a primary quantitation ion of known mass. By scanning for a selected number of masses, rather than the broad spectrum of masses, the sensitivity of the instrument is greatly increased. Detection limits are on the order of 0.5 to 5.0 µg/kg (ppb). Although the use of SIM is acceptable for applications requiring detection limits below the normal range of electron impact mass spectrometry, SIM may provide a lesser degree of confidence in the compound identification unless multiple ions are monitored for each compound (USEPA 1996). Because of lower detection limits, the information content and resolution capability (i.e., PAH category identification and source association) of the SIM method is considerably greater than the standard 8270 GC/MS method.[6] The primary disadvantage of this method is that the analytical costs are greater than the standard 8270 method and there are fewer laboratories that conduct these analyses.

A.8.4 Method GC/IRMS (Compound Specific Isotope Analysis)

Compound-specific isotope analysis (CSIA) provides complementary constraints for elucidating inputs of anthropogenic PAHs to aquatic environments (e.g., Stark *et al*. 2003; Walker *et al*. 2005; O'Malley *et al*., 1996; Ballentine *et al*., 1996; Hammer *et al*., 1998; McRae *et al*., 1999, 2000;; Mazeas and Budzinski, 2001). O'Malley *et al*. (1996) performed the first measurement of carbon isotopes of individual PAHs from modern depositional

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[6] If the electronic raw data files are available (e.g., gas chromatography coupled with mass spectrometer [GC/MS] acquisition data from EPA Method 8270), it is possible to quantitatively evaluate selected extracted ion profiles from these data to obtain useful fingerprinting information.

environments and various anthropogenic sources, demonstrating that when dominant PAH source characteristics are known, carbon isotopic ratios of individual PAH could be used to discriminate between inputs of PAH to sediments in individual depositional systems.

CSIA uses a somewhat different instrument and detector to accurately quantify ^{13}C and ^{12}C isotope ratios (typically reported as $\delta^{13}C$). This technique is advantageous in that different source materials have characteristic $\delta^{13}C$ ratios, which remain relatively consistent after being released to the environment. As such, data on $\delta^{13}C$ ratios can be very useful in providing a definitive association between specific sources and contaminated media.

To date however, this technique has generally been employed for academic research purposes and has only recently been applied in the area of PAH forensic investigation. The principal disadvantages of this method are the relatively high cost of analysis and few laboratories capable of performing the analysis. Presently, the CSIA method should be considered as a supplemental tool where it may be effectively employed (e.g., two petroleum refineries discharging into the same water body) and additional costs and time are warranted by project objectives.

A.9 Sample Collection

The collection of sediment samples for contaminant source studies is generally straightforward. Sediment samples can be collected using a range of surface (~0-10 cm; grab) and subsurface (core) sampling devices. The selection of sampling device is dependent on the specific objectives of the project. Most screening methods require approximately 10 grams of wet sediment whereas most ACF analyses require 50 grams or more (wet). Additional sample will be needed for other, complementary analyses (e.g., grain size, TOC).

Numerous references on sample collection techniques and equipments are available on the internet from the USEPA (epa.gov, clu-in.org) and the National Oceanic and Atmospheric (NOAA) Coastal Services Center (csc.noaa.gov).

A.10 Sample Analysis

Provided that sampling and analytical efforts are well coordinated, it is possible to perform the screening analyses, ACF sample selection, and sample extraction within regulatory mandated holding times (14 days for semi-volatile organic compounds such as PAHs).[7] In some instances, it will be useful to have the screening analyses conducted either in near real time in the field or at a nearby staging location. This analysis may increase the project's overall cost, but has the advantage of being able to alter the field sampling program on the basis of screening results as they become available. This will generally increase the cost-effectiveness of the project (i.e., ensure that appropriate samples are taken).

A.11 Screening Data Analysis

Analysis of screening data provides information needed for selection of samples to be analyzed further by ACF techniques. A useful first step is to evaluate the spatial relationships of the data (i.e., GIS-based maps) to identify contaminant trends and hotspots (possible sources). Screening data may even be contoured to interpolate concentrations across the study area.

Because chemical variations often follow changes in sediment texture, evaluating any physical properties data (e.g., grain size or TOC) can be useful in evaluating the RSC results. Cross-plots of RSC concentrations (y-axis) versus some physical property (x-axis) will often show that many samples fall along a single trend that, for example, demonstrates contaminant concentrations increasing proportionately with the percentage of fine-grained sediments. Such trends normally are representative of the ambient conditions within the study area. Samples that plot above any ambient trend typically indicate the presence of hotspots. To increase the spatial density of physical property

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[7] If regulatory holding times are not an issue, freezing of sediment aliquots is a technically viable option for extending the holding time of sediments for semivolatile organic analysis, and thereby permitting adequate time for screening analyses and data evaluation before selecting samples for ACF. If samples are frozen, aliquots for grain size and TOC should be removed before freezing to avoid any issue surrounding the affect that freezing may have on grain size.

data, simple proxies such as percent moisture may be used as a surrogate for grain size, if there is a strong enough correlation between the parameters.

It may be useful to use various statistical or numerical analyses such principal component analysis to identify trends or anomalies. These techniques are discussed in later sections.

A.12 ACF Sample Selection

The analytical strategy and budget will largely determine the number of screening samples selected for ACF. In any case, however, it is not necessary that the entire ACF budget be used if there is no technical basis to do so. For example, if screening data demonstrate an overwhelming consistency and predominance of background, ambient conditions in the study area, the ACF may simply include a few selected confirmation samples. Thus, selection of samples for ACF is largely a matter of selecting a reasonable and justified subset of the screening samples. General guidelines for the selection of samples for ACF are as follows:

- Select samples that provide ample spatial coverage of the entire study area. Try to represent all areas of the study and do not completely ignore any area on the basis of screening alone.

- Select a sufficient number of samples from within the study area to address project objectives. Select sufficient samples in areas of specific concern or interest, potentially including accessible upland sites of interest.

- Select samples that represent the range of screening concentrations observed, including those that are representative of the ambient/background conditions. Do not exclude all the low concentration samples as they may provide important information on background conditions.

A.13 Analysis of ACF Data

Selecting methods for analyzing ACF data depends on the type of data and study objectives. In general, analyses include the following:

- Visual inspection of chemical profile (fingerprint) data employing qualitative pattern recognition, sometimes compared to known standards,

- Graphical analysis of concentration histograms or source-specific diagnostic ratios or indices (e.g., cross-plots or ternary diagrams), and

- Quantitative chemometric analysis.

There are numerous standard graphing techniques for analyzing data, particularly useful with large datasets. Examples are population or individual sample histograms, population box-plots, or bivariate cross-plots. For example, histograms of sample concentrations can show the variability within samples. Box-plots of various parameters (concentrations or ratios) can be used to identify potential outliers and population quantiles. Diagnostic indices can be cross-plotted to reveal similar or dissimilar samples.

Some common data analysis techniques that can be used with ACF are described in the following sections. A general flowchart is provided in Figure 4.

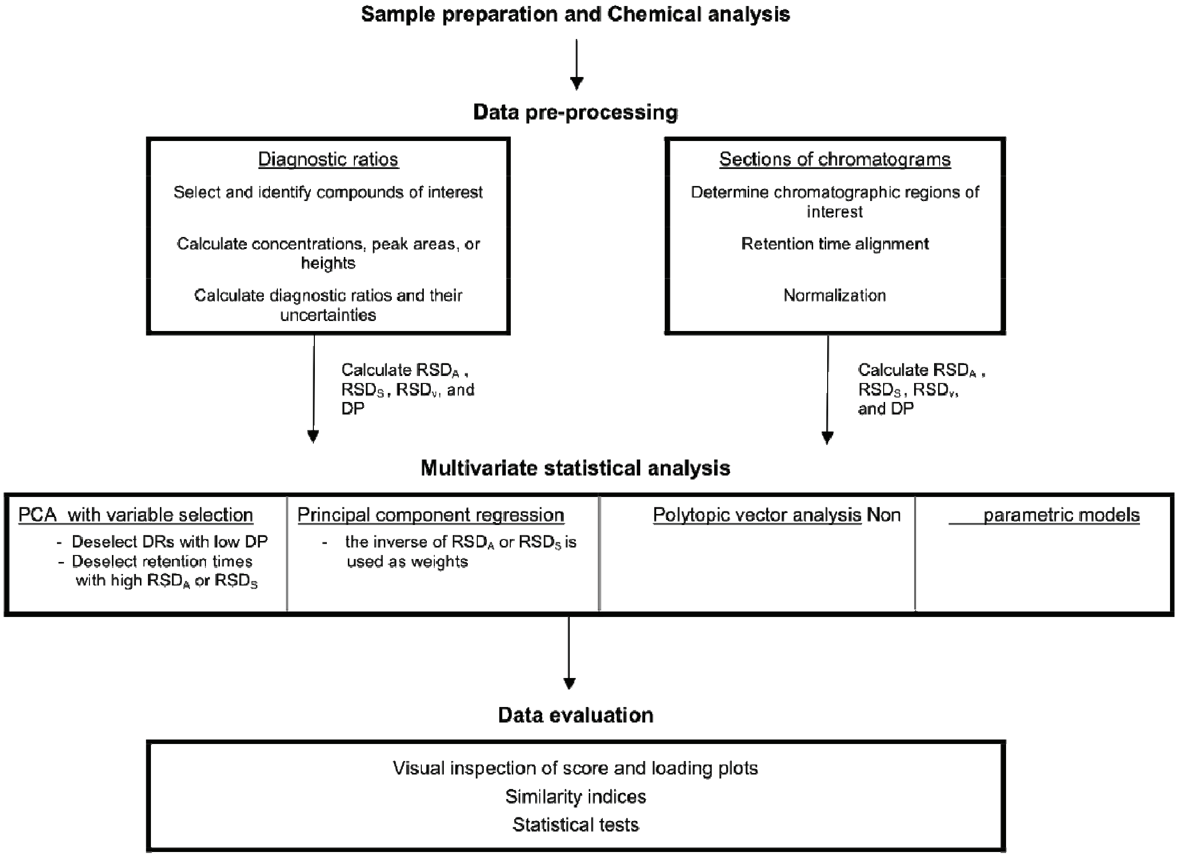


Figure 5. Flowchart of the general methodology for analysis of complex chemical mixtures with respect advanced chemical fingerprinting.

A.13.1 PAH Composition Profiles

Qualitative fingerprint assessment of chromatographic data can be extremely useful in interpretation of PAH concentration data, and is normally the first step in the analysis of PAHs in sediments. These fingerprints can include the GC/ FID or the total ion chromatograms (TICs) or extracted ion profiles (EIPs) from GC/MS analyses. These chromatographic data are typically not provided by the laboratory and must be requested. Historical GC/FID or GC/MS data (i.e., EPA Methods 8015 and 8270, respectively) may provide insight into PAH sources. In the case of PAHs (and other semi-volatile organic compounds), it is particularly valuable that the GC/FID fingerprint of the total extractable organic matter present in a sediment sample be interpreted by experienced chemists who can provide insight as to the specific nature of any hydrocarbons, including the presence of mixtures or naturally occurring, biogenic hydrocarbons associated with modern biomass and the degree of weathering.

PAH composition profiles are histograms of the normalized concentrations of individual PAHs in a given sample, ordered according to molecular weight (i.e., classes represent individual PAHs). Normalized concentrations are calculated as the ratio of individual PAH concentration to the total PAH concentration (i.e., the sum of individual PAH concentrations). PAH composition profiles can be prepared for either the priority pollutant list or an expanded forensic list.

Figures 5-9 provide a comparison of representative PAH histograms using the 16 priority pollutant PAHs as compared to an ACF expanded PAH list. These profiles are representative of samples from crude petroleum, coal tar, creosote, coal combustion cinders, and urban background. Although the information content of the ACF PAH histogram is significantly greater than the priority pollutant profile, Method 8270 nonetheless contains significant information that may be sufficient for source identification, depending on study objectives.

Although source-specific sampling is preferred, PAH composition profiles from the peer-reviewed literature are available for a number of source categories including refinery operations, oil spill differentiation, fuel source differentiation and weathering, tar evaluation, and urban runoff. In general, each of the broad PAHs sources (petrogenic, pyrogenic, diagenic) has different characteristic distributions that allow for the identification of specific categories of sources. General characteristics of petrogenic, pyrogenic, and diagenic PAHs are discussed in the following section.

A.13.1.1 Petrogenic PAHs

This group includes PAH mixtures that are generated by geological processes over millions of years at elevated temperatures, resulting in the formation of petroleum, coal, or oil shales. In the environment, these materials can be of either natural origin (oil seeps, coal outcrops) or anthropogenic sources (fossil fuel releases, coal stockpiles). Analyses of these materials indicate that alkylated-PAHs dominate over parent PAHs; low-molecular weight PAHs (2-ring and 3-ring PAHs) tend to dominate over high-molecular weight PAHs; and heterocyclic PAHs (e.g., benzo- and dibenzothiophenes) will tend to be present in petroleum at moderate concentrations. GC chromatograms tend to include a broad unresolved complex mixture (UCM) hump with the presence of distinct peaks representing PAHs, n-alkanes and isoprenoids. Where appropriate, analysis of alkanes, isoprenoids, and other polycyclic biomarkers can be utilized for additional differentiation.

A.13.1.2 Pyrogenic PAHs

This group includes PAH mixtures that are generated by the combustion or pyrolysis of organic matter such as grass, wood, petroleum, and coal. This group can be broadly differentiated between combustion products of wood, coal or petroleum fuels, and pyrolysis products such as tars that are generated during the production of coke, town gas, or other similar materials. Pyrogenic materials are characterized by the dominance of parent PAHs over alkylated-PAHs within homologue groups, the presence of kinetically vs. thermodynamically stable PAH assemblages, and very low proportions of heterocyclic PAHs. In combustion related PAH materials for grasses, wood and coals, 4-, 5-, and 6-ring PAHs tend to dominate over 2- and 3-ring PAH groups. Combustion related PAHs for fuels tend to include a greater relative proportion of 2- and 3-ring PAHs due to the presence of non-combusted fuel constituents. PAHs derived from the pyrolysis of coal, wood or oil will be rich in 2-, 3- and 4-ring PAHs relative to 5- and 6-ring PAHs, although the latter are typically present in relatively high total concentration. The dominant feature of pyrogenic materials, regardless of the source, is the dominance of parent PAHs over alkyl-PAHs with a decreasing relative abundance with increasing number of alkyl carbons. Urban runoff tends to be dominated by pyrogenic PAHs that are depleted in 2- and 3-ring PAHs, as well as heterocyclic PAHs. GC/FID chromatograms will tend to include multiple independent peaks, with a fairly low to negligible UCM. The relative abundance of n-alkanes and isoprenoids will be very low.

A.13.1.3 Diagenic PAHs

Diagenic/biogenic Materials – This group includes several selected high-molecular weight PAHs including perylene, retene, and other polycyclic biomarkers. These compounds are formed during plant growth, microbial degradation of original organic biomass, or through diagenesis of recent sediments. For the evaluation of PAH sources in forensic analysis, perylene is the most diagnostic compound.

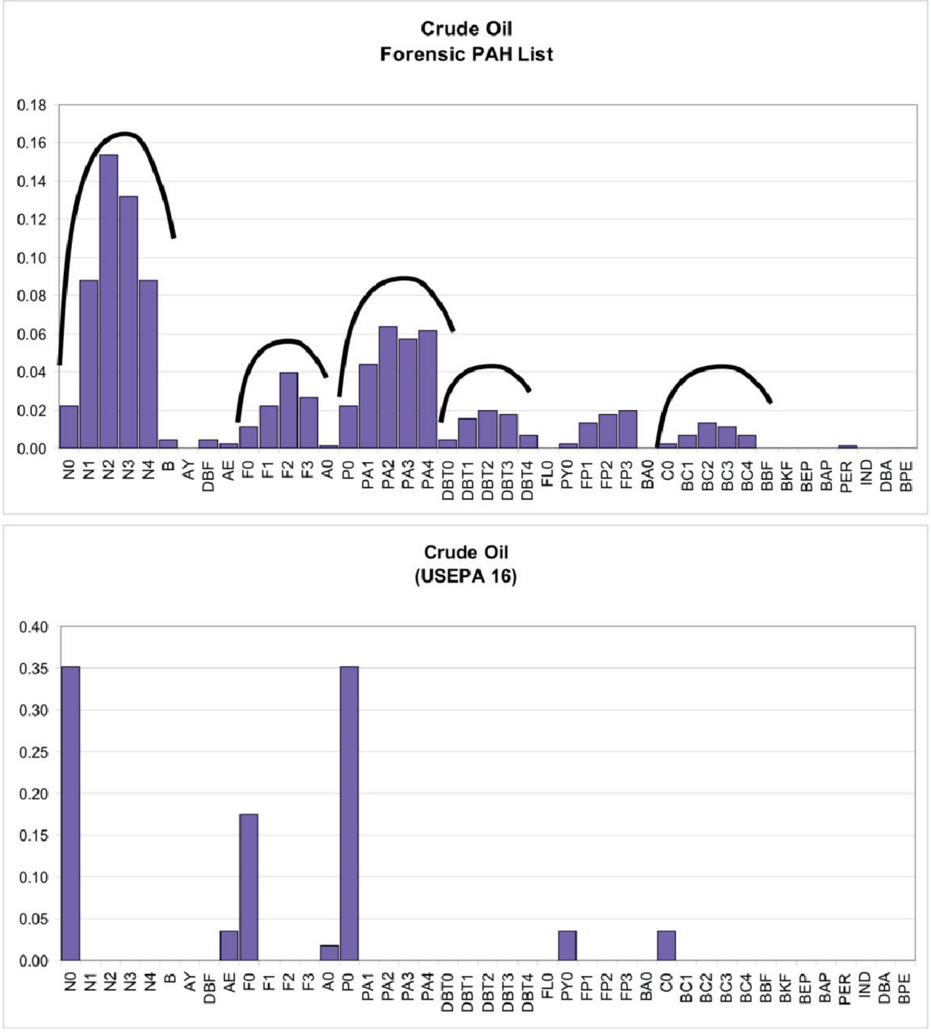


Figure 6. PAH Profile for crude oil with USEPA 16 Priority Pollutant PAHs and Forensic PAH target list. Note the presence hump where parent PAH (e.g. naphthalene) concentrations are lower than alkylated homologs. This is characteristic bell curve of petrogenic PAH sources including crude oil, refined petroleum fuels, lubricating oils, and coal. 2-ring and 3-ring PAHs dominate the profiles, with very low concentrations of 5-ring and 6-ring PAHs. The forensic PAH profile provides additional information content that allows for determination that the sample is from a petrogenic source.

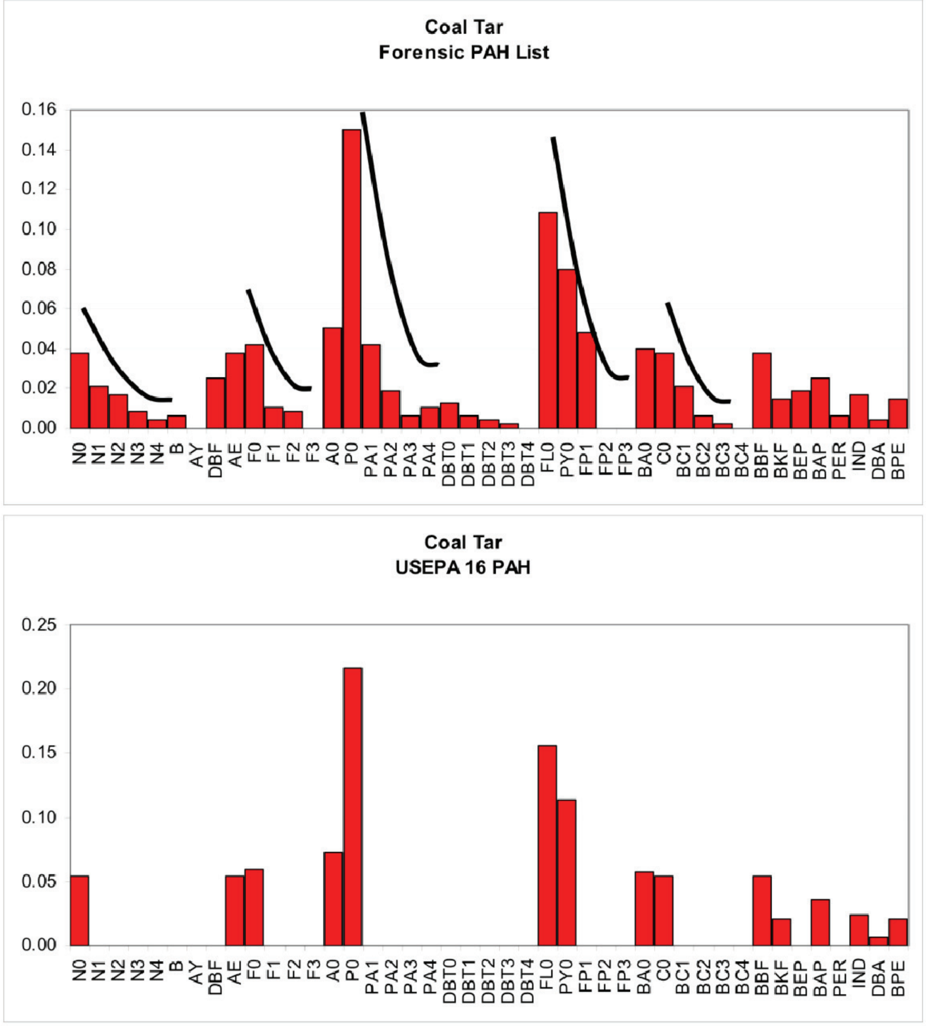


Figure 7. PAH Profile for Coal Tar with Forensic PAH list and USEPA 16 Priority Pollutant PAHs. This is characteristic sloping curve of pyrogenic PAH sources. Parent PAH compounds (e.g. naphthalene, pyrene, chrysene) have greater concentration than alkylated homologs with higher sequence homologs having decreasing concentration relative to lighter compound. Note higher relative concentrations of 4-ring and 5-ring PAHs relative to crude oil.

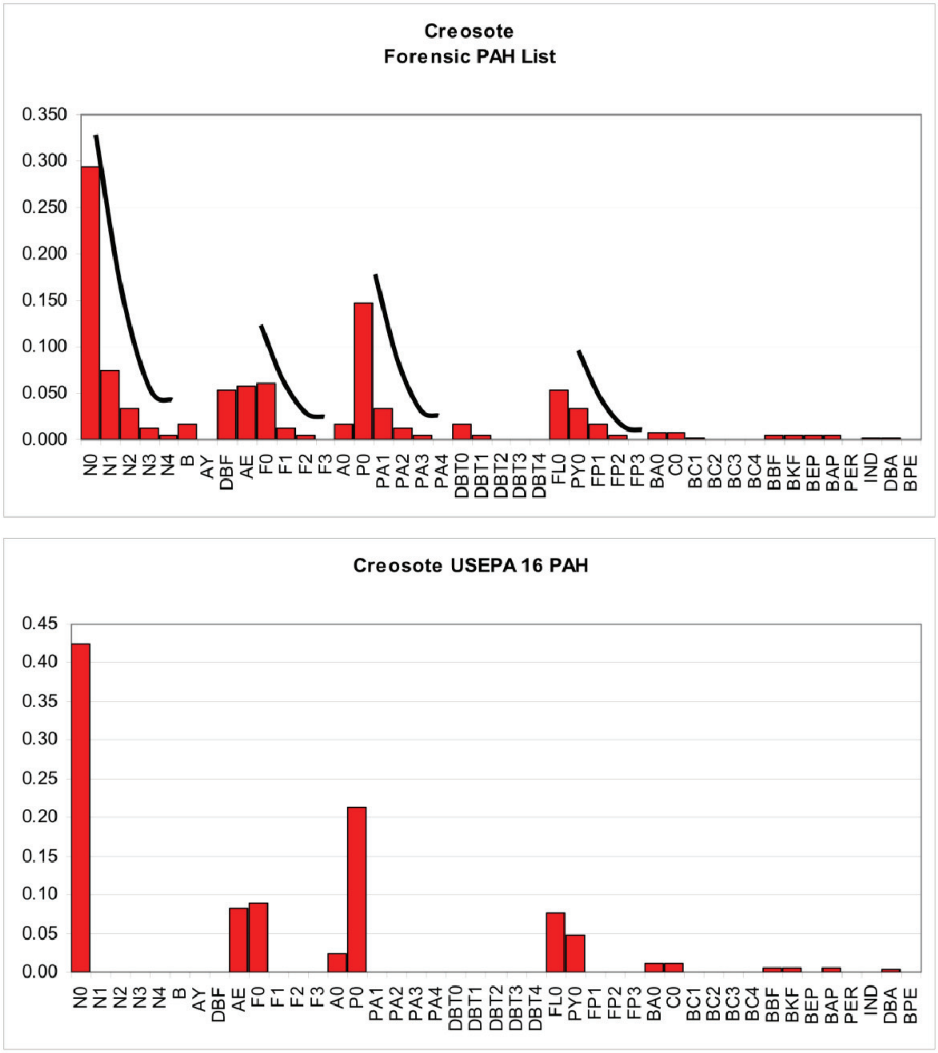


Figure 8. PAH Profile for Creosote with Forensic PAH list and USEPA 16 Priority Pollutant PAHs. This is characteristic of pyrogenic PAH sources. Parent PAH compounds (e.g. naphthalene, fluorene, phenanthrene/anthracene) have greater concentration than alkylated homologs with higher sequence homologs having decreasing concentration relative to lighter compound. Note that Creosote is distinguished from Coal Tar by increased concentrations of 2-and 3-ring PAHs and lower concentrations of 4- through 6-ring PAHs.

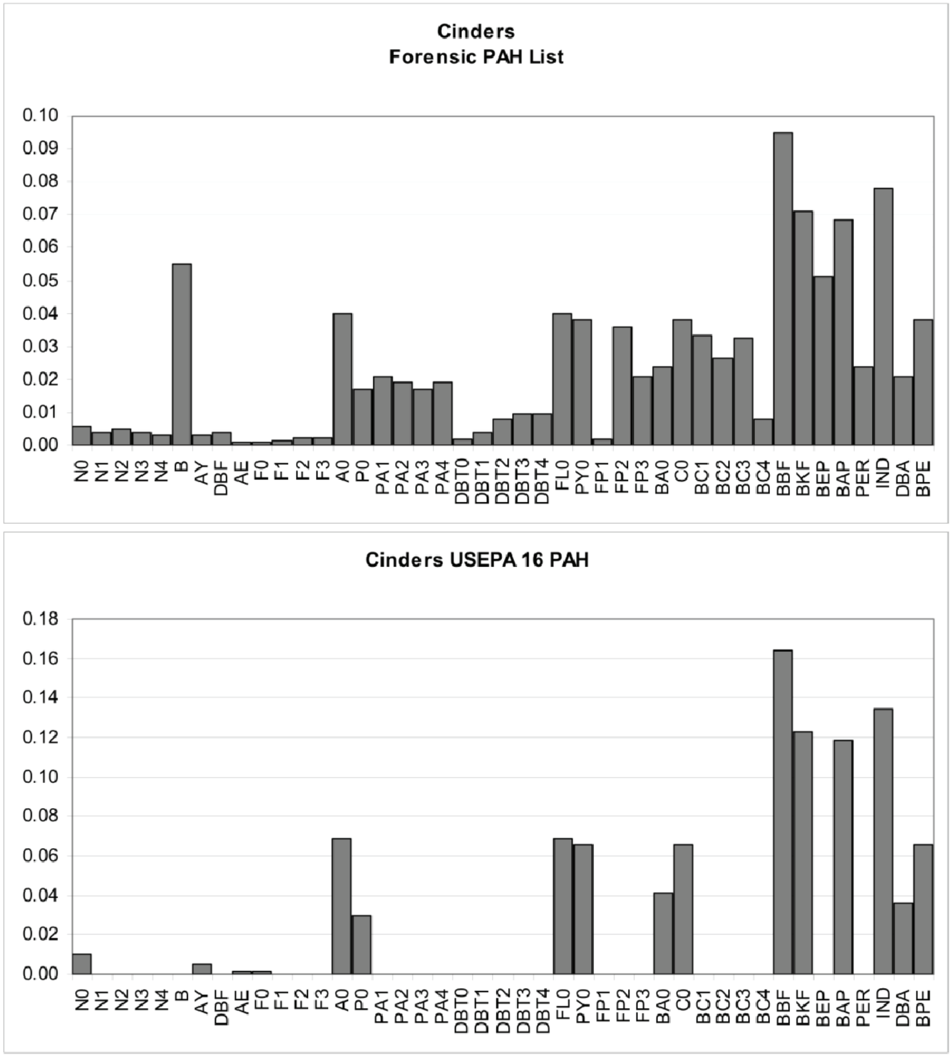
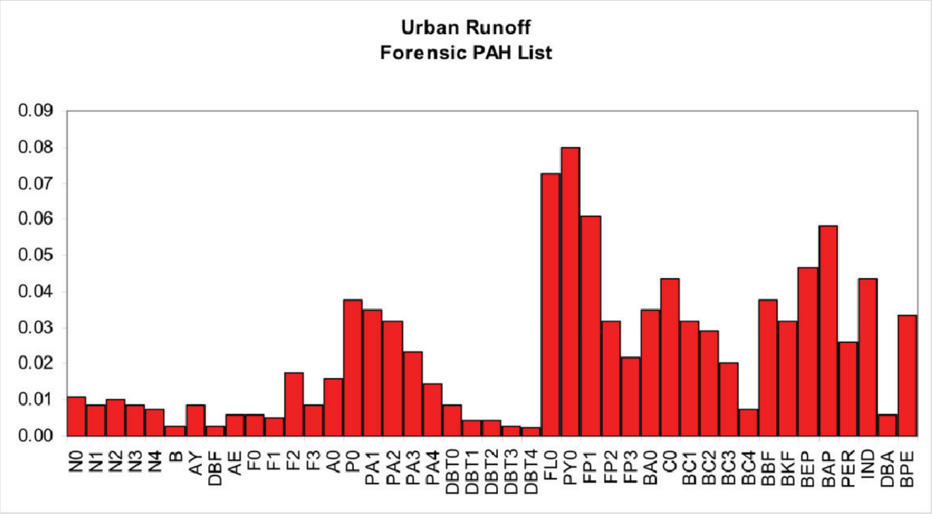


Figure 9. PAH Profile for Coal Combustion Cinders with Forensic PAH list and USEPA 16 Priority Pollutant PAHs. This is characteristic of pyrogenic PAH sources from non-petroleum materials. PAH profiles are dominated by 4-, 5- and 6-ring PAHs and are depleted in 2-and 3-ring compounds.



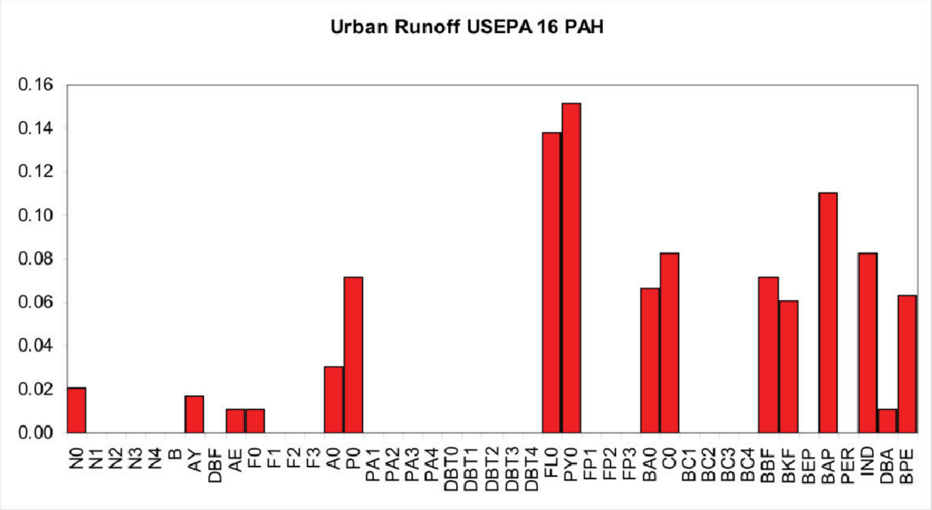


Figure 10. PAH Profile for general Urban Background with Forensic PAH list and USEPA 16 Priority Pollutant PAHs. PAH profiles tend to be dominated by 4-, 5- and 6-ring PAHs and are depleted in 2-and 3-ring compounds. However, the 2-and 3-ring compounds are more prevalent in sediments impacted by urban runoff due to the combined contribution of combustion by-products and petroleum derived PAHs associated with fuels and oils released from motor vehicle and other petroleum related sources.

A.13.2 PAH Diagnostic Ratios

Sources of PAHs may be differentiated by characteristics unique to their PAH profiles such the ratio of one PAH or PAH group to another. Below are some examples.

- Light PAHs/Heavy PAHs (LPAH/HPAH) – The ratio of light PAHs (2- to 3-ring PAHs) to heavy PAHs (4- to 6-ring PAHs). HPAH are preferentially formed by higher temperature processes characteristic of pyrogenic PAHs (i.e., combustion) and are less abundant in petrogenic sources, which formed at lower temperatures. In general, a ratio >1 indicates a petrogenic source and a ratio <1 a pyrogenic source.

- Fluorene/Fluoranthene (F/FL) – Fluorene, a 3-ring PAH, is abundant in petrogenic sources whereas fluoranthene, a 4-ring PAH, is virtually absent. Thus, in general, the F/FL ratio would be higher for petrogenic sources than for pyrogenic sources.

- Phenanthrene/Anthracene (P/A) – Formation of phenanthrene and anthracene, both 3-ring PAHs, is dependent on temperature. In general, the higher temperature processes associated with pyrogenic sources result in lower P/A ratios compared to petrogenic sources.

Diagnostic ratios reflect the general characteristics of the source. In general, diagnostic ratios are used to differentiate between pyrogenic and petrogenic source categories. Given that petrogenic formation of PAHs tends to form at considerably lower temperatures than pyrogenic processes, the PAH ratios from petrogenic sources will tend to reflect ratios that emphasize molecular stability at lower temperatures. In a similar manner, parent PAHs tend to be more stable at high temperatures relative to their alkylated homologues. Hence, these ratios can be used individually to differentiate between pyrogenic, petrogenic, and mixed source categories based on empirically derived cut points for the ratios.

Diagnostic ratios may be based on the comparison of PAH compounds having the same molecular weight (i.e. isomers), parent vs. alkylated homologue concentrations (e.g. anthracene/phenanthrene and C1-anthracene/phenanthrene), or a general comparison of lower vs. higher molecular weight PAHs (e.g., naphthalene vs. ΣPAH). Various diagnostic ratios have been developed to facilitate source identification and allocation and are generally based on empirical data obtained for know source materials. Recent reviews of diagnostic ratios are summarized in Simcik *et al*. (1999), Dickhut *et al*. (2000), Sanders *et al*. (2002), and Yunker *et al*. (2002). Table 12 provides some examples of diagnostic ratios obtained from the literature.

Table 12. Example Diagnostic Ratios

Ratio	Petrogenic Cut Point	Petroleum Combustion Cut Point	Mixed Source Cut Point	Combustion Cut Point	Other	Source Reference
Combustion PAH*/TotPAH	< 0.3	-	0.3 - 0.7	> 0.7	-	Hwang *et al*., 2003
P/A (178)	> 15	-	10 -15	< 10	-	De Luca *et al*., 2004
A/A + P (178)	< 0.1	-	-	> 0.1	-	Yunkers, 2002
FL/PY (202)	< 1.0	-	-	> 1.0	-	De Luca *et al*., 2004
FL/FL + PY (202)	< 0.4	0.4 - 0.5	-	> 0.5	-	Yunkers, 2002
BaA/C (228)	< 1.0	-	-	> 1.0	-	De Luca *et al*., 2004
BaA/BaA + C	< 0.2	0.2 - 0.35	-	> 0.35	-	Yunkers, 2002
IP/IP + BPE (278)	< 0.2	0.2 - 0.5	-	> 0.5	-	Yunkers, 2002
C0 / C0 + C1 P/A (178)	< 0.5	< 0.5	-	> 0.5	-	Yunkers, 2002
C0 / C0 + C1 FL/PY (202)	< 0.5	-	-	> 0.5	-	Yunkers, 2002

*Combustion PAHs include fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1 ,2,3-c,d)pyrene, dibenz(a, h)anthracene, and benzo(g, h, i)perylene.

If a forensic PAH evaluation is being conducted in an area where previous assessment used the standard 8270 GC/MS method, a preliminary evaluation of existing data using diagnostic ratios is appropriate. This information can subsequently be used to identify sample locations where a more detailed forensic PAH 8270 GC/MS analytical could be performed.

The primary advantage of using diagnostic ratios is that a significant amount of information can be derived from using only the 16 priority pollutant PAHs. A more robust expanded forensic PAH analysis list is not exclusively required to make the petrogenic versus pyrogenic differentiation. However, the use of the expanded forensic PAH list does provide several additional diagnostic ratios that include both parent and alkylated homologue compounds. These additional ratios can significantly improve the resolution of the final evaluation.

Several authors have utilized cross plots of diagnostic ratios (double ratio plots) to evaluate potential sources (Dickhut *et al*. 2000; Walker *et al*. 2005; Wang and Fingas 2003). Cross plots have the advantage over individual ratios of being able to simultaneously evaluate the relationship between lower and higher molecular weight isomer pairs (e.g. fluoranthene and pyrene with mass 202 compared to benz(a)anthracene and chrysene with mass 228), which can facilitate the classification of samples into source categories. A sample cross-plot is shown in Figure 10. Several authors have summarized PAH ratios for several specific sources, including mobile sources, coke and coal combustion, wood combustion and smelter operations. These cross plots can be used to evaluate potential mixing trends between two or more sources of PAHs (Walker *et al*. 2005).

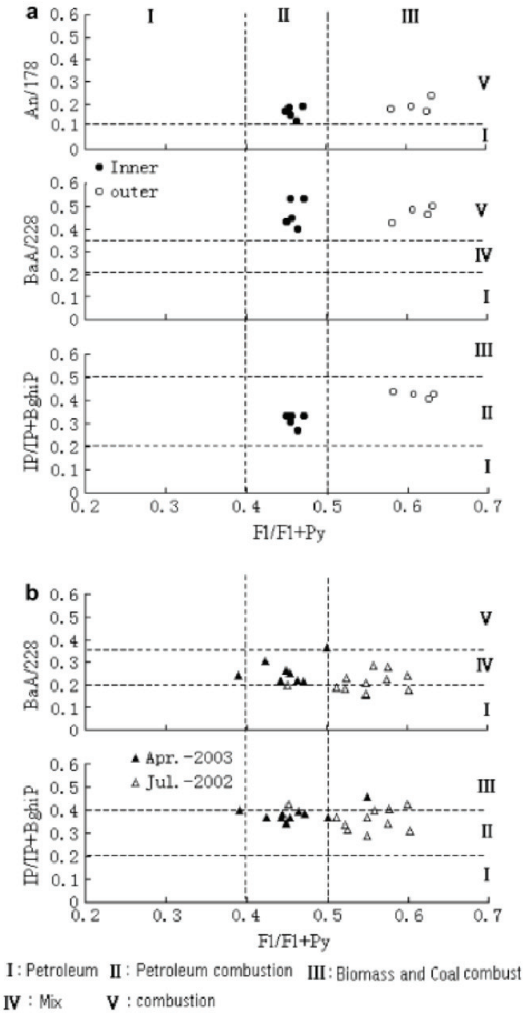


Fig 5. Plots of PAH isomer pair ratios for source identification: sediment samples; (b) suspended particular matter. Source bound lines are base on Yunker et al. (2002).

Figure 11. Example Cross Plots.
From Lou et al., 2006. Polycyclic Aromatic Hydrocarbons in Suspended Particulate Matter and Sediments from the Pearl River Estuary and Adjacent Coastal Areas, China. Env. Poll., v. 139, pp. 9-20

A.13.3 Principal Component Analysis

There are various statistical and numerical methods of data analyses performed on concentration data or ratios and other indices calculated from concentration data. These methods are collectively referred to as chemometrics. Chemometric analyses have proven to be an especially effective means of comparing chemical data from a large number of samples. An excellent summary of statistical and numerical methods commonly used can be found in Johnson and Ehrlich (2002). A particular and significant advantage of chemometric analyses is that they provide a strictly mathematical means of analyzing data, thus removing any biases of the interpreter. Chemometric analyses have the additional advantage of being able to convey the complex chemical differences among many samples with many individual chemical measurements in a visual manner that is more easily understood by the non-expert.

Principal components analysis (PCA) is a powerful chemometric technique for visualizing inter-sample and inter-variable relationships. It reduces the complexity of the data by finding linear combinations of the variables in the data set that account for the maximum amounts of variance. These linear combinations are called the principal components (PC). The first PC accounts for the maximum amount of variance and each successive PC accounts for less of the remaining variance. Various workers have investigated sources of the PAHs in sediments and other media using PCA (Uhler *et al*. 2005, Stark *et al*. 2003, Stout *et al*. 2003a, Krazanowski and Marriot 1994, Dillon and Goldstein 1984, Morrison 1976) with both raw, normalized, and transformed PAH compositions of sediment samples as input.

PCA yields a distribution of samples in n-dimensional space, where n is the number of variables (e.g., PAH analytes). The first PC is a line through this space upon which each sample point can be projected. The line's orientation is such that the variance of these projections is maximized. The second PC is another line defining the next highest variance. These first two lines define a plane. These planes are called factor score plots, which are one end product of PCA (Gabriel 1971). The Euclidean distances between sample points on these factor score plots are representative of the variance captured in each PC. In simpler terms, samples that cluster together are chemically similar and outliers are chemically distinct.

Figure 11 shows an example of a factor score plot for approximately 100 sediments from an urban waterway in which three sources of PAH were recognized: natural background (arising from pre-industrial, natural forest fires), urban runoff, and creosote (from a former coal tar distillation facility on the waterway) (Stout *et al*. 2001). Many sediment samples from this urban waterway contained only, or primarily only, one of these sources. These single-source samples tend to plot as clusters at or near the apices of the trends revealed by the PCA factor score plot. However, many other sediment samples tended to plot in locations intermediate between the clusters indicating that they contain a mixture of these. Spatial relationships among samples on a PCA score plot can be used to estimate or determine the proportions of each end-member in each sediment sample. Additional calculations involving spatial distributions, concentrations, and volumes of impacted sediments of each sample in the study could then be used to allocate responsibility among the sources.

A.13.4 Polytopic Vector Analysis

Polytopic vector analysis (PVA) is perhaps the most sophisticated statistical procedure that has been applied in the forensic investigation of sediment contamination (Barabas *et al*. 2004; Johnson *et al*. 2002;). This technique is a self-training receptor/mixing model that unmixes complex mixtures into several contributing patterns and their contribution to each sample (Johnson *et al*. 2002).

The fundamental, mathematical principles of PVA were developed for geological applications by Miesch (1976) and implemented by Full (1981). In more recent applications, it has been adopted in environmental forensics (Johnson *et al*. 2002). PVA has three objectives: (1) to determine the number of contributing sources in the system; (2) to resolve each fingerprint (with a sum of 1 or 100%); and (3) to resolve the loading or mixing proportion of each source on each sample. PVA starts with PCA and is a special case of factor analysis.

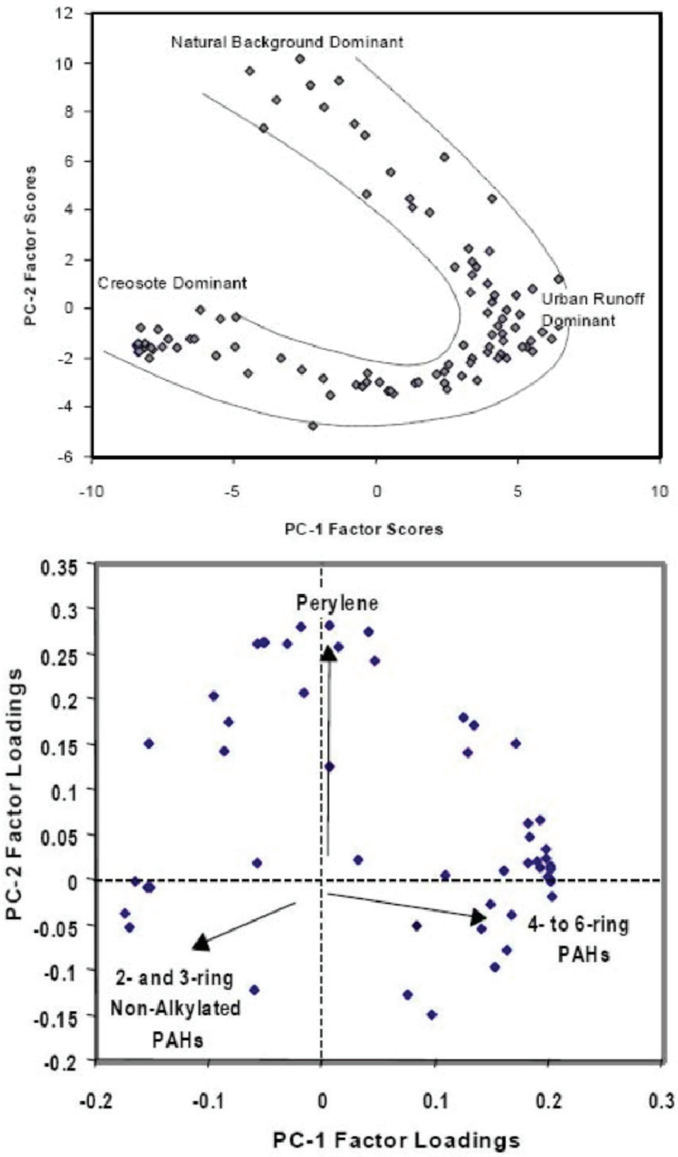


Figure 12. Factor score plot and corresponding factor loading plot for sediment PAH data. The PCA reveals three dominant PAH sources (natural background, urban runoff, and creosote) that were enriched in perylene, four- to six-ring PAHs, and two- and three-ring PAH, respectively. Samples plotting between the apices indicate a mixture of sources. Data from Stout et al. 2001.

A.13.5 Nonparametric methods

Nonparametric methods are best developed as study-specific methods as they can easily be adapted to fit the specific needs of a variety of petrogenic and pyrogenic sources. Carls (2006) recently developed a unique nonparametric approach to source identification that relies on scoring, not specific concentrations. In developing this approach, Carls (2006) investigated several nonparametric models including one designed to detect petroleum in general, one specific to Alaska North Slope crude oil (ANS), and one designed to detect pyrogenic PAH. The nonspecific method is simply based on the presence or absence of homologous PAH families and their constituents. Scoring in the specific version is based on the observation that fewer unsubstituted parent compounds are present in ANS than alkyl-substituted compounds in each of five homologous families (naphthalenes, fluorenes, dibenzothiophenes, phenanthrenes, and chrysenes). This relationship is generally true in unweathered oil (except for C3-fluorenes, C4-phenanthrenes, and C4-chrysenes) and remains (or becomes) true as the oil weathers. The same relationship was observed in other oils (Short 2002). The nonparametric pyrogenic model is based on the observation that unsubstituted parent homologue concentrations are typically much greater than alkyl-substituted concentrations.

Carls (2006) notes that oil identification was clearly difficult where composition was modified by physical or biological processes. Model results differed most in these cases, suggesting that a multiple model approach to source discrimination may be useful where data interpretation is contentious. However, a combined nonparametric model best described a broad range of hydrocarbon sources and may represent a useful new analytical assessment tool.

A.13.6 Synthesis and Presentation of Data

How the results of PAH data analysis are presented needs to consider the audience, which will dictate the level of technical detail. It is prudent to document the technical detail somewhere such as in a summary report or as appendices so that it is readily available. Because data analyses and interpretations typically lead to critical environmental decisions, it is important to properly maintain all data, field notes, reports, and calculations.

Chemical fingerprinting data can be very confusing, except to an experienced chemist. Their interpretation is much easier and useful when results are shown in easily interpreted graphs and figures such as PCA plots or cross-plots of diagnostic ratios. The value of a study will be undermined if the audience cannot easily grasp results or conclusions. Therefore, detailed data should be made available, but should be placed in appendices so that they do not detract from the main points of the study.

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