
A Guide to Polycyclic Aromatic Hydrocarbons for the Non-Specialist

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A Guide to Polycyclic Aromatic Hydrocarbons for the Non-Specialist

0 Overview

This report provides an introduction to polycyclic aromatic hydrocarbons (PAHs) for persons working in the petroleum industry. It describes what PAHs are and how they are formed; PAH environmental transport, fate, and health effects; regulatory requirements related to PAHs; and analytical methods for measuring PAH concentrations in the environment. This information is of particular relevance to the petroleum industry due to the natural presence of PAHs in crude oil, the formation of PAHs during some refining processes, and the production of PAHs throughout the combustion of petroleum products. The intended audience for this report includes environmental professionals who must address PAH regulatory issues, and field personnel who are responsible for the sampling and analyses of PAHs.

Concern about PAHs in the environment is due to their acute toxicity or carcinogenic properties, as well as their relative persistence. This concern has led to the regulation of PAHs under a number of U.S. laws, including the:

- Clean Air Act (CAA),
- Clean Water Act (CWA),
- Emergency Planning and Community Right-to-Know Act (EPCRA),
- Occupational Safety and Health Act (OSHA),
- Resource Conservation and Recovery Act (RCRA), and
- Safe Drinking Water Act (SDWA).

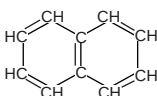
Several environmental regulations relate directly to petroleum products or petroleum processing. Polycyclic organic matter (POM) is one of the toxic air pollutants whose emissions reformulated gasoline is meant to reduce. POM (defined as the sum of the seven carcinogenic PAHs) is also on the list of mobile source hazardous air pollutants that the EPA is proposing for future regulation, as well as on the list of hazardous air pollutants for the EPA's Urban Air Toxics Strategy.

Toxic release inventory reporting (TRI) under EPCRA requires facilities, such as oil refineries that manufacture, process, or otherwise use as little as 10 lbs of the PAH benzo[ghi]perylene or 100 lbs of polycyclic aromatic compounds (a group of 21 PAHs, substituted PAHs, and heterocyclic compounds), to report their releases to the environment. Other laws and regulations on PAHs, which are described in Section 5 of this report, apply to their concentrations in the natural and workplace environment.

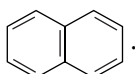
1 Introduction

1.1 WHAT ARE PAHS?

Polycyclic aromatic hydrocarbons (PAHs)—sometimes referred to as polynuclear aromatic hydrocarbons (PNAs), condensed ring aromatics, or fused ring aromatics—are a class of organic compounds consisting of two or more fused aromatic rings.

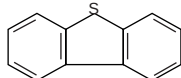
Naphthalene,  consisting of two fused benzene rings, is the simplest PAH. In this depiction, all of the

hydrogen and carbon atoms are labeled. More commonly, PAHs are shown without labeling the carbon and hydrogen

atoms: .

PAHs most commonly encountered in the environment contain two to seven fused benzene rings, although PAHs with a greater number of rings are also found. The “ultimate” PAH is graphite, an inert material comprised of planes of fused benzene rings.

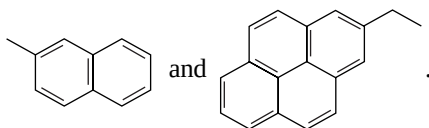
Like all hydrocarbons, PAHs contain only hydrogen and carbon. However, closely related compounds called heterocycles, in which an atom of nitrogen, oxygen, or sulfur replaces one of the carbon atoms in a ring, are commonly found with PAHs.

Dibenzothiophene,  for example, is a sulfur heterocycle. Names and structures of the list of 16 PAHs

considered “priority pollutants” under the “Clean Water Act” are found in Figure A-1 in the Appendix.

PAHs often occur with aliphatic (straight chain) hydrocarbons attached to the rings at one or more points. These compounds are referred to as “branched” or “alkylated” PAHs. The aliphatic chains are depicted as lines attached to the PAH with the end of the line representing a methyl group ($-CH_3$) and an angle representing an intermediate carbon ($-CH_2-$). Thus, methylnaphthalene

and ethylpyrene are depicted as



Because there are numerous possible combinations of the location of the alkyl chain on the parent PAH, the number of chains on the molecule, and the length of the chains, alkylated PAHs are often classified by the number of alkyl carbons they contain. Thus, methylnaphthalene, as depicted above, is a C_1 -naphthalene, while ethylpyrene is a C_2 -pyrene.

2 Sources of PAHs

PAHs are produced in nature through four generalized pathways: 1) low temperature diagenesis of organic matter (part of the changes undergone by a sediment after its initial deposition); 2) the formation of petroleum and coal; 3) incomplete or inefficient combustion at moderate to high temperatures (pyrolysis); and, 4) biosynthesis by plants and animals. These processes are the *primary sources* of PAHs. Primary sources of PAHs also include anthropogenic (man-made) sources. These include the combustion of fossil fuels and biomass, such as wood, as well as chemical production that results in the formation of PAHs.

Because the type distribution of PAHs depends on the temperature of formation, the characteristic distributions of these different sources can be used to help distinguish among different sources of PAHs in the environment. Once produced, PAHs are introduced or “delivered” into the environment through a number of pathways (i.e., *secondary sources*), which are described in Section 3.

2.1 PRIMARY SOURCES OF PAHs

Diagenic PAHs. *Diagenic* PAHs are those produced by natural processes that are set in motion when organic matter is deposited in nature—in soils or sediments. These processes, collectively called diagenesis, begin shortly after deposition of the organic matter. These are low temperature processes that occur after oxygen is depleted, and are believed to involve microorganisms, such as bacteria, though non-biological processes may occur in tandem. Relatively few individual PAHs are produced by these early diagenic processes. One of the most notable PAHs produced in this manner is the five-ringed PAH, perylene, shown in Figure 2-1. Perylene is commonly found in sediments of rivers, lakes, and oceans at a depth in the sediment where oxygen is reduced.

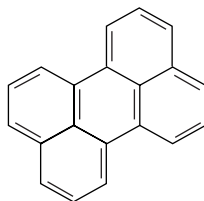


Figure 2-1. Perylene, a Five-Ringed Diagenic PAH

Fossil Fuel (Petroleum and Coal) PAHs. Over geological time and within petroleum reservoirs and coal beds in geological structures, another type of PAHs is produced—*petrogenic* PAHs. Petrogenic PAHs are formed at elevated pressures (and at higher temperatures than the formation of diagenic PAHs) within deeply buried layers of sediments. Petrogenic PAHs are formed, for example, when biological organic matter from plankton is converted to petroleum. These processes also can form coal, although the starting biological material (e.g., higher plants and animals) may be different. Petroleum or petrogenic PAHs and coal-derived PAHs are “fossil fuel” PAHs. The nature of the processes, which convert organic matter

to fossil fuels, involves semi-random chemical processes. This fact results in the complexity of many PAH structures that are found in fossil fuels. Hundreds to thousands of individual PAHs may be produced by nature during the processes that form petroleum. Nevertheless, while their compositions vary greatly, crude oils have in common the existence of two to six+ ringed PAHs, with a preponderance of alkylated structures associated with the two to four ringed compounds.

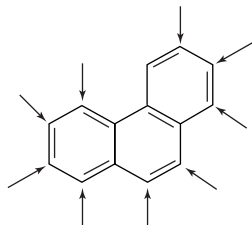


Figure 2-2. Phenanthrene
(↗ indicates possible site of alkylation)

The types of PAHs formed as fossil fuels include a complex variety of parent (i.e., unsubstituted), and alkylated PAHs. Series of PAHs comprised of parent and substituted PAHs form many families or *homologous series* of PAHs. The phenanthrene homologous series of PAHs includes, for example, phenanthrene itself, plus a series of alkylated homologues of phenanthrene with many alkyl substitutions (see Figure 2-2). The relative abundance of the alkylated PAHs of petrogenic PAHs far exceeds the abundance of the parent (i.e. unsubstituted) compound or C₀-phenanthrene. **The fact that alkylated PAHs “are much greater than” parent PAHs is a main feature of petrogenic PAHs.** This is illustrated in the first chart of Figure 2-3 for typical alkyl homologue distributions.

Pyrogenic PAHs. High temperature processes such as the combustion of fossil fuels or the burning of wood also form PAH (Figure 2-3). During higher temperature processes, those organic compounds that escape complete combustion (oxidation to carbon dioxide and water) include the *pyrogenic* PAHs. Diesel fuel combustion, forest fires, and the smoking of foods with certain woods are examples of pyrogenic processes. PAHs are also formed on meats by barbecuing (see Table 5-1). Included in this pyrogenic category are the products of high temperature processing of coals in coal gasification processes. The residuals of the coal gas processes are termed *coal tars*, and they are rich in the pyrogenic PAHs.

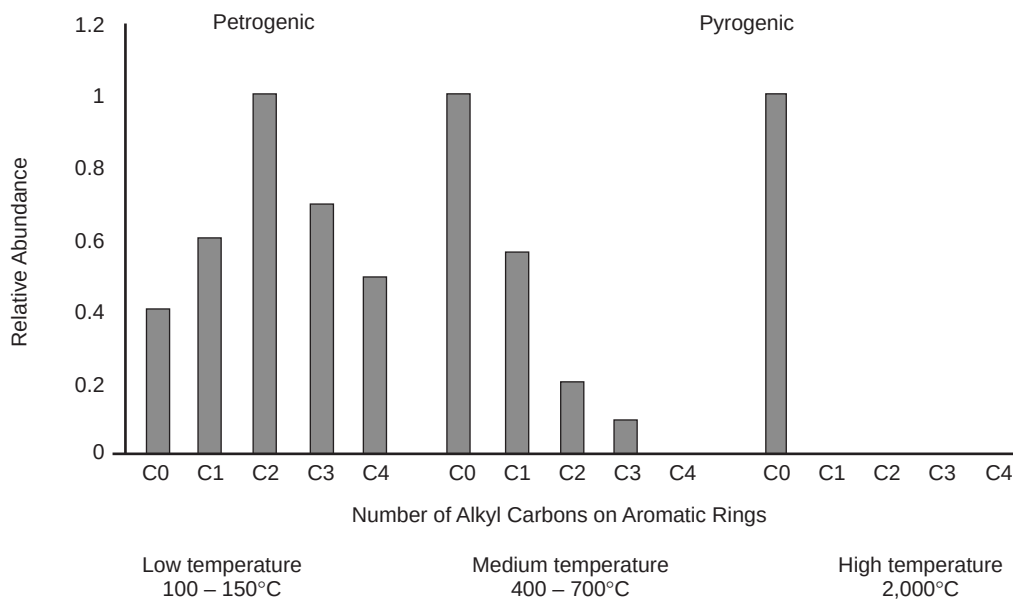


Figure 2-3. Representative Distribution of Alkylated PAHs Formed at Different Temperatures
(based on Chrysene)

Because the high temperature processes tend to destroy the more reactive alkylated PAHs, the production of unsubstituted PAHs are favored in pyrogenic processes. **Thus, a major feature of pyrogenic PAHs is that the parent PAHs “are much more numerous” than alkylated PAHs.** As a result, PAH distributions that are produced by the hotter and more rapid pyrolysis or combustion-related processes are markedly different from those produced by petrogenic processes (see Figure 2-3). Also, pyrogenic PAHs are characterized by the higher abundance of the four, five, and six+ ringed PAHs relative to PAHs found in most petroleums.

Biogenic PAHs. Certain PAH precursor compounds are biosynthesized in nature, although the direct biosynthesis of PAHs *per se*, remains uncertain. Although the contribution of microorganisms to the production of PAHs in nature has been reported, their contribution may be more to the oxygen-containing aromatic compounds rather than to PAHs themselves.

It is well-known that other PAH precursor compounds (e.g., abietic acid) exist in abundance in certain tree resins (e.g., conifer resins) and that specific PAHs are formed from the diagenesis or the combustion of these resins. For example, *retene*, (Figure 2-4), a specific C₄-phenanthrene isomer, is ubiquitous in residues from these plants and can be found in high relative abundance in sediments of pristine northern environments. Similarly, *simoneltite*, a substituted PAH compound, is found in abundance where organic conifer residues exist. These specific, singular PAHs are found in coastal sediments around the world.

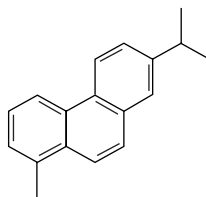


Figure 2-4. Retene

3 PAHs in the Environment

3.1 PAH “ENVIRONMENTAL DELIVERY SYSTEMS”

Once they are produced by primary processes, PAHs may be introduced into the environment through a number of pathways—secondary sources or “PAH delivery systems.” These include:

- Natural oil seeps and erosion of source rocks (shales)
- Petroleum spills and releases
- Urban runoff
- Industrial effluents
- Atmospheric deposition of combustion products
- Coal gasification (i.e., manufactured gas) plant residues, and runoff
- Creosote preservation

PAHs can enter the environment on local, regional, and global scales. Point sources, such as municipal or industrial outfalls, are on the local scale, and are generally made up of mixtures of PAHs that are combustion or oil-related. Non-point sources (e.g., rainfall runoff or atmospheric deposition) are found on regional scales, and are also made up of PAHs from multiple primary sources. Wide-field atmospheric deposition is a global source that distributes primarily pyrogenic PAHs (Ohkouchi *et al.*, 1999) to remote regions of the earth. Airborne transport of PAHs on soot particles from forest fires and the combustion of coal and oil has been established as a major mechanism for the distribution and delivery of PAHs to soils and sediments on regional and global scales.

Understanding how PAHs enter the environment is important in conducting environmental impact assessments and risk studies. On a global basis and in areas remote from urban influence, PAHs from pyrogenic processes transported over large distances are the principal source of background concentrations—more important than petrogenic PAH inputs—though the levels tend to be very low. On more localized scales, background PAH concentrations may be much higher, and PAHs from urban runoff together with combustion-related PAH inputs are very important contributors to most receiving environments. In selected geologically-active environments, oil seeps and erosion from oil source rocks and coal result in elevated

concentrations from natural sources of PAHs. The background concentrations of PAH are of particular significance when the potential effects (i.e., incremental addition) of PAHs from new oil and gas exploration projects or effects of oil spills are being evaluated as part of new project plans or environmental impact and damage assessments.

Natural Oil Seeps and Source Rock Erosion

In local areas (e.g., Santa Barbara Channel, Gulf of Alaska, Caspian Sea) and on a global basis, natural oil seeps from geologic formations that are exposed at the earth's surfaces contribute significant quantities of petrogenic PAHs to the environment. When these PAHs are bound tightly to particles by sorption they are deposited to sediments and become part of the natural PAH background. The significant background of PAHs in the sediments of Prince William Sound, the site of the *Exxon Valdez* oil spill, is almost totally the result of seep oil-related material and petroleum source rocks (shales) that are eroded by rivers and washed to the sea (Page *et al.*, 1995). In the Beaufort Sea area of the Alaskan and Canadian arctic, the input of PAHs from coal seam erosion mix with oil source rock erosion to establish a large PAH background concentration in the sediments.

Petroleum Spills and Releases

The PAHs that enter the environment from petroleum spills, leaks, and other releases are, by definition, petrogenic. Although oil spills receive considerable attention from industry, regulators, and the media, they typically do not account for a large fraction of PAHs entering the environment. This is so because spills account for only a fraction of the oil released into the environment, and because the concentrations of PAHs in the oil are less than those of other types of hydrocarbons. The PAH content of crude oils varies widely, ranging from <10% – >30% of the oil. Typical crude oils contain a small percentage of PAHs compared to other hydrocarbon fractions, as is shown in Figure 3-1. Similarly, while some refined products, such as diesel fuels, may consist of 25% – 30% aromatic compounds, most of these are monocyclic aromatics, not PAHs.

The concentration of individual PAHs may be as high as 5000 to 10,000 ppm in oils. The concentration of benzo[a]pyrene, a well-known and heavily monitored carcinogen, however, is typically <1 ppm in crude oil but up to roughly 50 ppm in some heavy refined products.

Composition and property data for crude oil and oil products can be found at:

<http://www.etcentre.org/main/e/db/db.html>

and in Volume 2 of the TPH Working Group Series: *Composition of Petroleum Mixture*, available under “ASP Publications” at the Association for Environmental Health and Sciences website:

<http://www.aehs.com/>

Urban Runoff and Municipal Wastewaters (Mixtures of PAH Sources)

A significant fraction (20% – 30%) of the petrogenic PAHs that enter the environment is from urban runoff that makes its way into coastal environments from stormwater runoff, which is often routed through municipal sewerage systems (NRC, 1985). The largest fractions of PAHs in many urban harbors (e.g., Boston, Los Angeles, San Francisco) come from chronic discharges of urban runoff through publicly-owned sewage treatment works and storm sewer outfalls.

Urban runoff consists of a considerable amount of pyrogenic PAHs, as well as petrogenic PAHs. The combustion of fossil fuels leads to soot, which when deposited to land leads to rainwater runoff with a significant presence of combustion-related PAHs. Runoff from parking lots and roadways are important local sources of PAHs to receiving waters and to municipal treatment plants, owing to the significant quantities of crankcase oil drippings, soot, and automotive tire particles that accumulate in heavily trafficked areas. (PAHs are present in carbon black used to make tires).

Industrial Pyrogenic PAH Sources: Aluminum Smelting, Manufactured Gas Plants, Creosote Pilings

The smelting of aluminum by the Soderberg and other processes produces waste materials, wastewaters, and air emissions that are rich in PAHs (Naes and Oug, 1998). These PAHs originate in the materials (i.e., coal tar pitches) used to make the electrodes utilized in the smelting process. Air emissions and wastewater sludges from these processes contain significant quantities of pyrogenic PAHs.

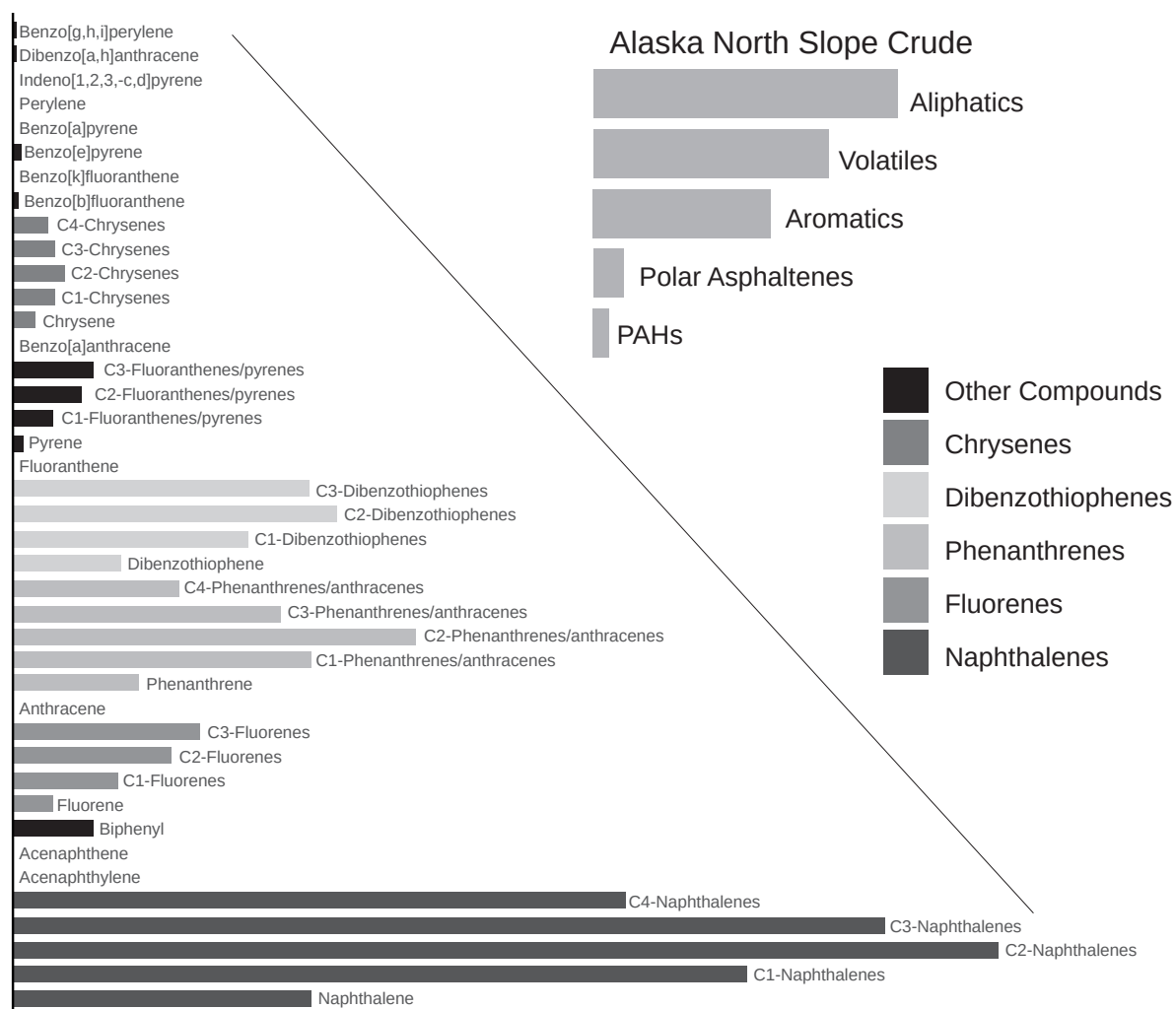


Figure 3-1. PAHs in Alaska North Slope Crude Oil

In the first half of the 20th century, manufactured gas plants (MGP) produced gas from coal, resulting in residues called “coal tar”. These coal tars contain large quantities (up to 70% – 80% by weight) of pyrogenic PAHs as a result of the high temperature processing of coal in the plants. These PAHs have entered the environment via groundwater flow and runoff to coastal rivers and sediments.

Also in the category of industrial pyrogenic PAHs are those derived from creosote, a coal tar derivative. The use of creosote as a wood preservative in wood pilings and telephone poles, especially in locations adjacent to urban harbors during the 20th century, has resulted in the release of creosote to the aquatic environment. Since creosote is heavier than water, once released it tends to become associated with sediments. Creosote-derived PAHs can be an important and dominant localized source of PAHs to the environment—in Puget Sound, in Boston Harbor, and even in parts of Prince William Sound.

Industrial Wastewaters and Waste Sites

Industrial wastewater effluents typically contain low quantities of PAHs, the levels of which are regulated by discharge permits. However, refineries, chemicals, plastics, and dyestuff manufacturing plants, among others, discharge PAHs to receiving waters and emit them to the atmosphere as fugitive emissions at low-to-moderate quantities. High molecular weight PAHs are also produced in modern petroleum coking operations.

At many waste disposal sites throughout the world, historically unregulated waste handling and disposal have resulted in the presence of a complex PAH “soup.” Typically, such sites were the scene of oily waste disposal operations, coking, or coal gasification. These PAHs can migrate from the site, enter groundwater, or seep into surface waters.