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Transport and Fate of Non- BTEX Petroleum Chemicals In Soils and Groundwater



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Transport and Fate of Non-BTEX Petroleum Chemicals in Soil and Groundwater

Health and Environmental Sciences Department

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ABSTRACT

In the assessment and remediation of petroleum contamination of soil and groundwater, the major research focus has been on the monoaromatics benzene, toluene, ethylbenzene, and xylene isomers (collectively, BTEX) from gasoline releases. This report presents the results of a literature survey of available information on the physical/chemical and toxicological properties, soil and groundwater mobility and fate, and laboratory analysis of non-BTEX components of petroleum products. To limit the research effort, a list of twelve compounds were selected for detailed review. Selection was based on abundance in petroleum products, expected mobility in the subsurface, and toxicity.

The survey found a lack of available information on the subsurface leaching of petroleum hydrocarbons and other compounds from the immiscible phase, and on the bulk migration of viscous petroleum products, such as lubricating oils, through the soil. The literature provided only limited data on the toxicology of highly alkylated saturated and aromatic hydrocarbons, which are among the most abundant components of many petroleum products. The study recommended research studies to address these gaps in the existing literature.



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EXECUTIVE SUMMARY

Introduction

In recent years, the major focus of concern about contamination of groundwater and soils with petroleum products has been releases of gasoline from underground storage tanks. Regulatory monitoring of soil and groundwater contamination has focused on benzene, toluene, ethylbenzene, and xylenes (BTEX), because they are major components of gasolines and other light distillate fuels, tend to migrate readily through porous soils, are slightly soluble in water, and are toxic to plants and animals, including humans. However, crude, refined, and residual petroleum products are extremely complex mixtures. Therefore, the American Petroleum Institute (API) is interested in identifying other organic components in crude and refined petroleum products that can be monitored in addition to BTEX as indicators of the behavior, fate, and potential environmental effects of petroleum products released to the soil/groundwater environment.

The objective of this report is to evaluate the migration, fate, and toxicity of non-BTEX petroleum chemicals released to soils and groundwater. The focus of this evaluation was on non-BTEX hydrocarbons and related hetero-organic compounds. A representative group of 12 components of petroleum products was selected for more intensive evaluation in this review, based on their abundance in petroleum products, toxicity to humans and aquatic organisms, physical/chemical properties that influence their migration through and accumulation in soils and groundwater, and the anticipated future interest of regulatory agencies in the compounds.

Study Methods

This study was performed using available literature and evaluation methods applied to the questions of interest. The universe of compounds considered for this study was limited to hydrocarbons and closely related sulfur-, nitrogen-, and oxygen-substituted compounds. Working within this universe, we reviewed all literature available to us, both open literature and information provided by API member companies, on composition of refined products and crude, residual, and used oils. Using the available data on chemical/physical properties and toxicity, three lists of compounds of potential interest were produced: one based on mammalian carcinogenic toxicity; one based on mammalian non-carcinogenic toxicity; and one based on a combination of abundance in petroleum products and properties favoring migration through soils. From these three lists, a set of 12 compounds that represented the range of environmental behavior and toxicity was selected.

The subsequent study elements then included a general review of the sources and fates of the 12 selected compounds in soil and groundwater (Section 4), a more detailed evaluation of subsurface transport (Section 5), a review of biological effects (toxicity) data (Section 6), and a review of available chemical analysis methods (Section 7). The general fate and subsurface transport evaluations were based on chemical properties reported in the literature and commonly used methodologies for evaluating subsurface chemical fate and transport. Based

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on the results of this work, recommendation for further work, including laboratory and field studies were developed (Section 8).

Chemical Composition and Properties

The chemical compositions of crude and refined oils are extremely complex and vary substantially. The most abundant and readily quantifiable non-BTEX hydrocarbons in all crude and refined products are the low molecular weight saturated and aromatic hydrocarbons. As a general rule, concentrations of individual hydrocarbons, and related oxygen-, sulfur-, and nitrogen-substituted hydrocarbons within an homologous series decrease as molecular weight increases. The major exception to this generalization is that C₁- through C₃-alkyl aromatic and heterocyclic compounds often are more abundant than the unalkylated parent compounds.

The most abundant non-BTEX aromatic hydrocarbons in most refined and crude oils include: trimethylbenzenes; tetralins/indans; tetramethylbenzenes; naphthalene; methylnaphthalenes; dimethylnaphthalenes; methylphenanthrenes; and dimethylphenanthrenes. Some used engine oils also contain relatively high concentrations of methylfluorenes/pyrenes, benz(a)anthracene, and methylbenzopyrenes.

The most abundant saturated hydrocarbons are the normal alkanes (paraffins) from hexane through decane; higher molecular weight n-alkanes also are abundant, but abundance tends to decrease with increasing molecular weight. Light refined products and light crude oils also contain high concentrations of cyclohexane, methylcyclohexane, isopentane, methylpentane, trimethylpentanes, dimethylbutane, and methylcyclopentane. Gasoline may contain percent concentrations of pentenes and methylpentenes (olefins).

The aqueous solubility decreases and octanol/water partition (K_{ow}) increases as molecular weight increases for all classes of hydrocarbons. As a general rule, chemicals with an aqueous solubility less than about 0.1 mg/L and a Log K_{ow} greater than about 5.0 will have limited mobility in soils and are unlikely to appear in groundwater at greater than ultratrace (low parts per billion) concentrations. By this definition, the most mobile hydrocarbons include monoaromatic hydrocarbons with molecular weights less than that of n-hexylbenzene, polycyclic aromatic hydrocarbons with molecular weights less than that of pyrene, saturated hydrocarbons with molecular weights less than that of n-nonane, alkenes with molecular weights less than that of 1-nonene, and heterocyclic compounds with molecular weights less than that of methyldibenzothiophenes. If bulk transport of a petroleum product occurs through subsurface soils, then higher molecular weight hydrocarbons may ultimately migrate to groundwater.

The 12 organic components of crude and refined petroleum chosen for more detailed evaluation in this report include:

Compound	Molecular Weight	Solubility (mg/L)	Log K_{ow}
Cyclohexane	84.2	57.5	3.44
n-Hexane	86.2	13.0	3.00
2,3-Dimethylbutane	86.2	19.1	3.85
2,2-Dimethylpentane	100.2	20.0	3.10
1,2,4-Trimethylbenzene	120.2	60.0	3.65
Naphthalene	128.2	34.4	3.37
2-Methylnaphthalene	142.2	25.5	4.11
Dibenzothiophene	184.3	1.47	5.08
1-Methylphenanthrene	192.3	0.27	5.14
Benz(a)anthracene	228.3	0.01	5.91
5-Methylchrysene	242.1	0.007	6.42
Benzo(a)pyrene	252.3	0.004	6.83

Seven of these compounds are abundant in crude oils: n-hexane, cyclohexane, 1,2,4-trimethylbenzene, naphthalene, 2-methylnaphthalene, 1-methylphenanthrene, and dibenzothiophene. Three potentially carcinogenic polynuclear aromatic hydrocarbons (PAH), benz(a)anthracene, benzo(a)pyrene, and 5-methylchrysene, are present at trace concentrations in most crude oils and at higher concentrations in some residual petroleum products and used engine oils. These higher molecular weight PAH generally are present at only trace concentrations in gasoline and middle distillate fuels. Gasoline and light middle distillate fuels, such as kerosene and jet fuels, contain high concentrations of hexane, cyclohexane, dimethylbutane, dimethylpentane, and 1,2,4-trimethylbenzene. Middle distillate fuels, particularly the heavier fuels, such as diesel fuel and No. 2 home heating oil, as well as many of the residual fuels, contain moderate concentrations of naphthalene, phenanthrene, dibenzothiophene, and their alkyl homologues.

The values for physical/chemical properties for the 12 compounds span the range of physical/chemical properties for the major chemical components of crude, refined, residual, and used oils. Therefore, their behavior in soils and groundwater should be characteristic of most mobile nonpolar organic compounds in petroleum.

Sources and Fate

Not all the hydrocarbons and related hetero-substituted compounds in soils are derived from petroleum products. Other fossil fuels, such as peat and coal, contain a wide variety of saturated, aromatic, and heterocyclic hydrocarbons. The burning (pyrolysis) of organic matter produces a wide variety of hydrocarbons, particularly high molecular weight PAH, similar to those in crude oil and refined or residual oil products. Normal and branched alkanes are synthesized by nearly all living organisms, particularly bacteria and plants. Some aromatic hydrocarbons or substituted aromatic hydrocarbons may be synthesized by living organisms. There probably are no mobile hydrocarbons or related heterocyclic compounds that are unique

to petroleum. However, hydrocarbon assemblages from different sources differ widely in composition and complexity. The most complex assemblages are from petroleum.

There are very few reliable data on the concentrations of petroleum-derived hydrocarbons in soils and sediments. Because aliphatic and olefinic hydrocarbons are readily biosynthesized by many species of microbes, plants, and animals, their concentrations in soils and sediments rich in organic matter often are high. Therefore, it is difficult to use saturated hydrocarbons as an indication of the level of contamination of soils with petroleum hydrocarbons.

Concentrations of individual and total PAH in soils and sediments vary widely primarily in relation to proximity to known sources. However, because of wide airborne dispersal of PAH-contaminated soot from anthropogenic and natural combustion sources, PAH are ubiquitous trace contaminants of all soils. Soils from remote areas may contain less than 1.0 mg/kg (ppm) total hydrocarbons; heavily-contaminated soils from industrial sites may contain more than 20 percent total hydrocarbons. Concentrations of total PAH range from less than about 0.1 mg/kg in clean soils to at least 25 mg/kg in some contaminated soils from industrial sites.

Nearly all soils contain colonies of bacteria and fungi that are capable of biodegrading at least some petroleum hydrocarbons. Soil bacteria and fungi show a tremendous diversity and adaptability in utilizing different types of organic molecules as a sole or supplemental carbon source. Many groups of microorganisms are able to oxidize saturated and, to a lesser extent, aromatic hydrocarbons and heterocyclic compounds completely to carbon dioxide and water and use them as a source of carbon for biomass accretion. In some cases, aromatic hydrocarbons and heterocyclics are metabolized only partially to a variety of polar, oxygenated metabolites. Rates of hydrocarbon degradation are much lower under anoxic than oxygen-rich conditions.

Following a release of crude or refined petroleum to soils, different hydrocarbon classes are degraded simultaneously, but at widely different rates by indigenous microbiota. Low molecular weight n-alkanes with chain lengths of 10 to 22 carbons are metabolized most rapidly, followed by isoalkanes and higher molecular weight n-alkanes, olefins, monoaromatics, PAH, and finally, highly condensed cycloalkanes, resins and asphaltenes. Sulfur heterocyclics seem to be more resistant to microbial degradation than PAHs of similar molecular weight.

Subsurface Transport

Several transport processes control the physical motion of petroleum chemicals through and between the NAPL (non aqueous phase liquid), aqueous, and sorbed solid phases in soils. When released to the subsurface environment, petroleum hydrocarbons are usually initially in the NAPL (oil) phase. NAPL transport, like any subsurface liquid motion, is driven by head gradients, the rate being a direct function of the permeability of the soil, and the travel distance being limited by the amount of liquid available. In the unsaturated zone, the NAPL gradients are predominantly vertical, producing a downward flow direction. As the NAPL

migrates downward, it leaves some material behind in the pores of the porous medium. The amount left behind is called the residual saturation and is held in place by capillary forces against the downward force of gravity. The NAPL will continue to migrate vertically through the unsaturated zone until one of the following three conditions is achieved:

- The mass of NAPL necessary to maintain flow is depleted due to the residual saturation left behind.
- The permeability declines to a level at which the downward gravitational force can not overcome the capillary force. This can occur either abruptly, at a stratigraphic discontinuity, or gradually.
- The top of the saturated zone is reached. At this point, the NAPL will float on the water if the density of the NAPL is less than water or sink through the water column if the density is greater than water.

Floating NAPL may accumulate in a mound on the groundwater surface and then travel radially in all directions outward from the mound center. The centroid of mass, however, will move down gradient with respect to the groundwater.

In general, the lower molecular weight hydrocarbons within the NAPL will evaporate and diffuse upward, while the higher molecular weight compounds will remain within the NAPL pool. In addition, chemicals with low oil/water partition coefficients will tend to diffuse outward and dissolve into the aqueous phase. These processes will eventually cause depletion of the NAPL in low molecular weight chemicals, although at a slow rate. Some chemicals and chemical fractions (e.g., resins and asphaltenes) in petroleum NAPL have such low environmental mobilities that they will remain as NAPL essentially indefinitely, or solidify as the lighter fractions are removed.

Compounds in petroleum products that boil at temperatures below about 250°C, or have vapor pressures greater than about 0.1 mm Hg, will tend to evaporate from the surface of an oil deposit or from oil-contaminated unsaturated soils. Included in this category are alkanes up through n-dodecane (vapor pressure, 0.12 mm Hg) and aromatics up through naphthalene (vapor pressure, 0.09 mm Hg as a solid and 0.24 mm Hg as a liquid). The rates of evaporation of different hydrocarbons are directly proportional to their vapor pressures.

Estimates were made of the equilibrium distribution among air, soil water, and soil particles for the dissolved (aqueous) phase of the 12 hydrocarbons evaluated in detail, for soils containing 0.1 and 5 percent total organic carbon and for both saturated and unsaturated soils. In unsaturated soils, the twelve hydrocarbons will be distributed primarily in the air and soil phases. As the concentration of total organic carbon in the soil increases, the fraction of each hydrocarbon sorbed to soil particles increases. The high molecular weight PAHs sorb nearly completely to soil particles under all conditions.

A majority of the compounds of interest also sorb to soil particles if the soil is saturated. As in unsaturated soils, the fraction of sorbed hydrocarbons increases as the concentration of total organic carbon in the soil increases. These results indicate that, once in the groundwater environment, the compounds of interest will remain primarily sorbed to soil particles. In the saturated zone, evaporation is negligible.

All of the selected hydrocarbons, however, particularly the more soluble low molecular weight ones, will migrate slowly through the soil, transported by groundwater. The rate of migration of hydrocarbons through soils in the aqueous phase is inversely proportional to the soil/water partition coefficient for the chemical and directly proportional to the permeability of the soil. The compounds of interest can be divided into two groups based on mobility in the aqueous phase. The more mobile compounds include 1,2,4-trimethylbenzene, naphthalene, 2-methylnaphthalene, cyclohexane, n-hexane, 2,3-dimethylbutane, and 2,2-dimethylpentane. The relatively less mobile compounds include benz(a)anthracene, benzo(a)pyrene, 5-methylchrysene, 1-methylphenanthrene, and dibenzothiophene. The single best criterion to use for assignment to a class is the value for $\log K_{ow}$. Compounds with $\log K_{ow}$ less than about 5.0 are in the first class. Compounds with $\log K_{ow}$ greater than about 5.0 are in the second class.

Biological Effects

Saturated and aromatic hydrocarbons have acute toxicities to aquatic organisms, expressed as the median effective dose (EC50), that span a range of 8,000 mmol/m³ or more. As a general rule, there is an inverse correlation between the aqueous solubility of a hydrocarbon and its acute toxicity to aquatic organisms. For most hydrocarbons, the toxic concentration in the water appears to lie between about 20 and 70 percent of the single-phase (aqueous) saturation concentration, irrespective of the solubility of the hydrocarbon. For higher molecular weight hydrocarbons, the toxic concentration is at or in excess of the saturation concentration. Concentrations of hydrocarbons in groundwater in equilibrium with surface or subsurface oil deposits will always be below the pure-phase (aqueous) saturation, and, further, concentrations of dissolved hydrocarbons will decrease away from the source, as the dissolved hydrocarbons are diluted in the groundwater. Only low molecular weight hydrocarbons might reach concentrations in groundwater that are potentially toxic to aquatic organisms.

Aquatic animals can accumulate petroleum hydrocarbons, particularly the higher molecular weight PAH, from very low concentrations in water to high concentrations in tissues. However, most aquatic organisms have an active mixed function oxygenase enzyme system capable of rapidly metabolizing and excreting accumulated PAH. Fish do not absorb PAH efficiently from their food and rapidly excrete accumulated hydrocarbons. Therefore, significant food chain biomagnification of PAH does not occur.

The major concern with respect to contamination of soils with petroleum products is that toxic hydrocarbons in the released materials may migrate into groundwater and pose a health hazard to humans via consumption of contaminated drinking water, agricultural products, and fishery

products. Three of the chemicals evaluated in detail are known animal carcinogens: benz(a)anthracene, 5-methylchrysene, and benzo(a)pyrene. These and other carcinogenic PAH are present at trace concentrations in crude and refined oils. Residual oil products and used crankcase oils may contain higher concentrations. The carcinogenic PAH have log K_{ow} values greater than 5.0 and so have a low mobility in soils and groundwater.

None of the other hydrocarbons evaluated in this report are carcinogenic, but some show some systemic and reproductive toxicity. There is little published information on the toxicity of individual hydrocarbons to higher animals, particularly humans. Some of these compounds have objectionable odors or tastes at concentrations below their toxic concentrations and heavily contaminated water and food would be unacceptable for human consumption.

Chemical Analysis

To accurately quantify concentrations of individual and total hydrocarbons derived from oil, and to differentiate petroleum hydrocarbons from hydrocarbons and other chemicals from different sources, methods for analysis of petroleum hydrocarbons in soils and groundwater should be highly sensitive and specific. Volatile hydrocarbons (e.g., 2,3-dimethylbutane, 2,2-dimethylpentane, n-hexane, cyclohexane, and 1,2,4-trimethylbenzene) should be analyzed by purge and trap extraction with separation and quantification by gas chromatography/mass spectrometry. Semivolatile aromatic hydrocarbons (e.g., naphthalene, 2-methylnaphthalene, 1-methylphenanthrene, dibenzothiophene, 5-methylchrysene, benz(a)anthracene, and benzo(a)pyrene) should be analyzed by solvent extraction, chromatographic cleanup, and separation and quantification by gas chromatography/mass spectrometry, preferably with the mass spectral detector in the selected ion mode to improve both sensitivity and specificity.

In order to differentiate between petroleum-derived and combustion- or biosynthesis-derived hydrocarbons in soils and groundwater, it is essential to quantify both parent aromatic hydrocarbons and the different alkyl congener groups (the latter are abundant in petroleum but not in combustion residues). Generally, parent and C_1 - through C_4 -alkyl homologues of naphthalene, fluoranthene, phenanthrene, dibenzothiophene, and chrysene should be used to fingerprint petroleum products in soils and groundwater and differentiate them from hydrocarbon assemblages from other sources.

Recommendations

Several recommendations for additional work were made based on the results of this evaluation. Accurate values are needed for physical/chemical properties of hydrocarbons affecting their behavior in soils and groundwater. Studies are needed of the rate of leaching of different hydrocarbons from NAPL into soil water. Similar studies should also measure the rate of penetration of bulk petroleum products of different types through soils with different permeabilities, moisture concentrations, and organic matter concentrations. Results of laboratory studies should be validated in field studies at oil-contaminated sites. Finally, additional information on the mammalian toxicity of parent hydrocarbons and their various alkyl derivatives would be useful.

Section 1

INTRODUCTION

The major focus of concern in recent years about petroleum product contamination of groundwater has been releases of gasoline from underground storage tanks. Regulatory monitoring of soil and groundwater contamination has focused on benzene, toluene, ethylbenzene, and xylenes (BTEX), because they are major components of gasolines and other light distillate fuels, tend to migrate readily through porous soils, are slightly soluble in water, and are toxic to plants and animals, including humans (Tucker and Hearne 1989; Thomas and Delfino 1991; Donaldson *et al.* 1992; Hartley and Englande 1992). However, crude, refined, and residual petroleum products are extremely complex mixtures. For example, gasoline contains more than 200 petroleum-derived chemicals plus several additives (Donaldson *et al.* 1992). Heavier distillate fuels, residual oils, used oils, and crude oils are much more complex and variable mixtures. Therefore, the American Petroleum Institute (API) is interested evaluating the behavior, fate, and potential effects of non-BTEX petroleum chemicals released to soil and groundwater.

The objective of this report is to evaluate the migration, fate, and toxicity of non-BTEX petroleum chemicals in soils and groundwater. This report contains a comprehensive critical review of the scientific literature on the composition, transport, fate, and possible biological effects (mammalian and aquatic toxicology) of selected non-BTEX petroleum chemicals. The organic components of petroleum products were selected for inclusion in this review based on their abundance in petroleum products, toxicity to mammals and aquatic organisms, physical/chemical properties that would favor their migration through soils and accumulation in groundwater, and the anticipated future interest of regulatory agencies in the compounds.

This reports includes:

- A description of the methods used to select candidate compounds;
- A summary of the hydrocarbon composition of various crude, refined, and residual petroleum products;
- A review of the sources and fates of the petroleum chemicals of concern in soils and groundwater;
- A discussion the current state of knowledge on the subsurface transport of petroleum hydrocarbons in soil/groundwater systems;
- The aquatic and mammalian toxicology of the selected petroleum hydrocarbons; and
- Recommended sensitive and specific analytical methods for the chemicals in soils and groundwater.

The final section of the report is a discussion of important gaps in our knowledge about the fate and behavior of non-BTEX petroleum compounds in soil/groundwater systems.

Section 2

METHODS

2.1 Chemical Classes Considered

This review was restricted to consideration of hydrocarbons and closely related sulfur-, nitrogen-, and oxygen-substituted organic compounds. These compounds, in particular the hydrocarbons, represent 50 - 98 percent of the total mass of most liquid petroleum (Neff, 1990). Additives to refined products and inorganic constituents of crude and used oils were not included in this review.

2.2 Selection of Candidate Chemicals for Detailed Evaluation

Twelve organic chemicals found frequently in petroleum products were selected for more intensive evaluation with respect to fate and possible effects in soil/groundwater systems, based on the assembled compositional, physical/chemical, and toxicological data. Selection was based on:

- abundance in refined petroleum products, and to a lesser extent in residual, used, and crude oils
- physical/chemical properties indicative of different degrees of mobility in soils and aqueous solubility
- and potential for high toxicity to mammals and aquatic organisms.

The compounds were selected to span a wide range of physical, chemical, and toxicological properties and, therefore, to be representative of the whole suite of the more abundant identified organic chemicals in petroleum. They do not include all the chemicals of environmental concern in petroleum products.

The candidate list of chemical constituents of petroleum products for detailed evaluation was submitted to API for review and approval. Following selection of the list of compounds, an in-depth assessment of the human health effects (carcinogenicity and systemic toxicity) and aquatic toxicology of the compounds was performed. An evaluation was also performed of the migratory behavior of each of the compounds in soils of different types, based on the scientific literature and published predictions from existing transport and fate models.

2.2.1 Chemical Composition of Petroleum Products

The published scientific literature, government documents, and oil industry reports were searched accessed and evaluated for information on the detailed chemical composition and

concentrations of nonpolar organic chemicals in various crude, refined, residual, and used petroleum products. Information on specific chemical constituents of petroleum products, rather than chemical classes or generic categories, was sought.

Limited detailed compositional data are available from the published literature. However, approximately 60 analyses were found. The petroleum products for which compositional data were found include; leaded and unleaded gasoline; kerosene; jet fuel; No. 2 fuel oil; Nos. 1 and 2 home heating oil; new and used engine oil (crankcase oil); rerefined engine oil; lube oil; bunker C residual oil; asphalts; and several crude oils. Concentrations of individual saturated, olefinic, and aromatic hydrocarbons; S-, N-, and O-substituted aliphatic compounds; and heterocyclic compounds in the petroleum products were summarized in tabular form (Appendix A).

2.2.2 Physical/Chemical Properties

The scientific literature was reviewed for selected physical and chemical properties of organic chemicals characteristic of crude and refined oils. Properties of greatest use in predicting the environmental fate of petroleum constituents include aqueous solubility, octanol/water partition coefficient (K_{ow}), sediment organic carbon/water partition coefficient (K_{oc}), specific gravity, physical form (gas, liquid, solid) at ambient temperatures, vapor pressure, and Henry's law constant. Physical and chemical properties of the most abundant hydrocarbons and heterocyclic compounds in the petroleum products were derived from a large number of scientific publications (e.g., Eastcott *et al.* 1988; Pearlman *et al.* 1984) and summarized in tabular form in Appendix B.

2.2.3 Mammalian and Aquatic Toxicology

Toxicology profiles were developed for the chemicals of concern. The toxicology profiles include a summary of published information about the acute, prechronic, and chronic toxicity, as well as carcinogenicity, reproductive effects, teratogenicity, and genetic toxicology to mammals. Toxicological profiles were prepared on the potential health effects of benz(a)anthracene, benzo(a)pyrene, 5-methylchrysene, 1-methylphenanthrene, dibenzothiophene, 1,2,4-trimethylbenzene, naphthalene, 2-methylnaphthalene, cyclohexane, n-hexane, 2,3-dimethylbutane, and 2,2-dimethylpentane. The databases searched in preparing these profiles include the Integrated Risk Information System (IRIS), Toxline, the Registry of Toxic Effects of Chemical Substances (RTECS), the Chemical Evaluation Search and Retrieval System (CESARS), and the Hazardous Substances Databank (HSDB). In addition, Agency for Toxic Substances Disease Registry (ATSDR) Profiles and EPA Drinking Water Quality Criteria Documents were used where available.

The compositional data summarized in Appendix A were used as a basis for a screen for the chemicals in crude and refined oils with the highest potential for mammalian toxicity (Appendix C). As a general rule, computer-based ranking systems rank chemicals that are known or suspected carcinogens or mutagens as more toxic than chemicals that possess

systemic toxicity alone. Therefore, it is not surprising that the most toxic petroleum constituents identified in the initial screening as highly toxic are the higher molecular weight aromatic compounds that are known carcinogens. The chemicals in crude and refined oils that are known or suspected to be carcinogens or mutagens include: 5-methylchrysene; benz(a)anthracene; 7,12-dimethylbenz(a)anthracene; benzo(a)pyrene; and indeno(1,2,3-cd)pyrene. Methylcholanthrene, a widely-studied carcinogenic polynuclear aromatic hydrocarbon (PAH), is not ordinarily found in petroleum and, therefore, was not considered further.

2.2.4 Transport and Fate

Transport and fate data for organic chemicals from petroleum products, particularly those identified for detailed evaluation, were summarized, based on physical/chemical properties and the published transport and fate processes that affect nonpolar organic chemicals in subsurface soils of different types. Published results of transport and fate models were used as the basis for predicting migration of the chemicals through different soils under different conditions. The effects of different physical/chemical properties of the 12 chemicals on their rates of migration through soils and tendency to accumulate in groundwater were evaluated. This evaluation was used as the basis for extrapolating the behavior of different classes of petroleum chemicals in soil/groundwater systems.

2.2.5 Analysis

Published methods for analysis of petroleum chemicals, particularly the 12 chemicals chosen for detailed evaluation, in soils and groundwater were described and evaluated. Standard EPA and ASTM methods, as well as non-conventional analytical methods were evaluated with respect to specificity for the compounds of concern, interferences, sensitivity, precision, and accuracy.

2.2.6 Information Needs

Based on the major findings of the literature review and synthesis, important gaps exist in our understanding of the soils and groundwater behavior, of human health and aquatic toxicology, and of the chemicals chosen for consideration in this study. Recommendations were made for additional research and assessment needed to improve our understanding of and ability to predict movements, fates, and effects of petroleum chemicals in soils and groundwater.

2.3 Chemicals Evaluated in Greater Detail

The two initial screens, based on mammalian toxicity and physical chemical properties favorable for migration through soils, produced two different lists of candidate petroleum compounds. The toxicological screen identified mainly high molecular weight polycyclic aromatic hydrocarbons. The physical/chemical screen identified primarily low molecular weight aromatic hydrocarbons, heterocyclic compounds, and cyclic alkanes. Therefore, it was

decided to select a few examples of each of the types of petroleum constituents for further evaluation in the literature review and synthesis.

The top-ranked chemicals identified by the different screening approaches are as follows.

Chemicals identified by mammalian toxicity/carcinogenicity screen:

- Benz(a)anthracene (including methyl- and dimethyl- congeners, particularly 7,12-dimethylbenz(a)anthracene)
- Dibenzanthracenes (different isomers as well as methyldibenzanthracenes)
- Benzo(a)fluoranthenes (all isomers as well as methylbenzo(a)fluoranthenes)
- Benzo(a)pyrene and methylbenzopyrenes
- Dibenzopyrenes
- Chrysene and methylchrysenes (particularly 5-methylchrysene)
- Cyclopenta(cd)pyrene
- Methyl- and dimethyl-phenanthrenes
- Indeno(1,2,3-cd)pyrene

Non-carcinogenic saturated compounds identified by the mammalian toxicity screen:

- | | |
|-------------------------|--------------------------|
| • 2,3-dimethylbutane | • 2,3-Dimethylpentane |
| • n-Hexane | • 2-Methylpentane |
| • 2-Methylhexane | • 2,2,4-Trimethylpentane |
| • 2,2,5-Trimethylhexane | |

Chemicals identified based on abundance in petroleum products and physical/chemical properties favoring migration in soils:

- Cyclopentane and methylcyclopentane
- Cyclohexane and methylcyclohexane

- Methyl- and dimethyl-pentanes
- n-Hexane
- 1,2,4-Trimethylbenzene
- Naphthalene, 2-methylnaphthalenes, and 2,6-dimethylnaphthalenes
- Phenanthrene and 1-methylphenanthrene

The list of candidate compounds was too long to evaluate in detail in the literature review. Therefore, a subset of characteristic chemicals representing the range of environmental behaviors and toxicities that might occur in oil-contaminated soils, was chosen. The chemicals chosen include three polycyclic aromatic hydrocarbons (PAH) (naphthalene, benz(a)anthracene, and benzo(a)pyrene), four alkyl-aromatic compounds (1,2,4-trimethylbenzene, 2-methylnaphthalene, 1-methylphenanthrene, and 5-methylchrysene), one heterocyclic compound (dibenzothiophene), and four low molecular weight alkanes (cyclohexane, n-hexane, 2,3-dimethylbutane, and 2,2-dimethylpentane). Three of the compounds are known carcinogens: benz(a)anthracene, 5-methylchrysene, and benzo(a)pyrene.

Section 3

CHEMICAL COMPOSITION AND PROPERTIES OF PETROLEUM PRODUCTS**3.1 General Properties**

The chemical compositions of crude and refined oils vary substantially, as expected. The most abundant and readily quantifiable non-BTEX hydrocarbons in all crude and refined products are the low molecular weight saturated and aromatic hydrocarbons (Neff 1990). As a general rule, concentrations of individual hydrocarbons, and related oxygen-, sulfur-, and nitrogen-substituted hydrocarbons within an homologous series, decrease as molecular weight increases. The major exception to this generalization is that C_1 - through C_3 -alkyl aromatics often are more abundant than the unalkylated parent compounds.

The most abundant non-BTEX aromatic hydrocarbons in most refined and crude oils include: trimethylbenzenes; tetralins/indans; tetramethylbenzenes; naphthalene; methylnaphthalenes; dimethylnaphthalenes; methylphenanthrenes; and dimethylphenanthrenes. Some used engine oils also contain relatively high concentrations of methylfluorenes/pyrenes, benz(a)anthracene, and methylbenzopyrenes.

The most abundant saturated hydrocarbons are the normal alkanes (paraffins) from hexane through decane; higher molecular weight n-alkanes also are abundant, but abundance tends to decrease with increasing molecular weight. Light refined products and light crude oils also contain high concentrations of cyclohexane, methylcyclohexane, isopentane, methylpentane, trimethylpentanes, dimethylbutane, and methylcyclopentane. Gasoline may contain percent concentrations of pentenes and methylpentenes (olefins).

The aqueous solubility decreases and K_{ow} increases as molecular weight increases for all classes of hydrocarbons. As a general rule, chemicals with an aqueous solubility less than about 0.1 mg/L and a Log K_{ow} greater than about 5.0 will have limited mobility in soils and are unlikely to appear in groundwater at greater than ultratrace (low parts per billion) concentrations. By this definition, the most mobile hydrocarbons include monoaromatic hydrocarbons with molecular weights less than that of n-hexylbenzene, polycyclic aromatic hydrocarbons with molecular weights less than that of methylfluorene and pyrene, saturated hydrocarbons with molecular weights less than that of n-nonane or n-hexane, alkenes with molecular weights less than that of 1-nonene, and heterocyclic compounds with molecular weights less than that of methylbibenzothiophenes. If bulk transport of a petroleum product occurs through subsurface soils, then higher molecular weight hydrocarbons may migrate to groundwater.

PAH carcinogens have log K_{ow} s greater than 5.0 (e.g., benz(a)anthracene, 5.91; 5-methylchrysene, 6.42; benzo(a)pyrene, 5.98; 7,12-dimethylbenz(a)anthracene, 6.93; and indeno(1,2,3-cd)pyrene, 7.0). Most have aqueous solubilities near or even below 1 $\mu\text{g/L}$ (parts per billion). Therefore, they are not likely to be very mobile in soils. Most of these

carcinogenic PAH are present at low concentrations (a fraction to a few parts per million) in crude and refined oils. They may be somewhat more abundant in used engine oil, residual oil and some asphalts (to a few tens of parts per million).

Toxicity of petroleum hydrocarbons to aquatic organisms usually increases with increasing molecular weight. The aromatic hydrocarbons are much more toxic than the saturated hydrocarbons of similar molecular weight. The limited data available seem to indicate that cyclic alkanes are more toxic to aquatic organisms than n-alkanes and branched alkanes. Heterocyclic compounds are approximately as toxic as the corresponding unsubstituted PAH compound (e.g., dibenzothiophene, carbazole, and dibenzofuran are about as toxic as fluorene to aquatic organisms). However, toxicity to aquatic organisms depends on bioavailability. Therefore, although toxicity increases with molecular weight, the point is reached when the aqueous solubility of the hydrocarbon, which decreases with increasing molecular weight, decreases to below the toxic concentration. Hydrocarbons for which the toxic concentration is greater than the aqueous solubility do not demonstrate acute toxicity to aquatic organisms. For PAH, the cutoff point is at about methylphenanthrenes, pyrene, and fluoranthene (aqueous solubility 0.1 to 0.2 mg/L). Thus, the light aromatic and heterocyclic hydrocarbons are the crude and refined oil components most acutely toxic to aquatic organisms.

3.2 Crude Petroleum

3.2.1 Complexity of Crude Oil

Crude petroleum is a mixture of organic chemicals of fossil, biogenic origin (Spears and Whitehead 1969). It contains thousands of organic and a smaller number of inorganic compounds (Neff 1990). No two crude oils are alike. They vary tremendously in chemical composition and relative concentrations of different chemicals, and in physical properties.

A particular crude oil may contain organic compounds ranging in molecular weight from methane (molecular weight 16), a gas at room temperature and pressure, to complex polymeric structures, such as asphaltenes with molecular weights up to at least 100,000 (Kallio 1976). Hydrocarbons are the most abundant components of crude oil, accounting, in most cases, for 50 to 98 weight percent of liquid crude petroleum (National Academy of Sciences 1985). The other organic components of petroleum include a wide variety of organic compounds containing sulfur, oxygen, or nitrogen. Figure 3-1 shows the molecular structures of the major classes of organic chemicals in petroleum.

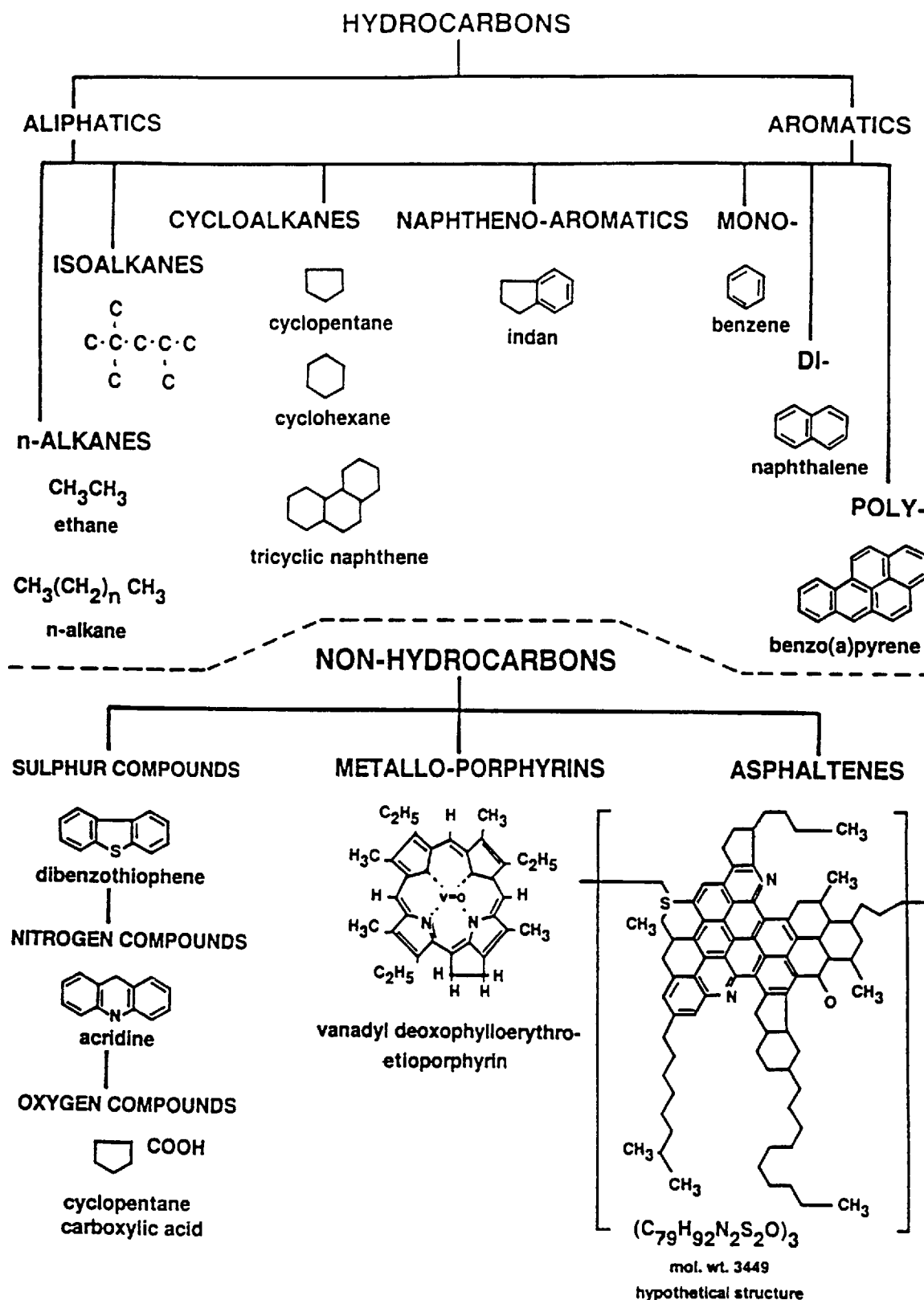


Figure 3-1. Structure of the most abundant classes of organic chemicals in crude and refined petroleum (from Neff, 1990)

3.2.2 Alkanes

Alkanes or paraffins are usually the most abundant hydrocarbons in crude oils. Crude oil may contain from a few percent to nearly 100 percent, but more typically about 30 to 70 percent alkanes (Spears and Whitehead 1969). There are three types of alkanes in petroleum, normal, branched, and cyclic. The normal and branched alkanes usually are present in about equal amounts; the cyclic alkanes often are the most abundant alkanes in crude oils.

Normal alkanes (n-alkanes) are linear chains of carbons linked by single covalent bonds. Two to four hydrogen atoms are covalently bonded to each carbon atom. Normal alkanes range in size from methane (C_1) to about C_{60} , and possibly as high as C_{78} . Branched alkanes, or iso-alkanes, contain one or more carbon chain branches; most are simple 2-, 3-, or 4-methylalkanes. The branched alkanes in crude oil may contain a series of hydrocarbons, based on isoprenoid (2-methyl-1,3-butadienylene) building blocks, extending from C_{10} to about C_{40} (Spears and Whitehead 1969, Thompson and Kennicutt 1992). The most abundant isoprenoid alkanes in petroleum are pristane (C_{19}) and phytane (C_{20}).

Cycloalkanes, also called cycloparaffins or naphthenes, may account for as much as 50 percent of the total hydrocarbons in crude oil. Most cycloalkanes are cyclopentane (C_5) and cyclohexane (C_6) derivatives (Zadro *et al.* 1985). Compounds containing seven- or eight-membered rings may also be present in small amounts. These saturated ring structures may be single, linked together by a single carbon-carbon covalent bond, or fused (sharing two carbons). They may contain aromatic ring structures, normal or branched alkane substituents, or non-hydrocarbon groups, such as one or more carboxylic acid groups. Cycloalkanes containing one or more carboxylic acid groups are called naphthenic acids. Steranes and triterpanes are complex cycloalkanes that are sometimes used as specific markers of the source and maturity of crude petroleum (Seifert and Moldowan 1978, Hughes and Holba 1988). The cycloalkanes are an extremely complex and heterogeneous group of hydrocarbons that pose serious analytical difficulties. As a result, they are the least well characterized of the major, mobile hydrocarbon classes in petroleum.

3.2.3 Aromatic Hydrocarbons

The other major class of hydrocarbons in petroleum is the aromatic hydrocarbons. Aromatic hydrocarbons are composed of one or more benzene rings. Aromatic hydrocarbons may account for up to about 20 percent of the total hydrocarbons in crude oil. Benzene may be present at a concentration of several percent in light crude oils. Benzene may contain one or more methyl or higher alkane substituents. Although benzenes with one or two methyl or ethyl groups (toluene, xylenes, ethylbenzene) are by far the most abundant alkyl benzenes in crude oils, mono- and di-alkyl benzenes with paraffin chains of 12 to 40 carbons have been identified in crude oils (Damsté *et al.* 1991).

Benzene may be linked to other benzene rings by single covalent bonds to form compounds such as biphenyl or terphenyl. More frequently, two or more benzenes are fused to form

polycyclic aromatic hydrocarbons (also called polynuclear aromatic hydrocarbons: PAH) (Neff 1979). Naphthalene ($C_{10}H_8$), consisting of two fused benzene rings is the lowest molecular weight PAH. Compounds such as fluorene, though not strictly aromatic, will be classified as PAH in this study as a matter of convenience. PAH with nine or more aromatic rings have been identified in the resin-asphaltene fractions of petroleum. Coronene (MW 300.4), composed of six fused aromatic rings in a highly condensed configuration, is the highest molecular weight PAH with sufficient environmental mobility (solubility $0.1 \mu\text{g/L}$) to be considered potentially toxic (Neff 1979).

The relative abundance of different aromatic hydrocarbons in crude petroleum usually decreases markedly with increasing molecular weight. In most cases, the one-ring (benzene) through three-ring (phenanthrene) aromatics in crude oil account for at least 90 percent of the aromatic hydrocarbons that can be resolved by conventional analytical techniques (Neff 1979). As a general rule, condensed PAH structures are much more abundant than linear structures of the same molecular weight (e.g., phenanthrene is much more abundant than anthracene).

PAH containing one or more methyl, ethyl, butyl, or occasionally higher alkane substituents on one or more aromatic carbons usually are more abundant in crude oils than the parent unalkylated PAH (Youngblood and Bloomer 1975). Homologues with two to four alkyl carbons usually are more abundant than the less or more highly alkylated homologues. The relative abundances in crude oils of different positional isomers of alkyl PAH (e.g., different trimethylnaphthalenes) are highly variable, depending on the source and maturity of the crude oil (Alexander *et al.* 1985; Strachan *et al.* 1988; Radke *et al.* 1990).

Aromatic hydrocarbons may contain saturated ring structures forming a wide variety of naphthenoaromatic compounds (Spears and Whitehead 1969). These may be combined further to produce complex polymeric structures that are important components of the resin/asphaltene fractions of petroleum. Although these complex, high molecular weight compounds are biologically inert, they do have a substantial influence on the environmental behavior and persistence of crude and residual oils.

3.2.4 Organic Compounds Containing Sulfur, Nitrogen, or Oxygen

Sulfur, nitrogen, and oxygen may be covalently bonded to alkane and aromatic compounds to form a wide variety of hetero-compounds. Organo-sulfur compounds usually are the most abundant. The concentration of sulfur in crude oil usually ranges from 0 to about 10 percent; nearly all the sulfur is organic (Spears and Whitehead 1969). Only the lower molecular weight organo-sulfur compounds in petroleum, boiling below about 350°C have been well characterized (Grimmer *et al.* 1983, Berthou and Vignier 1986, Damsté and de Leeuw 1987; Speight 1991). Types of organo-sulfur compounds that have been identified in crude oil include thiols, thiacycloalkanes, thiolanes, and thiophenes. Benzothiophenes, dibenzothiophenes, and naphthobenzothiophenes are the most toxic and persistent sulfur heterocyclic compounds in petroleum (Fedorak and Westlake 1984, Berthou and Vignier 1986). Because they have physical/chemical properties similar to the corresponding unsubstituted aliphatic and aromatic

hydrocarbons, sulfur compounds often are present with their unsubstituted counterparts in refined petroleum products, unless the refining process includes a desulfurization step.

The concentration of oxygen in crude oil rarely exceeds 2 percent and usually is in the range of 0.06 to 0.4 percent (Speers and Whitehead 1969). Nearly all the oxygen is present as organo-oxygen compounds boiling above about 400°C. The lower molecular weight organo-oxygen compounds that have been identified in crude oils include fatty acids, cycloalkane carboxylic acids (naphthenic acids), and oxygen-containing heterocyclic compounds, such as furan and dibenzofuran. Small amounts of ketones, phenols, ethers, lactones, esters, and anhydrides also may be present. The most abundant organo-oxygen compounds in crude oil usually are the naphthenic acids (Speers and Whitehead 1969). The most abundant naphthenic acids identified to date are the C₆ to C₁₉ acids. Because many organo-oxygen compounds, particularly the carboxylic acids and phenols, are polar and slightly soluble in water, they tend to be enriched in oil field produced waters (MacGowan and Surdam 1988, Barth 1991, Neff *et al.* 1992).

Crude petroleum may also contain from 0.01 to about 0.9 percent nitrogen. As with oxygen, most of the nitrogen in crude oil is in organic fractions boiling at temperatures greater than about 400°C (Speers and Whitehead 1969). Nitrogen is found in nitrogen-substituted hydrocarbons (e.g., pyridines, pyrroles, carbazoles, quinolines), and hydrocarbons also containing oxygen (quinolones), sulfur (thioquinolines), or oxygen and a metal (petroporphyrins) (Dorbon *et al.* 1984, Schmitter *et al.* 1984, Yamamoto *et al.* 1991). The petroporphyrins probably are derived from fossil plant chlorophylls and usually are present as vanadyl or nickel complexes.

3.2.5 Resins and Asphaltenes

The resin and asphaltene fractions of crude oil have not been characterized well (Speers and Whitehead 1969, Kallio 1976). These high-boiling fractions of oil are thought to consist of high molecular weight hydrocarbons and hetero compounds formed by thermally-induced condensation of lower molecular weight aromatic and heterocyclic compounds. Asphaltenes are thought to be present in colloidal suspension in petroleum and can be isolated from crude oil by precipitation with a low molecular weight alkane solvent, such as pentane. Asphaltenes have molecular weights of about 10,000 and possibly up to 100,000, and are thought to consist of stacked sheets of condensed aromatic ring structures similar to those in coal.

3.2.6 The Saturated Hydrocarbon Assemblage

Total alkanes represented 34 and 56 percent of two crude oils analyzed by Pancirov (1974) (Table 3-1). Cycloparaffins were the most abundant alkanes in both oils, followed by isoparaffins and n-paraffins. The relative abundance of cycloparaffins decreased with increasing ring number. Although this composition seems typical for crude oils, by far the best characterized alkane fraction of crude oils is the n-paraffins.

The dominant *n*- and iso-paraffins in crude oils usually are the low molecular weight six-through nine-carbon paraffins (Appendix Table A-1). In this molecular weight range, the *n*-paraffin usually is more abundant than any individual branched alkane isomer, though the sum of concentrations of all branched isomers for a given congener group may be greater than that of the *n*-alkane. Congeners are the different positional isomers of a compound. Among the longer chain *n*-paraffins, concentration in crude oils usually decreases with increasing chain length. For example, in Bent Horn and Cohasset (Canadian) crude oils, the most abundant *n*-alkane is octane, and concentrations decrease progressively with increasing chain length (Bobra and Callaghan 1990). The most abundant *n*-alkane in four Australian crude oils is heptane, octane, or nonane (Zadro *et al.* 1985). However, the most abundant *n*-alkane in a Prudhoe Bay crude oil is the C₁₁ *n*-paraffin (Riley *et al.* 1981).

3.2.7 The Aromatic/Heterocyclic Assemblage

One or more alkyl benzenes usually is more abundant than benzene in crude oils (Appendix Table A-2). This may be due in part to the great volatility of benzene (vapor pressure 76 mm Hg at 20°C), or to the fact that unalkylated parent aromatic hydrocarbons nearly always are less abundant than alkyl homologues in crude oil. Toluene or one of the isomers of xylene often is most abundant. The methylethyl- and trimethyl-benzenes also are abundant. Among the C₃-benzenes, 1,2,4-trimethyl-benzene often is the most abundant. Naphthalene and its alkyl homologues usually are less abundant than benzene and its alkyl homologues in most crude oils, except some heavy, naturally-weathered crudes.

Among the PAH and related sulfur heterocyclic compounds, abundance in crude oils usually decreases with increasing molecular weight (Appendix Tables A-3 and A-4).

Table 3-1. The saturated (alkane) hydrocarbon distribution of two crude and two refined oils. Concentrations are in weight percent. From Pancirov (1974).

Alkane Type	Kuwait	S. Louisiana	No. 2 Fuel	Bunker C
<i>n</i> -Paraffins	4.7	5.2	8.1	1.7
Iso-Paraffins	13.2	14.0	22.3	5.0
1-Ring Cycloparaffins	6.2	12.4	17.5	3.9
2-Ring Cycloparaffins	4.5	9.4	9.4	3.4
3-Ring Cycloparaffins	3.2	6.8	4.5	2.9
4-Ring Cycloparaffins	1.8	4.8	ND	2.7
5-Ring Cycloparaffins	0.4	2.3	ND	1.9
6-Ring Cycloparaffins	ND	1.1	ND	0.4
Total Cycloparaffins	16.1	36.6	31.4	15.2
Total Alkanes	34.0	56.0	61.8	21.9

ND, not detected

However, within each homologous series, the alkyl homologues usually are more abundant than the parent PAH. PAH with three to five alkyl carbons often are the most abundant. However, the number of possible positional isomers increases as the molecular weight of the parent PAH and the number of alkyl carbons increase, so it is difficult to quantify the sum of the more highly alkylated PAH. Thus, reported concentrations of C₃-, C₄-, and C₅-alkyl PAH usually are underestimates.

The two- and three-ring aromatic hydrocarbons (such as naphthalene, phenanthrene, and fluorene) and their alkyl homologues are nearly always much more abundant than higher molecular weight PAH in crude oils (Appendix Tables A-3 and A-4). The four- through six-ring PAH (pyrene/fluoranthene through coronene) usually are present at low or trace concentrations in crude oils (Appendix Table A-5). These high molecular weight PAH are much more characteristic of pyrogenic sources (soot, coal tars, engine exhaust) than petrogenic sources (Neff 1979; Edwards 1983). However, as with the two- and three-ring aromatics, the alkyl homologues of the higher molecular weight PAH in crude oil usually are more abundant than the parent compounds.

Among the well-known carcinogenic PAH (e.g., benzo(a)pyrene, benz(a)anthracene, 7,12-dimethylbenz(a)anthracene, indeno(1,2,3-cd)pyrene) only the methylchrysenes are likely to be present at greater than trace concentrations in crude oil (Appendix Table A-5). In eight crude oils analyzed by Grimmer *et al.* (1983), concentrations of benz(a)anthracene ranged from 1.0 to 6.7 mg/kg and concentrations of benzo(a)pyrene ranged from 0.1 to 3.6 mg/kg. The crude oils listed in Appendix Tables A-3 and A-4 contained non-detectable to 2.8 mg/kg benzo(a)pyrene.

There is a direct correlation in most crude oils between the concentration of total sulfur and the concentration of sulfur heterocyclic compounds (Grimmer *et al.* 1983). A large number of sulfur heterocyclics (Appendix Table A-5) and saturated organo-sulfur compounds (Appendix Table A-6) has been identified in high-sulfur crude oils. Dibenzothiophene and its alkyl homologues usually are the most abundant sulfur heterocyclics. As with the PAH, the alkyl homologues of dibenzothiophene are more abundant than the parent compound (Appendix Tables A-3 and A-4). Other relatively abundant sulfur heterocyclics that have been identified include benzonaphthothiophene and its C₁- and C₂-alkyl homologues. The most abundant sulfur-substituted alkanes in Wason crude oil are methanethiol, ethanethiol, and the thiacycloalkanes (Appendix Table A-6).

Carbazoles may also be abundant in some crude oils (Appendix Table A-5). The C₄-, C₅-, and C₆-carbazoles were the most abundant carbazoles in the Qatar crude oil analyzed by Grimmer *et al.* (1983). Other nitrogen heterocyclics were not detected or were not sought. In six crude oils analyzed by Dorbon *et al.* (1984), carbazole and 4-methylcarbazole were most abundant, and more highly alkylated carbazoles were rare. Benzocarbazoles and dibenzocarbazoles were as abundant as or more abundant than the carbazoles. Azafluorenes and azaphenanthrenes were abundant in two far eastern crude oils (Yamamoto *et al.* 1991).

Only traces of oxygen heterocyclic compounds were detected in Qatar crude oil (Appendix Table A-5). These included benzo(b)naphtho(2,1-d)furan and unidentified furan and methylfuran derivatives with masses of 242, 256, 262, 282, and 304.

3.3 Gasoline

3.3.1 Refining

Crude oils are refined to produce a wide variety of useful products, including gasoline, middle distillate fuels, and residual fuels. Refined and residual petroleum products contain all the chemical classes, except resins and asphaltenes, present in crude petroleum, as well as some compounds produced during refining or added to the finished product to improve its properties (Nyer and Skladany 1989; King 1992). Each refined or residual product contains primarily crude oil chemicals boiling over a narrow boiling point range (Figure 3-2). Gasoline has a boiling point range of about 40 to 205°C; middle distillate fuels have a boiling point range between about 175 and 375°C; residual fuel oils are blended from crude oil fractions boiling between about 350 and 700°C (CRCS, Inc. 1985a,b,c, Nyer and Sladany 1989). However, low concentrations of petroleum chemicals from outside the distillation range of the product may be present in different products. For example, gasolines sometimes contain traces of high molecular weight PAH, such as benzo(a)pyrene, and residual fuels may contain small amounts of alkylbenzenes (Pancirov 1974; Guerin 1977).

Gasoline is a blend of several refinery streams, composed primarily of volatile hydrocarbons (CRCS, Inc. 1985a). The refinery streams are processed in a variety of ways to increase yields from the crude oil stock and to improve anti-knock performance of the finished gasoline. These processes include: polymerization to produce olefinic dimers, trimers, and tetramers; alkylation to produce C₇ to C₉ branched paraffins to increase octane number; catalytic reforming to produce aromatic hydrocarbons by dehydrogenation of cycloparaffins; isomerization to convert n-pentane and n-hexane to branched isomers; and catalytic cracking and hydrocracking to break higher molecular weight hydrocarbons into gasoline boiling range hydrocarbons (King 1992). Olefins (alkenes) contain one or more carbon/carbon double bonds. Polymerization and catalytic cracking produce a variety of monoolefins, diolefins, cyclic monoolefins, and aromatic-olefin structures, such as styrenes, indenenes, and dihydronaphthalenes, not present in crude oils. Olefins are not desirable in finished gasoline; the olefinic feedstock usually is returned to the alkylation and polymerization units to produce more desirable alkyl-aromatic compounds. A variety of additives is added to gasoline to improve combustion performance, reduce emissions of potentially harmful combustion products, and protect internal engine parts.

3.3.2 Composition

Because of the variability in the relative concentrations of hydrocarbons in different crude oil feed stocks and the variety of refining processes used in each of several refinery streams that are blended to produce a finished gasoline, the relative concentrations of different

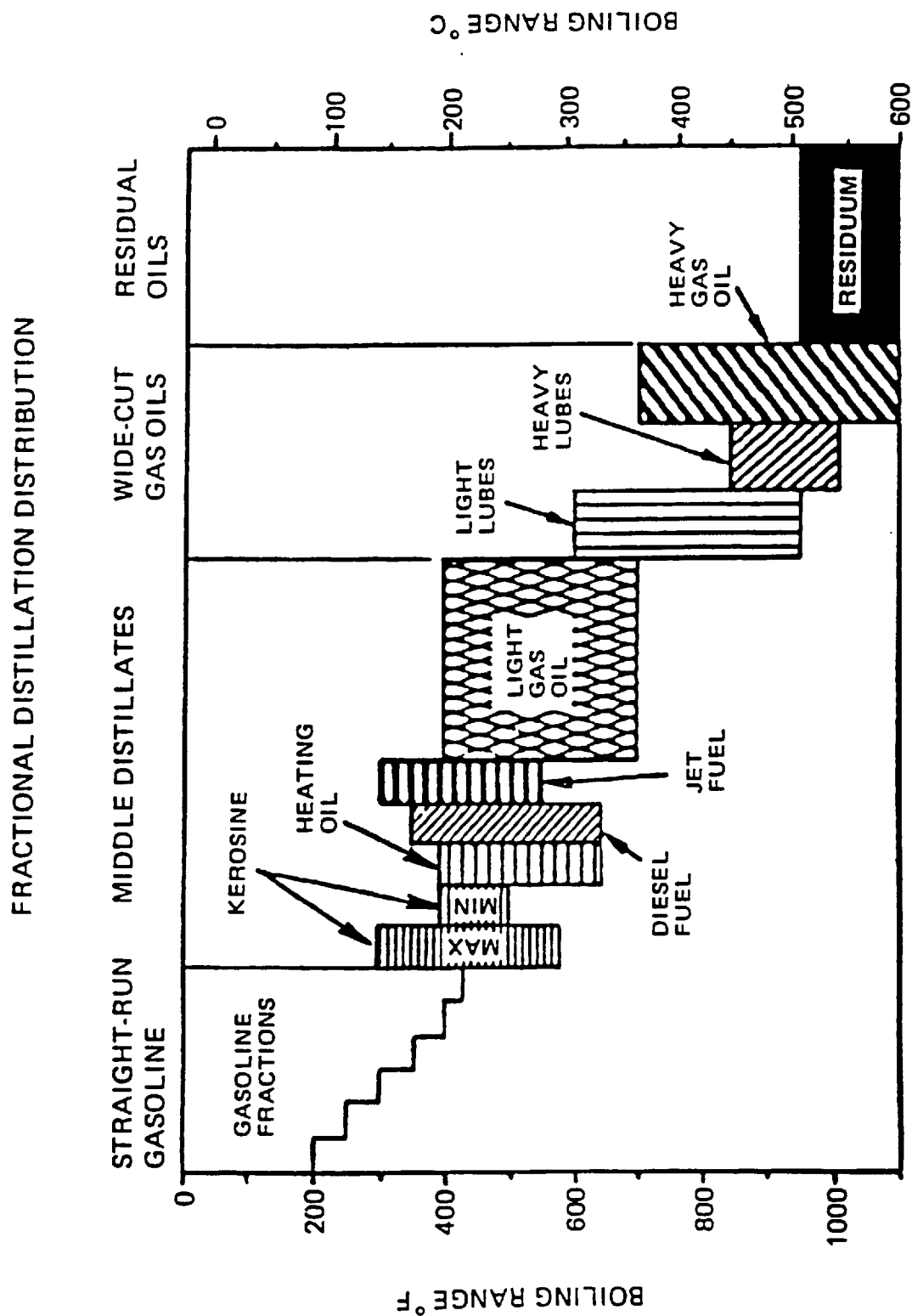


Figure 3-2. Boiling point range of fractions of crude petroleum (from National Academy of Sciences, 1985)

hydrocarbons in gasolines from different sources and during different seasons vary widely (Cline *et al.* 1991). The actual identity of the major ingredients, which may number about 200, does not vary much. Concentrations of individual aromatic hydrocarbons varied by as much as five-fold in 31 samples of summer and winter gasoline from north and central Florida (Appendix Table A-7: Cline *et al.* 1991). Between-sample variability was greatest for the lightest aromatics, benzene and toluene, and decreased with increasing molecular weight. Similar variability was noted for individual aromatics and n-alkanes in samples of gasoline from California (Donaldson *et al.* 1992).

The most abundant hydrocarbon class in gasoline is the isoalkanes (about 46 percent by volume), followed by the aromatic hydrocarbons (about 28 percent by volume) (CRCS, Inc. 1985a). Alkanes (about 11 percent), alkenes (about 9 percent), and cycloalkanes (about 5 percent) are less abundant.

As a general rule, the concentrations of individual gasoline constituents within a hydrocarbon class decrease with increasing molecular weight (Appendix Tables A-8 and A-9). High molecular weight alkanes, alkenes, and aromatics are present at trace or nondetectable concentrations (Appendix Table A-8). However, within a hydrocarbon class, one or a few compounds are present at much higher concentrations than other chemicals in that class. For example, isopentane, methylpentanes, and trimethylpentanes often are the most abundant components of the isoalkane fraction. 2,2,4-Trimethylpentane (isooctane) is an important octane-booster in gasolines.

Toluene, followed closely by *p*- and *m*-xylenes are the most abundant aromatic hydrocarbons in gasoline (Appendix Tables A-8 and A-9). Naphthalene usually is present at concentrations below about one percent. Higher molecular weight PAH are present at parts-per-million concentrations. n-Alkanes, particularly those above hexane, usually are present in gasoline at low concentrations.

The relative concentrations of cycloalkanes in gasoline are highly variable. The gasoline samples described in Appendix Tables A-8 and A-9 contain 0.07 to 9.39 weight percent cyclohexane. This may be due to the wide variability in the concentrations of total cycloalkanes in the gasoline fractions of different crude oils, ranging from 20 to 67 volume percent in the gasoline fraction of nine crude oils reviewed by Nyer and Skladany (1989). The olefinic fraction of gasoline also is quite variable. Some gasolines contain high concentrations of pentenes, methylpentenes, and higher molecular weight C₇-C₁₂-alkenes (Appendix Table A-8); others have low concentrations of these olefins, but are enriched in methylbutenes and C₆-alkenes (Appendix Table A-9). This variability is caused by variability in the refinery feed stocks and catalytic cracking processes used at different refineries to produce gasoline-range hydrocarbon mixtures. Ethyl- and dimethyl-styrenes have been detected in some gasolines at concentrations up to about 1.5 percent (Bobra and Callaghan 1990).

3.4 Middle Distillate Fuels

3.4.1 Refining

Middle distillate fuels are refined products of crude oil falling in the boiling point range of approximately 350°F to 700°F (177°C to 370°C) (CRCS, Inc. 1985b). They are blended from several refinery streams to produce a variety of fuels with different properties. Middle distillate fuels can be grouped into five general categories: aviation turbine fuels (jet fuels), kerosene, gas turbine fuel oils, diesel fuel oils, and home heating oils. Heavier fuel and heating oils, such as No. 4 fuel oil, often are blended from middle distillate fuels and residual oil. They have a composition intermediate between those of middle distillate and residual oils.

The middle distillate fuels have a more complex chemical composition than gasoline. They contain a wide variety of normal, branched, and cyclic alkanes, aromatic hydrocarbons, and heterocyclic compounds with between 9 and about 25 carbons. Most middle distillate fuels contain roughly 30 to 55 weight percent normal and iso-alkanes, 20 to 50 percent cycloparaffins, and 3 to 40 percent aromatic hydrocarbons. Small amounts (a few percent) of olefins may be present in some jet fuels and kerosenes. Middle distillate fuels also often contain a wide variety of additives, designed to improve specific properties of the products as fuels under different environmental conditions.

3.4.2 Jet Fuels

Jet fuels contain higher concentrations of alkanes and lower concentrations of aromatic hydrocarbons than gasolines do, because of the need to maximize energy content per unit mass of fuel. The abundance of individual n-alkanes in jet fuels increases to about octane (C_8), undecane (C_{11}), or dodecane (C_{12}), depending on the grade of fuel (Appendix Table A-10). Concentrations decrease with shorter or longer chain lengths. The distribution of isoalkanes in jet fuels is more complex. Prominent branched alkanes in JP-4 include methylhexanes, methylheptanes, and methyloctanes. JP-5 and JP-8 fuels contain alkyl homologues of longer chain alkanes. Prominent cycloparaffins in jet fuels include cyclohexane, trimethylcyclohexanes, n-butylcyclohexane, and heptylcyclohexane.

Toluene, xylenes, 1,2,4-trimethylbenzene, and diethylbenzenes are prominent monocyclic aromatic hydrocarbons in jet fuels. Naphthalene and its monomethyl and dimethyl homologues are quite abundant, particularly in the medium and heavier jet fuels.

3.4.3 Kerosene

Kerosene was the first commercially produced refined petroleum product (used primarily for illumination) and remained so until the adoption of electric illumination and the internal combustion engine, fueled with gasoline, early in this century. Kerosenes closely resemble jet fuels. Dominant hydrocarbons are paraffins and naphthenes (cycloparaffins) (Appendix Table A-11). Aromatic hydrocarbons may be present at concentrations up to about 30 percent. Dodecane (C_{12}) or tridecane (C_{13}) often is the most abundant n-paraffin. Among the aromatic

hydrocarbons, naphthalene and its monomethyl and dimethyl homologues are quite abundant. Alkylbenzenes undoubtedly also are abundant but were not analyzed by Goodman and Harbison (1997: Appendix Table A-11). Small amounts of acenaphthene, acenaphthalene, and phenanthrene are present, but most medium and high molecular weight PAH are present at concentrations below a few parts per million.

3.4.4 Heating Oils

Home heating oils contain 70 to 80 percent alkanes, and small amounts of olefins (Appendix Table A-12). Aromatic hydrocarbons are present at concentrations of about 18 to 30 percent. The dominant aromatic hydrocarbons are alkylbenzenes and naphthalenes. Small amounts of higher molecular weight PAH also may be present (Appendix Table A-13). A No. 2 home heating oil analyzed by Norris and Hill (1974) contained 1.3 and 2.4 ppm pyrene and fluoranthene, respectively, and 0.03 ppm benzo(a)pyrene.

3.4.5 Diesel Fuel

Diesel fuel or No. 2 fuel oil has an alkane composition similar to that of other middle distillate fuels (Pancirov and Brown 1875). The composition of the aromatic fraction of diesel fuel is complex and variable, depending on the composition of the source crude oil, the refining process, and the intended uses of the fuel (e.g., summer, winter, and marine diesel fuels have different compositions). Benzene and its alkyl homologues often are quite abundant (Appendix Tables A-13 and A-14). The more highly alkylated benzenes (C_3 and C_4) often are more abundant than the BTEX compounds. Naphthalene, phenanthrene and their C_1 through C_4 alkyl homologues also are quite abundant. The monomethyl or dimethyl isomer group usually is the most abundant. Most diesel fuels contain a few parts per million each of several common high molecular weight PAH, including methylfluorenes and pyrenes, chrysenes and methyl chrysenes. The samples summarized in Appendix Tables A-13 and A-14 contain benzo(a)pyrene to 0.6 ppm. If the crude oil feed stock contains organo-sulfur compounds and the refined product is not desulfurized, the diesel fuel will contain sulfur heterocyclics, particularly dibenzothiophenes.

3.5 Residual Petroleum Products

After the lighter fractions produced by various refinery process streams are recovered, high-boiling residues or bottoms remain that may be processed further to produce a wide variety of residual fuels and other residual petroleum products. Low viscosity blending stocks are added to high viscosity base stocks to produce several heavy residual fuels, including: No. 4, 5, and 6 fuel oil (No. 6 fuel oil also is called bunker C fuel oil); No. 4 diesel fuel; and No. 3 and 4 gas turbine fuel oils (CRCS, Inc. 1985c; IARC, 1989). Lubricating oils, asphalts, and petroleum tars also are made from high-boiling residual stocks. These residual petroleum products are extremely complex mixtures consisting primarily of moderately high molecular weight compounds (MW 600 to more than 1,000) with a boiling point range between 650 and 1,200°F (340 to 650°C). The most abundant components of residual petroleum products are asphaltenes, complex polar aromatic compounds, naphthenoaromatics, high molecular weight

normal, branched and cyclic saturated compounds, and a wide variety of hetero-derivatives of hydrocarbons, containing sulfur, oxygen, nitrogen, and metals (Boduszynski *et al.* 1981; CONCAWE 1985). These high molecular weight components of residual petroleum products, because of their high molecular weights and general insolubility, have a very limited mobility in the environment and generally are considered toxicologically inert. However, residual petroleum products also contain significant amounts of lower molecular weight hydrocarbons and related hetero-compounds. Particularly prominent in residual fuels and asphalts are relatively high concentrations (compared to lighter fuels) of three- through five-ring PAH (Appendix Table A-15). The composition and total concentration of the PAH fraction in a residual fuel oil depends on the nature and amount of the low viscosity blending stocks and the proportions of virgin (from crude distillation) and cracked (residues from thermal and catalytic cracking units) residues. Residues from catalytic cracking of heavy fractions of some oils may contain 50 percent or more of three- through five-ring PAH (CONCAWE 1985; Cruzan *et al.* 1986).

A sample of bunker C fuel oil analyzed by Neff and Anderson (1981) contained 34.2 percent aromatic hydrocarbons and 30.2 percent polar aromatics (mostly naphthoenaromatics). The most abundant PAH in No. 6 fuel oil include phenanthrene and its alkyl homologues, fluoranthene, chrysene, and benzo(a)pyrene (Appendix Table A-15). Unused lubricating oils generally contain much lower concentrations of PAH than residual fuel oils (Appendix Table A-16). During manufacture of lube oils, the base stocks are subjected to several hydrogen processes, such as hydrofinishing, hydrotreating, and hydrocracking, that convert aromatic hydrocarbons to naphthenes (cyclic alkanes) and break naphthenic rings to produce a product with better viscosity and temperature stability properties (Asseff 1987).

3.6 Used Lubricating Oils

During use in diesel and gasoline engines, lubricating oils or crankcase oils are subjected to high temperatures and friction from moving engine parts for long periods of time. They may be exposed to pyrolytic products of fuel combustion. As a result, used engine oils change in composition during use. One of the most important changes from an environmental perspective is the increase in the concentration of PAH, particularly the higher molecular weight, four- through six-ring PAH in the oil (Appendix Tables A-17 and A-18). The C₁ through C₃ alkyl homologues of the two- and three-ring PAH usually are more abundant than the parent compounds in the used oils (Appendix Table A-17). Concentrations of individual PAH tend to decrease as molecular weight increases, as is generally true for the unused oil (Appendix Table A-16). However, concentrations of individual higher molecular weight PAH in used crankcase oils are extremely variable, depending on the composition of the original unused oil, the length of use, engine condition and tuning, and whether the oil was used in a gasoline or diesel engine.

Some investigators have reported a tendency for the concentrations of some PAH to increase with length of use of the engine oil. For example, in two samples analyzed by Pruell and Quinn (1982), benzo(a)pyrene was not detectable in a sample of engine oil used in a gasoline engine for 3,928 miles, but it was present at a concentration of 22.3 mg/kg in a sample used

for 5,817 miles. Grimmer *et al.* (1981b) performed a detailed analysis of the PAH fraction of used engine oils from gasoline and diesel vehicles in Germany (Appendix Table A-18). A sample of crankcase oil used in a gasoline engine for 61,000 km contained 381 mg/kg methylphenanthrenes, 245 mg/kg benz(a)anthracene, 485 mg/kg methylchrysenes/methylbenz(a)anthracenes, and 217 mg/kg benzo(a)pyrene. Samples of engine oil used in gasoline and diesel engines for shorter times contained much lower concentrations of these and other PAH. However, API recently analyzed a large number used crankcase oil samples from service stations in Maryland, New York, and Texas and could find no correlation between concentrations of PAH, BTEX, and lead on the one hand and engine size, odometer reading, and miles driven since last oil change on the other (American Petroleum Institute, personal communication).

3.7 Petroleum Chemicals Chosen for Further Evaluation

In the initial screening of organic chemicals in crude, refined, residual, and used oils, 12 petroleum compounds were chosen for additional more intensive evaluation. These compounds were chosen to represent major classes of petroleum product constituents, and are among the more abundant members of their class in most products. They have a wide range of physical/chemical properties affecting their migration and persistence in soils and some of them also are among the more toxic petroleum hydrocarbons. The twelve compounds are listed in Table 3-2 along with some of their physical/chemical properties.

Of the 12 petroleum compounds selected for more detailed evaluation in this assessment, seven frequently are abundant in crude oils. These are n-hexane, cyclohexane, 1,2,4-trimethylbenzene, naphthalene, 2-methylnaphthalene, 1-methylphenanthrene, and dibenzothiophene. Three potentially carcinogenic PAH, benz(a)anthracene, benzo(a)pyrene, and 5-methylchrysene, are present at trace concentrations in most crude oils and at higher concentrations in some residual petroleum products and used engine oils. These higher molecular weight PAH generally are present at only trace concentrations in gasoline and middle distillate fuels. Gasoline and lighter middle distillate fuels, such as kerosene and jet fuels, contain high concentrations of hexane, cyclohexane, dimethylbutane, dimethylpentane, and 1,2,4-trimethylbenzene. Middle distillate fuels, particularly the heavier fuels, such as No. 2 diesel and No. 2 home heating oil, as well as many of the residual fuels contain high concentrations of naphthalene, phenanthrene, dibenzothiophene, and their alkyl homologues.

The 12 chemical constituents of petroleum products have molecular weights ranging from 86.2 to 252.3 (Table 3-2). They have aqueous solubilities ranging from about 60 mg/L to about 0.002 mg/L and log octanol/water partition coefficients (K_{ow}) ranging from about 2.8 to 6.8. The values for physical/chemical properties for the 12 compounds span the range of physical/chemical properties for the major chemical components of crude, refined, residual, and used oils (Appendix A). Therefore, their behavior and toxicity in soils and groundwater should be representative of the range for all the mobile nonpolar organic compounds in petroleum.

Table 3-2. Physical/Chemical Parameter Values

Compound	Molecular Weight	Log K_{ow}	Boiling Pt. °C	Melting Pt. °C	Density g/mL	Solubility		Henry's Law Const.	Henry's Law Const. $\text{Atm m}^3/\text{mol}$
						mg/L	mol/m^3		
benz(a)anthracene	228.3	5.91	435	160-162	1.2544	1.4×10^{-2}	6.1×10^{-6}	1.7×10^{-4}	4.1×10^{-6}
benzo(a)pyrene	252.3	6.83	311	175-179	1.11	1.5×10^{-3}	6.1×10^{-6}	1.7×10^{-4}	4.1×10^{-6}
5-methylchrysene	242.1	6.42	--	118-170	--	7.3×10^{-3}	3.0×10^{-5}	--	--
1-methylphenanthrene	192.3	5.14	390	119-123	--	2.69×10^{-1}	1.4×10^{-3}	--	--
dibenzothiophene	184.3	5.08	332	100	--	1.47×10^0	8.0×10^{-3}	--	--
1,2,4-trimethylbenzene	120.2	3.65	169	-44,-61	0.889	5.19×10^1	4.32×10^{-1}	2.53×10^{-1}	6.1×10^{-3}
naphthalene	128.2	3.37	210.8	80	1.145	3.06×10^1	2.39×10^{-1}	5.62×10^{-2}	1.4×10^{-3}
2-methylnaphthalene	142.2	4.11	240	34	1.029	2.56×10^1	1.80×10^{-1}	2.03×10^{-2}	4.9×10^{-4}
cyclohexane	84.2	3.44	80.7	6.47	0.779	5.75×10^1	6.83×10^{-1}	7.50×10^0	1.8×10^{-1}
n-hexane	86.2	3.00	68.7	-94.3	0.6594	1.23×10^1	1.43×10^{-1}	5.71×10^1	1.4×10^0
2,3-dimethylbutane	86.2	3.85	57.9	-129,-135	0.6616	1.91×10^1	2.22×10^{-1}	5.7×10^1	1.4×10^0
2,2-dimethylpentane	100.2	3.10	78	-123.8	0.6739	4.4×10^0	4.39×10^{-2}	1.29×10^2	3.1×10^0
benzene	78.1	2.1	80.1	5.5	0.88	1.79×10^3	2.24×10^1	2.3×10^{-1}	5.6×10^{-3}
toluene	92.1	2.7	110.6	-95	0.87	7.59×10^2	5.8×10^0	2.6×10^{-1}	6.4×10^{-3}
ethylbenzene	106.2	3.1	136.2	-94.97	0.87	1.35×10^2	1.4×10^0	2.7×10^{-1}	6.4×10^{-3}
m-xylene	106.2	3.3	139.1	-47.87	0.86	1.60×10^2	1.2×10^0	4.4×10^{-1}	1.1×10^{-2}
o-xylene	106.2	2.9	144.4	-25.18	0.88	2.15×10^2	1.6×10^0	2.1×10^{-1}	5.1×10^{-3}
p-xylene	106.2	3.1	138.4	13.26	0.86	2.21×10^2	1.9×10^0	2.9×10^{-1}	7.1×10^{-3}

Section 4

SOURCES AND FATES OF SELECTED CHEMICALS IN SOILS AND GROUNDWATER

4.1 Petroleum-Derived Chemicals in Soils and Groundwater

4.1.1 Petroleum Consumption

Petroleum and the wide variety of products derived from it are among the major consumer products in the world. Between 1988 and 1992, the average rate of consumption of petroleum in the United States alone was about 17 million barrels (714 million gallons) per day (Minerals Management Service 1991; Beck 1992). Domestic production of crude oil in 1990 averaged about 7.3 million barrels per day, the lowest level in 25 years (Minerals Management Service 1991). Projected average domestic production in 1992 is 7.2 million barrels per day (Beck 1992). The remaining crude oil, about 57 percent of total consumption, is imported.

Of the total consumed, about two-thirds was refined for use as fuel for land vehicles, airplanes, and ships. The consumption of automotive gasoline alone is approximately 305 million gallons per day (Beck 1992). Projected domestic consumption of middle distillate fuels (jet fuel, kerosine, and fuel oils) in 1992 is about 190 million gallons per day. Residual fuel oil consumption is expected to be about 48 million gallons per day. The remaining 171 million gallons consumed each day is used for other distillate and residual products as well as feed stocks for the petrochemical industry.

Several years ago, a typical car used about 9 gallons/year of crankcase oil (Vazquez-Duhalt 1989). Modern automobile engines require fewer oil changes and the amount of crankcase oil used per vehicle each year has decreased substantially. Annual world consumption (excluding China and eastern Europe) of lubricating oils for gasoline and diesel engines is about 26 billion gallons. About 65 percent of crankcase oil becomes used crankcase oil, the remainder being lost, mostly by combustion, during engine operation. Approximately 6.4 billion gallons of used automotive lubricating oils was generated annually in the United States in 1980 (Vazquez-Duhalt 1989). An estimated 31.7 to 50 percent of the used crankcase oil is used as fuel; 11.0 to 16.7 percent is incorporated into asphalt for roads; 3.3 to 9.2 percent is re-refined; and 23.0 to 30.0 percent of used crankcase oil (1.5 to 1.9 billion gallons) generated each year in the United States is disposed of in the environment, mostly by application to land.

4.1.2 Releases to Soil and Groundwater

The daily processing and utilization of more than 700 million gallons of petroleum each day in the United States requires an immense infrastructure for petroleum production, product manufacture, storage, and transportation. There are more than 700,000 above-ground storage tanks in oil production fields, and at refineries, terminals, and bulk plants (API 1992). More

than 75 percent of these are in the exploration and production sector. There are more than 1.7 million underground storage tanks at more than 200,000 service stations and end use facilities (EPA 1988; API 1993b). The United States has about 185 active refineries, 1,100 large product storage terminals (National Petroleum News 1992), 10,500 bulk plants (Hornbeck 1989), and 171,000 miles of petroleum pipelines (API 1993a).

Releases of refined oils, particularly gasoline, from underground storage tanks are the most widely recognized source of petroleum hydrocarbons in soils (Dowd 1984; Murphy *et al.* 1987). There are several other sources of crude and refined petroleum products releases to soils such as tank or pipeline leakage and releases during transfer from operations (EPA 1981). Releases on land of used crankcase oil by people who change the oil in their own cars (Hoffman *et al.* 1980) also results in contamination of surface and subsurface soils with petroleum. Estimates of the frequency and magnitude of hydrocarbon releases to soils from different sectors of the oil industry and from other industrial and domestic sources have been summarized in several reports (EPA 1986; Federal Register 1988; Riper and Früchtenicht 1989; Vasquez-Duhalt 1989; Oil Spill Intelligence Report 1991).

4.2 Petroleum-Type Chemicals from Other Sources in Soils

Not all the hydrocarbons and related hetero-substituted compounds in soils are derived from petroleum products. Other fossil fuels, such as peat and coal, contain a wide variety of saturated, aromatic, and heterocyclic hydrocarbons. The burning (pyrolysis) of organic matter produces a wide variety of hydrocarbons, particularly high molecular weight PAH, similar to those in crude oil and refined or residual oil products. Normal and branched alkanes are synthesized by nearly all living organisms, particularly bacteria and plants. Some aromatic hydrocarbons or substituted aromatic hydrocarbons may be synthesized by living organisms. There probably are no mobile hydrocarbons or related heterocyclic compounds that are unique to petroleum. However, hydrocarbon assemblages from different sources differ widely in composition and complexity. The most complex assemblages are from petroleum.

4.2.1 Other Fossil Fuels

Dead plant material, following its deposition in soils and sediments, undergoes a variety of diagenic reactions that change the chemical composition of the organic residues in various ways. Humic and fulvic acids are early diagenic products of plant matter. Humic acids are extremely complex, high molecular weight compounds that can be broken down pyrolytically into a large number of alkanes, olefins, and aromatic hydrocarbons (Schulten and Schnitzer 1992). Major breakdown products of humic acids include homologous series of alkanes and olefins to about C₃₀, n-alkylbenzenes to C₁₈, alkylphenols, and alkyl-naphthalenes. Unsubstituted heterocyclic compounds, such as furans, pyrroles and pyridines also are present. Humic acids may be abundant in organic-rich soils and sediments. However, most of the hydrocarbons and heterocyclic compounds in them are tightly bound to the acid matrix and are not easily leached out by water (Farrington 1986; Schulten and Schnitzer 1992).

Long-term diagenesis of plant matter produces first peat, and then perhaps soft and hard coals. Peat is a hydrocarbon material. The most abundant hydrocarbons identified in Canadian arctic peats are the C_{13} to C_{31} n-alkanes (average 160 $\mu\text{g/g}$) and medium molecular weight PAH (about 0.16 $\mu\text{g/g}$) (Yunker *et al.* 1991). Peats from the North Slope of Alaska contain a mean of 466 $\mu\text{g/g}$ total alkanes and 0.29 $\mu\text{g/g}$ total PAH (Steinhauer and Boehm 1992). The most abundant PAH in many peat samples, representing between 5 and 98 percent of the total PAH in the peat, is perylene (Venkatesan 1988; Steinhauer and Boehm 1992). Concentrations of perylene in peats tend to decrease with increasing age of the peat, suggesting that perylene is produced by early diagenesis of organic precursors in anoxic bog soils. Most peats contain high concentrations of lignin-based structures, high in substituted aromatic compounds (Cohen *et al.* 1991). Pyrolysates of peats from different sources may contain 3 to 6 percent furans, and a fraction to more than 1 percent benzene and alkylbenzenes (Cohen *et al.* 1991).

Coal is considered a predominantly aromatic material (Neff 1979). As much as 75 percent of the carbon in bituminous coal is aromatic (Ensminger 1977). Woo *et al.* (1978) used X-ray excited optical luminescence spectrometry to identify phenanthrene, perylene, benz(a)anthracene, benzo(a)pyrene, benzo(e)pyrene, and dibenzo(cd,mn)pyrene in samples of Iowa and Illinois coal. Tripp *et al.* (1981) reported that bituminous coal contains naphthalene, methylnaphthalene, dimethylnaphthalene, trimethylnaphthalenes, phenanthrene, and dimethylphenanthrenes. n-Alkanes from C_{10} to about C_{30} , and the isoalkane pristane also were abundant. Although coal contains high concentrations of aliphatic and aromatic hydrocarbons, most are tightly bound to the solid organic matrix of the coal and are toxicologically nearly inert (Bingham *et al.* 1979). However, coal dust may be a substantial source of analytical interference in monitoring programs designed to document the distribution and concentrations of released petroleum products in contaminated soils and sediments (Tripp *et al.* 1981).

4.2.2 Pyrosynthesis

Although fossil fuels are rich sources of saturated and aromatic hydrocarbons, it is generally agreed that most of the PAH and many of the aliphatic hydrocarbons in soils and sediments are derived from incomplete combustion of organic matter at high temperatures (Suess 1976; Neff 1979). Combustion of any organic material, including fossil fuels, will result in the generation of a wide variety of PAH, particularly if combustion takes place at temperatures above about 400 °C in an oxygen-deficient environment. PAH assemblages produced by pyrolysis of organic matter are complex and, unlike PAH assemblages in petroleum, usually are dominated by four-, five-, and six-ring PAH. In pyrolytic PAH assemblages, particularly those generated at temperatures above about 700°C, the dominant compound in each homologous series is the unalkylated parent compound or a homologue with only one or two alkyl substituents (Youngblood and Bloomer 1975; Boehm and Farrington 1984). In unburned petroleum products, alkyl homologues of most PAH are more abundant than the parent compound. These differences can be used to differentiate between petrogenic and pyrogenic PAH in soil samples.

PAH produced by pyrolysis accumulate in the particulate fraction produced during combustion and in any tarry or solid ash residues produced (Neff 1979). PAH up to pyrene are sufficiently volatile that small amounts may be present in the vapor phase of a combustion plume. The particulate fraction of a combustion plume is soot or carbon black. Soot can be thought of as an agglomerate of highly condensed PAH (Venkatesan and Dahl 1989). The fundamental chemical unit of a soot particle is thought to be a molecule with 61 or 91 fused aromatic rings (Thomas *et al.* 1968). The polycyclic matrix of soot is environmentally inert. However, PAH of environmental concern are quenched rapidly in the cooling smoke of the flame and sorb tightly through hydrogen bonding to the soot particles as they cool. PAH assemblages associated with soot are very stable and usually are not modified by photooxidation, dissolution, or biodegradation during transport in the air or water (Prahl and Carpenter 1983; Readman *et al.* 1984, 1987). As a result of this stability, pyrolytic PAH assemblages remain very stable over long periods of time after deposition in soils and sediments. PAH assemblages, thought to have been derived from ancient forest fires, have been identified in Cretaceous/Tertiary and Jurassic deposits (Venkatesan and Dahl 1989, Killops and Massoud 1992).

A great many domestic and industrial activities, as well as natural events such as forest fires, produce PAH by pyrolysis/pyrosynthesis. Pyrosynthesized PAH may be released to the environment in airborne particles or in the solid or aqueous byproducts of the pyrolysis process. Burning of fossil fuels is an important source of PAH in the environment. The particulate fractions of exhaust from gasoline and diesel-powered vehicles contained 16 to 332 µg/g total four- through six-ring PAH (Takada *et al.* 1991). Fluoranthene and pyrene represented between 46 and 88 percent of the total PAH in diesel exhaust and 15 to 17 percent of the total PAH in gasoline exhaust. Diesel exhaust also has high concentrations of alkylpyrenes. Other abundant PAH in gasoline exhaust include benzo(e)pyrene and coronene (Hoffmann and Wynder 1963). The ratio of benzo(a)pyrene (highly carcinogenic) to benzo(e)pyrene (non-carcinogenic) in gasoline exhaust is very low, about 0.075 (Hoffmann and Wynder 1963). Nearly all the PAH derived from vehicular exhaust are deposited within about 50 meters of roads (Harrison and Johnston 1985, Hewitt and Rashed 1990).

Many heat and electricity generating facilities burn fossil fuels and emit saturated and aromatic hydrocarbons in liquid, solid, and gaseous waste byproducts (Neff 1979; Heit 1985). Modern large-capacity electric generating facilities and heating plants usually have emission controls that decrease emissions of particulate PAH in stack gases. However, emissions from domestic furnaces usually are not controlled; old fashioned coal fired furnaces, in particular, may produce smoke with high concentrations of PAH. Incineration of solid and liquid wastes also is an important source of airborne particulate PAH (Davies *et al.* 1976). Several industrial processes, such as coal coking (Lao *et al.* 1975), carbonization of coal to produce coal tars, carbon black, and creosote (Merrill and Wade 1985) and aluminum smelting (Thrane 1987) produce airborne particles and solid wastes containing very high concentrations of PAH.

Wood burning stoves, used frequently for domestic heating, may produce large amounts of PAH that are concentrated primarily in the particle fraction of the smoke (Ramdahl *et al.* 1982; Knight *et al.* 1983). Forest fires and open burning of brush and plant wastes also are important sources of particulate emissions rich in PAH (Sullivan and Mix 1983; Freeman and Cattell 1990). Sullivan and Mix (1983) estimated that as much as 1.3 kg of total PAH were generated per hectare during burning at clear-cut logging sites in Oregon. Particulate matter from burning wood and different types of vegetation contained 4 to 60 $\mu\text{g/g}$ benz(a)anthracene and 2 to 194 $\mu\text{g/g}$ benzo(a)pyrene (Freeman and Cattell 1990). Smoked and charcoal broiled meats may contain up to about 164 ng/g total PAH (Panalaks 1976) derived from fuel combustion.

Because they are tightly bound to the solid phase, PAH sorbed to airborne soot particles are relatively stable. Soot containing sorbed PAH can be transported by air currents over vast distances and deposited on land or water bodies at sites remote from its source (Lunde and Bjorseth 1977; Bjorseth *et al.* 1979). For example, the Arctic haze over northern Alaska and Canada is thought to be derived from industrial emissions in the central United States and Europe (Daisey *et al.* 1981). Arctic haze collected in March at Point Barrow, AK, contained a mean of 1.25 $\mu\text{g/m}^3$ total PAH. This is much higher than in the lower atmosphere from remote, uninhabited areas in temperate and tropical environments but lower than the concentration of total particulate PAH in air samples from urban atmospheres. For example, air samples from Fairbanks, AK, where wood-burning stoves are used frequently for home heating, contained 2.9 to 155 $\mu\text{g/m}^3$ total PAH (Reichardt and Reidy 1980). Concentrations of total hydrocarbons, including saturated and aromatic hydrocarbons, in air samples over the sea surface of the tropical Atlantic Ocean west of central Africa were in the range of 2.8 to 133 ng/m³ (Bouchertall 1987).

Concentrations of soot particles in the air are quite variable, so hydrocarbon concentrations normalized to a unit volume of air do not give an indication of the magnitude of possible deposition of hydrocarbons on soils from airborne particles. Soot particles from air samples collected in several urban, industrial, and rural areas in Sweden contained 11 to 830 μg total PAH/g carbon (Näf *et al.* 1992). The most abundant PAH in most particulate samples were fluoranthene, pyrene, chrysene/triphenylene, benzo(a)pyrene, and indeno(1,2,3-cd)pyrene.

Atmospheric processes that result in deposition of airborne PAH on land and water include rainout, dry fallout, and vapor-phase deposition onto surfaces. The first two processes are quantitatively the most important for deposition of PAH. Residence time of particulate PAH in the atmosphere and, therefore, the aerial extent of their dispersal depends on meteorological conditions and particle size (Radding *et al.* 1977). Particles larger than about 1 μm , such as those from a coke oven emission (Broddin *et al.* 1977), usually are deposited within a few days under dry weather conditions, whereas submicron particles, such as the soot from vehicular exhaust (Katz and Pierce 1976), may persist in the lower atmosphere from a few days to as long as six weeks (Suess 1976). Concentrations of PAH in rain are inversely proportional to the length of the rain event, indicating that most of the particulate and some of the vapor-phase PAH are washed out of the atmosphere quickly during a shower (van Noort

and Wondergem 1985). Rainwater collected at the beginning of a rain event in the Netherlands contained 4.7 $\mu\text{g/L}$ total PAH. After 23 minutes of rainfall, the rain contained 0.047 $\mu\text{g/L}$ total PAH. The most abundant PAH in the rainfall were fluoranthene and pyrene, both slightly volatile.

Lower molecular weight PAH (naphthalene to pyrene) have sufficiently high vapor pressures that they can exist at significant concentrations in the vapor phase (Neff 1979). Vapor-phase PAH, being hydrophobic, have a strong tendency to sorb to solid surfaces, particularly those rich in organic matter. These lower molecular weight PAH tend to deposit onto surfaces of leaves, moist soil, and water (Grimmer and Duval 1970).

Rates of dry and wet deposition of airborne particulate and vapor-phase PAH and other hydrocarbons on land and water vary widely, depending primarily on proximity to major sources. Atmospheric deposition of saturated and aromatic hydrocarbons to soils in Rhode Island ranged from 58.5 and 61.4 $\mu\text{g/m}^2/\text{year}$, respectively, in rural areas to 3,220 and 4,120 $\mu\text{g/m}^2/\text{year}$, respectively, in an industrial area (Latimer *et al.* 1990). Tanaka *et al.* (1991) estimated flux rates of PAH to soils in the Hakyu-chi Experimental Forest in Tokyo between 333 and 666 $\mu\text{g/m}^2/\text{year}$. Fluxes of total PAH (primarily from airborne particles) to surface waters in several Swedish cities ranged from 1,400 to 61,000 $\mu\text{g/m}^2/\text{year}$, with highest deposition rates within 10 km of major point sources, such as aluminum smelters (Näf *et al.* 1992). An estimated total of 560 kg/year of PAH was deposited within a 10-km radius of an aluminum smelter at Sundsvall, Sweden. An average of 1,925 $\mu\text{g/m}^2/\text{year}$ of PAH was deposited in soils adjacent to a heavily-used roadway in Great Britain (Harrison and Johnston 1985). The rate of PAH deposition at a nearby reference site away from roads was about 88 $\mu\text{g/m}^2/\text{year}$. Thus, dry and wet deposition from the air can represent a substantial source of PAH to soils and sediments.

4.2.3 Biosynthesis

Aliphatic hydrocarbons are readily biosynthesized by living bacteria, plants, and animals (Kolattukudy 1976). Normal alkanes, methyl-branched alkanes, and normal alkenes (olefins) with an odd number of carbons are the main forms biosynthesized. These hydrocarbons are produced by decarboxylation of fatty acids. Assemblages of n-alkanes, dominated by chains with odd numbers of carbons between about 21 and 33 are characteristic of terrestrial plants and marsh grasses (Adlard *et al.* 1972). n-Alkane assemblages dominated by n-C₁₅ and n-C₁₇ are characteristic of phytoplankton (Blumer *et al.* 1971). Biogenic assemblages of aliphatic hydrocarbons in soils can be distinguished from those of petroleum or pyrogenic origin by the predominance of odd-numbered over even-numbered carbon chains in the former.

A wide variety of organic compounds containing fused-ring polycyclic aromatic structures are synthesized by organisms, particularly bacteria, fungi, and higher plants (Neff 1979). These compounds, such as vitamin K₂ (a naphthoquinone), are not true PAH, because they contain non-hydrocarbon substituents. However, some may be reduced by diagenic processes in soils to PAH. For example, perylene, thought to be derived from diagenesis of diatoms and other

plant material, often occurs at high concentrations in anoxic sediments and soils (Gschwend *et al.* 1983; Louda and Baker 1984; Venkatesan 1988). Under oxidizing conditions in soils and sediments, certain chemicals such as abietic acid from pine tree rosin and triterpenes (hopanes) from mosses and certain other plants can be oxidized to a PAH mixture called retene (Tan and Heit 1981, Ramdahl 1983). Retene (1-methyl-7-isopropylphenanthrene and small amounts of other alkyl phenanthrenes) also can be produced by combustion of coniferous woods. Other alkyl phenanthrenes are produced during diagenesis of abietic acid and retene. Jonsson (1968) identified small amounts of 1-methylphenanthrene, 2-ethylphenanthrene, 1,7-dimethylphenanthrene, and 1-methyl-7-ethylphenanthrene in crude pine tar retene. However, the PAH assemblages produced by the early diagenesis of suitable biogenic precursors have a simple composition and, for this reason, can be distinguished easily from petrogenic and pyrogenic PAH assemblages.

4.3 Concentrations of Hydrocarbons in Soils

There are very few reliable data on the concentrations of petroleum-derived hydrocarbons in soils and sediments. Because aliphatic and olefinic hydrocarbons are readily biosynthesized by many species of microbes, plants, and animals, their concentrations in soils and sediments rich in organic matter often are high (Readman *et al.* 1986). Therefore, it is difficult to use saturated hydrocarbons as an indication of the level of contamination of soils with petroleum hydrocarbons. Standard EPA methods for total oil and grease (Method 418.1) or equivalent methods for "total petroleum hydrocarbons" are extremely nonspecific and quantify any organic matter extracted with the extracting solvent. When used to monitor concentrations of petroleum hydrocarbons in water and soils, they invariably produce erroneously high values.

The saturated hydrocarbon fraction of a petroleum extract contains many hydrocarbons that can not easily be resolved by conventional gas chromatographic methods. This poorly resolved fraction of saturated hydrocarbons, composed of a wide variety of branched and cyclic alkanes and unique to petroleum, is called the unresolved complex mixture (UCM). The fraction of the total extract represented by the UCM increases during weathering of oil and, therefore, the UCM sometimes is used to differentiate between biogenic and petrogenic assemblages of saturated hydrocarbons (Readman *et al.* 1986). However, as the resolution of gas chromatographic columns has increased, the apparent concentration of the UCM in environmental samples has decreased. However, the UCM is most useful as an indication of weathered crude and heavy distillate and residual oils in soils.

Benzo(a)pyrene is the most extensively monitored PAH in the environment (Neff 1979). Benzo(a)pyrene in soils and sediments is derived almost exclusively from combustion sources. Therefore, its distribution does not reflect the environmental distribution of petrogenic and biogenic/diagenic PAH. Most surveys of the distribution of total PAH in soils and sediments have focused on the higher molecular weight, parent (unalkylated) PAH from pyrene/fluoranthene and higher (the so-called priority pollutant) PAH. These PAH come from both pyrogenic and petrogenic sources, but mainly from the former. Therefore, the standard EPA method for bases/neutrals/acids (Method 8270) or equivalent is not appropriate for

assessing the concentrations or distributions of petroleum-derived PAH in soils and sediments. Because methods for clearly identifying petroleum-derived hydrocarbons in soils and sediments (described in Section 7) have not been used extensively, it is difficult to assess the distribution and range of concentrations of petrogenic hydrocarbons in the environment.

Concentrations of individual and total PAH in soils and sediments vary widely primarily in relation to proximity to known sources. However, because of wide airborne dispersal of PAH-contaminated soot from anthropogenic and natural combustion sources, PAH are ubiquitous trace contaminants of all soils. The observations discussed below are examples of the range of concentrations of petrogenic and pyrogenic saturated and aromatic hydrocarbons that occur in clean and oil-contaminated soils.

The environmental distribution of benzo(a)pyrene has been studied extensively because it is a known animal carcinogen. Concentrations of benzo(a)pyrene in soils and sediments range from less than about 0.4 $\mu\text{g/kg}$ dry weight to greater than 500,000 $\mu\text{g/kg}$ (Neff 1979, Edwards 1983, Grimmer 1983). More typically, concentrations are in the range of about 100 to 1,000 $\mu\text{g/kg}$; measured concentrations greater than about 500 $\mu\text{g/kg}$ are exclusively from soils near known sources, such as heavily-used roadways, aluminum smelters, coke ovens, coal gasification works, and coal carbonization (creosote) plants.

Ambient soils in Norway contained an average of 188 $\mu\text{g/kg}$ total PAH; naphthalene, phenanthrene, and chrysene/triphenylene were the most abundant (Vogt *et al.* 1987). Contaminated soils contained an average of about 2,800 $\mu\text{g/kg}$ total PAH; the most abundant PAH were chrysene/triphenylene, fluoranthene, pyrene, phenanthrene, and benzo(a)pyrene. The most heavily contaminated soils were from the vicinity of an aluminum smelter.

Concentrations of total PAH in sediments of Cayuga Lake, NY, were in the range of 104 to 20,000 $\mu\text{g/kg}$ dry weight (Heit 1985). Highest concentrations were within about 1,000 meters of point sources of PAH: stacks of a coal-fired power plant; marinas; and highway bridges. These PAH were from both petrogenic and pyrogenic sources.

Latimer *et al.* (1990) identified used crankcase oil as the major source of petroleum hydrocarbons in urban runoff in Rhode Island. The concentrations of total hydrocarbons in soil particles in runoff ranged from an average of 24,800 mg/kg along an interstate highway and commercial area to 211,000 mg/kg in an industrial area. The dominant PAH in the particulate samples were phenanthrene, fluoranthene, and pyrene; benzo(a)pyrene and benzo(e)pyrene made up about 20 percent of the total PAH in the particles. Crankcase oil type hydrocarbons were present in bulk street dust and roadside soil at concentrations ranging from 39 to 3,490 mg/kg. Particles (mainly soot) derived from atmospheric deposition contained 2,280 to 125,000 mg/kg total hydrocarbons.

Soils at a refinery site in Germany were heavily contaminated with petroleum hydrocarbons to a depth of at least 6 meters (Ellis *et al.* 1990). Surface soils (0 to 2 meters) contained a mean of 12,980 mg/kg total hydrocarbons, as determined by infrared spectrometry. Groundwater