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

STEP
Strategies for Today's
Environmental Partnership

American Petroleum Institute
1220 L Street, Northwest
Washington, D.C. 20005

STEP

Strategies for Today's
Environmental Partnership

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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 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 C_1- through C_3-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 gravi-tational 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 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 PAH 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/m^3 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 petroleums (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-dimetylbutane, 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)
- Benzofluoranthenes (all isomers as well as methylbenzofluoranthenes)
- 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
- n-Hexane
- 2-Methylhexane
- 2,2,5-Trimethylhexane
- 2,3-Dimethylpentane
- 2-Methylpentane
- 2,2,4-Trimethylpentane

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

- Cylopentane 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 methyldibenzothiophenes. 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 µg/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.

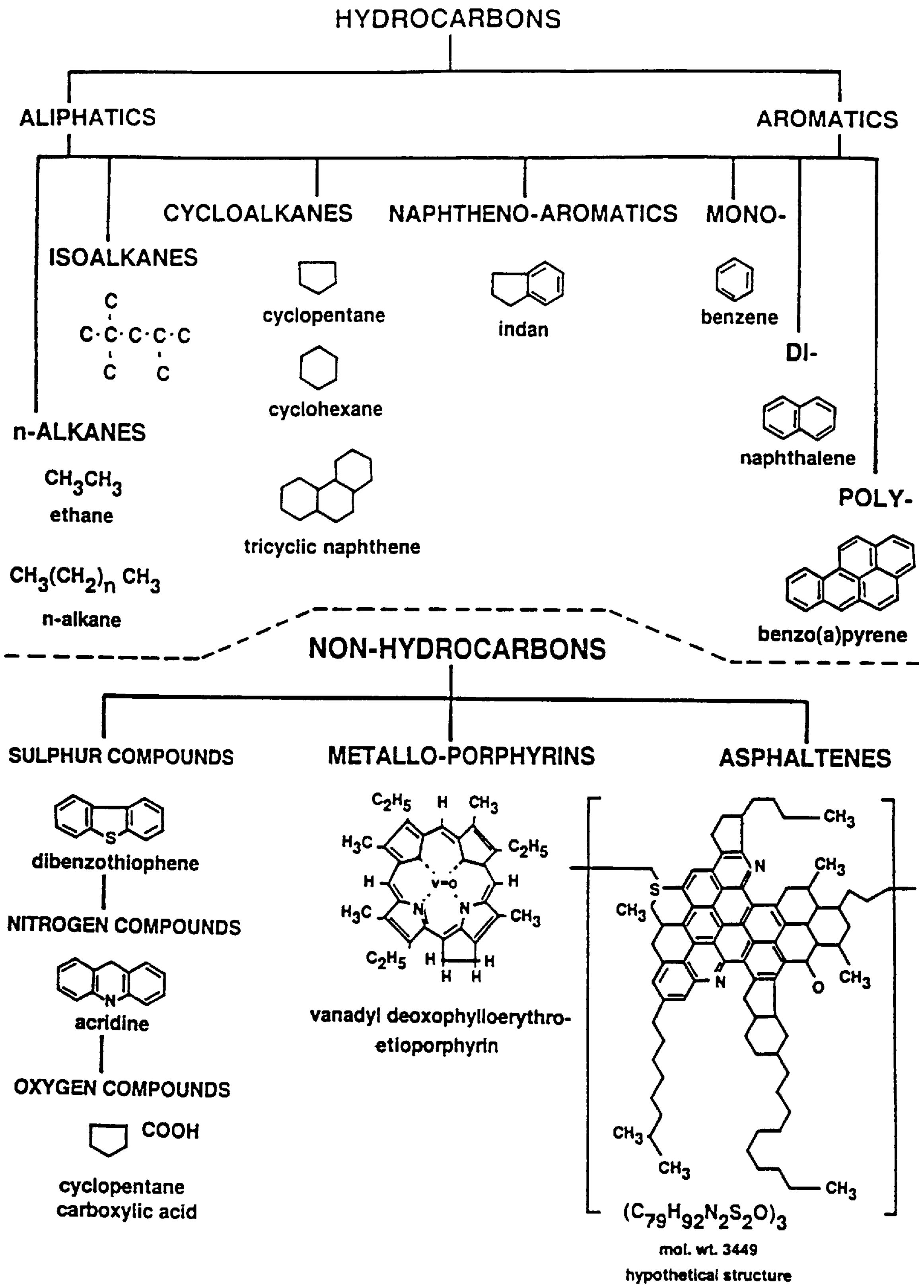

Figure 3-1. Structure of the most abundant classes of organic chemicals in crude and refined petroleum (from Neff, 1990)

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 μg/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 C_6 to C_{19} 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 C_{11} 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 C_3-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
n-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 C_3-, C_4-, and C_5-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 C_1- and C_2-alkyl homologues. The most abundant sulfur-substituted alkanes in Wasson 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 C_4-, C_5-, and C_6-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 C_7 to C_9 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, indenes, 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

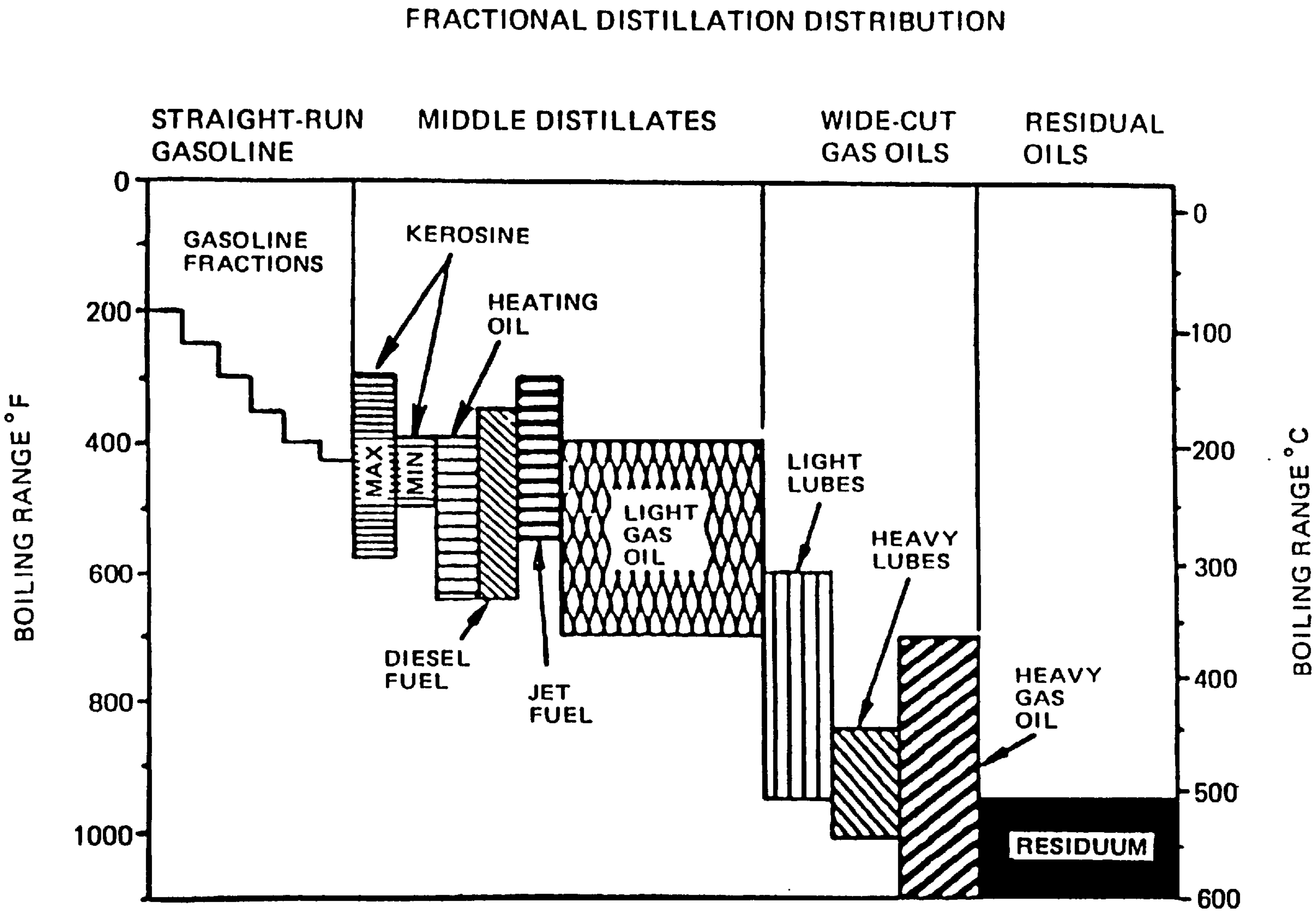

Figure 3-2. Boiling point range of fractions of crude petroleum (from National Academy of Sciences, 1985)

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 C_7-C_{12}-alkenes (Appendix Table A-8); others have low concentrations of these olefins, but are enriched in methylbutenes and C_6-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 that 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 (199?: 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 naphthenoaromatics). 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 198?).

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 C_1 through C_3 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 mg/L	Solubility mol/m³	Henry's Law Const.	Henry's Law Const. Atm m³/mol
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 C_{30}, n-alkylbenzenes to C_{18}, alkylphenols, and alkylnaphthalenes. 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 µg/g) and medium molecular weight PAH (about 0.16 µg/g) (Yunker *et al.* 1991) Peats from the North Slope of Alaska contain a mean of 466 µg/g total alkanes and 0.29 µg/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 forrest 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 μg/g benz(a)anthracene and 2 to 194 μg/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 μg/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 μg/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/m^3 (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 μg/L total PAH. After 23 minutes of rainfall, the rain contained 0.047 μg/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 μg/m^2/year, respectively, in rural areas to 3,220 and 4,120 μg/m^2/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 μg/m^2/year. Fluxes of total PAH (primarily from airborne particles) to surface waters in several Swedish cities ranged from 1,400 to 61,000 μg/m^2/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 μg/m^2/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 μg/m^2/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-C_{15} and n-C_{17} 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 K_2 (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 by 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 μg/kg dry weight to greater than 500,000 μg/kg (Neff 1979, Edwards 1983, Grimmer 1983). More typically, concentrations are in the range of about 100 to 1,000 μg/kg; measured concentrations greater than about 500 μg/kg are exclusively from to 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 μg/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 μg/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 μg/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 from the site contained about 0.5 mg/L total oil and grease. The infrared method for oil and grease is not specific for petroleum hydrocarbons and tends to overestimate oil contamination of slightly contaminated or clean soils. Soils at a creosote-contaminated site in Sweden contained 10 to 32,000 mg/kg creosote (mainly PAH) and 10 to 825 mg/kg petroleum hydrocarbons (Ellis *et al.* 1991). Creosote is a highly aromatic material containing as much as 93 g total PAH/kg (Lijinski *et al.* 1963). Sediments from the Elizabeth River, VA, contaminated with creosote, contained 1.4 to 13,000 mg/kg total PAH (phenanthrene through benzo[g,h,i]perylene) (Huggett *et al.* 1987).

By comparison, concentrations of total hydrocarbons in sediments of the Beaufort Sea off northern Alaska range from 0.3 to 20 mg/kg in nearshore sediments to 20 to 50 mg/kg in offshore sediments (Shaw *et al.* 1979, Venkatesan *et al.* 1983, Steinhauer and Boehm 1992). The dominant alkanes in the sediments are the odd-chain-length C_{21} through C_{33} n-alkanes, suggesting a biogenic origin. Concentrations of total PAH in Beaufort Sea sediments are in the range of 0.17 to 1.0 mg/kg, with perylene and alkyl naphthalenes and phenanthrenes being most abundant (Steinhauer and Boehm 1992). Particles entering the Beaufort Sea, Canada, in the Mackenzie River outflow contain an average of about 11.8 mg/kg total alkanes and about 2 mg/kg total PAH (Yunker *et al.* 1991).

4.4 Fates of Hydrocarbons in Soils and Groundwater

4.4.1 Distribution of Hydrocarbon Assemblages in Soils

Most theoretical studies of the behavior of nonpolar organic chemicals in soils and sediments are based on the assumption that individual chemicals enter a soil/water system in dissolved form (Liu *et al.* 1991; Uchrin *et al.* 1992). Under such conditions, nonpolar organic chemicals will tend to become distributed between the solid (primarily soil organic matter) and pore water phases of the soil; the equilibrium distribution under these conditions can be approximated by the soil organic matter/water partition coefficient, K_{oc} (Karickhoff *et al.* 1979). The value of K_{oc} for PAH and related heterocyclic compounds can be approximated by the formula:

$$\log K_{oc} = \log K_{ow} - 0.317 \qquad (4\text{-}1)$$

where K_{ow} is the octanol/water partition coefficient (Means *et al.* 1980). For higher molecular weight PAH with values for log K_{ow} greater than about 5.5, the relationship between K_{ow} and K_{oc} may be defined better by a parabolic equation of the form (Kayal and Connell 1990):

$$\log K_{oc} = 3.584 \log K_{ow} - 0.327(\log K_{ow})^2 - 3.523 \qquad (4\text{-}2)$$

However, the actual value of K_{oc} varies, depending on the texture of the soil and nature of the organic carbon in the soil. Both particulate and dissolved organic matter in soils compete for sorption of nonpolar organic chemicals; the two forms of soil organic matter often have roughly similar affinities for nonpolar organic chemicals in solution. However, sorption of

PAH to dissolved organic matter in soils may facilitate transport through the soil, whereas sorption to particulate organic matter will retard migration (Scheunert *et al.* 1992). Mass transfer of petroleum hydrocarbons among different phases (solid, soil water, non-aqueous phase liquids, etc.) in soil will be discussed at greater length in Section 5 of this report.

Actually, petroleum products and pyrogenic hydrocarbon assemblages nearly always enter soil/water systems as the extremely complex, hydrophobic mixtures discussed above. The fate of different chemicals in the petroleum mixture released on or mixed with soils depends on the total amount of petroleum product, its physical/chemical properties, and soil properties. Hydrocarbons will move from the petroleum product (called the non-aqueous phase liquid [NAPL] in Section 5) into soil water in contact with NAPL. The distribution at equilibrium of hydrocarbons among different phases in soils will depend on the oil/water partition coefficient of the hydrocarbon; the rate at which equilibrium is reached depends on the interphase mass transfer coefficient for the hydrocarbon (Payne and McNabb 1985; Shiu *et al.* 1990; Cline *et al.* 1991). The rate of transfer of hydrocarbons into the aqueous phase will depend primarily on the relative surface area of oil in contact with the water. Dissolution of low molecular weight hydrocarbons in the soil water may facilitate dissolution of higher molecular weight hydrocarbons through cosolvency (Burris and MacIntyre 1986; El-Zoobi *et al.* 1990).

Pyrogenic PAH and alkanes are tightly hydrogen-bonded to soot particles and do not readily transfer into the water phase when soot is deposited in water or soil/water systems (Readman *et al.* 1987). PAH associated with soot deposited in soils and sediments are relatively resistant to photooxidation by sunlight and biodegradation by soil microbes. They also are not readily bioavailable to aquatic organisms (Farrington 1986).

4.4.2 Migration

Several dispersal and weathering processes affect the fate of petroleum mixtures in soils. The most important of these are migration in the soil column, evaporation, dissolution in soil water, photochemical oxidation, and microbial degradation.

The rate and extent of migration of a petroleum product (NAPL) into and through soils depends on the viscosity, density, and interfacial tension of the oil, and the permeability of the soil (Strain 1986; Vandermeulen *et al.* 1988). Crude, refined, residual, and used petroleum products vary widely in density, interfacial tension, and viscosity (Table 4-1). Most crude oils and refined products have densities less than that of fresh water and, therefore, will tend to float on the upper interface of the subsurface water table. Any upward percolation of water through the soil column will tend to push the oil upward in the soil (Strain 1986). Some heavy crude oils and residual oils are more dense than water and sink when released in open water. They are so viscous that their rate of penetration into and migration through any but the coarsest gravel/cobble soils is very slow. The chronic or repeated nature of petroleum release or discharge to many terrestrial sites must be considered in predicting and evaluating migration of NAPL through soils.

Most crude oils and many intermediate and heavy distillate products are sufficiently viscous that they do not penetrate soils rapidly. Soils composed of fine-grained silt or clay particles, as well as sandy soils containing more than a few percent silt/clay, have very low permeabilities (Scheidegger 1957); migration and even diffusion of low molecular weight hydrocarbons and low-viscosity petroleum products is very slow in such soils (Mott and Weber 1991).

Table 4-1. Physical properties of crude, refined, residual, and waste oil that affect their behavior in soils. From Bobra and Callaghan (1990).

Oil Product	Density g/ml @ 10-20°C	Viscosity cP @ 15°C	Vapor Pressure kPa @ 37.8°C	Interfacial Tension dynes/cm
Crude Oil	0.790-0.988	2.06-34,000	<0.15-70.3	13.0-39.1
Naphtha (mineral spirits)	0.793	1.1	--	43.9
Naphtha (petroleum ether)	0.640	0.25	--	44.4
Aviation Gasoline	0.695-0.715	0.83	48	31.7-42.2
Gasoline	0.729	0.62	62-103	18.0
Kerosene	0.849	2.1	--	--
Jet Fuel, JP4	0.755	0.94	14-21	36.0
Jet Fuel, JP5	0.788	--	--	--
Jet Fuel, JP7	0.779	--	--	--
Jet Fuel, JP8	0.840	--	--	--
Jet Fuel, A	0.775	--	--	23.3
Jet Fuel, A1	0.804	1.26	--	40.4
Jet Fuel, B	0.757	1.02	21	12.4
No. 2 Fuel Oil	0.876	4.04	--	14.7
No. 2 Home Heating Oil	0.864	--	--	--
Marine Diesel	0.862	--	--	--
Diesel Fuel	0.827	2.7	--	29.4
No. 4 Fuel Oil	0.904	27.7	--	30.2
No. 5 Fuel Oil	0.923	--	--	--
Gas Turbine Fuel Oil	0.85-0.88	0.8-150	--	--
Lube Oil (gear oil)	0.883	975	--	3.4
Lube Oil (crankcase oil; new)	0.878	224.5	--	18.6
Lube Oil (crankcase oil; used)	0.885	175.2	--	24.4
Marine Intermediate Fuel	0.979	8,200	--	--
Bunker C (No. 6 Fuel Oil)	0.969	48,000	--	39.82
Bitumen	0.946-1.006	19,000->700,000	--	--
Crude Oil Condensate	0.823	2.02	--	29.6

Only products with low viscosities (less than about 3 centipoise at 15°C), such as naphtha, gasoline, kerosene, jet fuels, and some light crude oils may migrate through mixed grain size sand/silt/clay soils at moderate or high rates. Sandy soils and sediments have higher permeabilities and most distillate products and light to medium weight crude oils will migrate through them rapidly if the soils are not water-saturated. The interfacial tension between oil and water inhibits dispersal of oil into waterlogged soils. Because of the hydrophobicity of petroleum products, water-wet soils are not easily wetted by oils.

Weathering of crude and all but the lightest distillate fuels results in an increase in the viscosity and a decrease in the vapor pressure of the of the remaining petroleum material (Bobra and Callaghan 1990), further slowing penetration into and migration through the soil. Effects of weathering on interfacial tension are variable. However, all liquid petroleum products (those with pour points within the normal temperature range of soils) should be viewed as able to migrate through unsaturated soils at a finite rate. A heavy, viscous product that migrates through a soil at a rate of only about 1 mm/week will move about 2 feet in 10 years.

4.4.3 Evaporation

When a released petroleum product is exposed to air at the soil surface or in a moist, porous soil, the weathering process most affecting its fate in the environment is evaporation (Strain 1986). 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. 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) (Bobra *et al.* 1979). For homologous series, the rates of evaporation of different hydrocarbons are directly proportional to their vapor pressures, which are inversely proportional to their molecular weights (Mackay and Leinonen 1975). Aromatic hydrocarbons tend to evaporate more rapidly than alkanes of similar molecular weight, apparently because of the higher activity coefficients of aromatics than alkanes in the oil phase (Harrison *et al.* 1975). Thus, light aromatic hydrocarbons tend to be lost more rapidly than light alkanes from released oil. Park *et al.* (1990) found that between 15 and 30 percent of naphthalene and 1-methylnaphthalene were lost by volatilization from two PAH-contaminated soils; higher molecular weight PAH exhibited negligible (< 0.1 percent) volatilization in 48 hours. Gearing and Gearing (1982) found n-alkanes up through C_{20} in the air over a large outdoor seawater tank containing dispersed/dissolved No. 2 fuel oil. Prudhoe Bay crude oil exposed to the air and flowing water at low light intensity for 24 days lost all n-alkanes up through C_{10} and all monoaromatic hydrocarbons (Riley *et al.* 1981). Between 30 and 64 percent of the n-alkanes between C_{11} and C_{26} were lost, the relative amount decreasing with increasing chain length. Only about 45 percent of naphthalene and smaller amounts of higher molecular weight PAH were lost in 24 days. Thus, light aliphatic and aromatic hydrocarbons up to at least dodecane and methylnaphthalene readily evaporate from deposits of petroleum products on the soil or water surface. Hydrocarbons do not evaporate rapidly from petroleum deposits below the soil surface because of the limited flow of air over the petroleum (Wilson *et al.* 1981).

Light distillate fractions, such as gasoline, kerosine, and jet fuels and some very light crude oils, with boiling ranges mostly below about 250°C, may evaporate nearly completely from a soil or water surface or from a shallow porous deposit (Edgerton *et al.* 1987). Under typical environmental conditions, where the partial pressure of hydrocarbons in air is negligible, the rate of evaporation is proportional to the vapor pressure of the petroleum mixture, the mass transfer coefficient (which is proportional to the rate of air movement over the petroleum deposit), and the area of oil/air interface. Figure 4-1 shows the theoretical rate of evaporation of gasoline from a thick layer on the water surface, based on model calculations described by Nadeau and Mackay (1979). Nearly all the gasoline is predicted to evaporate within 14 hours. Thinner layers evaporate even more rapidly. As much as 50 to 60 percent of a light to medium crude oil on the water surface may be lost by evaporation in less than a week (Figure 4-2) if the layer of oil is thin (Wheeler 1978; Hurford and Buchanan 1989). The rate and maximum amount of crude oil that may evaporate from a surface deposit tend to decrease as the density of the oil increases (Mackay and McAuliffe 1988). For example, approximately 80 percent of Ekofisk crude oil (density, 0.804 g/ml) evaporates in 100 hours; approximately 10 percent of Tia Juana Pesado crude oil (density, 0.987 g/ml) evaporates in 100 hours. Most crude oils and refined products evaluated by Bobra and Callaghan (1990) have densities in this range (Table 4-1). Some residual oils and bitumens have higher densities and probably do not evaporate to a significant extent.

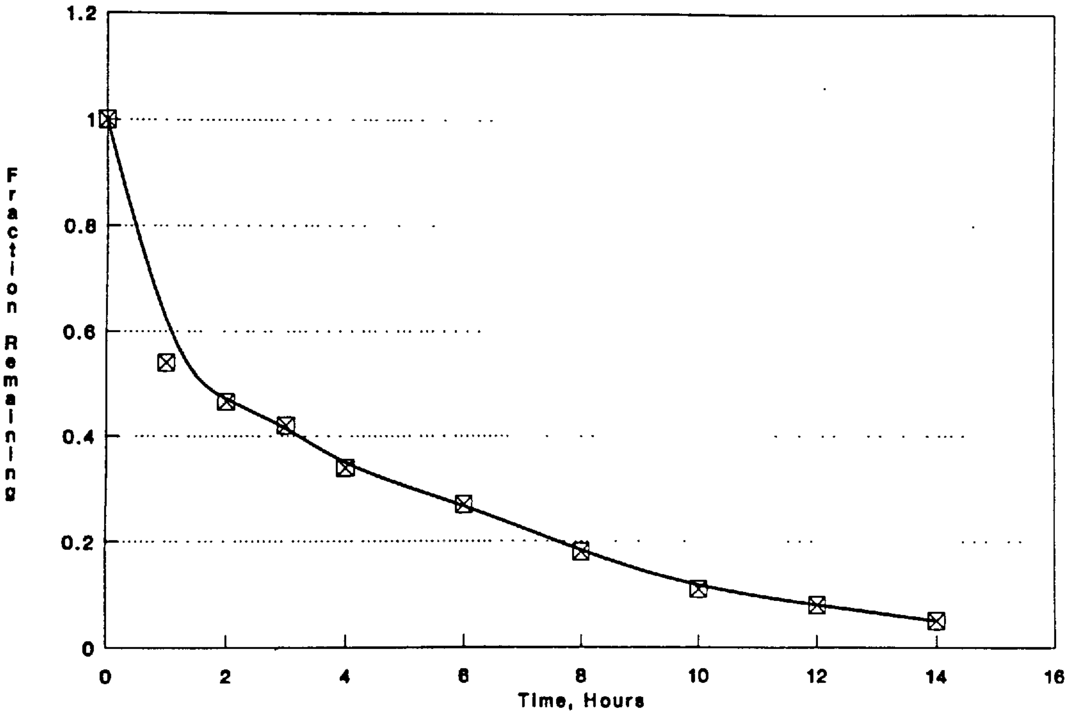

Figure 4-1. Gasoline evaporation from sea surface, assuming 20 MPH wind, 10°C temperature, 1000 BBL, boomed area 34,000 sq. ft. (Nadeau and Mackay, 1979)

Evaporation of gasoline-range hydrocarbons from the upper 20 cm of soil is quite rapid, particularly if the soil is slightly wet (Donaldson *et al.* 1992). Gasoline evaporated completely from moist soil in 8 to 16 days under summer conditions. Individual hydrocarbons from benzene to trimethylbenzene and n-dodecane behaved similarly.

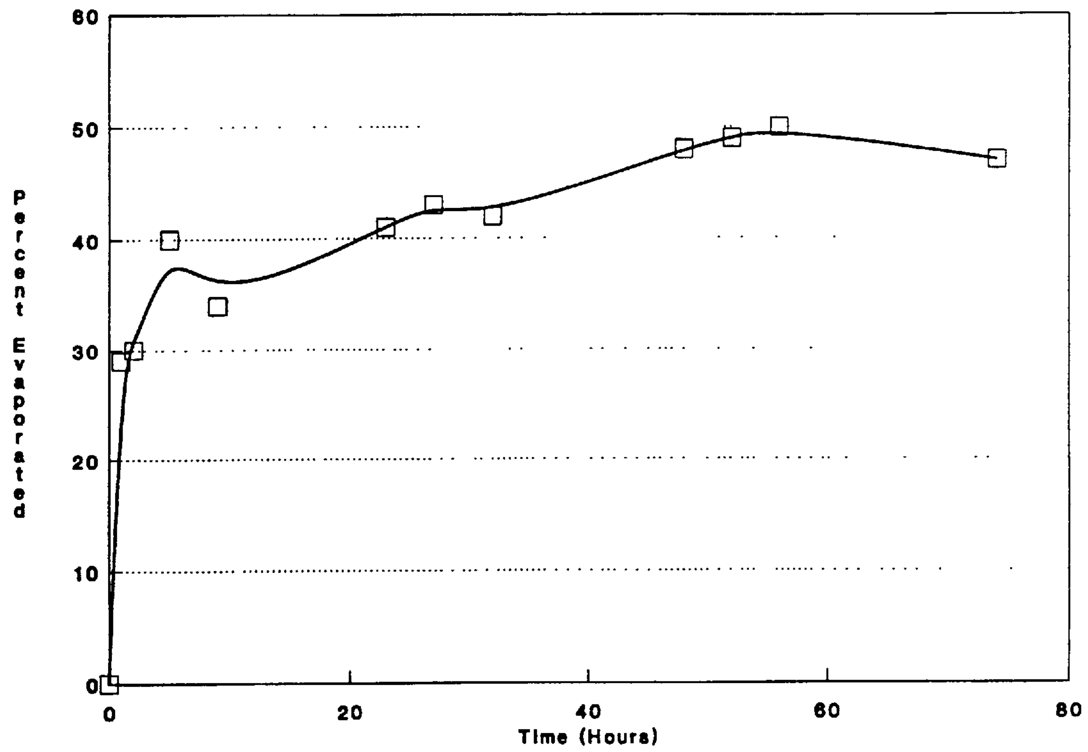

Figure 4-2. Evaporation of forties crude oil, 0.835 g/ml, 32.7% distilled at 180°C (Hurford and Buchanan, 1989)

Rates of evaporation of hydrocarbons from land-farmed petroleum sludges were affected by air velocity, temperature, organic loading, soil characteristics, and relative humidity (Thibodeaux and Hwang 1981). The rate of air movement over the surface of the petroleum deposit has a large effect on its rate of evaporation (Stiver and Mackay 1984). This relationship is expressed as the mass transfer coefficient, *k*, which has units of meters/second.

Evaporation of light hydrocarbons from the surface of an oil deposit increases the viscosity of the surface layer of the oil, inhibiting diffusion of light hydrocarbons to the surface from deeper in the deposit (Edgerton *et al.* 1987). In addition, as the lighter, more volatile components of the fuel are vaporized, net evaporation of the remaining fraction decreases (Mackay and Matsugu 1973).

There is a strong relationship between temperature and the vapor pressure of hydrocarbons, as expressed by the Clausius-Clapeyron equation. For most organic chemicals over a small range of vapor pressures, a plot of the log of vapor pressure versus the reciprocal of absolute temperature is essentially a straight line. The vapor pressure of benzene drops from 95.2 mm Hg at 25°C to 45.5 mm Hg at 10°C (Mackay and Leinonen 1975). The Henry's law constant (vapor pressure/solubility in water) of benzo(a)pyrene increases from 0.26 Pa m^3/mol at 10°C to 1.63 Pa m^3/mol at 35°C (ten Hulscher *et al.* 1992). Thus, temperature of the oil deposit on or in the soil has a marked influence on the rate of evaporation of volatile components from the oil (Reijnhart and Rose 1982; Edgerton *et al.* 1987). Gasoline released on ice evaporated completely after several days, but only 2 to 4 percent of diesel fuel released on ice evaporated in 10 days (Ramsler *et al.* 1973).

4.4.4 Dissolution

If oil deposited on land or percolating through soil comes in contact with water, some of the hydrocarbons in the petroleum will dissolve in the water phase. Dissolution is not as important as evaporation in removing hydrocarbons from released oil (Harrison *et al.* 1975). For example, in a crude oil release on water, rarely more than 5 percent of the oil goes into solution in the water phase (Payne *et al.* 1987). Even less oil would be expected to dissolve from oil on or mixed with soil. However, dissolution is very important with respect to contamination of groundwater. Because bulk petroleum products migrate slowly through any but the most permeable soils, the major mechanism for contamination of groundwater with petroleum hydrocarbons from all but the lowest viscosity petroleum products released on the surface is through transport in dissolved or finely dispersed form in water percolating through the soil column.

As discussed above, the tendency of a hydrocarbon to leave the oil phase and dissolve in water in contact with the oil is characterized by the partition coefficient between the oil and water phases. There is an inverse relationship among petroleum hydrocarbons between the value for K_{ow} and aqueous solubility (Appendix A). Hydrocarbons with values for log K_{ow} greater than about 4.5 (phenanthrene) and solubilities less than about 1 mg/L in fresh water do not partition effectively into water from oil, and only small amounts of these hydrocarbons will be transported through the soil column in solution.

Shiu *et al.* (1990) measured the relative solubility of several crude and refined oils in fresh water. When a petroleum product is layered on water and the two-phase system is stirred gently, hydrocarbons become distributed between the oil and water phases in relation to their relative solubilities in the two phases, defined by an equilibrium coefficient. None of the petroleum hydrocarbons reaches concentrations as high as their single-phase (aqueous) saturation concentration in the aqueous phase. The amounts of hydrocarbons that transfer into the aqueous phase depend on the water-to-oil volume ratio and the oil composition. As the water/oil ratio is increased by successive dilution for a given oil composition, the equilibrium concentrations of hydrocarbons in the aqueous phase decrease. Most of the decrease is caused by a marked decrease in concentrations of benzene, toluene, and xylenes in the water phase.

At water/oil ratios less than about 40 and a temperature of 22°C, between 7.75 and 58.0 mg/L total petroleum hydrocarbons from different crude oils go into solution (Table 4-2). Fuel and home heating oils have aqueous concentrations of about 2.5 to 6.5 mg/L. Gasolines produce the highest aqueous phase concentrations of the distillate products evaluated with equilibrium concentrations of 98 to 240 mg/L.

The most abundant hydrocarbons in most of the water-soluble fractions of crude and refined oils are the BTEX compounds (Shiu *et al.* 1990). These light aromatic compounds represent more than 90 percent of the total water-soluble fraction of some light distillate fuels. Naphthalene is present at trace concentrations in some water-soluble fractions. Water-soluble fractions of JP-4 and JP-8 jet fuels contain small amounts of cyclohexane, n-decane, and methylnaphthalenes (Smith *et al.* 1981). Water-soluble fractions of gasoline, kerosine, and diesel fuel contain small amounts (0.03 to 2.0 mg/L) of several alkylbenzenes, in addition to the dominant BTEX, as well as traces (0.03 to 0.1 mg/L) of methyl- and dimethylnaphthalenes (Thomas and Delfino 1991). Other components of the water-soluble fraction of crude and refined oils include light alkanes, ethane through heptane (total of about 0.1 to 10 mg/L), and traces of PAH with molecular weights higher than that of dimethylnaphthalenes (Anderson *et al.* 1974). Fluorene and phenanthrene may be present at concentrations up to about 0.01 mg/L. The solubility of oil decreases markedly as it

Table 4-2. Solubility of crude, refined, and residual petroleum products and the most abundant aromatic hydrocarbons in their water-soluble fractions. Concentrations are mg/L. From Shiu *et al.* (1990).

Petroleum Product	Total Petroleum Hydrocarbons	BTEX	Naphthalene
Norman Wells Crude (fresh)	29.39	20.84	0.1
(weathered)	0.36	0.05	0.03
Prudhoe Bay Crude	29.25	24.95	0.08
Kopanoar Crude	10.42	7.06	--
Hibernia Mobil B Crude	58.00	50.50	--
Hibernia J	7.75	6.68	0.02
Sable Island Gas Condensate	74.86	67.68	--
No. 2 Fuel Oil	2.76	1.28	0.11
No. 4 Fuel Oil	6.46	1.96	--
Home Heating Oil	3.12	1.16	--
Summer Gasoline	98.00	76.30	--
Unleaded Gasoline	112.00	84.40	0.20
Leaded Gasoline	240.00	215.50	0.20
Heavy Lube Oil	0.80	0.55	0.01
Crankcase Oil (new)	0.20	0.07	--
Crankcase Oil (used)	0.60	0.50	0.01
Diesel Fuel	2.80	1.56	0.09

weathers. Mackay and Shiu (1976) reported that the aqueous solubility of Norman Wells crude oil decreased from 32.3 to 0.14 mg/L during weathering, resulting in evaporation of 43 percent of the original mass of the oil. The decrease in solubility was caused by the loss of the more soluble lower molecular weight alkanes (C_1 through C_{12}) and light aromatic hydrocarbons by evaporation.

4.4.5 Photooxidation

Exposure of released crude or refined oil to solar radiation leads to a variety of photochemical reactions that produce a variety of mostly more polar organic compounds. These new compounds, although usually representing less than about one percent of the original oil (Ducreaux *et al.* 1986), have important effects on the behavior of the oil. Aromatic and heterocyclic compounds in oil are the most sensitive to photochemical reactions, though some alkanes also are photo-sensitive. The primary mechanism of photodegradation in a solid petroleum deposit is photo- oxidation involving singlet oxygen (Larson *et al.* 1977; Thominette and Verdu 1984a). The major photoreaction products are peroxides, aldehydes, ketones, alcohols, and fatty acids, all of which are more soluble than the parent compounds (Payne and McNabb 1985). Dibenzothiophene and its C_1 through C_3 alkyl homologues in released crude oil are photooxidized to their respective sulfoxides under natural conditions (Patel *et al.* 1979). Photooxidation also may lead to polymerization reactions to produce high molecular weight compounds that are not soluble in water or oil (Thominette and Verdu 1984b; Daling 1988). The rate of photooxidation seems to increase as the concentrations of PAH and sulfur compounds increase in the oil, and as light intensity at the oil surface increases. Among PAH, photodegradation rates increase as molecular weight increases (Mill *et al.* 1981 Valerio and Lazzarotto 1985). The half-time for photolysis of naphthalene in JP-4 jet fuel is about nine days (Smith *et al.* 1981). Oil deposits only a few millimeters below the soil or sediment surface do not photodegrade.

Photolysis has a variety of effects on the physical/chemical properties of released oil (Bobra and Tennyson 1989). The color of some oils, such as diesel fuel, changes. Precipitates may form at the oil/air or oil/water interface. Some crude and refined oils develop a hard surface crust. The density of some oils increases during photolysis, possibly due to polymerization of low molecular weight, low density compounds to more dense products. During photolysis, the viscosity of oils often increases and the interfacial tension decreases, at least initially. The decrease in interfacial tension may be caused by accumulation at the oil surface of surface-active agents (detergents) produced by photolysis. The concentration of the asphaltene fraction in the oil may increase due to precipitation of some photolysis products in the oil.

Evaporation, dissolution, and photooxidation have profound effects on the physical and chemical properties of a petroleum product on or in soils. Loss of low molecular weight saturated and aromatic hydrocarbons increases the density and viscosity of the oil and decreases its total solubility and vapor pressure (Bobra and Fingas 1986). Photooxidation converts some higher molecular weight components of the petroleum product to water-soluble products and polymerizes others to viscous, refractory residues. The viscosity of the petroleum product may increase by several orders of magnitude. The concentrations of the tarry resin and asphaltene fractions of middle and heavy distillate fuels and crude oils increase, favoring formation of asphalt pavements. Solidification occurs most rapidly at the surface of the oil deposit, slowing evaporation, dissolution, and photooxidation of residues deeper in the oil layer. Tar mats and asphalt pavements typically develop a crust composed primarily of non-volatile oil components, covering a core of less weathered oil containing high concentrations of light hydrocarbons (Payne and Phillips 1985).

4.4.6 Biodegradation

Nearly all soils and sediments contain colonies of bacteria and fungi that are capable of biodegrading at least some petroleum hydrocarbons (Leahy and Colwell 1990). 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 (Fedorak and Westlake 1984, Bossert and Bartha 1986, Kuhn and Suflita 1989, Qiu and McFarland 1991). For example, Qiu and McFarland (1991) showed that the soil fungus *Phanerochaete chrysosporium* caused benzo(a)pyrene to bind to soil (humification), rather than biodegrade to CO_2 and water. It is probable that the fungus converted the benzo(a)pyrene to oxygenated metabolites that bound covalently to soil humic material.

A wide variety of environmental and chemical factors affect the rate of biodegradation of petroleum products in soils and sediments, including oxygen concentration, temperature, nutrients (especially nitrogen and phosphorus), the physical state and chemical composition of the oil, and the previous history of oil pollution at the release site (Atlas 1981; Bartha and Atlas 1987; Leahy and Colwell 1990). Although many species of bacteria are able to metabolize petroleum hydrocarbons and hetero compounds in the absence of oxygen (Kuhn and Suflita 1989; McFarland and Sims 1991), all the available evidence indicates that rates of hydrocarbon degradation are much lower under anoxic than oxygen-rich conditions (Johnston 1970, Bauer and Capone 1985). Bauer and Capone (1985) observed that the rate of biodegradation of naphthalene in sediments increased as the concentration of oxygen increased (Figure 4-3). Oxygen stimulated naphthalene degradation most in acclimated sediments (sediments that already contained petroleum hydrocarbons).

Part of the negative effect of low oxygen concentrations on microbial degradation of hydrocarbons in soils and sediments may be related to availability of primary nutrients. Mineralization of organic matter, resulting in the release of inorganic nitrogen and phosphorus, is very slow in anoxic soils. Hydrocarbons, being rich in carbon but deficient in nitrogen and phosphorus, are an inadequate nutrient source for microbes in the absence of exogenous sources of available nitrogen and phosphorus. Scherrer and Mille (1989) showed that the rate of degradation of petroleum hydrocarbons was extremely slow in a peaty mangrove soil, despite the fact that the soil was periodically oxygenated. However, hydrocarbon degradation was stimulated by addition of an oleophilic fertilizer, indicating that the microbes were nutrient-limited. Thus, petroleum products may be extremely persistent in anoxic or hypoxic soils.

Although bacteria can degrade hydrocarbons over a wide temperature range, extending from below 0°C to 70°C (Atlas 1981), the rate of hydrocarbon degradation is highly temperature-dependent. The rate of hydrocarbon biodegradation in a gravel soil increased 3.3-fold between 6 and 16°C, and 2-fold between 11 and 21°C (Gibbs and Davis 1976). Coover and Sims (1987) reported that the rate of apparent biodegradation of two-, three-, and four-ring PAH, but not of five- and six-ring PAH, increased with increasing temperature between 10 and 30°C.

In some cases, the effect of temperature on microbial degradation is due to the presence in the oil of volatile, toxic hydrocarbons, such as benzene and toluene (Atlas and Bartha 1972). Low temperatures retard evaporation of some volatile hydrocarbons that are toxic to bacteria, delaying the onset of oil biodegradation. Light distillation products, such as gasoline, that are rich in BTEX compounds, may need to weather slightly before they can be biodegraded.

Following a release of crude or refined petroleum to soils or sediments, different hydrocarbon classes are degraded simultaneously, but at widely different rates by indigenous microbiota (Atlas *et al.* 1981; Bartha and Atlas 1987; Gough *et al.* 1992). 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 PAH of similar molecular weight (Fedorak and Westlake 1984, Kuhn and Suflita 1989). Indigenous microorganisms in the soil/groundwater of a creosote-contaminated site degraded 99, 94, 88, and 87 percent of the lower molecular

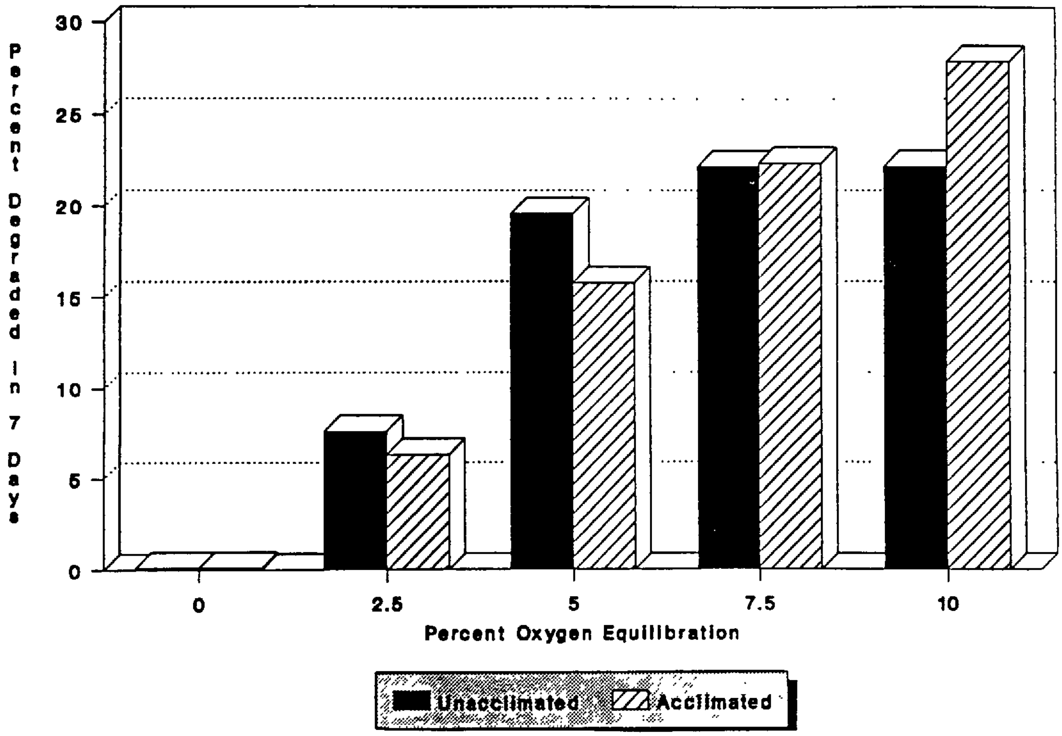

Figure 4-3. Bacterial Degradation of Naphthalene, Effect of Oxygen in Sediments (Bauer and Capone, 1985)

weight PAH, S-heterocyclics, N-heterocyclics, and O-heterocyclics, respectively in 14 days (Mueller *et al.* 1991). Only 53 percent of the higher molecular weight PAH were degraded. Some high molecular weight PAH, such as chrysene, dibenzanthracene, and perylene are degraded only very slowly in most soils (Bossert and Bartha 1986). Under anaerobic conditions, nitrogen and oxygen heterocyclics are more susceptible than sulfur heterocyclics to biodegradation (Kuhn and Suflita 1989). Soil microorganisms at a gasoline-contaminated site rapidly degraded benzene, toluene, xylenes, ethylbenzene, and tert-butanol (Thomas *et al.* 1988). m-Xylene was degraded more rapidly than o-xylene. Addition of peroxide (Thomas *et al.* 1988) or nitrate/nitrite (as an alternative terminal electron acceptor) (Gersberg *et al.* 1991) stimulated biodegradation, suggesting that the microbes were oxygen-limited.

Complex cycloalkanes, such as steranes and triterpanes are extremely resistant to microbial degradation (Hughes and Holba 1987). Because of the persistence of sulfur heterocyclics, such as dibenzothiophene and its alkyl homologues, and steranes and triterpanes, they are being used with increasing frequency to fingerprint and identify the sources of complex hydrocarbon mixtures in soils and sediments (Seifert and Moldowan 1978; Sinkkinen 1989).

In the scientific literature, there are several measurements in the scientific literature of the rates of degradation of petroleum hydrocarbons in soils and sediments. Often, microbial degradation is not differentiated from evaporation and dissolution/leaching. Thus, earlier studies probably overestimated the rate of biodegradation of petroleum hydrocarbons from soils. Kincannon (1972) reported that tank bottoms, residual fuel oil, and a waxy refined product, applied to surface soils, were degraded at a rate of 2.08 liters/m^2/month. Used crankcase oil applied to soil was degraded at an estimated rate of 2.98 liters/m^2/month (Francke and Clark 1974). However, Raymond *et al.* (1976) reported that, even under optimum conditions, degradation of oil by soil microorganisms rarely exceeded 0.6 liters/m^2/month. The rate of biodegradation of crude and refined oils in well-oxygenated surface sediments and soils has been estimated to be in the range of 0.006 to 0.12 liters/m^2/month (GESAMP 1977). Atlas and Bronner (1981) estimated that petroleum hydrocarbons were being degraded at a rate of 1.5 grams/m^2/month in the upper 5 cm of intertidal sediments along the Brittany coast of France, impacted by the *Amoco Cadiz* oil release. After eight years, concentrations of alkanes (originally present at concentrations of 2,400 to 17,000 μg/g) and aromatic hydrocarbons (originally present at concentrations of 740 to 5,500 μg/g) in intertidal soft sediments near the release site had dropped to near background levels (Page *et al.* 1989). Massie *et al.* (1985) estimated that the rate of degradation of naphthalene in offshore marine sediments ranged from 0.06 to 93.6 grams/m^2/month; the degradation rate of benzo(a)pyrene rarely exceeded 0.8 grams/m^2/month.

In most cases, the rate of degradation of petroleum hydrocarbons in contaminated soils is too slow under natural, undisturbed conditions for the hydrocarbons to disappear in a reasonable amount of time (within a few years). Activities that increase aeration of the soil, irrigate the soil with water, and provide essential primary nutrients (especially nitrogen and phosphorus) greatly accelerate the rate of loss of hydrocarbons from the soil by evaporation, leaching, photooxidation, and microbial action. For example, Dibble and Bartha (1979) studied the loss of petroleum hydrocarbons from a 1.5-hectare field that had been contaminated with 1.9 million liters of kerosene. The field was limed and fertilized periodically and tilled frequently.

Concentrations of hydrocarbons in the soil decrease rapidly and normal biological production of the field was resumed after one year; after two years, concentrations of petroleum hydrocarbons were at or near background.

4.4.7 Fate of Compounds of Concern in Soils

The chemicals chosen for more detailed evaluation in this study span a wide range of physical/chemical properties (Table 3-2). All the alkanes, as well as naphthalene have boiling points below about 250°C and relatively high Henry's law constants (above about 0.05 atm m^3/mol). Therefore, they will tend to evaporate rapidly from aerated soils. They also have high aqueous solubilities and low values for K_{ow}. Therefore, they will tend to be leached out of oily deposits into soil water and possibly migrate into groundwater. However, these compounds, particularly the alkanes, are highly biodegradable. In the presence of adequate supplies of oxygen and primary nutrients in the soil, they will be biodegraded by indigenous soil microbiota.

Dibenzothiophene and 1-methylphenanthrene are not sufficiently volatile to evaporate in significant amounts. However, they are sufficiently soluble that they may be leached into soil water and migrate with it to groundwater. With values for log K_{ow} of about 5.0, they will have a high affinity for the sorbed (particulate organic carbon) phase of the soil. However, significant migration through soils could occur if the concentration of organic carbon in the soil is very low or the concentration of dissolved organic carbon in the soil water is high.

The three higher molecular weight PAH, 5-methylchrysene, benzo(a)pyrene, and benz(a)anthracene, have very low aqueous solubilities and high values for log K_{ow}. Their mobility in soils will be very low. If exposed to sunlight at the soil surface, they will be photolyzed rapidly. However, they are relatively refractory to biodegradation by soil microbes. Therefore, they will tend to be immobile and persistent if present below the soil surface, particularly if the soils are hypoxic or anoxic.

The twelve model compounds, representative of the range of organic chemicals in crude, refined, residual, and used oils released on land, can be divided into three classes with respect to their fate in soils. These classes are:

- Moderately to highly mobile compounds that will readily evaporate, biodegrade, or leach into soil water: naphthalene, 2-methylnaphthalene, cyclohexane, n-hexane, 2,3-dimethylbutane, and 2,2-dimethylpentane.
- Slightly mobile compounds that could migrate through soils under some conditions and are moderately biodegradable. They will not evaporate to a significant extent: dibenzothiophene and 1-methylphenanthrene.

- Immobile or nearly immobile compounds that bind tightly to soil particles and are relatively refractory to biodegradation. They are sensitive to photolysis: benz(a)anthracene, benzo(a)pyrene, and 5-methylchrysene.

Section 5 considers subsurface transport issues in greater detail.

Section 5

SUBSURFACE TRANSPORT OF PETROLEUM HYDROCARBONS

5.1 Introduction

Predicting the behavior of crude, refined, residual, and used petroleum released to the environment is a fundamental part of understanding, and then evaluating and developing plans for mitigating their potential impacts. In order to qualitatively or quantitatively evaluate environmental behavior, the physical and chemical processes, together with the physical and chemical properties, of the complex petroleum products and the individual hydrocarbons in them must be known or estimated. Various natural physical, chemical, and biological processes control the transport and transformations of petroleum mixtures and individual hydrocarbons in the environment; the physical and chemical properties characterize the behavior of chemicals under different environmental conditions.

The processes that govern subsurface transport of petroleum hydrocarbons can be evaluated in terms of the following three basic processes, or groups of processes:

- Transport of oil phase petroleum hydrocarbons, also commonly referred to as non aqueous phase liquid (NAPL). In environmental situations where NAPL transport occurs, this process can produce substantially higher transport rates and lead to much more difficult remediation than transport of dissolved or adsorbed compounds.

- Mass transfer among various phases (solid, liquid, and gas) as well as among the three relevant environmental media (soil, water, and air). During mass transfer the hydrocarbons become dissolved in or adsorbed onto the various environmental media. Mass transfer among the three environmental media also occurs after the compounds have left the oil phase. Mass transfer processes result in a dynamic balance being achieved by petroleum hydrocarbons, or other chemicals, released into the subsurface environment.

- Transport of petroleum hydrocarbons with and within the environmental media with which they become associated through mass transfer processes. Examples of such transport include dissolved contaminant transport in groundwater and diffusion of vapors in the air.

The physical and chemical properties controlling subsurface hydrocarbon transport include a combination of intrinsic properties of the environmental media (such as soil permeability or porosity), ambient conditions (such as temperature and moisture content), and chemical specific properties (such as viscosity and density). In this report, we provide some discussion of the relevant properties of different environmental media and ambient conditions, but focus on the influence of the specific physical and chemical properties of the different non-BTEX organic components of petroleum products on their transport and fate in the soil/groundwater environment.

The chemical and biological transformation (degradation) processes discussed in Section 4 can change the chemical characteristics of the petroleum hydrocarbons during transport. Such transformations alter the chemical and physical properties that govern the transport processes. The effects of these transformation processes on subsurface transport of petroleum hydrocarbons is not addressed here because of the lack of adequate information regarding the identity and properties of the transformation products. Where the properties of these transformation products are known, however, the same evaluation as is applied here to the compounds chosen for evaluation in this report may be used.

The geologic medium available for hydrocarbon transport can be divided into unsaturated and saturated zones. The unsaturated zone of an aquifer extends from the groundsurface to the water table, a depth at which groundwater is at atmospheric pressure. In the unsaturated region, groundwater occupies only a fraction of the available geologic pore space with the remainder occupied by air. The unsaturated zone is further subdivided into the vadose zone typified by a low water content, a transition zone with intermediate water content levels, and the capillary fringe which is primarily saturated, but at a water pressure less than barometric, due to capillary suction of water from the water table. The saturated zone of an aquifer extends downward from the depth at which groundwater is at atmospheric pressure. In this zone there are no continuous, air filled pores.

Section 5 is organized into three subsections following this introduction. Initially, the section on General Subsurface Transport Processes (5.2) provides a background discussion of the processes and properties of greatest interest with regard to subsurface transport of petroleum hydrocarbons. The next section (5.3) then evaluates the behaviors of the compounds selected for review in this report (Table 3-2). Finally, Section 5.4 summarizes the results from the various evaluation methods presented in this Section.

5.2 General Subsurface Transport Processes

Transport processes control the physical motion of chemicals through and between different environmental media. The transport processes of primary interest are direct motion and advection of NAPL, NAPL/water dispersion, and diffusion of dissolved compounds. Advective transport is movement of a compound with an environmental medium with which it is associated. For example, movement of dissolved hydrocarbons with groundwater is considered to be advection. Dispersive and diffusive transport cause movement of compounds within environmental media. Both dispersion and diffusion typically cause spreading (dilution) of a plume and concurrently cause the leading edge of a plume to advance more rapidly than the centroid, which is governed by advective transport. Dispersion is caused by wide variability in actual flow paths within a porous medium. Dispersion is not, however, a fundamental transport process, but a concept used to provide quantitative adjustments related to the spatial scale at which transport in groundwater is typically evaluated. Diffusion is the molecular transport of a substance caused by concentration gradients.

When petroleum hydrocarbons are released to the subsurface environment, they are usually initially in the oil phase as NAPL. Direct NAPL transport is, therefore, the first key process to consider. Constituents of the NAPL subsequently dissolve in water, evaporate into air, and adsorb onto soil. The rate at which NAPL constituents transfer into these environmental media and the relative partitioning among these three media is the second key element to consider. Finally, motion of the dissolved and vapor phases within the unsaturated and saturated zones must be considered. These three issues, direct NAPL transport, constituent transfer into association with the various environmental media, and constituent dissolved phase transport, are discussed below.

5.2.1 NAPL Transport Processes

The basic processes governing subsurface NAPL transport are essentially the same as those governing subsurface water transport. The transport 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. Quantitative evaluation of NAPL transport is complicated, however, with respect to the procedures commonly used for water transport. The common methods for evaluating water transport are single-phase methods whereas multi-phase, generally two-phase, methods are frequently needed to quantify NAPL transport.

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 as it migrated downward.
- 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 aquifer 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.

NAPL that is denser than water (DNAPL) may disperse through the aquifer in droplets, sink to a level in the aquifer where the permeability is too low to be overcome by gravity, or it may segregate out into various fractions with different properties. The various fractions would then behave independently.

Either during its migration, or if relatively stable NAPL pools develop, diffusion between the NAPL mass and its surroundings will occur as a result of the large concentration gradients. If the NAPL is at or sufficiently near the ground surface to allow air exchange, the lower molecular weight hydrocarbons within the NAPL will evaporate into the air 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 transfer 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, as discussed in Section 4, that they will remain as NAPL essentially indefinitely, or solidify as the lighter fractions are removed.

The properties of petroleum products with the greatest influence on NAPL movement include viscosity, density, and interfacial tension. These properties are defined as follows. Numerical estimates for these parameters are presented later.

5.2.1.1 Viscosity. Viscosity is the resistance of a fluid to flow under an applied force. Fluids with higher viscosities will flow more slowly than those with lower viscosities, given the same head gradient and properties of the medium through which they are flowing. Liquid viscosity usually increases with decreasing temperature, though, in some complex organic mixtures, there may be a discontinuity in the temperature/viscosity relationship where there is a large change in viscosity over a very narrow temperature range. An ideal fluid is one that is devoid of viscosity. Materials with little internal structure tend to behave as ideal fluids. Therefore, water at room temperature and pressure tends to behave as an ideal fluid, whereas mixtures containing long chain molecules, such as many petroleum products, rarely do. The viscosity of petroleum products varies widely from about 0.25 to more than 50,000 cP at 15°C (Table 4-1).

Viscosity of petroleum products tends to increase sharply during natural weathering processes.

5.2.1.2 Density. Density is the ratio of mass to volume. As mentioned above, if the NAPL density is less than that of the ambient water, it will float; if greater, it will sink. The density of distilled water at standard temperature and pressure is 1.0 g/mL. Most crude, refined, residual, and used oils have densities in the range of about 0.6 to 1.0 g/mL (Table 4-1).

5.2.1.3 Surface or Interfacial Tension. Surface or interfacial tension is defined as the force per unit length which resists the expansion of a surface. This tensile force acts perpendicular to any reference line across the surface and is due to the cohesive properties of the molecules which comprise the fluid. Surface tension represents the work necessary to form an additional unit area of surface. Surface tension is often referred to as the interfacial tension resulting between a substance and its own vapor. Surface tension is frequently equated with interfacial tension in various literature sources. Although an important property, interfacial tension is difficult to quantify in a manner to be usable to evaluate environmental behavior of hydrocarbon mixtures. It is not, therefore, considered a primary property for evaluating the transport of individual hydrocarbons, and values are not presented in Table 3-2. Interfacial tension of different petroleum products are in the range of 3 to 50 dynes/cm. Direct measurements of residual saturation values for NAPL in various types of soil tend to be more useful than interfacial tension for predicting migration through soils.

Vapor pressure and solubility influence the NAPL depletion rate, but have little direct influence on NAPL movement.

5.2.2 Partitioning

The term partition is defined in chemical literature as the segregation of a compound, under equilibrium conditions, between two or more states of matter. For example, a substance may be partitioned between its liquid and gaseous state, or pertinent to this study, a compound can be referred to as being partitioned between the amount sorbed to a soil matrix and dissolved within soil moisture. The underlying assumption is that the partitioning represents equilibrium concentrations and is therefore independent of time. Commonly, the exchange of mass necessary to achieve equilibrium is referred to as partitioning, implying dynamics, and thus time dependent behavior. This may create confusion between the use of partitioning as a mass transfer process necessary to achieve equilibrium, and partitioning (or partitioned) as the ratio of concentrations present at equilibrium. In this report, the term 'partitioning' is used interchangeably to refer to the process necessary to achieve equilibrium as well as the concentration ratio between two states of matter. However, it should be kept in mind that partitioning is an equilibrium concept and partition coefficients used to numerically represent partitioning are applicable only under equilibrium conditions.

Two basic types of partitioning are significant when evaluating subsurface transport of petroleum hydrocarbons. The first is partitioning of a compound from the NAPL (oil phase) into the air and water. These are the processes of evaporation and dissolution discussed in Section 4. Second, after removal from the oil phase (NAPL), petroleum hydrocarbons dissolved in water or present in the vapor phase will partition among the three phases in the subsurface environment, solids (soils, rocks), liquid (predominantly water), and air. Mathematical representations of the equilibrium partitioning between these three phases have been developed in terms of fugacity by MacKay (1979), and MacKay and Paterson (1988). These relationships in Section 5.3 are used to assess environmental behavior. Fugacity has units of pressure, and its simplest definition can be regarded as the "escaping tendency" of a compound. A compound will transfer from areas of high fugacity to low fugacity in the same manner that heat is transferred from areas of high temperature to low temperature. Therefore, at compositional equilibrium, phase fugacities are equal since no mass transfer is occurring.

The MacKay (1979) equations relate the total amount of a compound available in terms of the amount of compound partitioned, the fugacity, and the available volume of each phase by:

$$M = \Sigma M_i = \Sigma (f_i V_i Z_i) \qquad (5\text{-}1)$$

where M is the total number of moles available, M_i is the moles associated with compartment i, f_i is the fugacity in compartment i, V_i is the volume of compartment i, and Z_i the Z value which quantifies the capacity of the phase for fugacity. Z values are related to the physical/chemical parameters as:

$$Z_1 = 1/RT \qquad (5\text{-}2)$$
$$Z_2 = 1/H \qquad (5\text{-}3)$$
$$Z_3 = (\rho K_d)/H \qquad (5\text{-}4)$$

where:

R = the ideal gas constant
T = temperature
H = Henry's law constant
K_d = soil partition coefficient
ρ = Soil bulk density

Under equilibrium conditions, the f_i values in each compartment are equal. Equilibrium of phase compositions is expressed by:

$$\int_0^{C_e} dC = \int_0^{f_e} Z df \qquad (5\text{-}5)$$

where:

C = concentration
C_e = equilibrium concentration
Z = fugacity capacity
f = fugacity
f_e = equilibrium fugacity

If the fugacity capacity is constant, the equation can be simply integrated. Otherwise, the fugacity capacity must be known as a function of the fugacity in order to integrate. For the purposes of this report, the fugacity capacity is assumed constant. Under equilibrium conditions, when $f_1 = f_2 = f_3$, the proportion in each phase can then be approximated as:

Soil Air Fraction: $M_1/M = f_1V_1Z_1/\Sigma(f_iV_iZ_i) = V_1Z_1/\Sigma(V_iZ_i)$ (5-6)
Soil Water Fraction: $M_2/M = f_2V_2Z_2/\Sigma(f_iV_iZ_i) = V_2Z_2/\Sigma(V_iZ_i)$ (5-7)
Soil Solids Fraction: $M_3/M = f_3V_3Z_3/\Sigma(f_iV_iZ_i) = V_3Z_3/\Sigma(V_iZ_i)$ (5-8)

If the phase concentration of a particular solute is high, the assumption of constant fugacity capacity no longer holds. For example, if the aqueous phase concentration at equilibrium is high, the assumption of constant $Z_2 = 1/H$ does not hold, since Henry's Law only applies for dilute solutions.

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Soil Water Fraction: $M_2/M = f_2V_2Z_2/\Sigma(f_iV_iZ_i)=V_2Z_2/\Sigma(V_iZ_i)$ (5-7)
Soil Solids Fraction: $M_3/M = f_3V_3Z_3/\Sigma(f_iV_iZ_i)=V_3Z_3/\Sigma(V_iZ_i)$ (5-8)

If the phase concentration of a particular solute is high, the assumption of constant fugacity capacity no longer holds. For example, if the aqueous phase concentration at equilibrium is high, the assumption of constant $Z_2 = 1/H$ does not hold, since Henry's Law only applies for dilute solutions.

Figure 5-1 is a triangular diagram that can be used to illustrate this equilibrium partitioning. This representation will be used later to represent the relative equilibrium partitioning, for the selected compounds as well as for BTEX. These partitioning diagrams can be used to characterize, in a simple way, some key general issues regarding subsurface transport. For example, compound X in Figure 5-1 has partitioned 70 percent to the soil matrix, 9 percent to water, and 21 percent to the air.

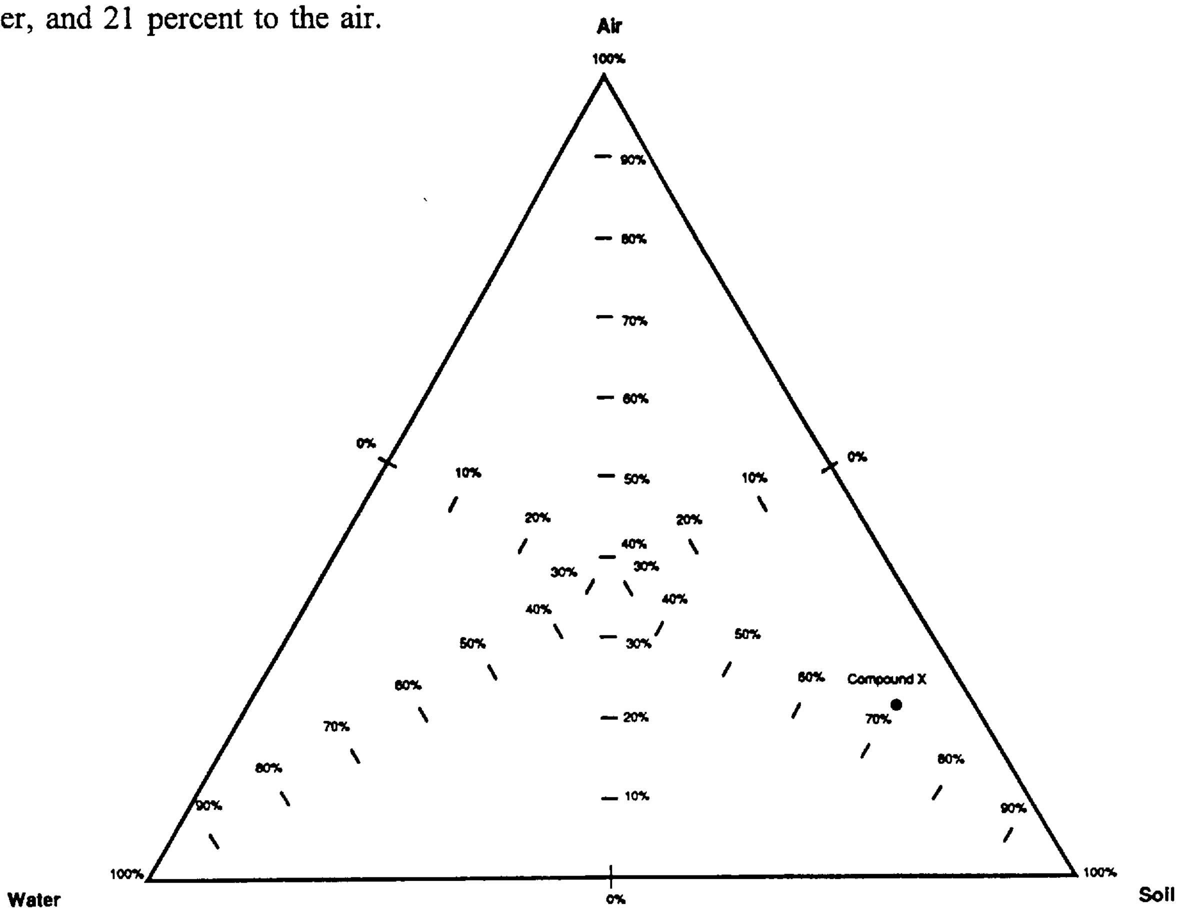


Figure 5-1. Triangular Diagram Used to Illustrate Equilibrium Partitioning (Compound X is partitioned 70% onto soil, 20% into air, and 10% into water)

In general compounds with a higher proportion in water will tend to be more mobile in groundwater; compounds with a higher proportion in air will tend to be more mobile in air (soil pores); and compounds with a higher proportion adsorbed to soils will tend to move with (or stay with) soils.

Partitioning of water-dissolved compounds onto solids and into air has been more thoroughly characterized than the partitioning process directly between the vapor and solid phases. These two partitioning processes are described in greater detail below.

Aqueous/Solid Phase Partitioning. This type of partitioning is commonly referred to as soil adsorption and quantified by a soil partition coefficient (K_d) which is the proportionality constant relating the amount of chemical sorbed ($C_s = \mu g$ adsorbed/g soil) to the concentration in water ($C_w = \mu g$ dissolved/ml of solution) as:

$$C_s = K_d C_w^{\ 1/n} \tag{5-9}$$

where values of 1/n typically range from 0.7 to 1.1 (Lyman, *et al.* 1982). 1/n is an exponential factor dependent on the abundance of binding sites on the sorbent relative to the abundance of sorbate molecules. It is an indication of the intensity of the sorptive reaction. For low molecular weight, nonpolar organic solutes with low aqueous solubilities at low concentrations in solution (less than 10^{-5}M or half their aqueous solubility, whichever is lower), the term, 1/n, approximates unity. Under these conditions (which will apply for all non-BTEX petroleum hydrocarbons partitioning from a petroleum NAPL into soil water), a plot of C_s versus C_w yields a straight line (a linear isotherm), the slope of which is K_d. The equation can be rewritten as:

$$K_d = C_s/C_w \tag{5-10}$$

Sorption studies on a wide variety of nonpolar organic compounds and soil and sediment types, indicate that organic matter dominates or controls sorption where there is sufficient organic matter present (more than about 0.1 percent organic carbon). K_d can also vary depending upon conditions such as pH, redox potential, and major ion composition of soil water.

The primary effect of aqueous/solid phase partitioning on contaminant transport is to retard chemical transport relative to water flow rates. This is typically represented in terms of a retardation factor (R) that is mathematically related to K_d as:

$$R = 1 + \frac{\rho_b K_d}{n} \tag{5-11}$$

where ρ_b is the bulk or mass density of the porous medium and n is the porosity of the medium.

Soils are extremely heterogeneous mixtures of different particle types and sizes. Because of this heterogeneity, the K_d for a particular chemical is likely to vary substantially, depending on the chemical composition and grain size of the soil used for the K_d determination. Therefore, many attempts have been made to normalize K_d values to some property of sediments that will allow effects of other properties of the soils to be canceled out, giving a partition coefficient that does not vary much with soil type. The normalizing factor had to be the soil property that most influenced the sorption of solutes to the soil particles. Lambert *et al.* (1965) and Lambert (1968) have shown that the sorption of a nonpolar organic compound to soils correlates well with the concentration of organic matter in the soil. This observation has been used as the basis for normalizing the linear partition coefficient to the concentration of total organic carbon in the soil (Karickhoff *et al.* 1979, Karickhoff 1981, Voice and Weber 1983, Weber *et al.* 1983). The normalized partition coefficient, K_{oc}, is calculated according to the following formula:

$$K_{oc} = \frac{K_d}{f_{oc}} \tag{5-12}$$

where f_{oc} is the fraction of organic carbon in the sediment. Karickhoff *et al.* (1979) plotted the K_d of phenanthrene and pyrene against fraction organic carbon in sediment samples from a wide variety of sources and found a linear relationship between the fraction organic carbon in the different sediments and the value for K_d. K_d values showed a 20- to 30-fold variation for the group of sediments with concentrations of organic carbon ranging from 0.11 to 2.38 percent (f_{oc} 0.001 to 0.0238). The corresponding values for K_{oc} varied by only about two-fold. Clays have a high binding capacity for organic solutes. In clay soils containing low concentrations of organic carbon, sorption is primarily to the surface of the clay particles or to hydrous iron and manganese oxide coatings on clay particles. However, if the clay soil contains more than about 0.1 percent organic carbon, most of the organic matter is present as surface coatings on the clay particles and serves as the site of sorption of nonpolar organic solutes (Weber *et al.* 1983).

The type of organic material associated with the sorbent phase does not seem to have much effect on partitioning (Voice and Weber 1983). Thus, normalization to organic carbon concentration in the soil or sediment substantially decreases the variability of the estimated partition coefficient. This relationship seems to hold for nonpolar organic compounds with aqueous solubilities less than about 10^{-3}M and for sediments containing more than about 0.1 percent organic carbon ($f_{oc} > 0.001$).

Outside this range of values, however, K_d cannot be reliably estimated through the relationship shown in Equation 5-12. In the absence of direct measurements, K_{oc} values can be estimated for a particular compound if a correlation can be found between K_{oc} and other widely-measured and catalogued parameters of nonpolar organic solutes. Two possibly applicable parameters are octanol/water partition coefficient (K_{ow}) (Briggs 1973, Hansch and

Leo 1979) and aqueous solubility (S) (Karickhoff *et al.* 1979). These empirical relationships often are expressed as regression equations of the form:

$$\log K_{oc} = a \log S + b \qquad (5\text{-}13)$$

$$\log K_{oc} = a \log K_{ow} + B \qquad (5\text{-}14)$$

where a and b are constants. The values for a and b vary, depending on the group of solutes being evaluated. A large number of different values for a and b have been reported in the literature for different groups of unionizable and ionizable nonpolar organic compounds (Farrington and Westall 1986). Equations applicable to the hydrocarbons of interest here are summarized in Table 5-1.

Table 5-1. Regression Equations for the Estimation of K_{oc}

Equation	Chemical Classes Represented	Ref.
Log K_{oc} = -0.54 logS + 0.44 (S in mole fraction)	Mostly aromatic or polynuclear aromatics; two chlorinated	1
Log K_{oc} = log K_{ow} - 0.317	PAH, and heterocyclic compounds	2
Log K_{oc} = 0.937 log K_{ow} - 0.006	Aromatics, polynuclear aromatics, triazines, and dinitroaniline herbicides	3
Log K_{oc} = 1.00 log K_{ow} - 0.21	Mostly aromatic or polynuclear aromatics; two chlorinated	1
Log K_{oc} = 3.584 log K_{ow} - 0.327 (log K_{ow})^2 - 3.523	Higher molecular weight with low K_{ow} >5.5	4

K_{oc} = soil (or sediment) adsorption coefficient
S = water solubility
K_{ow} = octanol-water partition coefficient

References

1. Karickhoff, S.W., D.S. Brown, and T.A. Scott, "Sorption of Hydrophobic Pollutants on Natural Sediments," *Water Res.*, 13:241-248 (1979).
2. Means, J.C., S.G. Wood, J.J. Hassett, and W.L. Banwart, "Sorption of Polynuclear Aromatic Hydrocarbons by Sediments and Soils," *Environ. Sci. Technol.* 14:1524-1528, 1980.
3. Brown, D.S., S.W. Karickhoff and E.W. Flagg, "Empirical Predication of Organic Pollutant Sorption in Natural Sediments," to be submitted to *J. Environ. Qual.*
4. Kayal, S.I. and D.W. Connell, "Partitioning of Unsubstituted Polycyclic Aromatic Hydrocarbons Between Surface Sediments and the Water Column in the Brisbane River Estuary," *Aust. J. Mar. Freshwater Res.* 41:443-456, 1990.

The value of 'a' remains near 1.0 for groups of highly nonpolar organic compounds, suggesting that the ratio of the fugacity constants for octanol and the organic phase of sediment is relatively constant for these solutes (Karickhoff 1981). The fugacity constant ratios for more polar solutes and for compounds containing a variety of different substituents are more variable, giving lower values for 'a'. The value of 'b' varies depending on the types of chemicals being evaluated. This means that the binding strength (affinity of the sorbent for the solute) of the organic phase of sediment and octanol are different and the degree of difference depends on properties of the organic solutes under investigation.

Aqueous/Gaseous Phase Partitioning. In general, aqueous/gaseous phase partitioning is quantified by relating the vapor pressure of a component of an ideal solution to the pure component vapor pressure of the solute and the solute concentration. This relationship is known as Raoult's Law and is expressed mathematically as:

$$P_i = x_i P_i^{o} \tag{5-15}$$

where P_i is the solution partial pressure, x_i is the mole fraction of solute, and P°_i is the solute pure component partial pressure.

For dilute solutions, typically of primary interest for hydrocarbon releases, the partitioning is adequately described by Henry's Law, which relates the gas vapor pressure of a solute to its mole fraction in solution as:

$$P_i = Hx_i \tag{5-16}$$

where H is commonly referred to as Henry's Law constant. Another form of Henry's Law also commonly used is:

$$H = \frac{C_{air}}{C_{water}} \tag{5-17}$$

where C_{air} is the chemical concentration in air and C_{water} is the chemical concentration in water.

Aqueous/gaseous phase partitioning is important for it characterizes how volatile a compound may be once in solution. Henry's Law constant is therefore a relative measure of volatility and of critical importance when evaluating the fate of volatile components of petroleum products in soils. A large value of H indicates a greater propensity for a compound to volatilize. As a rule of thumb, a contaminant with a Henry's Law constant of less than 5×10^{-5} atm m^3/mol will be more soluble and tend to remain in water, while a contaminant with Henry's constant greater than 5×10^{-3} atm m^3/mol will tend to be more volatile (Olson and David 1990).

5.2.3 Dissolved and Gaseous Phase Transport Processes

Dissolved phase transport can occur in either the unsaturated or saturated zone. The unsaturated zone extends from the ground surface to the top of the groundwater table. Dissolved hydrocarbons can enter the unsaturated zone through infiltration of water which contains hydrocarbons dissolved from an above-ground surface source, or hydrocarbons can become dissolved as infiltrating water passes over hydrocarbons adsorbed to soil particles or present as NAPL in the unsaturated zone. When NAPL or adsorbed hydrocarbons are present in the unsaturated zone, they typically form a long term source for dissolved phase hydrocarbons. Subsurface NAPL also provides a source for vapor phase hydrocarbons (from evaporation, as described in Section 4).

Dissolved hydrocarbon transport in the unsaturated zone occurs primarily by the advection and diffusion of hydrocarbon compounds dissolved in water (aqueous phase) or in air (gaseous phase). The predominant direction of motion is vertical. Dissolved hydrocarbon is advected downward by infiltrating moisture. Volatilized hydrocarbons are diffused upward as a result of concentration gradients between soil moisture and air-filled soil pore spaces, in addition to gradients between the air-filled pore spaces and air above the ground surface.

The transport rate of water-dissolved contaminants in the unsaturated zone is governed predominantly by the permeability of the medium, the water content, the concentration of the hydrocarbon in infiltrating water, and by vegetation when the water is in the root zone. In general, advection is the dominant transport process for the aqueous phase, though in low permeability environments, diffusion can also be significant. Even under ideal conditions, diffusion of nonpolar organic chemicals through an aqueous phase is very slow.

The transport of gas phase hydrocarbons in the unsaturated zone is governed primarily by the permeability of the medium, water content, air temperature, barometric pressure, and vegetation. In general, molecular diffusion is the dominant transport process for the gas phase.

The saturated zone of an aquifer extends from the groundwater table downward. Below the water table, there are no continuous air-filled pores. The primary transport mechanism for dissolved hydrocarbons in the saturated zone is advective transport, except in low groundwater flow environments where diffusion may dominate. The direction and rate of contaminant migration by advection and diffusion are controlled by the hydraulic gradients and concentration gradients, respectively.

Partitioning processes, as described in Section 5.2.2 apply in both the unsaturated and saturated zones. In the saturated zone, however, the only air interface at which partitioning can occur into the vapor phase is at the groundwater surface (the water table).

5.2.4 Special Conditions

Migration of hydrocarbons in the aqueous phase can be enhanced by processes of cosolvency and colloidal transport. Similarly, surfactants have the effect of increasing the mobility of hydrocarbons through micelle formation which decreases sorption of the hydrocarbons to soil particles. However, surfactants are not typically associated with hydrocarbon releases to land, although they may be added to the aquifer as a remedial measure to enhance pump-and-treat groundwater recovery systems.

Cosolvency is the process by which the solubility of one solute is enhanced by the presence in solution of another solute. In the presence of cosolvents, contaminants may, in theory, be present in the aqueous phase at concentrations greater than their aqueous solubility. Organic cosolvents are characterized into two categories according to their miscibility with water: completely-miscible organic solvents (CMOS), such as ethanol and acetone, and partially-miscible organic solvents (PMOS), such as benzene and xylene. When water and CMOS are mixed, the polarity of the mixed solvent decreases and, as a consequence, the solubility of hydrophobic organic chemicals increases, increasing their mobility. PMOS are better solvents for hydrophobic organic chemicals than CMOS and therefore have a higher potential for cosolvency, but their limited aqueous solubility prevents aqueous concentrations from achieving maximum cosolvency potential. Consequently, the lower the aqueous solubility of a PMOS the more negligible its cosolvent effects on both solubility and sorption of hydrophobic organic chemicals (Pinal *et al.* 1989).

Attempts to estimate the effects of cosolvency on hydrocarbon transport have been based on partition equations. The difficulties in applying linear partition equations to commercial gasoline mixtures include the large number of components involved and the problem of determining the moles of each in theoretically infinite combinations. Certain gasoline components may be cosolvents or change the activity coefficients in the solvent phase. Gasoline composition will also vary in different parts of the country and at different times of the year, and product composition may change daily depending on refinery operations (Section 3.2). Independent service stations also obtain product from different suppliers depending on market conditions.

Colloids may also enhance hydrocarbon transport. Colloids are particles with diameters less than 10 micrometers and may be composed of organic or inorganic material. Hydrocarbons can sorb to colloids in the same manner as they sorb to the solid matrix of a porous medium and subsequently be transported through an aquifer at the velocity of the colloids. If one or more of the following conditions are present in an aquifer, colloidal particles may significantly affect the rate of hydrocarbon transport (McCarthy and Zachara 1989):

- Groundwater flow rates are relatively high.
- Colloidal concentrations are relatively high (> 100 mg/l).
- The hydrocarbon in question is strongly hydrophobic.

- Aqueous chemistry is favorable to mobilization of colloids.
  Favorable conditions for colloidal transport include high sodium concentrations or chemical alternations that may be naturally occurring or contaminant induced.

It must be noted however, that information regarding concentrations of colloidal material and its transport in groundwater often are very limited and it is difficult to assess their impact on hydrocarbon transport.

5.3 Relative Subsurface Transport for Selected Petroleum Hydrocarbon Constituents

The actual behavior of petroleum hydrocarbons in the subsurface is highly dependent on specific characteristics of the environment into which they were released. Important characteristics include temperature, moisture content, permeability, tortuosity, groundwater flow rates, rainfall patterns, barometric pressure, and concentrations of organic materials in soil and water. These, and other factors, can vary widely and exist in a practically infinite variety of combinations. This review, therefore focusses principally on the relative behavior of the 12 selected compounds and for BTEX under a range of environmental conditions. Many of the factors that influence subsurface transport are interrelated, and absolute characterization of transport in a given environment requires simultaneous consideration of numerous issues. However, the behavior of different compounds can be addressed adequately by considering selected key parameters independently, or in carefully chosen groups.

5.3.1 NAPL Transport

NAPL transport in the context of this report simply refers to the transport of a liquid, other than water, through the environment. The liquid can be composed of only one "pure phase" compound, such as benzene, or more typically, a mixture of compounds.

At typical ambient subsurface temperatures, pure phase NAPL transport has little practical meaning for 7 of the 12 selected individual compounds because their melting points are higher than typical subsurface ambient temperatures, even in the warmest climates. For the other 5, which are liquid at typical ambient temperatures, there is little, if any, information about individual compound viscosities or interfacial tension. Therefore, essentially no useful information about pure phase NAPL transport of the selected individual compounds is available.

This lack of information, however, is not a significant issue because these compounds are essentially never released as individual compounds, but are rather components of complex mixtures, as described in Chapter 4. Even after substantial weathering, the remaining materials are complex mixtures, containing the most persistent compounds. NAPL migration issues must, therefore, be considered in the context of the petroleum hydrocarbon mixtures actually released to the environment. The data on viscosity and density, and interfacial tension shown in Table 4-1 for oil products are, therefore, the key data from which NAPL migration can be assessed. When available, data for residual saturation in soils is also useful. The individual compound characteristics become important, only when considering dissolved constituent behavior, discussed below.

5.3.2 NAPL Partitioning

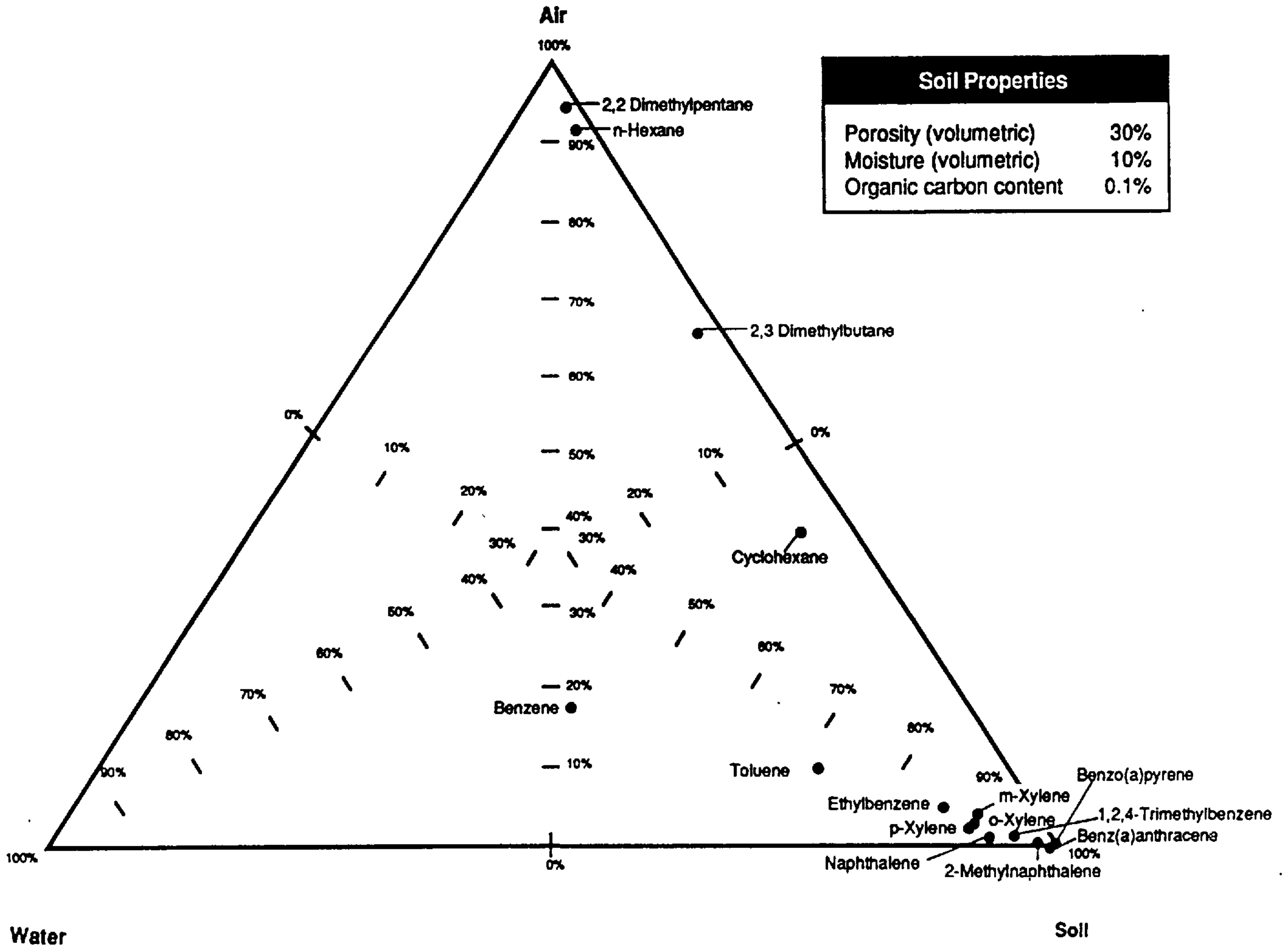
The rate of dissolution as infiltrating water passes over NAPL, or as groundwater in the saturated zone passes by NAPL, is a major unknown factor. As discussed in Section 4, the dissolution of petroleum hydrocarbons into water is limited by the partitioning process between NAPL and water. This partition coefficient has been shown to be approximately equal to K_{ow}, though it has also been shown to vary depending on the relative amounts of oil and water in the system and the hydrocarbon phase composition. This partitioning process will generally limit the aqueous dissolved concentration of a hydrocarbon to values lower than the hydrocarbon pure phase solubility because of the relative preference of these compounds to be associated with the oil phase. The effects of cosolvency, when significant, would tend to work in the opposite direction.

The overall dissolution rate probably is proportional to the NAPL/water surface contact area. For example, water passing through a porous medium in which the particles are coated with a petroleum product will have a relatively large contact area, whereas water forced around oil filled pores will have a much smaller contact area.

Most studies of dissolution and partitioning have been performed using simple linear interfaces in the absence of porous media.

5.3.3 Dissolved Phase Partitioning

The methods described earlier were used to estimate the relative partitioning for the 12 selected compounds and for BTEX among air, water, and soil, based on two sample soils with 0.1 percent and 5 percent organic carbon content. Tables 3-2 and 5-2 provide the chemical specific input parameter values needed. Soil porosity of 30 percent and moisture content of 10 percent were arbitrarily chosen as representative of a sandy soil. Figures 5-2 and 5-3 present the three-phase partitioning results for the two soil types. The two-phase partitioning was also estimated for the same compounds in a saturated soil (partitioning between water and soil). Figures 5-4 and 5-5 present these results. The three-phase numerical results used to develop Figures 5-2 and 5-3 are shown in Table 5-3. The two-phase numerical results are shown in Table 5-4, which corresponds to Figures 5-4 and 5-5. In developing these estimates, the potential impacts on solubility of dissolved organic carbon and other cosolvency effects were ignored. The estimates also neglect the apparent effect of adsorption on colloids, which would be measured as dissolved in water in commonly used sampling and analysis methods. The parameter values presented here were obtained from available literature sources. It should be noted, however, when estimating Henry's Law constant using the vapor pressure and solubilities for solutes which are solids under ambient conditions (e.g., naphthalene, 2-methylnaphthalene, benzo(a)antracene, benzo(a)pyrene, the Henry's Law should be based on hypothetically supercooled liquid vapor pressures and solubilities.



Soil Properties	
Porosity (volumetric)	30%
Moisture (volumetric)	10%
Organic carbon content	0.1%

Figure 5-2. Expected partitioning between air, water, and soil for a soil of relatively low organic carbon content. (Note: 5-methylchrysene, 1-methylphenanthrene, and dibenzothiophene are not shown because Henry's Law coefficient was not available.)

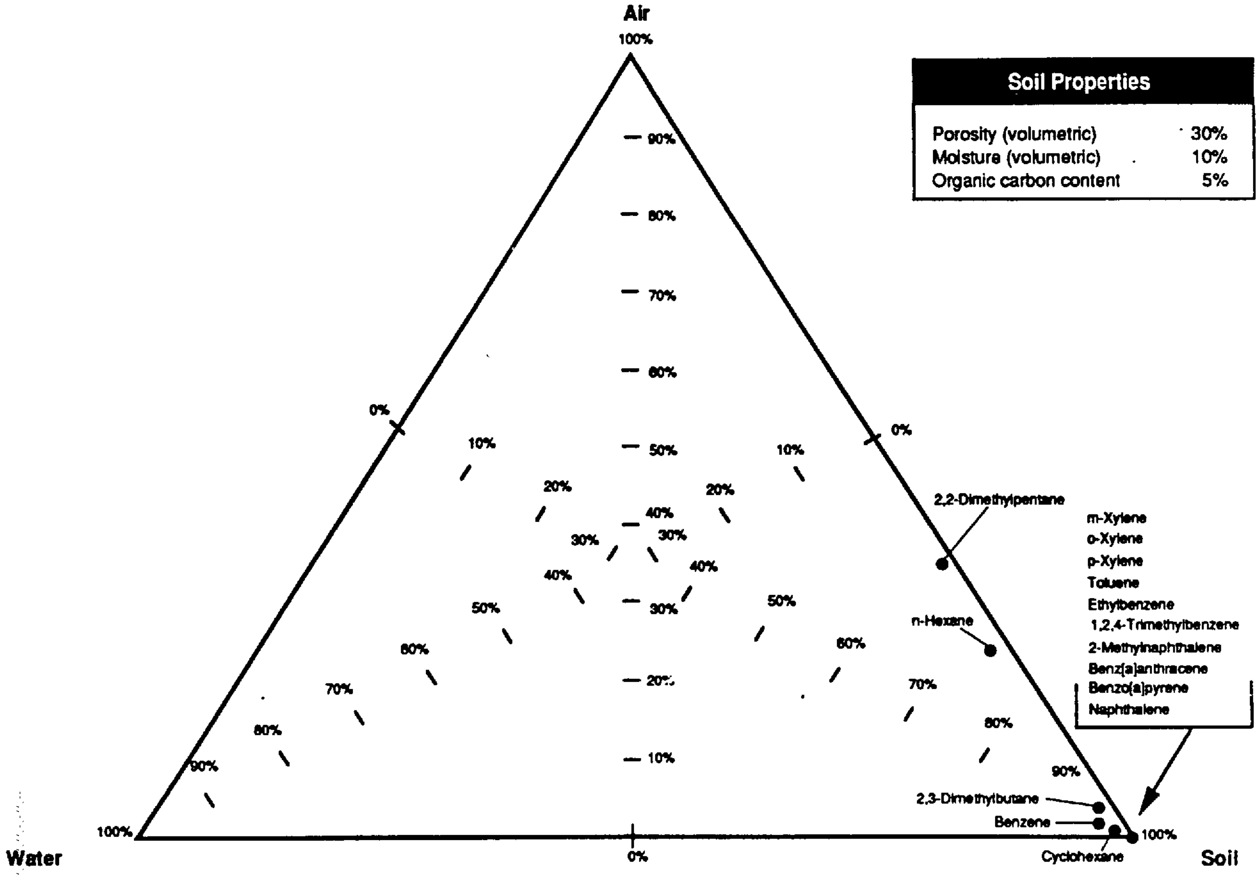


Figure 5-3. Expected partitioning between air, water, and soil for a soil of relatively high organic carbon content. (Note: 5-methylchrysene, 1-methylphenanthrene, and dibenzothiophene are not shown because Henry's Law coefficient was not available.)

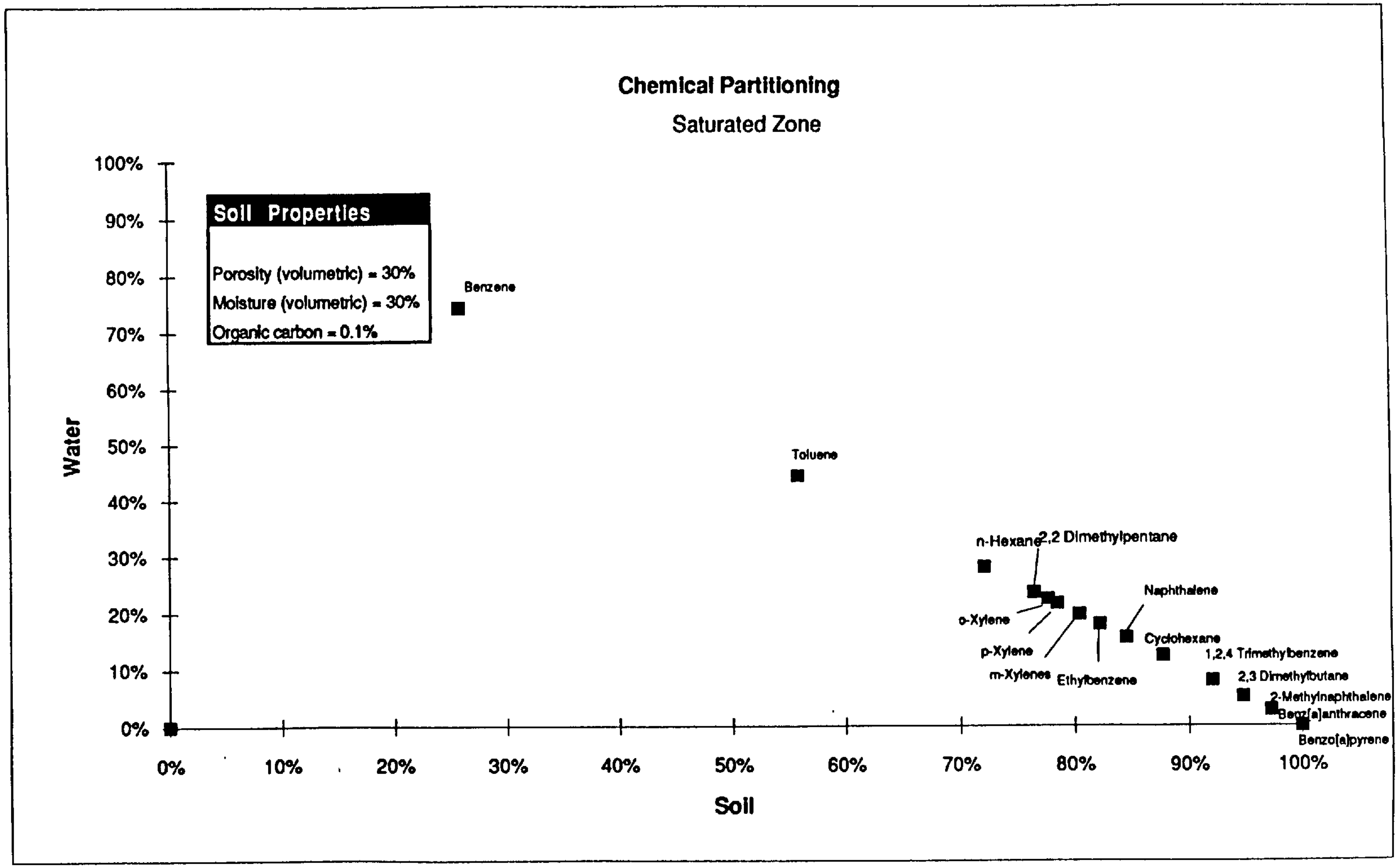


Figure 5-4. Expected partitioning between water and soil for a soil of relatively low organic carbon content.

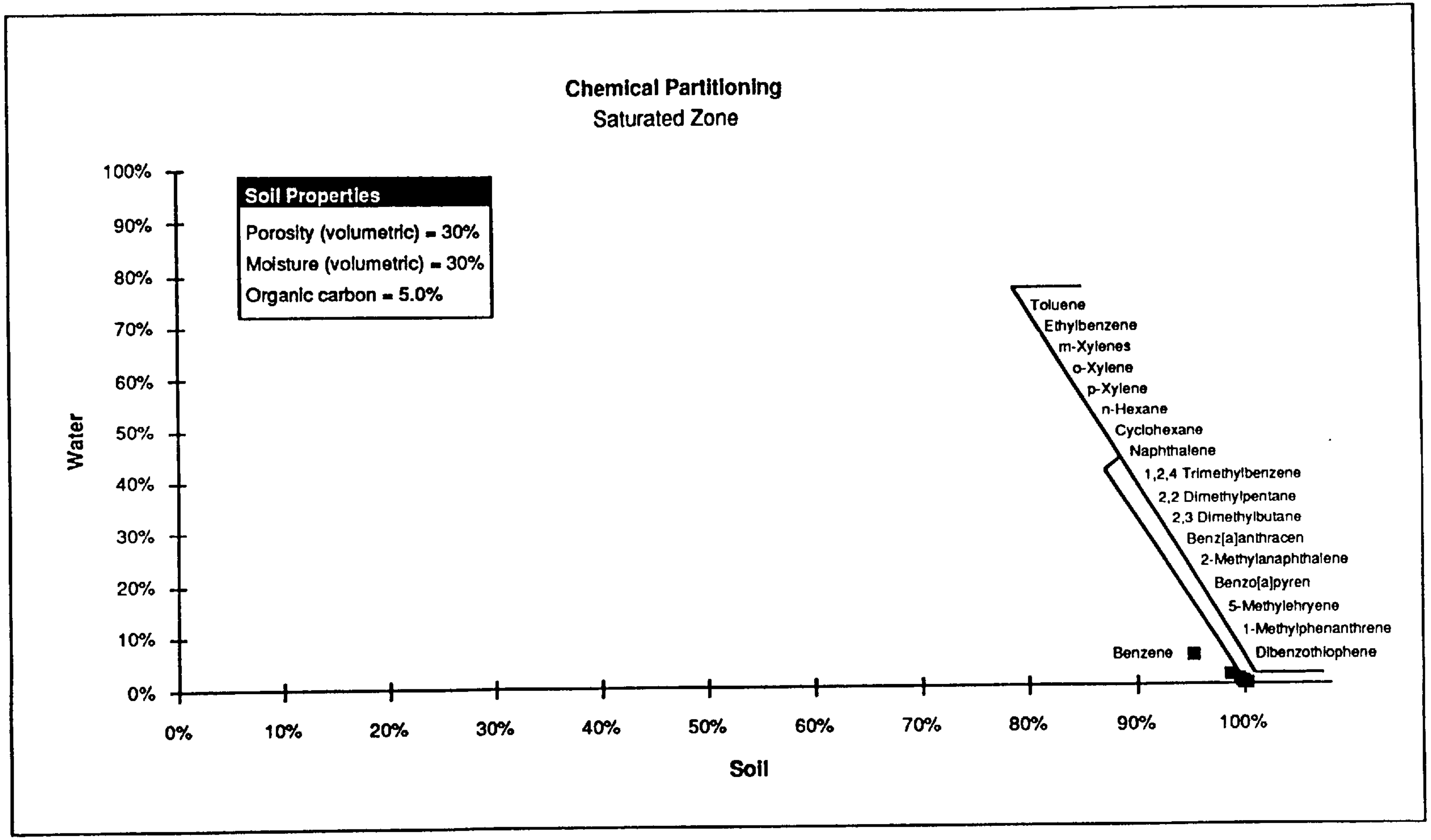


Figure 5-5. Expected partitioning between water and soil for a soil of relatively high organic carbon content.

Table 5-2. K_{oc}, K_d, and R values for the compounds of interest and BTEX

Compounds	Koc* (ml/g)	log Koc (ml/g)	Kd (ml/g) *0.1% organic carbon*	Kd (ml/g) *5% organic carbon*	R** *0.1% organic carbon*	R** *5% organic carbon*
Benz(a)anthracene	1,380,000	6.14	1380.00	69000	8,281	414,001
Benzo(a)pyrene	5,500,000	6.74	5500.00	275000	33,001	1,650,001
5-Methylchrysene	1,621,810	6.21	1621.81	81091	9,732	486,544
1-Methylphenanthrene	85,114	4.93	85.11	4256	512	25,535
dibenzothiophene	74,131	4.87	74.13	3707	446	22,240
1,2,4-Trimethylbenzene	2,754	3.44	2.75	138	18	827
Napthalene	1,300	3.11	1.30	65	9	391
2-Methylnapthalene	8,500	3.93	8.50	425	52	2,551
Cyclohexane	1,698	3.23	1.70	85	11	510
n-Hexane	617	2.79	0.62	31	5	186
2,3-Dimethylbutane	4,365	3.64	4.37	218	27	1,311
2,2-Dimethylpentane	776	2.89	0.78	39	6	234
Benzene	83	1.92	0.08	4	1	26
Ethylbenzene	1,100	3.04	1.10	55	8	331
m-Xylene	982	2.99	0.98	49	7	296
o-Xylene	830	2.92	0.83	42	6	250
p-Xylene	870	2.94	0.87	44	6	262

R values based on equation 5-11

*Koc was determined using Kow values from Table 3-2 and the fourth equation in Table 5-1.

**Soil properties:

Soil density (g/cc) = 1.80

Soil porosity = 0.30

Table 5-3. Numerical results of Three-phase Partitioning Calculations
(Graphical displays are presented in Figures 5-2 and 5-3)

Partitioning Calculations	Organic Carbon Content (0.1%)			Organic Carbon Content (5%)		
	Air Fraction	Water Fraction	Soil Fraction	Air Fraction	Water Fraction	Soil Fraction
Non-BTEX Compounds						
Benz[a]anthracene	0.0%	0.0%	100.0%	0.0%	0.0%	100.0%
Benzo[a]pyrene	0.0%	0.0%	100.0%	0.0%	0.0%	100.0%
5-Methylchrysene	NC	NC	NC	NC	NC	NC
1-Methylphenanthrene	NC	NC	NC	NC	NC	NC
dibenzothiophene	NC	NC	NC	NC	NC	NC
1,2,4-Trimethylbenzene	1.4%	2.8%	95.8%	0.0%	0.1%	99.9%
Naphthalene	0.6%	5.8%	93.6%	0.0%	0.1%	99.9%
2-Methylnapthalene	0.1%	0.9%	99.0%	0.0%	0.0%	100.0%
Cyclohexane	40.1%	2.7%	57.2%	1.4%	0.1%	98.5%
n-Hexane	92.9%	0.8%	6.3%	22.7%	0.2%	77.1%
2,3-Dimethylbutane	67.1%	0.6%	32.3%	4.0%	0.0%	96.0%
2,2-Dimethylpentane	96.0%	0.4%	3.6%	34.5%	0.1%	65.3%
BTEX Compounds						
Benzene	18.5%	39.8%	41.7%	0.9%	1.9%	97.3%
Toluene	10.0%	18.8%	71.2%	0.3%	0.5%	99.2%
Ethylbenzene	3.5%	6.5%	90.0%	0.1%	0.1%	99.8%
m-Xylene	6.2%	7.0%	86.8%	0.1%	0.2%	99.7%
o-Xylene	3.6%	8.4%	88.0%	0.1%	0.2%	99.7%
p-Xylene	4.7%	8.0%	87.4%	0.1%	0.2%	99.7%

Results based on applying equations 5-5, 6, and 7
NC = Not calculated

Soil Properties (volumetric)
Porosity = 30%
Moisture = 10%
Soil Bulk density = 1.8 g/cc

Table 5-4. Numerical results of Two-phase Partitioning Calculations
(Graphical displays are presented in Figures 5-4 and 5-5)

Partitioning Calculations	Organic Carbon Content (0.1%) Air			Organic Carbon Content (5%)		
	Air Fraction	Water Fraction	Soil Fraction	Air Fraction	Water Fraction	Soil Fraction
Non-BTEX Compounds						
Benz[a]anthracene	0.0%	0.0%	100.0%	0.0%	0.0%	100.0%
Benzo[a]pyrene	0.0%	0.0%	100.0%	0.0%	0.0%	100.0%
5-Methylchrysene	0.0%	0.0%	100.0%	0.0%	0.0%	100.0%
1-Methylphenanthrene	0.0%	0.3%	99.7%	0.0%	0.0%	100.0%
dibenzothiophene	0.0%	0.3%	99.7%	0.0%	0.0%	100.0%
1,2,4-Trimethylbenzene	0.0%	8.0%	92.0%	0.0%	0.2%	99.8%
Naphthalene	0.0%	15.5%	84.5%	0.0%	0.4%	99.6%
2-Methylnaphthalene	0.0%	2.7%	97.3%	0.0%	0.1%	99.9%
Cyclohexane	0.0%	12.3%	87.7%	0.0%	0.3%	99.7%
n-Hexane	0.0%	27.9%	72.1%	0.0%	0.8%	99.2%
2,3-Dimethylbutane	0.0%	5.2%	94.8%	0.0%	0.1%	99.9%
2,2-Dimethylpentane	0.0%	23.5%	76.5%	0.0%	0.6%	99.4%
BTEX Compounds						
Benzene	0.0%	74.2%	25.8%	0.0%	5.4%	94.6%
Toluene	0.0%	44.2%	55.8%	0.0%	1.6%	98.4%
Ethylbenzene	0.0%	17.8%	82.2%	0.0%	0.4%	99.6%
m-Xylene	0.0%	19.5%	80.5%	0.0%	0.5%	99.6%
o-Xylene	0.0%	22.3%	77.7%	0.0%	0.6%	99.4%
p-Xylene	0.0%	21.5%	78.5%	0.0%	0.5%	99.5%

Results based on applying equations 5-5, 6, and 7
NC = Not calculated

Soil Properties
Porosity = 30%
Moisture = 30%

As an example of how the estimates are developed, consider 1 cubic meter of soil with the following properties:

Porosity = 30%
Soil Moisture = 10% (by volume)
Soil Bulk Density = 1.8 g/cc
Organic Carbon Content = 0.1%
Temperature = 20°C

The corresponding volumes are therefore given as:

Volume of Soil Moisture = V_2 = 10% = 0.1 m^3
Volume of Soil Air = Porosity - V_2 = V_1 = 20% = 0.2 m^3
Volume of Soil Matrix = 100% - V_2 - V_1 = V_3 = 70% = 0.7 m^3

Then, using benzene as the compound of interest, we need to use the following properties:

$$\text{Henry's Law Constant} = 5.6 \times 10^{-3}\ \frac{\text{Atm m}^3}{\text{mol}} \quad \text{(see Table 3-2)}$$

$$K_{oc} = 83 \text{ mL/g} \quad \text{(see Table 5-2)}$$

$$K_d = 83 \times (0.001) = .083 \text{ mL/g} \quad \text{(see Equation 5-12)}$$

Using the ideal gas constant, R_i, (8.21×10^{-5} $m^3 \cdot$ atm / mole $\cdot$ K), the calculations of fugacity capacity (Z_i) are as follows:

$$Z_1 = \frac{1}{RT} = \frac{1}{(8.21 \times 10^{-5})(20 + 273.15)} = 41.5\ \frac{\text{mol}}{\text{Atm m}^3}$$

$$Z_2 = \frac{1}{H} = \frac{1}{5.6 \times 10^{-3}} = 5882.4\ \frac{\text{mol}}{\text{Atm m}^3}$$

$$Z_3 = \frac{\rho \times K_d}{H} = \frac{(1.8)(0.083)}{5.6 \times 10^{-3}} = 26.7 \frac{\text{mol}}{\text{Atm m}^3}$$

$$\frac{1}{\sum V_i Z_i} = \frac{1}{(V_1Z_1) + (V_2Z_2) + (V_3Z_3)}$$

$$= \frac{1}{[(0.2)(41.5)] + [(0.1)(5882.4)] + [(0.7)(26.7)]} = 0.02 \text{ atm}$$

and the fractions of contaminants in the various media are as follows:

$$\text{Air} = \frac{(Z_1)\ (V_1)}{\sum Z_i\ V_i} = 0.185 \quad \text{(see Equation 5-6)}$$

$$\text{Water} = \frac{(Z_2)\ (V_2)}{\sum Z_i\ V_i} = 0.398 \quad \text{(see Equation 5-7)}$$

$$\text{Soil Matrix} = \frac{(Z_3)\ (V_3)}{\sum Z_i\ V_i} = 0.417 \quad \text{(see Equation 5-8)}$$

As indicated in Figures 5-2 and 5-3, when present in the unsaturated zone, the compounds of interest partition primarily to the soil solids or air. In a soil of relatively low organic carbon content of 0.1 percent (Figure 5-2), the compounds of interest can be divided into three groups based on the relative degree of partitioning between soil and air.

Primarily to soil:
- 2-Methylnaphthalene
- Naphthalene
- 1,2,4 Trimethylbenzene
- Benz(a)anthracene
- Benzo(a)pyrene

Intermediate:
- Cyclohexane
- 2,3 Dimethylbutane

Primarily to air:
- 2,2-Dimethylpentane
- n-Hexane

Note that 5-methylchrysene, 1-methylphenanthrene, and dibenzothiophene are not plotted because an appropriate Henry's Law coefficient was not available. Figure 5-2 shows that the BTEX compounds generally partition to a greater extent into water than the compounds of interest. In soils with higher organic content (Figure 5-3) the compounds of interest sorb increasingly to soil particles: cyclohexane, 2,3 dimethylbutane, 1,2,4-trimethylbenzene, naphthalene, 2-methylnaphthalene, benz(a)anthracene, and benzo(a)pyrene partition primarily to soil. The remaining compounds of interest, 2,2-dimethylpentane and n-hexane, are less volatile, although a significant fraction remains partitioned to the air. In the soil of higher organic carbon content, BTEX also partitions primarily to soil particles.

In the saturated zone, the behavior of the chemicals of interest is similar to that in the unsaturated zone in that a majority of each compound partition to the soil solids. In a soil of relatively low organic content (Figure 5-4), the proportion of the compounds of interest partitioning to soil solids ranges from 72.1 percent for n-hexane to essentially 100 percent for benz(a)anthracene, benzo(a)pyrene, and 5-methylchrysene. In a soil of higher organic content (Figure 5-5) all of the compounds of interest partition almost completely to soil solids, with the lowest proportion all evaluated 99.2 percent for n-hexane.

The results presented in Figures 5-4 and 5-5 indicate that once in the groundwater environment the compounds of interest will partition primarily to soil solids. This does not necessarily imply, however, that they will be immobile. If colloidal transport is significant in the groundwater environment, these compounds may be transported greater distances than expected. Further, trace concentrations in the dissolved phase may in some circumstances be significant.

5.3.4 Dissolved Phase Transport Process

The principal issues governing the relative transport behavior of the selected compounds were discussed earlier in the context of partitioning. Partitioning dominates the behavior of these chemicals in both the unsaturated and saturated zones, though the relative tendency to volatilize is more significant in the unsaturated zone than the saturated zone. Other parameters that can be used to characterize relative subsurface mobility include the retardation coefficient for dissolved component flow rates, diffusion coefficients in air and water, and regulatory ranking schemes. Two methods of evaluation are presented, a Retardation Approach, and an EPA HRS (Hazard Ranking System) mobility approach.

5.3.4.1 Retardation Approach. The retardation coefficient, given in equation (5-11) is directly related to K_d, and, therefore, does not provide fundamentally new information regarding mobility. It does, however, provide a more direct representation of the amount by which dissolved component transport is retarded with respect to water movement. Table 5-2 shows organic carbon (K_{oc}), and soil (K_d) coefficients together with retardation (R) factors estimated using a representative soil bulk density of 1.8, a porosity of 0.3 and two representative organic carbon concentrations of 0.1 percent and 5 percent, the same values used for the partitioning computations presented earlier. As can be seen from Table 5-2, while the organic carbon content of the soil has a strong influence on the absolute value of R, it has little impact on the relative values of R between different compounds.

The estimated retardation factors are presented graphically in Figure 5-6. The compounds of interest can be divided roughly into the following two categories based on the calculated retardation factors.

Relatively more mobile in water:

- 1,2,4-trimethylbenzene
- naphthalene
- 2-methylnaphthalene
- cyclohexane
- n-hexane
- 2,3-dimethylbutane
- 2,2-dimethylpentane

Relatively less mobile in water:

- benz(a)anthracene
- benzo(a)pyrene
- 5-methylchrysene
- 1-methylphenanthrene
- dibenzothiophene

5.3.4.2 EPA HRS Mobility Approach. Another approach that can be used to evaluate relative mobility of different chemicals of interest is to calculate air and groundwater mobility values for each compound of interest, and for BTEX, using the EPA Hazard Ranking System (HRS) (EPA 1988). The air values are based on chemical vapor pressure, Henry's Law constant, and dry relative soil volatility. The groundwater values are based on solubility. The values from the HRS are presented in Table 5-5. A mobility value for of each compound of interest, and BTEX, was determined. The results are presented in Table 5-6. These numbers indicate the mobility value from the HRS if the compound was released in pure form at a site. These values do not address NAPL mobility and also do not address the issue of dissolution rates from NAPL into water which were discussed previously. They do, however, provide a reference framework for an approximate qualitative evaluation of subsurface mobility.

The mobility values are displayed graphically in Figure 5-7. Three values have been plotted: the groundwater value, air value, and total value which is the sum of the groundwater and air values. The maximum potential value for each is also presented as a dotted line.

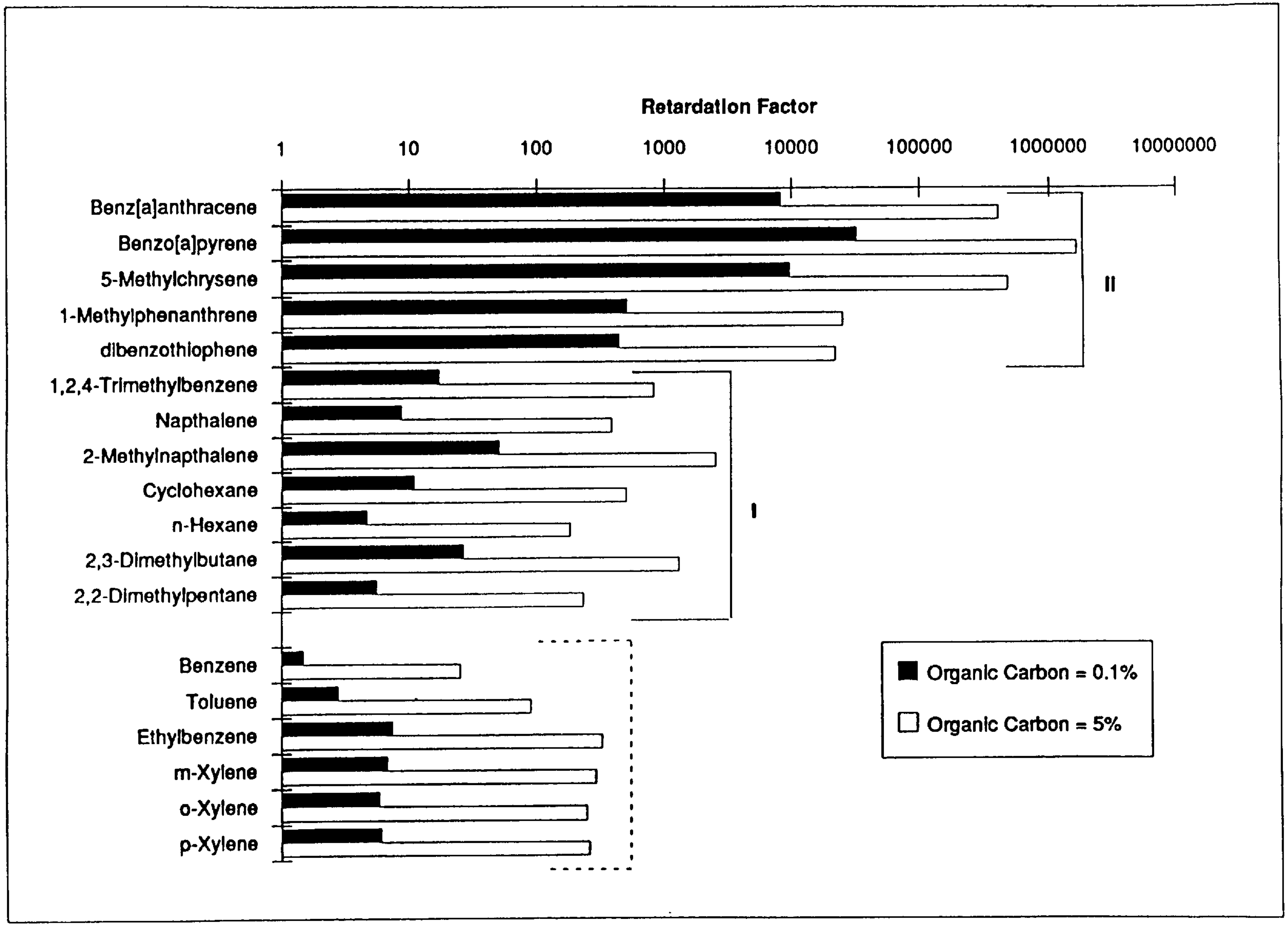


Figure 5-6. Retardation Factors Calculated for Two Different Soil Types (Numerical results and soil characteristics are presented in Table 5-4)

Table 5-5. Assigned Values for Mobility in the EPA Hazard Ranking System (EPA, 1988)

a. Gas Mobility Component Values (from Section 2.1.2.3.1, Table 2-7, of EPA, 1988)
b. Mobility Values for Organic Substances (from Section 3.2.12, Table 3-7, of EPA, 1988)

a. Air Mobility	EPA Assigned Value	b. Water Mobility	EPA Assigned Value
Vapor pressure		**Solubility (mg/l)**	
Above 10 torr*	3	Less than or equal to 10	0
Above 10-3 to 10 torr	2	Greater than 10 to 100	1
10-5 to 10-3 torr	1	Greater than 100 to 1,000	2
Less than 10-5 torr	0	Greater than 1,000	3
Henry's constant**			
Above 10-3	3		
Above 10-5 to 10-3	2		
10-7 to 10-5	1		
Less than 10-7	0		
Dry relative soil volatility***			
Above 1	3		
Above 10-3 to 1	2		
10-6 to 10-3	1		
Less than 10-6	0		

---

*Torr is a unit of pressure equal to 1/760 of an atmosphere (i.e., 1 mm Hg).

**Henry's constant in terms of atm-m3/mol.

***Dry relative soil volatility is a measure of the propensity of a gas to move through the air spaces in dry soil, as defined in U.S. Environmental Protection Agency, "Properties and Categorization of RCRA Wastes According to Volatility," as Pvp/MW1/4 where Pvp equals the vapor pressure of the substance at 25°C and MW equals the molecular weight of the substance.

Table 5-6. Mobility Values using the EPA Hazard Ranking System (EPA, 1988)

Compounds	Air							Ground Water		Air Score	Ground Water Score	Total Score (Max.=12)
	Molecular Weight	Vapor Pressure (torr)	Assigned Value	Henry's Law Constant (atm cu. m./mol)	Assigned Value	Dry Relative Soil Volatility	Assigned Value	Solubility (mg/l)	Assigned Value			
Benz(a)anthracene	228.3	1.5E-07	0	4.1E-06	1	3.9E-08	0	1.0E-02	0	1	0	1
Benzo(a)pyrene	252.3	5.7E-09	0	4.1E-06	1	1.4E-09	0	4.0E-03	0	1	0	1
5-Methylchrysene	242.1	NAV	NAV	NAV	NAV	NAV	NAV	7.3E-03	0	NAV	0	NAV
1-Methylphenanthrene	192.3	NAV	NAV	NAV	NAV	NAV	NAV	2.7E-01	0	NAV	0	NAV
dibenzothiophene	184.3	NAV	NAV	NAV	NAV	NAV	NAV	1.5E+00	0	NAV	0	NAV
1,2,4-Trimethylbenzene	120.2	1.9E+00	2	6.1E-03	3	5.6E-01	2	6.0E+01	1	7	1	8
Naphthalene	128.2	2.3E-01	2	1.4E-03	3	6.8E-02	2	3.4E+01	1	7	1	8
2-Methylnaphthalene	142.2	8.3E-03	2	4.9E-04	2	2.4E-03	2	2.6E+01	1	6	1	7
Cyclohexane	84.2	1.0E+02	3	1.8E-01	3	3.3E+01	3	5.8E+01	1	9	1	10
n-Hexane	86.2	1.5E+02	3	1.4E+00	3	4.9E+01	3	1.3E+01	1	9	1	10
2,3-Dimethylbutane	86.2	4.0E+02	3	1.4E+00	3	1.3E+02	3	1.9E+01	1	9	1	10
2,2-Dimethylpentane	100.2	4.0E+01	3	3.1E+00	3	1.3E+01	3	2.0E+01	1	9	1	10
Benzene	78.1	9.5E+01	3	5.6E-03	3	3.2E+01	3	1.8E+03	3	9	3	12
Toluene	92.1	3.0E+01	3	6.7E-03	3	9.7E+00	3	5.4E+02	2	9	2	11
Ethylbenzene	106.2	1.0E+01	2	6.4E-03	3	3.1E+00	3	1.5E+02	2	8	2	10
m-Xylene	106.2	8.6E-01	2	5.2E-03	3	2.7E-01	2	1.3E+02	2	7	2	9
o-Xylene	106.2	8.8E-01	2	5.3E-03	3	2.7E-01	2	1.8E+02	2	7	2	9
p-Xylene	106.2	8.6E-01	2	5.3E-03	3	2.7E-01	2	2.0E+02	2	7	2	9

NAV = Not available at typical ambient environmental temperatures

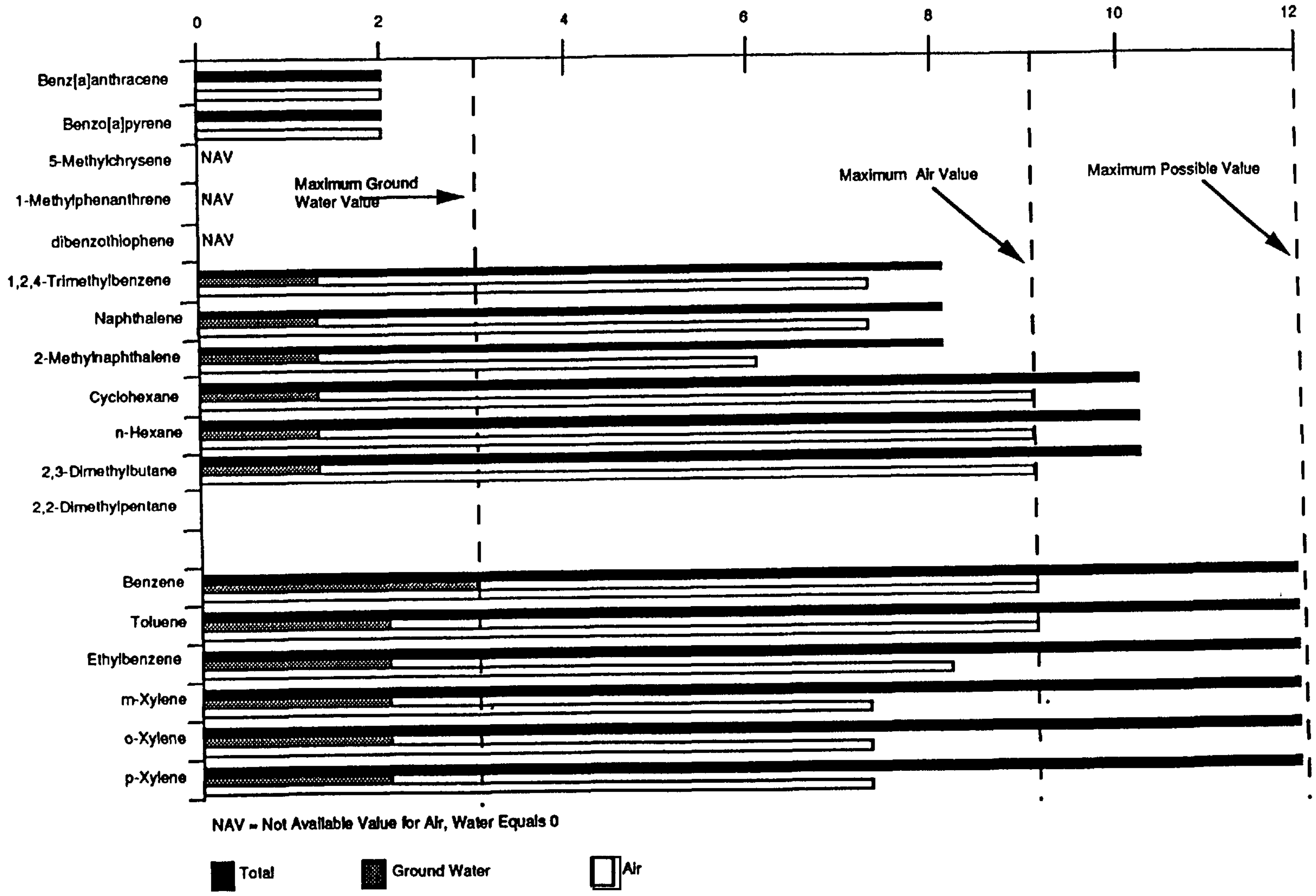


Figure 5-7. Mobility values using the EPA Hazard Ranking System (EPA 1988)

The results indicate that the compounds of interest would receive a relatively low mobility value for groundwater. The compounds benz(a)anthracene, benzo(a)pyrene, 5-methylchrysene, 1-methylphenanthrene, and dibenzothiophene would receive a 0 value. The compounds 1,2,4-trimethylbenzene, naphthalene, 2-methylnaphthalene, cyclohexane, n-hexane, 2,3-dimethylbutane, and 2,2-dimethylpentane would receive a value of 1, only one third the maximum value of 3. BTEX would receive higher values of 3, 2, 2, and 2, respectively. These results indicate that if the compounds of interest are released on a site, their potential to contaminate groundwater is generally less than that of BTEX. In addition, if all other factors (toxicity, site conditions, etc.) were equal, a site contaminated with BTEX would receive a higher groundwater ranking than if any of the compounds of interest were present.

The air values indicate similar results to those for water in that essentially two groups can be delineated. The compounds of interest with relatively low air mobility values are benz(a)anthracene, and benzo(a)pyrene; those receiving high values are 1,2,4-trimethylbenzene, naphthalene, 2-methylnaphthalene, cyclohexane, n-hexane, 2,3-dimethylbutane, and 2,2- dimethylpentane. 5-Methylchrysene, 1-methylphenanthrene, and dibenzothiophene were not assigned values because the physical parameters necessary for their evaluation were not available. With respect to BTEX, the group of higher valued compounds would be ranked in similar manner if all other factors were equal.

The total values essentially mimic the results of air and groundwater in that two groups of compounds of interest can be distinguished based on their assigned mobility values. With respect to these values, the compounds of interest comprising a group of lower mobility compounds include:

- benz(a)anthracene
- benzo(a)pyrene
- 5-methylchrysene
- 1-methylphenanthrene
- dibenzothiophene

5-methylchrysene, 1-methylphenanthrene, and dibenzothiophene were included in this group based solely on their groundwater value. Air values for these three compounds were not available. The compounds of interest comprising a group of higher mobility compounds include:

- 1,2,4-trimethylbenzene
- naphthalene
- 2-methylnaphthalene
- cyclohexane
- n-hexane
- 2,3-dimethylbutane
- 2,2-dimethylpentane

BTEX would be included in this higher mobility group also; benzene would receive the maximum total value, higher than any of the compounds of interest.

5.4 Summary

In summary, three methods for evaluating the behavior of the 12 compounds of interest have been presented. The methods include the partitioning calculations (Mackay 1979) presented in Section 5.3.3, the retardation coefficient approach in Section 5.3.4, and the mobility method used in the EPA Hazard Ranking system presented in Section 5.3.4 (USEPA 1988). A comparison of the results of the three methods indicates the 12 compounds of interest can be reasonably divided into three general categories based on saturated zone mobility and three categories based on partitioning in the unsaturated zone. Note that some compound categorization changes between the unsaturated and saturated zones. Category I includes compounds that are generally more mobile, and Category III includes compounds that are generally less mobile, with Category II in between. Table 5-7 summarizes the categorization developed from each of the approaches used to evaluate relative mobility. It is important to note that these categories are based on natural groupings of these compounds, not on fixed absolute criteria. The final summary categorization presented below is based on the average of the individual method categories drawn in Table 5-7.

Compound placement within the categories is as follows:

Water/Soil Behavior

Category I
- Naphthalene
- Cyclohexane
- n-Hexane

Category II
- 1,2,4-Trimethylbenzene
- 2-Methylnaphthalene
- 2,3-Dimethylbutane
- 2,2-Dimethylpentane

Category III
- Benz(a)anthracene
- Benzo(a)pyrene
- 5-Methylchrysene
- 1-Methylphenanthrene
- Dibenzothiophene

Water/Soil/Air Behavior

Category I
- n-Hexane
- 2,2-Dimethylpentane

Category II
- Cyclohexane
- 2,3 Dimethylbutane
- 2-Methylnaphthalene
- Naphthalene
- 1,2,4-Trimethylbenzene

Category III
- Benz(a)anthracene
- Benzo(a)pyrene

Table 5-7. Compound Categorization Based on Relative Subsurface Mobility

Compounds	Water/Soil			Air	
	Partitioning(1)	Retardation(2)	EPA/HRS(3)	Partitioning(4)	EPA(3)
1,2,4-Trimethylbenzene	II	I	II	III	II
Naphthalene	I	I	II	III	II
2-Methylnaphthalene	II	I	II	III	II
Cyclohexane	I	I	II	II	I
n-Hexane	I	I	II	I	I
2,3-Dimethylbutane	II	I	II	II	I
2,2-Dimethylpentane	I	I	II	I	I
Benz[a]anthracene	III	III	III	III	III
Benzo[a]pyrene	III	III	III	III	III
5-Methylchrysene	III	III	III	NR	NR
1-Methylphenanthrene	III	II	III	NR	NR
dibenzothiophene	III	II	III	NR	NR

(1)See Figure 5-4
(2)See Table 5-4
(3)See Table 5-6
(4)See Figure 5.2
NR - Not Reported
Categories I, II and III are relative groupings in order of decreasing mobility.

Section 6

BIOLOGICAL EFFECTS

6.1 Introduction

Bulk petroleum products, particularly the lighter distillate products, or individual chemical ingredients leached from oil released on land may percolate through permeable soils and contaminate groundwater. As discussed above, large amounts of groundwater in the United States are used as a direct source of domestic drinking water and for irrigated agriculture. In addition, many groundwater aquifers communicate directly with surface water bodies. Contamination of groundwater with petroleum chemicals could compromise many of the uses of this valuable resource. Many of the chemicals in petroleum products are toxic or carcinogenic to aquatic organisms and man, and could represent a hazard to aquatic organisms and man if their concentrations in groundwater supplies were high.

6.2 Aquatic Toxicology

6.2.1 Toxicity of Petroleum Products to Aquatic Organisms

Saturated and aromatic hydrocarbons have acute toxicities to aquatic organisms, expressed as the median effective dose (EC50) values (mmol/m^3), that span a range of 8,000 or more (Hutchinson *et al.* 1978, 1979; Abernethy *et al.* 1986). As a general rule, there is a direct correlation between the aqueous solubility of a hydrocarbon and its acute toxicity to aquatic organisms. This can be seen in a log-log plot of molar solubility versus molar toxicity (EC50) (Figure 6-1). As discussed earlier, there are inverse correlations between aqueous solubility of hydrocarbons and their molecular weights and K_{ow}s and a direct correlation between aqueous solubility and vapor pressure. Thus, these parameters also are correlated with acute toxicity. The toxicities of hydrocarbons in mixtures are additive (Warne *et al.* 1989), so a similar relationship will prevail for water soluble fractions of petroleum products.

These relationships indicate that most hydrocarbons are nonselective toxicants. Their toxicity depends on attainment of a critical volume or concentration is the tissues of the aquatic organism (Warne *et al.* 1991). The critical concentration of a hydrocarbon in tissues of aquatic organisms is attained (toxic effects occur) when the activity of the hydrocarbon in solution (proportional to the ratio of concentration in solution to saturation concentration) reaches a certain value. For most hydrocarbons the toxic concentration in the water appears to lie between about 20 and 70 percent of the saturation concentration, irrespective of the solubility of the hydrocarbon (Figure 6-1). For higher molecular weight hydrocarbons, the toxic concentration is at or in excess of the saturation concentration.

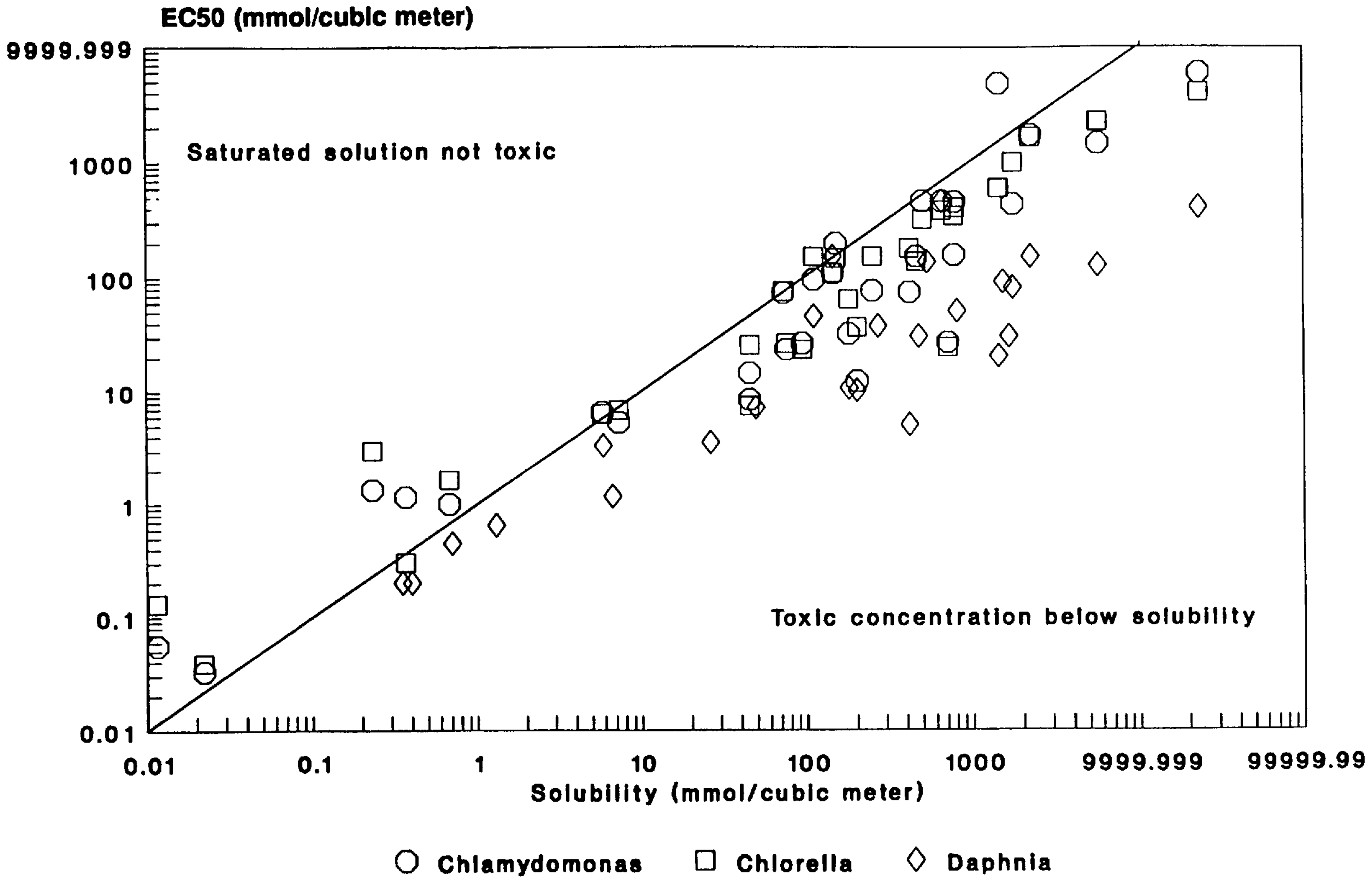


Figure 6-1. Relationship between aqueous solubility of petroleum hydrocarbons and their toxicity to freshwater organisms

Lower molecular weight hydrocarbons with aqueous solubilities of about 5 mmol/m^3 or more (with molecular weights lower than those of octane and phenanthrene) have acute toxicities that are lower than their aqueous solubilities. However, higher molecular weight alkanes and aromatics have acute toxicities approximately equal to or greater than their aqueous solubilities; saturated solutions of these compounds are not acutely toxic. EC50 values lying above the iso-concentration line in Figure 6-1 were extrapolated.

Concentrations of hydrocarbons in soil water in equilibrium with surface or subsurface oil deposits will nearly always be below saturation, and concentrations will tend to decrease as the dissolved hydrocarbons are carried away from the deposit and diluted in the soil water. As discussed above, the equilibrium concentrations of hydrocarbons in water in direct contact with oil depend on the oil/water partition coefficients of the hydrocarbons, not on their solubility alone in water. Equilibrium concentrations in water are always well below saturation. For example, a No. 2 fuel oil containing 4,000 mg/kg naphthalene (Appendix Table A-13), produced a water-soluble fraction containing 0.84 mg/L naphthalene (Anderson *et al.* 1974). This concentration is only about 4 percent of the saturation concentration of naphthalene in seawater (about 22 mg/L: Whitehouse 1984). Thus, concentrations of hydrocarbons in soil water and groundwater will always be below saturation. Only low molecular weight hydrocarbons might reach concentrations in groundwater that are potentially toxic to aquatic organisms. Abernethy *et al.* (1986) suggested that a 50-fold dilution of a saturated solution of any hydrocarbon should yield it completely nontoxic to aquatic organisms.

The water-soluble fractions of several crude, refined, residual, and used oil products are acutely toxic to freshwater animals at concentrations ranging from 0.12 to 50.3 mg/L (parts per million) (Table 6-1). The median lethal concentrations (LC50) were determined by different analytical methods than were used to analyze the concentrations of total petroleum hydrocarbons in full-strength water soluble fractions (Table 4-2). However, some general comparisons can be made. In cases where comparisons can be made, acutely toxic concentrations are in the range of about 30 to 100 percent of the full-strength water-soluble fractions. There is no consistent difference in the toxicity of any petroleum product to crustaceans (*Daphnia*) and fish. The most toxic products are weathered Norman Wells crude oil and new crankcase oil. Unleaded gasoline has the lowest acute toxicity. The differences in acute toxicity of different petroleum products are due to differences in the composition of the water-soluble fractions, not to the concentration of total hydrocarbons in it. Weathered crude oil and crankcase oil produce water-soluble fractions containing low concentrations of total hydrocarbons, dominated by naphthalenes and phenanthrenes; gasoline produces a water-soluble fraction containing a high concentration of total petroleum hydrocarbons, dominated by BTEX. These data suggest that leachate from an oil deposit in soils would have to be diluted only about 20-fold to be rendered nontoxic to aquatic organisms.

Table 6-1. Acute toxicity to freshwater organisms of water-soluble fractions of selected crude and refined petroleum products

Product	Organism	LC50 (mg/L)	Reference
Lago Medio crude	*Daphnia magna*	7.7	Babra 1983.
Norman Wells crude (fresh)	*Daphnia magna*	9.0	Bobra 1983.
(43.2% weatered)	*Daphnia magna*	0.12	Bobra 1983.
(fresh)	*Salmo gairdneri* larvae	11.6	Lockhart 1987.
Prudhoe Bay crude	*Daphnia magna*	9.4	Bobra 1983.
	Oncorhynchus tschawytscha	1.5	Moles 1979.
	Gasterosteus aculeatus	6.9	Moles 1979.
Diesel fuel	*Daphnia magna*	7.16	Maclean 1988.
	Salmo gairdneri larvae	2.52	Lockhart 1988.
No. 2 home heating oil	*Daphnia magna*	2.18	Maclean 1988.
Leaded gasoline	*Daphnia magna*	13.5	Maclean 1988.
Unleaded gasoline	*Daphnia magna*	50.3	Maclean 1988.
	Salmo gairdneri	5.40	Lockhart 1987.
Crankcase oil (new)	*Daphnia magna*	0.38	Maclean 1988.
(used)	*Daphnia magna*	4.87	Maclean 1988.

6.2.2 Bioavailability of Petroleum Hydrocarbons to Aquatic Organisms

Petroleum hydrocarbons, because of their hydrophobicity and lipophilicity, tend to be accumulated from aqueous solution into the lipids of aquatic organisms. Equilibrium concentrations of hydrocarbons and heterocyclic compounds in the tissues of aquatic organisms should be proportional to the octanol/water partition coefficients (K_{ow}) of the compounds (Schüürmann and Klein 1988; Warne *et al.* 1989; de Voogt *et al.* 1991). The equilibrium concentration of a compound in the tissues of an aquatic organism exposed to the compound in the water alone is expressed as the bioconcentration factor (BCF: the ratio of the concentration in tissues to the concentration in the water). There is an approximately linear relationship between log K_{ow} and log BCF in freshwater organisms for polycyclic aromatic hydrocarbons and heterocyclic compounds (Figure 6-2). Heterocyclic compounds appear to have higher values than PAH do for log BCF at a given log K_{ow}.

The PAH and dibenzothiophene among the compounds chosen for more detailed evaluation (Table 4-1) have values for log BCF that are in the middle range of the values shown in Figure 6-2. Log BCFs are:

• Naphthalene	2.63
• Methylphenanthrene	3.48
• Dibenzothiophene	3.80
• Benz(a)anthracene	4.00
• Benzo(a)pyrene	4.11

There are no published BCF values for the alkanes listed in Table 4-1. The alkanes are accumulated rapidly by aquatic organisms, but are metabolized by oxidation to carboxylic acids (fatty acids) and incorporated into the lipid pool of the organism (Cravedi and Tulliez 1986a,b; le Bon *et al.* 1987).

These results indicate that aquatic animals can accumulate petroleum hydrocarbons, particularly the higher molecular weight PAH, from very low concentrations in water to high concentrations in tissues. However, aquatic organisms have an active mixed function oxygenase enzyme system capable of rapidly metabolizing and excreting accumulated PAH (Lee 1981; Stegeman 1981). Fish do not absorb PAH efficiently from their food and rapidly excrete accumulated hydrocarbons (Niimi and Dookran 1989). Therefore, food chain biomagnification of PAH does not occur (Broman *et al.* 1990).

6.3 Mammalian Toxicology

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.

A toxicity screening analysis (Appendix C) was initially performed for a large number of non-BTEX petroleum hydrocarbons in order to develop the shorter list of petroleum products selected for more detailed evaluation. The initial screening was conducted using a hazard ranking system which was based on a toxicity scoring methodology developed as a collaborative effort between the Environmental Protection Agency (EPA) and the Oak Ridge National Laboratory (ORNL) (O'Bryan and Ross 1988).

The scoring system combines objective guidelines with professional judgment to evaluate chemicals and consists of 11 separate scoring parameters. For this toxicity screening analysis, a subset of these 11 parameters was chosen for evaluation: oncogenicity/carcinogenicity, genotoxicity, developmental/reproductive toxicity, and subchronic/chronic toxicity.

For each chemical, scoring was performed on all, or any combination, of these parameters, depending on the available data. For each parameter, scores ranged from 0 (no evidence of particular toxic effect) to 9 (confirmed evidence of particular toxic effect). Each parameter was scored independently of all others. Scores were not added, weighed, or combined. Rather, the entire set of scores for each chemical comprised a scoring profile for that chemical. Objective criteria were used to assign a numerical score when data were available. In certain cases, a score was raised or lowered based on professional judgment.

The final compounds were selected to be representative of the toxicities and fates of many major organic compounds in crude, refined, residual, and used oils. These compounds include the 12 compounds listed in Table 3-2. A toxicity profile was prepared for each selected compound.

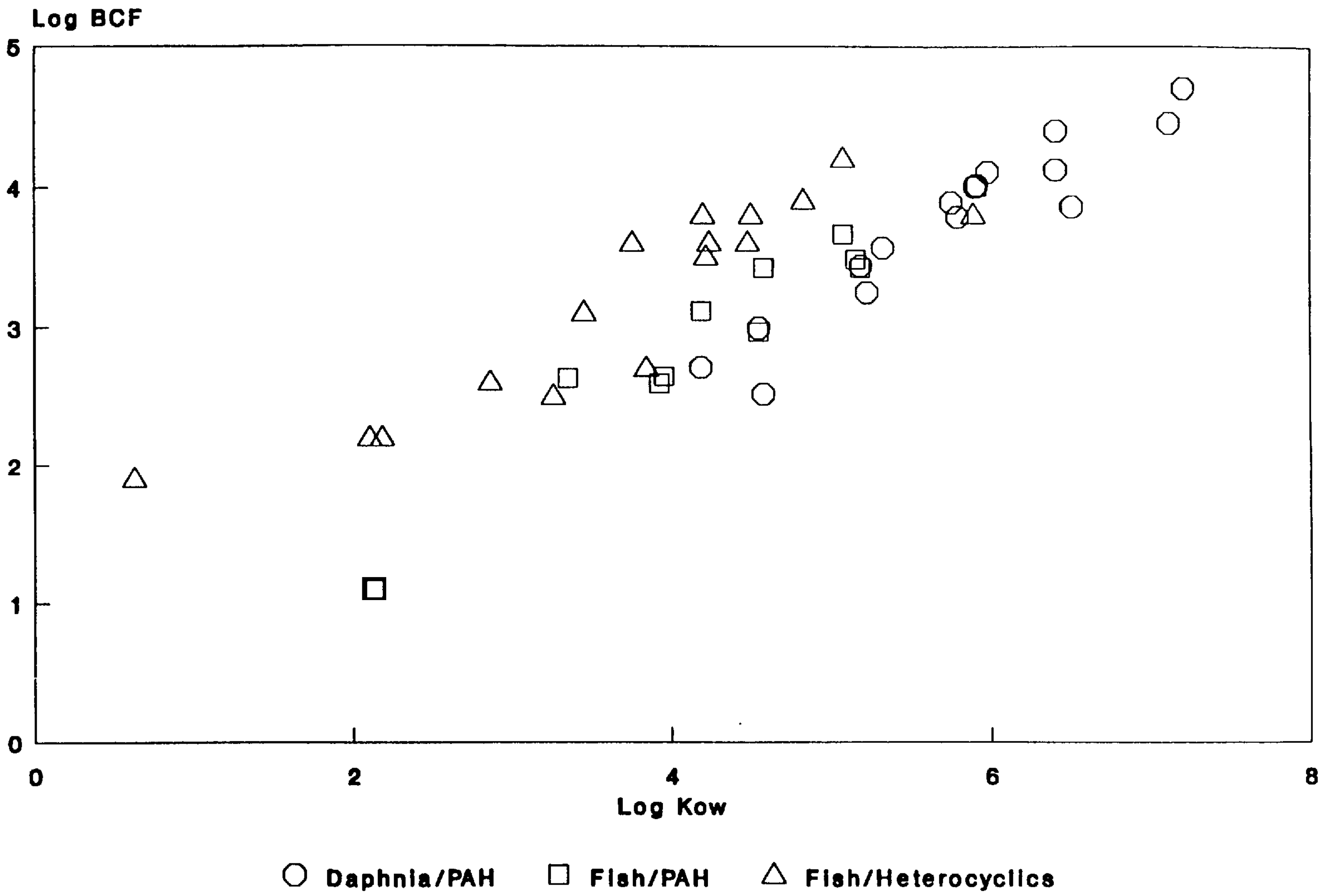


Figure 6-2. Relationship between log K_{ow} of selected PAH and sulfur heterocyctics and bioconcentration factors (BCF) in freshwater animals

Each toxicity profile addresses carcinogenicity/genotoxicity, reproductive/ developmental toxicity, and general toxicity. The section on general toxicity includes data on subchronic and chronic health effects, and to a limited degree, information on acute toxicity. Also included in this portion of the profile is information found in the literature on neurotoxicity and immunotoxicity. When available, human data were included in each profile. However, for most chemicals, data were limited primarily to animal studies. For the purposes of this human health effects evaluation, the primary exposure route of concern is ingestion resulting from the consumption of contaminated drinking water or fish. Therefore, greater emphasis and detail has been provided for those studies concerning the ingestion, or oral exposure route. However, toxic effects resulting from other routes of exposure (e.g., dermal, inhalation) have also been summarized briefly as appropriate.

For each chemical, information on its carcinogenicity classification by the EPA, the International Agency for Research on Cancer (IARC), and the National Toxicology program has been included. In addition, Federal water quality criteria values have been reported if available.

6.3.1 Benz(a)anthracene

Limited data are available on the health effects of benz(a)anthracene following oral exposure. This compound was shown to have some hepatic effects in rats, and was carcinogenic in mice. Benz(a)anthracene has also been reported as a mutagen in several test systems. The details of these studies are presented below. Both the IARC and the EPA have classified this compound as a probable human carcinogen (2A and B2, respectively), and the National Toxicology Program (NTP) lists benz(a)anthracene as a substance that can reasonably be anticipated to be a carcinogen.

The criteria recommended by EPA for the maximum acceptable concentration of PAHs, including benz(a)anthracene, in ambient water are 2.8×10^{-3} μg/l (water and fish consumption) and 3.11×10^{-2} μg/l (fish consumption only). In addition, the proposed maximum contaminant level (MCL) for PAHs in public water is 0.2 µg/l; however, based on the evidence of its carcinogenic potential, the maximum contaminant level goal (a non-enforceable concentration for drinking water) for PAHs, such as benz(a)anthracene, is 0 mg/l (IRIS 1992). The Agency for Toxic Substances and Disease Registry of the U.S. Department of Health and Human Services has reported that the minimum risk level (MRL) for PAHs in food is 3.6 ppm (ATSDR 1990a). This value is based on the animal studies described below.

6.3.1.1 General Toxicity. No case reports or epidemiological studies were found on the toxic effects of benz(a)anthracene in humans. In addition, the general toxicity data from animal bioassays is limited and reported effects from oral exposure include only moderate gastrointestinal and hepatic changes, as described below.

Intragastric administration of benz(a)anthracene at 50-100 mg/kg/day for four days suppressed intestinal carboxyesterase activity and induced hepatic carboxyesterase activity in rats.

Although enzyme alteration in the absence of other signs of gastrointestinal or liver toxicity is not considered an adverse health effect, it may precede the onset of more serious effects (Nousiainen *et al.* 1984). The higher dose (100 mg/kg/day) also resulted in a 19 percent increase in liver weight, and in the induction of cytosolic aldehyde dehydrogenase (ADH). The induction of ADH in animals has been correlated with carcinogenic potency (Torronen *et al.* 1981). In another study, oral exposure to benz(a)anthracene was associated with the induction of preneoplastic hepatocytes known as gamma glutamyl transpeptidase foci. Foci were induced in hepatectomized rats by the intragastric administration of 200 mg/kg of benz(a)anthracene, followed by a diet containing 2-acetylaminoflourene and carbon tetrachloride (Tsuda and Farber 1980).

6.3.1.2 Carcinogenicity/Genotoxicity. According to the IARC, there is *sufficient evidence* that benz(a)anthracene is carcinogenic to experimental animals; the IARC has placed this compound in group 2A, probably carcinogenic to humans (IARC 1987). The NTP has also classified this compound as a substance that may reasonably be anticipated to be a carcinogen (NTP 1991a). In addition, this compound is listed on the EPA Carcinogen Assessment Group's List of Carcinogens as a B2 compound, or a probable human carcinogen (IRIS 1992). These classifications are based on the lack of human data, as well as the experimental animal data and supporting genotoxicity data described below.

Mice administered two doses of benz(a)anthracene (2 mg) by oral gavage exhibited an increased incidence of hepatomas and pulmonary adenomas. In this study, mice were also given three doses of 1.5 mg benz(a)anthracene/week for five weeks by oral gavage. Treated animals developed lung adenomas, hepatomas, and papillomas of the forestomach (Klein 1963). However, in another study, a single gavage of 0.5 mg benz(a)anthracene did not produce tumors in mice, but 8 or 16 administrations by gavage at 3- to 7-day intervals over a 16 month period resulted in an increased incidence of forestomach papillomas (Bock and King 1959).

Benz(a)anthracene has also been shown to be carcinogenic in mice following dermal and subcutaneous exposure (IARC 1983).

Benz(a)anthracene was positive in mutagenicity tests with *Salmonella typhimurium* in the presence of metabolic activation (McCann *et al.* 1975, Coombs *et al.* 1976, Simmon 1979, Salamone *et al.* 1979, Bartsch *et al.* 1980, DeFlora *et al.* 1984, Norpoth *et al.* 1984, Utesch *et al.* 1987, Bos *et al.* 1988, Kaden *et al.* 1979) and with *Drosophila melanogaster* (Fahmy and Fahmy 1973). Results of *in vitro* tests with cultured mammalian cells show that this compound induced forward mutations (Slaga *et al.* 1978, Krahn and Heidelberger 1977, Amacher *et al.* 1980, Amacher and Turner 1980), sister chromatid exchange (Pal 1981), unscheduled DNA synthesis (Probst *et al.* 1981, Tong *et al.* 1981, Martin *et al.* 1978), and morphological transformations (Pienta *et al.* 1977, DiPaolo *et al.* 1969, Marquardt and Heidelberger 1972). Also, in an *in vivo* study, benz(a)anthracene induced sister chromatid exchange and micronuclei in hamsters (Peter *et al.* 1979). Based on these data, there is sufficient evidence that benz(a)anthracene is an active mutagen in short-term tests.

6.3.1.3 Reproductive/Developmental Toxicity. No data were found on the reproductive/developmental effect of benz(a)anthracene in humans or animals.

6.3.2 Benzo(a)pyrene

Human data on the health effects of oral exposure to benzo(a)pyrene are limited. However, oral administration of this compound has been reported to cause some systemic toxic effects (hepatic, gastrointestinal, renal, and hematological) in rats, and developmental and reproductive effects in rats and mice. In addition, benzo(a)pyrene was carcinogenic (inducing mostly forestomach tumors) in rats, mice, and hamsters following oral exposure, and has been reported as a mutagen in several test systems. Both the IARC and the EPA have classified this compound as a probable human carcinogen (2A and B2, respectively), and the NTP lists benzo(a)pyrene as a substance that can reasonably be anticipated to be a carcinogen.

The criteria recommended by EPA for the maximum acceptable concentration in ambient water of PAHs, including benzo(a)pyrene, are 2.8×10^{-3} μg/l (water and fish consumption) and 3.11×10^{-2} μg/l (fish consumption only). In addition, the proposed maximum contaminant level (MCL) for PAHs in public water is 0.2 μg/l; however, based on the evidence of its carcinogenic potential, the maximum contaminant level goal (a non-enforceable concentration for drinking water) for PAHs, such as benzo(a)pyrene, is 0 mg/l (IRIS 1992).The Agency for Toxic Substances and Disease Registry of the U.S. Department of Health and Human Services has reported that the minimum risk level (MRL) for PAHs in food is 3.6 ppm (ATSDR 1990a). The following are brief descriptions of studies examining the health effects of oral exposure to benzo(a)pyrene.

6.3.2.1 General Toxicity. No case reports or epidemiological studies were found on the toxic effects of benzo(a)pyrene in humans following oral exposure. Dermal exposure to this compound, however, has been shown to produce regressive verrucae and nucleolar enlargement in human volunteers and to aggravate preexisting skin conditions in patients (Cottini and Mazzone 1939, Rhoads *et al.* 1954). In addition, human bronchial mucosa treated *in vitro* with benzo(a)pyrene showed destruction of all cell types and distortion of cell morphology; this suggests that this compound could be toxic to the respiratory system of humans following inhalation exposure (Crocker *et al.* 1973, ATSDR 1990a). In animals, oral exposure to benzo(a)pyrene has been associated with mild hepatic, gastrointestinal, renal, and hematological toxicity, as described below.

Intragastric administration of benzo(a)pyrene at 50-150 mg/kg/day for four days suppressed carboxyesterase activity in the intestinal mucosa of rats and induced kidney microsomal and hepatic carboxyesterase activity. Although enzyme alteration in the absence of other signs of toxicity is not considered an adverse health effect, it may precede the onset of more serious effects (Nousiainen *et al.* 1984). Intragastric administration of 100 mg/kg/day also induced cytosolic aldehyde dehydrogenase (ADH) in the liver and increased liver weight by 27 percent. The induction of ADH in animals has been correlated with carcinogenic potency (Torronen *et al.* 1981). Another study showed the relationship between oral exposure to benzo(a)pyrene and the induction of preneoplastic hepatocytes known as gamma glutamyl transpeptidase foci. Foci were induced in hepatectomized rats by the intragastric administration of 200 mg/kg of benzo(a)pyrene (Tsuda and Farber 1980).

Oral exposure to benzo(a)pyrene has also been associated with hematological changes. In one study, a nonresponsive, or poorly inducible, strain of mice orally exposed to 120 mg benzo(a)pyrene/kg/day for 180 days developed adverse hematopoietic effects, including aplastic anemia and pancytopenia, that ultimately led to death. Responsive (markedly inducible) mice, however, remained healthy for at least six months following similar treatment (Robinson *et al.* 1975). In a similar study using the same dosing regimen, nonresponsive mice died within three weeks due to myelotoxic effects, while responsive mice exhibited no myelotoxicity (Legraverend *et al.* 1983).

6.3.2.2 Carcinogenicity/Genotoxicity. According to the IARC, there is *sufficient evidence* that benzo(a)pyrene is carcinogenic to experimental animals; the IARC has placed this compound in group 2A, probably carcinogenic to humans (IARC 1987). The NTP has also classified this compound as a substance which may reasonably be anticipated to be a carcinogen (NTP 1991a). In addition, this compound is listed on the EPA Carcinogen Assessment Group's List of Carcinogens as a B2 compound, or a probable human carcinogen (IRIS 1992). These classifications are based on the lack of human data, the experimental animal data, and the supporting genotoxicity data described below.

Several studies with mice have documented the relationship between the ingestion of benzo(a)pyrene (doses ranging from 1.5-400 mg/kg/day) and the development of benign and malignant tumors, mostly of the forestomach (Hartwell 1951, Shubik and Hartwell 1957, Thompson 1971, Tracor/Jitco 1973a, 1973b). Acute studies have shown that mice administered benzo(a)pyrene as an single intragastric dose, or as intermittent doses by gavage (doses ranging from 50-67 mg/kg) developed pulmonary adenomas and forestomach papillomas (Field and Roe 1965; Pierce 1961, Wattenberg and Bueding 1986, Wattenberg and Leong 1970). In subchronic studies (4-30 weeks), mice administered benzo(a)pyrene solutions by gavage also developed forestomach papillomas (Berenblum and Haran 1955, Biancifiori *et al.* 1967, El-Bayamy 1985, Robinson *et al.* 1987), as well as mammary tumors (Biancifiori *et al.* 1967), and lung adenomas (Biancifiori *et al.* 1967, Robinson *et al.* 1987). When this compound was orally administered to mice for 19 months (total dose of 0.10-100 mg/animal), the animals developed tumors of the liver, mesentery lymph nodes, peritoneum, and stomach (Fedorenko and Yansheva 1967).

A series of acute and subchronic feeding studies with mice also showed a relationship between exposure to benzo(a)pyrene and tumor incidence, which appeared related to the concentration used, and the duration of treatment (Neal and Rigdon 1967, Rigdon and Neal 1966, 1969). For example, 10 percent of mice fed 40-45 ppm benzo(a)pyrene for 110 days developed stomach tumors, compared to 70 percent of the animals fed 50-250 ppm for 122-197 days (Neal and Rigdon 1967). In a subsequent experiment, mice administered 250 and 1000 ppm of this compound in the diet had an increased incidence of stomach papillomas and carcinomas and lung adenomas. Animals in the 250 ppm dose group also developed leukemias. Again, tumor incidence increased with increasing dose (Rigdon and Neal 1966, 1969). In similar studies, mice were fed benzo(a)pyrene at concentrations of 0.4 or 1.26 mg/day for 28 days, 4.8 mg/day for 14 days, or 300 ppm for 35 days; all four groups had an increased incidence of forestomach tumors following an observation period of 10-14 weeks (Wattenberg 1972, 1974). Finally, a significant increase in stomach tumors was also seen in mice fed 0.2 or 0.3 mg benzo(a)pyrene in the diet for 12 weeks (Triolo *et al.* 1977).

Benzo(a)pyrene also has been shown to induce tumors in rats and hamsters. A single oral dose of benzo(a)pyrene (50 or 100 mg/kg), or subchronic exposure to this compound (eight weekly oral doses of 6.25 mg/kg), caused mammary tumors in female rats (Huggins and Yang 1962, McCormick 1981). Also, daily doses of 2.5 mg/rat have been reported to induce papillomas in the esophagus and forestomach (Gibel 1964). In a two-year study, rats administered benzo(a)pyrene by a caffeine gavage (6-39 mg/kg/year), or in the diet (39 mg/kg/year), had an increased incidence of benign and malignant forestomach tumors (Brune *et al.* 1981). Hamsters administered 2-5 mg benzo(a)pyrene by gavage for 1-11 months developed stomach papillomas and carcinomas (Dontenwill and Mohr 1962). When hamsters were fed this compound (500 ppm in the diet) for up to 14 months, they developed tumors in the esophagus, forestomach, and intestine (Chu and Malmgren 1965).

In addition to the data described above, the carcinogenic effects of benzo(a)pyrene have been reported for several species (mouse, rat, hamster, guinea pig, rabbit) following dermal, subcutaneous, intramuscular, intratracheal, inhalation, and intravenous administration. Most significantly, benzo(a)pyrene has been shown to be a potent experimental skin carcinogen, and is often used as a positive control in bioassays of other agents. There is also evidence that this compound produces local sarcomas in sub-human primates following repeated subcutaneous injections and lung carcinomas following intratracheal installations (IARC 1983, USEPA 1985, ATSDR 1990a).

In *in vitro* genotoxicity tests, oral exposure to 10 mg benzo(a)pyrene/kg produced gene mutations in mice in the mouse coat color spot test (Davidson and Dawson 1976, 1977); however, gene mutations were not induced in bacteria or yeast in a host-mediated assay in which benzo(a)pyrene was administered to mice by gavage (Simmon *et al.* 1979). Benzo(a)pyrene was positive in assays for forward mutations in *Salmonella* (in the presence of metabolic activation) (Kaden *et al.* 1979, Sakai *et al.* 1985), and for bacterial DNA repair, bacteriophage induction and bacterial mutation, and mutation in *Drosophila melanogaster. In vitro* tests with mammalian cells showed this compound induced DNA binding, DNA repair, sister chromatid exchange, chromosomal aberrations, and point mutations and transformations. This compound was also positive in several *in vivo* tests in mammals including DNA binding, sister chromatid exchange, chromosomal aberration, sperm abnormality, and the somatic specific locus test (Hollstein *et al.* 1979, de Serres and Ashby 1981, Tong *et al.* 1981).

Benzo(a)pyrene was also carcinogenic to two species of freshwater fish, the Japanese medaka (*Oryzias latipes*) and the guppy (*Poecilia retuculata*), when present in the water. Chronic exposure to concentrations about 100-fold higher than saturation aqueous solubility (produced by use of a carrier solvent) produced hepatocellular lesions classified as foci of cellular alteration, adenomas, and hepatocellular carcinomas (Hawkins *et al.* 1988, 1990). Exposure to concentrations of benzo(a)pyrene below its aqueous solubility produced no lesions.

6.3.2.3 Reproductive/Developmental Toxicity. No data were found on the reproductive or developmental toxicity of benzo(a)pyrene in humans. The results of animal studies, however, show that oral exposure to benzo(a)pyrene induces both reproductive and developmental effects in rats and mice.

In a two-generation study, benzo(a)pyrene was administered by gavage to pregnant mice during gestation. At the highest dose tested (160 mg/kg/day), there was a significant reduction in the percentage of pregnant females at parturition. In addition, F1 progeny from all treatment groups bred with untreated animals had significantly increased incidences of sterility. At the lowest dose tested (10 mg/kg/day), reduced fertility was associated with abnormalities in gonadal morphology and germ-cell development, while the higher doses resulted in complete sterility (Mackenzie and Angevine 1981). In another study, however, Swiss mice fed dietary benzo(a)pyrene at concentrations up to 133 mg/kg/day over varying times during mating, gestation, and parturition did not show adverse signs of sterility (Rigdon and Neal 1965). In a reproductive study with rats, dietary administration of benzo(a)pyrene for 28 days did not adversely affect the estrus cycle or fertility of females mated with untreated males. However, when treated male and female rats were mated, there was a reduction in the incidence of pregnancy, and an increase in stillborns and resorptions (Rigdon and Rennels 1964).

When benzo(a)pyrene was administered by gavage to pregnant mice during gestation, the viability of litters at parturition was significantly reduced in the highest dose group (160 mg/kg/day), and the mean pup weight was significantly reduced in all dose groups (10, 40, and 160 mg/kg/day) (Mackenzie and Angevine 1981). When aromatic hydrocarbon (Ah)-nonresponsive mice bred to Ah-responsive mice were administered dietary benzo(a)pyrene (120 mg/kg/day) during gestation, there was an increase in the incidence of stillborns, resorptions, and malformations in offspring (Legraverend *et al.* 1984).

Contrary to the data described above, negative results were obtained when dietary benzo(a)pyrene was administered to mice at a dose of 33.3-133.3 mg/kg/day at various times before and after mating. Although maternal weight gain was reduced in mice in the higher dose groups, no adverse effects on the developing embryos and no malformations were observed (Rigdon and Neal 1965). It should be noted, however, that the actual maternal exposure was difficult to quantify due to the method of administration (pellets containing the test material were rejected by the mothers, who eventually cannibalized their young).

In addition to oral exposure, subcutaneous and intraperitoneal injections of benzo(a)pyrene were shown to produce developmental (stillbirths, resorptions, malformations, testicular changes, immunosuppression, tumor induction) and reproductive effects (decreased number of corpora lutea, decreased uterine weights, increased resorptions, decreased fetal survival) in rats and mice (ATSDR 1990a).

6.3.3 5-Methylchrysene

No data were found on the general toxic effects or reproductive/developmental effects of 5-methylchrysene exposure (via any route) in humans or animals. However, this compound has been found to be carcinogenic to mice when administered dermally or subcutaneously. In addition, 5-methylchrysene has been reported as a mutagen in *Salmonella* and rat hepatocytes. The IARC has classified this compound as a possible human carcinogen (2B), and the NTP lists 5-methylchrysene as a substance that can reasonably be anticipated to be a carcinogen. Federal water quality criteria values have not been published for this compound.

6.3.3.1 General Toxicity. No data were found on the general toxicity of 5-methylchrysene in humans or animals.

6.3.3.2 Carcinogenicity. According to the IARC, there is *sufficient evidence* that 5-methylchrysene is carcinogenic to experimental animals; the IARC has placed this compound in group 2B, possibly carcinogenic to humans. The NTP has also classified this compound as a substance that may reasonably be anticipated to be a carcinogen (NTP 1991a). The EPA, however, has not evaluted 5-methylchrysene as to its potential carcinogenicity. The NTP and IARC classifications are based on the lack of human data, the experimental animal data, and the supporting genotoxicity data described below.

No data were found on the carcinogenicity of 5-methylchrysene in animals following oral exposure. However, subchronic skin painting studies have shown that this compound induces skin tumors in mice. In three similar studies, 5-methylchrysene was applied to the shaved backs of mice 3 times/week for up to 62 weeks at concentrations of either 100 μg/0.1 mL acetone (Hecht *et al.* 1974, Hoffmann *et al.* 1974), or 0.01 percent and 0.005 percent solutions in acetone (Hecht *et al.* 1976b). By week 25, all mice treated with 100 μg of 5-methylchrysene had developed skin tumors, and after 35 weeks all the mice in this dose group had died, with a total of 99 tumors, including 37 carcinomas. Three mice had, in addition to skin tumors, metastases to the lung, and one had metastases of the lung and spleen (Hecht *et al.* 1974, Hoffmann *et al.* 1974). Mice in the 0.01 and 0.005 percent dose groups had an increased incidence of skin tumors, including carcinomas, after 55 and 62 weeks of treatment, respectively (Hecht *et al.* 1976b). In other studies, mice were given initiating applications of 1-100 μg 5-methylchrysene in acetone every other day for a total of 10 doses. Ten days after the last dose, a promoter solution (TPA in acetone) was applied 3 times/week for 20 weeks. All dose groups showed an increased incidence of skin tumors that were classified as either keratoacanthomas, papillomas, or carcinomas (Hecht *et al.* 1974, 1976b, 1978, 1979, 1980, Amin *et al.* 1981). Similar results were found using the same methods and an initiating dose of 5-methylchrysene of 0.015-1.5 μmol/0.1 mL acetone (Amin *et al.* 1990, Rice *et al.* 1988).

In addition to the skin painting studies, two other investigations have found that subcutaneous administration of this compound is carcinogenic to mice. Mice given a single subcuteneous injection of 5-methylchrysene (2 mg) had an increased incidence of sarcomas at the injection site; the average latency for the tumors was 125-136 days (Dunlap and Warren 1943). When mice were given a subcutaneous injection of 0.05 mg 5-methylchrysene every two weeks for 20 weeks (total dose of 0.5 mg), 88 percent developed fibrosarcomas, with an average latent or latency period of 25 weeks (Hecht *et al.* 1976a).

Data from genotoxicity assays show that 5-methylchrysene was mutagenic to *Salmonella typhimurium* in the presence of an exogenous metabolic system (Coombs *et al.* 1976, Amin *et al.* 1979, Hecht *et al.* 1979), and induced DNA damage in primary rat hepatocytes (Tong *et al.* 1981).

6.3.3.3 Reproductive/Developmental Toxicity. No data were found on the reproductive or developmental toxicity of 5-methylchrysene in humans or animals.

6.3.4 1-Methylphenanthrene

No data were found on the general toxic effects or reproductive/developmental effects of 1-methylphenanthrene exposure (via any route) in humans or animals. This compound was not carcinogenic in one skin-painting study with mice, but was mutagenic in several test systems. These studies are described below. Because of the lack of human data and the inadequate animal data, the IARC has designated 1-methylphenanthrene as a class 3 compound (not classifiable as to carcinogenicity to humans). 1-Methylphenanthrene has not been classified by the EPA or the NTP as to its potential carcinogenicity. In addition, Federal water quality criteria values have not been published for this compound.

6.3.4.1 General Toxicity. No data were found on the general toxicity of 1-methylphenanthrene in humans or animals.

6.3.4.2 Carcinogenicity/Genotoxicity. The IARC has designated 1-methylphenanthrene as a class 3 compound (not classifiable as to carcinogenicity to humans). The EPA and the NTP have not classified this compound as to its potential carcinogenicity. The only carcinogenicity and mutagenicity data found on this compound are described below.

In a skin-painting study, mice were given initiating applications of 1-methylphenanthrene (0.1 percent solution in acetone) to the shaved back every other day for 20 days. Ten days after the last dose, a promoter solution (TPA in acetone) was applied 3 times/week for 20 weeks. Because no tumors were observed in these animals at the end of the study, it was concluded that 1-methylphenanthrene was inactive as an initiator (LaVoie *et al.* 1981).

Data from genotoxicity tests show that 1-methylphenanthrene was mutagenic to *Salmonella typhimurium* (Lavoie *et al.* 1981, Kaden *et al.* 1979, Sakai *et al.* 1985) and produced DNA damage and mutations in primary rat hepatocytes (Tong *et al.* 1981) and human lymphoblastoid cells (Barfknecht *et al.* 1981).

6.3.4.3 Reproductive/Developmental Toxicity. No data were found on the reproductive/developmental effect of 1-methylphenanthrene in humans or animals.

6.3.5 Dibenzothiophene

No data were found on the general toxic, carcinogenic, or reproductive/developmental effects of dibenzothiophene (via any route) in humans or animals. Dibenzothiophene has not been classified as to its potential carcinogenicity by the IARC, the EPA or the NTP. This compound was not mutagenic in several genotoxicity assays. In addition, Federal water quality criteria values have not been published for this compound.

6.3.5.1 General Toxicity. No data were found on the general toxicity of dibenzothiophene in humans or animals.

6.3.5.2 Carcinogenicity. The IARC, the EPA, and the NTP have not classified this compound as to its carcinogenicity. In addition, data from genotoxicity tests show that dibenzothiophene was not mutagenic to *Salmonella typhimurium* (Kaden *et al.* 1979, Pelroy *et al.* 1983, McFall *et al.* 1984), and did not produce mutations in Chinese hamster ovary cells (Rasmussen *et al.* 1991). No other data were found on the carcinogenicity of dibenzothiophene.

6.3.5.3 Reproductive/Developmental Toxicity. No data were found on the reproductive/developmental effects of dibenzothiophene in humans or animals.

6.3.6 1,2,4-Trimethylbenzene

Oral exposure to 1,2,4-trimethylbenzene did not result in kidney toxicity in rats. However, subchronic inhalation of this compound has caused diminished weight gain and toxic effects on the blood and nervous system of rats. The EPA, the NTP, and the IARC have not classified this compound as to its potential carcinogenicity. 1,2,4-Trimethylbenzene caused borderline" positive results in an oral rat carcinogenicity bioassay. No mutagenicity data specific to 1,2,4-trimethylbenzene were found. However, high flash naphtha, a mixture of predominantly 9-carbon aromatic molecules (primarily isomers of trimethylbenzene and ethyltoluene) has been found to be nongenotoxic in a battery of assays. Federal water quality criteria have not been published for 1,2,4-trimethylbenzene.

6.3.6.1 General Toxicity. In the only study found in the literature concerning oral exposure to this compound, 1,2,4-trimethylbenzene (0.5 and 2.0 g/kg) did not induce nephropathy in rats following gavage administration five days/week for four weeks (Halder *et al.* 1985). Short-term inhalation exposure to high concentrations of 1,2,4-trimethylbenzene has been found to result in central nervous system depression, thrombocytopenia, asthmatic bronchitis, chemical pneumonitis, and pulmonary edema. Headache, fatigue, nausea, and anxiety have also been noted. Rats that inhaled 1700 ppm 1,2,4-trimethylbenzene for four months were found to have diminished weight gain, lymphopenia, and neutrophilia. A marked depression in central nervous system activity was also observed (ACGIH 1986). No data were found on the toxic effects of this compound following oral exposure.

6.3.6.2 ***Carcinogenicity/Genotoxicity.*** The EPA, the IARC, and the NTP have not classified this compound as to its potential carcinogenicity. 1,2,4-Trimethylbenzene caused borderline" positive results in an oral rat carcinogenicity bioassay conducted at the Bologna Institute of Oncology (Maltoni *et al.* 1991). No other data on the carcinogenicity of this compound were found. No mutagenicity data specific to this compound were found in the literature surveyed. However, the mutagenic potential of high flash naphtha, a mixture of predominantly 9-carbon aromatic molecules (primarily isomers of trimethylbenzene and ethyltoluene) has been studied. High flash aromatic naphtha did not induce mutation in either the *Salmonella*/mammalian microsome mutagenicity test or the hypoxanthine-guanine phosphoribosyl transferase (HGPRT) assay in Chinese hamster ovary cells. This mixture was negative for sister chromatid exchange induction in Chinese hamster ovary cells, and did not produce chromatid or chromosomal abnormalities *in vitro*. In addition, there was no evidence of chromosomal abnormalities in rat bone marrow following exposure for five days to 1500 ppm. The authors reported that these data, in combination with previous studies of mixtures containing a substantial fraction of C9 aromatic hydrocarbons (American Petroleum Institute 1973, 1978), indicate that high flash aromatic naphtha, and similar materials, are not mutagenic, either *in vitro* or *in vivo*. They also noted that the lack of mutagenicity potential suggests that high flash aromatic naphtha is unlikely to be a genotoxic carcinogen (Schreiner *et al.* 1989).

6.3.6.3 Reproductive/Developmental Toxicity. No data were found on the developmental and reproductive toxicity of 1,2,4-trimethylbenzene. However, inhalation of high flash naphtha has been found to be teratogenic in rats at maternally toxic dose levels (1500 ppm), causing fetal mortality, reduced weight, delayed ossification, and an increase in the incidence of cleft palate. At 500 ppm, a level at which maternal weight gain was only slightly reduced, fetal weight gain was also decreased, but there was no other evidence of developmental effects. The lowest exposure level (100 ppm) did not cause any maternal or developmental toxicity. High flash naphtha was not found to cause reproductive effects following inhalation exposure in a 3-generation reproduction study (McKee *et al.* 1990).

6.3.7 Naphthalene

Human exposure to naphthalene occurs mainly through accidental or intentional (suicide attempts) ingestion of contaminated food or mothballs. Although the most common adverse effects of naphthalene ingestion are jaundice and hemolytic anemia, other effects include gastrointestinal, renal, neurological, and hepatic abnormalities. In animals, oral exposure to this compound was reported to cause various systemic toxic effects (hepatic, respiratory, immunological, renal, and ocular) in rats, mice, and rabbits. Naphthalene exposure did not cause developmental effects in animals, and resulted in only minimal reproductive effects in rats. This compound was not carcinogenic when administered orally, intraperitoneally, subcutaneously, or dermally, but did exhibit carcinogenic potential in animals when administered by inhalation.

The IARC has not evaluated the carcinogenic risk to humans associated with oral exposure to naphthalene, and the Carcinogen Assessment group of the USEPA has designated this chemical as a Group D, or not classifiable, compound. Naphthalene is not classified by the NTP, and Federal water quality criteria values have not been published for this compound.

6.3.7.1 General Toxicity. Human exposure to naphthalene has occurred from suicide attempts, accidental ingestion of contaminated food, and ingestion of mothballs by children. The primary target of naphthalene toxicity is the erythrocyte, and the most common adverse effects of naphthalene ingestion are jaundice and hemolytic anemia (decreased hemoglobin, hematocrit and erythrocyte values, and increased reticulocyte counts, heinz bodies, and serum bilirubin levels) (USEPA 1985, ATSDR 1990b). Infants appear to be more sensitive to the hemolytic effects of naphthalene than adults (Valaes *et al.* 1963).

Other reported effects in humans following oral exposure to naphthalene include the following: gastrointestinal symptoms, such as nausea, vomiting, diarrhea, intestinal bleeding and abdominal pain; renal effects, including tubular necrosis, hematuria, and renal failure; neurological effects such as sensorium, listlessness, lethargy, vertigo, convulsions, and coma; and hepatic effects, such as jaundice, hepatomegaly, and elevated serum enzyme levels (Bregman 1954, Chusid and Fried 1955, Dawson *et al.* 1958, Gidron and Leurer 1956 Gupta *et al.* 1979, Haggerty 1956, Kurz 1987, MacGregor 1954, Mackell *et al.* 1951, Ojwang *et al.* 1985, Shannon and Buchanan 1982, Zueler and Apt 1949). The majority of human deaths following naphthalene intoxication have resulted from attempted suicides. Due to the descriptive nature of these cases, the lethal dose could only be roughly estimated to range from 300-600 mg/kg (USEPA 1985, ATSDR 1990b). However, a lethal oral dose of 100 mg/kg has been reported for a child (RTECS 1992).

Similar effects to those described above have been reported in humans after inhaling mothball flakes (Valaes *et al.* 1963, Linick 1983, Harden and Baetjer 1978) and in infants dermally exposed to diapers or clothing treated with naphthalene mothballs (Schafer 1951, Cock 1957, Dawson 1958). Also, two cases have been reported of ocular effects including cataract formation, retinal hemorrhage, and chorioretinitis in workers who may have inhaled naphthalene (Van der Hoeve 1906, Ghetti and Mariana 1956).

In animals, systemic toxicity was seen following both acute and subchronic oral exposure to naphthalene, and included mild hepatic, respiratory, immunological, renal, and ocular effects. Acute oral administration of this compound (1000 mg/kg/day for 10-18 days) to rats caused modest increases in liver weight and hepatic enzyme activity (Rao and Pandya 1981, Yamauchi *et al.* 1986). When mice received similar treatment (267 mg/kg/day), no hepatic effects were observed, but the animals had increased lung weights and decreased thymus and spleen weights. In the same study, mice exposed to naphthalene (5.3-133 mg/kg/day) for 90 days had decreased spleen weights (highest dose only) and changes in clinical chemistry (increases in blood protein and decreases in calcium ion and BUN); no respiratory effects were observed (Shopp *et al.* 1984). Subchronic exposure of rats (200 or 400 mg/kg/day for 13 weeks) caused transient signs of toxicity (diarrhea, lethargy, hunched posture, roughened haircoats, decrease in body weight gain), and lesions of the kidney and thymus (high dose group only) (NTP 1980).

Several studies have documented that oral exposure to naphthalene causes ocular effects in rabbits, mice, and rats. In rabbits, oral doses of 1000-2000 mg naphthalene/kg/day for 1-28 days, resulted in cataract formation and reduced lens and capsule lactate dehydrogenase activities (Srivastava and Nath 1969, Rossa and Pau 1988, Van Heyningen and Pirie 1976 Ikemoto and Iwata 1978). At doses of 400-600 mg/kg, naphthalene caused ptosis and secretions around the eyes of mice (Shopp *et al.* 1984). Rats treated for four days with 1000 mg naphthalene/kg/day showed only a decrease in lens glutathione (Yamauchi *et al.* 1986), while rats orally administered this same dose for 75 days had cataract formation. No ocular effects were observed when this compound was tested on rats at concentrations of 41-750 mg/kg/day (Germansky and Jamall 1988, Schmahl 1955).

The acute oral LD_{50} values (dose that results in 50% mortality) for naphthalene in rats, mice, and guinea pigs were reported to be 2009-3310 mg/kg (Gaines 1969, Mallory *et al.* 1985a), 353-710 mg/kg (Shopp *et al.* 1984, Plasterer *et al.* 1985), and 1200 mg/kg (RTECS 1992), respectively. However, oral doses as low as 300 mg/kg have been found to be lethal to mice, and 1000 mg/kg doses were lethal to rats (Yamauchi *et al.* 1986) and rabbits (Rossa and Pau 1988). The no observable adverse affect levels (NOAEL) for general toxic effects were reported as 53-267 mg/kg/day for mice and 450 mg/kg/day for rats (ATSDR 1990b).

Dermal and intraperitoneal exposure to naphthalene have caused toxic effects in animals. For instance, naphthalene has been reported as a mild dermal irritant in rabbits at 500 mg/site (Mallory *et al.* 1985b), and causes ocular irritation in the eyes of rabbits at 0.1 mg/eye (Mallory *et al.* 1985c). Intraperitoneal injections of 125-400 mg/kg of this compound reportedly caused pulmonary necrosis to bronchiolar epithelial cells (Clara cells) in mice (Tong *et al.* 1981, 1982, Warren *et al.* 1982, O'Brien *et al.* 1985), and 400-600 mg/kg resulted in damage to renal cells (O'Brien *et al.* 1985) .

6.3.7.2 Carcinogenicity/Genotoxicity. The IARC has not evaluated the carcinogenic risk to humans associated with oral exposure to naphthalene. According to the EPA, there is no evidence for carcinogenicity in humans and the data from animal bioassays are inadequate (described below); therefore, the chemical is designated as a Group D, or not classifiable, compound (IRIS 1992). In addition, the NTP has not classified this compound as to its potential carcinogenicity (NTP 1991a).

The data from animal studies are limited, and only two studies were found that examined the carcinogenicity of oral exposure to naphthalene. The results of these studies show that naphthalene was not carcinogenic to rats when administered orally at a concentration of 41 mg/kg/day for two years (Schmahl 1955), or as a single gavage dose of 100 mg/kg (Tsuda *et al.* 1980). When mice were exposed to naphthalene by inhalation (10 or 30 ppm six hrs/day, five days/week for six months), however, there was a significant increase in the number of adenomas per tumor-bearing mouse lung, but not a significant increase in overall tumor incidence (Adkins *et al.* 1986). In another inhalation study, mice treated with 30 ppm naphthalene for six hrs/day, five days/week for 103 weeks had a significant increase in the incidence of bronchiolar adenomas (females only) and respiratory epithelial cell hyperplasia (males and females) (NTP 1991b). Finally, naphthalene was not carcinogenic to rats by intraperitoneal (Schmahl 1955) or subcutaneous injection (Knake 1956), and did not induce tumors in skin painting studies with mice (Kennaway 1930, Schmeltz *et al.* 1978).

In most cases, naphthalene was negative when tested in a variety of genotoxicity and mutagenicity assays. Naphthalene was not mutagenic in reverse and forward mutation assays using various strains of *Salmonella typhimurium* in the absence or presence of exogenous metabolic activation (Kraemer *et al.* 1974, McCann *et al.* 1975, Anderson and Styles 1978, Kaden *et al.* 1979, Florin *et al.* 1980, Gatehouse 1980, Connor *et al.* 1985, Ho *et al.* 1981, Seixas *et al.* 1982, Sakai *et al.* 1985, Mortelmans *et al.* 1986, Bos *et al.* 1988). Naphthalene was also negative in DNA damage assays (Nakamura *et al.* 1987, Mamber *et al.* 1983, Sina *et al.* 1983), and in phage induction assays (Ho and Ho 1981, Mamber *et al.* 1984). In addition, naphthalene did not cause cell transformations in rodent embryo cells (Freeman *et al.* 1973, Rhim *et al.* 1974), or in a murine mammary gland organ culture system (Tonelli *et al.* 1979).

6.3.7.3 Reproductive/Developmental Toxicity. No information was found on the reproductive effects of naphthalene in humans, and data from animal studies were limited. When naphthalene (300 mg/kg/day) was administered orally in corn oil to pregnant mice, there was a decrease in mean maternal body weight and in the number of pups per litter, and an increase in maternal lethality (Plasterere *et al.* 1985). However, when rabbits were treated with naphthalene (400 mg/kg/day) in a methylcellulose vehicle, no adverse effects were observed (Mallory *et al.* 1986). No effects on testicular weights were found when mice were treated with oral doses of naphthalene at concentrations up to 267 mg/kg/day for 14 days or 133 mg/kg/day for 90 days (Shopp *et al.* 1984).

Oral exposure of pregnant women to high levels of naphthalene could result in fetal (developmental) toxicity. For example, naphthalene ingested by the mother has been shown to cross the placenta and result in neonatal hemolytic anemia (Anziulewicz *et al.* 1959, Zinkham and Childs 1957, 1958). In addition, a positive association between the incidence of severe neonatal jaundice in infants and a history of naphthalene exposure (route undetermined) in the home has been reported in Nigeria (Familusi and Dawodu 1985). In the limited animal studies available, however, naphthalene exposure did not cause any developmental effects. No fetal abnormalities were observed when naphthalene was administered orally during gestation to pregnant mice (300 mg/kg/day) (Plasterer *et al.* 1985), and rabbits (40-400 mg/kg/day) (PRI 1986, Naismith and Matthews 1986), or injected intraperitoneally in pregnant rats (Hardin *et al.* 1981).

In additional to oral exposure, naphthalene has also been found to cause developmental abnormalities in rats following intraperitoneal administration (abnormalities of the musculoskeletal and cardiovascular systems) (RTECS 1992).

6.3.8 2-Methylnaphthalene

No information was found concerning the health effects posed by oral, inhalation, dermal, or subcutaneous exposure of humans or animals to 2-methylnaphthalene (ATSDR 1990). When administered intraperitoneally, however, this compound induced a slight respiratory effect in mice. Although no carcinogenicity data were found for this compound, 2-methylnaphthalene has been reported as mutagenic in human lymphocytes. The EPA, the IARC, and the NTP have not classified this compound as to its carcinogenicity. In addition, Federal water quality criteria values have not been published for this compound.

6.3.8.1 General Toxicity. No information was found on the general toxic effects of 2-methylnaphthalene in humans and the data from animal studies are very limited. A single intraperitoneal injection of 2-methylnaphthalene at 100-400 mg/kg caused exfoliation of the bronchial epithelium in mice (Griffen *et al.* 1981, 1983, Buckpitt *et al.* 1986). Intraperitoneal injections as high as 1000 mg/kg did not cause any other systemic toxic effects in the mice, and the lowest lethal dose was reported as 1000 mg/kg (Griffin *et al.* 1981, 1983). No data were found on the toxic effects of oral, dermal, inhalation, or subcutaneous exposure to 2-methylnaphthalene in animals. However, an oral LD_{50} (dose that resulted in 50% mortality) for 2-methylnaphthalene was reported as 1630 mg/kg (RTECS 1992).

6.3.8.2 Carcinogenicity/Genotoxicity. No data were found on the carcinogenic effects of 2-methylnaphthalne in humans or animals. In addition, the EPA, the IARC, and the NTP have not classified this compound as to its potential carcinogenicity. Except for one study that reported this compound as mutagenic in human lymphocytes (RTECS 1992), no data were found on the genotoxicity of 2-methylnaphthalene.

6.3.8.3 Reproductive/Developmental Toxicity. No data were found on the reproductive or carcinogenic effects of 2-methylnaphthalene in humans or animals.

6.3.9 Cyclohexane

No data are available on the effects associated with long-term ingestion of cyclohexane. Chronic inhalation exposure has induced microscopic changes in the liver and kidneys of experimental animals. The EPA, the IARC, and the NTP have not classified cyclohexane as to its potential carcinogenicity. This compound did not result in tumor induction when applied to the skin of mice and rabbits, or following inhalation exposure in rats and rabbits. However, in a recent study, cyclohexane was found to have tumor-promoting properties. Cyclohexane has induced chromosomal aberrations in the bone marrow cells of rats and caused DNA damage in *Escherichia coli*. However, this compound was nongenotoxic in *Salmonella typhimurium*, mouse lymphoma cells, and human lymphocytes. No Federal water quality criteria values have been published for this compound.

6.3.9.1 General Toxicity. No data were found in the literature on possible effects associated with long-term exposure to cyclohexane by the ingestion route. Limited data were available on chronic effects following inhalation of cyclohexane. Chronic inhalation exposure to concentrations above 300 ppm cyclohexane reportedly may produce mild irritation of the eyes and upper respiratory tract. Repeated inhalation exposure for 50 days to 786 ppm has resulted in microscopic changes in the liver and kidneys of rabbits; however, no toxic effects were observed among rabbits exposed to 434 ppm or 3330 ppm for the same duration (ACGIH 1980). In addition, exposure to 1243 ppm cyclohexane 6 hours/day for 50 days did not induce gross toxic effects in monkeys and tissues appeared normal on microscopic examination (Clayton and Clayton 1981).

In a subacute study, 1000 mg/kg cyclohexane caused kidney tubule injury as evidenced by an increase in β-$_2$-microglobulinuria following intraperitoneal administration (five times/week for two weeks). These renal tubular effects can most likely be attributed to cyclohexanol, the primary metabolite of cyclohexane (Bernard *et al.* 1989).

Acute oral exposure to high concentrations of cyclohexane may result in symptoms associated with central nervous system depression as well as gastrointestinal irritation. The oral LD_{50} for this compound is 29,800 mg/kg in rats. In experimental animals, short-term inhalation exposure to low concentrations of cyclohexane has caused irritation of the eyes, nose, and respiratory tract. Inhalation exposure to concentrations above 12,000 ppm may induce central nervous system depression with excitement, headache, dizziness, dullness, nausea, narcosis, coma and possibly death due to respiratory failure (Clayton and Clayton 1981).

6.3.9.2 Carcinogenicity/Genotoxicity. The EPA, the IARC, and the NTP have not classified cyclohexane as to its potential carcinogenicity. Cyclohexane was recently evaluated for its tumorigenic potential on mouse skin following multistage initiation-promotion protocols. The activity of ornithine decarboxylase (ODC), a marker of tumor promotion, was found to be induced by the topical application of cyclohexane (Gupta 1990). Kennaway *et al.* (1930) reported that mice exposed to cyclohexane via skin application did not develop tumors (dose and duration of exposure not reported). In addition, tumor development was not found to differ from controls among mice treated with 50-60 μl of cyclohexane applied to the shaved skin for 50 or 60 weeks (Horton *et al.* 1981, Easley *et al.* 1982). Fabre (1952 as reported in U.S. Department of Commerce 1984) reported that skin painting of rabbits using 10 mL of cyclohexane twice daily for 30 days did not result in tumor formation. Inhalation exposure to cyclohexane in rabbits (580-6400 ppm eight hours/day for 40 days) and rats (2330-5222 ppm eight hours/day for 40 days) was also nontumorigenic.

Cyclohexane induced chromosomal numerical aberrations in the bone marrow cells of female rats following inhalation exposure to 96.6 and 307.2 ppm for 6 hours/day, for five days. However, in this study, a dose-related response was not observed for this effect, and no significant differences were noted between treated and control animals with respect to structural aberration frequency and percentages of cells exhibiting one or more structural aberrations (Litton Bionetics 1982a). Cyclohexane was also found to cause DNA damage in *Escherichia coli* (RTECS 1992). Cyclohexane was nonmutagenic in all strains of *Salmonella typhimurium* tested in the presence and absence of metabolic activation (Mortelmans *et al.* 1986). In addition, this compound was negative when tested for the induction of unscheduled DNA synthesis in cultured human lymphocytes (Perocco *et al.* 1983) and did not cause specific locus mutations in mouse lymphoma cells (Litton Bionetics 1982b), or induce sister chromatid exchange in Chinese hamster ovary cells (Phillips 1984).

6.3.9.3 Reproductive/Developmental Toxicity. No data were found on the reproductive or developmental effects of cyclohexane in the literature surveyed.

6.3.10 n-Hexane

Limited data are available on the health effects of n-hexane resulting from oral exposure. Although n-hexane may be absorbed orally, exposure to this compound generally occurs by inhalation, and the majority of studies reported in the literature concern the inhalation exposure route. Chronic exposure to n-hexane has been found to cause peripheral neuropathy and axonal degeneration in humans. This compound has been found to be fetotoxic, but not teratogenic in animals. Both positive and negative results have been reported on its mutagenic potential. The EPA, the IARC, and the NTP have not classified n-hexane as to its potential carcinogenicity. In addition, Federal water quality criteria values have not been published for this compound.

6.3.10.1 General Toxicity. The EPA reports that there is considerable and compelling evidence that n-hexane is neurotoxic to humans. In many epidemiological studies reported, chronic inhalation exposure to n-hexane (concentrations varying between 500 and 1000 ppm) has been found to cause sensorimotor polyneuropathy with axonal degeneration of the distal parts of the peripheral nervous system, as well as the spinal cord, and the brain stem. Associated effects include weakness, memory loss, numbness, and headaches (Clement Associates 1985, IRIS 1992). Although limited data are available concerning the chronic effects associated with oral human exposure, ingestion of n-hexane has also been associated with central nervous system effects as well as nausea, anorexia, and general intestinal irritation. Studies of shoe factory workers have shown that n-hexane is metabolized to 2,5-hexanedione, a known neurotoxin (Perbillini *et al.* 1980). This primary metabolite of n-hexane is considered to most likely be responsible for the polyneuropathy associated with n-hexane exposure.

In experimental animals, subchronic and chronic oral n-hexane exposure has also been associated with neurotoxicity. In rats orally administered n-hexane at concentrations of 650 mg/kg for 90 days or more, axonal degeneration in peripheral nerve cells was observed. Peripheral neuropathy and distal nerve fiber degeneration were observed in an oral bioassay in which rats were given 400-600 mg/liter/day n-hexane (approximately 100-150 mg/kg/day) for five months (Spenser and Schaumburg 1977). In another rat study, neuropathy was induced following 101 days of n-hexane administration (4000 mg/kg, five days/week). Histological changes noted in this study included multi-focal axonal swellings, adaxonal myelin infolding, and paranodal myelin retraction. Histological examination of testicular tissue revealed varying stages of atrophy of the germinal epithelium. No neurological or testicular effects were reported at dose levels of 570 mg/kg or 1140 mg/kg n-hexane (Krasavage *et al.* 1980). Peripheral neuropathy has also been observed following inhalation exposure in animals (Spenser and Schaumburg 1977).

n-Hexane-induced renal toxicity (degenerated tubules) was observed in rats that received a single oral dose (1,290 mg/kg) of this compound. However, this dose produced no measurable effects on the following parameters after 42 hours: relative liver weight, relative kidney weight, plasma glutamic-pyruvic transaminase, plasma ornithine carbamyl transferase, blood urea nitrogen, and hepatic and renal histological changes (Hewatt *et al.* 1980).

6.3.10.2 Carcinogenicity/Genotoxicity. The IARC and the NTP have not classified n-hexane as to its potential carcinogenicity; classification by the EPA is pending. n-Hexane did not promote tumors when it was administered to mice topically and subcutaneously (Kraemer *et al.* 1974). No other data on the carcinogenicity of n-hexane were found.

n-Hexane induced chromosome aberrations in the bone marrow cells of rats (Hazelton Laboratories America, Inc. 1980) and in cultured hamster fibroblasts (RTECS 1992). However, n-hexane was negative when tested for mutagenicity in *Salmonella typhimurium* (Mortelmans *et al.* 1986). Negative results were also reported for the induction of specific locus mutations in mouse lymphoma cells (Hazelton Laboratories America, Inc. 1980).

6.3.10.3 Reproductive/Developmental Toxicity. n-Hexane has been found to be fetotoxic in animals; however, n-hexane does not appear to be a teratogen. In a study in which pregnant mice were administered up to 9.9 g/kg/day by gavage during gestational days 6 to 15, no teratogenic effects were observed. However, in this study, a dose-related reduction in fetal weight was observed at doses of 7.92 and 9.9 g/kg/day. No fetal malformations were noted (Marks *et al.* 1980). Similar results have been observed in inhalation studies carried out to assess the teratogenicity of n-hexane. Both oral (4000 mg/kg) and inhalation (1000 ppm) exposure to n-hexane have caused testicular damage in experimental animals (Nylen *et al.* 1989, Krasavage *et al.* 1980).

6.3.11 2,3-Dimethylbutane

Subchronic oral exposure to 2,3-dimethylbutane has been found to cause kidney toxicity in experimental animals. In the single mutagenicity study reported, this compound was found to be nongenotoxic. No other data were reported in the literature surveyed for any exposure route. The EPA, the IARC, and the NTP have not classified 2,3-dimethylbutane as to its potential carcinogenicity. Federal water quality criteria values have not been reported for this compound.

6.3.11.1 ***General Toxicity.*** Oral exposure to 2,3-dimethylbutane has induced kidney toxicity in experimental animals. The subchronic toxicity of 2,3-dimethylbutane was evaluated in rats that were administered 500 or 2000 mg/kg 2,3-dimethylbutane once daily by oral gavage, five days/week for four weeks. In this study, mean kidney weights were found to be significantly higher in both dose groups. Histopathological findings in the kidneys included hyaline droplet change, regenerative epithelium, and tubular dilation with granular material. Other effects associated with 2,3-dimethylbutane exposure included congested lungs, scattered pale and dark foci on the lungs, grey discoloration of the liver, moderately enlarged adrenals, and hemorrhages in the heart. The nephrotoxicity observed in this study was graded as 2+ on an activity scale ranging from inactive to highly active (- to 4+) (Borriston Laboratories 1985, Bomhard *et al.* 1990). Halder *et al.* (1985) dosed rats by oral gavage with 500 and 2000 mg/kg/day 2,3-dimethylbutane for five days/week for four weeks. 2,3-Dimethylbutane was nephrotoxic, inducing hyaline droplet accumulation, regenerative epithelium, and intratubular cast formation. Based on the severity of these effects, 2,3-dimethylbutane was assigned nephropathy scores of 77 and 73 (compared to 92 and 91 for the unleaded gasoline positive control), for the low and high test doses, respectively (Halder *et al.* 1985).

6.3.11.2 ***Carcinogenicity/Genotoxicity.*** The EPA, the IARC, and the NTP have not classified 2,3-dimethylbutane as to its potential carcinogenicity. In addition, no carcinogenicity data on this compound were found in the literature. In the single mutagenicity study reported, 2,3-dimethylbutane was negative in the L5178Y TK+/- mouse lymphoma assay in the presence and absence of metabolic activation (API 1987).

6.3.11.3 ***Reproductive/Developmental Toxicity.*** No data were found.

6.3.12 2,2-Dimethylpentane

One study was found in the literature surveyed concerning the toxic effects of 2,2-dimethylpentane. In this study, 2,2-dimethylpentane was found to induce kidney toxicity in rats. The EPA, the IARC, and the NTP have not classified 2,2-dimethylpentane as to its potential carcinogenicity; and Federal water quality criteria for 2,2-dimethylpentane have not been published.

6.3.12.1 ***General Toxicity.*** 2,2-Dimethylpentane has been found to induce morphological kidney changes in rats. This compound was included in a study in which 18 aliphatic/cycloaliphatic hydrocarbons were screened using male rats treated by oral gavage with 250 mg/kg/day for five days. Based on a predicted value for hyaline droplet formation related to presence of structure-based properties common to active aliphatic and alicyclic hydrocarbons, 2,2-dimethylpentane was assigned an activity score of 3 on a scale ranging from inactive to highly active (- to 4+) (Bomhard *et al.* 1990).

6.3.12.2 ***Carcinogenicity/Genotoxicity.*** The carcinogenicity of 2,2-dimethylpentane has not been evaluated by the EPA, the IARC, or the NTP. In addition, no data on carcinogenic effects associated with this compound were found in the literature.

6.3.12.3 ***Reproductive/Developmental Toxicity.*** No data were found.

6.4 Summary

The acute toxicity of petroleum hydrocarbons to aquatic organisms is inversely correlated with their aqueous solubilities and K_{ow}s. Hydrocarbons with solubilities lower than about 0.005 mMol/L are acutely toxic at concentrations equal to or greater than their aqueous solubilities; saturated solutions of these compounds are unlikely to be toxic to aquatic organisms. The acute toxicity of hydrocarbons with higher aqueous solubilities usually is in the range of 20 to 70 percent of aqueous solubility. Among the chemicals evaluated in greater detail in this review, the solubility/toxicity breakpoint occurs at about 1-methylphenanthrene (molecular weight 192.3). Aromatic hydrocarbons are more toxic than saturated hydrocarbons of similar molecular weight.

Water-soluble or water-accommodated fractions of crude and refined oils are not saturated with respect to any hydrocarbons. This is because equilibrium partitioning between the oil and aqueous phases favors retention of the hydrocarbons in the oil phase. The dominant hydrocarbons in water-soluble fractions are the BTEX compounds, some light alkanes, and small amounts of naphthalenes, phenanthrenes, and dibenzothiophenes. The acute toxicity of water-soluble fractions of crude, refined, residual, and used oils to freshwater organisms is in the range of 0.12 to 50.3 mg/L, reflecting the additive toxicity of the hydrocarbons in the aqueous mixture. Only rarely will water percolating through an oil-contaminated soil contain concentrations of total dissolved hydrocarbons as high as the acutely toxic concentrations.

There are limited published data available for the acute and chronic toxicity and carcinogenicity of individual petroleum hydrocarbons to humans and other mammals. The most data are available for the well-known PAH carcinogens, benzo(a)pyrene and benz(a)anthracene. These and other PAH carcinogens, such as 5-methylchrysene, 7,12-dimethylbenz(a)anthracene, dibenz(a,h)anthracene, 3-methylcholanthrene, and dibenzo(a,h)pyrene (Neff 1979), are only trace or ultratrace components in most crude oils, but are present at higher concentrations in some residual petroleum products and used engine oils (Appendix A).

The noncarcinogenic hydrocarbons have a moderate to low toxicity to mammals and man. However, a wide variety of toxic, reproductive, and histopathologic effects are produced in mammals by chronic exposure by various routes to high doses of some of these hydrocarbons.

The biggest problem associated with predicting possible harm to humans from consumption of groundwater contaminated with low concentrations of petroleum hydrocarbons is the general lack of published toxicological information about most of the major ingredients of petroleum products. As discussed above, the most abundant hydrocarbons in middle distillate and higher refined or residual products and in crude oil are highly alkylated alkanes (particularly cycloalkanes) and aromatic hydrocarbons. For example, 7,12-dimethylbenz(a)anthracene is much more carcinogenic than benz(a)anthracene (IARC 1983) and 5-methylchrysene is the most carcinogenic of the many isomers of monomethylchrysene (Hecht *et al.* 1976a). More data are needed on the mammalian toxicity of the more abundant alkyl hydrocarbons in petroleum products.

Section 7

ANALYSIS OF PETROLEUM HYDROCARBONS IN SOIL AND GROUNDWATER

7.1 Standard Analytical Methods

For this study, two major groups of petroleum hydrocarbons were identified as important to the assessment of migration and effects of petroleum releases in soils and groundwater. These two groups, which include the types of compounds listed in Table 3-2, are the volatile aliphatic and aromatic hydrocarbons (2,3-dimethylbutane, 2,2-dimethylpentane, n-hexane, cyclohexane, and 1,2,4-trimethylbenzene) and the semivolatile polycyclic aromatic hydrocarbons (naphthalene, 2-methylnaphthalene, 1-methylphenanthrene, dibenzothiophene, 5-methylchrysene, benz[a]anthracene, and benzo[a]pyrene).

Two different methodological approaches are required to analyze these two classes of hydrocarbons in soil and groundwater. Analysis of the volatile hydrocarbons involves sample preparation by purge and trap with analysis and quantification by gas chromatography/mass spectrometry (GC/MS). Analysis of semivolatile hydrocarbons in water and soils usually involves solvent extraction, extract cleanup, and analysis by GC/MS or High Pressure Liquid Chromatography (HPLC).

Standard analytical methods recommended by the U.S. EPA, such as EPA Method 624 and EPA SW-846 Method 8240 for the volatile hydrocarbons and EPA Method 625 and EPA SW-846 Method 8270 for the semivolatile hydrocarbons may be considered as practical methods for analysis of target compounds; however, there are some limitations to their use. The EPA methods were designed to determine selected priority pollutant compounds in hazardous wastes and environmental matrices suspected of being contaminated by priority pollutants.

Only 19 (of more than 100) of the organic chemicals on the priority pollutant list are hydrocarbons and only a few of these are abundant in crude, refined, residual, and waste oil products. Of the petroleum chemicals chosen for further evaluation in this report, only 4 are present on the semivolatile priority pollutant list: naphthalene, 2-methylnaphthalene, benz[a]anthracene, and benzo[a]pyrene. The volatile priority pollutant hydrocarbons include just BTEX. Because most of the abundant chemicals in petroleum products are not identified and quantified by the standard EPA analytical methods, the methods can not be used to effectively identify petroleum product contamination of soils and water or to differentiate among several possible sources of petroleum products (through fingerprinting) in environmental samples.

Quantitative identification of the sources, compositions, migration, and weathering of bulk petroleum products or aqueous extracts of petroleum products in soil and groundwater systems requires the adoption of analytical approaches that optimize the ability to differentiate among different petroleum source materials and non-petroleum sources of hydrocarbons. Such capabilities can then be used to fingerprint each specific source to the degree necessary to evaluate the potential contribution of other sources to the receiving environment.

Although commonly used solid waste analytical methods (i.e., SW-846 Method 8240, 8270; EPA Method 624, 625 using gas chromatography/mass spectrometry) provide for the quantification of specific petroleum hydrocarbons in a site assessment, only some of the objectives of source identification and hydrocarbon fate are satisfied.

These general organic chemical methods are deficient in chemical selectivity (i.e., types of compounds analyzed) and chemical sensitivity (i.e., analyte detection limits). Significant deficiencies in both of these areas may result in a larger problem: the inability to accurately match petroleum hydrocarbons in the environment with their respective sources, and to allocate the relative contribution of multiple sources in a contaminated environment. Other methods using gas chromatography with flame ionization detection or high-performance liquid chromatography with ultraviolet fluorescence detection limit the ability to fingerprint sources because of their lack of specificity.

Some aspects of the EPA methods are, however, are appropriate for sensitive and specific analysis of petroleum-contaminated environmental samples. These include the purge and trap procedures for the isolation and concentration of volatile organic compounds, and the extraction and extract cleanup procedures for the semivolatile compounds. These portions of the EPA methods can be used with modifications to other parts of the standard analysis protocols as the basis for very sensitive and specific analytical techniques for individual and total hydrocarbons and related hetero-compounds in environmental samples.

7.2 Volatile Hydrocarbons

Table 7-1 presents a recommended list of analytes when analyzing soil and groundwater samples for volatile hydrocarbons. This list includes the hydrocarbons currently in the 8240 analyte list, the study target analytes, and some other useful analytes. An effective method for measuring these analytes in soil and groundwater samples requires modification of EPA Method 8240 (EPA 1986). Samples are purged to volatilize the target analytes; analytes are trapped on a sorbent column. After the purging process, the target analytes are desorbed from the column and introduced into the GC/MS for quantitative analysis. Calibration standards of the target analytes are used to confirm peak identifications and to permit accurate quantification of the target analytes corresponding to the chromatographic peaks. Appropriate surrogate standards are spiked into samples prior to the purge and trap sequence to provide a measure of the efficiency of the procedure. The primary modification to Method 8240 involves expanding the list of target analytes determined by the GC/MS full scan analysis.

In addition to the Method 8240 analytes and this study's target analytes, analysis for volatile hydrocarbons should include the alkylated benzenes, EDB, and MTBE. These other compounds enhance the ability to fingerprint potential sources of hydrocarbon releases in receiving soil and groundwater.

Table 7-1. Volatile Hydrocarbons

EPA Method 8240 Hydrocarbon Analytes
- Benzene
- Toluene (C_1-benzene)
- Ethylbenzene (C_2-benzene)
- Xylenes (C_2-benzenes)

Target Analytes
- 2,3-dimethylbutane
- 2,2-dimethylpentane
- n-hexane
- cyclohexane
- 1,2,4-trimethylbenzene

Other Useful Analytes
- C_3-benzenes
- C_4-benzenes
- C_5-benzenes
- Ethylene dibromide (EDB)
- Methyl tertiary butyl ether (MTBE)

7.3 Semivolatile Hydrocarbons

Table 7-2 presents a recommended list of analytes when analyzing soil and groundwater samples for semivolatile hydrocarbons. This is a relatively long list that may be reduced, depending on the project needs. The PAHs listed include not only those evaluated in this study and those currently designated as EPA priority pollutants, but also several other PAHs and heterocyclic compounds frequently found at elevated concentrations in petroleum products. The additional alkylated PAHs and heterocyclics (e.g., C_1- through C_4-naphthalenes) are essential for differentiating between petrogenic and nonpetrogenic hydrocarbon sources or among different possible petrogenic sources, and for assessing the weathering and fate of petroleum hydrocarbon mixtures in the environment. These alkyl PAHs and dibenzothiophenes serve as sensitive indicators of weathering, providing a measure of how recent or "fresh" a release may be.

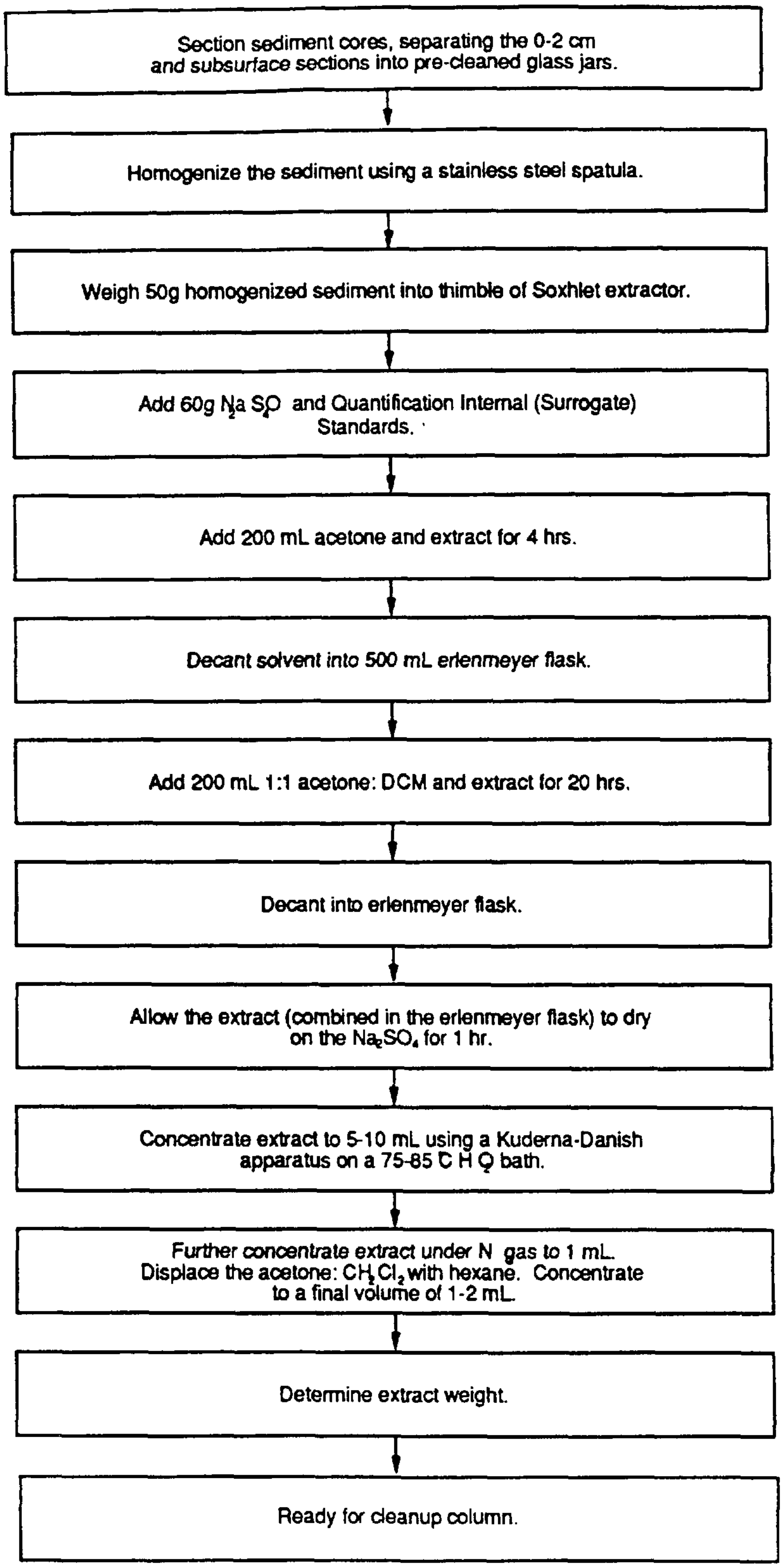
The analytical methods recommended for determining these PAHs include Soxhlet acetone/methylene chloride solvent extraction for sediment (EPA 1986) and liquid/liquid extraction with methylene chloride for water followed by cleanup by silica gel column chromatography (or HPLC), and instrumental analysis by GC/MS Full Scan or Selective Ion Monitoring (SIM). The major advantage of GC/MS SIM is that the method detection limits of these analytes are lower by almost an order of magnitude that those produced by conventional full-scan GC/MS. The recommended method for extraction of soil (sediment) and water samples is summarized in Figures 7-1 and 7-2; cleanup of the extracts is summarized in Figure 7-3; and methods for GC/MS instrumental analysis are summarized in Figure 7-4.

These recommended analytical methods have been applied successfully to a variety of sample matrices in numerous environmental studies (Atlas *et al.* 1981; Boehm 1981; Boehm *et al.* 1987; National Research Council 1985; Sauer and Boehm 1991). In implementing these methods a Quality Assurance/Quality Control Plan should be prepared that references specific laboratory standard operating procedures (SOPs) for all the specialty chemical analyses. The laboratory SOPs should provide the criteria for assessing data quality and specific requirements for quality control criteria and corrective measures. Quality control procedures should include precautions to preclude sample contamination in the laboratory, the analysis of procedural blanks, analysis of standard reference materials to provide an assessment of accuracy, and analysis of replicate samples to permit an assessment of precision. All chemistry data should be formally validated. Data validation ensures that the data quality objectives for accuracy and precision have been met, that the data have been generated in accordance with the Laboratory QA Plan, and that data are both traceable and defensible.

Table 7-2. PAH and Alkyl Homologue PAH Target Compounds

Compound Identification	Abbreviation^a	Compound Identification	Abbreviation^a
***Naphthalene**	**(C0N)**	*Fluoranthene	(FL)
C_1.Naphthalenes	(C1N)	C_1-Fluoranthenes^a	(C1FL)
C_2.Naphthalenes	(C2N)		
C_3.Naphthalenes	(C3N)	*Pyrene	(PY)
C_4.Naphthalenes	(C4N)	C_1-Pyrene	(C1PY)
***2-methylnaphthalene**			
		***Benz[a]anthracene**	**(BAA)**
*Acenaphthylene	(ACEY)		
		*Chrysene	(C0C)
*Acenaphthene	(ACE)	C_1-Chrysene	(C1C)
		C_2-Chrysene	(C2C)
Biphenyl	(BIP)	C_3-Chrysene	(C3C)
		C_4-Chrysene	(C4C)
*Fluorene	(C0F)	**5-Methylchrysene**	
C_1-Fluorenes	(C1F)		
C_2-Fluorenes	(C2F)	*Benzo[b]fluoranthene	(BBF)
C_3-Fluorenes	(C3F)		
		*Benzo[b]fluoranthene	(BKF)
Dibenzothiophene	**(C0D)**		
C_1-Dibenzothiophenes	(C1D)	***Benzo[a]pyrene**	**(BAP)**
C_2-Dibenzothiophenes	(C2D)		
C_3-Dibenzothiophenes	(C3D)	Benzo[a]pyrene	(BEP)
*Anthracene	(C0A)	Perylene	(PER)
*Phenanthrene	(C0P)		
C_1-Phenanthrenes/Anthracenes	(C1P/A)	*Indenol[1,2,3-c,d]pyrene	(IND)
C_2-Phenanthrenes/Anthracenes	(C2P/A)		
C_3-Phenanthrenes/Anthracenes	(C3P/A)	*Dibenz[a,h]anthracene (DAH)	(DAH)
C_4-Phenanthrenes/Anthracenes	(C4P/A)		
1-Methylphenanthene		*Benzo[g,hi]perylene	(BGHI)
		*7,12-Dimethylbenz(a)anthracene	

*EPA Method 8270 PAH Compounds
^{a} C1, C2, C3, C4 refer to number of alkyl carbon substituents on the parent compound
Bolded compounds are the PAH analytes that were evaluated for this study.



Section sediment cores, separating the 0-2 cm and subsurface sections into pre-cleaned glass jars.

Homogenize the sediment using a stainless steel spatula.

Weigh 50g homogenized sediment into thimble of Soxhlet extractor.

Add 60g Na_2SO_4 and Quantification Internal (Surrogate) Standards.

Add 200 mL acetone and extract for 4 hrs.

Decant solvent into 500 mL erlenmeyer flask.

Add 200 mL 1:1 acetone: DCM and extract for 20 hrs.

Decant into erlenmeyer flask.

Allow the extract (combined in the erlenmeyer flask) to dry on the Na_2SO_4 for 1 hr.

Concentrate extract to 5-10 mL using a Kuderna-Danish apparatus on a 75-85 C H_2O bath.

Further concentrate extract under N_2 gas to 1 mL. Displace the acetone: CH_2Cl_2 with hexane. Concentrate to a final volume of 1-2 mL.

Determine extract weight.

Ready for cleanup column.

Figure 7-1. Extraction Procedure for Sediment and Soil Samples

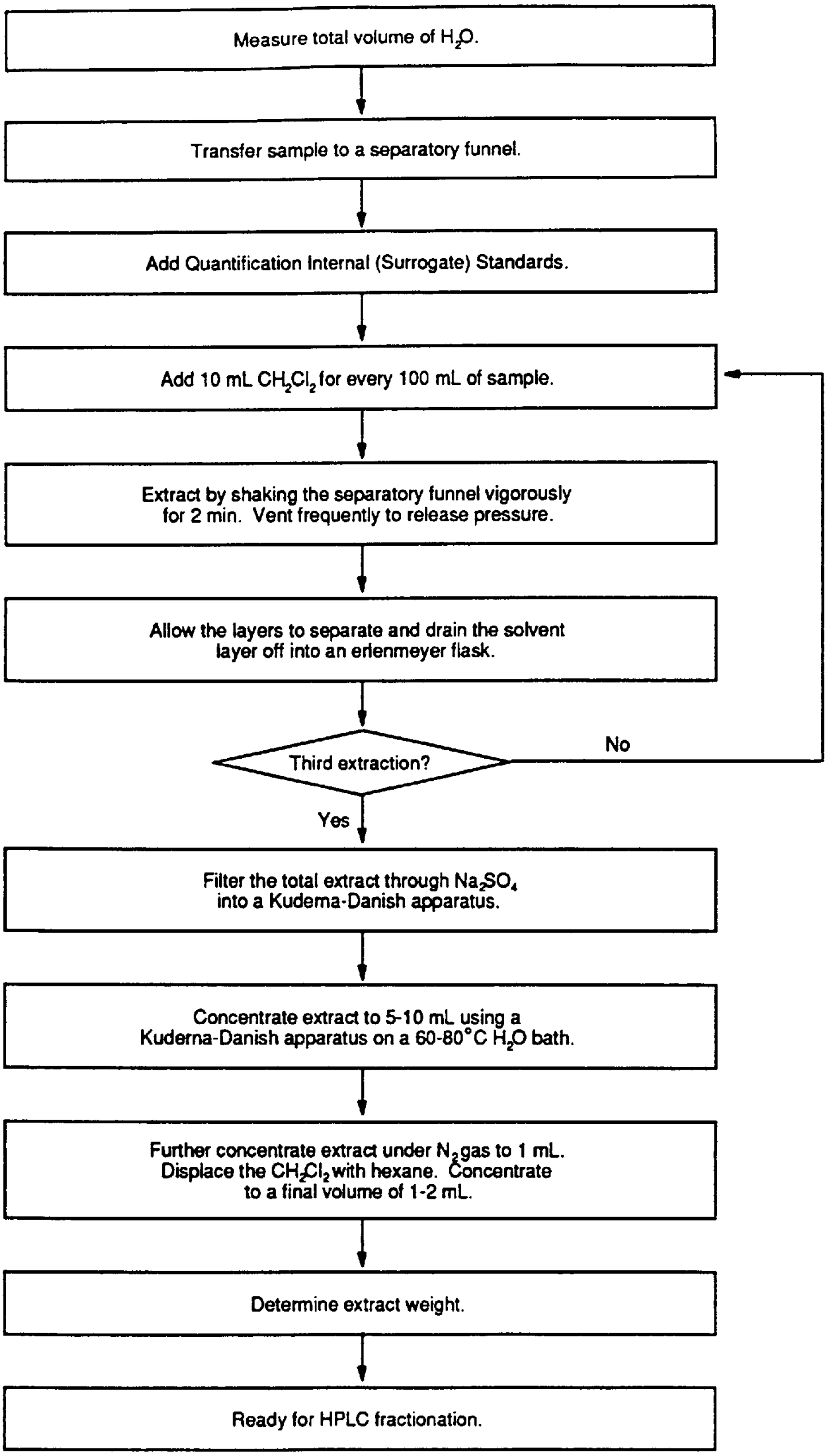
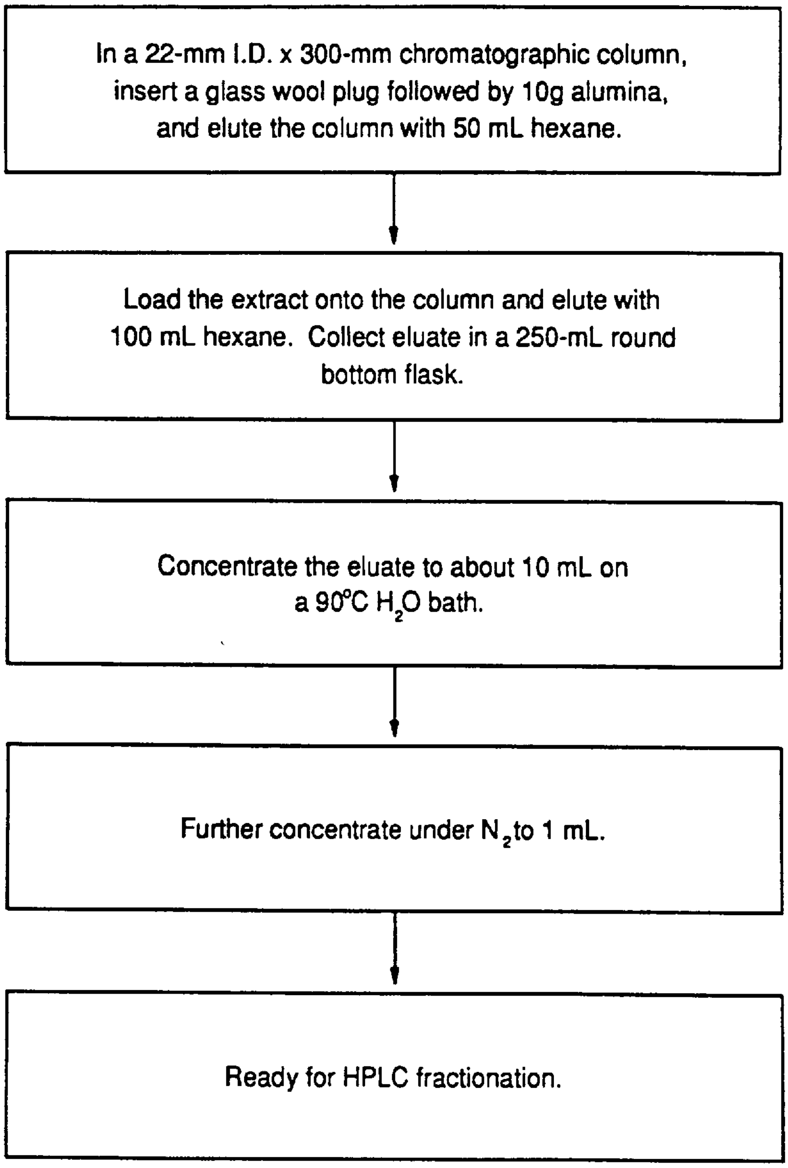


Figure 7-2. Extraction Procedure for Groundwater Samples



In a 22-mm I.D. x 300-mm chromatographic column, insert a glass wool plug followed by 10g alumina, and elute the column with 50 mL hexane.

Load the extract onto the column and elute with 100 mL hexane. Collect eluate in a 250-mL round bottom flask.

Concentrate the eluate to about 10 mL on a 90°C H_2O bath.

Further concentrate under N_2 to 1 mL.

Ready for HPLC fractionation.

Figure 7-3a. Extract Cleanup Column Procedure

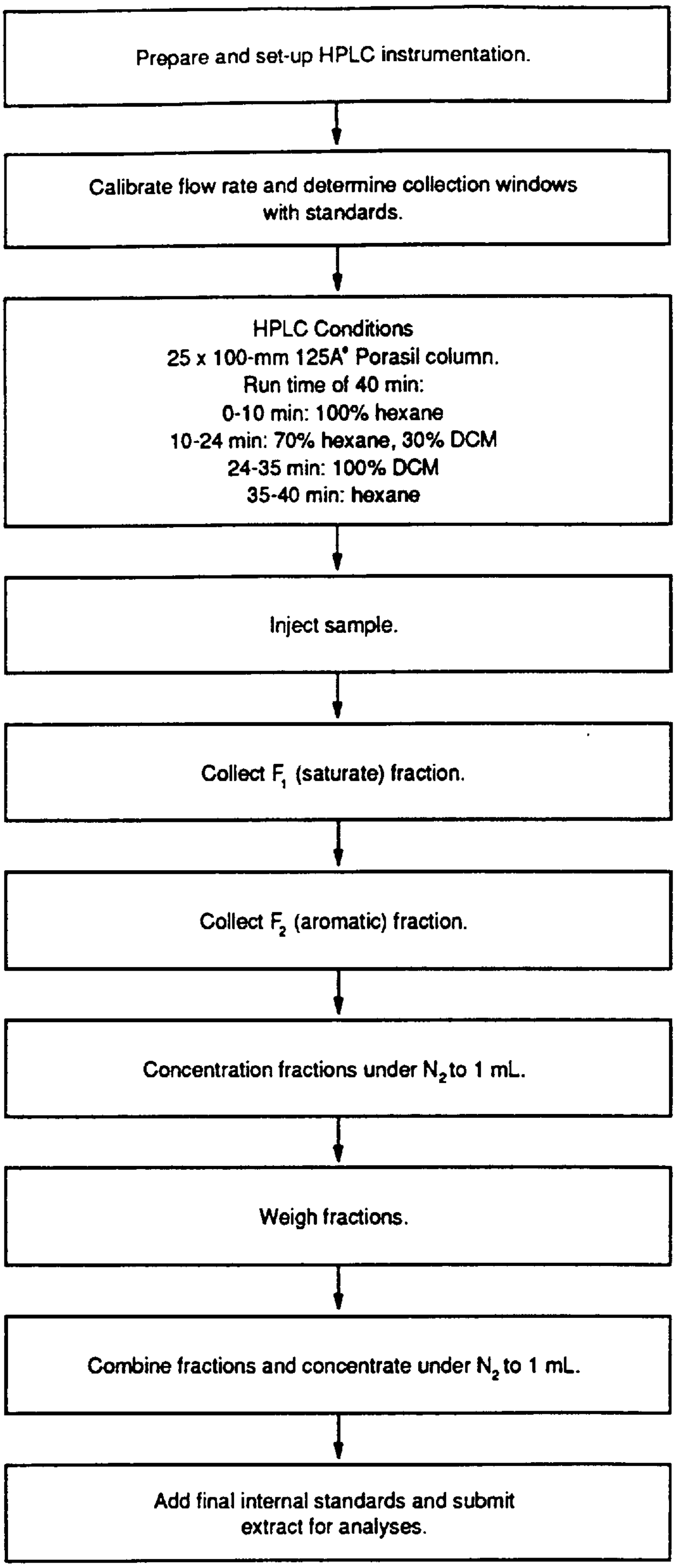


Figure 7-3b. Procedure for Fractionation of Extracts of Environmental Samples Containing Hydrocarbons by HPLC to Obtain F_1 (Saturated), F_2 (Aromatic), F_3 (Polar) Fractions for Gas Chromatic Analysis

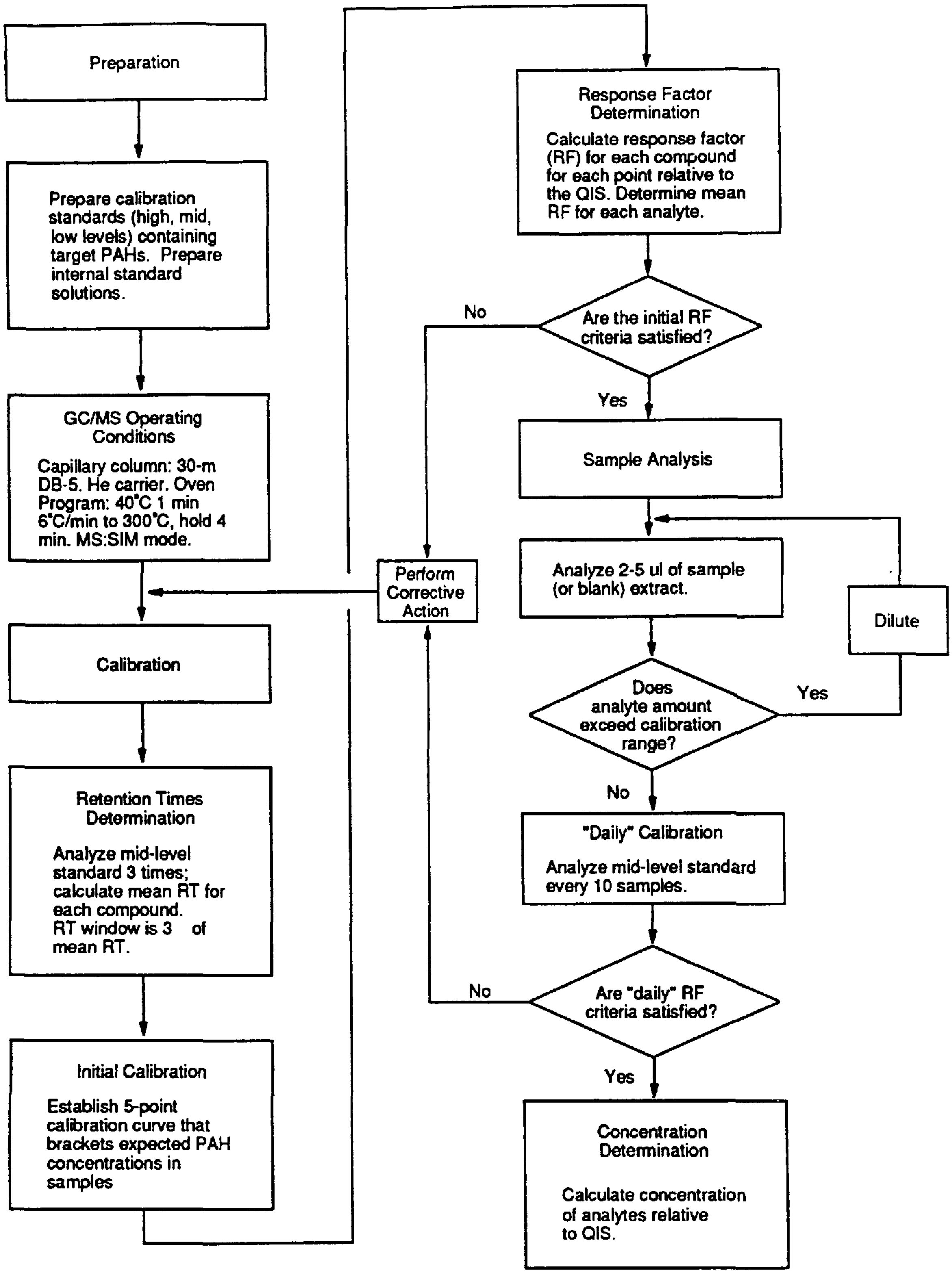


Figure 7-4. Instrumental Procedures for Analysis of Cleaned Up Extracts of Environmental Samples by Gas Chromatography with Quantification by Mass Spectrometry

Section 8

INFORMATION GAPS AND RECOMMENDATIONS

There exists a wide variety of uncertainties and information gaps with respect to the evaluation performed in this report on the transport, fate, and toxicity of selected petroleum hydrocarbons in soil/groundwater systems. Sections 8.1 through 8.4 describe selected information gaps and recommendations for addressing those gaps.

Section 8.1 addresses the lack of reliable values for many commonly measured parameters that are useful for assessing dissolved compound mobility. Sections 8.2 and 8.3 address issues related to subsurface behavior of non-aqueous phase liquid (NAPL) petroleum products that are generally not well known or characterized. Finally, Section 8.4 addresses toxicity issues. We have not presented recommendations related to analytical chemistry methods because adequate methods are known and available, although they may not be commonly available through the commercial laboratory business.

8.1 Physical/Chemical Parameter Values

8.1.1 Summary

The use of physical/chemical parameter values in mathematical models, for both predictive and interpretive purposes, is a well established part of evaluating behavior of chemicals in the environment, as described in Section 5.

Because models are being used with increasing frequency as the basis for the regulation of discharges to and cleanup of land and water resources, it is important that the parameters used in these models be of reasonable accuracy, generally at least within the correct order of magnitude.

Reliable values of certain parameters for the compounds of interest, however, are not readily available.

- Henry's Law coefficients within typical ambient environmental temperature ranges were not found in available literature for:
    - 5-methylchrysene
    - 1-methylphenanthrene
    - dibenzothiophene
    - benzo(a)pyrene

A value for the benzo(a)pyrene Henry's Law Constant was used in this report to assess transport behavior; however, a wide range of values are reported in the literature.

- K_{oc} values were not found in available literature for:
    - 5-methylchrysene
    - 1-methylphenanthrene
    - dibenzothiophene
    - 1,2,4-trimethylbenzene
    - cyclohexane

- n-hexane
- 2,3-dimethylbutane
- 2,2-dimethylpentane

To evaluate transport of these compounds in the report, published K_{ow} values were used to estimate K_{oc} from an empirical equation given in Lyman, *et al.* (1982).

8.1.2 Recommendation

A database of physical/chemical parameters, determined by validated, reliable empirical methods, should be developed for key petroleum-derived organic chemicals, such as those selected for study in this report. Values for additional chemicals can then be derived by use of chemical-class-specific linear regression equations and structure/activity models.

The literature values which are available should also be further reviewed for validity and consistency. There are relatively few empirically determined values for some parameters. Published values for K_{ow}, for example, may vary by two or three orders of magnitude for a single PAH (Güsten *et al.* 1991). Many of the values reported in the literature are calculated or estimated by various correlations, such as those discussed in Section 5 between K_{oc}, K_{ow}, and solubility, and by various structure/activity models. Errors in the measured values are propagated, and may even be magnified, through the use of such estimation methods.

8.2 Equilibrium Between Petroleum Products and Soil Water

8.2.1 Summary

Knowledge regarding the dissolution rate of petroleum product constituents from NAPL into water is very limited. As stated in Sections 4 and 5.3.1, the partitioning of nonpolar organic chemicals from NAPL into water at equilibrium can be approximated roughly by K_{ow}. However, there is considerable uncertainty concerning the rate at which equilibrium is reached in a soil/water environment. The rate of leaching of chemicals from NAPL into water is likely related to the relative surface area of contact between the NAPL and water phases in the soil. An additional complicating factor regarding the dissolution rate is that NAPL may be present in a variety of geometric configurations such as NAPL pools, globules, and residual droplets. These geometries probably have an effect on the dissolution rate because of the behavior of water associated with each of these geometries. Work has been conducted regarding partitioning of pure compounds among soil particles, water, and air, but little or no investigation has been conducted regarding the rates of partitioning of the compounds of concern between the complex NAPL mixture, represented by a released petroleum product, and soil water and particles.

8.2.2 Recommendation

Leaching studies should be performed in experimental soil columns with different types of petroleum products. Rate of leaching of the chemicals of interest into an aqueous phase would be monitored under different environmental conditions, particularly different degrees of soil saturation with water, different concentrations of soil organic carbon, and different soil types.

A component of this study would be a literature search and review of studies of the rate of leaching of various classes of hydrocarbons from releases and chronic discharges of different petroleum products on land. Most of the published work on this topic has dealt with migration of gasoline hydrocarbons, particularly BTEX, through soils. However, some work has been done with other petroleum products and other hydrocarbon classes.

8.3 Bulk Migration of Petroleum Products Through Soils

8.3.1 Summary

As discussed above, when released on land, crude, refined, residual, and used oils tend to migrate slowly down into the soil column. The rate of bulk movement of NAPL through the soil seems to depend in large part on the viscosity of the petroleum product and the permeability and moisture content of the soil. Although migration of gasoline through soils has been studied to some extent, migration of heavier, more viscous petroleum products has received little attention. Bulk transport of complex petroleum mixtures through soils may be an important mechanism of groundwater contamination, particularly at sites that have received chronic continuous or repeated discharges of petroleum products or oily wastes for many years.

8.3.2 Recommendation

Soil column studies, similar to those described above for partitioning of hydrocarbons from NAPL into soil water could be performed to measure the rate of penetration of bulk petroleum products of different types through soils with different permeabilities, moisture concentrations, and organic matter concentrations. The experimental system should be able to measure relatively low rates of penetration and transport of NAPL through the soil.

In addition, field surveys at release sites could be performed to measure the extent of penetration of different petroleum products into the soil column under natural conditions. Cores would be collected at different locations in the release area. Soil samples from several depths in the core would be analyzed for texture, moisture, total petroleum hydrocarbons, and the petroleum chemicals of interest. The total organic carbon should be measured on background soils, to help support evaluation of dissolved phase.

Somewhat similar studies frequently are performed as part of site assessments in support of corrective action evaluations. However, the study objectives and methods used are not the same. The study recommended here would be designed specifically to empirically measure the various transport and fate processes and the physical/chemical and environmental parameters controlling them, as discussed in earlier sections of this report.

8.4 Human Toxicology of Abundant Chemicals in Petroleum Products

8.4.1 Summary

As discussed in Section 6 of this report, there are very few reliable published data on the acute and chronic toxicity and possible carcinogenicity of low to medium molecular weight highly alkylated saturated and aromatic hydrocarbons which often are among the most abundant mobile chemicals in middle distillate and higher refined products, residual oils, and crude oils. Alkylated cycloalkanes and 2- to 3-ring aromatics and heterocyclic compounds (e.g., mono-, di-, and tri-methyl naphthalenes, phenanthrenes, and dibenzothiophenes) often are abundant in petroleum products. However, little published information is available about their aquatic and human toxicity. It is difficult to extrapolate from the toxicity of parent compounds to that of various positional isomers of alkylated congeners.

8.4.2 Recommendation

Systematic studies are needed of the relationship between position and number of alkyl carbons and the toxicity of cycloalkanes and aromatic hydrocarbons. There may be enough information available for a few compounds, such as alkylnaphthalenes, to serve as a basis for development of a structure/activity model that can be used to predict biological activity of a larger number of alkyl hydrocarbons.

Section 9

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Appendix A

Petroleum Hydrocarbon Composition Data

Table A-1 **Concentrations of normal, branched, and cyclic alkanes in U.S. crude oils. Concentrations are in mg/L. From Speight (1991) (Page 1 of 2).**

Compound	Ponca	n-Alkane Isoalkane	Santa Barbara	n-Alkane Isoalkane
Hexanes		2.2		0.76
n-hexane	18,000		7,230	
2-methylpentane	4,000		3,470	
3-methylpentane	3,000		4,180	
2,2-dimethylbutane	400		430	
2,3-dimethylbutane	800		1,400	
Heptanes		1.7		1.01
n-heptane	23,000		8,460	
3-methylhexane	5,000		1,880	
3-ethylpentane	500		--	
2-methylhexane	7,000		--	
2,3-dimethylpentane	1,000		6,010	
2,4-dimethylpentane	--		490	
Octanes		6.9		2.5
n-Octane	19,000		9,230	
2-methylheptane	--		--	
2,2-dimethylhexane	100		1,180	
2,3-dimethylhexane	600		1,630	
2,4-simethylhexane	600		--	
2,5-dimethylhexane	600		950	
3,3-dimethylhexane	300		--	
2-methyl-3-ethylpentane	400		--	
2,2,3-trimethylpentane	40		--	
2,3,3-trimethylpentane	60		--	
2,3,4-trimethylpentane	50		--	
Nonanes		2.6		0.87
n-nonane	18,000		5,800	
2-methyloctane	4,000		--	
3-methyloctane	1,000		4,200	
4-methyloctane	1,000		--	
2,3-dimethylheptane	500		--	
2,6-dimethylheptane	500		2,500	

Table A-1 Concentrations of normal, branched, and cyclic alkanes in U.S. crude oils. Concentrations are in mg/L. From Speight (1991). (Page 2 of 2)

Compound	Ponca	Santa Barbara
Higher n-paraffins		
n-decane	18,000	--
n-undecane	17,000	--
n-dodecane	17,000	--
Cycloparaffins		
cyclopentane	500	460
methylcyclopentane	9,000	3,030
cyclohexane	7,000	--
ethylcyclopentane	2,000	1,860
1,1-dimethylcyclopentane	2,000	630
1-t-2-dimethylcyclopentane	5,000	1,540
1-c-3-dimethylcyclopentane	2,000	--
1-t-3-dimethylcyclopentane	9,000	2,380
propylcyclopentane	--	--
ethylcyclohexane	2,000	--
1-t-2-dimethylcyclohexane	--	2,640
1-c-3-dimethylcyclohexane	--	--
1,1,3-trimethylcyclopentane	3,000	--
1-t-2-c-trimethylcyclopentane	3,000	3,600
1-t-2-c-4-trimethylcyclopentane	2,000	--
1,1,2-trimethylcyclopentane	600	--
1,1,3-trimethylcyclopentane	2,000	--
1-t-2-t-4-trimethylcyclohexane	2,000	--

Table A-2 Concentrations of benzenes and naphthalenes in U.S. crude oils. Concentrations are in mg/kg. From Speight (1991).

Compound	Ponca	Santa Barbara	East Texas	Bradford	Greendale	Winkler	Midway	Conroe
benzene	2,000	2,210	700	600	2,100	400	700	4,100
toluene	5,000	7,780	5,800	5,100	5,900	900	4,300	24,600
ethylbenzene	2,000	2,090	2,200	900	1,200	800	2,200	3,100
o-xylene	3,000	2,900	3,000	2,100	1,700	300	3,100	6,800
m-xylene	5,000	--	6,400	6,100	4,000	800	3,600	20,300
p-xylene	1,000	6,800	1,700	1,700	900	1,200	1,500	5,900
n-propylbenzene	900	2,600	800	500	300	200	400	1,200
isopropylbenzene	700	600	400	300	300	300	300	900
1-methyl-2-ethylbenzene	900	--	700	300	400	100	300	900
1-methyl-3-ethylbenzene	1,700	--	1,600	1,300	800	100	400	4,000
1-methyl-4-ethylbenzene	600	--	700	500	300	500	300	1,300
1,2,3-trimethylbenzene	1,000	--	--	--	--	--	--	--
1,2,4-trimethylbenzene	5,100	--	3,400	3,300	1,500	1,300	1,300	6,900
1,3,5-trimethylbenzene	1,200	1,800	900	1,700	500	500	500	3,600
t-butylbenzene	100	--	100	20	30	20	0	100
1,2,3,4-tetramethylbenzene	2,000							
tetrahydronaphthalene	300							
naphthalene	600							
1-methylnaphthalene	1,000							
2-methylnaphthalene	2,000							
5-methyltetrahydronaphthalene	800							
6-methyltetrahydronaphthalene	900							

Table A-3 **Concentrations of aromatic hydrocarbons in crude oils. Concentrations are in mg/kg. (Page 1 of 2)**

Compound	S.Louisiana$^{(1)}$	Kuwait$^{(1)}$	Prudhoe Bay$^{(2)}$	North Slope$^{(3)}$	VMI Crude$^{(4)}$	Wyoming Crude$^{(5)}$
C_3-C_6 benzenes						8,100
tetralins						2,400
toluene			820			
ethylbenzene			560			
xylenes			2,840			
trimethylbenzenes			2,140			
indane			670			nd
C_2-C_4 indanes						800
tetramethylbenzenes			1,400			
naphthalene			920	210	326	900
C_1-C_3 naphthalenes						17,500
methylnaphthalenes			4,300	770	1,663	
dimethlynaphthalenes			3,980	1,400	3,142	
trimethylnaphthalenes			510	870	1,899	
tetramethylnaphthalenes				500	994	
biphenyl				63		400
C_1-C_3 biphenyls						2,200
fluorene				30	72	600
C_1-C_2 fluorenes						1,000
methylfluorenes				110	264	
dimethylfluorenes				160	435	
trimethylfluorenes				190	389	
phenanthrene	70	26	380	91	189	500
C_1-C_2 phenanthrenes						700
methylphenanthrenes	255	89	540	460	635	
dimethylphenanthrenes			110	790	825	
trimethylphenanthrenes				540	631	
tetramethylphenanthrenes				280	217	
dibenzothiophene				80	271	
methyldibenzothiophenes				150	849	
dimethyldibenzothiophenes				220	732	
trimethyldibenzothiophenes				190	888	
tetramethyldibenzothiophenes					309	
fluoranthene	5.0	2.9		nd	3.0	
pyrene	3.5	4.5		3.4	4.0	
methylfluoranthenes/ pyrenes				46	35	
benz(a)anthracene	1.7	2.3		nd	2.0	

Table A-3 Concentrations of aromatic hydrocarbons in crude oils. Concentrations are in mg/kg. (Page 2 of 2)

Compound	S.Louisiana(1)	Kuwait(1)	Prudhoe Bay(2)	North Slope(3)	VMI Crude(4)	Wyoming Crude(5)
methyl/dimethyl-benzanthracene					nd	
chrysene	18	6.9		16	14	
methylchrysenes				23	26	
dimethylchrysenes				32	47	
trimethylchrysenes				30		
triphenylene	10	2.8				
benzofluoranthenes	1.0	<1.0		2.0		
benzo(a)pyrene	0.75	2.8		nd		
benzo(e)pyrene	2.5	0.5		4.9		
perylene	34.8	<0.1		nd		
benzo(ghi)perylene	1.6	<1.0		nd		

(1) Pancirov and Brown, 1975
(2) Riley et al., 1980
(3) Page et al., 1994
(4) Burns et al., 1991
(5) Woodward et al., 1981

Table A-4 Concentrations of alkylbenzenes, selected polycyclic aromatic hydrocarbons, and dibenzothiophenes in crude oils. Concentrations are in mg/kg.

Compound	Alberta Sweet(1)	Mega Borg(2)	Handil Crudes(3)
alkylbenzenes		600	
naphthalene		382	
methylnaphthalenes		1092	4860
ethylnaphthalenes			960
dimethylnaphthalenes		1428	9480
trimethylnaphthalenes		924	5100
tetramethylnaphthalenes		336	
acenaphthylene	13		
acenaphthene	57		
fluorene	59	66	
methylfluorenes	150	150	
dimethylfluorenes		228	
trimethylfluorenes		156	
phenanthrene	150	252	258
methylphenanthrenes	370	420	578
dimethylphenanthrenes	500	304	372
trimethylphenanthrenes		63	
dibenzothiophene		63	
methyldibenzothiophenes		143	
dimethyldibenzothiophenes		155	
trimethyldibenzothiophenes		63	
anthracene	11		
fluoranthene	6.0		
pyrene	17		
methylpyrene	39		
chrysene	30		
benzo(b)fluoranthene	4.0		
benzo(e)pyrene	5.0		
benzo(a)pyrene	nd		
methylcholanthrene	3.0		

(1) Benner et al., 1990

(2) Fawn and Barker, 1991

(3) Radke et al., 1990

Table A-5 **Concentrations of PAH and heterocyclic compounds in a sample of Qatar crude oil. Concentrations are mg/kg. Numbers in parentheses are number of isomers quantified. From Grimmer et al. (1983).**

Aromatics		Heterocyclics	
Compound	**Concentration**	**Compound**	**Concentration**
phenanthrene	>128.7	dibenzothiophene	>336.5
3-methylphenanthrene	>17.2	4-methyldibenzothiophene	>6.7
2-methylphenanthrene	>12.7	2-methyldibenzotheophene	>21.4
9-methylphenanthrene	>33.4	3-methyldibenzothiophene	>0.2
1-methylphenanthrene	>20.9	1-methyldibenzothiophene	>0.6
1-phenylnaphthalene	>0.1	C_2-carbazoles (6)	>2.7
fluoranthene	1.7	dimethdibenzotheophene	>3.5
pyrene	10.7	dimethylxanthene	>0.4
benzo(a)fluorene	10.8	C_3-carbazoles (8)	36.5
benzo(b&c)fluorenes	6.2	C_4-carbazoles (8)	56.5
4-methylpyrene	11.6	C_5-carbazoles (9)	49.8
1-methylpyrene	22.9	methylphenanthrothiophene	2.2
benzo(c)phenanthrene	0.4	C_6-carbazoles (9)	45.3
benz(a)anthracene	6.7	benzonaphthothiophene	122.3
chrysene/triphenyline	43.5	methylbenzonaphthothiophenes	200.4
3-methylchrysene	43.9	dimethylbenzonaphthothiophenes	9.8
2-methylchrysene	24.5	methylfuran derivatives (3)	13.6
4-/6-methylchrysene	15.6	thiophene derivative	39.2
other methylchrysenes (3)	27.6	triphenylene (4,4a,4b,5-bcd)-thiophene	6.2
dimethylchrysenes (8)	82.9	methylthiophene derivatives (9)	107.7
benzo(b&j)fluoranthenes	7.4	thiophene derivative	11.0
benzo(k)fluoranthene	15.9	methylfuran derivative	1.2
benzo(e)pyrene	28.9	methylthiophene derivatives (10)	30.7
benzo(a)pyrene	3.6	dithiophene derivatives (9)	13.7
methylbenzofluoranthenes (7)	58.0	sulfur-substituted PAHs (2)	6.3
dimethylbenzofluoranthenes (12)	27.2	methylfuran derivative	11.9
indeno(1,2,3-cd)pyrene	7.4	methylated sulfur-substituted PAHs (4)	13.7
benzo(ghi)perylene	5.0		
methylpicines (2)	6.4		
methylindeno(1,2,3-cd)pyrenes (2)	4.5		
coronene	0.3		

Table A-6 **Concentrations of sulfur-substituted alkanes in Wasson, Texas crude oil. Concentrations are in mg/L. From Speight (1991).**

Compound	Wasson Crude
methanethiol	24
ethanethiol	53
2-thiapropane	8.8
2-propanethiol	19.9
2-methyl-2-propanethiol	5.5
2-thiabutane	22.2
1-propanethiol	4.1
3-methyl-2-thiabutane	6.4
2-butanethiol	38.6
2-methyl-1-propanethiol	0.3
3-thiapentane	7.5
2-thaipentane	3.0
1-butanethiol	trace
2-methyl-2-butanethiol	6.4
2-pentanethiol	14.0
3-pentanethiol	5.7
3-thiahexane	1.2
2,4-dimethyl-3-thiapentane	5.3
2,2-dimethyl-3-thiapentane	0.58
thiacyclopentane	0.77
2-thiahexane	0.77
2-methyl-3-thiahexane	0.78
2-methylthiacyclopentane	23
4-methyl-3-thiahexane	5.0
3-methyltiacyclopentane	4.6
2-hexanethiol	28
thiacyclohexane	3.2
t-2,2-dimethylthiacyclopentane	25
c-2,5-dimethylthiacyclopentane	24
3-thiapentane	0.78
2-methylthiacyclohexane	29
3-methylthiacyclohexane	0.24
4-methylthiacyclohexane	0.48
cyclohexanethiol	12

Table A-7 Variability in the concentrations of major aromatic components of 31 samples of leaded and unleaded gasoline from north and central Florida. From Cline et al. (1991).

Compound	Concentration (wt%)			
	Mean	Minimum	Maximum	Standard Deviation
benzene	1.73	0.7	3.8	0.68
toluene	9.51	4.5	21.0	3.59
ethylbenzene	1.61	0.7	2.8	0.48
m-,p-xylenes	5.95	3.7	14.5	2.07
o-xylene	2.33	1.1	3.7	0.72
n-propylbenzene	0.57	0.13	0.85	0.14
3,4-ethyltoluene	2.20	1.5	3.2	0.40
1,2,3-trimethylbenzene	0.8	0.6	1.1	0.12

Table A-8 **Concentrations of alkanes, olefins, aromatic hydrocarbons, and additives in gasolines. Concentrations in volume or weight percent, except as indicated. (Page 1 of 3)**

Compound	PS-6(1)	Unleaded(2)	Leaded(2)	1974 Gasoline(3)	IARC(4)	36-117 US Cut(5)
n-alkanes						
butane	3.83	4-5	4-5		3-12	
pentane	3.11	2.6-2.7	2.6-2.7		1-9	
hexane	1.58				<1-6	
C_7-C_{10}-n-alkanes	1.21				<1-5	
Isoalkanes						
isobutane	1.14					
isopentane	8.72	9-11	9-11		5-10	
methhylpentanes	6.29				4-19	
2,3-dimethylbutane	1.66				<1-2	
C_6-isoalkanes	0.18					
dimethylpentane					<1-7	
methylhexanes	2.38					
dimethylhexanes	2.16					
C_7-isoalkanes	0.23					
trimethylpentanes	11.74				<1-14	
C_8-isoalkanes	4.98					
methyloctanes	1.51					
C_9-isoalkanes	0.50					
C_{10}-C_{13}-isoalkanes	2.65					
Cycloalkanes						
cyclopentane	0.15					1.13
methylcyclopentane	0.97				<1-3	7.27
ethylcyclopentane						2.92
trimethylcyclopentane						5.31
cyclohexane	0.08				<1-3	8.39
dimethylcyclopentane	0.77					
methylcyclohexane					<1-7	18.2
C_7-cycloalkanes	0.32					
C_8-cycloalkanes	0.74					
C_9-cycloalkanes	1.03					
C_{10}-C_{13}-cycloalkanes	0.62					

Table A-8 **Concentrations of alkanes, olefins, aromatic hydrocarbons, and additives in gasolines. Concentrations in volume or weight percent, except as indicated. (Page 2 of 3)**

Compound	PS-6(1)	Unleaded(2)	Leaded(2)	1974 Gasoline(3)	IARC(4)	36-117 US Cut(5)
Mono-olefins		5	10			
propylene	0.03					
butene	0.75					
C_4-alkenes	0.15					
methylbutenes					<1-4	
pentenes	1.22				<1-2	
C_5-alkenes	0.07					
C_6-alkenes	0.14					
methylpentenes	1.26					
C_7-C_{12}-alkenes	5.34					
Aromatics						
benzene	1.94	0.7-3.8	2-5		<1-4	3.03
toluene	4.73	4.5-21	6-7		5-22	12.05
ethylbenzene	2.00	0.7-2.8	5		<1-2	
o-xylene	2.27	1.1-3.7			1-10	
m-xylene	5.66	3.7-14.5				
p-xylene	1.72	"				
n-propylbenzene		0.13-0.85				
methylethylbenzenes	3.10	1.5-3.2			<1-2	
trimethylbenzene	3.26	0.6-1.1				
C_9-alkylbenzenes	2.51					
C_{10}-alkylbenzenes	2.21					
C_{11}-alkylbenzenes	0.57					
C_{12}-alkylbenzenes	0.21					
C_9-C_{13}-indans/ tetralins	1.59					
naphthalene		0.2-0.5	0.2-0.5			
C_{10}-C_{12}-naphthalenes	0.74					
anthracene		1.8 mg/L	1.8 mg/L			
fluoranthene				6.5 mg/L		
pyrene				4.4 mg/L		
benz(a)anthracene				4.3 mg/L		
chrysene				2.0 mg/L		
benzo(b)fluoranthene		3.9 mg/L	3.9 mg/L			
benzo(e)pyrene				0.8 mg/L		

Table A-8 **Concentrations of alkanes, olefins, aromatic hydrocarbons, and additives in gasolines. Concentrations in volume or weight percent, except as indicated. (Page 3 of 3)**

Compound	PS-6(1)	Unleaded(2)	Leaded(2)	1974 Gasoline(3)	IARC(4)	36-117 US Cut(5)
Aromatics (continued)						
benzo(a)pyrene				1.8 mg/L		
benzo(ghi)perylene				2.2 mg/L		
coronene				1.1 mg/L		
Nonhydrocarbons						
tetraethyllead			600 mg/L			
tetramethyllead			5 mg/L			
dichloroethane			210 mg/L			
dibromomethane			190 mg/L			
methyl *tert*butyl ether		to 15%			<1-4	

(1) Barker et al., 1991
(2) Cline et al., 1991
(3) Guerin, 1977
(4) IARC, 1989
(5) Nyer and Skladany, 1989

Table A-9 Variability in composition of gasolines from Houston, TX area in 1984. Concentrations are weight percent. From Diakun (1984). (Page 1 of 3)

Compound	Regular Blend	Lead-Free Blend	Super Unleaded	API Generic
Alkanes				
propane	0.10	0.04	0.04	0.07
iso-butane	0.59	0.77	0.90	0.75
n-butane	4.31	4.41	3.42	4.50
iso-pentane	7.77	10.13	8.02	9.25
n-pentane	5.05	5.09	1.94	4.91
2,2-dimethylbutane	0.61	0.41	0.10	0.48
cyclopentane	0.87	0.52	0.18	0.66
2,3-dimethylbutane	1.18	1.04	0.92	1.14
MTBE*	0.12	0.25	2.02	0.42
2-methylpentane	5.44	3.97	2.01	4.59
3-methylpentane	3.52	2.44	1.22	2.90
n-heptane	3.91	1.92	0.72	2.79
methylcyclopentane	2.10	1.48	0.82	1.74
2,2-dimethylpentane	0.52	0.56	0.72	0.59
cyclohexane	0.44	0.17	0.07	0.29
2-methylhexane	2.59	2.12	1.58	2.34
2,3-dimethylpentane	0.06	0.04	0.06	0.05
3-methylhexane	2.07	1.57	0.94	1.77
1-cis-3-dimethylcyclopentane	0.39	0.34	0.21	0.36
1-trans-3-dimethylcyclopentane	0.34	0.30	0.18	0.32
3-ethylpentane	0.54	0.40	0.25	0.46
2,2,4-trimethylpentane	1.21	2.43	5.02	2.26
n-heptane	1.42	0.91	0.51	1.12
methylcyclohexane	0.91	0.70	0.43	0.77
ethylcyclopentane	0.22	0.20	0.12	0.21
2,5-dimethylhexane	0.43	0.60	0.98	0.58
2,4-dimethylhexane	0.37	0.45	0.64	0.45
3,3-dimethylhexane	0.57	1.08	1.98	1.06
2,3-dimethylhexane	0.34	0.35	0.53	0.36
2-methylheptane	0.67	0.57	0.45	0.60
3-methylheptane	0.74	0.66	0.49	0.67
2,2,5-trimethylhexane	0.28	0.37	0.67	0.37
n-octane	0.62	0.49	0.41	0.54
n-nonane	0.36	0.22	0.17	0.28
n-decane	0.24	0.14	0.09	0.17
n-undecane	0.34	0.32	0.30	0.32
n-dodecane	0.19	0.12	0.07	0.13
C_{11}-C_{12}	3.21	2.38	1.97	2.13
C_{12} plus	1.21	2.12	1.37	0.92

Table A-9 **Variability in composition of gasolines from Houston, TX area in 1984. Concentrations are weight percent. From Diakun (1984). (Page 2 of 3)**

Compound	Regular Blend	Lead-Free Blend	Super Unleaded	API Generic
Olefins				
propylene	0.01	0.01	0.02	0.01
isobutylene	0.10	0.10	0.11	0.11
1-butene	0.14	0.20	0.27	0.19
trans-2-butene	0.28	0.38	0.45	0.37
cis-2-butene	0.28	0.35	0.39	0.34
3-methyl-1-butene	0.11	0.13	0.10	0.12
1-pentene	0.40	0.44	0.33	0.43
2-methyl-1-butene	0.63	0.75	0.58	0.71
isoprene	0.03	0.03	0.03	0.03
trans-2-pentene	0.98	1.05	0.90	1.05
cis-2-pentene	0.50	0.52	0.44	0.52
2-methyl-2-butene	1.14	1.19	1.06	1.21
trans-1,3-pentadiene	0.04	0.04	0.03	0.04
cyctopentadiene	0.02	0.02	0.03	0.02
cis-1,3-pentadiene	0.02	0.02	0.01	0.02
cyclopentene	0.21	0.21	0.24	0.22
3-methyl-1-pentene	0.12	0.12	0.09	0.12
4-methyl-2-pentene	0.13	0.12	0.10	0.13
2-methyl-1-pentene	0.23	0.21	0.17	0.22
1-hexene	0.16	0.15	0.11	0.15
C_6-olefins	1.85	1.67	1.68	1.84
1-methylcyclopentene	0.14	0.09	0.05	0.11
1-octene	0.14	0.12	0.08	0.12
1-nonene	0.04	0.09	0.01	0.10
1-decene	0.03	--	0.01	0.01
1-undecene	--	0.02	0.01	--
1-dodecene	0.22	0.13	0.10	0.14
Aromatics				
benzene	1.80	1.92	1.42	1.79
toluene	5.46	7.77	15.87	7.92
ethylbenzene	1.52	1.96	2.45	1.83
p- and m-xylenes	4.45	5.82	7.18	5.38
o-xylene	1.68	2.23	2.82	2.06
isopropylbenzene	0.16	0.18	0.27	0.17
n-propylbenzene	0.51	0.64	0.75	0.61
1-methyl-3-ethylbenzene	1.93	2.19	2.36	2.05

Table A-9 Variability in composition of gasolines from Houston, TX area in 1984. Concentrations are weight percent. From Diakun (1984). (Page 3 of 3)

Compound	Regular Blend	Lead-Free Blend	Super Unleaded	API Generic
Aromatics (continued)				
1-methyl-4-ethylbenzene	0.80	0.93	1.04	0.86
1-methyl-2-ethylbenzene	0.93	0.96	1.05	0.92
1,3,5-trimethylbenzene	0.63	0.74	0.86	0.69
1,2,4-trimethylbenzene	2.86	3.30	3.92	3.07
1,2,3-trimethlybenzene	0.69	0.80	0.98	0.47
1-methyl-2-isopropylbenzene	--	0.53	0.22	--
indane	0.48	0.46	0.44	0.09
tetralin	0.12	0.12	0.09	0.20
naphthalene	0.63	0.60	0.41	0.42

Table A-10 **Typical hydrocarbon composition of three grades of jet fuel. Concentrations are in weight percent. From Smith et al. (1981). (Page 1 of 3)**

Compound	JP-4	JP-5	JP-8
n-alkanes			
butane	0.12	--	--
pentane	1.06	--	--
hexane	2.21	--	--
heptane	3.67	--	0.03
octane	3.80	0.12	0.09
nonane	2.25	0.38	0.31
decane	2.16	1.79	1.31
undecane	2.32	3.95	4.13
dodecane	2.00	3.94	4.72
tridecane	1.52	3.45	4.43
tetradecane	0.73	2.72	2.99
pentadecane	--	1.67	1.61
hexadecane	--	1.07	0.45
heptadecane	--	0.12	0.08
octadecane	--	--	0.02
Isoalkanes			
isobutane	0.66	--	--
2,2-dimethylbutane	0.10	--	--
2-methylpentane	1.28	--	--
3-methylpentane	0.89	--	--
2,2-dimethylpentane	0.25	--	--
2-methylhexane	2.35	--	--
3-methylhexane	1.97	--	--
2,2,3,3-tetramethylbutane	0.24	--	--
2,5-dimethylhexane	0.37	--	--
2,4-dimethylhexane	0.58	--	--
3,3-dimethylhexane	0.26	--	--
2,2-dimethylhexane	0.71	--	--
2-methylheptane	2.70	--	--
4-methylheptane	0.92	--	--
3-methylheptane	3.04	--	--
2,5-dimethylheptane	0.52	--	--
2,4-dimethylheptane	0.43	--	--
4-ethylheptane	0.18	--	--
4-methyloctane	0.86	--	--
2-methyloctane	0.88	--	--

Table A-10 **Typical hydrocarbon composition of three grades of jet fuel. Concentrations are in weight percent. From Smith et al. (1981). (Page 2 of 3)**

Compound	JP-4	JP-5	JP-8
isoalkanes, continued			
3-methyloctane	0.79	0.07	0.04
2-methylundecane	0.64	--	--
2,6-dimethylundecane	0.71	--	--
2,4,6-trimethylheptane	--	0.07	0.07
4-methyldecane	--	0.78	--
2-methyldecane	--	0.61	0.41
2,6-dimethyldecane	--	0.72	0.66
2-methylundecane	--	1.39	1.16
2,6-dimethylundecane	--	2.00	2.06
cycloparaffins			
methylcyclopentane	1.16	--	--
cyclohexane	1.24	--	--
t-1,3-dimethylcyclopentane	0.36	--	--
c-1,3-dimethylcyclopentane	0.34	--	--
c-1,2-dimethylcyclopentane	0.54	--	--
methylcyclohexane	2.27	--	--
ethylcyclopentane	0.26	--	--
1,2,4-trimethylcyclopentane	0.25	--	--
1,2,3-trimethylcyclopentane	0.25	--	--
c-1,3-dimethylcyclohexane	0.42	--	--
1-methyl-3-ethylcyclohexane	0.17	--	--
1-methyl-2-ethylcyclohexane	0.39	--	--
dimethylcyclohexane	0.43	--	--
1,3,5-trimethylcyclohexane	0.99	0.09	0.06
1,1,3-trimethylcyclohexane	0.48	0.05	0.06
1-methyl-4-ethylcyclohexane	0.48	--	0.10
n-butylcyclohexane	0.70	0.90	0.74
propylcyclohexane	--	--	0.14
hexylcyclohexane	--	--	0.93
heptylcyclohexane	--	0.99	1.00
aromatic hydrocarbons			
benzene	0.50	--	--
toluene	1.33	--	--
ethylbenzene	0.37	--	--

Table A-10 **Typical hydrocarbon composition of three grades of jet fuel. Concentrations are in weight percent. From Smith et al. (1981). (Page 3 of 3)**

Compound	JP-4	JP-5	JP-8
aromatic hydrocarbons, continued			
m-xylene	0.96	0.13	0.06
p-xylene	0.35	--	--
o-xylene	1.01	0.09	0.06
isopropylbenzene	0.30	--	--
n-propylbenzene	0.71	--	--
1-methyl-3-ethylbenzene	0.49	--	--
1-methyl-4-ethylbenzene	0.43	--	--
1,3,5-trimethylbenzene	0.42	--	--
1-methyl-2-ethylbenzene	0.23	--	--
1,2,4-trimethylbenzene	1.01	0.37	0.27
1,3-diethylbenzene	0.46	0.61	--
1,4-diethylbenzene	--	0.77	--
1-methyl-4-propylbenzene	0.40	--	--
1,3-dimethyl-5-ethylbenzene	0.61	--	0.62
1-methyl-2-isopropylbenzene	0.29	--	0.56
1,4-dimethyl-2-ethylbenzene	0.70	--	--
1,2-dimethyl-4-ethylbenzene	0.77	--	--
1,2,3,4-titramethylbenzene	0.75	1.48	1.12
1-ethylpropylbenzene	--	1.16	0.99
1,2,4-triethylbenzene	--	0.72	0.99
1,3,5-triethylbenzene	--	--	0.60
phenylcyclohexane	--	0.82	0.87
1-t-butyl-3,4,5-trimethylbenzene	--	0.24	--
n-heptylbenzene	--	0.27	0.25
naphthalene	0.50	0.57	1.14
2-methylnaphthalene	0.56	1.38	1.46
1-methylnaphthalene	0.78	1.44	1.84
2,6-dimethylnaphthalene	0.25	1.12	1.34
biphenyl	--	0.70	0.63
1-ethylnaphthalene	--	0.32	0.33
2,3-dimethylnaphthalene	--	0.46	0.36
n-octylbenzene	--	0.78	0.61
olefins			
tridecene	--	0.45	0.73

Table A-11 **Hydrocarbon composition of two samples of kerosene. From Goodman and Harbison (198?). (Page 1 of 2)**

Compound/Class	Sample A	Sample B
hydrocarbon type (vol %)		
paraffins	50.5	42.7
monocycloparaffins & olefins	25.3	19.3
dicycloparaffins	5.6	8.9
alkylbenzenes	12.7	14.7
indans/tetralins	2.9	7.5
naphthalene & alkylnaphthalenes	3.0	6.9
n-paraffins (wt %)		
heptane	0.1	0.1
octane	0.2	0.3
nonane	0.4	0.8
decane	1.5	1.7
undecane	3.5	6.1
dodecane	2.8	5.7
tridecane	3.1	5.2
tetradecane	2.3	4.7
pentadecane	0.6	2.3
hexadecane	0.1	0.7
heptadecane	--	0.4
octadecane	--	0.3
nonadecane	--	0.2
eicosane	--	0.1
heneicosane	--	0.1
aromatic hydrocarbons (ppm, wt/vol)		
indene	<50	2.2
naphthalene	2,000	1,286
1-methylnaphthalene	2,200	2,160
2-methylnaphthalene	2,100	2,860
acenaphthene	51	40
acenaphthalene	25	38
fluorene	<2.0	36
1,4-dimethylnaphthalene	1,200	1,580
phenanthrene	1.9	493

Table A-11 **Hydrocarbon composition of two samples of kerosene. From Goodman and Harbison (198?). (Page 2 of 2)**

Compound/Class	Sample A	Sample B
anthracene	<2.0	7.3
fluoranthene	<4.0	1.0
pyrene	<2.0	2.0
benz(a)anthracene	<0.75	<0.09
chrysene	<2.0	<0.11
benzo(b)fluoranthene	<0.75	<0.20
benzo(k)fluoranthene	<0.50	<0.04
benzo(a)pyrene	<0.50	<0.30
benzo(g,h,i)perylene	<2.0	<0.30
indeno(1,2,3-c,d)pyrene	<2.0	<0.30
perylene	<3.0	<0.90
dibenz(a,h)anthracene	<0.75	<0.50
dibenzo(def,p)chrysene	<0.30	<0.15
9,10-dimethylanthracene	<4.0	6.0
2-methylanthracene	<4.0	3.9
benzo(b)fluorene	<4.0	1.0
benzo(a)fluorene	<4.0	0.78
7,12-dimethylbenz(a)anthracene	--	17.0
dibenzo(a,e)pyrene	<0.45	<0.30
benzo(b)chrysene	<0.45	<0.30
picene	<1.5	<1.4
p-quarterphenyl	<0.5	<0.50
coronene	<0.45	<0.30
dibenz(a,h)acridine	<0.2	<0.13
dibenzo(a,h)pyrene	<1.0	<0.70
3-methylcholanthrene	<0.1	<0.08
benzo(g,h,i)fluoranthene	<1.0	<0.04
naphtho(1,2,3,4,def)chrysene	<0.15	<0.10

Table A-12 Hydrocarbon composition of typical home heating oils. Concentrations are volume percent. From IARC (1989).

Hydrogen Type	Straight-run No. 1 Furnace Oils		Hydrotreated No. 1 Furnace Oil	Straight-run No. 2 Furnace Oil	No. 2 Furnace Oil 10% Catalytic	No. 2 Furnace Oil 50% Catalytic
	1	2				
n/iso-paraffins	50.5	54.3	42.6	41.3	61.2	57.2
monocycloparaffins	25.3	18.4	19.3	22.1	8.5	6.0
bicycloparaffins	5.6	4.5	8.9	9.6	8.3	5.0
tricycloparaffins	--	0.8	--	2.3	1.4	0.7
total alkanes	81.4	78	70.9	75.3	79.4	68.9
olefins	--	--	--	--	2.0	7.5
alkylbenzenes	12.7	14.3	14.7	5.9	5.3	8.0
indans/tetralins	2.9	3.8	7.5	4.1	4.3	5.4
dinaphthenobenzenes/indenes	--	0.9	--	1.8	1.3	1.0
naphthalenes	3.0	2.6	6.9	8.2	5.8	6.8
biphenyls/acenaphthanes	--	0.4	--	2.6	1.1	1.6
fluorenes/acenaphthylenes	--	--	--	1.4	0.6	0.3
phenanthrenes	--	--	--	0.7	0.2	0.5
total aromatic hydrocarbons	18.6	29.1	22.0	24.7	18.6	23.6

Table A-13 **Concentrations of benzenes and PAH in middle distillate fuels. Concentrations are in mg/kg.**

Compound	No. 2 Fuel Oil(1)	Artic Diesel(2)	Refined Spilled(3)	Diesel Fuel(4)	No. 2 Heating(4)
benzene	222,000[a]	<10			
toluene		2,549			
ethylbenzene		991			
xylenes		5,211			
naphthalene	4,000	4,086[a]	2,468		
methylnaphthalenes	27,100		23,312		
ethylnaphthalenes			5,576		
dimethylnaphthalenes	31,100		26,214		
trimethylnaphthalenes	18,400				
fluorene	3,600	302[a]			
anthracene				2.9	3.6
phenanthrene	429	171[a]			
methylanthracenes				9.3	15.7
methylphenanthrenes	7,850				
fluoranthene	37			0.57	2.4
pyrene	41			0.37	1.3
benz(a)anthracene	1.2			0.13	0.04
chrysene	2.2	<10[a]		0.45	0.54
triphenylene	1.4			3.3	0.73
benzo(a)pyrene	0.6			0.07	0.03
benzo(e)pyrene	0.1			0.18	0.02
benzo(g,h,i)perylene				0.03	0.03

(1) Pancirov and Brown, 1975
(2) Kennicutt et al., 1991
(3) Woodward et al., 1983
(4) Norris and Hill, 1974
a includes alkyl homologues

Table A-14 **Concentrations of benzenes and PAH in No. 2 diesel fuels. Concentrations are in mg/L or mg/kg.**

Compound	No. 2 Fuel Oil(1)	No. 2 Fuel Oil(2)	High S Diesel Fuel(2)	Low S Diesel Fuel(2)
toluene			8,300	nd
xylenes			200	2,700
trimethylbenzenes			27,000	17,000
C_4-benzenes			31,000	23,000
C_5-benzenes			13,000	11,000
C_6-benzenes			1,900	4,600
naphthalene	500	76	25,000	2,200
methylnaphthalenes	1,000	560	30,000	7,100
dimethylnaphthalenes	1,300	1,500	43,000	10,000
trimethylnaphthalenes	950	1,000	34,000	7,200
tetramethylnaphthalenes	550	520	1,200	900
biphenyl	75	52		
fluorene	38	40		
methylfluorenes	135	130		
dimethylfluorenes	305	240		
trimethylfluorenes	315	170		
phenanthrene	80	88	2,100	400
methylphenanthrenes	500	370	5,300	400
dimethylphenanthrenes	950	470	4,300	200
trimethylphenanthrenes	700	190	1,500	nd
tetramethylphenenthrenes	285	76		
dibenzothiophene	nd	150		
methyldibenzothiophenes	22	65		
dimethyldibenzothiophenes	80	84		
trimethyldibenzothiophenes	90	62		
fluoranthene	2.8	1.2		
pyrene	20	7.0		
methylfluoranthenes/pyrenes	80	15		
benz(a)anthracene	0.8	0.12		
chrysene	3.4	0.5		
methylchrysenes	6.0	0.8		
diemthylchrysenes	3.7	0.4		
trimethylchrysenes	1.6	0.08		
benzo(a)pyrene	nd	0.13		
benzo(e)pyrene	nd	nd		
benzo(g,h,i)perylene	nd	0.05		

(1) Page et al., 1994

(2) Boehm et al., 1989

Table A-15 **Concentrations of benzenes and PAH in residual petroleum products. Concentrations are in mg/L or mg/kg.**

Compound	Bunker C No. 6 Oil(1)	Bunker C(2)	Asphalts(3)	Paving Asphalts(4)
benzenes	60,000[a]			
naphthalene	1,000			
methylnaphthalenes	7,500	147		
dimethylnaphthalenes	12,300			
trimethylnaphthalenes	8,800			
biphenyls	<100			
fluorenes	2,400			3.0
phenanthrene	482	450	0.4-3.5	9.6
methylphenenthrenes	871			
dimethylphenanthrenes				
fluoranthene	240		nd-5	
pyrene	23		0.08-38	
benz(a)anthracene	90	1,520	nd-35	90
chrysene	196	3,090	0.04-34	80
triphenylene	31		0.25-7.6	
dimethylbenzanthracenes				4.3
benzo(k)fluoranthene		436		1.8
benzo(a)pyrene	44		nd-27	1.3
benzo(e)pyrene	10		0.03-52	
perylene	22		nd-39	1.5
benzo(g,h,i)perylene			tr-15	1.2
dibenz(a,h)anthracene				4.6
indeno(1,2,3-cd)pyrene		101		

(1) Pancirov and Brown, 1975
(2) Davani et al., 1989
(3) Wallcave et al., 1971
(4) Malaiyandi et al., 1982
[a] Includes benzene, toluene, ethylbenzene, and xylenes

Table A-16 **Concentrations of PAH in new engine oils and lube oil. Concentrations are in mg/kg.**

Compound	Engine Oil (new)(1)	Average(1)	Maximum	Rerefined(1)	Lube Oil(2)
dibenzo(b,d)thiophene	5				
fluorene					11.7
phenanthrene	7				46.5
anthracene	0.1				9.5
methyldibenzothiophenes	1				
methylphenanthrenes	8				
fluoranthene	0.7	0.3	3	69	2.0
phenanthrothiophene	0.4				
pyrene	2	0.7	7	12	2.5
benzonaphthofurans	1				
methylpyrenes/ fluoranthenes	1				
benzofluorenes	4				
methylbenzonaphthofurans	0.3				
methylpyrenes	3				
dimethylpyrenes/ fluoranthenes	1				
benzonaphthothiophenes	5	1	9	5	
benz(a)anthracene	0.3	0.2	2		0.68
triphenylene	3				
chrysene	1	1	12	30	3.2
methylbenzonaphtho-thiophenes	7				
methylchrysenes	1				
dimethylchrysenes	1				
benzofluoranthenes	0.4	0.1	0.2	8	0.62
triphenylenethiophene	0.1				
benzo(e)pyrene	0.25	0.2	0.4	4	
benzo(a)pyrene	0.03	0.06	0.3	1	0.23
methyltriphenylene/ thiophene	0.3				
methylbenzo(e)pyrenes	0.2				
methylbenzo(a)pyrenes	0.1				
dimethylbenzopyrenes	0.5				
indeno(1,2,3-c,d)pyrene	0.02	0.006	0.02	0.7	
dibenz(a)anthracene	0.1				
benzo(g,h,i)perylene	0.1	0.05	0.1	1	0.85
anthranthrene	0.01	0.03			
coronene		0.007	0.02	0.6	

(1) Grimmer et al., 1981a

(2) Eisenberg et al., 1988

Table A-17 **Concentrations of alkylbenzenes and PAH in used engine oils from North America. Concentrations are in mg/L or mg/kg. (Page 1 of 2)**

Compound	Winter Gas Engine Calgary$^{(1)}$	Gas Engine 3928 mi$^{(2)}$	Gas Engine 5817 mi	Waste Crankcase Oil (MD)$^{(3)}$
Σ alkylbenzenes	>900			
tetralin				24
naphthalene		2,350	2,520	368
methylnaphthalenes		6,350	4,150	57
dimethylnaphthalenes		4,470	3,000	114
trimethylnaphthalenes				37
Σ alkylnaphthalenes	440			
biphenyl		82.8	45.8	
methylbiphenyls	2.05			6
fluorene	1.47	98.3	109	6
methylfluorenes	2.45			
dimethylfluorenes	1.29			
trimethylfluorenes	1.10			
phenanthrene	7.80	186	193	33
anthracene	0.33	30.1	47.0	
phenylnaphthalene	0.90			
methylphenanthrenes	11.67	648	668	
dimethylphenanthrenes	10.59			
trimethylphenanthrenes	6.13			
diethylphenanthrenes	1.19			
ethylcyclopentaphenanthrene	1.42			
methylanthracenes	0.58			
dimethyanthracenes	0.26			
trimethylanthracenes	0.51			
dibenzothiophene	0.79			
methyldibenzothiophenes	2.26			
dimethyldibenzothiophenes	3.86			
trimethyldibenzothiophenes	1.94			
benzonaphthiophene	0.34			
methylbenzonaphthothiophene	0.54			
terphenyl	0.12			
fluoranthene	4.36	69.8	91.2	
pyrene	6.69	88.4	95.6	
methylpyrenes	4.25			
dimethylpyrenes	1.71			
ethylmethylpyrenes	0.14			
benzofluorenes	2.75			

Table A-17 Concentrations of alkylbenzenes and PAH in used engine oils from North America. Concentrations are in mg/L or mg/kg. (Page 2 of 2)

Compound	Winter Gas Engine Calgary(1)	Gas Engine 3928 ml(2)	Gas Engine 5817 ml	Waste Crankcase Oil (MD)(3)
benzo(c)phenanthrene	0.12			
benz(a)anthracene	0.87	32	47.4	
methylbenz(a)anthracene	2.45			
ethylbenz(a)anthracene	0.65			
chrysene/triphenylene	2.48	50	84.7	
cyclopenta(cd)pyrene	0.78			
benzo(b)fluoranthene	1.44			
methylbenzofluoranthenes	0.43			
benzo(e)pyrene	1.74	nd	27.1	
benzo(a)pyrene	0.36	nd	22.3	
methylbenzopyrenes	0.41			
perylene	0.13			
benzo(ghi)perylene	1.67			

(1) Peake and Parker, 1980
(2) Pruell and Quinn, 1988
(3) Hoffman et al., 1982

Table A-18 Concentrations of PAH in used engine oils (crankcase oils). Concentrations are in mg/kg. From Grimmer et al. (1981b).

Compound	Length of Use and Engine Type				
	610K km Gasoline	1-6K km Gasoline	0.5-6K km Diesel	3-30K km Diesel	9-31K Diesel
phenanthrene	158				
anthracene	46				
methylphenanthrenes	381				
2-phenylnaphthalene	44				
dimethylphenanthrenes (includes O-PAC)	56				
fluoranthene	178	109	59	3	3
pyrene	430	326	78	6	5
methylfluoranthenes /methylpyrenes	883				
dimethylfluoranthenes	263				
benz(a)anthracene	245				
benzo(b)naphtho-(2,1-d)thiophene			4	6	5
chrysene+triphenylene	223	74	43	6	8
methylchrysenes/ benz(a)anthracenes	485				
dimethylbenz(a)anthracene	21				
benzo(b+j)fluoranthenes	134	44	17	1	1
benzo(k)fluoranthene	37				
benzo(a)fluoranthene	19				
benzo(e)pyrene	278	49	11	1	1
benzo(a)pyrene	217	35	12	0.6	0.6
perylene	51	10	3	0.4	0.3
methylperylenes/ benzopyrenes/benzofluoranthenes	540				
dimethylperylenes/ benzopyrenes/benzofluoranthenes	62				
dibenz(a,j)anthracene	23				
indeno(1,2,3-cd)pyrene	89	12	9	0.3	0.2
dibenz(a,h)anthracene	14				
dibenz(a,c)anthracene	3				
benzo(ghi)perylene	334	85	16	0.8	0.6
anthranthrene	15	11	4	0.1	0.2
methyldibenzanthracenes	203				
dibenzo(b,k)fluoranthene	10				
coronene	60	29	6	0.1	0.1
dibenz(gf,op)naphthacene	41.32				
benzo(rst)pentaphene	7.51				

Appendix B

Physical/Chemical Properties of Petroleum Compounds

Table B-1 Physical/Chemical Properties of Petroleum Hydrocarbons (Page 1 of 4)

Compound	Molecular Weight	Aqueous Solubility		Log Kow	Henry's Law Const.*
		mg/L	M/cu. m.		
One-Ring Aromatic Hydrocarbons					
benzene	78.1	1.79E+03	2.24E+01	2.13E+00	2.30E-01
toluene	92.1	7.59E+02	5.80E+00	2.70E+00	2.60E-01
ethylbenzene	106.2	1.35E+02	1.40E+00	3.13E+00	2.70E-01
m-xylene	106.2	1.60E+02	1.20E+00	3.30E+00	4.40E-01
o-xylene	106.2	2.15E+02	1.60E+00	2.90E+00	2.10E-01
p-xylene	106.2	2.21E+02	1.90E+00	3.10E+00	2.90E-01
indan	118.1	1.09E+02	-	3.31E+00	-
isopropylbenzene	120.2	4.83E+01	4.02E-01	3.66E+00	6.14E-01
n-propylbenzene	120.2	5.22E+01	4.34E-01	3.69E+00	4.17E-01
1-ethyl 4-methyl benzene	120.2	9.49E+01	7.89E-01	-	2.01E-01
1-ethyl 2-methyl benzene	120.2	7.46E+01	6.21E-01	3.53E+00	2.15E-01
1,3,5-trimethyl benzene	120.2	4.82E+01	4.01E-01	3.55E+00	3.30E-01
1,2,4-trimethyl benzene	120.2	5.19E+01	4.32E-01	3.65E+00	2.53E-01
1,2,3-trimethyl benzene	120.2	6.55E+01	5.45E-01	3.58E+00	1.50E-01
t-butylbenzene	134.2	2.95E+01	2.20E-01	-	5.25E-01
isobutylbenzene	134.2	1.01E+01	7.53E-02	-	1.33E+00
s-butylbenzene	134.2	1.76E+01	1.31E-01	-	7.42E-01
1-isopropyl 4-methylbenzene	134.2	3.42E+01	2.54E-01	-	3.24E-01
n-butylbenzene	134.2	1.38E+01	1.03E-01	4.28E+00	5.38E-01
1,2,4,5-tetra-methylbenzene	134.2	3.48E+00	2.59E-02	4.00E+00	1.03E+00
n-pentylbenzene	148.3	1.05E+00	7.10E-03	4.90E+00	2.49E-01
n-hexylbenzene	162.3	1.02E+00	6.30E-03	5.52E+00	7.98E-01
Polycyclic Aromatic Hydrocarbons					
naphthalene	128.2	3.06E+01	2.39E-01	3.37E+00	5.62E-02
2-methyl naphthalene	142.2	2.56E+01	1.80E-01	4.11E+00	2.03E-02
1-methyl naphthalene	142.2	2.84E+01	2.00E-01	3.87E+00	1.60E-02
acenaphthylene	152.2	3.47E+00	2.28E-02	-	-
biphenyl	154.2	7.00E+00	4.54E-02	3.95E+00	3.48E-02
acenaphthene	154 2	3.93E+00	2.55E-02	3.92E+00	4.20E-03
2-ethyl naphthalene	156.2	8.00E+00	5.12E-02	3.86E+00	2.55E-02
1-ethyl naphthalene	156.2	1.07E+00	6.90E-03	3.87E+00	1.48E-02
1,3-dimethyl naphthalene	156.2	8.00E+00	5.12E-02	4.42E+00	-
1,4-dimethyl naphthalene	156.2	1.14E+01	7.30E-02	4.37E+00	-
1,5-dimethyl naphthalene	156.2	3.37E+00	2.16E-02	4.38E+00	-
2,6-dimethyl naphthalene	156.2	2.00E+00	1.28E-02	4.31E+00	6.50E-03
1,5-dimethyl naphthalene	156.2	3.37E+00	2.16E-02	4.38E+00	--
2,3-dimethyl naphthalene	156.2	3.00E+00	1.92E-02	4.40E+00	6.30E-03
fluorene	166.2	1.84E+00	1.11E-02	4.18E+00	3.60E-03
4-methylbiphenyl	168.2	4.05E+00	2.41E-02	-	-
1,4,5-trimethyl naphthalene	176.2	2.10E+00	1.19E-02	4.90E+00	9.50E-03

*Expressed as moles/cubic meter in air to moles/cubic meter in water

Table B-1 Physical/Chemical Properties of Petroleum Hydrocarbons (Page 2 of 4)

Compound	Molecular Weight	Aqueous Solubility		Log Kow	Henry's Law Const.*
		mg/L	M/cu. m.		
Polycyclic Aromatic Hydrocarbons (cont.)					
phenanthrene	178.2	1.18E+00	6.60E-03	4.57E+00	1.40E-03
anthracene	178.2	7.31E-02	4.00E-04	4.54E+00	6.63E-04
1-methylfluorene	180.0	1.09E+00	6.10E-03	4.97E+00	-
4,4'-dimethyl biphenyl	183.2	1.76E-01	9.59E-04	-	-
2-methyl anthracene	192.3	2.30E-02	1.20E-04	5.15E+00	-
9-methyl anthracene	192.3	2.61E-01	1.36E-03	5.07E+00	4.28E-02
1-methyl phenanthrene	192.3	2.69E-01	1.40E-03	5.14E+00	-
2-methyl anthracene	196.3	3.90E-02	2.00E-04	5.15E+00	-
pyrene	202.3	1.35E-01	7.00E-04	5.18E+00	3.47E-04
fluoranthene	202.3	2.63E-01	1.30E-03	5.22E+00	3.51E-04
2-ethylanthracene	206.3	2.70E-02	1.30E-04	-	-
9,10-dimethyl anthracene	206.3	5.57E-02	3.00E-04	5.25E+00	-
diisopropyl naphthalene	212.0	1.10E-01	5.19E-04	4.90E+00	-
dimethyl dibenzothiophenes	212.3	5.51E+00	-	-	-
2,3-benzofluorene	216.3	2.00E-03	9.20E-06	5.75E+00	-
1.2-benzofluorene	216.3	4.54E-02	2.10E-04	5.32E+00	-
benzo(ghi) fluoranthene	226.3	-	-	6.90E+00	-
trimethyl dibenzothiophenes	226.4	-	-	5.73E+00	-
chrysene	228.3	2.00E-03	8.80E-06	5.79E+00	1.80E-04
2,3-benz anthracene	228.3	5.71E-04	2.50E-06	5.90E+00	-
1,2-benz anthracene	228.3	1.40E-02	6.10E-06	5.91E+00	1.68E-04
triphenylene	228.3	6.60E-03	2.89E-05	-	-
2,6-diphenyl pyridine	232.3	-	-	4.82E+00	-
5-methylchrysene	242.1	7.30E-03	3.00E-05	6.42E+00	-
6-methylchrysene	242.1		3.00E-05	6.42E+00	-
benzo(b) fluoranthene	252.3	1.20E-03	4.80E-06	-	-
benzo(k) fluoranthene	252.3	5.50E-04	2.20E-06	6.40E+00	-
benzo(e)pyrene	252.3	-	-	6.40E+00	-
benzo(a)pyrene	252.3	1.54E-03	6.10E-06	6.83E+00	1.70E-04
perylene	252.3	4.04E-04	1.60E-06	6.50E+00	-
7,12-dimethyl benz(a)anthracene	256.1	-	1.00E-05	6.93E+00	-
3-methyl cholanthrene	268.4	2.95E-03	1.10E-05	7.11E+00	-
indeno(1,2,3-cd) pyrene	276.3	6.20E-02	2.24E-04	7.00E+00	-
benzo(ghi) perylene	276.3	2.60E-04	9.00E-07	7.10E+00	5.86E-06
picene	278.3	3.80E-04	1.34E-07	7.19E+00	-
1,2,5,6-dibenz anthracene	278.4	5.01E-04	1.80E-06	7.19E+00	3.07E-06
coronene	300.4	1.40E-04	5.00E-07	7.64E+00	-
Saturates					
cyclopentane	70.1	1.60E+02	2.28E+00	3.00E+00	7.50E+00
iso-pentane	72.2	4.80E+01	6.65E-01	-	5.62E+01

*Expressed as moles/cubic meter in air to moles/cubic meter in water

Table B-1 Physical/Chemical Properties of Petroleum Hydrocarbons (Page 3 of 4)

Compound	Molecular Weight	Aqueous Solubility		Log Kow	Henry's Law Const.*
		mg/L	M/cu. m.		
Saturates (cont.)					
n-pentane	72.2	4.08E+01	5.65E-01	3.62E+00	4.88E+01
methylcyclopentane	84.2	4.18E+01	4.98E-01	-	1.49E+01
cyclohexane	84.2	5.75E+01	6.83E-01	3.44E+00	7.50E+00
2,2-dimenthybutane	86.2	2.12E+01	2.46E-01	3.82E+00	6.99E+01
2,3-dimethylbutane	86.2	1.91E+01	2.22E-01	3.85E+00	5.70E+01
2-methylpentane	86.2	1.38E+01	1.60E-01	-	7.11E+01
n-hexane	86.2	1.23E+01	1.43E-01	3.00E+00	5.71E+01
1-hexane	86.2	6.16E+01	7.15E-01	2.78E+00	-
methylcyclohexane	98.2	1.60E+01	1.63E-01	2.82E+00	1.53E+01
n-heptane	100.2	3.06E+00	3.06E-02	4.66E+00	8.06E+01
2,2-dimethylpentane	100.2	4.40E+00	4.39E-02	3.10E+00	1.29E+02
2,4-dimethylpentane	100.2	4.41E+00	4.40E-02	3.10E+00	1.20E+02
3,3-dimethylpentane	100.2	5.94E+00	5.93E-02	-	7.49E+01
2,3-dimethylpentane	100.2	5.25E+00	5.24E-02	-	7.07E+01
2-methylhexane	100.2	2.54E+00	2.53E-02	-	1.40E+02
3-methylhexane	100.2	2.64E+00	2.63E-02	-	1.26E+02
1,1,3-trimethyl cyclopentane	112.2	3.73E+00	3.32E-02	-	6.43E+01
1,4-dimethyl cyclohexane	112.2	3.84E+00	3.42E-02	-	3.56E+01
1,2-dimethyl cyclohexane	112.2	6.00E+00	5.35E-02	-	1.46E+01
propylcyclopentane	112.2	2.04E+00	1.82E-02	-	3.64E+01
2,3,4-trimethyl pentane	114.2	2.30E+00	2.01E-02	-	7.21E+01
2,2,4-trimethyl pentane	114.2	2.44E+00	-	-	-
3-methylheptane	114.2	7.92E-01	6.93E-03	-	1.51E+02
n-octane	114.2	6.60E-01	5.77E-03	4.59E+00	-
4-methyloctane	128.3	1.15E-01	8.97E-04	-	4.06E+02
pentylcyclopentane	140.3	1.15E-01	8.20E-04	-	7.48E+01
n-decane	142.3	5.20E-02	4.05E-04	5.01E+00	1.74E+02
undecane	156.3	4.40E-02	2.81E-04	5.58E+00	7.49E+01
dodecane	170.3	3.40E-03	2.00E-05	6.10E+00	3.17E+02
tetradecane	198.4	6.55E-04	3.30E-06	7.20E+00	1.56E+02
hexadecane	226.4	5.21E-05	2.30E-07	8.25E+00	1.57E+02
octadecane	254.4	4.05E-06	1.59E-08	9.32E+00	2.51E+02
eicosane	282.6	3.11E-07	1.10E-09	-	8.00E+01
hexacosane	366.7	1.30E-10	3.63E-13	-	8.13E+00
Olefins (alkenes)					
1-pentyne	68.1	7.86E+02	1.15E+01	2.12E+00	-
1-pentene	70.1	1.48E+02	2.11E+00	-	1.63E+01
2-pentene	70.1	2.03E+02	2.89E+00	3.59E+00	9.20E+00
1-hexyne	82.2	6.88E+02	8.37E+00	2.73E+00	-
1-hexene	84.2	6.97E+01	8.28E-01	3.39E+00	1.68E+01

*Expressed as moles/cubic meter in air to moles/cubic meter in water

Table B-1 Physical/Chemical Properties of Petroleum Hydrocarbons (Page 4 of 4)

Compound	Molecular Weight	Aqueous Solubility mg/L	M/cu. m.	Log Kow	Henry's Law Const.*
Olefins (alkenes) (cont.)					
2-heptene	98.2	1.82E+01	1.85E-01	3.99E+00	1.70E+01
1-octene	112.2	4.09E+00	3.65E-02	4.57E+00	3.89E+01
1-nonene	126.2	1.12E+00	8.85E-03	5.15E+00	-
1-decene	140.3	-	-	5.70E+00	-
Heterocyclic Compounds					
quinoline	129.2	6.72E+03	5.20E+01	2.10E+00	-
isoquinoline	129.2	4.52E+03	3.50E+01	-	-
carbazole	167.2	1.00E+00	6.00E-03	3.84E+00	-
dibenzofuran	168.2	4.22E+00	2.51E-02	4.21E+00	-
acridine	179.2	-	-	3.45E+00	-
dibenzo(1,4)dioxin	183.2	2.67E-02	1.46E-04	-	4.19E+00
dibenzothiophene	184.3	1.47E+00	8.00E-03	5.08E+00	-
methyl dibenzothiophenes	198.3	-	-	4.86E+00	-
benzo(b)naphtho (2,3d)thiophene	234.3	-	-	5.07E+00	-
13H-dibenzo(a,i) carbozole	267.3	-	-	5.89E+00	-

*Expressed as moles/cubic meter in air to moles/cubic meter in water

Appendix C

Toxicity Data Summary

Table C-1: Toxicity Summary - Aromatics/Polynuclear Aromatics (Page 1 of 7)

Name	Subchronic /Chronic (S/C)	Carcinogenic Data (C)	Carcinogenic Classification	Genotoxicty In Vitro/In Vivo (G)	Developmental /Reproductive (R)	Hazard Ranking
acenaphthene	hepatotoxicity (M) {350 mg/kg/day} [1]		EPA-ND IARC-ND			S/C-3
acenaphthylene			EPA-D	pos/neg: S. typh [1]		C-2 G-2
alkylbenzenes (tri/tetramethylbenzenes, methylethylbenzenes, C3-C6 benzenes)	ND [1,2,3,4,5]		ND [1,2,3,4,5]	ND [1,2,3,4,5]	ND [1,2,3,4,5]	—
anthracene* {dimethylanthracenes, methylanthracenes, trimethylanthracenes}	no effects observed (M){1000 mg/kg/day} [1]	contra, inad, or neg (M, R, Rb) [2]	EPA-ND IARC-Group 3 H (ND), A (I)	neg: E. coli, B. subt, yeast; rat hepa, CHO, HeLa, CHV79, Mous lymp L5178Y, huma lymp, CHD6, rat live epit, mous, guin feta, SHE; pos/neg: S. typh [1] N [2]		C-1 G-0
anthranthrene		skin (pos in 1/4 studies {M}), injection site (rats) [2]	EPA-ND IARC-Group 3 H (ND), A (L)	pos: S. typh I [2]		C-4 G-3
benz[a]anthracene* {benzanthracenes, dimethylbenz[a]anthracene, dimethylbenzanthracenes, ethylbenz[a]anthracene, methylbenz[a]-anthracenes (see below)}		pulmonary, forestomach, liver, skin, injection site (M) [1]	EPA-B2 IARC-Group 2A H (ND), A (S)	Pos: S. typh, rat hepa, HeLa, CHV79, mous lymp L5178Y, rat live epit, CHO, SHE, mous prost C3HG23 neg: E. coli [1] S [2]		C-9 G-9
benz[a]anthracene, 6-methyl		injection site (M), skin (R) [5]	EPA-ND IARC-ND	pos: S. typh [5]		C-8 G-3

* Data summarized specific to chemical indicated

Table C-1: Toxicity Summary - Aromatics/Polynuclear Aromatics (Page 2 of 7)

benz[a]anthracene, 7-methyl		skin, injection site (R), skin, application site, respiratory (M) [5]	EPA-ND IARC-ND	pos: S. typh, B. subt, D. mela, mous fibr, mous embr, hams lung, hams embr, hams fibr, hams kidn, hams ovar, /pos: mous skin [5]		C-9 G-9
benz[a]anthracene, 7,12-dimethyl		brain, skin, blood, injection site, ovarian, uterine (R), ovarian, uterine, blood, injection site, skin, respiratory [5]	EPA-ND IARC-ND	pos: S. typh, E. coli, B. subt, D. mela, N. crass, S. cere, non-mamm test, huma mamm, huma embr, HeLa, huma lymp, huma live, huma fibr, huma leuk, rat embr, rat live, rat fibr, rat mamm /salm test, rat bone marr, rat ip, rat ip, rat oral, mous oral [5]	reproductive effects, teratogenic (R, M) [5]	C-9 G-9 R-9
benzo[a]fluorene* / benzo[b]fluorene* /benzo[c]fluorene*		I [2]	EPA-ND IARC-Group 3 H (ND) A (I)	pos/neg: S. typh [2] I [2]		C-2 G-2
benzo[b]fluoranthene* {methylbenzofluoranthenes}		lung, thorax (R), lung, liver, injection site, skin [1] (M)	EPA-B2 IARC-Group 2B H(ND), A (S)	pos/neg: S. typh [1] I [2]		C-8 G-2
benzo[j]fluoranthene* {methylbenzofluoranthenes}		skin (M), pulmonary (R) [2]	EPA-ND IARC-Group 2B H(ND), A (S)	pos: S. typh [2] I [2]		C-8 G-3
benzo[k]fluoranthene* {methylbenzofluoranthenes}		lung, thorax (R), lung, liver, skin (M)	EPA-B2 IARC-Group 2B H (ND), A (S)	pos: S. typh [1] I [2]		C-8 G-3
benzo[ghi]fluoranthene* {methylbenzofluoranthenes}		I [2]	IARC-Group 3 H (ND), A (I)	pos: S. typh [2] I [2]		C-3 G-3
benzonapthofuranes {methylbenzonapthofuranes}						

* Data summarized specific to chemical indicated

Table C-1: Toxicity Summary - Aromatics/Polynuclear Aromatics (Page 3 of 7)

benzo[b]naphtho-(2,3-d) thiophene, 6,11-dimethyl* {benzonapthothiophenes, methylbenzonaptho-thiophenes}		skin (M) [5]	EPA-ND IARC-ND			C-3
benzo[ghi]perylene		I [2]	EPA-D IARC- Group 3 H (ND) A (I)	pos: S. typh, CHO [1]; neg: mamm cells [2]		C-3 G-4
benzo[c]phenananthrene		I [2]	EPA-ND IARC-Group 3 H (ND), A (I)	pos: S. typh [2] I [2]		C-3 G-3
benzo[a]pyrene* {benzopyrenes, methylbenzo[a]pyrenes}	•	skin (M, R, Rb), injection site (M, R, GP, M, H) respiratory (H), stomach (R, H, M) [1]	EPA-B2 IARC- Group 2A H (ND), A (S)	pos: D. mela, CHV79, hams embr, mous / chin hams, mous bone marr [1] S [2]	embryotoxic, teratogenic, reproductive effects (M) [2], fetotoxic (R)	C-9 G-9 R-7
benzo[e]pyrene* {methylbenzo[e]pyrenes}		I [2]	EPA-ND IARC-Group 3 H(ND), A (I)	pos: S. typh, HeLa; neg: yeast, mamm cells, rat hepa, / pos: hams bone marr [2] L [2]		C-3 G-6
biphenyl* {biphenyls, methylbiphenyls}	kidney (R) {250 mg/kg/day} [1]		EPA-D IARC-ND	pos: mouse lymp; pos/neg: Chin hams; neg: S. typh, E. coli, rat hepa		S/C-3 G-4
chrysene* {dimethylchrysenes, methyl chrysenes (see below) trimethylchrysenes}		liver, lymphoma, lung (M) [1], skin (M) [2]	EPA-B2 IARC- Group 3 H (ND), A (L)	pos: S. typh, Chin hams, mous oocy, hams sperm, SHE; Neg: mous pros C3HG23 [1], yeast, rat hepa [2] L [2]		C-7 G-6
chrysene, 1-methyl		I [2]	EPA-ND IARC-Group 3 H (ND), A (I)	pos: S. typh [2] I [2]		C-3 G-3
chrysene, 2-methyl		skin {inter response} (M) [2]	EPA-ND IARC-Group 3 H (ND), A (L)	pos: S. typh [2] I [2]		C-4 G-3

* Data summarized specific to chemical indicated

Table C-1: Toxicity Summary - Aromatics/Polynuclear Aromatics (Page 4 of 7)

chrysene, 3-methyl		skin {inter response} (M) [2]	EPA-ND IARC-Group 3 H (ND), A (L)	pos: S. typh [2] I [2]		C-4 G-3
chrysene, 4-methyl		skin {inter response} (M) [2]	EPA-ND IARC-Group 3 H (ND), A (L)	pos: S. typh [2] I [2]		C-4 G-3
chrysene, 5-methyl		injection site, skin {high incidence} (M) [2]	EPA-ND IARC-Group 2B H (ND), A (S)	pos: S. typh, rat hepa [2] L [2]		C-8 G-5
chrysene, 6-methyl		skin {inter response} (M) [2]	EPA-ND IARC-Group 3 H (ND), A (L)	pos: S. typh [2] I [2]		C-4 G-3
coronene		I [2]	EPA-ND IARC- Group 3 H (ND), A (I)	pos: S. typh [2] I [2]		C-3 G-3
cyclopenta[cd]pyrene		skin (pos in 4/5 studies {M})[2]	EPA-ND IARC- Group 3 H (ND), A (L)	pos: S. typh, mamm cells [2] S [2]		C-4 G-8
dibenz[a,h]anthracene* {methyldibenzanthracenes}		pulmonary, mammary, forestomach, skin, injection site sarcomas[1]	EPA-B2 IARC- Group 2A H (ND), A (S)	pos: E. coli, B. subt, S. typh, huma epit, HeLa, CHO, SHE, mous C3H10T, mous pros [1] S [2]	embryotoxic (R) [2]	C-9 G-8 R-4
dibenz[a,c]anthracene* {methyldibenzanthracenes}		skin (M) [2]	EPA-ND IARC- Group 3 H (ND), A (L)	pos: S. typh, B. subt, mamm cells [2] S [2]		C-4 G-9
dibenz[a,j]anthracene* {methyldibenzanthracenes}		skin (M), injection site (M) [2]	EPA-ND IARC- Group 3 H (ND), A (L)	pos: S. typh [2] I [2]		C-4 G-3
dibenz[gf,op]napthacene {benzo[a]naptho(8,1,2-cde)naphthacene*)		application site (M)	EPA-ND IARC-ND			C-3

* Data summarized specific to chemical indicated

Table C-1: Toxicity Summary - Aromatics/Polynuclear Aromatics (Page 5 of 7)

dibenzo[a,e]fluoranthene* {dibenzo[b,k]fluoranthene}		skin (M), injection site (M) [2]	EPA-ND IARC- Group 3 {H(ND), A (L)}	ND [2]		C-4
dibenzo[a,e]pyrene*, dibenzo[a,h]pyrene*, dibenzo[a,i]pyrene* {benzo [rst]pentaphene}, dibenzo[a,l]pyrene* {dimethylbenzopyrenes}		S [2]	EPA-ND IARC- Group 2B H (NS), A (S)	pos: S. typh, neg: rat hepa [2] I [2]		C-8 G-3
dibenzo[bd]thiophene /dibenzothiophene(s), dimethyldibenzothiophenes, methyldibenzothiophenes, tetramethyldibenzothiophenes, trimethyldibenzothiophenes						
fluoranthene* {fluoranthenes, dimethylfluoranthenes}	nephropathy (M) {250 mg/kg/day} [1]	I [2]	EPA-D IARC- Group 3 H (ND), A (I)	pos/neg: S. typh, chin hams, CHO; neg: huma lymp [1] L [2]	embryotoxicity (in vitro {R}) [4]	S/C-3 C-3 G-4
fluoranthene, 2-methyl		skin (M) [2]	EPA-ND IARC-Group 3 H (ND), A (L)	pos: S. typh [2] I [2]		C-4 G-3
fluoranthene, 3-methyl		I [2]	EPA-ND IARC-Group 3 H (ND), A (I)	pos: S. typh [2] I [2]		G-3 G-3
fluorene* {fluorenes, dimethylfluorenes, methylfluorenes, trimethylflourenes}	dec. RBC, pack cell vol, hemo (M) {250 mg/kg/day} [1]	I [2]	EPA-D IARC- Group 3 H (ND), A (I)	pos/neg: mous lymp [2]; neg: S. typh, E. coli, rat, hepa [1] I [2]		S/C-2 C-2 G-2

* Data summarized specific to chemical indicated

Table C-1: Toxicity Summary - Aromatics/Polynuclear Aromatics (Page 6 of 7)

indanes (C2-C4)						
indans						
indeno [1,2,3-cd] pyrene		epidermoid (R), injection site (M), skin (M) [1]	EPA-B2 IARC- Group 2B H (ND), A (S)	pos: S. typh [1] I [2]		C-8 G-3
methylcholanthrene		blood, skin, injection site, respiratory, brain, prostrate (R), respiratory, blood, skin, musc-skel, injection site, uterine testicular (M) [5]	EPA-ND IARC-ND	pos: S. typh, E. coli, D. mela, N. crass, huma lung, HeLa, huma fibr, rat embr, rat live, rat lung, rat embr, /fish ip, salm test, rat oral, rat iv [5]	feto/embro toxicity (R), reproductive effects, teratogenic (M) [5]	C-9 G-9 R-8
napthalene* {alkylnapthalenes, napthalenes, dimethylnaphthalenes, methylnaphthalenes, ethylnaphthalenes, tetramethylnaphthalenes, trimethylnaphthalenes}		blood, uterine (R) [5]	EPA-D IARC-ND	neg: S. typh, E. coli, rat hepa, mous embr, rat embr [1]	nonteratogenic (M) [1], teratogenic (M) [5]	C-4 G-1 R-3
perylene* {dimethylperylenes, methylperylene(s)}		I [2]	EPA-ND IARC-Group 3 H (ND), A (I)	pos: S. typh; neg: huma lymp [2] I [2]		C-3 G-3

* Data summarized specific to chemical indicated

Table C-1: Toxicity Summary - Aromatics/Polynuclear Aromatics (Page 7 of 7)

phenanthrene* {diethylphenanthrenes, ethylcyclopentaphenanthrene, tetramethylphenanthrenes, trimethylphenanthrenes}		I [2]	EPA-D IARC- Group3 H (ND), A (I)	pos: huma lymp TK6; pos/neg: S. typh; neg: B. subt, E. coli, fungi, CHO, mamm cells [1] /pos: Chin hams bone marr [2] L [2]		C-3 G-4
phenanthrene, 1-methyl* {methylphenanthrenes}		I [2]	EPA-ND IARC-Group 3 H (ND), A (I)	pos: S. typh, rat hepa, huma lymp [2] S [2]		C-3 G-8
phenanthrene, 1,4-dimethyl {includes O-PAC}		I [2]	IARC-Group 3 H (ND), A (I)	pos: S typh, rat hepa [2] L [2]		C-3 G-5
phenanthrothiophene						
2-phenylnaphthalene						
pyrene* {dimethylpyrenes, methylpyrenes, ethylmethylpyrenes}	kidney effects (M) {125 mg/kg/day} [1]	I [2]	EPA-D IARC-Group 3 H (ND), A (I)	pos: mous lymph; neg: E.coli, B. Subt, dros, rat live epit: pos/neg: yeast, CHO [1]/neg:mous bone marr, other cell types [1] L [2]		S/C-3 C-3 G-4
tetralin* (tetrahydronaphthalene) {tetralins}	ND [1,2,3,5]	ND [1,2,3,5]	ND [1,2,3,5]	ND [1,2,3,5]	ND [1,2,3,4,5]	S/C C G
thiophene	ND [1,2,3,5]	ND [1,2,3,5]	ND [1,2,3,5]	ND [1,2,3,5]	ND [1,2,3,4,5]	S/C C G
terphenyl	ND [1,2,3,5]	ND [1,2,3,5]	ND [1,2,3,5]	ND [1,2,3,5]	ND [1,2,3,4,5]	S/C C G
triphenylene* {methyltriphenylene}			EPA-ND IARC-Group 3 H (ND), A (I)	pos: S. typh [2] I [2]		C-3 G-3

* Data summarized specific to chemical indicated

Table C-2: Toxicity Summary - n-Paraffins, Isoparaffins, Cycloparaffins, Olefins (Page 1 of 2)

Name	Subchronic /Chronic	Carcinogenic	Carcinogenic Classification	Genotoxicty In Vitro/In Vivo	Developmental /Reproductive	Hazard Ranking
cyclohexane	minor microscopic changes in liver and kidney (Rb) {786 ppm} [3]			pos: E. coli neg: SA7/SHE, S. typh [5]		S/C-2 G-2
decane	decreased WBC (R) {540 ppm}	skin (M) [5]				S/C-1 C-1
2,3-dimethyl butane	light hydrocarbon nephropathy (R) [6]					S/C-4
n-hexane	neurotoxicity (H) {73 mg/m3); nasal epithelial lesions (M) {77 mg/m3} [1]; neuropathy or testicular atrophy (R) {570 mg/kg/day} [3]		EPA-evaluation pending	pos:hams fibro [5]/unsp. in vivo cyto assay [7] neg: mous lymp [7]	pos: fetotoxic, reproductive effects [5] neg: nonembryotoxic, nonfetotoxic, no reproductive effects [7]	S/C-4 G-4 R-3
2-methyl butane	noninducer of light hydrocarbon nephropathy (R) [6]					S/C-0
2-methyl hexane	light hydrocarbon nephropathy (R) [8]					S/C-4
2,2,5-trimethyl hexane	light hydrocarbon nephropathy (R) [6]					S/C-4
2,3-dimethyl pentane	light hydrocarbon nephropathy (R) [6]					S/C-4
methylcyclopentane	noninducer of light hydrocarbon nephropathy (R) [6]					S/C-0

Table C-2: Toxicity Summary - n-Paraffins, Isoparaffins, Cycloparaffins, Olefins (Page 2 of 2)

Name	Subchronic /Chronic	Carcinogenic	Carcinogenic Classification	Genotoxicty In Vitro/In Vivo	Developmental /Reproductive	Hazard Ranking
2-methylpentane	light hydrocarbon nephropathy (R) [6]					S/C-4
2-methyl-2-pentene	noninducer of light hydrocarbon nephropathy (R) [6]					S/C-0
n-pentane	noninducer of light hydrocarbon nephropathy (R) [6]					S/C-0
trans-2-pentene	noninducer of light hydrocarbon nephropathy (R) [6]					S/C-0
2,2,4-trimethyl pentane	light hydrocarbon nephropathy (R) [6]			in vivo- pos: oral {unsc DNA synt} (R, M) [5]		S/C-4 G-4

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