ENVIRONMENTAL CONTAMINANTS ENCYCLOPEDIA
ENTRY ON PETROLEUM IN GENERAL

July 1, 1997

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Like a library or many large databases (such as EPA's national STORET water quality database), this document contains information of variable quality from very diverse sources. In compiling this document, mistakes were found in peer reviewed journal articles, as well as in databases with relatively elaborate quality control mechanisms [366,649,940]. A few of these were caught and marked with a "[sic]" notation, but undoubtedly others slipped through. The [sic] notation was inserted by the editors to indicate information or spelling that seemed wrong or misleading, but which was nevertheless cited verbatim rather than arbitrarily changing what the author said.

Most likely additional transcription errors and typos have been added in some of our efforts. Furthermore, with such complex subject matter, it is not always easy to determine what is correct and what is incorrect, especially with the "experts" often disagreeing. It is not uncommon in scientific research for two different researchers to come up with different results which lead them to different conclusions. In compiling the Encyclopedia, the editors did not try to resolve such conflicts, but rather simply reported it all.

It should be kept in mind that data comparability is a major problem in environmental toxicology since laboratory and field methods are constantly changing and since there are so many different "standard methods" published by EPA, other federal agencies, state agencies, and various private groups. What some laboratory and field investigators actually do for standard operating practice is often a unique combination of various standard protocols and impromptu "improvements." In fact, the interagency task force on water methods concluded that [1014]:

> It is the exception rather than the rule that water-quality monitoring data from different programs or time periods can be compared on a scientifically sound basis, and that...
>
> No nationally accepted standard definitions exist for water quality parameters. The different organizations may collect data using identical or standard methods, but identify them by different names, or use the same names for data collected by different methods [1014].

Differences in field and laboratory methods are also major issues related to (the lack of) data comparability from media other than water: soil, sediments, tissues, and air.

In spite of numerous problems and complexities, knowledge is often power in decisions related to chemical contamination. It is therefore often helpful to be aware of a broad universe of conflicting results or conflicting expert opinions rather than having a portion of this information arbitrarily censored by someone else. Frequently one wants to know of the existence of information, even if one later decides not to use it for a particular application. Many would like to see a high percentage of the information available and decide for themselves what to throw out, partly because they don't want to seem uniformed or be caught by surprise by potentially important information. They are in a better position if they can say: "I knew about that data, assessed it based on the following quality assurance criteria, and decided not to use it for this application." This is especially true for users near the end of long decision processes, such as hazardous site cleanups, lengthy ecological risk assessments, or complex natural resource damage assessments.

For some categories, the editors found no information and inserted the phrase "no information found." This does not necessarily mean that no information exists; it simply means that during our efforts, the editors found none. For many topics, there is probably information "out there" that is not in the Encyclopedia. The more time that passes without encyclopedia updates (none are planned at the moment), the more true this statement will become. Still, the Encyclopedia is unique in that it contains broad ecotoxicology information from more sources than many other reference documents. No updates of this document are currently planned. However, it is hoped that most of the information in the encyclopedia will be useful for some time to come even without updates, just as one can still find information in the 1972 EPA Blue Book [12] that does not seem well summarized anywhere else.

Although the editors of this document have done their best in the limited time available to insure accuracy of quotes or summaries as being "what the original author said," the proposed interagency funding of a bigger project with more elaborate peer review and quality control steps never materialized.

> The bottom line: The editors hope users find this document useful, but don't expect or depend on perfection herein. Neither the U.S. Government nor the National Park Service make any claims that this document is free of mistakes.

The following is one chemical topic entry (one file among 118). Before utilizing this entry, the reader is strongly encouraged to read the README file (in this subdirectory) for an introduction, an explanation of how to use this document in general, an explanation of how to search for power key section headings, an explanation of the organization of each entry, an information quality discussion, a discussion of copyright issues, and a listing of other entries (other topics) covered.

See the separate file entitled REFERENC for the identity of numbered references in brackets.

HOW TO CITE THIS DOCUMENT: As mentioned above, for critical applications it is better to obtain and cite the original publication after first verifying various data quality assurance concerns. For more routine applications, this document may be cited as:

> **Irwin, R.J., M. VanMouwerik, L. Stevens, M.D. Seese**, and **W. Basham.** 1997. Environmental Contaminants Encyclopedia. National Park Service, Water Resources Division, Fort Collins, Colorado. Distributed within the Federal Government as an Electronic Document (Projected public availability

on the internet or NTIS: 1998).

Petroleum, General

Brief Introduction:

Br.Class: General Introduction and Classification Information:

NOTE: The intent of this entry is to provide an overview of petroleum and petroleum products in general; the discussion includes many oil and oil product topics.

Petroleum is a complex mixture of thousands of different hydrocarbons and related substances, all with different physical and chemical properties [770]. As such, determination of the fate and toxicity of a particular oil is a difficult task. Since it is very difficult to generalize about the toxicity of crude oil, oil products, and/or "total petroleum hydrocarbons," issues related to specific petroleum compounds have been organized in this document under separate headings for individual petroleum product. Entries in this product include petroleum products such as unleaded gasoline, and Fuel Oil Number 6. Oil component compound entries include the individual product constituents, such as: Benzene, Naphthalene, Chrysene, Phenanthrene, and various other PAH, alkyl PAH, and BTEX compounds.

Petroleum is a liquid mixture of organic compounds obtained at certain regions of the upper strata of the earth [746]. Petroleum was formed by a complex and incompletely understood series of chemical reactions from organic material laid down in previous geological eras [753]. The word petroleum, derived from the Latin petra and oleum, means literally "rock oil" and refers to hydrocarbons that occur widely in the sedimentary rocks of the Earth's crust in the form of gases, liquids, semisolids, or solids [505].

Crude oil is rarely used in the form produced at the well, but is converted in refineries into a wide range of products, such as gasoline, kerosene, diesel fuel, jet fuel, domestic and industrial fuel oils, together with petrochemical feedstocks such as ethylene, propylene, the butenes, butadiene, and isoprene [753]. Petroleum is refined; that is, separated into useful products. Refining consists of essentially dividing the petroleum into fractions of different boiling ranges by distillation. Special treatment may be utilized during the refining process to remove undesirable components of petroleum [746]. The fractions themselves are often further distilled to produce the desired commercial product [661]. A variety of additives may be incorporated into some of the refined products to adjust the octane ratings or improve engine performance characteristics [746]. See also: Crude Oil entry.

The lightest hydrocarbons are gases at room temperature, and are collected and used as heating gas mixtures and in the petrochemical industry [661].

The next lightest hydrocarbons occur in the C4 to C9 range (also known as the light and heavy naphtha fraction), and are used in gasoline formulation [661]. Gasoline contains alkanes C6 to C10, cycloalkanes, alkenes, benzene, and lower molecular weight alkylbenzenes (toluene, xylenes). The branched alkanes make better gasoline than their straight chain isomers because they have better antiknock ratings [746].

Vapors condensing in the middle ranges or "middle distillates" are characteristic of kerosene hydrocarbons. These hydrocarbons are used for heavier fuels, diesel and jet fuels, and a variety of commercial products. These fuels contain paraffins (alkanes), cycloparaffins (cycloalkanes), aromatics, and olefins from approximately C9 to C20. Aromatic compounds of concern include alkylbenzenes, toluene, naphthalenes, and polyaromatic hydrocarbons (PAHs) [661].

The heaviest molecular weight compounds that do not vaporize at all are asphalts or paraffins, depending on the source of the crude. The highest boiling fractions are heavy, high molecular weight hydrocarbons suitable for lubricants and heating oils [661]. Lubricants may contain hydrocarbons ranging from C18 to C25. Paraffin wax and petroleum jelly typically contain C28 to C38 hydrocarbons. Other petroleum products include a wide variety of industrial solvents and asphaltenes [746].

Refined oils also may have a number of additives such as gelling inhibitors that are added to diesel fuels during cold weather. Certain additives may be of special concern in an injury assessment, either because they are toxic themselves or because they significantly change the behavior of the oil [771]. See the Forms section below for details on petroleum fractions and individual products.

Br.Haz: General Hazard/Toxicity Summary:

An oil product is a complex mixture of organic chemicals and contains within it less persistent and more persistent fractions. The range between these two extremes is greatest for crude oils [791]. Since petroleum is such a complex mixture of thousands of substances with different physical and chemical properties [770], summarizing the toxicity or general hazard of petroleum in general or even a particular oil is a difficult task.

While oil, as a mixture of hydrocarbons, is at least theoretically biodegradable, large-scale spills can overwhelm the ability of the ecosystem to break the oil down [505]. The toxicological implications from petroleum occur primarily from exposure to or biological metabolism of aromatic structures [770,773]. These implications change as an oil spill ages.

Some studies have indicated that pure naphthalene and alkylnaphthalenes are from 3 to 10 times more toxic to test animals than are benzene and alkylbenzene [770]. Because of the low water-solubility of tricyclic and polycyclic aromatic hydrocarbons (that is, those aromatic hydrocarbons heavier than naphthalene), these compounds are generally present at very low concentrations in the water soluble fraction of oil. Therefore, the results of this study and others conclude that the soluble aromatics of an oil (such as benzene, toluene, ethylbenzene, xylenes, and naphthalenes) produce the majority of its toxic effects in the environment [770,773].

Among PAHs, the toxicity of an oil is a function of its di- and tri-aromatic hydrocarbon content [770]. Like the single aromatic ring variations, including benzene, toluene, and the xylenes, all are "relatively" volatile compounds with "relatively" high water solubility.

> Note: many of these compounds are not particularly soluble in comparison with other chemicals in general, but are more soluble than many other heavier and more complex hydrocarbons.

Short-term (acute) hazards of lighter, more volatile and water soluble aromatic compounds (such as benzenes, toluene, and xylenes) include potential acute toxicity to aquatic life in the water column (especially in relatively confined areas) as well as potential inhalation hazards. However, the compounds which pass through the water column often tend to do so in small concentrations and/or for short periods of time, and fish and other pelagic or generally mobile species can often swim away to avoid impacts from spilled oil in "open waters." Most fish are mobile and probably avoid toxic concentrations of oil [774].

However, there are some potential effects of spilled oil on fish. The impacts to fish are primarily to the eggs and larvae, with limited effects on the adults. The sensitivity varies by species; pink salmon fry are affected by exposure to water-soluble fractions of crude oil, while pink salmon pink salmon eggs are very tolerant to benzene and water-soluble petroleum. The general effects are difficult to assess and quantitatively document due to the seasonal and natural variability of the species. Fish rapidly metabolize aromatic hydrocarbons due to their enzyme system [773]. See also: Crude Oil and Oil Spill entries.

At the initial stages of a release, when the naphthalene- and benzene-derived compounds are present at their highest concentrations, acute toxic effects are more common than later. These noncarcinogenic effects include subtle changes in detoxifying enzymes and liver damage [773].

Generally, the relative aquatic acute toxicity of an oil will be the result of the fractional toxicities of the different hydrocarbons present in the aqueous phase [770].

Long-term (chronic) potential hazards of lighter, more volatile and water soluble aromatic compounds include contamination of groundwater. Chronic effects of benzene, toluene, and xylene include changes in the liver and harmful effects on the kidneys, heart, lungs, and nervous system [609,764,765,767].

Except for short-term hazards from concentrated spills, BTEX compounds (benzene, toluene, ethyl benzene, and xylenes) have been more frequently associated with risk to humans than with risk to non-human species such as fish and wildlife. This is partly because only very small amounts are taken up by plants, fish, and birds and because this volatile compound tends to evaporate into the atmosphere rather than persisting in surface waters or soils [764]. However, volatiles such as this compound have can pose a drinking water hazard when they accumulate in ground water. See also, BTEX entry, and entries for benzene, toluene, ethyl benzene, and xylenes.

Both atmospheric and hydrospheric impacts must be assessed when considering toxic implications from a petroleum release containing significant quantities of these single-ring aromatic compounds.

The dibenzene ring structures, or naphthalene and its homologous series, are less acutely toxic than benzene but are more prevalent for a longer period during oil spills [773].

The toxicity of different crude oils and refined oils depends on not only the total concentration of hydrocarbons but also the hydrocarbon composition in the water soluble fraction (WSF) of an oil, water solubility, concentrations of individual components, and toxicity of the components [770]. The water soluble fractions prepared from different oils will vary in these parameters [770]. Water-soluble fractions (WSF) of refined oils (for example, No.2 fuel oil and Bunker C oil) are more toxic than water soluble fraction of crude oil to several species of fish (killifish and salmon) [774]. Compounds with either more rings or methyl substitutions are more toxic than less substituted compounds, but tend to be less water soluble and thus less plentiful in the water soluble fraction [774]. (See the Anderson et al. [770] for details on solubility, fate, and toxicity relationships).

One comprehensive study of oil product toxicity tests found that LC50 values that are from the same product class (classes include: Bunker, Crude, Lube oil, Diesel, Gasoline, Jet fuel) can vary over three orders of magnitude depending on the methods used in conducting the test [791].

In addition to large oil spills (such as the Ixtoco I, 1979; Exxon Valdez, 1989; and deliberate inputs during the Persian Gulf War, 1990), petroleum hydrocarbons are released into the aquatic environments from natural seeps as well as nonpoint source urban runoffs. Acute impacts from massive one-time spills are obvious and substantial. The impacts from small spills and chronic releases are the subject of much speculation and continued research. Clearly, these inputs of petroleum hydrocarbons have the potential for significant environmental impacts, but the effects of chronic low-level discharges can be minimized by the net assimilative capacities of many ecosystems, resulting in little detectable environmental harm [773].

Once the acutely toxic lighter compounds have been left the aquatic environment through volatilization or degradation, the main concern is chronic effects from heavier and more alkylated PAHs (see decision tree part of the laboratory section below, and see PAHs entry).

Bird species with water habitats are the species most commonly affected by oil spills and releases [773]. Oil itself breaks down the protective waxes and oils in the feathers and fur of birds and animals and disrupts the fine strand structure of the feathers resulting in a loss of heat retention and buoyancy and possible hypothermia and death [505,773]. Oiled birds often ingest petroleum while attempting to remove the petroleum from their feathers [773]. The effects of ingested petroleum include anemia, pneumonia, kidney, and liver damage, decreased growth, altered blood chemistry, and decreased egg production and viability [773]. Ingestion of the oil can also kill animals by interfering with their ability to digest food [505]. Chicks may be exposed to petroleum by ingesting food regurgitated by impacted adults [773].

Dynamics of the oil-in-water dispersion (OWD) are complex and have relevance related to potential toxicity or hazard. In comparing the toxicities to marine animals of oil-in-water dispersions prepared from different oils, not only the amount of oil added but also the concentrations of oil in the aqueous phase and the composition and dispersion-forming characteristics of the parent oil must be taken into consideration [770]. In comparing the potential impacts of spills of different oils on the marine biotic community, the amount of oil per unit water volume required to cause mortality is of greater importance than any other aspect of the oil's behavior [770]. For example, the magnitude and duration of oil effects to marine flora and fauna were not great following two large open water crude oil spills, namely the Torrey Canyon (1968) and the Santa Barbara (1971) incidents [770]. In contrast, the Tampico Maru (1965) and the West Falmouth (1970) spills, which involved much smaller spills of no. 2 fuel oil were reported to have been significantly more damaging to marine life [770]. Both of these incidents occurred in confined areas.

In the first spill, oil was held in a confined rocky area. Confinement of this toxic and dispersable oil in a relatively small body of water may have allowed aqueous hydrocarbon concentrations to rapidly reach toxic levels before volatilization and weathering could remove the more toxic aromatics [770]. In the second spill, the oil was incorporated into sediments in a shallow inlet. This situation might have resulted in slow leaching of soluble fractions from the sediments following the spill as well as the solubilization of other hydrocarbons by microbial activity [770].

Though most animals do not intentionally ingest petroleum, studies have shown that endangered sea turtles have ingested tar balls, apparently as a food source [773]. Marine mammals and pelagic species (those living in open seas rather than in water adjacent to land or inland) have similar routes of exposure: inhalation, surficial contact, and ingestion. The marine species include cetaceans, pinnipeds, and sea otters. Effects of petroleum on the pelagic species are varied [773].

The alkanes in gasoline and some other petroleum products are CNS depressants [855]. In fact, gasoline was once evaluated as an anesthetic agent [855]. However, sudden deaths, possibly as a result of irregular heartbeats, have been attributed to those inhaling vapors of hydrocarbons such as those in gasoline [855].

See also: crude oil entry.

Br.Car: Brief Summary of Carcinogenicity/Cancer Information:

Several compounds in petroleum products are carcinogenic. Certain carcinogenic effects have been associated with benzene and possibly naphthalene in laboratory animal studies [609,766,767]. Benzene is carcinogenic to humans [747].

The larger and heavier aromatic structures (with four to five aromatic rings), which are the more persistent in the environment, have the potential for chronic toxicological effects [773]. Since these compounds are nonvolatile and are relatively insoluble in water, their main routes of exposure are through ingestion and epidermal contact. Some of the compounds in this classification are considered possible human carcinogens; these include benzo(a and e)pyrene, benzo(a)anthracene, benzo(b,j,and k)fluorene, benzo(ghi)perylene, chrysene, dibenzo(ah)anthracene, and pyrene [773]. See individual PAH entries.

The debates on which PAHs and alkyl PAHs in complex mixtures such as this product to classify as carcinogens, and the details of exactly how to perform both ecological and human risk assessments on the complex mixtures of PAHs typically found at contaminated sites, are likely to continue. There are some clearly wrong ways to go about it, but defining clearly right ways is more difficult. PAHs usually occur in complex mixtures rather than alone. Perhaps the most unambiguous thing that can be said about complex PAH mixtures is that such mixtures are often carcinogenic and possibly phototoxic. One way to approach site specific risk assessments would be to collect the complex mixture of PAHs and other lipophilic contaminants in a semipermeable membrane device (SPMD, also known as a fat bag) [894,895,896], retrieve the contaminant mixture from the SPMD, then test the mixture for carcinogenicity, toxicity, and phototoxicity (James Huckins, National Biological Service, and Roy Irwin, National Park Service, personal communication, 1996).

See also: PAHs as a group entry.

Br.Dev: Brief Summary of Developmental, Reproductive, Endocrine, and Genotoxicity Information:

Commonly reported effects of petroleum and individual PAHs on living organisms are impaired immune systems for mammals and altered endocrine functions for fish and birds. Commonly reported effects of petroleum and individual PAHs also include impaired reproduction and reduced growth and development for plants, invertebrates, fish, reptiles, amphibians, and birds [835].

Effects of naphthalene- and benzene-derived compounds include interference with reproductive behavior [773].

Endocrine effects: Gulls, storm petrels, and guillemots had elevated corticosterone, thyroxin, and increased size of adrenal glands after ingestion of a single dose of 0.1% (of diet) crude oil [713]. Ingested doses of 0.5-3% crude oil over periods of 7-10 days, however, reduced corticosterone concentrations [713].

The results are mixed, but some immunological, reproductive, fetotoxic, and genotoxic effects have been associated with a few of the compounds found in crude oil [609,764,765,766,777] (see entries on individual compounds for more details).

Exposure to oil by birds also has been shown to lead to changes in behavior which ultimately cause reduced reproductive success [713]. Such effects include cessation or delay of egg laying, increased nesting phenology, nest abandonment, reduced feeding of young, mate switching, interruption of courtship behavior, egg rejection, parental rejection of chicks, impairment of incubation behavior, and reduced nest attentiveness [713].

Field studies have shown that external and internal exposures of oil to free-ranging wild birds causes several changes in behavior that lead to reduced reproductive success. Following application of 1 mL of weathered crude oil to breast feathers of nesting Cassin auklets (Ptychoramphus aleutica), a high proportion of them abandoned their nesting colony. Wedge-tailed shearwaters (Puffinus pacificus) also showed a high rate of colony abandonment following application of 0.1-2.0 mL of weathered crude oil to their breast feathers [713]. External exposure on one member of a pair of incubating Leach's storm petrels to 0.50 mL Prudhoe Bay crude oil caused rejection of 38% of the eggs, whereas none of the eggs of control pairs were rejected. Oiling of chicks by the externally treated adult also caused rejection of the chicks. (This reaction to oiled eggs and chicks may be limited to the procellariids, since species such as gulls [with reduced olfactory development] exhibit normal parental responses) [713].

Wedge-tailed shearwaters orally exposed to Santa Barbara crude oil had a laying and incubation frequency significantly lower than controls [713].

Oil concentrations as low as 1 uL/egg (1.3% of the surface of a mallard egg) are toxic. This appears to be a function of the aromatic component of crude oil rather than of impaired gas exchange [713].

Applications of naturally weathered North Slope crude oil to developing mallard eggs showed it to be less toxic than unweathered North Slope crude oil. Doses covering up to one-third of the shell area (92 mg) did not affect developing embryos. Eggs treated with the control material, petrolatum, were adversely affected by applications covering approximately one-sixth of the eggshell (24 mg), suggesting inhibition of gas exchange [789; Reprinted with permission from Environmental Toxicology and Chemistry, Vol.14(11), W.A. Stubblefield, G.A. Hancock, H.H. Prince, and R.K. Ringer, "Effects of Naturally Weathered Exxon Valdez Crude Oil on Mallard Reproduction." Copyright 1995 SETAC].

In general, gull eggs are most sensitive to external oiling when they are less than 10 days old. Beyond 10 days, oil doses as high as 100 uL crude oil/egg have no effect on hatchability of the eggs [713].

Mallards that had ingested 5% crude oil had delayed laying, decreased oviposition and decreased shell thickness [713]. Also, male mallards fed a 3% South Louisiana crude oil diet were less able to fertilize eggs successfully [713].

Mallards fed 0, 200, and 20,000 mg of naturally weathered North Slope crude oil (WEVC) per kg diet (food) exhibited no significant difference in reproductive or hatchling parameters. Significant decreases in mean serum phosphorous, serum total protein, albumin, bilirubin, and calcium concentrations were observed in high-dose-group females; no differences were noted among males. Eggshell strength and thickness in the high-dose group were significantly reduced [789; Reprinted with permission from Environmental Toxicology and Chemistry, Vol.14(11), W.A. Stubblefield, G.A. Hancock, H.H. Prince, and R.K. Ringer, "Effects of Naturally Weathered Exxon Valdez Crude Oil on Mallard Reproduction." Copyright 1995 SETAC].

The hatching success of herring and black-backed gull eggs decreased in response of 10 uL of crude or weathered crude oil applied externally to eggshells. This effect is most pronounced when eggs were exposed within 4-9 days of being laid. Although weathered oil was less toxic than fresh crude oil in laboratory exposures, the toxic effects of crude oil were the same if the crude oil applied to birds in the field was "fresh" or weathered.

Heron, tern and brown pelican eggs had reduced hatchability when oiled either directly or via the adult's feathers. Wedgetailed shearwaters fed 0.03-0.5 % weathered crude oil 30 days prior to egg laying exhibited decreased egg laying and breeding success, decreased survival of chicks, nest abandonment and less parental attentiveness [713].

The toxicity of crude oil may be affected by factors such as "weathering" time or the addition of oil dispersants. Weathered and "fresh" crude oil may have different toxicities, depending on oil type and weathering time. Prudhoe Bay crude oil (1 uL/egg) was less embryotoxic after 2-3 weeks of weathering, but hatchability was still significantly less than controls. Oil and dispersant mixtures appear to be equally as toxic as crude oil alone [713].

Following the Santa Barbara oil spill, an apparently large number of premature births were observed in sea lions [713].

See also: Tis.misc section below as well as naphthalene and benzene entries.

See also: Crude Oil entry and PAHs as a group entry.

Br.Fate: Brief Summary of Key Bioconcentration, Fate, Transport, Persistence, Pathway, and Chemical/Physical Information:

A comprehensive review of the physicochemical properties of several oils and oil products found their persistence in the aquatic environment to rank as follows (from most persistent to least persistent): Residual asphaltenes > Heavy crude oil > Medium crude oil > Fuel oil #6 > Light crude oil > Lube oils > Fuel oil #2 > Jet fuel > Gasoline [791].

The primary processes determining the fate of crude oils and oil products after a spill are spreading, evaporation, emulsification, dispersion, dissolution, reaction, and sedimentation. These processes are influenced by the spill characteristics, environmental conditions, and physicochemical properties of the spilled material [791].

Alkanes of various types of crude oils and various petroleum products were biodegraded faster than the "unresolved fractions" [975]. Different types of crude oils and products biodegraded at different rates in the same environments [975].

An oil product is a complex mixture of organic chemicals and contains within it less persistent and more persistent fractions. The range between these two extremes is greatest for crude oils [791]. Since the many different substances in petroleum have different physical and chemical properties [770], summarizing the fate of petroleum in general (or even a particular oil) is very difficult. Solubility-fate relationships must be considered.

Petroleum is naturally weathered according to its physical and chemical properties, but during this process living species within the local environment may be affected via one or more routes of exposure, including ingestion, inhalation, dermal contact, and, to a much lesser extent, bioconcentration through the food chain [773].

Large deposits of crude oil have been found in vastly different parts of the world and their chemical composition varies greatly. Consequently, no single composition of petroleum can be defined [753]. Thus petroleum-derived inputs to the environment vary considerably in composition; it is essential to bear this in mind when quantifying them in general terms such as an "oil" or the "total petroleum hydrocarbons" measurement [461]. The complexity of the inputs is matched by the range of properties of the components and the physical, chemical and biochemical processes that contribute to the distributive pathways and determine the fate of the inputs [461].

The composition of petroleum varies widely, depending on the area from which it is obtained. The principal components of the very complex mixtures of petroleum are hydrocarbons, which may be paraffinic, alicyclic, or aromatic in varying concentrations [746].

The relative proportions of hazardous compound constituents present in petroleum-based oil contamination is typically quite variable. The farther one progresses from lighter towards heavier oils (the general progression from light towards heavy is the following: Diesel, No. 2 Fuel Oil, Light Crudes, Medium Crude Oils, Heavy Crudes, No. 6 Fuel Oil, etc.) the greater the percentage of PAHs and other semi-volatiles (many of which are not so immediately toxic as the volatiles but which can result in long-term/chronic impacts). These heavier oils thus need to be analyzed for the semi volatile compounds which typically pose the greatest long-term risk, PAHs and alkylated PAHs.

The elemental compositions of petroleum vary greatly from crude oil to crude oil. Most compounds in petroleum (usually more than 75%) are types of hydrocarbons [461]. Most of the chemical components in petroleum are made up of five main elements [773]:

ELEMENT	RANGE (weight %)
Carbon	82-87
Hydrogen	11-15
Sulfur	0-8
Nitrogen	0-1
Oxygen	0.0-0.5

The elements are combined to form a complex mixture of organic compounds that range in molecular weight from 16 (methane; CH_4) to several thousand [753]. A wide range of metals are also found in trace amounts in crude oils [773]. All metals through the atomic number 42 (molybdenum) have been found, with the exception of rubidium and niobium; a few heavier elements also have been detected. Nickel and vanadium are the most important, because they are present in all crudes, usually at concentrations far higher than any other metal [753]. (See Chem.Detail section below for more details on the compounds in petroleum).

See also: Crude Oil and Oil Spills entries and PAHs as a group entry.

Synonyms/Substance Identification:

None found.

Associated Chemicals or Topics (Includes Transformation Products):

NOTE: Petroleum, both crude oil and refined products, is a very broad topic. It has been divided up into several different entries (although there is still some overlap on certain topics). Readers interested in Petroleum, General should also be aware of the following combination entries:

Crude Oil
Oil, Spills

See also entries on individual compounds in oil products:

PAHs as a group (Polycyclic Aromatic Hydrocarbons)
Benzene
Naphthalene
Phenanthrene
And Other PAHs, Alkyl PAHs,and BTEX compounds.

See Crude Oil entry for a more complete list of compounds in Petroleum.

See also entries on individual petroleum products:

Gasoline, Unleaded
Fuel Oil Number 6
Jet Fuel Number 4
etc.

For a list of 89 hazardous compounds suspected to be present in refinery wastes, see [815].

Water Data Interpretation, Concentrations and Toxicity (All Water Data Subsections Start with "W."):

W.Low (Water Concentrations Considered Low):

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound entries for summaries of information on individual components of this mixture.

W.High (Water Concentrations Considered High):

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound entries for summaries of information on individual components of this mixture.

W.Typical (Water Concentrations Considered Typical):

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound entries for summaries of information on individual components of this mixture.

W.Concern Levels, Water Quality Criteria, LC50 Values, Water Quality Standards, Screening Levels, Dose/Response Data, and Other Water Benchmarks:

W.General (General Water Quality Standards, Criteria, and Benchmarks Related to Protection of Aquatic Biota in General; Includes Water Concentrations Versus Mixed or General Aquatic Biota):

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound entries for summaries of information on individual components of this mixture.

W.Plants (Water Concentrations vs. Plants):

No information found; see Chem.Detail section for compounds in this product, then see applicable

individual compound entries for summaries of information on individual components of this mixture.

W.Invertebrates (Water Concentrations vs. Invertebrates):

The following tables are given to provide the reader with an idea of relative acute toxicity of various crude oils and refined products, by ranking the acute toxicity of the water soluble fraction of several oils to Artemia and Daphnia [684]. These fluorescence tests were older Canadian methods using only the product indicated and would be only roughly comparable to other fluorescence values. Fluorescence methods are not particularly desirable when unknown or mixed oil products are of concern (ranges in parentheses) [684]. The following tables indicate that light products, such as gasoline, have more potential for acute (short-term) toxicity than heavier oils; however, these findings do not relate to overall hazard since some of the heavier products contain heavy PAHs that would contribute to chronic (long-term) hazards including carcinogenicity. A product like used motor oil may also contain heavy metals that would add to its chronic toxicity potential [684]:

Table 1: Ranking of acute toxicity of water soluble fractions (WSF) of crude and refined oils to Artemia based on concentrations as % of water soluble fraction. Listed by rank. (Rank 1 = most toxic) [684]:
Note: Table reproduced with permission of author K.G Doe:

Editor's Comment: WSF values are of interest in looking at relative toxicity of different substances in the lab, but concentrations of total product mixtures (as opposed to individual compounds) or most WSF values are virtually impossible to replicate at field spill sites (Roy Irwin, National Park Service, Personal Communication, 1996).

The term "LC", or "lethal concentration" is basically inappropriate for oil products since there is no single concentration of any one compound within toxicity test solutions that are derived from oil products. The term "LC50" as applied to oil products is quite misleading to a reviewer of oil product toxicity data since one immediately assumes that the number associated with the concept (like, an LC50 of 1000 mg/L) represents the dissolved fraction which was the "effective concentration" [791].

RANK	4-HOUR EC50	48-HOUR EC50	48-HOUR LC50
1	Unleaded gasoline	Auto lube (new)	Leaded gasoline
2	Leaded gasoline	Unleaded gasoline	Unleaded gasoline
3	Sable Island Condensate(a)	Leaded gasoline	Furnace Fuel, Sable Island Condensate(a)
4	Venture Condensate(a), Furnace Fuel	Sable Island Condensate	---
5	---	Furnace Fuel	Venture Condensate
6	Western Sweet	Venture Condensate	Auto Lube (New)
7	Venezuelan BCF-22	Synthetic	Synthetic
8	Norman Wells	Diesel	Diesel
9	Transmountain	Venezuelan BCF-22	Venezuelan BCF-22
10	Diesel	Prudhoe Bay	Prudhoe Bay
11	Synthetic	Western Sweet, Hibernia	Norman Wells
12	Atkinson, Bent Horn, Amauligak, Lago Medio, Tarsuit, Bunker C-Light, Auto Lube (used), Auto Lube (new), Heavy Marine Lube, Hibernia, Prudhoe Bay	---	Hibernia
13	---	Bent Horn	Western Sweet
14	---	Transmountain, Norman Wells	Bent Horn
15	---	---	Lago Medio
16	---	Lago Medio	Transmountain, Atkinson, Amauligak, Tarsuit, Bunker C - Light, Auto Lube (used), Heavy Marine Lube
17	---	Amauligak	---
18	---	Heavy Marine Lube, Bunker C - Light, Atkinson, Auto Lube (used), Tarsuit	---

a = Condensate: a light hydrocarbon mixture produced as a liquid product in a gas-recycling plant through expansion and cooling of gas [684].

Table 2: Ranking of acute toxicity of water soluble fractions (WSF) of crude and refined oils to Daphnia magna based on concentrations as % of water soluble fraction. Listed by rank. (Rank 1 = most toxic) [684]:

RANK	4-HOUR EC50	48-HOUR EC50	48-HOUR LC50
1	Unleaded gasoline	Unleaded gasoline	Furnace fuel
2	Leaded gasoline	Sable Island Condensate, Furnace fuel	Leaded gasoline
3	Sable Island Condensate(a)	---	Unleaded gasoline
4	Venture Condensate(a)	Leaded gas, Venture Condensate	Diesel
5	Western Sweet	---	Sable Island Condensate
6	Synthetic	Western Sweet	Auto Lube (new)
7	Hibernia, Prudhoe Bay, Transmountain	Diesel, Synthetic	Auto Lube (used)
8	---	---	Bent Horn
9	---	Hibernia	Venture Condensate
10	Furnace fuel	Prudhoe Bay	Synthetic
11	Norman Wells	Transmountain, Norman Wells	Western Sweet
12	Venezuelan BCF-22	---	Transmountain
13	Diesel	Bent Horn, Venezuelan BCF-22	Norman Wells
14	Atkinson	---	Hibernia
15	Bent Horn, Amauligak	Amauligak	Prudhoe Bay
16	---	Auto Lube (New)	Amauligak
17	Lago Medio	Auto Lube (used)	Venezuelan BCF-22
18	Tarsuit	Lago Medio, Atkinson	Tarsuit
19	Bunker C, Heavy Marine Lube, Auto Lube (New), Auto Lube (used)	---	Heavy Marine Lube, Atkinson, Lago Medio, Bunker C - Light
20	---	Heavy Marine Lube	---
21	---	Tarsuit	---
22	---	Bunker C - Light	---

a = Condensate: a light hydrocarbon mixture produced as a liquid product in a gas-recycling plant through expansion and cooling of gas [684].

NOTES regarding above tables: In general, the water soluble fraction of the gasolines, condensates, furnace fuel and diesel oil turned out to be the most acutely toxic, while the water soluble fraction of bunker C - light, heavy marine lube and some of the crude oils such as Tarsuit, Lago Medio, Atkinson, Bent Horn and Amauligak were the least acutely toxic to both species of test animals [684].

> Editor's Comment: WSF values are of interest in looking at relative toxicity of different substances in the lab, but concentrations of total product mixtures (as opposed to individual

compounds) or most WSF values are virtually impossible to replicate at field spill sites (Roy Irwin, National Park Service, Personal Communication, 1996).

W.Fish (Water Concentrations vs. Fish):

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound entries for summaries of information on individual components of this mixture.

W.Wildlife (Water Concentrations vs. Wildlife or Domestic Animals):

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound entries for summaries of information on individual components of this mixture.

W.Human (Drinking Water and Other Human Concern Levels):

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound entries for summaries of information on individual components of this mixture.

W.Misc. (Other Non-concentration Water Information):

The water soluble fractions and oil-in-water dispersions of the no. 2 fuel oil and bunker C were considerably more toxic to the 6 test species than were those of the crude oils [770]. The test species can be ranked according to increasing sensitivity to oil as follows: Cyprinodon variegatus, Menidia beryllina, and Fundulus similus (all fish); and Penaeus aztecus postlarvae, Palaemonetes pugio and Mysidopsis almyra (all crustaceans) [770].

Misc. Abstract:

TI: TITLE
Petroleum hydrocarbons in urban runoff from a commercial land use area.
AU: AUTHOR
Hoffman EJ; Latimer JS; Mills GL; Quinn JG
SO: SOURCE
J. WATER POLLUT. CONTROL FED.; vol. 54, no. 11, pp. 1517-1524; 1982
AB: ABSTRACT
Storm runoff effluent from a shopping mall parking

lot was monitored for petroleum hydrocarbons and suspended solids during six storms over a 10-month period. The load of suspended solids (SS) and petroleum hydrocarbons in urban runoff varies widely during the progress of a storm. The highest concentrations and loads of SS and hydrocarbons in each storm are associated with the first major peak in flow rate, the first flush. Upon integration of the loads over time, a total hydrocarbon and SS load was calculated for each storm. The loading relationship was essentially linear with total rainfall, implying that the supply of solids available for incorporation in the runoff had not been exhausted in storms up to 4.06 cm (1.60 in.). There are indications, however, that the supply of hydrocarbons may be approaching a limit in storms greater than 4.82 cm (1.90 in.) of rainfall.

Sediment Data Interpretation, Concentrations and Toxicity (All Sediment Data Subsections Start with "Sed."):

Sed.Low (Sediment Concentrations Considered Low):

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound entries for summaries of information on individual components of this mixture.

Sed.High (Sediment Concentrations Considered High):

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound entries for summaries of information on individual components of this mixture.

Sed.Typical (Sediment Concentrations Considered Typical):

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound entries for summaries of information on individual components of this mixture.

Sed.Concern Levels, Sediment Quality Criteria, LC50 Values, Sediment Quality Standards, Screening Levels, Dose/Response Data and Other Sediment Benchmarks:

Sed.General (General Sediment Quality Standards, Criteria, and Benchmarks Related to Protection of Aquatic Biota in General; Includes Sediment Concentrations Versus Mixed or General Aquatic Biota):

No information found; see Chem.Detail section for compounds in this product, then see applicable

individual compound entries for summaries of information on individual components of this mixture.

Sed.Plants (Sediment Concentrations vs. Plants):

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound entries for summaries of information on individual components of this mixture.

Sed.Invertebrates (Sediment Concentrations vs. Invertebrates):

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound entries for summaries of information on individual components of this mixture.

Sed.Fish (Sediment Concentrations vs. Fish):

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound entries for summaries of information on individual components of this mixture.

Sed.Wildlife (Sediment Concentrations vs. Wildlife or Domestic Animals):

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound entries for summaries of information on individual components of this mixture.

Sed.Human (Sediment Concentrations vs. Human):

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound entries for summaries of information on individual components of this mixture.

Sed.Misc. (Other Non-concentration Sediment Information):

Some of the literature on sediment contamination by petroleum hydrocarbons was summarized in Olsen's 1984 annotated bibliography of the effects of contaminated sediments on fish and wildlife [449].

See also: Sed.Misc. section of the Crude Oil entry, for several case study examples of spills of crude oil which impacted sediments.

Misc. Abstract:

Hydrocarbon Concentrations in Water and Sediments from UK Marine Waters, Determined by Fluorescence Spectroscopy. Law RJ. MAR. POLLUT. BULL.; vol. 12, no. 5, pp. 153-157; 1981:

Between January 1978 and September 1979 samples of subsurface (1m) water and surface sediment were collected from sites in the North Sea, English Channel, Irish Sea and a number of estuarine areas. These have been analyzed by fluorescence spectroscopy (UVF) in order to provide information on the levels of hydrocarbons generally present in UK marine waters. Total hydrocarbon concentration (THCs) of water samples ranged from 1.1-74 mu g 1. super(-1) Ekofisk crude oil equivalents, all values greater than 3.5 mu g 1. super(-1) occurring inshore. In offshore areas the mean THCs were: 1.3 mu g 1. super(-1) in the northern North Sea, 1.5 mu g 1. super(-1)in the western Channel, 2.5 mu 1. super(-1) in the eastern Channel and southern North Sea, and 2.6 mu g 1. super(-1) in the Irish Sea. THCs of sediment samples ranged from 0.27-340 ug/g dry weight Ekofisk crude oil equivalents, the highest concentration being in the Queen's Channel, the main entrance to the River Mersey.

Soil Data Interpretation, Concentrations and Toxicity (All Soil Data Subsections Start with "Soil."):

Soil.Low (Soil Concentrations Considered Low):

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound entries for summaries of information on individual components of this mixture.

Soil.High (Soil Concentrations Considered High):

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound entries for summaries of information on individual components of this mixture.

Soil.Typical (Soil Concentrations Considered Typical):

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound entries for summaries of information on individual components of this mixture.

Soil.Concern Levels, Soil Quality Criteria, LC50 Values, Soil Quality Standards, Screening Levels, Dose/Response Data and Other Soil Benchmarks:

Soil.General (General Soil Quality Standards, Criteria, and Benchmarks Related to Protection of Soil-dwelling Biota in General; Includes Soil Concentrations Versus Mixed or General Soil-dwelling Biota):

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound entries for summaries of information on individual components of this mixture.

Soil.Plants (Soil Concentrations vs. Plants):

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound entries for summaries of information on individual components of this mixture.

Soil.Invertebrates (Soil Concentrations vs. Invertebrates):

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound entries for summaries of information on individual components of this mixture.

Soil.Wildlife (Soil Concentrations vs. Wildlife or Domestic Animals):

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound entries for summaries of information on individual components of this mixture.

Soil.Human (Soil Concentrations vs. Human):

No information found on this complex and variable mixture. See Chem.Detail section for chemicals found in this product, then look up information on each hazardous compound. Some individual compounds found in petroleum products have low-concentration human health benchmarks for soil (see individual entries).

Soil.Misc. (Other Non-concentration Soil Information):

Phytoremediation: To address the broader problem of oil contamination, Exxon and other companies (Science News: 8/5/95, p. 84) find that plants stimulate bacteria that break down hydrocarbons [1023]. However, researchers must then contend with herbicides that companies sometimes use on contaminated spots to prevent fires, says Evelyn Drake of Exxon in Annandale, N.J [1023].

The trend of thinking towards natural attenuation was given a boost by a Lawrence Livermore National Laboratory (LLNL) report entitled "Recommendations to Improve the Cleanup Process for California's Leaking Underground Fuel Tanks;" which stressed the use of passive bioremediation for petroleum product contaminated soils, whenever possible, based on the relatively low number of cases where drinking water was impacted [969]. EPA has pointed out some limitations of the LLNL report, including the lack of adequate consideration of PAHs and additives such as MTBE, as well limited consideration of (non-human) exposure pathways and various geologic conditions [969].

See also: Soil.Misc. section of the Crude Oil entry, for several case study examples of spills of crude oil which impacted soils.

No other information found; see Chem.Detail section for compounds in this product, then see applicable individual compound entries for summaries of information on individual components of this mixture.

Tissue and Food Concentrations (All Tissue Data Interpretation Subsections Start with "Tis."):

Tis.Plants:

A) As Food: Concentrations or Doses of Concern to Living Things Which Eat Plants:

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound entries for summaries of information on individual components of this mixture.

B) Body Burden Residues in Plants: Typical, Elevated, or of Concern Related to the Well-being of the Organism Itself:

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound entries for summaries of information on individual components of this mixture.

Tis.Invertebrates:

A) As Food: Concentrations or Doses of Concern to Living Things Which Eat Invertebrates:

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound entries for summaries of information on individual components of this mixture.

B) Concentrations or Doses of Concern in Food Items Eaten by Invertebrates:

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound entries for summaries of information on individual components of this mixture.

C) Body Burden Residues in Invertebrates: Typical, Elevated, or of Concern Related to the Well-being of the Organism Itself:

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound entries for summaries of information on individual components of this mixture.

Tis.Fish:

A) As Food: Concentrations or Doses of Concern to Living Things Which Eat Fish (Includes FDA Action Levels for Fish and Similar Benchmark Levels From Other Countries):

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound entries for summaries of information on individual components of this mixture.

B) Concentrations or Doses of Concern in Food Items Eaten by Fish:

No information found; see Chem.Detail section for compounds in this product, then see applicable

individual compound entries for summaries of information on individual components of this mixture.

C) Body Burden Residues in Fish: Typical, Elevated, or of Concern Related to the Well-being of the Organism Itself:

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound entries for summaries of information on individual components of this mixture.

Tis.Wildlife: Terrestrial and Aquatic Wildlife, Domestic Animals and all Birds Whether Aquatic or not:

A) As Food: Concentrations or Doses of Concern to Living Things Which Eat Wildlife, Domestic Animals, or Birds:

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound entries for summaries of information on individual components of this mixture.

B) Concentrations or Doses of Concern in Food Items Eaten by Wildlife, Birds, or Domestic Animals (Includes LD50 Values Which do not Fit Well into Other Categories, Includes Oral Doses Administered in Laboratory Experiments):

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound entries for summaries of information on individual components of this mixture.

C) Body Burden Residues in Wildlife, Birds, or Domestic Animals: Typical, Elevated, or of Concern Related to the Well-being of the Organism Itself:

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound entries for summaries of information on individual components of this mixture.

Tis.Human:

A) Typical Concentrations in Human Food Survey Items:

No information found; see Chem.Detail section for compounds in this product, then see applicable

individual compound entries for summaries of information on individual components of this mixture.

B) Concentrations or Doses of Concern in Food Items Eaten by Humans (Includes Allowable Tolerances in Human Food, FDA, State and Standards of Other Countries):

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound entries for summaries of information on individual components of this mixture.

C) Body Burden Residues in Humans: Typical, Elevated, or of Concern Related to the Well-being of Humans:

No information found; see Chem.Detail section for compounds in this product, then see applicable individual compound entries for summaries of information on individual components of this mixture.

Tis.Misc. (Other Tissue Information):

Factors to consider when interpreting residues of petroleum hydrocarbons in wildlife tissues were summarized by Hall and Coon in 1988 [128].

In birds, weathering may affect the MFO activity as birds fed 0.5 g fresh Kuwait crude oil/day had elevated MFO activity while weathered oil had no effect on MFO activity. MFO activity in young can also increase when the parents are exposed to oil. Chicks were found to have elevated MFO when the adults were fed South Louisiana crude oil prior to laying eggs [713].

In gray seals, MFO activity in the liver is less in young than in adults, thus young seals may be relatively more vulnerable to oil than adults [713].

In one study, ringed seals were fed C(14)-naphthalene-marked crude oil in fish at a rate of 5 mL/day, for up to four days. Aryl hydrocarbon hydroxylase (AHH) was induced in liver and particularly kidney tissue where activity increased three-fold. The seals appear to have a high MFO detoxifying capacity and high renal clearance of accumulated oils [713].

Misc. Abstract from Compact Cambridge CD-ROM: Life Sciences 1982 - 1985:

TI: TITLE

Ingestion of Petroleum by Breeding Mallard Ducks: Some Effects on Neonatal Progeny.
AU: AUTHOR
Gorsline J; Holmes WN
SO: SOURCE
ARCH. ENVIRON. CONTAM. TOXICOL.; vol. 11, no. 2, pp. 147-153; 1982
AB: ABSTRACT
Breeding female mallard ducks consuming petroleum-contaminated food show significant induced increases in the naphthalene-metabolizing properties of microsomes prepared from their livers. When incubated, fertilized eggs laid by the females consuming South Louisiana crude oil yielded ducklings that upon emergence possessed high levels of naphthalene-metabolizing activity associated with hepatic microsomes. In contrast, ducklings derived from eggs laid by females consuming food contaminated with Prudhoe Bay crude oil showed no increases in total hepatic naphthalene-metabolizing activity and only those ducklings hatched from eggs laid by females consuming food contaminated with 3% crude oil showed significantly induced levels of specific naphthalene-metabolizing activity at hatching.

Note: The following case study highlights were copied from NOAA Restoration Guidance Document [622] with permission of Eli Reinharz of the NOAA DART Team.

Case Study:

Approximately 30,000 barrels of crude oil were released as the result of a well blow-out in January 1983 at a Louisiana cypress swamp. Comparisons of control and affected sites one year after the discharge revealed that oil effects on vegetation were species-specific. Areas with high shading by mature trees had little or no understory and few effects of the oil were observed on the dominant woody vegetation. Perennial plants were returning to the sunlit areas. In contrast, oiled areas formerly covered with floating vascular vegetation were devoid of any vegetation. Similar effects were noted in a freshwater swamp discharge in Nigeria [622].

Case Study:

In July 1975, the tanker Garbis discharged 1,500 to 3,000 barrels of crude oil-water emulsion into the western edge of the Florida Current. Prevailing easterly winds drove the oil ashore along a 30 mile stretch of the Florida Keys from Boca Chica to

Little Pine Key [622].

Red mangroves with >50% of their leaves oiled were killed, and red mangrove propagules with >50% oil coverage died within 2 months. Black mangroves with >50% of pneumatophores oiled were killed. Thin oil coating left chemical burn scars, and germination of oiled seeds decreased by 30%. Batis and Salicornia spp. died when oil coated their leaves, stems or substrate. Lightly oiled mangrove areas appeared to exhibit normal growth 6 months after the discharge. However, young and dwarf mangroves apparently suffered permanent injury, indicated by deformed leaves, roots and stems. The discharge site was visited in May 1980, 5 years after the discharge, and it was reported that the oil had weathered significantly [622].

Case Study:

On April 27, 1986 a storage tank at the Texaco Refineria Panama on the Caribbean coast of Panama ruptured, releasing ~240,000 barrels of medium weight crude oil into Cativa Bay. On May 4, a storm broke the containment booms, releasing ~150,000 barrels of oil into the Atlantic Ocean. Winds, tides and rain runoff washed part of the oil onto exposed shorelines. Some of the oil was carried back into Cativa Bay, and some was washed into adjacent embayments with mangrove shorelines. By May 15, oil had spread along the coast and washed across fringing reefs and into mangrove forests and small estuaries. A total of 82 km of coastline (=11 linear km) was oiled to varying degrees. Approximately 75 ha of mangroves, primarily the red mangrove Rhizophora mangle, were killed by the discharge [622].

Prespill data on organismal distribution and abundance were available. In mangrove habitats, the discharge site was monitored between 1986 and 1992. Oiled and unoiled areas of 3 habitat types were monitored: open coast, lagoon, and river, for a total of 26 study sites, with replication. Three years after the discharge, there were no statistically significant differences in rates of leaf production and net canopy production in oiled and unoiled habitats [622].

Because a number of seedlings survived the discharge while adult trees died, it was concluded that adult mangrove mortality was the result of suffocation rather than oil toxicity. Their morphology (lack of prop roots) apparently allowed seedlings to survive immersion in oil [622].

It was noted that, in addition to direct mortality, oil altered the physical structure of the mangrove habitat. Defoliation removed the weight of leaves from mangrove branches. In some cases, branches flexed upward, lifting roots out of the water, with the result that root-living organisms that had survived oiling then died of desiccation or heat stress. In 1991, it was reported that the number of post-discharge recruits appeared to be sufficient for reforestation of the oil-impacted habitats. Three years after the discharge, dense growths of young seedlings were observed. Some of these were natural recruits and some had been planted. Significant reductions in the total length of shoreline fringed by red mangroves were reported 5 years after the discharge. In areas where mangroves survived or regenerated, submerged prop roots, an essential habitat for biota, were fewer in number and extended less deeply into the water than before the discharge [622].

Quarterly post-discharge monitoring began in August 1986, four months after the discharge. Quantitative surveys of oiled and unoiled areas of three intertidal habitats were surveyed: mangroves fronting on the open ocean, mangroves located along channel banks and lagoons, and mangroves located along brackish streams and man-made ditches. Rates of root mortality were 31%, 71% and 58% in oiled open coast, channel and stream sites respectively. The same rates in unoiled sites were 2%, 2% and 4%. Open coastal habitats exhibited persistent effects of oiling after 3 years: abundances of the prespill dominant crustose and foliose algae were reduced on oiled roots [622].

After 5 years the structure of the mangrove fringe changed significantly after oiling. The amount of shoreline fringed with mangroves decreased, with concomitant decreases in the density and sizes of submerged prop roots. Overall, the surface area of submerged mangrove roots decreased by 33% on the open coast, 38% in channels and 74% in streams [622].

Case Study:

The effects of the 1973 Zoe Colocotronis oil discharge in Puerto Rico were described on a variety of communities. These communities included sublittoral Thalassia beds and flats. Quantitative surveys were made in several affected Thalassia beds as well as in unoiled control sites one week and thirteen weeks after the discharge. Thirteen weeks later, diversity was increasing but still low, except in one area. It was only in these latter flats that grass injury was noted. Blades were killed and the rhizome matrix was exposed by erosion due to the loss of protecting grass blades. A year later, growth was underway. Three years later, there was renewed plant growth with sediment deposition [622].

Case Study:

The effects of experimental summer and winter crude oil discharges on tundra and taiga vegetation were studied at 6 sites in the Northwest Territories, Canada. Permafrost depth exceeded 200 feet at both sites [622[.

Norman Wells crude oil was applied by even surface spraying and as high intensity point discharges. Doses were 9 liters/m2 in sprayed areas and one single point 50 barrel discharge [622].

Oil effects were evident at both tundra and taiga sites within 48 hours of oil application. All surface discharges had a devastating effect on above-ground vegetation, but plant species differed markedly in their ability to survive and recover. Lichens, mosses and liverworts were killed outright and did not recover during the 3 years of the study. Some woody and dwarf shrubs were able to produce new shoots within a few weeks of initial defoliation. Reduced production of storage material resulted in increases in plant losses by winter-killing. Plants with thick, waxy cuticles exhibited the least initial injury, but died later. Regardless of discharge season, flowering and reproduction were severely reduced, even during the third summer after oiling. The permafrost was not significantly affected despite changes in energy budgets [622].

Overall, injury was greater in the exposed taiga sites than at tundra sites. Taiga species with deep or substantial below-ground storage organs were able to revegetate and recolonize. Tundra vegetation was better able to survive discharge effects and regenerate, despite losses of lichens and mosses. Recovery of these sites was attributed to the presence of several key species. Winter discharges had less effect than summer discharges in both tundra and taiga habitats due to the absence of actively growing foliage at the time of the discharge and to weathering of toxic oil components. Point discharges caused less injury than uniform spraying because the discharged oil was absorbed rapidly into the soil and then flowed beneath the surface. As long as a few inches of surface soil was clear of oil, vegetation was able to survive [622].

Case Study:

The Amoco Cadiz (crude oil) discharge off the Brittany coast provided an opportunity to study the impacts of an oil discharge on eelgrass beds in the path of the discharge. Zostera marina beds at Roscoff, France were monitored. Estimates were made of the production and biomass of eelgrass and the faunal composition of the grassbed community [622].

The subject eelgrass beds were hit by oil on March 20, 1978. The oil remained for weeks, covering the beds at low tide and loosening and floating off at high tide. Despite this heavy oil coverage, the impacts to the grass itself were not severe. In April and May, 1978, especially in the shallower study area, there was a blackening of the leaves and presence of transparent areas on them. These leaves were shed, but the plants were still alive. Production was judged to have continued normally and the general structure of the eelgrass beds was not altered [622].

Case Study:

An evaluation of the impacts of the Exxon Valdez oil discharge (crude oil) and consequent response efforts on the shoreline and eelgrass beds offshore of treated, untreated and unimpacted shorelines was performed. This study only considered eelgrass-specific impacts in the seagrass beds and did not evaluate impacts on other elements of this community. There appeared to be no impact by exposure to oil on the vegetative structures or processes, but there were some measurable impacts on reproductive processes. A year after the discharge, this effect (that is, low flowering shoot density) was generally evident at all oil-impacted sites. Two years later, only those sites offshore of oiled shoreline that were subjected to high-pressure hot water washing showed this effect. This presumably reflected incorporation of hydrocarbons into the sediments through the washing process [622].

Case Study:

Stimulation of plant growth was observed following oil discharges. An experimental evaluation of marsh plant growth was performed following treatment with 4 L/m2 and 8 L/m2 Kuwait crude oil atmospheric residue. Qualitatively, oiled plants were a darker green color than unoiled plants. Shoot lengths of Festuca rubra and dry weight of Puccinellia sp. increased after oiling [622].

Case Study:

A series of experiments in which Kuwait crude oil was sprayed on a Welsh saltmarsh at different times of year was performed. The field experiments were supplemented with greenhouse studies. Eighteen liters of Kuwait crude oil was applied to each of three 2m x 18m transects, a dose equivalent to light oiling. Most perennial marsh plant species suffered no long-term injury. The annual species Suaeda maritima and Salicornia sp., which do not possess underground roots, were injured by summer spraying. All plants exhibited a marked reduction in flower production if oiling occurred while flower buds were developing. Winter oiling of seeds reduced germination of some species in the spring. Overall, more adverse effects occurred when oil was applied during warm weather. However, recovery was rapid, regardless of the season when oil was applied: plants oiled in May recovered by September; plants oiled in August recovered by October; and plants oiled in November recovered by the following spring [622].

Case Study:

The effects of successive oilings on the recovery of vegetation were evaluated in a Welsh saltmarsh. The experimental design was a random block of five 2m x 5m plots located at each of three elevations in the marsh. Treatments included 2, 4, 8, and 12 successive monthly sprayings with 4.5 liters of fresh Kuwait crude oil. Vegetative cover was recorded between oilings and at intervals over 5 years [622].

Marsh plant responses to successive oilings were species-specific. For example, Spartina anglica recovered well by recolonizing from adjacent unoiled areas. In contrast, Puccinellia maritima showed little recovery on plots oiled 8 and 12 times. Juncus maritimus was reduced in all oiled plots located in upper marsh areas. Overall, marsh vegetation exhibited good recovery from up to 4 successive oilings, but underwent considerable changes in species composition following 8 to 12 successive oilings. In the latter cases, the changes persisted for at least 5 years following oiling [622].

Case Study:

A study, (1981), measured the rate of CO2 fixation of saltmarsh vegetation using portable light/dark chambers to evaluate physiological stress in marsh plots which were experimentally oiled with South Louisiana crude oil. Doses of 0.2 L/m2 and 8 L/m2 were applied to replicated 6 m2 enclosed plots. CO2 fixation was measured 7 and 14 days after oiling. Both oil doses decreased rates of CO2 fixation by 63-81% [622].

Case Study:

Several experiments were performed to determine the effects of fresh and artificially weathered south Louisiana crude oil on physically isolated plots in a York River, Virginia saltmarsh. All trophic levels were considered. Five 810 m2 contained experimental marsh units were constructed. Four of the units were dosed with oil; one unit served as an unoiled control treatment. Both weathered and unweathered oil had similar effects on Spartina alterniflora: standing stocks were lower than those in the unoiled control treatment [622].

Additional support exists for the contention that weathered oil is at least as toxic to plants as fresh oil. Weathered oil was found to be more toxic to kelp than fresh oil [622].

Case Study:

The effects of 4 types of oil on Spartina alterniflora in a Galveston Bay, Texas saltmarsh were examined: Arabian crude oil, Libyan crude oil, No. 6 fuel oil, and No. 2 fuel oil. Experimental treatments of each oil consisted of one liter applied to sediments, 1.5 liters applied to sediments and the lower 30 cm of plants, 2 liters applied to sediments and entire plants, and a control treatment in which no oil was applied. Oil was applied in autumn, and plant growth was evaluated after 5 months, one year and 2 years. All oils killed the aboveground portions of plants when applied to the entire plant surface. Partial oiling was detrimental only with No. 2 fuel oil.

All types of oil applied to sediments had no effect on Spartina. Five months after treatment, new root and rhizome growth occurred in plants treated with Arabian crude oil, Libyan crude oil, and No. 6 fuel oil; significantly less growth occurred in plants treated with No. 2 fuel oil. One year after oil treatment, plants treated with Arabian crude oil, Libyan crude oil, and No. 6 fuel oil had recovered completely [622].

Seasonal responses of Spartina alterniflora to oil also were evaluated in experimental plots in a Texas saltmarsh. Oil applications were in November or May. No influence of season was observed when any of the oil types was applied to sediments and lower plant parts. Season influenced plant response when oil was applied to whole plants: live plant biomass was reduced for a longer period when oil was applied in May. It was concluded that: (1) season need not be considered for Gulf Coast saltmarshes when only sediments or parts of Spartina are oiled; (2) complete oiling of S. alterniflora during seasons of increased growth caused longer-term reduction in live plant biomass than complete oiling during seasons of dormancy; and (3) cleanup is warranted for discharges of No. 2 fuel oil and for discharges of all types of oil resulting in complete plant coverage during the growing season [622].

Case Study:

Seasonal responses of Spartina alterniflora to oil were evaluated in experimental plots in a Texas saltmarsh. Four types of oil, Arabian crude oil, Libyan crude oil, No. 6 fuel oil, and No. 2 fuel oil, were applied to plants during November or May. Experimental treatments of each oil consisted of one liter applied to sediments, 1.5 liters applied to sediments and the lower 30 cm of plants, 2 liters applied to sediments and entire plants, and a control treatment in which no oil was applied. Live plant biomass and residual oil were measured periodically following treatment [622].

No influence of season was observed when any of the oil types was applied to sediments and lower plant parts. Reduction in live plant tissue occurred only with No. 2 fuel oil. Season influenced plant response when oil was applied to whole plants: live plant biomass was reduced for a longer period when oil was applied in May. The greatest decrease occurred with No. 2 fuel oil. It was concluded (1) that season need not be considered for Gulf Coast saltmarshes when only sediments or parts of Spartina are oiled; (2) complete oiling of S. alterniflora during seasons of increased growth caused longer-term reduction in live plant biomass than complete oiling during seasons of dormancy; and (3) cleanup is warranted for discharges of No. 2 fuel oil and for discharges of all types of oil resulting in complete plant coverage during the growing season [622].

Case Study:

A greenhouse study measured the responses to oil by two Spartina species. Effects on growth of a number of treatments, including weathering of oil, substrate penetration of oil, coating of plant aerial tissue with oil, continuous presence of the oil layer, duration of exposure to oil, and substratum type were evaluated [622].

The study concluded that the way in which oil comes into contact with marsh plant tissue or substrate is more important than weathering prior to exposure. Oil applied to the water layer did not affect existing plants, but completely inhibited growth. Oil applied to the substrate exhibited a significant effect on the plants, but had less effect on plants grown in marsh sediments (that is, peat) than those grown in sand, presumably because the fine textured marsh sediments reduced oil penetration [622].

Case Study:

In early February 1976, the Liberian tanker St. Peter, carrying a cargo of 243,000 barrels of Orito crude oil, sank in 1,000 m of water about 30 km off Cabo Manglares, Colombia. By mid-February, oil slicks reached mangrove habitats in Colombia. Mangrove roots and trunks located 20-70 m from the shoreline were oiled to heights of 2-3 m. Mangrove trees in the impacted area were partly defoliated [622].

By May and June 1976, most of the oil had washed off of the roots and trunks naturally in the less heavily oiled areas. New mangrove leaves, blooms, and seedlings were present in previously defoliated areas [622].

Case Study:

In April 1970, a pipeline broke on land near Tarut Bay, Saudi Arabia. A levee retained some of the oil, but 100,000 barrels of Arabian light crude oil were discharged into shallow Tarut Bay. Qualitative observations were made one week and 3 months following the discharge. In Avicennia (dwarf mangrove) marshes, some leaves were oiled, but the substrate did not appear to be heavily oiled. After 3 months, some mangroves were completely defoliated, but many survived, with some bearing flowers and fruit. It was concluded that after 3 months, mangroves and associated fauna exhibited little evidence of injury [622].

Case Study:

The effects of experimental oilings on 5 different arctic plant community types were studied in northwestern Canada. Plant communities differed with respect to species, soil, active layer depth, moisture, and microtopography. All were underlain by permafrost, with a biotic gradient ranging from a tree-covered area at Inuvik, located 115 km from the arctic coast, to tundra at Toktoyuktuk, located on the coast. In an experiment, light gravity sweet crude oil was applied at various doses during three different seasons. Spring and winter doses were 0, 0.25, 0.5, and 1.0 cm; summer doses were 0, 0.4, 0.75, and 1.5 cm. The maximum spring and winter doses were equivalent to 1,300 barrels per acre and the maximum summer dose was equivalent to 1,950 barrels per acre [622].

All actively growing plant tissue was destroyed. Plant recovery from latent buds on dwarf shrub species, especially Salix and Betula, was more rapid than for sedges. Lichens did not recover, and only one moss, Polytrichus junipernum exhibited any regrowth. Injury was greatest following summer applications, because the oil penetrated deeper into the soil. The extra energy absorbed on the contaminated plots was dissipated as latent heat of evaporation in spring and as sensible heat later in summer, rather than increasing active layer depth. Because total plant recovery was 20-55% on the treated plots after one full growing season, it was concluded that contaminated areas should be left undisturbed if possible [622].

Bio.Detail: Detailed Information on Bioconcentration, Biomagnification, or Bioavailability:

During the Exxon Valdez spill, bioconcentration explained the buildup of PAHs in tissues better than biomagnification; most accumulation was of an equilibrium partitioning nature across the gills rather than from the food chain [971]. Immature fish seem have higher bioconcentration of PAHs than adults, perhaps because their PAH breakdown systems are not fully developed and at times perhaps because of a higher percentage of lipid tissues (yolk tissues, etc) [971] (confirmed by Jerry Neff, Battelle Ocean Sciences, Duxbury, MA, personal communication 1996).

Species lower down on the food chain, such as certain zooplankton, phytoplankton, and invertebrates (like mussels and molluscs) can bioaccumulate PAHs. They will lose much of the accumulated hydrocarbon products if clean water is again available. However, if oil exposure is chronic, the hydrocarbons may enter more stable tissue (like depot lipids) and as long as the animal is in positive nutritional balance, will only very slowly release the hydrocarbons [713].

Biomagnification of petroleum hydrocarbons through the food chain has not been demonstrated in marine mammals, probably due to their cytochrome P450 system. The bioaccumulation and persistence of PAHs in the food chain is opposite of that seen for other chemicals such as some PCBs and certain other organochlorines which tend to concentrate in the top predators. Because it is the species lower in the food chain that concentrate PAHs, those species (like bowhead whales and walrus) that feed at that lower level are at higher risk of bioaccumulation than species (like killer whales) that feed higher in the food chain on fish. Fish also have an enzyme system for clearing hydrocarbons, and therefore are not likely to bioaccumulate hydrocarbons. However, colder waters can slow down the metabolism and elimination of hydrocarbons, thus animals feeding in arctic waters have a greater chance of bioaccumulating some hydrocarbons [713].

Log Kow values for PAHs [971]:

Naphthalene:	3.37
C1-Naphthalene:	3.87
C2-Naphthalene:	4.37
C3-Naphthalene:	5.0
C4-Naphthalene:	5.55
Acenaphthylene:	4.07
Acenaphthene:	3.92
Fluorene:	4.18
C1-Fluorene:	4.97
C2-Fluorene:	5.2
C3-Fluorene:	5.5
Anthracene:	4.54
Phenanthrene:	4.57
C1-Phenanthrene:	5.14
C2-Phenanthrene:	5.51
C3-Phenanthrene:	6
C4-Phenanthrene:	6.51
Dibenzothiophene:	4.49
C1-Dibenzothiophene:	4.86
C2-Dibenzothiophene:	5.5
C3-Dibenzothiophene:	5.73
Fluoranthene:	5.22

Pyrene:	5.18
C1-Fluoranthene/pyrene:	5.72
Benzo(a)anthracene:	5.91
Chrysene:	5.86
C1-Chrysene:	6.42
C2-Chrysene:	6.88
C3-Chrysene:	7.44
C4-Chrysene:	8
Benzo(b)fluoranthene	5.80
Benzo(k)fluoranthene:	6.0
Benzo(a)pyrene:	6.04
Indeno(1,2,3-c,d)pyrene:	7.0
Dibenz(a,h)anthracene:	6.75
Benzo(g,h,i)perylene:	6.50

Interactions:

Many PAHs found in petroleum products become more toxic in the presence of sunlight or other UV sources. See also: entry on PAHs and various entries on individual components of this mixture.

Uses/Sources:

Petroleum products have a vast array of uses. In approximate order of importance the uses are: fuels for vehicles and industry, heating oils, lubricants, raw materials in manufacturing petrochemicals and pharmaceuticals, and solvents. By a wide margin, most of the products derived from petroleum find use as fossil fuels to run vehicles, produce electricity, and to heat homes and business. About 65% of the petroleum used as fuel is consumed as gasoline in automobiles. Thus, petroleum products are ubiquitous in the modern environment which leads to contamination problems both for the environment and in sampling activities [661].

Forms/Preparations/Formulations:

There are several different ways to group various petroleum products. Refined oils are sometimes characterized by approximate boiling point range, which corresponds with the size (such as, number of carbon atoms) of the petroleum hydrocarbons in the refined oil [771]:

20-200 C:	4-12 carbons: Straight-run gasoline (meaning not produced through catalytic decomposition).
185-345 C:	10-20 carbons: Middle distillates, including kerosene, jet fuels, heating oil, diesel fuel.
345-540 C:	18-45 carbons: Wide cut gas oils, including light lube oils, heavy lube oils, waxes, and catalytic feed stock for production of

gasoline.

540 C:	>40 carbons: Residual oils, which may be cut with lighter oils to produce bunker oils.

Another way to group petroleum products is by generalized spill cleanup categories. Oil properties important for characterizing include flash point, specific gravity/API gravity, viscosity, emulsion formation, and adhesion [777] (see the Chem.Detail sections of individual oil product entries for this information). The following groupings are used by NOAA to identify basic cleanup options [741,771,777]:

Gasoline Products:

- Highly volatile.
- Evaporates quickly, often completely within 1 to 2 days.
- Highly soluble.
- Narrow cut fraction with no residue.
- Low viscosity, spreads rapidly to a thin sheen.
- High acute toxicity to biota.
- Do not emulsify.
- Will penetrate substrate; nonadhesive.

Diesel-like Products and Light Crudes (Jet Fuels, Diesel, No. 2 Fuel Oil, Kerosene, West Texas Crude):

- Moderately volatile.
- Refined products can evaporate with no residue.
- Light crude will leave residue (up to one-third of spill amount) after a few days.
- Moderately soluble, especially distilled products.
- Low and moderate viscosity; spread rapidly into thin slicks.
- Can form stable emulsions.
- Moderate to high acute toxicity to biota; product-specific toxicity related to type and concentration of aromatic compounds.
- Will "oil" intertidal resources with long-term contamination potential.
- Has potential for subtidal impacts (dissolution, mixing, sorption onto suspended sediments).
- Tend to penetrate substrate; fresh spills are not adhesive.
- Stranded light crudes tends to smother organisms.
- No dispersion necessary.
- Cleanup can be very effective.

Medium-grade Crude Oils and Intermediate Products (South Louisiana Crude, No. 4 Fuel Oil, Lube Oils):

- About one-third will evaporate within 24 hours.
- Typical water-soluble fraction 10-100 ppm.
- Moderate to high viscosity.

- -Variable acute toxicity; depending on amount of light fraction.
- -Can form stable emulsion.
- -May penetrate substrate and persist.
- -May be significant clean-up related impacts.
- -Oil contamination of intertidal areas can be severe/long term.
- -Stranded oil tends to smother organisms.
- -Impact to waterfowl and fur-bearing mammals can be severe.
- -Chemical dispersion is an option within 1-2 days.
- -Cleanup most effective if conducted quickly.

Heavy Crude Oils and Residual Products (Venezuela Crude, No. 6 Fuel Oil, Bunker C):

- -Heavy oils with little/no evaporation or dissolution.
- -Water-soluble fraction typically less than 10 ppm.
- -Heavy surface and intertidal area contamination likely.
- -Highly persistent, long-term sediment contamination possible.
- -Less acute toxicity relative to other oil types.
- -Very viscous to semisolid; may become less viscous when warmed.
- -Can form stable emulsions.
- -Weather very slowly. May form tarballs.
- -May sink depending on product density and water density.

> NOTE: For a detailed discussion of oil products sinking vs. floating, see the Fate.Detail section in the Oil Spills entry.

- -May be significant clean-up related impacts.
- -Heavy contamination of intertidal areas likely.
- -Severe impacts to waterfowl and fur-bearing mammals (coating and ingestion).
- -Stranded oil tends to smother organisms.
- -Dispersion seldom effective.
- -Little penetration of substrate likely, but can he highly adhesive.
- -Shoreline cleanup difficult under all conditions.

Low API Fuel Oils (LAPIO, Heavy Industrial fuel oils):

- -Neutrally buoyant or may sink depending on water density.
- -Weathers slowly; sunken oil has little potential for evaporation.
- -May accumulate on bottom under calm conditions and smother subtidal resources.
- -Sunken oil may be resuspended during storm events, providing a chronic source of shoreline oiling.
- -Highly variable and often blended with oils.
- -Blends may be unstable and the oil may separate when

spilled.

Chem.Detail: Detailed Information on Chemical/Physical Properties:

Since PAHs are important hazardous components of petroleum, risk assessments should include analyses of PAHs and alkyl PAHs utilizing the NOAA protocol expanded scan [828] or other rigorous GC/MS/SIM methods.

An important step in assessing the effects of petroleum products that have been released into the environment is to evaluate the nature of the particular mixture and eventually select an optimum remediation technology for that mixture [661].

As a general rule, all crude oils (unrefined petroleum) are complex mixtures composed of the same compounds, but the quantities of the individual compounds differ in crude oils from different locations. This rule of thumb implies that the quantities of some compounds can be zero in a given mixture of compounds that comprise a crude oil from a specific location [773].

A broad functional definition of petroleum hydrocarbons is that hydrocarbons are primarily composed of many organic compounds of natural origin and low water solubility. In general, petroleum is a complex mixture of hydrocarbons (molecules made up of only carbon and hydrogen) and nonhydrocarbons (molecules made up carbon, hydrogen, and other elements such as sulphur, nitrogen, and oxygen) that forms in the partial decomposition of biogenic material. The slow breakdown process, known as diagenesis, produces a range of hydrocarbons and hydrocarbon complexes significantly altered from the structure found in the original biomass [773].

Oils typically are described in terms of their physical properties (such as density and pour point) and chemical composition (such as percent composition of various petroleum hydrocarbons, asphaltenes, and sulfur). Although very complex in makeup, oils can be broken down into four basic classes of petroleum hydrocarbons [741]. Each class is distinguished on the basis of molecular composition, as described below [741,773]:

Alkanes (also called normal paraffins):

Alkanes are characterized by branched or unbranched chains of carbon atoms with attached hydrogen atoms, and contain no carbon-carbon double bonds (they are saturated). Common alkanes include methane, propane and isobutane [771].

Naphthenes (also called cycloalkanes or cycloparaffins):

Naphthenes typically comprise about 50% of the average crude oil. Naphthenes are similar to alkanes, but are characterized by the presence of simple closed rings of carbon atoms. Naphthenes are generally stable and relatively insoluble in water. Common naphthenes include cyclopropane and cyclopentane [771].

Alkenes (also called olefins or isoparaffins):

Alkenes are characterized by branched or unbranched chains of carbon atoms. Alkenes are not generally found in crude oils, but are common in refined products, such as gasoline. Common alkenes include ethene and propene [771].

Aromatics:

Aromatics are a class of hydrocarbons characterized by rings with six carbon atoms. Aromatics are considered to be the most acutely toxic component of crude oil, and are also associated with chronic and carcinogenic effects. Many low-weight aromatics also are soluble in water, increasing the potential for exposure to aquatic resources. Aromatics are often further distinguished by the number of rings, which may range from one to five. Aromatics with two or more rings are referred to as polycyclic aromatic hydrocarbons (PAHs). Common aromatics include benzene, naphthalene, and benzo(a)pyrene [771]. The most abundant aromatic hydrocarbon families have two and three fused rings with one to four carbon atom alkyl group substitutions [773].

NOTE: Crude oil contains, on the average, approximately 1% polynuclear aromatic hydrocarbons (PAHs). Concentrations of total carcinogenic PAHs (like benzo(a)pyrene) reported in the literature range from 12 ppm to <100 ppm [745].

Fresh crude oil will contain a fraction of volatile hydrocarbons, some of which may pose a threat to human health such as benzene, toluene, xylenes, and other aromatics. However, the relative mass fraction of volatile hydrocarbons in crude oil is significantly less than that found in crude oil distillate products such as gasoline. The volume percentage of benzene in gasoline may range up to 3% (30,000 ppm), while the benzene content of crude oil is approximately 0.2% (2000 ppm). As a result of the lower percentage of volatile aromatics, vapor emissions from crude oil-contaminated soils are expected to be much less than potential emissions from gasoline-contaminated soils [734].

Other components are also present in petroleum products. In addition to these four major classes of hydrocarbons, oils also are characterized by the following other components [771,773]:

Asphaltenes and resins:

Asphaltenes and resins can comprise a large fraction of crude oils and heavy fuel oils, making those oils very dense and viscous [771]. Composition is dependent upon source (these structures have the highest individual molecular weight of all crude oil components and are basically colloidal aggregates). Asphaltenes are substances in petroleum that are insoluble in solvents of low molecular weight such as pentane or hexane. These compounds are composed of very large cyclic and planar molecules and are solids at normal temperatures. Consequently, oils that have high asphaltene contents are very viscous, have a high pour point, and are generally nonvolatile in nature. The porphyrins, asphaltene, and resin compounds are considered the residual oil, or residuum. During the weathering process, this fraction is the last to degrade, and its persistence over years has been noted [773].

Polar:

Sulfur, Nitrogen, or Oxygen-containing aromatic compounds. Polar compounds are also known as "nonhydrocarbons" [773].

Porphyrins:

Complex large cyclic carbon structures derived form chlorophyll and characterized by the ability to contain a central metal atom (trace metals are commonly found within these compounds) [773].

Details of PAH content (mg/kg or ppm) in one fresh sample of Exxon Valdez Crude Oil [971]:

> Note: these values are wet weight (Jerry Neff, Battelle Ocean Sciences, Duxbury, MA, personal communication 1996):

Naphthalene:	622 mg/kg = ppm
C1-Naphthalene:	1400 mg/kg = ppm
C2-Naphthalene:	1780 mg/kg = ppm
C3-Naphthalene:	1410 mg/kg = ppm
C4-Naphthalene:	696 mg/kg = ppm
Acenaphthylene:	0 mg/kg = ppm
Acenaphthene:	2 mg/kg = ppm
Fluorene:	93 mg/kg = ppm
C1-Fluorene:	224 mg/kg = ppm
C2-Fluorene:	366 mg/kg = ppm
C3-Fluorene:	394 mg/kg = ppm
Anthracene:	0 mg/kg = ppm
Phenanthrene:	262 mg/kg = ppm
C1-Phenanthrene:	572 mg/kg = ppm
C2-Phenanthrene:	722 mg/kg = ppm
C3-Phenanthrene:	576 mg/kg = ppm
C4-Phenanthrene:	446 mg/kg = ppm
Dibenzothiophene:	217 mg/kg = ppm
C1-Dibenzothiophene:	449 mg/kg = ppm
C2-Dibenzothiophene:	635 mg/kg = ppm
C3-Dibenzothiophene:	579 mg/kg = ppm
Fluoranthene:	2 mg/kg = ppm
Pyrene:	10 mg/kg = ppm
C1-Fluoranthene/pyrene:	82 mg/kg = ppm
Benzo(a)anthracene:	2 mg/kg = ppm

Chrysene: 46 mg/kg = ppm
C1-Chrysene: 89 mg/kg = ppm
C2-Chrysene: 138 mg/kg = ppm
C3-Chrysene: 115 mg/kg = ppm
C4-Chrysene: 0 mg/kg = ppm
Benzo(b)fluoranthene 6 mg/kg = ppm
Benzo(k)fluoranthene: 0 mg/kg = ppm
Benzo(a)pyrene: 0 mg/kg = ppm
Indeno(1,2,3-c,d)pyrene: 1 mg/kg = ppm
Dibenz(a,h)anthracene: 1 mg/kg = ppm
Benzo(g,h,i)perylene: 2 mg/kg = ppm
Total PAHs 11,317 mg/kg = ppm

Details of PAH content (mg/kg or ppm) in salmon carcass (fatty viscera removed, so the concentrations may have been higher from whole body samples) from Snug Harbor, Alaska, an area heavily oiled by the Exxon Valdez Crude Oil, 4/15/89 [971]:

Note: Concurrent measurements of water quality, as well as equilibrium partitioning estimates of water quality based on concentrations in fish and mussels, both confirm that PAH concentrations did not exceed water quality criteria at the time these concentrations were measured in fish tissues [971]. These values are wet weight (Jerry Neff, Battelle Ocean Sciences, Duxbury, MA, personal communication 1996):

Naphthalene: 7.15 ug/kg = ppb
C1-Naphthalene: 65.11 ug/kg = ppb
C2-Naphthalene: 29.75 ug/kg = ppb
C3-Naphthalene: 93.95 ug/kg = ppb
C4-Naphthalene: 36.63 ug/kg = ppb
Acenaphthylene: 0 ug/kg = ppb
Acenaphthene: 0 ug/kg = ppb
Fluorene: 6.86 ug/kg = ppb
C1-Fluorene: 12.63 ug/kg = ppb
C2-Fluorene: 22.87 ug/kg = ppb
C3-Fluorene: 13.64 ug/kg = ppb
Anthracene: 0 ug/kg = ppb
Phenanthrene: 22.97 ug/kg = ppb
C1-Phenanthrene: 28.48 ug/kg = ppb
C2-Phenanthrene: 20.45 ug/kg = ppb
C3-Phenanthrene: 12.43 ug/kg = ppb
C4-Phenanthrene: 1.71 ug/kg = ppb
Dibenzothiophene: 19.65 ug/kg = ppb
C1-Dibenzothiophene: 19.68 ug/kg = ppb
C2-Dibenzothiophene: 15.96 ug/kg = ppb
C3-Dibenzothiophene: 7.44 ug/kg = ppb
Fluoranthene: 0 ug/kg = ppb
Pyrene: 0 ug/kg = ppb
C1-Fluoranthene/pyrene: 0.62 ug/kg = ppb
Benzo(a)anthracene: 0.72 ug/kg = ppb

Chrysene:	2.5 ug/kg = ppb
C1-Chrysene:	0.71 ug/kg = ppb
C2-Chrysene:	0.48 ug/kg = ppb
C3-Chrysene:	0.16 ug/kg = ppb
C4-Chrysene:	0.56 ug/kg = ppb
Benzo(b)fluoranthene	0 ug/kg = ppb
Benzo(k)fluoranthene:	0 ug/kg = ppb
Benzo(a)pyrene:	0 ug/kg = ppb
Indeno(1,2,3-c,d)pyrene:	0 ug/kg = ppb
Dibenz(a,h)anthracene:	0 ug/kg = ppb
Benzo(g,h,i)perylene:	0 ug/kg = ppb
Total PAHs	436 ug/kg = ppb

Details of PAH content (ug/kg or ppb) in whole body samples of mussels) from Snug Harbor, Alaska, an area heavily oiled by the Exxon Valdez Crude Oil, 4/15/89 [971]:

Note: Concurrent measurements of water quality, as well as equilibrium partitioning estimates of water quality based on concentrations in fish and mussels, both confirm that PAH concentrations did not exceed water quality criteria at the time these concentrations were measured in mussel tissues [971]. These values are wet weight (Jerry Neff, Battelle Ocean Sciences, Duxbury, MA, personal communication 1996):

Naphthalene:	12.9 ug/kg = ppb
C1-Naphthalene:	17.3 ug/kg = ppb
C2-Naphthalene:	247 ug/kg = ppb
C3-Naphthalene:	905 ug/kg = ppb
C4-Naphthalene:	850 ug/kg = ppb
Acenaphthylene:	0 ug/kg = ppb
Acenaphthene:	0 ug/kg = ppb
Fluorene:	38.3 ug/kg = ppb
C1-Fluorene:	383 ug/kg = ppb
C2-Fluorene:	1317 ug/kg = ppb
C3-Fluorene:	1535 ug/kg = ppb
Anthracene:	0 ug/kg = ppb
Phenanthrene:	356 ug/kg = ppb
C1-Phenanthrene:	1924 ug/kg = ppb
C2-Phenanthrene:	3834 ug/kg = ppb
C3-Phenanthrene:	2438 ug/kg = ppb
C4-Phenanthrene:	796 ug/kg = ppb
Dibenzothiophene:	260 ug/kg = ppb
C1-Dibenzothiophene:	1344 ug/kg = ppb
C2-Dibenzothiophene:	2743 ug/kg = ppb
C3-Dibenzothiophene:	2743 ug/kg = ppb
Fluoranthene:	10.7 ug/kg = ppb
Pyrene:	32.9 ug/kg = ppb
C1-Fluoranthene/pyrene:	302 ug/kg = ppb
Benzo(a)anthracene:	0 ug/kg = ppb
Chrysene:	411 ug/kg = ppb

C1-Chrysene:	658 ug/kg = ppb
C2-Chrysene:	521 ug/kg = ppb
C3-Chrysene:	239 ug/kg = ppb
C4-Chrysene:	43.9 ug/kg = ppb
Benzo(b)fluoranthene	27.4 ug/kg = ppb
Benzo(k)fluoranthene:	0 ug/kg = ppb
Benzo(a)pyrene:	65.8 ug/kg = ppb
Indeno(1,2,3-c,d)pyrene:	0 ug/kg = ppb
Dibenz(a,h)anthracene:	2.63 ug/kg = ppb
Benzo(g,h,i)perylene:	7.41 ug/kg = ppb
Total PAHs	24,051 ug/kg = ppb

The following table summarizes chemical component classes by percent weight for several representative petroleum products [773]:

CHEMICAL			REFINED OILS		
COMPONENT (wt %)	Gasoline	Kerosine	#2 Fuel Oil	10W/30 Motor Oil	#6 Fuel Oil
Saturates*	39.6	85.0	61.8	73.7	24.4
Aromatics	46.2	15.0	38.2	25.4	54.6
Polars	--	--	0.0	0.9	14.9
Asphaltenes	N/A	N/A	0.0	0.0	6.2
Sulfur (%)	0.07	0.5	0.32	0.37	2.0

NOTE: * Saturates includes alkanes, naphthenes, and alkenes [773].

The following table summarizes the physical properties of several representative petroleum products [773]:

PHYSICAL			REFINED OILS		
PROPERTIES	Gasoline	Kerosine	#2 Fuel Oil	10W/30 Motor Oil	#6 Fuel Oil
API Gravity*	60.0	37.0	31.6	29.0	10.0
Density (at 20C)	0.734	0.83	0.84	0.87	0.966
Pour point (C)	<-40.0	-18.0	-20.0	-37.0	6.0
Flash point (C)	-40.0	38.0	55.0	188.0	80.0

NOTE: * API gravity = (141.5/specific gravity at 60 F or 15.6 C) - 131.5.

Solubility of hydrocarbon components in petroleum products is an important property when assessing toxicity [661]. The water solubility of a substance determines the routes of exposure that are possible [773]. Solubility is approximately inversely proportional to molecular weight; lighter hydrocarbons are more soluble in water than higher molecular weight compounds. Lighter hydrocarbons, C4 to C8, including the aromatic are relatively soluble, up to about 2,000 ppm; heavier hydrocarbons are nearly insoluble [661]. The following list summarizes solubility in cold water (at 20 degrees C) for several representative petroleum products. Some of gasoline's more hazardous individual components are listed. The most soluble components are also the most toxic [661]:

PRODUCT	SOLUBILITY (ppm)
Gasoline (1)	50-100
1-Pentene	150
Benzene	1,791
Toluene	515
Ethylbenzene	75
Xylenes (2)	150
n-Hexane	12
Cyclohexane	210
i-Octane	8 ppb
JP-4 Jet Fuel	<1
Kerosene	<1
Diesel	<1
Light Fuel Oil #1 and #2	<1
Heavy Fuel Oil #4, #5, and #6	<1
Lubricating Oil	<1 ppb
Used Oil	<1 ppb
Methanol (for comparison)	>100,000

NOTES: (1) Solubilities of individual components may be higher; (2) Average data for a mixture of all isomers. Also, other sources list higher solubilities for various petroleum products [560].

For more specific information on solubility of a specific petroleum product, see that individual entry.

he water soluble fractions of the bunker C and fuel oil no. 2 contained significantly higher concentrations of naphthalenes and alkylnaphthalenes than those of the crudes. The concentrations, although low, of fluorene and methylfluorenes, phenanthrenes and methylphenanthrenes were also much higher in the water soluble fractions of the No. 2 fuel oil and bunker C oil than in the crude oils. Because aromatics are more water soluble than alkanes, water soluble fractions are enriched in aromatic hydrocarbons relative to the parent oil [770].

Fate.Detail: Detailed Information on Fate, Transport, Persistence, and/or Pathways:

In an often referenced study, the quantitative hydrocarbon composition and behavior in seawater of water-soluble fractions (WSF) and oil-in-water dispersions (OWD) of 4 oils was investigated (namely South Louisiana crude, Kuwait crude, and two refined oils - No. 2 fuel oil and bunker C residual oil) [770]. In the study, differences in the solubilities and composition of the test oils were described, as well as variations in sensitivity to oil of several marine species. A prediction of environmental impact must take into consideration the specific characteristics of the particular oil spilled as well as the particular spill environment (that is, whether the spill occurs in the open sea, or a confined water body) [770].

Biodegradation rates of hydrocarbons are dependent on the type of bacteria, presence of limiting nutrients, temperature, and types of hydrocarbons [657]. Most biodegradation occurs from about one week to many months after the spill [771]. Bacteria generally degrade hydrocarbons according to the following sequence (first to last): n-alkanes > branched alkanes > aromatic hydrocarbons > cyclic alkanes [657]. Within a PAH homologous series, bacteria degradation rates generally are inversely proportional to the degree of alkylation. So, the sequence of bacterial degradation within a PAH homologous series would be (from first to last degraded) [657]:

C0-PAH > C1-PAH > C2-PAH > C3-PAH > C4-PAH

The primary processes determining the fate of crude oils and oil products after a spill are spreading, evaporation, emulsification, dispersion, dissolution, reaction, and sedimentation. These processes are influenced by the spill characteristics, environmental conditions, and physicochemical properties of the spilled material. Due to the confounding effects of site-specific and spill-specific variables, physicochemical data will only provide a relative scale as to which oil and oil products will persist in the aquatic environment [791].

Oils and oil products with the least persistence in a water environment are those with low molecular weights, high solubilities, high vapor pressures, and low octanol/water partition coefficients (Kow). Oils and oil products with the greatest persistence are those with the opposite qualities [791]. (The low-molecular-weight hydrocarbons are more soluble, have a higher vapor pressure, and have a lower Kow than heavier products [791]).

See also: Bio.Detail section above for Kow values for various PAHs.

An oil product is a complex mixture of organic chemicals and contains within it less persistent and more persistent fractions. The range between these two extremes is greatest for crude oils, which are a mixture of everything from gasoline to asphaltenes [791].

In a study of various crude and residual oils, gentle aeration of the oil-in-water dispersions resulted in a loss of 80 to 90% of the total aqueous hydrocarbons in 24h [770]. Alkanes disappeared from the dispersion more rapidly than aromatics (for example, 1000 ppm oil-in-water dispersions of Kuwait crude, South LA crude, and fuel oil no. 2 experienced total alkanes decreases of 95%, 97%, and 81%, compared to total aromatic decreases of 69%, 52%, and 79%, respectively) [770]. More specifically, the concentrations of di-aromatic hydrocarbons (such as naphthalene) do not drop off as rapidly as that of the alkanes, which have lower water solubility [770].

A comprehensive review of the physicochemical properties of several oils and oil products found their persistence in the aquatic environment to rank as follows (from most persistent to least persistent): Residual asphaltenes > Heavy crude oil > Medium crude oil > Fuel oil #6 > Light crude oil > Lube oils > Fuel oil #2 > Jet fuel > Gasoline [791].

The water soluble fractions of the crude oils had higher total oil-hydrocarbon concentrations than the refined products in seawater (varying from a high of 18.9 ppm for South Louisiana crude to a low of 6.3 ppm for Bunker C, measured by infrared methods) [770]. The greater solubility of the crudes can be attributed to the fact that they were richer in light aliphatics (that is, the alkanes ethane to methylcyclohexane) and single-ring aromatics (benzene through xylene) than the refined products fuel no. 2 and bunker C [770]. The majority of these are removed from No. 2 fuel oil and bunker C during the refining process (that is, they are removed in the first fraction of the refining process, which is why gasoline, the first fraction, has the highest concentration of benzene, toluene, ethylbenzene, and xylenes (BTEX) of any refined product).

The following information summarizes oil weathering issues:

After oil is discharged into the environment, a wide variety of physical, chemical, and biological processes begin to transform the discharged oil. Collectively, these processes are referred to as weathering, and act to change the composition, behavior, routes of exposure, and toxicity of the discharged oil. For example, penetration of oil into marsh vegetation may depend on oil viscosity; weathered oils penetrate less than fresh oil. Weathered oil is composed of relatively insoluble compounds, and often coalesces into mats or tarballs. As a result, the potential for exposure to fish through water column toxicity is lessened, as is the potential for birds or mammals to encounter the oil. Alternatively, certain species are known to ingest tarballs and the potential for exposure to those resources may increase as the oil weathers. Also, the loss of the lighter fractions through dissolution and/or evaporation during the weathering process can cause normally buoyant oil to sink, thereby contaminating subtidal sediment and contributing to water column toxicity [771]. For a detailed discussion of sinking oil, see the Oil Spills entry.

After the loss of the volatile, soluble, and easily biodegraded compounds, the remaining compounds can become concentrated. Weathered oil becomes less acutely toxic, but due to polynuclear aromatic hydrocarbons (PAHs) of high molecular weight, it remains toxic [713].

The primary weathering processes are physical phenomena; these include spreading, evaporation, dissolution, dispersion, emulsification, and sedimentation [771]. (Chemical weathering processes include photodegradation and oxidation; biological weathering processes include (microbial) biodegradation and ingestion and depuration by organisms [713].) These processes occur for all discharges, but the rate and relative importance of each process depends on spill characteristics, environmental conditions, and physicochemical properties of the spilled material [771,791]. Note that due to the confounding effects of site-specific and spill-specific variables, however, the physicochemical data can only help by providing a rough estimate of the persistence of a crude oil or oil product in the aquatic environment [791].

That said, oils and oil products with the least persistence in a water environment would have low molecular weights, high solubilities, high vapor pressures, and low octanol/water partition coefficients (Kow). Oils and oil products with the greatest persistence would have the opposite. The low-molecular-weight hydrocarbons are more soluble, have a higher vapor pressure, and have a lower Kow than heavier products [791].

> NOTE: A comprehensive review of the physicochemical properties of several classes of crude oil and oil products found their persistence in the aquatic environment to rank as follows (from most persistent to least persistent): Residual asphaltenes > Heavy crude oil > Medium crude oil > Fuel oil #6 > Light crude oil > Lube oils > Fuel oil #2 > Jet fuel > Gasoline [791].

Several general compositional changes can be expected as an oil weathers [713]:

1. Loss of low boiling (less than 20 carbons) aromatic and saturated hydrocarbons through evaporation.
2. Loss of low boiling (less than 15 carbons) aromatic hydrocarbons through dissolution.
3. An increased relative importance of unresolved naphthenic and naphthenoaromatic compounds.
4. An increased importance of highly branched aliphatic hydrocarbons (like isoprenoids) relative to straight chain and singly methyl-branched molecules due to selective depletion of n-alkanes by biodegradation.
5. An increased importance of alkylated (dimethyl to tetramethyl) phenanthrene and dibenzothiophene compounds relative to other aromatics through combined weathering processes.
6. An increased importance of polycyclic aliphatic (like pentacyclic triterpanes) compounds relative to all saturated compounds [713].

The following table shows how the exposure of a spilled oil to the open environment speeds weathering. Note in the table below that the weathered oil PAH values (third column) are lower even though these samples were collected approximately 2 months sooner than the skimmer barge samples (second column):

Table: PAH concentrations (ug/g oil sampled) for three different crude oil sample types taken from the Exxon Valdez oil spill. Concentrations in 1) unweathered oil from the tanker itself (March 1989), 2) oil skimmed from the water immediately after the spill and held in the skimmer barge for about 90 days (July 1989), and 3) weathered oil from Prince

William Sound shorelines (May 1989) were, respectively [790; Reprinted with permission from Environmental Toxicology and Chemistry, Vol.14(11), W.A. Stubblefield, G.A. Hancock, W.H. Ford, and R.K. Ringer, "Acute and Subchronic Toxicity of Naturally Weathered Exxon Valdez Crude Oil in Mallards and Ferrets." Copyright 1995 SETAC]:

Naphthalene: 562, 14, 4
C1-Naphthalene: 1307, 150, 52
C2-Naphthalene: 1739, 740, 283
C3-Naphthalene: 1377, 970, 473
C4-Naphthalene: 767, 760, 423
Acenaphthylene: ND, ND, ND
Acenaphthene: ND, ND, ND
Fluorene: 80, 44, 27
C1-Fluorene: 208, 180, 98
C2-Fluorene: 306, 400, 198
C3-Fluorene: 310, 370, 245
Anthracene: ND, ND, ND
Phenanthrene: 222, 200, 124
C1-Phenanthrene/anthracene: 488, 660, 410
C2-Phenanthrene/anthracene: 629, 870, 564
C3-Phenanthrene/anthracene: 456, 640, 507
C4-Phenanthrene/anthracene: 256, 370, 263
Dibenzothiophene: 189, 150, 73
C1-Dibenzothiophene: 389, 460, 258
C2-Dibenzothiophene: 567, 860, 529
C3-Dibenzothiophene: 508, 880, 593
Fluoranthene: ND, ND, ND
Pyrene: 9, 7, 7
C1-Fluoranthene/pyrene: 63, 68, 70
Benzo(a)fluoranthene: ND, ND, 1
Chrysene: 41, ND, 54
C1-Chrysene: 73, 120, 120
C2-Chrysene: 93, 150, 144
C3-Chrysene: 79, 120, 101
C4-Chrysene: 64, 69, 58
Benzo(a)fluoranthene [sic]: 6, ND, 1
Benzo(k)fluoranthene: ND, ND, 2
Benzopyrene: 12, ND, 1
Indeno(1,2,3-c,d)pyrene: ND, ND, ND
Dibenz(a,h)anthracene: ND, ND, ND
Benzo(g,h,i)perylene: ND, ND, 1

ND = not detected.

For comparison, the following table lists some of the specific hydrocarbon content (ppm) of water soluble fraction from 10% oil-in-water solution of the 4 test oils (measured by gas chromatography) [770]:

COMPOUNDS	SOUTH LA CRUDE	KUWAIT CRUDE	NO. 2 FUEL OIL	BUNKER C RESIDUAL

Mono-aromatic				
Benzene	6.75	3.36	0.55	0.04
Toluene	4.13	3.62	1.04	0.08
Di- and tri- aromatics				
Naphthalene	0.12	0.02	0.84	0.21
1-Methylnaphthalene	0.06	0.02	0.34	0.19
2-Methylnaphthalene	0.05	0.008	0.48	0.20
Dimethylnaphthalenes	0.06	0.02	0.24	0.20
Trimethylnaphthalenes	0.008	0.003	0.03	0.10
Fluorene	0.001	0.001	0.009	0.005
Methylfluorenes	0.001	0.001	0.009	0.004
Phenanthrene	0.001	0.001	0.010	0.009
Methylphenanthrenes	0.002	0.001	0.007	0.011

The table below shows how as evaporation of a crude oil continues, its solubility decreases. (Although the solubility units in the table below are unfamiliar, the inversely proportional relationship of degree of weathering to solubility remains evident.):

Table: Relationship of weathering to solubility for several crude oils [683]:

CRUDE OIL	DEGREE OF WEATHERING (% evap'd)	SOLUBILITY* (g/m3)
Norman Wells	0	32.3
	6	27
	12	14.6
	20.4	7.3
	36.7	0.68
	43.2	0.14
Prudhoe Bay	0	29.25
	9.8	4.89
	18.2	0.15
	24.4	0.10
Lago Medio	0	25.5
	22.3	0.6

* = estimated subcooled liquid solubility

A brief discussion of each of the primary (physical) weathering processes mentioned above follows:

SPREADING: As oil enters the environment, it begins to spread immediately. The viscosity of the oil, its pour point, and the ambient temperature will determine how rapidly the oil will spread, but light oils typically spread more rapidly than heavy oils. The rate of spreading and ultimate thickness of the oil slick will affect the rates of the other weathering processes. For example, discharges that occur in geographically contained areas (such as a pond or slow-moving stream) will evaporate more slowly than if the oil were allowed to spread. Most of this process occurs within the first week after the spill [771].

EVAPORATION: Evaporative processes begin immediately after oil is discharged into the environment [771]. Some light products (like 1- to 2-ring aromatic hydrocarbons and/or low molecular weight alkanes less than n-C15) may evaporate entirely; a significant fraction of heavy refined oils also may evaporate [657,771]. For crude oils, the amount lost to evaporation can typically range from approximately 20 to 60 percent. The primary factors that control evaporation are the composition of the oil, slick thickness, temperature and solar radiation, windspeed and wave height. While evaporation rates increase with temperature, this process is not restricted to warm climates. For the Exxon Valdez incident, which occurred in cold conditions (March 1989), it has been estimated that appreciable evaporation occurred even before all the oil escaped from the ship, and that evaporation ultimately accounted for 20 percent of the oil. Most of this process occurs within the first few days after the spill [771].

DISSOLUTION: Dissolution is the loss of individual oil compounds into the water. Many of the acutely toxic components of oils such as benzene, toluene and xylene will readily dissolve into water. This process also occurs quickly after a discharge, but tends to be less important than evaporation. In a typical marine discharge, generally less than 5 percent of the benzene is lost to dissolution while greater than 95 percent is lost to evaporation. (For alkylated PAHs, solubility is inversely proportional to the number of rings and extent of alkylation [657].) The dissolution process is thought to be much more important in rivers because natural containment may prevent spreading, reducing the surface area of the slick and thus retarding evaporation. At the same time, river turbulence increases the potential for mixing and dissolution. Most of this process occurs within the first hour of the spill [771].

DISPERSION: The physical transport of oil droplets into the water column is referred to as dispersion. This is often a result of water surface turbulence, but also may result from the application of chemical agents (dispersants). These droplets may remain in the water column or coalesce with other droplets and gain enough buoyancy to resurface. Dispersed oil tends to biodegrade and dissolve more rapidly than floating slicks because of high surface area relative to volume. Most of this process occurs from about half an hour to half a day after the spill [771].

EMULSIFICATION: Certain oils tend to form water-in-oil emulsions (where water is incorporated into oil) or "mousse" as weathering occurs. This process is significant because, for example, the apparent volume of the oil may increase dramatically, and the emulsification will slow the other weathering processes, especially evaporation. Under certain conditions, these emulsions may separate and release relatively fresh oil. Most of this process occurs from about half a day to two days after the spill [771].

SEDIMENTATION or ADSORPTION: As mentioned above, most oils are buoyant in water. However, in areas with high suspended sediment levels, oils may be transported to the river, lake, or ocean floor through the process of sedimentation. Oil may adsorb to sediments and sink or be ingested by zooplankton and excreted in fecal pellets which may settle to the bottom. Oil stranded on shorelines also may pick up sediments, refloat with the tide, and then sink. Most of this process occurs from about two to seven days after the spill [771].

OTHER: Aeolian transport (relocation by wind) can also occur [771].

Case Study:

> The following case study illustrates how a crude oil trapped in mangrove sediments experienced very little weathering [622]:
>
> On April 27, 1986 a storage tank at the Texaco Refineria Panama on the Caribbean coast of Panama ruptured, releasing ~240,000 barrels of medium weight crude oil into Cativa Bay. On May 4, a storm broke the containment booms, releasing ~150,000 barrels of oil into the Atlantic Ocean. Winds, tides and rain runoff washed part of the oil onto exposed shorelines. Some of the oil was carried back into Cativa Bay, and some was washed into adjacent embayments with mangrove shorelines. By May 15, oil had spread along the coast and washed across fringing reefs and into mangrove forests and small estuaries [622].
>
> Initial weathering removed labile (unstable) oil components such as n-alkane hydrocarbons from oiled surface sediments within 6 months after the discharge. However, total oil concentrations remained high, up to 20% of dry weight in surface sediments, for at least the first 4 years following the discharge. Residual pools of oil in mangrove sediments were sufficiently fluid to flow out when sediments were cored or disturbed 5 years after the discharge. Most of the oozing oil was highly degraded, but one oiled stream contained a fresh oil residue with a full suite of n-alkanes. Subsequent chemical analysis confirmed that this oil was the crude oil mixture discharged in 1986. Release of oil from pools under and around the collapsed Refineria Panama storage tank and from mangrove sediments caused chronic reoiling for at least 5 years following the discharge, and undegraded oil residues were found in some heavily oiled sediments 6 years after the discharge. Thus, the

discharge site, initially injured by a single point-source of oil, became a chronic source of oil contamination. Hydrocarbon chemistry confirmed the long-term persistence of crude oil in mangrove sediments, with pools of trapped oil maintaining consistent hydrocarbon composition. The frequency and amount of reoiling differed among habitats. Secondary reoiling was heaviest in sheltered drainage systems of the mangrove environment, where oil continuously leaked from the sediment, but also occurred along the open coast and along channels. Seasonal variation in weather, water levels and tidal flushing affected the amount of oil released [622].

Laboratory and/or Field Analyses:

Recent (1991) studies have indicated that EPA approved methods used for oil spill assessments (including total petroleum hydrocarbons method 418.1, semivolatile priority pollutant organics methods 625 and 8270, and volatile organic priority pollutant methods 602, 1624, and 8240) are all inadequate for generating scientifically defensible information for Natural Resource Damage Assessments [468]. These general organic chemical methods are deficient in chemical selectivity (types of constituents analyzed) and sensitivity (detection limits); the deficiencies in these two areas lead to an inability to interpret the environmental significance of the data in a scientifically defensible manner [468].

PAHs are an important hazardous component of most petroleum products (See also: PAHs as a group entry).

The relative proportions of hazardous compound constituents present in petroleum-based oil contamination is typically quite variable. The lab analyses most appropriate for measuring different types of oil contamination depend upon the type of oil involved and the reason for measuring the contamination. The farther one progresses from lighter towards heavier oils (the general progression from light towards heavy is the following: Diesel, No. 2 Fuel Oil, Light Crudes, Medium Crude Oils, Heavy Crudes, No. 6 Fuel Oil, etc.) the greater the percentage of PAHs and other semi-volatiles (many of which are not so immediately toxic as the volatiles but which can result in long-term/chronic impacts). These heavier oils thus need to be analyzed for the semi volatile compounds which typically pose the greatest long-term risk, PAHs and alkylated PAHs.

Petroleum products consists of thousands of individual compounds. Therefore, the recommended lab analysis will depend upon the product of concern (for example, possible gasoline contamination would require a different set of scans than possible fuel oil no. 6 contamination). The decision to use a Total Petroleum Hydrocarbon (TPH) method, such as EPA 418.1 by Infrared Spectroscopy (IR) method or gas chromatography with flame ionization detection (GC/FID), vs. an expanded scan, such as gas chromatography with mass spectrometry detection (GC/MS) in the select ion mode (SIM), depends on desired precision, funding, and the question at hand. The term "LC", or "lethal concentration" is basically inappropriate for oil products since there is no single concentration of any one compound within toxicity test solutions that are derived from oil products. The term "LC50" as applied to oil products is quite misleading to a reviewer of oil product toxicity data since one immediately assumes that the number associated with the concept (like, an LC50 of 1000 mg/L) represents the dissolved fraction which was the "effective concentration" [791].

A comprehensive study of LC50 values for a variety of oil products found the comparability of these values to be limited due to the variability of test methodologies used. Variables in methodology include: the presence or absence of free product in the test chambers; whether test chambers were open or closed; if the test was conducted in freshwater or saltwater; how long the oil product-water solutions were mixed prior to adding test organisms; and how the actual concentration was calculated. The study found that reported LC50 values for oil products from the same product class (classes include: Bunker, Crude, Lube oil, Diesel, Gasoline, Jet fuel) can vary over three orders of magnitude depending on the methods used in conducting the test [791].

In interpreting data, it is important to understand that contaminants data from different labs, different states, and different agencies, collected by different people, are often not very comparable (see also, discussion in the disclaimer section at the top of this entry).

As of 1997, the problem of lack of data comparability (not only for water methods but also for soil, sediment, and tissue methods) between different "standard methods" recommended by different agencies seemed to be getting worse, if anything, rather than better. The trend in quality assurance seemed to be for various agencies, including the EPA and others, to insist on quality assurance plans for each project. In addition to quality control steps (blanks, duplicates, spikes, etc.), these quality assurance plans call for a step of insuring data comparability [1015,1017]. However, the data comparability step is often not given sufficient consideration. The tendency of agency guidance (such as EPA SW-846 methods and some other new EPA methods for bio-concentratable substances) to allow more and more flexibility to select options at various points along the way, makes it harder in insure data comparability or method validity. Even volunteer monitoring programs are now strongly encouraged to develop and use quality assurance project plans [1015,1017].

At minimum, before using contaminants data from diverse sources, one should determine that field collection methods, detection limits, and lab quality control techniques were acceptable and comparable. The goal is that the analysis in the concentration range of the comparison benchmark concentration should be very precise and accurate.

It should be kept in mind that quality control field and lab blanks and duplicates will not help in the data quality assurance goal as well as intended if one is using a method prone to false negatives. Methods may be prone to false negatives due to the use of detection limits that are too high, the loss of contaminants through inappropriate handling, or the use of inappropriate methods. The use of inappropriate methods is particularly common related to oil products.

A decision tree (dichotomous key) has been developed for the selection of lab methods for measuring contamination from light, midrange, and heavy oil products. Keys for light and heavy products can be found in the Gasoline General and Fuel Oil Number 6 entries, respectively. The midrange key is provided as follows as a typical example of an often necessary decision process (Roy Irwin, National Park Service, Personal Communication, 1997):

Draft Decision Tree (dichotomous key) for selection of lab methods for measuring contamination from light crude oils and middle distillate petroleum products (all diesels, jet fuels, kerosene, Fuel oil 2, Heating Oil 2):

1a. Your main concern is biological effects of petroleum products..2

1b. Your main concern is cleanup or remediation but no ecological or human resources are at risk............3

2a. The resource at risk is primarily humans via a drinking water pathway, either the contamination of groundwater used for drinking water, or the fresh* or continuing contamination of surface waters used as drinking water, or the risk is primarily to aquatic species in confined** surface waters from a fresh* spill, or the risk is to surface waters re-emerging from contaminated groundwater resources whether the spill is fresh* or not; the medium and/or pathway of concern is water rather than sediments, soil, or tissues 4

2b. The resource at risk is something else.....................5

3a. The spilled substance is a fresh* oil product of known composition: If required to do so by a regulatory authority, perform whichever Total Petroleum Hydrocarbon (TPH) analysis specified by the regulator. However, keep in mind that due to its numerous limitations, the use of the common EPA method 418.1 for Total Petroleum Hydrocarbons is not recommended as a stand-alone method unless the results can first be consistently correlated (over time, as the oil ages) with the better NOAA protocol expanded scan*** for polycyclic aromatic hydrocarbons (PAHs) and alkyl PAHs. If not required to perform an EPA method 418.1-based analysis for TPH, instead perform a Gas Chromatography/Flame Ionization Detection (GC/FID) analysis for TPH using the spilled substance as a calibration standard. GC/FID methods can be sufficient for screening purposes when the oil contamination is fresh*, unweathered oil and when one is fairly sure of the source [657]. If diesel 1D was spilled, perform TPH-D (1D) using California LUFT manual methods (typically a modified EPA method 8015) [465] or a locally available GC/FID method of equal utility for the product spilled. However, no matter which TPH method is used, whether based on various GC/FID or EPA method 418.1 protocols, the investigator should keep in mind that the effectiveness of the method typically changes as oil ages, that false positives or false negatives are possible, and that the better Gas Chromatography-Mass Spectrometry-Selected Ion Mode (GC/MS/SIM) scans (such as the NOAA expanded scan***) should probably be performed at the end of remediation to be sure that the contamination has truly been cleaned up.

3b. The spilled product is not fresh* or the contamination is of unknown or mixed composition........................6

4. Analyze for Benzene, Toluene, Ethyl Benzene, and Toluene (BTEX) compounds in water as part of a broader scan of volatiles using EPA GC/MS method 8260 (8260 is replacing the older 8240 method in SW-846 [1013]). The standard EPA GC/MS method 8260 protocol will be sufficient for some applications, but the standard EPA method 8240 (and especially the less rigorous EPA BTEX methods such as method 8020 for soil and method 602 for water) are all inadequate for generating scientifically defensible information for Natural Resource Damage Assessments [468]. The standard EPA methods are also inadequate for risk assessment purposes. Thus, when collecting information for possible use in a Natural Resource Damage Assessment or risk assessment, it is best to ask the lab to analyze for BTEX compounds and other volatile oil compounds using a modified EPA GC/MS method 8260 (8260 is replacing the older 8240 method in SW-846 [1013]) method using the lowest possible Selected Ion Mode detection limits and increasing the analyte list to include as many alkyl BTEX compounds as possible. Also analyze surface or (if applicable) ground water samples for polycyclic aromatic hydrocarbons (PAHs) and alkyl PAHs using the NOAA protocol expanded scan*** modified for water samples using methylene chloride extraction. If the contaminated water is groundwater, before the groundwater is determined to be remediated, also analyze some contaminated sub-surface soils in contact with the groundwater for BTEX compounds (EPA GC/MS method 8260 (8260 is replacing the older 8240 method in SW-846 [1013])), and PAHs (NOAA protocol expanded scan***). The magnitude of any residual soil contamination will provide insight about the likelihood of recontamination of groundwater resources through equilibria partitioning mechanisms moving contamination from soil to water.

5a. The medium of concern is sediments or soils.................6

5b. The medium of concern is biological tissues.................7

6. Perform the NOAA protocol expanded scan*** for polycyclic aromatic hydrocarbons (PAHs) and alkyl PAHs. If there is any

reason to suspect fresh* or continuing contamination of soils or sediments with lighter volatile compounds, also perform EPA GC/MS method 8260 (8260 is replacing the older 8240 method in SW-846 [1013]) using the lowest possible Selected Ion Mode (SIM) detection limits and increasing the analyte list to include as many alkyl Benzene, Toluene, Ethyl Benzene, and Xylene (BTEX) compounds as possible.

7a. The problem is direct coating (oiling) of wildlife or plants with spilled oil product....................................8

7b. The problem is something else...............................9

8. Perform NOAA protocol expanded scan*** for polycyclic aromatic hydrocarbons (PAHs) and alkyl PAHs and/or GC/FID fingerprinting of the coating oil only if necessary to identify the source or exact oil. If the source is known and no confirmation lab studies are necessary: dispense with additional chemical laboratory analyses and instead document direct effects of coating: lethality, blinding, decreased reproduction from eggshell coating, etc., and begin cleaning activities if deemed potentially productive after consolations with the Fish and Wildlife Agencies.

9a. The concern is for impacts on water column organisms (such as fish or plankton)..10

9b. The concern is for something else (including benthic organisms)...11

10. If exposure to fish is suspected, an HPLC/Fluorescence scan for polycyclic aromatic hydrocarbon (PAH) metabolites in bile may be performed to confirm exposure [844]. For bottom-dwelling fish such as flounders or catfish, also analyze the bottom sediments (see Step 6 above). Fish which spend most of their time free-swimming above the bottom in the water column can often avoid toxicity from toxic petroleum compounds in the water column, but if fish are expiring in a confined** habitat (small pond, etc.), EPA GC/MS method 8260 (8260 is replacing the older 8240 method in SW-846 [1013]) and the NOAA protocol expanded scan*** for PAHs could be performed to see if Benzene, Toluene, Ethyl Benzene, and Xylene (BTEX), naphthalene, and other potentially toxic compounds are above known acute toxicity benchmark concentrations. Zooplankton populations impacted by oil usually recover fairly quickly unless they are impacted in very confined** or shallow environments [835] and the above BTEX and PAH water methods are often recommended rather than direct analyses of zooplankton tissues.

11a. The concern is for benthic invertebrates: analyze invertebrate whole-body tissue samples and surrounding sediment samples for polycyclic aromatic hydrocarbons (PAHs) and alkyl PAHs using the NOAA protocol expanded scan***. If the spill is fresh* or the source continuous, risk assessment needs may also require that the sediments which form the habitat for benthic invertebrates be analyzed for Benzene, Toluene, Ethyl Benzene, and Xylene (BTEX) and other volatile compounds using EPA GC/MS method 8260 (8260 is replacing the older 8240 method in SW-846 [1013]) or modified EPA method 8260 in the Selected Ion Mode (SIM). Bivalve invertebrates such as clams and mussels do not break down PAHs as well or as quickly as do fish or many wildlife species. They are also less mobile. Thus, bivalve tissues are more often directly analyzed for PAH residues than are the tissues of fish or wildlife.

11b. The concern is for plants or for vertebrate wildlife including birds, mammals, reptiles, and amphibians: polycyclic aromatic hydrocarbons (PAHs) and other petroleum hydrocarbons break down fairly rapidly in many wildlife groups and tissues are not usually analyzed directly. Instead direct effects are investigated and water, soil, sediment, and food items encountered by wildlife are usually analyzed for PAHs and alkyl PAHs using the NOAA protocol expanded scan***. If the spill is fresh* or the source continuous, risk assessment needs may also require that these habitat media also be analyzed for Benzene, Toluene, Ethyl Benzene, and Xylene (BTEX) and other volatile compounds using EPA GC/MS method 8260 (8260 is replacing the older 8240 method in SW-846 [1013]) or modified EPA method 8260 in the Selected Ion Mode (SIM). Less is known about plant effects. However, the same methods recommended above for the analyses of water (Step 4 above) and for sediments or soils (Step 6 above) are usually also recommended for these same media in plant or wildlife habitats. If wildlife or plants are covered with oil, see also Step 8 (above) regarding oiling issues.

* Discussion of the significance of the word "fresh": The word "fresh" cannot be universally defined because oil breaks down faster in some environments than in others. In a hot, windy, sunny, oil-microbe-rich, environment in the tropics, some of the lighter and more volatile compounds (such as the Benzene, Toluene, Ethyl Benzene, and Xylene compounds) would be expected to disappear faster by evaporation into the environment and by biodegradation than in a cold, no-wind, cloudy, oil-microbe-poor environment in the arctic. In certain habitats, BTEX and other relatively water soluble compounds will tend to move to groundwater and/or subsurface soils (where degradation rates are typically slower than in a sunny well aerated surface environment). Thus, the judgement about whether or not oil contamination would be considered "fresh" is a professional judgement based on a continuum of possible scenarios. The closer in time to the original spill of non-degraded petroleum product, the greater degree the source is continuous rather than the result of a one-time event, and the more factors are present which would retard oil evaporation or breakdown (cold, no-wind, cloudy, oil-microbe-poor conditions, etc.) the more likely it would be that in the professional judgement experts the

oil would be considered "fresh." In other words, the degree of freshness is a continuum which depends on the specific product spilled and the specific habitat impacted. Except for groundwater resources (where the breakdown can be much slower), the fresher the middle distillate oil contamination is, the more one has to be concerned about potential impacts of BTEX compounds, and other lighter and more volatile petroleum compounds.

To assist the reader in making decisions based on the continuum of possible degrees of freshness, the following generalizations are provided: Some of the lightest middle distillates (such as Jet Fuels, Diesel, No. 2 Fuel Oil) are moderately volatile and soluble and up to two-thirds of the spill amount could disappear from surface waters after a few days [771,835]. Even heavier petroleum substances, such as medium oils and most crude oils will evaporate about one third of the product spilled within 24 hours [771]. Typically the volatile fractions disappear mostly by evaporating into the atmosphere. However, in some cases, certain water soluble fractions of oil including Benzene, Toluene, Ethyl Benzene, and Xylene (BTEX) compounds move down into groundwater. BTEX compounds are included in the more volatile and water soluble fractions, and BTEX compounds as well as the lighter alkanes are broken down more quickly by microbes than heavier semi-volatiles such as alkyl PAHs and some of the heavier and more complex aliphatic compounds. Thus after a week, or in some cases, after a few days, there is less reason to analyze surface waters for BTEX or other volatile compounds, and such analyses should be reserved more for potentially contaminated groundwaters. In the same manner, as the product ages, there is typically less reason to analyze for alkanes using GC/FID techniques or TPH using EPA 418.1 methods, and more reason to analyze for the more persistent alkyl PAHs using the NOAA protocol expanded scan***.

** Discussion of the significance of the word "confined": Like the word "fresh" the word "confined" is difficult to define precisely as there is a continuum of various degrees to which a habitat would be considered "confined" versus "open." However, if one is concerned about the well-being of ecological resources such as fish which spend most of their time swimming freely above the bottom, it makes more sense to spend a smaller proportion of analytical funding for water column and surface water analyses of Benzene, Toluene, Ethyl Benzene, and Xylene (BTEX) and other volatile or acutely toxic compounds if the spill is in open and/or deep waters rather than shallow or "confined" waters. This is because much of the oil tends to stay with a surface slick or becomes tied up in subsurface tar balls. The petroleum compounds which do pass through the water column often tend to do so in small concentrations and/or for short periods of time, and fish and other pelagic or generally mobile species can often swim away to avoid impacts from spilled oil in "open waters." Thus in many large oil spills in open or deep waters, it has often been difficult or impossible to attribute significant impacts to fish or other pelagic or strong swimming mobile species in open waters. Lethality has most often been associated with heavy exposure of juvenile fish to large amounts of oil products moving rapidly into shallow or confined waters [835]. Different fish species vary in their sensitivity to oil [835]. However, the bottom line is that in past ecological assessments of spills, often too much money has been spent on water column analyses in open water settings, when the majority of significant impacts tended to be concentrated in other habitats, such as benthic, shoreline, and surface microlayer habitats.

*** The lab protocols for the expanded scan of polycyclic aromatic hydrocarbons (PAHs) and alkyl PAHs have been published by NOAA [828].

End of decision tree key.

Other information:

Metals:

Since metals are a concern with used motor oil (see Chem.Detail Section,) an ICP scan for a general suite of metals should supplement organic analyses.

Organics:

Although EPA method 418.1: Petroleum Hydrocarbons expressed as Total Petroleum Hydrocarbons (TPH), is recommended by many State agencies, some consulting firms, and some laboratories for certain regulatory and screening applications (often leaking underground storage tanks), this method is not well suited to crude oil contamination or to the more persistent hazardous constituents in oil. (See entry entitled: Petroleum Hydrocarbons expressed as Total Petroleum Hydrocarbons). Low values tend to give the mistaken impression that a site is clean when it really isn't (a false negative). For example, a field test of bioremediation of soils contaminated with Bunker C (a heavy fuel) at a refinery in Beaumont, Texas, utilized oil and grease data, which (although the data was quite variable) seemed to indicate bioremediation was taking place [728]. A comparison of the oil and grease data at this site with TPH data at this site suggested the same thing, that the data was quite variable but if anything, the oil was being slowly being cleaned up by bioremediation (Bruce Herbert, Texas A. and M., Department of Geology, personal communication, 1995). However, a later study of the same site utilizing the expanded scan for PAHs [828] (a modified EPA 8270 including alkyl homologues and lower detection limits) [828], indicated that very little bioremediation of hazardous alkyl PAHs and multi-ring PAHs was actually taking place [727]. Thus, utilizing either oil and grease or TPH analyses would tend to lead one to the faulty conclusion that the harmful compounds were being naturally cleaned up at an acceptable rate. This is partly because the TPH and oil and grease methods tend to favor the lighter and less alkylated PAHs, whereas many of the carcinogenic and longer lasting PAHs are the heavier multi-ringed and alkylated compounds.

Abstracts on Fingerprinting:

> Wade, T.L., T.J. Jackson, T.J. McDonald, J.L. Sericano, and J.M. Brooks. 1993. Oyster Polynuclear Aromatic Hydrocarbon Fingerprinting Applied to the Apex Barge Oil Spill. Society of Environmental Toxicology and Chemistry (SETAC) 14th annual meeting. Westin Galleria and Oaks Houston, TX., (Nov. 14-18 1993), p. 17.
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> > An estimated 692,000 gallons of catalytic feed stock oil was spilled into Galveston Bay on July 28, 1990, when a tanker collided with three Apex barges in the Houston Ship Channel. Oysters were collected and analyzed from Galveston Bay Todd's Dump (GBTD) before the spill (235 days) and after the spill (6, 37, 132, 495, and 851 days). Oysters were also collected from Galveston Bay Redfish Island (GBRI), a site known to be impacted by the spill, 37 and 110 days after the spill. The spilled oil was also analyzed. The concentration of 18 polynuclear aromatic hydrocarbons (PAHs), measured as part of the National Oceanic and Atmospheric Administration's National Status & Trends (NS&T) showed a sharp increase from 100 ng/g (235 days before the spill) to over 600 ng/g (one week after the spill). Concentrations of these 19 PAHs were also found at GBRI. Fingerprinting techniques applied to data from oyster analyses demonstrated the presence of bioavailable Apex Barge oil 37, 110, 132 days after the spill at GBTD and GBRI. Fingerprinting becomes less diagnostic with time due to possible environmental weathering of the oil.
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> A.G. Requejo, T. McDonald, G. Denoux, M.C. Kennicutt, R. Sassen, and J.M. Brooks. 1993. Multivariate Analysis of Environmental Data: A tool for interpreting results of "fingerprinting" analyses. Society of Environmental Toxicology and Chemistry (SETAC) 14th annual meeting. Westin Galleria and Oaks, Houston, TX., (Nov. 14-18 1993), p. 17.
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> > Chemical Analyses of environmental samples

using "fingerprinting" techniques often result in large quantities of data for each sample. For example, a typical soil or sediment analysis might include concentrations of targeted saturated hydrocarbons, polynuclear aromatic hydrocarbons, chlorinated hydrocarbons, and trace metals, in addition to bulk parameters such as organic carbon and nitrogen content and grain size distributions. The sheer volume and diversity of this type of data can make its interpretation difficult. Multivariate analytical techniques such as Principal Components Analysis (PCA) are ideally suited for the reduction and synthesis of such data sets. PCA employs eigenvector analysis to evaluate the degree of similarity between samples and establish the interrelationship between measured analytes. The major advantages of PCA in comparison to traditional data interpretation approaches are that it is fast, objective, and employs all the data measured. The utility of this approach will be demonstrated using several different sets of environmental "fingerprinting " data. Included among these are fluorescence and polynuclear aromatic hydrocarbon data from bioremediated soil samples containing petroleum and trace organic and inorganic data from estuarine sediments (Casco Bay, Maine).

See also: lab sections of various petroleum products and lab sections on various components of oil products.

For additional details on protocols, including field collection protocols, see the Oil Spill entry.