ENVIRONMENTAL CONTAMINANTS ENCYCLOPEDIA

CRUDE OIL ENTRY

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Like a library or most 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 with out 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 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).

Crude Oil (CAS number 8002-05-9)

Brief Introduction:

Br.Class: General Introduction and Classification Information:

According to the U.S. Coast Guard Emergency Response Notification System (ERNS), crude oil is one of the most commonly spilled petroleum products in the United States, both by number of notifications and by volume [635].

Crude oils vary in physical characteristics such as color, viscosity, and specific gravity. Color ranges from light yellow-brown to black. Viscosity varies from free-flowing to a substance that will barely pour. Specific gravity is used to classify crude oil as light, medium (intermediate), or heavy [782].

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]. Crude petroleum, which may consist of hundreds of individual compounds must be refined to separate the constituent into useful fractions [661]. For more information on refining, see the "Petroleum, General" entry.

Each crude oil is a unique mixture, not matched exactly in composition or properties by any other sample of crude oil [747].

Br.Haz: General Hazard/Toxicity Summary:

In general, spilled oil is most harmful when shallow, productive waters, porous sediments, low energy aquatic environments, or special-use habitats are affected. Examples of high risk locations are wetlands, sheltered tidal flats, shallow bays, coarse sand and gravel beaches, and sites with concentrated reproductive and migratory activities [782].

Crude oil and petroleum products vary considerably in their toxicity, and the sensitivity of fish to petroleum varies according to species [782]. The water soluble fractions of crude oil can stunt fish growth (Denny Buckler, NBS, Columbia, MO, personal communication, 1995).

The impacts to fish are primarily to the eggs, larvae, and early juveniles, with limited effects on the adults [773,782]. 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.

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].

Nevertheless, there are several potential effects of oil on the fish or fishery industry [622]: One effect is depressed feeding. Another observed effect is decreased swimming activity and increased mortality. A third is mortality to eggs and larvae (such as after the Argo Merchant No.6 fuel oil discharge where 20% of the cod eggs and 46% of the pollock eggs in the discharge zone were dead) [622].

During the Torrey Canyon (Bunker C) discharge 90% of the pilchard eggs in the discharge area were killed. However, compared to the naturally high mortality rates of fish eggs these losses would be hard to detect in the commercial harvest. Following the Amoco Cadiz (Crude oil) discharge, a 1-year old class of flatfish was thought to have been reduced. A fourth effect is the exclusion of fishermen from the fishing grounds and other disruption of fishing which can change the population balance to date (such as salmon overescapement in Prince William Sound after the Exxon Valdez (crude oil)). Another effect is the fouling of fishing gear. Sixth, is the tainting of fish (such as change in flavor or smell) and the public's fear of tainting, mortality or other effects of non-motile inshore species, such as rockfish. Seventh is the mortality or other effects of fish maintained in mariculture enclosures (where escape of fish is prevented, like when the Braer oil discharge off the Shetlands affected salmon in mariculture enclosures). Finally, there are several sublethal effects such as fin erosion, ulceration of the integument, liver damage, lesions in the olfactory tissue, reduced hatching success, reduced growth, change in egg buoyancy, malformations that interfere with feeding, arrest of cell division, and genetic damage [622].

Oiling of feathers is considered to be the primary cause of most bird deaths following oil spills [713]. Oil disrupts the fine strand structure of the feathers, resulting in loss of water repellency and in decreased body insulation [773]. As the oiled plumage becomes matted, water penetrates the feathers and chills the body; the combined results are a loss of buoyancy and possible hypothermia [773]. The natural response to oil-matted plumage is preening; 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]. Chicks may be exposed to petroleum by ingesting food regurgitated by impacted adults [773].

No long-term population effects of oil pollution on pinnipeds have been documented (or rigorously examined for long enough periods to do so). Vulnerability of cetaceans to discharges is highest for species with small ranges (coastal, ice-dwelling, and/or riverine habitats), limited diets, poor behavioral flexibility, and small populations. For pinnipeds, stressed or nursing animals and recently weaned pups are most vulnerable. Sea otters and other fur-bearing mammals are the most vulnerable species [622].

The toxicity of crude oil can be interpreted as the toxicity of a complex mixture of inorganic and organic chemicals. However, a great deal of uncertainty exists in the use of dose-response relationships based on crude oil as a whole mixture [734]. An alternative approach which is often used is the "indicator chemical approach." This involves selecting a subset of chemicals from the whole mixture that represents the "worst-case" in terms of mobility and toxicity [745]. This approach can be used with crude oil with the subsets of chemicals being volatile organics such as benzene, toluene, ethylbenzene, and xylenes (known as BTEX; if present) and polycyclic aromatic hydrocarbons (PAHs). BTEX are of interest because they are soluble in water, highly mobile in the environment, and represent the more volatile and soluble components of crude oil. In addition, benzene is an EPA-defined class A carcinogen. PAHs are not highly mobile but are of interest because they are prevalent in crude oil, represent the heavier or less volatile crude oil components, and several are known animal carcinogens [745].

Little information is available on the toxicokinetics of crude oil as a chemical mixture; the effects of human exposure to crude petroleum oil has not been well studied [734].

Perhaps the most significant biological effects in marine fish are observed in embryos and larvae of certain species [781]. Many studies indicate that petroleum does cause damage in fish [781]. Some laboratory studies and field observations suggest that petroleum does not always damage marine biota [781].

PAHs and their transformation products are among the most hazardous constituents of crude oil. See also: PAHs as a group entry. Most of the toxicity data, however, is on the main parent compounds, rather than on the transformation products [773].

There are few data on oil effects on amphibians and reptiles (like sea turtles) [713]. Extrapolating results from tests of amphibians and reptiles is difficult because of the phylogenetic diversity within each group [713]. And, too little is known to extrapolate safety standards from other kinds of vertebrates. Amphibians are more sensitive to some chemicals than most fish that are commonly tested, but are also much more resistant to some cholinesterase-inhibiting compounds than other classes of vertebrates [713]. Reptiles have fewer routes of exposure and life stages than amphibians, but predictability from one group to another is still largely unknown [713]. 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].

Recovery from the effects of oil spills on local populations of invertebrates can require from a week to 10 years, depending on the type of oil, circumstances of the spill, and organisms affected. Invertebrates (zooplankton) in the water column of large bodies of water return to pre-spill conditions much faster than invertebrates in small bodies of water (fresh-water lakes, streams) [782].

Effects on plankton are short-lived, and zooplankton are more sensitive than phytoplankton. Epifauna, such as mussels and bivalves, often survive oiling as adults due to their protective shells, but they have no enzymatic system for purging. Therefore, bioaccumulation occurs, resulting in reduced feeding absorption efficiency followed by growth reductions [773]. For additional information on effects on invertebrates: see Tis.Misc. section below.

Effects on plants: In general, the data suggest that there is little direct effect of oil on kelps [713]. Eelgrass has been observed to be "almost unaffected" after an oil spill, and also to exhibit little impact from being chronically oiled in a polluted harbor [713]. In contrast, beds of Thallasia have been severely impacted after spills [713]. Also, surfgrass (Phyllospadix) has been observed to bleach and die following spills off California, Washington, and Alaska coasts [713].

Still, in almost all studies of oil spilled on seagrass habitats, the effects on associated biota were more pronounced than the effects on seagrass itself [713]. Recovery from the effects of oil spills on most local plant populations can require from a few weeks to 5 years, depending on the type of oil, circumstances of the spill, and species affected [782].

In the July 1975 spill from the tanker Garbis, discharging 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 [622]. For additional information on effects on plants: see Tis.Misc. section below.

See also: Oil Spills entry for more information on oil vs. wildlife.

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

It was determined that for crude oil there was inadequate evidence for carcinogenicity in humans and limited evidence for carcinogenicity in animals. Still, components of crude oil (certain PAHs like benz(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene, dibenz(a,h)anthracene, and indeno(1,2,3-cd)pyrene) have been found to be carcinogenic in animals and are classified as probable human carcinogens by both the EPA and IARC [734].

Certain carcinogenic effects also have been associated with benzene [609].

The debates on which PAHs, alkyl PAHs, and other aromatics found in crude oil 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.

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].

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).

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].

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: Petroleum, General entry and PAHs as a group entry.

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

Petroleum products contain within them 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].

Pathways for injuries due to incidents involving oil can be either direct or indirect. Direct pathways occur when the natural resource is exposed to the oil or to a chemical compound originating from the oil. Indirect pathways occur when the natural resource is not directly exposed to the oil or to any chemical compounds originating from the oil. Instead, the presence of the oil interferes with a physical, chemical or biological process important to the natural resource; or a use of the natural resource is impaired by the presence of the oil in that environment [713].

Biomagnification of petroleum hydrocarbons through the food chain has not been demonstrated in marine mammals, probably due to their cytochrome P450 system [713].

The following definitions are used in the NOAA HMRAD Shoreline Countermeasures Manual for tropical coastal environments [741]:

Light Oils (Diesel, No. 2 Fuel Oils, Light Crudes) [741]:

- Moderately volatile; will leave residue (up to 1/3 of spilled amount)
- Moderate concentrations of toxic (soluble) compounds
- Will "oil" intertidal resources with long-term contamination potential
- Has potential for subtidal impacts (dissolution, mixing, sorption onto suspended sediments)
- No dispersion necessary
- Cleanup can be very effective

Medium Oils (Most Crudes) [741]:

- About 1/3 will evaporate within 24 hours
- Maximum water-soluble fraction is 10-100 ppm
- Oil contamination of intertidal areas can be severe/long term
- 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 Oils (Heavy Crude Oils, No. 6 fuel, Bunker C) [741]:

- Heavy oils with little or no evaporation or dissolution
- Water-soluble fraction likely to be <10 ppm
- Heavy contamination of intertidal areas likely
- Severe impacts to waterfowl and fur-bearing mammals (coating and ingestion)
- Long-term contamination of sediments possible
- Weathers very slowly
- Dispersion seldom effective
- Shoreline cleanup difficult under all conditions

See also the following separate entries:

Petroleum, General
Oil Spill
PAHs as a group.

Synonyms/Substance Identification:

Petroleum [617]

NOTE: Although "petroleum" is sometimes considered a synonym of crude oil, it is used in this document to refer to petroleum products as a whole, not just as the crude oil from which these products are derived (for example, the "Petroleum, General" entry refers to both crude and refined oils (oil products)).

Base Oil [617]
Coal Liquid [617]
Coal Oil [617]
Crude Oil, Petroleum [617]
Crude Petroleum [617]
Petrol [617,747]
Petroleum Crude [617]
Petroleum Oil [617]
Rock Oil [617,747]
Seneca Oil [617,747]
Naphtha [747]

Associated Chemicals or Topics (Includes Transformation Products):

NOTE: Oil, both crude and refined, 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 Crude Oil also should be aware of the following entries:

Petroleum, General
Oil Spills

NOTE: Since crude oil is the most spilled petroleum product, and crude oil was the product spilled in the Exxon Valdez (resulting in the most oil spill research to date), there is naturally much overlap between Crude Oil topics and Oil Spill topics (see also: Oil Spills entry).

PAHs as a group

NOTE: The PAH section includes a recommended Expanded Scan listing of several PAH and alkyl homolog compounds that may be present in crude oil. For more information on these compounds, refer to the individual entry for the compound of interest.

TPH

Individual compounds of crude oil can be classified into the following two categories [713]:

1) Hydrocarbons, which include alkanes (normal and branched chains), cycloalkanes, alkenes, aromatics, naphthenoaromatics; and

2) Non-hydrocarbons, which include nitrogen, sulfur and oxygen (NSO) compounds, asphaltenes and resins (including NSO heterocyclics), metallo-organics, and inorganic metal salts.

Potential toxicity differs widely among the chemical constituents of oil. Therefore, as noted in the Brief Introduction, the "indicator chemical approach" is often used to evaluate the environmental effects of a chemical mixture [745]. Using this model, the reader may wish to refer to entries on some of the more toxic compounds found in crude oil such as [713]:

Benzene
Ethyl benzene
Toluene
Xylenes

The reader should also refer to individual entries on carcinogenic polyaromatic hydrocarbons (CaPNAs; of primary interest in terms of toxicity) such as [734]:

Benz(a)anthracene
Benzo(a)pyrene (B(a)P)
Benzo(b)fluoranthene
Benzo(k)fluoranthene
Chrysene
Dibenz(a,h)anthracene
Indeno(1,2,3-cd)pyrene

Other PAHs of interest with individual entries include [634] (NOTE: See the PAHs entry for a complete list of possible PAH and alkyl homologs in crude oil):

Naphthalene
Acenaphthylene
Acenaphthene
Anthracene
Fluorene
Phenanthrene
Fluoranthene
Pyrene
Benzo(g,h,i)perylene

See also Forms/Preparations/Formulations section below for a list of 153 existing crude oils.

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

NOTE: Water toxicity data for complex chemical mixtures such as crude oil can be difficult to interpret and use. Methodologies and analytical procedures used in controlled toxicity tests can vary greatly from test to test, thus causing test results to vary also. (One study found that LC50 values can vary over three orders of magnitude depending on the methods used in conducting the toxicity test [791].) They can also vary greatly from methodologies and procedures used in actual field-sample analyses, thus making a comparison of field sample values with toxicity data from the literature potentially difficult [791]. Nevertheless, toxicity data from the literature is included in this Crude Oil entry. This data is perhaps best used to understand the relative toxicity of individual crude oils or crude oil fractions (like the water-soluble fractions). It may also help the reader gain a "ballpark" understanding of his/her own data, depending on the type of data collected.

W.Low (Water Concentrations Considered Low):

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

W.Plants (Water Concentrations vs. Plants):

Acute toxicity data (96h LC50s) were summarized for aquatic macrophytes exposed to soluble hydrocarbons (esp. BTEX) derived from fresh crude oil. The range of concentrations was found to be 10 to 100 mg/L [624].

W.Invertebrates (Water Concentrations vs. Invertebrates):

Mature lobsters (Homarus americanus) were exposed to approximately 10 ppm crude oil for 5 consecutive days and exhibited an increase in response time to food stimulus [713].

Acute toxicity data (96h LC50s) were summarized for several types of invertebrates exposed to fresh crude oil. The ranges of concentrations were found to be: 0.1 to 100 mg/L for larvae and eggs; 100 to 40,000 mg/L for pelagic crustaceans; 56 mg/L for benthic crustaceans; and 1000 to 100,000 for bivalves [624].

Acute toxicity data (96h LC50s) were also summarized for several types of invertebrates exposed to soluble hydrocarbons (esp. BTEX) derived from fresh crude oil. The ranges of concentrations were found to be: 0.1 to 1.0 mg/L for larvae and eggs (all species); 1 to 10 mg/L for pelagic crustaceans; 1 to 100 for gastropods (snails); 5 to 50 for bivalves (oysters, clams); 1 to 10 for benthic crustaceans (lobsters, crabs, etc.); and 1 to 10 for other benthic invertebrates [624].

Table 1: Ranking of acute toxicity of water soluble fractions (WSF) of crude oils to Artemia based on concentrations as % of WSF. (Rank 1 = most toxic; 22 = least toxic) [684]. See "Petroleum, General" entry for complete ranking of 22 different crude and refined oils.

CRUDE OIL	4-HR EC50*	48-HR EC50	48-HR LC50**
Western Sweet	6	11	13
Synthetic	11	7	7
Hibernia	12	11	12
Prudhoe Bay	12	9	10
Transmountain	9	14	16

Norman Wells	8	14	11
Venezuelan BCF-22	7	9	9
Atkinson	12	18	16
Bent Horn	12	13	14
Amauligak	12	17	16
Lago Medio	12	16	15
Tarsuit	12	18	16

* = concentration at which 50% of the test population exhibited the effect of immobilization.
** = concentration at which 50% of the test population died.

Note: WSF values are of interest in looking at relative toxicity of different substances, but are not of much value for predicting what will happen at a new spill site (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].

Note from Roy Irwin: I don't know of any lab method which measures the concentration of crude oil as a whole after it has been spilled in open waters, concentrations may reflect lab concentrations estimated by dilution ratios (Roy Irwin, National Park Service, Personal Communication, 1996). Since this information can't be replicated in the field, it has questionable value related to spills and the information which one instead needs to obtain to compare to benchmarks and standards includes the concentrations of individual PAHs and alkyl PAHs [828].

Table 2: Ranking of the acute toxicity of water soluble fractions (WSF) of crude oils to Daphnia magna based on concentrations as % of WSF. (Rank 1 = most toxic; 22 = least toxic) [684]. See "Petroleum, General" entry for complete ranking of 22 different crude and refined oils.

	4-HR	48-HR	48-HR
CRUDE OIL	EC50	EC50	LC50
Western Sweet Blend	5	6	11

Synthetic Crude Oil	6	7	10
Hibernia	7	9	14
Prudhoe Bay	7	10	15
Transmountain	7	11	12
Norman Wells	11	11	13
Venezuelan BCF-22	12	13	17
Atkinson	14	18	19
Bent Horn	15	13	8
Amauligak	15	15	16
Lago Medio	17	18	19
Tarsuit	18	21	18

NOTE regarding tables 1 and 2 above:

> The ranking of these may have been different if measured concentrations (mg/L units) had been used as the basis for the ranking (instead of % of WSF) [684].

W.Fish (Water Concentrations vs. Fish):

> Note: WSF values are of interest in looking at relative toxicity of different substances, but are not of much value for predicting what will happen at a new spill site (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].

Pink salmon fry were exposed to the saltwater-soluble fraction (SWSF) of Prudhoe Bay crude oil in a saltwater medium. The threshold at which early-stage salmon avoided the contaminant was 16.0 mg total oil/L of water at a temperature of 7.5 C. The threshold for fry approximately 2.5 mos. older was only 1.6 mg total oil/L at a temperature of 11.5 C. Fry exposed to the freshwater-soluble fraction (FWSF) in a freshwater medium were much less sensitive, requiring exposure to 497 mg oil/L at 5.0 C before exhibiting avoidance [713].

Coho salmon were exposed (in a freshwater medium) to a mixture of monocyclic aromatic hydrocarbons similar to that found in the SWSF of fresh Prudhoe

Bay crude oil and AL50s (concentrations at which 50% of the test fish avoided the contaminant) for the mixture were determined. The AL50 for pre-smolt salmon was 3.7 mg/L at an average temperature of 6.9 C. The AL50 for late smolt salmon was 1.89 mg/L at 16.4 C. These results were consistent with other observations that threshold concentration declined with increased fish growth and temperature [713].

Pacific salmon were exposed to a mixture of monocyclic aromatic hydrocarbons (representing the SWSF of Prudhoe Bay crude oil) to one of two fish ladders. An AL50 of 3.2 mg/L was calculated. Artificial plumes similar in composition to the water-soluble fraction (WSF) of Prudhoe Bay crude also were generated in the home streams of the spawning salmon. Concentrations between 1.0 and 10.0 ppb resulted in disorientation and downstream movements of fish away from the contaminant [713].

Sand gobies (Pomatoschistus minutus) were exposed to concentrations of the WSF of North Sea crude oil ranging from 0.1 to 1 ppm. "Off bottom" activity for these nocturnal fish severely decreased beginning 1-2 days after the start of exposure; normal behavior was observed within 2 days of transferring the fish to clean water [713].

Juvenile coho and sockeye salmon exposed to 500 ppm to 3500 ppm equivalent crude oil exhibited abnormal locomotor activity by swimming through the oil at the surface of the water within 45 min of exposure. Eventually the fish became lethargic and were oriented vertically instead of horizontally [713].

Chum salmon exposed to less than 9 mg/L oil initially showed increased movements and rapid respiration followed by a gradual decline in activity toward immobility [713].

Some coho salmon exposed to 230-530 ug/L water-soluble fraction (WSF) of Cook Inlet crude oil exhibited behavior of reduced feeding [713].

Coho salmon were exposed to concentrations of up to 2 ppm of monocyclic aromatic hydrocarbons (simulating the saltwater-soluble fraction [SWSF] of Prudhoe Bay crude oil) for 8 to 22 hours. As the uptake of hydrocarbons into the fish increased, the percent return to their established "home base" declined and the time to return increased [713].

Cunners (Tautogolabrus adsperus) were exposed to

150 to 250 ug/L SWSF of Hibernia P-15 crude oil for 4-5 weeks and exhibited a reduction in feeding activity thereafter. When exposure was ended, recovery occurred in 2-3 weeks [713].

Adult atlantic silversides (Menidia), following exposure to 167 ppm of the WSF of Texas-Louisiana crude oil, exhibited a distinct loss of schooling behavior [713].

Freshwater minor carp (Puntius sophore) exposed to 200, 500, and 1000 ppm extracts of crude oil exhibited an increase in breathing rate and decrease in oxygen uptake [713].

One group of pink salmon fry was exposed to >or= 1.95 ppm Cook Inlet crude oil and another group to >or= 1.03 ppm Prudhoe Bay crude oil, each for 22 hrs. An increase in cough frequency was observed for both groups that reached a maximum after three hours and gradually declined until the end of the test [713].

Acute toxicity data (96h LC50s) were summarized for fish exposed to fresh crude oil. The range of concentrations was found to be 88 to 18,000 mg/L [624].

Cutthroat trout (Salmo clarki) were exposed for 90 days to four concentrations (ranging from 100 to 520 ug/L) of a Wyoming crude oil in water. Survival was reduced to 52% at 520 ug/L, but was not affected by the 3 lower concentrations. Growth was significantly slower than control fish at all four concentrations. Exposure concentrations of 520 and 450 ug/L induced gill lesions and development of lesions on the retina and lens of the eye. Accumulation of total hydrocarbons in fish tissue was directly related to water concentration, except for fish in the 520 ug/L concentration. Alkylated mono- and dicyclic aromatic hydrocarbons were accumulated most readily, and naphthalenes were the dominant aromatic component in oil, water, and fish. Evidence from this research suggests that discharges of 10 mg/L oil and grease allowed by several western states are too high [786].

Acute toxicity data (96h LC50s) were also summarized for finfish exposed to soluble hydrocarbons (esp. BTEX) derived from fresh crude oil. The range of concentrations was found to be 5 to 50 mg/L [624].

Concentrations of oil in water of 0.5 ppm or less can be lethal to cutthroat trout (Salmon clarki) [782].

It has been reported that crude oil in concentrations as weak as 0.4 mL/L (about 0.3 mg/L) is extremely toxic to freshwater fish [224].

> Note: WSF values and concentrations of crude oil as a whole (as compared to individual compounds) are difficult to measure at new spill sites and thus are of more interest in looking at relative toxicity of different substances, but are not of much value for predicting what will happen at a new spill site (Roy Irwin, National Park Service, Personal Communication, 1996).

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

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

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

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

Sed.Invertebrates (Sediment Concentrations vs. Invertebrates):

The amphipod Onisimus affinis strongly avoided 0.05 mL crude oil/15 g dry sediment. The response deteriorated both as the oil weathered and lost aromatics, and as the concentration of oil increased to 2.0 mL/15 g dry sediment--possibly due to sensory disruption or impairment at the higher concentration [713].

Sed.Fish (Sediment Concentrations vs. Fish):

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

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

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:

In March 1973, the Liberian tanker Zoe Colocotronis ran aground off La Parguera, Puerto Rico. In order to free the ship, approximately 4,500 tons of crude oil were pumped overboard. The wind drove about 60% of the oil into Bahia Sucia in southwestern Puerto Rico, where it affected a number of marine habitats, including red and black mangrove swamps [622].

The discharge site and an unoiled reference site were evaluated qualitatively one week, 13 weeks, and 3 years after the discharge. Observations were made of the degree of prop root oiling, of the prop root invertebrate community, and of oil in swamp sediments. After 3 years, dead mangroves were evident and oil remained in sediments [622].

It was noted, (1990), that although most petroleum released at sea in tropical environments degrades rapidly, contamination reaching intertidal sediments may persist for many years. They observed discrete subsurface layers of petroleum hydrocarbons in intertidal sediment cores collected from the discharge site in 1990, 13 years after the discharge. The uppermost such layer contained petroleum hydrocarbon concentrations greater than 200 mg/g, probably attributable to the 1977 [sic] Zoe Colocotronis discharge. A deeper layer with less concentrated petroleum hydrocarbons was believed to correspond to the Argea Prima discharge in 1962.

Sediments above, between and below these layers had low concentrations of typical biogenic hydrocarbons [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].

Oil slicks were observed frequently in Bahia Les Minas during the 4 years following the discharge. The slicks appeared to originate primarily from fringing mangrove areas which had been impacted by the discharge: as dead red mangroves decayed and their wooden structures disappeared, erosion of the associated oiled sediment occurred, releasing trapped oil [622].

Oil was present in mangrove sediments and continued to appear on mangrove roots during the three years following the discharge, with the highest levels of continued oiling occurring in stream habitats and the lowest levels along the open coast [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 re-oiling 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 re-oiling differed among habitats. Secondary re-oiling 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. The greatest amount of re-oiling occurred between February and August 1989 and appeared to be related to the collapse and cutting of dead mangroves and to replanting efforts by the Refineria Panama. It was suggested that the amount of oil released may have begun to decline at the time the monitoring program was terminated 5 years after the discharge, as mangroves became reestablished at oiled sites and developed root mats able to stabilize the substrate [622].

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

Soil.High (Soil Concentrations Considered High):

Seven large and medium size west coast ports were surveyed during August 1990 to determine their involvement with hydrocarbon contaminated soils and activities associated with the characterization and remediation of these soils [735]. All ports surveyed indicated that they have hydrocarbon contaminated soil problems [735]. At one site, a soil investigation revealed one or more of four underground petroleum pipelines, all idle or abandoned, near the center of the redevelopment area may have leaked. The presence of petroleum contamination in the soil was confirmed. The petroleum could not be identified, but appeared to be of a heavy petroleum type (diesel, bunker oil, or possibly very weathered crude) rather than gasoline [735]:

CONTAMINANT	CONCENTRATION (ppm)
Total Petroleum Hydrocarbon (TPH) EPA Method 418.1	69,300
Total Petroleum Hydrocarbon (TPH) EPA Method 8015	43,000

modified for diesel	
Benzene	40.7
Toluene	102
Xylene	67
Ethylbenzene	171

Soil.Typical (Soil Concentrations Considered Typical):

Five to fifteen ppm total petroleum hydrocarbons (TPH) in soil is a realistic background level on a Texas intercoastal waterways spoil island (Brian Cain, Fish and Wildlife Service Contaminants Specialist, Houston, personal communication, 1995).

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):

The inherent toxicity and environmental mobility of crude oil is vastly different from that of gasoline, and the designation of concentrations which are protective of public health should take these differences into consideration. As a result, the application of gasoline action levels to sites with crude oil contamination should not be considered appropriate [734].

Soil.Plants (Soil Concentrations vs. Plants):

One of the hazardous groups of compounds in crude oil is PAHs. PAHs may be translocated in plants and may accumulate in plants grown in contaminated soil [40]. See PAHs entry for more information.

Soil.Invertebrates (Soil Concentrations vs. Invertebrates):

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

Soil.Human (Soil Concentrations vs. Human):

Gasoline and crude oil: many states are known to have action levels consisting of a single concentration value which may vary from 10 to 100 ppm TPH [734]. Other states incorporate a range of action levels for addressing site-specific needs; values range from 10 to 1000 ppm TPH for gasoline soils [734].

It is important to stress that existing action levels are based on minimizing potential health risks associated with gasoline constituents such as benzene and the potential for groundwater impacts [734]. The inherent toxicity and environmental mobility of crude oil is vastly different from that of gasoline, and the designation of concentrations which are protective of public health should take these differences into account [734]. Furthermore, as a result of the lower percentage of volatile aromatics in crude oil, vapor emissions from crude oil-contaminated soils are expected to be much less than potential emissions from gasoline-contaminated soils [734]. As a result, the application of gasoline action levels to sites with crude oil contamination should not be considered appropriate [734].

No other 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):

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

Case Study:

The effect of Louisiana crude oil was examined on selected anaerobic soil processes in a Louisiana saltmarsh in controlled experiments. Redox potential did not vary with crude oil addition. The biological reduction of nitrate, manganese, iron and sulphate, and the production of methane and ammonium in stirred, reduced sediments were not affected by additions of up to

10% oil on a soil-weight basis. Oil placed on the water surface caused iron, manganese and ammonium released from the sediment to the overlying water column. It was concluded that crude oil discharged onto marsh surfaces or the surface of tidal water overlying Louisiana marshes probably has little or no influence on microbial processes because Louisiana's highly organic marsh sediments are anaerobic throughout the year. Hence, petroleum hydrocarbons had little importance as an energy source for microbial metabolism [622].

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 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 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 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 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 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 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 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 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 entries 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):

Oiled birds can readily ingest oil during preening. Mallards lightly coated with 6 g oil ingested 2 g within 3 days. Effects of ingested oil include anemia, pneumonia, intestinal irritation, kidney damage, altered blood chemistry, and impaired osmoregulation. The quantity of oil required to elicit these responses is highly variable. As little as 0.5 g was found to inhibit osmoregulation by intestines and nasal salt glands, but other physiological responses appear to be less sensitive [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 mortality, body weight, food consumption, reproductive parameters, 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 [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].

Mallards fed up to 50,000 ppm (5%) Exxon Valdez oil showed very little signs of toxicity or other deleterious effects, except for some decrease in serum calcium levels, some increase in number of cracked eggs, some decrease in thickness and strength of eggs. Oil painted onto eggs had limited effects, but eggs can be very sensitive to penetration of lighter compounds (a concern in diesel and lighter refined fuel products). Heavier oil products can coat eggs and reduce gas (including oxygen) exchange (Bill Stubblefield, personal communication, 1995).

No mortalities or toxic signs were noted in a 14-day feeding study with adult mallards at dietary concentrations up to 100,000 mg of naturally weathered North Slope crude oil (WEVC) per kg diet (food) [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].

Herring gulls receiving (internally) >or= 10 mL oil/kg body weight/day became lethargic beginning the fourth day of treatment. Following 5 days of treatment with 20 mL oil/kg body weight/day, herring gulls became moribund (at or near the point of death) and recumbent (resting, idle, lying down). Atlantic puffins (Fratercula arctica) provided 10 mL oil/kg body weight/day became weak by the fourth day of treatment. Sandhill cranes (Grus canadensis) provided 10 mg [sic] oil/kg body weight became more lethargic, appeared weaker, and maintained a different standing and walking posture than did controls [713].

Laboratory studies also have shown that oil exposure may reduce the ability of birds to respond to frightening stimuli. Mallard ducklings fed diets containing 0.25, 2.5, or 5.0% oil ran significantly shorter distances from frightening stimuli than controls did. The distance retreated from the frightening stimulus was significantly less in ducklings ingesting the higher oil concentrations [713].

Decreases in weight and length have been observed in mallards, guillemots, and gull chicks following forced ingestion of doses as low as 0.1-0.3 mL oil/kg body weight or a 5% crude oil diet. Peking ducks receiving a single 2 mL dose of South Louisiana crude oil in their diet exhibited depressed growth [713].

Breeding female mallard ducks consuming petroleum-contaminated food show significant induced increases in the naphthalene-metabolizing properties of microsomes prepared from their livers [806]. 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 [806]. 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 [806].

See also: Br.Dev section above.

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

In birds, ingested crude oils are mostly deposited in fat but also accumulated in a variety of tissues including liver, kidney, muscle, blood, and skin

[713]. Accumulation of oil in the brain is low [713].

After the 1989 Exxon Valdez spill, oil residues found in seal bile were five to six times higher in oiled areas compared with unoiled areas [622].

Tis.Human:

A) Typical Concentrations in Human Food Survey Items:

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

Tis.Misc. (Other Tissue Information):

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].

Note: The following case study highlights of effects on plants 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].

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

Case Study:

> In March 1973, the Liberian tanker Zoe Colocotronis ran aground off La Parguera, Puerto Rico. In order to free the ship, approximately 4,500 tons of crude oil were pumped overboard. The wind drove about 60% of the oil into Bahia Sucia in southwestern Puerto Rico, where it affected a number of marine habitats, including red and black mangrove swamps [622].
>
> The discharge site and an unoiled reference site were evaluated qualitatively one week, 13 weeks, and 3 years after the discharge. Observations were made of the prop root invertebrate community, and the oil in swamp sediments. They observed about half as many faunal groups on oiled prop roots one week after the discharge. Thirteen weeks after the discharge, repopulation of the prop root community began. After 3 years, dead mangroves were evident and oil remained in sediments [622].
>
> Both the discharge area and an unoiled reference area were examined in November 1978, 5 years after the discharge. Eleven transects in oiled areas and 5 transects in the unoiled area were designed to

transit three subhabitats: red mangrove fringe, black mangrove areas, and a salt lagoon. Cores were collected along each transect to sample infaunal benthic communities. Overall, mangrove prop root communities had recovered 5 years after the discharge. In black mangrove areas, there were more infaunal organisms > 1 mm in size in oiled areas than in the reference sites. In red mangrove habitats, there were fewer infaunal organisms > 1 mm in size in oiled areas, reflecting the red mangrove's greater susceptibility to oiling. In the lagoon, there were higher numbers of infaunal organisms > 1 mm in size in areas which had been oiled [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].

Invertebrates in 2 oiled sites and one unoiled reference site were compared during one year following the discharge. It was observed that intertidal invertebrates were killed immediately in many mangrove fringes. Immediately following the discharge, Uca sp., (crabs), migrated to unoiled habitats. Melalampus sp., (snails), did not ascend mangrove roots until the oil became tacky, about 4 weeks after the discharge.

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. Severe mortality of oysters and other invertebrates inhabiting mangrove roots was reported [622].

Oil slicks were observed frequently in Bahia Les Minas during the 4 years following the discharge.

The slicks appeared to originate primarily from fringing mangrove areas which had been impacted by the discharge: as dead red mangroves decayed and their wooden structures disappeared, erosion of the associated oiled sediment occurred, releasing trapped oil [622].

Oysters and mussels collected between 1986 and 1991 had high tissue levels of hydrocarbon residues associated with reduced population levels during the same period [622].

Distributions of sessile invertebrates were negatively correlated with the presence of oil, with the exception of the high intertidal barnacle Chthamalus sp. Mangrove root communities in channel and lagoon habitats also showed effects of oiling 3 years after the discharge. Before the discharge, root communities in these areas were dominated by the edible oyster Crassostrea rhizophorae and the barnacle Balanus improvisus. Abundances were lower after the discharge, with little evidence of recruitment, although oyster cover increased gradually on oiled roots. Mangrove root communities in drainage habitats were the most severely impacted by the discharge. The discharge completely eliminated the mussel Mytilopsis sallei, which dominated root communities in these habitats. Less common epibionts were also eliminated. Three years after the discharge, the root systems continued to be reoiled, and there was no evidence of recruitment of mussels or other epifauna [622].

In contrast, bivalves in channels and streams accumulated water soluble fractions of crude oil between 1986 and 1991 and remained heavily contaminated in May 1991, 5 years after the discharge. Levels of suspended oil after 5 years were high enough to reduce bivalve growth and respiratory rates. Oysters consistently accumulated about half as much total oil as mussels. Erosion is thought to be the principal process releasing tarry oils from sediments, while a combination of erosion and diffusion releases suspended oils from sediments. It was suggested that the observed continued high bivalve tissue concentrations of oil were indicative of dissolved and suspended hydrocarbons in the environment declining more slowly than visible, tarry residues and proposed that the processes controlling the two types of residue were partially uncoupled. It was concluded that the combination of chronic reoiling, injury to epibiotic assemblages, and reductions in submerged prop root substrate had decreased productivity in the mangrove habitat. They suggested that recovery would be a complex and prolonged process, and that reductions in productivity caused by oiling would persist until the amount of submerged prop root substrate returned to prespill levels [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 biomass of eelgrass and the faunal composition of the grassbed community [622].

A decrease in numbers of individuals and species was immediately apparent in the benthic infauna. Results in the shallower study area proved difficult to analyze due to natural changes in the bed. In the deeper bed these faunal changes were most apparent as a disappearance of amphipods, tanaids and echinoderms and a reduction in numbers of gastropods, polychaetes and bivalves. By the end of 1978, numbers of individuals had returned to levels present a year earlier, but diversity continued to change. The echinoderms were slow to recover, and none of the filter-feeding amphipods had returned. However, compared with some other habitats, it was concluded that the eelgrass community suffered relatively mild impacts since eelgrass blades and rhizome mat may have provided a protected habitat, reducing the impacts of the discharge on its residents [622].

Total numbers of individuals and species of mobile benthic fauna also decreased immediately following the discharge, an effect more evident a month later. Numbers of individuals increased throughout the following year but did not reach levels equalling those of a year earlier, and species numbers remained lower than before the discharge. Gastropods were not adversely affected. Cumaceans, tanaids and echinoderms had nearly recovered within a year. Amphipods were severely affected. There were 26 species of amphipods in the bed preceding the discharge, of which 21 had not returned a year later [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 and massive invertebrate mortality occurred: mangrove barnacles, mussels, and oysters were rare or absent 2 months after the discharge. Motile (capable of moving spontaneously) invertebrates migrated out of the affected area to zones above the oil line. Fiddler crab populations were reduced, particularly younger life history stages [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, and most crustaceans and mollusks had returned to prespill levels, presumably by migrating from unoiled areas [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 [713]. 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 [713]. The bioaccumulation and persistence of PAHs in the food chain is opposite that seen for other chemicals such as some PCBs and certain other organochlorines which tend to concentrate in the top predators [713]. 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 [713]. Fish also have an enzyme system for clearing hydrocarbons, thus are not likely to bioaccumulate hydrocarbons [713]. 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].

There is ample evidence that fish exposed to petroleum in sediments, water, or through the diet, accumulate hydrocarbons in tissues and body fluids [781]. Some of the aromatic hydrocarbons are converted metabolically to metabolites that remain in tissues for prolonged periods [781]. Some carcinogenic/mutagenic aromatic hydrocarbons, are actively taken up by fish and metabolized to derivatives that may lead to tumorous lesion [781]. Laboratory studies have revealed that the accumulation of hydrocarbons and the resulting metabolites in fish causes a deleterious effect on health and survival [781].

Cutthroat trout (Salmo clarki) were exposed for 90 days to four concentrations (ranging from 100 to 520 ug/L) of a Wyoming crude oil in water. Alkylated mono- and dicyclic aromatic hydrocarbons were accumulated most readily, and naphthalenes were the dominant aromatic component in oil, water, and fish. Accumulation of total hydrocarbons in fish tissue was directly related to water concentration, except for fish in the 520 ug/L concentration. Evidence from this research suggests that discharges of 10 mg/L oil and grease allowed by several western states are too high [786].

Oil was taken up by Acartia bifilosa and Eurytemora hirundoides copepod invertebrates in the gut system when exposed to Russian crude oil for 24 hours [900]. Super(14)C-1-naphthalene is also absorbed by E. hirundoides from emulsions in sea water [900]. Oil was present in E. hirundoides bodies after exposure for 24 hours to 1 ml/1 oil emulsion [900]. Naphthalene elimination from E. hirundoides bodies after being transferred into clean sea water was studied [900]. The half-life T sub(b) is 6.2 days and the consumption rate is 6.3 ng naphthalene/copepod from 1 mg/1 naphthalene emulsions [900]. It is therefore assumed that copepods eating oil form a potential danger to the components of the food chain, as part of the naphthalene accumulated in the bodies [900].

See log Kow figures in Chem.Detail section below.

Interactions:

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

See also: PAHs as a group entry.

Uses/Sources:

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

Forms/Preparations/Formulations:

Since having entries on various individual crude oils is beyond the scope of this document, the reader may wish to consult the report [560] from Environment Canada for chemical and physical data on a variety of specific crude oils (for an example, see the Chem.detail section below for information from [560] on Atkinson Crude). Individual crude oils referenced in [560] include: ADGO, Alaska North Slope, Alberta, Alberta Sweet Mixed Blend, Amauligak, Arabian, Arabian Heavy, Arabian Light, Argyl, Atkinson, Auk, Avalon, BCF 24, Beatrice, Belridge Heavy, Bent Horn, Bent Horn A-02, Beryl, Beta, Boscan, Bow River Blended, Bow River Heavy, Brae, Brent Blend, Brent, Buchan, California (API gravity 11), California (API gravity 15), Carpinteria, Cohasset, Cold Lake, Cook Inlet, Dos Cuadras, Dunlin, East Texas, Ekofisk, Empire, Endicott, Federated, Federated Light and Medium, Flotta Mix, Forties, Fosterton, Fulmar, Gorm, Granite Point, Gulf Alberta Light and Medium, Gullfaks, Heavy Louisiana Sweet, Heavy Reformate, Hibernia, Hibernia (EPA 86), Hondo, Hutton, Interprovincial, Iranian Heavy, Issungnak, Isthmus Blend, Koakoak 0-22, Koakoak 0-22A, Kopanoar 21-44, Kopanoar, Kopanoar M-13, Kopanoar M-13A, Kuparuk, Kuwait, La Rosa, Lago Medio, Lagotreco, Leduc Woodbend, Light Sour Blend, Lloydminster, Magnus, Maureen, Maya, Mayogiak, McArthur River, Menemota, Middle Ground Shoal, Mixed Sour Blend, Montrose, Murban, Murchison, Nektoralik K-59, Nektoralik K-59A, Nerlerk M-98A, B and C, Ninian Blend, Ninian, Norman Wells, North Cormorant, North East Texas, North Slope, Oseberg, Panuke, Perentis, Pembina, Piper, Pitas Point, Platform Irene, Port Hueneme, Prudhoe Bay, Ragusa, Rainbow Light and Medium, Rangeland-South Light and Medium, Redwater, Santa Clara, Sockeye, Sour Blend, South Cormorant, South Louisiana, South West Texas Light, Statfjord, Sumatran Heavy (Duri), Sumatran Light (Minas), Swanson River, Sweet Blend, Synthetic, Taching, Tarsiut, Tarsiut A-25, Tartan, Terra Nova, Terra Nova K-08 DST #s 1, 2, 3 and 4, Texas Gulf Coast Heavy, Texas Gulf Coast Light, Thistle, Tia Juana, Tia Juana Heavy, Tia Huana Light, Trading Bay, Trading Bay (Offshore Cook Inlet), Transmountain Blend, Udang, Ukalerk 2C-50, ULA, Uviluk, Uviluk P-66, Wainwright-Kinsella, West General Texas, West Sak, West Texas Ellenburger, West Texas Intermediate, West Texas Light, West Texas Sour, and Weyburn-Midale.

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

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

As a general rule, all crude oils are complex mixtures composed of the same compounds, but the quantities of the individual components differ in crude oils from different locations [773].

A light crude generally has an API gravity greater than 40 (specific gravity < 0.82), a medium crude between 15 and 40 (sp. gr. 0.82-0.97), and a heavy crude less than 15 (sp. gr. > 0.97)

[747].

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; CH4) 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].

Hydrocarbons generally dominate crude oil (for example, 50-98%) [713]. Individual compounds of crude oil can be classified into the following two categories: 1) Hydrocarbons, which include alkanes (normal and branched chains), cycloalkanes, alkenes, aromatics, naphthenoaromatics; and 2) Non-hydrocarbons, which include nitrogen, sulfur and oxygen (NSO) compounds, asphaltenes and resins (including NSO heterocyclics), metallo-organics, and inorganic metal salts [713].

Crude oil consists of thousands of individual compounds. The major groups include the saturated alkanes, alkenes, benzene, alkylated and aryl benzenes, polynuclear aromatics, heterocyclic aromatics, and hetro-atom substituted alkanes, alkenes and aromatics. The different types of crude oil will show different ratios of these compound types [783].

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].

> NOTE: Aromatics are often distinguished by the number of rings they possess, which may range from one to five [770]. Lighter, mono-aromatics (one ring) compounds include benzene, toluene, ethylbenzene, and xylenes [771]. Aromatics with two or more rings are referred to as polyaromatic hydrocarbons (PAHs) [770].

Crude oil is approximately 11% to 13% hydrogen and 84% to 87% carbon by weight. Crude oil contains on the average approximately 1 ppm B(a)P [734]. The B(a)P concentration in crude oils from the Persian Gulf, Libya, and Venezuela were measured at 0.04, 1.3, and 1.6 ppm, respectively. Estimates of total CaPNAs (carcinogenic PAHs) in crude oil ranges from 12 to < 100 ppm. Distillate fractions quantified by percent weight are commonly used to characterize crude oil. The relative percent weight of distillate fractions changes due to weathering with the loss of those fractions containing lighter hydrocarbons over time [734].

Table: Concentrations of individual polynuclear aromatic hydrocarbons (PAHs) in two crude oils (10[-6]g/g oil; ppm) [747]:

COMPOUND	South Louisiana Crude	Kuwait Crude
pyrene	4.3	4.5
fluoranthene	6.2	2.9
benz(a)anthracene	3.1	2.3
chrysene	23	6.9
triphenylene	13	2.8
benzo(a)pyrene	1.2	2.8
benzo(e)pyrene	3.3	0.5

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].

It is important to point out that crude oils contain primarily the alkyl homolog of aromatic compounds and relatively small quantities of the unsubstituted "parent" aromatic ring structures. It is these unsubstituted aromatic structures that are potentially responsible for the majority of the known toxic impacts of crude oils [773].

> NOTE: It is important to stress the word "known" in the previous sentence. In the past, most toxicity testing and EPA criteria focused on the "parent" aromatic ring structures, while the alkyl homologs were not individually assessed (Paulene Roberts, Louisiana State University, personal communication, 1995). Since technology has increased our ability to determine individual alkyl homologs, researchers are beginning to study the toxic effects of the individual alkyl homologs as well. Other sources now conclude that the alkylated PAHs are sometimes more toxic than the parent PAHs [468].

Table: PAH concentrations (ug/g oil sampled) were determined 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,ilperylene: ND, ND, 1

ND = not detected.

TABLE: Concentrations of PAHs in Two Crude Oils and Two Refined Oils [177]:

NOTE: The composition of chemicals making up petroleum hydrocarbon batches is quite variable, so in spill scenarios, it is often first necessary to determine the exact composition of the oil in the particular spill in question. The following concentrations in mg/kg (ppm) are from API reference oils:

Compound oil	South LA crude	Kuwait crude	No. 2 fuel oil	Bunker C residual
Naphthalene	400	400	4,000	1,000
1-Methylnaphthalene	800	500	8,200	2,800
2-Methylnaphthalene	900	700	18,900	4,700
Dimethylnaphthalenes	3,600	2,000	31,100	12,300
Trimethylnaphthalenes	2,400	1,900	18,400	8,800
Fluorenes	200	<100	3,600	2,400
Phenanthrene	70	26	429	482
1-Methylphenanthrene	111	-	173	43
2-Methylphenanthrene	144	89	7,677	828
Fluoranthene	5.	2.9	37	240
Pyrene	3.	4.5	41	23
Benz(a)anthracene	1.	2.3	1.2	90
Chrysene	17.56	6.9	2.2	196
Triphenylene	10	2.8	1.4	31
Benzo(ghi)fluoranthene	1	<1		
Benzo(b)fluoranthene	<0.5	<1		
Benzo[j]fluoranthene	<0.9	<1		
Benzo(k)fluoranthene	<1.3	<1		
Benzo(a)pyrene	0.75	2.8	0.6	44
Benzo(e)pyrene	2.5	0.5	0.1	10
Perylene	34.8	<O.l	-	22
Benzo(ghi)perylene	1.6	<1		

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

> NOTE: Although the solubility units below are unfamiliar, the inversely proportional relationship of degree of weathering to solubility remains evident (that is, as evaporation continues, solubility decreases).

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
Murban	0	28.6
Synthetic Oil Mixture	0	203.4

* = Estimated subcooled liquid solubility

Regarding TLC patterns for crude oil: The thin-layer chromatography (TLC) pattern, using hexane as the eluting solvent, will show a continuous streak stretching from R(f) 0.0 to 0.9 using iodine staining. There is often a large spot at R(f) 0.9 and a tail of material stretching to the origin. Portions of the tail will often be seen under short and long wave UV light, and crude oils can often be differentiated using the UV pattern [783].

The following is an example of the information available on specific crude oils in the Environment Canada document [560]. For similar information on 153 other crudes (listed under Forms/Preparations/Formulations section above) see the original reference [560].

NOTE: In this section, for properties with more than one value, each value came from its own source; in other words, if API Gravity at 60 F was measured several times and several different answers were obtained, all of the answers are provided:

MASS AND WEIGHT [560]

API Gravity (60/60 degrees F):

NOTE: API gravity = (141.5/specific gravity [60/60 degrees F]) - 131.5, where specific gravity [60/60 degrees F] is the oil density at 60 degrees F divided by the density of water at 60 degrees F.

23.7

Density (g/mL):

For temperatures of oil (T) between 0 and 30 C:
Density = 0.97871 - 0.000710 T

NOTE: The densities of crude oils and oil products are dependent on the temperature and degree of weathering. "0% Weathering Volume" means fresh Atkinson Crude Oil.

	(Weathering Volume %)			
Temp(C)	0	4	12	19.4
0	0.9219			0.9476
15	0.911			0.9438
20	0.9060	0.9172	0.9239	

SOLUBILITY [560]

Aqueous Solubility (mg/L): The solubility of oil in water can be determined by bringing to equilibrium a volume of oil and water, and then analyzing the water phase. Oil's aqueous solubility is expressed as the cumulative concentration of the individually dissolved components. Solubility is significantly reduced by weathering.

	Temp not given	22 C
Fresh Water	2.3	3.1
Seawater	2.5	

HYDROCARBON GROUP [560]

NOTE: The main constituents of oil are generally grouped into the below categories. Asphaltene content increases with increasing weathering, as does wax content.

Hydrocarbon Group Analysis (Weight %):

Saturates	82.7
Aromatics	13.2
Polars	1.5
Asphaltenes	2.6 2.39 2.2

Wax Content (Weight %):
1.1

METAL CONTENT [560]

Other Metals (ppm):

	Weathering (Volume %)	
	0	19.4
Molybdenum	0.6	<0.6
Potassium	2.0	2.0
Zinc	1.4	2.6
Lead	3.5	3.7
Nickel	1.8	2.7
Iron	6.7	66
Chromium	<1.5	<1.5
Magnesium	4.6	4.5
Vanadium	9.4	11
Copper	<0.6	0.6
Titanium	0.6	<0.6
Barium	0.6	0.6

VISCOSITY [560]

NOTE: The viscosities of crude oils and oil products are dependent on the temperature and degree of weathering. "0% Weathering Volume" means fresh Atkinson Crude Oil.

Dynamic Viscosity (mPa.s or cP):

	(Weathering Volume %)	
Temp(C)	0	19.4
15	65.1	533.3

Kinematic Viscosity (mm2/sec or cSt):

	(Weathering Volume %)		
Temp(C)	0	4	12
-10	304.8	762.7	2506
0	136.2	317.0	783.7
15	57.28	113.6	245.0
25	34.94	62.05	124.4

Pour Point (degrees C):

Pour point is the lowest temperature at which an oil sample is observed to flow when cooled under prescribed conditions. It is affected by weathering.

(Weathering Volume %)		
0	4	12
-38	-35	-28

INTERFACIAL TENSIONS [560]

NOTE: Interfacial tension is the force of attraction between molecules at the interface of a liquid. These tensions are essential for calculating the spreading rates and the likely extent to which the oil will form oil-in-water and water-in-oil emulsions. The interfacial tensions of crude oils and oil products are dependent on the temperature and degree of weathering. "0% Weathering Volume" means fresh Atkinson Crude Oil.

Air-Oil (mN/M or dynes/cm):

	(Weathering Volume %)	
Temp(C)	0	19.4
0	30.5	31.2
15	28.8	26.6

Oil-Seawater (mN/M or dynes/cm):

	(Weathering Volume %)	
Temp(C)	0	19.4
0	18.7	7.1
15	17.9	10.9

Oil-Water (mN/M or dynes/cm):

	(Weathering Volume %)	
Temp(C)	0	19.4
0	24.2	22.3
15	23.2	21.2

EMULSION [560]

NOTE: Water-in-oil emulsions are stable emulsions of small droplets of water incorporated in oil. Termed "chocolate mousse," these stable water-in-oil emulsions can have different characteristics than the parent crude oil. Emulsion characteristics of crude oils and oil products are dependent on the temperature and degree of weathering. "0% Weathering Volume" means fresh Atkinson Crude Oil. In general, Atkinson Crude Oil is very likely to form emulsions.

Emulsion Formation (in the VERY LIKELY range)

Fraction of oil that forms an emulsion (f initial)

	(Weathering Volume %)	
Temp(C)	0	19.4
0	1.0	1.0
15	1.0	1.0

Emulsion Stability (in the VERY STABLE range):

Fraction of oil that in the emulsion that remains after settling (f final)

	(Weathering Volume %)	
Temp(C)	0	19.4
0	1.0	1.0
15	1.0	1.0

Water Content of Emulsion (volume %):

	(Weathering Volume %)	
Temp(C)	0	19.4
0	83	53
15	88	73

DISPERSIBILITY [560]

Natural Dispersibility (% Dispersed):

Temp(C)	Naturally Dispersed
15	8

FIRE AND REACTIVITY [560]

Flash Point (C):

(Weathering Volume %)		
0	4	12
10	32	75

Fire Point (C):

(Weathering Volume %)		
0	4	12
26	50.5	95

DISTILLATION [560]

NOTE: Distillation data provides an indication of an oil's volatility and relative component distribution. Distillation data is reported as volume % recovered.

Distillation (C):

(Vol%)	Liquid Temp	Vapor Temp
IBP	173	58
5	210	106
10	252	123
15	290	129
17	304	201

NON-METAL CONTENT [560]

Sulphur (Weight %):

(Weathering	Volume %)
0	19.4
0.86	1.07

OTHER [560]

Reid method Vapor Pressure (kPa):

Temp(C)	Pressure
37.8	5.96

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

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

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

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 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.

Low molecular weight components evaporate readily; the amount of evaporation varies from about 10% of the spilled oil for very heavy crudes and refined products (No. 6 fuel oil) to as much as 75% for light crudes and refined products (No. 2 fuel oil, gasoline). Less than 5% of a crude oil or refined product will dissolve in water [782].

In general, microbial degradation is most rapid when dissolved oxygen, nutrients, and water temperature are elevated. Approximately 40-80% of a crude oil can be degraded by microbial action [782].

Pathways for injuries due to incidents involving oil can be either direct or indirect. Direct pathways occur when the natural resource is exposed to the oil or to a chemical compound originating from the oil. Indirect pathways occur when the natural resource is not directly exposed to the oil or to any chemical compounds originating from the oil: instead, the presence of the oil interferes with a physical, chemical or biological process important to the natural resource; or a use of the natural resource is impaired by the presence of the oil in that environment [713].

The following physical, chemical and biological processes can be involved in direct exposure pathways related to incidents involving oil [713]:
-coating of the external surface by oil
-uptake of dissolved oil components from water
-ingestion of oil droplets or blobs
-ingestion of non-living particles coated by oil

-ingestion of prey coated by oil
-ingestion of organisms in which oil components accumulated
-inhalation of volatile oil components [713]

Behavior and fate of discharged oil can be affected by the following physical, chemical and biological processes [713]:

-PHYSICAL: spreading (thinning of the oil slick); dispersion (by wind); movement (by currents or gravity flow); dissolution; sedimentation or settling; emulsification; evaporation or volatilization; aeolian transport (when oil droplets become airborne and are blown long distances by strong winds).
-CHEMICAL: photolysis or photooxidation or photodegradation; oxidation or chemical degradation.
-BIOLOGICAL: microbial degradation or biodegradation; ingestion and depuration by organisms [713].

In sedimentary environments (as opposed to gravel or rocky environments) such as sheltered tidal flats and salt marshes, the sediments are characterized by fine silts with high organic content. Here oil may be thoroughly incorporated into the sediments and persist for very long periods [784].

Information regarding the environmental half-life of whole crude oil in soil is limited. However, estimates of the half-lives of some crude oil constituents in soil have been published. The constituents of primary interest in terms of toxicity are the carcinogenic polyaromatic hydrocarbons (CaPNAs). The half-lives of PNAs (a.k.a. PAHs) in general are considered to be large, relative to other hydrocarbons such as benzene [734].

Benzo(a)pyrene (B(a)P), benz(a)anthracene (B(a)A), and benzo(b)fluoranthene (B(b)F) are all CaPNAs for which half-life estimates have been published. The primary fate mechanisms of these constituents is likely to be biodegradation. According to one source, 72% of B(a)P applied to soil remained after 16 months of incubation with bacteria. Based on first-order degradation, it is estimated that this would correspond to a half-life of approximately 1000 days for B(a)P. Another source estimated that the terrestrial half-life of B(a)P is approximately 290 days [734].

The half-life of B(b)F has been estimated to be 610 days in terrestrial environments. One source reported that 90% of an application of B(a)A remained after 11 months of incubation with bacteria. This would correspond to a half-life of approximately 2200 days for B(a)A based on first-order degradation. Another source estimated that the half-life of B(a)A in terrestrial environments is 430 days [734].

For the purpose of estimating safe concentrations of crude oil residues in residential soils, degradation of the toxic residues is assumed to occur with a half-life if 2200 days (6 years) [734].

Breeding female mallard ducks consuming petroleum-contaminated food show significant induced increases in the naphthalene-metabolizing properties of microsomes prepared from their livers [806]. 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 [806]. 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 [806].

Information on Weathering:

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].

A brief discussion of the primary (physical) weathering processes:

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].

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 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

See also: Chem.Detail section above for details of PAH content of Exxon Valdez oil as it weathers.

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]. See also: PAHs as a group entry.

A great deal of uncertainty remains in the use of dose-response relationships based on crude oil as a whole mixture [734].

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 (especially) alkylated PAHs.

Crude oil consists of thousands of individual compounds. The major groups include the saturated alkanes, alkenes, benzene, alkylated and aryl benzenes, polynuclear aromatics, heterocyclic aromatics, and hetro-atom substituted alkanes, alkenes and aromatics [783]. Some of the more toxic compound classes are: low molecular weight aromatics (such as benzene, toluene, xylene, other monocyclic aromatics), and polynuclear aromatic hydrocarbons (PAH) [713, 745]. Due to the presence of light aromatics and PAHs in fuel crude oil, we recommend the following decision tree:

Decision Tree (dichotomous key) for selection of lab methods for measuring contamination from midrange to heavy crude oils, number 6 and heavier fuel oils, bunker C and all other oils considered to be heavy):

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. Note: although heavy products have a lower percentage of BTEX and other relatively soluble compounds which typically threaten drinking water, ground water, or water column organisms, some heavy oils including crudes do contain some of these water soluble compounds, so they cannot be ignored........................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. Another option for fresh oil: in cases where an inexpensive screening scan is desired, consider using an HPLC/Fluorescence scan method for sediment or bile metabolite samples. Such scans are available from laboratories at Texas A. and M., Arthur D. Little, and the NOAA lab in Seattle. This scan is not much more expensive, and less prone to false negatives and various other problems than some of the more common screening methods (TPH-EPA 418.1 and Oil and Grease). Screening measures the total fluorescence of oil components while GC/MS measures individual aromatic compounds [521]. Thus, HPLC/fluorescence screening allowed detecting lower concentrations of petroleum-related aromatic compounds in samples contaminated by Prudhoe Bay Crude Oil than did analysis by GC/MS [521].

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 8240. The standard EPA GC/MS method 8240 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 8240 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 8240), 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 8240 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]. The

HPLC/fluorescence scan looks for the presence of metabolites of PAHs: naphthalene, phenanthrene, and benzo(a)pyrene. The technique does not identify or quantify actual PAH compounds, but subsequent gas chromatography analyses can be done to confirm the initial findings. Even the semi-quantitative Total Scanning Fluorescence (TSF) done inexpensively by labs such as GERG are a better measure of PAH contamination than GC/FID, which measures less persistent and less hazardous aliphatics. 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 8240 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 8240 or modified EPA method 8240 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 8240 or modified EPA method 8240 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 protocols for the expanded scan of polycyclic aromatic hydrocarbons (PAHs) and alkyl PAHs have been published by NOAA [828].

End of Decision Tree Key.

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 bioconcentratable 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 and oil spills.

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.
>
> > 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.

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.

> 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).

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. 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.

See also: Laboratory and/or Field Analyses section in Oil Spills entry for information on biological indicators of oil exposure. See also: PAHs as a group entry.