ENVIRONMENTAL CONTAMINANTS ENCYCLOPEDIA

FUEL OIL NUMBER 6 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 or summaries as being "what the original author said," the proposed interagency funding of a bigger project with more elaborate peer review and quality control steps never materialized.

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

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

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

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

> **Irwin, R.J., M. VanMouwerik, L. Stevens, M.D. Seese**, and **W. Basham.** 1997. Environmental Contaminants Encyclopedia. National Park Service, Water Resources Division, Fort Collins, Colorado. Distributed within the Federal Government as an Electronic Document (Projected public availability on the internet or NTIS: 1998).

Fuel Oil Number 6 (No 6 Fuel Oil, Fuel Oil No. 6, Bunker C, CAS number 68553-00-4)

Brief Introduction:

Br.Class: General Introduction and Classification Information:

Fuel oils are comprised of mixtures of petroleum distillate hydrocarbons [363,499]. Fuel oil #6 is a petroleum distillate fraction with a boiling point >400 degrees F [369]. Fuel oil No. 6 is the highest boiling fraction of the heavy distillates from petroleum. No. 6 oils represent approximately 5 to 8% of the original crude petroleum, but the exact yield depends on the source, refinery design and operations, and product requirements [557].

Fuel oil numbers 4, 5, and 6 are commonly known as "residual oils" since they are manufactured in whole or in part from distillation residues from refinery processing. Residual oils are complex and variable mixtures of relatively high molecular weight compounds and are difficult to characterize in detail. Molecular composition includes asphaltenes, polar aromatics, naphthalene aromatics, aromatics, saturated hydrocarbons and heteromolecules containing sulfur, oxygen, nitrogen and metals (see Chem.Detail for detailed analysis) [747]. Dimethyl and trimethyl naphthalenes are important components of Fuel No. 6. The viscous residuum fuel oils, numbers 5 and 6, sometimes referred to as bunker fuels, usually must be preheated before being burned [498].

Fuel oil No. 6 contains about 15% paraffins, 45% naphthenes, 25% aromatics, and 15% non-hydrocarbon compounds; the hydrocarbons contain 30 and greater carbon atoms [557]. It consists of straight-run and cracked distillates and residuals and contains aliphatics and aromatics [369].

Appreciable concentrations of polycyclic aromatic hydrocarbons (PAHs) are present in residual fuels because of the common practice of using both uncracked and cracked residues in their manufacture. Most blending stocks are likely to contain 5% or more of four- to six-ring condensed aromatic hydrocarbons (see the Chem.Detail section below for details). The exact identities and concentrations of PAHs in a particular sample depends on the nature and amounts of blending stocks as well as the virgin and cracked residues [747].

Oil-soluble compounds of calcium, cerium, iron, or manganese may be added to residual fuel oils to improve combustion [747]. Concentrations vary with fuel oil, but typically range between 50 to 300 ppm weight of the active material ingredient [747].

According the US Coast Guard Emergency Response Notification System (ERNS), fuel oil no. 6 is one of the most commonly spilled petroleum products the U.S [635].

Br.Haz: General Hazard/Toxicity Summary:

Hazards to Aquatic Biota, Wildlife, and Various Living Things Other than Humans:

In the aquatic environment, the main concern is the aromatics in Fuel oil 6. Benzene, Toluene, Ethyl Benzene, and Toluene (BTEX) compounds, although they do not make up a large percentage of this product, are present and could represent an acute toxicity risk. Due to their relative persistence and potential for various chronic effects (like carcinogenicity), the heavier aromatic PAHs, (and particularly the alkyl PAHs) in Fuel oil 6 can pose long term (chronic) hazards in contaminated soils, sediments, and groundwater.

Heavy oils (Including Heavy Crude Oils, No. 6 fuel, and Bunker C) are prone to severe impacts to waterfowl and fur-bearing mammals (coating and ingestion) [741,777]. They may weather slowly, and potentially sink (depending on product density and water density) to impact benthic organisms. However, in general, residual fuels are less acutely toxic relative to other oil types [777].

Many of the PAHs found in this product (see Chem.Detail section below) are more toxic in sunlight or other UV source than elsewhere (see PAHs as a group entry).

One of the hazardous groups of compounds in fuel oil is PAHs. PAHs may be translocated in plants and may accumulate in plants grown in contaminated soil [40]. Presumably this also occurs in sediments and aquatic plants and therefore might impact herbivorous species of fish and wildlife. Although some research seems to indicate that interior portions of above-ground vegetables do not accumulate high concentrations of PAHs, plants do translocate PAHs from roots to other plant parts, such as developing shoots [40]. Some plants can evidently catabolize benzo(a)pyrene, but metabolic pathways have not been clearly defined. This is an important factor since when PAHs do degrade through metabolism, they often break down into even more toxic, carcinogenic, and mutagenic compounds [40]. Metabolic transformations of PAHs into even more hazardous chemicals could also happen through microbial degradation of PAHs in soils or sediments. This provides an additional example of a situation where human health based standards are not protective of fish and wildlife, since it casts doubt on the environmental safety margin provided by EPA's human health-based soil guideline of =<100 ppm carcinogenic PAHs.

> However, in a series of soil and hydrocultures of the higher plants, tobacco, rye, and radish, as well as algae cultures of lower plants (Chlorella vulgaris, Scenedesmus obligurus, and Ankistrodesmus) /results indicate/ that certain polycyclic aromatic hydrocarbons (PAHs) have growth-promoting effects on plants. Further, the degree of the promoting effect corresponded to the oncogenic activity of the hydrocarbon. The six polycyclic aromatic hydrocarbons found in plants were tested one at a time or in combination. Considerable growth-promotion was noted (near to 100% in some cases) with the effectiveness of hydrocarbons ranked as follows: (1) Benzo(a)pyrene (2) Benzo(a)anthracene (3) Indeno (1,2,3-cd)pyrene, Benzo(b)fluoranthene (4) Fluoranthene (5) Benzo(ghi)perylene. [Graf W, Nowak W; Arch Hyg Bakt 150: 513-28 (1968) as cited in Health & Welfare Canada; Polycyclic Aromatic Hydrocarbons p.67 (1979) Report No. 80-EHD-50] [366].

For additional information on the effects of spilled Bunker C on plants, see Tis.Misc. section below.

Hazards to Humans:

Fuel oil #6 would be expected to be a skin, eye and respiratory irritant and a CNS depressant from inhalation of large amounts of the vapor or mist. Prolonged or repeated contact with the skin may produce a defatting dermatitis with dryness and cracking. This product may contain substances which have caused kidney damage in laboratory animals [369].

Chronic effects of some of the constituents in fuel

6 (such as naphthalenes) include changes in the liver and kidney [766].

Exposure to petroleum in soil is predominantly of concern through a number of possible exposure pathways, including dermal contact with soil, ingestion of soil, inhalation of soil particulates, and ingestion of contaminated groundwater [824].

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

No studies were found for fuel oil #6 [369]. The PAHs in this product include both carcinogenic and noncarcinogenic compounds. 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.

The debates on which PAHs, alkyl PAHs, and other aromatics in complex mixtures (such as this product) to classify as carcinogens, and the details of exactly how to perform both ecological and human risk assessments on the complex mixtures of PAHs typically found at contaminated sites, are likely to continue. There are some clearly wrong ways to go about it, but defining clearly right ways is more difficult. Perhaps the most unambiguous thing that can be said about complex mixtures of PAHs and other aromatics 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).

There is sufficient evidence for the carcinogenicity in experimental animals of residual (heavy) fuel oils and cracked residues derived from the oil refining of crude oil [747]. Residual (heavy) fuel oils are possibly carcinogenic to humans [747].

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

Some of the PAHs found in fuel oil are either AHH active or endocrine disruptors [561]. The experts disagree about the extent to which the two are synonomous (see PAHs as a group entry).

One investigator found increased lethality in rats exposed to fuel oil,but no increase in malformations were found [559].

Studies showed that contamination of quail eggs with Bunker C via maternal routes resulted in reduced egg production and reduced egg viability [558].

No reproductive studies were found for fuel oil #6 [369]. The results are mixed, but some reproductive and fetotoxic effects have been associated with a few of the compounds found in fuel no. 6 [766] (see sections on individual compounds for more details).

Exposure of avian eggs to hydrocarbons may be direct or maternal. Small amounts of exposure (50-100 uL) by direct transfer of oil on plumage to the eggs in the nest has been shown to be toxic to embryos. Studies showed that contamination of quail eggs with Bunker C via maternal routes resulted in reduced egg production and reduced egg viability (Grau et al., 1977) [558].

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

Fuel oil number 6 is a heavy oil with little or no evaporation or dissolution potential [741,777]. As such, fuel oil 6 may be highly persistent, with the potential for long-term sediment contamination. Other fate characteristics of heavy oils (Including Heavy Crude Oils, No. 6 fuel, and Bunker C) include the following [741]:

-Water-soluble fraction likely to be <10 ppm
-Heavy contamination of intertidal areas likely
-Long-term contamination of sediments possible
-Weathers very slowly
-Dispersion seldom effective
-Shoreline cleanup difficult under all conditions

Among the fuel oils, number 6 is the heaviest, with a specific gravity of about one. One of the three types of (unusual) scenarios in which one might tend to worry most about sinking fractions of oil includes spills of very heavy oils in freshwater, such as spills of heavy No. 6 fuel (Jackie Michel, Research Planning Inc., S. Carolina, Personal Communication,1995). For example, in the Mobil oil spill in the Columbia River near Portland, Oregon (03/19/84), spilled oil was distributed on the surface of the river, throughout the water column, and on the river bottom. Oil in the river bottom formed a pool in the eddy created by the hull of the Mobil oil [555].

In general, even though density of oil increases through weathering, the density will rarely increase to that of freshwater (approximately 1000 kg/m3) or marine water (about 1024 kg/m3). However, heavy fuels such as no. 6 may weather to densities heavier that water since the unweathered density already exceeds 900 kg/m3 (a typical No. 6 fuel oil is API 12.3 which corresponds to a density of 971 kg/m3 at 22 +or- 2 degrees Celsius) [554].

During a spill, the high viscosity of No. 6 fuel oil can often lead to the formation of "pancake" like tar globs when the temperature of the water is lower than the pour point of the oil [555]. These semi-solid, tar-like oils have low substrate penetrating ability, and are difficult to remove from contaminated surfaces. Emulsions formed by No. 6 fuel oils are very stable [555]. Examples of No. 6 fuel oil spills with pancake formation include the Presidente Rivera in the Delaware River (06/24/89), and the Argo Merchant near Nantucket Island, Massachusetts (12/15/76) [555]. For a more complete discussion of sinking oil, and oil spills in general, see the Oil Spill entry.

LAPIO, a particularly heavy kind of Fuel Oil 6, can float, sink, become neutrally buoyant, or fractionate and possess all three characteristics, it poses significantly different risks to natural resources, compared to floating oil spills [775]. For details see Fate.Detail section below.

Synonyms/Substance Identification:

BUNKER C [499,557,558,560]
GRADE 6 [499]
FUEL OIL NO. 6 [365,369]
FUEL OIL #6 [369]
HEATING OIL NO. 6 [369]
HEATING OIL #6 [369]
NO. 6 FUEL OIL [369,365,637]
NO. 6 HEATING OIL [369]
#6 FUEL OIL [369]
#6 HEATING OIL [369]

The United States Navy refers to bunker C as "Navy heavy" [637].

Associated Chemicals or Topics (Includes Transformation Products):

See also individual entries:

Fuel Oil, General
LAPIO (A very heavy #6 fuel oil) [775].

Oil Spills
Petroleum, General

See also entries on various PAHs and Alkyl PAHs. All 39 PAHs in the NOAA expanded scan [628] have been found in this product; these include, but are not limited to:

Phenanthrene
1-Methylphenanthrene
Fluoranthene
Pyrene
Benz(a)anthracene
Chrysene
Benzo(a)pyrene
Benzo(e)pyrene

Site Assessment-Related Information Provided by Shineldecker (Potential Site-Specific Contaminants that May be Associated with a Property Based on Current or Historical Use of the Property) [490]:

Raw Materials, Intermediate Products, Final Products, and Waste Products Generated During Manufacture and Use:

- Benzene
- Creosote
- Ethyl benzene
- Polynuclear aromatic hydrocarbons
- Toluene
- Xylenes

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

W.Low (Water Concentrations Considered Low):

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

Information from OHM/TADS [499]:

Aquatic toxicity:

Freshwater toxicity text (Conc.* in ppm):

Conc.	Expos (Hr)	Specie	Effect	Test Environment
2400	48	JUVENILE AMERICAN SHAD	TLM	
> 127	96	BLUEGILL	LC50	

Saltwater toxicity text (conc.* in ppm):

Conc.	Expos (Hr)	Specie	Effect	Test Environment
2,417	48	JUVENILE AMERICAN SHAD	TLM	
10	96	MENHADEN	LC50	
1,952	96	JUVENILE AMERICANSHAD	TLM	
26	96	GRASS SHRIMP	LC50	
1,302	96	JUVENILE AMERICAN SHAD	NO KILL	

Aquatic toxicity data from Environment Canada [560]:

Toxicity (mg/L):
Juvenile American shad-- 48h TLm*

1. Freshwater	2400	#1
2. Saltwater	2417	#2

*Note from Roy Irwin: I don't know of any lab method which measures the concentration of this product as a whole after it has been spilled in open waters, so these may reflect lab concentrations estimated by dilution ratios. 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].

W.Plants (Water Concentrations vs. Plants):

Information from OHM/TADS [499]:

Toxicity to plants:
Aquatic plants (ppm): 75*

*Note from Roy Irwin: I don't know of any lab method which measures the concentration of this product as a whole after it has been spilled in open waters, so these 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].

Abstract Contributed by Carol Schuler, Fish and Wildlife Service, Portland Oregon):

AUTHOR: Giddings JM; Washington JN
PUBLICATION YEAR: 1981
TITLE: Coal-Liquefaction Products, Shale Oil, and Petroleum. Acute Toxicity to Freshwater Algae
JOURNAL: Environmental Science and Technology
SOURCE: Vol 15, No 1, p 106-108, January, 1981. 2 Tab, 31 Ref.
KEYWORDS: Fuels; Toxicity; Synthetic fuels; Oil spills; Aquatic life; Aquatic algae; Aquatic plants; Coal liquefaction industry; Shale oil industry; Cyanophyta
KEYWORDS(*): *Oil pollution; *Water pollution effects; *Algae
MAJOR TOPIC: Water Quality Management, Protection - Effects of Pollution
ABSTRACT: Freshwater algae, Selenastrum capricornutum (a green alga) and Microcystis aeruginosa (a blue-green

alga), showed acute toxic effects from exposure to water soluble fractions (WSF) of oils in the following order: coal liquefaction products>shale oil products>petroleum products. WSF's were tested in concentrations of 0.1, 1, 10, and 100%. Most of the 11 coal liquefaction products were toxic at 1% and greater; 4 at 0.1%. Three unrefined shale oils inhibited photosynthesis at 10% and greater and were variably toxic at 1% and less. Two refined shale oils and the 5 petroleum products (DFM, No 2 diesel oil, and three No 6 fuel oils) showed little toxicity at all concentrations with the exception of some at 100% WSF. All samples were tested for absorbance at 254 nm, the absorption maximum for benzene and an approximation of aromatic content. The products with higher absorbances tended to be the most toxic to algae. (Cassar-FRC)
INST. AUTHOR: Oak Ridge National Lab.
AUTHOR ADDRESS: TN. Environmental Sciences Div.

W.Invertebrates (Water 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.

W.Fish (Water 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.

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):

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.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):

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 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 (bunker B is fuel oil no. 5, bunker C is fuel oil no. 6), or possibly very weathered crude) rather than gasoline [735]. The concentrations found [735]:

CONTAMINANT	CONCENTRATION (ppm)
Total Petroleum Hydrocarbon (TPH) EPA Method 418.1	69,300
Total Petroleum Hydrocarbon (TPH) EPA Method 8015 modified for diesel	43,000
Benzene	40.7
Toluene	102
Xylene	67
Ethylbenzene	171

Soil.Typical (Soil 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.

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):

In 1988, New Jersey started using a total petroleum hydrocarbon concentration of 100 ppm as a soil cleanup guideline thought to ensure that concentrations in ground water do not exceed drinking water standards; 100 ppm is thought to be relatively conservative and designed to identify potential problems [347]. More recently, the New Jersey standard was broken down by fuel type: if number 6 or 4 fuel oils, the guideline is 100 ppm; if number 2 fuel oil or diesel the guideline is 1,000 ppm (Steve Tatar, New Jersey Leaking Underground Storage Tank project, personal communication). The latest New Jersey values are part of a proposed cleanup standard (March 31, 1992, NJ Administrative Code) for all soil values (not just leaking underground tanks). Most New Jersey officials seem to believe the TPH guidelines in NJ are in dry weight, since soil values for other parameters are, but they hadn't yet been able to find the written confirmation as of this writing.

Soil.Plants (Soil 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.

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):

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

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

As of 1996, several States were considering allowing natural attenuation (the "do nothing and let nature clean up the mess through bioremediation" option) to proceed near leaking storage tanks in situations where drinking water was not being impacted and where human rather than environmental resources were the main resources in the immediate area (Roy Irwin, National Park Service, personal communication, 1996).

Others would point out that fuel oil spills into soils are not necessarily a trivial environmental threat related to ecotoxicology (emphasis on living things other than humans), due to the many hazardous compounds in fuel oils (see Chem.Detail section below).

Exposure to petroleum in soil is predominantly of concern through a number of possible exposure pathways, including dermal contact with soil, ingestion of soil, inhalation of soil particulates, and ingestion of contaminated groundwater [824].

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.

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 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 Wildlife, Birds, or Domestic Animals (Includes LD50 Values Which do not Fit Well into Other Categories, Includes Oral Doses Administered in Laboratory Experiments):

Information from RTECS [365]:

LD50/LC50 - LETHAL DOSE/CONC 50% KILL

RAT: LD50; ROUTE: Oral; DOSE: 5300 mg/kg; REFERENCE: Acute Toxicity Data. Journal of the American College of Toxicology, Part B 1:139, 1990.

LDLO/LCLO - LOWEST PUBLISHED LETHAL DOSE/CONC

RABBIT: LDLo; ROUTE: Skin; DOSE: 5200 mg/kg; REFERENCE: Acute Toxicity Data. Journal of the American College of Toxicology, Part B 1:139, 1990.

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

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

Tis.Human:

A) Typical Concentrations in Human Food Survey Items:

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

NOTE: Below are three case studies on the effects of spilled Bunker C on plants (Selected highlights copied from NOAA Restoration Guidance Document by permission of Eli Reinharz of NOAA DART Team) [622]:

Case Study 1:

In October 1978 the ship Howard Star released ~40,000 gallons of Bunker C and lubricating oils into Tampa Bay, Florida. At least 20 km of fringe mangrove shoreline was affected [622].

The oiled sites in Tampa Bay were visited 2 months, 9 months, 14 months and 16 months after the discharge. Each discharge site and adjacent reference sites were examined by aerial surveys to locate defoliated areas. Areas with obvious defoliation and reference areas were selected for subsequent ground surveys. The heaviest defoliation of mangroves, seedling mortalities, and mortalities of canopy-dwelling animals were observed where the heaviest oiling had occurred. The degree of oiling was controlled largely by geomorphic features of the forest [622].

On the basis of geomorphic features, two types of oil impacts were observed in Tampa Bay: outer fringe and an inner basin impacts. Impact to the outer fringe occurred at two sites where defoliation was concentrated in the outer mangroves. In these areas, mangrove mortality appeared to be related to (1) degree of exposure to waves and currents and (2) degree of oil penetration into the forest substrate. The latter was enhanced by the presence or absence of burrowing crabs. In Tampa Bay, exposed areas contained few burrows, and oil was removed by wave action within a few weeks. Impact to the inner basin was observed in two oiled areas of Tampa Bay where high tides moved oil up over coastal berms and into shallow basins behind them, spreading the oil over a wide area with a less well defined effects [622].

Case Study 2:

In December 1978 the barge Peck Slip released 440,000-460,000 gallons of Bunker C fuel oil into Bahia Medio Mundo, Puerto Rico, oiling at least 10 km of mangrove-dominated shoreline. In 1981 the oiled sites in Midia Mundo were visited immediately after the discharge, and 3-4 months and 10 months after the discharge. As in the Howard Star discharge, each discharge site and adjacent reference sites were examined by aerial surveys to locate defoliated areas. Areas with significant defoliation and reference areas were selected for subsequent ground surveys. The heaviest defoliation of mangroves, seedling mortalities, and mortalities of canopy-dwelling animals were observed where the heaviest oiling had occurred.

The degree of oiling was controlled largely by geomorphic features of the forest [622].

On the basis of geomorphic features, two areas of oil impact were observed at Media Mundo, an inner fringe impact and an inner basin impact. In the inner fringe impact, oil was concentrated on the inner mangroves, which are located on the inner berm of the forest. The affected inner berm site became heavily defoliated within 2 months of oiling, and remained so 18 months later, with the substrate and prop roots remaining oiled even after Hurricane David in 1979. An inner basin impact, similar to that described in Tampa Bay, was also observed at Media Mundo [622].

Case Study 3:

In December 1968, the tanker Witwater ran aground off the Caribbean coast of Panama, releasing 20,000 barrels of diesel oil and bunker C fuel oil. Injury to mangrove habitats was assessed qualitatively approximately 2 months after the discharge. The pneumatophores of black mangroves were thickly covered with a mixture of mud and oil. Prop roots of red Mangroves were coated with a thick layer of oil. Red mangrove seedlings were covered with oil and suffered massive mortality. Populations of crabs, Uca sp., were reduced relative to non-oiled areas [622].

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

The alkyl PAHs tend to bioaccumulate more than their parent compounds (see PAHs entry).

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.

Interactions:

May act as synergist to pesticides [499].

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.

Uses/Sources:

The viscous residuum fuel oils, numbers 5 and 6, sometimes referred to as bunker fuels, are used in furnaces and boilers of utility power plants, ships, locomotives, metallurgical operations, and industrial power plants, and usually must be preheated before being burned [498]. Bunker C is used primarily for firing steam boilers in the generation of electricity, large-scale heating, and powering marine vessels [557].

Bunker C fuel oil (fuel oil no. 6) is a heavy fuel oil used by ships, by industry, and for large-scale heating installations [637].

Forms/Preparations/Formulations:

Conventional #6 fuel oil is a mixture of the heavy residual oil left after the lighter components of crude oil are removed through a refining process, which is then blended with lighter oils to meet specifications for viscosity, pour point, and API gravity [775].

No. 2 fuel oil is a common blending agent, used to reduce the viscosity of conventional #6 fuel oils. Because #2 fuel oil (which is a good solvent for many blended residual fuel oils) is used as the cutter stock, #6 fuel oils are usually well-blended mixtures that are stable during long-term storage and do not tend to separate when spilled [775].

Like fuel oil #6, LAPIO (Low-API gravity oils) is a blend of heavy and light oil, but it generally contains more of the heavier components. Therefore, LAPIO could be considered as a very heavy #6 fuel oil [775]. Additional Details about LAPIO:

> A low-API gravity fuel oil, or LAPIO, is defined as an oil having an API gravity less than 10 degrees at 60 degrees F (see note below). This means that its specific gravity is less than or equal to 1.00 mg/L (which is the same as freshwater). Therefore, LAPIOs can float, be neutrally buoyant, or sink in water depending on the specific properties of the spilled oil and the salinity of the receiving waters [775]. LAPIO is an industry term [776].
>
> > 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 [560].

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. PAHs and alkyl PAHs in this product can be analyzed to risk assessment-appropriate (low; 1-10 ppb or lower) detection limits using the GC/MS/SIM NOAA protocol expanded scan [828].

> Caution: Every individual petroleum product has a unique "fingerprint," or distinct combination of concentrations of various PAHs and other petroleum constituents. Due to the varying properties of the same general category of a petroleum product (for example, each source and stage of a No. 6 fuel oil has a unique gas chromatograph "fingerprint"), careful assessment of the toxicity, specific gravity, and other physical characteristics of each individual oil must be taken into consideration to determine the exact effects of the product on the environment. For example, the API gravity of No. 6 fuel oils ranges from 7 to 14. Therefore, the below comments on No. 6 fuel oils are to be considered as representative, but not absolute values typical of every batch of the product with the same name.

Fuel oil No. 6 contains about 15% paraffins, 45% naphthenes, 25% aromatics, and 15% non-hydrocarbon compounds; the hydrocarbons contain 30 and greater carbon atoms [557]. Another source lists 21.1% saturates, 34.2% aromatics, 30.3% polar aromatics, and 14.4% asphaltenes [747]. Fuel oil No. 6 consists of straight-run and cracked distillates and residuals and contains aliphatics and aromatics [369].

Appreciable concentrations of PAHs are present in residual fuels because of the common practice of using both uncracked and cracked residues in their manufacture. Most blending stocks are likely to contain 5% or more of four- to six-ring condensed aromatic hydrocarbons. The following table lists the concentrations of three- to five-ring aromatics determined in one sample of No. 6 fuel oil (NOTE: The exact identities and concentrations of PAHs in a particular sample depends on the nature and amounts of blending stocks as well as the virgin and cracked residues) [747]:

Hydrocarbon	Concentration (ppm)
Phenanthrene	482
2-Methylphenanthrene	828
1-Methylphenanthrene	43
Fluoranthene	240
Pyrene	23
Benz(a)anthracene	90
Chrysene	196
Triphenylene	31
Benzo(a)pyrene	44
Benzo(e)pyrene	10
Perylene	22

Octanol Water Log: 3.3 to 7.06 [875].

Henry's Law Const. 5.9E-05 to 7.4 [875].

Physicochemical information from Environment Canada [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 [560]:

API GRAVITY (60/60 degrees F) [560]:

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 [560].

14.1
10
7.3
15.5
12.3

DENSITY (g/mL) [560]:

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. The following density values are at "0% Weathering Volume" - in other words, fresh No. 6 fuel oil.

Temp(C)	Density (at 0% Weathering Volume)
0	0.969 to 0.980
	0.986
	0.980
	0.9941
5	0.976
	0.9904
10	0.973
	0.963
	0.9867
15	0.974
	0.969
	0.9830
15.6	0.959 to 0.972
	0.9710
	0.963
20	0.956 to 0.970
	0.966
	0.9788

	0.9483 (estimated)
25	0.964
	0.9749
30	0.950 to 0.964
	0.9718

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	21.1
	21.1
	20.98
	15
	24.4
	21.1
Aromatics	34.2
	34.2
	33.83
	25
	54.6
	34.2
Polars	30.3
	30.3
	7.39
	15
	14.9
	30.3
Asphaltenes	14.4
	14.4
	6.17
	9.28
	14.4
	6.73
	6.5
Naphthenes	45

Wax Content (Weight %):

11.7
55.4

METAL CONTENT [560]:

Other Metals (ppm):

Nickel	62
	89
	35
	8.6
	34.3

Vanadium	25
	73
	272
	42
	270
Molybdenum	< 0.6
	272 ppb
Potassium	< 1.5
Zinc	1.61
	1.22
Lead	< 3
Iron	35
	13.2
Chromium	< 1.5
	440 ppb
Magnesium	23.9
Copper	1.2
	0.60
Titanium	< 0.6
Barium	< 0.3
Cobalt	197 ppb
Manganese	149 ppb

SOLUBILITY:

Aqueous Solubility (mg/L) [560]: 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)	20 C	22 C
Seawater	2.29	6.3	
Distilled Water	1.7		0.4
Fresh Water	4.45		

Solubility [554]:

1.95 mg/L (salt H2O3, at 22 +or- 2 degrees Celsius)
4.23 mg/L (d.d H2O, at 22 +or- 2 degrees Celsius)

Solubility: about 5 mg/L [875].

Concentrations of PAHs in a reference Bunker C residual oil versus Two Crude Oils Another Refined Oil [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	5.0	2.9	37	240
Pyrene	3.5	4.5	41	23
Benz(a)anthracene	1.7	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		

Physical Characteristics and Chemical Properties of Two Refined Products [558]:

Characteristic or Component	No. 2 Fuel Oil*	No.6 Bunker C Fuel oil
API gravity (20 C) (API)**	31.6	7.3
Sulfur (wt %)	0.32	1.46
Nitrogen (wt %)	0.024	0.94
Nickel (ppm)	0.5	89
Vanadium (ppm)	1.5	73
Saturates (wt %)	61.8	21.1
n-paraffins	8.07	1.73
C10 + C11	1.26	0
C12	0.84	0
C13	0.96	0.07
C14	1.03	0.11
C15	1.13	0.12
C16	1.05	0.14
C17	0.65	0.15
C18	0.55	0.12
C19	0.33	0.14
C20	0.18	0.12
C21	0.09	0.11

C22	0	0.10
C23	0	0.09
C24	0	0.08
C25	0	0.07
C26	0	0.05
C27	0	0.04
C28	0	0.05
C29	0	0.04
C30	0	0.04
C31	0	0.04
C32 Plus	0	0.05
Isoparaffins	22.3	5.0
1-ring cycloparaffins	17.5	3.9
2-ring cycloparaffins	9.4	3.4
3-ring cycloparaffins	4.5	2.9
4-ring cycloparaffins	0	2.7
5-ring cycloparaffins	0	1.9
6-ring cycloparaffins	0	0.4
Aromatics (wt %)	38.2	34.2
Benzenes	10.3	1.9
Indans and tetralins	7.3	2.1
Dinaphthenobenzenes	4.6	2.0
Naphthalenes	0.2 b	
Methylnaphthalenes	2.l b	2.6
Dimethylnaphthalenes	3.2 b	
Other naphthalenes	0.4	
Acenaphthenes	3.8	3.1
Acenaphthalenes	5.4	7.0
Phenanthrenes	0	11.6
Pyrenes	0	1.7
Chrysenes	0	0
Benzothiophenes	0.9	1.5
Dibenzothiophenes	0	0.7
Polar materials c (wt %)	0	30.3
Insolubles (pentane) c (wt %)	0	14.4

* This is a high aromatic material; a typical No. 2 fuel oil would have an aromatic content closer to 20-25%. From Vaughan (26).

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

NOTE: The above analyses represent typical values for two different refined products; variations in composition can be expected for similar materials from different crude oil stocks and different refineries.

PAHs in NSFO (Fuel Oil 5):

NOTE: The following information on fuel 5 is included for general information because fuel 5 is typically about 75-80% of fuel 6 [641].

A NOAA protocol [828] GC/MS/SIM expanded scan for PAHs in a sample of fresh NSFO (Fuel Oil 5) revealed the presence of all 39 PAHs and alkyl PAHs analyzed, with the lowest concentration being 0.6 ppm for Benzo(k)fluoranthene and the highest concentration being 4865 ppm for C2-Naphthalenes. A groundwater sample contaminated with weathered versions of the same NSFO product from Colonial National Historical Park also revealed the presence of all 39 PAHs and alkyl PAHs analyzed, with the lowest concentration being 39.7 ppt for Benzo(k)fluoranthene and the highest concentration being 48336 ppt for C4-Naphthalenes (Chuck Rafkind, National Park Service, Personal Communication, 1996). Total naphthalenes in these groundwater samples exceeded 107000 ppt, far above the 2.8 ppt cancer risk (10-6 level) benchmark given for human health (see naphthalene section).

Details of PAH content (ng/mg or ppm) in one fresh sample of NSFO (Fuel Oil 5, Chuck Rafkind, National Park Service, Personal Communication, 1996):

Naphthalene:	34.3	
C1-Naphthalene:	4086.9	
C2-Naphthalene:	4865.4	
C3-Naphthalene:	4793.7	
C4-Naphthalene:	2688.5	
Biphenyl:	3.5	
Acenaphthylene:	4.1	
Acenaphthene:	111.2	
Fluorene:	216.0	
C1-Fluorene:	658.8	
C2-Fluorene:	1277.0	
C3-Fluorene:	1243.8	
Anthracene:	96.4	
Phenanthrene:	778.2	
C1-Phenanthrene/anthracene:	2116.3	(includes both)
C2-Phenanthrene/anthracene:	2716.7	"
C3-Phenanthrene/anthracene:	1923.3	"
C4-Phenanthrene/anthracene:	820.5	"
Dibenzothiophene:	25.7	
C1-Dibenzothiophene:	1396.1	
C2-Dibenzothiophene:	2155.9	
C3-Dibenzothiophene:	1975.5	
Fluoranthene:	31.6	
Pyrene:	177.9	
C1-Fluoranthene/pyrene:	566.1	
Benzo(a)anthracene:	41.1	
Chrysene:	74.3	
C1-Chrysene:	312.1	
C2-Chrysene:	370.8	
C3-Chrysene:	29.9	
C4-Chrysene:	19.7	
Benzo(b)fluoranthene	11.0	
Benzo(k)fluoranthene:	0.6	
Benzo(e)pyrene:	29.8	
Benzo(a)pyrene:	19.3	

Perylene	10.6
Indeno[1,2,3-c,d]pyrene:	2.3
Dibenz(ah)anthracene:	4.0
Benzo(ghi)perylene:	11.4

> Note: The above PAHs and alkyl PAHs were analyzed by a GC/MS/SIM NOAA protocol [828] modified with methylene chloride extraction for use with water samples (Guy Denoux, Geochemical and Environmental Research Group, Texas A&M University, personal communication 1996).

Details of PAH content (ng/L or ppt, compare to the above listed ppm concentrations by dividing the below-listed ppt concentrations below by 1,000,000) in one sample of groundwater subjected to long term contamination of NSFO (Fuel Oil 5), possibly mixed with some JP-4, motorgas, and JP-8, Colonial National Historical Park Groundwater Site MW-10 (Chuck Rafkind, National Park Service, Personal Communication, 1996):

Naphthalene:	530.8	
C1-Naphthalene:	2463.7	
C2-Naphthalene:	12044.7	
C3-Naphthalene:	45345.1	
C4-Naphthalene:	48336.8	
Biphenyl:	129.7	
Acenaphthylene:	81.2	
Acenaphthene:	1517.6	
Fluorene:	1229.3	
C1-Fluorene:	11424.5	
C2-Fluorene:	28680.7	
C3-Fluorene:	32509.9	
Anthracene:	1972.5	
Phenanthrene:	7136.3	
C1-Phenanthrene/anthracene:	31377.0	(includes both)
C2-Phenanthrene/anthracene:	49447.3	"
C3-Phenanthrene/anthracene:	41754.1	"
C4-Phenanthrene/anthracene:	22250.2	"
Dibenzothiophene:	8377.8	
C1-Dibenzothiophene:	24742.0	
C2-Dibenzothiophene:	44033.0	
C3-Dibenzothiophene:	43900.3	
Fluoranthene:	818.8	
Pyrene:	5900.6	
C1-Fluoranthenes/pyrenes:	16248.3	(includes both)
Benzo(a)anthracene:	1053.5	
Chrysene:	1817.1	
C1-Chrysene:	7398.8	
C2-Chrysene:	9910.6	
C3-Chrysene:	1048.5	
C4-Chrysene:	625.9	
Benzo(b)fluoranthene	399.2	
Benzo(k)fluoranthene:	39.7	

Benzo(e)pyrene:	1062.3
Benzo(a)pyrene:	602.7
Perylene	428.6
Indeno[1,2,3-c,d]pyrene:	106.8
Dibenz(ah)anthracene:	117.1
Benzo(ghi)perylene:	421.4

Note: The above PAHs and alkyl PAHs were analyzed by a GC/MS/SIM NOAA protocol [828] modified with methylene chloride extraction for use with water samples (Guy Denoux, Geochemical and Environmental Research Group, Texas A&M University, personal communication 1996).

Additional Information on Physicochemical parameters [499]:

Physical parameters:
Location/state of material:
Dark, viscous, odiferous liquid. After 24 hour toc analysis revealed 11 ppm in solution; will float in slick on surface.
Melting point (degrees C):
-46
Boiling point (degrees C):
400
Reactivity:
Synergistic materials:
May act as synergist to pesticides.

Additional physicochemical parameters [554]:

Viscosity:
48000 cp (at 10 degrees Celsius)

Physicochemical Information on Specific Gravity:

Typical specific gravity of semi-solid tar like oils such as Fuel Oil 5, Fuel Oil 6, Fuel Oil 10, tall oil, asphalt, and heavy crude oil (the oils that tend to form tar balls) is 0.94 - 0.97 (at 15 degrees Celsius), translating to API gravity < 15 [556].

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 [560]. API gravity is < 15 for bunker C (usually in the range of 7 to 14) [558].

SPECIFIC GRAVITY is 1 (+/-) (for Fuel oil No 6) (NFPA, 1991)

NOTE: The specific gravity for the other fuel oils are:
A. Less than 1 (Fuel oils Nos 1, 2, 4, 5) (NFPA, 1991), and B. 0.85 (Fuel oil No 2) (OHM/TADS, 1992).

Additional Physicochemical Information [498]:

DENSITY

1 (+/-) g/cm(3) (Fuel oil No 6)
Note: the other fuel oils are: A. Less than 1 g/cm(3) (Fuel oils Nos 1, 2, 4, 5)

Note: a typical no. 6 fuel oil is API 12.3 which corresponds to a density of 971 kg/m3 at 22 +or- 2 degrees Celsius [554].

FLASH POINT (NFPA, 1991):
Fuel oil No 6: 150 to 270 degrees F
Note: the other fuel oils are:
Fuel oil No 1: 100 to 162 degrees F
Fuel oil No 2: 126 to 204 degrees F
Fuel oil No 4: 142 to 240 degrees F
Fuel oil No 5 (light): 156 to 336 degrees F
Fuel oil No 5 (heavy): 160 to 250 degrees F

EXPLOSIVE LIMITS: Not listed
IGNITION TEMPERATURE (NFPA, 1991):
Fuel oil No 6: 765 F
Note: the other fuel oils are:
1. Fuel oil No 1: 410 degrees F
2. Fuel oil No 2: 494 degrees F
3. Fuel oil No 4: 505 degrees F
4. Fuel oil No 5 (light): Not listed
5. Fuel oil No 5 (heavy): Not listed

ODOR: Petroleum-like odor (AAR, 1987).

TASTE: No information on the taste of fuel oil was found in available references at the time of this review.

COLOR: Fuel oils are straw yellow to dark colored liquids (AAR, 1987).

PH: No information on the pH of fuel oil was found in available references at the time of this review.

REACTIVITY: When heated to decomposition, fuel oils emit acrid smoke and irritating fumes (Sax & Lewis, 1989).

Fuel oils can react vigorously with oxidizing materials (Sax & Lewis, 1989).

Additional Physicochemical information from Environment Canada [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 [560]:

VISCOSITY

NOTE: The viscosities of crude oils and oil products are dependent on the temperature and degree of weathering. The following viscosity values are at "0% Weathering Volume" - in other words, fresh No. 6 fuel oil.

Dynamic Viscosity (mPa.s or cP):

Temp(C)	Dynamic Viscosity (at 0% Weathering Volume)
0	73500000
	1400000
10	28700000
15	48000
20	5980000
25	3180
50	545

Kinematic Viscosity (mm2/sec or cSt):

Temp(C)	Kinematic Viscosity (at 0% Weathering Volume)
10	> 1000
20	> 500
40	> 130
55	90 to 2000
60	65 to 1000
70	65 to 360
80	65 to 180

Note: Data obtained from a graph

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.

-4 to 13
2
< 16
-1
15
6
7

INTERFACIAL TENSIONS

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. The following tension values are at "0% Weathering Volume" - in other words, fresh No. 6 fuel oil.

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

Temp(C)	Air-Oil Tension (at 0% Weathering Volume)
0	N/M
15	N/M
Room Temp.	27
	25 (est.)

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

Temp(C)	Oil-Seawater Tension (at 0% Weathering Volume)
	N/M

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

Temp(C)	Oil-Water (at 0% Weathering Volume)
0	N/M
15	N/M
Room Temp	39.82
	50 (est.)

EMULSION

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. The following typical values are at "0% Weathering Volume" - in other words, fresh No. 6 fuel oil. In general, No. 6 fuel oil is not likely to form emulsions (although Bunker C from the Arrow incident did form stable emulsions).

Emulsion Formation Tendency (in the NOT LIKELY range):

Temp(C)	Fraction of oil that forms an emulsion (f initial)
0	0.1
	0
15	0
	0

Emulsion Stability (in the UNSTABLE range):

Fraction of oil in the emulsion:

Temp(C)	that remains after settling (f final)
0	0.2

	0
15	0.1
	0

Water Content of Emulsion (volume %):

Temp(C)	Water Content (at 0% Weathering Volume)
0	N/A
15	N/A

DISPERSIBILITY

Chemical Dispersibility (% Dispersed):

Dispersant	Dispersibility
C 9527:	0
Dasic:	0
EN 700:	0
CRX-8:	5

Natural Dispersibility (% Dispersed):

Temp(C)	Naturally Dispersed
15	0

FIRE AND REACTIVITY

Flash Point (C):
>110
66
60. MIN
174
80
> 66
99
98
> 65.5

Fire Point (C):
>257
164

Auto Ignition Temperature (C):
408
407

Combustion Results:
Relatively long ignition time (1.9 min);
26.4 vol% residue.

Flammability Limits (Volume %):
in air: 1 to 5

DISTILLATION

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	324	115
		151
		78
5	391	222
		126
10	414	310
		248
		166
15	422	259
		199
20	427	335
		267
		217
25	428	272
		225
30	432	345
		277
		231
35	435	282
		233
40	438	350
		286
		234
45	440	293
		235
50	441	355
		299
		235
55	445	304
		235
60	448	367
		312
		235
65	449	318
		235
70		370
		326
75		375
		333
80		344
85		357
90		387
95		417
FBP		441

Initial Boiling Point - IBP (C):

180 to 500

Final Boiling Point - FBP (C):

212 to >> 588
400

NON-METAL CONTENT

Carbon Residue - using the Ramsbottom method (Weight %):

12

Nitrogen (Weight %):

0.34
0.94
149 ppb

Sulphur (Weight %):

2.40
1.46
2.24
1.5

OTHER:

Ash (Weight %):

0.08

Reid method Vapor Pressure (kPa):

Temp(C)	Pressure
37.8	0.689 (estimated)

Compositional Analysis

Saturates:

n-Alkanes C13+	1.73
Isoalkanes	5.0
1-Ring Cycloalkanes	3.9
2-Ring Cycloalkanes	3.4
3-Ring Cycloalkanes	2.9
4-Ring Cycloalkanes	2.7
5-Ring Cycloalkanes	1.9
6-Ring Cycloalkanes	0.4

Aromatics:

Benzenes	1.9
Indans and Tetralins	2.1
Dinaphtheno Benzenes	2.0
Methylnaphthalenes	2.6
Acenaphthenes	3.1
Acenaphthalenes	7.0
Phenanthrenes	11.6
Pyrenes	1.7
Benzothiophenes	1.5
Dibenzothiophenes	0.7

Information on LAPIO, a particularly heavy kind of Fuel Oil 6: Like conventional fuel oil #6 (Bunker C), LAPIOs are mixtures of the heavy residual oil and lighter oils, but LAPIOs generally contain more of the heavier components [775]. The residual oils are derived primarily from three sources: 1) atmospheric reduced crude, 2) vacuum bottoms, and 3) heavy slurry oils. LAPIOs are heavy residual products blended with some other product to meet client specifications for viscosity, pour point, and sulfur content, but LAPIOs do not have to meet a minimum API gravity requirement. The amount and source of the cutter stock and/or lighter residual oil blended with the heavier residual oil to meet client specifications varies widely, so the chemical composition of LAPIO will vary case by case [775]. For example, fuel oil #2 is a commonly used blending agent to reduce viscosity in fuel oil #6, whereas LAPIO may be a blend of just residuals without any light cutter stock. Sometimes these residuals are incompatible, leading to asphaltene precipitation during transportation and storage. This can lead to changes in the physical properties of the oil and problems during combustion. Incompatible or non-homogenous blends can also physically separate into components that float, sink, and/or become neutrally buoyant when spilled on the water. When incompatible blends are simply poured into a beaker full of water, samples of visually homogenous oil will separate. The potential for physical separation appears to be unique to LAPIO [775]. For additional information on sinking oil, see the Oil Spills entry.

The pour point of a LAPIO is not always high (most < 45 degrees F) due to low paraffin content [776]. Although LAPIO has been compared to asphalt, this is a poor analogy. Asphalt rapidly cools to form solid masses, whereas most LAPIO will remain liquid at ambient temperatures, will act like fluid when spreading, and is less likely to be sticky [775].

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

Fuel oil 6 is less volatile than:

Petroleum ether or benzine
Gasoline
Naphtha
Mineral spirits
Kerosene, and
Lighter Fuel oils [363].

It is more volatile than:

Lubricating oils
Paraffin wax
Asphalt or tar [363].

Persistency [499]: Loss of fuel oil after 40 hour in bubbler apparatus - 2.% Evaporated, .005% Dissolved.

Experiments designed to study the effects of weathering on density of four common heavy fuel oils studied the five processes believed to contribute to an increase in oil density: evaporation, dissolution, photolysis, attachment of foreign matter, and water uptake. The study concluded that the primary causes of increased density are evaporation of the more volatile and less dense components of the oil (although the study results show that No. 6 fuel oil is unlikely to sink by evaporation alone), and the incorporation of denser-than-water mineral matter into the oil [554]. As a result of these two processes and the beginning high density of No. 6 fuel oil, these type of oil spills are at a higher risk of sinking. For example, a spill of Bunker C occurred in San Francisco Bay (1975). The spilled oil first increased in density by evaporative losses of its lighter fractions, and then was mixed through the water column by strong tidal currents and wind. Some of the oil globules carried to the bottom by the turbulence then mixed with sandy and gravelly sediments, thus causing the oil to remain near the bottom. The oil eventually moved to eastern San Pablo Bay after being transported landward by the near-bottom water currents [558].

The following information is from an assessment of potential risks associated with the shipment and transfer of LAPIO, a very heavy type of #6 fuel oil, in the St. John's River, Florida [775]:

> Because LAPIO can float, sink, become neutrally buoyant, or fractionate and possess all three characteristics, it poses significantly different risks to natural resources, compared to floating oil spills, for the following reasons [775]:
>
> 1. Neutrally buoyant or sinking LAPIO weathers very slowly by evaporation, a process that tends to remove the more toxic fractions from floating oil slicks and greatly reduces the acute toxicity of the spilled oil. As a result, the toxic components of a LAPIO spill are introduced directly into the water column at concentrations greater than traditional spills. Animals in the water column, such as fish, shellfish, and marine mammals, can be exposed to these higher concentrations [775].

2. LAPIO that is denser than the receiving waters is not expected to sink immediately to the bottom and remain there. More likely, it will be suspended in the water column by tidal and riverine currents, eventually exiting the river system with the net outflow of water. Accumulation of oil on the bottom is expected only in zones of low flow, such as dredged channels, dead-end waterways, and abandoned channels. Natural removal rates by physical flushing would be very slow for spills in the lacustrine section of the St. Johns River system [775].

3. Benthic organisms are seldom at risk from floating oil spills. However, with heavier-than-water spills, additional impacts to benthic resources are likely to occur from smothering as well as increased exposure to residual oil that was not recovered. As a corollary, impacts to shoreline habitats and animals that use both the shoreline and water surface should be less for sinking oil spills [775].

4. Containment and removal efforts for sinking oil will largely be ineffective. As recently experienced during the Morris J. Berman [Puerto Rico, 1994] oil spill, removing submerged oil is very slow, and usually generates large volumes of contaminated water and sediment. In fact, removal of the submerged oil in Puerto Rico was conducted only where the oil was contained by natural or existing features. Oil sank in other areas, but tidal currents dispersed the oil over large areas, making it impractical to recover [775].

5. Containment and removal efforts for neutrally buoyant oil will likely be ineffective. There are no proven techniques for containing oil in the water column, or for removing oil from such large volumes of water [775].

6. Even standard techniques for location, containment, and recovery will fail unless conducted by contractors experienced in the proper deployment and maintenance of the equipment and the

> special requirements of oil-spill response [775].

> The potential for spilled LAPIO on the water surface, in the water column, and on the river bottom will tend to affect a broad range of resources (fish, shellfish, manatees, and birds) in the St. Johns River. Manatees (a protected species) are unlikely to be found in the lower river segments in any great numbers, only as single individuals traveling to and from preferred habitats upstream [775]. Woodstorks (endangered) are also unlikely to be affected as they prefer to roost in trees and wade in upland freshwater marshes-areas unlikely to be oiled. Additional injuries to fishery and shellfish resources are more likely to occur. Present response technology is ill-equipped to deal with the potential water-column and benthic habitat impacts from a spill of LAPIO [775].

Laboratory and/or Field Analyses:

As mentioned in the Chem.Detail section above, fuel oil No. 6 contains about 15% paraffins, 45% naphthenes, 25% aromatics, and 15% non-hydrocarbon compounds; the hydrocarbons contain 30 and greater carbon atoms [557]. Appreciable concentrations of PAHs are present in residual fuels because of the common practice of using both uncracked and cracked residues in their manufacture [747].

Many lab methods have been used to determine PAHs, BTEX compounds, and other common components of this fuel [861], but when potential biological effects are to being considered, many of the methods historically used have been determined to be inferior to the NOAA protocol expanded scan [828] being recommended by many risk assessment experts in 1996. Many historically used methods, including EPA standard semi-volatile scan number 8270, do not cover important alkyl PAHs and do not utilize low-enough detection limits to use in ecological risk assessments. See also: PAHs as a group entry.

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].

Decision Tree (dichotomous key) for selection of lab methods for measuring contamination from midrange to heavy crude oils including Fuel Oil 6 (bunker C):

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.

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]. 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 expanded scan protocols for 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 bio-concentratable substances) to allow more and more flexibility to select options at various points along the way, makes it harder in insure data comparability or method validity. Even volunteer monitoring programs are now strongly encouraged to develop and use quality assurance project plans [1015,1017].

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

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

Additional details:

The relative proportions of hazardous compound constituents present in petroleum-based oil contamination is typically quite variable. The farther one progresses from lighter towards heavier oils (the general progression from light towards heavy is the following: Diesel, No. 2 Fuel Oil, Light Crudes, Medium Crude Oils, Heavy Crudes, No. 6 Fuel Oil, etc.) the greater the percentage of PAHs and other semi-volatiles (many of which are not so immediately toxic as the volatiles but which can result in long term/chronic impacts). Heavier oils such as fuel oil 5 thus need to be analyzed for the semi volatile compounds which typically pose the greatest long term risk, PAHs and alkylated PAHs.

Screening scans: Certain screening scans may be used to monitor the position and magnitude of contamination. Below are a few notes related to screening scans versus distillate fuels:

GC/FID:

While a screening analysis such as GC/FID should be adequate for mid-range products such as diesels, fuel oil no. 2, and possibly jet fuels, lighter gasoline fractions will be lost in a GC/FID analysis (which uses extraction and burning) [657]. Distillate fuels in the C9 to C16 range normally have a boiling range well above the boiling-point of benzene; accordingly, the benzene content of this fraction is usually low [747].

Method 8015:

EPA Method 8015 (for Non-halogenated Volatile Organics) is a gas chromatographic method sometimes recommended for the analysis of volatile and semivolatile compounds. It can be used to characterize light and midrange petroleum distillates such as gasoline, diesel, fuel oil, and kerosene. This method can be used to obtain some gross fingerprint information for differentiation between petroleum products, as well as detailed information that can be used to differentiate between different batches of the same product. The major limitation of Method 8015 is its inability to detect nonvolatile compounds. The State of California recommends a "modified method 8015" (different from EPA's method 8015 and also different from EPA method 418.1) for gasoline, kerosene, diesel oil, or other fuels in soil and groundwater, as specified in the Leaking Underground Fuel Tank (LUFT) Manual [465].

The California LUFT methods call for packed GC columns which have poor resolving power and make it difficult to obtain detailed information about the hydrocarbon type [810]. Superior GC columns and superior methods (such as ASTM 2887) are available [810]. For example, narrow-bore capillary columns can analyze most of the gasoline, entire diesel fractions, and a substantial portion of the crude oil range [810].

Using the California LUFT manual methods, only an experienced analyst will be able to differentiate diesel fractions from aged gasoline [810]. The oversimplified California methods and models are plagued with many problems [808,810]. Choosing an appropriate solvent for semivolatile analyses always presents a problem; some solvents extract certain compounds better than others and many present environmental or health risks [810].

HPLC screening scans:

In cases where a less expensive 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 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). HPLC/Fluorescence is less expensive than some of the more rigorous scans. The HPLC/fluorescence scan can be used for analyses of fish bile: the scan looks at bile directly 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.

> Additional Pros: HPLC Fluorescence screening methods have been performed extensively by NOAA to locate hotspots for crude oil contamination. NOAA's experience with the Exxon Valdez spill indicated that concentrations of aromatic hydrocarbons measured by HPLC/Fluorescence screening were highly correlated with the sums of Aromatic hydrocarbons determined by GC/MS, thus validating the screening method as an effective tool for estimating concentrations of petroleum-related aromatic hydrocarbons in sediments. Moreover, differences in HPLC chromatographic patterns among sediments suggested different sources of contamination, e.g., crude oil or diesel fuel. Allows crude determinations related to sources: HPLC/Fluorescence analyses allowed at least rough differentiation between aromatic hydrocarbons which may have originated from diesel fuel versus those from boat traffic [521] and The procedure was successfully applied to fingerprinting' gasolines, kerosines, diesel oils, heavy fuel oils, lubricating oils, and ship bilge oils [AUTHOR: Saner WA; Fitzgerald GE, II PUBLICATION YEAR: 1976 TITLE: Thin-Layer Chromatographic Technique for Identification of Waterborne Petroleum Oils JOURNAL: Environmental Science and Technology SOURCE: Vol. 10, No. 9, p 893-897, September 1976. 6 fig, 4 tab, 7 ref.].

EPA 418.1 for TPH:

> 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 fuel oil no. 6 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 (prone to false negatives). For example, a field test of bioremediation of soils contaminated with Bunker C 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 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 (a modified EPA 8270 including alkyl homologues and lower detection limits), 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. For more information, see Petroleum Hydrocarbons entry.

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 and Fuel Oil, general entries.