ENVIRONMENTAL CONTAMINANTS ENCYCLOPEDIA

FUEL OIL NUMBER 4 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 4 (No 4 Fuel Oil, Fuel Oil No. 4, CAS number 68476-31-3)

Brief Introduction:

Br.Class: General Introduction and Classification Information:

Fuel oils are comprised of mixtures of petroleum distillate hydrocarbons [363,499]. The various kinds of fuel oils are obtained by distilling crude oil, and removing the different fractions. Fuel oil no. 4 is a heavier distillate fuel oil than no. 2, yet lighter than no. 5 [641]. Fuel oil no. 4 is usually a 'light' residual, but sometimes is, or contains, a heavy distillate [747]. Fuel oil no. 4 can be prepared by combining 40 percent no. 2 fuel oil with 60 percent no. 6 fuel oil. It may also be prepared as a high-boiling distillate or light residual of crude oil [641].

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 [747]. These three heavy fuel oils are also known as gas oils and are composed of hydrocarbons ranging from C19 to C25 [872]. Residual oils are complex mixtures of relatively high molecular weight compounds and are difficult to characterize in detail. Molecular types include asphaltenes, polar aromatics, naphthalene aromatics, aromatics, saturated hydrocarbons and heteromolecules containing sulfur, oxygen, nitrogen, and metals [747].

Fuel oil no. 4 is intended for use in atomizing type burners that atomize oils of higher viscosity than domestic burners can handle. The permissible viscosity ranges of no. 4 fuel oil allow it to be pumped and atomized at relatively low storage temperatures. Therefore, in any weather (except extreme cold), it requires no preheating for handling in these burners [641].

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 [747]. Most blending stocks of residual fuel oils are likely to contain 5% or more of four- to six-ring condensed aromatic hydrocarbons. The exact identities and concentrations of various PAHs depend on the nature and amount of the low viscosity blending stocks and the proportions of 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 to the US Coast Guard Emergency Response Notification System (1993), fuel oil no. 4 was one of the top most spilled petroleum hydrocarbon products in U.S. waters, both by volume and the number of notifications [635].

ATSDR lists Diesel Fuel No. 4 as a synonym [962], but this product has a different CAS number and perhaps different additiives. However, specifications for both heating fuels and transportation fuels are at least somewhat similar [747]. Therefore, the reader may gain additional insight by reading the Diesel Oil #4 entry, since there will be some overlap in characteristics with Fuel Oil #4.

Br.Haz: General Hazard/Toxicity Summary:

Fuel oil no. 4 can be directly toxic to some forms of aquatic life, can coat birds, and is of concern as a potential source of PAHs, a potentially harmful class of aromatic hydrocarbons (see PAHs entry).

Chronic effects of some of the constituents in fuel 4 (such as naphthalenes) include changes in the liver and kidney [766]. Due to their relative persistence and potential for various chronic effects (like carcinogenicity) PAHs (and particularly the alkyl PAHs) can contribute to long-term (chronic) hazards of fuel 4 in contaminated soils, sediments, and groundwater (see PAHs entry).

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 oils is PAHs (see PAHs entry). 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].

See also: ATSDR toxicological profile on fuels oils in general, including this product [962].

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

Certain components of fuel no. 4, such as PAHs, may be carcinogenic to animals and humans. 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].

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

See also: ATSDR toxicological profile on fuels oils in general, including this product [962].

See also: PAHs as a group and Fuel Oil, General entries.

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 results are mixed, but some reproductive and fetotoxic effects have been associated with a few of the compounds found in fuel no. 5 [766] (see entries on individual compounds for more details).

See also: ATSDR toxicological profile on fuels oils in general, including this product [962].

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.

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

Fuel oil number 4 is considered to be a intermediate product, with an environmental fate similar to a medium-grade crude oil [777]. As such, about 1/3 of a spilled fuel no. 4 would be expected to evaporate within 24 hours. Fuel no. 4 has variable acute toxicity, depending on the specific amount of light fraction [777]. Fuel no. 4 may penetrate substrate and persist. Impacts to waterfowl and fur-bearing animals can be severe during a spill of residual oil due to coating and ingestion [777].

Petroleum distillates in order of decreasing volatility include [363]:

1. Petroleum ether or benzene
2. Gasoline
3. Naphtha
4. Mineral spirits
5. Kerosene
6. Fuel oils
7. Lubricating oils
8. Paraffin wax
9. Asphalt or tar.

See also: ATSDR toxicological profile on fuels oils in general, including this product [962].

Synonyms/ Substance Identification:

Light residual fuel oil [747]
Residual fuel oil [560]

NOTE: Fuel oil numbers 5 and 6 are also referred to as residual fuel oil.

ATSDR lists Diesel Fuel No. 4 as a synonym [962], but this product has a different CAS number and perhaps different additiives (see Diesel Oil #4 entry).

ATSDR lists heavy residual fuel oil, marine diesel fuel, and residual fuel oil number 4 as synonyms [962], but other references do not seem to agree [560,560].

Associated Chemicals or Topics (Includes Transformation Products):

See also individual entries:

Fuel Oil, General
Fuel Oil Number 2
Fuel Oil Number 6
Oil Spills
Petroleum, General
PAHs as a group
Naphthalene
C1-Naphthalene
C2-Naphthalene
C3-Naphthalene
C4-Naphthalene
Biphenyl
Acenaphthylene
Acenaphthene
Fluorene
C1-Fluorene

C2-Fluorene
C3-Fluorene
Anthracene
Phenanthrene
C1-Phenanthrene/anthracene
C2-Phenanthrene/anthracene
C3-Phenanthrene/anthracene
C4-Phenanthrene/anthracene
Dibenzothiophene
C1-Dibenzothiophene
C2-Dibenzothiophene
C3-Dibenzothiophene
Fluoranthene
Pyrene
C1-Fluoranthene/pyrene
Benzo(a)anthracene
Chrysene
C1-Chrysene
C2-Chrysene
C3-Chrysene
C4-Chrysene
Benzo(b)fluoranthene
Benzo(k)fluoranthene
Benzo(e)pyrene
Benzo(a)pyrene
Perylene
Indeno(1,2,3-c,d)pyrene
Dibenz(a,h)anthracene
Benzo(g,h,i)perylene

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]:

Pollution hazard:
Water pollution:
Persistency: Loss of fuel oil after 40 hour in bubbler apparatus - 2.% Evaporated, .005% Dissolved.

Effect on water treatment process:
Will interfere with settling and floc formation. May plug filters and exchange beds.

Water uses threatened:
Recreation, potable supply, fisheries, irrigation, industrial

Industrial fouling potential:
Boiler water feed should be limited to 7 ppm or less. Oil can result in poor heat transport, blistering, overheating and foaming. In reused cooling water, no oil is acceptable. Oil causes tastes in food processing water and is especially detrimental to cement and paper making operations.

W.Plants (Water 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.

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):

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.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 TPH 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. See also: Br.Haz section above.

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 this product (see Chem.Detail section below).

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 as yet. However, there is information available on some of the compounds found in this product (see individual PAH sections).

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]:

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.

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.

Irritation
Skin - standard draize test
Rabbit
route: Skin; Dose: 500 mg; Reaction: mild; 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):

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.

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

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.

Interactions:

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

Uses/Sources:

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

Forms/Preparations/Formulations:

Fuel oil no. 4 can be prepared by combining 40 percent no. 2 fuel oil with 60 percent no. 6 fuel oil. It may also be prepared as a high-boiling distillate or light residual of crude oil [641].

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

Caution: Every individual petroleum product has a unique "fingerprint," or distinct set of constituents most commonly identified by a gas chromatograph analysis. Due to the varying properties of the same general category of a petroleum product (each source and stage of a No. 4 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. Therefore, the below comments on No. 4 fuel oils are to be considered as representative, but not absolute values typical of every batch of the product with the same name.

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.

The heavy fuel oils (fuels oils number 4,5, and 6) contain 15-40% aromatics, dominated by alkyl phenanthrenes and naphthalenes [872]. Since fuel oils 4 and 5 are commonly produced by blending fuel oil 6 with lighter distillates. Therefore, most (probably all) of the PAHs and alkyl PAHs listed below would be expected to occur in Fuel 4, just as they are in fuel 5 (see the Fuel 5 entry for details):

Naphthalene
C1-Naphthalene
C2-Naphthalene
C3-Naphthalene
C4-Naphthalene
Biphenyl
Acenaphthylene
Acenaphthene
Fluorene
C1-Fluorene
C2-Fluorene
C3-Fluorene
Anthracene
Phenanthrene
C1-Phenanthrene/anthracene
C2-Phenanthrene/anthracene
C3-Phenanthrene/anthracene
C4-Phenanthrene/anthracene
Dibenzothiophene
C1-Dibenzothiophene
C2-Dibenzothiophene
C3-Dibenzothiophene
Fluoranthene
Pyrene
C1-Fluoranthene/pyrene
Benzo(a)anthracene
Chrysene
C1-Chrysene
C2-Chrysene
C3-Chrysene
C4-Chrysene
Benzo(b)fluoranthene
Benzo(k)fluoranthene
Benzo(e)pyrene
Benzo(a)pyrene
Perylene
Indeno(1,2,3-c,d)pyrene
Dibenz(a,h)anthracene
Benzo(g,h,i)perylene

Log KOW [875]: 3.3 to 7.06

Henry's Law Constant [875]: 5.9E-05 to 7.4

Solubility in Water [875,962]: ~5 mg/L.

Odor [875]: like kerosene.

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: Created by the American Petroleum Institute (API), API gravity is an arbitrary scale expressing the gravity or density of liquid petroleum products [637]. This scale was created in order to compare the densities of various oils. 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.

24.9 to 23.5
25.0

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 (i.e., as temperature goes down and/or the fraction of weathered oil increases, density increases). The following density values are at "0% Weathering Volume" - in other words, fresh No. 4 fuel oil.

Temp(C)	Density (at 0% Weathering Volume)
0	0.969 to 0.980
0	0.914 to 0.922
	0.938
15	0.904 to 0.912
	0.903
20	0.901 to 0.909
	0.925
30	0.895 to 0.902

HYDROCARBON GROUP [560]:

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

Hydrocarbon Group Analysis (Weight %):

Asphaltenes	3.2

Wax Content (Weight %):
5.5

METAL CONTENT [560]:

Other Metals (ppm):

Vanadium	35.0
Nickel	7.72
Chromium	44.1 ppb
Cobalt	32.8 ppb
Iron	0.226
Manganese	14.1 ppb
Zinc	0.263
Copper	0.0345

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.

	20 C
Water	6.46

Solubility [498]: Fuel oil is insoluble (sic, actually "relatively insoluble") in water (AAR, 1987).

NOTE on Solubility: No exact numbers can be given for solubilities of fuel oil in water because the composition of an oil varies from refinery to refinery. Generally, hydrocarbons of a lower molecular weight are more soluble than those of a higher molecular weight. Branching of hydrocarbon isomers, as well as ring formation, also tends to increase solubility. For two rings with the same carbon number, an unsaturated ring is more soluble in water than a saturated ring. The solubility of hydrocarbons in sea water is less than in fresh water. Also, an increase in temperature will greatly increase the amount of hydrocarbons which dissolve in water. Turbulence will also increase the rate of solubility [641].

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: Viscosity is a measure of the internal friction or the resistivity to flow of a liquid [637]. The viscosities of crude oils and oil products are dependent on the temperature and degree of weathering (as temperature goes down and/or the fraction of weathered oil increases, viscosity increases). The following viscosity values are at "0% Weathering Volume" - in other words, fresh No. 4 fuel oil.

Dynamic Viscosity (mPa.s or cP):

Temp(C)	Dynamic Viscosity (at 0% Weathering Volume)
10	47.2
20	22.7

Kinematic Viscosity (mm2/sec or cSt):

Temp(C)	Kinematic Viscosity (at 0% Weathering Volume)
10	40 to 101
15	33 to 79
20	27 to 60
30	18 to 38
38	5.8 to 26.4 2.0 to 5.8 for No.4 Light
40	11 to 26

Note: Data obtained from a graph (Curl 77)

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 (the larger the fraction of oil weathered, the higher the pour point).

-29 to -9
max -6
-7
5

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. 4 fuel oil.

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

Temp(C)	Air-Oil Tension (at 0% Weathering Volume)
20	32.1

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

Temp(C)	Oil-Seawater Tension (at 0% Weathering Volume)
20	30.23

EMULSION

NOTE: An emulsion is a suspension of small globules of one liquid in a second liquid with which the first will not mix [492]. Hence, 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. 4 fuel oil.

Emulsion Stability:

Forms stable emulsion (Curl 77)

FIRE AND REACTIVITY

NOTE: Flash point is the lowest temperature at which vapors arising from the oil will ignite momentarily (flash) on application of a flame under specific conditions [637].

Flash Point (degrees C):
54
78
min 55
min 38 for No.4 Light
> 54 (closed cup)

Auto Ignition Temperature (degrees C):
263

Flammability Limits (Volume %):
in air: 1.0 to 5.0

DISTILLATION

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

Distillation (degrees C):

(Vol%)	Liquid Temp
IBP	245
5	257
10	269
15	281
20	293
25	305
30	317

NOTE: IBP = initial boiling point

Boiling Range (degrees C):

101 to > 588

SENSATION

Color
Brown

OTHER
Reid method Vapor Pressure (kPa):

Temp(C)	Pressure
37.8	0.689 (estimated)

Information from Hazard Management Data Base [498]:

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).

Information from OHM/TADS [499]:

FIRE/EXPLOSION/CORROSION HAZARDS
Flammability: MODERATE. COMBUSTION WITH HEATING MODERATE HAZARD
Standard codes: NFPA - -,2,0
Toxic combustion products: NO GREAT HAZARD
Flash point (degrees C): 66
Autoignition temperature (degrees C): 408

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

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.

Laboratory and/or Field Analyses:

As mentioned in the Brief Introduction, fuel oil No. 4 may contain PAHs. PAHs are of concern in Fuel Oils in general [962] Appreciable concentrations of PAHs are present in residual fuels because on the common practice of using both uncracked and cracked residues in their manufacture [747]. See also: PAHs as a group and Fuel Oil, General entries.

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].

Due to the presence of light aromatics and PAHs in fuel oils, we recommend the following decision tree:

Decision Tree (dichotomous key) for selection of lab methods for measuring contamination from midrange fuel oils:

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

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

2a. The resource at risk is primarily humans via a drinking water pathway, either the contamination of groundwater used for drinking water, or the fresh* or continuing contamination of surface waters used as drinking water, or the risk is primarily to aquatic species in confined** surface waters from a fresh* spill, or the risk is to surface waters re-emerging from contaminated groundwater resources whether the spill is fresh* or not; the medium and/or pathway of concern is water rather than sediments, soil, or tissues. Note: although heavy products have a lower percentage of BTEX and other relatively soluble compounds which typically threaten drinking water, ground water, or water column organisms, some heavy oils including crudes do contain some of these water soluble compounds, so they cannot be ignored.......................4

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

3a. The spilled substance is a fresh* oil product of known composition: If required to do so by a regulatory authority, perform whichever Total Petroleum Hydrocarbon (TPH) analysis specified by the regulator. However, keep in mind that due to its numerous limitations, the use of the common EPA method 418.1 for Total Petroleum Hydrocarbons is not recommended as a stand-alone method unless the results can first be consistently correlated (over time, as the oil ages) with the better NOAA protocol expanded scan*** for polycyclic aromatic hydrocarbons (PAHs) and alkyl PAHs. If not required to perform an EPA method 418.1-based analysis for TPH, instead perform a Gas Chromatography/Flame Ionization Detection (GC/FID) analysis for TPH using the spilled substance as a calibration standard. GC/FID methods can be sufficient for screening purposes when the oil contamination is fresh*, unweathered oil and when one is fairly sure of the source [657]. If diesel 1D was spilled, perform TPH-D (1D) using California LUFT manual methods (typically a modified EPA method 8015) [465] or a locally available GC/FID method of equal utility for the product spilled. However, no matter which TPH method is used, whether based on various GC/FID or EPA method 418.1 protocols, the investigator should keep in mind that the effectiveness of the method typically changes as oil ages, that false positives or false negatives are possible, and that the better Gas Chromatography-Mass Spectrometry-Selected Ion Mode (GC/MS/SIM) scans (such as the NOAA expanded scan***) should probably be performed at the end of remediation to be sure that the contamination has truly been cleaned up. Another option for fresh oil: in cases where an inexpensive screening scan is desired, consider using an HPLC/Fluorescence scan method for sediment or bile metabolite samples. Such scans are available from laboratories at Texas A. and M., Arthur D. Little, and the NOAA lab in Seattle. This scan is not much more expensive, and less prone to false negatives and various other problems than some of the more common screening methods (TPH-EPA 418.1 and Oil and Grease). Screening measures the total fluorescence of oil components while GC/MS measures individual aromatic compounds [521]. Thus, HPLC/fluorescence screening allowed detecting lower concentrations of petroleum-related aromatic compounds in samples contaminated by Prudhoe Bay Crude Oil than did analysis by GC/MS [521].

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

4. Analyze for Benzene, Toluene, Ethyl Benzene, and Toluene (BTEX) compounds in water as part of a broader scan of volatiles using EPA GC/MS method 8240. The standard EPA GC/MS method 8240 protocol will be sufficient for some applications, but the standard EPA method 8240 (and especially the less rigorous EPA BTEX methods such as method 8020 for soil and

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

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

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

6. Perform the NOAA protocol expanded scan*** for polycyclic aromatic hydrocarbons (PAHs) and alkyl PAHs. If there is any reason to suspect fresh* or continuing contamination of soils or sediments with lighter volatile compounds, also perform EPA GC/MS method 8240 using the lowest possible Selected Ion Mode (SIM) detection limits and increasing the analyte list to include as many alkyl Benzene, Toluene, Ethyl Benzene, and Xylene (BTEX) compounds as possible.

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

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

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

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

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

10. If exposure to fish is suspected, an HPLC/Fluorescence scan for polycyclic aromatic hydrocarbon (PAH) metabolites in bile may be performed to confirm exposure [844]. The HPLC/fluorescence scan looks for the presence of metabolites of PAHs: naphthalene, phenanthrene, and benzo[a]pyrene. The technique does not identify or quantify actual PAH compounds, but subsequent gas chromatography analyses can be done to confirm the initial findings. Even the semi-quantitative Total Scanning Fluorescence (TSF) done inexpensively by labs such as GERG are a better measure of PAH contamination than GC/FID, which measures less persistent and less hazardous aliphatics. For bottom-dwelling fish such as flounders or catfish, also analyze the bottom sediments (see Step 6 above). Fish which spend most of their time free-swimming above the bottom in the water column can often avoid toxicity from toxic petroleum compounds in the water column, but if fish are expiring in a confined** habitat (small pond, etc.), EPA GC/MS method 8240 and the NOAA protocol expanded scan*** for PAHs could be performed to see if Benzene, Toluene, Ethyl Benzene, and Xylene (BTEX), naphthalene, and other potentially toxic compounds are above known acute toxicity benchmark concentrations. Zooplankton populations impacted by oil usually recover fairly quickly unless they are impacted in very confined** or shallow environments [835] and the above BTEX and PAH water methods are often recommended rather than direct analyses of zooplankton tissues.

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

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

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

To assist the reader in making decisions based on the continuum of possible degrees of freshness, the following generalizations are provided: Some of the lightest middle distillates (such as Jet Fuels, Diesel, No. 2 Fuel Oil) are moderately volatile and soluble and up to two-thirds of the spill amount could disappear from surface waters after a few days [771,835]. Even heavier petroleum substances, such as medium oils and most crude oils will evaporate about one third of the product spilled within 24 hours [771]. Typically the volatile fractions disappear mostly by evaporating into the atmosphere. However, in some cases, certain water soluble fractions of oil including Benzene, Toluene, Ethyl Benzene, and Xylene (BTEX) compounds move down into groundwater. BTEX compounds are included in the more volatile and water soluble fractions, and

BTEX compounds as well as the lighter alkanes are broken down more quickly by microbes than heavier semi-volatiles such as alkyl PAHs and some of the heavier and more complex aliphatic compounds. Thus after a week, or in some cases, after a few days, there is less reason to analyze surface waters for BTEX or other volatile compounds, and such analyses should be reserved more for potentially contaminated groundwaters. In the same manner, as the product ages, there is typically less reason to analyze for alkanes using GC/FID techniques or TPH using EPA 418.1 methods, and more reason to analyze for the more persistent alkyl PAHs using the NOAA protocol expanded scan***.

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

*** The 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.

Additonal detail:

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

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 analzye 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: ATSDR toxicological profile on fuels oils in general, including this product [962].

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.