ENVIRONMENTAL CONTAMINANTS ENCYCLOPEDIA

FUEL OIL, GENERAL 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, General

Brief Introduction:

Br.Class: General Introduction and Classification Information:

The purpose of this entry is to provide an overview on fuel oils in general. For specific information on a particular type of fuel oil, see the following entries: Kerosene (Fuel Oil Number 1), Fuel Oil Number 2, Fuel Oil Number 4, Fuel Oil Number 5, and Fuel Oil Number 6.

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 is any liquid petroleum product that is burned in a furnace for the generation of heat or used in an engine for the generation of power, except oils having a flash point of approximately 100 degrees F and oils burned in cotton or wool-wick burners. The oil may be a distillated fraction of a crude petroleum, a residuum from refinery operations, or a blend of these [498].

Fuel oil numbers 1 and 2 are referred to as distillate fuels oil, while fuel oil numbers 4, 5, and 6 are labelled residual [747] (see the Forms/Preparations/Formulations section below). Two major categories of fuel oil are burned by combustion sources: distillate oils and residual oils [663]. These oils are further distinguished by grade numbers, with Nos. 1 and 2 being distillate oils; Nos. 5 and 6 being residual oils; and No. 4 either distillate oil or a mixture of distillate and residual oils [663]. No. 6 fuel oil is sometimes referred to as Bunker C [663].

According to the USCG Emergency Response Notification System (1993), fuel oils are some of the top most spilled petroleum hydrocarbon products in U.S. waters, both by volume and the number of notifications [635].

Diesel oils are among the products considered "fuel oils" in a broad sense [962] (see Diesel Oil entries).

Br.Haz: General Hazard/Toxicity Summary:

The most toxic components of fuel oils are the aromatics, such as benzene, toluene, xylene, naphthalene and others. These aromatics are relatively highly soluble in water. After the aromatic fraction, toxicity decreases from

olefins through naphthenes to paraffins. Within each of these groups, the lower molecular weight hydrocarbon tends to be more acutely toxic [641].

Fuel oils have a moderately broad range of volatility and solubility [777]. For example, fuel 1 and 2 are moderately soluble and volatile, while fuel 4, 5, and 6 are not very soluble [777]. Short-term toxicity decreases as the type of fuel oil becomes less volatile (that is, no. 1 and 2 are moderately toxic, while toxicity decreases through no.4, no.5, and no.6) [641]. Fuel 1 and 2 possesses moderate to high acute toxicity to biota with product-specific toxicity related to the type and concentration of aromatic compounds, while fuels 5 and 6 are considered to be less acutely toxic relative to other oil types [777]. Fuel 4 has variable acute toxicity, depending on the amount of light fraction [777].

Short-term hazards of some of the lighter, more volatile and water soluble compounds (such as toluene, ethylbenzene, and xylenes) in fuel oils include potential acute toxicity to aquatic life in the water column (especially in relatively confined areas) as well as potential inhalation hazards. Fuel oil spills could result in potential acute toxicity to some forms of aquatic life. Oil coating of birds, sea otters, or other aquatic life which come in direct contact with the spilled oil is another potential short-term hazard. In the short term, spilled oil will tend to float on the surface; water uses threatened by spills include: recreation; fisheries; industrial, potable supply; and irrigation [608].

Long-term potential hazards of some of the lighter, more volatile and water soluble compounds (such as toluene and xylenes) in fuel oils include contamination of groundwater. Long-term water uses threatened by spills include potable (ground) water supply. Chronic effects associated with middle distillates are mainly due to exposure to aromatic compounds [661].

Long-term effects are also associated with polycyclic aromatic hydrocarbons (PAHs), alkyl PAHs, and alkyl benzene (such as xylene) constituents of fuel oil. Although PAHs, particularly heavy PAHs, do not make up a large percentage of distillate fuel oils by weight, there are some PAHs in these fuel oils, including naphthalene, alkyl naphthalenes, phenanthrene, and alkyl phenanthrenes [177,747]. Residual fuel oils may contain considerable amounts of PAHs [177,747]. Due to their relative persistence and potential for various chronic effects, PAHs (particularly the alkyl PAHs) can contribute to long-term (chronic) hazards of fuel oils in contaminated soils, sediments, and groundwater. Chronic effects of

some of the constituents in fuel oils (toluene, xylene, naphthalenes, alkyl benzenes, and various alkyl PAHs) include changes in the liver and harmful effects on the kidneys, heart, lungs, and nervous system. Increased rates of cancer, immunological, reproductive, fetotoxic, genotoxic effects have also been associated with some of the compounds found in fuel oils (see entries on individual compounds for more details).

> Further detail on potential risks for PAHs in this product: Acute toxicity is rarely reported in humans, fish, or wildlife, as a result of exposure to low levels of a single PAH compound. PAHs in general are more frequently associated with chronic risks. These risks include cancer and often are the result of exposures to complex mixtures of chronic-risk aromatics (such as PAHs, alkyl PAHs, benzenes, and alkyl benzenes), rather than exposures to low levels of a single compound. This product is an example of such a complex mixture (Roy Irwin, National Park Service, Personal Communication, 1996, based on an overview of literature on hand).

See also: PAHs as a group entry.

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].

Many of the PAHs found in this product (see Chem.Detail section below) are phototoxic, that is they display greatly enhanced toxicity in sunlight or other UV source than elsewhere (see PAHs as a group entry).

Summaries of the hazards to humans and animals of many of the aromatic and alkane constituents and additives in fuel oils were summarized by the Air Force Installation Restoration Program in 1990; hexane may be the most highly toxic of the alkanes [875]. Many of the alkanes are CNS depressants and general irritants [875].

See also: ATSDR toxicological profile on fuel oils 1 (kerosene), 1-D, 2, 2-D, and 4 [962].

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

Distillate fuel oils (no. 1 and 2) are not classifiable as to their carcinogenicity to humans [747]. However, certain carcinogenic effects have been associated with

some of the other compounds found in distillate fuel oils (see entries on individual compounds for more details).

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

Painting Fuel Oil 2 on mice was positive for carcinogenesis [875].

See also: the ATSDR toxicological profile on fuel oils 1 (kerosene), 1-D, 2, 2-D, and 4 [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.Dev: Brief Summary of Developmental, Reproductive, Endocrine, and Genotoxicity Information:

The results are mixed, but some immunological, reproductive, fetotoxic, and genotoxic effects have been associated with a few of the compounds found in fuel oils [764,765,766,767] (see entries on individual compounds for more details).

Some of the PAHs found in fuel oil are either AHH active or endocrine disruptors [561].

See also: ATSDR toxicological profile on fuel oils 1 (kerosene), 1-D, 2, 2-D, and 4 [962].

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

Distillate oils are more volatile and less viscous than residual oils. They have negligible nitrogen and ash contents and usually contain less than 0.3 percent sulfur (by weight) [663].

Because residual oils are produced from the residue remaining after the lighter fractions (gasoline, kerosene, and distillate oils) have been removed from the crude oil, they contain significant quantities of ash, nitrogen, and sulfur [663].

Fuel oils have a broad range of volatility and mobility [661]. Most fuel oils contain a combination of lighter, less persistent and more mobile compounds as well as heavier, more persistent and less mobile compounds. The general amount of these two groups of components varies by fuel type (for example, fuel 1 contains more lighter components, while fuel 6 contains more heavier components). These two different groups are associated with two distinctly different patterns of fate/pathway concerns:

The relatively lighter, more volatile, mobile, and water soluble compounds in fuel oils will tend to evaporate fairly quickly into the atmosphere or migrate to groundwater. When exposed to oxygen and sunlight, most of these compounds will tend to break down relatively quickly. However, in groundwater, many of these compounds tend to be more persistent than in surface water, and readily partition on an equilibria basis back and forth between water and solids (soil and sediment) media. Cleaning up groundwater without cleaning up soil contamination will usually result in a rebound of higher concentrations of these compounds partitioning from contaminated soils into groundwater (Roy Irwin, Personal Communication, 1995).

The compounds in fuel oils which will tend to be somewhat more persistent and more bound to solid particles will include the PAHs, alkyl PAHs, and alkyl benzenes. Higher concentrations of heavier PAHs will tend to be in adjacent contaminated soils than in groundwater, but cleaning up groundwater without cleaning up soil contamination will

nevertheless usually result in at least some rebound of higher concentrations of these compounds partitioning from contaminated soils into groundwater (Roy Irwin, personal communication).

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.

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.

See also: ATSDR toxicological profile on fuel oils 1 (kerosene), 1-D, 2, 2-D, and 4 [962].

Synonyms/Substance Identification:

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.

Associated Chemicals or Topics (Includes Transformation Products):

See also individual entries:

Kerosene (Fuel Oil Number 1)
Fuel Oil Number 2
Fuel Oil Number 4
Fuel Oil Number 5
Fuel Oil Number 6
LAPIO (A very heavy #6 fuel oil) [775].
Petroleum, General
Oil Spills
PAHs as a group

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):

Water Information on Fuel Oils from ATSDR [962] (see ATSDR for identification of embedded references):

Analysis of drinking water from Cincinnati, Ohio, in February of 1980, showed the presence of numerous hydrocarbons associated with petroleum products at concentrations ranging from 5 ng/L for naphthalene to 843 ng/L for benzene (Coleman et al. 1984). Kerosene was detected at monitoring wells (concentrations were not reported) located at the perimeter of a spent nuclear fuel processing plant in western New York State in 1983. The kerosene had been used as an extractant during plant operations from 1966 to 1972 (DOE 1989c). Groundwater samples taken from monitoring wells at gasoline stations undergoing remediation in Florida contained both kerosene and fuel oil at unspecified concentrations (Thomas and Delfino 1991a). Fuel oil no. 2 was detected along with gasoline in groundwater wells in Tiverton, Rhode Island. Over a 19-month period, total hydrocarbon concentrations in the water from one well decreased from 2,350 to 1,580 ug/L during which time the proportion of hydrocarbons associated with fuel oil increased from 42% (987 ug/L) to 78% (1,232 ug/L), probably as a result of the more rapid degradation of the gasoline (Zheng and Quinn 1988). Kerosene was detected in a whole water sample from monitoring wells for municipal intakes in California in the ug/L range (STORET 1992). Background concentrations of total hydrocarbons in

Narragansett Bay, Rhode Island, ranged from 0.7 to 4.0 ug/L (Gearing and Gearing 1982a). 5.4.3 Soil No data were located on levels of fuel oils detected in soils.

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

W.Typical (Water Concentrations Considered Typical):

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

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

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

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

W.Plants (Water Concentrations vs. Plants):

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):

Petroleum is a complex mixture of thousands of different hydrocarbons and related substances, all with different physical and chemical properties [770]. As such, determination of the fate and toxicity of a particular oil is a difficult task. Solubility-fate relationships must be considered. Generally, the relative toxicity of an oil will be the result of the fractional toxicities of the different hydrocarbons present in the aqueous phase [770]. In an often referenced study, the quantitative hydrocarbon composition and behavior in seawater of water-soluble fractions (WSF) and oil-in-water dispersions (OWD) of 4 oils was investigated (namely South Louisiana crude, Kuwait crude, and two refined oils - No. 2 fuel oil and bunker C residual oil) [770]. In the study, differences in the solubilities and composition of the test oils were described, as well as variations in sensitivity to oil of several marine species. One of the findings of this study is that, at least with the 4 oils tested in this study, the toxicity of an oil is largely a function of its di- and tri-aromatic hydrocarbon content [770]. This and other findings in this study demonstrate that a prediction of environmental impact must take into consideration the specific characteristics of the particular oil spilled as well as the particular spill environment (that is, whether the spill occurs in the open sea, or a confined water body). See the W.Misc section of the Petroleum, General entry for the complete summary of this study [770].

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):

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.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).

The trend of thinking towards natural attenuation was given a boost by a Lawrence Livermore National Laboratory (LLNL) report entitled "Recommendations to Improve the Cleanup Process for California's Leaking Underground Fuel Tanks;" which stressed the use of passive bioremediation for petroleum product contaminated soils, whenever possible, based on the relatively low number of cases

where drinking water was impacted [969]. EPA has pointed out some limitations of the LLNL report, including the lack of adequate consideration of PAHs and additives such as MTBE, as well limited consideration of (non-human) exposure pathways and various geologic conditions [969].

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:

Information on Fuel Oils from ATSDR [962] (see ATSDR for identification of embedded references):

Shellfish taken from unpolluted waters have been found to contain between 1 and 12 ug/g wet weight of total hydrocarbons while fish have been found to contain between 4 and 14 ug/g total hydrocarbons (steam distillables) (Connell and Miller 1980). Following a spill of fuel oil no. 2 in the Cape Cod Canal in Massachusetts, edible mussels (Mytilus edulis) contained average concentrations of various hydrocarbons up to 4.69 ug/g dry weight on day 1 of the spill; background hydrocarbon levels in the controls did not exceed 0.29 ug/g (Farrington et al. 1982a). Limpets in close proximity to onshore accumulations of hydrocarbon contaminants caused by diesel fuel spillage and leakage related to ship and boating activities in Arthur Harbor on the Antarctic Peninsula have incorporated PAHs into their tissues (Kennicutt et al. 1992b). However, 2 years after the release of 150,000 gallons of diesel fuel in the harbor, little spill-related contamination could be detected in intertidal limpets (Kennicutt and Sweet 1992). No data were located that discussed concentrations of fuel oils in other environmental media such as food or terrestrial plants and animals [962].

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.

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):

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 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:

Distillate oils are used mainly in domestic and small commercial applications [663]. Being more viscous and less volatile than distillate oils, the heavier residual oils (Nos. 5

and 6) must be heated for ease of handling and to facilitate proper atomization. Residual oils are used mainly in utility, industrial, and large commercial applications [663]. See the Forms/Preparations/Formulations section below.

Forms/Preparations/Formulations:

Because fuel oils are used with burners of various types and capacities, different grades are required. ASTM has developed specifications for six grades of fuel oil, namely numbers 1, 2, 4, 5, and 6 [498]:

> Fuel oil No 1 (essentially the same composition as kerosene) is a straight-run distillate used almost exclusively for domestic heating.
>
> Fuel oil No 2 (diesel oil and heating oil) is a straight-run or cracked distillate used as a general purpose domestic or commercial fuel in atomizing-type burners.
>
> Fuel oil No 4 is made up of heavier straight-run or cracked distillates and is used in commercial or industrial burner installations not equipped with preheating facilities.
>
> The viscous residuum fuel oils, Nos 5 and 6, sometimes referred to as bunker fuels B and C, respectively, usually must be preheated before being burned. These fuels are used in furnaces and boilers of utility power plants, ships, locomotives, metallurgical operations, and industrial power plants.

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:

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 weathering stage of a 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 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.

Octanol Water Log: 3.3 to 7.06 [875].

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

Physicochemical Information from Hazard Management Data Base [498]:

SPECIFIC GRAVITY
Less than 1 (Fuel oils Nos 1, 2, 4, 5)
1 (+/-) (Fuel oil No 6)

DENSITY
Less than 1 g/cm(3) (Fuel oils Nos 1, 2, 4, 5)
1 (+/-) g/cm(3) (Fuel oil No 6)

SOLUBILITY
Fuel oil is insoluble (sic, actually "relatively insoluble") in water.

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].

FLASH POINT
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
Fuel oil No 6: 150 to 270 degrees F

COLOR: Fuel oils are straw yellow to dark colored liquids.

REACTIVITY: When heated to decomposition, fuel oils emit acrid smoke and irritating fumes. Fuel oils can react vigorously with oxidizing materials.

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

CHEMICAL COMPONENT (wt %)	REFINED OILS			
	Gasoline	Kerosene*	#2 Fuel Oil	#6 Fuel Oil
Saturates	39.6	85.0	61.8	24.4
Aromatics	46.2	15.0	38.2	54.6
Polars	--	--	0.0	14.9
Asphaltenes	N/A	N/A	0.0	6.2
Sulfur (%)	0.07	0.5	0.32	2.0

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

PHYSICAL PROPERTIES	REFINED OILS			
	Gasoline	Kerosene*	#2 Fuel Oil	#6 Fuel Oil
API Gravity**	60.0	37.0	31.6	10.0
Density (at 20C)	0.734	0.83	0.84	0.966
Pour point (C)	<-40.0	-18.0	-20.0	6.0
Flash point (C)	-40.0	38.0	55.0	80.0

NOTES:
* Kerosene is essentially the same composition as Fuel Oil #1.
** API gravity = (141.5/specific gravity at 60 F or 15.6 C) - 131.5.

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 16 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.

Trimethyl benzenes may occur in this product [875].

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].

See also: ATSDR toxicological profile on fuel oils 1 (kerosene), 1-D, 2, 2-D, and 4 [962].

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

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].

See ATSDR toxicological profile on fuel oils 1 (kerosene), 1-D, 2, 2-D, and 4 [962].

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. See also: entries starting with the phrase fuel oil.

Laboratory and/or Field Analyses:

The recommended lab analyses method depends on the fuel oil type in question. For example, recommended lab methods for the detection of distillate fuel oils (1 and 2) differ slightly from recommended methods for residual fuel oils (4, 5, and 6). See the individual fuel oil entries for details.

See: ATSDR toxicological profile on fuel oils 1 (kerosene), 1-D, 2, 2-D, and 4 [962]. See also: lab sections of fuel oil products and lab sections on various components of fuel oils.

For additional details on protocols, including field collection protocols, see the Oil Spills entry and the PAHs entry.

PAHs are one of the big issues with fuel oil spills (See also: PAHs as a group entry). The following information relates to PAHs:

Recommended detection limits:

Most of the PAH methods which have been commonly used historically for routine monitoring, including PAH parent compound standard methods:

EPA 8270 (8270 includes several PAH parent compounds along with a long list of other organics) for solid waste/RCRA applications [1013], and

EPA NPDES method 610 as specified in 40 CFR Part 136 (method 610 includes 16 PAH parent compounds) [1010],

EPA method 625 for Base/Neutral Extractables (method 625 includes several PAH parent compounds along with a long list of other organics) as specified in 40 CFR Part 136 [1010],

are all inadequate for generating scientifically defensible information for Natural Resource Damage Assessments [468]. These standard EPA scans do not cover important alkyl PAHs and do not utilize low-enough detection limits. When biological effects, ecological risk assessment, damage assessment, or bio-remediation are being considered, detection limit should be no higher than 1-10 ng/L (ppt) for water and 1 ug/kg ppb dry weight for solids such as tissues, sediments, and soil.

Note: Utilizing up to date techniques, many of the better labs can use detection limits of 0.3 to 1 ppb for tissues, sediments, and soils. When no

biological resources are at risk, detection limits for solids should nevertheless generally not be above 10 ppb. One reason that low detection limits are needed for PAHs is that so many of the criteria, standards, and screening benchmarks are in the lower ppb range (see various entries on individual PAHs).

In the past, many methods have been used to analyze for PAHs [861,1010,1013]. However, 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].

For risk, damage assessment, drinking water, or to determine if biodegradation has occurred, the NOAA expanded scan for PAHs and alkyl PAHs [828], or equivalent rigorous and comprehensive scans. (such as SW-846 method 8270 modified for Selective Ion Mode detection limits and an equivalent list of parent compound and alkyl PAH analytes), are recommended.

If a Park Service groundwater investigation at Colonial National Historical Park performed in response to contamination by Fuel Oil 5 had utilized EPA semi-volatile scan 8270 or any of the other typical EPA scans (625, etc.) all of which only include parent compounds and typically utilize detection limits in the 170-600 ppb range, the false conclusion reached would have been that no PAHs were present in significant (detection limit) amounts. This false negative conclusion would have been made because the parent compound PAHs present constituted only 7.6% of the PAHs detected in groundwater by the expanded scan [828], and the highest concentration found for any parent compound was 8.4 ppb, far below the detection limits used on the older standard EPA scans. Utilizing the NOAA protocol expanded scan [828], it was determined that 92.4% of the total concentration values of the PAHs detected in groundwater were alkyl PAHs, and that all 39 PAHs and alkyl PAHs were present. Of course, all 39 PAHs were also present in the fresh product, in much higher concentrations, and also having alkyl compounds with the highest percentage of higher values compared to parent compounds (see Chem.Detail section above for more details).

In a similar vein, if the Park Service sediment investigation at Petersburg National Historical Battlefield (see Chem.Detail section above, this study was performed in response to contamination by Diesel) had utilized EPA semi-volatile scan 8270 or any of the other typical EPA scans (625, etc.), all of which only include parent compounds and often utilize detection limits no lower than the 170-600 ppb range, the false conclusion reached would have been that only one PAH was present in significant

(detection limit) amounts. This false negative conclusion would have been made because the parent compound PAHs present constituted only 2.4% of the PAHs detected in sediments, and the highest concentration found for any parent compound except pyrene was 85.5 ppb, far below the detection limits used on the older standard EPA scans. Pyrene was 185 ppb, which would have been non-detected on many of the EPA scans, but not all. However, utilizing the NOAA protocol expanded scan [828], it was determined that 97.6% of total quantity of PAHs detected in sediments were alkyl PAHs, and that all 39 PAHs and alkyl PAHs were present in these sediments.

When taking sediment samples for toxic organics such as PCBs, PAHs, and organochlorines, one should also routinely ask for total organic carbon analyses so that sediment values may be normalized for carbon. This will allow comparison with the newer EPA interim criteria [86,127]. TOC in sediments influences the dose at which many compounds are toxic (Dr. Denny Buckler, FWS Columbia, personal communication).

Analyses of sediments:

The past use of EPA method 8270 [861] for analyses of PAHs in sediments was often deficient because the detection limits used were too high. For example, the detection limit on phenanthrene in sediments analyzed from a Park Service site at Fort Darling was listed as 1600 ppb, whereas many now recommend using a detection limit no higher than 10 ppb (1 ppb is best). In this case, harmful levels of phenanthrene and other PAHs could have been present but the test would not have detected them, because the detection limit used was too high (Roy Irwin, National Park Service, personal commuication, 1997]. It is usually better to perform an expanded scan for PAHs and alkylated homologues [828], with detection limits no lower than 1 ppb dry weight in solids. In some cases where the expanded scans are too expensive, an alternative recommendation is that one screen sediments with a size-exclusion high-performance liquid chromatography (HPLC)/fluorescence method, utilizing sonic extraction.

The utility and practicality of the HPLC bile and sediment screening analyses were demonstrated on board the NOAA R/V Mt. Mitchell during the Arabian Gulf Project. Estimates of petroleum contamination in sediment and fish were available rapidly, allowing modification of the sampling strategy based on these results [522]. (see HPLC sections below for more detail).

Some labs (such as Coastal Environments Lab in Encinitas, California) have recommend P450 Reporter Gene System (RGS) screening for sediments to determine which are most severely contaminated with PAHs before proceeding to GC/MS testing. However, the system is also activated by certain PCBs, dioxins, and other compounds (see biomarker section below for details).

Compounds in Expanded Scans:

An "expanded scan of PAHs" done by the Geochemical and Environmental Research Group Laboratory includes parent compounds and various alkyl homologs [828]: The expanded list includes most

of the PAHs recommended by the NOAA's National Status and Trends program [680,828]:

Acenaphthene
Acenaphthylene
Anthracene
Benzo(a)anthracene
Benzo(a)fluoranthene
Benzo(k)fluoranthene
Benzo(g,h,i)perylene
Benzo(e)pyrene
Benzo(a)pyrene
Biphenyl
Chrysene
Chrysene, C1-
Chrysene, C2-
Chrysene, C3-
Chrysene, C4-
Dibenzo(a,h)anthracene
Dibenzothiophene

NOTE: Although opinions differ as to whether dibenzothiophene is a PAH, it is listed as such in several sources [795,468,495].

Dibenzothiophene, C1-
Dibenzothiophene, C2-
Dibenzothiophene, C3-
Fluoranthene
Fluoranthenes/Pyrenes, C1-
Fluorene
Fluorene, C1-
Fluorene, C2-
Fluorene, C3-
Ideno(1,2,3,c,d)pyrene
Naphthalene
Naphthalene, C1-
Naphthalene, C2-
Naphthalene, C3-
Naphthalene, C4-
Perylene
Phenanthrene
Phenanthrenes/Anthracenes, C1-
Phenanthrenes/Anthracenes, C2-
Phenanthrenes/Anthracenes, C3-
Phenanthrenes/Anthracenes, C4-

Additional Details on NOAA expanded scan: PAHs Lab Analyses, NOAA Protocol Expanded Scan for PAHs and Alkyl Homologues of PAHs Using Gas Chromatography-Mass Spectrometry with Selective Ion Mode Enhanced Detection Limits (GC/MS/SIM) [828]:

Recommended by: National Park Service Staff, Fish and Wildlife Service Contaminants Program, NOAA Status and Trends Program, EPA EMAP Program, Many Consultants working on Exxon Valdez Spill, Many Laboratories.

Pros: A more complete list of analytes including alkyl homologues, suitably low detection limits, good utility for both risk/hazard assessment and for obtaining basic clues about possible sources (provides a crude fingerprint).

Cons: A bit more expensive than EPA standard method 8270 and substantially more expensive than rough screening scans. Not all labs are set up to do it.

Detection limits:

Recommended water sample detection limits are 1-10 ng/L (ppt) while recommended tissue, soil, and sediment sample detection limits for the expanded scan for PAHs are 1 ug/kg (ppb) dry wt.

Typical Costs per Sample (based on a survey of several laboratories in 1995):

Lab 1 (BSEQ): $425 per sample including extraction.

Lab 2 (GERG): $250 to $400 per sample depending on details. For low numbers of samples with no previous extractions, $400 for water, $425 for sediment, and $450 for tissues. As low as $250 if extraction not included (less than standard 8270 scan).

Lab 3 (BNW): $425 including extraction, or as low as $225 each for 40 samples if extraction already done.

Lab 4 (CAS): $300 for one class of chemicals (PAHs), up to $600 for all 8270 method analytes and lower detection limits (Method 8270/SIM, detection limits 1 ppb water, 20 pb tissues, and 10 ppb sediments).

Lab 5 (ADL): $425 to $600 including extraction. If a lot of extra chemical classes or advance fingerprinting is specified: up to $1000 per sample.

Summary: An alternative which works for many purposes (hazard assessment, source determination, surveys of hazardous compounds in weathered as well as fresh oils.

Examples of standard method protocols for PAHs published by various parts of EPA as well as some other agencies are outlined below:

Holding Times:

Water Samples:

Both NPDES effluent discharge permit applications [1010] and RCRA (SW-846) solid and hazardous waste applications [1013] call for the following maximum holding times: 7 days until extraction and 40 days after extraction.

Solids Samples:

EPA RCRA methods for semi-volatiles in solids in SW-846 call for holding times of 14 days until extraction and 40 days after extraction [1013].

The need to get rid of headspace to prevent loss of certain PAHs (such as naphthalenes) tends to discourage the freezing of soil and other samples. However, the Fish and Wildlife Service and some other groups nevertheless freeze some soil samples. If this can be accomplished without compromising the sample (for example, breaking a glass container), the freezing tends to stop biodegradation. Once frozen, holding times for samples of semi-volatiles such as PAHs in solids is on the order of decades (John Moore, Fish and Wildlife Service, Personal Communication, 1997).

Containers:

Both EPA and APHA (Standards Methods Book) recommend glass containers for the collection of organic compounds [141,1010,1013]. EPA also recommends teflon lined caps for solids samples of semi-volatiles [1010,1013].

Guidance from other federal agencies (USGS, FWS, NOAA) also recommends glass containers for organics, and discourages the use of plastic containers for a variety of reasons (Roy Irwin, National Park Service, Personal Communication, 1997, based on a glance through recent internal guidance of several agencies).

Some federal agency quality control procedures call for voiding or red-flagging the results of organic analyses if the lab receives the sample in plastic containers (Roy Irwin, National Park Service, Personal Communication, 1997). The APHA pointed out some the potential hazards of the use of certain plastic containers for storing organic samples [141]:

A) Potential contamination of the sample via leaching of compounds from the plastic, and/or

B) The plastic container walls can sometimes be attacked by certain organics and fail, and/or

C) The possibility that some of organic compound will dissolve into the walls of the plastic container, reducing the concentration of the compound in the container [141].

For the relatively volatile PAHs such as naphthalenes, not even vials are not the best choice for avoiding false negatives in soil samples through volatilization losses, since the use of brass liners for collection resulted in 19 fold higher VOCs than when 40 mL vials were used [798] The third update of EPA's SW-846 RCRA guidance authorizes the storage of soil samples of volatiles in EnCore TM (or equivalent, no government endorsement implied) samplers as long the sample is analyzed within 48 hours after collection [1013]. Several states also authorize the use of EnCore TM or equivalent containers for temporary (48 hour) storage containers (Donalea Dinsmore, State of Wisconsin DNR, personal communication, 1997).

Certain plastic polymers present less of a problem related to potential losses of volatiles than others. Some plastic is found in the latest approved EnCore TM samplers. Some states also give the reader the option of using plastic in collecting devices. For example, related to methods for gasoline range petroleum hydrocarbons, Wisconsin states that organics can be collected using a 30 ml plastic syringe with the end sliced off, a brass tube, an EnCore TM sampler or other appropriate devices (Donalea Dinsmore, State of Wisconsin DNR, personal communication, 1997). A plastic syringe is also mentioned as an option in the third update of RCRA methods in SW-846 [1013]. The thinking appears to be that plastic is less of a threat in a collecting device, with momentary contact, than in a storage container where contact times are longer.

Typical "standard method" protocols recommend proper cleaning of glass containers before use. Some collectors simply use pre-cleaned jars from I-Chem, Eagle Pitcher, or other private suppliers (no government endorsement implied). EPA [1010], USGS, and most other federal agencies recommend cleaning procedures for the glass containers, usually involving detergent rinsing, baking, and sometimes HCL rinses (Roy Irwin, National Park Service, Personal Communication, 1997).

Field Protocols:

Standard field collection method protocols are published or internally distributed by the Fish and Wildlife Service, the USGS, DOE, NOAA, and EPA. These recommendations change over time, with the newest recommendations sometimes being quite different than the old, thereby producing different results. The USGS NAWQA

protocols call of sieving of sediment samples composites, a practice that might result in the loss of relatively volatile PAHs such as the naphthalenes.

The Fish and Wildlife Service methods are similar in many ways to NOAA field protocols [676]. Many recommended EPA field methods for organics are not very detailed, although the 3rd update of SW-846 for RCRA solid waste methods is becoming more detailed [1013].

The various EPA methods for organics are different from each other, with the selection of the appropriate method depending upon the specific application (RCRA vs. CERCLA vs. NPDES permits, vs. Drinking Water, etc.) [861,1010,1013]. The EPA-recommended field methods are scattered through various EPA and ASTM publications.

EPA methods typically include recommendations that grab samples rather than composites be utilized for organics, and require the proper cleaning of collection bottles and collecting gear for both volatile and semi-volatile organics [1010,1013]. In other publications, EPA recommends caution in the use of composite soil samples whether organic or inorganic, citing statistical complications and stating that the compositing of samples cannot, in general, be justified unless for a stated specific purpose and unless a justification is provided [1017].

For PAHs (lab method 610) and other semi-volatiles, EPA recommended in 1994: that "conventional sampling practices" be followed as specified by ASTM D-3370 (3370-95a is a recent number), "Standard Practices for Sampling Water from Closed Conduits" [1010,1012]. No field methods are specified when not sampling from pipes [1010,1012].

Regardless of what lab methods are used, the investigator should take special precautions to prevent the escape of relatively light PAHs during sample shipment, storage, extraction, and cleanup [798]. This is especially true for soil and sediment sampling. The results of analyses of the lighter semi-volatiles (such as naphthalenes) can be dramatically effected by small details such as how the samples are collected, stored, held, and analyzed in the lab, since volatile compounds can readily volatilize from samples in both field and lab procedures. If the investigator knows that the sample will contain significant quantities of the lighter semi-volatiles such as naphthalenes, field and lab precautions should be taken just as if the investigator were handling volatiles (see Benzene entry for details). For example, for the lighter semi-volatiles, it may be prudent to use EPA method 5021 in SW 846, a generic "headspace" method for

> the collection of volatiles in soils and sediments [1013].
>
> Standard field methods for sampling contaminated soils for various types of contaminants were summarized by EPA in 1991 [1020]. These methods seem generally consistent with SCS recommendations, but are not necessarily 100% consistent with other protocols suggested by other parts of EPA [1013], and are not consistent with methods suggested by other agencies, such as the Fish and Wildlife Service.

Variation in concentrations of organic contaminants may sometimes be due to the typically great differences in how individual investigators treat samples in the field and in the lab rather than true differences in environmental concentrations. This is particularly true for volatiles and for the relatively lighter semi-volatiles such as the naphthalene PAHs, which are so easily lost at various steps along the way. Contaminants data from different labs, different states, and different agencies, collected by different people, are often not very comparable. In fact, as mentioned in the disclaimers section, 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].

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]. The basics of these quality assurance plans for chemical analyses should include the following quality control steps:

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. Typical lab quality control techniques should have included the following considerations (Roy Irwin, National Park Service, Personal Communication, 1997, summary based on various EPA and FWS documents):

Procedural Blanks should be analyzed to assure that no contaminants are added during the field and lab processing of the samples. The standards for adequacy depend on the method and the media being measured.

> Different federal agencies publish different acceptable limits. For one program, NOAA stated that at least 8% of samples should be blanks, reference or control materials [676].
>
> The basic idea is that neither samples nor blanks should be contaminated. Because the only way to measure the performance of the modified procedures is through the collection and analysis of uncontaminated blank samples in accordance with this guidance and the referenced methods, it is highly recommended that any modifications be thoroughly evaluated and demonstrated to be effective before field samples are collected [1003].

Duplicate samples are analyzed to provide a measure of precision of the methods. The standards for adequacy depend on the method and the media being measured.

> Different federal agencies publish different acceptable limits. There appears to be an inverse relationship between precision and sensitivity [676].
>
> Some EPA methods state that a field duplicate must be collected at each sampling site, or one field duplicate per every ten samples, whichever is more frequent [1003]. Some protocols call for the preparation of one Ongoing precision and recovery (OPR) standard for every ten or fewer field samples. Great care should be taken in preparing ongoing precision and recovery standards [1003].

Spiked samples are analyzed to provide a measure of the accuracy of the analysis methods. The standards for adequacy depend on the method and the media being measured.

> Different federal agencies publish different acceptable limits.

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 an inappropriate methods such as many of the EPA standard scans. This is one reason for using the NOAA expanded scan for PAHs [828]; or method 8270 [1013] modified for SIM detection limits (10 ppt for water, 0.3 to 1 ppb for solids) and additional alkyl PAH analytes; or alternative rigorous scans. These types of rigorous scans are less prone to false negatives than many of the standard EPA parent compound PAH scans (Roy Irwin, National Park Service, Personal Communication, 1997).

PAHs are often analyzed when fuel oil products are spilled. This is as it should be, since PAHs are among the more hazardous of the constituents in fuel oils (see Chem.Detail sections of Fuel oil entries). However, it is not always easy to determine which combinations of lab methods to use for oil products. The following is a proposed decision Tree (dichotomous key) for selection of lab methods for measuring contamination from mid-range petroleum products (Roy Irwin, National Park Service, Personal Communication, 1997):

> In choosing a lab method, it should be kept in mind that many mid range products (such as Diesel, No. 2 Fuel Oils, and Light Crudes) can be expected to exhibit the following characteristics [741]:
>
> > -Moderately volatile; will leave residue (up to 1/3 of spilled amount)
> > -Moderate concentrations of toxic (soluble) compounds
> > -Will "oil" intertidal resources with long-term contamination potential
> > -Has potential for subtidal impacts (dissolution, mixing, sorption onto suspended sediments)
> > -No dispersion necessary
> > -Cleanup can be very effective

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

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

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

2a. The resource at risk is primarily humans via a drinking water pathway, either the contamination of groundwater used for

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

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

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

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

4. Analyze for Benzene, Toluene, Ethyl Benzene, and Toluene (BTEX) compounds in water as part of a broader scan of volatiles using EPA GC/MS method 8260. The older standard EPA GC/MS method 8240 protocol was sufficient for some applications, but the standard EPA method 8240 (and especially the less rigorous EPA BTEX methods such as method 8020 for soil and method 602 for water) are all inadequate for generating scientifically defensible information for Natural Resource Damage Assessments [468]. The standard EPA methods are also inadequate for risk assessment purposes. Thus, when collecting information for possible use in a Natural Resource

Damage Assessment or risk assessment, it is best to ask the lab to analyze for BTEX compounds and other volatile oil compounds using a modified EPA GC/MS method 8260 method using the lowest possible Selected Ion Mode detection limits and increasing the analyte list to include as many alkyl BTEX compounds as possible. Also analyze surface or (if applicable) ground water samples for polycyclic aromatic hydrocarbons (PAHs) and alkyl PAHs using the NOAA protocol expanded scan*** modified for water samples using methylene chloride extraction. If the contaminated water is groundwater, before the groundwater is determined to be remediated, also analyze some contaminated sub-surface soils in contact with the groundwater for BTEX compounds (EPA GC/MS method 8260) [1013], and PAHs (NOAA protocol expanded scan***). The magnitude of any residual soil contamination will provide insight about the likelihood of recontamination of groundwater resources through equilibria partitioning mechanisms moving contamination from soil to water.

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

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

6. Perform the NOAA protocol expanded scan*** for polycyclic aromatic hydrocarbons (PAHs) and alkyl PAHs. If there is any reason to suspect fresh* or continuing contamination of soils or sediments with lighter volatile compounds, also perform EPA GC/MS method 8260 [1013] using the lowest possible Selected Ion Mode (SIM) detection limits and increasing the analyte list to include as many alkyl Benzene, Toluene, Ethyl Benzene, and Xylene (BTEX) compounds as possible.

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

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

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

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

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

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

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

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

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

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

** Discussion of the significance of the word "confined": Like the

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

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

End of decision tree key.

In response to oil spills, it is important to analyze samples for petroleum PAHs, important alkyl PAHs, and the standard PAHs using the expanded scan of PAHs [828]. This degree of specificity is necessary because oil spill effects are related not so much to the gross amount of oil present as to the levels of key toxic components [468]. Expanded scans typically search for a long list of PAHs and alkylated PAHs at very low detection limits [828]. PAHs in such scans are typically identified by Gas Chromatography with Mass Spectrometry (GC/MS) in the selective ion mode (SIM). In the SIM mode, the GC/MS records intensify for ions that are diagnostic for specific PAHS. Modifications of older lab practices are necessary to get appropriately low detection limits.

Other information on analytical methods that are available for detecting and/or measuring and monitoring fuel oils in environmental media and in biological samples, information from the ATSDR Toxicological Profile (See ATSDR Profile for embedded reference identification) [962].

BIOLOGICAL MATERIALS [962]: Fuel oils are mixtures of

aliphatic and aromatic hydrocarbons (Air Force 1989). Most analytical methods for detecting fuel oils in biological media focus on the detection of kerosene components, as this is a commonly used fuel for residential heaters. Analytical methods for detecting other fuel oils in biological media were not located. .....For more analytical methods information, see the previous profiles on some of the individual components of fuel oils (e.g., benzene, toluene, total xylenes, and PAHs) (AT SDR 1989, 1990a, 1991a, 1991b). The primary method for detecting kerosene in biological materials such as blood is gas chromatography (GC). GC may be combined with mass spectroscopy (MS) for peak identification with the gas chromatograph in the electron impact mode (Kimura et al. 1988, 1991). Quantification methods include the use of mass fragmentography (Kimura et al. 1988). Hydrocarbon components of kerosene are determined based on analysis of headspace gas above the sample (Kimura et al. 1991). This method is useful for distinguishing between kerosene intoxication and gasoline intoxication as kerosene gives a high toluene peak and has a pseudocumene-to-toluene ratio only half that of gasoline. Capillary columns are used, with either Porapak, Chromosorb or Chemipak, giving acceptable results (Kimura et al. 1988). The percent recoveries of these methods were not provided. Wide-bore capillary columns have also been used (Hara et al. 1988) for GC/MS analysis combined with flame ionization detectors (FID). This method determined levels of m- and o-xylene (components of kerosene) in the blood, urine, and stomach contents. The sensitivity and precision of this method was generally good (93-100% recovery) [962].

ENVIRONMENTAL SAMPLES [962]: Because fuel oils are composed of a mixture of hydrocarbons, there are few methods for the environmental analysis of fuel oils as a whole, but methods are reported for the analysis of their component hydrocarbons. The methods most commonly used to detect the major hydrocarbon components of fuel oils in environmental samples are GC/FID and GC/MS.....Several of the components of fuel oils have been discussed in detail in their individual toxicological profiles (e.g., benzene, toluene, total xylenes, and PAHs), which should be consulted for more information on analytical methods (ATSDR 1989, 1990a, 1991a, 1991b). GC is the most commonly used method to selectively detect, identify, and quantify the volatile hydrocarbon components of fuel oils in air (Andrasko 1983; Baldwin 1977; NIOSH 1994). Air samples may be collected on adsorbent tubes such as charcoal, Florisil , Tenax , Porapak , or Chromosorb. Active carbons wires have also been used (Andrasko 1983). The hydrocarbons are extracted from the tubes by thermal desorption or with a liquid solvent such as carbon disulfide and

analyzed on the gas chromatograph. Precision is good (relative standard deviation=0.052) using the charcoal tubes (NIOSH 1994); recovery data were not reported for the other types of adsorption tubes, although desorption from the active carbon wires ranged between 90% and 99% recovery, with a detection limit in the ppb range. A Tenax-TA sorbent trap has been used with subsequent thermal desorption (Andrasko 1983). Combining sample concentration with the headspace method allows for sampling of smaller air volumes and for other environmental samples, such as kerosene combustion debris, that have undergone significant evaporation; the headspace method requires concentrating the sample prior to analysis (Andrasko 1983; Baldwin 1977). An exploratory study indicates that, with additional research, the microanalytical evolved gas analysis technique (EGA) can be further developed to measure kerosene soot in indoor aerosols (Daisey and Gundel 1991) [962].

Abbreviations: Al2O3=aluminum oxide; CCl 4 = carbon tetrachloride; CH 2 CS 2 = dichloromethane (methylene chloride); CS 2 = carbon disulfide; FID = flame ionization detector; GC = gas chromatography; GLC = gas liquid chromatography; KOH = potassium hydroxide; MS = mass spectrometry; Na 2 SO 4 = sodium sulfate; NaOH = sodium hydroxide; NR = not reported; PID = photoionization detector; TLC = thin-layer chromatography [962].

GC/FID and GC/MS have been used to measure the water-soluble components of fuel oils, particularly kerosene, in industrial effluents and estuarine water (Bianchi et al. 1991), sea water (Boyland and Tripp 1971), drinking water (Coleman et al. 1984; Dell' Acqua and Bush 1973), and groundwater (Thomas and Delfino 1991a). Purge-and-trap sample preparation methods have been used to determine purgeable (volatile) aromatic components of fuel oils. This method requires a trap with a Tenax / Chromosorb absorbent and the use of a gas chromatograph with a photoionization detector (PID) (EPA 1991c), an ion trap detector (ITD), or FID (Thomas and Delfino 1991a). A modification of the purge-and-trap method uses ambient temperatures, has the advantage of being applicable to a variety of waters, requires virtually no sample preparation (no solvents are required), and has an analysis time of approximately 30 minutes (Bianchi et al. 1991). While this method may be used for determining the presence of petroleum contaminants in water, it cannot distinguish between various sources of this contamination, e.g., between gasoline, kerosene, and diesel oil. Distinctions between water-soluble fractions of mixed hydrocarbons may be made by using solvent extraction of the water-soluble base/neutral and acid

fractions with methylene chloride (EPA 1991c; Thomas and Delfino 1991a). This separation of base/neutral and acid fractions will permit the GC resolution of the type of water soluble hydrocarbons present in the aqueous phase. Hexane has also been used as a solvent (Dell' Acqua and Bush 1973), as has pentane (Coleman et al. 1984). A dynamic thermal stripper has also been used to detect low levels (ppb range) of fuel oil no. 2 and kerosene present in water samples (Belkin and Esposito 1986). This method traps the fuels on an adsorption tube using helium gas for purging. The fuel is then thermally desorbed and backflushed to a gas chromatograph with FID. This method also does not require any solvent and needs only a 15 mL sample. Recovery for this method is good (91-114%) with precision ranging from 6.4 to 14.3% relative standard deviation. A modified Grob closed-loop-stripping method, which uses a wall-coated open tubular glass capillary column combined with GC/MS, has been used to extract and quantify low levels (ppt) of hydrocarbons in water samples. The method continually recirculates an ambient air stream through the 3.8-liter water sample for approximately 2 hours and collects the vapor on an activated carbon filter, followed by extraction with carbon disulfide and analysis (Coleman et al. 1981). An optical fiber fluorescence spectroscopy system has been used for real- time in situ measurements of low levels (at ppb of diesel fuel marine equivalent) of petroleum hydrocarbons in sea water, showing temporal and spatial variability (Lieberman et al 1993). A qualitative method for determining diesel oil in water has been proposed that is based on changes in the internal reflection of an optical fiber coated with an organophilic compound caused by the presence of hydrocarbons. The method does not require any sample preparation but is limited to relatively high concentrations of contaminants, e.g., 17 mg/L for diesel oil (Kawahara et al. 1983). An alternative method uses a Fourier transform infrared spectrometer (FTIR). This method has the advantage of no sample preparation, a short analysis time (20-30 seconds), and good accuracy (+ or -20%). A detection limit of 0.5 ppb has been determined for a 1-liter sample of sea water; 10 mL is sufficient if a detection limit of 0.05 ppm is acceptable. The FTIR may be coupled with a GC or liquid chromatography for the analysis of complex mixtures (Mille et al. 1985). GC/FID (Galin et al. 1990a), gas liquid chromatography (GLC) with FID (Midkiff and Washington 1972), and elevated temperature purge and trap with GC (Chang et al. 1990) have been used to measure fuel oils in soils. An enzyme immunoassay has been developed using a monoclonal antibody reagent that detects gasoline and diesel fuel in soil; commercialization of this assay will offer significant advantages over current testing methods of gasoline and

fuel contamination levels in soil (Allen et al. 1992b). GLC has also been used to determine fuel oils in marine sediments (Gearing et al. 1980) and other environmental samples such as paper, cloth, and wood (Midkiff and Washington 1972). Extraction is used to concentrate the sample because fuel oils do not provide sufficient vapors to allow the use of a headspace sampling method. Carbon tetrachloride is the recommended solvent as it causes less interference with the chromatographic peaks of the fuel oils (Galin et al. 1990a; Midkiff and Washington 1972). Quantification of fuel oil hydrocarbons from sediments is a more elaborate process. Following extraction, the saturated and olefinic hydrocarbon fraction is separated from the aromatic hydrocarbon fraction using thin-layer chromatography or column chromatography. Fractions are subsequently analyzed by GLC (Gearing et al. 1980). Recovery, sensitivity, and levels of detection data were not reported. Quantification of oils and grease, by gross weight only, in soils and sludges may be accomplished by extraction with a Soxhlet apparatus using either trichlorotrifluoroethane (APHA 1985) or methylene chloride (Martin et al. 1991) as the solvent, although this method may not be used to identify the specific type of oil or grease present in the soil sample. Synchronous scanning fluorescence spectroscopy can be used to identify kerosene, fuel oil number 2, fuel oil number 5, and other aromatic- containing products in groundwater and soil samples. This analytical method is more efficient than chromatographic methods, and its spectra are easier to interpret for identification purposes (Pharr et al. 1992). Fluorescence spectroscopy has been used for in situ detection of petroleum hydrocarbon plumes in soil; this technique allows for measurements in soils before monitoring wells are drilled and is thus independent of the fractionation and transport problems inherent when sampling well fluids (Apitz et al. 1992). The age of diesel oil in the subsurface soil environment can be determined by utilizing the fact that the composition of the diesel oil (the ratio between n-alkanes and isoprenoids) changes due to biodegradation. In one study, the ratio of C 17 to pristane was highly correlated with the residence time of diesel fuel at 12 test locations (Christensen et al 1993). A set of neural networks has been trained to identify seven classes of petroleum hydrocarbon based fuels from their fluorescence emission spectra; this technique correctly identified at least 90% of the test spectra (Andrews and Lieberman 1994). High-performance liquid chromatography (HPLC), followed by GC/MS, has been used to fractionate and then quantitate the aliphatic and aromatic hydrocarbons present in liquid fuel precursors in order to determine the fuel potential of the compounds. Kerosene had the advantage of not

requiring any sample preparation. Other light fuel oils may require the use of methylene chloride as a solvent prior to HPLC analysis (Lamey et al. 1991). The sensitivity, precision, and recovery of this method were not reported. An alternative method for fractionating and purifying petroleum hydrocarbons prior to GC or HPLC separation has been developed (Theobald 1988). The method uses small, prepacked, silica or C 18 columns that offer the advantage of rapid separation (approximately 15 minutes for a run); good recovery of hydrocarbons (85% for the C 18 column and 92% for the silica column); reusability of the columns; and for the silica column in particular, good separation of hydrocarbon from non-hydrocarbon matrices as may occur with environmental samples. Infrared analysis and ultraviolet spectroscopy were used to analyze the aromatic content in diesel fuels; these methods are relatively inexpensive and faster than other available methods, such as mass spectrometry, supercritical fluid chromotography, and nuclear magnetic resonance (Bailey and Kohl 1991). Due to the tendency of hydrocarbons in the soil to undergo subsurface oxidation, measuring CO 2 levels in the soil gas could be used as a cost-effective field screening tool. In one soil-gas survey, CO 2 levels in soil gas correlated well with petroleum hydrocarbons in the soil (Diem et al. 1988). A two-dimensional supercritical fluid chromotography (SFC) system has been developed for the determination of saturates, alkenes, and mono-, di-, and tri- aromatics in diesel fuel. This technique results in a short analysis time (less than 8 minutes) and good relative standard deviations at low alkene content (Andersson et al. 1992). The principal method for detecting kerosene or its components in biota is GC (Blumer et al. 1970; Farrington et al. 1982a; Newton et al. 1991). Aliphatic and aromatic hydrocarbon components of fuel oils taken up by shellfish (whole mussels without shells) were isolated by column chromatography following extraction. Both the alkane/cycloalkane and alkene/aromatic fractions were analyzed by GC with recoveries in the range of 67-100% for alkanes and 71-78% for some aromatics; these aromatics were also analyzed using GC/MS with recoveries between 49% and 74% (Farrington et al. 1982a). Determination of hydrocarbons may also be accomplished by fractionating the hydrocarbon components. Extraction of hydrocarbons from contaminated shellfish may be accomplished using Soxhlet extraction with methanol followed by reextraction with pentane. The extracts are then dried and concentrated prior to injection into the GC (Blumer et al. 1970). Other data on detection limits and precision were not provided [962].

Identification of Data Needs [962]: Methods for Determining Biomarkers of Exposure and Effect. No

biomarkers of exposure were identified for fuel oils because, while standard procedures exist for identifying or quantifying exposure to fuel oils based on hydrocarbon components in blood, urine, and stomach contents (Hara et al. 1988; Kimura et al. 1988, 1991), none of these are applicable solely to fuel oils. These methods are sensitive enough to measure the levels at which health effects occur and may be adequate for determining background levels in the population; however, they cannot distinguish between exposure to different fuel oils or other types of hydrocarbon mixtures. Analytical methods are needed for measuring the hydrocarbon components of fuel oils in lungs. Biomonitoring studies are needed to adequately assess exposure to fuel oils. No biomarkers of effects were identified for fuel oils because the effects associated with exposure to fuel oils are not unique for them, i.e., the effects may be caused by other chemicals or hydrocarbon mixtures. Analytical methods do exist for determining angiotensin-converting enzyme activity in the lungs. This enzyme may be used to determine the lung damage caused by a fuel oil. Analytical methods are needed to determine whether the tissue damage is specific to fuel oils and the target organs. Methods for Determining Parent Compounds and Degradation Products in Environmental Media. Methods exist to detect major hydrocarbon components of fuel oils in air (Andrasko 1983; Baldwin 1977; NIOSH 1994), water (Bianchi et al. 1991; Boyland and Tripp 1971; Dell'Acqua and Bush 1973; EPA 1991c), sediment (Gearing et al. 1980), and soil (Galin et al. 1990a; Midkiff and Washington 1972). The most commonly used methods are GC/FID and GC/MS. These methods are relatively sensitive, selective, and reliable, and can be used to detect the levels of the various components of fuel oils found in the environment and levels at which health effects occur. 6.3.2 On-going Studies No on-going analytical methods studies were located [962].