ENVIRONMENTAL CONTAMINANTS ENCYCLOPEDIA
DIESEL OIL ENTRY

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

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

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

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

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

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

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

Although the editors of this document have done their best in the limited time available to insure accuracy of quotes 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).

Diesel Oil, General (Diesel Fuels, CAS number 68334-30-5)

Brief Introduction:

Br.Class: General Introduction and Classification Information:

Note: Home heating oil is similar to diesel oil but has a separate CAS number (68476-30-2) and a separate discussion in this document (see entry "Fuel Oil Number 2 - Heating Oil"). Just as Diesel oil 1 is similar in chemical composition to Fuel oil 1, with the exception of additives, so is Diesel oil 2 similar in chemical composition to Fuel oil 2, with the exception of additives [962]. Diesel fuels, and typical home heating oil and high aromatic content home heating oil, are all forms of no. 2 fuel oil [498,560]. Diesel oils, as well as typical heating oil, fall under the broader category of Fuel Oil Number 2 (CAS 68476-30-2). See entry entitled "Fuel Oil Number 2" for details on this umbrella category.

Diesel oils are among the products considered "fuel oils" [962].

By the strictest definition, the term "diesel fuel" refers only to fuel oils which are intended for compression ignition engines. Such engines were invented in Germany in the nineteenth century by Rudolf Diesel and make use of the heat generated as the fuel-air mixture is compressed to 500 or 550 pounds per square inch as the sole ignition source. In theory, many different hydrocarbons and other highly flammable compounds could be used as fuel in a diesel engine, but in actuality nearly all diesel engines are fueled with a mixture of petroleum hydrocarbons which boil between 330 and 700 degrees Fahrenheit [822].

Diesel engines are more expensive to build than their gasoline-fueled counterparts. Their virtue lies in their sparing use of a relatively inexpensive fuel, and in their long life and low maintenance costs. Early diesel engines were mainly large, low rpm machines, but modern diesel engineering has seen the development of light, high speed engines. The major current (1991) uses of diesel engines are in: commercial trucks, propulsion of ships and boats, railroad locomotives, industrial engines, and private automobiles [822].

At a National Park Service spill site where sediments were contaminated by Diesel 1 and 2, the most common polycyclic aromatic hydrocarbons (PAHs) were alkyl PAHs (see Chem.Detail section below for details).

In terms of refining crude oil, diesel fuels are middle distillates. The middle distillates include kerosene, aviation fuels, diesel fuels, and fuel oil #1 and 2. These fuels contain paraffins (alkenes), cycloparaffins (cycloalkanes), aromatics, and olefins from approximately C9 to C20. Aromatic compounds of concern included alkylbenzenes, toluene, naphthalenes, and PAHs [661].

The term "diesel" is actually a catch-all for various diesel mixtures. The three most common forms of diesel are [560]:

> Grade 1-D: Straight-run fractions including kerosenes to intermediate distillates from mixed-base crudes. Used for mobile service such as trucks, railroads and submarines.
>
> Grade 2-D: Similar to Grade 1-D but with lower volatility. Used for industrial and heavy mobile service.
>
> Grade 4-D: Residual fuel oils blended with more viscous distillates. Used for larger stationary installations (ASTM D 975).

To some people, the term "diesel fuel" means any petroleum distillate which boils between 300 and 700 degrees Fahrenheit, and so includes another group of products which are more properly called heating oils (see also entry entitled Fuel Oil Number 2 - Heating Oil). Heating oils are intended for use in domestic or commercial space-heating furnaces, or as fuel for small steam or hot water boilers. In practice, some small petroleum refiners produce a single product which is marketed as both No. 2 diesel oil and No. 2 heating oil. The specifications for the two products overlap sufficiently that a dual-purpose product is possible. Larger refiners, however, make separate products with separate properties [822].

Diesel fuels are classed as middle distillates and are more dense than gasoline, thus providing more energy per unit volume than gasoline. The product definition for diesel oil in the U.S. Chemical Substances Inventory under the Toxic Substances Control Act is [747]:

> A complex combination of hydrocarbons produced by the distillation of crude oil. It consists of hydrocarbons having carbon numbers predominantly in the range of C9-C20 and boiling in the range of approximately 163-357 degrees C [747].

It has been stated that because of the way diesel is produced, most lighter weight hydrocarbons (C1 to C8) and most of the volatile aromatic compounds such as benzene, toluene, xylene, and ethylbenzene (BTEX), and most PAHs are removed from the diesel during the distillation process [497]. However, the proceeding statement is only true in a relative sense, since PAHs and BTEX are still important hazardous components of diesel spills (See Chem.detail section below for a complete list of PAHs, BTEX, and other compounds in diesel fuels).

Br.Haz: General Hazard/Toxicity Summary:

Short-term hazards of the some of the lighter, more volatile and water soluble compounds (such as toluene, ethylbenzene, and xylenes) in diesels include potential acute toxicity to aquatic life in the water column (especially in relatively confined areas) as well as potential inhalation hazards. Diesel fuels have moderate volatility and moderate solubility [777]. Diesel products possess moderate to high acute toxicity to biota with product-specific toxicity related to the type and concentration of aromatic compounds [777]. Diesel 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 the some of the lighter, more volatile and water soluble compounds (such as toluene and xylenes) in diesel fuels 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 PAHs, alkyl PAHs, and alkyl benzene (such as xylene) constituents of diesel fuels. Although PAHs, particularly heavy PAHs, have not been know to make up a huge percentage of diesel fuels by weight, previous scans have often ignored the important alkyl PAHs. It has been known previously that there are some PAHs in diesel fuels, including naphthalene, alkyl naphthalenes and phenanthrene [497,661,796,822,824].

At a National Park Service spill site where sediments were contaminated by Diesel 1 and 2, the most common PAHs were alkyl PAHs (see Chem.Detail section below). In this Park Service sediment investigation at Petersburg National Battlefield performed in response to contamination by Diesel Fuels (1D and 2D), 97.6% of the PAHs concentrations detected in sediments were alkyl PAHs. All 39 PAHs and alkyl PAHs analyzed were present in the contaminated sediments (Personal Communication, Roy Irwin, National Park Service, 1996). Since alkyl PAHs are such a high percentage of total PAHs in several petroleum products, they should not be ignored in hazard or risk assessments. Due to their relative persistence and potential for various chronic effects, PAHs (and particularly the alkyl PAHs) can contribute to long-term (chronic) hazards of diesel products in contaminated soils, sediments, and groundwater. Chronic effects of some of the constituents in diesels (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 diesel fuels (see entries on individual compounds for more details).

The term diesel fuel incorporates a broad range of petroleum products which vary significantly in exact chemical composition. In evaluating the effects of diesel fuel contamination on a particular site, some effort must be made to establish the nature of the diesel fuel which is present [822]. Although each batch will contain slightly different mixtures of hydrocarbons, one of the biggest environmental concerns with diesel oils is that they contain polyaromatic hydrocarbons (PAHs) such as fluoranthene and phenanthrene, which can be quite toxic in water [660] and sediments. Some of the PAHs in diesel oils are also suspected carcinogens, and some can persist for considerable periods of time in bottom sediments. Also, the heavier diesel fuels will tend to have higher levels of moderate and heavy PAHs [497]. Because the toxicity of diesel fuel is primarily related to PAH content, which is highly variable between the different diesel fuel types, the environmental impacts of different diesel fuels can vary by more than an order of magnitude [822].

The individual components of diesel which have independent health effects criteria are volatile aromatic hydrocarbons and polynuclear aromatic hydrocarbons. Of the volatile aromatic compounds (such as benzene, toluene, xylenes, and ethyl-benzene), toluene is the one most frequently found in diesel and results in the highest calculable risk due to inhalation. Of the polynuclear aromatic hydrocarbons, naphthalene, 2-methylnaphthalene, and phenanthrene are the most commonly found in diesel and are the individual compounds posing the highest calculable risk due to ingestion [497].

Many of the same compounds found in diesel are also found in jet fuels. As might be expected, there is therefore some overlap between the toxic effects potentially resulting from diesel spills and jet fuel spills (see the Jet Fuel, General 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 more toxic in sunlight or other UV source than elsewhere (see PAHs as a group entry).

For effects on plants, see case studies detailed in tis.misc. section below:

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

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

Painting either diesel fuel or closely related Fuel Oil 2 on mice was positive for carcinogenesis [875].

There is inadequate evidence for the carcinogenicity in humans of diesel fuels [747].

There is limited evidence for the carcinogenicity in experimental animals of marine diesel fuel [747]. Marine diesel fuel is possibly carcinogenic to humans (Group 2B) [747].

Distillate (light) diesel fuels are not classifiable as to their carcinogenicity to humans (Group 3) [747]. However, certain carcinogenic effects have been associated with some of the other compounds found in diesel fuels (see entries on individual compounds for more details).

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

The chemical composition of diesel fuels is highly variable, but it is generally not considered to be carcinogenic even though it contains PAHs at low concentrations. However, some positive evidence of carcinogenicity in animals has been reported. For example, a 2-year dermal study in mice by the National Toxicology Program concluded that chronic ingestion exposure to marine diesel fuel resulted in an increased incidence of skin neoplasms at a dose of 250 ppm [744].

Because the toxicity of diesel fuel itself following prolonged, low-level exposure has not been well studied, the toxicity of the chemicals that comprise diesel oil may be examined to determine if they suggest that chronic, low-level exposure to the mixture would present a hazard. Those constituents of diesel oil that have severe toxic effects, or effects that are most likely to manifest themselves at a lower level of exposure, are listed here [824]:

CHEMICAL	CPF (1/mg/kg/day)	RfD (mg/kg/day)
Benzene	0.029	
Benzo(a)pyrene	11.5	
N-Nitrosodiphenylamine	0.0049	
Quinoline	12.5	
Cresol (m-)		0.05
Cresol (o-)		0.05
Cresol (p-)		0.05
Ethylbenzene		0.1
Naphthalene		0.004
Phenol		0.6
Toluene		0.2
Total Xylene		2

NOTES:

1) CPF = Cancer Potency Factor; the higher the number (since CPF is reported as the inverse of mg/kg/day), the higher the threat of cancer due to exposure. Benzene is a known

human carcinogen. N-nitrosodiphenylamine causes bladder tumors in rats, and quinoline increases the incidence of liver tumors in laboratory animals. It is important to note that although benzo(a)pyrene (BaP) is carcinogenic to laboratory animals, it is likely to be present only as a trace constituent, if at all, in any particular diesel oil. Also, due to low water solubility, BaP is largely immobile in soil and unlikely to migrate significantly from a spill site in either soils or groundwater [824].

2) RfD = Reference Dose; similar to an Acceptable Daily Intake (ADI). Chemicals which have RfDs in the above table are regulated as noncarcinogens, although they may pose other threats. For example, naphthalene, which is a significant constituent of distillate oils, has been shown to cause hemolytic anemia in humans exposed for either short or long periods of time. Xylene and toluene have also been detected in distillate fuels; they both produce nervous system effects at high doses [824].

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.

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

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 diesel fuel [764,765,766,767] (see entries on individual compounds for more details).

Genotoxicity tests have provided equivocal results, with positive results in the rat bone marrow assay and negative results in the Ames assay [744].

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

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

See also: PAHs as a group entry.

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

Since alkyl PAHs make up such a big percentage of the PAHs in diesel contaminated sediments (see Chem.Detail section below for details), it should be kept in mind that these alkyl PAHs are heavier and behave differently than the parent compounds (see PAHs as a group entry).

Diesel in soil may migrate to drinking water supplies where it could present an adverse impact [497].

Jet fuels and diesels are middle distillate petroleum hydrocarbon products of intermediate volatility and mobility [661]. As intermediate products, diesel fuels have a combination of mostly lighter, less persistent and more mobile compounds as well as some heavier, more persistent and less mobile compounds. 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 diesel 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).
>
> The compounds in diesel 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. However, even for these heavier compounds, 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).

Concerning clean-up issues, diesel fuels in general fall into the Diesel-like Products and Light Crude category. The following grouping is used by NOAA to identify basic clean-up options [741,771,777]:

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

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

Diesel fuels are appreciably less volatile than gasoline [747].

In general, diesel fuel oil is not likely to form emulsions [560].

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

Synonyms/Substance Identification:

Automotive diesel oil (ADO) [607,747]
Diesel fuel (DOT) [607]
Diesel oil (petroleum) [607,747]
Diesel oils [607]
Diesel test fuel [607]
Fuels, diesel [607]
NA1993 (DOT) [607]
Olej napedowy III (Polish) [607]
Auto diesel [747]
Derv [747]
Diesel [747]
Diesel fuel oil [747]
Gas oil [747]

NOTE: RTECs [365] once listed Fuel Oil as a synonym for diesel. The more current RTECs [607], however, does not, because they are not the same thing. Confusion on CAS numbers is seen in the literature: CAS number 68512-90-3 is listed for diesel in RTECS but not in the Dictionary of CAS numbers [617] or some other sources. CAS 68476-34-6 is the number for diesel 2-D, not for diesel oil in general.

However, all diesel oils are considered types of fuel oils [962].

Associated Chemicals or Topics (Includes Transformation Products):

See also individual entries:

Diesel Oil #1
Diesel Oil #2
Diesel Oil #4
Fuel Oil, General
Fuel Oil Number 2
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):

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

W.Typical (Water Concentrations Considered Typical):

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

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

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

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

W.Plants (Water Concentrations vs. Plants):

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):

Aquatic saltwater toxicity data (mg/L) [560]:

GENUS/SPECIES:	24hr TLm:
Juvenile American Shad	204 (grade 1-D)
	204 (grade 2-D)

Acute toxicity of water-soluble fraction (mg/L) [560]:

GENUS/SPECIES	48h LC50
Larval Rainbow Trout	2.43 (closed cup)
	2.52 (open cup)

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

Aquatic toxicity data (mg/L) [560]:

GENUS/SPECIES	LD50
Mallard	20 mg/kg (1-D)

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

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

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

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

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

Sed.Low (Sediment Concentrations Considered Low):

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

Sed.High (Sediment Concentrations Considered High):

Details of contaminants (ng/g or ppb dry weight) in samples of sediments contaminated recently by Diesel Fuel (1D and 2D, historically possibly mixed with a few other petroleum products), two sites in Branch Creek, Petersburg National Battlefield (Ray Ahlbrandt, National Park Service, Personal Communication, 1996):

Site O = outfall area S1B, Sediments here smelled like Diesel.

Site DS = One mile downstream of S1B, still in Branch Creek, 50 feet upstream of confluence with Harrison Creek

Parameter	Site O	Site DS
Naphthalene:	15.1	10.3
C1-Naphthalene:	51.0	13.8
C2-Naphthalene:	910.5	25.1
C3-Naphthalene:	3698.1	52.1
C4-Naphthalene:	4915.9	26.1
	------	-----
Total Naphthalenes	9590.6	127.40

Note: there is some evidence of carcinogenicity for naphthlenes: see entries for naphthalenes and PAHs.

Biphenyl:	11.8	1.8
Acenaphthylene:	4.3	4.4
Acenaphthene:	21.7	29.7
Fluorene:	43.0	48.4
C1-Fluorene:	483.3	27.2
C2-Fluorene:	1371.2	22.5
C3-Fluorene:	1880.8	39.7
	-------	-----
Total Fluorenes	3,778.3	137.8
Anthracene:	17.4	88.4
Phenanthrene:	107.3	423.9
C1-Phenanthrene/anthracene:	1190.5	181.1
C2-Phenanthrene/anthracene:	1936.8	79.9
C3-Phenanthrene/anthracene:	1019.2	44.3
C4-Phenanthrene/anthracene:	318.3	17.7
	------	-----
Total P/A	4,455.8	323.0
Dibenzothiophene:	30.2	30.2
C1-Dibenzothiophene:	296.0	26.0
C2-Dibenzothiophene:	769.1	19.8
C3-Dibenzothiophene:	626.6	10.7
	------	-----
Total DBZT	1,721.9	86.7
Fluoranthene:	42.5	500.5
Pyrene:	78.6	421.0
C1-Fluoranthene/pyrene:	153.6	241.3

Heavy, Mostly More Carcinogenic PAHs:

Benzo(a)anthracene *:	12.3	183.7
Chrysene *:	21.5	173.9
C1-Chrysene *:	26.3	82.3
C2-Chrysene *:	39.1	31.9
C3-Chrysene *:	3.3	2.8
C4-Chrysene *:	5.5	22.1
	---	-----
Total Chrysenes *:	95.7	313.0
Benzo(b)fluoranthene *:	23.5	194.7
Benzo(k)fluoranthene *:	5.3	79.3
Benzo(e)pyrene **:	9.9	84.7
Benzo(a)pyrene *:	8.3	84.7
Perylene **:	2.5J	29.0
Indeno(1,2,3-c,d)pyrene *:	8.2	87.5

Dibenz(a,h)anthracene *:	2.4	25.9
Benzo(g,h,i)perylene **:	10.7	70.4

* Carcinogenic
** Not Able to Classify one way or the other (not sure about carcinogenicity, not classifiable, often due to lack of data, see PAHs entry for details)

Metals From Same Sites Listed above, but in ppm dry weight (mg/kg) rather than ppb:

Barium	27.65	2.62
Chromium	12.62	<1.0
Nickel	4.36	<2.0
Vanadium	25.1	<2.0
Lead	51.67	<10.0
Magnesium	583.97	12.29

For a brief analysis of the above data from Petersburg National Battlefield: See Chem.Detail section below.

Sed.Typical (Sediment Concentrations Considered Typical):

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

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

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

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

Sed.Plants (Sediment Concentrations vs. Plants):

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

Sed.Invertebrates (Sediment Concentrations vs. Invertebrates):

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

Sed.Fish (Sediment Concentrations vs. Fish):

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

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

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

Sed.Human (Sediment Concentrations vs. Human):

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

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

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

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

Soil.Low (Soil Concentrations Considered Low):

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

Soil.High (Soil Concentrations Considered High):

Seven large and medium size west coast ports were surveyed during August 1990 to determine their involvement with hydrocarbon contaminated soils and activities associated with the characterization and remediation of these soils. All ports surveyed indicated that they have hydrocarbon contaminated soil problems [735].

At one site, a soil investigation revealed one or more of four underground petroleum pipelines, all idle or abandoned, near the center of the redevelopment area may have leaked. The presence of petroleum contamination in the soil was confirmed. The petroleum could not be identified, but appeared to be of a heavy petroleum type (diesel, bunker oil, or possibly very weathered crude) rather than gasoline [735]:

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

Soil.Typical (Soil Concentrations Considered Typical):

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

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

Between 25 and 30 states, and 4 out of 10 Canadian provinces, have numerical cleanup criteria for petroleum contaminated soils. Until recently, most numerical criteria were expressed as maximum concentrations of certain gross contaminants such as oil and grease, total petroleum hydrocarbons, gasoline, or diesel fuel. Numerical criteria for these parameters range from 1,000 mg/kg to 20,000 mg/kg for oil and grease, 10 mg/kg to 1,000 mg/kg for gasoline and total petroleum hydrocarbons, and 100 mg/kg to 10,000 mg/kg for diesel fuel. Aesthetic or phytotoxicity considerations were typically the basis for the development of such standards; little or no consideration was given to the human health risks associated with the contaminant levels [738].

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):

State TPH Diesel (method not specified, Diesel

Range Organics?) cleanup guidance levels range from 100 to 10,000 ppm [806].

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):

One author stated that although diesel in soil is not a serious environmental threat, it may migrate to drinking water supplies where it could present an adverse impact [497]. 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 diesel 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 diesel (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].

In surface soils, diesel may have an impact on humans, animals, or plants. Diesel in surface and near-surface soils will biologically degrade, utilizing soil oxygen that would normally be available to plant roots, resulting in injury or death of the plants. The most common potential environmental impact, however, is migration of diesel to groundwater [497].

Health effects of diesel in soil [497]:

> No federal or professional industrial hygiene exposure standards have been established for diesel. Potential health effects of individual components present in diesel have been documented, however, and health risks of diesel can be evaluated based on these [497].
>
> The health risk from any carcinogenic components is extremely low or non-existent when diesel is present in soil. Consequently, requirements to remediate diesel-contaminated soil and the specific cleanup criteria mandated by regulatory agencies are not based on potential health effects of diesel-contaminated soil, but rather, on a desire to protect groundwater quality or on the assumption that diesel-contaminated soil is undesirable [497].

Remediation of diesel-contaminated soils [497]:

> Dineen [497] provides a discussion of 10 remediation options for diesel-contaminated soil: disposal, bioremediation, thermal treatment, road

base, asphalt batching, chemical oxidation, fixation, soil washing, containment, and no action. The option(s) selected for a specific site will be based on vertical and lateral depth of contamination, volume of contaminated soil, depth to groundwater, potential exposure pathways, soil type, surface usage, and local regulations [497].

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:

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 [962]. 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 [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):

An oral single-dose LD50 concentration of 5100 ppm has been calculated in rats. Sublethal effects include alopecia (hair loss), lethargy, diarrhea, skin irritation, and development of open sores [744].

RAT LD50 (oral) = 9 gm/kg. Toxic effects were gastrointestinal (Hypermotility, diarrhea) [607].

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):

See table in Carcinogenicity/Cancer/Tumors section below for Cancer Potency Factors (CPF) and Reference Doses (RfD) of various diesel components.

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):

Effects on Invertebrates:

In December 1968, the tanker Witwater ran aground off the Caribbean coast of Panama, releasing 20,000 barrels of diesel oil and bunker C fuel oil. Injury to mangrove habitats was assessed qualitatively approximately 2 months after the discharge. Populations of crabs, Uca sp., were reduced relative to non-oiled areas [622].

Effects on Plants:

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

In July 1991, a Japanese fishing vessel, Tenyo Maru, collided with the Chinese freighter, Tuo Hai, in northwest Washington state [860]. Approximately 380,000 liters of diesel fuel and intermediate fuel oil (IFO = 80% crude oil and 20% diesel oil) leaked from the sunken vessel. A study was initiated to investigate whether petroleum products, like those spilled from the Tenyo Maru, could result in the loss of coloration and death of bull kelp (Nereocystis luetkeana) as observed in the field. Kelp forests form ecosystems that are important for support of a variety of fish and shellfish species. The study tested the effects of three separate petroleum products, both unweathered and weathered: IFO, diesel fuel, and Prudoe Bay crude. All petroleum treatments resulted in a plant color loss, with a distinct bleached line being the most obvious visible indication of plant contact with petroleum. Intense bleaching was probably the result of chemical constituents in the petroleum that act as solvents. Chemical fractions of petroleum including cycloalkanes and aromatics are effective solvents for chlorophyll and other pigments. Direct damage to the tissue may have resulted from reduction in the protective mucus layer and subsequent drying, splitting, and microbial decay of the tissue. Based on the photosynthetic rate studies, whole-plant experiments, and blade growth-rate measurements, the relative ranking of petroleum-treatment effects to kelp are weathered diesel > unweathered IFO > unweathered diesel > weathered IFO > unweathered crude > weathered crude [860].

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

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.

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:

The major current (1991) uses of diesel engines are in: commercial trucks, propulsion of ships and boats, railroad locomotives, industrial engines, and private automobiles [822].

Depending on the major use, different types of diesel fuel may be utilized to obtain desired operating characteristics at the minimum cost. For example, Arctic Diesel is intended for use in low temperature areas, where pour point is critical. No. 1 diesel oil (more volatile than No. 2) is for high performance engines that require very good ignition characteristics [822]. No. 1 diesel also gives good performance in engines requiring frequent changes in speed and load, such as city buses [747]. No. 2 diesel oil (which has a higher specific gravity than No. 1) is used for industrial and heavy transportation service such as railroads, truck and river boats [747]. No. 4 diesel is used for low- and medium-speed engines [747]. Marine diesel is commonly used for large low-speed ship propulsion engines. And, SP type B diesel is a specification that was utilized by the Southern Pacific Railroad in the 1960s [822].

Diesel is used in the railroad industry to fuel locomotives and millions of gallons are stored and transported as part of daily operations. Diesel is also widely used as a solvent to clean moving parts. The widespread use of diesel in railroad yards has resulted in numerous occurrences of diesel-contaminated soil due to spillage, leakage from storage tanks, catastrophic leaks from tanker cars, absorption of diesel on sand used for traction, and past disposal of diesel into unlined ponds [497].

Forms/Preparations/Formulations:

The term "diesel" is actually a catch-all for various diesel mixtures. The three most common forms of diesel are: Diesel Oil #1 (Grade 1-D); Diesel Oil #2 (Grade 2-D); and Diesel Oil #4 (Grade 4-D) [560].

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

> Caution: Every individual petroleum product has a unique "fingerprint," or distinct combination of concentrations of various PAHs and other petroleum constituents. Due to the varying properties of the same general category of a petroleum product (that is, each source and weathering stage of a diesel oil has a unique gas chromatograph "fingerprint"), careful assessment of the toxicity, specific gravity, and other physical characteristics of each individual oil must be taken into consideration to determine the exact effects of the product on the environment. For example, the API gravity of diesel oils range from 35 to 42. Therefore, the below comments on diesel oils are to be considered as representative, but not absolute values typical of every batch of the product with the same name.

This product contains many additives [875,962]. Additives in diesel fuels include alkyl nitrates and nitrites; various nitro and nitroso compounds; peroxides; organic compounds of barium, calcium, manganese, and iron; aluminum compounds, various organic antioxidants, ethylene vinyl chloride polymers; various chlorinated hydrocarbons used as cold flow improvers; and various amines, alcohols, phenols, and sulfonates [875].

Metals content in diesel fuel products includes the following [875]:

Arsenic	Up to 0.13 ppm
Cadmium	Up to 0.89 ppm
Chromium	Up to 2.8 ppm
Iron	Up to 71 ppm
Lead	Up to 2 ppm
Manganese	Up to 6.2 ppm
Molybdenum	Up to 0.27 ppm
Vanadium	Up to 0.16 ppm
Zinc	Up to 4.8 ppm

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.

Details of contaminants (ng/g or ppb dry weight) in samples of sediments contaminated recently by Diesel Fuel (1D and 2D, historically possibly mixed with a few other petroleum products), two sites in Branch Creek, Petersburg National Battlefield (Ray Ahlbrandt, National Park Service, Personal Communication, 1996):

Site O = outfall area S1B, Sediments here smelled like Diesel.

Site DS = One mile downstream of S1B, still in Branch Creek, 50 feet upstream of confluence with Harrison Creek

Parameter	Site O	Site DS
Naphthalene:	15.1	10.3
C1-Naphthalene:	51.0	13.8
C2-Naphthalene:	910.5	25.1
C3-Naphthalene:	3698.1	52.1
C4-Naphthalene:	4915.9	26.1
	------	-----
Total Naphthalenes	9590.6	127.40

Note: there is some evidence of carcinogenicity for naphthlenes: see entries for naphthalenes and PAHs.

Parameter	Site O	Site DS
Biphenyl:	11.8	1.8
Acenaphthylene:	4.3	4.4
Acenaphthene:	21.7	29.7
Fluorene:	43.0	48.4
C1-Fluorene:	483.3	27.2
C2-Fluorene:	1371.2	22.5
C3-Fluorene:	1880.8	39.7
	-------	----

Total Fluorenes	3,778.3	137.8
Anthracene:	17.4	88.4
Phenanthrene:	107.3	423.9
C1-Phenanthrene/anthracene:	1190.5	181.1
C2-Phenanthrene/anthracene:	1936.8	79.9
C3-Phenanthrene/anthracene:	1019.2	44.3
C4-Phenanthrene/anthracene:	318.3	17.7
	-------	-----
Total P/A	4,455.8	323.0
Dibenzothiophene:	30.2	30.2
C1-Dibenzothiophene:	296.0	26.0
C2-Dibenzothiophene:	769.1	19.8
C3-Dibenzothiophene:	626.6	10.7
	------	-----
Total DBZT	1,721.9	86.7
Fluoranthene:	42.5	500.5
Pyrene:	78.6	421.0
C1-Fluoranthene/pyrene:	153.6	241.3

Heavy, Mostly More Carcinogenic PAHs:

Benzo(a)anthracene *:	12.3	183.7
Chrysene *:	21.5	173.9
C1-Chrysene *:	26.3	82.3
C2-Chrysene *:	39.1	31.9
C3-Chrysene *:	3.3	2.8
C4-Chrysene *:	5.5	22.1
	----	-----
Total Chrysenes *:	95.7	313.0
Benzo(b)fluoranthene *:	23.5	194.7
Benzo(k)fluoranthene *:	5.3	79.3
Benzo(e)pyrene **:	9.9	84.7
Benzo(a)pyrene *:	8.3	84.7
Perylene **:	2.5J	29.0
Indeno(1,2,3-c,d)pyrene *:	8.2	87.5
Dibenz(a,h)anthracene *:	2.4	25.9
Benzo(g,h,i)perylene **:	10.7	70.4

*	Carcinogenic
**	Not Able to Classify one way or the other (not sure about carcinogenicity, not classifiable, often due to lack of data, see PAHs entry for details)

Note: The above PAHs and alkyl PAHs were analyzed by a GC/MS/SIM NOAA protocol [828].

Metals From Same Sites Listed above, but in ppm dry weight (mg/kg) rather than ppb:

Barium	27.65	2.62
Chromium	12.62	<1.0
Nickel	4.36	<2.0
Vanadium	25.1	<2.0
Lead	51.67	<10.0
Magnesium	583.97	12.29

Brief Analysis of the Above Data from Petersburg National Battlefield (Roy Irwin, National Park Service, Personal Communication, 1996):

Overview: This was a one-time sampling, so not too much can be read into the results. However, the initial data seems generally consistent with a mixed petroleum product input with strong diesel component (as suspected) and it is of note that all 39 PAHs and alkyl PAHs were found in samples taken one mile downstream as well as even higher concentrations of many of the lighter (and less persistent) PAHs at the outfall. Magnesium, a known contaminant in diesel, is higher near the outfall and non-detected downstream. Other petroleum product suspect metals such as vanadium, nickel, and lead (from historic spills of leaded gas?) show the same trend. On the other hand, most of the heavier and more persistent PAHs had higher concentrations downstream. These heavier PAHs may be accumulating there after gradual transport downstream with sediment loads, while the lighter (and more prone to biodegradation) PAHs such as naphthalenes may be breaking down before they get so far downstream.

PAHs: Total naphthalenes of 9591 ppb dry weight at the outfall are far above concern effects benchmarks from Oakridge (407 ppb at 1% organic carbon). Only rough rather than precise comparisons can be made with Oakridge benchmarks since TOC was not analyzed along with the other contaminants listed in the above table. However, NOAA suggested that the potential for biological effects for naphthalene of this contaminant sorbed to sediments was highest in sediments where its concentration exceeded the 2100 ppb dry weight Effects Range-Median (ERM) concentration and was lowest in sediments where its concentration was less than the 160 ppb dry weight Effects Range-Low (ERL) concentration [664]. The ERL and ERM levels were developed for marine and estuarine sediments, so they are only a rough benchmark for freshwater sediments, though commonly used for that purpose due to the lack of many other benchmarks. Nevertheless, using both NOAA and Oakridge values, impacts would be suspected from the naphthalene levels in sediments near the outfall. Naphthalene is selectively phytotoxic, with alkyl compounds being most toxic [366], so effects on aquatic plants may be occurring in addition to effects on benthic aquatic invertebrates and fish. Anthracene concentrations of 17.4 ppb at the outfall and 88.4 one mile downstream are above the concern effects benchmark from Oakridge (0.3 ppb). Extractable organic matter was low (0.025) at the downstream site, so the 88.4 ppb level found there may be a concern. If the C1 to C4 Anthracenes were added, this exceedance would be more dramatic. Total chrysenes downstream are approaching but not exceeding the lowest published concern level: 386 ppb ERL NOAA level [664]. Benzo(a)anthracene levels in sediments downstream (183 ppb) somewhat exceeded the Oakridge Estimated equivalent sediment quality criterion of 108 ppb [652]. Benzo(a)pyrene levels in sediments downstream (157.6) exceed the OakRidge Estimated equivalent sediment quality criterion of 140 ppb [652]. Total fluorene sediment concentration of 3.778 ppm found upstream exceed 0.54 mg/kg dry weight (microtox) to 3.6 mg/kg dry weight (amphipod) AET benchmarks [416]. Fluoranthene levels downstream (500.5 ppb) were higher downstream, where this biodegradation resistant PAH may be accumulating; although 500 ppb is not extremely elevated, effects in sediments have been observed with mean fluoranthene concentrations as low as 382 ppb [444].

Total carcinogenic PAHs: in sediments downstream at site S6a, total carcinogenic PAHs just barely exceeded the 1 ppm level which had been shown to induce tumors in bullhead catfish [40]. Total carcinogenic PAHs were those in above tables from Benzo(a)anthracene, except for (excluding) the non-classifiable compounds Benzo(e)Pyrene, Perylene, and Benzo(g,h,i)perylene. Actually, none of the PAHs commonly analyzed by EPA method 8270 for semi-volatiles or even the NOAA expanded scan are clearly classified as non-carcinogens; the least damaging thing one can say about any of them is that they are not classifiable due to lack of data (see PAHs entry for details).

Metals: Lead in sediments upstream (51.7 ppm) slightly exceeds the NOAA ERL benchmark [664] and is approaching others. Otherwise, metals in sediments do not appear to be a concern.

In terms of refining crude oil, diesel fuel is a middle distillate. The middle distillates include kerosene, aviation fuels, diesel fuels, and fuel oil #1 and 2. These fuels contain paraffins (alkanes), cycloparaffins (cycloalkanes), aromatics, and olefins from approximately C9 to C20. Aromatic compounds of concern included alkylbenzenes, toluene, naphthalenes, and PAHs [661].

NOTE: According to one source, diesel fuels include high percentages of PAHs: naphthalenes, acenaphthalenes, anthracenes, and phenanthrenes [661]. However, reports of PAH content in diesel fuels varies; see short summary list just before the Environment Canada information [560] at end of this Chem.detail section.

In Europe, carbon numbers up to 28 and final boiling-points up to 390 degrees C can be found for automotive diesel oil [747].

Basic chemical composition groups in diesel (see also entry entitled Petroleum, General):

ALKANES: Normal, branched, and cyclic alkanes (paraffins) are the most abundant components found in diesel fuel (estimated 65 to 85 percent). Branched alkanes of particular interest include pristane and phytane, which are frequently present at a significant concentration and can be easily identified by gas chromatography. The ratio of pristane to heptadecane and phytane to octadecane for a given source of diesel fuel is frequently distinctive enough to enable source identification in a spill investigation. These ratios also increase during biological degradation and are useful in evaluating the age of environmental contamination [822].

AROMATICS: Aromatic compounds represent an estimated 10 to 30 percent of No. 2 diesel fuel. The flash point specification on No. 2 diesel is high enough that only trace quantities of BTEX components can be present. The lower flash point specifications on No. 1 diesel and on Arctic diesel do allow significant concentrations of these compounds, however. Alkyl benzenes, particularly C3 and C4 alkyl benzenes, are common light-end components of diesel fuel. Naphthalene, phenanthrene, acenaphthene, acenaphthylene, fluorene, fluoranthene, and pyrene, as well as a myriad of alkyl and cycloalkyl substituted positional-isomeric homologs of these compounds, are identified in this product. The most predominant compounds in this class are naphthalene and methyl substituted naphthalenes [822].

> NOTE: Because of the toxicity of this class of compounds they are frequently the target of analytes in environmental evaluation associated with petroleum contamination. Diesel fuels are considered to be somewhat carcinogenic, primarily as a result of their small contents of PAHs, although trace levels of BTEX must also be considered. This theory is supported by experimentation which shows that marine diesel is a causative tumorigenic substance to laboratory mice [822].

Reference [796] shows three polycyclic aromatic hydrocarbons to be in diesel: 0.07 ug/kg benzo(a)pyrene; 0.57-0.91 weight percent methylnaphthalene; and 0.13 weight percent naphthalene [796].

Some marine diesel fuels may contain more than 10% PAHs. Diesel fuels may also contain minor amounts of constituents such as n-hexane (below 0.1%), benzene (below 0.02%), toluene, xylenes and ethyl benzene (0.25-0.5%) [747].

Hydrocarbons class analysis for two different diesel samples [824]:

COMPOUND CLASS	SAMPLE 1 WEIGHT %	SAMPLE 2 WEIGHT %
Paraffins	42.70	41.70
Cycloparaffins	33.40	30.90
Aromatics	23.90	27.40

Specific constituents of no.2 fuel oil - diesel oil [824]:

CHEMICAL	CONCENTRATION RANGE (ppm)
Volatile Organics	
Benzene	6-82
Ethylbenzene	100-800
Toluene	100-800
Xylene	100-800
Polycyclic Aromatic Hydrocarbons	
Pyrene	ND-41
Fluoranthene	ND-37
Benzanthracene	0.001-1.2
Triphenylene	2.2
Chrysene	1.4
Benzo(a)pyrene	0.001-0.6
Benzo(e)pyrene	<0.1
2-Methylnaphthalene	6,700
Naphthalene	2,730
Phenanthrene	1,500

NOTE: ND = not detected

NOTE: Earlier in this document, it was stated that "Because of the way diesel is produced, all lighter weight hydrocarbons (C1 to C8) and most of the volatile aromatic compounds such as benzene, toluene, xylene, and ethylbenzene, are removed from the diesel during the distillation process" [497]. BTEX can be detected in diesel, but the BTEX concentrations listed in the table above are very low compared to typical gasoline BTEX concentrations [744]. Nonetheless, the presence of BTEX in diesel should be noted.

To summarize, diesel fuels contain the following PAH compounds [497,660,661,796,822,824]:

2-Methylnaphthalene*
Naphthalene*
Phenanthrene*
Pyrene
Fluoranthene
Benzanthracene
Triphenylene
Chrysene

Benzo(a)pyrene
Benzo(e)pyrene
Acenaphthene
Acenaphthylene
Flourene
* = predominant

and a myriad of alkyl- and cycloalkyl-substituted positional-isomeric homologs of several of these compounds [822].

Additional Physicochemical information from Environment Canada [560]:

NOTE: In this section, for properties with more than one value, each value came from its own source; in other words, if API Gravity at 60 F was measured several times and several different answers were obtained, all of the answers are provided [560]:

SOLUBILITY [560]:

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

	Temperature (not given)	22 C
Fresh Water	39.1	2.8
Gulf P20 Diesel in distilled water	2.3	
Gulf P40 Diesel in distilled water	8.3	
Seawater	60.4	

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

NOTE: Created by the American Petroleum Institute (API), API gravity is an arbitrary scale expressing the gravity or density of liquid petroleum products [637]. This scale was created in order to compare the densities of various oils. API gravity = (141.5/specific gravity [60/60 degrees F]) - 131.5, where specific gravity [60/60 degrees F] is the oil density at 60 degrees F divided by the density of water at 60 degrees F.

39.4
43.2 to 35.0 (grade 1-D)

METAL CONTENT [560]:

Other Metals (ppm):

Molybdenum	< 0.6
Potassium	2.8
Zinc	1.2
Lead	< 3
Nickel	< 1
Iron	4.6
Chromium	< 1.5
Magnesium	12.3
Vanadium	< 0.6
Copper	< 0.6
Titanium	< 0.6
Barium	< 0.3

DENSITY (g/mL) [560]:

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

NOTE: The densities of crude oils and oil products are dependent on the temperature and degree of weathering. The following density values are at "0% Weathering Volume" - in other words, fresh diesel fuel oil.

Temp(C)	Density (at 0% Weathering Volume)
0	0.838
15	0.809 to 0.849 (grade 1-D)
	0.827
20	0.868 to 0.898 (grade 2-D)

VISCOSITY [560]:

NOTE: The viscosities of crude oils and oil products are dependent on the temperature and degree of weathering. The following viscosity values are at "0% Weathering Volume" - in other words, fresh diesel fuel oil.

Dynamic Viscosity (mPa.s or cP):

Temp(C)	Dynamic Viscosity (at 0% Weathering Volume)
-1.1	2.8 (1-D)
0	3.9
	1.3 (grade 1-D)
	2.1 (grade 2-D)
1.7	1.9 (1-D)
15	2.7
	1.3 (1-D)
	2.1 (2-D)

Kinematic Viscosity (mm2/sec or cSt):

Temp(C)	Kinematic Viscosity (at 0% Weathering Volume)
15	1.5 to 1.6 (grade 1-D)

```
   40         1.3 to 2.4 (grade 1-D)
              1.9 to 4.1 (grade 2-D)
              5.5 to 24.0 (grade 4-D)
```

Pour Point (degrees C):

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

-20
-30
-34 (grade 1-D)
-17.8 (grade 2-D)

FIRE AND REACTIVITY [560]:

Flash Point (C):
55
min 38 (grade 1-D)
min 52 (grade 2-D)
min 55 (grade 4-D)
37.7 (closed cup tester) (grade 1-D)
51.7 (closed cup tester) (grade 2-D)

Flammability Limits (Volume %):

in air: 1.3 to 6 (grade 1-D)
1.3 to 6 (grade 2-D)

DISTILLATION [560]:

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

Initial Boiling Point - IBP (C):
180 to 360

Final Boiling Point - FBP (C):
193 to 293 (grade 1-D)
282 to 338 (grade 2-D)

SENSATION [560]:

Colour
Light brown (grade 1-D)
Light brown (grade 2-D)

Odour Threshold (ppm)
0.7 (grade 1-D)

OTHER [560]:

Reid method Vapor Pressure (kPa):

Temp(C)	Pressure
37.8	0.689 (estimated)
37.8	0.683 (grade 1-D)
	4.323 (grade 2-D)
38	1.51

Trimethyl benzenes may occur in this produce [875].

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

See also Br.Fate Section above.

Environmental fate in soil of "Diesel" [497]:

The most common potential environmental impact is migration of diesel to groundwater [497].

The mechanisms of diesel movement in soil are saturated or unsaturated flow of liquid or dissolved diesel in water, and diffusion (volatilization). Diffusion, however, is not a primary mechanism of diesel migration in soil [497].

Because of the heterogeneity inherent in soils, movement of diesel in the liquid state or dissolved diesel in water can only be described by very complex equations, and even these are of limited usefulness. Common sense and visible observations provide the best initial evaluation of the fate of diesel in soil. Since volatilization of diesel is limited, the primary direction of diesel movement is downward (leaching). Lateral movement can occur in a low-permeability zone or saturated zone of soil [497]. (For a summary of the fate of hydrocarbons in soil, see I. Bassert and R. Bartha, "The Fate of Petroleum in Soil Ecosystems," in Petroleum Microbiology, 1984.)

The most important soil characteristic affecting the movement of diesel is soil permeability, which is a function of soil porosity. Soil porosity, in turn, is usually a function of soil particle size. In unconsolidated soil, therefore, permeability decreases from sand to silt to clay. Macropore flow, soil density, and percent saturation make accurate predictions nearly impossible; however, under most circumstances, gross estimates of soil permeability based on particle size provide a reasonable estimate of the fate of diesel in soil [497].

Laboratory and/or Field Analyses:

Since PAHs and alkyl 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. If a Park Service sediment investigation at Petersburg National Historical Battlefield (see Chem.Detail section above, a study 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.

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

NOTE: As mentioned in the Chem.Detail section above, all 39 PAHs and alkyl PAHs [828] including all commonly analyzed parent compounds) have been reported in diesel fuels. Many alkyl homologs exist in diesel fuels [822, see Chem.Detail Section].

For metals see metals entries for details on lab methods.

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

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

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

6. Perform the NOAA protocol expanded scan*** for polycyclic aromatic hydrocarbons (PAHs) and alkyl PAHs. If there is any reason to suspect fresh* or continuing contamination of soils or sediments with lighter volatile compounds, also perform EPA GC/MS method 8240 (or 8260 update) using the lowest possible Selected Ion Mode (SIM) detection limits and increasing the analyte list to include as many alkyl Benzene, Toluene, Ethyl Benzene, and Xylene (BTEX) compounds as possible.

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

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

8. Perform NOAA protocol expanded scan*** for polycyclic aromatic hydrocarbons (PAHs) and alkyl PAHs and/or GC/FID

fingerprinting of the coating oil only if necessary to identify the source or exact oil. If the source is known and no confirmation lab studies are necessary: dispense with additional chemical laboratory analyses and instead document direct effects of coating: lethality, blinding, decreased reproduction from eggshell coating, etc., and begin cleaning activities if deemed potentially productive after consolations with the Fish and Wildlife Agencies.

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

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

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

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

11b. The concern is for plants or for vertebrate wildlife including birds, mammals, reptiles, and amphibians: polycyclic aromatic hydrocarbons (PAHs) and other petroleum hydrocarbons break down fairly rapidly in many wildlife groups and tissues are not usually analyzed directly. Instead direct effects are investigated and water, soil, sediment, and food items encountered by wildlife are usually analyzed for PAHs and alkyl PAHs using the NOAA protocol expanded scan***. If the spill is fresh* or the source continuous, risk assessment needs may also require that these habitat media also be analyzed for Benzene, Toluene, Ethyl Benzene, and Xylene (BTEX) and other volatile compounds using EPA GC/MS method 8240 (or 8260 update) or modified EPA method 8240 (or 8260 update) 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 Decison Tree Key.

See also: PAHs as a group entry.

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

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

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

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

A number of states, including California and Wisconsin, recommend the use of Diesel Range Organics (DRO) methods. Most DRO methods are modifications of method 8015b [1013]. Some states use alkane standards for DRO, while some use diesel fuel itself for calibration. National guidance is in SW-846 [1013]. One of the problems with DRO methods that concentrate on certain alkane standards is that the alkanes come from sources other than diesel, and the continued need to do occasional correlations with more rigorous scans of PAHs and alkyl PAHs. EPA has various alkane-related methods [861], but for risk assessment, alkane methods should usually be supplemented with GC/MS/SIM expanded scans for PAHs and alkyl PAHs [828].

Highlights from the Modified DRO (Method for Determining Diesel Range Organics) Recommended by Wisconsin DNR, September 1995 (Donalea Dinsmore, Wisconsin Department of Natural Resources, personal communication, 1997):

> This method is designed to measure the concentration of diesel range organics in water and soil. This corresponds to a

hydrocarbon range of C10 - C28 and a boiling point range between approximately 170°C and 430°C. As defined in the method, other organic compounds, including chlorinated hydrocarbons, phenols, phthalate esters, polynuclear aromatic hydrocarbons, kerosene, fuel oils and heavier oils are measurable. DRO results include these compounds/products.

...

The Limit of Quantitation (LOQ) of this method for diesel range organics is 10 mg/kg or less for soils and 0.1 mg/L or less for groundwater.

This method is based on a solvent extraction, Gas Chromatography (GC) procedure. This method should be used by, or under supervision of, analysts experienced in solvent extraction and the use of gas chromatographs. The analysts should be skilled in the interpretation of gas chromatograms and their use.

The method is designed to measure mid-range petroleum products such as diesel or fuel oil. Components greater than C28 present in products such as motor oils or lubricating oils are detectable under the conditions of the method. If, based on a review of the chromatogram, the presence of these product types is suspected, additional analyses may be necessary. These additional efforts are not contained within this method.

....

Summary of Method

This method provides gas chromatographic conditions for the detection of semivolatile petroleum fractions such as diesel, fuel oil #2, or kerosene. Samples are analyzed utilizing extraction to dissolve the organic constituents. The extract is dried, concentrated and injected into a capillary column gas chromatograph. The gas chromatograph is temperature programmed to facilitate separation of organic compounds. Detection is achieved by a flame ionization detector (FID). Quantitation is based on FID detector response to a diesel component standard.

This method is suitable for the analysis of waters, soils, or wastes.

Soil core samples are collected in wide mouth VOC vials with minimum handling to reduce loss of contaminants. Preservation by solvent addition is performed in the lab. This method is based in part on 1) USEPA SW-846: the 3rd edition of methods 8000 and 8100; 2) Method OA-2; 3) work by the EPA Total Petroleum Hydrocarbons Methods Committee; and 4) work by the Wisconsin Ad-Hoc Committee on LUST Program Analytical Requirements and Wisconsin State Laboratory of Hygiene.

....

Definitions

Diesel Range Organics (DRO): All the chromatographic response falling between the onset of the n-decane (n-C10) peak and the conclusion of the n-octacosane (n-C28) peak. Quantitation is based on a direct comparison of the total area within this range to the total area of the Diesel Component Standard.

Diesel Component Standard: A ten component blend of typical diesel compounds (Table 3). This standard serves as a quantitation standard and is used to establish a retention time window for diesel range organics.

Laboratory Control Spike - Water: A reagent water spiked with the Diesel Component Standard and run through the method with water samples as a quality control check. See Section 10.3.1.

Laboratory Control Spike - Soil: A reagent sand or soil sample spiked with the Diesel Component Standard and run through the method with soil samples as a quality control check. See Section 10.3.2.

Method Blank - Water: A reagent water sample extracted with the same volume of solvent used in samples, processed as a sample, and run as a quality control check. If contamination is found it is the lab's responsibility to determine its origin. See section 10.3.3 for method blank acceptance criteria.

Method Blank - Soil: A reagent sand or clean soil extracted with the same volume of solvent used in samples, processed as a sample, and run as a quality control check. If contamination is found it is the lab's responsibility to determine its origin. See section 10.3.4 for method blank acceptance criteria.

Calibration Check Standard (CCS): A calibration standard analyzed to verify the validity of the calibration curve. See section 10.3.5 for CCS acceptance criteria.

Temperature Blank: A vial of water supplied by the laboratory, treated in the same manner as sample vials and carried along with samples, to determine if proper cooling of samples has been achieved. A 40 ml or 60 ml vial will be adequate for this purpose.

......

Sample collection, Preservation, and Handling

Aqueous samples should be collected in a one liter amber bottle with a teflon lined cap. The Teflon liner must contact the sample. Samples must be preserved with 5 mls of 50% HCl at the time of collection, (acid must be added to the bottle prior to adding the sample). Cool samples to 4°C immediately after collection. Water samples must be held at 4°C and extracted within seven days of collection. Analysis must take place within 47 days of collection. Samples from carbonate aquifers should be preserved with sodium azide or extracted unpreserved within 48 hours of collection. Samples collected from carbonate aquifers must be flagged on the chain of custody. The pH of all water samples must be determined unless sample vials containing acid for field preservation were supplied by the lab. The pH measurement may be performed on left-over sample. If sample pH is greater than two, sample results must be flagged. Flagging is not required for carbonate aquifers samples preserved with sodium azide or extracted within 48 hours of collection.

Soils 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. Samples cannot be analyzed if the amount of soil in the vial exceeds the weight maxima listed in Table 1. A sufficient number of vials (three recommended) should be collected to provide for backup analyses in the event of breakage and to allow for screening. One vial must be collected for dry weight determination. Care must be taken to be sure the vial seals properly (no soil on the threads). This can be accomplished by using a clean toothbrush or other utensil to sweep particles off the threads of the vial.

Collect and preserve samples by one of the following techniques:

Collect soil into tared VOC vials following Table 1. Store samples on ice or at 4°C. Samplers should be aware that laboratories use a variety of vial taring methods so it is important to use only vials supplied by the laboratory performing the analysis.

Pack soil with no headspace into a brass tube. Cap the tube using plastic endcaps with teflon sheets placed between the endcaps and the sample. Store samples on ice or at 4°C. Immediately prior to solvent addition, the soil from the brass tube must be subsampled into a VOC vial following Table 1.

Subsampling involves removing one of the plastic endcaps, scrapping away the surface soil, and then scooping out, (with a spatula or other utensil), the appropriate weight of soil into the vial. Brass tubes must be cleaned appropriately prior to reuse.

Pack soil with no headspace into an EnCore TM sampler. Cap with the stainless steel "o-ring" cap. Store samples on ice or at 4°C. Soil stored in the EnCore TM sampler must be extruded from the device into a VOC vial immediately prior to solvent addition. The soil is extruded by using a pushrod supplied with the tool. Soil should not be scooped out of the sampler using a spatula, etc. EnCore TM samplers must be cleaned appropriately (following the manufacturers recommendations) prior to reuse.

Alternate sample storage devices equivalent or superior in performance to the brass tube or the EnCore TM sampler may be used for sample storage prior to preservation in the laboratory. Alternate sample storage devices must be approved by the Department prior to use.

Shipping time should be minimized. Samples must be received by the lab within 72 hours. Refer to Table 2 for soil sample holding times.

Extractant solvent must be added to soil vials within 72 hours of sample collection.

Upon receipt by the laboratory weigh the tared sample vial to determine the actual weight. Use Table 1 to determine the volume of solvent to add, or if the sample must be flagged or rejected. If the laboratory analyzes soil samples exceeding the weight maxima in Table 1, at the request of clients, the samples must not be reported as "DRO".

Add solvent to the sample in a 1:1 ratio (or greater) of mls solvent to grams of sample. Solvent can be injected through the septa, or the vial may be quickly opened to allow the appropriate volume of solvent to poured in. Solvent must be added to the sample within 72 hours of sample collection.

It is not necessary for the lab to complete the extraction at the time of injection of the solvent (addition of sodium sulfate, sonication, etc.) The date of solvent addition must be reported in lieu of the extraction date. Completion of the extraction (addition of sodium sulfate, sonication, etc.) need not be done until the time of analysis. Analysis must take place within 47 days of collection.

Sample temperature must be determined upon receipt to the lab. Sample temperature may be recorded as "received on ice" only if solid ice is present in the cooler at the time the samples are received. "Received on ice" means sample containers are surrounded by an ice slurry, or crushed, cubed or chipped ice at the time of receipt in the laboratory. It is acceptable to place the sample containers in plastic bags to preserve sample and label integrity. The use of bubble wrap or other insulating material is not allowed. Samples cooled during shipping with ice packs or "blue ice" may not be recorded as "received on ice". If samples are not "received on ice", temperature shall be determined from:

The temperature of an actual sample.

The temperature of a temperature blank shipped with samples.

The temperature of the melt water in the shipping container.

When no ice is in the cooler, no temperature blank is provided, and there is not sufficient sample volume to sacrifice for a temperature measurement, the laboratory must flag the sample result and state the condition of sample upon receipt (ie. not cooled during shipping, received at room temperature, etc.). Note: If blue ice packs or similar methods are used, precooling of samples to 4°C with ice or by refrigeration is required.

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References

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"Leaking Underground Fuel Tank (LUFT) Field Manual", State Water Resources Control Board, State of California, Sacramento, CA, May 1988.

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Diesel component standard and concentrations (other states use diesel fuel itself as the standard):

Component Concentration	ug/ml
Decane	1000
Dodecane	1000
Tetradecane	1000
Hexadecane	1000
Octadecane	1000
Eicosane	1000
Docosane	1000
Tetracosane	1000
Hexacosane	1000
Octacosane	1000
Total	10,000

Note: The concentration of the Diesel Component Standard may be varied as long as the concentration of each component is the same.

End of section on Wisconsin Method.

Abstracts on Fingerprinting:

Wade, T.L., T.J. Jackson, T.J. McDonald, J.L. Sericano, and J.M. Brooks. 1993. Oyster Polynuclear Aromatic Hydrocarbon Fingerprinting Applied to the Apex Barge Oil Spill. Society of Environmental Toxicology and Chemistry (SETAC) 14th annual meeting. Westin Galleria and Oaks Houston, TX., (Nov. 14-18 1993), p. 17.

> An estimated 692,000 gallons of catalytic feed stock oil was spilled into Galveston Bay on July 28, 1990, when a tanker collided with three Apex barges in the Houston Ship Channel. Oysters were collected and analyzed from Galveston Bay Todd's Dump (GBTD) before the spill (235 days) and after the spill (6, 37, 132, 495, and 851 days). Oysters were also collected from Galveston Bay Redfish Island (GBRI), a site known to be impacted by the spill, 37 and 110 days after the spill. The spilled oil was also analyzed. The concentration of 18 polynuclear aromatic hydrocarbons (PAHs), measured as part of the National Oceanic and Atmospheric Administration's National Status & Trends (NS&T) showed a sharp increase from 100 ng/g (235 days before the spill) to over 600 ng/g (one week after the spill). Concentrations of these 19 PAHs were also found at GBRI. Fingerprinting techniques applied to data from oyster analyses demonstrated the presence of bioavailable Apex Barge oil 37, 110, 132 days after the spill at GBTD and GBRI. Fingerprinting becomes less diagnostic with time due to possible environmental weathering of the oil.

A.G. Requejo, T. McDonald, G. Denoux, M.C. Kennicutt, R. Sassen, and J.M. Brooks. 1993. Multivariate Analysis of Environmental Data: A tool for interpreting results of "fingerprinting" analyses. Society of Environmental Toxicology and Chemistry (SETAC) 14th annual meeting. Westin Galleria and Oaks, Houston, TX., (Nov. 14-18 1993), p. 17.

> Chemical Analyses of environmental samples using "fingerprinting" techniques often result in large quantities of data for each sample. For example, a typical soil or sediment analysis might include concentrations of targeted saturated hydrocarbons, polynuclear aromatic hydrocarbons, chlorinated hydrocarbons, and trace metals, in addition to bulk parameters such as organic carbon and nitrogen content and grain size distributions. The sheer volume and diversity of this type of data can make its interpretation difficult. Multivariate analytical techniques such as Principal Components Analysis (PCA) are ideally suited for the reduction and synthesis of such data sets. PCA employs eigenvector analysis to evaluate the degree of similarity between samples and establish the interrelationship between measured

analytes. The major advantages of PCA in comparison to traditional data interpretation approaches are that it is fast, objective, and employs all the data measured. The utility of this approach will be demonstrated using several different sets of environmental "fingerprinting " data. Included among these are fluorescence and polynuclear aromatic hydrocarbon data from bioremediated soil samples containing petroleum and trace organic and inorganic data from estuarine sediments (Casco Bay, Maine).

Screening scans: if one is dealing with a fresh spill of known composition, or if one has already determined that a good correlation exists between the rigorous scans (as discussed above) and less rigorous screening scans, certain screening scans may be used to monitor the position and magnitude of contamination. Below are a few notes related to screening scans versus diesel fuels:

1) GC/FID:

While a screening analysis such as GC/FID should be adequate for mid-range products such as diesels and possibly jet fuels, lighter gasoline fractions will be lost in a GC/FID analysis (which uses extraction and burning) [657]. Middle distillates in the C9 to C16 range normally have a boiling range well above the boiling-point of benzene; accordingly, the benzene content of this fraction is usually low [747].

2) Method 8015:

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

In California, a "modified method 8015" (different from EPA's method 8015 and also different from EPA method 418.1) is used for gasoline, kerosene, diesel oil, or other fuels in soil and groundwater, as specified in the Leaking Underground Fuel Tank Manual [465]. Thus what is TPH in California is totally different from what may be reported as TPH in other states. In other States TPH often refers to something more similar to TRPH (EPA method 418.1 or some similar modification). One has to be careful with TPH or TRPH values because different labs use different methods for preparation of the samples. Most (but possibly not all) labs use a mixture of three different hydrocarbons (n-hexadecane, isooctane, and chlorobenzene) to calibrate instruments. California allows use of a "modified method 8015" wet weight method, which is different from EPA's method 8015, for TPH analysis of gasoline; this method detects volatile, non-halogenated hydrocarbons for TPH analysis [465].

3) Notes on the California LUFT Method:

In California, total petroleum hydrocarbons (TPH) reporting is usually a GC/FID California modified EPA method 8015, based on a diesel standard (diesel used to calibrate instruments). In California, this method is sometimes referred to method 8015 (diesel standard) [785]. The California Leaking Underground Fuel Tank (LUFT) manual, because of the predominance of diesel and gasoline in LUFTs, treats and reports all semi-volatiles as diesel and all volatiles as gasoline [810]. Thus in California, confusion often arises when [810]:

> Crude oil, kerosene, and hydraulic oil contamination is sometimes reported as diesel fuel, while
>
> Naphtha, mineral spirits, or jet fuel contamination is sometimes reported as gasoline.

According to the LUFT Manual [465], aromatic BTEX compounds represent 6.43 to 36.47% of gasoline by weight but account for less than 0.1% total weight of diesel fuel [809]. Since BTEX levels are typically 60 to 360 times higher in gasoline than in diesel, and since the clean-up criteria suggested in the LUFT manual are based solely on the presence of BTEX, the LUFT manual typically allows much higher amounts of diesel to remain in soil than gasoline [809]. Unless groundwater is very close, the LUFT manual usually allows even high levels of diesel fuel to remain in soil [809]. This appears to be ignoring the risk of PAHs and

> other (non-BTEX) compounds in diesel. The risk from BTEX compounds in diesel is only about 10 times lower for diesel-contaminated soil than for gasoline-contaminated soil if one looks at leaching potential, and even California regulatory agencies have been reluctant to always leave high levels of diesel fuel in contaminated soil [809].
>
> However, diesel fuel has approximately 35% of its components in the gasoline range [810]. Thus, when a diesel sample (or even a naphtha, paint thinner, mineral spirits, JP-4, stoddard solvent, Jet A, or crude oil sample) is purged, it will have a gasoline component and the laboratory using LUFT manual method will erroneously report the sample as gasoline [810].
>
> The California GC/FID methods also call for packed GC columns which have poor resolving power and make it difficult to obtain detailed information about the hydrocarbon type [810]. Superior GC columns and superior methods (such as ASTM 2887) are available [810]. For example, narrow-bore capillary columns can analyze most of the gasoline, entire diesel fractions, and a substantial portion of the crude oil range [810].
>
> Using the California LUFT manual methods, only an experienced analyst will be able to differentiate diesel fractions from aged gasoline [810]. The oversimplified California methods and models are plagued with many problems [808,810]. Choosing an appropriate solvent for semivolatile analyses always presents a problem; some solvents extract certain compounds better than others and many present environmental or health risks [810].

There are other analyses which have been used for measuring diesel, including various modifications of the standard EPA method 8100. For example, a Diesel Range Organics analysis is sometimes referred to as a DRO Modified EPA method 8100. The DIESEL FUEL TLC Method is discussed as follows [497]:

> The various types of diesel fuels will tend to have thin-layer chromatography (TLC) patterns that are different from each other and can be seen in the aromatic portion of the thin-layer chromatography (TLC) chromatogram. The ratio of saturated hydrocarbons to the PNA will vary from batch to batch. The heavier diesel fuels will tend to have higher levels of moderate and heavy PNAs. The thin-layer chromatography (TLC) pattern, using hexane as the eluting solvent, will show two spots, one oval shaped with an Rf of 0.9 (hexane) visible with iodine staining, and a second at about Rf 0.5 (hexane) visible under

> shortwave UV light, and iodine staining. Heavy diesel fuels will also contain material having an Rf of 0.3 to 0.5 (hexane) visible under short- and long-wave UV light, as well as iodine staining. The relative intensity of the saturated hydrocarbon spot to the aromatic hydrocarbon spot will vary from batch to batch.

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), an ion trap detector (ITD), or FID [972]. 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. 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 [962].

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 [962]. 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 [962].

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 [962].

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 C17 to pristane was highly correlated with the residence time of diesel fuel at 12 test locations [962].

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 [962].

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

See also: PAHs as a group entry.