ENVIRONMENTAL CONTAMINANTS ENCYCLOPEDIA

ENTRY ON
LAPIO (LOW-API GRAVITY FUEL OIL, A HEAVY TYPE OF #6 FUEL OIL)

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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).

LAPIO (Low-API gravity fuel oil, a Heavy Type of #6 Fuel Oil)

Brief Introduction:

Br.Class: General Introduction and Classification Information:

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

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

NOTE:

API gravity = (141.5/specific gravity [60/60 degrees F]) - 131.5

where specific gravity [60/60 degrees F] is the oil density at 60 degrees F divided by the density of water at 60 degrees F [560].

Br.Haz: General Hazard/Toxicity Summary:

Information from a spill in the St. Johns River:

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

No other information found. Since LAPIO could be considered as a very heavy #6 fuel oil, see Fuel

Oil Number 6 entry. See also: PAHs as a group entry.

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

No information found; since LAPIO could be considered as a very kind of heavy #6 fuel oil, see Fuel Oil Number 6 entry. See also: PAHs as a group entry.

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

No information found; since LAPIO could be considered as a very kind of heavy #6 fuel oil, see Fuel Oil Number 6 entry. See also: PAHs as a group entry.

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

The following information is from an assessment of potential risks associated with the shipment and transfer of LAPIO in the St. John's River, Florida [775]:

> Because LAPIO can float, sink, become neutrally buoyant, or fractionate and possess all three characteristics, it poses significantly different risks to natural resources, compared to floating oil spills, for the following reasons [775]:
>
> 1. Neutrally buoyant or sinking LAPIO weathers very slowly by evaporation, a process that tends to remove the more toxic fractions from floating oil slicks and greatly reduces the acute toxicity of the spilled oil. As a result, the toxic components of a LAPIO spill are introduced directly into the water column at concentrations greater than traditional spills. Animals in the water column, such as fish, shellfish, and marine mammals, can be exposed to these higher concentrations [775].
>
> 2. LAPIO that is denser than the receiving waters is not expected to sink immediately to the bottom and remain there. More likely, it will be suspended in the water column by tidal and riverine currents, eventually exiting the river system with the net outflow of water. Accumulation of oil on the bottom is expected only in zones of low flow, such as dredged channels, dead-end waterways, and abandoned channels. Natural removal rates by physical flushing would be very slow for spills in the

lacustrine section of the St. Johns River system [775].

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

4. Containment and removal efforts for sinking oil will largely be ineffective [775].

Synonyms/Substance Identification:

None found.

Associated Chemicals or Topics (Includes Transformation Products):

See also individual entries:

Oil Spills
Fuel Oil Number 6

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

W.Low (Water Concentrations Considered Low):

No information found; since LAPIO could be considered as a heavy kind of #6 fuel oil, see Fuel Oil Number 6 entry.

W.High (Water Concentrations Considered High):

No information found; since LAPIO could be considered as a heavy kind of #6 fuel oil, see Fuel Oil Number 6 entry.

W.Typical (Water Concentrations Considered Typical):

No information found; since LAPIO could be considered as a heavy kind of #6 fuel oil, see Fuel Oil Number 6 entry.

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; since LAPIO could be considered as a heavy kind of #6 fuel oil, see Fuel Oil Number 6 entry.

W.Plants (Water Concentrations vs. Plants):

No information found; since LAPIO could be considered as a heavy kind of #6 fuel oil, see Fuel Oil Number 6 entry.

W.Invertebrates (Water Concentrations vs. Invertebrates):

No information found; since LAPIO could be considered as a heavy kind of #6 fuel oil, see Fuel Oil Number 6 entry.

W.Fish (Water Concentrations vs. Fish):

No information found; since LAPIO could be considered as a heavy kind of #6 fuel oil, see Fuel Oil Number 6 entry.

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

No information found; since LAPIO could be considered as a heavy kind of #6 fuel oil, see Fuel Oil Number 6 entry.

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

No information found; since LAPIO could be considered as a heavy kind of #6 fuel oil, see Fuel Oil Number 6 entry.

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

No information found; since LAPIO could be considered as a heavy kind of #6 fuel oil, see Fuel Oil Number 6 entry.

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

Sed.Low (Sediment Concentrations Considered Low):

No information found; since LAPIO could be considered as a heavy kind of #6 fuel oil, see Fuel Oil Number 6 entry.

Sed.High (Sediment Concentrations Considered High):

No information found; since LAPIO could be considered as a heavy kind of #6 fuel oil, see Fuel Oil Number 6 entry.

Sed.Typical (Sediment Concentrations Considered Typical):

No information found; since LAPIO could be considered as a heavy kind of #6 fuel oil, see Fuel Oil Number 6 entry.

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; since LAPIO could be considered as a heavy kind of #6 fuel oil, see Fuel Oil Number 6 entry.

Sed.Plants (Sediment Concentrations vs. Plants):

No information found; since LAPIO could be considered as a heavy kind of #6 fuel oil, see Fuel Oil Number 6 entry.

Sed.Invertebrates (Sediment Concentrations vs. Invertebrates):

No information found; since LAPIO could be considered as a heavy kind of #6 fuel oil, see Fuel Oil Number 6 entry.

Sed.Fish (Sediment Concentrations vs. Fish):

No information found; since LAPIO could be considered as a heavy kind of #6 fuel oil, see Fuel Oil Number 6 entry.

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

No information found; since LAPIO could be considered as a heavy kind of #6 fuel oil, see Fuel Oil Number 6 entry.

Sed.Human (Sediment Concentrations vs. Human):

No information found; since LAPIO could be considered as a heavy kind of #6 fuel oil, see Fuel Oil Number 6 entry.

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

No information found; since LAPIO could be considered as a heavy kind of #6 fuel oil, see Fuel Oil Number 6 entry.

Soil Data Interpretation, Concentrations and Toxicity (All Soil

Data Subsections Start with "Soil."):

Soil.Low (Soil Concentrations Considered Low):

No information found; since LAPIO could be considered as a heavy kind of #6 fuel oil, see Fuel Oil Number 6 entry.

Soil.High (Soil Concentrations Considered High):

No information found; since LAPIO could be considered as a heavy kind of #6 fuel oil, see Fuel Oil Number 6 entry.

Soil.Typical (Soil Concentrations Considered Typical)

No information found; since LAPIO could be considered as a heavy kind of #6 fuel oil, see Fuel Oil Number 6 entry.

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

Soil.General (General Soil Quality Standards, Criteria, and Benchmarks Related to Protection of Soil-dwelling Biota in General; Includes Soil Concentrations Versus Mixed or General Soil-dwelling Biota):

No information found; since LAPIO could be considered as a heavy kind of #6 fuel oil, see Fuel Oil Number 6 entry.

Soil.Plants (Soil Concentrations vs. Plants):

No information found; since LAPIO could be considered as a heavy kind of #6 fuel oil, see Fuel Oil Number 6 entry.

Soil.Invertebrates (Soil Concentrations vs. Invertebrates):

No information found; since LAPIO could be considered as a heavy kind of #6 fuel oil, see Fuel Oil Number 6 entry.

Soil.Wildlife (Soil Concentrations vs. Wildlife or Domestic Animals):

No information found; since LAPIO could be considered as a heavy kind of #6 fuel oil, see Fuel Oil Number 6 entry.

Soil.Human (Soil Concentrations vs. Human):

No information found on this complex and variable mixture. Since LAPIO could be considered as a heavy kind of #6 fuel oil, see Fuel Oil Number 6 entry.

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

No information found; since LAPIO could be considered as a heavy kind of #6 fuel oil, see Fuel Oil Number 6 entry.

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; since LAPIO could be considered as a heavy kind of #6 fuel oil, see Fuel Oil Number 6 entry.

B) Body Burden Residues in Plants: Typical, Elevated, or of Concern Related to the Well-being of the Organism Itself:

No information found; since LAPIO could be considered as a heavy kind of #6 fuel oil, see Fuel Oil Number 6 entry.

Tis.Invertebrates:

A) As Food: Concentrations or Doses of Concern to Living Things Which Eat Invertebrates:

No information found; since LAPIO could be considered as a heavy kind of #6 fuel oil, see Fuel Oil Number 6 entry.

B) Concentrations or Doses of Concern in Food Items Eaten by Invertebrates:

No information found; since LAPIO could be considered as a heavy kind of #6 fuel oil, see Fuel Oil Number 6 entry.

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

No information found; since LAPIO could be considered as a heavy kind of #6 fuel oil, see Fuel Oil Number 6 entry.

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; since LAPIO could be considered as a heavy kind of #6 fuel oil, see Fuel Oil Number 6 entry.

B) Concentrations or Doses of Concern in Food Items Eaten by Fish:

No information found; since LAPIO could be considered as a heavy kind of #6 fuel oil, see Fuel Oil Number 6 entry.

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

No information found; since LAPIO could be considered as a heavy kind of #6 fuel oil, see Fuel Oil Number 6 entry.

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; since LAPIO could be considered as a heavy kind of #6 fuel oil, see Fuel Oil Number 6 entry.

B) Concentrations or Doses of Concern in Food Items Eaten by Wildlife, Birds, or Domestic Animals (Includes LD50 Values Which do not Fit Well into Other Categories, Includes Oral Doses Administered in Laboratory Experiments):

No information found; since LAPIO could be considered as a heavy kind of #6 fuel oil, see Fuel Oil Number 6 entry.

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; since LAPIO could be considered as a heavy kind of #6 fuel oil, see Fuel Oil Number 6 entry.

Tis.Human:

A) Typical Concentrations in Human Food Survey Items:

No information found; since LAPIO could be considered as a heavy kind of #6 fuel oil, see Fuel Oil Number 6 entry.

B) Concentrations or Doses of Concern in Food Items Eaten by Humans (Includes Allowable Tolerances in Human Food, FDA, State and Standards of Other Countries):

No information found; since LAPIO could be considered as a heavy kind of #6 fuel oil, see Fuel Oil Number 6 entry.

C) Body Burden Residues in Humans: Typical, Elevated, or of Concern Related to the Well-being of Humans:

No information found; since LAPIO could be considered as a heavy kind of #6 fuel oil, see Fuel Oil Number 6 entry.

Tis.Misc. (Other Tissue Information):

No information found; since LAPIO could be considered as a heavy kind of #6 fuel oil, see Fuel Oil Number 6 entry.

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

No information found; since LAPIO could be considered as a heavy kind of #6 fuel oil, see Fuel Oil Number 6 entry.

Interactions:

No information found; since LAPIO could be considered as a heavy kind of #6 fuel oil, see Fuel Oil Number 6 entry.

Uses/Sources:

Electric utilities are interested in using this type of oil due to its relative low cost and high BTU value [775]. Much of the residual oil sold today is obtained from foreign refiners who have not upgraded their refining processes. Oil jobbers are now the dominant suppliers, buying residual oils from refineries to blend them for resale on the spot market to electric utilities [775].

Forms/Preparations/Formulations:

LAPIO could be considered as a heavy kind of #6 fuel oil (see Fuel Oil Number 6 entry).

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

Since polycyclic aromatic hydrocarbons (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. See also: PAHs as a group entry.

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

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

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

The following information is from an assessment of potential risks associated with the shipment and transfer of LAPIO in the St. John's River, Florida [775]:

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

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

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

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

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

6. Even standard techniques for location, containment, and recovery will fail unless conducted by contractors experienced in the proper deployment and maintenance of the equipment and the special requirements of oil-spill response [775].

Present response technology is ill-equipped to deal with the potential water-column and benthic habitat impacts from a spill of LAPIO [775].

Since LAPIO could be considered as a heavy kind of #6 fuel oil, see also Fuel Oil Number 6 entry.

Laboratory and/or Field Analyses:

Recent (1991) studies have indicated that EPA approved methods used for oil spill assessments (including total petroleum hydrocarbons method 418.1, semivolatile priority pollutant organics methods 625 and 8270, and volatile organic priority pollutant methods 602, 1624, and 8240) are all inadequate for generating scientifically defensible information for Natural Resource Damage Assessments [468]. These general organic chemical methods are deficient in chemical selectivity (types of constituents analyzed) and sensitivity (detection limits); the deficiencies in these two areas lead to an inability to interpret the environmental significance of the data in a scientifically defensible manner [468]. A great deal of uncertainty remains in the use of dose-response relationships based on crude oil as a whole mixture [734].

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

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

Decision Tree (dichotomous key) for selection of lab methods for measuring contamination from number 6 and other oils considered to be heavy) (Roy Irwin, National Park Service, Personal Communication, 1996):

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

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

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

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

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

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

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

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

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

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

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

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

8. Perform NOAA protocol expanded scan*** for polycyclic aromatic hydrocarbons (PAHs) and alkyl PAHs and/or GC/FID fingerprinting of the coating oil only if necessary to identify the source or exact oil. If the source is known and

no confirmation lab studies are necessary: dispense with additional chemical laboratory analyses and instead document direct effects of coating: lethality, blinding, decreased reproduction from eggshell coating, etc., and begin cleaning activities if deemed potentially productive after consolations with the Fish and Wildlife Agencies.

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

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

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

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

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

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

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

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

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

End of Key.

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

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

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

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

Although EPA method 418.1: Petroleum Hydrocarbons expressed as Total Petroleum Hydrocarbons (TPH), is recommended by many State agencies, some consulting firms, and some laboratories for certain regulatory and screening applications (often leaking underground storage tanks), this method is not well suited to crude oil contamination or to the more persistent hazardous constituents in oil. (See entry entitled: Petroleum Hydrocarbons expressed as Total Petroleum Hydrocarbons). Low values tend to give the mistaken impression that a site is clean when it really isn't (a false negative). For example, a field test of bioremediation of soils contaminated with Bunker C (a heavy fuel) at a refinery in Beaumont, Texas, utilized oil and grease data, which (although the data was quite variable) seemed to indicate bioremediation was taking place [728]. A comparison of the oil and grease data at this site with TPH data at this site suggested the same thing, that the data was quite variable but if anything, the oil was being slowly being cleaned up by bioremediation (Bruce Herbert, Texas A. and M., Department of Geology, personal communication, 1995). However, a later study of the same site utilizing the expanded scan for PAHs

[828] (a modified EPA 8270 including alkyl homologues and lower detection limits), indicated that very little bioremediation of hazardous alkyl PAHs and multi-ring PAHs was actually taking place [727]. Thus, utilizing either oil and grease or TPH analyses would tend to lead one to the faulty conclusion that the harmful compounds were being naturally cleaned up at an acceptable rate. This is partly because the TPH and oil and grease methods tend to favor the lighter and less alkylated PAHs, whereas many of the carcinogenic and longer lasting PAHs are the heavier multi-ringed and alkylated compounds.

See also: PAHs as a group entry.