ENVIRONMENTAL CONTAMINANTS ENCYCLOPEDIA

TOTAL PETROLEUM HYDROCARBONS (TPH) ENTRY

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Like a library or many 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 without 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).

Petroleum Hydrocarbons expressed as Total Petroleum Hydrocarbons (TPH or TPHC)

Brief Introduction:

Br.Class: General Introduction and Classification Information:

Total Petroleum Hydrocarbons (TPH) refers to several rough laboratory tests which are relatively inexpensive, relatively quick, sometimes ineffective, and seldom very quantitative. TPH screening measures are done differently in various states, regions, and individual laboratories. What different labs and individuals report as "TPH" is so variable that much caution should be exercised when attempting to compare or interpret TPH data. Thus, the first order of business in analyzing TPH data is to determine exactly which one is being discussed.

Most often, total petroleum hydrocarbon methods are either EPA's method 418.1 or something like it (a modification of 418.1). However, many other methods are referred to as total petroleum hydrocarbons too.

When considering the results from EPA 418.1-based methods, one should take into account the inherent limitations of the method before using it, but many have not done so [657]. EPA has not officially changed method 418.1 for Total Recoverable Petroleum Hydrocarbons (TRPH) in water since revising their manual entitled "Methods for Chemical Analysis of Water and Wastes" (EPA-600/4-79-020) in 1983 [462]. A listing of problems with 418.1 was provided by Douglas et al. (Chapter 1 in Calabrese and Kostecki) in 1992 [657].

TPH analyses are frequently used for the goal of finding areas of gross contamination, but are often inadequate even for this task. If TPH concentrations are very high, it usually signifies that significant amounts of petroleum hydrocarbons are there. However, if TPH values are low or "non-detected," you cannot uniformly be sure that a significant petroleum hydrocarbon contamination problem is not present.

Few other environmental monitoring parameters have been so widely and consistently misapplied and misinterpreted. TPH tests have even (usually inappropriately) been used to test for things other than petroleum hydrocarbons, such as leakage of PCB-contaminated transformer oils and leakage from pesticide tanks. They typically don't work well for such tests, particularly if sonication extraction methods and/or inappropriate calibration oils are used, as they often are (Mike Martin, Orion Environmental Labs, Fife, Washington, personal communication to Roy Irwin).

TPH values done at the same lab from samples collected at only one site do not consistently give reliable insight about which part of the site is most contaminated, due to moisture content variability and other problems detailed below.

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]. Oil spill effects are related not so much to the gross amount of oil present as to the levels of key toxic components [468].

TPH methods are generally inappropriate when analyzing unknowns.

Due to numerous problems discussed in more detail below, many of the TPH methodologies have been prone to:

1) producing false negatives (reporting "non-detected" when there was really considerable petroleum hydrocarbons present), and

2) underestimating the extent of petroleum hydrocarbons present (true of virtually every TPH methodology), and

3) underestimating the overall risk from petroleum hydrocarbons due to missing significant amounts of some of the compounds of most concern (for example, PAHs), and

4) producing misleading data related to soil hot spots versus areas of less concern due to differing moisture concentrations of otherwise similar samples, and

5) producing misleading results because an inappropriate (not close enough to the unknown being sampled) standard (oil) was used in

calibration, and

6) producing soil or sediment data which cannot be directly compared with other TPH data or guidelines because one is expressed in dry weight and the other in wet weight, and

7) producing relatively accurate dry weight values for heavy petroleum hydrocarbons but questionable dry weight values for lighter, more volatile compounds, (Note: different labs dry the samples different ways and a sample with lots of lighter fraction hydrocarbons is more prone to hydrocarbon loss; the variable loss of volatile hydrocarbons in a drying step is therefore an additional area of lab and data variability), and

8) producing data which cannot be directly compared with other TPH data or guidelines because one data set is the result of a soxhlet extraction method and the other reflects a sonication or other alternative extraction method. [Note: TPH analyses using sonication extractions are most common but are only good for volatiles and miss most of the (especially hazardous) heavy petroleum hydrocarbons such as the heavier multi-ring PAHs], and

9) producing misleading data related to heavy fraction hydrocarbons (again such as the heavier PAHs) due to loss of the heavier compounds on filter paper, and

10) producing data prone to faulty interpretation of the environmental significance of the results (100 ppm of TPH from one type of oil may be practically non-toxic while 100 ppm of TPH from a different type of oil may be very toxic).

Another complication with TPH values is that petroleum-derived inputs vary considerably in composition; it is essential to bear this in mind when quantifying them in general terms such as an "oil" or the "total petroleum hydrocarbons" measurement [461]. Petroleum is complex, containing many thousands of compounds ranging from gases to residues boiling about 400 degree C [461]. Crude oils differ markedly in detailed composition, even during the lifetime of a single well, while distillates and petroleum products are enriched with certain compounds [461]. The complexity of the inputs is matched by the range of properties of the components and the physical, chemical and biochemical processes that contribute to the distributive pathways and determine the fate of the inputs [461]. Since different combinations of petroleum hydrocarbons typically contribute to "total petroleum hydrocarbons" at different sites, the toxicity and other ecological effects are also typically different at different sites, even if the total petroleum hydrocarbons concentration is the same.

The difficulty of standardizing and interpreting TPH levels is amplified by the following personal communications from laboratory scientists working with the TPH methods:

Many of TPH lab methods have been fairly generic (similar to oil and grease) and could easily be influenced by high biological lipids; weathered samples might be high in TPH but lower in biological effects than fresh samples (Chuck Kennicutt, Geochemical and Environmental Research Group, Texas A&M Laboratory, personal communication).

For more details about the various TPH methods, see the Laboratory and/or Field Analyses section below.

Br.Haz: General Hazard/Toxicity Summary:

The main hazards from elevated concentrations of Total Petroleum Hydrocarbons typically relate to the PAHs found in the oil contamination (see "PAHs as a group" entry).

Effects on birds and bioremediation aspects (Brian Cain, Fish and Wildlife Service, Houston, personal communication, 1995):

> Migratory birds can pick up some PAHs from soils, which is reflected in elevated metabolites in bile, but most of these birds are migratory and move on after the original oil insult. Thus, most workers have not found death or reproductive problems, or other chronic impacts upon the birds as a result from moderate oil contamination of soil.

Although PAHs are generally more hazardous than alkanes, alkanes do have some biological effects. The alkanes in gasoline are CNS depressants [855]. In fact, gasoline was once evaluated as an anesthetic agent [855]. However, sudden deaths, possibly as a result of irregular heartbeats, have been attributed to those inhaling vapors of hydrocarbons such as those in gasoline [855].

No other information found; most TPH methods are not very appropriate for measuring potential risks or hazards to living things.

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

The main carcinogenic hazards from elevated concentrations of Total Petroleum Hydrocarbons typically relate to the PAHs found in the oil contamination (see "PAHs as a group" entry).

No other information found; most TPH methods are not very appropriate as measures of potential carcinogenicity.

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

No information found; most TPH methods are not very appropriate for this application.

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

Many TPH methods are less than optimal when considering fate characteristics of the most hazardous compounds involved in typical oil spills. Consider the following example:

> In a simultaneous 11-week study of biodegradation at a Bunker C contaminated refinery in Beaumont, TX, one group of researchers used GC/MS SIM [727], while the other group used the standard TPH method for Oil and Grease [728] on the same weekly composite soil samples. Using the more simple TPH analysis, the researchers concluded that oil contents in the soil were reduced over time in general (the raw TPH data was very variable) [728].
>
> Using GC/MS SIM, the other researchers concluded that the highly weathered oil did not markedly change over the eleven weeks of the experiment, indicating little or no biodegradation. These researchers used GC/MS SIM to quantify a series of molecular biomarkers, such as hopane, in order to test ratios as indicators of in situ biodegradation. They also suggested that low bioavailability may have accounted for the lack of bioremediation at this site [727].

Since different combinations of petroleum hydrocarbons typically contribute to "total petroleum hydrocarbons" at different sites, the fate characteristics are also typically different at different sites, even if the total petroleum hydrocarbons concentration is the same.

Different methods used to generate total petroleum hydrocarbon concentrations, or other similar simple screening measures of petroleum contamination, all produce very different numbers [831]. For example, gasoline saturated soil produced the following concentrations (mg/kg = ppm) [831]:

Total Volatile Solids by EPA 160.4: 3,200
TPH by EPA 418.1: 140,110
TPH-G (GRO by GC/FID or GC/MS): 1,500
Naphthalene by EPA 8270: 13
Benzene by EPA 8260: 3.4
Ethyl Benzene by EPA 8260: 77
Toluene by EPA 8260: 150
Xylene by EPA 8260: 420
Original Gasoline by Column Mass Differences: 15,300

As the product spills or moves to or through different media, the above given proportions change. For example, aqueous leaching of the gasoline saturated soils documented above reduced TPH 418.1 more than it reduced TPH-G [831]. Following aqueous leaching, the concentrations were the following [831]:

Total Volatile Solids by EPA 160.4: 3,600
TPH by EPA 418.1: <25
TPH-G (GRO by GC/FID or GC/MS): 390-400
Naphthalene by EPA 8270: 2.7
Benzene by EPA 8260: <0.025
Ethyl Benzene by EPA 8260: 3.7
Toluene by EPA 8260: 0.13
Xylene by EPA 8260: 25
Original Gasoline by Column Mass Differences: 15,200

Synonyms/Substance Identification:

Many methods have been referred to as TPH methods, with new ones being created as time goes along. Most of these methods are different from one another and therefore not synonyms. See the Associated Chemicals or topics section for a partial listing.

Associated Chemicals or Topics (Includes Transformation Products):

TPH methods are usually not specific enough to measure transformation products. Although method 418.1 is the closest thing to a "standard TPH method" in the U.S. in 1992, many states and other groups have modified 418.1 for use with soils and other mediums. Some States (such as California) have come up with TPH methods totally different than 418.1 [465]. Various methods which have been used to generate TPH concentrations include:

1) EPA's national method 418.1 for total recoverable petroleum hydrocarbons in water, expressed in some places as wet weight and in others as dry weight, or

2) Method 418.1 "modified for soils" for total recoverable petroleum hydrocarbons, expressed in some places as wet weight and in others as dry weight, or

3) The Arizona-modified version of 418.1 (expressed as dry weight), or

4) California's Leaking Underground Fuel Tank (LUFT) Program version of 418.1 [465] (expressed as wet weight), or

5) California's more commonly recommended and used (different than 418.1) DHS (developed by the Department of Health Services) method for TPH, expressed as wet weight. The DHS method is spelled out in the California LUFT manual [465], but no specific oil calibration standards are required.

6) California also 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]. Although it doesn't call them TPH analyses and sometimes wants them in addition to TPH analyses, California also allows the following analyses for gasoline contamination: EPA method 8020 for BTX&E in soil, EPA method 602 for BTX&E in water, EPA method 8010 for halogenated volatile organics in soil, and EPA method 601 for halogenated volatile organics in water [465].

7) New Jersey's 418.1-based modified method for TPH (tphc) in soil (most officials believe it is commonly and should be expressed as dry weight), or

8) Washington's TPHG method for gasoline or TPHD method for Diesel, or

9) An alternative ASTM method, or

10) An older method (reported in the literature and used before the most recent silica gel modification steps) was added by most but not all labs, or

11) Some other method that someone has decided reflects something related to total petroleum hydrocarbons (new methods appear in the literature on a regular basis). See EPA EMMI database for a partial listing of various TPH methods [861].

See also: Chem.Detail section below.

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

NOTE: Benchmark values for TPH are typically not available. See entries on common individual PAHs of concern when measuring TPH, like naphthalene and fluoranthene.

W.Low (Water Concentrations Considered Low):

No information found; most TPH methods are not very appropriate for this application.

W.High (Water Concentrations Considered High):

No information found; most TPH methods are not very appropriate for this application.

W.Typical (Water Concentrations Considered Typical):

No information found; most TPH methods are not very appropriate for this application.

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; most TPH methods are not very appropriate for this application.

W.Plants (Water Concentrations vs. Plants):

Benchmark values for TPH are typically not available. See entries on common individual PAHs of concern when measuring TPH, like naphthalene and fluoranthene. See "PAHs as a group" entry for effects of oil on mangroves.

W.Invertebrates (Water Concentrations vs. Invertebrates):

No information found; most TPH methods are not very appropriate for this application.

W.Fish (Water Concentrations vs. Fish):

No information found; most TPH methods are not very appropriate for this application.

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

No information found; most TPH methods are not very appropriate for this application.

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

Contamination of drinking water supplies due to transport of toxic compounds from soils to groundwater is a legitimate concern that should be the focus of cleanup standards. Regrettably, our current understanding of this phenomenon is perhaps the greatest obstacle to the development of appropriate cleanup standards. Recent research on co-solubility/leaching phenomena is beginning to provide improved estimates of the release and transport of soil contaminants to groundwater. However, further characterization of these complex processes is required, as is an improvement in our ability to apply our knowledge of such processes on a site-specific basis. Largely because of this inadequate understanding of the leaching of organics from soils, dozens of different standards or guidelines currently exist at the state or local level for motor contaminated soils. They range from "background" (e.g. Michigan), or low ppb levels (e.g., 25 ppb benzene, Illinois), to tens or hundreds of parts per million (e.g., 100 ppm TPH, Washington; 10-500 ppm total BTEX, Tennessee) [736].

Total Petroleum Hydrocarbons (TPH), EPA method 418.1 suffers from several shortcomings as an index of potential groundwater contamination or health risk [497]:

> The analytical method for TPH (most commonly EPA method 418.1) does not actually measure "total" petroleum hydrocarbons, but rather a specific range of hydrocarbon compounds. The problems with Method 418.1 are caused by limitations of the extraction process (solvents used and the concentration steps) and the reference standards used for instrumental analysis. The method specifically states that it does not accurately measure the lighter fractions of gasoline (which would include BTEX). Further, there are no published performance data for the method when used on soil matrices (it is originally a water method that has been modified for solids), and it is subject to bias. These numerous technical procedural shortcomings limit its utility as an accurate and reliable analytical method.

TPH represents a summation of all the hydrocarbon compounds that may be present (and detected) in a soil sample. Because of differences in product composition between, for example, gasoline and diesel, or fresh versus weathered fuels, the types of compounds present at one site may be completely different than those present at another. Accordingly, TPH at a gasoline spill site will be comprised of mostly C6-C12 compounds, while TPH at an older site where the fuel has weathered will likely measure mostly C8-C12 compounds.

Because of this inherent variability in the method and the analyte, it is currently not possible to directly relate potential environmental or health risks with concentrations of TPH. The relative mobility or toxicity of contaminants represented by TPH analyses at one site may be completely different from that of another site (for example, C6-C12 vs. C10-C25). There is no easy way to say if 300 mg/kg of "TPH" form the former site will represent the same level of risk as 300 mg/kg TPH from the latter.

For these reasons, it is clear that TPH offers limited benefits as an indicator measure for cleanup criteria. Its current widespread use as a soil cleanup criterion is a function of a lack of understanding of its proper application and limitations, and its historical use as a simple and inexpensive indicator of general levels of contamination. When the regulatory objective is protection of groundwater quality, it would seem most appropriate to focus on specific and more mobile compounds like BTEX as the best indices of potential groundwater risks. Research needs in this area would include the development of improved measurement techniques for motor fuels in soil and the assessment of the relationship (if any) between TPH values and mobility of specific contaminants. Validation of the merits of BTEX as indicator compounds is also needed (i.e., do standards for BTEX provide adequate levels of protection from exposure to other soluble organics in fuels?) [497].

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

No information found.

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

Sed.Low (Sediment Concentrations Considered Low):

No information found; most TPH methods are not very appropriate for this application.

Sed.High (Sediment Concentrations Considered High):

No information found; most TPH methods are not very appropriate for this application.

Sed.Typical (Sediment Concentrations Considered Typical):

Keeping in mind that low levels of TPH do not always mean "no problem"; background levels for TPH at sites not considered pristine include:

Up to 30-40 ppm for sediments (Mark Ort, National Fisheries Contaminant Research Center, Fish and Wildlife Service (personal communication).

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; most TPH methods are not very appropriate for this application.

Sed.Plants (Sediment Concentrations vs. Plants):

No information found; most TPH methods are not very appropriate for this application.

Sed.Invertebrates (Sediment Concentrations vs. Invertebrates):

No information found; most TPH methods are not very appropriate for this application.

Sed.Fish (Sediment Concentrations vs. Fish):

No information found; most TPH methods are not very appropriate for this application.

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

No information found; most TPH methods are not very appropriate for this application.

Sed.Human (Sediment Concentrations vs. Human):

No information found; most TPH methods are not very appropriate for this application.

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

In some states there appears to be widespread confusion even in official circles about whether soil and sediment TPH guidelines as well as the TPH levels most often reported by various laboratories, are wet weight or dry weight values. The norm in most states appears to be dry weight (as it is for most reported concentrations of inorganic contaminants in soil), while in other states the norm is clearly wet weight.

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

Soil.Low (Soil Concentrations Considered Low):

Five to fifteen ppm TPH in soil is a realistic background level on a Texas intercostal waterways spoil island (Brian Cain, Fish and Wildlife Service Contaminants Specialist, Houston, personal communication, 1995).

Soil.High (Soil Concentrations Considered High):

No Information found; most TPH methods are not very appropriate for this application.

Soil.Typical (Soil Concentrations Considered Typical):

Five to 15 ppm for TPH is a realistic background level on a Texas spoil island. Although the islands are dirty when created, they clean up from bioremediation after creation. However, barge traffic, bilge leaks, etc. mean they always have a bit of oil around (Brian Cain, Fish and Wildlife Service, Houston, personal communication, 1995).

An analysis of 93 samples were taken from 31 different sites on Padre Island National Seashore and analyzed for Total Petroleum Hydrocarbons (TPH) using EPA Solid and Hazardous Waste method EPA SW 846, 9071--suggested that (Steven S. Barnes and Paul Eubank, Padre Island National Seashore, personal communication, 1995):

1) Most of the sites showed minimal contamination ranging from 180 ppm down to 30 ppm TPH. This latter group of samples with an average of 86 ppm probably represents a background level for this study area.

2) 300 parts per million would be considered moderate contamination "but nothing that should pose a threat to the environment."

3) One location which had been the site of a petroleum production facility (Convest) had a concentration of 36,400 ppm for the highest value determined.

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):

Cautions: TPH is a dubious parameter done differently in different states and different labs, and what it means is often in doubt. Perhaps 90 % of the TPH analyses for soils in the U.S. are done by the sonication process, which is only good for volatiles and misses most of the heavy petroleum hydrocarbons. Reporting limits for soils should also be scrutinized; in California the suggested reporting limits are 1-5 mg/L for liquids and 25-50 mg/kg for soils. Criteria developed more recently by a growing number of jurisdictions address specific constituents of motor fuels such as benzene, toluene, ethyl benzene, and xylenes (BTEX) [738] or individual PAHs, or total PAHs. See entries on BTEX, "PAHs as a group", and individual PAH entries.

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 TPH for gasoline contaminated soils and total petroleum hydrocarbons, and 100 mg/kg to 10,000 mg/kg for diesel fuel [738]. Many states are known to have action levels consisting of a single concentration value which may vary from 10 to 100 ppm TPH.

Many states are known to have soil action levels consisting of a single concentration value which may vary from 10 to 100 ppm TPH. Other states incorporate a range of action levels for addressing site-specific needs; values range from 10 to 1000 ppm TPH for gasoline soils [734].

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

Another site, located at a former petroleum tank farm, removed as part of the construction of a new cargo terminal, was also contaminated with petroleum hydrocarbon with associated BTEX. This product was identified as primarily gas-oil with a moderate percentage (20-45%) of lighter petroleum products [735]:

CONTAMINANT	CONCENTRATION (ppm)
Total Petroleum Hydrocarbon (TPH) EPA Method 418.1	37,000
Total Petroleum Hydrocarbon (TPH)	

EPA Method 8015 modified for diesel

Benzene	7.8
Toluene	1
Xylene	81
Ethylbenzene	29

Several States have specified 100 ppm TPH dry weight as a soil cleanup level and many of the states specify a method 418.1-based method. However, for the reasons stated above, various TRPH and TPH levels cannot be uniformly compared.

Between 25 and 30 states, and 4 out of 10 Canadian provinces, have numerical cleanup criteria for petroleum contaminated soils [738]. 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 [738]. Numerical criteria for these parameters range from 10 mg/kg to 1,000 mg/kg for gasoline and total petroleum hydrocarbons [738]. 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].

Guidelines for the New Jersey Environmental Cleanup Responsibility Act (1987): Petroleum hydrocarbons should not exceed 100 ppm [347]. In 1988, New Jersey started using a TPH concentration of 100 ppm as a soil cleanup guideline thought to ensure that concentrations in ground water do not exceed drinking water standards; 100 ppm is thought to be relatively conservative and designed to identify potential problems [347]. More recently, the New Jersey standard was broken down by fuel type: if number 6 or 4 fuel oils, the guideline is 100 ppm; if number 2 fuel oil or diesel the guideline is 1,000 ppm (Steve Tatar, New Jersey Leaking Underground Storage Tank project, personal communication). The latest New Jersey values are part of a proposed cleanup standard (March 31, 1992, NJ Administrative Code) for all soil values (not just leaking underground tanks). Most New Jersey officials seem to believe the TPH guidelines in NJ are in dry weight, since soil values for other parameters are, but they hadn't yet been able to find the written confirmation as of this writing.

Several other states, including Arizona, also use 100 ppm dry weight as some sort of guideline or benchmark for soil levels (Jerry Smith, Arizona

Department of Environmental Quality, personal communication). Arizona has their own standard operating procedure for TPH analysis, a dry weight modification of EPA method 418.1 for TRPH.

The California State Leaking Underground Fuel Task Force in 1987 stated that (to protect groundwater) soils having a low leaching potential should be removed if the total petroleum hydrocarbon concentrations exceed 1000 ppm; soils having a medium leaching potential should be removed if the total petroleum hydrocarbon concentrations exceed 100 ppm; and soils having a high leaching potential should be removed if the total petroleum hydrocarbon concentrations exceed 10 ppm [347]. Although most manuals [465] and written guidance documents in California do not specify whether wet or dry weight is to be reported, the State hazardous waste regulations say all lab analysis for hazardous waste identification shall be done on a wet weight basis (Bart Simmons, California Department of Health Services, Hazardous Materials Laboratory, personal communication). This is the exact opposite of most other states, so care should be taken in comparing California values with those generated elsewhere.

Some states have cleanup levels for TPH. For example, the soil TPH limit given by the Utah Department of Health for Hill AFB site near Logan was 38.1 mg/kg (Source: Draft Interagency Guide to Documenting Cost and Performance Information for Site Remediation Projects, EPA Contract 68-W#-0001, prepared by the Federal Remediation Roundtable, October, 1994). State soil cleanup levels tend to change, so the state in question would have to be contacted regarding latest levels. However, because of the many problems with TPH analyses (see discussion above), TPH cannot be used for effects or risk aspects (what does a certain concentration do to living things) of data interpretation. It is primarily a regulatory parameter.

Some states continued to have high regulatory levels of TPH in 1995. Texas Statewide Rule #91 for Oil, Gas, and Geothermal Operations (RCT, 1994) states that cleanup is required in non-sensitive areas when soil TPH levels exceed 10,000 ppm. Sensitive areas, such as parks would have lower limits (Bruce Heise, personal communication, 1995). However, lower levels are supposed to be used for sensitive areas, and 5,000 ppm was used for a rookery island in Corpus Christi Bay (Tom Schultz, Fish and Wildlife Service, Corpus Christi, personal communication, 1995).

> NOTE: The 10,000 ppm Texas Railroad Commission soil standard is still 1% oil, is mostly scoffed and laughed at in biological circles. However, with good bioremediation techniques used in sandy Texas soils, it would be realistic to target a progression for 10,000 ppm to under 100 ppm TPH within a 6 months period (Brian Cain, Fish and Wildlife Service, Houston, personal communication, 1995).

Soil.Plants (Soil Concentrations vs. Plants):

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

Although fresh oil spills often prevent terrestrial plant growth, once oil breaks down some of the oil compounds can be beneficial to some types of plants.

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

One common PAH, naphthalene, occurs naturally in the essential oils of the roots of Radix and Herba ononidis [PATTY. INDUS HYG & TOX 3RD ED VOL2A, 2B, 2C, 1981-1982 p.3333 [366].

Naphthalene, a common PAH, is SELECTIVELY PHYTOTOXIC [366, Spencer, E. Y. Guide to the Chemicals Used in Crop Protection. 7th ed. Publication 1093. Research Institute, Agriculture Canada, Ottawa, Canada: Information Canada, 1982. 411 [366].

The toxic effect of aromatic hydrocarbons, benzene, toluene, naphthalene, 1-methylnaphthalene, anthracene, 9-methylanthracene, phenanthrene, on the productivity of various marine planktonic algae (Dunaliela biocula, Phaeodactylum tricornutum, and Isochysis galbaya) increased with increasing number of aromatic rings. The methylated compounds were most toxic. Taxonomic differences in sensitivity to aromatic hydrocarbons /was investigated/. [Jensen K et al; Limnol 15 (2): 581-4 (1984) [366].

The effect of 10 organic chemicals on the growth and reproduction of the marine red alga was investigated. The test measured vegetative growth, formation of tetrasporangia (site of meiosis-asexual spore production), and production of cystocarps (evidence of sexual reproduction). The procedure was used to test the effects of ... naphthalene. Chronic values were determined for vegetative growth and formation of reproductive structures based on significant decreases from control levels. Absence of reproductive structures was also used to determine chronic values. No endpoint was consistently more sensitive than any other, and the ranking of the compounds from most to least toxic was similar regardless of the endpoint used. [Thusby GB et al; Environ Toxicol

Chem 4 (6): 797-805 (1985) [366].

According to AQUIRE Database (ERL-Duluth, U.S. EPA): The PAH "2-Naphthylamine has moderate acute toxicity to aquatic life. Insufficient data are available to evaluate or predict the short or long term effects of 2-Naphthylamine to plants."

Five to fifteen ppm TPH in soil is a realistic background level on a Texas intercostal waterways spoil island. Such levels should not be a problem for most plants (Brian Cain, Fish and Wildlife Service Contaminants Specialist, Houston, personal communication, 1995).

Soil.Invertebrates (Soil Concentrations vs. Invertebrates):

No information found; most TPH methods are not very appropriate for this application.

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

Five to fifteen ppm TPH in soil is a realistic background level on a Texas intercostal waterways spoil island. Such levels should not be a problem for most birds (Brian Cain, Fish and Wildlife Service Contaminants Specialist, Houston, personal communication, 1995).

Soil.Human (Soil Concentrations vs. Human):

Gasoline and crude oil: many states are known to have action levels consisting of a single concentration value which may vary from 10 to 100 ppm TPH [734]. Other states incorporate a range of action levels for addressing site-specific needs; values range from 10 to 1000 ppm TPH for gasoline soils [734].

It is important to stress that existing action levels are based on minimizing potential health risks associated with gasoline constituents such as benzene and the potential for groundwater impacts [734]. The inherent toxicity and environmental mobility of crude oil is vastly different from that of gasoline, and the designation of concentrations which are protective of public health should take these differences into account [734]. As a result, the application of these action levels to sites with crude oil contamination should not be considered appropriate [734].

The California State Leaking Underground Fuel Task Force in 1987 stated that (to protect groundwater) soils having a low leaching potential should be removed if the total petroleum hydrocarbon concentrations exceed 1000 ppm; soils having a medium leaching potential should be removed if the total petroleum hydrocarbon concentrations exceed 100 ppm; and soils having a high leaching potential should be removed if the total petroleum hydrocarbon concentrations exceed 10 ppm [347]. Although most manuals [465] and written guidance documents in California do not specify whether wet or dry weight is to be reported, the State hazardous waste regulations say all lab analysis for hazardous waste identification shall be done on a wet weight basis (Bart Simmons, California Department of Health Services, Hazardous Materials Laboratory, personal communication). This is the exact opposite of most other states, so care should be taken in comparing California values with those generated elsewhere.

The soil TPH limit given by the Utah Department of Health for Hill AFB site near Logan was 38.1 mg/kg (Source: Draft Interagency Guide to Documenting Cost and Performance Information for Site Remediation Projects, EPA Contract 68-W#-0001, prepared by the Federal Remediation Roundtable, October, 1994). State soil cleanup levels tend to change, so the state in question would have to be contacted regarding latest levels. However, because of the many problems with TPH analyses (see discussion above), TPH cannot be used for effects or risk aspects (what does a certain concentration do to living things) of data interpretation. It is primarily a regulatory parameter.

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

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]. TPH and other oversimplified methods which tend to underestimate hazards from PAHs and various alkyl aromatics may have helped to lead to the mistaken notion that if the aliphatics are cleaned up, the petroleum spill is cleaned up: this mistaken impression may be one reason that natural attenuation methods have become popular (Roy Irwin, National Park Service, personal communication, 1996).

In some states there appears to be widespread confusion even in official circles about whether soil and sediment TPH guidelines as well as the TPH levels most often reported by various laboratories, are wet weight or dry weight values. The norm in most states appears to be dry weight (as it is for most reported concentrations of inorganic contaminants in soil), while in other states the norm is clearly wet weight.

With the onset of nationwide underground storage tank removal, one of the most often performed analyses is the EPA 418.1 method for determination of petroleum hydrocarbons in water, modified for soils [464]. While the original water method spells out all extraction and analysis steps, the modified soil method is far less specific, allowing for several extraction techniques; thus with certain types of soils (clay, compacted, and wet) and certain types of hydrocarbons (bunker C, motor oils, and industrial greases) different extraction procedures can yield different results on the same sample.

Presently, two main extraction methods exist for 418.1 method modified for soils: soxhlet (very similar to the Goldfisch extraction method) and sonication; a key problem related to lab and data variability is that the sonication extraction for three minutes is not sufficient to extract thick hydrocarbons from dense soils [464]. Sonication is quicker and cheaper. Sonication tends to get preference due to price and turnaround considerations, yet can yield results 1,000 times too low and is also prone to yielding false negatives [464]. Negative (non-detected values <10 mg/kg) values for TPH done by sonication were found yield values of 595, 342, 132, 211, 81, <10, <10, 84, 837, 42, and 234 mg/kg, when done on the same samples by the Soxhlet method [464].

One sample of heavily compacted soil sent to a lab using soxhlet extraction yielded a TPH value of 10,741 mg/kg; the same sample sent to two labs using sonication extraction resulted in TPH concentrations of 38 and 220 mg/kg [464]. A second sample of heavily compacted soil sent to a lab using soxhlet extraction yielded a TPH value of 3,595.9 mg/kg; the same sample sent to two labs using sonication extraction resulted in TPH concentrations of <10 and 8.8 mg/kg [464]. A third sample of heavily compacted soil sent to a lab using soxhlet extraction yielded a TPH value of <10 mg/kg; the same sample sent to two labs using sonication extraction resulted in TPH concentrations of 13 and <10 mg/kg [464].

In soil modified procedures, wet or moist soils are usually dried by anhydrous sodium sulfate prior to extraction, yet how labs and regulatory guidelines treat reporting results in wet or dry weight is variable.

Due to all of the inherent variability, under the best of circumstances, TPH analyses are subject to numerous pitfalls and the data generated by them has limited environmental meaning. To be able to interpret TPH values at all, one must know which method was used to generate the values, whether wet weight or dry weight was reported, and whether the guidelines the TPH values are being compared to are in wet or dry weight.

Some have apparently interpreted and utilized data as though all TPH methods were the same as the Total Recoverable Petroleum Hydrocarbons (TRPH) methods, which is not true. When comparing data with soil guideline levels, it is necessary to ascertain whether or not the specific, correct laboratory analysis was done to measure compliance with the current specific guideline, whether or not both were expressed the same way (wet weight or dry weight), etc.

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; most TPH methods are not very appropriate for this application.

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

No information found; most TPH methods are not very appropriate for this application.

Tis.Invertebrates:

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

No information found; most TPH methods are not very appropriate for this application.

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

No information found; most TPH methods are not very appropriate for this application.

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

No information found; most TPH methods are not very appropriate for this application.

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; most TPH methods are not very appropriate for this application.

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

No information found; most TPH methods are not very appropriate for this application.

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

No information found; most TPH methods are not very appropriate for this application.

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; most TPH methods are not very appropriate for this application.

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; most TPH methods are not very appropriate for this application.

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; most TPH methods are not very appropriate for this application.

Tis.Human:

A) Typical Concentrations in Human Food Survey Items:

No information found; most TPH methods are not very appropriate for this application.

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; most TPH methods are not very appropriate for this application.

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

No information found; most TPH methods are not very appropriate for this application.

Tis.Misc. (Other Tissue Information):

No information found.

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

No information found; most TPH methods are not very appropriate for this application.

Interactions:

No information found; most TPH methods are not very appropriate for this application.

Uses/Sources:

One of the problems with many TPH methods is lack of specificity. Some of the methods which have been used for TPH pick up some vegetable and animal oils in addition to various fractions of petroleum oils.

Forms/Preparations/Formulations:

No information found.

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

When sampling in the environment, one is never quite sure which chemical mixtures are causing a TPH reading, which is one of the major weaknesses of the method.

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

A field test of bioremediation of soils contaminated with Bunker C at a refinery in Beaumont, Texas, utilized oil and grease data, which (although the data was quite variable) seemed to indicate bioremediation was taking place [728]. A comparison of the oil and grease data at this site with TPH data indicated that TPH was suggesting the same thing, that the data was quite variable but if anything, the oil was being slowly cleaned up by bioremediation (Bruce Herbert, Texas A. and M., Department of Geology, personal communication, 1995). However, a later study of the same site utilizing the expanded scan for PAHs (a modified EPA 8270 including alkyl homologues and lower detection limits), indicated that very little bioremediation of hazardous alkyl PAHs and multi-ring PAHs was actually taking place [727]. Thus, utilizing either oil and grease or TPH analyses would tend to lead one to the faulty conclusion that the harmful compounds were being naturally cleaned up at an acceptable rate. This is partly because the TPH and oil and grease methods tend to favor the lighter and less alkylated PAHs, whereas many of the carcinogenic and longer lasting PAHs are the heavier multi-ringed and alkylated compounds. See also Br.Fate section above.

Laboratory and/or Field Analyses:

It is important to understand that TPH 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 mentioned in the introduction, Total Petroleum Hydrocarbons (TPH) refers to several rough laboratory tests which are relatively inexpensive, relatively quick, sometimes ineffective, and seldom very quantitative. TPH screening measures are done differently in various states, regions, and individual laboratories. What different labs and individuals report as "TPH" is so variable that much caution should be exercised when attempting to compare or interpret TPH data. Thus, the first order of business in analyzing TPH data is to determine exactly which one is being discussed.

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 bioconcentratable 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 or regulatory critera concentrations 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 prone to false negatives (or false positives) is particularly common related to TPH and other general scans related oil products. This is one reason that more rigorous analyses (such as the NOAA expanded scan for PAHs and alkyl PAHs [828] are often recommended as alternatives to TPH analyses.

EPA Method 418.1 for total petroleum hydrocarbons measures the infrared (IR) absorbance (2930 cm-1, CH2 stretch) of Freon-extracted hydrocarbons relative to a mixed calibration standard of chlorobenzene, isooctane, and n-hexadecane (25%, 37.5%, 37.5%, V:V, respectively) [657]. EPA lists the following information for 418.1 [861]:

> EMSLC 418.1 Total Petroleum Hydrocarbons 1 MCAWW
> SPECTR mg/L DL "Petroleum Hydrocarbons, Total Recoverable"
> The sample is acidified to pH <2 and serially extracted with fluorocarbon-113 in a separatory funnel [861]. Interferences are removed with silica gel adsorbant [861]. Infrared analysis of the extract is performed by direct comparison with standards [861].

EPA also mentions the name petroleum hydrocarbons in some oil and grease methods (see oil and grease entry for details) [861].

EPA method 418.1 is often accepted as an accurate analytical measurement without taking into account limitations of the method [657]. One of the pitfalls of this method is the use of freon, which is soon to be banned, in the analysis. Also, soil types with large amounts of organic matter can interfere with IR results.

Although EPA Method 418.1 is one of the most widely used methods for the determination of total petroleum hydrocarbons in soils, it was originally intended solely for use with liquid waste. Studies performed by numerous groups have found the procedure to be prone to positive and negative biases. Natural organic and industrial materials, high inter-laboratory analytical variance, and the results obtained by different extraction processes can lead to possible positive biases. Inherent inaccuracies of the method are a result of the volatilization of low boiling point hydrocarbons, bias due to the soil matrix, and inappropriate standards. Solid bituminous materials such as asphalt and certain types of ash were shown to generate high TPH values with the EPA method 418.1. Naturally occurring soil organic humic compounds were also found to generate false positives [729].

> The following (indented) information on TPH was contributed by Mike Martin, Orion Environmental Labs, Fife, Washington (personal communication to Roy Irwin):
>
> > TPH usually means method 418.1 or something like it. The only remotely acceptable way to do it if you are unsure about the exact fuel in question, is to use a mixture of three compounds (light, intermediate, and heavy fractions) mixed together as a standard. Of course, if you are sure that a leaking tank contained diesel, you can calibrate on a diesel standard. If you are not sure, EPA's recommendation for a mixture of three standards should be used, and one can get relatively reproducible results on a variety of petroleum hydrocarbons, but only if soxhlet rather than the sonication extraction method is used. Attempting to get a dry weight is hard if there are light fractions (volatile) present; it only works well if you know your hydrocarbons are relatively heavy and thus relatively hard to drive off during the drying process.
> >
> > Probably 90 % of the TPH analyses for soils in the U.S. are done by the sonication process, which is only good for volatiles and misses most of the heavy petroleum hydrocarbons.
> >
> > Researchers have also used TPH methods in attempting to measure gross contamination of pesticides and PCB-contaminated transformer oils, but use of TPH for such purposes is generally not advisable, especially if sonication extractions are used. Using 418.1 methods with sonication for this purpose tends to produce a lot of false negatives, leading people to think little contamination is present when the reverse may be true. Utilities using TPH analyses on soils below transformers known to have been leaking have produced false negatives when using sonication-extraction TPH methods as a screening technique.
> >
> > In interpreting TPH data, one also cannot ignore % moisture, since moisture itself blocks the extraction of petroleum hydrocarbons by another hydrocarbon (freon). Sulfur or phthalate compounds also potentially interfere with TPH analyses. This is similar to the problem of strong interferences from phthalate esters or chlorinated solvents when one is using electron capture methods to

> look for chlorinated compounds such as PCBs or pesticides.
>
> State programs on TPH vary tremendously: Washington and Alaska state programs are pretty good. Those who rely too much on BTX or BTEX to measure gasoline or diesel contamination may be unaware that newer gasolines and diesels are better refined and contain fewer BTX compounds. Samples have also been known to be contaminated with newer gasoline or diesel fuels analyzed and coming up negative for the BTX compounds. BTX started as a measure of the more hazardous compounds in gasoline. Modern gas and diesel has a higher percentage of straight chain alkanes, non- volatiles, not as many aromatics, lots of long chain aliphatics, fewer BTX compounds. BTX also is not good for aged gasoline characterized by loss of BTX compounds over time. Thus the problem with many BTX analyses related to petroleum hydrocarbons is the danger on coming up with false negatives (The BTX test may indicate no contamination when significant contamination is present).
>
> Washington State uses the TPHG abbreviation for gasoline contamination, TPHD for diesel. Many older and existing TPH methods are inherently flawed and need to be changed.

The following (indented) information on TPH was contributed by or confirmed by Michael J. Wade, Arthur D. Little, Inc., Cambridge, MA (personal communication):

> Method 418.1 is a chlorinated hydrocarbon (freon) extraction method which extracts only the hydrocarbons picked up by the solvent. It has changed in the past and may change again when freon can no longer be used. Another complication is that some of the higher weight compounds (such as some of the PAH compounds of most concern) can be lost on the filter paper during a filtration step; this may cause a consistent underestimation of the high molecular weight hydrocarbons. Lipids other than petroleum hydrocarbons might contribute to TRPH analyzed as method 418.1. Method 418.1 was originally intended for wastewater effluent, and like oil and grease, picked up more than just petroleum hydrocarbons. Some of the better (but not all) labs have now added a modified silica gel step for separation of polar and non-polar material. This newer way to perform method 418.1 works better than the old in separating out petroleum hydrocarbons, but not all labs do it.
>
> TRPH, Like TPH, is methodologically defined and concentrations given as "TPH" or "TRPH" alone doesn't tell you much. To be able to understand the significance of the concentration, one needs to know exactly which

> method was used: Was it done by EPA TPH method 8015 for gasoline, EPA TPH method 8016 for Diesel, EPA method 418.1 for total recoverable petroleum hydrocarbons (TRPH), an ASTM method, an old method no longer used, a published EPA method with an added silica gel step (as many but not all labs now do), or some other method? Some have seemed to interpret and utilize data as though various TPH methods were the same as various TRPH methods, which is not true. When comparing data with soil guideline levels, it is necessary to ascertain which laboratory analysis was done to measure compliance with the current specific guideline.
>
> Many engineering and consulting companies use various TPH methods to try to find the hot spots or define the area of exposure because it is inexpensive, (about $50 a sample), but often a priority pollutant scan (about $200 a sample) or an expanded PAH scan (about $250 to $350 per sample) is preferable. Aliphatic and alkyl homologue scans are often also helpful to help "fingerprint" source and environmental petroleum hydrocarbons to determine the source.

The following information on TPH analyses was provided by Peter Wong, California Health Services Lab Certification Program (personal communication to Roy Irwin):

> Many TPH analyses are relatively new, some labs have relatively little experience with them; as a result there are many misidentifications. The analyst will assume most samples contain either diesel or gasoline but may misidentify samples that contain jet fuel, kerosene, or standard solvents. Labs should compare chromatograms to all possible hydrocarbon products.
>
> In California TPH now often refers to California's "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]. 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.
>
> Variability is introduced because a lot procedures are recommended but not required by the "standard methods," so different labs get creative in different ways. TPH

> and TRPH are thus relatively variable methods and should probably be considered to be qualitative or semi-quantitative. The solvents and filter papers used mean that some of the important petroleum hydrocarbon compounds are missed. It probably should be reported by labs as dry weight for comparison other values, but most labs report it as wet weight unless asked to do otherwise.

Additional problems with TPH methods (including method 418.1) include the following (Dr. Fred Kawahara, Research Scientist, EPA Environmental Monitoring and Support Laboratory, Cincinnati (personal communication to Roy Irwin):

> Most TPH measures are not good for looking for unknowns because the methods are only as good as the calibration standards and if you don't know what you are looking for you don't know which calibration standard to use. Using the wrong calibration standard can throw the answer off appreciably. The calibration issues include which working standards to use and which cell path length (method 318.1 forces you to chose a pathlength of 10 mm, 50 mm, or 100 mm).
>
> Some of the methods which have been used for TPH pick up some vegetable and animal oils. There can be a lot of laboratory and methodology variability related to volatility (light oils more susceptible, how long the oils are allowed to evaporate is a variable, how heat is used to calculate dry weight is a variable) issues. It is preferable to calculate wet weight TPH values first and then very carefully measure percentage moisture in a way which minimizes petroleum hydrocarbon losses.

Information on TPH analyses provided by Mark Ort, National Fisheries Contaminant Research Center, Fish and Wildlife Service (personal communication):

> The ASTM method for TPH (1990 ASTM book) is similar to EPA method 418.1 and calls for freon extraction. ASTM estimated the variability of the test (similar to round robin test of various labs). It appears from the ASTM equation that the method cannot reliably distinguish between 400 ppm and 0 ppm TPH. A regression plotted from Mark's work appeared to suggest even more variability as they could not reliably distinguish 800 ppm and a blank sample. The results are detailed in Mark Ort's 1992 M.S. thesis on file at Univ. of Missouri: The Effects of Crude Oil on the Mayfly: Hexagenia bilineata. 1992
>
> Mark's work with mayflies suggested mortality at 100 to 1400 ppm TPH (source: light American Amoco crude from Patoka Terminal, mixed with sediment). Mark has concluded that biota are probably sensitive above 800 to

> 1000 ppm TPH and that one method for TPH should be standardized nationally. Method 418.1 (similar to other ASTM methods) calls for use of freon 113, which only extracts certain petroleum hydrocarbons and leaves some others behind (to get them all multiple solvents and high lab costs would be necessary). In certain settings, 100 ppm TRPH is not real high compared to 30-40 ppm background levels. Mark used neither soxhlet nor sonication extraction.

Most TPH methods use inadequate detection limits [657]. Based on biological concerns, recommended water sample detection limits are 50 ug/L for total hydrocarbons [468]. Recommended tissue and sediment sample detection limits are 0.1 ug/g for total hydrocarbons [468].

A better (than EPA method 418.1) "total hydrocarbons" measure would include the sum of resolved and unresolved complex mixture of the chromatographic trace, extracted with methylene chloride, and using cleanup and instrumental analysis similar to methods used for rigorous PAH analyses [468].

Since TPH methods have so many problems, what are recommended alternatives? Currently recommended analyses include both a rigorous and expensive gas chromatography-mass spectrometry (GC-MS) "expanded" PAH scan [468,679,828], as well as a less expensive and more rapid modified GC/FID or a High-Performance Liquid Chromatographic/Fluorescence screening method [521,522,657]. Expanded PAH scans [including homologous series (alkylated) PAHs], aliphatic scans, and other analyses providing low detection limit (1 ppb dry weight for PAHs in soils, tissues and sediments) concentrations of the individual hydrocarbons of most concern are preferable for contaminated areas where one is not sure of the mix of petroleum hydrocarbons present [679,828].

Analytical expedience and costs are one reason why total petroleum hydrocarbons and other deficient gross screening methods have been used in the past. However, the choice of specific laboratory methods and the detection limit objectives should be derived from study objectives, not from analytical expedience [468].

A technical summary of associated analytical bias associated with EPA 418.1 is provided below [657]:

> "Briefly, negative method bias may result when samples are analyzed by this method because of (a) poor extraction efficiency of Freon for high molecular weight hydrocarbons, (b) loss of volatile hydrocarbons during extract concentration, (c) differences in molar absorptivity between the calibration standard and product type (Figure 1.2), (d) fractionation of soluble low IR absorbing aromatic hydrocarbons in groundwater during

> water washout, (e) removal of 5-to 6-ring alkylated aromatics during the silica cleanup procedure, and (f) preferential biodegradation of n-alkanes."
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> "Positive method bias may be introduced as a result of (a) product differences in molar absorptivity, (b) partitioning of soluble aromatics from the bulk product because of oil washout, (c) measurement of naturally occurring saturated hydrocarbons that exhibit a high molar absorptivity (e.g., plant waxes, n-C25, n-C27, n-C29, and n-C31 alkanes), and (d) IR dispersion of clay particles."

The following statement appears in the definition section of Method 418.1 [729]:

> "As in the case of Oil and Grease, the parameter of Petroleum Hydrocarbons is defined by the method. The measurement may be subject to interferences and the results should be evaluated accordingly."
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> > NOTE: The above statement appears to have been lost on some parts of the regulatory and industrial communities. The information gathered on Method 418.1 clearly demonstrates the procedure should not be used for the measurement of TPH in soils [729].

The use of two different oil analysis methods the same contaminated sample can result in two different conclusions. Listed below are two case studies demonstrating how different procedures can yield different results:

1) EPA Method 418.1 vs. GC/FID:

   CASE STUDY 1: Thomey and Bratberg (1989) conducted a comparison of TPH in soil by EPA 418.1 and GC/FID methods. They found fair agreement in sandy soils, but poor correlation with silt and clay soils. These researchers also theorized that colloidal and clay-sized particles could remain in suspension in the Freon extract, absorb infrared light, and cause a positive reading in the absence of petroleum hydrocarbons. They concluded that "EPA Method 418.1 is not an appropriate technique for measuring TPH concentrations in certain types of soils. These types of soil can be categorized as weathered limestone, clays, and silts" [729].

   CASE STUDY 2: GC/FID is often much better that the IR method (418.1). In one study where the 418.1 method was used at several different labs, they got results that were orders of magnitude different. The EPA method 418.1 controversy is not new, and most people in analytical chemistry business

> acknowledge all its faults. GC/FID includes an extraction technique that can reduce some of the noise of IR analysis. For example, in some spills, they add compost (hay and cow manure) to the soils (presumably to speed biodegradation?). EPA 418.1 analysis will pick up on these organics because it doesn't separate them from the oil. (Tom McDonald Texas A&M, personal communication, 1994).

Method 418.1 is applicable for the analysis of some semivolatile and nonvolatile petroleum hydrocarbons. This method readily detects the heavy petroleum products such as motor oil, tar, and asphalt. Occasionally, particulate materials present in the sample extract will scatter the infrared beam used in the quantitation step of this analysis. This results in instrument readings which may be incorrectly attributed to petroleum hydrocarbons. Quality assurance procedures can be implemented which would correct for this problem; however, the method does not require them, and so they are often not run by some laboratories. Subsequently, erroneous results are occasionally reported. A further limitation of this method is the general inability of the operators to differentiate between various petroleum products such as motor oil and asphalt. Nor can this analysis distinguish between hydrocarbons from biological processes and those contributed by anthropogenic or petrogenic sources. These distinctions can often be of importance to environmental projects [497].

DRO and GRO methods: See Diesel General and Gasoline entries.

Abstracts on Better (than TPH) methods for 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).