ENVIRONMENTAL CONTAMINANTS ENCYCLOPEDIA

GASOLINE, LEADED ENTRY

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

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

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

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

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

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

For some categories, the editors found no information and inserted the phrase "no information found." This does not necessarily mean that no information exists; it

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

Although the editors of this document have done their best in the limited time available to insure accuracy of quotes or summaries as being "what the original author said," the proposed interagency funding of a bigger project with more elaborate peer review and quality control steps never materialized.

> The bottom line: The editors hope users find this document useful, but don't expect or depend on perfection herein. Neither the U.S. Government nor the National Park Service make any claims that this document is free of mistakes.

The following is one chemical topic entry (one file among 118). Before utilizing this entry, the reader is strongly encouraged to read the README file (in this subdirectory) for an introduction, an explanation of how to use this document in general, an explanation of how to search for power key section headings, an explanation of the organization of each entry, an information quality discussion, a discussion of copyright issues, and a listing of other entries (other topics) covered.

See the separate file entitled REFERENC for the identity of numbered references in brackets.

HOW TO CITE THIS DOCUMENT: As mentioned above, for critical applications it is better to obtain and cite the original publication after first verifying various data quality assurance concerns. For more routine applications, this document may be cited as:

> **Irwin, R.J., M. VanMouwerik, L. Stevens, M.D. Seese**, and **W. Basham.** 1997. Environmental Contaminants Encyclopedia. National Park Service, Water Resources Division, Fort Collins, Colorado. Distributed within the Federal Government as an Electronic Document (Projected public availability on the internet or NTIS: 1998).

Gasoline, Leaded (CAS number 86290-81-5)

Brief Introduction:

Br.Class: General Introduction and Classification Information:

This entry contains information on leaded gasoline as well as some general information on gasoline in general The reader is encouraged to read the Gasoline, General entry as well.

Gasoline is a mixture of volatile hydrocarbons suitable for use in a spark-ignited internal combustion engine and having an octane number of at least 60 [498]. Octane number is a measure of burn rate, not power as is commonly assumed. Maximum power output is achieved by optimizing the rate at which a fuel burns inside the cylinders of an engine. The octane scale is defined such that pure n-heptane has an octane number of zero and iso-octane has an octane number of 100 [661].

Gasoline is a highly volatile petroleum product comprised primarily of light hydrocarbons, alkenes, benzene and alkyl substituted benzenes (toluene, xylenes, ethylbenzene) [497]. Benzene, toluene, ethylbenzene, and xylene are commonly referred to as BTEX.

There are two primary forms of gasoline: regular (leaded gasoline) and unleaded gasoline. The change from regular gasoline to unleaded gasoline was due to lead accumulation in the environment. By 1960, an estimated 200 million tons of lead went into gasoline annually and much of it escaped from tail pipes into the environment [818]. Lead has been proven to be extremely toxic to the ecosystem and humans (see the Lead entry for details).

All cars made after 1975 were equipped with catalytic convertors which run on unleaded gas. Unleaded gasoline may contain up to 0.013 g/L lead in the U.S. [818]. Since 1986, leaded gasoline cannot contain more than 0.025 g/L lead in the U.S. [820]. These lead phasedown regulations require a shift to increased gasoline processing , such as alkylation, isomerization, and catalytic reforming, to achieve the necessary octane levels [820].

In regular gasoline blends, lead compounds, such as tetramethyllead and tetraethyllead, are used to increase the octane number and to suppress pre-ignition [661,747]. Other hazardous compounds including ethylene dichloride, EDC, and ethylene dibromide, EDB, are added as lead

scavengers to prevent buildup of lead oxide deposits. In the combustion chamber, EDC combines with lead to produce lead chloride a volatile compound that is carried from the engine with the flow of exhaust gases [661]. See the Gasoline Additives entry for details.

Br.Haz: General Hazard/Toxicity Summary:

Gasoline is a mixture of approximately 280 different hydrocarbons in the range of C4 to C12; assessing the ecotoxicology of gasoline is tantamount to measuring the toxicity of the water soluble mono-aromatic components, particularly benzene, toluene, ethyl benzene, and xylenes (BTEX) [624]. Gasoline and its BTEX components clearly exhibit short-term toxicity effects to a variety of aquatic organisms, especially in closed or flow through systems [624].

From a toxicity profile standpoint, an important thing to realize about gasoline is that there are many different types: leaded, unleaded, aviation gasolines (avgas), various grades and octane ratings, and various additive contents. As a result, some gasolines have more content of the hazardous BTEX, naphthalene, metals, solvent additives, polyaromatic hydrocarbon (PAH), and alkyl PAH compounds than others. For example, super unleaded has higher concentrations of BTEX compounds than regular unleaded [560].

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

The toxicity profile of a particular gasoline varies tremendously with the exact gasoline in question. The most important hazardous components of most leaded gasolines are PAHs, alkyl PAHs, and the BTEX compounds (benzene and alkyl substituted benzenes such as toluene, xylenes, ethylbenzene); and metallic leaded gasoline additives such as Tetramethyllead (TML), Tetraethyllead (TEL), Ethylene dichloride (EDC), and Ethylene dibromide

(EDB). With lead additives, the acute toxicity of gasoline increases. Lead in large doses can damage the liver and kidneys. Lead is a heavy metal which is very toxic to aquatic organisms, especially fish [57]. Lead issues related to fish were summarized by Sorensen in 1991 [488]. Pain provided a 1995 summary of biological effects of lead [837] (the highlights have not yet been summarized herein). See the Gasoline Additives and Lead entries for details.

The effects of acute and chronic exposure to leaded regular gasoline are similar to those of gasoline in general, except that the hazard of effects on the central nervous system are even greater than for unleaded gasoline because of the presence of the alkyl lead compounds [606].

Mild exposure to tetraethyllead (TEL) leads to weakness, fatigue, headache, nausea, vomiting, and diarrhea. Prolonged exposure leads to confusion, delirium, manic excitement, and catatonia. Loss of consciousness and death follow [661].

Because of its effects on the nervous system, leaded regular gasoline is in Class 3 (may cause irreversible effects which can be life-threatening) for general toxicity [606].

The list of alkyl benzenes in gasoline is long, comprising many more compounds than just the better known BTEX alkyl benzenes (toluene, xylenes, and ethyl benzene) [796,797]. This is important because alkyl benzenes tend to be slow acting but potent carcinogens which may take years to induce cancer [797].

Gasolines also contain a small but significant amount of PAHs including naphthalene and alkyl naphthalenes [797]. Naphthalenes are particularly hazardous PAHs due to their particular combination of mobility, toxicity, and general environmental hazard [771]. Alkyl naphthalenes pose similar hazards and are usually found in the same petroleum products as naphthalenes, often in higher concentration than the parent compound (naphthalene). The parent compound naphthalene is the first to degrade, so as petroleum products age, the percentage of alkyl naphthalenes vs. naphthalene increases.

Heavier and more persistent PAHs are also found in gasolines [796]. Although they make up small percentages of gasolines, they are more persistent than most other constituents of gasoline and tend to have greater carcinogenic and other chronic impact potential.

Due to a high percentage of aromatics (generally from 25

to 50% [624,773,818,898]), gasoline is associated with many potential environmental hazards, both short- and long-term [747]:

> Short-term (acute) hazards of the some of the lighter, more volatile and water soluble aromatic compounds (such as benzenes, toluene, and xylenes) in gasoline include potential acute toxicity to aquatic life in the water column (especially in relatively confined areas) as well as potential inhalation hazards. Gasoline is highly volatile and soluble, and evaporates quickly [777]. Gasolines possess high acute toxicity to biota [777]. In the short term, spilled oil will tend to float on the surface; water uses threatened by spills include: recreation; fisheries; industrial; and irrigation [608].
>
> Long-term (chronic) potential hazards of the some of the lighter, more volatile and water soluble aromatic compounds in gasoline include contamination of groundwater. Chronic effects associated with gasoline are mainly due to exposure to aromatic compounds [661]. Chronic effects of some of the constituents in gasoline (benzene, toluene, xylene, naphthalenes, alkyl benzenes, and various alkyl PAHs) include changes in the liver and harmful effects on the kidneys, heart, lungs, and nervous system [609,764,765,766,767]. Although PAHs, particularly heavy PAHs, do not make up a large percentage of gasoline, there are some PAHs in gasoline. Due to their relative persistence and potential for various chronic effects (like carcinogenicity), PAHs (and particularly the alkyl PAHs) as well as alkyl benzenes such as xylenes, can contribute to long-term (chronic) hazards of gasolines in contaminated soils, sediments, and groundwaters (see "PAHs as a group" entry).

At high concentrations of gasoline, effects other than cancer can occur, even if exposure duration is short. These noncancer effects include headache; nausea; drowsiness; skin, eye, and throat irritation; loss of reflexes; and liver and kidney damage [898]. Inhalation of extremely high concentrations of gasoline can cause loss of consciousness, coma, and even sudden death. Over a number of years, inhalation of vapors can lead to severe blood damage (hemorrhaging and low blood cell levels), chromosomal alterations, or cerebral abnormalities [898].

Lead encephalopathy (acute lead poisoning) can occur from chronic high exposures to leaded gasoline such as those seen in abuse [606].

Because of its effects on the nervous system, leaded regular gasoline is in Class 3 (may cause irreversible effects which can be life-threatening) for general toxicity [606].

Some of the PAHs in this product can move into plants and some have either harmful or positive effects on plants (see PAHs as a group entry).

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

In humans, acute exposure to gasoline can produce skin, eye, and respiratory irritation, pulmonary edema, chemical pneumonitis from aspiration, CNS symptoms of nausea, headache, weakness, dizziness, giddiness or euphoria, loss of coordination or judgement, coma and death [606].

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].

Additional human health issues related to gasoline have been summarized by ATSDR [892]. Due to lack of time, important highlights from the ATSDR document have not yet been completely incorporated into this entry.

Biological effects of petroleum hydrocarbons on marine organisms and ecosystems are dependent on the persistence and bioavailability of specific hydrocarbons, the ability of organisms to accumulate and metabolize various hydrocarbons, the fate of the metabolized products, and the interference of specific hydrocarbons with normal metabolic processes that may alter an organism's chances for survival and reproduction in the environment. The responses of organisms to petroleum hydrocarbons can be manifested at four levels of biological organization: biochemical and cellular, organismal (including the integration of physiological, biochemical, and cellular), biochemical, and behavioral responses, population, and community [687].

Sublethal effects of petroleum hydrocarbons at the organismal and population levels include impairment of feeding, growth, development, energetics, and recruitment, alteration in reproductive and developmental potential of populations, and possible changes in population structure and dynamics [687].

In a study in Massachusetts there was a close correlation between the use of leaded gasoline and umbilical cord blood lead levels [897].

Several studies assessing the influence of lead on susceptibility to infectious agents have consistently shown that lead impairs both CMI and antibody-mediated host resistance (both animals and humans). Lead exposure also increased host susceptibility to viral infections [494].

Little toxicological data are available on leaded regular gasoline distinct from gasoline itself [606]. See also: Gasoline, General entry.

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

There is limited evidence for the carcinogenicity in experimental animals of unleaded automotive gasoline [747].

Gasoline is possibly carcinogenic to humans [747]. Gasoline is a suspected human carcinogen because it contains benzene, a known carcinogen [898]. Benzene is carcinogenic to humans [747]. Exposure, even at low levels, may result in the development of cancer [898].

Alkyl benzenes (a component of gasoline) tend to be slow acting but potent carcinogens which may take years to induce cancer [797].

Another component of gasoline [747,898], and one that reaches ground water [898], is 1,3-butadiene, a compound for which there is sufficient evidence of carcinogenicity for experimental animals but insufficient evidence for humans [747].

Gasoline exposure has been associated with kidney tumors in male rats, but not in female rats, mice, or humans [747,892]. Often mechanisms of action for such differences are not well understood, but in this case $10 million dollars worth of research has produced a somewhat better understanding of possible mechanisms of action (Hanspeter Witschi, University of California, Davis, personal communication, 1995). Gasoline, along with a diverse group of hydrocarbons, has been shown to induce alpha-2u globulin-mediated nephropathy and renal tumors in male rats [892]. The mechanism for kidney tumors is unique in male rats, involving binding of 2,4,4-trimethyl-2-pentanol (TMPOH), a metabolite of 2,2,4-trimethyl pentane (TMP), to alpha-2u globulin, a substance found only in male rats [892]. See WHO and ATSDR summaries [747,892] for details.

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

Some of the information on automotive gasoline versus cancer seems somewhat incriminating, but the information is too mixed and prone to potentially confounding co-factors to be totally conclusive [892].

Additional human health issues related to carcinogenicity of gasoline have been summarized by ATSDR [892].

See Chem.Detail section for compounds in this product, then see individual compound entries for summaries of information on individual components of this mixture. See also: PAHs as a group entry.

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

The results are mixed, but some immunological, reproductive, fetotoxic, and genotoxic effects have been associated with a few of the compounds found in gasoline [609,764,765,766,767] (see Chem.Detail section for compounds in this product, then see individual compound entries for summaries of information on individual components of this mixture).

Chronic exposure of men to leaded gasoline resulted in impotence, reduced number of sperm, and altered sperm shape, suggestive of effects seen in lead poisoning [606]. No other studies were found specifically for leaded regular gasoline [606].

Both gasoline and tetraethyl lead are Class A- (unconfirmed human reproductive hazards) [606]. Chronic

exposure of men to leaded gasoline resulted in impotence, reduced number of sperm, and altered sperm shape, suggestive of effects seen in lead poisoning [606].

All measured effects of lead on living organisms are adverse, including those negatively affecting survival, growth, learning, reproduction, development, behavior, and metabolism [66]. Effects of sublethal concentrations of lead in fish include increased mucous formation, delayed embryonic development, suppressed reproduction, inhibition of growth, and fin erosion [57].

One study noted a decrease in the weight of male rat pups subsequent to gasoline exposure by inhalation [688].

Information available is too incomplete to conclude that automobile gasoline causes birth defects or other reproductive problems in humans [892]. Additional human health issues related to this topic have been summarized by ATSDR [892].

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

There is no potential for concentration or accumulation in the food chain unless lead is present [499].

Combustion of gasoline additives is the major source of environmental pollution by lead. Thus lead is primarily an atmospheric pollutant that enters soil and water as fallout, a process determined by physical form and particle size. The net result is a buildup of lead near heavily traveled roads. This suggests that further reductions in leaded gasoline usage would result in lower human exposure. Lead enters aquatic systems from runoff or as fallout of insoluble (sic, actually relatively insoluble) precipitate and is found in sediment [897].

In aqueous solutions, tetraethyllead (TEL) and Tetramethyllead (TML) are first degraded to their respective ionic trialkyl lead species (TREL and TRML respectively), which are then degraded to ionic dialkyl lead species (DEL and DML respectively), and eventually to inorganic lead (Pb2+) [817, Reprinted with permission from Environmental Toxicology and Chemistry, Volume 14(4), L.-T. Ou, W. Jing and J.E. Thomas, "Biological and chemical degradation of ionic ethyllead compounds in soil." Copyright 1995 SETAC].

Gasoline contains primarily lighter, less persistent and more mobile compounds than other petroleum products. As such, gasoline is highly volatile and soluble [777]. The

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

After a release, gasoline tends to flow downward through the soil toward the groundwater table [898]. Soil characteristics and the depth to groundwater determine how quickly a gasoline and its constituents reach groundwater. Porous soil allows the gasoline to be transported quickly; dense soil slows the transport. Once the gasoline reaches the water table, it tends to accumulate on top of it, because it is less dense than water and is virtually insoluble in it. If the soil has a high resistance to lateral flow, accumulations of free product several feet deep can occur [898]. The aromatic compounds are the most water soluble constituents of gasoline. As a result, the composition of the dissolved groundwater contaminants is heavily dominated by aromatics, such as BTEX compounds [898]. See the Fate.Detail section of the Gasoline, General entry for more information. See also: BTEX entry.

Although heavy PAHs typically represent a small percentage of the total mass of volume of gasoline spilled, a few months later the PAHs represent a relatively large proportion of the hazardous components which still remain in contaminated soils or sediments. Through the weathering process, the hazardous but more mobile and volatile BTEX compounds have often migrated into the air or groundwater.

Additional issues related to this topic have been summarized by ATSDR [892]. See also: Oil Spills and Petroleum General entries, Benzene, BTEX, PAHs as a group, and other component entries.

Synonyms/Substance Identification:

Motor spirit [560]
Petrol [560]
Straight run [560]
Gas, leaded regular [606]
Gasoline, leaded regular [606]

Gasoline, regular [606]
Leaded petrol [606]
Leaded regular gasoline [606]
Petrol, leaded [606]
Regular gasoline [606]
Regular leaded gasoline [606]

Associated Chemicals or Topics (Includes Transformation Products):

See also individual entries:

Gasoline, General
Gasoline, Unleaded
Gas Additives
Oil Spills
Petroleum, General

See also individual entries on BTEX compounds:

BTEX
Benzene
Toluene
Ethylbenzene
Xylenes, Total

See also: PAHs, general and various PAH and alkyl PAH entries.

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

W.Low (Water Concentrations Considered Low):

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

W.High (Water Concentrations Considered High):

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

W.Typical (Water Concentrations Considered Typical):

Assuming a pre-1989 particle settling rate of 1 cm per second, a deposition of 0.3 gram per meter squared near the East Broadway Highway in Bermuda is responsible for the 1.2 ug/L and 110 ug/g of lead in Hamilton Harbor waters and sediments. If all transport and dilution processes that attenuate environmental lead concentration

remain equal (refers to the change in 1989 from unleaded gasoline to unleaded gasoline for automobiles), then airborne lead might now account for approximately 0.05 ug/L of lead in the harbor waters and approximately 4 ug/g of lead in harbor sediments [Simmons, J.A.K. and A.H. Knap. 1993. The impact of leaded to unleaded gasoline conversion on the oceanic island of Bermuda. Atmospheric Environment. 27A:1729-1733].

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

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

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

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

W.Plants (Water Concentrations vs. Plants):

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

W.Invertebrates (Water Concentrations vs. Invertebrates):

For a comparison of the acute toxicity of leaded and unleaded gasoline to Artemia and Daphnia magna, see the Gasoline, General entry.

Toxicity values from Environment Canada [560]:

NOTE: In this section, for properties with more than one value, each value came from its own source; in other words, if the 48h-EC50 for D. magna was measured several times and several different answers were obtained, all of the answers are provided [560]:

Acute Toxicity of Water Soluble Fraction (mg/L):

Genus/Species	48h-EC50	48h-LC50

Daphnia Magna	6.25	13.5
	8.88	19.2
Artemia spp.	19.2	21.3
	27.8	30.9

W.Fish (Water Concentrations vs. Fish):

Toxicity values from Environment Canada [560]:

NOTE: In this section, for properties with more than one value, each value came from its own source; in other words, if the 48h-EC50 for Juvenile Shad was measured several times and several different answers were obtained, all of the answers are provided [560]:

Acute Toxicity of Water Soluble Fraction (mg/L):

Genus/Species	48h-LC50	24h-TLm
Juvenile Shad	91	90 (freshwater) 91 (saltwater)

Freshwater Toxicity [498,499]:

Bluegill: LC50 8 ppm/96h, leaded and unleaded.

Saltwater Toxicity [498,499]:

Grass Shrimp: LC50 1.5 ppm/96h, leaded and unleaded

Mullet: LC50 4 ppm/96h, leaded

Menhaden: LC50, 2 ppm/96h, leaded

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

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

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

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

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

No information found; see Chem.Detail section for

compounds in this product, then see individual compound entries for summaries of information on individual components of this mixture.

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

Sed.Low (Sediment Concentrations Considered Low):

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

Sed.High (Sediment Concentrations Considered High):

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

Sed.Typical (Sediment Concentrations Considered Typical):

Assuming a pre-1989 particle settling rate of 1 cm per second, a deposition of 0.3 gram per meter squared near the East Broadway Highway in Bermuda is responsible for the 1.2 ug/L and 110 ug/g of lead in Hamilton Harbor waters and sediments. If all transport and dilution processes that attenuate environmental lead concentration remain equal (refers to the change in 1989 from unleaded gasoline to unleaded gasoline for automobiles), then airborne lead might now account for approximately 0.05 ug/L of lead in the harbor waters and approximately 4 ug/g of lead in harbor sediments [Simmons, J.A.K. and A.H. Knap. 1993. The impact of leaded to unleaded gasoline conversion on the oceanic island of Bermuda. Atmospheric Environment. 27A:1729-1733].

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

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

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

No information found; see Chem.Detail section for

compounds in this product, then see individual compound entries for summaries of information on individual components of this mixture.

Sed.Plants (Sediment Concentrations vs. Plants):

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

Sed.Invertebrates (Sediment Concentrations vs. Invertebrates):

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

Sed.Fish (Sediment Concentrations vs. Fish):

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

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

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

Sed.Human (Sediment Concentrations vs. Human):

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

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

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

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

Soil.Low (Soil Concentrations Considered Low):

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

Soil.High (Soil Concentrations Considered High):

No information found; see Chem.Detail section for compounds in this product, then see individual compound entries for summaries of information on individual components of this mixture. Lead may be a concern in soil, and does not bioremediate.

Soil.Typical (Soil Concentrations Considered Typical):

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

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

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

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 toluene, ethyl benzene, or xylene concentration exceeds 50 ppm; soils having a medium leaching potential should be removed if the concentration exceeds 0.3 ppm benzene, 0.3 ppm toluene, 1 ppm ethyl benzene, or 1 ppm xylene [347].

State TPH Gasoline cleanup guidance levels range from 10 to 1000 ppm [806].

Soil.Plants (Soil Concentrations vs. Plants):

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

Soil.Invertebrates (Soil Concentrations vs. Invertebrates):

No information found; see Chem.Detail section for compounds in this product, then see individual

compound entries for summaries of information on individual components of this mixture.

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

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

Soil.Human (Soil Concentrations vs. Human):

No information found on this complex and variable mixture. See Chem.Detail section for chemicals found in this product, then look up information on each hazardous compound. Some individual compounds found in petroleum products have low-concentration human health benchmarks for soil (see individual entries).

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

As of 1996, several States were considering allowing natural attenuation (the "do nothing and let nature clean up the mess through bioremediation" option) to proceed near leaking storage tanks in situations where drinking water was not being impacted and where human rather than environmental resources were the main resources in the immediate area (Roy Irwin, National Park Service, personal communication, 1996).

The trend of thinking towards natural attenuation was given a boost by a Lawrence Livermore National Laboratory (LLNL) report entitled "Recommendations to Improve the Cleanup Process for California's Leaking Underground Fuel Tanks;" which stressed the use of passive bioremediation for petroleum product contaminated soils, whenever possible, based on the relatively low number of cases where drinking water was impacted [969]. EPA has pointed out some limitations of the LLNL report, including the lack of adequate consideration of PAHs and additives such as MTBE, as well limited consideration of (non-human) exposure pathways and various geologic conditions [969].

Others would point out that petroleum product spills into soils are not necessarily a trivial environmental threat related to ecotoxicology (emphasis on living things other than humans), due to the many hazardous compounds in the product (see Chem.Detail section below).

Exposure to petroleum-source contamination in soils is predominantly of concern through a number of possible exposure pathways, including dermal contact with soil,

ingestion of soil, inhalation of soil particulates, and ingestion of contaminated groundwater [824].

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

Tissue and Food Concentrations (All Tissue Data Interpretation Subsections Start with "Tis."):

Tis.Plants:

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

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

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

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

Tis.Invertebrates:

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

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

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

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

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

No information found; see Chem.Detail section for

compounds in this product, then see individual compound entries for summaries of information on individual components of this mixture.

Tis.Fish:

A) As Food: Concentrations or Doses of Concern to Living Things Which Eat Fish (Includes FDA Action Levels for Fish and Similar Benchmark Levels From Other Countries):

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

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

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

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

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

Tis.Wildlife: Terrestrial and Aquatic Wildlife, Domestic Animals and all Birds Whether Aquatic or not:

A) As Food: Concentrations or Doses of Concern to Living Things Which Eat Wildlife, Domestic Animals, or Birds:

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

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

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

C) Body Burden Residues in Wildlife, Birds, or Domestic

Animals: Typical, Elevated, or of Concern Related to the Well-being of the Organism Itself:

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

Tis.Human:

A) Typical Concentrations in Human Food Survey Items:

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

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

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

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

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

Tis.Misc. (Other Tissue Information):

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

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

Certain of the organic compounds have some moderate bioaccumulation potential in certain kinds of organisms (see PAHs as a group and Alkane entries).

Lead tends to bioaccumulate in mussels and clams [90,95]. Benthic fish may accumulate lead directly from the sediments [95].

Food chain [499]:

Potential for accumulation: None (sic) noted unless lead

is present.

Potential Food chain concentration:
None (sic) noted unless lead is present.

Interactions:

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

Uses/Sources:

By a wide margin, most of the products derived from petroleum find use as fossil fuels to run vehicles, produce electricity, and to heat homes and businesses. About 65% of the petroleum used as fuel is consumed as gasoline in automobiles [661].

Forms/Preparations/Formulations:

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

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

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

Since PAHs are important hazardous components of this product, risk assessments should include analyses of PAHs and alkyl PAHs utilizing the NOAA protocol expanded scan [828] or other rigorous GC/MS/SIM methods.

Lead and other additives are important components of this product (see Br.Class and Br.Hazard sections above and Gasoline Additives entry for details).

Generally, the constituents of gasoline can be divided into three categories: paraffins, aromatics, and olefins. Paraffins, which are the largest class of compounds and often comprise about

66 percent of the gasoline, are composed of chains of carbons that are singly-bonded to atoms of hydrogen (that is, saturated hydrocarbons). Aromatics are those compounds whose structure includes a benzene ring. Aromatics often comprise approximately 25 percent of gasoline and are believed to be among its most toxic constituents (namely BTEX). Olefins are usually the smallest group of constituents, consisting of hydrocarbon chains that contain double or triple bonds (that is, unsaturated hydrocarbons) [898].

Other sources list very different proportions of constituents in gasoline [773]:

CHEMICAL COMPONENT (wt %)	REFINED OIL Gasoline
Saturates*	39.6
Aromatics	46.2
Polars	--
Asphaltenes	N/A
Sulfur (%)	0.07

NOTE: * = same as paraffins

Aromatics hydrocarbons account for between 87 to 95% of the water soluble fraction (WSF) derived from gasoline. However, these represent <50% of the volume of the parent gasoline. (Normal composition is approximately 50% aliphatic compounds + 50% aromatic + naphthenic ring compounds) [624].

Each commercial gasoline mixture has a different composition. The composition may vary in percent paraffins, naphthene, aromatics, olefins, and different additives. One gasoline sample, PS-6 gasoline, contained about 53% paraffins, 5% naphthenes, 36% aromatics, 6% olefins, and less than 1% unknowns by percent weight [818].

Vapor and liquid compositions of gasoline vary. Gasoline vapor is comprised mainly of short-chained, low molecular weight, and more volatile components such as the four and five carbon chain of light paraffins. Aromatic molecules are usually reduced to 2% since they are larger and heavier molecules [818]. See also the Fate.Detail section below.

Automotive gasoline may contain 0-7%, and typically 2-3%, benzene [747].

Naphthalenes make up from 0.09 to 0.49 weight percent of gasoline and from 0.08 to 0.5 volume percent of various gasolines [796].

The following PAHs are found in unleaded, premium unleaded, and leaded gasolines (ranges in %volume of gasoline given in parentheses) [796]:

Anthracene (1.55 to 1.84 % volume of gasoline)
Benzo(b)fluoranthene (3.9 % volume of gasoline)
Fluoranthene (1.84 % volume of gasoline)

Benzo(a)pyrene, a particularly carcinogenic and persistent heavy PAH, is found in gasoline in concentrations of 0.19 to 2.8

mg/kg (ppm), while benzo(e)pyrene, another heavy and persistent PAH is found in unleaded, premium unleaded, and leaded gasolines at a (presumably typical) concentration of 0.3 mg/kg (ppm) [796].

Pyrene is one of the polynuclear aromatics found in gasoline [366].

Additional issues related to this topic have been summarized by ATSDR [892].

See also the Petroleum, General entry for a description of the main classes of chemical constituents in petroleum products.

Gasoline Range Organic (GRO) standard, with component concentrations, used by Wisconsin (see Laboratory section for details, does not cover lead or other metals):

Component	Concentration
Methyl-t-butylether	1000 ug/mL
Benzene	1000 ug/mL
Toluene	1000 ug/mL
Ethylbenzene	1000 ug/mL
m-Xylene	1000 ug/mL
p-Xylene	1000 ug/mL
o-Xylene	1000 ug/mL
1,2,4-Trimethylbenzene	1000 ug/mL
1,3,5-Trimethylbenzene	1000 ug/mL
Naphthalene	1000 ug/mL
Total	10,000 ug/mL

Physicochemical information from Environment Canada [560]:

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

API GRAVITY (60/60 degrees F)

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

60
62.4
67.80 to 57.9 (straight run)

DENSITY (g/mL)

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

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

Temp(C)	Density (at 0% Weathering Volume)
0	0.746
5	0.7501
15	0.709 to 0.746 (straight run)
	0.729
20	0.7340

SOLUBILITY

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

	No temp reported	22 C
Freshwater	169	240
Distilled Water	186.7 #2	98 #1
Seawater	132.4	

KEY: #1 = summer gasoline, #2 = regular gasoline

HYDROCARBON GROUP

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

Hydrocarbon Group Analysis (Weight %):

		Straight-Run	Blended
Paraffins	50		
Naphthenes	40		
Aromatics	10		
Alkenes	< 30		
Saturates group		39.61	57.65
Aromatics group		46.24	32.56
Olefins group		14.15	7.03
Diolefins group			2.48
Benzene group			0.28

COMPOSITIONAL ANALYSIS (WEIGHT %)

Note: Detailed compositional analysis of petroleum can

be obtained through gas chromatography or gas chromatography/mass spectrometry.

isobutane	1.561
n-hexane	11.04
unknown	ND
n- & iso pentanes	8.320
2-pentanes	8.942
unknown	0.199
1-pentane	2.235
2-methylpentane	6.322
3-methylpentane	3.353
unknown (MW=86)	4.030
2-ethyl-1-butene	1.149
unknown	ND
methylcyclopentane	3.851
unknown (MW=100)	3.643
3-ethylpentane	2.736
isooctane	1.961
n-heptane	2.293
1-methyl-1-cyclohexane	1.022
benzene	3.879
unknown	0.355
unknown (MW=114)	1.916
unknown (MW=114)	1.380
unknown	ND
1,2-dimethylcyclohexane	0.643
2,4-dimethylheptane	1.801
unknown (MW=124)	0.466
toluene & 1,2-dichloroethane	4.457
4-methyloctane	0.766
4-n-propylheptane	0.536
n-nonane	0.796
ethylbenzene	1.239
p & m xylenes & 1,2-dibromomethane & phenylenediamine	3.985
3,4-dimethylheptane	0.114
o-xylene	1.571
2,6-dimethyloctane	0.266
n-propylbenzene	0.347
methyl ethyltoluene	1.723
cumene	1.118
1,2,4-trimethylbenzene & o-ethyltoluene	1.939
vinyl-2-ethyl hexyl ether	0.155
m-styrene & n-butylbenzene	1.403
dimethyl ethylbenzene	0.430
diethylbenzene	1.448
1,2,4,5-tetramethylbenzene	ND
n-dodecane	0.574
1,1-dimethyl ethylbenzene	1.000
ethyl styrene	0.589
2,6-dimethyl styrene	0.971

unknown	0.596
dimethyl isopropylbenzene	0.356
2,6-dimethylundecane	0.185

METAL CONTENT

Other Metals (ppm):

Molybdenum	< 0.6
Potassium	< 1.5
Zinc	0.5
Lead	1750
	1.1 g/L max
	1.1
Nickel	< 1
Iron	< 3
Chromium	< 1.5
Magnesium	< 1
Vanadium	< 0.6
Copper	< 0.6
Titanium	0.54
Barium	< 0.3

VISCOSITY

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

Dynamic Viscosity (mPa.s or cP):

Temp(C)	Dynamic Viscosity (at 0% Weathering Volume)
0	0.75
	0.519 (straight run)
5	0.53
15	0.62
	0.44 (straight run)
20	0.45

Kinematic Viscosity (mm2/sec or cSt):

Temp(C)	Kinematic Viscosity (at 0% Weathering Volume)
0	0.69 to 0.95
15	0.57 to 0.80
	0.59 to 0.62 (straight run)

INTERFACIAL TENSIONS

NOTE: Interfacial tension is the force of attraction between molecules at the interface of a liquid. These tensions are essential for calculating the spreading rates and the likely extent to which the oil will form oil-in-water and water-in-oil emulsions. The interfacial tensions of crude oils and oil

products are dependent on the temperature and degree of weathering. The following tension values are at "0% Weathering Volume" - in other words, fresh leaded gasoline.

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

Temp(C)	Air-Oil Tension (at 0% Weathering Volume)
0	20.9
15	19.8
20	19 to 23 (straight run)

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

Temp(C)	Oil-Seawater Tension (at 0% Weathering Volume)
0	19.8
15	18.6

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

Temp(C)	Oil-Water (at 0% Weathering Volume)
0	19.7
15	18.0
20	49 to 51 (straight run)

FIRE AND REACTIVITY

Flash Point (C):

-43
-43
-40
-17.8 (straight run) (C.C.)

Auto Ignition Temperature (C):

280
257

Explosion Limits of Vapour in Air:

Upper	Lower
7.6 %	1.4 %
7.1 % #1	1.3 % #1

KEY: #1 = Straight Run

DISTILLATION

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

Boiling Range (C):

14 to 135 (straight run)
30 to 200

Final Boiling Point (C):

38

NON-METAL CONTENT

Sulphur (Weight %):

max 0.15
0.07

SENSATION

Odour Threshold (ppm):

Upper	Lower
0.01	0.005
	0.25

OTHER

Reid method Vapor Pressure (kPa):

Temp(C)	Pressure
37.8	62 to 103
	51

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

See the Fate.Detail section of the Gasoline, General entry for information on the fate and transport of gasoline and its constituents following a release from an underground storage tank.

Laboratory and/or Field Analyses:

At spill sites, if Natural Resource Damage Assessment (NRDA), risk assessment, scientific inquiry, or various questions which might be argued in court are being investigated, state of the art methods must be used, and many of these exceed the requirements of regulatory agencies (Roy Irwin, National Park Service, Personal Communication, 1996).

Many lab methods have been used to analyze for gasoline contamination [861]. Volatile organic and related gasoline compounds have often been analyzed with EPA method 8240. However, for certain risk and Natural Resource Damage Assessment (NRDA) purposes using the standard EPA method 8240 for volatile organic components is inadequate [468]. The standard EPA method 8240

detection limits are not always low enough. Natural Resource Damage Assessment or ecological risk assessment may require lower detection limits for comparison with ecological benchmarks or criteria, although higher detection limits may be acceptable for plume monitoring in an industrial area where no biological resources are at risk.

Regardless of the detection limits utilized, the standard EPA 8240 (being replaced by method 8260) method often needs to be "enhanced" by the inclusion of analytes that would be expected in specific situations. For example, for tanks leaking gasoline and diesel, one should include rigorous analyses for alkyl benzenes (including but not limited to toluene, ethylbenzene, and xylene). Like alkyl PAHs, alkyl benzenes are more resistant to degradation than the parent compounds benzene). Other compounds which often need to be analyzed are MTBE, 1,2 Dichloroethane, alkyl lead isomers, and other compounds consistent with risk assessment needs. Enhanced 8240 (being replaced by method 8260) scans are available from various commercial labs (Gregory Douglas, Arthur D. Little, Inc., Cambridge, Massachusetts, personal communication, 1995).

EPA method 8240 (being replaced by method 8260) is not the only "standard method" used for gasoline compounds which is inadequate for assessing biological effects. 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]. Problems with these methods were further elucidated by Douglas et al. in 1992 [657]. 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].

When considering screening options, it should be kept in mind that 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, one sample of 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

TPH analysis 418.1 does not do a good job at picking up alkyl benzenes, nor do most other commonly used methods used to determine total petroleum hydrocarbons. Most TPH methods use standards which tend to favor aliphatic rather than aromatics compounds such as BTEX compounds and PAHs. Modified method 8015 as used in California does a better job at standard BTEX compounds, but it is not clear if it picks up all important alkyl benzenes.

Many of the hazardous compounds in gasoline, including all the organic lead compounds, are mostly or entirely missed by the most common TPH analysis (418.1). GC/FID is not a good TPH alternative for gasolines either, since in typical GC/FID (often modifications of EPA 8015) analyses, PAHs and metals are not covered at all and the lighter (BTEX) hazardous fractions typical of gasolines will be lost in extraction and burning steps. Thus, although GC/FID TPH analyses have some applicability for looking at aliphatic content of fresh mid-range products such as diesels and possibly jet fuels, they are not very appropriate for gasolines.

Although TPH analyses are sometimes done in addition to BTEX analyses in gasoline contaminated soil, the aliphatics emphasized by TPH are not only less hazardous than BTEX compounds, but also less mobile in soil [465], and some are longer lasting. Thus, typically when BTEX compounds have moved out of the soil and into groundwater pathways of concern to humans, some aliphatic compounds may still be in the soil and register in TPH analyses. After additional time, however, the lighter aliphatics in contaminated soils or sediments tend to break down and disappear as reflected by lower TPH values, but the more hazardous and persistent heavy alkyl PAHs remain in the soil and continue to pose a hazard even though TPH 418.1 values have become lower or non detected. The more recent improvements in GC/FID analyses for TPH have somewhat ameliorated but not totally changed this.

Alkyl naphthalenes pose similar hazards and are usually found in the same petroleum products as naphthalenes, often in higher concentration than the parent compound (naphthalene). The parent compound naphthalene is the first to degrade, so as petroleum products age, the percentage of alkyl naphthalenes vs. naphthalene increases, but most standard EPA standard scans (even 8270) do not pick up alkyl naphthalenes.

Methods for Sampling and Sample Preservation:

Regardless of what lab methods are used, the investigator must take special precautions to prevent the escape of volatiles during sample shipment, storage, extraction, and cleanup [798]. The results of analyses of volatiles can be dramatically effected by small details such as how the samples are collected, stored, held, and analyzed in the lab, since volatile compounds can readily volatilize from samples in both field and lab procedures. The realization that better methods were needed began when the lab results of EPA methods 8020 and 8240 were negative even when contamination by volatiles was obvious in the field, in other words, when investigators began seeing clearly false negative results [798]. The use of brass liners for collection resulted in 19 fold higher VOCs than when 40 mL vials were used [798]. After researching various papers which documented volatile losses of 9 to 99% during sampling and then finding 100% losses in samples held over 14 days in their own facilities, the Wisconsin DNR requires the following for soil sampling of volatiles:

1) methanol preservation be used for all samples [913], and

2) samples stored in brass tubes must be preserved in methanol within 2 hours and samples stored in EN CORE samplers must be preserved in 48 hours [913].

3) Detection limits should be no higher than 25 ug/Kg (ppb) dry weight for VOCs or petroleum volatiles in soil samples [913].

Proposed decision Tree (dichotomous key) for selection of lab methods for measuring contamination from gasoline and other light petroleum products (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 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 EPA method 8240 (being replaced by method 8260) (see item 4 of this key). For the most rigorous analysis, consider also performing the NOAA protocol expanded scan*** for polycyclic aromatic hydrocarbons (PAHs) and alkyl PAHs. If not required to perform an EPA method 418.1-based analysis for TPH, instead perform a Gas Chromatography/Flame Ionization Detection (GC/FID) analysis for TPH using the spilled substance as a calibration standard. GC/FID methods can be sufficient for screening purposes when the oil contamination is fresh*, unweathered oil and when one is fairly sure of the source [657]. If diesel 1D was spilled, perform TPH-D (1D) using California LUFT manual methods (typically a modified EPA method 8015) [465] or a locally available GC/FID method of equal utility for the product spilled. However, no matter which TPH method is used, whether based on various GC/FID or EPA method 418.1 protocols, the investigator should keep in mind that the effectiveness of the method typically changes as oil ages, that false positives or false negatives are possible, and that the better Gas Chromatography-Mass Spectrometry-Selected Ion Mode (GC/MS/SIM) scans (such as the NOAA expanded scan***) should probably be performed at the end of remediation to be sure that the contamination has truly been cleaned up.

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

4. Analyze for Benzene, Toluene, Ethyl Benzene, and Toluene (BTEX) compounds in water as part of a broader scan of volatiles using EPA GC/MS method 8260. The standard EPA GC/MS method 8240 (being replaced by method 8260) protocol will be sufficient for some applications, but the standard EPA method 8240 (being replaced by method 8260) (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 (being replaced by method 8260) method using the lowest possible Selected Ion Mode detection limits and increasing the analyte list to include as many alkyl BTEX compounds as possible. For the most rigorous analysis, 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 (being replaced by method 8260)), and (optional) 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. If there is any reason to suspect fresh* or continuing contamination of soils or sediments with lighter volatile compounds, perform EPA GC/MS method 8240 (being replaced by method 8260) 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. For the most rigorous analysis, consider also performing the NOAA protocol expanded scan*** for polycyclic aromatic hydrocarbons (PAHs) and alkyl PAHs.

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

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

8. Lighter petroleum products such as gasoline are less prone to coating problems than are heavy products, so that if coating is a problem, perhaps some unknown heavier product is contributing to the problem and an expanded scan of PAHs and alkyl PAHs [828] should be performed. 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, keep in mind that fish can often avoid oil compounds if not confined to the oil area. However, for the most rigorous analysis, a HPLC/Fluorescence

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

11a. The concern is for benthic invertebrates: If the spill is fresh* or the source continuous, risk assessment needs may 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 (being replaced by method 8260) or modified EPA method 8240 (being replaced by method 8260) in the Selected Ion Mode (SIM). Bivalve invertebrates such as clams and mussels do not break down PAHs as well or as quickly as do fish or many wildlife species. They are also less mobile. Thus, bivalve tissues are more often directly analyzed for PAH residues than are the tissues of fish or wildlife. For the most rigorous analysis, consider analyzing invertebrate whole-body tissue samples and surrounding sediment samples for polycyclic aromatic hydrocarbons (PAHs) and alkyl PAHs using the NOAA protocol expanded scan***.

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 (being replaced by method 8260) or modified EPA method 8240 (being replaced by method 8260) in the Selected Ion Mode (SIM). Less is known about plant effects. However, the same methods recommended above for the analyses of water (Step 4 above) and for sediments or soils (Step 6 above) are usually also recommended for these same media in plant or wildlife habitats. If wildlife or plants are covered with oil, see

also Step 8 (above) regarding oiling issues.

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

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

protocol expanded scan***.

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

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

End of Key.

Additional Details:

Modified Method 8270:

A modified (improved by internal standards, oven temperature profile and use of High resolution GC/MS - HRGC/MS) EPA method 8270 has been used to provide better results for MTBE, BTEX, and naphthalene compounds [801]. Using this method combined with cluster techniques can help fingerprint fresh gasolines, but with aged gasolines, some volatiles (including C2-benzenes, C1-naphthalenes, and C3 benzenes) were so standardized by refining and others (standard BTEX compounds, parent naphthalene) had changed so much with aging, that the only isomeric group which seemed to have relatively reliable fingerprinting for unleaded gasolines potential

was C8 alkanes [801].

Modified Method 8240 (being replaced by modified method 8260):

For volatiles, the standard EPA method 8240 has some of the same problems which plague EPA method 8270 for semivolatiles (inadequate choice of analytes, inadequate detection limits). Some labs attempt to address this by lowering detection limits to SIM specifications, adding analytes, and other modifications. For example, Columbia Analytical Services (no government endorsement implied) offers the following (Lee Wolfe, Columbia Analytical Services, personal communication, 1995):

Using a modified EPA method 8240 (about $200 per water sample in 1995), analyses can be done for the following volatile and gasoline additive compounds:

Note: detection limit = dl

Alkyl benzenes common in oils:

isopropyl benzene:	dl 1 ppb
n-propyl benzene:	dl 1 ppb
1,3,5-trimethyl:	dl 1 ppb
1,2,4-trimethyl:	dl 1 ppb
tert-butyl	dl 1 ppb
sec-butyl	dl 1 ppb
n-butyl	dl 1 ppb
MTBE	dl 1 ppb
BTEX	dl 0.5 ppb
1,2-DCA	dl 0.5 ppb

Description of EPA standard method 8260 for volatile organics from EPA EMMI Database on Lab methods [861]:

EPA Method 8260 (replacing 8240 for GC/MS Volatile Organics):

OSW 8260 Volatile Organics - CGCMS 58 SW-846 CGCMS ug/L MDL Method 8260 "Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS): Capillary Column Technique" The volatile compounds are introduced into the gas

chromatograph by the purge and trap method or by direct injection (in limited applications) [861]. Purged sample components are trapped in a tube containing suitable sorbent materials [861]. When purging is complete, the sorbent tube is heated and backflushed with helium to desorb trapped sample components [861]. The analytes are desorbed directly to a large bore capillary or cryofocussed on a capillary precolumn before being flash evaporated to a narrow bore capillary for analysis [861]. The column is temperature programmed to separate the analytes which are then detected with a mass spectrometer interfaced to the gas chromatograph [861]. Wide capillary columns require a jet separator, whereas narrow bore capillary columns can be directly interfaced to the ion source [861]. If the above sample introduction techniques are not applicable, a portion of the sample is dispersed in solvent to dissolve the volatile organic constituents [861]. A portion of the solution is combined with organic- free reagent water in the purge chamber [861]. It is then analyzed by purge and trap GC/MS following the normal water method [861]. Qualitative identifications are confirmed by analyzing standards under the same conditions used for samples and comparing resultant mass spectra and GC retention times [861]. Each identified component is quantified by relating the MS response for an appropriate selected ion produced by that compound to the MS response for another ion produced by an internal standard [861].

An organic lead test ($60 per water sample) can be used to look for alkyl lead isomers (compounds potentially found in gasoline samples); Detection limit 100 ppb water, 500 ppb soil.

Another option: doing a "tentative ID search" for other compounds using mass spectrometry.

HPLC Screening Methods:

Naphthalenes are important in gasolines, and some labs use screening HPLC fluorescence methods to screen for alkylated naphthalenes and dibenzothiophenes that fluoresce at naphthalene wavelengths and the alkylated phenanthrenes that fluoresce at phenanthrene wavelengths [521]. Other HPLC/fluorescence scans are used to examine fish bile directly for the presence of metabolites of PAHs such as naphthalene [523].

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. Some of the less rigorous procedures which have been used in include the following:

Description of Standard EPA Method 8240 (being replaced by 8260) for Volatile Organics [861] :

OSW 8240A S Volatile Organics - Soil, GCMS 73 SW-846 GCMS ug/kg EQL Method 8240A "Volatile Organics by Gas Chromatography/Mass Spectrometry (GC/MS): Packed Column Technique" The volatile compounds are introduced into the gas chromatograph by the purge and trap method or by direct injection (in limited applications) [861]. The components are separated via the gas chromatograph and detected using a mass spectrometer, which is used to provide both qualitative and quantitative information [861]. The chromatographic conditions, as well as typical mass spectrometer operating parameters, are given [861]. If the above sample introduction techniques are not applicable, a portion of the sample is dispersed in methanol to dissolve the volatile organic constituents [861]. A portion of the methanolic solution is combined with organic-free reagent water in a specially designed

purging chamber [861]. It is then analyzed by purge and trap GC/MS following the normal water method [861]. The purge and trap process - An inert gas is bubbled through the solution at ambient temperature, and the volatile components are efficiently transferred from the aqueous phase to the vapor phase [861]. The vapor is swept through a sorbent column where the volatile components are trapped [861]. After purging is complete, the sorbent column is heated and backflushed with inert gas to desorb the components, which are detected with a mass spectrometer [861].

OSW 8240A (being replaced by 8260) W Volatile Organics - Water, GCMS 73 SW-846 GCMS ug/L EQL Method 8240A "Volatile Organics by Gas Chromatography/Mass Spectrometry (GC/MS): Packed Column Technique" The volatile compounds are introduced into the gas chromatograph by the purge and trap method or by direct injection (in limited applications) [861]. The components are separated via the gas chromatograph and detected using a mass spectrometer, which is used to provide both qualitative and quantitative information [861]. The chromatographic conditions, as well as typical mass spectrometer operating parameters, are given [861]. If the above sample introduction techniques are not applicable, a portion of the sample is dispersed in methanol to dissolve the volatile organic constituents [861]. A portion of the methanolic solution is combined with organic-free reagent water in a specially designed purging chamber [861]. It is then analyzed by purge and trap GC/MS following the normal water method [861]. The purge and trap process - An inert gas is bubbled through the solution at ambient temperature, and the volatile components are efficiently transferred from the aqueous phase to the vapor phase [861]. The vapor is swept through a sorbent column where the volatile components are trapped [861]. After purging is complete, the sorbent column is heated and backflushed with inert gas to desorb the components, which are detected with a mass spectrometer [861].

Method 8240 vs. GC/FID:

If one is analyzing gasoline, one should use EPA method 8240 GC/MS (for VOCs) rather than GC/FID because the components would be lost to evaporation otherwise (Tom MacDonald, Texas A&M, personal communication, 1995).

Colorimetric Detector Tubes:

Colorimetric detector tubes for gasoline are available and a combination of gas chromatography-mass spectrometry can be used for the analytic quantitation of gasoline in the blood [498].

TLC Summary for Gasoline [783]:

The thin-layer chromatography (TLC) analysis of this material is generally unsuccessful because most of the gasoline will evaporate from the thin-layer chromatography (TLC) plate during the spotting procedure. Material that remains on the thin-layer chromatography (TLC) plate is the gasoline residue and is often as little as 0.1% of the amount initially placed on the thin-layer chromatography (TLC) plate. Gasoline contamination is easily detected by its odor. Using hexane as the eluting solvent, the thin-layer chromatography (TLC) pattern may show two spots, one very light spot at Rf 0.9 visible with iodine staining and comprised of saturated hydrocarbons. A second spot is sometimes seen at Rf 0.8 under shortwave UV light and it is comprised of benzene and the alkylated benzenes. This spot will disappear after a short time. Occasionally a sulfur band is seen with highly degraded gasolines and it appears as a spot just below the saturated hydrocarbons and is visible with iodine staining.

Notes on Gasoline from the California Leaking Underground Fuel Tank (LUFT) field manual [465]:

Gasoline is a mixture of over 200 petroleum-derived chemicals plus a few synthetic products that are added to improve fuel performance. the majority of gasoline components range from C4 to C12 hydrocarbons. Analysis of gasoline components is usually limited to detection of benzene, toluene, xylene, and ethylbenzene (BTX&E) because: 1) they are readily adaptable to gas chromatographic detection, 2) they pose a serious threat to human health (benzene is a carcinogen), 3) they have the potential to move through soil and contaminate ground water, and 4) their vapors are highly flammable and explosive.

In addition to BTX&E, analysis for total petroleum hydrocarbons (TPH) is commonly conducted. This analysis detects aliphatic (straight-chain hydrocarbons) and aromatic constituents (hydrocarbons made up of one or more benzene rings) contained in fuel. Detection is reported as the sum total of all hydrocarbons in the sample, rather than as individual chemicals. Because the lighter fractions (such as BTX&E) are more mobile, they can migrate or dissipate away from the main body of contamination. Initial analysis may show low detectable concentrations, even though significant concentrations exist at lower depths. Less mobile hydrocarbons, such as those detected in TPH analysis, may give a more accurate indication of the actual contamination. For these reasons, soils are analyzed for both BTX&E and TPH as indicators of contamination.

Where site-specific conditions warrant analysis of additional constituents, such as ethylene dibromide (EDB) and organic lead.

It is recognized that other groups or individuals have also used EDB and/or organic lead as indicators of leaded gasoline leaks. The LUFT Task Force recommends caution in the use of such indicators. EDB has been so widely used in rural areas that its detection may not be due to a gasoline leak. When it has been found affiliated with a gasoline leak, its levels often have been so low as to be of questionable validity. Analysis for EDB is only recommended where site-specific conditions warrant this additional step.

In the case of organic lead, one must recognize that many laboratories only analyze for total lead and cannot readily distinguish between organic and inorganic lead. It has been the experience of many LUFT Task Force members that when they request organic lead analysis, the results received are expressed in terms of total lead content (including inorganic lead). Because inorganic lead is native to many California soils, the use of total lead analysis has led to false readings of organic lead being reported.

Modified Method 8015:

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

Discussion of TPH-Gasoline (TPH-G):

Total petroleum hydrocarbons, usually a GC/FID California modified EPA method 8015, based on a gasoline standard (gasoline used to calibrate instruments). The California LUFT manual, because of the predominance of diesel and gasoline in leaking USTs, treats and reports all semi-

volatiles as diesel and all volatiles as gasoline [810]. Thus in California, confusion often arises when: crude oil, kerosene, and hydraulic oil contamination is sometimes reported as diesel fuel; while naphtha, mineral spirits, or jet fuel contamination is sometimes reported as gasoline [810].

Thus, in California, confusion often arises when [810]:

> Crude oil, kerosene, and hydraulic oil contamination is sometimes reported as diesel fuel, while
>
> Naphtha, mineral spirits, or jet fuel contamination is sometimes reported as gasoline.
>
> A naphtha, paint thinner, mineral spirits, JP-4, stoddard solvent, Jet A, diesel, or even crude oil sample is purged, it will have a gasoline component and the laboratory using LUFT manual method will erroneously report the sample as gasoline [810].
>
> The California GC/FID methods call for packed GC columns. These have poor resolving power and make it difficult to obtain detailed information about the hydrocarbon type [810].
>
> Fractions need to be differentiated: Using the California LUFT manual methods, only an experienced analyst will be able to differentiate diesel fractions from aged gasoline [810]. The oversimplified California methods and models are plagued with many problems [808,810].

GRO Methods:

A number of states, including California and Wisconsin, recommend the use of Gasoline Range Organics (GRO) methods. GRO methods are often similar or the same as TPH-G methods. Most GRO methods are modifications of method 8015b [1013]. Some states (like Wisconsin) use specific standards for GRO, while some use gasoline itself for calibration. National guidance is in SW-846 [1013].

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

> This method is designed to measure the concentration of gasoline range organics in water and soil. This corresponds to a hydrocarbon range of C6 - C10 and a boiling point range between

approximately 60°C and 220°C. As defined in the method, other organic compounds, including chlorinated solvents, ketones, ethers, mineral spirits, stoddard solvents, and napthas are measurable. GRO results include these compounds/products.

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

.... This method can be used to determine GRO and petroleum volatile organic compounds (PVOCs) concurrently. Laboratories must achieve a limit of detection (LOD) of 25 ug/kg or lower for soil PVOCs. Lower detection limits are achievable for water samples. The Department will use 25 ug/kg as a reporting limit for soil PVOCs. A 25 ug/kg reporting limit means that laboratories need not report detection of PVOC compounds below 25 ug/kg (on a wet weight basis). The Department will not accept the use of reporting limits in lieu of actual LODs in other tests unless specified. The requirements for the LOD applies to all samples analyzed to meet the requirements of the NR 700 series. Sample results will not be used to establish clean closure if the laboratory LOD for PVOCs is higher than 25 ug/kg for any reason. If sample detection limits are elevated because of dilution (or other reasons) the Department will consider the sample concentrations to be above levels acceptable for site closure. The LOD must not be adjusted for the dry weight of the sample, however, sample results must still be reported on a dry weight basis. The reported LOD must be adjusted if the volume of sample extract purged is less than the amount used to determine the LOD.

...

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

This method can be used to determine GRO and petroleum volatile organic compounds (PVOCs) concurrently. Section 9.4 (in the original Wisconsin document) contains requirements for analyzing GRO and PVOCs concurrently.

Summary of Method: This method provides gas chromatographic conditions for the detection of volatile petroleum fractions such as gasoline, stoddard solvent, or mineral spirits. Samples are analyzed utilizing purge-and-trap sample concentration. The gas chromatograph is temperature programmed to facilitate separation of organic compounds. Detection is achieved by a flame ionization detector (FID). Quantitation is based on FID detector response to a gasoline component standard.

This method is suitable for the analysis of waters, soils, or wastes. Water samples can be analyzed directly for gasoline range organics by purge-and-trap extraction and gas chromatography. Soil or waste samples are dispersed in methanol to dissolve the volatile organic constituents. A portion of the methanolic solution is then analyzed by purge-and-trap GC.

Soil core samples are collected in wide mouth VOC vials and preserved with methanol. Minimum handling is required to reduce loss of contaminants.

This method is based in part on 1) USEPA SW-846: Methods 5030, 8000, 8020, 8015; 2) a single laboratory method evaluation study conducted by the American Petroleum Institute; 3) work by the EPA Total Petroleum Hydrocarbons Committee; and 4) work by the Wisconsin Ad-Hoc Committee on LUST Program Analytical Requirements and Wisconsin State Laboratory of Hygiene.

...

Detector: Flame ionization (FID), or FID in series with a Photoionization detector (PID) if GRO/PVOCs are being determined concurrently.

Definitions: Gasoline Range Organics (GRO): All the chromatographic response falling between the onset of the methyl-tertiary-butyl ether peak and the conclusion of the naphthalene peak. Quantitation is based on a direct comparison of the total area within this range to the total area of the Gasoline Component Standard.

Gasoline Component Standard: A ten component blend of typical gasoline compounds. This standard serves as a quantitation standard and is used to establish a retention time window for gasoline range organics.

Gasoline Range Organic (GRO) component standard and concentrations:

Component	Concentration
Methyl-t-butylether	1000 ug/mL
Benzene	1000 ug/mL
Toluene	1000 ug/mL
Ethylbenzene	1000 ug/mL
m-Xylene	1000 ug/mL
p-Xylene	1000 ug/mL
o-Xylene	1000 ug/mL
1,2,4-Trimethylbenzene	1000 ug/mL
1,3,5-Trimethylbenzene	1000 ug/mL
Naphthalene	1000 ug/mL
Total	10,000 ug/mL

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

...

Samples can become contaminated by diffusion of volatile organics through the sample container septum during shipment and storage or by dissolution of volatiles into the methanol for preservation. Trip blanks prepared from both reagent water and methanol must be carried through sampling and subsequent storage and handling to serve as a check on such contamination.

....

Sample Collection, Preservation, and Handling: Aqueous samples should be collected in triplicate (or the number of bottles directed by the laboratory) without agitation and without headspace in contaminant-free glass VOC vials with Teflon-lined septa in the caps. The Teflon liner must contact the sample. Samples must be preserved with 500 ul of 50% HCl at the time of collection, (acid must be added to the vial prior to adding the sample). Cool samples to 4°C immediately after collection. Water samples must be held at 4°C and analyzed within 14 days from the date of collection. Samples from carbonate aquifers should be preserved with sodium azide or extracted unpreserved within 48 hours of collection. Samples collected from carbonate aquifers must be flagged on the chain of custody. The pH of all water samples must be determined unless sample vials containing acid for field preservation were

supplied by the lab. The pH measurement may be performed on left-over sample. If sample pH is greater than two, sample results must be flagged. Flagging is not required for carbonate aquifers samples preserved with sodium azide or extracted within 48 hours of collection.

Soil can be collected using a 30 ml plastic syringe with the end sliced off, a brass tube, an EnCoreTM sampler or other appropriate devices. Samples cannot be analyzed if the amount of soil in the vial exceeds the weight maxima listed in Table 1 (see original document). A sufficient number of vials (three recommended) should be collected to provide for backup analyses in the event of breakage and to allow for screening. One vial must be collected for dry weight determination (without methanol). A methanol trip blank must accompany each batch of samples (for each site and each day that samples are collected). See original Wisconsin document for further instructions on methanol trip blanks. Care must be taken to be sure the vial seals properly (no soil on the threads). This can be accomplished by using a clean toothbrush or other utensil to sweep particles off the threads of the vial.

Methanol preservation is mandatory for the Modified GRO method and must be noted on the chain of custody. Sample collection time must be verifiable from the chain of custody. Soil samples that arrive at the laboratory without methanol that have not been stored properly must be rejected. Flagging data for these samples will not be acceptable. (Proper storage is outlined in the Table 2 in the original Wisconsin document.) Results from soil samples not preserved in methanol will be rejected. If the laboratory analyzes soil samples not handled as indicated in Table 2 (original document), at the request of clients, the samples must not be reported as "GRO".

Collect and preserve soil samples by one of the following techniques. Methanol preservation techniques can be found in section 8.2.2 (in the original Wisconsin document).

Collect soil into tared VOC vials following Table 1 (see original document). Preserve immediately with methanol. Store samples on ice or at 4°C. Note that any samples collected in this fashion which

are not analyzed by a laboratory are considered hazardous waste. Vials should be shipped in an upright position. Vials can also be placed in separate "ziplock" bags to avoid any problems that might occur if a vial leaks (such as the ink being removed from vial labels). Samplers should be aware that laboratories use a variety of vial taring methods so it is important to use only vials supplied by the laboratory performing the analysis.

Pack soil with no headspace into a brass tube. Cap the tube using plastic endcaps with teflon sheets placed between the endcaps and the sample. Store samples on ice or at 4°C. Preserve with methanol within 2 hours of sample collection. Immediately prior to methanol preservation, the soil from the brass tube must be subsampled into a VOC vial following Table 1 (see original document). Subsampling involves removing one of the plastic endcaps, scrapping away the surface soil, and then scooping out, (with a spatula or other utensil), the appropriate weight of soil into the vial. Brass tubes must be cleaned appropriately prior to reuse.

Pack soil with no headspace into an EnCoreTM sampler. Cap with the stainless steel "o-ring" cap. Store samples on ice or at 4°C. Preserve with methanol within 48 hours of sample collection. Note that this allows the possibility of having the laboratory preserve the sample. If you intend to have the laboratory preserve the sample, it must be received at the laboratory within 40 hours of sample collection. Soil stored in the EnCoreTM sampler must be extruded from the device into a VOC vial immediately prior to methanol preservation. The soil is extruded by using a pushrod supplied with the tool. Soil should not be scooped out of the sampler using a spatula, etc. EnCoreTM samplers must be cleaned appropriately (following the manufacturers recommendations) prior to reuse.

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

Methanol can be added by one of the methods listed below. Vials must not be submitted to the

laboratory for analysis of any volatile parameter (GRO, PVOC, VOC) if any of the methanol has spilled in sampling. If the laboratory determines that a vial has leaked, by noting a visible reduction of volume, or an unusually low weight then this must be reported with analytical results. Only the vial that has leaked will be in question not the entire cooler or shipping package.

Samples collected directly into a VOC vial in the field can be placed into tared vials already containing the appropriate volume of methanol (see Table 1 in original document). Samples stored in the brass tube, EnCore TM sampler, or an approved alternate storage device, can be added to tared vials already containing the appropriate volume of methanol (see Table 1 in original document). Samples stored in the brass tube, EnCore TM sampler, or an approved alternate storage device, should be preserved after screening of collocated samples to determine which samples will be laboratory analyzed. Only those samples to be laboratory analyzed should be methanol preserved. Store samples on ice or at 4°C.

Methanol can be added from premeasured volumes provided by the laboratory or a commercial vendor. For samples collected directly into a VOC vial in the field or soils placed into a VOC vial after storage in an approved device, quickly open the soil vial and pour in the appropriate volume of methanol (see Table 1 in original document), closing the sample vial immediately. Store samples on ice or at 4°C. Unused vials of methanol may be used at other sites at the sampler's discretion. Professional judgement should be used in determining how long vials with methanol for preservation (or vials for trip blanks) can be stored. Labs may determine the shelf life for these vials if they wish to offer an exact time period for storage to their clients.

Premeasured volumes of methanol can be added via syringe from a septa vial provided by the laboratory or a private vendor containing the appropriate volume (see Table 1 in original document) or from bulk methanol in the laboratory. For samples collected directly into a VOC vial in the field or soils placed into a VOC vial after storage in an approved device, draw the appropriate volume of methanol into the syringe and add by

puncturing the vial septa. Depending on the vial size and volume of methanol added, venting of the vial may be necessary to facilitate adding the methanol. If necessary, vent the vial by partially unscrewing the vial top. A fresh syringe needle will be needed for each new vial to avoid cross contamination. Common laboratory glass syringes and noncoring type syringe needles should be used. Store samples on ice or at 4°C.

Methanol can be added using a teflon repeater pipet pump that attaches to a bottle of purge and trap grade methanol and delivers the appropriate volume of methanol (see Table 1 in original document). For samples collected directly into a VOC vial in the field or soils placed into a VOC vial after storage in an approved device, quickly open the soil vial and depress the pipet pump to deliver the methanol, closing the sample vial immediately. If this method is used it is important to make sure that purge and trap grade methanol be used. Store samples on ice or at 4°C. Note that the methanol in the bottle can become contaminated if stored near any source of volatile fumes. Storage and use of this apparatus must be away from petroleum products and other volatile contaminants.

Shipping time should be minimized. Samples must be received by the lab within 4 days. Refer to Table 2 in original document for soil sample holding times.

Upon receipt by the laboratory weigh the tared sample vial to determine the actual weight. Use Table 1 (see original document) to determine if the sample may be analyzed as is, requires addition of methanol, flagging, or must be rejected. If the laboratory analyzes soil samples exceeding the weight maxima in Table 1 (see original document), at the request of clients, the samples must not be reported as "GRO".

Sample temperature must be determined upon receipt to the lab. Sample temperature may be recorded as "received on ice" only if solid ice is present in the cooler at the time the samples are received. "Received on ice" means sample containers are surrounded by an ice slurry, or crushed, cubed or chipped ice at the time of receipt in the laboratory. It is acceptable to place the sample containers in plastic bags to preserve sample and

label integrity. The use of bubble wrap or other insulating material is not allowed. Samples cooled during shipping with ice packs or "blue ice" may not be recorded as "received on ice". If samples are not "received on ice", temperature shall be determined from:
The temperature of an actual sample.

The temperature of a temperature blank shipped with samples.

The temperature of the melt water in the shipping container.

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

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End of description of Wisconsin GRO method.

Details of other miscellaneous EPA (sometimes less rigorous) lab methods which have been used in the past in media such as drinking water for volatiles [893] (lab method description from EPA [861]):

EMSLC 502.2 ELCD VOA's - P&T/CGCELCD/CGCPID 44 DRINKING_WATER CGCELD ug/L MDL "Volatile Organic Compounds in Water by Purge and Trap Capillary Column Gas Chromatography with Photoionization and Electrolytic Conductivity Detectors in Series" This method is used for the identification and measurement of purgeable

volatile organic compounds in finished drinking water, raw source water, or drinking water in any treatment stage [861]. The method is applicable to a wide range of organic compounds, including the four trihalomethane disinfection by-products, that have sufficiently high volatility and low water solubility to be efficiently removed from water samples with purge and trap procedures [861]. An inert gas is bubbled through a 5 mL water sample [861]. The volatile compounds with low water solubility are purged from the sample and trapped in a tube containing suitable sorbent materials [861]. When purging is complete, the tube is heated and backflushed with helium to desorb trapped sample components onto a capillary gas chromatography (GC) column [861]. The column is temperature programmed to separate the analytes which are then detected with photoionization detector (PID) and halogen specific detectors in series [861]. Analytes are identified by comparing retention times with authentic standards and by comparing relative responses from the two detectors [861]. A GC/MS may be used for further confirmation [861].

EMSLC 502.2 PID VOA's - P&T/CGCELCD/CGCPID 33 DRINKING_WATER CGCPID ug/L MDL "Volatile Organic Compounds in Water by Purge and Trap Capillary Column Gas Chromatography with Photoionization and Electrolytic Conductivity Detectors in Series" This method is used for the identification and measurement of purgeable volatile organic compounds in finished drinking water, raw source water, or drinking water in any treatment stage [861]. The method is applicable to a wide range of organic compounds, including the four trihalomethane disinfection by-products, that have sufficiently high volatility and low water solubility to be efficiently removed from water samples with purge and trap procedures [861]. An inert gas is bubbled through a 5 mL water sample [861]. The volatile compounds with low water solubility are purged from the sample and trapped in a tube containing suitable sorbent materials [861]. When purging is complete, the tube is heated and backflushed with helium to desorb trapped sample components onto a capillary gas chromatography (GC) column [861]. The column is temperature programmed to separate the analytes which are then detected with photoionization detector (PID) and halogen specific detectors in

series [861]. Analytes are identified by comparing retention times with authentic standards and by comparing relative responses from the two detectors [861]. A GC/MS may be used for further confirmation [861].

EMSLC 503.1 Volatile Aromatics in Water 28 DRINKING_WATER GCPID ug/L MDL "Volatile Aromatic and Unsaturated Organic Compounds in Water by Purge and Trap Gas Chromatography" This method is applicable for the determination of various volatile aromatic and unsaturated compounds in finished drinking water, raw source water, or drinking water in any treatment stage [861]. Highly volatile organic compounds with low water solubility are extracted (purged) from a 5-ml sample by bubbling an inert gas through the aqueous sample [861]. Purged sample components are trapped in a tube containing a suitable sorbent material [861]. When purging is complete, the sorbent tube is heated and backflushed with an inert gas to desorb trapped sample components onto a gas chromatography (GC) column [861]. The gas chromatograph is temperature programmed to separate the method analytes which are then detected with a photoionization detector [861]. A second chromatographic column is described that can be used to help confirm GC identifications or resolve coeluting compounds [861]. Confirmation may be performed by gas chromatography/mass spectrometry (GC/MS) [861].

APHA 6230 D Volatile Halocarbons - CGCELCD STD_METHODS GCELCD "6230 Volatile Halocarbons" GCPID 6230 D [861]. Purge and Trap Capillary-Column Gas Chromatographic Method: This method is similar to Method 6230 C., except it uses a wide-bore capillary column, and requires a high-temperature photoionization detector in series with either an electrolytic conductivity or microcoulometric detector [861]. This method is equivalent to EPA method 502.2; see EMSLC\502.2 [861]. Detection limit data are not presented in this method, but the method is identical to 502.2; therefore, see EMSLC\502.2 for detection limit data [861]. Method 6230 B., 17th edition, corresponds to Method 514, 16th edition [861]. The other methods listed do not have a cross-reference in the 16th edition [861].

EMSLC 524.1 Purgeable Organics - GCMS 48

DRINKING_WATER GCMS ug/L MDL "Measurement of Purgeable Organic Compounds in Water by Packed Column Gas Chromatography/Mass Spectrometry" This is a general purpose method for the identification and simultaneous measurement of purgeable volatile organic compounds in finished drinking water, raw source water, or drinking water in any treatment stage [861]. Volatile organic compounds and surrogates with low water solubility are extracted (purged) from the sample matrix by bubbling an inert gas through the aqueous sample [861]. Purged sample components are trapped in a tube containing suitable sorbent materials [861]. When purging is complete, the trap is backflushed with helium to desorb the trapped sample components into a packed gas chromatography (GC) column interfaced to a mass spectrometer (MS) [861]. The column is temperature programmed to separate the method analytes which are then detected with the MS [861]. Compounds eluting from the GC column are identified by comparing their measured mass spectra and retention times to reference spectra and retention times in a data base [861]. Reference spectra and retention times for analytes are obtained by the measurement of calibration standards under the same conditions used for samples [861]. The concentration of each identified component is measured by relating the MS response of the quantitation ion produced by that compound to the MS response of the quantitation ion produced by a compound that is used as an internal standard [861]. Surrogate analytes, whose concentrations are known in every sample, are measured with the same internal standard calibration procedure [861].

EMSLC 524.2 Purgeable Organics - CGCMS 60 DRINKING_WATER CGCMS ug/L MDL "Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry" This is a general purpose method for the identification and simultaneous measurement of purgeable volatile organic compounds in finished drinking water, raw source water, or drinking water in any treatment stage [861]. Volatile organic compounds and surrogates with low water solubility are extracted (purged) from the sample matrix by bubbling an inert gas through the aqueous sample [861]. Purged sample components are trapped in a tube containing suitable sorbent materials [861]. When purging is complete, the sorbent tube is heated and backflushed with helium to desorb the trapped

sample components into a capillary gas chromatography (GC) column interfaced to a mass spectrometer (MS) [861]. The column is temperature programmed to separate the method analytes which are then detected with the MS [861]. Compounds eluting from the GC column are identified by comparing their measured mass spectra and retention times to reference spectra and retention times in a data base [861]. Reference spectra and retention times for analytes are obtained by the measurement of calibration standards under the same conditions used for samples [861]. The concentration of each identified component is measured by relating the MS response of the quantitation ion produced by that compound to the MS response of the quantitation ion produced by a compound that is used as an internal standard [861]. Surrogate analytes, whose concentrations are known in every sample, are measured with the same internal standard calibration procedure [861].

Additional issues related to this topic have been summarized by ATSDR [892].

See also: Oil Spills entry for detail on field protocols and study designs.

See also: PAHs as a group entry.