

ENVIRONMENTAL CONTAMINANTS ENCYCLOPEDIA
ENTRY ON GASOLINE, CASINGHEAD (NATURAL GASOLINE)

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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 uninformed 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, Casinghead (Natural Gasoline)

Brief Introduction:

Br.Class: General Introduction and Classification Information:

Casinghead gasoline is a mixture of liquid hydrocarbons extracted from natural gas, which issues from the casinghead (the mouth or opening) of an oil well, extracted by various methods and stabilized to obtain a liquid product suitable for blending with refinery gasoline. Methods of extraction include compression, absorption, or refrigeration [637].

According to the U.S. Coast Guard Emergency Response Notification System (ERNS), casinghead gasoline is one of the most commonly spilled petroleum products in the U.S. [635].

Br.Haz: General Hazard/Toxicity Summary:

Casinghead gasoline can be harmful to aquatic life in very low concentrations [615]. For humans, it is irritating to skin, eyes, nose and throat. If inhaled, it will cause dizziness, headache, difficult breathing or loss of consciousness [615].

Being a gasoline, casinghead gasoline probably contains a fairly high percentage of aromatic compounds. Therefore, acute toxicity is of greater concern than chronic toxicity. See the Gasoline, General and BTEX entries for more information on the toxicity of the light compounds in petroleum products.

Spillage of casinghead gasoline could cause fouling to shorelines, and may be dangerous if it enters water intakes [615].

No information found on the exact concentrations of PAHs and other aromatic compounds in this product. However, gasolines (in general) contain a small but significant amount of PAHs, alkyl PAHs, and other harmful aromatics such as BTEX compounds (see Chem.Detail section below). Therefore, unless proven otherwise at a given site, the chemical constituents and hazards associated with this product should be considered to be similar to other gasolines (see Gasoline, General and the PAHs as a group entries).

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 (Roy Irwin, National Park Service, Personal Communication, 1996, based on an overview of literature on hand). See also: PAHs as a group entry.

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].

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

No information found for this particular product. The following information was found for gasoline in general:

Gasoline (in general) is possibly carcinogenic to humans (IARC group 2B) [747]. Gasoline (in general) is a suspected human carcinogen because it contains benzene, a known carcinogen [898]. Benzene is carcinogenic to humans (IARC group 1) [747].

Gasoline (in general) is a suspected human carcinogen because it contains benzene, a known carcinogen. Exposure, even at low levels, may result in the development of cancer [898].

Another component of gasoline (in general) [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].

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

Gasoline (in general) 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-trimethylpentane (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 expected 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).

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

No other information found; see Gasoline, General entry for information on similar products.

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

No information found for this particular product. The following information was found for gasoline in general:

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

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 entries on individual compounds for more details). Gasoline is classified as an unconfirmed human reproductive hazard [606].

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].

No other information found; see Gasoline, General entry.

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

No information found; see Gasoline, General entry for information on other gasoline products.

Synonyms/Substance Identification:

Natural Gasoline [615]
Gasolines: Casinghead [615]
CHRIS Code GCS [615]

Associated Chemicals or Topics (Includes Transformation Products):

See also individual entries:

Gasoline, General
Petroleum, General
Oil Spills

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

W.Low (Water Concentrations Considered Low):

No information found; see Gasoline, General entry for information on other gasoline products.

W.High (Water Concentrations Considered High):

No information found; see Gasoline, General entry for information on other gasoline products.

W.Typical (Water Concentrations Considered Typical):

No information found; see Gasoline, General entry for

information on other gasoline products.

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 Gasoline, General entry for information on other gasoline products.

W.Plants (Water Concentrations vs. Plants):

No information found; see Gasoline, General entry for information on other gasoline products.

W.Invertebrates (Water Concentrations vs. Invertebrates):

No information found; see Gasoline, General entry for information on other gasoline products.

W.Fish (Water Concentrations vs. Fish):

Information from CHRIS [615]:

Aquatic toxicity: 90 ppm/24 hr/juvenile
American shad/Tlm/fresh water 91 ppm/24
hr/juvenile American shad/Tlm/salt water

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

No information found; see Gasoline, General entry for information on other gasoline products.

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

No information found; see Gasoline, General entry for information on other gasoline products.

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

No information found; see Gasoline, General entry for information on other gasoline products.

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

Sed.Low (Sediment Concentrations Considered Low):

No information found; see Gasoline, General entry for information on other gasoline products.

Sed.High (Sediment Concentrations Considered High):

No information found; see Gasoline, General entry for information on other gasoline products.

Sed.Typical (Sediment Concentrations Considered Typical):

No information found; see Gasoline, General entry for information on other gasoline products.

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 Gasoline, General entry for information on other gasoline products.

Sed.Plants (Sediment Concentrations vs. Plants):

No information found; see Gasoline, General entry for information on other gasoline products.

Sed.Invertebrates (Sediment Concentrations vs. Invertebrates):

No information found; see Gasoline, General entry for information on other gasoline products.

Sed.Fish (Sediment Concentrations vs. Fish):

No information found; see Gasoline, General entry for information on other gasoline products.

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

No information found; see Gasoline, General entry for information on other gasoline products.

Sed.Human (Sediment Concentrations vs. Human):

No information found; see Gasoline, General entry for information on other gasoline products.

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

No information found; see Gasoline, General entry for information on other gasoline products.

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

Soil.Low (Soil Concentrations Considered Low):

No information found; see Gasoline, General entry for information on other gasoline products.

Soil.High (Soil Concentrations Considered High):

No information found; see Gasoline, General entry for information on other gasoline products.

Soil.Typical (Soil Concentrations Considered Typical):

No information found; see Gasoline, General entry for information on other gasoline products.

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

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

No information found; see Gasoline, General entry for information on other gasoline products.

Soil.Plants (Soil Concentrations vs. Plants):

No information found; see Gasoline, General entry for information on other gasoline products.

Soil.Invertebrates (Soil Concentrations vs. Invertebrates):

No information found; see Gasoline, General entry for information on other gasoline products.

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

No information found; see Gasoline, General entry for information on other gasoline products.

Soil.Human (Soil Concentrations vs. Human):

No information found; see Gasoline, General entry

for information on other gasoline products.

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

No information found; see Gasoline, General entry for information on other gasoline products.

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 Gasoline, General entry for information on other gasoline products.

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

No information found; see Gasoline, General entry for information on other gasoline products.

Tis.Invertebrates:

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

No information found; see Gasoline, General entry for information on other gasoline products.

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

No information found; see Gasoline, General entry for information on other gasoline products.

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

No information found; see Gasoline, General entry for information on other gasoline products.

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 Gasoline, General entry

for information on other gasoline products.

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

No information found; see Gasoline, General entry for information on other gasoline products.

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

No information found; see Gasoline, General entry for information on other gasoline products.

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 Gasoline, General entry for information on other gasoline products.

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 Gasoline, General entry for information on other gasoline products.

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 Gasoline, General entry for information on other gasoline products.

Tis.Human:

A) Typical Concentrations in Human Food Survey Items:

No information found; see Gasoline, General entry for information on other gasoline products.

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 Gasoline, General entry for information on other gasoline products.

C) Body Burden Residues in Humans: Typical, Elevated, or

of Concern Related to the Well-being of Humans:

No information found; see Gasoline, General entry for information on other gasoline products.

Tis.Misc. (Other Tissue Information):

No information found; see Gasoline, General entry for information on other gasoline products.

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

No information found; see Gasoline, General entry for information on other gasoline products.

Interactions:

No information found; see Gasoline, General entry for information on other gasoline products.

Uses/Sources:

No information found; see Gasoline, General entry for information on other gasoline products.

Forms/Preparations/Formulations:

No information found; see Gasoline, General entry for information on other gasoline products.

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

No information found on the exact concentrations of PAHs and other aromatic compounds in this product. However, gasolines (in general) contain a small but significant amount of PAHs including naphthalene and alkyl naphthalenes [797]. 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.

Polycyclic aromatic hydrocarbons (PAHs), alkyl PAHs, and BTEX compounds tend to be important hazardous components of gasolines in general, especially as they age (See Gasoline, General entry). Therefore, risk assessments should include analyses of PAHs, alkyl PAHs, and alkyl Benzenes utilizing the NOAA protocol expanded scan [828] or other rigorous GC/MS/SIM methods (See PAHs as a Group, Benzene, and BTEX entries).

Caution: Every individual petroleum product has a unique "fingerprint," or distinct set of constituents most commonly identified by a gas chromatograph analysis. Due to the

varying properties of the same general category of a petroleum product (each source and weathering stage of casinghead 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. Therefore, the below comments on casinghead gasoline are to be considered as representative, but not absolute values typical of every batch of the product with the same name.

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

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

79.3

DENSITY (g/mL) [560]:

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

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

Temp(C)	Density (at 0% Weathering Volume)
15	0.670

SPECIFIC GRAVITY [615]: 0.671 at 15 degrees C (liquid)

Additional physicochemical information from Environment Canada [560]:

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

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 casinghead gasoline.

Dynamic Viscosity (mPa.s or cP):

Temp(C)	Dynamic Viscosity (at 0% Weathering Volume)
15	0.440 (estimated)

Kinematic Viscosity (mm²/sec or cSt):

Temp(C)	Kinematic Viscosity (at 0% Weathering Volume)
15	0.657 (estimated)

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 casinghead gasoline.

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

Temp(C)	Air-Oil Tension (at 0% Weathering Volume)
20	19 to 23

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

Temp(C)	Oil-Water (at 0% Weathering Volume)
20	49 to 51

FIRE AND REACTIVITY

Flash Point (C)

< -17.8 (O.C.)

Flammability Limits (Volume %):

in air: 1.3 to 7.1

DISTILLATION

NOTE: Distillation data provides an indication of an oil's volatility and relative component distribution.

Boiling Range (C):

14 to 135

COLOUR: COLOURLESS

Odour Threshold (ppm)

0.25

BIOLOGICAL OXYGEN DEMAND (BOD):

This is a standard way of describing how much oxygen dissolved in water is consumed by biological oxidation of the chemical during a stated period of time. In this case, BOD is expressed as a percent to indicate the number of pounds of oxygen consumed by each 100 pounds of the chemical during the stated time.

Percent (%)	Days
8	5

Information from CHRIS [615]:

Category:Flammable liquid

CHEMICAL DESIGNATIONS

CG compatibility class:Miscellaneous Hydrocarbon Mixtures

OBSERVABLE CHARACTERISTICS

Physical state:Liquid

Color:Colorless

Odor:Gasoline

FIRE HAZARDS

Flash point: <0 degrees F O.C.

Fire extinguishing agents: Dry chemical, foam, or carbon dioxide

Fire extinguishing agents NOT to be used: Water may be ineffective

Special hazards of combustion products: None

Behavior in fire: Vapor is heavier than air and may travel a considerable distance to a source of ignition and flash back.

Electrical hazard: Class I, group D

PHYSICAL AND CHEMICAL PROPERTIES

Physical state at 15 degrees C. and 1 ATM:Liquid

Boiling point at 1 ATM:58-275 degrees F = 14-135 degrees C = 287-408 degrees K

Liquid surface tension: 19-23 dynes/cm = 0.019-0.023 N/m
at 20 degrees C

Liquid water interfacial tension: 49-51 dynes/cm =
0.049-0.051 N/m at 20 degrees C

Vapor (gas) specific gravity: 3.4

Latent heat of vaporization: 130-150 Btu/lb = 71-81
cal/g = 3.0-3.4 X 10⁽⁵⁾ J/kg

Heat of combustion: -18,720 Btu/lb = -10,400 cal/g = -
435.4 X 10⁽⁵⁾ J/kg

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

No information found; see Gasoline, General entry for
information on other gasoline products.

Laboratory and/or Field Analyses:

Since polycyclic aromatic hydrocarbons (PAHs), alkyl PAHs, and BTEX compounds tend to be important hazardous components of gasolines in general (See Gasoline, General entry), risk assessments should include analyses these compound utilizing the NOAA protocol expanded scan [828] or other rigorous GC/MS/SIM methods (See PAHs as a Group, Benzene, and BTEX entries).

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].

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].

Draft decision Tree (dichotomous key) for selection of lab methods for measuring contamination from gasoline and other light petroleum products such as gasolines (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 tissues4
- 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 (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 8240. The standard EPA GC/MS method 8240 protocol will be sufficient for some applications, but the standard EPA method 8240 (and especially the less rigorous EPA BTEX methods such as method 8020 for soil and method 602 for water) are all inadequate for generating scientifically defensible information for Natural Resource Damage Assessments [468]. The standard EPA methods are also inadequate for risk assessment purposes. Thus, when collecting information for possible use in a Natural Resource Damage Assessment or risk assessment, it is best to ask the lab to analyze for BTEX compounds and other volatile oil compounds using a modified EPA GC/MS method 8240 method using the lowest possible Selected Ion Mode detection limits and increasing the analyte list to include as many alkyl BTEX compounds as possible. 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), 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 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. 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 consultations 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 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 or modified EPA method 8240 in the Selected Ion Mode (SIM). Bivalve invertebrates such as clams and mussels do not break down PAHs as well or as quickly as do fish or many wildlife species. They are also less mobile. Thus, bivalve tissues are more often directly analyzed for PAH residues than are the tissues of fish or wildlife. 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 or modified EPA method 8240 in the Selected Ion Mode (SIM). Less is known about plant effects. However, the same methods recommended above for the analyses of water (Step 4 above) and for sediments or soils (Step 6 above) are usually also recommended for these same media in plant or wildlife habitats. If wildlife or plants are covered with oil, see also Step 8 (above) regarding oiling issues.

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

To assist the reader in making decisions based on the continuum of possible degrees of freshness, the following generalizations are provided: Some of the lightest middle distillates (such as Jet Fuels, Diesel, No. 2 Fuel Oil) are moderately volatile and soluble and up to two-thirds of the spill amount could disappear from surface waters after a few days [771,835]. Even heavier petroleum substances, such as medium oils and most crude oils will evaporate about one third of the product spilled within 24 hours [771]. Typically the volatile fractions disappear mostly by evaporating into the atmosphere. However, in some cases, certain water soluble fractions of oil including Benzene, Toluene, Ethyl Benzene, and Xylene (BTEX) compounds move down into groundwater. BTEX compounds are included in the more volatile and water soluble fractions, and BTEX compounds as well as the lighter alkanes are broken down more

quickly by microbes than heavier semi-volatiles such as alkyl PAHs and some of the heavier and more complex aliphatic compounds. Thus after a week, or in some cases, after a few days, there is less reason to analyze surface waters for BTEX or other volatile compounds, and such analyses should be reserved more for potentially contaminated groundwaters. In the same manner, as the product ages, there is typically less reason to analyze for alkanes using GC/FID techniques or TPH using EPA 418.1 methods, and more reason to analyze for the more persistent alkyl PAHs using the NOAA protocol expanded scan***.

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

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

End of Key.

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

As of 1997, the problem of lack of data comparability (not only for water methods but also for soil, sediment, and tissue methods) between different "standard methods" recommended by

different agencies seemed to be getting worse, if anything, rather than better. The trend in quality assurance seemed to be for various agencies, including the EPA and others, to insist on quality assurance plans for each project. In addition to quality control steps (blanks, duplicates, spikes, etc.), these quality assurance plans call for a step of insuring data comparability [1015,1017]. However, the data comparability step is often not given sufficient consideration. The tendency of agency guidance (such as EPA SW-846 methods and some other new EPA methods for bio-concentratable substances) to allow more and more flexibility to select options at various points along the way, makes it harder to 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.

Scanning methods for various PAHs in drinking water have included methods which are much better than TPH but not necessarily better than the NOAA expanded scan: High pressure liquid chromatography (EPA 550, 550.1); gas chromatographic/mass spectrometry (EPA 525): PQL= 0.0002 mg/L [893].

See also: Gasoline, General entry.