ENVIRONMENTAL CONTAMINANTS ENCYCLOPEDIA

GASOLINE ADDITIVES ENTRY

July 1, 1997

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This document was put together by human beings, mostly by compiling or summarizing what other human beings have written. Therefore, it most likely contains some mistakes and/or potential misinterpretations and should be used primarily as a way to search quickly for basic information and information sources. It should not be viewed as an exhaustive, "last-word" source for critical applications (such as those requiring legally defensible information). For critical applications (such as litigation applications), it is best to use this document to find sources, and then to obtain the original documents and/or talk to the authors before depending too heavily on a particular piece of information.

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 (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 Additives (Including EDB = Ethylene dibromide, EDC = Ethylene dichloride, TEL = Tetraethyllead, TML = Tetramethyllead, MTBE = Methyl tertiary-butyl ether, Ethanol, Methanol)

Brief Introduction:

Br.Class: General Introduction and Classification Information:

There are two primary forms of gasoline: regular (leaded gasoline) and unleaded gasoline. Gasoline quality is controlled in three broad technical areas: volatility, octane quality, and additives. Volatility refers to the ability of the fuel to vaporize and mix with air to ensure combustion. Octane quality is a measure of the "smoothness" of combustion of the air/fuel mixture. Consequently, oxygenates, such as methanol (methyl alcohol) and ethanol (ethyl alcohol), are added to gasolines because they have definite effects on volatility and octane [820]. The process of combining a fuel with oxygen can be made more efficient by, in effect, "pre-burning" the fuel. Oxygenated fuel additives, such as methyl tertiary-butyl ether (MTBE) and tertiary-butyl ether (TBE) are already partially oxygenated and, therefore produce less carbon monoxide at the expense of slightly less power (fewer BTUs) per gram of fuel [820]. For additional information on MTBE, see also the separate entry on MTBE.

In "regular" or leaded gasoline blends, lead compounds, such as tetramethyllead (TML) and tetraethyllead (TEL), are used to increase the octane number [661]. Other hazardous compounds including ethylene dichloride (EDC) and ethylene dibromide (EDB) are added as lead scavengers to prevent buildup of lead oxide deposits [661]. 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].

Another lead scavenging agent additive in gasoline is 1,2 Dichloroethane [873,931]. See also 1,2-dichloroethane entry and the toxicological profile for 1,2-dichloroethane available from ATSDR [931].

The change from regular gasoline to unleaded gasoline was due to concern over lead accumulation in the environment (since lead has been proven to be extremely toxic to the ecosystem and humans - see the Lead entry for details). All cars manufactured in the year 1975 and following years were equipped with catalytic converters and therefore were required to operate on unleaded gasoline. Leaded gasoline after 1986 cannot contain more than 0.025 g/L (0.1 g/gal) lead. The lead phasedown regulations require a shift to increased gasoline processing, such as alkylation, isomerization, and catalytic reforming, to achieve the necessary octane levels. Selected oxygenates, such as alcohols and ethers, offer additional routes to high octane gasolines for unleaded mixtures [820].

Three of the more common oxygenated fuel additives that have been used with unleaded gasolines are methanol, ethanol, and methyl tertiary-butyl ether (MTBE). Methanol is obtained from petroleum (from methane or by reacting carbon monoxide and water); ethanol is obtained from corn by fermentation; and MTBE is made synthetically from petroleum feedstocks. The choice of which of the compounds commonly used in oxygenated fuels to use is dependent on region, cost of production, and availability of raw materials [661].

Ethanol, methanol, MTBE, and tert-butyl alcohol (TBA), are all also used as octane enhancers in unleaded gasoline [875].

The most widely used oxygenate is MTBE. Since it has a relatively low heat of vaporization, MTBE improves fuel mixing and atomization during cold operation and consequently reduces emissions. MTBE has been blended into both USA and European gasolines for many years, primarily because it has an extremely high octane value which has enabled it to take the place of lead compounds gradually being phased out [819]. See the MTBE entry for more information.

From a fuel manufacturer's standpoint aromatic compounds are desirable in gasolines since they increase the octane rating of gasoline blends. After the EPA's ban on lead additives in 1973, aromatic compounds, including benzene and alkylbenzenes have generally been used to increase the octane number. In present formulation up to 50% of a premium gasoline blend can be aromatic compounds [661]. Small amounts of aromatic hydrocarbons occur naturally in blends of gasoline. In addition, aromatic rich streams containing these hydrocarbons are added as blending agents in percent concentrations to unleaded gasoline to improve the antiknock characteristics of gasoline [818].

In addition to TEL and TML, methylcyclopentadienyl manganese tricarbonyl (MMT) is used as an anti-knock compound in leaded gasolines [875].

Anti-oxidants in gasoline include a wide variety of hindered phenols, Phenylenediamines, Aminophenols, and tetramines [747,875]. Metal deactivator additives include a wide variety of Disalicylidene amines [875].

Ignition controller additives include Tri-o-cresyl phosphates (TOCPs) [875]. Anti-icing additives include Isopropyl and other Alcohols, Amides/amines, Organophosphate ammonium salts, Glycols [747,875].

Detergents additives include Amino hydroxy amide, Amines, various long chain alkyl phenols, various long chain alcohols, long chain carboxylic acids, Alkyl ammonium dialkyl phosphate, Imidazolines, and Succinimides [747,875].

Anti-rust additives include various Fatty acid amines, Sulfonates, Amine/alkyl phosphates, carboxylic acids, phosphoric acids, sulfonic acids, and alkyl carboxylates [747,875].

Br.Haz: General Hazard/Toxicity Summary:

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, various additive contents. As a result, some gasolines have more content of hazardous BTEX compounds (namely benzene, toluene, ethyl benzene, and xylenes), naphthalene, metal, solvent additive, polycyclic aromatic hydrocarbon (PAH), and alkyl PAH compounds than others. For example, super unleaded has higher concentrations of BTEX compounds than regular unleaded [560].

Thus the toxicity or "hazard" of gasoline of interest to those reading a toxicity profile varies tremendously with the exact gasoline in question. The most important hazardous components of most gasolines are PAHs, alkyl PAHs, the BTEX compounds, especially benzene and alkyl substituted benzenes (toluene, xylenes, ethylbenzene), additives such as MTBE (Methyl tertiary-butyl ether), TBE (Tertiary butyl ether), Ethanol (Ethyl alcohol), Methanol (Methyl alcohol), and metallic leaded gasoline additives such as Tetramethyllead (TML), Tetraethyllead (TEL), Ethylene dichloride (EDC), and Ethylene dibromide (EDB).

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].

Although both alcohols and ethers can be used as vehicles for introducing oxygen into the gasoline pool, the alcohols (particularly methanol) display a variety of significant disadvantages relative to the ethers, including high vapor pressure, poor water tolerance, and high heat of vaporization. Of the three more common fuel additives, methanol is by far the most toxic and hazardous to handle since it is readily oxidized by liver enzymes to formaldehyde which can damage the liver and brain cells [661,819]. Fortunately, methanol is seldom used as an additive [661].

Benzene and its alkylbenzene relatives are generally considered to be the most toxic components of gasoline (except for methanol, which is a non-hydrocarbon additive). These compounds, which may be present at concentrations as high as 50% by weight in premium unleaded gasolines, exhibit both acute (prompt) and chronic (long-term) toxicity in humans [661]. Benzenes can occur in gasolines as part of the original mix or as additives.

Ethanol is also quite toxic. Ethanol exposure through gasohol or other ethanol blended fuel would be much lower than the amount associated with the acute toxic effects of straight ethanol, because the ethanol would be diluted with other fuels [818].

Acute exposure symptoms to EDB include vomiting, diarrhea, abdominal pain, and central nervous system (CNS) depression [661].

Tetraethyl Lead (TEL), a lead additive, is absorbed through the skin, inhaled as a vapor, or ingested. Exposure levels of 100 mg/m cubed for 1 hour causes acute symptoms.Mild exposure to 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]. See also: Lead Entry.

MTBE appears to have no adverse human health effects. There is little reason to assume this situation will change since similar ethers have been in commercial and industrial use for many years [661]. MTBE is acutely slightly toxic [818].

Not considered pure hydrocarbons, phenols comprise bout 0.3% of a typical gasoline blend [661]. Phenols are relatively soluble and quite toxic to humans and aquatic life [661]. Phenol is an aromatic alcohol derived from benzene by replacing a hydrogen with an hydroxide, -OH. The hydrogen associated with the OH group is acidic, that is, it ionizes to form H+ ions in solution [661]. Acids can attack tissues and other matter.

See also: entries for individual additives, such as MTBE, Lead, and 1,2- Dichloroethane.

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

Ethylene dibromide (EDB) has been identified as an experimental animal carcinogen [661].

Alkyl benzenes tend to be slow acting but potent carcinogens which may take years to induce cancer [797].

See also: entries for individual additives, such as MTBE, lead, and 1,2 Dichloroethane.

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

Exposure by inhalation of male and female rats to MTBE at up to 3400 ppm did not result in adverse effects on reproductive ability, litter size, or pup viability [606]. Teratology testing was negative in rats and mice with exposures up to 2500 ppm [606]. In a more recent report, MTBE did not produce embryotoxic effects in rabbits, even at doses of 8000 ppm, which were maternotoxic [606]. See the MTBE entry for more details.

See also: information listed for individual additives, such as MTBE, lead, and 1,2 Dichloroethane.

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

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

A study designed to determine the degradation and metabolism of the two ionic species, TREL and DEL, in soil under laboratory conditions concluded that both biological and chemical degradation of TREL and DEL in soil occurred, and that chemical degradation was probably the major factor contributing to the disappearance of TREL and DEL in soil. The exact extent of chemical degradation is not known. Attempts to isolate microorganisms capable of mineralizing TEL from the three soils and a leaded-gasoline contaminant soil were not successful [817, Reprinted with permission from Environmental Toxicology and Chemistry, Volume 14, Ou, L.-T., W. Jing and J.E. Thomas, "Biological and chemical degradation of ionic ethyllead compounds in soil." Copyright 1995 SETAC].

See also: entries for individual additives, such as MTBE, lead and 1,2 Dichloroethane.

Synonyms/Substance Identification:

No information found.

Associated Chemicals or Topics (Includes Transformation Products):

See also individual entries:

MTBE
Gasoline, General
Lead

Common unleaded gasoline additives [661]:

Methyl tertiary-butyl ether (MTBE)
Tertiary butyl ether (TBE) [818]
Ethanol (Ethyl alcohol)
Methanol (Methyl alcohol)

Common leaded gasoline additives [661]:

Tetramethyllead (TML)
Tetraethyllead (TEL)
Ethylene dichloride (EDC)
Ethylene dibromide (EDB)

Transformation products [817]:

Trimethyllead (TRML)
Dimethyllead (DML)
Triethyllead (TREL)
Diethyllead (DEL)
Inorganic lead (Pb^{2+})

Site Assessment-Related Information Provided by Shineldecker (Potential Site-Specific Contaminants that May be Associated with a Property Based on Current or Historical Use of the Property) [490]:

General Types of Associated Materials:

- Alcohols
- Gasoline

Raw Materials, Intermediate Products, Final Products, and

Waste Products Generated During Manufacture and Use:

- Benzyl chloride
- Boron hydrides
- Dibromoethane
- Dibromomethane
- Dichloroethane
- Ethyl alcohol
- Ethyl ether
- Ethylene oxide
- Hydroquinone
- Lead
- Lead, alkyl
- Methyl tertiary butyl ether
- Phosphorus
- Platinum
- Tricresyl phosphates

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

W.Low (Water Concentrations Considered Low):

No information found for additives in general; search for information under the individual entries such as MTBE, lead, or 1,2 dichloroethane.

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W.High (Water Concentrations Considered High):

No information found for additives in general; search for information under the name of the individual compound, such as MTBE, lead, or 1,2 dichloroethane.

W.Typical (Water Concentrations Considered Typical):

No information found for additives in general; search for information under the name of the individual compound, such as MTBE, lead, or 1,2 dichloroethane.

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 for additives in general; search for information under the name of the individual compound, such as MTBE, lead, or 1,2 dichloroethane.

W.Plants (Water Concentrations vs. Plants):

No information found for additives in general; search for information under the name of the individual compound, such as MTBE, lead, or 1,2 dichloroethane.

W.Invertebrates (Water Concentrations vs. Invertebrates):

No information found for additives in general; search for information under the name of the individual compound, such as MTBE, lead, or 1,2 dichloroethane.

W.Fish (Water Concentrations vs. Fish):

No information found for additives in general; search for information under the name of the individual compound, such as MTBE, lead, or 1,2 dichloroethane.

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

No information found for additives in general; search for information under the name of the individual compound, such as MTBE, lead, or 1,2 dichloroethane.

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

No information found for additives in general; search for information under the name of the individual compound, such as MTBE, lead, or 1,2 dichloroethane.

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

No information found for additives in general; search for information under the name of the individual compound, such as MTBE, lead, or 1,2 dichloroethane.

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

Sed.Low (Sediment Concentrations Considered Low):

No information found for additives in general; search for information under the name of the individual compound, such as MTBE, lead, or 1,2 dichloroethane.

Sed.High (Sediment Concentrations Considered High):

No information found for additives in general; search for information under the name of the individual compound, such as MTBE, lead, or 1,2 dichloroethane.

Sed.Typical (Sediment Concentrations Considered Typical):

No information found for additives in general; search for information under the name of the individual compound, such as MTBE, lead, or 1,2 dichloroethane.

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 for additives in general; search for information under the name of the individual compound, such as MTBE, lead, or 1,2 dichloroethane.

Sed.Plants (Sediment Concentrations vs. Plants):

No information found for additives in general; search for information under the name of the individual compound, such as MTBE, lead, or 1,2 dichloroethane.

Sed.Invertebrates (Sediment Concentrations vs. Invertebrates):

No information found for additives in general; search for information under the name of the individual compound, such as MTBE, lead, or 1,2 dichloroethane.

Sed.Fish (Sediment Concentrations vs. Fish):

No information found for additives in general; search for information under the name of the individual compound, such as MTBE, lead, or 1,2 dichloroethane.

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

No information found for additives in general; search for information under the name of the individual compound, such as MTBE, lead, or 1,2 dichloroethane.

Sed.Human (Sediment Concentrations vs. Human):

No information found for additives in general; search for information under the name of the individual compound, such as MTBE, lead, or 1,2 dichloroethane.

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

No information found for additives in general; search for information under the name of the individual compound, such as MTBE, lead, or 1,2 dichloroethane.

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

Soil.Low (Soil Concentrations Considered Low):

No information found for additives in general; search for information under the name of the individual compound, such as MTBE, lead, or 1,2 dichloroethane.

Soil.High (Soil Concentrations Considered High):

No information found for additives in general; search for information under the name of the individual compound, such as MTBE, lead, or 1,2 dichloroethane.

Soil.Typical (Soil Concentrations Considered Typical):

No information found for additives in general; search for information under the name of the individual compound, such as MTBE, lead, or 1,2 dichloroethane.

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):

EDC: State EDC cleanup guidance levels range from 0.025 to 130 ppm [806].

Soil.Plants (Soil Concentrations vs. Plants):

No information found for additives in general; search for information under the name of the individual compound, such as MTBE, lead, or 1,2 dichloroethane.

Soil.Invertebrates (Soil Concentrations vs. Invertebrates):

No information found for additives in general; search for information under the name of the individual compound, such as MTBE, lead, or 1,2 dichloroethane.

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

No information found for additives in general; search for information under the name of the individual compound, such as MTBE, lead, or 1,2 dichloroethane.

Soil.Human (Soil Concentrations vs. Human):

No information found for additives in general; search for information under the name of the individual compound, such as MTBE, lead, or 1,2 dichloroethane.

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

No information found for additives in general; search for information under the name of the individual compound, such as MTBE, lead, or 1,2 dichloroethane.

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 for additives in general; search for information under the name of the individual compound, such as MTBE, lead, or 1,2 dichloroethane.

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

No information found for additives in general; search for information under the name of the individual compound, such as MTBE, lead, or 1,2 dichloroethane.

Tis.Invertebrates:

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

No information found for additives in general; search for information under the name of the individual compound, such as MTBE, lead, or 1,2 dichloroethane.

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

No information found for additives in general; search for information under the name of the individual compound, such as MTBE, lead, or 1,2 dichloroethane.

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

No information found for additives in general; search for information under the name of the individual compound, such as MTBE, lead, or 1,2 dichloroethane.

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 for additives in general; search for information under the name of the individual compound, such as MTBE, lead, or 1,2 dichloroethane.

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

No information found for additives in general; search for information under the name of the individual compound, such as MTBE, lead, or 1,2 dichloroethane.

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

No information found for additives in general; search for information under the name of the individual compound, such as MTBE, lead, or 1,2 dichloroethane.

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 for additives in general; search for information under the name of the individual compound, such as MTBE, lead, or 1,2 dichloroethane.

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 for additives in general; search for information under the name of the individual compound, such as MTBE, lead, or 1,2 dichloroethane.

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 for additives in general; search for information under the name of the individual compound, such as MTBE, lead, or 1,2 dichloroethane.

Tis.Human:

A) Typical Concentrations in Human Food Survey Items:

No information found for additives in general; search for information under the name of the individual compound, such as MTBE, lead, or 1,2 dichloroethane.

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 for additives in general; search for information under the name of the individual compound, such as MTBE, lead, or 1,2 dichloroethane.

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

No information found for additives in general; search for information under the name of the individual compound, such as MTBE, lead, or 1,2 dichloroethane.

Tis.Misc. (Other Tissue Information):

No information found for additives in general; search for information under the name of the individual compound, such as MTBE, lead, or 1,2 dichloroethane.

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

Lead additives are toxic to the ecosystem and human health since lead bioaccumulates in the environment and in animal, marine, and human life (see the Lead entry for details). It is important to note again that it was due to lead's toxicity that it was banned in 1975 as a fuel additive [820].

Interactions:

No information found for additives in general; search for information under the name of the individual compound, such as MTBE, lead, or 1,2 dichloroethane.

Uses/Sources:

No information found for additives in general; search for information in the entries for individual compound, such as MTBE, lead, or 1,2 dichloroethane.

Forms/Preparations/Formulations:

Gasoline also contains other additives than the antiknock, lead scavengers, and oxygenates focused on in this entry. Other additives include [747]:

Detergents: Amino hydroxy amide, Amines, Alkyl ammonium dialkyl phosphate, Imidazolines, Succinimides

Anti-rust: Fatty acid amines, Sulfonates, Amine/alkyl phosphates, Alkyl carboxylates

Anti-oxidants: Hindered phenols, para-Phenylenediamine, Aminophenols

Dyes: Red (alkyl derivatives of azobenzene-4-azo-2-naphthol), Orange (benzene-azo-2-naphthol), Yellow (para-diethyl aminoazobenzene), Blue (1,4-diisopropylaminoanthraquinone)

Anti-icing: Alcohols, Amides/amines, Organophosphate ammonium salts, Glycols

Upper cylinder lubricants: Light mineral oils, Cycloparaffins

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

Various gasoline additives and the chemicals in them are listed above in the Br.Class and Forms sections.

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

Methanol is acidic and corrosive. It will attack ordinary soldered fitting and must be stored in underground storage tanks or other containers specifically designed to hold methanol. Fortunately, methanol is seldom used as an additive [661].

Oxygenates commonly used in Europe are methanol in conjunction with MTBE or tert-butyl alcohol (TBA). Typical oxygenate contents are 3% methanol plus 2% TBA or 5% MTBE. The methanol content in automotive gasolines should not exceed 3%, the MTBE content should not exceed 10%, and the total amount of oxygen should not exceed 2.5% [747].

Toluene makes up approximately 4-7% of gasoline [661]. Xylenes make up about 6-8% by weight of gasoline [661]. Alkanes also make up various parts of gasoline. n-Hexane is the most toxic of the alkanes [661]. It comprises 11-13% of gasoline by wight.

Phenols comprise bout 0.3% of a typical gasoline blend [661].

See the Chem.Detail section of the MTBE entry for chemical/physical information on MTBE [560].

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

Tetraethyllead (TEL) and tetramethyllead (TML) were the two major antiknock agents used in leaded gasoline [817]. Automobiles of 1975 and later models in the United States and other industrialized countries used only unleaded gasoline, resulting in a gradually phase out of the use of leaded gasoline through the early 1980s. As a result of the extensive use of leaded gas prior to the early 1980s, alkyllead species were found to be ubiquitous in the environment. Alkyllead compounds were detected in roadside soils, sediments, rain and surface waters, fish, and grass and tree leaves. Ionic triethyllead (TREL) and trimethyllead (TRML) were the dominant species found in the environment. In aqueous solutions, TEL and 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, Ou, L.-T., W. Jing and J.E. Thomas, "Biological and chemical degradation of ionic ethyllead compounds in soil." Copyright 1995 SETAC].

A study designed to determine the degradation and metabolism of the two ionic species, TREL and DEL, in soil under laboratory conditions concluded that both biological and chemical degradation of TREL and DEL in soil occurred, and that chemical degradation was probably the major factor contributing to the disappearance of TREL and DEL in soil. The exact extent of chemical degradation is not known. Attempts to isolate microorganisms capable of mineralizing TEL from the three soils and a leaded-gasoline contaminant soil were not successful [817, Reprinted with permission from Environmental Toxicology and Chemistry, Volume 14, Ou, L.-T., W. Jing and J.E. Thomas, "Biological and chemical degradation of ionic ethyllead compounds in soil." Copyright 1995 SETAC].

Laboratory and/or Field Analyses:

An ICP scan can be used for analyses of many metal additives including lead additives measured as total lead (see lead entry. Phosphates can be analyzed with total phosphate phosphorus and phenol additives as phenols. EDB, MTBE, 1,2 Dichoroethane can all be analyzed separately.

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

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

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

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

A standard TPH (Total Petroleum Hydrocarbon) analysis (EPA method 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 aromatic 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 compounds) 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.

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 compounds, 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].

Regardless of what lab methods are used, the investigator must take special precautions to prevent the escape of volatiles such as BTEX compounds 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].

Gasoline components showing up in GC chromatograms (whether state of the art GC/MS based on improved EPA Method 8270 [801] or more primitive GC/FID or GC/PID [804]) can be divided into three groups [801,804]:

> The first third includes relatively low boiling point (very volatile) lighter hydrocarbons such as some alkanes [804] and MTBE [801].
>
> The second third includes the still volatile but somewhat heavier BTEX hydrocarbons [801,804].
>
> The third third includes the heaviest (molecular weight greater than 110) and less volatile PAHs and alkyl PAHs [804] such as naphthalene and alkyl naphthalenes [801].

As gasoline spills age, the first third degrades first and the third third last, so as volatile MTBE and BTEX compounds disappear from soil (and appear in groundwater and air) the heavier PAHs become a greater percentage of the remaining petroleum contamination in soil [804].

If used as a measure of BTEX, the more lengthy scan referred to as standard EPA 8240 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 (like alkyl PAHs, alkyl benzenes are more resistant to degradation than parent compounds), MTBE and BTEX compounds, 1,2 Dichloroethane, alkyl lead isomers, and other compounds consistent with 1995 risk assessment needs. Enhanced 8240 scans are available from various commercial labs (Gregory Douglas, Arthur D. Little, Inc., Cambridge, Massachusetts, 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:

Alkyl benzenes common in oils:

isopropyl benzene:	detection limit (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

The California LUFT manual [465] discourages analyses for EDB in soils contaminated by gasoline spills, stating that EDB has wide uses other than gasoline [807].

The California LUFT manual [465] discourages analyses for organic lead contaminated soils related to gasoline spills, stating that most labs can measure only total, not organolead [807].

For more details on petroleum hydrocarbon analyses, see the Petroleum, General and Gasoline, General entries.

See also 1,2-dichloroethane entry and the toxicological profile for 1,2-dichloroethane available from ATSDR [931].