ENVIRONMENTAL CONTAMINANTS ENCYCLOPEDIA

ENTRY FOR BTEX AND BTEX COMPOUNDS

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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 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).

BTEX and BTEX Compounds (BTX, Analyses which Include Emphasis on Combinations of Benzene, Toluene, Ethyl Benzene, and Xylene compounds)

Brief Introduction:

NOTE: This section is intended to give an overview of BTEX (benzene, toluene, ethyl benzene, and xylenes) concerns and lab analyses. For specific toxicity information on the individual compounds in BTEX, see the individual benzene, toluene, ethyl benzene, and xylene entries.

Br.Class: General Introduction and Classification Information:

BTEX is a group of compounds including benzene, toluene, ethyl benzene, and xylenes. All are volatile organic compounds (VOCs) [903].

Motor fuels are complex organic mixtures comprised of hundreds of specific compounds. Indicator compounds are usually defined as those compounds which can be considered the most toxic and, the most mobile in soil and groundwater. For these reasons, many state cleanup standard or guidelines focus on benzene, toluene, ethylbenzene, and xylenes, commonly known as "BTEX or BTX." The relative mobility of these compounds is known, and they are widely recognized as the toxins of concern in fuels such as gasoline [497].

Br.Haz: General Hazard/Toxicity Summary:

The BTEX compounds represent some of the most hazardous components of gasoline. A variety of test are used to identify BTEX contamination (see the Laboratory section below for details).

Short term (acute) hazards of lighter, more volatile and water soluble aromatic compounds (such as benzenes, toluene, and xylenes) include potential acute toxicity to aquatic life in the water column (especially in relatively confined areas) as well as potential inhalation hazards.

Long term (chronic) potential hazards of lighter, more volatile and water soluble aromatic compounds include contamination of groundwater. Chronic effects of benzene, toluene, and xylene include changes in the liver and harmful effects on the kidneys, heart, lungs, and nervous system [609,764,765,767].

Except for short term hazards from concentrated spills,

BTEX compounds have been more frequently associated with risk to humans than with risk to non-human species such as fish and wildlife. This is partly because only very small amounts are taken up by plants, fish, and birds and because this volatile compound tends to evaporate into the atmosphere rather than persisting in surface waters or soils [764]. However, volatiles such as BTEX compounds can pose a drinking water hazard when they accumulate in ground water.

BTEX compounds are examples of hazardous substances commonly used in pesticides, but not listed on the label other than as "inerts" [549]. Although BTEX compounds such as toluene and xylenes are not officially recognized as part of the active ingredients of the pesticide containing it and are therefore part of the so-called "inerts," BTEX compounds are nevertheless far from "safe" at all concentrations to all life forms.

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

Certain carcinogenic effects have been associated with benzene [465,609,767] (see the Benzene entry for more details). BTEX compounds are often found in association with a mixture of PAH compounds, many of which are carcinogenic (see "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 some of the BTEX compounds [609,764,765,777] (see entries on individual compounds for more details).

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

Indicator compounds (such as BTEX) are usually defined as those compounds which are among the most acutely toxic and the most mobile in soil and groundwater [497]. See the individual benzene, toluene, ethyl benzene, and xylene entries for specific fate information.

BTEX compounds have the potential to move through soil and contaminate ground water, and their vapors are highly flammable and explosive [465].

At an aviation gasoline spill site in Traverse City, Michigan, a positive correlation was documented between significant rainfall events and increased concentrations

of slightly soluble organic compounds in the monitoring wells of the site [730]. Infiltrated water was determined to have transported organic constituents of the residual oil, specifically benzene, toluene, ethylbenzene, and ortho-xylene (BTEX), into the ground water beneath the water table, elevating the aqueous concentrations of these constituents in the saturated zone [730].

The biodegrability of MTBE in the subsurface is substantially slower than BTEX aromatic fuel components, due in part to the additive's tertiary bonds. It also tends to move faster. Therefore, towards the leading edge of a plume, MTBE's vertical distribution may be slightly deeper (and usually wider horizontally) than BTEX copounds (James Davidison, Alpine Environmental, Fort Collins, CO, personal communication, 1997; for details, see Davidson and Parsons, 1996. Remediating MTBE with current and emerging technologies. Proceedings of the Petroleum Hydrocarbons and Organic Chemicals in Groundwater Conference, November 13-15, 1996, Houston, pages 15-29).

Synonyms/Substance Identification:

No information found.

Associated Chemicals or Topics (Includes Transformation Products):

See also individual entries:

Benzene
Ethylbenzene
Toluene
Xylenes, Total

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

W.Low (Water Concentrations Considered Low):

No information found; see entries for individual BTEX compounds.

W.High (Water Concentrations Considered High):

Highest MTBE concentrations in surface water tend to be in marinas, where 2 cycle engines blow by MTBE along with gasoline. In a marina at California's Lake Shasta, concentrations as high as 84 ppb MTBE have been found along with BTEX concentrations of about 30 ppb (James Davidison, Alpine Environmental, Fort Collins, CO, personal communication, 1997).

W.Typical (Water Concentrations Considered Typical):

No information found; see entries for individual BTEX compounds.

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 entries for individual BTEX compounds.

W.Plants (Water Concentrations vs. Plants):

No information found; see entries for individual BTEX compounds.

W.Invertebrates (Water Concentrations vs. Invertebrates):

NOTE regarding the tables below from [684]:

The tables below contain results from toxicity tests conducted in closed systems with no air spaces. These conditions, of course, are unlike actual spill conditions in an open body of water, with the exception of: 1) the period of time immediately after the spill, and; 2) the un-evaporated solution of water and toxicants (the water soluble fraction, or WSF) just beneath the insoluble surface slick. Thus, given the controlled conditions of these toxicity tests, the values below are most useful when compared to other values in the same table (giving an idea of the compound's relative toxicity), or when compared to values from other tests conducted under the exact same conditions (personal communication, Kenneth Doe, Environment Canada, 1994).

The below table (reprinted with the permission of author Kenneth Doe) displays Acute toxicity of BTEX compounds to Artemia. These fluorescence tests were older Canadian methods using only the product indicated and would be only roughly comparable to other fluorescence values. Fluorescence methods are not particularly desirable when unknown or mixed oil products are of concern (ranges in parentheses) [684]. When you consider both that higher solubility leads to more bioavailability,

the following tables show that benzene has more potential for acute (short term) toxicity than the others listed (see the note below both tables). See also the "Petroleum, General" entry for toxicity comparison to other refined and crude oils.

HYDROCARBON	48-hr EC50 (% of WSF)	48-hr EC50 (Measured by Fluorescence in mg/L)
Benzene	4.6 (3.5-5.7)	67.7 (51.5-83.8)
Toluene*	6.9 (4.4-9.4)	35.2 (22.5-48)
Ethyl Benzene	8.5 (6.2-10.8)	9.2 (6.7-11.7)
p-Xylene*	15.0 (10.0-18.0)	18.4 (12.3-22.1)
o-Xylene	7.5 (5.5-9.4)	10.5 (7.7-13.1)
m-Xylene	7.0 (5.8-8.1)	7.2 (5.9-8.3)

* = Test Duration 24 hours

HYDROCARBON	48-hr LC50 (% of WSF)	48-hr LC50 (Measured by Fluorescence in mg/L)
Benzene	7.8 (6.3-9.2)	114.7 (92.7-135.3)
Toluene*	11.0 (9.4-12.6)	56.2 (48-64.3)
Ethyl Benzene	10.1 (7.3-13.0)	11.0 (7.9-14.1)
p-Xylene*	22.5 (18.0-32.0)	27.6 (22.1-39.2)
o-Xylene	16.2 (10.5-21.9)	22.6 (14.7-30.6)
m-Xylene	10.0 (8.0-12.0)	10.2 (8.2-12.3)

* = Test Duration 24 hours

The below table displays acute toxicity of BTEX compounds to Daphnia magna. Data from all valid replicates were combined (ranges in parentheses) [684]. Same remarks apply as for the table above.

HYDROCARBON	48-hr EC50 (% of WSF)	48-hr EC50 (Measured by Fluorescence in mg/L)
Benzene	0.81 (0.7-0.92)	12.9 (11.1-14.6)
Toluene	1.2 (1.0-1.8)	6.6 (5.5-9.8)
Ethyl Benzene	2.1 (1.8-3.2)	2.9 (2.5-4.4)
p-Xylene	2.5 (1.8-3.2)	4.7 (3.4-6.0)
o-Xylene	1.1 (0.56-1.8)	1.5 (0.78-2.5)
m-Xylene	2.7 (2.2-3.2)	4.1 (3.4-4.9)

48-hr LC50

HYDROCARBON	48-hr LC50 (% of WSF)	(Measured by Fluorescence in mg/L)
Benzene	5.9 (5.0-6.9)	88.9 (79.4-109.6)
Toluene	16.6 (10-32)	90.7 (54.6-174.8)
Ethyl Benzene	11.5 (9.1-13.9)	15.8 (12.5-19.1)
p-Xylene	18.0 (10-32)	33.7 (18.7-59.9)
o-Xylene	12.1 (7.7-16.5)	16.8 (10.7-22.9)
m-Xylene	17.4 (13.2-21.6)	26.5 (20.1-32.9)

NOTE regarding tables 1 and 2 above:
Based on measured concentrations (mg/L), m-xylene is the most toxic compound to Artemia. Another way to look at the toxicity of a compound is to consider its potency, that is, the amount a saturated solution can be diluted to (expressed as % of the WSF) and still produce the toxic effect. From this perspective, benzene would be the most toxic compound to Artemia since its LC50 (as % of WSF) is the lowest. Similarly for Daphnia magna, ethyl benzene and m-xylene are the most toxic compounds based on measured concentrations (mg/L), while benzene is the most toxic from a potency point of view [684].

W.Fish (Water Concentrations vs. Fish):

No information found; see entries for individual BTEX compounds.

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

No information found; see entries for individual BTEX compounds.

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

No information found; see entries for individual BTEX compounds.

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

No information found; see entries for individual BTEX compounds.

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

Sed.Low (Sediment Concentrations Considered Low):

No information found; see entries for individual BTEX compounds.

Sed.High (Sediment Concentrations Considered High):

No information found; see entries for individual BTEX compounds.

Sed.Typical (Sediment Concentrations Considered Typical):

No information found; see entries for individual BTEX compounds.

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 entries for individual BTEX compounds.

Sed.Plants (Sediment Concentrations vs. Plants):

No information found; see entries for individual BTEX compounds.

Sed.Invertebrates (Sediment Concentrations vs. Invertebrates):

No information found; see entries for individual BTEX compounds.

Sed.Fish (Sediment Concentrations vs. Fish):

No information found; see entries for individual BTEX compounds.

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

No information found; see entries for individual BTEX compounds.

Sed.Human (Sediment Concentrations vs. Human):

No information found; see entries for individual BTEX compounds.

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

No information found; see entries for individual BTEX compounds.

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

Soil.Low (Soil Concentrations Considered Low):

No information found; see entries for individual BTEX compounds.

Soil.High (Soil Concentrations Considered High):

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

CONTAMINANT	CONCENTRATION (ppm)
Total Petroleum Hydrocarbon (TPH) EPA Method 418.1	37,000
Total Petroleum Hydrocarbon (TPH) EPA Method 8015 modified for diesel	
Benzene	7.8
Toluene	1
Xylene	81
Ethylbenzene	29

Soil.Typical (Soil Concentrations Considered Typical):

No information found; see entries for individual BTEX compounds.

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 Total BTEX cleanup guidance levels range from 1 to 100 ppm [806].

Leaching potential analyses and additional lab analyses are required in California if petroleum contaminated sites have higher soil TPH levels than background or BTEX in soil above 0.3 mg/kg (ppm) [807].

Many state environmental regulations require the amount of BTEX in soils to be less than some regulated value [737]. In Texas, this value is 30 ppm by weight [737]. Contaminated soil above this level must be removed or treated so that groundwater contamination is avoided [737].

Less than 1000 mg/kg gasoline is considered to be a commonly accepted range of cleanup standards [736]. Contamination of drinking water supplies due to transport of toxic compounds from soils to groundwater is a legitimate concern that should be the focus of cleanup standards [736]. Regrettably, our current understanding of this phenomenon is perhaps the greatest obstacle to the development of appropriate cleanup standards [736].

Recent research on co-solubility/leaching phenomena is beginning to provide improved estimates of the release and transport of soil contaminants to groundwater [736]. However, further characterization of these complex processes is required, as is an improvement in our ability to apply our knowledge of such processes on a site-specific basis [736]. Largely because of this inadequate understanding of the leaching of organics from soils, dozens of different standards or guidelines currently exist at the state or local level for monitoring contaminated soils [736]. They range from "background" (Michigan), or low ppb levels (25 ppb benzene, Illinois), to tens or hundreds of parts per million (100 ppm TPH, Washington; 10-500 ppm total BTEX, Tennessee) [736]. In general, such values represent decisions based on the "best professional judgement" of the individuals or groups who have established them [736]. While each of these criteria exist to provide protection to groundwater supplies, because of the current scientific uncertainty surrounding the mobility of contaminants from soils, none are based on the direct knowledge of the relationship between soil contamination levels and leaching of contaminants

to the water table [736].

Until recently, most numerical criteria were expressed as maximum concentrations of certain gross contaminants such as oil and grease, total petroleum hydrocarbons, gasoline, or diesel fuel [738]. Aesthetic or phytotoxicity considerations were typically the basis for the development of such standards; little or no consideration was given to the human health risks associated with the contaminant levels [738]. Criteria developed more recently by a growing number of jurisdictions address specific constituents of motor fuels such as benzene, toluene, ethyl benzene, and xylenes (BTEX) [738]. These volatile aromatic compounds are generally considered to be of the greatest concern due to their mobility and toxicity [738]. Numerical criteria for these compounds are expressed either as maximum concentrations of individual constituents, or as the sum of benzene, toluene, ethyl benzene, and xylenes concentrations [738]. The derivation of these criteria is often based on multiples of background levels, detections limits, or allowable concentrations in groundwater [738].

Soil.Plants (Soil Concentrations vs. Plants):

Potential for plant uptake of BTEX is low and the half life of BTEX in soil is short, so except for perhaps phytotoxicity, a few hundred ppm of BTEX should not present much of a problem for crops [806].

Soil.Invertebrates (Soil Concentrations vs. Invertebrates):

No information found; see entries for individual BTEX compounds.

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

Soil cleanup levels for protection of wildlife, like protection levels for groundwater, will be very site specific for BTEX because of the variety of species that could be involved [806].

Soil.Human (Soil Concentrations vs. Human):

Benzene:
Health Based Cleanup Levels [806].

Residential: 2.5 ppm
Industrial: 14 ppm
Recreational: 250 ppm
Agricultural: 400 ppm
Groundwater: Site-Specific
Runoff: Site-Specific
Wildlife: Site-Specific

Toluene:
Health Based Cleanup Levels [806].

Residential: 2,000 ppm
Industrial: 10,000 ppm
Recreational: 170,000 ppm
Agricultural: 2,000 ppm
Groundwater: Site-Specific
Runoff: Site-Specific
Wildlife: Site-Specific

Xylene:
Health Based Cleanup Levels [806].

Residential: 300 ppm
Industrial: 1,400 ppm
Recreational: 25,000 ppm
Agricultural: 1,000 ppm
Groundwater: Site-Specific
Runoff: Site-Specific
Wildlife: Site-Specific

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

No information found; see entries for individual BTEX compounds.

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 entries for individual BTEX compounds.

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

No information found; see entries for individual BTEX compounds.

Tis.Invertebrates:

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

No information found; see entries for individual BTEX compounds.

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

No information found; see entries for individual BTEX compounds.

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

No information found; see entries for individual BTEX compounds.

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 entries for individual BTEX compounds.

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

No information found; see entries for individual BTEX compounds.

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

No information found; see entries for individual BTEX compounds.

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 entries for individual BTEX compounds.

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 entries for individual BTEX compounds.

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 entries for individual BTEX compounds.

Tis.Human:

A) Typical Concentrations in Human Food Survey Items:

No information found; see entries for individual BTEX compounds.

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 entries for individual BTEX compounds.

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

No information found; see entries for individual BTEX compounds.

Tis.Misc. (Other Tissue Information):

No information found; see entries for individual BTEX compounds.

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

No information found; see entries for individual BTEX compounds.

Interactions:

Although earlier information suggested that MTBE presence might tend to inhibit biodegradation of BTEX compounds, other information does not support this hypothesis (James Davidison, Alpine Environmental, Fort Collins, CO, personal communication, 1997).

Uses/Sources:

No information found; see entries for individual BTEX compounds.

Forms/Preparations/Formulations:

No information found; see entries for individual BTEX compounds.

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

According to the LUFT Manual [465], aromatic BTEX compounds represent 6.43 to 36.47% of gasoline by weight but account for less than 0.1% total weight of diesel fuel [809]. Since BTEX levels are typically 60 to 360 times higher in gasoline than in diesel, and since the clean up criteria suggested in the LUFT manual are based solely on the presence of BTEX, the LUFT manual typically allows much higher concentrations of diesel to remain in soil than gasoline [809].

The hazardous BTEX compounds typically constitute about 15% of unleaded gasolines [804]. Because of its relatively high water solubility, volatility, and toxicity, benzene, which makes up about 1% to 3% of gasoline, is normally targeted as a contaminant of concern [804].

Basic properties of BTEX [465]:

Benzene's water solubility is 1780 mg/L and it makes up 0.12 - 3.50 percent (by weight) of gasoline [465]. Benzene's California Department of Health Services Action Level (AL) is 0.7 ppb [465].

Toluene's water solubility is 535 mg/L and its weight percent in gasoline is 2.73 - 21.80 [465]. Toluene's California Dept. of Health Services Action Level is 100 ppb [465].

Ethylbenzene's water solubility is 152 mg/L and its weight percent in gasoline is 0.36 - 2.86 [465]. Ethylbenzene's Maximum Contaminant Level (MCL) Regulatory Threshold (Section 6444.5, Article 5.5, Division 4, Title 22 CCR) is 680 ppb [465].

Xylene's water solubility is 175 mg/L and its weight percent in gasoline is 0.68 - 2.86 for ortho-xylene, 1.77 - 3.87 for meta-xylene, and 0.77 -1.58 for para-xylene [465]. Xylene's Maximum Contaminant Level (MCL) Regulatory Threshold (Section 6444.5, Article 5.5, Division 4, Title 22 CCR) is 1750 ppb [465].

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

Basic fate characteristics of BTEX compounds have already been summarized in the following:

1) Br.Hazard, Br.Fate, and Laboratory sections of this entry.

2) Br.Hazard, Br.Fate, Fate.Detail, and Laboratory sections of the entries for individual BTEX compounds.

Case study [730]:

At an aviation gasoline spill site in Traverse City, Michigan, a positive correlation was documented between significant rainfall events and increased concentrations of slightly soluble organic compounds in the monitoring wells of the site [730]. Infiltrated water was determined to have transported organic constituents of the residual oil, specifically benzene, toluene, ethylbenzene, and ortho-xylene (BTEX), into the ground water beneath the water table, elevating the aqueous concentrations of these constituents in the saturated zone. It was concluded that water quality measurements are directly coupled to recharge events for the sandy type of aquifer with an overlying oil phase, which was studied in this work [730]. Ground water sampling strategies and data analysis need to reflect the effect of recharge from precipitation on shallow, unconfined aquifers where an oil phase may be present [730].

Laboratory and/or Field Analyses:

BTEX compounds are important in sampling strategies and contamination studies since: 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 [465].

For optimum risk or hazard assessment work, volatile compound lab methods with very low detection limits [such as EPA Method 8260 modified for Selective Ion Mode (SIM) Enhanced Detection Limits] should be used. The investigator should also specify the addition of any relevant compounds (such as related alkyl volatiles) suspected of being present but not typically found on the standard EPA scans. In concert with need to compare values with low benchmark concentrations, the regulatory requirements of States such as Wisconsin and the capabilities of better labs, detection limits should be as low as possible and in all cases no higher than 25 ppb [913] in soil, sediment, or tissue, and if possible no higher than 1 ppb (better labs can achieve 0.3 ppb) in water. Wisconsin requires a detection limit of 0.5 ug/L for all VOCs [923]. For more information on detection limits, see entries for various BTEX compounds: benzene, toluene, ethyl benzene, and xylenes.

For drinking water, in the past, EPA has recommended the following less rigorous methods for analyses of certain volatiles: Purge and trap capillary gas chromatography (EPA 502.2); gas chromatographic/mass spectrometry (EPA 524.2); purge and trap gas chromatography (EPA 503.1); gas chromatography/mass spectrometry (EPA 524.1); PQL= 0.005 mg/L [893].

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 [913,923], 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 [913,923].

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

BTEX compounds are most often measured in response to spills of gasoline and other light petroleum products. Draft decision Tree (dichotomous key) for selection of lab methods for measuring contamination from gasoline and other light petroleum products:

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 (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 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 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 decision tree key.

Variation in concentrations of organic contaminants may sometimes be due to the typically great differences in how individual investigators treat samples in the field and in the lab rather than true differences in environmental concentrations. This is particularly true for volatiles and for the relatively lighter semi-volatiles such as the naphthalene PAHs, which are so easily lost at various steps along the way. Contaminants data from different labs, different states, and different agencies, collected by different people, are often not very comparable. In fact, as mentioned in the disclaimers section at the top of this entry, 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].

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 an inappropriate methods, such BTEX scans when hydrocarbons other than BTEX hydrocarbons are the main suspects. This is one reason for using the NOAA expanded scan for PAHs and alkyl PAHs [828] (alkyl PAHs are much more resistent to degradation or volatility losses than BTEX compounds); or method 8260 [1013] for BTEX compounds modified for Selective Ion Mode (SIM) detection limits (to get lower detection limits), when dealing with oil spills. These types of rigorous scans are less prone to false negatives than many of the standard EPA scans for BTEX compounds (Roy Irwin, National Park Service, Personal Communication, 1997).

Other Details Related to BTEX methods:

Capillary gas chromatography with photo-ionization detection (PID) using a UV lamp emitting photons of the appropriate energy level discriminates effectively for aromatic hydrocarbons over non-aromatics. This is useful for determining the distribution of aromatics throughout the gasoline range. By convention, four groups of compounds are normally measured using EPA method 8020. They are benzene, toluene, ethyl benzene and the xylenes (BTEX). These can be measured with high precision in the ppb range of concentration. Difference in composition of various gasoline samples are easily noted by plotting their respective BTEX

components. Preferential loss of benzene and to a lesser degree toluene, is due in part to evaporation and in part to high water solubility of benzene and toluene [732].

Method 8020 is used to analyze for 8 aromatic VOCs. Samples are analyzed using direct injection or purge and trap methods. Groundwater must be analyzed by the purge and trap method. The method provides an optional GC column that is used for analyte configuration and that may help resolve analytes from interferences. There can be carry-over contamination with high and low level samples. Impurities may come from the purge and trap apparatus, organic compounds outgassing from the plumbing ahead of the trap, diffusion of VOCs through the sample bottle septum during shipping and storage, or from solvent vapors in the lab [731].

Capillary gas chromatography with photo-ionization detection (PID) using a UV lamp emitting photons of the appropriate energy level discriminates effectively for aromatic hydrocarbons over non-aromatics. This is useful for determining the distribution of aromatics throughout the gasoline range.

Although it doesn't call it TPH analyses and sometimes wants it in addition to TPH analyses, California sometimes allows the use of EPA method 8020 for BTX&E in soil [465]. Gas chromatograph, EPA method 8020, is appropriate for BTX or BTEX (benzene-toluene-xylene or benzene-toluene-xylene-ethyl benzene) if one knows for certain that gasoline is the contaminant; but it only works well measuring hydrocarbons within a certain size range (a range similar to gasoline). For example, jet fuel is a different range so you can't use BTX to measure jet fuel contamination. Some experts question whether or not BTEX or BTX analyses are appropriate when looking for modern gasoline or diesel fuels, since modern fuels are more highly refined and contain less BTX compounds (benzene, toluene, and xylenes, some of the most hazardous components of gasoline) (Roy Irwin, National Park Service, personal communication, 1994, based on conversations with various experts).

When the regulatory objective is protection of groundwater quality, it would seem most appropriate to focus on specific and more mobile compounds like BTEX as the best indices of potential groundwater risks. Research needs in this area would include the development of improved measurement techniques for motor fuels in soil and the assessment of the relationship (if any) between TPH values and mobility of specific contaminants. Validation of the merits of BTEX as indicator compounds is also needed (do standards for BTEX provide adequate levels of protection from exposure to other soluble organics in fuels?) [497].

See also: Lab sections in entries for individual BTEX compounds.

Description of EPA standard methods 8240 and 8260 from EPA EMMI Database on Lab methods [861]:

EPA Method 8240 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 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].

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

EPA description [861]:

> 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].

Other Misc. (mostly 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].

Other BTEX-related methods:

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

> Because BTX&E are more mobile than the remaining constituents, an analysis of BTX&E alone, without characterizing the entire contaminated soil profile, cannot be used to quantify the amount of fuel contamination in the soil. An analysis of Total Petroleum Hydrocarbons (TPH) should be included to check for other less mobile fuel constituents that could be absorbed onto the soil in higher concentrations. This additional analysis may serve as a check for the possibility that BTX&E have migrated to deeper depths.
>
> While TPH levels generally indicate fuel contamination, certain sites may have natural or historical use features (former oil field), that make interpretation difficult. Also, reported soil concentrations of volatile organic chemicals may vary with soil type. Complete recovery of volatiles during sample collection is difficult in sandy soil, due to losses from evaporation. Also, adsorption may limit extraction efficiency in clayey soils.
>
> In the leaching potential analysis suggested in the LUFT manual, that recommended detection limit for benzene, toluene, xylene, and ethylbenzene is 0.3 ppm for each compound. This 0.3 ppm value for BTX&E was determined to be a detection level that most laboratories can routinely achieve, based on a survey conducted by DHS.
>
> No BTX&E level is presented for the most sensitive sites (40

pts. or less). BTX&E levels should be below detection limits if TPH levels are 10 ppm or lower, therefore no BTX&E levels are presented to avoid the impression that detection limits are recommended as cleanup levels. Thus, the leaching potential analysis for sensitive sites relies exclusively on TPH values. If BTX or E are detectable, even though TPH is below 10 ppm, the site investigation should proceed to the General Risk Appraisal.

California also encourages the use of a modified EPA method 8015 or a alternative Department of Health Services method for TPH published in the LUFT manual [465], with added confirmation through use of a BTEX analyses.

If used as a measure of BTEX, the more lengthy scan referred to as standard EPA 8240 method often needs to "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).

EPA method 8020 PID is configured to have enhanced sensitivity to aromatics but also picks up aliphatics; a major problem with 8020 is that a compound may be identified as benzene when it is actually an aliphatic with the same retention time as benzene (false positive for benzene) [785]. EPA GC/MS method 8240 is superior to EPA method 8020 GC/PID in that 8240 is capable of identifying chemical compounds independent of compound retention times, thereby being less prone to false negatives for certain aromatics when in fact certain aliphatics are present instead [785]. Many identifications of benzene, xylene, toluene, and ethyl benzene as measured by GC/PID later turned out to be false (positives) when the samples were measured by GC/MS method 8240 [785]. When EPA method 8020 PID is used, it should be supplemented with EPA method 8240 [785].

The detectors used in a majority of portable analytical units used to detect contamination of petroleum hydrocarbons and various VOCs are primarily PID or FID detectors [803,804]. In addition to BTEX compounds, such portable units also respond to other VOCs [804].

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].

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