ENVIRONMENTAL CONTAMINANTS ENCYCLOPEDIA

BENZENE 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 (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).

Benzene (CAS number 71-43-2)

Brief Introduction:

Br.Class: General Introduction and Classification Information:

Benzene is a volatile organic compound (VOC) [868,903].

Common uses of benzene are as a solvent and as an intermediate for synthesis in the chemical and pharmaceutical industries. Approximately 86% of benzene production is used in the manufacturing of styrenes, phenols, cyclohexanes, and other organic chemicals. The remainder is used primarily in the manufacture of detergents, pesticides, solvents, and paint removers. Benzene occurs as a component of gasoline at less than 2% [368].

Benzene is usually present in gasoline and widely used in industry [335]. According to the USCG Emergency Response Notification System (1993), benzene was one of the most frequently spilled non-petroleum chemicals in U.S. waters, by number of notifications [635].

Benzene is a carcinogenic priority pollutant [302,446]. Benzene is a clear, colorless, flammable liquid that has limited solubility in water [261]. Although of limited solubility, benzene is one of the most soluble compounds in water of the petroleum hydrocarbons.

Br.Haz: General Hazard/Toxicity Summary:

Except for short term hazards from concentrated spills, this compound has 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 this compound have can pose a drinking water hazard when they accumulate in ground water.

Human populations are primarily exposed to benzene through inhalation of contaminated ambient air particularly in areas with heavy traffic and around filling stations. In addition, air close to manufacturing plants which produce or use benzene may contain high concentrations of benzene. Another source of exposure from inhalation is from tobacco smoke. Although most public drinking water supplies are free of benzene or contain <0.3 ppb, exposure can be very high

from consumption of contaminated sources drawn from wells contaminated by leaky gasoline storage tanks, landfills, etc. Although benzene has been detected in various food items, data is too scant to estimate exposure from ingestion of contaminated food. (IARC; Monograph, Some Industrial Chem and Dyestuffs 29: 99-106, 1982) [609].

Inhalation or ingestion of benzene causes acute irritation of the mucous membrane, producing restlessness and convulsions and sometimes resulting in death from respiratory failure [261].

While the major concern about the toxicity of benzene is its chronic effects, benzene is nevertheless an acutely toxic substance, with an estimated lethal oral dose being 1 teaspoon to 1 ounce for a normal adult [609]. Benzene is causally linked with central-nervous-system disorders [335].

Overall toxicity is "moderate" [870].

The U.S. Agency for Toxic Substances and Disease Registry (ATSDR) has recently completed a human health toxicity profile for benzene [767], which due to lack of time, has not yet been completely summarized herein. Toxicological profiles are revised and republished as necessary, but no less than once every three years [767]. For information regarding the update status of previously released profiles contact ATSDR at: Agency for Toxic Substances and Disease Registry Division of Toxicology/Toxicology Information Branch 1600 Clifton Road NE, E-29 Atlanta, Georgia [767].

Trimethyl benzenes are components of fuel oils and are CNS depressants for man or animals; see Air Force IRP guide for more details [875]. Although most other crude oil components biodegraded to non detectable levels following a spill in an experimentally polluted area, trimethyl benzenes (TMB) were detectable after three years [856].

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

EPA 1996 IRIS Database Information [893]:

> WEIGHT-OF-EVIDENCE CLASSIFICATION: Classification: A; human carcinogen.
>
> BASIS: Several studies of increased incidence of nonlymphocytic leukemia from occupational exposure, increased incidence of neoplasia in rats and mice exposed by inhalation and gavage, and some supporting data form the basis for this

classification.

ANIMAL CARCINOGENICITY DATA: Both gavage and inhalation exposure of rodents to benzene have resulted in development of neoplasia.

Classification of carcinogenicity: 1) evidence in humans: sufficient; 2) evidence in animals: sufficient; Overall summary evaluation of carcinogenic risk to humans is group 1: The chemical is carcinogenic to humans. /From table/ [IARC. Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man. Geneva: World Health Organization, International Agency for Research on Cancer,1972-PRESENT. (Multivolume work).,p. S7 120 (1987)] [609].

This compound is among 31 substances classified by the Chief of the Worker Health and Safety Unit of the California Department of Food and Agriculture as having "high carcinogenic or oncogenic potential" (Dr. Keith Maddy, personal communication).

Harmful amounts of benzene may be absorbed through the skin, causing leukemia and cancer [261]. A latent period of 2-50 years can occur between benzene exposure and development of the leukemia [606].

This compound has been treated as a carcinogen for model calculation purposes in some EPA risk-based (RBC and PRG) models [868,903].

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

Benzene is not teratogenic in experimental animals, although embryotoxic and fetotoxic effects have been reported at airborne concentrations less than those observed to be toxic to the mother rats [865].

Exposure to benzene has been associated with vaginal bleeding, hemorrhagic complications of pregnancy, heavy menstrual bleeding, menstrual cycle disorders, various obstetrical disorders including miscarriage, premature births, birth defects, and stillbirths [606,609].

Benzene crosses the human placenta, and similar levels are found in fetal and maternal blood [606,609].

In a few cases of benzene poisoning from high exposures during pregnancy, the fetus has seemed less sensitive than the mother [606].

Because of the poorly documented exposures and possible

mixed exposures, benzene is an unconfirmed human reproductive hazard [606,609].

Chromosome damage has been found among workers exposed to very low benzene levels [335]. Chromosome aberrations have been detected in animals and humans [368]. Occupational exposure to benzene has been associated with elevated frequencies of chromosome aberrations in peripheral lymphocytes (white blood cells) [606].

Human health issues related to this topic have been summarized by ATSDR [767].

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

Benzene does not bioconcentrate in aquatic biota to a significant degree [865]. Once the organisms are removed from contaminated water, benzene is rapidly cleared by the organisms [865]. Benzene is absorbed by any route of exposure and is metabolized via benzene epoxide to Phenol XREF and catechol, which are then conjugated with glutathione or glucuronic or sulfuric acids [366,606,609].

Accumulation of benzene is not expected to be important in any terrestrial organism and there are no reports indicating any significant bioconcentration in organisms or biomagnification in the food chain. The main route of exposure for terrestrial biota is, therefore, inhalation rather than exposure via the food chain [865].

Benzene does not persist in water or soil because it biodegrades and volatilizes rapidly to the atmosphere. It also does not persist in the atmosphere because it undergoes rapid photo-oxidation [865].

Biodegradation, principally under aerobic conditions, is the most important environmental fate process for water- and soil-associated benzene [767].

The biodegrability of MTBE (often found along with benzene in gasoline spills) in the subsurface is substantially slower than benzene and other 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 compounds such as benzene (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).

Environmental Fate/Exposure Summary [609]:

Benzene will enter the atmosphere primarily from fugitive emissions and exhaust connected with its use in gasoline. Another important source is emissions associated with its production and use as an industrial intermediate. In addition, there are discharges into water from industrial effluents and losses during spills. If benzene is released to soil, it will be subject to rapid volatilization near the surface and that which does not evaporate will be highly to very highly mobile in the soil and may leach to groundwater. It may be subject to biodegradation based on reported biodegradation of 24% and 47% of the initial 20 ppm benzene in a base-rich para-brownish soil in 1 and 10 weeks, respectively. It may be subject to biodegradation in shallow, aerobic groundwaters, but probably not under anaerobic conditions. If benzene is released to water, it will be subject to rapid volatilization; the half-life for evaporation in a wind-wave tank with a moderate wind speed of 7.09 m/sec was 5.23 hrs; the estimated half-life for volatilization of benzene from a model river one meter deep flowing 1 m/sec with a wind velocity of 3 m/sec is estimated to be 2.7 hrs at 20 deg C. It will not be expected to significantly adsorb to sediment, bioconcentrate in aquatic organisms or hydrolyze. It may be subject to biodegradation based on a reported biodegradation half-life of 16 days in an aerobic river die-away test. In a marine ecosystem biodegradation occurred in 2 days after an acclimation period of 2 days and 2 weeks in the summer and spring, respectively, whereas no degradation occurred in winter. According to one experiment, benzene has a half-life of 17 days due to photodegradation which could contribute to benzene's removal in situations of cold water, poor nutrients, or other conditions less conductive to microbial degradation. If benzene is released to the atmosphere, it will exist predominantly in the vapor phase. Gas-phase benzene will not be subject to direct photolysis but it will react with photochemically produced hydroxyl radicals with a half-life of 13.4 days calculated using an experimental rate constant for the reaction. The reaction time in polluted atmospheres which contain nitrogen oxides or sulfur dioxide is accelerated with the half-life being reported as 4-6 hours. Products of photooxidation include phenol,

nitrophenols, nitrobenzene, formic acid, and peroxyacetyl nitrate. Benzene is fairly soluble in water and is removed from the atmosphere in rain. The primary routes of exposure are inhalation of contaminated air, especially in areas with high traffic, and in the vicinity of gasoline service stations and consumption of contaminated drinking water.

Human health issues related to this topic have been summarized by ATSDR [767].

Synonyms/Substance Identification:

Information from HSDB [609]:

Benzeen (DUTCH) [609]
Benzen (POLISH) [609]
Benzin (OBS.) [607]
Benzine (OBS.) [607]

NOTE: According to one source, Benzine (Benzin) is not the same compound as benzene. Benzine is a heterogenous mixture of various hydrocarbons including pentanes, hexanes, heptanes, toluene, xylene, and small amounts of benzene [498].

Benzolene [607]
Benzol [609]
Benzole [609]
Benzolo (Italian) [609]
Bicarburet of hydrogen [609]
Carbon oil [607]
Cyclohexatriene [609]
Fenzen (Czech) [609]
Motor benzol [607]
NCI-C55276 [609]
Nitration benzene [607]
Polystream [609]
(6)Annulene [609]
Coal naphtha [609]
Phene [609]
Phenyl hydride [609]
Pyrobenzol [609]
Pyrobenzole [609]
RCRA waste number U019 [607]
UN1114 (DOT) [607]
AI3-00808 [609]
Caswell no 077 [609]
EPA pesticide chemical code 008801 [609]
Benzol 90 [609]

Molecular Formula [609]:

C6-H6

Associated Chemicals or Topics (Includes Transformation Products):

See also individual entries:

BTEX
Ethylbenzene
Toluene
Xylenes, Total

Major impurities are toluene and xylene. Others include: phenol, thiophene, carbon disulfide, acetylnitrile, and pyridine [609]. Alkyl benzenes such as ethylbenzene are also of concern.

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]:

Raw Materials, Intermediate Products, Final Products, and Waste Products Generated During Manufacture and Use:

- Cyclohexane
- Cyclohexene
- Cyclopropane
- Methylcyclohexene
- Phenols
- Toluene

A metabolite of benzene, 1,2,4-benzenetriol, has been shown to induce micronuclei and DNA damage in human lymphocytes and HL60 cells in culture. This metabolite forms a semiquinone radical and active oxygen, and may play a role in benzene-induced carcinogenesis [606]. The primary metabolite of benzene, benzene oxide, is mutagenic [606].

Metabolites [609]:

In human systems, benzene is metabolized through a variety of major & minor pathways. The primary site of action is the liver, where benzene is oxidized to phenol (hydroxybenzene), catechol (1,2-dihydroxybenzene), or quinol (1,4-dihydroxybenzene). Phenol is subsequently conjugated with inorganic sulfate to phenylsulfate, the other hydroxybenzenes are conjugated to a lesser extent, & all excreted in urine. Minor pathways incl further oxidation of catechol to hydroxyhydroquinol (1,2,4-trihydroxybenzene) or catabolism to cis, cis- or trans, trans-muconic acids, & phenol conjugation with glucuronic acid to form glucuronides, or with cysteine to produce 2-phenylmercapturic acid. [Clayton, G. D. and F. E. Clayton (eds.). Patty's Industrial Hygiene and

Toxicology: Volume 2A, 2B, 2C: Toxicology. 3rd ed. New York: John Wiley Sons, 1981-1982. 3273].

Yields n-acetyl-s-phenyl-cysteine in rat: Zbarsky SH, Young L; J Biol Chem 151: 587 (1943). Yields benzyl alcohol in guinea pigs: Sloane NH; Biochim Biophys Acta 107: 599 (1965); Gibson et al, Biochemistry 9: 1631 (1974). ... Yields cis-1,2-dihydro-1,2-dihydroxybenzene in pseudomonas: Gibson et al; Biochemistry 9: 1631 (1974); Gibson et al; Biochemistry 7: 2653 (1968). Phenol in pseudomonas & achromobacter: Claus D; J Gen Microbiol 36: 1 (1964). Yields cis,cis-muconic acid in rabbit: Park & Williams; Biochem J 54: 231 (1953). /From table/ [Goodwin, B.L. Handbook of Intermediary Metabolism of Aromatic Compounds. New York: Wiley, 1976.,p. B-4].

Metabolic products in rat ... Are phenol, hydroquinone, catechol, hydroxyhydroquinone, & phenylmercapturic acid. Conjugated phenols have been reported ... Except for a small amt of free phenol, all the phenolic metabolites were excreted in conjugated form. When (3)h-benzene was admin to mice, (3)H2O was also recovered from urine. [National Research Council. Drinking Water & Health Volume 1. Washington, DC: National Academy Press, 1977. 688].

In the rabbit, the major hydroxylation product of benzene was phenol, which along with some catechol and hydroquinone, was found in the urine conjugated with ethereal sulfate or glucuronic acid. [USEPA; Ambient Water Quality Criteria: Benzene p.C-11 (1980) EPA 440/5-80-018].

Unconjugated phenol has been found in mouse and rat urine after benzene administration. [USEPA; Ambient Water Quality Criteria: Benzene p.C-11 (1980) EPA 440/5-80-018].

The formation of benzene oxide, an epoxide of benzene is involved in the metabolism of benzene. This highly unstable intermediate rearranges non-enzymatically to form phenol. This step accounts for the occurrence of phenol as the major metabolite of benzene in urine. Catechol formation is thought to result from the hydration of benzene oxide by the enzyme epoxide hydratase followed by oxidation to catechol. It appears that catechol and phenol are formed by two distinctly different metabolic pathways. Hydroquinone is thought to result from a second passage of phenol through the mixed function oxidases. [Jerina D, Daly JW; Science 185: 573 (1974) as cited in USEPA; Ambient Water Quality Criteria: Benzene p.C-12 (1980) EPA 440/5-80-018].

Benzene, when administered sc at 880 mg/kg twice daily

for 3 days, decreased erythropoiesis much more markedly in DBA/2 mice than in C57BL/6 mice. Total urinary benzene metabolites and the % of the dose excreted in the urine were the same in both strains. Although the metabolic profile differed between the two strains, it was very similar when equitoxic doses of benzene were administered. The levels of both free and covalently bound benzene were higher in all organs of the DBA/2 mice. Phenol, hydroquinone, resorcinol, and catechol had no effect on erythopoiesis. [Snyder R et al; Adv Exp Biol 136A: 245-56 (1982)].

The urinary metabolites isolated by DEAE Sephadex A-24 anion-exchange chromatography from mice treated with radiolabeled benzene included phenol as the major component, as well as catechol, hydroquinone, and phenylmercapturic acid. The phenolic metabolites were excreted primarily as glucronides with the exception of a small amount of free phenol. [Longacre SL et al; Adv Exp Med Biol 136A: 307-17 (1982)].

A sensitive high performance liquid chromatography method is described which separates urinary metabolites from benzene-treated male CD-1 mice. Phenol, trans, trans-muconic acid and quino in the 48 hr urine, accounted, respectively for 12.8-22.8, 1.8-4.7 and 1.5-3.7% of the orally administered single dose of benzene (880, 440, and 220 mg/kg body wt). Catechol occurred in trace amounts. Trans, trans-muconic acid was identified and was unique to benzene as none was detected in urine of mice dosed orally with phenol, catechol, or quinol. The potential existence of a toxic metabolite in the form of an aldehyde precursor of muconic acid in vivo is discussed. [Gadel K et al; Xenobiotica 15: 211-20 (1985)].

In humans, phenol sulfate is the major metabolite of benzene until 400 mg/l levels are reached in the urine. Beyond that level, glucuronide conjugates are also present in the urine. [USEPA; Health Advisories for 25 Organics: Benzene p.19 (1987) PB 87-235578].

Male Wistar rats were tested to determine the effect of enzymes with different kinetic characteristics on the metabolism of benzene, in vitro. Kinetic analysis of the enzymes in the liver of rats fed a normal diet revealed the presence of two benzene hydroxylases with low Michaelis constant values of 0.01 millimolar and 0.07 millimolar, respectively. After 1 day of food deprivation, the isozyme with a constant equal to 0.01 millimolar disappeared while the activity of the second isozyme increased. Following the administration of phenobarbital there was evidence of a third benzene metabolizing enzyme in the liver of the animals exposed to benzene in concentrations ranging from 0.0055 to 6.25

millimolar, in vitro; the value of the Michaelis constant for this enzyme was equal to 4.5 millimolar and was not evident in control animals. Treatment with phenobarbital failed to affect the activity of the other low Michaelis constants of benzene hydroxylases identified in the liver of normal rats. Treatment with ethanol resulted in significant increase in the activity of both normally occurring benzene hydroxylases in the normal liver. [Nakajima T et al; Biochemical Pharmacol 36 (17): 2799-804 (1987)].

Mitoplasts (mitochondria with the outer membrane removed) from the bone marrow of rabbits were incubated sequentially with (3)H-labeled deoxyguanosine triphosphate and (14)C-labeled benzene to study the DNA adducts formed from benzene metabolites in mitochondria. Following isolation and isopycnic density gradient centrifugation in CsCl, the doubly labeled DNA was hydrolyzed to deoxynucleosides and separated on a Sephadex LH 20 column. At least seven deoxyguanosine adducts and one deoxyadenine adduct were present. [Snyder R et al; Arch Toxicol 60 (1-3): 61-4 (1987)].

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

W.Low (Water Concentrations Considered Low):

No information found.

W.High (Water Concentrations Considered High):

The highest reported mean concentration of benzene in Canadian effluents has been 65.3 ug/L, measured at an outfall from an organic chemicals industry [865].

Highest MTBE (additive often found along with benzene in gasoline spills) 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):

Concentration of benzene in Canadian surface waters are generally less than 1 ug/L. The mean concentration in untreated water measured in one study was 2 ug/L [865].

Information from HSDB [609]:

DRINKING WATER: 113 public supplies, 1976, 7 sites pos, avg of positive sites <0.2 ppb(1). 5 USA cities, 1974-5, 0-0.3 ppb(2). Contaminated drinking water wells in NY, NJ, CT, 30-300 ppb; highest concn in drinking water from surface source, 4.4 ppb(3). 3 surveys of community water supplies: 0 of 111 pos; 7 of 113 pos, mean 4 ppb; 4 of 16 pos (0.95 ppb-max)(4). USA Groundwater Supply Survey (GWS, 1982, finished drinking water), 466 samples selected at random from 1000 in survey, 0.6% pos, 3 ppb median, 15 ppb max(5). Wisconsin drinking water wells, data through Jun 1984, 1174 community wells, 0.34% pos, 617 private wells, 2.9% pos(6). [(1) Brass HJ et al; Drinking Water Qual Enhancement Source Prot pp. 393-416 (1977) (2) Coleman WE et al; Analysis and Identification of Organic Substances in Water. L Keith ed, Ann Arbor MI: Ann Arbor Press Chapt 21, pp. 305-27 (1976) (3) Burmaster DE; Environ 24: 6-13,33-6 (1982) (4) NAS; Drinking Water and Health, Vol 3 (1980) (5) Cotruvo JA; Sci Total Environ 47: 7-26 (1985) (6) Krill RM, Sonzogni WC; J Am Water Works Assoc 78: 70-5 (1986)].

GROUNDWATER: Chalk Aquifer (UK), 210 m from petrol storage, 1-10 ppb; Chalk Aquifer (UK), 120 m from petrol storage, >250 ppb; Chalk Aquifer (UK), 10 m from petrol storage, 1250 ppb; distances refer to benzene movement in groundwater(1). [(1) Tester DJ, Harker RJ; Water Pollut Control 80: 614-31 (1981)].

SURFACE WATER: 14 heavily industrialized with basins, 1975-1976, 20% samples >1 ppb and between 1 and 7 ppb(1). Lake Erie, 1975-6, 0-1 ppb, 1 of 2 sites positive; Lake Michigan, 1975-6, 0-7 ppb, 5 of 7 sites positive(2). 700 random sites in US, 1975, 5.4 ppb avg(3). US EPA STORET database, 1,271 samples, 15.0% pos, 5.0 ppb median(4). [(1) Ewing BB et al; Monitoring to Detect Previously Unrecognized Pollutants in Surface Waters. 75 pp. USEPA-560/6-77-015 (1977) (2) Konasewich D et al; Great Lake Water Qual Board (1978) (3) Kraybill HF; NY Acad Sci Annals 298: 80-9 (1977) (4) Staples CA et al; Environ Toxicol Chem 4: 131-42 (1985)].

SEAWATER: 5-15 parts per trillion Gulf of Mexico, 1977, unpolluted areas; 5-175 parts per trillion, Gulf of Mexico, 1977, anthropogenic influence(1). [(1) Sauer TC Jr; Org Geochem 3: 91-101 (1981)].

RAIN/SNOW: Detected in rainwater in Japan and in the UK (87.2 ppb)(1,2). [(1) Kato T et al; Yokohama Kokuritsu Daigaku Kankyo Kagaku Kenkyu

Senta Kiyo 6: 11-20 (1980) (2) IARC; Monograph. Some Industrial Chemicals and Dyestuffs. 29: 99-106 (1982)].

Benzene occurs in both ground water and surface public water supplies with higher levels occurring in ground water supplies. Based upon Federal drinking water surveys, approximately 1.3% of all ground water systems are estimated to contain benzene at levels greater than 0.5 ug/l. The highest level reported in the surveys for ground water was 80 ug/l. Approximately 3% of all surface water system are estimated to be contaminated at levels higher than 0.5 ug/l. None of the systems are expected to contain levels higher than 5 ug/l. [USEPA; Health Advisories for 25 Organics: Benzene p.19 (1987) PB 87-235578].

Effluents Concentrations [609]:

Wastewater from coal preparation plants, 0.3-48 ppb(1); wastewater from plants which manufacture or use benzene <1-179 parts per trillion(1); stack emissions from coking plants (Czechoslovakia), 15-50 ppm(2); stack emission estimates from chemical plants using emissions and worst case modeling at 150 m from source, less than or equal to 5 ppm(3). Groundwater at 178 CERCLA hazardous waste sites, 11.2% pos(4). US EPA STORET database, 1,474 samples, 16.4% pos, 2.50 ppb median(5). [(1) IARC; Monograph. Some Industrial Chemicals and Dyestuffs 29: 99-106 (1982) (2) SRI; Human Exposure to Atmospheric Benzene, Menlo Park, CA: SRI, Center for Resource and Environmental (1977) (3) Fentiman AF et al; Environmental Monitoring Benzene pp. 105-10 (PB-295641) (1979) (4) Plumb H Jr; Ground Water Monit Rev 7: 94-100 (1987) (5) Staples CA et al; Environ Toxicol Chem 4: 131-42 (1985)].

Industries in which mean or max levels in raw wastewater exceeded 1 ppm are (number of samples, percent pos, mean, max, in ppm): raw wastewater: auto and other laundries (20 samples, 70% pos, <1.4 ppm mean, 23 ppm max), iron and steal manufacturing (mfg) (9 samples, 77.8% pos, <8.0 mean, 46 max), aluminum forming (32 samples, 56.2% pos, 0.70 mean, 2.1 max), photographic equipment/supplies (48 samples, 54.2% pos, 0.16 mean, 2.1 max), pharmaceutical mfg (9 samples, 100% pos, 12 mean, 87 max), organic chemical/plastics mfg (number of samples not reported (NR), 63 detections, 22, NR), paint and ink formulation (36 samples, 63.9% pos, 1.2 mean, 9.9 max), petroleum refining (11 samples, number of pos NR, <0.10, 2.4), rubber processing (4

samples, 100% pos, 0.60 mean, 3.4 max), timber products processing (14 samples, 92.9% pos, 0.2 mean, 2.8 max); treated wastewater: auto and other laundries (4 samples, 50% pos, 0.1 ppm mean, 0.2 ppm max), iron and steal manufacturing (mfg) (13 samples, 76.9% pos, <14 mean, 120 max), aluminum forming (21 samples, 81.0% pos, <0.0058 mean, 0.040 max), photographic equipment/supplies (4 samples, 100% pos, 0.016 mean, 0.021 max), pharmaceutical mfg (6 samples, 100% pos, 1.8 mean, 10 max), organic chemical/plastics mfg (number of samples not reported (NR), 42 detections, 26, max NR), paint and ink formulation (24 samples, 62.5% pos, 0.39 mean, 3.8 max), petroleum refining (13 samples, NR, NR, 0.012), rubber processing (5 samples, 100% pos, <0.0077 mean, 0.010 max), timber products processing (5 samples, 60% pos, 0.010 mean, 0.033 max)(1). [(1) US EPA; Treatability Manual. p. I.9.1-1 to I.9.1-5 USEPA-600/2-82-001A (1981)].

Industrial sources of wastewater pollution from benzene in ug/l (avg; range): coal mining (2.6; 0-15), textile mills (<5; 0-200), timber products processing (350; 0-2,800), petroleum refining (>100; ND), paint and ink formulation (1,200; 0-9,900), gum and wood chemicals (180; 0-710), rubber processing (610; 0-3,400), auto and other laundries (840; 0-23,000), pharmaceuticals (220; 0-2,100), ore mining and dressing (2.1; 0-4.2), steam electric power (45, ND), foundries (200; ND), leather tanning and finishing (19; 0-150), nonferrous metals (11; 0-160), iron and steel (2,000; 0-43,000). /From table/ [Patterson JW; Industrial Wastewater Treatment Technolgy 2nd Edition p.309 (1985)].

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):

EPA 1996 IRIS database information, Ambient Water Quality Criteria for Aquatic Organisims [893]:

Acute Freshwater: 5.3E+3 ug/L LEC [893].

Older reference: Freshwater Acute Criteria: Insufficient data to develop

criteria. Lowest Observed Effect Level: 5300 ug/L [689].

Chronic Freshwater: None Given [893].

Marine Acute: 5.1E+3 ug/L LEC [893].

Older reference: Marine Acute Criteria: Insufficient data to develop criteria. Lowest Observed Effect Level: 5100 ug/L [446].

Marine Chronic: 7.0E+2 ug/L LEC [893].

Older reference: Marine Chronic Criteria: Insufficient data to develop criteria. Lowest Observed Effect Level: 700 ug/L [446].

Reference: 45 FR 79318 (11/28/80)

Contact: Criteria and Standards Division / OWRS / (202)260-1315

Discussion: The values that are indicated as "LEC" are not criteria, but are the lowest effect levels found in the literature. LECs are given when the minimum data required to derive water quality criteria are not available.

For aquatic biota, the leopard frog was the most sensitive organism identified in long-term tests. The reported LC50 was 3.7 mg/L for continuous 9-day exposure of the embryo-larval stages [865].

The Netherlands' Maximum Permissible Concentration (MPC) for the protection of all species in an aquatic ecosystem is 2400 ug/L [655].

NOTE: For carcinogens (like benzene), the MPC is based on a one-in-one-million acceptable risk of cancer.

The Netherlands' Negligible Concentration (NC) for benzene is 1% of the MPC, or 24 ug/L [655].

However, when harmonization between media is considered, the Netherlands benchmarks are lower:

The Netherlands' Harmonized (between media) Maximum Permissible Concentration (MPC) for benzene in water is 240 ug/L [655].

Note: Harmonization takes into account whether or not the MPC in one media (such as soil) would lead to exceeding the MPC in another media (such as air, water, or sediment) [655].

The Netherlands' Harmonized (between media) Negligible Concentration (NC) for benzene in water is 1% of the MPC, or 2.4 ug/L [655].

Oak Ridge National Lab, 1994: Ecological Risk Assessment Freshwater Screening Benchmarks for concentrations of contaminants in water [649]. For a definition of meaning of each benchmark, see entry entitled: Benchmarks, Ecological Risk Assessment Screening Benchmarks. To be considered unlikely to represent an ecological risk, field concentrations should be below all of the following benchmarks (ug/L) [649]:

CAS 71-43-2 BENZENE:

NATIONAL AMBIENT WATER QUALITY CRITERION - ACUTE: no information found

NATIONAL AMBIENT WATER QUALITY CRITERION - CHRONIC: no information found

SECONDARY ACUTE VALUE: 815

SECONDARY CHRONIC VALUE: 45.5

LOWEST CHRONIC VALUE - FISH: 8250

LOWEST CHRONIC VALUE - DAPHNIDS: > 98,000

LOWEST CHRONIC VALUE - NON-DAPHNID INVERTEBRATES: no information found

LOWEST CHRONIC VALUE - AQUATIC PLANTS: 525,000

LOWEST TEST EC20 - FISH: 21

LOWEST TEST EC20 - DAPHNIDS: no information found

SENSITIVE SPECIES TEST EC20: no information found

POPULATION EC2O: 229

Canada's Interim Assessment Criterion for benzene in water is 0.5 ug/L [656].

NOTE: a) For most of the organic chemical parameters in [656], criteria are based on analytical detection limits; b) criterion is considered "Interim" since complete supporting rationale do not exist.

Canada's Remediation Criteria for benzene for freshwater aquatic life is 300 ug/L [656].

NOTE: as of Sept 1991, this was a tentative water quality guideline.

W.Plants (Water Concentrations vs. Plants):

LC50 Chlorella algae 525 mg/l

W.Invertebrates (Water Concentrations vs. Invertebrates):

LC50 for Aedes aegypti (mosquito) was 200 mg/L (ppm) for a 48-hr exposure [998].

LC50 for Culex pipiens (mosquito) was 71 mg/L for a 48-hr exposure [998].

LC50 for Asellus aquaticus (aquatic sowbug) was 120 mg/L for a 48-hr exposure [998].

LC50s for Brachionus calyciflorus (rotifer) were >1 mg/L and >1000 mg/L for 24-hr exposures [998].

LC50 for Diaptomus forbesi (Calanoid copepod) was 710 mg/L for a 96-hr exposure [998]

LC50 for Chironomus thummi (midge) was 100 mg/L for a 48-hr exposure [998].

LC50 for Cloeon dipterum (mayfly) was 34 mg/L for a 48-hr exposure [998].

LC50 for Nemoura cinerea (stonefly) was 130 mg/L for a 48-hr exposure [998].

LC50 for Ischnura elegans (dragonfly) was 10 mg/L for a 48-hr exposure [998].

LC50 for Hydra oligactis (Hydra) was 34 mg/L for a 48-hr exposure [998].

LC50 for Lymnaea stagnalis (great pond snail) was 230 mg/L for a 48-hr exposure [998].

LC50s for Palaemonetes pugio (Daggerblade grass shrimp) were 43.5 and 33.0 mg/L for 24- and 48-hr

exposures, respectively [998].

LC50 for Crassostrea gigas (Pacific oyster) was 377 mg/L for a 48-hr exposure [998].

LC50s for Katelysia opima (marine bivalve) were 225, 205, 195 and 190 mg/L for 24-, 48-, 72- and 96-hr exposures, respectively [998].

LC50s for Daphnia magna (water flea) were 250 and 1130 mg/L for 24-hr exposures, and ranged from 200 to 682 mg/L for 48-hr exposures [998].

LC50 for Daphnia pulex (water flea) was 15.0 mg/L for a 96-hr exposure [998].

LC50 for Ceriodaphnia dubia (water flea) was 18.4 mg/L for a 24-hr exposure [998].

LC50 for Dugesia lugubris (Turbellarian, flatworm) was 74 mg/L for a 48-hr exposure [998].

Information from HSDB [609]:

> LC50 Palaemonetes pugio (grass shrimp) 27 ppm/96 hr /Conditions of bioassay not specified/ [Verschueren, K. Handbook of Environmental Data of Organic Chemicals. 2nd ed. New York, NY: Van Nostrand Reinhold Co., 1983. 241].
>
> LC50 Cancer magister (crab larvae) stage 1, 108 ppm/96 hr /Conditions of bioassay not specified/ [Verschueren, K. Handbook of Environmental Data of Organic Chemicals. 2nd ed. New York, NY: Van Nostrand Reinhold Co., 1983. 241].
>
> LC50 Crangon franciscorum (shrimp) 20 ppm/96 hr /Conditions of bioassay not specified/ [Verschueren, K. Handbook of Environmental Data of Organic Chemicals. 2nd ed. New York, NY: Van Nostrand Reinhold Co., 1983. 241].
>
> TLm Brine shrimp 66 mg/L/24 hr, 21 mg/L/48 hr /Conditions of bioassay not specified/ [Verschueren, K. Handbook of Environmental Data of Organic Chemicals. 2nd ed. New York, NY: Van Nostrand Reinhold Co., 1983. 241].

W.Fish (Water Concentrations vs. Fish):

LC50s for Carassius auratus (goldfish) were 34.42,

34.42 and 34.42 mg/L for 24-, 48- and 96-hr exposures, respectively [998].

LC50s for Clupea harengus pallasi (Pacific herring) ranged from 20 to 25 mg/L for 48-hr exposures, and from 40 to 45 mg/L for 96-hr exposures [998].

LC50s for Gambusia affinis (mosquitofish) were 395, 395 and 386 mg/L for 24-, 48- and 96-hr exposures, respectively [998].

LC50s for Lepomis macrochirus (bluegill) were 20 and 22.49 mg/L for both 24- and 48-hr exposures, and were 22.49 and 100 mg/L for 96-hr exposures [998].

LC50s for Oncorhynchus gorbuscha (pink salmon) ranged from 5.28 to 339 ul/L (ppm) for 96-hr exposures, with most values below 18 ul/L [998].

LC50s for Oncorhyncus kisutch (Coho salmon, silver salmon) were 9.8, 14.09 and 542 ul/L (ppm) for 96-hr exposures [998].

LC50s for Oncorhyncus mykiss (rainbow trout, donaldson trout) were 56.0 mg/L (ppm) for a 48-hr exposure, and 5.3, 5.9 and 9.2 mg/L for 96-hr exposures [998].

LC50s for Oncorhyncus nerka (sockeye salmon) were 10.76 and 5.5 ul/L (ppm) for 96-hr exposures [998].

LC50s for Oryzias latipes (Medaka, high-eyes) were 54, 70 and 74 mg/L for 24-hr exposures, and 54, 70, 74 and 250 mg/L for 48-hr exposures [998].

LC50s for Pimephales promelas (fathead minnow) were: 35.56 and 34.42 mg/L for 24-hr exposures; 32.00, 35.08 and 84.00 mg/L for 48-hr exposures; 12.60, 15.59, 24.6, 32.00 and 33.47 mg/L for 96-hr exposures; and 14.01 mg/L for a 7-day exposure. The lowest-observed-effect-concentration (LOEC) for death in fathead minnows was 17.2 mg/L, and the no-observed-effect-concentration (NOEC) for death was 10.2 mg/L 998].

Information from HSDB [609]:

> LC50 Morone saxatilis (bass) 5.8 to 10.9 ppm/96 hr /Conditions of bioassay not specified/ [Verschueren, K. Handbook of Environmental Data of Organic Chemicals. 2nd ed. New York, NY: Van Nostrand Reinhold Co., 1983. 241].

LC50 Poecilia reticulata (guppy) 63 ppm/14 days /Conditions of bioassay not specified/ [Verschueren, K. Handbook of Environmental Data of Organic Chemicals. 2nd ed. New York, NY: Van Nostrand Reinhold Co., 1983. 241].

LC50 Salmo trutta (brown trout yearlings) 12 mg/L/1 hr (static bioassay) [Verschueren, K. Handbook of Environmental Data of Organic Chemicals. 2nd ed. New York, NY: Van Nostrand Reinhold Co., 1983. 241].

LD50 Carassius auratus (goldfish) 46 mg/l/24 hr (modified ASTM D 1345) [Verschueren, K. Handbook of Environmental Data of Organic Chemicals. 2nd ed. New York, NY: Van Nostrand Reinhold Co., 1983. 241].

LD100 Lepomis macrochirus (bluegill sunfish) 34 mg/l/24 hr /Conditions of bioassay not specified/ [Verschueren, K. Handbook of Environmental Data of Organic Chemicals. 2nd ed. New York, NY: Van Nostrand Reinhold Co., 1983. 241].

LD100 Lepomis macrochirus (bluegill sunfish) 60 mg/l/2 hr /Conditions of bioassay not specified/ [Verschueren, K. Handbook of Environmental Data of Organic Chemicals. 2nd ed. New York, NY: Van Nostrand Reinhold Co., 1983. 241].

TLm Pimephales promelas (fathead minnow) 35.5 to 33.5 mg/l/24 hr, 96 hr (soft water) /Conditions of bioassay not specified/ [Verschueren, K. Handbook of Environmental Data of Organic Chemicals. 2nd ed. New York, NY: Van Nostrand Reinhold Co., 1983. 241].

TLm Pimephales promelas (fathead minnow) 24.4 to 32 mg/l/24 hr, 96 hr (hard water) /Conditions of bioassay not specified/ [Verschueren, K. Handbook of Environmental Data of Organic Chemicals. 2nd ed. New York, NY: Van Nostrand Reinhold Co., 1983. 241].

TLm Bluegill 22.5 mg/l/24 hr, 96 hr (soft water) /Conditions of bioassay not specified/ [Verschueren, K. Handbook of Environmental Data of Organic Chemicals. 2nd ed. New York, NY: Van Nostrand Reinhold Co., 1983. 241].

TLm Carassius auratus (goldfish) 34.4 mg/l/24 hr, 96 hr (soft water) /Conditions of bioassay

not specified/ [Verschueren, K. Handbook of Environmental Data of Organic Chemicals. 2nd ed. New York, NY: Van Nostrand Reinhold Co., 1983. 241].

TLm Lebistes reticulata (guppy) 36.6 mg/l/24 hr, 96 hr (soft water) /Conditions of bioassay not specified/ [Verschueren, K. Handbook of Environmental Data of Organic Chemicals. 2nd ed. New York, NY: Van Nostrand Reinhold Co., 1983. 241].

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

LC50 for Ambystoma mexicanum (Mexican axolotl salamander) was 370 mg/L (ppm) for a 48-hr exposure [998].

For aquatic biota, the leopard frog was the most sensitive organism identified in long-term tests. The reported LC50 was 3.7 mg/L for continuous 9-day exposure of the embryo-larval stages [865].

LC50 Clawed toad (3-4 wk after hatching) 190 mg/l/48 hr /Conditions of bioassay not specified/ [Verschueren, K. Handbook of Environmental Data of Organic Chemicals. 2nd ed. New York, NY: Van Nostrand Reinhold Co., 1983. 241] [609].

Oak Ridge National Lab, 1994: Risk Assessment Screening Benchmarks for Wildlife derived from No-Observed-Adverse-Effect (NOAEL) levels (see Tis.Wildlife, B) for these). To be considered unlikely to represent an ecological risk, water concentrations should be below the following benchmarks for each species present at the site [650]:

SPECIES	WATER CONCENTRATION (ppm)
Mouse (test species)	0.00000
Short-tailed Shrew	150.61300
Little Brown Bat	260.31800
White-footed Mouse	97.33600
Meadow Vole	170.35500
Cottontail Rabbit	80.72200
Mink	83.70800
Red Fox	59.74100
Whitetail Deer	33.42600

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

Human Health Water Quality Criteria (10E-6 Risk Level for Carcinogens):

IRIS 1996: Ambient Water Quality Criteria for Human Health Considering Water & Fish Routes of Exposure: 6.6E-1 ug/liter [893].

Older reference: published Criteria for Water and Organisms: 0.66 ug/L [689].

IRIS 1996 EPA: Ambient Water Quality Criteria for Human Health Considering Only Fish Ingestion Route of Exposure: 4.0E+1 ug/liter [893].

Older reference: published Criteria for Organisms Only: 40 ug/L [689].

EPA 1996 IRIS 1996 Value for MCL: Value: 0.005 mg/L Reference: 52 FR 25690 (07/08/87); 56 FR 30266 (07/01/91)[893].

Several older refernces gave the same concentration: Drinking Water MCL: 5.0 ug/L [302,446]. Maximum contaminant level (MCL) for benzene at 0.005 mg/l [609, 52 FR 25690 (7/8/87)].

Criteria Federal Register Notice Number: 45 FR 79326 [302,446].

MCLG value, EPA, 1996: Maximum contaminant level goal or MCLG means the maximum level of a contaminant in drinking water at which no known or anticipated adverse effect on the health of persons would occur, and which allows an adequate margin of safety. Maximum contaminant level goals are nonenforceable health goals. The MCLG for benzene is 0.0 mg/l [609,893, 40 CFR 141.50 (7/1/87), also 50 FR 46880 (11/13/85)].

IRIS Discussion: An MCLG of zero mg/L for benzene is proposed based on carcinogenic effects. In humans, exposure to benzene is associated with myelocytic anemia, thrombocytopenia and leukemia (acute myelogenous and monocytic leukemia). In animals, an increase in tumors and leukemia have been reported. EPA has classified benzene in Group A: sufficient evidence from epidemiological studies [893].

USEPA has estimated that excess upper-bound lifetime cancer risks of 10-4, 10-5, and 10-6 correspond to benzene in drinking water at concentrations of 70, 7 and 0.7 ug/l, respectively. [609, USEPA; Health Advisories for 25 Organics: Benzene p.26 (1987) PB 87-235578].

EPA IRIS 1996 Unit Risk: 8.3E-7 per ug/liter [893]. The unit risk is the quantitative estimate in terms of risk per ug/L drinking water [893]. The unit risk estimate is the geometric mean of four ML point estimates using pooled data from the Rinsky et al. (1981) and Ott et al. (1978) studies, which was then adjusted for the results of the Wong et al. (1983) study as described in the additional comments section for inhalation data. The unit risk should not be used if the water concentration exceeds 1E+4 ug/L, since above this concentration the unit risk may not be appropriate [893].

Taste threshold in water is 0.5-4.5 mg/l. [609,765] See also: USEPA; Supplement to Development Doc: Haz Subset Regs Sect 311, FWPCA, (1975) EPA 440/9-75-009.

Note: Before citing a concentration as EPA's water quality criteria, it is prudent to make sure you have the latest one. Work on the replacement for the Gold Book [302] was underway in March of 1996, and EPA IRIS database [893] is updated monthly.

Preliminary remediation goal (PRG) for tap water, EPA Region 9, 1995 [868]: 3.9E-01 ug/L [868].

The California State Department of Health Services Action Limit is 0.700 ug/L [767,859]. Many other states have standards of 1 ug/L, zero, or non-detected [767].

Other Drinking water standards [859]:

The U.S. EPA 1-day and 10-day health advisories for a 10-kg child consuming 1 L of water per day are both 235 ug/L.

The Florida State Maximum Contaminant Level (MCL) is 1.000 ug/L.

The Maximum Acceptable Concentration (MAC) for

Canada's Health and Welfare Department and for Ontario's Ministry of the Environment is 0.005 mg/L.

The U.S. National Academy of Science and NIOSH levels of a contaminant in drinking water at which adverse health effects would not be anticipated for seven days (also known as SNARL7) are both 250 ug/L.

The World Health Organization (WHO) Guideline Value is 10 ug/L (based on acceptable risk of <1 additional case cancer per 100,000 (1xE-5) people, and assuming daily water consumption of 2 L per day for a 70 kg man).

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

Toxic pollutant designated pursuant to section 307(a)(1) of the Clean Water Act and is subject to effluent limitations [609, 40 CFR 401.15, 7/1/87)].

Designated as a hazardous substance under section 311(b)(2)(A) of the Federal Water Pollution Control Act and further regulated by the Clean Water Act Amendments of 1977 and 1978. These regulations apply to discharges of this substance [609, 40 CFR 116.4, 7/1/87].

Industrial discharge, disposal of products containing benzene, and gasoline leaks from underground storage tanks can release benzene into water and soil [767].

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

Sed.Low (Sediment Concentrations Considered Low):

NY: no appreciable contamination: less than 0.014 ug/kg dry weight [761].

Soil criteria for evaluating the severity of contamination under the Dutch Soil Cleanup (Interim) Act (1982): 0.1 ppm indicates a background level for benzene [347].

Sed.High (Sediment Concentrations Considered High):

Benzene was detected in 3.3 % of urban-bay samples from the Puget Sound area. The mean concentration was 3.03 ug/kg dry weight (ppb), while the median concentration was 3 ug/kg (ppb) [852]. Note: these values based on only four samples where benzene was detected.

NOTE: The above values are not normalized for total organic carbon (TOC) content.

Analyses of sewage sludges from 50 publicly owned treatment works by the U.S. Environmental Protection Agency (1985): The mean concentration of benzene was 1.46 ppm (dry weight) [347].

NY: medium contamination: 0.014 to 10 ug/kg dry weight; high contamination, greater than 10 ug/kg dry wt. [761].

Sed.Typical (Sediment Concentrations Considered Typical):

Benzene was detected in 67% of non-urban-bay samples from the Puget Sound area. The mean concentration was 0.11 ug/kg dry weight (ppb), while the median concentration was 0.105 ug/kg (ppb) [852].

NOTE: The above values are not normalized for total organic carbon (TOC) content.

SEDIMENT: Surface sediments in Walvis Bay (off Capetown, SA)0-20 ppb(2). US EPA STORET database, 355 samples, 9% pos, <5.0 ppb median(3). [(2) Whelan JK et al; Geochim Cosmochim Acta 44: 1767-85 (1980) (3) Staples CA et al; Environ Toxicol Chem 4: 131-42 (1985)] [609].

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):

Based on equilibrium partitioning, the Netherlands' Maximum Permissible Concentration (MPC) for the protection of all sediment-dwelling organisms is 9.5 mg/kg dry weight [655]. For carcinogens (like benzene), the MPC is based on a one-in-one-million acceptable risk of cancer.

However, when harmonization between media is considered, the MPC is 10 times lower:

The Netherlands' Harmonized (between media) Maximum Permissible Concentration (MPC) for benzene in sediment is 0.95 mg/kg [655].

Note: Harmonization takes into account whether or not the MPC in one media (such as soil) would lead to exceeding the MPC in another

media (such as air, water, or sediment) [655].

Based on equilibrium partitioning, the Netherlands' Negligible Concentration (NC) for benzene is 1% of the MPC, or 0.095 mg/kg dry weight [655]. Considering harmonization factors, the NC is 0.0095 mg/kg [655].

Oak Ridge National Lab, 1994: Risk Assessment Screening Benchmarks for Sediment Concentrations. To be considered unlikely to represent an ecological risk, field concentrations should be below all of the following benchmarks in mg/kg (ppm) dry weight [652]:

0.052 is the ESTIMATED EQUIVALENT SEDIMENT QUALITY CRITERION at 1% Organic Carbon

Sed.Plants (Sediment Concentrations vs. Plants):

No information found.

Sed.Invertebrates (Sediment Concentrations vs. Invertebrates):

No information found.

Sed.Fish (Sediment Concentrations vs. Fish):

No information found.

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

No information found.

Sed.Human (Sediment Concentrations vs. Human):

No information found.

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

A mixed culture consortia obtained from subsurface sediments degraded 1 mg/L benzene in water to below detectable limits (detection limit not given) by a continuously recycled bioreactor within 8-10 days [767]. For details, see Fate.Detail section below.

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

Soil.Low (Soil Concentrations Considered Low):

No information found.

Soil.High (Soil Concentrations Considered High):

No information found.

Soil.Typical (Soil Concentrations Considered Typical):

SOIL: Soil near factories where benzene was used or produced, 2-191 ug/kg(1). [(1) IARC; Monograph. Some Industrial Chemicals and Dyestuffs 29: 99-106 (1982)] [609].

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):

Based on equilibrium partitioning, the Netherlands' Maximum Permissible Concentration (MPC) for the protection of all soil-dwelling organisms is 9.5 mg/kg dry weight [655].

However, when harmonization between media is considered, the MPC is 10 times lower:

The Netherlands' Harmonized (between media) Maximum Permissible Concentration (MPC) for benzene in soil is 0.95 mg/kg [655].

Note: Harmonization takes into account whether or not the MPC in one media (such as soil) would lead to exceeding the MPC in another media (such as air, water, or sediment) [655].

Based on equilibrium partitioning, the Netherlands' Negligible Concentration (NC) for benzene is 1% of the MPC (considering harmonization), so the NC is 0.0095 mg/kg [655].

Soil criteria for evaluating the severity of contamination under the Dutch Soil Cleanup (Interim) Act (1982): 0.1 ppm indicates a background level for benzene. 0.5 indicates a moderate contamination of benzene. 5 indicates a threshold value of benzene which will require immediate cleanup [347].

Acceptable on-site soil concentrations for benzene approved by the Ontario Ministry of the Environment for the Texaco and Shell refinery sites (1987): 0.040-0.13 ppm [347].

Based on equilibrium partitioning, the Netherlands' Negligible Concentration (NC) for benzene is 1% of the MPC, or 0.095 mg/kg dry weight [655].

> NOTE: For carcinogens (like benzene), the MPC is based on a one-in-one-million acceptable risk of cancer.

Recent research on cosolubility/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 motor fuel contaminated soils [736]. They range from "background" (Michigan), to low ppb levels (25 ppb benzene, Illinois) [736].

Soviet Union Maximum Allowable Concentration in Soils, 1984: 0.3 mg/kg [347].

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

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 benzene or BTEX concentration exceeds 50 ppm; soils having a medium leaching potential should be removed if the benzene concentration exceeds 0.3 ppm [347]. See also BTEX entry.

Canada's Interim Assessment Criterion for benzene in soil is 0.05 ug/g dry weight [656].

> NOTE: a) "Interim" means complete supporting rationale do not exist; b) for most of the organic parameters in [656], criteria are based on analytical detection limits and are intended to provide general guidance only for the protection of both human and environmental health [656].

Canada's Interim Remediation Criteria for benzene in soil for three different land-uses (ug/g dry weight) [656]:

Agricultural = 0.05
Residential/Parkland = 0.5
Commercial/Industrial = 5

NOTE: a) "Interim" means complete supporting rationale do not exist; b) if contaminant concentrations exceed the criterion for a current or anticipated land use at a site, then the need for further investigation and/or remediation exists; c) criteria are relevant to protection of both human and environmental health [656].

Soil.Plants (Soil Concentrations vs. Plants):

No information found.

Soil.Invertebrates (Soil Concentrations vs. Invertebrates):

No information found.

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

No information found.

Soil.Human (Soil Concentrations vs. Human):

EPA 1996 National Generic Soil Screening Level (SSL) designed to be conservative and protective at the majority of sites in the U.S. but not necessarily protective of all known human exposure pathways, land uses, or ecological threats [952]:

SSL = 22 mg/kg for ingestion pathway [952].

SSL = 0.8 mg/kg for inhalation pathway [952].

SSL = 0.002 to 0.03 mg/kg for protection from migration to groundwater at 1 to 20 Dilution-Attenuation Factor (DAF) [952].

EPA 1995 Region 9 Preliminary remediation goals (PRGs) [868]:

Residential Soil: 1.4 mg/kg wet weight
Industrial Soil: 3.2 mg/kg wet weight

NOTE:

1) Values are based on a one-in-one million cancer risk.
2) Non-cancer PRG is less than 100x the cancer PRG above.
3) PRGs focus on the human exposure pathways of ingestion, inhalation of particulates and volatiles, and dermal absorption. Values do not consider impact to groundwater or ecological receptors.

EPA Region III Risk Based Concentration (RBC): 0.03 mg/kg for protection from migration to groundwater [903].

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

See also Canada's Interim Criteria [656] in Soil.General section above.

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

Industrial discharge, disposal of products containing benzene, and gasoline leaks from underground storage tanks can release benzene into water and soil [767]. Benzene in water and soil breaks down more slowly than in air [767]. Benzene is slightly soluble in water and can pass through the soil into underground water [767].

A useful parameter for investigating the leachability of a chemical is the soil organic carbon sorption coefficient (Koc). According to Kenaga, compounds with a Koc of less than 100 are considered to be moderately to highly mobile [767]. Benzene, with a K oc value of 60-83, would be considered highly mobile [767]. See also: Fate.Detail section below.

A combination of steam stripping and air stripping, and a vapor extraction system that removes the separated benzene vapor may be suitable for the treatment of contaminated groundwater and soil [767]. An in situ bioremediation process has been used to decontaminate a site by delivering a controlled amount of nitrate (to accelerate biodegradation of benzene) to the site under

hydraulic control [767].

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.

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

2 species of macroalgae - 20 ppb(2). [(2) Whelan JK et al; Nature 299: 50-2 (1982)] [609].

BCFs for barley plants after 12, 33, 71, and 125 days were 17, 2.3, 2.9, and 4.6, respectively [767]. BCFs for cress plants after 12, 33, and 79 days were 10, 2.3, and 1.9, respectively [767]. The relative decrease in the BCFs with time was attributed to growth dilution [767]. However, since benzene exists primarily in the vapor phase, air-to-leaf transfer rather than root uptake is considered to be the major pathway of vegetative contamination [767]. Based on an equation to estimate vegetative contamination, the total concentration of benzene on exposed food crops consumed by humans and used as forage by animals was estimated to be 587 ng/kg, 81% of which was from air-to-leaf transfer and 19% from root uptake [767].

Tis.Invertebrates:

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

No information found.

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

No information found.

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

Seafood Concentrations [609]:

Lake Pontchartrain, LA seafood (ppb wet weight): oysters (Crassostra virginica), from the Inner Harbor Navigational Canal, avg of 5 samples, 220, clams composite samples (Rangia cuneata): from Chef Menteur Pass, 260, from The Rigolets, not detected(1). [(1) Ferrario JB et al; Bull Environ Contam Toxicol 34: 246-55 (1985)].

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.

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

No information found.

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

No information found.

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.

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):

Oak Ridge National Lab, 1994: Risk Assessment Screening Benchmarks for Wildlife derived from No-Observed-Adverse-Effect (NOAEL) levels (mg contaminant per kg body weight per day). To be considered unlikely to represent an ecological risk, wet-weight field concentrations should be below the following (right column) benchmarks for each species present at the site [650]:

SPECIES	NOAEL (mg/kg/day)	FOOD CONCEN-TRATION (ppm)
Mouse	26.36000	0.00000

(test species)		
Short-tailed Shrew	33.13500	55.22500
Little Brown Bat	41.65100	124.95300
White-footed Mouse	29.20100	188.94600
Meadow Vole	23.23000	204.42600
Cottontail Rabbit	7.80300	39.50900
Mink	8.28700	60.48900
Red Fox	5.04500	50.44800
Whitetail Deer	2.18900	71.07700

LDLo (lowest published lethal dose) Dog; ROUTE: Oral; DOSE: 2 gm/kg; REFERENCE: "Abdernalden's Handbuch der Biologischen Arbeitsmethoden." 4:1313, 1935. [607].

LDLo (lowest published lethal dose) Man; ROUTE: Oral; DOSE: 50 mg/kg; REFERENCE: Gekkan Yakuji. Pharmaceuticals Monthly 22:883, 1980. [607].

LD50 Rat; ROUTE: Oral; DOSE: 930 mg/kg; TOXIC EFFECTS: BEHAVIORAL - Tremor; BEHAVIORIAL- Convulsions or effect on seizure threshold; REFERENCE: Toxicology and Applied Pharmacology 7:767, 1965. [607].

LD50 Mouse; ROUTE: Oral; DOSE: 4700 mg/kg; REFERENCE: Hygiene and Sanitation 32(3):349, 1967. [607].

LD50 (unspecified mammal species); ROUTE: Oral; DOSE: 5700 mg/kg; REFERENCE: Gigiena i Sanitariya 39(4):86, 1974. [607].

LD50/LC50 PUBLISHED VALUES [498,607]:

1. TCLo (INHL) HUMAN: 100 ppm
2. TCLo (INHL) HUMAN: 210 ppm
3. TCLo (INHL) HUMAN: 10 ppm/8h/10yr-I
4. TCLo (INHL) MAN: 150 ppm/1yr-I
5. TCLo (INHL) MAN: 200 mg/m(3)/78wk-I
6. TCLo (INHL) MOUSE: 300 ppm/6H/16wk-I
7. TCLo (INHL) RAT: 670 mg/m(3)/24h
8. TCLo (INHL) RAT: 50 ppm/24h
9. TCLo (INHL) RAT: 1,200 ppm/6h/10wk-I
10. TCLo (INHL) RAT: 150 ppm/24h
11. TDLo (ORAL) HUMAN: 130 mg/kg
12. TDLo (ORAL) RAT: 52 g/kg/52wk-I
13. TDLo (SKIN) MOUSE: 1,200 g/kg/49wk-I
14. TDLo (SC) MOUSE: 600 mg/kg/17wk-I
15. TDLo (IP) MOUSE: 1,200 mg/kg/8wk-I
16. LCLo (INHL) HUMAN: 2 pph/5min
17. LCLo (INHL) HUMAN: 20,000 ppm/5min
18. LCLo (INHL) HUMAN: 2,000 ppm/5min

19. LCLo (INHL) HUMAN: 65 mg/m(3)/5yr
20. LDLo (ORAL) MAN: 50 mg/kg
21. LDLo (UNREPORTED) MAN: 194 mg/kg
22. LCLo (INHL) RABBIT: 45,000 ppm/30min
23. LDLo (IV) RABBIT: 88 mg/kg
24. LDLo (IP) GUINEA PIG: 527 mg/kg
25. LDLo (ORAL) DOG: 2 g/kg
26. LCLo (INHL) DOG: 146,000 mg/m(3)
27. LCLo (INHL) CAT: 170,000 mg/m(3)
28. LCLo (INHL) MAMMAL: 20,000 ppm/5min
29. LDLo (IP) MAMMAL: 1,500 mg/kg
30. LDLo (SC) FROG: 1,400 mg/kg
31. LD50 (ORAL) RAT: 930 mg/kg
32. LD50 (ORAL) RAT: 3,400 mg/kg
33. LD50 (ORAL) RAT: 3.8 mL/kg
34. LC50 (INHL) RAT: 10,000 ppm/7hr
35. LD50 (IP) RAT: 2,890 mcg/kg
36. LD50 (ORAL) MOUSE: 4,700 mg/kg
37. LD50 (ORAL) MOUSE: 18,250 mg/kg/2yr-C
38. LD50 (SKIN) MOUSE: 48 mg/kg
39. LC50 (INHL) MOUSE: 9,980 ppm
40. LD50 (IP) MOUSE: 340 mg/kg
41. LD50 (IP) MOUSE: 990 mcg/kg

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.

Tis.Human:

A) Typical Concentrations in Human Food Survey Items:

See also Tis.Invertebrates, C) above.

Food Survey Results [609]:

Heat treated or canned beef 2 ug/kg; Jamaican rum 120 ug/kg; eggs 500-1900 ug/kg; detected in fruits, nuts, vegetables, dairy products, meat, fish, poultry, eggs, and beverages(1). [(1) USEPA; Ambient Water Quality Criteria: Benzene p. C-5 EPA-440/5-80-018 (1980)].

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):

Oral RfD: 1.7E-03 mg/kd-d [868].

IRIS EPA 1996 quantitative estimate of carcinogenic risk from oral exposure ———— Slope Factor: 2.9E-2

per mg/(kg/day)[893]. The slope factor was derived from human data for inhalation exposure (see dose-response data for inhalation quantitative estimate). The human respiratory rate was assumed to be 20 cu.m/day and the human drinking water intake was assumed to be 2 L/day. The fraction of the administered dose absorbed systemically via inhalation and via drinking water were assumed to be equal [893].

For risk to human adults eating fish, separate carcinogenic and non-carcinogenic risk-based fish tissue concentrations were calculated [903]. The following EPA Region III fish tissue risk-based concentration (RBC) benchmark utilizes the lower of the two concentrations (carcinogenic), rounded to two significant figures [903]:

RBC = 0.11 mg/Kg wet weight.

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

Body Burdens [609]:

Detected in all 8 samples of mothers' milk from 4 USA urban areas(1). Breath of persons without specific exposure to benzene 8-20 ppb(2). Whole blood, 250 subjects (121 males, 129 females), not detected-5.9 ppb, 0.8 ppb avg(3). USA FY82 National Human Adipose Tissue Survey specimens, 46 composites, 96% pos, (>4 ppb, wet tissue concn), 97 ppb max(4). [(1) Pellizzari ED et al; Environ Sci Technol 16: 781-5 (1982) (2) IARC; Monograph. Some Industrial Chemicals and Dyestuffs. 29: 99-106 (1982) (3) Antoine SR et al; Bull Environ Contam Toxicol 36: 364-71 (1986) (4) Stanley JS; Broad Scan Analysis of the FY82 National Human Adipose Tissue Survey Specimens Vol. I Executive Summary p. 5 USEPA-560/5-86-035 (1986)].

Tis.Misc. (Other Tissue Information):

No information found.

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

Relatively low bioconcentration factors (BCFs) have been reported for aquatic bacteria, algae, macrophytes, and fish. The highest reported value was for Daphnia pulex, with a BCF of 225

(log BCF of 2.35) [865]. Six different studies found log BCF for several fish to be around 1.10 [902].

The depuration of benzene in Daphnia pulex and in fish is rapid: for Daphnia, 85% of accumulated benzene was removed during the 72 hours following withdrawal from contaminated water; and the half-life in striped bass was observed to be less than 1 day [865].

The bioconcentration/bioaccumulation potential of benzene in aquatic organisms of the open coastal ocean was investigated by sampling final effluent from the Los Angeles County waste water treatment plant quarterly from November 1980 to August 1981 [767]. The benzene concentration was 0.22 ppm [767]. The results show that the bioconcentration is related to the n - octanol/water partition coefficient (Kow) [767]. Benzene has a relatively low partition coefficient (log Kow = 2.13 or 2.15) [767]. Although its concentration in the effluent water was high, its bioaccumulation in fish liver was low (0.001-0.052 ug/g wet weight) [767]. In the alga Chlorella, a bioaccumulation factor of 30 was determined experimentally and a bioconcentration factor of 40 was estimated from regression equation using a value of Kow [767]. These findings suggest that bioaccumulation/bioconcentration in marine organisms is not significant and can be estimated by using the n - octanol/water partition coefficient [767]. Similar results were reported by Miller. who used a log octanol-water partition coefficient of 2.13 and an estimated bioconcentration factor (BCF) of 24 to conclude that benzene is not expected to bioconcentrate to any great extent in aquatic organisms [767]. An experimental BCF of 4.27 was measured in goldfish reared in water containing 1 ppm of benzene [767]. Based on these estimated and measured values, bioconcentration/bioaccumulation of benzene in the aquatic food chains does not appear to be important [767]. There is no evidence in the literature of biomagnification of benzene in aquatic food chain (e.g., increased accumulation from algae to algae-eating fish) [767]. Evidence exists for the uptake of benzene by cress and barley plants from soil [767]. BCFs for barley plants after 12, 33, 71, and 125 days were 17, 2.3, 2.9, and 4.6, respectively [767]. BCFs for cress plants after 12, 33, and 79 days were 10, 2.3, and 1.9, respectively [767]. The relative decrease in the BCFs with time was attributed to growth dilution [767].

BCF: eels (Anguilla japonica) 3.5(1); pacific herring (Clupea harengus pallasi) 4.4(2); goldfish 4.3(3). Based on a reported log Kow of 2.13(4), a BCF of 24 was estimated(5,SRC). Based on the reported and estimated BCF, benzene will not be expected to bioconcentrate in aquatic organisms. [(1) Ogata M, Miyake Y; Water Res 12: 1041-4 (1978) (2) Korn S et al; Fish Bull Natl Marine Fish Ser 75: 633-6 (1977) (3) Ogata M et al; Bull Environ Contam Toxicol 33: 561-7 (1984) (4) Hansch C, Leo AJ; Medchem Project Issue No. 26 Claremont, CA: Pomona College (1985) (5) Lyman WJ et al; Handbook of Chem Property Estimation Methods NY: McGraw-Hill p. 5-5 (1982)].

Biological Half-Life [609]: The excretion of unchanged benzene from the lung of rats was reported to be biphasic, suggesting a two-compartment model for distribution and a half-life of 0.7 hr. This agreed with experimental half-life values for various tissues that ranged from 0.4 to 1.6 hr. [Rickert DE et al; Toxicol Appl Pharmacol 49: 417 (1979) as cited in USEPA; Ambient

Water Quality Criteria: Benzene p.C-11 (1980) EPA 440/5-80-018].

Interactions:

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

The aerobic biodegradation of benzene is however, influenced by the presence of other aromatic hydrocarbons [767]. See fate.detail section below for details.

Information from HSDB [609]:

> DMSO pretreatment enhances benzene metabolism and toxicity in male Wistar rats. [Kocsis JJ et al; Science 160: 427 (1968)].
>
> Benzene & ethanol induced a common cytochrome P450 species in rabbit liver specifically effective in hydroxyl radical-mediated oxygenation of ethanol. Benzene oxidation by the benzene-inducible form of cytochrome P450 was almost completely inhibited by catalase, superoxide dismutase, dmso, & mannitol. [Ingelman-Sundberg M et al; Dev Biochem 23 (iss cytochrome P450, biochem biophys environ implic): 19-26 (1982).
>
> Simultaneous treatments with both benzene and toluene, or benzene and piperonyl butoxide, increased the excretion of unchanged benzene in the expired air. These compounds apparently act by inhibiting benzene metabolism. [USEPA; ECAO Atlas Document: Benzene IV-12 (1980)].
>
> The metabolism of benzene in vitro can be altered by the use of enzyme inducers administered to animals prior to sacrifice or by the addition of inhibitors to the mixtures. Benzene, phenobarbital, 3-methylcholanthrene and dimethyl sulfoxide are all microsomal stimulants for the metabolism of benzene. Benzene metabolism in vitro can be inhibited by carbon monoxide, aniline, metyrapone, SKF-525A, aminopyrine, cytochrome c, aminotriazole, or toluene. [USEPA; Ambient Water Quality Criteria: Benzene p.C-12 (1980) EPA 440/5-80-018].
>
> Benzene reduced the incorporation of (59)Fe into red cells by 75% at the higher dose when administered at 440 or 880 mg/kg to mice pretreated with (59)Fe 48 hr earlier. However, when toluene was administered simultaneously with benzene in a ratio of 2:1, the depression of (59)Fe uptake was prevented. Toluene reduced the appearance of benzene metabolites to 45% of controls at the higher dose and 30% at the lower dose. Thus toluene appears to inhibit benzene metabolism and by

so doing, alleviates its toxicity. [Snyder R et al; Adv Mod Environ Toxicol 4: 123-36 (1983)].

Uses/Sources:

Benzene is a component in gasoline. It is also an excellent solvent; its main use, however, is in the preparation of other compounds [261]. The compounds prepared from benzene, in the order of quantity produced, are styrene, for polymerization; phenol; detergents; aniline, for dyes; and chloro compounds [261]. Other uses of benzene include the production of pharmaceuticals, varnishes, and plastics [261].

The average content of benzene in premium and regular unleaded gasolines is 2.15% by weight or 1.76% by volume [865].

Major Uses [609]:

Mfr medicinal chem, dyes, org cmpd, artificial leather, linoleum, oil cloth, varnishes, lacquers; solvent for waxes, resins, oils /use as solvent is now discouraged/ [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 151].

Used for printing & lithography, paint, rubber, dry cleaning, adhesives & coatings, detergents [NIOSH; Criteria Document: Benzene p.20 (1974) DHEW Pub No 74-137].

Extraction and rectification; preparation and use of inks in the graphic arts industries; as a thinner for paints; as a degreasing agent [Fishbein L; Potential Indust Carcins & Mutagens p.96 (1977) USEPA 560/ 5-77-005].

Chem int for ethylbenzene, cumene, cyclohexane, nitrobenzene, maleic anhydride, chlorobenzenes, detergent alkylate, anthraquinone, benzene hexachloride, benzene sulfonic acid, biphenyl, hydroquinone, & resorcinol [SRI].

/Benzol for/ pesticidal uses /has been/ cancelled. /It/ was in use alone or in formulations for screwworm control on animals. /It was/ an ingredient of some early grain fumigants [Farm Chemicals Handbook 87. Willoughby, Ohio: Meister Publishing Co., 1987.,p. C-35].

In the tire industry (McMichael et al, 1975), & in shoe factories (Aksoy et al, 1974), benzene is used extensively. [Gilman, A.G., L.S.Goodman, and A. Gilman. (eds.). Goodman and Gilman's The Pharmacological Basis of Therapeutics. 7th ed. New York: Macmillan Publishing Co., Inc., 1985. 1638].

Used primarily as a raw material in the synthesis of

styrene (polystyrene plastics and synthetic rubber), phenol (phenolic resins), cyclohexane (nylon), aniline, maleic anhydride (polyester resins), alkylbenzenes (detergents), chlorobenzenes, and other products used in the production of drugs, dyes, insecticides, and plastics. [NTP; Toxicology and Carcinogenesis Studies of Benzene p.24 Report# 289 (1986) NIH Pub# 86-2545].

Natural Occurring Sources [609]:

Volcano, natural constituent of crude oil, forest fires, plant volatile(1,2). [(1) IARC; Monograph. Some Industrial Chemicals and Dyestuffs 29: 99-106 (1982) (2) Graedel TE; Chemical Cmpds in the Atmos, New York, NY: Academic Press (1978)].

Artificial Sources [609]:

Benzene enters the environment from production, storage, transport, venting, and combustion of gasoline; and from production, storage, and transport of benzene itself. Other sources result from its use as an intermediate in the production of other chemicals, and as a solvent, from spills, including oil spills; from its indirect production in coke ovens; from nonferrous metal manufacture, ore mining, wood processing, coal mining and textile manufacture; from cigarette smoke(1,2). [(1) IARC; Monograph. Some Industrial Chemicals and Dyestuffs 29: 99-106 (1982) (2) Graedel TE; Chemical Cmpds in the Atmos, New York, NY: Academic Press (1978)].

For late model cars it has been estimated that over 90% of automotive benzene comes from exhaust and less than 10% from fuel evaporation; this does not include any lost during tanker-to-station and station-to-car fuel transfers. [Verschueren, K. Handbook of Environmental Data of Organic Chemicals. 2nd ed. New York, NY: Van Nostrand Reinhold Co., 1983. 238].

In 1976, an estimated 1.3 billion pounds of benzene were released into the atmosphere from 132 million stationary and mobile sources. This included an estimated 240 million pounds per year from the production, transport, storage and use of benzene; 1 billion pounds per year from the refueling and operation of motor vehicles; and 22 million pounds per year from oil spills. [DHHS/NTP; Fourth Annual Report On Carcinogens p.35 (1985) NTP 85-002].

Forms/Preparations/Formulations:

Information from HSDB [609].

Nitration grade > 99% purity. [Environment Canada; Tech Info for Problem Spills: Benzene (Draft) p.20 (1981)].

"Benzol 90" contains 80-85% benzene, 13-15% toluene, 2-3% xylene. [NIOSH; Criteria Document: Benzene p.20 (1974) DHEW Pub No 74-137].

Commercial grades of benzene: Refined benzene-535 (free of H2S and SO2, 1 ppm max thiophene, 0.15% max nonaromatics); Refined benzene-485, Nitration-grade (free of H2S and SO2); Industrial-grade benzene (free of H2S and SO2) [Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed., Volumes 1-26. New York, NY: John Wiley and Sons, 1978-1984.,p. 3(78) 762].

Grade: crude, straw color; motor; industrial pure (2C); nitration (1C); thiophene-free; 99 mole%; 99.94 mole%; nanograde [Sax, N.I. and R.J. Lewis, Sr. (eds.). Hawley's Condensed Chemical Dictionary. 11th ed. New York: Van Nostrand Reinhold Co., 1987. 129].

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

Benzene is now known to have six identical carbon-carbon bonds, each intermediate between a single and double bond [261]. The structure is often written as a hexagon with a circle inside to represent this arrangement [261].

Solubilities:

0.180 g/100 g of water at 25 deg C [Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed., Volumes 1-26. New York, NY: John Wiley and Sons, 1978-1984.,p. V3(78) 746] [609].

820 ppm @ 25 degrees C; "slightly soluble" [368].

A "high water solubility" [865].

665 to 4006 mg/L at 25 degrees C (most values near 1780 mg/L) [902].

Miscible with alcohol, chloroform, ether, carbon disulfide, acetone, oils, carbon tetrachloride, & glacial acetic acid [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 151] [609].

Vapor Pressure:

100 MM HG AT 26.1 DEG C [Sax, N.I. Dangerous Properties of Industrial Materials. 6th ed. New] [609].

A "relatively high vapour pressure" [865].

10,133 to 13,172 Pa at 25 degrees C (most values near 12,700 Pa) [902].

Henry's Law Constant:

441 to 740 Pa m3/mol (most values near 555) [902].

Molecular Weight:

78.11 [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 151] [609].

Density/Specific Gravity:

0.8787 AT 15 DEG C/4 DEG C [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 151] [609].

Octanol/Water Partition Coefficient:

log Kow= 2.13 [Hansch C, Leo AJ; Medchem Project Issue No.26 Claremont, CA: Pomona College (1985)] [609].

A "low log octanol/water partition coefficient" [865].

log Kow = 1.56 to 2.69 (most values near 2.13) [902].

Sorption Partion Coefficient, log Koc:

1.09 to 2.33 (most values near 1.92) [902].

Boiling Point:

80.1 DEG C [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 151] [609].

Melting Point:

5.5 DEG C [IARC. Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man. Geneva: World Health Organization, International Agency for Research on Cancer,1972-PRESENT. (Multivolume work).,p. V7 203 (1974)] [609].

Viscosity:

0.6468 mPa's @ 20 C [Cheremisinoff PN; Benzene - Basic and Hazardous Props (1979) as cited in Environment Canada; Tech Info for Problem Spills: Benzene (Draft) p.4 (1981)] [609].

Color/Form:

CLEAR, COLORLESS LIQ [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 151] [609].

RHOMBIC PRISMS [Weast, R.C. (ed.) Handbook of Chemistry and Physics, 68th ed. Boca Raton, Florida: CRC Press Inc., 1987-1988.,p. C-105] [609].

Odor:

AROMATIC ODOR [National Fire Protection Association. Fire Protection Guide on Hazardous Materials. 9th ed. Boston, MA: National Fire Protection Association, 1986.,p. 49-20] [609].

Odor perception threshold (air) -- 4.9 mg/cu.m [337].

Odor perception threshold (water) -- 2.0 mg/L [337].

Coast Guard CHRIS database [367]:

Reactivity with water: No reaction.

Reactivity with common materials: No reaction.

Stability during transport: Stable.

Neutralizing agents for acids and caustics: Not pertinent.

Polymerization: Not pertinent.

Inhibitor of polymerization: Not pertinent.

Molar ratio (reactant to product): Data not available.

Reactivity group: 32.

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

Molecular weight: 78.11.

Boiling point at 1 ATM: 176 degrees F = 80.1 degrees C = 353.3 degrees K.

Freezing point: 42.0 degrees F = 5.5 degrees C = 278.7 degrees K.

Critical temperature: 552.0 degrees F = 288.9 degrees C = 562.1 degrees K.

Critical pressure: 710 psia = 48.3 atm = 4.89 MN/m(2).

Specific gravity: 0.879 at 20 degrees C (liquid).

Liquid surface tension: 28.9 dynes/cm = 0.0289 N/m at 20 degrees C.

Liquid water interfacial tension: 35.0 dynes/cm = 0.035 N/m at 20 degrees C.

Vapor (gas) specific gravity: 2.7.

Ratio of specific heats of vapor (gas): 1.061.

Latent heat of vaporization: 169 Btu/lb = 94.1 cal/g = 3.94 X 10(5) J/kg.

Heat of combustion: -17,460 Btu/lb = -9698 cal/g = -406.0 X 10(5) J/kg.

Heat of decomposition: Not pertinent.

Heat of solution: Not pertinent.

Heat of polymerization: Not pertinent.

Heat of fusion: 30.45 cal/g.

Limiting value: Data not available.

REID vapor pressure: 3.22 psia.

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

Half-lives in surface water [902]: 4.81 hours (based on evaporation loss at 25 deg C and 1 meter water depth; 120-384 hours (based on unacclimated aerobic biodegradation half-life).

Half-lives in ground water [902]: about 1 year; 240-17,280 hours (based on unacclimated aqueous aerobic biodegradation half-life).

Benzene is biodegradable in surface water and groundwater [767]. Microbial degradation of benzene in aquatic environments is influenced by many factors such as microbial population, dissolved oxygen, nutrients, other sources of carbon, inhibitors, temperature, and pH [767]. One study reported biodegradation half-lives for benzene in surface water (river water) and groundwater of 16 and 28 days, respectively [767]. Benzene was found to be resistant to biodegradation in surface water taken from a harbor and supplemented with either nutrients (nitrogen and phosphorus) or acclimated microbes [767]. Biodegradation did occur, with a half-life of 8 days, in surface water enriched with both nutrients and microbes [767].

Under aerobic conditions (pH 5.3, 20 o C), benzene was completely microbially degraded in 16 days in groundwater taken from a shallow well [767]. The aerobic biodegradation of benzene is also influenced by the presence of other aromatic hydrocarbons [767]. A bacterial culture grown with aromatic hydrocarbons plus nitrogen-, sulfur-, and oxygen-containing aromatic compounds was much less efficient in degrading benzene than the culture grown

with aromatic hydrocarbons alone [767]. Pyrrole strongly inhibited benzene degradation [767]. Benzene degradation was high when toluene and xylene were present [767].

An analysis of benzene, toluene, and xylene (BTX) in groundwater from a field site indicated that the amount of BTX in groundwater was inversely related to the availability of dissolved oxygen [767]. Results of biodegradation experiments in laboratory microcosms using groundwater from the field site showed the following results at BTX levels of 120-16,000 ppb: BTX degradation was 80-100% (half-life of 5-20 days) when the dissolved oxygen level was 2 ppm; BTX degradation was slowed (half-life of 20-60 days) when the dissolved oxygen level was 2 ppm; and little or no degradation of BTX occurred when the dissolved oxygen level was 0, 0.1, or 0.5 ppm [767]. Several pure cultures of microorganisms isolated from water including several Pseudomonas sp [767]. A strain of Pseudomonas fluorescens can catabolize benzene in water under aerobic conditions [767]. A strain of P. fluorescens can catabolize benzene under oxygen-limiting conditions (initial dissolved oxygen concentration of about 2 mg/L) with nitrate as alternate electron acceptor [767]. If the bacteria are ring-hydroxylating monooxygenases (e.g., P. fluorescens) they catabolize benzene to phenol; while ring dioxygenases (e.g., P. arviella) catabolize benzene to pyrocatechol and hydroquinone [767]. Ring cleavage by dioxygenases requires aromatic compounds carrying two hydroxyl groups, one in the ortho or para position [767].

Laboratory studies on microbial degradation of benzene with mixed cultures of microorganisms in gasoline-contaminated groundwater revealed that both oxygen and nitrogen concentrations are major controlling factors in the biodegradation of benzene [767]. A natural mix of adapted microorganisms, obtained by selective enrichment, was used as the inoculum to accelerate the biochemical breakdown of benzene in groundwater [767]. The inoculum plus nitrogen amendments enhanced the biodegradation rate of benzene 4.5-fold at 23 o C using a shaker flask system [767]. More than 95% of the benzene in groundwater was removed through microbial action within 73.5 hours [767].

A mixed culture consortia obtained from subsurface sediments degraded 1 mg/L benzene in water to below detectable limits (detection limit not given) by a continuously recycled bioreactor within 8-10 days [767]. Results of a biochemical oxygen demand (BOD) test determined that benzene was completely biodegradable after the second 6 [767].

Half-lives in soil [902]: 120-384 hours (based on unacclimated aqueous aerobic biodegradation half-life); < 10 days; 365 days; < 2.0 days.

Trimethyl benzenes (TMB) were still present three years after a spill, long after many other hydrocarbons had degraded [856].

Transport and Partitioning: The high volatility of benzene (vapor pressure, 95.2 mm Hg at 25 o C) is the controlling physical property in the environmental transport and partitioning of this chemical [767]. Benzene is considered to be highly volatile with a vapor pressure of 95.2 mm Hg at 25 o C [767]. Benzene is only slightly soluble in water, with a solubility of 1,780 mg/L at 25 o C, and the Henry's law constant for benzene (5.5x10 -3 atm-m 3

/mole at 20 o C) indicates that benzene partitions readily to the atmosphere from surface water [767]. Mackay and Leinonen estimated a volatilization half-life for benzene of 4.81 hours for a 1-meter-deep body of water at 25 o C [767]. Even though benzene is only slightly soluble in water, some minor removal from the atmosphere via wet deposition may occur [767]. A substantial portion of any benzene in rainwater that is deposited to soil or water will be returned to the atmosphere via volatilization [767]. Benzene released to soil surfaces partitions to the atmosphere through volatilization, to surface water through runoff, and to groundwater as a result of leaching [767]. A useful parameter for investigating the leachability of a chemical is the soil organic carbon sorption coefficient (Koc) [767].

According to Kenaga, compounds with a Koc of less than 100 are considered to be moderately to highly mobile [767]. Benzene, with a K oc value of 60-83, would be considered highly mobile [767]. Other parameters that influence leaching potential include the soil type (e.g., sand versus clay), the amount of rainfall, the depth of the groundwater, and the extent of degradation [767]. In a study of the sorptive characteristics of benzene to groundwater aquifer solids, benzene showed a tendency to adsorb to aquifer solids [767]. Greater adsorption was observed with increasing organic matter content [767].

A model developed to predict the environmental fate of benzene following leakage of gasoline from an underground storage tank at Vero Beach in Florida indicated that most (67%) of the benzene in the gasoline would volatilize from this shallow sandy soil within 17 months [767]. Of the remaining benzene, 29% would leach to groundwater, 3% would remain in the soil, and 1% would be degraded [767]. According to the model, the rate of volatilization and leaching would be the principal factors in determining the persistence of benzene in sandy soils [767]. The bioconcentration/bioaccumulation potential of benzene in aquatic organisms of the open coastal ocean was investigated by sampling final effluent from the Los Angeles County waste water treatment plant quarterly from November 1980 to August 1981 [767]. The benzene concentration was 0.22 ppm [767].

Information from HSDB [609]:

> TERRESTRIAL FATE: If benzene is released to soil it will be subject to rapid volatilization near the surface. That which does not evaporate will be highly to very highly mobile in soil and may leach to groundwater. The effective half-lives for volatilization without water evaporation from soil to benzene uniformly distributed to 1 and 10 cm in soil were 7.2 and 38.4 days, respectively(2). It may be subject to biodegradation based on reported biodegradation of 24% and 47% of the initial 20 ppm benzene in a based-rich para-brownish soil in 1 and 10 weeks, respectively(1). It may be subject to biodegradation in shallow, aerobic groundwaters, but probably not under anaerobic conditions. [(1) Haider K et al; Arch Microbiol 96: 183-200 (1974) (2) Jury WA et al; J Environ Qual 13: 573-9 (1984).

AQUATIC FATE: If benzene is released to water, it will be subject to rapid volatilization; the half-life for evaporation in a wind-wave tank with a wind speed of 7.09 m/sec was 5.23 hrs(1); the estimated half-life for volatilization of benzene from a model river one meter deep flowing 1 m/sec with a wind velocity of 3 m/sec is estimated to be 2.7 hrs at 20 deg C. It will not be expected to significantly adsorb to sediment, bioconcentrate in aquatic organisms or hydrolyze. It may be subject to biodegradation based on a reported biodegradation half-life of 16 days in an aerobic river die-away test(2). In a marine ecosystem, biodegradation occurred in 2 days after an acclimation period of 2 days and 2 weeks in the summer and spring, respectively, whereas no degradation occurred in winter(3). [(1) Mackay D, Yeun ATK; Environ Sci Technol 17: 211-7 (1983) (2) Vaishnav DD, Babeu L; Bull Environ Contam Toxicol 39: 237-44 (1987) (3) Wakeman SG et al; Bull Environ Contam Toxicol 31: 582-4 (1983)].

AQUATIC FATE: Evaporation was the primary loss mechanism in winter in a mesocosm experiment which simulated a northern bay where the half-life was 13 days(1). In spring and summer the half-lives were 23 and 3.1 days, respectively(1). In these cases biodegradation plays a major role and takes about 2 days(1). However, acclimation is critical and this takes much longer in the colder water in spring(1). According to one experiment, benzene has a half-life of 17 days due to photegradation(2) which could contribute to benzene's removal. In situations of cold water, poor nutrients, or other conditions less conducive to microbial, photolysis will play a important role in degradation. [(1) Wakeham SG et al; Bull Environ Contam Toxicol 31: 582-4 (1983) (2) Hustert K et al; Chemosphere 10: 995-8 (1981)].

ATMOSPHERIC FATE: If benzene is released to the atmosphere, it will exist predominantly in the vapor phase(3). Gas-phase benzene will not be subject to direct photolysis but it will react with photochemically produced hydroxyl radicals with a half-life of 13.4 days calculated using an experimental rate constant for the reaction. The reaction time in polluted atmospheres which contain nitrogen oxides or sulfur dioxide is accelerated with the half-life being reported as 4-6 hours(2). Products of photooxidation include phenol, nitrophenols, nitrobenzene, formic acid, and peroxyacetyl nitrate. Benzene is fairly soluble in water and is removed from the atmosphere in rain(1). [(1) Kato T et al; Yokohama Kokuritsu Diagaku Kankyo Kagaku Kenkyu Senta Kiyo 6: 11-20 (1980) (2) Korte F, Klein W; Ecotox Environ Saftey 6: 311-27 (1982) (3) Eisenreich SJ et al; Environ Sci Technol 15: 30-8 (1981)].

Biodegradation [609]:

No degradation of benzene as measured by BOD was reported in coarse-filtered (through 1 cm cotton layer) Superior harbor water incubated at 21 deg C for 12 days(1). Biodegradation half-lives of 28 and 16 days were reported in die-away tests for degradation of up to 3.2 ul/l benzene using groundwater and Lester River water, respectively, under aerobic conditions(2). The half-life in estuarine water was 6 days as measured by 14 C02 produced(3). In a marine ecosystem biodegradation occurred in 2 days after an acclimation period of 2 days and 2 weeks in the summer and spring, respectively, whereas no degradation occurred in winter(5). In a base-rich para-brownish soil, 20 ppm benzene was 24% degraded in 1 week, 44% in 5 weeks, and 47% in 10 weeks(4). [(1) Vaishnav DD, Babeu L; J Great Lakes Res 12: 184-91 (1986) (2) Vaishnav DD, Babeu L; Bull Environ Contam Toxicol 39: 237-44 (1987) (3) Lee RF, Ryan C; Microbial Degradation of Pollutants in Marine Environments. pp. 443-50 USEPA-600/9-72-012 (1979) (4) Haider K et al; Arch Microbiol 96: 183-200 (1974) (5) Wakeman SG et al; Bull Environ Contam Toxicol 31: 582-4 (1983)].

Benzene, in a mixture with toluene and xylenes, is readily biodegraded (total degradation of 7.5 ppm total mixture) in shallow ground water in the presence of oxygen in the unconfined sand aquifer at Canada Forces' Base Borden, Ontario; laboratory batch experiments demonstrated that the degradation could be attributed to biodegradation(1). Complete biodegradation in 16 days was reported under simulated aerobic groundwater conditions at 20 deg C(2). Reported metabolites of benzene using pure cultures of microorganisms include phenol and unidentified phenols(3), catechol and cis-1,2-dihydroxy-1,2-dihydrobenzene(4). [(1) Barker Jf et al; Ground Water Monit Rev 7: 64-72 (1987) (2) Delfino JJ, Miles CJ; Soil Crop Sci Soc FL Proc 44: 9-14 (1985) (3) Smith RV, Rosazza SP; Arch Biochem Biophys 161: 551-8 (1974) (4) Gibson DT et al; Biochem 7: 2653-62 (1968)].

Benzene at 50 ppm was 90% degraded by industrial wastewater seed incubated at 23 deg C for 6 hrs(1). Benzene inhibited industrial seed at concn of 100 ppm and above and municipal seed at 50 ppm and above(1). In a bench scale activated-sludge reactor with an 8 hour retention time, complete degradation occurred with 0.5% of the benzene being lost by air stripping(2). In laboratory systems, low concentrations of benzene are degraded in 6-14 days(3,4). 44-100% removal occurred at a sewage treatment plant; percentage by evaporation and biodegradation were not determined(5). [(1) Davis EM et al; Water Res 15: 1125-7 (1981) (2) Stover EL, Kincannon DF; J Water Pollut Control Fed 55: 97-109 (1983) (3)

Setzkorn EA, Huddleston RL; J Amer Oil Chem Soc 42: 1081-4 (1965) (4) Tabak HH et al; J Water Pollut Control Fed 53: 1503-18 (1981) (5) Feiler HD et al; Proc Natl Conf Munic Sludge Manag 8th, pp. 72-81 (1979)].

Abiotic Degradation [609]:

Since gas-phase benzene(1) or benzene dissolved in cyclohexane(2) does not absorb light of 290 nm or longer, it will not be expected to directly photolize in sunlight in these media. However, slight shifts in wavelength of absorption might be expected in more representative environmental media, such as water(3); eg, a half-life of 16.9 days was reported for photolysis of benzene dissolved in deionized water saturated with air exposed to sunlight(4). The rate constant for the vapor phase reaction of benzene with photochemically produced hydroxyl radicals has been reported to be 1.2x10-12 cu cm/molecule-sec at 25 deg C(5) which corresponds to an atmospheric half-life of 13.4 days at an atmospheric concentration of 5X10+5 hydroxyl radicals per cu cm. [(1) Noyes WA et al; J Chem Phys 44: 2100-6 (1966) (2) Silverstein RM, Bassler GC; p. 166 in: Spectrometric Identification of Organic Compounds 2nd ed. (1968) (3) Howard PH, Durkin PR; Sources of Contamination, ambient levels, and fate of benzene in the environment. pp. 65 USEPA-560/5-75-005 (1974) (4) Hustert K et al; Chemosphere 10: 995-8 (1981) (5) Perry RA et al; J Phys Chem 81: 296-304 (1977)].

While benzene is considered to be relatively unreactive in photochemical smog situations (in the presence of nitrogen oxides), its rate of degradation is accelerated with about 16% decrease in concentration in 5 hr(1). A typical experiment in the presence of active species such as NOx and SO2 showed that benzene photodegradation was considerably accelerated above that in air alone(2). Its half-life in the presence of active species was 4-6 hr with 50% mineralization to CO2 in approximately 2 days(3). Products of degradation include phenol, 2-nitrophenol, 4-nitrophenol, 2,4-dinitrophenol, 2,6-dinitrophenol, nitrobenzene, formic acid, and peroxyacetyl nitrate(4-6). Hydrolysis is not a significant process for benzene(7). [(1) Farley FF; Inter Conf on Photochemical Oxidant Pollution and Its Control. pp. 713-27 USEPA-600/3-77-001B (1977) (2) Yanagihara S et al; Proc Int Clean Air Cong 4th, pp. 472-7 (1977) (3) Korte F, Klein W; Ecotox Environ Saftey 6: 311-27 (1982) (4) Nojima K et al; Chemosphere 4: 77-82 (1975) (5) Hoshino M et al; Kokuritsu Kogai Kekyusho Kenkyu Hokoku 5: 43-59 (1978) (6) Kopczynski SL; Int J Air Water Pollut 8: 107-20 (1964) (7) Lyman WJ et al; Handbook of Chemical Property Estimation Methods. NY: McGraw-Hill pp. 7-4 (1982)].

Soil Adsorption/Mobility [609]:

Koc: Woodburn silt loam 31(1); 31.7-143(4); 83(8). Leaches in soil, passes through soil during bank infiltration(2,3). Based on a reported log Kow of 2.13(5), a Koc of 98 was estimated(6,SRC). Based on the reported and estimated Koc values, benzene will be expected to exhibit very high to high mobility in soil(7) and therefore may leach to groundwater. [(1) Chiou CT et al; Environ Sci Technol 17: 227-31 (1983) (2) Piet GJ, Morra CF; pp. 31-42 in Artifical Groundwater Recharge L Huisman, Tl Olsthorn eds Marshfield MA; Pitman Pub (1983) (3) Green WJ et al; J Water Pollut Control Fed 53: 1347-54 (1981) (4) Sabljic A; J Agric Food Chem 32: 243-6 (1984) (5) Hansch C, Leo AJ; Medchem Project Issue No. 26 Claremont, CA: Pomona College (1985) (6) Lyman WJ et al; Handbook of Chem Property Estimation Methods NY: McGraw-Hill p. 4-9 (1982) (7) Swann RL et al; Res Rev 85: 17-28 (1983) (8) Kenaga EE; Ecotox Environ Safety 4: 26-38 (1980)].

Volatilization from Water/Soil [609]:

Half-lives for evaporation of benzene from seawater in a mesocosm simulating Narragansett Bay, RI, containing the associated planktonic and microbial communities, varied with the seasons: spring (15 Apr-18 Jun) half-life 23 days, summer (19 Aug-8 Sept) 3.1 days, winter (4 Mar-4 May) 13 days(1). The effective half-lives for volatilization without water evaporation of benzene uniformly distributed at a rate of 1 kg/ha to 1 and 10 cm in soil with an organic carbon content of 1.25% were 7.2 and 38.4 days, respectively(2). The half-life for evaporation in a wind-wave tank with a wind speed of 7.09 m/sec was 5.23 hr(3). [(1) Wakeham SG et al; Environ Sci Technol 17: 611-7 (1983) (2) Jury WA et al; J Environ Qual 13: 573-9 (1984) (3) Mackay D, Yeun ATK; Environ Sci Technol 17: 211-7 (1983)].

The estimated half-life for volatilization of benzene from a river one meter deep flowing 1 m/sec with a wind velocity of 3 m/sec is estimated to be 2.7 hrs at 20 deg C(2,SRC) based on a reported Henry's Law constant of 5.3X10-3 atm-cu m/mole(1). Based on a reported vapor pressure of 95.2 mm Hg at 25 deg C(3), evaporation of benzene from surface soil and other surfaces is expected to be rapid. [(1) Hine J, Mookerjee PK; J Org Chem 40: 292-8 (1975) (2) Lyman WJ et al; Handbook of Chem Property Estimation Methods NY: McGraw-Hill pp. 15-9 to 15-31 (1982) (3) Riddick JA et al; Organic Solvents: Physical Properties and Methods of Purification. Techniques of Chemistry 4th ed. Wiley-Interscience pp. 1325 (1986)].

Absorption, Distribution and Excretion [609]:

Benzene is readily absorbed via lung, & about 40-50% is retained. ... It is taken up preferentially by fatty & nervous tissues, & about 30-50% ... Is excreted unchanged via lung; a 3-phase excretion pattern is seen at ... /Approx/ 0.7-1.7 Hr, 3-4 hr, & 20-30 hr. [IARC. Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man. Geneva: World Health Organization, International Agency for Research on Cancer,1972-PRESENT. (Multivolume work).,p. V7 211 (1974)].

When benzene was placed on skin under closed cup it was absorbed at rate of 0.4 mg/sq cm/hr (Hanke et al 1961) ... [IARC. Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man. Geneva: World Health Organization, International Agency for Research on Cancer,1972-PRESENT. (Multivolume work).,p. V29 117 (1982)].

Mice treated sc with 2 ml (3)h-labeled benzene/kg contained irreversibly bound radioactivity with decreasing binding magnitude in the following organs: liver, brain, kidney, spleen, fat. Mice treated with 2 daily SC doses of 0.5 Ml (3)h-benzene/kg for 1-10 days showed a radioactivity binding with liver & bone marrow residues which increased with treatment duration, except in the case of binding to bone marrow which decreased after day 6. [SNYDER R ET AL; RES COMMUN CHEM PATHOL PHARMACOL 20 (1): 191-4 (1978)].

When administered to mice subcutaneously, 72% of dose is recovered in expired air. [Andrews LS et al; Biochem Pharmacol 26: 293 (1977)].

Pharmacokinetic studies of humans experimentally exposed to approximately 50-60 ppm of benzene for four hours indicated that the absorption rate from the lung was approximately 47% with 30% being retained and 17% being exhaled unchanged. [USEPA; ECAO Atlas Document: Benzene IV-1 (1980)].

Rats were exposed to 500 ppm benzene for 30 min to eight hr. Benzene concentrations reached steady state within four hr in blood (steady-state concn= 11.5 ug/g), six hr in fat (concn= 164.4 ug/g), and two hr in bone marrow (concn= 37.0 ug/g). Lesser concn were detected in the kidney, lung, liver, brain, and spleen. [Rickert DE et al; Toxicol Appl Pharmacol 49: 417-23 (1979)].

Benzene is absorbed from the gastrointestinal tract when ingested. [Goodman LS, Gilmann A; The Pharm Basis of Therapeutics p.936 (1970)].

Benzene crosses the human placenta, & levels in cord blood are similar to those in maternal blood. ... The most frequent route by which humans are exposed to benzene is via inhalation. Toxic effects in humans have been attributed to combined exposure by both respiration & through the skin ... It is eliminated unchanged in expired air ... In men & women exposed to 52-62 ppm (166-198 MG/CU M) benzene for 4 hr, a mean of 46.9% Was taken up, 30.2% Was retained & the remaining 16.8% Excreted as unchanged benzene in expired air. ... When humans were exposed to 100 ppm (300 mg/cu m) benzene, it was detected in expired air 24 hr later, suggesting that it is possible to back-extrapolate to the benzene concentration in the inspired air. [IARC. Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man. Geneva: World Health Organization, International Agency for Research on Cancer,1972-PRESENT. (Multivolume work).,p. V29 117 (1982)].

... In female & male rats with large body fat content, benzene was eliminated more slowly & stored longer than in lean animals. ... Distribution in rabbit was highest in adipose tissue, high for bone marrow, & lower for brain, heart, kidney, lung, & muscle, although direct binding was higher in liver than in bone marrow. [Clayton, G. D. and F. E. Clayton (eds.). Patty's Industrial Hygiene and Toxicology: Volume 2A, 2B, 2C: Toxicology. 3rd ed. New York: John Wiley Sons, 1981-1982. 3279].

The solubility characteristics of benzene are such that it is easily taken up by the stratum corneum. Once in the stratum corneum, it does not meet many restraining forces to impede its movement and diffuses easily. The permeability constant for benzene, as determined in vitro, is higher than that of many other small molecules, particularly those having one or more polar groups. ... Even though these uncertainties exist, and more data are needed to support the ... conclusion that there is good overall agreement between in vitro and in vivo data. ... An adult working in ambient air containing 10 ppm of benzene, with 100 cm of glaborous skin in contact with gasoline containing 5% benzene, and his entire skin (2 sq m) in contact with ambient air, will absorb in an hr, 7.5 ul of benzene from inhalation, 7.0 ul from contact with gasoline, and 1.5 ul from body exposure to ambient air. Since ... in vitro techniques measure the penetration of benzene through strongly hydrated stratum corneum, the calculated flux may be higher than under some in vivo conditions. Nevertheless, it seems that unless good hygiene is maintained and care is taken to prevent lengthy exposure to solvents containing benzene, significant amounts of benzene may enter the body through the skin. [Blank IH, McAuliffe DJ; J Investigat Dermatol

85: 522-6 (1985)].

Laboratory and/or Field Analyses:

Detection limits should be as low as possible to avoid false negatives and (in any case) no higher than comparison benchmarks or criteria. USGS can achieve water detection limits of 0.1 ug/L or less for this compound using advanced methods such as USGS 1996 Custom Method 9090. Wisconsin requires a detection limit of 0.5 ug/L for all VOCs [923]. Several methods are available to achieve water detection limits below 1 ppb [767]. Soil and sediment methods are available with detection limits as low as 1 ppt.

If there is no reason to reason to use the lowest detection limits (for example, much higher levels are found or if no comparison benchmarks are that low), default detection limits should generally be no higher than 25 ppb [913] in soil, sediment, or tissue, and if possible, no higher than 1 ppb in water.

For optimum risk or hazard assessment work, volatile compound lab methods with very low detection limits [such as USGS 9090 or 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 the past, many methods have been used to analyze for this compound [861,1010,1011,1013]. Purgeable aromatics (such as benzene, ethylbenzene, and toluene have been analyzed using method 602 [1010] and 8240 or 8260 [1013]. However, 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]. EPA methods for NPDES permits are specified in 40 CFR Part 136 [1010]. EPA methods for drinking water are specified in 40 CFR Part 141 [1011].

EPA (RCRA Group) publishes requirements for solid waste methods in 40 CFR Part 261, Appendix III, with details in the following periodically updated publication [1013]:

> Environmental Protection Agency. 1997. Test methods for evaluating solid waste, physical/chemical methods, SW-846, EPA Office of Solid Waste and Emergency Response, EPA, Washington, D.C. Update 3 finalized in 1997. Available from NTIS or GPO. Previous 1995 update 2 was available on CD-ROM [1013].

RCRA (SW-846) methods tend to include provisions for using the specified method or something better. RCRA SW-846 methods typically require instrument calibration before analyses, but some labs don't do it, and many labs actually use some kind of hybrid between RCRA, CERCLA, or various other "standard protocols" (Roy Irwin, Park Service, Personal Communication, 1997, based on conversations with various EPA and private lab staff members). The guidance in SW-846 must be used in some states, but is considered "guidance of acceptable but not required methods" in most federal

applications. In the past, EPA has also published separate (not SW-846) guidance documents with suggestions on field sampling and data quality assurance related to sampling of sediments [1016] and soils [1017,1018,1019].

EPA (CERCLA) publishes various Contract Laboratory Program (CLP) methods documents periodically, available from EPA and NTIS. CLP methods were designed for use in contaminated areas and often have detection limits that are not low enough for use in relatively clean areas or where low detection levels are needed in comparison with low concentration criteria or benchmarks. CERCLA CLP methods tend to require things done exactly per contract specifications. A few examples of CLP publications (this list is not complete) [861]:

User's Guide CLP CERCLA User's Guide to the Contract Laboratory Program. USEPA - Office of Emergency and Remedial Response. Dec 1988

9240_0-0XFS Multi-Media/Conc Superfund OSWER CERCLA Multi-Media, Multi-Concentration Organic/Inorganic Analytical Service for Superfund, Quick Reference Fact Sheets, 9240.0-08FS (organic) and 9240-0-09FS (inorganic), August 1991. The organic/inorganic analytical service provides a technical and contractual framework for laboratories to apply EPA/Contract Laboratory Program (CLP) analytical methods for the isolation, detection and quantitative measurement of 33 volatile, 64 semi-volatile, 28 pesticide/Aroclor, and 24 inorganic target analytes in water and soil/ sediment environmental samples.

AOC/Contract Laboratory Program (CLP), Routine Analytical Services, Summary on EPA Home Page under Superfund Subdirectory, EPA Office of Remedial and Emergency Response, 1997, Internet.

Examples of standard method protocols published by various parts of EPA as well as some other agencies are outlined below:

Holding Times:

Water Samples: According to EPA protocols for NPDES permits, the maximum holding time for all purgeable aromatics (such as benzene, ethylbenzene, and toluene) is 14 days; samples should be kept iced or refrigerated, with no headspace or bubbles in the container (40 CFR, Part 136,3, 1994) [1010].

Samples of Solids: EPA RCRA methods for volatiles in solids in SW-846 also call for holding times of 14 days [1013].

Containers:

Both EPA and APHA (Standards Methods Book) recommend glass containers for the collection of organic compounds

[141,1010]. Guidance from other federal agencies (USGS, FWS, NOAA) also recommends glass containers for organics, and discourages the use of plastic containers for a variety of reasons (Roy Irwin, National Park Service, Personal Communication, 1997, based on a glance through recent internal guidance of several agencies). EPA specifies the use of teflon lined caps and teflon lined cap septums in glass vial containers for water samples of volatiles (VOCs and purgeable halocarbons such as the common organic solvents) [1010]. No headspace is allowed [1010]. Actually, vials are not the best choice for avoiding false negatives in soil samples through volatilization losses, since the use of brass liners for collection resulted in 19 fold higher VOCs than when 40 mL vials were used [798] (see Wisconsin protocol discussion below). The third update of EPA's SW-846 RCRA guidance authorizes the storage of soil samples of volatiles in EnCore TM (or equivalent, no government endorsement implied) samplers as long the sample is analyzed within 48 hours after collection [1013]. Several states also authorize the use of EnCore TM or equivalent containers (Donalea Dinsmore, State of Wisconsin DNR, personal communication, 1997).

Some federal agency quality control procedures call for voiding or red-flagging the results of organic analyses if the lab receives the sample in plastic containers (Roy Irwin, National Park Service, Personal Communication, 1997). The APHA pointed out some the potential hazards of the use of certain plastic containers for storing organic samples [141]:

> A) Potential contamination of the sample via leaching of compounds from the plastic, and/or
>
> B) The plastic container walls can sometimes be attacked by certain organics and fail, and/or
>
> C) The possibility that some of organic compound will dissolve into the walls of the plastic container, reducing the concentration of the compound in the container [141].

Certain plastic polymers present less of a problem related to potential losses of volatiles than others. Some plastic is found in the latest approved EnCore TM samplers. Some states also give the reader the option of using plastic in collecting devices. For example, related to methods for gasoline range petroleum hydrocarbons, Wisconsin states that organics can be collected using a 30 ml plastic syringe with the end sliced off, a brass tube, an EnCore TM sampler or other appropriate devices (Donalea Dinsmore, State of Wisconsin DNR, personal communication, 1997). A plastic syringe is

also mentioned as an option in SW-846 [1013]. The thinking appears to be that plastic is less of a threat in a collecting device, with momentary contact, than in a storage container where contact times are longer.

Typical "standard method" protocols recommend proper cleaning of glass containers before use. Some collectors simply use pre-cleaned jars from I-Chem or Eagle Pitcher (no government endorsement implied) or equivalent suppliers. EPA [1010], USGS, and most other federal agencies recommend cleaning procedures for the glass containers, usually involving detergent rinsing, baking, and sometimes HCL rinses (Roy Irwin, National Park Service, Personal Communication, 1997).

Field Protocols:

Standard field collection method protocols are published or internally distributed by the Fish and Wildlife Service, the USGS, DOE, NOAA, and EPA. These recommendations change over time, with the newest recommendations sometimes being quite different than the old, thereby producing different results. The Fish and Wildlife Service methods are similar in many ways to NOAA field protocols [676]. Many recommended EPA field methods for organics are not very detailed, although the 3rd update of SW-846 for RCRA solid waste methods is becoming more detailed [1013].

The various EPA methods for organics are different from each other, with the selection of the appropriate method depending upon the specific application (RCRA vs. CERCLA vs. NPDES permits, vs. Drinking Water, etc.) [861,1010,1013]. The EPA-recommended field methods are scattered through various EPA and ASTM publications.

EPA methods typically include recommendations that grab samples rather than composites be utilized for organics, and require the proper cleaning of collection bottles and collecting gear for both volatile and semi-volatile organics [1010,1013]. In other publications, EPA recommends caution in the use of composite soil samples whether organic or inorganic, citing statistical complications and stating that the compositing of samples cannot, in general, be justified unless for a stated specific purpose and unless a justification is provided [1017].

ASTM publishes standard method guidance for numerous very specific applications, like sampling from pipes (D 3370-95a) and sampling for VOCs in soils (ASTM method D 4547] [1018].

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]. This is especially true for soil and sediment sampling. 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]. In one study, the use of brass liners for collection of soil samples resulted in 19 fold higher VOCs than when 40 mL vials were used [798].

National guidance for minimizing loss of volatiles in field sampling is found in EPA RCRA method 5035 as described in update 3 of SW-846 [1013,1018]. Several states (WI,MN,NJ, and MI) have developed their own detailed guidance, often including the use of methanol as a preservative.

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 [913]:

1) Concentrated (1:1 by weight of preservative vs soil) 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 EnCoreTM 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].

Note: The use of methanol for soil sample preservation can make lower detection limits difficult, but the tradeoff can be worth it since otherwise high percentages of volatiles can be lost in very short periods of time, for example in 2 hours for benzene. In other words, low detection limits do not help much if you are losing all the volatiles from the soil sample before analysis. A possible alternative to using methanol for soil samples

of volatiles would be to use the EnCoreTM sampler and to analyze as soon as possible (no later than 48 hours) after collection using the methods that give lower detection limits (Donalea Dinsmore, State of Wisconsin DNR, personal communication, 1997).

The USGS NAWQA program also recognized the problem of potential losses of volatile compounds, and recommends the use of strong (1:1) HCL as preservative material. Some SW-846 methods call for the use of sulfuric acid [1013].

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, 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 (see 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]. The basics of these quality assurance plans for chemical analyses should include the following quality control steps:

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. Typical lab quality control techniques should have included the following considerations (Roy Irwin, National Park Service, Personal Communication, 1997, summary based on various EPA and FWS documents):

Procedural Blanks should be analyzed to assure that no

contaminants are added during the processing of the samples. The standards for adequacy depend on the method and the media being measured.

Different federal agencies publish different acceptable limits. For one program, NOAA stated that at least 8% of samples should be blanks, reference or control materials [676].

The basic idea is that neither samples nor blanks should be contaminated. Because the only way to measure the performance of the modified procedures is through the collection and analysis of uncontaminated blank samples in accordance with this guidance and the referenced methods, it is highly recommended that any modifications be thoroughly evaluated and demonstrated to be effective before field samples are collected [1003].

Duplicate samples are analyzed to provide a measure of precision of the methods. The standards for adequacy depend on the method and the media being measured.

Different federal agencies publish different acceptable limits. There appears to be an inverse relationship between precision and sensitivity [676].

Some EPA methods state that a field duplicate must be collected at each sampling site, or one field duplicate per every ten samples, whichever is more frequent [1003]. Some protocols call for the preparation of one Ongoing precision and recovery (OPR) standard for every ten or fewer field samples. Great care should be taken in preparing ongoing precision and recovery standards [1003].

Spiked samples are analyzed to provide a measure of the accuracy of the analysis methods. The standards for adequacy depend on the method and the media being measured.

Different federal agencies publish different acceptable limits.

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. This is one reason for using method 8260 modified for Selective Ion Mode (SIM) detection limits and using the NOAA expanded scan for PAHs and alkyl PAHs [828] when responding to oil spills. Alkyl PAHs are more persistent than benzene. The more rigorous scans are less prone to false negatives than many of the standard EPA scans (Roy Irwin, National Park Service, Personal

Communication, 1997).

However, benzene, ethylbenzene, toluene, and xylenes (the BTEX compounds) are often analyzed when light products such as gasoline are spilled. It is not always easy to determine which standard method to use. The following is a proposed decision Tree (dichotomous key) for selection of lab methods for measuring contamination from gasoline and other light petroleum products containing significant benzene, ethylbenzene, toluene, and xylenes (Roy Irwin, National Park Service, Personal Communication, 1997):

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 8260 (older method was 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 8260 (8260 is replacing older method 8240). The standard EPA GC/MS method 8260 protocol will be sufficient for some applications, but the standard EPA method 82400 (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 8260 (8260 is replacing older 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 8260), and (optional) PAHs (NOAA protocol expanded scan***). The magnitude of any residual soil contamination will provide insight about the likelihood of recontamination of groundwater resources through equilibria partitioning mechanisms moving contamination from soil to water.

5a. The medium of concern is sediments or soils.....6

5b. The medium of concern is biological tissues.....7

6. If there is any reason to suspect fresh* or continuing contamination of soils or sediments with lighter volatile compounds, perform EPA GC/MS method 8260 (8260 is replacing older 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 8260 (8260 is replacing older 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 8260 (8260 is replacing older method 8240) or modified EPA method 8260 (8260 is replacing older 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 8260 (8260 is replacing older method 8240) or modified EPA method 8260 in the Selected Ion Mode (SIM). Less is known about plant effects. However, the same methods recommended above for the analyses of water (Step 4 above) and for sediments or soils (Step 6 above) are usually also recommended for these same media in plant or wildlife habitats. If wildlife or plants are covered with oil, see also Step 8 (above) regarding oiling issues.

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

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

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

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

End of decision tree key.

For drinking water, in the past, EPA has recommended the following less rigorous methods for analyses of certain volatiles including benzene: 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); Older (no longer state of the art) PQL historically was 0.005 mg/L [893].

Methods for biological samples: Analytical methods have been developed to measure benzene levels in exhaled breath, blood, and various body tissues [767]. Methods are also available for determining metabolites of benzene in urine [767]. The primary method of analyzing for benzene in exhaled breath, body fluids and tissues is gas chromatography (GC) coupled with either flame ionization detection (FID), photoionization detection (PID), or mass spectrometry (MS) [767]. Both GC/FID and high-performance liquid chromatography (HPLC) with ultraviolet detection (UV) have been used to measure urinary metabolites [767]. Rigorous sample collection and preparation methods must be followed when analyzing for benzene and/or its metabolites to prevent contamination of the sample [767]. A summary of commonly used methods of measuring benzene in biological samples is presented in Table 6-1 [767]. Breath samples are collected on a solid sorbent, such as activated charcoal, silica gel, or Tenax GC, and thermally desorbed [767]. or collected in a breath sampling tube and directly injected [767]. A technique involving headspace analysis of adsorbed benzene has also been used with good results [767]. The sensitivity of the available methods ranges from the sub- to mid-ppb, with those using MS detection generally the most sensitive [767]. The selectivity of the methods is improved if high- resolution gas chromatographic (HRGC) columns are used [767].

Methods for environmental samples: Methods exist for determining benzene in air (ambient, occupational, and industrial), water, sediment, soil, foods, cigarette smoke, gasoline, and jet fuel [767]. Most involve separation by GC with detection by FID, PID, or MS [767]. HPLC/UV, spectrophotometry, and laser Raman spectroscopy (LRS) have also been used [767]. Table 6-2 summarizes several of the methods that have been used to analyze for benzene in environmental samples [767]. Numerous methods exist for detecting and measuring benzene in air [767]. Air samples for benzene analysis are usually preconcentrated by passing the sample through a trap containing a solid adsorbent [767]. Commonly used adsorbents are Tenax resins (e.g., Tenax TA, Tenax GR), silica gel, activated carbon, and carbonaceous polymeric compounds [767]. Benzene in air can be collected in stainless steel canisters (Summa polished canisters) or Tedlar bags [767], and can be analyzed with or without preconcentration [767]. Preconcentration of benzene can be accomplished by direct on-column cryogenic trapping [767], or

samples may be analyzed directly without preconcentration [767].

Description of Custom Method 9090: Basic Description of the Method (Brooke Connor, USGS Water Quality Lab, Denver, Personal Communication, 1996):

> Tue, 14 May 1996 From: "John S Zogorski, Supervisory Hydrologist, Rapid City, SD" Custom Method 9090: Basic Description of the Method, Identification and Quantification Strategy, and Data Transfer.
>
> General Description of the Method: Custom method 9090 uses capillary column gas chromatography / mass spectrometry (GC/MS) to identify and quantitate 87 analytes, and to tentatively identify unknowns. The method is intended to identify and measure low concentrations of VOCs that may occur in the environmental settings sampled in the NAWQA program, and which may be associated with either point and non-point sources, especially in urban areas. Fifty-five of the analytes included on 9090 are referred to as NAWQA VOC target analytes and were selected because of their known human health concern (A or B carcinogens), aquatic toxicity, frequency of occurrence, and/or emerging chemicals with a potential for wide-scale use and significance. Custom method 9090 builds on the same VOC analytical technology, GC/MS, that has been used at the NWQL and elsewhere for many years, and which is considered the conventional approach for high-quality analysis of VOCs in water...Persons unfamiliar with the GC/MS method for VOCs may wish to refer to 2 recent reports: Rose, D.L., and M.P. Schroeder, 1995, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory -- Determination of volatile organic compounds in water by purge and trap capillary gas chromatography/mass spectrometry: U.S. Geological Survey Open-File Report 94-708, 26 p. Raese, J.W., D.L Rose, and M.W. Sandstrom, 1995, U.S. Geological Survey Laboratory Method for Methyl tert-Butyl Ether and Other Fuel Oxygenates: U.S. Geological Survey Fact Sheet 219-95, 4 p.

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

> EPA Method 8240 for Volatile Organics [861]:
>
> > Method 8260 is replacing 8240 [1013].
> >
> > 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]. Method 8260 is replacing 8240 [1013].

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

Method 8260 is replacing 8240 [1013].

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].

This compound is one of the BTEX compounds. Notes on more generalized BTEX 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