# ENVIRONMENTAL CONTAMINANTS ENCYCLOPEDIA

# ETHYLBENZENE ENTRY

**July 1, 1997**


**COMPILERS/EDITORS:**

**ROY J. IRWIN, NATIONAL PARK SERVICE**

**WITH ASSISTANCE FROM COLORADO STATE UNIVERSITY**

**STUDENT ASSISTANT CONTAMINANTS SPECIALISTS:**

**MARK VAN MOUWERIK**

**LYNETTE STEVENS**

**MARION DUBLER SEESE**

**WENDY BASHAM**

**NATIONAL PARK SERVICE**

**WATER RESOURCES DIVISIONS, WATER OPERATIONS BRANCH**

**1201 Oakridge Drive, Suite 250**

**FORT COLLINS, COLORADO 80525**

**WARNING/DISCLAIMERS:**

Where specific products, books, or laboratories are mentioned, no official U.S. government endorsement is implied.

Digital format users: No software was independently developed for this project. Technical questions related to software should be directed to the manufacturer of whatever software is being used to read the files. Adobe Acrobat PDF files are supplied to allow use of this product with a wide variety of software and hardware (DOS, Windows, MAC, and UNIX).

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 or summaries as being "what the original author said," the proposed interagency funding of a bigger project with more elaborate peer review and quality control steps never materialized.

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

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

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

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

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

on the internet or NTIS: 1998).

Ethylbenzene (CAS number 100-41-4)

**Br**ief Introduction:

**Br.Class**: General Introduction and Classification Information:

Ethylbenzene is a volatile organic compound (VOC) [868,903]. Like toluene and xylenes, ethylbenzene is an alkyl benzene. It is different from benzene in having an ethyl group added to (substituted for a hydrogen) on the benzene ring.

Ethylbenzene has been 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 (40 CFR 116.4 (7/1/87)). These regulations apply to discharges of this substance [609]. It is also a toxic pollutant designated pursuant to section 307(a)(1) of the Clean Water Act and is subject to effluent limitations (40 CFR 401.15, 7/1/87) [609].

**Br.Haz**: General Hazard/Toxicity Summary:

Releases to water occur as a result of industrial discharges, the use of gasoline fuel for boating, fuel spillage, leaking underground storage tanks, landfill leachate, and the inappropriate disposal of waste [910]. Ocean releases occur as a result of offshore oil production, hydrocarbon venting, oil field brines, and tanker oil spills [910].

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.

Effects of this volatile solvent to non-human biota would often result from high concentrations immediately after a spill (before the compound has volatilized into the atmosphere) or as the indirect result of contamination of groundwater. For example, if highly polluted groundwater water comes into surface waters from springs or seeps, local effects may occur in the mixing zone where the groundwater enters surface water.

Human populations are primarily exposed to ethylbenzene from ambient air particularly in areas of heavy traffic, tunnels, parking lots, and around filling stations since it is a component of gasoline. High levels of exposure may exist near production and manufacturing facilities and in occupational settings where ethylbenzene is used as a solvent. Non-occupational exposure may result from indoor air containing cigarette smoke. Ethylbenzene is a contaminant in many drinking water supplies and levels can be quite high for wells near leaky gasoline storage tanks and for many surface supplies [609].

ATSDR has published a toxicity profile for this substance [910]. It states there are no reliable data on the effects in humans after eating, drinking, or breathing ethylbenzene or following direct exposure to the skin [910]. Additional human health issues related to this topic have been summarized by ATSDR [910]. Each profile will be revised and republished as necessary, but no less often than every three years, as required by CERCLA, as amended [910]. Due to lack of time, only part of the important highlights from this ATSDR document have as yet been incorporated into this current NPS entry.

This compound often occurs together with other aromatics (sometimes including alkyl PAHs), and a typical complex mixture of aromatics may be more toxic or hazardous in general than this compound would be alone (see "PAHs as a group" entry).

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

EPA 1996 IRIS Database [893]:

Classification as to human carcinogenicity weight-of-evidence classification:

Classification: D; not classifiable as to human carcinogenicity

BASIS: nonclassifiable due to lack of animal bioassays and human studies.

HUMAN CARCINOGENICITY DATA: None.

ANIMAL CARCINOGENICITY DATA: None. NTP has plans to initiate bioassay. Metabolism and excretion studies at 3.5, 35 and 350 mg/kg are to be conducted as well.

This compound often occurs together with other aromatics, some possibly more carcinogenic (see "PAHs as a group" and "Benzene" entries).

This compound has not been treated as a carcinogen for model calculation purposes in some EPA risk-based (RBC or risk-based concentration and PRG or Preliminary remediation goals) models [868,903].

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

One study indicated that acute oral exposure to 500 or 1000 mg/kg ethylbenzene decreases peripheral hormone levels and may block or delay the estrus cycle in female rats during the diestrus stage [910].

Ethylbenzene was not mutagenic in the range of concentrations tested (0.2, 2, 20, 50 and 200 ug/plate) for S. typhimurium TA98, TA100, TA1535, TA1537 and TA1538 or for Escherichia coli WP2 and WP2uvrA. Ethylbenzene also showed no response in the S. cerevisiae JD1 gene conversion assay. In contrast, ethylbenzene hydroperoxide showed positive responses with E. coli WP2 at 200 ug/plate in the presence of S9 and an equally significant response with the gene conversion system of yeast [893].

Additional human health issues related to this topic have been summarized by ATSDR [910].

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

The biodegrability of MTBE (often found along with ethyl benzene in gasoline spills) in the subsurface is substantially slower than ethyl 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]:

> Ethylbenzene will enter the atmosphere primarily from fugitive emissions and exhaust connected with its use in gasoline. More localized sources will be emissions, waste water and spills from its production and industrial use. Once in the

atmosphere, ethylbenzene will photochemically degrade by reaction with hydroxyl radicals (t1/2 hrs to 2 days) and partially return to earth in rain. Releases into water will decrease in concn by evaporation and biodegradation. The time for this decrease and the primary loss processes will depend on the season, and the turbulence and microbial populations in the particular body of water. Representative half-lives are several days to 2 weeks. Ethylbenzene is only adsorbed moderately by soil and may leach into groundwater where its biodegradation is possible. The primary source of exposure is from the air especially in areas of high traffic. However, exposure from drinking water is not uncommon [609].

**Syn**onyms/Substance Identification:

Aethylbenzol (German) [609]
Benzene, ethyl- [609]
EB [609]
Ethyl benzene [609]
Ethylbenzeen (Dutch) [609]
Ethylbenzol [609]
Etilbenzene (Italian) [609]
Etylobenzen (Polish) [609]
Phenylethane [609]
NCI-C56393 [609]

Molecular Formula:
C8-H10 [609]

**As**sociated Chemicals or Topics (Includes Transformation Products):

See also entries on:

BTEX
Gasoline, General
Petroleum, General
Benzene
Toluene
Xylene

See also: inforamtion on breakdown products in Fate.Detail section below.

Information from HSDB [609]:

Constituent components of typical commercial grade = 99.7% ethylbenzene, 0.1% m- and p-xylene, 0.1% cumene, and 0.1% toluene. [Sun Petroleum Prod Co; Material Safety Data Sheet (1981)].

Compounds identified in tars produced by the pyrolysis of ethylbenzene include the following suspected carcinogens: 1-benzanthracene, benzene, benzofluoranthene, 10,11-benzofluoranthene, 12-benzofluoranthene, 1-benzofluoranthene, 1-benzopyrene, 3,4-benzopyrene, chrysene, and 1,2:5,6-dibenzanthracene. [NAS; The Alkylbenzenes p.99 (1981)].

Metabolism/Metabolites [609]:

Ethyl benzene in man is metabolized 64% to mandelic and 25% to phenylglyoxylic acid and excreted into urine. [Thienes, C., and T.J. Haley. Clinical Toxicology. 5th ed. Philadelphia: Lea and Febiger, 1972. 126].

When admin orally to rabbits, it was ... Converted ... To a number of oxidation products & subsequently excreted. Major urinary metab was hippuric acid. Oxidation products were benzoic acid, phenylacetic acid & mandelic acid excreted as glycine conjugate, & ... Methylphenylcarbinol (1-phenylethanol) excreted as glucuronide. [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. 3304].

From a dose of 100 mg/kg admin orally to rats ... The urinary metabolites, p-ethylphenol, about 0.3%, & Smaller quantities of 1- & 2-phenylethanol /were identified/. [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. 3304].

In 3 lab technicians occupationally exposed to ethylbenzene, the urinary metabolites were amygdalic acid, phenylglyoxylic acid & 2-ethylphenol; within 24 hr more than 90% of metabolites had been excreted. [Hagemann J et al; Krebsgefaehrdung Arbeitsplatz/Arbeitsmed Kolloq, Ber Jahrestag Dtsch Ges Arbeitsmed, 19TH: 421 (1979)].

The oxidation of ethylbenzene to methylphenylcarbinol in animals ... Was confirmed ... With additional finding that both isomers of methyl phenyl carbinol (the + and - forms) in equal amt are result of its biological hydroxylation. [Browning, E. Toxicity and Metabolism of Industrial Solvents. New York: American Elsevier, 1965. 91].

Urinary sulfate ratio decreases are normally a rough est of dose-related alkylbenzene hydroxylation due mainly to side chain oxidation. ... This ... Does not hold with dose-action relationship for ethylbenzene. ... At high doses, ring hydroxylation increases, altering sulfate

ratio. [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. 3304].

Products of ring hydroxylation ... Detected for 1st time in rabbit urine. ... Identification of m- & p-hydroxyacetophenone & ... Acetophenone reveals that further oxidation in side-chain of acetophenone to phenacyl alcohol (& then to benzoic acid) is not only pathway. ... However, ring-hydroxylated products are only minor ones. [The Chemical Society. Foreign Compound Metabolism in Mammals. Volume 4: A Review of the Literature Published during 1974 and 1975. London: The Chemical Society, 1977. 247].

Since ... (1+) & (-1)Methylphenyl carbinol yielded (-1)mandelic acid /in rats/, as did acetophenone & omega-hydroxyacetophenone, the stereoselective step must occur during oxidation &/or reduction of latter ... Either pathway is possible, for ... Phenylglyoxal & ... Phenylethylene glycol ... Yielded (-)mandelic acid stereoselectively. [The Chemical Society. Foreign Compound Metabolism in Mammals. Volume 5: A Review of the Literature Published during 1976 and 1977. London: The Chemical Society, 1979. 505].

Benzoylformic acid was by-product in all ... Expt /in which rats were fed possible intermediates/. However, when this cmpd was fed, no mandelic acid was formed, & neither was (-1)mandelic acid converted into benzoylformic acid. [The Chemical Society. Foreign Compound Metabolism in Mammals. Volume 5: A Review of the Literature Published during 1976 and 1977. London: The Chemical Society, 1979. 505].

Female assistants using mixture of xylenes & ethylbenzene as solvent in histology lab were exam. Avg air concn of (m + p)-xylene & ethylbenzene was between 56-68 & 34-41 ppm. Approx 1.1 To 1.4% Of retained ethylbenzene was metabolized to 2-ethyl-phenol. [Angerer J et al; Int arch occup environ health 43 (2): 145 (1979)].

After ip administration of /4.45 g/ ethylbenzene /to rabbits/ ... o-, p-, and m-hydroxyacetophenone were identified in urine. The above hydroxyacetophenones represented 0.11, 0.13, and 0.03% of the dose ... respectively. [Kiese M, Lenk W; Xenobiotica 4: 337-43 (1974)].

When absorbed through skin, mandelic acid was excreted at 4.6%, Whereas after lung absorption majority of ethylbenzene was converted to mandelic acid & conjugated with glycine. [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. 3304].

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

**W.Lo**w (Water Concentrations Considered Low):

No information found.

**W.Hi**gh (Water Concentrations Considered High):

The geometric mean concentrations of ethylbenzene found at hazardous waste sites on the National Priorities List was 239 ppb in surface water and 69 ppb in groundwater (non-detect samples were not included in the mean calculations) [910].

Ethylbenzene has been detected in wells downgradient from landfills in Southern Ontario at concentrations ranging from 12 to 74 ug/L (ppb). Ethylbenzene was detected in private well water in Rhode Island with concentrations ranging from 1 to 156 ug/L. Groundwater near an underground coal gasification site in northeastern Wyoming contained concentrations of ethylbenzene ranging from 92 to 400 ug/L (ppb). Groundwater samples near a fuel spill in the Great Ouse Basin in Great Britain contained ethylbenzene concentrations as high as 1110 ug/L [910].

Highest MTBE (additive often found along with ethyl 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 (including ethyl benzene) concentrations of about 30 ppb (James Davidison, Alpine Environmental, Fort Collins, CO, personal communication, 1997).

**W.Typ**ical (Water Concentrations Considered Typical):

The median ethylbenzene concentration in ambient surface waters in the United States in 1980-82 was less than 5.0 ug/L (ppb) according to EPA's STORET water quality data base. The chemical was detected in 10% of 1101 samples collected during that period. Ethylbenzene was detected in 7.4% of the 1368 industrial effluent samples collected during 1980-1983 at a median concentration of less than 3.0 ug/L [910].

Ethylbenzene was measured in seawater at an average

concentration of 0.011 ug/L (ppb) and a concentration range of 0.0018-0.022 ug/L (ppb) over a 15-month observation period at Vineyard Sound, MA. It also has been reported in surface waters of the Gulf of Mexico at a concentration range of 0.0004-0.0045 ug/L (ppb) [910].

Ethylbenzene was measured in 4% of the municipal runoff samples collected in 15 cities of the United States as part of EPA's Nationwide Urban Runoff Program. The measured concentration range was 1-2 ug/L (ppb) [910].

Ethylbenzene does not appear to be widespread in groundwater used for public drinking water supplies. The 1982 Ground Water Supply Survey conducted by EPA reported ethylbenzene in only 3 out of 466 random samples at a mean concentration of 0.8 ug/L (ppb) and a maximum concentration of 1.1 ug/L [910].

Ethylbenzene was detected in public drinking water in Rhode Island with concentrations ranging from 1 ug/L (ppb) to 3 ug/L [910].

Ethylbenzene was measured in all three water plants sampled as part of the New Orleans Area Water Supply Study conducted by EPA in 1974 [910]. The reported concentrations were 1.6, 1.8, and 2.3 ug/L [910].

Water Concentrations [609]:

> DRINKING WATER: In surveys of representative US municipal water supplies, ethylbenzene has been detected in most cases(1,2,4-8,21). Values for 3 New Orleans finished drinking waters ranged 1.6 to 2.3 ppb(6). Chicago Central Water Works on Lake Michigan measured 4 ppb(8). It has been found in the water supply for Evansville, IN on the Ohio River(7). 6 of 10 US cities were found to be positive(1,4). One US city had 1 of 4 samples pos with a 1 ppb avg, while another reported no positive samples(5). Tap water from bank infiltrated Rhine River water in the Netherlands measured 30 ppb in one study(3). Zurich, Switzerland tap water - detected not quantified(9). [(1) NAS; The Alkylbenzenes p III-13 Contract 68-01-4655 (1980) (2) Shackelford WM, Keith, LH; Frequency of Organic Compounds in Surface Waters USEPA 600/4-76-062 (1976) (3) Piet GJ, Morra CF; p 31-42 in Artificial Groundwater Recharge; Huisman L, Olsthorn TN, eds (1983) (4) Bedding ND et al; Sci Total Environ 25: 143-67 (1982) (5) Callahan MA et al; p 55-61 in 8th Natl Conf Munic Sludge Manage Proc (1979) (6) Keith, LH et al; p 329-73 in Identification and Analysis of Organic Pollutants in Water. Keith LH ed (1976) (7) Kleopfer RD,

Fairless BJ; Environ Sci Technol 6: 1036-7 (1972) (8) Konasewich D et al; Status Report on Organic and Heavy Metal Contaminants in the Lakes Erie, Michigan, Huron and Superior Basins. Great Lakes Quality Review Board (1978) (9) Santodonato J et al; Investigation of selected potential environmental contaminants: styrene, ethylbenzene and related compounds 261 p USEPA 560/11-80-018 (1980)].

GROUNDWATER: A well in Ames, IA measured 15 ppb 50 yr after tar residues were buried at a nearby coal gas plant(5). Two aquifers near the Hoe Creek underground coal gasification site in Wyoming were sampled 15 mo after gasification was complete giving values of 82-400 ppb(2). In a US survey, 1970-76, it was detected but not quantified in well waters(1). In Jackson Township, NJ, drinking water wells measured 2000 ppb(4). Chalk aquifer in East Anglia, England - 210 m from petroleum storage - 0.15 ppb, 10 m distance - 1110 ppb, and 100-200 m - <250 ppb(3). [(1) Shackelford WM, Keith, LH; Frequency of Organic Compounds Identified in Water USEPA 600/4-76-062 (1976) (2) Stuermer DH et al; Environ Sci Technol 16: 582-7 (1982) (3) Tester DH, Harker RJ; Water Pollut Control 80: 614-31 (1981) (4) Burmaster DE; Environ 24: 6-13, 33-6 (1982) (5) Santodonato J et al; Investigation of Selected Potential Environmental Contaminants: Styrene, Ethylbenzene and Related Compounds 261 p USEPA 560/11-80-018 (1980)].

SURFACE WATER: Ethylbenzene has been detected but not quantified in a 1970-76 US survey(1,4). 14 heavily industrialized US river basins, 5 of 204 sites pos - 1-4 ppb; Chicago area and Illinois River Basin, 5 of 31 sites pos - 1-4 ppb(6). Two representative US cities, city A - 41% of 28 samples pos, 5.0 ppb avg, city B - 40% of 48 samples pos 3.2 ppb avg(2). Lower Tennessee River near Calvert City, KY reported 4.0 ppb(7). Lake Michigan, Chicago Sanitary and Ship Channel measured 1-2 ppb(3). River Glatt, Switzerland - detected, not quantified(5). [(1) Shackelford WM, Keith LH; Frequency of Organic Compounds Identified in Water USEPA 600/4-76-062 (1976) (2) Callahan MA et al; p 55-61 in 8th Natl Conf Munic Sludge Manage Proc (1979) (3) Konasewich D et al; Status Report on Organic and Heavy Metal Contaminants in the Lakes Erie, Michigan, Huron and Superior Basins. Great Lakes Quality Review Board (1978) (4) Bertsch W et al; J Chromatogr 112: 701-18 (1975) (5) Zuercher F, Giger W; Vom Wasser 47: 37-55 (1976) (6) Ewing BB et al; Monitoring to Detect Previously

Unrecognized Pollutants in Surface Waters 75 p USEPA 560/6-77-015 (appendix USEPA 560/6-77-015a) (1977) (7) Goodley PG, Gordon M; Kentucky Acad Sci 37: 11-5 (1976)].

SEAWATER: Gulf of Mexico anthropogenic influence ranged from 5 to 15 ppb(3). [(3) Sauer TC Jr; Org Geochem 3: 91-101 (1981)].

RAIN WATER: West Los Angeles, CA - 9 ppb(1). [(1) Kawamura K, Kaplan IR; Environ Sci Technol 17: 497-501 (1983)].

Effluents Concentrations [609]:

Industries with mean raw wastewater concentrations >2000 ppb: gum and wood chemicals (11,000 ppb), pharmaceutical manufacturing (10,000 ppb), paint and ink formulation, and auto and other laundries(1). Effluents from representative water treatment plants in Southern California were variable <10 ppb at San Diego City to 130 ppb at Los Angeles Co (both measurements following primary treatment)(2); <10 ppb detected following secondary treatment(2). In a US city survey, 17% of 6 samples were positive, 6.0 ppb avg(3), Lake Michigan, North Side sewage treatment plant - 1 ppb(4). [(1) USEPA; Treatability Manual p.I.9.8-3 USEPA 600/2-82-001a (1981) (2) Young DR; 1978 Ann Rep Southern Calif Coastal Water Res Proj p 103-12 (1978) (3) Callahan MA et al; p 55-61 in 8th Natl Conf Munic Sludge Manage Proc (1979) (4) Konasewich D et al; Status Report on Organic and Heavy Metal Contaminants in Lakes Erie, Michigan, Huron and Superior basins. Great Lakes Qual Board 373 p (1979)].

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

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

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. To be considered unlikely to represent an ecological risk, field concentrations should be below all of the following

benchmarks (ug/L) [649]:

National ambient water quality criterion - acute: no information found

National ambient water quality criterion - chronic: no information found

Secondary acute value: 6970

Secondary chronic value: 389

Lowest chronic value - fish: >440

Estimated lowest chronic value - daphnids: 12,922

Lowest chronic value - non-daphnid invertebrates: no information found

Lowest chronic value - aquatic plants: >438,000

All organisms: >440

Lowest test EC20 - fish: no information found

Lowest test EC20 - daphnids: no information found

Sensitive species test EC20: no information found

Population EC2O: 398

The Netherlands' Preliminary Maximum Permissible Concentration (MPC) for the protection of all species in an aquatic ecosystem is 370 ug/L [655].

The Netherlands' Negligible Concentration (NC) for toluene is 1% of the MPC, or 3.7 ug/L [655].

Note the above listed MPC and NC values are listed for this compound after harmonization is taken into account: Harmonization considers 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].

A limit of 0.25 mg/l has been recommended for the maximum level in ambient water to avoid tainting of fish and other organisms. [USEPA; Ambient Water Quality Criteria Document: Ethylbenzene (1980) EPA

No 440/5-8-048] [609].

Canada's Interim Assessment Criterion for ethylbenzene 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 ethylbenzene for freshwater aquatic life is 700 ug/L [656].

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

**W.Pl**ants (Water Concentrations vs. Plants):

The LC50 for algae is 33 mg/L [624].

**W.Inv**ertebrates (Water Concentrations vs. Invertebrates):

LC50s for Daphnia magna (water flea) were 77 and 190 mg/L for 24-hr exposures, and 75 mg/L for 48-hr exposures [998].

LC50s for Cancer magister (Dungeness or edible crab) were 40.0 and 13.0 mg/L (ppm) for 48- and 96-hr exposures, respectively [998].

LC50s for Crangon franciscorum (bay shrimp) were 2.2 and 0.49 ul/L (ppm) for 24- and 96-hr exposures, respectively [998].

LC50s for Mysidopsis bahia (Opossum shrimp) were >5.2, >5.2, 4.0 and 2.6 for 24-, 48-, 72- and 96-hr exposures. The lowest-observed-effect-concentration (LOEC) and the no-observed-effect-concentration for Opossum shrimp were 2.7 and 1.0 mg/L, respectively, both for 96-hr exposures [998].

LC50 for Crassostrea gigas (Pacific oyster) was 373 ul/L (ppm) for a 48-hr exposure [998].

Ecotoxicity Values [609]:

LC50 Mysidopsis bahia (shrimp) 87.6 mg/l 96 hr in a static unmeasured bioassay [USEPA; In-depth Studies on Health Environmental Impacts of Selected Water Pollutants (1978) EPA No 68-01-4646].

LC50 Palemonetes pugio (grass shrimp, adult) 14,400 ug/l/24 hr in a static unmeasured bioassay [USEPA; Ambient Water Quality Criteria Doc: Ethylbenzene p.3-7 (1980) EPA 440/5-80-048].

LC50 Palaemonetes pugio (grass shrimp, larva) 10,200 ug/l/24 hr in a static unmeasured bioassay [USEPA; Ambient Water Quality Criteria Doc: Ethylbenzene p.3-7 (1980) EPA 440/5-80-048].

**W.Fi**sh (Water Concentrations vs. Fish):

LC50s for Carassius auratus (goldfish) were 94.44 and 94.44 mg/L (ppm) for 24- and 48-hr exposures, respectively [998].

LC50s for Cyprinodon variegatus (sheepshead minnow) were 300, 360 and 320 mg/L for 24-, 48- and 72-hr exposures, respectively. The no-observed-effect-concentration (NOEC) for death is 88 mg/L for a 96-hr exposure [998].

LC50 for Ictalurus punctatus (channel catfish) is 210 mg/L for a 96-hr exposure [998].

LC50s for Lepomis macrochirus (bluegill) were: 35.08 and 169.0 mg/L for 24-hr exposures; 32.0 mg/L for a 48-hr exposure; and 150.0 and 88.0 mg/L for 96-hr exposures [998].

LC50s for Menidia menidia (Atlantic silverside) were 7.0, 6.4, 5.8 and 5.1 mg/L for 24-, 48-, 72- and 96-hr exposures, respectively. The no-observed-effect-concentration (NOEC) for death was 3.3 mg/L for a 96-hr exposure [998].

LC50s for Oncorhynchus mykiss (rainbow trout, donaldson trout) were 14.0 and 4.2 mg/L for 96-hr exposures [998].

LC50s for Pimephales promelas (fathead minnow) were: 48.51 and 42.33 mg/L for both 24- and 48-hr exposures; and 9.09 mg/L for a 96-hr exposure [998].

LC50s for Poecilia reticulata (guppy) were 97.1, 97.1 and 9.6 mg/L for 24-, 48- and 96-hr exposures [998].

Information from HSDB [609]:

A limit of 0.25 mg/l has been recommended for the maximum level in ambient water to avoid tainting of fish and other organisms. [USEPA; Ambient Water Quality Criteria Document: Ethylbenzene (1980) EPA No 440/5-8-048] [609].

LC50 Lepomis macrochirus (bluegill sunfish) 32 mg/l/96 hr /Conditions of bioassay not specified/ [Pickering QH, Henderson C; J Water Pollut Control Fed 38: 1419 (1966)].

LC50 Carassius auratus (goldfish) 94.44 mg/l/96 hr /Conditions of bioassay not specified/ [Pickering QH, Henderson C; J Water Pollut Control Fed 38: 1419 (1966)].

LC50 Lebistes reticulatus 97.10 mg/l/96 hr /Conditions of bioassay not specified/ [Pickering QH, Henderson C; J Water Pollut Control Fed 38: 1419 (1966)].

LC50 Cyprinodon variegatus (sheepshead minnow) 275 mg/l 96 hr in a static unmeasured bioassay [USEPA; In-depth Studies on Health Environmental Impacts of Selected Water Pollutants (1978) EPA No 68-01-4646].

LC50 Pimephales promelas (fathead minnow) 42.3 (hardwater) to 48.5 (softwater) mg/l 96 hr /Conditions of bioassay not specified/ [Pickering OH, Henderson C; J Water Pollut Control Fed 38: 1419 (1966)].

LC50 Poecilla reticulata (guppy) 97.1 mg/l/96 hr /Conditions of bioassay not specified/ [Pickering OH, Henderson C; J Water Pollut Control Fed 38: 1419 (1966)].

Test fish: Fathead minnows, age 34 days, were given 26.1 mg/l to 25.4 mg/l in 26.1 deg C water with 7.0 mg/l of dissolved oxygen at a pH of 7.39. LC50 12.1 mg/l/96 hr. [Geiger D.L., Poirier S.H., Brooke L.T., Call D.J., eds. Acute Toxicities of Organic Chemicals to Fathead Minnows (Pimephales Promelas). Vol. III. Superior,Wisconsin: University of Wisconsin-Superior, 1986. 189].

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

No information found.

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

EPA 1996 IRIS database information [893]:

Maximum Contaminant Level Goal

Value: 0.7 mg/L Status/Year: Final 1991 Econ/Tech?: No, does not consider economic or technical feasibility Reference: 56 FR 3526 (01/30/91).

Contact: Health and Ecological Criteria Division / (202)260-7571 Safe Drinking Water Hotline / (800)426-4791.

Discussion: An MCLG of 0.7 mg/L for ethylbenzene is promulgated based upon reported histopathological changes (lesion not specified) in a 6-month oral study in rats. The MCLG is based upon a DWEL of 3.4 mg/L and an assumed drinking water contribution of 20 percent.

Maximum Contaminant Level (MCL) 1996:

Value: 0.7 mg/L Status/Year: Final 1991 Econ/Tech?: Yes, does consider economic or technical feasibility Reference: 56 FR 3526 (01/30/91); 56 FR 30266 (07/01/91) [893].

Note from another reference: The U.S. EPA Maximum Contaminant Level (MCL) is 0.7 mg/L [859].

Contact: Drinking Water Standards Division / OGWDW / (202)260-7575 Safe Drinking Water Hotline / (800)426-4791

Discussion: The EPA has promulgated a MCL that is equal to the MCLG of 0.7 mg/L.

Note from another reference: The U.S. EPA Maximum Contaminant Level Goal (MCLG) is 0.680 mg/L [859].

Ambient Water Quality Criteria for Human Health: For the human route of exposure from both Water & Fish: 1.4E+3 ug/liter [893]. 45 FR 79318 (11/28/80).

Ambient Water Quality Criteria for Human

Health: For the human route of exposure from fish only: 3.28E+3 ug/liter [893]. 45 FR 79318 (11/28/80).

Preliminary remediation goals (PRGs) for Tap Water Published by EPA Region 9 and RBC for Region III [868,903]: 1300 ug/L [868].

Other information on drinking water standards and benchmarks [859]:

The Maximum Acceptable Concentration (MAC) in drinking water for Ontario's Ministry of the Environment is 2.400 ug/L.

The aesthetic objective (AO) in Canada for ethylbenzene in drinking water is 2.400 ug/L.

The U.S. EPA lifetime health advisories for a 70-kg adult assuming, first, that 100% of a person's exposure to the substance is from drinking water, and second, that only 20% of a person's exposure to the substance is from drinking water, are 3,400 ug/L and 680 ug/L, respectively.

The U.S. EPA 1-day, 10-day, and 7-year health advisories for a 10-kg child consuming 1 L of water per day are 32,000 ug/L, 3200 ug/L, and 970 ug/L, respectively.

State drinking water standards for this compound range from 1 ug/L (Illinois) to 1400 ug/L (WI and VT) [910].

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

No information found.

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

**Sed.Lo**w (Sediment Concentrations Considered Low):

No information found.

**Sed.Hi**gh (Sediment Concentrations Considered High):

Ethylbenzene was detected in 7% of urban-bay samples from the Puget Sound area. The mean concentration was 104 ug/kg dry weight (ppb), while the median concentration was 10 ug/kg (ppb) [852].

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

**Sed.Typ**ical (Sediment Concentrations Considered Typical):

Ethylbenzene was detected in 15% of non-urban-bay samples from the Puget Sound area. The mean concentration was 8.48 ug/kg dry weight (ppb), while the median concentration was 0.07 ug/kg (ppb) [852].

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

Sediments from the lower Tennessee River below Calvert City, KY measured 4.0 ppb(1). [(1) Goodley PC, Gordon M; Kentucky Acad Sci 37: 11-5 (1976)] [609].

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

**Sed.Gen**eral (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- and soil-dwelling organisms is 3.1 mg/kg dry weight [655].

Based on equilibrium partitioning, the Netherlands' Negligible Concentration (NC) for ethylbenzene is 1% of the MPC, or 0.031 mg/kg dry weight [655].

Note: The above listed MPC and NC values considered harmonization between media, taking 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].

**Sed.Pl**ants (Sediment Concentrations vs. Plants):

No information found.

**Sed.Inv**ertebrates (Sediment Concentrations vs. Invertebrates):

No information found.

**Sed.Fi**sh (Sediment Concentrations vs. Fish):

No information found.

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

No information found.

**Sed.Hum**an (Sediment Concentrations vs. Human):

No information found.

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

No information found.

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

**Soil.Lo**w (Soil Concentrations Considered Low):

No information found.

**Soil.Hi**gh (Soil Concentrations Considered High):

The geometric mean concentrations of ethylbenzene found in soil at hazardous waste sites that are on the National Priorities List was 697.59 ppb (non-detect samples were not included in the mean calculation) [910].

**Soil.Typ**ical (Soil Concentrations Considered Typical):

No information found.

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

**Soil.Gen**eral (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):

Canada's Interim Assessment Criterion for ethylbenzene in soil is 0.1 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 ethylbenzene in soil for three different land-uses (ug/g dry weight) [656]:

Agricultural = 0.1
Residential/Parkland = 5
Commercial/Industrial = 50

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].

Based on equilibrium partitioning, the Netherlands' Maximum Permissible Concentration (MPC) for the protection of all sediment- and soil-dwelling organisms is 3.1 mg/kg dry weight [655].

Based on equilibrium partitioning, the Netherlands' Negligible Concentration (NC) for ethylbenzene is 1% of the MPC, or 0.031 mg/kg dry weight [655].

Note: The above listed MPC and NC values considered harmonization between media, taking 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].

Soil criteria for evaluating the severity of contamination under the Dutch Soil Cleanup (Interim) Act (1982): 0.05 ppm of ethylbenzene indicates background concentrations. 5 ppm of ethylbenzene indicates a moderate soil contamination. 50 ppm indicates threshold values that require immediate cleanup [347].

State ethylbenzene cleanup guidance levels range from 1 to 68 ppm [806].

**Soil.Pl**ants (Soil Concentrations vs. Plants):

No information found.

**Soil.Inv**ertebrates (Soil Concentrations vs. Invertebrates):

No information found.

**Soil.Wild**life (Soil Concentrations vs. Wildlife or Domestic Animals):

No information found.

**Soil.Hum**an (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 = 7800 mg/kg for ingestion pathway [952].

SSL = 400 mg/kg for inhalation pathway [952].

SSL = 0.7 to 13 mg/kg for protection from migration to groundwater at 1 to 20 Dilution-Attenuation Factor (DAF) [952].

EPA 1996 Region 9 Preliminary remediation goals (PRGs) [868]:

Residential Soil: 6.9E+02 mg/kg wet weight
Industrial Soil: 6.9E+02 mg/kg wet weight

NOTE:

1) Values are based on a one-in-one million cancer risk.

2) 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.

3) PRGs for residential and industrial landuses are slightly lower concentrations than EPA Region III RBCs, which consider fewer aspects (more limited to ingestion pathway) [903].

EPA 1995 Region III Risk Based Concentration (RBC) to protect from transfers to groundwater:

5 mg/Kg dry weight [903].

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

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

Ethylbenzene can be released to soils through the spilling of gasoline and other fuels; through the disposal of solvents and household products such as paint, cleaning and degreasing solvents, varnishes, and pesticides; and through emissions from leaking underground storage tanks [910].

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

**Tis.Pl**ants:

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:

No information found.

**Tis.Inv**ertebrates:

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:

Ethylbenzene was detected at very low concentrations (0.008 mg/g) in oyster tissue but not in clam tissue from Lake Pontchartrain at Passes, LA. [910].

**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):

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 (carcinogenic), rounded to two significant figures [903]: 140 mg/Kg wet weight.

See also: Tis.human section for Rfd values.

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:

An average concentration of 0.01 mg ethylbenzene/kg body weight was measured in the tissue of bottomfish from commencement Bay in Tacoma, WA. [910].

**Tis.Wild**life: 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):

Liver & kidney wt increased in rats given subchronic oral doses of 408-680 mg/kg/day for 182 days. /From table/ [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. 3306] [609].

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.Hum**an:

A) Typical Concentrations in Human Food Survey Items:

Food Survey Results:

Trace concentrations of ethylbenzene have been reported in split peas (0.013 mg/kg), lentils (0.005 mg/kg), and beans (mean concentration 0.005 mg/kg; maximum concentration 0.01; mg/kg) [910]. Ethylbenzene was reported as one of 227 organic chemicals present in roasted filbert nuts [910].

Detected but not quantified in roasted filbert nuts (Santodonato J et al; Investigation of Selected Potential Environmental Contaminants: Styrene, Ethyl Benzene, and Related Compounds 261 p USEPA 560/11-80-018, 1980) [609].

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):

EPA 1996 IRIS database information [893]:

Crit. Dose: 97.1 mg/kg-day

RfD: 1E-1 mg/kg-day Confidence: Low

Acceptable daily intake: 1.6 mg/day [USEPA; Ambient Water Quality Criteria Doc: Ethylbenzene p.C-22 (1980) EPA 440/5-80-048] [609].

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 (carcinogenic), rounded to two significant figures [903]: 140 mg/Kg wet weight.

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

Detected, not quantified in 8 of 8 samples of mother's milk from 4 US urban areas(1). [(1) Pellizzari ED et al; Bull Environ Contam Toxicol 28: 322-8 (1982)] [609].

After 2 volunteers were exposed to 65 ppm ethylbenzene for 3 hr, the metabolites of ethylbenzene in their urine, mandelic acid, hippuric acid (HA), and phenylglyoxylic (PhGA) were analyzed. The metabolites were excreted in the urine in the order mandelic acid > hippuric acid > phenylglyoxylic. The highest value of excretion was observed 6-10 hr after the beginning of exposure. Mandelic acid/penylglyoxylic and hippuric/phenyglyoxylic mol ratios of total

excretion in urine were 3.5 and 2.6 respectively. [Yamasaki Y; Okayama Igakkai Zasshi 96 (5/6): 531-5 (1984)] [609].

**Tis.Misc.** (Other Tissue Information):

Ethylbenzene was not detected (at a detection limit of 0.025 mg/kg wet weight) in any of the 97 biota samples collected from all STORET stations in 1980-83 [910].

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

Bioconcentration factors (log BCF) in addition to those below are: 2.67 for microorganisms in water; 1.19 for goldfish; 1.2 for fish; and 2.31 for S. capricornutum [902].

In comparison to chemicals such as PCBs, DDT, and other chlorinated pesticides, which are of great concern with respect to bioaccumulation, ethylbenzene does not significantly bioaccumulate in aquatic food species [910]. A bioconcentration factor (BCF) in fish of 37.5 based on a log K ow of 3.15 has been estimated [910]. A 3% weighted average lipid content in fish and shellfish was assumed by EPA in the calculation [910]. The calculated BCF is a theoretical value based on known constants, and is a conservative estimate of the bioconcentration of this chemical in fish [910]. In a shellfish study, the ethylbenzene concentration in clam tissue was five times higher than that measured in water after an 8-day continuous-flow exposure to the water-soluble fraction of Cook Inlet crude oil [910]. Ethylbenzene also partitions into human adipose tissue [910].

Bioconcentration [609]:

The only experimental data on the bioconcentration of ethylbenzene is the low log BCF of 0.67 for clams exposed to the water-soluble fraction of crude oil(1). However, based on its octanol/water partition coefficient (log Kow= 3.15)(2) and using a recommended regression equation(3), one can calculate a log BCF in fish of 2.16 indicating that ethylbenzene should not significantly bioconcentrate in aquatic organisms(SRC). [(1) Nunes P, Benville PE Jr; Bull Environ Contam Toxicol 21: 719-24 (1979) (2) Hansch C, Leo AJ; Medchem Project Issue No 19 Claremont, CA Pomona College (1981) (3) Lyman WJ et al; Handbook of Chemical Property Estimation Methods. Environmental Behavior of Organic Compounds p 5-1 to 5-10 New York, NY McGraw Hill Co (1982)].

**Int**eractions:

In lab assistants using xylenes & ethylbenzene, 2,4-dimethylphenol, metab of m-xylene could not be detected. Competitive reaction between xylenes & ethylbenzene prevented m-

xylene from oxidation. ... [Angerer j et al; int arch occup environ health 43 (2): 145 (1979)] [609].

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

**Us**es/Sources:

Ethylbenzene makes up about 4.5% of gasoline [624].

Information from HSDB [609]:

> Used in ... The production of synthetic rubber ... As a solvent or diluent, a component of automotive and aviation fuels; mfr of cellulose acetate [International Labour Office. Encyclopedia of Occupational Health and Safety. Vols. I&II. Geneva, Switzerland: International Labour Office, 1983. 2114].
>
> Ethylbenzene is mainly used as a precursor to styrene. [Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed., Volumes 1-26. New York, NY: John Wiley and Sons, 1978-1984.,p. 24 (83) 740].
>
> ... Solvent-eg, for alkyd surface coatings, chem int for diethylbenzene & acetophenone, for ethyl anthraquinone, for ethylbenzene sulfonic acids (o-, m- & p-), for propylene oxide & alpha-methylbenzyl alcohol, unrecovered component of gasoline [SRI].
>
> Ethylbenzene is recovered from benzene-toluene-xylene (BTX) processing. [Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed., Volumes 1-26. New York, NY: John Wiley and Sons, 1978-1984.,p. 4 (78) 64].

Natural Occurring Sources [609]:

> Ethylbenzene is a product of biomass combustion(1), and a component of crude oil(2). [(1) Graedel TE; Atmospheric Chemical Compounds. New York NY Academic Press (1986) (2) Nunes P, Benville PE JR; Bull Environ Contam Toxicol 21: 71-24 (1979)].

Artificial Sources [609]:

> Emissions, waste water, leaks, and spills connected with its production, and use in the manufacture of styrene and use as a solvent(1); Emissions from petroleum refining; vaporization losses and spills of gasoline and diesel fuel at filling stations and during storage and transit

of these fuels; auto emissions; cigarette smoke(1-4). [(1) USEPA; Investigations of Selected Environmental Contaminants: Styrene, Ethylbenzene and Related Compounds, p.27-87 USEPA 560/11-80-018 (1980) (2) Verschueren K; Handbook of Environmental Data on Organic Chemicals 2nd ed p. 628-9, New York, NY Van Nostrand Reinhold Co, Inc (1983) (3) Graedel TE; Chemical Compounds in the Atmosphere p.110 New York, NY Academic Press (1978) (4) NAS; The Alkyl Benzenes p.I-1 to I-99 USEPA Contract 68-01-4655 (1980)].

Ethylbenzene is present at 0.02 wt% in coke-oven tars. [Kirk-Othmer encyc chem tech 3rd ed 1978-present V22 p.572].

Detected in cigarette smoke(1). [(1) NAS; The Alkylbenzenes p III-18 (1980)].

**Fo**rms/Preparations/Formulations:

Information from HSDB [609]:

Grade: Technical 99.0%; Pure 99.5%; Research 99.98%. [U.S. Coast Guard, Department of Transportation. CHRIS - Hazardous Chemical Data. Volume II. Washington, D.C.: U.S. Government Printing Office, 1984-5.].

Constituent components of typical commercial grade = 99.7% ethylbenzene, 0.1% m- and p-xylene, 0.1% cumene, and 0.1% toluene. [Sun Petroleum Prod Co; Material Safety Data Sheet (1981)].

AI3-09057

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

Solubilities:

60 to 655 mg/L at 25 degrees C (most values near 168) [902].

Solubility in water @ 15 deg c, 0.014 G/100 ml [Patty, F. (ed.). Industrial Hygiene and Toxicology: Volume II: Toxicology. 2nd ed. New York: Interscience Publishers, 1963. 1223] [609].

Sol in all proportions in ethyl alcohol and ethyl ether [International Labour Office. Encyclopedia of Occupational Health and Safety. Vols. I&II. Geneva, Switzerland: International Labour Office, 1983. 2114] [609].

Miscible with usual organic solvents [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 546] [609].

Vapor Pressure:

283 to 1329 Pa at 25 degrees C (most values near 1270) [902].

10 MM HG @ 25.90 DEG C [Browning, E. Toxicity and Metabolism of Industrial Solvents. New York: American Elsevier, 1965. 90] [609].

Henry's Law Constant:

669 to 1001 Pa m3/mol (most values near 854) [902].

Density/Specific Gravity:

0.8670 @ 20 DEG C/4 DEC C [Weast, R.C. (ed.) Handbook of Chemistry and Physics. 67th ed. Boca Raton, FL: CRC Press, Inc., 1986-87.,p. C-269] [609].

Octanol/Water Partition Coefficient, log Kow:

2.68 to 3.43 (most values were 3.15) [902].

Sorption Partition Coefficient, log Koc:

1.98 to 3.04 (most values near 2.41) [902].

Molecular Weight:

106.16 [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 546] [609].

Relative Evaporation Rate:

It evaporates about 94 times more slowly than ether [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. 3303] [609].

Color/Form:

Colorless liquid [Sax, N.I. and R.J. Lewis, Sr. (eds.). Hawley's Condensed Chemical Dictionary. 11th ed. New York: Van Nostrand Reinhold Co., 1987. 479] [609].

Odor:

Aromatic odor [Sax, N.I. and R.J. Lewis, Sr. (eds.). Hawley's Condensed Chemical Dictionary. 11th ed. New York: Van Nostrand Reinhold Co., 1987. 479] [609].

Pungent odor [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. 3303] [609].

Sweet, gasoline-like odor [U.S. Coast Guard, Department of Transportation. CHRIS - Hazardous Chemical Data. Volume II. Washington, D.C.: U.S. Government Printing Office, 1984-5.] [609].

Boiling Point:

136.2 DEG C @ 760 MM HG [Weast, R.C. (ed.) Handbook of Chemistry and Physics. 67th ed. Boca Raton, FL: CRC Press, Inc., 1986-87.,p. C-269] [609].

Melting Point:

-94.97 DEG C [Weast, R.C. (ed.) Handbook of Chemistry and Physics. 67th ed. Boca Raton, FL: CRC Press, Inc., 1986-87.,p. C-269] [609].

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

Note: Detailed information about the biocatlysis/biodegradation fate of this compound is included on the University of Minnesota Biocatlysis/Biodegradation Database (Available on the interet in July, 1997, www.nmsr.labmesd.umn.edu).

The photoreactivity of ethylbenzene is intermediate relative to other atmospheric hydrocarbons, and it is less reactive than gasoline, toluene, and alkenes such as propene [910].

Although ethylbenzene does not directly absorb light wavelengths that reach the troposphere, it is capable of undergoing photooxidation in water through an indirect reaction with other light- absorbing molecules, a process known as sensitized photolysis [910]. The compounds 1-phenylethanone, 1- phenylethanol, and benzaldehyde were identified from the laboratory photooxidation of ethylbenzene in both distilled water and seawater with acetophenone used as a sensitizer [910]. In the environment, similar degradation is expected to occur in the presence of ubiquitous, naturally occurring humic material sensitizers [910]. Biodegradation in aerobic surface water will compete with sensitized photolysis and transport processes such as volatilization [910]. Volatilization and biodegradation of ethylbenzene in seawater have been observed by Gschwend et al [910]. Migration from surface water to subsurface soil with low amounts of oxygen or to aquifers with lower microbial populations, however, will limit the rate of transformation [910]. No significant disappearance of ethylbenzene during 11 weeks of incubation with bacteria under low oxygen (anoxic) conditions was observed by Bouwer and McCarty in 1983 [910]. Slow degradation of ethylbenzene was reported in anaerobic aquifer materials known to support methanogenesis, although a long acclimation period or lag time was required [910]. Less than 1% of the initial concentration

of ethylbenzene remained after 120 weeks, indicating that, given sufficient time, ethylbenzene will be essentially completely biodegraded [910]. This contrast between biodegradation rates in the presence or absence of oxygen was demonstrated by a biofilm reactor study designed to simulate an aquifer [910]. Continuous-flow laboratory column studies under aerobic and methanogenic conditions were performed with mixed bacterial cultures on glass beads [910]. In the aerobic biofilm column, 99% of the ethylbenzene initially present was degraded within a 20-minute detention time, while under methanogenic (anaerobic) conditions, 7% was degraded within a 2-day detention time [910]. 5.3.2.3 Soil Biodegradation of ethylbenzene by aerobic soil microbes has been reported by various researchers [910]. The common soil microorganism Pseudomonasputida is able to utilize ethylbenzene as a sole source of carbon and energy [910]. In some instances, co-oxidation or co- metabolism was observed; i.e., ethylbenzene was degraded by Nocardia sp [910]. in the presence of other compounds that are more readily metabolized by the microorganism [910]. Anaerobic degradation of ethylbenzene in soil has not been reported, but based on observations from studies conducted under anaerobic conditions in other media as discussed above [910]. Transformation would be much slower than that observed under aerobic conditions [910]. Biotic transformations by aerobic soil microbes involve oxidation of the ethyl side chain to form phenylacetic acid and 1-phenylethanol; ring hydroxylation to form 2,3-dihydroxy-1-ethylbenzene, 2-hydroxyphenlacetic acid, 4-hydroxyphenylacetic acid, 2,5- and 3,4- dihydroxyphenylacetic acid; and ultimate ring cleavage to form straight chain carboxylic acids such as fumaric and acetoacetic acids [910]. No information was found on the rate at which such degradation occurs in the environment [910]. The kinetics of biodegradation are site specific, however, and depend upon factors such as the type and population of microbes present, the concentration of ethylbenzene, the presence of other compounds that may act as a substrate, and the amount of oxygen present [910]. Biodegradation in soil will also compete with migration processes such as volatilization and infiltration to groundwater [910]. Migration to anaerobic environments where biodegradation is limited may be faster than the rate of biotransformation in soil under certain site conditions [910].

The physicochemical properties of ethylbenzene reveal a strong tendency for ethylbenzene to partition into the atmosphere [910]. Depending upon site conditions, releases to surface soil can result in substantial losses to the atmosphere in addition to subsurface infiltration [910]. Vapor phase transport will occur from subsurface releases (i.e., from leaking underground storage tanks) and during migration through partitioning into air pockets within unsaturated soil pore spaces [910]. This vapor phase migration behavior is used in soil gas sampling methods [910]. The magnitude of the Henry's law constant, which measures partitioning between water and air, indicates that a significant proportion of ethylbenzene will partition from water into air [910]. Ethylbenzene dissolved in surface water, soil pore water, or groundwater will thus migrate into an available atmospheric compartment until its saturated vapor concentration is reached [910]. Sorption and

retardation by soil organic carbon will occur to a small extent, but sorption is not significant enough to prevent migration in most soils typically encountered in the environment [910]. In fact, solvent spills of chemicals such as ethylbenzene may enhance the mobility of other organic chemicals, which do strongly adsorb to soil [910]. Once in the atmosphere, ethylbenzene will be transported until it is removed by physical or chemical processes [910]. Physical removal processes, which involve partitioning into clouds or rainwater, are relevant to ethylbenzene, which has been measured in Los Angeles rainwater [910]. The concentrations of several dissolved organic chemicals in rainwater and in the atmosphere during rainfall events were measured by Ligocki et al [910]. The authors found that the concentration of ethylbenzene in rainwater was approximately equal to the inverse of the dimensionless Henry's law constant at atmospheric temperatures [910]. This indicates that ethylbenzene is removed from the atmosphere through precipitation to some extent, but it can re-enter the atmospheric environment upon evaporation [910].

Half-lives in surface water [902]: 5-6 hours, based on estimated evaporative loss of toluene at 25 degrees C and 1 m depth of water; 72-240 hours, based on unacclimated aqueous aerobic biodegradation half-life.

Half-lives in groundwater [902]: 144-5472 hours, based on unacclimated aqueous aerobic biodegradation half-life and seawater dieaway test data; 0.3 years (estimated from observed persistence in groundwater of the Netherlands).

Half-lives in soil [902]: 72-240 hours, based on unacclimated aqueous aerobic biodegradation half-life; <10 days.

Environmental Fate [609]:

> TERRESTRIAL FATE; When released onto soil, part of the ethylbenzene will evaporate into the atmosphere. It has a moderate adsorption in soil, but will probably leach into the groundwater especially in soil with a low organic carbon content. While there are no direct data concerning its biodegradability in soil, it is likely that it will biodegrade slowly after acclimation. (SRC).
>
> AQUATIC FATE: When released into water, ethylbenzene will evaporate fairly rapidly into the atmosphere with a t1/2 ranging from hrs to a few wks. Biodegradation will also be rapid (t1/2 2 days) after a population of degrading microorganisms becomes established which will depend on the particular body of water and the temperature. In one study, this acclimization took 2 days and 2 wks in summer and spring, respectively. Some ethylbenzene will be adsorbed by the sediment and bioconcentrated in fish. There is evidence that ethylbenzene slowly biodegrades in groundwater. In cases where large concn persists in groundwater over a yr after a spill, it is possible that resident microorganisms were killed by toxic concentrations. (SRC).

ATMOSPHERIC FATE: Ethylbenzene will be removed from the atmosphere principally by reaction with photochemically produced hydroxyl radicals (t1/2 hrs to 2 days). Additional quantities will be removed by rain. (SRC).

Biodegredation [609]:

After a period of adaptation, ethylbenzene is biodegraded fairly rapidly by sewage or activated sludge inoculums(1-3,9). As a component of gas oil, it is completely degraded in groundwater in 8 days(4) and seawater in 10 days(5). In a mesocosm experiment using simulated Narraganset Bay conditions, complete biodegradation occurred in approximately 2 days after a 2 week lag in spring and a 2 day lag in summer(6). Part of the attenuation in concn from a leaky gasoline storage tank in the chalk aquifer in England has been attributed to biodegradation(7). No degradation was observed in an anaerobic reactor even after 110 days acclimation(8) or at low concentrations in a batch reactor in 11 weeks under denitrifying conditions(10). [(1) Slave T et al; Rev Chim 25: 666-70 (1974) (2) Tabak HH et al; J Water Pollut Control Fed 53: 1503-18 (1981) (3) Malaney GW, McKinney RE; Water Sewage Works 113: 302-9 (1966) (4) Kappeler T, Wuhrmann K; Water Res 12: 327-33 (1978) (5) Van der Linden AC; Dev Biodegrad Hydrocarbons 1: 165-200 (1978) (6) Wakeham SG et al; Environ Sci Technol 17: 611-7 (1983) (7) Tester DJ, Harker RJ; Water Pollut Control 80: 614-31 (1981) (8) Chou WL et al; Biotechnol Bioeng Symp 8: 391-414 (1979) (9) USEPA; Treatability Manual p 1.9.8-1 to 1.9.8-5 USEPA 600/2-82-001a (1981) (10) Bouwer EJ, McCarty PL; Appl Environ Microbiol 45: 1295-99 (1983)].

Microorganisms, such as pseudomonas putida, are capable of oxidizing ethylbenzene to (+)-cis-3-ethyl-3,5-cyclohexadiene-1,2-diol & related compd. [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. 3304].

Abiotic Degredation [609]:

The predominant photochemical reaction of ethylbenzene in the atmosphere is with hydroxyl radicals; the tropospheric half-life for this reaction is 5.5 and 24 hr in the summer and winter, respectively(1,2). Degradation is somewhat faster under photochemical smog situations(3-5). Photooxidation products which have been identified include ethylphenol, benzaldehyde, acetophenone and m- and p-ethylnitrobenzene(6). Ethylbenzene is resistant to hydrolysis(7). [(1) Singh HB et al; Atmos Environ 15: 601-12 (1981) (2) Ravishankara AR et al; Int J Chem Kinet 10: 783-804 (1978) (3) Dilling WL et al; Environ Sci

Technol 10: 351-6 (1976) (4) Yanagihara S et al; 4th Int Clean Air Congr Proc p 472-7 (1977) (5) Washida N et al; Bull Chem Soc Japan 51: 2215-21 (1978) (6) Hoshino M et al; Kokuritsu Kogai Kenkyusho Kenkyu Hokoku 5: 43-59 (1978) (7) Lyman WJ et al; Handbook of Chemical Property Estimation Methods. Environmental Behavior of Organic Compounds p 7-1 to 7-4 New York, NY McGraw Hill Co (1982)].

Soil Adsorption/Mobility [609]:

Ethylbenzene has a moderate adsorption for soil. The measured Koc for silt loam was 164(1). Its presence in bank infiltrated water suggests that there is a good probability of its leaching through soil(2). [(1) Chiou CT et al; Environ Sci Technol 17: 227-31 (1983) (2) Piet GJ, Morra CF; p 31-42 in Artificial Groundwater Recharge; Hessman L, Olsthorn TN, ed (1983)].

Volatilization from Water/Soil [609]:

Ethylbenzene has a high Henry's Law constant and will evaporate rapidly from water; a half-life for evaporation from water with 1 m/sec current, 3 m/sec wind, and 1 m depth is 3.1 hr(1). In a mesocosm experiment using simulated conditions for Narragansit Bay, MA, and seasonal conditions, the loss of ethylbenzene was primarily by evaporation in winter (t1/2 13 days)(2). Since it has a moderately high vapor pressure, it will evaporate fairly rapidly from soil. [(1) Lyman WJ et al; Handbook of Chemical Property Estimation Methods. Environmental Behavior of Organic Compounds p 15-25 New York, NY McGraw Hill Co (1982) (2) Wakeham SG et al; Environ Sci Technol 17: 611-7 (1983)].

Absorption, Distribution and Excretion [609]:

Absorption is chiefly by inhalation. A small proportion ... That gets into the blood stream is exhaled unchanged, but most of it /70%/ is found in the urine as metabolites because of oxidation of the side chain. [Patty, F. (ed.). Industrial Hygiene and Toxicology: Volume II: Toxicology. 2nd ed. New York: Interscience Publishers, 1963. 1232].

It is absorbed ... Through skin at low rate. ... Has been detected in subcutaneous adipose tissue samples of workers 3 days after low to high exposure to styrene & related rubber mfr components. ... Has been detected in cord blood samples, indicating ... Transport through placenta. [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. 3304].

Traces ... Have been detected in human expiratory air at somewhat higher concn in smoker than nonsmoker. [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. 3303].

Three lab technicians exposed to 42 ppm & 1 to 34 ppm had avg steady state blood levels of 0.72 +/- 0.11 Mg/l. 30 Min after exposure concn had dropped to approx 0.5% Of original values. [Hagemann J et al, Krebsgefaehrdung Arbeitsplatz/Arbeitsmed Kolloq, Ber Jahrestag Dtsch Ges Arbeitsmed 19TH: 421 (1979)].

After exposure to 112-156 mg/l (aq) the skin absorption rate in humans (n=14) was 0.11 to 0.21 mg/sq m/hr. [Dutkiewicz T, Tyras H; Br J Ind Med 24 (4): 330-2 (1967)].

When administered sc to 40 rats (2.5 ml, 1:1 v/v), ethylbenzene was detected in the blood within 2 hours, and the levels of ethylbenzene (10-15 ppm in blood) were maintained for at least 16 hours. [USEPA; Ambient Water Quality Criteria Doc: Ethylbenzene p.C-6 (1980) EPA 440/5-80-048].

After exposure of rats to atmospheres of 50, 300, or 600 ppm ethylbenzene 6 hr/day, 5 days/wk, for maximum of 16 wk, the concn of ethylbenzene in perirenal fat and the urinary excretion of 1-phenylethanol, omega-hydroxyacetophenone, mandelic acid, phenylglyoxylic acid, hippuric acid, and phenaceturic acid were measured at the 2nd, 5th, and 9th weeks. Excretion of metabolites into urine increased in a dose-related manner, but less than linearly. the level of exposure, but not the pattern of the metabolites in the urine. The concn of ethylbenzene in perirenal fat was low at 50 ppm, high at 300 ppm and higher still at 600 ppm, but not in proportion to the increased dose. [Engstroem K et al; Xenobiotica 15 (4): 281-6 (1985)].

**Lab**oratory and/or Field Analyses:

For optimum risk or hazard assessment work, volatile compound lab methods with very low detection limits [such as EPA Method 8260 modified for Selective Ion Mode (SIM) Enhanced Detection Limits] should be used. The investigator should also specify the addition of any relevant compounds (such as alkyl volatiles) suspected of being present but not typically found on the standard EPA scans.

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 0.05 ug/L or less for this compound using advanced methods such as USGS 1996

Custom Method 9090. A detection limit of 0.3 ppm for this compound was determined to be a value that most California laboratories could routinely achieve, based on a survey conducted by the California DHS [465]. 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 [910]. Detection limits of less than 1 ug of ethylbenzene per liter of sample have been achieved using Methods 8010 and 8240 [910]. Tissue detection limits can be as low as 5 ppb [910]. The Environmental Health Laboratory Sciences Division of the Center for Environmental Health and Injury Control, Centers for Disease Control, is developing methods for the analysis of ethylbenzene and other volatile organic compounds in blood [910]. These methods use purge and trap methodology and magnetic sector mass spectrometry which gives detection limits in the low parts per trillion range. [910].

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.

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. In fact, as mentioned in the disclaimer section at the top of this entry, the interagency task force on water methods concluded that [1014]:

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

As of 1997, the problem of lack of data comparability (not only for water methods but also for soil, sediment, and tissue methods) between different "standard methods" recommended by different agencies seemed to be getting worse, if anything, rather than better. The trend in quality assurance seemed to be for various agencies, including the EPA and others, to insist on quality assurance plans for each project. In addition to quality control steps (blanks, duplicates, spikes, etc.), these quality assurance plans call for a step of insuring data comparability [1015,1017]. However, the data comparability step is often not given sufficient consideration. The tendency of agency guidance (such as EPA SW-846 methods and some other new EPA methods for bio-concentratable substances) to allow more and more flexibility to select options at various points along the way, makes it harder in insure data comparability or method validity. Even volunteer monitoring programs are now strongly encouraged to develop and use quality assurance project plans [1015,1017]. 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].
>
> It should be kept in mind that blanks will not help in the way intended if one is using a method prone to false negatives due to the use of detection limits that are too high, the loss of contaminants in handling, use of an inappropriate method, etc. (Roy Irwin, National Park Service, Personal Communication, 1997).

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.

Benzene, ethylbenzene, toluene, and xylenes (the BTEX compounds) are often analyzed when gasoline is spilled. However, 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.

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 by EPA and other agencies:

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

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].

For a descriptioin of USGS 1996 Custom Method 9090, see

Benzene Entry.

ATSDR Detailed Information [910]:

BIOLOGICAL MATERIALS:

Trace amounts of ethylbenzene in biological fluids can be detected by a number of analytical methods [910]. These include gas chromatography coupled with mass spectrometry (GC/MS), gas chromatography using a flame ionization detector (GC/FID), high performance liquid chromatography (HPLC), and isotachophoresis (ITP) [910].

Identification and quantitation of ethylbenzene in samples of whole blood taken from humans following occupational exposure to several volatile organic compounds was discussed by Antoine et al [910]. Gas purging-and- trapping on Tenax GC adsorbent was used to remove volatile organic components from blood for introduction into the GC/MS system [910]. The authors demonstrated that the inherent volatility of the organic compounds causes excessive foaming during purging, resulting in low yields of eluting components [910]. The use of an antifoaming agent, such as emulsion B, greatly reduced the foam and increased the accuracy and detection limits of the technique for ethylbenzene [910].

GC/MS = gas chromatography/mass spectrometry; GC/FID = gas chromatography/flame ionization detector; HPLC = high performance liquid chromatography; ITP = isotachophoresis; MA = mandelic acid; GC/ECD - gas chromatography/electron capture detector; GC/PID = gas chromatography/photoionization detector; GC/EICD = gas chromatography/electrolytic conductivity detector; UV = ultraviolet spectrophotometry; RSD = relative standard deviation; PGA = phenylglyoxylic acid; RSD = relative standard deviation; ppm = parts per million; ppb = parts per billion; and ppt = parts per trillion [910].

Ethylbenzene can be detected in whole human blood using a dynamic headspace purge and GC/MS [910]. Organic compounds are thermally desorbed from an adsorbent trap and onto the gas chromatography column in a GC/MS system where limited mass-scanning data are collected for qualitative and quantitative identification [910]. Limited mass-scanning involves scanning for a smaller number of ions than does full-scan GS/MS, thereby achieving better sensitivity of target volatile

organic compounds at low levels [910]. Furthermore, some analytes (e.g., ethylbenzene) can be detected by limited mass-scanning but not by full-scanning GC/MS because of the inherent differences in sensitivity between the two methods [910]. The absolute recoveries of the late-eluting volatile organic compounds can be increased by employing a capillary GC/MS as an alternative to the packed column approach and using a less vigorously heated purge analyzing system [910].

In addition to direct measurement of ethylbenzene in blood, concentrations of ethylbenzene metabolites can also be determined in the urine [910]. A simple, sensitive, and specific automated HPLC method for direct quantification of mandelic acid (MA) and phenylglyoxylic acid (PGA), which are the major urinary metabolites of ethylbenzene in humans, was developed by Ogata and Taguchi (1987, 1988) [910]. A possible disadvantage of the automated HPLC method is that at low concentrations (less than 1 mg/L) in urine these acids may not be distinguishable from other similar compounds [910].

A new HPLC method for the simultaneous determination of MA and PGA in the urine of rats was developed by Sollenberg et al in 1985 [910]. An isotachophoresis (ITP) technique may also be employed to quantify and detect MA and PGA in rat urine [910]. The authors indicated that there are essentially no significant difference between results obtained by the two methods [910]. However, the HPLC method is more sensitive for these analytes, and the ITP method is more rapid [910].

ENVIRONMENTAL SAMPLES:

Gas chromatography (GC) is the most widely used analytical technique for quantifying concentrations of ethylbenzene in air, water, soil, and fish [910]. Various detection devices used for GC include gas chromatograph (GC) equipped with a flame ionization detector (FID), mass spectrometer (MS), photoionization detector (PID), electron capture detector (ECD), or electrolytic conductivity detector (EICD) [910]. Because of the complexity of the samples matrix and the usually low concentrations of volatile organic components in environmental media, sample preconcentration is generally required prior to GC analysis [910]. Methods suitable for determining trace amounts of ethylbenzene in aqueous and other environmental media can be divided into three basic approaches that differ in the pretreatment of the sample and

the detection limit [910]. These include gas purging-and-trapping technique, headspace gas analysis, and extraction with organic solvent [910].

Gas purging-and-trapping is the most widely used method for the isolation, concentration, and quantification of volatile organic compounds in environmental samples [910]. The purge-and-trap technique offers advantages over other techniques in that it allows facile isolation and concentration of target compounds, thereby improving overall limits of detection and recovery of sample [910]. Detection limits of less than 1 ug of ethylbenzene per liter of sample have been achieved (Method 8010 and 8240) [910]. A serious drawback of this technique, particularly for quantitative analysis, is interference by impurities found in the stripping gas [910].

A headspace gas analyzer and GC has been employed by Drozd et al in 1978 and 1982 for the analysis and quantification of ethylbenzene in environmental samples [910]. This method is simple and does not require any sample preparation [910].

Extraction with organic solvents (liquid-liquid extraction) provides a simple, rapid screening method for semi-quantitative determination of ethylbenzene in aqueous samples containing limited number of volatile organic compounds but is less effective for aqueous samples containing large numbers of volatile organic compounds [910]. Furthermore, interference from the organic extraction solvent (hexane) makes it more difficult to completely identify all components [910].

A GC/MS and gas-purging-and-trapping technique has been recommended by EPA in 1986 (Method 8240) for determining ethylbenzene in water [910]. Following GC separation, compounds are ionized [910]. Upon ionization, fragmentation occurs, producing combinations of ions that are differentiated by their mass-to-charge (m/z) ratio [910]. Indications show that mass fragmentography offers a systematic, accurate, and highly selective method for quantitation of organic compounds at nanogram levels [910].

GC/PID is the method employed by NIOSH (1984, Method 1501) for determining ethylbenzene levels in air [910]. An automated GC/PID has been developed to identify gas-phase hydrocarbons (including ethylbenzene) for complex mixtures, such as vehicle

exhaust gas [910]. The GC/PID measures sub ppb concentrations without using trapping or freezing-concentration of samples before analysis [910]. These preconcentration steps are usually necessary because of the limited sensitivity of FID technique commonly used for analysis of air samples [910]. A modified capillary GC/PID in tandem with an FID to obtain a more sensitive method for detecting trace levels of ethylbenzene in the air was constructed by Nutmagul et al in 1983 [910].

A procedure to identify and quantify ethylbenzene in fish samples by GC/MS using a fused-silica capillary column (FSCC) and vacuum extraction was developed [910]. An advantage of the vacuum extraction technique is that the system does not require elevated temperatures or addition of reagents that could produce unwanted degradation products [910]. The FSCC provides a more attractive approach than a packed column for chromatographic analysis of volatile organic compounds because FSCC can be heated to a higher temperature (350 degrees C) than that recommended for packed column, thereby improving resolution and detection limits (at nanogram per gram level) of eluting compounds [910]. A physical limitation for compounds that can be detected, however, is that the vapor pressure of the compounds must be greater than 0.78 torr (~50 C) in the sample chamber [910].

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.

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 |