ENVIRONMENTAL CONTAMINANTS ENCYCLOPEDIA

ENTRY ON XYLENES (IN GENERAL)

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Like a library or many 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 without 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).

Xylenes, Total (Total Xylenes, Xylene Mixed Isomers, Methyl Toluene, Dimethylbenzene, Dimethyl Toluene, CAS number 1330-20-7)

Brief Introduction:

Br.Class: General Introduction and Classification Information:

Xylenes are volatile organic, monocyclic aromatic compounds with two methyl groups attached to a benzene ring [366]. Like toluene and ethylbenzenes, xylenes are alkyl benzenes. Xylenes are different from benzene in having two methyl groups added to (substituted for hydrogen) on the benzene ring, either in the ortho-, meta-, or para- positions.

Xylene, a widely used industrial solvent, is a mixture of ortho-, meta-, and para- isomers [366].

Xylenes (mixed) are considered volatile organic compounds (VOCs) [868,903]. Xylenes are alkyl benzenes and are also considered C2 benzenes.

Xylene produced from petroleum ... contains approx 20% o-xylene, 44% m-xylene, 20% p-xylene, and 15% ethylbenzene. Xylene from coal tar generally consists of 10-15% ortho-xylene, 45-70% meta-xylene, 23% para-xylene, and 6-10% ethylbenzene [366].

While o-xylene is recognized as a distinct product in chemical analyses, the m- and p- isomers are generally not separated during most routine analyses. Therefore, results of analyses of xylenes in environmental samples are usually presented as the concentration of the o-isomer and the total concentration of the combined m- and p- isomers [602].

p-Xylene and m-xylene cannot be separated by distillation because their boiling points are too close. [Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed., Volumes 1-26. New York, NY: John Wiley and Sons, 1978-1984.,p. 24(84) 711] [609].

Designated as a hazardous substance under section 311(b)(2)(A) of the Federal Water Pollution Control Act and further regulated by the Clean Water Act Amendments of 1977 and 1978. These regulations apply to discharges of this substance. [40 CFR 116.4 (7/1/88)] [366].

Br.Haz: General Hazard/Toxicity Summary:

This compound often occurs together with other aromatic compounds, some possibly more hazardous than this

compound alone (see entries for Benzene and "PAHs as a group").

In animals, large amounts of xylene can cause changes in the liver and harmful effects on the kidneys, heart, lungs, and nervous system [764].

Long term exposures of animals to low doses of xylene have not been well studied [764].

The Canadian government (1993) concluded that xylenes are not ordinarily entering the Canadian environment in concentrations that might be expected to cause adverse effects to aquatic biota, terrestrial wildlife, humans, or to depletion of stratospheric ozone (exceptions might be spills or other direct releases) [602].

Although most xylenes are released into the air, concentrations to which wildlife are exposed are at least 1000 times less than the effects threshold estimated for inhalation of xylenes by mammals. Concentrations in ambient air are at least 1 million times less than the effects threshold recorded for plants. 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.

This substance is an example of a hazardous substance commonly used in pesticides, but not listed on the label other than as "inerts" [549]. Although this substance is not officially recognized as part of the active ingredients of the pesticide containing it and is therefore part of the so-called "inerts," this substance is nevertheless not "safe" at all concentrations to all life forms.

Additional human health issues related to xylenes have been summarized by ATSDR (not all the highlights from ATSDR have been summarized in this entry) [764].

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

This compound often occurs together with other aromatic compounds, some possibly more carcinogenic than this compound alone (see entries for Benzene and "PAHs as a

group").

EPA 1996 IRIS database information [893]:

> Evidence for classification as to human carcinogenicity; weight-of-evidence classification
>
> Classification: D; not classifiable as to human carcinogenicity
>
> BASIS: Orally administered technical xylene mixtures did not result in significant increases in incidences in tumor responses in rats or mice of both sexes.
>
> HUMAN CARCINOGENICITY DATA
>
> None.
>
> ANIMAL CARCINOGENICITY DATA
>
> Inadequate.

Available animal data on the carcinogenicity of xylene(s) are inadequate to permit an evaluation [366].

Carcinogenicity information is too mixed and/or inadequate for definitive statements [764].

This compound has not been treated as a carcinogen for model calculation purposes in some EPA risk-based (RBC and PRG) models [868,903], but this tentative distinction was made for the purpose of choosing a modeling scenario based on current (often inadequate) knowledge rather than for the purpose of strongly stating that this compound is definitely not a carcinogen; the non-carcinogenic benchmarks are sometimes nearly as low as the carcinogenic benchmarks (Stan Smucker, personal communication, EPA, 1996).

Coal-based solvents (eg, xylene) have been suggested to be possible potent lymphocytic leukemogens, such as benzene, in a limited study of the relationship between lymphocytic leukemia and exposures to benzene and other solvents in the rubber industry. However, available animal data on the carcinogenicity of xylene(s) are inadequate to permit an evaluation [366].

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

Some information on immunological, reproductive, fetotoxic, and developmental effects points towards some

negative effects of xylene, but the information is limited and mixed [764].

Xylene does not appear to be particularly genotoxic [764]. In limited studies thus far, the individual isomers were not found genotoxic when tested in a number of short-term tests. (Fishbein L; Sci Total Environ; 43, 1-2: 165-83, 1985) [366].

In limited studies thus far, the individual isomers were not found to be genotoxic when tested in a number of short-term tests [366]. Negative results were observed in the Salmonella mutagenicity assay and in the mouse lymphoma L5179Y thymidine kinase forward mutation assay, and in chromosome damage in bone marrow cells after ip dosing with xylene [366].

In rats, exposure to xylene (50 or 500 mg/cu m) resulted in embryotoxic and teratogenic effects. The brain, liver, lung, and heart were affected. The number of postimplantation losses increased by 9.7 and 168% in the 50 and 500 mg/cu m xylene group, respectively. The incidence of fetal skeletal abnormalities was increased by 62 and 177%, respectively. (Mirkova E et al; J Hyg Epidemiol Microbiol Immunol 27, 3: 337-43, 1983) [366].

The placental crossing of benzene and its alkyl derivatives, their embryotoxic effects, and incidence of fetal anomalies were investigated in rats, mice, and rabbits. In rats all the components crossed the placenta and also appeared in the fetal blood and amniotic fluid. The concn were higher in the fetal blood than in the amniotic fluid, but both were lower than in the maternal blood. Xylenes and ethylbenzene increased the postimplantation loss, where as Aromatol had no such effect. All the organic solvents caused skeletal retardations of mouse fetus and increased the incidence of retarded fetuses at least at higher concn. Both ethylbenzene and Aromatol were moderately teratogenic in mice. The exposure of rabbits of 1000 mg/cu m solvent caused a mild toxic effect on mothers, fetal loss by abortion, and often a decrease in the wt of female fetus. [Ungvary G, Tatrai E; Arch Toxicol 8 (ISS Recept Other Targets Toxic Subst): 425-30, 1985) [366].

Pregnant CFY rats /were exposed/ by continuous inhalation to 1,000 mg/cu m (230 ppm) of a xylene mixture (10% o-, 50% m-, 20% p-xylene, and 20% ethylbenzene) on gestational days 9 through 14. At this concn, the xylene mixture produced skeletal effects including an increased incidence of supernumerary ribs (9/143 alizarin-stained fetuses in the dosed group compared to 2/143 in the control group). ... Two cases of agnathia (absence of mandible) /were reported/ in 286 pups. (Hudak A, Ungvary

G; Toxicol 11: 55-63, 1978) [366].

Reproductive effects in mice have been documented. See Tis.Wildlife, B) below.

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

Like benzene and toluene, xylenes are fairly volatile, and significant xylenes tend to quickly evaporate if exposed to the atmosphere [764]. However, xylenes can be more persistent when in groundwater, sediment, or soil media not directly exposed to atmosphere. Xylenes tend to migrate to groundwater, and persistence is an issue in groundwater, where in some cases, they may persist for months or years [764].

Most xylene in surface water evaporates into the air in less than a day. The rest of it biodegrades slowly into other chemicals. Only very small amounts are taken up by plants, fish, and birds. We do not know exactly how long xylene stays in water, but we do know that it stays longer in groundwater than in lakes and rivers, probably because it can evaporate from the latter [764].

Xylene evaporates from soil surfaces. Xylene below the soil surface stays there for several days and may travel down through the soil and enter groundwater. In the soil and groundwater it may be slowly biodegraded into less harmful compounds. It is not clearly known how long xylene trapped deep underground in soil or groundwater persists, but it may be months or years. Xylene stays longer in wet soil than in dry soil [764].

Xylenes are bioconcentrated in aquatic organisms to a limited extent. Although more information on bioconcentration would be helpful, the phenomenon of biomagnification is not expected to be important for xylene [764].

The biodegrability of MTBE (often found along with xylene and other BTEX compounds in gasoline spills) in the subsurface is substantially slower than BTEX aromatic fuel components, due in part to the additive's tertiary bonds. It also tends to move faster. Therefore, towards the leading edge of a plume, MTBE's vertical distribution may be slightly deeper (and usually wider horizontally) than BTEX compounds (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).

Some of the hydrocarbons making up jet fuel are soluble in water (e.g., the aromatics--benzene, toluene, and xylene). Under turbulent water conditions, the more soluble hydrocarbons remain dissolved longer and may partition to sediment or be biodegraded [876].

Environmental Fate/Exposure Summary [366]:

Xylenes will enter the atmosphere primarily from fugitive emissions and exhaust connected with their use in gasoline. Industrial sources include emissions from petroleum refining and their use as solvents and chemical intermediates. Discharges and spills on land and waterways result from their use in diesel fuel and gasoline, and storage and transport of petroleum products. Most of the xylenes are released into the atmosphere where they may photochemically degrade by reaction with hydroxyl radicals (half-life 1-18 hr). The dominant removal process in water is volatilization. Xylenes are moderately mobile in soil and may leach into groundwater where they are known to persist for several years, despite some evidence that they biodegrade in both soil and groundwater. Bioconcentration is not expected to be significant. The primary source of exposure is from air, especially at occupational sites where xylenes are used and in areas with high traffic.

Synonyms/Substance Identification:

AI3-02209-X [366]
Caswell No 906 [366]
Benzene, dimethyl- [366]
Dimethylbenzene [366]
EPA Pesticide Chemical Code 086802 [366]
Ksylen (POLISH) [366]
Xiloli (ITALIAN) [366]
Xylenen (DUTCH) [366]
Xylol [366]
Xylole (GERMAN) [366]
NCI-C55232 [366]
Methyltoluene [366]
Violet 3 [366]
Dimethylbenzene [580]
Xylene [580]

Molecular Formula:
C8-H10 [366]

Associated Chemicals or Topics (Includes Transformation Products):

NOTE: For more detailed information on the individual m-, o-, and p- isomers, see these individual entries.

See also the individual entries:

BTEX
Xylene, o-
Xylene, m-
Xylene, p-
Ethylbenzene
Benzene
Toluene

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

General Types of Associated Materials:

- Naphtha

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

- Phenols
- Pyridine
- Thiophene
- Trimethyl benzene

Impurities [366]:

Xylene produced from petroleum ... contains approx 20% o-xylene, 44% m-xylene, 20% p-xylene and 15% ethylbenzene. Xylene from coal tar generally consists of 10-15% ortho-, 45-70% meta-, 23% para-, and 6-10% ethylbenzene. Commercial xylenes may also contain small amt of toluene, trimethylbenzene, phenol, thiophene, pyridine, and nonaromatic hydrocarbons. [NIOSH; Criteria Document: Xylene p.14 (1975) DHEW Pub. NIOSH 75-168].

Unpurified xylene may contain ... pseudocumene ... . [International Labour Office. Encyclopedia of Occupational Health and Safety. Vols. I&II. Geneva, Switzerland: International Labour Office, 1983. 2335].

The possibility that commercial xylene may ... contain benzene should not be ignored. [NIOSH; Criteria Document: Xylene p.14 (1975) DHEW Pub. NIOSH 75-168].

Metabolites:

Xylenes are degraded by oxidation of both the aromatic ring and the methyl substituents. This yields products such as

dimethylphenols, methylsalicylic acid, toluic acids, and ring fission products of methylcatechols [602].

Xylene is metabolized to a toxic aldehyde, methylbenzaldehyde ... . [Riihimaki V et al; Scand J Work Environ Health 8: 77-9 (1982)] [366].

Metabolism/Metabolites [366]:

In humans ... Exposed to approx 0.2-0.4 mg/l xylene isomers (o-, m-, p-xylene) or 1:1:1 mixt for up to 8 hr ... pulmonary retention was 64%, which was ... independent of dosage or duration of exposure. After exposure, only 5% of retained xylenes were elim in expired air. More than 95% ... Excreted by humans into urine in form of methylhippuric acids. ... Small portion ... Excreted into urine as corresponding xylenols. [National Research Council. Drinking Water and Health. Volume 3. Washington, DC: National Academy Press, 1980. 179].

Quantitative determination of urinary metabolites in humans exposed to xylene using colorimetric determination is widely used. The metabolites of ... xylene are measured as ... methyl hippuric acid (MHA), paper chromatography and thin layer chromatography are necessary as pretreatments of samples. The addition of pyridine, p-dimethylaminobenzaldehyde (DAB) and acetic anhydride to glycine conjugates gives the most stable color development. Excellent analytical sensitivity and specificity with gas chromatographic methods requires pretreatment with diazomethane for methylesterification of methyl hippuric acid. [Ogata M; Acta Med Okayama 35 (6): 385-94 (1981)].

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

W.Low (Water Concentrations Considered Low):

No information found.

W.High (Water Concentrations Considered High):

The migration of petroleum products from leaking underground storage tanks and pipelines poses a groundwater contamination problem. Gasoline-contaminated groundwater in Los Angeles contained levels of xylenes as high as 153 ug/L (ppb) [764].

Highest MTBE (additive often found along with xylenes and other BTEX compounds 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 xylenes) concentrations of about 30 ppb (James Davidison, Alpine Environmental, Fort Collins, CO, personal communication, 1997).

W.Typical (Water Concentrations Considered Typical):

Limited monitoring data are available on ambient concentrations of xylenes in surface waters [764]. In view of the rapid volatilization of xylenes, their presence in surface waters is unlikely to be significant [764]. Surface waters generally contain average xylene concentrations of less than 1 ppb total xylenes except in areas where there are fuel processing activities, such as petroleum refining [764].

In Canada, concentration of xylenes in surface water are at least 100 times less than the effects threshold estimated for the most sensitive aquatic species [602].

Typical surface water concentrations range from not detected to 2 ug/L (ppb) [764]. Data on the occurrence of xylene in public drinking water supplies are available from several federal, regional, and state surveys [764].

In most cases, less than 6% of the groundwater and surface water systems sampled contained detectable levels of xylenes [764]. Typical xylene concentrations (all isomers) ranged from 0.2 to 9.9 ug/L (ppb) with mean concentrations of less than 2 ug/L (ppb) [764].

Concentrations of xylenes were not quantifiable in 824 water samples taken from surface water, groundwater wells, and treated drinking water in six Canadian provinces from 1985 to 1988 (detection limit of 0.5 ug/L for o-xylene and for m- and p-xylenes combined) [602].

DRINKING WATER [366]: According to a federal survey of drinking water from groundwater supplies, xylenes are present in < 5% of supplies(1). Xylenes have been detected in the drinking water in Canada with mean values of < 1 ppb(2) and in several USA cities including Washington, DC(3), Philadelphia, PA(4), Cleveland, OH(5), Tuscaloosa, AL(6), Houston, TX(6), and New Orleans, LA(9). Xylenes at 0.1-2.9 ppb have been found in drinking water wells in the vicinity of a landfill(7). A max of 0.1 ppb has been found in bank-filtered Rhine R water in the Netherlands(8). Detected in all 14 drinking water supplies studies, 10 surface and 4 ground in Great Britain(10). [(1) Dyksen JE, Hess AF III; J Amer Water Works Assoc 74: 394-403 (1982) (2) Otson R et al; J Assoc Off Anal Chem 65: 1370-4 (1982) (3) Saunders RA et al; Water Res 9: 1143-5 (1975) (4) Suffet IH et al; pp 375-97

in Identification and Analysis of Organic Pollutants in Water. Keith LH ed. Ann Arbor, MI: Ann Arbor Sci Publ (1976) (5) Sanjivamurthy VA; Water Res 12: 31-3 (1978) (6) Bertsch W et al; J Chromatogr 112: 701-8 (1975) (7) DeWalle FB, Chian ESK; J Water Works Assoc 73: 206-11 (1981) (8) Piet GJ, Morra CF; pp 31-42 in Artificial Groundwater Recharge (Water Res Eng Ser) Huisman L, Olsthorn TN eds. Pitman Publ (1983) (9) Dowty BJ et al; Environ Sci Technol 9: 762-5 (1975) (10) Fielding M et al; Organic Micropollutants in Drinking Water TR 159 p 49 Medmenham UK Water Res Ctre (1981)] [366].

GROUNDWATER [366]: Xylene isomers have been found in groundwater under landfills(1) and in the hundreds ppb range under a coal gasification site, 15 months after gasification was completed(2). [(1) DeWalle FB, Chian ESK; J Water Works Assoc 73: 206-11 (1981) (2) Stuermer DH et al; Environ Sci Technol 16: 582-7 (1982)] [366].

SURFACE WATER [366]: Detected, not quantified in the Mississippi River near New Orleans(1), the Black Warrior River in Tuscaloosa, AL(2), and the Glatt River in Switzerland(3). Xylenes have been found in Lakes Eire and Michigan(4). Detected at avg concn of < 1 ppb in the raw water sources of 30 Canadian cities(5). Detected in only 1 of 204 surface water samples in the USA(6). [(1) Dowty BJ et al; Environ Sci Technol 9: 762-5 (1975) (2) Bertsch W et al; J Chromatogr 112: 701-8 (1975) (3) Zuercher F, Giger W; Vom Wasser 47: 37-55 (1976) (4) Konasewich D; Status Report on Organic and Heavy Metal Contaminants in Lakes Erie, Michigan, Huron, and Superior Basins. Great Lakes Water Qual Rev Board (1978) (5) Otson R et al; J Assoc Off Anal Chem 65: 1370-4 (1982) (6) Ewing BB et al; Monitoring to Detect Previously Unrecognized Pollutants in Surface Waters USEPA-560/6-77-015, 015a p 75 (1977)] [366].

SEAWATER [366]: In Vineland Sound, MA(1) and the Gulf of Mexico(2). Valdez Harbor-Trans Alaskan Pipeline Terminal - 0.2 and 0.7 ppb in 2 of 7 sampling sites(3). [(1) Suffet IH et al; pp 375-97 in Identification and Analysis of Organic Pollutants in Water. Keith LH ed. Ann Arbor, MI: Ann Arbor Sci Publ (1976) (2) Sauer TC Jr et al; Mar Chem 7: 1-16 (1978) (3) Lysyj I et al; Environ Int 4: 407-16 (1980)] [366].

RAIN/SNOW: West Los Angeles, part per trillion range(1). [(1) Kamamura K, Kaplan IR; Environ Sci Technol 17: 497-501 (1983)] [366].

Effluents Concentrations [366]:

Low-level radioactive waste disposal site at Maxey Flats 0.12 and 0.48 ppm in 2 of 3 trench leachates(1).

Industrial plant in Philadelphia area 1000 ppb including all C2 benzenes (such as dimethyl benzene and ethylbenzene) (2). Effluent from containing ponds in Atigun River, Alaska 1.2 ppb, including ethyl benzene(3). Treated effluents from offshore oil drilling platforms in the Gulf of Mexico 0.3 ppm avg (concn includes ethylbenzene)(3). [(1) Francis AJ et al; Nuclear Technology 50: 158-63 (1980) (2) Hites RA; 8th Natl Conf Municp Sludge Manag: Sources and Fates of Industrial Organic Compounds; a case study; pp.107-19 (1979) (3) Lysyj I; Environ Int 4: 407-16 (1980)].

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

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

National EPA 1996 Water Quality Criteria [893]:

Freshwater Acute Criteria: None Published

Freshwater Chronic Criteria: None Published

Marine Acute Criteria: None Published

Marine Chronic Criteria: None Published

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

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

CAS 1330-20-7, XYLENE

National ambient water quality criterion - acute: no information found

National ambient water quality criterion - chronic: no information found

Secondary acute value: 1540

Secondary chronic value: 86.2

Estimated lowest chronic value - fish: 62,308

Lowest chronic value - daphnids: no information found

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

Lowest chronic value - aquatic plants: no information found

Lowest test EC20 - FISH: 2680

Lowest test EC20 - DAPHNIDS: no information found

Sensitive species test EC20: no information found

Population EC2O: no information found

Canada's Interim 1991 Assessment Criterion for xylene 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.

The Netherlands' Harmonized (between media) Maximum Permissible Concentration (MPC) for either 0-xylene, m-xylene, or p-xylene in water is 380 ug/L [655].

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

The Netherlands' Harmonized (between media) Negligible Concentration (NC) for either 0-xylene, m-xylene, or p-xylene in water is 1% of the MPC, or 3.8 ug/L [655].

W.Plants (Water Concentrations vs. Plants):

Shallow Groundwater Ecological Risk Assessment Screening Benchmark for Terrestrial Plants Listed

by Oak Ridge National Lab, 1994 [651]:

> To be considered unlikely to represent an ecological risk, field concentrations in shallow groundwater or porewater should be below the following benchmark for any aqueous solution in contact with terrestrial plants. Toxicity of groundwater to plants may be affected by many variables (pH, Eh, cation exchange capacity, moisture content, organic content of soil, clay content of soil, differing sensitivities of various plants, and various other factors). Thus, the following solution benchmark should be used as a screening benchmark only, and site specific tests would be necessary to develop a more rigorous benchmark for various combinations of specific soils and plant species [651]:
>
> > For CAS 1330-20-7, XYLENE, the benchmark is 100 mg/L (groundwater or porewater).

Growth of the alga Selenastrum capricornutum was reduced by 50% after 72 hours of exposure to 3.2 to 4.9 mg/L of each of the three xylene isomers. Exposure for 30 minutes to 300 mg/L resulted in a 65 to 100% kill of the freshwater macrophytes Elodea and Potamogeton [602].

The 8-day EC50 for growth of Selenastrum capricornutum ranged from 3.9 to 4.4 mg/L for each of the three xylene isomers [602].

W.Invertebrates (Water Concentrations vs. Invertebrates):

The most sensitive freshwater organism was the water flea (Daphnia magna) with 24-hour LC50s of 1.0 mg/L for o-xylene, 3.6 mg/L for p-xylene, and 4.7 mg/L for m-xylene. Among marine organisms, the most sensitive species was the bay shrimp (Crago franciscorum) with 96-hour LC50s 1.1 mg/L for o-xylene, 1.7 mg/L for p-xylene, and 3.2 mg/L for m-xylene [602].

LC50s for Brachionus calyciflorus (rotifer) were 253.0 and 252.7 mg/L (ppm) for 24-hr exposures, and 253.0 mg/L for a 48-hr exposure [998].

LC50s for Brachionus plicatilis (rotifer) were 495.9 and 496.0 mg/L (ppm) for 24-hr exposures [998].

LC50 for Daphnia magna (water flea) was 150 mg/L

for a 24-hr exposure [998].

LC50 for Diaptomus forbesi (Calanoid copepod) was 99.5 mg/L for a 96-hr exposure [998].

LC50s for Katelysia opima (marine bivalve) were 240, 220, 205 and 190 mg/L for 24-, 48-, 72- and 96-hr exposures, respectively [998].

LC50s for Palaemonetes pugio (daggerblade grass shrimp) were 14.0, 8.5 and 7.4 mg/L for 24-, 48- and 96-hr exposures, respectively [998].

W.Fish (Water Concentrations vs. Fish):

LC50s for Carassius auratus (goldfish) were: 75.0, 30.55 and 36.81 mg/L (ppm) for 24-hr exposures; 25.1 and 36.81 mg/L for 48-hr exposures; 20.72 mg/L for a 72-hr exposure; and 36.81 mg/L for a 96-hr exposure [998].

LC50 Carassius auratus (goldfish) 16.9 ppm/96 hr /Conditions of bioassay not specified, no specific isomer/ [Verschueren, K. Handbook of Environmental Data of Organic Chemicals. 2nd ed. New York, NY: Van Nostrand Reinhold Co., 1983. 1191] [366].

LD50 Goldfish 13 mg/l/24 hr /Conditions of bioassay not specified, no specific isomer/ [Verschueren, K. Handbook of Environmental Data of Organic Chemicals. 2nd ed. New York, NY: Van Nostrand Reinhold Co., 1983. 1191] [366].

LC50s for Cyprinus carpio (common, mirror, colored, carp) were 1080, 950 and 780 mg/L for 24-, 48- and 96-hr exposures, respectively [998].

LC50 Rainbow trout 13.5 mg/l/96 hr /Conditions of bioassay not specified, no specific isomer/ [Verschueren, K. Handbook of Environmental Data of Organic Chemicals. 2nd ed. New York, NY: Van Nostrand Reinhold Co., 1983. 1191] [366].

LC50s for Oncorhynchus mykiss (rainbow trout, donaldson trout) were 13.5 and 17.3 mg/L (ppm) for 24-hr exposures, and 8.2 and 17.3 mg/L for 96-hr exposures [998].

LC50 Fathead minnow 46 mg/l/1 hr; 42 mg/l/24-96 hr @ 18-22 deg C, in a static bioassay /No specific isomer/ [Verschueren, K. Handbook of Environmental Data of Organic Chemicals. 2nd ed. New York, NY: Van Nostrand Reinhold Co., 1983. 1191] [366].

LC50 for Pimephales promelas (fathead minnow) was 28.77 for both 24- and 48-hr exposures. LC50s were 13.4, 26.7 and 28.7 mg/L for 96-hr exposures [998].

LC50s for Poecilia reticulata (guppy) were 34.73 mg/L for 24-, 48- and 96-hr exposures [998].

LC50s for Lepomis macrochirus (bluegill) were: 30.5, 19.9, 15.9, 13.6 and 11.0 mg/L (ppm) for 1-, 2-, 4-, 8- and 16-hr exposures, respectively. LC50s ranged from: 10.4 to 36.0 mg/L for 24-hr exposures; 16.5 to 25.6 mg/L for 48-hr exposures; from 16.5 to 25.6 mg/L for 72-hr exposures; and from 13.5 to 24.5 mg/L for 96-hr exposures [998].

The most sensitive freshwater fish was the rainbow trout (Oncorhynchus mykiss), with 96-hour LC50s of 2.6, 7.6, and 8.4 mg/L for the p-, o-, and m- isomers, respectively. The most sensitive marine species tested was the young of the striped bass (Morone saxatilis), with 96-hour LC50s of 1.7, 8.0, and 9.7 mg/L for the p-, o-, and m- isomers, respectively [602].

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

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

CAS 1330-20-7, XYLENE (MIXED ISOMERS)

SPECIES	WATER CONCENTRATION (ppm)
Mouse (test species)	0.00000
Short-tailed Shrew	11.77000
Little Brown Bat	20.34400
White-footed Mouse	7.60700
Meadow Vole	13.31300
Cottontail Rabbit	6.30800
Mink	6.54200
Red Fox	4.66900
Whitetail Deer	2.61200

The toxicity of m-xylene to the early life stages of the leopard frog (Rana pipiens) and rainbow

trout was determined by exposing eggs of the species continuously from within 30 minutes of fertilization (embryos) to 4 days post-hatch (larvae). This resulted in a total continuous exposures of 9 days for the frog and 27 days for the trout. The LC50s for continuous exposure were 3.53 mg/L for the frog and 3.77 mg/L for the trout [602].

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

EPA 1996 IRIS database information [893]:

Maximum Contaminant Level Goal Value: 10.0 mg/L Reference: 56 FR 3526 (01/30/91)

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

Discussion: The EPA has promulgated a MCLG of 10.0 mg/L based upon potential adverse effects reported in a chronic oral study in rats. Cancer information on xylenes was reviewed and found to be inadequate for determining potential human carcinogenicity.

Maximum Contaminant Level (MCL)

Value: 10.0 mg/L Status/Year: Final 1991 56 FR 3526 (01/30/91); 56 FR 30266 (07/01/91)

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

Discussion: The EPA has promulgated a MCL equal to the MCLG of 10.0 mg/L.

National Water Quality Criteria [446,893]:

Human Health (1E-06 Risk Level for Carcinogens)

IRIS Criteria for Water and Organisms: None Published

IRIS Criteria for Organisms Only: None Published

Secondary Maximum Contaminant Level (SMCL)

Value: 0.02 Status/Year: Proposed 1989 Econ/Tech?: No, does not consider economic or technical feasibility Reference: 54 FR 22062 (05/22/89); 56 FR 3526 (01/30/91)

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

Discussion: SMCLs are non-enforceable and establish limits for contaminants which may affect the aesthetic qualities (e.g. taste and odor) of drinking water. It is recommended that systems monitor for these contaminants every three years. More frequent monitoring for contaminants such as pH, color, odor or others may be appropriate under certain circumstances. The SMCL for xylenes is based on odor qualities. Promulgation has been deferred following public comment (56 FR 3526).

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

EPA Region 9 Preliminary remediation goal (PRG) for Tap Water, 1995 [868]: 1.4E+03 ug/L.

EPA Region 3 risk based concentration (RBC) value for drinking water: 12,000 ug/L [903].

Older Drinking water information for xylene (CAS no. 1330-20-7) [859]:

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 2200 ug/L and 400 ug/L, respectively [859].

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 12,000 ug/L, 7800 ug/L, and (again) 7800 ug/L, respectively [859].

The U.S. EPA 7-year health advisories for a

70-kg adult consuming 2 L of water per day is 27,300 ug/L [859].

The aesthetic objective (AO) in Canada for xylene in drinking water is 0.300 mg/L [859].

New York State's Action Step Level 2 (ASL2) for public water systems is 10 ug/L. If this ASL2 is met or exceeded, the Bureau of Public Water Supply Protection must be notified and certain appropriate responses initiated [859].

New York State's Action Step Level 1 (ASL1) for public water systems is 50 ug/L. If this ASL1 is met or exceeded, the use of the water source must be discontinued and other appropriate responses initiated [859].

1 day EPA-calculated SNARL for xylenes = 12 mg/l; 10-day = 1.4 mg/l; and longer term exposure = 0.62 mg/l. [USEPA; Xylenes (Draft) p.6 (1981)] [366].

State Drinking Water Standards vary from 400 ug/L (several states) to 10,000 ug/L (NH) [764].

Canada's 1991 Interim Assessment Criterion for xylene in drinking water is equal to or less than 300 ug/L [656].

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

Concentration of xylenes in surface water are at least 100 times less than the effects threshold estimated for the most sensitive aquatic species [602].

Biological oxygen demand 5 (after 5 days @ 20 deg C): 0.64 (no stated isomer). [366, Verschueren, K. Handbook of Environmental Data of Organic Chemicals. 2nd ed. New York, NY: Van Nostrand Reinhold Co., 1983. 1190].

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

Sed.Low (Sediment Concentrations Considered Low):

No information found.

Sed.High (Sediment Concentrations Considered High):

Xylenes (total) was detected in 16% of urban-bay samples from the Puget Sound area. The mean concentration was 232 ug/kg dry weight (ppb), while the median

concentration was 9.6 ug/kg (ppb) [852].

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

Sed.Typical (Sediment Concentrations Considered Typical):

Xylenes (total) was detected in 27.5% of non-urban-bay samples from the Puget Sound area. The mean concentration was 27.88 ug/kg dry weight (ppb), while the median concentration was 0.28 ug/kg (ppb) [852].

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

Data on concentrations of xylenes in soils and sediments in Canada have not been identified [602].

13 samples of unspecified sediment 5.0 ppm max(1). [(1) Storet Data Base] [366].

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

Sed.General (General Sediment Quality Standards, Criteria, and Benchmarks Related to Protection of Aquatic Biota in General; Includes Sediment Concentrations Versus Mixed or General Aquatic Biota):

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

CAS 1330-20-7, XYLENE:

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

The Netherlands' Harmonized (between media) Maximum Permissible Concentration (MPC) for either 0-xylene, m-xylene, or p-xylene in sediments is 14 mg/kg [655].

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

The Netherlands' Harmonized (between media)

Negligible Concentration (NC) for either 0-xylene, m-xylene, or p-xylene in sediments is 1% of the MPC, or 0.14 mg/kg [655].

AET 1988: The apparent effects threshold concentrations for this compound in sediments proposed for Puget Sound ranged from 0.040 mg/kg dry weight (benthic species) to 0.016 mg/kg dry weight (amphipod) [416].

NOTE: Although the authors of the Puget Sound AETs have cautioned that Puget Sound AETs may not be appropriate for comparison with data from other geographic areas, so few sediment concern levels for this compound have been published that the proposed Puget Sound concern level is included in this text as an item of interest.

Sed.Plants (Sediment Concentrations vs. Plants):

No information found.

Sed.Invertebrates (Sediment Concentrations vs. Invertebrates):

No information found.

Sed.Fish (Sediment Concentrations vs. Fish):

No information found.

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

No information found.

Sed.Human (Sediment Concentrations vs. Human):

No information found.

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

No information found.

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

Soil.Low (Soil Concentrations Considered Low):

No information found.

Soil.High (Soil Concentrations Considered High):

No information found.

Soil.Typical (Soil Concentrations Considered Typical):

In Canada, data on concentrations of xylenes in soils and sediments have not been identified. In view of the sources and fate of xylenes in the environment, measurable concentrations of xylenes in soil would be expected to occur only near point sources such as spills, leaks, and waste disposal sites, or in areas with natural contamination from bituminous deposits [602].

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

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

The Netherlands' Harmonized (between media) Maximum Permissible Concentration (MPC) for either o-xylene, m-xylene, or p-xylene in soil is 14 mg/kg [655].

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

The Netherlands' Harmonized (between media) Negligible Concentration (NC) for either 0-xylene, m-xylene, or p-xylene in soil is 1% of the MPC, or 0.14 mg/kg [655].

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

The California State Leaking Underground Fuel Task Force in 1987 stated that (to protect groundwater) soils having a low leaching potential should be removed if the xylene concentration exceeds 50 ppm; soils having a medium leaching potential should be removed if the concentration exceeds 1 ppm xylene [347].

Canada's Interim Assessment Criterion for xylene 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 1991 Remediation Criteria for xylene 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].

State xylene cleanup guidance levels range from 1 to 50 ppm [806].

Soil.Plants (Soil Concentrations vs. Plants):

Oak Ridge National Lab, 1994: Risk Assessment Screening Benchmarks for Terrestrial Plants. To be considered unlikely to represent an ecological risk to terrestrial plants, field concentrations in soil should be below the following dry weight benchmark for soil [651]:

For CAS 001330-20-7 (XYLENE), no benchmark value exists.

Interim 1991 Canadian Remediation Criteria for Soil in cropland: 0.1 ug/g (ppm) [656].

Soil.Invertebrates (Soil Concentrations vs. Invertebrates):

No information found.

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

No information found.

Soil.Human (Soil Concentrations vs. Human):

Preliminary remediation goals (PRGs), 1995 [868]:

Residential Soil: 9.9E+02 mg/kg wet wt.
Industrial Soil: 9.9E+02 mg/kg wet wt.

NOTE:
1) 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.
2) Values are based on a non-carcinogenic hazard quotient of one.
3) PRGs for residential and industrial landuses are slightly lower concentrations than EPA Region III RBCs, which consider fewer aspects [903].

EPA Risk based concentration (RBC) to protect from transfers to groundwater:

74 mg/Kg dry weight [903].

Health Based Cleanup Levels [806]:

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

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

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

No information found.

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

Tis.Plants:

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

No information found.

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

No information found.

Tis.Invertebrates:

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

No information found.

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

No information found.

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

No information found.

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 vs. non-carcinogenic) concentrations, rounded to two significant figures [903]:

RBC Benchmark = 2700 mg/Kg wet weight. However, the reader should keep in mind that the concentrations would seldom get this high even in polluted areas.

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

No information found.

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

No information found.

Tis.Wildlife: Terrestrial and Aquatic Wildlife, Domestic Animals and all Birds Whether Aquatic or not:

A) As Food: Concentrations or Doses of Concern to Living Things Which Eat Wildlife, Domestic Animals, or Birds:

No information found.

B) Concentrations or Doses of Concern in Food Items Eaten by Wildlife, Birds, or Domestic Animals (Includes LD50 Values Which do not Fit Well into Other Categories, Includes Oral Doses Administered in Laboratory Experiments):

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

CAS 1330-20-7, XYLENE (MIXED ISOMERS)

SPECIES	NOAEL (mg/kg/day)	FOOD CONCEN-TRATION (ppm)
Mouse (test species)	2.06000	0.00000
Short-tailed Shrew	2.58900	4.31600
Little Brown Bat	3.25500	9.76500
White-footed Mouse	2.28200	14.76600
Meadow Vole	1.81500	15.97600
Cottontail Rabbit	0.61000	3.08800
Mink	0.64800	4.72700
Red Fox	0.39400	3.94200
Whitetail Deer	0.17100	5.55500

Although they do not speak to any potential this compound may have for long term (chronic) impacts, initial short term tests (acute oral toxicity) indicate xylene is relatively nontoxic to Japanese quail [185].

Pregnant outbred albino mice received by gavage, 3 times/day in cottonseed oil, a xylene mixt on days 6-15 of gestation. The mice where killed on day 18. At 3.6 Ml/kg/day, xylene killed 12 of 38 dams & caused a significantly smaller avg wt gain during pregnancy than did the cottonseed oil. Fetuses from

dams treated @ 2.4 Ml/kg/day had avg fetal wt significantly lower than that of control fetuses. At 2.4, 3.0, & 3.6 Ml/kg/day xylene produced a significantly greater avg % of malformed fetuses than did the control. Cleft palate was the major malformation at all 3 doses. When bilateral wavy ribs were counted as a malformation, the avg % of malformed fetuses incr from 7.8 To 10.5 @ 3.0 Ml/kg/day & from 9.1 To 13.4 @ 3.6 Ml/kg/day. Thus, xylene (mixed isomers) is teratogenic to mice @ 2.4 & 3.0 Ml/kg/day. [Marks ta et al; j toxicol environ health 9 (1): 97-105 (1982)] [366].

In single administration studies, groups of five F344/N rats and B6C3F1 mice of each sex received 500, 1,000, 2,000, 4,000, or 6,000 mg/kg /gavage in corn oil/. Administration of xylenes caused deaths at 6,000 mg/kg in rats and mice of each sex and at 4,000 mg/kg in male rats. Clinical signs observed /from 24 hr to 2 wk/ of dosing at 4,000 mg/kg included prostration, muscular incoordination, and loss of limb movement. Tremors, prone position, and slowed breathing were recorded for mice on day 3, but all mice appeared normal by the end of the 2 wk observation period. [NTP; Toxicology and Carcinogenesis Studies of Xylenes (Mixed) p.3 Report No TR 327 (1986) NIH Pub No 87-2583] [366].

In 14 day studies, groups of five /rats/ ... of each sex ... were administered 0, 125, 250, 500, 1,000, or 2,000 mg/kg and mice received 0, 250, 500, 1,000, 2,000, or 4,000 mg/kg. Chemical related mortality occurred only at 2,000 mg/kg in rats and 4,000 mg/kg in mice. Rats and mice exhibited shallow breathing and prostration within 48 hr following dosing at 2,000 mg/kg. These signs persisted until day 12 for rats, but no clinical signs were noted during the second wk for mice. [NTP; Toxicology and Carcinogenesis Studies of Xylenes (Mixed) p.3 Report No TR 327 (1986) NIH Pub No 87-2583] [366].

In 13 wk studies, groups of 10 rats of each sex received 0, 62.5, 125, 250, 500, or 1,000 mg/kg, and groups of 10 mice of each sex received 0, 125, 250, 500, 1,000, or 2,000 mg/kg. No deaths or clinical signs of toxicity were recorded in rats. However, high dose male rats gained 15% less and females gained 8% less weight than did the vehicle controls. Two female mice died at the 2,000 mg/kg level. Lethargy, short and shallow breathing, unsteadiness, tremors, and paresis were observed for both sexes in the 2,000 mg/kg group within 5-10 min after dosing and lasted for 15-60 min. [NTP;

Toxicology and Carcinogenesis Studies of Xylenes (Mixed) p.3 Report No TR 327 (1986) NIH Pub No 87-2583] [366].

Two yr toxicology and carcinogenesis studies were conducted by administering 0, 250, or 500 mg/kg xylenes in corn oil by gavage to groups of 50 F344/N rats of each sex, 5 days/wk for 103 wk. Groups of 50 B6C3F1 mice of each sex were administered 0, 500, or 1,000 mg/kg xylenes on the same schedule. Although the mortality was dose related in male rats (final survival: vehicle control, 36/50; low dose, 26/50; high dose, 20/50), many of the early deaths in the dosed males were gavage related. Body weights of the high dose male rats were 5-8% lower than those of the vehicle controls after wk 59. The mean body weights of low dose and vehicle control male rats and those of dosed and vehicle control female rats were comparable. Survival of dosed mice was not significantly different from that of the vehicle controls. The mean weights of dosed male and female mice were comparable to those of the vehicle controls. Hyperactivity lasting 5-30 min was observed after dosing in high dose mice, beginning after wk 4 and continuing through wk 103. At no site was the incidence of nonneoplastic or neoplastic effects in dosed rats or mice of either sex considered to be related to the administration of xylenes. ... Under the conditions of these 2 yr gavage studies, there was no evidence of carcinogenicity of xylenes (mixed) in male and female F344/N rats given 250 or 500 mg/kg or in male or female mice given 500 or 1,000 mg/kg. [NTP; Toxicology and Carcinogenesis Studies of Xylenes (Mixed) p.3 Report No TR 327 (1986) NIH Pub No 87-2583] [366].

LD50 Rat ingestion 4.3 g/kg [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. 3292] [366].

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

No information found.

Tis.Human:

A) Typical Concentrations in Human Food Survey Items:

No information found.

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: 179 mg/kg-day [Study 1 NOAEL(adj)] UF: 100

RfD: 2E+0 mg/kg-day Confidence: Medium

LDLo (lowest published lethal dose) Human oral 50 mg/kg [USEPA; Advisory Opinion for Xylenes (Dimethyl benzenes) (Draft) p.3 (1981)] [366].

Past oral Rfd (safe level) estimates have varied from 0.2 to 2.0 mg/kg/day [868].

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 vs. non-carcinogenic) concentrations, rounded to two significant figures [903]:

RBC Benchmark = 2700 mg/Kg wet weight. However, the reader should keep in mind that the concentrations would seldom get this high even in polluted areas.

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

Environmental pollutants in human milk were identified by gas chromatography/mass spectrometry. Xylene was one of the aromatics identified. [PELLIZZARI ED ET AL; BULL ENVIRON COMTAM TOXICOL 28: 322 (1982)] [366].

An adverse health effect disturbance to equilibrium has been observed in humans. ... This effect has been correlated with blood concn ... of 30 umol/l (equivalent to 318 ug/100 ml) ... . [USEPA; Advisory Opinion for Xylenes (Dimethyl benzenes) (Draft) p.6 (1981)] [366].

Tis.Misc. (Other Tissue Information):

No information found.

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

Bioconcentration [366]:

Little bioconcentration is expected. Based on the log octanol/water partition coefficient of 3.12-3.20 for the individual isomers(1) and using a regression relation(2), the log BCF for fish is calculated to be 2.14-2.20. The log BCF for eels is 1.3(3). [(1) Hansch C, Leo AJ; Medchem Project No 19 Claremont CA: Pomona College (1981) (2) Lyman WJ et al; Handbook of Chemical Property Estimation Methods McGraw Hill New York NY p 5-5 (1982) (3) Ogata M, Miyaka Y; Water Res 12: 1041-4 (1978)].

Interactions:

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

Information from HSDB [366]:

Concomitant ingestion of ethyl alcohol potentiated the deleterious behavioral effects of xylene in animals. Alcohol also potentiated the weak hepatic microsomal enzyme-inducing effects of xylene, and the combination produced liver damage at doses of xylene which were not effective alone. [Gosselin, R.E., R.P. Smith, H.C. Hodge. Clinical Toxicology of Commercial Products. 5th ed. Baltimore: Williams and Wilkins, 1984.,p. III-399].

Daily oral administration of 55 mg balagrin in xylene (20% balagrin-80% xylene) for 4 months, or administration of 235 mg xylene/kg stimulated rat serum ornithine carbamoyl transferase and leucine aminopeptidase, and decreased the relative weight of the liver. Only balagrin plus xylene decreased serum alpha-2 globulins, stimulated serum and liver cholinesterase, and decreased liver triglycerides, whereas xylene alone increased the blood leukocyte count and stimulated liver cytochrome oxidase, and inhibited it in the testes and brain. Xylene alone stimulated liver isocitrate dehydrogenase and glucose dehydrogenase more than did balagrin plus xylene. ... A 79% incr in hepatic DNA indicated repair. [Ivanova-Chemishanska L et al; Probl Khig 5: 50-7 (1980)].

When consumed prior to exposure, ethanol decreases the metabolic clearance of xylene by approximately one-half. [Ellenhorn, M.J. and D.G. Barceloux. Medical Toxicology - Diagnosis and Treatment of Human Poisoning. New York, NY: Elsevier Science Publishing Co., Inc. 1988. 963].

Uses/Sources:

Xylene (Dimethyl benzene) is used as an aquatic contact herbicide against pondweeds and algae such as Chara [187].

Major Uses [366]:

Raw material for production of benzoic acid; as solvent; manufacturing dyes & other organics; sterilizing catgut; production of phthalic anhydride, isophthalic & terephthalic acids & their dimethyl esters used in manufacture of polyester fibers; with canada balsam as oil-immersion in microscopy; cleaning agent in microscope technique [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 1448].

Manufacture of resins, paints, varnishes, general solvent for adhesives [Doull, J., C.D.Klassen, and M.D. Amdur (eds.). Casarett and Doull's Toxicology. 3rd ed., New York: Macmillan Co., Inc., 1986. 349].

In aviation gasoline; protective coatings; synthesis of org chemicals [Sax, N.I. and R.J. Lewis, Sr. (eds.). Hawley's Condensed Chemical Dictionary. 11th ed. New York: Van Nostrand Reinhold Co., 1987. 1243].

Source of o-xylene, m-xylene, p-xylene & ethylbenzene [SRI].

Solvent-eg, for paints, coatings, adhesives & rubber [SRI].

Back-blended into gasoline [SRI].

Unrecovered component of gasoline [SRI].

Used in manufacture of quartz crystal oscillators, hydrogen peroxide, perfumes, insect repellants, epoxy resins, pharmaceuticals, and in the leather industry. [Sittig, M. Handbook of Toxic And Hazardous Chemicals. Park Ridge, NJ: Noyes Data Corporation, 1981. 452].

/SRP:/ Used in histological laboratories.

Used as a solvent in phenoxyalkanoic herbicides. [Que Hee SS, Sutherland RG; The Phenoxyalkanoic Herbicides p.64 (1981)].

(MEDICATION) Used in manufacture of ... pharmaceuticals ... . [Sittig, M. Handbook of Toxic And Hazardous Chemicals. Park Ridge, NJ: Noyes Data Corporation, 1981. 452].

Used as an indirect food additive for use only as a component of adhesives. [21 CFR 175.105 (4/1/86)].

Used as an indirect food additive polymer for use as a basic component of single and repeated use food contact surfaces.

Xylene is used as a solvent in polysulfide polymer-polyepoxide resins. [21 CFR 177.1650 (4/1/86)].

Natural Occurring Sources [366]:

Petroleum, coal tar(1); forest fires, plant volatile(2). [(1) Verschueren K; Handbook on Environmental Data on Organic Chemicals; 2nd ed New York, NY VanNostrand Reinhold Co p.1188-94 (1982) (2) Graedel TE; Chemical Compounds in the Atmosphere; New York NY Academic Press p.108 (1978)].

Artificial Sources [366]:

Emissions from petroleum refining, gasoline and diesel engines(1). Emissions from its use as a solvent for alkyl resins, lacquers, enamels, rubber cement, pesticidal sprays and in organic synthesis(1,2). Leaks and evaporation losses during the transport and storage of gasoline and other fuels and from carburetor losses(1). [(1) NAS; The Alkyl Benzenes; p.I-1 to I-99 (1980) (2) The Condensed Chemical Dictionary; Ninth ed. p.931 (1977)].

Agricultural spraying. [NAS; The Alkyl Benzenes page I-1 to I-99 (1980)].

Forms/Preparations/Formulations:

Formulations/Preparations [366]:

The commercial product "mixed xylenes" is a technical product generally containing approximately 40% m-xylene and 20% each of o-xylene, p-xylene, and ethylbenzene, as well as small quantities of toluene ... . [Fishbein L; Sci Total Environ 43 (1-2): 165-83 (1985)].

70% of all mixed xylene grades produced are 3 deg and 5 deg grade. [DCE/NCI; Monograph On Human Exposure To Chemicals In The Workplace: Xylene p.1-1, 1985].

Solvent xylene, 2 deg C range [Kuney, J.H. and J.N. Nullican (eds.) Chemcyclopedia. Washington, DC: American Chemical Society, 1988. 119].

Grade: Nitration (bp range 137.2-140.5 deg C), 4 degrees (bp range 138-134 deg C), 5 degrees (bp range 137-142 deg C, high in m- isomer), 10 degrees (bp range 135-145 deg C); industrial (bp 90% 40 deg C, complete 160 deg C). Also other grades depending upon use. [Sax, N.I. and R.J. Lewis, Sr. (eds.). Hawley's Condensed Chemical Dictionary. 11th ed. New York: Van Nostrand Reinhold Co., 1987. 1243].

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

Xylene produced from petroleum ... contains approx 20% o-xylene, 44% m-xylene, 20% p-xylene and 15% ethylbenzene. Xylene from coal tar generally consists of 10-15% ortho-, 45-70% meta-, 23% para-, and 6-10% ethylbenzene. Commercial xylenes may also contain small amt of toluene, trimethylbenzene, phenol, thiophene, pyridine, and nonaromatic hydrocarbons. [NIOSH; Criteria Document: Xylene p.14 (1975) DHEW Pub. NIOSH 75-168] [366].

Jet Fuel 4 is among the many petroleum products contain xylenes. Composition (weight %) of Shale-Derived and Petroleum-Derived JP-4 [876]:

Disubstituted aromatics (xylenes)		
m -Xylene	2.60	2.71
p -Xylene	1.70	1.63
o -Xylene	2.00	1.89
Total	6.30	6.23

Solubilities:

Practically insol in water; miscible with absolute alcohol, ether, and many other organic liquids [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 1448] [366].

Density/Specific Gravity:

0.864 @ 20 DEG C/4 DEG C [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. 3556] [366].

Octanol/Water Partition Coefficient:

log Kow= 3.12-3.20 [Hansch, C., A. Leo. Substituent Constants for Correlation Analysis in Chemistry and Biology. New York, NY: John Wiley and Sons, 1979. 232] [366].

Boiling Point:

137-140 DEG C [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 1448] [366].

Molecular Weight:

106.16 [American Conference of Governmental Industrial Hygienists. Documentation of the Threshold Limit Values and Biological Exposure Indices. 5th ed. Cincinnati, OH:American Conference of Governmental Industrial Hygienists, 1986. 637] [366].

Corrosivity:

Xylene will attack some forms of plastics, rubber, and coatings. [Mackison, F. W., R. S. Stricoff, and L. J.

Partridge, Jr. (eds.). NIOSH/OSHA - Occupational Health Guidelines for Chemical Hazards. DHHS(NIOSH) PublicationNo. 81-123 (3 VOLS). Washington, DC: U.S. Government Printing Office, Jan. 1981. 2] [366].

Color/Form:

CLEAR LIQUID [American Conference of Governmental Industrial Hygienists. Documentation of the Threshold Limit Values and Biological Exposure Indices. 5th ed. Cincinnati, OH:American Conference of Governmental Industrial Hygienists, 1986. 6370] [366].

Odor:

Sweet odor [Environment Canada; Tech Info for Problem Spills: Xylenes (Draft) p.1 (1981)] [366].

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

Xylenes are rapidly lost from surface water by volatilization. The half-life in still water 1 meter deep has been estimated to be 5.6 hours; it would be shorter in turbulent water [602].

Volatilization rates were calculated for lakes (8 days) and rivers (1 to 2 days) and for streams and rivers (36 minutes to 47 days), with reported variations due to differences in conditions such as depth and flow rates of streams and rivers [602].

Xylenes can be degraded by micro-organisms in the water. Half-lives for biodegradation by unacclimated organisms in water have been estimated to be between 7 and 28 days for each of the three isomers in aerobic systems, and between 180 and 360 days for o-xylene and 28 and 112 days for m- and p-isomers in anaerobic systems [602].

Volatilization half-lives, ranging from less than 1 minute to 2.2 days, have been estimated for all three xylene isomers on the soil surface. Volatilization should be much slower for xylenes incorporated into soil, with rates decreasing rapidly with soil depth [602].

Although xylenes are only moderately soluble in water, they may leach through soils to groundwater. Movement through soils is expected to be slowed by the presence of organic matter, clay, and high moisture content. However, xylenes have been reported to move through clay soils [602].

Environmental Fate [366]:

TERRESTRIAL FATE: When spilled on land, xylenes will volatilize and leach into the ground. Xylenes may be degraded during their passage through soil(1). The extent of the degradation will undoubtedly depend on their concentration, residence time in the soil, the nature of the soil, and whether resident microbial populations have been acclimated.

[(1) Kappeler T, Wuhrmann K; Water Res 12: 327-33 (1978)].

AQUATIC FATE: In surface waters, volatilization appears to be the dominant removal process (half-life 1-5.5 days(2,SRC). Some adsorption to sediment will occur. Although xylenes are biodegradable and have been observed to degrade in seawater, there is insufficient data to access the rate of this process in surface waters. Although they have been observed to degrade in groundwater in one study, they are known to persist for many years in groundwater at least at sites where the concentration might have been quite high. In a field study of an oil spill from the Trans-Alaskan Pipeline which leaked into the Atigun River on June 10, 1979, aromatic hydrocarbons including xylenes were absent from the 40 km long river in contaminated area 18 days after the spill(1). [(1) Lysyj, I et al; Environ Int 4: 407-16 (1980) (2) Lyman WJ et al; Handbook of Chemical Property Estimation Methods McGraw-Hill NY p 15-1 to 15-34 (1982)].

ATMOSPHERIC FATE: When released into the atmosphere, xylenes may degrade by reaction with photochemically produced hydroxyl radicals (half-life 1.0-1.7 hr in summer and 10-18 hr in winter(1)). However, ambient levels are detected because of large emissions. [(1) Ravishankara AR et al; Int J Chem Kinetics 10: 783-804 (1978)].

Biodegradation [366]:

Xylenes are degraded in standard biodegradability tests using various inocula including sewage, activated sludge and sea water(1-4). They are completely degraded in 8 days in groundwater in a gas-oil mixtures; the acclimation period was 3-4 days(5). [(1) Bridie AL et al; Water Res 13: 627-30 (1979) (2) Kitano M; Biodegradation and Bioaccumulation Test on Chemical Substances. OECD Tokyo Mtg TSU-No. 3 (1978) (3) Malaney GW, McKinney RE; Water Sewage Works 113: 302-9 (1966) (4) Van der Linden AC; Dev Biodeg Hydrocarbons 1: 165-200 (1978) (5) Kappeler T, Wuhrmann K; Water Res 12: 327-33 (1978)].

Abiotic Degradation [366]:

Xylenes degrade in the atmosphere by reacting with photochemically produced hydroxyl radicals(1-3) with a half-life ranging from 1-1.7 hr in summer to 10-18 hr in winter(1) or a typical loss of 67-86% per day(3). They are moderately reactive under photochemical smog conditions with half-lives of several hours(5-7). Xylenes are resistant to hydrolysis, since there are no hydrolyzable functions. [(1) Ravishankara AR et al; Int J Chem Kinetics 10: 783-804 (1978) (2) Hansen DA et al; J Phys Chem 78: 1763-6 (1975) (3) Singh HB et al; Atmos Environ 15: 601-12 (1981) (4) Kopczynski SL et al; Environ Sci Technol 6: 342 (1972) (5) Yanagihara S et al; 4th Int Clean Air Conf Photochemical Reactivities of Hydrocarbons; p.472-7

(1977) (6) Van Aalst RM et al; Comm Eur Com Symp Phys Chem Behav Atmos Pollut EUR6621 1: 136-49 (1980) (7) Van Aalst RM et al; Comm Eur Com Symp Phys Chem Behav Atmos Pollut EUR 6621 1: 136-49 (1980)].

Soil Adsorption/Mobility [366]:

Xylenes have low to moderate adsorption to soil based on the KOC of o-xylene(48-68)(1) and similar chemicals. Xylenes have been observed to pass through soil at a dune-infiltration site on the Rhine River(2) and to leach into groundwater under a rapid infiltration site(3). [(1) Nathwani JS, Phillip CR; Chemosphere 6: 157-62 (1977) (2) Piet GJ et al; Quality of Groundwater Int Symp; Von Duyvenbouden W et al ed; Studies Env Sci 17: 557-64 (1981) (3) Tomson WB et al; Water Res 15: 1109-16 (1981)].

Volatilization from Water/Soil [366]:

Xylenes are volatile compounds with relatively high Henry's Law constant (0.22 for the ortho isomer and 0.32 for the m- and p- isomers)(1). The half-life for evaporation from water with a wind speed of 3 m/sec, a current of 1 m/sec, and a depth of 1 m is 3.2 hr for o-xylene and will be 2% higher for the m- and p-xylene(2). An experiment which measured the rate of evaporation of xylenes from a 1:1000 jet fuel:water mixture found that this rate averaged approximately 0.6 times the oxygen reaeration rate(3). Combining this ratio with oxygen reaeration rates for typical bodies of water(2), one estimates that the half-life for evaporation of xylenes from a typical river or pond is 29 and 144 hr, respectively(4,SRC). [(1) NAS; The Alkyl Benzenes; p.II-1 to II-51 (1980) (2) Lyman WJ et al; Handbook of Chemical Estimation Methods McGraw Hill New York NY p.15-1 to 15-34 (1982) (3) Smith JH, Harper JC; 12th Conf on Environ Toxicol: Behavior of Hydrocarbon Fuels in Aquatic Environment; p.336-53 (1980)].

Absorption, Distribution and Excretion [366]:

For exposure to xylene at concn averaging 100 ppm, the mean methyl hippuric acid concn should average 1.5 to 2 g/g creatinine (range 1.0-3.0) in a sample collected during the second part of the exposure period. Almost total urinary excretion of xylene occurs by 24 hours. The rapid xylene clearance from blood (plasma half-life of 4 hours) prevents adequate biological monitoring of serum samples. ... [Ellenhorn, M.J. and D.G. Barceloux. Medical Toxicology - Diagnosis and Treatment of Human Poisoning. New York, NY: Elsevier Science Publishing Co., Inc. 1988. 963].

Xylenes have been reported to cross the human placenta. [National Research Council. Drinking Water and Health. Volume 3. Washington, DC: National Academy Press, 1980. 180].

Xylene, when ingested, is readily absorbed by the human system, as has been shown in accidental ingestions. Absorption through intact & broken skin occurs readily. ... Xylene is absorbed mainly through mucous membranes & pulmonary system. ... Absorbed xylene is translocated through the vascular system. ... [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. 3296].

Urine of 134 persons exposed to organic solvents was analyzed with reference to albumin & beta-2 microglobulin excretion. Forty had been exposed mainly to xylene & toluene during paint mfr. Significantly greater amounts of albumin were excreted in exposed workers than in controls. No significant difference in beta-2-microglobulin excretion was demonstrated. [ASKERGREN A ET AL; ACTA MED SCAND 209: 479-84 (1981)].

The uptake of solvent by man during whole body exposure to toluene and xylene occurs almost exclusively through the lung; dermal uptake represents about 1% of the total uptake. [Wallen M et al; Brit J Indust Med 42: 111-6 (1985)].

Male rats were injected ip with benzene, toluene, or a mixt or xylene isomers at 20 mmol hydrocarbon/kg daily for 3 days. The effects of administration of these hydrocarbons upon their own in vitro metabolism, as well as upon cytochrome p450, NADPH-cytochrome c reductase, aminopyrine N-demethylase, aniline hydroxylase, glutathione, glutathione S-transferase, and UDP-glucuronyltransferase in liver were studied. [Pathiratne A et al; Toxicol Appl Pharmacol 82 (2): 272-80 (1986)].

The correlation between xylene exposure and urinary excretion of methyl hippuric acid (MHA) was studied in 40 workers (35 men, 5 women) employed in the paint industry. Subjects were exposed primarily to xylene although exposure to 11 other solvents was possible. Personal sampling showed 8 hr time weighted average for xylene ranged from 0-865 mg/cu m with a median exposure of 69 mg/cu m. Urine was collected over one 24 hr period for each worker. Personal air samples were collected for each worker over the course of a complete workday. Methyl hippuric acid excretion was linearly correlated to the 8 hr time weighted average for xylene exposure after adjustment for body weight. The total amount of methyl hippuric acid excreted in the urine over 24 hr showed virtually the same correlation to xylene exposure (r= 0.84) as the methyl hippuric acid excretion during the latter part of the workshift (r= 0.81, sampling time 4-5 hr) among 37 workers exposed to 8 hr time weighted average xylene concentrations of 0-200 mg/cu m. [Lundberg I, Sollenbert J; Scand J Work Environ Health 12: 149-53 (1986)].

Humans exposed to 46 or 92 ppm of o-, m-, p-xylene or a mixture (1:1:1) of the three for 8 hr absorbed approx 64% of

the inhaled xylene. No difference in the absorption rate was reported due to level of exposure, length of exposure, or the type and/or mixture of the xylene isomers. The absorption of xylene appeared to vary among individuals due to differences in ventilation rate. ... Individuals with an incr ventilation rate retained less xylene. [NCI; Monograph on Human Exposure to Chemicals in the Workplace: Xylene p.4-2 (July/1985)].

Male Wister rats exposed to xylene in air (80% m-xylene, 12% p-xylene) for 6 hr/day, 5 days/week for 2 weeks accumulated 64.8 mg/xylene/g of perirenal fat after five exposures and 127.0 mg/xylene/g of perirenal fat after 10 exposures to xylene. [NCI; Monograph on Human Exposure to Chemicals in the Workplace: Xylene p.4-4 (July/1985)].

Groups of five male Wister rats were exposed to 300 ppm of technical grade xylene (85% m-xylene, 15% other isomers) for 6 hr/day, 5 days a week for 5, 9, 14, or 18 weeks. Analysis of the perirenal fat by gas chromatography indicated that 67.6, 57.4, 40.7, and 36.6 mg/g of tissue was present after 5, 9, 14, or 18 weeks of exposure, respectively. The gradual decr in the xylene content of perirenal fat as the length of exposure was incr may have been the result of an incr metabolic rate. [NCI; Monograph on Human Exposure to Chemicals in the Workplace: Xylene p.4-4 (July/1985)].

Groups of six male human volunteers were exposed to 200 or 100 ppm of a xylene mixture (49.4% ethylbenzene) for 30 min through a breathing valve. The first group, while being exposed to 200 ppm of the xylene mixture, exercised on a bicycle ergometer for 90 min. The second group, exposed to 100 ppm, ... incr their level of exercise at 30 min intervals. At rest and during light work, pulmonary uptake ... was about 63% during the 2 hr exposure period. At a more strenuous work level, pulmonary uptake ... was only 51% after a correction had been applied for the incr breathing vol that occurs during heavy exercise. [NCI; Monograph on Human Exposure to Chemicals in the Workplace: Xylene p.4-1 (July/1985)].

15 human male volunteers exposed for 70 min periods to 100 and 300 ppm at rest and 300 ppm while exercising absorbed a mean of 180, 541, or 1210 mg of xylene, respectively. The xylene absorption rate for both exposure levels was 43% while resting and 64% while exercising, assuming inhalation volumes of 20 cu m/24 hr at rest and 10 cu m/8 hr at work. [NCI; Monograph on Human Exposure to Chemicals in the Workplace: Xylene p.4-2 (July/1985)].

Xylene possesses marked solubility in adipose tissue (distribution coefficient fat/blood approximately 100). ... [Riihimaki V et al; Arch Toxicol 49: 253-63 (1982)].

Laboratory and/or Field Analyses:

Detection limits should be as low as possible to avoid false negatives and (in any case) no higher than comparison benchmarks or criteria. Wisconsin requires a detection limit of 0.5 ug/L for all VOCs [923]. One GC/PID method is available to achieve water detection limit of 0.01 ug/L [764]. One GC/ECD method is available to achieve a soil detection limit of 1 ug/kg (ppb) [765].

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

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

In the past, many methods have been used to analyze for this compound [861,1010,1011,1013]. Volatiles such as the xylenes have been analyzed using method 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 for volatiles 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].

Contaminants data from different labs, different states, and different agencies, collected by different people, are often not very comparable (see also, discussion in the disclaimer section at the top of this entry).

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

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

It should be kept in mind that quality control field and lab blanks and duplicates will not help in the data quality assurance goal as well as intended if one is using a method prone to false negatives. Methods may be prone to false negatives due to the use of detection limits that are too high, the loss of contaminants through inappropriate handling, or the use of inappropriate methods such as many of the EPA standard scans. The use of inappropriate methods is particularly common related to oil products. This is one reason for using the NOAA expanded scan for PAHs [828]; or method 8270 [1013] modified for Selective Ion Mode (SIM) detection limits (10 ppt for water, 0.3 to 1 ppb for solids) and additional alkyl PAH analytes in response to oil spills. Alkyl PAHs are more persistent and less volatile than xylenes. Thus, rigorous low-detection-limit scans for alkyl PAHs are less prone to false negatives than many of the standard EPA high-detection-limit analyses for xylenes (Roy Irwin, National Park Service, Personal Communication, 1997).

The basics of quality assurance plans for chemical analyses should include the following quality control steps:

At minimum, before using contaminants data from diverse

sources, one should determine that field collection methods, detection limits, and lab quality control techniques were acceptable and comparable. The goal is that the analysis in the concentration range of the comparison benchmark concentration should be very precise and accurate. Typical lab quality control techniques should have included the following considerations (Roy Irwin, National Park Service, Personal Communication, 1997, summary based on various EPA and FWS documents):

Procedural Blanks should be analyzed to assure that no contaminants are added during the processing of the samples. The standards for adequacy depend on the method and the media being measured.

> Different federal agencies publish different acceptable limits. For one program, NOAA stated that at least 8% of samples should be blanks, reference or control materials [676].
>
> The basic idea is that neither samples nor blanks should be contaminated. Because the only way to measure the performance of the modified procedures is through the collection and analysis of uncontaminated blank samples in accordance with this guidance and the referenced methods, it is highly recommended that any modifications be thoroughly evaluated and demonstrated to be effective before field samples are collected [1003].

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

> Different federal agencies publish different acceptable limits. There appears to be an inverse relationship between precision and sensitivity [676].
>
> Some EPA methods state that a field duplicate must be collected at each sampling site, or one field duplicate per every ten samples, whichever is more frequent [1003]. Some protocols call for the preparation of one Ongoing precision and recovery (OPR) standard for every ten or fewer field samples. Great care should be taken in preparing ongoing precision and recovery standards [1003].

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

> Different federal agencies publish different acceptable limits.

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:

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].

Xylenes are a component of BTEX (see also BTEX entry). Notes on more generalized BTEX methods:

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

> Because BTX&E are more mobile than the remaining constituents, an analysis of BTX&E alone, without characterizing the entire contaminated soil profile, cannot be used to quantify the amount of fuel contamination in the soil. An analysis of Total Petroleum Hydrocarbons (TPH) should be included to check for other less mobile fuel constituents that could be absorbed onto the soil in higher concentrations. This additional analysis may serve as a check for the possibility that BTX&E have migrated to deeper depths.
>
> While TPH levels generally indicate fuel contamination, certain sites may have natural or historical use features (former oil field), that make interpretation difficult. Also, reported soil concentrations of volatile organic chemicals may vary with soil type. Complete recovery of volatiles during sample collection is difficult in sandy soil, due to losses from evaporation. Also, adsorption may limit extraction efficiency in clayey soils.
>
> In the leaching potential analysis suggested in the LUFT

manual, that recommended detection limit for benzene, toluene, xylene, and ethylbenzene is 0.3 ppm for each compound. This 0.3 ppm value for BTX&E was determined to be a detection level that most laboratories can routinely achieve, based on a survey conducted by DHS.

No BTX&E level is presented for the most sensitive sites (40 pts. or less). BTX&E levels should be below detection limits if TPH levels are 10 ppm or lower, therefore no BTX&E levels are presented to avoid the impression that detection limits are recommended as cleanup levels. Thus, the leaching potential analysis for sensitive sites relies exclusively on TPH values. If BTX or E are detectable, even though TPH is below 10 ppm, the site investigation should proceed to the General Risk Appraisal.

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

If used as a measure of BTEX, the more lengthy scan referred to as standard EPA 8240 method often needs to "enhanced" by the inclusion of analytes that would be expected in specific situations. For example, for tanks leaking gasoline and diesel, one should include rigorous analyses for alkyl benzenes (like alkyl PAHs, alkyl benzenes are more resistant to degradation than parent compounds), MTBE and BTEX compounds, 1,2 Dichloroethane, alkyl lead isomers, and other compounds consistent with 1995 risk assessment needs. Enhanced 8240 scans are available from various commercial labs (Gregory Douglas, Arthur D. Little, Inc., Cambridge, Massachusetts, personal communication, 1995).

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

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

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

The first third includes relatively low boiling point (very volatile) lighter hydrocarbons such as some alkanes [804] and MTBE [801].

The second third includes the still volatile but somewhat heavier BTEX hydrocarbons [801,804].

The third third includes the heaviest (molecular weight greater than 110) and less volatile PAHs and alkyl PAHs [804] such as naphthalene and alkyl naphthalenes [801].

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

Using a modified EPA method 8240 (about $200 per water sample in 1995), analyses can be done for the following volatile and gasoline additive compounds:

Alkyl benzenes common in oils:

isopropyl benzene:	detection limit (dl): 1 ppb
n-propyl benzene:	dl 1 ppb
1,3,5-trimethyl:	dl 1 ppb
1,2,4-trimethyl:	dl 1 ppb
tert-butyl	dl 1 ppb
sec-butyl	dl 1 ppb
n-butyl	dl 1 ppb
MTBE	dl 1 ppb
BTEX	dl 0.5 ppb
1,2-DCA	dl 0.5 ppb

Additional information on analytical methods for xylenes from ATSDR [764] (for information on embedded citations, see ATSDR Toxicological Profile) [764]:

BIOLOGICAL MATERIALS [764]:

> Extensive commercial, industrial, and domestic use of volatile organic chemicals such as xylene virtually assures that the general population will be exposed to this class of chemicals to some extent. The determination of trace amounts of xylene in biological tissues and fluids has been restricted to only a limited number of analytical methods. These include gas chromatography coupled with mass spectrometry (GC/MS), gas chromatography coupled with hydrogen flame ionization detection (GC/FID), and high-performance liquid chromatography (HPLC). Xylene can be detected at parts-per-trillion (ppt) levels in whole human blood using a purge and trap apparatus followed by GC/MS; however, this method does not distinguish between m- and p- xylene

((Ashley et al. 1992). Antifoam agents are frequently used, although a method has been developed that does not require this additive (Cramer et al. 1988). The use of a dynamic headspace purge at room temperature reduces the absolute recoveries of the late eluting compounds. An advantage of this GC/MS technique is that it can be used in conjunction with selected ion monitoring to obtain better sensitivity of target compounds (such as National Priority List Pollutants) at ppt levels (Cramer et al. 1988) [764].

To overcome the low recoveries obtained with the purge and trap method, another extraction procedure is recommended that uses Amberlite XAD-2 adsorbent resin present in the blood collection tube when the sampling takes place. This method dispenses with the readsorption of the hydrocarbon from the sampling tube to the polymer and gives recoveries of 77-98% (Norstrom and Scheepers 1990). The use of GC/FID followed by a combination of packed and open tubular capillary GC and GC/MS to detect and quantify the isomers of xylene in human tissues and fluids has been reported in the literature. Brain, liver, lung, kidney, and blood samples of individuals who died following occupational exposure to several organic solvents were analyzed using a combination of capillary columns (Bellanca et al. 1982). The sensitivity and resolution of the isomers of xylene were increased, and detection limits of 0.05 mg, 0.05 mg, and 0.01 mg per 100 grams of sample were obtained for m- , o , and p-xylene, respectively (Bellanca et al. 1982). Despite this increased resolving power, adequate separation of m-xylene and p- xylene was unattainable [764].

Exposure to xylene may also be indicated by its presence in exhaled breath. Xylene in mainstream breath may be determined by exhaling through a charcoal cloth (Glaser and Arnold 1989); xylene in sidestream breath is trapped using a two-stage Tenax TA sorbent sampler (Glaser et al. 1990) or a Tenax GC cartridge (Pellizzari et al. 1988). The Tenax cartridge is dried over calcium sulfate, and then the xylene is thermally desorbed for GC/MS. Correlations with carbon dioxide measurements were 90% and 60% for mainstream and sidestream breath, respectively (Glaser et al. 1990), with a quantification limit of 0.4 ug/L m-xylene for a 50-L sample (Glaser and Arnold 1989). The detection limit (LOD) was 0.50 ug/m3 with a quantification limit five times the LOD for a 15-L breath sample (Pellizzari et al. 1988) [764].

In addition to direct measurement of xylene in biological tissues and fluids, it is also possible to determine the concentration of its metabolites in biological fluids. A simple, sensitive, and specific automated HPLC technique was developed for direct and simultaneous quantification

of o- , m- , and p- methylhippuric acids, the metabolites of o- , m- , and p- xylene, respectively (Ogata and Taguchi 1987; Sugihara and Ogata 1978; Tardif et al. 1989). A possible disadvantage of the HPLC technique is that at low concentrations (less than 0.6 mg/L) in urine, these methylhippuric acids may not be distinguishable from similar compounds. However, addition of a mobile phase, consisting of mixture of acetonitrile and 1% phosphoric acid, has been used to distinguish between xylene metabolites and other solvents such as benzene and toluene in the urine (Astier 1992). Use of methanol as a solvent for the urine obviates the need for the customary ethylether extraction step and allows direct urine injection for HPLC (Ogata and Taguchi 1988). N -acetyl- S -xylyl-L-cysteine, a mercapturic acid, is also a urinary metabolite of xylene that may be detected by direct HPLC (Tanaka et al. 1990). The HPLC method recommended by NIOSH (1994) does not distinguish between p- and m- methyl hippuric acids. Other techniques that have been successful in quantitatively determining urinary concentrations of metabolites of xylene include GC/FID, GC/MS, and thin layer chromatography (TLC) [764].

GC/FID and GC/MS offer the possibility of excellent analytical sensitivity and specificity for urinary metabolites of xylene (Caperos and Fernandez 1977; de Carvalho et al. 1991; Engstrom et al. 1976; Kataoka et al. 1991; Kira 1977; Morin et al. 1981; Poggi et al. 1982). However, most GC analytical methods require the urinary metabolites to be chemically transformed into methyl esters or trimethyl silyl derivatives using ethylacetate or diazomethane. This transformation, however, is problematic and may subsequently cause low reproducibility (Caperos and Fernandez 1977; Engstrom et al. 1976; Morin et al. 1981; Poggi et al. 1982). The methylhippuric acid metabolites of the xylene isomers may be distinguished using an extractive alkylation procedure followed by capillary GC analysis (Kataoka et al. 1991). An extraction method using less toxic reagents (hydrochloric acid with methanol) has been developed (de Carvalho et al. 1991). A simple and highly reproducible TLC method has been developed for the detection and separation of m- or p- methylhippuric acid in the urine of individuals exposed to a mixture of volatile organic solvents (Bieniek and Wilczok 1981). However, the authors noted that this analytical technique is time consuming. Furthermore, the developing agent used in this technique (p- dimethylamine benzaldehyde in acetic acid) has the disadvantage that it is irritating to the eyes and mucous membranes. When measuring hippuric acids in the urine of workers exposed to xylenes, NIOSH (1994) recommends that a complete spot voiding sample be collected at the end of the shift after 2 days of

exposure. As a preservative, a few crystals of thymol should be added to the sample. It should be stored at 4 degrees C if analysis is within 1 week. The sample should remain stable for 2 months if it is stored at -20 [764].

ENVIRONMENTAL SAMPLES [764]:

A gas chromatograph equipped with an appropriate detector is the basic analytical instrument used for determining environmental levels of xylene. Precautions in the isolation, collection, and storage of xylene in environmental media are necessary to prevent loss of the volatile xylene compounds to the air. The most common method for detecting aromatic hydrocarbons in air is the adsorption of the vapors to either activated charcoal with extraction using carbon disulfide or adsorption to a polymer adsorbent, such as Tenax GC, with thermal desorption. Each method is then followed by injection of the desorbed sample into a gas chromatograph equipped with FID (Brown 1988a, 1988b; NIOSH 1994). The activated charcoal method requires a 12-L air sample, while the polymer adsorbent uses a smaller 5-L sample for determination of the xylene in the sub-parts-per-million range. A GC/MS method has also been developed which uses an adsorbent tube with layers of Tenax, Amberlite, and charcoal (Chan et al. 1990). The use of a molecular sieve to remove water vapor prior to adsorption has been recommended to increase recovery of the hydrocarbons (Whitman and Johnston 1964) [764].

A computer-controlled, high-speed GC system has been developed for rapid analysis of volatiles in air (and other media with appropriate vapor generation). The system combines an electrically heated cold-trap inlet (with a vacuum backflushing device on the GC) with a convention FID. The advantage of the system is that a complete analysis cycle requires only 10 seconds to detect p- xylene at a level of 13.4 ppb (Rankin and Sacks 1991). A differential optical absorption spectrophotometer has also been used to monitor o-xylene in air; this method gives a correlation coefficient of approximately 0.66 when compared with standard GC methods (Stevens and Vossler 1991). An automated gas chromatograph with photoionization detector (GC/PID) has been developed by Hester and Meyer (1979) to identify gas-phase hydrocarbons (including xylene) for complex systems such as vehicle exhaust gas. The GC/PID method allows for measurement of sub-parts-per-billion level concentrations of air contaminants and does not require trapping or freeze-concentration of samples before analysis. These latter preconcentration steps are usually necessary because of the limited sensitivity of FID techniques commonly used in the analysis of environmental samples [764].

A limitation of the GC/PID technique is that m- and p- xylene are detected but not well separated. GC/PID in tandem with FID was used to obtain a more sensitive method to determine xylene levels in the air. A detection limit of 1.3x10 -12 g of o- xylene per sample was achieved (Nutmagul et al. 1983) [764].