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6. POTENTIAL FOR HUMAN EXPOSURE

6.1 OVERVIEW

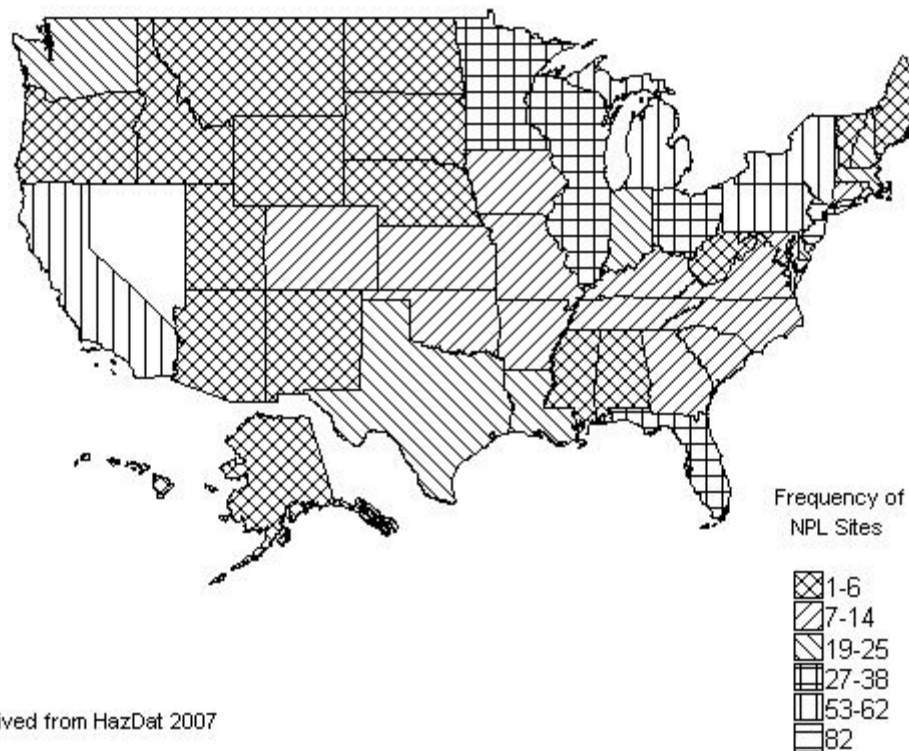
Ethylbenzene has been identified in at least 829 of the 1,689 hazardous waste sites that have been proposed for inclusion on the EPA National Priorities List (NPL) (HazDat 2007). However, the number of sites evaluated for ethylbenzene is not known. The frequency of these sites can be seen in Figure 6-1. Of these sites, 825 are located within the United States, 2 are located in the Commonwealth of Puerto Rico, and 2 are located in the Virgin Islands (not shown).

Ethylbenzene is an aromatic hydrocarbon naturally present in crude petroleum. It is also a combustion byproduct of biomass. It is widely distributed in the environment because of human activities such as the use of fuels and solvents (which account for the bulk of emissions) and through chemical manufacturing and production activities. Because of its volatile nature, ethylbenzene tends to partition to the atmosphere when it is released to the environment; therefore, exposure to this chemical is most likely to occur by inhalation. However, it is also present in trace amounts in some water supplies and food items. Thus, ingestion also may be an important exposure pathway in some cases. Exposures from contaminated water may also occur via inhalation and dermal absorption during showering and other household activities (Beavers et al. 1996).

Physical, chemical, and biological processes can remove ethylbenzene from the medium of concern and reduce human exposures. In the atmosphere, ethylbenzene exists primarily in the vapor phase. Vapor phase ethylbenzene is removed from air by reacting with photochemically produced hydroxyl radicals, with an approximate half-life of 2 days. Photolytic transformations may also take place in surface water in the presence of naturally occurring humic materials (sensitized photolysis). Biologically induced transformations take place largely in soil and surface water in the presence of oxygen; however, anaerobic degradation can also occur in soil, sediment, and groundwater, but at a much slower rate than aerobic biodegradation. Although chemical transformations can result in reduced exposures to ethylbenzene in the atmosphere, one toxic by-product of ethylbenzene photodegradation, peroxyacetyl nitrate (PAN), may be of concern. Ethylbenzene, as well as a variety of other hydrocarbons, has been implicated in the atmospheric formation of PAN in smog (Yanagihara et al. 1977).

The kinetics of partitioning and/or transformation processes are site-specific and depend upon many external factors. For example, the extent of biodegradation observed in an environmental medium depends upon the type and population of microorganisms present, the concentration of ethylbenzene, the

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Figure 6-1. Frequency of NPL Sites with Ethylbenzene Contamination

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presence of other compounds that may act as a substrate, and the presence or absence of oxygen. Biodegradation in soil will also compete with transport processes such as volatilization and infiltration to groundwater. Because ethylbenzene migration is only moderately retarded by adsorption onto soil, leaching of the compound to an anaerobic environment (groundwater) before biotransformation in soil is possible and may allow ethylbenzene to persist in an aquifer.

Although information is limited on dietary exposures, ethylbenzene does not appear to significantly bioaccumulate in aquatic or terrestrial food chains, and human exposure through this route is not likely to be of concern.

Exposure of the general population to ethylbenzene is possible through contact with gasoline, automobile emissions, solvents, pesticides, printing ink, varnishes, coatings, and paints. Cigarette smoke also has been identified as a source of exposure to this chemical. Ethylbenzene is widely present at low concentrations in rural, suburban, and urban atmospheres with the highest concentrations generally detected in areas of gasoline stations, tunnels, highways, and parking lots. Ethylbenzene is also present in indoor air. Very often ethylbenzene levels in indoor air exceed the levels typically found in outdoor air (Dodson et al. 2008). Occupational exposures are expected within the petroleum industry; within industries using solvents, paints, and coatings; and during the manufacture and handling of ethylbenzene and styrene (which is manufactured from ethylbenzene).

Several groups within the general population may have potentially higher exposures to ethylbenzene by inhalation, oral, or dermal contact with contaminated drinking water or soil. These groups include individuals living near manufacturing and processing facilities, petroleum refineries, and hazardous waste disposal sites and those working or residing in high traffic areas. Exposures associated with the consumption of contaminated drinking water as well as with inhalation and dermal exposure during showering and bathing in contaminated water would be expected for individuals that derive their primary drinking water supply from residential wells downgradient of uncontrolled landfills, hazardous waste sites, and leaking underground storage tanks that are contaminated with ethylbenzene. Individuals living near these sites may also be exposed via dermal contact with, or ingestion of soil contaminated with ethylbenzene.

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6.2 RELEASES TO THE ENVIRONMENT

The Toxics Release Inventory (TRI) data should be used with caution because only certain types of facilities are required to report (EPA 2005). This is not an exhaustive list. Manufacturing and processing facilities are required to report information to the TRI only if they employ 10 or more full-time employees; if their facility is included in Standard Industrial Classification (SIC) Codes 10 (except 1011, 1081, and 1094), 12 (except 1241), 20–39, 4911 (limited to facilities that combust coal and/or oil for the purpose of generating electricity for distribution in commerce), 4931 (limited to facilities that combust coal and/or oil for the purpose of generating electricity for distribution in commerce), 4939 (limited to facilities that combust coal and/or oil for the purpose of generating electricity for distribution in commerce), 4953 (limited to facilities regulated under RCRA Subtitle C, 42 U.S.C. section 6921 et seq.), 5169, 5171, and 7389 (limited S.C. section 6921 et seq.), 5169, 5171, and 7389 (limited to facilities primarily engaged in solvents recovery services on a contract or fee basis); and if their facility produces, imports, or processes $\geq 25,000$ pounds of any TRI chemical or otherwise uses $>10,000$ pounds of a TRI chemical in a calendar year (EPA 2005).

6.2.1 Air

Estimated releases of 4,586,441 pounds (~2,081 metric tons) of ethylbenzene to the atmosphere from 1,485 domestic manufacturing and processing facilities in 2006, accounted for about 82% of the estimated total environmental releases from facilities required to report to the TRI (TRI06 2008). These releases are summarized in Table 6-1.

The majority of ethylbenzene releases to the environment occur to the atmosphere. Because of its frequent use, and production in manufacturing operations, ethylbenzene is an important industrial chemical. Ethylbenzene is consistently ranked among the top 50 chemicals produced in the United States, with total production ranging from approximately 11 to 13 billion pounds annually (C&EN 1995, 2006; Kirschner 1995). In 2005, 11.6 billion pounds of ethylbenzene were produced by U.S. manufacturers (C&EN 2006). Its release can occur during manufacturing, processing, and handling. In 1978, emissions of ethylbenzene in the United States from catalytic reformat production alone were estimated at over 2 million pounds (Fishbein 1985). Ethylbenzene is also released to the air during processing of crude oil (Bratveit et al. 2007). Fuels and solvents, however, are considered to account for the bulk of emissions (Fishbein 1985). Exposure to ethylbenzene increases in areas high traffic areas (Smith et al. 2008). Ethylbenzene has been measured from tail pipe emissions of gasoline-powered vehicles at a weighted average rate of 12 mg/km (considering both catalyst and noncatalyst equipped cars) (Hampton et al.

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Table 6-1. Releases to the Environment from Facilities that Produce, Process, or Use Ethylbenzene^a

State ^c	RF ^d	Reported amounts released in pounds per year ^b								
		Air ^e	Water ^f	UI ^g	Land ^h	Other ⁱ	Total release			
							On-site ^j	Off-site ^k	On- and off-site	
AK	11	4,790	9	0	374	0	5,168	5	5,173	
AL	37	249,191	560	0	228	349	249,751	577	250,328	
AR	17	63,827	5	0	78	0	63,833	77	63,910	
AZ	19	33,661	12	0	0	0	33,673	0	33,673	
CA	99	91,863	11	500	1,733	1,407	92,331	3,184	95,515	
CO	10	2,435	0	0	10	0	2,435	10	2,445	
CT	12	4,504	1	0	10	729	4,505	739	5,244	
DE	3	7,175	0	0	1	0	7,175	1	7,176	
FL	39	104,231	8	0	5	268	104,239	273	104,512	
GA	33	80,852	1	0	229	1,742	80,853	1,971	82,824	
GU	2	2,436	0	0	0	255	2,436	255	2,691	
HI	10	3,312	53	0	170	78	3,365	248	3,613	
IA	25	72,532	0	0	3	0	72,535	0	72,535	
ID	2	111	No data	0	0	0	111	0	111	
IL	69	173,154	170	0	1,300	1,449	173,355	2,718	176,073	
IN	75	265,514	571	0	109	1,098	266,095	1,197	267,292	
KS	19	71,934	96	14	22,148	0	86,545	7,647	94,192	
KY	39	147,354	24	0	33,281	20,709	147,411	53,957	201,368	
LA	68	272,307	935	170	3,774	0	273,286	3,900	277,187	
MA	18	6,917	28	0	2,251	2,078	9,194	2,080	11,274	
MD	20	13,195	5	0	1	0	13,200	1	13,201	
ME	5	1,841	3	0	0	124	1,844	124	1,968	
MI	66	363,099	3	0	12,317	574	363,107	12,886	375,993	
MN	22	73,380	13	0	141	10	73,393	151	73,544	
MO	48	214,512	1	0	45	246	214,513	291	214,804	
MP	3	255	0	0	5	5	260	5	265	
MS	21	171,586	33	0	0	0	171,619	0	171,619	
MT	6	5,406	4	0	86	0	5,414	82	5,496	
NC	25	31,809	0	0	4	807	31,811	809	32,620	
ND	2	5,000	0	0	1	0	5,001	0	5,001	
NE	8	2,830	0	0	54	0	2,855	29	2,884	
NH	4	410	1	0	0	0	410	0	410	
NJ	41	37,281	230	0	2,010	8	38,247	1,282	39,529	
NM	8	10,585	5	5	186	1,334	10,772	1,343	12,115	
NV	4	2,821	No data	0	0	0	2,821	0	2,821	
NY	51	37,634	11	0	20	1,693	37,645	1,713	39,358	
OH	99	289,303	303	0	2,618	701	290,754	2,171	292,925	
OK	18	72,700	9	20	270	262	72,977	284	73,261	

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Table 6-1. Releases to the Environment from Facilities that Produce, Process, or Use Ethylbenzene^a

State ^c	RF ^d	Reported amounts released in pounds per year ^b								
		Air ^e	Water ^f	UI ^g	Land ^h	Other ⁱ	Total release			
							On-site ^j	Off-site ^k	On- and off-site	
OR	16	35,640	1	0	0	3	35,641	3	35,644	
PA	64	149,523	118	0	1,570	1,427	149,641	2,997	152,637	
PR	10	15,209	10	0	5	47	15,224	47	15,271	
RI	5	1,224	3	0	7	33	1,227	40	1,267	
SC	17	48,768	55	31	52	4,565	48,823	4,648	53,471	
SD	4	40,119	No data	0	0	0	40,119	0	40,119	
TN	33	412,260	45	0	502	250	412,306	751	413,057	
TX	158	627,282	1,625	843,929	13,835	2,262	1,462,679	26,254	1,488,933	
UT	15	6,812	5	0	98	97	6,822	190	7,012	
VA	25	66,825	99	0	180	79	66,924	259	67,183	
VI	3	12,390	3	0	12	0	12,393	12	12,406	
VT	1	608	No data	0	0	0	608	0	608	
WA	19	30,388	11	0	169	36	30,536	68	30,605	
WI	37	61,033	0	0	14	6,013	61,034	6,026	67,060	
WV	14	75,811	9	0	15	398	75,820	413	76,233	
WY	6	10,800	No data	0	261	0	10,805	256	11,061	
Total	1,485	4,586,441	5,088	844,670	100,181	51,134	5,445,543	141,972	5,587,515	

^aThe TRI data should be used with caution since only certain types of facilities are required to report. This is not an exhaustive list. Data are rounded to nearest whole number.

^bData in TRI are maximum amounts released by each facility.

^cPost office state abbreviations are used.

^dNumber of reporting facilities.

^eThe sum of fugitive and point source releases are included in releases to air by a given facility.

^fSurface water discharges, waste water treatment-(metals only), and publicly owned treatment works (POTWs) (metal and metal compounds).

^gClass I wells, Class II-V wells, and underground injection.

^hResource Conservation and Recovery Act (RCRA) subtitle C landfills; other on-site landfills, land treatment, surface impoundments, other land disposal, other landfills.

ⁱStorage only, solidification/stabilization (metals only), other off-site management, transfers to waste broker for disposal, unknown

^jThe sum of all releases of the chemical to air, land, water, and underground injection wells.

^kTotal amount of chemical transferred off-site, including to POTWs.

RF = reporting facilities; UI = underground injection

Source: TRI06 2008 (Data are from 2006)

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1983). Exposures to ethylbenzene can also occur while individuals are traveling in the passenger compartment of automobiles, and the chemical has been found at much higher concentrations during automobile engine malfunctions (Lawryk and Weisel 1996; Lawryk et al. 1995). Starting gasoline-powered vehicles in attached garages can contribute to increased indoor ethylbenzene exposure (Dodson et al. 2008). Emissions from gasoline-powered vehicles were found to be somewhat higher than from diesel trucks (Hampton et al. 1983). Similarly, ethylbenzene has been measured in jet fuel emissions (Katzman and Libby 1975) and has been reported in waste incinerator stack emissions (Jay and Steiglitz 1995; Junk and Ford 1980). Ethylbenzene has also been shown to be released into the atmosphere from volatile organic compound (VOC)-laden waste water in municipal sewer systems (Quigley and Corsi 1995).

Emissions of ethylbenzene can arise from transport of hot asphalt from a manufacturing plant to a paving site and from subsequent road paving operations. Kitto et al. (1997) measured the emissions of volatile organic compounds from Type I and Type II hot asphalts. At 150 °C, the concentration of the ethylbenzene emissions from Type I asphalt was 800 $\mu\text{g}/\text{m}^3$; at 200 °C, the concentration was 2,200 $\mu\text{g}/\text{m}^3$, an increase by a factor of 2.8. At 150 °C, the concentration of the ethylbenzene emissions from Type II asphalt was 7,000 $\mu\text{g}/\text{m}^3$; at 200 °C, the concentration was 21,000 $\mu\text{g}/\text{m}^3$, an increase by a factor of 3.

Mukund et al. (1996) conducted chemical mass balance source apportionment modeling on a data set of 142 3-hour integrated air samples collected at six different sites in three separate campaigns during the summer of 1989 in Columbus, Ohio. The contributions (\pm standard error) to the observed atmospheric levels of ethylbenzene from the sources considered, expressed as percentage of measured average concentration, were: 55 \pm 11 from vehicle exhaust; 0.7 \pm 0.2 from gasoline vapor; 0 \pm 3 from natural gas; 20 \pm 4 from industrial solvents; and 0 \pm 1 from the dry cleaning/degreasing/waste water composite source. These five sources contributed an estimated 76 \pm 12% of the measured average concentration of 1.1 $\mu\text{g}/\text{m}^3$.

Ethylbenzene releases to the air especially in indoor environments can occur with the use of consumer products such as pesticides, liquid process photocopiers and plotters, solvents, carpet glue, paints, varnishes, automotive products, adhesives, and fabric and leather treatments that contain ethylbenzene (Hodgson et al. 1991; Lillo et al. 1990; NAS 1980; Otson et al. 1994; Sack et al. 1992; Wallace et al. 1987b). Indoor exposure to ethylbenzene may also result from the start-up of gasoline-powered engines in attached garages (Dodson et al. 2008). Ethylbenzene (in addition to other aromatic hydrocarbons, such as benzene, styrene, and xylenes) has also been measured in cigarette smoke (Barrefors and Petersson 1993; Wallace et al. 1986, 1987c). An analysis of indoor air in a home using gasoline-contaminated tap

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water found that exposures to ethylbenzene could occur via inhalation during showering and other household activities (Beavers et al. 1996). Ethylbenzene concentrations in the shower area were often one to two orders of magnitude higher than in other areas of the home. Ethylbenzene has been identified in air samples collected at 121 of the 829 NPL hazardous waste sites respectively, where it was detected in some environmental media (HazDat 2007).

6.2.2 Water

Estimated releases of 5,088 pounds (~2.3 metric tons) of ethylbenzene to surface water from 1,485 domestic manufacturing and processing facilities in 2006, accounted for <1% of the estimated total environmental releases from facilities required to report to the TRI (TRI06 2008). An additional 141,972 pounds (~64.4 metric tons) were transferred off-site or released to publicly owned treatment works (POTWs) (TRI06 2008). These releases are summarized in Table 6-1.

Releases to water can occur as a result of industrial discharges (Snider and Manning 1982), fuel spillage (Gschwend et al. 1982; Tester and Harker 1981), leaking petroleum pipelines or underground storage tanks (Cotruvo 1985), landfill leachate (Barker 1987; Beavers et al. 1996; Chen and Zoltek 1995; Hallbourg et al. 1992), and the inappropriate disposal of wastes containing ethylbenzene (Eiceman et al. 1986). Ethylbenzene has been detected in both surface water and groundwater (EPA 2007i; Jin et al. 2007). Ethylbenzene emissions to oceans occur as a result of offshore oil production, hydrocarbon venting, oil field brines, and tanker oil spills (Sauer et al. 1978). Sauer and Tyler (1995) reported that ethylbenzene was one of the most commonly detected VOCs in motor vehicle waste fluids released from routine vehicle maintenance shops entering catch basins and septic tanks in Wisconsin. Ethylbenzene was detected at a mean concentration of 11 ppb (range 3–98 ppb) in catch basin waste water, 1.5 ppb (range 7–23 ppb) in septic tank effluent, and 8 ppb (range 9–53 ppb) in septic tank sludge.

Ethylbenzene has been identified in surface water at 123 sites and groundwater collected at 557 of the 829 NPL hazardous waste sites respectively, where it was detected in some environmental media (HazDat 2007).

6.2.3 Soil

Estimated releases of 100,181 pounds (~45.4 metric tons) of ethylbenzene to soils from 1,485 domestic manufacturing and processing facilities in 2006, accounted for about 2% of the estimated total environmental releases from facilities required to report to the TRI (TRI06 2008). An additional

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844,670 pounds (~383.2 metric tons), constituting about 15% of the total environmental emissions, were released via underground injection (TRI06 2008). These releases are summarized in Table 6-1.

Ethylbenzene can be released to soils through the spilling of gasoline and other fuels (Sauer and Tyler 1995; Tester and Harker 1981); through the disposal of solvents and household products such as paint, cleaning and degreasing solvents, varnishes, and pesticides; through emissions from leaking underground or aboveground storage tanks, well pumping units, or pipelines (Cotruvo 1985; Soukup et al. 2007); and leaching from landfills or contaminated industrial sites (Barker 1987; Soukup et al. 2007).

Ethylbenzene has been identified in soil and sediment samples collected at 469 and 144 of the 829 NPL hazardous waste sites respectively, where it was detected in some environmental media (HazDat 2007).

6.3 ENVIRONMENTAL FATE

6.3.1 Transport and Partitioning

The large vapor pressure and Henry's law constant of ethylbenzene (Table 4-2) suggests a moderate to strong tendency for ethylbenzene to partition into the atmosphere where it will exist predominantly in the vapor phase (Eisenreich et al. 1981; Mackay 1979; Masten et al. 1994). Depending upon site-specific conditions, releases to surface soil can result in substantial losses to the atmosphere in addition to subsurface infiltration. Since it has a moderately high vapor pressure, ethylbenzene will evaporate fairly rapidly from dry soil. Vapor phase transport will occur from subsurface releases (i.e., from leaking underground storage tanks) and during migration through unsaturated soil pore spaces (Rhue et al. 1988). Atmospheric reaction with hydroxyl radicals can limit the atmospheric transport of ethylbenzene (Dewulf and van Langenhove 1997).

The large Henry's law constant (Table 4-2), which measures partitioning between water and air, indicates that a significant proportion of ethylbenzene will partition from water into air (Mackay 1979; Masten et al. 1994). Ethylbenzene dissolved in surface water, soil pore water, or groundwater will thus migrate into an available atmospheric compartment until its saturated vapor concentration is reached. The volatilization half-life of ethylbenzene in a constructed wetland (length=228 m, width=60 m, depth=0.5–1.5 m) located in Phoenix, Arizona ranged from approximately 40 to 200 hours (Keefe et al. 2004).

Based on log K_{oc} values in the range of 2.2–2.4 (Table 4-2) and using the classification scheme of Swann et al. (1983), ethylbenzene is classified as having moderate mobility in soils. Sorption and retardation by

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soil organic carbon content will occur to a moderate extent, but sorption is not significant enough to completely prevent migration in most soils. Particularly in soils with low organic carbon content, ethylbenzene will tend to leach into groundwater. Mobility is also possible in aquifers that contain very little solid-phase organic matter, a condition common to sand and gravel aquifers (Ptacek et al. 1984). Sorption and desorption experiments performed by Dewulf et al. (1996) demonstrated that the sorption process of ethylbenzene on marine sediments is reversible and that the sorption is even lower than expected from the log K_{ow} data and the organic carbon content of the sediment. They concluded that the marine sediment compartment is not an important sink for the VOCs investigated when they are released to water.

When ethylbenzene is part of a complex mixture of hydrocarbons associated with a petroleum spill or leak, the proportion of ethylbenzene that will bind to soil versus the amount that will migrate toward groundwater depends primarily on the type of soil, the biological environment in the soil, the particular petroleum product in which the ethylbenzene is dissolved, the size of the spill, and the amount of rainfall (Stokman 1987; Soukup et al. 2007). For example, the solubility of ethylbenzene varies in accordance with the presence of other petroleum products (Ptacek et al. 1984). While the pure compound solubility of ethylbenzene in water is 180 mg/L, its solubility in water equilibrated with JP-jet fuel is 10.6 mg/L (Burris and MacIntyre 1984). Potter (1993) also reported that the equilibrium aqueous solubility of ethylbenzene was 2.4 mg/L with gasoline, 0.18 mg/L with diesel fuel, and 0.007 mg/L with #6 fuel oil equilibrated with groundwater. Both of these authors calculated the solubility concentrations of ethylbenzene in water equilibrated with various petroleum products. In addition, solvent spills of chemicals such as ethylbenzene may enhance the mobility of other organic chemicals, which do strongly adsorb to soil (Rao et al. 1985). No information was found concerning bioavailability of ethylbenzene from soil for human dermal or oral uptake.

Boyd et al. (1990) reported that corn residues high in organic matter that were left on the surface of a no tillage field, adsorbed a significantly greater amount of ethylbenzene as compared with surface soil. The authors suggested that the highly lipophilic plant cuticle appears to be the sorptive component. Kango and Quinn (1989) also reported that humic acid adsorbed higher amounts of ethylbenzene and xylenes ranging from 40 to 77 times greater than soil.

Once in the atmosphere, ethylbenzene will be transported until it is removed by physical or chemical processes. Physical removal processes, which involve partitioning into clouds or rainwater, are relevant to ethylbenzene, which has been measured in Los Angeles rainwater (Kawamura and Kaplan 1983). The

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concentrations of several dissolved organic chemicals in rainwater and in the atmosphere during rainfall events were measured by Ligocki et al. (1985). The authors found that the concentration of ethylbenzene in rain water was approximately equal to the inverse of the dimensionless Henry's law constant (Table 4-2) at atmospheric temperatures. This indicates that ethylbenzene is removed from the atmosphere through precipitation, but it can re-enter the atmospheric environment upon evaporation.

In comparison to chemicals such as polychlorinated biphenyls (PCBs), DDT, and other chlorinated pesticides, which are of great concern with respect to bioaccumulation, ethylbenzene does not significantly bioaccumulate in aquatic food chains. A measured bioconcentration factor (BCF) of 15 was reported for ethylbenzene in goldfish (Ogata et al. 1984). A BCF value of 53 was estimated in fish, using a log K_{ow} of 3.15 and a regression derived equation (Meylan et al. 1999). A 3% weighted average lipid content in fish and shellfish was assumed by EPA in the calculation. The calculated BCF is a theoretical value based on known constants, and is a conservative estimate of the bioconcentration of this chemical in fish. A calculated BCF of 167 was also estimated for fathead minnows (*Pimephales promelas*) (ASTER 1995). In a shellfish study, the ethylbenzene concentration in clam tissue was 5 times higher than that measured in water after an 8-day continuous-flow exposure to the water-soluble fraction of Cook Inlet crude oil (Nunes and Benville 1979).

Ethylbenzene has also been found to partition into human tissues; primarily as a result of inhalation exposures (see Section 6.5). Ethylbenzene has been detected in human adipose tissue (Sections 3.4.2.1 and 3.8.1), blood (Section 3.4.1.1), and in breast milk (Section 3.7). No information was located concerning the bioavailability of ethylbenzene from contaminated soil or sediment either with respect to dermal exposure or oral intake via consumption of soil particles from unwashed hands.

6.3.2 Transformation and Degradation

6.3.2.1 Air

Ethylbenzene undergoes atmospheric transformations through reaction with photochemically generated hydroxyl radicals (Atkinson et al. 1978; Ohta and Ohyama 1985; Ravishankara et al. 1978), NO_3 radicals (Atkinson et al. 1987), and atomic oxygen (Grovenstein and Mosher 1970; Herron and Huie 1973). Gas phase reactions with ozone and structurally similar molecules such as toluene have been observed (Atkinson and Carter 1984). The predominant degradation pathway for ethylbenzene in the atmosphere occurs via reaction with hydroxyl radicals and nitrate radicals (which are only present during non daylight hours), with the other degradation mechanisms being of only minor importance. The rate constant for the

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vapor phase reaction of ethylbenzene with photochemically generated hydroxyl radicals was measured as 7.1×10^{-12} cm³ per molecule-second (Kwok and Atkinson 1994). This corresponds to an atmospheric half-life of approximately 2 days using a hydroxyl radical concentration of 5×10^5 hydroxyl radicals per cm³. The rate constant for the degradation of ethylbenzene with nitrate radicals was measured as 6×10^{-16} cm³ per molecule-second (Atkinson et al. 1987). Using a nighttime nitrate radical concentration of 5×10^8 nitrate radicals per cm³, a half-life of approximately 26 days is estimated. Atmospheric degradation occurs more rapidly during summer months as opposed to winter since the concentration of hydroxyl radicals in the atmosphere peaks during summer (Ravishankara et al. 1978; Singh et al. 1981), and is also faster under photochemical smog conditions (Dilling et al. 1976). Oxidation by-products from the reaction with hydroxyl radicals and nitrogen oxides include ethylphenols, benzaldehyde, acetophenone, and *m*- and *p*-nitroethylbenzene (Hoshino et al. 1978). The major degradation pathways for ethylbenzene in the atmosphere are summarized in Figure 6-2.

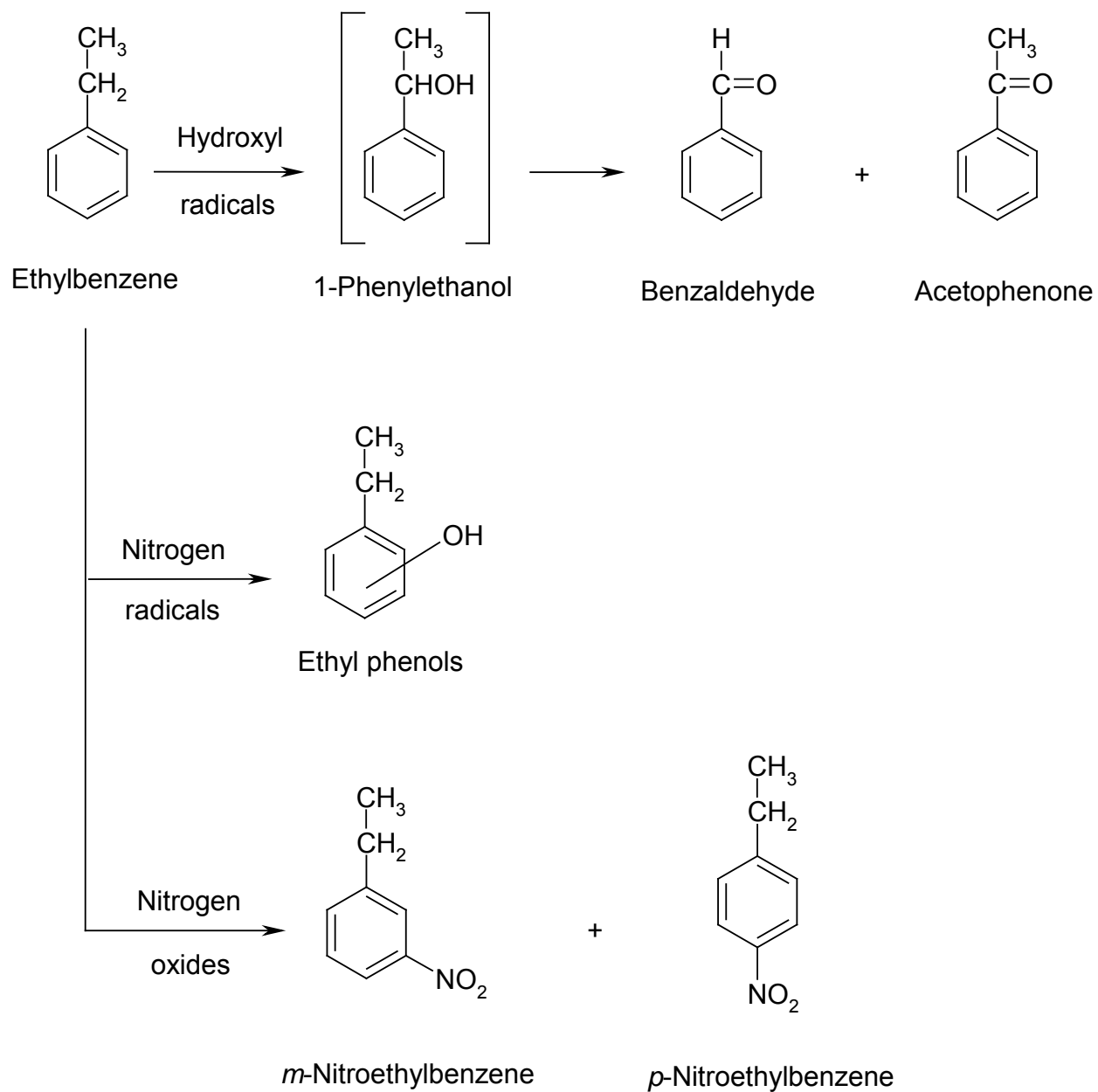
Experiments conducted with various hydrocarbons on the formation of photochemical aerosols or the haze associated with smog revealed that aromatics such as ethylbenzene produced only low yields of aerosol when compared with more reactive compounds such as alkenes (O'Brien et al. 1975). The formation of PAN is related to the photoreactivity of the reacting hydrocarbon. The photoreactivity of ethylbenzene is intermediate relative to other atmospheric hydrocarbons, and it is less reactive than gasoline, toluene, and alkenes such as propene (Yanagihara et al. 1977).

6.3.2.2 Water

In surface water, transformations of ethylbenzene may occur through two primary processes—photooxidation and biodegradation. Since ethylbenzene does not contain hydrolysable functional groups at environmental pH (pH 5–9), hydrolysis is not considered an important environmental fate process. Although ethylbenzene does not absorb light in the environmental ultraviolet spectrum, it is capable of undergoing photooxidation in water through an indirect reaction with other light-absorbing molecules, a process known as sensitized photolysis. The compounds 1-methylphenyl ketone (acetophenone), 1-phenylethanol, and benzaldehyde were identified as degradation products from the laboratory photooxidation of ethylbenzene in both distilled water and seawater with anthraquinone used as a sensitizer (Ehrhardt and Petrick 1984). In the environment, similar degradation is expected to occur in the presence of ubiquitous, naturally occurring humic material sensitizers. The major degradation pathways for ethylbenzene in water are summarized in Figure 6-3.

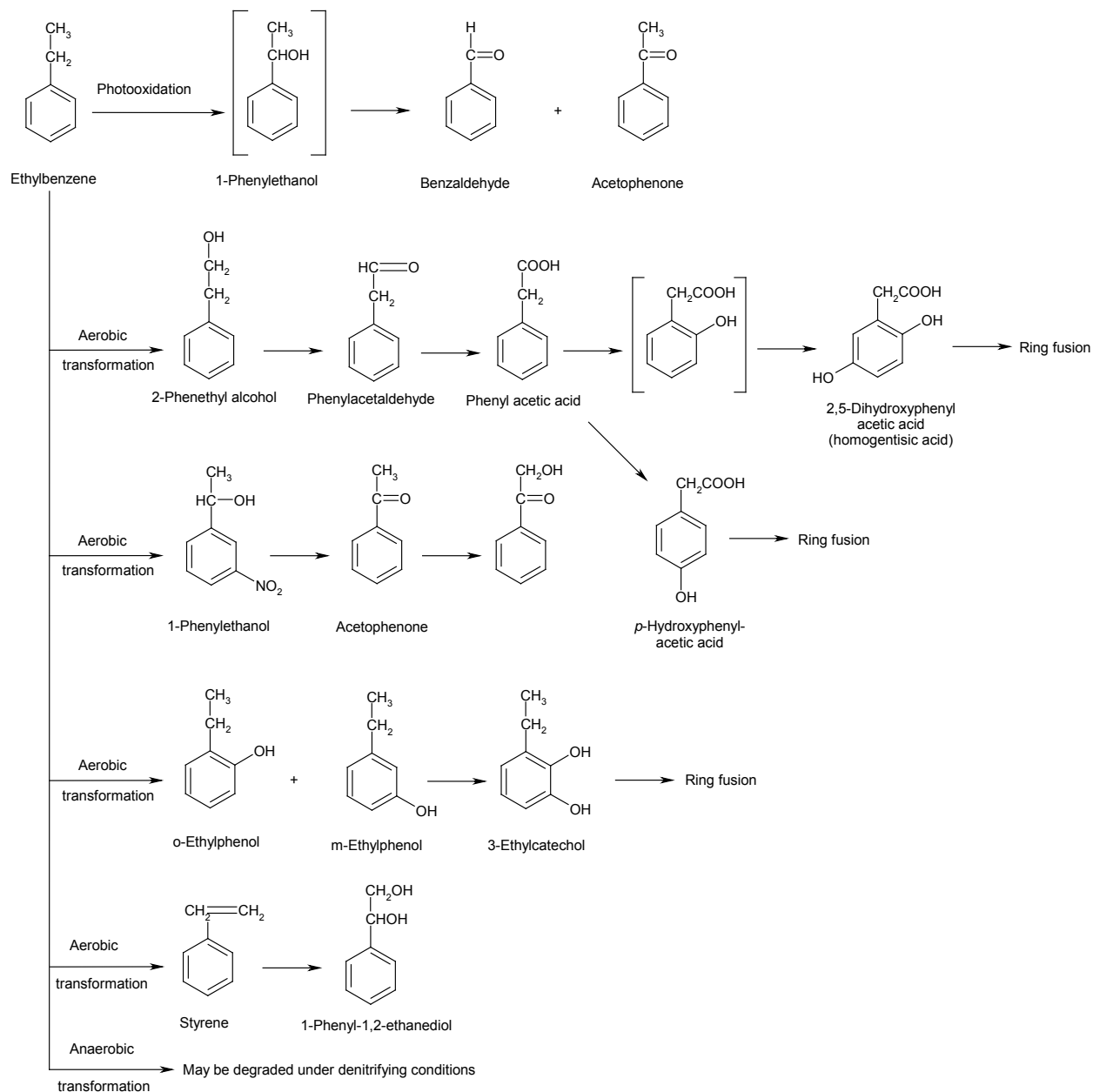
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Figure 6-2. Major Degradation Pathways for Ethylbenzene in the Atmosphere



Source: Hoshino et al. 1978

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Figure 6-3. Major Degradation Pathways for Ethylbenzene in Water, Sediment, and Soil

Source: Burback and Perry 1993; Ehrhardt and Petrick 1984; Van der Linden and Thijsse 1965

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Biodegradation in aerobic surface water will compete with sensitized photolysis and transport processes such as volatilization. Volatilization and biodegradation of ethylbenzene in seawater have been observed by Gschwend et al. (1982), Masten et al. (1994), and Wakeham et al. (1983). Migration from surface water to subsurface soil with low amounts of oxygen or to aquifers with lower microbial populations, however, will limit the rate of transformation. No significant disappearance of ethylbenzene during 11 weeks of incubation with bacteria under low oxygen (anoxic) conditions was observed by Bouwer and McCarty (1983). Slow degradation of ethylbenzene was reported in anaerobic aquifer materials known to support methanogenesis, although a long acclimation period or lag time was required (Wilson et al. 1986). Less than 1% of the initial concentration of ethylbenzene remained after 120 weeks, indicating that, given sufficient time, ethylbenzene will be essentially completely biodegraded.

Laboratory microcosm tests were conducted to determine optimum conditions for ethylbenzene biodegradation by aquifer microorganisms under denitrifying condition (Hutchins 1991). Ethylbenzene was degraded to $<5 \mu\text{g/L}$ when present as a sole source substrate and stoichiometric calculations indicated that nitrate removal was sufficient to account for 70–80% of the compound being mineralized. Biodegradation did not occur without the presence of nitrate, and nitrate removal was minimal without the presence of the ethylbenzene over a 55-day incubation period. In a laboratory microcosm containing aquifer material and groundwater from the North Bay site in Ontario, Canada, no significant loss of ethylbenzene was observed compared to unamended controls over a period of 187 days. In another experiment conducted at the North Bay site that used *in situ* biodegradation columns, ethylbenzene was completely degraded in at least 1 of the 8 *in situ* columns in <100 days (Acton and Barker 1992). In all cases, the authors attributed the ethylbenzene attenuation to biodegradation by methanogenic and fermentative bacteria. In another study using a laboratory scale flow-through aquifer column system, low dissolved oxygen ($<1 \text{ mg/L}$) conditions were initiated with the nitrate-amended column influent in order to mimic contaminated groundwater conditions distal from a nutrient injection well (Anid et al. 1993). The authors reported that 40% of the ethylbenzene was removed after several months of operation. In a similar study, using batch incubations seeded with four different aquifer materials, ethylbenzene was not degraded within 4 months in any of the denitrifying enrichments tested, even though nitrate reduction occurred. Burbach and Perry (1993) reported that *Mycobacterium vaccae* can catabolize a number of major groundwater pollutants, including ethylbenzene. At a concentration of 100 ppm, ethylbenzene was not measurably degraded; however, at 50 ppm, 80% of the added ethylbenzene was degraded. A product peak of 4-ethylphenol was detected as well as a small amount of 1-phenylethanol.

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The contrast between biodegradation rates in the presence or absence of oxygen was demonstrated by a biofilm reactor study designed to simulate an aquifer (Bouwer and McCarty 1984). Continuous-flow laboratory column studies under aerobic and methanogenic conditions were performed with mixed bacterial cultures on glass beads. In the aerobic biofilm column, 99% of the ethylbenzene initially present was degraded within a 20-minute detention time, while under methanogenic (anaerobic) conditions, only 7% was degraded within a 2-day detention time.

6.3.2.3 Sediment and Soil

Biodegradation of ethylbenzene by aerobic soil microbes has been reported by various researchers. The common soil microorganism *Pseudomonas putida* is able to utilize ethylbenzene as a sole source of carbon and energy (Fukuda et al. 1989; Gibson et al. 1973). In some instances, co-oxidation or co-metabolism was observed (i.e., ethylbenzene was degraded by *Nocardia sp.* in the presence of other compounds that are more readily metabolized by the microorganism) (Jamison et al. 1970; Van der Linden and Thijsse 1965). Yadav and Reddy (1993) reported that the white-rot fungus *Phanerochaete chrysosporium* efficiently degraded ethylbenzene as well as other benzene, toluene, ethylbenzene, and xylenes (BTEX) compounds when these chemicals were added either individually or as a composite mixture. In addition, substantially greater degradation of all the BTEX compounds was observed in static rather than in shaken liquid cultures. Furthermore, degradation was greater at 25 °C than at 37 °C, but pH variations between 4.5 and 7 had little effect on the extent of the degradation. Chen and Taylor (1995) reported that two thermophilic bacterial strains, *Thermus aquaticus* and an unidentified *Thermus sp.* degraded ethylbenzene (in a mixture with other BTEX chemicals) by 18% after 45 days of incubation at 70 °C and by 32% after 45 days of incubation at 60 °C, respectively. Zappi et al. (1996) reported that ethylbenzene degraded rapidly in a pilot scale bioslurry reactor under aerobic conditions. The initial concentration (0.35 mg/kg) was degraded by 94% in 2 days.

Biotic transformations by aerobic soil microbes involve oxidation of the ethyl side chain to form phenylacetic acid (Van der Linden and Thijsse 1965) and 1-phenylethanol (Bestetti and Galli 1984); ring hydroxylation to form 2,3-dihydroxy-1-ethylbenzene (Gibson et al. 1973), 2-hydroxyphenylacetic acid, 4-hydroxyphenylacetic acid, and 2,5- and 3,4-dihydroxyphenylacetic acid (Van der Linden and Thijsse 1965); and ultimate ring cleavage to form straight chain carboxylic acids such as fumaric and acetoacetic acids (Van der Linden and Thijsse 1965). The major degradation pathways for ethylbenzene are summarized in Figure 6-3.

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Anaerobic degradation of ethylbenzene based on observations from studies conducted under anaerobic conditions in other media and as discussed above (Bouwer and McCarty 1983, 1984; Wilson et al. 1986), would be much slower than that observed under aerobic conditions. Ramanand et al. (1995) studied the biodegradation of several organic pollutants including ethylbenzene in soil columns under denitrifying conditions. These authors reported that one of the significant factors governing biodegradation is the availability of suitable electron acceptors. The biodegradation of ethylbenzene, toluene, and xylenes has been demonstrated in laboratory samples obtained from subsurface habitats or in pure cultures under denitrifying conditions (Hutchins 1991; Hutchins et al. 1991). Ramanand et al. (1995) reported that soil column bacteria, after sufficient acclimation time, metabolized 100–500 μM of toluene and ethylbenzene in <6 days under denitrifying conditions. These compounds were successfully degraded under anoxic conditions by the addition of nitrate and by stimulating the indigenous soil denitrifying bacteria.

The kinetics of biodegradation appear to be site specific, and depend upon factors such as the type and population of microbes present, the environmental temperature, the concentration of ethylbenzene, the presence of other compounds that may act as a substrate, and the amount of oxygen and electron acceptors present. Biodegradation in soil will also compete with migration processes such as volatilization and infiltration to groundwater.

6.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

Reliable evaluation of the potential for human exposure to ethylbenzene depends in part on the reliability of supporting analytical data from environmental samples and biological specimens. Concentrations of ethylbenzene in unpolluted atmospheres and in pristine surface waters are often so low as to be near the limits of current analytical methods. In reviewing data on ethylbenzene levels monitored or estimated in the environment, it should also be noted that the amount of chemical identified analytically is not necessarily equivalent to the amount that is bioavailable. The analytical methods available for monitoring ethylbenzene in a variety of environmental media are detailed in Chapter 7.

6.4.1 Air

Ambient air levels of volatile organic compounds, including ethylbenzene, were monitored as a part of a multi-media study known as the Lower Rio Grande Valley Environmental Scoping Study. Monitoring was performed at a “central” site and at a “border” site in the Brownsville, Texas, air shed in the spring and summer of 1993. The median ambient concentration of ethylbenzene at the central site was $0.80 \mu\text{g}/\text{m}^3$ (0.18 ppbv) ($n=22$; range= 0.20 – $1.7 \mu\text{g}/\text{m}^3$ [0.046 – 0.39 ppbv]) in the spring and $0.4 \mu\text{g}/\text{m}^3$

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(0.09 ppb) ($n=14$; range= $0.2\text{--}1.0\ \mu\text{g}/\text{m}^3$ [$0.04\text{--}0.2$ ppbv]) in the summer. These concentrations are either lower or comparable to those found in previous EPA and other monitoring investigations (Ellenson et al. 1997). The median indoor concentration of ethylbenzene for nine Rio Grande Valley residences measured in the spring was $1.00\ \mu\text{g}/\text{m}^3$ (0.230 ppbv) compared to a median outdoor concentration of $0.70\ \mu\text{g}/\text{m}^3$ (0.16 ppbv); in the summer, the median indoor concentration of ethylbenzene for five residences was $1.40\ \mu\text{g}/\text{m}^3$ (0.321 ppbv) compared to a median outdoor concentration of $0.35\ \mu\text{g}/\text{m}^3$ (0.080 ppbv) (Mukerjee et al. 1997). The mean indoor concentration of ethylbenzene at the homes of 46 high school students residing in New York City was $3.57\ \mu\text{g}/\text{m}^3$ (0.821 ppbv) in the winter months as compared to a mean indoor concentration of $1.99\ \mu\text{g}/\text{m}^3$ (0.458 ppbv) during the summer months (Kinney et al. 2002). The corresponding mean outdoor levels of ethylbenzene were 1.27 (0.292 ppbv) and $1.88\ \mu\text{g}/\text{m}^3$ (0.432 ppbv) in the winter and summer months, respectively.

An update of the 1980 National Ambient Volatile Organic Compounds (VOC) database prepared for EPA summarized concentrations of ethylbenzene by site type (EPA 1988c). Median values are reported because they are less biased by a few high or low concentrations and, thus, may better represent the data than would average values. The median indoor concentration of ethylbenzene detected at 95 locations was 1.0 ppbv ($4.4\ \mu\text{g}/\text{m}^3$) (mean 2.9 ppbv), while personal air monitoring of 1,650 individuals found a median concentration of 1.3 ppbv ($5.6\ \mu\text{g}/\text{m}^3$) (mean 3.2 ppbv).

Of particular interest is that personal air monitoring of indoor air found higher concentrations of ethylbenzene than those observed in outdoor air. This was also observed during the Total Exposure Assessment Methodology (TEAM) Study conducted by EPA between 1979 and 1985 in an effort to measure exposures to 20 VOCs in personal air, outdoor air, and drinking water. The major cause for the higher personal air concentrations was felt to be the presence of ethylbenzene sources in the home. In the TEAM study, tobacco smoke was reported to be a main source of exposure to volatile aromatic compounds such as ethylbenzene (Wallace et al. 1987a, 1987c). Based on the results of a stepwise regression carried out on data collected during the fall in New Jersey from 352 participants, overnight geometric mean ethylbenzene exposures of persons living in homes with smokers were approximately 1.5 times the geometric mean exposures of persons living in homes without smokers. The amount of ethylbenzene measured in mainstream smoke of a single cigarette containing 16 mg of tar and nicotine was $8\ \mu\text{g}$ (Wallace et al. 1987c). Wallace et al. (1989) reported that a maximum outdoor air concentration of ethylbenzene of $7.4\ \mu\text{g}/\text{m}^3$ (1.7 ppbv) was detected in nine outdoor samples collected at each of three houses while maximum indoor air concentrations at these same residences ranged from 5 to $110\ \mu\text{g}/\text{m}^3$

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(1–25.3 ppbv). Mean personal exposures averaged $28 \mu\text{g}/\text{m}^3$ (6.4 ppbv) (range 4.6–144 $\mu\text{g}/\text{m}^3$ [1.0–33.1 ppbv]) and the personal/outdoor ratio for ethylbenzene was 16.

The poor quality of indoor air has been linked to a number of symptoms (headache; nausea; irritation of the eyes, mucous membranes, and respiratory system; drowsiness; fatigue; and general malaise) which have been defined as "sick building" syndrome. Kostianen (1995) identified over 200 VOCs in the indoor air of 26 normal houses. Ethylbenzene was detected in 100% of the houses studied at an average concentration of $3.2 \mu\text{g}/\text{m}^3$ [0.74 ppbv] (median $2.41 \mu\text{g}/\text{m}^3$ [0.554 ppbv], minimum $0.62 \mu\text{g}/\text{m}^3$ [0.14 ppbv], and maximum $10.54 \mu\text{g}/\text{m}^3$ [2.42 ppbv] concentration). The median concentration of ethylbenzene ($2.41 \mu\text{g}/\text{m}^3$ [0.554 ppbv]) in these normal houses was lower in all but one case than ethylbenzene concentrations detected in houses with "sick building" syndrome where the concentrations ranged from 2.25 to $747.24 \mu\text{g}/\text{m}^3$ (0.517–172 ppbv).

A nationwide study of indoor air concentration of 26 VOCs was conducted in Canada in 1991 (Fellin and Otson 1994). These authors reported that mean indoor ethylbenzene concentrations were $6.46 \mu\text{g}/\text{m}^3$ (1.48 ppbv), $8.15 \mu\text{g}/\text{m}^3$ (1.87 ppbv), $4.35 \mu\text{g}/\text{m}^3$ (1.00 ppbv), and $13.98 \mu\text{g}/\text{m}^3$ (3.21 ppbv) in the winter, spring, summer and fall months, respectively and that the concentrations declined with an increase in ambient air temperature. At ≤ 0 , 0–15, and ≥ 15 °C, the mean ethylbenzene concentrations were $12.76 \mu\text{g}/\text{m}^3$ (2.93 ppbv), $7.78 \mu\text{g}/\text{m}^3$ (1.79 ppbv), and $6.46 \mu\text{g}/\text{m}^3$ (1.48 ppbv), respectively. These authors concluded that indoor sources of ethylbenzene (primarily from household products) are likely to have a more significant influence on indoor air concentrations than climatic variables.

Concentrations of ethylbenzene were measured in soil gas, and indoor and outdoor air of a home located near a landfill in California (Hodgson et al. 1992). During the first sampling in September, ethylbenzene concentrations were not detected in soil gas or outdoor air, but were detected at 0.6 ppbv ($3 \mu\text{g}/\text{m}^3$) in basement air. In October, ethylbenzene concentrations averaged 3.3 ppbv ($14 \mu\text{g}/\text{m}^3$) in soil gas, 0.8 ppbv ($4 \mu\text{g}/\text{m}^3$) in basement air, and 0.7 ppbv ($3 \mu\text{g}/\text{m}^3$) in bedroom air. In this study, the authors found that the existence of soil gas contamination alone is not sufficient to result in significantly elevated indoor exposures. The entry rate of ethylbenzene and VOCs from the soil into the house was low. The limited entry that occurred at the conditions of the study was apparently the result of diffusive and advective flux of VOC through the cement blocks used in the basement wall construction. The authors suggest that there is a general need to identify variables associated with residential sites with the highest potential for significantly elevated indoor exposures resulting from soil gas contamination.

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Indoor VOC concentrations were analyzed in 12 California office buildings as part of the California Healthy Building Study (Daisey et al. 1994). These authors reported that ethylbenzene was detected at a geometric mean of $0.50 \mu\text{g}/\text{m}^3$ (0.11 ppbv) (range $0.27\text{--}0.98 \mu\text{g}/\text{m}^3$ [0.062–0.22 ppbv]). These authors also reported that an estimated 82% of indoor air concentrations were contributed from motor vehicle emissions. Hodgson et al. (1991) reported that concentrations of ethylbenzene in indoor air of a new office building ranged from 7 to $18.7 \mu\text{g}/\text{m}^3$ (2–4.30 ppbv) over the course of a 14-month sampling period. Furthermore, ethylbenzene indoor air concentrations were higher than those in outdoor air and that the dominant source of VOCs in the building was liquid-process photocopiers and plotters which emitted a characteristic mixture of $\text{C}_{10}\text{--}\text{C}_{11}$ isoparaffinic hydrocarbons.

VOC concentrations were monitored both indoors and outdoors, including garages, basements, and common spaces, for 55 Boston area residences as part of the Boston Exposure Assessment in Microenvironmental (BEAM) study. Indoor and outdoor arithmetic mean ethylbenzene concentrations of 2.4 and $0.42 \mu\text{g}/\text{m}^3$, respectively, were reported. Arithmetic mean ethylbenzene concentrations in garages, basements, and common hallways were 35, 4.1, and $2.1 \mu\text{g}/\text{m}^3$, respectively. VOC concentrations also varied seasonally, tending to be higher in summer than winter (arithmetic mean ethylbenzene concentrations of 0.06 and $0.04 \mu\text{g}/\text{m}^3$, respectively). Attached garages attributed to approximately 20–40% of gasoline-associated indoor VOC concentrations, while basements contributed approximately 10–20% and common hallways contributed 5–10% of indoor concentrations (Dodson et al. 2008).

Wadden et al. (1995) reported average VOC concentrations for indoor air monitored in a sheetfed offset printing shop. These authors reported mean ethylbenzene concentrations ranging from 0.27 to $0.84 \text{mg}/\text{m}^3$ (0.062–0.19 ppmv) based on 12 1-hour samples.

Levels of ethylbenzene monitored in ambient air show great variation (Jonsson et al. 1985). Generally, air concentrations are much lower in rural areas than in urban areas, where vehicle emissions are thought to be a major contributor of ethylbenzene to ambient air. Ethylbenzene concentrations range from below detection limits in rural areas to $100 \mu\text{g}/\text{m}^3$ (23.0 ppbv) on busy urban streets (Jonsson et al. 1985). Kelly et al. (1994) reported a median concentration of ethylbenzene of $1.1 \mu\text{g}/\text{m}^3$ (0.25 ppbv) for 8,723 samples collected from 93 locations throughout the United States.

Ambient air concentrations reported for Deer Park, Texas suggest a correlation between high traffic areas and VOC concentrations. The mean ethylbenzene concentration for 12 sites was $0.51 \mu\text{g}/\text{m}^3$ (0.12 ppbv).

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High correlations between toluene, ethylbenzene, and xylenes suggest petroleum-related sources (Smith et al. 2008).

Median outdoor air concentrations of ethylbenzene for 6 remote and 122 rural locations are reported as 0.156 and 0.013 ppbv (0.679 and 0.056 $\mu\text{g}/\text{m}^3$), respectively (EPA 1988c). Median concentrations of 0.62 ppbv (2.7 $\mu\text{g}/\text{m}^3$) were reported for 886 suburban and 1,532 urban locations. The daily median concentration of ethylbenzene considering all site types including source dominated areas and workplace air was 0.60 ppbv (2.6 $\mu\text{g}/\text{m}^3$). Table 6-2 lists some monitoring results reported for ethylbenzene in various cities.

Ethylbenzene concentrations at four locations along U.S. Highway 70 near Raleigh, North Carolina, during the month of May were reported to range from 10 to 16 ppbv (44–70 $\mu\text{g}/\text{m}^3$) that were corrected to include upwind concentrations (Zweidinger et al. 1988).

Concentrations of ethylbenzene were measured in two tunnels: the Fort McHenry Tunnel in Baltimore, Maryland (June 18–24, 1992) and the Tuscarora Mountain Tunnel in Pennsylvania (September 2–8, 1992) (Zielinska et al. 1996). These authors reported minimum and maximum ethylbenzene concentrations (on a carbon basis) for the Fort McHenry Tunnel of 6.3 and 89.2 ppbC (0.79 and 11.2 ppbv) for bore #3, respectively, and 0.5 and 114.1 ppbC (0.06 and 14.26 ppbv) for bore #4, respectively, and concentrations for the Tuscarora Tunnel of 1.2 and 11.1 ppbC (0.15 and 6.04 ppbv), respectively. The total number of light-duty vehicles (LDV) and heavy-duty vehicles (HDV) that passed through each tunnel was 12,273 LDV and 187 HDV for bore #3 and 11,788 LDV and 2,417 HDV for bore #4 of the Fort McHenry Tunnel and 4,887 LDV and 1,041 HDV for the Tuscarora Tunnel.

Ethylbenzene is released during processing of crude oil. Bratveit et al. (2007) reported air concentrations ranging from an average of 0.01–0.09 ppm of ethylbenzene over a 12-hour period, with individual measurements reported as high as 1.11 ppm (Bratveit et al. 2007).

Ethylbenzene and other VOCs have been found to be removed from waste water in municipal sewers and were emitted to the ambient atmosphere prior to entering a downstream waste water treatment facility in Toronto, Ontario (Quigley and Corsi 1995). These authors measured concentrations of ethylbenzene during four monitoring events and found that concentrations ranged from not detectable to 5 ppm. Headspace concentrations of ethylbenzene exhibited a significant weekday/weekend trend. Significant emissions of all VOCs monitored occurred during three of the four monitoring events. Ethylbenzene had

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Table 6-2. Ethylbenzene Concentrations in Ambient Air Samples Collected in the United States

Location	Concentration	Comments	Reference
Downey, California	4.6±3.7 ppb (mean±SD) 16.1 ppb ^a	February 18–27, 1984; n=100	Singh et al. 1985
Los Angeles, California	3–12 ppb (range)	September 29– November 13, 1981	Grosjean and Fung 1984
Riverside, California	1.3±0.8 ppb (mean±SD) 4.0 ppb ^a	July 1–13, 1980; n=100	Singh et al. 1985
Denver, Colorado	2.2±3.1 ppb (mean±SD) 18.5 ppb ^a	June 15–28, 1980; n=100	Singh et al. 1985
Chicago, Illinois	0.8±1.2 ppb (mean±SD) 9.5 ppb ^a	April 20–May 2, 1981; n=100	Singh et al. 1985
St. Louis, Missouri	0.6±0.5 ppb (mean±SD) 2.1 ppb ^a	May 29–June 9, 1980; n=100	Singh et al. 1985
Camden, New Jersey	0.17 ppb (mean)	July 6–August 16, 1981; n=35	Harkov et al. 1983
Elizabeth, New Jersey	0.26 ppb (mean)	July 6–August 16, 1981; n=37	Harkov et al. 1983
Newark, New Jersey	0.33 ppb (mean)	July 6–August 16, 1981; n=38	Harkov et al. 1983
Staten Island, New York	1.7±2.5 ppb (mean±SD) 17.2 ppb ^a	March 26–April 5, 1981; n=100	Singh et al. 1985
Staten Island, New York	2.7±4.2 ppb (mean±SD) 16.7 ppb ^a	April 25–May 1, 1984; n=100	Singh et al. 1985
Philadelphia, Pennsylvania	0.8±0.8 ppb (mean±SD) 7.3 ppb ^a	April 4–22, 1983 n=100	Singh et al. 1985
Pittsburgh, Pennsylvania	0.8±1.6 ppb (mean±SD) 10.5 ppb ^a	April 7–17, 1981; n=100	Singh et al. 1985
Houston, Texas	1.5±1.6 ppb (mean±SD) 8.2 ppb ^a	March 8–17, 1984; n=100	Singh et al. 1985
Jones State Forest, Texas	2.8 ppb ^b	January 4–6, 1978	EPA 1979

^aMaximum measured concentration^bMedian concentration in 10 bag samples (median concentration in 5 can samples was 1.0 ppb)

n = number of samples; SD = standard deviation

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the second highest emissions during all periods and ranged from 7 to 14 g/hour (62–130 kg/year) for event 1 and from 1 to 13 g/hour (9–115 kg/year) for event 2. Ethylbenzene emissions at five municipal treatment facilities ranged from 0.08 to 93 g/day (0.003–3.9 g/hour). Results of this study suggest that sewers that accept VOC-laden waste water, and that are characterized by significant ventilation and drop structures, can be significant sources of VOC emissions (including ethylbenzene) relative to municipal waste water treatment facilities.

Assmuth and Kalevi (1992) reported that ethylbenzene was detected in municipal solid waste landfill gas at minimum and maximum concentrations of 6.6–7.6 mg/m³ (1.5–1.7 ppmv), <0.1–9.6 mg/m³ (<0.02–2.2 ppmv), 0.2–1.2 mg/m³ (0.04–0.28 ppmv), and 85–98 mg/m³ (20–22 ppmv) at four different landfill sites in Finland. Concentrations of ethylbenzene measured in a biogas collection system at the Miron Quarry Municipal Waste Landfill Site in Montreal, Quebec ranged from 2 to 36 mg/m³ (0.5–8.3 ppmv) (Goldberg et al. 1995).

6.4.2 Water

The median ethylbenzene concentration in ambient surface waters in the United States in 1980–1982 was <5.0 µg/L (ppb) according to EPA's STORET water quality database (Staples et al. 1985). The chemical was detected in 10% of the 1,101 samples collected during that period. Ethylbenzene was also detected in 7.4% of the 1,368 industrial effluent samples collected during 1980–1982 at a median concentration of <3.0 µg/L (ppb). More recent data from the STORET database indicated that ethylbenzene was only detected in 15 out of 548 surface water samples obtained from January 2005 to March 2007, at a maximum concentration of 2 ppb (EPA 2007i).

From 1989 to 1993, New York City municipal waste waters were analyzed to determine the frequency of detection of organic priority pollutants, including ethylbenzene (Stubin et al. 1996). Ethylbenzene was detected in 14 of 84 (17%) influent samples at concentrations ranging from 1 to 11 µg/L (ppb) and in only 1 of 84 (1%) effluent samples at a concentration of 2 µg/L (ppb).

Ethylbenzene and other VOCs have been detected in waste water in municipal sewers prior to entering a downstream waste water treatment facility in Toronto, Ontario (Quigley and Corsi 1995). These authors measured concentrations of ethylbenzene in waste water during several monitoring events and found that concentrations ranged from 0.059 to 0.086 mg/L (ppm) in one event and from 7 to 11 mg/L (ppm) in another event. The authors also determined that the stripping efficiency across two drop structures with

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waste water fall heights of 1.4–3 meters within the sewer system removed 31–36% of the ethylbenzene in the waste water. Results of this study suggest that sewers that accept VOC-laden waste water, and that are characterized by significant ventilation and drop structures, can be significant sources of VOC emissions (including ethylbenzene) relative to municipal waste water treatment facilities.

As part of EPA's Nationwide Urban Runoff Program, ethylbenzene was measured in 4% of the municipal runoff samples collected in 15 cities throughout the United States (Cole et al. 1984). The measured ethylbenzene concentration range was 1–2 µg/L (ppb). Ethylbenzene was detected in 41 out of 249 (16.5%) storm water runoff samples collected at 46 different sampling locations in North Carolina over a 1-year period (Borden et al. 2002). The mean, median, and maximum ethylbenzene levels were 0.10, 0.07, and 0.36 µg/L (ppb), respectively.

Ethylbenzene was measured in seawater at an average concentration of 0.011 µg/L (ppb) and a concentration range of 0.0018–0.022 µg/L (ppb) over a 15-month observation period at Vineyard Sound, Massachusetts (Gschwend et al. 1982). Ethylbenzene also has been reported in surface waters of the Gulf of Mexico at a concentration range of 0.0004–0.0045 µg/L (ppb) (Sauer et al. 1978).

Ethylbenzene has been detected in a relatively remote location (Mt. Mitchell, North Carolina) in cloud water at a mean concentration of 170 ng/L (range 0–450 ng/L) (Aneja 1993). The average concentration of ethylbenzene in precipitation was 34 ng/L. Ethylbenzene has also been detected in snow samples from two remote sites in the province of Québec, Canada (Kos and Ariya 2006). Ethylbenzene levels reported in µg/L±3σ were: 2.65±1.28 (Resolute Bay); 0.22±0.02 (Gaspé Peninsula); and 0.31±0.06 (Gaspé Peninsula).

From 1989 to 1990 and from 1992 to 1993, ethylbenzene was monitored in wetland-treated leachate water at a municipal solid waste landfill in central Florida (Chen and Zoltek 1995). During the first sampling period, ethylbenzene was detected in surface water samples ranging from 0.06 to 0.09 ppb and in groundwater samples ranging from 0.06 to 9.75 ppb. During the second sampling period (1992–1993), ethylbenzene was not detected in surface water samples, but was detected in groundwater samples at concentrations ranging from below detection limits to 10.55 ppb. Ethylbenzene was detected in a study of three landfills in central Florida (Hallbourg et al. 1992). These authors reported concentrations of ethylbenzene in groundwater of 1.63–9.75, <1–83.8, and <1–8.6 µg/L (ppb) at the three different landfill sites. The mean concentration of ethylbenzene detected in landfill leachate from these disposal areas was 17.5 µg/L.

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Ethylbenzene was measured in all three drinking water plants sampled as part of the New Orleans Area Water Supply Study conducted by EPA in 1974 (Keith et al. 1976). The reported concentrations were 1.6, 1.8, and 2.3 $\mu\text{g/L}$ (ppb). The 1982 Ground Water Supply Survey conducted by EPA reported ethylbenzene in only 3 out of 466 random samples at a mean concentration of 0.8 $\mu\text{g/L}$ (ppb) and a maximum concentration of 1.1 $\mu\text{g/L}$ (ppb) (Cotruvo 1985). Chemical monitoring of 617 private and 1,174 public groundwater wells in the state of Wisconsin revealed that ethylbenzene was detected in 3 community and 12 private wells. The concentration of ethylbenzene detected exceeded the state's recommended drinking water advisory limit of 1,400 $\mu\text{g/L}$ (ppb) in 9 of the 12 private wells, but no exceedences were observed in the public wells (Krill and Sonzogni 1986).

Ethylbenzene was infrequently detected in a comprehensive survey conducted by the United States Geological Survey (USGS) of volatile organic compounds in private and public groundwater wells used for drinking water (USGS 2006). Ethylbenzene was identified in 18 out of 3,497 aquifer samples at a median concentration of 0.035 $\mu\text{g/L}$ for the 18 samples having positive detections. In an analysis of domestic groundwater wells, the median concentration of ethylbenzene was reported as 0.041 $\mu\text{g/L}$ for samples having positive detections. Ethylbenzene was identified in 7 out of 1,083 samples obtained from public wells across the United States at a median concentration of 0.32 $\mu\text{g/L}$ for samples having positive detections.

Although ethylbenzene does not appear to be a frequent contaminant in public water supplies, private residential wells near landfills, hazardous waste sites, or gas stations are more likely to contain detectable levels of this compound. Ethylbenzene was listed as one of the 58 most frequently detected chemicals associated with groundwater contamination near superfund sites (Knox and Canter 1994). Ethylbenzene was listed as having a medium priority with respect to its frequency of occurrence. Ethylbenzene has been detected in wells downgradient from landfills in Southern Ontario at concentrations ranging from 12 to 74 $\mu\text{g/L}$ (ppb) (Barker 1987). Ethylbenzene was detected at levels of 1–22, 1–5, and <1 $\mu\text{g/L}$ in groundwater 0–37, 50–114, and 170–254 meters, respectively, downgradient from a municipal landfill located in Grindsted, Denmark (Baun et al. 2000). Ethylbenzene was detected in groundwater from a representative monitoring well on a former gas-compressor site near South Lovedale, Oklahoma at a concentration of 220 $\mu\text{g/L}$ (Jin et al. 2007).

Borden and Yanoschak (1990) compared ground and surface water quality impacts associated with North Carolina sanitary landfills. These authors found that ethylbenzene was detected at $\approx 25\%$ of the waste

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water effluents (receiving secondary treatment) and only 3% of the groundwater sampled in the vicinity of sanitary landfill sites. Groundwater monitoring at 479 hazardous waste disposal sites indicated that ethylbenzene, like the other 9 VOCs monitored, was detected at more than 100 of the 479 sites tested (Plumb 1991). Ethylbenzene was also one of the VOCs detected in groundwater samples from hazardous waste sites in all 10 EPA regions. Rosenfeld and Plumb (1991) reported that ethylbenzene was detected in groundwater at 19% of wood-treatment industry sites based on its frequency of detection and average concentration. Groundwater near an underground coal gasification site in northeastern Wyoming contained concentrations of ethylbenzene ranging from 92 to 400 µg/L (ppb) (Stuermer et al. 1982). Groundwater samples near a fuel spill in the Great Ouse Basin in Great Britain contained ethylbenzene concentrations as high as 1,110 µg/L (ppb) (Tester and Harker 1981).

6.4.3 Sediment and Soil

The median ethylbenzene concentration (dry weight) detected in sediment in the United States in 1980–1982 was 5 µg/kg (ppb) according to EPA's STORET water quality database (Staples et al. 1985). The compound was detected in 11% of 350 sediment samples analyzed. More recent data from the STORET database indicated that ethylbenzene was identified, but not quantified, in 25 out of 68 sediment samples obtained from January 2005 to March 2007 (EPA 2007i).

Ethylbenzene concentrations were analyzed in contaminated soil samples obtained from the site of a former crude oil and natural gas production facility near Los Angeles, California. Concentrations ranged from the limit of detection (0.005 mg/kg) to 160 mg/kg. Subsurface samples were collected from trenches, boreholes, and excavations; the highest concentrations were found in samples obtained through a borehole (Soukup et al. 2007).

6.4.4 Other Environmental Media

Data from the FDA Total Diet Study Market Basket Surveys collected between September 1991 and October 2003 indicate that ethylbenzene was detected in 82 different food items at a maximum concentration of 0.129 ppm (FDA 2006b). In a previous Market Basket Survey, ethylbenzene was identified in 15 out of 234 table-ready food items at an average concentration of 0.0146 ppm and a range of 0.00637–0.0387 ppm (Heikes et al. 1995). Trace concentrations of ethylbenzene have been reported in split peas (0.013 mg/kg [ppm]), lentils (0.005 mg/kg [ppm]), and beans (mean concentration 0.005 mg/kg [ppm]; maximum concentration 0.011 mg/kg [ppm]) (Lovegren et al. 1979). Ethylbenzene was reported as one of 227 organic chemicals present in roasted filbert nuts (Kinlin et al. 1972). Gorna-Binkul et al.

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(1996) reported concentrations of ethylbenzene in orange peel (0.0236 $\mu\text{g/g}$ [ppm] dry weight) and in parsley leaves (0.2567 $\mu\text{g/g}$ [ppm] dry weight). The author reported that the differences in concentrations of the VOCs were dependent on the plant species and the morphological part of the plant analyzed. In underground parts (i.e., roots and bulbs) not directly exposed to polluted ambient air during growth, no VOC concentrations were detected. Biedermann et al. (1995) reported concentrations of several VOCs in extra virgin olive oil collected in northwest Italy. These authors measured ethylbenzene levels in raw olives of 6 $\mu\text{g/kg}$ (ppb), which increased with time as they were milled to 25 $\mu\text{g/kg}$ (ppb). Levels in the finished olive oils ranged from 11 to 27 $\mu\text{g/kg}$ (ppb) depending on the preparation method used. These authors reported that while some of the ethylbenzene was accumulated in the olives in the orchards, a larger proportion was accumulated as a result of exposure of the oil to air in the milling areas. Ethylbenzene concentrations in olive oil increased from 6 to 235 ppb after 2 days of exposure. The authors concluded that the production process increased the concentration of ethylbenzene in the oil as a result of uptake from the air that was likely to be contaminated with gasoline vapors associated with small vehicles used to move the olives from area to area within the olive oil mill.

Ethylbenzene was also found to migrate from thermoset polyester cooking containers (composed of cross-linking chains of styrene) into belly pork during cooking (Gramshaw and Vandenburg 1995). Migration ranged from <6 to 34 $\mu\text{g/kg}$ for ethylbenzene. The authors also found that the migration measured during the second use of the cookware was generally higher than that during the first use. These authors also reported that ethylbenzene concentrations in food cooked in foil-covered dishes was higher than that in the same food cooked uncovered. This was especially true for ethylbenzene that was more volatile than the styrene tested. Ehret-Henry et al. (1994) also reported migration of ethylbenzene from polystyrene containers into dairy products. Concentrations of ethylbenzene were 2–4 $\mu\text{g/kg}$ for yogurt and 4 $\mu\text{g/kg}$ for chocolate dessert.

Sack et al. (1992) conducted a survey of VOCs in 1,159 household items, including automotive products, household cleaners and polishes, paint related products, fabric and leather treatments, cleaners for electronic equipment, oils, greases, and lubricants, adhesive-related products, and miscellaneous products. Ethylbenzene was detected in 157 of 658 (24%) of the products tested. The highest mean ethylbenzene concentrations and percentage of products in each category in which ethylbenzene was detected are as follows; 7.2% w/w (wet weight) in 7.5% of automotive products, 2.4% w/w in 47.8% of paint-related products, and 1.0% w/w in 11.8% of fabric and leather treatments.

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Hodgson et al. (1996) determined the contribution of environmental tobacco smoke (ETS) to concentrations of VOCs in smoking environments. These authors reported that the average emission factor for ethylbenzene for six brands of cigarettes was 101 $\mu\text{g}/\text{cigarette}$ (range 83–142 $\mu\text{g}/\text{cigarette}$). The average concentration of ethylbenzene in five smoking areas ranged from 1.3 to 8.7 $\mu\text{g}/\text{m}^3$ (0.3–2 ppbv). Martin et al. (1997) determined the ETS yield of selected analytes, including ethylbenzene, for the 50 top-selling U.S. cigarette brand styles in 1991 and for the University of Kentucky Research cigarette, K1R4F. The ETS was generated by smokers in an environmental test chamber. The ethylbenzene concentrations measured were 8.68 $\mu\text{g}/\text{m}^3$ for full flavor cigarettes, 8.24 $\mu\text{g}/\text{m}^3$ for full flavor low tar cigarettes, and 8.72 $\mu\text{g}/\text{m}^3$ for ultra-low-tar cigarettes. The mean ethylbenzene concentration for all cigarettes was 8.50 $\mu\text{g}/\text{m}^3$. The mean ethylbenzene yields by tar category weighted by market share were 81.18 $\mu\text{g}/\text{cigarette}$ for full flavor cigarettes, 76.79 $\mu\text{g}/\text{cigarette}$ for full flavor low tar cigarettes, and 81.66 $\mu\text{g}/\text{cigarette}$ for ultra low tar cigarettes. The mean ethylbenzene yield for all cigarettes was 79.57 $\mu\text{g}/\text{cigarette}$.

Ethylbenzene was not detected (at a detection limit of 0.025 mg/kg [ppm] wet weight) in any of the 97 biota samples collected from all STORET stations in 1980–1983 (Staples et al. 1985). Ethylbenzene was detected at low concentrations (0.8 ng/g [0.8 ppb]) in oyster tissue, but not in clam tissue from Lake Pontchartrain at Passes, Louisiana (Ferrario et al. 1985). The highest average ethylbenzene concentration measured in tissue of bottomfish from Commencement Bay in Tacoma, Washington was reported as 0.01 mg /kg (ppm) (Nicola et al. 1987).

6.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

The highest exposure to ethylbenzene for the general public is most likely to occur via inhalation associated with the use of self-service gasoline pumps or while driving a gasoline-powered motor vehicle especially in high traffic areas or in tunnels (Lawryk et al. 1995; Smith et al. 2008). Backer et al. (1997) performed a study that measured exposures associated with the pumping two different blends of fuel under cold conditions in Fairbanks, Alaska. The subjects in the study had significantly higher levels of gasoline components in their blood after pumping gasoline than before. The changes in VOC levels in blood were similar whether the individuals pumped regular or oxygenated gasoline. Prior to pumping regular gasoline, the median concentration of ethylbenzene in blood was 0.10 ppb (n=26) with a range of 0.02–0.73 ppb; after pumping, the median concentration was 0.16 ppb with a range of 0.06–1.40 ppb. Before pumping an oxygenated fuel blend that was 10% ethanol, the median concentration of

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ethylbenzene in blood was 0.11 ppb (n=22) with a range of 0.04–0.55 ppb; after pumping, the ethanol blend, the median concentration was 0.16 ppb with a range of 0.06–0.64 ppb.

Janasik et al (2008) studied ethylbenzene exposure in six male volunteers who were subjected to an exposure chamber containing ethylbenzene as well as toluene, xylene, and mesitylene at concentrations emulating Polish occupational exposure standards of 100 mg/m³. Blood and urine samples obtained from the volunteers were analyzed. Ethylbenzene concentrations in the blood ranged from 20 to 200 µg/L, while urine concentrations ranged from 1 to 152 µg/L (Janasik et al. 2008).

Lawryk and Weisel (1996) measured in-vehicle concentrations of selected gasoline-derived volatile organic compounds on 113 commutes through suburban New Jersey and 33 New Jersey/New York commutes. In a typical suburban commute, the mean in-vehicle concentration of ethylbenzene was 11.5±18.8 µg/m³ (2.64±4.32 ppbv; n=52) under low ventilation conditions and 8.5±11.2 µg/m³ (1.9±2.57 ppbv; n=43) under high ventilation conditions. On the New Jersey turnpike and in the Lincoln Tunnel, the mean in-vehicle concentrations of ethylbenzene were 8.8±10.8 µg/m³ (2.0±2.48 ppbv; n=32) and 14.3±10.2 µg/m³ (3.29±2.34 ppbv; n=32), respectively.

Ethylbenzene is ubiquitous in urban and rural atmosphere resulting from vehicular and industrial emissions (EPA 1988c). Tobacco smoke also provides a general source of exposure to ethylbenzene in indoor air (Wallace et al. 1987c). Wallace et al. (1989) also reported that two activities, painting and the use of automotive products (carburetor cleaner), led to increased indoor exposure to ethylbenzene by 100-fold. Indoor exposure to ethylbenzene may also be increased resulting from the start-up of gasoline-powered engines in attached garages (Dodson et al. 2008). Information on exposure from foods is limited, but is not likely to be a significant source of ethylbenzene for the general population.

Human exposure to styrene and ethylbenzene was assessed by considering inhalation exposure (including cigarette smoking) and food intake (Tang et al. 2000). The daily exposure to ethylbenzene for the general population was calculated as 1.8 µg/kg bodyweight/day, with up to 99% of the exposure due to inhalation routes and only 1–2% caused by food consumption.

One-half of the household drinking water used in the United States is supplied by groundwater, and contamination of groundwater by petroleum products is an increasingly common problem (Beavers et al. 1996). Beavers et al. (1996) conducted a study in a New England household that used groundwater contaminated by gasoline from a leaking underground storage tank. A total daily dose of 379 µg

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ethylbenzene (204 µg ingested and 175 µg inhaled) was estimated for an exposed subject compared to a median daily dose of 32 µg for unexposed subjects. Of the 175 µg inhaled by the exposed subject, 108 µg was attributed to shower activities. The exposed subject and the three non-exposed subjects all were smokers.

The 1982 National Human Adipose Tissue Survey conducted by EPA measured ethylbenzene in 96% of the 46 composite samples analyzed for VOCs (EPA 1986). A wet tissue concentration range of not detected (detection limit=2 ng/g) to 280 ng/g (ppb) was reported, but an average concentration was not provided.

Ethylbenzene has been detected in breast milk samples collected from 8 of 12 women from various cities in the United States; however, the concentrations were not reported (Pellizzari et al. 1982). The 12 women sampled in the study were residents of Bayonne, New Jersey (6 women), Jersey City, New Jersey (2 women), Bridgeville, Pennsylvania (2 women), and Baton Rouge, Louisiana (2 women).

Mean and median concentrations of ethylbenzene detected in 631 blood samples from participants in the Third National Health and Nutrition Examination Survey (NHANES III 1998–1994 data) were 0.11 and 0.06 ppb (95 percentile value of 0.25 ppb), respectively (Ashley et al. 1994). In an earlier study (Ashley et al. 1992), these authors reported a mean ethylbenzene concentration of 0.12 ppb in 13 blood samples. Hajimiragha et al. (1989) conducted a study of 13 nonsmokers and 14 smokers with no known occupational or hobby-related exposure to volatile organic hydrocarbons. These authors reported a mean and median ethylbenzene concentration of 651 ng/L (0.651 ppb) and 431 ng/L (0.431 ppb) for the nonsmokers and 837 ng/L (0.837 ppb) and 533 ng/L (0.533 ppb) for the smokers. Ethylbenzene concentrations tended to occur at higher concentrations in the blood of smokers than in nonsmokers; however, the difference was not significant. Ashley et al. (1995) also reported that smoking elevated the blood levels of ethylbenzene and was highly correlated with blood levels of 2,5-dimethylfuran. These authors reported a mean concentration of 0.10 ng/mL (ppb) (median 0.048 ng/mL; range from below detection limit to 2.7 ng/mL) for nonsmokers and a mean concentration of 0.17 ng/mL (ppb) (median 0.16 ng/mL; range 0.036–0.88 ng/mL) for smokers. To aid in understanding the kinetics of uptake and elimination of volatile organics (including ethylbenzene), Ashley and Prah (1997) measured blood concentrations before, during, and after exposure of five individuals to a mixture of volatile organics in a controlled chamber. The half-lives of the compounds measured were <0.5 hour, but the elimination time courses were multiexponential and suggested that, with repeated exposure, bioaccumulation may occur in humans.

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Occupational exposure to ethylbenzene in the petroleum industry has been reported in a study that measured ethylbenzene concentrations in air for 49–56 workers during the summer of 1984 (Rappaport et al. 1987). The average air concentrations of ethylbenzene measured over the full work shift for gasoline service station attendants, transport drivers, and outdoor refinery personnel were comparable at 0.063, 0.079, and 0.079 mg/m³, respectively (14.5, 18.2, and 18.2 ppbv, respectively). The authors noted that exposures of service station attendants were significantly lower when vapor recovery systems were present. Crude oil process operators at an offshore processing plant near Norway were found to be exposed to 0.01–0.09 ppm of ethylbenzene in air during a full 12-hour work shift. Short-term exposure to ethylbenzene was dependent upon the specific work task and ranged from <0.01 to 1.11 ppm. Workers on the flotation package were found to be exposed to the highest ethylbenzene concentrations (Bratveit et al. 2007).

Personal air monitoring of 35 varnish workers (spraymen) has revealed an average ethylbenzene concentrations of 4.0 ppm, while the average concentration in blood was 61.4 µg/L (Angerer and Wulf 1985). Concentrations of ethylbenzene were monitored in auto paint shops in Spain that used organic solvents (de Medinilla and Espigares 1988). These authors reported air concentrations of ethylbenzene ranging from 0.50 to 125.0 mg/m³ (0.12–28.75 ppmv).

The indoor air of screen printing plant workrooms located directly below houses in Amsterdam, Holland was found to contain median TWA concentrations of ethylbenzene ranging from <0.03 mg/m³ (7 ppbv) to 1.30 mg/m³ (299 ppbv) and maximum TWA concentrations ranging from 0.11 mg/m³ (25 ppbv) to 3.21 mg/m³ (738 ppbv) (Verhoeff et al. 1988).

Spray-painting and gluing operations can also result in exposure to ethylbenzene; personal air monitoring of workers measured average exposures of approximately 0.50 ppmv (2.2 mg/m³) (Whitehead et al. 1984). Most of the operations measured during the study were performed in ventilation hoods.

Holz et al. (1995) reported that ethylbenzene air concentrations detected from air sampling in all areas of a styrene production facility located in the former German Democratic Republic ranged from 365 to 2,340 µg/m³ (0.08–0.53 ppmv).

According to the National Occupational Exposure Study (NOES) conducted by NIOSH from 1981 to 1983, an estimated 201,838 workers were potentially exposed to ethylbenzene in the workplace (NIOSH

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1990). The NOES database does not contain information on the frequency, concentration, or duration of occupational exposure to any of the chemicals listed. The survey provides only estimates of the numbers of workers for whom potential exposure in the workplace is an issue.

The Occupational Safety and Health Administration (OSHA) has set a Permissible Exposure Limit (PEL) based on a TWA of 100 ppm ($\approx 435 \text{ mg/m}^3$ at 1 atm and 25 °C) in the workplace (OSHA 1974). The American Conference of Governmental Industrial Hygienists also recommends a Threshold Limit Value (TLV-TWA) of 100 ppm ($\approx 435 \text{ mg/m}^3$) for occupational exposures (ACGIH 1992). The recommended exposure limit (REL) for occupational exposures (TWA) set by the NIOSH is also 100 ppm ($\approx 435 \text{ mg/m}^3$) for ethylbenzene based on a 10-hour average workday and a 40-hour workweek (NIOSH 2005).

6.6 EXPOSURES OF CHILDREN

This section focuses on exposures from conception to maturity at 18 years in humans. Differences from adults in susceptibility to hazardous substances are discussed in Section 3.7, Children's Susceptibility.

Children are not small adults. A child's exposure may differ from an adult's exposure in many ways. Children drink more fluids, eat more food, breathe more air per kilogram of body weight, and have a larger skin surface in proportion to their body volume. A child's diet often differs from that of adults. The developing human's source of nutrition changes with age: from placental nourishment to breast milk or formula to the diet of older children who eat more of certain types of foods than adults. A child's behavior and lifestyle also influence exposure. Children crawl on the floor, put things in their mouths, sometimes eat inappropriate things (such as dirt or paint chips), and spend more time outdoors. Children also are closer to the ground, and they do not use the judgment of adults to avoid hazards (NRC 1993).

Children can be exposed to ethylbenzene by inhalation in urban and rural atmospheres contaminated by vehicular and industrial emissions. Tobacco smoke also provides a general source for exposure of children to ethylbenzene in indoor air, especially in the homes where one or both parents smoke. Children may also be exposed to ethylbenzene-containing consumer products, such as carpet glues, paints, and varnishes. Household activities, such as painting, can lead to short-term exposures to higher levels of ethylbenzene if ventilation is inadequate. The limited information available on exposure from foods indicates that food is not likely to be a significant source of ethylbenzene for children.

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Ethylbenzene is heavier than air, and since young children are closer to the ground or floor because of their height, during accidental exposures they may be exposed to more ethylbenzene vapors than adults. A 2-year monitoring study (2000–2001) involving 134 children aged 6–10 was conducted in Minneapolis, Minnesota in order to assess exposure to VOCs, including ethylbenzene (Sexton et al. 2005). The distribution of ethylbenzene measured in the blood of these children (416 samples) is provided in Table 6-3. Comparing these data to monitoring results from NHANES III, the levels of ethylbenzene in children's blood is approximately 2 or more times lower than in non-occupationally exposed adults (Sexton et al. 2005). Ethylbenzene has been detected in breast milk samples collected from 8 of 12 women from various cities in the United States; however, the concentrations were not reported (Pellizzari et al. 1982). The 12 women sampled in the study were residents of Bayonne, New Jersey (6 women); Jersey City, New Jersey (2 women); Bridgeville, Pennsylvania (2 women); and Baton Rouge, Louisiana (2 women). No direct pharmacokinetic experiments have been done to investigate whether significant amounts of ethylbenzene are transferred to breast milk in mammals. No studies were located that expressed the level of ethylbenzene or its metabolites in amniotic fluid, meconium, cord blood or neonatal blood.

Although no data were found in the literature, it is possible that children playing near hazardous waste sites could be dermally exposed to ethylbenzene in soil or orally exposed by hand-to-mouth activity and/or soil pica. Ethylbenzene, however, is only moderately adsorbed by soil. Since it has a moderately high vapor pressure, it will evaporate fairly rapidly from dry soil. However, under certain soil conditions, ethylbenzene may persist for longer periods of time; it has been detected in soil samples collected at 469 of the 829 NPL hazardous waste sites where it has been detected in some environmental media (HazDat 2007). It was also detected in high concentrations in soil at a former crude oil and natural gas production facility, which was being considered for redevelopment (Soukup et al. 2007). No information was found concerning dermal and oral bioavailability of ethylbenzene in soil.

In the home, intentionally sniffing solvents could lead to high levels of exposure. Household products containing ethylbenzene, such as gasoline, paints, and glue, are widely available to children. Radhouame et al. (2008) studied inhalant abuse among 40 male and 4 female children and young adults (aged 11–23 years) suspected of drug abuse in Tunisia. Solvent metabolites were measured in urine samples to indicate exposure to VOC compounds through sniffing of various products. The authors concluded that the particular children in the study abused substances that ultimately resulted in high toluene and hexane exposures, as opposed to those resulting in high ethylbenzene exposure (Chakroun et al. 2008). However, abuse of household products could still be a concern for exposure of children to ethylbenzene.

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Table 6-3. Distribution of Blood Ethylbenzene Concentrations in Children (ng/mL)

Sampling period	Samples	Percentage							
		above detection limit	10th	25th	50th	75th	90th	95th	99th
February 2000	92	79.1	0.02	0.02	0.03	0.05	0.07	0.08	0.12
May 2000	86	66.7	0.01	0.02	0.03	0.04	0.05	0.07	0.17
February 2001	63	61.1	0.02	0.02	0.02	0.03	0.03	0.03	0.04
May 2001	88	98.9	0.03	0.04	0.05	0.06	0.08	0.09	0.10

Source: Sexton et al. 2005

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No information was found concerning differences in the weight-adjusted intakes of ethylbenzene by children.

No exposures of children to ethylbenzene by contamination of workers' homes were found in the Workers' Home Contamination Study conducted under the Worker's Family Protection Act (NIOSH 1995).

6.7 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

In addition to individuals who are occupationally exposed to ethylbenzene (see Section 6.5), there are several groups within the general population that may receive potentially high exposures (higher than background levels) to ethylbenzene. These populations include individuals living in proximity to sites where ethylbenzene is produced or used in manufacturing or sites where ethylbenzene is disposed, and includes individuals living near the 829 NPL hazardous waste sites where ethylbenzene has been detected in some environmental media (HazDat 2007). Ethylbenzene has been detected in air and groundwater at 121 and 557 NPL hazardous waste sites, respectively.

Individuals living or working near petroleum refineries or chemical manufacturing plants may receive higher inhalation exposures than those experienced by the general population. Residents living in the vicinity of gasoline stations, high traffic areas, tunnels, parking lots, and highways may also receive a higher than average inhalation exposure since ethylbenzene is a component of gasoline (Smith et al. 2008). Residential wells downgradient of leaking underground storage tanks, landfills, and hazardous waste sites contaminated with petroleum products and solvents may contain high levels of ethylbenzene. If these residential wells are the primary source of drinking water, this may pose a risk to human health via consumption of contaminated water as well as increased inhalation of and dermal contact with ethylbenzene during showering and bathing. A study of indoor air in a home using gasoline-contaminated drinking water found that exposures to ethylbenzene could occur via inhalation during showering and other household activities (Beavers et al. 1996). Ethylbenzene concentrations in shower air were often one to two orders of magnitude higher than non-shower air. These authors reported a total daily household dose of ethylbenzene of 379 μg , with 204 μg derived from ingestion of drinking water and 175 μg derived from inhalation (108 μg from shower-related inhalation and 67 μg from non-shower-related inhalation) to the exposed subject living in the home. The daily dose of ethylbenzene for an unexposed smoker by comparison was estimated to be 32 μg .

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6.8 ADEQUACY OF THE DATABASE

Section 104(i)(5) of CERCLA, as amended, directs the Administrator of ATSDR (in consultation with the Administrator of EPA and agencies and programs of the Public Health Service) to assess whether adequate information on the health effects of ethylbenzene is available. Where adequate information is not available, ATSDR, in conjunction with NTP, is required to assure the initiation of a program of research designed to determine the health effects (and techniques for developing methods to determine such health effects) of ethylbenzene.

The following categories of possible data needs have been identified by a joint team of scientists from ATSDR, NTP, and EPA. They are defined as substance-specific informational needs that if met would reduce the uncertainties of human health assessment. This definition should not be interpreted to mean that all data needs discussed in this section must be filled. In the future, the identified data needs will be evaluated and prioritized, and a substance-specific research agenda will be proposed.

6.8.1 Identification of Data Needs

Physical and Chemical Properties. The physical and chemical properties of ethylbenzene are well characterized (see Table 4-2) and allow prediction of the transport and transformation of the compound in the environment (Amoore and Hautala 1983; Bohon and Claussen 1951; Chiou et al. 1983; EPA 1982; Hansch and Leo 1979; Hodson and Williams 1988; Mackay and Shiu 1981; Polak and Lu 1973; Sutton and Calder 1975; Verschueren 1983). No additional studies are needed at the present time.

Production, Import/Export, Use, Release, and Disposal. According to the Emergency Planning and Community Right-to-Know Act of 1986, 42 U.S.C. Section 11023, industries are required to submit substance release and off-site transfer information to the EPA. The TRI, which contains this information for 2006, became available in May of 2008. This database is updated yearly and should provide a list of industrial production facilities and emissions.

Ethylbenzene has numerous uses (ACGIH 2002; Ransley 1984; Verschueren 1983), and production of the chemical has steadily increased since 1983 (C&EN 1994a, 1994b, 1995, 2006; Kirschner 1995). Releases occur from a variety of common sources including manufacturing and production (TRI06 2008), fuels, automobile exhaust, and fumes from paints, varnishes, solvents, carpet glue, and hot asphalt (Fishbein 1985; Hampton et al. 1983; Junk and Ford 1980; Katzman and Libby 1975; Kitto et al. 1997; Mukund et al. 1996; NAS 1980; Wallace et al. 1987b). Ethylbenzene also is released from waste waters to the

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atmosphere in municipal sewer systems (Quigley and Corsi 1995). Therefore, the potential for human exposure to ethylbenzene is considerable. The medium most likely to be contaminated is air, although ethylbenzene has also been detected in trace amounts in water supplies. Some ethylbenzene-containing wastes are designated as hazardous and are subject to EPA handling and recordkeeping requirements. Recommended methods for the disposal of ethylbenzene include burial in a landfill and rotary kiln incineration, liquid injection incineration, and fluidized bed incineration (EPA 1981d). No data need is identified at this time.

Environmental Fate. Ethylbenzene is primarily partitioned to and transported in air (Dewulf and van Langenhove 1997; Eisenreich et al. 1981; Mackay 1979; Masten et al. 1994). The partitioning and transport processes in water, soil, and aquatic life are also well characterized (ASTER 1995; Dewulf et al. 1996; Kawamura and Kaplan 1983; Ligocki et al. 1985; Swann et al. 1983). Transformation and degradation processes have also been well characterized in air (Atkinson and Carter 1984; Atkinson et al. 1978; Grovenstein and Mosher 1970; Herron and Huie 1973; Hoshino et al. 1978; O'Brien et al. 1975; Ohta and Ohyama 1985; Ravishankara et al. 1978; Yanagihara et al. 1977), water (Acton and Barker 1992; Anid et al. 1993; Bouwer and McCarty 1984; Burbach and Perry 1993; Ehrhardt and Petrick 1984; Gschwend et al. 1982; Hutchins 1991; Masten et al. 1994; Wakeham et al. 1983; Wilson et al. 1986), and in soil and sediment (Bestetti and Galli 1984; Chen and Taylor 1995; Hutchins 1991; Hutchins et al. 1991; Jamison et al. 1970; Ramanand et al. 1995; Van der Linden and Thijsse 1965; Yadav and Reddy 1993; Zappi et al. 1996). No data need is identified at this time.

Bioavailability from Environmental Media. Ethylbenzene is absorbed following inhalation, oral, and dermal exposures. Information is available on its absorption from air and water, but little data exist regarding dermal bioavailability and absorption from soil and food. Due to its large vapor pressure and Henry's law constant, ethylbenzene is expected to volatilize fairly rapidly from soil surfaces. Based on the moderate affinity of ethylbenzene for soil, especially soils with relatively high organic carbon content, the amount of ethylbenzene in bioavailable form in soil is expected to be low to moderate. Because of the low BCF values calculated for ethylbenzene, food chain bioaccumulation would not be expected to be significant sources of ethylbenzene exposure. No data need is identified at this time.

Food Chain Bioaccumulation. Limited data suggests that ethylbenzene does not bioconcentrate in aquatic organisms (Ogata et al. 1984), and is not likely to bioaccumulate in aquatic or terrestrial food chains. However, little information on food residues in commercially important fish and shellfish species

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is currently available. Additional monitoring data regarding the levels of ethylbenzene would be helpful for several commercially important fish and shellfish species.

Exposure Levels in Environmental Media. Reliable monitoring data for the levels of ethylbenzene in contaminated media at hazardous waste sites are needed so that the information obtained on levels of ethylbenzene in the environment can be used in combination with the known body burden of ethylbenzene to assess the potential risk of adverse health effects in populations living in the vicinity of hazardous waste sites.

An extensive amount of atmospheric monitoring data exists (EPA 1988c; Goldberg et al. 1995; Kinney et al. 2002; Kostianen 1995; Mukerjee et al. 1997; Quigley and Corsi 1995; Wallace et al. 1987a, 1987c; Zielinska et al. 1996; Zweidinger et al. 1988). Ethylbenzene has also been detected in surface water and groundwater (Barker 1987; Borden and Yanoschak 1990; Chen and Zoltek 1995; Cole et al. 1984; Cotruvo 1985; Gschwend et al. 1982; Krill and Sonzogni 1986; Quigley and Corsi 1995; Staples et al. 1985; Stubin et al. 1996; Stuermer et al. 1982; Tester and Harker 1981), sediment (Staples et al. 1985), a limited number of foodstuffs (Ferrario et al. 1985; Górna-Binkul et al. 1996; Kinlin et al. 1972; Lovegren et al. 1979; Nicola et al. 1987), and in cigarette smoke (Hodgson et al. 1996; Martin et al. 1997; Wallace 1986; Wallace et al. 1987c). Continued monitoring data at or around hazardous waste sites are needed in order to assess human exposure for populations residing in these areas.

Exposure Levels in Humans. Ethylbenzene and its metabolites have been detected in human blood (Angerer and Wulf 1985; Ashley et al. 1994), urine (Bardodej and Bardodevova 1970; Dutkiewicz and Tyras 1967; Engstrom and Bjurstrom 1978; Gromiec and Piotrowski 1984; Kiese and Lenk 1974; Sullivan et al. 1976; Yamasaki 1984), breast milk (Pellizzari et al. 1982), and adipose tissue (Engstrom and Bjurstrom 1978; EPA 1986). Most of the monitoring data have come from occupational studies of specific worker populations exposed by inhalation. Members of the general population can be exposed to ethylbenzene through inhalation of fumes while pumping gas, riding in gasoline-powered vehicles, and routinely starting vehicles in enclosed garages (Backer et al. 1997; Dodson et al. 2008; Lawryk and Weisel 1996; Lawryk et al. 1995), as well as exposure to ethylbenzene-containing consumer products (Hodgson et al. 1991; Lillo et al. 1990; NAS 1980; Otson et al. 1994; Sack et al. 1992; Wallace et al. 1987b). Additional information regarding the general population's exposure to ethylbenzene would be useful. Dietary intake is expected to be insignificant as compared to inhalation exposure (Tang et al. 2000). Oral exposures are likely to be low, except for the consumption of contaminated drinking water by populations living in the vicinity of hazardous waste sites, leaking underground storage tanks, or

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municipal landfills. This information is necessary for assessing the need to conduct health studies on these populations.

Exposures of Children. Children are exposed to ethylbenzene by the same routes that affect adults. Biomonitoring data suggest that blood levels of ethylbenzene are lower in children than non-- occupationally exposed adults (Sexton et al. 2005). Ethylbenzene has been detected in breast milk samples collected from 8 or 12 women from various cities in the United States; however, the concentrations were not reported (Pellizzari et al. 1982). There do not appear to be any childhood specific means to decrease exposure to ethylbenzene, aside from educating children about the dangers of inhalant abuse (Chakroun et al. 2008). A data need exists to determine current ethylbenzene residues and their sources in breast milk of members of the general population.

Child health data needs relating to susceptibility are discussed in Section 3.12.2, Identification of Data Needs: Children's Susceptibility.

Exposure Registries. No exposure registries for ethylbenzene were located. This substance is not currently one of the compounds for which a sub-registry has been established in the National Exposure Registry. The substance will be considered in the future when chemical selection is made for sub- registries to be established. The information that is amassed in the National Exposure Registry facilitates the epidemiological research needed to assess adverse health outcomes that may be related to exposure to this substance.

6.8.2 Ongoing Studies

The Federal Research in Progress (FEDRIP 2007) database provides additional information obtainable from a few ongoing studies that may fill in some of the data needs identified in Section 6.8.1. These studies are summarized in Table 6-4.

As part of the Third National Health and Nutrition Evaluation Survey (NHANES III), the Environmental Health Laboratory Sciences Division of the National Center for Environmental Health, Centers for Disease Control and Prevention, will be analyzing human blood samples for ethylbenzene and other volatile organic compounds. These data will give an indication of the frequency of occurrence and background levels of these compounds in the general population.

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Table 6-4. Ongoing Research Regarding the Environmental Fate and Exposure to Ethylbenzene

Investigator	Affiliation	Description	Sponsor
Thrall KD	Battelle Pacific Northwest Laboratories, Richland, Washington	The overall research objective for this project is to expand prior studies to evaluate the percutaneous absorption of compounds commonly encountered within similar industries (styrene and ethylbenzene) along with focused studies to evaluate the dermal bioavailability of compounds with both lipophilic and hydrophilic properties.	NIOSH
Burke J	EPA	The development of a human exposure model has been initiated to characterize population exposures to air toxics in support of risk assessment activities in the National Air Toxics Program. This research will develop probabilistic inputs for exposure to chemicals such as benzene and ethylbenzene for use in the model.	EPA

EPA = Environmental Protection Agency; NIOSH = National Institute for Occupational Safety and Health

Source: FEDRIP 2007