

6. POTENTIAL FOR HUMAN EXPOSURE

6.1 OVERVIEW

Benzene has been identified in at least 1,000 of the 1,684 hazardous waste sites that have been proposed for inclusion on the EPA National Priorities List (NPL) (HazDat 2006). However, the number of sites evaluated for benzene is not known. The frequency of these sites can be seen in Figure 6-1. Of these sites, 995 are located within the United States, 3 are located in the Commonwealth of Puerto Rico (not shown), and 2 are located in the Virgin Islands (not shown).

Benzene is released to the environment by both natural and industrial sources, although the anthropogenic emissions are undoubtedly the most important. Emissions of benzene to the atmosphere result from gasoline vapors, auto exhaust, and chemical production and user facilities. EPA's estimate of nationwide benzene atmospheric emissions from various sources was 34,000 metric tons/year (EPA 1989).

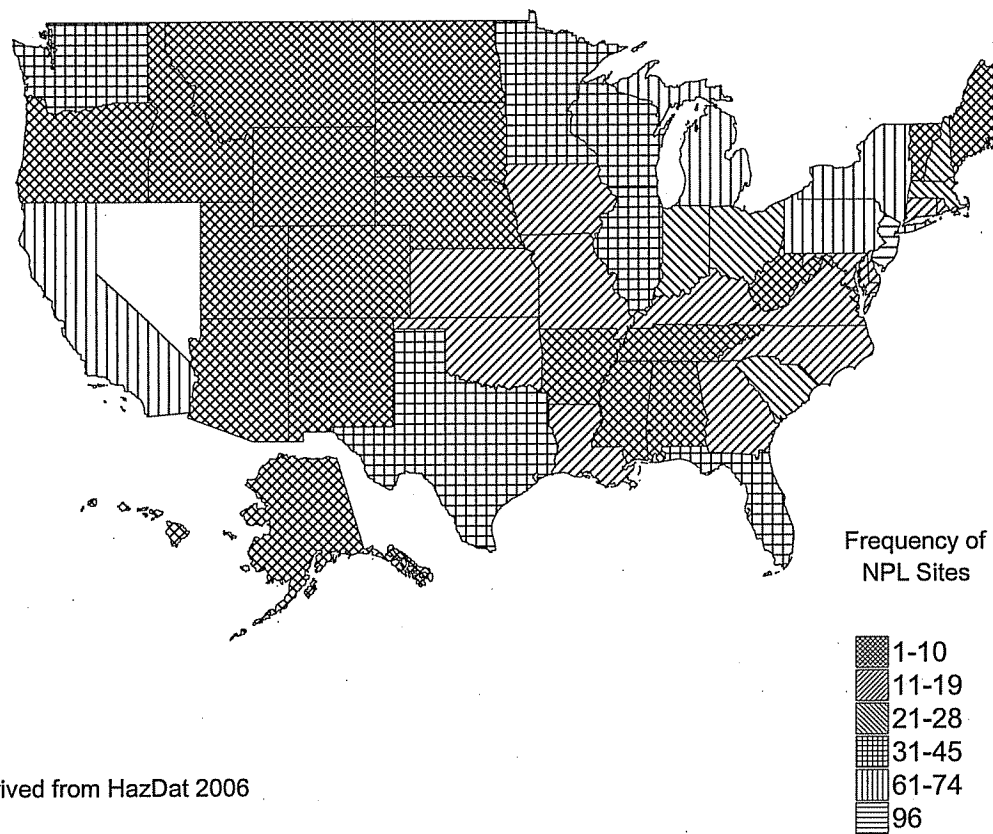
According to the Toxics Release Inventory, releases to the air from manufacturing and processing facilities were about 6.7 million pounds (3,055 metric tons) in 2004 (TRI04 2006). Releases to air accounted for about 93% of the total industry-related releases to the environment (TRI04 2006). Benzene is released to water and soil from industrial discharges, landfill leachate, and gasoline leaks from underground storage tanks.

Chemical degradation reactions, primarily reaction with hydroxyl radicals, limit the atmospheric residence time of benzene to only a few days, and possibly to only a few hours. Benzene released to soil or waterways is subject to volatilization, photooxidation, and biodegradation. Biodegradation, principally under aerobic conditions, is an important environmental fate process for water- and soil-associated benzene.

Benzene is ubiquitous in the atmosphere. It has been identified in air samples of both rural and urban environments and in indoor air. Although a large volume of benzene is released to the environment, environmental levels are low because of efficient removal and degradation processes. Benzene partitions mainly into air (99.9%) and inhalation is the dominant pathway of human exposure accounting for >99% of the total daily intake of benzene (Hattemer-Frey et al. 1990; MacLeod and MacKay 1999). The general population is exposed to benzene primarily by tobacco smoke (both active and passive smoking) and by inhaling contaminated air (particularly in areas with heavy motor vehicle traffic and around filling stations). Air around manufacturing plants that produce or use benzene and air around landfills and hazardous waste sites that contain benzene are additional sources of exposure. Exposure to benzene can

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



Derived from HazDat 2006

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also result from ingestion of contaminated food or water. Use of contaminated tap water for cooking, showering, etc., can also be a source of inhalation exposure since benzene can volatilize from water. Compared to inhalation, dermal exposure accounts for a minor portion of the total exposure of the general population. The magnitude of exposure is greatest for those individuals occupationally exposed to benzene; however, a far greater number of individuals are exposed as a result of benzene released from smoking tobacco products, from gasoline filling stations, and from auto exhaust. Smoking was found to be the largest anthropogenic source of direct human exposure to benzene (Duarte-Davidson et al. 2001; Hattemer-Frey et al. 1990).

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 2005g). 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 2005g).

6.2.1 Air

Estimated releases of 6.7 million pounds (~ 3,055 metric tons) of benzene to the atmosphere from 968 domestic manufacturing and processing facilities in 2004, accounted for about 93% of the estimated total environmental releases from facilities required to report to the TRI (TRI04 2006). These releases are summarized in Table 6-1.

Benzene is released into the atmosphere from both natural and industrial sources. Natural sources include crude oil seeps, forest fires, and plant volatiles (Brief et al. 1980; Graedel 1978). Major anthropogenic sources of benzene include environmental tobacco smoke, automobile exhaust, automobile refueling

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

State ^c	RF ^d	Reported amounts released in pounds per year ^b							Total release	
		Air ^e	Water ^f	UI ^g	Land ^h	Other ⁱ	On-site ^j	Off-site ^k	On- and off-site	
AK	7	19,568	19	0	375	0	19,962	0	19,962	
AL	15	290,660	290	0	280	2	290,955	277	291,232	
AR	8	33,137	66	0	0	0	33,203	0	33,203	
AZ	13	4,910	0	0	9	0	4,915	4	4,919	
CA	65	57,611	129	228	1,292	598	57,970	1,888	59,858	
CO	11	19,630	0	0	10	36	19,630	46	19,676	
CT	9	2,552	2	0	0	2	2,554	2	2,556	
DE	5	3,425	6,006	0	26	0	9,431	26	9,457	
FL	26	396,187	41	0	0	157	396,228	157	396,385	
GA	15	36,893	128	0	9	0	37,026	4	37,030	
GU	3	7,106	1	0	0	401	7,107	401	7,508	
HI	9	11,171	30	0	12	0	11,201	12	11,213	
IA	14	42,671	1	0	0	0	42,672	0	42,672	
ID	2	1,732	No data	0	0	0	1,732	0	1,732	
IL	35	171,104	102	0	2,152	104	172,227	1,235	173,462	
IN	30	211,476	805	14,001	4,654	29	227,079	3,886	230,965	
KS	19	69,823	164	231	259	0	70,226	251	70,477	
KY	22	77,345	799	0	766	20	78,904	26	78,930	
LA	62	605,128	1,075	122,723	1,688	968	729,109	2,473	731,582	
MA	10	5,556	55	0	26	537	5,611	563	6,173	
MD	11	12,644	8	0	184	1	12,821	15	12,836	
ME	5	3,027	23	0	0	467	3,049	467	3,516	
MI	41	345,255	8	0	127	2,295	345,363	2,322	347,686	
MN	16	16,614	2,724	0	131	1,561	19,360	1,670	21,030	
MO	17	98,498	0	0	0	0	98,498	0	98,498	
MP	2	710	0	0	0	0	710	0	710	
MS	13	59,076	25	0	14	0	59,102	13	59,115	
MT	5	17,242	5	0	15	0	17,248	14	17,262	
NC	12	17,290	0	0	5	48	17,295	48	17,343	
ND	2	6,400	0	0	1	0	6,400	1	6,401	
NE	9	1,333	No data	0	0	6	1,333	6	1,339	
NJ	20	51,054	443	0	150	169	51,510	306	51,816	
NM	9	38,730	No data	7	2	0	38,739	0	38,739	
NV	3	1,005	No data	0	0	0	1,005	0	1,005	
NY	44	60,682	56	0	10	1,335	60,738	1,345	62,084	
OH	52	183,972	67	5	730	82	184,049	807	184,856	
OK	11	114,701	14	0	278	71	114,984	80	115,064	

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OR	6	4,651	8	0	41	0	4,659	41	4,700	
PA	39	234,647	419	0	345	11,389	235,066	11,733	246,800	
PR	10	49,879	7	0	0	0	49,886	0	49,886	
RI	2	1,841	4	0	0	820	1,845	820	2,665	
SC	6	64,627	6	0	250	1,023	64,883	1,023	65,906	
SD	11	272	1	0	0	0	273	0	273	
TN	17	73,926	63	0	280	0	73,989	280	74,269	
TX	150	2,681,863	621	298,595	8,326	1,713	2,935,539	55,579	2,991,118	
UT	11	31,314	750	0	809	233	32,069	1,038	33,107	
VA	17	183,748	787	0	26	0	184,535	26	184,561	
VI	3	20,576	0	0	9	0	20,576	9	20,585	
WA	18	50,667	14	0	95	48	50,770	54	50,824	
WI	14	141,183	0	0	251	63	141,183	314	141,496	
WV	5	76,556	284	0	393	0	76,840	393	77,233	
WY	7	24,986	0	0	1	0	24,986	1	24,987	
Total	968	6,736,655	16,051	435,790	24,033	24,179	7,147,049	89,659	7,236,707	

^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: TRI04 2006 (Data are from 2004)

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operations, and industrial emissions. Using source exposure modeling, it was estimated that benzene emissions were highest from coke oven blast furnaces (Edgerton and Shah 1992). Other sources that contributed to emissions of benzene include automobiles, petrochemical industries, waste water treatment plants, and petroleum industries (Edgerton and Shah 1992).

Industrial and automotive sources of benzene are well monitored. EPA (1989) estimates of nationwide benzene atmospheric emissions, in metric tons/year (kkg/year), from various industrial sources include: (1) coke byproduct recovery plants (17,000 kkg/year), (2) benzene waste operations (5,300 kkg/year), (3) gasoline marketing systems, including bulk gasoline terminals and plants, service stations, and delivery tank trucks (4,800 kkg/year), (4) transfer operations at chemical production facilities, bulk terminals, and coke byproduct recovery plants (4,600 kkg/year), (5) benzene storage vessels (620–1,290 kkg/year), (6) industrial solvent use (450 kkg/year), (7) chemical manufacturing process vents (340 kkg/year), and (8) ethylbenzene/styrene process vents (135 kkg/year). Benzene is present in passenger car tailpipe emissions at compositions ranging from 2.9 to 15% of the total tailpipe hydrocarbon composition (Black et al. 1980). The 2002 benzene industrial emission inventory for California totaled 266 metric tons/year (CARB 2005); these numbers did not include motor vehicle exhaust, which accounted for 71% of emissions in 1984 (Cal EPA 1987). The contribution of mobile source hazardous air pollutant emissions has been compared to that of stationary sources in the Seattle-Tacoma area. Mobile sources were estimated to contribute approximately 83% of the benzene from stationary areas and mobile sources combined, with major stationary point sources excluded (EPA 1994d). Benzene is also released by off-gassing from particle board (Glass et al. 1986), vaporization from oil spills, and emissions from landfills (Bennett 1987; Wood and Porter 1987). While all of these sources release more benzene into the environment, a large percentage of the benzene inhaled by humans comes from cigarette smoke. Exhaled breath of smokers contains benzene (Wallace 1989a, 1989b; Wallace and Pellizzari 1986; Wester et al. 1986).

According to the Texas Natural Resource Conservation Commission (TNRCC), of the 93 districts in Texas reporting benzene emissions from industrial sources, in 1980, 1985, and 1988, 10 districts reported 0 tons/year, 79 districts reported 0.1–100 tons/year, 4 districts reported 100–400 tons/year, 2 districts reported 400–1,000 tons/year, and 1 district had emissions projected at above 1,000 tons/year (Pendleton 1995).

The natural sources most monitored for benzene released to air are fires (Austin et al. 2001; Lowry et al. 1985). A study of nine municipal fires in Canada found a mean concentration of 3.45 ppm of benzene

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and had very high relative concentration of other volatile organic compounds (VOCs) monitored (Austin et al. 2001).

There is a potential for atmospheric release of benzene from hazardous waste sites. Benzene has been detected in air in 200 of the 1,684 current and former NPL sites where it has been detected in some medium (HazDat 2006).

6.2.2 Water

Estimated releases of 16,051 pounds (~7 metric tons) of benzene to surface water from 968 domestic manufacturing and processing facilities in 2004, accounted for about 0.2% of the estimated total environmental releases from facilities required to report to the TRI (TRI04 2006). These releases are summarized in Table 6-1.

Benzene is released to water from the discharges of both treated and untreated industrial waste water, gasoline leaks from underground storage tanks, accidental spills during marine transportation of chemical products, and leachate from landfills and other contaminated soils, (CDC 1994; Crawford et al. 1995; EPA 1979; NESCAUM 1989; Staples et al. 1985). A fire in a tire dump site in western Frederick County, Virginia, produced a free-flowing oily tar containing benzene among other chemicals. The seepage from this site contaminated nearby surface water (EPA 1993). Between 1986 and 1991, 3,000 gallons of benzene were accidentally released into Newark Bay and its major tributaries. Another 3,000 gallons were released in 1991 (Crawford et al. 1995).

There is a potential for release of benzene to water from hazardous waste sites. Benzene has been detected in groundwater samples collected at 832 of the 1,684 current and former NPL sites and in surface water samples collected at 208 of the 1,684 sites (HazDat 2006).

6.2.3 Soil

Estimated releases of 24,033 pounds (~11 metric tons) of benzene to soils from 968 domestic manufacturing and processing facilities in 2004, accounted for about 0.3% of the estimated total environmental releases from facilities required to report to the TRI (TRI04 2006). An additional 435,000 pounds (~197 metric tons), constituting about 6% of the total environmental emissions, were released via underground injection (TRI04 2006). These releases are summarized in Table 6-1.

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Benzene is released to soils through industrial discharges, land disposal of benzene-containing wastes, and gasoline leaks from underground storage tanks. In northern Virginia, approximately 200,000 gallons of liquid hydrocarbons were released from a fuel-storage terminal into the underlying soil (Mushrush et al. 1994).

There is a potential for release of benzene to soil from hazardous waste sites. Benzene has been detected in soil samples collected at 436 of the 1,684 sites, and in sediment samples collected at 145 of the 1,684 sites where benzene has been detected in some medium (HazDat 2006).

6.3 ENVIRONMENTAL FATE

6.3.1 Transport and Partitioning

The high volatility of benzene is the controlling physical property in the environmental transport and partitioning of this chemical. Benzene is considered to be highly volatile with a vapor pressure of 95.2 mm Hg at 25 °C. Benzene is moderately soluble in water, with a solubility of 1,780 mg/L at 25 °C, and the Henry's law constant for benzene (5.5×10^{-3} atm-m³/mole at 25 °C) indicates that benzene partitions readily to the atmosphere from surface water (Mackay and Leinonen 1975). Since benzene is soluble in water, some minor removal from the atmosphere via wet deposition may occur. A substantial portion of any benzene in rainwater that is deposited to soil or water will be returned to the atmosphere via volatilization.

Benzene released to soil surfaces partitions to the atmosphere through volatilization, to surface water through runoff, and to groundwater as a result of leaching. The soil organic carbon sorption coefficient (K_{oc}) for benzene has been measured with a range of 60–83 (Karickhoff 1981; Kenaga 1980), indicating that benzene is highly mobile in soil and readily leaches into groundwater. Other parameters that influence leaching potential include the soil type (e.g., sand versus clay), amount of rainfall, depth of the groundwater, and extent of degradation. In a study of the sorptive characteristics of benzene to groundwater aquifer solids, benzene showed a tendency to adsorb to aquifer solids. Greater soil adsorption was observed with increasing organic matter content (Uchrin and Mangels 1987). An investigation of the mechanisms governing the rates of adsorption and desorption of benzene by dry soil grains revealed that periods of hours are required to achieve equilibrium and that adsorption is much faster than desorption (Lin et al. 1994). The rate of volatilization and leaching are the principal factors that determine overall persistence of benzene in sandy soils (Tucker et al. 1986).

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Studies suggest that benzene does not bioaccumulate in marine organisms. The bioconcentration/bioaccumulation potential of benzene in aquatic organisms of the open coastal ocean was investigated by sampling final effluent from the Los Angeles County waste water treatment plant quarterly from November 1980 to August 1981 (Gossett et al. 1983). Benzene has a relatively low octanol/water partition coefficient ($\log K_{ow}=2.13$ or 2.15) (Gossett et al. 1983; HSDB 2007). In the alga, *Chlorella*, a bioaccumulation factor of 30 was determined experimentally (Geyer et al. 1984). An experimental bioconcentration factor (BCF) of 4.27 was measured in goldfish reared in water containing 1 ppm of benzene (Ogata et al. 1984). Based on these measured values, bioconcentration/bioaccumulation of benzene in the aquatic food chains does not appear to be important. These results are consistent with the fact that benzene has a relatively low octanol/water partition coefficient (Gossett et al. 1983; HSDB 2007), suggesting relatively low bioaccumulation. There is no evidence in the literature of biomagnification of benzene in aquatic food chain.

Evidence exists for the uptake of benzene by cress and barley plants from soil (Scheunert et al. 1985; Topp et al. 1989). BCFs for barley plants after 12, 33, 71, and 125 days were 17, 2.3, 2.9, and 4.6, respectively. BCFs for cress plants after 12, 33, and 79 days were 10, 2.3, and 1.9, respectively. The relative decrease in the BCFs with time was attributed to growth dilution (Topp et al. 1989). Since benzene exists primarily in the vapor phase, air-to-leaf transfer is considered to be the major pathway of vegetative contamination (Hattemer-Frey et al. 1990). Based on an equation to estimate vegetative contamination, the total concentration of benzene on exposed food crops consumed by humans and used as forage by animals was estimated to be 587 ng/kg, 81% of which was from air-to-leaf transfer and 19% was from root uptake (Hattemer-Frey et al. 1990).

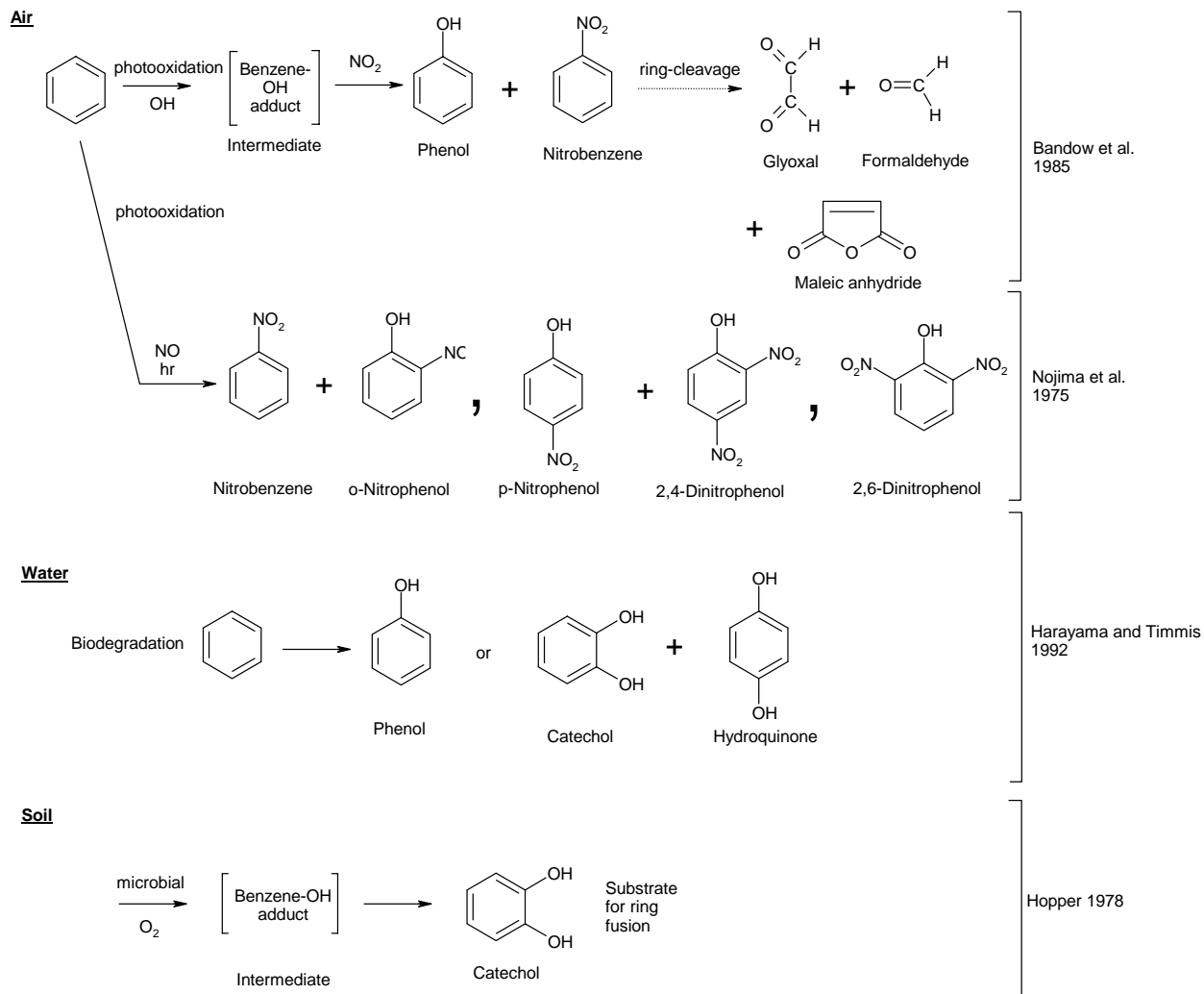
Benzene also accumulates in leaves and fruits of plants. After 40 days, plants grown in benzene-rich environments showed bioaccumulation in the leaves and fruit that were greater than the air partitioning coefficient of benzene in the atmosphere. Blackberries exposed to 0.313 ppm and apples exposed to 2.75 ppm contained about 1,000 and 36 ng/g of benzene, respectively (Collins et al. 2000).

6.3.2 Transformation and Degradation

Benzene undergoes a number of different transformation and degradation reactions in the environment as discussed in the following sections. The resulting environmental transformation products within different media are shown in Figure 6-2.

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Figure 6-2. Environmental Transformation Products of Benzene in Various Media



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6.3.2.1 Air

Benzene in the atmosphere exists predominantly in the vapor phase (Eisenreich et al. 1981). The most significant degradation process for benzene is its reaction with atmospheric hydroxyl radicals. The rate constant for the vapor phase reaction of benzene with photochemically produced hydroxyl radicals has been determined to be 1.3×10^{-12} cm³/molecule-second, which corresponds to a residence time of 8 days at an atmospheric hydroxyl radical concentration of 1.1×10^6 molecules/cm³ (Gaffney and Levine 1979; Lyman 1982). With a hydroxyl radical concentration of 1×10^8 molecules/cm³, corresponding to a polluted atmosphere, the estimated residence time is shortened to 2.1 hours (Lyman 1982). Benzene may also react with other oxidants in the atmosphere such as nitrate radicals and ozone; however, the rate of degradation is considered insignificant compared to the rate of reaction with hydroxyl radicals. Residence times of 472 years for rural atmospheres and 152 years for urban atmospheres were calculated for the reaction of benzene with ozone (O₃) using a rate constant for O₃ of 7×10^{-23} cm³/molecule-second (Pate et al. 1976) and atmospheric concentrations for O₃ of 9.6×10^{11} molecules/cm³ (rural) and 3×10^{12} molecules/cm³ (urban) (Lyman 1982).

The reaction of benzene and nitric oxide in a smog chamber was investigated to determine the role of benzene in photochemical smog formation (Levy 1973). The results showed that benzene exhibited low photochemical smog reactivity in the four categories tested: rate of photooxidation of nitric oxide, maximum oxidant produced, eye-irritation response time, and formaldehyde formation. The authors concluded that benzene probably does not play a significant role in photochemical smog formation (Levy 1973). In the presence of active species such as nitrogen oxides and sulfur dioxide, the rate of photodegradation of benzene in the gas phase was greater than that in air alone. Its half-life in the presence of such active species (100 ppm benzene in the presence of 10–110 ppm NO_x or 10–100 ppm SO₂) was 4–6 hours with 50% mineralization to carbon dioxide in approximately 2 days (Korte and Klein 1982). Some of the products of the reaction of benzene with nitrogen monoxide gas (e.g., nitrobenzene, *o*- and *p*-nitrophenol, and 2,4- and 2,6-dinitrophenol) may have potentially adverse effects on human health (Nojima et al. 1975); however, these species also have relatively short atmospheric lifetimes, which should limit the potential exposure to these compounds. Photooxidation of benzene in a nitrogen monoxide/nitrogen dioxide-air system formed formaldehyde, formic acid, maleic anhydride, phenol, nitrobenzene, and glyoxal (ethane-1,2-dione) (Bandow et al. 1985).

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Direct photolysis of benzene in the atmosphere is not likely because the upper atmosphere effectively filters out wavelengths of light <290 nm, and benzene does not absorb wavelengths of light >260 nm (Bryce-Smith and Gilbert 1976).

6.3.2.2 Water

Benzene is subject to indirect photolysis in sunlit surface water, but does not undergo direct photolysis. For direct photolysis to occur, a substance must absorb photons of light >290 nm. During indirect photolysis, light energy is absorbed by other constituents (photosensitizers) of the media (water, soil) and the excited species can then transfer energy to benzene (indirectly promoting it to an excited electronic state), or lead to the formation of reactive species, such as singlet oxygen or hydroxy radicals, which react with benzene. Humic and fulvic acids are well-known photosensitizing agents and are practically ubiquitous in natural waters. A half-life of 16.9 days was reported for photolysis of benzene dissolved in oxygen-saturated deionized water and exposed to sunlight (Hustert et al. 1981).

Benzene is readily degraded in water under aerobic conditions. Results of a biochemical oxygen demand (BOD) test determined that benzene was completely biodegradable after the second week of static incubation at 25 °C at benzene concentrations of 5 and 10 mg/L using domestic waste water as the microbial inoculum (Tabak et al. 1981). A study of the degradation of benzene by the microbial population of industrial waste water at 23 °C using a shaker flask system showed that after 6 hours, only 8% (4 mg/L) of the initial 50 mg/L dose of benzene remained (Davis et al. 1981). Water from a petroleum production site was successfully biotreated for complete removal of benzene using a flocculated culture of *Thiobacillus denitrificans* strain F and mixed heterotrophs (Rajganesht et al. 1995).

Microbial degradation of benzene in aquatic environments is influenced by many factors including microbial population, dissolved oxygen, nutrients, other sources of carbon, inhibitors, temperature, pH, and initial concentration of benzene. Vaishnav and Babeu (1987) reported biodegradation half-lives for benzene in surface water (river water) and groundwater of 16 and 28 days, respectively. Benzene was found to be resistant to biodegradation in surface water taken from a harbor and supplemented with either nutrients (nitrogen and phosphorus) or acclimated microbes, however, biodegradation did occur, with a half-life of 8 days, in surface water enriched with both nutrients and microbes (Vaishnav and Babeu 1987). At very high levels, as may be the case of a petroleum spill, benzene (and other compounds contained in petroleum) is toxic to microorganisms and the rate of degradation is slow compared to low initial starting concentrations. In another study, Davis et al. (1994) observed rapid aerobic biodegradation

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of benzene in aquifer groundwater samples and measured times for 50% disappearance ranging from 4 days for an initial benzene concentration of 1 mg/kg to 14 days for an initial benzene concentration of 10 mg/kg. Under acidic conditions (pH 5.3, 20 °C), benzene was completely microbially degraded in 16 days in groundwater taken from a shallow well (Delfino and Miles 1985).

The aerobic biodegradation of benzene is also influenced by the presence of other aromatic hydrocarbons. A bacterial culture grown with aromatic hydrocarbons plus nitrogen-, sulfur-, and oxygen-containing aromatic compounds was much less efficient in degrading benzene than the culture grown with aromatic hydrocarbons alone. Pyrrole strongly inhibited benzene degradation. Benzene degradation was high when toluene and xylene were present (Arvin et al. 1989).

Laboratory studies on microbial degradation of benzene with mixed cultures of microorganisms in gasoline-contaminated groundwater revealed that both oxygen and nitrogen concentrations are major controlling factors in the biodegradation of benzene. Nitrogen enhanced the biodegradation rate of benzene 4.5-fold, over inoculum-enriched water alone. More than 95% of the benzene in groundwater was removed through microbial action within 73.5 hours (Karlson and Frankenberger 1989).

Benzene biodegradation under anaerobic conditions does not readily occur. When dissolved oxygen is depleted, an alternative electron acceptor such as nitrate, carbonate, or iron(III) must be available, and microbes capable of using the alternative electron acceptor to degrade the benzene must be present (McAllister and Chiang 1994). Using aquifer material obtained from a landfill from Norman, Oklahoma, no significant benzene biodegradation was reported during the first 20 weeks of incubation under anaerobic conditions at 17 °C; however, after 40 weeks of incubation, benzene concentrations were reduced by 72 and 99% of the benzene was degraded after 120 weeks (Wilson et al. 1986). No degradation of benzene was observed in 96 days under anaerobic conditions (20 °C) using raw water intake from a water treatment plant (Delfino and Miles 1985).

Use of water as an oxygen source in the anaerobic degradation of benzene has been demonstrated. Experiments indicated that incorporation of ^{18}O from ^{18}O -labeled water is the initial step in the anaerobic oxidation of benzene by acclimated methanogenic cultures. Phenol was the first major product (Vogel and Grbić-Galić 1986).

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6.3.2.3 Sediment and Soil

Benzene is biodegraded in soil under aerobic conditions. Microbial metabolism of benzene proceeds through the formation of *cis*-dihydrodiols and, with further metabolism, to catechols, which are the substrates for ring fission (Gibson 1980; Hopper 1978). *Pseudomonas putida* oxidized benzene through *cis*-1,2-dihydroxy-1,2-dihydrobenzene (Gibson 1977; Hopper 1978). After acclimation, *Norcardia* species and *Pseudomonas* species, effectively degraded benzene to carbon dioxide within 7 days (45–90%). A strain of *Rhodococcus* isolated from contaminated river sediment mineralized 71% of benzene at an initial concentration of 0.7 mg/L in 14 days (Malachowsky et al. 1994). The soil bacterium *Nitrosomonas europaea* catabolized benzene to phenol and hydroquinone (Keener and Arp 1994). Another new mixotrophic bacteria, a strain of *Pseudomonas sp.* isolated from contaminated soil, grew under both anaerobic and aerobic conditions and used benzene for its growth (Morikawa and Imanaka 1993). The biodegradation of 2 mg of radiolabeled benzene in 100 g of soil with a mixed microbial population transformed 47% of the added radioactivity to carbon dioxide after 10 weeks (Haider et al. 1981). The authors concluded that specific organisms that mineralize benzene were present in the soil in only small numbers.

ULTRA, a fate and transport model used to predict the environmental fate of benzene following leakage of gasoline from an underground storage tank into shallow sandy soil, indicated that only about 1% of the benzene in the gasoline would be degraded over a 17-month period, and 3% would remain in the soil (Tucker et al. 1986). According to this model, most of the benzene that would be leaked in soil would either volatilize (67%) or move into groundwater (29%).

Salanitro (1993) summarized the aerobic degradation rates for BTEX in laboratory subsoil-groundwater slurries and aquifers. The data indicate that decay rates for benzene are highest (19–52% per day) for benzene concentrations <1 ppm when initial dissolved oxygen levels are about 8 ppm. Rates are significantly reduced (0–1.1% per day) when benzene levels are 1–2 ppm, and no degradation was observed when benzene levels were >2 ppm. This is particularly relevant in the case of petroleum spills as high concentrations of petroleum compounds are toxic to organisms and decrease the rate of biodegradation.

Benzene has been shown to be anaerobically transformed by mixed methanogenic cultures derived from ferulic acid-degrading sewage sludge enrichments. In most of the experiments, benzene was the only semicontinuously supplied energy sources in the defined mineral medium (Grbić-Galić and Vogel 1987).

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After an initial acclimation time of 11 days, at least 50% of the substrate was converted to CO₂ and methane. The intermediates were consistent with benzene degradation via initial oxidation by ring hydroxylation.

It has been demonstrated that when mixtures of benzene, toluene, xylenes, and ethylbenzene are present in an anaerobic environment, there is a sequential utilization of the substrate hydrocarbons, with toluene usually being the first to be degraded, followed by the isomers of xylene in varying order. Benzene and ethylbenzene tend to be degraded last, if they are degraded at all (Edwards and Grbić-Galić 1992). Similar studies using only benzene at initial concentrations ranging from 40 to 200 µM showed degradation rates ranging from 0.36 to 3.7 µM/day depending upon substrate concentration and the presence of other carbon sources (Edwards and Grbić-Galić 1992).

6.3.2.4 Other Media

Twenty-day-old spinach leaves placed in a hermetic chamber containing vapors of ¹⁴C-labeled benzene were shown to assimilate benzene, which was subsequently metabolized to various nonvolatile organic acids (Ugrekhelidze et al. 1997).

6.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

Reliable evaluation of the potential for human exposure to benzene depends in part on the reliability of supporting analytical data from environmental samples and biological specimens. Concentrations of benzene 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 benzene 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 benzene in a variety of environmental media are detailed in Chapter 7.

6.4.1 Air

Benzene is ubiquitous in the atmosphere. It has been identified in outdoor air samples of both rural and urban environments and in indoor air. Table 6-2 lists benzene levels in outdoor air from various cities in the United States.

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Table 6-2. Benzene Levels in Air Samples

Location	Concentration (ppb)	Comments	References
Outdoor air			
San Francisco, California	0.8–5.2 (range); 2.6±1.3 ^a	Data from six different urban locations in 1984; n=25	Wester et al. 1986
Stinson Beach, California	0.38±0.39 ^a	Data from remote coastal area in 1984; n=21	Wester et al. 1986
Houston, Texas	1.2–18.7 (range); 37.5 ^b	EPA survey, urban area; n=14; summer 1986	EPA 1987a ^c
Houston, Texas	0.55–6.3; 1.73 ^b	Semirural area; n=22; 1990–1991	Kelly et al. 1993
St. Louis, Missouri	0.63–12.1 (range); 1.85 ^b	EPA survey, urban area; n=18; summer 1985	EPA 1987a ^c
Denver, Colorado	3.0–6.6 (range); 4.1 ^b	EPA survey, urban area; n=13; summer 1986	EPA 1987a ^c
Philadelphia, Pennsylvania	0.32–3.0 (range); 1 ^b	EPA survey, urban area; n=14; summer 1985	EPA 1987a ^c
New York (Manhattan), New York	0.88–5.3 (range); 1.75 ^b	EPA survey, urban area; n=12; summer 1986	EPA 1987a ^c
Chicago, Illinois	0.63–5.05 (range); 3.45 ^b	EPA survey, urban area; n=14; summer 1986	EPA 1987a ^c
Boston, Massachusetts	0.69–3.1; 1.06 ^b	Urban area; n=22; 1990–1991	Kelly et al. 1993
New York (Staten Island), New York	0.1–34 (range); 4.4±6.6 ^a	Urban area; spring 1984	Singh et al. 1985
73 km northwest of Denver, Colorado	0.02–0.85 (range)	Rural area; May 1981–December 1982	Roberts et al. 1985
Elizabeth and Bayonne, New Jersey	Night 2.7 ^d , 28.5 (max); day, 3.0 ^d , 13.8 (max)	Night, n=81–86; day, n=86–90; fall 1981	Wallace et al. 1985
Personal air			
Elizabeth and Bayonne, New Jersey	Night 9.7 ^d , 159.6 (max); day, 8.5 ^d , 84.5 (max)	Night, n=346–348; day, n=339–341; fall 1981	Wallace et al. 1985
Elizabeth and Bayonne, New Jersey	Winter 5.2, summer 2.7, fall 4.8		Rappaport and Kupper 2004
Los Angeles, California	Winter 4.5, spring 2.2, fall 2.8		Rappaport and Kupper 2004

^aAverage±standard deviation^bMedian^cConcentrations reported as ppb carbon; values presented in table represent conversion equivalents as ppb benzene.^dWeighted average

EPA = Environmental Protection Agency; max = maximum; N = number of samples

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Volatile organic compounds, including benzene, were measured at 11 monitoring sites in Anchorage, Alaska, in a year-long study ending in April 1994 (Taylor and Morris 1995). Average annual benzene concentrations ranged from a minimum of 1.15 parts per billion by volume (ppbv) in a low density residential area to 5.44 ppbv near a major midtown intersection. In a neighborhood where residents were complaining of petroleum odors, the highest benzene concentrations (annual average 3.74 ppbv) were measured on a cliff over the petroleum tank farm, within 50 meters of a petroleum storage tank.

Ambient air samples from 44 sites in 39 U.S. urban areas were collected from 6 to 9 a.m. during June through September of 1984, 1985, and 1986. Benzene was present in every sample. The median benzene site concentrations ranged from 0.8 to 6 ppb, with the overall median being 2.1 ppb (estimated detection limit ~0.04 ppb carbon; conversion equivalent ≈ 0.007 ppb benzene). The data indicated that mobile sources were the major source of benzene in the vast majority of samples (EPA 1987a). Benzene concentrations were in the range of >1 – <5 ppbv for all of the 13 sites tested in a 1996 study. The sites included: Baton Rouge, Louisiana; Brownsville, Texas; Brattleboro, Vermont; Burlington, Vermont; Camden, New Jersey; El Paso, Texas; Garyville, Louisiana; Galveston, Texas; Hanville, Louisiana; Port Neches, Texas; Rutland, Vermont; Underhill, Vermont; and Winooski, Vermont (Mohamed et al. 2002).

The following daily median benzene air concentrations were reported in the Volatile Organic Compound National Ambient Database (1975–1985): remote (0.16 ppb), rural (0.47 ppb), suburban (1.8 ppb), urban (1.8 ppb), indoor air (1.8 ppb), and workplace air (2.1 ppb). The outdoor air data represent 300 cities in 42 states while the indoor air data represent 30 cities in 16 states (Shah and Singh 1988). In a NHEXAS study of six states in the Great Lakes region, benzene was found in 99.7% of the 386 personal air samples taken with an average concentration of 2.35 ppb. Benzene was also found in 100% of both indoor and outdoor samples with concentrations averaging 2.25 and 1.13 ppb, respectively (Clayton et al. 1999).

An EPA study of the concentration of various pollutants in 1990 showed an average concentration of benzene of 0.948 ppb. The source of benzene included manufacturing facilities and manufacturers that emit benzene to the environment (17%), mobile (60%), and background (23%) sources (Morello-Frosch et al. 2000).

In California, motor vehicle exhaust accounted for over 70% of the nonsmoking population's exposure to ambient benzene (Cal EPA 1987). The 1984 population-weighted average benzene concentration in California was estimated to be 3.3 ppb (Cal EPA 1987). Benzene emissions in a Los Angeles roadway tunnel were measured at a concentration of 382 mg/L (118,420 ppm) (Fraser et al. 1998).

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Industrial sites that produce benzene are monitored often. Analysis of ambient air samples collected in industrial areas showed benzene levels ranging from 0.13 to 5 ppb in Iberville Parish, Louisiana, an area that included many organic chemical and petroleum producer, user, and storage facilities located along the Mississippi River (Pellizzari 1982). Indoor and outdoor air measurements were made in August 1987 in the Kanawha Valley region of West Virginia, which is the center of a heavily industrialized area known for its chemical manufacturing. The mean, maximum, and median indoor concentrations of benzene were 2.1, 14.9, and 0.64 ppb, respectively. The median outdoor ambient air concentration of benzene was 0.78 ppb (Cohen et al. 1989).

An analysis of gas from 20 Class II (municipal) landfills revealed a maximum concentration of 32 ppm for benzene (Wood and Porter 1987). Benzene was measured in the vicinity of the BKK landfill, a hazardous waste landfill in California, at a maximum concentration of 1.2 ppb (Bennett 1987). Maximum estimated levels of benzene in air near uncontrolled (Superfund) hazardous waste sites were 59.5 ppb at the Kin-Buc Landfill (Edison, New Jersey) and 162.8 ppb in Love Canal basements (Niagara Falls, New York) (Bennett 1987; Pellizzari 1982).

According to the National Cancer Institute, the average concentration of benzene in 1998 was 0.58 ppb in metropolitan areas (NCI 2003). A study of New York City air found mean values of 0.80, 1.87, and 1.47 ppb for outdoor (home), indoor (home), and personal air, respectively (Kinney et al. 2002). According to the New York Department of Health, the air from about 50% of oil fuel heated homes between the years 1997 and 2003 contained benzene concentrations ≥ 0.69 ppb inside the home, and 0.47 ppb in the area outside their homes. New York City was not included in this study (NYSDOH 2005). Concentrations of VOCs were measured in 12 northern California office buildings with three different types of ventilation. Benzene concentrations ranged from <0.1 to 2.7 ppb, with a geometric mean of 0.98 ppb (Daisey et al. 1994).

Population-weighted personal exposures to benzene exceeded the outdoor air concentrations in data from EPA's Total Exposure Assessment Methodology (TEAM) study. The overall mean personal exposure was about 4.7 ppb, compared to an overall mean outdoor concentration of only 1.9 ppb (Wallace 1989a). The study also reported that the median level of benzene in 185 homes without smokers was 2.2 ppb, and the median level of benzene in 343 homes with one or more smokers was 3.3 ppb (Wallace 1989a). This finding points to the possible significance of passive smoking as a source of benzene exposure. Indoor air samples taken from a smoke-filled bar contained 8.08–11.3 ppb of benzene (Brunnemann et al. 1989). A

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study conducted by R.J. Reynolds Tobacco Company in smoking and nonsmoking homes revealed that benzene levels were elevated in smoking homes. In 24 nonsmoking homes, the mean benzene concentration was 1.21 ppb with a maximum of 5.93 ppb. In 25 smoking homes, the mean benzene concentration was 1.73 ppb, with a maximum of 8.43 ppb. However, benzene was not significantly correlated or associated with 3-ethenylpyridine, a proposed vapor phase environmental tobacco smoke marker (Heavner et al. 1995).

A British study measured benzene concentrations from both rural and urban areas in 1995. The highest concentrations of benzene were in Southampton urban center, London roadside, and Liverpool, which contained measured benzene levels of 2.53, 1.69, and 1.60 ppb, respectively. The lowest measured benzene concentrations were in rural Hartwell and urban Edinborough, which contained 0.4 and 0.69 ppb of benzene, respectively (Duarte-Davidson 2001).

6.4.2 Water

Data from EPA's STOrage and RETrieval (STORET) database (2003–2005) showed that benzene was positively detected in 38% of the surface water samples collected at 571 observation stations ranging from concentrations too low to quantify to 100 µg/L (100 ppb) in one Utah test site. The sampling sites in the STORET database include both ambient and pipe sites. Ambient sites include streams, lakes, ponds, wells, reservoirs, canals, estuaries, and oceans and are intended to be indicative of general U.S. waterway conditions. Pipe sites refer to municipal or industrial influents or effluents (EPA 2005f).

Benzene was found in 904 of the 8,200 samples tested by the U.S. Geological Survey across the United States and Canada (USGS 2005). The EPA found benzene in 13,919 and 1,119 groundwater and surface water samples, respectively (EPA 2001).

Benzene is found in both polluted and unpolluted waters and rainwater. Measured benzene levels in open ocean from the Gulf of Mexico in 1977 in relatively unpolluted and polluted waters were 5–15 ng/kg (5–15 parts per trillion [ppt]), and 5–40 ng/kg (5–40 ppt), respectively (Sauer 1981). Benzene levels measured in coastal surface waters of the Gulf of Mexico were 6 ng/kg (6 ppt) in relatively unpolluted waters and 50–175 ng/kg (50–175 ppt) in polluted coastal waters (Sauer 1981). Benzene has been detected in rainwater in the United Kingdom at a concentration of 87.2 ppb (Colenutt and Thorburn 1980).

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Benzene levels in water in the vicinity of five industrial facilities using or producing benzene ranged from <1 ppb to a high of 179 ppb found in plant effluent. In general, benzene in plant effluents quickly dispersed in rivers or streams to levels of 1–2 ppb or less (EPA 1979). The maximum benzene levels observed in monitoring wells in plumes from fuel spills at gasoline service stations ranged from 1,200 to 19,000 ppb (Salanitro 1993). A monitoring well in the vicinity of a bulk storage facility had a maximum benzene level of 45,000 ppb (Salanitro 1993). In northern Virginia, approximately 200,000 gallons of liquid hydrocarbons were released from a fuel-storage terminal into the underlying soil. A dichloromethane extract of groundwater from a monitoring well in the same area gave a benzene concentration of 52.1 ppm (Mushrush et al. 1994). Benzene has been detected at concentrations ranging from 16 to 110 ppb in landfill leachate from a landfill that accepted both municipal and industrial wastes (Cline and Viste 1985).

Composite data from the Comprehensive Emergency Response, Compensation, and Liability Act (CERCLA) monitoring program indicate that benzene was detected at a frequency of 11.2% in groundwater in the vicinity of 178 inactive hazardous waste disposal sites (Plumb 1987). Data from a 1980 national survey by the Council on Environmental Quality on groundwater and surface water contamination showed benzene concentrations in contaminated drinking water wells in New York, New Jersey, and Connecticut ranged from 30 to 330 ppb, with the highest concentration in drinking water from surface water sources reported to be 4.4 ppb (Burmester 1982). Benzene has also been identified but not quantified as one of the major organic constituents in commercially bottled artisan water in the United States (Dowty et al. 1975). At detection limits ranging from 0.2 to 1.0 ppb, benzene was detected at a concentration of 2 ppb in only one sample of 182 samples of bottled drinking water (Page et al. 1993). In six states of the Great Lakes region, unspecified amounts of benzene were found in 5.7% of the 247 drinking water sites tested (Clayton et al. 1999).

Because the New Jersey Department of Environmental Protection identified serious water issues in a 930 km² area within metropolitan Philadelphia, tests have been done to find other water sources such as the Kirkwood-Cohansey aquifer system. A study of 57 water samples taken from the shallow ground water supply at Kirkwood Cohansey aquifer in New Jersey showed that the majority of samples (50) contained between 0.2 and 1 ppbv of benzene, three samples contained <0.1 ppbv, and four samples contained >1 ppbv (Baehr et al. 1999).

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6.4.3 Sediment and Soil

A Canadian study estimated that benzene is absorbed by the soil at a rate of 100 tons/year (MacLeod and MacKay 1999). Data from EPA's STORET database (2003–2005) showed that benzene had been positively detected in sediment samples taken at 9% of 355 observation stations with a median level of <5 ppb (EPA 2005f). The concentration of benzene in soil near factories where benzene was produced or used ranged from 2 to 191 ppb (IARC 1982).

Benzene levels ranging from <2 to 191 ppb were recorded in the vicinity of five industrial facilities using or producing benzene (EPA 1979). Sediment levels ranging from 8 to 21 ppb were detected in Lake Pontchartrain in Louisiana (Ferrario et al. 1985). In northern Virginia, approximately 200,000 gallons of liquid hydrocarbons were released from a fuel-storage terminal into the underlying soil. Soil about 1,000 feet from that storage terminal contained benzene gas at a concentration of 1,500 ppm at a depth of 10 feet (Mushrush et al. 1994).

6.4.4 Other Environmental Media

Benzene has been detected in a variety of food. Benzene has been reported to occur in fruits, fish, vegetables, nuts, dairy products, beverages, and eggs (EPA 1982a). Although benzene has been detected in dairy products, there is no evidence of the presence of benzene in either cow's milk or human breast milk (Hattemer-Frey et al. 1990). Eggs had the highest concentrations (2,100 ppb [uncooked] and 500–1,900 ppb [hard-boiled]), followed by haddock (100–200 ppb), Jamaican rum (120 ppb), irradiated beef (19 ppb), heat-treated canned beef (2 ppb), and butter (0.5 ppb). Lamb, mutton, veal, and chicken all had <10 ppb benzene (when the meats were cooked) (EPA 1980b, 1982a). A survey of more than 50 foods collected and analyzed from 1991 to early 1992 (McNeal et al. 1993) revealed that foods (including eggs) without added benzoates contained benzene at levels ≤ 2 ng/g. The level of benzene in foods containing added benzoates in addition to ascorbates (e.g., imitation strawberry preserves, taco sauce, and duck sauce) ranged from <1 to 38 ng/g. In many foods, the presence of benzene is likely to be due to uptake from the air (Grob et al. 1990). This conclusion was supported by the fact that the uptake decreased with a decrease in exposed surface area of foods and contact time with air (Grob et al. 1990).

The U.S. Food and Drug Administration sponsored a 5-year study to determine the amount of volatile organics in food from 1996 to 2000. The results are shown in Table 6-3 (Fleming-Jones and Smith 2003). Benzene was found in cheddar cheese, cream cheese, margarine, butter, sour cream, ground beef, bologna, hamburger, cheeseburger, pork, beef frankfurters, tuna canned in oil, chicken nuggets, chocolate

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Table 6-3. Benzene in Food^a

Food	Number of cases found (n=14)	Concentration minimum- maximum in ppb
Cheddar cheese	2	20–47
Mixed nuts	3	1–6
Ground beef	12	9–190
Pork bacon	6	2–17
Banana, raw	13	11–132
Frankfurters, beef	4	2–11
Cream cheese	3	1–17
Chocolate cake icing	2	2–23
Tuna canned in oil	7	4–13
Fruit flavored cereal	5	2–21
Eggs scrambled	4	2–40
Peanut butter	5	2–25
Avocado, raw	10	3–30
Popcorn, popped in oil	3	4–22
Blueberry muffin	3	3–8
Strawberries, raw	1	1
Cola carbonated	3	1–138
Orange, raw	2	11–15
Coleslaw with dressing	14	11–102
Sweet roll danish	1	3–3
Potato chips	2	2–7
Fruit flavored sherbet	3	3–61
Quarter pound hamburger cooked	11	4–47
Margarine	1	7
Sandwich cookies	3	1–39
Butter	6	4–22
Chocolate chip cookies	2	1–8
Sour cream	2	3–15
Apple pie fresh/frozen	4	2–11
Chicken nuggets fast food	4	2–5
Graham crackers	2	1–9
French fries fast food	3	2–56
Cheeseburger quarter pound	8	5–44
Cheese pizza	2	1–2
Bologna	4	2–44
Cheese and pepperoni pizza	4	8–30
Olive/safflower oil	6	1–46
Sugar cookies	3	8–30
Cake doughnuts with icing	2	3
Popscicle	4	1–10

^aDerived from Fleming-Jones and Smith 2003

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cake icing, sandwich cookie, chocolate chip cookies, graham crackers, sugar cookies, cake doughnuts with icing, french fries, apple pie, cola carbonated beverages, sweet roll Danish, potato chips, cheese pizza, cheese and pepperoni pizza, mixed nuts, fruit-flavored cereal, fruit flavored sorbet, popsicles, olive/safflower oil, scrambled eggs, peanut butter, popcorn popped in oil, blueberry muffins, coleslaw with dressing, raw banana, avocado, oranges, and strawberries. American cheese was the only food tested that did not contain benzene. Foods with the greatest maximum concentration of benzene included ground beef (maximum 190 ppb), raw bananas (maximum 132 ppb), carbonated cola (maximum 138 ppb), and coleslaw with dressing (maximum 102 ppb).

As part of a program to identify possible exposures that may be important in the high incidence of lung cancer among women in Shanghai, China, Pellizzari et al. (1995) qualitatively identified the volatile components emitted during heating of cooking oils to 265 °C. This study found that, on a relative basis, the intensity of the benzene peak in the total ion current chromatogram of vapors from Chinese rapeseed oil (commonly used in wok cooking) was 14-, 6.6-, and 1.7-fold greater than in vapors from peanut, soybean, and other canola (rapeseed) oils, respectively.

Cigarette smoke remains an important source of human exposure to benzene. The amount of benzene measured in mainstream smoke ranged from 5.9 to 73 µg/cigarette (Brunnemann et al. 1990). Larger amounts of benzene were found in sidestream smoke, ranging from 345 to 653 µg/cigarette (Brunnemann et al. 1990). Benzene has been found in vapor from cigarette smoke in concentrations ranging from 3.2 to 61.2 µg/cigarette depending on the brand of cigarette. The amount of tar in the cigarette was not directly related to the benzene concentration (Darrall et al. 1998).

6.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

Exposure to low levels of environmental benzene is unavoidable due to the ubiquitous presence of benzene in the environment from a variety of anthropogenic sources. Benzene can be detected in blood samples. In a study designed to establish reference blood concentrations of benzene and other selected volatile organic compounds in the general population of the United States, Ashley et al. (1994) measured blood benzene levels in 883 people (not occupationally exposed) in the United States who had participated in the Third National Health and Nutrition Examination Survey (NHANES III). Within this group of nonoccupationally exposed subjects, the mean and median blood benzene levels were 0.13 and 0.061 ppb, respectively. Seven nonsmoking subjects from this study group were assessed for blood benzene levels just prior to entering examination vans with limited potential for benzene exposure and at

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the end of a 3-hour period in this environment. Mean blood benzene levels prior to van entry and after 3 hours in the van measured 0.046 ppb (range from not detected to 0.061 ppb) and 0.033 ppb (range from not detected to 0.055 ppb), respectively. Lemire et al. (2004) reported a median blood benzene level of 0.047 ppb in a subgroup of 546 nonsmoking and nonoccupationally exposed subjects from the NHANES III study group. Elevated blood benzene levels may be expected among subjects with potential for elevated exposure to benzene, such as smokers, commuters, gas station attendants, and people who use products that emit benzene.

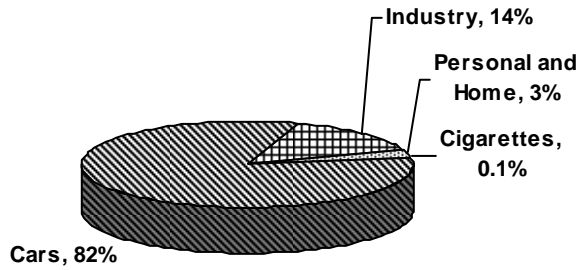
The Total Exposure Assessment Monitoring (TEAM) studies, carried out by the EPA between 1980 and 1990, suggested that for many chemicals, including benzene, the most important sources of pollution are small and close to the person, and that exposures are not clearly correlated with emissions. For example, the TEAM study findings indicated that nearly 85% of atmospheric benzene in outdoor air is produced by cars burning petroleum products and the remaining 15% is produced by industry. Despite the fact that petroleum products contribute to the majority of benzene in the atmosphere, half of the total national personal exposure to benzene comes from cigarette smoke (Wallace 1995). In fact, breath measurements of benzene provided by the TEAM study between 1979 and 1988 identified smoking as the single most important source of benzene exposure for about 40 million U.S. smokers (Wallace 1989b). Even passive exposure to cigarette smoke is responsible for more benzene exposure (about 5% of the total) than the emissions from the entire industrial capacity of the United States (about 3% of the total) (Wallace 1995). A breakdown of the emissions and exposure sources for benzene that was derived from the Los Angeles TEAM study data (Wallace et al. 1991) is given in Figure 6-3. The reason that a relatively small source of emissions can have such a large effect on exposure is the efficiency of delivery. Wallace (1995) reports that one cigarette delivers an average of 55 μg of benzene with nearly 100% efficiency to the smoker. Benzene from industrial sources is dissipated into the atmosphere.

Smokers ($n=200$) in the TEAM study had a mean breath concentration of 15 $\mu\text{g}/\text{m}^3$ (4.7 ppb), almost 10 times the level of 1.5–2 $\mu\text{g}/\text{m}^3$ (0.47–0.63 ppb) observed in more than 300 nonsmokers (Wallace 1989b). Smokers also had about 6–10 times as much benzene in their blood as non-smokers (Wallace 1995). In another study, benzene concentrations were compared in the breath of smokers and nonsmokers and in ambient air in both an urban area of San Francisco and in a more remote area of Stinson Beach, California (Wester et al. 1986). In the urban area, benzene in smokers' breath (6.8 ± 3.0 ppb) was greater than in nonsmokers' breath (2.5 ± 0.8 ppb) and smokers' ambient air (3.3 ± 0.8 ppb). In the remote area, the same pattern was observed. This suggests that smoking represented an additional source of benzene above that of outdoor ambient air (Wester et al. 1986). In 10 of 11 homes inhabited by tobacco smokers,

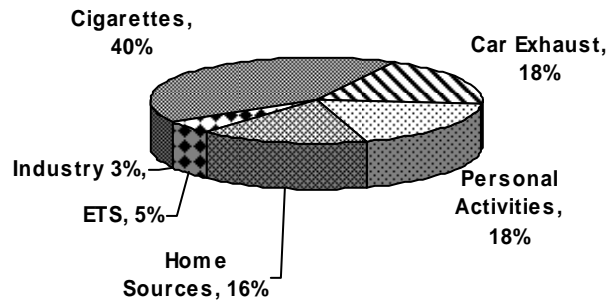
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Figure 6-3. Benzene Emissions and Exposures

Benzene Emissions



Benzene Exposures



Note: A comparison of benzene emission sources (home sources include paints and petroleum products; personal activities include driving and use of consumer products that contain benzene). Data taken from Wallace et al. (1991).

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mean indoor and personal benzene concentrations were 2–5 times higher than outdoor levels (Thomas et al. 1993).

Assuming that the average sales-weighted tar and nicotine cigarette yields 57 μg benzene in mainstream smoke, Wallace (1989a) estimated that the average smoker (32 cigarettes per day) takes in about 1.8 mg benzene per day from smoking. This is nearly 10 times the average daily intake of nonsmokers (Wallace 1989a). On the assumption that intake of benzene from each cigarette is 30 μg , Fishbein (1992) has calculated that a smoker who consumes two packs of cigarettes per day will have an additional daily intake of 1,200 μg .

A British study of rural and urban environments suggests that benzene exposure is greatly affected by proximity to smokers (Duarte-Davidson et al. 2001). Air concentrations of benzene at an urban center in South Hampton averaged about 2.5 ppb, while in a rural location in Hartwell, the average amount of benzene in the air was 0.41 ppb. Air at a smoky pub was found to contain 22 ppb of benzene. Comparing the daily doses of rural nonsmokers, urban nonsmokers, urban passive smokers, and urban smokers, very little difference between the rural nonsmokers' 24 ppb daily dose and the urban nonsmokers' 30 ppb daily dose was found. Passive urban smokers, on average, have a daily benzene exposure dose of 38 ppb of benzene while smokers have a daily exposure dose of benzene of 163 ppb. On average, nonsmokers in urban and rural environments have estimated benzene intakes of 1.15 and 1.5 $\mu\text{g}/\text{kg}$ body weight/day.

Women tend to intake more of benzene per kg body weight than men. Passive smokers' estimated daily intake averages are 2.10 and 1.74 $\mu\text{g}/\text{kg}$ body weight/day for women and men, respectively. Urban women and men smokers' estimated intakes are estimated at 9.00 and 7.46 $\mu\text{g}/\text{kg}$ body weight/day, respectively; this is equivalent to an atmospheric concentration of 8.2 ppb (Duarte-Davidson et al. 2001).

In 1990, a study in Germany analyzed factors that predicted people's exposures to VOCs and found that while smoking was the most significant determinant of benzene exposure, automobile-related activities, such as refueling and driving, were also significant (Hoffmann et al. 2000). Virtually all (99.9%) of the benzene released into the environment finally distributes itself into the air. The general population may be exposed to benzene through inhalation of contaminated air, particularly in areas of heavy motor vehicle traffic and around gas stations. Compared to inhalation, dermal exposure probably constitutes a minor portion of benzene exposure for the general population. Personal sources account for 18% of the total exposure of the general population to benzene. The main personal sources (other than smoking

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cigarettes) are driving or riding in automobiles and using products that emit benzene (paints, adhesives, marking pens, rubber products, and tapes) (Wallace 1989a).

Benzene constitutes 1–2% of most blends of gasoline and is released as a vapor from vehicular emissions. Since benzene is a constituent of auto exhaust and fuel evaporation, people who spend more time in cars or in areas of heavy traffic have increased personal exposure to benzene. Assuming an average benzene concentration of $40 \mu\text{g}/\text{m}^3$ (12.5 ppb) for a moving automobile and an exposure duration of 1 hour/day, the calculated intake for driving or riding in an automobile is $40 \mu\text{g}/\text{day}$ (Wallace 1989a). In an investigation of exposure to methyl *tertiary*-butyl ether (MTBE) in oxygenated gasoline in Stamford, Connecticut, venous blood samples were collected from 14 commuters and from 30 other persons who worked in the vicinity of traffic or automobiles. In addition to MTBE, the samples were analyzed for five chemicals, including benzene. Levels of benzene in the blood of 11 nonsmoking men and women commuters ranged from 0.10 to 0.20 $\mu\text{g}/\text{L}$ (median=0.12 $\mu\text{g}/\text{L}$). Blood benzene levels of 0.29, 0.14, and 0.58 $\mu\text{g}/\text{L}$ were measured in one female and two male smoking commuters, respectively. In 12 nonsmoking male car repair workers, blood benzene levels ranged from 0.11 to 0.98 $\mu\text{g}/\text{L}$ (median=0.19 $\mu\text{g}/\text{L}$); in 8 smoking male car repair workers, levels ranged from 0.17 to 0.67 $\mu\text{g}/\text{L}$ (median=0.42 $\mu\text{g}/\text{L}$). Three nonsmoking male gasoline attendants had blood benzene levels ranging from 0.32 to 0.47 $\mu\text{g}/\text{L}$ (median=0.36 $\mu\text{g}/\text{L}$) (White et al. 1993).

Pumping gasoline can also be a significant source of exposure to benzene. A study conducted between July 1998 and March 1999 that comprised of 39 customers of gasoline self service stations from North Carolina, measured the benzene level in the air around the station as well as the levels of benzene in customers' breath prior to and immediately after fueling (Egeghy et al. 2000). Benzene levels in the air around the station ranged from <0.02 to 11.16 ppm, with a mean (± 1 standard deviation) of 0.91 (± 1.8) ppm. The range of benzene levels in the breath of customers prior to fueling was <0.001–0.022 ppm with a mean (± 1 standard deviation) of 0.0027 (± 0.0034) ppm while the range of benzene levels in the breath of customers after re-fueling was <0.001–0.434 ppm with a mean (± 1 standard deviation) of 0.05 (± 0.081) ppm (Egeghy et al. 2000). Another study reported a benzene concentration of 1 ppm at the breathing-level of a person pumping gas (EPA 1986). Using this concentration and an estimated 70 minutes/year of time spent pumping gasoline, a benzene intake of $10 \mu\text{g}/\text{day}$ has been calculated (Wallace 1989a). In a group of 26 subjects who were not occupationally exposed to benzene, but were exposed to benzene during refueling in Fairbanks, Alaska, median blood benzene levels prior to and immediately following refueling were 0.19 ppb (range 0.08–0.65 ppb) and 0.54 ppb (range 0.13–1.70 ppb), respectively (Backer et al. 1997).

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Gasoline vapors vented into the home from attached garages can also increase indoor air exposure to benzene (Wallace 1989a, 1989b). Depending on airflow from garage to living areas, mean indoor benzene concentrations in houses with a garage were 2–5 times higher than outdoor levels in most homes (Thomas et al. 1993). Benzene levels in four garages during different times in a day ranged from 0.94 to 61.3 ppb. The higher concentrations of benzene in these garages were not only from vehicular activity, but also in varying proportions from stored gasoline, paints, and benzene-containing consumer products (Thomas et al. 1993). Inhalation exposure to off-gassing from benzene-containing products and to evaporative emissions from automobiles in attached garages has been estimated to be 150 µg/day (Wallace 1989a).

A study of human exposure to benzene in the California South Coast Air Basin showed that benzene exposure in that area has decreased greatly since 1989. Adult smokers saw a 28% decrease in benzene exposure from 1989 to 1997, while adult nonsmokers and adolescents saw a decrease in benzene exposure of 67 and 55%, respectively. Where people were being exposed to benzene also changed during that time. Ambient air was the source of 49% of the benzene that nonsmokers were exposed to in 1997, which is less than the 59% from 1987. For smokers in the region, 85% of their benzene exposure was from smoking and 4% was from the ambient air in 1997. This shows an increase in benzene exposure from smoking since 1987 (78%) and a decrease in exposure from the ambient air (12%) (Fruin et al. 2001). The main sources credited with this decrease in exposure are reformulated gasoline and stricter air emission laws as well as smoking control measures.

Another source of exposure to benzene for the general population is the use of domestic wood stoves. It has been estimated that approximately 10% of the space heating in urban areas of the northern United States is from wood burning, with up to 50% in smaller, rural towns (Larson and Koenig 1994). Benzene has been found to be a major component of the emissions from wood burning, especially from efficient flame combustion, and constituted roughly 10–20% by weight of total non-methane hydrocarbons (Barrefors and Petersson 1995). It should be noted, however, that chimney emissions result in much lower human exposure than equally large emissions at the ground level.

Other sources of inhalation exposure to benzene include air around hazardous waste sites, industrial facilities, off-gassing from particle board, and off-gassing from contaminated water during showering and cooking. Based on the TEAM study findings, it appears that the following are not important sources of

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exposure to benzene on a nationwide basis: chemical manufacturing facilities, petroleum refining operations, oil storage tanks, drinking water, food, and beverages (Wallace 1989a).

Average water intake of benzene (assuming a typical drinking water concentration of 0.1 ppb and a consumption of 2 L/day) is 0.2 $\mu\text{g/day}$ (HSDB 2007). According to another estimate, the daily intakes of benzene for a nonsmoking individual (not exposed to secondary smoke) are 1–550 μg (Fishbein 1992).

While most human exposure to benzene is believed to be through inhalation, studies show that benzene can permeate skin with a permeability factor of about 0.14–0.18 cm/hour at 25 °C. The permeability factor was not affected by moisturizer, baby oil, or insect repellent; however, it was affected by temperature (50 °C) and sunscreen with the permeability factors increasing to 0.26 and 0.24 cm/hour, respectively (Nakai et al. 1997).

Individuals employed in industries that use or make benzene or products containing benzene may be exposed to the highest concentrations of benzene. The National Occupational Exposure Survey (NOES), conducted by NIOSH from 1981 to 1983, estimated that approximately 272,300 workers employed in various professions were potentially exposed to benzene in the United States. Approximately half of these workers were employed in general medical and surgical hospitals, and their occupations included nurses and aides, physicians, technicians, technologists, therapists, dieticians, pharmacists, and janitors (NIOSH 1990). The NOES database does not contain information on the frequency, concentration, or duration of exposure; the survey provides only estimates of workers potentially exposed to chemicals in the workplace. The current OSHA permissible limit for an 8-hour TWA exposure to benzene is 1 ppm and a short-term exposure limit in any 15-minute period is 5 ppm (OSHA 2003). The NIOSH recommended exposure limit is 0.1 ppm for an 8-hour TWA and 1 ppm for short-term exposure (NIOSH 1992b). In 1987, OSHA estimated that approximately 238,000 workers were exposed to benzene in seven major industry sectors, including petrochemical plants, petroleum refineries, coke and coal chemicals, tire manufacturers, bulk terminals, bulk plants, and transportation via tank trucks (Table 6-4) (OSHA 1987). Approximately 10,000 workers were estimated to be exposed to TWA concentrations in excess of the 1 ppm standard. This estimate did not include firms covered by the exclusions, firms under jurisdiction of other agencies, or firms involved in the use of products containing small quantities of benzene. The uptake of benzene by workers in a municipal waste incinerator in Germany was assessed by measuring benzene levels in blood (Angerer et al. 1991). No significant difference ($p < 0.05$) in blood benzene levels between workers and controls were detected (mean 0.22 $\mu\text{g/L}$ for nonsmoking workers versus 0.25 $\mu\text{g/L}$

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Table 6-4. Percentage of Employees Exposed to Benzene by Exposure Level and Industry Division^a

Industry sector	Percentage of observations in each exposure category according to range of 8-hour TWA benzene concentrations (ppm)						Total number of employees
	0.0–0.1	0.11–0.5	0.51–1.0	1.1–5.0	5.1–10	10+	
Petrochemical plants ^b		74.6		23.0	2.4	0.0	4,300
Petroleum refineries ^{c,d}	64.6	26.1	4.6	3.8	0.5	0.4	47,547
Coke and coal chemicals ^e	0.0	39.3	27.6	27.5	4.4	1.3	947 ^f
Tire manufacturers ^c	53.4	37.5	6.3	2.8	0.0	0.0	65,000
Bulk terminals ^c	57.8	32.8	5.3	3.7	0.3	0.1	27,095
Bulk plants ^c	57.8	32.8	5.3	3.7	0.3	0.1	45,323
Transportation via tank truck ^c	68.4	23.1	5.3	2.9	0.1	0.2	47,600
Total							237,812

^aDerived from OSHA 1987

^bPercentages represent the portion of workers whose average exposures are in each category.

^cPercentages represent the portion of sampling results in each category.

^dData do not reflect respirator use and sampling biases.

^ePercentages represent the portion of workers whose average exposures are in each category.

^fExcludes workers employed at the coke ovens.

TWA = time-weighted average

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for nonsmoking controls). OSHA requires the use of engineering controls and/or respiratory protection in situations where compliance with the TWA is not feasible (OSHA 1987).

Certain jobs, such as gasoline station workers, firefighters, and dry cleaners, are believed to put people at a higher risk of benzene exposure. In an analysis of literature, it was estimated that workers in the area of crude petroleum and natural gas are exposed to 0.04 ppm benzene, while workers in petroleum refining, gas stations, and crude petroleum pipelines are exposed to 0.22, 0.12 and 0.25 ppm benzene, respectively. This study also showed that fire fighters are exposed to an average of 0.38 ppm benzene (van Wijngaarden and Stewart 2003). Workers from four different dry cleaning facilities in Korea had mean benzene air concentrations ranging from 2.7 to 3.2 ppb. Their exposure to benzene was dependent upon the type of solvent used for cleaning (Jo and Kim 2001). Benzene concentrations of 25.46 and 1,331.29 ppb were found near the kiln and at the rotary line, respectively, inside a hazardous waste incinerator in Turkey (Bakoglu et al. 2004).

A study comparing workers who were exposed to benzene regularly at work to people who were not exposed to benzene at work showed that while the general population in Italy had average blood benzene concentration of 165 ng/L, the people who were exposed to high benzene levels at work had an average benzene blood concentration of 186 ng/L. Immediately following their shift, the average benzene blood level samples from of benzene-exposed workers was 420 ng/L. The average blood benzene levels for smoking and nonsmoking occupationally exposed workers were 264 and 123 ng/L respectively (Brugnone et al. 1998).

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,

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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 subject to increased benzene exposure by inhalation of second-hand smoke. In a study of nonsmoking rural families, urban families, and urban smoking families, infant exposure to benzene was estimated at doses of 15.3, 19.7, and 25.9 $\mu\text{g}/\text{day}$, respectively, with daily intakes of 1.68, 2.16, and 2.55 $\mu\text{g}/\text{kg}$ body weight/day, respectively. For children of the same classification, benzene exposure was measured at doses of 29.3, 37.6, and 49.3 $\mu\text{g}/\text{day}$, respectively, with daily intakes of 0.71, 0.91, and 1.20 $\mu\text{g}/\text{kg}$ bodyweight/day, respectively. For all infants and children, benzene exposure predominantly comes from the indoors (Duarte-Davidson et al. 2001).

Depending on a child's living environment, they may have higher exposure to benzene than adults. In a study of two lower-income areas of Minneapolis, children were found to have average personal benzene exposures of 0.66 and 0.53 ppb in the winter and spring, respectively. The highest concentration of benzene in their environment came from the home with winter and spring concentrations of 0.69 and 0.66 ppb respectively, while the outdoor and school benzene concentrations were 0.41 and 0.19 ppb, respectively (Adgate et al. 2004). In Italy, concentrations of the benzene metabolite, *trans,trans*-muconic acid (MA), was measured in the urine of children from both urban areas in Naples and rural areas in Pollica. The mean urinary concentrations of MA detected for rural and urban children were 48.4 and 98.7 $\mu\text{g}/\text{L}$ (Amodio-Cocchieri et al. 2001). These studies also found no strong link between passive smoking and MA levels. The only factor that affected levels of MA in urine samples was how close the family lived to the road. A study in Rouen, France, compared benzene exposure and concentrations in nonsmoking parents and their children. Despite the fact that the children were exposed to slightly less benzene 3.47 ppb ($11.1 \mu\text{g}/\text{m}^3$) than their parents 4.51 ppb ($14.4 \mu\text{g}/\text{m}^3$), there was no significant correlation between exposure means and urinary metabolite levels (Kouniali et al. 2003).

Benzene concentrations in women and their tissue as well as breast milk have been a major concern. In a study of South Korean housewives living near service stations, indoor, outdoor and breath benzene concentrations averaged 5.73, 3.63, and 3.29 ppm, respectively (Jo and Moon 1999). Benzene has been found in mother's milk (Pellizzari 1982). Benzene was found at mean concentrations of 0.06 $\mu\text{g}/\text{kg}$ in 23 samples of breast milk taken from a children's hospital in Rome (Fabiatti et al. 2004). While this may provide a mechanism by which infants are exposed to benzene, these concentrations are lower than in other foods.

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6.7 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

Individuals who live near hazardous waste sites or near leaking underground fuel storage tanks might be exposed to potentially high concentrations of benzene in their drinking water if they obtain tap water from wells located near these sources. In a series of experiments conducted in a single-family residence from June 11 to 13, 1991, exposure to benzene through contaminated residential water was monitored (Lindstrom et al. 1994). The residential water was contaminated with benzene and other hydrocarbons in 1986. Periodic testing conducted from 1986 to 1991 showed benzene concentrations ranging from 33 to 673 $\mu\text{g/L}$ (ppb). The experiment involved an individual taking a 20-minute shower with the bathroom door closed, followed by 5 minutes for drying and dressing; then the bathroom door was opened and this individual was allowed to leave the house. Integrated 60- and 240-minute whole-air samples were collected from the bathroom, an adjacent bedroom, living room, and in ambient air. Glass, gas-tight syringe grab samples were simultaneously collected from the shower, bathroom, bedroom, and living room at 0, 10, 18, 20, 25, 25.5, and 30 minutes. Two members of the monitoring team were measured for 6 hours using personal Tenax gas GC monitors. For the first 30 minutes of each experiment, one member was based in the bathroom and the other in the living room. Benzene concentrations in the shower head ranged from 185 to 367 $\mu\text{g/L}$ (ppb), while drain level samples ranged from below the detectable limit (0.6 $\mu\text{g/L}$ or ppb) to 198 $\mu\text{g/L}$ (ppb). Analysis of the syringe samples suggested a pulse of benzene moving from the shower stall to the rest of the house over approximately 60 minutes. Peak benzene levels were measured in the shower stall at 18–20 minutes (758–1,670 $\mu\text{g/m}^3$), in the bathroom at 10–25 minutes (366–498 $\mu\text{g/m}^3$), in the bedroom at 25.5–30 minutes (81–146 $\mu\text{g/m}^3$), and in the living room at 36–70 minutes (40–62 $\mu\text{g/m}^3$). The total benzene dose resulting from the shower was estimated to be approximately 281 μg , with 40% via inhalation and 60% via the dermal pathway (Lindstrom et al. 1994).

The major source of exposure to benzene is cigarette smoke. A smoker of 32 cigarettes per day (the U.S. average per smoker) would have a benzene intake of approximately 1.8 mg/day (at least 10 times the average nonsmoker's intake) (Wallace 1989a). Median benzene concentrations in 343 homes with smokers averaged 3.3 ppb compared to 2.2 ppb in 185 homes without smokers. This represents a 50% increase in benzene exposure for nonsmokers exposed to passive smoke compared to nonsmokers not exposed to passive smoke (Wallace 1989a). In a study in Germany, the mean benzene concentrations for frequent smokers and nonsmokers were 6.1 and 2.4 ppb, respectively (Hoffmann et al. 2000).

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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 benzene 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 benzene.

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 benzene are well characterized and allow prediction of the transport and transformation of the compound in the environment.

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 2004, became available in May of 2006. This database is updated yearly and should provide a list of industrial production facilities and emissions.

Benzene is one of the top 20 highest volume chemicals produced in the United States. In 1994, the U.S. production volume of benzene was 14.7 billion pounds (C&EN 1995). The production volume during the 1984–1994 period has increased by 4% annually (C&EN 1995). The United States currently has a benzene production capacity of 11.8 billion liters (SRI 2004). Imports of benzene into the United States have generally ranged from 10,176 to 11,672 million pounds during 2002–2004 (USITC 2005). Exports increased from 21 million pounds in 2002 to 290 million pounds in 2003, but decreased to 145 million pounds in 2004 (USITC 2005). The major use of benzene is in the production of other chemicals (primarily ethylbenzene, cumene, and cyclohexane), accounting for approximately 91% of benzene

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production volume. Benzene is also used in chemical laboratories as a solvent and a reactant (OSHA 1977, 1987), and as an anti-knock agent in unleaded gasoline (Brief et al. 1980; EPA 1985a). The widespread use of benzene as a solvent has decreased in recent years. Many products that used benzene as a solvent in the past have replaced it with other organic solvents; however, benzene may still occur as a trace impurity in these products. Less than 2% of the amount of benzene produced is used as a solvent in such products as trade and industrial paints, rubber cements, adhesives, paint removers, artificial leather, and rubber goods. Benzene has also been used in the shoe manufacturing and rotogravure printing industries (EPA 1978; OSHA 1977). In the past, certain consumer products (such as some paint strippers, carburetor cleaners, denatured alcohol, and rubber cement used in tire patch kits and arts and crafts supplies) contained small amounts of benzene (Young et al. 1978). Other consumer products that contained benzene were certain types of carpet glue, textured carpet liquid detergent, and furniture wax (Wallace et al. 1987). The use of benzene in certain pesticides has been canceled. Benzene-containing wastes, such as commercial chemical products, manufacturing chemical intermediates, and spent solvents, are subject to federal and/or state hazardous waste regulations (HSDB 2007). Currently, the recommended method of disposal is to incinerate solvent mixtures and sludges at a temperature that ensures complete combustion. No additional information on the production, import/export, use, release, or disposal of benzene is needed at this time.

Environmental Fate. Benzene released to the environment partitions mainly to the atmosphere (Mackay and Leinonen 1975). However, the compound can also be found in surface water and groundwater. Benzene is mobile in soil (Karickhoff 1981; Kenaga 1980); however, there is a need for more information on the leachability potential of benzene to groundwater in different soil types. Benzene is transformed in the atmosphere by photooxidation. Biodegradation, principally aerobic, is the most important fate process of benzene in water (Delfino and Miles 1985; McAllister and Chiang 1994; Salanitro 1993) and soil (Gibson 1980; Hopper 1978; Salanitro 1993). Benzene can persist in groundwater. No additional information on the environmental fate of benzene is needed at this time.

Bioavailability from Environmental Media. Benzene can be absorbed following oral exposure (Thienes and Haley 1972), dermal exposure (Blank and McAuliffe 1985; Franz 1984; Laitinen et al. 1994; Lindstrom et al. 1994; Lodén 1986; Susten et al. 1985), and inhalation exposure (Ashley et al. 1994; Avis and Hutton 1993; Boogaard and van Sittert 1995; Brunnemann et al. 1989; Byrd et al. 1990; Etzel and Ashley 1994; Fustinoni et al. 1995; Ghittori et al. 1995; Gordian and Guay 1995; Hajimiragha et al. 1989; Hanzlick 1995; HazDat 2006; Karacic et al. 1995; Kok and Ong 1994; Lagorio et al. 1994a; Laitinen et al. 1994; Lauwerys et al. 1994; Lindstrom et al. 1994; Mannino et al. 1995; Nomiyama and

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Nomiyama 1974a; Ong and Lee 1994; Ong et al. 1995; Pekari et al. 1992; Popp et al. 1994; Rauscher et al. 1994; Rothman et al. 1995; Ruppert et al. 1995; Scherer et al. 1995; Shamy et al. 1994; Srbova et al. 1950). These routes of exposure may be of concern to humans because of the potential for benzene to contaminate the air (Bennett 1987; Black et al. 1980; Brief et al. 1980; Cal EPA 1987; Edgerton and Shah 1992; EPA 1989, 1994d; Glass et al. 1986; Graedel 1978; Mayer et al. 1994; TRI02 2005; Wallace 1989a, 1989b; Wallace and Pellizzari 1986; Wester et al. 1986; Wood and Porter 1987), drinking water (CDC 1994; EPA 1979), and soil (HazDat 2006; Mushrush et al. 1994; TRI02 2005). Information on inhalation exposure and on the absorption of benzene following ingestion of plants grown in contaminated environments near hazardous waste sites would be helpful in determining bioavailability of the compound in these media.

Food Chain Bioaccumulation. Benzene has an estimated low-to-moderate bioconcentration potential in aquatic organisms (Miller et al. 1985; Ogata et al. 1984) and some plants (Geyer et al. 1984). Most of the benzene accumulation on vegetation results from air-to-leaf transfer. Root uptake is not believed to be important (Hattemer-Frey et al. 1990). Biomagnification in aquatic food chains does not appear to be important (Ogata et al. 1984). No further information appears to be needed.

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

Benzene is widely distributed in the environment and has been detected in air (Clayton et al. 1999; EPA 1987a; Mohamed et al. 2002; Morello-Frosch et al. 2000), water (EPA 2001, 2005f; Sauer 1981, USGS 2005), soil (EPA 1979; Ferrario et al. 1985; MacLeod and MacKay 1999; Staples et al. 1985), sediment, and some foods (EPA 1980b, 1982a; Fleming-Jones and Smith 2003). The levels of benzene in air and water are well documented, but there is a need for more current information. Benzene is not expected to be a significant contaminant in aquatic foods (Geyer et al. 1984; Gossett et al. 1983; Miller et al. 1985; Ogata et al. 1984); however, some contamination of food crops consumed by humans may occur, primarily from air-to-leaf transfer (Hattemer-Frey et al. 1990). The total concentration of benzene on exposed food crops consumed by humans was estimated to be 587 ng/kg (Hattemer-Frey et al. 1990). Humans are at risk of exposure to benzene because of its widespread distribution in the environment, particularly in the atmosphere. Releases to the air from gasoline, smoking, and automobile exhaust constitute the major risk of potential exposure for the general population (Wallace 1995). Additional data

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characterizing the concentration of benzene in drinking water, air, and soil surrounding hazardous waste sites would be helpful in assessing human exposure for populations living near these waste sites. In addition, more current data on levels of benzene in foods would be helpful in estimating intake of benzene from food.

Exposure Levels in Humans. Benzene has been detected in human body fluids and tissues such as blood, urine, and fat (Brugnone et al. 1989; Chao et al. 1993; Karacic et al. 1987). Most of the monitoring data have come from occupational studies of specific worker populations exposed to benzene (Inoue et al. 1989b; Karacic et al. 1987; OSHA 1987; van Wijngaarden and Stewart 2003). Biological monitoring studies exist for the general population (Melikian et al. 1994). There is information for background levels in breath of smokers and nonsmokers (Wallace 1989b), baseline blood levels (Karacic et al. 1987), and levels of urinary metabolites in unexposed people (Inoue et al. 1989b). Information on exposure levels for populations living in the vicinity of hazardous waste sites would be helpful in estimating exposure in these groups.

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

Exposures of Children. Benzene levels have been monitored in children and the environments in which they live. This information gives levels found for infants and children in rural and urban area as well as the levels found for children in homes of parents who smoke (Duarte-Davidson et al. 2001). There have been many studies relating oil and petroleum exposure to childhood leukemia and other diseases; however, the majority of these studies have not recorded benzene levels. More information about the exposures of children, particularly those subject to high exposures such as smoking, busy roads, and gasoline stations, are needed.

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

Exposure Registries. In 2001, 1,143 people were included in the benzene subset of the Volatile Organics Compounds subregistry of the National Exposure Registry. These people were exposed to benzene at a site in Texas. Demographic and health information was obtained on all the exposed persons; the information will be updated longitudinally. For those who were identified as exposed and were deceased, a death certificate will be obtained to ascertain cause of death. This activity was carried out by the Exposure and Disease Registry Branch (EDRB), Division of Health Studies (DHS), ATSDR. The

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data became part of public-user data files maintained by ATSDR. The statistical analyses of the baseline data was completed and published (Agency for Toxic Substances and Disease Registry 1995). The information that was amassed in the National Exposure Registry will be used to facilitate the epidemiological research needs to assess adverse health outcomes that may be related to the exposure to this substance.

6.8.2 Ongoing Studies

The Federal Research in Progress (FEDRIP 2005) 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 6-5.

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Table 6-5. Ongoing Studies on the Potential for Human Exposure to Benzene^a

Investigator	Affiliation	Research description	Sponsor
Cho, CY	CHA Corporation; Laramie, Wyoming	Study of the use of microwave technology for superfund site remediation	NIEHS
Fischer, LJ		Understanding potential health hazards from groundwater and soil contamination of chemicals commonly found at hazardous waste sites	USDA
Greenberg, A		Study of critical steps in the ring-opening metabolism of the human carcinogen benzene to muconaldehyde	USDA
Gurian, PL	University of El Paso Texas; El Paso, Texas	Modeling of organic compounds in drinking water	National Institute of General Medical Sciences
Nylander-French, LA	University of North Carolina; Chapel Hill, North Carolina	Assessment of dermal exposure to benzene and naphthalene	NIEHS
Rothman, N		Study of occupational and environmental exposures	Division of cancer epidemiology and genetics
Scow, KM	University of California; Davis, California	Molecular characterization of aquifer microbial communities	NIEHS
Stenzel, PS	National Institute of Health	Study of the link between occupational exposure of carcinogens and cancer	Division of cancer epidemiology and genetics
Thrall, KD	Oregon Health and Science University; Portland, Oregon	Assessment of human volatile organic compounds exposure near Superfund sites	NIEHS
Weisel, CP		Study of the modulation of benzene metabolism by exposure to environmental mixtures	USDA

^aFEDRIP 2005

NIEHS = National Institute of Environmental Health Sciences; USDA = U.S. Department of Agriculture