6. POTENTIAL FOR HUMAN EXPOSURE

6.1   OVERVIEW

Hexachlorobenzene has been identified in at least 107 of the 1,613 hazardous waste sites that have been proposed for inclusion on the EPA National Priorities List (NPL) (HazDat 2002). However, the number of sites evaluated for hexachlorobenzene is not known. The frequency of these sites can be seen in Figure 6-1. All of these sites are located within the United States and none are located in the Commonwealth of Puerto Rico (not shown).

Hexachlorobenzene has not been sold in the United States (as an end-product) since its last registered use as a pesticide was voluntarily canceled in 1984. Hexachlorobenzene is released to the environment almost entirely by industrial activities. Currently, it is released as a by-product during the manufacture of several chlorinated solvents (carbon tetrachloride, perchloroethylene, trichloroethylene, and chlorinated benzenes) or as an impurity in several currently registered pesticides. Additional amounts of hexachloro-benzene are also formed during combustion processes such as incineration of municipal refuse (EPA 1986e) or through use of pyrotechnic mixtures (Karlsson et al. 1991).

Hexachlorobenzene may enter the environment through air emissions and in waste water from facilities involved in the production of solvents or pesticides, combustion products (i.e., flue gases and fly ash) from municipal incinerators, and air emissions released from the use of pyrotechnic mixtures. Nonpoint source dispersal of hexachlorobenzene in both agricultural and urban settings results from its presence as a contaminant in several widely used pesticides. These sources, in addition to hazardous waste site sources, account for the majority of human exposures to hexachlorobenzene.

Hexachlorobenzene is among the most persistent environmental pollutants because of its chemical stability and resistance to degradation. If released to the atmosphere, hexachlorobenzene exists primarily in the vapor phase and degradation is extremely slow. Half-life estimations for hexachlorobenzene in the atmosphere are highly variable, ranging from 0.63 years in tropical/subtropical regions, to 1.94 years in temperate/boreal regions, to 6.28 years in polar regions. A calculated half-life of 1.69 years was attained from a measured hydroxyl rate constant ($2.7x10^{-14}$ cm^3/molecule-second). Long-range global transport is possible from the temperate to the polar regions. Physical removal of hexachlorobenzene from the air

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

Frequency of
NPL Sites

	1-2
	3-4
	5-6
	7-8
	18

Derived from HazDat 2002

may occur via washout by rainfall or snowfall, or via dry deposition. If released to water, hexachloro-benzene will partition from the water column into sediment and suspended particulate matter.

In water, it is a persistent chemical not readily degraded by either abiotic or biotic processes. The half-life value of hexachlorobenzene is estimated to range from 2.7 to 5.7 years in surface water and from 5.3 to 11.4 years in groundwater. Volatilization from the water column is moderately rapid; however, the compound's strong adsorption to particulates and organic matter in water can result in lengthy persistence in the sediment. If released to soil, hexachlorobenzene can volatilize from the soil surface relatively quickly, but will be strongly adsorbed to organic matter and is generally considered immobile with respect to leaching. Its half-life value in soils is estimated to range from 3 to 6 years. Hexachlorobenzene bioaccumulates significantly in both terrestrial and aquatic food chains. Bioconcentration factors (BCFs) as high as 17,000,000 and 21,900 have been reported for lichens and fish, respectively.

Monitoring for hexachlorobenzene has focused primarily in the Great Lakes region where production of chlorobenzenes was historically high. Atmospheric monitoring detected the compound at mean and median concentrations of 36.68 (0.03668 ng/m^3) and 30.94 (0.03094 ng/m^3) pg/m^3, respectively, from 56 air samples in Villeroy, Quebec in 1992 (Poissant et al. 1997). Hexachlorobenzene has also been detected in minute amounts (up to 0.174 ng/L [ppt]) in precipitation samples from the Great Lakes region (Chan et al. 1994) and in precipitation samples collected from Villeroy, Quebec in 1992 (0.04 ng/L) (Poissant et al. 1997). It was also detected in drinking water in three cities on Lake Ontario at a mean concentration of 0.1 ppt (Oliver and Nichol 1982a). Hexachlorobenzene has also been detected in soil and sediment samples in both agricultural areas where it was used as a fungicide on seed grains and in urban soils near production and waste disposal sites (EPA 1985g). Sediment samples (2 cm depth) collected from lakes (Allen-Gil et al. 1997a) and landfills have also been contaminated with hexachloro-benzene (Yasuhara et al. 1999).

Concentrations of hexachlorobenzene have been reported for a variety of commercial fish species in the Great Lakes (Allen-Gil et al. 1997a; Kuchlick and Baker 1998) with concentrations up to 17 ppb in raw fish fillets (Newsome and Andrews 1993; Zabik et al. 1995). In the National Pesticide Monitoring Program, concentrations as high as 700 ppb were reported in whole fish samples collected from contaminated areas (Schmitt et al. 1990). This chemical has also been detected in the fatty tissues and muscle of a wide variety of waterfowl (Foley 1992; Gebauer and Weseloh 1993; Swift et al. 1993), marine mammals (Becker et al. 1997; Langlois and Langis 1995), and mammals (Corsolini et al. 1999). In terrestrial ecosystems, hexachlorobenzene has been detected in lichens (Muir et al. 1993) and in

caribou that graze primarily on lichens (Elkin and Bethke 1995). Concentrations of hexachlorobenzene in these fish and wild game species can be a source of hexachlorobenzene exposure to man.

Hexachlorobenzene residues have been detected in 76% of samples analyzed as part of the National Human Adipose Tissue Survey (FY82) (EPA 1986f). These hexachlorobenzene residues are most likely the result of consumption of low levels of hexachlorobenzene in food, with a calculated yearly intake of 68, 22, and 5 µg for adults, toddlers, and infants, respectively (EPA 1986e). Compared to this, exposure to hexachlorobenzene via inhalation or through drinking water is relatively low. Human exposure may also occur via dermal contact with contaminated soil or sediment or via ingestion of contaminated soil by children. In occupational settings, exposure occurs primarily via inhalation or dermal contact.

Hexachlorobenzene has been identified in at least 107 of 1,613 current or former NPL hazardous waste sites (HazDat 2002). However, the number of sites evaluated for hexachlorobenzene is not known. The frequency of these sites within the United States can be seen in Figure 6-1.

Due to extensive research conducted on hexachlorobenzene, the data reported herein do not encompass complete and thorough research for this chemical.

6.2   RELEASES TO THE ENVIRONMENT

Releases of hexachlorobenzene are required to be reported under SARA Section 313; consequently, data are available for this compound in the Toxics Release Inventory (TRI) (EPA 1995c). According to the TRI, a total of 13,818 pounds (6,267 kg) of hexachlorobenzene was released to the environment in 1998. In addition, an estimated 490 pounds (222 kg) were released by manufacturing and processing facilities to publicly owned treatment works (POTWs) and an estimated 13,328 pounds (6,045 kg) were transferred off-site (TRI98 2000). The TRI data should be used with caution because only certain types of facilities are required to report. This is not an exhaustive list.

Hexachlorobenzene has been identified in a variety of environmental media (air, surface water, leachate, groundwater, soil, and sediment) collected at 107 of 1,613 current or former NPL hazardous waste sites (HazDat 2002).

6.2.1   Air

Releases to the air from the production of chlorinated solvents, where hexachlorobenzene is a minor by-product, have been estimated at 0.3 kg (0.7 pounds) annually and emissions from municipal refuse incineration have been estimated at 85–8,512 kg (187–1,870 pounds) annually (Bailey 2001). Table 6-1 Part B summarizes U.S. hexachlorobenzene emissions in the mid 1990s. As incineration has emerged as a prevalent technology for reducing the bulk of hazardous and nonhazardous wastes, investigations have shown that even with careful controls it is virtually impossible to eliminate unwanted by-products (Products of Incomplete Combustion [PICs]) (Martens et al. 1998). Slight temperature differences on the surfaces of incinerator kiln and reactor components, or other reactions in flues, can lead to the formation of numerous chemical compounds. Where the original wastes contain organochlorines, one type of toxicant may be transformed into another (Dellinger et al. 1989). Hexachlorobenzene, for example, has been detected at concentrations ranging from 20 to 70 ppm in gases emitted by the thermal degradation of toxaphene (Lahaniatis et al. 1992). Since incineration of wastes is a growing global phenomenon, there are concerns that inadequate management attention is given to minimizing PICs. For hexachlorobenzene, and many other organochlorines that can be dispersed widely through atmospheric transport pathways, the virtual absence of data on PICs can lead to complications in estimating environmental releases and mass balances of hexachlorobenzene for regional areas or on a global scale (Lahaniatis et al. 1992).

Nonpoint source dispersal of hexachlorobenzene historically has resulted from its use as a seed fungicide (Beyer 1996) and results from the use of a number of registered pesticides in which it is a contaminant. Eight major pesticides (chlorothalonil, DCPA or Dacthal®, pentachlorophenol or PCP, picloram, PNCB or quintozene, atrazine, simazine, and lindane) in current use contain up to 0.3% hexachlorobenzene as an impurity (see Section 6.2.3 and Table 6-1 Part A). When these pesticides are applied in sprays, they have the greatest potential for release into the air. Most of the pesticide, and the hexachlorobenzene impurities, end up on the top layer of the soil and can become airborne through volatilization of the vapor or adsorbed onto soil particles. The hexachlorobenzene agriculturally applied through the use of these eight pesticides amounts to an estimated 1,270 kg/year (2,790 pounds/year); however, the total amount of hexa-chlorobenzene actually released into the air could not be estimated (Bailey 2001).

Another minor source of hexachlorobenzene releases to the air comes from the use of pyrotechnic mixtures that produce white obscurant screening smokes (Karlsson et al. 1991). These screening smokes

Table 6-1. U.S. Hexachlorobenzene Emissions Summary, Mid 1990s, Part A

	HCB concentration	Average annual U.S. use (kg/year)	HCB emissions (kg/year)
Products containing HCB			
Pesticides			
DCPA (dacthal)	1,000 ppm	677,791	677.8
Atrazine	1 ppm	32,233,523	32.2
Simazine	1 ppm	1,825,391	1.8
Picloram	50 ppm	655,922	32.8
PCNB	500 ppm	627,338	313.7
Chlorothalonil	40 ppm	4,928,591	197.1
Lindane	50 ppm	51,345	2.6
Pentachlorophenol	50 ppm	4,000,000	12.0[a]
Pesticides subtotal			**1,270.0**
Chlorinated solvent usage	1 ppb	282,600,000	0.3
Manufacturing			
U.S. Chemical manufacturing			**399**

Table 6-1. U.S. Hexachlorobenzene Emissions Summary, Mid 1990s, Part B

	Emissions factors (kg HCB/kg)				Calculated emissions (kg/year)		
	Low	Mean	High	Product (kg/year)	Using low factors	Using mean factors	Using high factors
Metals							
Aluminum casting	86	$2.2x10^{-3}$	$4.3x10^{-3}$	HCE $5.88x10^{4}$	51	129	253
Secondary copper	$3.9x10^{-9}$	$3.9x10^{-8}$	$3.9x10^{-7}$	$6.95x10^{8}$	3	27	271
Metals subtotals					**53**	**156**	**524**
Combustion							
Municipal	$2.9x10^{-9}$	$2.9x10^{-8}$	$2.9x10^{-7}$	$2.93x10^{9}$	85	851	8,512
Hazardous wastes	$1.9x10^{-9}$	$1.9x10^{-8}$	$1.9x10^{-7}$	$1.5x10^{6}$	3	29	285
Medical	$2.9x10^{-9}$	$2.9x10^{-9}$	$2.9X10^{-9}$	$7.7x10^{8}$	2	22	223
Coal	$1.3x10^{-12}$	$1.3x10^{-11}$	$1.3x10^{-10}$	$7.91x10^{11}$	1	10	103
Cement	$1.7x10^{-11}$	$1.7x10^{-10}$	$1.7x10^{-9}$	$6.76x10^{10}$	1	11	115
Iron sintering	$1.5x10^{-10}$	$1.5x10^{-9}$	$1.5x10^{-8}$	$1.22x10^{10}$	2	18	183
Sewage sludge	$4.7x10^{-10}$	$4.7x10^{-9}$	$4.7x10^{-8}$	$8.65x10^{8}$	0	4	41
Biomass	$6.0x10^{-12}$	$6.0x10^{-11}$	$6.0x10^{-10}$	$2.28x10^{11}$	1	14	137
Combustion subtotals					**96**	**960**	**9,598**
Total U.S. HCB emissions (kg/year)					**1,818**	**2,785**	**11,791**

[a]Based on 6% volatilization of HCB from pentachlorophenol-treated wood.

Source: Bailey 2001

are used by the military to obscure vision and hide targets, and are used by civilian firefighters during fire training sessions.

The estimated release of 1,535 pounds (698 kg) of hexachlorobenzene to the atmosphere from 12 manufacturing, processing, and waste disposal facilities in 1999 accounted for about 10.5% of the estimated total environmental releases (TRI99 2001). These releases are summarized in Table 6-2. The data from the TRI listed in Table 6-2 should be used with caution, however, since only certain types of facilities are required to report (EPA 1995c). This is not a comprehensive list.

Hexachlorobenzene has been identified in air samples at 7 sites, collected from 1,613 NPL hazardous waste sites, where it was detected in some environmental media (HazDat 2002).

6.2.2 Water

The principal release of hexachlorobenzene into water in the past has been through direct discharges from chemical solvent manufacturing facilities. Total production of chlorobenzenes in the United States has declined from more than 300,000 metric tons (300 million kg or 661 million pounds) in 1970 to about 200,000 metric tons (200 million kg or 441 million pounds) in 1980. The total amount of hexachloro-benzene released as a by-product in production of all chlorinated solvents has been estimated to range from 70,343 to 241,311 kg/year (154,000–532,000 pounds/year) (EPA 1986e). Estimated hexachloro-benzene releases into water from these sources, however, were only 70 kg/year (154 pounds/year) (EPA 1986e).

The estimated release of 8 pounds (4 kg) of hexachlorobenzene to water from two domestic manufacturing and processing facilities in 1999 accounted for about 0.055% of the estimated total environmental releases (TRI99 2001). An additional 13,559 pounds (6,045 kg) were transferred off-site, including to POTWs (TRI99 2001). These releases are summarized in Table 6-2. The data from the TRI listed in Table 6-2 should be used with caution, however, since only certain types of facilities are required to report (EPA 1995c). This is not a comprehensive list.

Hexachlorobenzene has been identified in surface and groundwater samples at 10 and 42 sites, respectively, collected from 1,613 NPL hazardous waste sites, where it was detected in some environmental media (HazDat 2002).

Table 6-2. Releases to the Environment From Facilities That Produce, Process, or Use Hexachlorobenzene

State[b]	Number of facilities	Reported amounts released in pounds per year[a]						
		Air[c]	Water	Underground injection	Land	Total on-site release[d]	Total off-site release[e]	Total on and off-site release
CA	4	7	0	No data	0	7	No data	7
KY	2	0	No data	No data	No data	0	No data	0
LA	5	1,387	7	No data	13,003	14,397	1	14,398
NE	1	5	No data	No data	0	5	No data	5
NJ	1	3	0	No data	0	3	4	7
OH	1	2	1	No data	No data	3	5	8
TN	1	0	No data	No data	No data	0	No data	0
TX	5	131	0	No data	20	151	13,549	13,700
Total	21	1,535	8	0	13,023	14,566	13,559	28,125

Source: TRI99 2001

[a]Data in TRI are maximum amounts released by each facility.
[b]Post office state abbreviations are used.
[c]The sum of fugitive and stack releases are included in releases to air by a given facility.
[d]The sum of all releases of the chemical to air, land, water, and underground injection wells.
[e]Total amount of chemical transferred off-site, including to publicly owned treatment works (POTW).

6.2.3   Soil

Historically, hexachlorobenzene was released to soils directly through its application as a fungicide on
seed grains. Even after use of hexachlorobenzene as a pesticide ceased, an estimated 95% of hexachloro-
benzene produced in the manufacture of chemical solvents was disposed of in land applications (EPA
1986e). Current releases to soils may occur through land disposal of hexachlorobenzene-containing
wastes, from discharges from manufactured facilities, and from use of currently registered pesticides
containing small amounts of hexachlorobenzene. Contamination of soil and sediment with hexachloro-
benzene is frequently secondary to the discharge of contaminated water, from which the hexachloro-
benzene is then adsorbed by the soil or sediment. Sediment samples (2 cm depth) were collected from
four lakes (Feniak, Desperation, Schrader, and Elusive) from the foothills of the Brooks Range, Alaska.
All lakes were oligotrophic, and the pH was neutral to slightly alkaline. The mean concentration among
the six samples was 0.17 ng/g dry weight, derived from the concentrations of the sediments from Lakes
Feniak (0.27 ng/g dry weight), Desperation (0.08 ng/g dry weight), Schrader (0.11 ng/g dry weight), and
Elusive (0.21 ng/g dry weight) (Allen-Gil et al. 1997a). Substantial levels of hexachlorobenzene, ranging
from 0.5 to 460 ppb, have been detected in sediment cores sampled at 1 cm intervals to a sediment depth
of 8 cm in Lake Ontario. The highest sediment contamination in Lake Ontario was found in sediments
1–2 cm in depth which correspond to sediments laid down from 1971 to 1976 during a period of high
U.S. production of chlorobenzenes (Oliver and Nichol 1982a). Although no studies concerning the
release of hexachlorobenzene from landfills have been located for the United States, Yasuhara et al.
(1999) sampled leachates from 11 landfills in Japan. Leachates were sampled at the outlet of the leachate
collecting pipe from open and controlled landfills. Hexachlorobenzene concentrations in the 11 leachate
samples from 11 landfills ranged from not detected to 0.054 ng/L. Of the 11 sites, 6 are currently under
reclamation and at least 3 sites were sampled 12–17 years after completion of reclamation. Site 2, which
was sampled after 14 years of reclamation, had no detectable levels of hexachlorobenzene. Leachates
from sites 3 and 4, which were sampled after 17 and 12 years of reclamation, had hexachlorobenzene
concentrations of 0.033 and 0.054 ng/L, respectively. Site 4 had the highest detection of hexachloro-
benzene concentration. The median concentration among these sites was 0.03 ng/L.

The presence of hexachlorobenzene as an impurity in several currently registered pesticides appears to be
a continuing source of exposure for the general population. The pesticides containing impurities of hexa-
chlorobenzene include: picloram, PCNB or quintozene, chlorothalonil, DCPA or Dacthal®, pentachloro-
phenol or PCP, atrazine, simazine, and lindane (Bailey 2001; Kutz et al. 1991). Estimated emissions of
these eight pesticides is summarized in Table 6-1 Part A. Picloram is a herbicide used in agriculture and

silviculture to control broad-leaf weeds and conifers in grasses (Tomlin 1997). PCNB is used as a fungicide, herbicide, disinfectant, and antifouling ingredient in paint and wood preservatives. It is also a seed dressing agent widely used on turf and ornamental plants (EPA 1986e). PCNB, or quintozene, is used as a soil fungicide on lawns and ornamental crops, as a seed treatment of field crops and vegetables (e.g., barley, corn, cotton, oats, rice, and wheat), and as a slime inhibitor in industrial waters (Budavari 1996; IARC 1974). Chlorothalonil, and Dacthal® are used widely in agriculture, but also are used in home gardens, lawn care, or other applications around residences or in urban areas (Farm Chemicals Handbook 1993). Chlorothalonil (sold under the trade name Bravo®) is a fungicide used on horticultural crops, golf courses, and residential turf, and as a biocide in paints and wood preservatives. Dacthal® is a pre-emergent herbicide widely used on lawns and turf grass (EPA 1986e). Pentachlorophenol (PCP) is a insecticide and fungicide used to protect timber from fungal rot and wood-boring insects (Tomlin 1997). Atrazine and simazine are selective herbicides used to control broadleaf and grassy weeds in corn and other crops (Tomlin 1997). Lindane is an insecticide and fumigant that has been used on a wide range of soil-dwelling and plant-eating insects. It is commonly used on a wide variety of crops, in warehouses, in public health to control insect-borne diseases, and (with fungicides) as a seed treatment (Tomlin 1997).

Although hexachlorobenzene impurities in Dacthal® were as much as 10% in the early 1970s, current levels of hexachlorobenzene contamination in all five pesticides are much lower. A registration standard was issued for picloram in 1985 that specified a maximum hexachlorobenzene content of 0.02%. By the terms of an EPA PCNB rebuttal presumption against registration in 1982, PCNB registrants agreed to reduce hexachlorobenzene contamination levels in PCNB to 0.5% by 1983 and to 0.1% by April 1988. A registration standard was issued by EPA for chlorothalonil in 1984 requiring that hexachlorobenzene contamination not exceed 0.05%. Since 1973, the maximum allowable hexachlorobenzene content of technical grade DCPA (Dacthal®) has been 0.3% (EPA 1986e). As a result of a settlement agreement between the EPA and chemical producers of PCP, the producers agreed to reduce hexachlorobenzene contamination in PCP to no more than 75 ppm (0.0075%). Recent surveillance monitoring by EPA has generally detected <50 ppm (0.005%) hexachlorobenzene contamination in PCP samples (EPA 1994c).

In 1999, 13,023 pounds of hexachlorobenzene were released to land from 21 domestic manufacturing, processing, and waste disposal facilities reporting releases of the compound to the environment (TRI99 2001). No releases (0 pounds) of hexachlorobenzene occurred via underground injection (TRI99 2001). Releases to the environment from facilities that produce, process, or use hexachlorobenzene are summarized in Table 6-2. The data from the TRI should be used with caution since only certain types of facilities are required to report (EPA 1995c). This is not a comprehensive list.

The annual total emissions of hexachlorobenzene in the United States was estimated to be on average 2,785 kg (Bailey 2001). This estimated total was calculated using emission subtotals of 1,270 kg for pesticide use, 0.3 kg for chlorinated solvent use, 399 kg from manufacturing processes, 156 kg from metal industries (using mean emission factors), and 960 kg from combustion sources (using mean emission factors). These data are summarized in Table 6-1.

Hexachlorobenzene has been identified in soil and sediment samples at 76 and 33 sites, respectively, collected from 1,613 NPL hazardous waste sites, where it was detected in some environmental media (HazDat 2002).

6.3 ENVIRONMENTAL FATE

6.3.1 Transport and Partitioning

Hexachlorobenzene has a moderate vapor pressure (1.09×10^{-5} mmHg) (Budavari 1996) and has a very low solubility (0.005815 mg/L) (Yalkowsky 1992) in water (see Table 4-2). If released to the atmosphere, hexachlorobenzene can exist in both the vapor phase in association with particulates (Eisenreich et al. 1981); however, monitoring studies have demonstrated that the vapor phase generally predominates (Ballschmiter and Wittlinger 1991; Bidleman et al. 1989; Lane et al. 1992). Hexachloro-benzene concentrations in the vapor phase represented 92–100% of the total hexachlorobenzene concentration in air samples collected in a monitoring study conducted in Ontario, Canada (Lane et al. 1992). Although physical removal of hexachlorobenzene from the atmosphere is possible via both wet and dry deposition (Howard 1990), the compound is hydrophobic, and somewhat resistant to wet deposition scouring unless it becomes sorbed to airborne dust or cloud condensation nuclei. Its resistance to wet deposition tends to slow down its transfer across the equatorial areas between the northern and southern hemispheres. At high latitudes, the typically cold air conditions encourage dry deposition of aerosols (Ballschmiter and Wittlinger 1991; Lane et al. 1992; Wania and Mackay 1993). These factors lead to atmospheric pathways as a major transport mechanism for hexachlorobenzene. The net residence time of hexachlorobenzene in the atmosphere is significantly less than 1 year, and is based on physical translocation and not on chemical transformation (Ballschmiter and Wittlinger 1991). The atmospheric mechanisms can operate over large distances, perhaps on a hemispheric scale (Kelly et al. 1991). At higher latitudes, transfers and partitioning back to aqueous systems may be accentuated by the cold, dry air. Since these areas are not zones of hexachlorobenzene production or use, the presence of such contaminants has attracted considerable attention in research studies (Ballschmiter and Wittlinger 1991).

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The Henry's law constant value for this compound (5.8×10^{-4} atm-m^3/mol) (Ten Hulscher et al. 1992) suggests that releases of hexachlorobenzene to surface water will volatilize at a moderate rate, and that volatilization can be a significant transfer mechanism (Thomas 1990). If released to water, adsorption of hexachlorobenzene to sediment or soil particulates is also expected to be significant on the basis of the high organic carbon partition coefficient (K_{oc}) value (EPA 1981a) (see Table 4-2). Since hexachloro-benzene will adsorb strongly to soil particles and sediments, it may build up in the bottom sediments of large aquatic systems such as the Great Lakes. The concentration of hexachlorobenzene in Lake Ontario sediment is about 1 million times higher than in Lake Ontario water (Oliver and Nichols 1982a). In Lakes Superior, Michigan, and Huron, the very large sizes, considerable depths, and appreciable retention times have allowed much of the historical organochlorine burden to become immobilized in bottom sediments, with a concomitant reduction in the levels of hexachlorobenzene found in surface waters. In the upper Great Lakes, the vast majority of the ongoing mass balance inputs seem related to atmospheric deposition (Eisenreich et al. 1981). For other parts of the Great Lakes system, and especially the connecting waters and Lakes Erie and Ontario, mass balance studies can give different impressions. Detailed studies on Lake Erie suggest that well over half of the hexachlorobenzene inputs come from wet or dry atmospheric deposition processes (270 kg/year or 600 pounds/year) (Kelly et al. 1991). However, a significant portion (110 kg/year or 240 pounds/year) also comes from river pathways such as the highly polluted Detroit River via surface runoff and contaminated sediments resuspended during their passage through the connecting waters. Because of its strong adsorption to sediment, most of the hexachloro-benzene is transported with silt and sediment particles during floods, and very little is dissolved in the water. Quemerais et al. (1994) reported that 23% of the hexachlorobenzene in whole water samples collected from the St. Lawrence River was associated with the dissolved phase, while 77% was associated with the particulate phase. Although Rostad et al. (1988) did not quantify the percentage of hexachloro-benzene found in the dissolved versus the particulate phase, they reported that hexachlorobenzene was one of the organic compounds associated with suspended sediment particles in several river systems within the Mississippi River drainage area. In a 1999 study, Rostad et al. (1999) measured hexachloro-benzene concentrations in suspended sediment particles within the Mississippi River in the spring and summer of 1989 and 1990. Concentrations of hexachlorobenzene fluctuated between Winfield, Missouri and Belle Chasse, Louisiana during the spring and the summer; however, in both seasons, the concentration was higher at Chasse, Louisiana (1.9 ng/g in the spring; 2.1 ng/g in the summer) than at Winfield, Missouri (1.2 ng/g in the spring; 0.13 ng/g in the summer). Furthermore, Rostad et al. (1999) estimated annual transport of hexachlorobenzene via suspended sediments to the Gulf of Mexico by averaging the St. Francisville, Louisiana and Belle Chasse, Louisiana daily loads, averaging the spring and summer values for hexachlorobenzene, and projecting annual transport. The Gulf of Mexico receives

an estimated 145 kg/year hexachlorobenzene via suspended sediment particles of the Mississippi River
(Rostad et al. 1999).

Because of its high sorption characteristics, hexachlorobenzene is expected to be immobile in soil and
unlikely to leach into groundwater (Swann et al. 1983). At waste disposal sites, where bioremediation
techniques are proposed to reduce the mass of carbon-containing contaminants, there is the potential for
augmenting the leaching properties of hexachlorobenzene and other organochlorines. The lipid materials
in bacterial cell membranes may lead to a repartitioning of hexachlorobenzene sorbed to soil colloids.
This can lead to a phenomenon called facilitated transport where the mobility of hydrophobic pollutants
such as hexachlorobenzene adsorbed to soils may be enhanced by biosorption on bacteria and move into
aquifers along with the bioremedial bacterial cultures (Lindqvist and Enfield 1992). Except at NPL sites,
however, this potential source of groundwater pollution would seem to be remote.

The Henry's law constant value (5.8×10^{-4} atm-m^3/mol) (Ten Hulscher et al. 1992) suggests that hexa-
chlorobenzene released to moist soil will volatilize at a moderate rate. Several studies have indicated that
volatilization may be a significant mechanism for loss of hexachlorobenzene released to soils. Beall
(1976) studied the persistence of aerially applied hexachlorobenzene (equivalent to 10 ppm in the top
5 cm of soil) in a simulated pasture maintained for 19 months in a greenhouse. Twenty hours post-
application, the top 2 cm of soil contained 5.6 ppm (air-dry basis). Hexachlorobenzene concentrations in
the top 2 cm of soil found after 0.5, 1, 6.5, 12, and 19 months were 45.2, 24.4, 7.9, 4.7, and 3.4% of
day 1 values, respectively. However, no significant change in the deeper 2–4 cm layer of soil which
averaged hexachlorobenzene residues of 0.11 ppm was observed over the 19-month study.
Concentrations of hexachlorobenzene in pasture grass on day 1 were 1,060 ppm, but 2 weeks
postapplication only 15.6 ppm (1.5% of day 1 residues) were detected. Although hexachlorobenzene
volatilized fairly rapidly from plant and soil surfaces, it could be persistent within the soil if treated
surface soil were mixed into deeper soil layers by plowing. Nash and Gish (1989) studied the
volatilization and dissipation of several halogenated pesticides from moist sandy loam soil under
controlled conditions in micro-agroecosystem chambers maintained in a greenhouse for 154 days. As soil
temperature increased from 5 to 35 EC, the percentage of originally applied hexachlorobenzene that was
detected in the soil compartment decreased, while the percentage detected in the air increased suggesting
that hexachlorobenzene volatilizes more rapidly with increased soil temperature.

The high octanol/water partition coefficient (K_{ow}) value (Hansch et al. 1995) for hexachlorobenzene (see
Table 4-2) suggests that bioconcentration and biomagnification of hexachlorobenzene are likely to occur

to a significant degree. Veith et al. (1979) measured biological concentration factor (BCF) values of 16,200 for fathead minnows, 21,900 for green sunfish, and 5,500 for rainbow trout exposed to hexa-chlorobenzene at 15 EC for 32 days. Oliver and Niimi (1983) studied bioconcentration in rainbow trout exposed to water containing 2 concentrations of hexachlorobenzene (0.32 and 8 ng/g [ppb]) for 119 and 105 days, respectively. The BCF values were 12,000 and 20,000 at the 0.32 and 8 ng/g (ppb) exposure levels, respectively. Chaisuksant et al. (1997) conducted a bioconcentration experiment using mosquito fish (*Gambusia affinis*) as well. The fish were exposed to three concentrations of eight chemicals, and the highest concentration used consisted of a mixture with each chemical present in a concentration equal to 1/20 of the LC_{50}. After 96 hours of exposure, the BCF of hexachlorobenzene in mosquito fish was 3,730. In 1992, the Chemicals Inspection and Testing Institute (1992) conducted a bioconcentration experiment using carp (*Cyprinus carpio*). After an 8-week exposure period to concentrations of 0.5 and 0.05 µg/L of hexachlorobenzene, the BCFs in carp were 11,000–27,000 and 6,000–30,000, respectively.

In a model aquatic ecosystem to which hexachlorobenzene was introduced, the BCF averaged 740 for algae *(Oedogonium cardiacum)*, 1,500 for the snail *(Helisoma sp.)*, 910 for the daphnid *(Daphnia magna)*, 1,610 for the mosquitofish *(G. affinis)*, and 10,610 for the catfish *(Ictalurus punctatus)* (Isensee et al. 1976). The authors concluded that biomagnification was also occurring within the food chain because the catfish (highest trophic level species) accumulated over 10 times more hexachlorobenzene than the next highest trophic level (snails and mosquitofish), and these species accumulated 1.5–2 times more than the lowest food chain species, the daphnids (primary consumers) and the algae (primary producers). In studies of natural populations of white bass in Lake Erie, Russell et al. (1995) concluded that biomagnification of hexachlorobenzene did not occur. These authors did report biomagnification in Lake Erie fish populations was occurring for several other organic chemicals with log K_{ow} values greater than 6.1. Hexachlorobenzene bioaccumulation factors (BAFs) in aquatic fish species has been measured by Burkhard et al. (1997) in the Bayou d'Inde of the Calcasieu River system near Lake Charles, Louisiana. This field study resulted in log BAF values of 5.80 for blue crab (*Callinectes Sapidus*), 6.03 for mummichog fish (*Fundulus Heteroclitus*), 6.30 for Atlantic croaker (*Micropoganias undulatus*), and 6.68 for gulf menhaden (*Brevoortia Patronus*). The author further compared the measured values obtained to previously reported and predicted BAF values. A comparison of these data with that of Pereria et al. (1988) reveals a difference that was not considered significant by the author. Pereria et al. (1988) determined log BAF values of 4.03 for blue crab, 4.56 for Atlantic croaker, 4.12 for spotted sea trout *(Cynoscion nebulosis)*, and 4.61 for blue catfish (*Ictalurus furcatus*).

Connell et al. (1988), using data derived from terrestrial laboratory microcosm studies with two oligochaete worms (*Limnodrilus hoffmeisteri* and *Tubifex*), suggest that interstitial water may be the source from which lipophilic compounds such as hexachlorobenzene in sediment are bioconcentrated by oligochaetes. The concentration factor was 0.54 for hexachlorobenzene during a 110-day exposure test. In a similar study of the earthworm *(Eisenia andrei)* raised in field-contaminated soil, Belfroid (1995) reported a biota-to-soil accumulation factor of 0.507 for hexachlorobenzene. These authors also noted an initial elimination half-life of 1.9 days followed by a period of slower elimination with a half-life of 47 days. In a terrestrial food web study conducted on the Niagara Peninsula of Ontario, Canada from 1987 to 1989, Hebert et al. (1994) reported concentrations of hexachlorobenzene increased from the lower trophic level species to higher trophic level predator species. Concentrations of hexachlorobenzene were not detected in soil or plant material; however, concentration ranges were 0.2–0.3 µg/kg (ppb) (wet weight) in earthworms, not detected to 1.0 µg/kg (ppb) in mammals, 2.0–2.4 µg/kg (ppb) in starlings, 1.8–2.5 µg/kg (ppb) in robins, and 2.1–5.1 µg/kg (ppb) in kestrels at the top of the food web.

Several agricultural species of plants have been shown to bioaccumulate hexachlorobenzene in their roots and in portions of the plant growing closest to the soil (Scheunert et al. 1983; Smelt and Leistra 1974). There were marked differences in the BCFs among the various plant species with higher residues associated with those species with the higher lipid content (Schroll et al. 1994; Smelt and Leistra 1974). The roots of the plants generally accumulate higher concentrations of soil-applied hexachlorobenzene than do the aerial parts of the plants. This has been demonstrated for hexachlorobenzene in sugar beets, carrots, turnips, wheat, and pasture grass (Scheunert et al. 1983; Smelt and Leistra 1974). The edible root portion of carrots accumulated the highest concentration of hexachlorobenzene (1,250 ppb with a plant/soil BCF of 19) for a human food source. The measured BCF for hexachlorobenzene was 210 and 470 in soy bean plants via root uptake from water containing 0.2 and 0.4 µg/L hexachlorobenzene, respectively (Kraaij and Connell 1997). Concentrations of hexachlorobenzene were also high in grass roots (810 ppb) and the lower (0–5 cm) part of the blade (220 ppb) (Smelt and Leistra 1974). It is assumed that hexachlorobenzene in soil is mobile mainly in the gas phase. Gaseous hexachlorobenzene can diffuse directly into the plant root or evaporated hexachlorobenzene can be taken up by plant foliage (Ecker and Horak 1994). Some studies have reported no marked translocation of the hexachlorobenzene from roots to shoots or vice versa (Schroll et al. 1994). Residues in the roots were associated only with root uptake from the soil; those residues in the shoots were only from foliar uptake from the air. Recent studies by Ecker and Horak (1994), however, suggest that root uptake of hexachlorobenzene by oil pumpkins occurred and that the hexachlorobenzene was translocated into the shoots. These authors believe that uptake of dissolved hexachlorobenzene from soil solution into the roots may not have been

considered earlier as a source for the translocated compound. Pollutants entering the plant from contaminated soil via roots would be translocated in the plant by the xylem while gas- and particle-phase deposition onto leaves or uptake by the stomata would be translocated by the phloem (Simonich and Hites 1995). Concentrations of hexachlorobenzene in agricultural crops can be directly transferred to humans via direct consumption, while concentrations in grass and other forage crops can be indirectly transferred to humans via consumption of dairy products or meat from cattle grazing on contaminated pastures.

Lichen from Northwestern Ontario and South Central Ontario exhibited BCF values of 1.7×10^7 and 8.8×10^6, respectively, for hexachlorobenzene. These BCF values were calculated as the concentration of hexachlorobenzene in the lichen (ng/m^3 wet weight) compared to the concentration in the air (ng/m^3) (Muir et al. 1993). Furthermore, bioconcentration of hexachlorobenzene by lichen, a major forage food for caribou can transfer hexachlorobenzene to recreational hunters and natives peoples that consume caribou in their diets (Elkin and Bethke 1995).

6.3.2   Transformation and Degradation

6.3.2.1   Air

Few studies regarding atmospheric degradation of hexachlorobenzene have been located. Photodegradation of hexachlorobenzene in its vapor phase, or as an adsorbable on silica gel, has been reported as not occurring when hexachlorobenzene was irradiated with ultraviolet radiation of wavelength 290 nm for 6 days (Parlar 1978); however, production of HCl and CO_2 was observed when hexachlorobenzene was irradiated at 230 nm (Parlar 1978). In the troposphere, hexachlorobenzene is probably photochemically stable, but degradation in the stratosphere by photo-dissociation by shorter-wavelength, higher energy-ultraviolet light may be a mechanism for atmospheric degradation in the stratosphere.

The photo-oxidation half-life (first-order kinetics) of hexachlorobenzene based on the vapor phase reaction with hydroxyl radicals in air was estimated to range from 156.4 days to 4.2 years by Howard et al. (1991) and from 158 days to 4.3 years by Kwok and Atkinson (1995). Wania and Mackay (1995) estimated the degradation half-life (first-order kinetics) of hexachlorobenzene to be 0.63 years (230 days), 1.94 years (708 days), and 6.28 years (2,292 days) in air in tropical/subtropical regions, temperate/boreal regions, and polar regions, respectively. Brubaker and Hites (1998) measured a hydroxyl rate constant of 2.7×10^{-14} cm^3/molecule-second at 25 EC, corresponding to a calculated half-life of 1.69 years. Thus, atmospheric degradation is extremely slow and is not an efficient method of hexachlorobenzene removal.

6.3.2.2   Water

Hexachlorobenzene is a persistent compound and is not significantly degraded by either abiotic or biodegradation processes in water. It is resistant to the types of hydrolysis reactions that can help degrade other organochlorines or organophosphates, and it is not markedly subject to photolytic decay (Mill and Haag 1986). Biodegradation of organic priority pollutants in a waste water inoculum system was studied by Tabak et al. (1981). Among the 57 environmental pollutants tested, hexachlorobenzene at concentrations of 5 and 10 ppm was among the more slowly biodegraded compounds tested, with only 21–56% degradation in 1 week. Further biodegradation after the first week was minimal in three subsequent 7-day subcultures with settled domestic waste water as microbial inoculum. Biodegradation of hexachlorobenzene in waste water treatment systems is expected to be slow.

An aquatic ecosystem study conducted by Schauerte et al. (1982) shows that hexachlorobenzene will mainly absorb onto particulate matter in the water and then be transported to the bottom sediment. After 145 weeks, the study found a significant amount (10–20%) of hexachlorobenzene remaining in the upper sediment layers (0–10 cm). The half-life (first-order kinetics) of hexachlorobenzene was estimated to range from 2.7 to 5.7 years in surface water and from 5.3 to 11.4 years in groundwater based on unacclimated aqueous aerobic biodegradation (Howard et al. 1991).

Hirsch and Hutzinger (1989) conducted surface water photolysis test with hexachlorobenzene in a laboratory setting and found that this process may occur. A first order rate constant (1.3×10^{-6}/sec) corresponding to a half-life of 6.17 days for the photolysis of hexachlorobenzene in distilled water in a photochemical reactor equipped with mercury arc lamps was reported. Hexachlorobenzene in an acetonitrile:water mixture exposed to wavelengths of 290 nm for 8 hours resulted in a 33.5% loss of hexa-chlorobenzene. 1,2,3,4,5-Pentachlorobenzene (76.8%), 1,2,3,5-tetrachlorobenzene (1.2%), 1,2,4,5-tetrachlorobenzene (1.7%), and 1,2,4-trichlorobenzene (0.2%) were found as hexachlorobenzene transformation products (Choudhry et al. 1986). In another experiment, hexachlorobenzene in a water:acetonitrile solution was exposed to sunlight and resulted in a half-life of 70 days (Mill and Haag 1986). The studies above found photolysis of hexachlorobenzene a feasible loss process with half-lives ranging from 6.17 to 70 days.

Hydrolysis is not expected to be an important fate process. EPA (1987g) observed zero hydrolysis after 13 days for pH values of 3, 7, and 11 at 85 EC.

Hexachlorobenzene can also be eliminated by ozone reactions. Roche and Prados (1995) conducted a study and compared the efficiencies of ozone and ozone-hydrogen peroxide systems in removing hexachlorobenzene from water treatment processes. The concentration of ozone during the experiments was 70 mg O_3/L. When ozone was applied, 11–14% of an initial concentration of 1.0 µg/L hexachlorobenzene was removed. This removal increased to 15–48% when hydrogen peroxide and ozone were applied together.

6.3.2.3   Sediment and Soil

Hexachlorobenzene is a persistent compound and is not significantly degraded in soils by either abiotic or biodegradation processes. In a year-long laboratory study, soil treated with 0.1, 1.0, and 10 ppm of hexachlorobenzene was stored under aerobic (sterile and nonsterile) conditions and under anaerobic nonsterile conditions in covered containers to retard hexachlorobenzene volatilization (Isensee et al. 1976). No loss in the soil-incorporated hexachlorobenzene was observed at any treatment concentration or under any storage condition. Beck and Hansen (1974) measured a half-life (first-order kinetics) of 3–6 years for hexachlorobenzene in soils. Anaerobic biological dechlorination of hexachlorobenzene has also been demonstrated in anaerobic sewage sludge (Fathepure et al. 1988). These authors reported that hexachlorobenzene was dechlorinated to tri- and dichlorobenzenes under anaerobic conditions when sewage sludge was maintained in serum bottles and incubated in the laboratory. Complete biotransformation of a 50 ppm inoculum occurred within 3 weeks. Two routes of dechlorination were observed. The major route was hexachlorobenzene → pentachlorobenzene → 1,2,3,5-tetrachlorobenzene → 1,3,5-trichlorobenzene; the minor route was hexachlorobenzene → pentachlorobenzene → 1,2,4,5-tetrachlorobenzene → 1,2,4-trichlorobenzene → dichlorobenzenes (i.e., 1,2-, 1,3-, and 1,4-dichlorobenzene). Yuan et al. (1999) also conducted an anaerobic biological dechlorination study using sewage sludge obtained from the Di-Hua Municipal Sewage Treatment Plant in Taipei, Japan. All experiments were performed using 25 mL serum bottles containing 9 mL of sewage sludge and various concentrations of hexachlorobenzene. After a 20-day incubation period, 98% of the 2 mg/L hexachlorobenzene remained, while addition of 1,2,3-trichlorobenzene adapted consortium accelerated dechlorination which occurred at a calculated rate of 0.29 mg/L/day. At hexachlorobenzene concentrations of 2, 5, and 10 mg/L, complete dechlorination occurred within 6 days and at the 50 mg/L concentration, dechlorination occurred in 8 days. Optimal dechlorination occurred at a rate of 0.29 mg/L/day, pH of 7.0, and 30 EC. According to Yuan et al. (1999), dechlorination occurred via the following path: hexachlorobenzene → pentachloro-benzene → 1,2,3,4-tetrachlorobenzene + 1,2,3,5-tetrachlorobenzene → 1,2,4-trichlorobenzene + 1,2,3-trichlorobenzene + 1,3,5-trichlorobenzene → 1,2-dichlorobenzene + 1,4-dichlorobenzene. From this and other

studies, it is clear that in a time frame of days to years, anaerobic biodegradation may remove hexachloro-benzene from soils.

The Chemicals Inspection and Testing Institute (1992) of Japan conducted an aerobic sludge study to test hexachlorobenzene biodegradation. Hexachlorobenzene, present at 100 mg/L, reached 0% of its theoretical biological oxygen demand (BOD) in 2 weeks using an activated sludge inoculum at 30 mg/L and the Japanese Ministry of International Trade and Industry (MITI) test; thus, aerobic degradation is not an important fate process.

Likewise, in areas of the Great Lakes region with a long history of hexachlorobenzene contaminated waste water discharges affecting aquatic sediments, the concentrations of hexachlorobenzene in the sediments can be significant (see Section 6.4.2). Susarla et al. (1997) examined the transformation of hexachlorobenzene in fresh water lake (Lake Kasumigaura, Japan) sediments under anaerobic conditions. Dechlorination occurred after a 4-day lag phase and was complete in 32 days. The calculated rate of dechlorination was 0.110/day. Hexachlorobenzene transformation pathway under sulfidogenic conditions resulted in hexachlorobenzene 6 pentachlorobenzene 6 1,2,3,5-tetrachlorobenzene 6 1,3,5-tri-chlorobenzene 6 1,3-dichlorobenzene. Under methanogenic conditions the pathway was as follows: hexachlorobenzene 6 pentachlorobenzene 6 1,2,3,4-tetrachlorobenzene 6 1,2,4-trichlorobenzene 6 1,4-dichlorobenzene. After almost a year, 98% of the hexachlorobenzene was dechlorinated to 1,3- and 1,4-dichlorobenzene (Susarla et al. 1997). In another experiment, dechlorination of hexachlorobenzene in an estuary sediment collected from the mouth of Tsurumi river occurred at a rate of 0.0256/day with a half-life of 27.1 days (Masunaga et al. 1996). Thus, aquatic sediment degradation of hexachlorobenzene occurs in a month to a year.

6.4   LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

Reliable evaluation of the potential for human exposure to hexachlorobenzene depends in part on the reliability of supporting analytical data from environmental samples and biological specimens. In reviewing data on hexachlorobenzene levels monitored 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.

6.4.1 Air

Hexachlorobenzene is moderately volatile, but is usually not detected in ambient air samples except at very low concentrations. Ambient air sampling was conducted by the EPA at selected locations in the United States from 1976 to 1979. In 1976, 49% of the 43 composite samples collected in four locations contained detectable concentrations of hexachlorobenzene, with a mean value of 0.1 ng/m^3. In 1977, 12% of the 34 samples collected in three locations contained hexachlorobenzene, with a mean concentration of 1.5 ng/m^3. In 1978, the compound was not detected in any of the 33 samples collected at three locations and in 1979, hexachlorobenzene was detected in 31% of the 89 samples collected in eight locations, with a mean of 0.5 ng/m^3 (detection limit: 0.1 ng/m^3) (EPA 1985g). Eisenreich et al. (1981) reported atmospheric concentrations of hexachlorobenzene in the Great Lakes region ranging from 0.09 to 0.28 ng/m^3. Results of airborne samples collected between 1990 and 1993 from the Great Lakes region by the Integrated Atmospheric Deposition Network are provided by Hoff et al. (1996). The annual mean gas-phase and particulate-phase concentrations of hexachlorobenzene were 98 and 0.2 pg/m^3, respectively, in samples from Lake Superior near Eagle Harbor, Michigan, 120 and 0.1 pg/m^3, respectively, in samples from Lake Michigan near Sleeping Bear Dunes, Michigan, 80 and 0.2 pg/m^3, respectively, in samples from Lake Erie near Sturgeon Point, New York, and 130 and <0.1 pg/m^3, respectively, in samples from Lake Ontario near Point Petre, Ontario. From July 1988 to September 1989, 143 air samples were collected at Egbert, Ontario, Canada and were analyzed for PCB and organochlorine concentrations. Hexachlorobenzene was detected at concentrations ranging from a minimum of 0.04 pg/m^3 (0.00004 ng/m^3) to a maximum of 640 pg/m^3 (0.64 ng/m^3) (annual mean >54 pg/m^3 (0.054 ng/m^3) (Hoff et al. 1992). Inhalation exposure was estimated to be 0.3 ng/m^3 in urban air (Burton and Bennett 1987). Hexachlorobenzene measured in air in Villeroy, Quebec in 1992 found mean and median concentrations of 36.68 (0.03668) and 30.94 pg/m^3 (0.03094 ng/m^3), respectively, from 56 air samples (Poissant et al. 1997). A meteorological station located in a semirural area outside Lancaster, England was the site of air samples. Four air samples per day (taken at 6-hour intervals) were taken for 7 days. The minimum, maximum, and mean concentrations of hexachlorobenzene in these samples were <28.8, 76.1, and 39.3 pg/m^3, respectively. The authors found an absence of a cycle in the concentrations of hexachlorobenzene and concluded that the compound was breaking through the polyurethane foam plugs due to its relatively high vapor pressure (Lee et al. 2000).

Hexachlorobenzene air concentrations have also been measured in urban and rural areas in France. Atmospheric fallout from the urban area, Paris, and the rural area, La Ferté-sous-Jouarre, was collected in raw form as bulk precipitation. Hexachlorobenzene concentration in rural fallout measured in

February–July 1992 and January –September 1993 ranged from 2.5 to 4.5 ng/L and from 0.3 to 4 ng/L, respectively. For the same time periods, urban fallout measured 1.8–17 and 0.3–5.6 ng/L, respectively (Chevreuil et al. 1996). The mean concentrations of hexachlorobenzene in precipitation samples collected in the Great Lakes region from 1986 to 1991 ranged from 0.145 ng/L (ppt) at Sibley Park on Lake Superior, to 0.108 ng/L (ppt) at Pelee Island in Lake Erie, to 0.174 ng/L (ppt) at Wolfe Island in Lake Ontario (Chan et al. 1994). The mean and median concentrations of hexachlorobenzene from eight precipitation samples collected from Villeroy, Quebec in 1992 were 0.04 and 0.05 ng/L, respectively (Poissant et al. 1997). Precipitation samples collected between 1990 and 1993 from the Great Lakes region by the Integrated Atmospheric Deposition Network were analyzed. The annual mean concentration of hexachlorobenzene in these precipitation samples were 0.1 ng/L in samples from Lake Superior near Eagle Harbor, Michigan, 0.06 ng/L in samples from Lake Michigan near Sleeping Bear Dunes, Michigan, 0.04 ng/L in samples from Lake Erie near Sturgeon Point, New York, and 0.3 ng/L in samples from Lake Ontario near Point Petre, Ontario (Hoff et al. 1996). The concentrations of hexa-chlorobenzene in air, particulate matter, and rain from Galveston Bay, Texas were 87.3±103.3, 0.4±0.5, and 42.5 pg/m^3 (not detected–48.1 pg/m^3), respectively, between 1995 and 1996 (Park et al. 2001). The median levels of hexachlorobenzene in ambient air samples collected in Zagreb, Croatia in 1997 were 29 pg/m^3 (range, 0.5–49 pg/m^3) in the northern residential region of Ksaverska and 31 pg/m^3 (range, 15–61 pg/m^3) in the southern region near a landfill (Romaníc and Krauthacker 2000). The average concentration of hexachlorobenzene in air at Lake Malawi, in southeast Africa, from February 1997 to May 1998, was 11±7.5 pg/m^3 (Karlsson et al. 2000).

Nonoccupational exposure to hexachlorobenzene for residents of two U.S. cities (Jacksonville, Florida and Springfield, Massachusetts) was studied over three seasons: summer 1986, spring 1987, and winter 1988 (Whitmore et al. 1994). The study focused primarily on inhalation exposures with primary environmental monitoring consisting of 24-hour indoor and outdoor air. For the Jacksonville, Florida, population, the estimated mean hexachlorobenzene concentration ranged from 0.3 to 1.3 ng/m^3 for indoor air and from not detected to 0.2 ng/m^3 for outdoor air. For the Springfield, Massachusetts population, mean exposures were much less. The estimated hexachlorobenzene concentrations ranged from not detected to 0.1 ng/m^3 for indoor air and no detectable concentrations of hexachlorobenzene for outdoor air.

Extremely high concentrations of hexachlorobenzene in air have been detected in areas close to production and disposal sites in both outdoor and indoor air. Mann et al. (1974) measured hexachloro-benzene concentrations ranging from 70 to 23,296 ng/m^3 near chlorinated solvent and pesticide

manufacturing facilities; air levels near a chemical waste landfill were as high as 16,000 ng/m^3 (EPA

1975b). Hexachlorobenzene has been detected at 11,000 ng/m^3 in flue gas effluents from a municipal

refuse-fired steam boiler in Virginia, and at 9.5 ng/m^3 in flue gas effluents from a refuse-derived fuel fired

power plant in Ohio (Tiernan et al. 1985). Air concentrations of hexachlorobenzene inside industrial

plants can be as high as 150,000 ng/m^3 (Currier et al. 1980); air concentrations inside a pesticide

production facility were measured at 22,000 ng/m^3 (Davis and Morgan 1986).

6.4.2   Water

Drinking water in three cities in the Lake Ontario vicinity contained hexachlorobenzene ranging from

0.06 to 0.2 ppt (mean of 0.1 ppb), about the same as water from the lake (Oliver and Nichol 1982a).

Hexachlorobenzene was detected in ambient water samples from two of the Great Lakes and their

tributary rivers. Mean concentrations of hexachlorobenzene in Lake Ontario, Lake Huron, and the Grand

River were 0.06 ppt (range, 0.02–0.1 ppt), 0.04 ppt (range, 0.02–0.1 ppt), and 0.06 ppt (range,

0.02–0.1 ppt), respectively. In the Niagara River, concentrations of 0.02–17 ppt were detected with the

highest value measured downstream of a waste disposal site (Oliver and Nichol 1982a). Widely varying

measurements in this river may be attributed to the fact that measurements were near the limit of the

analytical detection limits. More recently, hexachlorobenzene was detected in 42% of whole water

samples (dissolved plus particulate phases) collected during 1991 in the St. Lawrence River and several of

its tributaries. Hexachlorobenzene concentrations detected in the St. Lawrence River ranged from not

detected to 0.09 ng/L (mean 0.01 ng/L [ppt]) (Quemerais et al. 1994). Hoff et al. (1996) obtained and

presented water concentration data from a 1992 sampling study. Hexachlorobenzene concentrations in

Lakes Superior, Michigan, Huron, Erie, and Ontario were 0.01, 0.014, 0.007, 0.014, and 0.045 ng/L,

respectively. In remote European mountain lake waters, the concentrations of hexachlorobenzene were

8.4±11 pg/L at Redó, Spain, 4.0±1.8 pg/L at Gossenkölle, Austria, and 6.2±1.0 pg/L at Øvre Neådalsvatn,

Norway (Vilanova et al. 2001). The concentrations of hexachlorobenzene in microlayer and subsurface

Mediterranean seawater off the coast of Alexandria, Egypt were on average, 27.3±17 and 12±6.9 ng/L,

respectively (Abd-Allah 1999).

A study was conducted from 1974 to 1975 to collect and analyze surface water samples from sites of

known hexachlorobenzene contamination along the Mississippi River near an industrial area in Geismar,

Louisiana (EPA 1976a). The maximum hexachlorobenzene concentration detected in water was

90.3 ppb. A concentration of 2 ppb has been measured in the Mississippi River near Baton Rouge,
Louisiana (Laska et al. 1976).

Industrial waste water samples contained hexachlorobenzene levels as high as 300 ppb (EPA 1976b;
Schmitt et al. 1990). Effluent concentrations of hexachlorobenzene from four Canadian plants in the
Great Lakes region ranged from 0.001 to 0.002 ppb (0.0015 ppb mean) (Oliver and Nichol 1982a).

Hexachlorobenzene concentrations were measured in water at an uncontrolled hazardous waste site near
Bayou Baton Rouge, Louisiana (Davis and Morgan 1986). Surface water samples collected from a
containment pond used for disposal of wastes from both rubber production and manufacture of
chlorinated organics at the site contained up to 8,100,000 ppb hexachlorobenzene.

6.4.3   Sediment and Soil

Mean concentrations of hexachlorobenzene in lake sediments in the Great Lakes ranged from 0.2 to
97 ppb with the highest values measured in Lake Ontario. Deeper sediment layers (1–2 cm) had even
higher concentrations of hexachlorobenzene (460 ppb) than surface (0–1 cm) samples (270 ppb), with the
peak value corresponding to deposition in the years 1971–1976 declining to 270 ppb in 1976–1980
(Oliver and Nichol 1982a). In 1992, 2 cm deep bed sediment samples were collected from the South
Platte River at Henderson, Colorado and Cache La Poudre River near Greeley, Colorado. The sediment
contained 1.5 and <1 µg/kg, dry weight, hexachlorobenzene, respectively. The authors concluded that
this concentration was correlated to the hexachlorobenzene concentrations found in urban and agricultural
lands in the South Platte River Basin (Tate and Heiny 1996). Outside of the United States, 12 sediment
samples were collected in June 1993 near known discharges from municipalities and industries from Lake
Ladoga, Russia. Hexachlorobenzene concentrations were 3.58 and 14.6 ng/g in 2 out of the 12 samples,
and was not detected in the remaining 10 samples (Ristola et al. 1996).

In 1972, hexachlorobenzene levels in soil were detected in 11 of 1,485 agricultural sites (0.7%) in
37 states, ranging from 0.01 to 0.44 mg/kg (10–440 ppb). In 1973, only 1 of 1,470 sites (0.1%) contained
hexachlorobenzene at 10 ppb, while in a 1976 study of 11 states, only 2 of 391 sites (0.5%) contained
hexachlorobenzene at concentrations ranging from 10 to 20 ppb (EPA 1985g). The majority of these
agricultural sites with hexachlorobenzene detections were under cultivation with wheat or other seed
grains (e.g., barley, oats, rye), which is consistent with the registered agricultural uses of hexachloro-
benzene at that time. The authors concluded that the occurrence of hexachlorobenzene residues in

agricultural soils was associated with hexachlorobenzene's registered pesticide uses rather than general environmental or industrial contamination.

In a study of 40 urban areas sampled during the 1970s, 7 sites (17.5%) contained detectable hexachlorobenzene concentration in soil ranging from 0.01 to 0.59 mg/kg (10–590 ppb) (EPA 1985g). In the levees of the Mississippi River near Baton Rouge, where the river water contained 2 ppb hexachlorobenzene, the soil contained 167 ppb (Laska et al. 1976). In contrast to agricultural soils, hexachlorobenzene residues in urban soils resulted from releases during the manufacture, use, or disposal of hexachlorobenzene or hexachlorobenzene-containing wastes rather than the use of hexachlorobenzene as a pesticide (EPA 1985g).

Hexachlorobenzene concentrations were measured in soil and sediment at several uncontrolled hazardous waste sites in several states (Davis and Morgan 1986). Hexachlorobenzene concentrations of up to 20,000 ppb were measured in soil at a scenic highway site near Bayou Baton Rouge, Louisiana, while concentrations in sediment of 39,500 ppb were measured from a bayou bank downstream of the site. Soil cores from a monitoring well (25–27 feet deep) were as high as 400,000 ppb, and as high as 90,000 ppb in soils collected at 40–41 feet deep (Davis and Morgan 1986). Soil and sediment collected from a disposal site near Sorrento, Louisiana contained 62,000 and 130,000 ppb hexachlorobenzene, respectively. Soil collected at a Crystal City, Texas pesticide disposal site was found to contain 20,000 ppb hexachlorobenzene. A maximum hexachlorobenzene concentration detected in soil at an industrial site of known contamination near Geismar, Louisiana was 53,130 ppb (Laseter et al. 1976).

Sediment concentrations of hexachlorobenzene vary widely from relatively unpolluted areas to those areas used extensively for disposal of hexachlorobenzene-containing wastes. Sediment hexachlorobenzene concentrations from San Luis Pass, located near industrial areas of West Galveston Bay, Texas ranged from 0.05 to 1.5 ppb (dry weight) with a mean of 0.49 ppb (Murray et al. 1981).

Hexachlorobenzene concentrations in marine sediment samples collected from an industrialized area of the harbor in Portland, Maine ranged from <0.03 to 0.37 ppb (mean 0.14 ppb) (Ray et al. 1983). Concentrations of hexachlorobenzene in sediment from the Niagara River watershed in the vicinity of several hazardous waste disposal areas ranged from 8,000 to 30,000 ppb (Elder et al. 1981). The average concentration of hexachlorobenzene in surficial sediments of the Kaohsiung coast (southwestern Taiwan), which receives wastewater from the largest industrial city in Taiwan (Kaohsiung City), ranged from 1.7 to 24.7 ng/g (Lee et al. 2000a).

6.4.4   Other Environmental Media

Concentrations of hexachlorobenzene have been detected in several species of fish and shellfish. Hexa-
chlorobenzene concentrations were determined for several species of marine organisms collected from
San Luis Pass near Galveston Bay, Texas (Murray et al. 1981). Mean concentrations of hexachloro-
benzene at were 0.49 ppb wet weight for flounder (species unspecified), 0.65 ppb for longnose killifish
(Fundulus similis), 0.88 ppb for brown shrimp *(Penaeus aztecus)*, 9.6 ppb for blue crab *(Callinectes
sapidus)*, and 0.71 ppb for the dwarf squid *(Lollingnucula brevis)*. Oysters *(Crassotrea virginica)*
collected at the lower end of the Houston Ship Channel were found to contain hexachlorobenzene
concentrations ranging from 0.31 to 1.41 ppb with a mean of 0.63±0.39 ppb (Murray et al. 1980). The
Sheboygan River in Wisconsin is another area of concern for contamination of organochlorine pesticides
in fish due to the existence of wetlands, urban and developed land, woodland, and agricultural land
surrounding this river. In addition, the lower segment of the river has a history of shipping, industrial and
municipal activities, and dredging, including the existence of a landfill designated as a federal superfund
site. Schrank et al. (1997) collected white suckers (*Catostomus commersoni*) from two sites of the
Sheboygan River; one site was 1 to 2 km from the mouth of the river and the other was 50 km from the
mouth of the river, which served as the reference site. The fish collected from both sites contained less
than detectable residues of hexachlorobenzene along with other organochlorine compounds, thus
minimizing the risk of exposure to hexachlorobenzene from this river.

DeVault (1985) reported concentrations of hexachlorobenzene in whole fish composites collected from
the Great Lakes during 1980 and 1981 ranged from <0.002 to 3.47 mg/kg (<2–347 ppb). Hexachloro-
benzene concentrations in fresh water trout (4–6+ years old) from the Great Lakes region ranged from
8 to 127 ppb with the highest concentration found in a fish collected near the discharge of the Niagara
river into Lake Ontario (Oliver and Nichol 1982a). In another study of Great Lakes fish species,
Newsome and Andrews (1993) reported hexachlorobenzene concentrations in fish fillet composites
ranged from 0.22 ng/g (ppb) in bullhead to 9.05 ng/g (ppb) wet weight in trout in lake areas with open
fisheries. Zabik et al. (1995) reported that skin-off processing and selected cooking methods reduced
hexachlorobenzene residues in chinook salmon and carp harvested from the Great Lakes. Concentrations
of hexachlorobenzene averaged 0.017 ppm (17 ppb) and 0.011 ppm (11 ppb) (wet weight) in raw and
cooked salmon fillets, respectively, and averaged 0.005 ppm (5 ppb) and 0.003 ppm (3 ppb) in skin-on
and skin-off fillets, respectively. The average percentage loss of hexachlorobenzene from chinook
salmon fillets by baking, charbroiling, and canning was 40%. Losses of hexachlorobenzene residues from
carp fillets were slightly greater than 40% (Zabik et al. 1995). Walleye, siscowet, carp, and whitefish

were collected for organochlorine pesticides analysis from Lake Superior along the Apostle Islands region during 1991 and 1992. Walleye and carp had hexachlorobenzene concentrations below the limit of quantification, while siscowet and whitefish measured concentrations of 3.2 and 2.8 ng/g wet weight of tissue, respectively (Gerstenberger et al. 1997). Organisms sampled during the summer of 1994, from the Keweenaw Peninsula of Lake Superior, contained measured hexachlorobenzene concentrations ranging from 0.8 to 1.8 ng/g wet weight in smelts, 3.0–4.3 ng/g wet weight in herrings, 4.7–8.4 ng/g wet weight in bloaters, 1.1–4.1 ng/g wet weight sculpins, <0.1–0.2 ng/g wet weight in mysis, 0.8–1.4 ng/g wet weight in limnocalanus, 0.8 ng/g wet weight in amphipods, and 1.7–3.1 ng/g wet weight in lake trout (Kuchklick and Baker 1998). Grayling and lake trout were collected from four lakes (Feniak, Desperation, Schrader, and Elusive) from the foothills of the Brooks Range, Alaska. All lakes were oligotrophic, and the pH was neutral to slightly alkaline. Fifty-six grayling liver samples and 39 grayling muscle samples were analyzed for hexachlorobenzene concentration, and mean and median values were derived. In the 56 grayling liver samples, the mean and median concentrations were 0.65 and 0.48 ng/g dry weight, respectively. The 39 grayling muscle samples had mean and median concentrations of 0.33 and 0.22 ng/g dry weight, respectively. In lake trout, the mean and median concentrations in 33 liver samples were 1.15 and 0.87 ng/g dry weight, respectively, and in 34 muscle samples were 0.46 and 0.26 ng/g dry weight, respectively (Allen-Gil et al. 1997a). Hexachlorobenzene concentrations in sea organisms from the Barents Sea were as follows (units=ng/g lipid weight): copepods (13.5), euphausids (16.5), amphipods (19.5), polar cod (39±1.7), and cod (65±7.7) (Borgå et al. 2001). In 1991, the concentrations of hexa-chlorobenzene in amphipods, isopods, and sculpins from the Bothnian Bay (Baltic Sea) were 340 (n=3), 370 (n=5), and 37 (n=3) ng/g dry weight, respectively (Strandberg et al. 2000).

The bioaccumulative tendencies of hexachlorobenzene have made it a candidate for monitoring in the U.S. Fish and Wildlife Service National Pesticide Monitoring Program (Schmitt et al. 1990) and the National Study of Chemical Residues in Fish which was started in 1986 (NSCRF) (EPA 1992b). Maximum hexachlorobenzene tissue concentrations (wet weight) detected in whole fish were 700, 130, 120, and 410 ppb in the 1976–1977, 1978–1979, 1980–1981, and 1984 sampling years, respectively. The geometric mean tissue concentration was 10 ppb for 1976–1977 and <10 ppb for all other sampling years (Schmitt et al. 1990). The highest hexachlorobenzene concentrations in the 1984 sampling period (410 ppb) were detected in whole fish from the Tombigbee River, Alabama in the vicinity of a pesticide production facility where concentrations during all sampling years had been the highest nationally. The most recent national results from the ongoing study conducted by NSCRF show that hexachlorobenzene was detected at 46% of the 362 sites surveyed for fish tissue analysis. The mean hexachlorobenzene concentration for fish tissue samples analyzed in this program was 5.8 ppb. The five sites with the

highest concentrations are listed in Table 6-3 (EPA 1992b). The Freeport, Texas site is near a pesticide

plant and the other four sites are close to a variety of chemical manufacturing plants. The Calcasieu

River, Louisiana site is close to a Superfund site involving a variety of organic solvents (EPA 1992b).

Hazardous waste dumping during the early 1940s and 1950s contaminated the Devil's Swamp, Louisiana

with chlorinated hydrocarbons, which has greatly affected fish species. As fish is an important food

6. POTENTIAL FOR HUMAN EXPOSURE

Table 6-3. Sites with the Five Highest Concentrations of Hexachlorobenzene in Fish[a]

Whole body hexachlorobenzene concentration (ppb; wet weight)	Type of sample (fish)	Location
913	Sea catfish	Brazos River, Freeport, Texas
202	Catfish	Bayou D'Inde, Sulfur, Louisiana
93.7	Carp	Mississippi River, St. Francisville, Louisiana
85.5	White sucker	Quinipiac River, North Haven, Connecticut
75	Sea catfish	Calcasieu River, Moss Lake, Louisiana

[a]From the EPA 1992b National Study of Chemical Residues in Fish

source for the community surrounding this area, concentrations of contaminants are of great concern.
Levels of hexachlorobenzene in various fish species collected from Devil's Swamp, Louisiana, was
compared to those from a control site, Tunica's Swamp, Louisiana. Mean hexachlorobenzene
concentrations calculated from concentrations of 13 different edible fish species tissues were 23.65 ng/g
compared to 2.0 ng/g calculated from 10 different edible fish species from Tunica's Swamp (Tchounwou
et al. 1998).

Hexachlorobenzene has been detected in tissues of various wildlife species throughout North America,
but especially in wildlife indigenous to the Great Lakes region. Swift et al. (1993) reported mean
concentrations of hexachlorobenzene of 0.02 ppm (20 ppb) wet weight (0.04 ppm [40 ppb] lipid weight
basis) and 0 ppm wet weight (0.07 ppm [70 ppb] lipid weight basis) in mesenteric and subcutaneous fat
and breast tissue, respectively, of common goldeneye waterfowl wintering in New York state. The
detection limit in this study was 0.002 ppm. Gebauer and Weseloh (1993) reported that the geometric
mean hexachlorobenzene concentrations of 0.4 and 0.9 µg/kg (ppb) in muscle tissue in mallard ducks
using a contaminated sediment site, and sewage lagoon site, respectively, as a resting and feeding area
were significantly greater than levels found in ducks using a natural marsh area. Foley (1992) reported
hexachlorobenzene residues in muscle tissues of several species of ducks and geese collected in New
York State in 1983–1984. Statewide residues were 64 ppb (wet weight) for buffleheads, 49 ppb for
scaups, 26 ppb for mallards, 20 ppb for black ducks, 6 ppb for wood ducks, and 11 ppb for Canada geese.
Adult sea otters that had died along the coast of California were collected by the U.S. Fish and Wildlife
Service and the California Department of Fish and Game. Hexachlorobenzene concentrations in liver,
kidney, and brain tissues were 0.74–8, 0.28–2.6, and 0.28–0.74 ng/g wet weight, respectively (Nakata et
al. 1998). The mean hexachlorobenzene concentration for 207 wild mink liver tissue samples, collected
from 1991 to 1995 in the Northwest Territories, Canada from seven mink communities, ranged from
0.21 to 0.67 ng/g wet weight (Poole et al. 1998). Snail composite samples, without shells, were collected
from two lakes (Feniak and Elusive) from the foothills of the Brooks Range, Alaska. All lakes were
oligotrophic, and the pH was neutral to slightly alkaline. The mean concentration among these six
samples was 0.15 ng/g dry weight with a median of 0.10 ng/g dry weight (Allen-Gil et al. 1997a).

Hexachlorobenzene has also been detected in the eggs of various wildlife species in the Great Lakes
region and Canada. Yamashita et al. (1992) reported hexachlorobenzene residues ranges of 8–36 ng/g
(ppb) and 18–26 ng/g (ppb) on a wet weight basis in the eggs of the double-crested cormorant and the
Caspian tern, respectively, collected during 1988 from the Great Lakes region. Somers et al. (1993)
reported geometric mean concentrations of 0.013 µg/g (13 ppb) (wet weight) of hexachlorobenzene in

double-crested cormorant eggs collected in southern Alberta, Canada. Elliott and Martin (1994) reported mean hexachlorobenzene concentrations in sharp-shinned hawk eggs in south central Ontario ranging from 0.010 to 0.051 mg/kg (10–51 ppb) from 1986 to 1989. Hexachlorobenzene concentrations in Cooper's hawk eggs ranged from 0.005 to 0.012 mg/kg (5–12 ppb) during the same period. Cobb et al. (1994) reported mean residues of 18.0 ng/g (18 ppb) in the chorio-allantoic membranes removed from great blue heron eggs collected from Puget Sound, Washington. Jarman et al. (1996) conducted an experiment with prairie falcon eggs that were collected from eyries in northern and central California between 1989 and 1991. Addled and unhatched eggs were frozen until chemical analysis. The following are the geometric mean concentrations (in mg/kg wet weight) of hexachlorobenzene at their respective sampling sites: Frog/Hand Nest 800; Pig Cyn 17; Crowley Tower 11; Willow Sp. 8.0; Goat Rock 10; Mt. Dome 20; and Mt. Diablo 81. Mean hexachlorobenzene residues in peregrine falcon eggs from Rankin Inlet (Hudson Bay, Canada) were 0.03 µg/g wet weight (n=2; range 0–0.15 µg/g wet weight) between 1982 and 1986, and 0.030 µg/g wet weight (n=20; range 0–0.165 µg/g wet weight) between 1991 and 1994 (Braune et al. 1999).

Hexachlorobenzene residues were also detected in snapping turtle eggs collected from a wetland area on Lake Ontario. Residues ranged from 43.9, 16.6, and 20.9 ng/g (ppb) (wet weight) to 494.7, 282.1, and 262.2 ng/g (ppb) (lipid weight) for the first five eggs, a composite of five eggs, and the last five eggs, respectively (Bishop et al. 1995). Bishop et al. (1996) conducted another study with snapping turtle eggs that were collected from nests at five locations from the Great Lakes Basin in 1990–1991. Thee eggs were analyzed for hexachlorobenzene and the results were compared to data collected from the same sites in the years 1981, 1984, 1988, and 1989. Residue concentrations for all locations and their respective years are listed in Table 6-4. Based on the results, the hexachlorobenzene concentration was the highest in eggs from Cootes Paradise and lowest in eggs from Algonquin Park. Although the concentration of hexachlorobenzene at Cootes Paradise has been continuously declining since 1984, residues in eggs from this site are consistently higher than those from the other sites, and are at least 3 times higher than eggs from the next most contaminated site, Lynde Creek. On the whole, the hexachlorobenzene mean concentration from the five sites in the Great Lakes Basin showed a decrease from the year 1984 to 1990 (Bishop et al. 1996).

Langlois and Langis (1995) reported that the concentration of hexachlorobenzene in the blubber of beluga whales from the St. Lawrence Estuary to Northern Quebec Province ranged from 0.22 to

Table 6-4. Residue Concentrations (ng/g) in Snapping Turtle Eggs
from Five Locations Collected in 1981–1991

	Year				
Sites	1981	1984	1988	1989	1990/1991
Algonquin Park	20	NA	10	3	NA
Cranberry Park	NA	NA	40	30	NA
Lynde Creek	NA	70	80	60	80
Cootes Paradise	NA	350	300	170	170
Big Creek Marsh	50	NA	NA	40	NA
Rondeau Park	NA	60	NA	20	NA

NA = Snapping turtle eggs were not available or were not collected during those years.

Source: Bishop et al. 1996

0.93 mg/kg (220–930 ppb) wet weight. Consumption of blubber and organ meats from these whales by native peoples may constitute a potential health risk if these tissues are a significant part of the diet (Langlois and Langis 1995). In 1997, Gauthier et al. (1997) analyzed blubber biopsies from Northwestern Atlantic Balaenopterid whales summering in the Gulf of St. Lawrence. Samples were collected in the summer and fall of 1991 and 1992 from 21 minke, 15 fin, 6 blue, and 8 humpback whales. Hexachlorobenzene concentrations in the blubber of these whales were 101, 96, 110, and 177 ng/g lipid, respectively, and in all species, the concentrations were higher in males (140 ng/g lipid) than in females (103 ng/g lipid).

Becker et al. (1997) analyzed the blubber of 7 pilot whales, 5 harbor porpoises, 12 beluga whales, 2 northern fur seals, and 2 ringed seals that were obtained from the U.S. National Biomonitoring Specimen Bank. Hexachlorobenzene concentration ranges were 43–465 ng/g wet weight for pilot whales, 223–1,070 ng/g wet weight for harbor porpoises, 81.9–952 ng/g wet weight for beluga whales, 138–741 ng/g wet weight for northern fur seals, and 125–156 ng/g wet weight for ringed seals (Becker et al. 1997). Elkin and Bethke (1995) reported that hexachlorobenzene was the most predominant organo-chlorine residue present in tissues of the caribou collected in the Northwest Territory of Canada. Residues ranged from a lipid corrected mean of 32.83 ng/g (ppb) in fat from Bathurst caribou to 129.41 ng/g (ppb) in Lake Harbor animals (Baffin Island). Consumption of meat and organs from these range animals by native peoples, including native American populations of Inuits in Alaska, may constitute a potential human health risk if these tissues are a significant part of the diet.

The Florida Department of Environmental Protection and the Florida Marine Research Facility in St. Petersburg, Florida maintain archives of tissues obtained from dead Florida Manatees (*Trichechus manatus latirostris*). In 1996, Ames and Van Vleet (1996) obtained and analyzed 19 manatee samples from the Florida EPA. Of these samples, hexachlorobenzene was found at concentrations of 0.038 and 0.085 µg/g in one blubber and one liver sample, respectively. The authors did not find a correlation between the contamination in manatees by hexachlorobenzene and other pesticides and the location in which the manatees were found dead; thus, the authors concluded that these manatees must have been contaminated elsewhere, especially since manatees are known to travel long distances.

Corsolini et al. (1999) analyzed chlorinated hydrocarbon concentrations in muscle and fat samples of the red fox collected from Sienna, Italy in 1992. Hexachlorobenzene mean concentrations in muscle and fat were 0.47 and 0.23 µg/g lipid basis, respectively, and were the lowest of all of the chlorinated hydrocarbons that were tested (Corsolini et al. 1999).

Sitarska et al. (1995) collected tissue samples from 18 cows just after slaughtering, always from the same parts of the studied organs. Hexachlorobenzene mean concentrations were 1.394 µg/kg wet mass in the ovaries, 1.061 µg/kg wet mass in the mammary glands, and 0.550 µg/kg wet mass in the liver.

Beyer (1996) subjected earthworms (*Lubricous terrestris*) to hexachlorobenzene in artificial soil. Over the course of 28 weeks, hexachlorobenzene concentrations in these earthworms ranged from 1.8 to 3 ppm. Beyer (1996) also conducted three 8-week experiments in which earthworm survival rates were 97, 99, and 100%, respectively.

Hexachlorobenzene was detected in composited milk samples collected through the U.S. Pasteurized Milk Network during 1990–1991 (Trotter and Dickerson 1993). The milk samples were collected at approximately 63 sites located in the United States, Puerto Rico, and the Panama Canal Zone. Hexa-chlorobenzene was detected in trace amounts in one sample collected in each of seven metropolitan areas (Cristobal, Panama Canal Zone; Kansas City, Missouri; Los Angeles, California; Memphis, Tennessee; Portland, Oregon; Spokane, Washington; Wichita, Kansas) and was detected at 0.001 ppm (1 ppb) in one sample from Rapid City, South Dakota.

Pesticide residue data from the FDA Adult Total Diet Study conducted from 1980 to 1982 were evaluated by Gartrell et al. (1986). These authors reported that hexachlorobenzene was detected in a wide variety of domestic foods: dairy products, meat, fish and poultry, oils and fats, and sugar and adjuncts. The highest mean concentrations of hexachlorobenzene were detected in oils and fats (0.9 ppb) and in meat, poultry, and fish (0.2 ppb). Concentrations of hexachlorobenzene in ready-to-eat foods were monitored for 10 years from 1982–1991 through the FDA's Revised Market Basket Survey. Hexachlorobenzene was detected in 618 samples of 81 different foods at a mean concentration of 0.0006 µg/g (0.6 ppb) (KAN-DO Office and Pesticide Teams 1995). In food composites from six Canadian cities, the mean concentration of hexachlorobenzene in positive samples (4.8% of 913 total analysis) was 0.5 ng/g (Newsome et al. 2000). The U.S. Food and Drug Administration monitored domestic and imported apples and rice by collecting random samples for a period of 12 months beginning in October, 1993. Hexachlorobenzene was not determined to be in violation according to the concentration limits set for this compound in any of the domestic and imported apple and rice samples; however, it was found in 1 out of 612 imported rice samples (0.02 ppm), but this concentration does not violate any limit set by the EPA (Roy et al. 1997). The concentrations and occurrences of hexachlorobenzene residues in butter from Spain (n=36, 89% positive) and the rest of Europe (n=20, 70% positive) were 5.864±3.171 ng/g wet weight and 3.022±3.964 ng/g wet weight, respectively (Badia-Vila et al. 2000).

The frequency of detection of hexachlorobenzene in the FDA Total Diet Study conducted in 1982–1984 was 9% (Gunderson 1988). Hexachlorobenzene intakes, in µg/kg body weight/day, estimated for these total diet analyses were 0.0020 and 0.0011 for 14–16-year-old males and 60–65-year-old females, respectively. In more recent FDA Total Diet Studies, the frequency of detection of hexachlorobenzene residues declined to 7% in 1988 (FDA 1989), 5% in 1989 (FDA 1990), 4% in 1990 (FDA 1991), 2% in 1991 (FDA 1992), <2% on 1991–1993 (FDA 1994), and <2% in 1994 (FDA 1995). Hexachlorobenzene intakes (µg/kg body weight/day) estimated for the Total Diet Analyses also declined from intakes estimated in the 1982–1984 analysis and were 0.0011 and 0.0006 in 1988 (FDA 1989); 0.0009 and 0.0005 in 1989 (FDA 1990); 0.0005 and 0.0002 in 1990 (FDA 1991); and 0.0004 and 0.0002 in 1991 (FDA 1992) for 14–16-year-old males and 60–65-year-old women, respectively.

Domestic samples of mixed feed rations were collected and analyzed by the FDA for pesticide surveillance during fiscal years 1989–1994. Hexachlorobenzene residue was detected in 1 of 457 samples in trace amounts (Lovell et al. 1996).

Burton and Bennett (1987) estimated a human body burden for hexachlorobenzene of 0.7 mg derived primarily from dietary intake of fatty foods (0.2 µg/day). Inhalation was estimated to contribute 100 times less than dietary intake (0.002 µg/day) and consumption of drinking water was also considered to contribute only negligible amounts of hexachlorobenzene (0.06 µg/year).

An exploratory study of chemical exposure was conducted among Vietnamese, Bangladeshi, and local resident sportfish consumers in the Montreal region of the St. Lawrence River. The concentration ranges for the respective groups are as follows: 0.01–0.04; 0.01–0.02; and 0.01–0.07 µg/L, indicating a positive correlation between local residents consuming sportfish from the St. Lawrence River and hexachloro-benzene concentrations (Kosatsky et al. 1999). Anderson et al. (1998) conducted a study to assess hexa-chlorobenzene contamination in human serum and urine samples from frequent consumers of sport fish from Lakes Michigan, Erie, and Huron. A telephone survey was conducted requesting fish eating habits with special attention to lake trout, brown trout, rainbow trout, or chinook or coho salmon, carp or catfish, and walleye or perch or smelt. After the survey, each angler was invited to give a serum sample. The minimum and maximum hexachlorobenzene concentrations of all 30 participating subjects were 0.02 and 0.2 ppb, respectively, with a median concentration of 0.1 ppb. Eight participants from Lake Michigan had minimum and maximum concentrations of 0.09 and 0.2 ppb, respectively, with a median concentrations of 0.1 ppb, and 11 participants from Lake Huron and Lake Erie had respective minimum and maximum concentrations of 0.04 and 0.2 ppb and 0.02 and 0.2 ppb with median concentrations of

0.1 and 0.09 ppb. A comparison group from Arkansas (180 serum samples) had hexachlorobenzene concentrations ranging from not detected to 0.3 ppb with a median of 0.1 ppb (Anderson et al. 1998). This study illustrates that since the comparison group had the highest range in concentration, there is a wide spread of hexachlorobenzene contamination and any population may possibly be affected.

Sinkkonen et al. (1995b) discovered concentrations of hexachlorobenzene in pine needles in the vicinity of a metal reclamation plant. Five sites sampled and analyzed for hexachlorobenzene in the wax of the needles and the rest of the needles in 1991 (0.257–0.731 ng/g; 0.758–3.170 ng/g), 1992 (0.142–0.692 ng/g; 0.255–1.785 ng/g), and 1993 (0 concentration found in the wax of the needles; 0.217–0.885 ng/g) show decreasing concentrations (Sinkkonen et al. 1995b). In 1996, Sinkkonen et al. (1996) analyzed pine needles in and around the metal reclamation plant again. Composite samples from the years 1993, 1994, and 1995 had hexachlorobenzene concentrations of 6.9–8.3 ng/g in the wax of the needles and 0.2–2.2 ng/g in the rest of the needles, contrary to the decreasing trends found from the analysis conducted during 1991–1993.

6.5   GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

Hexachlorobenzene is no longer produced (as an end-product) or used as a pesticide in the United States. Consequently, the current potential for exposure of the general population appears to be very limited. Members of the general population may be exposed to very low concentrations of hexachlorobenzene through ingestion of contaminated foodstuffs, particularly those with high lipid content such as meat, poultry, and fish. General population exposure to hexachlorobenzene via inhalation or dermal contact would be much less. Occupational exposure is possible for workers involved in the production of chlorinated hydrocarbons, which releases hexachlorobenzene as a by-product. One recent study has also shown farmers to be susceptible to hexachlorobenzene.

Brock et al. (1998) investigated four families in Iowa and two families in North Carolina for exposure to several organochlorine pesticides by analyzing the pesticide levels in their serum. Among the farmers from Iowa, mean hexachlorobenzene concentrations in serum ranged from 0.12 to 0.26 ng/mL, and their spouses had mean levels ranging from 0.05 to 0.24 ng/mL. The two farmers from North Carolina had mean levels of 0.15 and <0.05 ng/mL, and their respective spouses had levels of 0.16 and 0.17 ng/mL. It was shown that in one family, the pesticide serum level in the spouse (0.17 ng/mL) was higher than that in the farmer (<0.05). Glynn et al. (2000) studied the serum concentration of hexachlorobenzene in a group of 790 men ages 40–75 who were randomly selected from both rural and urban areas of Uppsala,

Sweden. The mean concentration of hexachlorobenzene was 83.1±133.6 ng/g lipid for this group. This study group had lower serum concentrations than males who had recent occupational exposure or high environmental exposure. Hagmar et al. (2001) examined blood samples from 110 men who consumed varying amounts of fish from the Baltic sea. The median plasma levels of hexachlorobenzene in the 43 Swedish and 67 Latvian adult males in this study group was 84 ng/g lipid. Recently, the serum concentrations of pregnant women from the Disko Bay area, Greenland were studied by Bjerregaard and Hansen (2000). The women in this study consume a high level of meat and blubber from marine animals. The concentration of hexachlorobenzene in plasma taken from these women between the years 1994 and 1996 was 1.2 ng/mL wet weight (range, 0.1–7.0 ng/mL wet weight). Hexachlorobenzene concentrations in serum in study groups of active smoking mothers, passive smoking mothers, and nonsmoking mothers from Germany were 0.87 ng/mL (range, 0.23–4.38 ng/mL), 0.55 ng/mL (range, <0.10–3.27 ng/mL), and 0.46 ng/mL (range, <0.10–2.73 ng/mL) (Lackman et al. 2000). The mean concentration of hexachloro-benzene in whole blood from infant children ranged from 0.13 to 0.23 ng/mL (Karmaus et al. 2001). The highest concentration was observed in children who were breastfed for over 12 weeks after birth.

Nonoccupational exposure to hexachlorobenzene for residents of two U.S. cities (Jacksonville, Florida and Springfield, Massachusetts) were studied over three seasons; summer 1986, spring 1987, and winter 1988 (Whitmore et al. 1994). The study focused primarily on inhalation exposures with primary environmental monitoring consisting of 24-hour indoor, personal, and outdoor air. For the Jacksonville, Florida population, the estimated mean hexachlorobenzene concentration ranged from 0.3 to 1.3 ng/m^3 for indoor air, from not detected to 0.2 ng/m^3 for outdoor air, and from 0.4 to 0.9 ng/m^3 for personal air. For the Springfield, Massachusetts population, mean exposures were much less. The estimated hexachloro-benzene concentrations ranged from not detected to 0.1 ng/m^3 for indoor air, were not detected in outdoor air, and ranged from not detected to <0.05 ng/m^3 for personal air. The mean air exposure estimated for hexachlorobenzene in Jacksonville, Florida, was 10 ng/day, while dietary exposure ranged from 70 to 120 ng/day. The mean air exposure for Springfield, Massachusetts, was not detected in the personal air samplers, while the dietary exposure was 105 ng/day. In both the Jacksonville, Florida population, characterized as a high pesticide use area, and in the Springfield, Massachusetts population, characterized as a low pesticide use area, the dietary exposure to hexachlorobenzene was the predominant exposure pathway.

In the most recent National Human Adipose Tissue Survey, hexachlorobenzene was found in 35 of 46 human adipose tissue samples from all regions of the United States at levels ranging from 12 to 1,300 ppb (EPA 1986f). In other studies of the general population, hexachlorobenzene has been found in

human fat samples from residents of the Texas Gulf Coast at concentrations ranging from 18 to 35 ppb (Ansari et al. 1986). Kutz et al. (1991) summarized data on hexachlorobenzene residues in human adipose tissue collected in the United States from 1973 through 1983. The geometric mean concentrations increased slightly from 0.02 ppm (20 ppb) in 1973 to 0.05 ppm (50 ppb) in 1976, and then declined to 0.031 ppm (31 ppb) in 1983.

Human breast adipose tissue samples from 36 females of 50–80 years in age were collected from the Yale-New Haven hospital in Connecticut. A correlation was made between breast adipose tissue and serum residues using Pearson's correlation coefficient. On a lipid adjusted basis, all 36 human adipose tissue samples were found to contain residues of hexachlorobenzene. The range of concentration was 2.5–33.3 ng/g with a median of 17.7 ng/g (Archibeque-Engle et al. 1997). A study conducted in British Columbia, Canada, Mes (1992) reported median and maximum hexachlorobenzene residues in biopsied fatty tissue of 18.8 and 87 ng/g (ppb), respectively. In a more recent study, small amounts of breast tissue were collected from 60 women undergoing breast surgery at Stanford University, California. The mean hexachlorobenzene concentration was 46 ng/g fat with a minimum and maximum of 14 and 170 ng/g fat, respectively (Petreas et al. 1998). Weistrand and Noren (1998) collected adipose tissue and liver samples from five Swedish men and two Swedish women. Hexachlorobenzene concentrations ranged from 12 to 129 ng/g lipids with a mean of 56 ng/g lipids in adipose tissue and 17 to 156 ng/g lipids with a mean of 58 ng/g lipids in the liver. Hexachlorobenzene levels in human adipose tissue from 64 mothers living in Veracruz, Mexico averaged 0.065 mg/kg (range, 0.010–0.401 mg/kg) on a lipid adjusted basis (Waliszewski et al. 2000a). The mean concentrations of hexachlorobenzene in autopsy tissue samples from Greenlanders were 594 μg/kg lipid (range, 476–742 μg/kg lipid), 588 μg/kg lipid (range, 156–1,890 μg/kg lipid), 260 μg/kg lipid (range, 175–387 μg/kg lipid), and 754 μg/kg lipid (range, 603–943 μg/kg lipid) for subcutaneous fat, omental fat, brain, and liver tissues, respectively (Dewailly et al. 1999).

In the National Health and Nutrition Examination Survey (NHANES II) conducted by the EPA, hexachlorobenzene levels in blood from the general population collected from 1976 to 1980 revealed a median concentration of 1.7 ppb, which did not vary among the three age groups studied (Murphy and Harvey 1993). Hexachlorobenzene levels in normal human blood serum samples were reported to be 2.2 ppb and were higher (4.6 ppb) in uremic serum samples (Rutten et al. 1988). In a recent study conducted in British Columbia, Canada, Mes (1992), reported median and maximum whole blood levels of 0.11 and 0.34 ng/g (ppb) in individuals from the general population.

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Although all uses of hexachlorobenzene as a pesticide in the United States were voluntarily canceled in 1984, occupational exposures may still occur among workers in the chlorinated solvent manufacturing industry, and workers currently involved in the manufacture and application of pesticides contaminated with hexachlorobenzene. Military or firefighting personnel who use pyrotechnic mixtures that release hexachlorobenzene and workers involved in the disposal of hexachlorobenzene contaminated materials, via combustion processes associated with municipal incinerators or those involved in the handling and treatment of wastes at hazardous waste sites, may be exposed to higher than background concentrations.

No information was located on concentrations of hexachlorobenzene in occupationally exposed populations in the United States. However, in a 10-year study (1976–1985), human adipose tissue samples and human milk from patients exposed to PCBs or pesticides in Ontario, Canada were analyzed for a variety of pesticides and industrial chemicals (Frank et al. 1988). Residues of hexachlorobenzene in adipose tissues averaged at or below 0.2 ppb in the extractable fat. Concentrations of hexachlorobenzene in milk ranged from a mean of 0.52 ppb (in whole milk) in 1983–1984 to a mean of 0.26 ppb (in whole milk) in 1985. The highest mean concentration (1.33 ppb) was observed in central Ontario residents. Urban residents had a higher mean concentration (0.57 ppb) as compared to rural residents with a mean of 0.27 ppb.

Plasma hexachlorobenzene concentrations in a Louisiana population living in a hexachlorobenzene-contaminated area averaged 3.6±4.3 ppb. The highest plasma level (345 ppb) was detected in a waste disposal facility worker, while the highest plasma level in the general population was 23 ppb (Burns and Miller 1975). Workers at a carbon tetrachloride and perchloroethylene production facility had plasma hexachlorobenzene levels of up to 223 ppb. Hexachlorobenzene blood levels were determined over a 4-year period in men employed in the manufacture of chlorinated solvents (Currier et al. 1980). Blood levels ranged from 5 to 1,121 ppb (310.7 ppb mean) in 1974, 30–990 ppb (311.5 mean) in 1975, 3–600 ppb (159.9 mean) in 1976, and 22–467 ppb (170.3 mean) in 1977. The hexachlorobenzene blood levels were strongly associated with the number of years worked in the chlorinated solvents plant, but they were poorly correlated with airborne hexachlorobenzene concentrations ranging from <1 to 13 ppb or wipe samples from work areas ranging from 0.03 to 124 μg/100 m^2.

Vegetable sprayers applying hexachlorobenzene-contaminated dimethyltetrachloroterephthalate (DCPA) had plasma levels of hexachlorobenzene ranging from 0 to 310 ppb (mean 40±63 ppb), accompanied by elevated levels of delta-aminolevulinic acid, but no health related adverse effects (Burns et al. 1974).

Elevated urinary uroporphyrin and coproporphyrin were found in 1 of 54 men occupationally exposed to hexachlorobenzene (Morley et al. 1973).

Workers at a new hazardous waste incinerator in Constanti, Spain had mean plasma levels of hexachloro-benzene at 152 µg/kg lipid (range, 19.4–854.0 µg/kg lipid) (Domingo et al. 2001). Residents (n=608) living near an electrochemical factory in Catalonia, Spain had mean serum concentrations of hexachloro-benzene as follows (units ng/mL): general population, male (50.2), female (48.0), all (48.9); nonfactory workers, male (39.8), female (47.9), all (46.3); and living with a worker of the factory, yes (46.8), no (46.8) (Ballester et al. 2000).

Individuals employed in industries that manufacture or process hexachlorobenzene or products containing hexachlorobenzene may be exposed to the highest concentrations. The National Occupational Exposure Survey (NOES), conducted by NIOSH from 1981 to 1983, estimated that 1,038 workers employed at 10 facilities were potentially exposed to hexachlorobenzene in the United States (NOES 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.

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 3.7 Children's Susceptibility.

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

Children are particularly susceptible to hexachlorobenzene by ingestion of breast milk. Table 6-5 summarizes the concentrations of hexachlorobenzene in human breast milk taken from women living in different regions of the world. Hexachlorobenzene was detected in human milk samples collected from

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54 residents of Hawaii during 1979–1980 (Takei et al. 1983). The incidence of detection of hexachloro-
benzene in the sampled population was 100% and the mean concentration of positive detections was
46±49 ppb (ng/g lipid basis) with residues ranging from 18 to 38 ppb (ng/g lipid basis). The authors state
that the levels of hexachlorobenzene in human milk from residents of Hawaii are consistent with levels
detected in an earlier human milk study conducted on women on the mainland United States. Schecter et
al. (1998) found that hexachlorobenzene residues in the breast milk of a mother with nursing twins
decreased from 10.7 ng/g lipid to not detectable in 30 months. Thus, nursing infants are particularly
susceptible to hexachlorobenzene poisoning due to the mother's decrease in body burden and the infant's
intake (Schecter et al. 1998). A recent study of organochlorine pesticide concentrations in human milk
sampled throughout Canada during 1992 found that hexachlorobenzene was present in all 497 milk
samples at a mean concentrations of 0.44 ng/g (ppb) in whole milk and 14.5 ng/g (ppb) in milk fat
(Newsome et al. 1995). A comparison by Canada Health of human milk contamination in whole milk
from 1967 to 1992 was conducted in Canada, Quebec and Ontario. This study showed a decrease in
hexachlorobenzene concentration in Canada (mean concentration; 2–0.44 ng/g), Quebec (median
concentration; 2–0.40 ng/g), and Ontario (median concentration; 2–0.48 ng/g) (Craan and Haines 1998).
Newsome et al. (1995) reported that concentrations of hexachlorobenzene were higher in women from

Table 6-5. Mean Levels of Hexachlorobenzene in Breast Milk

Location of study	N/n	Concentration[a]	Reference
New Zealand			Bates et al. (1994)
Auckland, urban	11/n/a	0.020	
Northland, rural	10/n/a	0.021	
Christchurch, urban	9/n/a	0.030	
Canterbury, rural	8/n/a	0.063	
Porto Alegre, Brazil	30/19	0.02	Beretta and Dick (1994)
France (multiple locations)	20/19	0.147	Bordet et al. (1993)
Madrid, Spain	63/52	1.0	Conde et al. (1993)
Industrialized area		1.74	
Canada (1967–1992)	no data	0.002–0.00044[b]	Craan and Haines (1998)
Quebec		0.002–0.00040[b]	
Ontario		0.002–0.00048[b]	
Arctic Quebec			Dewailly et al. (1993)
Inuit women	107/107	0.136	
Caucasian women	50/48	0.028	
Italy	27/no data		Larsen et al. (1994)
Rome		0.25	
Pavia		0.12	
Milan		0.20	
Florence		0.14	
Arkansas, USA	942/57	0.03	Mattison et al. (1992)
Canada	412/no data	0.026	Mes et al. (1993)
Victoria, Australia (1985/1986)	158/153	0.005[b]	Monheit and Luke (1990)
Canada (multiple locations, in 1992)	497/497	0.0044[b] 0.015[c]	Newsome et al (1995)
Sweden (1972–80)	227–1,500/ no data	0.110–220	Norén and Meironyté (2000)
Akumadan, Ghana	20/19	0.04	Ntow (2001)
Bratislava, Slovak Republic	26/26	0.339	Prachar et al (1993)
Victoria, Australia	60/59	0.41	Quinsey et al (1995)
Czech Republic			Schoula et al (1996)
Prague	17	0.639	
Kladno	12	0.570	
Uherske Hradiste	7	0.482	
Northern Thailand	25/9	0.0051[b]	Stuetz et al (2001)
Hawaii, USA (1979–1980)	54/54	0.046±0.049	Takei et al. (1983)
Veracruz, Mexico	43/43	0.047	Waliszewski et al (1996)

Source: Pohl and Tylenda (2000)

[a]µg/g on lipid basis
[b]whole milk sample
[c]milk fat sample
N = number of samples; n = number of samples with measurable levels

the Great Lakes Basin area as compared to the rest of Canada. Concentrations of hexachlorobenzene were higher in the breast milk of women who consumed more than 100 g of fish weekly.

Children may also be exposed to chemicals via ingestion of contaminated foods. Hexachlorobenzene residues have been detected in 76% of samples analyzed as part of the National Human Adipose Tissue Survey (FY82) (EPA 1986f). These hexachlorobenzene residues are most likely the result of consumption of low levels of hexachlorobenzene in food, with calculated yearly intakes of 68, 22, and 5 µg for adults, toddlers, and infants, respectively (EPA 1986e). More recently, Yess et al. (1993) evaluated hexachlorobenzene residues from 1985 to 1991 detected in the Total Diet Studies of infant and adult foods that are consumed by infants and young children. These authors reported maximum hexa-chlorobenzene residues detected in various food groups as follows: combination meat dinners—pork (0.4 ppb), beef (0.3 ppb), chicken/turkey (0.3 ppb), chicken/turkey/vegetable (0.3 ppb), beef and vegetable (0.1 ppb); vegetables and fruits—pears (1.0 ppb), apples (0.4 ppb), and carrots (0.2 ppb); milk products—canned evaporated milk (0.5 ppb), whole milk (0.2 ppb), and low-fat (2%) milk (0.1 ppb); and peanut butter (5.0 ppb).

Hexachlorobenzene intakes, in µg/kg body weight/day, estimated for these total diet analyses (1982–1984) were 0.0015 for 6–11-month-old infants. A follow-up study found a decrease in intakes that were estimated in 1982–1984. Hexachlorobenzene intakes(µg/kg body weight/day) were estimated to be 0.0016 in 1988 (FDA 1989); 0.0007 in 1989 (FDA 1990); 0.0004 in 1990 (FDA 1991); and 0.0003 in 1991 (FDA 1992) for 6–11-month-old infants.

Although inhalation exposures of hexachlorobenzene in children have not been studied, it is anticipated that exposure by this route will not be significant in outdoor environments. The Henry's law constant of hexachlorobenzene is $5.8x10^{-4}$ atm-m^3/mol (Ten Hulscher et al. 1992), indicating that this compound will volatilize rapidly, especially in moist soils with low organic content. Hexachlorobenzene's high log K_{oc} of 6.08 (EPA 1981a), however, indicates that volatilization from soil surfaces will be greatly attenuated. Considering that hexachlorobenzene concentrations in the environment are extremely low, exposure of children by inhalation is expected to be insignificant. After a hexachlorobenzene spill, inhalation exposure may be important before environmental equilibrium is attained. Under these conditions, high concentrations of hexachlorobenzene would be found in the atmosphere, due to hexachlorobenzene's calculated vapor density of 10. This situation, however, is not expected to occur since hexachlorobenzene is no longer produced or used commercially and is only found as an impurity in pesticides and as a by-product of chlorinated hydrocarbons.

The EPA issued a warning regarding pesticides and advised that potential exposure of pesticides to young children via dermal absorption and ingestion was more important than inhalation routes (Jantunen et al. 1997).

6.7   POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

In addition to those individuals occupationally exposed to hexachlorobenzene identified in Section 6.5, several groups within the general population may receive potentially higher exposures to hexachloro-benzene. These groups within the general population include individuals living near facilities where hexachlorobenzene is produced as a byproduct, individuals living near the 101 current or former NPL hazardous waste sites where this compound is present, recreational and subsistence fishermen who consume higher amounts of fish than the general population, and native populations (including Native American populations such as the Inuits of Alaska) who may be exposed to higher levels of hexachloro-benzene associated with dietary intakes of caribou and other game species.

Consumption of contaminated groundwater by individuals living in the vicinity of production facilities or hazardous waste sites may be an important source of exposure for both adults and children. Hexachloro-benzene has been detected in 42 groundwater samples from 107 NPL hazardous waste sites (HazDat 2002). Skin contact with or ingestion of hexachlorobenzene contaminated soil on their hands may be an additional source of exposure for children living near hazardous waste facilities. Hexachlorobenzene has been detected in 76 soil samples from 107 NPL hazardous waste sites (HazDat 2002).

Recreational and subsistence fishermen who consume appreciably higher amounts of locally caught fish from contaminated water bodies may be exposed to higher levels of hexachlorobenzene associated with dietary intake than members of the general population (EPA 1995b). Hexachlorobenzene contamination in fish and shellfish has triggered the issuance of several human health advisories. As of September 1994, hexachlorobenzene was identified as the causative pollutant in fish consumption advisories in Louisiana and Ohio. This information is summarized in Table 6-6. EPA has identified hexachlorobenzene as a target analyte and recommended that this chemical be monitored in fish and shellfish tissue samples collected as part of state toxics monitoring programs. EPA recommends that

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Table 6-6. Fish Consumption Advisories[a]

State	Waterbody	Extent	Species
Louisiana	Devil's Swamp Lake and Bayou Baton Rouge	7 miles	All fish
	Calcasieu and Cameron parishes	6 miles	All fish and shellfish
Ohio	Tuscarawas River	Turkey Foot Rd. (SR 619), Barberton, to South Broadway St (SR 416), New Philadelphia (Tuscarawas County)	Carp-common, bass-smallmouth, bullhead-yellow, bass-rock, catfish-channel, bass-largemouth

[a]From EPA 1997b National Listing of Fish Consumption Advisories

residue data obtained from these monitoring programs should then be used by the states to conduct risk assessments to determine the need for issuing fish and shellfish consumption advisories for the protection of the general public as well as recreational and subsistence fishermen (EPA 1997b).

Native American populations such as the Inuits of Alaska or other subsistence hunters living in high latitude areas of the United States and Canada may be exposed to hexachlorobenzene residues in caribou, beluga whales, polar bears, seals, and other game species. Significantly higher concentrations of hexa-chlorobenzene (mean 136 ng/g [ppb]) were reported in breast milk of Inuit mothers from eastern Canada (Quebec Province) as compared with residues of 28 ng/g (ppb) in Caucasian mothers (Dewailly et al. 1993). By analogy, it is possible that Inuit populations in western North America (Alaska) may receive potentially higher hexachlorobenzene exposures from their dietary habits. In a follow-up study by Dewailly et al. (1999) 26 subcutaneous fat samples, 41 omental fat samples, 17 brain samples, and 26 liver samples were collected in November 1992 to Mid-October 1994 from Inuit Greenlanders. Mean hexachlorobenzene concentrations were 594, 588, 260, and 754 µg/kg lipid basis, respectively. A comparison of these data clearly suggest an increase in Inuit population's hexachlorobenzene levels from dietary habits. Maternal body burden and lactational transfer of hexachlorobenzene can increase tissue levels in the neonate (Ando et al. 1985; Frank et al. 1988).

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 hexachlorobenzene is available. Where adequate information is not available, ATSDR, in conjunction with the National Toxicology Program (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 hexachlorobenzene.

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 hexachlorobenzene are sufficiently well documented to permit estimation of the compound's environmental fate (Budavari 1996; EPA 1981a; Hansch et al. 1995; Lide 1998; Ten Hulscher et al. 1992; Verschueren 1996). No further information is needed.

Production, Import/Export, Use, Release, and Disposal.   Hexachlorobenzene is not currently manufactured as a commercial end-product in the United States and has not been commercially produced since the late 1970s (EPA 1986e). However, hexachlorobenzene currently is produced as a by-product or impurity in the manufacture of chlorinated solvents, other chlorinated compounds, and several currently registered pesticides (Bailey 2001; EPA 1986e, 1994c; IARC 1979).

The total amount of hexachlorobenzene released as a by-product in the production of all chlorinated solvents was estimated as 0.3 kg/year in the mid 1990s (Bailey 2001), while hexachlorobenzene released through use of eight major pesticides containing hexachlorobenzene accounted for 1,270 kg/year (Bailey 2001). Current production estimates for hexachlorobenzene as a by-product or impurity are not available. Current, quantitative estimates of production of hexachlorobenzene from all sources are needed to evaluate potential exposures and risks to human health.

There are no current commercial uses of hexachlorobenzene in the United States, although the compound was used as a fungicide until 1984 when the last registered use as a pesticide was voluntarily cancelled (Beyer 1996). Prior to the registration cancellations, hexachlorobenzene was registered as a seed protecting for use on several grains (principally wheat) and field crops (EPA 1986e). Hexachlorobenzene was also used in pyrotechnic and ordinance materials and in synthetic rubber production (EPA 1986e). Impurities of hexachlorobenzene in currently registered pesticides (picloram, PNCB, chlorothalonil, Dacthal®, atrazine, simazine, lindane, and PCP) (Bailey 2001; EPA 1986e, 1993a; Farm Chemicals Handbook 1993) appear to be a continuing source of hexachlorobenzene exposure for the general population. Five of the pesticides containing impurities of hexachlorobenzene (PCNB, chlorothalonil, Dacthal®, lindane, and PCP) are used in home gardens, lawn care, and other applications around residences and in urban areas (Farm Chemicals Handbook 1993). Currently, data regarding the release of hexachlorobenzene into the environment as an impurity via the use of other pesticides is not available.

No current information was located on import/export volumes for hexachlorobenzene, although import/export volumes for hexachlorobenzene/DDT combined are available (NTDB 1995).

Hexachlorobenzene is listed as a hazardous waste. It is regulated under the Clean Water Effluent Guidelines as stated in Title 40, Section 400–475, of the Code of Federal Regulations and the Resource Conservation and Recovery Act (RCRA) (see Chapter 8). Past disposal methods have included incineration, landfills, discharges to municipal sewage treatment plants, and emissions to the atmosphere. The recommended method of disposal for hexachlorobenzene is incineration (Clayton and Clayton 1981; EPA 1988a, 1989a; IRPTC 1985; Lamb et al. 1994). No further information on disposal practices is needed; however, estimates on the volume of hexachlorobenzene disposed of annually and the disposal method used are needed to assess exposure pathways.

According to the Emergency Planning and Community Right-to-Know Act of 1986, 42 U.S.C. Section 11023, industries are required to submit chemical release and off-site transfer information to the EPA. The TRI, which contains this information for 1999, became available in 2001. This database will be updated yearly and should provide a list of industrial production facilities and emissions.

Environmental Fate.   Hexachlorobenzene released to the environment partitions to several environmental compartments (air, water, soil and sediment, and biological organisms). Hexachloro-benzene partitions to the atmosphere from soil surfaces through volatilization (Nash and Gish 1989). The remainder is adsorbed strongly to soil where it persists for extended periods (half-life of months to years) due to its resistance to biodegradation (Beall 1976; Beck and Hansen 1974; Isensee et al. 1976). Leaching of hexachlorobenzene into groundwater is not expected to occur very rapidly under most circumstances due to the compound's high sorption characteristics (Swann et al. 1983). Yuan et al. (1999) have recently reported that hexachlorobenzene can be dechlorinated to dichlorobenzenes under anaerobic conditions in the laboratory using sewage sludge as inoculum.

Once in the atmosphere, hexachlorobenzene exists in both the vapor and particulate phase; however, the vapor phase predominates (Ballschmiter and Wittlinger 1991; Bidleman et al. 1989; Lane et al. 1992). Degradation of hexachlorobenzene in the atmosphere is quite slow (1.69 years) (Brubaker and Hites 1998). Since hexachlorobenzene is hydrophobic, wet deposition will not be an important loss process. In cold high latitude zones, dry deposition of hexachlorobenzene aerosols is encouraged (Ballschmiter and Wittlinger 1991; Lane et al. 1992; Wania and Mackay 1993). Atmospheric transport of hexachloro-benzene is a major mechanism for global translocation of this compound (Eisenreich et al. 1981; Kelly et

al. 1991). Long-range global transport of hexachlorobenzene released anywhere in the world can occur
via atmospheric or oceanic systems (Ballschmiter and Wittlinger 1991; Wania and MacKay 1993).

Hexachlorobenzene released to water will volatilize, adsorb to sediments, or bioaccumulate in fish and
other aquatic organisms (Bishop et al. 1995; EPA 1992b; Kelly et al. 1991; Langlois and Langis 1995;
Oliver and Nichol 1982a; Quemerais et al. 1994; Rostad et al. 1993; Schmitt et al. 1990; Zabik et al.
1995). Hydrolysis and biodegradation are not significant processes in water. Information on biodegra-
dation of hexachlorobenzene under anaerobic conditions in a laboratory study exists (Yuan et al. 1999),
but degradation under field conditions were not found. Further information on these processes, including
degradation products, are needed to determine potential mechanisms and sources of hexachlorobenzene
releases from soils and the potential for the compound and its degradation products to contaminate
groundwater.

Both bioaccumulation and biomagnification of hexachlorobenzene were reported to occur in an aquatic
laboratory microcosm system (Burkhard et al. 1997; Isensee et al. 1976); however, data by Russell et al.
(1995) suggests that hexachlorobenzene bioaccumulates, but is not biomagnified in certain fish
populations in Lake Erie. In terrestrial ecosystems, hexachlorobenzene can also be accumulated in
several agricultural plant species in the roots and parts of the plants closest to the soil (Kraaij and Connell
1997; Scheunert et al. 1983; Schroll et al. 1994; Smelt and Leistra 1974). In lichens, a high latitude
forage food for caribou, hexachlorobenzene was found to be bioconcentrated 8,800,000–17,000,000 times
the concentration in the atmosphere (Muir et al. 1993). Although the issue of biomagnification in some
ecosystems needs to be clarified, there are adequate data on the bioconcentration of hexachlorobenzene in
both aquatic and terrestrial ecosystems.

Bioavailability from Environmental Media.   Hexachlorobenzene can be absorbed following
inhalation of contaminated workplace air (Burns et al. 1974; Currier et al. 1980; Richter et al. 1994).
Since hexachlorobenzene is only moderately volatile, inhalation may not be a major concern except at
hazardous waste sites or in industrial settings. Hexachlorobenzene can be absorbed following ingestion
of contaminated food or water. Exposure to hexachlorobenzene through ingestion of food contaminated
with low levels of the compound is probably the greatest source of exposure for the general population.
Exposure to hexachlorobenzene through ingestion of contaminated drinking water is not expected to be
an important source of concern since the compound is not very soluble in water. Although there are no
quantitative data on the human absorption of orally administered hexachlorobenzene, gastrointestinal
absorption has been demonstrated for rats (Albro and Thomas 1974; Ingebrigtsen and Nafstad 1983;

Ingebrigtsen et al. 1981). The lymphatic system has also been shown to play an important part in the absorption of hexachlorobenzene in the intestines. Hexachlorobenzene is absorbed by the lymphatic system in the region of the duodenum and jejuno-ileum and is deposited in the adipose tissue, bypassing the portal circulation (Iatropoulos et al. 1975). Since hexachlorobenzene is tightly bound to soil particles, ingestion of hexachlorobenzene-contaminated soil, particularly by children, may also be an important route of exposure near production and processing facilities or near hazardous waste disposal sites. No information was available regarding absorption of hexachlorobenzene following dermal contact. Information regarding the bioavailability of hexachlorobenzene from both ingestion of soil-bound hexachlorobenzene particularly in children and from dermal contact with contaminated soils are needed, particularly in assessing health risks to populations living near hazardous waste sites.

Food Chain Bioaccumulation.   Like many of the other organochlorine pesticides, hexachlorobenzene is lipophilic and has a high bioaccumulation potential. Hexachlorobenzene is bioaccumulated in fish and other aquatic organisms (Bishop et al. 1995; EPA 1992b; Langlois and Langis 1995; Murray et al. 1980, 1981; Oliver and Nichol 1982a; Schmitt et al. 1990; Zabik et al. 1995) as well as waterfowl (Cobb et al. 1994; Foley 1992; Gebauer and Weseloh 1993; Somers et al. 1993; Swift et al. 1993; Yamashita et al. 1992). Hexachlorobenzene is bioaccumulated in aquatic food chains with virtually no degradation of the compound by the exposed organisms (Isensee et al. 1976). The results of a laboratory aquatic ecosystem study suggest that bioaccumulation as well as biomagnification of hexachlorobenzene occurs (Isensee et al. 1976); however, authors of a more recent study conducted in natural fish populations suggest that hexachlorobenzene is not biomagnified (Russell et al. 1995). In terrestrial ecosystems, several agricultural crops have been found to accumulate hexachlorobenzene in their roots and in portions growing closest to soil level (Ecker and Horak 1994; Scheunert et al. 1983; Schroll et al. 1994; Smelt and Leistra 1974). The edible root portion of carrots accumulated the highest hexachlorobenzene concentration with a BCF of 19 (Smelt and Leistra 1974). Lichens, a primary forage for caribou, were also shown to bioaccumulate hexachlorobenzene (Muir et al. 1993). A field study on a terrestrial ecosystem suggested that hexachlorobenzene was biomagnified through various trophic levels of the food web (Hebert et al. 1994). Further studies are needed to resolve whether hexachlorobenzene is biomagnified in both aquatic and terrestrial ecosystems.

Exposure Levels in Environmental Media.   Environmental monitoring data are available for hexachlorobenzene in air (Currier et al. 1980; Davis and Morgan 1986; Eisenreich et al. 1981; EPA 1975b, 1985g; Hoff et al. 1996; Lee et al. 2000; Mann et al. 1974; Poissant et al. 1997; Tiernan et al. 1985), water (Chan et al. 1994; Davis and Morgan 1986; EPA 1976a; Hoff et al. 1996; Laska et al. 1976;

Oliver and Nichol 1982a; Quemerais et al. 1994), soil (Elder et al. 1981; EPA 1985g; Laseter et al. 1976; Laska et al. 1976), and sediment (Davis and Morgan 1986; Elder et al. 1981; Murray et al. 1981; Oliver and Nichol 1982a; Ray et al. 1983; Rostad et al. 1999). Groundwater monitoring data are lacking; however, hexachlorobenzene has been detected in 42 groundwater samples from 107 NPL hazardous waste sites. Current information on hexachlorobenzene concentrations in groundwater is needed. Human intake estimates for exposure from environmental media are available (Whitmore et al. 1994), but are limited. In general, while monitoring data are available for most environmental media, much of the information on environmental levels was collected during the 1970s through the mid 1980s. More recent monitoring data from all environmental media would provide more accurate information for estimating human and animal intakes.

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

Exposure Levels in Humans.   Hexachlorobenzene has been detected in human adipose tissue (Ansari et al. 1986; EPA 1986f; Frank et al. 1988; Kutz et al. 1991; Mes 1992;), blood (Burns and Miller 1975; Burns et al. 1974; Currier et al. 1980; Murphy and Harvey 1993; Rutten et al. 1988), and milk (Craan and Haines 1998; Frank et al. 1988; Newsome et al. 1995; Schecter et al. 1998; Takei et al. 1983). Studies exist that relate occupational exposure to blood levels of hexachlorobenzene (Burns et al. 1974; Currier et al. 1980). Studies to compare the steady-state intake of hexachlorobenzene as measured by urinary and fecal excretion as it relates to blood levels in occupationally exposed workers would be particularly useful. Since hexachlorobenzene has been detected in both urine and feces, a study of this nature could be conducted. These studies might also address possible individual differences in the metabolism of this compound. This information is necessary for assessing the need to conduct health studies on these populations.

Exposures of Children.   Exposure pathways for children have been well documented in breast milk (Newsome et al. 1995; Schecter et al. 1998) and diet (FDA 1992; Yess et al. 1993). Data documenting body burdens for children are needed. Data addressing exposure to children who live, play, or attend school near NPL sites, industrial sites, such as chlorinated hydrocarbon production factories, or on farmlands where hexachlorobenzene is being released as an impurity of another pesticide would allow for a better assessment of hexachlorobenzene exposure. As hexachlorobenzene is released due to the use of

other pesticides on foods, an evaluation of possible hexachlorobenzene residues in children's food substances would further enhance the ability to construct a complete picture of exposure. Studies revealing contamination of drinking water or groundwater would also prove essential in this assessment. Attention should also focus on the use of tap water as a contaminant source when used to prepare infant formulas from condensed or powdered forms. As children are often bound to pick up soil off the ground and maybe even put this soil in their mouths, studies regarding exposure to children through soil would be helpful. Information concerning childhood-specific means to decrease exposure would be useful.

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

Exposure Registries.   No exposure registries for hexachlorobenzene were located. This substance is not currently one of the compounds for which a subregistry has been established in the National Exposure Registry. The substance will be considered in the future when chemical selection is made for subregistries to be established. The information that is amassed in the National Exposure Registry facilitates the epidemiological research needed to assess adverse health outcomes that may be related to exposure to this substance. Currently, Inuit communities appear to have potentially higher exposures to hexachlorobenzene and should be further monitored (Dewailly et al. 1993, 1999).

6.8.2   Ongoing Studies

As part of the Third National Health and Nutrition Evaluation Survey, the Environmental Health Laboratory Sciences Division of the National Center for Environmental Health and Injury Control, Centers for Disease Control and Prevention, will be analyzing human blood samples for hexachloro-benzene and other volatile organic compounds. These data will give a more current indication of the frequency of occurrence and background levels of these compounds in the general population.

According to FEDRIP (2001), there is one ongoing study on hexachlorobenzene being conducted at the Virginia Polytechnic Institute. This study involves an effort to reveal the aryl dehalogenation mechanism and to evaluate the ability of carbon monoxide reduced carbon monoxide dehydrogenase to reductively dehalogenate hexachlorobenzene.