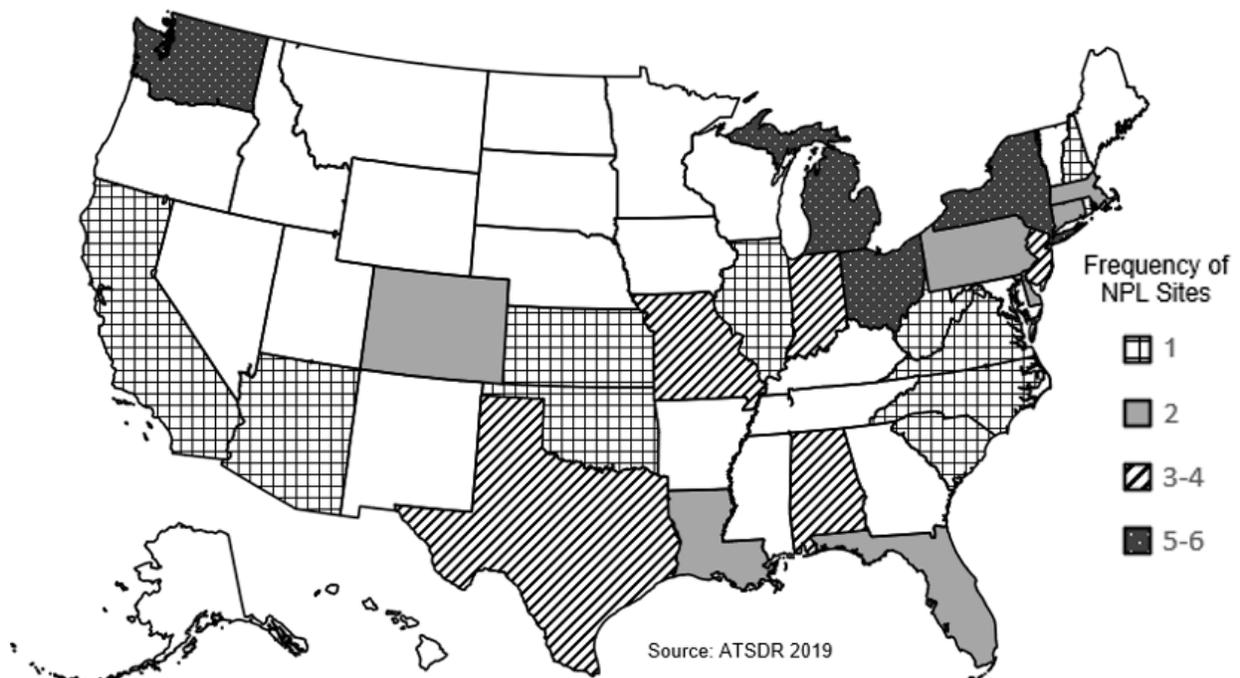


CHAPTER 5. POTENTIAL FOR HUMAN EXPOSURE

5.1 OVERVIEW

Hexachlorobutadiene has been identified in at least 62 of the 1,867 hazardous waste sites that have been proposed for inclusion on the EPA National Priorities List (NPL) (ATSDR 2019). However, the number of sites in which hexachlorobutadiene has been evaluated is not known. The number of sites in each state is shown in Figure 5-1.

Figure 5-1. Number of NPL Sites with Hexachlorobutadiene Contamination



- The most likely route of exposure for the general public to hexachlorobutadiene is through ingestion of contaminated food and water and inhalation.
- There are no natural sources of hexachlorobutadiene that contribute to environmental levels. The main source is its production as a byproduct of chlorinated hydrocarbon synthesis.
- Its principal use is as a chemical intermediate in the manufacture of rubber compounds.
- There are limited data on the fate and transport of hexachlorobutadiene. The available data suggest that it will bind to soil particles and sediments and particulates in air and water. Some volatilization of hexachlorobutadiene from surface waters and soils may also occur.

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- In air, it will likely react with reactive oxygen species and have a half-life ranging from 60 days to 1.6 years. The estimated half-life in surface water is estimated to be between 3 and 300 days.

5.2 PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

5.2.1 Production

Hexachlorobutadiene was first prepared in 1877 by the chlorination of hexyl oxide (IARC 1979). Commercial quantities of hexachlorobutadiene have never been produced in the United States. The primary source of hexachlorobutadiene found in the United States is inadvertent production as a waste byproduct of the manufacture of certain chlorinated hydrocarbons, such as tetrachloroethylene, trichloroethylene, and carbon tetrachloride (EPA 1980; Yang 1988). In 1982, EPA reported an annual volume of about 28 million pounds of hexachlorobutadiene inadvertently produced as a waste byproduct from this source (EPA 1982a; NLM 2020). Table 5-1 summarizes information on U.S. companies that manufactured or used hexachlorobutadiene in 2018 (TRI18 2020).

Table 5-1. Facilities that Produce, Process, or Use Hexachlorobutadiene

State ^a	Number of facilities	Minimum amount on site in pounds ^b	Maximum amount on site in pounds ^b	Activities and uses ^c
IN	1	100	999	12
KY	1	100,000	999,999	1, 3, 6
LA	5	10,000	9,999,999	1, 5, 6, 12, 13
OH	1	1,000	9,999	12
TX	4	100	999,999	1, 5, 6, 12, 13, 14

^aPost office state abbreviations used.

^bAmounts on site reported by facilities in each state.

^cActivities/Uses:

- | | | |
|----------------------|-----------------------------|--------------------------|
| 1. Produce | 6. Reactant | 11. Manufacture Aid |
| 2. Import | 7. Formulation Component | 12. Ancillary |
| 3. Used Processing | 8. Article Component | 13. Manufacture Impurity |
| 4. Sale/Distribution | 9. Repackaging | 14. Process Impurity |
| 5. Byproduct | 10. Chemical Processing Aid | |

Source: TRI18 2020 (Data are from 2018)

5.2.2 Import/Export

Since 1974, most hexachlorobutadiene used commercially in the United States has been imported from Germany. Imported quantities remained fairly constant in the late 1970s, averaging about

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500,000 pounds annually, but dropped to 145,000 pounds in 1981 (EPA 1980, 1982b). More recent information on the volume of imported or exported hexachlorobutadiene is not available.

5.2.3 Use

Hexachlorobutadiene is used as a chemical intermediate in the manufacture of rubber compounds (EPA 1982b). Lesser quantities of hexachlorobutadiene are used as a solvent, a fluid for gyroscopes, a heat transfer liquid, a hydraulic fluid, and a chemical intermediate in the production of chlorofluorocarbons and lubricants (EPA 1980; IARC 1979; Verschueren 1983). Small quantities are also used as a laboratory reagent (EPA 1982b). In the international market, Russia is reported to be one of the major users of hexachlorobutadiene, where it is used as a fumigant on grape crops. Hexachlorobutadiene is also used as a fumigant in France, Italy, Greece, Spain, and Argentina (IARC 1979; NTP 1991). Prior to 1975, the largest domestic use of hexachlorobutadiene was for the recovery of “snift” (chlorine-containing) gas in chlorine plants (NLM 2020). More recent information from U.S. chlorine producers indicates that hexachlorobutadiene is no longer used for this process (EPA 1982b; IARC 1979).

5.2.4 Disposal

Waste streams resulting from the inadvertent production of hexachlorobutadiene as a byproduct of certain chlorinated hydrocarbons typically contain 33–80% hexachlorobutadiene. These wastes are disposed of by various methods. Disposal practices have shifted from landfilling to incineration. Incineration, which is considered the preferred method of disposal, reportedly achieves >99.9% destruction efficiency (EPA 1982b). In 1982, approximately 68% of an estimated 27 million pounds of hexachlorobutadiene wastes were disposed of by incineration, 32% by deep well injection, and <0.2% by hazardous waste landfill operations (EPA 1982b).

The generation, treatment, storage, and disposal of hexachlorobutadiene-containing wastes are subject to regulation under the Resource Conservation and Recovery Act (RCRA). Underground injection of hexachlorobutadiene is subject to permits issued under an Underground Injection Control program promulgated under the Safe Drinking Water Act (EPA 1982b).

5.3 RELEASES TO THE ENVIRONMENT

The Toxics Release Inventory (TRI) data should be used with caution because only certain types of facilities are required to report (EPA 2005). This is not an exhaustive list. Manufacturing and processing

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Table 5-2. Releases to the Environment from Facilities that Produce, Process, or Use Hexachlorobutadiene^a

State ^c	RF ^d	Reported amounts released in pounds per year ^b							Total release	
		Air ^e	Water ^f	UI ^g	Land ^h	Other ⁱ	On-site ^j	Off-site ^k	On- and off-site	
TX	4	15	0	0	0	0	15	0	15	
Total	12	2,192	0	0	13	0	2,192	13	2,205	

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

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

^cPost office state abbreviations are used.

^dNumber of reporting facilities.

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

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

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

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

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

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

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

RF = reporting facilities; UI = underground injection

Source: TRI18 2020 (Data are from 2018)

There are no known natural sources of hexachlorobutadiene that contribute to environmental levels. The predominant source of hexachlorobutadiene is inadvertent production from the synthesis of certain chlorinated hydrocarbons (EPA 1982a). In 1975, the production of hexachlorobutadiene in the United States was estimated to be 8 million pounds, with 0.1 million pounds released to the environment (NSF 1975). Sixty-eight percent of the 27 million pounds of hexachlorobutadiene waste generated in the United States in 1982 was disposed of by incineration. This process typically obtains a 99.99% destruction efficiency, indicating that approximately 1,900 pounds were released to the atmosphere.

5.3.2 Water

There were no releases of hexachlorobutadiene to surface water or publicly owned treatment works (POTWs) from 12 domestic manufacturing and processing facilities in 2018 required to report to the TRI (TRI18 2020). These releases are summarized in Table 5-2.

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Hexachlorobutadiene may be released to underground and surface waters through discharge from industrial facilities, by leaching from industrial discharges, by leaching from landfills or soils, or by urban runoff. Hexachlorobutadiene was detectable in 1.6% of 1,190 industrial effluent samples reported in the EPA Storage and Retrieval (STORET) database (Staples et al. 1985). The median concentration for all samples, including nondetects was <6 ppb. This chemical was also detected in leachate from an industrial landfill at a concentration of 0.109 ppm (Brown and Donnelly 1988) and from a hazardous waste site (Hauser and Bromberg 1982). In 1982, of the 27 million pounds of hexachlorobutadiene waste produced in the United States as a byproduct of chlorinated hydrocarbon production, 9 million pounds were disposed of by deep well injection (EPA 1982a).

5.3.3 Soil

Estimated releases of 13 pounds (~0.006 metric tons) of hexachlorobutadiene to soils from 12 domestic manufacturing and processing facilities in 2018, accounted for ~0.6% of the estimated total environmental releases from facilities required to report to the TRI (TRI18 2020). No hexachlorobutadiene was released via underground injection (TRI18 2020). These releases are summarized in Table 5-2.

Hexachlorobutadiene may be released to soil by disposal of wastes in landfill operations. In 1982, only 0.2% of the 27 million pounds of hexachlorobutadiene waste produced as a byproduct of chlorinated hydrocarbon-synthesis was disposed of in landfill operations (EPA 1982a). These data indicate that the release to soil was approximately 54,000 pounds.

5.4 ENVIRONMENTAL FATE

5.4.1 Transport and Partitioning

Air. Hexachlorobutadiene can exist in the atmosphere as a vapor or adsorbed to airborne particulate matter. The atmospheric burden of hexachlorobutadiene has been estimated to be 3.2 and 1.3 million kg/year for the northern and southern hemispheres, respectively (Class and Ballschmiter 1987). Significant dispersion of hexachlorobutadiene has been confirmed by the detection of hexachlorobutadiene at areas that are far removed from release sources (Class and Ballschmiter 1987). A high partition coefficient ($\log K_{oc}$) value of 3.67 (Montgomery and Welkom 1990) for hexachlorobutadiene indicates that adsorption to soils with high organic carbon content can occur. Wind erosion of contaminated surface soils can then lead to airborne hexachlorobutadiene-containing particulate matter.

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Levels of hexachlorobutadiene have been detected in fly ash from the incineration of hexachlorobutadiene-containing hazardous waste (Junk and Ford 1980). The transport of particulate matter is a function of particle size and wind speed; however, no data were located regarding the transport of hexachlorobutadiene-containing particles in air.

Water. Transport and partitioning of hexachlorobutadiene in water involves volatilization to the atmosphere and sorption to soil and sediments particulates. The high partition coefficient ($\log K_{ow}$) of 4.78 (Montgomery and Welkom 1990) for hexachlorobutadiene leads to preferential partitioning to sediments and biota over water. Environmental surveys generally report higher levels of hexachlorobutadiene in sediments than in the waters that contain them (Elder et al. 1981; EPA 1976a; Oliver and Charlton 1984). Hexachlorobutadiene has a vapor pressure of 0.15 mmHg (25°C) (Montgomery and Welkom 1990), indicating that volatilization from water occurs. Volatilization is reduced by adsorption to organic material in the water.

Sediment and Soil. The transport and partitioning of hexachlorobutadiene in soils involve volatilization and adsorption. An estimated high partition coefficient ($\log K_{oc}$) of 3.67 (Montgomery and Welkom 1990) for hexachlorobutadiene in soil indicates that soil adsorption can occur, particularly in soils with a high organic carbon content. Sorption was the predominant fate process for hexachlorobutadiene during anaerobic digestion of sludges (Govind et al. 1991). Data indicate that hexachlorobutadiene is mobile in sandy soils, which have relatively low organic-carbon contents (Piet and Zoeteman 1980). Volatilization from surface soils is relatively low; binding to the organic carbon content of the soil further reduces hexachlorobutadiene release.

The desorption of hexachlorobutadiene from field samples of contaminated soil to water was shown to occur in two stages: a loosely bound stage and a tightly bound stage, exhibiting a hysteresis effect on desorption. The initial partitioning from desorption of loosely bound hexachlorobutadiene in soil is quicker than the more tightly bound hexachlorobutadiene desorption characterized as a long-term resistant phase (Chen et al. 1999; Kommalapati et al. 2002).

Other Media. In rainbow trout, the bioconcentration factor (BCF) was dependent on water concentration (Oliver and Niimi 1983). At low concentrations of 0.10 ng/L, a BCF of 5,800 was obtained, compared to a value of 17,000 obtained with higher water concentrations of 3.4 ng/L. Hexachlorobutadiene preferentially accumulates in the liver of fish (Pearson and McConnell 1975). In mussels, the BCF was determined to be between 900 and 2,000 (Pearson and McConnell 1975).

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However, lower values were obtained for algae, crayfish, and bass (160, 60, and 29, respectively) (EPA 1976a). The EPA reviewed new BCF data and recommended a value of 392 (EPA 1989).

Bioaccumulation factors based on freely dissolved lipid-normalized concentrations in water for hexachlorobutadiene range from 6,761 to 575,440 in various aquatic species including *Callinectes sapidus*, *Fundulus heteroclitus*, *Micropogonias undulates*, and *Brevoortia patronus* (Burkhard et al. 1997).

The mean concentration of hexachlorobutadiene found in fish in a contaminated swamp in the lower Mississippi River in Baton Rouge, Louisiana was more than 300 times greater than the mean sediment concentrations suggesting high bioaccumulation (Bart et al. 1998).

5.4.2 Transformation and Degradation

Air. No data were located regarding the transformation and degradation of hexachlorobutadiene in air. Based on the monitoring data, the tropospheric half-life of hexachlorobutadiene was estimated by one author to be 1.6 years in the northern hemisphere (Class and Ballschmiter 1987). However, analogy to structurally similar compounds such as tetrachloroethylene indicates that the half-life of hexachlorobutadiene may be as short as 60 days, predominantly due to reactions with photochemically produced hydroxyl radicals and ozone (Atkinson 1987; Atkinson and Carter 1984). Oxidation constants of $<10^3$ and $6 \text{ (m}\cdot\text{hr)}^{-1}$ were estimated for reactions with singlet oxygen and peroxy radicals, respectively (EPA 1982c).

Water. Data concerning the transformation and degradation of hexachlorobutadiene in waters are limited. Under aerobic conditions, hexachlorobutadiene underwent complete biodegradation after 7 days in water inoculated with domestic sewage (Tabak et al. 1981). Biodegradation of hexachlorobutadiene also occurred during anaerobic digestion of wastewater sludges, although sorption was the predominant fate process (Govind et al. 1991). However, biodegradation did not occur in anaerobic waters (Johnson and Young 1983). Based on monitoring data, the half-life of hexachlorobutadiene in rivers and lakes was estimated to be 3–30 and 30–300 days, respectively (Zoeteman et al. 1980). Data regarding the hydrolysis or photolysis of hexachlorobutadiene in water were not located.

Sediment and Soil. Data regarding the transformation and degradation of hexachlorobutadiene in soil were not located. However, based on the observation that hexachlorobutadiene was completely

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biodegraded in water under aerobic conditions (Tabak et al. 1981), biodegradation probably occurs in nonarid soils as well.

5.5 LEVELS IN THE ENVIRONMENT

Reliable evaluation of the potential for human exposure to hexachlorobutadiene depends, in part, on the reliability of supporting analytical data from environmental samples and biological specimens.

Concentrations of hexachlorobutadiene in unpolluted atmospheres and in pristine surface waters are often so low as to be near the limits of current analytical methods. In reviewing data on hexachlorobutadiene levels monitored or estimated in the environment, it should also be noted that the amount of chemical identified analytically is not necessarily equivalent to the amount that is bioavailable.

Table 5-3 shows the lowest limit of detections that are achieved by analytical analysis in environmental media. An overview summary of the range of concentrations detected in environmental media is presented in Table 5-4.

Table 5-3. Lowest Limit of Detection Based on Standards^a

Media	Detection limit	Reference
Air	0.02 µg/sample	NIOSH 1994
Water	0.11 µg/L	EPA 1992
Soil/solid waste	Laboratory specific	EPA 2006
Whole blood	18 ng/L	Kastl and Hermann 1983

^aDetection limits based on using appropriate preparation and analytics. These limits may not be possible in all situations.

Table 5-4. Summary of Environmental Levels of Hexachlorobutadiene

Media	Low	High	For more information
Outdoor air (ppt)	2	37	Section 5.5.1
Indoor air (ppt)	–	38	Section 5.5.1
Surface water (ppb)	0.82	22	Section 5.5.2
Drinking water (ppt)	1.6	2.7	Section 5.5.2
Sediment (µg/kg)	2.9	11	Section 5.5.3
Food (mg/kg)	0.06	0.3	Section 5.5.4

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Detections of hexachlorobutadiene in air, water, and soil at NPL sites are summarized in Table 5-5.

Table 5-5. Hexachlorobutadiene Levels in Water, Soil, and Air of National Priorities List (NPL) Sites

Medium	Median ^a	Geometric mean ^a	Geometric standard deviation ^a	Number of quantitative measurements	NPL sites
Water (ppb)	120	560	5,600	8	6
Soil (ppb)	230,000	23,000	220	10	6
Air (ppbv)	7.2	6.8	420	15	7

^aConcentrations found in ATSDR site documents from 1981 to 2019 for 1,867 NPL sites (ATSDR 2019). Maximum concentrations were abstracted for types of environmental media for which exposure is likely. Pathways do not necessarily involve exposure or levels of concern.

5.5.1 Air

In the United States, the reported average concentration of hexachlorobutadiene, based on 72 samples from urban and source dominated areas, was 36 ppt (0.38 µg/m³) (EPA 1988a; Shah and Singh 1988). Hexachlorobutadiene levels ranging from 2 to 11 ppt were reported in a number of cities (EPA 1978; Singh et al. 1980, 1982). Higher levels of hexachlorobutadiene were reported in Niagara Falls, with concentrations of up to 37 ppt detected in ambient air levels and up to 38 ppt detected in the basement air of homes near industrial and chemical waste disposal sites (Pellizzari 1982). Hexachlorobutadiene was not detected in 31 ambient air samples from two superfund sites (Intermountain Waste Oil Refinery; Ogden Railyard) (WQP 2020).

Occupational exposures can be significantly higher for individuals who work at plants that produce chlorinated hydrocarbons. Maximum air levels off plant property, at a plant boundary, and within a plant were reported to be 22, 938, and 43,000 ppt, respectively (EPA 1976b).

5.5.2 Water

Hexachlorobutadiene has been detected in some surface waters, but the incidence of detection is low. It was detected in about 4% of 2,518 ambient water samples compiled from the STORage and RETrieval (STORET) and National Water Information System (NWIS) databases, but levels were below the lower reporting limit (WQP 2020). Historically, hexachlorobutadiene was detected in 1 of 204 surface water sites sampled across the United States with a concentration of 22 ppb (EPA 1977). Low levels of

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hexachlorobutadiene were detected in the Niagara River at 0.82 ppt (Oliver and Charlton 1984). Hexachlorobutadiene was not detected in rainwater (Pankow et al. 1984) or urban storm water runoff (Cole et al. 1984; WQP 2020) in a number of U.S. cities. It has not been detected in open ocean waters; however, the coastal waters of the Gulf of Mexico were reported to contain 3–15 ppt (Sauer 1981).

Low levels of hexachlorobutadiene (<1 ppb) may be found in drinking water (EPA 1989). Finished drinking water samples from two U.S. cities were found to contain 1.6 and 2.7 ppt, respectively (EPA 1984). Hexachlorobutadiene was detected in about 31% of 4,329 groundwater samples, with only about 10% of samples testing above the reporting limit with a maximum concentration of 6.38 ppm (WQP 2020).

5.5.3 Sediment and Soil

Hexachlorobutadiene adsorbs to sediments in contaminated water. Sediments from the Niagara River were found to contain 2.9–11 µg/kg (Oliver and Charlton 1984). Hexachlorobutadiene was analyzed for, but not detected, above the quantitation limit in >2,500 sediment samples reported from the Great Lakes National Program (WQP 2020). The median quantitation limit was <300 ppb. Hexachlorobutadiene was not detected in 84 sediment samples from the city and county of Honolulu with lower reporting levels of 26–42 ppb, nor was it detected in 43 ocean site sediment samples.

Abdelghani et al. (1995) conducted field and laboratory studies to determine the levels of hexachlorobutadiene in various samples collected from a swamp area in Louisiana. Hexachlorobutadiene levels ranged from <0.05 to 0.40 ppb in sediment samples.

Hexachlorobutadiene was not detected in 333 soil samples tested in response to Hurricane Katrina, in 133 soil samples from superfund site Ogden Railyard or in 325 soil samples reported from U.S. Geological Survey sites in Alabama, Florida, Hawaii, Indiana, New Mexico, and Texas (WQP 2020).

5.5.4 Other Media

Hexachlorobutadiene was detected in several foodstuffs in the United Kingdom (McConnell et al. 1975) and Germany (Kotzias et al. 1975), but it was not detected in the United States in milk, eggs, or vegetables even when the samples were obtained from within a 25-mile radius of facilities producing chlorinated hydrocarbons (Yip 1976; Yurawecz et al. 1976). Fish from the Great Lakes generally did not contain detectable levels of hexachlorobutadiene (Camanzo et al. 1987; DeVault 1985), with the

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exception of trout from Lake Ontario, which were reported to contain 0.06–0.3 mg/kg (Oliver and Niimi 1983). Hexachlorobutadiene was not detectable in any of 993 fish tissue samples collected from 2000 to 2020 reported on the STORET database including data from 39 U.S. states in 60 species of fish (WQP 2020).

Macgregor et al. (2010) investigated concentrations of persistent organic pollutants (POPs), including hexachlorobutadiene, in eels from 30 sites across Scotland. While several of the other POPs were detected in all samples, hexachlorobutadiene was detected in only one sample. Eels were used as an ideal biomonitor because of their high lipid content.

Hexachlorobutadiene was not detected in sewage influents (EPA 1979), in sewage samples (EPA 1990), or landfill leachate (WQP 2020).

In a study of black tattoo ink, hexachlorobutadiene was detected in 6 of 14 samples; the levels ranged from 0.08 to 4.52 $\mu\text{g/g}$ (Lehner et al. 2011).

5.6 GENERAL POPULATION EXPOSURE

The general population can be exposed to low levels of hexachlorobutadiene in air, food, and water. Estimates of source or route-specific exposures to humans were not located. Hexachlorobutadiene has been detected in human adipose tissue with a concentration ranging from 0.8 to 8 $\mu\text{g/kg}$ wet weight (McConnell et al. 1975; Mes et al. 1982). Higher concentrations were reported in human liver samples, with values ranging from 5.7 to 13.7 $\mu\text{g/kg}$ wet weight (McConnell et al. 1975). These data indicate that exposure to hexachlorobutadiene occurs in humans, but do not identify sources or routes of exposure. Although exposure from foods is probably a minor route of exposure, people who consume large amounts of fish obtained from contaminated waters may be exposed to significant quantities of hexachlorobutadiene. Similarly, persons who live in source-dominated areas or work in plants that produce chlorinated hydrocarbons may be exposed to significant levels of hexachlorobutadiene in the air. No information was found on the number of workers potentially exposed to hexachlorobutadiene.

Fat tissue samples from 50 children living in farm areas in the Murcia region of Spain were found to have mean concentrations of hexachlorobutadiene of 0.70 $\mu\text{g/g}$ (from 13 positive samples) ranging from 0.23 to 2.43 $\mu\text{g/g}$ (Olea et al. 1999).

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5.7 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

People who live in source-dominated areas (at or near hazardous waste sites or chlorinated hydrocarbon production plants) and workers in these areas are potentially exposed to high levels of hexachlorobutadiene. Individuals who consume large amounts of fish from contaminated waters may also be exposed to above-average levels of hexachlorobutadiene.