

6. POTENTIAL FOR HUMAN EXPOSURE

6.1 OVERVIEW

Carbon tetrachloride has been identified in at least 430 of the 1,662 hazardous waste sites that have been proposed for inclusion on the EPA National Priorities List (NPL) (HazDat 2005). However, the number of sites evaluated for carbon tetrachloride is not known. The frequency of these sites can be seen in Figure 6-1. Of these sites, 425 are located within the United States, 1 is located in Guam, 2 are located in the Virgin Islands, and 2 are located in the Commonwealth of Puerto Rico (not shown).

Carbon tetrachloride is a stable chemical that is degraded very slowly, so there has been a gradual accumulation of carbon tetrachloride in the environment as a consequence of releases from human activities. Until 1986, the largest source of release was from the use of carbon tetrachloride as a grain fumigant, but this practice has now been stopped. Other releases of carbon tetrachloride may occur during carbon tetrachloride production or during the use of carbon tetrachloride in the manufacture of chlorofluorocarbons and other chemical products.

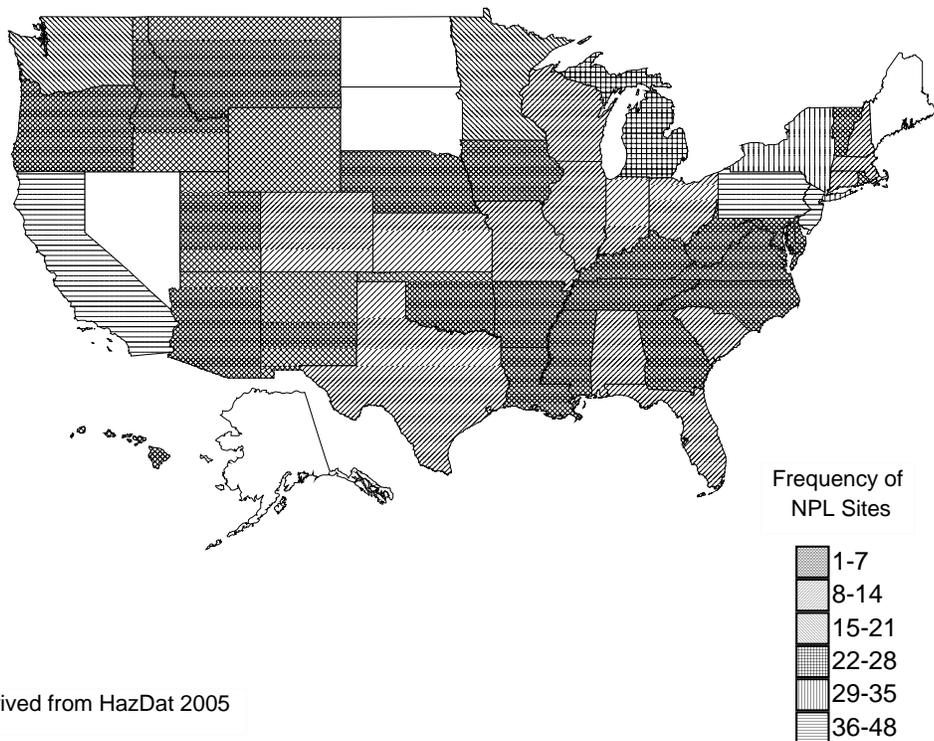
Because carbon tetrachloride is volatile at ambient temperature, most carbon tetrachloride in the environment exists in the air. Typical levels in rural areas are about $1 \mu\text{g}/\text{m}^3$, with somewhat higher values in urban areas and near industrial sources (Brodzinski and Singh 1983; Simmonds et al. 1983; Wallace et al. 1986). Low levels of carbon tetrachloride have been detected in many water systems (particularly surface water systems), with typical values of $<0.5 \mu\text{g}/\text{L}$ (Letkiewicz et al. 1983). Less than 1% of all groundwater-derived drinking water systems has levels of carbon tetrachloride $>0.5 \mu\text{g}/\text{L}$ and $<0.2\%$ have levels $>5 \text{ mg}/\text{L}$ (EPA 1987a).

6.2 RELEASES TO THE ENVIRONMENT

The TRI data should be used with caution because only certain types of facilities are required to report (EPA 1997). This is not an exhaustive list. Manufacturing and processing facilities are required to report information to the Toxics Release Inventory only if they employ 10 or more full-time employees; if their facility is classified under Standard Industrial Classification (SIC) codes 20–39; and if their facility

6. POTENTIAL FOR HUMAN EXPOSURE

Figure 6-1. Frequency of NPL Sites with Carbon Tetrachloride Contamination



6. POTENTIAL FOR HUMAN EXPOSURE

produces, imports, or processes $\geq 25,000$ pounds of any TRI chemical or otherwise uses $>10,000$ pounds of a TRI chemical in a calendar year (EPA 1997).

6.2.1 Air

Estimated releases of 4.44 million pounds (202 metric tons) of carbon tetrachloride to the atmosphere from 55 domestic manufacturing and processing facilities in 2002, accounted for about 71% of the estimated total environmental releases from facilities required to report to the TRI (TRI02 2004). These releases are summarized in Table 6-1.

Although sources of carbon tetrachloride including marine algae, oceans, volcanoes, and drill wells have been cited (Gribble 1994), the majority of carbon tetrachloride in the environment is due to direct release to the atmosphere during production, disposal, or use of the compound. The estimated annual global release of carbon tetrachloride was about 60,000–80,000 metric tons/year during the period 1965–1977 (Singh et al. 1979a). Based on measurements of the rate of change of carbon tetrachloride levels in air around the globe, the calculated total atmospheric releases of carbon tetrachloride during the period 1978–1985 were around 90,000 metric tons/year (Simmonds et al. 1988). Some carbon tetrachloride may also be formed in air by photochemical decomposition of perchloroethylene (Singh et al. 1975) or by incomplete combustion of this chemical during waste incineration (Katami et al. 1992), although the magnitude of this contribution is difficult to estimate (Singh et al. 1979a).

Releases of carbon tetrachloride to air in the United States from manufacturing and processing ranged from 3.7 to 4.6 million pounds during 1987–1989, but were substantially reduced in 1990 and years after (EPA 1990, 1991b; TRI02 2004). According to the TRI02 (2004), an estimated total of 444,436 pounds (202 metric tons) of carbon tetrachloride, amounting to 71% of the total environmental release, was discharged to the air from manufacturing and processing facilities in the United States in 2001 (TRI02 2004) (see Table 6-1). The TRI data should be used with caution since only certain types of facilities are required to report. This is not an exhaustive list.

6.2.2 Water

Estimated releases of 320 pounds (0.145 metric tons) of carbon tetrachloride to surface water from 55 domestic manufacturing and processing facilities in 2002, accounted for about $<1\%$ of the estimated

6. POTENTIAL FOR HUMAN EXPOSURE

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

State ^c	RF ^d	Reported amounts released in pounds per year ^b							
		Air ^e	Water ^f	UI ^g	Land ^h	Other ⁱ	Total release		On- and off-site
							On-site ^j	Off-site ^k	
AL	1	10	0	0	0	0	0	10	10
AR	3	4,031	0	0	0	0	0	4,031	4,031
CA	1	1,000	0	0	0	0	0	1,000	1,000
IL	1	11	0	0	215	168	383	11	394
IN	2	500	250	0	5	0	0	755	755
KS	1	12,239	0	32,922	0	0	0	45,161	45,161
KY	2	854	0	0	5	0	5	854	859
LA	12	304,984	55	139,323	45	38	44	444,401	444,445
MD	1	119	0	0	0	0	0	119	119
MI	1	250	0	0	0	0	0	250	250
MS	1	500	0	0	0	0	0	500	500
NC	1	41	0	0	0	0	0	41	41
NE	1	255	0	0	0	0	0	255	255
OH	4	4,530	5	2	255	61	316	4,537	4,853
PA	2	6,983	0	0	500	1,564	2,064	6,983	9,047
TN	2	21	0	0	0	0	0	21	21
TX	15	107,605	10	5,568	8	28	5,604	107,618	113,223
UT	1	65	0	0	0	0	0	65	65
WV	2	438	0	0	0	0	0	438	438
WY	1	No data	No data	No data	No data	No data	No data	No data	No data
Total	55	444,436	320	177,815	1,033	1,860	8,417	617,050	625,467

Source: TRI02 2004 (Data are from 2002)

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

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

^cPost office state abbreviations are used.

^dNumber of reporting facilities.

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

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

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

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

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

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

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

RF = reporting facilities; UI = underground injection

6. POTENTIAL FOR HUMAN EXPOSURE

total environmental releases from facilities required to report to the TRI (TRI02 2004). These releases are summarized in Table 6-1.

Relatively small amounts of carbon tetrachloride are released to water. The total in 1978 was estimated to be 2.5 metric tons, due almost entirely to discharges from carbon tetrachloride production facilities (Rams et al. 1979). Analysis of data from EPA's Storage and Retrieval (STORET) database for the early 1980s indicate that carbon tetrachloride was detectable in 5.5% of 1,343 industrial effluent samples (Staples et al. 1985). The median concentration of all samples was <5 µg/L. Carbon tetrachloride was also detected in leachates from industrial landfills at concentrations ranging from <10 to 92 µg/L (Brown and Donnelly 1988).

In 1989, approximately 320 pounds (0.145 metric tons) of carbon tetrachloride was released in the United States to surface waters (EPA 1991b). An estimated total of 178,135 pounds (81 metric tons) of carbon tetrachloride, amounting to about 28% of the total environmental release, was discharged to the water and underground injection (potential groundwater release) from manufacturing and processing facilities in the United States in 2002 (TRI02 2004, see Table 6-1).

6.2.3 Soil

Estimated releases of 1,033 pounds (0.47 metric tons) of carbon tetrachloride to soils from 55 domestic manufacturing and processing facilities in 2002, accounted for about 0.0016% of the estimated total environmental releases from facilities required to report to the TRI (TRI02 2004). An additional 1.78 million pounds (81 metric tons), constituting about 28% of the total environmental emissions, were released via underground injection (TRI02 2004). These releases are summarized in Table 6-1.

Release of carbon tetrachloride to soil during carbon tetrachloride production was estimated to be 200,000 pounds (92 metric tons) in 1978 (Letkiewicz et al. 1983). Other sources of carbon tetrachloride discharged to soil include wastes associated with production and use of chlorofluorocarbons, metal cleaning compounds, adhesives, paints and other products. Total emissions to soil were estimated to be 2.6 million pounds (1,200 metric tons) in 1978 (Letkiewicz et al. 1983). In 1989, approximately 1,800 pounds (0.8 metric tons) of carbon tetrachloride were released in the United States to land (EPA 1991b). An estimated total of 1,033 pounds (0.47 metric tons) of carbon tetrachloride, amounting to <1%

6. POTENTIAL FOR HUMAN EXPOSURE

of the total environmental release, was discharged to the soil from manufacturing and processing facilities in the United States in 2002 (TRI02 2004).

6.3 ENVIRONMENTAL FATE

6.3.1 Transport and Partitioning

Nearly all carbon tetrachloride released to the environment exists in the atmosphere (73% is released to the atmosphere directly). Most of the carbon tetrachloride released to soil and water evaporates within a few days (EPA 1991b). Because carbon tetrachloride does not degrade readily in the atmosphere, significant global transport is expected. Although carbon tetrachloride is moderately soluble in water (800 mg/L at 20 °C) (Verschuere 1983), only about 1% of the total carbon tetrachloride in the environment exists dissolved in surface waters and oceans (Galbally 1976). This is attributable to the relatively high rate of volatilization of low molecular weight chlorinated hydrocarbons from water (Dilling 1977; Dilling et al. 1975). Because of this, carbon tetrachloride also tends to volatilize from tap water used for showering, bathing, cooking, and other household uses inside a home (McKone 1987; Tancrede et al. 1992).

Most carbon tetrachloride released to soil is expected to volatilize rapidly due to its high vapor pressure (91.3 mmHg at 20 °C) (Howard 1990; IARC 1979). A fraction of the carbon tetrachloride remaining in the soil may adsorb to the soil organic matter, based on a calculated soil sorption coefficient of 110 ($\log K_{oc}$ of 2.04) (Kenaga 1980). Nevertheless, carbon tetrachloride is expected to be moderately mobile in most soils, depending on the organic carbon content, and leaching to groundwater is possible (Howard 1990). Marine sediments high in organic matter tended to have higher concentrations of carbon tetrachloride than did sediments with lower organic matter (McConnell et al. 1975). The composition of the soil organic matter and the water content of the soil may also affect sorption of carbon tetrachloride (Rutherford and Chiou 1992; Rutherford et al. 1992). Experimentally determined K_{oc} values for sorption of carbon tetrachloride on soils with organic carbon contents of 1.49 and 0.66% were 143.6 and 48.89 ($\log K_{oc} = 2.16$ and 1.69), respectively (Walton et al. 1992). The retardation factor of carbon tetrachloride in breakthrough sampling in groundwater ranged from 1.4 to 1.7, indicating that soil adsorption is a relatively minor fate process (Mackay et al. 1983). Retardation factors for carbon tetrachloride measured in a flow-through system studying sorption of organics to aquifer materials with very low organic carbon (0.07–0.025%) ranged from 1.10 to 1.46 (Larsen et al. 1992), confirming this conclusion.

6. POTENTIAL FOR HUMAN EXPOSURE

There is little tendency for carbon tetrachloride to bioconcentrate in aquatic or marine organisms. Reported log bioconcentration factors (BCFs) were 1.24 and 1.48 in trout and bluegill sunfish, respectively (HSDB 2004; Neely et al. 1974; Pearson and McConnell 1975). However, the log octanol/water partition coefficient ($\log K_{ow}$) of 2.64 for carbon tetrachloride (EPA 1984) suggests that bioaccumulation is at least possible under conditions of constant exposure and may occur in occupational settings or in people living at or near hazardous waste sites. No data were located on the biomagnification of carbon tetrachloride. However, since most animals readily metabolize and excrete carbon tetrachloride following exposure (see Section 3.4.3), biomagnification is not expected.

6.3.2 Transformation and Degradation

6.3.2.1 Air

Carbon tetrachloride is very stable in the troposphere (Cox et al. 1976; Lillian et al. 1975; Singh et al. 1980). This is primarily because carbon tetrachloride does not react with hydroxyl radicals that initiate breakdown and transformation reactions of other volatile hydrocarbons. In addition, carbon tetrachloride does not photodissociate in the troposphere because, in the vapor state, it has no chromophores that absorb light in those visible or near ultraviolet regions of the electromagnetic spectrum, which prevail in the troposphere (Davis et al. 1975). The rate of oxidation of carbon tetrachloride is thought to be so slow that its estimated tropospheric half-life exceeds 330 years (Cox et al. 1976). Ultimately, carbon tetrachloride that is not removed from the troposphere by rainfall (Pearson and McConnell 1975) diffuses upward into the stratosphere where it may be photodegraded by shorter wavelength ultraviolet light (185–225 nm) more prevalent in this region of the atmosphere to form the trichloromethyl radical and chlorine atoms (Molina and Rowland 1974). The rate of photodissociation begins to become important at altitudes >20 km, and increases as altitude increases (Molina and Rowland 1974). Estimates of the atmospheric lifetime (the overall persistence of carbon tetrachloride in the troposphere and the stratosphere combined) are variable, but most values range from 30 to 100 years (EPA 1991b; Molina and Rowland 1974; Simmonds et al. 1983, 1988; Singh et al. 1979a), with 50 years generally being accepted as the most reasonable value.

Chlorine atoms and other chlorine species formed by photodecomposition of carbon tetrachloride in the stratosphere can catalyze reactions that destroy ozone. As the manufacture of carbon tetrachloride for use

6. POTENTIAL FOR HUMAN EXPOSURE

in chlorofluorocarbons is phased out according to an international agreement (EPA 1987e), the impact of carbon tetrachloride on atmospheric ozone is likely to decrease.

6.3.2.2 Water

Carbon tetrachloride dissolved in water does not photodegrade or oxidize in any measurable amounts (Howard et al. 1991). The rate of hydrolysis in water is second order with respect to carbon tetrachloride, but is extremely slow, with a calculated half-life of 7,000 years at a concentration of 1 ppm (Mabey and Mill 1978). The reported aqueous hydrolysis rate calculated from gas phase measurements was $<2 \times 10^{-6} \text{M}^{-1} \text{s}^{-1}$ (Haag and Yao 1992), 1–2 orders of magnitude less than other chlorinated alkanes. Others have suggested that hydrolysis may be the cause of decreasing carbon tetrachloride concentrations with depth in the ocean (Lovell et al. 1973). However, this observation might also be explained by the biodegradation of carbon tetrachloride, which occurs much more rapidly than hydrolysis, particularly under anaerobic conditions. Biodegradation may occur within 16 days under anaerobic conditions (Tabak et al. 1981). Based upon acclimated aerobic screening test data, the aqueous aerobic half-life of carbon tetrachloride was estimated to be 6–12 months (Howard et al. 1991). Based upon unacclimated anaerobic screening test data and acclimated aerobic sediment/aquifer grab sample data, the aqueous anaerobic half-life of carbon tetrachloride was estimated to be 7–28 days (Howard et al. 1991).

The carbon atom in carbon tetrachloride is in its most oxidized state, therefore it is much more likely to undergo reductive degradation, as opposed to oxidative degradation (McCarty 1996a; McCarty and Reinhart 1993; McCarty and Semprini 1994; McCarty et al. 1996b). Carbon tetrachloride may undergo reductive dechlorination in aquatic systems in the presence of free sulfide and ferrous ions, or naturally occurring minerals providing those ions (Kriegman-King and Reinhard 1991). The transformation rate of carbon tetrachloride to chloroform and other products under simulated groundwater conditions at 50 °C was evaluated for the chemical alone, with minerals (biotite and vermiculite) providing ferrous ions and free sulfide ions, and with natural iron sulfides (pyrite and marcasite). Reported half-lives for carbon tetrachloride were 380 days for carbon tetrachloride alone, 2.9–4.5 days with minerals and sulfide ion present, and 0.44–0.85 days in the presence of natural iron sulfides. The effects noted with free ferrous or free sulfide ions were two orders of magnitude less than with natural minerals. Another recent study found degradation of 84% of the carbon tetrachloride present in aqueous solution containing ferrous ions 33 days, but no effect with sulfide ions (Doong and Wu 1992). Additional studies indicated that the abiotic reductive dechlorination of carbon tetrachloride could involve microbial cofactors or metabolites. Reductive dechlorination also occurs by anaerobic microbial transformation (Edwards et al. 1942).

6. POTENTIAL FOR HUMAN EXPOSURE

Carbon tetrachloride removal via reductive dechlorination has also been observed under sulfate reducing conditions in an anaerobic system (de Best et al. 1998). Complete removal of carbon tetrachloride was observed, with chloroform and dichloromethane as the main transformation products; however, some unknown degradation products were also observed.

6.3.2.3 Sediment and Soil

No studies were located on the degradation of carbon tetrachloride in soil or sediment. Based on the estimated aqueous aerobic biodegradation half-life of carbon tetrachloride, the half-life of carbon tetrachloride in soil is estimated to be 6–12 months (Howard et al. 1991).

6.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

Reliable evaluation of the potential for human exposure to carbon tetrachloride depends in part on the reliability of supporting analytical data from environmental samples and biological specimens. Concentrations of carbon tetrachloride 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 carbon tetrachloride levels monitored or estimated in the environment, it should also be noted that the amount of chemical identified analytically is not necessarily equivalent to the amount that is bioavailable. The analytical methods available for monitoring carbon tetrachloride in a variety of environmental media are detailed in Chapter 7.

6.4.1 Air

Carbon tetrachloride appears to be ubiquitous in ambient air. Based on analysis of 4,913 ambient air samples reported in the National Ambient Volatile Organic Compounds Database (including remote, rural, suburban, urban, and source dominated sites in the United States), the average concentration of carbon tetrachloride was 0.168 ppb ($1.1 \mu\text{g}/\text{m}^3$) (Shah and Heyerdahl 1988). Carbon tetrachloride was detected in air at 76 NPL hazardous waste sites (HazDat 2005). Average values reported in four U.S. cities ranged from 0.144 to 0.291 ppb (Singh et al. 1992). Similar results were reported by Simmonds et al. (1983), who found average concentrations of 0.6–0.8 $\mu\text{g}/\text{m}^3$ (0.10–0.13 ppb) at five coastal monitoring stations around the world, and Kelly et al. (1994), who reported a median ambient

6. POTENTIAL FOR HUMAN EXPOSURE

concentration of $0.8 \mu\text{g}/\text{m}^3$ based on a compilation of ambient data from 1964 through 1992. Continued monitoring studies by Simmonds et al. (1988) reveal that global atmospheric levels of carbon tetrachloride have been steadily increasing by about 1.3% per year, reaching 0.12–0.14 ppb by 1985. Similar concentrations of carbon tetrachloride were also reported in air at five hazardous waste sites and one landfill in New Jersey, where average values ranged from 0.02 to 0.12 ppb (LaRegina et al. 1986). A study done involving the Toxic Air Monitoring System (TAMS) network showed concentrations of carbon tetrachloride in urban locations in Boston, Chicago, Houston, and the Seattle/Tacoma area (Evans et al. 1992). The median 24-hour concentrations were 0.12, 0.13, and 0.13 ppb at the three Boston sites, 0.12, 0.12, and 0.13 ppb at the three Chicago sites, 0.15, 0.13, and 0.12 ppb at the three Houston sites, and 0.12 ppb at the Seattle/Tacoma site. Sweet and Vermette (1990, 1992) have shown that carbon tetrachloride is present in areas of urban Illinois including southeast Chicago and east St. Louis at average concentrations of $0.7\text{--}1.0 \mu\text{g}/\text{m}^3$ (0.11–0.16 ppb). It was determined in this study that point sources of carbon tetrachloride from industry and wind direction are responsible for localized increases in concentration. The Arizona hazardous air pollutants monitoring program has demonstrated average concentrations of carbon tetrachloride ranging from 0.7 to $0.75 \mu\text{g}/\text{m}^3$ (0.11–0.12 ppb) (Zielinska et al. 1998). A study on air toxics in Minnesota has shown a carbon tetrachloride median concentration of $0.77 \mu\text{g}/\text{m}^3$ (0.12 ppb). This concentration exceeded health benchmark values in 88% of monitoring sites (Pratt et al. 2000). A study monitoring levels of carbon tetrachloride in 13 urban areas of the United States during September 1996 to August 1997 provided a mean concentration of 0.072–0.09 ppbv throughout the areas (Mohamed et al. 2002). The more recent studies demonstrate a decrease in levels of carbon tetrachloride in the ambient air, which could be a reflection of the current drop in production; however, the resistance to atmospheric degradation allows for levels to remain somewhat constant. Ambient air concentrations of carbon tetrachloride were unaffected by changes in temperature and season (Mohamed et al. 2002), or day of the week (Austin 2003).

Studies have revealed that carbon tetrachloride is also a common contaminant of indoor air. Typical concentrations in homes in several U.S. cities were about $1 \mu\text{g}/\text{m}^3$ (0.16 ppb), with some values up to $9 \mu\text{g}/\text{m}^3$ (1.4 ppb) (Wallace et al. 1986). Concentrations in indoor air were usually higher than in outdoor air, indicating that the source of the carbon tetrachloride was building materials or products (pesticides, cleaning agents) inside the home (Wallace et al. 1986, 1987). Based on 2,120 indoor air samples in the United States, the average concentration of carbon tetrachloride was 0.4 ppb ($2.6 \mu\text{g}/\text{m}^3$) (Shah and Heyerdahl 1988). However, the median value was 0 ppb, indicating that carbon tetrachloride was not detected in more than half of the samples. A later study determined backyard outdoor air concentrations of carbon tetrachloride taken from 175 home sites in 6 urban areas to be $0.6 \mu\text{g}/\text{m}^3$ (Wallace 1991). In

6. POTENTIAL FOR HUMAN EXPOSURE

this same study, 24-hour average exposures of 750 people in 6 urban areas were determined to be $1 \mu\text{g}/\text{m}^3$ (0.16 ppb). This indicates that for carbon tetrachloride, outdoor sources account for a majority of the airborne risk; however, indoor sources are still a concern (Acquavella et al. 1994; Wallace 1991). These data may reflect the effects of the discontinuation of the use of carbon tetrachloride in consumer products.

6.4.2 Water

There have been a number of surveys performed by the federal government to define typical levels of carbon tetrachloride in water supplies in this country. The results of these studies reveal that about 99% of all groundwater supplies and about 95% of all surface water supplies contain $<0.5 \mu\text{g}/\text{L}$ of carbon tetrachloride (Letkiewicz et al. 1983). Carbon tetrachloride was detected in groundwater at 310 NPL hazardous waste sites, and in surface water at 53 NPL hazardous waste sites (HazDat 2005). Analysis of 945 drinking water samples from cities around the United States found detectable levels ($>0.2 \mu\text{g}/\text{L}$) in 30 (3.2%) of the samples (Westrick et al. 1984). The highest value reported was $16 \mu\text{g}/\text{L}$, and the median value of the positive samples ranged from 0.3 to $0.7 \mu\text{g}/\text{L}$ in different sample groups. Carbon tetrachloride has also been detected in some private drinking water wells, at levels ranging from 1 to $720 \mu\text{g}/\text{L}$ (RIDOH 1989). Based on a survey of groundwater monitoring data from 479 waste sites, carbon tetrachloride was also detectable in groundwater (concentration not reported) at 32 sites in 9 EPA regions (Plumb 1991, 1992). A U.S. Geological Survey study of pesticide compounds present in well water around the United States showed the presence of carbon tetrachloride in $<5\%$ of the wells, but no concentration data were provided (Kolpin et al. 1997). A study on chemicals in California drinking water from 1984 to 1990 showed organic pollutants in 921 of 7,712 wells sampled (Lam et al. 1994). Of these contaminated wells, 45 were contaminated with carbon tetrachloride, at a maximum concentration of $29 \mu\text{g}/\text{L}$ (Lam et al. 1994). A survey of data by the National Academy of Sciences (NAS 1978) reported a range of carbon tetrachloride concentrations in seawaters of 0.2– $0.7 \text{ ng}/\text{L}$. Based on analysis of data from the STORET database, carbon tetrachloride was detectable in 12% of 8,858 ambient water samples (Staples et al. 1985). The median concentration in all samples was $0.1 \mu\text{g}/\text{L}$.

6.4.3 Sediment and Soil

Because carbon tetrachloride is ubiquitous in air, it is likely that trace levels of carbon tetrachloride are present in surface soils around the globe. Carbon tetrachloride was detected in soil at 103 NPL hazardous waste sites, and in sediment at 23 NPL hazardous waste sites (HazDat 2005). Based on information from

6. POTENTIAL FOR HUMAN EXPOSURE

the STORET database, carbon tetrachloride was detected in 0.8% of sediment samples across the United States (Staples et al. 1985). The median concentration of all samples was <5 mg/kg dry weight.

6.4.4 Other Environmental Media

Until 1986, one of the major uses of carbon tetrachloride was as a fumigant for grain, and consequently, low levels of carbon tetrachloride occurred in grain or food products derived from such grain. Estimates of carbon tetrachloride residue levels in treated grain varied as a function of fumigation conditions and the amount of aeration after fumigation, but values of 1–100 mg/kg were typical (Deer et al. 1987; Letkiewicz et al. 1983; Lynn and Vorches 1957; McMahon 1971). Levels in finished food prepared from fumigated grains were considerably lower, with typical concentrations below 0.1 mg/kg (Berck 1974). Carbon tetrachloride was detected in 44 of 549 food items at an average concentration of 0.031 mg/kg in a Food and Drug Administration (FDA) survey (Daft 1991). However, carbon tetrachloride is no longer used for this purpose in the United States, so exposure from this source is no longer of concern, but certain foods may absorb small amounts of carbon tetrachloride from the air during processing (Daft 1991). Carbon tetrachloride does not appear to occur in significant quantities in most other foods (Letkiewicz et al. 1983; McConnell et al. 1975).

Carbon tetrachloride was detected in 11 of 1,159 household cleaning and related products in a survey conducted during the late 1980s (Sack et al. 1992). Since this chemical is no longer used in consumer products, exposure from this source is not likely to be of concern.

6.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

Members of the general population are most likely to be exposed to carbon tetrachloride through ambient air and drinking water. Despite being banned from consumer products, the long lifetime of carbon tetrachloride in the atmosphere contributes to the background level to which the general population is exposed (Wallace 1991). Assuming inhalation of 20 m³/day by a 70-kg adult and 40% absorption of carbon tetrachloride across the lung (IRIS 2003), typical levels of carbon tetrachloride in ambient air (about 1 µg/m³) yield systemically absorbed doses of about 0.1 µg/kg/day. Somewhat higher exposures could occur near point sources such as industries that produce or use carbon tetrachloride or hazardous waste sites contaminated with carbon tetrachloride. Estimates of daily intake from air and water range from 12 to 511 µg/day and from 0.2 to 60 µg/day, respectively, based on average concentrations of 0.1–

6. POTENTIAL FOR HUMAN EXPOSURE

4 ppb (0.64–25.6 $\mu\text{g}/\text{m}^3$) in air and 0.1–30 $\mu\text{g}/\text{L}$ in water (Howard 1990). For water, consumption of 2 L/day by a 70-kg adult containing a typical carbon tetrachloride concentration of 0.5 $\mu\text{g}/\text{L}$ yields a typical daily intake of about 0.01 $\mu\text{g}/\text{kg}/\text{day}$.

A study by Hartwell et al. (1992) analyzed the levels of carbon tetrachloride breath, personal air, and fixed indoor and outdoor sites in the Los Angeles area of California. The percentages of samples in which carbon tetrachloride was detected overnight, during the winter season were 2.13% in breath, 81.4% in personal air, 90.5% in kitchen, and 91.3% in outdoor air. Based on these results, carbon tetrachloride is considered often found, but not at relatively high concentrations in the winter season, and therefore, concentrations were not provided. Similar results were determined for daytime and summer months.

Exposure to carbon tetrachloride may also occur by dermal and inhalation routes while using tap water for bathing and other household purposes (McKone 1987; Tancrede et al. 1992).

Exposure to carbon tetrachloride via food is not likely to be of significance, since levels in most foods are below analytical detection limits. Ingestion of bread or other products made with carbon tetrachloride-fumigated grain may have contributed to dietary exposure in the past, but this route of exposure is no longer believed to be of significance.

In the workplace, the most likely route of exposure is by inhalation. Air concentrations at a number of locations where fumigated grain was stored were well below 5 ppm, while some samples contained over 60 ppm (Deer et al. 1987). The average exposure of workers in the grain facilities ranged from 0.002 to 0.1 ppm, depending on job activity. For a worker exposed to 0.1 ppm (630 $\mu\text{g}/\text{m}^3$), the intake during an 8-hour day corresponds to a dose of about 35 $\mu\text{g}/\text{kg}/\text{day}$. Based on results of the National Occupational Exposure Survey (NOES) conducted during 1981–1983, the National Institute for Occupational Safety and Health (NIOSH) estimated that 58,208 workers were potentially exposed to carbon tetrachloride in the United States at that time (HSDB 2004). A study showing the baseline for potential emissions in the extrusion of polycarbonate resin at 304 °C showed that carbon tetrachloride was either undetectable or present at very low levels (Rhodes et al. 2002).

6. POTENTIAL FOR HUMAN EXPOSURE

6.6 EXPOSURES OF CHILDREN

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

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

Young children often play close to the ground and frequently play in the dirt, which increases their dermal exposure to toxicants in dust and soil. They also tend to ingest soil, either intentionally through pica, or unintentionally through hand-to-mouth activity. Children, thus, may be orally dosed and dermally exposed to carbon tetrachloride present as a contaminant in soil and dust. It has been demonstrated that carbon tetrachloride vapors are absorbed by the skin slowly (HSDB 2004). In addition, carbon tetrachloride has a log K_{oc} value (organic carbon-water partition coefficient) of 2.04 (Kenaga 1980) indicating that it is not expected to adsorb to soil and sediment (HSDB 2004). Most of the carbon tetrachloride in the upper layers of the soil will be rapidly volatilized to air (vapor pressure=90 mmHg at 20 °C). Loss of carbon tetrachloride from the soil decreases the potential of dermal and oral exposure to children, but its rapid volatilization results in inhalation being the most likely route of exposure during play on the ground.

Children breathe in more air per kilogram of body weight than adults. Therefore, a child in the same micro-environment as an adult is likely to be exposed to a higher dosage of carbon tetrachloride from ambient air. Young children are closer to the ground or floor because of their height. The carbon tetrachloride vapors being heavier than air (vapor density=5.32, air=1, HSDB 2004) tend to concentrate near the ground. Children are therefore at a greater risk of exposure than adults during accidental spills or through indoor use of carbon tetrachloride in an unventilated area.

6. POTENTIAL FOR HUMAN EXPOSURE

Exposures of the embryo or fetus to volatile organic compounds such as carbon tetrachloride may occur if the expectant mother is exposed. A newborn infant may be exposed by breathing contaminated air and by ingestion of mother's milk, which can contain small amounts of carbon tetrachloride. Children may be exposed through accidental ingestion of products containing carbon tetrachloride. Because of the toxicity of carbon tetrachloride, consumer uses have been discontinued, and only industrial uses remain (Section 5.3); therefore, the occurrence of products containing carbon tetrachloride being in the home should be low. Older children and adolescents may be exposed to carbon tetrachloride in their jobs or hobbies, or through deliberate solvent abuse by "sniffing." Inhalant abuse during pregnancy poses significant risks to the pregnancy and endangers both the mother and the fetus. Solvent abuse of carbon tetrachloride for euphoric effects would result in exposure levels that exceed those producing adverse effects in animals.

A study has been done in the Kanawha Valley in West Virginia observing children from 74 elementary schools in the this area (Ware et al. 1993). The Kanawha Valley region is one of the largest areas of chemical manufacturing in the United States. Concentrations of 5 petroleum-related compounds and 10 compounds more specific to industrially related processes, including carbon tetrachloride, were determined at the different schools in groups based on proximity to industry. It was determined that the mean concentration values of both the petroleum-related compounds and the process-related compounds for schools in the valley, near the chemical companies, were higher than for schools in the valley further away from the chemical companies, as well as schools out of the valley, both near and further away from the chemical companies. These values ($19.71 \mu\text{g}/\text{m}^3$ for the petroleum-related compounds and $5 \mu\text{g}/\text{m}^3$ for the process-related compounds) are also higher than normally found in outdoor air around the country. A correlation was drawn between these higher concentrations of chemicals and an increased incidence of respiratory symptoms, including asthma, wheeze-related symptoms, and symptoms characteristic of reactive airway disease. It should be noted, however, that these data are for mixtures of volatile organic compounds and are not specific to carbon tetrachloride. Also, the observed data do not show direct causation of the observed symptoms; therefore, a need exists for further investigation of the effects of carbon tetrachloride on children (Donnelly et al. 1995).

6.7 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

Workers involved in the manufacture or use of carbon tetrachloride are the population most likely to have exposures to carbon tetrachloride significantly higher than members of the general public. Workers exposed to concentrations in air ranging from 20 to 125 ppm for intermediate durations have experienced

6. POTENTIAL FOR HUMAN EXPOSURE

a variety of neurological effects (see Section 3.2.1.4). Current regulations restrict the acceptable concentration of carbon tetrachloride in workplace air to 2 ppm, but this is still much higher than commonly encountered in the ambient environment. Fugitive emissions of carbon tetrachloride from chemical plants may expose area residents to elevated levels of this halocarbon, although concentrations outside the plant are typically much lower than in the chemical plant itself. Other populations that might have above average exposure include persons living near hazardous waste sites contaminated with carbon tetrachloride.

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 carbon tetrachloride is available. Where adequate information is not available, ATSDR, in conjunction with NTP, is required to assure the initiation of a program of research designed to determine the health effects (and techniques for developing methods to determine such health effects) of carbon tetrachloride.

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 carbon tetrachloride have been well studied, and reliable values for key parameters are available for use in environmental fate and transport models. On this basis, it does not appear that further studies of the physical-chemical properties of carbon tetrachloride are essential.

Production, Import/Export, Use, Release, and Disposal. According to the Emergency Planning and Community Right-to-Know Act of 1986, 42 U.S.C. Section 11023, industries are required to submit substance release and off-site transfer information to the EPA. The TRI, which contains this information

6. POTENTIAL FOR HUMAN EXPOSURE

for 2002, became available in May of 2004. This database is updated yearly and should provide a list of industrial production facilities and emissions.

Although the production of carbon tetrachloride has been declining, humans are at risk of exposure to the compound at specific industrial locations where the compound is used or near chemical waste sites where emission to the environment may occur. Available data indicate that most carbon tetrachloride manufactured in this country is consumed in the synthesis of chlorofluorocarbons, but current quantitative data on the amounts of carbon tetrachloride imported and exported into and from the United States are sparse (HSDB 2004; USITC 2003). According to the Emergency Planning and Community Right-to-Know Act of 1986, 43 U.S.C. Section 11023, Industries are required to submit substance release and off-site transfer information to the EPA. TRI, which contains this information for 2002, became available in 2004. This database is updated yearly and should provide a list of industrial production facilities and emissions.

In 2002, the United States released approximately 414,000 pounds (188 metric tons) of carbon tetrachloride to the environment from manufacturing and processing facilities, most of which (70%) was released directly to the atmosphere (TRIO2 2004). Carbon tetrachloride is considered a hazardous waste and is subject to disposal regulations. Information on current disposal practices for used containers, sludges, and soils containing carbon tetrachloride waste are lacking. Because carbon tetrachloride is so stable in the environment, collection of this information on production, use, release, and disposal are needed to evaluate the effect of current industrial practices on local and global levels of carbon tetrachloride. Further, this information would be useful in the overall evaluation of human health risk of carbon tetrachloride.

Environmental Fate. The environmental fate of carbon tetrachloride has been investigated by a number of workers, and available data are adequate to conclude that one main fate process is volatilization followed by photodecomposition in the stratosphere (Pearson and McConnell 1975). However, there is some uncertainty in available estimates of atmospheric lifetime, and more detailed studies of the rate of carbon tetrachloride decomposition, and how this depends on altitude, geographic location, and other atmospheric components, are needed to refine models predicting global and local trends in carbon tetrachloride levels. Although only a small fraction of environmental carbon tetrachloride is thought to exist in surface waters, the possibility exists that hydrolysis, bioaccumulation, or adsorption, while slow, could compete with the slow photodecomposition occurring in the atmosphere. Estimates on the aerobic and anaerobic biodegradation half-lives of carbon tetrachloride in water have

6. POTENTIAL FOR HUMAN EXPOSURE

been made based on limited data. For this reason, additional studies on carbon tetrachloride flux rates into and out of surface water, as well as refined quantitative estimates of aquatic fate processes would be valuable. The chemical is expected to evaporate rapidly from soil due to its high vapor pressure and may migrate into groundwater due to its low soil adsorption coefficient. No data are available on biodegradation in soil. Additional studies to determine degradation rates and the extent to which adsorption has occurred are needed. These data are also useful in evaluating the impact of carbon tetrachloride leaching from hazardous waste sites.

Bioavailability from Environmental Media. Carbon tetrachloride can be absorbed following oral dosing and inhalation, or dermal exposure. No data were located regarding the potential effects of environmental media (air, water, soil) on the absorption of carbon tetrachloride. However, since soil adsorption is considered to be relatively low for carbon tetrachloride, it seems unlikely that soil would have a significant effect on its bioavailability. Additional studies are needed to determine the extent of bioavailability from contaminated air, drinking water, and soil at hazardous waste sites.

Food Chain Bioaccumulation. Limited data indicate that carbon tetrachloride has a low tendency to bioconcentrate in the food chain, even though it is a lipophilic compound (Neely et al. 1974; Pearson and McConnell 1975). The lack of bioconcentration is mainly due to the volatility of carbon tetrachloride, which facilitates clearance from exposed organisms. Nevertheless, carbon tetrachloride does tend to become concentrated in fatty tissues, and further studies on the levels of carbon tetrachloride in the fat of fish would help evaluate the risk of carbon tetrachloride exposure by this pathway. No data are available on the bioconcentration in plants. Additional studies would be useful in assessing potential for human exposure from ingestion of plant foodstuff. Data are also needed on the biomagnification of the compound in the aquatic and terrestrial food chain. These data would be useful in assessing food chain bioaccumulation as a potential human exposure pathway.

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

Levels of carbon tetrachloride in air, water, and sediments have been measured at numerous locations in the United States, and typical or average exposure levels in ambient air and drinking water are fairly well

6. POTENTIAL FOR HUMAN EXPOSURE

defined (Letkiewicz et al. 1983; Shah and Heyerdahl 1988; Singh et al. 1992; Westrick et al. 1984). There is considerable local variation, with higher-than-average levels occurring in some industrial areas and near some waste sites. However, much of this information is no longer current. Consequently, further monitoring of carbon tetrachloride in the workplace and in ambient water and air near known or potential sources of carbon tetrachloride would be valuable in identifying locations where human exposure could be elevated.

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

Exposure Levels in Humans. Detection of carbon tetrachloride in blood, urine, and expired air has been used as an indicator of exposure to the compound in occupational settings. Similar information on the general population, particularly in the vicinity of hazardous waste sites, are needed to estimate levels of the compound to which the general population has been exposed and perhaps some correlation of these levels with levels of carbon tetrachloride in contaminated air, drinking water, and soil.

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

Exposures of Children. There are very limited data on the effects of carbon tetrachloride exposure on children. As stated earlier (Section 6.6), adult data cannot simply be extrapolated to children for a variety of different reasons. Data on children's exposure are needed.

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

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

6. POTENTIAL FOR HUMAN EXPOSURE

6.8.2 Ongoing Studies

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

The Federal Research in Progress (FEDRIP 2004) database provides additional information obtainable from a few ongoing studies that may fill in some of the data needs identified in Section 6.8.2. These studies that include one which deals with the phytoremediation of toxic waste sites using poplar trees to remove toxic solvents from influent waters. Over a 4-year period, 98–99% of trichloroethylene was removed, with similar results shown for carbon tetrachloride and perchloroethylene. Further study is being done using this methodology to determine the fate of the carbon from these chemicals.