

## 6. POTENTIAL FOR HUMAN EXPOSURE

### 6.1 OVERVIEW

1,4-Dioxane has been identified in at least 31 of the 1,689 hazardous waste sites that have been proposed for inclusion on the EPA National Priorities List (NPL) (HazDat 2007). However, the number of sites evaluated for 1,4-dioxane is not known. The frequency of these sites can be seen in Figure 6-1. Of these sites, all are located within the United States.

1,4-Dioxane is released into the environment during its production, the processing of other chemicals, its use, and with its unintentional formation during the manufacture of ethoxylated surfactants (EC 2002). In the past, 1,4-dioxane was released into the environment with its use as a stabilizer for 1,1,1-trichloroethane (TCA). Since the use of TCA has been discontinued, current releases from this source are expected to be very low.

Given its vapor pressure and Henry's Law constant, the rate of volatilization of 1,4-dioxane from water and soil surfaces is expected to be moderate. In air, it is subject to photooxidation with an estimated half-life of 1–3 days. 1,4-Dioxane biodegrades very slowly in water and soils and is considered recalcitrant. It adsorbs weakly to soil and will move quickly into groundwater. Bioconcentration, bioaccumulation, and biomagnification are not considered important environmental fate processes for 1,4-dioxane.

Current levels of 1,4-dioxane in the environment are unavailable. Historical data (i.e., 1980s or earlier) suggest that ambient levels were 0.1–0.4  $\mu\text{g}/\text{m}^3$  in air and 1  $\mu\text{g}/\text{L}$  in water. Higher concentrations of 1,4-dioxane have been observed primarily in groundwaters.

The general population is exposed to negligible levels of 1,4-dioxane. The primary routes of human exposure to 1,4-dioxane are inhalation of 1,4-dioxane in air, ingestion of contaminated food and drinking water containing 1,4-dioxane, and dermal contact with contaminated consumer products (e.g., products containing ethoxylated surfactants). Because 1,4-dioxane may be found in tap water, human exposure to 1,4-dioxane may also occur during activities such as showering, bathing, and laundering. Occupational exposure occurs during the production, processing, and use of 1,4-dioxane, which results in inhalation or dermal exposure.



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**6.2 RELEASES TO THE ENVIRONMENT**

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

1,4-Dioxane is released into the environment during its production, processing, use, and with its unintentional formation during the manufacture of ethoxylated surfactants (EC 2002). In the past, 1,4-dioxane was released into the environment with its use as a stabilizer for TCA. Since the use of TCA has been discontinued, current releases from this source are expected to be very low.

1,4-Dioxane is unintentionally formed as an impurity during the manufacture of alkyl ether sulphates (AES) and other ethoxylated substances. However, much of the 1,4-dioxane impurity in these chemicals is removed through a stripping process during their manufacture. The stripper condensates from the manufacturing processes are discharged through normal plant effluents, where they are diluted by other waste streams and discharged as industrial wastes (NICNAS 1998). 1,4-Dioxane remaining as a by-product in end-use products (a large percentage of which may be used in domestic detergents and personal care products) will be released to publicly owned treatment works (POTWs) along with the surfactants, although this release will be far more diffuse.

According to the TRI, a total of 182,338 pounds (82,693 kg) of 1,4-dioxane were released to the environment in 2007 from facilities required to report to the TRI (TRI07 2009). In addition, an estimated 2,794 pounds (361 kg) were transferred off-site, including to POTWs (TRI07 2009). The TRI data should

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be used with caution, because only certain types of facilities are required to report. This is not an exhaustive list. Since 1988, total on-site releases of 1,4-dioxane appear to be decreasing from a high of 1,234,968 pounds (560,172 kg) in 1993 to a low of 182,338 (82, 707) pounds in 2007.

**6.2.1 Air**

Estimated releases of 125,341 pounds (~57 metric tons) of 1,4-dioxane to the atmosphere from 45 domestic manufacturing and processing facilities in 2007 accounted for about 69% of the estimated total on-site environmental releases from facilities required to report to the TRI (TRI07 2009). These releases are summarized in Table 6-1.

1,4-Dioxane may be released to air during its production, the processing of other chemicals (e.g., pharmaceuticals/pesticides), and its use (EC 2002). The total emissions of 1,4-dioxane from stationary sources in California are estimated to be at least 210,000 pounds per year, based on data reported under the Air Toxics “Hot Spots” Program (California ARB 1997).

No further information was located on the emissions of 1,4-dioxane to air.

1,4-Dioxane has been identified in air samples collected at 6 of the 1,689 NPL hazardous waste sites, where it was detected in some environmental media (air, groundwater, surface water, soil, and sediment) (HazDat 2007).

**6.2.2 Water**

Estimated releases of 56,996 pounds (~26 metric tons) of 1,4-dioxane to surface water from 45 domestic manufacturing and processing facilities in 2006 accounted for about 31% of the estimated total on-site environmental releases from facilities required to report to the TRI (TRI07 2009). An additional 2,794 pounds (~1 metric ton) were transferred off-site, which included releases to POTWs (TRI07 2009). These releases are summarized in Table 6-1.

1,4-Dioxane may be released to surface water and groundwater during its production, the processing of other chemicals, its use, and with its unintentional formation during the manufacture of ethoxylated surfactants (EC 2002).

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**Table 6-1. Releases to the Environment from Facilities that Produce, Process, or Use 1,4-Dioxane<sup>a</sup>**

State <sup>c</sup>	RF <sup>d</sup>	Reported amounts released in pounds per year <sup>b</sup>							
		Air <sup>e</sup>	Water <sup>f</sup>	UI <sup>g</sup>	Land <sup>h</sup>	Other <sup>i</sup>	Total release		
							On-site <sup>j</sup>	Off-site <sup>k</sup>	On- and off-site
AL	1	1,038	0	0	0	0	1,038	0	1,038
AR	2	7,383	49	0	0	490	7,432	490	7,922
CA	2	2,554	0	0	0	0	2,554	0	2,554
CO	1	1,000	0	0	0	0	1,000	0	1,000
CT	1	0	No data	0	0	0	0	0	0
IL	1	6,209	0	0	2	0	6,211	0	6,211
LA	4	3,702	13,711	0	3	840	17,413	843	18,256
MI	1	0	No data	0	0	0	0	0	0
MN	1	1,950	No data	0	0	870	1,950	870	2,820
MO	2	20	1	0	0	0	21	0	21
MS	1	1,508	0	0	2	0	1,508	2	1,511
NC	4	20,230	4,926	0	12	0	25,156	12	25,168
OH	1	250	0	0	500	0	250	500	750
OR	1	908	0	0	24	0	908	24	932
PA	1	1,660	No data	0	0	0	1,660	0	1,660
PR	1	156	0	0	34	0	156	34	190
SC	8	38,818	13,876	0	18	0	52,694	18	52,713
TN	2	7,840	23,167	0	0	0	31,007	0	31,007
TX	5	30,088	1,266	0	0	0	31,354	0	31,354
WI	2	10	0	0	0	0	10	0	10

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State <sup>c</sup>	RF <sup>d</sup>	Reported amounts released in pounds per year <sup>b</sup>							
		Air <sup>e</sup>	Water <sup>f</sup>	UI <sup>g</sup>	Land <sup>h</sup>	Other <sup>i</sup>	Total release		
							On-site <sup>j</sup>	Off-site <sup>k</sup>	On- and off-site
WV	2	16	0	0	0	0	16	0	16
Total	44	125,341	56,996	0	596	2,200	182,338	2,794	185,132

<sup>a</sup>The 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.

<sup>b</sup>Data in TRI are maximum amounts released by each facility.

<sup>c</sup>Post office state abbreviations are used.

<sup>d</sup>Number of reporting facilities.

<sup>e</sup>The sum of fugitive and point source releases are included in releases to air by a given facility.

<sup>f</sup>Surface water discharges, waste water treatment-(metals only), and publicly owned treatment works (POTWs) (metal and metal compounds).

<sup>g</sup>Class I wells, Class II-V wells, and underground injection.

<sup>h</sup>Resource Conservation and Recovery Act (RCRA) subtitle C landfills; other on-site landfills, land treatment, surface impoundments, other land disposal, other landfills.

<sup>i</sup>Storage only, solidification/stabilization (metals only), other off-site management, transfers to waste broker for disposal, unknown

<sup>j</sup>The sum of all releases of the chemical to air, land, water, and underground injection wells.

<sup>k</sup>Total amount of chemical transferred off-site, including to POTWs.

RF = reporting facilities; UI = underground injection

Source: TRI07 2009 (Data are from 2007)

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1,4-Dioxane was detected at 1 µg/L in effluents from the North Side and Calumet sewage treatment plants on the Lake Michigan Basin (Konasewich et al. 1978). 1,4-Dioxane has been detected in discharges into Lake Michigan near Chicago in 1977 (Konasewich et al. 1978) and in the Haw River in North Carolina (Dietrich et al. 1988). However, no information about the concentration of 1,4-dioxane or detection limit was provided in these sources.

The U.S. Geological Survey (USGS) sampled groundwater and surface water in the vicinity of a former waste-oil refinery near Westville, Indiana from 1997 to 2000 (USGS 2002). The site was operational from the mid 1930s until 1987, and included numerous storage tanks, a filter press, several cracking towers, a cannery, and waste oil storage lagoons. 1,4-Dioxane concentrations in the groundwater plume ranged from 3 to 31,000 µg/L and eventually discharged to a ditch approximately half a mile away from the refinery. 1,4-Dioxane levels ranged from 8 to 140 µg/L in the surface water collected from the network of ditches surrounding the site.

Effluent of a sewage treatment plant discharging into the River Lee (United Kingdom) contained <1 ng/L in 8-hour mixed samples (EC 2002). Effluent of a sewage treatment plant from a polyethylene terephthalate (PET) manufacturing process contained 100 mg/L of 1,4-dioxane in 1995 (EC 2002).

In Kanagawa prefecture, Japan, Abe (1999) reported that 1,4-dioxane concentrations in effluents from chemical plants that used the compound as a solvent ranged from 0.4 to 4,020 µg/L the combined collection treatments of apartment houses and river basin sewage systems were 0.8–46 and 1.0–97 µg/L, respectively. No further data were located for emissions of 1,4-dioxane to water.

1,4-Dioxane has been identified in surface water and groundwater samples, collected at 5 and 18 sites, respectively, of the 1,689 NPL hazardous waste sites, where it was detected in some environmental media (HazDat 2007).

### 6.2.3 Soil

Estimated releases of 596 pounds (<1 metric ton) of 1,4-dioxane to soils from 45 domestic manufacturing and processing facilities in 2007 accounted for <1% of the estimated total on-site environmental releases from facilities required to report to the TRI (TRI07 2009). These releases are summarized in Table 6-1.

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1,4-Dioxane may be released to soil during its production, the processing of other chemicals, its use, and with its unintentional formation during the manufacture of ethoxylated surfactants (EC 2002).

Between 1976 and 1985, Pall Life Sciences' (PLS) predecessor, Gelman Sciences in Ann Arbor, Michigan disposed of large quantities of waste water containing 1,4-dioxane on soil in a holding pond and through a waste injection well. 1,4-Dioxane was used as a solvent for cellulose acetate, a component of micro-porous filters. This chemical contaminated soil and rock layers and seeped into the groundwater. Disposal of this chemical in this way was stopped in 1986 (City of Ann Arbor 2003; MSU 2001). No further data were located for emissions of 1,4-dioxane to soil.

1,4-Dioxane has been identified in soil samples collected at 6 of the 1,689 NPL hazardous waste sites, where it was detected in some environmental media (HazDat 2007).

### 6.3 ENVIRONMENTAL FATE

1,4-Dioxane is expected to volatilize at a moderate rate from water and soil surfaces. In air, it is subject to photooxidation with an estimated half-life of 1–3 days. 1,4-Dioxane is relatively resistant to biodegradation in water and soils. It binds weakly to soils and will therefore move readily into groundwater. Bioconcentration, bioaccumulation, and biomagnification are not significant for 1,4-dioxane.

#### 6.3.1 Transport and Partitioning

The Henry's law constant for 1,4-dioxane is  $4.8 \times 10^{-6}$  atm m<sup>3</sup>/mole, which indicates that 1,4-dioxane is expected to volatilize from water surfaces (Park et al. 1987; Thomas 1990). Based on this Henry's law constant, the volatilization half-life from a model river (1 m deep, flowing 1 m/second, wind velocity of 3 m/second) is estimated as 7 days. The volatilization half-life from a model lake (1 m deep, flowing 0.05 m/second, wind velocity of 0.5 m/sec) is estimated as 56 days (EPA 2000b). The Henry's law constant for 1,4-dioxane also indicates that volatilization from moist soil surfaces may occur. The potential for volatilization of 1,4-dioxane from dry soil surfaces may exist based upon a vapor pressure of 38.1 mm Hg (Daubert and Danner 1985). Even though volatilization of 1,4-dioxane may occur, risks to human health from inhalation exposures are expected to be low under environmental conditions.

According to a classification scheme, an estimated  $K_{oc}$  value of 17 suggests that 1,4-dioxane is expected to have very high mobility in soil (Swann et al. 1983). This estimated  $K_{oc}$  value was calculated using a

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log  $K_{ow}$  of -0.27 and a regression-derived equation (Hansch et al. 1995; Thomas 1990). In the absence of significant degradation processes (see Section 6.3.2), 1,4-dioxane is susceptible to leaching from soil into groundwater. In clay soils, 1,4-dioxane will not be adsorbed as a result of any specific interaction with the surface of clay minerals. However, 1,4-dioxane can get trapped in the interfacial region of clay soils due to its strong interaction with water molecules. This may result in a lower than expected mobility for 1,4-dioxane in clay soils (Zhang et al. 1990). Groundwater retardation factors ( $R_f$ ) for 1,4-dioxane range from 1.0 to 1.6. These values indicate that 1,4-dioxane is expected to be a mobile compound (e.g.,  $R_f$  for chloride=1.0, which is indicative of no retardation) in groundwater (Priddle and Jackson 1991).

According to a classification scheme, a bioconcentration factor (BCF) value of 3 for 1,4-dioxane suggests that the potential for bioconcentration in aquatic organisms is low (Franke et al. 1994). This estimated BCF (the BCF is the concentration of the chemical in fish tissues over concentration of chemical in water) was calculated using a log  $K_{ow}$  of -0.27 and a regression-derived equation (Hansch et al. 1995; Meylan et al. 1999). The results of an experimental bioconcentration study also reported very low BCF values (e.g., 0.2–0.7) for 1,4-dioxane (EC 2002). Therefore, bioconcentration, bioaccumulation, and biomagnification are unlikely to be significant for 1,4-dioxane.

### 6.3.2 Transformation and Degradation

#### 6.3.2.1 Air

The primary loss mechanism for 1,4-dioxane in the atmosphere is photooxidation with OH radicals, while photolysis, reaction with ozone molecules, and reaction with nitrate radicals are insignificant in comparison (Grosjean 1990). The second-order rate constant for OH radical photooxidation of 1,4-dioxane is  $1.09 \times 10^{-11}$  cm<sup>3</sup>/molecule-sec (Atkinson 1989). Using OH radical concentrations between  $0.5 \times 10^6$  and  $1.5 \times 10^6$  OH radicals/cm<sup>3</sup> and a 12-hour day, the atmospheric half-lives for 1,4-dioxane are 2.9 and 1.0 days, respectively. A reaction product from OH radical photooxidation is 2-oxodioxane (or c-C<sub>4</sub>H<sub>7</sub>O<sub>2</sub>). The lifetime of this alkyl radical, 2-oxodioxane in air at 1 atm is 0.02 microseconds with respect to the addition of O<sub>2</sub> to give the corresponding peroxy radical (c-C<sub>4</sub>H<sub>7</sub>O<sub>2</sub>)O<sub>2</sub>. These radicals react rapidly ( $t_{1/2}$ =6 minutes based on NO concentration of  $2.5 \times 10^8$  molecules/cm<sup>3</sup>) with NO to produce NO<sub>2</sub> and by inference (c-C<sub>4</sub>H<sub>7</sub>O<sub>2</sub>)O alkoxy radicals. The sole atmospheric fate of this alkoxy radical is decomposition *via* C-C bond scission, leading to the formation of ethylene glycol diformate (Platz et al. 1997). There are no known reactions for the *in situ* formation of 1,4-dioxane in the atmosphere (Grosjean 1990).

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**6.3.2.2 Water**

Since 1,4-dioxane does not have functional groups that are susceptible to hydrolysis (Wolfe and Jeffers 2000), hydrolysis of 1,4-dioxane is not expected to occur in the environment. Since 1,4-dioxane does not adsorb light in the environmental spectrum (i.e., >290 nm), 1,4-dioxane is not expected to undergo direct photolysis in aqueous media. 1,4-Dioxane may undergo indirect photolysis by aqueous hydroxyl radicals near the water surface. The half-life for this reaction is 336 days at pH 7 (Anbar and Neta 1967). However, the extent of this reaction of OH radicals with 1,4-dioxane in the environment is unknown.

1,4-Dioxane has been found to be resistant to biodegradation (Alexander 1973; Dow Chemical Co. 1989; Fincher and Payne 1962; Heukelekian and Rand 1955; Mills and Stack 1954). Results of a biological oxygen demand (BOD) test for 1,4-dioxane indicate that negligible oxygen was consumed over a 20-day test period (Swope and Kenna 1950). Mills and Stack (1954) noted that degradation of 1,4-dioxane was not observed in cultures of sewage microorganisms exposed for 1 year to waste water treatment plant effluents adjusted to contain 1,4-dioxane at concentrations ranging from 100 to 900 mg/L. In a different study, microorganisms present in either municipal or industrial activated sludge were unable to degrade 1,4-dioxane during 2 days of continuous exposure to concentrations ranging from 10 to 100 mg/L (Dow Chemical Co. 1989). Accordingly, it appears that 1,4-dioxane will not undergo significant degradation in conventional biological treatment systems. Thus, 1,4-dioxane has been classified as not readily biodegradable, and it is not expected to rapidly biodegrade in the environment (Kawasaki 1980; Lyman et al. 1982).

Acclimated microbial cultures may be capable of degrading 1,4-dioxane under certain conditions. Roy et al. (1994) investigated the biodegradability of 1,4-dioxane in industrial wastes using microorganisms obtained from acclimated industrial waste. These authors found that pure 1,4-dioxane and industrial wastes containing 1,4-dioxane are biodegradable. Following a 10-day lag period, complete degradation of 150 mg/L of 1,4-dioxane was observed after 32 days of treatment using an electrolytic respirometer cell. However, partial degradation of 1,4-dioxane was observed at higher concentrations, which may have resulted from the build up of intermediates inhibitory to the biodegradation process (Roy et al. 1994, 1995). Zenker et al. (2000) reported that a mixed microbial culture enriched from a 1,4-dioxane contaminated aquifer was capable of aerobically degrading 1,4-dioxane in the presence of tetrahydrofuran (THF). No biodegradation of 1,4-dioxane was observed in the absence of THF, and the measured cell yield was similar during degradation of 1,4-dioxane with THF or with THF alone. This suggests that

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1,4-dioxane was biodegraded via a co-metabolic process (i.e., transformation of a non-growth substance [1,4-dioxane] in the presence of a growth substrate [THF] or another transformable compound).

Zenker et al. (1999) reported that a mixed microbial culture enriched from a 1,4-dioxane contaminated soil was capable of aerobically degrading 1,4-dioxane in the presence of THF. 1,4-Dioxane and THF were added to the soil microcosm at a concentration of 200 mg/L under enhanced conditions, which included incubation at 35 °C and the addition of nitrogen, phosphorus, and trace minerals. Both 1,4-dioxane and THF were completely degraded within 100 days, while 1,4-dioxane alone degraded completely after 300 days of incubation. Microcosms incubated under ambient conditions exhibited no biodegradation of 1,4-dioxane or THF (Zenker et al. 1999).

### 6.3.2.3 Sediment and Soil

Limited information was located on the transformation and degradation of 1,4-dioxane in soils and sediment. Kelley et al. (2001) investigated the potential to enhance 1,4-dioxane biodegradation in both planted and unplanted soil, by adding the 1,4-dioxane-degrading actinomycete, *Amycolata* sp. CB1190. 1,4-Dioxane was not removed within 120 days in sterile controls or in viable microcosms not amended with CB1190. Poplar root extract (40 mg/L as chemical oxygen demand [COD]) stimulated 1,4-dioxane degradation in bioaugmented soil, and 100 mg/L of 1,4-dioxane was removed within 45 days. Other co-substrates that enhanced 1,4-dioxane degradation by CB1190 included THF and 1-butanol, while glucose and soil extract did not affect 1,4-dioxane degradation (Kelley et al. 2001). While long-term enrichments eventually yield cultures of CB1190 that are capable of growth on 1,4-dioxane alone, THF appears to be the preferred growth substrate for CB1190 (Parales et al. 1994).

### 6.3.2.4 Other Media

Pure 1,4-dioxane is known to react with molecular oxygen at ambient temperatures to form peroxides and hydroperoxides in the course of long-term storage and handling (Howard and Ingold 1969). Peroxides are formed primarily with exposure to air and UV light. Formate esters are formed from subsequent transformations of peroxides and hydroperoxides by way of free-radical mechanisms (Jewett and Lawless 1980).

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**6.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT**

Reliable evaluation of the potential for human exposure to 1,4-dioxane depends in part on the reliability of supporting analytical data from environmental samples and biological specimens. Concentrations of 1,4-dioxane 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 1,4-dioxane 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 1,4-dioxane in a variety of environmental media are detailed in Chapter 7.

Recent information on the levels of 1,4-dioxane in the ambient environment are unavailable. Historical data (i.e., 1980s or earlier) suggest that ambient levels were 0.1–0.4  $\mu\text{g}/\text{m}^3$  in air and 1  $\mu\text{g}/\text{L}$  in water. Higher concentrations of 1,4-dioxane in groundwaters have been observed in aquifers contaminated with TCA.

**6.4.1 Air**

Recent information on the ambient levels of 1,4-dioxane in air is unavailable. Because the use of 1,4-dioxane has declined in recent years, current levels of 1,4-dioxane in the ambient air are likely to be less than levels reported in the 1980s or in earlier periods. In 1984, the concentration of 1,4-dioxane ranged from 0.1–0.4  $\mu\text{g}/\text{m}^3$  in ambient air sampled from the United States. No information was provided in this source on the locations where the air sampling occurred (EC 2002). In the early to mid 1980s, the mean ambient levels of 1,4-dioxane in outdoor air was measured as part of the VOC National Ambient Database in the United States (Shah and Singh 1988). The mean concentration of 1,4-dioxane was 0.107 ppbv or 0.385  $\mu\text{g}/\text{m}^3$  (n=617; median, 0.000 ppbv). 1,4-Dioxane was detected in outdoor air samples from the United States between 1981 and 1984 (detection limit unspecified). In the winter of 1984, 1,4-dioxane was detected in 67% of outdoor air samples from Los Angeles communities (n=25) at a median concentration of 0.27  $\mu\text{g}/\text{m}^3$ . In the summer of 1984, 1,4-dioxane was detected in 22% of outdoor air samples from Los Angeles communities (n=23) at a median concentration of 0.02  $\mu\text{g}/\text{m}^3$ . In the summer of 1984, 1,4-dioxane was detected in 20% of outdoor air samples from Antioch/West Pittsburg, California (n=10) at a median concentration of 0.03  $\mu\text{g}/\text{m}^3$  (Pellizzari et al. 1986). Between 1979 and 1984, the mean concentration of 1,4-dioxane in ambient air was 0.44  $\mu\text{g}/\text{m}^3$  (range, 0–30  $\mu\text{g}/\text{m}^3$ ; detected in 187 of 533 samples) in samples collected from 12 unspecified urban/suburban locations in the United States (EPA 1993).

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In the summer of 1981 (July 6–August 16), the geometric mean concentrations of 1,4-dioxane in air near three industrialized urban areas (i.e., Newark, Elizabeth, and Camden, New Jersey) of the United States were 0.01 (21 of 38 samples positive), 0.02 (15 of 38 samples positive), and 0.005  $\mu\text{g}/\text{m}^3$  (21 of 35 samples positive), respectively (Harkov et al. 1983). The three same sites were also sampled from January 18–February 26, 1982. The geometric means of these samples ranged from 0 to 0.01  $\mu\text{g}/\text{m}^3$ ; 20% of samples were positive, with a maximum value of 5.31  $\mu\text{g}/\text{m}^3$  (Harkov et al. 1984; EC 2002). Two ambient air samples taken in New Jersey were reported to contain 1,4-dioxane (Harkov et al. 1985). In 1983, near the Kramer Landfill in New Jersey, sampled ambient air contained 1,4-dioxane at a geometric mean concentration of 0.01 ppbv or 0.4  $\mu\text{g}/\text{m}^3$  (maximum, 0.09 ppbv or 0.3  $\mu\text{g}/\text{m}^3$ ). In 1982, at an urban/industrial site in Newark, New Jersey, ambient air contained 1,4-dioxane at a geometric mean concentration of 0.01 ppbv, or 0.4  $\mu\text{g}/\text{m}^3$  (n=26; maximum, 1.45 ppbv or 5.22  $\mu\text{g}/\text{m}^3$ ). At various landfills in the United States, the concentration of 1,4-dioxane in landfill gas was reported to be 0.62  $\mu\text{g}/\text{m}^3$  and 0.33  $\text{g}/\text{m}^3$  (EC 2002).

In the early to mid 1980s, the mean ambient levels of 1,4-dioxane in indoor air was measured as part of the VOC National Ambient Database in the United States (Shah and Singh 1988). The mean concentration of 1,4-dioxane in indoor air was 1.029 ppbv, or 3.704  $\mu\text{g}/\text{m}^3$  (n=585; median, 0.000 ppbv). 1,4-Dioxane was detected in indoor air samples from the United States between 1981 and 1984 (detection limit unspecified). In the winter of 1984, 1,4-dioxane was detected in 64% of indoor air samples from Los Angeles communities (n=25) at a median concentration of 0.26  $\mu\text{g}/\text{m}^3$ . In the summer of 1984, 1,4-dioxane was detected in 17% of indoor air samples from Los Angeles communities (n=23) at a median concentration of 0.02  $\mu\text{g}/\text{m}^3$ . In the summer of 1984, 1,4-dioxane was detected in 10% of indoor air samples from Antioch/West Pittsburg, California (n=10) at a median concentration of 0.07  $\mu\text{g}/\text{m}^3$  (Pellizzari et al. 1986). In a multi-national survey taken between 1978 and 1990, mean 1,4-dioxane levels were 11  $\mu\text{g}/\text{m}^3$  in indoor air samples taken from buildings (i.e., schools and offices) with reported unspecified complaints among the occupants (Brown et al. 1994). In June of 1990, 125 households in Woodland, California were monitored for a variety of toxic air contaminants. Approximately 21% of the indoor samples collected contained measurable amounts of 1,4-dioxane. The average concentration of 1,4-dioxane was below the quantifiable limit of 0.11  $\mu\text{g}/\text{m}^3$ , and the measurements ranged from below the quantifiable limit to 140  $\mu\text{g}/\text{m}^3$  (California ARB 1997).

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**6.4.2 Water**

Recent information on the concentration levels of 1,4-dioxane in groundwater, surface water, and drinking water is limited. However, because the use of 1,4-dioxane has declined in recent years, current levels of 1,4-dioxane in aqueous media are likely to be less than levels reported in the 1980s or in earlier periods.

In the 1970s, municipal water supplies in the United States were reported to contain 1 µg/L of 1,4-dioxane (Kraybill 1978); however, the frequency of this level was not provided. In a drinking water well in Massachusetts, a concentration of 2,100 µg/L was reported (Burmester 1982). However, this well appeared to be contaminated. In six drinking water wells (37% of samples) near a solid waste landfill located 60 miles southwest of Wilmington, Delaware, two wells were found to contain 0.1 and 0.5 µg/L 1,4-dioxane, but no 1,4-dioxane was detectable in the finished drinking water in the municipality using that well field (DeWalle and Chian 1981). Concentrations in private wells ranged from 0.001–1 to 200 mg/L (from 1–1,000 to 200,000 µg/L). The concentration of 1,4-dioxane in five wells near Circleville, Ohio ranged from <1 to 360 µg/L after contamination of groundwater following treatment of industrial waste water (Hartung 1989). Drinking water from the Netherlands contained 1,4-dioxane at a concentration of 0.5 µg/L (EC 2002). Drinking water samples from homes near the Durham Meadows Superfund site in Durham, Connecticut had maximum 1,4-dioxane concentrations of 26 µg/L in untreated water in one residential well and 12 µg/L in treated water from another residential well (EPA 2004g).

1,4-Dioxane was determined at 1.1–109 µg/L in contaminated groundwater in California (Draper et al. 2000). Extensive groundwater contamination (<0.01–220 mg/L or <10–220,000 µg/L) with more limited surface water contamination (<0.01–0.29 mg/L or <10–290 µg/L) resulted from treatment of industrial waste water in an unlined oxidation lagoon in Ann Arbor, Michigan (DeRosa et al. 1996). Current levels of 1,4-dioxane were about 1 µg/L in eight groundwater wells located in the vicinity of this site. However, the number of non-detects was not provided in this source (Michigan DEQ 2004). 1,4-Dioxane was discovered in groundwater at more than 250 ppm (mg/L) at a San Jose, California solvent recycling facility in 1998. In a survey of TCA release sites in California, it was found that 1,4-dioxane was present in a majority of these sites (concentrations unspecified) (Mohr 2004). At the Stanford Linear Accelerator Center (SLAC) in Menlo Park, California, the occurrence of 1,4-dioxane in groundwater is closely associated with TCA and its abiotic degradation product, 1,1-dichloroethane. It was found at this location at a maximum concentration of 7,300 ppb (Mohr 2004). Leachates from wells located near low level radioactive waste disposal sites contained 1,4-dioxane, but no quantitative data were presented (Francis et

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al. 1980). Between 1983 and 1986, 1,4-dioxane was detected in groundwater near three landfills in Canada at concentrations  $<1 \mu\text{g/L}$  (EC 2002). In groundwater beneath a landfill, the concentration of 1,4-dioxane was  $500 \mu\text{g/L}$  at a site in Canada sampled in 1982 (EC 2002). Groundwater samples obtained from an abandoned waste-oil refinery near Westville, Indiana contained 1,4-dioxane at levels ranging from approximately 3 to  $31,000 \mu\text{g/L}$  (USGS 2002).

In 1982, 1,4-dioxane was detected in samples of river water from the Haw River in North Carolina, which flows through an industrialized section of the North Carolina Piedmont (Dietrich et al. 1988). However, no information on the levels of 1,4-dioxane in these samples were reported by the authors. 1,4-Dioxane at  $1 \mu\text{g/L}$  was detected in the Chicago Sanitary and Ship Channel in the Lake Michigan basin (Konasewich et al. 1978). Surface water from the provincial area of Drenthe in the Netherlands contained 1,4-dioxane at concentrations ranging from 1 to  $10 \mu\text{g/L}$  (EC 2002). At five different locations near the banks of the Rhine River in Germany, surface water contained  $<10 \mu\text{g/L}$  1,4-dioxane in 1996 (EC 2002). River water collected from an unspecified river in the United Kingdom contained 1,4-dioxane, but no quantitative data were presented (Gelman Sciences 1989c). Dioxane concentrations in river water ranged from  $<0.024$  to  $0.69 \mu\text{g/L}$  in Kitakyushu, Japan (Kawata et al. 2003) and from 0.1 to  $16 \mu\text{g/L}$  in Kanagawa, Japan (Abe 1999). The Japanese Ministry of the Environment reported that 1,4-dioxane in river and coastal waters ranged from  $<0.08$  to  $46 \mu\text{g/L}$  at 34–35 sites in Japan during fiscal years 1997–1999 (Kawata et al. 2003). 1,4-Dioxane was detected in surface water samples from 11 of 19 sites from Niigata, Japan at concentrations ranging from  $<0.03$  to  $0.39 \mu\text{g/L}$  (Kawata et al. 2003).

During the period of 1988–1991, the maximum concentration of 1,4-dioxane detected at Superfund sites in 21 states was  $10 \mu\text{g/L}$  (Canter and Sabatinti 1994). 1,4-Dioxane ranged in concentration from 1.1 to  $109 \mu\text{g/L}$  in leachate from hazardous waste disposal sites in Japan (Yasuhara et al. 1997). In 2000–2001, the concentration of 1,4-dioxane in leachate from a closed hazardous waste landfill in Japan ranged from 0.16 to  $0.50 \mu\text{g/L}$ . At an open hazardous waste landfill, the concentration of 1,4-dioxane in leachate ranged from 0.91 to  $10.6 \mu\text{g/L}$  (Yasuhara et al. 2003). At these landfills, waste plastics were disposed after either incineration or crushing and pressing under heat. The heating process appears to have resulted in the formation of 1,4-dioxane, although a mechanism for this process was not provided (Yasuhara et al. 2003). The concentration of 1,4-dioxane in landfill leachates from eight hazardous disposal sites in Japan ranged from 1.100 to  $109 \mu\text{g/L}$  (median,  $3.900 \mu\text{g/L}$ ) (Yasuhara et al. 1997). In May 1988, the concentration of 1,4-dioxane in an outwash aquifer near the Gloucester Hazardous Waste Landfill (Ottawa, Canada) ranged from  $\sim 300$  to  $2,000 \mu\text{g/L}$ , with a 13% frequency of detection (detection

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limit=150 µg/L) (Lesage et al. 1990). The concentrations of 1,4-dioxane were reported to be 11, 8, and 36 µg/L in landfill leachates sampled from three municipal landfills in Göteborg, Sweden (Paxéus 2000).

In an industrial/urban area of Japan (i.e., Kanagawa prefecture), the concentration of 1,4-dioxane in river water ranged from 0.3 to 0.9 µg/L during the period of 1996–1998; the concentration in groundwater ranged from 0.2 to 0.4 µg/L during the period of 1995–1997 in the same area (Abe 1999). High concentrations of 1,4-dioxane in polluted groundwater from this area ranged from <0.1 (not detected) to 52 µg/L and were correlated with TCA contamination of groundwater (Abe 1999). Romero et al. (1998) measured the concentration of 1,4-dioxane in industrial waste waters from producers of polyester resins in Barcelona, Spain. The polymer resins were polymerized using different glycols in acid catalyzed condensation reactions. In these waste water samples, 1,4-dioxane was detected at a mean concentration of 6,400 µg/L (range, <100–31,400 µg/L) and a frequency of 48.6% (Romero et al. 1998).

### 6.4.3 Sediment and Soil

No quantitative data were located on the concentrations of 1,4-dioxane in sediments or soil.

### 6.4.4 Other Environmental Media

There have been no systematic studies designed to determine the levels of 1,4-dioxane in foods. However, 1,4-dioxane has been detected in some foods, which may indicate that 1,4-dioxane may be a natural constituent. 1,4-Dioxane was identified, but not quantified, in chicken flavor and meat volatiles (Shahidi et al. 1986). 1,4-Dioxane was also identified in volatile flavor compounds from fried chicken (Tang et al. 1983); however, no concentration levels were reported. Chung et al. (1983) identified 1,4-dioxane in the volatile components of tomato juices and tomato juice products by mass spectrometry, although levels of 1,4-dioxane were not quantified. 1,4-Dioxane was formed in trilinolein (a component of fat oil used in deep-frying foods) after deep-fry heating (Chang et al. 1978). However, the concentration of 1,4-dioxane was not specified. Odor from cooked small shrimp was reported to contain 1,4-dioxane at unquantified levels (Choi et al. 1983). Sanceda et al. (1984) detected 1,4-dioxane in patis, a Philippine fermented fish sauce, which is a commonly used food condiment in the diet of Southeast Asian people. Patis also may be readily available in some gourmet food stores in the United States. The concentration of 1,4-dioxane in patis was not specified. A study of the Japanese diet found that samples of a representative basket of foods contained 1,4-dioxane in levels from undetected to 13 ppm (mg/kg) (Nishimura et al. 2004). 1,4-Dioxane was identified, but not quantified, in adipose tissue of pasture-

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raised or concentrate-fed lambs (Sivadier et al. 2008). No further information on the detection of 1,4-dioxane in foods was located.

Food additives have been reported to contain 1,4-dioxane, although current levels were unavailable. For example, polysorbate 60 and polysorbate 80, which are used as food additives, have historically been found to contain 1,4-dioxane (Birkel et al. 1979). Polysorbate 60 and polysorbate 80 are produced from the polymerization of polyoxyethylene. Levels of 1,4-dioxane in these compounds have been reported to range from 4.8 to 6.0 ppm (mg/L) and from 5.3 to 5.8 ppm (mg/L), respectively. No further information on the levels of 1,4-dioxane in food additives was located.

In the FDA Cosmetic Handbook, it was reported that “cosmetics containing as ingredients ethoxylated surface active agents, i.e., detergents, foaming agents, emulsifiers, and certain solvents identifiable by the prefix, word or ‘PEG,’ ‘Polyethylene,’ ‘Polyethylene glycol,’ ‘Polyoxyethylene,’ ‘-eth-,’ or ‘-oxynol-,’ may be contaminated with 1,4-dioxane.” It is also reported that “it (1,4-dioxane) may be removed from ethoxylated compounds by means of vacuum stripping at the end of the polymerizations process without unreasonable increase in raw material cost” (FDA 1992).

Although manufacturers are able to remove 1,4-dioxane from ethoxylated raw materials by vacuum stripping, studies by FDA indicate that some ethoxylated raw materials may still contain 1,4-dioxane at significant levels. Since 1979, FDA has conducted periodic surveys of levels of 1,4-dioxane in ethoxylated raw materials used in cosmetic products and finished cosmetic products (Black et al. 2001). In 1997, the average concentration of 1,4-dioxane in ethoxylated raw materials used in cosmetic products was 348 ppm (range, 45–1,102 ppm). In previous years, the average concentrations of 1,4-dioxane were 49 ppm (1979), 207 ppm (1980), 71 ppm (1993), and 180 ppm (1996). The average concentration of 1,4-dioxane in ethoxylated alkyl sulfate surfactants was reported to be 229 ppm (range, 71–580 ppm), 226 ppm (range, 6–1,410 ppm), 80 ppm (range, 16–243 ppm), 188 ppm (range, 20–653 ppm), and 348 ppm (range, 45–1,102 ppm) in the years 1979, 1980, 1983, 1993, 1996, and 1997, respectively (Black et al. 2001).

Although industry has taken steps to reduce 1,4-dioxane in ethoxylated surfactants, some cosmetic and household products may contain 1,4-dioxane at levels >10 ppm. For example, EPA (1992) examined 1,159 household products for chemical contaminants such as 1,4-dioxane. In one of six samples of laundry presoak spray analyzed, 1,4-dioxane was reported at a concentration of 15.0 w/w%. In an FDA survey of cosmetic finished products in the United States, the average concentrations of 1,4-dioxane were

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reported to be 50 ppm (range, 2–279 ppm), 19 ppm (range, 2–36 ppm), and 2 ppm (range, 1–8 ppm) for the years 1981, 1982, and 1983, respectively (Black et al. 2001). After a 10-year break, FDA resumed its surveys of cosmetic finished products in 1992. The number of products analyzed for 1,4-dioxane between 1992 and 1997 totaled 99. Since 1994, the focus was on children's shampoos and bubble baths, which are typically formulated with ethoxylated raw materials. FDA observed that the previous downward trend in the levels of 1,4-dioxane in products in the late 1980s was no longer evident in the 1990s. The average concentrations of 1,4-dioxane in cosmetic finished products were reported to be 41 ppm (range, 5–141 ppm), 79 ppm (range, 50–112 ppm), 45 ppm (range, 20–107 ppm), 74 ppm (range, 42–90 ppm), 14 ppm (range, 6–34 ppm), and 19 ppm (range, 6–34 ppm) in the years 1992, 1993, 1994, 1995, 1996, and 1997, respectively (Black et al. 2001). Although these levels are considered low and not expected to pose a hazard for consumers, the authors of the study commented that some raw material producers were not effectively controlling the levels of 1,4-dioxane in certain products. A more recent survey reported by the Campaign for Safe Cosmetics (2007) found that the levels of 1,4-dioxane in cosmetic products that were tested were slightly lower than in the survey conducted by the FDA in the 1990s. The levels of 1,4-dioxane in these products ranged from 1.5 to 12 ppm in baby and children's products and from 2 to 23 ppm in adult products. A second survey released in March of 2009 had similar results. Thirty-two out of 48 consumer products had detectable levels of 1,4-dioxane, with levels ranging from 0.27 to 35 ppm (Campaign for Safe Cosmetics 2009). Other studies reported that household laundry detergents, shampoos, soaps, and skin cleansers were found to contain 1,4-dioxane at levels ranging from 6 to 160 ppm (Gelman Sciences 1989a, 1989b). In Denmark, cosmetic products and dishwashing detergent, which used polyethoxylated surfactants, contained 1,4-dioxane at levels ranging from 0.3 to 96 ppm and from 1.8 to 65 ppm, respectively (Rastogi 1990). The FDA has indicated that the levels of 1,4-dioxane found in their monitoring of cosmetics do not present a hazard to consumers (FDA 2009).

1,4-Dioxane has been reported to be a contaminant in other consumer products. For example, 1,4-dioxane was found to be an impurity at concentrations of 0.5 and 1–3% in two household adhesive products from the United States (NIH 2004). 1,4-Dioxane was detected in 2 of 62 samples of household adhesives at concentrations of 1.0 w/w% for boot cement and 2.8 w/w% for universal cement (EPA 1992). 1,4-Dioxane was identified, but not quantified, in the headspace gas phase of a sample of dishwashing detergent, but was not identified in 58 other consumer products tested (Kwon et al. 2007).

1,4-Dioxane is formed from the breakdown of diethylene glycol. In 1988, consumer anti-freeze products contained 1,4-dioxane at concentrations ranging from 100 to 3,400 ppb (Gelman Sciences 1989c).

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Radiator fluids have been found to contain slightly higher levels of 1,4-dioxane at concentrations ranging from 10 to 22,000 ppb (Gelman Sciences 1989c).

1,4-Dioxane was detected in 39 household aerosol products from Japan. In each of these samples, TCA was detected. The range of 1,4-dioxane concentration was 0.17–2.25% (Mori et al. 1992). A good correlation between the contents of 1,4-dioxane and TCA suggest that TCA containing 3% of 1,4-dioxane was used historically in the manufacture of aerosol products. However, because the use of TCA has been phased out in the United States since 1996, current levels of 1,4-dioxane in aerosol products should be limited.

1,4-Dioxane was identified but not quantified in human feces obtained from a healthy male individual from the former Soviet Union (Dmitriev et al. 1985). However, no information was provided in this study on the possible source of 1,4-dioxane in this feces sample or whether or not the individual was occupationally exposed to 1,4-dioxane.

Krotosznski et al. (1979) found 1,4-dioxane in the expired air of 24.8% of the samples taken from 54 healthy humans. The geometric mean concentration was  $0.253 \mu\text{g}/\text{m}^3$ . This concentration is significantly higher than those reported in the ambient air studies in New Jersey (see Section 6.4.1). However, no attempt was made to correlate the concentrations in the expired air with those found in the ambient air, nor was there an attempt to correlate these concentrations with life style or occupational exposures. Conkle et al. (1975) also found 1,4-dioxane ( $0.41 \mu\text{g}/\text{hour}$ ) in the expired air of one out of eight volunteers. These authors speculated that 1,4-dioxane was a normal metabolic product, although neither this study nor the former monitoring study cited above had undertaken rigorous steps to prevent contamination with 1,4-dioxane during the analysis.

In 1989, 1,4-dioxane was detected in highway rest-stop radiator boil-over pools at concentrations ranging from <10 to 2,300 ppb (Gelman Sciences 1989a, 1989b).

## 6.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

The primary routes of human exposure to 1,4-dioxane for the general population are inhalation of 1,4-dioxane in air, ingestion of contaminated food and drinking water containing 1,4-dioxane, and dermal contact with consumer products. Because 1,4-dioxane may be found in tap water, human exposure to 1,4-dioxane may also occur during activities such as showering, bathing, and laundering.

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A study conducted by the Centers for Disease Control and Prevention (CDC) collected human blood specimens in 2007–2008 from a geographically-diverse population of U.S. residents  $\geq 12$  years old. No detectable concentrations of 1,4-dioxane were found in 2,053 human blood specimens analyzed (Wang et al. 2009). The authors concluded that despite the potential for human exposure to 1,4-dioxane from consumer products, the low dermal penetrability is likely to result in a negligible internal dose.

Recent levels of 1,4-dioxane in air are not available. In 1984, the concentration of 1,4-dioxane ranged from 0.1 to 0.4  $\mu\text{g}/\text{m}^3$  in ambient air sampled from the United States. Assuming that an adult breathes approximately 20  $\text{m}^3$  of air per day, the inhalation exposure would be 2–8  $\mu\text{g}$  of 1,4-dioxane per day. Current exposure from air is likely to be less than this value. Exposure may be somewhat higher for persons living near sources of 1,4-dioxane emission. Individuals employed at industrial facilities that produce, process, and use 1,4-dioxane will also have higher exposures. Similarly, 1,4-dioxane is taken into the body by ingestion of drinking water. Current levels of 1,4-dioxane in drinking water are not available. In the 1970s, drinking waters in the United States were reported to contain 1  $\mu\text{g}/\text{L}$  of 1,4-dioxane (Kraybill 1978). Using this concentration and the consumption rate as 2 L/day, the 1,4-dioxane intake from drinking water would be 2  $\mu\text{g}/\text{day}$ . Current exposure from drinking water may likely be less than this value. Recently, a Total Diet Study in Japan determined the intake of 1,4-dioxane in food based on the average intake of food in the Kanto area of Japan (Nishimura et al. 2004). The 1,4-dioxane content of 12 food groups ranged between 2 and 15  $\mu\text{g}/\text{kg}$  inclusive. From these results, the total daily intake of 1,4-dioxane was calculated to be 0.440  $\mu\text{g}$ . This study indicates that the amount of 1,4-dioxane intake contributed from food is very low. FDA has estimated the exposure to 1,4-dioxane from the use of polyethylene glycol mono-isotridecyl ether sulfate sodium salt as a surfactant in adhesives intended for use in contact with food. Based on a daily diet of 3 kg, exposure to 1,4-dioxane has been estimated to be 0.2 ppb of daily diet or 0.6  $\mu\text{g}/\text{person}/\text{day}$  (FDA 1998). Since most consumer products (e.g., detergents, shampoos, and cosmetic products) containing 1,4-dioxane may be diluted with water prior to application, dermal exposure is expected to be small in comparison to other exposures such as air, drinking water, and food.

The National Industrial Chemicals Notification and Assessment Scheme (NICNAS) administered by the National Occupational Health and Safety Commission of Australia developed a ‘worst-case scenario’ for daily intake (inhalation and dermal exposure) for 1,4-dioxane from consumer products (not including pharmaceuticals or food products). The average daily intake from these exposures was calculated at around 7  $\mu\text{g}/\text{kg}$ , based on an assumed level of 30 ppm 1,4-dioxane in end-use products (NICNAS 1998).

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Occupational exposure of individuals involved in the production, processing, or use of 1,4-dioxane may result from inhalation or dermal exposure (De Rosa et al. 1996). The National Occupational Exposure Survey (1981–1983) indicated that 86,489 individuals, including 30,542 women, potentially were exposed to 1,4-dioxane (NIOSH 1977). This estimate was derived from observations of the actual use of the compound (25% of total observations) and the use of trade name products known to contain the compound (75%). The National Occupation Hazard Survey conducted by NIOSH from 1972 to 1974 estimated that 334,000 individuals were occupationally exposed to 1,4-dioxane, including 100,000 individuals occupationally exposed as a result of 1,4-dioxane used as a stabilizer in TCA (NIOSH 1976). In 1977, NIOSH estimated that 2,500 individuals were occupationally exposed to 1,4-dioxane, in addition to the 100,000 individuals occupationally exposed to both TCA and 1,4-dioxane (NIOSH 1977). OSHA reported that as many as 466,000 individuals may be occupationally exposed to 1,4-dioxane.

Individuals employed at chemical plants may be exposed to 1,4-dioxane as solvent vapors (Buffler et al. 1978). Between the period of 1994–1996, a survey in Hiroshima Prefecture, Japan was conducted to determine the levels of solvent vapors in 196 workplace areas. The survey was repeated every 6 months during this 3-year period. 1,4-Dioxane was reported in 6 of 1,176 cases at median and maximum concentrations of 0.5 and 0.8 ppm, respectively. 1,4-Dioxane was only detected in work areas where degreasing, cleaning, and wiping operations had occurred (Yasugi et al. 1998). During 1979, industrial hygiene monitoring was conducted at several plants which produced alcohol ethoxysulfate salts (Shell Oil Co. 1988). Time-weighted-average concentrations of 1,4-dioxane in air samples collected for five different jobs and locations within these plants were at or below the detection limit of <0.1 ppm. A maximum TWA concentration of 0.4 ppm reported in this monitoring study. In another study, 1,4-Dioxane and HEAA were detected in the urine of individuals occupationally exposed to 1,4-dioxane. Individuals were exposed to a time-weighted average concentration of 1.6 ppm 1,4-dioxane for 7.5 hours. The mean concentration of 1,4-dioxane and HEAA in urine samples from exposed individuals at the end of each workday were 3.5 and 414  $\mu\text{mol/L}$  (0.31 and 36.5 mg/L), respectively (Young et al. 1976).

Individuals involved in the manufacture of ethoxylated chemicals may be exposed to 1,4-dioxane from its occurrence as a by-product, and in particular during the stripping process, which is carried out to remove 1,4-dioxane from certain ethoxylated chemicals (mainly surfactants and emulsifiers) (EC 2002). Because of large quantities of TCA were previously used, past occupational exposure to 1,4-dioxane (used as a

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stabilizer) may have been significant, particularly in metal degreasing operations. As the manufacture of TCA is currently restricted, only limited exposure from this exposure source is expected to occur.

### 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, then 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 have the judgment of adults to avoid hazards (NRC 1993).

Specific information on the exposure of children to 1,4-dioxane does not exist. As for adults in the general population, small exposures occur from the normal ingestion of food and drinking water, inhaling air, and dermal contact with contaminated consumer products (e.g., containing ethoxylated surfactants). Home exposures may result from the unintentional consumption of consumer products (e.g., baby shampoo, household detergents) containing 1,4-dioxane. However, the extent of this possible exposure route in the general population is unknown.

### 6.7 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

Individuals who consume drinking water from contaminated wells may be exposed to higher levels of 1,4-dioxane. For example, groundwater has been reported to be contaminated with 1,4-dioxane in the following locations: Ann Arbor, Michigan; San Jose, California; and Menlo Park, California (DeRosa et al. 1996; Mohr 2004). The extent of 1,4-dioxane exposure for these populations is not known.

Individuals employed in occupations involved in the manufacture, processing and handling, and use of 1,4-dioxane will have potentially higher exposures to this chemicals. In addition, individuals involved in analytical science and research and development activities, which may utilize 1,4-dioxane as a solvent, may be exposed to higher levels of 1,4-dioxane.

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**6.8 ADEQUACY OF THE DATABASE**

Section 104(i)(5) of CERCLA, as amended, directs the Administrator of ATSDR (in consultation with the Administrator of EPA and agencies and programs of the Public Health Service) to assess whether adequate information on the health effects of 1,4-dioxane 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 1,4-dioxane.

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.** Sufficient information regarding the chemical and physical properties (i.e., log  $K_{ow}$ , log  $K_{oc}$ , Henry's law constant, vapor pressure, etc.) of 1,4-dioxane is available to evaluate its environmental fate (see Table 4-2). There are no data needs at this time.

**Production, Import/Export, Use, Release, and Disposal.** According to the Emergency Planning and Community Right-to-Know Act of 1986, 42 U.S.C. Section 11023, industries are required to submit substance release and off-site transfer information to the EPA. The TRI, which contains this information for 2007, became available in February of 2009. This database is updated yearly and should provide a list of industrial production facilities and emissions.

1,4-Dioxane is currently produced in the United States, although current production volumes are not available. Information on current and future production and importation levels of 1,4-dioxane are needed to determine whether the risk for human exposure to 1,4-dioxane is significant. Although 1,4-dioxane is not widely used in the home, environment, or most workplaces, it can be present as a contaminant in materials that are found or used in these environments and, therefore, human exposures to 1,4-dioxane can occur. 1,4-Dioxane is used primarily as a solvent. 1,4-Dioxane has been found as an impurity in cosmetics, household and industrial detergents, and pharmaceuticals due to its occurrence as a by-product

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in ethoxylated emulsifiers. 1,4-Dioxane may be present as a contaminant of food. However, no information is available that quantifies actual levels of 1,4-dioxane in food. Water is the most likely media to be contaminated with significant quantities of 1,4-dioxane (EC 2003; Hartung 1989).

Pure or nearly pure 1,4-dioxane is disposed of by incineration. It is expected that 1,4-dioxane is completely destroyed by this method. Aqueous solutions of 1,4-dioxane are disposed in waste water treatment facilities. Because 1,4-dioxane is resistant to biodegradation, complete mineralization of this chemical is not efficient. Thus, there may be need to develop effective methods of disposal for aqueous solutions of 1,4-dioxane. Additional information is needed on the amounts of 1,4-dioxane disposed of by each method.

**Environmental Fate.** There are no data needs regarding the environmental fate of 1,4-dioxane. 1,4-Dioxane is miscible in water and partitions primarily to the aqueous media in the environment. 1,4-Dioxane has high mobility in soil and has the potential to migrate into groundwater. In air, 1,4-dioxane will degrade by reaction with OH radicals with a half-life of <1 day (EPA 2000b). 1,4-Dioxane has been found to be resistant to biodegradation in the environment (Alexander 1973; Dow Chemical Co. 1989; Fincher and Payne 1962; Heukelekian and Rand 1955; Mills and Stack 1954). 1,4-Dioxane is expected to persist in both water and soil.

**Bioavailability from Environmental Media.** 1,4-Dioxane is absorbed following inhalation, oral, and dermal contact (see Chapter 3). However, 1,4-dioxane is not bioconcentrated. Based on dermal penetration studies, dermal absorption of 1,4-dioxane is limited. No data needs have been identified at this time.

**Food Chain Bioaccumulation.** Because 1,4-dioxane is miscible in water, it is not bioconcentrated in plants, aquatic organisms, or animals. 1,4-Dioxane is not biomagnified to any extent in prey organisms. No data needs have been identified at this time.

**Exposure Levels in Environmental Media.** Reliable monitoring data for the levels of 1,4-dioxane in contaminated media at hazardous waste sites are needed so that the information obtained on levels of 1,4-dioxane in the environment can be used in combination with the known body burden of 1,4-dioxane to assess the potential risk of adverse health effects in populations living in the vicinity of hazardous waste sites.

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1,4-Dioxane has been detected in air, water, and foodstuff. Although historical data are available (e.g., 1980s and earlier), recent information on the levels of 1,4-dioxane in these media are not available. Reliable monitoring data for the levels of 1,4-dioxane in contaminated media at hazardous waste sites are needed so that the information obtained on levels of 1,4-dioxane in the environment can be used in combination with the known body burden of 1,4-dioxane to assess the potential risk of adverse health effects in populations living in the vicinity of hazardous waste sites. Estimates have been made for human intakes of 1,4-dioxane from air and drinking water. However, these estimates are based on historical monitoring data which may not be representative of current levels of 1,4-dioxane in environmental media. It is unclear how extensive the human exposure to 1,4-dioxane is indoors and from consumer products. Additional data that determines current levels of 1,4-dioxane in air, drinking water, food, and consumer products are necessary to assess human exposure to 1,4-dioxane.

**Exposure Levels in Humans.** 1,4-Dioxane has been detected in the urine of individuals who are occupationally exposed to 1,4-dioxane (Young et al. 1976). Two studies conducted by Conkle et al. (1975) and Krotosznski et al. (1979) involving 54 and 8 volunteers, respectively, detected 1,4-dioxane in a small number of expired air samples collected from these volunteers, but the source of the measured 1,4-dioxane could not be determined because the studies did not adequately document lifestyle or occupation. No other biological monitoring studies have been done in populations surrounding hazardous waste sites or in the general population. This information is necessary for assessing the need to conduct health studies on these populations. No estimates have been made for human intake of 1,4-dioxane from various environmental media. This information is necessary for determining the routes of exposure to 1,4-dioxane from these various media.

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

**Exposures of Children.** Children are exposed to 1,4-dioxane in the same manner as adults. Exposure and body burden studies on children would be useful. Children who take frequent bubble baths may be exposed to higher levels of 1,4-dioxane than adults due to possible contamination of ethoxylated surfactants found in some of these commercial products. Additional studies are needed to determine whether this is a significant exposure route for children. It is not known whether children are different in their weight-adjusted intake of 1,4-dioxane. Additional studies would help to determine if children are more or less exposed to 1,4-dioxane compared to adults.

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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 1,4-dioxane 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.

Historically, 1,4-dioxane has been used as a stabilizer in TCA at concentrations up to 4%. Often 1,4-dioxane is present at sites where TCA has been found as a contaminant. TCA is currently one of the compounds for which a Subregistry has been established in the Volatile Organic Compounds (VOCs) Registry. The VOCs Registry is part of the National Exposure Registry (NER), which was created and is being maintained by the Agency for Toxic Substances and Disease Registry.

### 6.8.2 Ongoing Studies

The FEDRIP (2009) database provides additional information obtainable from a few ongoing studies that may fill in some of the data needs identified in Section 6.8.1.

Researchers at North Carolina State University are investigating the intermediates and pathways of the microbial degradation of several important ether pollutants including 1,4-dioxane. In addition, the key enzymes responsible involved in the biodegradation of these important pollutants are to be characterized and subsequently identify and characterize the genes encoding these enzymes.