

## 6. POTENTIAL FOR HUMAN EXPOSURE

### 6.1 OVERVIEW

Chlorine dioxide and chlorite have not been identified in any of the 1,647 waste sites that have been proposed for inclusion on the EPA National Priorities List (NPL) (HazDat 2004). However, the number of sites evaluated for chlorine dioxide and chlorite are not known. The frequency of these sites can be seen in Figure 6-1.

Chlorine dioxide is a highly reactive chemical (see Section 6.3.2) that will exist only in the immediate vicinity of where it is produced or used. In the United States, the primary route of exposure to chlorine dioxide and chlorite (ions and salts) is from the consumption of drinking water. Chlorine dioxide is added to drinking water as a disinfectant in some municipal water-treatment systems in the United States. In 1995, 5.1% of community water-treatment systems in the United States reported that chlorine dioxide was used (Hoehn et al. 2000). However, the total number people exposed will be higher if smaller facilities (i.e., those serving less than 50,000 people) are also included in this value (see Section 5.3). As regulated by EPA (as of January 1, 2002), the maximum residual disinfectant levels in drinking water for chlorine dioxide and chlorite ion are 0.8 and 1.0 mg/L, respectively (EPA 2002e, 2002g).

### 6.2 RELEASES TO THE ENVIRONMENT

Releases of chlorine dioxide are required to be reported under Superfund Amendment Reauthorization Act (SARA) Section 313; consequently, data are available for this compound in the Toxics Release Inventory (TRI) (EPA 1995). According to the TRI, a total of 582,315 pounds (264,134 kg) of chlorine dioxide was released to the environment in 2001 (TRI01 2003). The TRI data should be used with caution because only certain types of facilities are required to report. This is not an exhaustive list.

#### 6.2.1 Air

The estimated release of 582,005 pounds (263,993 kg) of chlorine dioxide to the atmosphere from over 100 manufacturing, processing, and waste-disposal facilities in 2001 accounted for about 99.9% of the

6. POTENTIAL FOR HUMAN EXPOSURE

**Figure 6-1. Frequency of NPL Sites with Chlorine Dioxide and Chlorite Contamination**



Derived from HazDat 2004

\*No data are available in HazDat 2004

## 6. POTENTIAL FOR HUMAN EXPOSURE

estimated total environmental releases (TRI01 2003). These releases are summarized in Table 6-1. The data from the TRI listed in Table 6-1 should be used with caution, however, since only certain types of facilities are required to report (EPA 1995). This is not a comprehensive list.

No other information was found in the literature about the releases of chlorine dioxide and chlorite (ions or salts) into air.

**6.2.2 Water**

The estimated release of 310 pounds (141 kg) of chlorine dioxide to water from one electric power facility in Florida accounted for <0.1% of the estimated total environmental releases in 2001 (TRI01 2003). No releases (0 pounds) of chlorine dioxide occurred via underground injection (TRI01 2003). These releases are summarized in Table 6-1. The data from the TRI listed in Table 6-1 should be used with caution, however, since only certain types of facilities are required to report (EPA 1995). This is not a comprehensive list.

No other information was found in the literature about the releases of chlorine dioxide and chlorite (ions or salts) into water.

**6.2.3 Soil**

One manufacturing facility reported releases of chlorine dioxide to the environment in 2001; no chlorine dioxide was reportedly released to land (TRI01 2003). Releases to the environment from facilities that produce, process, or use chlorine dioxide are summarized in Table 6-1. The data from the TRI should be used with caution since only certain types of facilities are required to report (EPA 1995). This is not a comprehensive list.

No other information was found in the literature about the releases of chlorine dioxide and chlorite (ions and salts) to soils and sediment.

## 6. POTENTIAL FOR HUMAN EXPOSURE

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

State <sup>c</sup>	Number of facilities	Reported amounts released in pounds per year <sup>b</sup>						
		Air <sup>d</sup>	Water	Under-ground injection	Land	Total on-site release <sup>e</sup>	Total off-site release <sup>f</sup>	Total on and off-site release
AL	9	53,789	0	0	0	53,789	0	53,789
AR	5	18,848	0	0	0	18,848	0	18,848
CA	3	3,391	0	0	0	3,391	0	3,391
CO	1	255	No data	0	0	255	0	255
FL	8	110,496	310	0	0	110,806	0	110,806
GA	8	6,924	0	0	0	6,924	0	6,924
ID	1	6,105	No data	0	0	6,105	0	6,105
IL	2	9,714	No data	0	0	9,714	0	9,714
KY	3	5,147	0	0	0	5,147	0	5,147
LA	6	19,861	0	0	0	19,861	0	19,861
MA	1	0	No data	0	0	0	0	0
MD	1	19,005	No data	0	0	19,005	0	19,005
ME	6	8,936	0	0	0	8,936	0	8,936
MI	3	1,563	0	0	0	1,563	0	1,563
MN	2	23,229	0	0	0	23,229	0	23,229
MS	4	35,758	0	0	0	35,758	0	35,758
NC	8	66,695	0	0	0	66,695	0	66,695
NY	2	6,560	0	0	0	6,560	0	6,560
OH	1	22,005	0	0	0	22,005	0	22,005
OR	3	15,295	No data	0	0	15,295	0	15,295
PA	6	34,555	0	0	0	34,555	0	34,555
SC	6	56,967	0	0	0	56,967	0	56,967
TN	2	13,403	No data	0	0	13,403	0	13,403
TX	4	6,259	0	0	0	6,259	0	6,259
VA	3	14,105	0	0	0	14,105	0	14,105
VT	1	0	0	0	0	0	0	0
WA	7	15,846	0	0	0	15,846	0	15,846
WI	5	7,294	No data	0	0	7,294	0	7,294
<b>Total</b>	<b>111</b>	<b>582,005</b>	<b>310</b>	<b>0</b>	<b>0</b>	<b>582,315</b>	<b>0</b>	<b>582,315</b>

Source: TRI01 2003

<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>The sum of fugitive and stack releases are included in releases to air by a given facility.

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

<sup>f</sup>Total amount of chemical transferred off-site, including to publicly owned treatment works (POTW).

## 6. POTENTIAL FOR HUMAN EXPOSURE

**6.3 ENVIRONMENTAL FATE****6.3.1 Transport and Partitioning**

Chlorine dioxide is a very reactive compound and may exist in the environment for only short periods of time (see Section 6.3.2). Chlorine dioxide is readily soluble as a gas. However, chlorine dioxide can be easily driven out of aqueous solutions with a strong stream of air. The partition coefficient between water and  $\text{ClO}_2(\text{g})$  is about 21.5 at 35 °C and 70.0 at 0 °C (Aieta and Berg 1986; Kaczur and Cawfield 1993; Stevens 1982). Transport and partition of chlorine dioxide in soils and sediments will not be significant. Chlorine dioxide is expected to be reduced to chlorite ions in aqueous systems (see Section 6.3.2.2).

Like chlorine dioxide, the chlorite ion is a strong oxidizer (Rav-Acha 1998). Since chlorite is an ionic species, it is not expected to volatilize and will not exist in the atmosphere in the vapor phase. Thus, volatilization of chlorite ions from moist soil and water surfaces or dry soil surfaces will not occur. Because chlorite is an anion, sorption of chlorite ions onto suspend particles, sediment, or clay surfaces is expected to be limited under environmental conditions. Thus, chlorite ions will be mobile in soils and leach into groundwater. However, chlorite (ions and salts) will undergo oxidation-reduction reactions with components in soils, suspend particles, and sediments (e.g.,  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$  ions; see Section 6.3.2.2). Thus, oxidation-reduction reactions may reduce the concentration of chlorite ions capable of leaching into groundwater.

No additional information was located in the literature on the transport and partitioning of chlorine dioxide and chlorite (ions and salts).

**6.3.2 Transformation and Degradation**

Chlorine dioxide is an unstable gas that rapidly decomposes in air. In water, chlorine dioxide is a strong oxidizer; 50–70% of the chlorine dioxide that reacts with organic and inorganic compounds will immediately appear as chlorite ( $\text{ClO}_2^-$ ) and chloride ( $\text{Cl}^-$ ) ions. Chlorine dioxide does not form trihalo-methanes as disinfection by-products (DBPs). However, chlorine dioxide does result in the formation of other DBPs (e.g., lower chlorinated organics, chlorate, and chlorite) which may be found in drinking water treated with chlorine dioxide (Aieta and Berg 1986; Chang 1982; Stevens 1982). Suh and Abdel-

## 6. POTENTIAL FOR HUMAN EXPOSURE

Rahman (1985) reported that the presence of  $\text{ClO}_2$  and  $\text{HOCl}$  ( $\text{Cl}_2$  dissolved in water) inhibit the formation of trihalomethanes, and the degree of inhibition depends on the ratio of  $\text{ClO}_2$  to  $\text{HOCl}$ .

**6.3.2.1 Air**

Chlorine dioxide gas is unstable and can rapidly decompose at high concentrations ( $>40$  kPa partial pressure). It also decomposes to chlorine and oxygen with exposure to mild heat, noise, flame, and a minor pressure wave at low concentrations (Dobson and Cary 2002). Chlorine dioxide will decompose upon exposure to sunlight (Vogt et al. 1986). The gas-phase absorption spectrum for chlorine dioxide is the same as in aqueous solution (Kaczur and Cawfield 1993). The primary photochemical reaction of  $\text{ClO}_2$  in the gas phase corresponds to homolytic scission of one of the chlorine-oxygen bonds (i.e.,  $\text{ClO}_2 \rightarrow \text{ClO} + \text{O}$ ). Products of this initial reaction generate secondary products including doublet-state oxygen ( $\text{O}_2^*$ ), chlorine ( $\text{Cl}_2$ ), and chlorine trioxide ( $\text{Cl}_2\text{O}_3$ ) (Griese et al. 1992; Zika et al. 1984). If chlorine dioxide gas is diluted in air to  $<15$  volume percent, it can be relatively stable in darkness (Vogt et al. 1986).

**6.3.2.2 Water**

Chlorine dioxide is readily soluble in water, forming a greenish-yellow solution. It is not unusual to simultaneously have multiple chlorine species present in chlorine dioxide solutions originating from by-products or unreacted precursors. Table 6-2 lists the various chlorine species that might be present in solutions of chlorine dioxide (Gordon 2001).

Chlorine dioxide alone will not hydrolyze in solution to any appreciable extent between pH 2 and 10. Dilute neutral or acidic aqueous solutions of chlorine dioxide are stable if kept cool, well sealed, and protected from sunlight. In the absence of oxidizable substances and in the presence of hydroxyl ions, chlorine dioxide will dissolve in water and then decompose with the slow formation of chlorite and chlorate ions (e.g.,  $2\text{ClO}_2 + 2\text{OH}^- \rightarrow \text{ClO}_2^- + \text{ClO}_3^- + \text{H}_2\text{O}$ ). At chlorine dioxide concentrations in the 5–10 mg/L range at pH 12, the decomposition half-life of chlorine dioxide in solution ranges from 20 to 180 minutes (Aieta and Berg 1986; Stevens 1982; WHO 2000). Lee et al. (2004) found that the concentration of chlorate ions formed from chlorine dioxide were higher at low pHs. For example,

## 6. POTENTIAL FOR HUMAN EXPOSURE

**Table 6-2. Chlorine Speciation in Aqueous Solutions**

Oxidation State	Species	Formula
+7	Perchlorate ion	$\text{ClO}_4^-$
+5	Chlorate ion	$\text{ClO}_3^-$
+4	Chlorine dioxide	$\text{ClO}_2$
+3	Chlorite ion	$\text{ClO}_2^-$
+3	Hypochlorous acid	$\text{HClO}_2$
+1	Hypochlorite ion	$\text{OCl}^-$
+1	Hypochlorous acid	$\text{HOCl}$
0	Chlorine	$\text{Cl}_2$
-1	Chloride ion	$\text{Cl}^-$

## 6. POTENTIAL FOR HUMAN EXPOSURE

10 and 15% chlorate ions were formed from chlorine dioxide at pHs 4 and 7, respectively. At pH 10, chlorate ions were not formed at all.

Chlorine dioxide has a positive chlorine-oxidation state of four (+4), which is intermediate between chlorite (+3) and chlorate (+5) ions. Reduction of chlorine dioxide usually results in the formation of chlorite ions (e.g.,  $\text{ClO}_2 + e^- \times \text{ClO}_2^-$ ;  $E^{\text{pH}=7}=0.95$  volts). Chlorite ions ( $\text{ClO}_2^-$ ) are also effective oxidizing agents, although they react much slower than chlorine dioxide. The reduction of chlorite results in the formation of chloride ions (e.g.,  $\text{ClO}_2^- + 4\text{H}^+ + 4e^- \times \text{Cl}^- + 2\text{H}_2\text{O}$ ;  $E^{\text{pH}=7}=0.37$  volts). The redox potential at pH 7 (i.e.,  $E^{\text{pH}=7}$ ) indicates that chlorine dioxide is a stronger oxidizer than chlorite ions (Rav-Acha 1998). During water-treatment, approximately 50–70% of the chlorine dioxide reacted will immediately appear as chlorite and chloride (Aieta and Berg 1986; Stevens 1982).

Chlorine dioxide, like other strong oxidants, will oxidize manganese (II), iron (II), iodide ( $\text{I}^-$ ), and sulfide ( $\text{S}^{2-}$ ), forming insoluble manganese dioxide ( $\text{MnO}_2$ ), iron hydroxides precipitates, iodine ( $\text{I}_2$ ), and sulfate ( $\text{SO}_4^{2-}$ ), respectively (Dernat and Pouillot 1992). In the absence of sunlight, bromide ( $\text{Br}^-$ ) is not oxidized by chlorine dioxide. Thus, chlorine dioxide will not transform bromide into hypobromite ( $\text{OBr}^-$ ), which could react with organic matter to form bromoform ( $\text{CHBr}_3$ ) or bromate ( $\text{BrO}_3^-$ ). This is a significant difference between the use of chlorine dioxide as an oxidant and the use of chlorine or ozone as oxidants in water-treatment systems (Aieta and Berg 1986; Stevens 1982; WHO 2000).

Since chlorine dioxide reacts generally as an electron acceptor, hydrogen atoms present in activated organic CH or NH bonds do not react by electrophilic substitution with chlorine (Hoigne and Bader 1994). As a result, chlorine dioxide will form fewer chlorinated compounds compared to  $\text{Cl}_2$  when it reacts with organic matter. In contrast, chlorine ( $\text{Cl}_2$ ) reacts not only by oxidation, but also by electrophilic substitution, resulting in a variety of volatile and nonvolatile chlorinated organic products; for example, trihalomethanes (THMs). It has been well established that “chlorine-free” chlorine dioxide in reaction with both humic and fulvic acids does not form THMs. However, some other types of chlorinated organics may be formed from the reaction of chlorine dioxide with humic and fulvic acids (Aieta and Berg 1986; Stevens 1982). The reactions of chlorine dioxide with olefin compounds in wastewater are apparently very complex and produce a host of chlorinated and nonchlorinated products. No evidence exists that chlorine dioxide undergoes reactions with saturated aliphatic hydrocarbons under mild conditions. Chlorine dioxide does not seem to cause the formation of odorous compounds with phenol. Chlorine dioxide treatment of phenols can cause chlorine substitution, ring cleavage, or both, depending on the particular phenol reacted and the conditions of the reaction. Through complex



## 6. POTENTIAL FOR HUMAN EXPOSURE

mechanisms, chlorine dioxide reacts rapidly with phenols and phenoxide anions to form quinones and chloroquinones, and when in excess, oxalic and maleic acids. Chlorine substitution in the products, however, is not entirely absent (Aieta and Berg 1986; Rav-Acha and Choshen 1987; Stevens 1982). Chlorine dioxide reacts with natural organic matter (NOM; i.e., humic and fulvic acids) mainly on the aromatic part. Formaldehyde and acetaldehyde are the main byproducts of oxidation of NOM by chlorine dioxide; pH does not have any significant influence on this reaction (Dąbrowska et al. 2003).

At a waste water-treatment pilot plant in Evansville, Indiana, which used chlorine dioxide as a primary disinfectant, more than 40 different organic disinfection by-products (DBPs) were identified at very low concentrations. Eleven of these DBPs are regulated chemicals by EPA (i.e., bromodichloromethane, carbon tetrachloride, dibromochloromethane, 1,1,1-trichloro-2-propanone, maleic anhydride, bromoform, 1,4-dichlorobenzene, benzyl cyanide, benzoic acid, naphthalene, and decylphenol) (Richardson et al. 1994). Chlorine dioxide will not react with ammonia and reacts only slowly with primary amines. In general, amines produce the respective aldehyde upon reaction with chlorine dioxide in the following order of reactivity: tertiary>secondary>primary (Aieta and Berg 1986; Stevens 1982).

Chlorine dioxide readily degrades in aqueous solutions under ultraviolet light. It has a broad UV absorption band with a maximum near 360 nm and a molar extinction coefficient of about  $1,150 \text{ (M} \times \text{cm)}^{-1}$  (Aieta and Berg 1986). It is postulated that the reaction in solution proceeds as in the gas phase, to give ClO and O. The initial photodissociation reaction is followed by rapid dark and light reactions to produce chlorate ( $\text{ClO}_3^-$ ), hypochlorite ( $\text{OCl}^-$ ), and chloride ( $\text{Cl}^-$ ) (Zika et al. 1984). Solution speciation can have a marked effect on the mechanism and products generated from photolysis of chlorine dioxide. In the absence of light, chlorine dioxide will not oxidize bromide ion into hypobromite ( $\text{OBr}^-$ ) and will not form bromoform ( $\text{CHBr}_3$ ) or bromate ( $\text{BrO}_3^-$ ). However, under sunlight, some photolysis intermediates of chlorine dioxide with long half-lives are capable of oxidizing bromide to hypobromite, which will result in the formation of bromate. Thus, if labile organic materials are present during illumination, bromoform may be generated by the reaction of organic matter with hypobromite formed by intermediates of chlorine dioxide photolysis (Aieta and Berg 1986; Bolyard et al. 1993; Griese et al. 1992; Stevens 1982; WHO 2000; Zika et al. 1984).

Chlorite and chlorate ions have been shown to undergo reduction by bacteria under anaerobic conditions. Anaerobic degradation is an important process in anoxic groundwater, sediments, and some soils. It has been known for over 40 years that chlorate ions can be reduced by mixed cultures under anaerobic conditions (Logan 1998). Chlorate-respiring bacteria are widely distributed in the environment and

## 6. POTENTIAL FOR HUMAN EXPOSURE

utilize electron acceptors (e.g., chlorate ions) in lieu of oxygen to generate energy and produce carbon-based building blocks. The reduction of chlorate ions occurs in two steps; chlorate reduction with chlorate reductase enzyme followed by chlorite disproportionation catalyzed by chlorite dismutase (a non-respiratory enzyme). Oxygen and chloride are formed as the end products (Danielsson et al. 2003; Xu et al. 2004). Although oxygen is produced during reduction processes, it is rapidly consumed by the bacteria such that oxygen does not accumulate to high levels. Chlorate dismutase activity is unaffected by oxygen, but expression of this enzyme does not occur under aerobic conditions even in the presence of perchlorate or chlorate ion (Xu et al. 2004). Several dinitrifying bacteria reduce chlorate but, in general, this reduction is not coupled to microbial growth (Wolterink et al. 2002). Moreover, these organisms lack chlorite dismutase enzyme, which is required for reduction of chlorite. Thus, it is likely that the nitrate and chlorate pathways for chlorate-reduction are not necessarily related (Wolterink et al. 2002). No quantitative information was located on the biodegradation rate of chlorate or chlorite ions in the environment. However, the rate of chlorate ion degradation appears to be rapid under anaerobic conditions in waste-water treatment facilities (Logan 1998).

### 6.3.2.3 Sediment and Soil

No information was located in the literature on the transformation and degradation of chlorine dioxide or chlorite (ions and salts) in sediment and soils.

### 6.3.2.4 Other Media

No information was located in the literature on the transformation and degradation of chlorine dioxide or chlorite (ions and salts) in other environmental media.

## 6.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

### 6.4.1 Air

Chlorine dioxide degrades rapidly in air (see Section 6.3.2.1) and should be measurable only near its source of production or use (e.g., pulp and paper-mill plants, water-treatment facilities). As part of an international study of workers in the pulp and paper industry, the concentration of chlorine dioxide was measured in the workplace air of pulp and paper mills in 19 countries. The concentration of chlorine dioxide was measured in the following work areas: steam and power generation (range, <1–60 ppb);

## 6. POTENTIAL FOR HUMAN EXPOSURE

effluent water-treatment (range, not detected to 3 ppb); and maintenance (range, < detection limit to 5.8 ppb) (Kauppinen et al. 1997; Teschke et al. 1999). In another study, the concentration of chlorine dioxide was measured in the workplace air at a pulp mill in British Columbia, Canada between May and June, 1988. The concentration of chlorine dioxide was <10 ppb in area samples and personal full-shift samples. The exception was in the bleach/chemical preparation area sample in which the concentration of chlorine dioxide ranged from <10 to 300 ppb (Kennedy et al. 1991).

The formation of offensive odors in indoor air, such as “kerosene-like” and “cat-urine-like” odors, have been attributed to drinking water treated with chlorine dioxide. The “kerosene-like” and “cat-urine-like” odors are produced by reactions between chlorine dioxide escaping from water and volatile organic compounds found in homes, primarily from new carpeting. This has been ascribed to over-dosing drinking water with residual chlorine dioxide (or chlorite ions), which is used as a postdisinfectant to prevent microbial growth in water-distribution systems (Dluzniewski 2002; Hoehn et al. 1990, 2003).

No other information was located in the literature on the concentrations of chlorine dioxide or chlorite (ions and salts) in air.

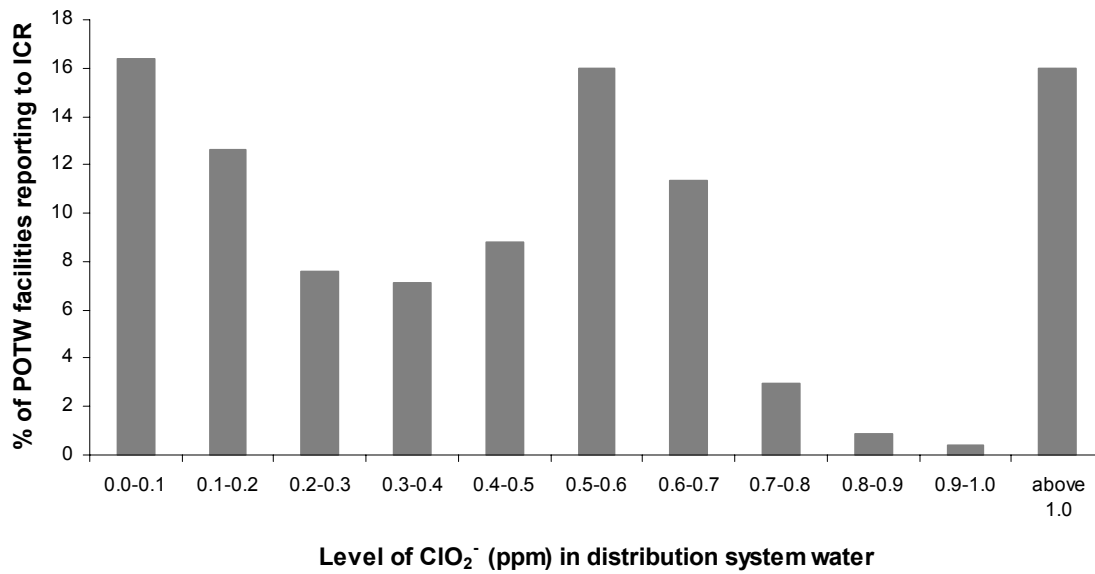
#### 6.4.2 Water

Chlorine dioxide is added to drinking water as a disinfectant in some municipal water-treatment systems in the United States. In 1995, 5.1% of community water-treatment systems in the United States reported that chlorine dioxide was used (Hoehn et al. 2000). This would translate to about 12 million people who may be exposed to chlorine dioxide and chlorite ions in the United States. However, the total number of people exposed will be higher if smaller facilities (i.e., those serving <50,000 people) are also included in this value.

As regulated by EPA (as of January 1, 2002), the maximum residual-disinfectant level (MRDL) for chlorine dioxide is 0.8 mg/L (EPA 2002g); the maximum contaminant level (MCL) for its oxidation product, chlorite ion, in drinking water is 1.0 mg/L (EPA 2002e). The levels of chlorite ion in distribution system waters have been reported as part of the Information Collection Rule (ICR), a research project used to support the development of national drinking-water standards in the United States (EPA 2002d). Figure 6-2 illustrates the levels of chlorite ion in drinking waters sampled from distribution systems versus the percentage of publicly-owned treatment works (POTW) facilities in the United States

6. POTENTIAL FOR HUMAN EXPOSURE

**Figure 6-2. Percentage of POTW Facilities Reporting to ICR vs. Level of Chlorite in Distribution System Water\***



Source: EPA 2002d

\*Samples were taken from the distribution system of POTW facilities that utilized chlorine dioxide.

ClO<sub>2</sub><sup>-</sup> = chlorite; ICR = Information Collection Rule; POTW = publicly owned treatment works

## 6. POTENTIAL FOR HUMAN EXPOSURE

that reported as part of the ICR in 1998. Approximately 16% of this group had levels of chlorite ion over the MCL of 1 mg/L.

In a 12-week epidemiological study conducted in a small town in Ohio, the ranges of concentrations of chlorine dioxide, chlorite ion, and chlorate ion in drinking water were 0.3–1.1, 3.2–7.0, and 0.3–1.1 mg/L, respectively (Lykins et al. 1990; Michael et al. 1981). In one study using a sensitive analytical method, the average concentration of chlorine dioxide in tap water from the city of Brest, France was  $1.8 \times 10^{-7}$  mol/L (0.012 mg/L) (Quentel et al. 1994).

Bolyard et al. (1993) analyzed samples from four water-treatment facilities in the United States that use chlorine dioxide as a disinfectant. Source water samples were also analyzed from each facility and no chlorite or chlorate ions were detected. At these water-treatment facilities, additional gaseous  $\text{Cl}_2$  was added to provide a residual disinfectant in the distribution systems. Water taken from these distribution systems (i.e., water sampled at water-treatment plant) had measurable concentrations of both chlorite and chlorate ions. The ranges of concentrations were 15–740 and 21–330  $\mu\text{g/L}$  for chlorite and chlorate, respectively (Bolyard et al. 1993). In general, chlorite ion was the predominate disinfection by-product. However, at two sites where water was chlorinated prior to passing through secondary sedimentation basins containing activated carbon, concentrations of chlorate ion concentrations were higher than chlorite ions. At these sites, residual  $\text{Cl}_2$  and activated carbon likely oxidized chlorite to chlorate, which resulted in elevated levels of chlorate in finish water samples (Bolyard et al. 1993).

No other information was located in the literature on the concentrations of chlorine dioxide or chlorite (ions and salts) in water.

### 6.4.3 Sediment and Soil

No information was located in the literature on the concentrations of chlorine dioxide or chlorite (ions and salts) in sediments and soil. Due to the high reactivity of chlorine dioxide and chlorite (ions and salts), however, concentrations of these compounds are expected to be small or nil.

## 6. POTENTIAL FOR HUMAN EXPOSURE

**6.4.4 Other Environmental Media**

No information was located in the literature on the concentrations of chlorine dioxide or chlorite (ions and salts) in other environmental media.

**6.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE**

The general population may be exposed to chlorine dioxide and chlorite (ions or salts) by the ingestion of drinking water. As part of the ICR, 5.1% of the water-treatment facilities serving more than 100,000 people in the United States reported that chlorine dioxide was used in 1995 (Hoehn et al. 2000). However, the percentage of facilities using chlorine dioxide would be higher if smaller facilities (i.e., those serving <50,000 people) were also included in this value. Individuals who live in communities with water-treatment facilities using chlorine dioxide will have a higher exposure to chlorine dioxide and chlorite ions than other segments of the population.

For communities that utilize chlorine dioxide as a drinking-water disinfectant, an exposure estimate may be calculated based on the maximum residual-disinfectant levels for chlorine dioxide and chlorite ion. If the concentration of chlorine dioxide in U.S. drinking water is assumed to be 0.8 mg/L (the maximum residual disinfectant level [EPA 2002g]) and the consumption rate of drinking water by a normal adult is assumed to be 2 L/day, then the exposure to chlorine dioxide from drinking water would be 1.6 mg/day. Similarly, if the concentration of chlorite ion in U.S. drinking water is assumed to be 1.0 mg/L (the maximum contaminant level [EPA 2002e]), and the consumption rate of drinking water by a normal adult is assumed to be 2 L/day, then the exposure from drinking water would be 2.0 mg/day. However, the exposure to chlorine dioxide and chlorite ion may be much lower than these estimated levels depending on individual conditions for each community. Other sources of exposure to chlorine dioxide and chlorite (ions and salts) are not significant for the general population.

Occupational exposure to chlorine dioxide and chlorite may occur at facilities that utilize these chemicals as bleaching agents (e.g., pulp and paper mills) or water disinfectants (e.g., water-treatment facilities). The primary route of occupational exposure will be by inhalation of these compounds in the immediate vicinity of their use. As part of an international study of workers in the pulp and paper industry, the concentration of chlorine dioxide was measured in the workplace air of pulp and paper mills from 19 countries. The concentration of chlorine dioxide was measured in the following work areas: steam and power generation (range, <1–60 ppb); effluent water-treatment (range, not detected to 3 ppb); and

## 6. POTENTIAL FOR HUMAN EXPOSURE

maintenance (range, <detection limit to 5.8 ppb) (Kauppinen et al. 1997; Teschke et al. 1999). In another study, the concentration of chlorine dioxide was measured in the workplace air at a pulp mill in British Columbia, Canada between May and June in 1988. The concentration of chlorine dioxide was <10 ppb in area samples and personal full-shift samples. The exception was in the bleach/chemical preparation area sample, in which the concentration of chlorine dioxide ranged from <10 to 300 ppb (Kennedy et al. 1991).

## 6.6 EXPOSURES OF CHILDREN

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

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

Specific information on the exposure of children to chlorine dioxide and chlorite (ions and salts) was not located. Like adults, the primary route of exposure for children will be from drinking water. Water consumption among children is higher on a proportional body weight basis than for adults. Therefore, children may have a higher exposure to chlorine dioxide and chlorite (ions and salts). Other sources of exposure to chlorine dioxide and chlorite (ions and salts) will not be significant. Chlorine dioxide and chlorite (ions and salts) are reactive chemicals and will not be found in amniotic fluid, meconium, neonatal blood, or breast milk.

## 6. POTENTIAL FOR HUMAN EXPOSURE

**6.7 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES**

Individuals who are employed at pulp and paper mills, municipal water-treatment facilities, and other facilities that use chlorine dioxide as a disinfectant may have high exposures to chlorine dioxide and chlorite (ions and salts) (see Section 6.5).

**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 chlorine dioxide and chlorite are available. Where adequate information is not available, ATSDR, in conjunction with the National Toxicology Program (NTP), is required to assure the initiation of a program of research designed to determine the health effects (and techniques for developing methods to determine such health effects) of chlorine dioxide and chlorite.

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 relevant physical and chemical properties of chlorine dioxide and chlorite (ions and salts) are well known and permit estimation of its environmental fate. Physical and chemical properties are presented in Table 4-2 (Dobson and Cary 2002; HSDB 2002; Kaczur and Cawfield 1993; O'Neil 2001; NIOSH 2002; Vogt et al. 1986).

**Production, Import/Export, Use, Release, and Disposal.** Data regarding the production of chlorine dioxide and chlorite (ions and salts) are available, but are limited (Kaczur and Cawfield 1993). Annual production of chlorine dioxide in the United States has increased from 79 to 361 kilotons between the years 1970 and 1990 (Kaczur and Cawfield 1993). Additional production information for chlorite (ions and salts) specifically whether the production amount (7,700 metric tons in 1991; Kaczur and Cawfield 1993) is larger or smaller than in the past would be useful. Information on future production of



## 6. POTENTIAL FOR HUMAN EXPOSURE

chlorine dioxide and chlorite (ions and salts) would also be helpful. Chlorine dioxide and chlorite (ions and salts) are not widely used in the home or environment. Some municipal waste water-treatment facilities use chlorine dioxide or chlorite (ions and salts) to disinfect drinking water (EPA 2002c; Kaczur and Cawfield 1993; Vogt et al. 1986). Wood-pulp bleaching is the largest industrial use of chlorine dioxide (EPA 2002c; Kaczur and Cawfield 1993; Vogt et al. 1986). Air is the medium most likely contaminated with chlorine dioxide near facilities where it is used (TRI01 2003). Additional information on disposal methods is not warranted since chlorine dioxide and chlorite (ions and salts) are reactive and will not exist for long periods of time in the environment (see Section 6.3).

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. TRI, which contains this information for 2001, became available in July of 2003. This database is updated yearly and should provide a list of industrial facilities and emissions.

**Environmental Fate.** Chlorine dioxide and chlorite (ions and salts) are strong oxidizers and will not exist in the environment for long periods of time (Dobson and Cary 2002); therefore, transport and partitioning of chlorine dioxide and chlorite (ions and salts) are not important. Chlorine dioxide reacts immediately in water to form chlorite and chlorate ions, and in air to form chlorine and oxygen (Dobson and Cary 2002). Information on the half-life of chlorite (ions and salts) in environmental media would be useful.

**Bioavailability from Environmental Media.** Chlorine dioxide and chlorite (ions and salts) are strong oxidizers. Chlorine dioxide is highly reactive and will not be bioavailable in environmental media. Additional information concerning the bioavailability of chlorite (ions and salts) would be helpful.

**Food Chain Bioaccumulation.** Chlorine dioxide and chlorite (ions and salts) are strong oxidizers and will not bioconcentrate or biomagnify in plants, aquatic organisms, or animals.

**Exposure Levels in Environmental Media.** Chlorine dioxide and chlorite (ions and salts) are strong oxidizers and react quickly in air, water, soil, plant material, and foodstuffs. No environmental monitoring studies are available. The general population may be exposed to chlorine dioxide and chlorite (ions and salts) by the ingestion of drinking water. As part of the ICR, 5.1% of the water-treatment facilities serving more than 100,000 people in the United States reported that chlorine dioxide was used in 1995 (Hoehn et al. 2000). Using the maximum contaminant level (EPA 2002e) for chlorine dioxide and

## 6. POTENTIAL FOR HUMAN EXPOSURE

chlorite, exposure from drinking water for these populations would be 1.6 and 2.0 mg/day, respectively. Additional monitoring data are needed for populations exposed to chlorine dioxide and chlorite (ions and salts) from drinking water. Reliable monitoring data for the levels of chlorine dioxide and chlorite (ions and salts) in contaminated media at hazardous waste sites are needed so that the information obtained on levels chlorine dioxide and chlorite (ions and salts) in the environment can be used in combination with the known body burden of chlorine dioxide and chlorite (ions and salts) to assess the potential risk of adverse health effects in populations living in the vicinity of hazardous waste sites.

**Exposure Levels in Humans.** Chlorine dioxide and chlorite (ions and salts) are strong oxidizers and react quickly in water or moist body tissues to form chloride ions. Consequently, chlorine dioxide and chlorite (ions and salts) are not detected in human tissues (e.g., blood, urine, fat, or breast milk). Biological monitoring studies are not available for these compounds near hazardous waste sites. This information is necessary for assessing the need to conduct health studies on these populations.

**Exposures of Children.** There are no unique exposure pathways for children. Children will be exposed to chlorine dioxide and chlorite (ions and salts) in the same manner as adults in the general population (i.e., ingestion of water). Studies focusing on the exposure of children to drinking waters containing chlorine dioxide and chlorite (ions and salts) would be useful. Additional information on whether children are different in their weight-adjusted intake of chlorine dioxide and chlorite (ions and salts) is needed. Data on childhood specific means to decrease exposure would also be useful. Chlorine dioxide and chlorite (ions and salts) are strong oxidizers and react quickly in water or moist body tissues to form chloride ions. Consequently, chlorine dioxide and chlorite (ions and salts) will not be detected in tissues of children (e.g., blood, urine, or fat).

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

**Exposure Registries.** No exposure registries for chlorine dioxide and chlorite (ions and salts) were located. These substances are not currently compounds for which a sub-registry has been established in the National Exposure Registry. These substances will be considered in the future when chemical selections are 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**

The Federal Research in Progress (FEDRIP 2003) 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. A National Science Foundation study exploring the photochemistry of chlorine dioxide relevant to stratospheric ozone depletion is currently being conducted by Dr. Prezhdo at the University of Washington. No other studies on the environmental fate of chlorine dioxide or chlorite (ions and salts) are reported to be currently in progress (FEDRIP 2003).