

## 6. POTENTIAL FOR HUMAN EXPOSURE

### 6.1 OVERVIEW

Chlorine dioxide and chlorite have not been identified in any of the 1,613 hazardous waste sites that have been proposed for inclusion on the EPA NPL (HazDat 2002). 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 2002g, 2002e).

### 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 1,021,346 pounds (463,275 kg) of chlorine dioxide was released to the environment in 2000 (TRI00 2002). 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 743,015 pounds (337,026 kg) of chlorine dioxide to the atmosphere from over 100 manufacturing, processing, and waste disposal facilities in 2000 accounted for about 72.7% of the estimated total environmental releases (TRI00 2002). These releases are summarized in Table 6-1. The

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



\*No data are available in HazDat 2002

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

| State <sup>b</sup> | Number of facilities | Reported amounts released in pounds per year <sup>a</sup> |         |                       |         |                                    |                                     | Total on and off-site release |
|--------------------|----------------------|---|---------|-----------------------|---------|------------------------------------|-------------------------------------|-------------------------------|
|                    |                      | Air <sup>c</sup>  | Water   | Underground injection | Land    | Total on-site release <sup>d</sup> | Total off-site release <sup>e</sup> |                               |
| AL                 | 9                    | 143,834   | 0       | No data               | 0       | 143,834                            | No data                             | 143,834                       |
| AR                 | 4                    | 17,839  | 0       | No data               | 0       | 17,839                             | No data                             | 17,839                        |
| CA                 | 1                    | 6,014   | 0       | No data               | No data | 6,014                              | 0                                   | 6,014                         |
| CO                 | 2                    | 3,955   | No data | No data               | No data | 3,955                              | No data                             | 3,955                         |
| FL                 | 8                    | 53,932  | 584     | No data               | 0       | 54,516                             | No data                             | 54,516                        |
| GA                 | 9                    | 6,789   | 0       | No data               | 0       | 6,789                              | No data                             | 6,789                         |
| ID                 | 2                    | 6,145   | No data | No data               | No data | 6,145                              | No data                             | 6,145                         |
| IL                 | 1                    | 12,545  | No data | No data               | No data | 12,545                             | No data                             | 12,545                        |
| KY                 | 3                    | 4,625   | 277,747 | No data               | 0       | 282,372                            | No data                             | 282,372                       |
| LA                 | 4                    | 33,265  | 0       | No data               | 0       | 33,265                             | No data                             | 33,265                        |
| MA                 | 1                    | No data   | No data | No data               | No data | No data                            | No data                             | 0                             |
| MD                 | 1                    | 185   | No data | No data               | No data | 185                                | No data                             | 185                           |
| ME                 | 6                    | 6,972   | 0       | No data               | 0       | 6,972                              | No data                             | 6,972                         |
| MI                 | 3                    | 21,204  | 0       | No data               | 0       | 21,204                             | No data                             | 21,204                        |
| MN                 | 2                    | 28,952  | 0       | No data               | No data | 28,952                             | 0                                   | 28,952                        |
| MS                 | 4                    | 39,696  | No data | No data               | No data | 39,696                             | No data                             | 39,696                        |
| NC                 | 6                    | 149,255   | 0       | No data               | No data | 149,255                            | No data                             | 149,255                       |
| NH                 | 1                    | 51  | 0       | No data               | No data | 51                                 | No data                             | 51                            |
| NY                 | 2                    | 12,010  | 0       | No data               | No data | 12,010                             | 0                                   | 12,010                        |
| OH                 | 2                    | 25,007  | 0       | No data               | No data | 25,007                             | 0                                   | 25,007                        |
| OR                 | 3                    | 5,930   | No data | No data               | 0       | 5,930                              | No data                             | 5,930                         |
| PA                 | 6                    | 36,606  | 0       | No data               | 0       | 36,606                             | No data                             | 36,606                        |
| SC                 | 5                    | 71,699  | 0       | No data               | No data | 71,699                             | No data                             | 71,699                        |

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

| State <sup>b</sup> | Number of facilities | Reported amounts released in pounds per year <sup>a</sup> |         |                       |         |                                    |                                     | Total on and off-site release |
|--------------------|----------------------|---|---------|-----------------------|---------|------------------------------------|-------------------------------------|-------------------------------|
|                    |                      | Air <sup>c</sup>  | Water   | Underground injection | Land    | Total on-site release <sup>d</sup> | Total off-site release <sup>e</sup> |                               |
| TN                 | 2                    | 12,944  | No data | No data               | No data | 12,944                             | No data                             | 12,944                        |
| TX                 | 3                    | 9,542   | 0       | No data               | 0       | 9,542                              | No data                             | 9,542                         |
| VA                 | 3                    | 14,429  | 0       | No data               | 0       | 14,429                             | No data                             | 14,429                        |
| WA                 | 8                    | 8,335   | 0       | No data               | No data | 8,335                              | No data                             | 8,335                         |
| WI                 | 3                    | 11,255  | No data | No data               | No data | 11,255                             | No data                             | 11,255                        |
| Total              | 104                  | 743,015   | 278,331 | No data               | 0       | 1,021,346                          | 0                                   | 1,021,346                     |

Source: TRI00 2002

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

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

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

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

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

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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 278,331 pounds (126,249 kg) of chlorine dioxide to water from three domestic manufacturing and processing facilities in 2000 accounted for about 27.3% of the estimated total environmental releases (TRI00 2002). No releases (0 pounds) of chlorine dioxide occurred via underground injection (TRI00 2002). 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.

Chlorate and chlorite ions are disinfection by-products (DBPs) from water treatment using chlorine dioxide. Table 6-2 contains data 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. In all water treatment plants, water taken from the distribution system (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 µg/L for chlorite and chlorate, respectively (Bolyard et al. 1993).

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

In 2000, 0 pounds of chlorine dioxide were released to land from one manufacturing facility reporting releases of the compound to the environment (TRI00 2002). 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.

**Table 6-2. Occurrence of Chlorite and Chlorate Ions in Finished Water From Utilities That Use Chlorine Dioxide**

| Site number | Date sampled | Type of source         | Source-water quality |     |                   | Chlorine dioxide dose (estimated) (mg/L) | Free chlorine Residual <sup>a</sup> (mg/L) | Plant Finish Water concentration <sup>b</sup> (µg/L) |          |
|-------------|--------------|------------------------|----------------------|-----|-------------------|--|--|--|----------|
|             |              |                        | Turbidity            | pH  | Alkalinity (mg/L) |  |  | Chlorite   | Chlorate |
| 37          | 9/90         | Stream                 | 19                   | 7.0 | 33                | 2  | NA   | 580  | 110      |
| 37          | 9/91         | Stream                 | 6                    | 6.9 | 31                | 1  | 2.4  | 740  | 140      |
| 44          | 8/91         | Reservoir <sup>c</sup> | 3.4                  | 7.2 | 39                | 0.1–0.2                                  | NA   | 15   | 330      |
| 62          | 8/91         | Stream <sup>c</sup>    | 15                   | 7.7 | 84                | 1  | 3.1  | 170  | 310      |
| 80          | 9/91         | Mixed <sup>c</sup>     | 27                   | 7.8 | 196               | 0.07                                     | 1.8  | 52   | 21       |

Source: Bolyard et al. 1993

<sup>a</sup>Free residual chlorine concentration leaving the treatment plant as finished water.

<sup>b</sup>The samples were assumed to have no detectable chlorine dioxide residual on the basis of information from utility personnel. All samples contained 50 mg EDA/L as a preservative.

<sup>c</sup>Source water was analyzed for chlorite and chlorate, and none was detected above the 10 µg/L reporting limit.

EDA = ethylenediamine; NA = not analyzed

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

### 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 dissolved gas. However, chlorine dioxide can be easily driven out of aqueous solutions with a strong stream of air. The partition coefficient between water and  $\text{ClO}_{2(g)}$  is about 21.5 at 35 EC and 70.0 at 0 EC (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 may be mobile in soils and leach into groundwater. However, chlorite (ions or 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

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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-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. It also decomposes rapidly to chlorine and oxygen with exposure to mild heat. 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 6-3 lists the various chlorine species that might be present in solutions of chlorine dioxide (Gordon 2001).

Chlorine dioxide does not hydrolyze to any appreciable extent between pH 2 and 10 but remains in solution. Dilute neutral or acidic aqueous solutions are stable if kept cool, well sealed, and protected from sunlight. In the absence of oxidizable substances and in the presence of hydroxide 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).

Chlorine dioxide has a positive chlorine oxidation state of four (+4), which is intermediate between chlorite (+3) and chlorate (+5) ions. Oxidation of chlorine dioxide usually results in the formation of chlorite ions (e.g.,  $\text{ClO}_2 + \text{e}^- \rightarrow \text{ClO}_2^-$ ;  $E^{\text{pH}=7} = 0.95$  volts). Chlorite ions ( $\text{ClO}_2^-$ ) are also effective oxidizing

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**Table 6-3. 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      | $\text{Cl}^-$    |

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agents, although they react much slower than chlorine dioxide. The oxidation of chlorite results in the formation of chloride ions (e.g.,  $\text{ClO}_2^- + 4\text{H}^+ + 4\text{e}^- \rightarrow \text{Cl}^- + 2\text{H}_2\text{O}$ ;  $E^{\text{pH}=7}=0.37$  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 (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 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, trihalo-methanes (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 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 alkenes 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 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). At a waste water treatment pilot plant in Evansville, Indiana, which used chlorine dioxide as a primary disinfectant, more than 40 different organic DBPs were identified at very low concentrations. Ten of these DBPs are regulated chemicals by EPA. Some of the compounds identified were maleic anhydrides and halopropanones (Richardson et al. 1994). Chlorine dioxide will not react with ammonia

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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  $\text{ClO}_4$  and  $\text{O}_4$ . The initial photodissociation reaction is followed by rapid dark and light reactions to produce the products, 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).

### 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 or salts) in sediment and soils. However, chlorine dioxide and chlorite ions should degrade rapidly in soil in an analogous manner to the reactions described in water (see Section 6.3.2.2).

### 6.3.2.4 Other Media

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

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**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 from 19 countries. The concentration of chlorine dioxide was measured in the following work areas: steam and power generation (range, <0.001–0.06 ppm); effluent water treatment (range, not detected to 0.003 ppm); 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 <0.01 ppm 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 <0.01 to 0.3 ppm (Kennedy et al. 1991).

Chlorine dioxide-treated drinking water has been attributed to the formation of offensive odors in indoor air, such as “kerosene-like” and “cat-urine-like” odors. This has been ascribed to over-dosing drinking water with residual chlorine dioxide, which is used as a postdisinfectant to prevent microbial growth in water distribution systems. 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 (Hoehn et al. 1990).

No other information was located in the literature on the concentrations of chlorine dioxide or chlorite (ions or 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

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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 water sampled from the distribution system versus the percentage of publically owned treatment works (POTW) facilities in the United States 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).

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

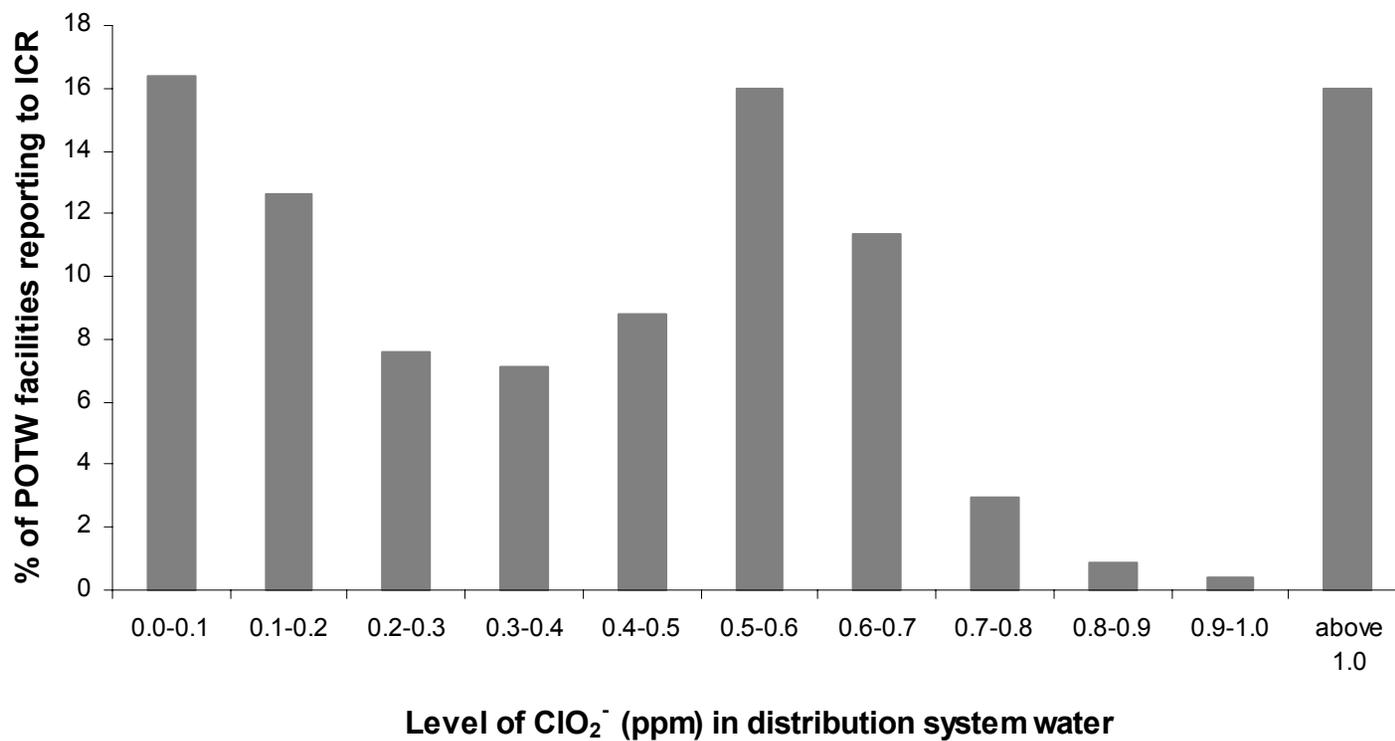
#### **6.4.3 Sediment and Soil**

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

#### **6.4.4 Other Environmental Media**

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

**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

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## 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 these communities 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 or salts) will not be 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, <0.001–0.06 ppm); effluent water treatment (range, not detected to 0.003 ppm); 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 <0.01 ppm 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 <0.01 to 0.3 ppm (Kennedy et al. 1991).

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**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 or 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 or salts). Other sources of exposure to chlorine dioxide and chlorite (ions or salts) will not be significant. Chlorine dioxide and chlorite (ions or salts) are reactive chemicals and will not be found in amniotic fluid, meconium, neonatal blood, or breast milk.

**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 or 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 is available. Where adequate information is not available, ATSDR, in conjunction with the National Toxicology Program (NTP), is required to

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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.

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 (see Section 4.2).

**Production, Import/Export, Use, Release, and Disposal.** Data regarding the production, import/export, and use of chlorine dioxide and chlorite (ions or salts) are available (see Sections 5.1–5.3), but are limited. Additional information on the facilities (e.g., water treatment) and industries that use chlorine dioxide and chlorite (ions or salts), the production amounts, and disposal methods are needed.

**Environmental Fate.** Little experimental data on the residence time and half-life of chlorine dioxide and chlorite (ions or salts) in the atmosphere are available. Additional information on the transport of chlorine dioxide in the atmosphere may be useful, considering that over 900,000 pounds are released annually to air (TRI00 2002). Additional information about the mechanism of reformation of chlorine dioxide in water distribution systems from chlorite ion is needed (Hoehn et al. 1990). Additional information concerning the transport and partitioning of chlorite (ions or salts) is also needed.

**Bioavailability from Environmental Media.** Chlorine dioxide and chlorite (ions or 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 or salts) is needed.

**Food Chain Bioaccumulation.** Chlorine dioxide and chlorite (ions and salts) are strong oxidizers and will not bioaccumulate.

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**Exposure Levels in Environmental Media.** No data are available in the literature for the exposure levels of flora and fauna to chlorine dioxide or chlorite (ions or salts). Additional information on the exposure of flora and fauna to chlorine dioxide and chlorite may be useful.

**Exposure Levels in Humans.** Ingestion of water is the primary route of exposure to chlorine dioxide and chlorite ions by the general population. Only limited information is available. Additional information about the levels of chlorite ion in tap water and other human exposure sources is needed.

**Exposures of Children.** Children will be exposed to chlorine dioxide and chlorite ions in the same manner as adults in the general population (i.e., ingestion of water). Additional information about possible differences in exposure pathways for children versus adults would be useful.

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

**Exposure Registries.** No exposure registries exist for chlorine dioxide and chlorite.

### 6.8.2 Ongoing Studies

The Federal Research in Progress (FEDRIP 2002) 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. No ongoing studies on the environmental fate of chlorine dioxide or chlorite (ions or salts) are currently in progress (FEDRIP 2002).