

## 6. POTENTIAL FOR HUMAN EXPOSURE

### 6.1 OVERVIEW

Although it has multiple uses and is released to the environment, chlorine is too reactive to be identified in any of the 1,704 hazardous waste sites that have been proposed for inclusion on the EPA National Priorities List (NPL) (HazDat 2007).

Chlorine may be released into the environment during accidents such as a chlorine gas leak from an industrial facility or a chlorine tank spill or rupture. Low concentrations of chlorine gas (<600 ppt) appear to be produced by the photolysis of seawater aerosol. Chlorine gas injected into the water during water chlorination quickly dissolves and forms chloride and hypochlorous acid within seconds. Liquid chlorine in a ruptured tank or spilled onto the ground or into water during an accident is expected to volatilize rapidly, forming a greenish-yellow cloud of chlorine gas. This gas cloud can be carried several miles away from the source of release while maintaining dangerous levels of chlorine.

Since chlorine gas is so reactive, it is not expected to remain in the environment very long after it is released. Chlorine immediately reacts with both organic and inorganic materials that it comes into contact with. As mentioned above, it is converted within seconds once it dissolves in water. Chlorine undergoes direct photolysis in the air and its half-life in the troposphere is on the order of several minutes. Chlorine levels in the ambient atmosphere, water, soil, or sediment are not available.

Exposure of the general population to chlorine gas is not expected except in the case of an accidental spill or industrial mishap. There have been several documented incidents in which large amounts of chlorine gas have been released, thereby exposing workers and the members of the general population following the derailment of trains carrying liquefied chlorine gas (Agency for Toxic Substances and Disease Registry 1998; NTSB 1998, 2005, 2006). Other accidental exposures may occur when individuals mix acidic household chemicals with bleach or pool sanitizing agents (see Section 6.3.2.2). Occupational exposure to low levels of chlorine gas may occur for individuals who work at facilities where it is produced or used. These individuals may be exposed to higher levels if an accidental release occurs within the facility. Children are expected to be affected by the same routes of exposure as adults, except for occupational exposure.

The general public is not exposed to molecular chlorine in drinking water as a result of water sanitation practices, even though chlorine gas may be used in these processes. Free chlorine in drinking water is

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defined as the sum of dissolved chlorine gas, hypochlorous acid, and hypochlorite anion. As discussed in Chapter 4 and in Section 6.3.2.2, the level of dissolved chlorine in water is very low, except under acidic conditions. As a consequence, the term free chlorine in public water systems or swimming pools usually refers to the concentration of hypochlorous acid and hypochlorite anion (APHA 1998a, 1998b).

## 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 2005). 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 2005).

### 6.2.1 Air

Estimated releases of 5,050,000 pounds (2,290 metric tons) of chlorine to the atmosphere from 915 domestic manufacturing and processing facilities in 2006, accounted for about 88% of the estimated total environmental releases from facilities required to report to the TRI (TRI06 2008). These releases are summarized in Table 6-1.

Chlorine may be released into the air in fugitive emissions from industrial facilities where it is produced or used. It may also be released into the air as a result of a spill or tank rupture (Henry et al. 2005; Horton et al. 2002). Between January 1993 and December 2000, 952 chlorine-related events (865 involved chlorine only) were reported to the ATSDR's Hazardous Substances Emergency Events Surveillance system (Horton et al. 2002). Of the 865 chlorine-only events, 592 (68.4%) involved air emissions. Of the 564 events for which release amount information was available in pounds, 511 events involved releases of  $\leq 250$  pounds. Examples of some recent large scale accidents involving the release of chlorine gas follow.

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**Table 6-1. Releases to the Environment from Facilities that Produce, Process, or Use Chlorine<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
AK	2	0	No data	0	0	0	0	0	0
AL	39	43,765	1,208	0	0	0	44,973	0	44,973
AR	23	54,016	637	0	0	0	54,653	0	54,653
AZ	10	668	250	0	517	0	1,435	0	1,435
CA	28	3,192	0	0	8,100	0	11,292	0	11,292
CO	9	45,635	0	0	0	0	45,635	0	45,635
CT	4	972	816	0	0	0	1,788	0	1,788
DC	2	1,008	0	0	0	0	1,008	0	1,008
DE	5	4,662	No data	0	0	0	4,662	0	4,662
FL	34	5,749	22	0	27,734	0	18,055	15,450	33,505
GA	34	5,332	2,702	0	0	0	8,034	0	8,034
HI	1	5	No data	0	0	0	5	0	5
IA	16	12,873	16,825	0	1,620	0	31,318	0	31,318
ID	6	8,965	250	0	5	0	9,215	5	9,220
IL	31	186,356	121,209	0	0	0	307,565	0	307,565
IN	34	77,356	1,501	0	278	0	78,862	273	79,135
KS	10	2,681	0	146,240	0	0	148,921	0	148,921
KY	21	78,635	490	0	0	0	79,125	0	79,125
LA	63	179,943	13,056	0	269	72	192,999	341	193,340
MA	5	385	No data	0	0	0	385	0	385
MD	9	781	0	0	0	0	781	0	781
ME	5	1,510	0	0	0	0	1,510	0	1,510
MI	26	30,950	679	0	0	0	31,628	0	31,628
MN	16	12,165	0	0	0	0	12,165	0	12,165
MO	20	15,545	1,157	0	0	0	16,702	0	16,702
MS	18	61,839	676	0	0	0	62,515	0	62,515
NC	23	121,870	12,308	0	8	0	134,186	0	134,186
ND	4	715	0	0	0	0	715	0	715
NE	9	2,126	220	0	0	0	2,346	0	2,346
NH	2	11	0	0	0	0	11	0	11
NJ	12	8,251	6,431	0	0	0	14,682	0	14,682
NM	6	3,133	No data	3,166	0	109	6,299	109	6,408
NV	9	5,246	No data	0	252,035	0	257,281	0	257,281
NY	23	61,884	1,209	0	0	694	63,093	694	63,787
OH	42	51,278	1,206	0	0	7	52,484	7	52,491

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		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
OK	12	1,448	250	0	0	0	1,698	0	1,698
OR	10	10,744	301	0	0	0	11,045	0	11,045
PA	31	68,834	2,919	0	0	0	71,753	0	71,753
PR	7	3,644	No data	0	0	0	3,644	0	3,644
RI	3	1,796	No data	0	0	0	1,796	0	1,796
SC	18	12,836	23	0	0	0	12,859	0	12,859
SD	2	0	186	0	144	0	330	0	330
TN	26	138,054	0	0	0	0	138,054	0	138,054
TX	116	242,531	31,610	13,908	160	0	288,209	0	288,209
UT	6	3,330,619	0	0	0	0	3,330,619	0	3,330,619
VA	25	31,766	11,173	0	0	0	42,939	0	42,939
VT	1	0	No data	0	0	0	0	0	0
WA	18	2,268	17,006	0	5	0	19,279	0	19,279
WI	21	40,691	3,540	0	14	0	44,245	0	44,245
WV	14	17,997	4,000	0	0	0	21,997	0	21,997
WY	4	57,019	0	0	114	0	57,133	0	57,133
<b>Total</b>	<b>915</b>	<b>5,049,751</b>	<b>253,859</b>	<b>163,314</b>	<b>291,003</b>	<b>882</b>	<b>5,741,931</b>	<b>16,879</b>	<b>5,758,810</b>

<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: TRI06 2008 (Data are from 2006)

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A freight train derailment, which took place on April 11, 1996, 2 miles west of Alberton, Montana resulted in a spill releasing 64.8 tons of chlorine into the environment (Agency for Toxic Substances and Disease Registry 1998; NTSB 1998). On January 6, 2005, a train carrying sodium hydroxide, cresol, and liquefied chlorine collided with another train in Graniteville, South Carolina releasing approximately 120,000 pounds of chlorine gas to the surrounding atmosphere (NTSB 2005). On June 28, 2004, a westbound Union Pacific Railroad freight train collided with an eastbound freight train in Macdona, Texas (NTSB 2006). Consequently, a tank car carrying 180,000 pounds of liquefied chlorine was punctured, releasing a cloud of chlorine gas to the immediate area (NTSB 2006). An accident involving a broken cargo transfer pipe at the ATOFINA Chemicals plant in Riverview, Michigan, resulted in the release of flammable methyl mercaptan gas (NTSB 2002). A subsequent fire resulted in damage to an adjacent tank car loaded with chlorine. It was estimated that approximately 26,500 of the 178,560 pounds of chlorine in the tank car were released in this incident, which occurred in July 2001 (NTSB 2002).

Chlorine appears to be generated in very low concentrations by the photolysis of seawater aerosols above seawater (California Environmental Protection Agency 2002; Chang et al. 2004; Knipping and Dabdub 2003).

Based on its instability and reactivity, it is not expected to be identified in air at any of the 1,704 hazardous waste sites that have been proposed for inclusion on the EPA National Priorities List (NPL) (HazDat 2007).

### 6.2.2 Water

Estimated releases of 254,000 pounds (115 metric tons) of chlorine to surface water from 915 domestic manufacturing and processing facilities in 2006, accounted for about 4% of the estimated total environmental releases from facilities required to report to the TRI (TRI06 2008). These releases are summarized in Table 6-1.

Activities at industrial facilities where chlorine is produced or used may result in its unintentional release to surface water. Chlorine may also be released into water as a result of a spill or tank rupture. Chlorine gas is injected directly into water during certain disinfection processes; however, these processes take place under controlled conditions within treatment facilities to prevent the release of chlorine into the environment (Das 2002; Tchobanoglous and Schroeder 1985). Furthermore, the chlorine gas is

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immediately converted into hypochlorous acid, chloride ion, and hypochlorite as soon as it enters the water. Chlorine may be formed in waters containing hypochlorite if the pH is lowered to levels below 4 (Farr et al. 2003).

Chlorine is too reactive to be identified in surface water or groundwater at any of the 1,704 hazardous waste sites that have been proposed for inclusion on the EPA National Priorities List (NPL) (HazDat 2007).

### 6.2.3 Soil

Estimated releases of 291,000 pounds (132 metric tons) of chlorine to soils from 915 domestic manufacturing and processing facilities in 2006, accounted for about 5% of the estimated total environmental releases from facilities required to report to the TRI (TRI06 2008). An additional 163,000 pounds (74 metric tons), constituting about 3% of the total environmental emissions, were released via underground injection (TRI06 2008). These releases are summarized in Table 6-1.

Activities at industrial facilities where chlorine is produced or used may result in its release to soil. Chlorine may also be released onto soil as a result of a spill. Of the 865 chlorine-only events reported to the ATSDR's Hazardous Substances Emergency Events Surveillance system between January 1993 and December 2000, 134 (15.5%) involved spills (Horton et al. 2002).

Chlorine is too reactive to be identified in soil or sediment at any of the 1,704 hazardous waste sites that have been proposed for inclusion on the EPA National Priorities List (NPL) (HazDat 2007).

## 6.3 ENVIRONMENTAL FATE

### 6.3.1 Transport and Partitioning

The boiling point of chlorine is  $-34.04\text{ }^{\circ}\text{C}$ ; therefore, chlorine is a gas under environmental conditions (HSDB 2009). Chlorine gas dissolves in water (7.3 g/L at  $20\text{ }^{\circ}\text{C}$ ) and is immediately converted to hypochlorous acid and chloride ion at environmental pH. However, this conversion is hindered under very acidic conditions ( $\text{pH}<4$ ). Molecular chlorine in water at this low pH is expected to volatilize rapidly based on a Henry's law constant of  $1.17 \times 10^{-2}\text{ atm}\cdot\text{m}^3/\text{mol}$  (Staudinger and Roberts 1996).

Chlorine is not expected to bioaccumulate in plants or animals since it reacts with the moist tissues of living systems (Compton 1987; Schreuder and Brewer 2001; Schmittinger et al. 2006). Schreuder and Brewer (2001) observed severe damage to the foliage of two conifer species exposed to a chlorine gas

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cloud released during an accidental spill. All buds on exposed trees located within 50 m of the release were killed.

If a large amount of liquid chlorine is released to a body of water, such as during a spill or an underwater release from a ruptured tank, some of the chlorine is expected to escape into the air before it can mix and react with the water. Similarly, when liquid chlorine is spilled onto the ground or when a tank containing liquid chlorine is ruptured, much of the chlorine will volatilize rapidly into the air creating a greenish-yellow cloud of chlorine gas (Agency for Toxic Substances and Disease Registry 1998; DOE 2005b). Since chlorine gas is heavier than air, a chlorine gas cloud will remain low to the ground. Movement and dissipation of the gas cloud is determined by such factors as the release volume, type of release, terrain, topography, temperature, humidity, atmospheric stability, and wind speed and direction (DOE 2005b; U.S. Chemical Safety and Hazard Investigation Board 2003).

Analysis of the chlorine gas cloud released during the 2005 Graniteville, South Carolina train derailment indicates that the dense cloud was initially driven southwest by gravity toward lower elevation, but was later dispersed by the wind toward the north and northeast as the boundary layer of the plume grew and as the gas began to mix with the surrounding air (DOE 2005a, 2005b). Wenck et al. (2007) reported that there were approximately 40 severe outcomes ( $\geq 3$  nights of hospitalization and 9 deaths) and approximately 120 less severe outcomes ( $\leq 2$  nights hospitalization) that occurred within a half-mile radius of the incident (Wenck et al. 2007). According to these authors, only a few less severe outcomes occurred between a half-mile and three-quarters of a mile from incident.

Movement of chlorine through soil is not expected to be relevant since chlorine will react and volatilize so quickly when spilled onto the ground (Agency for Toxic Substances and Disease Registry 1998; Schulte 1999).

### **6.3.2 Transformation and Degradation**

#### **6.3.2.1 Air**

The primary removal mechanism for chlorine in air is direct photolysis (EPA 1993; Graedel 1978; Graedel et al. 1986). Sunlight at tropospheric wavelengths ( $< 430$  nm) breaks apart the chlorine molecule to form two chlorine radicals. These radicals then react with any available organic molecule to form hydrochloric acid. The mean atmospheric lifetime of chlorine has been reported as 440 seconds (the atmospheric half-life can be approximated by multiplying the lifetime by the natural logarithm of 2)

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(Graedel 1978). A tropospheric lifetime of <15 minutes was calculated by Tanaka et al. (2003) under smog conditions in Houston, Texas. The rate of direct photolysis for any chemical species is dependent upon the intensity of sunlight, and therefore, factors such as time of year, geographic location, and time of day affect the photolysis rate. Hov (1985) discussed the diurnal variation of the photolysis rate of chlorine in an analysis of the effect that atmospheric chlorine had on the formation of various photochemical oxidants in southern Telemark, Norway. It was generally concluded that the photodissociation rate is rapid under both winter and summer sunlight conditions. Using absorption cross section data for chlorine at 330 nm, a maximum photodissociation rate constant of approximately  $1.6 \times 10^{-3} \text{ second}^{-1}$  was calculated for midsummer, midday sunlight conditions. This corresponds to a tropospheric half-life of approximately 7.2 minutes and a mean lifetime of slightly over 10 minutes. Using a photodissociation rate constant of approximately  $0.2 \times 10^{-3} \text{ second}^{-1}$  calculated for midday winter sunlight conditions, a half-life of 58 minutes is estimated.

Chlorine is also expected to react with cloud particulates and rain drops that it comes into contact with in the atmosphere, forming hydrochloric and hypochlorous acids (Vetrano 2001). These acids can then be washed out of the atmosphere by precipitation (Vetrano 2001).

### 6.3.2.2 Water

Water disinfection through chlorination has been in regular use since the early 1900s; consequently, the fate of chlorine in water has been well studied (Das 2002). Chlorine gas released into water first dissolves and then undergoes a disproportionation within seconds at environmental pH to form hydrochloric ( $\text{H}^+ + \text{Cl}^-$ ) and hypochlorous acid (HOCl) (Cotton et al. 1999; Das 2002; EPA 1999; Farr et al. 2003; Morris 1946; Snoeyink and Jenkins 1980; Tchobanoglous and Schroeder 1985; Wang and Margerum 1994). The equilibrium that exists between hypochlorous acid and the hypochlorite anion is controlled by the pH of the water. Since the  $\text{pK}_a$  of hypochlorous acid is 7.49 (O'Neil et al. 2001), the formation of the conjugate base (hypochlorite anion) is favored under alkaline conditions and the protonated species (hypochlorous acid) is favored under neutral and mildly acidic conditions. Under strongly acidic conditions ( $\text{pH} \leq 2$ ), the formation of molecular chlorine is possible (see Chapter 4).

As illustrated in Figure 4-1, the equilibrium between chlorine, hypochlorous acid, and hypochlorite acid is dependant on the pH of the solution (Farr et al. 2003). As the pH is lowered to 4, the equilibrium begins to shift to the left, and small amounts of  $\text{Cl}_2$  are present. At pH below 2, chlorine becomes the dominant species. Therefore, molecular chlorine will be formed in chlorinated water (containing hypochlorous



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acid) that has been made very acidic. Under these conditions, chlorine is expected to react rapidly with both organic and inorganic mater that it comes into contact with in the water; it is also expected to volatilize rapidly into the air based on a Henry's law constant of  $1.17 \times 10^{-2}$  atm-m<sup>3</sup>/mol (Staudinger and Roberts 1996). Chlorine is toxic to microbial communities; therefore, biodegradation is not considered to be a relevant fate process (Vetrano 2001). The hypochlorous acid formed during the disproportionation of chlorine in natural waters reacts with organic and inorganic materials, ultimately forming chloride, oxidized inorganics, chloramines, trihalomethanes, oxygen, and nitrogen (IARC 1991; Vetrano 2001).

**6.3.2.3 Sediment and Soil**

If liquid chlorine is spilled onto soil, it will react with both organic and inorganic mater in the soil; however, much of the chlorine is expected to volatilize immediately (Agency for Toxic Substances and Disease Registry 1998; Schulte 1999). Chlorine is expected to dissolve and disproportionate in the water of moist soils to form chloride and hypochlorite (Cotton et al. 1999). Chlorine in a gas cloud is expected to react with soil surfaces that it comes into contact with. Chlorine is toxic to microbial communities; therefore, biodegradation is not considered to be a relevant fate process (Vetrano 2001).

When released into water, chlorine is expected to react with suspended solids and sediments that it comes into contact with.

**6.3.2.4 Other Media**

Specific information on the transformation of chlorine in other media is not available; however, chlorine is very unstable and is expected to react with most substances that it comes into contact with.

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

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

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**6.4.1 Air**

Levels of chlorine monitored in the ambient atmosphere have not been located. Scientists have proposed that chlorine is generated during the photolysis of seawater aerosol (California Environmental Protection Agency 2002; Chang et al. 2004; Knipping and Dabdub 2003). According to California Environmental Protection Agency (2002), chlorine was detected in the air at a New York coastal site with a maximum concentration of 150 ppt. Chang et al. (2004) reported a maximum chlorine concentration of 580 ppt in air samples collected from coastal locations in Taiwan.

Little information is available regarding the levels of chlorine measured in air surrounding areas of accidental release. The concentrations of chlorine monitored in the air surrounding a chlorine release from a railroad tank car near Festus, Missouri were >1,000 ppm (U.S. Chemical Safety and Hazard Investigation Board 2003). Chlorine concentrations as high as 1,000 ppm were measured in the air at a train derailment chemical spill near Alberton, Montana that released chlorine gas in April 1996 (Agency for Toxic Substances and Disease Registry 1998).

**6.4.2 Water**

Levels of chlorine monitored in water are not available. Chlorine is not a predominant species in water at environmental pH since it disproportionates within seconds to form chloride anion and hypochlorous acid; therefore, chlorine is not expected to be detected in the aquatic environment (Das 2002; Morris 1946; Wang and Margerum 1994).

**6.4.3 Sediment and Soil**

Levels of chlorine monitored in sediment and soil are not available. Chlorine is not expected to be found in soil since it reacts and volatilizes so rapidly.

**6.4.4 Other Environmental Media**

Levels of chlorine monitored in food, animals, vegetation, and consumer products are not available. Chlorine is not expected to be found in these media because of its very high reactivity.

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**6.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE**

Chlorine is not normally detected in ambient air, soil, surface water, groundwater, or drinking water. Therefore, background exposure of the general population to chlorine is not expected. Greater than 95% of the chlorine that is inhaled (over a 1–5 ppm range) reacts in the upper respiratory tract (Nodelman and Ultman 1999a, 1999b; Winder 2001) and eventually joins the chloride pool in the body. Therefore, analysis of human biological materials such as blood, urine, and body tissue for chlorine is not considered relevant. The amount of chlorine that needs to be inhaled to induce a significant increase in extracellular chloride in the body is probably a lethal amount. Current procedures for gauging an individual's exposure to chlorine gas involve analysis of the lungs and respiratory airways for physical and functional damage (Lawson 1981; Winder 2001).

Members of the general population may be exposed to chlorine if they mix an acid with a solution containing sodium hypochlorite (CDC 1991). Examples include mixing toilet bowl cleaners containing hydrochloric, phosphoric, or oxalic acid with bleach (Becker and Forrester, 2008; CDC 1991; Gapany-Gapanavicius et al. 1982; Howard et al. 2007; Mrvos et al. 1993). If enough acid is added to lower the pH of the hypochlorite solution to below 4, chlorine gas will be released (Farr et al. 2003). Individuals may also be exposed to chlorine if swimming pool chemicals are accidentally mixed with acids or too much sodium hypochlorite is added to the water over a short period of time (Agabiti et al. 2001; Becker and Forrester 2008; Bonetto et al. 2006; Ngo et al. 2007; Sexton and Pronchik 1998). On October 22, 1998, hydrochloric acid accidentally spilled onto chlorinated swimming pool water at a recreational facility in Rome, Italy causing the liberation of chlorine gas to the entire center and exposing nearly 300 people to the gas (Agabiti et al. 2001). The exact amount of chlorine released in this accident was not reported. A similar accident occurred on February 17, 2004 in Parma, Italy in which 18 children were exposed to chlorine gas (Bonetto et al. 2006). In this case, the improper addition of an excessive amount of sodium hypochlorite was added to a chlorinated swimming pool to shock the system, resulting in the emission of chlorine gas.

Occupational exposure to low levels of chlorine gas in air may occur for individuals who work at facilities that produce, transport, or use chlorine (Gautrin et al. 1995). These individuals may also be exposed to high chlorine concentrations if an accidental release occurs at the facility (Beach et al. 1969; Chester et al. 1969; Gautrin et al. 1999; Kennedy et al. 1991; NTSB 2002, 2005, 2006; USB 2007).

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Of the 865 chlorine-only events reported to the ATSDR's Hazardous Substances Emergency Events Surveillance system between January 1993 and December 2000, 275 events involved victims (1,071 individuals) (Horton et al. 2002). Of these, 759 were occupational exposures and 68 were first responders.

### 6.6 EXPOSURES OF CHILDREN

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

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

As with adults, biomonitoring is not considered relevant for assessing childhood exposure to chlorine. Therefore, information on chlorine levels in blood, urine, tissue, breast milk, neonatal blood, cord blood, and meconium fluid is not available. Children may be exposed to chlorine through the same routes that affect adults, except for occupational exposures. Children located near an accidental release of chlorine such as a leak from a factory or a chlorine tank spill or rupture may be exposed to high concentrations of chlorine through inhalation, skin contact, or eye contact. Children may be exposed to high levels of chlorine if they are in an area where swimming pool chemicals are being improperly used or where certain household chemicals are mixed together. Mixing an acid, such as toilet cleaner, with bleach can generate chlorine gas if the pH of the bleach is lowered to below 4.

### 6.7 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

Individuals located near an accidental release of chlorine may be exposed to high concentrations of this gas through inhalation, skin contact, and eye contact if the cloud travels in their direction (Horton et al. 2002; Wenck et al. 2007). Individuals who live near industrial facilities where chlorine gas is produced or used may be exposed to high concentrations if there is an accidental release of a large amount of

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chlorine gas from the facility (USB 2007). Of the 865 chlorine-only events reported to ATSDR's Hazardous Substances Emergency Events Surveillance system between January 1993 and December 2000, 275 events involved victims (1,071 individuals) (Horton et al. 2002). Of these, 235 were members of the general public. A train derailment near Alberton, Montana on April 11, 1996 released approximately 130,000 pounds of chlorine gas to the atmosphere (NTSB 1998). According to the National Transportation Safety Board (NTSB), approximately 350 people were treated for chlorine inhalation. Nine people, including members of the train crew, were hospitalized. The NTSB reported that a transient riding the train died from acute chlorine toxicity (NTSB 1998). On January 6, 2005, a northbound Norfolk Southern Railway Company freight train traveling through Graniteville, South Carolina, encountered an improperly lined switch that diverted the train from the main track onto an industrial track, where it struck an unoccupied, parked train releasing approximately 120,000 pounds of chlorine gas from one of the cars of the northbound train (NTSB 2005). The train engineer and 8 other people died as a result of chlorine gas exposure and an additional 554 nearby residents were treated at local hospitals for respiratory illness as a result of this accident. On June 28, 2004 a westbound Union Pacific Railroad freight train collided with an eastbound freight train in Macdona, Texas (NTSB 2006). Consequently, a tank car loaded with liquefied chlorine was punctured, releasing a cloud of chlorine gas that surrounded the accident area. Three persons, including the conductor of the Union Pacific train and two local residents, died as a result of acute chlorine gas inhalation. The Union Pacific train engineer, 23 local residents, and 6 emergency responders were treated for respiratory illness or other injuries related to the collision and derailment.

### 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 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 chlorine.

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

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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 important chemical and physical properties for elemental chlorine are available (EPA 1999; HSDB 2009; Staudinger and Roberts 1996), as well as the important equilibrium constants describing the equilibrium reaction of chlorine in water (Cotton et al. 1999; Farr et al. 2003). No data need is identified 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 2005, became available in May of 2007. This database is updated yearly and should provide a list of industrial production facilities and emissions.

Current production and U.S. import/export volumes are available for chlorine (CMR 2006; HSDB 2009; ITA 2007; The Chlorine Institute 2008; U.S. Census Bureau 2008), as well as adequate disposal methods (HSDB 2009). No data need is identified at this time.

**Environmental Fate.** The environmental fate of chlorine is understood. Chlorine is extremely reactive and will not remain in environmental media for long periods of time. The important equilibrium properties of chlorine in water are understood (Cotton et al. 1999; Farr et al. 2003). Scientists have proposed that minute quantities of chlorine are generated naturally during the photolysis of seawater aerosols (California Environmental Protection Agency 2002; Chang et al. 2004; Knipping and Dabdub 2003). Sunlight at tropospheric wavelengths (<430 nm) dissociates the chlorine molecule to form two chlorine radicals; a lifetime of <15 minutes (half-life of <11 minutes) was calculated for this reaction (Tanaka et al. 2003). No data need is identified at this time.

**Bioavailability from Environmental Media.** Chlorine is too reactive to be bioavailable from soil, water, or other environmental media. No data need is identified at this time.

**Food Chain Bioaccumulation.** Chlorine is too reactive to bioaccumulate in the food chain. No data need is identified at this time.

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

Chlorine is too reactive to monitor for background levels in the environment. In the case of an accidental spill, levels >1,000 ppm have been observed in air around the accident site (U.S. Chemical Safety and Hazard Investigation Board 2003). Very low levels of chlorine (parts per trillion) are generated naturally during the photolysis of seawater aerosols (California Environmental Protection Agency 2002; Chang et al. 2004). No data need is identified at this time.

**Exposure Levels in Humans.** Humans can be exposed to chlorine following the accidental release at a manufacturing facility or an accident involving the transportation of liquefied chlorine gas (NTSB 1998, 2002, 2005, 2006); however, molecular chlorine levels in human tissues cannot be quantitatively assessed (see Chapter 7). In addition, people may be exposed to chlorine if they mix common household chemicals that are acidic with bleach or pool sanitizing chemicals (Agabiti et al. 2001; Bonetto et al. 2006). Continued monitoring of accidental chlorine releases and the health affects observed in humans is necessary.

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

**Exposures of Children.** Similar to adults, exposure of children to chlorine gas primarily occurs from accidental industrial or transportation releases (NTSB 1998, 2002, 2005, 2006), or the inadvertent mixing of common household chemicals with bleach or pool sanitizing chemicals, resulting in the liberation of chlorine (Agabiti et al. 2001; Bonetto et al. 2006). Continued monitoring of accidental chlorine releases and the health affects observed in children is necessary.

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 chlorine 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-

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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.

**6.8.2 Ongoing Studies**

Two ongoing studies have been located in the Federal Research in Progress Database (FEDRIP 2009) that will measure levels of chlorine in the marine atmosphere. These are listed in Table 6-2. No other ongoing studies regarding the potential for human exposure to chlorine were located.



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**Table 6-2. Ongoing Studies Regarding the Potential for Human Exposure to Chlorine**

Investigator	Affiliation	Research description	Sponsor
R. Talbot and A. Pszeny	University of New Hampshire	Study of reactive halogens in the marine boundary layer overlying the eastern tropical north Atlantic Ocean. This research will include measurement of inorganic chlorine gases.	National Science Foundation
E. Saltzman	University of California-Irvine	Study of the source, presence, and distribution of inorganic dihalogen gases in the marine atmosphere. This research will include measurement of chlorine gas in coastal and marine air.	National Science Foundation

Source: FEDRIP 2009