

## 6. POTENTIAL FOR HUMAN EXPOSURE

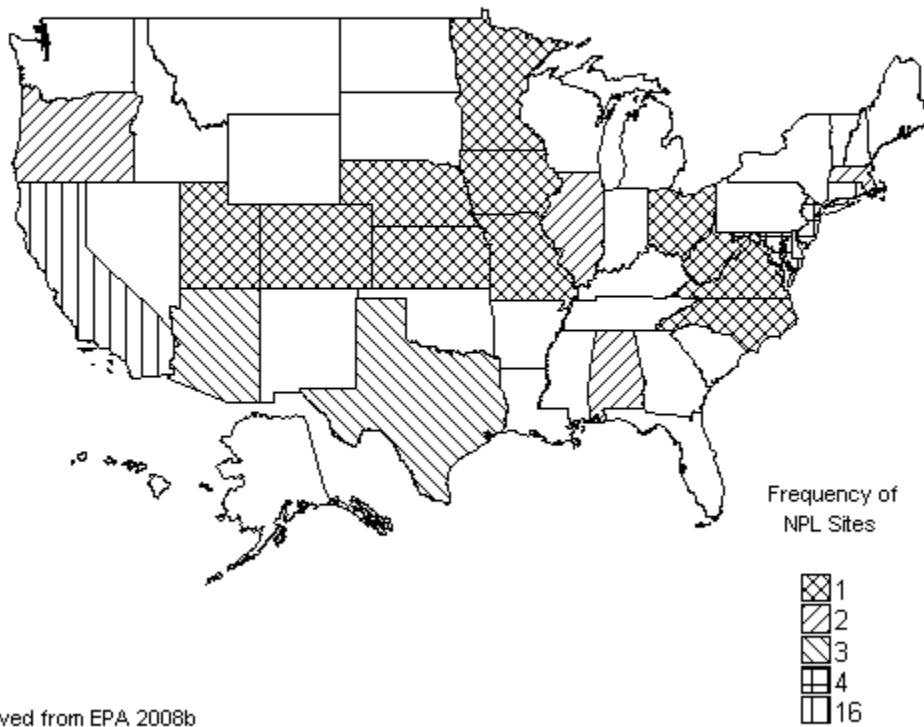
### 6.1 OVERVIEW

Perchlorates have been identified in at least 49 of the 1,581 hazardous waste sites that have been proposed for inclusion on the EPA National Priorities List (NPL) (EPA 2008b, 2008c). However, the number of sites evaluated for perchlorates is not known. The frequency of these sites can be seen in Figure 6-1.

Perchlorates are high melting inorganic salts that are soluble in water at environmentally significant concentrations. They are found in or released to the environment in two forms. In the absence of water, the perchlorate salts listed in Table 4-1 will be found (or released) as a solid. In water, perchlorates will rapidly dissolve and completely dissociate into the perchlorate anion and the corresponding cation (e.g., for potassium perchlorate, the corresponding cation would be  $K^+$ ). The cations of the perchlorates listed in Table 4-1, magnesium, potassium, ammonium, sodium, and lithium, are ubiquitous in the environment. Given that perchlorates completely dissociate at environmentally significant concentrations, their cations are, for all practical purposes, spectators in the aqueous fate of perchlorates. Therefore, the environmental fate of the perchlorate salts listed in Table 4-1 is dominated by the perchlorate anion.

Perchlorates are known to be highly reactive thermodynamically and therefore, they may react vigorously under the proper conditions. The activation energy of ammonium perchlorate is 123.8 kJ/mol below 240 °C, 79.1 kJ/mol above 240 °C, and 307.1 kJ/mol between 400 and 440 °C (Mendiratta et al. 1996). The decomposition of perchlorates is usually initiated using a high temperature source, such as a glow wire, to overcome the thermodynamic barrier. Once decomposition of some perchlorate molecules is initiated, the resulting reaction produces a large amount of heat. Between 200 and 300 °C, ammonium perchlorate undergoes an autocatalytic decomposition (Singh et al. 2000). At about 400 °C, ammonium perchlorate decomposes very fast and suddenly explodes. The reactivity is a function of the reaction pathway. Different reaction pathways for perchlorates would have different barriers than the thermal decomposition discussed above. Nevertheless, the existence of a large thermodynamic barrier for the decomposition of a reactive compound such as perchlorate is important in understanding its persistence in the environment.

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**Figure 6-1. Frequency of NPL Sites with Perchlorate Contamination**

Derived from EPA 2008b

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When the perchlorate anion is detected in water, it is not always possible to determine the perchlorate salt that represents the original source of the contamination. That is, potassium perchlorate may be the compound that was released to the environment, yet some other perchlorate salt, such as sodium perchlorate, may be the "charge neutral" species present in the analyzed sample. For ammonium perchlorate, this is of particular relevance as the ammonium ion biodegrades in the environment and, therefore, must be replaced with some other cation to maintain the overall neutrality of the solution. From a practical standpoint, however, the concentration of the perchlorate ion is the most important factor when determining the potential for adverse effects to the perchlorates. It is the perchlorate ion that is analyzed for in environmental samples.

In Chapter 5 of this profile, the uses of the perchlorates listed in Table 4-1 were provided. Many of these uses result from the high reactivity and strong oxidizing power of perchlorates. The environmental fate of perchlorate is also dominated by this reactivity, yet its persistence is much longer than might be expected for a strong oxidizing agent. This apparent discrepancy can, in part, be explained by differences in its high energy of activation.

When released to the environment, perchlorates are expected to be highly mobile in soil and to partition to surface water or groundwater. They are not expected to significantly adsorb to sediment or suspended organic matter. They are also expected to readily settle from the atmosphere by wet and dry deposition. No degradation process for perchlorates in the environment has been unambiguously established. Laboratory experiments suggest that they may be reduced by anaerobic microbes in soil and water, although the presence of sulfates and nitrates in the environment attenuates this process. Laboratory experiments also suggest that perchlorates may undergo uptake by some plants and may be subsequently reduced to chloride. Neither the types of plants that take up perchlorate nor the types capable of reducing it have been well categorized. The mechanism for uptake by plants has not been established.

The potential for contamination resulting from discharges at facilities that manufacture and use perchlorate was studied following the accidental fire and subsequent explosion at the PEPCON rocket fuel plant, located in Henderson, Nevada in May 1988 (Urbansky 1998). This plant was one of the principal manufacturing facilities for ammonium perchlorate in the United States. Perchlorate concentrations as high as 630,000  $\mu\text{g/L}$  were observed in nearby surface water samples following the accident (Urbansky 1998). Nearby groundwater samples were also contaminated with perchlorate at concentrations ranging from 51,400 to 630,000  $\mu\text{g/L}$ . Monitoring data from 50 wells obtained near the

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Kerr-McGee ammonium perchlorate producing facility, also located in Henderson, Nevada, had perchlorate levels as high as 3.7 g/L (Urbansky 1998). The EPA has published a list of federal and private facilities in the United States from 25 states with known perchlorate releases to environmental media such as surface water, groundwater, and soil (EPA 2003, 2005c).

Perchlorate can also be released to the environment from the use of other commodities such as safety flares and fireworks. For example, following a July 4<sup>th</sup> fireworks display near a small lake in Oklahoma, a maximum perchlorate concentration of 44.2 µg/L was measured in the lake (Wilkin et al. 2007). This maximum level was roughly 1,000 times greater than the mean perchlorate concentration (0.043 µg/L) that was observed in the lake prior to the fireworks display.

In addition to the potential anthropogenic sources of perchlorate discussed in Chapter 5 and the use of products for which perchlorate is found as an impurity, there are natural sources of perchlorate in the environment (Dasgupta et al. 2006; Rajagopalan et al. 2006). Traces of perchlorate found in rain and snow may be caused by a series of reactions that result in the formation of atmospheric perchlorate (Dasgupta et al. 2006). In addition, perchlorate has been detected in laboratory experiments upon passage of sodium chloride aerosols through an electrical discharge that simulates lightening. Kang et al. (2006) demonstrated that perchlorate can be generated as an end-product of chlorine precursors such as aqueous salt solutions of hypochlorite, chlorite, and chlorate, following exposure to UV radiation. Using perchlorate levels observed in rainfall samples and estimated rainfall rates in the United States, the rate of natural atmospheric perchlorate deposition was estimated to range from  $1.3 \times 10^5$  to  $6.4 \times 10^5$  kg per year (Dasgupta et al. 2006). Further evidence of natural sources of perchlorate is the widespread occurrence in the arid Southwestern United States in places where no anthropogenic sources of perchlorate exist (Dasgupta et al. 2006; Rajagopalan et al. 2006). Perchlorate was detected in groundwater from several counties located in western Texas and eastern New Mexico at relatively low concentrations ( $<4$  µg/L); however, some samples had levels of nearly 200 µg/L (Rajagopalan et al. 2006). The primary source of perchlorate in this area was postulated as deposition of naturally occurring atmospheric perchlorate.

Humans are primarily exposed to perchlorate through the ingestion of food items and also through the consumption of drinking water that contains perchlorate. Efforts are being made to determine the relative contribution of perchlorates from food and water. There are also consumer products that are widely available to the general population that also contain perchlorate. For example, household bleach has been shown to contain perchlorate, with concentrations ranging from 89 to 8,000 ppb (MassDEP 2006a). A correlation was observed between storage time of the bleach and higher levels of perchlorate. Perchlorate

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has also been detected in tobacco products (Ellington et al. 2001) and nutritional supplements (Snyder et al. 2006). General population and occupational exposure to perchlorate is discussed in greater detail in Section 6.5.

## 6.2 RELEASES TO THE ENVIRONMENT

### 6.2.1 Air

There is no information in the TRI database on releases of perchlorates to the atmosphere from manufacturing and processing facilities because these releases are not required to be reported (EPA 1997a).

The perchlorates listed in Table 4-1 are high melting inorganic salts that have very low vapor pressures. Therefore, solid perchlorates are not expected to directly volatilize to air as fugitive emissions during their manufacture, processing, transport, disposal, or use. Release to the air through volatilization from water is also not expected for perchlorates as dissociated inorganic ions are known to not be stripped from water (Bodek et al. 1988).

Solid perchlorate aerosols may be released to the atmosphere as fugitive emissions in dust-forming operations during manufacture, processing, and use. Gibbs et al. (1998) reported an occupational exposure investigation where they noted that dust was generated in an ammonium perchlorate production facility. Lamm et al. (1999) classified dust-forming manipulations at an ammonium perchlorate production facility as low for perchlorate solutions or slurries, moderate for limited quantities for dry perchlorates, and high when large quantities of dry perchlorates were used.

One documented major use of perchlorates is as a component of solid rocket boosters (Vogt et al. 1986). Solid rocket boosters rapidly release gases to provide propulsion through the atmosphere, and the release of unspent perchlorates may occur during this process. However, engineered design of rocket boosters target efficient and complete reaction of the perchlorate as a fundamental requirement to ensure successful launches. Studies on particulate emissions from propulsion systems have been performed (Hindman and Finnegan 1980), although it is not known if perchlorate was a targeted analyte. Perchlorates may be released to the environment from booster rockets during a catastrophic failure (Merrill and O'Drobinak 1998) or aborted flight. Following the Delta II flight failure that occurred at Cape Canaveral in January 1997, it was estimated that 200,000 pounds of perchlorate-containing hydroxyl-terminated polybutadiene (HTPB) solid propellant was released (Merrill and O'Drobinak 1998).

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Release of perchlorates to the atmosphere may also occur during open-burn decommissioning of rocket booster propellants or munitions (Chan et al. 2000). Emissions of regulated substances have been measured during tests of this disposal process (DOD 1995), although perchlorate was not one of the targeted analytes.

Perchlorates also find extensive use in fireworks and other pyrotechnic devices (Conkling 1996; Dasgupta et al. 2005; Lindner 1993; Schilt 1979). Release of unspent perchlorate may occur during the detonation of fireworks, flares, oxygen generators, flash-pots, smoke bombs, and other pyrotechnic devices, although very little information on the amounts, if any, was located in the available literature. Dasgupta et al. (2005) calculated an annual source strength of  $1.4 \times 10^5$  kg/year for perchlorate in road flares used in the United States, which is estimated as 1.4% of the production of total oxidizer perchlorate. These authors were not able to estimate perchlorate released from fireworks, since fireworks vary greatly in their type and composition. Release of perchlorate may also occur during catastrophic explosions at firework facilities (CSB 1999) or at facilities that manufacture other pyrotechnic devices based on this oxidant.

It has been postulated that perchlorate may be formed naturally in the atmosphere during photochemical transformation reactions involving chlorine precursors. Some possible mechanisms include the reaction of ClO radicals with sulfuric acid aerosols, electrical discharge through chloride aerosol, reaction of aqueous chloride with high concentrations of ozone, and direct photolysis of aqueous chlorite (Dasgupta et al. 2005; Jaegle et al. 1996; Kang et al. 2006). Accordingly, perchlorate may be produced in the atmosphere after volcanic eruptions. The authors suggest that perchlorate produced in volcanic eruptions similar to Mt. Pinatubo may represent a significant reservoir of chlorine in the lower stratosphere.

In an effort to locate the source of perchlorate contamination in the southern high plains desert in the Texas panhandle where there has been no known anthropogenic release of perchlorates nearby, Dasgupta et al. (2005) explored the possibility of perchlorate generation through atmospheric processes. The authors reported that perchlorate was formed during experiments where chloride aerosol was exposed to electrical discharge (lightning simulation) and where aqueous chloride was exposed to high amounts of ozone. Natural atmospheric perchlorate deposition was estimated to range from  $1.3 \times 10^5$  to  $6.4 \times 10^5$  kg per year in the United States (Dasgupta et al. 2006). However, additional testing is needed to determine whether these atmospheric processes are indeed natural pathways by which perchlorates enter the environment (Dasgupta et al. 2005; Erickson 2004; Renner 2005a).

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**6.2.2 Water**

There are no data in the TRI database on releases of perchlorates to the water from manufacturing and processing facilities because these releases are not required to be reported (EPA 1997a).

Perchlorates may be released to water in emissions from their manufacture, processing, or use. Waste water treatment processes used by POTWs and onsite treatment facilities, including stripping, precipitation, filtration, oxidation, or aerobic biodegradation, do not effectively remove perchlorates from waste streams (Urbansky 1998). Therefore, perchlorate in waste water may eventually be released to surface water.

EPA published a list of facilities from 25 states with perchlorate releases related to the manufacture, disposal, or research of explosives, propellants, or pyrotechnics (EPA 2003, 2005c). Maximum perchlorate concentrations observed in monitoring wells for several of these facilities exceeded 1,000 µg/L, with some observed concentrations in excess of 100,000 µg/L (EPA 2003, 2005c). Propellant removal during decommissioning or maintenance (reloading with new propellant) of solid rockets is known to have been accomplished using high pressure water sprays (Chan et al. 2000). The amount of ammonium perchlorate-laden washout from decommissioning rockets was expected to reach 8.5 million pounds in the first decade of the twenty-first century (Buckley et al. 1999), but since this estimate was made, significant changes in decommissioning and maintenance practices of rocket motors have substantially reduced the potential for future releases of perchlorate to the environment. According to the ITRC (2008), “There are times when rocket propellant must be removed from the rocket motor casing. To do so the rocket motor was taken to the ‘hog-out’ facility, where the propellant was removed using a water knife to avoid explosion hazards. The water containing ammonium perchlorate in both solid and dissolved forms was discharged to unlined and lined ponds (Aerojet Case Study)...Perchlorate is also found at areas where waste ammonium perchlorate rocket propellant was taken to be destroyed by burning and detonation (Aerojet Case Study)...Past management practices were not concerned with the release of perchlorate to the environment because it was not recognized or regarded as a contaminant of concern. Widespread perchlorate presence in the United States was observed after the spring of 1997 when an analytical method was developed with a quantitation level of 4 parts per billion. Subsequent advances in analytical chemistry have proven perchlorate to be more widespread in the environment than previously thought.”

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The catastrophic failure of a Delta II rocket in 1997 over the Atlantic Ocean resulted in unspent propellant falling into the ocean (Merrill and O'Drobinak 1998). Subsequent laboratory tests indicated that ammonium perchlorate will migrate from the propellant matrix to seawater. Similarly, perchlorates that have been released to the atmosphere may also enter environmental waters by deposition onto the surface of oceans, rivers, lakes, or ponds by either gravitational (dry settling) or wet (rain wash-out) processes.

Perchlorates may ultimately be released to surface water from the runoff from or erosion of perchlorate-laden sand or soil (Herman and Frankenberger 1998). The percolation of water through contaminated sand or soil is expected to bring perchlorate into underground aquifers; this is consistent with monitoring studies in wells sampled near known sites of its use (see Section 6.4.2). Runoff from perchlorate-laden soil is expected to lead to surface water contamination as determined by its detection in surface water samples down gradient from facilities that manufactured, maintained, decommissioned, or tested solid rocket boosters (Herman and Frankenberger 1998; Mendiratta et al. 1996; Urbansky 1998). The use of fireworks may also contaminate nearby water bodies. A small lake near Ada, Oklahoma had baseline perchlorate concentrations in surface water ranging from 0.005 to 0.081  $\mu\text{g/L}$ , with a mean value of 0.043  $\mu\text{g/L}$ . Following the release of a fireworks display (14 hours after the fireworks), perchlorate concentrations spiked to values ranging from 24 to 1,028 times the mean baseline value (Wilkin et al. 2007). A maximum perchlorate concentration of 44.2  $\mu\text{g/L}$  was determined following the July 4<sup>th</sup> event in 2006. After the fireworks displays, perchlorate concentrations decreased toward the background level within 20–80 days, with the rate of attenuation correlating to surface water temperature.

### 6.2.3 Soil

There are no data in the TRI database on releases of perchlorates to the soil from manufacturing and processing facilities because these releases are not required to be reported (EPA 1997a). As discussed in Section 6.2.2, facilities that manufactured, maintained, decommissioned, or tested solid rocket boosters likely released perchlorates to the environment. Their detection in groundwater wells at some of these sites (see Section 6.4.3) suggests that the initial release was to soil, and subsequent transport led to contamination of the aquifer. Information on the amount of perchlorate released to soil as a result of its manufacture, processing, and use in aerospace and military applications could not be located in the available literature.

The use of explosives that contain perchlorates in underground applications, such as mining (Vogt et al. 1986), may result in the release of unspent oxidant to soil. The amount of perchlorate used in explosives,



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the frequency of use in underground applications, and the amount of unspent oxidant released are not available.

Perchlorates that have been released to the atmosphere may be deposited directly on the Earth's surface by either dry or wet deposition processes. The catastrophic failure of a Delta II rocket was found to release unspent ammonium perchlorate propellant to land (Merrill and O'Drobinak 1998). Deposition of perchlorate to soil from the use of fireworks is also expected to be significant.

Perchlorate has been detected in fertilizers derived from Chilean caliche (Ellington et al. 2001; Urbansky et al. 2001). It was also detected in other fertilizer products (Susarla et al. 1999), although follow-up studies failed to detect perchlorate in the 40 products tested (Urbansky and Collette 2001). Fertilizer derived from Chilean saltpeter has been traditionally applied mainly to tobacco plants, but is also marketed for citrus fruits, cotton, and some vegetable crops (Urbansky et al. 2001). Perchlorate containing fertilizers would result in the contamination of soil as a direct result of their intended use. Using a perchlorate concentration of 0.2% and a total importation volume of  $2.4 \times 10^{10}$  kg of Chilean nitrate fertilizer (Dasgupta et al. 2006),  $4.8 \times 10^7$  kg of perchlorate may have been released directly to soil over the period from 1930 to 1993.

### 6.3 ENVIRONMENTAL FATE

Only a limited number of studies investigating the environmental fate of perchlorate were located in the peer-reviewed literature. Key aspects of its environmental fate have been assessed based on the analysis of physical and chemical properties, available monitoring data, and known sources of release. Although substantial research efforts are currently underway (see Section 6.8.2, Ongoing Studies), much has been learned concerning the behavior of perchlorates in the environment.

In water, perchlorates are expected to readily dissolve and dissociate into their component ions. Thermodynamic data on the dissolution of the perchlorates (Schilt 1979) indicate that the rate of this process should be rapid for all of the perchlorates listed in Table 4-1. The cations of the perchlorates listed in Table 4-1, magnesium, potassium, ammonium, sodium, and lithium, are ubiquitous in the environment. Given that perchlorates completely dissociate at environmentally significant concentrations, their cations are, for all practical purposes, spectators in the environmental fate of perchlorates dissolved in water. Therefore, when in water, the cations do not participate in, nor do they substantially influence, the fate of the perchlorate anion in the environment.

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**6.3.1 Transport and Partitioning**

Perchlorates are water soluble and the anion does not typically form insoluble metal complexes in solution (Cotton and Wilkinson 1980). Since the perchlorate ion is only weakly adsorbed to mineral surfaces in solutions of moderate ionic strength, its movement through soil is not retarded (Logan 2001; Urbansky and Brown 2003; Urbansky and Collette 2001). These two properties indicate that perchlorate will travel rapidly over soil with surface water runoff or be transported through soil with infiltration. Therefore, if released to soil, perchlorates are expected to be highly mobile and travel to groundwater and surface water receptors. This is consistent with surface water and groundwater monitoring data that indicate that perchlorates have been found far from known sites of their release to soil (see Section 6.4.2). Although data quantifying the extent of perchlorate adsorption to soil were not located in the available literature, a study on willow decontamination in sand bioreactors (Nzengung et al. 1999) established, through a mass-balance assessment, that perchlorates were not adsorbed by sand under the conditions of the experiment.

Perchlorates are not expected to volatilize from soil to the atmosphere given their very low vapor pressure. Moreover, dissociated inorganic ions do not undergo volatilization (Bodek et al. 1988). Perchlorates may be transported from soil to the atmosphere by wind-borne erosion. This convective process may release either aerosols or particulate matter to which dry perchlorate salts are adsorbed.

If released to water, perchlorates are not expected to volatilize to the atmosphere based on the extensive data set available for soluble inorganic ions that indicates this process does not occur (Bodek et al. 1988). The water solubility of perchlorates indicates that they will not be removed from the water column by physical processes and become adsorbed to sediment and suspended organic matter. Since the perchlorate ion is only weakly adsorbed to mineral surfaces in solutions of moderate ionic strength (Logan 2001; Urbansky and Brown 2003; Urbansky and Collette 2001), perchlorate is not expected to adsorb to sediment and organic matter. Since perchlorate does not serve as a ligand in aqueous solutions (Cotton and Wilkinson 1980), it is not expected to undergo removal from water through the formation of insoluble metal complexes. The water solubility and degree of complex formation of perchlorate do not change significantly as a function of acidity (Bodek et al. 1988), indicating that its fate is not expected to change within the pH range typically found in the environment. In cases where high concentration perchlorate brines enter the subsurface, the movement of perchlorate is expected to be controlled by gravity and the topography of confining layers (DOD 2006a). Perchlorate brines may sink through the

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subsurface and accumulate on or in confining layers where its release into groundwater is limited by diffusion.

Limited data indicate that perchlorate may accumulate in living organisms, as it has been detected in vegetation, fish, amphibian, insect, and rodent samples collected near a site of known contamination (Smith et al. 2001). The concentrations of perchlorate in male threespine stickleback fish (*Gasterosteus aculeatus*) were 0.63, 0.54, and 4.47 µg/g, corresponding to aquarium water perchlorate concentrations of 0, 1, and 10 ppm, respectively (U.S. Air Force Space Missile Systems Center 2002). Dean et al. (2004) reported bioconcentration factors of 1.854 for Asiatic clam (*Corbicula fluminea*) and 0.70 for bluegill (*Lepomis macrochirus*), indicating that bioconcentration of perchlorates in aquatic organisms is low. Theodorakis et al. (2006) analyzed fillets and heads of fish collected from Lakes Waco and Belton in Texas for perchlorates. These lakes are located near the Naval Weapons Industrial Reserve Plant where solid fuel rocket motors are manufactured. Perchlorate concentrations in positive samples ranged from 146 to 2,740 µg/kg wet weight in fillets and from 626 to 4,560 µg/kg wet weight in heads. Perchlorates were not detected in water samples from these lakes except for one instance at one of the three sampling sites in Lake Belton (14 µg/L) indicating that food chain transfer is possible. Possible routes of exposure for these fish include ingestion of contaminated periphyton (algae film), ingestion of contaminated detritus, and ingestion of perchlorate-containing invertebrates.

In a study on plant-mediated treatment of perchlorate-contaminated water (Nzengung et al. 1999), it was reported that uptake occurred in eastern cottonwoods (*Populus deltoides* and hybrid *populus*), *Eucalyptus cineria*, and willow (*Salix nigra*) in sand bioreactors. Willow was the only tree studied in detail. Perchlorate uptake was found to be initially rapid at a rate that was linear with the volume of water evapotranspired by the tree until a plateau was reached where perchlorate uptake ceased. At an initial application of 88.8 mg (at 96.4 mg/L), the total amounts of perchlorate in the root, lower stem, upper stem, and leaf after 26 days were 0.04, 0.18, 0.34, and 0.48 mg, respectively. In addition, 11% of the perchlorate was not accounted for, and was believed to be degraded to chloride in the leaves. Perchlorate uptake has also been established in salt cedar (*Tamarix ramosissima*) although the rate of uptake, excretion, and/or reduction was not determined (Urbansky et al. 2000c). Yu et al. (2004) observed uptake of perchlorate from sand in cucumber (*Cucumis sativus* L.), lettuce (*Lactuca sativa* L.), and soybean (*Glycine max*). Concentrations of perchlorate were higher in the lettuce (750 ppm) than in the cucumber (41 ppm) and soybean (18 ppm). It was reported that the presence of external nutrients such as nitrate may hinder uptake of perchlorate. The percent recovery of perchlorate in lettuce after it was applied at

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500, 1,000, 5,000, and 10,000 ppb to lettuce pots in a greenhouse was 82, 74, 76, and 73%, respectively (EPA 2004b).

A study on the uptake of perchlorate by tobacco plants from soil amended with Chilean-nitrate derived fertilizer (containing perchlorate at 36–1,544 mg/kg) found that extracts of the green and flue-cured leaves contained perchlorate at 12.4–164.6 mg/kg (dry weight) (Ellington et al. 2001). The authors point out that the available data set is not sufficient at this point in time to predict which plants undergo perchlorate uptake and accumulation and which ones are capable of completely reducing it to chloride, an important factor to consider given that food crops may be irrigated with contaminated water containing perchlorate. The uptake and transport of perchlorate from contaminated soil to the leaves of tobacco plants was also demonstrated over a wide range of initial soil concentrations (Sundberg et al. 2003). The results of this study indicate that perchlorates are taken up by the root system, transported up the stem via the xylem, and accumulate in the leaves and stems.

If released to the atmosphere, the perchlorate salts are expected to exist as a solid aerosol or be adsorbed to suspended particulate matter. Removal from the atmosphere is expected to occur by both dry and wet deposition to the Earth's surface. The water solubility and rapid rate of dissolution of perchlorates indicate that they may partition to clouds or fog, although subsequent deposition to the Earth's surface would be expected.

### **6.3.2 Transformation and Degradation**

#### **6.3.2.1 Air**

No data were located on the transformation or degradation of perchlorates in air. The dominant mechanism for the degradative removal of chemical compounds from the atmosphere is via their reaction with gas-phase oxidants (Lyman et al. 1990). Gas-phase oxidants include the neutral molecules, ozone and singlet oxygen, as well as hydroxyl radicals during the day or nitrate radicals at night. However, these species are all weaker oxidants than perchlorate, and atmospheric degradation via this pathway is, therefore, not expected to occur.

The other major atmospheric degradation process for chemical compounds is through direct photolysis. In general, this reaction is not sufficiently facile for solid phase materials for it to occur to any significant extent in the atmosphere. Since perchlorates are expected to exist as a solid dust in the atmosphere or be

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adsorbed to suspended particulate matter, direct photolysis is not expected to occur. Jaegle et al. (1996) estimated that the photolytic loss of perchloric acid in the atmosphere would be negligible.

**6.3.2.2 Water**

The ability of bacteria to utilize perchlorate as a terminal electron acceptor was first reported in 1976 (Logan et al. 2001b). Reviews by Logan (1998) and Herman and Frankenberger (1998) provide an extensive set of examples where laboratory experiments using microorganisms biodegrade (respire) perchlorate under anaerobic conditions. In the environment, anaerobic degradation has been found to be an important process in anoxic groundwater, sediments, and some soils. Microorganisms utilize alternative electron acceptors such as nitrate or sulfate anions in lieu of oxygen to generate energy and produce carbon-based building blocks in these anaerobic environs. In laboratory studies, the perchlorate anion has also been found to serve as an alternative electron acceptor in anaerobic microbial respiration. The reduction of perchlorate by microorganisms has been found to be inhibited by the electron acceptors most commonly found in anaerobic environments, most notably nitrate and/or sulfate. In a few cases, they were found to be reduced preferentially. The initial product from the respiration of perchlorate is chlorate ( $\text{ClO}_3^-$ ), which, in turn, is reduced by some of the isolates to chlorite ( $\text{ClO}_2^-$ ) and ultimately chloride ( $\text{Cl}^-$ ) and either oxygen or bicarbonate. A confounding aspect of the complete reduction of perchlorate is the production of oxygen, the absence of which defines a medium as anaerobic. For some microorganisms (obligate or strict anaerobes), perchlorate reduction was completely inhibited by the presence of oxygen. For others (facultative anaerobes), perchlorate reduction would subside with the introduction of oxygen and reoccur once it had been removed from the system via other processes.

Nzengung et al. (1999, 2004) studied the use of willows and other trees for the phytoremediation of perchlorate-contaminated water using hydroponic bioreactors. These investigators found that reduction of perchlorate to chloride occurred rapidly in the root zone (rhizosphere) after a relatively short acclimation period. Added nitrate inhibited the degradation of perchlorate indicating that reduction was occurring anaerobically, presumably in oxygen free micro-environments. The level of nitrate found to result in inhibition, 100 mg/L, is on the low end of the range typically found in soils, 0–1,200 mg/L. Tan et al. (2004b) reported that in the absence of nitrate, perchlorate was removed to levels below the detection limit ( $<4 \mu\text{g/L}$ ) in wetland columns with perchlorate influents of 4, 8, 16, and 32 mg/L. van Aken and Schnoor (2002) studied poplar tree cuttings (*Populus deltoides* x *nigra*) grown in the presence of radiolabeled perchlorate at 25 mg/L. These authors reported that 50% of the perchlorate was reduced 30 days after perchlorate application.

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Despite the numerous observations that perchlorate is readily reduced by microorganisms in laboratory cultures and the perceived ubiquity of these microorganisms in the environment (Bruce et al. 1999; Coates et al. 1999), it has been found to be persistent in the environment (Logan et al. 1998). *In situ* removal of perchlorate has not yet been demonstrated (Coates and Anderson 2000). This is likely due to the ubiquitous presence of nitrate and sulfate in the environment and the preferential utilization of these electron acceptors by anaerobes. Nevertheless, work in this area is continuing and recent studies are available on the reduction of perchlorate by hydrogen utilizing bacteria (Giblin et al. 2000) in the presence of acetate (Bruce et al. 1999; Coates et al. 1999; Kim and Logan 2001; Logan et al. 2001b) and in the presence of nitrate (Giblin and Frankenberger 2001; Herman and Frankenberger 1999). Biodegradation of perchlorate has also been demonstrated in salt solutions (11% brine) (Logan et al. 2001a).

No other degradation processes that are likely to remove perchlorates from water were identified. Photo-oxidation in water by alkoxy, peroxy, or other reactive species (Mill 1982) is not expected to occur as these species are weaker oxidants than perchlorate. Millero (1990) studied the rates of the indirect photochemical oxidation of Cu(I) and Fe(II) by hydroxyl radicals in artificial seawater solutions prepared using sodium perchlorate. No correction for a hydroxyl radical reaction with perchlorate was included in the detailed kinetic analysis performed by the authors, indicating that the reaction of perchlorate with hydroxyl radicals did not occur to any significant extent.

Another common removal process in the environment is biodegradation under aerobic conditions. In this process, the substrate is oxidized by microorganisms. Given that the perchlorate anion is at its highest oxidation state, this process is not expected to occur.

No studies on the direct photochemical degradation of perchlorates in water were located in the available literature. One of the requirements for direct photolysis to occur is the possession of a suitable chromophore that absorbs light in the environmentally significant range of >290 nm (i.e., wavelengths not blocked by the ozone layer); it does not address to what extent, if any, a reaction will ensue after a quantum of light has been adsorbed. Aqueous solutions of sodium perchlorate have a broad absorption at 605–700 nm (GMELIN 1999). This wavelength of light is on the long-wavelength (red), low energy side of the visible spectrum. A quantum of light at this wavelength does not typically have sufficient energy to result in the direct photochemical degradation of chemical compounds.

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The other major removal process for chemical compounds in environmental waters is through hydrolysis. Hydrolysis does not occur for inorganic salts that ionize in aqueous solutions, and it will not occur for perchlorates.

**6.3.2.3 Sediment and Soil**

Very few studies on the degradation of perchlorates in sediment or soil have been located in the available literature. Microorganisms isolated from soil have been found to reduce perchlorates under anaerobic conditions in the laboratory (Herman and Frankenberger 1998; Logan 1998) suggesting the potential for removal from anoxic soils and sediments. As noted for the degradation and removal from water (Section 6.3.2.2), perchlorates have been found to be persistent; the importance of this process in anoxic sediment and soils is not known. Tipton et al. (2003) have stated that the necessary criteria for perchlorate degradation in soil are anaerobic conditions, an adequate carbon source, and an active perchlorate-degrading microbial population. Perchlorate applied to Yolo loam at 180 mg/L during an anaerobic flooded batch experiment was completely biodegraded after 30 days (Tipton et al. 2003). During an analysis of perchlorate contaminated streambed sediment located near the Naval Weapons Industrial Reserve Plant in McGregor, Texas, it was concluded that microbial degradation of perchlorate was taking place based on a sequential depletion of electron acceptors and a constant  $\text{Cl}^-$  concentration in the sediment (Tan et al. 2005). While studying the natural biodegradation of perchlorate in the Las Vegas Wash area in Nevada, Zhang et al. (2002) concluded that this process is hindered by the lack of an electron donor, the presence of nitrate, and salinity levels in the area.

No other degradation process can be predicted for perchlorates in soil or sediment.

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

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

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**6.4.1 Air**

No monitoring data on the atmospheric concentration of perchlorates were located in the available literature.

**6.4.2 Water**

Drinking water samples from 3,858 public water systems located across the United States were collected from 2000 to 2004 as part of the Unregulated Contaminants Monitoring Rule (UCMR) (EPA 2005g). EPA found that approximately 4.1% (or 160) of these systems had at least one analytical detection of perchlorate (in at least one entry/sampling point) at levels greater than or equal to the minimum reporting level of 4 micrograms per liter ( $\mu\text{g/L}$ ). These 160 systems are located in 26 states and 2 territories. Perchlorate was detected at  $>4 \mu\text{g/L}$  in 365 of 13,401 (2.7%) samples from 67 of 1,247 (5.4%) surface water systems that serve  $>10,000$  people with a mean (range) concentration of  $15.6 \mu\text{g/L}$  ( $4.0\text{--}420 \mu\text{g/L}$ ). Perchlorate was detected at  $>4 \mu\text{g/L}$  in 29 of 1,496 (1.9%) samples from 5 of 236 (2.1%) surface water systems that serve  $<10,000$  people with a mean (range) concentration of  $6.4 \mu\text{g/L}$  ( $4.1\text{--}17 \mu\text{g/L}$ ). Perchlorate was detected at  $>4 \mu\text{g/L}$  in 214 of 14,972 (1.4%) samples from 69 of 962 (7.2%) groundwater systems that serve  $>10,000$  people with a mean (range) concentration of  $11.3 \mu\text{g/L}$  ( $4.0\text{--}200 \mu\text{g/L}$ ). Perchlorate was detected at  $>4 \mu\text{g/L}$  in 6 of 2,459 (0.2%) samples from 5 of 485 (1%) groundwater systems that serve  $<10,000$  people with a mean (range) concentration of  $7.8 \mu\text{g/L}$  ( $4.3\text{--}20 \mu\text{g/L}$ ). Based on analysis of 2004 UCMR data, NAS (2005) estimated that more than 11 million people are served by public drinking water supplies from which samples containing at least  $4 \mu\text{g/L}$  of perchlorate were collected.

According to information provided by the California Department of Health Services (CADHS 2007), perchlorate has been detected above  $4 \mu\text{g/L}$  in 267 out of approximately 7,000 drinking water sources located across California during monitoring conducted between March 2002 and March 2007. The greatest numbers of detections were in Los Angeles, Riverside, San Bernardino, and Orange Counties where perchlorate was found in 106, 64, 57, and 18 sources, respectively. The peak concentrations reported for these counties were 100, 73, 88, and  $10.6 \mu\text{g/L}$ , respectively. Perchlorate was detected drinking water from only four sources in Sacramento County; however, the peak concentration reported was  $95.9 \mu\text{g/L}$ .

In drinking water wells tested in Riverside and San Bernardino Counties, California, the maximum perchlorate concentration measured was  $216 \mu\text{g/L}$  (Herman and Frankenberger 1998). Five of six well-



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water samples obtained near Sacramento, California, March–April 1997, contained 4–260 µg/L of perchlorate (Okamoto et al. 1999). The concentrations of perchlorate measured in six water supply wells that serve the city of Loma Linda, California during 1997–1998 ranged from <4 to 29 µg/L (Agency for Toxic Substances and Disease Registry 2000). Jackson et al. (2005b) detected perchlorate above 0.5 µg/L in 179 out of 254 public water system and private wells in nine counties in the Texas Southern High Plains. Perchlorate concentrations were >4 µg/L in 88 wells. The maximum concentrations were 58.8 µg/L for private wells and 45.6 µg/L for public water system wells. The Massachusetts Department of Environmental Protection (MassDEP 2006a) reported that perchlorate concentrations were at or above the analytical reporting limit of 1 µg/L in only 9 of 600 tested public water supply systems in that state. Elevated perchlorate concentrations (maximum 1.5–1,300 µg/L) were measured near areas where blasting agents and fireworks were used.

Snyder et al. (2005) measured perchlorate concentrations ranging from 0.06 to 6.8 µg/L in 12 of 13 waters from various sources (seven surface waters, one groundwater, one spring water, and four treated waters) in the United States. The level in the spring water sample was reported to be “clearly visible” but below the reporting limit of 0.05 µg/L. These authors also detected perchlorate in 10 of 21 bottled water samples from various sources at levels ranging from 0.07 to 0.74 µg/L. Eleven of these samples were below the method reporting limit of 0.05 µg/L. In a separate study, perchlorate was not detected in 16 brands of imported and domestic bottled water (Urbansky et al. 2000a).

During a 1997–1998 drinking water survey, perchlorate was not detected (reporting limit=4.0 µg/L) in surface water samples from 40 sites in 11 states (Gullick et al. 2001). Out of 367 groundwater wells in 17 states tested during this survey, only 9 wells located in California and New Mexico contained perchlorate. Concentrations in samples from these wells ranged from <4–7 µg/L. The Southern Nevada Water Authority detected perchlorate at 11 µg/L in tap water samples (Urbansky 1998). Perchlorate was detected in the drinking water supply for Clark County, Nevada, at 4–15 µg/L (Li et al. 2000a). The perchlorate level in finished drinking water supplies in Yuma, Arizona, 1999, was 6 µg/L (Brechner et al. 2000). Drinking water advisory levels for perchlorate have been set in Arizona (14 µg/L), Maryland (1 µg/L), Nevada (18 µg/L), New Mexico (1 µg/L), New York (5 and 18 µg/L), and Texas (17 and 51 µg/L) (Dasgupta et al. 2005; EPA 2005c; Tikkanen 2006). Drinking water standards have been set in California (6 µg/L) and Massachusetts (2 µg/L). Perchlorate was generally not detected in surface water samples collected from 50 sites across the Great Lakes Basin (Backus et al. 2005). Concentrations were near the method detection limit of 0.2 µg/L in two samples from Hamilton Harbour and six creek/river water samples from the Maitland Valley and the Upper Thames River watersheds in Canada.

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Perchlorate contamination in drinking water has been reported at 12 DOD facilities and 2 other federal agency facilities located in California, Illinois, Maryland, Massachusetts, New Mexico, Ohio, and Utah as of March, 2005 (EPA 2005c). Maximum reported perchlorate concentrations in surface water at these sites range from approximately 1 to 720  $\mu\text{g/L}$ . Perchlorate contamination in drinking water has been reported at 16 private facilities located in Arizona, California, Iowa, Nebraska, New Mexico, Nevada, New York, and Utah as of March, 2005 (EPA 2005c). Maximum reported perchlorate concentrations in surface water at these sites range from approximately 5 to 811  $\mu\text{g/L}$ .

Surface water samples taken in August 1997 from the Las Vegas Wash, which feeds into Lake Mead, had perchlorate concentrations of 1,500–1,680  $\mu\text{g/L}$  (Herman and Frankenberger 1998; Urbansky 1998). Smith et al. (2004) reported a mean perchlorate concentration of 450  $\mu\text{g/L}$  in 24 water samples from 3 sites at the Las Vegas Wash collected in March, 2002 near Henderson, Clark County, Nevada. The Los Angeles Metropolitan Water District has detected perchlorate at 8  $\mu\text{g/L}$  at an intake located in Lake Mead (Urbansky 1998). In a separate study, perchlorate was detected in 57% of 147 surface water samples and 50% of 10 pore water samples collected in the Lake Mead area with average (maximum) concentrations of 10.5 (130) and 19.6 (98.0)  $\text{mg/kg}$ , respectively (Dean et al. 2004). Reported concentrations of perchlorate in the Colorado River are 5–9  $\mu\text{g/L}$  (Sanchez et al. 2005b, 2006). In Utah, perchlorate concentrations in groundwater wells at Alliant Techsystems, a rocket manufacturing site, ranged from 4 to 200  $\mu\text{g/L}$  (Urbansky 1998). According to a report issued by the EPA in December 2005, surface water concentrations in Las Vegas Wash, Lake Mead, and the Lower Colorado River have declined by 85, 70, and 60%, respectively, since the inception of a seep capture and treatment program at the Kerr-McGee site in Henderson, Nevada began in November 1999 (EPA 2006a).

Groundwater samples from a shallow aquifer near the Aerojet General Corporation's solid rocket fuel facility near Sacramento, California had maximum perchlorate levels of 8,000  $\mu\text{g/L}$  (Herman and Frankenberger 1998). Sampling wells at the Kennecott Utah Copper mines in Magna, Utah had perchlorate levels of 13  $\mu\text{g/L}$ . In well water samples in California, 30% had detectable levels of perchlorate (detection limit presumably 4  $\mu\text{g/L}$ ) and the concentration of perchlorate in 9% of them was over 18  $\mu\text{g/L}$ .

Perchlorate has been detected in surface and groundwater samples in Texas, Arkansas, Maryland, New York, California, Utah, and Nevada (Coates et al. 1999). It was detected in 30 groundwater wells by the California Department of Health Services at concentrations >18  $\mu\text{g/L}$  and in 50% of the wells test in

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Suffolk County, New York at concentrations up to 40 µg/L (Kim and Logan 2001; Logan et al. 2001b). In 1998, a survey by the California Department of Health Services found at 144 wells were contaminated at levels >18 µg/L (Giblin et al. 2000).

Perchlorate contamination in surface water has been reported at 17 DOD facilities located in Alabama, Arizona, Indiana, Maryland, New Mexico, Ohio, Oklahoma, Texas, and West Virginia as of March, 2005 (EPA 2005c). Maximum reported perchlorate concentrations in surface water at these sites vary widely, ranging from approximately 1 to 16,000 µg/L. Maximum reported concentrations of perchlorate in surface water at three private locations, Aerojet Company in Arkansas, Boeing/Rocketdyne in Nevada, and Elf Atochem in Oregon, were 12,500, 120,000, and 14 µg/L, respectively.

Perchlorate contamination in groundwater has been reported at 48 DOD facilities and 5 other federal agency facilities located in Alabama, Arizona, Arkansas, California, Colorado, Illinois, Indiana, Iowa, Maryland, Massachusetts, Minnesota, Missouri, New Jersey, New Mexico, Oregon, South Carolina, South Dakota, Tennessee, Texas, Utah, Virginia, Washington, and West Virginia as of March, 2005 (EPA 2005c). Maximum reported perchlorate concentrations in groundwater at these sites vary widely, ranging from approximately 1 to 276,000 µg/L. Perchlorate contamination in groundwater has been reported at 29 private facilities located in Arizona, Arkansas, California, Iowa, Kansas, Missouri, Nebraska, Nevada, New York, Oregon, and Utah as of March, 2005 (EPA 2005c). Maximum reported perchlorate concentrations in surface water at these sites vary widely, ranging from approximately 5 to 3,700,000 µg/L. Similar data listing concentrations of perchlorate in surface and groundwater at both federal and private facilities in the United States as of April, 2003 have been reported by EPA (2003, 2005c). The suspected source of these high levels of perchlorate in groundwater was usually related to the manufacture, disposal, testing, or research of explosives, rockets, or propellants (EPA 2003, 2005c).

Perchlorate levels in 8 of 12 groundwater and surface water samples at the Longhorn Army Ammunition plant, Texas, 1999, ranged from 3 to 776 µg/L (Smith et al. 2001). The concentration of perchlorate near the McGregor, Texas Naval Weapons Industrial Reserve Plant was 5,600 µg/L in tributary surface water samples collected at the site boundary and <4.0–91,000 µg/L in groundwater samples taken in the area (Cowan 2000). In a nearby wet weather spring connected to a boundary tributary, the concentration was 22,000 µg/L, while approximately 1 and 3 miles downstream in a creek, the concentrations were 200 and 56 µg/L, respectively. Perchlorate was detected in 13 of 25 local groundwater samples collected in Livermore, California, at 1–37 µg/L (Koester et al. 2000) and in drinking water from southern Nevada at 8–9 µg/L (Magnuson et al. 2000). Perchlorate concentrations measured in groundwater from remote

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locations in the Middle Rio Grande Basin in north-central New Mexico ranged from 0.12 to 1.8 µg/L (Plummer et al. 2006).

A study of 54 counties in west Texas and 2 adjacent counties in New Mexico found perchlorate levels in several groundwater samples (Rajagopalan et al. 2006). The concentration of perchlorate was generally low (<4 µg/L); however, some samples had detectable levels approaching 200 µg/L. While a single definitive source for these perchlorate levels could not be identified, the authors concluded that the majority of perchlorate detected at these sites could result from atmospheric deposition.

The U.S. Government Accountability Office listed perchlorate concentrations measured in surface water, groundwater, and drinking water samples from 395 sites from 35 states, the District of Columbia, and two commonwealths of the United States (GAO 2005). The concentrations at these locations ranged from 4 to 3,700,000 µg/L. According to the survey, 110 sites were located near defense-related activities, 36 sites were located near perchlorate manufacturing and handling operations, 16 sites were located near fireworks and flare manufacturing, general manufacturing, and hazardous waste sites, 6 sites were located near agricultural operations, and 227 sites were not located near activities linked to perchlorate.

Seawater samples collected off the coasts of Texas, Massachusetts, California, Hawaii, Oregon, Maine, and Mexico contained perchlorate at concentrations ranging from below the detection limit (0.07 µg/L) to 0.345 µg/L (Martinelango et al. 2006). The concentrations of perchlorate measured in 22 rain and 4 snow samples collected in Lubbock, Texas ranged from <0.01 to 1.6 and from <0.01 to 0.4 µg/L, respectively (Dasgupta et al. 2005).

#### 6.4.3 Sediment and Soil

Perchlorate contamination in soil or sediment has been reported at 27 DOD facilities and 2 other federal agency facilities located in Alabama, Arizona, California, Indiana, Massachusetts, Maryland, New Jersey, New Mexico, Texas, Utah, Washington, and West Virginia as of March, 2005 (EPA 2005c). Maximum reported perchlorate concentrations in soil at these sites vary widely, ranging from approximately 32 to 2,000,000 ppb. Maximum reported concentrations of perchlorate in sediment were 17 ppb at the Aberdeen Proving Ground in Maryland, 230 ppb at the Naval Surface Warfare Center in Maryland, 186 ppb at the Lone Star Army Ammunition Plant in Texas, and 190 ppb at the Allegheny Ballistics Laboratory in West Virginia. Perchlorate contamination in soil was also reported at two private sites in Arizona and one private site in Arkansas; however, concentrations were not provided.

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Perchlorate levels in 4 of 12 sediment samples at the Longhorn Army Ammunition plant, Texas, 1999, ranged from 12 to 704 µg/L (Smith et al. 2001). It was also detected in 4 of 18 soil samples near a single building at the facility at 50–322 µg/kg. The concentration of perchlorate in soil samples underneath the foundations of former propellant mixing facilities at the McGregor, Texas Naval Weapons Industrial Reserve Plant ranged from 23 to 1,800,000 µg/kg (Cowan 2000). Perchlorate was detected in 38% of 113 soil samples and 93% of 93 sediment samples collected from the Lake Mead area of Nevada with average (maximum) concentrations of 57.7 (1,470) mg/kg and 12.8 (56.0) mg/kg, respectively (Dean et al. 2004). Smith et al. (2004) reported a mean perchlorate concentration of 24.7 µg/g in 51 soil samples from 3 sites at the Las Vegas Wash near Henderson, Clark County, Nevada.

The concentration of perchlorate in soil samples taken from a tobacco field, December 1999, was 340 µg/kg (Ellington et al. 2001). Tobacco plants grown in this field had been fertilized that summer using products derived from Chilean caliche (which contained perchlorate at 35,800 and 1,544,000 µg/kg). The concentrations of perchlorate measured in the saturation extract of six soil samples from the Mission Valley Formation in San Diego, California ranged from below the detection limit (2 µg/L) to 40.2 µg/L (Duncan et al. 2005).

#### 6.4.4 Other Media

FDA (2007b) presented measurements of perchlorate in 27 foods and beverages obtained in fiscal years 2004–2005. Lettuce samples were collected from growers in various locations in Arizona, California, Texas, New Jersey, and/or Florida. Mean perchlorate levels were 10.6 ppb (µg/kg) in green leaf lettuce, 8.06 ppb (µg/kg) in iceberg lettuce, 11.19 ppb (µg/kg) in red leaf lettuce, and 11.75 ppb (µg/kg) in romaine lettuce (fresh/dry weight not specified). Bottled water with location sources from Georgia, Missouri, California, North Carolina, Texas, Colorado, Maryland, Minnesota, Nebraska, South Carolina, Arkansas, Kansas, Wisconsin, and Pennsylvania generally contained no detectable perchlorate. Milk samples from Maryland, California, Pennsylvania, Virginia, Arizona, Georgia, Kansas, Louisiana, New Jersey, North Carolina, Texas, and Washington had a mean perchlorate level of 5.81 ppb. For comparison, Dyke et al. (2007) provide concentrations of perchlorate in dairy milk from Japan that are higher than the preliminary data values reported for the United States by FDA. Perchlorate concentrations in the Japanese samples ranged from 5.47 to 16.40 µg/L with a mean value of 9.39 µg/L and a median value of 9.34 µg/L. Sanchez et al. (2007) compared perchlorate levels in broccoli, cauliflower, and cabbage grown in fields irrigated with water from the Colorado River, which contains

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perchlorate, with levels of thiocyanate and nitrate, two other anions that inhibit iodide uptake. The authors concluded that brassica irrigated with Colorado River water do accumulate trace levels of perchlorate. However, the levels of perchlorate observed are much lower than the levels of nitrate and thiocyanate, which are naturally present in these food plants.

Perchlorate concentrations in other foods reported by FDA (2007b) are listed in Table 6-1.

Following the preliminary assessment on perchlorate exposure (FDA 2007b), FDA completed its Total Diet Study (TDS) and released estimated dietary intakes for perchlorate and iodine for 14 age and gender groups (Murray et al. 2008). These perchlorate intakes are based on data collected from the TDS from 2005 to 2006. TDS sampling is conducted four times annually, once in each of the major geographical regions of the country (west, north central, south, and northeast). Each round of sampling is referred to as an individual market basket survey and for each market basket survey, samples of 285 selected food and beverages are obtained from three cities within the region. The TDS results found that detectable levels of perchlorate were observed in 59% of all samples analyzed, with 74% (211 of the 285) of the TDS foods having at least one positive sample. Perchlorate was not detected in 26% (74 of 285) of TDS foods. The contribution by food groups to the total intake of perchlorate for these age/gender groups are illustrated in Table 6-2. Table 6-3 provides the actual estimated dietary intake of perchlorate for these groups.

During a study of perchlorate concentrations in lettuce irrigated with Colorado River water (5 mg/L perchlorate concentration), perchlorate concentrations ranged from below quantifiable levels to 142 µg/kg (fresh weight) in the total above ground plant, 195 µg/kg (fresh weight) in the frame and wrapper leaves, and below detection to 26 µg/kg (fresh weight) in the edible head (Sanchez et al. 2005b). Perchlorate was detected above 0.2 µg/L in 144 out of 438 leafy vegetable samples produced in California (outside the Colorado River region), Colorado, New Jersey, New Mexico, New York, Michigan, Ohio, and Quebec (Sanchez et al. 2005a). Quantifiable perchlorate concentrations ranged from 18 to 104 µg/kg fresh weight in conventionally grown vegetables and from 21 to 628 µg/kg fresh weight in organically grown vegetables. Sanchez et al. (2006) measured perchlorate in citrus fruit grown from trees in the Southwest that were irrigated with perchlorate contaminated water (mean concentration of approximately 6 µg/L). Mean, median, and maximum perchlorate concentrations were 2.3, 1.3, and 14.8 µg/L fresh weight, respectively, in 33 lemon samples, 3.3, 1.3, and 16.2 µg/L fresh weight, respectively, in 15 grapefruit samples, and 7.4, 4.8, and 37.6 µg/L fresh weight, respectively, in 28 orange samples. Krynetsky et al. (2004) detected perchlorate in 11 edible cantaloupe and 10 whole cantaloupe samples with median

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**Table 6-1. Measurements of Perchlorate in Samples of 27 Types of Food and Beverages Collected From Various Locations in the United States**

Type of food or beverage	Mean residue ( $\mu\text{g/kg}$ ) <sup>a</sup>	Number of samples
Lettuce (green leaf)	10.3 4.4 <sup>b</sup>	137 2 <sup>b</sup>
Lettuce (iceberg)	8.1 2.1 <sup>b</sup>	43 4 <sup>b</sup>
Milk	5.81 <sup>c</sup> 7 <sup>b</sup>	125 8 <sup>b</sup>
Tomatoes	13.7 78 <sup>b</sup>	73 4 <sup>b</sup>
Carrots	15.8	59
Spinach	115 40 <sup>b</sup>	36 4 <sup>b</sup>
Collards	95.1 17.7 <sup>b</sup>	13 4 <sup>b</sup>
Cantaloupes	28.6 24.4 <sup>b</sup>	48 4 <sup>b</sup>
Apples	0.15 <sup>c</sup>	9
Grapes	8.58	12
Oranges	3.47 2.7 <sup>b</sup>	10 4 <sup>b</sup>
Strawberries	2.14	19
Watermelon	1.96	19
Fruit juices (apple and orange)	2.31 <sup>c</sup>	14
Broccoli	8.49	14
Cabbage	8.80	13
Greens	92.4	14
Cucumber	6.64 19.1 <sup>b</sup>	20 4 <sup>b</sup>
Green beans	6.12	19
Onions	0.53	12
Potatoes	0.15 <sup>d</sup>	6
Sweet potatoes	1.24	6
Corn meal	1.16	22
Oatmeal	3.96	22
Rice (brown and white)	0.50 <sup>d</sup>	19
Whole wheat flour	4.27	19
Catfish	1.02	7
Salmon	1.06	11
Shrimp	19.83	5

<sup>a</sup>Mean values are reported as ppb in source. Mean values were calculated treating non-detections as equal to one-half the detection limit. Fresh/dry weight not specified.

<sup>b</sup>Murray et al. 2008

<sup>c</sup>Mean value is in  $\mu\text{g/L}$ .

<sup>d</sup>All samples were non-detects.

Source: FDA 2007b

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**Table 6-2. Percent Contribution Organized by Food Group to the Total Estimated Daily Intake for Perchlorate for 2005–2006**

Food group	Intake (percent of total)						
	Infants 6–11 months	Children 2 years	Children 6 years	Children 10 years	Females 14–16 years	Males 14–16 years	Women 25–30 years
Baby food	49	0	0	0	0	0	0
Beverages	1	3	3	4	7	7	12
Dairy	32	51	50	47	29	37	20
Egg	0	0	0	0	0	0	0
Fat/oil	0	0	0	0	0	0	0
Fruit	4	15	11	9	11	7	8
Grain	2	6	8	8	8	9	8
Legume	0	0	0	0	0	0	0
Mixture	6	8	9	10	14	12	14
Meat, poultry, fish	1	4	6	5	7	7	11
Sweets	0	1	1	1	1	1	1
Vegetables	5	12	12	16	23	20	26

Food group	Men 25–30 years	Women 40–45 years	Men 40–45 years	Women 60–65 years	Men 60–65 years	Women 70+ years	Men 70+ years
Baby food	0	0	0	0	0	0	0
Beverages	12	12	11	9	9	6	7
Dairy	20	17	21	17	19	23	22
Egg	0	0	0	0	0	0	0
Fat/Oil	0	0	0	0	0	0	0
Fruit	5	11	8	12	9	12	12
Grain	8	8	9	8	8	8	9
Legume	0	0	0	0	0	0	0
Mixture	16	13	13	9	10	10	10
Meat, poultry, fish	9	7	8	7	8	5	7
Sweets	0	1	1	0	0	0	0
Vegetables	30	31	29	38	37	36	33

Source: Murray et al. 2008



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**Table 6-3. Range of Estimated Lower and Upper Bound Average Perchlorate Intake for 2005–2006**

Food group	Intake (µg/person/day)						
	Infants 6–11 months	Children 2 years	Children 6 years	Children 10 years	Females 14–16 years	Males 14–16 years	Women 25–30 years
Baby food	1.1–1.3	0.0–0.0	0.0–0.0	0.0–0.0	0.0–0.0	0.0–0.0	0.0–0.0
Beverages	0.0–0.1	0.0–0.3	0.0–0.4	0.0–0.5	0.02–0.8	0.0–0.1	0.2–1.2
Dairy	0.8–0.8	2.6–2.6	2.9–2.9	3.1–3.1	1.6–1.6	3.1–3.1	1.2–1.2
Egg	0.0–0.0	0.0–0.0	0.0–0.0	0.0–0.0	0.0–0.0	0.0–0.0	0.0–0.0
Fat/oil	0.0–0.0	0.0–0.0	0.0–0.0	0.0–0.0	0.0–0.0	0.0–0.0	0.0–0.0
Fruit	0.1–0.1	0.7–0.9	0.6–0.7	0.5–0.6	0.6–0.7	0.5–0.6	0.5–0.6
Grain	0.0–0.1	0.3–0.3	0.4–0.5	0.5–0.5	0.4–0.5	0.7–0.8	0.4–0.5
Legume	0.0–0.0	0.0–0.0	0.0–0.0	0.0–0.0	0.0–0.0	0.0–0.0	0.0–0.0
Mixture	0.1–0.1	0.4–0.5	0.5–0.6	0.6–0.7	0.8–0.8	1.0–1.1	0.9–0.9
Meat, poultry, fish	0.0–0.0	0.2–0.2	0.3–0.3	0.3–0.4	0.3–0.4	0.5–0.6	0.7–0.7
Sweets	0.0–0.0	0.0–0.0	0.0–0.1	0.0–0.1	0.0–0.1	0.0–0.1	0.0–0.1
Vegetables	0.1–0.1	0.6–0.6	0.7–0.7	1.0–1.0	1.2–1.3	1.7–1.7	1.5–1.5
Total intake	2.4–2.7	4.9–5.5	5.4–6.1	6.1–6.9	5.1–6.1	7.7–9.1	5.4–6.8
Total intake (µg/kg/day)	0.26–0.29	0.35–0.39	0.25–0.28	0.17–0.20	0.09–0.11	0.12–0.14	0.09–0.11
Food group	Men 25–30 years	Women 40–45 years	Men 40–45 years	Women 60–65 years	Men 60–65 years	Women 70+ years	Men 70+ years
Baby food	0.0–0.0	0.0–0.0	0.0–0.0	0.0–0.0	0.0–0.0	0.0–0.0	0.0–0.0
Beverages	0.2–1.6	0.3–1.3	0.2–1.7	0.2–1.0	0.2–1.3	0.1–0.7	0.1–0.9
Dairy	1.5–1.5	1.1–1.1	1.8–1.8	1.1–1.1	1.5–1.5	1.4–1.4	1.7–1.7
Egg	0.0–0.0	0.0–0.0	0.0–0.0	0.0–0.0	0.0–0.0	0.0–0.0	0.0–0.0
Fat/oil	0.0–0.0	0.0–0.0	0.0–0.0	0.0–0.0	0.0–0.0	0.0–0.0	0.0–0.0
Fruit	0.3–0.4	0.7–0.8	0.6–0.7	0.7–0.8	0.6–0.8	0.7–0.8	0.8–1.0
Grain	0.6–0.7	0.5–0.6	0.7–0.8	0.5–0.5	0.6–0.7	0.5–0.6	0.6–0.7
Legume	0.0–0.0	0.0–0.0	0.0–0.0	0.0–0.0	0.0–0.0	0.0–0.0	0.0–0.0
Mixture	1.2–1.3	0.8–0.9	1.1–1.1	0.6–0.6	0.8–0.9	0.6–0.6	0.7–0.8
Meat, poultry, fish	0.7–0.7	0.5–0.5	0.6–0.7	0.4–0.5	0.6–0.7	0.3–0.4	0.5–0.6
Sweets	0.0–0.0	0.0–0.0	0.1–0.1	0.0–0.0	0.0–0.0	0.0–0.0	0.0–0.0
Vegetables	2.2–2.2	1.9–2.0	2.4–2.4	2.4–2.4	2.8–2.9	2.2–2.2	2.5–2.5
Total intake	6.7–8.6	5.9–7.3	7.4–9.4	5.9–7.1	7.2–8.8	5.8–6.9	7.1–8.3
Total intake (µg/kg/day)	0.08–0.11	0.09–0.11	0.09–0.11	0.09–0.10	0.09–0.11	0.09–0.11	0.11–0.12

Source: Murray et al. 2008

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(range) concentrations of 9.6 (<2.0–18.2) and 23.9 (<2.0–39.3) µg/kg, respectively (fresh/dry weight not specified).

According to El Aribi et al. (2006), perchlorate was detected in all produce, wine, and beer samples purchased in grocery and liquor stores located in the greater Toronto, Ontario area between January 2005 and February 2006. These products were harvested or produced in many parts of the world. Median concentrations reported for perchlorate in products from each country ranged from 0.047 to 169.698 µg/kg in 63 produce samples, 0.013–15.54 µg/L in 77 wine samples, and 0.03–10.663 µg/L in 144 beer samples, and below detection (5 ng/L). Perchlorate was detected above 5 ng/L in 11 out of 12 beverage samples and in 7 out of 10 bottled water samples from around the world at reportable concentrations of 0.067–5.098 µg/L and 0.021–4.795 µg/L, respectively. Median, minimum, and maximum perchlorate concentrations in samples harvested or produced in the United States were 0.252, 0.094, and 19.29 µg/kg, respectively, in 8 produce samples, 20.9, 0.197, and 4.593 µg/L, respectively, in 12 wine samples, and 0.662, 0.364, and 2.014 µg/L, respectively, in 8 beer samples.

Perchlorate was detected in 20 out of 31 dietary supplements with mean, median, and maximum reportable concentrations of 247, 25, and 2,420 ng/g, respectively (Snyder et al. 2006). The limits of detection ranged from 2 to 15 ng/g. Perchlorate was also detected in two samples of kelp granules, a flavor enhancing ingredient, at concentrations of 709 and 740 ng/g.

In a survey of 10 randomly selected off-the-shelf tobacco products, perchlorate was detected in six of seven brands of different plug chewing tobacco at 2.3–149.3 mg/kg (dry weight), two of two brands of cigarettes at 15.1–71.7 mg/kg, and one of one brand of cigars at 7.1 mg/kg (Ellington et al. 2001).

Mean perchlorate concentrations measured in the blood, milk, urine, and feces of cows with calculated perchlorate intakes of 0.46 mg/day from feed and 0.03 mg/day from water were 0.24, 4.37, 3.68, and 5.84 ng/mL, respectively (Capuco et al. 2005). Perchlorate concentrations were monitored in vegetation and animal samples collected at various locations at the Longhorn Army Ammunition plant, Texas, 1999. It was detected in green tree frog samples (86–153 µg/kg), harvest mouse samples (1,120–2,328 µg/kg), cotton mouse samples (356 µg/kg), mosquitofish samples (83–206 µg/kg), juvenile sunfish samples (132 µg/kg), blackstripe minnow samples (104 µg/kg), bullfrog tadpole samples (1,130–2,567 µg/kg), chorus frog samples (580 µg/kg), *Notropis spp.* samples (77 µg/kg), weed shiner samples (100 µg/kg), bullrush samples (555–9,487 µg/kg dry weight), crabgrass samples (1,060,000–5,557,000 µg/kg dry weight), and damselfly larvae (811–2,036 µg/kg) (Smith et al. 2001). Perchlorate was not detected in

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Northern cricket frog samples, American toad sample, bullfrog samples, or largemouth bass samples. For most of these samples, it was not specified whether measurements were conducted on a wet- or dry-weight basis. The concentrations of perchlorate were below the detection limit of 2.5 µg/L wet weight in most fish samples (tissue extracts) collected from lakes, rivers, and streams located near the Naval Weapons Industrial Reserve Plant in McLennan County, Texas (Theodorakis et al. 2006). Concentrations in fish with quantifiable levels ranged from 10.8 to 4,560 µg/kg wet weight. Perchlorate was detected in 18% of 88 terrestrial mammals, 3% of 107 fish, and 12% of 42 terrestrial birds sampled in the Lake Mead area, Nevada with average (maximum) concentrations of 13.4 (53.0), 16.4 (44.3), and 1.5 (4.2) mg/kg, respectively (Dean et al. 2004). It was not specified whether these measurements were conducted on a wet or dry-weight basis.

In wood samples from dormant salt cedars near the Las Vegas Wash, Nevada, date not provided, perchlorate concentrations ranged from 5 to 6 mg/kg in twigs extending above the water and at 300 mg/kg in submersed stalks (Urbansky et al. 2000c). The rate and selectivity of perchlorate uptake by the salt cedars was not determined. The mean concentration of perchlorate was 289.3 µg/g in 71 vegetation samples collected from 3 sites at the Las Vegas Wash during March, 2002 (Smith et al. 2004). Perchlorate has been detected in 50% of 177 terrestrial vegetation samples and 24% of 50 aquatic vegetation samples from the Lake Mead area in Nevada with average (maximum) concentrations of 34.7 (428) and 38.8 (176) mg/kg, respectively (Dean et al. 2004). Tan et al. (2004b) tested several plants and trees (smartweed [*Polygonum spp.*], watercress (*Nasturtium spp.*), ash (*Fraxinus greggii* A. Gray), chinaberry (*Melia azedarach* L.), elm (*Ulmus parvifolia* Jacq.), willow (*Salix nigra* Marshall), mulberry (*Broussonetia papyrifera* [L.] Vent.), and hackberry (*Celtis laevigata* Willd.) that were growing beside streams near the Naval Weapons Industrial Reserve Plant at McGregor, Texas for perchlorate. Perchlorate was detected above 1 µg/L in streamwater at five out of six locations with average concentrations ranging from <1 to 281 µg/L. The average concentrations of perchlorate in the plants and trees at these locations ranged from <1 to 40,600 µg/kg dry weight. Martinelango et al. (2006) measured perchlorate concentrations ranging from 29 to 878 µg/kg dry weight in 13 commercially available seaweed species.

## 6.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

The general population is likely to be exposed to perchlorate through some dietary routes, drinking water sources, and consumer products.

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Data from the FDA TDS indicated that 74% (211 of the 285) of the foods analyzed had at least one sample in which perchlorate was detected (Murray et al. 2008). The perchlorate dietary intake was estimated to range from 0.08 to 0.11  $\mu\text{g/kg/day}$  for males aged 25–30 years to 0.35–0.39  $\mu\text{g/kg/day}$  for children 2 years old (see Table 6-3). These estimates are in good agreement with previous estimates based upon limited sets of data. Daily dose for perchlorate exposure via ingestion of lettuce, dietary supplements, and citrus fruit have been calculated (Sanchez et al. 2005a, 2005b, 2006; Snyder et al. 2006). None of these estimates were above the EPA reference dose (0.7  $\mu\text{g/kg/day}$ ). Blount et al. (2007) estimated a daily perchlorate dose based on measured concentrations in urine, which account for the combined exposure from all sources. Reported geometric mean and 95th percentile urinary perchlorate concentrations of 3.35 and 12  $\mu\text{g/L}$ , respectively, were measured in a nationally representative population of 1,618 U.S. residents, ages  $\geq 20$  years, during 2001 and 2002 as part of the National Health and Nutrition Survey (NHANES). Based on these monitoring data, the geometric mean and 95th percentile values of the estimated perchlorate dose in adults were 0.066 and 0.234  $\mu\text{g/kg/day}$ , respectively. Only 11 adults had estimated doses greater than the EPA reference dose.

The detection of perchlorate in drinking water supplies (Brechner et al. 2000; Giblin et al. 2000; Herman and Frankenberger 1998; Li et al. 2000a; Urbansky 1998) and in tap water samples (Urbansky 1998) indicates that members of the general population may be exposed by ingestion of water containing perchlorate. Perchlorate has been identified at least once in approximately 4% of over 3800 community water systems from 26 different states and 2 territories, with detectable levels averaging 9.8  $\mu\text{g/L}$  and ranging from the method detection limit of 4  $\mu\text{g/L}$  to a maximum at 420  $\mu\text{g/L}$  (EPA 2007).

Contaminated groundwater sources near known ammonium perchlorate production or use sites (Giblin et al. 2000; Herman and Frankenberger 1998; Kim and Logan 2001; Logan et al. 2001b; Smith et al. 2001; Urbansky 1998) suggest that populations that obtain drinking water from down gradient wells at such sites may also be exposed to perchlorates. Since more sensitive analytical techniques have been developed, perchlorate is also being found in areas other than where it has been manufactured, used, or released by humans, suggesting that exposure from natural sources are possible (Dasgupta et al. 2005; Rajagopalan et al. 2006; Urbansky 2002; Valentín-Blasini et al. 2005).

Valentín-Blasini et al. (2005) measured perchlorate concentrations ranging from 0.66 to 21 (median 32)  $\text{ng/mL}$  in urine samples from 61 healthy adult donors from Atlanta, Georgia with no known perchlorate exposure. These authors also measured perchlorate in urine samples from 60 pregnant women from 3 Chilean cities (Antofagasta, Chañaral, and Taltal) where perchlorate concentrations in tap

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water range from approximately 0.4 to 114 ng/mL. The median and range of concentrations of perchlorate in the samples were 35 and 0.49–1,100 ng/mL, respectively. Pearce et al. (2007) reported perchlorate concentrations ranging from 0.37 to 127 µg/L measured in 56 urine samples from 57 Boston-area nursing mothers.

Perchlorate has been detected in different types of tobacco products (Ellington et al. 2001). It is likely that smokeless tobacco products (chewing tobacco) will result in greater exposure than cigarettes since the combustion of the perchlorate upon lighting will result in a reaction before it is inhaled. Individuals that reload their own ammunition may also be exposed to perchlorates due to their presence in gunpowder (Lindner 1993). Members of the general population undergoing some types of medical imaging may be exposed to small amounts (200–400 mg orally) of perchlorate (Gibbs et al. 1998). Perchlorate has also been identified in certain common household products such as bleach. Perchlorate levels in bleach were reported to range from 89 to 8,000 ppb, with concentrations increasing with time of product storage (MassDEP 2006a). Perchlorate has also been detected in dietary (vitamin and mineral) supplements and flavor-enhancing ingredients collected from various commercial vendors in two large U.S. cities (Snyder et al. 2006). The highest level of perchlorate was found in a supplement recommended for pregnant women as a prenatal vitamin/mineral supplement.

Workers at facilities where perchlorates are manufactured or used may be exposed by inhalation. Workers at an ammonium perchlorate facility were exposed to calculated single-shift absorbed doses of 0.2–436 µg/kg with a 35 µg/kg average (Gibbs et al. 1998). Lifetime cumulative doses for workers over an average of 8.3 years ranged from 8,000 to 88,000 µg/kg. Workers may also be exposed to perchlorate dusts through oral routes through deposition of particles via mouth breathing (Gibbs et al. 1998). In a survey at an ammonium perchlorate manufacturing facility, respirable air samples had an average perchlorate concentration of 0.091 mg/day for workers at low dust-forming operations. The average perchlorate concentration for moderate and high dust-forming operations was 0.601 and 8.591 mg/day, respectively (Lamm et al. 1999). Exposure through inhalation or dermal contact may also occur from aqueous perchlorate solutions if aerosol-producing operations, such as spray drying, are used; however, dermal absorption of perchlorate is expected to be low since electrolytes applied from aqueous solutions do not readily penetrate the skin (Scheuplein and Bronaugh 1983).

The National Occupational Exposure Survey (NOES), conducted from 1981 to 1983, indicates that 2,641 total workers were exposed to potassium perchlorate, 1,452 to sodium perchlorate, 1,445 to ammonium perchlorate, and 1,906 to magnesium perchlorate in the United States (NIOSH 1995). No

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values were reported for lithium perchlorate. Exposure for female workers was reported as 1,948 (potassium), 230 (sodium), 230 (ammonium), and 713 (magnesium). It is not known why females represented a higher percentage of the total worker exposure for lithium and magnesium perchlorates relative to that for the sodium and ammonium salts.

These NOES data suggest that the highest production volume salts, sodium and ammonium perchlorates, were used in operations involving fewer people than magnesium and potassium perchlorates. These data also suggest that magnesium and potassium perchlorates were used either in a wider range of applications, in processes requiring more human manipulation, or in applications that were performed at multiple sites in the United States.

## 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).

Children are expected to undergo environmental exposure to perchlorates via the same routes predicted for adult members of the general population in Section 6.5, primarily through the ingestion of food and drinking water containing perchlorate. Blount et al. (2007) reported geometric mean and 95<sup>th</sup> percentile urinary perchlorate concentrations of 4.93 and 19 µg/L, respectively, measured in 374 children living in the United States, ages 6–11 years, during 2001 and 2002 as part of the NHANES. Geometric mean and 95th percentile concentrations in 828 children ages 12–19 years measured during this study were 3.80 and 12 µg/L, respectively. The authors note that the adjusted geometric mean of urinary perchlorate concentrations is higher for children (5.40 µg/L) than for adolescents (3.30 µg/L) and adults (3.41 µg/L). Possible explanations for this are differences in pharmacokinetics, the relationship of dose per body

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weight, and differences in dietary habits between children and adults such as the consumption of milk and green leafy vegetables.

The estimated dietary intakes for children have been calculated based upon the FDA TDS (see Table 6-3). These data indicate that children have the highest estimated intake on a body weight basis as compared to the other age groups because they consume more food per body weight and have different food consumption patterns when compared to the other age groups (Murray et al. 2008). Children 2 years of age had the highest estimated intake ranging from 0.35 to 0.39  $\mu\text{g/kg/day}$ , which is roughly 50–56% of the EPA reference dose (RfD). Dairy products provided over 50% of the total perchlorate intake in their diets. Using measured urinary concentration data, Blount et al. (2007) estimated the daily dose of perchlorate for women of reproductive age to give an indication of possible fetal exposure to perchlorate. The median and 95th percentile values of the estimated perchlorate dose were 0.057 and 0.214  $\mu\text{g/kg/day}$ , respectively, in 662 women of reproductive age. The median of the estimated dose was 0.066  $\mu\text{g/kg/day}$  in 110 pregnant women (95th percentile value was not reported).

Measurements of perchlorate concentration in mother's milk, a potential route of exposure for infants, indicated a mean level of 10.5  $\mu\text{g/L}$  and a maximum level of 92  $\mu\text{g/L}$  in 35 human milk samples from 18 states (Kirk et al. 2005). Kirk et al. (2007) reported perchlorate concentrations ranging from 0.5 to 39.5  $\mu\text{g/L}$  measured in the breast milk of 10 women (from Texas, Colorado, Florida, Missouri, New Mexico, and North Carolina). Mean and median concentrations were 5.8 and 4.0  $\mu\text{g/L}$ , respectively. Téllez et al. (2005) reported mean perchlorate concentrations of 81.6, 18.3, and 85.6  $\mu\text{g/L}$  measured in the breast milk of women from the Chilean cities of Antofagasta (14 samples), Chañaral (16 samples), and Taltal (25 samples), respectively. Perchlorate was detected in all 49 breast milk samples from 57 Boston-area women ranged at concentrations ranging from 1.3 to 411  $\mu\text{g/L}$  (Pearce et al. 2007). These authors also measured perchlorate in infant formulae; perchlorate was detected in all 17 samples measured at concentrations ranging from 0.22 to 4.1  $\mu\text{g/L}$ . Using data from Kirk et al. (2005) for levels of perchlorate in human milk and exposure factors described in EPA (1997b), Baier-Anderson et al. (2006) estimated that infants breastfed for 6 months may have daily doses of perchlorate that exceed the NAS recommended RfD of 0.7  $\mu\text{g/kg/day}$ . This information needs to be put in context by reiterating that the RfD is, by definition, an estimate spanning as much as an order of magnitude, and that the perchlorate RfD is based on a precursor to an adverse effect.

Perchlorate has also been detected in dairy milk, another source of exposure of children and adults (Kirk et al. 2005). The mean level of perchlorate in 47 cow's milk samples from 11 states was 2  $\mu\text{g/L}$ , with a

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maximum level of 11 µg/L. The FDA has reported a mean concentration of 5.81 ppb measured in 125 dairy milk samples collected from 12 states (FDA 2007b). Data from the most recent FDA TDS found a mean concentration of 7 ppb measured in 8 samples of milk (Murray et al. 2008). Rice et al. (2007) demonstrated the transfer of perchlorate from feed to cows was a significant source of perchlorate in subsequent milk samples. Analysis of the ingredients of the total mixed ration (TMR) determined that the majority of perchlorate arose from corn silage, alfalfa, and hay.

Perchlorates may be released to soil by a number of pathways. Because children sometimes eat inappropriate things and put dirt in their mouths, they may be exposed to perchlorates through ingestion of contaminated soil. The presence of certain household products that contain perchlorates could also lead to a child being exposed. Children may be exposed to perchlorates if they use or disassemble flares; infants may be exposed orally if they put them in their mouths.

**6.7 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES**

Members of the general population who live near hazardous waste sites containing perchlorates and draw their drinking water from underground wells may potentially receive high exposure to perchlorates. Similarly, people who live near facilities that manufacture, process, use, or dispose of large amount of perchlorates may also receive potentially higher exposures.

Workers in facilities that manufacture or use large amounts of solid perchlorates may receive potentially high inhalation exposures. Twenty-nine individuals were tested for perchlorate exposure after 3 consecutive days of 12-hour shifts working at an ammonium perchlorate production facility near Cedar City, Utah (Braverman et al. 2005). The mean and median concentrations of perchlorates in serum samples collected from the workers were 2 and 0 µg/L, respectively, before exposure and 838.4 and 358.9 µg/L, respectively, after exposure. The mean and median concentrations of perchlorates in urine samples were 0.16 and 0.11 mg/g creatinine, respectively, before exposure and 43.0 and 19.2 mg/g creatinine, respectively, after exposure. Gibbs et al. (1998) calculated that workers at an ammonium perchlorate manufacturing facility may receive doses that are 2–3 orders of magnitude greater than a person might receive from drinking water obtained from Lake Mead or the Colorado River and 2–3 orders of magnitude less than that historically prescribed for the treatment of Grave's disease.

Due to their presence and potential emission in signal flares, members of the population that use these devices on a frequent basis, such as law enforcement officers, may be exposed to higher levels of



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perchlorates than the general public. Similarly, frequent users of perchlorate-based civilian explosives, fireworks display technicians, and related occupations may be exposed to higher levels.

## 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 perchlorates 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 perchlorates.

The following categories of possible data needs have been identified. 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.** Perchlorates have been manufactured commercially for nearly 100 years (Schilt 1979). Their fundamental physical and chemical properties have been well described in the literature. Vapor pressure data are not available for the perchlorate salts listed in Table 4-1; however, they are high melting ionic solids and would be expected to be nonvolatile. No further investigation of the physical/chemical properties of perchlorates is required to assess their potential for human and environmental exposure.

**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. Reliable data on the production of perchlorates are not available. Reasonable estimates are available for past ammonium perchlorate production, although current values are not available. Past or present production data for the remainder of the perchlorates listed in Table 4-1 are not available. Accurate production data may not become available because perchlorates are considered strategic chemicals due to their extensive use in military and aerospace applications and there are no requirements to track and report for the numerous industrial and

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commercial applications for perchlorate. Accordingly, available worldwide perchlorate production data are unlikely to be complete. Accurate production data is one factor that is required to establish the foundation from which potential human and environmental exposure to perchlorates can be determined.

The techniques used in manufacturing perchlorates have been well described in the available literature and there are no data needs in this area.

Accurate import and export data on perchlorate are not readily available. Perchlorates are not listed as a separate, reportable item on U.S. Census Bureau's schedule B book on imports. Production, import and export data are available for certain products that may contain perchlorate. For example, large amounts of fireworks (approximately  $1 \times 10^8$  kg) are imported into the United States (USITC 2008). The actual volume of perchlorates represented by these figures is not known since the content of perchlorate varies by firework type and origin. Reliable data on the importation of fireworks as well as the amount of perchlorate they contain are important in determining human exposure.

The numerous uses of perchlorates have been described in the available literature. However, the amount of perchlorates used in these applications is not always available. Determining the amount of perchlorates in these products is essential in fully establishing the extent, level, and route of potential occupational exposures. Moreover, the amount of perchlorate contained in pyrotechnic devices, especially consumer products (i.e., small fireworks, flares, and gunpowder) is required to establish worker exposure as well as potential exposure to members of the general population. This data gap requires additional research to characterize and document potential significant sources of perchlorate released to the environment.

Limited data on the release of perchlorates to the environment were located. Releases are known to be associated with the perchlorate production for propellants as well as rocket manufacture, testing, and decommissioning. The amount, frequency, and duration of these releases are not well documented. Researchers have speculated that the current extent of perchlorate contamination in western waters is a direct result of these activities. A better understanding of historical releases, used in combination with an extensive monitoring database, will allow the development of robust models that can be used to predict the potential for human and environmental exposure

The wide variety of uses for perchlorates suggests that other releases are likely during production, processing, formulation, transport, use, and disposal. No data on the resulting release of perchlorates were located in the available literature. The water solubility of perchlorates suggests that disposal in

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aqueous waste streams may occur during their production and use. Given that perchlorates are not known to be removed from waste water streams in POTWs or other common treatment processes, release to waste water represents a point source release to surface water. Since perchlorates are known to persist in surface water, a comprehensive understanding of point source releases to the environment is required to fully establish the potential for human exposure.

Perchlorates are explosive chemicals that see extensive use in pyrotechnic devices including fireworks. Catastrophic accidents resulting from manufacturing of perchlorates (Urbansky 1998) and products in which it is contained (CSB 1999) are known to have occurred. Release of unspent perchlorates to the environment is a likely result of these events. Members of the general population who live near these facilities may therefore be exposed to perchlorates as a result of a catastrophic explosion. Similarly, perchlorates are known to be released during the catastrophic explosion of booster rockets (Merrill and O'Drobinak 1998). Determining the amount released during these events is required to estimate potential human and environmental exposure.

Unspent perchlorates may be released to the environment in the effluent of propulsion systems in solid propellant rockets and fireworks. Unspent oxidant may also be released during the “burst” at fireworks displays. The amount of perchlorates released via these mechanisms, if any, is not known but may be significant. Given the large volume of perchlorates used in rockets and that members of the general population frequent firework displays, the amount released from these potential pathways is required for a comprehensive determination of general population exposure.

Concern over the disposal of perchlorate has not arisen until recently (Urbansky 1998). DOD recovers much of the perchlorate that is used in weapon systems and returns it to the manufacturer for use in commercial applications (DOD 2007). More information on the level, frequency, amount, composition, method, route, duration, and chronology of perchlorate disposal would be needed for a thorough assessment of the environmental burden of perchlorates.

**Environmental Fate.** Studies of sufficient number and breadth to rigorously establish the environmental fate of perchlorates have not been performed, and currently, there are no regulations in place that restrict their use. Very few studies on the transport and partitioning of perchlorates in the environment were located. Moreover, current methodologies for estimating key predictors of fate processes, including the octanol/water partition coefficient, soil adsorption coefficient, and

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bioconcentration factor are not sufficiently robust to provide accurate results for inorganic ions in general and perchlorates specifically.

Some aspects of the environmental fate of perchlorates can be reliably predicted. Volatilization from water or soil to the atmosphere is not expected to occur to a significant extent. If released directly to the atmosphere, deposition through wet and dry process is expected to return perchlorates to the Earth's surface (although the importance of long-range transport in air was not located in the available literature). Analysis of physical/chemical properties and available monitoring data indicate that perchlorates are unlikely to be strongly adsorbed to soil or sediment.

There is also a paucity of data available on the degradation of perchlorate in the environment. Given that they are fully oxidized, perchlorates are not expected to react with the common environmental oxidants found in air and surface waters. Direct photolysis is also not expected to be a significant process.

Numerous workers have demonstrated that in laboratory studies, isolated microorganisms can respire perchlorates, although to date, no evidence of the biodegradation of perchlorate in the environment has been located. The anaerobic biodegradation of perchlorates would be expected to occur in anoxic soils and groundwater. Because members of the general population may be exposed to perchlorates through the ingestion of contaminated well water, aerobic biodegradation studies that establish its potential removal from drinking water sources are important. Ingestion of perchlorate-contaminated drinking water may be a route of exposure for those members of the general population living near hazardous waste sites containing perchlorates.

The available data on the fate of perchlorates in the environment do not allow an accurate prediction of their lifetime in soil and water.

**Bioavailability from Environmental Media.** No data are available to determine the bioavailability of perchlorate from environmental media. It has been detected in plants (Nzengung et al. 1999) and tobacco products (Ellington et al. 2001) and may be present in food crops irrigated with perchlorate contaminated water. The bioavailability of perchlorate from environmental media would provide additional information to help determine potential levels of human exposure.

**Food Chain Bioaccumulation.** Limited data are available on the uptake of perchlorates in biota. A laboratory study (Nzengung et al. 1999) provides evidence for the uptake and depuration of perchlorates

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in willows. It has been detected in vegetation, fish, amphibian, insect, and rodent samples near a site of known contamination (Smith et al. 2001). Few studies of perchlorate bioconcentration in fish and aquatic organisms or food chain bioaccumulation have been identified. These data are required in order to determine the potential exposure of higher organisms to perchlorates.

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

No monitoring data are available on the concentration or frequency of detection of perchlorates in air, or plant materials, while there are data on the concentration of perchlorates in soil, surface water and groundwater at various sites where perchlorates have been used or disposed or are naturally occurring.

**Exposure Levels in Humans.** Recent data are available on perchlorate exposure levels in humans for both age and gender groups (Blount et al. 2007; Murray et al. 2008). Continued monitoring data and estimates of human exposure are necessary to compare exposure levels and observed health effects in the population.

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

**Exposures of Children.** Children are expected to be exposed to perchlorates primarily through the ingestion of food (including milk) and drinking water containing perchlorate. Infants may be exposed through mother's milk. Since younger children have the propensity to place objects in their mouths, the levels of perchlorate in soil and consumer items needs to be determined.

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 perchlorates were located. This substance is not currently one of the compounds for which a sub-registry has been established in the National Exposure Registry. The substance will be considered in the future when chemical selection is made for sub-registries to be established. The information that is amassed in the National Exposure Registry facilitates

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the epidemiological research needed to assess adverse health outcomes that may be related to exposure to this substance.

**6.8.2 Ongoing Studies**

The Federal Research in Progress (FEDRIP 2008) database and the Current Research and Information System database funded by the U.S. Department of Agriculture (CRIS 2008) provide additional information obtainable from a few ongoing studies that may fill in some of the data needs identified in Section 6.8.1. These studies are summarized in Table 6-4.

In addition, DOD is pursuing recycling technology to recover ammonium perchlorate from demilitarized rocket motors for military reuse, which should significantly reduce the amount of propellants that must be destroyed by open burn/open detonation (DOD 2008).

It should be noted that additional information on the potential for human exposure to perchlorates is continually appearing in the scientific literature. Much of this work is being performed by both private and governmental laboratories and, therefore, would not be cited in FEDRIP. Interested readers who require the latest information on the potential for human exposure to perchlorates are urged to consult the scientific literature.

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**Table 6-4. Ongoing Studies on the Potential for Human Exposure to Perchlorates (Including Studies on Fate and Occurrence)**

Investigator	Affiliation	Research description
EPA	EPA, Office of Research and Development, National Exposure Research Lab	Survey of industrial and foodgrade chemicals for perchlorate content
CDC	CDC, NCEH	Perchlorate exposure in the US population (ages 6+ using NHANES data (2001–)
CDC	CDC, NCEH	Maternal and perinatal fetal perchlorate exposure
CDC	CDC, NCEH	Perchlorate exposure of infants consuming either breastmilk or infant formula
CDC	CDC, NCEH	Mechanisms of active transport of perchlorate in cultured mammalian cells
CDC	CDC, NCEH	Perchlorate exposure and thyroid hormone levels in a population of women with low iodine intake
FDA	FDA	Ongoing FDA Total Diet Survey analysis for perchlorate
Follet RF	Agricultural Research Service	Improving soil and nutrient management systems for sustained productive and environmental quality
Mylon S	Lafayette College	Removal and destruction of perchlorate from aqueous systems using polymer ligand technology and packed bed reactors
Raskin LM	University of Illinois at Urbana-Champaign, Department of Civil and Environmental Engineering	Process optimization, molecular microbial characterization, and biofilm modeling of a bioreactor for perchlorate removal from drinking water
Sanchez CA	University of Arizona	Assessment of perchlorate content of food crops irrigated with water from the Colorado River
Sanchez CA	University of Arizona	Study of the fate and transport of perchlorate in the soil of the lower Colorado River region of Arizona
Scow KM	University of California	Study of microbial degradation of contaminants in soil, vadose, and groundwater
Stewart VJ	University of California	Study of bacterial anaerobic respiration in relation to its use and application in environmental microbiology and bioremediation
Strathmann T	University of Illinois at Urbana-Champaign	Development of a sustainable catalytic treatment process for perchlorate

CDC = Centers for Disease Control and Prevention; EPA = Environmental Protection Agency; FDA = Food and Drug Administration; NCEH = National Center for Environmental Health; NHANES = National Health and Nutrition Examination Survey

Source: CRIS 2008; FEDRIP 2008; SI/EPA 2008