

6. POTENTIAL FOR HUMAN EXPOSURE

6.1 OVERVIEW

Perchlorates have been identified in at least 8 of the 1,662 hazardous waste sites that have been proposed for inclusion on the EPA National Priorities List (NPL) (HazDat 2005). However, the number of sites evaluated for perchlorates is not known. The frequency of these sites can be seen in Figure 6-1.

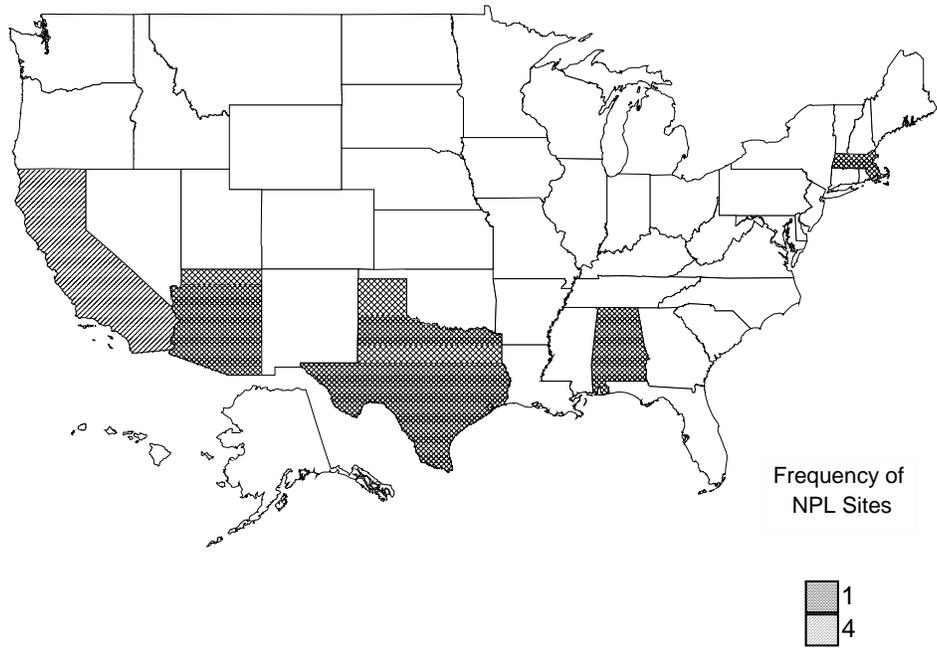
Perchlorates are high melting inorganic salts that are soluble in water at environmentally significant concentrations. They are found in or released to the environment in two forms. In the absence of water, the perchlorate salts listed in Table 4-1 will be found (or released) as a solid. In water, perchlorates 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.

This results in a significant consequence when determining the potential for human exposure to perchlorates. 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

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



Derived from HazDat 2005

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for a strong oxidizing agent. This apparent discrepancy can, in part, be explained by differences in its kinetic and thermodynamic reactivity.

Thermodynamic reactivity is an indication of how favorable the energetics of a reaction are. Perchlorates are known to be highly reactive thermodynamically and, therefore, they may react vigorously under the proper conditions. The kinetic reactivity indicates how fast a reaction will occur at a given temperature. For perchlorates, this value is relatively low at ambient temperature and they react slowly at room temperature. The rate at which chemical reactions proceed increases with increasing temperature. The decomposition of perchlorates is usually initiated using a high temperature source, such as a glow wire, to overcome the kinetic barrier. Once decomposition of some perchlorates 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 kinetic reactivity is a function of the reaction pathway. Different reaction pathways for perchlorates would have different kinetic barriers than the thermal decomposition discussed above. Nevertheless, the existence of a large kinetic barrier for the decomposition of a reactive compound such as perchlorate is important in understanding its persistence in the environment.

The potential for perchlorate contamination was first realized after monitoring at the PEPCON rocket fuel plant, which exploded in 1988, revealing that nearby surface water samples had perchlorate concentrations as high as 630 µg/L (Urbansky 1998). Nearby groundwater samples were also contaminated with perchlorate. In January 1997, the California Department of Health Services began to test for perchlorates at the Aerojet aerospace facility outside of Sacramento as regulators became aware of groundwater contamination at the site (EPA 1999; Okamoto et al. 1999). To perform a complete assessment at the site, new methods to detect the perchlorate anion were developed that improved the detection limits by 2 orders of magnitude from 400 to 4 µg/L. Groundwater samples were found to contain perchlorate at up to 8,000 µg/L (Okamoto et al. 1999). In February 1997, monitoring studies in nearby communities detected perchlorate in drinking water wells at concentrations up to 280 µg/L. Subsequent monitoring with this more sensitive method detected perchlorate contamination far from known sources of its production and use. Within a short time, it was detected in surface water, groundwater, and drinking water samples in California, Nevada, and Utah (Koester et al. 2000; Okamoto et al. 1999; Urbansky 1998). Additional data are currently being evaluated to assess the degree to which available peer reviewed data adequately reflect the scope and levels of perchlorate contamination.

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Limited data are available in the peer reviewed literature on the potential for human exposure to perchlorates. No data on the amount of perchlorates released to air, soil, or water were located in the available literature. The major source of release is generally thought to have resulted from the manufacture of perchlorates for rocket booster engines as well as their testing and decommissioning (removing aged propellants). Release of perchlorate has also occurred during the manufacture of munitions. Perchlorates have been detected in fertilizers derived from Chilean saltpeter a source of naturally occurring perchlorates. These fertilizers have been traditionally used mainly to grow tobacco.

Release of unspent perchlorates to the environment is known to have occurred during the catastrophic explosion of a booster rocket. Perchlorates may also be released to the environment during a catastrophic explosion in a facility in which they are manufactured or used.

Small amounts of perchlorates may also be released directly to the environment during their use in pyrotechnic devices. They may also be released to waste water during electroplating operations, pyrotechnic manufacture, and other sites of their manufacture and use. Since perchlorates are not removed in publicly owned treatment works (POTWs), their presence in waste water will likely result in their eventual release to surface water. No information on the amount of perchlorate released to POTWs could be located in the available literature. Recent studies have suggested that atmospheric processes involving interaction of chloride with lightning or ozone may be a natural source of perchlorates in the environment.

Limited data on the environmental fate of perchlorates were located in the available literature. The available data indicate that perchlorates are expected to be highly mobile in soil and to partition to surface water or groundwater. They are not expected to significantly absorb to sediment or suspended organic matter. They are also expected and to readily settle from the atmosphere.

No degradation process for perchlorates in the environment has been unambiguously established. Laboratory experiments suggest that they may biodegrade under anaerobic conditions in soil and water although there is no evidence that this will occur in the environment. 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.

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There are limited data available in the peer reviewed literature on the concentration of perchlorates found in the environment. Perchlorate has been found in groundwater and surface water near facilities where it was manufactured and used at maximum concentrations of 1,500 and 8,000 µg/L, respectively.

Perchlorate has also been found in drinking water wells far removed from known sources of contamination at a maximum concentration of 216 µg/L. It has also been found in tap water at up to 11 µg/L. As of January, 2001, drinking water facilities are required to monitor for perchlorate and more data on its concentration may be available in the future.

There are also limited data available in the peer reviewed literature on the concentration of perchlorates in other environmental media. Perchlorate has been detected in plants, mammals, amphibians, fish, and insects near a site of known contamination. The potential for perchlorate to bioconcentrate in fish and aquatic organisms or bioaccumulate in higher organisms has not been established.

The general population may be exposed to perchlorates by the ingestion of contaminated drinking water. Members of the general population may also be exposed through the use of tobacco products, the ingestion of contaminated food, or the use of pyrotechnic devices in which perchlorates are contained. Members of the general population who live near hazardous wastes sites containing perchlorate may be exposed through the ingestion of contaminated drinking water or dermal exposure when coming in contact with contaminated soil. Occupational exposure to perchlorates may occur through the inhalation of dusts (or from dust settling in the mouth) produced during the manufacture, processing, use, or disposal of perchlorate-containing materials, or through the use of pyrotechnic devices.

6.2 RELEASES TO THE ENVIRONMENT

The TRI data should be used with caution because only certain types of facilities are required to report (EPA 1997). This is not an exhaustive list. Manufacturing and processing facilities are required to report information to the Toxics Release Inventory only if they employ 10 or more full-time employees; if their facility is classified under Standard Industrial Classification (SIC) codes 20–39; and if their facility produces, imports, or processes $\geq 25,000$ pounds of any TRI chemical or otherwise uses $>10,000$ pounds of a TRI chemical in a calendar year (EPA 1997).

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6.2.1 Air

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

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. There is no information on releases of perchlorates to the atmosphere from manufacturing and processing facilities because these releases are not required to be reported (TRI02 2005).

The major use of perchlorates is as a component of solid rocket boosters (Vogt 1986). Solid rocket boosters rapidly release gases to provide propulsion through the atmosphere, and the release of unspent perchlorates may occur during this process. 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 also be released to the atmosphere from booster rockets during a catastrophic failure (Merrill and O'Drobinak 1998) or aborted flight. 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 (Einfeld et al. 1995), although perchlorate was not one of the targeted analytes.

Perchlorates also find extensive use in fireworks and other pyrotechnic devices (Conkling 1996; 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 no information on the amount, if any, was located in the available literature. Release of perchlorate may also occur during

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catastrophic explosions at firework facilities (CSB 1999) or at facilities that manufacture other pyrotechnic devices based on this oxidant.

Perchlorates may also enter the atmosphere through the wind-borne erosion of contaminated sand, soil, or particulate matter. This process may also occur at hazardous waste sites or after a large spill of solid perchlorates. No atmospheric monitoring data on the quantity of perchlorates in air near hazardous waste sites were located.

It has been postulated that perchlorate may be formed in the atmosphere by the reaction of ClO radicals with sulfuric acid aerosols (Jaegle et al. 1996). 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. 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 2005).

6.2.2 Water

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

Perchlorates may be released to water in emissions from their manufacture, processing, or use. No data on the amounts of perchlorate released in waste water were located in the available literature. 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. There is no information on releases of perchlorates to water from manufacturing and processing facilities because these releases are not required to be reported (TRI02 2005).

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There is limited information available on the release of ammonium perchlorate to water. Although no quantitative information focusing on the release of ammonium perchlorate to water from the manufacture, maintenance, decommissioning, or testing of solid rocket propellants was located in the available literature, perchlorate concentrations resulting from these activities have been reported to have reached the g/L level (Herman and Frankenberger 1998). 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 is expected to reach 8.5 million pounds in the first decade of the twenty-first century (Buckley et al. 1999). Although this waste water may be disposed of by incineration (Buckley et al. 1999), information on the historical methods that have been used to treat this type of waste water is not available.

No information on the release of perchlorates to surface or waste water during the manufacture of fireworks, explosives, and other pyrotechnic devices or during their use in electroplating baths and related uses were located in the available literature. 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).

6.2.3 Soil

There is no information on releases of perchlorates to soil from manufacturing and processing facilities because these releases are not required to be reported (TRI02 2005). As discussed in Section 6.2.2,

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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 1986), may result in the release of unspent oxidant to soil. The amount of perchlorate used in explosives, 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).

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 Collete 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.

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

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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.

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

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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.

Limited data indicate that perchlorate may accumulate in living organisms, as it has been detected in vegetation, fish, amphibian, insect, and rodent samples 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.

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 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

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important factor to consider given that food crops may be irrigated with contaminated water containing perchlorate.

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. No monitoring data for the presence of perchlorates in rain, fog, or clouds were located in the available literature.

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 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

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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 (ClO_3^-), which, in turn, is reduced by some of the isolates to chlorite (ClO_2^-) and ultimately chloride (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.

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

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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 and, therefore, perchlorates are not expected to undergo direct photolysis in water.

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

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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 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 depend 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 perchlorate 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.

6.4.1 Air

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

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6.4.2 Water

Drinking water samples from 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).

Perchlorate was detected above 4 µg/L in 67 out of 1,247 (5.4%) surface water systems (365 out of 13,401 [2.7%] samples) that serve >10,000 people with a mean (range) concentration of 15.6 (4.0–420) µg/L. Perchlorate was detected above 4 µg/L in 5 out of 236 (2.1%) surface water systems (29 out of 1,496 [1.9%] samples) that serve <10,000 people with a mean (range) concentration of 6.4 (4.1–17) µg/L. Perchlorate was detected above 4 µg/L in 69 out of 962 (7.2%) groundwater systems (214 out of 14,972 [1.4%] samples) that serve >10,000 people with a mean (range) concentration of 11.3 (4.0–200) µg/L. Perchlorate was detected above 4 µg/L in 5 out of 485 (1%) groundwater systems (6 out of 2,459 [0.2%] samples) that serve <10,000 people with a mean (range) concentration of 7.8 (4.3–20) µg/L.

In drinking water wells tested in Riverside and San Bernardino Counties, California, the maximum perchlorate concentration measured was 216 µg/L (Herman and Frankenberger 1998). Five of six well-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 ppb (Agency for Toxic Substances and Disease Registry 2000). 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 has been 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 ppb), California (6 ppb), Maryland (1 ppb), Massachusetts (1 ppb), Nevada (18 ppb), New Mexico (1 ppb), New York (5 and 18 ppb), and Texas (17 and 51 ppb) (Dasgupta et al. 2005; EPA 2005c).

Perchlorate contamination in drinking water has been reported at 12 DoD facilities and 2 other federal agency facilities located in California, Illinois, Massachusetts, Maryland, 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 ppb. Perchlorate contamination in drinking water has been

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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 ppb.

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 0.45 $\mu\text{g/mL}$ 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) mg/kg , respectively (Dean et al. 2004). 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). 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 Suffolk Country, New York at concentrations up to 40 $\mu\text{g/L}$ (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 $>18 \mu\text{g/L}$ (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 ppb. 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 ppb, respectively.

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Perchlorate contamination in groundwater has been reported at 48 DoD facilities and 5 other federal agency facilities located in Alabama, Arkansas, Arizona, California, Colorado, Iowa, Illinois, Indiana, Massachusetts, Maryland, Minnesota, Missouri, New Jersey, New Mexico, Oregon, South Carolina, South Dakota, Tennessee, Utah, Texas, Virginia, Washington, and West Virginia as of March, 2005 (EPA 2005c). Maximum reported perchlorate concentrations in surface water at these sites vary widely, ranging from approximately 1–276,000 ppb. Perchlorate contamination in surface water has been reported at 29 private facilities located in Arkansas, Arizona, 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 ppb. 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).

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).

The concentration 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). No monitoring data on the concentration of perchlorates in seawater, fog, or clouds were located in the available literature.

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

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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.

Perchlorate levels in 4 of 12 sediment samples at the Longhorn Army Ammunition plant, Texas, 1999, ranged from 12 to 704 $\mu\text{g/L}$ (Smith et al. 2001). It was also detected in 4 of 18 soil samples near a single building at the facility at 50–322 $\mu\text{g/kg}$. 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 $\mu\text{g/kg}$ (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 $\mu\text{g/g}$ 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 $\mu\text{g/kg}$ (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 $\mu\text{g/kg}$).

6.4.4 Other Environmental Media

FDA (2004) presented measurements of perchlorate in lettuce, bottled water, and milk, but cautions that these data are exploratory and should not be understood to be a reflection of distribution of perchlorate in the U.S. food supply. The consumer is further cautioned that the perchlorate levels should not be viewed as indicators of exposure. Lettuce samples were collected from growers in various locations in Arizona, California, Texas, New Jersey, and/or Florida. Mean perchlorate levels were 10.7 ppb in green leaf lettuce, 7.76 ppb in iceberg lettuce, 11.6 ppb in red leaf lettuce, and 11.9 ppb in romaine lettuce. 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 5.75 ppb. Perchlorates were detected in 11 edible cantaloupe and 10 whole cantaloupe samples with median (range) concentrations of 9.6 (<2.0–18.2) and 23.9 (<2.0–39.3) $\mu\text{g/kg}$,

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respectively (Krynitsky et al. 2004). 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 brands of cigars at 7.1 mg/kg (Ellington et al. 2001). Perchlorate was not detected in 16 brands of imported and domestic bottled water (Urbansky et al. 2000a).

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.

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), crabgrass samples (1,060,000–5,557,000 µg/kg), and damselfly larvae (811–2,036 µg/kg) (Smith et al. 2001). It was not detected in Northern cricket frog samples, American toad sample, bullfrog samples, or largemouth bass samples. 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).

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The average (maximum) concentration of perchlorate detected in 12% of 33 terrestrial insects collected near the Allegany Ballistics Laboratory in West Virginia was 12.6 (6.2) mg/kg (Dean et al. 2004).

6.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

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 contaminated water. 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 members of the general population that draw drinking water from down gradient wells may also be exposed to perchlorates. The general population may also be exposed to contaminated food and milk (FDA 2004).

Members of the general population living near hazardous waste sites, facilities that manufacture fireworks and other pyrotechnic devices, or farms using perchlorate-containing fertilizers may also be exposed to perchlorates. Contamination of soil at these sites is expected to subsequently lead to contamination of nearby groundwater and/or surface water, which may ultimately lead to exposure through ingestion of contaminated water. Members of the general population who live near these areas may also be exposed through the inhalation of wind-borne perchlorate dusts. Acute inhalation exposure to higher levels may occur immediately after a catastrophic explosion at a fireworks facility.

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, although at lower concentrations (Dasgupta et al. 2005; Urbansky 2002; Valentin-Blasini et al. 2005). Humans living in these areas may be exposed to perchlorates; however, the source and nature of this type of contamination are unclear and must be studied further before the extent of this exposure can be understood.

Valentin-Basini et al. (2005) measured perchlorate concentrations ranging from 0.66 to 21 (median 32) 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, Chanaral, and Taltal) where perchlorate concentrations in tap 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 to 1,100 ng/mL, respectively.

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Perchlorate has been detected in different types of tobacco products (Ellington et al. 2001) and members of the general population that use these products are likely to be exposed. 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).

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 $\mu\text{g}/\text{kg}$ with a 35 $\mu\text{g}/\text{kg}$ average (Gibbs et al. 1998). Lifetime cumulative doses for workers over an average of 8.3 years ranged from 8,000 to 88,000 $\mu\text{g}/\text{kg}$. Workers may also be exposed to perchlorate dusts through dermal and possibly 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.

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 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.

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6.6 EXPOSURES OF CHILDREN

This section focuses on exposures from conception to maturity at 18 years in humans. Differences from adults in susceptibility to hazardous substances are discussed in 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).

No information explicitly discussing perchlorate exposure to children was located in the available literature. 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 contaminated drinking water and food. No perchlorate body burden measurements for children are available. Measurements of perchlorate concentration in mother's milk, a potential route of exposure for infants, indicated a mean level of 10.5 ppb and a maximum level of 92 ppb in 35 human milk sample from 18 states (Kirk et al. 2005). 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 ppb, with a maximum level of 11 ppb. Given the relatively small number of samples taken, the results should be considered preliminary.

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. They may also be dermally exposed if they crawl over perchlorate-contaminated soil.

The presence of gunpowder or small fireworks in the home may lead to a child being exposed to perchlorates. Children may be exposed to perchlorate-containing dust when their parents reload their own ammunition, and mischievous entry into the gunpowder container may also lead to exposure. Children

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may be exposed to perchlorates by dermal contact if they use or disassemble fireworks; infants may be exposed orally if they put them their mouth.

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 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

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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 by a joint team of scientists from ATSDR, NTP, and EPA. They are defined as substance-specific informational needs that if met would reduce the uncertainties of human health assessment. This definition should not be interpreted to mean that all data needs discussed in this section must be filled. In the future, the identified data needs will be evaluated and prioritized, and a substance-specific research agenda will be proposed.

6.8.1 Identification of Data Needs

Physical and Chemical Properties. 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. The TRI, which contains this information for 2002, became available in May of 2004. This database is updated yearly and should provide a list of industrial production facilities and emissions.

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. Accordingly, available worldwide perchlorate production data are unlikely to be complete. Accurate production data are 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.

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No data on the import or export of perchlorates were located. Perchlorates are not listed as a separate, reportable item on U.S. Census Bureau's schedule B book on imports. The largest source of perchlorates imported into the United States likely results from its use in fireworks. Large amounts of fireworks are imported into the United States, as the value of these imports in 1997 was \$93 million (U.S. Census Bureau 1999). However, the amount of perchlorates represented by this value is not available. Fireworks may represent a significant source of perchlorate exposure to children and members of the general population. Therefore, 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 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.

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 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.

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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. 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.

No information is available on the amount of perchlorates released to hazardous waste sites. Knowledge of the amount of perchlorates at hazardous waste sites is required for risk assessors to establish an accurate understanding of their potential for human exposure.

It has been reported in the available literature that perchlorates are widely used in automobile airbags inflation systems. However, no information was located indicating the degree to which these devices have been commercialized or the number of cars in which they have been installed. No information could be located on the amount of perchlorates present in these devices. Given the well-understood life-cycle of automobiles, their ubiquitous nature, and the potential for extensive human and environmental exposure from this source, more information is required.

There is reason to believe that from a historical perspective, concern over appropriate perchlorate disposal has not arisen until recently (Urbansky 1998). Comprehensive information on the level, frequency, amount, composition, method, route, duration, and chronology of perchlorate disposal is not present in the available literature and cannot be accurately synthesized. Without this information, a thorough assessment of the environmental burden of perchlorates cannot be established.

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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 bioconcentration factor are not sufficiently robust to provide accurate results for inorganic ions in general and perchlorates specifically. The high solubility of perchlorates in both organic solvents, including organic alcohols, and water indicates that broad predictions made solely on water solubility should be viewed with caution in the absence of experimental data.

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.

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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 is required 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 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, soil, or plant materials. Limited data on the concentration of perchlorates in surface water and groundwater were located; however, the available data are limited to Western states. Information that addresses environmental exposure to perchlorates throughout the United States is not available. No data on the concentration of perchlorates found at hazardous waste sites were located. This information is necessary for assessing the need to conduct health studies on these populations.

Exposure Levels in Humans. Only limited data are available on potential exposure levels of members of the general population through the ingestion of contaminated drinking water, food, and milk. No data are available on potential exposure to humans through other routes of exposure nor are the levels of perchlorates in food or consumer products available. The amount of information only allows a speculative determinative of the potential human exposure to perchlorates. There is a clear data need in this area as there is only a paucity of data currently available to predict human exposure to perchlorates.

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Exposures of Children. Children are expected to be exposed to perchlorates primarily through the ingestion of contaminated drinking water, food, and milk. 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 need to be determined. Sufficient data addressing the concentration of perchlorates in soil, especially in and around hazardous waste sites, are not available. The amount of perchlorates in consumer items in the home is not known, nor is the amount in gunpowder, or in fireworks, which are a potential source of exposure to children. The available data set does not yet allow the levels of perchlorate exposure to children and infants to be determined.

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

Exposure Registries. No exposure registries for perchlorates were located. Perchlorates are not currently identified as one of the compounds for which a subregistry has been established in the National Exposure Registry. The substances will be considered in the future when chemical selection is made for subregistries to be established. The information that is amassed in the National Exposure Registry facilitates the epidemiological research needed to assess adverse health outcomes that may be related to exposure to these substances.

6.8.2 Ongoing Studies

The Federal Research in Progress (FEDRIP 2005) database, the Current Research and Information System database funded by the U.S. Department of Agriculture (CRIS/USDA 2002), the U.S. Department of Energy (DOE 2002), and the National Science Foundation Awards (NSF Awards 2002) 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 6-1.

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 6-1. Ongoing Studies on the Potential for Human Exposure to Perchlorates (Including Studies on Fate and Occurrence)

| Investigator | Affiliation | Research description |
|--------------|---|---|
| RF Follet | Agricultural Research Service | Impact study of improved nitrogen management on soil and water quality |
| RF Follet | Agricultural Research Service | Study of improved nitrogen use efficiency and its effects on water quality and the environment |
| P Kofinas | University of Maryland | Toxic and nutrient pollution prevention by use of anion binding polymeric hydrogels |
| LM Raskin | 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 |
| DE Rolston | University of California, Davis | Exposure assessment method involving transport, transformation, and remediation of volatile organic compounds in the vadose zone and ground waste |
| CA Sanchez | University of Arizona | Assessment of perchlorate content of food crops irrigated with water from the Colorado River |
| CA Sanchez | University of Arizona | Study of the fate and transport of perchlorate in the soil of the lower Colorado River region of Arizona |
| KM Scow | University of California | Study of microbial degradation of contaminants in soil, vadose, and groundwater |
| VJ Stewart | University of California | Study of bacterial anaerobic respiration in relation to its use and application in environmental microbiology and bioremediation |
| FR Shirazi | Stratum Engineering, Inc. | Development of a biological permeable barrier for use in groundwater bioremediation |
| U.S. EPA | U.S. EPA, Office of Research and Development, National Exposure Research Lab | Survey of industrial and foodgrade chemicals for perchlorate content |

Source: FEDR&D 2005; FEDRIP 2005

EPA = Environmental Protection Agency